Ising-like Models with Energy-Volume Coupling

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We consider a regular assembly of singly occupied cells with two accessible volumes. Coupled to cell volumes are interaction energies between nearest neighbors that lead to a phase transition with a critical point. We find that these compressible cell models can serve as Ising-like prototypes of the one-component liquid-liquid and isostructural solid-solid phase transitions that originate in the short-range features of the intermolecular potential. The mean-field solutions provide hints concerning the analytical form of the equation of state of liquid water.

The gas-liquid phase transition of pure substances is caused by the attractive, long-ranged section of the intermolecular potential. The details of this potential at shorter distances can lead to phase transitions between condensed phases with distinct densities. Stell and Hemmer first predicted [1] that a pair potential with a "core-softened" repulsive part can induce a second phase transition in addition to the usual gas-liquid transition. They also found that this sort of intermolecular potential underlies isostructural solid-solid transitions such as that experimentally observed in cerium [2]. Simulations for the "step" potential soon confirmed the Stell-Hemmer predictions [3]. Also, isostructural solid-solid transitions for hard-core square-well potentials with an extremely short-ranged attractive region have been reported [4].

Basically the same phenomenon—that is, the coexistence of two condensed phases with distinct densities for a one-component system—has been found in liquids interacting via a variety of core-softened pair potentials [5,6], as well as for a number of water force fields used in simulations [7,8], most of which support the hypothesis of a liquid-liquid critical point [9] which is also supported by a variety of experiments (see Ref. [10] and references therein). As shown by Stell and Hemmer for isostructural solid-solid transitions, the existence of *two length scales* characterizing the short-range section of the intermolecular potential is essential for the occurrence of a liquid-liquid phase transition for a one-component system [11].

In recent years, critical behavior in liquid-liquid transitions has been studied assuming that such transitions belong to the universality class of the three-dimensional Ising model [12,13]. In support, a finite-size scaling analysis of the liquid-liquid phase transition of the Jagla "ramp" potential [5] reveals Ising-like behavior [14].

Also recently, a "two-structure" molecular thermodynamic approach has been proposed to describe experimental data on supercooled water [15] and also simulation results for a number of water force fields [16,17], thereby extending mean-field-level work on the equation of state [18,19].

Here we ask if we can devise Ising-like models to describe this phenomenology. The *compressible cell* (CC) models presented here indicate that we can, and we will show that they are consistent with the accumulated findings on one-component liquid-liquid and isostructural solid-solid phase transitions. Mean-field solutions yield an analytical equation of state relevant to understanding the unusual thermodynamics of liquid water at low temperatures. We shall also see that these Ising-like CC models allow an "exact" treatment of *criticality*.

Model description and nature.—Using the concept recently introduced by Fisher *et al.* [20,21] of "fluctuating cell volumes" in lattice models, we examine a three-dimensional regular assembly with N sites and a coordination number c. Associated with each site is a "cell" inside of which is a moving particle. Akin to the Ising model, in which spins point either up or down, and the standard lattice gas (SLG) model [22], in which cells of a fixed volume are either vacant or contain one particle, each cell has *two* accessible volumes, $v_- = v_0$ and $v_+ = v_0 + \delta v$, with $\delta v > 0$. Although there are primitive versions of this with vanishing attractive forces between particles, we focus on more general models in which $\varepsilon_{--} = \varepsilon_{+-} = \varepsilon_0$ and $\varepsilon_{++} = \varepsilon_0 - \delta\varepsilon$, where the sign and magnitude of ε_0 are unrestricted and $\delta\varepsilon > 0$.

