

Freezing and orientational order in weakly anisotropic fluids

Hyung-June Woo and Xueyu Song

Department of Chemistry, Iowa State University, Ames, Iowa 50011

(Received 7 November 2000; published 6 April 2001)

A simple theoretical method of studying the effect of weak anisotropy on the freezing of classical fluids is discussed. Free energy of the solid phase is separated into contributions due to the formation of the regular lattice and the remaining orientational part. The former is calculated by the density-functional theory, while a mean-field theory of orientational order is developed for the latter. An application to the freezing of hard dumbbell fluids yields results in good agreement with simulations.

DOI: 10.1103/PhysRevE.63.051501

PACS number(s): 64.70.Dv, 05.20.Jj, 64.60.Cn

Freezing of simple isotropic liquids such as Lennard-Jones fluids is now fairly well-understood, largely due to the successful application of density-functional theory to the freezing of the hard-sphere system [1,2]. Ramakrishnan and Yussouff (RY) pioneered the early perturbative treatments [3], and refinements were made later by various weighted density approximations [4–6]. Quantitative agreements with simulation data have been achieved.

Many of the real molecular systems are modeled by anisotropic potentials. Although many authors have applied generalizations of the RY-type density-functional theory to the freezing of weakly anisotropic hard dumbbell and spheroid fluids [7], satisfactory results have been obtained only for small anisotropies [8]. In particular, the various levels of nontrivial effects of increasing anisotropy uncovered by simulations, such as orientational ordering of solid phases in coexistence with fluids [9,10] and the appearance of liquid crystalline phases for higher anisotropies [10], have not been captured theoretically. An efficient theoretical method to treat the fluid-solid equilibria of anisotropic systems would be of interest not only in the general theories of freezing in molecular fluids, but also in the study of phase behavior of various colloidal systems [11] and globular protein solutions [12].

In this paper, we describe a method that combines the density-functional theory and a mean-field treatment of orientational ordering appropriate for studies of the phase behavior of weakly anisotropic model fluids. As an application of the formalism, the freezing transitions in hard dumbbell fluids are considered. The calculated phase diagram agrees well with existing simulation results.

Although precise sources of difficulties encountered in the extensions of the density-functional theories are currently unclear, it is likely that the packing effects associated with the anisotropic interactions in the solid phases are not easily captured in density-functional approaches based on homogeneous liquid properties.

An alternative, albeit phenomenological, approach to freezing is provided by application of the cell theory [13]. The free energy of a solid is simply assumed to be the logarithm of the “free volume” accessible to a particle confined inside a cage formed by its nearest neighbors fixed on their equilibrium positions. Although generally unacceptable as a theory of liquids mainly due to the problem of the communal entropy [14,15], a surprisingly good agreement of coexist-

ence densities with simulation data is obtained when applied to the hard-sphere solid [15]. Extensions of the cell theory have been applied to freezing in hard dumbbell fluids [16].

It thus appears worthwhile to attempt a systematic development of a formalism suitable for studies of the effect of anisotropy on freezing, which avoids both the limitations and technical complexities of the straightforwardly extended density-functional approach, and the *ad hoc* empirical assumptions of the cell theory.

We consider a classical molecular fluid with potential energy,

$$V[\{\mathbf{r}_i, \omega_i\}] = \frac{1}{2} \sum_{i \neq j}^N v(\mathbf{r}_i, \omega_i, \mathbf{r}_j, \omega_j), \quad (1)$$

where $\{\mathbf{r}_i, \omega_i\}$ is the set of molecular center coordinates and orientations, N is the total number of molecules, and $v(\mathbf{r}_i, \omega_i, \mathbf{r}_j, \omega_j)$ is the pairwise interaction potential between molecules i and j . To achieve an effective separation of the translational and orientational free-energy contributions, we separate the full interaction potential into an isotropic reference part and the anisotropic remainder:

$$v(\mathbf{r}_i, \omega_i, \mathbf{r}_j, \omega_j) = v_0(r_{ij}) + v_1(\mathbf{r}_i, \omega_i, \mathbf{r}_j, \omega_j), \quad (2)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Equation (1) is separated correspondingly as $V[\{\mathbf{r}_i, \omega_i\}] = V_0[\{\mathbf{r}_i\}] + V_1[\{\mathbf{r}_i, \omega_i\}]$. The appropriate choice of the isotropic reference potential would depend on the particular case being considered, but in general would have to be made such that the reference fluid closely mimics the homogeneous low-density behavior of the full anisotropic fluid. The full partition function can be written as

