P H Y S I C A L   R E V I E W   L E T T E R S

Structural Order for One-Scale and Two-Scale Potentials

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We perform molecular dynamics simulations to investigate the relationship between structural order and waterlike dynamic and thermodynamic anomalies in spherically symmetric potentials having either one or two characteristic length scales. Structural order is characterized by translational and orientational order parameters. We find that (i) dynamic and thermodynamic anomalies exist for both one-scale and two-scale ramp potentials, and (ii) waterlike structural order anomalies exist only for the two-scale ramp potential. Our findings suggest that the waterlike relationship between structural order and anomalies is related to the presence of two different length scales in the potential.

Most liquids become denser upon cooling and more viscous upon compression. However, water and many other liquids with local tetrahedral order [1] (e.g., silica, silicon, carbon, and phosphorous) show a decrease in density upon cooling (density anomaly) and an increase of diffusivity upon pressurizing (diffusion anomaly). These liquids share many other thermodynamical anomalous properties than those mentioned above. For instance, experiments in phosphorous indicate the presence of a liquid-liquid phase transition [2] and similar results are obtained from computer simulations in silica [3], silicon [4], and water [5]. A possible explanation of these anomalies is the tendency of these liquids to form bonds resulting in local open structures not present in simple liquids. Therefore, much effort has been expended to understand the relationship between the structure and the dynamical and thermodynamic anomalies observed in tetrahedral liquids.

Simple spherically symmetric potentials with a "core softened" or a repulsive interaction at short distances are able to generate waterlike density and diffusion anomalies [6–13], and can even show a liquid-liquid transition [12]. These findings in simple liquids imply that strong orientational interactions (as observed in water or silica) are not a *necessary* condition for a liquid to have thermodynamic and dynamical anomalies. It is still not clear whether such strong orientational interactions are necessary for a liquid to have structural anomalies. Here we address the question of whether spherically symmetric potentials are also able to reproduce the structural anomalies found in systems with local tetrahedral order.

Errington and Debenedetti [14] (ED) have studied the microscopic structural order in liquid water by using simple geometrical metrics or order parameters. The structural order was characterized using two different metrics: a translational order parameter t [15], quantifying the tendency of particle pairs to adopt preferential separations, and a bond-orientational order parameter q [14,16], quantifying the extent to which a molecule and its four nearest

neighbors arrange in a tetrahedral local structure, as is the case in hexagonal ice. A useful way of investigating structural order in liquids is to map state points onto the t-q plane. Such a representation was introduced by Torquato and co-workers [17], who applied it to sphere packings and referred to it as an *order map*. ED used the order map to investigate structural order in water [14]. Because of the distinctive features discovered in that study, in what follows we refer to waterlike order maps as the *ED order map*. ED found that the state points accessible to the liquid state in the order map fall into a two-dimensional area, meaning that in general t and q are independent. However, for those state points where the dynamical and thermodynamical anomalies occur, the t-q parameters fall on a line in the ED order map, meaning that they are strictly correlated. This is clear evidence of the relationship between structure and water anomalies. Shell *et al.* [18] tested the ED order map in silica and found it qualitatively similar to water. However, t-q points corresponding to anomalies do not fall on a single line as in water but fall on a stripe region.

The ED order map was studied for hard spheres [17,19] and Lennard-Jones [15] systems. In these systems, where no dynamical or thermodynamic anomalies are observed, the liquid state points *always* fall on a single line on the ED order map. In other words, in contrast to the case of silica or water, the q-t parameters are *always* strongly correlated. In light of these findings, it is natural to inquire about the ED order map of systems that are spherically symmetric and, in addition, exhibit waterlike anomalies in their thermodynamic and transport properties.

