On the stability of the plastic crystal phase of hard dumbbell solids

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We consider the thermodynamic properties of the solid phase and solid–fluid phase equilibria of hard dumbbells. The focus of the present work is a more detailed study of the stability of the orientationally disordered (plastic crystal) solid phase relative to other solid phases and to the fluid. Our results indicate that the plastic crystal is not stable for values of L^* (the separation of the two spheres of the dumbbell reduced by the sphere diameter) greater than about 0.38. For larger anisotropies than this the hard dumbbell fluid freezes into an orientationally ordered structure. The disappearance of the plastic crystal phase is accompanied by the approach to zero of the density difference between the fluid and the plastic crystal at coexistence and sharp increases in the coexistence pressure and densities. At high pressures the plastic crystal phase transforms into an orientationally ordered structure. These results and those of previous studies allow us to present a fairly complete description of the phase diagram of hard dumbbells.

I. INTRODUCTION

In a recent paper,[1] hereafter referred to as I we presented a Monte Carlo simulation study of the solid phase thermodynamics and solid–fluid phase equilibria for systems of hard dumbbells. The purpose of the study was to investigate the dependence of the solid phase properties and solid–fluid equilibria upon the dumbbell anisotropy as a model for the influence of molecular shape upon these properties. We studied three values of the dumbbell bond length, $L^*=0.3$, 0.6, and 1.0 ($L^*=L/\sigma$ is the dumbbell bond length divided by the dumbbell sphere diameter). For $L^*=0.3$ we found that the stable solid structure on freezing is a face centered cubic (fcc) plastic crystal, in which the dumbbells have a high degree of translational order but a low degree of orientational order. At higher pressures this phase becomes unstable with respect to orientationally ordered base centered monoclinic structures which allow the hard dumbbells to achieve their maximum packing density. Our results for this system are consistent with an earlier study by Singer and Mumaugh[2] who considered freezing into the plastic crystal phase for mildly anisotropic hard dumbbells. For $L^*=0.6$ our results are consistent with freezing into an orientationally ordered solid. For $L^*=1.0$ we studied orientationally ordered solid phases, although in this case there is also the possibility of formation of an aperiodic crystal due to the large structural degeneracy in this case.[3] Leaving aside the issue of formation of aperiodic structures, the key feature of dependence of the solid–fluid equilibria for hard dumbbells upon L^* is that at low anisotropies the system freezes into a plastic crystal but at larger anisotropies, freezing into orientationally ordered phases occurs.

On the basis of the results in I we can conclude that the broad features of the solid–fluid equilibria for hard dumbbells are similar to those for hard prolate ellipsoids as studied by Frenkel *et al.*[4] The principal difference seems to be the observation of a clear density change in the transition between plastic crystal and orientationally ordered structures for hard dumbbells, indicative of a first order transition. Frenkel and Mulder[4] observed a second order or weak first order phase transition between these solid phases for a mildly anisotropic hard ellipsoid model.

Experimental data indicate that for diatomic molecules the condition for the formation of a plastic crystal phase is the possession of a mild anisotropy[5] in terms of molecular shape. Thus short molecules like N_2 exhibit a plastic crystal phase but more anisotropic molecules such as Cl_2 do not.[5] The fact that the hard dumbbell model with $L^*=0.30$ freezes into a plastic crystal phase and that with $L^*=0.60$ freezes into an orientationally ordered phase indicates that there is an intermediate elongation beyond which it is not possible to have a plastic crystal phase. This was in fact shown by Singer and Mumaugh[2] in their study of the plastic crystal–fluid equilibria of mildly anisotropic hard dumbbells. They found that only when $L^*<0.40$ could the plastic crystal phase be in equilibrium with the fluid.