A particle moves in a *free volume* in its cell. When this volume is sufficiently small, the system is in a *condensed* state. Hence we have two characteristic free volumes, $0 < \dot{v}_+ < v_+$ and $0 < \dot{v}_- < v_-$, and the ratio $\lambda = \dot{v}_+/\dot{v}_-$ quantifies the local entropic effects, being thus an essential parameter. Note that such geometrical features as cell volume and shape as well as particle size and shape strongly affect the free volumes [21]. Figure 1 shows two examples in which cell volumes and free volumes
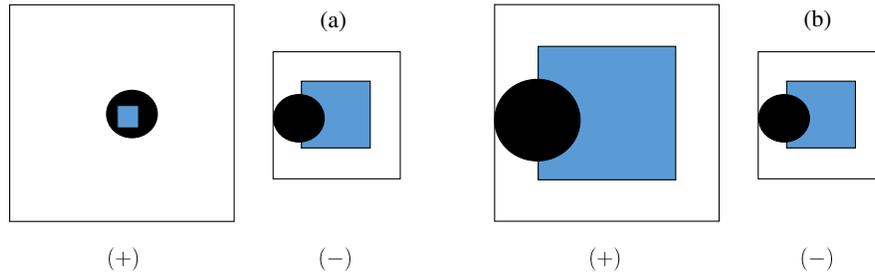
FIG. 1.   Single-cell (+) and (−) states for two situations, (a) and (b). Pictures are two-dimensional for the sake of simplicity, and the shaded (blue) areas are the free volumes a particle can explore in its cell. The relative proportions of particle sizes, volumes, and free volumes are schematic. In (a), we choose—because we have the freedom to do so—to consider that the free volume of particles in (+) cells is restricted so that $\lambda < 1$. In (b), two particle sizes are used while $\lambda > 1$.

are coupled in distinct ways, illustrating that their values can be chosen independently.

We assign $n_i = 1$ and $n_i = 0$ to cell i when it is in the (+) and (−) states, respectively. Thus, for the configuration $\{n_i; i = 1, ..., N\}$, the system energy and volume are

$$E\{n_i\} = \frac{c}{2}N\varepsilon_0 - \delta\varepsilon \sum_{\langle ij \rangle} n_i n_j \qquad (1)$$

and

$$V\{n_i\} = Nv_0 + \delta v \sum_{i=1}^{N} n_i. \qquad (2)$$

We define $\bar{\beta} \equiv 1/k_B T$ and $\bar{p} \equiv \bar{\beta}p$, with T being the temperature, p the pressure, and k_B the Boltzmann constant, and examine the isothermal-isobaric ensemble, summing the $e^{-\bar{\beta}E}$ and $e^{-\bar{p}V}$ Boltzmann factors over microstates. The resulting partition function $Y(N, p, T)$ has the mathematical structure of the Ising canonical partition function. Thus, when using $\mu = -k_B T \ln Y$ as the chemical potential and the standard Ising variables $\bar{f} \equiv -F/Nk_B T$, $K \equiv J/k_B T$, and $h \equiv H/k_B T$ (with F, J, and H as the free energy, coupling constant, and magnetic field, respectively), we find the mapping [23]

$$\bar{f} = \bar{p}\left(v_0 + \frac{1}{2}\delta v\right) - \frac{1}{2}\ln\lambda - \bar{\mu} + \frac{c}{2}\bar{\beta}\left(\varepsilon_0 - \frac{1}{4}\delta\varepsilon\right), \qquad (3)$$

$$K = \frac{1}{4}\bar{\beta}\delta\varepsilon, \qquad h = -\frac{1}{2}\bar{p}\delta v + \frac{1}{2}\ln\lambda + \frac{c}{4}\bar{\beta}\delta\varepsilon, \qquad (4)$$

where $\bar{\mu} \equiv \mu/k_B T - \ln[\Lambda_T^3/v_-]$, with $\Lambda_T \equiv \hbar\sqrt{2\pi/mk_B T}$ being the de Broglie thermal wavelength for particles of mass m.

We will later use known solutions of the Ising model to exploit Eqs. (3) and (4) and analyze mean-field-approximation solutions, but first we finish our description of our models.

Note that CC models differ *fundamentally* from lattice gases. In lattice gases, the coupling between cell occupancy and interaction energy is essential. In CC models, the analogous mechanism is local *energy-volume coupling*. On the other hand, when measured in terms of lattice spacings, distances are discrete in lattice models, implying that associated with the *two accessible volumes* for a cell in CC models there are two lattice spacings. In the Ising paradigm, this appears as the *two length scales* underlying the phase transitions. In addition, the larger lattice spacings characteristic of (+) states make (++) interactions longer range. Because these interactions lower the energy by $\delta\varepsilon$ from the arbitrary value ε_0, this is the essential feature of a pair potential with a softened core [24,25].