$$Z = Z_0 \langle e^{-\beta V_1[\{\mathbf{r}_i, \omega_i\}]} \rangle_0, \quad (3)$$

where Z_0 is the reference system partition function, $\beta = 1/k_B T$, and the angled brackets in Eq. (3) represent the average over the probability distribution of the reference system,

$$\langle \cdots \rangle_0 \equiv \int d^N \mathbf{r}_i \mathcal{P}_0[\{\mathbf{r}_i\}] \int \frac{d^N \omega_i}{\Omega^N} (\cdots), \quad (4)$$

where Ω is the total area of angular elements. The translational probability distribution is given by

$$\mathcal{P}_0[\{\mathbf{r}_i\}] = \frac{e^{-\beta V_0[\{\mathbf{r}_i\}]}}{\int d^N \mathbf{r}_i e^{-\beta V_0[\{\mathbf{r}_i\}]}}. \quad (5)$$

For a crystalline solid phase, the translational distribution is dominated by the small neighborhood in the configurational space of the regular lattice structure. The single-particle density possessing translational long-range order thus accounts for most of the structural features contained in the full distribution function. A functional form of the single-particle density invariably used in the density-functional theories, and shown to be highly accurate in describing the real solid structures, is the sum of Gaussians centered on the lattice sites. The corresponding distribution function can be written as

$$\mathcal{P}_0[\{\mathbf{r}_i\}] = (\alpha/\pi)^{3N/2} \exp\left[-\alpha \sum_{n=1}^N (\mathbf{r}_n - \mathbf{R}_n)^2\right], \quad (6)$$

where $\{\mathbf{R}_n\}$ is the set of lattice vectors and α is the Gaussian width parameter directly related to the Lindemann ratio. With Eq. (6), the molecule n is localized to the neighborhood of the lattice site \mathbf{R}_n .

From Eq. (3), the total free energy per molecule can be written as

$$f = f_0 + f_\omega, \quad (7)$$

where $N\beta f_0 = -\ln Z_0$ and $N\beta f_\omega = -\ln(Y_N/\Omega^N)$ with the ‘‘orientational partition function’’ Y_N defined as

$$Y_N = \int d^N \mathbf{r}_i \mathcal{P}_0[\{\mathbf{r}_i\}] \int d^N \omega_i e^{-\beta V_1[\{\mathbf{r}_i, \omega_i\}]}. \quad (8)$$

Conventional methods of density-functional theory can be applied to obtain the reference free energy, or the free energy of lattice formation, f_0 , and the parameter α .

The orientational free energy f_ω serves as the ‘‘correction term’’ compensating the total neglect of the orientational correlations in the isotropic reference system free energy f_0 . To simplify the presentation of the remainder, we take $\alpha \approx \infty$ in Eq. (6), upon which we get

$$Y_N = \int d^N \omega_i \prod_{\langle nm \rangle} Q_{nm}(\omega_n, \omega_m), \quad (9)$$

where the interactions beyond the nearest-neighbor pairs $\langle nm \rangle$ were neglected, and $Q_{nm}(\omega_n, \omega_m) = \exp[-\beta v_1(\mathbf{R}_n, \omega_n, \mathbf{R}_m, \omega_m)]$.

With the translational distribution localized around the regular lattice sites, a self-consistent mean-field-like formalism can be used to obtain the orientational free energy by considering the hierarchy of many-particle distributions. A

similar approach has been used by Tareeva and Trapezina [17] to treat orientational ordering in the solid. It requires, however, a nonsingular energy expression, and therefore is not appropriate for systems dominated by hard-core interactions.

The n -particle reduced probability distribution function is given by

$$P_N^{(n)}[\{\omega_n\}] = \frac{1}{Y_N} \int d^{N-n} \omega_i \prod_{\langle nm \rangle} Q_{nm}(\omega_n, \omega_m), \quad (10)$$

and the single-particle distribution function for a central site, $p_0(\omega_0) = P_N^{(1)}[\omega_0]$, can be written as

$$\begin{aligned} p_0(\omega_0) &= \frac{1}{Y_N} \int \prod_n d\omega_n Q_{0n}(\omega_0, \omega_n) \\ &\times \int d^{N-n_c-1} \omega_i \prod_{\langle ml \rangle'} Q_{ml}(\omega_m, \omega_l) \quad (11a) \\ &= \frac{1}{\Omega \xi} \int \prod_n d\omega_n Q_{0n}(\omega_0, \omega_n) P_{N-1}^{(n_c)}[\{\omega_n\}]. \quad (11b) \end{aligned}$$

In Eq. (11a), the first and second integrations are over the nearest neighbors of the central site and the rest of the sites, respectively, the second product excludes pairs involving the central site, and n_c is the coordination number. Equation (10) was used to get Eq. (11b), and $\xi = Y_N^{1/N}/\Omega = \exp(-\beta f_\omega)$.