In this paper we consider in more detail the stability of the plastic crystal both with respect to orientationally ordered solid phases and with respect to the fluid. To that purpose we have obtained new Monte Carlo results which supplement those of Refs. 1 and 2 with special emphasis on mildly anisotropic dumbbells. We have studied the dependence upon L^* of both the plastic crystal–fluid equilibria and the plastic crystal-orientationally ordered solid equilibria. We have located the upper limit in L^* for which a plastic crystal phase is possible and found good agreement with the value proposed by Singer and Mumaugh.[2] These results and those of the previous studies allow us to present a fairly complete description of the phase diagram of hard dumbbells.

II. SIMULATION METHODOLOGY

The simulation methodology used in this paper is that used in I and we refer the reader to that paper for a more

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detailed description. We shall briefly outline the main features of the simulations. To simulate the solid phase we used the Monte Carlo (MC) equivalent of the molecular dynamics method developed by Parrinello and Rahman.[6] The method is a constant pressure MC simulation[7] with changes in the unit cell shape to allow the system to equilibrate to the correct crystal structure.[8,9]

In contrast to our work in I we considered only two solid structures, the fcc plastic crystal and an orientationally ordered base centered monoclinic structure. The fcc plastic crystal phase was obtained as follows. We started with an α-N_2 structure at high pressure. This phase is mechanically stable although thermodynamically unstable for the elongations considered here. We gradually reduced the pressure until the α-N_2 spontaneously transformed into a plastic crystal phase with the same centers of mass arrangement as the α-N_2 but with the dumbbells orientationally disordered. The equation of state (EOS) at lower pressure was obtained by expanding from this initial state. Some high pressure points were obtained by compressing the initial plastic crystal (PC) state. The orientationally ordered base centered monoclinic structure used was that denoted as CP1 in I. This structure is easily visualized for the case of $L^*=1.0$ at close packing. It consists of hexagonally close packed layers of dumbbells stacked so that the dumbbell spheres are in an ABC arrangement. In I we found that the properties of two other orientationally ordered monoclinic structures were essentially indistinguishable from those of the CP1 structure within the precision of the simulations.

In these simulations we used 108 particles for the PC structure and 144 ($6\times6\times4$) particles for the close packed structure. A run typically involved 20 000 cycles for equilibration and 20 000 cycles for thermodynamic averages where a cycle consist of an attempt to move each particle and an attempt to change the volume and/or shape of the system. Calculations involving larger numbers of particles were presented in I and did not show qualitatively different behavior. The free energy was obtained using the method proposed by Frenkel and Ladd[10] as extended to molecular fluids by Frenkel and Mulder.[4] This method creates a reversible path between the solid under consideration and a noninteracting Einstein crystal with fixed center of mass for which the partition function is known in a closed form. For each solid phase we choose a reference point and performed the free energy calculations. For the PC we used typically 20 values of the coupling parameter and for the CP1 phase we used 10 values. In both cases Gauss–Legendre quadrature was used to evaluate the difference in free energy between the solid phase under consideration and the reference Einstein crystal (see I). In the case of the PC crystal phase the reference Einstein crystal was an α-N_2 structure at the same density. The phase transition between the PC phase and the α-N_2 phase is suppressed by the presence of the external field. Once the free energy is known at a given reference state then the free energy along the isotherm is obtained through thermodynamic integration of the EOS.

The fluid phase was described by using the EOS pro-

TABLE I. Equation of state of hard dumbbell solids as obtained from MC simulations.

| L^*	p^*	$\langle \rho^* \rangle$ (PC)	$\langle \rho^* \rangle$ (CP1)
0.15	13.0	1.041	
	15.0	1.078	
	17.5	1.097	
	20.0	1.131	
0.35	25.0	1.111	1.135
	30.0	1.145	1.191
	32.5	1.156	1.212
	36.0	1.165	1.242
	38.0	1.177	1.256
0.375	30.0	1.138	1.185
	33.0	1.153	1.212
	35.0	1.157	1.234
	38.0	1.172	1.254
	40.0	1.184	1.260
	45.0	1.202	1.281
0.40	30.0		1.192
	35.0		1.234
	40.0		1.256
	45.0		1.279
0.50	30.0		1.198
	35.0		1.226
	40.0		1.260
	45.0		1.279
	50.0		1.309
0.80	30.0		1.168
	35.0		1.222
	40.0		1.239
	45.0		1.260
	50		1.284