Here we perform discrete molecular dynamics simulations to study the model introduced by Jagla [8] (see Fig. 1). We will identify the model with $\lambda \equiv \sigma_1/\sigma_0 = 1.76$ as the two-scale ramp potential (2SRP) model, and the model with $\sigma_0 = 0$ as the one-scale ramp potential (1SRP) model. We use *NVT* ensemble for a system composed by $N = 1728$ (2SRP) or 850 (1SRP) particles with periodic boundary conditions and control the temperature with the
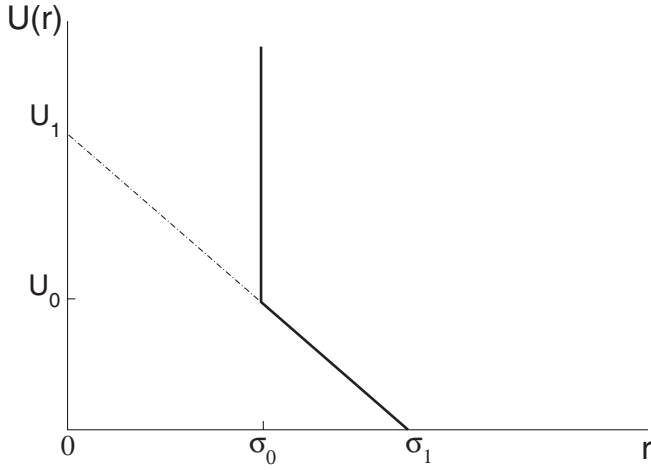
FIG. 1.   The ramp potential introduced by Jagla [8]. σ_0 corresponds to the hard-core distance; σ_1 characterizes a softer repulsion range that can be overcome at high pressure. The 1SRP has $\sigma_0 = 0$, while the 2SRP has two length scales with $\sigma_1/\sigma_0 = 1.76$.

Berendsen thermostat. The details of the simulation are given in Ref. [13]. However, we note that we use different units than in Ref. [13]: lengths are measured in units of σ_1 and energy is measured in units of U_1. We also check that the results do not depend on the number of particles and the value of σ_1 and U_1 after renormalization.

We use the translational order parameter [14,15,18],

$$t \equiv \int_0^{s_c} |g(s) - 1| ds. \tag{1}$$

Here $s \equiv r\rho_n^{1/3}$ is the radial distance scaled by the mean interparticle distance, $g(s)$ is the pair correlation function, and s_c is a numerical cutoff that can be set to a suitable value (we choose s_c so that it corresponds to one-half the simulation box size). For a completely uncorrelated system, $g(s) \equiv 1$, and thus $t = 0$. For systems with long-range order, the modulations in $g(s)$ persist over large distances, causing t to grow.

An orientational order parameter introduced by Steinhardt *et al.* [20] and used in Refs. [15,17,19,21] is modified to characterize the average local order of the system [22]. For each particle, we define 12 vectors (or bonds) connecting the central particle with each of its 12 nearest neighbors. Each bond is characterized by two angles (θ, φ) and the corresponding spherical harmonic $Y_{\ell m}(\theta, \varphi)$ can be computed. The orientational order parameter associated with each particle i is

$$Q_{\ell i} \equiv \left[\frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{m=\ell} |\bar{Y}_{\ell m}|^2 \right]^{1/2}. \tag{2}$$

Here, $\bar{Y}_{\ell m}(\theta, \varphi)$ denotes the average of $Y_{\ell m}(\theta, \varphi)$ over the 12 bonds associated with particle i. For $\ell = 6$ [15], Q_ℓ has maximum value for most crystals such as fcc, hcp, and bcc

[20]. The values of Q_{6i} for each molecule in the system obey a Gaussian distribution, and the averaged value of Q_{6i} over all the particles [22], Q_{6s}, is used to characterize the local order of the system. In general, Q_{6s} grows in value as the crystallinity of a system increases. For example, in fcc lattice, $Q_{6s}^{\text{fcc}} = 0.574$, and for uncorrelated system, $Q_{6s} = 1/\sqrt{12} \approx 0.289$. Thus, Q_{6s} provides a measure of orientational order in the system. We note that fcc is the structure of the stable crystal at low pressure in the 1SRP and 2SRP models [13].

