Phase Diagram of a System of Hard Ellipsoids

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The phase diagram of a system of hard ellipsoids of revolution was investigated by means of constant-pressure Monte Carlo simulation. Prolate as well as oblate ellipsoids were considered. The results for the isotherms of the system at several different values of the length-to-breadth ratio are presented. Four different phases of the system are identified and a tentative picture of the phase diagram is given.

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At present our knowledge of systems composed of nonspherical particles is very limited compared to what we know about the hard-sphere system. Since nonsphericity is expected to give rise to new types of behavior such as liquid-crystalline order, it is of considerable interest to study its effects. Several theories have to date been proposed to describe the possibility of long-range orientational order in nonspherical-hard-particle fluids.[1] Thus far the predictions of such theories could not be tested, as no numerical data were available on the orientationally and/or translationally ordered phases of these systems. (For the isotropic phase see, however, Vieillard-Baron.[2]) More seriously the existing hard-particle theories ignore the possibility of freezing altogether. As a consequence these theories might well predict a transition to an orientationally ordered fluid phase at a pressure where the solid phase is actually thermodynamically more stable.

In this Letter we present a Monte Carlo study of different systems composed of hard ellipsoids of revolution conveniently parametrized by the length-to-breadth ratio $x=a/b$, where a and b denote the lengths of the major and minor axes of the ellipsoids. This model includes as limiting cases, the hard-sphere, hard-platelet, and hard-needle systems, about which independent information is available.[3,4] Before presenting our results, we briefly describe the computational procedure.

We used constant-pressure Monte Carlo[5] simulation on systems of $N\approx 10^2$ particles. The high-density runs were started from a close-packed configuration obtained by expanding an fcc sphere packing by a factor of x along the (111) direction, yielding an orthorhombic lattice structure. We did not investigate the possibility that another crystal structure yields a more stable solid; experience with the hard-sphere solid suggests that the free-energy difference between different closed-packed structures is slight.[6] Periodic boundary conditions were employed. The number of particles was chosen such that the shape of the periodic box closely approximated a cube. Allowed configurations were generated with use of an overlap criterion for ellipsoids given by Vieillard-Baron.[7] The volume-changing move was made after every sweep of particle moves. In the high-density region the different side lengths of the box were allowed to fluctuate independently, to allow for a possible nonisotropic density dependence of the shape of the unit cell. A typical number of 10^3 sweeps (10^5 particle moves) was used to obtain equilibrated configurations, starting from equilibrated samples at a slightly higher or lower density. Averages calculated from typically 10^4 equilibrium configurations included the density ρ, the orientation-averaged pair distribution function $g_{00}^{(2)}(\vec{r}_{ij})$, the short-range second-rank order parameters $g_{22}^{(2)}(\vec{r}_{ij})=\langle P_2(\hat{\Omega}_i\cdot\hat{\Omega}_j)\rangle$, and the structure factor $S(\vec{k})$ for three orthogonal Bragg vectors. The unit of volume chosen was $V_u=8ab^2=8xb^3$. This yields the following dimensionless pressure $P^*=\beta PV_u$ and density $\rho^*=\rho V_u$.

