The direct correlation function in nematic liquid crystals from computer simulation

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Abstract

We compare the direct correlation function (DCF) in the nematic phase of uniaxial molecules modelled as soft ellipsoids with DCFs of the same system in the isotropic phase from simulation and Percus-Yevick theory. The nematic DCF is determined without approximations from computer simulations, using a scheme that takes into account explicitly the dependence of the pair correlation on the orientation of the director. The method was validated by calculating the Frank elastic constants from the DCF through the Poniewierski-Stecki equations and comparing them with the values obtained from an analysis of order fluctuations.

1. Introduction

The direct correlation function (DCF) is important in the statistical mechanics of fluids[1,2]. While the DCF of isotropic phases has been well studied theoretically [3–10] and by simulation [11], few studies have been devoted to the DCF of nematic mesophases [12]. Nematic DCFs from simulation have been obtained by Stelzer et al. [13,14] and Zakharov et al. [15]. However, they neglected the explicit angular dependence of the pair correlation on the orientation of the director, i.e. the axis of preferential molecular alignment.

Longa et al. [16] objected to this approximation. Indeed, when Stelzer et al. used their DCF to estimate the Frank elastic constants [12,17] of the system via the Poniewierski-Stecki (PS) expressions [18], their results disagreed significantly from the values published soon after by Allen et al. [19], who analysed the order tensor fluctuations in the same model liquid crystal. Since the latter method is straightforward, the mismatch was most likely due to an error in the DCF.

Recently, we proposed a way to calculate the DCF in a uniaxial nematic liquid crystal without any approximation from a spherical harmonics expansion of the two-particle density [20]. We reformulated the PS equations so that the Frank elastic constants can be computed directly from the expansion coefficients of the DCF in Fourier space. We applied the method to the nematic phase of a model system of soft ellipsoids. For comparison we also computed the Frank elastic constants from the fluctuations of the order tensor. We found good agreement between the values, indicating that our method of calculating the DCF is reliable.

In this paper we show data for the two-particle density and the DCF in the nematic phase. We also calculate the DCF for the isotropic phase, and compare it with the nematic DCF, as well as the isotropic DCF from Percus-Yevick theory.

2. Finding the direct correlation function

In a homogeneous system at equilibrium, the total correlation function h is defined from the one- and two-particle densities $\rho^{(1)}$ and $\rho^{(2)}$:

$$h(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12}) = \frac{\rho^{(2)}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})}{\rho^{(1)}(\mathbf{u}_1)\rho^{(1)}(\mathbf{u}_2)} - 1, \qquad (1)$$

where $\mathbf{u}_i$ is a molecular axis versor and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. The shorter-ranged DCF c is extracted from h through the Ornstein-Zernike equation [1]

$$h(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12}) = c(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12}) + \qquad (2)$$
$$+ \int c(\mathbf{u}_1, \mathbf{u}_3, \mathbf{r}_{13}) \, \rho^{(1)}(\mathbf{u}_3) \, h(\mathbf{u}_3, \mathbf{u}_2, \mathbf{r}_{32}) d\mathbf{u}_3 d\mathbf{r}_3 .$$

In a frame where the z-axis points along the director, all orientation-dependent functions can be expanded in a basis of spherical harmonics:

$$\rho^{(1)}(\mathbf{u}) = \varrho \sum_{l \text{ even}} f_l \, Y_{l0}(\mathbf{u}) \qquad (3)$$

$$F(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12}) = \sum_{\substack{l_1, l_2, l \\ m_1, m_2, m}} F_{l_1 m_1 l_2 m_2 l m}(r) \qquad (4)$$
$$\times Y_{l_1 m_1}(\mathbf{u}_1) \, Y_{l_2 m_2}(\mathbf{u}_2) \, Y_{lm}(\hat{\mathbf{r}}_{12}).$$

where $F = \rho^{(2)}$, h or c, $r = |\mathbf{r}_{12}|$, and $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r$. Because of the symmetry of the nematic phase, only real coefficients with $m_1 + m_2 + m = 0$ and $l_1 + l_2 + l$ even enter the expansion; if the molecules have uniaxial symmetry, every l_i is even, too.

The expansions in Eqns. (3) and (4) allow Eqns. (1) and (2) to be put in matrix form. Eqn. (1) becomes a linear system that can be solved for the coefficients of h by standard numerical methods, once the coefficients of $\rho^{(1)}$ and $\rho^{(2)}$ are known from simulation. The Ornstein-Zernike Eqn. (2) is most conveniently solved in Fourier space. This requires a Hankel transformation [21] of the coefficients of h from the previous step, and a back transformation of the coefficients of c.

