

Plastic crystal phases of hard dumbbells and hard spherocylinders

C. Vega

Departamento de Química-Física, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

P. A. Monson^{a)}

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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Mildly anisotropic nonspherical molecules like nitrogen and carbon monoxide can form solid phases which exhibit long range translational order without long range orientational order. Such phases are referred to as rotator phases or plastic crystals. Recent studies using Monte Carlo and molecular dynamics computer simulation have shown that this kind of phase occurs on freezing of slightly nonspherical model particles with hard core potentials such as hard dumbbells,¹⁻⁴ hard spherocylinders⁵⁻⁷ and hard ellipsoids.⁸ For larger anisotropies or at high pressure such phases become unstable with respect to orientationally ordered solids.³⁻⁷ The phase diagram of hard dumbbells in the region where the plastic crystal phase becomes unstable was studied by Vega *et al.*⁴ In this work evidence was presented indicating that the density change on freezing of the fluid into the plastic crystal phase becomes very small at a triple point where the fluid phase, the plastic crystal phase and an orientationally ordered solid phase coexist.

Recently Bolhuis and Frenkel⁷ have presented an extensive computer simulation study of the phase diagram of the hard spherocylinder model. This study covered a wide range of molecular anisotropies including very long particles which can form liquid crystalline phases in addition to solids and isotropic fluids. For mild anisotropies the molecular shapes represented by the hard dumbbell and hard spherocylinder models are quite similar and it might be anticipated that the solid-fluid phase diagram would reflect this. Indeed, Bolhuis and Frenkel⁷ presented a comparison of some of their results for hard spherocylinders with those for hard dumbbells²⁻⁴ and the agreement was seen to be very close. However, the Gibbs-Duhem integration procedure^{7,9} used in their work is not reliable near the limit of stability of the plastic crystal phase. Thus their data was only sufficient to make a rough estimate of the phase diagram in this rather narrow but nevertheless important region of molecular anisotropy. The manner in which Bolhuis and Frenkel drew the termination of the plastic crystal phase differs from that presented for hard dumbbells.⁴ In particular they show a substantial density change on freezing of the fluid into the plastic crystal phase at the triple point. In view of the otherwise good agreement with the results for hard dumbbells and the rather clear evidence for a small fluid to plastic crystal density change in the hard dumbbell model⁴ we have undertaken a closer comparison of the results for the two models. We have also calculated the solid-fluid coexistence properties for a hard spherocylinder model near the limit of stability of the plastic crystal phase using a method which is more reliable in this region. These new results and the comparisons we

will present between hard dumbbells and hard spherocylinders indicate that the two model systems behave in a similar way in the region where plastic crystal phase becomes unstable. Below we present this comparison and also a few brief remarks on the significance of these results.

Figures 1 and 2 show the density vs anisotropy and pressure vs anisotropy phase diagrams of hard dumbbells and hard spherocylinders from the computer simulation data. The reduced units for pressure, density and length are defined by

$$p^* = pd^3/kT; \quad \rho^* = \rho d^3; \quad L^* = L/\sigma \quad (1)$$

where d is the diameter of the sphere with the same volume as the dumbbell or spherocylinder, L is the cylinder length of the spherocylinder or the bond length of the dumbbell and σ is the cylinder diameter for the spherocylinder or the atom diameter for the dumbbell. We have calculated additional coexistence points for hard spherocylinders with $L^* = 0.30, 0.35$ and 0.37 .¹⁰ The solid phase equations of state and free energies were computed using Monte Carlo simulations with 108 molecules using the same methods as those employed by Vega *et al.*⁴ The fluid phase equation of state and free energies were computed from the accurate equation of state of Nezbeda.¹¹ Notice that the agreement between the data for the two models is very good when plotted in this way. The dependence of the coexistence properties upon L^* for the two models is very similar in the region where the plastic crystal phase becomes unstable. In both models the density difference between the plastic crystal and the fluid becomes very small and the coexistence pressure rises sharply with increasing L^* . Clearly the existence of a triple point where the fluid, plastic crystal and an orientationally ordered solid phase coexist is a distinct possibility for both systems.

