Molecular Crystals and Liquid Crystals

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

Theory of Translational and Orientational Melting with Application to Liquid Crystals

Kenji K. Kobayashi [a]

[a] Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo, Japan

To cite this article: Kenji K. Kobayashi (1971): Theory of Translational and Orientational Melting with Application to Liquid Crystals, Molecular Crystals and Liquid Crystals, 13:2, 137-148

To link to this article: http://dx.doi.org/10.1080/15421407108084959

Molecular Crystals and Liquid Crystals. 1971. Vol. 13, pp. 137–148

Theory of Translational and Orientational Melting with Application to Liquid Crystals†

KENJI K. KOBAYASHI

Institute for Solid State Physics
University of Tokyo
Roppongi
Tokyo, Japan

Received October 6, 1970; *in revised form December* 2, 1970

Abstract—A theory of melting with application to liquid crystals in which both translational and orientational order parameters are taken into account is developed in a manner similar to that of Kirkwood and Monroe.

1. Introduction

Liquid crystals are characterized by the presence of an orientational order of rod-like molecules of which centers of gravity are completely disordered as in a classical liquid.(1)

The recent revival of interest in liquid crystals has much urged various experimental investigations. From the theoretical point of view, however, there is as yet no satisfactory microscopic treatment of the ordered state. The most celebrated theory is a phenomenological continuum theory developed by Oseen, Zocher and Frank(2) which has been very often employed in explaining successfully the effects of a magnetic field on liquid crystals and their distortions as well as the strong scattering and depolarization of light.(3)

On the other hand, Maier and Saupe(4) presented a microscopic statistical theory of orientational melting based on an interaction between molecules possessing quadrupole–quadrupole type symmetry and nicely described the first order nematic–isotropic liquid phase transition in a molecular field approximation. It should be noted, however, that in their theory only the orientational order parameter was taken into account, so that it cannot describe a crystal–nematic phase transition.

† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

In order to describe the crystal–nematic phase transition as well as the smectic liquid crystal, one needs to introduce another order parameter, i.e. a translational or positional order parameter.

In 1961, Pople and Karasz⁽⁵⁾ developed a theory of fusion which allows for order–disorder phenomena in both the orientations and positions of molecules. The two lattice model used by Lennard-Jones and Devonshire⁽⁶⁾ was extended so that molecules may take up two orientations on any site. By introducing a coupling between orientational and positional disorder a rotational phase transition and a lattice melting transition were obtained. This pioneering work based on the lattice or " discrete " model of the liquid state has for the first time succeeded in a unified treatment of the phase transitions in molecular crystals such as plastic crystals and liquid crystals. Although only the nematic state is predicted in its original form, a smectic phase could be obtained by extending their theory so as to include a third order parameter, i.e. a lamellar order parameter.

It seems, however, of some worth to develop another theory of translational and orientational melting based on the " continuous " model of the liquid state. The purpose of the present paper is to extend the Kirkwood–Monroe theory⁽⁷⁾ of fusion to the case of anisotropic molecules and to present a theory of melting in which both the translational and orientational order parameters are taken into account. We shall here be concerned with the nematic and smectic liquid crystals. In Sec. 2, a brief summary of the theory developed by the author⁽⁸⁾ will be made and some results will be given in Sec. 3. Thermal fluctuations in liquid crystals are described in the Appendix.

2. A Brief Summary of the Theory

In order to develop a microscopic theory of liquid crystals the knowledge of an intermolecular force is needed. It is now widely accepted that dispersion and repulsion forces make a predominant contribution to the stability of the nematic mesophase.⁽¹,⁹⁾

Let each molecule be characterized by the coordinates $\mathbf{q} = (ax, ay, az)$ of its center of mass and by the angular coordinates (θ, ϕ) which determine the orientation of the molecule. Let us also assume that the molecule is elongated and rod-like. Then, an interaction energy between two molecules may be written as,

$$U(\mathbf{q}_1, \theta_1, \phi_1; \mathbf{q}_2, \theta_2, \phi_2) = V(|\mathbf{q}_1 - \mathbf{q}_2|) + W(|\mathbf{q}_1 - \mathbf{q}_2|) \cdot P_2(\cos\gamma). \quad (1)$$

where V describes the usual short-range central forces and the second term represents orientational forces (anisotropic part of the dispersion force and a quadrupole–quadrupole interaction), γ being the angle between the molecular axes and P_2 the Legendre polynomial of the second order.

