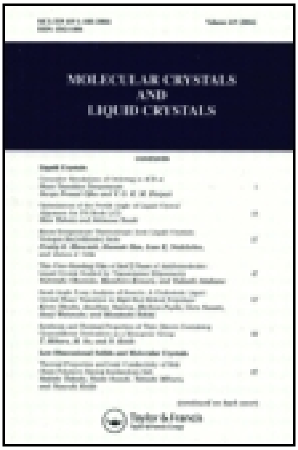

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Phase Diagram of Hard Ellipsoids of Revolution

Daan Frenkel [a] , Bela M. Mulder [b] & John P. Mctague [c d]

[a] Fysisch Laboratorium, Rijksuniversiteit Utrecht, 3508, TA, Utrecht, The Netherlands

[b] Institute for Theoretical Physics, Rijksuniversiteit Utrecht, 3508, TA, Utrecht, The Netherlands

[c] National Synchrotron Light Source, Brookhoven National Laboratory, Upton, NY, 11973, U.S.A.

[d] Executive Office of the President, Office of Science and Technology, Washington, DC, 20506, U.S.A.

Version of record first published: 17 Oct 2011.

To cite this article: Daan Frenkel , Bela M. Mulder & John P. Mctague (1985): Phase Diagram of Hard Ellipsoids of Revolution, Molecular Crystals and Liquid Crystals, 123:1, 119-128

To link to this article: http://dx.doi.org/10.1080/00268948508074770

*Mol. Cryst. Liq. Cryst.*, 1985, Vol. 123, pp. 119–128
0026-8941/85/1234-0119/$15.00/0

Printed in the United States of America

# Phase Diagram of Hard Ellipsoids of Revolution†

DAAN FRENKEL

*Fysisch Laboratorium, Rijksuniversiteit Utrecht 3508 TA Utrecht, The Netherlands.*

*BELA M. MULDER*

*Institute for Theoretical Physics, Rijksuniversiteit Utrecht 3508 TA Utrecht, The Netherlands*

and

JOHN P. McTAGUE‡

*National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.*

(*Received August 6, 1984*)

We present the results of Monte Carlo simulations of the equation of state of hard ellipsoids of revolution with axial ratio's $a/b$ = 3, 2.75, 2, 1.25, 0.8, 0.5, 0.3636 and 0.3333. We identify four distinct phases, *viz.* isotropic fluid, nematic fluid, ordered solid and plastic solid. In all cases the thermodynamic phase transitions are located by free energy computation. We find nematic phases only for $a/b \geqslant 2.75$ and $a/b \leqslant 1/2.75$. A plastic solid phase is observed for $1.25 \geqslant a/b \geqslant 0.8$. It is found that the phase diagram is surprisingly symmetric under interchange of the major and minor axes of the ellipsoids.

## INTRODUCTION

Since the work of Onsager[1] it has been known that liquid crystalline order can be induced by purely repulsive anisotropic intermolecular

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†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

‡Present Address: Executive Office of the President, Office of Science and Technology, Washington, DC 20506, U.S.A.

interactions. In the particular case considered by Onsager, viz. that of thin spherocylinders of length $L$ and diameter $D$ with $L/D \rightarrow \infty$ the transition from the isotropic to the nematic phase takes place at a number density $\rho$, such that $\rho L^2 D = O(1)$. At the transition the packing fraction, i.e. the fraction of the volume occupied by molecules, is of order $D/L$, which vanishes in the limit $L/D \rightarrow \infty$. However, if we consider values of $L/D \approx 3$-$4$, typical of real liquid crystal forming molecules it is obvious that the isotropic-nematic and liquid-solid transitions occur at densities that are comparable. In fact, below a certain minimum anisometry one should expect that the isotropic-nematic transition is pre-empted by the isotropic-solid transition. Unfortunately, at finite packing fractions all hard-core models for simple nematogens defy exact solution. Hence the range of stability of the nematic phase as a function of the molecular shape is not known *a priori*. In fact, most approximate theories of the equation of state of hard, non-spherical particles fix the minimum anisometry to form a nematic phase in a rather *ad hoc* way, namely as that value of $L/D$ for which the transition to the nematic phase occurs at the density of the corresponding close packed solid.

