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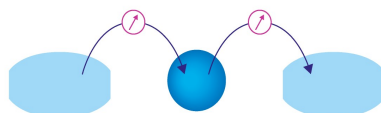
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The equation of state and the collision rate for systems ranging in size from four to 500 particles are described. The dependence of the results on the number of particles is qualitatively discussed and in this way insight is gained as to what is required of more accurate analytical theories. By comparing the results to various analytical theories now available their region of validity is established. The number of particles necessary at various densities to obtain a quantitative description of the equilibrium properties is delineated. Whether a first-order phase transition exists for hard spheres remains open until larger systems are investigated.

INTRODUCTION

IN the previous paper[1] a program for digital computers has been described which reproduces the detailed motions of a system of interacting classical particles. In this paper some of the results of such a calculation as applied to a relatively small number of hard sphere molecules is presented. The aim of such a study was to learn how many particles are required to adequately represent the equilibrium behavior of a real system.

In order to answer this question it is necessary to study the dependence of the results on the number of particles. Thus, systems as small as four particles and as large as 500 particles are reported on. The four-particle system was studied in the hope that it would reproduce the two-state behavior at a density near 1.5 times close-packing noted previously[2-5] for larger systems. If this were the case then it would have been worthwhile to attempt an analytical solution for the four-particle system, and determine from it what the proper average behavior between the two states is at that density. Since a larger number of particles than four were required to bring about a two-state behavior, analytical treatment is out of the question; even dealing with three independent particles would have been a hard task (three particles are placed relative to the fourth). This also means that any analytic treatment to even qualitatively describe the behavior near this density would be extremely difficult.

The larger systems were studied in the hope that the two states would eventually coexist. Only then can one be sure that hard spheres have a first-order phase transition between a fluid and a solid state. The fact that this was not achieved with systems as large as 500 particles is not surprising. The best hope of getting the two phases to coexist for a small number of particles is in two-dimensional systems, since fewer particles are

perturbed by the boundary. In two-dimensional systems the same two-state behavior was found as in three-dimensional systems and a study is now under way to determine whether a 1000- or a 2000-particle system does have the two phases coexisting.

Before it can be said that a large enough number of particles have been used to adequately represent an infinite system, the boundary conditions used should not influence the results. This has by no means been achieved with a 500-particle system. Periodic boundary conditions have been used throughout for the systems presented in this report in the belief that they give the most realistic results. They are certainly natural boundary conditions in condensed or solid systems where the structure is periodic. They also can be shown to cause the least error in the equilibrium properties at low density. Other boundary conditions have been studied also, and will be reported on subsequently. Although qualitatively the results are the same, they differ quantitatively and they will continue to do so until the number of particles on the surface is a small fraction of the total number of particles. In the more favorable situation of two-dimensional systems this will not occur until systems containing more than 10 000 particles can be handled. This is, however, quite feasible with the latest generation of computers.

With a system so large that boundary conditions do not significantly influence the results, it would be possible to represent an arbitrary number of particles at solid densities provided the system is run long enough to rearrange itself to the state of lowest free energy from some arbitrary initial configuration. In the fluid region the number of particles does not affect the results as long as there are enough particles to establish the proper local order. For solids, however, long-range order can only be obtained for a small number of particles if the order extends across the boundaries of the system. In the case of periodic boundary conditions this means that the particles on one side of the cell have to be perfectly arranged relative to the other side of the cell. For large systems, however, fairly long-range order can be established within a given cell and even if the boundaries do not match, this does not seriously influence the results. Thus a crystal can form

[1] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **31**, 459 (1959).

[2] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **27**, 1208 (1957).

[3] T. E. Wainwright and B. J. Alder, Nuovo cimento Suppl. **9**, Ser. 10, 116 (1958).

[4] W. W. Wood and J. D. Jacobson, J. Chem. Phys. **27**, 1207 (1957).

[5] W. W. Wood, R. R. Parker and J. D. Jacobson, Nuovo cimento Suppl. **9**, Ser. 10, 133 (1958).

TABLE I. Equation of state and the collision rate for four particles.

v/v_0	$(pv/NkT)-1$	Γ/Γ_0	R^a	C^b
1.250	13.35	5.03	0.89	2
1.400	8.88	3.73	0.89	2
1.500	7.41	3.36	0.89	7
1.525	7.12	3.27	0.89	5
1.550	6.86	3.23	0.90	3
1.600	6.40	3.08	0.89	5
1.700	5.76	2.93	0.88	2
1.800	5.28	2.88	0.90	2
1.850	5.09	2.87	0.91	5
1.900	4.99	2.83	0.88	5
2.000	4.61	2.80	0.90	2
2.100	4.33	2.73	0.89	5
2.200	4.20	2.74	0.88	2
2.300	3.94	2.74	0.90	5
2.400	4.00	2.87	0.88	5
2.500	3.68	2.82	0.91	2
3.000	3.02	2.72	0.89	2

ᵃ R is the ratio of the experimental to theoretical collision rate, if the latter is calculated from the Enskog theory with the machine determined equation of state.

ᵇ C is the number of 1000 collisions the problem has been run.

in any direction relative to the boundary, which is not the case in the smaller systems. However, there are still serious problems in large systems with respect to the calculating time involved to transform an arbitrary initial state to the final equilibrium state. Just as in real systems, glasses can be stable for very long times, so an arbitrary initial configuration can be metastable for as long a time as one cares to calculate.

For small systems it is thus necessary to study that precise number of particles which fit exactly into the cell in order to represent a solid as realistically as possible. This number of particles also has to be placed into the chosen lattice positions; otherwise it has been found that the system will not convert to the state of lowest free energy in reasonable calculating time.

TABLE II. Equation of state and the collision rate for eight particles.

$v/v_0{}^a$	$(pv/NkT)-1$	Γ/Γ_0	R^b	C^c
1.500(s)	7.56	3.59	0.94	0–5.0
1.525(s)	7.37	3.61	0.95	0–5.0
1.550(s)	7.07	3.50	0.95	0–20.0
1.570(s)	6.88	3.46	0.95	0–7.5
1.580(s)	6.82	3.46	0.95	0–6.6
1.580(f)	9.90	4.14	0.79	6.6–10.0
1.590(s)	6.78	3.41	0.94	0–5.0
1.600(s)	6.67	3.42	0.95	0–1.4
1.600(f)	9.72	4.14	0.79	1.4–5.0
1.610(s)	6.56	3.36	0.95	0–10.0
1.620(s)	6.50	3.40	0.96	0–5.0
1.650(s)	6.34	3.37	0.96	0–10.0
1.700(s)	5.99	3.28	0.96	0–7.6
1.800(s)	5.55	3.17	0.94	0–10.0
2.000(s)	4.71	3.09	0.97	0–1.3
2.000(f)	5.16	3.34	0.96	1.3–5

ᵃ The brackets symbolize the solid (s) and the fluid (f) branch, respectively.

ᵇ As defined in Table I.

ᶜ C stands for the range in units of 1000 collisions the problem has run in each branch.

Although only the two close-packed lattices for hard spheres were studied and they both, as expected, gave the same results, it is believed that they yield the state of lowest free energy at least at the highest densities. If metastability is a problem, the most efficient way to avoid long calculations is to study various initial states and select the one of lowest free energy at various densities. This has not as yet been done extensively. Thus a body-centered crystal should be examined in the two-state region.

It is, however, possible even in small systems to slightly change the number of particles studied and still get a solid with long-range order. One example of this is given when a perfect solid with one imperfection, namely with one missing particle, is described. Of course, not too many such holes could be introduced in small systems or they would lose their long-range character.

