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Freezing of a two-dimensional fluid into a crystalline phase: Density functional approach

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A free-energy functional for a crystal proposed by Singh and Singh [Europhys. Lett. **88**, 16005 (2009)] which contains both the symmetry conserved and symmetry broken parts of the direct pair correlation function has been used to investigate the crystallization of a two-dimensional fluid. The results found for fluids interacting via the inverse power potential $u(r) = \epsilon\,(\sigma/r)^n$ for $n = 3$, 6, and 12 are in good agreement with experimental and simulation results. The contribution made by the symmetry broken part to the grand thermodynamic potential at the freezing point is found to increase with the softness of the potential. Our results explain why the Ramakrishnan-Yussouff [Phys. Rev. B **19**, 2775 (1979)] free-energy functional gave good account of freezing transitions of hard-core potentials but failed for potentials that have soft core and/or attractive tail.

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I. INTRODUCTION

Freezing is a basic phenomenon, the most inevitable of all phase changes. When a liquid freezes into a crystalline solid its continuous symmetry of translation and rotation is broken into one of the Bravais lattices. A crystalline solid has a discrete set of vectors $\mathbf{R_i}$ such that any function of position, such as one particle density $\rho(\mathbf{r})$, satisfies $\rho(\mathbf{r}+\mathbf{R_i}) = \rho(\mathbf{r})$ for all $\mathbf{R_i}$ [1]. Because of localization of particles on lattice sites, a crystal is a system of extreme inhomogeneities where values of $\rho(\mathbf{r})$ show extreme differences between its values on the lattice sites and in the interstitial regions. The density functional formalism of classical statistical mechanics has been used to develop theories for liquid-solid transitions [2,3]. This kind of approach was initiated in 1979 by Ramakrishnan and Yussouff [4].

The central quantity in this formulation is the excess reduced Helmholtz free energy arising due to interparticle interactions of both the crystal $A_{\text{ex}}[\rho]$ and the liquid $A_{\text{ex}}[\rho_l]$ [4,5]. For the crystal $A_{\text{ex}}[\rho]$ is a unique functional of $\rho(\mathbf{r})$, whereas for the liquid $A_{\text{ex}}(\rho_l)$ is simply a function of liquid density ρ_l. The density functional formalism is used to write an expression for $A_{\text{ex}}[\rho]$ in terms of one- and two-particle distribution functions of the solid [2–5]. The direct pair correlation function (DPCF) that appears in this expression is a functional of $\rho(\mathbf{r})$ [2]. When this functional dependence is ignored and the DPCF is replaced by that of the coexisting uniform liquid [4,5] or by that of an “effective uniform fluid” [6,7] the free energy functional becomes approximate and fails to provide an accurate description of freezing transitions for a large class of intermolecular potentials. Attempts to include a term involving the three-body direct correlation function of the coexisting liquid in the free energy functional failed to improve the situation [8,9].

It has recently been emphasized [10–12] that at the freezing point a qualitatively new contribution to the correlations in distribution of particles emerges due to spontaneous symmetry breaking. This fact has been used to write the DPCF of a frozen phase as a sum of two qualitatively different contributions; one that preserves the continuous symmetry of uniform liquid and the other that breaks it and vanishes in the liquid. The double functional integration in density space of a relation that connects $A_{\text{ex}}[\rho]$ to the DPCF led to an exact expression for $A_{\text{ex}}[\rho]$. The freezing transitions in three dimensions have been investigated using this new free energy functional. The results found for the isotropic-nematic transition [10], crystallization of power-law fluids [11] and the freezing of fluids of hard spheres into crystalline and glassy phases [12], are very encouraging.

In this paper we apply the free energy functional to investigate the liquid-solid transition in two dimensions. It may, however, be noted that in contrast to a three-dimensional solid, a two-dimensional solid melts in two steps; the intermediate phase known as hexatic has a very narrow stability region in between liquid and crystal [13–15]. Since inclusion of the hexatic phase in the density functional formalism has not so far been possible, we neglect its presence and focus on the freezing of a fluid into the crystalline phase. A similar approach has been taken by others [16–21]. Here, our motivation is to examine how well this new free energy functional (described briefly in the following section) compares with other free energy functionals in describing the crystallization of two-dimensional fluids.

The paper is organized as follows: In Sec. II we give a brief description of the free-energy functional for a symmetry broken phase that contains both the symmetry conserving and symmetry broken parts of the DPCF. In Sec. III we describe methods to calculate these correlation functions for a two-dimensional system. The theory is applied in Sec. IV to investigate the freezing of power-law fluids into a crystalline solid of hexagonal lattice. The paper ends with a brief summary and perspectives in Sec. V.

II. FREE ENERGY FUNCTIONAL

The reduced free energy functional $A[\rho]$ of an inhomogeneous system is a functional of $\rho(\mathbf{r})$ and is written as [2]

$$A[\rho] = A_{\text{id}}[\rho] + A_{\text{ex}}[\rho]. \tag{2.1}$$

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The ideal gas part $A_{\rm id}$ is exactly known and is written in terms of $\rho(\mathbf{r})$ as

$$A_{\rm id}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\{\ln[\rho(\mathbf{r})\Lambda] - 1\}, \tag{2.2}$$

where Λ is cube of the thermal wavelength associated with a molecule. The second functional derivative of the excess part $A_{\rm ex}[\rho]$ with respect to $\rho(\mathbf{r})$ defines the DPCF $c(\mathbf{r}_1,\mathbf{r}_2)$ of the system [2],

$$\frac{\delta^2 A_{\rm ex}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} = -c(\mathbf{r}_1,\mathbf{r}_2;[\rho]). \tag{2.3}$$

The function c that appears in this equation is related to the total correlation function $h(\mathbf{r}_1,\mathbf{r}_2)$ through the Ornstein-Zernike (OZ) equation,

$$h(\mathbf{r}_1,\mathbf{r}_2) = c(\mathbf{r}_1,\mathbf{r}_2) + \int d\mathbf{r}_3 c(\mathbf{r}_1,\mathbf{r}_3)\rho(\mathbf{r}_3)h(\mathbf{r}_2,\mathbf{r}_3). \tag{2.4}$$

Both functions h and c are functionals of $\rho(\mathbf{r})$.

Since breaking of continuous symmetry of a uniform liquid at the freezing point gives rise to a qualitatively new contribution to correlations in the distribution of particles [10–12], the DPCF of the frozen phase is written as a sum of two contributions:

$$c(\mathbf{r}_1,\mathbf{r}_2;[\rho]) = c^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|,\rho_0) + c^{(b)}(\mathbf{r}_1,\mathbf{r}_2;[\rho]), \tag{2.5}$$

where $c^{(0)}$ is symmetry conserving and $c^{(b)}$ symmetry broken parts of the DPCF. While $c^{(0)}$ depends on the magnitude of interparticle separation r and is a function of average density $\rho_0 = \langle\rho(\mathbf{r})\rangle$, $c^{(b)}$ is invariant only under a discrete set of translations and rotations and is a functional of $\rho(\mathbf{r})$.

