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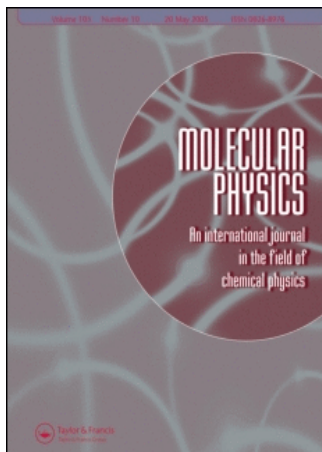
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## Application of cell theory to the thermodynamic properties of hard dumbbell solids

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The cell model of Lennard-Jones and Devonshire has been applied to the calculation of the free energy of hard dumbbell solids. The effective single particle partition functions were evaluated by Monte Carlo integration. The calculations have been carried out for several dumbbell bond lengths and crystal structures. The crystal structures included orientationally ordered base centred monoclinic structures which allow the dumbbells to achieve their maximum packing density and also the  $\alpha$ -N<sub>2</sub> structure. For the shortest bond length studied, an f.c.c. plastic crystal was also considered. The plastic crystal was treated as an f.c.c. array of spheres interacting via the pair potential derived from the reference averaged Mayer function (RAM) perturbation theory. By using an accurate equation of state for the hard dumbbell fluid the solid–fluid equilibria were determined. Good agreement with Monte Carlo simulations was found for both the solid free energy and equation of state, as well as the properties of the solid and fluid phases in equilibrium. The approach correctly predicts the dependence upon molecular anisotropy of the freezing properties. We also consider the stability of an aperiodic crystal for the case of dumbbells formed from tangent spheres.

### 1. Introduction

There has been considerable interest recently in the theory of freezing for simple systems. Much of this interest has been catalysed by the application of classical density functional theory which treats the solid as a highly inhomogeneous liquid [1, 2]. The free energy of the solid is related to that of the liquid via expressions which require knowledge of the direct correlation functions of the liquid. This theory has been quite successful for hard spheres, which can serve as an excellent reference system for perturbation or mean field studies of the freezing of the rare gases [1, 3]. Accurate and simple expressions for the fluid properties may be obtained from theories such as the Percus–Yevick theory [4]. For hard spheres the density functional theory in its most recent implementations is quantitatively accurate in its predictions [2].

It is also to be expected that studies of model systems of hard nonspherical particles such as hard dumbbells or hard ellipsoids will provide information about the role of molecular shape in determining the freezing properties of anisotropic molecules. Frenkel *et al.* [5–7] have made a comprehensive Monte Carlo simulation study of hard ellipsoids. This study focused principally upon the isotropic–nematic

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transition in the fluid phase for more anisotropic systems, but the solid–fluid equilibria were also obtained. The principal findings for the anisotropy dependence of the solid–fluid equilibria was the existence of a maximum in the solid–fluid coexistence densities and pressure when expressed as a function of the ellipsoid axis ratio. For mildly anisotropic ellipsoids, a plastic crystal phase was found to be the stable solid structure at lower pressures. The transition from plastic crystal to orientationally ordered crystal was found to be weakly first order or second order.

We have recently made a Monte Carlo simulation study of solid–fluid equilibria in systems of hard dumbbells and have investigated the dependence of the freezing properties upon the molecular anisotropy [8]. We have found that for the moderate anisotropies the hard dumbbells freeze into orientationally ordered base centred monoclinic structures. For the largest anisotropies there is also the possibility of the formation of solids in which the dumbbell spheres lie in an ordered structure but the centres of mass are on an aperiodic structure [9–11]. We used our results for orientationally ordered structures to estimate the properties of this aperiodic structure. For anisotropies similar to that of nitrogen we found that an f.c.c. plastic crystal was stable at lower pressures and the orientationally ordered structures were stable at high pressures. In this case our results are consistent with those from an earlier Monte Carlo simulation study by Singer and Mumaugh [12] of freezing into the plastic crystal. Our results are consistent with a first order transition between the plastic crystal and the orientationally ordered crystal.

Density functional theory has been applied to the freezing of hard dumbbells by Haymet and coworkers [13] (who also studied hard ellipsoids) and by Chandler and coworkers [14]. In both cases, a freezing transition into an f.c.c. plastic crystal was predicted for mildly anisotropic systems. However, for anisotropies appropriate to  $N_2$ , the plastic crystal phase could not be stabilized relative to the fluid. Orientationally ordered solids were studied by Haymet and coworkers [13] but were not found to be stable in the context of the theory. The discrepancy between the predictions from density functional theory and simulation results [8, 12] have an as yet unknown origin. We may speculate that this is due to the extra complexity in applying the theory to nonspherical molecules and also the lack of information about the direct correlation functions of hard nonspherical molecules in the fluid state which is both tractable and truly accurate. However, more analysis of the various approximations made in constructing these theories is required before firm conclusions are reached.

The purpose of the present paper is to show that quite accurate predictions of the freezing properties for hard dumbbell systems can actually be made by using a somewhat less ambitious approach. In particular, we use the simple Lennard-Jones and Devonshire cell theory [15] for the solid phase properties and an accurate equation of state for the fluid phase. This kind of approach has been used previously with some success for hard spheres [16] and also for the Lennard-Jones 12-6 potential [17]. Cell theory has been applied to an interaction site model of solid  $CO_2$  by Gibbons and Klein [18], but solid–fluid equilibrium was not considered. Our motivation for this study was to see whether a relatively simple approach could be developed for studying the solid phase properties of hard nonspherical particles. Such an approach might then be used to develop a mean field theory for the freezing properties of more complex systems. This would parallel the manner in which Longuet-Higgins and Widom [3] used the freezing properties of hard spheres as a reference system for the freezing of the rare gases. Hoover and Ree [16], in their definitive study of the hard sphere phase diagram, showed that quite accurate predictions could be made by using

Table 1. Coexistence data for the freezing of hard spheres into an f.c.c. solid, obtained from cell theory, Monte Carlo simulations and various density functional theories (DFT).  $\rho_f^*$  and  $\rho_s^*$  refer to equilibrium fluid and solid densities, respectively, while  $P^*$  denotes the equilibrium pressure.  $\Delta\rho/\rho_f$  is the fractional density change upon freezing.

	$\rho_f^*$	$\rho_s^*$	$\Delta\rho/\rho_f$	$P^*$
Monte Carlo <sup>a</sup>	0.943	1.041	0.103	11.7
Cell theory <sup>a</sup>	0.933	1.049	0.124	11.2
DFT <sup>b</sup>	0.968	1.150	0.188	14.2
DFT <sup>c</sup>	0.912	1.044	0.145	10.9
DFT <sup>d</sup>	0.945	1.041	0.102	11.9

<sup>a</sup> Hoover and Ree [16]. The row marked cell theory was calculated using a Padé approximant for the fluid phase free energy and cell theory [19] for the solid phase free energy.

<sup>b</sup> Density-functional theory, Smithline *et al.* [13].

<sup>c</sup> Density-functional theory, Denton and Ashcroft [31].

<sup>d</sup> Density-functional theory, Lutsko and Baus [32].

the cell theory for the solid phase properties and the Padé approximant for the fluid phase equation of state. These are shown in comparison with the computer simulation results and with the results from different versions of density functional theory in table 1. We have found comparably good agreement for the freezing properties of hard dumbbells. The best results from density functional theory seem to come from nonperturbative approaches [2] which do not rely upon the truncation of a functional Taylor expansion of the Helmholtz free energy, as is done in the versions of the theory which have been applied thus far to hard dumbbells [13, 14].