posed for hard dumbbells by Tildesley and Streett.[11] In I we checked that this EOS is reliable at densities of the fluid higher than those where the parameters in the equation of state were fitted. Throughout our discussion of the results we will use the following reduced units for density and pressure: $\rho^*=\rho d^3$ and $p^*=pd^3/kT$, where $d^3=\sigma^3(1+3/2L^*-1/2L^{*3})$. Thus d is the diameter of a sphere with the same volume as the dumbbell. Systems with different values of L^* but the same value of ρ^* are at the same volume fraction.

III. RESULTS

In Table I we present the results for the EOS of hard dumbbell solids in the PC and CP1 phases. In addition to our studies of mildly anisotropic dumbbells we have also included results for $L^*=0.5$ and 0.8 which were not presented in I. For the case of $L^*=0.15$ we only considered the PC solid phase, since it was shown in I that for $L^*=0.30$ the fluid freezes into the PC phase and such behavior should be anticipated for any value of L^* less than this. In Table I it is clear that the density of the PC is intermediate between that of the fluid and that of the orientationally ordered phase CP1. The density of the PC crystal phase gets closer to that of the fluid phase when the molecular anisotropy increases. This is illustrated in Fig. 1 where we show the EOS for $L^*=0.35$ and 0.375. The value of the orientational order parameter, as defined in I, in the PC phase was characteristic of an orientationally disordered structure.
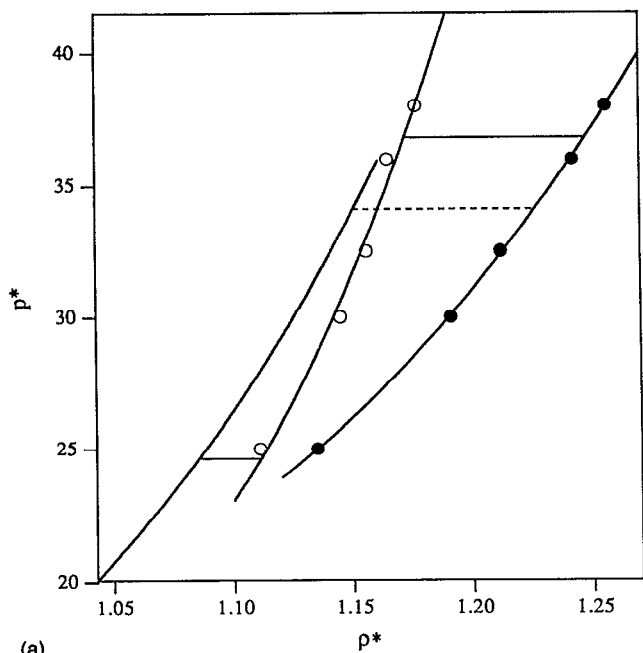
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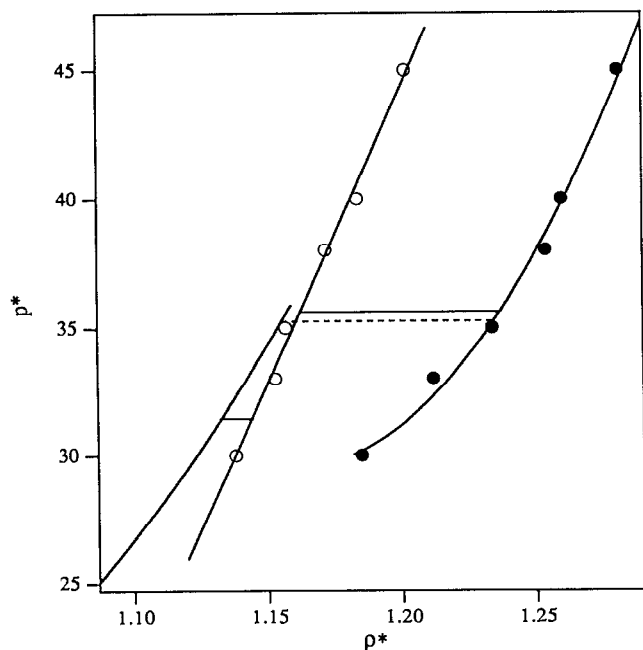
(b)