3. Model, simulations and data analysis

The particles in our simulations interact through a simple repulsive pair potential $V_{ij}(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r}_{ij})$,

$$V_{ij} = \begin{cases} 4\epsilon_0 \, (\tilde{r}_{ij}^{-12} - \tilde{r}_{ij}^{-6}) + \epsilon_0, & \tilde{r}_{ij}^{-6} < 2 \\ 0, & \text{otherwise} \end{cases}, \qquad (5)$$

where $\tilde{r}_{ij} = (r_{ij} - \sigma_{ij} + \sigma_0)/\sigma_0$; the shape function

$$\sigma_{ij}(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}_{ij}) = \sigma_0 \left\{ 1 - \frac{\chi}{2} \left[\frac{(\mathbf{u}_i \cdot \hat{\mathbf{r}}_{ij} + \mathbf{u}_j \cdot \hat{\mathbf{r}}_{ij})^2}{1 + \chi \mathbf{u}_i \cdot \mathbf{u}_j} \right. \right.$$
$$\left. \left. + \frac{(\mathbf{u}_i \cdot \hat{\mathbf{r}}_{ij} - \mathbf{u}_j \cdot \hat{\mathbf{r}}_{ij})^2}{1 - \chi \mathbf{u}_i \cdot \mathbf{u}_j} \right] \right\}^{-1/2} \qquad (6)$$

approximates the contact distance between two ellipsoids of elongation $\kappa = \sigma_{\text{end-end}}/\sigma_{\text{side-side}} = \sqrt{(1+\chi)/(1-\chi)}$ [22]. We use scaled units defined in terms of ϵ_0, σ_0, the particle mass and the Boltzmann constant k_B. We chose $\kappa = 3$, a temperature $T = 0.5$, and number densities $\varrho = 0.24$ and $\varrho = 0.30$, that correspond to isotropic and nematic ($\langle P_2 \rangle = 0.69, \langle P_4 \rangle = 0.31$) states, respectively, the phase transition happening at $\varrho = 0.29$.

The pair density $\rho^{(2)}$ of the isotropic phase was determined in a system of $N = 1000$ particles, that of the nematic phase in systems of $N = 1000, 4000$, 8000 and 16000 particles. For $N = 1000$ we used Monte Carlo (MC) on a workstation, for the larger systems we resorted to a domain decomposition molecular dynamics (MD) program on a Cray T3E. Run lengths were 5–10 million MC or MD steps depending on system size.

The expansion coefficients of $\rho^{(2)}$ were computed from simulation configurations using [23]

$$\rho^{(2)}_{l_1 m_1 l_2 m_2 l m}(r) = 4\pi \, \varrho^2 \, g(r) \qquad (7)$$
$$\times \langle \, Y^*_{l_1 m_1}(\mathbf{u}_1) \, Y^*_{l_2 m_2}(\mathbf{u}_2) \, Y^*_{lm}(\hat{\mathbf{r}}) \, \rangle_{\delta r},$$

where $g(r)$ is the radial distribution function, i.e. the number of molecular pairs at distances between r and $r + \delta r$, divided by $4\pi \varrho \, r^2 \delta r$. These time-consuming averages were calculated in part on a Cray T3E. We have determined coefficients for l_i, l up to $l_{max} = 6$ (there are 469) in all systems, and up to $l_{max} = 8$ (there are 1447) in the smallest system (nematic phase), with $\delta r = 0.04$.
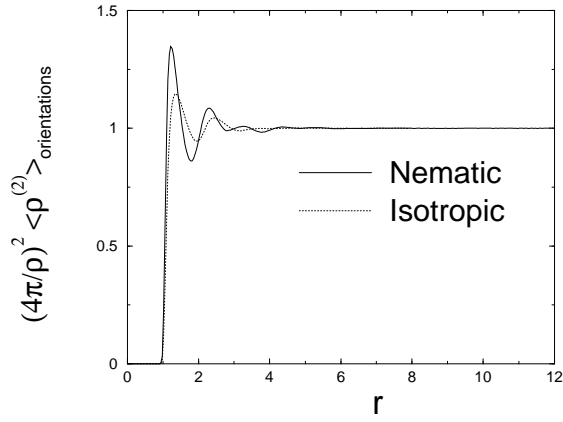
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Fig. 1. Average over all orientations $\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}_{12}$ of the two-particle density $\rho^{(2)}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})$ multiplied by $(4\pi/\varrho)^2$.
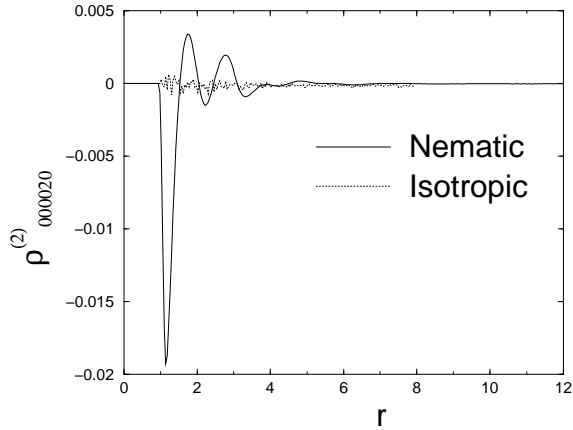

