

Percus-Yevick approximation for fluids with spontaneous partial order

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In this paper we present a Percus-Yevick approximation which can be applied to a system in which a phase transition has occurred, resulting in spontaneous breaking of a continuous symmetry and partial spontaneous order. Previous methods have allowed calculations only for molecules which are in the isotropic phase or all perfectly aligned. For the orientationally disordered isotropic phase, our technique gives identical results to previous work. The appropriate treatment for systems with spontaneously broken continuous symmetry has been appreciated for some time in the magnetic and field theoretic literature. We adapt these treatments to the anisotropic fluid system with a diagrammatic implementation of a Ward identity. This technique is demonstrated on a simplified model of a nematic liquid crystal in which molecules can move in three dimensions and have a two-dimensional "orientation" interaction through a pair potential which depends only on the molecular separation and relative orientation. We solve the Ornstein-Zernike equation with the modified Percus-Yevick closure for the pair correlation functions of the orientationally anisotropic system. Our equations correctly result in Goldstone modes, characteristic of systems with spontaneously broken symmetries.

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I. INTRODUCTION

The pair correlation function plays a very important role in physics. It is measurable by scattering experiments and virtually all thermodynamic properties can be expressed in terms of it if the particles in systems interact through pairwise forces. Integral-equation methods, which generally involve solving the Ornstein-Zernike equation with the Percus-Yevick or hypernetted-chain closure approximation, have led to reasonably good results for the pair correlation functions of classical simple liquids [1]. More recently, these methods have been used to study the structural properties of the isotropic fluids of hard nonspherical particles [2], and spherical and nonspherical isotropic dipolar fluids [3, 4]. Using the correlation functions obtained in the isotropic phase, the isotropic-nematic phase transition is also studied [4, 5] by applying the stability criterion and the second-order density functional theory. For anisotropic fluids, only cases where the molecules are all perfectly aligned in one particular direction have been studied [6]. Our goal is to extend the integral-equation method to systems such as nematic liquid crystals, having partial spontaneous order as a consequence of sufficiently strong interparticle interactions.

Spontaneous symmetry breaking is particularly well studied in magnetic systems below the critical temperature. The Hamiltonian in some model n -dimensional ferromagnets is invariant under the group of rotations in spin space, $O(n)$ if the external field and the spins are simultaneously rotated. When the field is zero any spontaneous magnetization breaks a continuous symmetry in such a ferromagnet in which $n \geq 2$. The direction of the magnetization is not predetermined and there exist spin wave excitations, or Goldstone modes, which rotate the direction of the magnetization without any energy cost. Therefore in this and other systems with spontaneously

broken continuous symmetries some susceptibilities are infinite.

The invariance of the Hamiltonian leads to the so-called Ward identities [7, 8]. The study of the singular behavior, induced by the Goldstone modes, in equation of state and susceptibilities near the coexistence curve has attracted theoretical interest for many years. Analogously, the essential feature of the Goldstone modes in a nematic fluid system is that under a uniform rotation the system is unchanged. This implies that the susceptibility (or density response function) is infinite in the limit of zero wave vector. As typical (e.g., Ornstein-Zernike) methods calculate the inverse susceptibility, it seems clear that careful treatment of these modes is prudent as small errors in the correct answer, resulting in a negative rather than zero inverse susceptibility, will clearly lead to unphysical results. We show that a Ward identity, which relates the one-point probability density to an integral of the two-point correlation function, can be implemented with a modified version of the Percus-Yevick approximation [9] and correctly results in exactly zero inverse susceptibility for the Goldstone modes. We illustrate our theory first with a simple non-self-consistent calculation which demonstrates the relationship between the Ward identity and the Goldstone modes. We then apply the method using the modified Percus-Yevick approximation in which the pair correlation functions are determined self-consistently given an interaction potential between the two molecules.

Previous studies have suggested [4, 5] that the Percus-Yevick approximation does not lead to isotropic-nematic phase transitions. This conclusion was drawn by substituting the direct correlation functions of the *isotropic* state obtained from solving the Ornstein-Zernike equation with the Percus-Yevick closure into a stability criterion or into a truncated density functional formula of the second order. We believe a more direct and more

reliable way to study the isotropic-nematic phase transition is through examining the probability functions of both the isotropic and the nematic phase directly. As far as we know the single-particle probability function or the correlation function of a nematic system with a partial order has never been obtained using the integral-equation method in any of the previous studies. In this paper, we show how one can apply a modified Percus-Yevick closure to self-consistently determine the probability function and the correlation function of such a partially ordered system, resulting from a spontaneous broken symmetry *after* a phase transition has occurred. Only simple model calculations are illustrated here. Phase transition studies with Percus-Yevick and/or hypernetted-chain approximations will be conducted in more realistic model calculations in the future. In our simple model calculations we assume that the molecules, having axial symmetry, move in three dimensions yet their orientations are confined to a plane, i.e., the orientation directions can be specified in terms of an angle θ with respect to a fixed axis, rather than the more general case where the orientation must be specified by a set of Euler angles, $\Omega = (\theta, \phi, \chi)$. Moreover, the pair potential $u(r, \theta - \theta')$ is assumed to depend only on the spatial separation between the molecules, r , and their relative orientations, $\theta - \theta'$.

The paper is organized as follows. In the next section we describe a Ward identity in a nematic fluid system with spontaneously broken symmetry and discuss the modified Percus-Yevick closure. Section III contains the model calculations and Sec. IV is a summary.

II. THEORY

A. Definitions

We follow the standard definitions [10] for the n -particle reduced probability densities and correlation functions. Assuming the spatial coordinate and the orientation are the only relevant variables to specify a particle, the single-particle probability density $\rho(1)$ can be written as

$$\rho(1) = \rho(\vec{r}, \Omega) = \sum_i \langle \delta(\vec{r} - \vec{r}_i) \delta(\Omega_i - \Omega) \rangle, \quad (1)$$

where \vec{r}_i and Ω_i are the spatial coordinate and the orientation of the i th particle, and $\langle \rangle$ stands for thermal average. Specifically, in a nematic liquid crystal the single-particle probability density ρ is only a function of the orientation of the particles, Ω .

