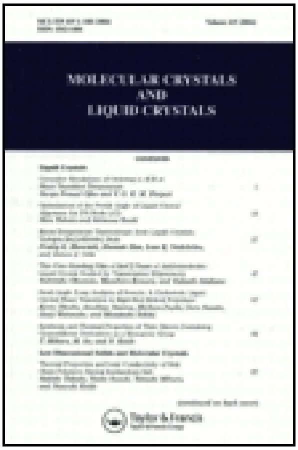

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Theory of Homologous Liquid Crystals. II. Orientation Correlation Functions

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Theory of Homologous Liquid Crystals. II. Orientation Correlation Functions†

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Molecular correlation functions of homologous liquid crystals are calculated statistical mechanically from a generalized McMillan hamiltonian. It goes beyond the mean-field approximation and includes the nematic and smectic fluctuations on the same footing. The expressions obtained are valid for either the isotropic(I), nematic(N) or smectic A(A) phase and are equally applicable to I-N or I-A transitions. When specified to the isotropic phase the inverse correlation function G_0^{-1} shows a smooth "bending down" near T_{NI} or T_{AI} for all homologues in accordance with most experiments. The variation of the "degree" of the "bending down" with different members of a homologous series is in agreement with, e.g., the *n*CB and *n*OCB data of Muta et al. For 9CB and 11CB our G_0^{-1} curve, without "inflection", "saturation" or "dip", agrees with the experiments of Zhang et al., but not those of Coles and Strazielle, or Pouligny et al. Supercooling temperature T^* [defined by $G_0^{-1}(T^*) = 0$] as function of molecular length is also calculated. Our theory is compared with others (including that of Gohin et al.).

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I. INTRODUCTION

When liquid crystals are still in the isotropic(I) phase but near the nematic(N) phase, due to the fluctuation of the order parameter, some properties of the N phase already show up. This is the so-called pretransitional effect. It manifests experimentally as the anomalous increase of the Cotton–Mouton coefficient, light scattering intensities, etc.[1] These measured quantities are related to the correlation function G_0 of the molecular orientations.

In the mean-field approximation(MFA), the Landau-deGennes model[2] gives, in the I phase, a G_0^{-1} linear in the temperature T. Yet, in 1970, Stinson and Litster[3] observed that in the I phase of MBBA (methoxybenzylidene butylaniline) there is a "bending down" of the $G_0^{-1} \sim T$ curve very near T_{NI}, the transition temperature between the N and I phases, in violation of the MFA results. This anomaly has since been confirmed by other experiments[4–15] on different compounds with various measurements (including depolarized Rayleigh scattering, magnetic or electric birefringence). More recently, the trend of the anomalous "bending down" in a homologous series has been investigated by Muta et al.,[16] Coles and Straziell,[17] Gohin et al.,[18] Pouligny et al.,[19] Zhang et al.,[20] respectively. Similar studies on nematic solutions or mixtures are also reported.[13,21,22]

In some of these studies, extra structures (in the "bending down" region) are observed very near T_{NI} and they are not always consistent with each other. For example, in 9CB and 11CB (alkylcyanobiphenyl), "inflection" points are observed in the light scattering measurements;[17] "saturation" or even a "dip" is found in the optical Kerr effects data,[19] while a smooth "bending down" (i.e., no extra structure) is reported in the Cotton–Mouton experiments.[20] Note that these three conflicting experimental results are all for the same materials and the same temperature regions (although different but supposedly "equivalent" physical quantities and measuring techniques are used). To our knowledge, there is yet no satisfactory explanation or resolution of this glaring contradiction.

On the theoretical side, the "bending down" in G_0^{-1} was first attributed by Stinson and Litster[3] to the failure of the MFA in the critical region very close to T_{NI}. The same point of view was held by Fan and Stephen[23] who, by inclusion of the cubic and quartic terms in the free energy, managed to give a finite series expression for G_0^{-1} containing the "bending down" feature. Unfortunately, each correction term in this series is divergent in itself, rendering the validity of the expression questionable and not very useful in practice, in our opinion. (See Section VI for a discussion of the related work of Chandrasekhar et al.)

It was not until 1978 that Lin[24] succeeded in deriving a G_k (valid for *both* I and N phases) that goes beyond the MFA but still satisfies the required sum rule. This result was immediately generalized[25] to include the presence of an external (magnetic or electric) field and was used to calculate the apparent gap exponent [see Ref. (26) for the definition of apparent exponents]. In this beyond-mean-field theory[24,25] based on the Maier–Saupe type hamiltonian the "bending down" anomaly was naturally explained [see Ref. (27) for more details including discussions on Ref. (28)]. Pouligny and Lalanne[8] have since used this theory to reinterpret their previous data on MBPB (*p*-methoxy-benzoate-*p*-*n*-pentylbenzene)[7] with equal success. Lately, Lin's theory was generalized[29] to the case of nematic mixtures or impure nematics [see also Ref. (8)] and found to be in agreement with experiments.

In spite of these successes, Lin's previous theory[25] is limited by the facts that (i) it cannot be applied to I-A transitions (A represents smectic A phase); (ii) for numerical calculations, the molecules are fixed in an artificial lattice; (iii) the quantity $(T_{NI} - T^*)/T_{NI}$, as in all other existing theories, is too large compared to experimental value. The last two points are the main obstacles in obtaining unambiguous *quantitative* comparisons between theory and experiments [see Ref. (27)]. Point (i) is due to the fact that the theory is based on the Maier–Saupe hamiltonian which describes only the I-N transition.

The aim of this paper is to generalize Lin's theory[25] to the generalized McMillan hamiltonian of Ref. (30) [referred to as (I) in the following] so that limitations of (i) and (ii) are overcome and the variations with different members in a homologue can be calculated. In our approach, the smectic and nematic fluctuations are treated on an equal footing (Section III), in contrary to the work of Gohin et al.[18] Despite much effort, we are not able to overcome point (iii) (see Section V). Our calculations for the orientational correlation function show a smooth "bending down" region for all members of any homologue (Section IV), in agreement with the findings of Zhang et al.[20] [but not that of Refs. (18) and (19) in this particular aspect] and that of Muta et al.[16] Our results are compared with those of Refs. (18) and (19) in relation to the relevant experiments of homologous series[16–20] (Sections V and VI).

Calculations of T^* as function of molecular length are presented in Section V. Apparent exponents will be discussed elsewhere.[27]

II. BASIC FORMULAS

For simplicity, following Ref. (31), we set $\delta = 0$ in Eq. I (2.4) [representing Eq. (2.4) of Ref. (30)] and obtain the hamiltonian

$$H = -(4\pi^{1/2})^{-1} JF(d/r_0)\sum_{i,j}{}' \exp(-r_{ij}^2/r_0^2) S_i S_j \tag{2.1}$$

where J is a coupling constant, d the molecular length (or smectic layer thickness), r_0 the effective range of interaction between two molecules, $S_i = P_2(\cos\theta_i)$, θ_i the angle between the director of the ith molecule and the smectic layer normal (the z-axis). The prime in the summation indicates the absence of $i = j$ terms. In Eq. (2.1), only the $S_i S_j$ part of $P_2(\cos\theta_{ij})$ is kept [see Appendix A of (I)] since the other parts are ineffective in the following calculations [see Refs. (25) and (32)]. Let $\mathbf{r}_i \equiv (x_i, y_i, z_i)$, $x_{ij} \equiv x_i - x_j$, etc., $\rho_{ij}^2 \equiv x_{ij}^2 + y_{ij}^2$. Then the exponential in Eq. (2.1) can be separated into two parts related to ρ_{ij} and z_{ij}, respectively. When $\exp(-z_{ij}^2/r_0^2)$ is considered as a function of z_j and assuming $\{g_n(z_j)\}$, $n = 0, 1, \ldots,$ to be a complete basis function of z_j, we obtain

$$\exp(-z_{ij}^2/r_0^2) = \sum_n Af_n(z_i) g_n(z_j) \tag{2.2}$$

where $Af_n(z_i)$ is the coefficient of expansion. Here, the introduction of A is purely for the sake of notational convenience. Eq. (2.2) may be rewritten as

$$H = -\frac{1}{2}\sum_{i,j}{}' \sum_n J_{ij}(\rho_{ij}) f_n(z_i) g_n(z_j) S_i S_j \tag{2.3}$$

where

$$\begin{aligned} J_{ij} &\equiv (J/2\pi^{1/2}) AF(d/r_0)\exp(-\rho_{ij}^2/r_0^2), \qquad i \neq j \\ J_{ii} &\equiv 0 \end{aligned} \tag{2.4}$$

In the following, three basic formulas [Theorems A, B and C corresponding to Eqs. (2.5), (2.9) and (2.15)] are given.

Theorem A.

$$\langle f(x, y)\, g(\mathbf{r}, \boldsymbol{\Omega})\rangle = \langle f(x, y) \langle g(\mathbf{r}, \boldsymbol{\Omega})\rangle_1 \rangle \tag{2.5}$$

where f and g are arbitrary functions, $x \equiv (x_1, \ldots, x_N)$, etc. [similarly for $\mathbf{r}$ and $\boldsymbol{\Omega}$, with $\boldsymbol{\Omega}$ being the angular angles (θ, φ) of the molecules], N the total number of molecules. $\langle \cdots \rangle$ is the thermal average and

$$\langle g(\mathbf{r}, \Omega) \rangle_1 \equiv \frac{\int dz_1 \ldots dz_N \int d\boldsymbol{\Omega}_1 \ldots d\boldsymbol{\Omega}_N \exp(-\beta H) g(\mathbf{r}, \boldsymbol{\Omega})}{\int dz_1 \ldots dz_N \int d\boldsymbol{\Omega}_1 \ldots d\boldsymbol{\Omega}_N \exp(-\beta H)} \tag{2.6}$$

where $\beta = 1/k_B T$.

The proof of Eq. (2.5) is given in Appendix A.

Comparing Eq. (2.5) with Eq. (6) of Ref. (32) we see that in the latter it is the operators of the different molecules that have been separated while in the former case here, it is the degree of freedom of the molecules.

Let

$$\begin{aligned} M_n(i) &\equiv f_n(z_i) S_i \\ M_{nj} &\equiv \sum_i M_n(i) J_{ij} \end{aligned} \tag{2.7}$$

and $-E_j$ be the parts in H that are related to the jth molecule, i.e.,

$$E_j = \sum_n M_{nj} g_n(j) S_j \tag{2.8}$$

we then obtain (see Appendix B):

Theorem B.

$$\langle \{\bar{j}\} \{j\} \rangle_1 = \langle \{\bar{j}\} \langle \{j\} \rangle_{E_j} \rangle_1 \tag{2.9}$$

where $\{j\}$ $(\{\bar{j}\})$ represents any function of operators related (unrelated) to the jth molecule,

$$\langle \{j\} \rangle_{E_j} \equiv \frac{\int dz_j \, d\boldsymbol{\Omega}_j \exp(\beta E_j) \{j\}}{\int dz_j \, d\boldsymbol{\Omega}_j \exp(\beta E_j)} \tag{2.10}$$

Here, in Eq. (2.9), it is an average with respect to three types of degrees of freedom (i.e., $z, \boldsymbol{\Omega}$) while in Eq. (6) of Ref. (32), it is only two (i.e., $\boldsymbol{\Omega}$).