TABLE III. Equation of state and the collision rate for 16 particles.

$v/v_0{}^a$	$(pv/NkT)-1$	Γ/Γ_0	R^a	C^a
1.500	7.71	3.77	0.97	0–5.0
1.525(s)	7.49	3.72	0.97	0–8.6, 9.0–10.0
1.525(f)ᵇ	...	...	...	8.6–9.0
1.550	7.31	3.74	0.97	0–10.0
1.600(s)	6.98	3.67	0.97	0–1.9, 2.0–10.0
1.600(f)ᵇ	...	...	...	1.9–2.0
1.650(s)	6.63	3.57	0.97	2.5–6.0, 8.6–10.0
1.650(f)	9.0	4.84	0.97	0–2.5, 6.0–8.6

ᵃ The symbols have been defined in the previous tables.

ᵇ For the cases $v/v_0=1.525$ and 1.600, the fluid branch existed for too few collisions to determine the pressure adequately.

RESULTS

Since the machine is made to calculate the actual motion of each particle, this program has been principally designed to study the transport properties of systems. Some preliminary results[6] of these have been previously given. In this report, however, attention is focused on the equilibrium properties because these are much better understood and hence confidence in the method can be established, especially since direct comparison with the Monte Carlo results[4,5] can be made.

The thermodynamic properties of a hard sphere system are completely described by the pressure since the internal energy is that of a perfect gas. The pressure is calculated by a direct application of the virial theorem which states that

$$(pv/NkT)-1=(1/Nu^2)(d\Xi/dt), \qquad (1)$$

where u^2 is the mean square velocity,

$$\Xi = \sum_{\text{collisions}} b_{ij},$$

[6] B. J. Alder and T. E. Wainwright, *Transport Processes in Statistical Mechanics*, I. Prigogine (Interscience Publishers, New York, 1958), p. 97.

TABLE IV. Equation of state and the collision rate for 32 particles.

v/v_0[a]	$(pv/NkT)-1$	rmsd[b]	Γ/Γ_0	R[a]	C[a]
1.03139	97.2	0.21	34.1	1.01	0–2.0
1.25000	13.62		5.72	1.00	0–10.0
1.40000	9.33	0.16	4.37	0.99	0–11.0
1.50000	8.12		4.06	0.99	0–42.0
1.52500(s)	7.92		4.04	0.99	0–29.0, 30.0–93.0, 106.0–107.0, 204.0–205.0
1.52500(f)	10.51		5.42	1.00	29.0–30.0, 93.0–106.0, 107.0–204.0, 205.0–263.0
1.53000(s)	7.88		4.03	0.99	0–76.0
1.53000(f)	10.47		5.41	1.00	76.0–200.0
1.53125(s)	7.90		4.04	0.99	0–4.2
1.53125(f)	10.54		5.41	0.99	4.2–28.0
1.53250(s)	7.84		4.00	0.99	0–9.0
1.53250(f)	10.45		5.35	0.99	9.0–52.0
1.53500(s)	7.78		4.01	1.00	0–2.5
1.53500(f)	10.30		5.28	0.99	2.5–52.0
1.54000(s)	7.72		4.01	1.00	0–0.4
1.54000(f)	10.23		5.26	0.99	0.4–47.0
1.55000(s)	7.63	0.77	3.95	0.99	0–5.0, 6.5–25.0, 179.0–180.0
1.55000(f)	10.02		5.19	0.99	5.0–6.5, 25.0–179.0, 180.0–220.0
1.60000(s)	7.57		4.02	0.98	0–5.0
1.60000(f)	9.06		4.87	1.00	5.0–53.0
1.65000	8.41	0.82	4.63	0.99	0–50.0
1.70000	7.83	0.37	4.40	0.98	0–15.0
1.75000	7.13	0.47	4.19	1.00	0–15.0
1.80000	6.59	0.88	3.99	1.00	0–15.0
2.00000	4.89	0.50	3.28	1.00	0–5.0
3.00000	2.09		2.07	0.98	0–39.0
9.00000	0.409		1.23	0.99	0–9.0
10.00000	0.343		1.17	1.01	0–1.5
14.14214	0.249		1.05	0.97	0–3.0

[a] The symbols have been defined in the previous tables.
[b] rmsd stands for the root-mean-square deviation in $(pv/NkT)-1$.

and $b_{ij}=r_{ij}\cdot\mathbf{u}_{ij}$ has been defined previously[1] as the scalar product of the relative positions and relative velocities of particles i and j which are involved in a collision. The pressure is graphically determined from the slope of a plot Ξ vs t, and can for a sufficiently long run be obtained within an accuracy of 1% in pv/NkT.

The only property involving the time which shall be discussed here is the collision rate Γ. According to the theory of Enskog,[7] Γ is intimately related to the equation of state,

$$\Gamma/\Gamma_0 = (pv/NkT-1)/(B/v), \qquad (2)$$

where B is the second virial coefficient and Γ_0 is the collision rate at infinite dilution

$$\Gamma_0 = 2N(N-1)\sigma^2(\pi u^2/3)^{\frac{1}{2}}. \qquad (3)$$

N is the number of particles per unit volume. Since finite systems are dealt with, it is strictly speaking necessary to use the value of B for finite systems also. Hence the expression given in Sec. E was used for B. σ is the diameter of the particles. The collision rate and the equation of state are tabulated at various compressions expressed in terms of v/v_0, where v_0 is the volume of the system at close packing.

[7] D. Enskog, Kgl. Svenska Ventenskapsakad. Handl. 64, No. 4 (1922).

(A) Intermediate Densities

The results are presented in Tables I through XI and in graphs 1 through 4. Figure 1 shows the results for various sized systems in the intermediate density region where the two-state behavior is found. As the

TABLE V. Equation of state and the collision rate for 96 particles.

v/v_0[a]	$(pv/NkT)-1$	$\Gamma\Gamma_0$	R[a]	C[a]
1.0306	99.55	34.4	1.00	0–2.0
1.1000	31.54	11.90	1.02	0–2.9
1.1600	20.27	7.85	0.99	0–2.0
1.2500	13.66	5.75	1.00	0–3.0
1.3448	10.53	4.83	1.01	0–2.0
1.4200	9.22	4.36	0.99	0–2.0
1.5000	8.41	4.25	1.00	0–7.0
1.6000(s)	7.77	4.18	1.00	0–2.6
1.6000(f)	8.96	4.88	1.01	2.6–10.0
1.7000(s)[b]	...	...	...	0–1.0
1.7000(f)	7.54	4.25	0.98	1.0–6.5
1.8000(s)	6.14	3.75	1.01	0–3.8
1.8000(f)	6.80	4.10	0.99	3.8–6.0
1.9000	5.44	3.50	1.00	0–4.0
2.0000	4.72	3.22	1.01	0–3.6
2.7220	2.63	2.31	0.96	0–3.0
14.1422	0.240	1.14	0.99	0–3.0

[a] The symbols have been defined in previous tables.
[b] The solid branch is too short to determine the pressure with any accuracy.

TABLE VI. Equation of state and the collision rate for 108 particles.

