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Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: M. Wsdati & A. Isihara (1972): Theory of Liquid Crystals, Molecular Crystals and Liquid Crystals, 17:2, 95-108

To link to this article: http://dx.doi.org/10.1080/15421407208083833

Molecular Crystals and Liquid Crystals. 1972. Vol. 17, pp. 95–108

Theory of Liquid Crystals†

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Received January 8, 1971; *in revised form April* 4, 1971

Abstract—A formalism based on cluster expansions for non-uniform fluids is found useful for the discussion of various theories of liquid crystals. Using the general formalism the equations which determine the order parameters for transitions in three-dimensional liquid crystals are derived. The proof by Lakatos that there is no phase transition within the approximation of the Onsager integral equation is found not to be correct in general. The isotropic–nematic and nematic–smectic transitions in a two-dimensional system of rod-like molecules are estimated, the latter transition point agrees with what Alder and Wainwright estimated for a hard-sphere molecule in two-dimensions.

1. Introduction

Since Onsager discussed the appearance of an anisotropic phase in dilute system of rod-like molecules,(1) phase transitions in liquid crystals have attracted many theoretical attentions. For instance, Isihara further developed the Onsager theory in a more systematic and elegant way,(2) Zwanzig viewed the transitions from a slightly different angle based on the Onsager theory but by restricting the

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† This work was supported partly by the National Science Foundation through Grant GP-19740 to the State University of New York and partly by the Advanced Research Agency through Contract No. N00014–67–A–0398 (monitored by the Office of Naval Research) with the University of Rochester.

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molecular orientations into three mutually perpendicular directions and taking the limit of infinitely thin rods,⁽³⁾ and more recently Lakatos took up the Onsager–Isihara approach with detailed numerical analyses.⁽⁴⁾ On the other hand, Kobayashi proposed recently⁽⁵⁾ use of the integral equation which Kirkwood and Monroe⁽⁶⁾ derived for the discussion of a phase transition in simple liquids. The integral equation of Kirkwood and Monroe differs from Onsager's in the appearance of the direct potential instead of Mayer's f function in the integrand. Maier and Saupe⁽⁷⁾ proposed an effective field approach in which an orientational dependent potential determined an order parameter. A more elaborate work along this line has been worked out by McMillan,⁽⁸⁾ who succeeded to reproduce the nematic and smectic phases by adding short ranged coordinate dependent potential to the angle dependent potential.

A natural question arises then whether or not one can unify these three different theories, i.e., two integral equation methods and one effective field approach. In the next section we shall try to answer this question. We shall then derive closed equations similar to McMillan's but avoiding his phenomenological approach. Kobayashi tried to make a similar approach, but his equations are not closed and therefore unsatisfactory. We shall then consider a two-dimensional system. Recently, Lakatos concluded that a system of long thin rod-like molecules in two-dimensions does not show a phase transition. We shall show that the proof by Lakatos,⁽⁹⁾ being based on an undesirable approximation, is not valid and the result is misleading. We shall then make an approach which is similar to Kobayashi and McMillan's but is more satisfactory in theoretical structure and will estimate critical concentrations, one of which corresponding to what Alder and Wainwright⁽¹⁰⁾ obtained for a hard-sphere system by numerical analyses. In fact, the nature of this transition is essentially the same as theirs.

2. Cluster Expansion for a Non-Uniform System

Consider N anisotropic molecules in volume V with mass m and moments of inertia I_1, I_2 and I_3. Each molecule has six degrees of freedom, its position and orientation being designated by a variable τ. In the grand canonical ensemble the n-particle distribution function $\rho_n(\tau_1, \tau_2, \ldots, \tau_N)$ and the grand partition function Ξ are given by

$$\rho_n(\tau_1, \tau_2, \ldots \tau_N) = \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} \frac{1}{\Xi} \frac{z^{*N}}{N!} \int \mathrm{d}\tau_{n+1} \ldots \mathrm{d}\tau_N \exp(-\Phi/kT) \tag{2.1}$$

