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Systematic Solution of the Mean Field Equation for Liquid Crystals

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Systematic Solution of the Mean Field Equation for Liquid Crystals[†]

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Starting with a pairwise, spatially and orientationally dependent intermolecular potential of the Kobayashi-McMillan form, we carry out a systematic solution of the mean field equation for liquid crystals. The mean field equation, presented as first of a hierarchy of BBGKY equations, is first reduced to a set of coupled integrodifferential equations by means of expanding the distribution function $f(\mathbf{r}, \theta)$ and $\ln f(\mathbf{r}, \theta)$ in Legendre polynomials and the reciprocal lattice space. In the first level of approximation, the expansion retains only the lowest-order coefficients, permitting a complete decoupling of the equations. In the second level of approximation, the leading coefficient which couples spatial order to orientational order is included. In the third level of approximation two more higher order coefficients are included. At each level, the free energy functional is evaluated to determine the equilibrium phase at given temperatures and chainlengths of a homologous series. It is shown that the expansion converges very rapidly, the second level of approximation being entirely sufficient. This lends support to our earlier variational calculation which contained only three variational parameters.

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I INTRODUCTION

An obvious generalization of the Maier–Saupe model[1] of liquid crystals calls for the introduction of spatially dependent coefficients in the two-particle potential. Thus Kobayashi[2] wrote

$$v(1, 2) = v_0(r_{12}) + v_2(r_{12})P_2(\hat{\Omega}_1 \cdot \hat{\Omega}_2) \tag{1}$$

for the interaction between a pair of molecules at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, with orientations $\hat{\Omega}_1$ and $\hat{\Omega}_2$. Actually the most general form for the interaction potential is a function of five variables.[3] Considerations of translational and rotational symmetry lead to the formation of the five scalars r_{12}, $\hat{\Omega}_1 \cdot \hat{r}_{12}$, $\hat{\Omega}_2 \cdot \hat{r}_{12}$, $\hat{\Omega}_1 \cdot \hat{\Omega}_2$, and $\hat{\Omega}_1 \times \hat{\Omega}_2 \cdot \hat{r}_{12}$, of which only two have been selected[4] for use in Eq. (1). So the potential given is a long way from being general. Nevertheless, it has been shown to account well for properties such as the phase diagram for a homologous series and order parameters,[5–7] and more detailed phase transition information like the volume change, latent heat, and maximum supercooling temperature.[8,9] While the latter quantities require a more sophisticated analysis involving pair correlation functions,[7] the former can be obtained with the most primitive mean field technique: either that of McMillan,[5] or our own.[6,7] Both calculational methods are time-consuming, and neither has been shown to be fool-proof. For this reason we offer here a systematic and accurate procedure, along with numerical results, which turned out to give complete support to our earlier variational work.[6] Couplings between various spatial order parameters turned out to be *un*important. This has some bearing on the first or second order nature of the nematic–smectic A transition as discussed by Meyer and Lubensky in a recent analysis.[10]

The mean field calculational techniques of McMillan[5] and our own[6,7] have been amply reviewed in recent articles,[10–12] and will not be reviewed here.

II MEAN FIELD EQUATION

The statistical mechanics begins with the partition function

$$\Xi = \int \exp\left[-\frac{1}{kT}\sum_{i<j} v(i,j)\right] d\mathbf{r}_1\, d\hat{\Omega}_1 \cdots d\mathbf{r}_N\, d\hat{\Omega}_N. \tag{2}$$

We define the v-particle distribution function as follows:

$$P^{(v)}(1, \ldots, v) = \frac{(4\pi)^v N!}{(N-v)!\,\Xi} \int \exp\left[-\frac{1}{kT}\sum_{i<j} v(i,j)\right] d\mathbf{r}_{v+1}\, d\hat{\Omega}_{v+1} \cdots d\mathbf{r}_N\, d\hat{\Omega}_N. \tag{3}$$

