

Statistical-mechanical study of the pair correlations for the dipolar Gay-Berne model

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A statistical-mechanical theory based upon the method of conditional distribution function has been applied to calculations of the nearest-neighbor (NN) and next NN correlators as well as order parameters. The method takes into account translational and orientational correlations as well as their coupling. Using the dipolar Gay-Berne interaction potential, calculations have been carried out for temperatures and densities corresponding to a nematic phase. The results in orientational distribution functions indicate a significant effect of the dipole-dipole interactions on the orientational order of the liquid crystal. It was found that NN particles tend to be mutually antiparallel, whereas a reversed tendency is observed for next NN particles. These results are in agreement with computer simulations and with interpretations of experimental data. [S1063-651X(99)50508-4]

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The problem of predicting phase behavior of liquid crystals (LCs) based on information about molecular shape and intermolecular interactions remains one of the most fundamental in LC physics. In recent years, the Gay-Berne (GB) [1] model has been frequently used for describing interactions between anisotropic particles. In particular, this potential was employed in many computer simulations of liquid crystalline phases. Frequently, molecules that form the LC system possess strongly polar groups. Satoh, Mita, and Kondo [2] have examined the dipole effect on phase equilibria using GB model and found that the I - N transition is shifted towards higher temperatures when the dipole moment is located near the end of the molecule. Vanakaras and Photinos showed, in the framework of the variational cluster expansion [3], that the dipole interactions substantially shift the I - N transition temperature and strongly promote antiparallel molecular association. Rull and coworkers [4] found that the dipolar model predicts only I - Sm - B transition, whereas in the absence of dipolar interactions the model exhibits I - N - Sm - B phases at the same temperature. Zannoni and coworkers [5] showed using a Monte Carlo (MC) simulation that dipolar GB system with an axial dipole at the center or near the end of molecules can form antiferroelectric bilayer stripe domains. Furthermore, ferroelectric and antiferroelectric smectic phases were observed in a MC simulation of a polar GB system [6].

Recently, a modification of Bethe theory [7,8], which takes account of intercell pair correlations, has been pro-

posed for describing LC systems composed of dipolar GB particles [9]. Using this approach, the influence of the dipolar forces on the order parameters (OPs) and the elastic properties of the system have been investigated. The aim of the present Rapid Communication is to apply the above mentioned approach to investigate the influence of these forces on short-range correlations between molecules in a nematic phase.

We consider here a classical one-component fluid, consisting of cylindrically symmetric particles. Let \mathbf{q}_i denote their center-of-mass coordinates, and let \mathbf{e}_i denote unit vectors defining their orientations; in the following the collective symbol $i \equiv (\mathbf{q}_i, \mathbf{e}_i)$ will also be used. Particles can be identified, to a certain approximation, with prolate ellipsoids of revolution [1], with major semiaxes σ_{\parallel} and minor semiaxes σ_{\perp} , respectively. We consider N such particles occupying a volume V at the temperature T ; ideally one can subdivide the total volume into N cells, each with volume $v = V/N$, arranged in a simple-cubic lattice. The treatment used here further assumes that each cell is occupied by only one molecule; this seems to be a reasonable approximation for a condensed system. Particles are assumed to interact via a pairwise additive potential $\Phi(ij)$, so that the total interaction energy for the N particles is $U = \sum_{i < j} \Phi(ij)$. The quantity $\exp[-U/(k_B T)]$ is the canonical probability density; upon integrating out the coordinates of remaining particles, one can define single-particle probability densities $F_i(i)$, two-particle probability densities $F_{ij}(ij)$, and so on [7-9]. The infinite hierarchy is truncated here at two-particle level. By the partitioning of space mentioned above, $F_i(i)$ is the probability density for a single particle confined inside a cell of volume v , and $F_{ij}(ij)$ is a probability density for two particles confined in two different cells. These functions can also be written in terms of mean-force potentials (MFPs)

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$\psi_{i,j}(i)$. Following the approach outlined in Refs. [7,8], one obtains a closed system of nonlinear integral equations involving MFP's [7–9],

$$\psi_{i,j}(i) = \int_j d(j) \exp[-\Phi(ij)/(k_B T)] \psi_{j,i}^{-1}(j) F_j(j), \quad (1)$$

where

$$F_j(j) = \frac{\psi_j(j)}{\int_j d(j) \psi_j(j)},$$

$$\psi_j(j) = \prod_{i \neq j} \psi_{j,i}(j), \quad \int_j d(j) = \int_w d\mathbf{q}_j d\mathbf{e}_j,$$

$$w = \mathbf{v} \otimes \alpha.$$

Here α denotes the volume associated with orientations.