$v/v_0{}^a$	$(pv/NkT)-1$	Γ/Γ_0	R^a	C^a
1.0306	99.02	34.3	1.00	0–5.0
1.2500	13.68	5.70	1.00	0–5.5
1.3448	10.65	4.89	1.02	0–4.6
1.4200	9.34	4.48	1.01	0–2.6
1.5000	8.36	4.24	1.01	0–13.9
1.5500(s)	8.20	4.31	1.01	0–3.0
1.5500(f)	9.84	5.09	1.00	3.7–29.7
1.6000(s)[b]	8.13	4.36	1.00	0–1.9
1.6000(f)	8.87	4.67	0.98	2.2–34.0
1.6500(s)[b]	7.73	4.01	...	0–0.7
1.6500(f)	8.30	4.58	1.00	0.7–4.2
1.7000	7.61	4.35	1.00	0–33.0
1.7678	6.83	3.90	0.97	0–5.4

[a] The symbols have been defined in previous tables.
[b] The accuracy of the results at these densities is poor due to the short existence of these branches.

TABLE VII. Equation of state and the collision rate for 256 particles.

$v/v_0{}^a$	$(pv/NkT)-1$	Γ/Γ_0	R^a	C^a
1.5000	8.34	4.12	0.98	0–3.0
1.6000(s)	7.52	3.98	0.99	0–2.5
1.6000(f)	8.96	4.87	1.01	4.9–9.5
1.7678(s)	6.37	3.87	1.02	0–3.7
1.7678(f)	6.88	4.09	1.00	5.0–9.2
2.0000	4.81	3.21	0.99	0–3.0

[a] The symbols have been defined in previous tables.

TABLE VIII. Equation of state and the collision rate for 500 particles.

$v/v_0{}^a$	$(pv/NkT)-1$	Γ/Γ_0	R^a	C^a
1.6000(s)	7.68	4.07	0.98	0–6.2
1.6000(f)	8.91	4.82	1.00	11.0–22.5
1.6500	7.06	3.84	0.98	0–3.0
1.7000	6.67	3.79	0.99	0–3.2
1.7678	6.36	3.73	0.99	0–2.8

[a] The symbols have been defined in previous tables.

TABLE IX. Equation of state and the collision rate for 32 particles in the compressed-fluid region.

v/v_0	$(pv/NkT)-1$	Γ/Γ_0	R^b	C^b	$v/v_0-0.1506$
1.1546[a]	700	300	1.10	0–1.4	1.0040
1.1987	64.1	26.2	1.01	0–1.1	1.0481
1.2496	30.8	13.1	1.01	0–1.4	1.0990
1.2982	22.5	9.37	0.95	0–1.2	1.1476
1.3443	18.3	8.10	0.98	0–1.4	1.1937
1.4017	14.7	6.93	1.00	0–1.4	1.2511
1.4948	11.2	5.55	0.99	0–1.3	1.3442
1.5981	9.20	4.98	1.00	0–1.2	1.4475

[a] The system was carried to a density of $v/v_0=1.1546$, but $(pv/NkT)-1$ was so high that with the short run available the pressure could not be determined accurately.
[b] The symbols have been defined in previous tables.

TABLE X. Equation of state for 100 particles, initially always in a random configuration.

v/v_0	$(pv/NkT)-1$	C^a	$(pv^b/NkT)-1$
1.2279	21.5	0–4.0	
1.3448	13.3	0–3.5	
1.7678	6.70	0–4.3	
2.0000	4.81	0–5.6	
2.722	2.47	0–1.9	
14.142	0.237	0–2.8	0.240
30.43	0.104	0–3.2	0.104
86.07	0.0359	0–1.9	0.0352

[a] The number of collisions in units of 1000 collisions the problem has been run.
[b] From the five-term virial expansion.

TABLE XI. Equation of state for 31 particles, initially in a face-centered lattice with one particle left out.

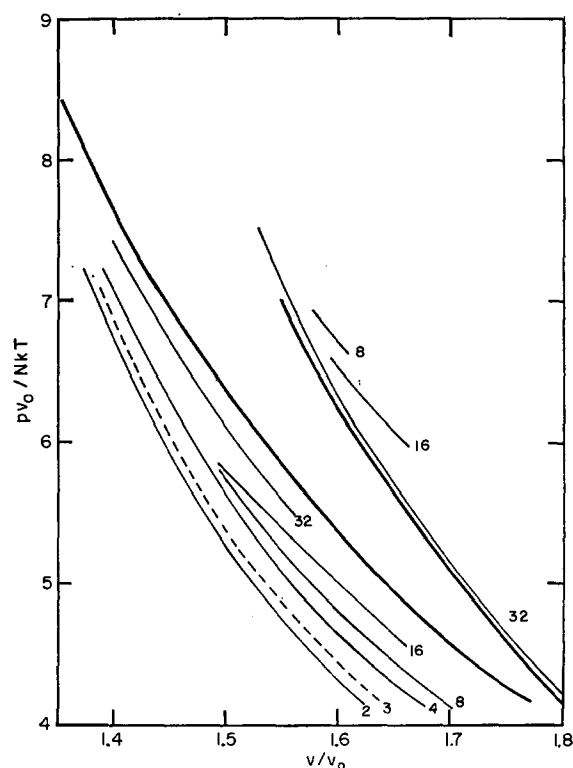| v/v_0	$v/v_0{}^a$	pv_0/NkT	$(pv/NkT)-1$	C
1.2903	1.2500	11.4	13.75	0–2.0
1.4464	1.4012	7.28	9.53	0–7.2
1.5484(s)	1.5000	5.88	8.11	0–1.0
1.5484(f)	1.5000	7.23	10.19	3.0–7.0

[a] The value of v/v_0 if there were 32 particles present.

FIG. 1. Equation of state in the transition region. Both the fluid and solid branches are plotted for those numbers of particles where each was found. The curves are labeled by the number of particles. The heavy lines refer to systems which contain 96 or more particles.

cathode ray tube pictures displayed in paper I[1] clearly showed, the lower branch of the system is solidlike and the upper branch is fluidlike. It was found that the system stayed in the lower branch for quite a long calculating time, then suddenly jumped to the upper branch and stayed there for quite a long calculating time before jumping back to the solid branch again. The transition between the two branches occurs so infrequently that it was not possible to get enough statistics to establish the average time the system spends in each branch. Thus, each branch is plotted separately. Even if an average pressure could be established in this density region its significance would not be clear.

Thus, in these small systems it is not possible to have solid and fluid together in equilibrium, but the whole system is in either one phase or the other. The accessible region of phase space might be considered as consisting of two pockets, one solid, the other liquid, connected by a narrow passage. The narrow passage represents the relatively improbable cooperative motion among the particles necessary to let a particles escape out of its cell and turn a solid into a liquid. The reverse process also is improbable since a cooperative motion among a set of particles is required to form a small ordered region. For these small systems such processes are made more unlikely, because the solid has to crystallize in a particular orientation. For larger systems this is not necessary so that presumably the passage between the two pockets enlarges for this reason. On the other hand, the crystallites could be bigger so that more particles might be involved in the cooperative motion, causing a narrowing of the passage. If there is to be a first-order phase change, crystals must exist in equilibrium with the fluid; that means that the passage must not be choked off in larger systems. The passage can, however, be still quite narrow so that it might take a large amount of calculating time to establish equilibrium, but the system is large enough so that part of the system is in the solid phase and part in the liquid one.

The question of what actually happens is not settled yet, but can probably be settled by the study of large two dimensional systems. From the results presented in

TABLE XII. Occurrence of the first transition from the solid to the fluid state at a given density ($v/v_0=1.60$) for various numbers of particles and the duration of the transition.

N	collisions/particle	duration[a] (collisions/particle)
8	350	
16	240	
32	310	
96	54	. . .
108	35	6
256	20	19
500	25	19

[a] For the small systems the duration of the transition is too short to be accurately determined, but they are of the order of one collision per particle.