In particular, we have

$$P^{(1)}(1) \equiv P^{(1)}(\mathbf{r}_1, \hat{\Omega}_1) \equiv nf(\mathbf{r}_1, \hat{\Omega}_1)$$
$$= \frac{4\pi N}{\Xi} \int \exp\left[-\frac{1}{kT} \sum_{i<j} v(i,j) \right] \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\hat{\Omega}_2 \cdots \mathrm{d}\mathbf{r}_N \, \mathrm{d}\hat{\Omega}_N, \tag{4}$$

and

$$P^{(2)}(1, 2) = P^{(2)}(\mathbf{r}_1, \hat{\Omega}_1, \mathbf{r}_2, \hat{\Omega}_2) \equiv n^2 f(\mathbf{r}_1, \hat{\Omega}_1) f(\mathbf{r}_2, \hat{\Omega}_2) g(1, 2)$$
$$= \frac{(4\pi)^2 N(N-1)}{\Xi} \int \exp\left[-\frac{1}{kT} \sum_{i<j} v(i,j) \right] \mathrm{d}\mathbf{r}_3 \, \mathrm{d}\hat{\Omega}_3 \cdots \mathrm{d}\mathbf{r}_N \, \mathrm{d}\hat{\Omega}_N, \tag{5}$$

n being the mean number density of the system: $N/\mathscr{V}$.

Equation (4) can be immediately differentiated, either with respect to the spatial coordinates to obtain the integrodifferential equation:

$$-kT\nabla_1 \ln f(\mathbf{r}_1, \hat{\Omega}_1) = \frac{n}{4\pi} \int f(\mathbf{r}_2, \hat{\Omega}_2) g(1, 2) \nabla_1 v(1, 2) \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\hat{\Omega}_2, \tag{6}$$

or with respect to the angular coordinates to obtain:

$$-kT\nabla_{\Omega_1} \ln f(\mathbf{r}_1, \hat{\Omega}_1) = \frac{n}{4\pi} \int f(\mathbf{r}_2, \hat{\Omega}_2) g(1, 2) \nabla_{\Omega_1} v(1, 2) \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\hat{\Omega}_2. \tag{7}$$

In either case, the two-particle distribution function appears on the right as a result of the straightforward mathematical operation.

The solution of these equations requires the knowledge of $g(1, 2)$, which in turn creates horrendous tasks.[8,13] Fortunately, in the primitive mean field calculation, short range correlations are completely ignored. This goes for spatial correlations as well.[14] In other words, $g(1, 2)$ is set equal to 1. Under these conditions, Equations (6) and (7) can be integrated directly. Writing the integration constant as $kT\lambda$, we find

$$-kT \ln \lambda f(\mathbf{r}_1, \hat{\Omega}_1) = \frac{n}{4\pi} \int f(\mathbf{r}_2, \hat{\Omega}_2) v(1, 2) \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\hat{\Omega}_2.$$

This is the equation that we intend to solve accurately and systematically in the present paper. It is of course just the self-consistency equation given by McMillan:[5]

$$f(\mathbf{r}_1, \hat{\Omega}_1) = \frac{1}{\lambda} \exp\left[-\frac{1}{kT} V(\mathbf{r}_1, \hat{\Omega}_1) \right], \tag{9}$$

with

$$V(\mathbf{r}_1, \hat{\Omega}_1) = \frac{n}{4\pi} \int f(\mathbf{r}_2, \hat{\Omega}_2) v(1, 2) \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\hat{\Omega}_2. \tag{10}$$

The appearance of the factor $1/4\pi$ in the definition of the mean field V results from our particular choice of normalization. From Eq. (4),

$$\int P^{(1)}(\mathbf{r}_1, \hat{\Omega}_1)\mathrm{d}\mathbf{r}_1\, \mathrm{d}\hat{\Omega}_1 = 4\pi N, \tag{11}$$

or

$$\int f(\mathbf{r}_1, \hat{\Omega}_1)\mathrm{d}\mathbf{r}_1\, \mathrm{d}\hat{\Omega}_1 = 4\pi\mathscr{V}. \tag{12}$$