The aim of the present work is to obtain essentially exact numerical information on the phase diagram of a class of very simple non-spherical molecules, *viz.* hard ellipsoids of revolution. Ellipsoids of revolution are convex bodies. The equation describing the surface of a hard ellipsoid of revolution is: $(x^2 + y^2)/b^2 + z^2/a^2 = 1$ where $a$ and $b$ denote the length of the major and minor axes of the ellipsoid. The shape of the ellipsoid is conveniently parametrized by $x \equiv (a/b)$. As $x$ varies from 0 to $\infty$ we go from extremely oblate ellipsoids ("hard platelets")[2] through hard-spheres ($x = 1$) to extremely prolate ellipsoids. The latter system is equivalent to the hard-rod system investigated by Onsager.[1] In what follows we shall be using reduced units to express the thermodynamic quantities of the hard-ellipsoid system. The units of energy is fixed at $kT$ and the unit of volume is given by $8\,ab^2$. This latter definition has the advantage that it reduces to $(2a)^3 = \sigma^3$ for hard-spheres. In these units the density of close periodic packing is equal to $\sqrt{2}$.

## COMPUTATIONAL METHOD

We performed Monte-Carlo simulations on an assembly of $N \approx 10^2$ ellipsoids for values of $x = 0.3333, 0.3636, 0.5, 0.8, 1.25, 2, 2.75$ and

3; note that for every value of $x = a/b$ studied, we also studied the corresponding system with $x = b/a$. In all cases periodic boundary conditions were employed. The initial configuration was obtained by distorting a *FCC* lattice along the 111-axis by a factor $x$. In our simulations the 111-plane was the basal plane of the periodic box. We chose the number of particles such that the distorted (orthorhombic) box was approximately cubic. We did not investigate whether the solid thus obtained was indeed thermodynamically more stable than other possible solid structures; it is known, at least for the hard sphere solid[3,4] that the free energy difference between *FCC* and *HCP* phases is almost undetectable. The computational details of the simulations will be described in a separate publication.[5] Here we only mention some general points about the computational technique. First of all one needs an efficient numerical method to detect overlaps of the hard ellipsoids; this problem was solved in computationally convenient way by Vieillard-Baron, over a decade ago.[6] At that time Vieillard-Baron's efforts to study hard ellipsoids by computer simulation failed because his method of computing the pressure in a constant volume system turned out to be rather cumbersome. We circumvented this problem by employing the constant-pressure Monte Carlo method[7] and a new constant volume method[2] both of which are far easier to implement than the method described in ref. 6. The length of the simulations was at least $10^4$ sweeps (i.e. attempted moves/particle) for every state point excluding equilibration. But in the vicinity of the isotropic-nematic transition much longer runs were required. The phase diagram was traversed both in the direction of increasing and decreasing density, i.e. one set of simulations was started from the ordered solid phase while the other was started from the dilute gas. For the systems with $x = 3, 2.75, 0.3636$ and $0.3333$ we found that spontaneous nematic ordering set in as the isotropic fluid was compressed. There are several ways to monitor the onset of nematic order; in the present simulation we monitored the behavior of the correlation function $g_2(r) \equiv \langle P_2\,(\vec{\mathbf{l}}(\mathbf{0}) \cdot \vec{\mathbf{l}}(\vec{\mathbf{r}}))\rangle$. In the isotropic phase $g_2(r)$ decays rapidly to zero while in the nematic phase $g_2(r)$ tends to $\langle P_2\rangle^2$ as $r \rightarrow \infty$. Of course, as the systems studied in the simulations are finite we can only probe the behavior of $g_2(r)$ at distances smaller than half the diameter, $D$, of the periodic box. However, this is no real drawback as we observe that once nematic ordering takes place $g_2(r)$ reaches its limiting value within a few particle diameters. Hence the value of $g_2(r)$ at $r = D/2$ is a good measure for $\langle P_2\rangle^2$.