Following Kirkwood and Monroe, we expand a one-particle distribution function $f(\mathbf{q}, \theta, \phi)$ in the Fourier series in reciprocal lattice vectors. We shall here consider a simple cubic lattice (a the lattice constant).

$$f(\mathbf{q}, \theta, \phi) = \sum_{l_1 l_2 l_3 = -\infty}^{+\infty} S_{l_1 l_2 l_3}(\theta, \phi) \cdot \exp(2\pi i[l_1 x + l_2 y + l_3 z]). \quad (2)$$

The minimization condition for the free energy with respect to the function $f(\mathbf{q}, \theta, \phi)$ leads to the following equation for f.[7]

$$\log\lambda \cdot f(\mathbf{q}, \theta, \phi) = -\frac{1}{4\pi v k_B T} \int^{v} d^3q' \int d\Omega' \, (V(|\mathbf{q} - \mathbf{q}'|) + W(|\mathbf{q} - \mathbf{q}'|) \cdot P_2(\cos\gamma)) \cdot f(\mathbf{q}', \theta', \phi') \cdot g(|\mathbf{q} - \mathbf{q}'|, \cos\gamma) \quad (3)$$

for the system confined in a volume v (unit cell), $d\Omega$ denotes the element of solid angle, λ being the normalization constant for f.

$$\frac{1}{4\pi v} \int^{v} d^3 q \int d\Omega \cdot f(\mathbf{q}, \theta, \phi) = 1 \quad (4)$$

$g(|\mathbf{q} - \mathbf{q}'|, \cos\gamma)$ is the pair correlation function which is approximately expressed by two terms.

$$g(|\mathbf{q}|, \cos\gamma) = g_0(|\mathbf{q}|) + g_2(|\mathbf{q}|) \cdot P_2(\cos\gamma) + \cdots \quad (5)$$

we may approximately use $g_0(|\mathbf{q}|)$ of isotropic liquid phase in considering the nematic phase, whereas $g_0(|\mathbf{q}|)$ and $g_2(|\mathbf{q}|)$ of the nematic phase may be used for the smectic phase.

Substitution of Eq. (2) into Eq. (3) and assumption of an axial symmetry of the system on the average (i.e., $S(\theta, \phi) = S(\theta)$) yield

$$\log\lambda \cdot f(\mathbf{q}, \theta, \phi) = \sum_{l_1 l_2 l_3 = -\infty}^{+\infty} \left[\alpha_{l_1 l_2 l_3} \cdot \frac{1}{4\pi} \int d\Omega' \cdot S_{l_1 l_2 l_3}(\theta') + \beta_{l_1 l_2 l_3} \cdot P_2(\cos\theta) \cdot \frac{1}{4\pi} \int d\Omega' \cdot P_2(\cos\theta') \, S_{l_1 l_2 l_3}(\theta')\right] \cdot \exp(2\pi i[l_1 x + l_2 y + l_3 z]), \quad (6)$$

where $\alpha_{l_1 l_2 l_3}$ and $\beta_{l_1 l_2 l_3}$ are defined as follows.

$$\alpha_{l_1 l_2 l_3} = -\frac{1}{vk_BT}\int^{v} d^3q[V(|\mathbf{q}|)g_0(|\mathbf{q}|)+\tfrac{1}{5}W(|\mathbf{q}|)\cdot g_2(|\mathbf{q}|)] \cdot \exp(2\pi i[l_1x+l_2y+l_3z]), \tag{7}$$

$$\beta_{l_1 l_2 l_3} = -\frac{1}{vk_BT}\int^{v} d^3q[W(|\mathbf{q}|)g_0(|\mathbf{q}|)+V(|\mathbf{q}|)\cdot g_2(|\mathbf{q}|) + \tfrac{2}{7}W(|\mathbf{q}|)\cdot g_2(|\mathbf{q}|)]\cdot\exp(2\pi i[l_1x+l_2y+l_3z]). \tag{8}$$