The two-particle density $\rho^{(2)}(1, 2)$ is the probability of finding two particles \vec{r} apart (translational symmetry is assumed) with orientations Ω and Ω' , respectively. Explicitly, it is defined as

$$\begin{aligned} \rho^{(2)}(1, 2) &= \rho^{(2)}(\vec{r}, \Omega, \Omega') \\ &= \sum_{i \neq j} \langle \delta(\vec{r}_i) \delta(\Omega_i - \Omega) \delta(\vec{r}_j - \vec{r}) \delta(\Omega_j - \Omega') \rangle. \end{aligned} \quad (2)$$

The total correlation function, $h(1, 2)$, or $h(\vec{r}, \Omega, \Omega')$ is defined to be

$$h(1, 2) = h(\vec{r}, \Omega, \Omega') = \rho^{-1}(\Omega) \rho^{-1}(\Omega') \rho^{(2)}(\vec{r}, \Omega, \Omega') - 1. \quad (3)$$

The direct correlation function $c(1, 2)$ is defined through the Ornstein-Zernike equation,

$$h(1, 2) = c(1, 2) + \int d3c(1, 3)\rho(3)h(3, 2). \quad (4)$$

To compute the correlation functions, it is more convenient to write the Ornstein-Zernike equation in Fourier space,

$$\begin{aligned} h(\vec{k}, \Omega, \Omega') &= c(\vec{k}, \Omega, \Omega') \\ &+ \int d\Omega_1 c(\vec{k}, \Omega, \Omega_1) \rho(\Omega_1) h(\vec{k}, \Omega_1, \Omega'). \end{aligned} \quad (5)$$

For simple isotropic fluids, $\rho(\Omega) = \rho_0$, the above Ornstein-Zernike equation is often solved in conjunction with the Percus-Yevick or hypernetted-chain closure for the correlation functions. To understand the closures and later implement the Ward identity, it is useful to briefly review the Ursell-Mayer perturbation expansion [11, 12] in diagrammatic terms.

We follow the notations used in Ref. [1] and review only basic concepts here. In statistical mechanics, diagrams are often used to conveniently represent complicated and many-dimensional integrals over the particle coordinates which appear in the pair correlation functions and many other important physical quantities. They are commonly drawn as white circles (root points), black circles (field points), and bonds. In the following discussion, if not specified otherwise, a factor of $\rho(1)$ is associated with each black circle and a factor $f(1, 2) = \exp[-\beta u(1, 2)] - 1$ is associated with each bond, where $\beta = 1/k_B T$ is the inverse temperature and $u(1, 2)$ is the interparticle potential. A circle can also be a (1) connecting circle: removal of such a circle causes the diagram to become disconnected; (2) articulation circle: removal of such a circle causes the diagram to separate into two or more parts of which one of them contains no white circle; or (3) nodal circle: one through which all paths between two particular white circles pass. A diagram is called irreducible if it is free of articulation circles. A bridge diagram is free of nodal circles and contains two white circles which are not an articulation pair and are not connected by a bond. For example, the direct correlation function $c(1, 2)$ is the sum of the diagrams that consist of two white circles, 1 and 2, black ρ circles, f bonds, and which are free of connecting circles. Some of the diagrams in $c(1, 2)$ which are allowed in both Percus-Yevick and hypernetted-chain approximations are shown in Fig. 1(a). The total correlation function $h(1, 2)$ is the sum of all simple diagrams that consist of two white circles, 1 and 2, black ρ circles, f bonds, and which are free of articulation circles. Approximations are usually made when calculating $h(1, 2)$. If all the bridge diagrams [a typical bridge diagram is shown in Fig. 1(b)] are ignored, one obtains the hypernetted-chain closure,

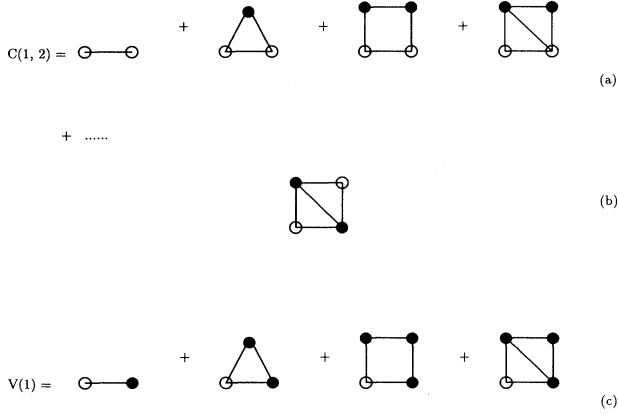


FIG. 1. (a) Some diagrams in the direct correlation function $c(1, 2)$ which are included in both Percus-Yevick and hypernetted-chain approximations. (b) A typical bridge diagram which is excluded in Percus-Yevick or hypernetted-chain closure. (c) The function $v(1)$, which is defined in the text, in terms of diagrams. (a) and (c) also illustrate that a functional derivative of v with respect to ρ in the Ward identity is simply to replace any single black circle in (c) with a white one.

$$h(1, 2) = \beta u(1, 2) + c(1, 2) + \ln[h(1, 2) + 1]. \quad (6)$$

Further, if all other diagrams without direct links between the two white circles are omitted, the Percus-Yevick closure,

$$c(1, 2) = f(1, 2)[1 + h(1, 2) - c(1, 2)], \quad (7)$$

is obtained. These (and other) closures combined with the Ornstein-Zernike equation have been solved for isotropic fluids as well as fluids with perfect alignment. We show in the following how we can extend the Percus-Yevick approximation to fluids with partial orientational order due to spontaneous symmetry breaking.

B. Ward identity

In a nematic system with spontaneously broken symmetries the Goldstone modes are present. In such a system a simple uniform rotation of the direction of the directors does not change the energy of the system. Therefore the susceptibility is infinite at the $\vec{k} \rightarrow 0$ limit. As the susceptibility and the pair correlation function are closely related [1], this implies that the total correlation function $h(\vec{k}, \Omega, \Omega')$ also becomes infinite as $\vec{k} \rightarrow 0$. The implication for the direct correlation function $c(\vec{k}, \Omega, \Omega')$ can be examined through the Ornstein-Zernike equation. It is convenient to define $H(\vec{k}, \Omega, \Omega') = \rho^{1/2}(\Omega)\rho^{1/2}(\Omega')h(\vec{k}, \Omega, \Omega')$ and $C(\vec{k}, \Omega, \Omega') = \rho^{1/2}(\Omega)\rho^{1/2}(\Omega')c(\vec{k}, \Omega, \Omega')$. The Ornstein-Zernike equation, Eq. (5), can then be written in a symmetric form,

$$H(\vec{k}, \Omega, \Omega') = C(\vec{k}, \Omega, \Omega') + \int d\Omega_1 C(\vec{k}, \Omega, \Omega_1)H(\vec{k}, \Omega_1, \Omega'). \quad (8)$$

Taking both H and C as integral operators, symbolically we can write $h \sim H \sim (1 - C)^{-1}C$. Clearly, to guarantee that the Goldstone modes are treated correctly, so that $h(\vec{k} \rightarrow 0, \Omega, \Omega') \rightarrow \infty$, we need to ensure that the operator C has a unit eigenvalue.

