Pair Correlation Functions in Nematics: Free-Energy Functional and Isotropic-Nematic Transition

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We develop a free-energy functional for an inhomogeneous system that contains both symmetry conserved and symmetry broken parts of the direct pair correlation function. These correlation functions are found by solving the Ornstein-Zernike equation with the Percus-Yevick closure relation. The method developed here gives the pair correlation functions in the ordered phase with features that agree well with the results found by computer simulations. The theory predicts accurately the isotropic-nematic transition in a system of anisotropic molecules and can be extended to study other ordered phases such as smectics and crystalline solids.

The freezing of a fluid of anisotropic molecules into a nematic phase is a typical example of a first-order phase transition in which the continuous symmetry of the isotropic phase is broken [1]. In a nematic phase, molecules are aligned along a particular but arbitrary direction so as to have a long-range order in orientation while the translational degrees of freedom remain disordered as in an isotropic fluid. At the isotropic-nematic transition the isotropy of the space is spontaneously broken and, as a consequence, correlations in distribution of molecules lose their rotational invariance. By computer simulations of a system of ellipsoids Phuong and Schmid [2] evaluated the effect of breaking of rotational symmetry on pair correlation functions (PCFs) and showed that in a nematic phase there are two qualitatively different contributions: one that preserves rotational invariance and the other that breaks it and vanishes in the isotropic phase. The symmetry preserving part of PCFs passes smoothly without any abrupt change through the transition.

The correlation functions which describe the distribution of molecules in a classical fluid can be given as the simultaneous solutions of an integral equation, the Ornstein-Zernike (OZ) equation, and a closure relation that relates correlation functions to the pair potential. Well-known closure relations are the Percus-Yevick (PY) relation, the hypernetted-chain (HNC) relation, and the mean spherical approximation (MSA) [3]. This approach has been used quite successfully to describe the structure of isotropic fluids. However, the application of the theory to ordered phases has so far been very limited, though no feature of the theory inherently prevents it from being used to describe structures of the ordered phases. Holovko and Sokolovska [4] have used the MSA and the Lovett equation [5] which relates one-particle density to PCFs to solve analytically the OZ equation for a model of spherical particles with the long-range anisotropic interaction and determined the PCFs in a nematic phase. However, when Phuong and Schmid [2] used the PY and the Lovett equa-

tions and solved the OZ equation numerically for a system of soft ellipsoids, nematic phase was not found and for this the PY closure was blamed. Here we adopt a method based on density-functional formalism and show that the PY relation gives nematic phase with PCFs harmonic coefficients that have features similar to those found by simulations [2] and by analytical solution [4].

A density-functional theory (DFT) requires an expression of the grand thermodynamic potential of the system in terms of one- and two-particle distribution functions and a relation that relates the one-particle density distribution $\rho(\mathbf{x})$ to PCFs. Such a relation is found by minimizing the grand thermodynamic potential with respect to $\rho(\mathbf{x})$ with appropriate constraints [6]. The correlation functions that appear in these equations are of the ordered phase and are functional of $\rho(\mathbf{x})$. The free-energy functionals that exist in the literature [7,8] and have been used to study the freezing transitions replace these correlations by that of the isotropic fluids [6]. This approximation limits the applicability of the theory and needs improvement.

We first show how the fact that PCFs in the nematic phase have two distinct parts leads us to divide the OZ equation and the closure relation into two sets of equations. The solutions of these equations give both the symmetry conserving and the symmetry breaking parts of PCFs. Using these correlation functions we construct a free-energy functional. This free-energy functional is then used to locate the isotropic-nematic transition in a model system of elongated rigid molecules interacting via the Gay-Berne (GB) pair potential [9]. The GB potential between a pair of molecules (i, j) is written as $u(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j) = 4\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j)(R^{-12} - R^{-6})$, where $R = (r_{ij} - \sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j) + \sigma_0)/\sigma_0$ and $\hat{\mathbf{e}}_i$ is the unit vector specifying the axis of symmetry of the ith molecule. The expressions for the angle dependent range parameter σ and potential well depth function ϵ contain four parameters x_0, k', μ, and ν. These parameters measure the anisotropy in the repulsive and attractive forces. The parameters σ_0 and ϵ_0 scale

the distance and energy, respectively. The value of x_0, k', μ, and ν are taken 3.0, 5.0, 2.0, and 1.0, respectively.

