Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 16 Jun 2011

To cite this article: Masashi Torikai (2011): Excluded Volume Effect on the Nematic Phase of Hard Spherocylinder Fluid in Contact with a Hard Wall, Molecular Crystals and Liquid Crystals, 546:1, 72/[1542]-78/[1548]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.571918

Mol. Cryst. Liq. Cryst., Vol. 546: pp. 72/[1542]–78/[1548], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.571918

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Excluded Volume Effect on the Nematic Phase of Hard Spherocylinder Fluid in Contact with a Hard Wall

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The nematic phase of hard spherocylinder fluid in contact with a hard wall is calculated using a density functional theory. A new trial distribution function with explicit consideration of the excluded volume effect between the spherocylinders and the wall is proposed. The new trial function gives a lower surface tension than without the excluded volume effect, but it results in a less-plausible tilted nematic director with respect to the wall.

Keywords Density functional theory; excluded volume effect; nematic phase

1. Introduction

Theoretical studies on the interfacial properties of the nematic phases of rod-like liquid crystal have been carried out by using the mean field theory [1], density functional theory [2–9], and computer simulations [10]. These studies show that the nematic director of hard rod-like molecular liquids at the interface with the isotropic liquid phase [2–5] and with a hard wall [1, 6–8, 10] is parallel to the interface.

The equilibrium density profile of a system can be derived by minimizing the free energy defined in the density-functional theory. Other than solving the Euler-Lagrange equation derived from the functional derivative of the free energy functional, we may obtain an approximate density profile by assuming a possible functional form with some variational parameters as a trial function and minimizing the free energy with respect to the parameters. The trial function with fewer variational parameters is better since multidimensional minimization of the free energy is numerically demanding. In order to make a relatively accurate density profile, it is necessary to reduce the number of the variational parameters without loosing important properties of the density profile. For instance, the coupling of the translational and orientational degrees of freedom in the density profile is one of the essential properties of non-spherical molecular liquids under the existence of an interface. If we reduce the number of variational parameters in the trial function by using a

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so-called decoupling approximation, we can significantly simplify the minimization process but we will obtain less satisfactory results, as pointed out in [11,12].

In the present paper, I propose a simple method to make a trial function that explicitly takes into account the excluded volume effect between the molecules and wall. This method, based on that proposed by Shinomoto [13] for hard sphere fluids, introduces an effective attractive force due to the excluded volume effect, and can include the coupling between the translational and orientational degrees of freedom in a natural way. We find that this method gives a lower surface tension than without the excluded volume effect. But the stable state given by this method is less plausible: the nematic phase with tilted director with respect to the wall. Thus we must conclude that this method is not satisfactory at this stage, but it can be a preliminary step to considering the excluded volume effect on the interfacial phenomena of liquid crystals.

2. Theory

The system consists of a hard plain wall and the fluid of hard spherocylinders (SPCs) with the cylinder length L and breadth D. The spherocylinder is characterized with the position of its center $\boldsymbol{r}=(x, y, z)$ and the orientation of the molecule $\boldsymbol{\omega}=(\theta, \varphi)$, where θ and φ are the polar and the azimuthal angle of the molecule axis with respect to the Cartesian axis. The interaction between SPCs i and j is $u(i, j)=\infty$ if i and j overlap and otherwise zero, where i as the argument of a function denotes $(\boldsymbol{r}_i, \boldsymbol{\omega}_i)$. The interaction between an SPC i and the wall at $z=0$ is $\mathrm{u_w}(z_i, \theta_i)=\infty$ if $z_i \leq z_\mathrm{m}(\theta_i)=D/2+(L/2)|\cos\theta_i|$ and otherwise zero. We may assume that the distribution function does not depend on x and y due to symmetry of the system.