Mathematically, the eigenequation of the integral operator C is written as

$$\int d\Omega_1 C(\vec{k}, \Omega, \Omega_1)\Psi_i(\vec{k}, \Omega_1) = \lambda_i(\vec{k})\Psi_i(\vec{k}, \Omega). \quad (9)$$

This is a homogenous Fredholm equation of the second kind [13]. The kernel $C(\vec{k}, \Omega, \Omega_1)$ defined above is real and symmetric with respect to Ω . Hilbert-Schmidt theory has shown that if the kernel is real and symmetric, the integral equation has real eigenvalues λ_i and the corresponding eigenfunctions are orthogonal, as for other Hermitian operators. These eigenfunctions form a complete set, in particular, the kernel can be written as $C(\vec{k}, \Omega, \Omega_1) = \sum_i \lambda_i(\vec{k})\Psi_i(\vec{k}, \Omega)\Psi_i(\vec{k}, \Omega_1)$. If one also expands $H(\vec{k}, \Omega, \Omega')$ in terms of the same basis set, substitutes in Eq. (8), and uses the orthonormal relation for the basis functions, the Ornstein-Zernike equation can be written as

$$H(\vec{k}, \Omega, \Omega') = \sum_i \frac{\lambda_i(\vec{k})}{1 - \lambda_i(\vec{k})} \Psi_i(\vec{k}, \Omega)\Psi_i(\vec{k}, \Omega'). \quad (10)$$

From the above equation it is easy to see that if C has a unit eigenvalue in the $\vec{k} \rightarrow 0$ limit, $\lambda_i(\vec{k} \rightarrow 0) \rightarrow 1$, the correlation function $h(\vec{k}, \Omega, \Omega')$ is infinite.

We refer to the eigenvector corresponding to unit eigenvalue as Ψ . Since the Goldstone modes are the direct consequence of the spontaneously broken rotational symmetry, this eigenvector must be simply related to ρ . Moreover, we can heuristically argue the functional dependence of Ψ on ρ . In the equilibrium system we are considering, the single-particle probability function can be written as $\rho(\vec{r}, \Omega) = \rho(\hat{\Omega} \cdot \hat{n}(\vec{r}))$, where $\hat{n}(\vec{r})$ is the direction of the director at position \vec{r} and $\hat{\Omega}$ is the unit vector oriented in direction Ω . The two-particle reduced density, $\rho^{(2)}(\vec{r}, \Omega, \Omega')$, defined in Sec. II A, is the probability of finding two particles \vec{r} apart and oriented in directions Ω and Ω' , respectively. In the system we are considering, it is proportional to $\langle \rho(\hat{\Omega} \cdot (\hat{n} + \delta\hat{n}(\vec{r}_1)))\rho(\hat{\Omega}' \cdot (\hat{n} + \delta\hat{n}(\vec{r}_2))) \rangle$, where \hat{n} is the director of the nematics, $\delta\hat{n}(\vec{r}_1)$, is the fluctuation of the director at position \vec{r}_1 and $\vec{r}_1 - \vec{r}_2 = \vec{r}$. In the state corresponding to the Goldstone modes, the director varies slowly in space, $\rho(\hat{\Omega} \cdot (\hat{n} + \delta\hat{n}(\vec{r}_1))) \approx \rho(\Omega) + \frac{\partial \rho}{\partial \hat{\Omega}} \hat{\Omega} \cdot \delta\hat{n}(\vec{r}_1) \sim \rho(\Omega) + \delta\rho(\Omega)$, where $\delta\rho(\Omega)$ is the change of the density $\rho(\Omega)$ due to a rotation of the director. Taking the thermal average, the two-particle density becomes $\rho^{(2)}(\vec{r}, \Omega, \Omega') \sim \rho(\Omega)\rho(\Omega') + \delta\rho(\Omega)\delta\rho(\Omega')$. From the definition of the total correlation function, Eq. (3), we obtain $h(\vec{r}, \Omega, \Omega') \sim \rho^{-1}(\Omega)\rho^{-1}(\Omega')\delta\rho(\Omega)\delta\rho(\Omega')$. Using Eq. (10), we therefore expect the eigenvector Ψ which

corresponds to the Goldstone modes to be proportional to $\rho^{-1}(\Omega)\delta\rho(\Omega)$.

In order to realize these physical results mathematically we introduce a Ward identity in nematic systems with spontaneously broken symmetries. First we examine the one-point probability density, $\rho(1)$. Using the definition Eq. (1), one can express $\rho(1)$ in terms of the grand partition function Ξ , $\rho(1) = z(1)\delta\ln\Xi/\delta z(1)$, where z is the activity, related to the chemical potential μ and the thermal wavelength λ_T by $z = \lambda_T^{-3}\exp(\beta\mu)$. In diagrammatic nomenclature, $\rho(1)$ is the sum of $z(1)$ plus all simple connected diagrams consisting of one white circle and one or more black z circles and f bonds. Star product rules and topological reduction can be applied to these connected diagrams and lead to the following important conclusion:

$$\ln[\rho(1)/z(1)] = v(1), \quad (11)$$

where $v(1)$ is the sum of all simple irreducible diagrams consisting of one white circle, one or more black ρ circles, and f bonds. We show some of the possible diagrams in $v(1)$ in Fig. 1(c). In a nematic system, $\rho(1)$ or $v(1)$ is only a function of Ω , and we write

$$\rho(\Omega) = \rho_0 e^{v(\Omega)}/Z, \quad (12)$$

where the normalization coefficient Z ensures that $\int d\Omega \rho(\Omega) = \rho_0$. Using the above equation, it is straightforward to write

