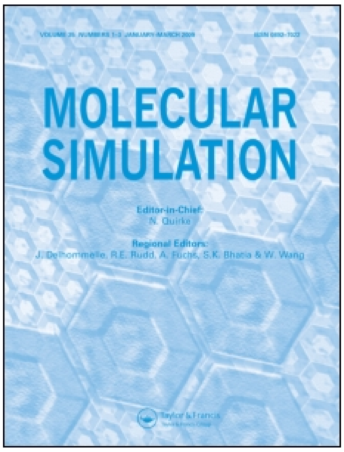

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Frank van Swol[a]; Leslie V. Woodcock[b]
[a] School of Chemical Engineering, Cornell University, Ithaca, New York, USA [b] School of Studies in Chemical Engineering, University of Bradford, W. Yorkshire, UK

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PERCOLATION TRANSITION IN THE PARALLEL HARD-CUBE MODEL FLUID

FRANK VAN SWOL

School of Chemical Engineering, Cornell University, Ithaca, New York, USA

and

LESLIE V. WOODCOCK

School of Studies in Chemical Engineering, University of Bradford, Bradford, W. Yorkshire, UK

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Pressure and self-diffusion calculations for a model fluid system of parallel hard cubes are reported. When viewed alongside equations of state incorporating the known coefficients in the virial expansion (b_2 to b_7), a weak phase change is postulated around $\frac{1}{4}$ close-packing. Changes in behaviour are also seen at the same density for the self-diffusion coefficient and an associated single-particle free volume. It is conjectured that a transition may be identifiable with the low-density percolation transition that occurs in all hard-core fluids when the single particle configurational volume becomes extensive. If the hard-sphere model were to behave similarly, the observations may have implications for the general development of liquid-state theory.

KEY WORDS: Hard-cube, fluid, percolation, virial series, equations of state, diffusion.

1. INTRODUCTION

The equilibrium theory of liquids has traditionally been approached either from the dilute gas reference state, using Mayer cluster expansions, or from the regular lattice state using cell cluster techniques [1]. The lack of success of the former approach in the high-density fluid range, and of the latter approach in the low-density fluid range, raises the question whether either of these two approaches, if evaluated to sufficient order, could constitute an accurate analytic theory of fluids over the whole density range.

The difficulty with these theories is generally thought to be the complexity in approximating the higher-order terms, rather than problems related to convergence. It is possible, however, that there may be a bifurcation point associated with the known low-density percolation transition for hard-core systems [2, 3]. Such a transition could represent a higher order phase change above and below which the virial series or cell-cluster expansions, respectively, even if full evaluation were possible, would fail to converge.

In order to explore further this interesting possibility, we have embarked upon a computer study of the parallel hard-cube model, particularly in the region of its low density percolation transition. This is the state point when an average particle in a static ensemble configuration can diffuse over the whole volume occupied by the fluid. It is defined and discussed in section 2. The parallel hard-cube model has, to our knowledge, not previously been investigated by computer simulation.

The first seven virial coefficients of the parallel hard-cube model are exactly known; the model appears to be exceptional in that b_6 and b_7 are negative. Clearly, if the subsequent higher virial coefficients are all negative, there must indeed be a point of non-convergence, possibly associated with a thermodynamic or transport discontinuity, since it can be proved that convergence of the virial series is obtained up to a finite density [4].

It is for this reason, together with the advantage of computational expediency over spheres for the free-volume contours, that this uncommon model is initially chosen to examine the low-density percolation transition in fluids and any thermodynamic or transport manifestations. Recent work has suggested that the transition also occurs in colloidal suspensions of spherical particles and could have a determining influence on the non-Newtonian rheology of these materials [5].

2. PERCOLATION AND FREE VOLUME

Hoover *et al.* [2] derived a relationship for the pressure of a general hard-core system of rods, discs and spheres

$$\frac{pV}{NkT} = 1 + \frac{\sigma}{2D}\langle s_f/v_f\rangle \tag{1}$$

where D is the dimensionality and v_f is the free volume accessible to a single particle when the remaining N-1 particles are fixed; s_f is the corresponding surface area. The angular brackets denote an ensemble average. Speedy [6] had derived a very similar relation using the "spare volume" concept, i.e. that volume accessible to an additional $(N + 1)$ st. particle averaged over an ensemble:

$$\frac{pV}{NkT} = 1 + \frac{\sigma}{2D}\langle s_s\rangle/\langle v_s\rangle. \tag{2}$$

The relation between $\langle v_s\rangle$ and the chemical potential is well-known [7]:

$$\mu = -kT\log_e\frac{\langle v_s\rangle}{V}. \tag{3}$$

At low densities, Hoover's $\langle v_f\rangle$ is an extensive property, since a single particle can percolate the whole system, whereupon $s_s \equiv s_f$, $v_s \equiv v_f$ and Equations (1) and (2) are identical.

At high densities, $\langle v_f\rangle$ is intensive and, in the thermodynamic limit, there must be a point at which $\langle v_f\rangle$ changes from being extensive to intensive; this is the percolation transition. Specific numerical calculations of $\langle v_f\rangle$ for hard discs show the transition occurs at a packing fraction of $(22 \pm 2\%)$ [3]. The thermodynamic variations through the transition have not been investigated.

