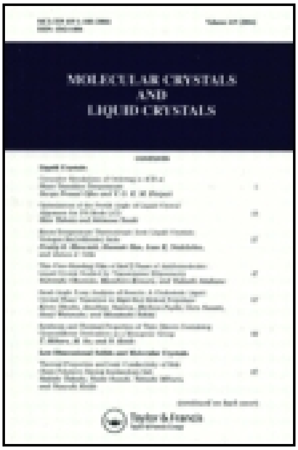

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Statistical Theory of Smectic A and Columnar Phases in Hard Rod Fluids

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Statistical Theory of Smectic A and Columnar Phases in Hard Rod Fluids

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The free energy of smectic A and columnar phases in parallel hard cylinders with length L and width D are calculated as functions of the order parameters. In the third virial approximation we find the second order nematic to smectic A (N-S_A) lyotropic phase transition at a packing fraction $\eta = \eta_{NA} = 0.355$ where the smectic layer spacing d is $d_c = 1.35L$. These values agree with results by computer simulation: $\eta_{NA} = 0.35$ and $d_c = 1.27L$. Incorporating an attractive potential, we show the system exhibits the second order N-S_A phase transition at a temperature T_{NA}, and find for $T < T_{NA}$ the relation $(d/d_c - 1)/(1 - T/T_{NA}) \sim 10^{-1}$ and the layer compression modulus $B \sim 15(kT/v_{mol})(1 - T/T_{NA})$, where v_{mol} is the molecular volume. The stability of the columnar phase due to the hard core repulsion cannot be proved in the second virial approximation.

Keywords: statistical theory, hard rod fluids, columnar phases, excluded volume effect, lyotropic SA phase, thermotropic SA phase

INTRODUCTION

As has been shown theoretically by Onsager more than forty years ago,[1] systems of long hard rods can form the nematic (N) liquid crystal phase due to the hard core repulsion among the rods. In many systems of rod like polymers the intermolecular force is mainly the hard core repulsion; and recently in these systems not only the nematic and the cholesteric (Ch) phases but also more ordered the smectic A (S_A) and the columnar (Co) phases have been found experimentally.[2] Therefore, what types of liquid crystal phase can be stabilized by only the hard core repulsion is not an academic problem but quite actual question. Moreover, the study of this problem is very important to understand the role of the excluded volume effect as the common molecular mechanism of liquid crystalline phases including ordinary thermotropic ones.

Previously, the possibility of the S_A phase due to the hard core repulsion has been shown theoretically by Wadati and Isihara[3] using a two-dimensional model, and further by Hosino, Nakano and Kimura[4] for a three-dimensional system of hard square rods; and recent computer simulations proved it in system of hard spherocylinders.[5] Further, Hosino, Nakano and Kimura have suggested the possibility of the Co phase in the system of square rods and also the simulation found the phase in the spherocylinders of large length to width ratio.

In recent theoretical works, the stability of the smectic A phase in parallel hard cylinders has been predicted by several different methods. However, the stability of the Co phase is yet an open question. In the present paper, we calculate the free energy of the S_A phase for the system of hard cylindrical rods in the third virial approximation as a function of the order parameter. We find the second order lyotropic N-S_A phase transition likely as in the second virial approximation, and obtain those numerical values of the phase transition density and the layer spacing which agree quite well with the computer simulation. Then, by introducing a simple type of attractive intermolecular potential in the model, we discuss the thermotropic N-S_A phase transition and calculate the transition temperature, the order parameter, the layer spacing, and the layer compression modulus of the S_A phase. The results give good explanations for real behavior of ordinary thermotropic liquid crystals.

Further, we discuss by the second virial approximation the stability of Co phase in parallel hard cylinders. However, we cannot find the possibility of N-Co phase transition in the purely repulsive system.

