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Theoretical analysis of isotropic-nematic transition properties*

Yu Ming Shih and Y. R. Lin-Liu
Department of Physics, Northwestern University, Evanston, Illinois 60201

Chia-Wei Woo
Department of Physics, Northwestern University, Evanston, Illinois 60201
and Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439

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With the aid of a modified mean-field model, one in which the spatial correlations are handled by means of a conventional classical liquid theory and the orientational ordering alone is subjected to the mean-field approximation, we find it possible to correlate thermodynamic data near the isotropic-nematic transition region. In contrast with the Maier-Saupe theory, we deduce accurately the volume change, latent heat, and maximum supercooling temperature. The theoretical analysis when applied to PAA and MBBA leads to results in *quantitative* agreement with experiment. We propose that measured data on other nematic and cholesteric liquid cystals be subjected to tests under the same scheme.

I. INTRODUCTION

We wish to address ourselves to the question of how much one can extract from a mean-field theory for liquid crystals. It is generally conceded that the mean field theory does quite well in predicting qualitative features such as order-parameter changes and phase diagrams.[1-3] When it comes to understanding thermodynamics *quantitatively* near phase-transition regions, however, the approximation is thought to falter.[4] We disagree. Our view is that if the approximation is introduced in the right context, and if the thermodynamic analysis is carried out correctly, the mean-field theory can go a long way.

By the *right context*, we mean that in dealing with nematogens, the mean-field approximation should be applied only to determining the *orientational* order. At liquid-crystalline densities, which are essentially classical liquid or solid densities, it is clearly inappropriate to apply a mean-field approximation to the description of *spatial* ordering. The latter should be treated with a lattice model, or better yet, with a conventional classical liquid theory. Now, the lattice model, or any model which fixes the intermolecular distance in an averaging process,[1] is not only unrealistic, but also assumes as input a rather restricted spatial distribution of molecules: one which in all likelihood is *not* consistent with the calculated orientational distribution. References 2 and 3 did away with such a model. The spatial dependence of the intermolecular potential was of forms susceptible to mean-field treatment, but did not contain short-range repulsions. Such models cannot sustain configurational equilibrium: They collapse under pressure. Thus the resulting spatial distribution of molecules, even when made consistent with the orientational distribution, should be regarded as input to the theory.

In this paper, we present a more sophisticated model: one that accounts for short-range repulsive interactions. We view the spatial distribution of molecules as having resulted from a conventional classical liquid theory. Instead of carrying out detailed calculations, however, we determine the relevant parameters in the model by using established experimental data. A mean-field analysis is then carried out to obtain orientational ordering, and subsequently physical quantities related to the isotropic-nematic (I-N) transition. As far as liquid-crystalline properties are concerned, this is still a *mean-field theory*. Statistical mechanicians with background rooted in Ising and other lattice models may feel uncomfortable with our usage of the terminology, but they must surely recognize that liquid crystals are after all just classical liquids endowed with orientational order. Thus in a mean-field approximation, although a density function will suffice in describing the orientational distribution, pair-distribution functions must still make their presence felt to properly account for spatial correlations.

Our theory begins with a pairwise potential

$$V(1,2)=V_0(r_{12})+V_2(r_{12})P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2)+V_4(r_{12})P_4(\hat{\Omega}_1\cdot\hat{\Omega}_2), \tag{1}$$

where the unit vector $\hat{\Omega}_i$ denotes the orientation (θ_i,φ_i) of the ith molecule, and P_2 and P_4 are Legendre polynomials. A potential of this form is not the most-general expansion formula, but is sufficiently general at the present stage of development of microscopic theories for liquid crystals, and is a most tractable expression as we shall soon see. V_2 and V_4 are assumed weak compared to V_0. Other than that, we need no information about the exact nature of the forces.

