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WATER AND AMORPHOUS ICE
UNSOLVED PROBLEMS OF LIQUID WATER

Static and Dynamic Puzzles

H. E. Stanley, S. V. Buldyrev, N. Giovambattista, E. La Nave, A. Scala, F. Sciortino, F. W. Starr

[HeS,SVB,NG,ElaN,AS] Center for Polymer Studies and Department of Physics
Boston University, Boston, MA 02215 USA
[ELaN,AS,FS] Dipartimento di Fisica Università di Roma La Sapienza,
Istituto Nazionale di Fisica della Materia and
INFM Center for Statistical Mechanics and Complexity,
Piazzale Aldo Moro 2, 00185 Roma, Italy
[FW] Polymers Division and Center for Theoretical
and Computational Materials Science
National Institute of Standards and Technology, Gaithersburg, MD 20899 USA

Abstract

We present an overview of recent research applying ideas of statistical mechanics to try to better understand the statics and especially the dynamic puzzles regarding liquid water. The take-home message for the static aspects is that what seems to "matter" more than previously appreciated is local tetrahedral order, so that liquid water has features—such as a liquid-liquid phase transition—in common with SiO2 and P4 as well as perhaps Si and C. For the dynamic aspects, what may "matter" is the number of diffusive directions in the potential energy landscape.

1. The goal: Understanding “what matters”

Many physicists are attracted to physics because of the focus on understanding just enough of a subject to comprehend the key features that really matter. As soon as some physicists feel they understand “what matters”, insatiable appetites for novelty force attention to new puzzles. At the 1968 Kyoto STATPHYS-8 conference, among the most exciting new developments was the degree to which the principle of scale invariance provided increased understanding of “what matters” near a
critical point. The key point was that what matters near a critical point is the correlation length for statics, and the correlation time for dynamics. An exciting question these days is "what matters" in understanding the statics and dynamics of liquid water, and important clues are emerging when one focuses on behavior in the deeply supercooled region, especially just above—and just below—the "critical" temperature $T_{\text{MCT}}$ predicted by mode coupling theory (MCT).

2. Statics: "What matters" is local tetrahedral geometry

2.1 Introduction

Liquid water is not a typical liquid. However, some progress has occurred in understanding its highly anomalous equilibrium and dynamical properties [1, 2, 3, 4]. Water is a space-filling hydrogen bond network, as expected from continuum models of water. However when we focus on the well-bonded molecules, we find that water can be regarded as having certain clustering features—the clusters being not isolated "icebergs" in a sea of dissociated liquid (as postulated in mixture models dating back to Röntgen) but rather patches of well-bonded molecules embedded in a highly connected network or "transient gel" [5, 6, 7, 8, 9, 10, 11]. Similar physical reasoning applies if we generalize the concept of well-bonded molecules to molecules with a smaller than average energy [12] or to molecules with a more ordered than average "local structure" [13].

2.2 Liquid-liquid phase transition hypothesis

A few years ago, Poole, Sciortino, and Essmann made computer simulations of the ST2 model of water, with the goal of exploring in detail what might happen in the low-temperature region [14]. What they discovered in computer water was the apparent existence of a second critical point $C'$, below which the liquid phase separates into two distinct phases—a low-density liquid (LDL) and a high-density liquid (HDL).

Although in experiments we cannot get closer than 5–15°, $C'$ nonetheless exerts a strong effect in the experimentally-accessible region of the phase diagram. If we have a singularity in our phase diagram at a well-defined critical point, it's going to have an effect on an entire region around it—a "critical region." The size of this critical region depends on the material, but it is usually somewhere between 10 percent and 100 percent above the critical temperature and pressure that response functions are significantly affected. It is not required that the system is exactly at its critical point for the system to exhibit remarkable be-
behavior, such as the phenomenon of critical opalescence discovered and correctly explained in 1869 by Andrews [15] in terms of increased fluctuations away from (but close to) the critical point. It is for this reason that critical phenomena are particularly interesting.

2.3 Experimental work

When liquid water is supercooled below the homogeneous nucleation temperature \( T_H \) (\(-38^\circ\text{C}\) at \( P = 1\) atm), crystal phases nucleate homogeneously, and the liquid freezes spontaneously to the crystalline phase. Mishima creates 1 cm\(^3\) high-pressure ices in a piston-cylinder apparatus, decompresses the sample at a constant rate of 0.2 GPa/min, and—because melting is endothermic—observes melting transitions of the ice polymorphs using a thermocouple to detect a change in the sample temperature during the decompression [16, 17]. He then determines melting pressures at different temperatures. The melting curves he obtains agree with previously-reported data for stable melting lines [18, 19], and extend our knowledge of the location of metastable melting lines to much lower temperatures.

The Gibbs potential \( G \) of the ice polymorphs is known. Since \( G \) is identical in coexisting phases, locating the melting lines of the ice polymorphs is sufficient to learn \( G \) for water along these lines. By interpolating data for \( G \) obtained along these melting lines, one can find the approximate experimental \( G \) for a wide range of temperatures and pressures in the no-man’s land below \( T_H \) [16]). After finding \( G \) as a function of pressure \( P \) and temperature \( T \), one can find by differentiation the volume as a function of \( P \) and \( T \). Volume as a function of \( T \) is just what we want—this is the equation of state of liquid water. The P-V-T relation found is consistent with the existence of a line of first-order liquid-liquid transitions which continues from the line of low-density amorphous - high-density amorphous transitions and terminates at an apparent critical point \( C' \). The P-V-T relation is also consistent with other known experimental data [20, 21, 22, 23, 24, 25, 26] and also with a number of theoretical and simulation results [13, 14, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36].

2.4 Theoretical work

The most natural response to the concept of a second critical point in a liquid is bafflement—such a thing just does not make sense. To make the concept more plausible, we offer the following remarks. Consider a typical member of the class of intermolecular potentials that go by the name of core-softened potentials [37, 38, 39]. Recently such potentials have
been re-visited [28, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53]; they are attractive to study because they can be solved analytically in one-dimension and are tractable to study using approximation procedures (and simulations) in higher dimensions. They are also more realistic than one might imagine at first sight, and indeed may reflect "what matters" in water-water interactions, since the repulsive soft core mimics the effect of the small number (4) of nearest neighbors in liquids with a local tetrahedral structure. Although such a picture may seem to be oversimplified, it is consistent with neutron data [22, 23, 24, 25].

Also, simulation results are in good accord with neutron results (see, e.g., [54]), and Sasai relates these two distinct local structures to dynamic properties [55].

One can characterize (or at least "caricature") the local structural heterogeneities that appear in liquid water by simulations. Specifically, Canpolat and collaborators [56] considered state points of liquid water at different pressures—especially near its phase boundaries with ice Ih and with ice VI. In the spirit of the "Walraffen pentamer," they develop a model of interacting water pentamers, and find two distinct local energy minima which they identify with two well-defined configurations of neighboring pentamers. The "Walraffen pentamer" is defined by four water molecules located at the corners of a tetrahedron that are hydrogen-bonded to a central molecule—see, e.g., [57, 58]; the corner molecules are separated from the central molecule by 2.8Å, corresponding to the first peak in the oxygen-oxygen radial distribution function. Canpolat and collaborators advance the hypothesis that these configurations may be related to the local "high-density" and "low-density" structural heterogeneities occurring in liquid water.

2.5 Outlook

Before concluding this brief discussion of statics, we ask "What is the requirement for a liquid to have such a second critical point?" By the arguments presented above, some other liquids should display second critical points, namely systems that at low temperature and low pressure have anticorrelated entropy and specific volume fluctuations. Thus a natural extension to our work is to consider other tetrahedrally-coordinated liquids. Since other tetrahedral liquids have that similar features, we might anticipate similar critical points occur on the liquid free energy surface of these liquids. Evidence in favor of this possibility has been reported for SiO2 [59, 60], amorphous GaSb [61, 62], C [63, 64], and Si [65]. Recently, clear experimental evidence for a liquid-liquid phase transition has been reported in phosphorus, where the low-
density liquid phase is a molecular liquid of tetrahedral P₄ “molecules” [66, 67]. With a change in pressure, the low-pressure, low-density molecular liquid transforms to a high-pressure, high-density polymeric liquid. During the transformation, two forms of liquid coexist, showing that phosphorus has a first-order liquid-liquid phase transition.

3. Dynamics on the potential energy landscape: “What matters” is the number of diffusive directions

3.1 Introduction

The study of the dynamics in supercooled liquids is receiving great interest [68] due novel experimental techniques [69, 70], detailed theoretical predictions [71], and by the opportunity to follow the microscopic dynamics via computer simulation [72, 73]. MCT [71] quantitatively predicts the time evolution of correlation functions and the dependence on temperature T of characteristic correlation times. Unfortunately, the temperature region in which MCT is able to make such predictions for the long time dynamics is limited to weakly supercooled states. Parallel with the development of MCT, theoretical work [74, 75, 76, 77, 78] has called attention to thermodynamic approaches to the glass transition, and to the role of configurational entropy in the slowing down of dynamics [79, 80, 81]. These theories, which build on ideas put forward some time ago [82, 83, 84], stress the relevance of the topology of the potential energy landscape (PEL) explored in supercooled states. Detailed studies of the PEL may provide insights into the slow dynamics of liquids, and new ideas for extending the present theories to the deep supercooling regime.

3.2 Instantaneous normal modes and the topology of the PEL

One approach to understanding the role of the PEL is to study the connectivity between different local configurations using the instantaneous normal mode (INM) formalism [85]. Analogous to the standard normal mode theory for solids, an INM is the eigenfunction of the Hessian, which is the matrix of the second derivatives of the potential energy with respect to all 6N atomic coordinates. In a liquid state, the eigenvalues of the Hessian matrix are not all generally positive; the negative eigenvalues indicate a downward curvature of the PEL, i.e., indicate unstable directions for the system. Previous studies using the INM formalism indicate that the number of directions with negative curvature is
reduced on cooling, motivating theories relating diffusion in liquids to the INM density of states [86, 87]. Low temperature liquid dynamics involve the superposition of fast oscillations around quasi-equilibrium positions (intra-basin motion) and the rearrangement of the system between these positions (inter-basin motion). The typical oscillation period is much shorter than the typical time needed by the system to rearrange itself, i.e., the structural relaxation time. INM theories for diffusion relate the diffusion of the system in configuration space to activated processes of inter-basin motion. In this respect, the unstable modes are considered representative of the barriers crossed when the system changes basins.

Figure 1. Schematic sketch of the possible shapes of the PEL associated with imaginary eigenvalues. Unstable modes are first separated into shoulder and double well modes. Furthermore, double well modes are split into diffusive and non-diffusive ones. Adapted from Ref. [89].

One approach [88, 89] among many [90, 91] for separating the diffusive modes (basin changes in configuration space) from the non-diffusive modes (no basin changes) is classifying the modes according to their potential energy profile (Fig. 1), and partition those unstable modes into two groups: (i) unstable normal modes due to the anharmonicities
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(shoulder modes) and (ii) modes along which the system is crossing a saddle (double-well modes) [90]. In order to distinguish between shoulder and double-well modes, the potential energy profile is calculated along straight paths that follow the direction of the eigenvector. Furthermore, to distinguish the false and true double wells, we calculate the steepest descent trajectories starting from the opposite sides of the saddle. A mode represents true double well, called a diffusive mode, if these trajectories end up in two distinct local minima.

3.3 Results

Next we discuss the numerical relationship between $D$ and the number of diffusive modes $f_{\text{diff}}$ in the vicinity of the fragile-to-strong crossover temperature $T_X$. We review recent work on two different models of tetrahedral liquids, the SPC/E extended simple point charge model for water [89, 92] and the BKS model of silica [93]. For silica (Fig. 2), the fragile-to-strong transition temperature $T_X$ coincides numerically [93, 94, 96] with the critical temperature $T_{\text{MCT}}$ identified by MCT. For both models, it appears that $D$ depends on $T$ and $P$ only through $f_{\text{diff}}$—the analog of the magnetization $M(H,T)$ of a ferromagnet depending on magnetic field $H$ and temperature $T$ only through the correlation length $\xi$. Specifically, for both models it appears that $D$ follows a general power-law relation of the form

$$D/T \sim (f_{\text{diff}})^\alpha,$$

for roughly two decades in $f_{\text{diff}}$ and three decades in $D/T$. For the water model, $\alpha \approx 2$ while for the silica model it appears that $\alpha \approx 1.3$. In the case of silica, the identical functional form describes the relationship between $D$ and $f_{\text{diff}}$ both above and below $T_X$, showing that while the $T$ dependence of both $D$ and $f_{\text{diff}}$ is sensitive to the microscopic mechanisms controlling the dynamics, the fragile-to-strong transition does not affect the relation between $D$ and $f_{\text{diff}}$. The exponent value $\alpha = 2$ found for water has recently been theoretically interpreted [95].

In summary, then, two different dynamical mechanisms affect the slowing down of the dynamics in supercooled states [89]:

(i) In the weakly supercooled region, the slowing down of the dynamics arises from the progressive reduction in the number of directions where free exploration of configuration space is possible. The system is always located close to a multi-dimensional ridge between different basins, and the time scale of the long-time dynamics is set by the time required to probe one of the free directions. In this
Figure 2. Arrhenius plot of (a) the diffusion constant $D$ for Si atoms in SiO$_2$ and (b) $f_{\text{diff}}$. The crossover to the straight line Arrhenius behavior below $T_x$ represents the fragile-to-strong crossover for silica. Part (c) shows the parametric relation $D/T$ vs $f_{\text{diff}}$ in a log-log scale. The data are smooth through the "mode-coupling" crossover temperature $T_x$. Adapted from Ref. [93]
range of $T$, the diffusion is not limited by the presence of energy barriers that must be overcome by thermally activated processes, but is controlled by the limited number of directions leading to different basins along almost constant potential energy paths. Furthermore, the number of free directions completely determines the value of $D$, independent of the thermodynamic parameters $T$ and $\rho$.

(ii) Close to $T_{\text{MCT}}$, the system starts to sample regions of configuration space that have no free directions. The change in the dynamics above and below $T_{\text{MCT}}$ can be viewed as a change in the properties of the PEL sampled in equilibrium, from configurations always close to a ridge of progressively lower and lower dimension to configurations far from any ridge [96, 97]. Below $T_{\text{MCT}}$, the system must go close to the ridge and then select the right direction. The search for the ridge below $T_{\text{MCT}}$, i.e., the search for a rare event, can be probably described as an activated process, which corresponds to Arrhenius behavior of the diffusion constant.

(iii) The relation between connectivity and number of local minima in the PEL—which can be calculated in theoretical models as recently done for the random energy model [98]—may help build on the existing ideas bridging thermodynamics and dynamics [99].

4. Dynamics below the MCT: “What matters” is cooperative motion

4.1 Introduction

As a supercooled liquid is cooled toward the glassy state, the system is increasingly found near local potential energy minima, called inherent structure configurations [82]. In this description, in the glassy state, the system is localized in one of the potential energy basins [94, 100, 101, 102]. While such a picture of liquid dynamics is difficult to verify experimentally, computer simulation offers an excellent opportunity to explore these ideas. For a pre-defined liquid potential, a liquid trajectory can be generated via molecular dynamics simulation and the local potential energy minima can be evaluated by an energy minimization method [82]. With this procedure, the motion in phase space is converted into a minimum-to-minimum trajectory, or inherent structure trajectory. A general picture of the system moving among a set of basins surrounding the multitude of local minima has evolved. More specifically, simulations have shown that both the depth of the minima sampled by the system, as well as the number of these minima, decrease on cooling [102, 103].
Figure 3. (a) Displacement of each of the 216 molecules during the course of a transition from one inherent structure to another. (b) Distribution of displacements $u$ of the oxygen atoms between inherent structure changes, $P(u)$, sampled along a 30 ns trajectory in 20,000 inherent structure changes. The exponential tail of $P(u)$, with a characteristic length of about 0.02 nm, is mostly due to the highly mobile molecules, while the power law with exponent 2.5 would correspond to an "elastic" response of the system to these highly mobile molecules [115]. Adapted from Ref. [105].

The description of the real motion of the system as an inherent structure trajectory becomes a powerful way of separating the vibrational contribution, responsible for the thermal broadening of instantaneous measurements from the slow structural component [104]. Such an approach becomes even more powerful below $T_{\text{MCT}}$, since most of the instantaneous configurations are far from saddles, making correlation functions calculated from the inherent structure trajectory fully account for the $\alpha$-relaxation dynamics [100].

4.2 Results

Recent results [105] are based on molecular dynamics simulations of the SPC/E model [106] of water for 216 molecules, at fixed density $\rho = 1 \text{ g/cm}^3$. The numerical procedure is described in Ref. [107]. The
Figure 4. Snapshot of the system in one IS. Only the eight molecules with displacement larger than 0.025 nm [Fig. 3(a)] are shown here. Hydrogen-bonded molecules are connected by tubes. Note that all 8 molecules are nearby and form a cluster, which unlike the Lennard-Jones case, are bounded and less string-like. Adapted from Ref. [105].

Trajectories are analyzed at $T = 180$ K, and the mode coupling temperature for this density is $T_{MCT} = 193.6$ K [107], so the system is in the deep supercooled liquid state. At this temperature, the diffusion coefficient is four orders of magnitude smaller than its value at $T = 300$ K and only a few molecules move significantly (with displacements larger than 0.025 nm) at each simulation time step.

To aid in understanding the distribution of the displacements during the IS changes, Fig. 3(a) shows the displacements $u$ of all 216 individual molecules for a typical inherent structure transition. In fact, there is a relatively small set of molecules with a large displacement. A snapshot of the eight molecules with the largest displacement is shown in Fig. 4. Interestingly, this set of molecules forms a cluster of bonded molecules. Indeed, for all cases studied, the set of molecules which displace most forms a cluster of bonded molecules. The observed clustering phenomenon characterizes the inherent structure transitions in water and can be interpreted as the analog of the string-like motion observed in simple atomistic liquids [100], connected to the presence of dynam-
ical heterogeneities [108, 109, 110, 111]. Similar results were found by Ohmine et al. using the TIP4P and TIPS2 models for water [112].

To characterize the distribution of individual molecular displacements between different inherent structures more carefully, Fig. 3(b) shows the distribution of displacements u of the oxygen atoms P(u). Note that P(u) was previously studied by Schroder et al. for a binary Lennard-Jones mixture [100].

Analysis of the changes in hydrogen bond connectivity associated with inherent structure changes reveals that these transitions are associated with the breaking and reformation of hydrogen bonds.

Reference [105] further shows that the transitions associated with an increase in the energy correspond to the breaking of linear bonds and to the simultaneous formation of bifurcated bonds [113, 114]. Similarly, the transitions associated with a decrease in the energy correspond to the breaking of bifurcated bonds and to the simultaneous formation of linear bonds. This result supports the hypothesis that the linear to bifurcated transition can be considered as an elementary step in the rearrangement of the hydrogen bond network.

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References

Unsolved problems of liquid water: Static and dynamic puzzles

NEW PHASE TRANSITIONS

Unsolved problems of liquid water: Static and dynamic puzzles


Erwin Mayer.
HIGH-DENSITY AMORPHOUS ICE AND ITS PHASE TRANSITION TO ICE XII

I. Kohl, T. Loerting, C. Salzmann, E. Mayer, A. Hallbrucker

Institute of General, Inorganic and Theoretical Chemistry
University of Innsbruck, A-6020 Innsbruck, Austria

Abstract

High-density amorphous ice, HDA, was heated in a pressure vessel with indium linings at constant pressures of between 0.52 to 1.9 GPa from 77 K up to 240 K. The formed phases were characterized by X-ray diffractograms of samples recovered under liquid N₂ at 1 bar. The metastable domain of ice XII thus revealed extends between \( \approx 158-212 \) K from \( \approx 0.7 \) to \( \approx 1.5 \) GPa, and is in a different region of water’s phase diagram than that shown by Koza et al. [Phys. Rev. Lett. 85, 334 (2000)]. When HDA, or hexagonal ice, is compressed without using indium linings, ice XII can form even when the pressure vessel is immersed in liquid N₂, but it requires a pronounced apparent pressure drop at pressures \( \geq 1.1 \) GPa. These apparent pressure drops can be caused by buildup of friction. We propose that shock-waves generated by apparent pressure drops cause transient local heating up to the temperature range of the ice XII metastable domain, and that this induces nucleation and crystal growth. Pressure-displacement curves obtained on compression of ice Ih are consistent with formation of ice XII from HDA only, and not from ice Ih.

1. Introduction

Studies of the water/ice phase diagram and of the crystalline phases of ice, in which the water molecules form tetrahedral networks by hydrogen bonding, are important not only for further understanding of the hydrogen bond itself, but also for its relevance in the interaction of water molecules with biological structures. The polymorphic forms of ice illustrate the structural variety possible for the hydrogen-bonded polymers of four-coordinated water [1]. The recent discovery of a new phase of ice, crystallizing in the much investigated medium pressure range [2], came as a surprise. This new high-pressure phase of ice, called ice XII, was
first prepared by Lobban et al. [3], by slow crystallization from the liquid phase at 260 K at a pressure of 0.55 GPa, which is within the stability region of ice V [2]. Ice XII “contains only seven- and eight-membered rings and is the first example of a 4-connected net of this type” [4]. Ice XII is metastable with respect to ice V [5], like metastable ice IV which is also found within the stability region of ice V [2, 6, 7, 8], and its density is similar to that of ice IV [3].

Subsequently to its formation from the liquid phase, Koza et al. [9] reported formation of ice XII in a completely different region of water’s phase diagram, namely as an incidental product in the preparation of high-density amorphous ice (HDA) [10, 11, 12, 13] at 77 K on compression of hexagonal ice (ice Ih) up to 1.8 GPa. However, the decisive conditions favoring ice XII or HDA formation were not clear. In their study the relative amounts of HDA and ice XII were scattered more or less randomly. They concluded that they “have been unsuccessful in identifying a route that would predictably allow to separate the production of HDA from the production of ice XII.” Similar findings were later reported in an abstract by Hallbrucker [14]. In retrospect Bragg peaks of ice XII had been observed and reported before in samples prepared on compression of ice Ih for formation of HDA [15, 16, 17] and attributed to “some metastable form of high-pressure crystalline ice” [17], but they have not been assigned to a new phase of ice. Kohl et al. [18] then showed that in this route ice XII forms on compression of ice Ih at 77 K only via HDA, and not directly from ice Ih, and that its formation requires a sudden pronounced apparent pressure drop at pressures \( \approx 1.1 \) GPa. They further proposed that shock-waves generated by the apparent pressure drops cause transient local heating, and that this induces nucleation and crystal growth of ice XII.

Apparent pressure drops and shock-wave heating can be avoided by using indium linings [10, 11, 12, 13]. This allowed us to determine the metastable domain of ice XII by heating HDA at constant pressures of between 0.52 and 1.9 GPa from 77 K up to 240 K. The metastable domain of ice XII thus revealed lies in the ice VI domain and extends between \( \approx 158–212 \) K from \( \approx 0.7 \) to \( \approx 1.5 \) GPa [19]. Thus, the observation of a “second regime of metastability” of ice XII, postulated by Koza et al. [20] between 77 to \( \approx 150 \) K and 1.0 to 1.8 GPa in order to account for its unexpected formation on compression of ice Ih at low temperatures (see Fig. 1 in Ref. [20]), seems to be an effect of apparent pressure drops and shock-wave heating.

We note that several other high-pressure ice phases form on heating HDA under pressure [21, 22, 23], and on compression of ice Ih at various temperatures [13, 20, 24]. For example, Suzuki et al. [23] recently
reported that on heating HDA at 1.5 GPa up to 180 K, a high-pressure ice forms which they tentatively assumed to be either ice IV, ice VI or ice XII.

2. Experimental methods

HDA samples were prepared by compression of ice Ih at 77 K in a commercially available piston-cylinder apparatus with an 8 mm (up to 1.8 GPa) or 10 mm (up to 1.3 GPa) diameter piston (from Specac Company), and pressure-displacement curves were recorded with the TestXpert V 7.1 Software. Controlled compression was achieved with a computerized “universal testing machine” (Zwick, Model BZ100/TL3S). Samples were recovered after compression from the piston-cylinder apparatus under liquid N₂ and characterized by X-ray diffraction. The characterized HDA samples were thereafter reloaded under liquid N₂ into the piston-cylinder apparatus and compressed for a second time. The compressed samples were further characterized by differential scanning calorimetry. As reported recently [5], this allows to determine the relative amounts of HDA and ice XII more accurately than by evaluation of X-ray diffractograms. The isobaric HDA → ice XII phase transition was studied in a controlled manner by using indium linings as described in Ref. [18] to avoid pressure drops and transient shock-wave heating. X-ray diffractograms were recorded on a diffractometer in θ-θ geometry (Siemens, model D 5000, Cu-Kα), equipped with a low-temperature camera from Paar. The sample plate was in horizontal position during the whole measurement. Installation of a “Goebel mirror” allowed to record small amounts of sample without distortion of the Bragg peaks.

3. Results and discussion

We first show that compression of HDA without indium linings can lead to formation of ice XII even when the pressure vessel is immersed in liquid N₂, and that this requires an apparent pressure drop presumably causing transient shock-wave heating [18]. We then proceed to the HDA → ice XII phase transition and the metastable domain of ice XII which was determined by isobaric heating of HDA at pressures of between 0.52 and 1.9 GPa in the absence of apparent pressure drops by using indium linings [19]. Thus, indium has a pronounced effect because its malleability is high even at 77 K.

Figure 1 shows that HDA can transform on compression into ice XII. Figure 1a is the pressure-displacement curve obtained on compression of ice Ih at 77 K which is similar to curves reported, e.g., by Mishima et al. [10, 11] The plateau region between 1.11 and 1.35 GPa is due to the
Figure 1. Ice XII formation on compression of HDA at 77 K. (a) Formation and characterization of HDA as shown by the pressure-displacement curve of ice Ih and (b) X-ray diffraction pattern (Cu-\(K\alpha\)) of recovered HDA recorded at 1 zero pressure; (c) is the pressure-displacement curve of HDA compressed up to 1.8 GPa, and (d) the X-ray diffraction pattern of ice XII recovered after (c). Note the pressure drop at 1.23 GPa. (e) Pressure-displacement curve of HDA, with pressure drop at 0.86 GPa, and (f) X-ray diffraction pattern of HDA recovered after compression. Ice Ih peaks are marked by the asterisks. HDA was compressed without indium linings. (From Ref. [18].)
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phase transition of ice Ih to HDA. Figure 1b shows the characteristic X-ray diffraction pattern of a HDA sample which was recovered after compression under liquid N$_2$ at 1 bar. Bragg peaks marked with asterisks are from a small amount of ice Ih condensed onto the sample during the transfer. The diffraction curve is shown only up to $2\theta = 43^\circ$, because intense peaks from the substrate interfere at higher $2\theta$ values. Therefore, the shoulder on the HDA peak at high $2\theta$ values is not observable [10, 11, 15]. This HDA sample was subsequently compressed and Fig. 1c shows the pressure-displacement curve, with a pronounced pressure drop at 1.23 GPa. The compressed material was thereafter identified by its X-ray diffraction pattern as nearly pure ice XII (Fig. 1d), contaminated only with a small amount of ice Ih (marked with asterisks). In a further experiment, a pressure drop on compression of HDA up to 1.5 GPa occurred at 0.86 GPa, but the recovered phase was unchanged HDA (cf. Figs. 1e and 1f). Apparently it requires not only a pressure drop, but also a minimum pressure for inducing formation of ice XII.

The curvatures at the beginning of all three pressure-displacement curves is due to densification of ice Ih on first compression (Fig. 1a) or of the HDA pieces filled into the piston cylinder apparatus (Figs. 1c and 1e). These curvatures are followed by fairly straight lines: for Figure 1a this indicates compression of ice Ih until its phase transition to HDA starts at 1.11 GPa, for Figs. 1c and 1e it indicates compression of HDA.

In Fig. 2 we show that pressure-displacement curves of ice Ih samples are also consistent with formation of ice XII from HDA, and not directly from ice Ih. In the pressure-displacement curve of ice Ih shown in Fig. 2a the second, intense, pressure drop occurs at 1.08 GPa. The recovered phase characterized by X-ray diffraction is some untransformed ice Ih (Fig. 2b, marked with asterisks) and HDA. In the pressure-displacement curve of another ice Ih sample shown in Figure 2c the pressure drop occurs at 1.29 GPa. The recovered phase now is nearly pure ice XII (cf. Fig. 2d) containing only a small amount of ice Ih. Thus ice XII is formed on pressure drop only when conversion of ice Ih to HDA had already occurred. From the shape of these pressure-displacement curves we conclude that for Fig. 2c the ice Ih→HDA transition had been nearly completed when the pressure drop occurred at 1.29 GPa. However, for Fig. 2a the pressure drop at 1.08 GPa occurred at the beginning of the transition, and further compression without pressure drop resulted in formation of HDA and not of ice XII.

In our experience the decisive factor for formation of ice XII on compression of HDA at 77 K is a massive apparent pressure drop at a sufficiently high pressure. This pressure drop is caused by sudden release of friction. Build-up of friction between the piston and the pressure vessel
containing ice Ih and/or HDA can occur because the sample creeps on compression between piston and pressure vessel [25]. To minimize or avoid this friction build-up, Mishima et al. [10, 11, 12, 13] held samples enclosed in an indium cup. Sudden release of friction generates a shockwave which causes the enormous bang and presumably heating of the sample. Johari [26] reported that in his studies of compression of ice Ih “the sudden release of the mechanical energy also produces a spike of temperature from 77 K up to ≈ 170 K, lasting for only a few seconds, as indicated by the thermocouple inserted into the plug and kept ≈ 1 mm away from the ice sample.” This temperature then is within the metastable domain of ice XII shown in Fig. 3.

Shock wave generation is a necessary requirement for formation of ice XII at 77 K bath temperature on compression of ice Ih, or HDA, but it is not sufficient: Figs. 1e and 1f show that HDA has to be com-
pressed above 0.86 GPa before a pressure drop induces formation of ice XII. The threshold value necessary for ice XII formation estimated from these pressure-displacement curves is $0.86 < \leq 1.23$ GPa. In a further experiment (not shown) HDA was transformed on compression by a pressure drop at 1.1 GPa which narrows the range of the threshold value. On compression of HDA its density increases in a nearly linear manner [10, 11, 25]. Thus, it is really the density of HDA which has to be above a threshold value before a shock wave can induce formation of ice XII.

In a next step we determined the (meta-)stability domain of ice XII by isobaric heating of HDA at pressures of between 0.52 and 1.9 GPa in the absence of apparent pressure drops by using indium linings [19]. The experimental evidence is shown in Figure 2 of Ref. [19] in form of isobaric volume change versus temperature plots, and of X-Ray diffractograms of samples recovered at 77 K and 1 bar. Figure 3 shows our

**Figure 3.** The medium pressure range of the phase diagram of water/ice. The empty circle in the ice V domain denotes the region where ice XII formed from the liquid [3]. The hatched region indicates the $p, T$ region where ice XII was observed in our study [19]. Vertical arrows below the pressure axis indicate the pressures used for isobaric heating of HDA by using indium linings. Full circles characterize the temperature region where ice XII formed from HDA, and empty circles denote the region of its phase transition to another high-pressure phase. Full and empty triangle indicate where at 0.52 GPa ice V and ice II are formed, and the full square indicates formation of ice VI from HDA at 1.91 GPa. Horizontal broken arrows indicate for comparison the temperatures used by Koza et al. [20] for isothermal compression of ice Ih. (From Ref. [19]')
results within the relevant part of water’s phase diagram, and the difference to the approach applied by Koza et al. [20]. The empty circle in the ice $V$ domain indicates the region where ice XII was first obtained from the liquid [3]. Vertical arrows on the pressure axis indicate the pressures at which we heated HDA isobarically from 77 K at a rate decreasing from $\approx 6$ to $\approx 1.5 \text{ Kmin}^{-1}$. Formation of ice XII is indicated by full circles, and its phase transition to ice VI on further heating by empty circles. The hatched region in between thus constitutes the $p,T$ area where (meta-)stable ice XII can exist. For comparison Koza et al.’s [20] approach, which they presumed to be isothermal, is indicated on the temperature axis by horizontal dotted arrows. At these temperatures, and additional temperatures of 77 and 100 K, samples of ice Ih were pressurized up to 1.8 GPa. Koza et al. [20] report that “the observation of explosive sound accompanied by abrupt loss of pressure indicates the development of shock waves during the compression which could play a major role in the transformation process.” Due to the nature of their experiments, transition pressures and temperatures can not be determined unambiguously, and their postulated “second regime of metastability” of ice XII lies below the temperature scale of Fig. 3.

It is intriguing that HDA transforms over such a wide range of pressures first into ice XII before on further heating stable ice VI is formed. Figure 2 in Ref. [19] demonstrates that HDA densifies further on isobaric heating before its phase transition to ice XII occurs. In a similar manner, Figure 1 shows that HDA requires at 77 K a minimal pressure of $\approx 1.1$ GPa, or a minimal density, before pressure drop and shock-wave heating can lead to formation of ice XII. According to Mishima et al. [10, 11] the density of HDA at 77 K and 1.0 GPa is $1.31 \pm 0.02 \text{ g/cm}^{-3}$, and an even higher density results on isobaric heating of HDA at 1.1 or 1.9 GPa (see Fig. 2 in Ref. [19]). Thus, the density difference between low-density amorphous ice (LDA) and HDA at 77 K and 1 bar is similar to that of the latter and, for example, HDA at 1.0 GPa and 150 K, shortly before its phase transition to ice XII. Therefore, the structural state of densified HDA at a density of $\geq 1.31 \text{ g/cm}^{-3}$ has to be considered in attempts to understand the HDA$\rightarrow$ice XII phase transition in terms of local structural elements. X-Ray [15, 16] and neutron [17] diffraction studies of the structure of HDA do not seem to be helpful here because they were done at 1 bar, and the density of HDA at this pressure is only $1.17 \pm 0.02 \text{ g/cm}^{-3}$ [10, 11]. The problems in interpreting the structures of LDA and HDA on the basis of the available diffraction data are lucidly illustrated by Pusztai [27].
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References

STRUCTURE AND DYNAMICS OF CONFINED WATER

Marie-Claire Bellissent-Funel
Laboratoire Léon-Brillouin (CEA-CNRS)
CEA Saclay, 91191 Gif-sur-Yvette cedex, France

Abstract
This paper accounts for recent results about structure and dynamics of confined water obtained by neutron scattering and molecular dynamic simulations. First we recall the structural results obtained by x-ray and neutron diffraction on supercooled and glassy water. We compare the structure of water confined in a porous silica glass to that of water in supercooled and glassy states. Second the dynamics of confined water is interpreted in terms of the relaxing cage model. The nucleation properties of water as well as the dynamics are modified, particularly when the level of hydration of the porous medium decreases down to a monolayer of water molecules.

1. Introduction

The structural properties of water are now mostly well understood in some range of temperatures and pressures using different techniques such as X-ray diffraction [1-3], neutron scattering [4-11], molecular dynamics (M-D) [12-18], and Monte Carlo (MC) [19] simulations. The number of models of its structure is very large and the number of experimental results enormous. The result for such an interest lies on the fact that water has unusual physical and chemical properties due mainly to the presence of H-bonds. An illustration is given by the phase diagram of water [20] presented in Fig. 1.

The polymorphism of water is indeed remarkable and besides all these crystalline phases one must add two amorphous solids, the low density amorphous ice (LDA) and the high density amorphous ice (HDA). The microscopic structure of these two forms of amorphous ice has been studied both by X-ray [21,22] and neutron scattering [23] as well as the low density amorphous ice, prepared by different techniques [24-27].
this paper, we compare the structure of confined water with that of supercooled water and amorphous ice. Then we report on some unusual nucleation and dynamic properties of water confined in a porous silica glass.

2. Theory

For a molecular liquid, the structure factor may be split into two parts [28]:

\[ S_M(Q) = f_1(Q) + D_M(Q), \quad (1) \]
where \( f_1(Q) \) is defined as the molecular form factor

\[
f_1(Q) = \frac{b_0^2 + 4b_Ob_Dj_0(Qr_{OD})e^{-\gamma DDQ^2} + 2b_D^2j_0(Qr_{DD})e^{-\gamma DDQ^2}}{(b_O + 2b_D)^2}.
\] (2)

The \( D_M(Q) \) function contains all the intermolecular contributions. Thus, at large \( Q(Q > 8 \text{Å}^{-1}) \), the main contribution to \( S_M(Q) \) comes from \( f_1(Q) \) whereas \( D_M(Q) \) goes to zero.

Moreover, at \( Q = 0 \), \( f_1(Q) \) is equal to unity and the interference function \( S_M(Q) \) has the thermodynamic limit \( S_M(0) = \rho_Mk_BT\chi_T \), where \( \rho_M \) is the density, \( k_B \) the Boltzmann constant, \( T \) the temperature, and \( \chi_T \) the isothermal compressibility.

The total pair correlation function \( g(r) \) is related to the Fourier transform of \( S_M(Q) \) by the relation:

\[
4\pi\rho_M(g(r) - 1) = \frac{2}{\pi} \int_0^\infty Q(S_M(Q) - S_M(\infty)) \sin(Qr)dQ,
\] (3)

where \( S_M(\infty) = (b_0^2 + 2b_O^2)/ (b_O + 2b_D)^2 = 0.3346 \) is the asymptotic value of \( f_1(Q) \) at large \( Q \) and \( \rho_M \) is the molecular density.

The function \( g(r) \) is a combination of the different pair partial correlation functions and includes both the intramolecular and intermolecular distances. It is more convenient to remove the intramolecular terms by subtracting the molecular form factor from \( S_M(Q) \) to obtain \( D_M(Q) \), which may be Fourier transformed in order to obtain the pair correlation function \( g_L(r) \) for intermolecular terms only:

\[
d_L(r) = 4\pi\rho_M(g_L(r) - 1) = \frac{2}{\pi} \int_0^\infty QD_M(Q) \sin(Qr)dQ.
\] (4)

In this way, no truncation effect arises; moreover the first peaks due to the intramolecular distances disappear in the low \( r \) range.

The composite \( g_L(r) \) function is thus defined as:

\[
g_L(r) = 0.489g_{DD}(r) + 0.421g_{OD}(r) + 0.90g_{OO}(r),
\] (5)

where the dominant contributions concern the \( DD \) and \( OD \) spatial correlations.

3. The microscopic structure of water

3.1 Amorphous ices

We report on the amorphous state of water that has been obtained by compressing \( I_h \)-ice to high pressure at 77 K [26]. On pressure relaxation,
the transition is not reversible and the phase which took place at pressure higher than 11 kbar can be recovered at atmospheric pressure. Since this amorphous form has a density equal to 1.17 gcm\(^{-3}\) at normal pressure, this new variety is labeled high-density amorphous ice in contrast with the low density form obtained from vapor or liquid state. This high density form has also been prepared from the low density amorphous ice [27].

3.1.1 X-ray scattering study [21-22]. The X-ray data have been collected by use of a standard \(\theta - 2\theta\) diffractometer operating in the transmission mode with a monochromated Mo\(_{\alpha}\) radiation (\(\lambda = 0.7093\) \(\text{Å}\)). The structure factor \(S_M(Q)\) versus the momentum transfer \(Q\) (\(Q = 4\pi \sin(\theta) / \lambda\), where \(2\theta\) is the diffraction angle) has been determined after the usual corrections, the water molecule being treated as a spherical entity.

The pair correlation function \(g(r)\) of the molecular centres (which can be assimilated to the oxygen atoms) is calculated by Fourier transformation of \(S_M(Q)\) according to the relation:

\[
g(r) = 1 + \frac{1}{2\pi^2 \rho_M} \int Q[S_M(Q) - 1]M(Q) \sin(Qr) dQ, \tag{6}\]

where \(\rho_M\) is the number density of the sample and \(M(Q)\) a damping function [21-22].

a) Low density amorphous water: the structure factor of the phase formed after heating the high-density amorphous sample at 140 K and subsequently cooled to 77 K is shown in figure 2a. It is very similar to those of a sample obtained either from vapor deposition on a cold substrate [29] or by hyperquenching of water [24].

b) Figure 3a displays the weighted function \(d_L(r) = 4\pi r \rho_M [g(r) - 1]\) of the low-density amorphous ice. One can see that the first nearest neighbours, located at the mean value \(r = 2.8\) \(\text{Å}\), are clearly separated from the second ones; the coordination number is equal to 4.0. The second nearest neighbours distance, around 4.6 \(\text{Å}\), indicates a local tetrahedral hydrogen-bonding network of the water molecules, with an angle O-O-O of about 109°.

c) High-density amorphous water: figure 2b shows the structure factor of the phase obtained after compression of \(I_h\) ice and decompression to zero pressure, at 77 K: clearly, no evidence for long-range structural order can be detected which is the proof that the transition crystal \(\rightarrow\) amorphous solid has been achieved under pressure. Compared to the data shown in fig.2a, \(S_M(Q)\) exhibits dramatic differences both in the shapes and in positions of the first two peaks in the low- \(Q\)-range. On the contrary,
the structure factors of both forms of amorphous ices are quite identical for $Q > 7\text{Å}^{-1}$; this feature involves a similar nearest neighbouring. Indeed, the weighted function $4\pi r \rho_M[g(r) - 1]$ (fig. 3b) shows that the first neighbours are located at 2.8Å and that the tetrahedrally-bonded structure persists as in the low-density form. However, the second shell is broad and split into two peaks located near 3.7 and 4.65Å: the distribution of the molecular centres at the level of the second shell involves distortion and a complexity in the packing of the tetrahedral entities.
3.1.2 Neutron scattering study [23]. The measurements have been performed at the Reactor Orphée of the laboratoire Léon Brillouin at Saclay, on the 7C2 spectrometer. The wavelength used $\lambda = 0.70\text{Å}$ allowed us to cover a $Q$ range extending from 0.3 to $16\text{Å}^{-1}$. All measurements were performed at 77 K. For each measurement, the temperature was increased until the desired transition was apparent and then reduced to 77 K and kept constant during the run. Figure 4 gives the structure factors $S_M(Q)$ relative to low density and high density amorphous ices. Figure 5 shows the functions $d_L(r)$ for the same two forms of water.

a) Low density amorphous ice: the weighted function $d_L(r)$ (fig.5a) is characterized by structural peaks which are well identified up to the second neighbour shell, a deep minimum at 6.5Å, and oscillations ex-
Figure 4. The structure factor $S(q)$ of amorphous $D_2O$ ice at 77K as determined by neutron scattering a) low density form; b) high density form [23].

tending far beyond these distances. The interatomic distances are very close to those found in an ideal tetrahedral symmetry with the oxygen-oxygen distance around 2.8Å and the intramolecular distance O-D equal to 0.97Å [23]. The hydrogen bond distance is close to 1.80Å showing that each deuterium atom is close to the alignment O-D.

The comparison between the experimental $d_L(r)$ for low density amorphous ice and that of supercooled water at $-10.5^\circ$ C and $-31.5^\circ$ C [30] is given fig. 7. Let us only mention that in the last case, $d_L(r)$ presents some features characteristic of amorphous ice, which shows that we have
at this low temperature, an increase effect of hydrogen bonding, leading to a greater spatial correlation between second and third-bonded molecules. The fully hydrogen bonded network which is present in the low density amorphous ice is therefore a natural end product of the structural evolution of the system with decreasing temperature if crystallisation can be suppressed. An appropriate description of the structure of low density amorphous ice has been given in terms of a continuous random network model [31]. In this model the basic building unit is a water pentamer. This is equivalent to a description of the molecular arrangement in water by a continuous random network of tetrahedrally coordinated H-bonds [31].

b) High density amorphous ice: the weighted function $d_L(r)$ (fig.5b) of the high density form is completely different from that of the low density form. Beyond the first neighbours distance, a very broad peak is present at 3.35 Å and a minimum exists at 5.0 Å, i.e. in the region where there is a maximum for the low density form. The intermolecular O-O distance appears as a shoulder at 2.8 Å and is in agreement with the X-ray scattering.

From the analysis of the data, it can be inferred that the deuterium atoms are not in the O-O alignment and that the intramolecular angle DOD is around 106°, i.e. about 4° smaller than the regular tetrahedral angle. We interpret the pair correlation function $d_L(r)$ of the high-density form of amorphous ice by the loss of the main O-O-O angular correlations; at normal pressure, this function looks close to that of liquid water at high temperature [11].

3.2 Supercooled water [32]

3.2.1 Structure factors $S_M(Q)$. Figure 6 gives the structure factors of supercooled water [30], at respectively, −10.5° C and −31.5° C as compared with that of low density amorphous ice. When the temperature is decreased it appears that the main peak position $Q_0$ of the structure factor of supercooled water tends toward the value 1.69 Å which is characteristic of low density amorphous ice [23].

3.2.2 Pair correlation functions $d_L(r)$. The composite pair correlation functions of supercooled water [30] at −10.5° C and −31.5° C are displayed in figure 7 and compared with that of low density amorphous ice [23].

At −31.5° C, in the small-$r$ range, some features characteristic of low density amorphous ice show up. In particular, the O-D hydrogen bond distance at 1.82 Å, and the D-D intermolecular distance at 2.31 Å are present. In the large-$r$ range one observes additional small oscillations
Figure 5. The weighted pair correlation function $d_L(r)$ of amorphous $D_2O$ ice at 77K as determined by neutron scattering: (b) low density form as compared with supercooled water at $-31.5^\circ$ C (a); (d) high density form as compared with room temperature water (c) [23],

which are not present at $-10.5^\circ$ C and an out of phase behaviour of the broad oscillations for values of $r$ higher than 10 Å. These features are similar to those observed in low density amorphous ice.

At normal pressure and low temperature, the measurements confirm the increasing spatial correlations in deeply supercooled water as the temperature is decreased and the tendency to evolve toward the structure of low density amorphous ice. In supercooled water, the structure present between 4.5 and 6.0 Å is connected to the formation of tetrahedrally coordinated patches [31]. It is clear that such patches are not present in the high pressure liquid water, either because the hydrogen
Figure 6. Structure factors $S_m(Q)$ of supercooled $D_2O$, at normal pressure, as compared with that of low density amorphous ice (LDA) at 77 K [30].

bonds are broken, i.e. the molecular energy is on average too low or, more likely because the hydrogen bond network is distorted.
4. Microscopic structure of confined water

Water in confined space has attracted a considerable interest in the recent years. It is commonly believed that the structure and dynamics of water are modified by the presence of solid surfaces, both by a change of hydrogen bonding and by modification of the molecular motion which depends on the distance of water molecules from the surface.

Among the hydrophilic model systems, let us mention clay minerals [33-34], and various types of porous silica [35-36]. In the last case, the authors have interpreted their results in terms of a thin layer of surface
water with more extensive H-bonding, lower density and mobility and lower nucleation temperature as compared to bulk water.

We present now results about the structure of water confined in a Vycor glass [37] which is a porous silica glass, characterized by a quite sharp distribution of cylindrical interconnected pores, and hydrophilic surfaces. We present here some of our results which have been obtained as functions of level of hydration from full hydration (0.25g water/g dry vycor) down to 25% and temperature [38-39]. Based on the information that the dry density of Vycor is 1.45 g/ml, the porosity 28% and the internal cylindrical pores of cross sectional diameter 50Å, the 50% hydrated sample has 3 layers of water molecules on its internal surface and a 25% hydrated sample corresponds roughly to a mono-layer coverage.

Results for two levels of hydration of Vycor demonstrate that the fully hydrated case is almost identical to the bulk water and the partially hydrated case is of little difference. However, the three site-site radial correlation functions are indeed required for a sensible study of the orientational correlations between neighboring molecules [40]. An interesting feature is that we observe like in the differential analysis measurements, supercooling of water to a much lower temperature of $-27^\circ$ C in a partially hydrated samples compared to a fully hydrated sample ($-18^\circ$ C) [38]. It seems that the confinement of the water favors the nucleation of cubic ice which appears superimposed on the spectrum of liquid water and whose proportion can be deduced from the intensity of the (111) Bragg peak. The proportion of cubic ice increases with decreasing temperature. In fact, at $-100^\circ$ C, the spectrum of confined water looks similar to that of cubic ice (Fig. 8). This is in sharp contrast to bulk water which always nucleates into hexagonal ice. In Fig. 9, we show a spectrum which gives a clear evidence of water which is present below the Bragg peaks at $-18^\circ$ C obtained by subtraction of the weighted spectrum of the same sample cooled down to $-100^\circ$ C.

Results relative to a 25% hydrated Vycor sample indicates that, at room temperature, interfacial water has a structure similar to that of bulk supercooled water at a temperature of about 0$^\circ$ C which corresponds to a shift of about 25 K [39]. Therefore the structure of interfacial water is characterized by an increase of the long range correlations which corresponds to the building of the H-bond network as it appears in low density amorphous ice [28]. There is no evidence of ice formation when the sample is cooled from room temperature down to $-196^\circ$ C (liquid nitrogen temperature).
5. Translational motions of interfacial water

5.1 The relaxing cage model

The description of the translational diffusional dynamics in confined or interfacial water has been the subject of several publications using the model of Volino and Dianoux (see the reference 41). Recently nanosecond time Molecular Dynamics simulations of supercooled water have been performed. The data have been described with success in terms of the relaxing cage model. The relaxing cage model uses an idea bor-
rowed from mode-coupling theory (MCT) of supercooled liquids. Mode-coupling theory focuses its attention on the cage effect in the liquid state which can be pictured as a transient trapping of molecules by their neighbours as a result of lowering of the temperature [42]. In supercooled or interfacial water due to the reduced thermal energy of the molecule and for water due to the formation of a stabler, hydrogen-bonded cage around each molecule, a molecule can translate a substantial distance only by rearranging positions of a large number of molecules around it. Thus the diffusion is strongly coupled to the local structural rearrangements or the structural relaxation. The usual, Markovian, Brownian-like diffusion is no longer valid in the case of supercooled water. The relaxing cage model appears now the more appropriate one to describe the diffusional dynamics in supercooled and interfacial water.

A detailed discussion of the intermediate scattering function $F_2(Q, t)$ for bulk water and its extension to the case of confined water is given in

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**Figure 9.** Spectrum of confined $D_2O$ at $-18^\circ$ C from fully hydrated Vycor after subtraction of Bragg peaks. There is 23% liquid water [38].
References [43-45]. One shows that in the time interval \(10^{-3} < t < 10^4\) ps, the CMD data using an Extended Simple Point Charge (SPCE) model potential for water [45] have been fitted by the following expression [43]

\[
F_s(Q, t) = (1 - A(Q)) \exp(-t/\tau_s^2) + A(Q) \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right), \quad (7)
\]

in which the initial decorrelation associated with the motion in the cage (first term) is followed by a stretched exponential decay (second term). The slow relaxation is characterised by a correlation time \(\tau\), related to the lifetime of the cage and a stretched exponent \(\beta\). \(A(Q)\) is the so-called Debye-Waller factor (DWF) which has a Gaussian shape. This implies that the short time dynamics of interfacial or supercooled water is, to a good approximation, harmonic.

\[
A(Q) = \exp\left(-\frac{1}{3}Q^2a^2\right), \quad (8)
\]

where \(a\) is the root mean square vibrational amplitude of water molecules in the cage in which the particle is constrained during its short time movements. From the results of the MD simulation of the SPC/E water at supercooled temperature, \(a\) is found to be about 0.5Å. Thus for a \(Q\)-range between 0 and 1.0Å\(^{-1}\), applicable to high resolution QENS spectra, the DWF in Eq. (8) is very nearly unity. Thus in Eq. (7) the contribution of the first term on the right hand side is negligible. We can thus write with a good approximation the final intermediate scattering function as:

\[
F_s(Q, t) = A(Q) \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right). \quad (9)
\]

The dynamic structure factor of the interfacial water is given by the expression:

\[
S_s^{H_2O}(Q, \omega) = \frac{A(Q)}{\pi} \int_0^\infty dt \cos(\omega t) \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right), \quad (10)
\]

where the Fourier transform is carried out numerically. The theoretical model is convoluted by the resolution of the spectrometer.

In the following the relaxing cage model has been applied in the case of water from fully hydrated Vycor.

5.2 Water molecules in hydrated Vycor

The quasi-elastic neutron scattering experiments have been performed at the High Flux Reactor of the Institut Laue Langevin in Grenoble using the IN5 time of flight spectrometer. The energy resolution (FWHM)
at the elastic position was 10$\mu$eV and the $Q$ range covered was from $0.15\,\text{Å}^{-1}$ to $0.99\,\text{Å}^{-1}$ (using 10 Å neutrons). The sample consists of $H_2O$-hydrated Vycor rectangular plates of thickness 1.9 mm and surface area of $32 \times 36$ mm$^2$. Vycor plates are thin enough to ensure that neutron transmission with water inside is 90%.

According to the relaxing cage model, the self dynamic structure factor, $S_s(Q, \omega)$, which is a time Fourier transform of the stretched exponential function in Eq. (9), shows a sharp line near $\omega = 0$ with an extended slowly decaying side wing [44]. The procedure of fitting the spectra is described into details in Ref. [44]. In particular, the structural relaxation rate and the stretch exponent $\beta$ are obtained.

