is being pressure broadened at the higher pressures.

For these reasons, it is concluded that pressure-induced transitions do not significantly affect the value of the transition rate taken at 0.05 Torr but may become important at pressures greater than 0.3 Torr.

The experimentally determined spontaneous transition rate is 2.35×10^{-4} sec^{-1}. At present, the experimental uncertainties (a factor of 3) are sufficiently high that this cannot be considered to be in disagreement with the predicted value[5] of 1.27×10^{-4} sec^{-1}. Further work to reduce the experimental uncertainties is in progress.

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Phase Transitions in a Fluid of Biaxial Particles*

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A model is solved for a fluid of biaxial particles within a type of mean-field approximation. The results suggest that the phase diagram of such a fluid exhibits a special critical point where two second-order critical lines meet a first-order phase boundary in a sharp cusp. The features of the phase diagram suggest a new way to look for critical phase transitions and biaxial phases in liquid crystals.

Recently there has been a great deal of interest in critical phenomena in systems with phase diagrams of topological structures which indicate unusual critical behavior.[1,2] There has also been some interest in an as yet unobserved liquid-crystal phase with no long-range order in the position of the constituent molecules,[3] but with long-range orientational order of biaxial (i.e., nonuniaxial) rather than uniaxial symmetry.[4,5] In this Letter, we consider a model for a fluid of biaxial particles within a type of mean-field approximation. The results indicate that the phase diagram of such a fluid contains a critical point different from both ordinary critical points and tricritical points.[6] The special point occurs where two second-order critical lines meet a first-order phase boundary in a sharp cusp. The cusp, which occurs as the behavior of the molecules of the fluid crosses over from rodlike to platelike, is a region of enhanced stability for a biaxial phase. Thus, in addition to special critical behavior, our results also indicate a novel way to change the character of the nematic-isotropic transition and to search for biaxial liquid crystals.

The specific model which we have studied is a lattice model for steric interactions among hard rectangular plates.[5] The structure of the phase diagram, however, is the natural result of the Landau theory of phase transitions for a rotation-

ally invariant Hamiltonian with states described by a second-rank tensor order parameter. In particular, our results apply to models with anisotropic energies of interaction,[4] as well as to steric models. Although models can be constructed in which first-order phase transitions intervene to give different phase diagrams, we feel that the proposed diagram is the most likely one to occur for liquid-crystal systems which might exhibit a biaxial phase.

The hard-plate lattice model has already been described in Ref. 5. It is a much idealized model for a fluid of platelike particles, but even so it cannot be solved exactly by any known method. Thus, a type of mean-field approximation was employed which has been used for understanding excluded-volume effects in polymers.[7] The drawbacks of such a mean-field approximation include a lack of any good measure of quantitative errors and a tendency to indicate phase transitions to states with long-range order in systems for which the order is known to be of finite range. Nonetheless, the mean-field method has had well-established success in indicating qualitative features of phase diagrams.[2]

In Ref. 5, Shih obtained results which indicate that states of the model can be classified according to the long-range orientational order of the constituent particles as follows: biaxial states in which both the longest axes and the flat faces of the particles tend to be parallel, prolate uniaxial states in which the longest axes tend to be parallel, oblate uniaxial states in which the flat faces tend to be parallel, and isotropic states for which all orientations occur equally. Not surprisingly, biaxial states can occur only if the particles are neither very rodlike nor very much like square plates and then only at relatively high density. Prolate uniaxial states occur for rodlike particles (length/width $\gtrsim 0.3$) at intermediate densities, and oblate uniaxial states occur for platelike particles (length/width $\lesssim 0.3$) also at intermediate densities. Isotropic states occur at low density.

We now consider results for a case which elucidates the interesting crossover region between rodlike and platelike behavior. We consider particles that are just marginally platelike (oblate) in their excluded-volume interactions. We then include an orientation-dependent interaction energy which favors rodlike (prolate) order. Since excluded-volume interactions contribute to the entropy, they dominate at high temperature. Rodlike interactions dominate at low temperature, and the crossover region occurs in between. This model should serve to elucidate what may be physically more relevant cases in which factors other than temperature control the effective asymmetry of the molecules. The model corresponds to the following Gibbs free energy:

$$G' = -D[(\alpha_1+\alpha_2)^2 + (\alpha_3+\alpha_4)^2 + (\alpha_5+\alpha_6)^2] + G(\{\alpha\}), \quad (1)$$

where the α's are the fractions of molecules with each orientation, and $G(\{\alpha\})$ is given by Eq. (7) of Ref. 5 with the parameters l and w in previous equations set equal to 6 and 2.3, respectively. The parameter which determines the effective molecular asymmetry can be taken as RT/D, which we denote T^*, with R the gas constant and where extensive quantities, like D, refer to one mole of molecules.