## 2. Theoretical background and numerical methods

In the cell theory of Lennard-Jones and Devonshire [15], the canonical partition function is factorized into single particle partition functions describing the motion of the molecules in cells formed by the other molecules of the solid in a static configuration on their lattice sites. We have

$$Q_N = \left(\frac{q}{V}\right)^N (Z_1)^N, \quad (1)$$

where  $N$  is the number of molecules,  $q$  is the molecular partition function which includes all the contributions from the internal degree of freedom, and  $V$  is the volume. The single particle partition function  $Z_1$  is given for a linear molecule by

$$Z_1 = \frac{1}{4\pi} \int \int \exp(-\beta\phi(\mathbf{r}_1, \boldsymbol{\omega}_1)) d\mathbf{r}_1 d\boldsymbol{\omega}_1, \quad (2)$$

where  $\phi(\mathbf{r}_1, \boldsymbol{\omega}_1)$  is the potential energy of interaction of the molecule with its neighbors expressed as a function of position in the cell,  $\mathbf{r}_1$ , and orientation,  $\boldsymbol{\omega}_1$ , and  $\beta = 1/kT$  where  $T$  is absolute temperature and  $k$  is Boltzmann's constant. For the case of hard core potentials (e.g. hard spheres or hard dumb-bells) the Boltzmann factor is either zero or unity so that, for hard spheres, the integral then measures the free volume available to the central molecule in its cell. This free volume can be obtained analytically, as was shown many years ago by Buehler *et al.* [19]. For hard nonspherical particles we have also to consider the orientational degrees of freedom, so that integral might be more correctly described by the term free configuration space rather

than free volume. Moreover, it is necessary to evaluate the integral numerically. To do this we use Monte Carlo integration. Once  $Z_1$  has been determined, we can readily obtain the free energy and then the pressure by differentiation. Since we are determining  $Z_1$  numerically, it is convenient to fit the results to a function in order to differentiate them and use them in phase equilibrium calculations. For this purpose we use the expression

$$Z_1 = C\alpha^D \exp(a_1\alpha + a_2\alpha^2 + a_3\alpha^3), \quad (3)$$

where  $C$ ,  $a_1$ ,  $a_2$ , and  $a_3$  are adjustable constants, and  $\alpha$  is given by

$$\alpha = \frac{\rho_0 - \rho}{\rho_0}, \quad (4)$$

where  $\rho$  is the number density and  $\rho_0$  is its value at close packing. Values of the densities at close packing for the structures considered in this work are given in reference [8]. Equation (3) is a generalization of the expression used by Alder *et al.* [20] to fit the  $PVT$  properties of hard spheres from molecular dynamics simulations at high pressure. The exponent  $D$  is the number of degrees of freedom of the central molecule [21], so that  $D = 3$  for hard spheres and  $D = 5$  for hard dumbbells in orientationally ordered structures. In some cases it was necessary to treat  $D$  as an adjustable parameter in order to obtain a good fit of the values of  $Z_1$  at high density.

We have evaluated equation (2) by Monte Carlo integration so that

$$Z_1 = v \langle \exp(-\beta\Phi(\mathbf{r},\omega)) \rangle, \quad (5)$$

where  $v$  is the volume of the cell and the angled brackets denote an average of the Boltzmann factor over randomly generated configurations of the central particle in its cell. This average is equal to the fraction of configurations where there is no overlap between the central particle and its nearest neighbors. Direct use of this expression becomes difficult at densities approaching close packing, where the free configuration space approaches zero, and the overwhelming proportion of randomly generated configurations of the central molecule result in overlap. Some kind of importance sampling is therefore necessary. What we have done is to perform a random walk simulation of the central molecule in its cell. During the course of this simulation we kept track of the maximum displacement of the particle away from its static lattice configuration (both in position and orientation). Some care in choosing the step size for the random walk was necessary in order to sample the accessible configuration space effectively in a reasonable amount of time. We adopted a procedure whereby the random walks with  $5 \times 10^4$  steps were repeated several (2–4) times until the maximum displacements obtained increased by no more than one part in  $10^4$ . The maximum displacement from the random walk simulation was then used to define a restricted sample space for the Monte Carlo integration of equation (1). We write

$$Z_1 = \frac{\Delta\phi}{4\pi} \Delta\cos\theta \Delta x \Delta y \Delta z \langle \exp(-\beta\Phi(\mathbf{r},\omega)) \rangle \quad (6)$$

Here  $\Delta\cos\theta$ ,  $\Delta\phi$ ,  $\Delta x$ ,  $\Delta y$  and  $\Delta z$  define the size of the interval centred on the static lattice configuration in which the coordinates were sampled ( $\theta$  and  $\phi$  refer to the usual orientation angles defined relative to the  $z$  axis). Since the random walk simulation must lead to a maximum displacement which is less than the exact value, we have applied a safety factor of 1.05 to the displacements obtained in this way. For hard spheres the maximum displacement is known analytically, and we have checked that

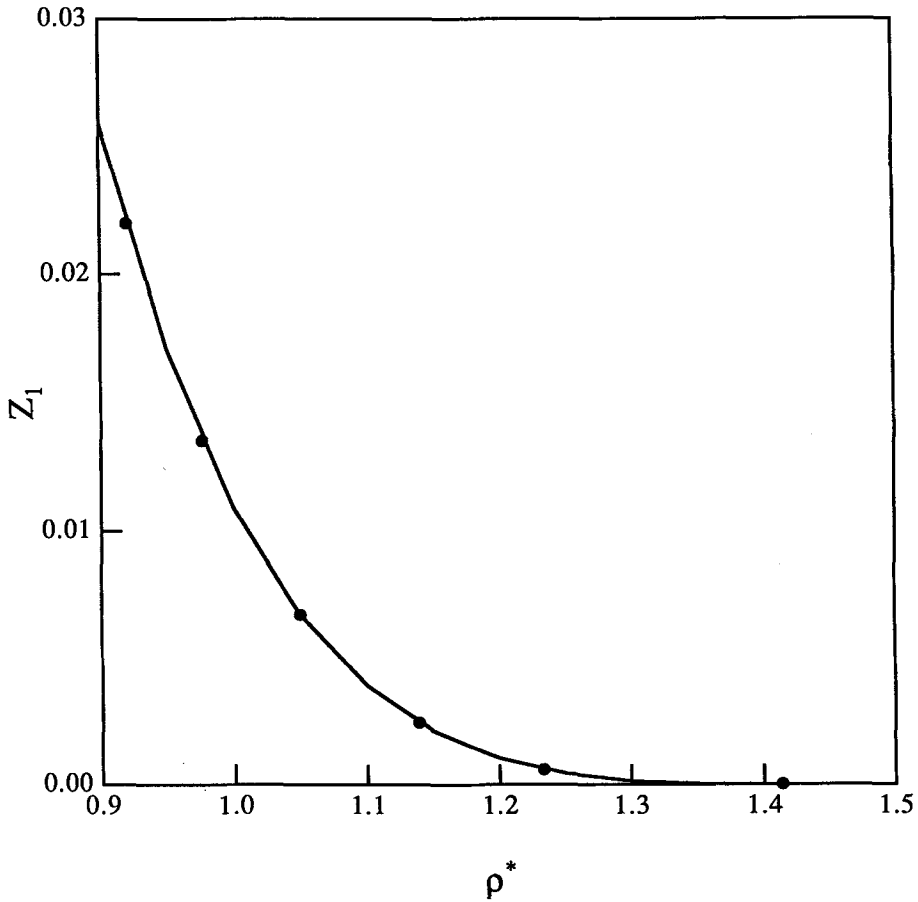


Figure 1. The free volume for hard spheres. The line gives results from our numerical calculations while the points are the analytical results from Buehler *et al.* [19].

the random walk method yields accurate results in this case. In this way, we have been able to evaluate accurate values of  $Z_1$  for densities up to values approaching close packing. Typically, we used  $10^6$  random samples to determine the average in equation (6), which led to estimates which are accurate to at least three significant figures. As an illustration of this accuracy, figure 1 shows values of  $Z_1$  for hard spheres obtained in this way together with the analytical results [19].