Figure 10 shows a plot of the structural relaxation rate as a function of $Q$ in log-log scale for 100% hydrated sample at five temperatures, three of the lower ones are supercooled. It looks obvious that the structural relaxation rate has a power law dependence on $Q$ given by

$$1/\tau \propto Q^\gamma.$$  

(11)

The values of exponent $\gamma$ are given in the inset for each temperature. One observes that values of $\gamma$ are larger than but not far from 2. In principle, for a sufficiently small value of $Q$, $\gamma$ should reduces to 2 so that a correct hydrodynamic behaviour is recovered. The $Q$-dependence of the stretch exponent $\beta$ for the same sample shows that values of $\beta$ are significantly below unity for large $Q$, but approaching unity for $Q$ less than $0.1\,\text{Å}^{-1}$. One can infer from these results that even at the highest temperature measured, the hydrodynamic limit is probably reached for $Q$ only below $0.1\,\text{Å}^{-1}$.

Since both $\tau$ and $\beta$ control the quasi-elastic line shape and have $Q$ dependences, it is convenient to try to combine the two to obtain a single parameter which characterise the structural relaxation. In the case of an exponential relaxation as a result of a continuous diffusion, one has

$$F_s(Q, t) = \exp \left( -DQ^2 t \right).$$  

(12)

For this case, one can characterise the relaxation by its first cumulant (initial slope) which is $DQ^2$ or by its area, which is $1/DQ^2$. The two are equivalent. In the case of a stretched exponential relaxation, the first cumulant diverges for $\beta < 1$, but the area under the curve is [43]:

$$\bar{\tau} = \int_0^\infty dt \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right] = \frac{\tau}{\beta} \Gamma \left( \frac{1}{\beta} \right).$$  

(13)

Figure 11 is a log-log plot of the average relaxation time $\bar{\tau}$ as a function of $Q$. One sees that the average relaxation time has, within this $Q$ range,
Figure 10. Evidence of a power-law dependence of the structural relaxation rate on $Q$ (equation 13), measured with 10 $\mu$eV resolution, in the 100% hydrated sample. This graph shows a log-log plot of $1/\tau$ vs $Q$. Within a $Q$ range of $0.1 - 1 \text{Å}^{-1}$ the exponent $\gamma$, which is the slope of the solid lines joining the data points, seems to be a constant. The corresponding data from MD simulation [45] show that the exponent $\gamma$ is $Q$-dependent, approaching 2 as $Q$ goes below $0.1 \text{Å}^{-1}$.

a power law dependence,

$$\tau \approx Q^{-\gamma},$$

with an exponent $\gamma'$ approximately equal to 2 at room temperature, similar to the simple diffusion case. One may then define an average diffusion constant by the relation

$$\tau = 1/\bar{D}Q^{2},$$

and use it to estimate the average diffusion coefficient $\bar{D}$. From Fig. 11, for 100% hydrated sample at 293 K, we get $\gamma' = -1.95, \tau = 944$ ps at $Q = 0.1 \text{Å}^{-1}$. Substituting these two numbers into the above relation, we get $\bar{D} = 1.1 \times 10^{-5} \text{cm}^{2}/\text{sec}$, compared to the measured self diffusion constant for bulk water at this temperature which is $D = 2.0 \times 10^{-5} \text{cm}^{2}/\text{sec}$ [46]. We thus arrive at a ratio $D/\bar{D} = 1.8$, agreeing with estimate of Lee and Rossky [47]. We may also say that as far as the single-particle dynamics is concerned, water in Vycor at 293 K behaves as that in a
bulk water at 273 K (20 degrees below). As the temperature goes below the freezing point, the exponent $\gamma'$ becomes less than 2, indicating a deviation from simple diffusion.

![Graphs showing relaxation time $\tau$ vs. $Q$ at different temperatures](image)

Figure 11. Average relaxation time $\tau$ [defined in Eq.13] for the 100% hydrated sample plotted against $Q$ in log-log scales. It can be seen that the slope is approximately $-2$ at room temperature.

The recent results from neutron scattering experiments [43-44,48] and molecular dynamics simulations [45] establish clearly the existence of alpha relaxation in supercooled or interfacial water suggesting that the dynamics of supercooled water can be described in the general frame of the MCT scheme of glass-forming liquids.

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[37] General information on Vycor Brand Porous “thirsty glass”, n° 7930, Corning Glass Works, is available from OEM Sales Service, Box 5000, Corning, NY 14830, USA.
NEUTRON DIFFRACTION STUDY OF WATER POLYMORPHISM

M. A. Ricci
Dipartimento di Fisica “E. Amaldi,” Università di Roma Tre
and
INFM, Unità di Roma Tre. Via della Vasca Navale 84, 00146 Roma, Italy

A. K. Soper
ISIS Facility, Rutherford Appleton Laboratory
Chilton, Didcot, Oxford, OX11 0QX, UK
and
Department of Physics and Astronomy, University College London
Gower Street, London WC1E 6BT, UK

Abstract

A continuous evolution of the microscopic structure of water between two polymorph forms is observed, by increasing the pressure at isothermal conditions in the supercooled phase. The three site-site partial structure factors of two polymorphs of water have been extrapolated from neutron diffraction experiments exploiting the isotopic H/D substitution. The low density polymorph has an open hydrogen-bonded structure, while the high density polymorph has non-tetrahedral O–O–O angles and a collapsed second coordination shell, which implies broken hydrogen bonds between the first and second neighbouring shells.

1. Introduction

H. E. Stanley, in a paper published in this book [1], has pointed out that what matters to explain the “mysteries” of water is tetrahedral-ity, i.e., the peculiar microscopic structure of water when it forms an extended hydrogen bond (HB) network. As a matter of fact tetrahedrality seems to be a common feature of most liquids experiencing liquid-liquid phase transitions [2].
Molecular dynamics simulations [3], performed on SPC/E water [4] have indeed predicted such phase transition to occur for water at thermodynamic states below the homogeneous nucleation curve, where experiments on real pure bulk water are not feasible. As a matter of fact the first experimental evidence for the possible existence of a liquid-liquid phase transition in supercooled metastable water has been found using a water emulsion, where water is confined to droplets of the order of 1 µ [5, 6, 7]. The apparently discontinuous behaviour of the compression induced melting of ice IV and V when confined in the emulsion, is consistent with the transition of water from a low density phase (LDW) to a high density phase (HDW), ending at a liquid-liquid critical point in the region between the ice III and ice IV melting curves (at about 500 bar and 230 K).

Here we want to address the issue of a possible liquid-liquid phase transition in water performing experiments in the stable liquid phase. In particular we want to assess whether it is possible to identify the structures of the two polymorphs of water, namely HDW and LDW, by neutron diffraction experiments. In the hypothesis of existence of a liquid-liquid critical point, water is expected to undergo a phase separation at temperatures lower than the critical one and to continuously transform from its low density to its high density form above this point. Studies of the microscopic structure of water over an extended density range can in this hypothesis allow the extrapolation of the structure of the two polymorphs. The experiment [8] has been performed at T=268 K, to avoid crystal nucleation and explore a wide density range, increasing the pressure from 260 to 4000 bar. On the other hand there is already some evidence from transport properties [9] and x-ray diffraction [10] that, in the vicinity of the ice I/ice III triple point (T=251 K, P= 2090 bar), the anomalous properties of water are best visible and the HB network of low temperature water undergoes a relevant modification. Moreover, according to J. R. Errington and P. Debenedetti [11], the region where the transport properties of water are anomalous is well inside the region of structural anomalies.

2. Experimental details and data analysis

The experiment has been performed at the SANDALS diffractometer [12], installed at the Isis pulsed neutron source in the U.K.. Details about the sample container and experimental set up can be found in ref. [8]. Diffraction data have been recorded for the empty instrument, for a
Neutron diffraction study of water polymorphism

standard vanadium slab, for the empty sample container, for D_2O, H_2O, and for an equimolar mixture of the two liquids (HDO). Measurements on H_2O have been performed at three pressure states (P = 260, 2090 and 4000 bar) at T = 268 K, corresponding to densities of 0.0338, 0.0362 and 0.0381 molecules/Å^3, respectively [13]. The temperatures and pressures for D_2O and HDO have been increased in order to account for the slightly higher pressure and temperature of the triple point of D_2O compared to H_2O.

Data analysis, as far as multiple scattering, absorption, inelastic contributions and conversion to absolute units are concerned, has been performed following the standard routines available on SANDALS [14, 15] and the interference cross sections, F_α(Q), have been obtained for the three isotopically substituted samples. These functions are shown in Fig. 1a at P=4000 bar, as an example. Among these data the D_2O and HDO ones show the largest pressure dependence: this is however confined below 4 Å⁻¹ (see Fig. 1b and c).

For each sample α the F_α(Q) function is a linear combination of three partial structure factors (PSF), S_{ij}(Q):

\[ F_\alpha(Q) = b_0^2 S_{OO}(Q) + 4b_0b_H S_{OH}(Q) + 4b_H^2 S_{jj}(Q) \]  

where \( b_0 \) is the scattering length of the oxygen atoms and \( b_j \) is the scattering length of the deuterons, or hydrogens [16], or their average, when \( \alpha \) is D_2O, H_2O, or HDO, respectively. Given the large difference between \( b_D \) and \( b_H \), and the good contrast between the three cross sections shown in Fig. 1, the three partial structure factors can be extracted from the neutron diffraction experiment. The availability of the PSF is the real advantage of a neutron diffraction experiment with isotopic substitution with respect to experiments performed on the deuterated species alone. They are indeed necessary to deepen the knowledge of the orientational correlations in the liquid, since they act as strong constraints to molecular dynamics simulations aimed at recording molecular configurations compatible with the experimental data.

The observation that at each \( Q \) value the intensity of the PSF is a linear function of the density, \( \rho \), (as evidenced in Fig. 2) suggests that, following the idea of ref. [21], we can go further and express the density, the PSF and their Fourier transforms, namely the site-site radial distribution functions (RDF), as linear combinations of their counterparts for HDW and LDW:

\[ \rho(T,P) = \alpha(T,P)\rho_H(T) + [1 - \alpha(T,P)]\rho_L(T) \]  
\[ S_{ij}(Q) = \alpha(T,P) S_{ij}^H(T) + [1 - \alpha(T,P)] S_{ij}^L(T) \]
Figure 1. (a) $F_s(Q)$ functions for D$_2$O (solid line), HDO (line plus symbols) and H$_2$O (open symbols) at 4000 bar; (b) $F_s(Q)$ functions for D$_2$O at $P = 260$ bar (solid line), $P = 2990$ bar (dashed line) and at $P = 4000$ bar (thick line); (c) same as (b) for HDO.

\[
\rho(T, P)g_{ij}(r) = \alpha(T, P)\rho_H(T)g_{ij}^H(r) + [1 - \alpha(T, P)]\rho_L(T)g_{ij}^L(r) \quad (4)
\]
Figure 2.  PSF as a function of density at selected Q values in the $0.9 - 4 \text{ Å}^{-1}$ range.
where \( \alpha(T, P) \) represents the volume fraction of high density structure in the liquid and \( \rho_H(T) \), \( \rho_L(T) \) are the molecular number densities of HDW and LDW, respectively.

A further requirement on both extrapolated and measured PSF is that they must be compatible with model distributions of molecules. An empirical potential structural refinement (EPSR) simulation [17, 18] has been then applied to all PSF data. Details about the EPSR method can be found in the above quoted references. Here we want to mention only that this method has the advantage of fitting all measured data simultaneously, instead of traditional Fourier transform of individual PSF; moreover structural properties not readily available from the experiment can be evaluated from the MD trajectories. The limiting values of \( \rho_H(T) \) and \( \rho_L(T) \) can be obtained by the requirement that any extrapolated structure factors and radial distribution functions must satisfy the physical constraints: \( g_H^P(r) \geq 0 \) and \( S_H^O(Q), S_L^O(Q) \geq -1 \). After this fitting we got for the two polymorphs density values quite close to the densities of HDA and LDA ices, reported in the literature [19], namely \( \rho_H(T) = 0.0402 \text{ molecules/Å}^3 \) and \( \rho_L(T) = 0.0295 \text{ molecules/Å}^3 \).

Figure 3 shows the PSF of the two polymorphs, extrapolated according to Eq. (3). Density effects are confined in the region of the first peak. In the \( HH \) PSF this peak moves to shorter \( Q \) values in LDW; in the \( OH \) PSF it moves in the same direction and develops a shoulder. In the \( OO \) PSF we see the major effect, with the first peak that splits into two well resolved peaks: notably the \( S_{OO}(Q) \) functions of HDW and LDW closely resemble those measured by x-ray diffraction from HDA and LDA ices [20], although they have been obtained by a quite separate procedure.

3. Discussion

In Fig. 4a the oxygen-oxygen radial distribution functions, \( g_{OO}(r) \), obtained at \( T = 268K \) are compared with those of ambient water. We notice that low pressure RDF is almost identical to the ambient one, while strong modifications take place as the pressure increases. In particular the Ii peak moves to shorter distances and becomes a shoulder of the I one at the highest pressure state: this indicates that the tetrahedral coordination is lost at the higher densities. On the other two RDF (see Fig. 4b and c) we notice a clear sharpening of the peaks, compared to ambient water, due to trivial temperature effects, while density effects are less evident, although present. These are indeed best visible in the extrapolated RDF of HDW compared with LDW (see Fig. 5). In particular we notice that the H-bond length, as measured by the position of the first peak of the \( g_{OH}(r) \) function, decreases from 1.81 Å in LDW to
1.77 Å in HDW, thus implying a more linear H-bond in HDW compared to LDW.

From the recorded molecular configurations we can also plot the probability that, given a molecule in the origin of the reference frame, lying in the $x, z$ plane with the dipole moment oriented along the $z$–axis, the molecules belonging to its I and II neighboring shell are found at a dis-
Figure 4. Site-site RDF for water at $T = 268$ K at various densities, compared with those of ambient water.

tance $r = r(\theta, \phi)$. This spatial density function (SDF) is plotted in a 10 Å × 10 Å window in Fig. 6 for LDW and HDW. The lobes shown are a 3-dimensional rendering of contours of the SDF at a level 1.9 times the average density of the liquid in each case. Pronounced lobes are observed opposite to each $OH$ vector on the central molecule and in a broad band of density at right angles to these underneath the central molecule: these lobes correspond to the I shell of approximately tetrahedrally bonded water molecules. A II shell, in antiphase with the I, is seen. Notably this II shell collapses in going from LDW to HDW and almost merges with the I one: this collapse is the primary signature of the structural transformation that occurs as water density increases.

4. Conclusions

We have shown that it is possible to determine the microscopic structure of the two polymorph phases of supercooled water from neutron diffraction measurements performed in the stable liquid phase, provided that the isotopic substitution technique is employed to extract the three PSF and that a wide density range is explored. In particular the structure of HDW differs from that of LDW because of the collapse of the II neighboring shell close to the I one. This observation, together with the evidence for shorter H-bonds, implies the absence of H-bonds between
the I and II shell of molecules. This means that HDW cannot be modelled as a percolating network of bonds, contrary to LDW, where the second shell of molecules sits at approximately the tetrahedral distance and the H-bonds are long enough to form a network.

Our data are compatible with the existence of a liquid-liquid phase transition in supercooled water, although they cannot unambiguously prove the existence of such transition. They are indeed interpreted in
terms of a continuous evolution of the water structure from its low density, tetrahedrally ordered, phase to its high density phase, as the pressure increases above the predicted liquid-liquid critical point. The configurational entropy increases with pressure toward the state where the diffusion coefficient is maximum and then both recover their "normal" behaviour at higher densities.
Figure 7. SDF functions for HDW as determined from the EPSR simulation.

References

LIQUID-VAPOUR PHASE DIAGRAMS OF WATER IN NANOPORES

Confinement vs. surface effects

I. Brovchenko, A. Geiger, A. Oleinikova
Physikalische Chemie, Universität Dortmund
44221 Dortmund, Germany

Abstract

Coexistence curves of water in nanopores were simulated in the Gibbs ensemble. Evolution of the coexistence curves with strength of the water-pore interaction and pore size is analysed. The surface effect is found to be the dominant factor, which determines the water phase diagrams in nanopores. The possible ranges of critical temperatures of liquid-vapour and layering transitions of water in pores are estimated. A new low-temperature surface transition is found in the pore with a model superhydrophobic wall.

1. Introduction

Phase diagrams of fluids in pores are strongly modified by a combination of the influence of the finite size of the system and surface effects, such as changes of the structure of the fluid due to interactions with the wall [1]. Moreover, surface phase transitions, such as layering, may split from the remaining liquid-vapour transition [2]. To understand the expected rich phase behaviour of fluids in pores, these effects have to be analysed for possible ranges of pore size, shape, fluid-wall and fluid-fluid interaction. Molecular simulations provide a realistic (although difficult) way for studying the phase behaviour of fluids. Two direct methods were applied for the simulation of coexistence curves of fluids in pores: Molecular Dynamics [3] and Gibbs ensemble Monte Carlo simulations [4]. Until now only very few simulated coexistence curves of simple fluids in pores are available [5], prohibiting a systematic analysis.

The phase behaviour of water in pores is of special interest in view of its importance for understanding biological and industrial processes.
Localization of the regions of two-phase coexistence in the T-\(\varphi\) plane
and knowledge of the densities of the coexisting phases is the basis for a
correct simulation of the properties of water in pores. This is especially
important for understanding the water properties in incompletely filled
pores. (Another practically important situation is the equilibrium of
water in a pore with an external bulk reservoir. See [6,7] and reference
therein.)

We report a study of the coexistence line of water in nanopores with
smooth surface, obtained by simulations in the Gibbs ensemble. The
strength of the water-pore interaction varied from hydrophobic to hydrophilic.
The evolution of the coexistence curve (critical temperature, shape of the coexistence curve, appearance of surface transitions) with
varying water-pore interaction and pore size is analysed. Besides, a nar-
row cylindrical pore with a repulsive step near the pore wall was used
to analyse the effect of a model superhydrophobic surface [8] on the
coexistence curve of water.

2. Method

TIP4P water [9] in cylindrical and slit-like pores of 24 to 60 Å diam-
ters (width) was simulated with periodic boundary conditions applied in
one (cylindrical pores) and two (slit-like pores) dimensions. The water-
pore interaction was simulated as Lennard-Jones (LJ) (9-3) potential,
which depends on the distance between the oxygen atom and the pore
surface only. The parameter \(\sigma\) of this potential was fixed at 2.5 Å,
whereas the parameter \(\epsilon\) was varied to change the well-depth \(U = -0.39\)
\(\epsilon\) from -0.39 kcal/mol to -4.62 kcal/mol. That approximately covers
the range from hydrophobic to hydrophilic substrates. Gibbs ensemble
Monte Carlo simulations [4] were used to obtain water phase coexistence.
The two coexisting phases are represented in two simulation boxes. The
water in both boxes is kept at the same temperature and the equality of
pressure is provided by simultaneous changes of the box volumes. The
total number \(N\) of molecules in the two boxes is fixed during the simul-
ation (\(N\) ranges from 400 to 3000 depending on pore size and shape). The
distribution of molecules between the two boxes changes in the course
of a simulation due to the molecular transfers, which provide equality of
the chemical potential in the two coexisting phases.

Low efficiency of molecular insertion (deletion) in (from) the dense
phase, especially at low temperatures, is the main factor, which limits
the applicability of the Gibbs ensemble simulation. The efficiency
of molecule deletions was improved by a biased choice of more loosely
bound molecules [6]. The efficiency of molecule insertions was improved
by early rejection of the new configuration if at least one of the interatomic distances between the inserted molecule and other molecules is shorter than some reference value [10]. The acceptance probability was corrected by a factor, equal to the probability to find at random a molecule with energy higher than the chosen reference energy (in the case of deletion) or with shortest interatomic distances, exceeding the chosen reference distances (in the case of insertion). These techniques allow to extended the simulation of the liquid-vapour coexistence curve of bulk water in the supercooled region down to 200 K [10] (see Fig. 1.a).

The water density in the pore was calculated by assuming that a shell of width $\sigma/2$ near the pore wall is inaccessible to water.

3. Results

3.1 Coexistence curves of water in hydrophobic and hydrophilic pores

The obtained coexistence curves of water in cylindrical pores with radius $R_C = 12 \, \text{Å}$ are presented in Fig.1. The liquid-vapour critical temperature in the pore $T_P$ strongly decreases with respect to the bulk value ($T_{3D} \approx 579 \, \text{K}$, [10]) with strengthening of the water-pore interaction (Fig.1, b-d): $T_P \approx 0.93 T_{3D}$ at $U = -0.39 \, \text{kcal/mol}$, $T_P \approx 0.90 T_{3D}$ at $U = -1.93 \, \text{kcal/mol}$, $T_P \approx 0.80 T_{3D}$ at $U = -3.08 \, \text{kcal/mol}$. The shape of the liquid-vapour coexistence curve also strongly depends on $U$. Strengthening water-pore interaction makes the top of the coexistence curve more flat.

When the parameter $U$ achieves -3.85 kcal/mol, the coexistence curve splits into two regions (Fig.1.e): coexistence between vapour and two water layers, adsorbed on the pore wall (solid circles) and liquid-vapour coexistence in the inner part of the pore (open circles). In the low temperature region of Fig.1.e only liquid-vapour coexistence is observed. This suggests the existence of a triple point near $T \approx 250 \, \text{K}$ and $\rho \approx 0.8 \, \text{g/cm}^3$.

Further strengthening of the water-pore interaction ($U = -4.62 \, \text{kcal/mol}$) results in the appearance of three kinds of phase coexistence in the pore (Fig.1.f): 1st layering transition, i.e. liquid-vapour coexistence in the first outer layer (low density region); 2nd layering transition (open circles) and liquid-vapour coexistence in the inner part of the pore. The same three regions of two-phase coexistence are observed also for slit-like pores.

The critical temperature of the 1st layering transition $T_{1L}$ is not very sensitive to pore size and shape and varies in the range 0.68 to 0.70 $T_{3D}$. The critical temperature of the 2nd layering transition $T_{2L}$ is always
lower than $T_{1L}$. With increasing pore size the 2nd layering transition disappears (for cylindrical pores between $R_C = 15$ Å and $R_C = 20$ Å).

The density interval of the two-phase coexistence, corresponding to the 1st layering transition, is proportional to the ratio of the volume of the first water layer to the total pore volume. This ratio decreases
with increasing pore size, going to zero at $R_c \to \infty$. In parallel, the density interval, corresponding to the liquid-vapour coexistence in the inner part of the pore, extends and becomes the most typical two-phase coexistence in larger hydrophilic pores (Fig.2, bottom panel).

The critical temperature $T_f$ of the liquid-vapour phase transition of this “inner” water confined within two water layers in hydrophilic pores ($U = -4.62$ kcal/mol), varies strongly with changes of the pore size. In cylindrical pores $T_f$ changes from $0.59T_{3D}$ at $R_c = 12$ Å to $0.80T_{3D}$ at $R_c = 20$ Å and to $\geq 0.96T_{3D}$ at $R_c = 25$ Å. Contrary to this, in hydrophobic pores ($U = -0.39$ kcal/mol) the liquid-vapour critical temperature $T_P$ is surprisingly insensitive to variations of the pore size in the considered range. When the radius $R_C$ of hydrophobic cylindrical pores changes from 12 Å to 20 Å, $T_P$ varies from 0.92 to 0.94$T_{3D}$, which is not distinguishable within the accuracy of the simulation method.

### 3.2 Structural properties of water in pores

Structural properties of water in pores were calculated on the basis of the obtained water densities along the coexistence curves. The density distributions of oxygen and hydrogen atoms in the liquid phase along the pore radius are shown in Fig.3 for pores with different strengths of water-pore interaction. Strong density variations, indicating the appearance of two pronounced water layers near the pore wall, are observed in all considered pores, except the hydrophobic one (Fig3.c). Despite an orientational independent interaction of the water molecules with the wall, strengthening water-pore interaction causes strong orientational ordering of water molecules near the hydrophilic wall. This is reflected in specific maxima of the hydrogen atom density in between the two water layers.

The specific structure of the first outer layer of water in hydrophilic pores is shown in Fig. 4. Hydrogen-bonded quasi-planar water polygons dominate at low temperatures, whereas at higher temperatures there are hydrogen-bonded chains of water molecules. This structure reflects also in the oxygen-oxygen pair correlation functions $g_{OO}(r)$ (Fig.5). A pronounced maximum at 5.5 Å of $g_{OO}(r)$ in the first layer, that corresponds to the doubling of the first maximum position, is observed for all pores, excluding the hydrophobic one only. Decrease of the temperature improves the tetrahedral water structure, this is indicated by the increase of the tetrahedral maximum at 4.40 Å, whereas the maximum of $g_{OO}(r)$ at 5.5 Å persists in a wider temperature range than the tetrahedral maximum does.
3.3 Coexistence curve of water in a superhydrophobic pore

We have simulated the coexistence curve of water in a cylindrical pore with $R_C = 10 \, \text{Å}$ and a wall potential which should model a superhydrophobic surface. A repulsive step of 0.2 kcal/mol height and 3 Å width (between 7 and 10 Å from the pore axis) was added to a hard wall at 10 Å from the pore axis (see Fig. 7, lower panel), modelling in a simplified
Figure 3. Oxygen (solid lines) and hydrogen (dashed lines) atom density distribution of water along the radius of cylindrical pores with $R_C = 12 \, \text{Å}$. Liquid branch of the coexistence curve at $T = 300 \, \text{K}$. a) $U = -4.62 \, \text{kcal/mol}$; b) $U = -3.85 \, \text{kcal/mol}$; c) $U = -3.08 \, \text{kcal/mol}$; d) $U = -1.93 \, \text{kcal/mol}$; e) $U = -0.39 \, \text{kcal/mol}$. 
way the interaction of water with a hydrophobic surface of appropriate roughness to hinder the approach of water [8].

The obtained coexistence curve is shown in Fig. 6. A pronounced density maximum of the liquid branch of the liquid-vapour coexistence curve at the temperature about 290 K is clearly seen. In addition, a new low-temperature two-phase region is observed at high densities (Fig. 6, open circles). The critical point of this transition is located around 240 K. The corresponding coexisting phases differ mainly by the densities in the surface layer (see Fig. 7, upper panel). An accurate analysis of the structural properties of water in this pore is complicated by its narrowness and cylindrical shape.

4. Discussion

The simulated coexistence curves of water in pores show two-phase states of confined water in wide intervals of temperature and density. This indicates the necessity to take into account typical two-phase states of water in pores both in computer simulations and in the analysis of ex-
Experimental results. Neglecting the possibility of water phase separation in pores may result in the simulation of thermodynamically unstable states.

By varying the strength of water-pore interaction in a wide range we can trace the evolution of the coexistence curve of water in pores in detail. In hydrophobic pores with a surface close to a hard wall the liquid-vapour coexistence curve is narrower than in the bulk. To charac-
Figure 6. Coexistence curve of water in a superhydrophobic cylindrical pore ($R_C = 10\ A$) with a repulsive step near the pore wall.

To characterize the evolution of the shape of the coexistence curve quantitatively, we use the effective exponent $\beta_{eff}$ that describes the temperature dependence of the order parameter $\Delta \rho = (\varrho_1 - \varrho_2)/2$ in a wide temperature range via $\Delta \rho \sim (T_C - T)^{\beta_{eff}}$, where $\varrho_1$ and $\varrho_2$ are average or local densities of the coexisting phases. An analysis of the local order parameter along the pore radius shows [10], that water in the surface layer of hydrophobic pore disorders with temperature more strongly than the water in the interior of the pore, obeying a power law with an effective critical exponent $\beta_{eff}$ value close to the surface critical exponent $\beta_1 \approx 0.8$ of a semi-infinite Ising magnet at an ordinary transition [11]. As a result, the effective exponent $\beta_{eff}$ of the pore coexistence curve, determined for
the average densities, essentially exceeds the 3D-Ising value. In particular, the apparent “mean-field behaviour” with the exponent $\beta_{\text{eff}} \approx 0.5$ observed experimentally [12,13] may be attributed to the surface effect discussed above. A normal (with non-zero surface field) and not ordinary (with zero surface field) transition is expected for the asymptotic critical behaviour of fluids near boundaries [14]. But in the limit of a weak surface field, fluids may show features of an ordinary transition at temperatures not too close to the critical temperature [15].

The critical temperature $T_P$ in hydrophobic pores is found to be slightly below the bulk value $T_{3D}$ ($T_P = 0.93T_{3D}$), and insensitive to changes of the pore size in the considered range, in apparent disagreement with theoretical expectations. This result may be connected with a
strong distortion of the shape of the coexistence curve due to the specific critical behaviour of the surface layer in hydrophobic pores.

Strengthening water-pore interaction increases the oscillations of the water density normal to the pore wall (Fig.3). Due to this layered structure, the system gets feature of two-dimensionality [16]. This results in a decrease of the value of the effective exponent $\beta_{\text{eff}}$ towards the 2D Ising value and a flattening of the coexistence curve. The value $\beta_{\text{eff}}$ in the cylindrical pores with $R_C = 12 \, \text{Å}$ decreases from $\beta_{\text{eff}} = 0.46$ at $U = -0.39 \, \text{kcal/mol}$ to $\beta_{\text{eff}} = 0.16$ at $U = -3.08 \, \text{kcal/mol}$. In parallel the shift $\Delta T_P$ of the pore critical temperature $T_P$ changes from $\Delta T_P = 0.07T_{3D}$ to $\Delta T_P = 0.20T_{3D}$, respectively. This covers approximately the interval of possible shifts of the liquid-vapour critical temperature due to the variation of the strength of the water-pore interaction, as far as it is limited from below by the hard wall interaction and from above by the appearance of the layering transition. The obtained ratio of the maximal and minimal $\Delta T_P$ of about 2.9 is comparable with the theoretical predictions [17].

A layering transition with critical temperature $T_{1L} = 0.69T_{3D}$ separates from the liquid-vapour transition when the parameter $U$ of the water-pore potential gets close to the typical energy of pair interaction between water molecules (-4 to -5 kcal/mol). In order to clarify the effect of water-substrate interaction on the critical temperature of the layering transition we simulated the coexistence curve of water at a substrate with quasi-infinite attraction. This system was modelled by placing all water oxygens in one plane. Such quasi-2D-water shows a critical temperature $T_{2D} \approx 0.57T_{3D}$, a ratio $T_{2D}/T_{3D}$ which is essentially higher than for LJ fluids. So, the critical temperature of the water layering transition at a smooth surface may vary in the interval from $0.69T_{3D}$ to $0.57T_{3D}$.

The existence of a triple point, where vapour, liquid and surface layers coexist (Fig. 1.e) indicates the possibility of an additional phase transition, caused by the destabilization of the surface layers with respect to the vapour or liquid phase (depending on the average water density in the pore) below the triple point. This agrees with the recent observation of an additional low-temperature phase transition in pores, incompletely filled with water [18].

In hydrophilic pores the liquid-vapour phase transition of the “inner” water takes place in a cavity with a wall consisting of two highly ordered water layers (see Fig.2, lower panel). In this case the liquid-vapour pore critical temperature $T_f$ proves to be highly sensitive to a variation of the pore size. $T_f$ varies from $0.59T_{3D}$ to $\geq 0.96T_{3D}$, when the radius of the cylindrical pores changes from $R_C = 12 \, \text{Å}$ to $R_C = 25 \, \text{Å}$, in qualitative
agreement with theoretical predictions for the finite-size effect [17]. This may be attributed to a significant reduction of the density oscillations of the “inner” water due to the specific wall, formed by two water layers.

The water molecules in the first outer layer in hydrophilic pores show a specific arrangement with an appearance of hydrogen bonded chains and polygons (Fig.4). This causes the appearance of an additional pair correlation of oxygen atoms at 5.5 Å (Fig.5).

In the model superhydrophobic pore with a repulsive step near the pore wall an additional low-temperature liquid-liquid coexistence was found (Fig.6). This phase transition may be the analogue of the layering surface transition near a hydrophilic wall and (or) may be caused by water polymorphism at low temperatures (note, that the critical temperature of this transition $T \approx 240$ K is close to the expected liquid-liquid critical point of bulk water [19,20]). Simulations with larger pores with superhydrophobic surface are necessary in order to clarify the origin of this transition.

5. Conclusions

Coexistence curves of water in nanopores with smooth surface were simulated for a wide range of water-pore interaction. Strong changes of the pore critical temperature and the shape of the coexistence curve are found. The range of the possible variations of the critical temperatures of the liquid-vapour and layering transitions are estimated. New low-temperature phase transitions are found in a superhydrophobic pore.

The presented results show that the surface effect is the dominant factor, which determines the rich phase behaviour of water in nanopores. Analysis of the surface critical behaviour of fluids in the framework of the existing theory of boundary critical phenomena [14] is difficult because of the strong variation of density and intermolecular interaction near the surface. The shift of the critical parameters of the fluid in the pore makes this analysis even more complicated. Extended computer simulations of the fluid phase behaviour in pores allow to clarify these problems.

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References

RELAXATIONS IN SUPERCOOLED CONFINED WATER

P. Gallo
Dipartimento di Fisica “E. Amaldi,” Università Roma Tre
and
INFM, Unità di Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italy

Abstract

Studies of single particle dynamics of supercooled water confined in silica pores performed with computer molecular dynamics and inelastic neutron scattering are presented and analyzed in the framework of the mode coupling theory for the glass transition. The computer study highlights two well distinct dynamical regimes. Close to the hydrophilic substrate molecules are below the mode coupling crossover temperature, $T_c$, already at ambient temperature (bound water). The water closer to the center of the pore (free water) approaches $T_c$ upon supercooling as predicted by mode coupling theory. Inelastic neutron scattering data are analyzed upon supercooling for hydration levels of 12 and 8%. Also these data are discussed in the framework of the mode coupling theory, in the region of the fast, $\beta$, relaxation. Strong deviations from the theoretical predictions are found and ascribed to the existence of a low frequency scattering excess also visible in the simulation.

1. Introduction

The study of the dynamics of water at interfaces or confined in nanopores as a function of temperature and hydration level is relevant in understanding important effects in systems of interest to biology, chemistry and geophysics.

It is well known that liquid water shows a very peculiar behavior in the supercooled phase. The study of water approaching a glass phase is still a challenging problem since below 235 K one enters the so called no man’s land [1], where nucleation processes take place and drive the liquid to the solid crystalline phase, preventing the observation of the glass transition [2, 3]. It is unclear until now how confinement could change this scenario. It would be particularly important to understand
whether the glass transition temperature could be experimentally accessible for confined water. In this respect the modifications induced by the confinement on the dynamics of water on supercooling are of extreme interest.

In the many experimental studies of confined water that have been performed in Vycor is of particular interest [4], since Vycor is a porous silica glass characterized by a quite sharp distribution of pore sizes with an average diameter of 40 Å. The pore size does not depend on the hydration level and the surface of the pore is strongly hydrophilic. Moreover, the water-in-Vycor system can be considered as a prototype for more complex situations of interfacial water.

In particular the dynamics of water confined in Vycor glass has been studied by different experimental techniques such as neutron diffraction and nuclear magnetic resonance [5, 6]. A slowing down of the dynamics with respect to the bulk phase is observed. In ref. [6] experimental data in the region of the slow relaxation (late α) have been successfully analyzed upon supercooling in terms of mode coupling theory, MCT [7].

In the following section I briefly recall the glass transition scenario for a supercooled liquid focusing on MCT. In the next section results of a molecular dynamics, MD, simulation of water confined in a silica pore are presented. The pore is modeled to mimic the properties of a real pore of Vycor glass. The analysis of the slow relaxation for high hydration levels of the pore indicates that water approaches the crossover temperature $T_C$ as predicted by MCT upon supercooling [8, 9, 10, 11]. The fourth section is devoted to the presentation of inelastic neutron scattering data of water confined in Vycor glass, also analyzed in the framework of MCT upon supercooling. These results of low hydrated samples indicate that the region of the fast relaxation, $\beta$, is masked by the existence of low frequency scattering excess, LFSE, typical of strong glass formers [12]. The last section contains the concluding remarks.


As one starts supercooling a liquid (i.e. cooling the system below the melting temperature $T_m$) the system approaches an important crossover temperature $T_C$ referred to as the temperature of “kinetic glass transition” or crossover temperature. MCT [7] in its idealized version is able to describe the dynamics of the liquid in great detail with precise predictions on the behavior and the analytical shape of the density correlators for systems sufficiently close to, yet above $T_C$. $T_C$ represents a cross-over temperature from a liquid-like regime to a solid-like regime.
where only hopping processes can restore ergodicity. $T_C$ is above the Kauzmann temperature $T_K$ where the ideal liquid-glass transition occurs. The transition at $T_K$ would take place only at an infinitely slow cooling rate, where it would be signaled by the divergence of the viscosity. This ideal second order transition is related to the singularities which are found at finite cooling rate in experiments at the conventional glass transition temperature, $T_g$, where $T_K < T_g < T_C$.

In this paper I will focus on the relatively high temperature region where dynamics can be studied by equilibrium MD, i.e. the supercooled region where $T$ is above and approaches $T_C$. Here MCT in its idealized version works very well for many systems [7].

MCT is able to describe the dynamics of a liquid when the single entity, molecule or atom, is trapped by the transient cage formed by its nearest neighbors. This transient caging is responsible for the stretching of the relaxation laws and the separation of time scales. In its idealized version MCT does not take into account the hopping processes. This version predicts a transition to a non-ergodic system at $T_C$, when all the cages are frozen. Nonetheless, since hopping processes are not relevant for most liquids above $T_C$, in this region of the phase diagram the prediction of MCT are fulfilled by most of the glass formers.

When approaching $T_C$ from the liquid side, the Fourier transform of the density correlator, the self intermediate scattering function (ISF), $F_S(Q,t)$, has a two step relaxation behavior with a fast and a slow decay. After the fast decay it enters a plateau region, corresponding to the rattling of the particle in the nearest-neighbor cage, which is called the $\beta$-relaxation region. After the time interval of the plateau, which becomes longer when approaching $T_C$, the function $F_S(Q,t)$ decays to zero. This long time relaxation is called $\alpha$-relaxation. In the $\alpha$-relaxation region it has been shown that the relaxation process is well described by a stretched exponential

$$ F_S(Q,t \to \infty) \sim e^{-t/\tau_\beta} \quad (1) $$

where $\tau$ is the long relaxation time and $\beta$ is called the Kohlrausch exponent. MCT predicts that, when $T_C$ is approached, the $\alpha$-relaxation takes place on increasingly longer time scales, so that the relaxation time $\tau$ diverges with a power law

$$ \tau \sim (T - T_C)^{-\gamma} \quad (2) $$
As a consequence, the diffusion coefficient $D$, which is predicted to be proportional to $\tau_1^{-1}$, goes to zero at $T_C$ with the power law $D \sim (T - T_C)^\gamma$.

Finally, we recall that, since the MCT description of the kinetic glass transition is based on the cage effect, the relevant length scales are of the order of the nearest-neighbor distances. Consequently the dynamical quantities in $Q$ space display this effect most clearly for values of $Q$ close to the maximum of the static structure factor $S(Q)$.

2.1 Bulk supercooled water and MCT

In recent years it was discovered that SPC/E supercooled water has a temperature of structural arrest $T_C$ [13] coinciding with the so called singular temperature $T_s$ of Speedy and Angell [14]. As stated above, MCT predicts that close to $T_C$ the liquid dynamics is dominated by the "cage effect". Water does not behave like normal glass-forming fluids in this respect, since the cage effect is not a consequence of an increase of density upon supercooling but rather seems to be determined by the increase of the hydrogen bond stiffness, which makes the cage more rigid as the temperature is lowered below room temperature. The long time behavior of the single particle dynamics is well described in terms of the MCT and the dependence of $\tau_1$ (and $D$) on temperature are found to agree with the power law, Eq.(2). Successive simulations over a wide range of pressures and temperatures [15] and theoretical studies [16] fully confirmed the MCT behavior of this potential.

3. MD study of the dynamics of confined water

A cubic cell of silica glass with a cylindrical cavity has been constructed as described in detail in previous works [9]. Water molecules described by the SPC/E model are introduced into the pore of radius $R = 20$ Å. The water sites interact with the atoms of the rigid matrix by means of an empirical potential model. The MD calculations are performed with periodic boundary conditions along the $z$-direction. Water is considered at densities corresponding to the experimentally determined level of roughly full and half hydrations. In the chosen geometry this corresponds to $N_w = 2600$ water molecules and to a density $\rho = 0.8788$ g/cm$^3$ and $N_w = 1500$ and a density $\rho = 0.4971$ g/cm$^3$ respectively. The dynamical behavior of the confined water is investigated for five temperatures, namely $T = 298, 270, 240, 220$ and $210$ K. The single particle dynamics of the water molecules contained in the pore is analyzed and some of the main predictions of MCT are tested. The radial density profile of the water oxygen atoms shows the high hy-
Figure 1. Intermediate scattering function (ISF) for free water in the $xy$-direction at the peak of the structure factor ($Q_{MAX} = 2.25 \text{ Å}^{-1}$) for the five investigated temperatures. Curves on the top correspond to lower temperatures. Full lines are the MD data and long-dashed lines are the fit by Eq. (3). In the inset the full layer analysis is shown for $T = 240 \text{ K}$.

drophilicity of the pore in the form of density oscillations close to the substrate. Due to the presence of strong inhomogeneities in this system, a fit of the total correlators to an analytic shape can be carried out only by excluding the subset of molecules in the double layer close to the substrate ($R > 15 \text{ Å}$) which is identified with the so called bound water. The self intermediate scattering function, ISF, is calculated separately for bound water and for the remaining inner layers ($R < 15 \text{ Å}$), which are identified with the free water. Since no asymptotic free motion is possible in the $xy$ plane, the dynamics within this plane and along the pore z-axis is separately analyzed. In Fig. 1 the ISF of free water is shown along the $xy$-direction at the peak of the oxygen-oxygen structure factor, $Q_{MAX} = 2.25 \text{ Å}^{-1}$, as a function of temperature. The free water molecules inside the pore exhibit, as in the case of SPC/E bulk water [13, 15, 16], a diversification of the relaxation times as supercooling proceeds. The plateau region stretches as $T_C$ is approached. The long time region, the so-calld late $\alpha$ region, is expected to have a stretched exponential decay for a liquid approaching $T_C$. In the same figure, the fit of the function

$$F_S(Q, t) = [1 - A(Q)] e^{-(t/\tau_\alpha)^2} + A(Q)e^{-(t/\tau_\alpha)^2}$$  \hspace{1cm} (3)
to the data points is shown, where \( A(Q) = e^{-a^2Q^2/3} \) is the Debye-Waller factor arising from the cage effect with \( a \) the effective cage radius. \( \tau_s \) and \( \tau_l \) are, respectively, the short and the long relaxation times, and \( \beta \) is the Kohlrausch exponent. Obviously the Gaussian form of the fast relaxation can be only an approximate one.

In the inset of Fig. 1 the full layer analysis for \( T = 240 \) K is showed as a representative case. The topmost curve shows the behavior of bound water, while the lower curve is the ISF of free water (identical to the curve in the main picture). It is clearly seen that bound water is below \( T_C \), since the correlation function does not decay to zero on the nanosecond time scale. The central curve is the total ISF of confined water. It displays a strong non-exponential tail, which cannot be fitted by a stretched exponential function. The layer analysis introduced clearly shows that the contribution of free water can be separated from the one of bound water and that the stretched exponential function is able to give a very good fit to the late part of the \( \alpha \) region in the free water subsystem upon supercooling. The \( T \) dependence of \( \beta \) and \( \tau_l \) is in agreement with MCT. MCT also predicts that the inverse of the \( \alpha \)-relaxation time \( \tau_l \) vanishes with the same power law as the diffusion coefficient \( 1/\tau_l \sim (T - T_C)^{\gamma} \). Also this property is verified by the MD data. For the full hydration case the values \( T_C^{\beta} = 194.5 \), \( \gamma^{\beta} = 1.90 \), \( T_C^{\alpha} = 185.3 \) and \( \gamma^{\alpha} = 2.21 \) [8] are found. Similar results hold for the half hydration case where \( T_C^{\beta} = 170.4K \) and \( \gamma^{\beta} = 3.4 \). \( T_C^{\alpha} = 167.6K \), \( \gamma^{\alpha} = 3.8 \) [9]. At ambient pressure SPC/E bulk water undergoes a kinetic glass transition at \( T = 186.3 \) K with \( \gamma = 2.29 \) [13]. These values are not very different from the ones found for the full hydration in the \( z \) direction.

In Fig. 2 the same layer analysis is carried out for the van Hove correlation function calculated as a function of distance for a given time corresponding to the late \( \alpha \) regime. It is evident in the total correlator the existence of two peaks that are exactly split in two separate ones by the layer analysis. A similar result is obtained at ambient temperature (not shown) [17]. This confirms that the division into two subsets of this system is robust and able to account for the dynamical behavior of the system also on supercooling.

4. Experimental test of the \( \beta \) relaxation scaling law

An INS experiment on an incoherent scatterer measures the space-time Fourier transform of the density correlator, namely the self-dynamic structure factor, \( S_S(Q, \omega) \). In the framework of MCT this correlator mul-
**Figure 2.** Angular average of the van Hove self-correlation function. The total correlator (long dashed line) is shown together with the bound water contribution (long-short dashed line) and the free water contribution (continuous line).

**Figure 3.** Log-log plot of $\chi/\chi_{\text{min}}$ vs $\omega/\omega_{\text{min}}$ at $Q = 1.9 \text{ Å}^{-1}$ for 12 hydration level. In the inset one of the curves of the main frame is shown (triangles) together with the fit (continuous lines), performed according to Eq. 4.
tiplied by the frequency is proportional to the response function $\chi(Q, \omega)$ which exhibits a minimum between two regions asymptotically approaching $\chi \sim \omega^{-b}$ and $\chi \sim \omega^{\alpha}$. The analytic shape of the susceptibility as a function of temperature around the minimum follows a scaling law when normalized to the values of the function in the minimum between the two peaks:

$$\frac{\chi}{\chi_{\text{min}}} = C_1 \left(\frac{\omega}{\omega_{\text{min}}}\right)^{a_{\text{eff}}} + C_2 \left(\frac{\omega}{\omega_{\text{min}}}\right)^{-b}$$  \hspace{1cm} (4)$$

Eq. 4 is the interpolation formula for an ad-hoc data fitting procedure used for the $\beta$-relaxation scaling law test. Two series of INS experiments have been performed. The first series was taken at the ISIS facility on the MARI spectrometer and the second at the ILL facility using the IN5 spectrometer. Constant $Q$ data for $S_S(Q, \omega)$ have been interpolated at $Q$ values of 1.7, 1.9 and 2.1 Å$^{-1}$ for three temperatures, $T = 220, 248$ and 268 K, and two hydration levels, namely 8% and 12%. These values have been selected in the vicinity of the first peak of the oxygen-oxygen static structure factor. All the curves have been fitted to Eq. 4. In Fig. 3 the curves are shown for one of the two hydration level investigated, namely 12%. The value of the $b$ exponent has been fixed to 0.4. This value was estimated from simulations [9] and has, however, a little influence in the fit. In fact the $\alpha$ relaxation region is completely, or almost completely buried in the experimental resolution. As an example a fit to Eq. 4 is shown in the inset of Fig. 3. The values of $a_{\text{eff}}$ for the three selected $Q$ values are $a_{\text{eff}} > 1$ for all the $Q$ investigated (not reported) [12], while MCT indicates for this exponent a topmost value of 0.395. As already stated in the introduction the existence of an MCT $\alpha$ relaxation region has been clearly shown for water-in-Vycor both with experiments [5, 6] and in the MD simulations [8, 9, 10, 11]. Therefore, given the present state-of-art on the subject, the INS findings appear to be compatible with the existence of a low frequency scattering excess, LFSE, analogous to that observed already in strong glass formers [7]. The value of $a_{\text{eff}}$ increases with decreasing temperature, as expected for the LFSE. The overshoot visible in the MD ISF in the early region of the plateau for the lowest temperatures in Fig. 1 can also be related to the existence of a LFSE.

5. Concluding remarks

For confined water both experiments and simulations indicate a modification of behavior with respect to the bulk. We show evidence that the hydration level together with the hydrophilicity of the substrate play, through the layering effect, an important role in determining the dynamical properties of confined water. Provided that the effect of confinement
and interaction with the substrate are properly taken into account it is nonetheless still possible to fit the observed behavior in the theoretical framework of typical glass formers in analogy with previous findings on SPC/E water in the bulk phase.

We would like to stress, however, that in the present work we have considered a much more complex system than the bulk, where an additional anisotropic effect and a perturbation by the substrate is present. Therefore the fact that MCT could be used in this framework as a unifying theoretical approach is highly relevant as a guideline for the systematic study of the important phenomenology of confined and interfacial water.

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References


TRANSFORMATIONS, DYNAMICS, AND STRUCTURES OF AMORPHOUS ICES

Is it a glass or an amorphous solid?

[DDK, JST, VS, IS, ECS] Steacie Institute for Molecular Sciences
National Research Council of Canada, Ontario K1A 0R6 Canada
[CAT] University of Reading, Reading, United Kingdom RG6 2AD
[CKL] Argonne National Laboratory, Argonne, IL 60439 USA

Abstract

The relationship of the amorphous ices to the liquid state of water is discussed in view of recent theoretical and experimental studies. In addition to characterizing the transformations of high density amorphous ice (HDA), the dynamical properties, and structures of HDA ice and related phases, the phenomenon of pressure induced amorphization is examined in view of recent experimental and theoretical results.

1. Introduction

The discovery of high-density amorphous (HDA) ice by Mishima [1] and coworkers in 1984 led to a new and exciting areas of research on a number of topics related to the study of water and ice as well as amorphous solids in general. When ice Ih is compressed at low temperature, a sharp transition was observed that resulted in a dense form of amorphous ice (HDA ice) that could be recovered at 77 K. When HDA is warmed at low pressure it transforms to a low density amorphous (LDA) ice [2] that can also be recovered at low temperatures. There have been many significant contributions and new ideas that have directly resulted from the discovery of Mishima and his coworkers. In this article, recent results that reveal the relationship of the amorphous ices to the liquid and crystalline phases of ice will be discussed. The question of the relationship of HDA and the low-density amorphous ice to the crystalline forms or the liquid is an important one since the existence of these phases has led
to the suggestion that there may exist two phases of liquid water under certain conditions of moderately high pressure and low temperatures [3]. This intriguing possibility has resulted in numerous excellent critical investigations. It is clear that there is a very real possibility that water or many other liquids may in fact have two or more liquid phases. The existence of two or more liquid phases for a single material has in fact been reported for several materials [4, 5]. The question that now remains is whether the amorphous ices and their thermodynamic behavior can provide a basis for this suggestion. In this paper, the properties of the amorphous ices and related phases will be discussed in detail. In particular, the questions addressed are the relationship of the amorphous ices to liquid water and crystalline ice phases, the mechanism of the transformation of ice and related materials to high density amorphous solids at low temperatures, and the origin of excess low-frequency vibrational modes in amorphous ice at low temperatures. This report will focus mainly on the work reported by or in progress at our laboratory.

![Figure 1. Calculated [15] and experimental [14] phase transformation line for ice Ih.](image)
2. Mechanisms for pressure induced amorphization

The mechanism for the pressure induced transformation of ice Ih to HDA as been discussed frequently since the original discovery [1] of the phenomenon by Mishima et al. in 1984. It at first appeared to occur close to the point on the phase diagram where the extrapolated melting line of ice Ih predicted a transformation may occur. This very interesting suggestion led to several studies where HDA ice was suggested to have a structure expected for a dense quenched liquid form of water. A number of experimental and theoretical studies began to suggest that the phenomenon was perhaps more complex. The experimental data on the thermodynamic properties of the phase transition in ice Ih and similar behavior observed in related solids such a clathrate hydrates [6] and SiO₂ [7, 8] made it apparent that more detailed and critical examination was required. In addition, a number of theoretical studies on pressure induced amorphization in SiO₂ [9, 10], ice Ih [11] and clathrates [6] indicated that this phenomenon may not be closely related to conventional thermodynamic melting. In fact, an alternate mechanism for pressure induced melting had been suggested earlier in the work of S. Yip and colleagues [12]. Thermodynamic measurements of the phase transition behavior have indicated that the equilibrium pressure between HDA and the dense liquid are a factor of about 2 lower than observed [13]. If one examines the phase transition behavior of ice Ih [14] as it is pressurized over the temperature range 100 K - 253 K (Fig. 1), it is clear that there is a distinct change in melting transformation line at about 160 K. This feature led to a re-examination of the phase transformation to determine the possible origin of this behavior [15]. First, a combination of quasi-harmonic lattice dynamics and the Lindeman criterion for melting was used to compute the melting line for ice Ih. This method was previously applied successfully to several related systems. The melting line is reproduced with reasonable parameters as shown in Fig. 1. At low temperatures ( < 160 K), where another mechanism has been indicated, the elastic constants of ice Ih at finite temperature have been calculated and examination of certain Born stability conditions [16] show a mechanical instability line is obtained in excellent agreement with experiment. This suggests that the transformation at low temperature is due to a compaction of the crystalline ice structure with a filling of voids in the open lattice and does not correspond to the formation of a dense liquidlike structure.