## RESULTS AND DISCUSSION

The equations of state of the hard ellipsoid systems studied are shown in figures 1, 2, and 3. The systems with $2 \geqslant x \geqslant \frac{1}{2}$ have a phase diagram which consists of a single isotropic fluid branch and a solid branch.

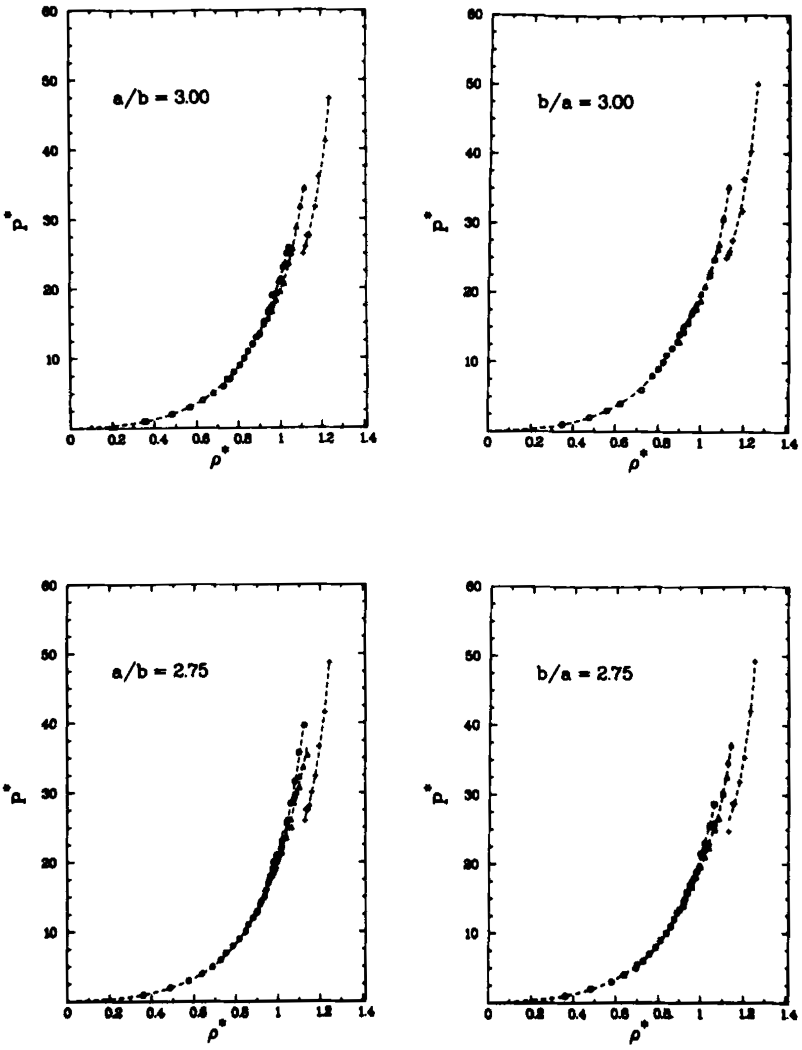

FIGURE 1 Equation of state of hard ellipsoids of revolution with $a/b = 3, 2.75$ and $b/a = 3, 2.75$. The pressure is in units $kT/8ab^2$, the density in units $(8ab^2)^{-1}$. (0): isotropic branch, (Δ): nematic branch, (+): solid branch. The continuous curves are polynomial fits to the Monte Carlo data.