The relationship between v_f and v_s at densities above the percolation transition, where v_s takes the form of cavities, has also been examined by Speedy [8]. It was shown that

$$\langle v_s\rangle \leqslant \langle v_f\rangle$$

and, further, that

$$\langle v_f \rangle = \langle v_s \rangle \left(1 + \frac{\langle \Delta v_s \rangle^2}{\langle v_s \rangle^2}\right) \tag{4}$$

where $\langle \Delta v_s \rangle^2$ is the square of the mean fluctuation in v_s. At the percolation transition $\langle V_f \rangle / \langle V_s \rangle$ increases abruptly from unity. Equations (1)–(4) suggest that the percolation transition may be associated with a thermodynamic break depending on the variation in s_f and s_s through the transition.

Using a dimensional scaling agreement (which is not exact) Speedy finds [8]

$$\langle s_f \rangle = \langle s_s \rangle \left(1 + \tfrac{1}{2} \frac{\langle \Delta v_s \rangle^2}{\langle v_s \rangle^2}\right). \tag{5}$$

Since both s_f and v_f change discontinuously, there could be a thermodynamic transition of some higher order at the percolation transition.

Even if the fluid equation of state were to be continuous through this transition point in the thermodynamic limit, there is no reason to expect continuous behaviour through the transition when the fluid is subjected to some kind of external perturbation. For example, the geometric constraints imposed by periodic boundary conditions on an infinite system, or the imposition of a shear gradient, could be expected to influence the configurational behaviour differently on either side of the transition resulting in phase transition behaviour.

3. PARALLEL CUBE MODEL

3.1 Virial Coefficients

The parallel hard-cube model is formally defined by the pair potential

$$\phi_{ij}(x_{ij}, y_{ij}, z_{ij}) = 0 \quad \text{for} \quad x_{ij} > \sigma, y_{ij} > \sigma \quad \text{and} \quad z_{ij} > \sigma$$

and

$$\phi_{ij}(x_{ij}, y_{ij}, z_{ij}) = \infty \quad \text{if} \quad x_{ij} < \sigma, y_{ij} < \sigma \quad \text{or} \quad z_{ij} < \sigma$$

where σ is the length of the cube edge. In the hard-sphere model only the scalar distance r_{ij} defines the excluded volume. As a consequence of the cubic symmetry, the virial coefficients and free volume contours are much easier to evaluate in the parallel hard-cube model.

When the equation of state is expanded in powers of the relative density (ϱ/ϱ_0) the virial coefficients are defined as

$$\frac{pV}{NkT} = 1 + \sum_{n=2}^{\infty} b_n \left(\frac{\varrho}{\varrho_0}\right)^{n-1} \tag{6}$$

where ϱ is the density N/V and ϱ_0 is the maximum packing density; in reduced units $\varrho_0\sigma^3$ for cubes is unity. The corresponding ϱ_0 values for hard-spheres and circles are $\sqrt{2}$ and $2/\sqrt{3}$ respectively.

Table 1 gives the known virial coefficients for the various 2- and 3-dimensional hard-core model fluids as defined by Equation (6), together with the references to the

Table 1 Virial coefficients for the expansion in powers of density relative to close packing for hard-core models.

	circles (*a, e, f*)	*squares* (*c, d*)	*spheres* (*b, e, f*)	*cubes* (*c, d*)
1	1	1	1	1
2	1.8138	2	2.9619	4
3	2.5727	3	5.4831	9
4	3.1759	$3\frac{2}{3}$	7.4563	$11\frac{1}{3}$
5	3.613	3.722	8.489	3.160
6	3.093	3.025	8.87	−18.88
7	4.088	1.65	9.25	−43.5

(a) L. Tonks, *Phys. Rev.* **50,** 955 (1936).
(b) L. Boltzmann, *Proc. Roy. Dutch Acad. Sci.*, **7,** 484 (1899).
(c) R.W. Zwanzig, *J. Chem. Phys.*, **24,** 855 (1956).
(d) W.G. Hoover and A.G. de Rocco, *J. Chem. Phys.*, **36,** 3141 (1962).
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original calculations. For circles and spheres the virial coefficients b_2–b_7 increase monotonically up to the highest known; the ultimate destination of b_n has been the subject of considerable speculation in the development of accurate hard-sphere equations of state [9].

It is noteworthy that for two-dimensional squares the highest virial coefficient is b_5 and then there is a decrease through b_7. For the parallel hard-cube model, however, b_4 is the maximum-value coefficient, and the subsequent decrease is so abrupt that the two highest known coefficients, b_6 and b_7, actually go negative. If this were to be the general pattern of behaviour, albeit less pronounced for circles and spheres at low n values, the implication is that all those hard-core model fluids should exhibit a density above which the virial equations of state would fail to converge on the physical result from a grand partition function, or an "exact" computer simulation.