TABLE XIII. Occurrence of the first major transition from the solid to the fluid state for a given number of particles (32) as a function of density.

v/v_0	collisions/particle
1.52500	5800
1.53000	4700
1.53125	260
1.53250	560
1.53500	150
1.54000	25
1.55000	310
1.60000	310

Table XII it appears that the passage widens as the number of particles increase. Table XII shows that as the number of particles increases it takes fewer and fewer collisions per particle to go from an initial solid state to the fluid state at a given density. These results are for a single run for all the different systems and hence large statistical fluctuations can be expected. Nevertheless the trend is clearly established. Table XII also shows the number of collisions necessary to go from the lower branch to the upper branch as judged by the interval from the point at which the pressure first increases to the point at which the pressure steadies down to the upper branch value. The fact that the transition region between these two states persists longer as the number of particles increases also indicates that the passage widens, because the systems spend more time in the partially melted state. Without referring to the picture just presented one can say that the partially melted region becomes more stable for larger systems, so that for large enough systems that state might become stable for very long times and a first-order phase transition would then exist.

Returning to the picture of phase space, as the density changes the pockets change relatively in size. Thus, at higher densities the solid pocket grows at the expense of the liquid pocket. This means that the system spends more time in the solid pocket and attempts fewer entries into the passage to the liquid side. At the same time, however, the passage also narrows, since a more improbable fluctuation is involved in turning a denser solid at least partially into a fluid. This picture is confirmed by the results in Table XIII, where the density dependence of the transition is studied for a set number of particles. At higher densities the transition from the solid to the fluid state requires many more collisions, until finally at v/v_0 of 1.50 it was impossible to cause the transition to take place. Since the passage is wider for larger systems, it can be expected that at higher densities than for smaller systems it will still be possible to reach the fluid state. Eventually, however, the passage should be choked off at high but finite densities, but, as will be seen, the liquid pocket can still persist as a metastable state. In any case these considerations are in accordance with the sensitive dependence of the results on density.

Figure 1 also demonstrates the systematic variation of the results with the number of particles. It is found that the larger systems have a higher pressure in the solid phase than the smaller systems, while in the fluid phase just the reverse is true. However, for systems greater than about 100 particles the pressure is no longer different within the accuracy of the results. These systems form the heavy curve drawn in Fig. 1. For 100 or more particles all the second neighbors of a given particle are in the same cell, while for 32 particles some of these second neighbors are in the adjacent cell. Because of the periodic boundary condition this means that these second neighbors are not all independent of each other in their motion, that is, some of them have identical histories. For systems with less than 32 particles even the nearest neighbors are not independent. This apparently causes the fairly large change in the results for very small systems. Once the first neighbors are correctly treated the results are close to the behavior of larger systems. Whether third neighbors are treated independently or not is apparently of not much quantitative significance except as far as the phase transition is concerned. There many particles are needed to represent a crystallite in equilibrium with a fluid.

The two-state behavior was found over a region of density of $1.5 < v/v_0 < 1.7$. Above v/v_0 of about 1.7 the solid system which was initially set up almost immediately lost the ordered configuration, and hence did not stay on the lower pressure branch for an observable time. Systems with $v/v_0 < 1.525$ remained in the lower branch and in the original configuration for very long runs.

The results of the free volume theory[8] are given in Fig. 1 by the curve labeled 2. From the point of view of periodic boundary conditions one particle surrounded by its neighbors at fixed positions is generated by a two-particle system, the second particle representing all the neighbors. A one-particle-per-cell system with periodic boundary conditions leads to no collisions and hence a perfect gas equation of state. This free-volume theory uses the smeared-out neighbor approximation, that is, the central particle is confined to an equivalent sphere rather than the exact, but geometrically complex, region that is accessible in between the neighboring spheres when they are located on lattice positions. If the latter free volume is calculated[9] the pressure is raised but not nearly enough to bring it into agreement with the larger system results.

The dotted curve labeled 3 in Fig. 1 refers similarly to a free-volume theory, but one in which two particles are confined to a cell determined by their neighbors.[10] The curve is dotted because it is not the accurate result of such a calculation. Because of the complexity of the

calculation some mathematical approximations had to be used in order to apply the theory to this region of density. Again the results are in the right direction from the two-particle theory but not large enough.

A characteristic of the free-volume theory and of very small periodic systems is that density fluctuations are suppressed. This could make the pressure too low as compared to an infinite system. Thus, if $P(\rho)$ is the pressure as a function of density, according to the free volume theory, then the effect of fluctuations can be calculated as a perturbation. Let ρ_0 be the average density and let $f(\rho)$ be the distribution of densities in the region of an atom. That is, $f(\rho)$ is related to the distribution of nearest-neighbor configurations or cell sizes which would be found in an infinite system. Then,

$$\bar{P} = \int_0^\infty P(\rho) f(\rho) d\rho.$$

Expanding $P(\rho)$ in a Taylor series about ρ_0 yields

$$\bar{P} = P(\rho_0) \int_0^\infty f(\rho) d\rho + (dP/d\rho) |_{\rho_0} \int_0^\infty (\rho - \rho_0) f(\rho) d\rho$$

$$+ \tfrac{1}{2} (d^2 P/d\rho^2) |_{\rho_0} \int_0^\infty (\rho - \rho_0)^2 f(\rho) d\rho + \cdots,$$

and since

$$\int_0^\infty f(\rho) d\rho = 1$$

and

$$\int_0^\infty \rho f(\rho) d\rho = \rho_0,$$

$$\bar{P} = P(\rho_0) + \tfrac{1}{2} (d^2 P/d\rho^2) |_{\rho_0} \int_0^\infty (\rho - \rho_0)^2 f(\rho) d\rho$$

$$+ \text{ higher order terms.}$$

At very high densities where density fluctuations are inhibited, $f(\rho)$ is a delta function centered at ρ_0 so the integral in the above equation vanishes.

Thus, as can be seen from Fig. 1 and particularly from Fig. 3, at densities near close-packing, the free-volume theory calculates the pressure very accurately. At densities lower than that of close-packing, the integral is positive so that P is larger than $P(\rho_0)$ since $d^2 P/d\rho^2$ is positive. The amount of fluctuation in density, that is the width of the function $f(\rho)$, grows with increasing system size so that the larger systems in this density range should show higher pressures.

The free-volume theory is a model applicable in the solid state in as much as the neighboring particles are strictly confined to a lattice. It is, therefore, not surprising that the two-state behavior is not found for this theory. The larger systems investigated on the calculating machine are akin to the cell theory, as previously implied, when periodic boundary condi-

[8] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A163**, 53 (1937).

[9] R. J. Buehler, R. H. Wentorf, J. O. Hirschfelder, and C. F. Curtiss, J. Chem. Phys. **19**, 61 (1951).

[10] J. de Boer, Physica **20**, 655 (1954); **21**, 137 (1955).

tions are used. For example, the same results for the equation of state are obtained when two particles are studied on a body-centered cubic lattice with periodic boundary conditions and when the free-volume theory for that situation is worked out. Thus larger systems are merely cell theories with more particles per cell. The question is, then, how many particles per cell are necessary to get away from an ordered state and create the opportunity to produce a disordered state. As Fig. 1 shows, the three-particle analytical theory did not show a disordered state; neither does the four-particle system worked out on the computer.