Let $\overline{M}_{nj}$ be a certain (to be defined) type of thermal average of M_{nj}

[see Eq. (4.9)]. When Eq. (2.10) is Taylor expanded one gets

$$\langle\{j\}\rangle_{E_j} = K(\{M_{nj}\}) \equiv \langle\{j\}\rangle_0 + \sum_n \beta\Delta_{jn}\left(M_{nj} - \overline{M}_{nj}\right) + \frac{1}{2}\sum_{n,n'} \beta^2\Delta_{jnn'}\left(M_{nj} - \overline{M}_{nj}\right)\left(M_{n'j} - \overline{M}_{n'j}\right) + \cdots \tag{2.11}$$

where

$$\langle\{j\}\rangle_0 = K\left(\left\{\overline{M}_{nj}\right\}\right) \equiv \frac{\int dz_j\, d\Omega_j\, \{j\} \exp\left(\beta\sum_n \overline{M}_{nj} g_n(z_j) S_j\right)}{\int dz_j\, d\Omega_j \exp\left(\beta\sum_n \overline{M}_{nj} g_n(z_j) S_j\right)} \tag{2.12}$$

$$\beta\Delta_{jn} = \left(\frac{\partial K}{\partial M_{nj}}\right) M_{nj} = \overline{M}_{nj} = \beta\left[\langle\{j\}\, g_n(z_j) S_j\rangle_0 - \langle\{j\}\rangle_0 \langle g_n(z_j) S_j\rangle_0\right] \tag{2.13}$$

$$\begin{aligned}\beta^2\Delta_{jnn'} &= \left(\frac{\partial^2 K}{\partial M_{nj}\,\partial M_{n'j}}\right)_{M_{nj} = \overline{M}_{nj},\, M_{nj} = \overline{M}_{nj}} \\ &= \beta^2\left[\langle\{j\}\, g_n(z_j) g_{n'}(z_j) S_j\rangle_0 - \langle\{j\}\, g_n(z_j) S_j\rangle_0 \langle g_{n'}(z_j) S_j\rangle_0\right. \\ &\quad - \langle\{j\}\, g_{n'}(z_j) S_j\rangle_0 \langle g_n(z_j) S_j\rangle_0 + \langle\{j\}\rangle_0 \langle g_{n'}(z_j) S_j\rangle_0^2 \\ &\quad \left. + \langle\{j\}\rangle_0 \langle g_n(z_j) S_j\rangle_0^2 - \langle\{j\}\rangle_0 \langle g_n(z_j) g_{n'}(z_j) S_j^2\rangle_0\right]\end{aligned} \tag{2.14}$$

Substituting Eqs. (2.11)–(2.14) into Eq. (2.9) we obtain an expansion up to second order of the generalized Suzuki formula:

Theorem C.

$$\begin{aligned}\langle\{\bar{j}\}\{j\}\rangle_1 &= \langle\{\bar{j}\}\rangle_1 \langle\{j\}\rangle_0 + \beta\sum_n \Delta_{jn}\left(\langle\{\bar{j}\}\, M_{nj}\rangle_1 - \langle\{\bar{j}\}\rangle_1 \overline{M}_{nj}\right) \\ &\quad + \frac{1}{2}\beta^2 \sum_{n,n'} \Delta_{jnn'}\left(\langle\{\bar{j}\}\, M_{nj} M_{n'j}\rangle_1 - \langle\{\bar{j}\}\, M_{nj}\rangle_1 \overline{M}_{n'j}\right. \\ &\quad - \langle\{\bar{j}\}\, M_{n'j}\rangle_1 \overline{M}_{nj} \\ &\quad \left. + \langle\{\bar{j}\}\rangle_1 \overline{M}_{nj} \overline{M}_{n'j}\right) + \cdots\end{aligned} \tag{2.15}$$

In this paper, Eq. (2.15) is used up to the β term.

III. ORIENTATIONAL CORRELATION FUNCTION

Orientational correlation function is defined by

$$G_{\mathbf{k}} \equiv N^{-1}\sum_{i,j}(S_i - \langle S_i\rangle)(S_j - \langle S_j\rangle)e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} \tag{3.1}$$

$$\bar{G}_{\mathbf{k}} \equiv N^{-1}\sum_{i,j}\langle S_i S_j e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)}\rangle \tag{3.2}$$

In the I phase, $\langle S_i\rangle = 0$ and hence $\bar{G}_{\mathbf{k}} = G_{\mathbf{k}}$. By Eqs. (2.5) and (3.2),

$$\bar{G}_{\mathbf{k}} = N^{-1}\sum_{i,j}\langle\langle A_i A_j^{+}\rangle_1 e^{i(k_x x_{ij} + k_y y_{ij})}\rangle \tag{3.3}$$

where

$$A_i \equiv S_i \exp(ik_z z_i) \tag{3.4}$$

and A_i^+ is the conjugate operator of A_i. In Eq. (2.15), neglecting the β^2 term and taking $\{j\} = A_j^+$, $\{\bar{j}\} = A_i$ (denoting Δ_{jn} in this case by Δ_n for notational simplicity), one has

$$(i \neq j) \qquad \langle A_i A_j^{+}\rangle_1 = \langle A_i\rangle_1\langle A_j^{+}\rangle_0 + \beta\sum_n \Delta_n \sum_\lambda J_{\lambda j}\langle A_i B_{n\lambda}\rangle_1 - \beta\sum_n \Delta_n\langle A_i\rangle_1 \bar{M}_{nj} \tag{3.5}$$

where

$$B_{n\lambda} \equiv f_n(z_\lambda)S_\lambda$$

In Eq. (2.15), neglecting the β^2 term, taking $j = \lambda$, $\{\lambda\} = B_{n\lambda}$, $\{\bar{\lambda}\} = A_i$ and denoting $\Delta_{nn'}$ in this case by $\Delta_{\lambda n'}$, i.e.,

$$\begin{aligned} \Delta_n &= \langle A_j^{+} g_n(z_j)S_j\rangle_0 - \langle A_j^{+}\rangle_0\langle g_n(z_j)S_j\rangle_0 \\ \Delta_{nn'} &= \langle B_{n\lambda} g_{n'}(z_j)S_j\rangle_0 - \langle B_{n\lambda}\rangle_0\langle g_{n'}(z_j)S_j\rangle_0 \end{aligned} \tag{3.6}$$

we have

$$(i \neq \lambda) \qquad \langle A_i B_{n\lambda}\rangle_1 = \langle A_i\rangle_1\langle B_{n\lambda}\rangle_0 + \beta\sum_{n'} \Delta_{nn'} \sum_{\lambda'} J_{\lambda'\lambda}\langle A_i B_{n'\lambda'}\rangle_1 - \beta\sum_{n'} \Delta_{nn'}\langle A_i\rangle_1 \bar{M}_{n'\lambda} \tag{3.7}$$

In the following, $\bar{G}_{\mathbf{k}}$ is obtained by solving Eq. (3.7) to obtain the Fourier transforms of $\langle A_i B_{n\lambda}\rangle_1$ and substituting into Eq. (3.5). Let

$$F_n(k_z; i,\lambda) \equiv \langle A_i B_{n\lambda}\rangle_1 \tag{3.8}$$

$$F_n(\mathbf{k}) \equiv F_n(k_z, k_\perp) = N^{-1}\sum_{i,\lambda} F_n(k_z; i,\lambda)e^{ik_x x_{i\lambda} + ik_y y_{i\lambda}} \tag{3.9}$$

where $k_\perp \equiv (k_x, k_y)$. Note that (see Appendix C)

$$N^{-1}\sum_{\substack{i,\lambda,\lambda' \\ (i\neq\lambda)}} J_{\lambda\lambda'}F_n(k_z; i,\lambda)e^{ik_x x_{i\lambda} + ik_y y_{i\lambda}}$$

$$= J_{k_\perp}F_n(k_z, k_\perp) - N'^{-1}\sum_{p_\perp} F_n(k_z, p_\perp)J_{p_\perp} \tag{3.10}$$

where

$$J_{p_\perp} \equiv \sum_j J_{ij}e^{ip_x x_{ij} + ip_y y_{ij}}, \qquad p_\perp \equiv (p_x, p_y), \quad N' \equiv N^{2/3} \tag{3.11}$$

In the following, in Eqs. (3.5) and (3.7) only the terms corresponding to $n' = 0, 1$ and $n = 0, 1$ are kept (see Section IV). When both sides of Eq. (3.7) are multiplied by $\exp i(p_x x_{i\lambda} + p_y y_{i\lambda})$ and then operated by $N^{-1}\sum_{i,\lambda}$, by Eqs. (3.8) and (3.9), one obtains for $n = 0$:

$$(1 - \beta\Delta_{00}J_{k_\perp})F_0(\mathbf{k}) - \beta\Delta_{01}J_{k_\perp}F_1(\mathbf{k}) = X_0 + C_0(\mathbf{k}) \tag{3.12}$$

When $n = 1$, we obtain similarly:

$$-\beta\Delta_{10}J_{k_\perp}F_0(\mathbf{k}) + (1 - \beta\Delta_{11}J_{k_\perp})F_1(\mathbf{k}) = X_1 + C_1(\mathbf{k}) \tag{3.13}$$

where

$$C_n(\mathbf{k}) \equiv \langle A_i\rangle_1\Big(\langle B_{n\lambda}\rangle_0 - \beta\sum_{n'}\Delta_{nn'}\bar{M}_{n'\lambda}\Big)N^{-1}\sum_{\substack{i,\lambda \\ (i\neq\lambda)}} e^{ik_x x_{i\lambda} + ik_y y_{i\lambda}},$$

$$n, n' = 0, 1 \tag{3.14}$$

$$X_0 \equiv -\beta\Delta_{00}N'^{-1}\sum_{p_\perp} J_{p_\perp}F_0(k_z, p_\perp) - \beta\Delta_{01}N'^{-1}\sum_{p_\perp} J_{p_\perp}F_1(k_z, p_\perp)$$

$$+ F_0(k_z; i, i)$$

$$X_1 \equiv -\beta\Delta_{10}N'^{-1}\sum_{p_\perp} J_{p_\perp}F_0(k_z, p_\perp) - \beta\Delta_{11}N'^{-1}\sum_{p_\perp} J_{p_\perp}F_1(k_z, p_\perp)$$

$$+ F_1(k_z; i, i) \tag{3.15}$$

Noting that X_0 and X_1 are independent of $k_\perp$ we may obtain $F_0(\mathbf{k})$ and $F_1(\mathbf{k})$ by solving the simultaneous equations (3.12) and (3.13), resulting in (see Appendix D):