LYOTROPIC SMECTIC A PHASE

Let us consider a system of N hard cylindrical molecules with the length L and diameter D aligning parallel to the z-axis of the space. We define the order parameter of the smectic A phase, i.e. the density wave along the z-axis with a wavelength d which is called as the layer spacing, in the following form

$$\sigma \equiv \left\langle \frac{1}{\mathrm{N}} \sum_{i}^{N} \cos\left(\frac{2\pi}{d} z_i\right) \right\rangle, \tag{1}$$

where z_i is the z-component of the position vector $\mathbf{r}_i$ of the center of mass of the i-th rod, $\langle \ldots \rangle$ indicates the thermal average. Assuming between molecules only the hard core potential

$$\phi_{ij}^{h} = \begin{cases} +\infty & \text{if } i \text{ and } j\text{-th molecules intersect,} \\ 0 & \text{otherwise,} \end{cases} \tag{2}$$

we calculate the free energy of the system using the method of symmetry breaking potential up to the fourth order in the order parameter. The detail of the calculations are described elsewhere.[6] In the third virial approximation, we get the result

$$\frac{F(\sigma) - F(0)}{\mathrm{NkT}} = \mathrm{D}_1(\eta, d)\sigma^2 + \mathrm{D}_3(\eta, d)\sigma^4, \tag{3}$$

where

$$\begin{aligned} \mathrm{D}_1(\eta, d) &= 1 + 8\eta j_0\left(\frac{2\pi}{d}\mathrm{L}\right) \\ &\quad + 16\eta^2\zeta\left\{j_0^2\left(\frac{\pi}{d}\mathrm{L}\right) + 2j_0\left(\frac{2\pi}{d}\mathrm{L}\right)\right\}, \end{aligned} \tag{4}$$

$$\begin{aligned} \mathrm{D}_3(\eta, d) &= \frac{1}{16}\left(1 + 8\eta j_0\left(\frac{4\pi}{d}\mathrm{L}\right) - 16\eta^2\left[\zeta\left\{2j_0^2\left(\frac{\pi}{d}\mathrm{L}\right)\right.\right.\right. \\ &\quad \left.\left.\left. - 9j_0^2\left(\frac{2\pi}{d}\mathrm{L}\right) - 2j_0\left(\frac{4\pi}{d}\mathrm{L}\right)\right\} + 4j_0^2\left(\frac{4\pi}{d}\mathrm{L}\right)\right]\right), \end{aligned} \tag{5}$$

and $\eta \equiv \rho v_{mol}$ is the packing fraction, $\rho \equiv N/V$ the number density, $v_{mol} \equiv \pi D^2 L/4$ the molecular volume, $j_0(x) \equiv x^{-1}\sin x$ the zeroth order spherical Bessel function, and $\zeta \equiv 0.5865$.

Minimizing the expression (3), where $F(0)$ is the free energy of the nematic phase, against σ and d, respectively, we can calculate the equilibrium free energy and also the equilibrium values of σ and d as functions of η. Then, we can conclude the system shows a lyotropic second order N-S$_A$ phase transition at a density $\eta_{NA} = 0.355$ and the layer spacing at the point is $d_c = 1.35L$ from the condition $F(\sigma) = F(0)$ for equilibrium of two phases. These values agree remarkably well with the results of recent computer simulation on the same system[5]: $\eta_{NA} = 0.35$ and $d_c = 1.27L$. The values given by the second virial approximation are, on the other hand, $\eta_{NA} = 0.575$ and $d_c = 1.398L$. Clearly the latter η_{NA} value is too large but the d_c value is not so bad. Thus we can see that the second virial theory is qualitatively correct to describe the present problem but quantitatively not so good; in comparison with this, the third virial theory is very accurate not only qualitatively but also quantitatively.

In the lowest order in $(\eta - \eta_{NA})/\eta_{NA}$, we found the order parameter

$$\sigma = 2.89\,\{(\eta - \eta_{NA})/\eta_{NA}\}^{1/2}, \tag{6}$$

and the layer spacing

$$d = d_c\{1 - 0.161\,(\eta - \eta_{NA})/\eta_{NA}\}. \tag{7}$$

It is desired to verify experimentally such density dependences.