The properties of the system are completely determined by the ν-particle distribution functions

$$P^{(\nu)}(1,\ldots,\nu)\equiv P^{(\nu)}(\vec{r}_1,\hat{\Omega}_1,\ldots,\vec{r}_\nu,\hat{\Omega}_\nu)=\frac{N!}{(N-\nu)!}\,\frac{\int\exp[-\sum_{i<j}V(i,j)/kT]\,d\vec{r}_{\nu+1}\,d\hat{\Omega}_{\nu+1}\cdots d\vec{r}_N\,d\hat{\Omega}_N}{\int\exp[-\sum_{i<j}V(i,j)/kT]\,d\vec{r}_1\,d\hat{\Omega}_1\cdots d\vec{r}_N\,d\hat{\Omega}_N}. \tag{2}$$

The one-particle distribution function, or the density function $P^{(1)}(1)\equiv P^{(1)}(\vec{r}_1,\hat{\Omega}_1)$, can be separated, thus: $n(\vec{r})f(\theta)$. For isotropic and nematic phases, $n(\vec{r})=\rho\equiv 1/v$. The two-particle distribution function $P^{(2)}(1,2)\equiv P^{(2)}(\vec{r}_1,\hat{\Omega}_1,\vec{r}_2,\hat{\Omega}_2)$ deviates from a product of two density functions by a factor

$$g(1,2)\equiv P^{(2)}(1,2)/[P^{(1)}(1)P^{(1)}(2)], \tag{3}$$

known as the pair-correlation function. $g(1,2)$ depends on the positions and orientations of molecules 1 and 2. For a system characterized by pairwise interactions, $g(1,2)$ is of fundamental importance. Strictly speaking it should be calculated either from its definition, or by means of an approximate integral equation.[5] In the crudest approximation where all correlations are ignored, $g(1,2)$ is set to unity. We feel that this is too drastic a move. If such an approximation is used for a system in which the potential contains a repulsive core, the internal energy will diverge. In our mean-field model, it will be replaced by an effective g: one that is obtained by averaging $g(1,2)$ in some reasonable way over all orientations. The averaging process leads to a simple formula

$$g(1,2)\to g_e(r_{12})\equiv g_s(r_{12}\,|\,[V_0+V_2\sigma_2^2+V_4\sigma_4^2]/kT), \tag{4}$$

where $g_s(r\,|\,V/kT)$ denotes the radial distribution function for a system of spherically symmetric particles interacting via a pairwise potential V, and

$$\sigma_i\equiv\int f(\theta)P_i(\cos\theta)\,d\hat{\Omega} \tag{5}$$

denotes the ith orientational order parameter. While we have no intention of actually postulating V and calculating $g(1,2)$, the result shown in Eq. (4) is crucial in our analysis. We shall for this reason end our introduction by "deriving" the equation that governs the orientationally averaged g, and show that the solution is approximately given by Eq. (4).

Differentiate $P^{(2)}$, using the defining equation (2):

$$\nabla_1P^{(2)}(1,2)=P^{(2)}(1,2)\nabla_1\left(\frac{-V(1,2)}{kT}\right)+\int P^{(3)}(1,2,3)\nabla_1\left(\frac{-V(1,3)}{kT}\right)d\vec{r}_3\,d\hat{\Omega}_3. \tag{6}$$

In the isotropic and nematic phases, we can write

$$P^{(2)}(1,2)\equiv\rho^2f(\theta_1)f(\theta_2)g(1,2)\to\rho^2f(\theta_1)f(\theta_2)g_e(r_{12}) \tag{7}$$

and

$$P^{(3)}(1,2,3)\equiv\rho^3f(\theta_1)f(\theta_2)f(\theta_3)g(1,2,3)\to\rho^3f(\theta_1)f(\theta_2)f(\theta_3)g_e^{(3)}(r_{12},r_{23},r_{31}). \tag{8}$$

Substituting these expressions into Eq. (6) and integrating the resultant equation over $\hat{\Omega}_1$ and $\hat{\Omega}_2$, we find

$$\nabla_1g_e(r_{12})=g_e(r_{12})\nabla_1\left(\frac{-\bar{V}(r_{12})}{kT}\right)+\rho\int g_e^{(3)}(r_{12},r_{23},r_{31})\nabla_1\left(\frac{-\bar{V}(r_{13})}{kT}\right)d\vec{r}_3, \tag{9}$$

where

$$\bar{V}(r_{12})=V_0(r_{12})+V_2(r_{12})\sigma_2^2+V_4(r_{12})\sigma_4^2. \tag{10}$$