Using Eq. (2.5) we rewrite Eq. (2.3) as

$$\frac{\delta^2 A^{(0)}{}_{\rm ex}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} = -c^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|,\rho_0), \tag{2.6}$$

$$\frac{\delta^2 A^{(b)}{}_{\rm ex}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} = -c^{(b)}(\mathbf{r}_1,\mathbf{r}_2;[\rho]), \tag{2.7}$$

where $A^{(0)}{}_{\rm ex}[\rho] + A^{(b)}{}_{\rm ex}[\rho] = A_{\rm ex}[\rho]$. The expressions for $A^{(0)}{}_{\rm ex}[\rho]$ and $A^{(b)}{}_{\rm ex}[\rho]$ are found from functional integrations of Eqs. (2.6) and (2.7), respectively. In this integration, as described elsewhere [10–12], the system is taken from some initial density to the final density along a path in the density space; the result is independent of the path of integration. These integrations give

$$\begin{aligned} A^{(0)}{}_{\rm ex}[\rho] = {} & A_{\rm ex}(\rho_l) + \beta\mu - \ln(\rho_l\Lambda) \\ & -\frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2[\rho(\mathbf{r}_1)-\rho_l][\rho(\mathbf{r}_2)-\rho_l] \\ & \times \overline{c}^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|), \end{aligned} \tag{2.8}$$

and

$$\begin{aligned} A^{(b)}{}_{\rm ex}[\rho] = {} & -\frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2[\rho(\mathbf{r}_1)-\rho_0][\rho(\mathbf{r}_2) \\ & -\rho_0]\overline{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2), \end{aligned} \tag{2.9}$$

where

$$\begin{aligned} \overline{c}^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|) = {} & 2\int_0^1 d\lambda\lambda \int_0^1 d\lambda' c^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|; \\ & \rho_l + \lambda\lambda'(\rho_0-\rho_l)), \end{aligned} \tag{2.10}$$

$$\begin{aligned} \overline{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2) = {} & 4\int_0^1 d\xi\xi \int_0^1 d\xi' \int_0^1 d\lambda\lambda \int_0^1 d\lambda' \\ & \times c^{(b)}(\mathbf{r}_1,\mathbf{r}_2;\lambda\lambda'\rho_0;\xi\xi'\rho_G). \end{aligned} \tag{2.11}$$

Here $A_{\rm ex}(\rho_l)$ is excess reduced free energy of the coexisting uniform liquid of density ρ_l and chemical potential μ, $\rho_0 = \rho_l(1+\Delta\rho^*)$ is average density of the solid and $\beta = (\frac{1}{k_BT})$, k_B being the Boltzmann constant, T is the temperature, and ρ_G is an order parameter arising due to the breaking of symmetry.

The expression for $A_{\rm ex}{}^{(0)}[\rho]$ given by Eq. (2.8) is found from functional integrations when density ρ_l of the coexisting fluid is taken as a reference. The expression for $A_{\rm ex}{}^{(b)}[\rho]$ given by Eq. (2.9) is found by performing double functional integrations in the density space corresponding to the symmetry broken phase. The path of integration in this space is characterized by two parameters λ and ξ. These parameters vary from 0 to 1. The parameter λ raises the density from zero to the final value ρ_0 as it varies from 0 to 1, whereas the parameter ξ raises the order parameters from zero to their final values ρ_G. The result is independent of the order of integration.

The free energy functional for the symmetry broken phase is the sum of $A_{\rm id}[\rho]$, $A_{\rm ex}{}^{(0)}[\rho]$, and $A_{\rm ex}{}^{(b)}[\rho]$ Thus,

$$\begin{aligned} A[\rho] = {} & \int d\mathbf{r}\rho(\mathbf{r})\{\ln[\rho(\mathbf{r})\Lambda] - 1\} + A_{\rm ex}(\rho_l) \\ & + \beta[\mu - \ln(\rho_l\Lambda)]\int d\mathbf{r}[\rho(\mathbf{r}) - \rho_l] \\ & - \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2[\rho(\mathbf{r}_1)-\rho_l] \\ & \times[\rho(\mathbf{r}_2)-\rho_l]\overline{c}^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|) \\ & - \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2[\rho(\mathbf{r}_1)-\rho_0][\rho(\mathbf{r}_2)-\rho_0]\overline{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2), \end{aligned} \tag{2.12}$$

where $\overline{c}^{(0)}$ and $\overline{c}^{(b)}$ are given, respectively by (2.10) and (2.11). In deriving Eq. (2.12) no approximation has been introduced. In the Ramakrishnan-Yussouff free energy functional $\overline{c}^{(b)}$ is neglected and $\overline{c}^{(0)}$ is replaced by $c^{(0)}$.

In locating transition the grand thermodynamic potential defined as

$$-W = A - \beta\mu\int d\mathbf{r}\rho(\mathbf{r}) \tag{2.13}$$

is generally used as it ensures that the pressure and the chemical potential (μ) of the two phases remain equal at the transition. The transition point is determined by the condition $\Delta W = W_l - W = 0$, where W_l is the grand thermodynamic potential of the coexisting liquid. From the above expressions one gets the following expression for ΔW:

$$\begin{aligned} \Delta W = {} & \int d\mathbf{r}\left(\rho(\mathbf{r})\ln\frac{\rho(\mathbf{r})}{\rho_l} - [\rho(\mathbf{r})-\rho_l]\right) \\ & - \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2[\rho(\mathbf{r}_1)-\rho_l] \end{aligned}$$

$$\times\,[\rho(\mathbf{r}_2)-\rho_l]\overline{\mathbf{c}}^{(\mathbf{0})}(|\mathbf{r}_2-\mathbf{r}_1|) -\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2[\rho(\mathbf{r}_1)-\rho_0][\rho(\mathbf{r}_2)-\rho_0]\overline{\mathbf{c}}^{(\mathbf{b})}(\mathbf{r}_1,\mathbf{r}_2). \tag{2.14}$$