3.2 MD Calculations

Some computer simulation studies of the two-dimensional parallel square model have been previously reported [10], but we have found no reference to MC or MD computations for cubes. The present algorithm is based on the original hard-sphere method [11], which lists the predictions to the next collision time, with the adaptation that the three collision directions (X, Y and Z) are calculated separately. The Fortran algorithm for the inner-cycle of the program is listed in the Appendix.

All the computations reported here were carried out for a system of $N = 512$ cubes with the usual periodic boundary conditions. The uncertainty limits on the pressure equation-of-state results quoted in Table 1 are the standard deviations taken over approximately 10 subaverages from MD subruns of 50 000 collisions each.

The equation-of-state data is calculated from the virial theorem

$$\frac{pV}{NkT}(MD) = 1 + \sum_{st}^{n_c} \frac{r_\alpha v_\alpha}{3N\Delta t} \tag{7}$$

where α is the collision direction and the summation is over all the collisions (n_c) in the time interval Δt.

The MD results for the pressure have been compared with a number of theoretical and empirical equations of state for hard-cube models.

3.3 Equations of State

The most accurate equations of state are shown in Figure 1 together with the MD data points. The high density pressure data is also shown and the results indicate that, as expected, the parallel hard-cube model exhibits a first-order freezing/melting transition in the vicinity of $\varrho = 0.5\varrho_0$ and $pV/NKT \sim 6$. We are unable to obtain the

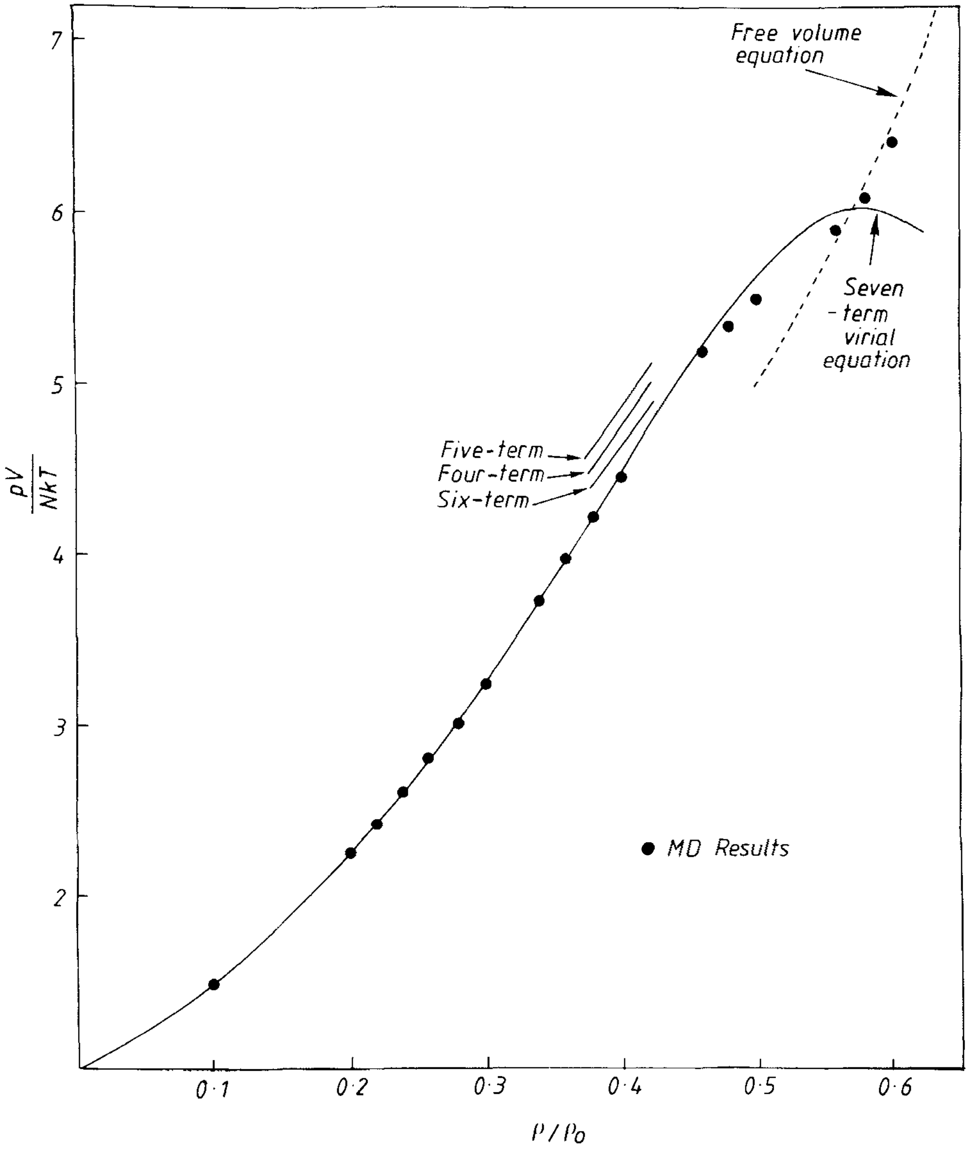

Figure 1 A comparison between the calculated MD pressures for the parallel hard-cube model and analytic equations of state; the free volume and seven-term virial equations accurately represent the crystal and fluid branches respectively. An inspection of the four-, five- and six-term virial equations shows that the excellent agreement of the seven-term virial equation is probably fortuitous.

the precise freezing and melting parameters from the present data without knowledge of the relative free energies of the two phases.