Fig. 2. Expansion coefficient $\rho^{(2)}_{000020}(r)$ of the two-particle density $\rho^{(2)}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})$.
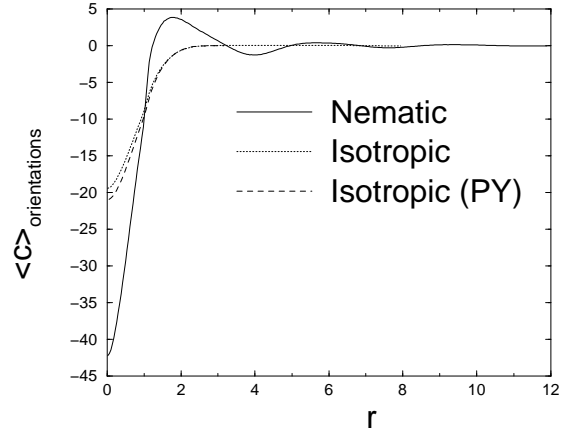

Fig. 3. Average over all orientations of the direct correlation function $c(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})$ from simulation, and the Percus-Yevick approximation for the isotropic phase.
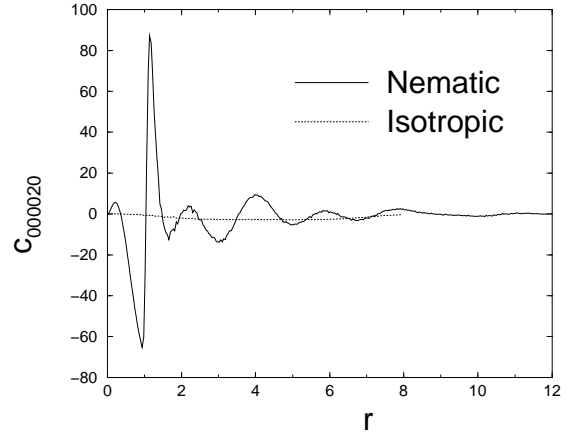

Fig. 4. Expansion coefficient $c_{000020}(r)$ of the direct correlation function $c(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})$.

4. Results and discussion

Fig. 1 shows the pair density $\rho^{(2)}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})$ averaged over all orientations $\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}_{12}$. This function changes little from isotropic to nematic, in spite of the difference between the overall densities ϱ. In both phases, the only structure in this function is at distances corresponding to the dimension $\kappa = 3$ of the particles, indicating the lack of long range translational order.

Fig. 2 shows the coefficient of $\rho^{(2)}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})$ with $(l_1, m_1, l_2, m_2, l, m) = (0, 0, 0, 0, 2, 0)$, that describes the correlation between the director and the intermolecular vector $\mathbf{r}_{12}$ irrespective of the molecular orientations $\mathbf{u}_1$ and $\mathbf{u}_2$. This coefficient is zero in the isotropic phase, that is rotationally invariant, but non zero in the nematic phase, reflecting the anisotropy of the latter.

Fig. 3 and Fig. 4 show the corresponding curves for the DCF. The amplitude difference between the orientations-averaged DCFs in the two phases is enhanced with respect to that of the orientations-averaged two-particle densities. The isotropic DCF is shorter-ranged and flattens out for $r > \kappa$, while the nematic DCF shows large oscillations that persist longer. This can be attributed to the increase

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Table 1

Elastic constants for systems with different number of particles N. PS: Poniewerski-Stecki expressions based on a DCF from a spherical harmonics expansion of $\rho^{(2)}$ up to $l_{max} = 6$ (8 for $N = 1000$; with $l_{max} < 6$ the results are about 20% worse). OF: order fluctuation analysis. The statistical error on the last digit is given within parentheses.

N	method	$\langle K_{11} \rangle$	$\langle K_{22} \rangle$	$\langle K_{33} \rangle$
1000	PS	0.55 (2)	0.35 (3)	1.56 (4)
4000	PS	0.52 (2)	0.31 (1)	1.51 (3)
	OF	0.53 (1)	0.30 (1)	1.60 (1)
8000	PS	0.51 (2)	0.33 (2)	1.48 (3)
16000	PS	0.51 (1)	0.32 (1)	1.43 (2)
	OF	0.53 (1)	0.30 (1)	1.59 (1)

in the local order, that allows particles to pack more efficiently in the side-by-side configuration of the nematic phase. For comparison, we have also calculated the isotropic DCF connecting Eqns. (2) and (5) with the Percus-Yevick closure [10]:

$$c(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12}) = [h(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12}) + 1] \tag{8}$$
$$\times \{1 - \exp[V_{12}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12})/k_B T]\}.$$

Agreement with the simulation result for the isotropic phase is quite good. Again, the coefficient $c_{000020}(r)$ is zero in the isotropic case and non-zero in the nematic case.

Various physical quantities can be obtained from the DCF, e.g. the Frank elastic constants via the PS theory, as mentioned in the introduction. The results are summarized in Table 1, together with those obtained from an order tensor analysis following Allen et al. [19]. The elastic constants are important phenomenological parameters for a quantitative description of bulk liquid crystals. Here they were used as a test to check our new approach to the DCF in oriented systems. Indeed, for the sole purpose of finding the elastic constants, the order tensor method is computationally more efficient, while of course the DCF, being a central quantity in density functional theory, has applications far beyond the calculations of elastic constants.

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