Percus-Yevick approximation for fluids with spontaneous partial order: Results for a separable model

Hua Zhong and Rolfe G. Petschek
Department of Physics, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106-7079

(Received 14 August 1995)

Recently we have applied the Percus-Yevick approximation to nematic fluids with partial spontaneous order using a diagrammatic implementation of a Ward identity. In this paper we apply the method to study the isotropic-nematic phase transition of a separable model, where the interparticle potential independently depends on the spatial separation and the relative orientation of the particles. This approach allows us to study the transition directly without other approximations besides the Percus-Yevick closure itself. Previous works of the integral equation method on phase transitions were based on the stability criterion or coexistence condition derived from a truncated density functional expansion. By calculating the correlation functions of the *isotropic* phase and applying the stability criterion, we find that within the Percus-Yevick approximation there are *no* numerical solutions indicating an isotropic-nematic phase transition, in agreement with the work by Perera and co-workers [Mol. Phys. **60**, 77 (1987); J. Chem. Phys. **89**, 6941 (1988)]. With this approach, however, we can determine the orientationally dependent probability density ρ self-consistently and we *find* the orientationally partially ordered nematic phase within the Percus-Yevick approximation. With a general qualitative analysis, we show that the stability limit within the Percus-Yevick approximation is highly unstable numerically, which may explain why no numerical solutions reaching the stability limit have been found in previous works for either isotropic-nematic or nematic-smectic phase transitions. We also show analytically that the stability criterion can be derived from the Ward identity. [S1063-651X(96)05705-4]

PACS number(s): 64.70.Md, 05.40.+j

I. INTRODUCTION

Integral-equation methods, which generally involve solving the Ornstein-Zernike equation with the Percus-Yevick (PY) or hypernetted-chain closure approximation, have been widely used to study the pair correlation functions of classical simple liquids [1]. They have also been applied to isotropic fluids of nonspherical particles [2,3] and anisotropic fluids of perfectly aligned molecules [4,5]. These methods have made significant contributions to our understanding of simple fluid systems. It is therefore worthwhile to generalize and apply these useful techniques to the study of the liquid crystals that have partial orientational orders. Recently we have developed an approach [6] to extend the Percus-Yevick approximation to anisotropic nematic fluids with partial spontaneous orientational order. This approach is basically a diagrammatic implementation of a Ward identity of the nematic fluid system with spontaneously broken symmetries. The Ward identity relates the one-point probability density to an integral of the two-point correlation function, which enables us to determine the orientationally dependent probabilities self-consistently. With a simple XY model, where the orientations of the axial molecules in three dimensions are confined to a plane and the interactions between the molecules depend only on their spatial separation and relative orientations, we have shown that the Ward identity can be implemented with a modified version of the Percus-Yevick approximation [7] and correctly yields an infinite susceptibility in the limit of zero wave vector for the Goldstone modes. In this paper we apply this method to an investigation of the isotropic-nematic phase transition. To avoid mathematical complications, we concentrate on a separable model, where the interparticle potential is of the form $u(r,(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')^2)$, with r being the interparticle separation and $\hat{\mathbf{\Omega}}$, $\hat{\mathbf{\Omega}}'$ the orientations of the molecules. Note, however, that this approach can be applied to more complicated and realistic (such as Gay-Berne [8], hard spherocylinders or hard ellipsoids) nonseparable model potentials.

In 1973, Workman and Fixman [9] generalized the Ornstein-Zernike and Percus-Yevick equations and applied the integral-equation method to study the isotropic-anisotropic phase transitions in liquid crystals. The generalized Ornstein-Zernike equation obtained through the functional differentiation of the grand canonical partition function is identical to the one we used in our current approach. The generalized Percus-Yevick equation in Workman and Fixman's work was based on density functional theory. In general, in terms of the density functional theory, the difference of the grand potential $\Delta\Omega=\Omega[\rho]-\Omega[\rho_0]$ between two states can be expanded [10] as

$$\begin{aligned}\beta\Delta\Omega=&\int d(1)\{\rho(1)\ln[\rho(1)/\rho_0(1)]-[\rho(1)-\rho_0(1)]\}\\&-\frac{1}{2!}\int\int d(1)d(2)c(1,2,\rho_0)[\rho(1)-\rho_0(1)]\\&\times[\rho(2)-\rho_0(2)]-\cdots,\end{aligned}\tag{1}$$

where $d(1)=d\mathbf{r}_1 d\hat{\mathbf{\Omega}}_1$ and $c(1,2,\rho_0)$ is the direct correlation functions of the reference state with density ρ_0. Usually this expansion is truncated at the two-particle direct correlation function, $c(1,2,\rho_0)$. The free energy F can also be expanded in a similar fashion [9,11]. In Workman and Fixman's paper, the one-point probability function $\rho(1)$ was written in terms of reference state density $\rho_0(1)$, mean field potential, and an additional function S [Eq. (13) of Ref. [9]], which was then determined by minimizing the free energy expression. With a repulsive potential for rodlike particles they predicted an isotropic-anisotropic phase transition. More recently, also based on the density functional expansion of the free energy, Stecki and Kloczkowski [11] derived a stability criterion. A coexistence condition was also obtained by setting $\beta\Delta\Omega=0$ in Eq. (1), from which the location of the isotropic-nematic transition [12] can be determined by using the *isotropic* phase as the reference state. Perera and co-workers [12,13] have found that using the correlation function calculated in the *isotropic* phase through the hypernetted chain approximation and the referenced hypernetted chain approximation, and applying the stability criterion or coexistence condition described above, they can obtain transition temperatures in good agreement with the Monte Carlo simulation results [14]. However, they also found that the Percus-Yevick approximation does not predict an isotropic-nematic transition regardless of the form of the model interaction potential. In studying the nematic-smectic phase transition, Caillol and Weis [4,5] also found that there are no numerical solutions reaching the stability limit within the Percus-Yevick approximation.

With a simple analysis we show that the calculations near the stability limit are highly unstable in the Percus-Yevick approximation. This is a general argument that should apply to isotropic-nematic, nematic-smectic, or other phase transitions. Compared to the truncated density functional theory described above, our method does not impose any additional approximations other than the Percus-Yevick approximation itself. The orientational dependent density $\rho(\mathbf{\Omega})$ is directly determined by the Ward identity, Ornstein-Zernike equation, and Percus-Yevick closure altogether, self-consistently. More importantly, our approach gives qualitatively correct treatment for the Goldstone modes. Thus a perturbative theory based on our treatment and taking into account graphs (or effects) not included in the PY treatment is possible in principle and consistent with rotational invariance.

The paper is organized as follows. In the next section we review briefly the Ward identity and the extended Percus-Yevick approximation for a nematic fluid with spontaneously broken symmetries. We discuss the basis function and other implementation details in Sec. III. We will show analytically that we can derive the stability criterion [13] from the Ward identity. We also give a qualitative argument to show that the (physical) stability limit is numerically unstable within the Percus-Yevick approximation. Results of the model calculations are presented in Sec. IV. Section V is a summary.