Figure 1 shows that the solid branch is reasonably represented by the self-consistent free volume theory (SCFV) equation of state.

$$\frac{pV}{NkT}(SCFV) = \frac{3\varrho/\varrho_0}{(1 - \varrho/\varrho_0)} + 2, \tag{8}$$

A form that has been shown to be exact analytically for cubes in the limit that $\varrho \to \varrho_0$ [12]. The data in Table 2 show that this simple question is also a reasonable representation of the fluid phase data, to within a few percent. This is fortuitously due to a crossover effect at $\varrho/\varrho_0 = 0.3$, the density below which it becomes an increasingly poor representation.

When the virial equation of state (Equation 6) is truncated at the highest known virial coefficient (b_7), a very accurate representation of the fluid phase MD data over the whole fluid range is obtained. This is useful for the calculation of other thermodynamic properties, but it may give a misleading impression regarding the convergence of the virial series. Figure 1 shows that when we consider the corresponding 4-, 5- and 6-term truncated virial equations the agreement obtained by truncation beyond b_7 is fortuitous. It seems unlikely that the higher virial series should entirely cancel.

An alternate representation of the fluid equation of state with a very simple analytic

Table 2 Equation-of-state data for the parallel hard-cube model fluid.

$\varrho\sigma^3$	$NCOL^a$	$EQUIL^b$	$\frac{pV}{NkT}$			
			MD	*SCF V*	*EQ. 12*	*7-VIRIAL*
0.06	100	20	1.2737 ± 0.026	2.191	1.309	1.2749
0.10	120	66	1.5016 ± 0.0041	2.333	1.493	1.5014
0.18	500	100	2.0754 ± 0.0026	2.659	2.070	2.0760
0.20	500	420	2.2463 ± 0.0051	2.750	2.250	2.2469
0.22	650	200	2.2484 ± 0.0058	2.846	2.446	2.4290
0.24	600	200	2.6237 ± 0.0079	2.947	2.662	2.6220
0.26	650	200	2.8268 ± 0.0094	3.054	2.899	2.8262
0.27	500	200	2.9317 ± 0.0054	3.110	3.026	2.9320
0.28	400	200	3.0391 ± 0.0134	3.167	3.160	3.0404
0.30	550	400	3.2664 ± 0.010	3.286	3.449	3.2640
0.34	400	200	3.7277 ± 0.013	3.545	4.122	3.7351
0.36	500	200	3.9866 ± 0.016	3.688	4.515	3.9794
0.38	500	200	4.2335 ± 0.021	3.839	4.954	4.2268
0.40	500	400	4.9869 ± 0.012	4.000	5.444	4.9592
0.46	500	200	5.2149 ± 0.058	4.556		5.1880
0.48	500	200	5.339 ± $\frac{1}{2}$%	4.769		5.4016
0.50	500	200	5.490 ± $\frac{1}{2}$%	5.000		5.5944
0.56	500	200	5.899 ± $\frac{1}{2}$%	5.818		5.9820
0.58	500	200	6.088 ± $\frac{1}{2}$%	6.143		6.0211
0.60	500	200	6.405 ± $\frac{1}{2}$%	6.500		5.9996
0.70	500	200	8.915 ± $\frac{1}{2}$%	9.000		
0.80	500	200	13.912 ± $\frac{1}{2}$%	14.000		
0.90	500	200	28.419 ± $\frac{1}{2}$%	29.000		
0.95	500	200	57.200 ± $\frac{1}{2}$%	59.000		

[a] Number of collisions used to obtain the data in this table (thousands).

[b] Number of collisions used for equilibration (EQUIL is *not* included in NCOL).

form can be obtained by a modification to the derivation of van der Waals equation of state for hard spheres [13]

$$\frac{Q}{Q_0} = \left(\frac{v - b^2}{v}\right)^N \tag{9}$$

where $v = V/N$, Q is the partition function and Q_0 is the partition function for the ideal gas. At high density the equation is more accurate by replacing v by a free volume $v - v_0$ where v_0 is a molecular volume;
then

$$\begin{aligned} \frac{Q}{Q_0} &= [(v - v_0 - b_2)/(v - v_0)]^N \\ &= \exp(-b_2/(v - v_0)). \end{aligned} \tag{10}$$

since

$$A = -kT \log_e Q$$

the excess Helmholtz free energy is

$$\frac{A^+}{kT} = \frac{b_2}{(v - v_0)} \tag{11}$$

and

$$\frac{pV}{NKT} = 1 - V\left(\frac{\mathrm{d}A^+}{\mathrm{d}V}\right)_T = 1 + \frac{b_2 v}{(v - v_0)^2}, \tag{12}$$

reduced units $b_2 = 4$ and $v_0 = 1$ for cubes.