In the decoupling approximation, the following simple trial distribution function (with a variation parameter α) is used:

$$\rho(z, \boldsymbol{\omega}; \alpha) = \rho_\mathrm{b} f(\boldsymbol{\omega}; \alpha) f_\mathrm{w}(z, \theta), \tag{1a}$$

$$f_\mathrm{w}(z, \theta) = \exp[-\beta u_\mathrm{w}(z, \theta)]. \tag{1b}$$

Strictly speaking, the translational and the orientational degrees of freedom *couple* via the factor $f_\mathrm{w}(z, \theta)$ which assures that the distribution vanishes in the excluded volume $V_\mathrm{w}(\theta)$. But the effect of the wall remains where the SPCs directly contact with the wall and thus this approximation is crude.

We can improve the distribution function (1) by taking into account an effective force due to the excluded volumes, in a similar way to the theory for hard sphere fluids by Shinomoto [13]. In our system, we can define two excluded volumes: $V(i, \boldsymbol{\omega}_j)$ between an SPC i and another SPC j, and $V_\mathrm{w}(\theta)$ between the hard wall and an SPC with the polar angle θ. An SPC i feels the pressure from the surrounding SPCs due to the collision at the surface of the excluded volume $V(i, \boldsymbol{\omega}_j)$. The pressure is isotropic in the region far from the wall. Near the wall, however, the pressure is no longer isotropic since any collision between the SPC i and SPCs with the orientation $\boldsymbol{\omega}_j$ cannot occur where $V(i, \boldsymbol{\omega}_j)$ and $V_\mathrm{w}(\theta_j)$ overlap. Due to the anisotropy of the pressure, the SPC i feels an effective attractive force toward the wall. This mechanism for the effective force is similar to that of the so-called depletion force between particles suspended in solutions of macromolecules [14].

The increase of the distribution function of SPCs near the wall due to the effective force can be estimated [13] by the Boltzmann factor

$$\exp[-\beta\Psi(z,\boldsymbol{\omega})], \tag{2}$$

where $\beta = 1/kT$ is the inverse temperature with the Boltzmann constant k and temperature T, and $\Psi(z, \boldsymbol{\omega})$ denotes the minimum work required to move an SPC with the direction $\boldsymbol{\omega}$ from infinity to z under the influence of the effective force. As a zeroth approximation of the density distribution, we start from the decoupling approximation (1). Then we can conclude from the pressure sum rule [15] that the pressure p obeys the ideal gas equation of state $p = \rho_b kT$ with bulk density of SPC ρ_b. We can then readily show [13]

$$\beta\Psi(z,\boldsymbol{\omega}) = -\rho_b\langle \mathrm{V_{ov}}(\mathrm{z},\boldsymbol{\omega},\boldsymbol{\omega}')\rangle_{f(\boldsymbol{\omega}';\alpha)}, \tag{3}$$

where $V_{ov}(z_i, \boldsymbol{\omega}_i, \boldsymbol{\omega}')$ denotes the overlap volume between $V(i, \boldsymbol{\omega}')$ and $V_w(\boldsymbol{\omega}')$, and the angular brackets $\langle\rangle_{f(\boldsymbol{\omega};\alpha)}$ denote an average over the z-independent orientational distribution $f(\boldsymbol{\omega};\alpha)$. In this paper, I choose the Onsager trial distribution function [16] as the z-independent orientational distribution:

$$f(\boldsymbol{\omega};\alpha) = \frac{\alpha}{4\pi\sinh\alpha}\cosh(\alpha\cos\Theta), \tag{4}$$

where Θ is the angle between the director and the orientation $\boldsymbol{\omega}$ and α defines the distribution width around the director. From the Eqs. (2), (3), and (4), the trial distribution function used in this paper is

$$\rho(z,\boldsymbol{\omega};\alpha) = \rho_b f(\boldsymbol{\omega};\alpha) f_w(z,\boldsymbol{\omega})\exp\lfloor\rho_b\langle V_{ov}(z,\boldsymbol{\omega},\boldsymbol{\omega}')\rangle_{f(\boldsymbol{\omega}';\alpha)}\rfloor. \tag{5}$$

In this distribution function, the translational and the orientational degrees of freedom couple in a natural way.

