by numerically integrating the dynamical equations. They include the effects of boundaries, which increases the difficulty and may explain part of the complicated motion they report. Still, the mechanism seems clear: The system evolves toward a local minimum of $\tilde{f}$ at $\beta = 0$ or π; upon reaching the local minimum, $\tilde{f}$ changes, with the local minimum now a local maximum. The external source of the heat current provides the energy dissipated by this process.

The preceding analysis, based on helical solutions, cannot be quantitatively correct, for it is likely that the unstable helices develop into more complicated time-dependent states. Nevertheless, we expect the qualitative behavior to confirm our second basic result that an applied parallel magnetic field $H > H_c$ should induce a marked time-dependent deformation, whose character depends on the nature of the experiment: A persistent current in a torus should lead to a stable wide-angle helix with reversed but diminished supercurrent, whereas heat flow should produce anharmonic but periodic oscillations of the texture.

This work was supported in part by the National Science Foundation Grant No. DMR78-25258.

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Nematic-Isotropic Transition in Liquid Crystals

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(Received 6 June 1979)

Correlation functions and the Cotton-Mouton coefficient are calculated for liquid crystals beyond the mean-field approximation. My results in the context of a first-order transition are compared with the recent experiments of Keyes and Shane for N-[*p*-methoxybenzylidine]-*p*-butylaniline (MBBA) connecting with the possible tricritical nature of the nematic-isotropic transition.

Recently, Keyes and Shane[1] measured the gap exponent Δ for the nematic-isotropic (N-I) phase transition in N-[*p*-methoxybenzylidine]-*p*-butylaniline (MBBA) in the isotropic phase. They found $\Delta = 1.26 + 0.10$ which is consistent with the tricritical value $\Delta = 1.25$ but differs from the mean-field prediction $\Delta = 2$, giving the impression that the N-I transition is actually tricritical in nature. In this Letter, among other things, we show that by going beyond the mean-field approximation the so-called gap exponent Δ is not a constant but in general a function of temperature T. Depending on the temperature range under consideration, the effective exponent can deviate from the mean-field value and may be equal to 1.59, for example. Therefore, the measurement of Δ alone is insufficient in determining the critical or tricritical nature of the N-I transition. In addition, the deviation of the inverse of the Cotton-Mouton coefficient from linearity just above T_c is explained.

It has been known for some time that the de Gennes-Landau theory[2] is inapplicable near T_c in the isotropic phase. More recently, contrary to the current belief,[3] Lin and Cai[4] have shown that, quantitatively speaking, the same

de Gennes–Landau theory is also inapplicable in the nematic phase (although it does predict correctly[4,5] the asymmetry of the correlation-length exponents on the two sides of T_c as confirmed experimentally by Dong and Tomchuk[3]). The inadequacy of the mean-field approximation in describing the N-I transition is thus clear and there is obviously the need for a better theory.

Let us consider the simple Maier-Saupe Hamiltonian with an external magnetic field added,

$$H=-\sum_{i>j} J_{ij}P_2(\cos\theta_{ij})-h\sum_i P_2(\cos\theta_i),$$

where $J_{ij}=J_{ji}$, $J_{ii}=0$, and h is proportional to the square of the external field. For our purpose it is sufficient to work with the modified form:

$$H=-\sum_{i>j} J_{ij}P_2(\cos\theta_i)P_2(\cos\theta_j) - h\sum_i P_2(\cos\theta_i). \quad (1)$$

In fact, within our approximation to be presented below, the two forms have the same effects.[6]

In the mean-field approximation, when $h=0$ ($k_B=1$) one has $T_c=0.220\,19J_0$ and the supercooling temperature $T^*=0.2J_0$, where $J_0=\sum_j J_{ij}$. Also

$$S_1\equiv\left(\frac{\partial S}{\partial\alpha}\right)_{\alpha=0,\,S=0}=\frac{\beta J_0/5}{1-\beta J_0/5}=\epsilon^{-1}\sim\epsilon^{-\gamma} \quad (2)$$

and

$$S_2\equiv\left(\frac{\partial^2 S}{\partial\alpha^2}\right)_{\alpha=0,\,S=0}=\tfrac{10}{7}(1+\epsilon)\epsilon^{-3}\sim\epsilon^{-(\gamma+\Delta)}, \quad (3)$$

where the order parameter is $S\equiv\langle P_2(\cos\theta_i)\rangle$, $h\equiv J_0\alpha$, $\epsilon\equiv(T-T^*)/T^*$, and $\beta\equiv 1/T$. With use of Eqs. (2) and (3), one obtains immediately the mean-field value $\Delta=2$, in agreement with that from the de Gennes–Landau theory.