Isotherms were calculated for the following

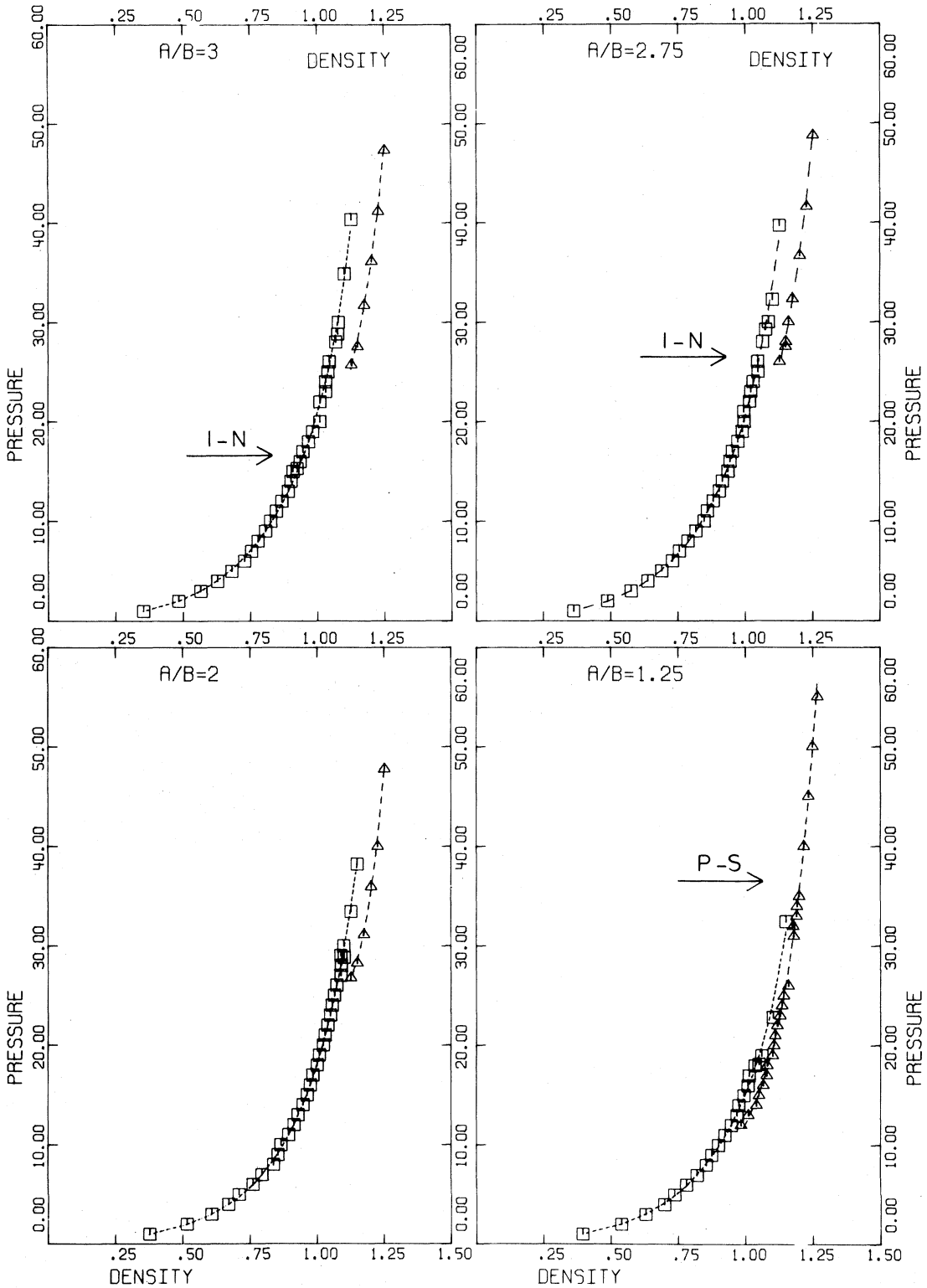

FIG. 1. Isotherms for systems of prolate ellipsoids with $x = 3.00$, 2.75, 2.00, and 1.25 (fluid branch, open squares; solid branch, open triangles). All dashed lines are polynomial fits to guide the eye. Pressure and density are given in the reduced units as explained in the text. The arrows indicate the approximate location of the isotropic-fluid to nematic-liquid-crystal transition in the cases $x = 3.00$ and $x = 2.75$. For $x = 1.25$ the plastic to ordered-solid transitions is likewise indicated.

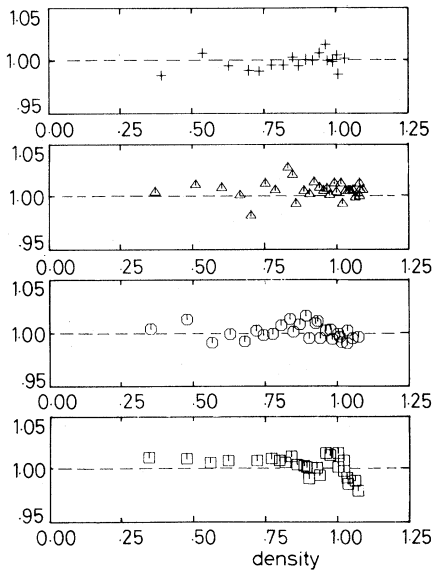

FIG. 2. The ratios of the densities at equal pressure of systems with inverse length-to-breadth ratios, plotted as a function of the density of the system with $x > 1$. From top to bottom we have crosses, $x = 1.25$ and $x = 0.8$; triangles, $x = 2.00$ and $x = 0.5$; circles, $x = 2.75$ and $x = 0.3636$; squares, $x = 3.00$ and $x = 0.3333$.

length-to-breadth ratios: $x = 1.25$, 2.00, 2.75, 3.00 (prolate) and $x = 0.8$, 0.5, 0.3636..., 0.3333... (oblate). The results for the prolate systems are shown in Fig. 1.