For $x \geqslant 2.75$ and $x \leqslant 0.3636$ we also observe a nematic fluid branch. In all cases the density gap separating solid and fluid branches is rather wide (6–8%). It is easy to compress the fluid to densities where it is metastable. The lower end of the solid branch corresponds to the lowest pressure at which we found the solid to be mechanically

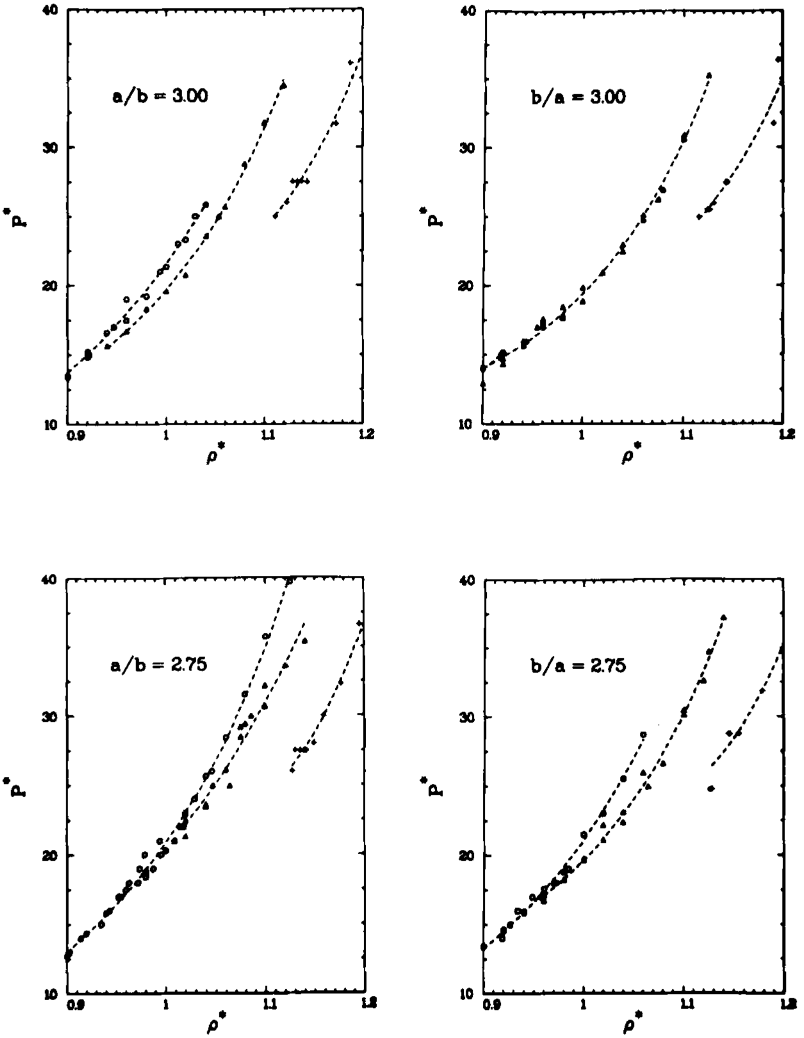

FIGURE 2 Detail of the equation of state of hard ellipses of revolution with $a/b$ = 3, 2.75 and $b/a$ = 3, 2.75. Same units as in figure 1. In this figure the isotropic (0) and nematic (Δ) branches can be clearly distinguished. The lowest points on the solid branch (+) are close to the point of mechanical instability of the solid phase. The continuous curves are polynomial fits to the Monte Carlo data.

stable. Spontaneous freezing of the super-compressed fluid was observed only in the case of the strongly over-compressed fluids with $x = 1.25$ and $x = 0.8$. The transition from the isotropic to the nematic phase is quite different in nature from the fluid-solid transition. First of all the density change on going from the isotropic to the nematic

