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A STUDY OF TWO PARTICLE CLUSTER APPROXIMATION FOR NEMATIC LIQUID CRYSTAL FILMS

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A two-particle cluster variation theory is presented here to treat the inhomogeneous nematic phase. This theory is used to study nematic liquid crystal films. The internal energy per molecule in each layer is calculated and results are in agreement with those of the simulation. It is found that within the two-particle cluster theory, the surface excess free energy in both the nematic phase and the isotropic phase increases with the temperature. This behavior is in contradiction with that of the simulation and the mean field theory.

1. Introduction

The importance of short range correlations between molecules in the homogeneous nematic phase of liquid crystals has been demonstrated by experimental data and computer simulations.[1] There have been a few forms of molecular theories published on the subject of the short range correlations, including the Bethe method,[2] the constant coupling theory[3] and our functional variation theory based on the cell mode.[4] Compared with the simple mean field theory, all these theories lead to improved values for all quantities — characteristic for the nematic — isotropic phase transition within the Maier–Saupe model.[5]

Recently, M. M. Telo da Gama *et al.*[6] investigated nematic liquid crystal films by a molecular theory within the Bethe approximation. More specifically, they considered a slab of finite width, having parallel surfaces at the top and bottom, and being infinite extent in the other two directions. This confined system, which was first studied by G. R. Luckhurst *et al.* through the Monte Carlo method and the mean field theory,[7] is especially interesting because short range correlations

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appearing in bulk make it difficult to understand the effects of finite system size. Calculations were carried out in Ref. 6, with attention focused on the shift of the transition temperatures, averaged energies per particle, order parameter profiles and absorption for a range of slab widths. However, the temperature dependence of the surface excess free energy, which relates to the surface tension when the slab width tends to infinite, was not given.

In this letter, we present a two-particle cluster variation theory which can be used to treat the inhomogeneous nematic phase and include some effects of the local short range correlations between molecules. As an example, we also study the nematic films described above. The numerical results are in accordance with those of the Bethe approximation. But it appears that the temperature dependence of the surface excess free energy is in a sense unexpected.

2. Theory

Let us consider a system of N liquid crystal molecules. The direction of the long axis of a molecule is described by the spherical coordinates θ, ϕ. Denote $\Omega \equiv (\theta, \phi)$. We define one body and two body distribution functions $g^{[f]}(\Omega_i)$ and $g[ij](\Omega_i, \Omega_j)$, where superscript $[i]$ refers to the definite molecule i and $[ij]$ to the definite molecules i and j. It is implied that molecules may have different distributions when the system is inhomogeneous. The distribution functions satisfy the normalization condition and the consistency condition

$$\int g^{[i]}(\Omega_i) d\Omega_i = 1 , \tag{1}$$

$$\int g^{[ij]}(\Omega_i, \Omega_j) d\Omega_j = g^{[i]}(\Omega_i) , \tag{2}$$

where $d\Omega = \sin\theta d\theta d\phi$ and the angular integration is taken over the whole solid angle. Within the two particle cluster approximation, the free energy of the system is expressed as[4,8]

$$\begin{aligned} \beta F = \frac{1}{2} \sum_i \sum_{j=1}^{z^{[i]}} \iint & [\beta V(\Omega_i, \Omega_j) + \ln g^{[ij]}(\Omega_i, \Omega_j) \\ & - (1 - 1/z^{[i]}) \ln g^{[i]}(\Omega_i) g^{[j]}(\Omega_j)] g^{[ij]}(\Omega_i, \Omega_j) d\Omega_i d\Omega_j , \end{aligned} \tag{3}$$

where $\beta \equiv 1/kT$; the first summation is taken over all molecules of the system and the second over $z^{[i]}$ neighbors of the molecule i. The orientational pair potential $V(\Omega_i, \Omega_j)$ is taken as[1–4]

$$V(\Omega_i, \Omega_j) = J P_z(\cos\theta_{ij}) . \tag{4}$$

Here J is aa positive constant reflecting the strength of the interaction, θ_{ij} is the angle between the long axes of the neighboring molecules i and j, and P_z is the second order Legendre polynomial. The equilibrium distribution results from the minimization of the free energy with respect to the variations of the distribution functions. So we have

$$\sum_{j=1}^{z^{[i]}}[\beta V(\Omega_i,\,\Omega_j)+\ln g^{[ij]}(\Omega_i,\,\Omega_j)-(1-1/z^{[i]})\ln g^{[i]}(\Omega_i)g^{[j]}(\Omega_j)]-\lambda^{[i]}=0\,, \quad (5)$$

where $\lambda^{[i]}$ is a variational constant.