The surface tension of the system can be calculated as the excess grand thermodynamic potential per unit area over the bulk value. For simplicity, we use the Onsager approximation [16], i.e., the second-virial approximation in this paper. The expression of the surface tension is then

$$\beta\gamma = -\beta\Delta\mu\Gamma - (S_{rot} + S_{tr:id} + S_{tr:ex})/k - S_{eff}/k, \tag{6}$$

where $\beta\Delta\mu = \beta\mu - \ln(\Lambda^3\rho_b/4\pi)$ with the de Broglie thermal wavelength Λ, $\Gamma = -\rho_b\langle\lambda(\omega)\rangle_{f(\omega)}$,

$$\lambda(\boldsymbol{\omega}_i) = z_m(\theta_i) - \int_{z_m(\theta_i)}^{\infty}\psi(i)\,\mathrm{d}z_i, \tag{7a}$$

$$\psi(i) = \exp\lfloor\rho_b\langle V_{ov}(z,\boldsymbol{\omega},\boldsymbol{\omega}')\rangle_{f(\boldsymbol{\omega}';\alpha)}\rfloor - 1, \tag{7b}$$

$$S_{rot}/k = \rho_b\langle\lambda(\boldsymbol{\omega})\ln[4\pi f(\boldsymbol{\omega})]\rangle_{f(\boldsymbol{\omega})}, \tag{8a}$$

$$S_{\text{tr:id}}/k = -\rho_b \langle \lambda(\boldsymbol{\omega}) \rangle_{f(\boldsymbol{\omega})}, \tag{8b}$$

$$\frac{S_{\text{tr:ex}}}{k} = \frac{\rho_b^2}{2} \left\langle \int_{z_m(\theta_2)-z_m(\theta_1)}^{\infty} dz_{12} A(|z_{12}|, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)[z_{12} - z_m(\theta_2) + z_m(\theta_1)] \right\rangle_{f(\omega_1)f(\omega_2)} + \frac{\rho_b^2}{2} \langle z_m(\theta_1) \int dr_1 V(1, \omega_2) \rangle_{f(\boldsymbol{\omega}_1)f(\boldsymbol{\omega}_2)} \tag{9}$$

and

$$\frac{S_{\text{eff}}}{k} = \frac{\rho_b^2}{2} \left\langle \int_{z_m(\theta_1)}^{\infty} dz_1 \int_{z_m(\theta_2)}^{\infty} dz_2 A(|z_{12}|, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)[\psi(1)\psi(2) + \psi(1) + \psi(2)] \right\rangle_{f(\boldsymbol{\omega}_1)f(\boldsymbol{\omega}_2)} \tag{10}$$

with $A(|z_{ij}|, \boldsymbol{\omega}_i, \boldsymbol{\omega}_j)$ being the intersection of the $V(i, \boldsymbol{\omega}_j)$ with the $z = z_j$ plane. In performing the numerical calculation, I used the approximation for $A(|z_{ij}|, \boldsymbol{\omega}_i, \boldsymbol{\omega}_j)$ used in [6], in which the spherical and cylindrical parts of the excluded volume $V(i, \boldsymbol{\omega})$ are ignored. The equations (6)–(10) can be derived in a similar way to that in [6]. We recover the same expression as in [6] for the surface tension if we totally ignore the effective force toward the wall, i.e., $\psi(i) \equiv 0$.

3. Results and Discussions

I used the bulk isotropic-nematic phase coexistence condition when I calculated the surface tension of the nematic phase of the SPC fluid. The bulk coexistence conditions for the length-to-breadth ratio $L/D = 5$, 10, and 20 are listed in Table 1. The nematic order parameters, defined as $s = \langle 3\cos^2\theta - 1 \rangle/2$, at the transition are also shown in the table.