FIG. 1. Equation of state (EOS) and phase equilibria for hard dumbbells with (a) $L^*=0.35$ and (b) $L^*=0.375$. The filled circles are MC results for the CP1 phase and the open circles are for the PC phase. The lines through the MC results are fits to the data. The fluid is described with Tildesley and Streett (Ref. 11) EOS. The solid tie lines correspond to transitions between stable phases and the dashed tie line corresponds to a transition between metastable phases.

In Table II we show the free energy calculations for all the solid phases considered. From the EOS data of Table I and the free energy calculations of Table II the phase equilibria can be obtained. The coexistence densities, pressures, and chemical potentials for the different transitions found are shown in Table III. We have also included the transitions between metastable phases. The translational order parameter, as defined in I, at melting was always in the

range (0.60–0.70) when the melting occurs from the PC phase and of about 0.90 or higher when it occurs from the CP1 structure. The orientational order parameter at melting for the CP1 increases from 0.70 to 0.98 as L^* increases from 0.40 to 0.80.

For $L^*=0.15$ we see that the densities of the fluid and solid at coexistence are very similar to the ones of hard spheres which are respectively $\rho_f^* = 0.94$ and $\rho_s^* = 1.04$.[12] The pressure is slightly higher than that of hard spheres at coexistence which is $p^*=11.7$. Our results suggest that between $L^*=0$ (hard spheres) and $L^*=0.15$ the fractional density change $\Delta = (\rho_s^* - \rho_f^*)/\rho_f^*$ decreases slightly and the coexistence pressure increases slightly. For $L^*=0.15$ the fractional density change is $\sim 9\%$.

As L^* is increased to 0.30 there is a significant increase in the densities of the fluid and solid at coexistence and also in the coexistence pressure. The fractional density change is reduced to $\sim 5\%$. From $L^*=0.30$ to 0.35 there is a sharp increase in the coexistence pressure. The fractional density change decreases from 5% to 2.5% while both the densities of the fluid and solid at coexistence increase significantly. In I we suggested that the fractional density change of hard dumbbells with $L^*=0.30$ was relatively close to that of N_2 which is experimentally found to be of $\sim 2.5\%$.[13] Here we see that for $L^*=0.35$ the fractional density change of hard dumbbells is of $\sim 2.5\%$ which is closer to that of nitrogen. Nitrogen is often modeled with the two center Lennard-Jones model using a reduced length of $L^*=0.33$.[14] It seems clear from these results that the fractional density change of N_2 at freezing can be well described by a hard dumbbell model, assuming that the differences between an fcc plastic crystal (the present case) and a hexagonal-close-packed (hcp) plastic crystal (β-N_2) are small as we would anticipate. For $L^*=0.35$ the fluid freezes into a plastic crystal phase, which upon compression transforms into a close packed structure at higher pressures. This is illustrated in Fig. 1(a). Note also that the fluid to CP1 solid transition occurs in the metastable branch of both phases.

For $L^*=0.375$ the fluid also freezes into a PC phase. The fractional density change is now only $\sim 1\%$. Some snapshots of liquid and PC phases at equilibrium clearly show disordered distribution of the molecular center of mass for the liquid phase and ordered distribution of the centers of masses in the solid phase. The center of mass radial distribution function is also very different in the two phases at equilibrium. However the site–site distribution function of liquid and PC phases are very similar for distances between the sites $<2.5\sigma$. Upon compression the PC phase again becomes unstable with respect to the CP1 structure. The fluid-CP1 transition occurs again in the metastable branch of both phases. This is illustrated in Fig. 1(b). The pressures at the fluid to PC phase and PC-CP1 phase are now very close. This suggests that there will be a crossing between the fluid-PC and PC-CP1 coexistence lines at an elongation slightly larger than $L^*=0.375$.