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} z^{*N} \int \mathrm{d}\tau^N \exp(-\Phi/kT) \tag{2.2}$$

where Φ is the potential energy and z^*, the activity, is related to the absolute activity z by

$$z^* = z \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \left(\frac{2\pi kT(I_1 I_2 I_3)^{1/3}}{h^2}\right)^{3/2}. \tag{2.3}$$

The potential energy will be assumed to be

$$\Phi(\tau^N) = \sum_{i=1}^{N} \psi(\tau_i) + \sum_{i>j} \phi(\tau_i, \tau_j) \tag{2.4}$$

where $\psi(\tau)$ is the potential due to external forces and $\phi(\tau_i, \tau_j)$ is the interaction energy of two particles.

In what follows we shall mostly use one-body and two-body reduced distribution functions. The former is related to the average number of particles N by

$$N = \int \mathrm{d}\tau \rho_1(\tau). \tag{2.5}$$

To simplify notations, we shall omit the suffix 1 to the one-body distribution function from now on. Like the case of uniform fluids, the grand partition function can be rewritten as follows

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \mathrm{d}\tau^N \prod_{i=1}^{N} z^*(\tau_i) \prod_{1 \leq i < j \leq N} \{1 + b(\tau_i, \tau_j)\} \tag{2.6}$$

where

$$z^*(\tau) = z^* e^{-\psi(\tau)/kT},$$

$$b(\tau_i, \tau_j) = e^{-\phi(\tau_i, \tau_j)/kT} - 1. \tag{2.7}$$

The cluster expansions of thermodynamic functions which follow from Eq. (2.7) have been discussed elsewhere$^{(11)}$ and we shall quote only the results. The free energy is

$$\begin{aligned}F = F_0 &+ \int d\tau \rho(\tau)\psi(\tau) + kT\int d\tau \rho(\tau)\ln\rho(\tau)\\ &+\frac{kT}{2}\iint d\tau\, d\tau' \rho(\tau)\rho(\tau')\left[\{1+v(\tau,\tau')\}\ln\frac{1+v(\tau,\tau')}{1+b(\tau,\tau')} - v(\tau,\tau')\right]\\ &- kT\ (\text{sum of closed polygons})\\ &- kT\ (\text{sum of connected graphs with multiple } v\text{-bonds}). \qquad (2.8)\end{aligned}$$

The internal energy is

$$\begin{aligned}U = U_0 &+ \int d\tau \rho(\tau)\psi(\tau)\\ &-\frac{kT}{2}\iint d\tau\, d\tau' \rho(\tau)\rho(\tau')\{1+v(\tau,\tau')\}\ln\{1+b(\tau,\tau')\} \qquad (2.9)\end{aligned}$$

and the entropy is

$$\begin{aligned}S = S_0 &- k\int d\tau \rho(\tau)\ln\rho(\tau)\\ &-\frac{k}{2}\iint d\tau\, d\tau' \rho(\tau)\rho(\tau')[\{1+v(\tau,\tau')\}\ln\{1+v(\tau,\tau')\} - v(\tau,\tau')]\\ &+ k\ (\text{sum of closed polygons})\\ &+ k\ (\text{sum of connected graphs with multiple } v\text{-bonds}). \qquad (2.10)\end{aligned}$$

In these expressions, F_0, E_0 and S_0 represent the contributions from the kinetic energy part of the Hamiltonian and $\{1+v(\tau,\tau')\}$ is the correlation function defined by

$$\begin{aligned}1+v(\tau,\tau') &= \frac{\rho_2(\tau,\tau')}{\rho(\tau)\rho(\tau')}\\ &= \{1+b(\tau,\tau')\}[1+(\text{sum of connected graphs with}\\ &\qquad b\text{-bonds and two labels})]. \qquad (2.11)\end{aligned}$$