THERMOTROPIC SMECTIC A PHASE

In the Maier-Saupe theory of the nematic phase,[7] an attractive dispersion potential such as

$$\phi_{ij}^{a} = -C(r_{ij}) - A(r_{ij})P_2(\cos\theta_{ij}) \tag{8}$$

has been assumed between molecules, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the centers of mass of i and j-th molecules, θ_{ij} the angle between the molecular axes, $P_2(x) = (3x^2 - 1)/2$ the second order Legendre polynomial. Later using this type of potential, McMillan[8] has discussed the smectic A phase in a molecular field approximation when he assumed simply the r_{ij} dependence of the coefficients $C(r_{ij})$ and $A(r_{ij})$ as $\exp\{-(r_{ij}/r_0)^2\}$. For the present model in which all the molecules align parallel to each other, we can assume the attractive potential simply as

$$\phi_{ij}^{a} = -A\exp\{-(r_{ij}/r_0)^2\}, \tag{8'}$$

where A and r_0 are positive constants. We treat this potential in a molecular field approximation as same as McMillan. The free energy of the system is now given by changing the factors $\mathrm{D}_1(\eta, d)$ and $\mathrm{D}_3(\eta, d)$ in the Equation (3) as

$$\mathrm{D}_1(\eta, d) \rightarrow \mathrm{D}_1(\eta, d) - \eta\frac{\tilde{A}}{\mathrm{kT}}\exp\{-(\pi r_0/d)^2\}, \tag{9}$$

$$\mathrm{D}_3(\eta, d) \rightarrow \mathrm{D}_3(\eta, d) - \eta\frac{\tilde{A}}{\mathrm{kT}}\exp\{-4(\pi r_0/d)^2\}, \tag{10}$$

where $\tilde{A} = A(\sqrt{\pi}r_0)^3/\mathrm{v}_{\mathrm{mol}}$.

On the basis of this free energy, we can conclude the system exhibits the second order N-$\mathrm{S_A}$ thermotropic phase transition at a temperature

$$\mathrm{T}_{\mathrm{NA}} = \eta\frac{\tilde{A}}{\mathrm{k}}\frac{\exp\{-(\pi r_0/d_c)^2\}}{1 + \mathrm{D}_1(\eta, d_c)}$$

$$\cong 0.255\frac{\eta}{\eta_{\mathrm{NA}} - \eta}\frac{\tilde{A}}{\mathrm{k}}\exp\{-5.38(r_0/\mathrm{L})^2\}, \tag{11}$$

where $d_c = 1.35\mathrm{L}\,[1 + \{0.161 + 0.594(r_0/\mathrm{L})^2\}(\eta_{\mathrm{NA}} - \eta)/\eta_{\mathrm{NA}}]$ and $\eta_{\mathrm{NA}} = 0.355$. Further we can find the following expressions for the order parameter σ, the layer spacing d, and the layer compression modulus B which is defined by the equation

$$\frac{\delta F}{V} = \frac{1}{2}B\left(\frac{\delta d}{d}\right)^2, \tag{12}$$

where δF is the increase of the free energy for a small variation δd of the layer spacing.

$$\sigma \cong 2.89 \left\{\frac{\eta_{NA} - \eta}{\eta_{NA}}\right\}^{1/2} \left\{\frac{T_{NA} - T}{T_{NA}}\right\}^{1/2}, \tag{13}$$

$$d \cong d_c \left[1 + 0.594\left\{\frac{\eta_{NA} - \eta}{\eta_{NA}}\right\}\left\{\frac{T_{NA} - T}{T_{NA}}\right\}\left(\frac{r_0}{L}\right)^2\right], \tag{14}$$

$$B \cong 149.4 \frac{kT}{v_{mol}} \left\{\frac{\eta_{NA} - \eta}{\eta_{NA}}\right\}\left\{\frac{T_{NA} - T}{T_{NA}}\right\}. \tag{15}$$

All these expressions are valid for the first order in $(\eta_{NA} - \eta)/\eta_{NA}$ and $(T_{NA} - T)/T_{NA}$. The density and temperature dependences of σ given by the Equations (6) and (13) are the same as the well known results of Landau theory of the second order phase transition.

