b_F is the Foldy term due to the interaction of the neutron with the electrostatic potential of a bound electronic charge, Z is the atomic number, b_{ne} is the neutron-electron scattering length, and $f(\sin\theta/2\lambda)$ is the electronic form factor. For forward scattering $f=1$. Using the value $b_F = -1.468\times10^{-3}$ fm calculated by Foldy[14] and the value $b_{ne} = (-1.38 \pm 0.02)\times10^{-3}$ fm measured by Koester, Nistler, and Waschkowski,[13] one obtains a nonnuclear term $b_e = 8.28\times10^{-3}$ fm whose value is greater than the experimental error on the measured b value. Then the nuclear force scattering length for uranium is given by $b_{NF} = (8.409 \pm 0.0062)\times10^{-13}$ cm.

In conclusion, the very accurate determination of the neutron coherent scattering length of natural uranium makes it possible to obtain an accurate determination of the neutron coherent scattering length of the isotope ^{238}U. We intend to continue these fundamental constant measurements in the actinide series, in particular for ^{235}U and ^{232}Th (for which contradictory results exist).

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Monte Carlo Study of the Isotropic-Nematic Transition in a Fluid of Thin Hard Disks

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The first numerical determination of the thermodynamic isotropic-nematic transition in a simple three-dimensional model fluid, viz., a system of infinitely thin hard platelets, is reported. Thermodynamic properties were studied with use of the constant-pressure Monte Carlo method; Widom's particle-insertion method was used to measure the chemical potential. The phase diagram is found to differ considerably from predictions of a second-virial ("Onsager") theory. Virial coefficients up to the fifth were computed; b_5 is found to be negative.

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Beginning with the work of Onsager[1] a great variety of theoretical models have been proposed that aim to link the thermodynamic properties of liquid-crystal-forming fluids to the intermolecular interactions of the constituent molecules.[2] In assessing the relative merits of these models, direct comparison with experiments on real liquid crystals has often been less than conclusive because disagreement between theory and experiment could be blamed on the use of unrealistic models for the intermolecular interactions, rather than on fundamental deficiencies of the theoretical approach used. For lack of exact results there is clearly a great need for numerical data on simple model systems. Surprisingly enough, though some simulations on the isotropic-nematic transition have been reported,[3] these have been limited to lattice models. Such models leave out an essential characteristic of liquid crystals (viz., the fact that it is a *liquid*). A fluid of hard spherocylinders was studied by Veillard-Baron,[4] but the isotropic-nematic (I-N) transition was not located.

In this Letter we report, what is to our knowledge, the first determination of the thermodynamic I-N transition in a simple three-dimensional model fluid. The model that we have chosen to study is a fluid of infinitely thin, hard platelets of diameter σ (see Fig. 1). There are several reasons for studying this particular system: First of all, it is *guaranteed* to have a nematic phase at high densities. As the platelets have zero volume, this system cannot crystallize. In contrast, in model systems with a finite density of closest packing one must first make sure whether a thermodynamically stable nematic phase can exist at all. Secondly, the hard-platelet fluid is a "one-parameter" system; there is only one independent thermodynamic variable, viz., the density $\rho^* = \rho\sigma^3$. In this respect the hard-platelet system is similar to the hard-sphere fluid, and one may hope that the hard-platelet fluid could serve as a reference system for a whole class of nematogens, viz., those that consist of disklike molecules. Finally, and perhaps most importantly, results on the hard-platelet system provide a direct test of the Onsager model.[1] To be more precise, the Onsager model aims to describe the I-N transition in a system of thin hard rods; it neglects contributions to the free energy that involve virial coefficients higher than the second. In the limit that the length-to-width ratio of the rods goes to infinity, higher virial coefficients are indeed negligible. The special feature of the hard-platelet system is that if one neglects virial coefficients higher than the second, it is isomorphous with a system consisting of infinitely thin rods.[5] But in the hard-platelet fluid higher virial coefficients are nonnegligible (see Table I). Consequently, a study of the latter system enables us to assess to what extent the presence of higher virial coefficients affects the validity of the Onsager predictions. In view of what follows, it is useful to briefly summarize these predictions: At low densities (i.e., below the I-N transition) the equation of state is of the form

$$P = \rho^* + \rho^{*2} b_2 \tag{1}$$

(for disks, $b_2 = \pi^2/16$). In Eq. (1), and in what follows, we use reduced units: $kT = 1$ and $\sigma = 1$. A phase transition is predicted at $P = 22.89$, $\rho_I = 5.334$, and $\rho_N = 6.846$. Here we have used the values that Kayser and Raveché obtained by numerically solving the Onsager model.[6] The order parameter in the nematic phase is defined as

$$S = N^{-1} \sum_{i=1}^{N} P_2(\vec{u}_i \cdot \vec{n}), \tag{2}$$

where $\vec{u}_i$ is the unit vector describing the orientation of molecule i, and $\vec{n}$ is the nematic director. At the I-N transition the value of S is predicted to jump discontinuously from 0 to 0.784. Note that the Onsager theory predicts a very strong first-order transition ($\Delta\rho^*/\rho^* = 26\%$).