The particular derivation offered here has the advantage of framing the equation as first of a series: the BBGKY hierarchy. It emphasizes the role of $g(1, 2)$ and explains why the primitive mean field theory fails when one deals with quantities dependent upon short range spatial correlations.[14]

III REDUCTION OF THE EQUATION AND THE FREE ENERGY FUNCTIONAL

Assuming uniaxiality, the distribution function $f(\mathbf{r}, \hat{\Omega})$ reduces to a function of $\mathbf{r}$ and θ, where θ is the orientation as measured from the molecular axis to the director. It is natural to expand $f(\mathbf{r}, \theta)$ as follows:

$$f(\mathbf{r}, \theta) = \sum_{\mathbf{q}} \sum_{l=1}^{\infty} \alpha_{\mathbf{q},2l} P_{2l}(\cos\theta)\exp(i\mathbf{q}\cdot\mathbf{r}), \tag{13}$$

where $\mathbf{q}$ stands for a complete set of reciprocal lattice vectors. The coefficients $\alpha_{\mathbf{q},2l}$ are order parameters:

$$\alpha_{\mathbf{q},2l} = \frac{4l+1}{4\pi\mathscr{V}} \int f(\mathbf{r}, \theta)P_{2l}(\cos\theta)\exp(-i\mathbf{q}\cdot\mathbf{r})\mathrm{d}\mathbf{r}\, \mathrm{d}\hat{\Omega}. \tag{14}$$

It is convenient to introduce another set of parameters $\beta_{\mathbf{q},2l}$ by defining

$$\ln \lambda f(\mathbf{r}, \theta) = \sum_{\mathbf{q}} \sum_{l=1}^{\infty} \beta_{\mathbf{q},2l} P_{2l}(\cos\theta)\exp(i\mathbf{q}\cdot\mathbf{r}). \tag{15}$$

From the normalization condition Eq. (12), we find

$$\lambda = \frac{1}{4\pi\mathscr{V}} \int \exp\left[\sum_{\mathbf{q}} \sum_{l} \beta_{\mathbf{q},2l} P_{2l}(\cos\theta)\exp(i\mathbf{q}\cdot\mathbf{r})\right]\mathrm{d}\mathbf{r}\, \mathrm{d}\hat{\Omega}. \tag{16}$$

Substituting these expressions into the mean field equation (8) and expanding the Legendre polynomials in spherical harmonics, we find that Eq. (8) can be decoupled:

$$i\mathbf{q}\beta_{\mathbf{q},0} = \frac{-n}{kT}\int \exp(i\mathbf{q}\cdot\mathbf{r}_{21})\nabla_1 v_0(r_{12})d\mathbf{r}_2\cdot\alpha_{\mathbf{q},0}, \tag{17}$$

$$i\mathbf{q}\beta_{\mathbf{q},2} = -\frac{n}{5kT}\int \exp(i\mathbf{q}\cdot\mathbf{r}_{21})\nabla_1 v_2(r_{12})d\mathbf{r}_2\cdot\alpha_{\mathbf{q},2}, \tag{18}$$

$$\beta_{\mathbf{q},2l} = 0, \qquad l > 2. \tag{19}$$

Or, in more detail, by combining Eqs. (13), (15)–(18) we obtain

$$\beta_{\mathbf{q},0} = \frac{n}{kT}\frac{i\mathbf{q}}{q^2}\cdot\int d\mathbf{r}_2 \exp(i\mathbf{q}\cdot\mathbf{r}_{21})\nabla_1 v_0(r_{12})$$
$$\times\frac{\int_{\Delta\mathscr{V}}\int_{-1}^{1}\exp[-i\mathbf{q}\cdot\mathbf{r}+\sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\,\mathbf{p}\cdot\mathbf{r})]d\mathbf{r}\,d\cos\theta}{\int_{\Delta\mathscr{V}}\int_{-1}^{1}\exp[\sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\mathbf{p}\cdot\mathbf{r})]d\mathbf{r}\,d\cos\theta} \tag{20}$$