We have found the states of minimum G' by varying the density together with the α's to find numerically the state of lowest Gibbs free energy at given T^* and effective pressure p^*, where $p^* = \text{pressure} \times V_0/RT$, with V_0 being a standard volume. Our results for the phase diagram are summarized in Fig. 1. The structure of the phase diagram is rather remarkable in that in the narrow crossover region between rodlike and platelike behavior the biaxial phase is predicted to occur for a wide range of p^*. Also, the transition from the isotropic to the uniaxial phases,

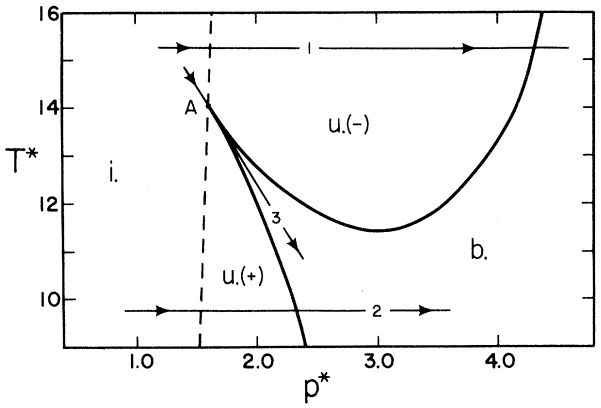

FIG. 1. Phase diagram of a fluid of biaxial particles showing the crossover region between rodlike and platelike behavior. The phases indicated are i, isotropic; $u(-)$, oblate uniaxial; $u(+)$, prolate uniaxial; b, biaxial. First-order phase-transition boundaries, dashed lines; second-order boundaries, heavy solid lines. T^* is the effective molecular asymmetry; p^* is the effective pressure. The point A is a special critical point. The behaviors of the order parameters along the paths 1, 2, and 3 are discussed in the text.

which is usually first order, occurs in a special type of second-order transition at the point marked A. All this behavior can be readily understood in terms of the Landau theory of phase transitions.

The basis of the Landau theory is the assumption that there is a free energy $\tilde{G}$ which can be regarded as an analytic function of an appropriate order parameter whose value is determined by minimizing $\tilde{G}$. The first step in applying the theory is the identification of the order parameter. It turns out that, although our model is of cubic symmetry, its behavior can be understood by proceeding directly to the physically relevant case in which the order parameter is a second-rank tensor property of a system with full rotational symmetry. Essentially any traceless second-rank tensor property which is an average of a molecular property of biaxial symmetry could serve as an order parameter. For example, in our calculations we have used the following molecular tensor:

$$\overleftrightarrow{Q}_m = \vec{n}\vec{n} - \vec{m}\vec{m}, \tag{2}$$

where $\vec{n}$ is a unit vector along the longest axis of the molecule, and $\vec{m}$ is a unit vector normal to the plane of the molecule. The average of $\overleftrightarrow{Q}_m$ over molecular orientations, $\overleftrightarrow{Q}_{av}$, reflects the overall symmetry of the state of system. Without loss of generality, we may write $\overleftrightarrow{Q}_{av}$ in the following representation[4]:

$$\overleftrightarrow{Q}_{av} = U \begin{bmatrix} -\frac{1}{2}r(\cos\theta + \sqrt{3}\sin\theta) & 0 & 0 \\ 0 & -\frac{1}{2}r(\cos\theta - \sqrt{3}\sin\theta) & 0 \\ 0 & 0 & r\cos\theta \end{bmatrix} U^{\dagger}, \tag{3}$$

where U is a unitary rotation matrix. It can be seen that for isotropic states $r = 0$, for prolate uniaxial states $r > 0$ and $\cos(3\theta) = 1$, for oblate uniaxial states $r > 0$ and $\cos(3\theta) = -1$, and for biaxial states $r > 0$ and $|\cos(3\theta)| \neq 1$.

Having specified the order parameter, we may now consider the Landau expansion for $\tilde{G}$. It can be shown that since $\tilde{G}$ must be invariant under rotations, its expansion must be a polynomial in the two invariants $r^2\cos(3\theta) = 4\det\overleftrightarrow{Q}_{av}$ and $r^2 = \frac{2}{3}\mathrm{tr}\overleftrightarrow{Q}_{av}^2$. For our model, with p^* and T^* in the neighborhood of the point A, the expansion of $\tilde{G}$ to sixth order in r is well approximated by

$$\tilde{G} = -a(p^* - p_A^*)r^2 + b(T^* - T_A^*)r^3\cos(3\theta) + cr^4 + dr^5\cos(3\theta) + er^6 + fr^6\cos^2(3\theta), \tag{4}$$

where (p_A^*, T_A^*) corresponds to the point A and the constants a through f turn out to be positive. It is readily verified that the structure of Eq. (4) implies all of the major features of the phase diagram.