We now define the correlation function $G_{ij}\equiv\langle S_iS_j\rangle-S^2$ and its Fourier transform

$$G_{\vec{k}}\equiv N^{-1}\sum_{i,j} G_{ij}\exp[i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)],$$

where $S_i\equiv P_2(\cos\theta_i)$, N is the total number of molecules, and $\vec{R}_i$ is the position of the ith molecule. By definition, $G_{\vec{k}}$ satisfies the rigorous sum rule

$$N^{-1}\sum_{\vec{k}} G_{\vec{k}}=\langle\delta S^2\rangle\equiv\langle S_i^2\rangle-S^2. \quad (4)$$

Parallel to the procedure used in Ref. 5, the exact formula of Suzuki[6,7] for classical systems is used. When $i\neq j$, we have the following rigorous result:

$$\langle S_iS_j\rangle=\langle S_iF(\beta E_j)\rangle, \quad (5)$$

where $E_j\equiv\sum_i J_{ij}S_i$, and

$$F(\beta E_j)\equiv\frac{\int d\theta_j S_j\exp[\beta(E_j+h)S_j]\sin\theta_j}{\int d\theta_j\exp[\beta(E_j+h)S_j]\sin\theta_j}. \quad (6)$$

To obtain a closed equation for $\langle S_iS_j\rangle$, expand $F(\beta E_j)$ in a Taylor series and keep the fluctuation to linear terms so that

$$F(\beta E_j)=F(\langle\beta E_j\rangle) + \langle\delta S^2\rangle(\beta E_j-\langle\beta E_j\rangle)+\ldots, \quad (7)$$

where the thermal averages are taken in the mean-field approximation. Combining (5) and (7) and noting that $F(\langle\beta E_j\rangle)=S$, we have

$$\langle S_iS_j\rangle=S^2+\beta\langle\delta S^2\rangle(\textstyle\sum_{\vec{k}} J_{kj}\langle S_iS_k\rangle-J_0S^2), \quad i\neq j. \quad (8)$$

Equation (8) can be easily solved to give

$$G_{\vec{k}}=\left[\frac{\beta J_0\langle\delta S^2\rangle/g(\beta J_0\langle\delta S^2\rangle)}{1-\langle\delta S^2\rangle\beta J_{\vec{k}}}\right]\langle\delta S^2\rangle, \quad (9)$$

where $g(y)\equiv N^{-1}\sum_{\vec{k}}(1/y-J_{\vec{k}}/J_0)^{-1}$. $G_{\vec{k}}$ in (9) goes beyond the mean-field approximation and obviously satisfies the sum rule (4). For $\vec{k}=0$,

$$G_0=\frac{x}{1-x}\frac{1}{g(x)}\langle\delta S^2\rangle, \quad (10)$$

with $x\equiv\beta J_0\langle\delta S^2\rangle$.

In the high-temperature phase in the presence of external field H, the Cotton-Mouton coefficient $C=\delta n/H^2$ (where δn is the anisotropy of the refractive index) is proportional to S/h or S/α. Hence,

$$C\sim S/\alpha=S_1+\tfrac{1}{2}S_2\alpha+\ldots. \quad (11)$$

Note that the results for S_1 and S_2 given by Eqs. (2) and (3) involve the mean-field approximation, while rigorously we have

$$S_1/J_0=\beta(G_0)_{h=0,\,S=0}\equiv\beta G_1$$

and

$$S_2/J_0^2=\beta(\partial G_0/\partial h)_{h=0,\,S=0}\equiv\beta G_2.$$

Consequently,

$$C\sim C_1+C_2\alpha, \quad (12)$$

where $C_1=G_1(J_0/T)$ and $C_2=\frac{1}{2}G_2(J_0^2/T)$.