The cell theory described above is strictly applicable only to orientationally ordered crystals. For mildly anisotropic particles it can be expected that orientationally disordered (plastic crystal) structures will be stable in the solid phase. In order to provide some treatment of these systems at a comparable level of approximation, we decided to approximate the plastic crystal as a system of spherical particles interacting via the reference averaged Mayer function reference potential [22]

$$\beta u_0(r_{12}) = -\ln \left[ \frac{1}{4\pi} \int \int \exp(-\beta u(r_{12}, \omega_1, \omega_2)) d\omega_1 d\omega_2 \right]. \quad (7)$$

For hard dumbbells this potential can be calculated by a combination of numerical and analytical techniques [22]. The potential  $u_0(r_{12})$  has a hard sphere core for  $r_{12}$  less than the distance of closest approach between two hard dumbbells. It is zero for

$r_{12} > L + \sigma$  (where  $L$  is the separation between the spheres of the dumbbell and  $\sigma$  the sphere diameter), the maximum distance at which overlap of two dumbbells can occur. Between these separations  $u_0(r_{12})$  is a smoothly decreasing repulsive potential. Naturally, this approximation can only be expected to be accurate for mildly anisotropic dumbbells. Moreover, the solid phase of such a system has a maximum packing density which is determined by the size of the hard core in  $u_0(r_{12})$ , and this density will be significantly higher than that of the hard dumbbell system being approximated. This will lead to an overestimation of the solid compressibility. Thus, we may expect significant errors in the equation of state for the solid at high pressures. Nevertheless, as will be clear later, we do obtain some useful results by applying it to the plastic crystal phase for mildly anisotropic dumbbells.

For nonspherical molecules we have, in addition to changes of crystal structure with density, the possibility of small but significant changes in the unit cell shape with density, and these have been observed in our Monte Carlo simulation work [8]. Such

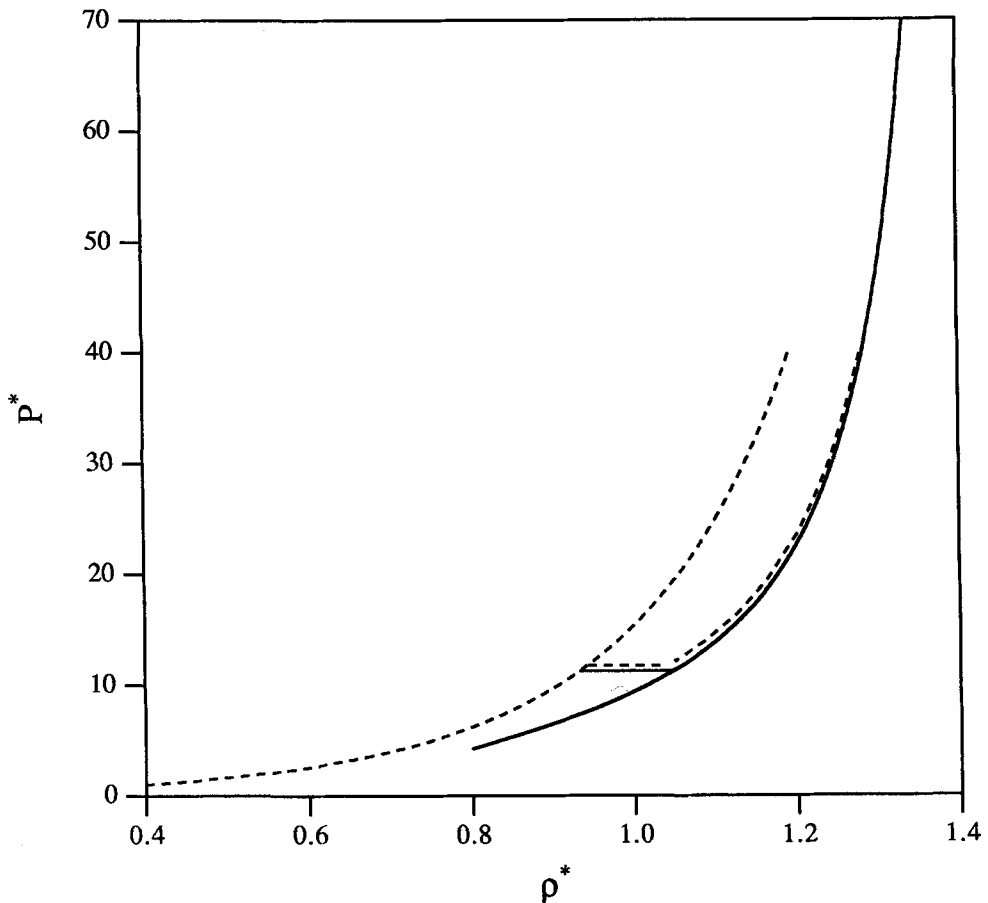


Figure 2. The equation of state and phase equilibria for hard spheres. The dashed line gives results for the fluid and solid phases using the Carnahan–Starling [26] and Hall [27] equations of state, respectively. The solid line gives the result for the solid phase from cell theory. The dashed tie line is the result of Hoover and Ree [16], and the solid line is the result obtained by using cell theory for the solid phase and the Carnahan–Starling equation of state for the fluid phase.

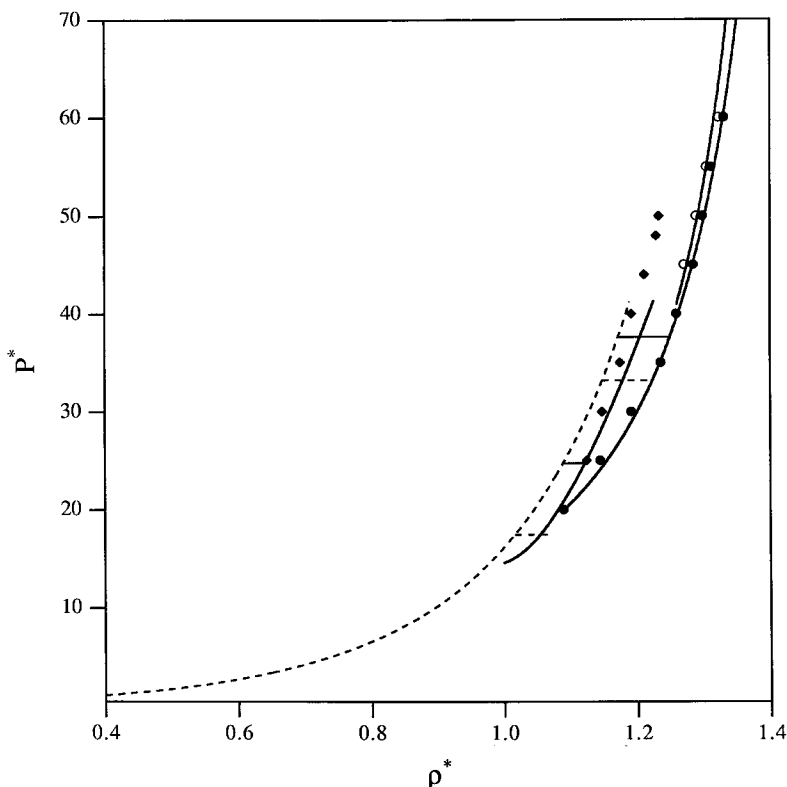


Figure 3. The equation of state and phase equilibria for hard dumbbells with  $L^* = 0.3$ . The dashed line is the fluid phase equation of state calculated from the Tildesley–Streett equation [28]. The points are the simulation results for the f.c.c. plastic crystal (diamonds), the  $\alpha\text{-N}_2$  structure (open circles) and the CP1 structure (filled circles). The solid lines give the equation of state for the solid from cell theory for (from left to right) the f.c.c. plastic crystal, the  $\alpha\text{-N}_2$  structure and the CP1 structure. The thermodynamic properties of the three CP structures are essentially identical within the precision of both the simulations [8] and the cell theory calculations. Tie lines are shown between equilibrium phases obtained by using cell theory (solid line) and Monte Carlo simulation (dashed line) for the solid phase properties.

effects can be incorporated into cell theory by carrying out a free energy minimization with respect to unit cell geometry at each density, but at the cost of an increase in the computer time required. In most of the present studies we have used the unit cell shape at close packing for all other densities, but we will describe some studies of the effect of relaxing this restriction.

In addition to the f.c.c. plastic crystal and the  $\alpha$ -nitrogen structure, we have chosen other crystal structures to study in this work by consideration of the ways in which hard dumbbells are arranged at their maximum packing density [8]. A simple way to picture the geometry of hard dumbbell solids at closest packing is to note that dumbbells can be arranged into hexagonally packed layers in which each sphere of the dumbbell also lies in a hexagonally packed layer. In these layers the dumbbell axes are tilted from the normal to the plane of the layer by an angle given by  $\arcsin(L^*/\sqrt{3})$ , where  $L^* = L/\sigma$ . Since each of these layer exposes a hexagonal array of spheres to the layers above and below it, the dumbbell layers may be stacked in any manner



Table 2. Solid–fluid equilibria for  $L^* = 0.3$  as obtained from cell theory (CT) calculations and compared with Monte Carlo (MC) results [8]. PC refers to the plastic crystal phase.