$$\beta_{\mathbf{q},2} = \frac{n}{kT}\,\frac{i\mathbf{q}}{q^2}\cdot\int d\mathbf{r}_2 \exp(i\mathbf{q}\cdot\mathbf{r}_{21})\nabla_1 v_2(r_{12})$$
$$\times\frac{\int_{\Delta\mathscr{V}}\int_{-1}^{1}\exp[-i\mathbf{q}\cdot\mathbf{r}+\sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\mathbf{p}\cdot\mathbf{r})]P_2(\cos\theta)d\mathbf{r}\,d\cos\theta}{\int_{\Delta\mathscr{V}}\int_{-1}^{1}\exp[\sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\mathbf{p}\cdot\mathbf{r})]d\mathbf{r}\,d\cos\theta} \tag{21}$$

$$\beta_{\mathbf{q},2l} = 0, \qquad l > 2,$$

where $\Delta\mathscr{V}$ denotes a unit cell.

At this point we carry out a further step of reduction. A specific form of the potential is introduced following McMillan[5] and our own earlier work:[6,7]

$$v_0(r) = -v_0\delta\exp\left[-\left(\frac{x}{x_0}\right)^2-\left(\frac{y}{y_0}\right)^2-\left(\frac{z}{z_0}\right)^2\right], \tag{23}$$

$$v_2(r) = -v_0\exp\left[-\left(\frac{x}{x_0}\right)^2-\left(\frac{y}{y_0}\right)^2-\left(\frac{z}{z_0}\right)^2\right]. \tag{24}$$

Equations (20)–(22) become:

$$\beta_{\mathbf{q}.0} = \frac{v_0}{kT}\,\pi^{3/2}x_0y_0z_0n\delta\exp[-\tfrac{1}{4}(x_0^2q_x^2+y_0^2q_y^2+z_0^2q_z^2)]$$
$$\times\frac{\int_{\Delta\mathscr{V}}\int_{-1}^{1}\exp[-i\mathbf{q}\cdot\mathbf{r}+\sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\mathbf{p}\cdot\mathbf{r})]d\mathbf{r}\,d\cos\theta}{\int_{\Delta\mathscr{V}}\int_{-1}^{1}\exp[\sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\mathbf{p}\cdot\mathbf{r})]d\mathbf{r}\,d\cos\theta}, \tag{25}$$

$$\beta_{\mathbf{q},2} = \frac{v_0}{kT}\pi^{3/2}x_0 y_0 z_0 n \exp[-\tfrac{1}{4}(x_0^2 q_x^2 + y_0^2 q_y^2 + z_0^2 q_z^2)]$$

$$\times \frac{\int_{\Delta\mathscr{V}}\int_{-1}^{1} \exp[-i\mathbf{q}\cdot\mathbf{r} + \sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\mathbf{p}\cdot\mathbf{r})]P_2(\cos\theta)\mathrm{d}\mathbf{r}\,\mathrm{d}\cos\theta}{\int_{\Delta\mathscr{V}}\int_{-1}^{1} \exp[\sum_{\mathbf{p}}\sum_l \beta_{\mathbf{p},2l}P_{2l}(\cos\theta)\exp(i\mathbf{p}\cdot\mathbf{r})]\mathrm{d}\mathbf{r}\,\mathrm{d}\cos\theta}$$

$$\beta_{\mathbf{q},2l} = 0, \qquad l > 2. \tag{26}$$

A couple of comments are in order. First, coefficients of order $l > 2$ vanish because our potential, at v_2, is of a truncated form. That is already obvious from Eqs. (17)–(18). Next, the equations in general strongly couple the coefficients. Only in one special case are the coefficients decoupled. That case will be discussed in Section IV.