Minimization of ΔW with respect to $\rho(\mathbf{r})$ subject to the perfect crystal constraint leads to

$$\ln\frac{\rho(\mathbf{r})}{\rho_l}=\phi+\int d\mathbf{r}_2[\rho(\mathbf{r}_2)-\rho_l]\tilde{c}^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|) +\int d\mathbf{r}_2[\rho(\mathbf{r}_2)-\rho_0]\tilde{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2), \tag{2.15}$$

where

$$\tilde{c}^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|)=\int_0^1 d\lambda c^{(0)}(|\mathbf{r}_2-\mathbf{r}_1|,\rho_l+\lambda(\rho_0-\rho_l)),$$

and

$$\tilde{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2)=\int_0^1 d\xi\int_0^1 d\lambda c^{(b)}(\mathbf{r}_1,\mathbf{r}_2,\lambda\rho_0,\xi\rho_G).$$

The value of Lagrange multiplier ϕ in Eq. (2.15) is found from the condition

$$\frac{1}{V}\int d\mathbf{r}\frac{\rho(\mathbf{r})}{\rho_0}=1. \tag{2.16}$$

One needs, in principle, the values of $c^{(0)}$ and $c^{(b)}$ to calculate self-consistently the value of $\rho(\mathbf{r})$ that minimizes W. In practice, however, one finds it convenient to do minimization with an assumed form of $\rho(\mathbf{r})$. The ideal part is calculated using a form for $\rho(\mathbf{r})$ which is a superposition of normalized Gaussians centered around the lattice sites,

$$\rho(\mathbf{r})=\frac{\alpha}{\pi}\sum_n \exp[-\alpha(\mathbf{r}-\mathbf{R_n})^2], \tag{2.17}$$

where α is the localization parameter. For the interaction part it is convenient to use the Fourier expansion,

$$\rho(\mathbf{r})=\rho_0+\sum_{G\neq 0}\rho_G e^{i\mathbf{G}\cdot\mathbf{r}} \tag{2.18}$$

where $\mathbf{G}$ are reciprocal lattice vectors (RLV's) of the lattice and $\rho_G=\rho_0\mu_G$ are order parameters. Taking Fourier transform of Eq. (2.17) one finds $\mu_G=e^{(-G^2/4\alpha)}$.

III. APPLICATION TO CRYSTALLIZATION OF POWER-LAW FLUIDS

A. Potential model

We consider model fluids interacting via inverse power pair potentials $u(r)=\epsilon(\sigma/r)^n$ where ϵ, σ, and n are potential parameters and r is molecular separation. The parameter n measures softness of the repulsion; $n=\infty$ corresponds to the hard disk and $n=1$ to the one component plasma. Such repulsive potentials can be realized in colloidal suspensions. One such system in two dimensions has been provided by paramagnetic colloidal particles in a pendant water droplet, which are confined to the air-water interface [13]. By applying an external magnetic field perpendicular to the interface, a magnetic moment is introduced in the particles resulting in a tunable mutual dipolar repulsion between them. The pair interaction thus created is repulsive and proportional to r^{-3}. The crystallization of this system has been investigated by van Teeffelen and co-workers [20,21] using several versions of density functional theory (DFT). Another example where short range repulsion between molecules is found is microgel spheres whose diameter could be temperature tuned [15]. Most computer simulation studies on these systems suffer from the finite-size effects. In the case of hard disks recently a large scale Monte Carlo simulation, large enough to access the thermodynamic regime, has been performed [22]. The result confirms two-step transitions from liquid to solid with the intermediate hexatic phase [23,24]. However, the liquid-hexatic transition, in contrast to the prediction of Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory [23,24] is found to be first order while the hexatic-solid transition is second order. The density functional theory predicts the liquid-solid transition to be first order.

In addition to being a pair potential that can be realized in a real system, it has a well known scaling property according to which the reduced excess thermodynamic properties depend on a single variable (or coupling constant) which for a two-dimensional system is defined as

$$\gamma=(\rho\sigma^2)(\beta\epsilon)^{2/n}=\rho^*T^{*(-2/n)}.$$

Using this scaling the potential is written as

$$\beta u(r)=\frac{\Gamma}{r^n},$$

where $\Gamma=\gamma^{n/2}$ and r is measured in units of $a_0=(1/\rho)^{1/2}$.

B. Calculation of $c^{(0)}(r)$ and its derivatives with respect to ρ

The pair correlation functions of a classical system can be found in any spatial dimensions as a simultaneous solution of the OZ equation [Eq. (2.4)] and a closure relation that relates functions h, c, and the potential $u(r)$. Several closure relations including the Percus-Yevick (PY) relation, the hypernetted chain (HNC) relation, modified hypernetted chain (MHNC) relation, etc., have been used to describe the structure of a uniform fluid [25]. We may, however, note that while the OZ equation is general and connects the total and direct pair correlation functions of liquids as well as of symmetry broken phases, the closure relations that exist in the literature have been derived assuming translational invariance [25]. They are therefore valid only for normal fluids. We use the integral equation theory involving suitable closure relations to find the symmetry conserving part of pair correlation functions $h^{(0)}(r)$ and $c^{(0)}(r)$ and their derivatives with respect to density, The symmetry broken part of the DPCF is calculated using a method described in Ref. [11].

The OZ equation for a uniform system of density ρ reduces to

$$h^{(0)}(r)=c^{(0)}(r)+\rho\int d\mathbf{r}'c^{(0)}(r')h^{(0)}(|\mathbf{r}'-\mathbf{r}|). \tag{3.1}$$

The HNC closure relation and a closure relation proposed by Roger and Young [26] by mixing the PY and the HNC relations, in such a way that at $r=0$ it reduces to the PY and for $r\rightarrow\infty$ it reduces to the HNC relation, can be written together as

$$h^{(0)}(r) = \exp[-\beta u(r)]\left[1 + \frac{\exp\{\chi(r) f(r)\} - 1}{f(r)}\right] - 1, \tag{3.2}$$

where $\chi(r) = h^{(0)}(r) - c^{(0)}(r)$ and $f(r) = 1 - \exp(-\psi r)$ is a mixing function with an adjustable parameter $0 \leqslant \psi \leqslant \infty$. For $\psi = \infty$ or $f(r) = 1$, Eq. (3.2) reduces to the HNC closure relation. In the Roger-Young relation, ψ is chosen to guarantee thermodynamic consistency between the virial and compressibility routes to the equation of state.