Equation (9) is the familiar Born-Green-Kirkwood-Yvon (BGKY) integral equation for a classical isotropic liquid characterized by the pair potential $\bar{V}$. The solution $g_s(r_{12})$ can be calculated in a number of ways.[6] We thus obtain

$$g_e(r_{12})=g_s(r_{12}\,|\,[V_0+V_2\sigma_2^2+V_4\sigma_4^2]/kT). \tag{11}$$

The appearance of g_e affects the values of several thermodynamic parameters. The determination of the parameters will however remain empirical. We do not intend to solve Eqs. (9)–(11) in this paper.

II. THERMODYNAMIC FUNCTIONS

The identification of v and T, rather than P and T, as the independent thermodynamic variables is a most direct choice to make in a molecular theory. It implies that one should work with the Helmholtz free energy F, rather than the Gibbs free energy G. This gets a bit awkward when phase transitions are under consideration. Extreme care must be taken. For example, it will not do to ignore the difference between $\Delta G\equiv G_I-G_N$ and $\Delta F\equiv F_I-F_N$ (where I and N denote isotropic and nematic phases, respectively) by claiming that $P\Delta v\equiv P(v_I-v_N)$ makes an insignificant contribution, since quantities of such magnitudes are precisely the objects under study. Here lies one of the common pitfalls in interpreting molecular theoretic results.

In this section we further develop our mean-field analysis. The Helmholtz free energy and other relevant thermodynamic functions will be derived and expressed in terms of a small number of parameters.

We begin by defining an internal energy functional $\mathcal{U}$ and an entropy functional $\mathcal{S}$ in the usual way,[7] and cluster expanding the latter. The results are

$$\mathcal{U} = \mathcal{U}_{\text{ideal}} + \tfrac{1}{2}N\rho\tilde{\gamma}_0 + \tfrac{1}{2}N\rho\tilde{\gamma}_2\sigma_2^2 + \tfrac{1}{2}N\rho\tilde{\gamma}_4\sigma_4^2, \tag{12}$$

where

$$\tilde{\gamma}_i = \int V_i(r)g_e(r)\,d\vec{r}, \tag{13}$$

and

$$\mathcal{S} = \mathcal{S}_{\text{ideal}} - Nk\ln\rho + k\ln N! - Nk\int f(\theta)\ln f(\theta)\,d\hat{\Omega} - \tfrac{1}{2}N\rho k\int g_e(r)\ln g_e(r)\,d\vec{r} + \cdots . \tag{14}$$

We shall not go beyond the terms explicitly shown in Eq. (14). The last term is all important, as we shall soon see. A free-energy functional $\mathfrak{F}$ may now be defined. A few steps of algebra ensue, in which g_e is expanded in powers of V_2/V_0 and V_4/V_0, or equivalently V_2/kT and V_4/kT since $V_0 \approx kT$. Equation (4) allows us, then, to write

$$g_e(r) \approx g_0(r) + \sigma_2^2 g_2(r) + \sigma_4^2 g_4(r). \tag{15}$$

Such an expansion is valid since V_2 and V_4 are from the outset assumed weak compared to V_0, and thus

$$\left|\frac{g_s(r\,|\,(V_0 + V_2\sigma_2^2 + V_4\sigma_4^2)/kT) - g_s(r\,|\,V_0/kT)}{g_s(r\,|\,V_0/kT)}\right| \ll 1. \tag{16}$$

Finally,

$$\mathfrak{F} = \mathfrak{F}_0 + NkT\int f(\theta)\ln f(\theta)\,d\hat{\Omega} + \tfrac{1}{2}N\rho\gamma_2\sigma_2^2 + \tfrac{1}{2}N\rho\gamma_4\sigma_4^2, \tag{17}$$

where $\mathfrak{F}_0$ simply gathers all terms which do not vary with the distribution function $f(\theta)$, and

$$\gamma_i = \int g_0(r)V_i(r)\,d\vec{r} + \int g_i(r)V_0(r)\,d\vec{r} + kT\int g_i(r)[1 + \ln g_0(r)]\,d\vec{r}. \tag{18}$$