Based on these results let us now discuss theories of liquid crystals. For this purpose we take only the lowest order terms and use

$$\begin{aligned}F = F_0 &+ \int d\tau \rho(\tau)\psi(\tau) + kT\int d\tau \rho(\tau)\ln\rho(\tau)\\ &-\frac{kT}{2}\int d\tau\, d\tau' \rho(\tau)\rho(\tau')b(\tau,\tau'). \qquad (2.12)\end{aligned}$$

Minimizing the free energy we obtain

$$\rho(\tau) = A^{-1}\exp\left[-\frac{1}{kT}\psi(\tau) + \int \mathrm{d}\tau'\rho(\tau')b(\tau,\tau')\right] \tag{2.13}$$

where the constant A is determined by the normalization condition (2.5).

(i) ONSAGER'S INTEGRAL EQUATION

It is convenient to use the distribution function $f(\tau)$ which is normalized as

$$\int f(\tau)\,\mathrm{d}\tau = V. \tag{2.14}$$

That is

$$\rho(\tau) = cf(\tau), \qquad c = \frac{\mathrm{N}}{V}. \tag{2.15}$$

Then, Eq. (2.13) is rewritten as follows

$$f(\tau) = A^{-1}\exp\left[-\frac{1}{kT}\psi(\tau) + c\int \mathrm{d}\tau' f(\tau')b(\tau,\tau')\right] \tag{2.16}$$

where now A is determined by Eq. (2.14). For $\psi(\tau) = 0$, Eq. (2.16) is what Onsager used.

(ii) KIRKWOOD–MONROE'S INTEGRAL EQUATION

We consider the weak field case and expand the exponential function in $b(\tau,\tau')$. The first order term gives an integral equation:

$$\rho(\tau) = A^{-1}\exp\left[-\frac{1}{kT}\psi(\tau) - \frac{1}{kT}\int \mathrm{d}\tau'\rho(\tau')\phi(\tau,\tau')\right]. \tag{2.17}$$

(iii) MOLECULAR FIELD EQUATION

The second term on the right side of Eq. (2.17) may be considered as an average molecular field due to those particles around a given particle. Denoting

$$\rho(\tau) = A^{-1}\exp(-\bar{\psi}/kT) \tag{2.18}$$

we arrive at

$$\bar{\psi}(\tau) = A^{-1}\int \mathrm{d}\tau'\phi(\tau,\tau')\exp\left[-\frac{1}{kT}\{\bar{\psi}(\tau')\}\right] + \psi(\tau') \tag{2.19}$$

which is the equation used by McMillan.

(iv) KOBAYASHI'S APPROACH

In the absence of the external field one is led to

$$F = F_0 + kT \int \rho(\tau) \ln \rho(\tau)\, \mathrm{d}\tau + \frac{1}{2} \iint \rho(\tau)\rho(\tau')g(\tau, \tau')\phi(\tau, \tau')\, \mathrm{d}\tau\, \mathrm{d}\tau'. \quad (2.20)$$

Minimization of this expression with respect to $\rho(\tau)$ gives

$$\rho(\tau) = A^{-1} \exp\left[-\frac{1}{kT} \int \mathrm{d}\tau' \phi(\tau, \tau')\rho(\tau')g(\tau, \tau') \right]. \quad (2.21)$$

These expressions have been used often. Kobayashi applied these to liquid crystals, but did not obtain explicit results such as McMillan's. The essential difficulty with Eq. (2.21) is in the appearance of the pair correlation function on the right side. That is, the equation is not closed.