The four-particle system is the smallest cubic unit of a face-centered lattice. Since the system is so small, it was necessary in the calculation to anticipate collisions with a particle and also with its periodic continuations in neighboring boxes. This causes such small systems to be not nearly so fast to run on the computers as one might at first think. Nevertheless, quite long runs were made without finding a transition to a fluid-like state. However, a comparison of the positions of particles initially and after some collisions had taken place, showed that particles had switched positions for values of $v/v_0 \geq 1.80$ while they were still in their original order for $v/v_0 \leq 1.7-$ at the end of the run. This means that although particles are free to interchange, it is not possible to create any disorder in the system, because after the interchange the particles are again in a regular arrangement near lattice positions. The value of v/v_0 at which interchange can first take place is a reasonable one. Interchange can first occur roughly when two particles can slip past each other along the diagonal of the unit cube after a third one is placed on the corner. This means that the diagonal length $(\sqrt{3})$ has to be equal to 3σ or $v/v_0 = 1.837$. By cooperative motion of three particles a rotation of the three (equivalent to an interchange) can occur at slightly higher densities in agreement with the facts.

For systems containing eight or more particles the two-state behavior was obtained, though with eight-particle systems the fluid state was reached in only a few cases, and then after rather long runs. The eight-particle system consisted of two unit cubes containing four particles each placed next to each other. The resulting periodic space consisted of rectangular parallelopipeds. Similarly for the 16-particle system two of the eight-particle cells were placed next to each other. The 32-particle system again has a cubic cell when two of these 16-particle cells are combined. Figure 1 shows that the difference in the pressure for the two states is larger for the smaller systems. An explanation of why the fluid pressure is higher for the smaller system might be that when these systems get into the disordered state it is impossible to establish the proper local order. Because for the eight- and 16-particle systems the nearest neighbors are not independent, it is not possible to relax the position of one neighbor if the other neighbor is in a favorable position. In other words, there is
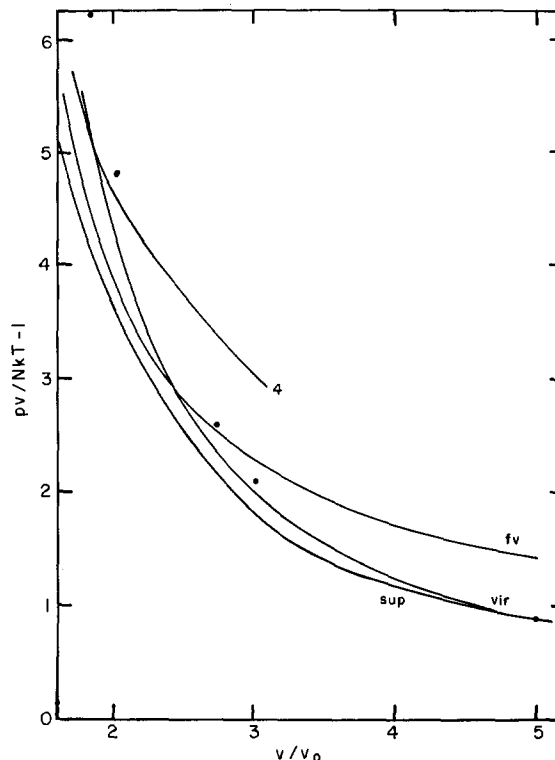

FIG. 2. Equation of state in the low-density region. The symbols labeling the curve mean: sup=superposition theory, vir=five-term virial expansion, fv=free-volume theory, 4=four-particle results, and the dots refer to the machine calculations for systems with 32 or more particles.

order among the correlated neighbors but the system overall is more jammed up than in larger systems because less flexibility is available. This jamming causes a higher pressure.[11] The very same reason caused a lower pressure in the solid branch. Less flexibility in the solid phase meant that the correlated neighbors were always the same distance apart so that if a particle collides with one member of a correlated set it will certainly be far away from some of the others. This effect was described previously as an inhibition of fluctuation in cell size.

(B) Low Densities

Figure 2 compares the molecular dynamics results with various analytical theories in the dense-gas region. The dots refer to the results for larger systems. The free-volume theory (labeled fv) is just not applicable in this region and results in pressures which are too high. Because the curves for small systems cross the curve for larger systems at different densities it misleadingly appears that the four-particle theory gives a worse result than the two-particle theory at low densities. The four-particle theory is probably in better

[11] See the next paragraph which explains the same phenomena in an equivalent way, namely, the inability of the system to form clusters.

TABLE XIV. Excess entropy of a fluid of rigid spheres, S^E/Nk, as a function of density.

v/v_0	Sup	Present	fv
8.38	0.03	0.03	1.36
4.74	0.11	0.10	1.81
3.48	0.23	0.21	2.16
2.83	0.37	0.36	2.45
2.42	0.56	0.55	2.73
2.15	0.76	0.77	2.98
1.94	1.00	1.04	3.24
1.78	1.23	1.35	3.49
1.64	1.49	1.76	3.77
1.53	1.77	2.21	4.05

agreement with the large-system results than the "smeared" free-volume theory at still lower densities, but may not be any better than the "average" free volume theory[9] which also gives too high a pressure in this region ($v/v_0 > 2.5$). The reason that the pressure is now higher than the more accurate results while in the solid region it was lower, can be restated in the following manner. In the fluid region hard spheres like to cluster so as to have as large as possible an attractive potential of average force. When two spheres are close together this effective attractive potential arises from the geometric consideration that there are more collisions forcing the two spheres together than forcing them apart. The cell theory prevents this clustering by confining the neighboring particles to their lattice positions; the effective attractive potential is hence less and the pressure higher.

The superposition theory of Kirkwood[12] treats the distribution of particles in a much more satisfactory manner, as can be seen by the better results in Fig. 2. (The curve labeled sup) In fact, it was the prediction of the superposition theory[13] that hard spheres have a solid-fluid-like phase transition at a v/v_0 of about 1.5 that lead originally to this investigation. That something unusual happens there is demonstrated in this report. We hope in a later report to make a more detailed comparison of the superposition theory with the present results for both the pair and triplet distribution function. This allows a direct checking of the validity of the Kirkwood approximation. It can be anticipated that the pair and triplet distribution functions compare almost quantitatively but that some finer details are left out in the superposition approximation. This can be ascribed to the fact[14] that the superposition approximation is equivalent to leaving out some of the highly linked cluster diagrams in the rigorous Mayer cluster expansion. It is because of these omitted terms that the pressure calculated from the theory for hard spheres is too low. These highly linked diagrams become relatively more important at high densities, so

that at lower densities the theory is quantitatively correct. Unfortunately, however, in the interesting liquid-density region the theory is only semiquantitative, but still the best analytic theory available.

To carry the theory logically one step further by making the superposition approximation in the space of four molecules (the free-volume theory carries it out in the space of only two molecules[15]) is a formidable mathematical problem. Even if this were done, as the previous discussion showed, it would not yet lead to quantitative results. In order to get quantitative results the superposition approximation would have to be made in the space of 20 or so molecules. Even a solution of the equation resulting from the superposition approximation with four particles would require extensive use of computers, so it was felt best to try the present calculational approach to learn more about what is ultimately required of an analytical description of the classical many-body problem.

The study of the entropy clearly shows the superiority of the superposition theory over the free-volume theory. Table XIV makes such a comparison of the excess entropy, S^E, defined as follows,

$$S = -Nk \ln p + S^*(T) + S^E,$$

where

$$S^E/Nk = \int_\infty^{v/v_0} [(pv/NkT) - 1](v_0/v) d(v/v_0)$$

$$+ \ln(pv/NkT), \quad (4)$$

and

$$S^*(T) = \lim_{p \to 0} [S + Nk \ln p].$$

S^E is the excess entropy at constant pressure over that of an ideal gas. The free-volume theory gives much too low an entropy because the particles are ordered on lattice positions. However, when the free-volume theory is considered from the point view of a two-particle periodic boundary-condition problem then the entropy is considerably raised even though the equation of state is the same for the body-centered cubic lattice. We hope to discuss this more fully in a later paper. The excess entropy calculated from the superposition theory is in quite good agreement with the present results. Only at the highest density does any discrepancy appear.