II. BRIEF REVIEW

A. Ward identity

Spontaneous symmetry breaking is most frequently used in describing n-dimensional ferromagnets [15], where for $n\geqslant 2$ without the presence of an external field, the direction of the magnetization is not predetermined. The spontaneous magnetization breaks the continuous symmetry and leads to spin wave excitations, or Goldstone modes, which rotate the direction of the magnetization without any energy cost. In such a system, the susceptibilities are infinite. Analogously, in nematic fluids with sufficiently strong interparticle interactions, after the isotropic-nematic phase transition, the orientations of the molecules break the continuous rotational symmetry and result in a spontaneous partial order. Therefore the susceptibility is infinite in the limit of zero wave vector. In the Ornstein-Zernike equation,

$$h(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=c(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')+\frac{1}{4\pi}\int d\hat{\mathbf{\Omega}}_1 c(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}_1)\times\rho(\hat{\mathbf{\Omega}}_1)h(\mathbf{k},\hat{\mathbf{\Omega}}_1,\hat{\mathbf{\Omega}}'), \tag{2}$$

the total correlation function $h(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$ is directly related to the susceptibility, which implies that $h(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$ also becomes infinite as $\mathbf{k}\to 0$. Defining $H(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=\rho^{1/2}(\hat{\mathbf{\Omega}})\rho^{1/2}(\hat{\mathbf{\Omega}}')h(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$ and $C(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=\rho^{1/2}(\hat{\mathbf{\Omega}})\rho^{1/2}(\hat{\mathbf{\Omega}}')c(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$, the above Ornstein-Zernike equation can be written in a symmetric form,

$$H(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=C(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')+\frac{1}{4\pi}\int d\hat{\mathbf{\Omega}}_1 C(\mathbf{k},\hat{\Omega},\hat{\mathbf{\Omega}}_1)H(\mathbf{k},\hat{\mathbf{\Omega}}_1,\hat{\mathbf{\Omega}}'). \tag{3}$$

Taking both H and C as integral operators, we can write [6] symbolically $h\sim H\sim(1-C)^{-1}C$. If the eigenequation of the operator C is written as

$$\frac{1}{4\pi}\int d\hat{\mathbf{\Omega}}_1 C(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}_1,)\hat{\mathbf{\Psi}}_i(\mathbf{k},\hat{\mathbf{\Omega}}_1)=\lambda_i(\mathbf{k})\hat{\Psi}_i(\mathbf{k},\hat{\mathbf{\Omega}}), \tag{4}$$

the Ornstein-Zernike equation, (3) can be reexpressed as

$$H(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=\sum_i \frac{\lambda_i(\mathbf{k})}{1-\lambda_i(\mathbf{k})}\hat{\mathbf{\Psi}}_i(\mathbf{k},\hat{\mathbf{\Omega}})_i(\mathbf{k},\hat{\mathbf{\Omega}}'). \tag{5}$$

Clearly, to guarantee that the Goldstone modes are treated correctly so that $h(\mathbf{k}\to\mathbf{0},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')\to\infty$, we need to ensure that the operator C has a unit eigenvalue. By further studying the relation between the one-particle probability function and the two-particle direct correlation function $c(\mathbf{k}\to\mathbf{0},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$, we obtain a relation

$$\frac{\delta v(\hat{\mathbf{\Omega}})}{\delta\rho(\hat{\mathbf{\Omega}}')}=c(\mathbf{k}\to\mathbf{0},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}'), \tag{6}$$

where

$$\rho(\hat{\mathbf{\Omega}})=\rho_0\exp[v(\hat{\mathbf{\Omega}})]/Z, \tag{7}$$

and Z is a normalization constant such that $\int d\hat{\mathbf{\Omega}}\rho(\hat{\mathbf{\Omega}})/(4\pi)=\rho_0$. This is a typical Ward identity related to Goldstone modes due to the spontaneously broken continuous rotational symmetries. It is easy to show that [6], provided ρ depends on $\hat{\mathbf{\Omega}}$ so that $\delta\rho(\hat{\mathbf{\Omega}})$ (changes in ρ due to a rotation of the director) is not zero and the eigenvector with unit eigenvalue in Eq. (4) is $\Psi\propto\rho^{-1/2}(\hat{\mathbf{\Omega}})\delta\rho(\hat{\mathbf{\Omega}})$, the singularity in $H(\mathbf{k},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$ [or $h(\mathbf{k},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$] as $\mathbf{k}\to\mathbf{0}$ due to the Goldstone modes can be treated correctly with proper implementation of the Ward identity.

B. Percus-Yevick closure

The Ward identity, Eq. (6), is an *exact* relation between the one-point probability density and the two-point correlation function. However, in terms of diagrammatic nomenclature, the Percus-Yevick closure only includes some of the possible diagrams of $c(1,2)$, therefore [6] the Percus-Yevick closure commonly used in systems without a spontaneous partial order does *not* satisfy the Ward identity. To make the closure consistent with the Ward identity, the rotational average on the correlation functions is needed. In Percus and Yevick's original paper [7], they considered a system of interacting spherical particles and derived a classical many-body Hamiltonian in terms of the collective coordinates, which are the Fourier components of the particle density. In their derivation, translational invariance of the system was imposed. If nonspherical particles are considered, additional energy terms due to the rotational freedom of the particles should also be included in the Hamiltonian. We would need to introduce new collective coordinates and both rotational and translational invariances of the whole system should be applied in deriving a generalized Percus-Yevick closure. In other words, physically, the underlying effective potential defined in Percus and Yevick's original paper [7] is rotationally invariant. Therefore the correlation function entering the Percus-Yevick closure must be rotationally invariant.

We define $\langle h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')\rangle_{\mathrm{rot}}$ to be the rotational average of the correlation function $h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$, the modified Percus-Yevick closure is written as

$$c(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')=f(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')[1+\langle h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')\rangle_{\mathrm{rot}}-c(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')], \tag{8}$$

where $f(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')=e^{-\beta u(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')}-1$ is the Mayer function and $u(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$ is the interparticle potential.

III. IMPLEMENTATION DETAILS, WARD IDENTITY, AND THE STABILITY CRITERION

A. Basis functions

We assume that the molecules in the system of our interest have axial symmetry and their orientations can be specified by angles $\hat{\boldsymbol{\Omega}}=(\theta,\phi)$. We choose a coordinate system such that the z axis is along the nematic director direction. The single particle density in nematic fluids ρ is therefore only a function of θ,

$$\rho(\hat{\boldsymbol{\Omega}})=\sum_{l}\rho_l Y_{l0}(\hat{\boldsymbol{\Omega}}) \tag{9}$$

[the $l=0$ component of ρ_l is related to ρ_0 defined in Eq. (7) by relation $\rho_{l=0}=\sqrt{4\pi}\rho_0$], where $Y_{lm}(\hat{\boldsymbol{\Omega}})$ are the commonly used spherical harmonics,

$$Y_{lm}(\theta,\phi)=(-1)^m\left(\frac{2l+1}{4\pi}\right)^{1/2}\left(\frac{(l-m)!}{(l+m)!}\right)^{1/2}P_{lm}(\cos\theta)e^{im\phi} \tag{10}$$

for $m\geqslant 0$, and for $m<0$, $Y_{l,-m}=(-)^m Y^{\star}_{lm}$. The total correlation function $h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$ can also be expanded in terms of spherical harmonics, in general:

$$h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')=\sum_{l_1l_2l}\sum_{m_1m_2m}h_{l_1l_2lm_1m_2m}(\mathbf{r})Y_{l_1m_1}(\hat{\boldsymbol{\Omega}})\times Y_{l_2m_2}(\hat{\boldsymbol{\Omega}}')Y^{*}_{lm}(\hat{\mathbf{r}}). \tag{11}$$

For a nematic system, $h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$ is invariant under a rotation along the direction of the director (z axis). This condition leads to the relation $m=m_1+m_2$, and therefore the expansion coefficients $h_{l_1l_2lm_1m_2m}(r)$ are real functions.

It is convenient to expand the interparticle potential, correlation functions $c(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$, and $\langle h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')\rangle_{\mathrm{rot}}$ in terms of rotational invariants [16]. In general, a rotationally invariant function $F(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')$ can be written as

$$F(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')=\sum_{l_1l_2l}F_{l_1l_2l}(\mathbf{r})\Phi_{l_1l_2l}(\hat{\mathbf{r}},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}'), \tag{12}$$

where

$$\Phi_{l_1l_2l}(\hat{\mathbf{r}},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')=\sum_{m_1,m_2}C(l_1l_2l,m_1m_2m)Y_{l_1m_1}(\hat{\boldsymbol{\Omega}}_1)\times Y_{l_2m_2}(\hat{\boldsymbol{\Omega}}_2)Y^{\star}_{lm}(\hat{r}) \tag{13}$$

is a rotational invariant and $C(l_1l_2l,m_1m_2m)$ is a Clebsch-Gordan coefficient. Discussions of expanding correlation functions in terms of rotational invariants have been well documented in Refs. [16] and [17], and will not be repeated here. For a nonpolar molecule, orientation of the molecule $\hat{\boldsymbol{\Omega}}_1$ is equivalent to $-\hat{\boldsymbol{\Omega}}_1$. Since $Y_{l_1m_1}(\hat{\boldsymbol{\Omega}}_1)=(-1)^{l_1}Y_{l_1m_1}(-\hat{\boldsymbol{\Omega}}_1)$, using Eqs. (12) and (13) we find that l_1 must be even. Symmetry requires that l_1, l_2, and l must all be even.