Figure 2 shows all the available results for coexistence pressures of hard dumbbells plotted vs L^*. The results of Singer and Mumaugh[2] for mild anisotropies are also in-

TABLE II. Free energy calculations for hard dumbbells in the PC and CP1 solid phases. N is the number or particles used, λ_{max} is the maximum value of the coupling parameter in the Frenkel–Ladd method (Refs. 4 and 10). N_λ is the number or values of λ used in the Frenkel–Ladd method. R is the ratio of the unit cell axes c/a divided by its value at close packing [i.e., $R=(c/a)/(c/a)_p$]. ΔA_2 is the free energy difference between the hard dumbbell solid and an interacting Einstein crystal with fixed center of mass. ΔA_1 is the free energy difference between the interacting and the noninteracting Einstein crystal obtained using umbrella sampling. A_{ref} is the absolute Helmholtz free energy at the reference density. All free energies are divided by NkT.

L^*	Lattice	N	λ_{max}	N_λ	R	p^*	ΔA_2	ΔA_1	A_{ref}
0.15	PC	108	1000	20	1.00	1.041	−11.23	0.0003	5.15
0.35	PC	108	1000	20	1.00	1.113	−9.44	0.0018	7.16
0.35	PC	108	1000	20	1.00	1.178	−8.02	0.0214	8.59
0.35	CP1	144	8000	10	0.91	1.191	−12.63	0.0102	9.17
0.375	PC	108	1000	20	1.00	1.151	−8.44	0.0086	8.18
0.375	CP1	144	8000	10	0.94	1.237	−11.48	0.0002	10.32
0.40	CP1	144	8000	10	0.93	1.234	−11.45	0.0077	10.38
0.50	CP1	144	8000	10	0.94	1.260	−10.43	0.0004	11.47
0.80	CP1	144	8000	10	0.96	1.239	−9.06	0.0002	12.98

cluded and good agreement between both sets of data is observed. The results indicate a crossing between the fluid-PC and the PC-CP1 coexistence lines, which is associated with a very sharp increase in the coexistence pressure of the fluid-PC transition and a significant decrease of the coexistence pressure of the PC-CP1 transition for elongations larger than $L^*=0.30$. We estimate that the three coexistence curves (fluid-PC, PC-CP1, and fluid-CP1) intersect at approximately $L^*=0.38$ and $p^*=35$ (we have illustrated this crossing by means of dashed lines). At about this elongation the PC phase disappears. This is in good agreement with the value $L^*=0.40$ found in Ref. 2. Figure 3 shows the corresponding coexistence densities for the transitions. The key feature here is the steep rise in the coexistence densities for the solid–fluid transition between about $L^*=0.15$ and 0.4, which is accompanied by a sharp decrease in the density change between the fluid and PC phases. We conjecture that this density difference vanishes at about $L^*=0.38$, where the PC phase disappears, although our calculations do not rule out the possibility that it remains finite if quite small. In Fig. 4 we show the difference between the reduced pressures at coexistence of the PC-CP1 transition and of the fluid-PC transition plotted together with the density change in the fluid-PC transition. Both quantities plotted approach zero at about $L^*=0.38$.

The termination of the coexistence region between the fluid and PC phases at a point does not mean that they become the same phase. As an illustration of this, the translational order parameter of the PC phase at melting is always in the range (0.6–0.7) for all the values of L^* up to 0.38.