This very simple equation of state actually turns out to be rather insensitive to the choice of v_0, provided it lies roughly in the range of the particle volume or the close-packed volume per particle. For squares and cubes, both these quantities take the value unity. Alternatively, to obtain the exact third virial coefficient v_0 could be set equal to $b_3/2b_2$ to give a value of 1.25 for cubes, which would be in the vicinity of an amorphous close packing. The equation of state given by Equation (12) is almost exact up to about 30% packing and deviates up to about 10% approaching freezing (Table 2).

The higher virial coefficients predicted by Equation (12) are obtained from the expansion

$$\frac{pV}{NkT} = 1 + b_2 v^{-1} + 2b_2 v_0 v^{-2} + \ldots (n - 1) v_0^{(n-1)} b_2 v^{-(n-1)} \ldots \tag{13}$$

where n is the general term. It is clear from the general term that all the predicted virial coefficients are positive and that this approach cannot represent the true series as it is bound to fail for the higher coefficients, despite the accuracy up to high density. This limitation applies to all previous analytic equations for hard spheres also.

Further light can be shed on the virial equation of state by considering closed-form representations to the whole virial series. In Figure 2 we show what happens if all the higher virial coefficients b_8–b_∞ take the same negative value as b_7. This hypothetical equation of state is

$$\frac{pV}{NkT}(b_7\text{-Closure}) = 1 + \frac{b_7 \varrho/\varrho_0}{1 - \varrho/\varrho_0} + \sum_{n=2}^{7} (b_n - b_7)\left(\frac{\varrho}{\varrho_0}\right)^{n-1}. \tag{14}$$

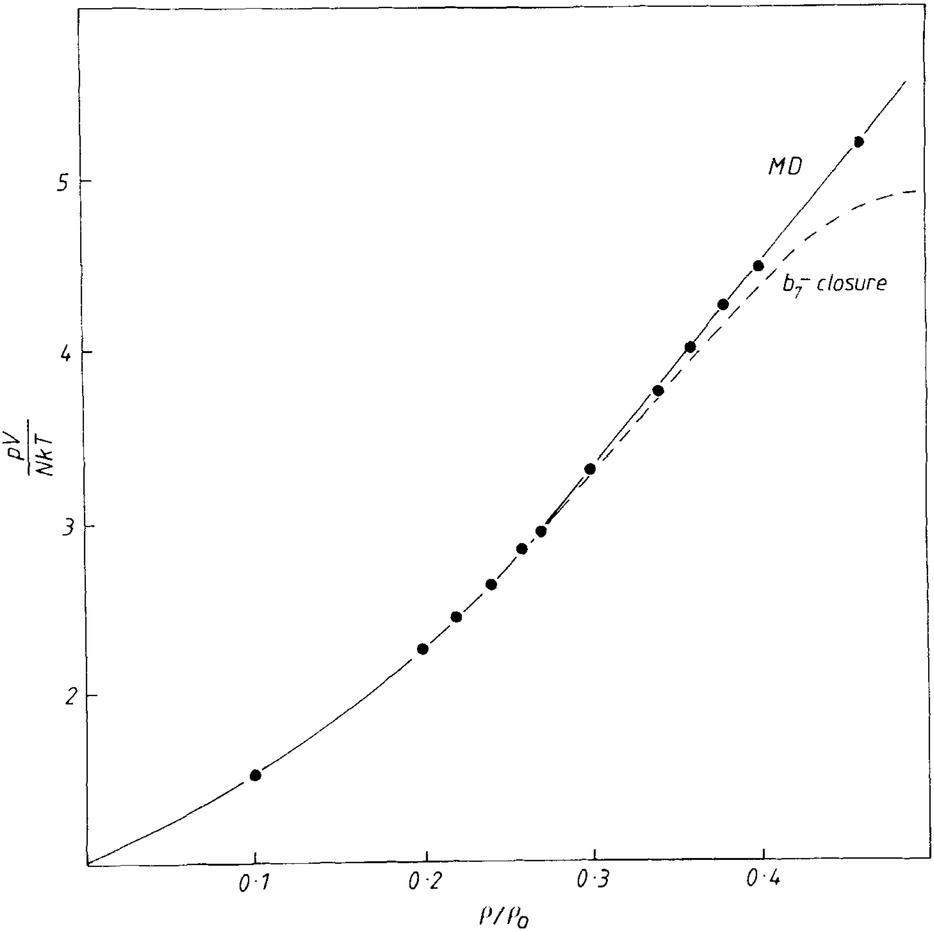

Figure 2 A comparison between the calculated MD pressures for the parallel hard-cube and the b_7-closure equation showing the non-convergence of the virial equation of state if the higher coefficients remain negative.

When the values b_2–b_7 from Table 1 are substituted into Equation (14), the virial equation diverges from the MD data around the density $0.25\varrho_0$ as shown in Figure 2.

Thus, we conclude that, if the higher coefficients remain negative, the virial equation of state fails to converge at an intermediate density in the fluid range. This density is actually rather insensitive to the precise closure form but would shift to somewhat lower values if the higher virial coefficients were to be negatively divergent as indicated by the ratio b_7/b_6.