$$\begin{aligned} F_0(\mathbf{k}) = {} & \left[D_1(k_\perp)D_2(k_z)\right]^{-1} \\ & \times \Big\{(1-\beta\Delta_{11}J_{k_\perp})\left[\overline{C}_0(k_z)+\beta h_2(k_z)q_1-\beta^2\overline{C}_0(k_z)\Delta q_2\right] \\ & +\beta\Delta_{01}J_{k_\perp}\left[\overline{C}_1(k_z)+\beta h_1(k_z)q_1-\beta^2\overline{C}_1(k_z)\Delta q_2\right] \\ & +\left[(1-\beta\Delta_{11}J_{k_\perp})C_0(\mathbf{k})+\beta\Delta_{01}J_{k_\perp}C_1(\mathbf{k})\right]/D_1(k_\perp)\Big\} \end{aligned} \tag{3.16}$$

$$\begin{aligned} F_1(\mathbf{k}) = {} & \left[D_1(k_\perp)D_2(k_z)\right]^{-1} \\ & \times \Big\{\beta\Delta_{10}J_{k_\perp}\left[\overline{C}_0(k_z)+\beta h_2(k_z)q_1-\beta^2\overline{C}_0(k_z)\Delta q_2\right] \\ & +(1-\beta\Delta_{00}J_{k_\perp})\left[\overline{C}_1(k_z)+\beta h_1(k_z)q_1-\beta^2\overline{C}_1(k_z)\Delta q_2\right] \\ & +\left[\beta\Delta_{10}J_{k_\perp}C_0(\mathbf{k})+(1-\beta\Delta_{11}J_{k_\perp})C_1(\mathbf{k})\right]/D_1(k_\perp)\Big\} \end{aligned} \tag{3.17}$$

where

$$\begin{aligned} h_1(k_z) &\equiv \overline{C}_1(k_z)\Delta_{00}-\overline{C}_0(k_z)\Delta_{10} \\ h_2(k_z) &\equiv \overline{C}_0(k_z)\Delta_{11}-\overline{C}_1(k_z)\Delta_{01} \end{aligned} \tag{3.18}$$

$$q_1 \equiv N'^{-1}\sum_{p_\perp} J_{p_\perp}/D_1(p_\perp) \tag{3.19}$$

$$q_2 \equiv N'^{-1}\sum_{p_\perp} J_{p_\perp}^2/D_1(p_\perp) \tag{3.20}$$

$$\Delta \equiv \Delta_{00}\Delta_{11}-\Delta_{01}\Delta_{10} \tag{3.21}$$

$$\begin{aligned} \overline{C}_n(k_z) \equiv {} & -\beta\Delta_{n0}N'^{-1}\sum_{p_\perp} J_{p_\perp}C_0(k_z,p_\perp)/D_1(p_\perp) \\ & +\beta^2\Delta N'^{-1}\sum_{p_\perp} J_{p_\perp}^2 C_n(k_z,p_\perp)/D_1(p_\perp) \\ & -\beta\Delta_{n1}N'^{-1}\sum_{p_\perp} J_{p_\perp}C_1(k_z,p_\perp)/D_1(p_\perp)+F_n(k_z;i,i), \\ & \qquad n=0,1 \end{aligned} \tag{3.22}$$

$$D_1(k_\perp) \equiv (1-\beta\Delta_{00}J_{k_\perp})(1-\beta\Delta_{11}J_{k_\perp})-\beta^2\Delta_{10}\Delta_{01}J_{k_\perp}^2 \tag{3.23}$$

$$D_2(k_z) \equiv (1+\beta\Delta_{00}q_1-\beta^2\Delta q_2)(1+\beta\Delta_{11}q_1-\beta^2\Delta q_2)-\beta^2\Delta_{10}\Delta_{01}q_1^2 \tag{3.24}$$

When both sides of Eq. (3.5) is multiplied by $\exp(ip_x x_{ij} + ip_y y_{ij})$ and operated by $N^{-1}\sum_{i,\lambda}$, using Eqs. (3.16) and (3.17) and then substituting into Eq. (3.3), one obtains

$$\bar{G}_{\mathbf{k}} = \langle\langle S_i^2\rangle_1 + C_3(\mathbf{k}) + \beta\Delta_0 F_0(\mathbf{k}) J_{k_\perp} - \beta\Delta_0 N'^{-1}\sum_{p_\perp} F_0(k_z, p_\perp) J_{p_\perp}$$

$$+ \beta\Delta_1 F_1(\mathbf{k}) J_{k_\perp} - \beta\Delta_1 N'^{-1}\sum_{p_\perp} F_1(k_z, p_\perp) J_{p_\perp}\rangle \tag{3.25}$$

where

$$C_3(\mathbf{k}) \equiv \langle A_i\rangle_1 \langle A_j^+\rangle_0 N^{-1}\sum_{i,j} e^{ik_x x_{ij} + ik_y y_{ij}} \tag{3.26}$$

Eq. (3.25) is rather complicated and has to be simplified to be practically useful. One possible way of simplification is to apply the random-phase approximation (RPA), i.e., taking the thermal averages of both sides of Eqs. (3.12) and (3.13) with the approximations:

$$\begin{aligned} \langle J_{k_\perp} F_0(\mathbf{k})\rangle &\simeq \langle J_{k_\perp}\rangle\langle F_0(\mathbf{k})\rangle \\ \langle J_{k_\perp} F_1(\mathbf{k})\rangle &\simeq \langle J_{k_\perp}\rangle\langle F_1(\mathbf{k})\rangle \end{aligned} \tag{3.27}$$

We then obtain $\langle F_0(\mathbf{k})\rangle$ and $\langle F_1(\mathbf{k})\rangle$ by using the same procedure in the derivation of Eqs. (3.16) and (3.17) above. The results thus obtained are the same as replacing directly $J_{k_\perp}$ by $\langle J_{k_\perp}\rangle$, $C_0(\mathbf{k})$ by $\langle C_0(\mathbf{k})\rangle$ and $C_1(\mathbf{k})$ by $\langle C_1(\mathbf{k})\rangle$ in Eqs. (3.16) and (3.17). Therefore, in RPA, Eq. (3.25) becomes

$$\bar{G}_{\mathbf{k}} = \langle S_i^2\rangle + \langle C_3(\mathbf{k})\rangle + \beta\Delta_0\langle F_0(\mathbf{k})\rangle\langle J_{k_\perp}\rangle - \beta\Delta_0 N'^{-1}$$

$$\times \sum_{p_\perp}\langle F_0(k_z, p_\perp)\rangle\langle J_{p_\perp}\rangle + \beta\Delta_1\langle F_1(k)\rangle\langle J_{k_\perp}\rangle$$

$$- \beta\Delta_1 N'^{-1}\sum_{p_\perp}\langle F_1(k_z, p_\perp)\rangle\langle J_{p_\perp}\rangle \tag{3.28}$$

Note that Eqs. (3.25) or (3.28) [and Eqs. (4.1)–(4.13)] is valid in either I, N or A phase.

IV. NUMERICAL CALCULATIONS

In order to calculate $\bar{G}_{\mathbf{k}}$ numerically, it is necessary to give the explicit forms of the functions g_n and f_n. Since $\{g_n(z_j)\}$ is just a complete set of basis functions, we may assume

$$\{ g_n(z_j)\} = \{\cos(n2\pi z_i/d), \sin(n2\pi z_i/d)\} \tag{4.1}$$

where n is non-negative integer. If only $n = 0, 1$ terms are retained then the term $\sin(2\pi z_i/d)$ needs not be considered (see Appendix E). Consequently,

$$\begin{aligned} g_0(z_j) &= 1 \\ g_1(z_j) &= \bar{\alpha}\cos(2\pi z_i/d) \end{aligned} \tag{4.2}$$

where

$$\bar{\alpha} \equiv 2\exp\left[-(\pi/t)^2\right]w(t) \tag{4.3}$$

$$t \equiv d/r_0 \tag{4.4}$$

and $w(t)$ is defined by Eq. I (2.13) [see Figure 1 of (I)]. In Eq. (4.2), the factor $\bar{\alpha}$ is included for notational convenience.

According to the definition of f_n in Eq. (2.2), one has

$$f_0(z_i) = 1 \tag{4.5}$$

$$f_1(z_i) = \cos(2\pi z_i/d) \tag{4.6}$$

$$A = a_0 \equiv (\pi^{1/2}/t)R(t/2) \tag{4.7}$$

where $R(x)$ is defined by Eq. I (2.14). Eq. (2.4) becomes

$$\begin{aligned} J_{ij} &= \tfrac{1}{2}JF(t)R(t/2)t^{-1}\exp\left(-\rho_{ij}^2/r_0^2\right), \qquad i \neq j \\ J_{ii} &= 0 \end{aligned} \tag{4.8}$$

In Eq. (2.13) the thermal average $\overline{M}_{nj}$ is arbitrary. We now substitute Eqs. (4.5) and (4.6) into Eq. (2.7) and define

$$\begin{aligned} \overline{M}_{0j} &\equiv \langle J_0\rangle\eta \\ \overline{M}_{1j} &\equiv \langle J_0\rangle\sigma \end{aligned} \tag{4.9}$$

where

$$\begin{aligned} J_0 &\equiv \sum_j J_{ij} \\ \eta &\equiv \langle S_i \rangle \\ \sigma &\equiv \langle \cos(2\pi z_i/d) S_i \rangle \\ \langle J_0 \rangle &= \frac{1}{2} J F(t) R(t/2) t^{-1} \sum_j \langle \exp(-\rho_{ij}^2/r_0^2) \rangle \end{aligned} \tag{4.10}$$

Eq. (4.8) is used in Eq. (4.10). Eq. (2.12) becomes

$$\langle \{j\} \rangle_0 = \frac{\int_0^d dz_j \int d\boldsymbol{\Omega}_j \{j\} \exp(-\beta V)}{\int_0^d dz_j \int d\boldsymbol{\Omega}_j \exp(-\beta V)} \tag{4.11}$$

$$V \equiv -\langle J_0 \rangle \left[\eta + \bar{\alpha} \sigma \cos(2\pi z_i/d) \right] S_i \tag{4.12}$$

By comparison, we note immediately that Eq. (4.12) is nothing but Eq. I (2.8) with $\delta = 0$. Comparing Eq. (4.10) with Eq. I (A19), we have

$$\bar{J} = \langle J_0 \rangle \tag{4.13}$$

Therefore, $\langle \cdots \rangle_0$ is just the mean-field thermal average defined in (I).