As discussed in Sec. II, we need to obtain the rotationally averaged total correlation function $\langle h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')\rangle_{\mathrm{rot}}$ in the extended Percus-Yevick closure. The rotational average is defined as

$$\langle h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')\rangle_{\mathrm{rot}}=\int d\hat{\omega}R(\hat{\omega})h(\mathbf{r},\hat{\boldsymbol{\Omega}},\hat{\boldsymbol{\Omega}}')\bigg/\int d\hat{\omega}, \tag{14}$$

where $R(\hat{\omega})$ is the rotational operator for a rotation along direction $\hat{\omega}$. Using the relation $Y_{lm'}(\hat{\boldsymbol{\Omega}}')=\Sigma_m D^{l}_{mm'}(\hat{\omega})Y_{lm}(\hat{\boldsymbol{\Omega}})$, where the $D^{l}_{mm'}(\hat{\omega})$ are the standard Wigner's generalized spherical harmonics [16,17], $\hat{\boldsymbol{\Omega}}$ and $\hat{\boldsymbol{\Omega}}'$ are the angles before and after the rotation, we can further write Eq. (14) as

$$\begin{aligned}\langle h(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')\rangle_{\mathrm{rot}}=&\sum_{l_1l_2l}\sum_{m_1',m_2'} h_{l_1l_2lm_1'm_2'}Y_{l_1m_1}(\hat{\mathbf{\Omega}}_1)Y_{l_2m_2}(\hat{\mathbf{\Omega}}_2)\\ &\times Y^\star_{lm}(\hat{\mathbf{\Omega}})\sum_{m_1m_2}\int d\hat{\omega}D^{l_1}_{m_1m_1'}(\hat{\omega})D^{l_2}_{m_2m_2'}(\hat{\omega})\\ &\times D^{l,\star}_{mm'}(\hat{\omega})\bigg/\int d\hat{\omega}\\ =&\sum_{l_1l_2l}\sum_{m_1'm_2'}C(l_1l_2l,m_1'm_2'm')\\ &\times h_{l_1l_2lm_1'm_2'm'}/(2l+1)\\ &\times\sum_{m_1m_2}C(l_1l_2l,m_1m_2m)\\ &\times Y_{l_1m_1}(\hat{\mathbf{\Omega}}_1)Y_{l_2m_2}(\hat{\mathbf{\Omega}}_2)Y^\star_{lm}(\hat{\mathbf{\Omega}}).\end{aligned}\tag{15}$$

Comparing the above equation with Eqs. (12) and (13) for expansion $\langle h(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')\rangle_{\mathrm{rot}}$, we obtain relation

$$\langle h\rangle_{\mathrm{rot},l_1'l_2'l}=\sum_{m_1'm_2'}C(l_1l_2l,m_1'm_2'm')h_{l_1l_2lm_1'm_2'm'}/(2l+1).\tag{16}$$

In this paper, we consider a ‘‘separable’’ model, where the potential depends upon the separation of the molecules and their relative orientations in the form of $u(r,(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')^2)$. In particular, we assume the Mayer function can be written as

$$\begin{aligned}f(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')&=\sum_l\frac{2l+1}{4\pi}f_l(\mathbf{r})P_l(\cos\gamma)\\ &=\sum_{l,m}f_l(\mathbf{r})Y^*_{lm}(\hat{\mathbf{\Omega}})Y_{lm}(\hat{\mathbf{\Omega}}'),\end{aligned}\tag{17}$$

where γ is the angle between $\hat{\mathbf{\Omega}}$ and $\hat{\mathbf{\Omega}}'$ and the addition theorem for the spherical harmonics has been used. For separable models, the basis functions and the indices for the expansion coefficients can be simplified. Explicitly, the expansion coefficients $F_{l_1l_2l}(r)$ in Eq. (12) are nonzero only when $l_1=l_2$ and $l=0$. Substituting the value of the Clebsch-Gordan coefficient, $C(ll0,m,-m,0)=(-1)^{l+m}/\sqrt{2l+1}$ into the expansion, Eq. (13), we have

$$\begin{aligned}F(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=&\sum_{l_1}F_{l_1l_10}(\mathbf{r})/\sqrt{4\pi(2l_1+1)}\sum_{m_1}Y^*_{l_1m_1}(\hat{\mathbf{\Omega}})\\ &\times Y_{l_1m_1}(\hat{\mathbf{\Omega}}'),\end{aligned}\tag{18}$$

where F can be the Mayer function, the rotationally averaged total correlation function $\langle h\rangle_{\mathrm{rot}}$, or the correlation function c. The total correlation function h in Eq. (11) can also be simplified as

$$\begin{aligned}h(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=&\sum_{l_1l_2m_1}(-1)^{m_1}h_{l_1l_20,m_1,-m_1,0}(\mathbf{r})/\sqrt{4\pi}Y^*_{l_1m_1}\\ &\times(\hat{\mathbf{\Omega}})Y_{l_2m_1}(\hat{\mathbf{\Omega}}')\\ =&\sum_{l_1l_2m_1}(-1)^{m_1}h_{l_1l_2m_1}(r)/\sqrt{4\pi}Y^\star_{l_1m_1}\\ &\times(\hat{\mathbf{\Omega}})Y_{l_2m_1}(\hat{\mathbf{\Omega}}').\end{aligned}\tag{19}$$

B. Ward identity and the stability criterion

We discussed in the Introduction that from a truncated density functional expansion of the free energy one can derive a stability condition [11]. If the direct correlation function $c(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$ is expanded in the form of Eq. (18), the stability condition can be written as

$$1-\frac{\rho_0c_{ll0}(\mathbf{k}=\mathbf{0})}{4\pi\sqrt{4\pi(2l+1)}}>0.\tag{20}$$

Practically, the $l=2$ component of c_{ll0} is checked to determine the phase transition, i.e.,

$$1-\frac{\rho_0c_{220}(\mathbf{k}=\mathbf{0})}{8\pi\sqrt{5\pi}}>0.\tag{21}$$

We will show that we can reach the same condition from the Ward identity. In Sec. II A we mentioned that the operator $C(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$ must have a unit eigenvalue with eigenvector $\Psi(\hat{\mathbf{\Omega}})\propto\delta\rho(\hat{\mathbf{\Omega}})/\rho^{1/2}(\hat{\mathbf{\Omega}})$, or equivalently Eq. (4) can be written as

$$\delta\rho(\hat{\mathbf{\Omega}})=\frac{1}{4\pi}\rho(\hat{\mathbf{\Omega}})\int d\hat{\mathbf{\Omega}}'c(\mathbf{k}=\mathbf{0},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')\delta\rho(\hat{\mathbf{\Omega}}'),\tag{22}$$

where $\delta\rho(\hat{\mathbf{\Omega}})$ is the change of $\rho(\hat{\mathbf{\Omega}})$ due to a rotation. $\delta\rho(\hat{\mathbf{\Omega}})$ can be written [6] as a linear combination of $\hat{L}_+\rho(\hat{\mathbf{\Omega}})=\Sigma_l\sqrt{l(l+1)}\rho_lY_{l,1}(\hat{\mathbf{\Omega}})$ and $\hat{L}_-\rho(\hat{\mathbf{\Omega}})=\Sigma_l\sqrt{l(l+1)}\rho_lY_{l,-1}(\hat{\mathbf{\Omega}})$, where we have used Eq. (9). It is straightforward to substitute expansions for $c(\mathbf{k},\Omega,\Omega')$, $\rho(\hat{\mathbf{\Omega}})$, and $\delta\rho(\hat{\mathbf{\Omega}})$ into Eq. (22) and obtain the following self-consistent relation for various components of ρ_l,

$$\begin{aligned}\rho_{l_2}=&\frac{1}{(4\pi)^2}\sum_{l_1,l}\sqrt{\frac{l_1(l_1+1)(2l+1)}{l_2(l_2+1)(2l_2+1)}}C(ll_1l_2,000)\\ &\times C(ll_1l_2,011)c_{l_1l_10}(\mathbf{k}=\mathbf{0})\rho_{l_1}\rho_l.\end{aligned}\tag{23}$$