Lattice	$\rho_f^*$		$\rho_s^*$		$P^*$		$\mu/kT$	
	CT	MC	CT	MC	CT	MC	CT	MC
PC	1.089	1.017	1.122	1.070	24.74	17.45	29.28	22.37
CP1	1.173	1.148	1.250	1.221	37.60	33.22	40.62	36.85
CP2	1.173	1.148	1.251	1.222	37.61	33.22	40.63	36.85
CP3	1.173	1.143	1.250	1.218	37.60	32.32	40.63	36.08

which facilitates the closest packing of the exposed spheres. We have identified three different ways in which the dumbbell layers may be stacked, and these are readily understood for the case where  $L^* = 1.0$  (tangent spheres) which, at closest packing, is identical in structure to a close packed array of spheres. In two of these the dumbbell axes are all parallel. One of these two structures has the dumbbell spheres arranged in an ABC sequence so that the structure is an f.c.c. array of spheres. We label this structure CP1. In the other, the dumbbell spheres are stacked in an ABAB sequence so that the structure is an h.c.p. array of spheres. We label this structure CP2. The layers may also be stacked so that the tilt angle alternates between successive layers. We label this structure CP3. The three structures are illustrated in figure 1 of reference [8]. These structures are closely related to those of the solid halogens [24].

For the case of  $L^* = 1.0$  it is possible to achieve maximum packing without orientational order due to the structural degeneracy of the system at close packing. Such structures may be generated by randomly assigning bonds to an f.c.c. or h.c.p. array of spheres at close packing. They have the property that while the atoms of the dumbbells show a high degree of translational order the centers of mass do not. For this reason, such structures are referred to as aperiodic solids. The 2-dimensional hard dumbbell case has been studied in detail using a variety of methods by Wojciechowski *et al.* [9–11]. The key result is that the structural degeneracy lowers the free energy of this phase relative to the orientationally ordered structures. In the present case of hard dumbbells in 3 dimensions, determination of the structural degeneracy at close packing is the dimer problem for an f.c.c. lattice [25].

We have applied cell theory to the case of the aperiodic structure for hard dumbbells with  $L^* = 1.0$  as follows. We start with an f.c.c. array of spheres and choose two adjacent spheres as the central dumbbell. We then make a random assignment of bonds to the spheres surrounding these two in such a way that each sphere is bonded to one, and only one, other sphere. The centre of mass coordinates and orientations of all the dumbbells resulting from this process are then determined.

Table 3. Solid–fluid equilibria for  $L^* = 0.6$  as obtained from cell theory (CT) calculations and compared with Monte Carlo results [8].

Lattice	$\rho_f^*$		$\rho_s^*$		$P^*$		$\mu/kT$	
	CT	MC	CT	MC	CT	MC	CT	MC
$\alpha$ -N <sub>2</sub>	1.211	1.193	1.256	1.255	54.41	48.59	56.13	51.29
CP1	1.162	1.146	1.276	1.249	41.23	37.97	45.05	42.22
CP2	1.162	1.143	1.276	1.244	41.24	37.37	45.06	41.70
CP3	1.162	1.148	1.275	1.252	41.08	38.33	44.92	42.53

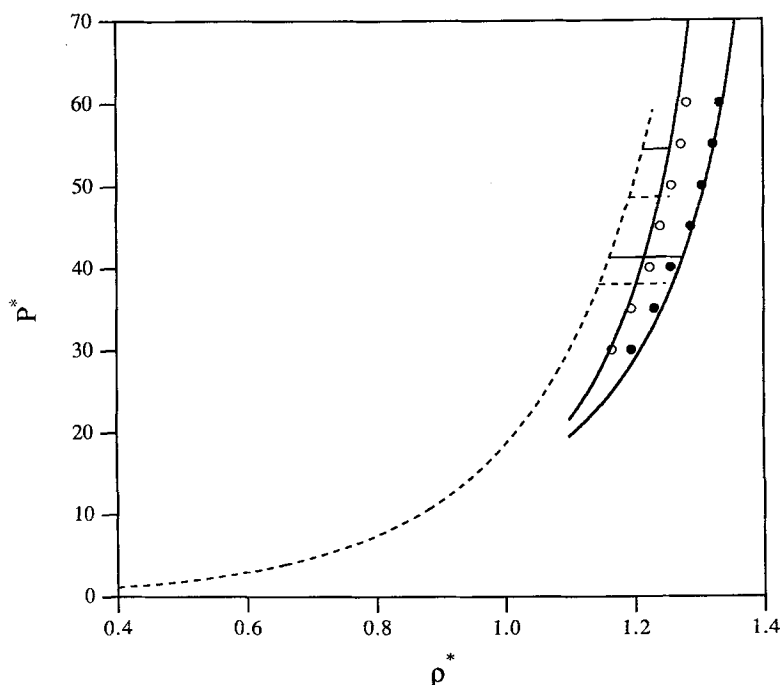


Figure 4. The equation of state and phase equilibria for hard dumbbells with  $L^* = 0.6$ . The dashed line is the fluid phase equation of state calculated from the Tildesley–Streett equation [28]. The points are the simulation results for the  $\alpha$ -N<sub>2</sub> structure (open circles) and the CP1 structure (filled circles). The solid lines give the equation of state for the solid from cell theory for (from left to right) the  $\alpha$ -N<sub>2</sub> structure and the CP1 structure. The thermodynamic properties of the three CP structures are essentially identical within the precision of both the simulations [8] and the cell theory calculations. Tie lines are shown between equilibrium phases obtained by using cell theory (solid line) and Monte Carlo simulation (dashed line) for the solid phase properties.

These coordinates then define the cell for determination of  $Z_1$ . At each density we have averaged the free energy over  $10^3$  realizations of this random cell structure, using  $10^4$  samples in the determination of  $Z_1$  for each realization.

In presenting results for these hard dumb-bell systems we shall use the following reduced units for density and pressure:

$$\rho^* = \rho d^3; \quad P^* = Pd^3/kT,$$

where  $d^3 = \sigma^3(1 + 3/2L^* - 1/2L^{*3})$ , so that  $d$  is the diameter of a sphere with the same volume as the dumbbell. In this way, systems with different values of  $L^*$  but the same value of  $\rho^*$  are at the same volume fraction.

### 3. Solid–fluid equilibria for hard dumbbells

To begin with we show in figure 2 the solid and fluid branches of the equation of state for hard spheres from cell theory and from empirical fits of the molecular simulation data [26, 27]. Cell theory slightly underestimates the solid phase pressure as well as the freezing pressure, and slightly overestimates the density change on freezing. Nevertheless, the overall results are quite satisfactory.

Figure 3 shows the corresponding results for hard dumbbells with  $L^* = 0.3$ , and

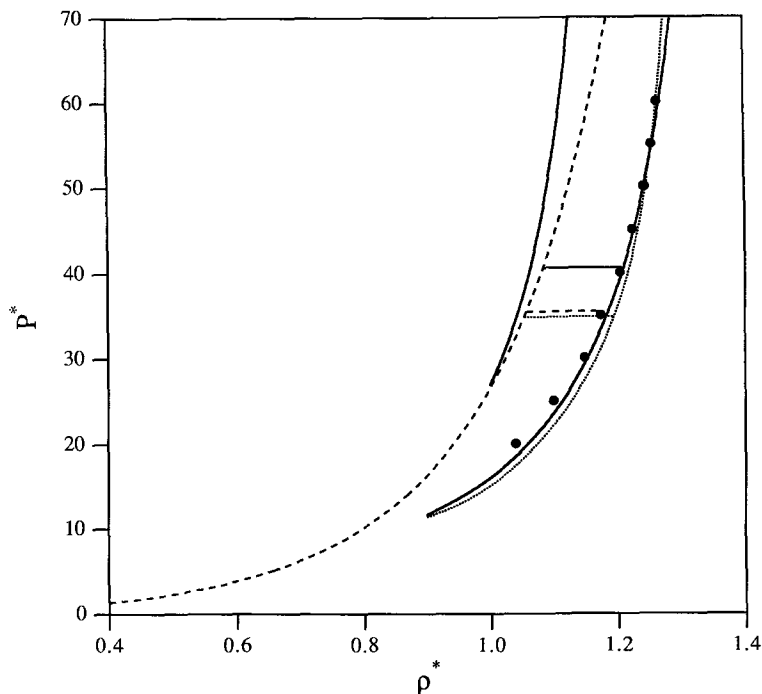


Figure 5. The equation of state and phase equilibria for hard dumbbells with  $L^* = 1.0$ . The dashed line is the fluid phase equation of state calculated from the Tildesley-Street equation [28]. The points are the simulation results for the CP1 structure. The solid lines give the equation of state for the solid from cell theory for (from left to right) the  $\alpha$ -N<sub>2</sub> structure and the CP1 structure. The thermodynamic properties of the three CP structures are essentially identical within the precision of both the simulations [8] and the cell theory calculations. The dotted line gives the results from cell theory for the CP1 structure with  $c/a$  given by its value from the Monte Carlo simulation of the solid near the melting density. Tie lines are shown between equilibrium phases obtained by using cell theory (solid and dotted lines) and Monte Carlo simulation (dashed line) for the solid phase properties.