$$\delta\rho(\Omega) = \rho(\Omega)\delta v(\Omega). \quad (13)$$

The relation between the one-particle probability density and the two-particle density is obtained by simply examining the variations of $v(\Omega)$ as a functional of ρ . In terms of diagrams, the functional derivative $\delta v(\Omega)/\delta\rho(\Omega')$ is the sum of those diagrams of $v(\Omega)$ where a black ρ circle is replaced by a white circle [refer to Figs. 1(a) and 1(c)]. In other words, $\delta v(\Omega)/\delta\rho(\Omega')$ is the sum of all simple diagrams with two white circles, possible black ρ circles, f bonds, and which are free of connecting circles. One can show that the sum of this group of diagrams is indeed the two-particle direct correlation function $c(\vec{k} \rightarrow 0, \Omega, \Omega')$. The relation

$$\frac{\delta v(\Omega)}{\delta\rho(\Omega')} = c(\vec{k} \rightarrow 0, \Omega, \Omega') \quad (14)$$

can be regarded as a special case of the definition of the direct correlation function, $c(1,2) = \delta v(1)/\delta\rho(2)$, which is also equivalent to the Ornstein-Zernike equation, Eq. (4). Equation (14) is a typical Ward identity which relates the one-particle function $\rho(\Omega)$ to the two-particle correlation function $c(k, \Omega, \Omega')$. Using Eqs. (12), (13), and the Ward identity, Eq. (14), it is easy to show that, provided ρ depends on Ω so that $\delta\rho(\Omega)$, changes in ρ due to a rotation of the director, is not zero that there is an eigenvector Ψ with unit eigenvalue in Eq. (9) and $\Psi = z\rho^{-1}(\Omega)\delta\rho(\Omega)$, where z is a normalization coefficient.

To summarize, through the Ward identity we find that the integral operator C does have a unit eigenvalue in

the $\vec{k} \rightarrow 0$ limit. Its corresponding eigenvector is proportional to $\delta\rho(\Omega)/\rho(\Omega)$, where $\delta\rho(\Omega)$ is the change of the density $\rho(\Omega)$ due to a rotation of the director. Therefore the singularity in $H(\vec{k}, \Omega, \Omega')$, or $h(\vec{k}, \Omega, \Omega')$ as $\vec{k} \rightarrow 0$ due to the Goldstone modes can be treated correctly with proper implementation of the Ward identity.

C. Percus-Yevick closure

In this paper we solve the Ornstein-Zernike equation only with the Percus-Yevick closure. In this case the direct correlation function c is expected to be short ranged and complications with long-range fluctuations known to be important in systems with spontaneously broken continuous symmetries and to require careful treatment are absent. We expect $h \sim 1/k^2$ in the $k \rightarrow 0$ limit, the same as the transverse susceptibility in ferromagnetic systems [7, 8].

To ensure the consistency of the closure scheme with the Ward identity, care must be taken. We will show through the diagrammatic language that the correlation function h in the commonly used Percus-Yevick closure must be replaced by its rotational average $\langle h \rangle_{rot}$. The rotational average on h is physically related to the rotational invariance in these systems. To understand this physically, it is worthwhile to briefly review the original paper on the Percus-Yevick approximation [9]. In that paper, Percus and Yevick analyzed a classical many-body system by the use of the collective coordinates in which the potential energy is approximated by an effective potential in terms of force constants for phonon oscillations. Using the assumption of the separability of the collective coordinates, they derived the Percus-Yevick closure and directly related the correlation function h in the closure and the Ornstein-Zernike equation to the effective potential. In a system with spontaneously broken symmetries the underlying effective potential should still be rotationally invariant. Therefore the correlation function entering the Percus-Yevick closure must be rotationally invariant.

Diagrammatically, the Ward identity, Eq. (14), is an *exact* relation between the one-point probability density and the two-point correlation function. However, the Percus-Yevick closure only includes part of all of the possible diagrams of $c(1,2)$, as reviewed earlier in Sec. II B. It is easy to see that naive extension of the Percus-Yevick closure commonly used in systems without a spontaneous partial order does not satisfy the Ward identity. For example, in Fig. 1(c) we illustrate a few possible diagrams in the one-point density function $v(\Omega)$. The diagrammatic rule for a functional derivative with respect to ρ in the Ward identity is simply to replace any (single) black circle with a white one. Therefore one possible diagram derived from the last diagram in Fig. 1(c) is the bridge diagram shown in Fig. 1(b). This diagram is clearly excluded in the Percus-Yevick closure. To make the closure consistent with the Ward identity, rotational average on the correlation functions is needed. We define $\langle h(\vec{r}, \Omega, \Omega') \rangle_{rot}$ to be the rotational average of the correlation function $h(\vec{r}, \Omega, \Omega')$, and the modified Percus-Yevick closure is written as

$$c(\vec{r}, \Omega, \Omega') = f(\vec{r}, \Omega, \Omega')[1 + \langle h(\vec{r}, \Omega, \Omega') \rangle_{rot} - c(\vec{r}, \Omega, \Omega')]. \quad (15)$$

Once this rotational average has been performed the Ward identity is satisfied, at least for $\delta\rho$ proportional to $\delta\rho_{rot}$, changes in ρ which can be realized by rotations. Fortunately it is precisely such changes which are relevant to appropriate behavior with Goldstone modes. Since the Ursell-Mayer function $f(r, \Omega, \Omega')$ is rotationally invariant, $c(r, \Omega, \Omega')$ is also rotationally invariant in Eq. (15). We demonstrate the correct treatment of the Goldstone modes with the Ward identity and show how one can solve for the correlation functions with the modified Percus-Yevick closure using model calculations.

III. MODEL CALCULATIONS

In order to illustrate the principles without unnecessary mathematical complications, in the models we assume the orientations of the molecules are confined in a plane, which can be specified with a single variable θ about a fixed axis. The interaction potential is only a function of the spatial separation r (in three dimensions) and the relative orientation $\theta - \theta'$.