When the higher order expansion coefficients ρ_l for $l>2$ are negligible, the above equation leads to

$$\begin{aligned}&\rho_2C(222,000)C(222,011)c_{220}(\mathbf{k}=\mathbf{0})/(4\pi)^2\\ &\qquad=1-\frac{\rho_0c_{220}(\mathbf{k}=\mathbf{0})}{8\pi\sqrt{5\pi}}.\end{aligned}\tag{24}$$

A physically meaningful positive solution for ρ_2 can only be found when the right hand side of Eq. (24) is greater than zero, which is exactly the stability condition, Eq. (21).

For numerical computations, it is more convenient to write the Ward identity Eq. (6) as [6]

$$v(\hat{\mathbf{\Omega}}_1)=\frac{1}{4\pi}\int d\hat{\mathbf{\Omega}}_2 c(\mathbf{k}\rightarrow\mathbf{0},\hat{\mathbf{\Omega}}_1,\hat{\mathbf{\Omega}}_2)\rho(\hat{\mathbf{\Omega}}_2). \tag{25}$$

Using the expansions, Eqs. (9) and (18), we obtain

$$v_{l_1}=\frac{c_{l_1 l_1 0}(k\rightarrow 0)\rho_{l_1}}{(4\pi)^{3/2}\sqrt{2l+1}}. \tag{26}$$

Also from Eq. (7) we find

$$\rho_{l_1}=2\pi\rho_0\int_{-1}^{1}\left(\frac{2l_1+1}{4\pi}\right)^{1/2}P_{l_1}(x)\times\exp\sum_{l_1'}\left(\frac{2l_1'+1}{4\pi}\right)^{1/2}v_{l_1'}(x)P_{l_1'}(x)/Z, \tag{27}$$

where

$$Z=\int_{-1}^{1}dx\exp\sum_{l_1'}\left(\frac{2l_1'+1}{4\pi}\right)^{1/2}v_{l_1'}(x)P_{l_1'}(x). \tag{28}$$

Equations (26)–(28) are to be solved self-consistently.

C. Ornstein-Zernike equation and Percus-Yevick closure

Substituting the expansion for the correlation function $c(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$ of the form (18), probability density $\rho(\hat{\mathbf{\Omega}})$ of the form (9), and the total correlation function Eq. (19) into the Ornstein-Zernike equation (2), we obtain the relation

$$\sum_{l_3}A_{l_1 l_3 m_1}(k)h_{l_3 l_2 m_1}(k)=(-1)^{m_1}c_{l_1 l_1 0}(k)\delta_{l_1 l_2}/\sqrt{2l_1+1}, \tag{29}$$

where

$$A_{l_1 l_3 m_1}(k)=\delta_{l_1 l_3}-\sum_{l}\frac{1}{(4\pi)^2}\left(\frac{2l+1}{2l_3+1}\right)^{1/2}C(l_1 l l_3,000)C(l_1 l l_3,m_1 0 m_1)c_{l_1 l_1 0}(k)\rho_l. \tag{30}$$

We can therefore invert the matrix A to obtain the correlation function h using Eq. (29).

For $k\rightarrow 0$ and in the presence of a Goldstone mode, the determinant of the matrix A is very close to zero, which might lead to a large numerical discrepancy in inverting the matrix. In this case, we solve the Ornstein-Zernike equation in terms of the eigenvalues and eigenvectors of the integral equation (4). Expanding the correlation functions and density in terms of basis functions discussed in Sec. III A, the integral equation can be written explicitly as

$$\sum_{l'm'}B_{lml'm'}(k)\psi^{i}_{l'm'}(k)=\lambda^{i}_{lm}(k)\psi^{i}_{lm}(k), \tag{31}$$

where

$$B_{lml'm'}(k)=\frac{\delta_{mm'}}{4\pi}\sum_{l_1}\frac{c_{l_1 l_1 0}(k)}{\sqrt{4\pi(2l_1+1)}}\int d\hat{\mathbf{\Omega}}Y_{l_1 m}(\hat{\mathbf{\Omega}})\rho^{1/2}(\hat{\mathbf{\Omega}})Y_{lm}(\hat{\mathbf{\Omega}})\int d\hat{\mathbf{\Omega}}'Y_{l_1 m}(\hat{\mathbf{\Omega}}')\rho^{1/2}(\hat{\mathbf{\Omega}}')Y_{l'm}(\hat{\mathbf{\Omega}}'). \tag{32}$$

The correlation function h can be expressed as

$$h_{l_1 l_2 m_1}(k)=(-1)^{m_1}\sqrt{4\pi}\sum_{lm}\sum_{l'm'}\sum_{i}\frac{\lambda^{i}_{lm}(k)}{1-\lambda^{i}_{lm}(k)}\psi^{i}_{lm}(k)\psi^{i}_{l'm'}(k)\times\int d\hat{\mathbf{\Omega}}Y_{l_1 m}(\hat{\mathbf{\Omega}})\rho^{-1/2}(\hat{\mathbf{\Omega}})Y_{lm}(\hat{\mathbf{\Omega}})\int d\hat{\mathbf{\Omega}}'Y_{l_2 m}(\hat{\mathbf{\Omega}}')\rho^{-1/2}(\hat{\mathbf{\Omega}}')Y_{l'm}(\hat{\mathbf{\Omega}}'). \tag{33}$$

We have checked numerical results using both the matrix inverting and the eigenequation methods; they agree with each other as expected.

In terms of the expansion coefficients in Eq. (18), the extended Percus-Yevick closure, Eq. (8), can be written as

$$c_{l_1 l_1 0}(r)=f_{l_1 l_1 0}(r)+\sum_{l_1',l_1''}\frac{(2l_1'+1)^{1/2}(2l_1''+1)^{1/2}}{(4\pi)^{3/2}(2l_1+1)^{1/2}}C^{2}(l_1' l_1'' l_1,000)f_{l_1' l_1' 0}(r)\eta_{l_1'' l_1'' 0}(r), \tag{34}$$

where we have used relations summarized in Gray and Gubbin's book [17] for the Clebsch-Gordan coefficients, and η is defined as

$$\eta = \langle h \rangle_{\text{rot}} - c. \tag{35}$$

In order to solve the Ornstein-Zernike equation, Percus-Yevick closure and the Ward identity self-consistently, we have adopted the iterative method. We begin the iteration with the initial guess $c^{(1)}(r, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')$, where the superscript indicates the iteration number. In general for the nth iteration, we first obtain $c^{(n)}(k, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')$ through a Fourier transform. Its limit at $k \to 0$ is used in the Ward identity, Eq. (25), to determine $\rho^{(n)}(\hat{\mathbf{\Omega}})$. This involves solving Eqs. (26)–(28) self-consistently. The converged values of ρ_l are then substituted into the Ornstein-Zernike equation to obtain the correlation function $h^{(n)}(k, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')$ using Eqs. (29)–(33). Its rotational average $\langle h \rangle_{\text{rot}}$ is then performed and $\langle h \rangle_{\text{rot}}^{(n)}(r, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')$ is substituted in the modified Percus-Yevick closure, Eq. (34), to compute $c^{(n+1)}(r, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')$. This ends the nth iteration. This procedure is repeated many times until the correlation functions converge.