For simplicity, we assume for purpose of approximation that the Fourier transforms $\alpha_{l_1 l_2 l_3}$ and $\beta_{l_1 l_2 l_3}$ can be treated as negligibly small for $|l_1|^2+|l_2|^2+|l_3|^2>1$. Then, by symmetry, Eq. (6) yields

$$\log\lambda\cdot f(\mathbf{q},\theta,\phi) = \alpha_0\cdot\frac{1}{4\pi}\int d\Omega'\, S_{000}(\theta') + 2\alpha_1(\cos 2\pi x+\cos 2\pi y + \cos 2\pi z)\cdot\frac{1}{4\pi}\int d\Omega'\cdot S_{100}(\theta') + \beta_0\cdot P_2(\cos\theta) \cdot\frac{1}{4\pi}\int d\Omega'\cdot P_2(\cos\theta')\,S_{000}(\theta') + 2\beta_1\cdot P_2(\cos\theta) \cdot(\cos 2\pi x+\cos 2\pi y+\cos 2\pi z)\cdot\frac{1}{4\pi}\int d\Omega' \cdot P_2(\cos\theta')\,S_{100}(\theta') \tag{9}$$

where for simplicity in notation α_{000}, α_{100}, β_{000} and β_{100} are written as α_0, α_1, β_0 and β_1, respectively.

Equation (4) leads to the following equality.

$$\frac{1}{4\pi}\int d\Omega\cdot S_{000}(\theta) = 1. \tag{10}$$

We shall define parameters σ, τ and η as follows.

$$\sigma \equiv \frac{1}{4\pi}\int d\Omega\cdot S_{100}(\theta), \tag{11}$$

$$\tau \equiv \frac{1}{4\pi}\int d\Omega\cdot P_2(\cos\theta)\cdot S_{000}(\theta), \tag{12}$$

$$\eta \equiv \frac{1}{4\pi}\int d\Omega\cdot P_2(\cos\theta)\cdot S_{100}(\theta). \tag{13}$$

σ and τ represent the translational and orientational order parameters, respectively and η stands for a kind of mixing order parameter as will be shown below. Noting the following expression for $S_{l_1 l_2 l_3}$,

$$S_{l_1 l_2 l_3} = \frac{1}{v}\int^{v} d^3 q \cdot f \cdot \exp\left(-2\pi i[l_1 x + l_2 y + l_3 z]\right)$$

we have the basic equations to determine the order parameters with the use of new parameters: $t = \beta_0 \tau$, $s = 2\alpha_1 \sigma$ and $m = 2\beta_1 \eta$.

$$\frac{t}{\beta_0} = \frac{\mathrm{d}\log \lambda(t, s, m)}{\mathrm{d}t}, \tag{14}$$

$$\frac{3s}{2\alpha_1} = \frac{\mathrm{d}\log \lambda(t, s, m)}{\mathrm{d}s}, \tag{15}$$

$$\frac{3m}{2\beta_1} = \frac{\mathrm{d}\log \lambda(t, s, m)}{\mathrm{d}m} \tag{16}$$

where the normalization constant λ for f is given by

$$\lambda = \int_0^1 \mathrm{d}z \cdot \exp\left(t \cdot P_2(z)\right) \cdot I_0^3(s + m \cdot P_2(z)) \cdot \exp(\alpha_0) \tag{17}$$

where I_0 is the modified Bessel function of the zeroth order.