Figure 2 also shows the pressure resulting from the five term virial expansion (labeled vir)

$$(pv/NkT) - 1 = (b/v) + 0.625(b/v)^2 + 0.287(b/v)^3$$

$$+ 0.115(b/v).^4 \quad (5)$$

At low density perfect agreement with this expression is obtained as it must be (see Table X). At higher densities the expansion no longer converges; however further terms are hard to evaluate analytically. These further terms are also hard to get from the numerical results

[12] J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).
[13] J. G. Kirkwood, E. K. Maun, and B. J. Alder, J. Chem. Phys. 18, 1040 (1950).
[14] B. R. A. Nijboer and L. van Hove, Phys. Rev. 85, 777 (1952).
[15] J. G. Kirkwood, J. Chem. Phys. 18, 380 (1950).

because no effort has been made to obtain precise and more data points in the intermediate-density region. The precision required of the data is very high in order to say with confidence what the next virial coefficients are going to be. All that can be said with confidence with the available results is that the sixth and seventh virial coefficients are positive. The data can be empirically fitted up to the transition density adding a term $0.079(b/v)^5$ to Eq. (5). Only slight improvement can be obtained over this fit by adding two terms $0.046(b/v)^5 + 0.02(b/v)^6$ These terms may not have any relation to the theoretical higher virial coefficients.

The fact that all the known virial coefficients are positive has theoretical impact on the question of the divergence of the virial expansion for hard spheres. If they were all positive it would be of course impossible to get a flat pressure volume region or a van der Waals loop indicative of a first-order phase transition. If there then is a phase transition, with all the coefficients positive, the series either diverges at the phase transition or, what appears more likely, the series continues into a metastable fluid region. This region can be artifically generated on the calculator and will be discussed in the next section. The earlier Monte Carlo results[16] had indicated that some of the higher virial
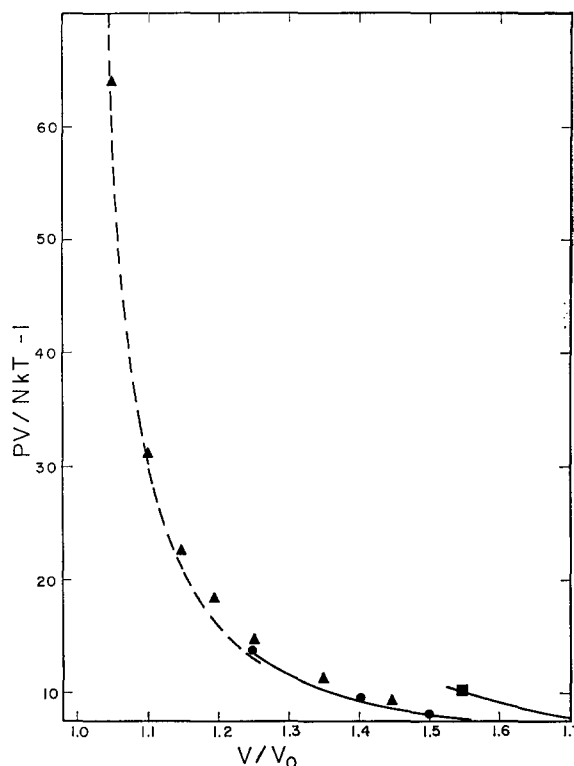

FIG. 4. Equation of state in the high-density region. The solid lines represent the data for the 32-particle system in the solid and fluid branches. The dashed line is calculated by the free-volume theory in the region where it is accurate. The triangles represent the equation of state for 32 particles in the extended fluid branch when that data has been corrected by subtracting an empirically determined constant from v/v_0 (Table IX). The dots represent the equation of state for 31 particles when their close-packed volume has been corrected to that of 32 particles. The square represents an uncorrected point on the fluid branch of the 31-particle system.

coefficients are negative. This was in error due to insufficiently long runs.[4]

(C) High-Density Region

The high-density results for the equation of state are shown in Fig. 3. As mentioned before, there is a systematic trend in the pressure with the number of particles (solid lines) but the differences vanish at high enough densities. The 96-particle results are plotted explicitly although they do not significantly differ from the other large-system results. This is of interest because the 96-particle system was placed into a hexagonal closed-packed lattice with a rectangular parallelopiped box while all the other large systems were in a cubic box containing a face-centered crystal. These two lattices differ only in the arrangement of the third nearest neighbors of a particle. As has already been seen, these third neighbors do not significantly affect the results and hence it is not surprising that the hexagonal and face-centered lattice results agree over the entire density region.

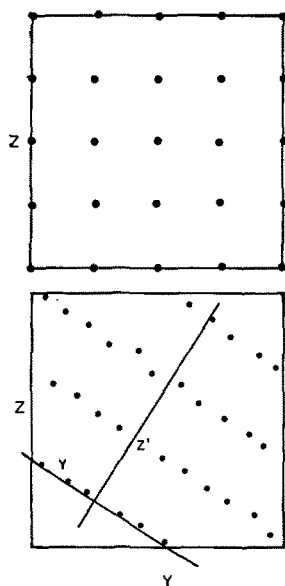The dotted curves in Fig. 3 demonstrate that in the

FIG. 3. Equation of state in the high-density region. The curves are labeled by the number of particles which were used. For 32 particles both the solid and fluid branch are graphed. The significance of the dotted lines is that these curves were obtained by using unusual initial configurations and hence these curves do not represent a usual equilibrium state of the system.

[16] M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. 22, 881 (1954).

FIG. 5. Upper graph: The configuration of a 32-particle system in the yz projection for a face-centered lattice. Each dot represents two particles on top of each other. Lower graph: The configuration of the 32-particle system at the end of the run in the extended fluid branch. The $y'z'$ axis refers to the projection graphed in Fig. 6.

solid region for these small systems the results depend on the number of particles studied as well as their initial configuration. In the fluid phase these factors did not influence the pressure, as the results for 100 particles in Table X show. The 100 particles were initially placed in some random configuration, but one which allowed the spheres to be quite tightly packed, so that quite high densities could be achieved. The density could then be lowered by shrinking the diameter of the spheres, keeping the cubic box the same dimensions. At high densities the system could not rearrange itself to a perfect crystal as the higher pressure in Fig. 3 indicates. Even if this system were able to unjam itself it could not form a perfect crystal but only one with eight holes, since that is required by the periodic boundary conditions for a face-centered cubic lattice. However, when the density was lowered to that of a fluid, the system was able to rearrange itself to obtain the proper local order.

A system with an artifically introduced single hole was then set up to study its behavior in this region. The resultant 31-particle pressure is shown in Fig. 3, and it is again higher in the solid region, but not as high as the 100-particle system since it is much more ordered. However, again, as the square point in Fig. 4 shows, in the fluid region the pressure is the same as that of a 32-particle system. The results on the solid side can, however, be understood if it is considered that the hole is just an inaccessible region to the system, in other words, the 31-particle system behaves like a 32-particle system. Thus, if the close-packed volume, v_0, is converted to that of a 32-particle system, the dots in

Fig. 4 result, yielding perfect agreement in the pressure with that of the perfect crystal. Actually the agreement should not be perfect since the particles surrounding the hole have a slightly larger volume accessible to them, so that the pressure should be slightly smaller than that of a perfect crystal. At high densities of the solid even this difference should disappear, since the particles surrounding the hole are completely locked in. Within the accuracy of the present results this difference could not be picked up even at the lowest solid densities.