The differentiation of Eqs. (3.1) and (3.2) with respect to density ρ yields the following two relations:

$$\begin{aligned}\frac{\partial h^{(0)}(r)}{\partial \rho} &= \frac{\partial c^{(0)}(r)}{\partial \rho} + \int d\mathbf{r}' c^{(0)}(r') h^{(0)}(|\mathbf{r}' - \mathbf{r}|) \\ &\quad + \rho \int d\mathbf{r}' \frac{\partial c^{(0)}(r')}{\partial \rho} h^{(0)}(|\mathbf{r}' - \mathbf{r}|) \\ &\quad + \rho \int d\mathbf{r}' c^{(0)}(r') \frac{\partial h^{(0)}(|\mathbf{r}' - \mathbf{r}|)}{\partial \rho}\end{aligned} \tag{3.3}$$

and

$$\frac{\partial h^{(0)}(r)}{\partial \rho} = \exp[-\beta u(r)] \exp[\chi(r) f(r)] \frac{\partial \chi(r)}{\partial \rho}. \tag{3.4}$$

The closed set of coupled equations (3.1)–(3.4) have been solved for four unknowns $h^{(0)}$, $c^{(0)}$, $\frac{\partial h^{(0)}(r)}{\partial \rho}$, and $\frac{\partial c^{(0)}(r)}{\partial \rho}$. The method can be extended to include higher order derivatives. In Fig. 1 we plot the Fourier transform of $c^{(0)}(\mathbf{r})$ defied as

$$\hat{c}^{(0)}(\mathbf{q}) = \rho \int d\mathbf{r} c^{(0)}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{3.5}$$

for $(n,\gamma) = (3,4.30), (6,1.30)$, and $(12,0.90)$. The values given in Fig. 1(a) for $n = 3$ are in good agreement with values found by van Teeffelen and co-workers [20,21] (see Fig. 1 of their paper). As has been reported in Ref. [21] the HNC closure underestimates values of $\hat{c}^{(0)}(q)$ whereas the Roger-Young (RY) closure gives relatively better but not very accurate values. In Fig. 1 we also give values found from an approach proposed by Kang and Ree (KR) [27].

The exact closure relation which one finds from the liquid state theory [25] can be written as

$$1 + h^{(0)}(r) = g^{(0)}(r) = \exp[-\beta u(r) + \chi(r) + B(r)], \tag{3.6}$$

where $B(r)$ is the bridge function. In the HNC closure relation $B(r)$ is taken equal to zero. In the KR approach the bridge function calculated for a reference potential and denoted as $B_0(r)$ is used for $B(r)$ in Eq. (3.6). The evaluation of $B_0(r)$ is done prior to and separated from the main integral equation by solving the Martynov-Sarkisov [28] integral equation. We briefly summarize here the way this is done for soft repulsive potentials in two dimensions.

The potential $u(r)$ is first divided into a reference $u_0(r)$ and a perturbation part $u_p(r)$.

$$u(r) = u_0(r) + u_p(r), \tag{3.7}$$

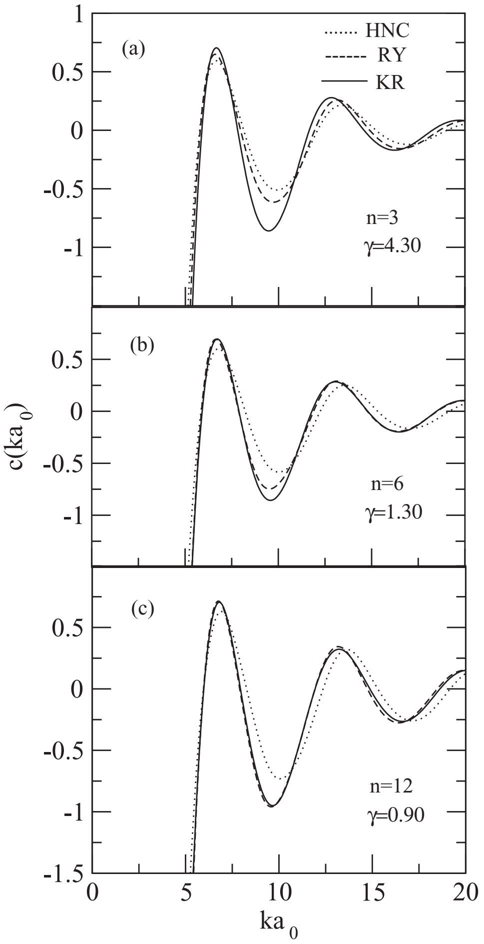

FIG. 1. The dimensionless Fourier transform $\hat{c}^{(0)}(q)$ of the direct pair correlation function of $c^{(0)}(r)$ plotted against $ka_0 (a_0 = (1/\rho)^{1/2})$ shown are data found from the integral equation theory using the RY closure (dashed line), HNC closure (dotted line), and KR closure (full line) at values of γ shown in (a)–(c) for $n = 3$, 6, and 12, respectively.

where

$$\begin{aligned} u_0(r) &= u(r) - F(r) \quad \text{if} \quad r \leqslant a, \\ &= 0 \quad \text{if} \quad r > a, \end{aligned} \tag{3.8}$$

$$\begin{aligned} u_p(r) &= F(r) \quad \text{if} \quad r \leqslant a, \\ &= u(r) \quad \text{if} \quad r > a. \end{aligned} \tag{3.9}$$

Here $F(r) = u(a) - u'(a)(a - r)$ and a is the nearest neighbor distance for hexagonal lattice at given density ρ. The $B_0(r)$ for the reference potential is evaluated using the OZ equation

$$h_0{}^{(0)}(r) - c_0{}^{(0)}(r) = \chi_0{}^{(0)}(r) = \rho \int d\mathbf{r}' c_0{}^{(0)}(r') h_0{}^{(0)}(|\mathbf{r}' - \mathbf{r}|) \tag{3.10}$$

and closure relation

$$1 + h_0{}^{(0)}(r) = \exp[-\beta u_0(r) + \chi_0(r) + B_0(r)]. \tag{3.11}$$

For $B_0(r)$ the Mortynov-Sarkisov [28] relation

$$B_0(r) = [1 + s\chi_0(r)]^{1/s} - 1 - \chi_0(r) \tag{3.12}$$

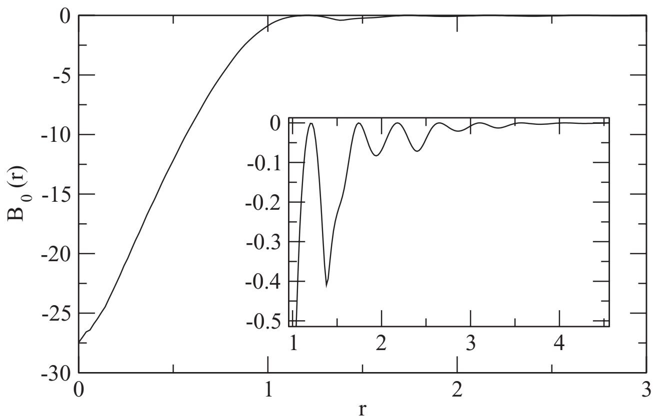

FIG. 2. Bridge function $B_0(r)$ for $n = 3$ at $\gamma = 4.30$. The distance r is in units of $a_0 = (1/\rho)^{1/2}$. Inset magnifies the values of $B_0(r)$ for $r \geqslant 1$.

with $s = 2$ is used. The values of $B_0(r)$ are found by solving Eqs. (3.10)–(3.12) self-consistently. The value of $B_0(r)$ as a function of r for $n = 3$ is plotted in Fig. 2. The nature of $B_0(r)$ is the same as was found in the case of three dimensions [27]. This value of $B_0(r)$ found for the reference potentials is used in relation (3.6) which is used to solve the OZ equation self-consistently to get values of $h^{(0)}(r)$ and $c^{(0)}(r)$. The values of $\hat{c}^{(0)}(q)$ found by this method are shown in Fig. 1 by full lines. These values are close to the simulation values given by van Teeffelen and co-workers [20,21] for $n = 3$. For $n = 6$ and 12 values found from the RY closure and values found from the KR method are close, showing that for short-range repulsive potentials the RY closure yields good values of pair correlation functions.