That Eq. (17) has the same functional dependence on the order parameters, as the Maier-Saupe theory came from the fact that $\mathcal{S}$ was expanded in powers of V_2/kT and V_4/kT. It preserves for us the correct prediction of order-parameter discontinuities at transition. There are, however, major differences in interpretation. The entropy functional, as seen from Eq. (14), no longer contains $Nk\int f(\theta)\ln f(\theta)\,d\hat{\Omega}$ alone. Also, γ_2 and γ_4 in Eq. (17) now depend on temperatures and volume — not so much through the dependence of $g_i(r)$ on T and v as through the direct temperature dependence of the last term in Eq. (18). However, the Maier-Saupe theory, which yields latent heats off by a factor of as much as 3, cannot be repaired by simply allowing γ_2 and γ_4 to depend on T and v, since such a move would necessarily render inconsistent statistical and thermodynamic [Eq. (24)] definitions of the entropy.

From Eq. (17) we recognize that $\mathfrak{F}$ depends on $f(\theta)$ explicitly through the second term, and implicitly through σ_2 and σ_4. The minimization of $\mathfrak{F}$ with respect to $f(\theta)$ leads now to the usual transcendental equations made up of Eq. (5) and

$$B_i = \rho\gamma_i\sigma_i/kT, \tag{19}$$

with

$$f(\theta) = (1/4\pi Z)\exp[-B_2P_2(\cos\theta) - B_4P_4(\cos\theta)]. \tag{20}$$

Z is a normalization constant:

$$Z = \frac{1}{4\pi}\int \exp[-B_2P_2(\cos\theta) - B_4P_4(\cos\theta)]\,d\hat{\Omega}. \tag{21}$$

The Helmholtz free energy F is given by the minimized $\mathfrak{F}$, or

$$\begin{aligned} F &= (F_0 - NkT\ln 4\pi) \\ &\quad + (-NkT\ln Z - \tfrac{1}{2}N\rho\gamma_2\sigma_2^2 - \tfrac{1}{2}N\rho\gamma_4\sigma_4^2) \\ &\equiv F_1 + F_2. \end{aligned} \tag{22}$$

Thermodynamic definitions of pressure and entropy then yield

$$\begin{aligned} P &= \left\{-\left(\frac{\partial F_0}{\partial v}\right)_T\right\} + \left\{\tfrac{1}{2}\rho^2(\gamma_2\sigma_2^2 + \gamma_4\sigma_4^2) + \tfrac{1}{2}\rho^3\left[\left(\frac{\partial\gamma_2}{\partial\rho}\right)_T\sigma_2^2 + \left(\frac{\partial\gamma_4}{\partial\rho}\right)_T\sigma_4^2\right]\right\} \\ &\equiv P_1 + P_2 \end{aligned} \tag{23}$$

and

$$\begin{aligned} S &= \left\{-\left(\frac{\partial F_0}{\partial T}\right)_v + Nk\ln 4\pi\right\} \\ &\quad + \left\{Nk\ln Z + \frac{1}{T}(N\rho\gamma_2\sigma_2^2 + N\rho\gamma_4\sigma_4^2) - \frac{1}{2}\left[N\rho\sigma_2^2\left(\frac{\partial\gamma_2}{\partial T}\right)_v + N\rho\sigma_4^2\left(\frac{\partial\gamma_4}{\partial T}\right)_v\right]\right\} \\ &\equiv S_1 + S_2, \end{aligned} \tag{24}$$

where $\ln Z$ depends on $f(\theta)$ and vanishes when $\sigma_2 = \sigma_4 = 0$.

The "constant-volume phase-transition point" at given temperature T can now be determined by equating F_I and F_N. Since $F_I = F_1$ and $F_N = F_1 + F_2$, we require F_2 to vanish. In particular, at the transition temperature $T_{I\text{-}N}$,

$$F_2(\rho^*, T_{I\text{-}N}) = 0, \tag{25}$$

where $\rho^* \approx \rho_I \approx \rho_N$ at $T_{I\text{-}N}$.