(v) OUR APPROACH

Based on our above observations let us now try to construct a satisfactory theory of liquid crystals within the context of the Onsager approximation. For this purpose it is convenient to introduce position vectors $\mathbf{r}$ and orientation vectors $\mathbf{n}$ for the τ variables. Our problem is to solve the non-linear integral equation:

$$f(\mathbf{r}, \mathbf{n}) = A^{-1} \exp\left[c \iint \mathrm{d}\mathbf{r}'\, \mathrm{d}\mathbf{n}\, b(\mathbf{rn}, \mathbf{r}'\mathbf{n}') f(\mathbf{r}', \mathbf{n}') \right]. \quad (2.22)$$

We assume that the kernel can be expanded in a complete set of orthonormalized functions as follows

$$b(\mathbf{rn}, \mathbf{r}'\mathbf{n}') = \sum_{lm} a_{lm} R_l(\mathbf{R}) \Phi_m(\mathbf{N}) \quad (2.23)$$

where

$$\mathbf{R} = \mathbf{r} - \mathbf{r}', \qquad \mathbf{N} = \mathbf{n} - \mathbf{n}'. \quad (2.24)$$

In expanding b as in Eq. (2.23) we are considering that R_l will be describing changes in the density and Φ_m those in the molecular orientations.

Anticipating that the solution $f(\mathbf{r}, \mathbf{n})$ will represent phase transitions characteristic of liquid crystals we assume

$$f(\mathbf{r}, \mathbf{n}) = A^{-1} \exp\left[N \sum_{lm} a_{lm} S_{lm} R_l(\mathbf{r}) \Phi_m(\mathbf{n}) \right] \quad (2.25)$$

where S_{lm} are order parameters to be determined. Using the normalization condition of Eq. (2.14) we find

$$A = \frac{1}{V}\iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{n}\exp\left[\sum_{lm} Na_{lm}S_{lm}R_l(\mathbf{r})\Phi_m(\mathbf{n})\right] \tag{2.26}$$

and the equations of self-consistency

$$\begin{aligned} NS_{lm}a_{lm} &= \frac{ca_{lm}}{A}\iint \mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{n}' R_l(\mathbf{r}')\Phi_m(\mathbf{n}')\exp\left[\sum_{lm} Na_{lm}S_{lm}R_l(\mathbf{r}')\Phi_m(n')\right] \\ &= \frac{ca_{lm}V}{A}\frac{\partial A}{\partial(Na_{lm}S_{lm})}. \end{aligned} \tag{2.27}$$

That is

$$S_{lm} = \partial \ln A/\partial(Na_{lm}S_{lm}) \tag{2.28}$$

from which the order parameters can be determined. In deriving Eq. (2.27) we have used the additive theorem for orthogonal functions.

Our problem is now reduced to finding non-trivial solutions of Eq. (2.28). While explicit results depend on the potentials we can prove that S_{lm} are the averages of $R_l\Phi_m$ and may indeed be considered as order parameters. In fact, using Eq. (2.28) and then Eq. (2.26) we find

$$\begin{aligned} S_{lm} &= \frac{1}{A}\frac{\partial A}{\partial(Na_{lm}S_{lm})} \\ &= \frac{\iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{n}\,R_l(\mathbf{r})\Phi_m(\mathbf{n})\exp\left[\sum_{lm} Na_{lm}S_{lm}R_l(\mathbf{r})\Phi_m(\mathbf{n})\right]}{\iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{n}\exp\left[\sum_{lm} Na_{lm}S_{lm}R_l(\mathbf{r})\Phi_m(\mathbf{n})\right]} \\ &= \frac{\iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{n}\,R_l(r)\Phi_m(\mathbf{n})f(\mathbf{r},\mathbf{n})}{\iint f(\mathbf{r},\mathbf{n})\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{n}} \\ &= \langle R_l\Phi_m\rangle. \end{aligned} \tag{2.29}$$

3. Difficulties in Lakatos' Approach

As we mentioned in the Introduction, Lakatos proved the nonexistence of a phase transition in a two-dimensional system of rod-like molecules. Before going into details of her proof, we must remember that the Onsager integral equation is not rigorous at all. Therefore, it is not appropriate to keep using the equation if our interest is in discussing phase transitions. Although there is no real two-dimensional system, experiments on rod-like molecules on a surface have actually shown phase transitions. Therefore, in what follows we shall first examine the theory of Lakatos mathematically within the framework of the Onsager approach, and after showing mathematical difficulties in her proof, we shall use our formalism in the previous section and try to reproduce phase transitions.