4. DIFFUSION AND FREE VOLUME

The diffusion coefficients were calculated from a least square fit of the mean-square displacement against time according to

$$D = \frac{\langle \Delta r^2 \rangle}{6t}. \tag{15}$$

The numerical values are given in Table 3. Since we are looking for phase variations in the diffusion coefficients against density we will specify precisely the method of estimating the uncertainties quoted in Table 3, as calculated from Equation (15).

The slope of a regression line for n data points X, Y is

$$g = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\Sigma(x - \bar{x})^2} = \frac{n\Sigma xy - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2},$$

$$S_x^2 = \frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)} \quad \text{and} \quad S_y^2 = \frac{n\Sigma y^2 - (\Sigma y)^2}{n(n-1)},$$

$$S_{x|y}^2 = \frac{n-1}{n-2}(S_y^2 - g^2 S_x^2).$$

$S_{y|x}$ measures the scatter about the regression line. The standard errors of the slope q are then estimated from $S_{y|x}$ and S_x.

$$S_g \equiv \frac{S_{y|x}}{S_x\sqrt{n-1}},$$

$$\therefore (n-2)S_g^2 = \Sigma y^2 - \frac{(\Sigma y)^2}{n} - \frac{\left(\Sigma xy - \frac{\Sigma x \Sigma y}{n}\right)}{\Sigma x^2 - \frac{(\Sigma x)^2}{n}}.$$

A 100 (1-α)% confidence interval for the true slope β is

$$g \pm t_{\alpha/2}, (n-2)S_g.$$

$t_{\alpha/2}$, $(n - 2)$ follows from a t-distribution

Table 3 Diffusion coefficients and free volumes for the parallel cube model from MD calculations.

$\varrho\sigma^3$	D^a	v_f/σ^{3b}
0.06	1.843 ± 0.012	16.14 ± 0.32
0.10	0.7606 ± 0.0039	2.641 ± 0.047
0.18	0.4124 ± 0.0094	0.2736 ± 0.0033
0.20	0.3587 ± 0.0020	0.17563 ± 0.0021
0.22	0.3248 ± 0.0018	0.11684 ± 0.00097
0.24	0.2620 ± 0.0012	0.07975 ± 0.00092
0.26	0.2028 ± 0.0012	0.05588 ± 0.00073
0.27	0.2154 ± 0.0015	0.0473 ± 0.00044
0.28	0.1984 ± 0.0010	0.04015 ± 0.00051
0.30	0.1537 ± 0.0011	0.02925 ± 0.00032
0.34	0.1126 ± 0.00076	0.01674 ± 0.00022
0.36	0.1018 ± 0.0012	0.01284 ± 0.00024
0.38	0.07082 ± 0.00059	0.01010 ± 0.00021
0.40	0.06156 ± 0.00057	0.008028 ± 0.000099
0.46	0.0300 ± 0.00039	0.0045 ± 0.0002

[a] D is in reduced units of $(\sigma^2 kT/m)^{1/2}$

[b] The v_f values in this table are defined by Equations (16) and (17).

$$t_{\alpha/2}, (n-2) = \begin{cases} \sim 2.02 \text{ for a } 95\% \text{ interval} \\ \sim 2.70 \text{ for a } 99\% \text{ interval} \end{cases}$$

whence $n = 50$ was used.

Thus $g \pm 2.70S_g$ represents a 99% confidence interval for the true slope.

The data for the diffusion coefficients are plotted in Figure 3 in the standard Arrhenius form, giving a clear indication of anomalous behaviour at the reciprocal temperature (pV_0/NkT) 20.6, possibly a discontinuity. The equation-of-state data shows that this corresponds to a density $0.26\varrho_0$.

In order to obtain an estimate of the high-density free volume behaviour, we have calculated the mean free paths (λ_x, λ_y, λ_z) in the X, Y, Z directions from the average speed ($\bar{c}$) in that direction divided by the corresponding reversal frequencies (f_x, f_y, f_z).

$$\lambda_x = \bar{c}_x f_x^{-1} \tag{16}$$

where

$$\bar{c}_x = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{kT}{m}\right)^{1/2} \tag{17}$$