We now specify our calculations to the I phase. In the I phase,

$$\eta = 0 \tag{4.14}$$

$$\sigma = 0 \tag{4.15}$$

By Eqs. (4.9), (4.14) and (4.15),

$$\overline{M}_{0j} = \overline{M}_{1j} = 0 \tag{4.16}$$

Taking

$$\mathbf{k} = 0 \tag{4.17}$$

and by Eqs. (4.2), (4.5), (4.6), (4.11), (4.14) and (4.15), the different terms in Eq. (3.6) may be calculated, resulting in

$$\begin{aligned} \Delta_0 = \Delta_{00} &= \langle S_j^2 \rangle_0 = 1/5 \\ \Delta_{01} = \Delta_1 &= \langle S_j^2 \cos(2\pi z_j/d) \rangle_0 \bar{\alpha} = 0 \\ \Delta_{10} &= \langle S_j^2 \cos(2\pi z_j/d) \rangle_0 = 0 \\ \Delta_{11} &= \langle S_j^2 \cos^2(2\pi z_j/d) \rangle_0 \bar{\alpha} = \bar{\alpha}/10 \end{aligned} \tag{4.18}$$

By Eqs. (4.11), (4.14)–(4.16) and (3.14) we obtain

$$C_0(0, p_\perp) = 0 = C_1(0, p_\perp) \tag{4.19}$$

By Eqs. (4.18), (4.19) and (3.8),

$$\begin{aligned} \overline{C}_0(0) &= F_0(0; i, i) = \langle S_i^2 \rangle_1 \\ \overline{C}_1(0) &= F_1(0; i, i) = \langle S_i^2 \cos(2\pi z_i/d) \rangle_1 \end{aligned} \tag{4.20}$$

Similarly, by (3.18)–(3.20), (3.23) and (3.26) we have

$$\begin{aligned} D_1(p_\perp) &= (1 - \beta\Delta_{00}J_{p_\perp})(1 - \beta\Delta_{11}J_{p_\perp}) \\ D_2(p_\perp) &= (1 + \beta\Delta_{00}q_1 - \beta^2\Delta_{00}\Delta_{11}q_2)(1 + \beta\Delta_{11}q_1 - \beta^2\Delta_{00}\Delta_{11}q_2) \\ q_1 &\equiv [\beta(\Delta_{00} - \Delta_{11})]^{-1}[q(\beta\Delta_{00}J_0)/\beta\Delta_{00}J_0 - q(\beta\Delta_{11}J_0)/\beta\Delta_{11}J_0] \\ q_2 &\equiv [\beta^2\Delta_{00}\Delta_{11}]^{-1} + [\beta^2(\Delta_{00} - \Delta_{11})]^{-1} \\ &\quad \times [q(\beta\Delta_{00}J_0)/\beta\Delta_{00}^2J_0 - q(\beta\Delta_{11}J_0)/\beta\Delta_{11}^2J_0] \\ h_1(0) &= \Delta_{00}\langle S_i^2 \cos(2\pi z_i/d) \rangle_1 \\ h_2(0) &= \Delta_{11}\langle S_i^2 \rangle_1 \\ C_3(0, p_\perp) &= 0 \\ q(u) &\equiv N'^{-1}\sum_{p_\perp}(1/u - J_{p_\perp}/J_0)^{-1}, \qquad u \equiv \beta\Delta_{00}J_0 \end{aligned} \tag{4.21}$$

Putting Eqs. (4.18)–(4.21) into Eqs. (3.16) and (3.17) we have

$$\begin{aligned} F_0(0, p_\perp) &= (1 - \beta\Delta_0 J_{p_\perp})^{-1} u [q(u)]^{-1} \langle S_i^2 \rangle_1 \\ F_1(0, p_\perp) &= [D_1(p_\perp) D_2(p_\perp)]^{-1}(1 - \beta\Delta_{00}J_{p_\perp}) \\ &\quad \times [\overline{C}_1(0) + \beta h_1(0) q_1 - \beta^2 \overline{C}_1(0)\Delta q_2] \end{aligned} \tag{4.22}$$

Substituting Eq. (4.22) into Eq. (3.25) and noting that Eq. (3.1) and

Eq. (3.2) are identical under the conditions of Eqs. (4.14) and (4.15) we have

$$G_0 = \left\langle \frac{u}{1-u} \frac{\langle S_i^2 \rangle_1}{q(u)} \right\rangle \tag{4.23}$$

Since both u and $q(u)$ are operator functions of $\mathbf{r}[\equiv(r_1, \ldots, r_N)]$ (but not $\boldsymbol{\Omega}$) only, the $\langle \cdots \rangle$ in Eq. (4.23) is effectively a thermal average of the different possible translational configuration of the molecules, similar to the situation in amorphous materials, and is difficult to calculate.

In the following, we make the appropriate approximation such that Eq. (4.23) is replaced by

$$G_0 = \frac{v/g(v)}{1-v} \langle S_i^2 \rangle \tag{4.24}$$

where

$$v \equiv \langle u \rangle = \beta \Delta_{00} \langle J_0 \rangle = \beta \bar{J}/5 \tag{4.25a}$$

$$g(v) \equiv N'^{-1} \sum_{p_\perp} \left(1/v - \langle J_{p_\perp} \rangle / \bar{J}\right)^{-1} \tag{4.25b}$$

This approximation is equivalent to RPA because Eq. (4.24) is obtained if we start directly from the RPA results of Eq. (3.28) and then repeat the procedure of deriving Eq. (4.23).

Eq. (4.24) is the final result that will be used in our numerical calculations below. It is identical in form to Eq. (10) of Ref. (25) [or Eq. (25) of Ref. (32)]. There are two important points of difference: (i) The function g here is two-dimensional while that in Ref. (25) is three-dimensional; (ii) $\bar{J}$ here depends on d/r_0 while J_0 in Ref. (25) does not.

Function $g(v)$ is calculated explicitly (see Appendix F) to be

$$g(v) = (v/4)\left\{(36\pi)^{1/3} - \ln(1-v) + \ln\left[1 - v\exp(-36\pi)^{1/3}\right]\right\} \tag{4.26}$$

and shown numerically in Figure 1. For comparison, $g(v)$ of Ref. (25) [denoted by $g_L(v)$ in Figure 1] is also plotted. $g(v)$ is calculated in a continuum with a cut-off wave-vector while $g_L(v)$ is calculated for

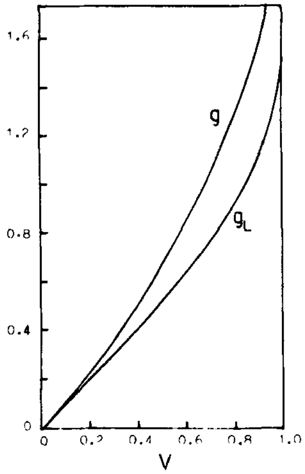


FIGURE 1 The function $g(v)$. $g_L(v)$ is g in Ref. 25.

a simple square lattice. When $v \to 1$, $g_L(v) = 1.516$ while $g(v) \to -\frac{1}{4}\ln(1-v)$ which diverges logarithmically.

The experimental supercooling temperature T^* is defined by $G_0^{-1}(T^*) = 0$. By Eq. (4.24), we have ($k_B = 1$)

$$T^* = 0.2\bar{J} \tag{4.27}$$

Note that $\bar{J}$ and hence T^* varies with t ($\equiv d/r_0$). Corresponding to different functional forms of $F(t)$ in Eq. (2.1), $T^* \sim t$ curves of different characteristics are obtained. The discussion is similar to the case of $T_{\mathrm{NI}} \sim t$ in (I). For example, when $F(t) = t^\lambda$, with $\lambda = 0$ ($= 1$) T^* will decrease (increase) slowly with d/r_0 increasing; for $\lambda = 2$, T^* increases rapidly with d/r_0, etc. [see also (I)].

If we assume approximately that $\langle S_i^2 \rangle \simeq \langle S_i^2 \rangle_0 = 1/5$, by Eq. (4.24), one may obtain $G_0^{-1}(T)$. The curve $G_0^{-1} \sim T/\bar{J}$ is plotted as curve a in Figure 2, which already bends down in the I phase, in

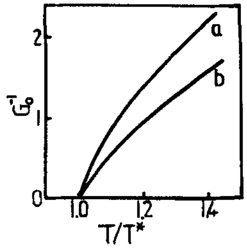


FIGURE 2 Function G_0^{-1} vs T/T^*. a is the present theory; b from Ref. 25.

accordance with experiments.[3-22] Curve b is from Ref. (25). Here, $\bar{J}$ corresponds to J_0 of Ref. (25) and is given by [see Eq. I (4.1)]:

$$\bar{J} = 2JR(t/2)F(t)t^{-1}\exp(-D^2/r_0^2) \tag{4.28}$$

where D is the width of the molecule. The two curves a and b agree with each other in shape and differ only numerically. Note that in the usual practical use (see Section V) only the relative values of G_0^{-1} matter. From Figure 2 it is easily seen that curve a, after multiplied by an approximate constant, may be made to almost coincide with curve b. The two curves are therefore basically the same from this point of view.

Using Eq. (4.28) it is possible to obtain from Figure 2 the variation of $G_0^{-1} \sim T$ curve in relation to the molecular length (and width) (see Section V). The fact that there exists a universal $G_0^{-1} \sim T$ curve when T is expressed in units of $\bar{J}$ results partly from the assumption of only *one* (coupling) energy constant J in the hamiltonian of Eq. (2.1) (as is also the case in the Maier–Saupe case[25]) and partly from the nature of the first-order expansion of Eq. (2.15) used here. One should not be surprised if this universality is violated in real materials as one knows that sometimes it is necessary to include higher-order terms (such as P_4) and hence other coupling constants into the hamiltonian. In fact, this universality is indeed broken when the full expansion (to second-order) form of Eq. (2.15) is used.[33,34]

It should be pointed out that in the high temperature regime ($v \to 0$), by Eq. (4.26), we have $g(v) \simeq 1.2v(1 + 0.2v)$. By Eqs. (4.24) and (4.27), $G_0^{-1} \sim (T - 0.8T^*)$, in agreement with mean-field results. When $T \to T^*$ ($v \to 1$), we have $g(v) \simeq -\frac{1}{4}\ln(1 - v)$, or

$$G_0^{-1} \sim -(T - T^*)\ln(T - T^*) \tag{4.29}$$

which differs from the mean-field results [but still satisfies $G_0^{-1}(T^*) = 0$, as expected]. In contrast, in the Maier–Saupe case,[25] one still has $G_0^{-1} \sim (T - T^*)$ (but with a different slope compared to the $v \to 0$ regime[27]) when $v \to 1$. Note that the logarithmic divergence of G_0 [and $g(v)$] at $v \to 1$ follows from the two-dimensional integral of $g(v)$ of Eq. (4.25b).