The surface tensions (6) under these bulk isotropic-nematic coexistence parameters are shown in Figure 1 as functions of θ_d, the polar angle of the nematic director. For all values of L/D, our new trial function (5) gives better (i.e., lower) surface tension than the result from the approximation (1). The most stable tilt angle of the director for the SPC fluid with $L/D = 5$ is $\theta_d = 90°$, i.e., the director is parallel to the wall. The surface tensions of the SPC fluids with $L/D = 10$ and 20, however, show minima at tilted angles $\theta_d \approx 60° - 70°$.

Table 1. The coexistence conditions for the bulk isotropic and nematic phases of the hard SPC fluids with length-to-breadth ratio $L/D = 5$, 10, and 20. ρ_b denotes the density of the nematic phase

L/D	μ	ρ_b	α	s
5	9.24	0.200	11.35	0.76
10	4.26	0.0519	13.41	0.79
20	1.20	0.0134	15.06	0.81

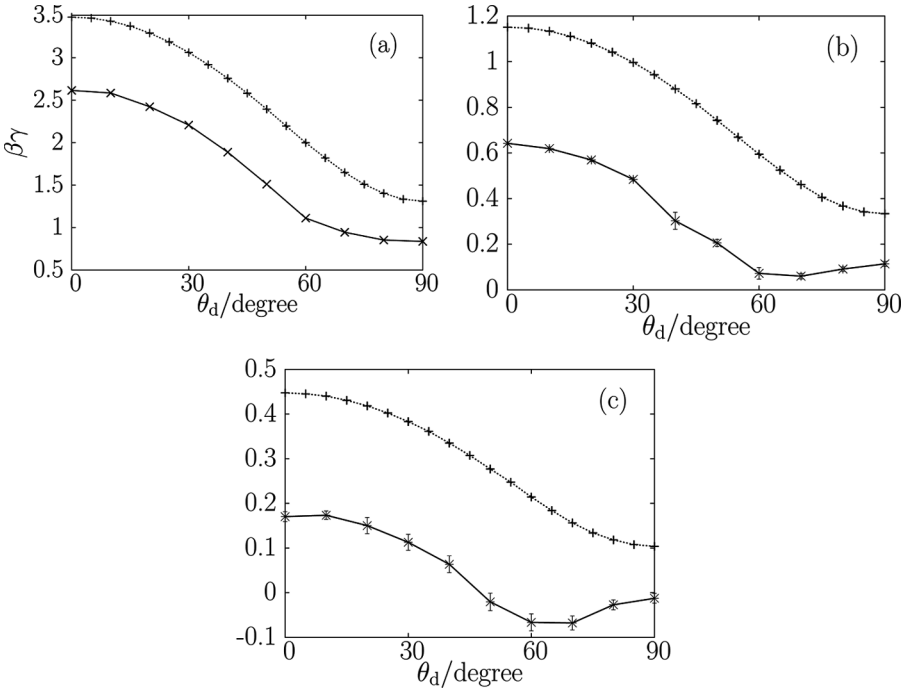

Figure 1. The director-dependence of the surface tension of the nematic phase of SPC fluids with (a) $L/D = 5$, (b) 10, and (c) 20. θ_d denotes the angle between the director and the z axis. Solid and dashed lines are the surface tensions calculated using the trial distribution functions (5) and (1), respectively.

The spatial distribution $\rho(z)$ is shown in Figure 2 for SPC with $L/D = 20$ and $\theta_d = 70°$. The rapid increase near the wall can be clearly seen in this figure. The density decreases monotonically with z. If we apply the Shinomoto method recursively [17], we will be able to obtain a more realistic oscillatory behavior of the density. The nematic order parameter $s(z)$ shown in Figure 2 is defined using the polar angle of SPCs with respect to the director, not to the z-axis. $s(z)$ weakly increases along with the increase of the density.

