Solid-Fluid Phase Coexistence of Hard Heteronuclear Dumbbells via Cell Theory and Monte Carlo Simulation

S. C. Gay[(a),(b)], Paul D. Beale[(b)], James C. Rainwater[(a)]

[(a)] Physical and Chemical Properties Division, 838.08, National Institute of Standards and Technology*, 325 Broadway, Boulder, CO 80303

[(b)] Department of Physics, University of Colorado at Boulder, Box 390, Boulder, CO 80309

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ABSTRACT

We study the solid-fluid equilibria of hard heteronuclear dumbbells using cell theory and isobaric ensemble Monte Carlo simulations. Calculations for six cases of L^* (bond length) and σ^* (sphere diameter ratio) near the homonuclear limit are discussed with two base-centered monoclinic orientationally-ordered crystal structures which have been considered. The two crystal structures exhibit nearly identical properties at freezing within the accuracy of the calculations for the cases we present. The reduced pressure at coexistence increases with decreasing σ^*.

KEY WORDS: cell model; hard dumbbells; heteronuclear; Monte Carlo simulation; solid-fluid equilibrium

1. INTRODUCTION

Problems of considerable current interest are determinations of solid-liquid equilibrium and the structure of the coexisting solid from molecular shape and intermolecular interactions. Since the phase transition is strongly influenced by the steric interactions of the molecules, a purely repulsive model can serve as a basis to which perturbations of van der Waals and multipole forces can be added.

Recently, Monson and co-workers have modeled the solid phase of systems of hard homonuclear dumbbells [1,2] and other rigid assemblies of hard spheres [3] by Monte Carlo simulations and, for dumbbells, by the much more computationally economical cell theory of Lennard-Jones and Devonshire [4,5]. For the liquid they used the Tildesley-Streett equation of state [6] which was checked with Monte Carlo simulation. Of particular interest is the ratio of triple-point temperature to critical-point temperature, and with perturbative additions to the hard-body models they have qualitatively predicted some of the highest [2] and lowest values [3] of that ratio occurring in nature. In addition, the method has been used to distinguish the relative stability of orientationally ordered and disordered solids as a function of bond length [7,8] and have qualitatively predicted density changes on melting.

Our objective is to follow Monson's very promising methods to study molecules without reflection symmetry perpendicular to the primary molecular axis, such as methyl fluoride. In the present work we consider heteronuclear hard dumbbells, initially as a small variation from the homonuclear case. For the solid, we use constant pressure Monte Carlo simulation with a box shape change [9] and the Frenkel-Ladd lattice coupling technique [10] as extended to nonspherical particles by Frenkel and Mulder [11] and, independently, the cell theory of Lennard-Jones and Devonshire [4] to determine the free energy of two orientationally ordered lattice structures. For the fluid phase, we use Monte Carlo simulations in the isobaric ensemble and compare with the equation of state (EOS) of Maeso and Solana [12]. We then equate the pressures and chemical potentials of each

phase to determine thermodynamic phase equilibrium. We also consider the high pressure limit of the solid structure in the parameter space of heteronuclear molecules.

2. CRYSTAL STRUCTURES OF HETERONUCLEAR DUMBBELLS

Heteronuclear dumbbells are described by two parameters $L^* = L/\sigma_A$ and $\sigma^* = \sigma_a/\sigma_A$ where L is the separation of the centers of the two spheres composing the dumbbell, and σ_A and σ_a are the diameters of the larger and smaller spheres respectively. The molecule becomes two tangent spheres when $L^* = (1+\sigma^*)/2$ and becomes spherical when $L^* \le (1-\sigma^*)/2$. For these reasons, we address only dumbbells with $(1-\sigma^*)/2 \le L^* \le (1+\sigma^*)/2$ in this paper.

If we place molecules in layers with the larger spheres forming a two-dimensional hexagonal close-packed array, the dumbbells orient so that the small spheres fall into the valleys formed by the larger spheres. The angle which the directors of the molecules make with respect to the normal to the layer is

$$\theta_L = \sin^{-1}\left(\frac{L^{*2} + 3/4 - \sigma^*/2 - \sigma^{*2}/4}{\sqrt{3}L^*}\right). \tag{1}$$

When $\sin\theta_L = 1$ the smaller spheres may freely fall into the gaps between the larger spheres. In this case the dumbbell becomes something resembling a sphere with a "pimple". The pimple can rest in any of the gaps between the larger spheres in a close-packed arrangement. In the area between the curve $\sin\theta_L = 1$ and the line $L^* = (1-\sigma^*)/2$ in the plane of the heteronuclear dumbbell parameters (see Fig. 1), the solid structure will be close-packed spheres with the pimples randomly distributed into the gaps between the larger spheres.