In practice, we use a solution of the standard Lennard-Jones isotropic fluids, or a converged result with the same density at a temperature nearby as an initial guess for $c^{(1)}(r, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')$. To avoid divergence and expedite the computation, we have implemented the mixing scheme,

$$c^{i+1}(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') = (1-\alpha) c^{i}(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') + \alpha c^{\text{new}}(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}'), \tag{36}$$

where $c^{\text{new}}(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')$ is the direct correlation function obtained at the $(i+1)$th cycle, $0 < \alpha < 1.0$ is a mixing parameter. We adjust the mixing parameter α automatically according to the difference of $|c^{i}(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') - c^{\text{new}}(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')|$, such that α is small when the difference is very large and vice versa. We have also used the Shanks transformation to try to attenuate large differences in the iterative process.

D. Thermodynamic quantities of interest

We use $\langle P_2(\cos\theta) \rangle$ as the order parameter,

$$\begin{aligned} \langle P_2(\cos\theta) \rangle &= \int d\hat{\mathbf{\Omega}} \rho(\hat{\mathbf{\Omega}}) P_2(\cos\theta) \Bigg/ \int d\hat{\mathbf{\Omega}} \rho(\hat{\mathbf{\Omega}}) \\ &= \rho_2 / (\sqrt{5} \rho_0). \end{aligned} \tag{37}$$

In a nematic liquid crystal, the single-particle probability density ρ is only a function of the orientation of the particles $\hat{\mathbf{\Omega}}$ and the two-particle density, $\rho^{(2)}(1,2) = \rho^{(2)}(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') = \rho(\hat{\mathbf{\Omega}}) \rho(\hat{\mathbf{\Omega}}') [h(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') + 1]$. For systems with Goldstone modes, the rotational average of the correlation function h is needed and the internal energy U can be expressed [1] as

$$\begin{aligned} U &= \frac{1}{2} \int \rho^{(2)}(1,2) u(1,2) d(1) d(2) \\ &= \frac{V}{2} \int dr d\hat{\mathbf{\Omega}} d\hat{\mathbf{\Omega}}' \rho(\hat{\mathbf{\Omega}}) \rho(\hat{\mathbf{\Omega}}') [\langle h(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') \rangle_{\text{rot}} + 1] u(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}'). \end{aligned} \tag{38}$$

We can also obtain the pressure equation

$$\begin{aligned} \frac{\beta P}{\rho_0} &= 1 - \frac{\beta}{6\rho_0} \int dr d\hat{\mathbf{\Omega}} d\hat{\mathbf{\Omega}}' [\mathbf{r} \cdot \nabla_r u(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')] \rho(\hat{\mathbf{\Omega}}) \rho(\hat{\mathbf{\Omega}}') [\langle h(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') \rangle_{\text{rot}} + 1] \\ &= 1 - \frac{2\pi\beta}{3\rho_0} \int d\hat{\mathbf{\Omega}} d\hat{\mathbf{\Omega}}' \rho(\hat{\mathbf{\Omega}}) \rho(\hat{\mathbf{\Omega}}') \int_0^\infty dr r^3 \frac{\partial u(r, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}')}{\partial r} [\langle h(\mathbf{r}, \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') \rangle_{\text{rot}} + 1], \end{aligned} \tag{39}$$

where the last equation is specifically written for a system interacting through a separable potential.

E. Stability limit

Using a simple qualitative analysis, we made an effort to understand whether we can reach the stability limit within the Percus-Yevick closure. We are mainly interested in the $\mathbf{k} \to \mathbf{0}$ limit, which contributes the most in the following argument. Close to transition in the *isotropic* phase we can write

$$\begin{aligned} h_{000}(k \to 0) &= -a_1, \\ h_{220}(k \to 0) &= \frac{a_2}{k^2 + a}, \end{aligned} \tag{40}$$

where a and a_i are positive parameters, $a \to 0$ is the stability limit. We assume that components $h_{l_1 l_1 0}$ for $l_1 > 2$ are small enough to be negligible, or at least that they do not vary rapidly as the stability limit is approached. The Ornstein-Zernike equation, Eq. (2), takes a simple form in isotropic phase,

$$h_{l_1 l_1 0}(k) - c_{l_1 l_1 0}(k) = \frac{\rho_0 h_{l_1 l_1 0}(k) c_{l_1 l_1 0}(k)}{4\pi \sqrt{4\pi(2l_1 + 1)}}. \tag{41}$$

Using Eqs. (40) and (41), we find

$$c_{000}(k\rightarrow 0)=\frac{4\pi a_1\sqrt{4\pi}}{a_1\rho_0-4\pi\sqrt{4\pi}},$$

$$c_{220}(k\rightarrow 0)=\frac{a_2}{k^2+a+\rho_0 a_2/(8\pi\sqrt{5\pi})}. \tag{42}$$

For convenience, we express the Percus-Yevick closure Eq. (8) as

$$\begin{aligned}c(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')&=\{1-\exp[\beta u(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')]\}[1+h(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')]\\&=\mathscr{F}(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')[1+h(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')],\end{aligned} \tag{43}$$

where we have defined $\mathscr{F}(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=1-\exp[\beta u(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')]$. The Fourier transform of Eq. (43) is simply

$$\begin{aligned}c(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')&=\mathscr{F}(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')\\&\quad+\int dk_1\mathscr{F}(\mathbf{k}-\mathbf{k}_1,\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')h(\mathbf{k}_1,\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}').\end{aligned} \tag{44}$$

More explicitly, using the expansion for the rotational invariants shown in Sec. III, Eq. (18), the above equation can be written as

$$\begin{aligned}c_{l_1l_10}(k)&=\mathscr{F}_{l_1l_10}(k)\\&\quad+\sum_{l_1',l_2'}\frac{(2l_1'+1)^{1/2}(2l_2'+1)^{1/2}}{(4\pi)^{3/2}(2l_1+1)^{1/2}}C^2(l_1'l_2'l_1,000)\\&\quad\times\int d\mathbf{k}_1\mathscr{F}_{l_1'l_1'0}(\mathbf{k}-\mathbf{k}_1)h_{l_2'l_2'0}(\mathbf{k}_1).\end{aligned} \tag{45}$$

To make progress for strong interacting potentials discussed in the paper, we can assume that

$$\mathscr{F}_{000}(k\rightarrow 0)=-a_3,$$

$$\mathscr{F}_{220}(k\rightarrow 0)=a_4, \tag{46}$$

where a_i are again positive constants. The main contribution to the integral in Eq. (45) is from the $k_1\rightarrow 0$ limit. It is therefore straightforward to use Eqs. (40), (42), (46), and (45) to find the following relation:

$$\begin{aligned}\frac{a_2}{k^2+a+\rho_0a_2/(8\pi\sqrt{5\pi})}&=a_4+\left(-a_3+\frac{2\sqrt{5}}{7}a_4\right)\frac{a_2}{(4\pi)^{3/2}}\\&\quad\times\int d\mathbf{k}_1\frac{1}{\mathbf{k}_1^2+a}-\frac{a_1a_4}{(4\pi)^{3/2}}.\end{aligned} \tag{47}$$

Since $\int d\mathbf{k}_1 1/(\mathbf{k}_1^2+a)\propto a_5+\sqrt{a}$, it is easy to see that when $k\rightarrow 0$, $a=0$ can be a solution if the interaction potential and the parameters of the system satisfy Eq. (47).