The mean internal energy $\bar{U}$ is given by

$$\begin{aligned} \frac{\bar{U}}{k_B T} &= \frac{1}{(4\pi v)^2 k_B T}\int \mathrm{d}\Omega \int \mathrm{d}\Omega' \int^{v} d^3 q \int^{v} d^3 q' \cdot U(|\mathbf{q}-\mathbf{q}'|;\, \theta, \phi;\, \theta', \phi') \\ &\quad \times f(\mathbf{q}, \theta, \phi) \cdot f(\mathbf{q}', \theta', \phi') \cdot g(|\mathbf{q}-\mathbf{q}'|, \cos\gamma) \\ &= -\sum_{l_1 l_2 l_3} \alpha_{l_1 l_2 l_3} \cdot \frac{1}{(4\pi)^2}\int \mathrm{d}\Omega \int \mathrm{d}\Omega' \cdot S_l(\theta) \cdot S_{-l}(\theta') \\ &\quad - \sum_{l_1 l_2 l_3} \beta_{l_1 l_2 l_3} \cdot \frac{1}{(4\pi)^2}\int \mathrm{d}\Omega \int \mathrm{d}\Omega' \cdot (P_2(\cos\theta) \cdot S_l(\theta)) \\ &\qquad \cdot (P_2(\cos\theta') \cdot S_{-l}(\theta')) \\ &= -\alpha_0 - 6\alpha_1 \cdot \sigma^2 - \beta_0 \tau^2 - 6\beta_1 \cdot \eta^2. \end{aligned} \tag{18}$$

The Gibbs free energy of the system is given by

$$\frac{(G - G_0)}{RT} = -\log \lambda(t, s, m) \tag{19}$$

where G_0 is the free energy for the system of free molecules.

3. Results and Discussion

Let us consider, first of all, the case for $\beta_1 = 0$. Then, λ can be factorized into two parts.

$$\lambda = \lambda_s \cdot \lambda_t;\ \lambda_s = I_0^3(s) \cdot \exp(\alpha_0),\ \lambda_t = \int_0^1 \mathrm{d}z \cdot \exp\left(t \cdot P_2(z)\right). \tag{20}$$

The order parameters t and s are determined from the following equations.

$$\frac{t}{\beta_0}=\frac{\int_0^1 \mathrm{d}z\cdot P_2(z)\cdot \exp\left(t\cdot P_2(z)\right)}{\int_0^1 \mathrm{d}z\cdot \exp\left(t\cdot P_2(z)\right)}, \tag{21}$$

$$\frac{s}{2\alpha_1}=\frac{I_1(s)}{I_0(s)}. \tag{22}$$

Equation (21) just coincides with that of Maier and Saupe, while Eq. (22) corresponds to that of Kirkwood and Monroe for the simple cubic lattice.

In practice, however, β_1 does not reduce to zero and the presence of β_1 does not allow us to factorize λ into two parts and mixes the translational and orientational motions of molecules. In other words, η represents a kind of mixing order parameter.

It seems a rather formidable task to solve three coupled transcendental Eqs. (14)–(16) exactly, so that we present an approximate solution.

Assuming $\beta_1 \ll 1$ and making the cumulant expansion only with respect to m, retaining up to the second order terms in m and eliminating m from Eqs. (14)–(16), we have the following coupled equations for σ and τ.

$$\tau=\frac{\int_0^1 \mathrm{d}z\cdot P_2(z)\cdot \exp\left(\beta_0\tau\cdot P_2(z)\right)}{\int_0^1 \mathrm{d}z\cdot \exp\left(\beta_0\tau\cdot P_2(z)\right)}+12\frac{\beta_1}{\beta_0}\cdot\tau\cdot\sigma^2, \tag{23}$$

$$\sigma=\frac{I_1(2\alpha_1\sigma)}{I_0(2\alpha_1\sigma)}+\frac{\beta_1}{\beta_0}\cdot\frac{\beta_0}{\alpha_1}\cdot\sigma\cdot\tau^2. \tag{24}$$

These equations are solved graphically for the case of $\beta_1/\beta_0 = 1/80$ and $\beta_0/\alpha_1 = 6$ and the result is shown in Fig. 1.

Owing to the presence of a coupling between translational and orientational motions, the translational or positional order parameter appears at somewhat higher temperature (T^σ) than in the case without coupling (T_0^σ). It should be emphasized that the gradual appearance of the translational order parameter (σ) is not essential to this theory. The result comes from the assumption of the simple cubic lattice and the neglection of higher order Fourier transforms of α and β. For the case of a face centered cubic lattice, as was shown by Kirkwood and Monroe,(7) the melting transition turns out to be of the first order. In this respect, it is to be noted that Bulkin