A. Model I

We first illustrate the relationship between Goldstone modes and the Ward identity using a simple, non-self-consistent model which can be solved analytically. Assume a very weak but possibly long-ranged interaction potential such that the direct correlation function $c(r, \theta - \theta') \approx f(r, \theta - \theta')$, where $f(r, \theta - \theta')$ is the Ursell-Mayer function mentioned above. For simplicity, we assume

$$f(r, \theta - \theta') = \frac{e^{-\epsilon r}}{4\pi r} [a + b \cos^2(\theta - \theta')]. \quad (16)$$

Its Fourier transform $f(k, \theta - \theta')$, or $c(k, \theta - \theta')$ can be readily obtained,

$$c(k, \theta - \theta') = \frac{1}{k^2 + \epsilon^2} [a + b \cos^2(\theta - \theta')]. \quad (17)$$

Since the direct correlation function c is a function of $\theta - \theta'$, the Ward identity, Eq. (14), can be simplified and written as

$$v(\theta) = \int d\theta' c(k \rightarrow 0, \theta - \theta') \rho(\theta'). \quad (18)$$

Using Eqs. (12), (17), and (18), we can solve for the probability density $\rho(\theta)$,

$$\rho(\theta) = \frac{\rho_0}{2\pi I_0(A)} e^{A \cos 2\theta}, \quad (19)$$

where $I_n(x)$ is the modified Bessel function and A satisfies the relation

$$A = \frac{\rho_0 b I_1(A)}{2\epsilon^2 I_0(A)}. \quad (20)$$

Notice that the above equation only has solutions when

$\rho_0 b \epsilon^{-2} > 1$. This is essentially the condition to have an isotropic-nematic phase transition for this model. Equation (19) can be substituted into the Ornstein-Zernike equation to solve for the pair correlation function h . As we consider the particles are confined to be oriented in a plane, we can expand both c and h in terms of sin and cos functions and obtain h by solving an integral equation which is approximated numerically by a finite matrix inversion, or by solving a Fredholm eigenvalue problem. We illustrate the matrix inversion technique in Sec. III B and here we use the eigenvalue method. The matrix inversion technique is faster than the eigenvalue method, yet the eigenvalue calculation is clearer. Both techniques yield the same results.

As mentioned above in Sec. II B, for convenience we define

$$H(k, \theta, \theta') = \rho^{1/2}(\theta) \rho^{1/2}(\theta') h(k, \theta, \theta') \quad (21)$$

and

$$C(k, \theta, \theta') = \rho^{1/2}(\theta) \rho^{1/2}(\theta') c(k, \theta, \theta'), \quad (22)$$

the Ornstein-Zernike equation

$$h(k, \theta, \theta') = c(k, \theta, \theta') + \int d\theta_1 c(k, \theta, \theta_1) \rho(\theta_1) h(k, \theta_1, \theta') \quad (23)$$

can then be written as

$$H(k, \theta, \theta') = C(k, \theta, \theta') + \int d\theta_1 C(k, \theta, \theta_1) H(k, \theta_1, \theta'), \quad (24)$$

and it is symmetric with respect to interchange of the variables θ and θ' . Defining the eigenvalues and eigenvectors of the operator $C(k, \theta, \theta')$ to be $\lambda_i(k)$ and $\Psi_i(k, \theta)$,

$$\int d\theta_1 C(k, \theta, \theta_1) \Psi_i(k, \theta_1) = \lambda_i(k) \Psi_i(k, \theta), \quad (25)$$

we can write $H(k, \theta, \theta')$ as

$$H(k, \theta, \theta') = \sum_i \frac{\lambda_i(k)}{1 - \lambda_i(k)} \Psi_i(k, \theta) \Psi_i(k, \theta') \quad (26)$$

according to Eq. (24).

We define the coordinate system such that the axis is along the nematic director \hat{n} . Since in nematic systems there is no difference between the direction \hat{n} and $-\hat{n}$, the relation $C(k, \theta, \theta') = C(k, -\theta, -\theta')$ holds. Therefore its eigenfunction $\Psi(k, \theta)$ must be even, $\Psi^{(e)}(k, \theta) = \Psi^{(e)}(k, -\theta)$ or odd, $\Psi^{(o)}(k, \theta) = -\Psi^{(o)}(k, -\theta)$. As $d\rho(\theta)/d\theta \sim \sin 2\theta$, to examine the Goldstone modes we look at the odd solution in particular. Using Eqs. (17), (19), (22), and (25), it is easy to see that if $\lambda \neq 0$, $\Psi^{(o)}(k, \theta) \sim e^{\frac{A}{2} \cos 2\theta} \sin 2\theta$. With the normalization factor the odd solution is written as

$$\Psi^{(o)}(k, \theta) = -\sqrt{\frac{A}{2\pi I_1(A)}} e^{\frac{A}{2} \cos 2\theta} \sin 2\theta \quad (27)$$

and its corresponding eigenvalue is

$$\lambda^{(o)}(k) = \frac{\epsilon^2}{k^2 + \epsilon^2}. \quad (28)$$

Substituting Eqs. (27) and (28) into Eq. (26) and using Eq. (21), we find the odd part of the solution contributes a term $\frac{b}{2} \sin 2\theta \sin 2\theta' / k^2$ in $h(k, \theta, \theta')$. This is the solution for the Goldstone modes. It is easy to check that

$$\begin{aligned} h(k, \theta, \theta') = & \frac{b}{2k^2} \sin 2\theta \sin 2\theta' + \frac{b(a+2b)(2k^2+4\epsilon^2-b\rho_0)}{2b(k^2+\epsilon^2-a\rho_0)(2k^2+4\epsilon^2-b\rho_0)-4(b+2a)\epsilon^4 A^2} \\ & - \frac{b(2a+b)\epsilon^2 A}{b(k^2+\epsilon^2-a\rho_0)(2k^2+4\epsilon^2-b\rho_0)-2(b+2a)\epsilon^4 A^2} (\cos 2\theta + \cos 2\theta') \\ & + \frac{b^2(2k^2+4\epsilon^2-b\rho_0)}{2b(k^2+\epsilon^2-a\rho_0)(2k^2+4\epsilon^2-b\rho_0)-4(b+2a)\epsilon^4 A^2} \cos 2\theta \cos 2\theta'. \end{aligned} \quad (29)$$

The first term is the contribution of the Goldstone modes. This simple analytic model shows that the Goldstone modes can be treated correctly with the use of the Ward identity. We have also performed a self-consistent calculation with the modified Percus-Yevick closure using the same Ursell-Mayer function, Eq. (16). These calculations were performed in the weak, long-range potential limit in which self-consistency is not expected to make a significant change in the results. We confirmed this and will not present detailed results here.