To investigate whether we can reach the stability limit, we consider a perturbation to the solution discussed above. Assume

$$\begin{aligned}c_{000}(k\rightarrow 0)&=\frac{4\pi a_1\sqrt{4\pi}}{a_1\rho_0-4\pi\sqrt{4\pi}}+\delta_0\\&=c_{000}^{sol}(k\rightarrow 0)+\delta_0,\end{aligned}$$

$$\begin{aligned}c_{220}(k\rightarrow 0)&=\frac{a_2}{k^2+a+\rho_0a_2/(8\pi\sqrt{5\pi})}+\delta_2\\&=c_{220}^{\text{sol}}(k\rightarrow 0)+\delta_2,\end{aligned} \tag{48}$$

where $c_{000}^{\text{sol}}(k\rightarrow 0)$ and $c_{220}^{\text{sol}}(k\rightarrow 0)$ are the solutions within the Percus-Yevick closure, δ_0 and δ_2 are small perturbations. Using Eqs. (48) and (41), to the lowest order in δ_0 and δ_2 we find

$$h_{000}(k\rightarrow 0)=-a_1+\delta_0\left(1-\frac{a_1\rho_0}{2\pi\sqrt{4\pi}}+\frac{a_1^2\rho_0^2}{64\pi^3}\right),$$

$$h_{220}(k\rightarrow 0)=\frac{a_2}{k^2+a}+\delta_2\left(1+\frac{a_2\rho_0}{4\pi\sqrt{5\pi}(k^2+a^2)}+\frac{a_2^2\rho_0^2}{320\pi^3(k^2+a^2)^2}\right). \tag{49}$$

We denote the direct correlation functions obtained using the Percus-Yevick closure and h written in the equation above as c'. It is easy to find

$$\begin{aligned}c_{000}'(k\rightarrow 0)&=c_{000}^{\text{sol}}(k\rightarrow 0)-\frac{a_3}{(4\pi)^{3/2}}\delta_0\left(1-\frac{a_1\rho_0}{2\pi\sqrt{4\pi}}+\frac{a_1^2\rho_0^2}{64\pi^3}\right)\\&\quad+\frac{a_4}{7(4\pi)^3}\delta_2\left(1+\frac{a_2\rho_0}{4\pi\sqrt{5\pi}}\int d\mathbf{k}_1\frac{1}{\mathbf{k}_1^2+a^2}+\frac{a_2^2\rho_0^2}{320\pi^2}\int d\mathbf{k}_1\frac{1}{(\mathbf{k}_1^2+a^2)^2}\right)\\&=c_{000}^{\text{sol}}(k\rightarrow 0)+\delta_0'\end{aligned} \tag{50}$$

$$c'_{220}(k\rightarrow 0)=c^{\mathrm{sol}}_{220}+\frac{a_4}{(4\pi)^{3/2})}\,\delta_0\left(1-\frac{a_1\rho_0}{2\pi\sqrt{4\pi}}+\frac{a_1^2\rho_0^2}{64\pi^3}\right)+\left(-a_3+\frac{2\sqrt{5}}{7}a_4\right)$$

$$\times\,\delta_2\left(1+\frac{a_2\rho_0}{4\pi\sqrt{5\pi}}\int d\mathbf{k}_1\,\frac{1}{\mathbf{k}_1^2+a^2}+\frac{a_2^2\rho_0^2}{320\pi^3}\int d\mathbf{k}_1\,\frac{1}{(\mathbf{k}_1^2+a^2)^2}\right)$$

$$=c^{\mathrm{sol}}_{220}(k\rightarrow 0)+\delta'_2\,.$$

Notice that both δ'_0 and δ'_2 contain an integral $\int d\mathbf{k}_1 1/(\mathbf{k}_1^2+a^2)^2\approx 1/\sqrt{a}$, which diverges as $a\rightarrow 0$. From the analysis above, it is easy to see that the stability limit within the Percus-Yevick approximation is numerically highly unstable. This might explain why there have been no numerical solutions, found in previous studies [4,12,13] that reach the stability limit, found in previous studies [4,12,13]. The arguments presented here are not confined to the isotropic-nematic phase transitions. They are completely general and should apply to other kinds of phase transitions (i.e., nematic-smectic phase transition) as well.

IV. COMPUTATIONAL RESULTS

We consider a separable model. In particular, we assume the Mayer function $f(r,\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=e^{-\beta u(r,\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')}-1$, can be written as

$$f_{\mathrm{tot}}(r,\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')=f_{\mathrm{iso}}(r)+f_{\mathrm{aniso}}(r)P_2(\cos(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')). \tag{51}$$

And we have chosen

$$f_{\mathrm{iso}}(r)=\exp\left\{-4\beta\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]\right\}-1, \tag{52}$$

which is the Mayer function for the standard Lennard-Jones potential, ϵ is the potential depth and σ the potential width. The anisotropic part of the potential is chosen to be

$$f_{\mathrm{aniso}}(r)=4\beta\epsilon\lambda\,\Theta(r-\sigma)\,\frac{(r-\sigma)}{r^6}, \tag{53}$$

where λ is a parameter and $\Theta(r-\sigma)$ is the step function. Some of the results are shown in Figs. 1 to 7. The parameters are written in terms of the reduced density and temperature which have standard definitions: $\rho_0^\star=N\sigma^3/V$ and $T^\star=k_BT/\epsilon$. All the results presented here are done with 1024 points with $\Delta r=0.02\sigma$ and λ is set to be 0.75.

Using the Lennard-Jones–like anisotropic interaction potentials, Luckhurst and Romano have investigated the isotropic-nematic transition with Monte Carlo simulations [14] and they *found* the system in nematic phase before it freezes. With the same model potentials using stability criterion and coexistence condition, Perera and co-workers [12,13] also calculated the transition temperature with mean spherical approximation, hypernetted chain closure, and the referenced hypernetted chain approximation. Results obtained from the hypernetted chain and referenced hypernetted chain approximations agree reasonably well with the Monte Carlo results. However, they found similar computation with the Percus-Yevick closure does *not* predict an isotropic-nematic transition.

We also studied the stability criterion with our model potential using the Percus-Yevick closure. When we restrict the system to be in the isotropic phase [angular dependent coefficients ρ_l in Eq. (9) for $l\neq 0$ are set to be zero], we found that we cannot obtain converged numerical results at or beyond the stability limit. In other words, using the stability criterion there is *no* solution that indicates an isotropic-nematic phase transition. For example, when $\rho_0^\star=0.79$ the stability criterion, Eq. (21), implies that the system has a phase transition when $c_{220}(k=0)$ exceeds 126.088. We have plotted $c_{220}(k=0)$ as a function of temperature $T^\star$ in Fig. 1. Notice that we stop getting converged numerical solutions around $T^\star=1.01$, before $c_{220}(k=0)$ exceeds the stability limit. This is consistent with what was found by Perera, Kusalik, and Patey [12].

However, with the Ward identity we can determine an orientationally dependent density $\rho(\Omega)$ self-consistently. And using this new approach we have obtained numerically converged solutions within the Percus-Yevick closure beyond the temperature where the curve in Fig. 1 stops. And we *found* the orientationally partially ordered nematic state. To estimate the transition temperature, we have tried to use either the solution obtained from a lower temperature or the one from a higher temperature as an initial guess to start a self-consistent run. More precisely, we have tried to gradually ''cool down'' the system from an isotropic state as well

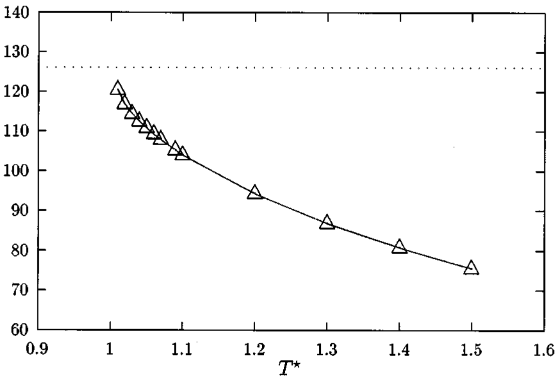

FIG. 1. If the probability density $\rho(\hat{\mathbf{\Omega}})$ is restricted to be rotationally invariant, we stop getting converged numerical solutions for the Ornstein-Zernike equation within the Percus-Yevick closure before the system reaches its stability limit (dashed line). We have plotted $c_{220}(k=0)$ as a function of the temperature for $\rho_0^\star=0.79$ and $\lambda=0.75$, $T^\star$ is in reduced unit defined in the text.