For liquid crystal films, following Refs. 6 and 7, the molecules interacting with the pair potential (4) are located at the sites of a simple cubic lattice. The surfaces of the film are assumed to be normal to the z-axis and they remove the homogeneity in the z-direction but not in the XY-plane. We label the layers parallel to the surfaces with the letter m, with $m = 1$ and $m = n$ denote the two surface layers. The one-body distribution function is localized according to the layer in which the molecule is located; i.e. we have $g^{[i]}(\Omega_i) = g^{(m)}(\Omega_i)$, if the molecule i is in the mth layer. From Eqs. (1), (2) and (5), we obtain a set of equations for the one body distribution functions,

$$\begin{aligned} g^{(m)}(\Omega_1) = A^{(m)} &\left\{\int [g^{(m)}(\Omega_2)]^{1-1/z^{(m)}} \exp[-\beta V(\Omega_1,\,\Omega_2)]d\Omega_2\right\}^4 \\ &\times\left\{\int [g^{(m-1)}(\Omega_2)]^{1-1/z^{(m)}} \exp[-\beta V(\Omega_1,\,\Omega_2)]d\Omega_2\right\}^{1-\delta_{m1}} \\ &\times\left\{\int [g^{(m+1)}(\Omega_2)]^{1-1/z^{(m)}} \exp[-\beta V(\Omega_1,\,\Omega_2)]d\Omega_2\right\}^{1-\delta_{mn}}, \\ &\qquad\qquad (m=1,2,\ldots,n) \end{aligned} \quad (6)$$

where $z^{(m)}$ is equal to 5 for $m = 1,\ n$, otherwise it is equal to 6; $A^{(m)}$'s are the constants determined by Eq. (1).

In order to solve this set of equations, we choose a representation for $g^{(m)}(\Omega)$; i.e. we expand $\ln g^{(m)}(\Omega)$ in Legendre polynomials.[2,4] For the simple pair potential (4), we retain only the leading term of the expansion and write[4,9]

$$g^{(m)}(\Omega) = \exp[\beta J\sigma^{(m)}P_2(\cos\theta)]/Z_1^{(m)}\,, \quad (7)$$

$$Z_1^{(m)} = \int \exp[\beta J\sigma^{(m)}P_2(\cos\theta)]d\Omega\,, \quad (8)$$

where θ is the angle of the molecule with respect to the director. $\sigma^{(m)}$'s are functions of temperature and are determined by requiring that this set of equations will give the orientational order parameters

$$\langle P_2^{(m)}\rangle = \int P_2(\cos\theta)\,g^{(m)}(\Omega)d\Omega\,, \quad (9)$$

consistently. It should be noted that $\sigma^{(m)} = 0$ is a set of solutions for any temperature, it corresponds to the isotropic phase. When two sets of solutions appear, the one with lower free energy is more stable. The free energy can be written as

$$\begin{aligned}\beta F(n) = \sum_{m=1}^{n} \beta F^{(m)} = \frac{1}{2} L \sum_{m=1}^{n} \Big[& 4(1 - 1/Z^{(m)}) \ln Z_1^{(m)} \\ & + (1 - \delta_{m1})(1 - 1/z^{(m)}) \ln Z_1^{(m-1)} \\ & + (1 - \delta_{mn})(1 - 1/z^{(m)}) \ln Z_1^{(m+1)} - \ln Z_2^{(m)} \Big] ,\end{aligned} \tag{10}$$

where $L = N/n$ is the number of molecules in each layer and

$$\begin{aligned} Z_2^{(m)} = \int & \left\{ \int \exp[\beta J(1 - 1/z^{(m)})\sigma^{(m)} P_2(\cos\theta_1) + \beta J P_2(\cos\theta_{12})] d\Omega_2 \right\}^4 \\ & \times \left\{ \int \exp[\beta J(1 - 1/z^{(m)})\sigma^{(m-1)} P_2(\cos\theta_1) + \beta J P_2(\cos\theta_{12})] d\Omega_2 \right\}^{1-\delta_{m1}} \\ & \times \left\{ \int \exp[\beta J(1 - 1/z^{(m)})\sigma^{(m+1)} P_2(\cos\theta_1) + \beta J P_2(\cos\theta_{12}) d\Omega_2 \right\}^{1-\delta_{mn}} d\Omega_1 . \end{aligned} \tag{11}$$