We base the orientationally ordered structures studied in this work on the monoclinic CP1 structure for homonuclear dumbbells described by Vega *et al.* [1]. One heteronuclear structure, which we call CP1a, is obtained by shrinking the top spheres of the dumbbells in each layer so that the molecules all have the same orientation. The crystal structure for CP1a is base-centered monoclinic with a one-molecule basis. A second

structure which we considered (CP1b) is obtained by shrinking the top sphere of dumbbells in one layer and the bottom sphere in layers adjacent to it. The result is alternating layers of dumbbells pointing up or down. The structure is base-centered monoclinic with a basis of two molecules. Examples of the above structures are shown in Fig. 2. For $\sigma^* = 1$ the two structures have identical close-packing densities, but for $\sigma^* < 1$, CP1b has a slightly greater close-packing density than CP1a, with the difference increasing with decreasing σ^*.

3. COMPUTATIONAL METHODS

3.1. CELL THEORY

We use the approach described in [5] modified appropriately for heteronuclear dumbbells. In simple cell theory, the configurational partition function of the solid is approximated as

$$Q_N = N!Q_1^N \tag{2}$$

where

$$Q_1 = \frac{1}{4\pi}\int d\Omega \int_{cell} d\mathbf{r} \exp\left[-\beta u(\mathbf{r},\Omega)\right], \tag{3}$$

$\beta = 1/k_B T$, and $u(\mathbf{r},\Omega)$ is the potential energy of a molecule in the cell formed by its neighboring molecules *fixed* at their lattice positions. The five-dimensional integral is evaluated by Monte Carlo integration where, for efficiency in sampling, the sample volume for the integration is determined by a random walk of the central molecule in its cell [5]. Also, we employed a Sobol sequence [13] to generate the translational coordinates used in the integration which gives slightly lower error in the integration than a pseudorandom number generator for an equivalent number of sample points. In order to sample the entire range of solid angle, we found it necessary to perform two random walks: one with the central molecule starting in its equilibrium orientation, and one with it starting in a "flipped" orientation. At high enough densities the flipped orientation often did not contribute to the free volume. (This is especially true for molecules with significantly different sphere diameters.) The geometry of the cell was chosen to be that of the close-

packed structure expanded to the appropriate density. We checked our code by comparing results for homonuclear molecules with those in [5].

3.2. MONTE CARLO SIMULATION METHODS

In order to determine phase equilibria from Monte Carlo (MC) simulation, we must calculate the pressure versus density equation of state and the absolute Helmholtz free energy F at some reference density. The free energy at all densities then follows by thermodynamic integration:

$$f\left(\rho_2^*\right) = f\left(\rho_1^*\right) + \int_{\rho_1^*}^{\rho_2^*} d\rho^* \frac{p^*\left(\rho^*\right)}{\rho^{*2}} \tag{4}$$

where $f\left(\rho^*\right) = F\left(\rho^*\right)/NkT$, $\rho^* = \rho d^3$, $p^* = pd^3/kT$, and d is the diameter of a sphere with the same volume as the dumbbell. For heteronuclear dumbbells we find

$$d^3 = \sigma_A^3 \left[\frac{1+\sigma^{*3}}{2} + \frac{3}{4} L^*\left(1+\sigma^{*2}\right) - \frac{L^{*3}}{2} + \frac{3\left(1-\sigma^{*2}\right)^2}{32L^*} \right]. \tag{5}$$

We used constant pressure MC simulation with a box shape change [9] as described in [1] to calculate $p^*\left(\rho^*\right)$ for the various structures. Most of the simulations were performed on systems of 96 particles formed by stacking 4 particles in the crystallographic **a** and **c** directions and 6 particles in the **b** direction. To examine finite size effects, some calculations were done for a 192 particle system obtained by doubling the number of particles in the **c** direction. We set the initial **a** and **b** directions to coincide with the $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ directions respectively. One MC step (MCS) consisted of an attempt to move each particle twice and to change the box shape once on average, where a particle move was chosen to be a simultaneous translation and rotation move. In a typical simulation we used from 6×10^3 to 10^4 MCS for equilibration and 2×10^4 MCS for calculating thermodynamic averages. We adjusted the step sizes to achieve a translation/rotation acceptance ratio of approximately 0.3 and a volume change acceptance ratio of 0.05. We used the order parameter given in [14] to study orientational ordering and the order parameter in [1] to study translational order.