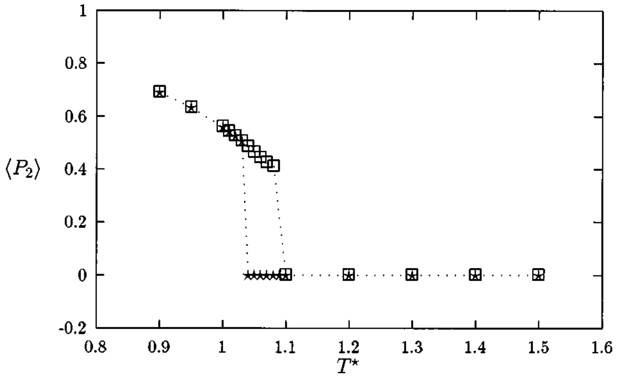

FIG. 2. Order parameter $\langle P_2(\cos\theta)\rangle$ as a function of the temperature for $\rho_0^\star = 0.79$ and $\lambda = 0.75$. Squares are the solutions obtained by “heating up” the system while the stars are the ones by “cooling down” the system. The dotted lines connect the two sets of the data points as a guide to the eyes. Notice the hysteresis close to the phase transition. The temperature $T^\star$ is again in reduced unit defined in the text.

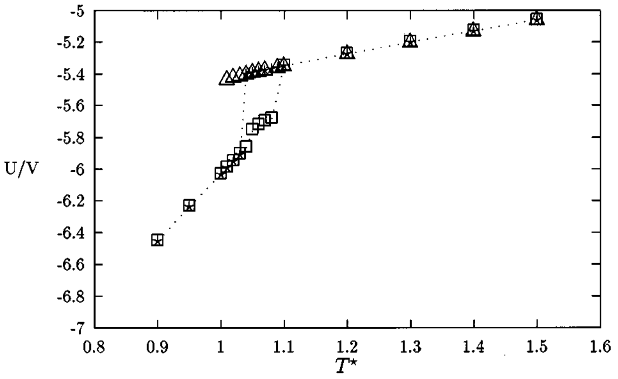

FIG. 4. Internal energy as a function of the temperature. Triangles are the results obtained if the system is restricted to be in isotropic phase. Squares are the solutions obtained by “heating up” the system while the stars are the ones by “cooling down” the system. Dotted lines connect the data points as a guide to the eyes. All relevant quantities are in reduced units defined in the text.

as gradually “heat up” the system from an ordered state. We found a narrow hysteresis in the region close to the phase transition. In Fig. 2 we show the order parameter as a function of the temperature. Crosses are the results we obtained by “cooling down” the system from an isotropic phase and the squares are the ones obtained by “heating up” the system from an orientationally partially ordered nematic phase. There is an abrupt change in the order parameter in both the “heating” and “cooling” processes, shown in Fig. 2 as discontinuities in both curves. This is due to the nature of the first order phase transition. The discontinuities occur at $T^\star = 1.04$ when “cooling” and at $T^\star = 1.09$ when “heating.” The isotropic-nematic phase transition temperature should be between 1.04 to 1.09 within the hysteresis region.

To compare to the data shown in Fig. 1, where the system is *restricted* to be in an isotropic phase, we again plotted $c_{220}(k=0)$ as a function of the temperature through both “heating” and “cooling” processes. In this case, however, the probability density of the system, $\rho(\hat{\boldsymbol{\Omega}})$ is allowed to adjust itself to satisfy the Ward identity. We show that as expected, the phase transition takes place before the system reaches its stability limit. The curve obtained from the “cooling” process in Fig. 3 overlaps with the curve shown in Fig. 1 from $T^\star = 1.04$ and above. Below this temperature, the system prefers to be in a partially ordered nematic phase. This is clearly shown in Fig. 4 where we have plotted the internal energy as a function of temperature. Below the “supercooling” temperature, the internal energy of the isotropic system (triangles) is much higher than that of the partially ordered nematic system. In Fig. 5 we show the pressure of system as temperature varies. Both internal energy and the pressure show a visible discontinuity around the phase transition.

When the continuous rotational symmetry in the system is broken and results in a partial orientational order, the susceptibility or $\langle h(k=0)\rangle_{\mathrm{rot},220}$ goes to infinity. To compare the correlation functions before and after the isotropic-nematic phase transition, we have plotted $\langle h(k)\rangle_{\mathrm{rot},220}$ at $T^\star = 1.05$ obtained through both the “heating” and “cooling” pro-

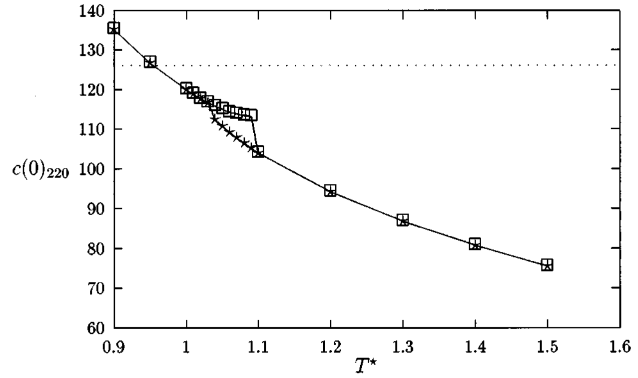

FIG. 3. Direct correlation function $c_{220}(k=0)$ as a function of the temperature for $\rho_0^\star = 0.79$ and $\lambda = 0.75$. The probability density is self-adjusted to satisfy the Ward identity, not restricted to be rotationally invariant as in the case of Fig. 1. Squares are the solutions obtained by “heating up” the system while the stars are the ones by “cooling down” the system. Lines connect the two sets of the data points as a guide to the eyes, $T^\star$ is in reduced unit defined in the text.

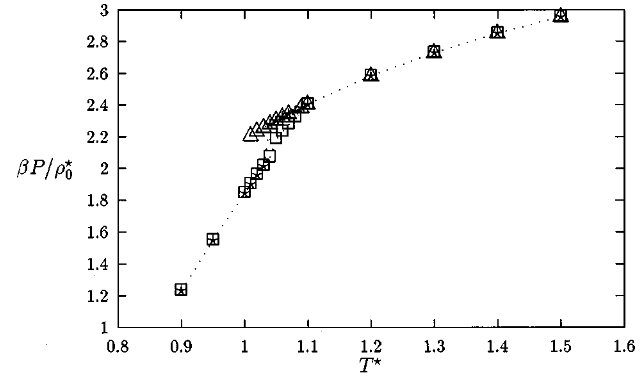

FIG. 5. Pressure as a function of the temperature. The parameters and symbols are the same as the ones used in Fig. 4. All relevant quantities are in reduced units defined in the text.

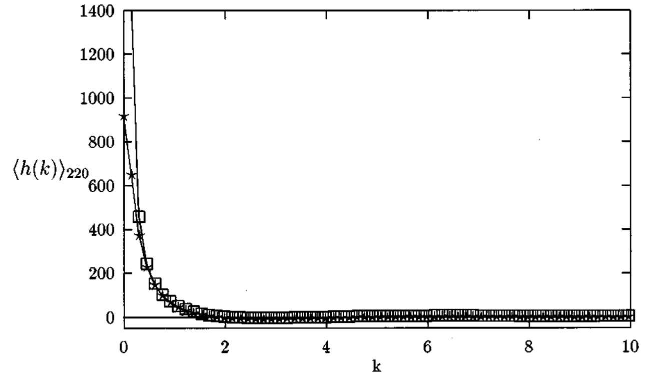

FIG. 6. The correlation function $\langle h(k)\rangle_{\mathrm{rot},220}$ at $T^\star=1.05$. As shown in Fig. 2, $T^\star=1.05$ is in the hysteresis region. The system can be found either in an isotropic phase (stars) or in a partially ordered nematic phase (squares) depending on the initial conditions. The figure shows that the singularity at $k\to0$ limit is present only when the system has a broken spontaneous rotational symmetry. k is in reduced unit defined in the text.