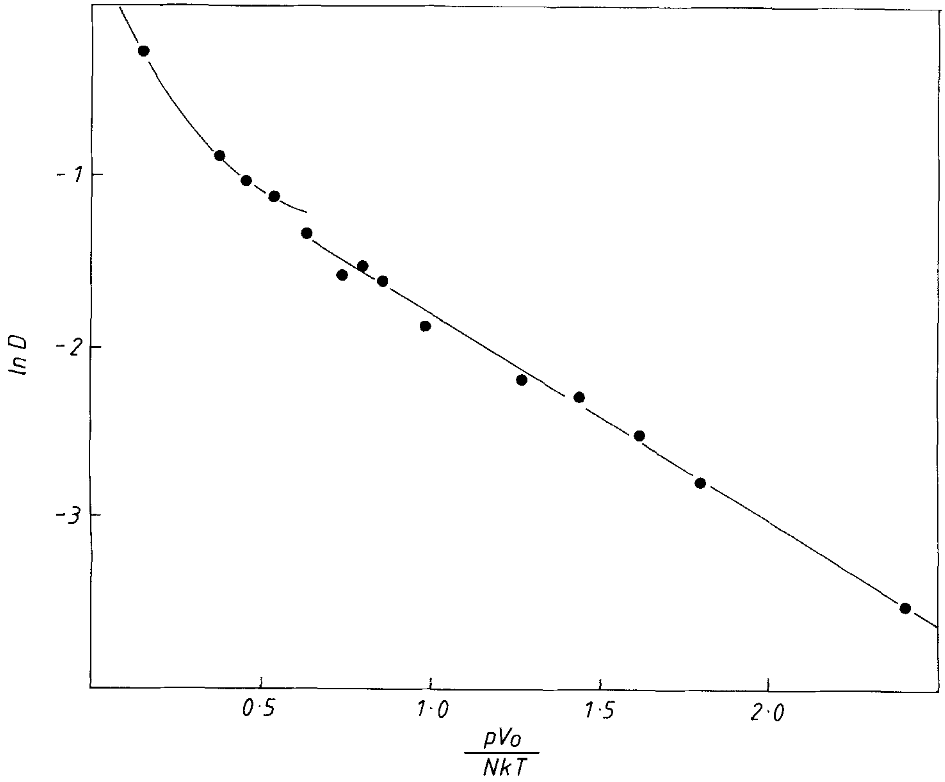

Figure 3 Calculated behaviour of the diffusion coefficient of the hard parallel-cube model plotted in Arrhenius form; a discontinuity is in evidence at the reduced pressure-temperature $pV_0/NkT \sim 0.6$.

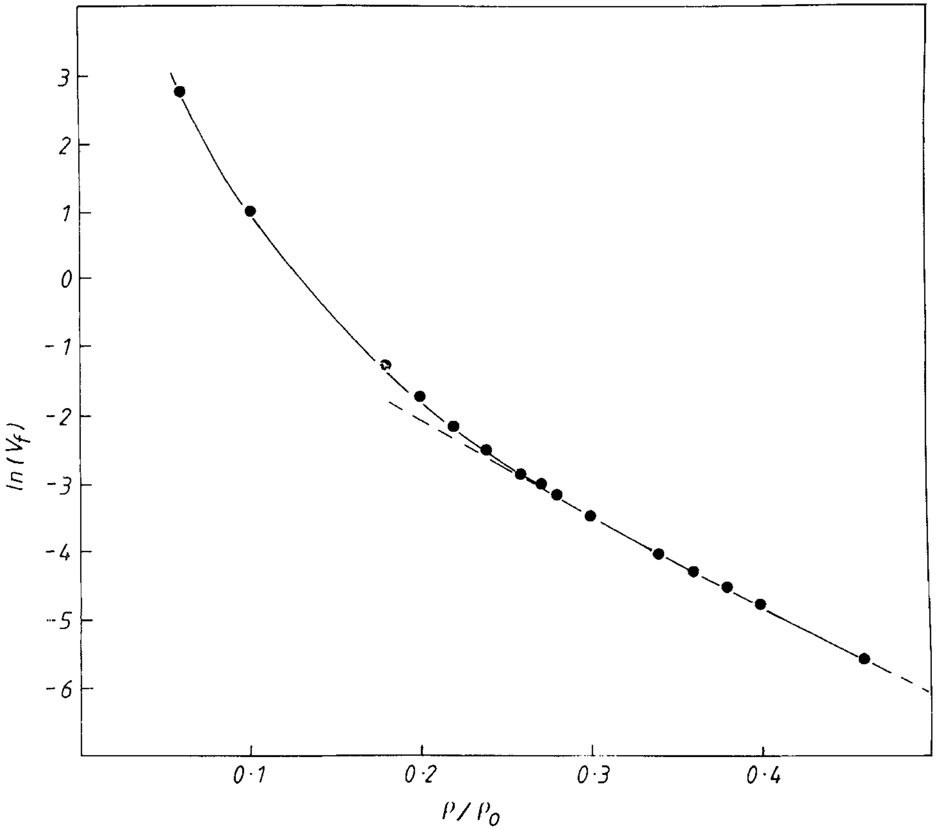

Figure 4 Single-particle free volumes for the hard parallel cube model as a function of density: the data shows a change in functional behaviour around 25% packing.

The v_f values given in Table 3 and plotted in Figure 4 correspond to the product $\lambda_x\lambda_y\lambda_z$. Figure 4 shows that the logarithm of the free volume, which is proportional to the entropy at high density, varies with density down to around $\varrho/\varrho_0 \sim 0.25$ and thereafter increases much faster than this simple law. The main observation is the change in the behaviour of this free volume attending the previously discussed changes in pressure and diffusivity.

5. CONCLUSIONS

The present results represent a preliminary determination of the properties of the parallel hard-cube model. The importance of the model, in the theory of fluids generally, rests in its geometric simplicity and the exaggerated behaviour of the known virial series compared to spheres. Phase transition behaviour is more pronounced than in the two-dimensional analogue parallel squares and therefore more amenable to observation by simulations.

The equation-of-state data for the pressure suggests that the virial series may fail to converge at an intermediate density and that this state point is associated with the percolation transition defined by the extensive/intensive free volume discontinuity occurring in all hard-core models. The data for the diffusion coefficient is also indicative of a phase change in transport properties.