The manner in which we have plotted the intersection of the coexistence curves and regions in Figs. 2 and 3 deserves some further discussion from the point of view of the phase rule. For a single phase, single component hard dumbbell system with a given value of L^*, only one intensive configurational property is independently variable. From this result it might be deduced that coexistence between more than two phases is not possible in a hard particle system. At first glance Figs. 2 and 3 contradict this since they imply the possibility of three phase fluid-PC-CP1 coexistence for a value of L^* around 0.38. However, in order to apply the phase rule correctly here we must consider L^* as a parameter in the free energy of the system, which can be viewed a field variable. Then a single phase hard dumbbell system has two independently variable intensive properties, one of which is L^*. It is then possible to observe three phase coexistence at specific values of L^*. Viewed from this perspective, two phase equilibrium is a line in an all field space (P vs L^*) and three phase equilibrium is a point of intersection of three two phase lines.

TABLE III. Phase transitions of hard dumbbells. The transitions between metastable phases are labeled with an asterisk. We have also included the results for $L^*=0.30$ from I.

| L^*	Phase 1	Phase 2	ρ_1^*	ρ_2^*	p^*	μ/kT
0.15	Fluid	PC	0.950	1.032	12.45	17.11
0.30	Fluid	PC	1.017	1.070	17.45	22.37
0.30	PC	CP1	1.208	1.275	43.15	44.80
0.30*	Fluid	CP1	1.148	1.221	33.22	36.85
0.35	Fluid	PC	1.085	1.111	24.64	29.30
0.35	PC	CP1	1.172	1.247	36.80	39.90
0.35*	Fluid	CP1	1.150	1.226	34.08	37.74
0.375	Fluid	PC	1.132	1.144	31.44	35.48
0.375	PC	CP1	1.162	1.237	35.63	39.12
0.375*	Fluid	CP1	1.155	1.234	35.25	38.82
0.40	Fluid	CP1	1.157	1.237	35.95	39.51
0.50	Fluid	CP1	1.150	1.235	36.37	40.29
0.80	Fluid	CP1	1.105	1.224	36.47	42.40
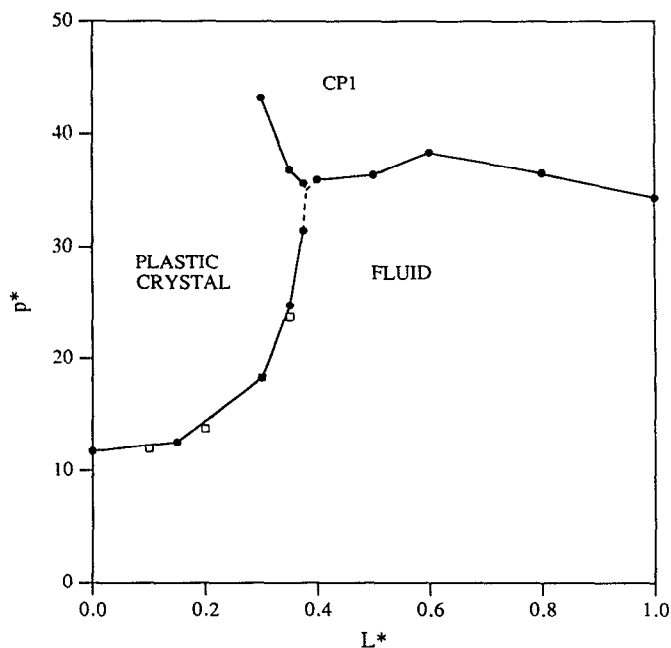
FIG. 2. Pressure at coexistence vs L^* for hard dumbbells. The points correspond to equilibrium transitions (fluid-PC, fluid-CP1, and PC-CP1) determined from the MC results of I and of this work. The lines through the points are a guide to the eye. The three lines intersect at approximately $L^*=0.38$ and $p^*=35$. The regions where the fluid, the plastic crystal and the close packed structure CP1 are the stable phases are illustrated. The results for $L^*=0.0$ are those of Hoover and Ree (Ref. 12). The open squares correspond to the results of Singer and Mumaugh (Ref. 2).
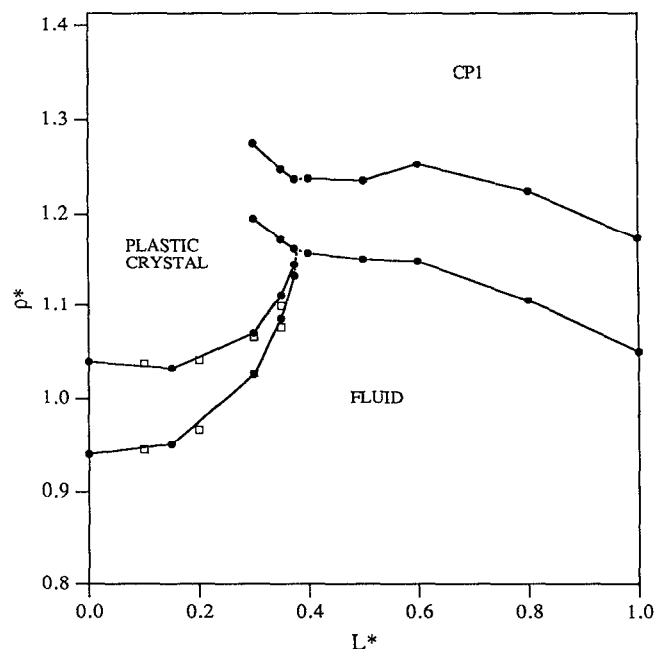
FIG. 3. Densities at coexistence vs L^* for hard dumbbells from the MC results of I and of this work. The lines through the points are a guide to the eye. The regions labeled as fluid, plastic crystal, and CP1 correspond to the densities and elongations at which these phases are stable. The regions without any label correspond to the coexistence regions between these phases. The coordinates of the point where the fluid-PC coexistence region terminates are approximately $L^*=0.38$ and $\rho^*=1.150$. The results for $L^*=0.0$ are those of Hoover and Ree (Ref. 12). The open squares correspond to the results of Singer and Mumaugh (Ref. 2).