Mean-field solutions and the Widom line in a waterlike model.—The mean-field pvT equation of state, in which v is the volume per particle, is [23]

$$p = Tg(v) + c\frac{\delta\varepsilon}{\delta v}\frac{v - v_0}{\delta v}, \qquad (5)$$

with

$$g(v) = \frac{k_B}{\delta v}\ln\left(\lambda\frac{v_0 + \delta v - v}{v - v_0}\right). \qquad (6)$$

This has the mathematical structure of the mean-field standard lattice gas (SLG) equation of state, which is not surprising because both the CC and SLG models are equivalent to the Ising model. The coordinates of the (mean-field) critical point are

$$v_c = v_0 + \frac{1}{2}\delta v, \qquad T_c = \frac{1}{4}c\frac{\delta\varepsilon}{k_B}, \qquad p_c = \frac{1}{4}c(2 + \ln\lambda)\frac{\delta\varepsilon}{\delta v}. \qquad (7)$$

Figure 2 shows how the phase transition builds up in the $p - v$ plane. Thus, the $Tg(v)$ contribution indicates that system compressibility approaches zero at the edges of the v range (from $v_- = v_0$ to $v_+ = v_0 + \delta v$). Combining this with thermodynamic convexity, i.e., $(\partial p/\partial v)_T < 0$, yields
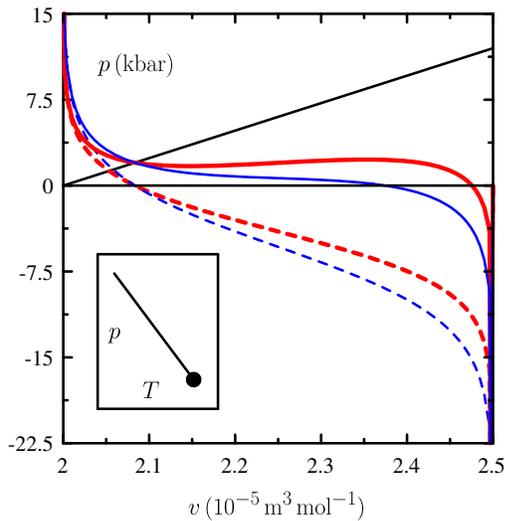
FIG. 2. Isotherms in the pressure-volume plane calculated from Eqs. (5) and (6) for the model in Fig. 1(a) with parameters $c = 6$, $\delta\epsilon = 1000$ J mol^{-1}, $v_0 = 2 \times 10^{-5}$ m^3 mol^{-1}, $\delta v = 0.5 \times 10^{-5}$ m^3 mol^{-1}, and $\lambda = 0.2$. According to Eq. (7), these parameters yield $T_c = 184.4$ K and $p_c = 1.17$ k bar. The straight line is the $c\delta\epsilon(v - v_0)/\delta v^2$ contribution, while the dashed lines are the $Tg(v)$ contributions for $T = 150$ K (bold dashed line, red) and $T = 200$ K (thin dashed line, blue), with the two remaining solid curves representing, according to Eq. (5), the resulting $p(v)$ values; hence, the bold (red) line corresponds to $T = 150$ K and the thin (blue) line to $T = 200$ K. The inset shows that the coexistence curve in the pressure-temperature plane has a negative slope and ends at a critical point.

mimics the structural scheme characteristic of supercooled water [28]. We choose the values of the model parameters by matching the critical coordinates to those at which the liquid-liquid critical point of real water has been hypothesized to exist ($T_c \sim 200$ K and p_c a few hundred bars) [12].

Note that according to the Clapeyron equation, the slope of the coexistence curve in the p-T plane dp_σ/dT is negative in this waterlike model, since the phase with a higher volume—i.e., the phase with a higher proportion of (+) cells—has a lower entropy because $\lambda < 1$ (see also the inset in Fig. 2). This negative dp_σ/dT is consistent with what has been found for water force fields [29]. Thus, because it is a continuation of the coexistence curve, the Widom line also has a negative slope. Figure 3 illustrates that this is the case: isobaric $C_p(T)$ and $\alpha_p(T)$ plots reveal that extrema move toward lower T as p increases.