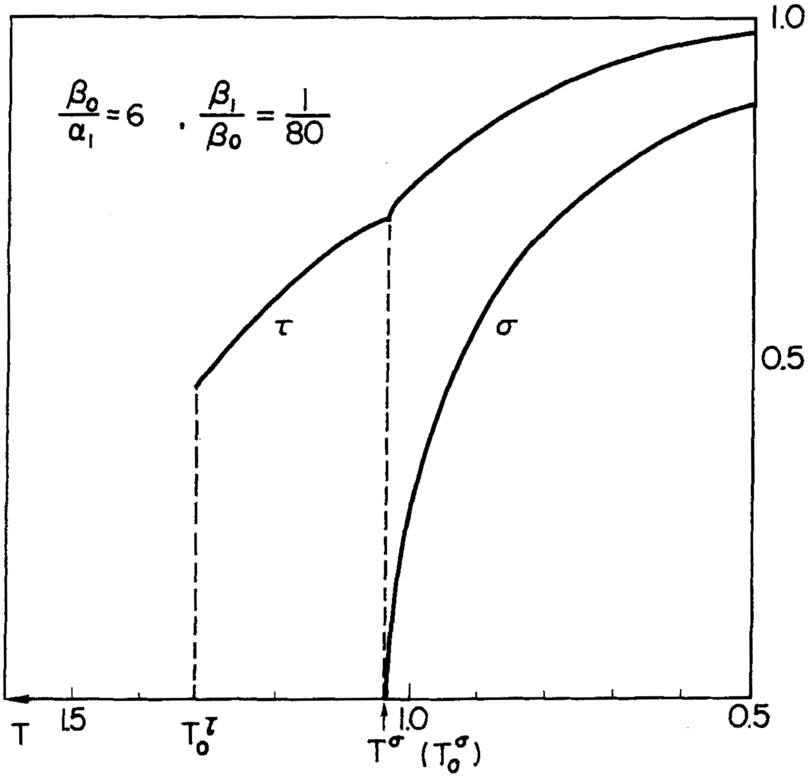

Figure 1. The calculated temperature dependence of orientational (τ) and translational (σ) order parameters.

et al.⁽¹⁰⁾ have examined the infrared spectra of 4, 4′-*bis*(alkoxy) azoxybenzenes as a function of temperature through the crystal-nematic transition and have observed that several bands disappear gradually (not abruptly) as this transition is approached, concluding that the crystal-nematic transition is not a first order one. It should be remarked that if the transition were nearly of the second order, a non-propagating soft mode suggested by the author⁽¹¹⁾ might be observed in the vicinity of the transition point.

Let us consider the ordered state. If the aligned direction of molecules is taken as z-axis, it can be concluded that the term $\langle P_2(\cos\theta)\cos 2\pi z\rangle$ is considerably larger than $\langle P_2(\cos\theta)(\cos 2\pi x + \cos 2\pi y)\rangle$ in the ordered state. Consequently, we need to distinguish the mixing order parameter parallel to z-axis: $\eta^{\parallel}$ from that perpendicular to z-axis: $\eta^{\perp}$. Correspondingly, translational order parameters $\sigma^{\parallel}$ and $\sigma^{\perp}$ can be introduced and Eq. (9) may be expressed effectively as follows.

$$\begin{aligned}\lambda \cdot f(\mathbf{q}, \theta, \phi) = \exp[&\alpha_0 + 2\alpha_1^{\perp} \cdot \sigma^{\perp}(\cos 2\pi x + \cos 2\pi y) \\ &+ 2\alpha_1^{\parallel} \cdot \sigma^{\parallel} \cdot \cos 2\pi z + \beta_0 \tau \cdot P_2(\cos\theta)]. \end{aligned} \tag{25}$$

Therefore, an intermediate state ($\sigma^{\perp} = 0$, $\sigma^{\parallel} \neq 0$, $\tau \neq 0$) can be found between the crystal ($\sigma^{\perp} \neq 0$, $\sigma^{\parallel} \neq 0$, $\tau \neq 0$) and the nematic phase ($\sigma^{\perp} = 0$, $\sigma^{\parallel} = 0$, $\tau \neq 0$). This state just corresponds to the smectic liquid crystal which possesses both orientational order and one-dimensional translational order along the preferred direction of molecules. Generally speaking, the aligned direction of molecules does not necessarily coincide with the z-axis, which indicates the possible existence of tilted smectic mesophase as has been pointed out by Saupe.(12)