LDA ice that is prepared by annealing HDA ice at 120 K at 1 bar has also been studied for its relationship to quenched liquid water [17].
Quenched liquid water can be prepared by cooling micron sized drops of water [18] at a high rate of about $10^{-6} \text{s}^{-1}$. The LDA ice can be converted to an HDA ice by application of pressure [2, 19] but the precise mechanism of this transformation is not well understood. In this case also the transformation pressure at 77 K is well above that predicted from thermodynamic measurements [13] In the next section the structures of HDA and LDA ice will be examined critically.

It is also important to note that amorphous ices can also be prepared from depressurizing and heating of several crystalline phase of ice. In particular, ice VIII and more recently [20] ice XII, has been shown to become amorphous upon careful heating. The appearance of an amorphous ice when ice XII is heated is of particular importance since ice XII is frequently accidentally prepared when ice Ih is pressurized.

3. Structure of amorphous ices and their relation to liquid water and crystalline phases of ice

There have been numerous studies of the structures of the amorphous ices and these studies have led to several interesting suggestions for the possible structures of liquid water at low temperatures and moderated temperatures. In this section we will review the current experimental and theoretical results which are yielding insight into the structures of these materials.

It is now known that the method used to prepare HDA ice can also often yield a crystalline impurity that has been identified as ice XII [21, 22]. Since the mechanism for transformation is most likely a mechanical collapse of the ice Ih lattice, it may be suggested that HDA ice is an intermediate kinetic or metastable state related to an underlying crystalline phase such as ice XII. In Fig. 2, the radial distribution function for the oxygen atoms in HDA ice and ice XII are compared. The O - O - O angular distributions are also compared in Fig. 3. There are clear similarities that support this conjecture if one allows for the extra broadening and low angle compression that is expected for the amorphous material. The relation of HDA ice to liquid water can be examined by comparison with the O - O - O angular distribution for a dense cooled water [23] and it was shown that there are significant structural differences. Another sensitive method for examining subtle but distinct structural differences is the vibrational mode spectrum that can be obtained from incoherent inelastic neutron scattering [17] and Raman spectroscopy [24]. It is well known that the vibrational frequencies of both the internal modes and
vibrational modes for water molecules in ice and water are are very strong function of the O-H - - O hydrogen bond lengths and to a lesser extent to the O-H - - H bond angle and other environmental features of the condensed phase. This has resulted in demonstrating that the hydrogen bond interactions in LDA ice differ significantly from those in the glass obtained by rapid quenching of the liquid.
4. Dynamical properties and low-frequency vibrational modes in amorphous ices

The understanding of the excess density of low-frequency modes in many amorphous solids has been a challenging problem for many years. The amorphous ices are an ideal material for study since there is a very large density variation of about 25 % as well as several forms. The origin of excess low-frequency modes in amorphous solids has been suggested to be a result of several sources including damped acoustic modes, interacting soft harmonic oscillators, or quasilocalized vibrations [25]. Excess low-frequency vibrational modes have been observed in HDA ice by infrared and incoherent inelastic neutron scattering techniques. A recent analysis of this data has resulted in a characterization and an atomic picture of the origin of these modes. The large amount of both optical spectroscopic data as well as incoherent inelastic neutron scattering and elastic scattering data as well as reliable theoretical models for water potentials has made this possible [26].

HDA ice that was prepared as large diameter (70 mm) thin (2mm) disks were used for incoherent inelastic neutron scattering measurements carried out at temperatures in the range 5 - 80 K. Spectra were obtained
Figure 4. The low-frequency vibrational density of state for HDA ice as determined from incoherent inelastic neutron scattering.

at the Chalk River Laboratory in Canada. A symmetric transmission geometry was used with a range of frequency transfer -0.10 ≤ ν ≤ 4.10 THz for a momentum transfer of Q = 2.5 Å⁻¹. The data were corrected for absorption and shielding, multiphonon scattering, multiple scattering, beam profile, higher order contaminations, and background scattering. The results for the vibrational density of states at 5, 20, 40, 60, and 80 K are shown in Fig. 4.

The lattice dynamics of HDA ice was then calculated using the TIP4P potential model for water. The water molecule configurations were obtained from a reverse Monte Carlo (RMC) [27, 28] analysis on neutron structure factor data [29]. In order to test for consistency and eliminate bias from the analysis, two structural models were used for the starting configurations in the RMC analysis. A crystalline ice Ih and a liquid water configuration were used. Both starting configurations yielded structure factors and radial distribution functions that were essentially identical. The RMC analysis gave results in good agreement with previous analysis that used both neutron and x-ray diffraction data. The ”experimental” structure derived from the RMC analysis with 1536 water molecules was then relaxed to eliminate imaginary modes using
a conjugate gradient calculation. The normal mode frequencies and eigenvectors for the optimized structure were then obtained. The local frequency spectrum (LFS) was calculated for all molecules in the HDA simulation cell.

![Frequency Distribution](image_url)

**Figure 5.** The temperature dependence of the excess vibrational density of states $\Delta g(\omega)$ at 24 cm$^{-1}$ versus the population difference parameter [26].

The experimental results are consistent with recent far-infrared absorption measurements [30, 31] that report absorption in HDA to be similar to that found in other amorphous systems. The infrared measurement detected a much weaker absorption in LDA that could be enhanced when the samples were doped with LiCl or methanol. In addition, the “fragility” the doped LDA increased as the number of excess modes increases. The infrared active modes have a temperature dependence that is consistent with a two-level system model. This temperature dependence is also obtained for the modes detected by neutron scattering as shown in Fig. 5. A two-level system is described by a model potential with an asymmetric double minimum [32] and this model has been suggested to support the viewpoint that there may be a common origin for the low-frequency modes in amorphous solids.

Lattice dynamics calculations on the structure obtained from the RMC analysis provides a means for the characterization of the origin
of the vibrational modes at low frequencies in HDA. The comparison of the calculated vibrational density of states for HDA and ice Ih in the frequency region \(0 - 100 \text{ cm}^{-1}\) shows the excess density of states in HDA and good agreement with experiment [33].

An analysis of the calculated LFS for each of the 1536 molecules in the simulation cell indicated that about 20 % had strong contributions to the frequency region between 5 - 40 \(\text{cm}^{-1}\). The amplitude of these peaks were twice as large as the average contribution to the local LFS spectrum for molecules in the simulation cell. The strong peaks indicate that the molecules participating in the low-frequency vibrations have larger amplitudes than other molecules. Water molecules with the strongest peaks in the local frequency spectrum are therefore to be viewed as defects in an otherwise uniform structure.

![Figure 6](image)

**Figure 6.** The calculated frequency distribution for selected molecules showing strong (solid lines), moderate (dashed lines), and essentially Debye frequency distributions (dotted lines).

A set of 65 molecules that had an excess amplitude in the local frequency spectrum greater than four times the average amplitude were selected and their structural features were examined. The most distinct feature for this set of molecules was the appearance of short localized chains of hydrogen bonded molecules. Thirty-one of the 65 molecules
in the set were in chains or dimers. The longest chain was branched and consisted of 6 molecules in addition to several chains of 3 water molecules. The longest hydrogen bond length was 3.5 Å and this was in a single dimer. There were 11 O-H - - O hydrogen bond lengths < 2.7 Å. The low frequency modes contributing to the excess density of states result from the contributions of these chains and dimers. The low-frequency modes involve the collective motions of the chains in addition to those of the dimers and isolated molecules. This result is remarkably similar to the suggested low-frequency relaxations in soft-sphere model systems [34]. The interatomic potential for the soft-sphere model consists of a simple inverse sixth-power interatomic potential that reproduces the main features observed in several amorphous systems including the contribution of isolated chainlike structures to the low frequency spectrum. Other features of the structure of the 65 selected molecules such as the slightly lower coordination number and shorter intrachain bond lengths are remarkably similar to those obtained from analysis of the soft-sphere model system. In Figure 6 the frequency distribution for 10 selected water molecules with strong, moderate, and weak contributions to the frequency distribution in the frequency region < 50 cm\(^{-1}\).

One method for obtaining the localized nature of a vibrational mode in a solid is the participation ratio defined as

\[ p_j = \left( \frac{\sum_{i=1}^{N} |u_i^j|^2}{N \sum_{i=1}^{N} |u_i^j|^4} \right)^{-1} \]

where \(u_i^j\) is the displacement of atom \(i\) in normal mode \(j\). The participation ratio \(\approx 1\) for extended modes and \(1/N\) for a mode where only one molecule contributes. The frequency dependent participation ratio for HDA (Fig.7) shows a gradual decline below 40 cm\(^{-1}\) and a distinct dip between 10 and 20 cm\(^{-1}\), in contrast to ice Ih where no drop is calculated. The region below 10 cm\(^{-1}\) could not be used due to the limited sample size. This study demonstrates the feasibility for characterizing the source of excess vibrational modes seen in amorphous solids. HDA ice has provided an excellent material for this study due to the complete sets of diffraction data, inelastic neutron scattering data, as well as reliable potentials for performing the required lattice dynamics for characterization of the low-frequency vibrational modes.

5. Summary

This review of recent studies of several phase of amorphous ices has attempted to summarize studies that characterize the the mechanism for
the pressure-induced transformation of ice Ih and related materials as well as their structures. A unique method used to determine the atom-scale origin of the excess vibrational density of states in the high density form of amorphous ice has been described. The exact relationship of the amorphous ices to dense supercooled water or normal density water and the very real possibilities of a second critical point and the existence two phases of liquid water remains as a challenging subject for research.

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PURE WATER STRUCTURE
AND HYDRATION FORCES
FOR PROTEIN FOLDING

Teresa Head-Gordon
Department of Bioengineering, University of California
Berkeley, CA 94720

Greg Hura
Graduate Group in Biophysics, University of California, Berkeley
and Life Sciences Division, Lawrence Berkeley National Laboratory
Berkeley, CA 94720

Jon M. Sorenson
Department of Chemistry, University of California
Berkeley CA 94720

Robert M. Glaeser
Department of Molecular and Cell Biology, University of California, Berkeley
and Life Sciences Division, Lawrence Berkeley National Laboratory
Berkeley, CA 94720

Abstract
This paper summarizes results of our recent work on pure water scattering and models for aqueous hydration potentials of mean force for protein folding.

1. Introduction
Experimental and theoretical studies on the folding of small globular proteins have established that they fold by a two-state mechanism, finding that the resulting folding is very cooperative, similar to a first-
order phase transition in bulk materials. The cooperativity of folding is fundamentally connected to a free energy landscape thought to be funneled due to the presence of sufficient energetic biases that ultimately win over the loss of conformational entropy of the unfolded chain\textsuperscript{1,2}. The free energy landscape theory has now provided a theoretical framework within which to develop minimalist protein folding models or all-atom protein folding simulations that have stronger quantitative connections to experiment \textsuperscript{3–8}.

Quantitative comparisons to protein folding experiments must of course connect back to the development of a free energy surface describing both the protein and its aqueous environment. Typically experiments guide the development of the underlying potential energy functions, but the experimental repertoire for characterizing aspects of this free energy surface are primarily focused on either the protein itself or separately on the pure water fluid. Our group has been involved in developing a better connection between the two systems through the combined use of both neutron and x-ray scattering experiments, molecular dynamics simulations and theoretical analysis on aqueous solutions of biological molecules over a range of concentrations to deepen our understanding of hydration in protein folding\textsuperscript{9–11}.

The scattering intensity contains information about the solute-solute correlations in water through the radial distribution function between solute centers, $g_{c}(r)$. The solute-solute radial distribution function in aqueous solution, $g_{c}(r)$, can be equated with the Boltzmann factor, $g_{c}(r) = e^{-W(r)/k_{B}T}$, where $W(r)$ defines an averaged potential, or a "potential of mean force", between the two solutes separated by a distance $r$. The information content of the solution scattering experiments is the net correlations between solute pairs that takes into account the complicated solvent environment, which can be extracted with the aid of simulations and equated with the thermodynamics of amino acid association in water.

One outcome of this approach is the discovery of "reduced" descriptions of hydrophobic solvation, i.e. the extraction of hydrophobic potentials of mean force (pmf) from the experimental intensity using simulation. We have focused on solutions of a common hydrophobic amino acid solute, N-acetyl-leucine-amide (NALA) or -methylamide (NALMA)\textsuperscript{9–11} as a function of its concentration in water to demonstrate this approach.

Dilute solution scattering studies of this amino acid monomer constitutes a model of the solvation structure and free energy of hydrophobic solute association during early protein self-assembly events when the local concentration of amino acids is relatively dilute and residues are well-hydrated\textsuperscript{9,10}. We also have reported x-ray solution scattering re-
sults on the behavior of the hydrophobic NALMA solute in water at high concentrations\textsuperscript{10,11} as a model of later folding events when significant spatial domains of the protein are driving toward the formation of the hydrophobic core. We have used these experimentally derived pmfs as reduced solvation descriptions to define new energy surfaces on which we have performed global optimizations to predict protein structure in the recent CASP4 competition with significant success in the more difficult protein targets of this contest\textsuperscript{14}. In the results we briefly review this published work for the concentrated NALMA solutions.

At the same time, the simulations of the experimental intensity observable that are needed to extract the solute-solute correlations for these solutions also gives a direct assessment of the quality of the protein and water force fields themselves. We have determined that while the underlying force fields appear to be qualitatively consistent with experiment (we believe), the quantitative agreement is sometimes poor depending on the combination of protein force field and water model used. Certainly some of the error resides in the water model itself, and the quality of a given water model can be judged against a battery of experiments for structure and dynamics. In the results we describe how the ambiguity in past structural experiments has led us perform a high quality synchrotron experiment\textsuperscript{12} and corresponding theoretical analysis\textsuperscript{13} of the structure of ambient neat water that has proved important for vetting existing water potentials, new non-polarizable and polarizable water models, and emerging simulation methodologies such as Car-Parrinello molecular dynamics.

2. Results

X-ray solution scattering measurements at concentration ratios of NALMA solute to water of 1:25 through to 1:100 were obtained, as well as that for pure water, some of which are shown in Figure 1. The x-ray curve for the more dilute concentrations is dominated by the main x-ray diffraction peak of water at room temperature at $Q \sim 2.0\text{Å}^{-1}$. However, at a concentration of 1:50, a new feature appears at $Q \sim 0.8\text{Å}^{-1}$, and develops into a peak at 1:25, the maximum concentration studied. The new diffraction at $Q \sim 0.8\text{Å}^{-1}$ reflects the formation of a fluid, but ordered, phase, the amount of which depends upon the total solute concentration, but whose internal structure is not sensitive to solute concentration.

We have used molecular dynamics simulations to interpret this new experimental feature at $Q \sim 0.8\text{Å}^{-1}$. While we cannot simulate the time progression involved in the formation of solute distributions seen experimentally, as this would require MD simulations over very long
time scales in order to reach the final equilibrated distribution of solutes, considerations of the mechanisms of how these solute configurations are reached are not important for this experiment. What is important is determining the final configurations of solutes that reproduce the static experimental observable.

We have focused therefore on what we view is a rough but complete representation of the possible distributions of solutes seen experimentally. First, we considered a fully dispersed and hydrated configuration of NALMA molecules in water at concentrations of solute to water of 1:24 and 1:48. A second class of solute configuration involves the formation of small molecular aggregates of solutes that range from mono-dispersed to clusters containing roughly two to six NALMAs in the most concentrated solutions. Concentration ratios of solute to water considered were
in the range 1:24 to 1:100. Finally, we consider the case that all NALMAs are configured into one cluster, for concentrations of 1:24, 1:42, and 1:48.

![Graph](image)

**Figure 2.** Comparison of the x-ray solution scattering experiment and three simulated intensity curves for three different \( g(r) \) models for NALMA in SPC water at concentrations of solute to water of 1:24.

Figure 2 shows a comparison of the simulated data with the experimental data at the highest concentration of 1:25. The concentration dependence seen experimentally (all data not shown) is best reproduced by configurations of NALMA in which the solutes are maximally dispersed or involving small molecular clusters on the order of two to six NALMAs. When considering the best single cluster data, the scattering predicted for the smallest single cluster is too sharply defined and slightly shifted to a smaller \( Q \)-value. This gets worse for the larger-sized cluster (which is simulated in a larger box and is therefore more dilute) where
there is a significant rise in intensity and shift away from $Q \sim 0.8\AA^{-1}$ (data not shown).

![Graph](image)

*Figure 3.* The potential of mean force consistent with the aqueous models of $g_\ell(r)$ that reproduce the leucine-leucine correlations over a range of concentrations.

Our experimental and simulation results over a range of hydrophobic amino acid concentrations imply aqueous potentials of mean force with two free energy minima such as that shown in Figure 3, and by our model indicate the type of aqueous free energy biases in the folding free energy landscape for protein self-assembly. The importance of this result is that even at late stages of folding when the local concentration of hydrophobic amino acids is very high, significant water is still present and stabilizing hydrophobic amino acids at length scales where they are separated by a water layer. To further strengthen the connection between our monomer systems and proteins, we have found that simple order-of-magnitude estimates for the change in configurational entropy arising from the collapse of a dense solution are the same as estimates of the conformational entropy change experienced by a polymer chain in the later stages of collapse.

Figure 4 shows the better quantitative agreement with experiment using the TIP-FQ water model at mole ratios of solute to water of 1:25 when it is compared to the SPC simulation (Figure 2). A better quantitative comparison between simulation and experiment gives us more confidence in the result that dispersed to small molecular aggregates are formed at these high concentrations of hydrophobic solutes in water.
Because these are the newest generation force fields, we might ask how well they reproduce something as basic as ambient pure water structure.

To answer this question we have recently performed a new x-ray diffraction study at the Advanced Light Source (ALS) in Berkeley of liquid water under ambient conditions that takes advantage of various state-of-the-art features of a modern day experiment. Improvements include a well characterized polarization correction, a high-level Compton scattering correction, higher energy x-rays that permit the use of thinner samples and reduces the need for a multiple scattering correction, more accurate intensities using a modern CCD image plate detector, and careful attention to the evaluation of the atomic form factors for extraction of radial distribution functions. The error bars show that our data has accuracy exceeding the differences when compared to the scattering curves of past x-ray in Figure 5.
Figure 5. Comparison of current experimental $g_{OO}(r)$ with previous work. The fit was obtained with $\alpha = 1.333$ and $\delta = 2.2\text{Å}$\textsuperscript{-1}. Legend: Narten and Levy, x-ray (grey line); Soper, Bruni, and Ricci, neutron (dash line); ALS data, x-ray (black line).

We have found that the true charge density of the water molecule in the condensed phase requires a modification of the isolated atom scattering factors commonly used in the extraction of radial distribution functions from neutron and x-ray scattering data\textsuperscript{13} according to:

$$I(Q) = \sum_{ij} x_i x_j f_i(Q) f_j(Q) \frac{\sin Q r_{ij}}{Q r_{ij}} + \sum_{i \leq j} x_i x_j f_i(Q) f_j(Q) h_{ij}(Q).$$  \hspace{1cm} (1)

We know that the Debye approximation, the assumption of superposition of the standard atomic scattering factors, $f(Q)$, performs inadequately for gas phase water. A simple modification is to scale the atomic scattering factors by the proper factor which gives a value of 1.86D for the dipole moment of gas-phase water, i.e. multiply $f_O(Q)$ by 1.11 and $f_H(Q)$ by 0.56. The result is that this simple adjustment greatly im-
proves agreement at small $Q$, but at the sacrifice of agreement at large $Q$. The reason for this is that the large $Q$ tails of the atomic scattering factors probe the density profile of the core electrons of the individual atoms. The core density would be expected to change much less upon chemical bonding, and in fact the Debye expression gives excellent agreement with the essentially exact result at large $Q$. This suggests a modification of the atomic scattering factors which rescales them properly at low $Q$, but retains their values at large $Q$. Such a modification is the following:

$$ f'(Q) = [I + (\alpha - I) \exp(-Q^2/2\delta^2)] f(Q), $$

where $f'(Q)$ is the modified atomic scattering factor (MASF), $f(Q)$ is the atomic scattering factor for the isolated atom, $\alpha$ is a scaling factor giving the redistribution of charge, and $\delta$ is a parameter to be fit, representing the extent of valence-electron delocalization induced by chemical bonding. For gas phase water, we choose $\alpha$ to correspond to the gas phase dipole moment. The unknown parameter $\delta$ can be fit by requiring the Debye expression curve to agree with the best available ab initio CI result. A single parameter choice of $\delta = 2.2\AA^{-1}$ for both oxygen and hydrogen MASF’s was found to give excellent agreement when Eq. 2 was used to reproduce gas phase water scattering. The advantage of the MASF formalism lies in the firmer foundation it provides for extraction of the oxygen-oxygen (OO) and possibly oxygen-hydrogen (OH) correlations from the experimental scattering curves. With the proper scaling, they allow the correct weighting of OO and OH correlations, allowing one to extract $g_{OO}(r)$ and not only a molecular centers radial distribution function.

Using the MASF’s and a fitting of the x-ray intensity based on a linear combination of a representative basis set of $g_{OO}(r)$’s, we have determined a $g_{OO}(r)$ for water consistent with our recent experimental data gathered at the ALS that is different than the $g_{OO}(r)$ reported by other x-ray and neutron scattering experiments. Compared to past experiments, the ALS data supports a $g_{OO}(r)$ exhibiting a taller and sharper first peak, and systematic shifts in all peak positions to smaller $r$ (Figure 6). In what follows we evaluate the performance of various water models and simulation methodologies in reproducing this one property at this one thermodynamic state, with the reminder that this is where most models of water should perform quite well with the understanding that this is only one of many important properties of liquid water.

In the non-polarizable water model category we find that TIP3P, SPC, ST2, ST4, as well as MCY (data not shown) are inadequate structural descriptions of ambient water, while SPC/E and TIP4P are
Figure 6. A comparison of x-ray scattering experimental data on pure water at 25°C and 1 atm as determined by our recent synchrotron ALS work (black), that of Narten (gray), and of Nishikawa (light gray).

give good agreement with our ALS experiment. The recently introduced TIP5P five-site model[22] gives excellent agreement with our ALS data (Figure 7), and with its robust performance for accurate densities over a large temperature range, makes it possibly the current non-polarizable water model of choice in classical simulation. We find that the NCC-vib[24], PPC[25], and TIP4P-FQ[26], and TIP4P-Pol[27] polarizable models perform well, but with some problems in the vicinity of the first peak. The CC model[28] has similar problems to the former polarizable models, but also shows shifts in all peak positions to larger r than what we determine from experiment.

In Figure 8 we show a comparison of our ALS-derived data with several recently reported ab initio simulated g_{oo}(r)'s. These include a 10ps, 64 water molecule MD run with a gradient-corrected BLYP functional
with an average ionic temperature of 318K\textsuperscript{29}, a 5ps, 32 water molecule MD run with the gradient-corrected BLYP functional and average ionic temperature of 303K\textsuperscript{30}, a 2ps, 54 water molecule MD run with the PBE functional, and at a temperature of \(\sim 300K\textsuperscript{31}\), and a new 6.4ps \textit{ab initio} simulation with the PBE functional at \(\sim 294K\) by Schwegler and co-workers\textsuperscript{32}, to be reported in a future publication. The quantitative agreement is quite poor. The problems with the reported \textit{ab initio} results arise from several sources that typically have been investigated and overcome in the classical simulation literature. These include dependence on initial conditions, length of the simulations, variation in system properties that arise with temperature or density, and finite size effects. Given the current computational expense of \textit{ab initio} molecular dynamics that prohibit box sizes typically used in empirical force field
simulations at present, these are largely technical limitations that will clearly diminish over time, and we would expect quantitative agreement to improve in the future.

3. Conclusions

The unification of our theoretical and experimental work is the development or discovery of effective protein interactions that implicitly includes the effects of aqueous solvent, and that potentially deeply influences the kinetics, thermodynamics, and their role in defining the intermediates on the folding pathway of proteins. While the experimen-
tal repertoire of protein-based structural techniques has resulted in a good understanding of a folding or folded protein’s secondary structure and tertiary structure contacts, approaches to characterize the role of the hydration environment in terms of structure and forces in folding are comparatively minimal at present. We have combined our expertise in solution scattering experiments, simulations, and theory to address this deficiency. Furthermore, the benchmarking of protein simulations as to the quality of the underlying empirical force fields is naturally addressed in the simulation and experimental research proposed here. We hope that this work will lead forward to understanding and quantifying protein folding energy landscape biases and improvements in potential functions for water and proteins, but with an even longer term objective of taking protein-aqueous systems out of the context biology and towards design of a new biomaterials.

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References

DYNAMIC PROPERTIES OF STRETCHED WATER

P. A. Netz, F. W. Starr, H. E. Stanley, M. C. Barbosa

[PA] Departamento de Química, Universidade Federal do Rio Grande do Sul
91500-280, Canoas , RS, Brazil

[FWS] Polymers Division and Center for Theoretical
and Computational Materials Science
National Institute of Standards and Technology
Gaithersburg, MD 20899, USA

[HES,MCB] Center for Polymer Studies and Department of Physics
Boston University, Boston, MA 02215, USA

[MCB] Instituto de Física, Universidade Federal do Rio Grande do Sul
Caixa Postal 15051, 91501-970, Porto Alegre, RS, Brazil

Abstract

We investigate the dynamics of the extended simple point charge
(SPC/E) model of water in the supercooled region. The dynamics at
negative pressures show a minimum in the diffusion constant D when
the density is decreased at constant temperature, complementary to
the known maximum of D at higher pressures. A similar trend in the
rotational diffusion is also observed.

1. Introduction

The thermodynamic description of supercooled water has been a ma-
jor topic of research already for many years. Most of this scientific effort
has been concentrated in understanding the static anomalies present in
this complex fluid. It expands on freezing and, at a pressure of 1 atm,
the density has a maximum at 4°C. Additionally, there is a minimum of
the isothermal compressibility at 46°C and a minimum of the isobaric
heat capacity at 35°C [1]. These anomalies are linked with the micro-
scopic structure of liquid water, which can be regarded as a transient
gel—a highly associated liquid with strongly directional hydrogen bonds
[2, 3]. Each water molecule acts as both a donor and an acceptor of
bonds, generating a structure that is locally ordered, similar to that of ice, but maintaining the long-range disorder typical of liquids.

Several scenarios have been proposed to explain these anomalies. In the "stability limit conjecture" [4, 5], the liquid spinodal line for water is reentrant. It has a minimum at negative pressures and passes back to positive $P$ as the temperature decreases. The increasingly anomalous thermodynamic behavior of liquid water as it is cooled at positive pressures can be interpreted in terms of approaching this spinodal. The "critical point hypothesis" proposes a second critical point as the terminus of a phase coexistence between a high density and a low density liquids. The increase in the response functions is then interpreted as a signature of being in the vicinity of this critical region. The "singularity-free hypothesis" suggests that there is no divergence in the response functions. They grow but stay finite [3, 6, 7].

Recently, dynamic properties of water have gained attention both experimentally [8, 9] and in computer simulations [10, 11, 12, 13, 14, 15, 16]. The surprising result of these works is that water also exhibits an anomalous dynamical behavior. The increase of the applied pressure leads to an increase in water translational diffusion coefficient and to a faster rotational diffusion [17, 8, 9]. These effects can be understood as follows. The increase of pressure leads to an increase in the number of defects and in the presence of interstitial water. This disrupts the tetrahedral local structure, weakening the hydrogen bonds, and thus increasing the diffusion constant [15, 16]. A further increase in the pressure leads to steric effects which works in the direction of lowering the mobility. The interplay of these factors leads to a maximum in the diffusion constant [15, 16] at some high density $\rho_{\text{max}}$. As a result, for each isotherm a maximum of the diffusion coefficient and a minimum in the rotational correlation time are found. However, the behavior at very low $\rho$ is less well understood.

In this manuscript, we present our recent studies of how the dynamics of low-temperature water are affected by the decrease of the density [18]. We perform molecular dynamics (MD) simulations of the SPC/E model of water in the range $210 \text{ K} < T < 280 \text{ K}$ and $0.825 \text{ g/cm}^3 < \rho < 0.95 \text{ g/cm}^3$. We calculate the rotational and translational diffusion coefficients in this region. A relationship between the behavior of the two coefficients is suggested.

2. Results

We performed molecular dynamics simulations using 216 water molecules described by the extended simple point charge (SPC/E) model [19], in
Dynamic properties of stretched water

Figure 1. (a) Dependence of the diffusion constant $D$ on $\rho$ along isotherms (for $\rho \leq 1.0$ g/cm$^3$). Open symbols are from Ref. [18], and filled symbols are from Ref. [15]. The dotted line separates liquid state points from phase separated state points, but is not an indication of the exact $\rho_{P}(T)$, which varies slightly with $T$. (b) Full $\rho$ dependence of $D$, also showing the maxima.
the canonical ensemble (NVT), in a cubic simulation box using periodic boundary conditions. The diffusion coefficient \( D \) was calculated using the slope of the linear regression of the mean square displacement versus time using a range of time long enough to assure that the molecules have reached a diffusional behavior. We show \( D \) along isotherms in Figure 1. For \( T \leq 260 \text{ K} \), \( D \) has a minimum value at \( \rho \approx 0.9 \text{ g/cm}^3 \), which becomes more pronounced at lower \( T \) (Figure 1). This behavior can be understood considering the structural changes that occur with decreasing density. At low \( T \), the decreased density enhances the local tetrahedral ordering, which leads to a decrease in \( D \). Further decreases in density reduces the stability of the tetrahedral structure and causes an increase of \( D \). The location of the minimum is near the ice Ih density \( \approx 0.915 \text{ g/cm}^3 \), which is the density where the perfect tetrahedral order occurs. The orientational relaxation was analyzed using the rotational autocorrelation functions [20, 21]:

\[
C^{(1)}(\mathbf{e}) = \langle P_1(\mathbf{e}(t) \cdot \mathbf{e}(0)) \rangle 
\]

where \( \mathbf{e} \) is a chosen unity vector describing the orientation of the molecules and \( P_i \) is the \( i \)-th order Legendre Polynomial (we restrict ourselves only to the study of the first two correlations):

\[
P_1(x) = x
\]

\[
P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}
\]

We choose three vectors to describe the orientation. The first vector is the unit vector with the same orientation as the dipole moment. The second corresponds to the O-H bond direction and the third is a vector perpendicular to the plane of the molecule.

The correlation functions were fitted to a biexponential decay function [21], and two relaxation times were calculated, corresponding to a slower (I) and a faster (II) mode.

\[
C = a_0 \exp(-bt^2/2) + a_I \exp(-t/\tau^I) + a_{II} \exp(-t/\tau^{II})
\]

For each correlation using a given vector, two times were calculated, leading to a rather complicated symbology. For example, the slower relaxation time for the second-order correlation using the third vector would be \( \tau_3^{II(2)} \). With few exceptions, however, we have found only one relaxation time, for correlation in a given vector, that is \( \tau_y^{I(x)} = \tau_y^{II(x)} \). We obtain therefore six correlation times for each simulated point, \( \tau_1^{(1)} \).
and $\tau_1^{(2)}$ for the first orientation vector and similarly $\tau_2^{(1)}$, $\tau_2^{(2)}$, $\tau_3^{(1)}$ and $\tau_3^{(2)}$. At $T = 240$ K where a detailed analysis was carried out, we find a maximum in the orientational time as illustrated in Figure 2.

3. Conclusions

We analyze the dynamic properties of supercooled water. For high densities ($\rho > \rho_{\text{max}}$), water behaves as a normal liquid and the decrease of translational diffusion coefficient, $D$, with increasing pressure is governed by steric effects. For $\rho_{\text{min}} < \rho < \rho_{\text{max}}$, as the pressure is decreased, the presence of defects and interstitial water decrease, the tetrahedral structure dominates, with stronger hydrogen bonds. This process reaches its maximum at $\rho = \rho_{\text{min}} \approx \rho_{\text{cc}}$. Further stretching destabilizes the hydrogen bond network, leading to an increase in mobility. Preliminary studies of the rotational diffusion show a maximum in the orientational time at low density region in compass with the behavior of $D$.

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References

COMPUTER SIMULATION OF SUPERCOOLED WATER AND AMORPHOUS ICES

G. G. Malenkov
Institute of Physical Chemistry, Russian Academy of Sciences
Leninskii prosp. 31, Moscow, 119991 Russia

Abstract

Molecular dynamics computer simulation of supercooled liquid water of various density as well as of low-density amorphous (LDA) and high-density amorphous (HDA) ices revealed heterogeneity of their structure. This heterogeneity is manifested in non-homogeneous spacial distribution of molecules with small and large value of tetrahedricity and Voronoi polyhedron volumes. Diffusion in LDA ice model begins to be observable at 220 K, very slow diffusion accompanied by the change of hydrogen bonded partners can be seen at lower temperature. The HDA ice model starts to soften at 130-140 K, sharp increase of diffusion coefficient occurs also at about 220 K.

1. Introduction

Water is a very unusual and interesting substance. Its volume decreases during the melting and reaches its minimum at 4° C. The volume of liquid water, when supercooled below 0° C, continues to increase when the temperature decreases and reaches 19.15 cm³/mol (an extrapolated value; it is remarkable that it is very close to the volume of low density amorphous ice) at -45° C. This temperature corresponds to the start of homogeneous crystallization (T_H) and it is practically impossible to obtain liquid water below it.

Polymorphism of water is extremely rich. Apart from a dozen of crystalline phases two amorphous solid modifications are known. Practically all the crystalline modifications can exist at temperatures and pressures lying beyond the fields of their thermodynamic stability, i.e., can be metastable. Both amorphous modifications are metastable by definition. Existence of the two amorphous modification of solid water, whose densities at atmospheric pressure differ by 20%, gave birth to the
Figure 1. Snapshot of HDA ice obtained from quenched molten ice III (768 molecules).

idea of the possibility of coexistence of the two liquid phases below $T_H$. All these fascinating facts and ideas have attracted considerable interest of the scientific community and generated a lot of discussions (see, e.g. [1, 2, 3, 4] and references therein).

For a long time our group has been involved in computer simulation of various aqueous systems. In recent years our efforts were mainly directed to the study of dependence of dynamical characteristics of water molecules on their local environment and on structural and dynamic heterogeneity of hydrogen-bonded networks. Bulk liquid water [5, 6], aqueous small droplets [6], high-pressure ice crystalline polymorphs [7, 8] as well as low- and high-density amorphous ices [9] have been studied.
In this communication some results relevant to the above-mentioned problems will be presented and discussed. Most part of this material was not included into published or submitted papers.

2. Methods

Molecular dynamics simulation was performed using the algorithm proposed by Allan Grivtsov for simulation of the systems consisting of the rigid molecules [10]. Intermolecular interactions were described by the atom–atom potential functions elaborated by Poltev, Grokhлина and Malenkov [11] for simulation of DNA–water system. The same functions were used in our simulations of aqueous systems mentioned in the introduction. Periodic boundary conditions were used in all our simulations.
The model of high density amorphous (HDA) ice was prepared by melting ice II or ice III models with subsequent quenching of the obtained melts. Rectangular independent cells contained 576 molecules in the case of ice II and 768 molecules in the case of ice III. Before the quenching the cell was converted into cubic one and parameters were adjusted to obtain density equal to 1.17 g/cm$^3$ (density of HDA ice at atmospheric pressure).

The models of low density amorphous (LDA) ice were obtained by "stretching" of the models of liquid water (729 molecules in the cubic independent cell [5]) or of heated HDA ice to obtain system with density close to 0.94 g/cm$^3$. Several simulations of amorphous ice with density intermediate between 0.94 and 1.17 were performed as well. Typical
snapshots of the instantaneous structures of some simulated systems are shown in Figs. 1, 2, 3, and 4.

3. Structural heterogeneity

Local environment of the molecules in the simulated systems was characterized by two parameters: index of tetrahedricity ($\tau$) and volume of Voronoi polyhedron (VVP). The tetrahedricity index is the measure of the regularity of the environment. It is determined as

$$
\tau = \sum_{j=i+1}^{6} \sum_{i=1}^{5} \frac{(l_i - l_j)^2}{15(l)^2}
$$

where $l_i$ is the length of the tetrahedron edges, $\tau$ is equal to zero if all the edges of tetrahedron are the same, i.e., the tetrahedron is regular. The
greater is $\tau$, the less regular is the environment of a particular molecule. VVP is the measure of local density. Concept of Voronoï polyhedra is widely used when describing structure of non-crystalline systems [13, 14]. The greater is VVP the less dense is local surrounding of a particular molecule.

We have demonstrated for ST2 liquid water that molecules with small and large values of $\tau$ group together forming branched three-dimensional clusters, which pierce all the volume [12]. Qualitatively the same picture is seen when space distribution of molecules with small or large values of $\tau$ and with small and large values of VVP are studied in liquid wa-
Computer simulation of supercooled water and amorphous ices

Figure 6. Dependence of centre of mass mean square displacement on time for LDA ice, molecules with different VVP values.

ter and amorphous ices when intermolecular interactions are described by the potential functions proposed in [11]. Correlation between $\tau$ and VVP values is very poor and clusters formed by molecules with large $\tau$ and VVP or by small $\tau$ and VVP do not coincide. We can say that molecules with large and small values of $\tau$ or VVP form two interpenetrating three-dimensional networks of the higher order in relation to primary H-bonded network. Structural heterogeneity is more pronounced at low temperature but it is difficult to define the degree of heterogeneity quantitatively when studying space distribution of molecules with various $\tau$ or VVP values in instantaneous structures. Structural hetero-
Figure 7. Density of vibrational state for HDA ice for molecules with different tetrahedricities.

Figure 8. Same as Fig. 7 for molecules with different VVP values.
Figure 9. Dependence of diffusion coefficient on temperature with density 0.94 g/cm$^3$.

Figure 10. Same as Fig. 9 with density 1.17 g/cm$^3$. 
Figure 11. Change of the hydrogen bond partner in krypton amorphous ice at low temperature (137 K). R1-C and R2-C are distances of the oxygen atoms of two water molecules from the centre of the cell. R1-2 is the distance between these two oxygen atoms. Hydrogen bond was formed at the 7100th fs from the start of the simulation.

geneity is illustrated by a space distribution of molecules with large and small VVP values in an HDA ice instantaneous structure. Corresponding distribution for molecules with different $\tau$ and VVP values for other simulated systems look qualitatively similar. Molecules sharing Voronoï polyhedra faces are connected by straight lines.

4. Dynamic heterogeneity

It is quite natural that dynamic properties of the molecules depend on their local environment. It was shown by us for the case of proton-ordered crystalline ices II and IX [7, 8]. In the structure of each of these ices there are two crystallographically different sorts of molecules.
Amplitudes and frequencies of vibrations for molecules of these two sorts were shown to be different.

Distribution of the properties that describe local environment of the molecules (such as \( \tau \) and VVP) are continuous for the non-crystalline phases. That is why it is impossible to divide molecules into discrete unambiguously defined structural classes. We calculated time dependence of the centre-of-mass mean-square displacement \( < R^2(t) > \) and velocity autocorrelation function (both for centres of mass and protons) separately for the molecules whose \( \tau \) values are greater (molecules with regular or "good" tetrahedral surrounding) or less (molecules with irregular or "bad" surrounding) than some ambiguously chosen values. The same procedure was done for the molecules with small or large VVP values (Fig. 6). From \( < R^2(t) > \), the amplitudes of vibrations and (in the case of positive slope of \( < R^2(t) > \) at \( t > 0.5 \) ps long times) the diffusion coefficient could be estimated. Fourier transformation of the velocity autocorrelation function gives us the density of vibrational states of centres of mass or protons.

In all the studied cases, dynamical characteristics of the molecules depended on their local environment (Figs. 5, 6, 7, and 8). Amplitudes of vibration of molecules with large values of \( \tau \) and of VVP were always greater than of the molecules with small \( \tau \) and VVP values. This is no surprise since molecules with irregular or less dense surrounding are expected to have greater mobility. Vibrational spectra depend on local density not so strongly as on regularity of environment. \(^1\)

5. Diffusion at different temperatures

We could not observe any detectable diffusion in the system with 0.94 g/cm\(^3\) density at temperatures below 220 K: slopes of \( < R^2(t) > \) (\( t > 0.5 \) ps) are close to zero at these temperatures (Fig. 9). But it does not mean that there are not any diffusive motions in the ld amorphous ice model at low temperature. We compared lists of H-bonds found using geometric criterion formulated in [5]. After several picoseconds some of the molecules changed the H-bond partners (Fig. 11). Sometimes, VVP of some molecules changed abruptly and boundaries between the regions of high (small VVP values) and low (large VVP values) density moved a little during the simulation. We observed these events mainly at the temperature higher than 130 K. At about 220 K, the \( < R^2(t) > \) slope

\(^1\)Calculations of the dependence of dynamic characteristics on local environment were performed by E.A. Zheligovskaya.
becomes positive and the diffusion coefficient of softened LDA ice starts to noticeably increase (Fig. 5a).

In the case of the system with 1.17 g/cm³ density, the positive slope of $< R^2(t) >$ started to be detectable at temperature about 130–140 K (Fig. 10). Our HDA ice changed to something like liquid with very low diffusion coefficient ($D$). There was a kink in the $D(T)$ dependence at $T$ about 220 K, after which diffusion increased more sharply with temperature (Fig. 10). Change of HB-partners occurred more often in our hd model than in the ld one.

6. Conclusions

In computer models of hd (quenched molten ices II and III, d=1.17 g/cm³) and of ld (quenched stretched liquid water, d=0.94 g/cm³) amorphous ices structural heterogeneity was found. This heterogeneity manifests itself as a non-uniform spatial distribution of molecules with close values of the tetrahedricity index or of the Voronoï polyhedron volume. Regions with molecules having high or low values of these parameters have the shape of branched three-dimensional network that pierces all the volume. Mobility of molecules with less dense or less regular surrounding is higher than mobility in more dense or more regular regions. Low density amorphous model ice softens at 220 K. In the case of high density model diffusion begins to be observed at 130–140 K, but sharp increase of diffusion coefficient takes place at 220 K. But at low temperature, when there is no noticeable diffusion, chance of hydrogen bonded partners rarely occurs in both forms of amorphous ice.

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References


IV

GLASSES AND AMORPHOUS SOLIDS
AMORPHOUS-AMORPHOUS PHASE TRANSITIONS IN ELEMENTAL GROUP-IV SEMICONDUCTORS

P. C. Kelires
Physics Department, University of Crete
P.O. Box 2208, 710 03 Heraklion, Crete, Greece
and
Foundation for Research and Technology-Hellas (FORTH)
P.O. Box 1587, 711 10 Heraklion, Crete, Greece

Abstract
We study the nature of amorphous to amorphous phase transitions in silicon and germanium through Monte Carlo simulations within the empirical potential approach. We find that there is a transformation to a high-density amorphous (HDA) phase, but there is no evidence for a discontinuous volume change. On the other hand, the free energy curves of the low-density and high-density phases versus pressure show definite crossings that indicate first-order transitions between the two amorphous phases. It seems that the transition proceeds via a kind of spinodal decomposition, which is manifested as a continuous change in structure.

1. Introduction
Amorphous to amorphous phase transformations, induced by applied pressure, are interesting phenomena that have extensively been studied in the past, but are yet not as well understood as the analogous crystal to crystal phase transitions. A typical example is the transformation observed in amorphous H$_2$O, which is of first order and exhibits a discontinuous volume change [1]. In silica glass, SiO$_2$, the first-order transition seems to be kinetically hindered with no evidence for a discontinuous volume change at the transition pressure [2]. In the case of the elemental amorphous semiconductors a-Si and a-Ge under pressure,
it was found experimentally that the transition is either accompanied by a sharp drop in the resistivity and the optical gap (evaporated films), or by a continuous decrease in resistivity (reactively sputtered a-Si:H and a-Ge:H films) [3]. In both cases, little is known about the structural modifications of the high-pressure phases, the elastic moduli under pressure, and the nature of the volume change during the transition.

Here, we report preliminary theoretical studies of this problem. We attempt to address the above mentioned issues by carrying out continuous-space Monte Carlo simulations. At the moment, we restrict our research to the structural properties of a-Ge and a-Si under pressure. Our aim is to unravel the equilibrium properties of these systems at finite temperatures. In the following, we describe the methodology on which our simulations are based. We then give our results and discuss their implications. We conclude with some notions about future work.

2. Methodology

The present investigations are based on continuous-space Monte Carlo (MC) simulations. The underlying statistical ensemble is the isobaric-isothermal (N,P,T) ensemble, that allows for the accurate equilibration of the density (volume) as the pressure on the system is kept constant. (Equilibration is performed under conditions of constant number of atoms N in the system, constant pressure P, and constant temperature T. These conditions are the most appropriate as they mimic usual experimental conditions in the laboratory.) The implementation of this ensemble for MC simulations is done through the Metropolis algorithm [4]. We have two types of moves: random atomic displacements ($s^N \rightarrow s'^N$), where $s^N$ is symbolic for the 3N scaled atomic coordinates in the cell, and volume changes $V \rightarrow V'$. These moves are accepted with a probability

$$P_{\text{acc}} = \text{Min}[1, \exp(-\beta \Delta W)] \sim e^{-\Delta W/k_B T},$$

(1)

where

$$\Delta W = \Delta U_{\text{disp}}(s^N \rightarrow s'^N) + P(V' - V) - Nk_B T \ln(V'/V).$$

(2)

$\Delta U_{\text{disp}}$ is the change in potential energy due to the atomic displacements both during the random moves and the volume changes. The volume involving terms (the last two terms) operate only during the volume changes.

It is advantageous to use the (N,P,T) ensemble because it allows volume and density fluctuations and leads to equilibration of the cell density. Thus, it avoids the a priori fixing of density and the a posteriori
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calculation of pressure (use of the microcanonical (N,V,E) or canonical
(N,V,T) ensembles), which is a common practice in molecular dynamics
(MD) simulations. The latter approach involves the risk of not relaxing
completely the external forces applied to the system.

In order to make the extensive simulations feasible, we model the in-
teratomic interactions within the empirical potential approach. While
this is less accurate than ab initio methods, that treat the energetics of
the system at a quantum mechanical level, it is by far more accurate for
the overall statistical equilibration, i.e., for a reliable minimization of
Gibbs free energy at finite temperatures. We use the empirical poten-
tials of Tersoff for Si and Ge [5] that have been well tested and applied
The potentials describe the elastic properties of Si and Ge reasonably
accurately. Since they were fitted to the energies of various bulk phases,
it is expected that they can also describe accurately the energetics of the
high pressure phases. Another attractive feature of this method is the
ability for calculating atomic level quantities, such as energies [8] and
bulk moduli [9]. This is based on the decomposition of the total energy
of the system into atomic contributions, something inaccessible by ab
initio methods.

We use simational cells with 512 atoms with periodic boundary con-
ditions. We have two types of cells to start as zero pressure structures.
The first type is produced by quenching from the liquid and contains
some intrinsic defects (threefold and fivefold atoms). The second type
is based on the Wooten-Winer-Waire (WWW) model [10] of a-Si(Ge),
which is a hypothetical model, completely tetrahedral, constructed from
the diamond lattice by a bond-switching mechanism. We use cells con-
structed by Djordjević, Thorpe, and Wooten [11], which we relax with
the Tersoff potential. The results obtained by these two types of cells
are indistinguishable.

3. Results and discussion

We first address the issue whether we can achieve a high pressure
phase of a-Ge(Si), and attempt to identify the nature of this transfor-
mation. The results of the MC simulations for a-Ge at 300 K, as summa-
rized by compression–decompression curves, are shown in the pressure
vs. volume graph of Fig. 1. In this case, the starting low-density amor-
phous (LDA) phase is generated by quenching the liquid.

We observe that there is a large hysteresis upon decompression, i.e.,
the system does not reverse its path, leading irreversibly to a densified
state at the end zero pressure, that we designate as high-density amor-
phous (HDA) phase. Interestingly, it seems that the final state does not depend strongly on the decompression path, and that more or less there is a unique HDA phase with only minor modifications (even for the decompression starting from 100 GPa). The LDA phase has a mass density $\rho_m = 5.1 \text{ g/cm}^3$, while the HDA phase is $\sim 30\%$ more dense than the LDA structure. Another prominent feature in this figure is the absence of a clear evidence for a discontinuous volume change. The increasing rate in volume change above 20 GPa can be hardly taken as such an evidence. A similar behavior was found in simulations of amorphous silica under pressure [2]. It is clear, however, in Fig. 1 that decompression from 20 GPa nearly reverses the path, so the gradual transformation to a HDA phase occurs dynamically above this pressure. For a-Si, we use the WWW cells as the starting LDA phase. We find the same trends. Compression–decompression (not shown due to space limits) leads to a HDA phase (25\% denser than the LDA phase). Again, the transition seems to be gradual.

A ball and stick 3-D model showing the HDA structure of Ge is depicted in Fig. 2. Atoms are shaded according to their coordination. The great majority of atoms have high coordination (mainly sixfold and
sevenfold), and the average coordination is 6.6. There is a clustering of atoms with the same coordination. Thus, the HDA phase in this case, as in a-Si as well (the mean coordination is 5.5), differs from a-SiO₂ where the coordination of Si atoms remains tetrahedral [2].

The bond-angle distribution function (BADF) of the HDA phase of Si, shown in Fig. 3, confirms the strong departure from tetrahedral coordination. Most evident is the peak at 60 degrees and the shoulder at ~ 150 degrees, that are reminiscent of similar features in l-Si. From the pair distribution function (not shown) we extract an average bond length of 2.52 (2.70) Å for Si and Ge, respectively. These observations suggest that the HDA phases possess the high-coordinated, metallic-like local geometries characterizing l-Si.

Our approach gives us the opportunity to study the energetics of the HDA phases at the local level by decomposing the total (cohesive) energy and assigning to each atom an atomic energy [8]. The probability distributions of atomic energies of the HDA Si phase is plotted
Figure 3. The bond-angle distribution function of the HDA Si phase after decompression from 60 GPa.

in Fig. 4. The total distribution is peaked at -4.18 eV/atom, about 0.2 eV higher than the cohesive energy of the LDA phase, and 0.4 eV higher than the crystalline energy. Actually, the energy of the remaining fourfold atoms in the network reflects the LDA energy and it is the lowest among all coordinations. With increasing coordination the energy becomes progressively higher, suggesting that atoms with higher coordinations are unstable geometries in the network. Indeed, annealing at successively higher temperatures eliminates progressively the highly coordinated atoms and relaxes the density. Annealing becomes effective above 700 K. At 1200 K, the HDA structure of both Si and Ge nearly relaxes to the starting LDA structure.

Fig. 5 shows the variation of Gibbs free energies of the LDA and HDA phases of Si at zero temperature, $G = E + PV$, as a function of pressure. The crossing of the curves at 9.8 GPa indicates a first-order transition at thermodynamic equilibrium. This, by account to the above results, seems to be kinetically hindered at room temperature, and it rather proceeds via a kind of spinodal decomposition, which is manifested as a continuous change in structure in the same manner found in SiO$_2$. The calculated equilibrium transition pressure $P_t$ is very close to the experimental value of 10 GPa [3]. For Ge, the $P_t$ is calculated at 5.5 GPa compared to the experimental 6 GPa. We conclude that for both
Si and Ge the transition is well defined, although kinetically hindered, and that the HDA structures are the stable phases above $P_{tr}$.

Finally, an independent verification of the $P_{tr}$ is provided by analyzing energy vs. volume curves, such as the one shown in Fig. 6 for Si. Using the common tangent method, one extracts a $P_{tr}$ at 9.7 GPa, in excellent agreement with the above result.

4. Conclusions

Monte Carlo simulations of a-Si and a-Ge under pressure find an equilibrium transition pressure between a low-density and a high-density amorphous phase at 9.8 and 5.5 GPa, respectively. The transition is kinetically hindered in the simulations and it proceeds via a gradual change in the structure. The characteristics of the high pressure phase are metallic-like, resembling those found in liquid Si and Ge. We are in the process of studying the elastic properties of this high density phase.

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Figure 5. Variation of Gibbs free energy with pressure at 0 K for the LDA and HDA phases of Si.

Figure 6. Energy versus volume curves at 0 K for the LDA and HDA phases of Si.
References

KINETICS AND NON-ERGODIC NATURE OF AMORPHOUS-AMORPHOUS TRANSFORMATIONS UNDER PRESSURE

A. G. Lyapin, V. V. Brazhkin, E. L. Gromnitskaya, V. V. Mukhamadiarov, O. V. Stal’gorova, O. B. Tsiok
Institute for High Pressure Physics, Russian Academy of Sciences
Troitsk, Moscow region, 142190, Russia

Abstract
To probe the nature of amorphous-amorphous transformations, we have carried out the detailed study of the kinetics of such type transformations in SiO$_2$ and GeO$_2$ glasses and H$_2$O ice under pressure. A number of anomalous features, such as the logarithmic law of densification at a fixed pressure, inelastic behavior long before volume anomaly, and the overlap of pressure ranges of the direct and reverse coordination changes in the GeO$_2$ network (negative hysteresis), were found to distinguish the amorphous-amorphous transformation in $g$-GeO$_2$ and presumably $g$-SiO$_2$ from that of ordinary first order transitions. Elastic softening was established to be the common precursor for transformation between the LDA and HDA amorphous phases of H$_2$O ice. Three distinct stages (shear elastic softening, bulk softening, and main volume jump) were found for the temperature-induced HDA — LDA transformation. Similarity in elastic softening of the pressurized Ih lattice and LDA network clarifies the differences in the structural and dynamic nature of LDA and HDA ices. The detailed picture of amorphous-amorphous transformations shows their complicated nonergodic nature combining the features typical for both the first-order transition and singularity-free scenario.