At this stage, the evidence for a thermodynamic transition in conjunction with the percolation transition remains weak. Hoover's work [3] on 2-D discs shows that at the low density percolation transition the thermodynamic virial series is still very accurate seemingly applicable. It is likely that the thermodynamic manifestations of the percolation transition appear when the model is subjected to an external perturbation, i.e. boundary conditions, or an attractive perturbation in the potential, giving rise to critical phenomena for example, or a shear gradient.

Should this behaviour be confirmed by more substantial computations in the future, the hard-sphere model might also show a similar trend, with the higher virial coefficients going negative and the virial equations failing to converge. While this remains a speculative assertion, the implications for the development of analytic theories of liquids based on the cluster expansion, e.g. Percus-Yevick and CHNC [1], are such that the topic is worthy of continued investigation.

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APPENDIX

The Fortran coding for parallel hard-cube dynamics proceeds as for hard spheres except that a list of the time to the next collision in each of the three dimensions has to be evaluated. The present method also uses Link-cell coding. Both the general one-cycle hard-sphere algorithms and the Link-cell method used in this work have been described in detail in an informal newsletter.[†].

[†] *SERC Daresbury Laboratory Information Quarterly for Computer Simulation of Condensed Phases.* D.M. Heyes, No. 10, p. 21 (September 1982). W. Smith, No. 20, p. 52 (March 1986).

The coding section for the listing of the time to the next collision for the parallel hard-cube model is as follows. Note that a table of neighbouring cells is stored: NCELL(IP,N1).

```
C COLLISION PREDICTION TABLES
29      1=1
        DT = 1.0D0
9       CONTINUE
        IF(1.EQ.K)GO TO 21
        IF(I.EQ.L)GO TO 21
        IF(NJ(I).EQ.K)GO TO 21
        IF(NJ(I).EQ.L)TO TO 21
        IF(NCT.EQ.O)GO TO 21
        GO TO 23
21      CONTINUE
        TC(I)=1.ODO
        IP=IX(I)
        DO 40 NI=1,27
        JP=NCELL(IP,N1)
        J=LO(JP)
        IF(J.EQ.O)GO TO 40
41      CONTINUE
        IF(J.EQ.I)GO TO 7
        X=RX(I)-RX(J)
        Y=RY(I)-RY(J)
        Z=RZ(I)-RZ(J)
        IF(X.GR.O.5D0)X=X-1.0D0
        IF(Y.GT.O.5DO)Y=Y-1.0D0
        IF(Z.GT.O.5D0)Z=Z-1.0D0
        IF(X.LT.-O.5DO)X=X+1.ODO
        IF(Y.LT.-O.5DO)Y=Y+1.ODO
        IF(Z.LT.-O.5DO)Z=Z+1.ODO
        XX=X+X
        YY=Y+Y
        ZZ=Z+Z
        U=VX(I)-VX(J)
        V=VY(I)-VY(J)
        W=VZ(I)-VZ(J)
        BX=X*U
        BY=Y*V
        BZ=Z*W
        IF(XX.LT.SSEPS.AND.YY.LT.SSEPS.AND.ZZ.LT.SSEPS)GO TO 17
C   X- COLLISION
        IF(XX.LT.SS)GO TO 300
        IF(BX.GE.O.O)D=(S-X)/U
        IF(X.LT.O.O)D=-(S+X)/U
        IF(D.GT.TC(I)TO TO 300
        YSEP=(Y+D*V)**2
        ZSEP=(Z+D*W)**2
        IF(YSEP.GT.SS.OR.ZSEP.GT.SS)GO TO 300
```

```
      TC(I)=D
      NJ(I)=J
      GO TO 7
C  Y- COLLISION
300   IF(YY.LT.SS)GO TO 301
      IF(BY.GE.O.O)GO TO 301
      IF(Y.GT.O.O)D=(S-Y).V
      IF(Y.LT.O.O)D=-(S+Y).V
      IF(D.GT.TC(I)GO TO 301
      XSEP=(X+D*U)**2
      ZSEP=(Z+D*W)**2
      IF(XSEP.GT.SS.OR.ZSEP.GT.SS)GO TO 301
      TC(I)=D
      NJ(I)=J
      GO TO 7
C  Z- COLLISION
301   IF(ZZ.LT.SS)GO TO 7
      IF(BZ.GE.O.O)GO TO 7
      IF(Z.GT.O.O)D=(S-Z)/W
      IF(Z.LT.O.O)D=(S+Z)/W
      IF(D.GT.TC(I)GO TO 7
      XSEP=(X+D*U)**2
      YSEP=(Y+D*V)**2
      IF(XSEP.GT.SS.OR.YSEP.GT.SS)GO TO 7
      TC(I)=D
      NJ(I)=J
7     CONTINUE
      J=LINK(J)
      IF(J.NE.LO(JP)GO TO 41
40    CONTINUE
23    CONTINUE
      IF(TC(I).GT.DT)GO TO 20
      DT=TC(I)
      KS=I
      LS=NJ(I)
20    I=I+1
      IF(I.LE.N)GO TO 9
      K=KS
      L=LS
```