When $h=0$ and $S=0$, $\langle\delta S^2\rangle=\frac{1}{5}$ so that $x=T^*/T$ and

$$C_1=x^2/[(1-x)g(x)]. \quad (13)$$

For simplicity, we assume that the molecules are to be positioned in a simple-cubic lattice. In this case, $g(y)$ is a monotonic increasing function

such that $g(y) \geq y$ with $g(0) = 0$ and $g(1) = 1.516$. For $T \gg T^*$ ($x \ll 1$), $g(x) \simeq x$ so that $C_1 \simeq x/(1-x) = T^*/(T - T^*)$ and we recover the mean-field result. However, for $T \sim T^*$ ($x \sim 1$), $g(x)$ deviates very much from linearity and has most impact on the shape of C_1. In Fig. 1, the dots are calculated values of C_1^{-1} from (13). The straight line is there to guide the eye. The bending down of the dots near T_c corresponds exactly to what is observed[1,8] as presented in the inset (taken from Fig. 2 of Ref. 1). The unit of $H^2/\delta n$ in the inset is arbitrary.

In Fig. 2, our calculated C_2 as function of T is plotted. In the inset, the experimental value of C_2 is deduced from Fig. 1 of Ref. 1. The unit is arbitrary. The shape of the two curves definitely agree with each other (although a quantitative comparison is unjustified at this point; see discussion below).

Combining (10) and (13), we have

$$\frac{C_2}{C_1} = \frac{5}{7}\frac{1}{\epsilon^2}\left(1 + 2\epsilon - \frac{\epsilon}{1+\epsilon}\frac{g'(1/(1+\epsilon))}{g(1/(1+\epsilon))}\right), \tag{14}$$

where $g'(x) \equiv dg(x)/dx$. Note that when $g(x)$ is approximated by x, Eq. (14) reduces to $C_2/C_1 = \frac{5}{7}(1+\epsilon)/\epsilon^2$ which is nothing but the mean-field result $\frac{1}{2}S_2/S_1$ with use of Eqs. (2) and (3). However, as shown in (9) the exact form of the function $g(x)$ is what guaranteed the fulfillment of the sum rule (4). Furthermore, as is evident in (13) and Fig. 1, it is the deviation of $g(x)$ from x that gives rise to the bending down of the curve C_1^{-1} near T_c.

We may write (14) as

$$C_2/C_1 \sim \epsilon^{\Delta(\epsilon)} \tag{15}$$

emphasizing that the exponent Δ is, in fact, a function of ϵ, or equivalently, T. In Fig. 3, $\ln(C_2/C_1)$ is plotted against $-\ln\epsilon$. The dots are calculated from (14). The slope of the linear fit gives the effective Δ for the temperature range under consideration. We find $\Delta = 1.59$.

Compared with experimental value[1] of $\Delta = 1.26 \pm 0.10$, our calculated value of 1.59 does not seem to be close enough. However, this is not surprising at all. The simple Maier-Saupe Hamiltonian used here is known to be an oversimplification as far as numerical results are concerned. For example, it gives $(T_c - T^*)/T_c \sim 10^{-1}$ compared with the experimental value of 10^{-3}. The important point we want to bring out is that as Δ is concerned, the mean-field approximation is not reliable. And when one goes beyond this approximation, as we demonstrated above with the

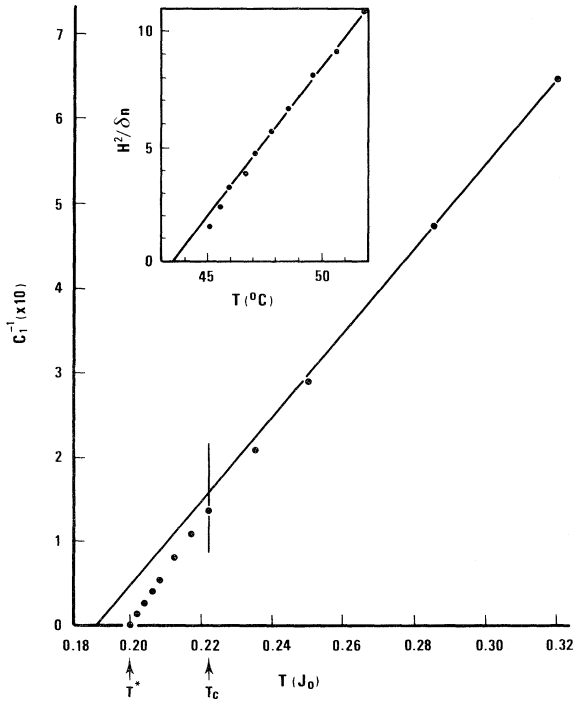

FIG. 1. Inverse of the calculated Cotton-Mouton coefficient C_1 vs temperature. The straight line is there to guide the eye. The inset is the experimental result from Fig. 2 of Ref. 1