The OZ equation which relates the total PCF, $h(\mathbf{x_1}, \mathbf{x_2})$, with DPCF, $c(\mathbf{x_1}, \mathbf{x_2})$, in an inhomogeneous system is written as [6,10] $h(\mathbf{x_1}, \mathbf{x_2}) = c(\mathbf{x_1}, \mathbf{x_2}) + \int c(\mathbf{x_1}, \mathbf{x_3}) \times \rho(\mathbf{x_3})h(\mathbf{x_3}, \mathbf{x_2})d\mathbf{x_3}$, where $\mathbf{x_i}$ indicates both position $\mathbf{r_i}$ and orientation $\mathbf{\Omega_i}$ of the ith molecule, $d\mathbf{x_3} = d\mathbf{r_3}d\mathbf{\Omega_3}$. The PY relation is expressed as $c(\mathbf{x_1}, \mathbf{x_2}) = [e(\mathbf{x_1}, \mathbf{x_2}) - 1][1 + h(\mathbf{x_1}, \mathbf{x_2}) - c(\mathbf{x_1}, \mathbf{x_2})]$, where $e(\mathbf{x_1}, \mathbf{x_2}) = \exp[-\beta\mathbf{u}(\mathbf{x_1}, \mathbf{x_2})]$. We now write the pair correlation functions h and c as a sum of symmetry conserved and symmetry broken parts, i.e., $h = h^{(0)} + h^{(n)}$ and $c =$

$c^{(0)} + c^{(n)}$. This allows us to write the OZ and PY equations as

$$h^{(0)}(\mathbf{x_1}, \mathbf{x_2}) = c^{(0)}(\mathbf{x_1}, \mathbf{x_2})$$
$$+ \rho_0 \int c^{(0)}(\mathbf{x_1}, \mathbf{x_3})h^{(0)}(\mathbf{x_3}, \mathbf{x_2})d\mathbf{x_3} \quad (1)$$

$$c^{(0)}(\mathbf{x_1}, \mathbf{x_2}) = [e(\mathbf{x_1}, \mathbf{x_2}) - 1][1 + h^{(0)}(\mathbf{x_1}, \mathbf{x_2})$$
$$- c^{(0)}(\mathbf{x_1}, \mathbf{x_2})] \quad (2)$$

and

$$h^{(n)}(\mathbf{x_1}, \mathbf{x_2}) = c^{(n)}(\mathbf{x_1}, \mathbf{x_2}) + \int c^{(0)}(\mathbf{x_1}, \mathbf{x_3})\rho_n(\mathbf{x_3})h^{(0)}(\mathbf{x_3}, \mathbf{x_2})d\mathbf{x_3} + \int [\rho_0 + \rho_n(\mathbf{x_3})][c^{(0)}(\mathbf{x_1}, \mathbf{x_3})h^{(n)}(\mathbf{x_3}, \mathbf{x_2})$$
$$+ c^{(n)}(\mathbf{x_1}, \mathbf{x_3})h^{(0)}(\mathbf{x_3}, \mathbf{x_2}) + c^{(n)}(\mathbf{x_1}, \mathbf{x_3})h^{(n)}(\mathbf{x_3}, \mathbf{x_2})]d\mathbf{x_3} \quad (3)$$

$$c^{(n)}(\mathbf{x_1}, \mathbf{x_2}) = [e(\mathbf{x_1}, \mathbf{x_2}) - 1][h^{(n)}(\mathbf{x_1}, \mathbf{x_2}) - c^{(n)}(\mathbf{x_1}, \mathbf{x_2})].$$
$$(4)$$

Here $\rho(\mathbf{x_3}) = [\rho_0 + \rho_n(\mathbf{x_3})]$, where ρ_0 is the bulk number density and $\rho_n(\mathbf{x_3}) = \rho_0[f(\mathbf{\Omega_3}) - 1]$. $f(\mathbf{\Omega})$ is the single particle orientation distribution function normalized to unity.