Table 4. Solid-fluid equilibria for hard dumb-bells with  $L^* = 1.0$  as obtained from cell theory (CT) and from Monte Carlo (MC) simulations [8].

Lattice	$\rho_f^*$		$\rho_s^*$		$P^*$		$\mu/kT$	
	CT	MC	CT	MC	CT	MC	CT	MC
CP1	1.084	1.053 <sup>a</sup>	1.210	1.174 <sup>a</sup>	40.58	34.57 <sup>a</sup>	48.26	42.64 <sup>a</sup>
CP1		1.058 <sup>b</sup>		1.179 <sup>b</sup>		35.45 <sup>b</sup>		43.48 <sup>b</sup>
CP2	1.086	1.052 <sup>a</sup>	1.212	1.177 <sup>a</sup>	40.98	34.37 <sup>a</sup>	48.63	42.45 <sup>a</sup>
CP2		1.071 <sup>c</sup>		1.194 <sup>c</sup>		37.83 <sup>c</sup>		45.71 <sup>c</sup>
CP3	1.082	1.051 <sup>a</sup>	1.209	1.173 <sup>a</sup>	40.30	34.25 <sup>a</sup>	48.00	42.34 <sup>a</sup>
Aperiodic	0.985	0.936 <sup>d</sup>	1.112	1.030 <sup>d</sup>	24.71	19.4 <sup>d</sup>	32.97	27.45 <sup>d</sup>

<sup>a</sup> Monte Carlo simulation results for 144 particles.

<sup>b</sup> Monte Carlo simulation results for 486 particles.

<sup>c</sup> Monte Carlo simulation results for the CP1 lattice with the restriction that the lattice assumes the same structure as at close-packing.

<sup>d</sup> Estimate based on Monte Carlo simulation results for the CP3 lattice with an added contribution to the free energy from the structural degeneracy of the aperiodic structure at close packing.

Table 5. Solid-fluid equilibria for  $L^* = 1.0$  as obtained from cell theory (CT) calculations, using the values of  $(c/a)/(c/a)_{cp} = 0.97, 0.98,$  and  $0.985$  for CP1, CP2, and CP3, respectively. Monte Carlo simulation results for CP1 are for 486 particles while CP2 and CP3 results are for 144 particles [8].

Lattice	$\rho_f^*$		$\rho_s^*$		$P^*$		$\mu/kT$	
	CT	MC	CT	MC	CT	MC	CT	MC
CP1	1.054	1.058	1.195	1.179	34.80	35.45	42.85	43.48
CP2	1.061	1.052	1.205	1.177	36.09	34.47	44.08	42.45
CP3	1.056	1.051	1.198	1.173	35.17	34.25	43.21	42.34

the estimates of the freezing properties are given in table 2. The fluid phase properties of hard dumbbells were determined from the accurate equation of state of Tildesley and Streett [86], which was obtained by fitting data from Monte Carlo simulations. In this case, we have considered the stability of three types of solid phase: an f.c.c. plastic crystal; the  $\alpha$ -nitrogen structure and three base centered monoclinic structures. These latter three structures have thermodynamic properties which are almost indistinguishable within the numerical accuracy of our cell theory calculations and within

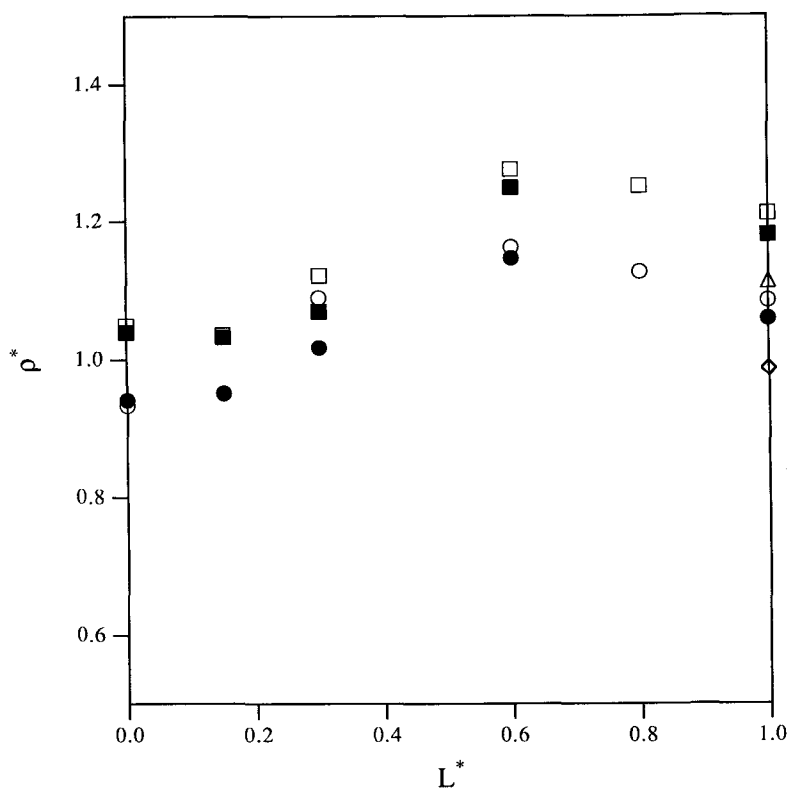


Figure 6. Coexisting fluid (circles) and solid (squares) densities for hard dumbbells versus  $L^*$ . Comparison between cell theory results (open symbols) and Monte Carlo simulations (filled symbols) is shown. For  $L^* = 1.0$ , cell theory results for freezing into an aperiodic structure are also shown by a triangle (solid density) and diamond (fluid density).

Table 6. Dependence of the free energy  $A/NkT$  upon unit cell shape of the CP1 lattice from cell theory at  $\rho^* = 1.179$  for  $L^* = 1.0$ . From Monte Carlo simulations [8] with the same average density we find that the average value of  $\theta$  is  $32.6^\circ$  and the average value of  $(c/a)/(c/a)_{cp}$  is 0.974.

$\theta$	$(c/a)/(c/a)_{cp}$							
	0.93	0.94	0.95	0.962	0.97	0.98	1.00	1.02
35.26	13.82	13.40	13.27	13.27	13.33	13.51	13.89	14.46
33.08	13.86	13.46	13.24	13.15	13.14	13.17	13.39	13.72
31.00	14.22	13.93	13.75	13.61	13.57	13.51	13.51	13.65

the precision of the Monte Carlo simulations [8]. Cell theory is most accurate for the orientationally ordered structures since, for the plastic crystal, there is the additional approximation of using the sphericalized reference potential. An important consequence of this latter approximation is to overestimate the compressibility of the solid at high density. Nevertheless, the theory does correctly predict freezing into the plastic crystal rather than the orientationally ordered structures, and also that the  $\alpha\text{-N}_2$  structure appears only as a metastable state.