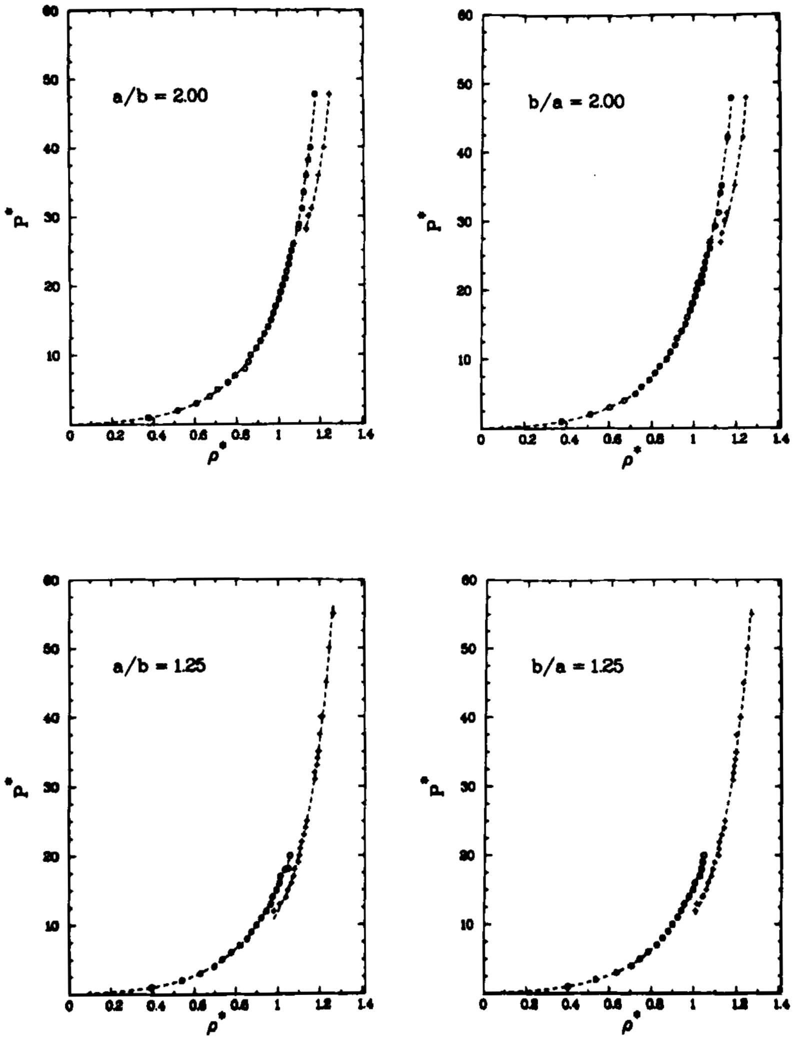

FIGURE 3 Equation of state of hard ellipsoids of revolution with $a/b = 2, 1.25$ and $b/a = 2, 1.25$. Same units as in figure 1. For these $a/b$-ratio's only isotropic (0) and solid (+) phases are observed. The continuous curves are polynomial fits to the Monte Carlo data.

branch is quite small (~1%) and, moreover, the range of metastability of the isotropic and nematic phases is quite limited. The upper end of the isotropic branch end the lower and of the nematic branch correspond to the highest (lowest) pressure at which the respective phases could be maintained in a metastable state for at least 2 × $10^4$ passes. We observe that the range of metastability is appreciably less for oblate than for prolate ellipsoids. Why this should be so is not obvious although we recall that the I-N transition in extremely prolate ellipsoids is strongly first order[1] whereas the transition in extremely oblate ellipsoids is very weakly first order.[2]

The determination of the location of the thermodynamic phase transitions is a major problem, because it requires the determination of the absolute free energy of all phases involved. In general this requires the construction of a reversible path from a state of known free energy to the phase under consideration. We determined the free energy of the isotropic, nematic and solid phases. For the isotropic phase we used standard techniques but for the nematic and solid phases novel techniques were developed. Here we only sketch the approach used in the different free energy construction. For details we refer the reader to refs. 4 and 5. The free energy of the isotropic phase at a density $\rho_H$ was computed by integrating $(\partial F/\partial V) = -P$ along an isotherm from the dilute gas at density $\rho_L$:

$$F(\rho_H) = F(\rho_L) + \int_{1/\rho_H}^{1/\rho_L} P\,dV$$

For sufficiently low values of $\rho_L$, $F(\rho_L)$ approaches the free energy of an ideal gas at the same density.

