JOURNAL OF COMPUTATIONAL PHYSICS 7, 361–366 (1971)

Hard Sphere Equation of State in the Close-Packed Limit*

B. J. ALDER, D. A. YOUNG, AND M. R. MANSIGH

Lawrence Radiation Laboratory, University of California, Livermore, California 94550

AND

Z. W. SALSBURG

Chemistry Department, Rice University, Houston, Texas 77001

Received January 12, 1971

In the expansion of the hard sphere equation of state about close-packing, $pV/NkT = 3/\alpha + C_0 + C_1\alpha + \cdots$, where $\alpha = V/V_0 - 1$, the first two perturbation terms C_0 and C_1 have been evaluated by molecular dynamics averages for systems of hard dodecahedra in the fcc and hcp configurations. The two lattices have identical values of C_0 within the precision of the calculation, but the fcc value of C_1 is lower than the hcp value by about 10%.

1. INTRODUCTION

In the summer of 1969 we were discussing different approaches to the high density expansion of the hard sphere equation of state when it became apparent that by means of molecular dynamics it would be very simple to evaluate accurately the rigorous expressions for the expansion coefficients which Zevi Salsburg had recently formulated [1]. These expansion coefficients had previously been obtained [2] only from the difference between the total value of pV/NkT and the known high density limiting value given by the free volume theory $3/\alpha$, where $\alpha = V/V_0 - 1$. This way of obtaining C_0 and C_1 in the expansion

$$pV/NkT = 3/\alpha + C_0 + C_1\alpha + \cdots \tag{1}$$

is relatively inaccurate in as much as C_0 and C_1 are obtained as the difference between two very large numbers, with the resultant loss of significant figures.

---

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

This difficulty is analogous to that encountered in obtaining higher virial coefficients from computer data on the equation of state at low density as opposed to a direct evaluation of the theoretical expression for each virial coefficient.

There are a number of reasons for wanting to have accurate C_0 and C_1 values. The obvious one is to test various models that have been proposed for the high density solid equation of state. The need for very accurate values, however, arises principally from a desire to settle the problem of which of the two possible close-packed structures of hard spheres, namely face-centered cubic or hexagonal, is the more stable. By previous methods [2] no reliable difference between the equations of state of these two crystal structures could be detected. Although the high density equation of state by itself cannot resolve this problem (one needs the equation of state over the entire solid phase, so that by integration the free energy can be evaluated) it nevertheless is indicative of the difference to be expected.

It was thus decided that in the summer of 1970 we would attack this problem as well as a number of related ones. One of these was the evaluation of the elastic constants in the high density limit. We were then going to evaluate the elastic constants, including their frequency dependence, in general for these very anharmonic hard sphere crystals. Our intent was to investigate the difference in high frequency elastic behavior between a solid and a fluid. Zevi Salsburg was on his way to Livermore to start this investigation when he died. We have decided to carry out this program without his patiently given explanations, his sage counsel, his contagious enthusiasm, his clear thinking, his vast expertise, and above all his devotion to imaginative scientific investigations.

2. THEORY

The theory for the perturbation expansion will only be outlined here. The starting point is the partition function, written as the integral of a product of unit step functions $H(r_{ij} - \sigma)$, where H is zero if the argument of H is less than 0 and H is 1 if the argument is greater than 0. The separation of particles i and j of diameter σ is r_{ij} in general and "a" if i and j are nearest neighbors at their lattice positions. The argument of H can now be expanded near close-packing in terms of small displacements from the lattice sites, that is, in powers of $(a - \sigma)/\sigma$. The coefficients in this expansion contribute only when $\mathbf{r}_{ij} \cdot \mathbf{w}_{ij} = \sigma$, where $\mathbf{w}_{ij}$ is the unit vector joining the lattice sites belonging to particles i and j. In other words, a contribution to the expansion coefficients is obtained only when the projection of the vector joining the centers of the particles onto the axis joining their lattice sites is σ. But that is precisely the condition under which dodecahedra would have collisions, if the faces of the dodecahedra are determined in the usual manner, as for example in the Wigner–Seitz cell theory, in which at close-packing, planes are drawn perpendicular to the lines joining lattice sites.