Equations (1) and (2) give relations that are identical to the ones used in calculating PCFs in an isotropic

phase. Relations given by (3) and (4) are new and give PCFs arising due to the breaking of symmetry. We chose a coordinate frame where the z axis points in the direction of director $\hat{n}$ (director frame). All orientation dependent functions are expanded in spherical harmonics $Y_{lm}(\Omega)$ [2,11]. This yields (for uniaxial nematic phase of axially symmetric molecules) $f(\Omega) = \sum_{l(\text{even})} \sqrt{(2l + 1)} P_l Y_{l0}(\Omega)/\sqrt{4\pi}$ and

$$\psi(r, \Omega_1, \Omega_2) = \sum_{l_1 l_2 l m_1 m_2 m} \psi_{l_1 l_2 l m_1 m_2 m}(r)Y_{l_1 m_1}(\Omega_1)Y_{l_2 m_2}(\Omega_2)Y_{lm}^*(\hat{r}), \quad (5)$$

where ψ stands for h, c, or e. P_l is the order parameter; its value is zero in the isotropic phase and nonzero in the nematic phase. In a uniaxial symmetric phase of axially symmetric molecules, $m_1 + m_2 - m = 0$ and $l_1 + l_2 + l$ as well as each l are even. Because $h^{(0)}$, $c^{(0)}$, and e preserve the rotational symmetry, for them $\psi_{l_1 l_2 l m_1 m_2 m}(r) = \psi_{l_1 l_2 l}(r)C_g(l_1 l_2 l m_1 m_2 m)$, where C_g is the Clebsch-Gordan coefficient.

We solved (1) and (2) for the GB potential using a method described in [12] and determined the values of $c^{(0)}_{l_1 l_2 l m_1 m_2 m}(r^*)$ and $h^{(0)}_{l_1 l_2 l m_1 m_2 m}(r^*)$ for values of l, l_i up to $l_{\max} = 8$ at reduced temperature $T^*(\equiv k_B T/\epsilon_0) = 1.0$ and for densities $0 \leq \rho^*(\equiv \rho\sigma_0^3) \leq 0.36$. To solve (3) and (4) we first set up linear equations for $h^{(n)}_{l_1 l_2 l m_1 m_2 m}(r^*)$ and $c^{(n)}_{l_1 l_2 l m_1 m_2 m}(r^*)$, using the expansions described above. In these equations $h^{(0)}_{l_1 l_2 l m_1 m_2 m}(r^*)$, $c^{(0)}_{l_1 l_2 l m_1 m_2 m}(r^*)$ and the order parameters P_l appear. Here we restrict ourselves to only one order parameter P_2 and solve these equations for $0 \leq P_2 \leq 0.70$ at the interval of $\Delta P_2 = 0.05$ for all densities between 0 and 0.34 and for l, l_i up to $l_{\max} = 4$. The solution is found using the same iterative method [12] as in the case of (1) and (2) but with two additional precautions: as coefficients $h^{(n)}_{l_1 l_2 l m_1 m_2 m}(r^*)$ show oscillations (Fig. 2) which extend to $r^*(\equiv r/\sigma_0) \sim 20$ we extended the range of

r^*(i.e., $r^*_{\max} = 40$) to ensure proper convergence. The other point which needed special care is related to the pronounced long-range tail which occurs in coefficients $h^{(n)}_{l_1 l_2 l m_1 m_2 m}(r^*)$ with m_1, $m_2 = \pm 1$ (Fig. 3). For this we adopted a method discussed in [2,13]. This ensured that the finite size effect on the tail as well as its effect on other harmonic coefficients are accounted for accurately.

The reduced free energy $A[\rho]$ of an inhomogeneous system is a functional of density $\rho(\mathbf{x})$ and is written as [6] $A[\rho] = A_{\text{id}}[\rho] + A_{\text{ex}}[\rho]$, where $A_{\text{id}}[\rho] = \int d\mathbf{x}\rho(\mathbf{x}) \times [\ln\{\rho(\mathbf{x})\Lambda\} - 1]$ is the ideal gas part. The excess part $A_{\text{ex}}[\rho]$ is related with the DPCF of the system as

$$\frac{\delta^2 A_{\text{ex}}}{\delta\rho(\mathbf{x_1})\delta\rho(\mathbf{x_2})} = -c^{(0)}(\mathbf{x_1}, \mathbf{x_2}; \rho_0) - c^{(n)}(\mathbf{x_1}, \mathbf{x_2}; [\rho]).$$
$$(6)$$