V. COMPARISON WITH EXPERIMENTS

In the presence of an external magnetic field B, the hamiltonian becomes

$$H = H_0 - h\sum_i S_i \tag{5.1}$$

where H_0 is that of Eq. (2.1) and

$$h = \tfrac{1}{2}\chi_a B^2 \tag{5.2}$$

Here, χ_a is the anisotropic part of magnetic susceptibility. The Cotton–Mouton coefficient in the high temperature phase is given by

$$C \equiv \delta n / B^2 = m_0 \langle S_i \rangle_H / h \tag{5.3}$$

where m_0 is a material constant,[29] δn the anisotropic part of the refractive index, $\langle \cdots \rangle_H$ the thermal average under the hamiltonian H (in the previous Sections, $\langle \cdots \rangle = \langle \cdots \rangle_{H_0}$). In weak field, one may expand $\langle S_i \rangle_H$ with respect to h.

$$\langle S_i \rangle_H = \left(\frac{\partial \langle S_i \rangle_H}{\partial h} \right)_{h=0,\, S=0} h + \frac{1}{2} \left(\frac{\partial^2 \langle S_i \rangle_H}{\partial h^2} \right)_{h=0,\, S=0} h^2$$

$$= \beta h G_0 + \frac{1}{2} \beta^2 h^2 N^{-1} \sum_{i,j,\mu} S_i S_j S_\mu \tag{5.4}$$

Therefore,

$$C = m(A_1 + \alpha A_2) \tag{5.5}$$

$$A_1 \equiv \beta \bar{J} G_0 \tag{5.6}$$

$$A_2 \equiv \frac{1}{2} \beta^2 \bar{J}^2 N^{-1} \sum_{i,j,\mu} \langle S_i S_j S_\mu \rangle \tag{5.7}$$

$$m = m_0 / \bar{J}, \qquad \alpha \equiv h / \bar{J} \tag{5.8}$$

The introduction of the energy unit $\bar{J}$ [$= \langle J_0 \rangle$, see Eq. (4.13)] here is a matter of convenience so that A_1, A_2 and α are dimensionless quantities. In fact, $\bar{J}$ may be replaced by any other quantity (e.g. J) with energy dimension.

In light scattering in the I phase, the intensity of scattered light is given by

$$\mathrm{I} = M G_0 \tag{5.9}$$

where M is a material constant.[29] By Eqs. (5.5) and (5.9) we see that both magnetic birefringence and light scattering may be used to determine G_0. The important point which is often overlooked is that in a homologous series, m (and M) may vary from molecule to molecule and they are usually not known a apriori. Therefore, in comparison with experiments of homologues, we prefer to use the quantity $C(T)/C(T_0)$ [instead of $C(T)$ itself] where T_0 is an arbitrary reference temperature.

When B is very weak, $C \simeq mA_1$ and

$$C(T)/C(T_0) = A_1(T)/A_1(T_0) = (T_0/T)G_0(T)/G_0(T_0) \quad (5.10)$$

For simplicity, we assume that we are dealing with rod-like molecules of zero width ($D = 0$) so that Eq. (4.28) becomes

$$\bar{J} = 2JR(t/2)F(t)t^{-1} \quad (5.11)$$

Assuming $F(t) = t^2$ and $T_0 = T_c$ ($= T_{\mathrm{NI}}$ or $\mathrm{T_{AI}}$) and using Eqs. (4.24), (5.10) and (5.11), $[A_1(T,t)/A_1(T_c,t)]^{-1}$ is calculated in the I phase ($\langle S_i^2\rangle = 1/5$) and shown in Figure 3. The two curves a and b correspond respectively to $t = 2.4$ and 2.58. Note that when the molecular length t increases the transition temperature T_c also increases but the curvature (i.e. the "degree" of the "bending down") of the curve decreases.

If $F(t)$ assumes different form, $T_c(t)$ will change accordingly [see (I)] but the trend of the curvature in Figure 3 remains unchanged. Also, Figure 3 is unaffected by the particular choice of the reference temperature T_0.

Since, by Eq. (5.6), G_0 differs from A_1 by only a temperature dependent factor $\beta\bar{J}$ the curve $G_0^{-1}(T)/G_0^{-1}(T_0) \sim T$ is basically the same as in Figure 3.

As the odd and the even series of a homologue may correspond to different $F(t)$ [see (I)] we shall discuss the two series separately.

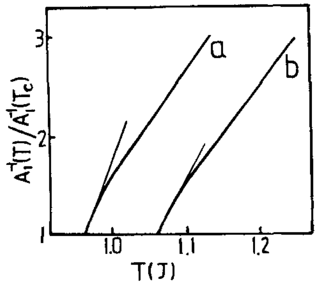
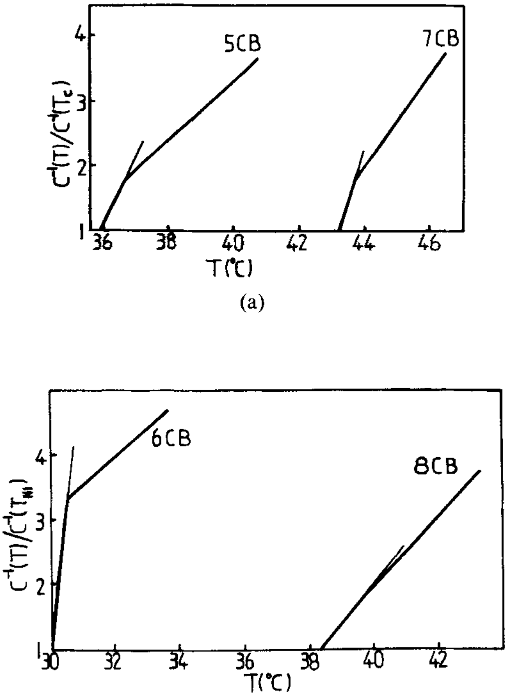


FIGURE 3 Theoretical curve $A_I^{-1}(T,t)/A_I(T_c,t)$. Curves a and b correspond to $t = 2.4$ and 2.58, respectively. The thin lines are drawn to guide the eye.



(a)

(b)

FIGURE 4 Experimental $C^{-1}(T)/C^{-1}(T_c)$ curves derived from Ref. 16 for the odd series (a) and the even series (b) of *n*CB.

Figure 4 is calculated from the experimental data of *n*CB (alkyl cyanobiphenyl) reported in Figure 4 of Ref. (16). *n*CB belongs to the case of $F(t) = t^2$ [see (I)]. The agreement between our theory of Figure 3 and the experimental data of Figure 4 is obvious.

Figure 5 is derived from the experimental data of *n*OCB (alkoxy cyanobiphenyl) depicted in Figure 5 of Ref. (16). Here, we assume $T_0 = 1.02T_c$. This is because the experimental value[16] of $C^{-1}(T_c)$ is too small to be used accurately. According to (I), the phase diagram of *n*OCB corresponds to the type of $F(t)$ of Eq. I (3.3) (i.e., not the $F(t) = t^2$ type). However, when $n > 3$, T_{NI} increases monotonically with n and the resulting theoretical curve of $[A_1(T,t)/A_1(T_0,t)]^{-1}$ will have the same trend as shown in Figure 3 which obviously agrees with Figures 5(a) and 5(b).

It should be emphasized that since the material constant m may depend on n the curvature of the experimental curve of $C^{-1} \sim T$,

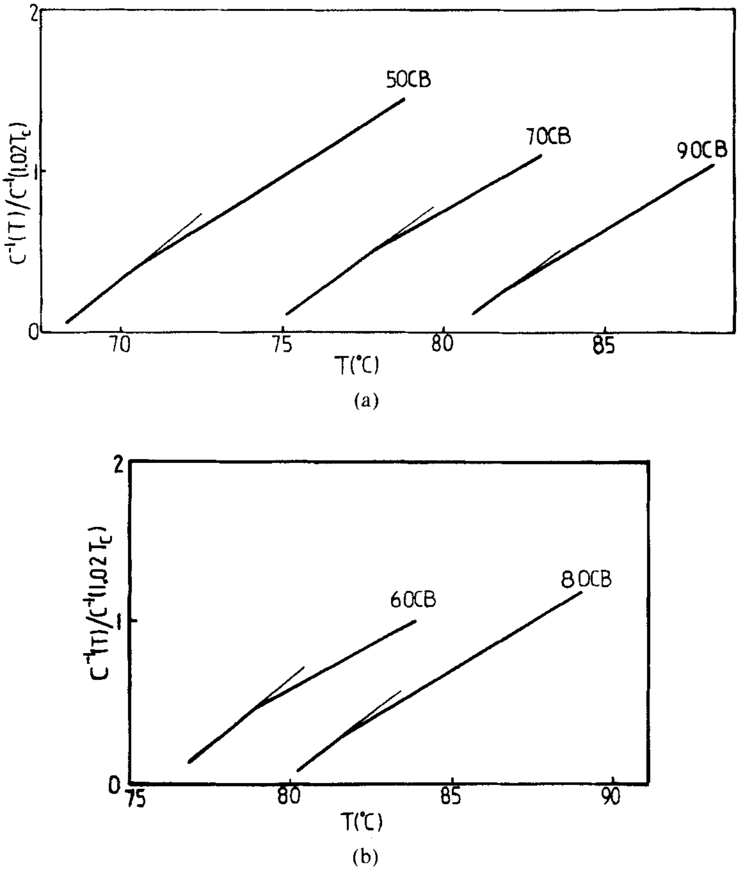


FIGURE 5 Experimental $C^{-1}(T)/C^{-1}(1.02T_c)$ curves derived from Ref. 16 for the odd series (a) and the even series (b) of *n*OCB.

unlike that of $C^{-1}(T)/C^{-1}(T_0) \sim T$, needs not decrease appreciably or at all [e.g. the $C^{-1}(T)$ of the odd series of *n*OCB, see Figure 5 of Ref. (16)]. This shows the importance of using the experimental $C^{-1}(T)/C^{-1}(T_0)$ instead of $C^{-1}(T)$ in comparing with theory. Consequently, in the work of Gohin et al.[18] the direct comparison between experimental results of T/I with theory must be exercised with caution (see Section VI).

The light scattering results of *n*CB by Coles and Strazielle[17] are more complicated. The curves plotted in Figure 2 of Ref. (17), in our notation, are T/I, or equivalently, $\bar{J}(MA_1)^{-1}$. There are two peculiar features about this result.[17] (i) $I^{-1}(T_c) = 0$, which is at odd with our theoretical prediction of $I^{-1}(T_c) > 0$ and $I^{-1}(T^*) = 0$ ($T^* < T_c$), and also in contradiction to the light scattering result of $I^{-1}(T_c) > 0$ on MBBA by Stinson and Litster.[3] All the Cotton–Mouton measurements [e.g. Ref. (16)] also give $C^{-1}(T_c) > 0$. (ii) In both 9CB and 11CB, the curve $I^{-1} \sim T$ bends *up* near T_{NI} and then increases monotonically and linearly with T. This implies an apparent exponent $\bar{\gamma} > 1$ [$\bar{\gamma}$ defined by[26] $G_0 \sim (T - T^*)^{-\bar{\gamma}}$] and the existence of an inflection point. Note that in other nCB, I^{-1} bends down as usual.

In comparison, "saturation" of "dip" are found by Pouligny et al.[19] in 9CB and 11CB. Our results in Figure 3 giving a smooth bending down agrees with those of Zhang et al.[20] but not those of Refs. (17) and (19).