Figures 2(a) and 2(b) show the density dependence of t for both the 1SRP and 2SRP at different temperatures T. The behavior of $t(\rho)$ is qualitatively the same in both models. At low T, $t(\rho)$ shows a clear minimum and maximum and, hence, a range of ρ where t decreases with increasing ρ. This anomaly implies that the system becomes less ordered upon compression. As T increases, the extrema in $t(\rho)$ disappear. At high T, for the 2SRP, t is a monotonically increasing function of ρ, as is the case in normal liquids. However, for the 1SRP, t decreases with ρ. This behavior at high T is probably a consequence of the absence of a hard core in the pair interaction potential. Therefore, upon compression, particles can pass through each other, and, as ρ increases, the structure of the liquid resembles more the structure of the gas. As expected, $t(T)$ and $Q_{6s}(T)$ in both models decreases with T at fixed ρ, meaning that the system becomes more disordered upon heating (Fig. 2).
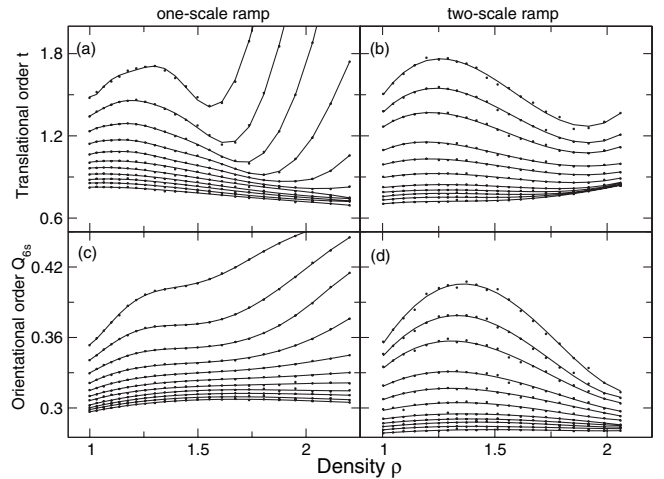

FIG. 2.   The upper panels show the density dependence of the translational order parameter t. The solid lines are polynomial fits to the data, introduced as a guide to the eye. (a) One-scale ramp potential ($\sigma_0 = 0$). From top to bottom isotherms correspond to $T = 0.03$, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12, and 0.13. (b) Two-scale ramp potential with $\sigma_1/\sigma_0 = 1.76$. From top to bottom isotherms correspond to $T = 0.027$, 0.036, 0.045, 0.063, 0.082, 0.109, 0.145, 0.172, 0.2, 0.236, and 0.290. The lower panels (c) and (d) show the density dependence of the orientational order parameter Q_{6s} for same sets of isotherms.

Q_{6s} as a function of density for both models is shown in Figs. 2(c) and 2(d). At low T, $Q_{6s}(\rho)$ for the 1SRP is a monotonically increasing function of ρ, i.e., orientational order increases upon compression. Instead, $Q_{6s}(\rho)$ for the 2SRP at low T shows a clear maximum, indicating a range of density for which $Q_{6s}(\rho)$ decreases with ρ. We also note that, at high pressure or density, the two models have different crystal structures, hcp for 1SRP and rhombohedral for 2SRP. Thus the different $Q_{6s}(\rho)$ in liquid state may be related to the difference in crystal formation.