C. Calculation of $c^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$

For a crystal $c^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ is invariant only under a discrete set of translations corresponding to lattice vectors $\{\mathbf{R_n}\}$. If one chooses a center of mass variable $\mathbf{r}_c = \frac{(\mathbf{r}_1+\mathbf{r}_2)}{2}$ and difference variable $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, the $c^{(b)}$ can be written as [11,12]

$$c^{(b)}(\mathbf{r}_1,\mathbf{r}_2;[\rho]) = \sum_G \exp(i\mathbf{G}\cdot\mathbf{r}_c)c^{(G)}(\mathbf{r};[\rho]), \quad (3.13)$$

where G are RLV's. Since $c^{(b)}$ is real and symmetric with respect to interchange of $\mathbf{r}_1$ and $\mathbf{r}_2$, $c^{(G)}(\mathbf{r}) = c^{(-G)}(\mathbf{r})$ and $c^{(G)}(\mathbf{r}) = c^{(G)}(-\mathbf{r})$. The function $c^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ can be expanded in terms of higher body direct correlation functions of uniform liquid [2];

$$\begin{aligned} c^{(b)}(\mathbf{r}_1,\mathbf{r}_2;[\rho]) &= \int d\mathbf{r}_3 {c_3}^{(0)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\rho_0)[\rho(\mathbf{r}_3)-\rho_0] \\ &\quad + \frac{1}{2}\int d\mathbf{r}_3 d\mathbf{r}_4 {c_4}^{(0)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4;\rho_0) \\ &\quad \times [\rho(\mathbf{r}_3)-\rho_0][\rho(\mathbf{r}_4)-\rho_0] + \cdots, \end{aligned} \quad (3.14)$$

where $\rho(\mathbf{r}_n) - \rho_0 = \sum_G \rho_G e^{i\mathbf{G}\cdot\mathbf{r_n}}$, and ${c_n}^{(0)}$ are the n-body direct correlation functions of a uniform liquid of density ρ_0. These correlation functions are related to derivatives of $c^{(0)}(r,\rho_0)$ with respect to density ρ_0 as follows [2]:

$$\begin{aligned} \frac{\partial c^{(0)}(r)}{\partial \rho_0} &= \int d\mathbf{r}_3 {c_3}^{(0)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\rho_0), \\ \frac{\partial^2 c^{(0)}(r)}{\partial {\rho_0}^2} &= \int d\mathbf{r}_3 \int d\mathbf{r}_4 {c_4}^{(0)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4;\rho_0), \end{aligned} \quad (3.15)$$

etc.

The values of derivatives of $c^{(0)}(r)$ appearing on the left hand side of the above equations can be found using the integral equation theory described above. The usefulness of this method to find $c^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ depends on convergence of the series (3.14), which is a series in ascending powers of order parameters, and our ability to find values of n-body ($n \geqslant 3$) direct correlation functions from Eq. (3.15). Barrat *et al.* [8] have shown that ${c_3}^{(0)}$ can be factored as ${c_3}^{(0)}(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{13}) = t(r_{12})t(r_{13})t(r_{23})$ and the function $t(r)$ can be determined from the relation [see Eq. (3.15)]

$$\frac{\partial c^{(0)}(r)}{\partial \rho_0} = t(r)\int d\mathbf{r}' t(r')t(|\mathbf{r}'-\mathbf{r}|). \quad (3.16)$$

This method can be extended for higher ${c_n}^{(0)}$ [29]. Since $\overline{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ is averaged over density ρ and over order parameters ρ_G, the contributions made by successive terms of Eq. (3.14) in ${A_{\text{ex}}}^{(b)}[\rho]$ is expected to decrease rapidly [11]. In the case of three dimensions it was found that it is only the first term of the series (3.14) which needs to be considered to describe accurately the fluid-solid transition [11,29]. In two dimensions the convergence is expected to be faster as the number of nearest neighbors is less compared to the three dimensions and therefore the higher body correlation functions are expected to be less important. In view of this, we consider here the first term of the series (3.14) only and examine its contribution in stabilizing the hexagonal lattice at the transition point.

From known values of $\frac{\partial c^{(0)}(r)}{\partial \rho}$ we solved numerically Eq. (3.16) to find values of $t(r)$ for different values of γ. In Fig. 3, we plot values of $t(r)$ for $n = 3$, 6, and 12 at values of γ close to the freezing point.

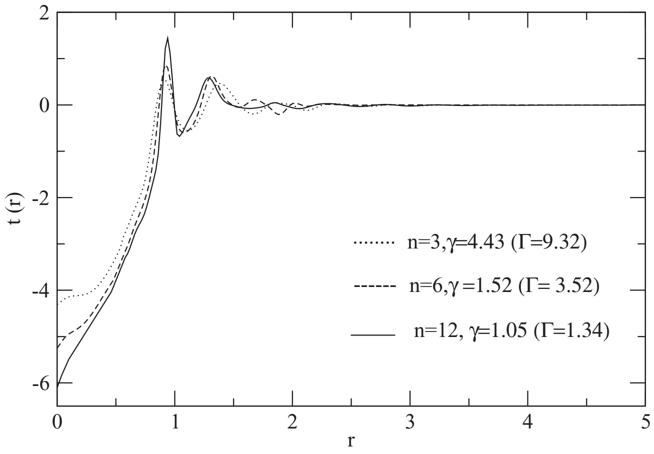

FIG. 3. Function $t(r)$ vs r for $n = 3$, 6, and 12 at the values of γ above the fluid-solid transition point; r is in units of $a_0 = (1/\rho)^{1/2}$.