In this sense L^* plays an analogous role to that played by the temperature in a single component system with attractive interactions.

In Fig. 5 we show the fractional density change as a function of L^*. The trends are clearly illustrated. From $L^*=0$ to about $L^*=0.38$ there is a sharp decrease in the fractional density in the fluid-PC phase transition. At elongations higher than about $L^*=0.38$ the fractional density change takes values typical of the fluid-CP1 phase transition. At about $L^*=0.38$ there is a discontinuity in the fractional density change. For a real substance a discontinuity in the fractional density change on freezing at a given temperature may occur whenever there is a solid–solid–liquid triple point.[15]

In concluding this section we should note that for elongations close to $L^*=1.0$ the possibility of an aperiodic crystal exists.[16,17] For the two-dimensional case Wojciechowski et al.[3] have shown that the aperiodic crystal is the stable phase. Estimates[1,18] suggest that this may also be the case for three-dimensional hard dumbbells. In that case the phase diagram in the proximity of $L^*=1.0$ will be more complicated than the one presented in Figs. 2 and 3. This issue is discussed in more detail in I.

IV. CONCLUSIONS

We have presented further MC simulation results for the fluid–solid and solid–solid phase transitions in hard
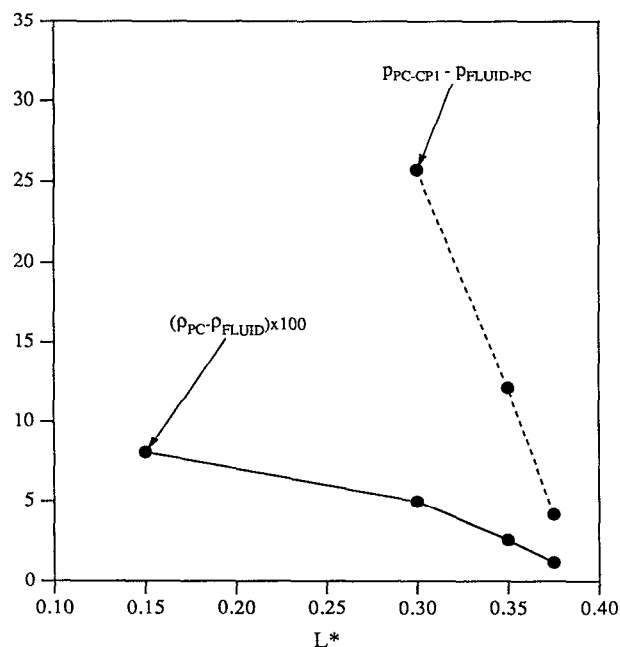