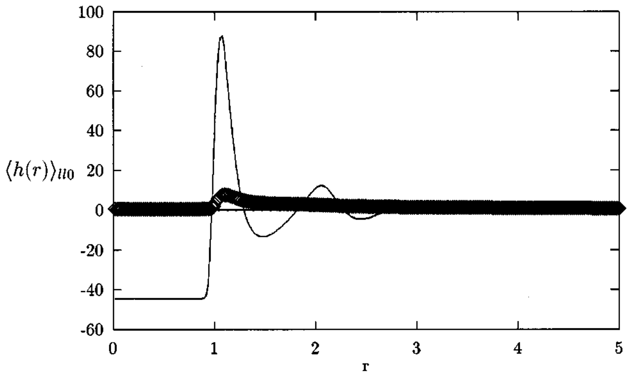

FIG. 7. Correlation function $\langle h(r)\rangle_{\mathrm{rot},ll0}$ for $\rho_0^\star=0.79$ and $\lambda=0.75$ at $T^\star=1.0$. The $l=0$ component is indicated by the solid line, the $l=2$ component is marked by squares, other components are too small to be seen in the figure. r is in reduced unit defined in the text.

cesses. As shown in Fig. 2 this temperature is in the hysteresis region. The solution obtained through ''heating'' (squares) shows that the system has partial orientational order while the solution obtained through ''cooling'' (stars) indicates that the system is in isotropic phase. We show in Fig. 6 that when the system has a partial orientational order, $\lim_{k\to0}\langle h(k)\rangle_{\mathrm{rot},220}$ approaches infinity, which demonstrates the presence of the Goldstone modes. When the system is in the isotropic phase, however, $\langle h(k)\rangle_{\mathrm{rot},220}$ in the $k\to0$ limit has a large but finite value. It is reasonable to expect that the susceptibility is large as the system approaches the stability limit. However, we must emphasize that to treat the Goldstone modes resulting from a spontaneous breaking of the rotational symmetry correctly, it is crucial [6] that the susceptibility diverges instead of having a finite value, and the Ward identity is the key to achieve that.

In Fig. 7 we show $\langle h(r)\rangle_{\mathrm{rot},ll0}$ as a function of r for $T^\star=1.0$, $\rho_0^\star=0.79$, and $\lambda=0.75$. The oscillations of the correlation function as a function of r are typical of a fluid with a highly repulsive core. Since the angular dependent part of the interaction is outside the core, in the core region $r<\sigma$, the total correlation function $h(r,\theta,\theta')$ is -1. In other words, as shown in Fig. 7 $\langle h(r)\rangle_{\mathrm{rot},000}=-4\pi\sqrt{4\pi}$ and $\langle h(r)\rangle_{\mathrm{rot},ll0}=0$ for $l>0$ in the core region. All components for $l\neq0$ vary on a relatively small scale compared to their $l=0$ counterparts and components for $l>2$ are too small to be seen in the figure. The $l=0$ component of the direct correlation function $c_{000}(r)$ shows a sharp rise inside the core and the $l=2$ component $c_{220}(r)$ has a sharp peak just outside the core. Both components die down rapidly outside the peak and the components $c_{ll0}(r)$ for $l>2$ are much smaller. These features are essentially the same as the ones we observed in an earlier model calculation [6] and therefore we shall not include these figures in the paper. With different parameters within reasonable range, the correlation functions retain the same qualitative features described above.

V. SUMMARY AND DISCUSSION

We have shown that a Ward identity that relates the one-particle probability density to the integral of the two-particle density in nematic fluids can be used in conjunction with the Ornstein-Zernike equation and Percus-Yevick closure to determine the one-particle probability density $\rho(\hat{\mathbf{\Omega}})$ and correlation functions self-consistently. This approach allows us to study the isotropic-nematic transition using an integral equation method without further approximations other than the closure itself. This is different from the early studies based on a truncated density functional theory, which showed [12,13] that one cannot find a numerical solution within the Percus-Yevick closure that indicates a phase transition. We give a qualitative general analysis that explains why the stability limit within the Percus-Yevick approximation is numerically highly unstable. Using this approach, we find the orientationally partially ordered nematic state, in which the total correlation function $h(k)$ diverges when $k\to0$, as expected for systems with the presence of the Goldstone modes. We also reported the order parameter and other thermodynamic properties of the system in both isotropic and orientationally partially ordered nematic phases.

In principle our approach can be used in other models with strong interparticle interactions. Our experience shows, however, that one needs a considerable amount of numerical effort for such calculations. Compared to similar calculations in which $\rho(\hat{\mathbf{\Omega}})$ is restricted to be isotropic in each self-consistent computational cycle two additional tasks must be accomplished. One is that $\rho(\hat{\mathbf{\Omega}})$ must be determined self-consistently, the other is that we must solve for director-direction dependent correlation function $h(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')$ first before calculating the rotationally invariant correlation function $\langle h(\mathbf{k},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}')\rangle_{\mathrm{rot}}$. In the process of pursuing a converged numerical solution, large deviations from the final solution might occur, especially close to the phase transition condition. In such a case, a large basis set is needed. For the model potential we used, a basis set with l up to 6 and 1024 radial mesh points is necessary. The anisotropic potential we used here is rather ''soft'' compared to, for example, the Lennard-Jones–like potential [14] or hard spherocylinder and hard ellipsoid potentials. We expect that a sharp anisotropic interacting potential in general leads to large fluctuations in the computational process. Therefore perhaps a rather large basis set and long computational time are required to obtain converged results. We attempted to use the anisotropic potential in the same form (also same parameters) as the ones used in Luckhurst and Romano's Monte Carlo work [14] and were not able to find a converged numerical solution within the Percus-Yevick approximation in the nematic phase. One possibility is that there is no numerical solution in this case, the other possibility is that more elaborate computational efforts are needed. It certainly would be helpful if it could be shown analytically whether there exists a solution given an interaction potential and parameters of the system.

So far we have only considered how to apply Percus-Yevick closure to systems with spontaneously orientational order, in which we have assumed that the direct correlation function c is short ranged. In order to take into account long-range fluctuations, important in studying isotropic-nematic phase transitions, it seems necessary to consider how one can correctly apply a more complete closure (such as hypernetted-chain approximation) in systems with spontaneously broken rotational symmetries.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation through ALCOM, the Advanced Liquid Crystalline Optical Materials Science and Technology Center through Grant No. DMR8920147 and by the Ohio Board of Regents.

---

[1] For a review, see for example, J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, Boston, 1986).

[2] P. H. Fries and G. N. Patey, J. Chem. Phys. **82**, 429 (1985); **85**, 7307 (1986); A. Perera, P. G. Kusalik, and G. N. Patey, *ibid.* **87**, 1295 (1987); **87**, 5969E (1988).

[3] A. Perera and G. N. Patey, J. Chem Phys. **89**, 5861 (1988); **91**, 3045 (1989).

[4] J. M. Caillol and J. J. Weis, J. Chem. Phys. **90**, 7403 (1989).

[5] J. M. Caillol, J. J. Weis, and G. N. Patey, Phys. Rev A **38**, 4772 (1988); J. M. Caillol and J. J. Weis, J. Chem. Phys. **92**, 3197 (1990).

[6] H. Zhong and R. G. Petschek, Phys. Rev. E **51**, 2263 (1995).

[7] J. E. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958).

[8] J. G. Gay and B. J. Berne, J. Chem. Phys. **74**, 3316 (1981).

[9] H. Workman and M. Fixman, J. Chem. Phys. **58**, 5024 (1973).

[10] See, for example, M. Baus, J. Stat. Phys. **48**, 1129 (1987).

[11] J. Stecki and A. Kloczkowski, J. Phys. C **3**, 40 (1979); Mol. Phys. **51**, 42 (1981).

[12] A. Perera, G. N. Patey, and J. J. Weis, J. Chem. Phys. **89**, 6941 (1988).

[13] A. Perera, P. G. Kusalik, and G. N. Patey, Mol. Phys. **60**, 77 (1987).

[14] G. R. Luckhurst and S. Romano, Proc. R. Soc. London A **373**, 111 (1980).

[15] E. Brezin and D. J. Wallace, Phys. Rev B **7**, 1967 (1973); L. Schäfer and H. Horner, Z. Phys. B **29**, 251 (1978).

[16] L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1972).

[17] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon, Oxford, 1984).