A number of approximations are possible for decoupling the hierarchy represented by Eq. (11b). One obvious choice is to ignore the correlations between the sites and approximate the multiparticle distribution as the product of the single-particle distributions. The other extreme is to ignore the fluctuations instead:

$$P_{N-1}^{(n_c)}[\{\omega_n\}] \approx p_1(\omega_1) \prod_{n \neq 1} \delta(\omega_n - \omega_1), \quad (12)$$

where ‘‘1’’ is any one of the coordination sites. A more realistic approach would be to take the combination of the two limits based on the classification of the coordination sites into M symmetry-related sublattice groups. Fluctuations between sites within a subgroup, and the correlations between sites belonging to different groups, are ignored. The n_c -particle distribution function in Eq. (11b) is thus approximated as

$$P_{N-1}^{(n_c)}[\{\omega_n\}] \approx \prod_{m=1}^M \left[p_m(\omega_{m_1}) \prod_{l \neq m_1} \delta(\omega_l - \omega_{m_1}) \right], \quad (13)$$

where $p_m(\omega_{m_1})$ is the single-particle distribution function of a site belonging to the m th sublattice, m_1 is any one of the sites of the m th group, and the second product runs over the rest of the sites within the sublattice group.

With Eq. (13), Eq. (11b) becomes

$$p_0(\omega_0) = \frac{1}{\Omega \xi} \prod_{m=1}^M \int d\omega_1 p_m(\omega_1) \prod_{n \in m} Q_{0n}(\omega_0, \omega_1). \quad (14)$$

Equation (14) relates the central site distribution function to those of its neighbors. A self-consistent solution can be obtained by assuming a certain parametrized form of the angular distribution, and solving Eq. (14) by iterative procedures.

The formalism developed above is quite general, and could be applied to any short-ranged fluids with relatively weak anisotropy. On the other hand, phases without translational order such as liquid crystals would require different approaches to Eq. (5). In the following, we specifically consider the hard dumbbell fluids, whose phase behavior seems to reveal canonical features of general trends observed in the weak anisotropy regime [10,18]. The hard dumbbell fluids consist of pairs of fused hard spheres with diameter σ and bond length L . The reduced bond length $L^* = L/\sigma$ serves as the ‘‘anisotropy parameter.’’ With computer simulation [8,9], it has been shown that the fluid freezes into the orientationally disordered plastic phase for $L^* < 0.38$, whereas the orientationally ordered phase coexists with the fluid for larger anisotropies.

We use the simple analytical expression of the hard dumbbell fluid free energy devised by Tildesley and Street (TS) [21]. The modified weighted density approximation (MWDA) [6] with the generalization proposed by Khein and Ashcroft [19] was used for the calculation of f_0 . To closely approximate the translational free energy of the full system by those of the reference, the TS form of the free energy and the direct correlation function of an effective hard-sphere system were used as inputs to the MWDA. The effective hard-sphere diameter d was determined by the compressibility thermodynamic consistency.

The perturbation potential in Eq. (2) can in fact be replaced by the full potential since we have assumed perfect localization of molecular centers to lattice sites. For the hard dumbbell potential, the Boltzmann factor $Q_{0n}(\omega_0, \omega_1)$ is either 0 or 1 depending on whether the two dumbbells overlap or not with given orientations. To solve Eq. (14), we choose the following form of $p_m(\omega) \equiv p(\omega; \bar{\omega}_m)$:

$$p(\omega; \bar{\omega}_m) = A^{-1} \exp[b \cos^2 \delta\theta_m + c \cos \delta\phi_m], \quad (15)$$

where θ and ϕ are the angles in the spherical coordinate system, $\delta\theta_m = \theta - \bar{\theta}_m$, $\delta\phi_m = \phi - \bar{\phi}_m$, and A is the normalization factor. Nonzero values of b and c signify the preference of the molecular orientation to directions close to $\bar{\theta}_m$ and $\bar{\phi}_m$. A convenient bounded set of orientational-order parameters can be defined as

$$\begin{aligned} q &= \langle P_2(\cos \delta\theta_m) \rangle_p, \\ z &= \langle \cos \delta\phi_m \rangle_p, \end{aligned} \quad (16)$$

where the angled brackets are the averages over $p_m(\omega)$ and $P_2(x) = (3x^2 - 1)/2$. The order parameters are determined self-consistently by the set of equations obtained from Eq. (14),