It should be pointed out that Eq. (1) is valid for various liquid crystalline phases, which are characterized by translational and orientational correlations as well as their coupling. The solutions, $\psi_{i,j}(i)$, are functions of position and orientation of the particle. Since we take into account only singlet- and two-particle functions of the infinite hierarchy, i.e., pair correlations between cells, the following expression for binary function is obtained:

$$F_{ij}(ij) = F_i(i) F_j(j) \exp[-\Phi(ij)/(k_B T)] \psi_{i,j}(i)^{-1} \psi_{j,i}(j)^{-1}. \quad (2)$$

The last three factors in Eq. (2) reflect correlations between cells, which distinguishes the approach used here from mean-field approximations. After solving Eq. (1), a number of correlators relevant for a liquid crystalline system, and expressed in terms of one- and two-particle functions, can be calculated,

$$\bar{P}_{2L} = \langle P_{2L}(\cos \beta) \rangle = \int_i d(i) F_i(i) P_{2L}(\cos \beta), \quad (3)$$

$$\bar{\kappa} = \left\langle P_2(\cos \beta) \cos \frac{2\pi z}{d} \right\rangle = \int_i d(i) F_i(i) P_2(\cos \beta) \cos \frac{2\pi z}{d}, \quad (4)$$

$$\langle \mathbf{e}_i \cdot \mathbf{e}_j \rangle = \int_i d(i) \int_j d(j) F_{ij}(ij) \mathbf{e}_i \cdot \mathbf{e}_j. \quad (5)$$

Here P_{2L} denote Legendre polynomials of even rank and \bar{P}_{2L} are the corresponding order parameters. The polar angle β specifies the relative orientation of the long axis of the molecule and the director, the latter taken to coincide with the cell z axis, and d is the layer spacing of the smectic- A phase. The set of OPs \bar{P}_{2L} defines the orientational order, while $\bar{\kappa}$ is a measure of the amplitude of the density wave describing the layered structure. The nematic phase is characterized by $\bar{\kappa} = 0$ and $\bar{P}_{2L} \neq 0$ [10].

Solving five-dimensional problem (1) is very complicated, and there are no good general methods for systems of

more than one nonlinear equation. The solution $\psi_{i,j}(i)$ is invariably obtained by a numerical iterative procedure, using the formula

$$\psi^{[k+1]}(\mathcal{Q}_i) = \{\psi^{[k]}(\mathcal{Q}_i) \hat{L} \psi^{[k]}(\mathcal{Q}_i)\}^{1/2}, \quad (6)$$

where \hat{L} , $\|\hat{L}\| \leq 1$ is the five-dimensional nonlinear integral operator defined by Eq. (1) in the space $w_i = \mathbf{v} \otimes \alpha$, \mathcal{Q}_i is a five-dimensional vector in the same space, and k is the iteration number. The numerical procedure for construction of the MFP $\psi_j(j)$ has been described in Refs. [8,9]. It can be repeated for various neighbors of the i th cell; in order to keep the treatment numerically tractable, we took the drastic step of truncating the interaction potential at second neighbors.

Two points should be noted: first, in the present calculation we considered only a simple cubic structure, with six neighbors and twelve next neighbors; this implies that we deal with a system of 18 nonlinear equations in a five-dimensional space.

We are aware of the fact that the correlations are strong beyond the next-nearest neighbors (NNN), the computations become, however very heavy and suffer, in addition, from numerical instabilities. The second point concerns convergence of the iterative procedure; the algorithm Eq. (6) exhibited a poor convergence in the vicinity of N -Sm- A phase transition points, because the function $\psi_{i,j}(i)$ was not a smoothly varying one. Taken these points into account, we restrict the present Rapid Communication to investigations of the nematic phase.