To calculate the free energy at a reference density we employed the lattice coupling method described by Vega *et al*. [1] due to Frenkel and Mulder [11]. In this procedure the free energy is written as

$$f = f_{eins}^{cm}(\lambda_{\max}) + \Delta f_1(\lambda_{\max}) + \Delta f_2(\lambda_{\max}) + \Delta f_3 \tag{6}$$

where $f_{eins}^{cm}(\lambda_{\max})$ is the free energy of a non-interacting Einstein crystal with translational and torsional spring constants λ_1 and λ_2 having reduced values equal to $\lambda_{\max}$. The first correction Δf_1 accounts for the fact that there is always some interaction of dumbbells at $\lambda = \lambda_{\max}$. The second correction Δf_2 links the crystal with spring constant $\lambda = \lambda_{\max}$ with that at $\lambda = 0$. Finally, to account for the fact that the center of mass of the crystal is fixed in calculating Δf_2, we add the correction Δf_3. The reader is referred to [1] and [11] for further details.

In our calculations, the integral to determine Δf_2 was determined by 10 point Gaussian quadrature with the integrand transformed as suggested in [10]. $\lambda_{\max}$ was chosen to have a value of 8000 in reduced units. We checked our code by checking results in the homonuclear and spherical limits [1,10] and by checking for thermodynamic consistency in the integration of the pressure equation of state. The values of the reference free energies we obtained are shown in Table I.

3.3. FLUID EQUATION OF STATE

In order to reduce the total computation required to compute the solid-fluid equilibrium, we investigated the suitability of the analytic equation of state given by Maeso and Solana [12] for the heteronuclear dumbbell fluid. To test its accuracy we performed constant pressure MC simulations of the fluid phase for each (L^*, σ^*) studied and also looked for agreement with the Tildesley-Streett equation in the homonuclear limit [6]. At low pressures the analytic EOS and the MC data agree well with each other, but at moderate to high pressures the agreement worsens with the analytic equation overestimating the isothermal compressibility of the fluid (see Fig. 3). The analytic equation still proved useful, in that we could use it to calculate the free energy at a density low enough that the

analytic and MC pressures agreed well, and then only perform MC simulations at higher pressures to obtain the necessary data to find the phase equilibrium.

4. RESULTS

As the pressure in the constant pressure (MC-NPT) simulations was decreased, small changes occurred in the solid structure that were important to include in the lattice coupling procedure. In addition to small changes in the simulation box shape, θ_L also tended toward smaller values than it assumes at close-packing. A summary of the coexistence properties between the ordered solid structures and the fluid is shown in Table II. We estimate that the coexistence densities determined by Monte Carlo simulations are accurate to about 1%, the largest source of error coming in the quadrature involved in the lattice coupling. The cell theory calculations, where we took the geometry to be that at close-packing expanded to the desired density, overestimate the densities at freezing by 1 to 6% when compared to the MC results. The results for CP1a and CP1b structures are indistinguishable within the statistical error of the Monte Carlo calculations for $\sigma^* = 0.95$ and $\sigma^* = 0.90$. This is similar to the results of Vega *et al*. with the CP1, CP2 and CP3 structures in the homonuclear case [1]. Both the Monte Carlo and cell theory results show an increase in pressure with decreasing σ^* at solid-fluid coexistence (Fig. 4).

5. CONCLUSIONS

This work has investigated solid-fluid equilibria of hard heteronuclear dumbbells using both Monte Carlo simulation and cell theory to calculate independently the solid phase free energy. In particular, two ordered solid structures were studied (CP1a and CP1b). The equation of state of Maeso and Solana, while agreeing well with Monte Carlo results at low pressures, was found to be insufficiently accurate for calculating solid-fluid equilibrium without using MC data to extend its range.