The Helmholts free energy functional in the mean field approximation can be expressed as

$$F = F_0 + kT\frac{n}{4\pi}\int f(\mathbf{r},\hat{\Omega})\ln\frac{nf(\mathbf{r},\hat{\Omega})}{4\pi}\mathrm{d}\mathbf{r}\,\mathrm{d}\hat{\Omega}$$

$$+ \frac{n^2}{32\pi^2}\int f(\mathbf{r}_1,\hat{\Omega}_1)f(\mathbf{r}_2,\hat{\Omega}_2)v(1,2)\mathrm{d}\mathbf{r}_1\,\mathrm{d}\hat{\Omega}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\hat{\Omega}_2, \tag{28}$$

where F_0 contains all parts independent of $f(\mathbf{r},\hat{\Omega})$. After some lengthy but straightforward algebra, we find

$$F = F_0 + kTN\left\{\ln\frac{\mathrm{n}}{4\pi} - \ln A + \frac{4\pi^{3/2}}{\zeta_x\zeta_y\zeta_z t}\right.$$

$$\left.\times\left[2\alpha^2 + \frac{1}{\delta}\left(\beta_1^2\exp\left(\frac{\zeta_x^2}{4}\right) + \beta_2^2\exp\left(\frac{\zeta_y^2}{4}\right) + \beta_3^2\exp\left(\frac{\zeta_z^2}{4}\right)\right)\right]\right\}$$

$$-kTN\left\{\frac{1}{128\pi^6A^2t}\left[\delta G_0^2\left(\frac{\alpha}{t}\right) + G_1^2\left(\frac{\alpha}{t}\right)\right]J\left(\frac{\beta_1}{t},\zeta_x\right)J\left(\frac{\beta_2}{t},\zeta_y\right)J\left(\frac{\beta_3}{t},\zeta_z\right)\right\}, \tag{29}$$

where $t \equiv kT/v_0$,

$$\alpha \equiv t\beta_{000,2}, \qquad \beta_1 \equiv 2t\beta_{100,0}, \qquad \beta_2 \equiv 2t\beta_{010,0}, \qquad \beta_3 \equiv 2t\beta_{001,0},$$

$$n \equiv n_x n_y n_z \equiv \frac{1}{\mathrm{d}_x}\frac{1}{\mathrm{d}_y}\frac{1}{\mathrm{d}_z},$$

$$\zeta_x \equiv \frac{2\pi x_0}{\mathrm{d}_x}, \qquad \zeta_y \equiv \frac{2\pi y_0}{\mathrm{d}_y}, \qquad \zeta_z \equiv \frac{2\pi z_0}{\mathrm{d}_z},$$

$$G_0\left(\frac{\alpha}{t}\right) = \int_0^1 \exp\left[\frac{\alpha}{t}P_2(\cos\theta)\right]\mathrm{d}\cos\theta = \int_0^1 \exp\left[\frac{\alpha}{t}\frac{1}{2}(3x^2 - 1)\right]\mathrm{d}x, \tag{30}$$

$$G_1\left(\frac{\alpha}{t}\right) = \int_0^1 \exp\left[\frac{\alpha}{t}\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\right]\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\mathrm{d}x, \tag{31}$$

$$J\left(\frac{\beta}{t}, \eta\right) = \int_{-\pi}^{\pi} \mathrm{d}\xi_1 \int_{-\infty}^{\infty} \mathrm{d}\xi_2 \exp\left[\frac{\beta}{t}(\cos\xi_1 + \cos\xi_2) - \frac{(\xi_1 - \xi_2)^2}{\eta^2}\right], \tag{32}$$

$$A = G_0\left(\frac{\alpha}{t}\right) I_0\left(\frac{\beta_1}{t}\right) I_0\left(\frac{\beta_2}{t}\right) I_0\left(\frac{\beta_3}{t}\right), \tag{33}$$

and

$$I_\nu(\zeta) = \frac{1}{\pi^{1/2}(\nu - \frac{1}{2})!}\left(\frac{\zeta}{2}\right)^\nu \int_0^\pi \exp(\pm\zeta\cos\theta)\sin^{2\nu}\theta\,\mathrm{d}\theta, \qquad \nu > -\tfrac{1}{2}, \tag{34}$$

with the last line defining modified Bessel functions.