The equation of state and solid–fluid equilibria results for the case of  $L^* = 0.6$  are shown in figure 4, with the numerical values of the freezing properties given in

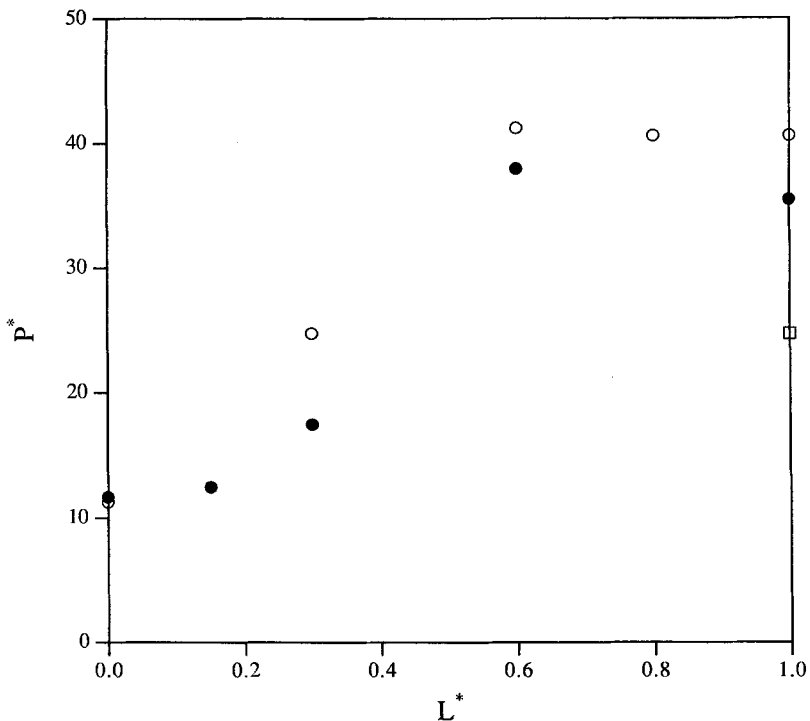


Figure 7. The freezing pressure for hard dumbbells versus  $L^*$ . Comparison between the cell theory results (open circles) and Monte Carlo simulations (filled circles) is shown. For  $L^* = 1.0$ , the cell theory result for freezing into an aperiodic structure is also shown by a square.

Table 7. Solid–fluid equilibria for hard dumb-bells with  $L^* = 0.15$  as obtained from cell theory (CT) using the RAM potential, from density functional theory (DFT) [14], and from Monte Carlo simulations [30].

	$\rho_t^*$	$\rho_s^*$	$P^*$	$\mu/kT$
MC	0.950	1.033	12.45	17.11
CT	0.951	1.036	12.45	17.11
DFT	1.005	1.523		

table 3. Results for the solid in a close packed structure and in  $\alpha\text{-N}_2$  are shown. The theory predicts, again correctly, that the fluid freezes into the close packed structure and that the  $\alpha\text{-N}_2$  structure is metastable.

Figure 5 shows the corresponding results for  $L^* = 1.0$ , with the numerical values of the freezing properties given in table 4. The first point to be noted here is the very high pressure obtained for the  $\alpha\text{-N}_2$  structure from cell theory, which is even higher than that of the fluid phase at high density. This is consistent with the fact that in our simulation work we found that the  $\alpha\text{-N}_2$  structure was not mechanically stable. We have also included our predictions of the freezing properties for the case of freezing into an aperiodic structure. Notice that, in this case, the freezing pressure and densities are much lower. This is a consequence of the extra stability added to the aperiodic structure as a consequence of its structural degeneracy. It is this aperiodic structure which is likely to be the stable structure on freezing hard dumbbells with  $L^* = 1.0$ . Within the cell theory approximation the equation of state and free energy of the aperiodic solid without the degeneracy contribution are very close to those of the orientationally ordered structures.

As can be seen from table 4 and figure 5, the agreement between theory and simulation for  $L^* = 1.0$  is generally quite good. One of the most important sources of error in cell theory is the neglect of changes in the unit cell geometry with density. For the close packed structures we also repeated the cell theory calculations with the unit cell having the same shape as that obtained from the simulation results near the melting density. This improves the prediction of the freezing properties (see table 5) but leads to a slightly poorer prediction of the equation of state as shown in figure 5. In table 4 we also show results obtained for the CP2 structure from simulations where the unit cell shape was constrained to the shape at close packing. These results are in much better agreement with the cell theory predictions made with the same restrictions. It should be noted that there is a contribution to the pressure which comes from the change in unit cell shape with density, and this has not been included in either of our cell theory calculations. There are two important ways in which the unit cell changes with density. If we label the basis vectors of the unit cell as  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$ , with the understanding that  $\mathbf{a}$  and  $\mathbf{b}$  lie in the plane of the hexagonally packed layers, then we find that the ratio  $c/a$  decreases with density relative to its value at close packing. Second, the angle of orientation of the molecular axes relative to the normal to the  $\mathbf{a}\text{-}\mathbf{b}$  plane decreases as the density is decreased away from close packing [8]. To investigate whether cell theory could correctly predict the effect of such distortions, we carried out a set of calculations at one density where we looked at the effect of changing both the orientation angle and the ratio  $c/a$  upon the solid free energy. Some results are shown in table 6 for the CP1 structure. The cell theory results are consistent with an optimum unit cell geometry which is close to that obtained from the Monte

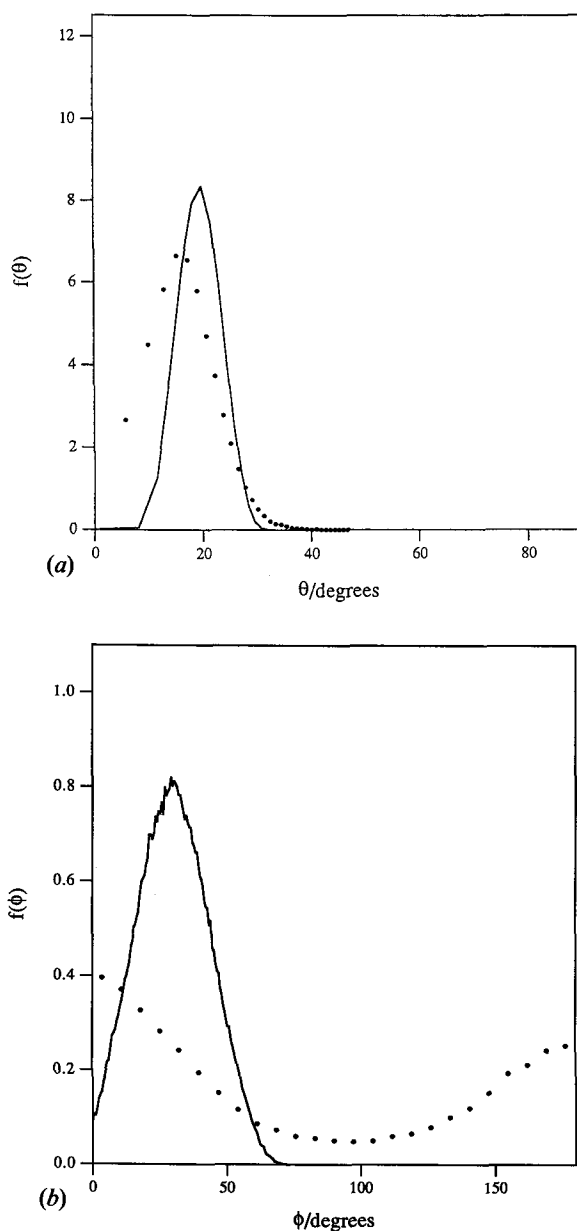


Figure 8. Angular distribution functions (a)  $f(\theta)$  and (b)  $f(\phi)$  for hard dumbbells with  $L^* = 0.6$ . The line gives the results from cell theory for the CP1 structure at the reduced pressure  $P^* = 37.5$ . The points are the corresponding Monte Carlo simulation results.

Carlo simulations [8] using the Parinello–Rahman [29] method for changing the simulation cell shape.