The kernel of the integral equations (1) is determined by the pair interaction potential; this was chosen to be the sum of a Gay-Berne and dipole-dipole interactions

$$\Phi(ij) = \Phi_{GB}(ij) + \Phi_{dd}(ij).$$

The GB term has the form [1]

$$\Phi_{GB}(ij) = 4\epsilon_0 \epsilon \left(\left\{ \frac{\sigma_0}{q_{ij} - \sigma + \sigma_0} \right\}^{12} - \left\{ \frac{\sigma_0}{q_{ij} - \sigma + \sigma_0} \right\}^6 \right), \quad (7)$$

and the dipolar term is defined by

$$\Phi_{dd}(ij) = \frac{\Delta^2}{q_{ij}^3} \{ \mathbf{e}_i \cdot \mathbf{e}_j - 3(\mathbf{r}_{ij} \cdot \mathbf{e}_i)(\mathbf{r}_{ij} \cdot \mathbf{e}_j) \}, \quad (8)$$

where

$$\mathbf{q}_{ij} = \mathbf{q}_i - \mathbf{q}_j, \quad q_{ij} = |\mathbf{q}_{ij}|, \quad \mathbf{r}_{ij} = \mathbf{q}_{ij}/q_{ij}.$$

Here, \mathbf{e}_i , \mathbf{e}_j are unit vectors defining molecular orientations, whereas \mathbf{r}_{ij} denotes the intermolecular unit vector. The quantities $\sigma = \sigma(\mathbf{r}_{ij}, \mathbf{e}_i, \mathbf{e}_j)$ and $\epsilon = \epsilon(\mathbf{r}_{ij}, \mathbf{e}_i, \mathbf{e}_j)$ depend on mutual orientations but not on distance between centers of mass, and their expressions can be found in Ref. [1]. In our calculations, the parameters μ and ν of Ref. [1] have been fixed to the values 1 and 2, respectively.

It should be pointed out that the comparison with the nonpolar GB model has been done at the original parametrization of the GB potential [1], with $\nu = 1$ and $\mu = 2$. As for the dipolar interaction, we are considering axial dipoles placed

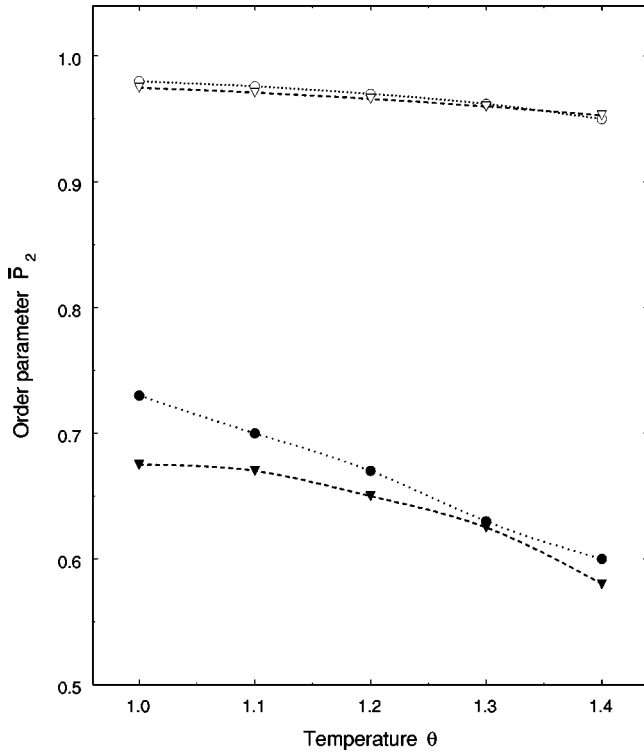


FIG. 1. Temperature dependence of orientational order parameter \bar{P}_2 for both polar and nonpolar GB models, at constant density $\rho=0.33$. Open and closed symbols refer to polar and nonpolar systems, respectively. Our computations are shown using circles, the open triangles represent results from MC simulations [2], while closed triangles correspond to MD [11] simulations.

in molecular centers; the symbol Δ denotes their common absolute magnitude, and $\mu^* = \Delta / \sqrt{\epsilon_0 \sigma_0^3}$.

Our calculations have been performed at temperatures and densities corresponding to the nematic phase. Dimensionless (reduced) units have been used for number density $\rho = N\sigma_0^3/V$, temperature $\theta = k_B T / \epsilon_0$, and dipole moment μ^* ; for the anisotropy parameter in the GB potential term, we chose the ratio $\sigma_{\parallel} / \sigma_{\perp} = 3$. We examined the effect of different truncation radii; for example, when $\rho = 0.33$, $\theta = 1$, and $\mu^* = 2$, we found a change in \bar{P}_2 from 0.9695 (nearest neighbors) to 0.9806 (nearest and next-nearest neighbors). Results quoted in the following were obtained by taking into account first and second neighbors.

Figure 1 shows the temperature dependence of order parameter \bar{P}_2 for both nonpolar ($\mu^* = 0$) and polar ($\mu^* = 2$) GB models, at fixed density $\rho = 0.33$. The results of our calculations show a rather good agreement with computer simulation results, both for polar [2], and nonpolar [11] GB models.