Let us next consider the librational motion in liquid crystals. This kind of mode was first treated by Frenkel(13) and was called as "rotation-oscillation wave". Assuming the intermolecular potential of Eq. (1), we can easily obtain the following expression for the frequency of the collective librational mode in the ordered state in the molecular field approximation (I the moment of inertia of the molecule).

$$\omega = \sqrt{\frac{3\beta_0 k_B T \langle P_2(\cos\theta)\rangle}{2I}} = \sqrt{\frac{3\beta_0 k_B T \tau}{2I}}. \tag{26}$$

The frequency of the collective librational mode is found to decrease as the nematic-isotropic phase transition is approached. This result seems to correspond to the increase of the librational amplitude as the temperature is approached to this transition point as has been given by Chandrasekhar *et al.*,(9) although their treatment corresponds to the Einstein model of lattice vibrations whereas the one presented here corresponds to the Debye model. It should be noted that this classical librational mode has little resemblance to a "libron" proposed by Honma *et al.*(14) The "libron" is valid only for "quantum" solids such as solid H_2 and D_2, its frequency being independent of the moment of inertia of constituent molecules.(14)

Finally, it should be remarked that the primitive theory presented here could be made more realistic in some respects. For example, the effect of dipole moment of molecules could be taken into account by including a term $P_1(\cos\gamma)$ in Eq. (1).(15)

Acknowledgements

The author would like to express his sincere thanks to Dr Y. Furuhata for the stimulating review talk about liquid crystals. He is also indebted to Prof. T. Nakamura, Prof. H. Inokuchi, Prof. I. Nakada, Prof. E. Hanamura, Dr T. Nakagiri and Dr F. Sugawara for helpful discussions and references. This work has been supported by the Sakkokai Foundation.

Appendix

We shall consider here thermal fluctuations in liquid crystals from the microscopic point of view.

Let us first define the Fourier transform $\delta S_{\mathbf{k}}$ of a fluctuation part of the one-particle distribution function: $f = f_0 + \delta f$ as follows.

$$\delta f(\mathbf{q}, \theta, \phi) = \int d^3 k \cdot \delta S_{\mathbf{k}}(\theta, \phi) \cdot \exp(2\pi i \mathbf{k} \cdot \mathbf{q}). \tag{A.1}$$

Let us further define $\gamma_{\mathbf{k}}$ as follows.

$$\frac{1}{f_0(\mathbf{q}, \theta, \phi)} = \int d^3 k \cdot \gamma_{\mathbf{k}}(\theta, \phi) \cdot \exp(2\pi i \mathbf{k} \cdot \mathbf{q}). \tag{A.2}$$

Then, the fluctuation part of the free energy $F = U - TS$ may be written as follows with the use of α and β of Eqs. (7), (8).

$$\begin{aligned}
\frac{\delta^2 F}{RT} = {} & \frac{1}{8\pi}\int \mathrm{d}\Omega \int d^3 k \int d^3 k' \cdot \gamma_{\mathbf{k}'-\mathbf{k}} \cdot \delta S_{\mathbf{k}}(\theta, \phi) \cdot \delta S_{-\mathbf{k}'}(\theta, \phi) \\
& + \frac{1}{2}\Bigg[\int d^3 k \Bigg\{ \alpha_{\mathbf{k}} \left(\frac{1}{4\pi}\int \mathrm{d}\Omega \cdot \delta S_{\mathbf{k}}(\theta, \phi)\right) \cdot \left(\frac{1}{4\pi}\int \mathrm{d}\Omega' \cdot \delta S_{-\mathbf{k}}(\theta', \phi')\right) \\
& + \beta_{\mathbf{k}} \left(\frac{1}{4\pi}\int \mathrm{d}\Omega \cdot P_2(\cos\theta) \cdot \delta S_{\mathbf{k}}(\theta, \phi)\right) \cdot \Bigg(\frac{1}{4\pi}\int \mathrm{d}\Omega' \cdot P_2(\cos\theta') \\
& \qquad \cdot \delta S_{-\mathbf{k}}(\theta', \phi')\Bigg) \\
& + 2\beta_{\mathbf{k}} \sum_{m=1}^{2} \frac{(2-m)!}{(2+m)!} \left(\frac{1}{4\pi}\int \mathrm{d}\Omega \cdot P_2^m(\cos\theta)\, \delta S_{\mathbf{k}}(\theta, \phi) \cdot \exp(im\phi)\right) \\
& \times \left(\frac{1}{4\pi}\int \mathrm{d}\Omega' \cdot P_2^m(\cos\theta') \cdot \delta S_{-\mathbf{k}}(\theta', \phi') \cdot \exp(-im\phi')\right)\Bigg\}\Bigg]
\end{aligned} \tag{A.3}$$