Let a and b be the minor and major axes of each molecule. For a two-dimensional rigid rod system one can find the exact kernel of the integral equation as follows (for the reason explained in the next section, we use here $\beta(\gamma)$ instead of $b(\gamma)$):

$$\beta(\gamma) = -2(a^2+b^2)|\sin\gamma| - 4ab|\cos\gamma| - 5ab \tag{3.1}$$

The proof by Lakatos is based on the approximate kernel:

$$\beta(\gamma) = -2b^2|\sin\gamma| \tag{3.2}$$

While this approximation is attractive, one observes the following difference in the two expressions:

$$\lim_{\gamma\to 0}\beta(\gamma) = \begin{cases}\text{finite}, & \text{from Eq. (3.1)} \qquad (3.3\text{a})\\ 0, & \text{from Eq. (3.2)} \qquad (3.3\text{b})\end{cases}$$

Physically, this difference is significant because in the Lakatos approximation, i.e. Eq. (3.3b), the effect of molecular correlation disappears when exactly the opposite is expected. What is missing in accepting the approximation is an additional condition that

$$(a+b)^2|\sin\gamma| \gg 4ab|\cos\gamma| \tag{3.4}$$

which is certainly not valid for small angles. If, however, we take the limit of $b \to \infty$ for a finite a and γ the upper limit of γ indeed approaches zero. But, as we approach this limit the system becomes more and more easily oriented. Finally, in the very limit $b \to \infty$ the system can be oriented automatically with even one molecule (zero concentration!).

The Onsager integral equation can be rewritten in the form

$$\frac{\partial f(\theta)}{\partial\theta} = f(\theta)g(\theta), \tag{3.5}$$

where

$$g(\theta) = c\int_0^\pi \frac{\partial\beta(\theta,\theta')}{\partial\theta} f(\theta')\,d\theta'. \tag{3.6}$$

By introducing the exact kernel we find

$$\frac{\partial g(\theta)}{\partial \theta} = -c\int_0^\pi \beta(\theta,\theta')f(\theta')\,\mathrm{d}\theta' + 5abc - 4c(a^2+b^2)f(\theta) - 16abcf\left(\theta+\frac{\pi}{2}\right) \tag{3.7}$$

and

$$\frac{\partial^2 g(\theta)}{\partial \theta^2} = -g(\theta) - 4c(a^2+b^2)\frac{\partial f}{\partial \theta} - 16abc\frac{\partial f(\theta+\pi/2)}{\partial \theta}. \tag{3.8}$$

Using Eq. (3.5) we arrive at

$$\frac{\partial^2 g(\theta)}{\partial \theta^2} = -g(\theta) - 4c(a^2+b^2)f(\theta)g(\theta) - 16abcf\left(\theta+\frac{\pi}{2}\right)g\left(\theta+\frac{\pi}{2}\right). \tag{3.9}$$

This equation is exact and differs in structure from Eq. (33) of Lakatos. The last term of Eq. (3.9) did not appear in Lakatos' equation. With this term the proof by Lakatos does not hold as it is. For instance, Eq. (34) of Lakatos is no longer correct.