$A_{\text{ex}}[\rho]$ is found by functional integration of (6). In this integration the system is taken from some initial density to the final density $\rho(\mathbf{x})$ along a path in the density space; the result is independent of the path of the integration [14]. For the symmetry conserving part $c^{(0)}$ the integration in density space is done taking isotropic fluid of density ρ_l (the density of coexistence fluid) as reference. This leads to

$$A_{ex}^{(0)}[\rho] = A_{ex}(\rho_l) - \frac{1}{2}$$
$$\times \int d\mathbf{x_1} \int d\mathbf{x_2} \Delta\rho(\mathbf{x_1})\Delta\rho(\mathbf{x_2})\bar{c}(\mathbf{x_1}, \mathbf{x_2}), \quad (7)$$

where $\bar{c}(\mathbf{x_1}, \mathbf{x_2}) = 2\int d\lambda\lambda \int d\lambda' c^{(0)}\{\mathbf{x_1}, \mathbf{x_2}; \rho_l + \lambda\lambda'(\rho_0 - \rho_l)\}$, $\Delta\rho(\mathbf{x}) = \rho(\mathbf{x}) - \rho_l$, $A_{ex}(\rho_l)$ is the excess reduced free energy of the isotropic fluid of density ρ_l and ρ_0 is the average density of the ordered phase.

In order to integrate over $c^{(n)}[\rho]$, we characterize the density space by two parameters λ and ξ which vary from 0 to 1. The parameter λ raises density from 0 to ρ_0 as it varies from 0 to 1 whereas parameter ξ raises the order parameter from 0 to P_2 as it varies from 0 to 1. This integration gives

$$A_{ex}^{(n)}[\rho] = -\frac{1}{2}\int d\mathbf{x_1} \int d\mathbf{x_2}\rho(\mathbf{x_1})\rho(\mathbf{x_2})\tilde{c}(\mathbf{x_1}, \mathbf{x_2}), \quad (8)$$

where

$$\tilde{c}(\mathbf{x_1}, \mathbf{x_2}) = 4\int_0^1 d\xi\xi \int_0^1 d\xi' \int_0^1 d\lambda\lambda \int_0^1 d\lambda'$$
$$\times c^{(n)}(\mathbf{x_1}, \mathbf{x_2}, \lambda\lambda'\rho_0; \xi\xi'P_2).$$

Note that while integrating over λ, P_2 is kept fixed and while integrating over ξ, ρ_0 is kept fixed. The result does not depend on the order of integration. The free-energy functional of an ordered phase is the sum of A_{id}, $A_{ex}^{(0)}$, and $A_{ex}^{(n)}$. Note that the RY [7] free-energy functional is the sum of only A_{id}^0 and A_{ex}^0 and contains an additional approximation in which $\bar{c}(\mathbf{x_1}, \mathbf{x_2})$ in (7) is replaced by $c(\mathbf{x_1}, \mathbf{x_2}; \rho_l)$.

The grand thermodynamic potential defined as $-W = A - \beta\mu \int d\mathbf{x}\rho(\mathbf{x})$, where μ is the chemical potential, is preferred to locate the transition as it ensures that the pressure and chemical potential of the two phases remain equal at the transition. The transition point is determined by the condition $\Delta W = W_l - W = 0$. The order parameters are determined from equations found by minimizing the grand thermodynamic potential with appropriate constraints [6,13]. The isotropic-nematic transition at $T^* = 1.0$ with one order parameter is found to take place at $\rho_l^*(= \rho_l\sigma_0^3) = 0.3325$ with $\Delta\rho^*[\equiv (\rho_o - \rho_l)/\rho_l] = 0.0086$ and order parameter $P_2 = 0.40$. For the RY free-energy functional the transition takes place at $\rho_l^* = 0.3570$ with $\Delta\rho^* = 0.0055$ and $P_2 = 0.439$. The symmetry breaking part of PCFs makes the isotropic phase unstable and induces the emergence of the ordered phase at lower density.