The lower panels in Fig. 3 compare, at constant p, the model predictions with experimental values of κ_T and κ_S. We use literature values of κ_T for T down to 239 K [30], while we calculate κ_S from data of κ_T, α_p, and C_p [30] by using the exact thermodynamic relation $\kappa_S = \kappa_T - Tv\alpha_p^2/C_p$. Interestingly, additional κ_T experimental data down to even lower temperatures reported recently [10] reveal a $\kappa_T(T)$ maximum around 228 K. On the other hand, the shape of the $\kappa_S(T)$ experimental curve strongly suggests that this property should exhibit a maximum at about 238 K. In this context, it is to be remarked, as is
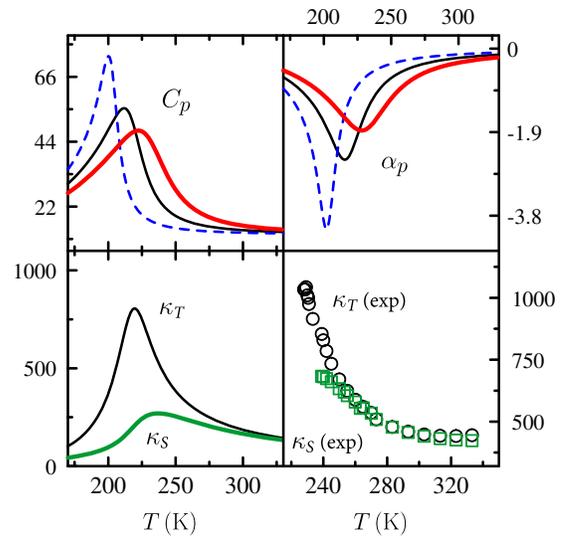
negative $Tg(v)$ values for large v. When the *positive* contribution from interactions between particles in nearest-neighbor (+) cells is added, a van der Waals loop appears at temperatures below the critical temperature T_c.

The mean-field equation of state enables a quantitative study of the Widom line, which has received considerable attention in connection with one-component liquid-liquid phase transitions [13,26,27]. This line is an extension of the coexistence curve in the p-T plane to the one-phase region (i.e., $T > T_c$) at which thermodynamic response functions (e.g., heat capacity) exhibit extrema when evaluated along a given path (e.g., isobaric). Asymptotically close to the critical point, all such extrema converge into a single line. In practice, however, the behavior of response functions upon "crossing the Widom line" is explored at a greater distance from T_c. We next ask how CC models behave when the Widom line is crossed.

To address this question, we use Eqs. (5) and (6) to measure the isobaric heat capacity C_p, the isothermal (κ_T) and isentropic (κ_S) compressibilities, and the isobaric thermal expansivity α_p of the model described in Fig. 1(a). This model builds up a geometrical selectivity in which the free volume in (+) cells is constrained, i.e., $\lambda < 1$, so that (++) configurations are open, low-density structures with small local entropy and small energy. This

FIG. 3. Temperature dependence of the isobaric heat capacity C_p (in J K^{-1} mol^{-1}), the isobaric thermal expansivity α_p (in 10^{-3} K^{-1}), and the isothermal (κ_T) and isentropic (κ_S) compressibilities (in 10^{-12} Pa^{-1}) for the waterlike model in Fig. 1(a), with the model parameters and critical coordinates specified in the caption of Fig. 2, at −500 bar (bold solid line, red), 1 bar (thin solid line), and 500 bar (thin dashed line, blue). Data for compressibilities correspond to 1 bar, with the literature experimental data in the lower-right panel obtained from Refs. [10] and [30].

clearly perceptible from Fig. 3, that the model likewise predicts that the temperature of the $\kappa_S(T)$ maximum is greater than that of the $\kappa_T(T)$ maximum.

Hence [23], our waterlike CC model reproduces with significant detail the experimentally observed low-temperature anomalies of the response functions of supercooled water [31,32]. Because such a model exhibits a phase transition with a critical point, it supports the experimental observation that the behavior of supercooled water is consistent with that of a liquid with critical coordinates around 200 K and a few hundred bars. Indeed, the existence of a second liquid-liquid critical point in water has been hypothesized [7], but experimental constraints make its direct observation difficult [28]. In any event, Fig. 3 shows that our CC model offers the possibility of studying this criticality.

Before discussing critical behavior, we note that Fig. 2 reveals, in accord with observations [33], that the model contemplates the existence of states with a negative pressure which is large in magnitude. We thus find further support to the conclusion that, even at a mean-field level, a model with the microscopic attributes of low-temperature water exhibits a macroscopic behavior consistent with experimental results. Therefore, we conclude that Eqs. (5) and (6) may allow us to develop a physically based equation of state for liquid water.