Taking only the first term of Eq. (3.14), the expression for $c^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ in terms of $t(r)$ can be written as

$$c^{(b)}(\mathbf{r}_1,\mathbf{r}_2) = \sum_G \rho_G \int d\mathbf{r}_3 t(|\mathbf{r}_2-\mathbf{r}_1|)t(|\mathbf{r}_3-\mathbf{r}_1|)e^{i\mathbf{G}\cdot\mathbf{r}_3} \times t(|\mathbf{r}_3-\mathbf{r}_2|). \qquad (3.17)$$

Using the relation

$$\mathbf{r}_3 = \tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2) + (\mathbf{r}_3-\mathbf{r}_1) - \tfrac{1}{2}(\mathbf{r}_2-\mathbf{r}_1) = \mathbf{r}_c + \mathbf{r}' - \tfrac{1}{2}\mathbf{r},$$

Eq. (3.17) reduces to Eq. (3.13), i.e.,

$$c^{(b)}(\mathbf{r}_1,\mathbf{r}_2) = \sum_G e^{i\mathbf{G}\cdot\mathbf{r_c}} c^{(G)}(\mathbf{r}),$$

where

$$c^{(G)}(\mathbf{r}) = \rho_G t(r) e^{-(1/2)i\mathbf{G}\cdot\mathbf{r}} \int d\mathbf{r}' t(r') e^{i\mathbf{G}\cdot\mathbf{r}'} t(|\mathbf{r}'-\mathbf{r}|). \qquad (3.18)$$

Using the relation $e^{i\mathbf{G}\cdot\mathbf{r}} = \sum_m (i)^m J_m(Gr) e^{im(\phi_G-\phi_r)}$ where $J_m(Gr)$ is the Bessel function of the first kind of integral order m we find following expression for $c^{(G)}(r)$:

$$c^{(G)}(\mathbf{r}) = \sum_M (i)^M c_M{}^{(G)}(r) e^{iM\phi_G} e^{-iM\phi_r}, \qquad (3.19)$$

where

$$c_M{}^{(G)}(r) = \rho_G t(r) \sum_m B_m(r,G) J_{m+M}\left(\frac{1}{2}Gr\right) \qquad (3.20)$$

and

$$B_m(r,G) = \int dk k t(k) J_m(kr) \int dr' r' J_m(kr') J_m(Gr') t(r'). \qquad (3.21)$$

For hexagonal lattice $M = 0, \pm 6$. The value of $c_M{}^{(G)}(r)$ depends on values of order parameters μ_G and on the values of RLV's. In Figs. 4–6, we plot harmonic coefficients $c_0{}^{(G)}(r)/\mu_G$ and $c_6{}^{(G)}(r)/\mu_G$ for $n = 3$, 6, and 12 for RLV's of the first four sets, respectively. For a different set of RLV's $c_M{}^{(G)}(r)$ varies with r in a different way; the values in all cases become negligible for r [measured in units of $a_0 = (1/\rho)^{1/2}$] >1.5. For any given value of G, the value of $c_0{}^{(G)}(r)$ is about an order of magnitude larger than $c_6{}^{(G)}(r)$ at their maxima and minima. As the magnitude of G increases the value of $c_M{}^{(G)}(r)$ decreases and after the sixth set of RLV's values of $c_M{}^{(G)}(r)$ become negligible for all values of n.

D. Calculation of $\bar{c}^{(0)}(r)$ and $\bar{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$

The values of $\bar{c}^{(0)}(r)$ for a given liquid density ρ_l and a solid density ρ_0 are found from the known values of $c^{(0)}(r,\rho)$ where ρ varies from ρ_l to ρ_0 by performing integrations in Eq. (2.10) which can be rewritten as

$$\bar{c}^{(0)}(r,\rho_0) = 2\int_0^1 d\lambda\lambda \int_0^1 d\lambda' c^{(0)}(r,\rho_l + \lambda\lambda'\rho_l\Delta\rho^*), \qquad (3.22)$$

where $\Delta\rho^* = (\rho_0-\rho_l)/\rho_l$. The integrations are performed numerically using a very fine grid for variables λ and λ'. Since $\rho_l\Delta\rho^* \ll \rho_l$ one can use Taylor expansion to solve Eq. (3.22).

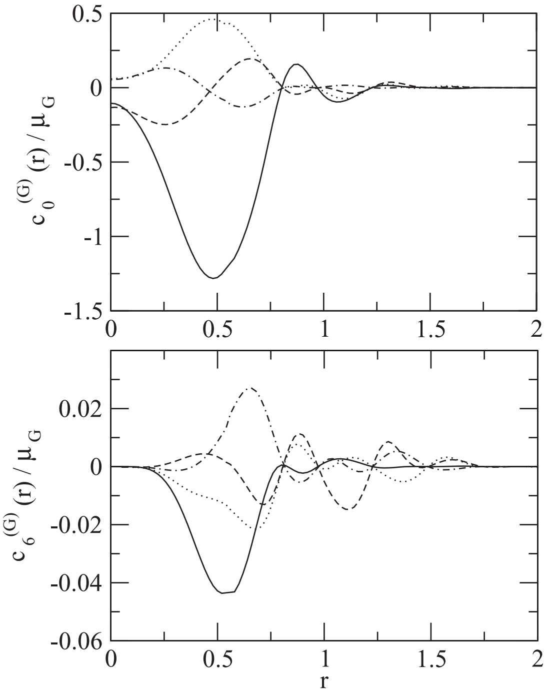

FIG. 4. Harmonic coefficients $c_M{}^{(G)}(r)/\mu_G$ for RLV's of first four sets for $n = 3, \gamma = 4.42$ ($\Gamma = 9.32$). Notations are as follows: Full line represents values of the first set, the dotted line of the second set, dashed line of the third set, and dashed-dotted line of the fourth set. The distance r is expressed in units a_0, where $a_0(= 1/\rho)^{1/2}$.

Thus

$$\bar{c}^{(0)}(r,\rho_0) = c^{(0)}(r,\rho_l) + \frac{1}{3}\rho_l\Delta\rho^* \frac{\partial c^{(0)}(r,\rho_l)}{\partial\rho_l} + O(\rho_l{}^2\Delta\rho^{*2}). \qquad (3.23)$$

For $\Delta\rho^* \lesssim 0.1$ which is the case at the transition point the first two terms written explicitly in Eq. (3.23) are enough and give values which are in very good agreement with the values found numerically from Eq. (3.22).