For all temperatures, values of the first-rank orientational order parameter were found to be $\bar{P}_1 \approx 0.02$, suggesting no ferroelectricity, in agreement with the purely dipolar model composed of a simple cubic lattice [12]. Values of the coupling OP, at the same temperatures, were found to be $\bar{\kappa} \approx 0.01$, confirming the nematic character of the phase.

The orientational order of LCs is traditionally quantified in terms of OPs; however, the most complete description of the order is provided by the singlet orientational distribution

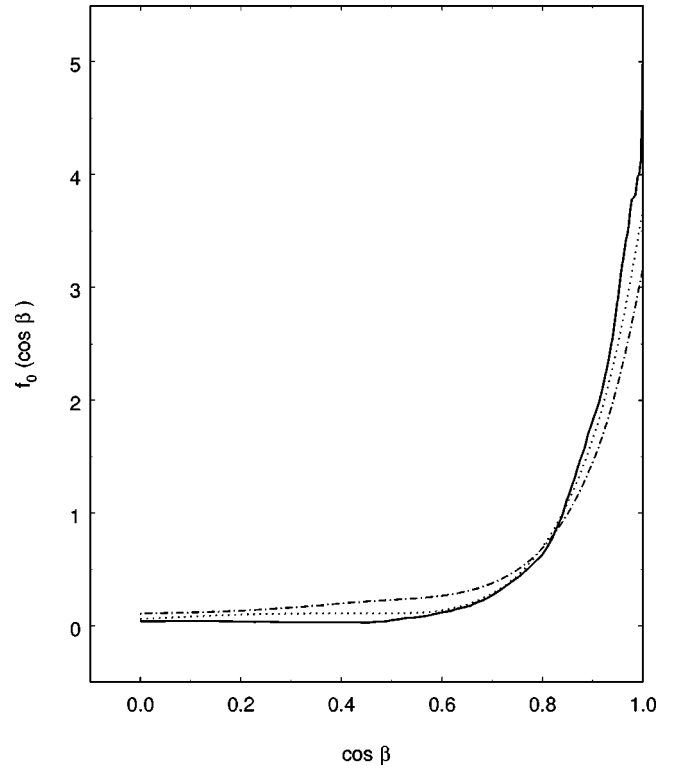


FIG. 2. Orientational distribution functions at fixed density, $\rho = 0.33$, and temperature $\theta = 1.0$, for polar and nonpolar GB models; dashed line for $\mu^* = 2$, dashed-dotted line for $\mu^* = 0$, respectively. The solid line corresponds to the MD simulation of 5CB in the nematic phase, at $T = 300$ K and density 1 g cm^{-3} .

function (ODF). In Fig. 2 we compare the ODFs $f_0(\cos \beta) = \int d\mathbf{q}_i d\varphi F_i(\mathbf{q}_i, \mathbf{e}_i)$, for both polar and nonpolar models, with one determined in the molecular dynamics (MD) simulation for 5CB (4-*n*-pentyl-4'-cyanobiphenyl) [13]. The MD simulation was carried out using the conventional potential energy function composed of intra and intermolecular contributions [14]. The comparison of the ODFs determined using the two methods seems justified since the experimental value of the dipole moment for 5CB molecule is $4.77 D$ [15], corresponding to $\mu^* = 2$. Furthermore, the temperature and density in the MD simulation (300 K and 1 g cm^{-3}) corresponds to the dimensionless parameters $\theta = 1.0$ and $\rho = 0.33$, respectively. Comparing the values of the OP \bar{P}_2 obtained from the MD simulation with realistic atom-atom interaction (i), with one obtained from the integral equation (ii) and MC (iii) approaches, both for the dipolar GB model, show the following results: (i) $\bar{P}_2 = 0.66$, (ii) $\bar{P}_2 = 0.98$, and (iii) $\bar{P}_2 = 0.98$, respectively. In view of completely different interaction models used in (i) and (ii,iii) such a deviation is not surprising.