where the $P_2^m(\cos\theta)$ are the associated Legendre polynomials of the second order. The first term on the right hand side of Eq. (A.3) represents the entropy fluctuations, the second one expresses the thermal fluctuations of the translational order parameter, the third one the fluctuations of the orientational order parameter and the last one the fluctuations arising from its azimuthal parts which are neglected in the molecular field approximation.

The above expression is rewritten as follows for the purpose of convenience.

$$\frac{\delta^2 F}{RT} = \frac{1}{2}\int d^3k \left[\gamma_0 |\delta\xi_{\mathbf{k}}|^2 + \alpha_{\mathbf{k}} |\delta\sigma_{\mathbf{k}}|^2 + \beta_{\mathbf{k}} \sum_{m=-2}^{+2} |\delta\tau_{\mathbf{k}}^{(m)}|^2\right] \tag{A.4}$$

where the random phase approximation (i.e., the retention of only the term $\mathbf{k} = \mathbf{k}'$) is used in the term involving $\gamma_{\mathbf{k}}$. $\delta\xi$, $\delta\sigma$ and $\delta\tau$ are defined as follows.

$$|\delta\xi_{\mathbf{k}}|^2 \equiv \frac{1}{4\pi}\int \mathrm{d}\Omega \cdot \delta S_{\mathbf{k}}(\theta,\phi)\cdot \delta S_{-\mathbf{k}}(\theta,\phi), \tag{A.5}$$

$$|\delta\sigma_{\mathbf{k}}|^2 \equiv \left(\frac{1}{4\pi}\int \mathrm{d}\Omega \cdot \delta S_{\mathbf{k}}(\theta,\phi)\right)\cdot\left(\frac{1}{4\pi}\int \mathrm{d}\Omega' \cdot \delta S_{-\mathbf{k}}(\theta',\phi')\right) \tag{A.6}$$

$$|\delta\tau_{\mathbf{k}}^{(m)}|^2 \equiv \frac{(2-|m|)!}{(2+|m|)!}\left(\frac{1}{4\pi}\int \mathrm{d}\Omega \cdot P_2^m(\cos\theta)\cdot \delta S_{\mathbf{k}}(\theta,\phi)\exp(im\phi)\right) \times \left(\frac{1}{4\pi}\int \mathrm{d}\Omega' \cdot P_2^m(\cos\theta')\cdot \delta S_{-\mathbf{k}}(\theta',\phi')\exp(-im\phi')\right). \tag{A.7}$$

The normalization condition for f yields

$$\frac{1}{4\pi v}\int \mathrm{d}\Omega \int d^3q \cdot \delta f(\mathbf{q},\theta,\phi) = 0,$$

which leads to the following equality.

$$\frac{1}{4\pi}\int \mathrm{d}\Omega \cdot \delta S_0(\theta,\phi) = 0. \tag{A.8}$$

Hereafter we restrict our attention to long wavelength fluctuations in liquid crystals. Then, all the terms may be expanded as a power series in wave vector $\mathbf{k}$. Equations (A.6) and (A.8) lead us to the conclusion that the fluctuations of the translational order parameter $|\delta\sigma_{\mathbf{k}}|^2$ are much smaller than the other fluctuations since its zeroth-order term $|\delta\sigma_0|^2$ vanishes, which indicates that the orientational fluctuations make a predominant contribution to those in liquid crystals.