1. Introduction
First-order phase transitions initiated in crystals by pressure $P$ or temperature $T$ change constitute a class of phenomena that have been thoroughly studied both experimentally and theoretically. In particular, the high-pressure phase polymorphism has been much studied for many crystalline solids [1]. The existence of reversible transformations
between amorphous modifications involving changes of the local-order structure and the density (in the subsequent discussion also referred to as structural or coordination transitions) has been firmly established by different experimental techniques for SiO$_2$ and GeO$_2$ oxide glasses and amorphous H$_2$O ice [2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Moreover, there is experimental evidence for the structural transitions under pressure in other amorphous materials, for example, between amorphous modifications of carbon [12, 13].

Nevertheless, the nature of phase transformations in topologically disordered systems such as amorphous solids has not been adequately studied as yet [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 14, 15, 16, 17, 18, 19, 20]. Being a metastable and nonergodic system, the amorphous solid can be well described in many respects by the traditional thermodynamics at relatively low temperatures. The sharp transformation between the low density and high density forms of amorphous ice is considered now as a first-order transition [9, 10, 11, 16]. However, a great number of experiments show a wide range of amorphous-amorphous transformation (AAT) in silica and germania glasses under pressure [2, 3, 4, 5, 6, 7, 8, 21, 22, 23, 24, 25].

Most intriguing is elucidation of the mechanism of the AAT. The phase transitions in crystals occur through nucleation and diffusive growth of the new phase (diffusive transformations) or as coherent atomic displacements in the lattice (martensite transformations). Neither of the two possibilities can be realized in the case of transformations between amorphous phases. Long-range diffusion is forbidden in the temperature range of existence of metastable amorphous phases, whereas coherent movement of atoms is impossible in the geometrically disordered system. While the thermodynamic of first order phase transition between crystalline phases can be described by two-level model for Gibbs’ free energies [Fig. 1 (a)], where the barrier between two levels illustrates qualitatively the kinetic factor for the transition, the interaction between amorphous phases is quite complicated. First, there is native dispersion of energies for individual elementary atomic clusters (or individual atoms for simple substances) in amorphous phases, and consequently the energy relation between idealized two amorphous phases is complicated because the transitions between elementary clusters of different structural types are possible for both directions [Fig. 1 (b)]. Moreover, the distributions of local energy minima for the amorphous basins can correspond to energy bands [Fig. 1 (c)], and the interaction between these bands assumes complicated scenario of transformation. This means, for example, a possibility of continuous transformation between amorphous phases (Fig. 2), in contrast to crystals, when the point of transition is clearly defined by intersection of the Gibbs’ free energy curves (Fig. 2).
Figure 1. Energy diagram for phase interaction between (a) crystalline phases and (b-c) amorphous phases. The diagrams for amorphous phases show energy levels for individual elementary clusters or atoms (b) as the discrete dispersed levels or (c) as the energy bands for amorphous megabasins, where the individual levels show defect atomic states with respect to the ideal amorphous phase.

In this paper we present the kinetic study of AAT by precision measurements on the density of SiO₂ and GeO₂ glasses under pressure and ultrasonic measurements on the transformation between low- and high-
density amorphous modifications (LDA and HDA) of H₂O ice. Conceptual approaches to the description of transformations between amorphous phases are also considered.

Silica is the most important glass-forming material. The AAT in g-SiO₂ with the change from tetrahedral- to octahedral-Si coordination was studied in situ by x-ray diffraction [4] and optical spectroscopic techniques [2, 3, 5, 21, 22], and was found to occur in the range 10–25 GPa. Vitreous germania g-GeO₂ is the excellent chemical and structural analog of silica glass. Its high-pressure elastic properties and fourfold-to-sixfold AAT were studied by different techniques [6, 7, 8, 24, 25, 26, 27]. The coordination change for g-GeO₂ was observed between 4 and 13 GPa, and the equation of state was directly studied by the optical method in the range $P \leq 7.1$ GPa [8].

The discovery by Mishima et al. of the pressure-driven crystal-to-amorphous transformation in ice [28] and first-order–like transition between the LDA and HDA phases [9, 28] emphasizes the importance of water ice as a model hydrogen-bonded system in studying general aspects of the structural evolution of amorphous solids under pressure.
The mechanism of AAT is of specific relevance for our understanding of puzzling water properties and for discussing a possible first-order liquid-liquid phase transition with the boundary line terminating at the second critical point in the supercooled region [17].

2. Experimental techniques

Structure of $g$-SiO$_2$ and $g$-GeO$_2$ samples was tested by x-ray diffraction. The bulk and shear elastic moduli were determined at ambient conditions from the measured values of transverse and longitudinal sound velocities. The high-pressure experiments with $g$-SiO$_2$ and $g$-GeO$_2$ were carried out in the “toroid” device [29] capable to generate hydrostatic pressure (4:1 methanol-ethanol) up to 9 GPa [30]. The precise volumetric studies were accomplished using the strain gauge technique. All details concerning the preparation of gauges and high-pressure assembly, as well as high-pressure experiments, are presented elsewhere [30]. The absolute accuracy of volume measurements by the strain gauge technique to be about 0.3%. At the same time, the relative sensitivity of this method, which is particularly critical for time dependent relaxation measurements, is much better, $\Delta V/V \sim 10^{-5}$ [30].

The elastic properties of H$_2$O ice were measured in the pressure range up to 2.0 GPa and temperature range 77–300 K by an ultrasonic technique using high-pressure device of the cylinder-piston type [31]. Ice samples were prepared from distilled water by rapid cooling. The measurements were performed by the pulsed ultrasonic method [32] using $x$-cut and $y$-cut quartz plates as piezoelectric sensors with carrier frequencies of 5 MHz. During the experiment, the pulse transit time changes of longitudinal ultrasonic waves or of transverse ultrasound waves were determined by the method of visual signal superposition. [33] The sample height change was determined by means of the dial-gauge indicating device remote from the low-temperature zone. The detail description of the high-pressure setup and experimental procedure, including specific information on low-temperature measurements and friction correction, is presented in [31]. The bulk, $B$, and shear, $G$, elastic moduli were calculated from the values of transverse, $v_t$, and longitudinal, $v_l$, wave velocities using the standard equations for the isotropic elastic medium.

3. Kinetics of amorphous-amorphous transformation in glassy GeO$_2$ and SiO$_2$

Fig. 3 (a) shows the equations of state for $g$-SiO$_2$, obtained by the strain gauge technique. The initial density was determined by the Archimedes method, $\rho_0 = 2.20 \pm 0.03$ g/cm$^3$. The pressure dependence
of bulk modulus [Fig. 3 (b)] was calculated from the direct derivative of the equation of state, \( B = -V(dP/dV) \). The initial bulk modulus \( B \approx 40 \pm 3 \) GPa is in good accordance with the ultrasonic bulk modulus for the same sample, \( B_0 \approx 37 \pm 1 \) GPa (the ultrasonic shear modulus \( G_0 \approx 30 \pm 1 \) GPa). The main features of \( B(P) \) curve, including the anomalous minimum at \( P \approx 2 \) GPa, are the same as those from the Brillouin scattering [26] and ultrasonic [27] studies.

The all above data have been obtained for slow continuous increase or decrease of pressure \( (dP/dt \sim 0.1 \) GPa/min). After pressurization the sample of \( g \)-SiO\( _2 \) was kept at \( P = 9.0 \) GPa during one hour. We have found an irreversible densification of the sample, which can be described by the logarithmic law, \( \Delta V/V \propto \log t \), with a high accuracy (Fig. 4). The density vs pressure curve for decompression is evidently shifted toward higher densities [Fig. 3 (a)].

Two kinds of experiments were carried out for \( g \)-GeO\( _2 \) under pressure. In the first experiment, the glass sample was pressurized and depressurized under a continuous pressure change \( (dP/dt \sim 0.1 \) GPa/min), and in the second experiment the pressure increase was interrupted by the volume vs time measurements at fixed pressures during \( \sim 100 \) min or longer. The direct (up to 9 GPa) and reverse equations of state are presented in Fig. 5 (a). The samples have the initial density 3.7 \( \pm 0.1 \) g/cm\(^3\) (by the Archimedes method) and the bulk modulus 30 \( \pm 2 \) GPa slightly higher than those obtained in the previous studies. The main features of volume high-pressure behavior are similar to those from [8].

The volume vs pressure curves for the continuous and intermittent pressure increase experiments are very close to each other [Fig. 5 (b)]. The important feature for the second type of experiments is that the pressure increase between time measurement results in the returning of \( V(P) \) curve to the dependence observed for a continuous pressure increase [Fig. 5 (b)]. Such behavior corresponds to the variation of bulk modulus between the pauses for time-dependent volume measurements [Fig. 5 (c)]. From the compressibility curve the reverse transformation begins at \( P \approx 4 \) GPa, where we have directly found the irreversible volume change with time.

The results of volume vs time measurements are shown in Fig. 6. We have found the direct evidence of time-dependent irreversible relaxation at \( P = 3 \) GPa, in the region of divergence between the quasistatic and ultrasonic (or Brillouin) equations of state. However, the inelastic behavior seems to appear in \( g \)-GeO\( _2 \) even below, at \( P \approx 2 \) GPa, where the relaxed compressibility starts to increase [Fig. 5 (c)]. The time dependence of volume decrease (Fig. 6) is described by the curves, which
are nearly linear at a sufficiently long time interval in the $\Delta V/V$ vs $\log t$ coordinates.
4. Mechanism and non-ergodic nature of amorphous- amorphous transformation in $g$-GeO$_2$ and $g$-SiO$_2$

The use of the precision tensometric technique made it possible to establish that the behavior of compressibility of the SiO$_2$ glass becomes inelastic even at $P \approx 6$–7 GPa [Fig. 3 (b)], while a tangible logarithmic volume relaxation is observed at $P = 9.1$ GPa (Fig. 4). Therefore, the a- SiO$_2$ transformation kinetics are supposedly similar to the kinetics of the coordination transition in $g$-GeO$_2$.

The following four major features of the AAT in $g$-GeO$_2$ and $g$- SiO$_2$ stand out. (i) The anomaly corresponding to the coordination compaction of the amorphous GeO$_2$ network was recorded over a broad pressure range [Figs. 3 (a) and 5 (a)]. (ii) For a fixed pressure, a logarithmic with time change of volume is observed in the transition range [Figs. 4 and 6]. The typical amplitude of the relaxation depends only slightly on the pressure. (iii) On prolonged exposure to a fixed pressure, in response to the relaxation, the quasi-static compressibility decreases sharply [Fig. 5 (c)] to the values resulting from ultrasonic and Brillouin
Figure 5. (a) The equation of state of \( g\)-GeO\(_2\) in comparison with the volumetric data of Smith et al. [8] (c) and the Brillouin [25] (dashed and dotted) and ultrasonic [27] (dotted) equations of state. (b) Volume change in the experiment with a continuous variation of the pressure (dashed line) compared with that in the experiment with the intermittent compression (solid line). (c) Variation of compressibility of \( g\)-GeO\(_2\) for different experimental conditions.

experiments at these pressures [25, 27]. On further pressure increase, the compressibility re-increases, i.e. the amorphous network “forgets”
Figure 6. Time dependence of relative volume for $g$-GeO$_2$ at the different pressures.

about the preceding relaxation. (iv) A "negative" hysteresis is observed for the coordination transition in $g$-GeO$_2$, i.e. the inverse transformation commences at $P \approx 4$ GPa in the pressure range of the direct transition, the onset of which was recorded at $P \approx 3$ GPa.

The above-specified features of the transformation in $g$-GeO$_2$ and the relaxation in $g$-SiO$_2$ at the onset of the coordination transition differ radically from the features of conventional first-order phase transitions. The understanding of the nature of amorphous-amorphous transformations should be based on the point of view, that glass is a non-ergodic system and the basic feature of an amorphous solid (glass), distinguishing it from a crystal, is a wide variation of geometric characteristics for individual atoms and small clusters. Indeed, the logarithmic kinetics is not a unique phenomenon and is inherent to various disordered systems [34, 35, 36, 37]. The logarithmic relaxation is connected with the existence of a continuous spectrum of relaxation times having the uniform distribution of its logarithm [38]. As far as the structural transformations are concerned, this means a wide hierarchy of structural processes with the uniform distribution of energy barriers.
Amorphous-amorphous transformations: Kinetics, non-ergodic nature

The wide variation of geometric characteristics results in the wide distribution of atomic energies and stresses (for example, see [39, 40]). The distribution of intertetrahedral Si-O-Si (Ge-O-Ge) angles [41] and torsional angles of adjacent tetrahedra are of particular importance for the fourfold-to-sixfold transformation in \( g \)-SiO\(_2\) (\( g \)-GeO\(_2\)). The increase of external pressure should upset the distribution of energy barriers for the reconstruction of short range order and soften the open-packed networks of SiO\(_2\) and GeO\(_2\) glasses. The wide distribution of local pressure spinodals [8, 18] with respect to the coordination change corresponds to the softening of different network parts at different pressures.

The atomic level stress tensor [42] seems to be a governing parameter for the instability of local network parts. The simplest model for the amorphous-amorphous transformation may take into account the trace of atomic level stress tensor, associated with atoms, or the local compression of individual atoms, \( \sigma_i \sim p_i \Omega_i \) (\( p_i \) is the atomic pressure and \( \Omega_i \) is the volume for the \( i \)-th atom). If the pressure position of spinodal for a local network part is defined by the local atomic stress \( \sigma \), the distribution of atomic stresses \( \xi(\sigma) \) should directly correspond to the distribution of transformation spinodals for different network parts. Thus, a small part of the network is involved into the transformation at a fixed pressure.

Thus, the local instability approach allows one to explain the observed anomalous features of AAT's on the basis of distributions of energy (transformation barriers) and dynamic (tensor of atomic level stresses) characteristics and considering glasses as non-ergodic systems.

5. Kinetics of \( LDA \leftrightarrow HDA \) transformations in \( H_2O \) ice

The picture of the changes of elastic moduli and density during heating \( HDA \) ice (Fig. 7) is directly connected with the \( HDA \rightarrow LDA \rightarrow 1c \rightarrow 1h \) sequence of transformations [11, 28, 43, 44]. The known data for the temperatures of \( HDA \rightarrow LDA, T =114-128 \) K, and \( LDA \rightarrow 1c, T =143-162 \) K, transitions allowed one to establish the correspondence between these phase transitions and the observed anomalies in elastic properties.

One can select three distinct stages of \( HDA \rightarrow LDA \) transformation (Fig. 7), namely the shear elastic softening (from \( \approx 100 \) K), the bulk softening (from \( \approx 115 \) K), and the main volume jump (starting at \( \approx 127 \) K). The data on the \( G \) modulus point out that the shear instability plays an important role in the AAT mechanism. However, one should take into account that the shear and bulk softening may be not only a precursor of the \( HDA \rightarrow LDA \) transformation, but is a natural consequence of the
Figure 7. Relative volume $\Delta V/V_0$, bulk modulus $B$, and shear modulus $G$ at 0.05 GPa during temperature-induced $HDA \rightarrow LDA$ transformation.

structural transformation to a less dense and softer $LDA$ phase. The time-dependent study of $HDA$ ice at fixed temperatures indicates that some irreversible relaxation occurs in the interval $\approx 100$ to $130$ K that is accompanied by a decrease of $\rho$ and $G$ values. But reverse thermocycles (when the temperature was decreased and than increased again)
showed that the transverse velocity \( v_t \) and \( G \) modulus softening with temperature (in the interval 100–130 K) was partially reversible in the interval 100–120 K (Fig. 8). Thus, the elastic softening of \( HDA \) ice is not only a result of irreversible relaxation, but it is also an inherent property of the \( HDA \) amorphous network and should be considered as an elastic precursor for the \( HDA \rightarrow LDA \) transformation.

*Figure 8.* Temperature dependences of the density, transverse sound velocity \( V_t \), and shear modulus for thermocycles during \( HDA \rightarrow LDA \) transformations.
The transverse ultrasonic velocity and density, measured upon compression of \(LDA\) ice and then upon its decompression, as well as the calculated shear modulus, are presented in Fig. 9. The \(LDA \rightarrow HDA\) transition begins at \(\approx 0.4\) GPa \((T = 110\) K\) in accordance with the previous studies [9, 11]. The irreversible changes of \(\rho\) and \(v_t\) at the points \(A\) \((P = 0.5\) GPa\) and \(B\) \((P = 0.53\) GPa\) are the direct evidence of the transformation (Fig. 9). But the transformation does not finish at these pressures and continues at least up to 1.4 GPa. This is proved, first, by the comparison of the direct and reverse dependences in Fig. 9 and, second, by the relaxation measurements. We kept the pressure during \(\sim 1-2\) minutes at the points, marked in Fig. 9, and found the following relaxation changes: \(\sim 0.2-1.0\) % for \(\rho\) and \(\sim 0.3-2.0\) % for \(v_t\).

The most striking observation consists in the shear elastic softening of the \(LDA\) phase up to the \(LDA \rightarrow HDA\) transition beginning. The pressure derivative for the shear modulus for \(LDA\) phase, \(G'_p \sim -(0.3-0.6)\), is very close to that for \(1h\) ice, \(G'_p \sim -(0.4-0.6)\). There is a clear similarity between the \(1h \rightarrow HDA\) and \(LDA \rightarrow HDA\) transformations (Fig. 9).

6. On the nature of \(LDA \leftrightarrow HDA\) transformations

The common feature of the \(LDA \rightarrow HDA\) and \(HDA \rightarrow LDA\) transformations is the elastic softening as a structural change precursor. However, there is a clear difference in the scenarios of these transformations. The \(HDA \rightarrow LDA\) transition is of a gradual stepwise character (Fig. 8), because before the volume jump, the transformation starts from the elastic softening as both an inherent property of the amorphous network and as a result of the irreversible relaxation. The \(LDA \rightarrow HDA\) transition is quite different, and one can choose two distinct stages (Fig. 9). The first stage corresponds to the pressurizing of \(LDA\) phase with the predominantly reversible elastic softening as an inherent property of the \(LDA\) network, and the second one is the structural transformation starting rather abruptly.

The reasons for the ice \(1h\) evolution under pressure (Fig. 9) are clear. Up to the amorphization onset ice \(1h\) is geometrically and topologically rigid against any structure rearrangement. So, the data on \(LDA\) ice (Fig. 9) compel us to suppose that this amorphous phase has also the topologically and geometrically rigid structure practically up to the moment of \(LDA \rightarrow HDA\) transformation. This point of view is supported by the recent far infrared absorption study [45]. According to this measurement, \(LDA\) ice has a negligible density of low-frequency modes
Figure 9. Pressure dependences of the transverse sound velocity $v_t$, density, and shear modulus $G$ for direct (filled squares) and reverse (open squares) LDA $\rightarrow$ HDA transformations at 110 K. The arrows A and B indicate the points, where pressure was maintained for 9 and 20 min, respectively. Vertical bars indicate the points, where relaxation changes were detected. The segment $ab$ of the reverse transformation corresponds to temperatures 120–130 K. The pressure dependences $\rho(P)$ and $G(P)$ for the AAT LDA $\rightarrow$ HDA are compared with those for Ih $\rightarrow$ HDA transition (circles).
corresponding to low-energy excitations similarly to ice Ih and Ic, but in contrast to \( HDA \) ice \[45\] and glassy SiO\(_2\) \[46\] with a high density of low-frequency modes.

It is natural to consider the \( LDA \rightarrow HDA \) transition as a low-temperature continuation of the first-order transition in supercooled water (Fig. 10) \[17\]. The difference in the volumes and atomic packings in \( LDA \) and \( HDA \) ices clearly suggest the concept of polyamorphism, however the concept of thermodynamic first order transition cannot be completely applied to the transformations between amorphous ices. The wide tail of pressure-induces \( LDA \rightarrow HDA \) transformation, as well as a complicated picture of temperature-induced \( HDA \rightarrow LDA \) with the relaxation precursor (Fig. 10) cannot be interpreted in the framework of an ordinary first order transition.

The complicated kinetics of the AAT’s in ice can be naturally related to the nonergodic and structurally dispersed nature of amorphous ices. At the same time, the first-order features of the \( LDA \rightarrow HDA \) transition correspond to two predominant types of the short-range atomic packing in ice, the existence of which is controlled by the energy of chemical bonding between H\(_2\)O molecules and the \( PV \) contribution to the Gibbs’ free energy. The \( LDA \rightarrow HDA \) transition, a possible first order transition in supercooled water \[17\], and the evolution from low-density water to high-density water with the intermediate two-state structure \[47, 48\] (Fig. 10) reflect in this case the general trend of alternating the two types of atomic packing preferable at lower and higher pressures, respectively. The packing trend in amorphous ice leads to the transformation similar to the transitions in the crystal, but the frozen atomic stresses provide the pressure-dispersed features and a wide interval of the AAT’s in ice.

7. General remarks and conclusions

Thus, the kinetics of AAT in SiO\(_2\) and GeO\(_2\) glasses display a number of anomalous phenomena, particularly, the logarithmic kinetics of densification at a fixed pressure. Ultrasonic study of H\(_2\)O ice also shows a number of unusual features in the kinetics of \( LDA \leftrightarrow HDA \) transformations, such as the three-stage (shear and bulk softening and volume jump) scenario of the temperature-induced \( HDA \rightarrow LDA \) transformation, precursor relaxations, and the relaxation tail after the transformation. The approach, considering amorphous phases as non-ergodic systems with the distributed atomic level parameters, allowed us to explain the observed anomalous features.

The amorphous phases and glasses should be treated as a nonergodic system with the intrinsic frozen dispersion (due to the topological dis-
Figure 10. Hypothetical phase diagram of supercooled water on the equilibrium phase diagram of ice. The line of first-order phase transition (the thick solid line) between low density (LDW) and high density water (HDW) terminates at the critical point K [17]. At a higher temperature it transforms to the region of anomalous properties of liquid water (dotted lines), at lower temperatures (below the glass transition or crystallization temperature $T_g$) to the line (short dashed line) of thermodynamic equilibrium between glassy LDA and HDA ices. The real LDA ↔ HDA transformations are shown by the arrows, indicating the transition width and including the relaxation precursor, interval of softening, and relaxation tail. The position of the main volume jump for AAT's and its width are shown by the long dot-and-dash lines, respectively.

order) of structural and dynamic characteristics on the atomic scale. Thermodynamically, this means that it would be problematic to introduce some uniform structural or dynamic property, which, in particular, can serve as the order parameter for a possible phase transition. Kinetically, this implies, first of all, a wide interval of the transformation, really observed in the experiments.

The AAT's can be clearly interpreted in terms of static atomic stresses characterized quantitatively by the atomic level stress tensor. It is clear that in the disordered liquid state, like glass, large atomic stresses exist at any moment. But for long times, these stresses have negligible averages for the shear components. For this reason, the liquids includ-
ing their supercooled states are elastically relaxing systems without the macroscopic static shear elasticity. In the glassy states atomic stresses are frozen, and amorphous phases have the elasticity similar to that in crystals.

Therefore, consideration of the distributions of geometric and dynamic atomic characteristics is an adequate way to describe the nature of amorphous solids and their response to pressure. Taking into consideration the local nature of soft phonon modes and spinodals in disordered networks makes it possible to account for the specific features of coordination transformations in amorphous phases under pressure. At the same time, the general rules, which associate the geometry of an amorphous network and the bond type with the character of AAT, have hardly been formulated thus far.

In summary, the picture of the AAT’s in the studied disordered solids displays the features typical for both the first-order phase transitions (volume anomaly, etc.) and the singularity-free scenario [17] (the latter feature is the direct consequence of the dispersion of structural and dynamic nature on the atomic scale of amorphous states).

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PHASE RELATIONS FOR WATER AND ICE IN CONFINED GEOMETRY

John Dore, Beau Webber
*School of Physical Sciences, University of Kent, Canterbury CT2 7NR, UK*

Peter Behrens, Christian Haggenmuller
*Anorganische Chemie, Universität Hannover, D-30167, Germany*

Dan Montague
*Department of Physics, Willamette University, Salem, OR 97301 USA*

Abstract

A brief survey is given of the structural characteristics of water at low temperatures in the normal and super-cooled states using neutron diffraction. Similar studies are presented for D$_2$O water in mesoporous sol-gel silicas showing the depression of the nucleation temperature, the effects of fractional filling and the formation of cubic ice I$_c$ in the pores. Preliminary data is also presented for both neutron and x-ray diffraction studies of water in the ordered MCM41 silica, showing the deep super-cooling and the reversible phase transformation between water and cubic ice. The importance of hydrogen-bonded networks and the development of long-range correlations are used to provide an explanation of the observations. Further work is in progress.

1. Introduction

The phase diagram for ice consists of a large number of crystalline phases dependent on various geometries of hydrogen-bonded networks. The importance of the hydrogen-bond remains in the disordered phases of liquid water and amorphous ices. The effects are clearly displayed in the super-cooled regime where there are significant structural changes as a function of temperature. The liquid density is reduced towards that of ice I and there is a steady evolution of the hydrogen-bonded connectiv-
ity towards the continuous random network of tetrahedral bonds that characterises the structure of low-density amorphous ice.

If the water is confined within the geometry of a mesoporous solid (usually silica), the nucleation temperature is depressed by an amount that is inversely proportional to the pore size. Furthermore, the ice formed under these conditions is not normally of the form ice Ih produced from the bulk phase. The phase relationships for ice in confined geometry are therefore of interest and have been investigated by neutron and x-ray diffraction studies. The following sections describe some of the recent results.

2. Diffraction formalism

For neutron diffraction by heavy water, D$_2$O, the measured molecular structure factor $S_M(Q)$ may be written as

$$S_M(Q) = f_1(Q) + D_M(Q)$$

where $f_1(Q)$ is the form-factor and $D_M(Q)$ represents inter-molecular terms that define the liquid structure. The composite pair correlation function, $g(r)$, may be evaluated from the Fourier-Bessel transform

$$d(r) = 4\pi r \rho_M [g(r) - 1] = \frac{2}{\pi} \int_0^\infty Q D_M(Q) \sin Qr \, dQ$$

where $\rho_M$ is the molecular density. For D$_2$O, the partial functions are weighted according to

$$g(r) = 0.092 \, g_{OO}(r) + 0.422 \, g_{OD}(r) + 0.486 \, g_{DD}(r).$$

For temperature variation studies it is convenient to use a difference function analysis procedure where

$$\Delta S_M(Q,T,T_0) = S_M(Q,T) - S_M(Q,T_0) = \Delta D_M(Q,T,T_0)$$

for a temperature $T$ relative to a reference temperature $T_0$. The corresponding spatial function, $\Delta d_L(r;T,T_0)$, may be evaluated from the transform of $\Delta D_M(Q,T,T_0)$. Equivalent expressions may be written for the x-ray case where the scattering is predominantly from the oxygen atoms and the b-values are replaced by the appropriate atomic form-factors, which are $Q$-dependent.

3. Structural characterisation of low-temperature water and amorphous ice

Neutron diffraction studies have been made of ‘bulk’ super-cooled water down to temperatures 35° below the normal nucleation temperature.
Phase relations for water and ice in confined geometry

The density decreases by 8% and the structure changes significantly with temperature due to the development of long-range correlations [1] as shown in Fig 1. Low-density amorphous ice is made by vapour-deposition onto a cold substrate plate. The neutron diffraction pattern has a pronounced peak at 1.7 A\(^{-1}\) and the \(d(r)\) function has well-developed features extending to 20 Å and beyond. The structure corresponds to that of a fourfold co-ordinated random network based on approximately linear hydrogen-bonds. All of the specific features in the \(d(r)\) curve (Fig.1) can be explained by correlations within the network. In this context it can be seen that the structural changes in super-cooled water can be viewed as an increasing build-up of hydrogen-bond connectivity as the temperature is reduced. In effect the structure of the deeply-supercritical liquid is evolving towards that of amorphous ice but this metastable state is interrupted by the process of nucleation and crystallite growth. It is also clear that the amorphous ice phase undergoes a phase transition to cubic ice at 140K so although the structural characteristics seem closely related there is a temperature regime where neither phase can exist on an experimental timescale.

4. Experimental results for water/ice in mesoporous silicas

4.1 Sol-gel silicas

Neutron diffraction results for D\(_2\)O in sol-gel silicas have been presented previously [2] and also covered in a recent review [3]. The main effect is a shift in the position of the main diffraction peak \(Q_0(T)\) as a function of temperature. This feature indicates an enhanced hydrogen-bonding for the confined water compared with that of the bulk liquid and corresponds to a shift of approximately 15°C for 90 Å pores, as shown in Fig 2. The nucleation temperature is also depressed and depends on the pore size.

4.2 Partially-filled pores

It has been suggested that water in the interfacial region close to the hydrophilic interface has different properties due to the bonding to surface siloxyl groups. The effective range of this influence has remained a controversial topic for many years but the current consensus is that it is restricted to a few molecular layers. Comparative studies [3, 4] using the temperature difference approach for fractional fillings of 0.4, 0.6 and 1.0 were unable to detect any significant variations and showed that the separate \(\Delta D_M(Q; T, T_0)\) and \(\Delta d_L(r; T, T_0)\) curves scaled almost exactly
Figure 1. Spatial correlations in deeply-supercooled water and low-density amorphous ice from neutron diffraction measurements[1].

according to the filling factor. This surprising result suggests that there is minimal perturbation to the water structure in the interface region. The significance of this observation will be discussed in Sec 5.

4.3 Ice nucleation in sol-gel silicas

Neutron diffraction results [4, 5] have shown that the super-cooled water nucleates with the formation of cubic ice $I_c$ rather than hexagonal ice $I_h$ formed from the bulk state. This unexpected behaviour appears
Figure 2. Variation in the position of the main diffraction peak $Q_0(T)$ as a function of temperature for bulk and confined water.

to be related to the nucleation and growth mechanism in the pores as ice $I_h$ is formed in large pores. The effect can be most conveniently demonstrated for the partial filling of differently-sized pores and the use of a high-resolution diffractometer. Fig. 3 shows the diffraction pattern in the region of $1.7 \text{ Å}^{-1}$ from several samples where the effective thickness of the water layer is approximately 20 Å. The characteristic signal for ice $I_h$ consists of a triplet whereas that of ice $I_c$ comprises a single central peak. The results show that a thin water layer in a large pore nucleates to form pure hexagonal ice but in a more restricted volume there is an asymmetric peak profile suggesting a defective form of cubic ice. There is a possibility that this profile can be explained on the basis of stacking faults in the 'abcabc' layers but the situation is complicated and there
is no convincing explanation of the observed results. Further discussion is deferred to Sec 5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diffraction_peak.png}
\caption{The main diffraction peak after nucleation of ice in different pore-size silicas.}
\end{figure}

4.4 Water/ice in mesoporous silicas; neutron diffraction

The MCM-type silicas [6] provide an important class of ordered mesoporous solids where the geometry is well defined. They are produced via the sol-gel process using a liquid crystal template and are calcined to give an ordered array of channels with diameters in the 25-35 Å range. There are two forms shown in Fig.4 based on the hexagonal array of parallel pores (MCM41) or an inter-twined array of branched pores based on the cubic phase (MCM48).

Neutron diffraction data [3, 6] have been taken for both systems and results are shown in Fig.5a for D₂O in MCM41 at several temperatures after subtraction of the substrate scattering contribution. The liquid undergoes deep supercooling and nucleates to cubic ice at approximately 45°C below the normal freezing point of the bulk sample. Furthermore, the transformation between the liquid and crystal phases is completely reversible without any hysteresis. Consequently, there appears to be a
Phase relations for water and ice in confined geometry

first-order phase transition between two states that would both be in a metastable condition for the bulk state at this temperature. The use of a difference function procedure gives the \( \Delta d_k(r; T, T_0) \) function shown in Fig.5b, where the build-up of long-range spatial correlations can be seen to be similar to the features of Fig 2. It is clear that there is a continual enhancement of the hydrogen-bonding network as the temperature is reduced.

\[ \text{Figure 4. The mesoporous structure of MCM41 and MCM48 silicas.} \]

4.5 Water/ice in mesoporous silicas; x-ray diffraction

In order to study other aspects of the deeply-supercooled state and nucleation characteristics, an x-ray diffraction study \cite{7} using synchrotron radiation was undertaken. A sample of the preliminary results is given.
(a) diffraction results.

(b) the change in the spatial function $\Delta d_i(r; T, T_0)$.

Figure 5. Neutron diffraction data for supercooled water in MCM41 silica.
in Fig. 6 based on a difference function analysis. It was found that ice nucleation occurred at a higher temperature than expected but it is unclear whether this occurrence is due to the perturbation of the sample by the x-ray beam or due to excess water on the outside of the pores. The figure shows that hexagonal ice is initially formed but also that the central peak of the triplet increases in intensity at the lower temperatures corresponding to the formation of cubic ice. A puzzling feature of the measurements was an apparent change in the relative intensities of the triplet peak even when the temperature was stable. This behaviour suggests that there are dynamic changes in the ice structure on a timescale of minutes. The beam-size was 2 x 3 mm so many crystallites contribute to the diffraction pattern and it seems unlikely that this observation can be the result of any preferred orientation in the sample. The natural conclusion is that the ice structure is itself changing and that the average over the fluctuating Bragg intensity is being observed in the datasets. Clearly, a more detailed investigation will be needed to isolate the separate time and temperature dependence but the obvious conclusion is that the nucleating ice is not in a stable equilibrium state.

The changes with temperature can also be seen in the small-angle scattering region. At low Q-values, the SAXS intensity profile results from the ordered array of the cylindrical pores and has a similar shape to that for the liquid crystal used as the template. The intensity for this region shows a systematic variation with temperature and is highest below 200K, the lowest temperatures of measurement. Furthermore the intensity falls as the sample is warmed to its original temperature.

The origin of the SAXS signal is from the contrast between the \( \rho \)-value of silica and ice, typical relative values are 9.3 for ice \( I_h \) and approximately 24 for the silica substrate. The large change in intensity is therefore difficult to understand as the \( \rho \)-values are not expected to change much with temperature. The only other possibility is that there are inhomogeneities within the ice itself leading to a variation in density across the pore volume that is then convoluted with the liquid crystal form-factor. If so, this phenomenon would imply a partial fragmentation of the ice at low temperatures and a healing or annealing effect on warming. It is, of course, possible that the ice is under pressure from the changes in density within the restricted volume but it is still difficult to provide a self-consistent picture that fully explains the observations. Further measurements under carefully controlled conditions and checks for reproducibility will be required to understand these complex new results. It is hoped to make these measurements in the near future [8].
5. Conclusions and Future Work

The picture that emerges from these investigations is that the deeply-supercooled liquid state depends on the systematic evolution of the hydrogen-bonded network with reducing temperature. The properties vary in a predictable manner despite the density maximum and the unusual behaviour of the super-cooled state. In a similar manner, the properties of low-density amorphous ice can be understood in terms of a continuous random network of hydrogen-bonds. Although quantitative agreement with the experimental results has not been obtained from simulation studies, it is well recognised that the space-filling characteristics of the tetrahedral bonding play a central role in the behaviour. What remains as a challenge to present understanding centres on the phase relations between the ordered and disordered states, whether in the crystalline solid, amorphous solid or liquid. The present work ad-
dresses the relationship between water and amorphous ice with crystalline ice I, using confined geometry to provide deep supercooling of the liquid.

Under bulk conditions, hexagonal ice $I_h$ forms naturally as water is cooled. However, it appears that the initial phases of nucleation and growth involve the formation of a defective seed crystallite of ice $I_c$. The reasons for this behaviour are unclear and are probably linked to the stability of small H-bonded clusters in the liquid. As the temperature is further reduced, the network connectivity is increased and the longer-range correlations become more important. The effects of the confined geometry give an effective temperature shift so that the network becomes more developed, molecular motion is more restricted and the nucleation process is inhibited. The effect of pressure within the capillaries cannot be ignored but it cannot be simply evaluated. The most important parameter is the density of the confined water in the pores and its variation with temperature but experimental methods to determine this value are problematic; one possibility is currently under investigation [9].

The effect of the pore size (Fig 3) suggests that ice $I_h$ is the preferred crystalline phase for large extensions of connected water, whether as a volume (3D) or a thin layer (2D). It seems likely that this principle will remain for hydrophobic as well as hydrophilic interfaces but there is, as yet, no experimental verification since most of the studies are naturally based on the wide range of silicas that are available. Some additional studies on partially-hydrophobic samples are needed but are difficult and have not been attempted in any systematic manner. The obvious extension to systems of biological significance is a natural development and also the associated prevention of crystallization in cryo-protection processes.

Another puzzling aspect of the current studies is the apparent changes that occur in the diffraction [and SAS] pattern below the onset of ice nucleation. This phenomenon suggests that there is a much more complex behaviour of the confined ice than might have been expected. The fact that the water/ice system continues to give unexpected results is, itself, possibly no surprise – it seems that the more we learn about this fascinating system, the less we understand about the nature of collective hydrogen-bonded systems. The next decade should see further advances in the linking together of experimental, simulation and theoretical developments to provide a clearer picture but it seems inevitable that water and ice will continue to baffle us for a little while longer. The mysteries of water will remain as a major scientific challenge for the foreseeable future.
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References

[8] Neutron and x-ray experiments for water in MCM silicas are already planned.
[9] The use of variable isotopic substitution for H₂O/D₂O mixtures can be used in SANS studies to give the temperature dependence of the density but the determination of absolute values poses significant problems.
ENERGY LANDSCAPES AND AMORPHOUS-AMORPHOUS TRANSITIONS

Daniel J. Lacks  
Department of Chemical Engineering, Tulane University  
New Orleans, LA 70118 USA

Abstract  
Stress is shown to lead to major changes in energy landscapes, such as the disappearance of energy minima. These changes in the energy landscape alter the system dynamics, which in turn alters the system properties. In particular, these landscape changes are shown to lead to amorphous-amorphous phase transitions, enhanced diffusion in flowing liquids, plastic deformation in glassy materials, and a critical polydispersity for colloidal crystals.

1. Introduction  
The effects of stress on disordered systems are still not fully understood, despite their importance. Two obstacles to this understanding are the difficulties of (i) describing the dynamics of disordered systems in terms of a simple molecular-level picture (in contrast, the dynamics of crystals can largely be described in terms of vibrational motion about well-defined structures and the motion of defects such as dislocations), and (ii) addressing long-time phenomena in molecular-level simulations. Although molecular dynamics simulations are widely used to study disordered systems, it is often difficult to extract physical understandings of the phenomena solely from such simulation results, and to address phenomena occurring with time scales longer than several nanoseconds.

Recently, the energy landscape or "inherent structure" formalism has emerged as a framework that allows the dynamics of disordered systems to be physically described in a simple way [11]. The system dynamics can be considered the sum of vibrational motion within local minima and transitions between local minima. The vibrational motion is similar to that in a crystal, while the transitions between minima manifest in fluid-like properties such as diffusion and flow. For crystal phases, the
system remains in the energy minimum corresponding to that crystal structure, and the system dynamics consists of vibrations within this energy minimum (for perfect crystals). For liquid and glassy phases, the system moves between local energy minima corresponding to disordered structures - the transitions between local minima are relatively frequent in liquids, whereas the transitions are relatively infrequent in glasses.

The present paper will describe how stress changes the potential energy landscape, and how these landscape changes are shown to lead to amorphous-amorphous phase transitions, enhanced diffusion in flowing liquids, plastic deformation in glassy materials, and a critical polydispersity for colloidal crystals.

2. Computational methods

The present simulations are carried out for systems of 100-2000 particles interacting through empirical force fields, with periodic boundary conditions. The strain-induced changes in the potential energy landscape are determined as follows: Local potential energy minima corresponding to disordered structures are first obtained by quenching liquid systems to zero temperature using a variable-metric minimization algorithm. Strains are then imposed in extremely small increments (on the order of 0.0001-0.001). After each strain increment, the potential energy is minimized with respect to the atomic coordinates (at constant strain). System properties are calculated at these minimum energy configurations, to see how the local minima change with strain. Saddle points between local minima are obtained with a conjugate gradient algorithm.

2.1 Strain-induced disappearances of energy minima

The strains resulting from applied stresses lead to disappearances of energy minima and barriers in disordered systems, as shown schematically in Fig. 1 [7, 8]. The evidence for these disappearances, as shown in Fig. 2 (for a monatomic glass), is that at certain strains: (1) The curvature of the local minimum decreases to zero in one direction (equivalently, a normal mode frequency decreases to zero). (2) The height of an energy barrier that separates this local minimum from another decreases to zero. (3) The curvature of the barrier decreases to zero. (4) The distance between this barrier and the local minimum decreases to zero. These changes in the potential energy landscape establish that a local energy minimum disappears when the system is strained.
These disappearances of local energy minima give rise to locally discontinuous and irreversible changes in the structure and properties of the system, as the system suddenly moves to another energy minimum.

The strain-induced disappearance of energy minima is found to be a localized phenomenon; this localization contrasts to mechanical instabilities in crystals, which are delocalized [10]. Based on the localization of the mechanical instabilities to finite-sized groups of atoms, as the system-size increases: (1) the disappearance of energy minima occur more frequently because the number of groups of atoms which undergo instabilities is an extensive quantity, and (2) the magnitudes of the discontinuous property changes will decrease because a decreasing fraction of the system is involved in the instability. For these two reasons, the properties will appear continuous for macroscopic systems.
Figure 2. Disappearances of energy minima and barriers in disordered systems for a monatomic glass.

2.2 Plastic deformation in glassy materials

As a glassy material is strained, the stress usually increases continuously and nearly linearly with strain, but discontinuous stress drops punctuate these increases. These stress drops correspond to the disappearance of energy minima, as described above, and are irreversible. In this way, the strain-induced disappearances of energy minima give rise to yielding and plastic flow in glassy materials [9].

2.3 Enhanced diffusion in flowing liquids

Shear stresses and strains are generated in liquids by flow (due to viscous effects at the boundaries). These flow-induced strains lead to
disappearances of energy minima [8]. After an energy minimum disappears, the system relaxes towards another energy minimum, with an associated change in atomic positions.

The atomic displacements associated with the disappearances of energy minima correspond to steps in a random walk (in the directions perpendicular to the shear); the sum of these steps gives rise to self-diffusion that is strain-activated rather than thermally activated. These strain-activated contributions to diffusion augment the usual thermally activated contributions.

![Graph](image)

*Figure 3.* NEMD results demonstrating that the dependence of the diffusion constants on shear rate extrapolates in the low temperature limit towards the result based only on the disappearance of energy minima.

To demonstrate the validity of the proposed mechanism for enhanced self-diffusion in liquids, NEMD simulations are carried out to determine the self-diffusion constants as a function of shear rate and temperature, using the solid equations of motion with the temperature maintained by a Gaussian thermostat. The NEMD results, shown in Fig. 3, demonstrate that the dependence of the diffusion constants on shear rate extrapolates in the low temperature limit towards the result based only on the disappearance of energy minima [8].
Figure 4. Results for the pressure as the glass is compressed and then decompressed (at zero temperature).

2.4 Amorphous-amorphous phase transitions

The results for the pressure as the glass is compressed and then decompressed (at zero temperature) are shown in Fig. 4. The path followed by the system is not reversed on decompression due to the strain-induced disappearance of local minima of the potential energy surface [3] (these disappearances give rise to the discontinuities in the pressure-volume curve evident in Fig. 4). The low density (high volume) branch of this pressure-volume curve can be associated with a low-density amorphous
(lda) phase, and the high density (low volume) branch can be associated with a high-density amorphous (lda) phase.

A comparison of the Gibbs free energies $G$ of the lda and hda phases gives insight in regard to the long time dynamics of the system, which cannot be addressed by molecular dynamics [4]. These free energies are evaluated at the lda and hda energy minima described above, and are calculated in the limit of zero temperature such that $G = E + PV$. As shown in Figure 2, the free energy curves of the lda and hda phases cross at $P=3$ GPa, suggests that a first-order transition may occur between the lda and hda phases at $P=3$ GPa.

The first-order transition from lda to hda requires thermal activation, because a barrier exists between these energy minima. The first-order phase transition will therefore be kinetically hindered at some “low temperatures”. If the first-order transformation is kinetically hindered, the lda phase will persist until the pressure exceeds its spinodal (i.e., metastability limits). The transformation from lda to hda at zero temperature, as shown in Fig. 4, occurs by what can be considered spinodal decomposition - i.e., the energy minima corresponding to the lda phase disappear above certain pressures. This spinodal decomposition takes place over a broad pressure range due to the variety of local environments in an amorphous system (i.e., different local atomic arrangements become unstable at different pressures), and is thus manifested as a continuous change in structure.

In summary, we predict that there is a pressure-induced first-order phase transitions from lda to hda in silica, characterized by a discontinuous change in volume. The first-order phase transition can be kinetically hindered at low temperatures, in which case the lda phase persists until it undergoes a gradual spinodal decomposition at a higher pressure.

### 2.5 Order-disorder transitions in polydisperse colloids

We have also shown for colloidal systems that increases in polydispersity lead to the disappearance of energy minima corresponding to ordered structures, analogously to the effects of stress [6]. The disappearances are detected by the decrease to zero of the curvature of the energy minimum and the ensuing discontinuous decrease in the extent of order. These results demonstrate that there is a terminal polydispersity above which the crystal phase cannot possibly exist, even as a metastable state.
2.6 Biological evolution

The dynamics of evolutionary processes and the dynamics of liquids and glasses have both been described in terms of landscapes [1]. The dynamics of evolutionary processes are determined by a fitness landscape, which is the success of an entity in reproducing as a function of genotype (or phenotype) [12]; populations are localized about fitness maxima at low mutation rates, and become increasingly delocalized throughout larger regions of the fitness landscape at higher mutation rates [2]. The dynamics of liquids and glasses are determined by an energy landscape, which is the energy as a function of atomic configuration [11]; the system is localized about energy minima at low temperatures, and becomes increasingly delocalized throughout larger regions of the energy landscape at higher temperatures. The fitness and energy landscapes are both rugged landscapes, in that there are many local optima.

Simulation results suggest that regressive evolution (i.e., evolution to a less adapted state) will often occur in response to environmental change, by a process analogous to the stress-induced reversal of aging in glassy materials [5]. The key to this process is the stress-induced disappearance of fitness optima that lead to irreversible changes in the location of a population in genotype space. Even though the population may always evolve to higher fitness states, this irreversible process will often act to bring an initially well-adapted system to a less adapted state upon a return to initial conditions.

Punctuated equilibrium in biological evolution and first-order amorphous-amorphous phase transitions in liquids and glasses are both characterized by sharp property changes that punctuate periods of little property change. The landscape paradigm is used to suggest that punctuated equilibrium can occur by a mechanism analogous to that underlying first-order amorphous-amorphous phase transitions. In this mechanism, the population suddenly moves to a different region of the fitness landscape after environmental change causes that region of the landscape to become more favorable. This mechanism is an equilibrium (rather than kinetic) mechanism, and is applicable if the mutation rates are sufficiently high such that the fitness valleys are readily traversed on the time scales of the environmental change.

3. Conclusions

Stress leads to important changes in energy landscapes, which alter the system dynamics and ultimately the system properties. For example, stress can lead to the disappearance of local minima of the potential energy landscape. These landscape changes are shown to lead to
amorphous-amorphous phase transitions, enhanced diffusion in flowing liquids, plastic deformation in glassy materials, and a critical polydispersity for colloidal crystals. Similar landscape ideas may give insights into biological evolution.

Acknowledgments

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References

LOCALIZED LOW-ENERGY EXCITATIONS IN GLASSES

Effect of pressure

V. Hizhnyakov,* J. Kikas, An. Kuznetsov,
A. Laisaar,† A. Suisalu

[VH,AK,AL,AS] Institute of Physics, University of Tartu, Rüüt Street 142,
51014 Tartu, Estonia

[VH,JK] Department of Physics, University of Tartu, Tõnise Street 4,
51010 Tartu, Estonia

Abstract

We show that the external pressure reduces the number of localized low-energy excitations in glasses. We also explain the experimentally observed narrowing of spectral holes in glasses under hydrostatic pressure.

1. Introduction

It is well known that in any glass, besides the ordinary phonons, there are also specific low-energy excitations: tunneling two-level systems (TLSs) and quasi-harmonic soft localized modes (SLMs) (see Refs. [1, 2, 3] and reviews [4, 5, 6, 7]). At very low temperatures \( T < 2-4 \) K, various properties of glasses, e.g., their specific heat \( C_P \), are mainly determined by TLSs, whereas at somewhat higher temperatures \( 4 \) K \( < T < 20 \) K the prevailing contribution comes from SLMs (see, e.g., a review [5] and Chapters 8 and 9 in Ref. [6]).

A notable feature of the low-energy localized excitations, especially of SLMs, in a glass is their rather high sensitivity to external pressure, as was shown by the measurements of heat capacity, thermal conductivity, optical spectra, neutron scattering, etc. The first evidences came from studying the pressure dependence of the well-known peak in the plot of

*E-mail address: hizh@fi.tartu.ee
†E-mail address: laisaar@fi.tartu.ee

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$C_p/T^3$ versus $T$ at $T_1 = 3 - 5$ K in glassy polymers [8, 9] (see also [10]). It was found that this peak was markedly suppressed and slightly shifted to higher $T$ at pressures of a few kilobars. An independent confirmation was given by our observation of a notable (1.8-fold) decrease in the width of spectral holes burned in a chlorin-doped glassy polystyrene under pressure of 5.1 kbar at 4.2 K [11]. Afterwards it was found [12, 13, 14, 15] that at somewhat higher temperature (8 and 15 K) this effect of the hole narrowing with pressure is even more pronounced. Certain (although not so strong per unit pressure) suppression of the width of spectral holes has also been observed at temperatures $T < 4.2$ K [16, 17].

At low temperatures the width of spectral holes $\gamma$ (being a measure of the homogeneous width $\gamma_{\text{hom}}$ of the respective zero-phonon lines: $\gamma \approx 2\gamma_{\text{hom}}$) is mainly determined by the interaction of an electronic transition in an impurity center with TLSs and SLMs. At $T$ around 4.2 K, both TLSs and SLMs contribute roughly equally to the width of the spectral hole [14]; at lower temperatures the main contribution comes from the TLSs, while at higher temperatures the contribution from SLMs dominates. Thus, the observed pressure narrowing of holes, more pronounced at 15 K than at 4.2 K, points to a reduction in the number of soft localized excitations, especially of SLMs. In this paper, we show that such a reduction of the SLMs is a consequence of the pressure-induced transformations of the low-energy excitations in a glass with the predominance of the conversion of soft localized excitations into non-soft TLSs over the opposite process.

2. Soft anharmonic potential model

Our consideration is based on the soft anharmonic potential (SAP) model [18, 19], which offers a unified description of both TLSs and SLMs within the scope of the general theory. In this model, the low-energy excitations are described by the single-coordinate anharmonic oscillator potentials

$$U(x) = E_0(\eta x^2 + \xi x^3 + x^4).$$

Here $x$ is the dimensionless collective coordinate of a group of atoms involved in a TLS or SLM ($x$ is expressed in the length units $a_0 \sim 1$ Å on the atomic scale), $E_0 \sim 10$ eV is of the order of the binding energy of atoms in a glass, while $\eta$ and $\xi$ are randomly distributed dimensionless parameters, smaller than unity. As is known, the SLMs in this model are described by a single-well potential and they must have a small positive $\eta$ value and a small positive or negative $\xi$ value so that the condition $\xi^2 < 32\eta/9$ would be satisfied. On the contrary, TLSs have a double-well potential and they must satisfy the reverse inequality $\xi^2 > 32\eta/9$. 


2.1 Distribution function

The SLMs in the SAP model are described by the tail of a broad distribution function $F(\eta, \xi)$. According to [18, 19] this function has a positive mean value $\bar{\eta} \sim 0.3 - 1$, whereas the distribution of $\xi$ is centered around the mean value $\bar{x} = 0$, and is assumed to be an even function of $\xi$, i.e. $F(\eta, \xi) = F(\eta, -\xi)$. However, it was shown by us [20, 12, 14]) that the last statement should be revised: $F(\eta, \xi)$ is no longer an even function of $\xi$ if one relates the sign of the coordinate variation to the sign of the local volume change – the decrease of $x$ corresponds to the decrease of the local volume. If the sign of $x$ is defined in such a manner, then for the majority of SLMs $\xi$ must be negative, i.e., $\xi < 0$ (note that ordinary pair potentials for atoms also have a negative cubic anharmonicity parameter $\xi$).

To further elucidate the properties of the $F(\eta, \xi)$ function we take into account that the potential $U(x)$ of a SAP results from the contributions of a number ($z$) of pair potentials [18, 21]:

$$U(x) = \sum_{j=1}^{z} \Phi_j(x - x_j).$$  \hspace{1cm} (2)

Here $x_j$ is a position of the atom $j$ interacting with the "central atom".