The free energy of the nematic phase is less easily computed. Neither by compression nor by expansion can a state of known free energy be reached reversibly. Hence we devised the following reversible path to the nematic phase: we studied the isotherm of a fluid of hard ellipsoids in a strong "magnetic" field H along the z-axis. The Hamiltonian of this system is equal to the Hamiltonian of the field-free system, $H_0$, plus a term of the form $V = \sum_{i=1}^{N} H^2 \sin^2 \theta_i$. The absolute free energy of an ideal gas in such a magnetic field can be evaluated exactly. The absolute free energy of the nematic phase is obtained by first integrating $(\partial F/\partial V) = -P$ from the low density phase to a density where, even without a field, the nematic phase is stable. Next we slowly switch off the magnetic field H, and compute the integral of $(\partial F/\partial H') = 2H'N\langle\sin^2\theta\rangle_{H'}$, from $H' = H$ to $H' = 0$. The situation with $H' = 0$ corresponds to the normal nematic phase. This route to the nematic phase is reversible as it goes around the isotropic-nematic critical point.

Finally we compute the absolute free energy of the solid by constructing a reversible path from an Einstein crystal to the solid under consideration by slowly switching off the spring constants. This method is explained in some detail in ref. 4 where it has been applied to atomic solids. Here we have generalized the method to molecular solids. The main difference is that, in addition to the springs which constrain the molecular centers of mass in the Einstein crystal, we also apply a magnetic field to constrain the molecular orientations. Details about the free energy computations and the subtleties involved will be described in ref. 5. Here we just quote the main result that was obtained with these new techniques, *viz.* the absolute location of the isotropic-nematic and fluid-solid phase transition of hard ellipsoids. The "phase diagram" of hard-ellipsoids is shown in figure 4. In table I we have collected the thermodynamic data on the phase transition. In this table (and in figure 4) we have also included the well-known hard-sphere results of ref. 8.

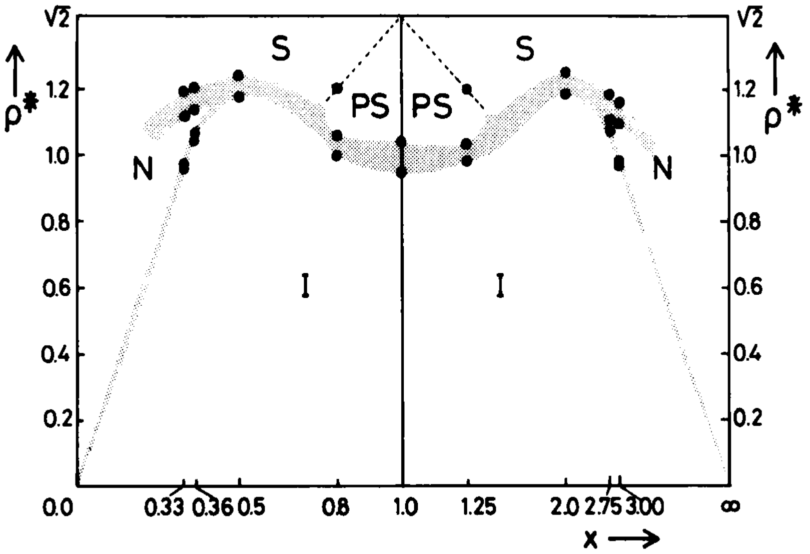

FIGURE 4 "Phase diagram" of hard ellipsoids of revolution. Vertical axis: $\rho^*$ in units $(8ab^2)^{-1}$, horizontal axis: $a/b \equiv x$. The shaded areas correspond to two-phase regions. The dots correspond to computed phase coexistence points (see Table I). The points for $x = 1$ were taken from ref. 8. The following phases can be distinguished. I: isotropic fluid, N: nematic fluid, S:orientationally ordered solid, PS: plastic solid.