The thermal average of the orientational fluctuations $|\delta\tau_{\mathbf{k}}^{(m)}|^2$ can be derived from the equipartition theorem.

$$\langle|\delta\tau_{\mathbf{k}}^{(m)}|^2\rangle = \frac{1}{\beta_{\mathbf{k}}}. \tag{A.9}$$

Expanding $\beta_{\mathbf{k}}$ as a power series in **k**, we obtain the following Ornstein-Zernike type formula.

$$\langle|\delta\tau_{\mathbf{k}}^{(m)}|^2\rangle = \frac{1}{\beta_0 + (\beta_z^{\|} \cdot k_z^2 + \beta_{\perp}^{\|} \cdot k_{\perp}^2)/2}. \tag{A.10}$$

These results seem to confirm a derivation of the thermal fluctuations in liquid crystals given by de Gennes⁽³⁾ with the use of the continuum theory.

REFERENCES

1. Gray, G. W., " Molecular Structure and the Properties of Liquid Crystals " Academic Press, New York, 1962; Saupe, A., *Angew. Chem. Internat. Edit.* **7**, 92 (1968); Chistyakov, I. G., *Soviet-Phys. Uspekhi* **9**, 551 (1967).
2. Oseen, C. W., *Trans. Faraday Soc.* **29**, 883 (1933); Zocher, H., *ibid.* **29**, 945 (1933); Frank, F. C., *Disc. Faraday Soc.* **25**, 19 (1958).
3. de Gennes, P. G., *Mol. Cryst. and Liq. Cryst.* **7**, 325 (1969).
4. Maier, W. and Saupe, A., *Z. Naturforsch.* **14a**, 882 (1959); **15a**, 287 (1960); **16a**, 816 (1961).
5. Pople, J. A. and Karasz, F. E., *J. Phys. Chem. Solids* **18**, 28 (1961); Karasz, F. E. and Pople, J. A., *ibid.* **20**, 294 (1961).
6. Lennard-Jones, J. E. and Devonshire, A. F., *Proc. Roy. Soc.* **A169**, 317 (1939); **A170**, 464 (1939).
7. Kirkwood, J. G. and Monroe, E., *J. Chem. Phys.* **9**, 514 (1941).
8. Kobayashi, K. K., *Phys. Letters* **31A**, 125 (1970); *J. Phys. Soc. Japan* **29**, 101 (1970).
9. Chandrasekhar, S., Krishnamurti, D. and Madhusudana, N. V., *Mol. Cryst. and Liq. Cryst.* **8**, 45 (1969).
10. Bulkin, B. J., Grunbaum, D. and Santoro, A. V., *J. Chem. Phys.* **51**, 1602 (1969).
11. Kobayashi, K. K., *J. Phys. Soc. Japan* **27**, 1116 (1969).
12. Saupe, A., *Mol. Cryst. and Liq. Cryst.* **7**, 59 (1969).
13. Frenkel, J., " Kinetic Theory of Liquids", Dover Publications, New York, 1955, p. 84.
14. Honma, S., Okada, K. and Matsuda, H., *Progr. Theor. Phys.* (*Kyoto*) **37**, 1310 (1966); **38**, 767 (1967).
15. Krieger, T. J. and James, H. M., *J. Chem. Phys.* **22**, 796 (1954); Kobayashi, K. K., Hanamura, E. and Shishido, F., *Phys. Letters* **28A**, 718 (1969).

Note Added in Proof

Recently, Chandrasekhar *et al.* (*Mol. Cryst. and Liq. Cryst.* **10,** 151 (1970)) have extended the Pople–Karasz theory so as to take into account the right volume dependence of intra-site repulsive force, obtaining a good agreement with experiments. They also have made an extension of the Maier–Saupe theory by taking a quadrupole–dipole type interaction into consideration (*Mol. Cryst. and Liq. Cryst.* **10,** 337 (1970)).

As regards the non-propagating (relaxational) soft mode associated with the liquid–solid transition suggested by the author, it should be noted that Amer, Shen and Rosen (*Phys. Rev. Letters* **24,** 718 (1970)) have recently observed abrupt broadening of the central Rayleigh–wing component (i.e., with no change in frequency) at the solid–nematic phase transition which might be related to the above-mentioned mode.