In order to make comparison with the predictions of density functional theory [14], we have made some calculations for the case  $L^* = 0.15$  using both cell theory and Monte Carlo simulation [30]. Only the plastic crystal solid phase was considered. The cell theory was again carried out by using the RAM potential for the solid. This

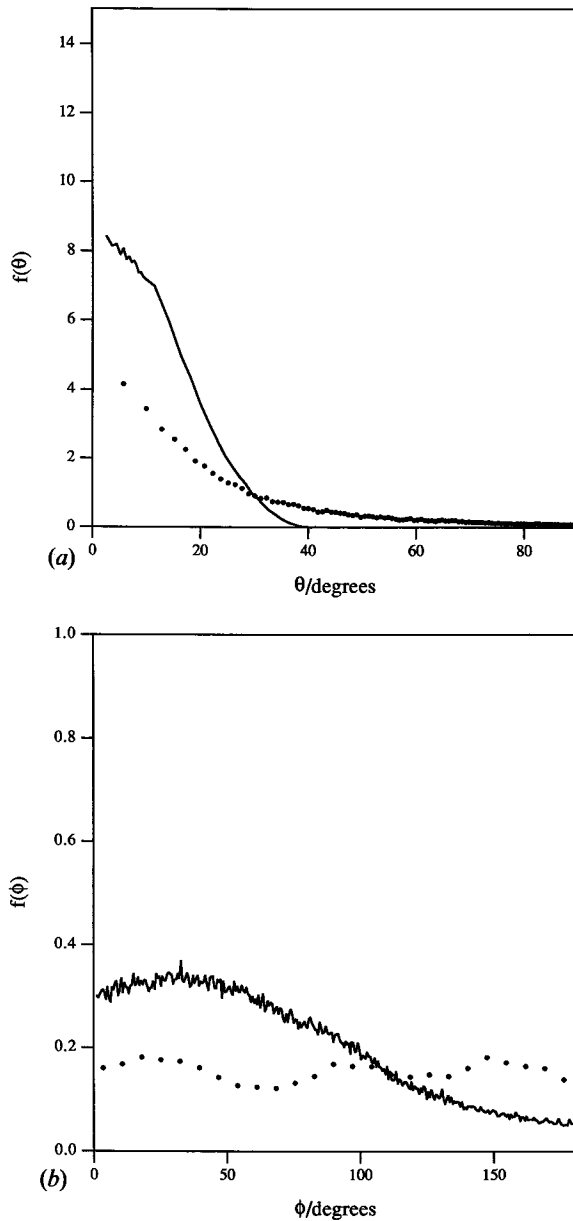


Figure 9. Angular distribution functions (a)  $f(\theta)$  and (b)  $f(\phi)$  for hard dumbbells with  $L^* = 0.3$ . The line gives the results from cell theory for the CPI structure at the reduced pressure  $P^* = 30$ . The points are the corresponding Monte Carlo simulation results.

should be much more accurate for a system of this very slight molecular anisotropy. A comparison of the freezing properties for this system is shown in table 7. Cell theory is in excellent agreement with the simulation results, whereas the density functional theory substantially overestimates the coexistence densities. It should be noted that this version of the density functional theory [14] is perturbative in form, and it is quite possible that improved agreement would be obtained by using a nonperturbative



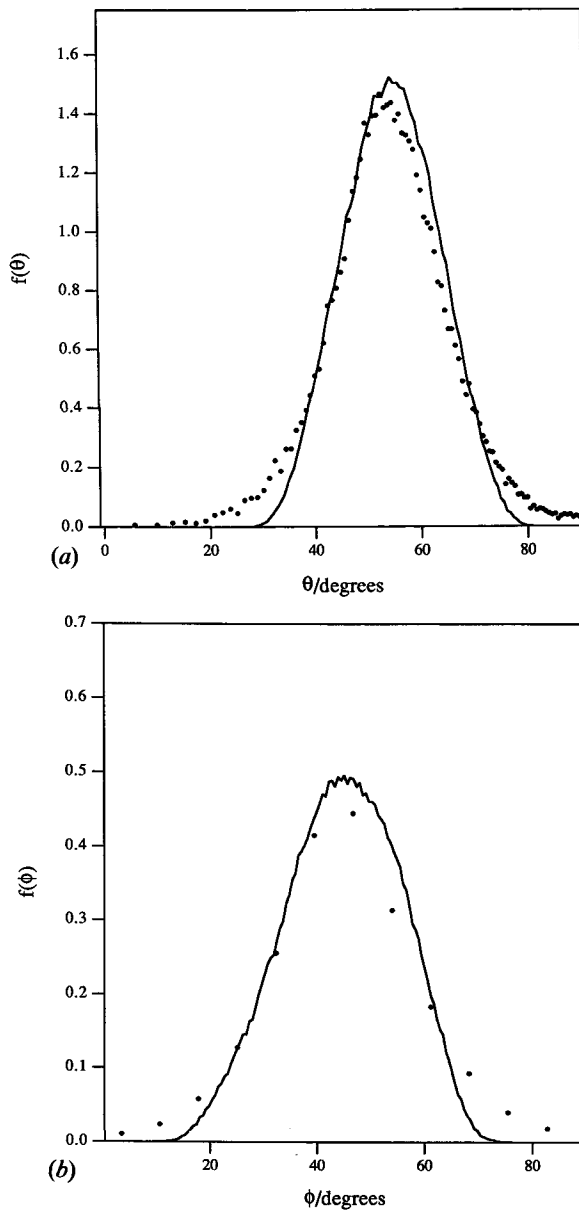


Figure 10. Angular distribution functions (a)  $f(\theta)$  and (b)  $f(\phi)$  for hard dumbbells with  $L^* = 0.3$ . The line gives the results from cell theory for the  $\alpha$ -N<sub>2</sub> structure at the reduced pressure  $P^* = 45$ . The points are the corresponding Monte Carlo simulation results.

approach [2, 31, 32], should this prove feasible. A more detailed comparison between density functional theory and Monte Carlo simulation for freezing into the plastic crystal has been given by Singer and Mumaugh [12].

The predictions of the freezing properties as a function of  $L^*$  are shown together with simulation results in figure 6 for the coexistence densities and in figure 7 for the coexistence pressures. For  $L^* = 1.0$  we have included the results for freezing into both orientationally ordered structure as well as the aperiodic structure. Notice that the cell theory results agree very well with the trends seen in the simulation results.

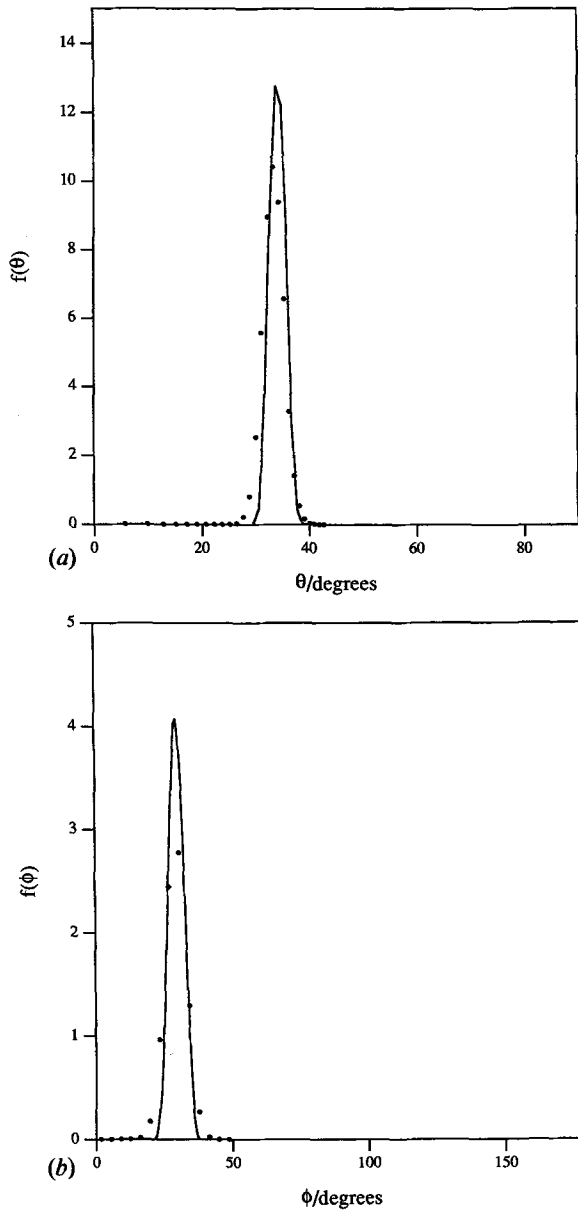


Figure 11. Angular distribution functions (a)  $f(\theta)$  and (b)  $f(\phi)$  for hard dumbbells with  $L^* = 1.0$ . The line gives the results from cell theory for the CP1 structure at the reduced pressure  $P^* = 60$ . The points are the corresponding Monte Carlo simulation results.