TABLE I

Densities of coexisting phases and pressures at phase transition for hard ellipsoids of revolution. The ratio of the axes (*a*/*b*) is denoted by $x$. $\rho_I$ and $\rho_N$ denote the densities of the coexisting isotropic and nematic fluid phases, $P_{IN}$ is the corresponding pressure at coexistence. $\rho_F$ and $\rho_S$ denote the densities of the coexisting (isotropic or nematic) fluid phase with the (plastic or ordered) solid phase; $P_{FS}$ is the pressure at the freezing point. The units are as in figure 1. The estimated errors in the densities at coexistence is $\leqslant 1\%$ for the FS-transitions, but $\sim 3\%$ for the IN-transitions. Figure 2 suggests that the actual IN-transition for $x = 0.33$ takes place at a slightly lower density than indicated in the present table.

| $x$ | $\rho_I$ | $\rho_N$ | $P_{IN}$ | $\rho_F$ | $\rho_S$ | $P_{FS}$ |
|---|---|---|---|---|---|---|
| 3.00 | 0.969 | 0.988 | 18.69 | 1.096 | 1.163 | 30.84 |
| 2.75 | 1.072 | 1.089 | 30.00 | 1.118 | 1.182 | 33.36 |
| 2.00 | — | — | — | 1.185 | 1.252 | 46.97 |
| 1.25 | — | — | — | 0.983 | 1.039 | 14.34 |
| 1.00 | — | — | — | 0.943 | 1.041 | 11.70 |
| 0.80 | — | — | — | 0.998 | 1.060 | 15.51 |
| 0.50 | — | — | — | 1.175 | 1.245 | 45.79 |
| 0.36 | 1.040 | 1.066 | 25.69 | 1.137 | 1.206 | 36.54 |
| 0.33 | 0.956 | 0.972 | 17.75 | 1.119 | 1.194 | 34.17 |

We wish to stress the following salient features of figure 4. First of all, no stable nematic is possible for $2 \geqslant x \geqslant ½$. Actually the limits on the stability of the nematic phase must be rather close to $x = 2.75$ and $x = 0.3636$. Secondly we find that melting transition for $1.25 \geqslant x\ 1/2 \geqslant 0.8$ takes place at a much lower density than for $x = 2$ and $x = 0.5$. The reason is that the almost spherical ellipsoids freeze into an orientationally disordered ("plastic") solid (which, incidentally has cubic symmetry). In contrast, the systems with $x = 2$ and $x = ½$ freeze directly from the isotropic fluid to the orientationally ordered solid, this involves a large loss of orientational entropy. This explains why freezing in this case, takes place at high pressures: a large $P\Delta V$ term is required to offset the $T\Delta S$ contribution. Another interesting trend is that the density of the freezing point of the nematic phases appears to decrease with increasing anisometry. It is natural to ask at what $\rho$ freezing will occur in the limit $x \to \infty$ and $x^{-1} \to \infty$. An approximate scaling argument[9] suggests that freezing of nematic fluids of needles and platelets takes place at the same density, $\rho_F$. This density is somewhat lower than the density of hard-sphere fluid at freezing. Finally we wish to point out that the ellipsoids with $x = 1.25$ and $x = 0.8$ undergo a transition from an orientationally disordered to orientationally ordered solid phase at $\rho = 1.20$ (both for $x = 1.25$ and $x = 0.8$). We have not observed any density change at this transition and tentatively identify it as a second-order phase transition.

Probably the most striking feature of the phase diagram of hard-ellipsoids is its striking symmetry under the transformation $x \rightarrow x^{-1}$. The symmetry, which incidentally is *not* exact, can be understood at the level of the second virial coefficient[10] which is in fact invariant under permutation of long and short axes. However, all higher virial coefficients lack this symmetry and hence the apparent symmetry of the phase diagram at higher densities is fortuitous.

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