4. Rod-like Molecules in Two-Dimensions

Let us consider very dilute cases and try to explain the isotropic–nematic phase transition. We may assume that the system has *translational uniformity and shall use the distribution function* $f(\mathbf{n})$ instead of $f(\mathbf{r}, \mathbf{n})$. The exact kernel which we gave by Eq. (3.1) represents the total excluded volume of two molecules. In view of our derivations of the fundamental equations, let us use the excluded volume which is determined by the locus of the center of gravity of a second molecule moving around a first molecule, the mutual orientation of these two molecules being fixed at γ. Then

$$b(\gamma) = -2ab - 2ab\,|\cos\gamma| - (a^2+b^2)\,|\sin\gamma|. \tag{4.1}$$

The difference between Eqs. (3.1) and (4.1) is only academic. It will be possible to obtain similar results if one used the former. We can use

$$b(\gamma) = B_0 + B_1\cos 2\gamma \tag{4.2}$$

where

$$B_0 = -2ab - \frac{2}{\pi}(a+b)^2,$$

$$B_1 = \frac{4}{3\pi}(b-a)^2. \tag{4.3}$$

As in Section 2 we express the solution in terms of an orientational order parameter S as

$$Af(\theta) = e^{cB_1S\cos 2\theta}. \tag{4.4}$$

Then, the normalization condition gives

$$A = \pi I_0(cB_1S). \tag{4.5}$$

The order parameter is determined in terms of the modified Bessel functions by

$$S = \frac{I_1(cB_1S)}{I_0(cB_1S)}. \tag{4.6}$$

Upon inspecting Eq. (4.6) we find that there can be no solutions for $cB_1/2 > 1$. Hence, the critical concentration is

$$c^{i\to n} = \frac{2}{B_1} = \frac{3\pi}{2}\frac{1}{(b-a)^2}. \tag{4.7}$$

In terms of the volume concentration, which is dimensionless, the critical concentration is

$$c_v{}^{i\to n} = c^{i\to n}ab = \frac{3\pi}{2}\frac{ab}{(a-b)^2}. \tag{4.8}$$

In the limit of large b this critical concentration approaches zero, as we expected in the previous section.

Using the distribution function given by Eq. (4.4) one obtains the free energy (apart from the rotational kinetic energy)

$$F = -N\rho kT\left[1+\ln\frac{V}{N\rho}-\ln\frac{4\pi}{A}-\frac{c}{2}B_1s_1{}^2+\frac{c}{z}B_0\right]. \tag{4.9}$$

from which the pressure is found to be

$$p = ckT\left[1-\frac{c}{2}\{B_0+B_1s^2\}\right]. \tag{4.10}$$

For $x = 2/cB_1$ and $z = cB_1S_1$ Eq. (4.6) becomes

$$1-x = \frac{I_2(z)}{I_0(z)} \tag{4.11}$$

where we have used the property of the Bessel function. In the limit $b \gg a$ we have $B_0 = -(3/2)B_1$ and

$$p = \frac{p_0}{x}\left[1+\frac{3}{2}\frac{1}{x}-\frac{1}{4}xz^2\right], \qquad p_0 = \frac{2kT}{B_1}. \tag{4.12}$$