It is of interest to check whether this hole has moved during a run from the point of view of diffusion theory. A mechanism of diffusion in solids is by means of a particle moving into the hole leaving a hole in its stead. Even if this did not take place it would not alter the above argument for changing v_0. An examination of the positions of the particles at the end of the rather short run at the lowest solid density showed that this phenomenon had not occurred. This is not surprising since such a motion would involve a highly cooperative movement of the particles surrounding the hole. Furthermore, the few particles used seriously restrict such fluctuations.

The extension of the fluid branch to solid volumes for 32 particles was accomplished by still other means. The dashed curve labeled 32F in Fig. 3 was generated by a gradual compression of a fluid 32-particle system. This gradual compression was achieved by a slow swelling of the particles, keeping the volume of the system unchanged. The striking feature of these results is that no two-state behavior is found and that a smooth extension of the fluid branch can be generated at much higher pressures than the crystal branch. The fact that a two-state behavior was not observed is not surprising since at the lowest compressed density studied, $v/v_0 = 1.4948$ (see Table IX), it was also not possible to effect the transition from the solid to the fluid branch. The reverse transition also requires a large fluctuation which is not very probable under these jammed conditions. The liquid and solid regions of phase space have thus been isolated, if not at this density certainly at slightly higher densities. No matter how long the calculator would run, no transition between the two states is possible for these finite systems.

The higher pressure for the extended fluid curve compared to the 100-particle system indicates that at a given density the 100 particles are less jammed up. This is because the larger system has more voids (the equivalent of eight holes) which are at least partially accessible to the particles. The uniqueness of the extended fluid branch has not been investigated, since only a single run has been made. It might be expected that there exists a fairly narrow band of curves extending the fluid branch depending on from what particular configuration the compression was started. The only relevant data on this was obtained by the Monte Carlo
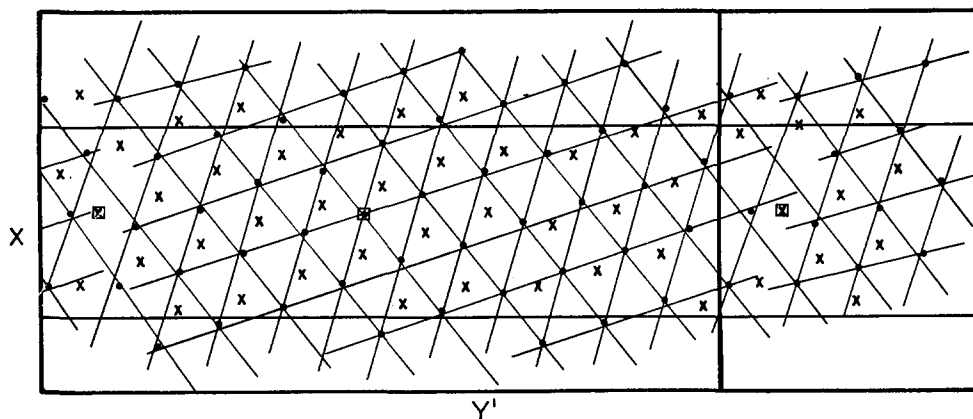
FIG. 6. The xy' projection of the positions of the 32-particle system referred to in Fig. 5. The horizontal and vertical lines refer to the repeat planes due to the periodic boundary conditions. The crosshatched lines connect positions of atoms in the lower layer (dots). The crosses represent positions of atoms in the layer above. The squares represent location of atoms which are missing.

method[17] using a similar procedure for 32 particles. The curves do differ in some detail but are over-all in substantial agreement.

Since it was possible to understand the behavior of the 31-particle system by correcting its close-packed volume, it should be possible to do the same thing for these other disordered systems except that the close-packed volume has to be found empirically. In other words, a free-volume type of theory should still work since the particles are localized, but the average free-volume per particle cannot be calculated from a crystal lattice model. The free volume could be calculated if the volume taken up by the imperfections were known. The close-packed volume for the extended fluid branch system was determined from the point at which the pressure became infinite (about $v/v_0 = 1.1506$). If the pressure is plotted against $v/v_0 - 0.1506$ (Table IX and Fig. 4) good agreement with the crystal branch is obtained in the region where the free-volume theory is accurate.

An examination of the positions of the particles at the highest density studied on the extended fluid branch reveals that they are not in a completely disordered array but rather in a slightly imperfect hexagonal close-packed lattice. Figure 5 compares the positions projected in the yz plane of a perfect face-centered cubic crystal (upper graph) to that found at the end of the compression run (lower graph). It is obvious that on an over-all basis the lower graph shows quite a bit of order. However, where the z' symbol is located on the graph an atom is missing, and in the plane above and below that hole some disorder exists. The projection in the xy' plane given in Fig. 6 makes this clearer. Two planes of particles each perpendicular to the z' axis are plotted. The missing atom is indicated by a square. The crystal does not repeat every cube in the y' direction but every three cubes as indicated by the heavy vertical line. However, in the x direction the repetition distance is the usual one of every cube as indicated by the horizon-

tal lines. The crossed lines connecting the particles in one layer are drawn to emphasize the nearly hexagonal nature of the lattice. The crosses for the location of the particles in the layer above fall near the center of the triangles formed by the crosshatched lines as they should for a hexagonal lattice. There appears to be one fault in the crystal which might be described as a slip in addition to the hole. It is associated with the hole in the plane below (on the very left of Fig. 6 and repeated periodically just to the right of the heavy vertical line for purposes of clearer demonstration). The particles above the hole are quite regularly arranged as shown in the middle of the box in Fig. 6. The slip also appears very clearly again (about $\frac{3}{4}$ over in the box) in the upper layer of particles marked by crosses.

Undoubtedly these same imperfections would not appear each time such a compression was tried, as mentioned earlier. However, there are only a limited number of ways to have imperfections in such small systems. What would happen if the same thing were tried on larger systems is pure speculation. Very likely, however, a similar slightly disordered system would result if the fluid state compressed so fast that not enough time were allowed to reach the equilibrium state at each density. This behavior is quite analogous to cooling a liquid so fast that a glass forms. A glass is also believed to give a high degree of local order. Larger systems can, of course, have more complicated imperfections; however, it is the instantaneous local arrangements in the fluid that primarily determines what sort of faults are frozen in.

(D) Collision Rate

The results for the collision rate relative to the collision rate at infinite dilution for the various systems are given in Tables I through IX, and some of the results are graphically presented in Fig. 7. The collision rate ratio generally conforms to the behavior of the equation of state. Thus, as Fig. 7 shows, the collision rates for systems of less than 96 particles are low on the

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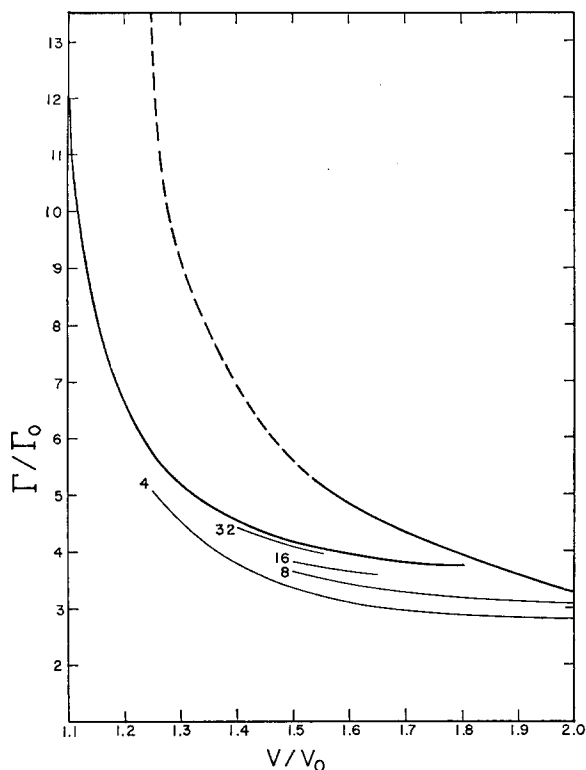[17] W. W. Wood, (private communication).