The kinds of variations of r and θ with p^* and T^* are illustrated by the behaviors along the three paths 1, 2, and 3 in Fig. 1. On path 1, with T^* constant and $> T_A^*$ and p^* increasing, there is a first-order transition to an oblate uniaxial state followed by a second-order transition to a biaxial state. On path 2, with T constant and $< T_A^*$, there is a first-order transition to a prolate uniaxial state followed for a second-order transition to a biaxial state. (This corresponds to the case studied by Freiser.[4]) For paths such as 1 and 2, the discontinuity in r at the isotropic-uniaxial transition is roughly proportional to $|T^* - T_A^*|$. Finally on path 3 with p^* and T^* varied together so that $T^* - T_A^* = -4.1(p^* - p_A^*)$, we observe a second-order transition directly to a biaxial phase. The biaxial phase region extends for T^* above and below the path within limits proportional to the $\frac{3}{2}$ power of the distance along the path from A.

In the context of the simple Landau theory, the point A corresponds to an "accidental" second-order phase transition. In order to see the special nature of this transition, it is necessary to consider fluctuations at the various transitions. The second-order phase transitions from uniaxial to biaxial phases involve the establishment of an ordering axis in a plane perpendicular to the unique axis, and thus the dimensionality of the critical order parameter is 2, as in an XY model. At the point A, however, there are fluctuations in all the elements of $\overleftrightarrow{Q}_{av}$, indicating a five-dimensional critical order parameter. In contrast to the situation at tricritical points, there are no fluctuations indicated for any nonordering density.

The special critical behavior at A is of course only indicated by a mean-field approximation to an idealized model. It remains to discover liquid crystals or other physical systems which might manifest the predicted behavior. The structure of the predicted phase diagram suggests an ap-

proach in this quest. First, note that the extensive biaxial phase region on the right side of Fig. 1 corresponds to high density and/or low temperature. Experience with ordinary nematic liquid crystals indicates that these conditions are likely to lead to crystallization before a biaxial phase could appear. However, according to Fig. 1, it should also be possible to reach the biaxial phase by adjusting T^*, the effective molecular asymmetry parameter, without necessarily decreasing the range of stability of the liquid crystal phases or changing conditions likely to affect crystallization. The biaxial phase and the special critical behavior should both appear when we achieve a crossover between rodlike and platelike behavior. One way to do this would be to make mixtures of rodlike and platelike molecules[8] with similar melting points and favorable dispersion interactions.[9] The phase diagram for such a two-component fluid would be similar to that in Fig. 1 with concentration playing the role of T^*. Furthermore, such a mixture would ameliorate the ever-present chance that crystallization might intervene before a biaxial phase could be achieved. Even before a biaxial phase appears, the onset of the crossover region might be investigated by measuring the behavior in the discontinuity in the order parameter r at the isotropic-uniaxial transition and looking for a linear decrease as the point A is approached.

In conclusion, we have solved a model in a mean-field approximation, and the results suggest that a fluid of biaxial particles might be a most interesting system for both theoretical and experimental study of phase transitions.

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Neutron-Scattering Observations of Critical Slowing Down of an Ising System

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We have studied the dynamics of the order-disorder phase transition in Ni_3Mn by neutron-scattering techniques. The relaxation time constant for the long-range order is about 90 min at a temperature 15°C below the critical temperature, but closer to the critical temperature it increases by more than an order of magnitude. This critical slowing down varies as the reduced temperature to a power of 1.04 ± 0.09.

The full dynamic behavior of Ising systems is not built into the Hamiltonian since the Hamiltonian does not provide a mechanism for changing the z component of spin on any atom. A number of recent theoretical treatments[1-6] have introduced an external spin-flipping mechanism to bring the system to equilibrium and, on this basis, have predicted critical slowing down with a time constant given by the reduced temperature raised to some power.

Order-disorder critical phase transitions in binary alloys are believed to be excellent examples of Ising-type phase transitions.[7,8] The Hamiltonian for the alloy ordering process is equivalent to the Ising Hamiltonian if it is assumed that the ordering energy varies linearly with the number of neighbors of a given type. The mechanism which actually moves the atoms from one lattice