B. Model II

The potential for model II consists of the Lennard-Jones potential and an additional angular dependent potential outside of the "core" region. In other words, we assume the Ursell-Mayer function in the form of

$$\begin{aligned} f(r, \theta - \theta') = & \exp \left\{ -4\beta\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \right\} - 1 \\ & + b\Theta(r - \sigma) \frac{(r - \sigma)}{r^6} \cos^2(\theta - \theta'), \end{aligned} \quad (30)$$

where the $\Theta(r - \sigma)$ function indicates that the angular dependent part of the potential is only effective outside the "core" region σ . When $b = 0$ the system is simply a Lennard-Jones fluid. To test our programs, we have solved the Ornstein-Zernike equation with the Percus-Yevick closure and computed the pair correlation function $h(r)$, inverse compressibility $\beta\partial p/\partial\rho = 1/[1+\rho h(0)]$, and other related quantities for the simple Lennard-Jones fluids. These quantities all agree well with others' results [14].

In systems where the orientations of the molecules are confined in two dimensions, the modified Percus-Yevick closure, Eq. (15), can be written as

$$\begin{aligned} c(r, \theta - \theta') = & f(r, \theta - \theta') \\ & \times [1 + \langle h(r, \theta - \theta') \rangle_{rot} - c(r, \theta - \theta')], \end{aligned} \quad (31)$$

where $\langle h(r, \theta - \theta') \rangle_{rot}$ is the rotational average of $h(r, \theta, \theta')$ defined as

the eigenvalue corresponding to the Goldstone modes $\lambda^{(o)}(k \rightarrow 0)$ is unity and $h(k \rightarrow 0, \theta, \theta')$ indeed is proportional to $1/k^2$. Also using Eqs. (19) and (27), one can verify that the eigenvector is proportional to $\rho^{-1}(\theta)\partial\rho(\theta)/\partial\theta$ as predicted by our theory. Combining both the even and odd eigenvalue solutions for Eq. (25), we obtain the total correlation function,

$$\langle h(r, \theta - \theta') \rangle_{rot} = \frac{1}{2\pi} \int_0^{2\pi} d\bar{\theta} h(r, \theta + \bar{\theta}, \theta' + \bar{\theta}). \quad (32)$$

Due to the rotational invariance of $c(k, \theta - \theta')$, the Ward identity can again be written in the simplified form shown in Eq. (18). To obtain the pair correlation functions and the probability density for the model when $b \neq 0$, we need to solve the Ornstein-Zernike equation, (23), Ward identity, Eq. (18), and the Percus-Yevick closure, Eq. (31), self-consistently. We have adopted the iterative method to solve this set of the equations. In the model we have assumed the angular dependent part of the potential to be proportional to $\cos^2(\theta - \theta')$. Therefore when the angular dependent quantities are expanded in terms of $\sin l\theta$ and $\cos l\theta$, all terms with odd l are zero due to the symmetries in the system. Explicitly, we write

$$v(\theta) = \sum_l v_l \cos 2l\theta, \quad (33)$$

$$c(r, \theta - \theta') = \sum_l c_l(r) \cos 2l(\theta - \theta'), \quad (34)$$

$$h(r, \theta, \theta') = \sum_{l, l'} h_{ll'}^{(e)} \cos 2l\theta \cos 2l'\theta' + h_{ll'}^{(o)} \sin 2l\theta \sin 2l'\theta', \quad (35)$$

and

$$\langle h(r, \theta - \theta') \rangle_{rot} = \sum_l \langle h(r) \rangle_{rot, l} \cos 2l(\theta - \theta'), \quad (36)$$

where the relation

$$\langle h(r) \rangle_{rot, l} = \frac{1}{2} [h_{ll}^{(e)}(r) + h_{ll}^{(o)}(r)] \quad (37)$$

holds. The above expansions also apply to their Fourier transform counterparts. We begin the iteration with the initial guess $c^{(1)}(r, \theta - \theta') = f(r, \theta - \theta')$ where the superscript indicates the iteration number. In general for the n th iteration, we first obtain the Fourier component $c^{(n)}(k, \theta - \theta')$. Its limit at $k \rightarrow 0$ is used in the Ward

identity, Eq. (18), to determine $\rho^{(n)}(\theta)$. This involves solving the following set of integral equations:

$$v_l = c_l(k) \int d\theta' \cos 2l\theta' e^{\sum_{i=1}^n v_i \cos 2i\theta'} / Z, \quad l = 0, \dots, n \quad (38)$$

$$Z = \int d\theta' e^{\sum_{i=1}^n v_i \cos 2i\theta'}. \quad (39)$$

The converged values of v_l are then used to calculate the angular part of the integrals in the Ornstein-Zernike equation. The total correlation function obtained from the Ornstein-Zernike equation $h^{(n)}(k, \theta, \theta')$ is Fourier transformed to $h^{(n)}(r, \theta, \theta')$ and its rotational average is substituted in the modified Percus-Yevick closure, Eq. (31), to compute $c^{(n+1)}(r, \theta - \theta')$. This ends the n th iteration. This procedure is repeated many times until the correlation functions converge.

The Ornstein-Zernike equation can be solved as an eigenvalue problem as illustrated in Sec. III A or by directly inverting matrices. Using expansions (33)–(35), the Ornstein-Zernike equation, Eq. (23), can be written as

$$A_{ll'}(k) h_{ll'}(k) = c_l(k) \delta_{ll'}, \quad (40)$$

where for even solutions, $h_{ll'}^{(e)}(k)$,

$$A_{ll'}(k) = \delta_{ll'} - c_l(k) \int d\theta \rho(\theta) \cos 2l\theta \cos 2l_1\theta \quad (41)$$

and for odd solutions, $h_{ll'}^{(o)}(k)$,

$$A_{ll'}(k) = \delta_{ll'} - c_l(k) \int d\theta \rho(\theta) \sin 2l\theta \sin 2l_1\theta. \quad (42)$$

One can invert the matrix $A_{ll'}$ and multiply matrix $c_l(k) \delta_{ll'}$ to obtain $h_{ll'}$ using Eq. (40). To ensure numerical accuracy to the Ornstein-Zernike equation, we have taken a large basis set, i.e., large enough l_{max} such that the coefficients for $l > l_{max}$ are numerically zero.