The physical argument for this happenstance rests on the observation that at close-packing the curvature of the spheres can be neglected. Thus, at close-packing the spheres can be considered as having flat sides, namely the faces of the dodecahedra. Away from close-packing the curvature must be taken into account but can be treated as small in the sense that the perturbation terms are evaluated as statistical mechanical averages over collisions of dodecahedra. Formally, this means that ensemble averages involving $\delta(\mathbf{r}_{ij} \cdot \mathbf{w}_{ij} - \sigma)$ can be replaced by collision averages:

$$\delta(\mathbf{r}_{ij} \cdot \mathbf{w}_{ij} - \sigma) = \beta m \mid \mathbf{v}_{ij} \mid \delta(t - t_c), \tag{2}$$

where $\beta = 1/kT = 3/mu^2$, u is the rms velocity, and $\mathbf{v}_{ij}$ is the change of velocity upon collision at $t = t_c$, which, by the manner the dodecahedra have been determined, is necessarily in the direction of $\mathbf{w}_{ij}$.

The equation of state can be obtained by differentiation of the free energy with respect to volume, leading to

$$C_0 = 2 + \frac{1}{2(a - \sigma)\, Nu^2} \frac{1}{t} \sum_{\text{coll}}^{t} (r_{12}^2 - \sigma^2)\, v_{12}\,, \tag{3}$$

where t is the time elapsed in the sum over collisions. Similarly,

$$C_1 = -8/9 + C_0/3 + \frac{N}{4(a - \sigma)^2 (Nu^2)^2} \lim_{s \to 0} \frac{1}{t} \sum_{\text{coll}}^{t} \left[R_{12}^2 v_{12} \frac{1}{s} \sum_{\text{coll}}^{s} \mathbf{w}_{12} \cdot \mathbf{w}_{23} v_{23} \right]$$
$$+ \frac{N}{4(a - \sigma)^2 (Nu^2)^2} \lim_{s \to 0} \frac{1}{t} \sum_{\text{coll}}^{t} \left\{ [R_{12} v_{12} - \langle R_{12} v_{12} \rangle] \frac{1}{s} \sum_{\text{coll}}^{s} [R_{34} v_{34} - \langle R_{12} v_{12} \rangle] \right\}, \tag{4}$$

where $R_{12} = (r_{12}^2 - \sigma^2)$. The last term represents a fluctuation in the quantity calculated for C_0 for two different pairs of particles labeled 12 and 34, colliding a time s apart. This fluctuation has to be extrapolated to zero time between collisions, i.e., to $s = 0$. The second to last term in C_1 correlates pairs of colliding particles involving a common particle, and it also must be extrapolated to zero time between collisions. Higher coefficients C_n would require evaluation of higher order fluctuation terms, which would be increasingly difficult to calculate.

3. PROGRAMMING

The system of dodecahedra is set up at an arbitrary density, but sufficiently high so that only nearest neighbors can collide. Furthermore, only those faces can have collisions that can touch at close-packing, and no rotation of the particles is allowed. The initial configuration is either an fcc or hcp lattice. In order to prevent number and shape dependent effects from interfering with accurate comparison between the two crystals, two systems of $6 \times 6 \times 6 = 216$ particles with periodic boundary conditions are set up which differ only in the order of stacking of layers of dodecahedra.

The molecular dynamics program for spheres can be somewhat simplified for this system by keeping track of the position of each particle relative to its own lattice position and by keeping a permanent table of the twelve nearest neighbor lattice sites relative to the central one. In the hcp case care must be taken to distinguish between two types of neighbor arrangements. This information is then used in the usual way to find the smallest time to the next collision. This involves only the solution of a linear instead of a quadratic algebraic equation. The change of velocity upon collision is also simpler than previously, involving only a simple exchange in the direction perpendicular to the colliding faces. The 216 particle program ran at 1 million collisions/hr on the CDC 6600. A $12 \times 12 \times 12 = 1728$ particle program on the CDC 7600 ran at 3 million collisions/hr.

The coefficient C_0 is a simple sum over all collisions, analogous to the virial average previously used to determine the pressure. The sum is accumulated as each collision occurs. This is also done for C_1 except that in addition averages over as many as 20 successive collisions between different pairs of particles are accumulated at a small number (10) of even time intervals apart. Even time intervals (about 0.01 mean collision times) are chosen in order to have an efficient scheme for placing the value of the time between successive collisions into its appropriate time location. The choice of the number of intervals as well as the size of the interval itself is made on the basis that a sufficient number of collisions occur in each interval to get good statistics and yet the interval is small enough so that a reliable extrapolation to zero time is possible. For the term involving successive collisions between pairs of particles of which one is a common particle only one successive collision was taken into account since the collisions occur on the average already one mean collision time apart.