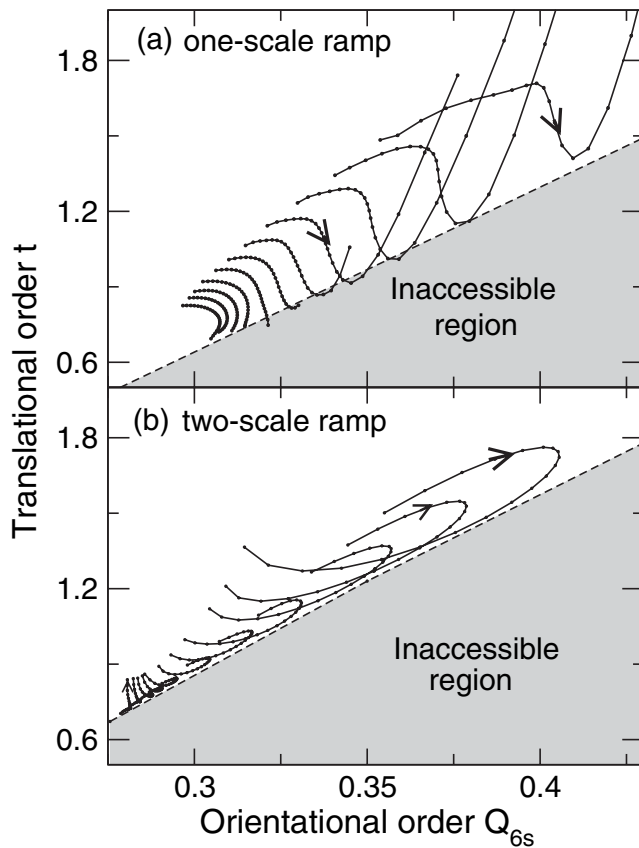Figure 3 shows the isotherms from Fig. 2 in the ED order map representation. For both the 1SRP and 2SRP, the state points fall on a two-dimensional region; i.e., t and Q_{6s} can be changed independently. As in the case of silica and water [14,18], we also find an inaccessible region in the ED order map where no liquid state points can be found. The structural anomalies correspond to the section of the isotherms in Fig. 2 where both Q_{6s} and t decrease upon compression. Only for the 2SRP do we find such anomalies, as has been observed in both silica and water. The state points corresponding to the structural anomalies do not fall, strictly speaking, on a single line delimiting the inaccessible region in the ED order map [Fig. 3(b)]. Instead, these state points form a narrow stripe region, resembling the water ED order map much more closely than the ED order map found for silica [18].

Next, we discuss the regions in the phase diagram where the structural, dynamical, and thermodynamic anomalies occur. In water, the region in the T-ρ or P-T plane corresponding to both structural anomalies contains the region corresponding to the diffusion anomaly which in its turn contains the region corresponding to the density anomaly. In silica, the diffusion anomaly region contains the structural anomaly region, which also contains the density anomaly region. Figure 4 shows the temperature of maximum density (TMD) line and the diffusivity maxima-minima (DM) line. The TMD defines the boundary where the density anomaly occurs, while the DM defines the boundary where the diffusion anomaly occurs. By definition, the structural anomaly region in the T-ρ plane is delimited by the location in the T-ρ plane of the Q_{6s} maximum and the t minimum. Figure 5(b) shows that the relation among the regions of various anomalies for the 2SRP is the same as in the case of water [14]; i.e., the
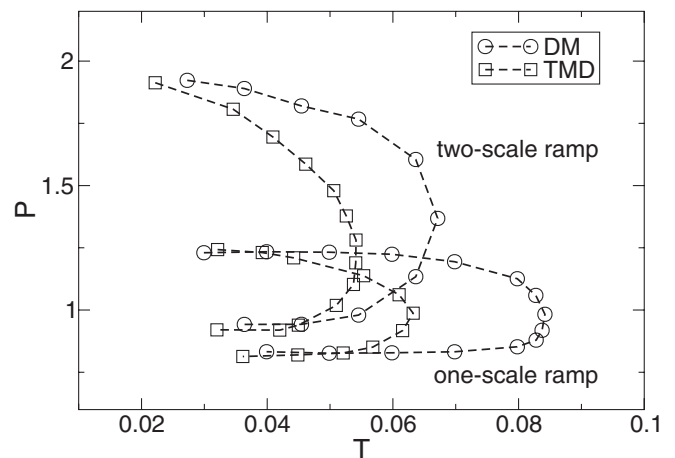

FIG. 3. (a) The ED order map for the one-scale ramp liquid. Isotherms correspond to $T = 0.03$, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12, and 0.13 (from top to bottom), and the arrow indicates the direction of increasing density. For $T \leq 0.08$, t has a maximum at a low density and a minimum at a high density but Q_{6s} shows no maximum. (b) The ED order map for the two-scale ramp liquid. Isotherms correspond to $T = 0.027$, 0.036, 0.045, 0.063, 0.082, 0.109, 0.145, 0.172, 0.2, 0.236, and 0.290 (from top to bottom). Q_{6s} and t have maxima at low densities, and t has minima at high densities. We can identify a structurally anomalous region bounded by loci of maximum orientational order (at low densities) and minimum translational order (at high densities) in which both t and Q_{6s} decrease upon compression. All state points within the structurally anomalous region fall in a narrow stripe region adjacent to the inaccessible region where no liquid state point can be found.