We find that a change in σ^* of only 5-10% from the homonuclear limit has a significant effect on the coexistence properties. For the dumbbell shapes we considered, the CP1a and CP1b structures were indistinguishable by their thermodynamic properties at freezing, which is not surprising since the structures have nearly identical close-packing

densities for $\sigma^* \cong 1$. For lower σ^* where the close-packing densities of the two structures differ more, simulation and/or cell theory may be able to distinguish the thermodynamically preferred structure. For these cases and for dumbbells with lower L^* it will likely be important to consider the possibility of a plastic crystal phase. We will investigate this in future work.

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Table I. Free Energy Calculations for hard heteronuclear dumbbells for the CP1a and CP1b solid phases. ρ^* is the reduced density. R_c and R_b are the ratios $(c/a)/(c/a)_0$ and $(b/a)/(b/a)_0$ (ratios of box length ratios to box length ratios at close-packing) respectively, f_{ref} is the absolute Helmholtz free energy divided by NkT, and f_{CT} is the free energy divided by NkT at ρ^* calculated by cell theory with $R_c = R_b = 1$ The result labeled by a dagger (†)is from reference [1]. NA means "not available" as the information was not given in the reference. All calculations are for 96 particle systems except for those marked with (*) (144 particles) and with (**) (192 particles).

L^*	σ^*	Lattice	ρ^*	R_c	R_b	f_{ref}	f_{CT}
0.8	0.95	CP1a	1.219	0.97	0.97	12.19	12.55
0.8	0.95	CP1b	1.215	0.96	0.98	12.04	12.82
0.8	0.90	CP1a	1.212	0.99	0.99	12.86	13.89
0.8	0.90	CP1b	1.215	0.97	0.99	12.87	14.23
$0.6^{\dagger(*)}$	1.00	CP1	1.289	0.96	NA	12.28	12.49
$0.6^{(*)}$	1.00	CP1	1.289	0.96	1.00	12.30	12.49
0.6	0.95	CP1a	1.277	0.97	0.98	12.47	12.63
$0.6^{(**)}$	0.95	CP1b	1.289	0.98	0.99	12.80	13.47
0.6	0.95	CP1b	1.243	0.96	0.98	11.40	12.00
0.6	0.90	CP1a	1.288	0.99	0.99	13.59	14.81
0.6	0.90	CP1b	1.281	0.97	0.99	13.11	14.47
0.5	0.95	CP1a	1.253	0.97	0.98	11.09	11.46
0.5	0.95	CP1b	1.252	0.96	0.98	11.18	11.65
0.5	0.90	CP1a	1.231	0.97	0.99	11.09	12.00
0.5	0.90	CP1b	1.212	0.97	0.98	10.51	11.64

Table II. Solid-fluid equilibria of hard heteronuclear dumbbells as obtained from MC simulation and cell theory (CT). The results labeled by (a), (b) and (c) are from references [1], [7], and [5] respectively. Results for a 192 particle system are labeled by (**).

L^*	σ^*	Lattice	ρ_f^*(CT)	ρ_f^*(MC)	ρ_s^*(CT)	ρ_s^*(MC)	p^*(CT)	p^*(MC)
0.8	1.00	CP1	1.124	1.105[(b)]	1.251	1.224[(b)]	40.02	36.47[(b)]
0.8	0.95	CP1a	1.125	1.101	1.220	1.205	40.90	36.09
0.8	0.95	CP1b	1.150	1.097	1.238	1.196	46.72	35.36
0.8	0.90	CP1a	1.158	1.105	1.232	1.181	59.45	40.62
0.8	0.90	CP1b	1.168	1.098	1.236	1.174	64.69	38.94
0.6	1.00	CP1	1.162[(c)]	1.146[(a)]	1.276[(c)]	1.249[(a)]	41.23[(c)]	37.97[(a)]
0.6	0.95	CP1a	1.158	1.150	1.255	1.243	42.85	40.71
0.6	0.95	CP1b	1.176	1.151[(**)]	1.262	1.254[(**)]	48.39	40.84[(**)]
0.6	0.95	CP1b	1.176	1.143	1.262	1.237	48.39	38.86
0.6	0.90	CP1a	1.229	1.172	1.288	1.247	77.76	49.92
0.6	0.90	CP1b	1.228	1.163	1.283	1.231	77.50	46.46
0.5	1.00	CP1	1.174	1.150[(b)]	1.279	1.235[(b)]	41.13	36.37[(b)]
0.5	0.95	CP1a	1.161	1.142	1.275	1.250	42.43	38.06
0.5	0.95	CP1b	1.189	1.149	1.263	1.252	50.72	39.62
0.5	0.90	CP1a	1.231	1.167	1.285	1.244	69.76	44.98
0.5	0.90	CP1b	1.242	1.165	1.304	1.232	76.20	44.42