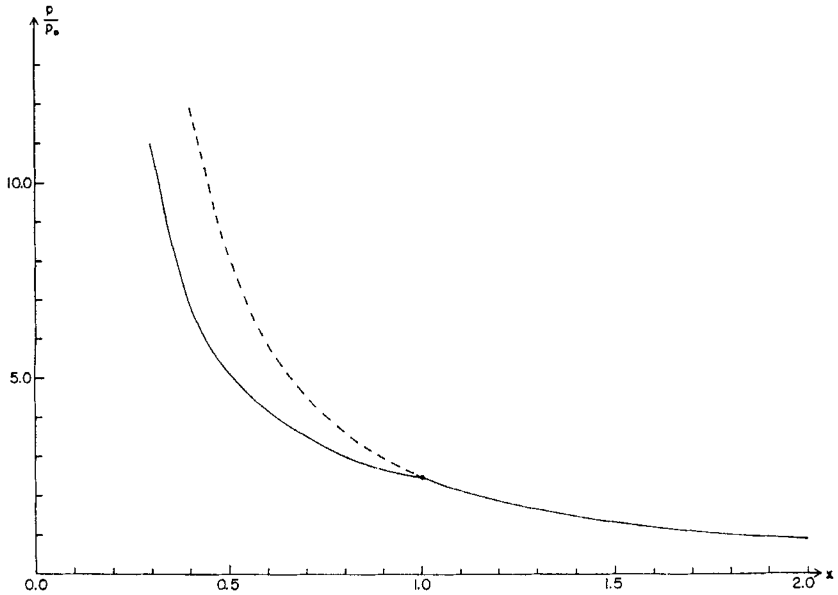

Figure 1. Reduced pressure p/p_0 as a function of reduced area.

Numerical results for the pressure are illustrated in Fig. 1. Here, the solid curve represents the stable phases and a black circle corresponds to a critical point.

The distribution function is shown in Fig. 2 for various values of the concentration. The straight line I corresponds to the isotropic phase. As the concentration increases, the distribution function shows an orientational dependence.

When the concentration of the system further increases beyond this critical value the distribution function will have a sharp peak at $\theta = 0$ as a consequence of the exponential form. Therefore, in the region we assume

$$f(\mathbf{r}, \mathbf{n}) = f(\mathbf{r})\,\delta(\theta). \tag{4.13}$$

The integral equation is reduced to

$$f(\mathbf{r}) = A^{-1} \exp\left[c \int b(\mathbf{r}, \mathbf{r}') f(\mathbf{r}')\, d\mathbf{r}'\right] \tag{4.14}$$

where

$$b(\mathbf{r}, \mathbf{r}') = b(r) = -1 \quad (\text{for } |x| \leqslant a, \quad y \leqslant b). \tag{4.15}$$

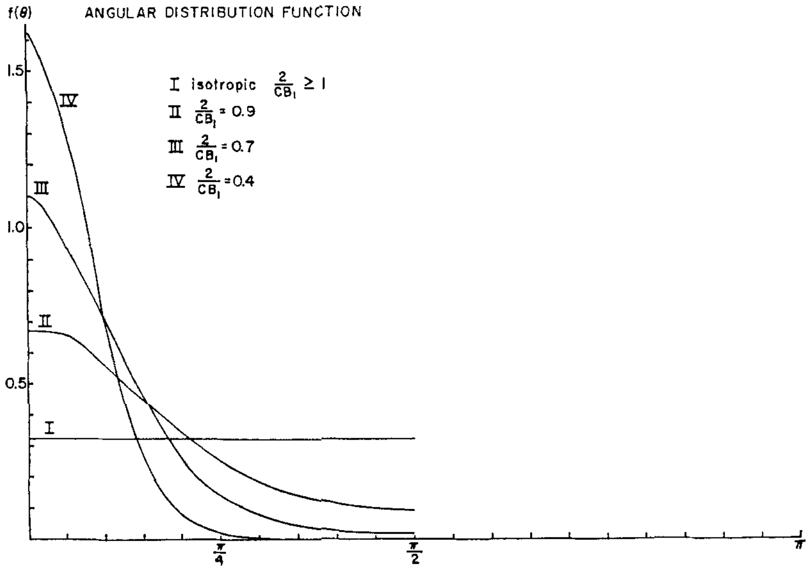

Figure 2. Orientational distribution function for various parameters.

Let us now try to describe a translational phase transition in the y-direction because this is the direction in which the molecules are oriented. Let us use

$$b(r) = \bar{B}_0 + \bar{B}_1 \cos\left(\frac{2\pi}{y_0} y\right) \tag{4.16}$$

with

$$\begin{aligned} \bar{B}_0 &= \frac{2}{L}\frac{2}{L}\int_0^L \mathrm{d}x \int_0^L \mathrm{d}y\, b(r) = -\frac{16}{V}ab, \\ \bar{B}_1 &= \frac{2}{L}\frac{2}{L}\int_0^L \mathrm{d}x \int_0^L \mathrm{d}y\, b(r)\cos\frac{2\pi y}{y_0} = -\frac{8ay_0}{\pi V}\sin\left(\frac{2\pi b}{y_0}\right), \\ V &= 4L^2, \end{aligned} \tag{4.17}$$

and let us introduce a translational order parameter t into the solution:

$$f(\mathbf{r}) = A^{-1}\exp\left[N\bar{B}_1 t\cos\left(\frac{2\pi}{y_0}y\right)\right]. \tag{4.18}$$