III. MEAN-FIELD THEORY AND INPUT EXPERIMENTAL DATA

Let us now summarize our procedure for carrying out the mean-field analysis. It is clear that at every T and ρ, by specifying γ_2 and γ_4, we can solve Eqs. (5), (19), and (20) simultaneously to determine the parameters B_2, B_4, σ_2, and σ_4. Subsequently, Eq. (22) can be used to evaluate F_2. If the T and ρ chosen happen to fall on the transition curve, F_2 should vanish. In particular, this should be the case at $T_{I\text{-}N}$ and ρ^*. If not, something must have gone wrong in choosing the effective interaction parameters γ_2 and γ_4. Also, the order parameter σ_2 at transition is rather well known experimentally, and should be reproducible from the mean-field analysis. Using as input the experimental data $T_{I\text{-}N}$, $\rho^*[\approx \rho_I(T_{I\text{-}N}) \approx \rho_N(T_{I\text{-}N})]$, and $\sigma_2(T_{I\text{-}N})$, we determine $\gamma_2(T_{I\text{-}N}, \rho^*)$ and $\gamma_4(T_{I\text{-}N}, \rho^*)$ by requiring the calculated F_2 to vanish and the calculated σ_2 to agree with experiment. This concludes the first stage of our analysis.

If γ_2 and γ_4 were independent of temperature and density, the extension of the above procedure to all T and ρ should complete the story. Equation (18), however, indicates that such is not the case. We must once again rely on experimental data for determining these dependences. The task turns out to be simpler than might be expected. First of all, as we mentioned earlier, most of the temperature and density dependence of γ_i enter through the last term of Eq. (18). The reason is that, while $g_i(r)$ does depend on T and ρ, the variations in its value are small since we are not considering a very wide range of T and ρ. Also, such dependences enter γ_i indirectly, whereas in the last term there is a direct, linear dependence on T. In principle, then, we should ignore the density dependence and write γ_i in the form $(a_i + b_i T)$. Experiment,[8] however, indicates that it is preferable to write

$$\gamma_i = \gamma_{i0} T^{\alpha}. \tag{26}$$

For the transition curve can be fitted quite well by the relation

$$\rho = A T^{1/\Gamma}, \tag{27}$$

with Γ in the range 4–5. Also, along the transition curve, σ_2 remains virtually constant.[9] In anticipation of the dominance of the σ_2 and B_2 terms over the σ_4 and B_4 terms, respectively, Eqs. (5) and (20) then imply that B_2 remains virtually constant. Equation (19), when rewritten in the form

$$\rho = (B_2 k/\sigma_2) T/\gamma_2, \tag{28}$$

and compared with Eq. (27), subsequently requires γ_2 to take the form (26), with

$$\alpha = 1 - 1/\Gamma. \tag{29}$$

TABLE I. Input information.

		PAA	MBBA
	σ_2	0.35–0.40 [a,b]	0.31–0.35 [c]
Inferred:	σ_4	0.067–0.099	0.044–0.067
	B_2/σ_2	−4.622 – −4.571	−4.680 – −4.622
	B_4/σ_4	1.503–0.430	3.374–1.503
$T_{I\text{-}N}$ (K)		408 [a]	318 [d]
$v_I \approx v_N$ (cm^3/mole)		225 [e]	260 [f]
κ (10^{-11}cm^2/dyn)		7.5 [g]	4.87 [h]
β (10^{-4} K^{-1})		9 [g]	8.7 [f]
Γ		4.0 [a]	4.7 [h]

[a] Reference 10.
[b] Reference 9.
[c] Reference 11.
[d] Reference 12.
[e] Reference 13.
[f] Reference 14.
[g] Reference 15.
[h] Reference 8.

Since the range of T and ρ considered is rather small, it is immaterial as to which form is the most appropriate for γ_i. We accept the more convenient form (26), which is also that preferred by experiment. Thus,

$$(\partial \gamma_i/\partial \rho)_T = 0 \tag{30}$$

and

$$(\partial \gamma_i/\partial T)_v = (\alpha/T)\gamma_i = (1 - 1/\Gamma)\gamma_i/T. \tag{31}$$

This concludes the second stage of our analysis.