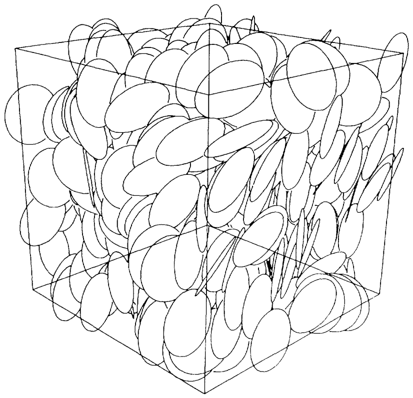

FIG. 1. A typical configuration of a system of 400 hard platelets at a density $\rho = 4.8$. This configuration has nematic order.

From a computational point of view the constant-pressure Monte Carlo (MC) method[7] is best suited to study the equilibrium properties of the hard-platelet system. The chemical potential of the hard-platelet fluid was measured *directly*, employing Widom's relation between the excess chemical potential, $\mu_{\rm ex}$, and the probability, $P_{\rm acc}$, that a platelet, added at random to the system, will be accepted[8]: $\mu_{\rm ex} = -kT \ln\langle P_{\rm acc}\rangle$. In this particular system the probability of acceptance is such that, even at the highest densities studied, the estimated error in $\mu_{\rm ex}$ was less than 2%. In fact, we devised several methods to improve the statistics on $\mu_{\rm ex}$; these will be described in a future publication.[9] As a check on the reliability of the MC data we computed the virial coefficients of the hard-platelet fluid up to b_5, using the diagram techniques developed by

Ree and Hoover.[10] The results are shown in Table I. Note that b_5 is *negative*. We know of no other example of a three-dimensional, purely repulsive hard-core system that has a negative virial coefficient as early as b_5. We find that at low pressures ($P < 5$), the MC results are, to within the computational error, indistinguishable from the predictions of a five-term virial series. We performed constant-pressure MC simulations on a system consisting of 100 hard platelets at pressures in the range $1 < P < 25$; in all cases periodic boundary conditions were employed. Additional simulations with $N = 50$ and $N = 400$ were carried out to test for systematic system size dependences, especially around the phase transition. Initially, the system was prepared in a configuration with all platelets oriented parallel; the centers of mass were distributed randomly over the box. Subsequent runs were started from previously equilibrated lower or higher density configurations. In every case at least 10^4 passes ($= 10^6$ moves for $N = 100$) were reserved for equilibration (considerably more close to the I-N transition). Equilibrium averages were accumulated in runs lasting between 2×10^4 and 10^5 passes.

The dependence of ρ^* and μ on P is shown in Fig. 2. For the sake of comparison the five-term virial series is also shown. Note that at higher pressures the virial series predicts a lower density than was observed in the MC simulations; this implies that at least some of the higher virial coefficients must also be negative. Around $P = 14.25$ we observe a small discontinuity in the density ($\rho^* = 3.78 \rightarrow \rho^* = 4.07$ for $N = 400$). The width of the density gap is strongly system-size dependent: It is largest for $N = 400$ and is completely absent for $N = 50$. We wish to emphasize that, even for the largest systems studied, we never observed any systematic dependence of the measured equilibirum properties on the density of the initial configuration (i.e., no hysteresis). On the basis of Landau's symmetry arguments (see, e.g., Ref. 5) one would expect a first-order isotropic-nematic transition in three dimensions. The MC results are certainly compatible with a weak first-order transition but on the basis of the simulation results alone we cannot rule out other possibilities. At $P = 14.25$ the chemical potential of the high- and low-density phases is equal to within experimental accuracy. The precise location of the phase transition was determined in the following way: Polynomial fits were made to the high- and low-density branches of the equation of state. We then computed μ at high densities by integrating $\partial\mu/\partial P = 1/\rho^*$ along the isotherm, keeping $P_{I\text{-}N}$ (the transition pressure) as an adjustable parameter. The value of $P_{I\text{-}N}$ quoted above is the one that yielded the best agreement between μ obtained by integration and μ obtained directly by use of the particle-insertion method. Even so the uncertainty in the transition pressure is still ±3%. Note that the discontinuity in slope of μ vs P is barely visible in Fig. 2. The order parameter S, defined as the

TABLE I. Virial coefficients b_n ($n = 2$–5) for hard platelets, expressed in units $\sigma^{3(n-1)}$ (column I) and in units $b_2^{\,n-1}$ (column II).