Since our theoretical value of $(T_c - T^*)/T_c$ differs significantly from experiment (see below) we do not expect our theory, at this level, will completely agree with experiments quantitatively.

In contrary to the Maier–Saupe case,[25] our theory here can give G_0^{-1} for both I-N and I-A transitions which depends on t, as well as phase diagrams [see (I)] and t-dependent T^*. In Figure 6, phase diagrams from Figure 4(c) of (I) and T^* from Eqs. (4.27) and (4.28) ($D = 0$) are plotted. Here, $F(t) = t^2$ and $\delta = 0.65$ [δ is ignored in Eq. (2.1) but appears in Eq. I (2.4)]. Rigorously speaking, to be consistent with Eq. (2.1) we should depict a phase diagram in Figure 6 corresponding to $\delta = 0$, but the result is more or less the same.

The phase diagram in Figure 6 corresponds to nCB.[16,17] In agreement with Figure 3(b) of Ref. (20) our T^* increases with t for both the even and the odd series. Note that T^* in Table I of Ref. (17) [called T_1^* in Ref. (8)] is not our T^*; our T^* is called T_{CL}^* in Refs. (16) and (20) or T_2^* in Ref. (8). From Figure 6, $(T_c - T^*)$ increases with t ($T_c = T_{\mathrm{NI}}$ or T_{AI}) which agrees with the experimental results for the even series but at odd with that of the odd series [see Table II of Ref. (16)]. In our theory, $T_{\mathrm{NI}}/T^* \simeq 1.1$, irrespective of the form of $F(t)$. In all cases, our $(T_c - T^*)/T_c$ is much larger than the experimental value. In this regard, T^* has been calculated from the second-order

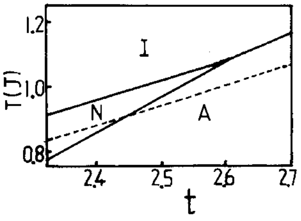


FIGURE 6 Theoretical phase diagram (solid lines) and the supercooling temperature T^* (broken line) as function of molecular length t.

expression of G_0 and T_{NI} from beyond-mean-field approximation (in the fashion of Vertogen and van der Meer[35]) but the above conclusion remains essentially unchanged (see Section 3.4 of Shu's Thesis[34]).

VI. DISCUSSION

1. Starting from the generalized McMillan hamiltonian of Eq. (2.1), we obtained the molecular correlation function $\bar{G}_k$ of Eq. (3.25) using first-order expansion of the generalized Suzuki formula of Eq. (2.15). Under RPA of Eq. (3.27), $\bar{G}_k$ is simplified to Eq. (3.28) which along with Eq. (3.25) is valid in the I, N or A phase. In the I phase, G_0 assumes the simple form of Eq. (4.23). Applying RPA again, Eq. (4.23) is further reduced to Eq. (4.24) which [together with Eqs. (4.25), (4.26) and (5.11)] is the formula used in our numerical calculations. By Eqs. (3.4), (4.5) and (4.6) and the definition of $B_{n\lambda}$ we see that the orientational and translational order parameters are coupled together in Eqs. (3.5) and (3.7). Therefore, our G_k does contain the nematic and smectic fluctuations on the same footing [in contrast to the theory of Ref. (18)].

Our theory, being based on a hamiltonian, is valid, in principle, for the whole temperature range. In contrast, the theory of Gohin et al.,[18] starting from a free energy of order parameters, is confined to the temperature region near T_c (see Senbetu and Woo[36] for a related discussion).

2. To make contact between experimental data and our theory, in addition to the methods discussed in Section V, one may proceed as follows. To be specific, let us assume that one has measured either the Cotton–Mouton coefficient $C(T,n)$ [of Eq. (5.3)] or the depolarized light scattering intensity $I(T,n)$ [of Eq. (5.9)]. Here, n denotes the particular member of a homoloque. In the former case, for each n, a series of $C(T,n) \sim B^2$ curves with T as parameter is usually plotted.[10,11] The value of each of these curves at $B^2 \to 0$ gives $\frac{1}{2} m_0 \chi_a G_0/T$, according to Eqs. (5.2)–(5.4). We then plot $2(m_0 \chi a)^{-1}(T/G_0) \sim T$ for each n. In the latter case, $T/I = M^{-1}(T/G_0) \sim T$ for each n is usually plotted.[17-19]

i. What to plot from experimental data—For notational sake, let us denote

$$Q(T,n) \equiv a(n)[T/G_0(T,n)] \tag{6.1}$$

where

$$\begin{aligned} a(n) &= 2(m_0\chi_a)^{-1} && \text{for magnetic bifrefringence} \\ &= M^{-1} && \text{for light scattering} \end{aligned} \tag{6.2}$$

Note that all m_0, χ_a and M are functions of n and may even depend on T, in principle. The T-dependence is usually assumed to be weak for the temperature range of a few decades covered in the experiments. We thus assume that they depend on n only. The curve $Q(T,n) \sim T$ is what should be and is plotted, for example, in Figure 4 and 5 of Ref. (16), Figure 2 of Ref. (17), and Figure 1a of Ref. (18).

ii. Determination of $a(n)$—In the I phase, with $\langle S_i^2\rangle \simeq \langle S_i^2\rangle_0 = 1/5$, Eqs. (4.24), (4.25a) and (4.27) may be rewritten as

$$1/G_0 = 5(1-v)g(v)/v \tag{6.3}$$

$$v = T^*/T \tag{6.4}$$

At high temperature $(T^*/T \to 0)$,

$$g(v) \simeq 1.2v(1+0.2v) \tag{6.5}$$

resulting in

$$\begin{aligned} 1/G_0 &\simeq 1/G_0' \equiv 6(T-0.8T^*)/T \\ Q(T,n) &\simeq Q'(T,n) \equiv 6a(n)(T-0.8T^*) \end{aligned} \tag{6.6}$$

Therefore, $a(n)$ may be determined from the slope of the high-temperature linear part of $Q(T,n) \sim T$.

The dots in Figure 3 of Gohin et al.[18] are therefore $6a(n)$. It should be emphasized that in here the even and the odd series should be considered separately (so that the physical quantity involved is a smooth function of n). From the above Figure, we note that for the n04(p-n-alkoxybenzilidene-p'-n-butylaniline) series $a(n)$ indeed varies with n [implying $a_N = a_N(n)$ where a_N is defined in Eq. (14) of Ref. (18)].

It is appropriate to point out that according to our Figure 1, Eq. (6.5) [and hence Eq. (6.6)] is satisfied only when $0 \leqslant v \leqslant 0.2$ or $\infty > \epsilon \geqslant 4$ [$\epsilon(T) \equiv (T-T^*)/T^*$]. Experimentally, $T^* \simeq 300$ K and $Q(T,n)$ is linear for $T > T^* + 10°\mathrm{C}$ (at most), or $\epsilon > 3.3 \times 10^{-2}$. This discrepancy of the theory is related closedly to the fact that our theory gives $\epsilon(T_c) \simeq 10^{-1}$ which also differs from the experimental value of $\epsilon(T_c) \simeq 10^{-3}$ by two orders of magnitude [see Ref. (27) for further discussions].

iii. Determination of T^*—By extrapolating the low-temperature part of the $Q(T,n) \sim T$ curve near T_c to intercept the T axis (which can be done only approximately since due to the first-order nature of the N-I transition, no experimental points exists below T_c) one obtains $T^*(n)$. If the high-temperature linear part of $Q(T,n)$ is extrapolated instead, one obtains an intercept equal to $0.8T^*$. T^*'s determined by these two methods are not consistent with each other numerically by reason given at the end of (ii) above. The first method should be used.

iv. Determination of $\bar{J}(t,u)$ or $JF(t)$—From $T^*(n)$ and Eq. (4.27) one has $\bar{J}(n)$ and hence $JF(n)$ if the molecules are assumed to be of zero width and Eq. (5.11) is used. The (t,u) values for each n may be estimated from the conformation of the molecules; or, lacking this information, some reasonable linear functions of $t(n)$ and $u(n)$ [$u \equiv D/r_0$, $t \equiv d/r_0$] may be assumed to obtain a trial function of $\bar{J}(t,u)$ from $\bar{J}(n)$. By Eqs. I (4.2) and (4.28) [see (I) for definition of v_0],

$$v_0 = \pi^{-1/2} t \bar{J}(t,u) \tag{6.7}$$

We may then use the procedure outlined in (I) to obtain the I-N-A phase diagram of the even and the odd series of the homologue and compare it with experiments.

v. Comparing experiment with our theory—For this purpose, since our theory calculates only G_0 (but not Q or a), one method is to obtain $[Q(T,n) - Q'(T,n)]/[Ta(n)] = 1/G_0(T,n) - 1/G_0'(T,n)$

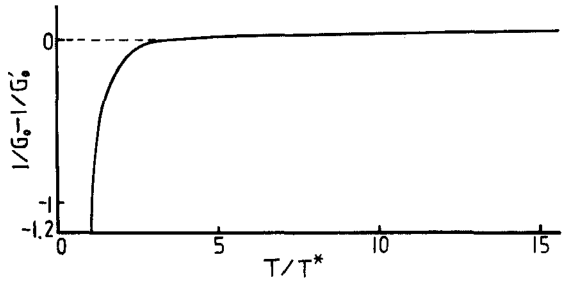


FIGURE 7 Theoretical $1/G_0 - 1/G_0'$ vs T/T^* curve.

$\equiv P(T,n)$ where Q' represents the high-temperature linear part of Q from (i) and $a(n)$ from (ii). The curve $P(T,n) \sim T/T^*(n)$ is then plotted and compared with our theoretical universal curve as shown in Figure 7. Since we know only that $T_c/T^* > 1$ and do not have an analytic form of T_c (in contrary to the Maier–Saupe case[25]) we have refrained from drawing T_c in Figure 7. Note that T_c/T^* is not a constant and may vary with n. As is discussed in Section IV, the universality of $G_0(T) = G_0(T/T^*)$ [which is as good as the order parameter $\langle P_2 \rangle$ being a function of T/T_{NI} of T/T^* in the Maier–Saupe model[1]] may break down in reality, the next more qualitative method should also be attempted.

The second method is to plot $P(T,n) \sim T$ and compare it with our Figure 8. It is easy to see that Figure 8 follows directly from Figure 7, in which the two curves correspond to different n. The one with $T^* = T_2^*$ changes more slowly compared to the one with $T^* = T_1^*$ $(< T_2^*)$ [see Figure 2 of Ref. (29) for a related discussion].

In the above analysis, the even and the odd series may be plotted on the same diagram. Note that the case that $T_c - T^*$ is large such that a large part of the bending down in Figure 8 is hidden from sight cannot be precluded.

Only qualitative agreement between experimental data and our Figures 7 and 8 are expected. A systematic analysis of the data[18] of n04 and others[16,17,19,20] in this fashion remains to be done and is most desired.