4. Results

A check on the accuracy of the calculation was made by comparing the pressure calculated by means of the virial theorem with that predicted by the self-consistent free volume theory [2]. Table I shows the comparison to be within the precision of the calculation. The accuracy in C_0 is only somewhat smaller than in the virial pressure, while C_1 is much less accurately determined. The reason for this is that the fluctuation term in C_1 is the difference of two large terms. An additional uncertainty is caused by a graphical extrapolation to zero time.

TABLE I

Calculated values of PV/NkT from the molecular dynamics dodecahedron systems compared with the prediction of the self-consistent free volume theory at $V/V_0 = 1.05$.

	Molecular Dynamics[a]		Self-Consistent Free Volume Theory
N	216	1728	
fcc	61.9892 (3)	61.989 (1)	61.98916
hcp	61.9892 (3)	61.989 (1)	61.98916

[a] The numbers in parentheses are the uncertainties in the last digits of the preceding numbers.

TABLE II

Calculated values of C_0 from the molecular dynamics dodecahedron system compared with hard sphere molecular dynamics and the predictions of the cell cluster and Fixman theories

	Molecular Dynamics[a]			Cell Cluster	Fixman
	Dodecahedron Calculation		Hard Sphere		
N	216	1728	500		
fcc	2.5649(4)	2.5658(4)	2.56(2)	2.442	2.55634
hcp	2.5646(4)	2.5658(2)	2.56(2)	2.458	2.55634

[a] The numbers in parentheses are the uncertainties in the last digits of the preceding numbers.

TABLE III

Calculated values of C_1 from the molecular dynamics dodecahedron systems compared with hard sphere molecular dynamics calculations

	Dodecahedron Calculation[a]	Hard Sphere[a]
fcc	0.52(1)	0.56(8)
hcp	0.57(1)	0.56(8)

[a] The numbers in parentheses are the uncertainties in the last digits of the preceding numbers.

In Table II the values of C_0 computed by dodecahedron dynamics are compared to those previously obtained by hard sphere dynamics [2]. The computed values of C_0 are seen to increase slightly with increasing number of particles. There is no observable difference in the values of C_0 for the two lattices. The two theoretical predictions [1, 4] are accurate but not exact. The accurate prediction of the Fixman theory [4] is possibly fortuitous since a higher approximation in this theory leads to a less accurate prediction, namely, $C_0 = 2.40 \pm 0.04$.

The computer predictions for C_1 are given in Table III for the 216 particle system. The 1728 particle system was not run sufficiently long to yield reliable values for the fluctuation term. If in Eq. (4) the factor of N is removed from the term involving correlation of successive collisions with a common particle, the 216 particle value is larger than the 1728 particle value by a factor of 7.86 ± 0.16 for fcc and by a factor of 7.94 ± 0.16 for hcp. If there were no intrinsic number dependence effects, this term should be $1728/216 = 8.0$ times larger for the 216 particle system than for the 1728 particle system. The slightly lower values for the ratio indicate a slightly higher value of C_1 for the larger systems.

The slightly higher pressure of the hard sphere hcp solid near close-packing is suggestive, but not conclusive proof, that the fcc phase has the higher entropy and is therefore the more stable phase. If the difference in the pressure between the two phases is considered to be due to C_1 at high pressure up to a volume $(V/V_0 = 1.1)$, where it exceeds the known bound and at larger volume the difference is taken to be the bound itself $((V\,\Delta p/NkT) = 0.005)$, the expected entropy difference at close-packing would be $(S_{\text{fcc}} - S_{\text{hcp}})/Nk = 0.002$. The greater stability of the fcc phase and an entropy difference of the same magnitude were suggested by earlier considerations [5].

REFERENCES

1. W. G. RUDD, Z. W. SALSBURG, A. P. YU, AND F. H. STILLINGER, *J. Chem. Phys.* **49** (1968), 4857.
2. B. J. ALDER, W. G. HOOVER, AND D. A. YOUNG, *J. Chem. Phys.* **49** (1968), 3688.
3. B. J. ALDER AND T. E. WAINWRIGHT, *J. Chem. Phys.* **31** (1959), 459.
4. F. H. REE, *J. Chem. Phys.* **53** (1970), 920.
5. B. J. ALDER, B. P. CARTER, AND D. A. YOUNG, *Phys. Rev.* **183** (1969), 831.