Using the expressions given above [Eqs. (3.13), (3.19), (3.20)] we rewrite Eq. (2.11) as

$$\bar{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2) = 4\sum_G e^{i\mathbf{G}\cdot\mathbf{r_c}} \sum_M \sum_m (i)^M e^{iM\phi_G} e^{-iM\phi_r} \times J_{M+m}\left(\frac{1}{2}Gr\right) \int_0^1 d\xi\xi \int_0^1 d\xi'\xi'\rho_G \int_0^1 d\lambda\lambda \times \int_0^1 d\lambda' L_m(r,G,\lambda\lambda'\rho), \qquad (3.24)$$

where $L_m(r,G;\rho) = t(r,\rho)B_m(r,G,\rho)$ depends on density ρ which is scaled from zero to ρ_0 by varying λ and λ' between 0 and 1. The integration over ξ and ξ' are done analytically leading to

$$\bar{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{3}\sum_G \rho_G e^{i\mathbf{G}\cdot\mathbf{r_c}} \sum_M \sum_m (i)^M e^{iM\phi_G} e^{-iM\phi_r} \times J_{M+m}\left(\frac{1}{2}Gr\right) I_m(r,G,\rho_0), \qquad (3.25)$$

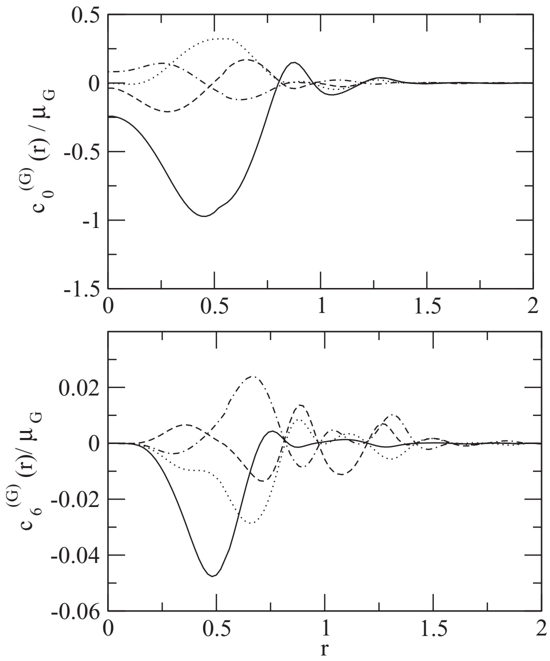

FIG. 5. Harmonic coefficients $c_M{}^{(G)}(r)/\mu_G$ for RLV's of first four sets for $n = 6, \gamma = 1.52$ $(\Gamma = 3.52)$. Notations are same as in Fig. 4.

where $\rho_G = \rho_0 \mu_G$ and

$$I_m(r,G,\rho_0) = 2\int_0^1 d\lambda\lambda \int_0^1 d\lambda' L_m(r,G;\lambda\lambda'\rho). \qquad (3.26)$$

These integrals are evaluated numerically for a given density ρ_0 from known values of $L_m(r,G;\rho)$ for density varying from zero to ρ_0. Since $L_m(r,G;\rho)$ varies smoothly with density and its values have been evaluated at closely spaced values of density, the result found for $\overline{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ is expected to be accurate.

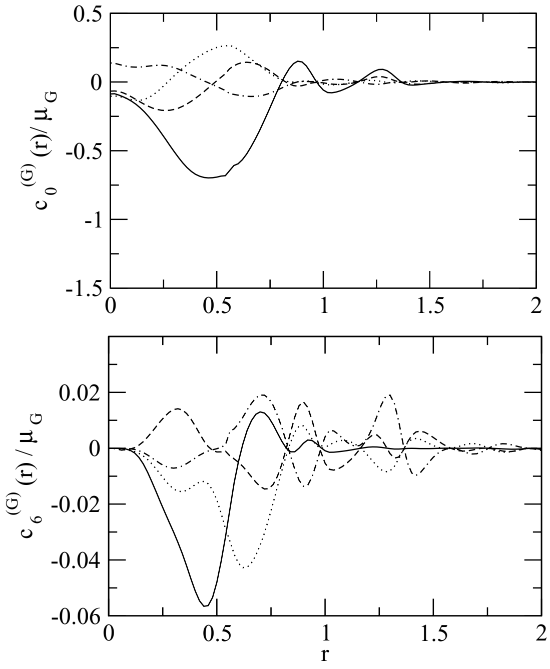

FIG. 6. Harmonic coefficients $c_M{}^{(G)}(r)/\mu_G$ for RLV's of first four sets for $n = 12, \gamma = 1.05$ $(\Gamma = 1.34)$. Notations are same as in Fig 4.

IV. LIQUID-SOLID TRANSITION

Substituting expressions of $\rho(r)$ given by Eqs. (2.17) and (2.18) and of $\overline{c}^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ given by Eq. (3.19) in Eq. (2.14) we find

$$\frac{\Delta W}{N} = \frac{\Delta W_{\rm id}}{N} + \frac{\Delta W_0}{N} + \frac{\Delta W_b}{N}, \qquad (4.1)$$

where

$$\frac{\Delta W_{\rm id}}{N} = (1+\Delta\gamma)\left[1 + \ln\left(\frac{\alpha}{\pi}\right) - 2 - \ln\rho_0\right] + 1, \qquad (4.2)$$

$$\frac{\Delta W_0}{N} = -\frac{1}{2}\Delta\gamma\hat{\hat{c}}^{(0)}(0) - \frac{1}{2}(1+\Delta\gamma)^2 \sum_{G\neq 0} |\mu_G|^2 \hat{\hat{c}}^{(0)}(G), \qquad (4.3)$$

$$\frac{\Delta W_b}{N} = -\frac{1}{2}(1+\Delta\gamma)^3 {\sum_G}' {\sum_{G_1}}' \mu_{G_1}\mu_{-G-G_1} \hat{\hat{c}}\left(\mathbf{G_1} + \frac{\mathbf{1}}{\mathbf{2}}\mathbf{G}\right), \qquad (4.4)$$

where $\Delta\gamma = (\frac{\gamma_s - \gamma_l}{\gamma_l})$; the subscripts s and l refer to solid and liquid respectively. Here $\Delta W_{\rm id}$, ΔW_0, and ΔW_b are respectively, the ideal, symmetry conserving, and symmetry broken contributions to ΔW. The prime on a summation in Eq. (4.4) indicates the condition $\mathbf{G} \neq 0$, $\mathbf{G}_1 \neq 0$, and $\mathbf{G} + \mathbf{G}_1 \neq 0$, and

$$\hat{\hat{c}}^{(0)}(\mathbf{G}) = \int \overline{c}^{(0)}(r,\gamma_l)e^{i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r},$$

$$\hat{\hat{c}}\left(\mathbf{G_1} + \frac{\mathbf{1}}{\mathbf{2}}\mathbf{G}\right) = \int \overline{c}^{(G)}(\mathbf{r},\gamma_s)e^{-i[\mathbf{G_1}+(\mathbf{1}/\mathbf{2})\mathbf{G}]\cdot\mathbf{r}}d\mathbf{r}$$

We used the above expressions to locate the liquid-crystal (hexagonal lattice) transition by varying values of γ, $\Delta\gamma$, and α. For a given γ_l and $\Delta\gamma$, $\frac{\Delta W}{N}$ is minimized with respect to the localization parameter α; next $\Delta\gamma$ is varied until the lowest value of $\frac{\Delta W}{N}$ at its minimum is found. If this lowest value of $\frac{\Delta W}{N}$ is not zero then γ_l is varied until $\frac{\Delta W}{N}$ is zero. The values of the transition parameters can also be found from simultaneous solution of equations, $\frac{\partial}{\partial\Delta\gamma}(\frac{\Delta W}{N}) = 0$, $\frac{\partial}{\partial\alpha}(\frac{\Delta W}{N}) = 0$, and $\frac{\Delta W}{N} = 0$.