In Fig. 1 we show some harmonic coefficients of DPCF in the director space for $T^* = 1.0$, $\rho^* = 0.3361$, and $P_2 = 0.44$. While the coefficients $c_{220\,000}(r^*)$ and $c_{2201-10}(r^*)$ shown in Fig. 1(a) survive both in isotropic and nematic phases, the coefficients $c_{200\,000}(r^*)$ and $c_{002\,000}(r^*)$ shown in 1(b) survive only in the nematic phase and vanish in the isotropic phase. The contribution arising due to symmetry breaking to coefficients $c_{220\,000}(r^*)$ and $c_{2201-10}(r^*)$ is
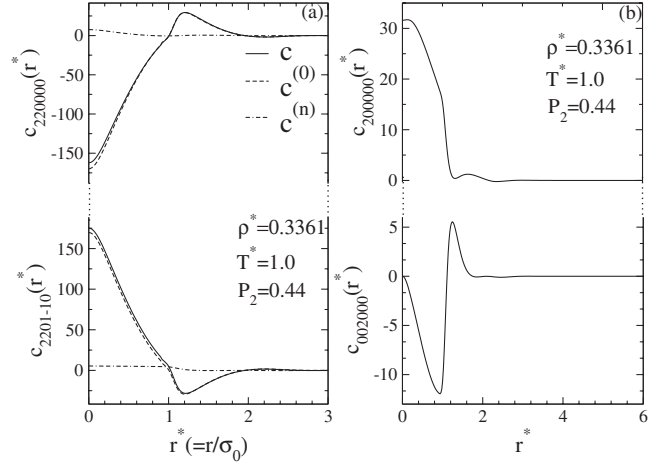

FIG. 1.   Harmonic coefficients $c_{l_1l_2lm_1m_2m}(r^*)$ in the director frame. In (a) we show two those coefficients which preserve the rotational invariance while in (b) the coefficients that arise due to symmetry breaking. In [2] harmonic coefficients are labeled as $c_{l_1m_1l_2m_2lm}(r^*)$.

found to be small compared to the symmetry conserving part. Few selected harmonic coefficients of h are shown in Figs. 2 and 3 in director space. In Fig. 2 we plot the harmonic coefficients $h_{200\,000}(r^*)$ and $h_{002\,000}(r^*)$ which survive only in the nematic phase and note the oscillatory behavior which continues to survive for large values of r^*. In Fig. 3 we plot coefficient $h_{2201-10}(r^*)$ which is of fundamental importance as it defines nematic elastic constants [1] and decays as $1/r^*$ at large distance. This long-range tail behavior is attributed to the director transverse fluctuations [4] which give rise to orientational wave excitations, i.e., the Goldstone modes. This can be seen by taking the tensor order parameter $Q_{\alpha\beta} = \frac{1}{N}\sum_{i=1}^N \frac{3}{2} \times (e_{i\alpha}e_{i\beta} - \frac{1}{3}\delta_{\alpha\beta})$, where α, $\beta = x, y, z$, and $e_{i\alpha}$ is the α component of the molecular axis vector $\mathbf{e_i}$ of each molecule and $\delta_{\alpha\beta}$ the Kronecker symbol and calculating (assuming that the director is along z and the y axis is perpendicular to wave vector $\mathbf{q}$) the correlation $\langle Q_{xz}(q)Q_{xz}(-q)\rangle$. The result involves coefficients
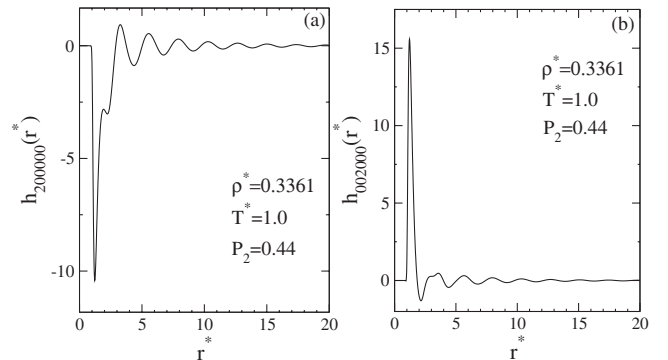