IV FIRST LEVEL OF APPROXIMATION: DECOUPLED PARAMETERS

In the lowest level of approximation, only the following coefficients will be retained: $\beta_{000,0}$, $\beta_{100,0} = \beta_{-100,0}$, $\beta_{010,0} = \beta_{0-10,0}$, $\beta_{001,0} = \beta_{00-1,0}$, and $\beta_{000,2}$. This is a particularly crude approximation. Its only virtue is simplicity. We use it to illustrate some of the algebraic manipulations, and to make contact with our earlier work. Using the notations given in the last section, we obtain

$$\begin{aligned} &\text{i) } \beta_{000,0} = \frac{\zeta_x\zeta_y\zeta_z\delta}{8\pi^{3/2}t}, \\ &\text{ii) } \beta_{000,2} = \frac{\zeta_x\zeta_y\zeta_z K(\beta_{000,2})}{8\pi^{3/2}t}, \end{aligned} \tag{35}$$

where

$$K(\beta_{000,2}) = \frac{\int_{-1}^{1}\exp[\beta_{000,2}P_2(\cos\theta)]P_2(\cos\theta)\mathrm{d}\cos\theta}{\int_{-1}^{1}\exp[\beta_{000,2}P_2(\cos\theta)]\mathrm{d}\cos\theta},$$

and thus

$$\beta_{000,2} = \frac{\zeta_x\zeta_y\zeta_z}{16\pi^{3/2}t}\left[\frac{1}{\beta_{000,2}\int_0^1\exp[\frac{3}{2}\beta_{000,2}(x^2 - 1)]\mathrm{d}x} - \left(\frac{1}{\beta_{000,2}} + 1\right)\right]; \tag{36}$$

$$\text{iii) } \beta_{100,2} = \frac{\zeta_x\zeta_y\zeta_z\delta}{8\pi^{3/2}t}\exp\left[-\left(\frac{\pi x_0}{\mathrm{d}_x}\right)^2\right]\left[\frac{I_1(2\beta_{100,0})}{I_0(2\beta_{100,0})}\right]; \tag{37}$$

$$\text{iv)}\ \beta_{010,0} = \frac{\zeta_x\zeta_y\zeta_z\delta}{8\pi^{3/2}t}\exp\left[-\left(\frac{\pi y_0}{\mathrm{d}_y}\right)^2\right]\left[\frac{I_1(2\beta_{010,0})}{I_0(2\beta_{010,0})}\right]; \tag{38}$$

$$\text{v)}\ \beta_{001,0} = \frac{\zeta_x\zeta_y\zeta_z\delta}{8\pi^{2/3}t}\exp\left[-\left(\frac{\pi z_0}{\mathrm{d}_z}\right)^2\right]\left[\frac{I_1(2\beta_{001,0})}{I_0(2\beta_{001,0})}\right]. \tag{39}$$

Thus, in this lowest level of approximation, all coefficients are decoupled. With $\beta_{000,0}$ given definitely by Eq. (35), there are only four separate transcendental equations to solve. The procedure is extremely rapid to carry out numerically. The only problem is that the accuracy attained is very low. Using the same potential parameters as in Ref. 6, we found the phase diagram distorted.

Offhand it appears that our earlier work in Ref. 7 was carried out at precisely the same level of approximation. Yet we claimed that the effect of neglecting the coefficient coupling the spatial and orientational order, $\beta_{001,2}$, was insignificant. Actually there is no real contradiction. The calculation in Ref. 7 was *variational*, whereas the present calculation is based on a sequential development which entertains no free parameters. Just how the variational procedure compensated the deficient decoupling scheme is not known, but certainly there is no *a priori* reason to expect agreement between the results of Ref. 7 and the present calculation unless *all* the omitted coefficients are unimportant.