Figure 3 displays the temperature dependence of the average correlators for nearest and next nearest neighbors. The average correlators for nearest-neighbors are defined by $\xi_{\lambda} = [1/(2\lambda)] \sum_l \langle \mathbf{e}_0 \cdot \mathbf{e}_l \rangle$, where $\lambda = 1$ denotes the average of two ‘‘vertical’’ nearest neighbors of the central particle indicated by subscript 0, whereas label $\lambda = 2$ correspond to the average of four ‘‘horizontal’’ neighbors. The ‘‘vertical’’ correlators are characterized by a common positive value, while almost identical negative values were obtained for all four

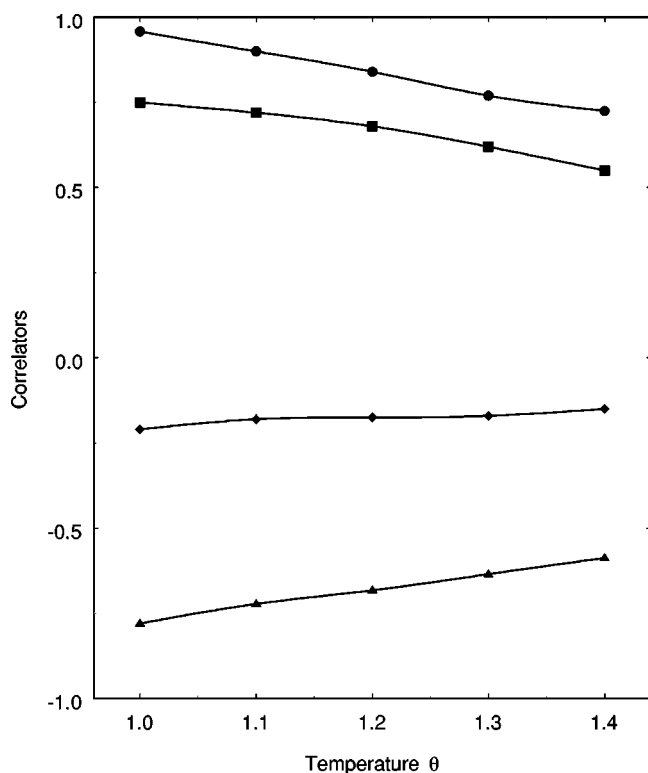


FIG. 3. Temperature dependence of the orientational correlators, ξ_λ , for the nearest neighbors; circles correspond to the “vertical” ξ_1 , whereas triangles correspond to the “horizontal” ξ_2 , respectively. The same dependence of the average orientational correlators $\bar{\xi}$ (squares) and $\bar{\eta}$ (rhombus), for the nearest and next nearest neighbors, respectively.

“horizontal” correlators. The average nearest neighbor correlator $\bar{\xi} = (1/3)\sum_\lambda \xi_\lambda$ shown in Fig. (3), is therefore negative for all temperatures indicating an antiparallel orientation of the dipoles in neighbor cells.

We note that the agreement between integral equation approach (ii) and the computer simulation (iii), concerning the orientational order parameter is good. This leads us to the conclusion the anisotropy of the nematic phase is not im-

posed by the symmetry of the system (cubic lattice), but rather is a consequence of the (GB) potential. In analogy with nearest neighbors, the correlations between next-nearest neighbors are defined $\eta_\lambda = \langle \mathbf{e}_0 \cdot \mathbf{e}_\lambda \rangle$, where $\lambda = 1, \dots, 12$ labels the neighbors of the central particle. We have found these quantities to be rather insensitive to λ , and therefore report in Fig. 3 the temperature dependence of their average over the twelve neighbors, i.e., $\bar{\eta} = (1/12)\sum_\lambda \eta_\lambda$. The average correlator $\bar{\eta}$, is positive for all temperatures.

It should be noted out that the MC simulation (iii) [2] predicts a smectic structure below $\theta = 1.6$, while our calculations indicate a nematic phase. Such disagreement require a more careful investigation of the phase diagram of the modified GB potentials. In the original formulation of the strength parameter $\epsilon = \epsilon(\mathbf{r}_{ij}, \mathbf{e}_i, \mathbf{e}_j)$, with exponents $\nu = 1$ and $\mu = 2$ [1], the computer simulation predicts a nematic phase [16], in the temperature range that corresponds to our calculations. We also do not know *a priori* what effect the changes of the exponents will have on the stability of the liquid crystalline phases.

We conclude this Rapid Communication by noting that a dipole moment attached to a GB particle significantly increases the orientational order of the system. Furthermore, the average correlators for neighbors and next neighbors are negative and positive, respectively. The former result indicate an antiparallel average orientation of the neighbor molecules. This observation is in fact in agreement with MC computer simulations [2,17], and with interpretations of experimental data for polar nematogens [18]. Of course, the head-tail symmetry in the conventional GB particles prevents investigation of this important structural effect. Finally, it should also be pointed out that the absence of long-range translational order in the nematic fluid precludes the possibility of antiferroelectric long-range order.

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