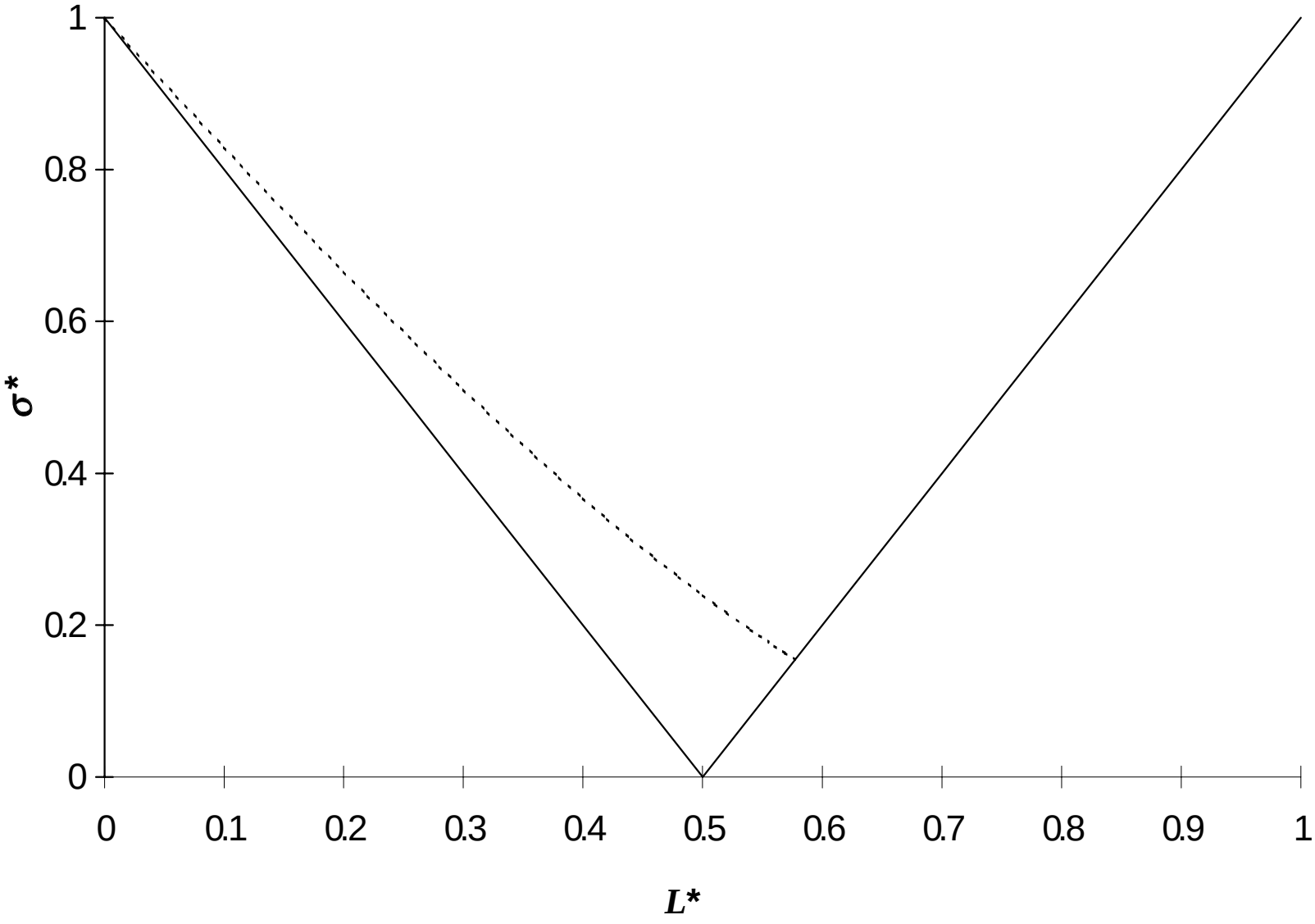
FIGURE CAPTIONS

Fig. 1 The L^*, σ^* parameter plane. The solid lines are $L^* = (1+\sigma^*)/2$ and $L^* = (1-\sigma^*)/2$. The dotted line is where $\sin(\theta_L) = 1$.