Let us first consider SAPs with $\xi = 0$. We choose all $x_j$ so that the value $\xi = 0$ would be realized at the point $\{x_j = 0\}$. In this case $\eta = \sum_j \Phi_j'(0)/2E_0$; the linear term is absent if $\sum_j \Phi_j'(0) = 0$. If the atoms $j$ are slightly shifted, then the central atom is slightly displaced, too. One can find the latter displacement $x_0$ as follows: at small $x_j$ the main contribution to the appearing of a small linear term in the potential is given by $-\sum_j \Phi_j'(0)x_j$. This term is equal to $-2E_0\mu x_0$, which gives $x_0 = \sum_j \Phi_j'(0)x_j/2E_0\eta$. The displacement leads to the cubic term $4E_0\mu x_0^3$; i.e. the new value of $\xi$ equals $2 \sum_j \Phi_j''(0)x_j/E_0\eta$. Consequently, the probability of finding a SAP with the cubic anharmonicity parameter $\xi$ and given $\eta$ can be written as

$$F(\eta, \xi) \approx \int\cdots\int \delta(\xi - 2 \sum_j \frac{\Phi_j''(0)x_j}{E_0\eta}) P(\{x_j\}) \Pi_j dx_j,$$  \hspace{1cm} (3)

where $P(\{x_j\})$ is the probability of finding the atoms with the coordinates $\{x_j\}$ (it has no peculiarities). One should distinguish the cases 1) $|\eta| \ll \bar{\eta}$ and 2) $\eta \sim \bar{\eta}$. In the first case the actual $\eta$ value is the sum of a number of sign-alternating terms $\Phi_j''(0)/2E_0$. In this case the quantities $\eta$ and $\Phi_j''(0)$ in Eq. (3) are practically independent. Therefore $F(\eta, \xi) \sim |\eta| f(\eta \xi)$, where the function $f$ has no peculiarities. One
can see that the distribution function has the $|\eta|$-type (or "sea gull") singularity [21, 19, 5] and it depends only on the product of $\xi$ and $\eta$ [20]. The latter dependence may be approximated by a straight line with a negative slope. Therefore in the small $|\eta|$ and $|\xi|$ limit

$$F(\eta, \xi) \propto |\eta|(1 - \beta_1 \eta \xi),$$

where $\beta_1 > 0$ is a parameter. In the second case, the most probable are the values of the $\Phi_j''(0)$ being close to the mean value of $\Phi''(0) \approx E_0 \eta / \bar{z}$. Then in Eq. (3) the factor $E_0 \eta$ cancels out. Therefore in the $F$-function the factor $|\eta|$ vanishes and the $|\eta|$ and $|\xi|$ values become uncorrelated.

The range of applicability of Eq. (4) is characterized by the parameter $\eta_1$. According to our consideration it is determined by fluctuations of the local structure of a glass. Note also another opinion (see, e.g. [5]): $\eta_1$ is determined by the interaction of TLSs via phonon exchange.

3. Density of states for SLMs

In the case when $\xi^2 < 32\eta/9$, the shape around the bottom of SAPs only weakly depends on $\xi$. Therefore the effect of anharmonicity in their lowest vibrational states may be neglected. In such a case, the DOS of the SLMs with a given frequency $\omega$, $\rho(\omega)$, is defined by the number of SAPs with the corresponding $\eta = (\omega/\omega_D)^2$ value and with all $\xi$ values between $-\sqrt{32\eta/9} \sqrt{32\eta/9}$ [5, 20] or, in terms of a variable $\nu = \xi^2/32\eta$ with all $\nu$ between $-1$ and $1$:

$$\rho(\omega) \propto \int_1^1 \tilde{F}(\eta, \xi) d\nu; \; \eta = (\omega/\omega_D)^2, \; \xi = \nu \sqrt{32\eta/9}. \; (5)$$

Here $\tilde{F}(\eta, \xi) = \eta F(\eta, \xi), \omega_D = \sqrt{2E_0/Ma_0^2}$ is a characteristic frequency of glass (close to the Debye frequency). Inserting here Eq. (4), one finds that for small $\omega \ll \Omega = \omega_D \sqrt{\bar{m}}$, due to the $|\eta|$-type singularity of the distribution function, we have $\rho(\omega) \propto \omega^4$. To write $\rho(\omega)$ in an explicit form, we apply the quasi-Lorentzian density of states [22]

$$\rho(\omega) \propto \frac{\omega \Gamma_\omega}{\Gamma_\omega^2 + (\omega^2 - \omega_0^2)^2}, \; (6)$$

where $\omega_0 \sim \omega_D$ and $\Gamma_\omega = \omega^3/\Omega$. This expression for $\rho(\omega)$ allows one to describe the contribution of SLMs to the heat capacity of glasses in a broad temperature interval (e.g., for polystyrene between 1 K and 50 K).
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4. Effect of Pressure on SLMs

The effect of pressure $P$ on a SAP in the low $P$ limit may be described by adding to $U(x)$ a term linear in $P$ and $x$, $E_0\kappa P x$, so that

$$U_P(x) = E_0(\eta x^2 + \xi x^3 + x^4 + \kappa P x).$$

Here $\kappa > 0$ is the material parameter related to the local compressibility of a glass. To estimate this term, $\kappa$ may be replaced by the bulk compressibility, which for organic solids is $\sim 10^{-5}\text{bar}^{-1}$. Introducing a new coordinate $X = x + \kappa P/2\eta$, one can obtain (up to an additive constant)

$$U_P(X) \approx E_0(\eta P X^2 + \xi P X^3 + X^4),$$

(7)

where $\eta_P \approx \eta - 3\xi\kappa P/2\eta$ and $\xi_P \approx \xi - 2\kappa P/\eta$. Here the terms higher than linear in $P$ are neglected. It can be seen that pressure leads to the following changes in the $\eta$ and $\xi$ values: $\Delta \eta_P \approx -3\xi\kappa P/2\eta$ and $\Delta \xi_P \approx -2\kappa P/\eta$. The pressure-induced increase of $\bar{\eta}$ (which requires that $\Delta \eta_P$ should on average be positive) can be realized only if $\bar{\xi} < 0$.

Under pressure the distribution function will alter and take the form

$$\tilde{F}_P(\eta, \xi) = \int \int \tilde{F}(\eta', \xi') \delta(\eta - \eta_P) \delta(\xi - \xi_P) d\eta' d\xi'.

(8)

In the low $P$ limit one gets

$$\tilde{F}_P(\eta, \xi) \approx \tilde{F}(\eta - \Delta \eta_P, \xi - \Delta \xi_P).

(9)

Consequently, the DOS under pressure can be obtained by replacing in Eq. (5) $\eta$ and $\xi$ by their prior-to-pressure-application values $\eta + 3\kappa P/2\eta$ and $\xi + 2\kappa P/\eta$. Thus the $\tilde{F}_P(\eta, \xi)$ function becomes shifted with respect to $\tilde{F}(\eta, \xi)$ towards smaller $\xi$ values. As a result, TLSs above the upper integration limit will enter the integration region, i.e. will transform into SLMs (the latter process was demonstrated in Ref. [23] by computer simulations). At the same time, SLMs near the lower integration limit will transform into TLSs and will leave the integration region. In the case of an asymmetric $F(\xi)$ function with negative $\bar{\xi}$, SAPs with negative $\xi$ prevail over those with positive $\xi$. Therefore more SLMs will disappear than emerge under pressure, i.e. on the whole the SLM system will be suppressed [24].

To find the effect of pressure on the SLMs DOS in the region of its maximum we take into account that $F(\eta, \xi)$ is a broad function of $\xi$ [5], which allows one to use the approximation $F(\eta, \xi) \approx F(\eta, 0)(1 - \beta \xi)$ [14]. We get

$$\rho_P(\omega) \approx \rho(\omega_P)(1 - 2\kappa \beta P \omega_0^2/\omega^2),$$

(10)
where \( \omega_0 = \omega_D \sqrt{\eta_0} \), \( \omega_P = \omega - \omega_0^2 \sigma P / 2 \omega \), \( \sigma = 16 \kappa \beta / 9 \). We can see that under pressure the DOS of SLMs is both attenuated and shifted towards higher frequencies. Both effects are stronger for lower frequencies. In the low frequency limit we use Eq. (4), which gives

\[
\rho_P(\omega) \propto \omega^4 (1 - \sigma_1 P),
\]

where \( \sigma_1 = 22 \kappa \beta_1 / 3 \). One can see that the DOS is suppressed without changing its \( \omega^4 \) power dependence. To write \( \rho_P(\omega) \) in an explicit form we suppose that at moderate pressures of the order of a few kilobars the DOS given by Eq. (6) can be used, however, with modified parameters \( \omega_0 \) and \( \Omega \) and with a modified peak value of \( \rho(\omega) \). All of them can be obtained from Eqs. (10) and (11). Eventually we get

\[
\rho_P(\omega) \propto \frac{\omega^4 \Omega_P (1 - \sigma_0 P)}{\omega^6 + \Omega_P^2 (\omega^2 - \omega_0^2)^2},
\]

where \( \omega_0^2 \approx \omega_0^2 (1 + \alpha P) \), \( \Omega_P \approx \Omega (1 + \sigma_1 P / 2 - 17 \alpha P / 16) \), \( \sigma_0 \approx \sigma_1 / 2 - 15 \alpha / 16 \) and \( \alpha = 16 \kappa \beta \omega_0^2 / 9 \omega_0^2 \).

Figure 1 shows the DOS of SLMs for polystyrene at various pressures, calculated by using Eq. (12). The values of the parameters \( \omega_0 \approx 70 \) cm\(^{-1} \) and \( \Omega \approx 9 \) cm\(^{-1} \) were derived from the fit between the calculated and the experimental [25] \( C_P(T) \) values from 2 to 30 K at 1 atm in this material. The calculated \( \rho(\omega) \) is in very good agreement with the DOS of the low-frequency vibrational modes in glassy polystyrene obtained from site-selective fluorescence spectra [26]. For the pressure parameters \( \sigma_0 \) and \( \alpha \) we chose the values \( \sigma_0 = 0 \) and \( \alpha \approx 0.2 \) kbar\(^{-1} \) [this value of \( \alpha \) corresponds to the above estimations \( \kappa \sim 10^{-5} \) bar\(^{-1} \) and \( \beta \sim 1 \), and to the ratio \( (\omega_0/\omega_1)^2 = \eta_0 \sim 0.1 \) (see Sect. 3.3 in Ref. [5]); it agrees well with our experimental data (see below)]. It is evident from Fig. 1 that the calculated DOS of SLMs is remarkably suppressed and shifted to higher frequencies already at 3 kbar. In a qualitative agreement with the Raman scattering results in vitreous GeS\(_2\) [27] and inelastic neutron scattering in pressure-densified SiO\(_2\) glass [28], the calculated DOS is reduced at all \( \omega \) values; the strongest reduction occurs around the peak of \( \rho_P(\omega) \) and on the left of it, while at large \( \omega \) values the reduction tends to zero.

Recently we studied a pseudophonon sideband in the hole-burning spectrum of chlorin-doped glassy polystyrene under pressure up to 3.7 kbar at 4.8 K. As a result of a prolonged (~30 min) laser irradiation at the peak of the chlorin 0 – 0 absorption band near 636 nm, a pseudophonon sideband appeared with its peak being located at ~ 13 cm\(^{-1} \) to the red from the purely electronic hole (see Fig. 2). At high pressure
of 3.7 kbar this sideband was somewhat suppressed in its low-frequency part and shifted by 2 cm\(^{-1}\) further away from the 0-0 hole. As is known [21], the phonon sideband represents the weighted DOS for all low-energy excitations, interacting with the electronic transition (including phonons and SLMs). Thus our experimental result may be considered as an additional support to our theoretical treatment of the pressure variation of DOS for SLMs in glasses.

5. Effect of pressure on TLSs

In the SAP model the TLS correspond to two-well potentials. The low-energy TLSs take place in two cases: 1) \(\eta \approx \eta' = \xi^2/4\) \((\eta > 0)\), 2) \(\eta < 0\), \(\xi^2 < 32|\eta|/9\). Here we consider only the first case, while the second case can be reduced to this case by a proper shift of the

Figure 1. Theoretical DOS for soft localized modes in a glassy polystyrene at various pressures as calculated from Eq. (12). The parameter values are given in the text.
coordinate. Let us rewrite the potential in the form

\[ U(x) = E_0 x^2 [(x + \xi/2)^2 + \delta], \]

where \( \delta = \eta - \eta', \eta' = \xi^2/4. \) We are interested in the almost equally deep potential wells (minima) when \( \delta/\eta' \ll 1. \) In this case the minima are in the coordinates \( x_1 = 0, \ x_2 \approx -(\xi/2). \) The energy difference of the minima is \( \Delta \approx E_0 \eta/\delta, \) the tunneling probability equals \( \Gamma \approx \varepsilon e^{-\lambda}, \) where \( \varepsilon \approx (2E_0 \eta_1/M)^{1/2}/a_0 \) is the energy of the zero-point vibrations, \( \lambda \approx (MV_0 \eta_2)^{1/2}/a_0 \hbar = E_0 \eta^2/4 \varepsilon. \) Energy of the TLS equals \( E \approx \sqrt{\Delta^2 + \Gamma^2}. \)

We are interested in the TLSs with \( E \approx 10^{-5} E_0 \sim 10^{-4} - 10^{-5} \text{eV}, \ \lambda \approx 5 - 8, \ \eta' \approx \eta_2 \approx 0.2 - 0.3. \) The DOS of such TLSs, \( W(E), \) is

\[ W(E) \sim \frac{1}{\sqrt{E}}. \]
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determined by the integral [1]:

\[ W(E) \propto \int_0^E d\Delta \int_{\lambda_1}^{\infty} d\lambda \phi(|\Delta|) \delta(E - \sqrt{\Delta^2 + \Gamma^2}) \]

\[ \sim \phi(E) \int_{\Gamma_1}^E d\Gamma / \Gamma \sim \phi(E) \ln E \approx \text{const.} \]

where \( \lambda_1 \approx 5 - 8 \) is the lower value of \( \lambda \) consistent with the condition \( \Gamma \sim E \sim 10^{-5} E_0 \), whereas \( \Gamma_1 \ll E \) and \( \phi(|\Delta|) \) is the distribution function of the parameter \( |\Delta| \). For \( \Delta < 10^{-5} E_0 \), \( \phi(|\Delta|) \approx \Phi(\eta_2) \), where

\[ \Phi(\eta_2) \equiv F(\eta_2; -2\sqrt{\eta_2}). \]

Here we take into account that the SAPs with negative \( \xi \approx -2\sqrt{\eta_2} \) mainly contribute to the TLSs and that \( \Phi(\eta_2) \) is a very broad function of \( \eta_2 \) (as compared to \( E/E_0 \)).

One can find the dependence of \( W(E) \) on pressure by replacing \( \eta_2 \) in the function \( \Phi(\eta_2) \) with \( \eta_{2P} = \eta_2 - \kappa P / \sqrt{\eta_2} \). One gets

\[ W_P(E) \approx W(E) - \kappa P \Phi'(\eta_2) / \sqrt{\eta_2}. \tag{13} \]

The above estimations show that \( \eta_2 \) is smaller than \( \bar{\eta} \). Therefore the derivative \( \Phi'(\eta_2) \) is positive and the difference \( W_P(E) - W(E) \) is negative, i.e. the DOS of the low-energy TLSs decreases with pressure. By the order of magnitude, \( |W(E) - W_P(E)| / W(E) \sim \kappa P \). This is smaller than \( \rho(\omega) - \rho_P(\omega) / \rho(\omega) \sim \kappa P / \eta_1 \), i.e. the relative change of the DOS for SLMs with low frequencies \( \omega < \Omega \sim 5 \ \text{cm}^{-1} \). This can be understood as follows: the low-energy TLSs, as distinct from the low-frequency SLMs, are not very soft systems – their zero-point frequency \( \varepsilon / \hbar \gg \Omega \) is relatively high, the barrier between the minima \( V_b = E_0 \eta_2^2 / 16 \sim 10^{-1} - 10^{-2} \ \text{eV} \) being also rather high. Therefore they are less sensitive to the external pressure than very soft SLMs.

6. Width of a spectral hole

Knowing \( \rho_P(\omega) \) for SLMs and \( W_P(E) \) for TLSs, we can calculate their contribution to the width of spectral holes at different \( P \) and \( T \) values. To this end, we shall take into account that at low temperatures the thermal broadening of holes, induced either by SLMs or by TLSs, is governed by the same mechanism: both broadenings arise from the fluctuations of the frequency of the zero-phonon electronic transition in an impurity center due to thermally activated transitions between the energy levels of SLMs or TLSs [21]. Supposing that the characteristic time of these transitions is short as compared to the time interval between burning
and measuring the hole, the contribution of SLMs to the holewidth is
determined [21] by the quantity $\rho(|\Delta\omega(n - n')|^{3/2}) \rho(\omega) d\omega)^{k/3}$. Here $n$
($n'$) is the nth ($n'$th) level of a SLM which was occupied when the hole
was burned (measured), $\{(\cdot \cdot \cdot T)$ denotes the thermal averaging, $\Delta\omega$ is the
change of the SLM's frequency on the electronic transition, $k = 3$ if the
interaction of centers with SLMs is of the dipole-dipole type, $k = 4$ if it is
of the dipole-quadrupole type, etc. The difference between the most relevant
cases $k = 3$ and $k = 4$ is rather small. So we can confine ourselves
to a simpler case $k = 3$. The thermal averaging of the quantity $|n - n'|$
yields $1/\sinh(\hbar\omega/k_B T)$. Supposing that the changes of the parameter
$\eta$ for SLMs due to the electronic transition in the impurity center do
not depend on the values of $\eta$, one finds $\Delta\omega \propto 1/\omega$. As a result, the
contribution of SLMs to the holewidth can be written as

$$\gamma_{\text{SLM}}(P, T) = \text{const} \times \int_0^{\Delta \omega^2} \frac{\rho_P(\omega) d\omega}{\omega \sinh(\hbar\omega/k_B T)}. \tag{14}$$

According to this formula $\gamma_{\text{SLM}} \propto T^4$ at $T \ll \hbar\Omega/k_B$ and $\gamma_{\text{SLM}} \propto T$ at
$T \gg \hbar\Omega/k_B$. The contribution of the TLSs is described by an analo-
gous formula, where $\rho_P(\omega) d\omega$ and $\omega \sinh(\hbar\omega/k_B T)$ have been replaced
by $W_P(E) dE$ and $2 \cosh(E/2k_B T)^2$, respectively. For TLSs one gets
$\gamma_{\text{TLS}} \propto T^{k/3}$ at any $T$.

In Fig. 3 we compare the calculated holewidths with our data points
obtained for chlorin-doped polystyrene in isobaric-isothermal experi-
ments (no $P$ or $T$ variations between burning and measuring the hole).
The curves show calculated $P$ dependence of the holewidths at three
fixed $T$ values. The contribution of SLMs to the holewidth, $\gamma_{\text{SLM}}$, was
found from Eqs. (12) and (14), using the same parameter values as in
Fig. 1. The contribution from TLSs was taken to vary with $T$ and $P$
as $\gamma_{\text{TLS}} \approx 0.5 T^{1.3}/(1 + 0.03 P)$ GHz, with $T$ expressed in K and $P$ in
kbar. Here the $T$ term, $0.5 T^{1.3}$, was taken from Ref. [29] for chlorin in
polystyrene, while the $P$ term, $1/(1 + 0.03 P)$, was estimated from our
high-pressure data at 4.2 K, where contributions from SLMs and TLSs
to $\gamma = \gamma_{\text{SLM}} + \gamma_{\text{TLS}}$ are roughly equal. The constant in Eq. (14) is the
fitting parameter. As can be seen from Fig. 3, both theory and exper-
iment show that the higher the temperature, the stronger the effect of
pressure-induced narrowing of spectral holes.

7. Conclusion

We have presented a model which describes the effect of pressure on
soft localized modes in glasses. According to this model, the external
pressure, in addition to increasing, on average, the frequencies of SLMs,
also decreases their number. This happens because SLMs with a neg-
Figure 3. Pressure variation of the width $\gamma$ of the spectral holes burned at the peak of the $S_1 \rightarrow S_0$ 0–0 absorption band (\sim636 nm) of chlorin molecules in polystyrene at 4.2, 8, and 15 K. Points - experiment; curves - theory (solid lines: $\gamma = \gamma_{\text{SLM}} + \gamma_{\text{TLS}}$; dashed lines: $\gamma_{\text{TLS}}$).

ative cubic anharmonicity $\xi$ are more abundant than the SLMs with a positive $\xi$. Owing to this, the applied pressure not only enhances the stiffness of SLMs, but also predominantly (over the reverse process) induces their transformation into two-level systems. We have calculated the contribution of SLMs into the width of spectral holes in a dye-doped polystyrene as a function of pressure at different temperatures and have found that the proposed model explains the observed pressure-induced narrowing of holes, rather strongly depending on the temperature of a sample.

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[24] The pressure-generated TLSs are not low-energy ones.
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AMORPHOUS PRESSURE-INDUCED ALLOYS

Formation, stability, and crystallisation

V. F. Degtyareva

Institute of Solid State Physics Russian Academy of Science,
Chernogolskoe, Moscow district, 142432

Abstract

An amorphous state of materials is a metastable state which can be produced by different ways, as for instance, by quenching from the liquid, sputtering thin films, ion implantation, ball milling or action of high pressure. Intensively studied amorphized materials, both experimentally and theoretically, are tetrahedral semiconductors—group IV elements and III-V compounds. This paper concerns a special case of pressure-induced amorphization in binary alloy systems. Discussed are some general features of amorphous pressure-induced state in binary alloy systems, the conditions providing alloy amorphization and crystallization processes of amorphous phases. An ability of binary alloy systems to form an amorphous phase is regarded to valence electron concentration in spirit of known Hume-Rothery phases. The subject of discussion is amorphous state primarily in alloys with a two-phase mixture at ambient conditions as in Al-Ge, Cd-Sb and Zn-Sb alloys. Alloy amorphization is considered by pressure quenching and in situ under pressure.

1. Formation of amorphous phases in binary alloys by “pressure quenching”

Systematic studies of binary alloys under high pressure have been developed in the group of Ponyatovskii (in the Institute of Solid State Physics Russian Academy of Science) using a method of “pressure quenching” [1]. The samples of alloy are exposed at pressure/temperature to allow a formation of new high-pressure intermetallic phases and then quenched to liquid nitrogen temperature. The quenched alloys are studied by X-ray diffraction at ambient pressure at low temperature. In the binary alloys of group II to V elements several intermediate phases
were obtained by “pressure quenching” and their crystal structure was determined [1]. Some additional intermediate phases were registered during the annealing of quenched alloys to room temperature. This corresponds to the known Ostwald’s step rule allowing for a system on the way from a metastable to an equilibrium state the formation of intermediate metastable states (with local energy minima). Of particular interest is that these intermediate states can be as crystalline as well as amorphous.

**Figure 1.** Diffraction patterns of (a) Al$_{30}$Ge$_{70}$ and (b) Zn$_{45}$Sb$_{55}$ alloys after exposure to pressure/temperature annealing and pressure quenching, taken at room temperature/ambient pressure on Cu $K_{\alpha}$ radiation (Ref. [5]). Two diffuse haloes are a characteristic of an amorphous state in both alloys. A small admixture of the crystalline phase ZnSb in the Zn-Sb alloy indicates that composition of the amorphous phase is $\sim$ Zn$_{40}$Sb$_{60}$.

Amorphous alloys have been obtained after pressure quenching of metallic high-pressure phases and returning to room temperature. Amorphization of alloys occurs as a result of solid-solid reaction like as a spontaneous process. An amorphous state has been obtained in the following binary alloy systems: Al-Ge [2], Cd-Sb and Zn-Sb [3], and Ga-Sb [4]. There are some common features for these alloys systematised in Ref. [5]. Amorphous states in binary alloy studied have similarity in their diffraction patterns characterized by two broaden peaks of relatively strong intensity as shown in Fig. 1 for Al$_{30}$Ge$_{70}$ and Zn$_{45}$Sb$_{55}$. An initial state of alloys in both cases was a two-phase mixture Al+Ge and ZnSb+Sb, respectively. After exposure to pressure/temperature annealing and pressure quenching metallic high-pressure phases are retained at
ambient pressure/low temperature and amorphous phases are observed in both alloys after heating to room temperature.

It was shown that the alloy amorphization appears under certain conditions, among which the important one is an existence of a semiconducting phase in the equilibrium alloy. This can be a semiconducting phase of a constituent element (Ge in Al-Ge) or an intermediate semiconducting compound (CdSb, ZnSb, GaSb). Amorphous phase composition ranges with respect to that of a semiconducting phase can cover this range (GaSb) or lie beyond the range of a semiconducting phase (Al-Ge, Cd-Sb, Zn-Sb). In the latter case the amorphous phases correlate in composition to high-pressure metallic phases. There is a common characteristic of an amorphous phase for all cases discussed that it occurs at a particular alloy composition, which is referred to an average number of valence electrons in the alloy, i.e. valence electron concentration, equal to 3.7 - 4 electron per atom.

![Diffraction patterns](image)

*Figure 2.* Diffraction patterns of ZnSb and CdSb taken in a diamond anvil cell on Mo Kα radiation (Ref. [6]). Left: (a) CdSb compound, 0 GPa; (b) sh+ Cd, 7.5 GPa; (c) amorphous phase, 0 GPa, decompression; (d) crystalline phase Cd₃Sb₂, 0 GPa, in 2 days. Right: (a) ZnSb compound, 0 GPa; (b) sh+ Zn, 7.5 GPa; (c) amorphous phase, 0 GPa, decompression; (d) sh+ Zn, 105 GPa, recompression. Stars denote diffraction peaks from Cd or Zn.

2. **Alloy amorphization under pressure: in situ x-ray diffraction**

Crystal-to-amorphous transition was observed in situ under pressure by X-ray diffraction studies of alloys Cd-Sb and Zn-Sb [6]. A diamond
anvil cell was used with the laboratory X-ray source (Mo radiation). Polycrystalline compounds CdSb and ZnSb with orthorhombic structure $\sigma P16$ were pressurized in quasihydrostatic conditions up to $\sim 15$ GPa at room temperature. Previous studies on these systems by pressure quenching [3] have shown that these 50/50 compounds of semiconducting type decompose under pressure and new intermediate phases of metallic type form around a composition $\sim 60$ at.% Sb with an excess Cd or Zn. This process of decomposition was observed in situ by structural high-pressure studies. Diffraction patterns taken with increasing pressure (Fig. 2) show in both alloys above 7 GPa a new phase with a simple hexagonal structure, $sh$, with admixture of Cd or Zn. On decompression, the high-pressure phase transformed to an amorphous phase in both alloys. On recompression, the crystalline high-pressure phase recovered and by decompression returned again to the amorphous state. The "stability" of amorphous phases under ambient conditions is different in different systems. Relatively unstable is the amorphous phase in Cd-Sb, it began to crystallize in two days (see Fig. 2), first into a metastable compound Cd$_3$Sb$_2$ and then into the equilibrium compound CdSb. This process of crystallization via a metastable state is also in accordance with the Ostwald's step rule.

Relatively stable at room temperature are amorphous phases in ZnSb and Al-Ge. Crystallization of these amorphous alloys was observed under pressure or by temperature annealing.

3. Amorphous alloy crystallization: two ways

Crystallization of amorphous alloy under pressure was studied for Al$_{30}$Ge$_{70}$ alloy with diamond anvil cell using energy dispersive diffraction on synchrotron radiation [7]. An initial state of alloy was amorphous obtained by pressure quenching [2] after exposure to 9 GPa at 320° C. Diffraction patterns show the transition above 5 GPa from the amorphous phase to a crystalline phase with a simple hexagonal structure - the same phase that was previously obtained by pressure quenching [2]. This amorphous-crystalline transition is reversible, it reproduced several times by loading and unloading the cell as shown on Fig. 3. The crystallisation process of amorphous phase occurs during quite a short time (just after a change in pressure, within few minutes) implying a non-diffusion character of this transformation. It follows that both amorphous and high-pressure crystalline phases are of the same composition. This conclusion is supported by in situ under pressure observations of amorphous-crystalline transitions in Zn-Sb and Cd-Sb described above.
Amorphous pressure-induced alloys: Formation, stability, crystallisation

*Figure 3.* Series of diffraction patterns of Al<sub>30</sub>Ge<sub>70</sub> taken in a diamond anvil cell by energy-dispersive diffraction on synchrotron radiation, 2θ = 9.68°, E · d = 7346 KeV-pm (Ref. [7]). Starting alloy is amorphous. Stars denote diffraction peak of Au, a pressure marker. Left: On compression the amorphous phase transforms above 5 GPa to a crystalline high-pressure phase, sh, and another high-pressure phase, hcp, appears above 40 GPa. Middle: On decompression the amorphous phase recovers. Right: After recompression the crystalline sh phase recovers and on decompression the sample returns to the initial amorphous state. Weak diffraction peaks at 2-0.3 GPa belong to an intermediate metastable crystalline phase tentatively with the white tin structure.

Another process of crystallization in amorphous alloy occurs by temperature annealing at ambient pressure [8]. The amorphous Al<sub>30</sub>Ge<sub>70</sub> alloy was annealed at T = 200° C and diffraction patterns were registered in ~ 0.5 h steps. The annealing results in appearance of sharp crystalline peaks of Al and Ge phases corresponding to the equilibrium. A complete amorphous to crystalline transformation was observed after an annealing time of ~ 17 hours. For each step a fraction of crystalline material was evaluated from the relative intensity of crystalline diffraction peaks. This transformation follows the Avrami equation describing thermally activated processes and it appears to be a diffusion controlled process. Thus, the amorphous Al<sub>30</sub>Ge<sub>70</sub> alloy was crystallized by two ways:

(1) into the high-pressure phase of the same composition by a non-diffusion process;
(2) into the ambient-pressure phase mixture Al + Ge by a diffusion process at annealing.

Figure 4. Diffraction patterns of the amorphous Al$_{30}$Ge$_{70}$ alloy after annealing at $T = 200^\circ$ C taken at ambient pressure/room temperature on Cu $K_\alpha$ radiation (Ref. [8]). The amorphous phase transforms into an equilibrium phase mixture Al (fcc) and Ge (diamond-like).

These observations provide an evidence for the “stability” of amorphous state in quenched alloys because of existing of energy barrier hindering the alloy relaxation to the equilibrium. A temperature annealing allows the system to overcome this barrier kinetically. A formation of an amorphous alloy is associated with a chemical disorder of the stoichiometric compound, which occurs by its destabilization under pressure and formation of a metallic high-pressure phase. The metallic phase is usually not strictly ordered and has not as deep and narrow energetic minimum, as the stoichiometric compounds do, especially those of semi-
conducting type. Therefore, to return to the equilibrium state a diffusion process is necessary to separate elements to compositions, which would correspond to initial phases.

4. Stability of amorphous state as an electronic phase of Hume-Rothery type

Special regions for stability of amorphous alloys with respect to alloy electron concentration imply an existence of structural energy minimum for amorphous state as a specially organized structural form. A classical example of crystal structure determination by the number of valence electrons provides the sequence of so-called Hume-Rothery phases in the noble-metal based alloys: $\alpha$ (fcc), $\beta$ (bcc), $\gamma$ (complex cubic), and $\epsilon$ (hcp) along the valence electron concentration 1.35, 1.5, 1.62, and 1.75 [9]. The stability for these phases was explained by Brillouin zone fitting to the Fermi surface [10, 11]. Those Brillouin zones are considered that formed by planes with strong structure factor. These planes lie close to the Fermi sphere. As in the case of complex $\gamma$-phase the Brillouin zone forms many-faced polyhedron lying close to the sphere.

This concept was applied to the family of amorphous alloys with special stability around 1.8 el./atom [12]. It was assumed, that (i) the Fermi momentum, $k_F$, to be spherical; (ii) the reciprocal-lattice vector $q$ corresponding to the first diffraction peak is spherically symmetric; (iii) the stability criteria (Nagel-Tauc) is $q = 2k_F$. Amorphous phases at 1.8 el./atom follow the Hume-Rothery phases in their sequence along the electron concentration with evolution of Brillouin zone to a sphere.

These ideas of phase stability can be extended to higher values of electron concentration with a structural sequence involving phases as simple hexagonal, white tin and simple cubic [13]. In some cases the structure of intermediate phases is rather complex, as for example, the structure of so-called X-phase in Bi-based alloys with orthorhombic cell, $\alpha$C16-$\text{Cmca}$, [14]. Stability of this phase has apparently the same reasoning as for the Hume-Rothery $\gamma$-brass phase.

In a similar manner one could expect a formation of a new class of amorphous phases in this extended range of electron concentration approaching 4 el./atom. Amorphous alloys occurred at $\sim 3.8 - 4$ el./atom correspond to the Nagel-Tauc criteria $q \approx 2k_F$, if $q$ is referred to the second diffraction peak. Within the nearly-free-electron approach the Fermi sphere radius is determined as $k_F = (3\pi^2n/V)^{1/3}$ where $n$ is valence electron number and $V$ is atomic volume estimated approximately to be equal to that of the nearest crystalline semiconducting phase. Experimentally observed $q$ values comparing to estimated values of $k_F$ are
as follows:

<table>
<thead>
<tr>
<th></th>
<th>Al₉₀Ge₇₀</th>
<th>Zn₄₀Sb₆₀</th>
<th>GaSb</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (el./at)</td>
<td>3.7</td>
<td>3.8</td>
<td>4.0</td>
</tr>
<tr>
<td>q (Å⁻¹)</td>
<td>3.4</td>
<td>3.1</td>
<td>3.2</td>
</tr>
<tr>
<td>k_F (Å⁻¹)</td>
<td>1.74</td>
<td>1.64</td>
<td>1.62</td>
</tr>
</tbody>
</table>

The Nagel-Tauc criteria \( q \approx 2k_F \) is satisfied taking into account uncertainties in atomic volumes (see more details in Ref. 5). As far as the first Brillouin zone is considered with the number of electron states not exceeding 2, the first family of amorphous alloys can be located on the scale of electron concentration approaching the boundary of 2 electron per atom. Similarly, for the discussed family of amorphous alloys with \( 3.7 - 4 \text{ el.}/\text{atom} \) the apparent valence concentration boundary is close to 4—the maximum number of electron states allowed to fill the second Brillouin zone.

The known crystalline phases of group IV elements and III-V compounds, with the average 4 valence electrons, are semiconductors and they form covalent bonds of tetrahedral type. The coordination number is 4 in the first coordination shell and is 12 in the second coordination shell. To some extend the amorphous phases discussed can be considered as distorted tetrahedral nets with coordination shells approaching to that of crystalline diamond-like structure, as was shown by recent neutron diffraction studies on bulk amorphous alloys [15, 16]. Therefore the of group IV elements and III-V compounds with diamond-like structure are quite easily amorphized materials in sputtered thin films, by ion implantation or under high pressure. An example of pressure-amorphized III-V compound provides GaSb [4]. In this system the amorphous phase and the high-pressure metallic phase overlap in composition with the initial semiconducting compound. Of special interest is amorphization in Cd-Sb and Zn-Sb where the high-pressure phase and consequently the amorphous phase located in composition range beyond that of semiconducting compounds with the average \( n = 3.5 \text{ el.}/\text{atom} \). This case clearly demonstrates a separation in composition of the amorphous and semiconducting phases. Nonetheless the amorphous phases formed under pressure in binary alloys Zn-Sb, Cd-Sb and Al-Ge are close to tetrahedral nets and correspond to nearly 4 el./atom composition.

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**References**
Amorphous pressure-induced alloys: Formation, stability, crystallisation


MONTE CARLO STUDY OF THE DYNAMIC
AND STATIC GLASS TRANSITIONS
IN THE 10-STATE POTTS GLASS

A scenario for the structural glass transition?

C. Brangian, W. Kob, K. Binder
[CB, WK, KB] Institut für Physik, Johannes-Gutenberg-Universität,
Staudinger Weg 7, 55099 Mainz, Germany
[WK] Laboratoire des Verres, Université Montpellier II,
34095 Montpellier, France

Abstract

It is still an unsolved problem whether or not there is a static phase
transition from a (metastable) supercooled fluid to a (metastable) ideal
glass underlying the structural glass transition, or whether the latter
is purely a dynamical transition (such as described by mode coupling
theory). The $p$-state infinite range Potts glass with $p > 4$ is known as
an example where both a static and a dynamic transition occur in the
thermodynamic limit, $N \to \infty$. In the present paper, we use Monte
Carlo simulations to study for the case $p = 10$ how this limit is ap-
proached by considering values of $N$ in the range $160 \leq N \leq 2560$.
While the mean-field scenario is recovered qualitatively, unexpectedly
large finite-size effects are found. Near the dynamic transition, evidence
for dynamic finite size scaling is found, but the exponents describing the
$N$-dependence of the relaxation time and other quantities are not un-
derstood analytically. The extent to which this model can mimic the
glass transition of real systems is discussed.

1. Introduction

Despite longstanding efforts [1, 2, 3, 4, 5, 6, 7, 8, 9, 10], the under-
standing of why and how an supercooled fluid freezes into a glass (an
amorphous solid) remains controversial. In a rather narrow temperature
range, the viscosity $\eta(T)$ and other measures of the structural relax-
atation time increase typically 15 orders of magnitude, before the fluid
falls out of (metastable) equilibrium and the structure gets arrested, see
Fig. 1. However, there is no consensus on the interpretation of these observations. One theory [2, 3], addressing the decrease of the fluid “configurational entropy” $\Delta S$ as $T$ is lowered, postulates a static transition at $T_0$ where $\Delta S(T)$ for an “ideal” supercooled fluid should vanish. Assuming that the free energy barriers (that need to be overcome by the structural relaxation) scale inversely in $\Delta S$, the relaxation time $\tau$ becomes $\tau \propto \exp\left[E_{\text{act}}/(T\Delta S)\right] = \exp\left[C/(T - T_0)\right]$, where $\Delta S = c(T - T_0)$ and the constant $C$ is related to the energy $E_{\text{act}}$ as $C = E_{\text{act}}/(cT_0)$. This relation $\tau \propto \exp[C/(T - T_0)]$, known as Vogel-Fulcher law [4] is a popular description of the slowing down near $T_g$, but its accuracy is rather doubtful.

Also there are ideas attributing the slowing down to a growing static correlation length $\xi$, similar to Ising spin glasses [11] where $\tau \propto \xi^z$, with a dynamic exponent $z$ that is unusually large [11]. However, we consider the evidence that such an idea works also for the structural glass transition as not very convincing.

Probably the most successful approach is mode coupling theory (MCT) [5, 6]. This microscopic description for the dynamics of density fluctuations in supercooled fluids in its idealized form leads to a sharp transition from an ergodic to a non-ergodic behavior at a critical temperature $T_c > T_g$ (Fig. 1). Of course, the predicted power law divergence of $\eta \propto (T/T_c - 1)^{-\gamma}$ is not in agreement with experiment since usually $\eta(T)$ remains finite even a bit below $T_c$. Therefore it is argued that this divergence occurs only when the atoms are strictly arrested in cages formed by their neighbors, but gets rounded off when hopping “processes” (i.e., thermally activated crossing of barriers in configuration space) are included. But MCT does not make any predictions about a further transition at $T < T_c$.

While these concepts seem very disparate, it is interesting to note that there do exist exactly soluble models where several transitions of the type shown in Fig. 1 occur. One such model is the $p$-state Potts glass with $p > 4$ in the mean field (infinite-range) limit [12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. The Hamiltonian is

$$ H = - \sum_{i<j} J_{ij} \left( \sum_{\sigma_i \sigma_j} - 1 \right), \quad \sigma_i \in \{1, 2, \ldots, p\}, \quad i = 1, 2, \ldots, N, \quad (1) $$

where the bonds $J_{ij}$ are quenched random variables distributed according to a Gaussian,

$$ P(J_{ij}) = \frac{1}{\sqrt{2\pi} \Delta J} \exp \left[ - \frac{(J_{ij} - J_0)^2}{2(\Delta J)^2} \right], \quad (2) $$
Figure 1. Schematic plot of the viscosity $\eta(T)$ of a fluid vs inverse temperature $1/T$. Characteristic temperatures are indicated: melting temperature $T_m$, critical temperature $T_c$ of mode coupling theory (MCT), glass transition temperature $T_g$-defined operationally requiring $\eta(T = T_g) = 10^{13}$ Poise - and Vogel-Fulcher temperature $T_0$, respectively. Upper left inset shows the schematic behavior of the Fourier transform of density correlations $\Phi_q(t)$ for wave-vector $q$ according to idealized MCT: for $T > T_c$ this correlator decays to zero as function of time $t$, in two steps ($\beta$-relaxation, $\alpha$-relaxation). For $T < T_c$ only the first step remains, the system is frozen at a plateau value $f$ (“non-ergodicity parameter”). Lower right inset shows the normalized entropy difference $\Delta S/S_m$ between fluid and crystal [$S_m = \Delta S(T_m)$] as function of $T$: often these data are compatible with a linear extrapolation according to which $\Delta S$ vanishes at $T_0$ (“Kauzmann paradox” [1]).

The mean $J_0$ and width $\Delta J$ are chosen as

$$J_0 \equiv [J_{ij}]_{av} = \frac{\tilde{J}_0}{(N-1)}, \quad (\Delta J)^2 \equiv \left[\frac{J_{ij}^2}{\langle J_{ij}^2 \rangle}_{av} = \frac{(\Delta \tilde{J})^2}{N-1} \quad (3)$$

to ensure a sensible thermodynamic limit. (Here $\langle \rangle_{av}$ stands for the average over the distribution $P$.) We can fix the temperature scale by $\Delta \tilde{J} = 1$, and take $\tilde{J}_0 = 3 - p$ because for this choice the system is far off from any tendency to ferromagnetic order [20].
Fig. 2 presents a qualitative sketch of the mean-field predictions for this model for $N \to \infty$. As usual, the $p$ states are described in the “simplex representation” in which $(p - 1)$-dimensional vectors $\vec{S}$ point towards the corners of a $p$-simplex, $\vec{S}_\lambda \cdot \vec{S}_\lambda^\prime = p \delta_{\lambda \lambda'} - 1$ with $\lambda, \lambda' = 1, 2, \ldots, p$. We can then define an order parameter $q$ as

$$q = \left[ \frac{1}{p - 1} \sum_{\mu, \nu = 1}^{p - 1} (q^{\mu \nu})^2 \right]^{1/2}, \quad q^{\mu \nu} = \frac{1}{N} \sum_{i=1}^{N} \left( \bar{S}_{i, \alpha}^{\mu} \right) \left( \bar{S}_{i, \beta}^{\nu} \right), \quad \mu, \nu = 1, 2, \ldots, p - 1.$$  \hspace{1cm} (4)

Here $\alpha$ and $\beta$ are two “replicas”, that is two systems that have identical bond configuration and evolve according to two independent Monte Carlo simulations.

The reduced spin glass susceptibility $\bar{\chi}_{SG}$ is related to the second moment of the order parameter distribution by

$$\bar{\chi}_{SG} = \frac{N}{p - 1} \left[ \langle q^2 \rangle \right]_{av} = \frac{N}{p - 1} \int_0^1 q^2 p(q) dq. \hspace{1cm} (5)$$

Note that by $\langle \ldots \rangle$ we mean the thermal average in the canonical ensemble. For an Ising spin glass, $p = 2$, we would have a second order freezing transition at $T_s = 1$, where $\bar{\chi}_{SG}$ diverges according to a Curie-Weiss law, $\bar{\chi}_{SG} \propto (T/T_s - 1)^{-\lambda}$, and the order parameter rises continuously, $q \propto (1 - T/T_s)^{\beta_{SG}}$ with $\beta_{SG} = 1$ in mean field theory [11].

For $p > 4$, however, the transition sets in discontinuously at a temperature $T_0 > T_s$, so $\bar{\chi}_{SG}$ is still finite at the transition, and $T_S$ gets only the meaning of an (extrapolated) spinodal. And while for $p \leq 4$ there is a divergence of the relaxation time $\tau$ at $T_S$, i.e. we have ordinary critical slowing down [11], for $p > 4$ the relaxation time diverges already at a still higher temperature $T_D$, where a dynamical transition from ergodic to non-ergodic behavior occurs,

$$\tau \propto (T/T_D - 1)^{-\lambda}, \quad T_D > T_0. \hspace{1cm} (6)$$

This divergence is caused by the occurrence of a long lived plateau in the spin autocorrelation function,

$$C(t) = [N(p - 1)]^{-1} \sum_{i=1}^{N} \left[ \langle \bar{S}_i(t) \cdot \bar{S}_i(t' + t) \rangle \right]_{av}. \hspace{1cm} (7)$$

The behavior of $C(t)$ near $T_D$ is described precisely by the same type of idealized MCT as the structural glass transition [14, 15]. Of course, in mean-field theory the barriers between the valleys in phase space
Figure 2. Mean-field predictions for the $p$-state Potts glass with $p > 4$. The spin glass order parameter, $q_{E,A}$, is nonzero only for $T < T_0$ and jumps to zero discontinuously at $T = T_0$. The spin glass susceptibility $\chi_{SG}$ follows a Curie-Weißenberg-type relation with an apparent divergence at $T_c < T_0$. The relaxation time $t$ diverges already at the dynamical transition temperature $T_D$. This divergence is due to the occurrence of a long lived plateau of height $q_{E,A}$ in the time-dependent spin autocorrelation function $C(t)$. The discontinuous transition of the order parameter, however, is not accompanied by a latent heat: therefore, there is no jump in the entropy at $T_0$, only a kink singularity occurs. The extrapolation of the high-temperature branch of the entropy would vanish at a “Kauzmann temperature” $T_K = [(1/4)(p - 1)/ \ln p]^{1/2} T_s$. 

for $T_0 < T < T_D$ are all infinitely high, and hence unlike in real glasses (Fig. 1) there is no hopping over these barriers possible on finite timescales. Since for our fully connected model with finite $N$ the barriers are finite, however, one expects that Eqs. (1-3) for $N$ finite will be closer in behavior to a real glass [22]. In addition, it is of interest to understand how the mean-field limit is approached as $N$ goes towards $N \to \infty$. These questions are the motivation for the Monte Carlo study that is described in the next section.
2. Monte Carlo results

Simulations were carried out for \(N = 160\) (using 500 samples, that is different sets of \(J_{ij}\)), 320 (200 samples), 640 (100 samples), 1280 (100 samples) and 2560 (up to 50 samples), implementing the Metropolis algorithm, and (for static properties at \(T < 1\)) parallel tempering techniques [23].

![Figure 3](image_url)

Figure 3. Entropy per spin \(s\), normalized by its high temperature value, plotted vs inverse temperature (left hand side), for different system sizes (curves with symbols). The bold dashed and the bold solid curve are the replica symmetric and the one-step replica symmetry-broken solution, respectively. Vertical arrows indicate \(\beta_0 = 1/T_0\) and \(\beta_K = 1/T_K\). The right hand side shows the inverse of the reduced spin glass susceptibility \(\chi_{SG}^{-1}\) vs \(T^{-2}\). Inset: Plot of \(\chi_{SG}^{-1} + T^{-2}\) vs \(T^{-2}\). From Brangian et al. [24].

Figure 3 shows our results for static properties such as the entropy and the inverse spin glass susceptibility [24]. One sees unexpectedly large finite size effects: only for \(1/T \geq 0.7\) a clear convergence to the replica theory (that describes the behavior of the system in the thermodynamic limit) occurs. Although the static glass transition is not a critical phenomenon in this model, but a first order transition, there is a pronounced finite size rounding. But for \(T_0/T \geq 1\) it is quite plausible that convergence occurs towards the 1-step replica-symmetry-broken solution. In fact, both for \(T\) well above \(T_0\) and for \(T\) well below \(T_0\) the convergence seems to scale like \(S(N) - S(\infty) \propto 1/N\), while near \(T_0\) we find [24] for energy and entropy a scaling as \(N^{-2/3}\), and related results are also found for \(\langle q^2 \rangle_{av}\). While such a scaling is expected for Potts glasses with a second-order transition [19, 20, 25] finite size scaling for
first order glass transitions without latent heat still needs to be developed [20]. In any case, our results support the assertion that at the static transition temperature both $\chi_{SG}$ and $s$ are still nonzero.

Fig. 4 shows typical data for the autocorrelation function (see [24] for more details) and autocorrelation times $\tau$. The latter have been defined by $C(t = \tau) = 0.2$, i.e. by the time it takes to fall significantly under the plateau (if it exists) which has a height of $q_{EA}(T = T_D) = 0.328$ [18]. Surprisingly, contrary to expectation (Fig. 2), a clear cut plateau is not detected for $T \geq T_D = 1.142$ but only for $T$ distinctly lower than $T_D$. (Here the value of $T_D$ is obtained from the calculation of De Santis et al. [18].) Furthermore we find that the time-temperature superposition principle [4, 5] is not satisfied, i.e. in the $\alpha$-relaxation regime the correlator $C(t)$ are not just a function of $t/\tau$, as can be seen from the slight spreading of the curves in Fig. 4. Only for $T \leq 0.85$ the principle seems to hold (see inset in the upper panel of Fig. 4). Note, however, that the temperature dependence of $\tau$, see lower panel of Fig. 4, is indeed remarkably similar to the behavior of real glasses (Fig. 1): on the plot $\tau$ vs $1/T$ there is an appreciable curvature, due to the crossover of the power law above $T_D$, Eq. (6), to a presumably Arrhenius behavior for $T < T_D$. These results are, however, again due to finite size effects, as a finite size scaling analysis of the relaxation time shows [21]. Fig. 5 shows that the data for $T > T_D$ indeed are compatible with the predicted power law. Here we use a dynamic finite size scaling Ansatz [21, 26],

$$\tau = N^{z^*} \tau \left\{ N(T/T_D - 1)^{\Delta/z^*} \right\} \text{ for } N \to \infty \text{ and } (T/T_D - 1) \to 0. \quad (8)$$

The scaling function $\tau(\zeta \to \infty)$ is proportional to $\zeta^{-z^*}$, such that for $N \to \infty$, fixed $T > T_D$, the $N$-dependence cancels out and Eq. (6) is recovered.

The resulting estimate for $\Delta(\approx 2)$ is similar to what one finds from MCT analysis for structural glasses. Again, however, we do not understand the exponent $z^*$ describing the size dependence (for second order transitions of mean field spin glasses one has [11, 21, 24] $z^* = 2/3$). Note also that Eq. (8) has a sound theoretical basis for ordinary critical phenomena only [26], while for a dynamical transition Eq. (8) merely is a speculative hypothesis.

3. Conclusions

Extensive Monte Carlo simulations for the $p = 10$ Potts glass model with mean-field interactions, Eqs. (1)-(3), were presented for a range of system sizes $N$, and static properties were found to be compatible with the theoretical predictions that are available for $N \to \infty$. For finite
Figure 4. Plot of $C(t)$ vs $t/\tau$ for $N = 160$ (upper part). The temperatures are $T = 0.7, 0.765, 0.85, 0.9, 0.95, 1.0, 1.142$ and $1.17$ (left to right). The inset shows the same data, but including only the three lowest temperatures. In the lower panel we plot the relaxation time $\tau$ vs. inverse temperature for different system sizes. The broken vertical line indicates the location of the dynamical transition. Note the choice of a logarithmic scale for the ordinate. Error bars of $\tau$ are mostly due to sample-to-sample fluctuations. From Bragian et al. [24]
Figure 5. Log-log plot of the scaled relaxation time $\tau/N^{z^*}$ vs. the scaled distance $N(T/T_D - 1)^{\Delta/z^*}$ from the dynamical transition temperature $T_D$, choosing $z^* = 1.5$ and $\Delta/z^* = 1.3$. The inset is a log-log plot of $\tau(T = T_D)$ vs. $N$. From Brangian et al. [21]

$N$ the temperature dependence of the relaxation time $\tau$ is compatible with a crossover near $T_D$ from a power law (as described by idealized MCT) to an Arrhenius behavior for $T < T_D$. At the same time, this model has a static glass transition but the entropy stays non-vanishing (and there is also no divergent static glass susceptibility) and thus it does present a reasonable scenario for what might happen at the glass transition of structural glasses. Hence we hope that further studies of this model may indeed lead to a better understanding of real glasses, although there clearly is no quenched disorder (for $T > T_g$) present in the latter, while the present model exhibits quenched disorder at all temperatures.

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TRANSITIONS IN SIMPLE LIQUIDS:  
CORRELATION FUNCTION APPROACH

V. N. Ryzhov, E. E. Tareyeva  
*Institute for High Pressure Physics, Russian Academy of Sciences*  
142 190 Troitsk, Moscow Region, Russia

**Abstract**  
We briefly describe the relations between the symmetry of correlation functions and phase transitions in simple liquids. The special attention is paid to the dependence of the transitions on the shape of the interparticle potential.

1. **Introduction**

Despite the growing interest to the possible polymorphic phase transitions in liquids and glasses [1, 2, 3] the nature of different phases which can be found in dense (and possibly metastable) liquids is still puzzling. The coexistence of different phases, while common for mixtures, is unexpected for a simple fluid. In principle, the rules of thermodynamics do not forbid the existence of more than two different fluid phases in a simple fluid, however, from a common experience only two of them are well known: a low density fluid (vapor) and a high density fluid (liquid) phases. At the same time in recent years experimental evidences of such features of phase diagram as liquid-liquid transitions, polyamorphism, etc. appeared for a wide range of systems including water, Si, I, Se, S, C, P, etc [3, 4, 5, 2, 6, 7, 8, 9]. The complexity of the phase diagrams in these substances may be a result of complex interactions depending on the intermolecular orientations. At the same time exploring the possibility that simple fluids interacting through isotropic potentials may exhibit the similar behaviour represent a serious challenge for theorists.