Finally, as input to thermodynamic work to be discussed in Sec. IV, we need experimental data on the compressibility $\kappa \approx \kappa_I \approx \kappa_N$ and the coefficient of thermal expansion $\beta \approx \beta_I \approx \beta_N$ near the transition. All input data are listed in Table I for PAA and MBBA, along with references. The inferred mean field parameters are shown in the same table.

Even though a large body of empirical information is called upon, none has been, or indeed can be, *contrived* to fit the phase-transition properties (volume change, latent heat, and maximum supercooling temperature) desired. To a large extent the information quoted in this paper was known to previous authors, but has not been put to proper use.

IV. PHASE-TRANSITION PROPERTIES

The rest of our analysis relies heavily on the aid rendered in Fig. 1. The curves labeled I and N are presumably molecular theoretic results if one were to actually calculate them. Both curves contain unphysical portions (shown as dashed curves). The actual isotherm, with its transition region greatly exaggerated, is depicted as the continuous solid line. The flat segment ($A'C'$) comes out of an equal-area, or Maxwell, construction.

The volume change at transition is given by

$$\begin{aligned}\Delta v/v &\equiv (v_I - v_N)/v \\ &\approx \kappa_I(P_C - P_E) + \kappa_N(P_E - P_A) \approx \kappa(P_C - P_A),\end{aligned} \tag{32}$$

where the P's denote pressures calculated via Eq. (23) at the subscripted points. $\kappa \approx \kappa_I \approx \kappa_N$ results from the narrowness of the transition region. Equations (23) and (30) yield

$$\begin{aligned}P_C - P_A &= P_1(\rho^*) - [P_1(\rho^*) + P_2(\rho^*)] \\ &= (-1/2v^{*2})(\gamma_2\sigma_2^2 + \gamma_4\sigma_4^2).\end{aligned} \tag{33}$$

Next, the latent heat is given by

$$\Delta H = T[(S_{C'} - S_C) - (S_{A'} - S_A)] + T(S_C - S_A), \tag{34}$$

where the S's denote entropies calculated via Eq. (24) at the subscripted points. But since

$$S_{C'} - S_C \approx (v_{C'} - v_C)\left(\frac{\partial S}{\partial v}\right)_T\bigg|_{C'} \tag{35}$$

and

$$S_{A'} - S_A \approx (v_{A'} - v_A)\left(\frac{\partial S}{\partial v}\right)_T\bigg|_{A'}, \tag{36}$$

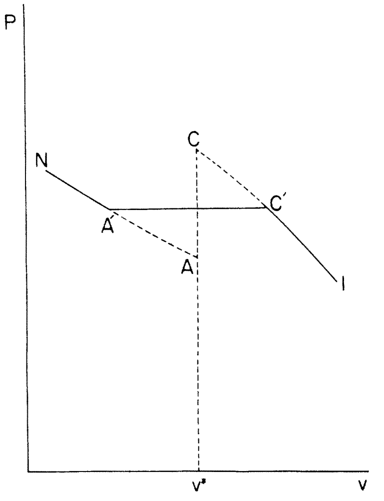

FIG. 1. Isotherm near the I-N transition (not to scale).

and since

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v = \frac{\beta}{\kappa}, \tag{37}$$

we find

$$[(S_{C'} - S_C) - (S_{A'} - S_A)] \approx (\beta/\kappa)\Delta v, \tag{38}$$

with $\beta \approx \beta_I \approx \beta_N$ near transition. Equation (24), which yields

$$\begin{aligned}S_C - S_A &= S_1(\rho^*) - [S_1(\rho^*) + S_2(\rho^*)] \\ &= \frac{-N}{2Tv^*}(\gamma_2\sigma_2^2 + \gamma_4\sigma_4^2) \\ &\quad + \frac{N}{2v^*}\left[\sigma_2^2\left(\frac{\partial\gamma_2}{\partial T}\right)_v + \sigma_4^2\left(\frac{\partial\gamma_4}{\partial T}\right)_v\right],\end{aligned} \tag{39}$$

now gives us ΔH with the aid of Eq. (31).