3. The essence of our result of Eq. (4.24) is easy to understand. The different molecules correspond to different $\bar{J}$ (or T^*) and sample different temperature regions in the curve of Figure 7. The derivations in Sections III and IV indicate how this result comes about and point to the way of its improvement. For example, the transition from Eq. (4.23) to Eq. (4.24) may be too rough an approximation.

In our theory, the orientational part is treated beyond MFA but the

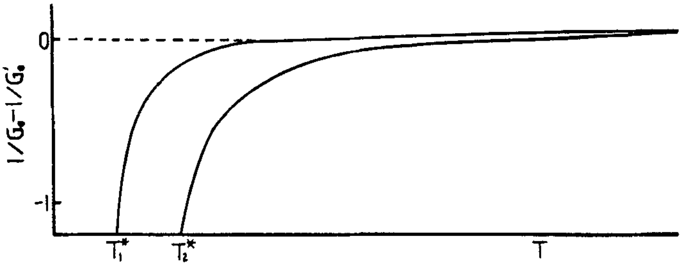


FIGURE 8 Sketch of theoretical $1/G_0 - 1/G_0'$ vs T curve.

translational part remains in MFA. The opposite is true in the OAPC (orientationally-averaged-pair-correlations) treatment of Woo et al.[37] (which consequently does not have bending down in G_0^{-1}).[38] A synthesis of the two approaches should be attempted.

Note that fluctuation of the smectic layer normal (the z axis) has not been taken into account here.

4. A second-order calculation[33,34] (using the full expansion of Eq. (2.15) to β^2 term) of G_0 shows the same behavior as in Figure 3.

5. In cyano compounds with intrinsic polarization (such as nCB and nOCB) pairing of molecules may be important. In this case, a $P_1(\cos\theta_{ij})$ term is suggested to be included in the hamiltonian.[39] Madhusudana and Chandrasekhar have included such a term in the Maier–Saupe hamiltonian and calculated $S = S(h)$ in the Bethe approximation; an apparent exponent $\bar{\gamma} < 1$ was obtained but no $G^{-1}(T)$ curve described.[39] Later, the same Bethe approximation was used in a treatment of the Maier–Saupe hamiltonian (without the P_1 term) by Chandrasekhar et al. [see §2.5.1 of Ref. (40)]. We have calculated the curve $(S/h)^{-1} \sim T$ from Eq. (2.5.23) of Ref. (40) and found a small bending *up* (i.e. $\bar{\gamma} > 1$) [see §3.5 of Ref. (34)]. This result is in opposite to that of Ref. (25) using a different approximation for the same hamiltonian, and certainly at odd with the experimental result of[3,10,11] $\bar{\gamma} < 1$ in MBBA (in which P_1 is not important). We therefore conclude that the Bethe approximation is unreliable as orientational correlation function is concerned (irrespective of the absence or presence of P_1 in the hamiltonian).

In the calculation of Pouligny and Lalanne,[8] J_{ij} is allowed to be a function of the translational degrees of freedom r. The $\langle \cdots \rangle$ in Ref. (8) is thus in fact a thermal average over the angular variable Ω only and not the real thermal average (over both r and Ω). This is the consideration of putting the molecules in a fixed lattice in Ref. (25) and shows the need to go through the tedious treatment in this paper when both r and Ω are included in the hamiltonian.

6. A calculation[41] of the orientational relaxation time τ in the Glauber model[42] consistent with the approximation used here gives the mean-field result $\nu(T - T^*)^{-1}$ (ν is a viscosity constant) [see also Ref. (8)].

7. In Figure 7 (and correspondingly in Figure 8), for $\infty > T/T^* \gtrsim 4.3$, $P(T, n)$ is slightly positive (almost unnoticeable in the scale of the Figure) and tends to zero as $T \to \infty$. This is due to the fact that $G_0^{-1} = G_0'^{-1} + 0.12(T^*/T)^2 + 0[(T^*/T)^3]$ and the chosen definition of G_0' (so that T/G_0' represents the approximate straight-line part of T/G_0 at large T) in Eq. (6.6). We note that in Refs. (18) and (19) there are indeed some experimental points that lie above the straight-

line part of T/G_0 at large T. But experimental inaccuracy precludes more detailed comparison.

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APPENDIX A. PROOF OF EQ. (2.5)

Let

$$Z \equiv \mathrm{Tr}_{(r,\Omega)} \exp(-\beta H) \tag{A.1}$$

where

$$\mathrm{Tr}_{(r,\Omega)} \equiv \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \int d\Omega_1 \ldots d\Omega_N \tag{A.2}$$

Similarly, define

$$\mathrm{Tr}_{(x,y)} \equiv \int dx_1 \ldots dx_N \int dy_1 \ldots dy_N \tag{A.3}$$

$$\mathrm{Tr}_{(z,\Omega)} \equiv \int dz_1 \ldots dz_n \int d\Omega_1 \ldots d\Omega_N \tag{A.4}$$

We then have

$$\begin{aligned}
&\langle f(x,y)\, g(\mathbf{r},\mathbf{\Omega})\rangle \\
&= Z^{-1}\mathrm{Tr}_{(r,\Omega)} f(x,y)\, g(\mathbf{r},\mathbf{\Omega}) \exp(-\beta H) \\
&= Z^{-1}\mathrm{Tr}_{(x,y)}\{ f(x,y)[\mathrm{Tr}_{(z,\Omega)}\, g(\mathbf{r},\mathbf{\Omega}) \exp(-\beta H)]\} \\
&= Z^{-1}\mathrm{Tr}_{(r,\Omega)}\left\{ f(x,y)\mathrm{Tr}_{(z,\Omega)} \right. \\
&\qquad\qquad \left. \times \left[\frac{\mathrm{Tr}_{(z,\Omega)}\, g(\mathbf{r},\mathbf{\Omega})\exp(-\beta H)}{\mathrm{Tr}_{(z,\Omega)} \exp(-\beta H)} \exp(-\beta H) \right] \right\} \\
&= Z^{-1}\mathrm{Tr}_{(r,\Omega)}\{ f(x,y) \langle g(\mathbf{r},\mathbf{\Omega})\rangle_1 \exp(-\beta H)\} \\
&= \langle f(x,y) \langle g(\mathbf{r},\mathbf{\Omega})\rangle_1 \rangle
\end{aligned}$$

which is Eq. (2.5).

APPENDIX B. PROOF OF EQ. (2.9)

$$
\begin{aligned}
\langle\{\dot{j}\}\{j\}\rangle_1 &= Z^{-1}\mathrm{Tr}_{(z,\Omega)}\Big[\{\dot{j}\}\{j\}\exp(-\beta H' + \beta E_j)\Big] \\
&= Z^{-1}\mathrm{Tr}_{(z,\Omega),(i\neq j)} \\
&\quad \times \Bigg\{\exp(-\beta H')\{\dot{j}\}\Bigg[\mathrm{Tr}_{(j)}\exp(-\beta E_j) \\
&\qquad\qquad \times \frac{\mathrm{Tr}_{(j)}\{j\}\exp(-\beta E_j)}{\mathrm{Tr}_{(j)}\exp(-\beta E_j)}\Bigg]\Bigg\} \\
&= Z^{-1}\mathrm{Tr}_{(z,\Omega)}\Big\{\exp(-\beta H)\{\dot{j}\}\langle\{j\}\rangle_{E_j}\Big\} \\
&= \langle\{\dot{j}\}\langle\{j\}\rangle_{E_j}\rangle_1
\end{aligned}
$$

which is Eq. (2.9), and $H' \equiv H + E_j$, $\mathrm{Tr}_{(j)} \equiv \mathrm{Tr}_{(z_j,\boldsymbol{\Omega}_j)} \equiv \int dz_j\, d\boldsymbol{\Omega}_j$.

APPENDIX C. DERIVATION OF EQ. (3.10)

$$
\begin{aligned}
N^{-1}\sum_{\substack{i,\lambda,\lambda' \\ (i\neq\lambda)}} J_{\lambda'\lambda}F_n(k_z;i,\lambda')e^{ik_x x_{i\lambda}+ik_y y_{i\lambda}} \\
= A - N^{-1}\sum_{i,\lambda'} J_{\lambda' i}F_n(k_z;i,\lambda') \qquad \text{(C.1)}
\end{aligned}
$$

where

$$
\begin{aligned}
A &\equiv N^{-1}\sum_{i,\lambda,\lambda'} J_{\lambda'\lambda}F_n(k_z;i,\lambda')e^{ik_x x_{i\lambda}+ik_y y_{i\lambda}} \\
&= N^{-1}\sum_{i,\lambda'}\left(\sum_{\lambda} J_{\lambda'\lambda}e^{ik_x x_{\lambda'\lambda}+ik_y y_{\lambda'\lambda}}\right)F_n(k_z;i,\lambda)e^{ik_x x_{i\lambda'}+ik_y y_{i\lambda'}} \\
&= J_{k_\perp}N^{-1}\sum_{i,\lambda'} F_n(k_z;i,\lambda)e^{ik_x x_{i\lambda'}+ik_y y_{i\lambda'}} \\
&= J_{k_\perp}F_n(\mathbf{k}) \qquad \text{(C.2)}
\end{aligned}
$$

In the last two lines of Eq. (C.2), definitions given in Eqs. (3.11) and (3.9) have been used. Note that

$$\begin{aligned}
&\sum_{p_\perp} J_{p_\perp} F_n(k_z, p_\perp) \\
&\quad = N^{-1} \sum_{p_\perp} \left(\sum_{\lambda} J_{\lambda'\lambda} e^{ip_x x_{\lambda'\lambda} + ip_y y_{\lambda'\lambda}} \right) \left(\sum_{i,\lambda'} F_n(k_z; i, \lambda) e^{ip_x x_{i\lambda'} + ip_y y_{i\lambda'}} \right) \\
&\quad = N^{-1} \sum_{i,\lambda,\lambda'} J_{\lambda'\lambda} F_n(k_z; i, \lambda') \left(\sum_{p_\perp} e^{ip_x x_{i\lambda} + ip_y y_{i\lambda}} \right) \\
&\quad = N^{-1/3} \sum_{i,\lambda'} J_{\lambda' i} F_n(k_z; i, \lambda') \qquad \text{(C.3)}
\end{aligned}$$

Substituting Eq. (C.3) into Eq. (C.2) and defining $N' \equiv N^{2/3}$ one obtains Eq. (3.10)

APPENDIX D. DERIVATIONS OF EQS. (3.16) AND (3.17)

Solving Eqs. (3.12) and (3.13) one has

$$\begin{aligned}
F_0(\mathbf{k}) = \left[D_1(k_\perp) \right]^{-1} \big[&(1 - \beta\Delta_{11} J_{k_\perp}) X_0 + \beta\Delta_{01} J_{k_\perp} X_1 + (1 - \beta\Delta_{11} J_{k_\perp}) \\
&\times C_0(\mathbf{k}) + \beta\Delta_{01} J_{k_\perp} C_1(\mathbf{k}) \big] \qquad \text{(D.1)}
\end{aligned}$$

$$\begin{aligned}
F_1(\mathbf{k}) = \left[D_1(k_\perp) \right]^{-1} \big[&\beta\Delta_{10} J_{k_\perp} X_0 + (1 - \beta\Delta_{00} J_{k_\perp}) X_1 + \beta\Delta_{10} J_{k_\perp} C_0(\mathbf{k}) \\
&+ (1 - \beta\Delta_{00} J_{k_\perp}) C_1(\mathbf{k}) \big] \qquad \text{(D.2)}
\end{aligned}$$