The constant A is found to be

$$A = \frac{4}{V}\iint_0^L \mathrm{d}x\,\mathrm{d}y \exp\left[N\bar{B}_1 t \cos\frac{2\pi}{y_0}y\right] \tag{4.19}$$

$$= 1 + (N\bar{B}_1 t)^2/4 + (N\bar{B}_1 t)^4/64 + \dots \tag{4.20}$$

The equation for consistency becomes

$$N\bar{B}_1 t = \frac{C\bar{B}_1 V}{A}\frac{\partial A}{\partial(N\bar{B}_1 t)}. \tag{4.21}$$

The first approximation to this equation gives

$$t = \frac{N\bar{B}_1}{2}t\left[1 - \frac{1}{8}(N\bar{B}_1 t)^2\right]. \tag{4.22}$$

Therefore, in this approximation the condition for phase transition is

$$\bar{B}_1 > 0, \qquad \frac{N\bar{B}_1}{2} > 1. \tag{4.23}$$

The case $y_0 = b$ corresponds to closed packing. The quantity B_1 oscillates sinusoidally in the domain $b < y_0 < 2b$. Therefore, we put

$$y_0 = \alpha b \quad (1 < \alpha < 2). \tag{4.24}$$

In the domain, the density is

$$\rho = \frac{\pi}{4\alpha}\frac{1}{ab}\frac{1}{|\sin 2\pi/\alpha|}. \tag{4.25}$$

The ratio between $A_0 = ab$, the volume of a particle, and $A = V/N$, the volume per particle is

$$\frac{A}{A_0} = 1.27\alpha \sin\left(\frac{360^\circ}{\alpha} - 180^\circ\right). \tag{4.26}$$

Numerical values of this ratio are tabulated in Table 1. As one sees from the table, the maximum of the ratio appears at $\alpha = 1.4$. The maximum value 1.7 is close to what Alder and Wainwright obtained for hard-disk particles in two-dimensions: (10) Their value is approximately 1.30. Therefore, we estimate the critical concentration for nematic–smectic transition to be

$$c^{n\to s} = \frac{\pi}{5.6}\frac{1}{ab}. \tag{4.27}$$

TABLE 1 The Volume per Particle in the Unit of Molecular Volume

α	$360°/\alpha - 180°$	$\sin(360/\alpha - 180)$	$1.27\alpha \sin(360/\alpha - 180)$
1.0	180°	0	0
1.1	147	0.68	0.95
1.2	120	$3^{1/2}/2$	1.65
4/3	90	1.00	1.69
1.4	77	0.97	1.72
1.5	60	$3^{1/2}/2$	1.65
1.6	45	0.71	1.44
1.7	32	0.53	1.14
1.8	20	0.34	0.77
1.9	4	0.07	0.18
2.0	0	0	0

In contrast to the isotropic–nematic critical concentration given by Eq. (4.7) the above critical concentration is much larger. In fact,

$$\frac{c^{i\to n}}{c^{n\to s}} = 8.4\frac{a}{b}. \tag{4.28}$$

The mechanism for the nematic–smectic phase transition is the same as that for a hard-sphere particle. For anisotropic molecules we may expect two such transitions. The role played by hard-core potentials in these transitions is important. For improvements of the theory it is of course necessary to consider higher order terms and approximations. Nevertheless, various phase transitions in liquid crystals can be understood in terms of our formalism.

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