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In this article we are going to briefly analyze the relations between
the symmetry of correlation functions and phase transitions in simple
fluids [10] with the special attention to the dependence of the transitions
on the shape of the interparticle potential.

2. Liquid-liquid transition without changing the
symmetry of correlation functions

Recently a lot of attention is paid to the exploring the hypothesis
that in addition to the known gas-liquid critical point the second critical
point may occur in (may be metastable) liquid phase at low temperatures
and high densities [3, 11, 12, 13, 14]. As at the ordinary critical point,
no symmetry of the correlation functions is broken at this transition. In
this case the order parameter is the difference of densities of high and
low density phases \( \Delta \rho = \rho_1 - \rho_2 \).

The possibility of the existence of the second critical point drastically
depends on the shape of the interparticle potential. After the pioneering
work by Hemmer and Stell [15], a lot of attention was paid to the investi-
gation of the properties of the systems with the so called core-softened
potentials—the potentials that have a region of negative curvature in
their repulsive core. As was shown, depending on the parameters of the
potentials one can observe the waterlike thermodynamic anomalies and
the second critical point [16, 17, 18, 19, 20].

From the intuitive point of view liquid-liquid phase transition between
low density and high density phases may be related to the competition
between expanded and compact structures. This suggests that the poten-
tial should have two equilibrium positions. The most obvious form
of the potential with such a feature is the potential with two wells:

\[
\Phi(r) = \begin{cases} 
\infty, & r \leq \sigma \\
0, & \sigma < r \leq a \\
-\varepsilon_1, & a < r \leq b \\
0, & b < r \leq c \\
-\varepsilon_2, & c < r \leq d.
\end{cases}
\]  

(1)

The potential (1) \((\varepsilon_1 = 1.0; \varepsilon_2 = 1.5; a = 1.5; b = 1.55; c = 1.98; d = 2.0)\) is shown in Fig. 1 along with the radial distribution function of
the hard sphere system for two reduced densities \(\eta = 0.2\) and \(\eta = 0.5\)
(here \(\eta = \pi \rho \sigma^3 / 6\), \(\rho\) is the density of the system and \(\sigma\) is the diameter
of the hard core). This potential may be considered as the first-order
approximation for the water potential [3].

To our knowledge, there are no evidences for the existence of the
second critical point in the case of the two-well potential \(\Phi(r)\). To inves-
Figure 1. The double-well potential along with the radial distribution function of hard sphere system for two reduced densities $\eta = 0.2$ and $\eta = 0.5$. 
tigate this possibility, we developed the mean-field (van der Waals-like) theory for the two-well potential system.

Using the well-known Bogoliubov inequality for the free energy $F \leq F_{HS} < U - U_{HS} >_{HS}$, where $F_{HS}$ is the free energy of the system of hard spheres with diameter $\sigma$, one can estimate the free energy of the two-well potential system. Here $U = \frac{1}{2} \sum_{i \neq j}^{N} \Phi(r_{ij})$ and $U_{HS} = \frac{1}{2} \sum_{i \neq j}^{N} \Phi_{HS}(r_{ij})$. The average over the hard sphere potential has the form

$$< U - U_{HS} >_{HS} = 2\pi \rho N \int_{0}^{\infty} \Phi_{atr}(r) g_{HS}(r)r^2 dr,$$

where $\Phi_{atr}(r) = \Phi(r) - \Phi_{HS}(r)$ is the attractive part of the potential, $g_{HS}(r)$ is the radial distribution function of the hard sphere system which is taken in the Percus-Yevick approximation [21]. To calculate $F_{HS}$, one can use, for example, the approximate Carnahan-Starling equation [22]

$$\frac{F_{HS}}{k_B T N} = 3 \ln \lambda - 1 + \ln \rho + \frac{4\eta - 3\eta^2}{(1 - \eta)^2}.$$

Here $\lambda = h/(2\pi m k_B T)^{1/2}$.

The equation of state is given by $P = \rho^2 \partial (F/N)/\partial \rho$. In Fig. 2 the two families of isotherms are shown for the temperatures close to two critical points which, for the parameters of the potential corresponding to Fig. 1, are given by $\beta_1 = \epsilon_1/k_B T_{c1} = 6.3$ and $\beta_2 = \epsilon_1/k_B T_{c2} = 3.8$. Fig. 2 shows that at low temperatures ($\beta = \epsilon_1/k_B T > \beta_1$) there are two van der Waals-like loops in the equation of state which correspond to two fluid-fluid transitions. In the temperature region $\beta_2 < \beta < \beta_1$ there is only one loop which corresponds to the well known gas-liquid transition, $\beta_2$ being the gas-liquid critical point temperature. $\beta_1$ is the liquid-liquid critical temperature.

Fig. 1 is helpful for understanding the mechanism of appearance of the second critical point. As is well known, even the presence of the gas-liquid transition in the phase diagram of a simple fluid is not a universal feature and strongly depends on the range of the interparticle potential. It is only when a range of the attraction is sufficiently long compared to the range of the repulsion that the gas-liquid transition appears. The situation with the second critical point is more complex. From Fig. 1 and Eq. (2) one can see that upon increasing the density the contribution to the free energy from the second well is always negative and increases in absolute value because it is located near the second maximum of the radial distribution function which grows when the density increases. On the other hand, the contribution from the first well is negative but nonmonotonic because the location of the first minimum of the radial distribution function depends on the density and at some
Figure 2. The isotherms for the double-well potential (1) for different values of \( \beta = \varepsilon_1/(k_B T) \).

density coincides with the position of the first well of the potential. Fig.
3 illustrates the behaviour of the total free energy \( F \) (minus \( F_0 \), where
\( F_0/(k_B T N) = 3 \ln \lambda - 1 + \ln(6/(\pi \sigma^3)) \)) and different contributions to \( F \)
as functions of \( \eta \).
Changing the parameters of the potential one can change the positions of the critical points and the form of the phase diagram. For example, the critical temperatures may be easily made equal or even reversed.
However, from Figs. 1 and 3 it is obvious that the second critical point appears due to the negative curvature of the potential near the position of the first well. So one can conclude that the shape of the potential plays the crucial role in appearance of the second critical point.

It should be noted (see Fig. 2) that the second critical point may appear at high densities corresponding to the metastable supercooled liquid state of the two-well system, because pure hard sphere system freezes at the density \( \eta \approx 0.49 \), and attractive part of the potential stabilizes the solid phase and shifts the freezing point to low densities.

3. Transitions with the change of the symmetry of correlation functions

In the previous section we discussed the transition in liquids which is not accompanied by the change of a symmetry of correlation functions. However, there are phase transitions (real or hypothetical) at which the local structure of the system changes drastically. The broken symmetry of the correlation functions is related to these transitions. In this section we discuss some examples of such transitions.

3.1 Crystallization

Crystallization is the most common phase transition liquids undergo at increasing density or at decreasing temperature. In the solid phase the local density, proportional to the one-particle distribution function, has the symmetry of a crystal lattice and can be expanded in a Fourier series in reciprocal lattice vectors \( \mathbf{G} \):

\[
\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}},
\]

where the Fourier coefficients \( \rho_{\mathbf{G}} \) are the order parameters for the transition.

The equations for the local density (or order parameters) may be obtained in the framework of the density functional theory of freezing [23, 24, 25, 26]. The most important for our purposes feature of the freezing transition is that all classical systems with repulsive potentials seem to crystallize through the first-order transition at low enough temperatures or high densities. In three dimensions attraction does not play qualitative role in nature of the transition (however, it can change the quantitative characteristic of the transition).

On the other hand, it should be noted that in two dimensions the transition scenario depends on the shape of the potential. This feature of two dimensional melting is closely related to the existence of the new
liquid state - the so-called hexatic phase or the phase with the bond orientational order. We shall discuss the properties of this phase in the next subsection.

### 3.2 Local structure and bond orientational order in simple liquids

It should be noted, that higher-order correlation functions are the functionals of the lower-order ones [27, 28, 29], so the broken symmetry of the one-particle distribution function (crystallization) leads to the disruption of the symmetry of two-particle correlation function. However, there is a state of matter which is characterized by the uniform local density, but the broken symmetry of a two-particle correlation function. Let us discuss the transition to this state in detail.

There are two broken symmetries in crystalline solid state - translational and orientational. These symmetries are not independent because rotation of a part of a crystal disrupts the translational symmetry. However, one can imagine the state of matter with long range correlations in directions of the local crystallographic axes but without translational order. Such type of order is called the bond orientational order, where ”bond” is the vector joining a particle with its nearest neighbour. This type of order is well known in theories of two-dimensional melting (hexatic phase) [30, 31]. In this state the density of the system which is proportional to one-particle distribution function is uniform $\rho(r) = const$, but the rotational symmetry of two-particle correlation function is broken:

$$
F_2(r_1 | r_1^0) = g(|r_1 - r_1^0|)(1 + f(r_1 - r_1^0)),
$$

(5)

where $f(r_1 - r_1^0)$ has the symmetry of local environment of the particle at $r_1^0$ and may be written in the form $f(r_1 - r_1^0) = f(|r_1 - r_1^0|, \Omega)$, where $\Omega$ determines the direction of the vector $r_1 - r_1^0$. In the case of three dimensions function $f(r, \Omega)$ may be expanded in a series in spherical harmonics:

$$
f(r, \Omega) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_{lm}(r) Y_{lm}(\Omega).
$$

(6)

In two dimensions the expansion has the form:

$$
f(r, \Omega) = \sum_{m=\infty}^{-\infty} f_m(r) e^{im\Omega}.
$$

(7)

Here $f_{lm}(r)$ and $f_m(r)$ are the order parameters for the transition.

Microscopic equations for the order parameters (6) can be obtained from the exact non-linear equation for many-particle distribution functions [27, 28, 29]. The equation which determines the stability of an
isotropic liquid with respect to the formation of the state with bond orientational order has the form [27, 28, 29]:

\[
f_{lm}(r) - \frac{4\pi}{2l+1} \int \Gamma_1(r, r') g(r') f_{lm}(r') r'^2 dr' = 0. \tag{8}
\]

Here \( \Gamma_1(r, r') \) is obtained from:

\[
\Gamma(r_1, r_1^0, r_2) = \sum_{k \geq 1} \frac{\rho_k}{(k-1)!} \int S_{k+1}(r_1 \ldots r_{k+1}) \times \nonumber
g(|r_3 - r_1^0|) \ldots g(|r_{k+1} - r_1^0|) dr_3 \ldots dr_{k+1}. \tag{9}
\]

\( S_{k+1}(r_1 \ldots r_{k+1}) \) is the irreducible cluster sum of Mayer functions connecting (at least doubly) \( k + 1 \) particles. In the isotropic liquid one has:

\[
\Gamma(r_1, r_1^0, r_2) = \Gamma(r, r', \theta), \tag{10}
\]

where \( r = |r_1 - r_1^0|, r' = |r_2 - r_1^0|, \theta \) - the angle between vectors \( r \) and \( r' \).

\[
\Gamma(r, r', \theta) = \sum_{l=-m}^{\infty} \frac{4\pi}{2l+1} \Gamma_l(r, r') \sum_{l=-m}^{l} Y_{lm}(\Omega_1) Y_{lm}^{*}(\Omega_2), \tag{11}
\]

The angles \( \Omega_1 \) and \( \Omega_2 \) determine the directions of the vectors \( r \) and \( r' \).

It should be emphasized that the state with bond-orientational order is a liquid, because in the framework of the equilibrium theory the shear modulus is proportional to the Fourier coefficients of the one-particle distribution function (4) [31], so the shear modulus of the state with bond-orientational order is equal to zero.

Before calculating the line of the transition for a Lennard-Jones system, let us discuss the correlation function of orientational fluctuations of two-particle distribution function which determines the local structure of a liquid. The correlation function of orientational fluctuations is described by the four-particle correlation function which can be written in the form:

\[
F_3(r_1, r_1^0, r_2, r_3^0) = g(|r_1 - r_1^0|) g(|r_2^0 - r_3^0|) (1 + f_4(r_1, r_1^0, r_2, r_3^0)), \tag{12}
\]

\[
f_4(r_1, r_1^0, r_2, r_3^0) = f(r, R, k, \theta_1, \theta_2, \phi_1 - \phi_2), \tag{13}
\]

where \( r = |r| = |r_1 - r_1^0|, k = |k| = |r_2^0 - r_3^0|, R = |R| = |r_1 - r_3^0|, \theta_1 \) and \( \theta_2 \) are the angles of \( r \) and \( k \) with \( R \), \( \phi_1 - \phi_2 \) - the angle between the planes \( \langle r, R \rangle \) and \( \langle k, R \rangle \). Function \( f(r, R, k, \theta_1, \theta_2, \phi_1 - \phi_2) \to 0 \) for
$R \to \infty$ and can be expanded in a double series in spherical harmonics:

$$f(r, R, k, \theta_1, \theta_2, \phi_1 - \phi_2) =$$

$$= \sum_{m=-\infty}^{\infty} \sum_{l'=-|m|}^{\infty} B_{l',m}^m(r, R, k) Y_{l m}(\theta_1, \phi_1) Y_{l',-m}(\theta_2, \phi_2).$$ (14)

Function $B_{l',m}^m(r, R, k)$ determines the correlations between the regions which local symmetry is described by the indices $(l, m)$. Using the gradient expansion technique [27, 28, 29] one can obtain the set of differential equations for $B_{l',m}^m(r, R, k)$. The solution of these equations may be written in the form [29]:

$$B_{l',m}^m(r_s, R, r_s) = C \exp(-R/\xi_{l,m}),$$ (15)

where $r_s$ is the nearest neighbour distance, and $\xi_{l,m}$ is the correlation length of the orientational fluctuations. $\xi_{l,m} \to \infty$ when approaching the instability line given by Eq. (8).

Steinhardt, Nelson and Ronchetti [33] have studied bond orientational order in a computer simulation of a supercooled Lennard-Jones liquid. They concluded that increase in icosahedral ordering occurs as the liquid is supercooled about 10% below the equilibrium melting temperatures. In this case, extended orientational correlations appear, with little or no increase in the translational correlation length. The symmetry of the icosahedral state is not perfectly icosahedral, however. This result is in agreement with early works by Frank [34], Bernal [35, 36], and Scott [37] who proposed that the local symmetry of simple liquids is determined by defective or fragmented icosahedral building blocks that exhibit a five-fold symmetry.

Fig. 3 represents the behaviour of the correlation length $\xi_{l,m}$ for $l = 6, m = 5$ (icosahedral local symmetry) and $l = 6, m = 4$ (cubic local symmetry) [29]. It should be noted that there is no solution of Eq. (8) for the case $l = 4$ corresponding to the pure cubic local symmetry.

To compare our results with those obtained by Steinhardt et al [33], we made our calculations for the dimensionless density $\rho^* = \rho \sigma^3 = 0.973$. The calculated instability temperature $T^* = k_B T/\varepsilon = 0.683$ is in agreement with the one obtained in [33] in framework of molecular dynamics $T^* = 0.626$. This instability temperature is about 10% below the melting temperature $T^* = 0.701$. It should be noted that recently the five-fold local symmetry was directly observed in a liquid lead by X-ray scattering [32].

The phase diagram of the Lennard-Jones system is shown in Fig. 5. One can see that the bond-orientational order can exist in limited region of the $T^* - \rho^*$ plane. To explain this we calculated the correlation
Figure 4. Orientational correlation lengths $\xi_{6,5}$ (icosahedral local symmetry) - (solid line) and $\xi_{6,4}$ (cubic local symmetry) (dashed line) for Lennard-Jones liquid with the dimensionless density $\rho^* = 0.973$.

lengths $\xi_{i,m}$ for the hard sphere system and found the tendency of the increasing of the correlation for $l = 6$, but no instability was found. So one can conclude that it is the attractive part of the potential that is responsible for the appearance of a bond-orientational order. When density or temperature increase, the role of attraction decreases, and the ordered state becomes destroyed.

It should be noted that the line in Fig. 5 is the spinodal, however due to symmetry reasons, the transition is of the first order, so the actual transition line is above the line in Fig. 5.

The role of the shape of the potential is even more pronounced in two dimensions where the bond orientational order state is called a hexatic phase. More than 20 years ago Halperin and Nelson [30] and Young [38] have developed a theory of two-dimensional melting based on the ideas of Kosterlitz and Thouless [39]. This KTHNY theory predicts that the transition may be fundamentally different from that observed in ordinary three-dimensional systems. It was found that the transition between two-dimensional solid and isotropic liquid can occur via two continuous transitions corresponding, respectively, to dissociation
of dislocations and disclinations. The low-temperature solid phase is characterized by algebraic decay of translational order. Dislocations unbind at a temperature $T_m$ into a phase with short-range translational order, but with algebraic decay of bond-orientational order. This intermediate phase is called the hexatic phase. The properties of the hexatic phase are similar to those of a nematic liquid crystal, except that triangular lattices melt into a phase with persistent sixfold, rather than twofold order. Paired disclinations in the hexatic phase ultimately unbind themselves, driving a second transition at a higher temperature $T_i$ into an isotropic liquid.

A conventional first-order transition between the two-dimensional solid and isotropic liquid is also a possibility [40, 41].

As was shown in our previous works [42], systems with soft-core potentials should melt in accordance with KTHNY scenario, while the hard disk system melts through the first order transition without hexatic phase. To elucidate the influence of the attraction on the possible scenario of two-dimensional melting, let us consider melting of the sys-


tem with square-well potential:

\[
\Phi(r) = \begin{cases} 
\infty, & r \leq \sigma \\
-\varepsilon, & \sigma < r \leq h \\
0, & r > h 
\end{cases}
\]  

(16)

From the intuitive point of view attraction should stabilize the crystal and decrease the melting density, so making the appearance of free dislocations more plausible and favoring the KTHNY scenario. In Fig. 6 the melting density \( \rho_m \) is shown as a function of the attraction radius \( h \) for \( \varepsilon/(k_BT) = 0.5 \) [43].

![Graph showing the melting density \( \rho_m \) as a function of the attraction radius \( h \).](image)

Figure 6. Two dimensional melting density \( \rho_m \) as a function of the attractive part of the potential \( h \) (see details in text).

In Fig. 6 the solid line corresponds to the line of the absolute instability of the solid phase which is close to the line of the first-order transition, dashed lines describe the continuous KTHNY transition (two lines correspond to two different values of the phenomenological parameter - a dislocation core energy). Triangles are the results of the Monte-Carlo simulation of the first-order phase transition. Dotted lines schematically show the lines of the hexatic phase - isotropic liquid phase transitions.

The melting curve in Fig. 6 has a rather exotic form, but there are simple physical reasons which explain such kind of behaviour. It seems
that sharp increase of the transition density in the vicinity of $h \approx 1.5-1.7$ takes place because the square-well potential (16) does not have the true minimum. The re-appearance of the continuous transition at large $h$ occurs because the second neighbours are in the range of the attraction well and stabilize the crystal [43]. It should be noted that the exotic behaviour of the system in the vicinity of $h \approx 1.7$ was also found in the work by Stanley et al. [44].

3.3 Hidden symmetry – broken symmetry of higher order correlation functions

The crystalline solid state is characterized by a long-range positional order of the atomic density and associated bond orientational order belonging to one of the well-known allowed crystalline symmetries. In a diffraction experiment, $\delta$-function Bragg reflections are observed in the structure factor $S(\mathbf{q})$ that show the associated point symmetry of the lattice. In the case of the long range bond-orientational order, one can observe the modulation of the structure factor which corresponds to the symmetry of the nearest neighbour environment of a particle.

However, one can imagine the situation when the isotropy of three or four-particle correlation function is broken, but the symmetry of one and two-particle correlation functions is unchanged. In this case the structure factor of the system is the same as for the isotropic liquid because it depends only on the two-particle correlation function. This is why we call this type of the symmetry a "hidden symmetry" - it can not be detected in diffraction experiments.

So, using the diffraction experiments it is impossible to distinguish a liquid-liquid transition without changing the symmetry of the correlation functions (see Sec. 2) and the transition accompanied by the breaking of a hidden symmetry. It seems that the only way to answer the question what kind of transition one observes in an experiment is to analyze the whole phase diagram. In principle the hidden symmetry transition may be of the first order, but in contrast to the liquid-liquid transition discussed in Sec. 2, it separates the phases with different symmetries and can not end at the critical point. There are two possibilities for the hidden symmetry phase transition:(1) it may end at the tricritical point, and measurements above the tricritical point should reveal the thermodynamic anomalies but no density change; (2) it may intersect the gas-liquid transition line (see also the article by V.V. Brazhkin in this issue). In this case one can expect a sharp bend on the gas-liquid transition line at the point of intersection.
Transitions in simple liquids: Correlation function approach

To our knowledge there are no calculations exploring the idea of breaking the symmetry of higher order distribution functions. In principle it may be done using the method described in Sec. 3.2 as was proposed in Ref. [45].

4. Conclusions

In this article we briefly discussed the possible phase transitions which may exist in (supercritical) simple liquids. It was shown that there are two types of liquid-liquid transitions: the former is not accompanied by the breaking of the correlation functions symmetry, and the latter is accompanied. When the symmetry of a pair correlation function is disrupted (bond orientational order) the transition may be easily detected in diffraction experiments, however in the case of the breaking of the symmetry of higher order correlation functions ("hidden symmetry") more subtle analysis is necessary to distinguish between two types of transitions. It was emphasized that the very existence of liquid-liquid transitions in simple liquids in a crucial manner depends on the shape of the potential.

It should be noted that in the case of hidden symmetry there is only a very approximate qualitative understanding of the problem, and further investigations are necessary to develop satisfactory theory which could confirm or reject this possibility.

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References

[10] Simple fluids are the fluids consisting of the particles of the same sort and interacting through an isotropic potential.
Transitions in simple liquids: Correlation function approach


Elena Tareyeva and Valentin Ryzhov.
PHASE TRANSITIONS INDUCED OR SUPPRESSED BY CONFINEMENT

Jacqueline Quintana  
*I Instituto de Químic*a, Universidad Nacional Autónoma de México, México 04510 DF, Mexico

Alberto Robled*o  
*I Instituto de Física, Universidad Nacional Autónoma de México  
Apartment Postal 20-364, México DF, 01000, Mexico

Abstract  
The consequences of confinement on the phase diagram of various systems are described for a slab geometry and for both cases of identical and competing walls. We emphasize the occurrence of enrichment of phase behavior or the suppression of bulk phase transitions rather than the generic shift of phase boundaries known as capillary condensation as described by finite-size scaling theory. We illustrate these phenomena with two examples, i) phase separation in a symmetric fluid mixture representative of enantiomeric species, and ii) suppression of the first-order nematic-isotropic transition for a certain range of wall-field parameters. Finally we speculate on the consequences of similar confinement effects in network forming systems as it is the case of water.

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1. Introduction
A prototypical model geometry for the study of the combined effects of finite size and surface fields on phase transitions is that of two-phase coexistence occurring between parallel planar walls separated by a distance $L$. Because in this slab geometry the system can remain infinite in two spatial dimensions the free energy singularities of bulk phase transitions do not become rounded by confinement. One distinguishes two situations: 1) Identical or alike walls, when the interaction between the fluid molecules and the walls, the wall fields, favor the same phase
at both walls, \( h_1 \simeq h_2 \). And, 2) opposing walls, when one wall favors one phase but the other the second phase, \( h_1 \simeq -h_2 \). In the first case one observes “capillary condensation,” descriptions of which date back to Lord Kelvin [1]. There is a familiar [2] convergence of the coexistence curve and its associated critical point \( T_c^{(L)} \) to the bulk coexistence curve with critical temperature \( T_c^{(\infty)} \), of the form \( T_c^{(L)} - T_c^{(\infty)} \sim L^{-1/\nu} \) when \( L \to \infty \), where \( \nu \) is the bulk correlation length exponent. In the second case, for symmetrically-opposed wall fields, \( h_1 = -h_2 \), a more surprising effect takes place [3]–[8], for any wall separation \( L \) phase coexistence occurs only at temperatures \( T < T_c^{(L)} \) located below and near the wetting transition temperature \( T_w \) of the semi-infinite one-wall system. There is now a convergence of \( T_c^{(L)} \) to \( T_w \) as \( L \to \infty \) [2]–[8], and, remarkably, a single phase with long-ranged correlations in the directions parallel to the walls is found for the entire range \( T_c^{(L)} < T < T_c^{(\infty)} \), with \( T_c^{(L)} < T_w \). Since \( T_w \) is generally located far away from the bulk \( T_c^{(\infty)} \) the consequences of confinement are striking. The appearance of the single-phase states at \( T_c^{(L)} \) can be described as a shifted wetting transition [5], and this can be either continuous or of the first order [5]. Interestingly, depending on the choice of types of wall fields the phase behavior of the finite system resembles either that of the bulk or that of the one-wall semi-infinite system, and this indicates the underlying connection between the properties of the confined system and those of the related infinite-size systems. As described, the wetting phenomena associated to the one-wall system is clearly discernible in the behavior of systems confined by opposing walls, but not in that of confinement by alike walls. However, the phenomenon of capillary condensation is not completely insensitive to the wetting properties of the substrates. The leading scaling term that describes the field shift \( h_L - h_\infty \) of the phase transition locus in the phase diagram, the Kelvin equation, does not depend on the wetting regime, but the next correction term to scaling has been shown [9], [10] to depend on whether the temperature is above or below \( T_w \).  

Whereas it is experimentally trivial to prepare identical substrates and observe the small phase boundary shifts predicted by the theoretical arguments of finite size scaling, this is not the case for competing substrates with symmetrically opposed surface effects. It is not simple to construct or arrange substrates that will interact with the fluid molecules in such a way as to favor a different phase close to each substrate with equal strength. However, this is feasible when there is some underlying symmetry in the fluid system. Here we make reference to two such examples [11], [12] and use them to illustrate how the sur-
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face phase transitions occurring in semi-infinite systems manifest in the confined system. The first example is that of racemic mixtures of enantiomers [11], a symmetric fluid mixture of equal amounts of molecular species that are nonsuperimposable mirror images of each other. In this case each substrate can be prepared with an oriented layer of one of the pure enantiomeric species each and the resulting arrangement is that of symmetrically opposed wall fields acting on the symmetric mixture with equal concentration and chemical potentials. The second example is that of a liquid-crystalline fluid at the conditions for coexistence of the isotropic and nematic phases [12]. In this case one substrate is prepared to promote parallel (or planar, random or homogeneous) molecular alignment while the other enforces perpendicular (or homeotropic) alignment with equal intensity. In the following sections we provide a brief recollection of the phase transition properties of these systems and describe the conditions for which 1) transitions absent in the bulk can be induced under confinement or 2) existing bulk transitions can be suppressed for certain ranges of the wall interaction parameters. Practical applications are implied for the separation of enantiomeric species in racemic mixtures and for the control over the presence or absence of the nematic-isotropic transition according to wall separation. At the end of this article we mention briefly the analog effects that confinement, under similar slab geometry and wall interactions, would have in models for network forming fluids such as those for hydrogen-bonded water.

The analytical method in our calculations is the most basic density functional variational method for inhomogeneous systems where the basic ingredients is a Landau-type free energy with square gradient terms. In the slab geometry the minimization of this functional can be carried out successfully since the inhomogeneity takes place only along one dimension in space. Even though the limitations due to the approximate nature of this phenomenological, mean-field-like, approach are well understood, many interesting questions involving phase transitions have been rationalized through its use, and often this method is the first option in the study of a given problem [13], [14].

2. The Landau free energy method

The variational scheme set by the Landau density functional applies to a rich collection [15] of statistical-mechanical phenomena often related to the properties of interfaces, such as the kinetics of phase change, wetting and other surface phase transitions, and the interplay of these with the effects of finite size in confined systems. Consider the standard free energy functional in the language of a simple magnet with magnetization
$m(z)$ and external field $h$,

$$F[m] = \int_{z_1}^{z_2} \left[ f_b(m) - hm + \frac{A}{2} \left( \frac{dm}{dx} \right)^2 \right] dz + \Phi_1(z_1) + \Phi_2(z_2), \quad (1)$$

with

$$f_b(m) = am^2 + bm^4, \quad (2)$$

where $a$ and $b$ are constants and $t \equiv (T - T_c)/T_c$ is the temperature distance to the critical temperature $T_c$. In Eq. (1) $A$ is taken to be a constant and $\Phi_{1,2}$ are boundary or surface terms of the form

$$\Phi_{1,2} = -\frac{1}{2}g_{1,2}m_{1,2}^2 - h_{1,2}m_{1,2}, \quad (3)$$

where $m_{1,2} = m(z_{1,2})$, $g_{1,2}$ are the surface coupling enhancement parameters and $h_{1,2}$ are the surface fields. For a $d$-dimensional system $F$ is a free energy density in $d - 1$-dimensional space. The related properties of the finite-size system with slab geometry of width $L \equiv z_2 - z_1$, the semi-infinite one-surface system, and the boundaryless infinite system, can be determined, respectively, by allowing $z_1$ and $z_2$ to be both finite, one of them infinite, or both infinite, and by correspondingly eliminating unnecessary surface terms.

The vanishing of the first variation $\delta F = 0$ yields the Euler-Lagrange equation

$$A \frac{d^2 m}{dz^2} = f'_b - h, \quad (4)$$

where the prime indicates derivative with respect to $m$, together with the boundary conditions

$$\pm \frac{dm}{dz} \bigg|_{z_{1,2}} = -g_{1,2}m_{1,2} - h_{1,2}, \quad (5)$$

where the plus and minus signs correspond to the surfaces at $z_1$ and $z_2$, respectively. The thermodynamic stability of the profiles $m(z)$ obtained from the above equations can be determined by considering that the second variation of the free energy functional evaluated at $m(z)$ be positive. This analysis requires that the sign of the eigenvalues $\lambda_r$ associated to the eigenvalue equation

$$\int K(z, z') \varphi_r(z') dz' = \lambda_r \varphi_r(z), \quad (6)$$

be positive, where $K(z, z')$ is the second functional derivative of $F[m(z)]$, and for which we obtain, from Eq. (1),

$$K(z, z') \equiv \frac{\delta^2 F}{\delta m(z) \delta m(z')} = f''_b(m(z'))\delta(z - z') - A\delta''(z - z') +$$
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\[ A \delta (z - z') [\delta (z - z_2) - \delta (z - z_1)], \]

where \( \delta (z) \) is the Dirac delta function. Accordingly, the stability of the uniform bulk states with respect to uniform order-parameter fluctuations is determined only by the sign of \( f''_b(m) \).

When \( h \) is uniform Eq. (4) can be integrated once to yield

\[ m' \equiv \frac{dm}{dz} = \pm \sqrt{\frac{2}{A}} (f_b - hm - C_L), \]

where the constant \( C_L \) is determined by the walls separation via

\[ L = \int_{m_0}^{m_L} \frac{dm}{\sqrt{\frac{2}{A} [f_b(m) - hm - C_L]}}. \]

Substitution of this equation into Eq. (1) gives the expression for the equilibrium free energy,

\[ F_{eq} = \int_{m_0}^{m_L} m' dm + C_L L - \frac{1}{2} g_L m_L^2 - h_L m_L - \frac{1}{2} g_0 m_0^2 - h_0 m_0. \]

Bulk phase coexistence takes place at \( T < T_c \) and \( h = 0 \) and the values of the order parameter for these phases, denoted by \(-m_t\) and \( m_t\), are the minima of Eq. (2). It is useful to write the constant of integration \( C_L \) as \( C_L = C_\infty + \Delta C_L \), where \( C_\infty = f_b(-m_t) = f_b(m_t) \). When \( T > T_c \) and \( h = 0 \) the minimum of \( f_b \) is at \( m = 0 \) and \( C_\infty = f_b(0) \). Ref. [15] provides a detailed description of how this free energy density formalism is applied to describe different problems in infinite, semi-infinite, and finite systems involving inhomogeneous situations, ranging from nucleation and spinodal decomposition, to wetting and surface phase transitions, and to phase diagram shifts as produced by confinement produced by two parallel walls.

3. Confined mixtures of enantiomers

Enantiomers, termed “right-handed” or “left-handed”, \( d \) or \( l \), are molecules that differ structurally only in the spatial arrangement of atoms around a chiral center, macroscopic samples of them have essentially identical physical properties except when acting in chiral environments. Thus, the pure species have the same melting and boiling points, solubility, molecular spectra, etc. The majority of molecules in living systems are chiral. Generally, only one enantiomeric species is present in a given biological system, and this often recognizes right-handed drugs more readily than left-handed ones, or vice versa. In contrast, when the compounds are made via ‘normal’ laboratory chemical synthesis a
racemic mixture is obtained, i.e., a mixture with equal amounts of the two species [16].

Recently [11] we studied the properties of an elemental statistical-mechanical model for a mixture of enantiomers, and we found that phase separation of the two compounds can be induced in the racemic mixture via confinement by means of suitable - chiral - substrates. Our model mixture in mean-field approximation is a van der Waals symmetric mixture model [17] of equal-sized molecules with negative heat of mixing, i.e., unlike pair attractions are stronger than like pair attractions. In conformity with real enantiomeric mixture behavior the model bulk phase diagram lacks liquid-liquid immiscibility and the racemic mixture is an azeotrope [16]. We studied the inhomogeneous states of the racemic mixture for the slab geometry, with identical and symmetrically-opposed surface chemical potentials. The specific strength of the surface chemical potentials and the selective enhancement of interactions at the walls can be conceived to be the result of the preparation of the substrates by a uniform, oriented, coating of one of the enantiomeric species or by another suitable pure enantiomer. Two different sets of identical substrates are realized with use of either the $l$ or the $d$ species, whereas the symmetrically opposed walls are constructed by coating one wall with the $l$ species and the other with the $d$ species. The free energy of the model fluid mixture at constant density is equivalent to that of a magnetic spin-1/2 system with negative (antiferromagnetic) coupling. And we took advantage of this fact to study the order parameter profiles and the phase properties of the confined states with the familiar language and techniques of the Landau density functional for one-dimensional inhomogeneities described in the previous section [15].

In this equivalence the magnetization $m$ measures the concentration of species $m = 1 - 2 \rho_l(\rho_l + \rho_d)^{-1}$ where $\rho_l$ and $\rho_d$ are the number densities of the two species. The field $h$ measures the difference $h = (\mu_d - \mu_l)/2$ between the chemical potentials $\mu_l$ and $\mu_d$ of the two species, whereas the coupling $J$ relates to the difference $J = (\alpha - \alpha')(\rho_l + \rho_d)/2$ between the strengths $\alpha$ and $\alpha'$ of the attractive interactions for like and unlike molecular pairs. Therefore liquid-liquid immiscibility for a racemic mixture corresponds to the onset of spontaneous magnetization, and this is only possible for a ferromagnetic coupling $J > 0$. (As it is customary, the term $at$ in $f_0(m)$ in Eq. (2) is given by $at = J - kT/2$).

A brief description of our main results is the following: It was found that there is local phase separation of the racemic mixture ($h = 0$) in the neighborhood of the substrates for the unconfined system ($L \to \infty$) with vanishing wall fields ($h_{1,2} = 0$) but in the presence of sufficiently large surface coupling enhancement ($g > g_c$). The wall fields $h_{1,2}$ and the
enhancement \( q \) indicate surface departures from the bulk \( h \) and \( J \), respectively. Technically, the equilibrium state is a degenerate four-phase state, i.e. four concentration profiles (two symmetric and two antisymmetric) have the same minimum free energy. This state is analogous to that obtained at temperatures \( T \) below the so-called purely-surface transition in semi-infinite systems with ferromagnetic interactions [18]. When the system becomes confined \( (L < \infty) \) the four-phase state splits into two different two-phase states, one is the coexistence of states with profiles that show local excess concentration of the same enantiomer at both walls (symmetric profiles), and the other is the coexistence of states with profiles that show local excess concentration of a different species at each wall (antisymmetric profiles). The former is the equilibrium state and the latter is metastable, and as \( L \) decreases the free energy difference between the two types of coexisting states increases. When the wall fields are turned on one of those coexistence states splits into two one-phase states whereas the other remains a two-phase state. For identical walls it is the symmetric two-phase state that splits and the new equilibrium one-phase state is that rich in the enantiomer species favored by the walls, the enrichment takes place all across the slit although it is more pronounced at the walls. For symmetrically-opposing walls it is the antisymmetric two-phase state that splits, and of these, it is the state which exhibits wall enrichment in the enantiomer species favored by the field at each wall that attains the lower free energy. For large \( L \) this is the equilibrium state. The enrichment takes place only at the walls and the mixture remains racemic at the middle of the slit. As the wall separation \( L \) decreases the free energy difference between this state and the symmetric two-phase state decreases and at a given separation there is a first order transition below which the equilibrium configuration is that of the symmetric two-phase state.

Thus we find that the effect of confinement of the racemic mixture model with use of our representation of chiral substrates via surface fields and surface interaction enhancements leads to a phase behavior considerably more complex than that displayed by the bulk racemic mixture.

4. **Nematics under competing-wall confinement**

Surface alignment has been widely used to favor particular director configurations in nematic liquid crystal films and special cell construction and surface treatment methods have been developed to this purpose [19]. The control over the molecular alignment induced by substrates is important because of competition of director orientation between sur-
face and bulk. Consequently, the capacity to modify the orientation of the nematic axis by means of weak surface external fields has become the basis for several important applications of nematic liquid crystals in optical display and related devices [19].

We describe now results [12] on the modifications that the bulk isotropic-nematic transition suffers when confinement takes place via parallel walls with competing surface fields. We choose the surface field at one wall to favor molecular orientations parallel to the plane of the wall, with no specific preference within that plane (random parallel alignment) and that at the other wall to promote orientations normal to the plane (homeotropic alignment). We have obtained the order parameter profiles that correspond to this arrangement within the Landau-de Gennes theory (with vanishing enhancement parameter $g$), and we have determined the phase diagram as a function of temperature $T$, surface field strength $\mu_s$ and wall separation $L$ [12]. We chose symmetrically opposing walls with equal field strengths but opposite signs, $\mu_L = -\mu_0 = \mu_s$.

The Landau-de Gennes free energy density functional (for the special case of uniform director orientation) that describes the confined system is given [19] by Eq. (1) where the magnetization $m$ is replaced by the nematic alignment order parameter $S$, the magnetic field $h$ is replaced by the ordering field $\mu$, and where the free energy $f_b$ is now given by

$$f_b(S) = -\mu S + a(T - T^*) S^2 + b S^3 + c S^4.$$  \hspace{1cm} (11)

The external field strength $\mu$ is necessarily positive (since it is proportional to the square of either an electric or magnetic field applied along the $z$ axis).

Our study [12] indicates that the isotropic-nematic transition does not experience a temperature shift under confinement ($T_{IN}^{(L)} = T_{IN}$ for all $L$) but its occurrence is severely restricted to lie below a maximum wall separation $L_{qw}(\mu_s)$. The curve $L_{qw}(\mu_s)$ demarcates the transformation of “bulk-like” isotropic-nematic two-phase coexistence states into “interface-like” one-phase states. $L_{qw}$ diverges when $\mu_s \rightarrow \mu_{s}^{w}$ where $\mu_{s}^{w}$ is the wall field strength required for the wetting transition of the semi-infinite system to occur at $T_{IN}$. The transition is of the 1st order ($L_{qw}$) when $\mu_s$ is smaller than a special value $\mu_{s}^{t_{c}}$ and it is critical ($L_{qw}^{t_{c}}$) when $\mu_s$ is larger than $\mu_{s}^{t_{c}}$, the two branches join at a tricritical point when $\mu_s$ equals $\mu_{s}^{t_{c}}$. The IN coexistence states for $\mu_s > \mu_{s}^{t_{c}}$ undergo an additional continuous transition between low and high wall adsorption states at the locus $L_{qw}^{t_{c}}(\mu_s)$ that originates at $L_{qw}(\mu_{s}^{t_{c}})$ and extends towards smaller $L$ and larger $\mu_s$. A similar phase diagram in the $(L, \mu_s)$-plane is obtained when the temperature is varied moderately both below and above $T_{IN}$. When $T < T_{IN}$ the transition at the wall separation $L_{qw}(\mu_s)$ is
between nematic-like and interface-like states, whereas for $T > T_{IN}$ the transition involves isotropic-like and interface-like states. In both cases $L_{H \rho \omega}$ diverges when $\mu_s \rightarrow \mu_s^{pw}$ where $\mu_s^{pw}$ is the wall field strength for a prewetting transition of the semi-infinite system at $T$.

This application of the Landau-de Gennes free energy when $T = T_{IN}$ and $\mu = 0$ is equivalent to that of a magnetic slab described by a symmetric double-well Landau free energy when $h = 0$ with opposing surface fields and vanishing coupling surface enhancement $g$, however, the phase properties are displayed differently since the temperature in the nematic takes the role of the external field $h$ of the magnet. This is a consequence of the cubic term in $f_0(S)$ in Eq. (11) that makes $T$ the adjusting parameter for the difference in height of the minima of $f_0(S)$ and for their appearance or disappearance. Thus, $T_{IN}$ remains fixed under opposing wall confinement just as spontaneous magnetization $m_0$ takes place at vanishing $h$ under similar circumstances, and the isotropic-nematic transition continues to be of the first order under confinement as it is the counterpart for the coexistence of oppositely magnetized states. Also, the phase behavior observed in the nematic with variation of $T$ across $T_{IN}$ can be observed in the magnetic slab under the application of an external field, as $h$ passes through zero.

The competing walls introduce interfacial-like states that occupy large regions of the phase diagram where the isotropic and the nematic phase would be found otherwise. However, when the IN transition is not suppressed by symmetrically opposing walls the transition does not suffer a temperature shift and remains at $T_{IN}$ (in contrast to confinement via identical walls).

5. Possible confinement effects on network-forming fluids

Transitions between distinct amorphous forms of pure substances have been observed in network-forming fluids involving amorphous solids [20]. It is commonly acknowledged that the hydrogen bond interaction between water molecules creates in the pure liquid a space-filling tetrahedral network of first neighbors at all times and that the subsistence or degradation of this singularly open structure is the origin of all anomalies in the liquid and the ice polymorphs [21], [22]. It has been suggested that two forms of liquid water may coexist at very low temperatures [23],
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[24], possibly shedding light on why water has such unusual properties compared to other liquids.

Anomalies in both equilibrium and dynamical properties of liquid water, that become more pronounced in the metastable region below the melting pressure curve, might be the result of an underlying equilibrium phase separation between two forms of liquid water terminating at a critical point. There appear major experimental difficulties in corroborating the conjectured singular behavior because its possible location in the temperature region below the nucleation limit of the solid is not accessible. The hydrogen bond interaction between water molecules creates in the pure liquid a space-filling tetrahedral network of first neighbors at all times. The two conjectured low temperature metastable types of liquid water, like the two known forms of amorphous ice, correspond to a low density structure of straight bonds and a high density structure of distorted, nonlinear bonds.

The two examples in the previous sections that illustrate the induction or suppression of phase transitions via appropriate confinement conditions might be of use in either: a) extending the range of the conjectured liquid-liquid phase boundary via enhancement of fluid interactions close to the walls, or b) in displacing to lower temperatures the melting curve via the use of competing wall fields. For these effects to take place the substrates should have the capacity to modify in their vicinity the average length and strength of the hydrogen bonds, or the capacity to affect the long range order of these bonds [25].

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References

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FREE ENERGY FOR LIQUIDS OUT OF EQUILIBRIUM

Effective temperatures from time-scale separation.

A. Scala, F. Sciortino
Dipartimento di Fisica ed Istituto Nazionale di Fisica della Materia
Università degli studi di Roma “La Sapienza”
P.le Aldo Moro 2, I-00185, Roma, Italy

Abstract
Starting with the Stillinger and Weber expression for the free energy of supercooled liquids, we extend the free energy to the case in which two time scales separate and the system is in quasi-equilibrium. The concept of an effective temperature, different from the kinetic temperature, is naturally introduced. An example of hypothetical quasi-equilibrium phase diagram is presented for the case of SPC/E water.

1. Introduction
The study of the properties of undercooled liquids is a topic of current research. Under the name of undercooled liquids we will indicate liquids whose relaxations start to show a separation between different timescales. The idea of considering the dynamics of undercooled liquids similar to the vibrations of a disordered solid on short timescales, while attributing the slow dynamics to rare change in the global structure (i.e. the atomic position of the disordered solid assumed as the reference for short time vibrations) is old [1]; in particular, the fruitful reformulation of Goldstein [2] of these ideas in terms of an energy landscape has led to the introduction of a formalism [3] that is particularly suitable for the study of liquids via Monte Carlo or Molecular Dynamics simulations [4].

In Sec. 2 we describe such formalism, showing that it is particularly suitable to investigate the connections between the statics and the dynamics of equilibrium systems. In Sec. 3 we show that such formalism can be extended to systems in quasi-equilibrium via the introduction of a temperature for the slow degrees of freedom that can be measured both
via dynamics and via statics. In Sec. 4 we speculate on the possibility of quasi-equilibrium, quench-rate dependent critical points.

2. Free energy for a supercooled liquid

The phase space of a system can be in general partitioned in different ways, giving rise to equivalent rewritings of the free energy [5]. In general, we will consider systems with an hamiltonian $\mathcal{H}$ and disregard the momentum space as it can be trivially integrated out; we will therefore concentrate on the $fN$-dimensional configuration space $W$, where $f$ is the number of spatial degrees of freedoms of a particle and $N$ is the number of particles. What makes us prefer or introduce a particular partition is its physical relevance and interpretation.

Stillinger and Weber introduced such a partition [3] in the spirit of the Goldstein picture of undercooled liquids dynamics (see Fig. 1). They associate to each configuration the configuration reached following a steepest descent path to minimize the potential energy. Such configuration is called an inherent structure (IS) and corresponds to a local minimum of the potential energy (Fig. 2). While to each IS we can associate its potential energy $e_{IS}$, the converse is not true: to each energy level $e_{IS}$ there will be associated a degeneracy $\Omega(e_{IS})$ counting the number of local minima with energy $e_{IS}$ [6] (Fig. 3). Following the reasoning of Goldstein we can already argue that $e_{IS}$ is a good candidate to be a slow variables of the system, as it is associated to the global structure of a liquid and not to its vibrational excitations. Defining the configurational entropy $s_{\text{conf}} = k_B\ln(\Omega(e_{IS}))$, we can write the Helmotz free energy of the system at temperature $T$ and volume $V$ as [3].
Free energy for liquids out of equilibrium

\[ F(T, V) = e_{IS}(T, V) - T s_{\text{con}}(e_{IS}, V) + f_{\text{vib}}(e_{IS}, T, V) \]  

(1)

Figure 2. Sketch of the Stillinger-Weber partition of the configuration space \( W \). The configurations indicated as \( IS^i \) are local minima of the potential energy; all the configurations of the basin \( W^i \) are associated to \( IS^i \) via steepest descent.

where \( e_{IS} \) is the energy of the typical minima at \( (T, V) \), \( s_{\text{con}} \) for each fixed \( V \) will depend implicitly on the temperature via the T dependence of \( e_{IS} \) and \( f_{vib} \) is the average free energy of the typical basins at \( (T, V) \). At fixed \( V \), \( f_{vib} \) will depend on the shape of the basins (we assume that the shape of the basin can be parametrized by \( e_{IS} \)) and on the average kinetic energy (therefore on \( T \)). The validity of such approximations has been carefully checked and confirmed via numerical simulations of different atomic and molecular model systems [7, 8, 9, 10, 11, 12]

For real systems \( s_{\text{con}} \) has been often approximated by the difference of the entropy of the liquid and the entropy of some reference solid phase [13]. For computer liquids we have access to the IS configurations and can therefore estimate the “true” \( s_{\text{con}} \). In particular, we can use thermodynamic integrations using the relation

\[ ds_{\text{con}} = \frac{de_{IS}}{T} + \frac{df_{vib}}{T} = \frac{de_{IS}}{T} \left( 1 + \frac{\partial f_{vib}}{\partial e_{IS}} \right) \]  

(2)

for the differential of \( s_{\text{con}} \) obtained using the extremum condition \( \delta F = 0 \). To calculate \( F \), first an accurate estimate of \( e_{IS} \) must be obtained by minimizing the potential energy of equilibrium configurations of the liquids. The estimate of \( f_{vib} \) includes two steps: first, the harmonic
contribution $f^h$ valid at low temperatures is obtained calculating the normal mode frequencies $\omega_i$ ($i = 1, fN$ [14]) near the IS minima; the exact calculation for a collection of harmonic oscillators gives us the estimate [15]

$$f^h = -k_B T <\ln \left( \frac{\hbar \omega}{2\pi k_B T} \right) >>$$

where the average $<\ldots>$ [16] is intended both on the IS configurations and on all the $fN$ modes. For systems like the binary Lennard-Jones mixture, $f^h$ is already a good estimate for $f_{\text{vib}}$ [7]. In the case of a molecular liquid, the SPC/E model for water [17], measurable deviations are found [8]. Still, deviations are small and can be estimated as perturbative corrections to the ideal harmonic oscillator behavior [18]. In practice, what it is found is that heating up IS's one can estimate the anharmonic corrections $e_{\text{anharm}} = aT^2 + bT^3 + \ldots$ to the ideal harmonic behavior $e = e_{\text{IS}} + (f/2) k_B T$.

\[ \begin{aligned}
\text{Figure 3.} & \quad \text{The free energy of undercooled liquids can be expressed in terms of the energy levels } e_{\text{IS}} \text{ of the inherent structures IS, to their degeneracy } \Omega(e_{\text{IS}}) \text{ and to the shape (in harmonic approximation, to the curvature } \omega) \text{ of the associated basins.}
\end{aligned} \]

Therefore, once $e_{\text{IS}}$ and $f_{\text{vib}}$ have been estimated, we can reconstruct $s_{\text{conf}}$ by thermodynamic integrations. The behavior of $s_{\text{conf}}$ is related to the possibility of an ideal glass transition [13]. If $s_{\text{conf}}$ becomes zero at some finite temperature $T_K$ (the so-called Kauzmann temperature [19]), this means that the liquid is in a metastable state, trapped in the basin of a single minima; therefore diffusivity is zero and the thermal vibrations around the disordered structure (the IS of the minimum) are the only sort of motion taking place. A precise functional dependence has been proposed by Adam and Gibbs [20] among $s_{\text{conf}}$ (a static quantity) and the diffusion coefficient $D$ (a dynamic quantity):
where $A$ is almost constant with $T$ [20, 21]. Up to now, the Adam-Gibbs relation (Eq. 4) has always been found to be consistent with simulation results [8, 11, 12, 9] (see Fig. 4).

\[ D \propto e^{-\frac{A}{T_{s,conf}}} \]  \hspace{1cm} (4)

Figure 4. Adam-Gibbs plot of diffusivity $D$ versus $1/T_{s,conf}$ [8]. The plot shows that there is a strong correspondence among the dynamics and the statics of undercooled liquids [22, 23]. For the sake of clarity, the values of $D$ have been shifted by multiplying by powers of 5 from $5^0$ (the lowermost curve $\rho = 0.95 \text{ g/cm}^3$) to $5^5$ (the uppermost curve $\rho = 1.40 \text{ g/cm}^3$).

3. Free energy for quasi-equilibrium states

Attempts to construct thermodynamics for out-of-equilibrium states have not yet come to a success; in particular, for glassy systems the history of the system cannot in general be disregarded so that no static theory with a small number of parameters can be constructed [5]. In the case of undercooled systems, where a separation between two different time scales becomes sharper and sharper, it is possible to generalize in
a straightforward way the expression for the free energy. In the case of simulated liquids, quenching at low $T$, the time evolution of $e_{IS}$ is slow, with a decay compatible with a logarithmic or a very small power-law decay [7], while the short time dynamics has a much faster timescale and is vibrational in character (see Fig. 5). We can then treat our system as two subsystems in contact: a vibrational subsystem, linked to the fast vibrations in a basin, and the configurational subsystem of the local minima $IS$'s, whose dynamics is reflected by the slow decay of $e_{IS}$ (see Fig. 5). On the timescales where the vibrational subsystem comes in equilibrium with the external heat-bath at temperature $T_{bath}$ (in this sense, the vibrational subsystem is canonical [24]), $e_{IS}$ is almost constant (in this sense, the configurational subsystem is almost microcanonical [24]) (see Fig. 6).