The results given in Table I for $n = 3$, 6, and 12 correspond to the RY closure relation. We note that the contribution arising due to the symmetry broken part of the DPCF is far

TABLE I. Freezing parameters α, γ_l, $\Delta\gamma$ and the pressure P at coexistence along with the contributions of ideal, symmetry conserving, and symmetry broken parts of $\frac{\Delta W}{N}$. These results correspond to the Roger-Young closure [26].

n	α	γ_l	$\Delta\gamma$	$\frac{\Delta W_{\rm id}}{N}$	$\frac{\Delta W_0}{N}$	$\frac{\Delta W_b}{N}$	$\frac{\beta P}{\rho}$
3	100	4.96	0.025	2.50	−1.74	−0.76	75
6	100	1.55	0.040	2.50	−2.10	−0.40	31
12	96	1.00	0.050	2.49	−2.32	−0.17	22

TABLE II. Freezing parameters $\Gamma_f(=\gamma_f{}^{n/2})$, $\Gamma_s(=\gamma_s{}^{n/2})$, the width of coexistence region $\Delta\Gamma = \Gamma_s - \Gamma_f$, and the relative displacement parameter $\xi(\simeq 2/\alpha)$ at the coexistence obtained from various density functional schemes. The MWDA stands for modified weighted density approximation, EMA stands for extended modified weighted density approximation, RY and KR refer to, respectively, the Roger-Young closure [26] and the Kang and Ree [27] closure.

	Γ_l	Γ_s	$\Delta\Gamma$	ξ
Present result with RY	11.04	11.46	0.42	0.020
Present result with KR	9.20	9.61	0.41	0.022
MWDA with RY [21]	41.07	41.13	0.06	0.017
EMA with RY [21]	23.00	23.08	0.09	0.020
EMA with Verlet [21]	9.33	9.49	0.16	0.020
Simulation [31]	12.0	12.25	0.025	
Experiment [13]	10.0	10.75	0.75	0.038

from negligible and its importance increases with the softness of the potential. While it is about 7.3% to the symmetry conserving term for $n = 12$, it increases about 44% for $n = 3$. This explains why the Ramakrishnan-Yussouff theory gives good results for hard core potentials but fails for potentials that have soft core and/or attractive tail. As the contribution of $\frac{\Delta W_b}{N}$ is negative, it stabilizes the solid phase. Without it the theory strongly overestimates the stability of the fluid phase especially for softer potentials [20,21]. The contribution made by the symmetry broken part of the DPCF is, as expected, small compared to that in three dimensions (3D) at the freezing point for the same potential. For example, the contribution in 3D [11] for $n = 12$ is 22.2% compared to 7.3% in 2D whereas for $n = 6$ the contribution is 37% in 3D and 18% in 2D.

In Table II we compare results of the present calculation using both the RY closure and the KR procedure to calculate pair correlation functions for $n = 3$ with the results found from other free-energy functionals as reported in Ref. [21]. The experimental results obtained from real-space microscopy measurements of magnetic colloids confined to an air-water interface [13] and values found from numerical simulations [30,31] are also given in the table. While the RY closure gives slightly higher values of Γ_f and Γ_s compared to the experimental values, the KR closure gives slightly lower values. But these values along with the values of other parameters, particularly the value of $\Delta\Gamma = \Gamma_s - \Gamma_f$, are in better agreement with the experimental values compared to any other versions of the DFT. Although the extended modified weighted-density approximation (EMA) [32] with Verlet closure [33] gives values of Γ_f which is close to the one found by us using the KR closure, but the values of $\Delta\Gamma$ are significantly lower: $\Delta\Gamma_{\text{EMA}} = 0.16$ compared to the values found by us, $\Delta\Gamma = 0.41$, and the experimental value, 0.75.

The real-space experimental data are not available for other systems. The computer simulation results [34,35] show the liquid-solid transition at $\gamma_l = 1.51$ and 0.986 respectively for $n = 6$ and 12. These values are close to the one given in Table I.

V. SUMMARY AND PERSPECTIVES

We used a free energy functional that contains both the symmetry conserving part of the DPCF $c^{(0)}(r)$ and the symmetry broken part $c^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$ to investigate the freezing of a two-dimensional fluid into a two-dimensional crystal of hexagonal lattice. The values of $c^{(0)}(r)$ and its derivatives with respect to density ρ as a function of interparticle separation r have been determined using an integral equation theory comprising the OZ equation and the closure relations of Roger and Young [26] and of Kang and Ree [27]. For soft potential ($n = 3$) the two results are found to differ; the KR closure seems to give a better result. For more repulsive potentials the two results are close as shown in Fig. 1. For $c^{(b)}(\mathbf{r}_1,\mathbf{r}_2)$, which is a functional of $\rho(\mathbf{r})$ and is invariant only under a discrete set of translations and rotations, we used an expansion in ascending powers of order parameters. This expansion involves higher body direct correlation functions of isotropic phase, which in turn were found from the density derivatives of $c^{(0)}(r)$ using a method proposed by Barrat *et al.* [8].

The contribution of the symmetry broken part of DPCF to the free energy is found to depend on the nature of pair potentials; the contribution increases with softness of potentials. This result is in agreement with that found in three dimensions and explains why the Ramakrishnan-Yussouff free-energy functional was found to give a reasonably good description of the freezing transition of hard core potentials but failed for potentials that have soft core and/or attractive tail. The results found here and the results reported for 3D indicate that the theory described here can be used to investigate the freezing transitions of all kinds of fluids.

Since our free energy functional takes into account the spontaneous symmetry breaking it can be used to study various phenomena of ordered phases. The results indicate that the density functional approach provides an effective framework for theoretical study of a large variety of problems involving inhomogeneities. However, the question not adequately addressed yet is the size of fluctuations effect which plays an important role in two-dimensional systems. The other important question is the inclusion of the hexatic phase in the theory [36].

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