Each term in (6) except for S_{eff} (which vanishes if we ignore the effect of the effective force) shows a qualitatively similar θ_d-dependence to its counterpart obtained by setting $\psi(i) \equiv 0$. The term $-S_{\text{eff}}/k$ of (6) is almost constant in $0° \leq \theta_d \leq 50°$ and it increases monotonically from $\theta_d = 60°$ up to 90°. The fact that $\beta\gamma$ does not have a minimum at $\theta_d = 90°$ would be partially accounted for by this increase in $-S_{\text{eff}}/k$. But it cannot be fully attributed to the S_{eff} behavior since $\beta\gamma$ still has a minimum around $\theta_d \approx 60° - 70°$ even if we omit S_{eff} from (6).

The tilted nematic director at a hard substrate we observed here is not consistent with the result in [6], in which an approximation equivalent to (1) was used; furthermore, a computer simulation does not seem to exhibit the stable tilted nematic director of hard SPC fluid with $L/D = 15$ against a hard wall [10]. Since the Onsager approximation becomes better for longer SPC fluids, it will not be the main cause of such a questionable minimum in the surface tension at a tilted angle. In fact, a spurious minimum in the isotropic-nematic interface tension due to the Onsager

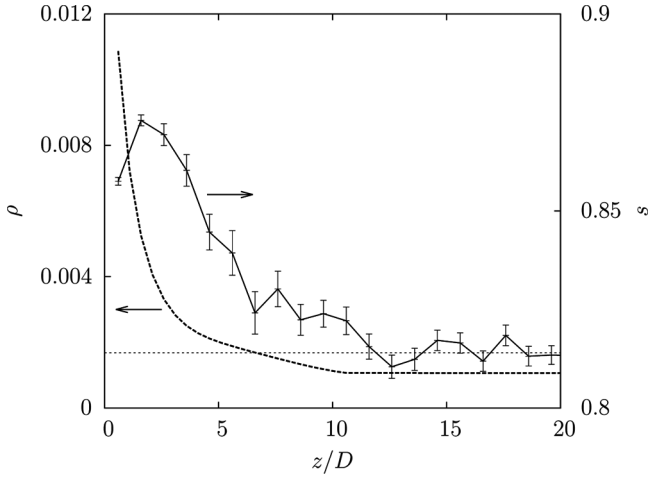

Figure 2. The z-dependence of the nematic order parameter s (solid line) and density ρ (dashed line) for SPC fluid with $L/D = 20$. The horizontal dotted line indicates the bulk nematic order parameter.

approximation is observed for $L/D = 5$ SPC fluid, but such minimum disappears for longer SPC fluids [2,3].

The director tilt in our result would be a direct consequence of the effective attractive force toward the hard wall. As shown in Figure 2, the SPC density rapidly increases near the wall due to the effective force. Although the density profile obtained using the computer simulation [10] also increases as z decreases, the behavior is not monotonic but the density rapidly decreases very close to the wall. This is because of the fluctuation of the molecular orientation around the nematic director. In our theory, however, it seems that the density increase near the wall introduced by the factor (2) is too significant and the decrease due to the molecular orientational fluctuation is not enough; thus the density cannot decrease in the vicinity of the wall. Since a steep gradient in the density contributes to the increase in the free energy, the tilted director is preferable with respect to this contribution because the tilt keeps the SPC centers away from the wall and depresses the steep increase of the density near the wall.

To conclude, the distribution function (5), in which the translational and the orientational degrees of freedom couple in a natural way, gives a lower surface tension than the decoupling approximation (1), but it predicts a questionable tilted director against the wall. This result may be because the expression (5) emphasizes the density increase near the wall too much. Our results might be improved by taking into account the oscillatory behavior by using the Shinomoto method recursively [17] and depressing the density increase. We can also expect that a different choice of the orientational distribution function (4) will give better results.

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