The internal energy per molecule associated with each layer m is given by

$$\langle u^{(m)} \rangle = \partial(\beta F^{(m)}/L)/\partial\beta . \tag{12}$$

Equation (12) gives half the averages of four pairs of interactions within layer m, one pair of interaction in adjacent layers m and $m - 1$ (with $m \neq 1$), and one pair of interaction in adjacent layers m and $m + 1$ (with $m \neq n$), which is expected from thermodynamics.

In the absence of boundaries, Eqs. (6) and (10) reduce to those for the bulk system in the two-particle cluster variation theory,[4,8] i.e.

$$g(\Omega_1) = A \left\{ \int [g(\Omega_2)]^{1-1/z} \exp[-\beta V(\Omega_1, \Omega_2] d\Omega_2 \right\}^z , \tag{13}$$

$$\beta F_b = \frac{1}{2} N[(z - 1) \ln Z_1 - \ln Z_2] \tag{14}$$

where

$$Z_1 = \int \exp[\beta J \sigma P_2(\cos\theta)] d\Omega , \tag{15}$$

$$Z_2 = \int \left\{ \int \exp[\beta J(1 - 1/z)\sigma P_2(\cos\theta_1) + \beta J P_2(\cos\theta_{12})] d\Omega_2 \right\}^2 d\Omega_1 . \tag{16}$$

Those equations give also the results which is identical to the constant coupling theory.[3,9]

The surface excess free energy is defined by,[6,7]

$$F_{\rm ex}(n) = F(n) - F(b)\,. \tag{17}$$

Note that $2\gamma \equiv \lim_{n\to\infty}[F_{\rm ex}(n)/L]$ defines the surface tension γ for both the nematic phase and the isotropic phase.

3. Numerical Results and Discussion

We have made numerical calculations for the film composed of 10 molecular layers. The theory predicts a first order nematic-isotropic phase transition at $t_c = 1.1373$ ($t = kT/J$). For comparison, the value predicted by the Monte Carlo simulation[7] is 1.095 and that by the mean field theory is 1.2990. The temperature dependence of the internal energy per molecule $\langle u^{(m)}\rangle$ in each layer is calculated and the results are shown in Fig. 1. Because of the short range correlations concerned, $\langle u^{(m)}\rangle$ given by Eq. (12) is not zero even in the isotropic phase, which is in agreement with that of the Monte Carlo simulation,[7] in addition, the curves in the isotropic phase for m = 2, 3, 4, 5 are the same in accordance with the conclusion of the Bethe approximation.[6] Order parameter profile and the other quantities including their variations with the slab width, about which our theory reaches a consensus with the Bethe approximation,[6] will be published elsewhere.

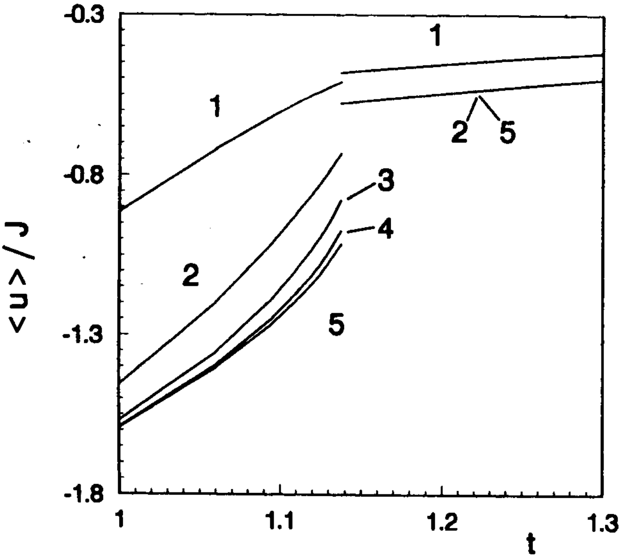

Fig. 1. Temperature dependence of the internal energy per molecule for the layers.