We found a remarkable symmetry between the systems with inverse length-to-breadth ratios. This is evident from Fig. 2, where we plot the ratio of the densities at equal pressure of pairs of systems having inverse length-to-breadth ratios. At low pressures, such symmetry is to be expected, as in the present units the second virial coefficients for x and $1/x$ ellipsoids are equal.[8] At higher pressures the observed symmetry, which even persists in the solid phase, is quite surprising. However, knowledge about the limiting cases $x = 0$ and $x = \infty$ indicates that this symmetry can be only approximate.[4] The Monte Carlo runs were made starting from either a high-density solid, yielding the solid branch of the isotherms, or by compressing a low-density fluid. (Spontaneous nucleation has been observed, but not characterized, for $a/b = 1.25$ and for $b/a = 1.25$.) The typical density difference between the fluid and solid branches was of the order of (5–10)%. In the cases with $x = 2.75$ and 3.00 and their inverses $x = 0.36...$ and 0.33..., an orientationally ordered fluid phase was found in the higher-density part of the fluid branch.

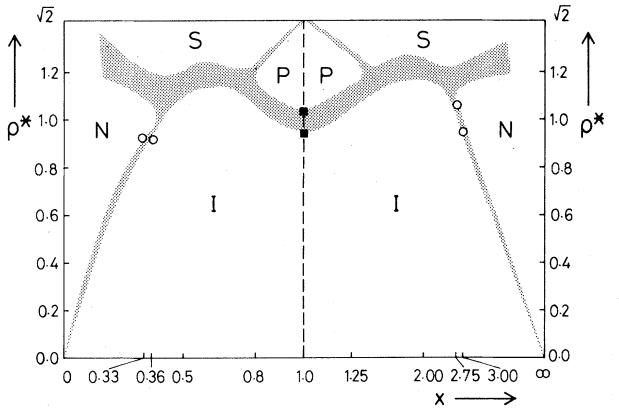

FIG. 3. Tentative picture of the phase diagram. Oblate ellipsoid systems correspond to $x < 1$. Open circles indicate the location of the observed isotropic to nematic transitions. The black squares are the values for the coexistence densities of the hard-sphere liquid to plastic-solid transition. The upper limit of the density, $\rho_u = \sqrt{2}$, corresponds to close packing.

The transition from the isotropic fluid towards this ordered phase shows no observable hysteresis in an expansion-compression cycle. The density change at the transition was too small to be detected with the present computational accuracy [(1–2)%]. The appearance of the orientationally ordered phase could be monitored by the tail of the short-range second-rank order parameter, which approaches the square of the long-range order parameter $\langle P_2 \rangle$ for large separations.

No ordered fluid phase was found for $0.5 \leq x \leq 2$ indicating that the bounds on the nematic region in the phase diagram must lie somewhere between $x = 2.75$ and $x = 2.00$ for the prolate ellipsoids, and $x = 0.36...$ and $x = 0.5$ for the oblate case. For the cases $x = 1.25$ and $x = 0.8$ the lower-density part of the solid branch was found to be a plastic solid, i.e., the particles were translationally ordered, but the order parameter $\langle P_2 \rangle$ was zero, suggesting that the particles are free to reorient. The density change at the transition from this plastic solid to the ordered solid phase (around $\rho = 1.21$) was too small to be observed. No evidence was found for other types of liquid-crystalline order (e.g., smectic) in any of the cases studied. The precise location of the thermodynamic liquid-to-solid transition, which requires the computation of the absolute free energy of the solid phase, is a point which we are currently investigating. Combining all the information up to now we arrive at the following tentative picture of the phase diagram (Fig. 3). Note that

in the present units the isotropic-nematic transitions for hard platelets ($x = 0$) and hard needles ($x = \infty$) occur at zero density. Details of the calculations as well as comparison with current theories will be presented elsewhere.

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