Criticality.—Equations (3) and (4) show that the Ising "thermal" field K is strongly connected to the temperature, that the "ordering field" h is affected by contributions from both the pressure and the temperature, and that the chemical potential only enters (or "mixes in") the free energy. Thus [23], $\mu(p, T)$ is a reasonable choice of the thermodynamic potential in CC models [34]. This *mirrors* the situation found in the SLG, which leads to $p(\mu, T)$. Note also that the scheme in Eqs. (3) and (4) is consistent with that proposed phenomenologically for one-component liquid-liquid criticality [12,13]. The only difference is the lack of "pressure mixing" in K, but this pressure mixing occurs in decorated models with vacant *bond* cells of variable volume [23].

Focusing on phase boundaries, we set $h = 0$ in Eq. (4) and find [23]

$$p_\sigma = p_c + (k_B T_c \ln \lambda / 4 \delta v) t + O(t^2) \quad \text{and} \quad (8)$$

$$\mu_\sigma = \mu_c + (v_c k_B T_c \ln \lambda / 4 \delta v - s_c) t + O(|t|^{2-\alpha}), \quad (9)$$

where $\alpha \simeq 0.109$, s_c is the critical entropy per particle, and $t \equiv (T - T_c)/T_c$. Note that the pressure remains analytical at the critical point while the second temperature derivative of the chemical potential diverges as $|t|^{-\alpha}$. The opposite is true for the SLG, for which only p is nonanalytical [21]. This has implications for the shape of the coexistence curve, which displays *full* symmetry in the v-T plane. In particular [23], the specific volumes of the coexisting phases are given by

$$v^\pm = v_c[1 \pm B|t|^\beta + O(|t|)], \quad (10)$$

with $B > 0$ and $\beta \simeq 0.326$. For the number density $\rho = v^{-1}$, we find

$$\rho^\pm = \rho_c[1 \mp B|t|^\beta + B^2|t|^{2\beta} + O(|t|^{3\beta})]. \quad (11)$$

Hence, the coexistence curve diameter in the density-temperature plane, $\rho_d \equiv (\rho^+ + \rho^-)/2$, curves as the critical point is approached, showing a $|t|^{2\beta}$ singularity which is absent for $v_d \equiv (v^+ + v^-)/2$. The coexistence curve of CC models is, indeed, symmetric in the volume-temperature plane, and this symmetry property is related to the analyticity of the pressure, as the symmetry of the SLG coexistence curve in the ρ-T plane is related to the analyticity of the chemical potential [21].

Using Eq. (8), we find that the value of the slope of the coexistence curve in the p-T plane evaluated at criticality, $(dp_\sigma/dT)_c$, is positive when cell volumes and free volumes are correlated, i.e., when $\lambda > 1$, but that anticorrelation ($\lambda < 1$) yields a negative slope. In addition, $(dp_\sigma/dT)_c = 0$ for constant free volumes, i.e., $\lambda = 1$.

The waterlike model in Fig. 1(a) is, as noted above, characterized by a negative value of dp_σ/dT. Figure 1(b), in contrast, shows a connection with the isostructural solid-solid phase transitions supported by experiments, simulations, and theoretical analyses [1–3]. For cerium, this kind of transition has been attributed to the ultrahigh-pressure promotion of $4f$ electrons to the conduction band ($5d$), which decreases the effective ionic radius and increases the energy [1,2]. Because $(dp_\sigma/dT)_c > 0$ [3], a CC version with $\lambda > 1$ is needed. Thus, we expect that larger ions explore a larger free volume.

In the borderline case $(dp_\sigma/dT)_c = 0$, Jagla model simulations reveal that significant anomalies are present only for κ_T [13,27]. The performance of the model along the critical isobar is consistent with these results [23].

Final remarks.—We cannot use $\delta\varepsilon$, $\delta v > 0$ to describe the isostructural solid-solid transitions in systems composed of particles interacting via hard-core square-well pair potentials with an extremely short-ranged attractive section [4]. Thus, we might use a modified CC model with $-v_0 < \delta v < 0$ to approach this problem. On the other hand, we cannot use CC models to probe the recently discovered one-component liquid-liquid transitions caused by "network interpenetration" in systems with highly directional interactions [35].

But because much of our understanding of the gas-liquid phase transition is based on the standard lattice gas, the evidence provided here confirms that our compressible cell models can serve as *basic* prototypes for the one-component liquid-liquid and isostructural solid-solid phase transitions we have examined in this work.

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