Now we devote our attention to the surface excess free energy given by Eq. (17). In Fig. 2, we give the result as a function of the scaled temperature for the slab thickness $n = 10$, a case which has been studied by using the simulation and the mean field theory.[7] We note that the excess free energy in both the nematic phase

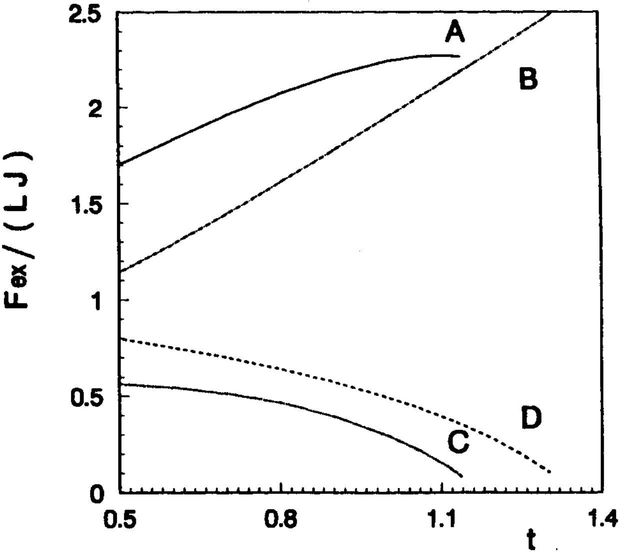

Fig. 2. Temperature dependence of the surface excess free energy. (A) For the nematic phase; (B) For the isotropic phase and it has been extended to the range of $t < t_c$; (C) The difference between A and B; (D) Predicted by the mean field theory for the nematic phase and it is zero for the isotropic phase.

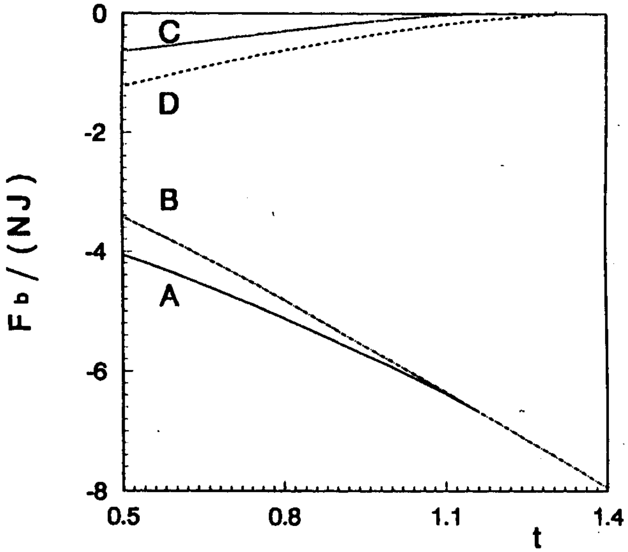

Fig. 3. Temperature dependence of the bulk free energy. (A) For the nematic phase; (B) For the isotropic phase and it has been extended to the range of $t < t_c$; (C) The difference between A and B; (D) Predicted by the mean field theory for the nematic phase and it has been taken zero for the isotropic phase.

and the isotropic phase increases with the temperature. This behavior and the specific values are in contradiction with the results of the simulation and those of the mean field theory.[7] The difference between the excess free energy in the nematic phase and that in the isotropic phase seems, however, normal and it is 0.082 (LJ) at the phase transition. The value predicted by the simulation is 0.022 (LJ) and that by the mean field theory is 0.106 (LJ).

It is profitable to recall the bulk free energy in the two-particle cluster theory of nematics. The results calculated from Eq. (14) are shown in Fig. 3. We can see that the temperature variation of the bulk free energy in both the nematic phase and the isotropic phase is abnormal (only the slope of the curves is definite and two curves can move along vertical direction simultaneously), but the difference between them is normal. As a matter of fact, this characteristics is universal in the molecular theories of nematics which takes account of two-body correlations. When we treat the bulk system, we use the free energy to determine the phase transition and the temperature dependence of it is unimportant at all. However, when we describe the films, the surface excess free energy relates to the surface tension, so both its value and temperature dependence are important. We believe that the abnormal behavior of the bulk free energy in the two-particle cluster theory is the latent reason why the theory fails to predict the surface excess free energy. The results of this letter give a limit to the application of the two-particle cluster theory and the other equivalent theory (the constant coupling theory, etc.) when these theories are used to treat the films and to study the surface properties of nematic liquid crystals.

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