The definition of a maximum supercooling temperature requires a bit of reasoning. We shall begin by explaining the physical meaning of the point C in Fig. 1.

Let us imagine a hypothetical experiment being carried out at fixed temperature $T_{I\text{-}N}$ and decreasing volume. The state of the system will move leftward along the isotherm labeled I in Fig. 1, toward the point C'. As it reaches C', there is nothing to tell the system that a phase transition should occur. Each molecule looks around itself and finds the volume allotted to it being decreased; but as long as its specific Helmholtz free energy continues to favor the isotropic phase, it will remain on the I curve. The breakdown takes place at C, where F_N becomes lower than F_I. Thus at C the system must go over to the nematic phase. $v_C(T)$, or $v^*(T)$, is thus the smallest volume that the system can attain in the isotropic phase at temperature $T_{I\text{-}N}$.

Now, construct a series of such "isotherms" at decreasing temperatures T_1, $T_2, \ldots,$ all below $T_{I\text{-}N}$. There will be *some* temperature T^* at which the smallest attainable isotropic volume $v^*(T^*)$ equals $v_{C'}$ at temperature $T_{I\text{-}N}$, i.e., $v^*(T^*) = v_{C'}(T_{I\text{-}N})$. Had we started the system at C' and decreased temperature at constant volume, the system if undisturbed would have remained isotropic all the way down to T^*. At T^*, however, the comparison between F_I and F_N requires the system to turn nematic. Thus T^* is the maximum supercooling temperature at constant volume, starting from $T_{I\text{-}N}$.

In actual experiments, sometimes it is more reasonable to look at the maximum supercooling temperature at constant *pressure*. In that case, we identify yet a different temperature T', $T_{I\text{-}N} > T' > T^*$, at which the maximum pressure $P_C(T')$ barely touches the flat segment of the actual $T_{I\text{-}N}$ isotherm, i.e., $P_C(T') = P_{C'}(T_{I\text{-}N})$. Starting from

TABLE II. Calculated results vs experiment.

	PAA		MBBA	
	Calc.	Expt.	Calc.	Expt.
$\Delta v/v$ (%)	0.32–0.41	0.30–0.36 [a]	0.11–0.14	0.11–0.14 [b,c]
ΔH_{I-N} (J/mole)	635–821	574–760 [a]	280–360	284–381 [d,e]
$T_{I-N} - T^*$ (K)	2.6–3.4	3.3 [f]	0.8–1.0	0.8 [f]

[a] Reference 9.
[b] Reference 12.
[c] Reference 14.
[d] Reference 17.
[e] Reference 18.
[f] Reference 16.

C' at T_{I-N}, then, reducing temperature at constant pressure moves the system leftward along $C'A'$, intersecting all the while the dashed portions of the isotherms below T_{I-N}. At T', the system turns nematic spontaneously.

In order to compare with the experiment of Ref. 16 (Table II), it is not totally clear as to whether T^* or T' should be used. Since the two values are reasonably close, and we are seeking only an order-of-magnitude agreement for this quantity, either will be satisfactory. T^*, being easier to identify and calculate, is given by

$$T^* - T_{I-N} \approx \frac{\Delta v}{2}\left(\frac{dv^*}{dT}\right)^{-1}\Bigg|_{T_{I-N}}, \qquad (40)$$

and is shown in Table II. Actually the so-called maximum supercooling temperature is often defined as the temperature at which the correlation length of scattering intensity diverges in a light-scattering experiment. Since this is rather outside the present scope of investigation, we publish it elsewhere.[19]

The collection of data and the calculation are done for the two most popular nematogens: PAA and MBBA. The phase-transition properties obtained are seen to be in excellent agreement with experiment. What we have presented is then a new scheme based on the mean-field model for checking consistencies among experimental — or predicting phase transition properties where none has been measured. We propose that measured properties for other nematic and cholesteric liquid crystals be subjected to similar analyses as presented here as soon as sufficient thermodynamic data are accumulated.

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