Fig. 2 CP1a (top) and CP1b (bottom) structures shown in the initial configurations of the MC-NPT simulations.

Fig. 3 The equation of state of Maeso-Solana [12] (solid line) and points with error bars from MC-NPT calculation for $L^* = 0.6$, $\sigma^* = 0.90$.

Fig. 4 The dependence of pressure at coexistence on σ^*. Note that here we have plotted $p\sigma_A/kT$ instead of p^*. The solid circles are due to Vega *et al.* [1,7] and represent the homonuclear limit ($\sigma^* = 1$). The squares and triangles are the Monte Carlo results for $\sigma^* = 0.95$ and $\sigma^* = 0.90$ respectively. The hollow (solid) shapes represent CP1a (CP1b) results. PC denotes a plastic crystal phase.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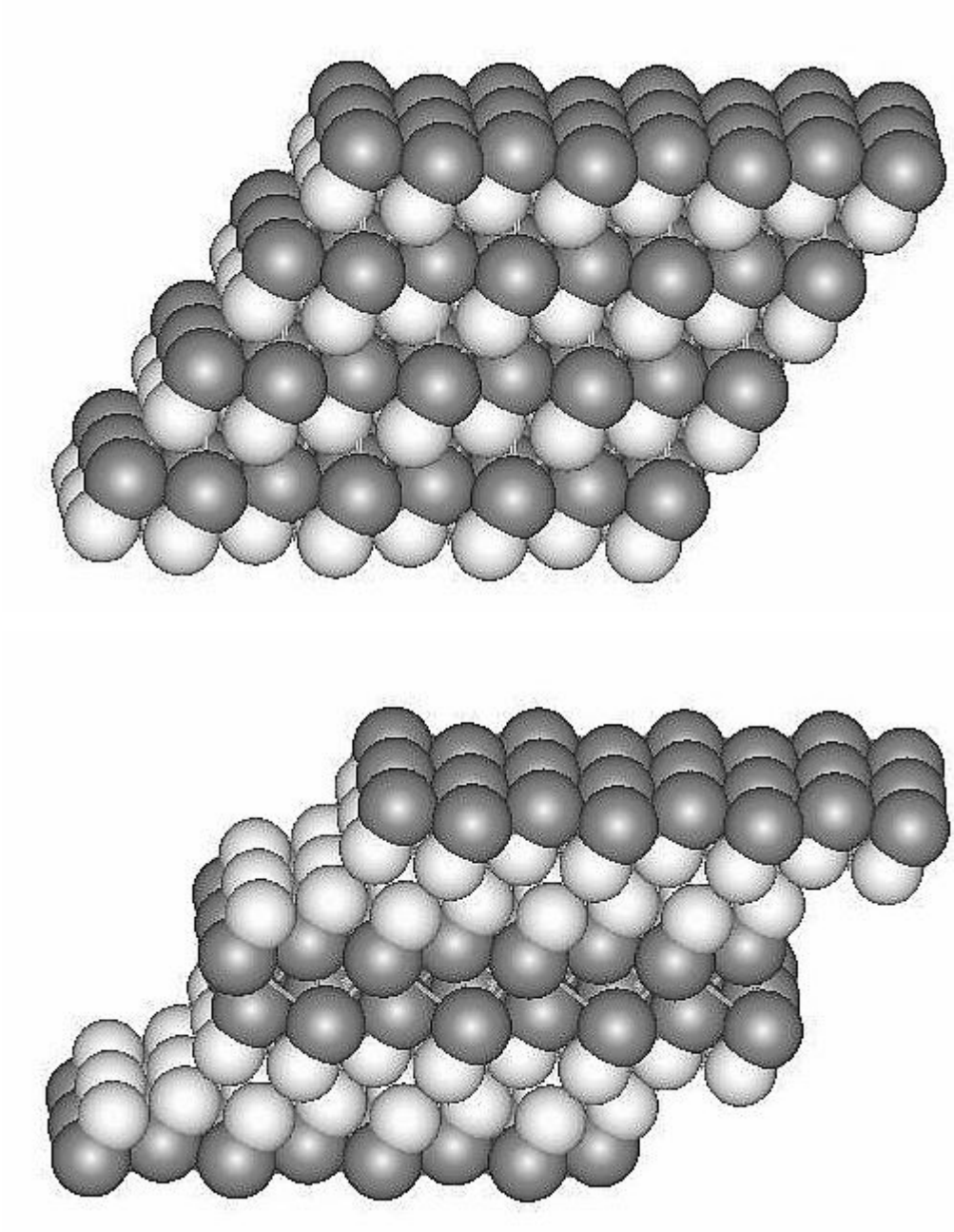