If we assume tentatively the order of magnitude $(\eta_{NA} - \eta)/\eta_{NA} \sim 0.1$ and $r_0 \sim L$, then Equations (14) and (15) reproduce fairly well the empirical sizes and the temperature dependences of the respective quantities for real liquid crystals.[9]

LYOTROPIC COLUMNAR PHASE

The columnar phase, i.e. a two-dimensional long range translational order in the *xy*-plane, has been found in many disc like molecules. Can such a columnar phase be formed by hard core repulsion in rod like molecules? For low molecular weight thermotropic liquid crystals of rod like molecules this phase seems not yet be observed to today, but a recent experiment shows the columnar phase exists in concentrated solution of long rod like DNA.[2] In order to study the problem, we calculate the free energy of the system of parallel hard cylinders as a function of the order parameter which is defined as

$$\tau \equiv \left\langle \frac{1}{3N} \sum_i^N \{\cos \mathbf{k}_I \cdot \mathbf{r}_i + \cos \mathbf{k}_{II} \cdot \mathbf{r}_i + \cos \mathbf{k}_{III} \cdot \mathbf{r}_i\} \right\rangle, \tag{16}$$

where

$$\mathbf{k}_I \equiv \frac{4\pi}{\sqrt{3}\,a}(1, 0, 0), \quad \mathbf{k}_{II} \equiv \frac{4\pi}{\sqrt{3}\,a}\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right)$$

$$\mathbf{k}_{III} \equiv \mathbf{k}_I + \mathbf{k}_{II}. \tag{17}$$

In cases $1 \geqslant \tau > 0$, the columns of rods form a triangular lattice with the lattice constant a in the *xy*-plane, whereas in the nematic phase $\tau = 0$.

The calculation method is the same as for the smectic A phase; considering only the hard core repulsions, we obtain the free energy by the second virial approximation in a power series of τ up to the fourth order,

$$\frac{F(\tau) - F(0)}{N\mathrm{kT}} = A(\eta, a)\,\tau^2 - 2\tau^3 + C(\eta, a)\,\tau^4, \tag{18}$$

where

$$A(\eta, a) = 3\left\{1 + 16\eta \frac{\sqrt{3}\,a}{4\pi \mathrm{D}} J_1\left(\frac{4\pi\mathrm{D}}{\sqrt{3}\,a}\right)\right\}, \tag{19}$$

$$C(\eta, a) = \frac{15}{4} + 3\eta\left\{4\frac{\sqrt{3}\,a}{8\pi\mathrm{D}} J_1\left(\frac{8\pi\mathrm{D}}{\sqrt{3}\,a}\right),\right.$$

$$\left. + 16\frac{a}{4\pi\mathrm{D}} J_1\left(\frac{4\pi\mathrm{D}}{a}\right)\right\}, \tag{20}$$

and $J_1(x)$ is the first order Bessel function. The minimum value of the density at which the coefficient $A(\eta, a)$ changes its sign is found to be $\eta = \eta^* = 0.945$ for $a = a_c = 1.41\mathrm{D}$. As the free energy (18) contains the third order term of the order parameter τ and $C(\eta, a_c) > 0$, the system is now expected to exhibit the first order N-Co phase transition at a density near η^*. Using the free energy, we find the columnar phase is stable only for $\eta > \eta_{\mathrm{NC}} = 0.88$. However, the density η_{NC} seems to be unphysical because it is almost the same as the close packing value $\eta_{cp} = 0.907$. Thus, in the second virial approximation, we cannot prove the stability of the columnar phase. An improvement of the calculation in the third virial approximation is in progress.

CONCLUDING REMARKS

In the third virial approximation, we have clearly shown that the systems of parallel long cylinders can form stable smectic A phase due to the hard core repulsions. In recent theoretical works very similar results to the present ones have been obtained for the stability of the smectic A phase in parallel hard cylinders by several different methods[10,11,12,13].

On the other hand, the stability of the columnar phase in the same system has not been proved here by the second virial approximation. On the columnar phase, however, the existing theories do not agree with each other; Somoza and Tarazona[14] predicted the smectic A to columnar phase transition at $\eta \cong 0.55$, and Holyst and Poniewierski[15] argued that the columnar phase is more stable than the solid phase for $0.76 < \eta < 1$. Both results have been obtained by calculations based on density functional formalism. We expect that our progressing calculations in the third virial approximation throw light on this problem.

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