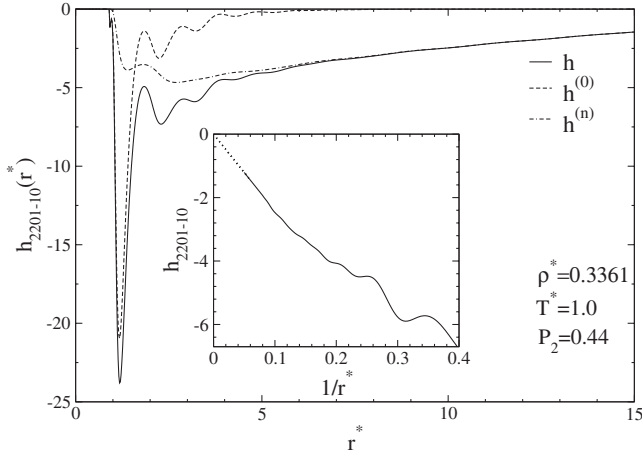FIG. 2.   Coefficients $h_{l_1l_2lm_1m_2m}(r)$ which survive only in the nematic phase.

FIG. 3. Harmonic coefficient $h_{2201-10}$ in the director frame. Details are same as in Fig. 1. Inset shows the plot of $h_{2201-10}$ harmonics with respect to $1/r^*$; the dotted line shows the extrapolated part.

$h^{(n)}_{l_1 l_2 l m_1 m_2 m}(q)$ with $|m_1|$, $|m_2| = 1$. These coefficients which are the Fourier transform of $h^{(n)}_{l_1 l_2 l m_1 m_2 m}(r^*)$ (Fig. 3) behave as $1/q^2$ for $q \to 0$. This is the case of the Goldstone mode of zero mass.

When the Ward identity which must be satisfied in the nematic phase is expressed in the functional differential form it reduces to the Lovett equation [4] and is written as

$$
\begin{aligned}
1 = -\rho \sum_{l_1} \sum_{l'} & \sqrt{2l' + 1}\, P_{l'} \sqrt{\frac{(2l_1 + 1)(2l' + 1)}{20\pi}} \\
& \times C_g(l_1, l', 2, 0, 0, 0) C_g(l_1, l', 2, 1, 0, 1) \\
& \times \int r^2 dr c_{l_1 201-10}(r).
\end{aligned}
\tag{9}
$$

Using the values of $c_{2201-10}(r^*)$, $c_{4201-10}(r^*)$, and P_2 in the nematic region we find the relation is fully satisfied.

The density-functional approach allows one to include more order parameters in the theory even though they are not included in calculating the PCFs. This is done through the parametrization of $\rho(\mathbf{x})$ [6]. When we take two order parameters P_2 and P_4 and use the free-energy functional developed here the transition takes place at $T^* = 1$ with $\rho_l^* = 0.317$, $\Delta\rho^* = 0.026$, $P_2 = 0.644$, and $P_4 = 0.332$. These values compare well with the simulation values, $\rho_l^* = 0.32$, $P_2 = 0.66$, and $P_4 = 0.29$ [15]. This comparison suggests that the effect of order parameter P_4 on PCFs is small.

We now briefly comment on how the theory developed here can be applied to the ordered phases which need for their description $n(n \geq 2)$ number of order parameters. In such a case we can think of a n-dimensional order parameter space; a point in this space defines the values of all the n

order parameters. To obtain $\tilde{c}$, the integration in (8) can be done along a straight line path that connects origin to a point corresponding to the final values of the n order parameters. This path is parametrized by a single variable ξ. However, $c^{(n)}$ appearing in (8) has to be written as $c^{(n)}(x_1 x_2; \lambda\lambda'\rho_0; \xi\xi'\sqrt{\sum_{i=1}^{n} \mu_i^2})$, where μ_i is the ith order parameter.

In conclusion, we developed a method of solving the OZ equation with a closure relation to get both the symmetry conserving and symmetry breaking parts of PCFs. Using these correlation functions we constructed a free-energy functional to study the freezing transition and other properties of an ordered phase. Since the symmetry breaking parts of PCFs have features of the ordered phase including its geometrical packing, the free-energy functional proposed here will allow us to study various phenomena of the ordered phases [13].

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