FIG. 4. Difference in the reduced pressure between the plastic crystal-CP1 phase transition and fluid–plastic crystal phase transition as a function of the elongation of the hard dumbbell. We also show the jump in the reduced density (with a factor of 100 for plotting convenience) of the fluid–plastic crystal phase transition as a function of the elongation.
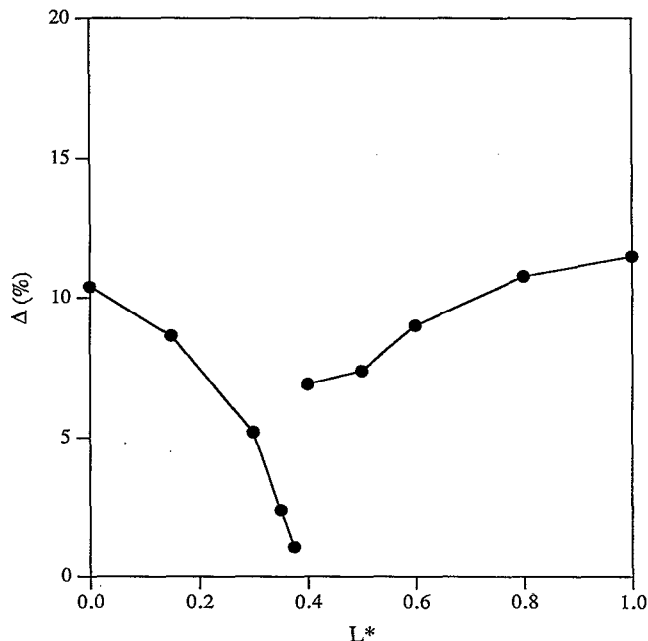
FIG. 5. Fractional density change at freezing, $\Delta = (\rho_s^* - \rho_f^*)/\rho_f^*$, plotted vs L^*. The discontinuity around $L^*=0.38$ is due to the change in nature of the fluid–solid transition, from a fluid-PC phase transition to a fluid-CP1 phase transition. The results for $L^*=0.0$ are those of Hoover and Ree (Ref. 12).

dumbbell systems. This simulation study indicates that mildly anisotropic hard dumbbells freeze into a PC phase which becomes unstable with respect to an orientationally ordered phase at higher densities. The properties at freezing of hard dumbbells with $L^* \lesssim 0.15$ are similar to those of hard spheres with the same molecular volume. For values of L^* between ~0.15 and 0.38 the fluid freezes into a PC structure with a sharp decrease in the fractional density change and a sharp increase in the coexistence density and pressure with increasing L^*. At $L^*=0.38$ our results suggest that the plastic crystal phase disappears. This is in good agreement with the value $L^*=0.40$ found by Singer and Mumaugh.[2] At higher elongations the fluid freezes into an orientationally ordered crystal and the PC phase is

not thermodynamically stable. The available results lead to a fairly complete description of the phase diagram of hard dumbbell.

Based on these results and those of earlier studies,[1,2] we believe that the fluid-PC phase transition in the hard dumbbell model with L^* close to 0.3–0.35 is a good structural model for the freezing of liquid N_2. However, the sharp changes in freezing properties with L^* in this range suggest that the quantitative accuracy of any dumbbell model (e.g., the two center Lennard-Jones potential) for the freezing of N_2 may be quite sensitive to the value of L^* used.

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