If we assume that the basins corresponding to a given $e_{IS}$ visited in out-of equilibrium are the same (or have the same characteristics) of the ones visited in equilibrium, we can use the expression of $f_{vib}(e_{IS}, T)$ obtained in equilibrium to take account of the vibrational part of the free energy. Obviously, the vibrational temperature will be equall to the external bath temperature $T_{bath}$. The configurational part corresponds to the almost microcanonical subsystem of the energy levels $e_{IS}$ together with their degeneracies $\Omega(e_{IS})$. Now, we can write in general the free energy of this subsystem as $e_{IS} - T_{int} \delta_{con}(e_{IS})$ where $T_{int}$ (we will indicate $T_{int}$ as the internal temperature) can be in general different from $T_{bath}$ [5]:

$$F = e_{IS} - T_{int} \delta_{con}(e_{IS}) + f_{vib}(e_{IS}, T_{bath}).$$

(5)

$T_{int}$ is interpreted as a parameter that "optimizes" the free energy [26] given the constraints that the energy of the minima is $e_{IS}$ and that the vibrational subsystem has temperature $T_{bath}$. Therefore, we can derive an expression of $T_{int}$ [7] extremizing the generalized free energy:

$$\frac{\partial F}{\partial e_{IS}} = 0 \rightarrow T_{int}(e_{IS}, T_{bath}) = 1 + \frac{\partial f_{vib}}{\partial e_{IS}} \frac{\partial \delta_{con}}{\partial e_{IS}}.$$

(6)

Up to now, we have a theoretical prescription for $T_{int}$ that is self consistent with our writing of the generalized free energy. At this point, two questions naturally arise: first, is it possible to write the free energy in terms of experimentally measurable quantities? And then, can we measure $T_{int}$?

Regarding the first problem, we recognize that already in the 30's an approach to the construction of an out-of-equilibrium free energy for
Figure 5. (a) The typical decay of a correlation function in undercooled liquids. The fast relaxation corresponds to the vibrational dynamics and can be treated in the harmonic approximation using the instantaneous normal mode approach (b) Typical decay of $e_{IS}$ after a deep quench. A slow logarithmic law is compatible with numerical data [7, 25].

experimental glasses had been attempted by Davies and Jones [27] in terms of “frozen observables”, i.e. quantities that maintain values typical of high temperatures after quenching; a successful implementation of
such ideas is found in [28], who uses the “more” concrete enthalpies of shock compressed hard-sphere liquids [29] to calculate the equilibrium configurational entropy.

Regarding the measurement of $T_{\text{int}}$, we can resort to dynamics measurements: it is in fact known both from theory [30], numerical simulations [7] and experiments [31], that out of equilibrium systems can exhibit at least two temperatures. A simple way to measure such temperatures is through the application of linear response theory [32]. Let’s consider a perturbed Hamiltonian $H_P = H - \lambda B$, where $H$ is the unperturbed Hamiltonian, $B$ is a generic observable and $\lambda$ is a small parameter. Linear response theory predicts [33] that, switching on the perturbation at time $t = 0$, we have

$$<A(t)>_P = -\frac{\lambda}{k_BT}[C_{AB}(t) - C_{AB}(0)]$$  

(7)

where $<A(t)>_P$ (the response of the system) is the time evolution of the average of an observable $A$ in presence of the perturbation and $C_{AB}(t) = <A(t)B(0)>$ is the correlation function (the decay of fluctuations) between the observables $A$ and $B$ in absence of the perturbation. Therefore, from the slope of a parametric plot of $<A>_P$ versus $\lambda C_{AB}$, the temperature is measured from the dynamics of the system (see Fig. 7).

While at short times such temperature coincides with $T_{bath}$, at long times a temperature $T_{eff} \neq T_{bath}$ is measured in quenching experiments.

Figure 6. Quenching the system (i.e. lowering rapidly the external temperature $T_{bath}$ of the heat bath), vibrational degrees of freedom come rapidly at a canonical (NVT) equilibrium with the bath, while the subsystem corresponding to structural changes (the IS’s) relaxes slowly and can be treated as an almost microcanonical (NVE) system in which $e_{IS}$ does not change over the characteristic vibrational timescales.
Figure 7. Fluctuation-dissipation plot of the response $\langle A \rangle_P$ of the system to a small perturbation versus the equilibrium, unperturbed decay of the cross correlations $C_{AB}$ among observables $A$ and $B$. According to Eq. 7, the slope of the plot gives a measure of the temperature of the system. While at short times (i.e. high values of $C_{AB}$) the temperature of the system is in equilibrium with the bath temperature, at long times (high values of the response $\langle A \rangle_P$) the system reveals that slow degrees of freedom are at a temperature higher (lower slope of the plot) than the bath.

In the case of binary-mixture Lennard Jones system, it has been verified that $T_{eff} = T_{int}(e_{IS},T_{bath})$ [7]. In general, $T_{eff}$ tends to be higher than $T_{bath}$ and of the order of the temperature at which the system is in equilibrium exploring basins of depth $e_{IS}$. Somehow, the configurational part of the system “remembers” the temperature at which was originated.

4. Out of equilibrium phase diagram for SPC/E water

Equation 5 and 6 allow to develop, using the inherent structure formalism, an expression for the free energy for disordered materials even in
out-of-equilibrium states; for such free energy, the “history” of the system is described by its $e_{IS}$ value. In this section we present a preliminary application to the case of SPC/E water.

The low temperature of SPC/E water has been object of a massive computational investigations in order to investigate the slow dynamics of molecular liquids [34] and to check the liquid-liquid critical point scenario [35]. In particular, the properties of the energy landscape have been thoroughly analyzed in order to find connections between the dynamics and the statics of such a system [8, 22, 36].

The profile of the energy of SPC/E versus the volume develops a change in concavity already in the region numerically accessible (see Fig. 4), suggesting the possibility of a phase transition hindered by the entropic terms. Low temperature extrapolations predict indeed a liquid-liquid critical point a temperature of $\sim 130 \, K$ and a specific density of $\sim 1.1 \, g/cm^3$ [37]. Such a transition would be located beyond the predicted Kauzmann line for SPCE water [8] and therefore unaccessible to equilibrium studies [38].

To derive an expression for the free energy in the low temperature region of SPC/E water, we select for simplicity the harmonic approximation, where $f_{vib}(e_{IS}, V, T_{bath}) \approx f^h = -k_BT_{bath} << ln \left( \frac{\hbar^2(e_{IS}, V)}{2\pi k_BT_{bath}} \right) \gg \left( \text{Eq. 3} \right)$. We use the data for $s_{conf}$ at $T = 210 \, [8]$ as reference entropy to obtain an expression for $s_{conf}^h$:

$$s_{conf}^h(e_{IS}, V) = s_{conf}^{T=210}(V) + \int_{210}^{T(e_{IS}, V)} \frac{d\epsilon_{IS} + df^h}{T}, \quad (8)$$

where $T(e_{IS}, V)$ is the temperature at which a system at volume $V$ in equilibrium has $IS$'s of energy $e_{IS}$. We obtain then the generic expression for the free energy in harmonic approximation:

$$F^h(e_{IS}, T_{bath}, V) = e_{IS} - T_{int}(e_{IS}, T_{bath}, V)s_{conf}^h(e_{IS}, V) + f^h(e_{IS}, T_{bath}, V). \quad (9)$$

First, we check the equilibrium phase diagram for $F^h$. No phase transition is found in the physical region where $s_{conf} > 0$. We then perform an ideal experiment: we consider the free energy of state points in equilibrium at a temperature $T_{eq}$ after a sudden quench at $T_{bath} = 100K$ (well below the Kauzmann locus). After a rapid quench, $e_{IS}$ has not time to change on the timescales of vibrations, so that $e_{IS}$ and $s_{conf}$ remain to their equilibrium values, while $f_{vib} \approx f^h(e_{IS}(T_{eq}), T_{bath} = 100K)$. 


Free energy for liquids out of equilibrium

![Graph showing the contributions of $e_{IS}$, $s_{conf}$, and $f_{vib}$ to the free energy of SPC/E water at $T = 210$ K. The shape of $e_{IS}$ indicates that the system would phase separate if it was not for the strong $-T s_{conf}$ term which avoids the change of concavity in the free energy. For SPC/E water, $f_{vib}$ is practically irrelevant to change the concavity of the free energy.]

The value of the internal $T_{int}$ can be calculated from Eq. 6 and will be in general different from the temperature $T_{eq}$ at which the quench has started. In the harmonic approximation, Eq. 6 becomes

$$T_{int} = T_{eq} \frac{1 - a T_{bath}}{1 - a T_{eq}}$$

where $a = \frac{\partial \langle k_B \ln[\omega(e_{IS}, V)] \rangle}{\partial e_{IS}}$ and $T_{eq}$ is the temperature at which minima of depth $e_{IS}$ are populated in equilibrium.

In the case of SPC/E water, as can be inferred from Fig. 8, $a$ is small (order $10^{-2} K^{-1}$) such that $T_{int} \approx T_{eq}$, differing from the case of the binary mixture Lennard-Jones [7] where $a$ is relevant and $T_{int} < T_{eq}$ significantly.

Therefore, for SPC/E water in the harmonic approximation, it is not possible to “shift up” the critical point above the Kauzmann line. This is true for two reasons: first, in SPC/E water the vibrational part $f_{vib}$ of the
Figure 9. (a) example of the linear dependence of $e_{IS}$ versus $1/T$ (b) the average logarithm of the basin’s curvature is approximately linear in $e_{IS}$.
free energy has a very small dependence both on \( V \) and on \( e_{IS} \) compared to the remaining term. Therefore, if we ignore \( f_{vib} \), the phase diagram stays almost unchanged. The only way then to get a phase transition is to “kill” the entropic term \( T_{int} s_{conf} \); but from Eq. 6 we see that, as \( \partial f_{vib} / \partial e_{IS} << 1 \), \( T_{int} \approx T_{eq} \) where \( T_{eq} \) will be approximatively equal to the temperature at which the quench is started as the change of \( e_{IS} \) is logarithmically slow. So, for systems where \( f_{vib} \) does not vary much with \( e_{IS} \) (i.e. the shape of the basins does not vary much), the temperature of the slow degrees of freedom of the systems after a quench stays almost the same as the starting temperature of the quench. In order to decrease drastically the internal temperature (and therefore decrease the entropic term of the free energy hindering eventual critical points), one has to resort is a system with a strong dependence of the shape of the basins with \( e_{IS} \). In the extreme case \( \partial f_{vib} / \partial e_{IS} >> 1 \), we would have the ideal situation \( T_{vib} \approx T_{bath} \). The possibility of the appearance of critical points in out-of-equilibrium situation is a new issue that deserves to be further addressed and investigated.

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References

[6] Note that a rigorous analysis requires the definition of a density of states \( d(e_{IS}) \) such that \( d(e_{IS}) \Delta \) are the number of IS with energy between \( e_{IS} \) and \( e_{IS} + \Delta \) [39].
Note that there are three spurious zero frequency modes corresponding to the translation of the system.


Note that for the derivation of the free energy of the equilibrium liquid we are always assuming that self averaging for all observables. This is not in general the case for systems with complex landscapes at low temperatures [40]


According to the Adam-Gibbs expression (Eq. 4), at the Kauzmann line corresponding to $\kappa_{\text{conf}}(V,T) = 0$ diffusion becomes zero and the system cannot evolve anymore.
Free energy for liquids out of equilibrium


WATER AND ICE IN
QUASI-TWO-DIMENSIONAL GEOMETRIES

Phase transitions, phase equilibria, and solvation forces

K. Koga
Department of Chemistry, Fukuoka University of Education
Fukuoka 811-4192 Japan

Abstract
Phase transitions and phase equilibria of water confined between parallel hydrophobic surfaces studied by molecular dynamics simulations are reviewed. When the separation distance between the surfaces is as small as a thickness of two molecular layers, the thin film of water freezes into a bilayer crystalline phase or a bilayer amorphous phase both having a quasi-two-dimensional completely hydrogen-bonded network. The existence of two distinct disordered phases—the liquid and the bilayer amorphous phases—demonstrates the polymorphism of confined water. This polymorphism is compared with that of the bulk water. The liquid-bilayer amorphous transition is also observed when two large parallel hydrophobic plates are immersed in bulk water and one plate approaches the other at a fixed temperature and a fixed bulk pressure. The solvation force between the plates exhibits discontinuous jumps and hysteresis, suggesting special hydrophobic interactions due to the liquid-amorphous phase transition of confined water.

1. Introduction
When liquid water is confined in a hydrophobic pore, the hydrogen-bonded network is largely perturbed near the surface since water molecules cannot form hydrogen bonds to the surface; that is, the three-dimensional network, which would otherwise extend infinitely, is forced to terminate at the surface. In particular, in a space as narrow as a few molecular diameters, the entire hydrogen-bonded network would be so frustrated that the increase in potential energy per molecule due to confinement amounts to a few \(kT\), where \(k\) is Boltzmann’s constant and \(T\) the temperature. Phase equilibria and phase transitions of water—one of the
representatives of the network-forming substances—under such extreme confinement are the topics of this presentation.

Some recent studies of confined water based on molecular dynamics (MD) simulations have revealed first-order phase transitions from liquid to several kinds of solid phases which have completely hydrogen-bonded network [1, 2]. In quasi-two-dimensional (Q2D) systems of a particular width, liquid water freezes into either bilayer ice or bilayer amorphous solid (or solid-like form). Relation among liquid, ice, and amorphous phases in the Q2D system resembles that among high-density liquid (HDL), ice Ih, and low-density liquid (LDL) in a bulk system. However, the liquid-amorphous phase transition in the Q2D system is accompanied by changes in potential energy and diffusivity much larger and shaper than those by which the HDL-LDL transitions of bulk water is accompanied [3, 4, 5, 6, 7]. The liquid-amorphous phase transition is observed not only by varying temperature or pressure but also by varying width of the parallel walls at a fixed temperature and a fixed pressure [8]. In a system in which two large parallel hydrophobic plates are immersed in liquid water, the solvation force between the plates exhibits discontinuous changes when water between the plates undergoes the liquid-amorphous phase transition.

\[ P_{zz} \]
\[ \text{(a) System A} \]

\[ P_{xx} \]
\[ \text{(b) System B} \]

\[ P \]
\[ \text{(c) System C} \]

*Figure 1.* Three types of confined systems studied by the MD simulations. (a) \((P_{zz}, T)\)-controlled system; (b) \((P_{xx}, T)\)-controlled system; (c) \((P, T)\)-controlled system.

2. Systems and equilibrium conditions

We consider three types of Q2D systems as shown in Fig. 1. The first two (system A and B) consist of \(N\) water molecules confined between two parallel surfaces of area \(A\) whereas the other consists of water molecules between and surrounding two parallel plate-like solutes. Each system represents a different equilibrium condition, mimicking a different experiment. In system A, the pressure acting on the surfaces, \(P_{zz}\), is controlled by allowing fluctuations in the inter-surface distance \(h\), i.e., a
volume work in the direction normal to the surfaces (Fig. 1a). Thus $h$ is given as an average over a simulation time. This condition is similar to the experimental condition realized in the surface force apparatus (SFA) [9] in which a thin film of liquid between two surfaces is under a fixed load. It is, however, not exactly the same as the experimental condition because system A has a constraint that the area per molecule $a = A/N$ is fixed. In system B, on the other hand, $h$ is fixed (i.e., no volume work is allowed in the normal direction) but the lateral pressure $P_{xx}$ (the pressure tensor components parallel to the surfaces) is controlled by allowing a volume work in the direction parallel to the surfaces (Fig. 1b). Thus $a$ is not fixed but is given as an average over a simulation time. In order to carry out a real experiment controlling $P_{xx}$ of the thin film, one might need to introduce a nanometer-size piston between two surfaces. In computer simulations, however, it is easy to control $P_{xx}$ by allowing $A$ to fluctuate provided that the two parallel surfaces are structureless. In system C, the confined water is a subsystem open to the bulk environment. Here the bulk pressure $P$ is controlled rather than a pressure tensor $P_{xx}$ or $P_{zz}$ of the thin film.

The fundamental differential for systems A and B is given by

$$dU = TdS + \mu dN - P_{xx}hdA - P_{zz}Ah$$

where $U$ is the internal energy and $S$ is the entropy. The appropriate thermodynamic potential for system A is given by

$$\Phi_x = U - TS + P_{zz}Ah,$$

because any state of equilibrium is achieved under the condition of a fixed $N$, $T$, $A$, and $P_{zz}$. Likewise, the appropriate thermodynamic potential for system B is given by

$$\Phi_x = U - TS + P_{xx}Ah.$$  

Then their differentials are given, respectively, by

$$d\Phi_x = -SdT + h\Delta PdA + AhdP_{zz} + \mu dN$$

and

$$d\Phi_x = -SdT - A\Delta Pdh + AhdP_{xx} + \mu dN$$

where $\Delta P = P_{zz} - P_{xx}$, and the equilibrium conditions for system A and B are $[\delta\Phi_x]_{N,P_{zz},A,T} = 0$ and $[\delta\Phi_x]_{N,h,P_{xx},T} = 0$, respectively.

The thermodynamic description for system C is essentially the same as that for the $\mu VT$-controlled confined system [10].

The phase diagrams for the one-component confined systems A, B, and C are given in a three-dimensional thermodynamic space, such as
$P_{zz}$-$a$-$T$, $P_{xx}$-$h$-$T$ and $P$-$h$-$T$ (or $\mu$-$h$-$T$) spaces. Slopes of the phase boundaries and differences of certain molar quantities between two distinct phases are related with each other by Clapeyron equations for the confined system [8]. (For system C, see Ref. [10].)

In MD simulations reported below, the water-water intermolecular interactions are taken to be the TIP4P potential [11]. The water-hydrophobic surface interactions (in system A, B, and C) are modeled by the 9-3 Lennard-Jones potential with appropriate parameters for hydrocarbon surfaces [1]. The pressure-tensor ($P_{zz}$ or $P_{xx}$) and temperature are controlled by a modified Nosé-Andersen’s method. Other details on the simulation method are given elsewhere [1, 2, 8].

3. Bilayer ice phase

It is very difficult to observe freezing of bulk water in MD simulations as the freezing process is too slow to occur in simulation time scales. (Because of this fact one can study the HDL-LDL phase transition in the supercooled region.) However, a thin film of water in system A (with a fixed area density $a^{-1} = N/A$) freezes easily in the MD simulation [1]. The resulting phase is the bilayer ice, which has a Q2D completely hydrogen-bonded network. Each layer consists of identical distorted hexagonal hydrogen-bonded rings, and the distorted honeycomb lattice of one layer is superimposed on the other in the top view (See Fig. 5). Every water molecule is hydrogen-bonded to three neighbors in the same layer and to its partner in the other layer. The freezing and melting observed in the simulations exhibit typical characteristics of the first-order phase transition: the potential energy and the wall-wall separation distance suddenly decrease at the freezing temperature, and a large hysteresis loop is observed upon heating. The bilayer ice satisfies the common ice rules and two additional ice rules, violation of which causes significant increase in the potential energy. Because of the bilayer ice rules, the residual entropy of the bilayer ice crystal is calculated exactly as $S_{\text{b}} = (Nk/4)\ln 2$. This means that $S_{\text{b}}/S_{\text{c}} = 0.43$, where $S_{\text{c}}$ is the residual entropy of ice Ih.

Using the MD simulation results and the Clapeyron equations, we can qualitatively draw the first-order phase boundary between the confined liquid and the bilayer ice in the $T$-$P_{zz}$ plane. For example, from Eq. (4) and the equilibrium condition $d\Phi = d\Phi$ along a phase boundary between two phases $\alpha$ and $\beta$, one has

$$
\left( \frac{\partial P_{zz}}{\partial T} \right)_{T} = \frac{s^\alpha - s^\beta}{(h^\alpha - h^\beta)a},
$$

(6)
where \( s = S/N \). At 50 MPa and 150 MPa, the wall-wall separation distance \( h \) decreases upon freezing, i.e., the film of water shrinks when it freezes, and the entropy decreases at the same time; on the other hand, \( h \) increases, i.e., the film expands at 1 GPa. Thus the slope is positive at low and medium \( P_{zz} \) and negative at a high \( P_{zz} \).

![Figure 2](image.png)

*Figure 2.* Temperature-dependence of the potential energy for system B. The lateral pressure \( P_{zz} \) is kept constant at 0.1 MPa. The filled and unfilled marks denote results in the cooling and heating processes, respectively.

### 4. Bilayer amorphous phase

Figure 2 shows the temperature dependence of the potential energy of system B at \( P_{zz} = 0.1 \) MPa. The inter-surface distance \( h \) was set to 8.7 Å. As the system is cooled, the potential energy first gradually decreases and then suddenly drops by about 5.6 kJ/mol to a lower value at 270 K. This large energy drop within a small temperature range (5 K) is comparable both to that (7.0 kJ/mol) [12] at the freezing transition of TIP4P bulk water and to that (4.6 kJ/mol) [1] at the freezing transition of the confined water in system A, but is much larger than that (1.2
Table 1. Diffusion constants (in units of cm²s⁻¹) for water confined in the hydrophobic pore (Q2D), supercooled water (3D), and ice (3D ice) obtained from MD simulations of TIP4P model.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Q2D (0.1MPa)</th>
<th>3D (0.1MPa)</th>
<th>3D (200MPa)</th>
<th>3D ice</th>
</tr>
</thead>
<tbody>
<tr>
<td>275K</td>
<td>1.3 x 10⁻⁹</td>
<td>233K: 2 x 10⁻⁹</td>
<td>193K: 3.0 x 10⁻⁷</td>
<td>240K: 3 x 10⁻¹⁰</td>
</tr>
<tr>
<td>270K</td>
<td>3.0 x 10⁻⁹</td>
<td>213K: 9 x 10⁻⁸</td>
<td>183K: 1.4 x 10⁻⁷</td>
<td>230K: &lt;10⁻¹¹</td>
</tr>
<tr>
<td>250K</td>
<td>7.9 x 10⁻¹¹</td>
<td>193K: 6 x 10⁻⁸</td>
<td>173K: 9 x 10⁻⁹</td>
<td></td>
</tr>
</tbody>
</table>

kJ/mol at 200 MPa) [6] at the HDL-LDL liquid-liquid transition in supercooled TIP4P bulk water. In the heating process, the potential energy jumps to a higher value at around 300 K. Discontinuous changes in density are also observed: sudden expansion and contraction in the cooling and heating processes, respectively. The discontinuous changes in energy and density, and the large hysteresis, suggest a strong first-order phase transition in the confined system.

The diffusion constants calculated prior and after the transition (at 275 K and 270 K respectively) differ by four orders of magnitudes. This order-of-magnitude change in diffusivity is comparable to that of liquid-to-crystalline ice transition in the bulk TIP4P system (Table 1), as well as to that of the real water at liquid-to-crystalline ice transition [13, 14]. The drastic change in diffusivity within a small temperature range (5 K) suggests that the confined liquid water transforms into a very viscous "solid-like" amorphous phase around 270 K, which is significantly higher than the melting temperature of the TIP4P ice at 0.1 MPa. In contrast, diffusivity of bulk water changes only about one order of magnitude within a temperature range (213-233 K at 0.1 MPa and 173-183 K at 200 MPa) where the possible HDL-LDL transition occurs (Table 1).

Inherent structures of (a) the liquid (Fig. 3), (b) the bilayer amorphous (Fig. 4), and (c) the bilayer ice crystal phases (Fig. 5) are shown. In the amorphous phase, the two molecular layers are nearly flat; the spatial arrangements of oxygen atoms in both layers are being superimposed on each other (i.e., having a symmetry of reflection). These two features do not show up in the liquid phase. More crucial is the difference in the hydrogen-bonded network structure. In the bilayer amorphous phase, every molecule is hydrogen-bonded with four nearest-neighbour molecules (except a few defects) in a way that three neighbours are in the same layer whereas the fourth one is in the opposite layer. Consequently, the hydrogen-bonded network of the amorphous phase is almost perfect. The substantial decrease in potential energy and the loss of fluidity upon the phase transition can be attributed mainly to the formation of the perfectly hydrogen-bonded network. No liquid-to-bilayer amorphous phase
transition has been observed in a wider hydrophobic pore [15] or in the model hydrophilic pore in which water molecules form hydrogen bonds to hydrophilic sites on the surfaces. Effects of the wall-wall separation distance on the phase transition will be discussed below.

The quasi-two-dimensional network structures of the bilayer amorphous [2] and the bilayer crystal [1] are parallel to the 2D continuous-random network model of glass and the regular honeycomb network model of crystal [16]. First, the bilayer amorphous structure lacks long-range order in the configuration of oxygen atoms, although the local network structure is very similar. Second, there appears a significant spread in hydrogen-bond angles in the 2D network. The most notable structural difference between the bilayer amorphous and the bilayer crystalline ice is the variation in the shape of the polygonal rings of hydrogen bond in each layer. Figure 4 shows that there are not only hexagonal rings but also pentagonal and heptagonal rings, and even some of octagonal
Figure 4. Same as Fig. 3 for bilayer amorphous phase.

rings. The distribution of the $n$-membered rings, which was evaluated based on three independent sets of 100 inherent structures, shows 77% of hexagon ($n=6$), 11% of pentagon ($n=5$), 11% of heptagon ($n=7$) and 1% of the rest ($n=4, 8, 9, 10$). The appearance of a large number of pentagonal and heptagonal rings indicates that these rings are not exceptional imperfections in a crystal but characteristic constituents of the solid-like phase.

The liquid-to-bilayer amorphous transition is not an ordinary glass transition accompanied by no changes in enthalpy and density; it is a first-order transition between two distinct disordered phases, which is referred to as “polyamorphic transition” [17]. The polyamorphic transition for water has been observed as the solid-solid transition between the high density amorphous (HDA) and the low-density amorphous (LDA) by Mishima and co-workers [18, 19], whereas molecular simulation studies indicate existence of the liquid-liquid (HDL-LDL) transition [3, 4, 5, 6, 7]. The liquid-liquid transitions have also been reported for covalent tetrahedral substances [20] including liquid silicon [21, 22], car-
Figure 5. Same as Fig. 3 for bilayer ice.

Table 2. Thermodynamic and structural properties for quasi-2D and 3D water.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Potential energy* (kJ/mol)</th>
<th>4 H-bond species* (%)</th>
<th>6-membered rings* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDL</td>
<td>-47.6</td>
<td>-53.5</td>
<td>73.1</td>
</tr>
<tr>
<td>LDL/LDA</td>
<td>-51.9</td>
<td>-55.0</td>
<td>99.7</td>
</tr>
<tr>
<td>Ice</td>
<td>-53.0</td>
<td>-55.9</td>
<td>100.0</td>
</tr>
</tbody>
</table>

1. Average potential energy of inherent structures. (kJ/mol)
2. Average fraction of molecules having four hydrogen-bonding neighbours.
3. Average number of 6-membered rings normalized by the number in a corresponding crystal.

bon [23, 24], and phosphorus [25]. The phase transition of model water confined in the hydrophobic nanopore [2] seems to belong to another type, i.e., the liquid-solid polyamorphic transition, since the diffusivity comparable to that of crystalline ice and the perfect hydrogen-bonded network strongly suggest the low-temperature phase is solid.
5. **Similarity and difference between Q2D water and 3D water**

Here we consider what are the common features of the polyamorphic transition for the Q2D water and 3D (bulk) water, and what are the main differences. Comparing the potential energy and structural properties of three phases (2D: liquid, bilayer amorphous, and bilayer ice phases; and 3D: LDL, HDL, and ice phases) for each system (see Table 2), we find the following similarities between Q2D and 3D water:

(i) The potential energy differs more between the higher-energy liquid phase and the lower-energy amorphous (or liquid) phase than between the lower-energy amorphous (or liquid) phase and the crystalline solid phase.

(ii) Upon the transition, the population of molecules having a coordination number other than 4 nearly vanishes in the Q2D system, and decreases substantially as well in the 3D system.

(iii) The number of six-membered rings in the hydrogen-bonded network differs significantly among the three phases, thus possibly being a suitable order parameter characterizing the three phases.

There are, however, several significant differences between Q2D and 3D systems. First, the polyamorphic phase transition is very sharp and drastic in the Q2D water as shown in Fig. 2; and the large hysteresis appears. These are the features never observed in simulations of bulk water. Second, the lower-energy disordered phase is an amorphous solid in the Q2D system. It was mentioned earlier that the diffusion constant changes by at least four orders of magnitude from 275 K to 270 K (Table 1). The hydrogen-bonded network is nearly perfect so that water molecules lose their mobility abruptly. The finite diffusivity at the low temperature is due to exceptional defects in the network; the diffusivity would be too small to be observed if the network is perfectly-connected without defects. From a dynamical point of view, the polyamorphic transition of the confined Q2D water may be described as follows. The system is no longer exploring the potential-energy surfaces in the configurational space [26]; rather it is trapped in one of the deep minima corresponding to completely hydrogen-bonded yet non-periodic network structures. Once trapped, the system cannot move to other minima but basically remains at the same minimum, which is a fundamental characteristic of solids. Furthermore, in the Q2D system the minima are very deep so that the bilayer amorphous phase does not melt even at 290 K at $P_{x}=0.1$ MPa. In bulk water, in contrast, the HDL-LDL transition is not as sharp as in the Q2D system: the potential energy change (1.5 kJ/mol) and the diffusivity change (two orders of magnitude) are
much smaller than those in the Q2D system, and a significant number of molecules are not completely hydrogen-bonded to four neighbors even in the LDL phase.

Why does the confined water exhibit the polyamorphic liquid-amorphous transition in such an unequivocal manner? It seems two conditions are necessary for the liquid-bilayer amorphous transition. One is the geometry of confinement: it should be such that width of the slit or of the surface-surface distance be in a very narrow range that can accommodate two layers but not three layers or more. There might be other type of amorphous phases in confined water; but the bilayer amorphous phase seems to form only in the particular geometry. The other necessary condition is hydrophobicity of the surface. Hydrophilic surfaces to which water molecules are hydrogen-bonded inhibit formation of the closed network of water itself whereas hydrophobic surfaces promote the formation. It is analogous to the formation of clathrate hydrates since only hydrophobic guest molecules enable host water molecules to form the completely hydrogen-bonded network. Under these two conditions — geometry and hydrophobicity — formation of the completely hydrogen-bonded network is made possible, and thus the confined water undergoes the strong first-order transition.

The phase boundary between liquid and bilayer amorphous phases in the $T$-$P_{xx}$ plane for a fixed $h$ is obtained qualitatively (Fig. 6) from MD simulations of cooling and heating processes at different fixed pressures and those of compressing and decompressing processes at a fixed $T$. The transition temperatures upon cooling at -100 MPa, 0.1 MPa, 100 MPa, and 300 MPa are 260 K, 270 K, 265 K, and 260 K. No transition is observed at 1 GPa at least up to 190 K. The transition pressure upon decompressing at 250 K is 500 MPa. These results of MD simulations indicate that the slope of phase boundary is negative when $P_{xx} \geq 0.1$ MPa. This is consistent with the Clapeyron equation for the system B:

$$\left(\frac{\partial P_{xx}}{\partial T}\right)_h = \frac{s^\alpha - s^\beta}{(a^\alpha - a^\beta)h},$$

(7)

for the change in entropy is negative ($\Delta s < 0$) and the change in volume is positive ($\Delta v = h\Delta a > 0$) at the liquid-to-bilayer amorphous phase transition. The phase boundary extends into a metastable region of negative pressures ($P_{xx} < 0$), where the slope becomes positive.

6. Phase transition and solvation force induced by confinement

Now we consider the phase behavior of the confined water with changing $h$, the wall-wall separation distance [8]. In this case the force acting
on the walls is an important quantity for monitoring not only the structure of the confined fluid but also the phase behavior. From the $NP_{xx}T$ MD simulation of system B, one can directly obtain the normal pressure $P_{zz}$ acting on the walls by the confined fluid. Two series of simulations, one at 280 K and the other at 270 K, were carried out in which $h$ was reduced stepwise and increased reversely. At both temperatures, $P_{xx}$ was set to 0.1 MPa. The simulation time at each state point ranges from 4 ns to 18 ns, depending on the time required for equilibration.

Figures 7 and 8 show $P_{zz}(h)$ curves for confined water. At 280 K, with reducing $h$, the force $P_{zz}$ oscillates reflecting the structure of the confined liquid (Fig. 7). The highest peak corresponds to the force required for squeezing a bilayer to a monolayer. The potential energy also changes continuously at this temperature. Thus no phase transition is observed by changing $h$ at $T = 280$ K and at $P_{xx} = 0.1$ MPa. At 270 K, however, the force curve is discontinuous at several distances and a large hysteresis is observed when $h$ is reduced and increased. The first discontinuous change in $P_{zz}$ with reducing $h$ is observed as an abrupt drop at around $h = 9$ Å, and then $P_{zz}$ increases rapidly until $h = 7.5$
Å, where again a sudden drop is observed. Structural analysis confirms that the confined water undergoes the liquid-to-bilayer amorphous phase transition at around 9 Å, and that the amorphous phase is compressed until it melts at 7.5 Å. When $h$ is increased, $P_{zz}$ changes continuously showing a peak at around 8 Å (a peak similar to the one at 280 K) and then suddenly jumps to a higher value at 8.2 Å. This jump corresponds to the liquid-to-amorphous transition upon increasing $h$. After the transition, $P_{zz}$ decreases with increasing $h$ and eventually takes negative values; but it suddenly jumps at 9.4 Å. The last jump corresponds to the amorphous-to-liquid phase transition. In this way, the confined water undergoes the liquid-to-amorphous and amorphous-to-liquid transitions with decreasing $h$, and exhibit the transitions in reverse order showing a large hysteresis. The discontinuous force curve and the hysteresis reflect the first-order phase transition of confined water.

Preliminary results for the system C ($N = 3350$) show that the liquid-bilayer amorphous phase transition is also observed for the water cond
fined between two semi-finite parallel walls immersed in bulk water when bringing one wall to the other at \( P = 0.1 \text{ MPa} \) and at \( T = 250 \text{ K} \). In this system, the force acting on the wall is regarded as the solvation force due to the fluid and it is directly obtained from the simulation. As shown in Fig. 9, the solvation force is discontinuous at the phase transition and exhibits a hysteresis. This result suggests a possibility of special hydrophobic interactions due to the polyamorphic transition of water. When \( T = 270 \text{ K} \), however, cavitation and a subsequent drying transition are observed at \( h = 9 \text{ Å} \) instead of the liquid-amorphous transition. Recent studies based on molecular theory suggests that the drying transition gives rise to an attractive solvation force between the two walls at large length scales [27]. In the timescale of simulation, however, the drying transition has been observed only at a small \( h \). Whether the liquid-amorphous transition or the drying transition takes place at small length scales would depend on \( P \) and \( T \) of the bulk environment;
Figure 9. The solvation force between model hydrophobic plates immersed in TIP4P water (system C) at $P = 0.1$ MPa and $T = 250$ K.

the former should be observed in a low $T$ and high $P$ region whereas the latter seems to occur in a high $T$ and low $P$ region.

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References

FRAGILITY, CONFIGURATIONAL ENTROPY, AND THE ENERGY LANDSCAPE OF GLASS-FORMING LIQUIDS

Srikanth Sastry
Jawaharlal Nehru Centre for Advanced Scientific Research
Jakkur Campus, Bangalore 560064, India

Abstract

Fragility is a quantitative index of the rapidity of change of dynamical properties such as viscosity in glass forming liquids. In addition to this kinetic definition, various thermodynamic quantifications of fragility have also been explored in recent years. An analysis of thermodynamic fragility is presented here, based on the study of local energy minima (inherent structures) sampled by the liquid. An expression is derived for the thermodynamic fragility, relating it to parameters that quantify the distribution of inherent structures and the vibrational properties of basins of individual inherent structures. A comparison is made with the kinetic fragilities obtained for a model glass forming liquid from computer simulations. Some open questions and future directions are discussed.

1. Introduction

When cooled to low temperatures in a manner that avoids crystallization, most liquids transform to a glass, an amorphous solid form lacking the long range periodic structure characterizing crystalline solids. The transformation process is referred to as the glass transition. Near the glass transition, liquids display many unusual dynamical features, such as a rapid rise in the viscosity and relaxation times as temperature is reduced, stretched exponential relaxation and heterogeneous dynamics [1, 2, 3, 4, 5]. The glass transition observed in experiments (the “laboratory glass transition”) is understood to be not a transition in the thermodynamic sense but a falling out of equilibrium of the liquid. Whether a thermodynamic transition underlies the laboratory transition, and how an explanation of such a thermodynamic transition is linked (or not) to
a detailed understanding of the unusual dynamics displayed by liquids at low temperatures, is a topic is considerable current research [5]. In this paper, a specific aspect of the latter question is addressed, namely the relationship between fragility and configurational entropy, a thermodynamic quantity that is central to much of the thermodynamic analyses of glass forming liquids. The relationship is addressed by studying quantitatively the distribution and properties of local energy minima, or inherent structures, sampled by the liquid. The inherent structure approach, as well as the concepts of fragility and configurational entropy, are described in the next section. Section 3 describes the comparison of the kinetic and thermodynamic fragilities obtained from computer simulations of a model liquid. Section 4 contains a discussion of open questions, and a summary.

2. The inherent structure approach

The disordered structure of a liquid has the implication that the energies of interaction between particles will generally be very complicated, and that the part of configuration space explored by the material in the liquid state is characterized by the presence of many local minima of the potential energy. Such is the case also, e.g., in a crystalline solid if one allows for the presence of defects. The use of the phrase “energy landscape” to describe the complicated interactions in a glass forming liquid (and other disordered systems) therefore contains in addition the expectation that the complicated potential energy topography plays an essential role in determining the properties of the system. If such is the case, it is desirable to attempt a description of glass forming liquids in terms of quantities that define the nature of the potential energy landscape. In the inherent structure approach, one considers the decomposition of the 3N dimensional (for an atomic liquid) configuration space of the liquid into basins of individual local potential energy minima. A basin of a given minimum is defined as the set of points in the configuration space (or configurations) which map to that minimum under a local energy minimization. The canonical partition function of the liquid can then be expressed as a sum over inherent structure basins, the summand being partial partition functions defined for individual basins. In the following, the equations are written for a two-component atomic liquid, since the model liquid described in the next section is such a liquid. In turn, the sum over basins is written in terms of (a) a distribution of minima in energy, and (b) the free energies of basins, as follows:

\[
Q(N, \rho, T) = \Lambda^{-3N} \frac{1}{N_A!N_B!} \int d\mathbf{r}^N \exp \left[ -\beta \Phi \right]
\]

(1)
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\[
e = \sum_{\alpha} e^{\lambda} \exp \left[ -\beta \Phi_{\alpha} \right] \Lambda^{-3N} \int_{V_{\alpha}} d\Phi \exp \left( -\beta (\Phi - \Phi_{\alpha}) \right)
\]

\[
= \int d\Phi \Omega(\Phi) \exp \left[ -\beta (\Phi + F_{\text{vib}}(\Phi, T)) \right]
\]

\[
= \int d\Phi \exp \left[ -\beta (\Phi + F_{\text{vib}}(\Phi, T) - T S_c(\Phi)) \right]
\]

where \( \Phi \) is the total potential energy of the system, \( \alpha \) indexes individual inherent structures, \( \Phi_{\alpha} \) is the potential energy at the minimum, \( \Omega(\Phi) \) is the number density of inherent structures with energy \( \Phi \), and the configurational entropy density \( S_c = k_B \ln \Omega \). The basin free energy \( F_{\text{vib}}(\Phi_{\alpha}, T) \) is obtained by a restricted partition function sum over a given inherent structure basin, \( V_{\alpha} \). \( \Lambda \) is the de Broglie wavelength, \( N_A \) and \( N_B \) are the number of \( A \) and \( B \) type atoms in the two component liquid, \( T \) is the temperature, and \( \rho \) the density of the liquid. In the following, the dependence on \( \rho \) is not explicitly stated always since the interest is in \( T \) dependent behavior at constant density. The configurational entropy of the liquid arises from the multiplicity of local potential energy minima sampled by the liquid at temperature \( T \), and is related to the configurational entropy density above by

\[
S_c(T) = \int d\Phi S_c(\Phi) P(\Phi, T),
\]

where

\[
P(\Phi, T) = \Omega(\Phi) \exp \left[ -\beta (\Phi + F_{\text{vib}}(\Phi, T)) \right] / Q(N, \rho, T),
\]

\[
= \exp \left[ -\beta (\Phi + F_{\text{vib}}(\Phi, T) - T S_c(\Phi)) \right] / Q(N, \rho, T),
\]

is the probability density that inherent structures of energy \( \Phi \) are sampled at temperature \( T \). In the above expression for the partition function, an assumption has been made that the basin free energy does not differ for different basins of the same inherent structure energy. Without reference to the distribution of minima, the configurational entropy can be defined as the difference of the total entropy of the liquid and the vibrational entropy of typical minima sampled at a given temperature:

\[
S_c(\rho, T) = S_{\text{total}}(\rho, T) - S_{\text{vib}}(\rho, T).
\]

The “entropy theory” of Gibbs, Di Marzio and Adam [7, 8] define the ideal glass transition, underlying the laboratory transition, as an “entropy vanishing” transition where the configurational entropy vanishes (the configurational entropy is not, however, defined in precisely
the same way in [7, 8]). A similar picture also emerges from the study of mean field spin glass models and calculations motivated by them [9, 10, 11]. Whether such a transition exists for real materials is still a matter of debate [12, 13, 14]. The calculations below produce such an entropy vanishing transition but it must be kept in mind that they result from extrapolations which may not be valid.

Further, the Adam-Gibbs [8] theory relates the configurational entropy to relaxation times in the liquid:

$$\tau = \tau_0 \exp \left[ \frac{A}{TS_c} \right], \quad (5)$$

where $A$ is a material specific constant. The validity of this relation has been verified by numerous experimental studies (which typically use the excess entropy of the liquid over the crystal in place of $S_c$) and computer simulation studies [15, 16, 17, 18] (where configurational entropy is evaluated). Further, if $S_c$ has the form $TS_c = K_A (T/T_K - 1)$, the Adam-Gibbs relation results in the Vogel-Fulcher-Tammann-Hesse (VFT) form, observed to describe the $T$ dependence of viscosity, as well as diffusivity and relaxation times, in many glass formers. The VFT relation may be written as

$$\tau = \tau_0 \exp \left[ \frac{1}{K_{VFT} (T/T_0 - 1)} \right], \quad (6)$$

where $T_0$ is the temperature of apparent divergence of viscosity. $K_{VFT}$ is a material specific parameter quantifying the kinetic fragility. Fragility is a measure of how rapidly the viscosity, relaxation times, etc, of a liquid changes as the glassy state is approached [20]. For small values of $K_{VFT}$ (strong case), Eq.(6) yields close to Arrhenius behaviour; large $K_{VFT}$ values yield deviations from Arrhenius behaviour.

That the basin free energy $F_{\text{vib}}$ arises from “vibrational” motion within individual basins is emphasized by the suffix $\text{vib}$. If this motion is sufficiently localized around the minima, a suitable procedure would be to approximate the basins as harmonic wells, and to evaluate the basin free energy within this approximation. The validity of such a procedure has been tested recently in various studies [21, 22, 10, 17, 18, 23]. It is found that below the temperature where the liquid begins to exhibit aspects of slow dynamics, (non-Arrhenius behaviour of relaxation times, and stretched exponential relaxation) [25, 21, 23, 24], a harmonic approximation of the basins is reasonable. Evidence that indicates the applicability of the classical (as opposed to quantum mechanical) basin entropy calculation to real systems is presented in [24]. A classical cal-
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culation of the basin free energy yields
\[ F_{\text{vib}} = k_B T \sum_{i=1}^{3N} \ln \frac{h \nu_i}{k_B T}, \]  
(7)

or equivalently, the basin entropy,
\[ \frac{S_{\text{vib}}}{k_B} = \sum_{i=1}^{3N} 1 - \log \left( \frac{h \nu_i}{k_B T} \right), \]  
(8)

where \( \nu_i \) are the vibrational frequencies of the given basin, and \( h \) is Plank’s constant. From the form of \( S_{\text{vib}} \) it is apparent that the entropy difference between two basins arises solely due to the difference in their frequencies. Thus, such entropy differences remain finite as \( T \to 0 \) which is unphysical as the basin entropy of each basin and therefore their difference must go to zero for \( T = 0 \). Results in [24] show that this artifact does not qualitatively affect the conclusions that can be drawn from the classical analysis. Calculations based on Eq. (8), where the vibrational frequencies are obtained numerically for energy minima generated in simulations, indicate [18] (see also [26, 27]) that the difference in \( S_{\text{vib}} \) between basins is roughly linear in the basin energy. Thus one can write
\[ \Delta S_{\text{vib}}(\Phi) = S_{\text{vib}}(\Phi, T) - S_{\text{vib}}(\Phi_0, T) = \delta S (\Phi - \Phi_0), \]  
(9)

and correspondingly,
\[ F_{\text{vib}}(\Phi, T) = F_{\text{vib}}(\Phi_0, T) - T \delta S (\Phi - \Phi_0) \]  
(10)

where \( \Phi_0 \) is a reference basin energy. The latter expression follows since the internal energy \( U_{\text{vib}} = 3Nk_B T \) for all basins.

In addition to the basin free energy, the partition function in Eq.(1) requires knowledge of the configurational entropy density \( S_c \). Various recent studies have explored methods for estimating \( S_c \) from computer simulations [28, 21, 22, 29, 18, 19]. It has been observed that the distribution \( \Omega(\Phi) \) is well described by a Gaussian [28, 30, 18] (equivalently, \( S_c(\Phi) \) an inverted parabola). Although the arguments [28, 30] may not apply to low energy minima, a Gaussian form for \( \Omega(\Phi) \) allows for a straightforward evaluation of the partition function Eq.(1), and whose validity has been tested in the range of temperatures where simulations are performed [18, 23]. The configurational entropy density is written as
\[ \frac{S_c(\Phi)}{Nk_B} = \alpha - \frac{(\Phi - \Phi_0)^2}{\sigma^2} \]  
(11)
where $\alpha$ is the height of the parabola and determines the total number of configurational states, i.e. energy minima (the total number is proportional to $\exp(\alpha N)$), $\Phi_0$ and $\sigma^2$ respectively define the mean and the variance of the distribution. The parameters $\alpha$, $\Phi_0$ and $\sigma$ have been estimated from simulation data [18]. With the above form for $S_c(\Phi)$ and Eq.\,(10) for the vibrational free energy, the partition function can be evaluated, from which the following temperature dependence of the inherent structure energies, the configurational entropy, the fragility index, and the ideal glass transition temperature $T_K$ (defined by $S_c(T_K) = 0$) are obtained:

$$< \Phi > (T) = \Phi_0^{eff} - \frac{\sigma^2}{2Nk_B T},$$

where $\Phi_0^{eff} = \Phi_0 + \frac{\sigma^2 \delta S}{2Nk_B}$,

$$TS_c(T) = K_{AG}^{PEL}(T) \left( \frac{T}{T_K} - 1 \right),$$

where $K_{AG}^{PEL}$ is the thermodynamic fragility index, given by,

$$K_{AG}^{PEL}(T) = \left( \frac{\sigma \sqrt{\alpha}}{2} \frac{\sigma^2 \delta S}{4Nk_B} \right) \left( 1 + \frac{T_K}{T} \right) - \frac{\sigma^2 \delta S}{2Nk_B},$$

and

$$T_K = \sigma (2Nk_B \sqrt{\alpha} + \sigma \delta S)^{-1}.$$

These equations constitute relations that express quantities relevant to the thermodynamics of glass forming liquids, the configurational entropy and the ideal glass transition temperature, in terms of parameters that describe the “energy landscape” of the liquid, namely the distribution of local energy minima, and the topography of individual minima in the form of vibrational frequencies. In particular, the expressions for $TS_c$ shows that the fragility of the liquid can be expressed in terms of parameters that quantify the “energy landscape” of the liquid. The expression for the fragility parameter $K$ shows that when vibrational frequencies are the same for all basins, fragility is governed by the spread of the configurational density of states. Further, an increase(decrease) of vibrational entropy with the energy of the minima (quantified by $\delta S$) leads to a decrease(increase) in the fragility.

In experimental studies, the quantity that is typically used is the “excess entropy” $S_{ex}$ (defined with respect to the crystal) rather than the configurational entropy. Recently, Martinez and Angell [34] have discussed the use of excess vs. configurational entropy in obtaining experimental fragilities. In the model liquid described below, the crystal phase is not known. It is reasonable however, to use the lowest energy...
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inherent structure as the reference state to calculate excess entropy. To this end, the excess vibrational entropy is defined as:

\[ \Delta S_{\text{vib}}'(\Phi(T)) = S_{\text{vib}}(\Phi, T) - S_{\text{vib}}(\Phi_{\text{min}}, T) = \delta S(\Phi - \Phi_{\text{min}}). \quad (16) \]

where \( \Phi_{\text{min}} \) is the lowest energy inherent structure.

From the temperature dependence of \( \Phi \) above, the temperature dependence of \( \Delta S_{\text{vib}} \) can easily be calculated, and results in

\[ T \Delta S_{\text{vib}}'(T) = \left( \frac{\sigma^2 \delta S}{2Nk_B} \right) \left( \frac{T}{T_K} - 1 \right). \quad (17) \]

The “excess” entropy is then,

\[ S_{\text{ex}}(T) = S_{\text{total}}(T) - S_{\text{vib}}(\Phi_{\text{min}}, T) \]

\[ = S_{\text{conf}}(T) + S_{\text{vib}}(T) - S_{\text{vib}}(\Phi_{\text{min}}, T) = S_{\text{conf}}(T) + \Delta S_{\text{vib}}'(T). \quad (18) \]

The expression for the excess entropy is therefore

\[ TS_{\text{ex}}(T) = K_{\text{ex}}^{PEL}(T) \left( \frac{T}{T_K} - 1 \right), \quad (19) \]

where \( K_{\text{ex}} \) is the fragility index based on the excess entropy, given by,

\[ K_{\text{ex}}^{PEL}(T) = \left( \frac{\sigma^2 \sqrt{a}}{2} + \frac{\sigma^2 \delta S}{4Nk_B} \right) \left( 1 + \frac{T_K}{T} \right). \quad (20) \]

It can be seen that when the vibrational frequencies of different basins differ substantially, the fragility estimated from the configurational entropy and the excess entropy lead to different values.

Note that the thermodynamic index \( K \) above is temperature dependent, and cannot therefore be compared directly with the kinetic index in Eq. (6). However, the \( 1/T \) dependence becomes weak at temperatures sufficiently bigger than \( T_K \), and in that limit, the VFT form (Eq. (6)) is obtained.

3. Computer simulation results

Many recent computer simulation studies of dynamics and thermodynamics aspects of glass forming liquids have employed a binary mixture of atomic particles as a model system [31, 32, 25, 21, 10, 17], as this system has been parametrized to prevent crystallization. Results presented here are from molecular dynamics simulations of 204 type \( A \) and 52 type \( B \) particles. The particles interact via the Lennard-Jones (LJ) potential, with parameters \( \epsilon_{AB}/\epsilon_{AA} = 1.5, \epsilon_{BB}/\epsilon_{AA} = 0.5, \sigma_{AB}/\sigma_{AA} = 0.8, \)
and $\sigma_{BB}/\sigma_{AA} = 0.88$, and $m_B/m_A = 1$. The LJ potential is modified with a quadratic cutoff and shifting at $r_c^\alpha = 2.5\sigma_\alpha^0$ [33]. All quantities are reported in reduced units, length in units of $\sigma_{AA}$, volume $V$ in units of $\sigma_{AA}^3$ (density $\rho \equiv N/V$, where $N$ is the number of particles, in units of $\sigma_{AA}^3 \equiv \rho_0$), temperature in units of $\epsilon_{AA}/k_B$, energy in units of $\epsilon_{AA}$ and time in units of $\tau_m \equiv (\sigma_{AA}^2 m/\epsilon_{AA})^{1/2}$, where $m = m_A = m_B$ is the mass of the particles. Argon units are used for the $A$ type particles when it is desirable to state values in SI units, i.e. $\epsilon_{AA} = 119.8 K \times k_B$, $\sigma_{AA} = 0.3405 nm$, $m_A = 6.6337 \times 10^{-20} kg$. Molecular dynamics simulations are performed over a wide range of temperatures at each density, with run lengths ranging from $1.3 ns$ to $0.4 \mu s$. Local energy minimizations are performed for 1000 ($k_B T/\epsilon_{AA} < 1$) or 100 ($k_B T/\epsilon_{AA} > 1$) configurations to obtain typical local energy minima or ‘inherent struc-

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Figure 1. (a): Inverse diffusivities vs. scaled (inverse) temperature for the binary LJ liquid for a series of densities. $T_r$ is the temperature where $D$ reaches a fixed, small value. (b) The Adam-Gibbs plot for the same set of densities [see Eq. (5)].
Figure 2. Kinetic and thermodynamic fragilities for the binary LJ liquid at a series of densities. See Eqs. (5), (6).

atures’ [6] sampled by the liquid. The Hessian (matrix of second derivatives of the potential energy) evaluated at the minima are diagonalized to obtain the vibrational frequencies. As the binary LJ liquid has mostly been studied at low temperatures and high densities, the location of the liquid-gas critical point has not previously been estimated. A rough estimate, obtained by performing simulations in the appropriate range of ρ and T of length 2.912 ns, is $k_B T_c/\epsilon_{AA} \sim 1.1$, $\rho_c/\rho_0 \sim 0.416$ [24]. The binary LJ liquid is studied at a series of densities, for a number of temperatures (details in [17, 18]). Fig. 1(a) shows the inverse diffusivities plotted against a scaled (inverse) temperature (the scaling temperature $T_s$ is chosen such that the diffusivities for each density reach a common, low, value). It can be seen that as the density of the liquid increases, the behaviour of the diffusivity is farther from Arrhenius; the liquid becomes more fragile with increasing density. Fig. 2 shows the kinetic fragility values obtained from data in Fig. 1(a). Fig. 1(b) shows (details above, and in [18]) an “Adam-Gibbs” plot, where log(diffusivity) is plotted against $(T S_v)^{-1}$; according to the Adam-Gibbs relation, the result ought to be a straight line, which is indeed observed to be the case (note, however, that the slopes for different densities are different). Based on approach described in the previous section, the density of states (DOS) of energy minima is constructed, from data obtained from computer simulations, as described in [18]. The DOS so obtained are shown in Fig. 3, which shows (see previous section) that (a) the number
of energy minima decreases, and (b) the spread in energy increases, with increasing density. These trends are to be compared with the trend in fragility. Fig. 2 shows the thermodynamic fragility obtained from Eq. (14) above. As $K^{PEL}_{AG}(T)$ are $T$ dependent, the average value, in the range of $T$ where diffusivities are measured, is plotted. It is seen that the thermodynamic fragilities, obtained from parameters describing the energy landscape of the liquid, compare well with the kinetic fragilities.