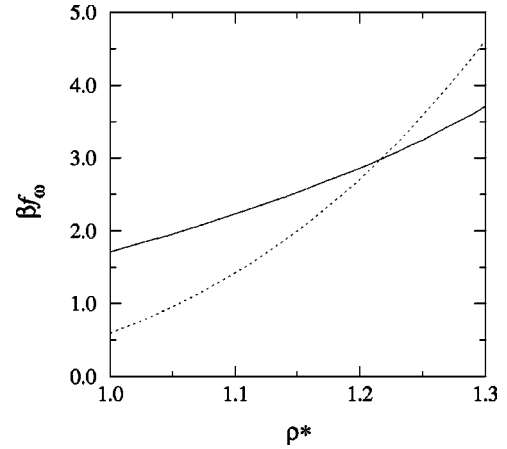


FIG. 1. Orientational free energy f_ω for the fcc and hcp phases as a function of the reduced density $\rho^* = \rho\sigma^3[1 + 3L^*/2 - (L^*)^3/2]$ for $L^* = 0.4$. Solid and dotted lines are the hcp and fcc values, respectively.

$$\xi = \int \frac{d\omega_0}{4\pi} \prod_{m=1}^M \int d\omega_1 p(\omega_1; \bar{\omega}_m) Q_m(\omega_0, \omega_1),$$

$$q = \int \frac{d\omega_0}{4\pi\xi} P_2(\delta\theta_0) \prod_{m=1}^M \int d\omega_1 p(\omega_1; \bar{\omega}_m) Q_m(\omega_0, \omega_1), \quad (17)$$

$$z = \int \frac{d\omega_0}{4\pi\xi} \cos \delta\phi_0 \prod_{m=1}^M \int d\omega_1 p(\omega_1; \bar{\omega}_m) Q_m(\omega_0, \omega_1),$$

where $Q_m(\omega_0, \omega_1) = \prod_{n \in m} Q_{0n}(\omega_0, \omega_1)$. Equations (17) can be iterated with an initial guess of q and z .

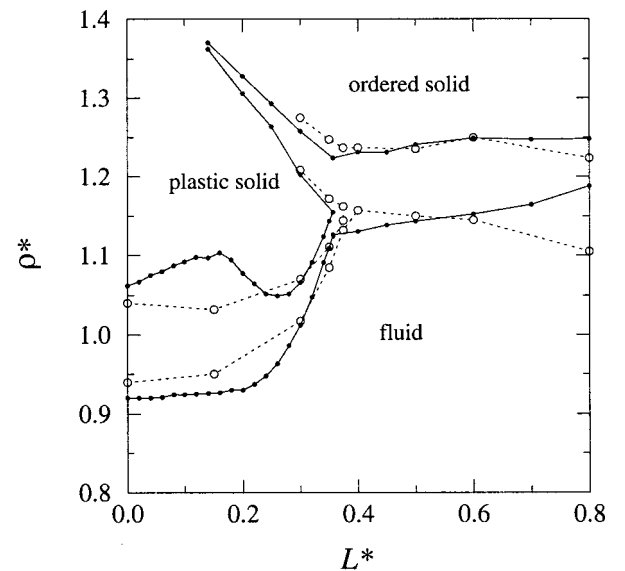


FIG. 2. Phase diagram of hard dumbbell fluids. Dots are the coexistence densities calculated. Open circles are the simulation results from Ref. [9]. Solid and dotted lines are guides to the eye.

For the plastic phase, each molecular centers were assumed to be in face-centered-cubic (fcc) symmetries. Coordination sites of a central site would consist of three sublattice groups, and $M=3$ in Eqs. (17). Preferred angular orientations were taken as those of the α -N₂ structure [20]. We assumed that for the ordered phase, molecular centers are arranged in the hexagonal-close-packed (hcp) symmetry, with the preferred orientation along the c direction. The lattice constant ratio was taken as the close-packing value. All of the coordination sites have the same preferred orientation, namely the direction perpendicular to the hexagonal planes, and $M=1$ in Eqs. (17). Angular integrals in Eqs. (17) were evaluated by a 30-point Gauss-Legendre quadrature in each dimension. For the fcc solid phase, no appreciable orientational ordering into α -N₂ structure was observed in our calculations, whereas the order parameter of the hcp phase was found to increase monotonically with density, approaching 1 near close packing.