For Goldstone modes where the matrix A becomes nearly singular for k values close to zero, care must be taken. Instead of inverting the original matrix, we construct a matrix $B = \Psi\Psi^\dagger$, where Ψ is the eigenvector corresponding to the Goldstone modes, and invert the matrix $A + B$. The inverse of A is obtained through the relation

$$A^{-1} = (A + B)^{-1} + (A + B)^{-1} \Psi \left(\frac{1}{1 - \Psi^\dagger (A + B)^{-1} \Psi} \right) \times \Psi^\dagger (A + B)^{-1}. \quad (43)$$

We expect $h(k, \theta, \theta') \sim \Psi(\theta)\Psi(\theta')/k^2$ as $k \rightarrow 0$ due to the Goldstone modes and $h(k, \theta, \theta')$ approach to a constant as $k \rightarrow \infty$. In order to increase the numerical accuracy and to require fewer points in the Fourier transform, we therefore write $h(k, \theta, \theta') = a\Psi(\theta)\Psi(\theta')/k^2 - a\Psi(\theta)\Psi(\theta')/(k^2 + \eta^2) + h'(k, \theta, \theta')$. Fourier transforms of the first two terms are done analytically. The term including η is included to make this analytic transformation finite and give the length scale over which the Goldstone modes cease to have susceptibilities $\sim k^{-2}$. The parameter a is in principle related to the normalization of Ψ and the Goldstone mode stiffness and implies h' is small and slowly varying as $k \rightarrow 0$. It was fixed by insisting that h' for the first two nonzero values of k be equal. The results are insensitive to a and η within reasonable bounds.

Some of the results are shown in Figs. 2–5. The parameters are written in terms of the reduced density and temperature which have standard definitions: $\rho_0^* = N\sigma^3/V$ and $T^* = k_B T/\epsilon$. The qualitative features of the pair correlation functions are the same for all the calculations we have performed with different sets of the parameters. All the results presented here are done with 1024 points with $\Delta r = 0.02\sigma$. The correlation function $\langle h(k) \rangle_{rot,l}$ for $\rho_0^* = 0.8$, $T^* = 1.0$, and $b = 3.0$ is shown in Fig. 2. Components for l higher than unity are too small to be seen with the scale used in the figure. In the $k \rightarrow 0$ limit, the singularity of the $l = 1$ component is quite prominent, indicating the presence of the Goldstone modes. The oscillations of the correlation function as a function of k are typical of a fluid with a highly repulsive core. Higher

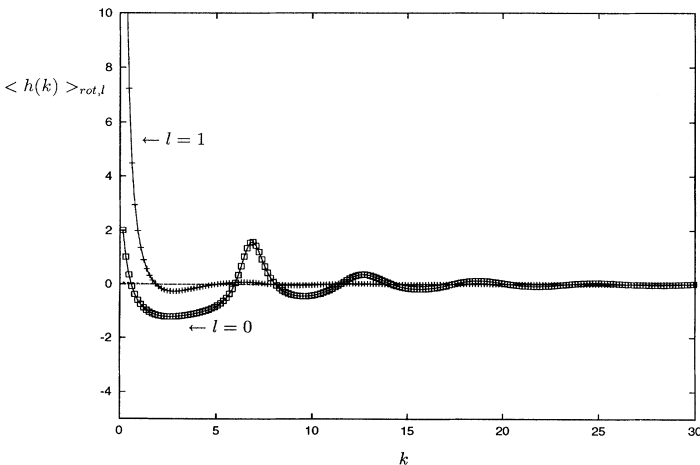


FIG. 2. The total correlation function $\langle h(k) \rangle_{rot,l}$ for $\rho_0^* = 0.8$, $T^* = 1.0$, and $b = 3.0$. The divergence of the $l = 1$ component as $k \rightarrow 0$ is due to the presence of the Goldstone modes.

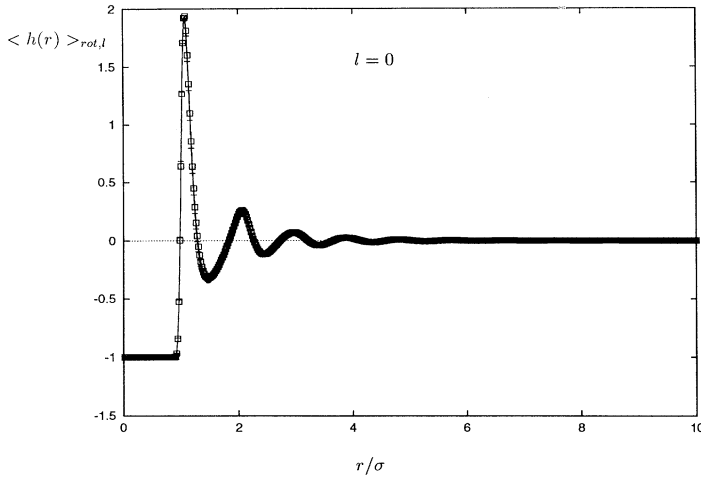


FIG. 3. The total correlation function h in real space for the $l = 0$ component with $b = 0$ (crosses) and $b = 3.0$ (squares). The parameters for ρ_0^* and T^* are the same as in Fig. 2.

density and larger values of b lead to longer range of the oscillations. In Fig. 3 we directly compare the $l = 0$ component of the total correlation function $h(r)$ with $b = 0$ and $b = 3$ for the same values of ρ_0^* and T^* as those used in Fig. 2. With the scale we used in the figure we cannot tell the difference between the two curves. The $l = 0$ component of the direct correlation function $c_l(r)$ is essentially the same as the ones for the pure Lennard-Jones fluid and is not shown here. For $r < \sigma$, the curve shows a large dip due to the hard core and it rises sharply close to σ and then quickly vanishes. Figure 4 shows the $l = 1$ components of $\langle h(r) \rangle_{rot,l}$ and $c_l(r)$ for $\rho_0^* = 0.85$, $T^* = 1.0$, and $b = 3.5$. Both quantities vary on a relatively small scale compared to their $l = 0$ counterparts. Since the angular dependent part of the interaction is outside the core, in the core region the total correlation function $h(r, \theta, \theta')$ is strictly -1 as expected and there-