In addition to the predictions of the thermodynamic properties, it is interesting to examine how well cell theory handles the structural effects in the solid. We should of course anticipate that the assumption of molecular motion in a cell consisting of neighboring molecules on a static lattice is a considerable oversimplification. We have calculated the normalized distribution of orientations which arise in cell theory and have compared this with results from Monte Carlo simulations [8]. Representative results are shown for the orientationally ordered solid structures in figures 8–11. Cell

theory provides its best description of the orientational order for the  $\alpha$ -N<sub>2</sub> structure for  $L^* = 0.3$  (see figure 10(a)). This is partly a consequence of the cubic unit cell in this case. For the CP structures there is, as noted earlier, some distortion of the unit cell as the density is decreased from close packing, and this has not been included in these cell theory calculations. For  $L^* = 1.0$  (see figure 11) the agreement between simulation and theory is also quite good, since the molecular anisotropy restricts the molecular orientations in a similar way to that imposed by cell theory. For the CP1 structure for  $L^* = 0.6$  and  $L^* = 0.3$ , the agreement is quite good for the  $\theta$  distribution but less good for the  $\phi$  distribution. This is because the orientational order in the  $\phi$  is lost more quickly in  $\phi$  as the density is lowered from close packing. For moderately anisotropic molecules there is generally less orientational order in the CP1 structure than that imposed on the system in cell theory. In fact, for  $L^* = 0.3$ , and to a lesser extent for  $L^* = 0.6$ , there is considerable reorientation of the molecules via precession about the axis normal to the hexagonally packed layers in the CP1 structure.

#### 4. Summary and discussion

We have presented a study of cell theory applied to the solid phases of hard dumbbells. The equation of state obtained from cell theory is in quite good agreement with the results from Monte Carlo simulations. The relative stability of the different crystal structures considered also agrees with simulation. The theory has been extended to the case of a plastic crystal by treating such a phase as a collection of particles interacting via an effective spherical reference potential obtained from RAM theory. This works quite well near to the melting density but overestimates the compressibility of the solid at high densities. By using the Tildesley–Streett [28] equation of state for the hard dumbbell fluid we have been able to estimate the solid–fluid equilibria. The estimates are in quite good agreement with the Monte Carlo simulation results. The theoretical estimates correctly reflect the overall dependence of the freezing properties upon the dumbbell anisotropy. The results for hard dumbbells are not quite as accurate as those for hard spheres, but this is due principally to the neglect in our calculations of the density dependence of the unit cell shape. We have shown that cell theory can be used to determine an optimum unit cell shape which agrees well with that obtained in Monte Carlo simulations [8].

For the case of  $L^* = 1.0$  we have also applied cell theory to the aperiodic solid. The configurational degeneracy makes this structure more stable than the orientationally ordered structures considered. Within the cell theory approximation the equation of state and free energy without the degeneracy contribution are very close to those of the orientationally ordered structures. This is consistent with results from a recent study for the case of hard dumbbells in 2 dimensions [11].

This work has demonstrated the utility of the simple cell theory for providing economical and reliable estimates of solid phase properties of hard dumbbells. For hard spheres the approach is about as accurate as the best density functional theory available. For hard dumbbells it is more accurate than the density functional theories which have been developed thus far [13, 14], although improvements on these approaches can be anticipated [2, 31, 32]. The present approach may well prove quite useful in the study of more complex molecular solids when the detailed study by Monte Carlo simulations or density functional theories is not feasible. We are currently using the present results together with results from Monte Carlo simulations

to extend the generalized van der Waals theory of Longuet-Higgins and Widom [3] to the freezing of molecular liquids.

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### References

- [1] HAYMET, A. D. J., 1987, *Science*, **236**, 1076; HAYMET, A. D. J., 1987, *Ann. Rev. Phys. Chem.*, **38**, 89.
- [2] BAUS, M., 1990, *J. Phys. Condensed Matter*, **2**, 2111.
- [3] LONGUET-HIGGINS, H. C., and WIDOM, B., 1964, *Molec. Phys.*, **8**, 549.
- [4] PERCUS, J. K., and YEVICK, G. J., 1958, *Phys. Rev.*, **110**, 1.
- [5] FRENKEL, D., and MULDER, B. M., 1985, *Molec. Phys.*, **55**, 1171.
- [6] FRENKEL, D., MULDER, B. M., and MCTAGUE, J. P., 1984, *Phys. Rev. Lett.*, **52**, 287.
- [7] FRENKEL, D., MULDER, B. M., and MCTAGUE, J. P., 1985, *Molec. Crystals liq. Crystals*, **123**, 119.
- [8] VEGA, C., PARAS, E. P. A., and MONSON, P. A., 1992, *J. chem. Phys.*, **96**, 9060.
- [9] BRANKA, A. C., WOJCIECHOWSKI, K. W., 1985, *Molec. Phys.*, **56**, 1149.
- [10] WOJCIECHOWSKI, K. W., 1987, *Phys. Lett. A*, **122**, 377.
- [11] WOJCIECHOWSKI, K. W., FRENKEL, D., and BRANKA, A. C., 1991, *Phys. Rev. Lett.*, **66**, 3168.
- [12] SINGER, S. J., and MUMAUGH, R., 1990, *J. chem. Phys.*, **93**, 1278.
- [13] SMITHLINE, S. J., RICK, S. W., and HAYMET, A. D. J., 1988, *J. chem. Phys.*, **88**, 2004.
- [14] MCCOY, J. D., SINGER, S., and CHANDLER, D., 1987, *J. chem. Phys.*, **87**, 4853.
- [15] LENNARD-JONES, J. E., and DEVONSHIRE, A. F., 1937, *Proc. R. Soc. Lond. A*, **168**, 53.
- [16] HOOVER, W. G., and REE, F. H., 1968, *J. chem. Phys.*, **49**, 3609.
- [17] HENDERSON, D., and BARKER, J. A., 1968, *Molec. Phys.*, **14**, 587.
- [18] GIBBONS, T. G., and KLEIN, M. L., 1974, *J. chem. Phys.*, **60**, 112.
- [19] BUEHLER, R. J., WENTORF, R. H., HIRSCHFELDER, J. O., and CURTISS, C. F., 1951, *J. chem. Phys.*, **19**, 61.
- [20] ALDER, B. J., HOOVER, W. G., and YOUNG, D. A., 1968, *J. chem. Phys.*, **49**, 3688.
- [21] VIEILLARD-BARON, J., 1974, *Molec. Phys.*, **28**, 809.
- [22] PERRAM, J. W., and WHITE, L. R., 1974, *Molec. Phys.*, **28**, 527.
- [23] KOHLER, F., QUIRKE, N., and PERRAM, J. W., 1979, *J. chem. Phys.*, **71**, 4128.
- [24] ENGLISH, C. A., and VENABLES, J. A., 1974, *Proc. R. Soc. Lond. A*, **340**, 57.
- [25] NAGLE, J. F., 1966, *Phys. Rev.*, **152**, 190.
- [26] CARNAHAN, N. F., and STARLING, K. E., 1969, *J. chem. Phys.*, **51**, 635.
- [27] HALL, K. R., 1972, *J. chem. Phys.*, **57**, 2252; JACKSON, G., and VAN SWOL, F., 1988, *Molec. Phys.*, **65**, 161.
- [28] TILDESLEY, D. J., and STRETT, W. B., 1980, *Molec. Phys.*, **41**, 85.
- [29] PARRINELLO, M., and RAHMAN, A., 1980, *Phys. Rev. Lett.*, **45**, 1196.
- [30] VEGA, C., PARAS, E. P. A., and MONSON, P. A., *J. chem. Phys.* (in press).
- [31] DENTON, A. R., and ASHCROFT, N. W., 1989, *Phys. Rev. A*, **42**, 7312.
- [32] LUTSKO, J. F., and BAUS, M., 1990, *Phys. Rev. A*, **41**, 6647.