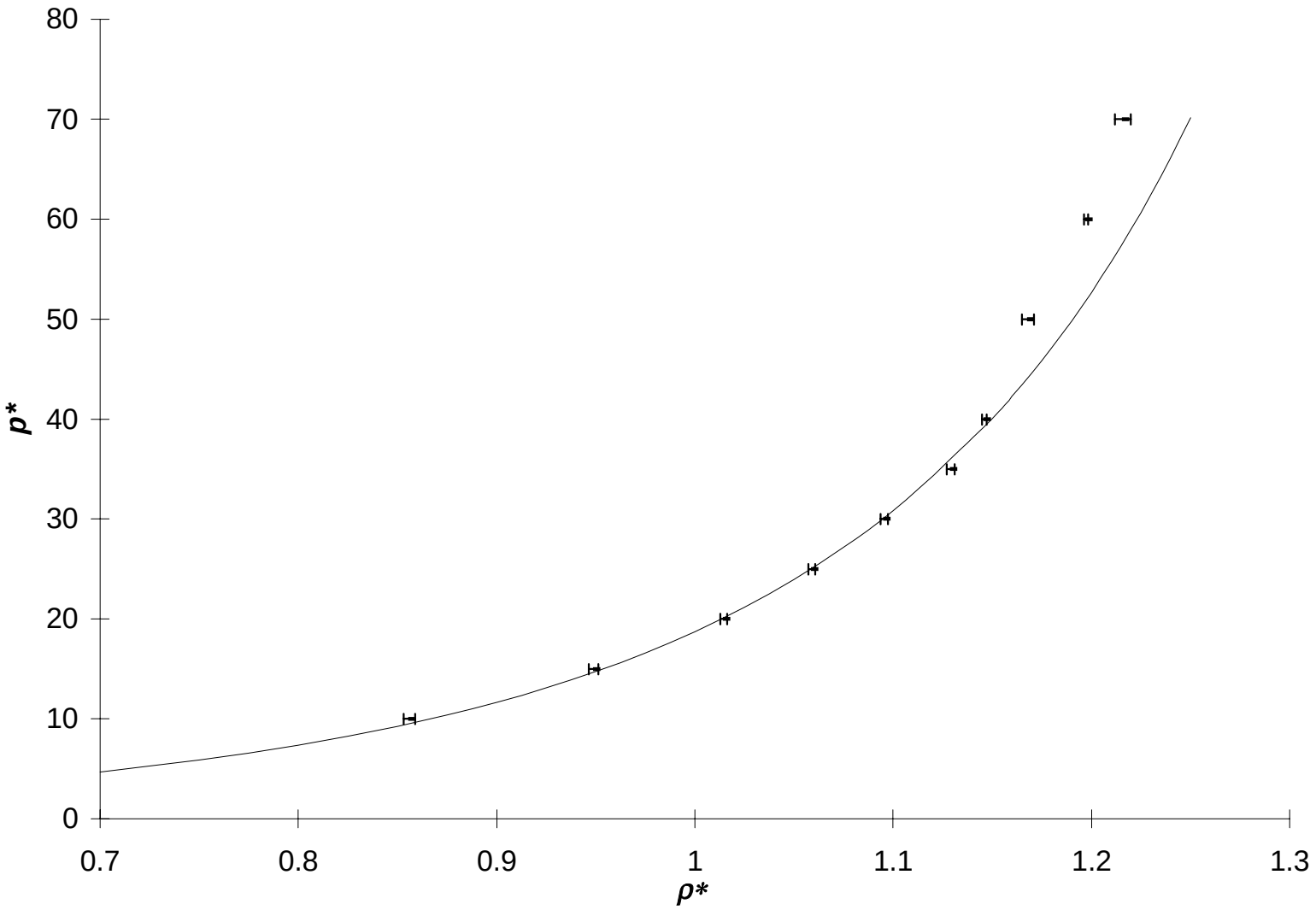
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