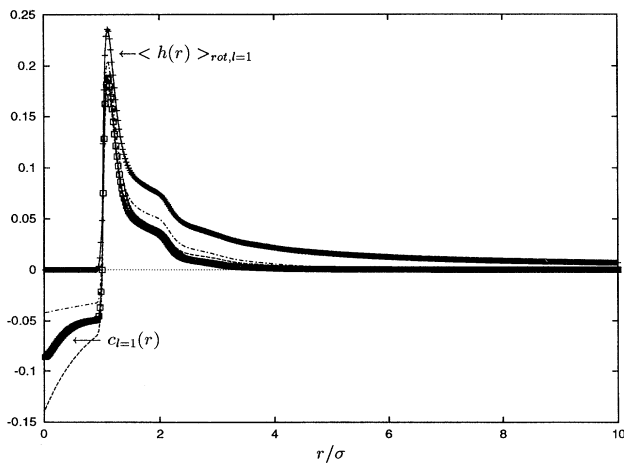


FIG. 4. The $l = 1$ component of the total correlation function, $\langle h(r) \rangle_{rot,l}$ (crosses) and the direct correlation function $c_l(r)$ (squares) with $\rho_0^* = 0.85$, $T^* = 1.0$, and $b = 3.5$. $\langle h'(r) \rangle_{rot,l=1}$ obtained with two sets of the parameters $a = 0.9$, $\eta = 0.6$ (dash-dotted line) and $a = 0.9$, $\eta = 2.0$ (dashed line) are also shown in the figure.

fore $\langle h(r) \rangle_{rot,l=1}$ is zero for $r < \sigma$. The direct correlation function $c_{l=1}(r)$ shows a sharp rise as for the $l = 0$ component of $c_l(r)$. After the sharp peak just outside the core, both $\langle h(r) \rangle_{rot,l=1}$ and $c_{l=1}(r)$ die down rapidly. The fine structures for both $\langle h(r) \rangle_{rot,l=1}$ and $c_{l=1}(r)$ outside of the core are not an artifact of the numerical calculation because their Fourier transforms $\langle h(k) \rangle_{rot,l=1}$ and $c_{l=1}(k)$ are both smooth curves as shown in Fig. 5. We also show the rotationally averaged, $l = 1$ component of $h'(k, \theta, \theta')$ (defined earlier in the text) and its Fourier transform in Figs. 4 and 5. $\langle h'(k) \rangle_{rot,l=1}$ calculated with two sets of the parameters a and η are explicitly shown in Fig. 5. With reasonable choices of a and η , $\langle h'(k) \rangle_{rot,l=1}$ is a slowly varying function and therefore requires fewer points in the Fourier transform. The final results of h and c are independent of choices of the parameters.

This model calculation shows that the Ornstein-Zernike equation can be solved in conjunction with the modified Percus-Yevick closure for a nematic system with spontaneously broken symmetries. With the proper implementation of the Ward identity, the singularity of the

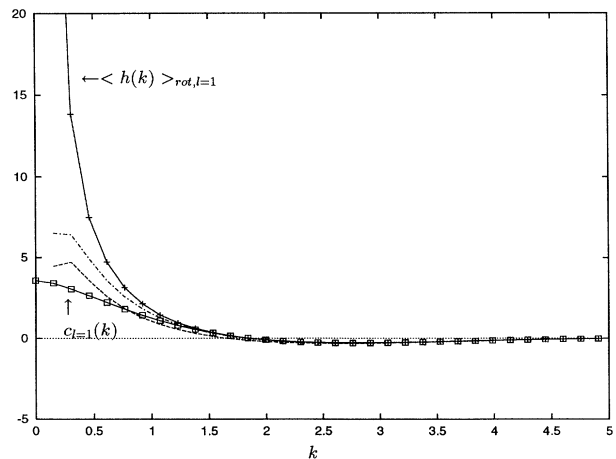


FIG. 5. The same quantities shown in Fig. 4 plotted in Fourier space.

correlation function at $k \rightarrow 0$ due to the Goldstone modes can be treated correctly.

IV. SUMMARY AND DISCUSSION

For systems with sufficiently strong interparticle interactions, there exists partial orientational order after the isotropic-nematic phase transition due to spontaneous breaking of the continuous rotational symmetry. Adapting the techniques used in ferromagnetic systems with spontaneously broken symmetries, we derive a Ward identity, which relates the one-particle probability density to the integral of the two-particle density in nematic systems. We show that the rotational average of the correlation functions is needed in the Percus-Yevick closure to ensure the correct consequences of rotational invariance due to the Goldstone modes. The modified Percus-Yevick approximation can be solved with the Ward identity and the Ornstein-Zernike equation for probability density and correlation functions of a spontaneously partially ordered system. As our model calculations show, proper use of the Ward identity results in the correct treatment of the Goldstone modes, which leads to infinite susceptibility as $k \rightarrow 0$. We believe that with more realistic model interparticle potentials, this technique can be applied to study the thermodynamic properties of nematic liquid crystals through the pair correlation functions. This technique differs from the use of the stability criterion or truncated density functional theory [4, 5], in that it uses the ordered state to calculate the self-consistent two-point function. Thus self-consistency can be used even (as in this paper) beyond the stability limit. Additionally it is possible that the ordered state may not be terribly closely related to the disordered state—this is likely in systems with large first-order transitions. In this case the ability to deal directly with the ordered state

may find transitions lacking in other approaches. As in an ordered state most of the molecules are, actually, ordered, using the ordered state correlation function seems more likely to result in good interparticle interactions.

It is straightforward to generalize our approach to more realistic models of a nematic system. For example, calculations of the Lebwohl-Lasher [15] type of models (similar to model II discussed in Sec. III) with three-dimensional “orientation” interactions can be carried out directly following similar procedures described in the paper. In general, our approach can be applied to any nematic models with strong interparticle interactions, such as hard spherocylinders, hard ellipsoids, or the Gay-Berne [16] type of models. Mathematically it is easier to treat “separable” models (such as the Lebwohl-Lasher model) where the interparticle potential is of the form $u(r, (\hat{\Omega} \cdot \hat{\Omega}')^2)$ than those more realistic hard spherocylinders, hard ellipsoids, or Gay-Berne [16] types of models. The mathematical complications involved in computations of the correlation functions with more realistic models are comparable to those of *isotropic* systems consisting of hard particles, which have been well detailed in Refs. [2–5]. The main differences would be that the single-particle probability density ρ must be self-consistently determined by the Ward identity, Eq. (14), and the Ornstein-Zernike equation to be solved, Eq. (5), depends on the angular dependent particle density ρ . Such calculations are in progress.

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