Putting Eqs. (D.1) and (D.2) into Eqs. (3.14) and (3.15), and noting that X_0 and X_1 are independent of $k_\perp$ one has

$$(1 + \beta\Delta_{00} q_1 - \beta^2 \Delta q_2) X_0 + \beta\Delta_{01} q_1 X_1 = \overline{C}_0(k_z) \qquad \text{(D.3)}$$

$$\beta\Delta_{10} q_1 X_0 + (1 + \beta\Delta_{11} q_1 - \beta^2 \Delta q_2) X_1 = \overline{C}_1(k_z) \qquad \text{(D.4)}$$

where $\overline{C}_0$ and $\overline{C}_1$ are defined in Eq. (3.22). By Eqs. (D.3) and (D.4) and denoting the determinant by $D_2(k_z)$ [defined in Eq. (3.24)] one obtains

$$X_0 = \left[D_2(k_z)\right]^{-1}\left[\bar{C}_0(k_z) + \beta\left(\bar{C}_0(k_z)\Delta_{11} - \bar{C}_1(k_z)\Delta_{01}\right)q_1 - \beta^2\bar{C}_0(k_z)\Delta q_2\right] \tag{D.5}$$

$$X_1 = \left[D_2(k_z)\right]^{-1}\left[\bar{C}_1(k_z) + \beta\left(\bar{C}_1(k_z)\Delta_{00} - \bar{C}_0(k_z)\Delta_{10}\right)q_1 - \beta^2\bar{C}_1(k_z)\Delta q_2\right] \tag{D.6}$$

Putting Eqs. (D.5) and (D.6) into Eqs. (D.1) and (D.2) we obtain Eqs. (3.16) and (3.17).

APPENDIX E. DISCUSSION OF EQ. (4.2)

By Eq. (4.1), define $g_2(z_j) = \sin(2\pi z_i/d)$. Assume that in $\{g_n\}$ we keep only the g_0, g_1 and g_2 terms [g_0 and g_1 are defined by Eq. (4.2)]. By the definition of Δ_2 in Eq. (3.6) we know that under space inversion, because $k_z \to -k_z$, $z_j \to -z_j$, one has $\Delta_2 \to -\Delta_2$, resulting in $\Delta_2 = 0$.

By the definition of f_n in Eq. (2.2), we have $f_2(z_i) \sim \sin(2\pi z_i/d)$. Similar to the discussion of space inversion above one can prove that $\Delta_{n2} = 0$, $n = 0, 1$. Therefore, a set of simultaneous equations for $\langle A_i B_{0\lambda}\rangle_1$ and $\langle A_i B_{1\lambda}\rangle_1$ can be obtained from Eq. (3.7), which does not involve $\langle A_i B_{2\lambda}\rangle_1$. Also, in Eq. (3.5), since $\Delta_2 = 0$, one does not have to know $\langle A_i B_{2\lambda}\rangle_1$. In short, $n = 2$ is ineffective in Eqs. (3.5) and (3.7).

APPENDIX F. DERIVATION OF EQ. (4.26)

To calculate the explicit form of $g(v)$ of Eq. (4.25b) we first calculate $\langle J_{p_\perp}\rangle / \langle J_0\rangle$. According to Appendix B of (I) and similar to Eq. I (B4), we have

$$\langle \exp(-\rho_{ij}^2/r_0^2 + ip_x x_{ij} + ip_y y_{ij})\rangle$$

$$= \frac{1}{L_x L_y}\int_{-L_x/2}^{L_x/2}\int_{-L_y/2}^{L_y/2} dx_{ij}\, dy_{ij}\, h(\rho_{ij})\exp\left(-\rho_{ij}^2/r_0^2 + ip_x x_{ij} + ip_y y_{ij}\right)$$

where L_x, L_y are the dimensions of the sample in the x and y

directions, h the pair correlation function in two-dimension [see Appendix B of (I)]. If we assume $h(\rho_{ij}) \simeq 1$ approximately, then

$$\langle \exp(-\rho_{ij}^2/r_0^2 + ip_x x_{ij} + ip_y y_{ij}) \rangle = \frac{\pi r_0^2}{L_x L_y} \exp(-r_0^2 p_\perp^2/4) \tag{F.2}$$

By Eqs. (2.4), (3.11) and (F.2),

$$\langle J_{p_\perp} \rangle = \langle J_0 \rangle \exp(-r_0^2 p_\perp^2/4) \tag{F.3}$$

$$\langle J_0 \rangle = \tfrac{1}{2} J F(t) R(t/2) t^{-1} N' \pi r_0^2 / L_x L_y \tag{F.4}$$

The appearance of N' here and elsewhere is explained at the end of Appendix A of (I). We now calculate $g(v)$. Putting Eq. (F.3) into Eq. (4.25b) and replacing the summation in $P_\perp$ space by integral, we have

$$g(v) = \frac{L_x L_y}{N'(2\pi)^2} \int_0^{p_m} dp_\perp \, p_\perp 2\pi \left[v^{-1} - \exp(-r_0^2 p_\perp^2/4) \right]^{-1} \tag{F.5}$$

where p_m is the cut-off in the p space. It follows that

$$g(v) = \frac{L_x L_y}{N'} \frac{v}{\pi r_0^2} \left\{ r_0^2 p_m^2/4 + \ln\left[1 - v \exp(-r_0^2 p_m^2/4) \right] - \ln(1 - v) \right\} \tag{F.6}$$

Noting that $V^{2/3} = L_x L_y$ and $N' d\pi (r_0/2)^2 = L_x L_y L_z$ approximately [see Eq. I (B7)], we have

$$p_m = (6\pi^2 N/V)^{1/3} \tag{F.7}$$

Combining Eqs. (F.6) and (F.7) we obtain Eq. (4.26).

References

1. P. G. deGennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
2. P. G. deGennes, *Mol. Cryst. Liq. Cryst.* **12**, 193 (1971).
3. Y. W. Stinson and J. D. Litster, *Phys. Rev. Lett.* **25**, 503 (1970).
4. M. Schadt and W. Helfrich, *Mol. Cryst. Liq. Cryst.* **17**, 335 (1972).
5. J. C. Filippini and Y. Poggi, *J. Physique Lett.* **37**, L17 (1976); B. Malraison, Y. Poggi, and J. C. Filippini, *Solid State Commun.* **31**, 843 (1979).
6. J. Prost and J. R. Lalanne, *Phys. Rev.* **A8**, 2090 (1973); J. P. Marcerou and J. Prost, *Phys. Lett.* **66A**, 218 (1978).

7. B. Pouligny, E. Sein and J. R. Lalanne, *Phys. Rev.* **A21**, 1528 (1980).
8. B. Pouligny and J. R. Lalanne, *Phys. Rev.* **A26**, 3679 (1982).
9. P. V. Kolinski and B. R. Jennings, *Mol. Phys.* **40**, 979 (1980).
10. P. H. Keyes and J. R. Shane, *Phys. Rev. Lett.* **42**, 2073 (1979).
11. C. Rosenblatt, *Phys. Rev.* **A27**, 1234 (1983).
12. B. R. Ratna and R. Shashidhar, 8th Int. Liq. Cryst. Conf., Kyoto, June 30–July 4, 1980.
13. Zhang Shulin et al., *Mol. Cryst. Liq. Cryst.* **70**, 183 (1981).
14. H. J. Coles, *Mol. Cryst. Liq. Cryst. Lett.* **49**, 67 (1978).
15. D. A. Dummur and A. E. Tomes, *Mol. Cryst. Liq. Cryst.* **76**, 231 (1981).
16. K. Muta, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **18**, 2073 (1979).
17. H. J. Coles and C. Strazielle, *Mol. Cryst. Liq. Cryst.* **55**, 237 (1979).
18. A. Gohin, C. Destrade, H. Gasparoux and J. Prost, *J. Physique* **44**, 427 (1983).
19. B. Pouligny, J. P. Marcerou, J. R. Lalanne and H. J. Coles, 9th Int. Liq. Cryst. Conf., Bangalore, Dec. 6–10, 1982.
20. Zhang Shulin et al., *Mol. Cryst. Liq. Cryst.* **91**, 295 (1983).
21. K. Muta, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **20**, 503 (1981).
22. C. Strazielle and H. J. Coles, *J. Physique* **40**, 895 (1979).
23. C.-p. Fan and M. J. Stephen, *Phys. Rev. Lett.* **25**, 500 (1970).
24. Lin Lei, *Kexue Tongbao* **23**, 715 (1978).
25. Lin Lei, *Phys. Rev. Lett.* **43**, 1604 (1979).
26. Lin Lei, *J. Physique* **43**, 251 (1982).
27. Lin Lei and Shu Changqing, to be published.
28. P. H. Keyes, *Phys. Rev.* **A23**, 2075 (1981).
29. Lin Lei and Huang Yun, *Phys. Lett.* **89A**, 287 (1982).
30. Shu Changqing and Lin Lei, the preceding paper [(I) in this series].
31. M. L. McMillan, *Phys. Rev.* **A4**, 1238 (1971).
32. Zhang Zhaoqing, Feng Kean and Lin Lei, *Acta Physica Sinica* **29**, 807 (1980) [*Chinese Phys. (U.S.A.)*] **1**, 110 (1981).
33. Shu Changquing and Lin Lei, *Acta Physica Sinica* **31**, 915 (1982).
34. Shu Changqing, M. Sc. Thesis, Institute of Physics, Chinese Academy of Sciences, Beijing (1981).
35. G. Vertogen and B. W. van der Meer, *Phys. Rev.* **A19**, 370 (1979).
36. L. Senbetu and C.-W. Woo, *Mol. Cryst. Liq. Cryst.* **84**, 101 (1982).
37. L. Feijoo, V. T. Rajan and C.-W. Woo, *Phys. Rev.* **A19**, 1263 (1979); J. L. Shen, L. Lin, L. Yu and C.-W. Woo, *Mol. Cryst. Liq. Cryst.* **70**, 301 (1981).
38. J. L. Shen and C.-W Woo, *Phys. Rev.* **A24**, 493 (1981).
39. N. V. Mahusudana and S. Chandrasekhar, *Pramana, Suppl.* **1**, 57 (1975).
40. S. Chandrasekhar, *Liquid Crystals* (Cambridge U.P., London, 1977).
41. Lin Lei, 8th Int. Liq. Cryst. Conf., Kyoto, June 30–July 4, 1980.
42. R. J. Glauber, *J. Math. Phys.* **4**, 294 (1963).