In order to understand the behavior in Figs. 1 and 2 it is useful to include L^* in the thermodynamics as a parameter in the Gibbs or Helmholtz free energies that plays the role of an additional field variable.^{2,7} For example the Gibbs-Duhem equation becomes

$$d\mu = v dp + \kappa dL, \quad (2)$$

where $\kappa = (\partial\mu/\partial L)_p = (\partial A/\partial L)_v$, μ is the chemical potential, A is the Helmholtz free energy per molecule and v is the volume per molecule. A first order phase transition would be one with non zero differences in v and/or κ between the phases. The Clapeyron equation takes the form^{2,7}

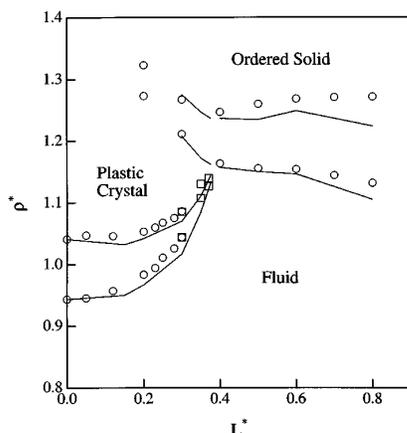


FIG. 1. Reduced coexistence densities as a function of L^* for hard dumbbells (solid lines) and hard spherocylinders (open symbols). Results for hard dumbbells were taken from Vega *et al.* (Refs. 3, 4). The data of Singer and Mumaugh (Ref. 2) are in good agreement with these. The open circles correspond to the results of Bolhuis and Frenkel for hard spherocylinders (Ref. 7) and the open squares correspond to the results of this work for hard spherocylinders.

$$[dp/dL] = -(\Delta\kappa/\Delta v). \quad (3)$$

Integration of Eq. (3) provides a method of calculating coexistence properties as a function of L given an initial condition.^{7,9} Clearly the sharp rise in the solid-fluid coexistence pressure and the sharp decrease in the density change on freezing as the stability limit of the plastic crystal is approached shown in Figs. 1 and 2 correlate well with the above expression. These observations also point to the difficulty of using the integration of Eq. (3) for calculating coexistence properties in this region of L , as was noted by Bolhuis and Frenkel.⁷

The phase rule for an n component hard nonspherical particle system made up of particles with identical diameters (i.e., values of σ) can be written as

$$F = 2n + 1 - \pi, \quad (4)$$

where F is the number of degrees of freedom and π the number of phases. The term $2n$ comes from the need to specify an anisotropy variable plus a composition variable (or chemical potential) for each component in fixing the state of a mixture of hard nonspherical particles. The phase rule is consistent with the occurrence of triple points for a single component hard dumbbell or hard spherocylinder system at particular values of L .

On the basis of Fig. 1 there are two scenarios for the precise form of the phase diagram in the region where the plastic crystal becomes unstable that are consistent with the phase rule. One possibility is that the density change between fluid and plastic crystal could vanish prior to a triple point being reached. This would lead to reentrant fluid to plastic crystal to fluid behavior for a very narrow region of L .¹² A vanishing density change is unusual behavior for a first order transition but is not forbidden since $\Delta\kappa \neq 0$. Interestingly, Singer and Mumaugh² provide data for κ for different values of L for hard dumbbells and it is evident that

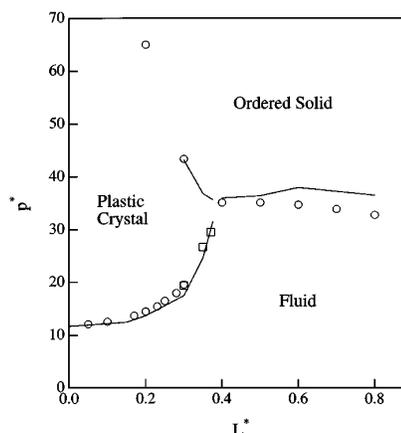


FIG. 2. Reduced coexistence pressures as a function of L^* for hard dumbbells (solid lines) and hard spherocylinders (open symbols). Results for hard dumbbells were taken from Vega *et al.* (Ref. 3, 4). The data of Singer and Mumaugh (Ref. 2) are in good agreement with these. The open circles correspond to the results of Bolhuis and Frenkel for hard spherocylinders (Ref. 7) and the open squares correspond to the results of this work for hard spherocylinders.

$\Delta\kappa$ changes sign in the neighborhood of $L^* = 0.12$ but Δv remains nonzero (in this region a plot of $p\sigma^3/kT$ vs L^* exhibits a minimum). The second possibility is a triple point with a very small but finite density change between the fluid and plastic crystal phases.¹³ This is fully consistent with the available simulation results and on existing evidence would appear to be the more likely scenario.

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^{a1}Author to whom correspondence should be addressed.

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¹⁰The reduced pressures at coexistence that we calculated for these values of L^* are 19.35, 26.68, and 29.47. The reduced solid densities are 1.085, 1.131, and 1.140. The reduced fluid densities are 1.044, 1.108, and 1.127.

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¹³In Ref. 4 it was suggested that the density difference between plastic crystal and fluid might vanish at the triple point. This would violate the phase rule since the equality of densities between two phases reduces the number of degrees of freedom by one.