The orientational free energy f_ω as a function of density for the two phases is shown in Fig. 1. It is seen that in general there exists a switch of stability from the fcc to hcp solid as density increases. To calculate the values of the coexistence densities, the translational part of the free energy f_0 should be added along with the ideal part to f_ω for each of the lattice symmetries.

The obtained phase diagram is shown in Fig. 2. For low anisotropy, the dumbbell fluid freezes into the plastic phase, while the fluid coexists with the orientationally ordered phase at higher bond-length parameters. The triple point, where the fluid, plastic, and the ordered phases coexist, is found to be at $L^*=0.36$, in good agreement with simulations. The general level of agreement with simulations is similar to that of the hard-sphere limit, except the small L^* region of the fluid-plastic phase boundaries. For $L^*\leq 0.2$, the dumbbells on the fcc lattice do not interact within the present approximations for densities near coexistence, and $f_\omega=0$. The resulting overestimation of the stability of the plastic phase is manifested as the broadening of the coexistence region. In reality, the effect of anisotropic interactions would still be felt for these small values of L^* , mainly due to the finite size of the Lindemann ratio. Equation (14) can be readily generalized to include translational distribution functions with a nonzero width α .

The current method could be applied fairly straightforwardly to study the phase behavior of the ‘‘soft’’ anisotropic model fluids. A choice of the isotropic reference system for a given potential model determines the anisotropic perturbation potential, which serves as the input to the mean-field theory of orientational order.

-
- [1] D. W. Oxtoby, *Nature (London)* **347**, 725 (1990).
 [2] R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (M. Dekker, New York, 1992).
 [3] T. V. Ramakrishnan and M. Yusouff, *Phys. Rev. B* **19**, 2775 (1979); A. D. J. Haymet and D. W. Oxtoby, *J. Chem. Phys.* **74**, 2559 (1981).
 [4] P. Tarazona, *Mol. Phys.* **52**, 81 (1984).
 [5] W. A. Curtin and N. W. Ashcroft, *Phys. Rev. A* **32**, 2909 (1985); *Phys. Rev. Lett.* **56**, 2775 (1986).
 [6] A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **39**, 4701 (1989).
 [7] J. D. McCoy, S. J. Singer, and D. Chandler, *J. Chem. Phys.* **87**, 4853 (1987); J. F. Marko, *Phys. Rev. Lett.* **60**, 325 (1988); S. J. Smithline, S. W. Rich, and A. D. J. Haymet, *J. Chem. Phys.* **88**, 2004 (1988); U. P. Singh, U. Mohanty, and Y. Singh, *Phys. Rev. A* **38**, 4377 (1988).
 [8] S. J. Singer and R. Mumaugh, *J. Chem. Phys.* **93**, 1278 (1990).
 [9] C. Vega, E. P. A. Paras, and P. A. Monson, *J. Chem. Phys.* **96**, 9060 (1992); **97**, 8543 (1992).
 [10] P. Bolhuis and D. Frenkel, *J. Chem. Phys.* **106**, 666 (1997).
 [11] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, New York 1994).
 [12] P. R. ten Wolde and D. Frenkel, *Science* **277**, 1975 (1997); V. Talanquer and D. W. Oxtoby, *J. Chem. Phys.* **109**, 223 (1998).
 [13] J. E. Lennard-Jones and A. F. Devonshire, *Proc. R. Soc. London, Ser. A* **168**, 53 (1937).
 [14] J. G. Kirkwood, *J. Chem. Phys.* **18**, 380 (1950).
 [15] W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **49**, 3609 (1968).
 [16] E. P. A. Paras, C. Vega, and P. A. Monson, *Mol. Phys.* **77**, 803 (1992); S. C. Gay, J. C. Rainwater, and P. D. Beale, *J. Chem. Phys.* **112**, 9841 (2000).
 [17] E. E. Tareeva and T. I. Trapezina, *Dokl. Akad. Nauk SSSR* **223**, 823 (1975) [*Sov. Phys. Dokl.* **20**, 548 (1976)].
 [18] C. Vega and P. A. Monson, *J. Chem. Phys.* **107**, 2696 (1997).
 [19] A. Khein and N. W. Ashcroft, *Phys. Rev. Lett.* **78**, 3346 (1997); *Phys. Rev. E* **60**, 2875 (1999).
 [20] T. A. Scott, *Phys. Rep.* **27**, 89 (1976).
 [21] D. J. Tildesley and W. B. Streett, *Mol. Phys.* **41**, 85 (1980).