V HIGHER LEVELS OF APPROXIMATION

In the next level of approximation, we include the coupling parameters $\beta_{100,2}$, $\beta_{010,2}$, and $\beta_{001,2}$ in the expansion, and continue to omit all higher order coefficients. Going back to Eqs. (25)–(27), it is immediately clear that the equations are now coupled, and that the solution will take some work. The method that we employed was iterative. Taking the solution from the last section as a starting point, $\beta_{100,2}$, $\beta_{010,2}$ and $\beta_{001,2}$ were evaluated. After that the entire set of coefficients were returned into the right hand sides of Eqs. (25)–(26) for improvement. This process went on until convergence was reached. (There are of course more efficient ways of iteration, but even in the presence of the double integrations the numerical computation was not very demanding.) Actually we did very little work on the smectic A-crystalline transition. Most of the results were obtained for the isotropic–nematic (I–N) and nematic–smectic A (N–A) transitions, for which only three coefficients had to be determined: $\beta_{000,2}$, $\beta_{001,0}$, and $\beta_{001,2}$.

We adopt here the potential parameters[15] of Ref. 6:

$$\zeta_x = \pi, \qquad \delta = 0.65,$$
$$\zeta_y = \pi, \qquad x_0 = y_0 = z_0.$$

Noting that the factor $1/z_0^2 \pi n_x n_y$ in Eq. (6) of Ref. 6, which works out to be $4/\pi$, does not appear in the present (more natural) form of the potential, the reduced temperature t in Ref. 6 must be multiplied by $\pi/4$ for comparison with the reduced temperature in present work. Also, rewriting Eq. (15):

$$f(z,\theta) = \frac{\exp(\beta_{000,0})}{\lambda}$$

$$\times \exp\left[\beta_{000,2} P_2(\cos\theta) + 2\beta_{001,2} P_2(\cos\theta)\cos\frac{2\pi z}{d_z} + 2\beta_{001,0}\cos\frac{2\pi z}{d_z}\right]$$

and comparing to Eq. (8) of Ref. 6 gives us the correspondence:

$$\beta_{000,2} \leftrightarrow \frac{a}{t},$$

$$\beta_{001,0} \leftrightarrow \frac{c\delta}{2t},$$

$$\beta_{001,2} \leftrightarrow \frac{b}{2t}.$$

There is no other notational difference besides these.

TABLE I

Typical results at the second level of approximation. $\zeta_z^{-1} = 0.40$ in this case.

t	$\beta_{000,2}$	$\beta_{001,0}$	$\beta_{001,2}$	$F - F_0$	Equilibrium Phase Determined
0.126	0	0	0	−3.26657	I
0.124	0	0	0	−3.28961	I
0.122	0	0	0	−3.31341	I
	1.94195	0	0	−3.31329	
0.120	0	0	0	−3.33800	N
	2.22785	0	0	−3.34581	
0.118	0	0	0	−3.36343	N
	2.44733	0	0	−3.38113	
0.116	0	0	0	−3.38973	A
	2.96646	0	0	−3.41694	
	2.96646	0.23537	0.25230	−3.42056	
0.114	0	0	0	−3.41695	A
	3.25437	0	0	−3.45560	
	3.25437	0.31605	0.35356	−3.46920	

Table I shows a set of solutions and the corresponding free energies, at a typical "chainlength" $\zeta_z^{-1} = 0.40$ (or $\zeta_z = 2.5$) over a range of temperature t. The equilibrium phase at each temperature is determined by comparing the free energies.

Table II shows how the present results compare with the results of Ref. 6 at a representative set of ζ_z^{-1} and t. The notations correspond to those used in the present paper. As is obvious from Table II, the agreement is striking. We found no noticeable change at all in the phase diagram. For this reason, the phase diagram is not shown. This calculation, then, demonstrated the importance of the parameter which couples spatial order to orientational order.