The study above has been conducted at constant density. In order to readily compare with experimental results, one must study the behaviour at constant pressure. A preliminary comparison is made here between these two cases. From Eq. (8), it is clear that the non-trivial part of the vibrational entropy arises from the vibrational frequencies, in the form $-\sum_{i=1}^{3N} \log(\nu_i)$. This quantity is plotted in Fig. 4(a) for the constant density case, against inherent structure energies $\Phi - \Phi_0$ (with reference to the value for inherent structures of energy $\Phi_0$, which

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**Figure 3.** The density of states of energy minima for different densities. In each case, the zero of the $x$-axis has been shifted to the lowest possible energy according to the Gaussian extrapolation. See Eq. (11).
results in $\Delta S_{\text{vib}}$; see Eqs (8), (9)). In the constant pressure case, the appropriate configurational density of states is not available. Hence, $-\sum_{i=1}^{3N} \ln(\nu_i)$ is plotted (without subtraction of a reference value) by itself, against temperature. As $\Phi - \Phi_0$ increases with $T$, Figs 4(a),(b) permit a qualitative comparison; it is seen that vibrational entropy decreases with $T$ in the constant density case, while it increases in the constant pressure case. These opposite trends arise from the path in the phase diagram taken. However, a full analysis of the constant pressure case requires the evaluation of the appropriate density of configurational states.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4a}
\caption{(a) Comparison of constant density and constant pressure behaviours of the vibrational entropies. In the constant pressure case, the non-trivial part of the vibrational entropy [see Eq. (8)] is plotted as the reference high temperature value is not known. Further, in this case, the data are plotted against temperature instead of the inherent structure energy.}
\end{figure}
4. Summary and conclusions

Results are presented here that show that a thermodynamic evaluation of fragility, which compares well with the kinetic estimates, is possible within analysis accessible to computer simulations. The expression for the thermodynamic fragility shows that fragility depends on the spread in energy of the inherent structure energies, as well as variation of the vibrational properties of individual inherent structures. While the results shown support the applicability of the Adam-Gibbs relation to the liquid studied (such agreement is also found in [15, 16]), the difference in the slopes in Fig. 1(b) for different densities need to be understood. Results in Fig. 4 show that the constant pressure and density cases can be quite different, which calls for an analysis of the constant pressure case. Finally, the DOS of inherent structures, while accessible in computer simulations, is not readily measurable from experimental data, although some attempts to extract the DOS from experimentally measured have been made [35, 36]. Further research along these lines, as well as the possibility of extracting information about the energy landscape from the study of aging behaviour [26] need to be explored.

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[*] Email: sastry@jnrasr.ac.in
Glass-forming liquids: Fragility, entropy, energy landscape


THERMODYNAMICS OF LIQUIDS AND GLASSES

What do discs, spheres and ethylbenzene have in common?

Robin J. Speedy
504/120 Courtenay Place, Wellington, New Zealand.

Abstract

The thermodynamic properties of a liquid can be expressed in terms of the properties of the glasses that it samples which provides a unified description of liquids, glasses and the glass transition. The description is shown to be remarkably similar, in some quantitative detail, for systems as diverse as hard spheres, hard discs and real ethylbenzene.

1. Introduction

The thermodynamic properties of a liquid can be expressed in terms of the properties of the glasses that it samples which provides a unified description [1] of liquids, glasses and the glass transition. The aim of this paper is to show that the description is remarkably similar, in quantitative detail, for systems as diverse as hard spheres [2], hard discs [3-5] and real ethylbenzene [6-7].

Figure 1 shows the enthalpy of liquid, crystalline and glassy ethylbenzene. When the liquid is cooled at the rates typical of laboratory studies [6], a few degrees per minute, it becomes stuck in a glass at the experimental kinetic glass transition temperature, $T_g = 115K$, and the measured enthalpy of that glass is shown as a solid line which tends to the limiting enthalpy $H_0(T_g)$ at absolute zero. Other glasses with different enthalpies could be made by cooling the liquid at different rates [8,9] and two of these are shown as dashed lines which are estimated elsewhere [10]. The fictive temperature [1,11], $T_f$, of a glass can be defined as the temperature where it has the same enthalpy and density as the equilibrium liquid. Simulation studies suggest that cooling rates
in excess of $10^{15}$ degrees per second would be needed to make the glass with a fictive temperature $T_f = 240K$. The lower dashed line shows a hypothetical [12,13] ideal glass, which has the same entropy as the liquid at its fictive temperature. That glass could be formed only by cooling the liquid at an infinitesimally slow rate to allow the liquid to equilibrate near the Kauzmann [14] temperature $T_K$.

\[ T_f \]

\[ H/RK \]

\[ T/K \]

\[ H_0(T_f) \]

\[ \text{ethylbenzene} \]

\[ \text{liquid} \]

\[ \text{glasses} \]

\[ \text{crystal} \]

\[ 0 \]

\[ 100 \]

\[ 200 \]

\[ 300 \]

\[ 0 \]

\[ 2000 \]

\[ 4000 \]

\[ H/RK\]

\[ T/K\]

Figure 1. The enthalpy, $H$, of ethylbenzene versus temperature at atmospheric pressure. $H$ is expressed in units $RK = 8.314 J/mol$ relative to the crystal at absolute zero. Solid lines are from experimental measurements. The upper dashed line shows an estimate of the enthalpy of a glass with fictive temperature $T_f = 240K$. The lower dashed line shows an estimate of the enthalpy of an “ideal glass” whose entropy is equal to that of the liquid at the Kauzmann temperature $T_K = 98K$. 
2. Thermodynamics

The vibrational Gibbs free energy of an individual glass can be expressed as

$$G_g(H_0, T) = H_0 + \int_0^T C_{P,g}(H_0, T')(1 - T/T')dT',$$  \hspace{1cm} (1)

where $C_{P,g}(H_0, T)$, the heat capacity of the glass, is the slope of a glass line in figure (1). The vibrational entropy of a glass is zero \(^7,^{10}\) at absolute zero. The entropy of the liquid is greater than that of one glass because the liquid can sample $N_g(H_0)$ structurally distinct glasses with the same $H_0$. The assumption that all glasses with the same $H_0$ have the same bulk properties is supported the reproducibility \(^2,^{4,15}\) of glasses formed in simulation studies.

The extra entropy of the liquid

$$S_c(H_0) = k_B \ln \{N_g(H_0)\},$$  \hspace{1cm} (2)

is called the configurational \(^{16}\) entropy. $S_c(H_0)$ is the residual calorimetric entropy of the glass at absolute zero. $k_B$ is the Boltzmann constant. The free energy of the liquid is then

$$G_l(T) = G_g(H_0, T) - TS_c(H_0),$$  \hspace{1cm} (3)

where $H_0(T)$ is determined implicitly by the condition

$$\left(\frac{\partial[G_g(H_0, T) - TS_c(H_0)]}{\partial H_0}\right)_{T,P} = 0,$$  \hspace{1cm} (4)

which minimizes the free energy of the liquid \(^1\).

Equations (1)–(4) show that a full description of the thermal properties of a liquid and its glasses on an isobar requires knowledge of $C_{P,g}(H_0, T)$ and $S_c(H_0)$. $C_{P,g}(H_0, T)$ is material specific but $S_c(H_0)$ is likely \(^7\) to have a similar form for simple materials and the object of this paper is to highlight the qualitative and quantitative similarities between the form of $S_c(H_0)$ in substances as diverse as hard discs and ethylbenzene.

The number, $N_g(H_0)$, of structurally distinct, mechanically stable, amorphous packings of $N$ particles with enthalpy $H_0$ at absolute zero is expected to be extensive \(^{17}\) and to have a maximum at some value $H_m$ of $H_0$. If each macroscopic structure can be viewed as a collection of independent microscopic parts then the central limit theorem suggests the normal distribution $N_g(H_0) = \exp\{N[\alpha - \gamma(H_m - H_0)^2]\}$ so that, from Eq (2),

$$S_c(H_0)/R = \alpha - \gamma(H_m - H_0)^2,$$  \hspace{1cm} (5)

where $R = Nk_B$.  

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*Thermodynamics of liquids and glasses*
3. Discs & spheres

It is difficult to cool a real liquid [9] fast enough to make glasses with a wide range of fictive temperatures and glasses with $T_f > T_g$ are likely relax irreversibly [8] below $T_f$ so that they are difficult to characterise. However, instantaneous cooling [19] is easy in computer simulation experiments and constraints [4,5,20] can be used in simulations to prevent an unstable glass from relaxing, so that model glasses with a wide range of fictive temperatures can be made and characterised. Figure 2 shows the enthalpy of a hard disc fluid, crystal and some glasses.

For discs or spheres the energy, $U$, is all kinetic, $U = DRT/2$, where $D$ is the dimensionality, so the enthalpy $H = U + PV$ is

$$H = DRT/2 + PV$$  \hspace{1cm} (6)$$

where $V$ is the volume of the system and $P$ is the pressure. The volume occupied by the discs or spheres, $V_\text{m}$, provides a natural unit of volume. The energy unit, $PV_\text{u}$, and the temperature unit, $PV_\text{u}/R$, are constant on an isobar. The enthalpy of the perfect crystal at absolute zero is chosen as the zero for enthalpy, as is customary in experimental studies [8].

There is a qualitative difference between figures 1 and 2 because the heat capacity of real substances goes to zero at absolute zero whereas the simulated model is classical and the heat capacity stays finite, but otherwise the figures are qualitatively similar. An important difference is that the properties of hard disc glasses with different fictive temperatures can be measured, from zero to infinite temperature so the long dashed lines shown in figure 2 are from direct measurement [5], whereas assumptions and extrapolation [6,7,10] are needed to estimate the long dashed line in figure 1.

Most of the measurements shown in figure 2 are for an equimolar mixture of discs with diameters in the ratio 1.4:1, because pure discs freeze quickly when $RT/PV_\text{u} < 0.14$, but the enthalpy of the mixture is the same as that of pure discs on the scale of the figure.

Figure 3 shows that hard spheres follow the same pattern. For spheres the properties of glasses with fictive temperatures above 0.07 were inferred [2] by assuming that the equation of state of glasses with different fictive temperatures has the same form as that of the kinetically stable glasses (with $RT_f/PV_\text{u} \approx 0.07$) and by fitting the known properties of the fluid to equations (2 - 5). For discs the same procedure [3] led to results that agree well with more direct measurements [5].
4. Configurational entropy

Figure 4 shows the configurational entropy of ethyl benzene [6]. To estimate \( S_c \) the heat capacity of the experimental glass [6] (the slope of the short solid line in fig 1) was extrapolated to 300 K to provide a reference glass whose properties are known. The heat capacity of glasses with different limiting enthalpies was assumed [10] to vary linearly with \( H_0 \) with a coefficient that varies as \( 1/T \) so that

\[
C_{P,g}(H_0, T) = C_{P,g}(H_r, T)[1 + (\theta/T)(H_0 - H_r)],
\]  

(7)
Figure 3. Enthalpy, $H$, versus temperature, $T$, for hard spheres [2] on an isobar.

where $H_r$ is the value of $H_0$ for the reference glass and $\theta$ is a material specific constant. The values of $\theta$ and the three constants $\alpha$, $\gamma$ and $H_m$ in equation (5) were chosen [10] to represent the measured enthalpy and entropy of the liquid precisely, from 115 K to 300 K, in terms of equations (1-5). The same procedure yields the dashed lines shown in figure 1.

Figure 5 shows $S_c$ for hard discs. In this case the free energy of glasses with fictive temperatures in the range $0.05 < RT_f / PV_u < \infty$ are measured directly [5].

To compare the forms of $S_c(H_0)$ for models and real substances the different energy units need to be scaled out. Equation (5) can be written as

$$S_c/R = \alpha - \gamma^*(1 - H_0 / H_m)^2,$$  

(8)
so that $\gamma^* = \gamma H_m^2$ is dimensionless. At the Kauzmann temperature, where $S_c = 0$ and $H_0 = H_K$, equation (8) yields

$$1 - H_K/H_m = \sqrt{\alpha/\gamma^*}. \quad (9)$$

and this provides a dimensionless measure of the width of the distributions shown in figures 4 and 5.

Table 1 lists the terms in equation (9) for the few models and real substances for which estimates of $S_c(H_0)$ on an isobar are available. There are many other estimates of $S_c$ for real substances but they rely
Figure 5. The configurational entropy, $S_c$, versus the limiting enthalpy, $H_0$, on an isobar, for an equimolar mixture of hard discs [5] with diameters in the ratio 1.4:1. $H_m$ is the value of $H_0$ for the most numerous glasses and $H_K$ is the value of $H_0$ for the hypothetical ideal glass with $T_f = T_K$. The dotted line estimates $S_c$ for pure discs by shifting the solid line down by the entropy of mixing, $0.69R$.

on the assumption [7,10] that $C_{P,g}(H_0,T)$ is independent of $H_0$. In the case of ethylbenzene, for instance, that assumption leads to an estimate [7,8,10] of $\alpha$ that is 2.8 times higher than the peak shown in figure 4. $S_c$ has been calculated on isochors for some other simulated models [21-24].

The total number of structurally distinct glasses that a material can form is about $\exp(\alpha N)$. For ethylbenzene and toluene $\alpha$ is higher than for spheres which is expected because the asymmetric molecules can

\[ \text{H}_0 / \text{PV}_u \]

\[ H_K \]

\[ H_m \]

\[ S_c / R \]
Table 1. Values of the dimensionless constants in equation (9).  

<table>
<thead>
<tr>
<th>Material</th>
<th>( \alpha )</th>
<th>( \gamma^* )</th>
<th>( (\alpha/\gamma^*)^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheres (pure) [2]</td>
<td>2.0</td>
<td>5.6</td>
<td>0.60</td>
</tr>
<tr>
<td>Disks (pure) [3,5]</td>
<td>0.9</td>
<td>2.3</td>
<td>0.62</td>
</tr>
<tr>
<td>SSW ((N_v = 4, \varepsilon = 0)) [15]</td>
<td>2.2</td>
<td>4.8</td>
<td>0.68</td>
</tr>
<tr>
<td>Ethylbenzene [10]</td>
<td>2.7</td>
<td>6.3</td>
<td>0.65</td>
</tr>
<tr>
<td>Toluene [10]</td>
<td>3.3</td>
<td>5.5</td>
<td>0.77</td>
</tr>
</tbody>
</table>

*Table 1 notes.* For pure discs \( \gamma \) is assumed to be the same as in the mixture but \( \alpha \) is lower [2] by \( S_{mix}/R \) where \( S_{mix} \) is the entropy of mixing. SSW \((N_v = 4, \varepsilon = 0)\) is a tetravalent \((N_v = 4)\) saturated square well model [15] with zero well depth \((\varepsilon = 0)\). Measured values of \( S_c \) (from the first 10 rows in table 4 of ref 15. ) were fitted to a quadratic in \( H_0 \) to get \( \alpha \) and \( \gamma \) for SSW \((N_v = 4, \varepsilon = 0)\). Most of the values of \( \alpha \) and \( \gamma^* \) have an uncertainty of about 20%. The estimates for toluene are less reliable than those for ethylbenzene [10].

Form glasses with structures that are distinguishable on account of the orientation of the molecules, as well as on their positions.

The last two columns of table 1 show the interesting results. Firstly, \( \gamma^* \approx 5.5 \) is the same for all the three dimensional materials to within the likely uncertainties. Secondly, the width of the distribution of glasses \( \sqrt{\alpha/\gamma^*} \approx 2/3 \) is about the same for all the materials, including discs.

5. Conclusions

Table 1 shows remarkable similarities between the form of \( S_c(H_0) \) for diverse materials. For instance, the last column implies, from equation (9), that \( H_K \approx H_m/3 \) to within the likely uncertainties. It also locates the distribution of glasses relative their crystals, because \( H_K \) and \( H_m \) are expressed relative the crystals at absolute zero.

For discs and spheres \( S_c(H_0) \) is determined solely by geometrical factors, since the potential energy is zero. The isobaric results shown in figures 2 and 3 are presented with temperature as the independent variable, to highlight the similarity to figure 1, but varying the temperature serves only to vary the density. The approximate constancy of \( \sqrt{\alpha/\gamma^*} \) suggests that at least some features of the “potential energy landscape” [17,19] for real materials are primarily determined by geometry and density rather than by energy and temperature.

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References

NEW PHASE TRANSITIONS

LANDSCAPE OF WATER DYNAMICS AND CHEMICAL REACTIONS

I. Ohmine, M. Matsumoto, S. Saito, A. Baba, Y. Yonekura, S. Ogasawara, H. Inagaki, C. Kobayashi

Chemistry Department, Nagoya University, Chikusa-ku
Nagoya, JAPAN 464-8602
[YY] Hoshizaki Electric Ltd. Sakae, Toyooka, Aichi, JAPAN
[CK] Physics Department, University of California, San Diego
9500 Gilman Drive, La Jolla, CA 9203 USA

Abstract

The potential energy landscape of water dynamics and chemical reactions is analyzed. We have been studying the following three subjects of liquid water dynamics: (1) What is the nature of the global potential energy surface involved in the liquid water dynamics, which characterized by collective motions and long-time relaxation/ fluctuations? How can we detect directly these collective motions and relaxations experimentally? (2) How does water freeze into a crystalline ice structure? (3) How does an excess proton move in water (liquid water and ice)? We briefly discuss what is now known for (1) and (3), and mainly focus on (2).

1. Introduction

1.1 Liquid water dynamics and its landscape

Liquid water is amorphous gel-like in a short time scale, while it exhibits diffusional motion as an ordinal liquid in a very longer time scale. In between these time scales (about few to tens pico-seconds), the hydrogen bond network rearrangement (HBNR) occurs intermittently and locally in space, involving local collective motions accompanied with large fluctuations. [4, 5, 1, 2, 3] In order to identify these intermittent local collective molecular motions and to explore the nature of the global potential energy surface involved in HBNR of water, the inherent structure analysis [6] and various analyses based on normal modes (quenched nor-
mal mode, instantaneous normal mode, [7] and normal mode excitation) and reaction coordinates were performed. [4, 8, 9, 10] The inherent structures are local minima of the potential energy wells. In trajectory, the system undergoes well to well transitions (inherent structure transitions) after exhibiting vibrational motions in individual wells. Certain sets of inherent structures sequentially visited by the system are found to form island structures (i.e., basins); they are mutually separated with small energy barriers and small structure differences. The transitions among inherent structures within a basin (minor inherent structure transitions) occur easily and frequently. The transitions among the islands (called the basin-basin transitions) occur intermittently. [8, 9] The basin-basin transitions comprise large inherent structure changes but involve relatively small energy barriers. These transitions were found to take place only when the system finds a phase-dynamics matching to pass through narrow and entangled long pathways without large energy barriers. Until the system finds such a phase-dynamics matching, numerous minor inherent structure transitions take place within a basin. [8, 9] It is very interesting to see that the characteristics of these liquid water properties are much common with those found recently for the supercooled state of water. [11, 12, 13]

Various relaxations associated with these collective motions in liquid water yield so-called 1/f spectra, which appears in potential energy fluctuation [5], the low frequency profile of Raman signal (associated with the polarization fluctuation) [14, 15], and others. The spatial-temporal nature of the intermittent local collective motions can be detected by using the neutron scattering [15, 16, 17] and X-ray scattering [18], when they can measure for the smaller \( \omega \) and larger \( k \) values (i.e., the lower energy and smaller spatial region) than the present ones. [3] One of the methods, which may detect these intermittent collective motions, is a higher nonlinear flash photolysis experiment, [19, 20] since this method deals with the phase space dynamics of a system. [10, 21] This technique is analogous to the spin-echo experiment but uses photons [19, 20, 25, 26], and distinguishes the homogeneous and the inhomogeneous elements in liquid dynamics [10, 22, 23, 24]. The problem of applying these higher order nonlinear experiments to water at present is that the signal intensity from water must be very weak, as its polarizability is one order of magnitude smaller than CS₂. As the development of this field is very fast, it may become soon possible that we detect these collective motions and their relaxation of water directly.
1.2 Water freezing

As the water potential energy surface (PES) along the liquid dynamics has the characteristic of a “fragile” liquid, involving various deep energy minima with different hydrogen bond network structures [27, 1, 2, 3]. Upon cooling, water may be trapped into one of such local minima and form an amorphous structure. Nevertheless, liquid water always freezes into crystalline ice in the ambient condition [28]. In the following section, we will present the results of Monte Carlo (MC) and MD calculations, a global PES analysis, and other analyses for the water freezing process.

The freezing mechanisms of liquids have been intensively investigated. A van der Waals atomic liquid was shown to be rather easily crystallized upon cooling. It first forms a body centered cubic structure (BCC), and then changes to a face centered cubic (FCC) lattice [29]. NaCl liquid, a typical ionic atomic liquid, quickly freezes into a rock salt structure upon cooling. [30] The global potential energy surface of its clusters was shown to have a so-called funnel structure smoothly converging to the energy minimum of a rock salt structure. In contrast with these simple liquids, the hydrogen bonds in water have very strong directionality and both the rotation and translation motions of water molecules involve large energy barriers. Liquid water is thus expected not easily form a crystalline structure upon cooling. The mechanism of water crystallization has been investigated by many authors. [31] There have been, however, only three cases in which liquid water freezes into a crystalline structures. Examples are (1) water freezing on an ice surface [32], (2) that under a electric field [33], and (3) that in the pseudo-two-dimensional condition. [34] Although these studies have revealed the mechanism of freezing in a great extent, there have been no studies, as far as our knowledge concerned, on the homogeneous freezing mechanism of pure water.

1.3 Proton transfer in liquid water, ice, and biomolecules

The proton transfer is a most basic reaction in chemistry and biochemistry. It is the basis of the RedOx reaction and almost all the energy of biological activities is created by the proton transfer as the first step. Proton transfer in liquid water is known to be very fast in comparison with other ions. To explain this fast transfer, the mechanism of sequential concerted proton transfers along the hydrogen bond network in water has been proposed. [35] It is only very recent that the mechanism of the excess protons in water becomes clear [36, 37, 38, 39, 40, 41]. It was found that the proton transfer is driven by the hydrogen-bond-coordination fluctuation caused by the hydrogen bond network rear-
rangement (HBNR). [3, 1, 2] The proton transfer takes place almost solely on the three-coordinated water molecules induced by HBNR. [42] Those three-coordinated hydrogen bond water molecules appear in the structure fluctuation caused by the hydrogen bond network rearrangement dynamics. [36, 37, 38, 39] The fast proton transfer in liquid water is thus a typical example of the fluctuation-induced chemical reactions. [37]

The proton transfer in ice is also known to be very fast; [43] its rate is considered to be about half of that in liquid water [44]. But its mechanism must be quite different from the liquid water case. The geometry and the motions of water molecules in ice are confined due to the strong structural constraint from the surrounding water molecules and thus no significant hydrogen bond network rearrangement takes place, but the proton transfer is still very fast in ice. We have investigated the mechanism of the excess-proton transfer in ice by analyzing the potential energy surface, the normal modes and the interaction with a defect. It is found that the solvation from water molecules in long-distance shells is essential for the smooth transport of the proton. The details of the global potential energy surface of the excess proton transfer in ice and in biomolecules are given in our recent articles [45, 46, 47].

2. Water freezing mechanism

We have first investigated the nature of the global potential energy surface related with the water freezing by using annealing and sequential reaction coordinated analyses for water molecular clusters. We then examined the freezing dynamics of liquid water by Monte Carlo (MC) and Molecular Dynamics (MD) calculations. TIP4P potential is used. This potential is known to provide 'temperate results' for many physical quantities of liquid water. The phase transition temperature of liquid water to ice was estimated, by the free energy calculation, to be around 230 K for this potential. [48] Some potentials such as ST2 and TIP5P overemphasize the tendency of the freezing.

2.1 Global potential energy surface of water molecular clusters for freezing

We investigated the global potential energy surfaces (GPES) of (intermediate-size) water molecular clusters to understand how the hydrogen bond network (HBN) structure alters upon cooling [49, 50, 51]. We have determined the sequential "lowest"-energy-barrier reaction coordinates (SLEBRC) of a (H$_2$O)$_{64}$ cluster till reached to a deepest energy minimum [49]. Figure 1 shows that the overall potential energy surface,
starting from a liquid-state inherent structure, decreases slowly toward lower energy states although each RC step often involves a rugged path. The system thus may be conveyed to a deepest energy minimum structure with a sufficiently slow cooling. Indeed, the deepest energy minima obtained by very slow annealing are found to be about equal to those obtained by SLEBRC calculations. Near the bottom, the HBNR involve distinct HB breaking and thus the system yields “strong character,” while it does the “fragile character” in the higher energy, liquid, region. [27, 52, 12] It is noted that SLEBRCs were often trapped in an intermediate energy basin and thus can not reach deep minima. When it happens, the next (the next-next,.....) lowest-energy-barrier reaction coordinates were determined. The GEPSSs thus obtained are found to be very similar to that shown in Fig. 1.

2.2 Molecular dynamics and Monte Carlo studies on liquid water freezing process

We have performed MC and MD calculations for the freezing process of liquid water, by imposing the constant temperature, constant pressure/volume and the periodic boundary condition for the systems containing 64, 96, 216, 512, 4096 water molecules (using TIP4P potential). In MD calculation, the freezing process is monitored after the jumping the system temperature from high value (300 or 400 K) to the lower one (230 or 220 K).

In MD calculations for smaller-size systems (with 512 water molecules or less), we have found that there exists a very long induction period (few hundred nanoseconds ~ microseconds) before the potential energy lowering starts in the freezing process. Once taking place, the overall profile of the total potential energy (PE) decreases almost monotonically. This “freezing period” lasts only few to ten nanoseconds, depending on the size of systems. It is found that the PE fluctuation in this “freezing period” is much smaller than that in the induction period. This means that the system wanders through vast configurational space before getting into a definite “freezing period,” whose global potential energy profile has a funnel structure like shown in Fig. 1. The fluctuation in the freezing period is suppressed by this “funnel force.” Figure 2 shows an example of such a MD trajectory.

In larger systems, the formation of the initial “cluster” with an ice structure (“seed” formation) may take place, by the mechanism described just above, at anywhere of the system, and thus the freezing period starts almost immediately after the temperature jump. We have found in the system with 4096 water molecules that the “ice clusters”
Figure 1. Potential energy landscape curve obtained by sequential reaction coordinate analysis, which passes through the lowest energy barrier minima each steps, started from liquid state, and ending up a very deep energy minimum of the global potential energy surface. This curve connects among SLEBRC steps, that is, a minimum (an inherent structure) – a transition state (TS) – next minimum – another TS – and so force. The deepest minimum, indicated by an arrow, locates at 280 SLEBRC step. Potential energy surface (PES) is fairly sluggish around 80-280 steps. PESs in many other SLERCs are more rugged than the present one.

appear and disappears all over the place and starts glow as a sort of the nucleation process. This nucleus “growing” is, however, not a simple nucleation process, in which particles attach to a nucleus individually, but several water molecules cooperatively form six-member-rings (the basic units of ice), which percolate spatially to form a crystal (Fig. 3). In this “growing” period, a kinetic energy flow must play a crucial role in forming a right crystal structure. The kinetic energy is released when the potential energy is lowered by a local ice structure formation. If this kinetic energy is not dissipated properly, the structure of local segments might be melted. On the other hand, large rearrangements of locally
ordered-structures are needed from time to time to form a crystalline structure. In order to have such rearrangements, local excess kinetic energy must exist.

There are various kinds of simulation techniques, such as Multi-Canonical MC, annealing, J-walking, Replica-Exchange methods, to explore global potential energy surfaces of complex systems. We have also applied these methods to deal with global potential energy surface and sought for an order parameter of water freezing. It is found that there is a sharp separation between the liquid state and the ice state. It is very hard to find a proper order parameter smoothly connecting these states and determine the free energy barrier height between them. For example, $Q_6$ parameter, that is, an index of the tetrahedrality of HB network structure, suddenly changes from liquid value (near zero) to a crystal value only when the crystallization becomes almost complete, and thus can not be a good index to deal with the entire freezing process. We found that the density fluctuation is one of key factor to initiate the freezing, [53] but it alone can not be the order parameter.
Although these simulation techniques, Multi-Canonical MC, J-walking, Replica-Exchange methods, have been found to be very efficient to deal with global potential energy surfaces of relatively small systems, they often have a difficulty to deal with larger systems, like water. Further studies are needed to find new methods and proper order parameters in order to understand the mechanism of freezing process of liquid water (liquid of molecules having the very strong three-dimensional directionality).

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POLYANIONS IN CRystALLINE, PLASTIC
AND MOLTEN PHASES OF ZINTL COMPOUNDS

Jürgen Hafner
Institut für Materialphysik and Center for Computational Materials Science,
Universität Wien, Sensengasse 8, A-1090 Wien, Austria
e-mail: juergen.hafner@univie.ac.at

Abstract

For certain intermetallic compounds of alkali metals and group IV elements containing tetrahedral polyions, a two stage melting process has been reported. Ab-initio molecular dynamics simulations have been used to investigate the stability of polyions in the crystalline, the translationally and rotationally disordered high-temperature solid phase, and in the liquid phase of KSn. Investigations of the structural, dynamic, and electronic properties in all three states are reported.

1. Introduction

Over many decades, the Zintl-alloys formed by a strongly electropositive (alkaline or alkaline-earth) metal and a strongly electronegative polyvalent main-group element have attracted the interest of physicists and chemists because of their highly unusual structural, thermodynamic and electronic properties. The general building principle of these compounds has been formulated already in the thirties: Assuming a complete electron transfer, the more electronegative element B becomes isoelectronic to an element placed to its right in the Periodic Table. In the AB alloy, the B-ions form a sublattice that is isostructural to the crystal structure of the isoelectronic element. Prominent examples illustrating the Zintl-principle [1] are the diamond-type sublattice of the Al-ions in an LiAl alloy with the B32 structure and the tetrahedral polyions isoelectronic and isostructural to P4 molecules found in many I-IV compounds [2]. Although sometimes violently criticized, the Zintl principle has received striking confirmation by ab-initio quantum mechanical calculations of the crystalline and electronic structures [3, 4, 5], provided that a charge-transfer compound is defined as a system in which the va-
ience band is describable in terms of linear combinations of the atomic orbitals of the electronegative element only. Recently, the interest in Zintl-phases has been revived by the discovery that polyanions can survive melting. X-ray and neutron-diffraction studies have revealed the existence of a high degree of topological and chemical short-range order in the liquid [6]. Ab-initio density-functional molecular dynamics simulations [7, 8] have confirmed the existence of a certain fraction of polyanions in the liquid where they are formed and re-destroyed in a dynamical equilibrium. An equally exciting discovery was that melting of certain I-IV compounds occurs through a two-stage process [9, 10, 11, 12]. In the first step the ordered crystalline compound undergoes a transformation to a high-temperature solid phase characterized by rapidly changing dynamical disorder. In NaSn and CsPb compounds the tetrahedral Sn\textsuperscript{4+} and Pb\textsuperscript{4+} polyanions are thought to remain intact and fixed at their crystalline positions while the alkali cations diffuse rapidly among the polyanions, the diffusive motion being supported by the librational and diffusive motion of the polyanions (the “paddle-wheeld” effect [12]). In the second step of the melting process, the crystalline arrangement of the polyanions breaks down and they begin to disintegrate. The intermediate state of the polyanionic compounds is referred to as the “plastic” phase (in reference to its mechanical properties) or as the “rotor” phase (in reference to its dynamical properties). Both transitions (solid → plastic and plastic → liquid) have been described as being first order.

The present paper describes ab-initio molecular dynamics (MD) simulations of KSn, leading to the prediction that a plastic phase exists also in this alloy system. MD simulations of polyanionic compounds are a particularly difficult task. The chemical bonding has been characterized as ionic-covalent, with strong covalent bonds within the polyanions (and, in the crystalline phase, a semiconducting gap between states that are bonding and antibonding within the clusters) and weaker electrostatic interactions between polyanions and alkali cations. The covalent forces holding the polyanions together depend very strongly on the structural perfection of the tetrahedral polyanions and their coordination by polyanions. Even modest distortions of the local arrangement of polyanions and cations are able to weaken the covalent bonds. Hence a survival of polyanions in a dynamically disordered (plastic or liquid phase) requires a correlated motion of polyanions and alkali-atoms. Hence a simulation using classical-force fields is almost hopeless and one has to adopt ab-initio density-functional techniques which allow to calculate via the Hellman-Feynman theorem the full set of quantum-mechanical many-body forces [13, 14]. In Sec. II we summarize very briefly the com-
putational method and the setup used in our simulations of the liquid and plastic phases of KSn, our results are presented in Sec. III and we summarize in Sec. IV.

1.1 Ab-initio Hellmann-Feynman molecular-dynamics

The cornerstone of ab-initio MD is the fast and efficient calculation of the electronic groundstate within the local-density approximation. This is achieved by an iterative diagonalization of the Kohn-Sham Hamiltonian in a plane-wave basis (the electron-ion interaction being described by ultrasoft pseudopotentials [15]), using a residuum-minimization approach and efficient charge- and potential mixing algorithms [16]. Once the electronic ground-state is known, the forces acting on the atoms can be calculated analytically via the Hellmann-Feynman theorem. These forces can then be used in a conventional canonical MD simulation using Nosé-dynamics. For a system as close to a semiconductor-metal transition as KSn, the exact calculation of the groundstate after each ionic move is essential to avoid that the system drifts away from the adiabatic surface.

For KSn, MD simulations have been performed for ensembles containing 64, 96 and 124 atoms, at two slightly different densities, \( n = 0.023 \, \text{\AA}^{-3} \) and \( n = 0.0026 \, \text{\AA}^{-3} \). The former value corresponds to the zero-pressure density derived from short exploratory MD runs, the latter value is close to the density estimated from the experimental diffraction data [17]. The simulation was started at a temperature of 1500 K, using different starting configurations and gradually lowered to 1150 K. To ensure complete equilibration, the simulations where extended to about 60 ps. Details may be found elsewhere [8].

1.2 Results

The results revealed a remarkable difference between the 64-atom high-density ensemble and those obtained with larger ensembles at the same or lower densities. The differences are relatively modest at the level of pair-correlation functions and structure factors where only a sharpening of the first few peaks is observed. In the bond-angle distributions, however, one finds a single narrow peak centered at about 60° for the smaller high-density ensemble and a much broader peak with a broad high-angle distribution extending to 180° in all other cases. This suggests that the tetrahedral polyanions are rather well preserved in the small ensemble, but largely destroyed in the other ensembles. A detailed account of the structure functions and diffraction data has been given by
Figure 1. The instantaneous configuration of the 64-atom ensemble representing liquid KSn at a density of $n = 0.26 \, \text{Å}^{-3}$. Large grey circles represent K atoms, smaller dark circles Sn atoms. Sn-Sn bonds shorter than 3Å are drawn as solid bars. The lines represent the boundaries of the MD box. Note that almost all Sn atoms belong to one of the Sn$_4$ tetrahedra.

Genser and Hafner [8], here we only illustrate the two different states of KSn in the form of snapshots of instantaneous configurations and of the trajectories of the center of gravity of Sn$_4$-nearest neighbor tetrahedra. In state I ($N=64$ atoms, $n= \, 0.026 \, \text{Å}^{-3}$) we find that the majority of the Sn-atoms belongs to rather regular Sn$_4$ tetrahedra (Fig. 1). These tetrahedra are arranged on a regular lattice, the projection of the trajectories of the centres of the tetrahedra (see Fig. 2) shows that they remain
Polyanions In crystalline, plastic and molten phases of zintl compounds

KSn 64

![Graph showing trajectories of the centre of gravity of tetrahedral Sn₄ polyanions in KSn 64, projected on three coordinate planes. The trajectories represent the dynamical evolution of the system during a 7.5 ps time interval.]

Figure 2. Trajectories of the centre of gravity of the tetrahedral Sn₄ polyanions formed in the 64-atom ensemble of KSn at n = 0.026 Å⁻³, projected on the three coordinate planes. The trajectories represent the dynamical evolution of the system during a time interval of 7.5 ps.

fixed at their positions within the MD cell and perform only vibrational movements of relatively small amplitude. In state II (N=124 atoms, n=0.023 Å⁻³) only a much smaller fraction of the Sn-atoms belong to one of the relatively rare polyanions, the majority forms irregular clusters in an entangled network (Fig. 2). Tetrahedra are formed and broken at a rapid rate, trajectories corresponding to those shown in Fig. 2 are broken into short fragments and scattered over the entire cell.

Thus it appears that state II corresponds to the normal liquid state of KSn, while state I corresponds to the “plastic” or “rotor” phase. More pronounced differences between the two phases exist in the dynamic and
Figure 3. The instantaneous configuration of the 124-atoms ensemble representing liquid KSn at a density of \( n = 0.026\text{Å}^{-3} \). See figure 1.

electronic properties. Fig. 3 shows the total and partial frequency spectra calculated from the Fourier-transformed velocity autocorrelation functions. While the K-spectra show only a single peak related to the vibrations of K-atoms in the cage of surrounding atoms, the Sn-spectra show two distinct peaks and a high-frequency shoulder assigned - in the order of increasing frequencies - to librational or translational movements of polyanions (not necessarily only Sn\(_4\) tetrahedra), vibrations of Sn atoms unbound to polyanions, and distortions of the polyanions (their frequency agrees reasonably well with optical modes in \( \alpha\)-tin). In the inelastic spectra, there are only gradual differences between states I and II, but substantial differences appear in the low-frequency limit related to the interdiffusion constants. While for state II we derive high diffusion constants of \( D_K \sim 0.8\text{Å}^2\text{ps}^{-1} \) and \( D_{Sn} \sim 0.5\text{Å}^2\text{ps}^{-1} \), state I is characterized by a lower diffusion constant for K, \( D_K \sim 0.5\text{Å}^2\text{ps}^{-1} \) and an almost vanishing diffusivity of the Sn-atoms \( D_{Sn} \lesssim 0.1\text{Å} \text{ps}^{-1} \). In
Figure 4. Frequency distribution functions $\Psi_i(\omega)$ for molten KSn at $T = 1150$ K: (a) total $\Psi(\omega)$; (b), (c): partial $\Psi_i(\omega)$, $i = K, Sn$. Bold lines: $N_{at} = 64$, $n = 0.026\text{Å}^{-3}$; thin lines: $N_{at} = 64$, $n = 0.023\text{Å}^{-3}$; dotted lines: $N_{at} = 96$, $n = 0.023\text{Å}^{-3}$.

In this case diffusion of Sn occurs almost exclusively by contacts between neighbouring Sn-polyanions.
Even more striking differences exist in the electronic properties: State I is identified as almost semiconducting with a nearly vanishing electronic density of states (DOS) at the Fermi-level (Fig. 4). It is also important to emphasize that although the local DOS at the K-sites is non-zero, the detailed analysis of the partial (angular-momentum decomposed) DOS and of the charge distributions demonstrates that the valence bonds are entirely dominated by Sn-states, the local DOS appearing at the K-sites resulting from the overlap of the rather extended eigenstates of the Sn$^{4-}$ polyanions to the K-spheres (see also Ref. [8]). For state II on the other hand, the structural disorder and the destruction of the polyanions results in a closing of the pseudo-gap at the Fermi level and a definitely metallic character of the alloy (Fig. 5). This agrees
with the dramatic change of the electrical transport properties at the order-disorder transition.

![Graph](image)

*Figure 6.* Total electronic densities of states for the 96- and 124-atom ensembles (parts (a) and (b), respectively) of K-Sn at $n = 0.023\text{Å}^{-3}$ representing the liquid phase.

### 1.3 Discussion and conclusion

Using ab-initio MD simulations we have succeeded in demonstrating the co-existence of a normal liquid and a “plastic” or “rotor” phase in the Zintl compound KSn. The “rotor” phase is characterized by the formation of a lattice of almost perfect Sn$_4^-$ polyanions and a rapid diffusive motion of the K-atoms. The increase in static and dynamic disorder has also dramatic consequences on the electronic properties.

Computationally, the formation of the “rotor” phase from the normal liquid depends on the choice of the boundary conditions (the shape of the cell must be compatible with an ordered arrangement of the polyanions) and on the ability to saturate the covalent bonds within the polyanions. Isolated Sn-atoms or incomplete polyanions represent a rather aggressive chemical species capable of attacking and destabilizing already formed Sn$_4$-clusters. It is also important to emphasize that the process of formation of polyanions is a rather slow one (being diffusion-limited) and that rather long simulation times are also required for reaching a frequency resolution sufficient to allow to deduce diffusion constants from
the low-frequency limit of the frequency distributions compatible with
the analysis of the mean-square displacements.

The existence of dynamical disorder in high-temperature solids is of
course not a novel phenomenon: translational disorder on a sublattice is
known from fast-ion conductors, dynamical disorder of molecules or ions
exist in molecular “rotor” phases. The polyanionic I-IV Zintl phases,
however, are unique in so far as they are constituted by two metallic
elements only and the interaction with the alkali counter-ions involves
covalent, ionic as well as metallic elements. The existence of a transla-
tionally as well as orientationally disordered phase demonstrates the
polyanions represent well-defined chemical entities of sufficient stability
to survive in a dynamically disordered environment.

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(1993).
LOW TEMPERATURE PROPERTIES
OF A SPIN MODEL
WITH VARYING FERROMAGNETIC AND
ANTIFERROMAGNETIC COUPLINGS

Chin-Kun Hu
Institute of Physics, Academia Sinica, Taipei 11529, Taiwan
e-mail address: huck@phys.sinica.edu.tw

Abstract
We briefly review Monte Carlo results for low temperature properties of a spin model with varying ferromagnetic and antiferromagnetic nearest-neighbor coupling constants. The fraction of antiferromagnetic coupling constants is $R$. $R = 0$ and $R = 0.5$ are corresponding to a ferromagnetic Ising model and a spin glass model, respectively. In 1999, Hartmann found that as $R$ increases from 0 to 0.5, the system has a crossover from ferromagnetic behavior to spin glass behavior at $R_c = 0.222 \pm 0.005$. More recently, Lin, Hu, and Hausmann found that for $R$ near and smaller than $R_c$, there are some protein-like ground states, which could be “designed” by many realizations of coupling constants. This leads to the idea of “spin protein” sitting between a ferromagnet and a spin glass.

1. Introduction
Ferromagnet, antiferromagnet, spin glass, and protein are important materials and they have quite different low temperature properties. As the temperature $T$ decreases to very low values, a ferromagnet (and an antiferromagnet) can easily reach its unique lowest energy ground state. The ground state of a ferromagnet (and an antiferromagnet) has no frustration and the energy landscape near the ground state is smooth. As the temperature $T$ decreases to very low values, a spin glass can easily trap in one of its many metastable states. The ground state or metastable states of a spin glass have frustrations and the energy landscapes near such states are rugged. As the temperature $T$ decreases to very low values, a protein can easily reach its ground state. However,
a protein has frustration and rugged energy landscape with an overall slope towards the ground state (funnel). It seems that the behavior of a protein is in-between those of a ferromagnet and a spin glass.

The behavior of a ferromagnet can be well represented by a ferromagnetic Ising model. A spin glass can be prepared by mixing magnetic atoms with non-magnetic atoms. Although the distribution of magnetic atoms in the sample is random, the behavior of a spin glass can be well represented by the Edward-Anderson model [1] with Ising spins on a lattice and the nearest-neighbor coupling constants of the Ising spins are ferromagnetic or antiferromagnetic with equal probability. Dasgupta, Ma, and Hu [2] have found that at very low temperatures, the Edward-Anderson model has many metastable states which could be related to each other by flipping of clusters and the dynamic properties of the model at low temperatures could be understood from flipping of clusters with a distribution of barrier heights.

For proteins, there are also interesting lattice models (see [3] and references therein). There are 20 different amino acids in protein sequences. However, in lattice protein models, it has been usually assumed that there are only two kinds of amino acids: polar (P) and hydrophobic (H) amino acids. Recently, Li et al. have found stimulating results for a H-P protein model on a $3 \times 3 \times 3$ simple cubic (sc) lattice with free boundary conditions. In their model, a protein structure is specified by a set of coordinates of all the monomers. There are a total of 51,704 compact structures unrelated by rotational, reflection, or reverse-labeling symmetries on the $3 \times 3 \times 3$ sc lattice. The energy of a sequence folded into a particular structure is given by short-range contact interactions

$$H = \sum_{i<j} E_{\sigma_i \sigma_j} \Delta(r_i - r_j).$$

Here $E_{HH} = -2.3$, $E_{HP} = -1$, and $E_{PP} = 0$ so that HH pairs prefer to stay inside the lattice. They found that 4.75% of the $2^{27}$ sequences have unique ground states. From the correspondence between sequences with an unique ground state and structures, they obtained designability $N_s$ of each structure. Most structures have very small values of $N_s$. However, there are a few structures which have very large $N_s$. Such structures are protein-like and the existence of the structures with large $N_s$ could explain that under mutation proteins are either stable or change from one stable structure to another.

Since the behavior of a protein seems to be in-between those of a ferromagnet and a spin glass as discussed above, it is of interest to know whether between the ferromagnet and the spin glass, there are states
Spin model with couplings: Low-temperature properties

which are similar to protein states. For this purpose, recently Lin, Hu, and Hansmann (LHH) [4] used a simulated annealing method to study low temperature behavior of an Ising model on a $4 \times 4 \times 4$ sc lattice with periodic boundary conditions and with varying fraction $R$ of antiferromagnetic bonds; $R = 0$ and $R = 0.5$ are corresponding to the ferromagnetic Ising model and spin glass model, respectively. This model was studied by Hartmann [5] in 1999. From calculation of Binder parameter [6], Hartmann found that as $R$ increases from 0 to 0.5, the system has a crossover from ferromagnetic behavior to spin glass behavior at $R_c = 0.222 \pm 0.005$ [5]. Lin, Hu, and Hansmann found that for $R$ near and smaller than $R_c$, there are some protein-like ground states, which could be “designed” by many realizations of coupling constants [4]. This leads to the idea of “spin protein” sitting between a ferromagnet and a spin glass.

This paper is organized as follows: In Sec. 2, the model studied by LHH and the simulation procedures are introduced. In Sec. 3, some simulation results are presented and discussed. Some problems for further studied are addressed in Sec. 4.

![Figure 1. The fraction $f_{SG} = N_{SG}/N_T$ of realizations with single ground state as a function $R$.](image-url)
Figure 2. The average number of ground states, \( \langle N_g \rangle \), as a function of \( R \)

2. Model and simulation procedure

LHH considered following Hamiltonian for Ising spins on a sc lattice of \( N \) sites:

\[
H = - \sum_{\langle lm \rangle}^{3N} J_{lm} \sigma_l \sigma_m
\]  

(2)

where \( \sigma_i = \pm 1 \). A certain number \( M \) of randomly chosen bond variables, \( J_{lm} \), are set to \( J_{lm} = -1 \) while the remaining \( 3N - M \) bonds are assigned the value \( J_{lm} = 1 \). The ratio \( R = M/3N \) is a measure for the randomness in the Ising system and leads to the frustration in the system:

\[
F = \frac{1}{3N} \sum_{i} \delta(F_{\square_i} , -1) \quad \text{with} \quad F_{\square_i} = J_{12}J_{23}J_{34}J_{14} .
\]  

(3)

Here, \( J_{12}, J_{23}, J_{34}, J_{14} \) are the four bond variables of the \( i \)-th elementary plaquette \( \square_i \) of the lattice. It is easy to show that the average value of \( F, \langle F \rangle \), is related to \( R \) by [7].

\[
\langle F \rangle = 4[R^{3}(1 - R) + R(1 - R)^{3}] .
\]  

(4)

The simulation follows the following steps:
Figure 3. The number $N_D$ of truly different single ground state configurations, as a function of $R$.

1 Generate 2000 realizations of $\{J_{lm}\}$ for a $4 \times 4 \times 4$ sc lattice.

2 For each $\{J_{lm}\}$, $N_1$ simulated annealing (SA) runs are performed to cool down the system from $T = 3.0$ to $T = 0.3$ with step size $\Delta T = 0.1$ and MCS=40. The ground state $C_g$ of one realization is the spin configuration with the lowest energy $E_g$ obtained in the $N_1$ runs.

3 It is required that $E_g$ is found in at least $N_2$ SA runs with $N_2 \geq 10^4$ and define the failure rate:

$$N_F = (N_1 - N_2)/N_1.$$  \hspace{1cm} (5)

4 $N_2$ ground state configurations are checked for rotational and translational symmetries, and in this way the number $N_g$ of distinct ground state configurations for the given realization of bond randomness, $\{J_{lm}\}$, is identified.
Figure 4. The average number of failing rate, $<N_F>$, as a function of $R$

5 A realization $\{J_{im}\}$ is protein-like if $N_g=1$. The number of protein-like realization $\{J_{im}\}$ among 2000 realizations is denoted by $N_{SG}$. LHH then define

$$f_{SG} = N_{SG}/2000.$$ (6)

6 LHH check $N_{SG}$ protein-like ground states on translational and rotational symmetries to find the number $N_D$ of distinct ground states.

3. Simulation results

In [4], most quantities are plotted as a function of frustration, $F$. Here the calculated quantities are plotted as a function of $R$.

The calculated fraction of protein-like realizations among 2000 total realizations as a function of $R$ is plotted in Fig. 1 which shows that $f_{SG}$ rapidly decreases in the interval $0.1 < R < 0.2$ and $f_{SG}$ is almost constant for $R > 0.2$.

The calculated average number of ground states, $<N_g>$, among 2000 realizations as a function of $R$ is plotted in Fig. 2 which shows
that $<N_g>$ has rapid increase near $R_c$. The calculated number $N_D$ of truly different single ground state configurations, as a function of $R$ is plotted in Fig. 3 which shows that $N_D$ has rapid increase in the interval $0.1 < R < 0.19$. The calculated average failure rate $<N_F>$ as a function of $R$ for all realizations and realizations with $N_g = 1$ is plotted in Fig. 4 which shows that $<N_F>$ for realizations with $N_g = 1$ has rapid increase at $R_c$.

The calculated ratio $N_D/N_{SG}$ as a function of $R$ is plotted in Fig. 5 which shows that $N_D/N_{SG}$ is almost 0 for $R < 0.1$ and 1 for $R > 0.21$. In the former case, there is only one or very small number of truly different single ground state. This could not be the idea model for protein state because it is difficult for the system to evolve into another protein-like state under mutation (on configurations of coupling constants). In later case, each single ground state is only designed by one realization of coupling constants and such single ground state is not stable under mutation, i.e. the original protein-like realization can easily become not protein-like realization under mutation. In the small region near $R_p = 0.17 \pm 0.02$, there are several truly different single
ground states and each of such states is designed by many realizations of coupling constants. Such single ground states have properties similar to those of “protein” states as discussed in [3].

4. Summary and further research problems

The results presented above can be summarized as follows:

1. The crossover from the ferromagnet to the spin glass at $R_c = 0.222 \pm 0.005$ found by Hartmann could be related to the rapid increases of $<N_F>$ ($N_g = 1$) and $<N_g>$ near $R_c$.

2. For $R$ slightly smaller than $R_c$ and near $R_p = 0.17 \pm 0.02$, there are spin states whose properties are very similar to those of “protein” states, i.e. there are spin protein sitting between a ferromagnet and a spin glass.

The results presented above suggests following problems for further studies.

1. Exact enumeration of the present model on smaller lattices. The fast algorithm proposed by Chen and Hu [8] to find exact geometrical factors for a $q$ bond-correlated percolation model corresponding to the $q$-state Potts model would be useful for this purpose.

2. Simulation of a bond-diluted and site-diluted frustrated Ising model on $sc$ lattices, in which some lattice sites are vacant and represent solvent, and some ferromagnetic or antiferromagnetic bonds between occupied sites are replaced by weaker interactions, similar to those considered by H. Li et al [3]. In such a dilute spin model, it is possible to generate more realistic protein-like structures with backbone and side chains.

3. Chemical evolution of biological molecules. The structures with large $N_s$ suggest that such structures can be realized more easily in random environments. This might be a useful mechanism for chemical evolution of biological molecules.

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