FIG. 4. Temperature of maximum density (TMD) and diffusivity minima and maxima (DM) lines for the two potentials in the P-T plane. The region of diffusion anomaly is defined by the loci of DM inside which the diffusivity increases with density. The thermodynamically anomalous region is defined by the TMD line, inside which the density increases when the system is heated at constant pressure.
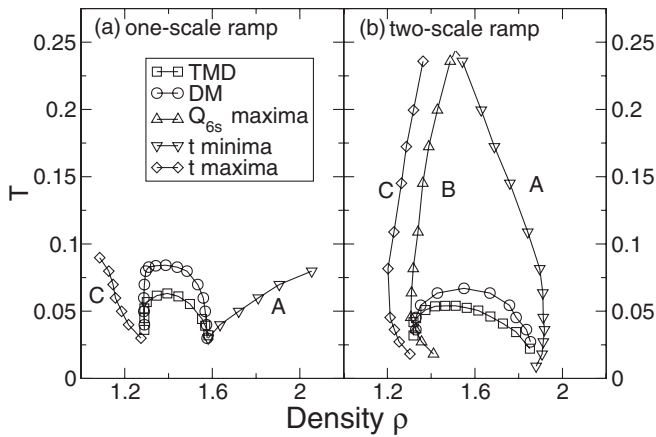
FIG. 5. Relationship between the structural order and the density and diffusion anomalies. (a) For the one-scale ramp liquid, the open region bounded by the loci of t minima (curve A) and t maxima (curve C) [see Fig. 3(a)] defines the structurally anomalous region. This region contains the diffusion anomaly (delimited by the DM) and the density anomaly (delimited by the TMD). (b) For the two-scale ramp liquid, the structurally anomalous region can be defined by the region between the loci of t minima (curve A) and by the loci of either t maxima (curve C) or Q_{6s} maxima (curve B) [see Fig. 3(b)]. The structurally anomalous region contains the diffusion anomaly region which also contains the density anomaly region. Only the two-scale ramp potential shows the same relation between the structural, diffusion, and density anomaly regions as observed in water.

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For the 1SRP, there is no clear Q_{6s} maximum (i.e., Q_{6s} shows no anomaly), so we are not able to identify a structural anomaly region. However, in this case the structural anomaly can be identified by those state points along an isotherm where t decreases upon compression. Therefore, the maximum and minimum values of t in Fig. 3(a) define the structural anomaly region. Figure 5(a) shows that with this definition the structural anomaly region contains the diffusion anomaly region which also contains the density anomaly region. We show in Fig. 5(b) that for the 2SRP, defining the structural anomaly boundaries using the extrema of t does not alter the relationship between the regions of various anomalies. Furthermore, comparing Figs. 5(a) and 5(b), we observe that the effect of reducing the hard-core distance σ_0 is to open the structural anomaly region (curves C and A).

In summary, we find that the 2SRP shows not only density and diffusion anomalies but also the same structural anomalies found in tetrahedral liquids such as silica

and water. Furthermore, the 2SRP also shows the same relation among structural, dynamical, and density anomalies. Our finding suggests that the waterlike relationship between structural order and anomalies may be due to the presence of two different repulsive length scales. When eliminating the hard-core interaction, we find no waterlike relation between structure and dynamics. This suggests that the ratio between the two length scales in the 2SRP, σ_1/σ_0, is the relevant variable in the interaction potential.

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[22] In Refs. [15,17,19], $\bar{Y}_{\ell m}(\theta, \varphi)$ denotes the average over *all* the bonds in the *system*, and the orientational order is defined for the whole system, and not just for single molecules. However, for water and silica [14,18] the orientational order is defined for each molecule and its average is used.