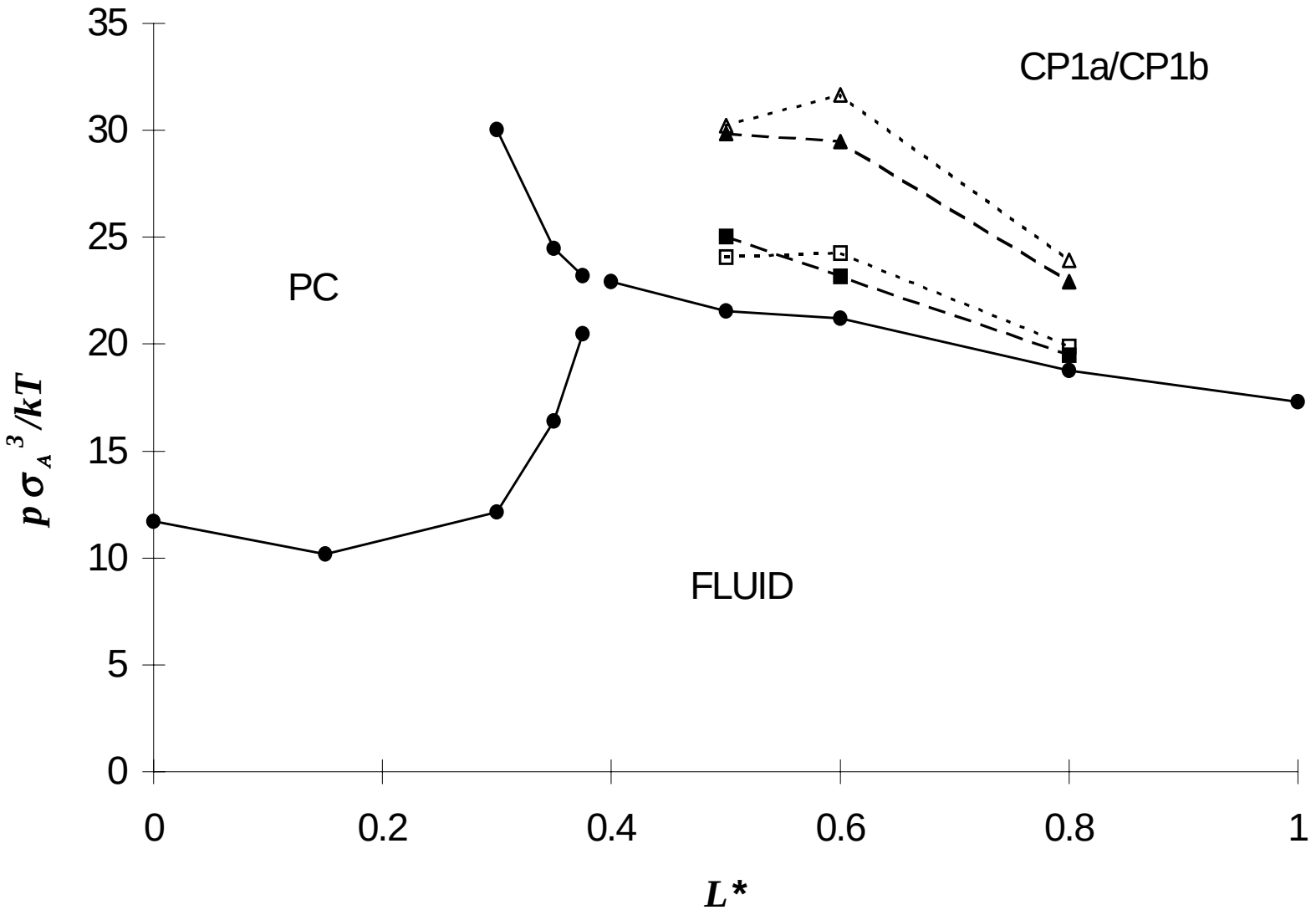
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