n	b_n I	b_n II
2	$\pi^2/16$	1
3	$0.1692 \pm 1 \times 10^{-4}$	$0.4442 \pm 4 \times 10^{-4}$
4	$0.004\,80 \pm 1 \times 10^{-4}$	$0.0205 \pm 5 \times 10^{-4}$
5	$-0.008\,67 \pm 3 \times 10^{-4}$	$-0.060 \pm 1 \times 10^{-3}$

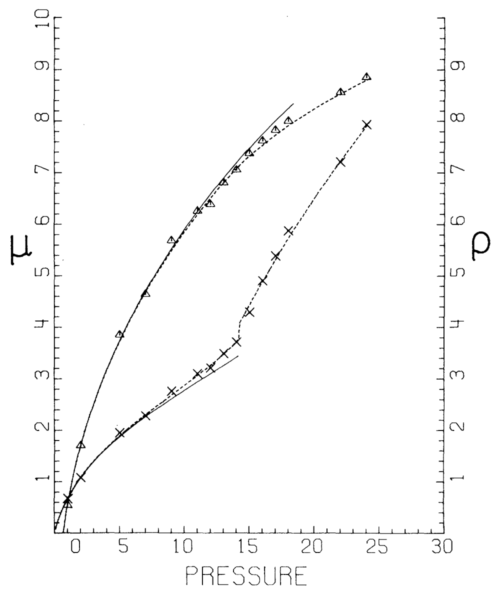

FIG. 2. Pressure dependence of the average density ρ (crosses) and the chemical potential μ (triangles), as obtained from constant-pressure MC simulations. To improve the legibility of the figure only a fraction of the measured points has been included. Dashed lines: polynomial fits to ρ and μ. Solid lines: five-term virial series expressions for ρ and μ. All quantities are in reduced units.

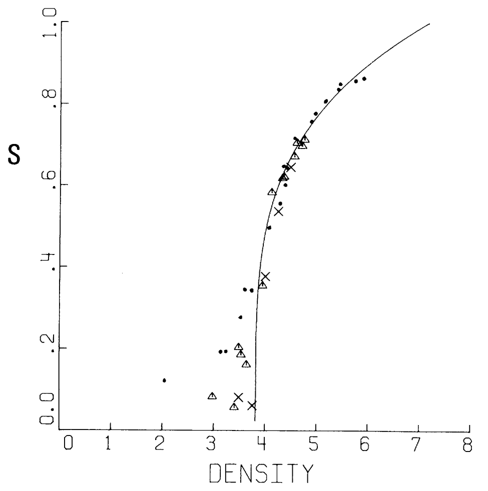

FIG. 3. Density dependence of the nematic order parameter S, for different system sizes: $N = 100$ (points), $N = 400$ (triangles), $N = 800$ (crosses). The drawn line is the best single-power-law fit to the MC data (exponent $\beta \simeq 0.25$). Points at densities below the estimated density of the nematic phase at coexistence were not included in the fit.

largest eigenvalue of the matrix

$$Q_{\alpha\beta}=N^{-1}\sum_{i=1}^{N}(3u_i^{\alpha}u_i^{\beta}-\delta_{\alpha\beta})/2,$$

was studied as a function of density. Near the I-N transition a very strong system size dependence of S was observed (see Fig. 3). We attempted to fit the density dependence of S just above the I-N transition by a power law of the form $S=A(\rho^*-\rho_0^*)^{\beta}$. Strictly speaking, there is no reason to expect a power-law dependence of the order parameter close to a first-order transition. However, in real liquid crystals of rodlike molecules the density dependence of the order parameter agrees quite well with a mean-field description, which implies that close to the transition $\beta=\frac{1}{2}$. This behavior was not observed in the present simulation; in fact, it was found that $\beta=\frac{1}{2}$ gave a rather poor fit. The best fit was obtained with $\beta \simeq 0.25$. We do not consider this as evidence for nonclassical behavior of the exponent β; more likely it signifies that the range of densities over which S follows a simple power law is rather narrower than the range over which we tried to fit it. At ρ_N^* we find a value $S \simeq 0.37 \pm 0.1$.

In summary, we find that the real phase diagram of the hard-platelet fluid differs dramatically from the phase diagram that one would predict if all virial coefficients higher than the second vanish. We observe an I-N transition at $P=14.25$ with $\rho_I^*=3.78$ and $\rho_N^*=4.07$ (compared with $P=23.01$, $\rho_I^*=5.35$, $\rho_N^*=6.75$ for the Onsager theory). In contrast to the Onsager model the phase transition in the hard-platelet system is quite weak: The jump in density is 7% (cf. 26%) and the jump in the order parameter is 0.37 (cf. 0.784). At high densities we find that $P \simeq 3\rho^*$, in agreement with the Onsager prediction. It is, however, easy to show that this result is independent of the details of the model; any model that treats the geometrical constraints on the molecular orientations in a dense hard-platelet nematic correctly should lead to this prediction.

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