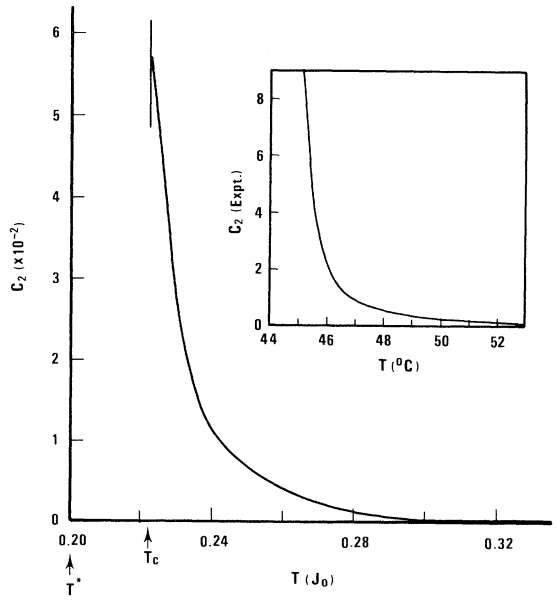

FIG. 2. Calculated coefficient C_2 vs temperature. The inset is the experimental result deduced from Fig. 1 of Ref. 1.

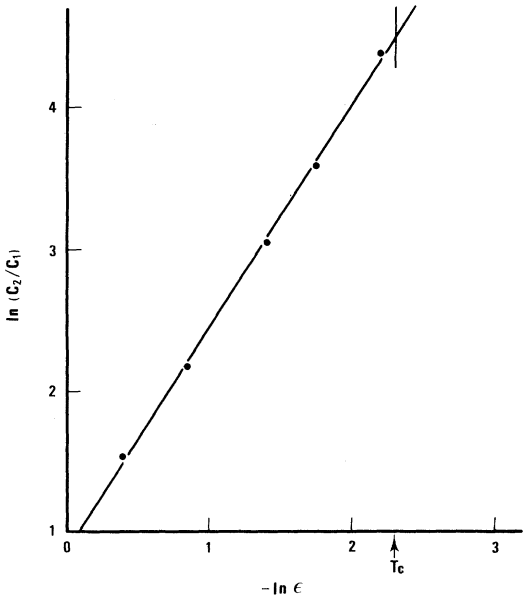

FIG. 3. Calulated $\ln(C_2/C_1)$ vs $\ln\epsilon$. The straight line is a linear fit.

simple Hamiltonian, Δ can indeed deviate greatly from the mean-field value. Therefore, a measured Δ (even if it is close to tricritical exponent) that disagrees with the mean-field value does not constitute a conclusive verification that the nematic-isotropic transition is not an ordinary critical point. It only says that the mean-field approximation is not good enough in describing this transition. Of course, the possibility of a tricritical point is not precluded. But this needs other evidence. In this regard, theoretical investigations along the line presented here with use of a more realistic Hamiltonian is most desired. In fact, preliminary results are rather encouraging and will be reported elsewhere.

We thank Glenn H. Brown, William L. McMillan, and Chia-Wei Woo for helpful discussions and various people at Northwestern University for their kind hospitality during the author's stay. This work is supported in part by the National Science Foundation through Grant No. DMR 76-18375.

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Special Phonons and Superconductivity in the Hexagonal Tungsten Bronzes

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(Received 13 December 1978; revised manuscript received 2 October 1979)

Neutron scattering measurements on single crystals of hexagonal tungsten bronzes $M_{0.33}WO_3$ reveal low-frequency, relatively dispersionless phonon branches which can be associated with the vibrations of the metal atoms M in the large open channels they occupy in the crystal structure. An analysis based on Eliashberg theory shows that the strong dependence of the superconducting transition temperature on the species M arises from these special phonons.

The possibility that the superconducting transition temperature within a group of materials could be raised substantially by varying lattice-dynamical properties has been explored in many studies. However, the direct relation between changing phonon properties and higher T_c's, although in principle understood within strong-coupling theory,[1] is difficult to verify experimentally. In this article, experimental results and a suitable analysis are presented showing that, for the