At this stage, we can already conclude that higher order coefficients in the expansion of $\ln \lambda f(\mathbf{r}, \hat{\Omega})$ are not imortant, for otherwise they would be expected to make their presence felt in $\beta_{000,2}$, $\beta_{001,0}$, and $\beta_{001,2}$ of Ref. 6. The variational nature of the latter would have called for compensating adjustments in the parameters to account for the missing coefficients. That did not occur.

To be certain, we moved on to a third level of approximation and included the higher order spatial parameters $\beta_{002,0}$ and $\beta_{002,2}$. There were now five coupled transcendental equations to solve. Once again an iteration procedure was employed, with the starting input taken from the output of the second level calculation. Table III lists representative results. It is clear that the effect of these higher order spatial parameters is almost totally negligible.

It can be argued that our particular choice of the form of the potential, or perhaps the potential parameters, is such that the effects of the higher order spatial parameters are *made* insignificant. In particular, since the first set of parameters ($\beta_{001,0}$, $\beta_{001,2}$) determine the layered structure and the second set ($\beta_{002,0}$, $\beta_{002,2}$) only help to *shape* the distribution function, for a relatively

TABLE II

Comparison of present results at the second level of approximation with those of Ref. 6.

			Present			Ref. 6		
ζ_z^{-1}	t	Phase	$\beta_{000,2}$	$\beta_{001,0}$	$\beta_{001,2}$	$\beta_{000,2}$	$\beta_{001,0}$	$\beta_{001,2}$
0.35	0.139	N	2.005	0	0	1.980	0	0
	0.099	A	5.021	0.187	0.235	5.000	0.20	0.28
0.38	0.125	N	2.369	0	0	2.327	0	0
	0.112	A	3.559	0.198	0.226	3.579	0.31	0.21
0.40	0.118	N	2.447	0	0	2.467	0	0
	0.115	A	3.132	0.284	0.313	3.144	0.48	0.31
0.42	0.115	A	3.068	0.416	0.461	3.140	0.68	0.51
0.45	0.116	A	2.838	0.530	0.584	2.879	0.81	0.64

TABLE III

Significance of higher order spatial parameters.

ζ_z^{-1}	t	$\beta_{000,2}$	$\beta_{001,0}$	$\beta_{001,2}$	$\beta_{002,0}$	$\beta_{002,2}$
0.36	0.105	4.381	0.169	0.205	0.000085	0.000106
0.38	0.110	3.765	0.258	0.301	0.000336	0.000409
0.40	0.114	3.254	0.316	0.354	0.000797	0.000941
	0.115	3.131	0.284	0.312	0.000640	0.000748
	0.116	2.970	0.237	0.254	0.000442	0.000508

smooth spatial dependence in the potential the second set of parameters will be left with very little role to play. Nevertheless, what the mean field theory offers here is a universal phase diagram. As long as *some* potential can be found to fit the phase diagram well, it is difficult to imagine that fine details in the form of the potential should matter, when the present case yields higher-order parameters at two orders of magnitude (or more) smaller than the leading-order parameters.

In a recent paper by Meyer and Lubensky[10] examining the first or second order nature of the N–A transition, it is suggested that the coupling between first and second spatial order parameters is important, and that it would have been safer in our earlier calculation to include more terms in the mean field. By coincidence the present work did precisely that. We found it unnecessary to include more terms. The order parameters $\alpha_{\mathbf{q},2l}$ will not be affected to any perceptible extent by the inclusion of more $\beta_{\mathbf{q},2l}$. However, the disagreement may not really be there since Meyer and Lubensky looked at the region $\zeta_z^{-1} > 0.5$, while our calculations are for $\zeta_z^{-1} < 0.5$. Also, it may be worthwhile to look at other potentials and do the analysis more exhaustively using our present procedure, which is not only systematic but also very efficient, the computer time required being an order of magnitude less than our earlier variational procedure.[6]

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15. In Ref. 7, $\zeta_x = \zeta_y = 3.0$ instead of π.