FIG. 7. Collision rate relative to the Boltzmann collision rate as a function of v/v_0. The fluid branch is represented by the upper curve for systems of 32 particles and larger. The dashed curve represents the extended fluid branch. The solid branch is represented by the heavy curve for systems of 96 particles and larger, and by the labeled curves for smaller systems.

FIG. 9. Dependence of the equation of state on the number of particles at higher density. Curves A, B, C, D, and E refer to, respectively, $v/v_0 = 1.4$, 1.5, 1.525, 1.55, and 1.65 in the solid branch.

ratio of the experimental value of Γ/Γ_0 to the theoretical one. The theoretical one is determined by the use of the equation of state as obtained by the computer work for the same system. A striking confirmation of the Enskog theory of collision rates is obtained for systems larger than 32 particles, which shows that this ratio is unity within statistical significance at all densities. This in turn implies that the molecular chaos approximation made by the Enskog theory is a valid one insofar as the collision rate is concerned. The validity of this assumption[7] at solid densities is certainly doubtful. The result then probably means that the collision rate is insensitive to this approximation. However, when artificial velocity correlations are introduced among the nearest neighbors of a particle as in small systems, the experimental to theoretical collision rate does reflect this correlation. This ratio is less than unity and the deviation is the largest for the smallest system. It is remarkable that this deviation is independent of density within the accuracy of the results; although the eight-

solid branch just as the equation of state is. The collision rates for eight-particle systems in the fluid branch seem unusually low (Table II) although the pressures are high.

As Eq. (2) shows, the collision rate ratio is purely a function of the equation of state according to the theory of Enskog. The R column in Tables I through IX is the
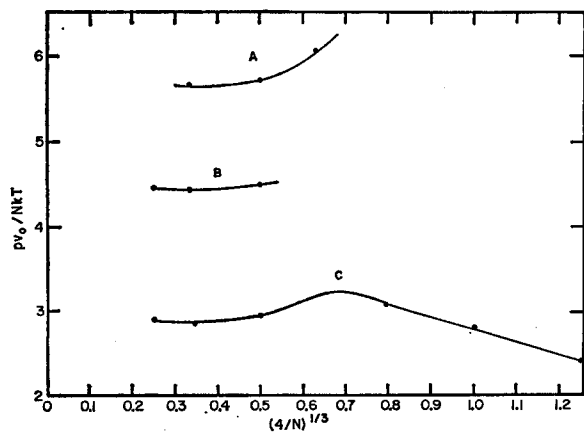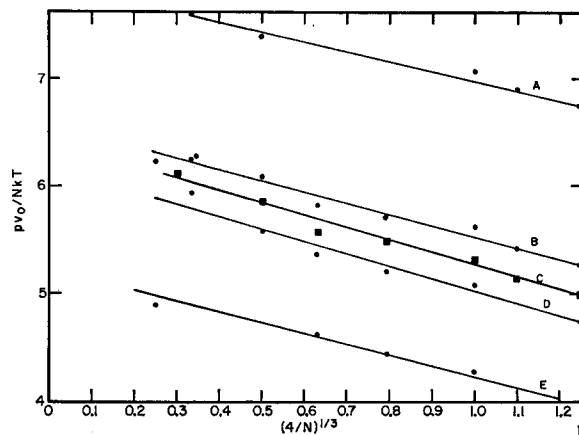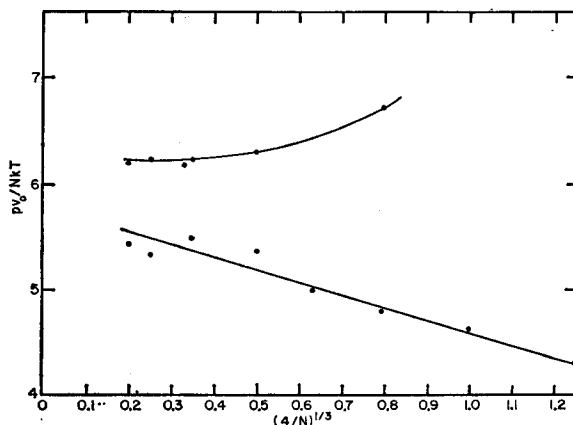

FIG. 8. Dependence of the equation of state on the number of particles at lower density. Curve A refers to $v/v_0 = 1.65$, curve B to $v/v_0 = 1.7678$ and curve C to $v/v_0 = 2.0$ in the fluid branch.

FIG. 10. Dependence of the equation of state on the number of particles for $v/v_0 = 1.60$ in both the fluid and solid branch.

particle case is a spurious exception, the deviation was much larger in the fluid phase than in the solid phase.

(E) Dependence of the Results on the Number of Particles

Although we intend to discuss the dependence of the results on the number of particles more fully when the study of larger systems in both two and three dimensions is completed, Figs. 8–10 are presented to demonstrate the dependence found so far which was previously discussed qualitatively. The results are plotted against $(4/N)^{\frac{1}{3}}$. The factor four is of not much significance except that it normalizes the results to the smallest cubic cell that can generate a face-centered lattice. The choice of the reciprocal one-third power of the number of particles which is characteristic of the linear dimensions of the system has been chosen empirically as the power which makes the graphs most nearly linear.

It is only at low density that it has been possible to investigate theoretically the dependence of the results on the number of particles. The first few virial coefficients for an infinite system (subscript ∞) of hard spheres are related to those of a finite periodic system[18] (subscript N) by

$$B_N = B_\infty(1 - 1/N)$$

$$C_N = C_\infty[1 + (1/5N) - (6/5N^2)],$$

where B and C are the second and third virial coefficients. For one particle these expressions correctly reduce the virial coefficients to zero and for a system as small as 32 particles the corrections are already small. For dense gas systems the results are given in Fig. 8 and show that the pressure first increases as N increases and then decreases very slightly (curve C). At higher densities, but still in the fluid region, the pressure decreases monotonically as N increases (curves A and B).

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[18] I. Oppenheim and P. Mazur, Physica 23, 197 (1957).

All curves show that the results have become pretty independent of N for the larger systems.

Figure 9 shows the dependence of the pressure on N for the solid branch at various densities. The lines drawn are the best ones to fit the data and show that the pressure increases as the N increases. An extrapolation to an infinite system along these straight lines is, however, not justified. At the densities where the most extensive runs were made and the largest systems were studied (curve B) and lower curve in Fig. 10, the results appear within the accuracy of the results to be independent of N for larger systems justifying the previous discussions. Figure 10 plots the dependence of the results on N for both the fluid and solid branch of a system and shows that even under the worst condition of extrapolation of the solid branch the pressure difference between the two branches does not vanish.

CONCLUSION

It appears that systems as small as 100 particles are sufficient to describe accurately the equilibrium behavior in the fluid region of hard spheres. In the two-state region four particles are insufficient to establish both states and 500 particles are insufficient to make the two states coexist. In the solid region for these small systems the initial state of the system and the number of particles must be selected so as to achieve the lowest free energy.

The Enskog theory for the collision rate is valid over the entire density region, while the free-volume theory is valid only at high densities and the superposition theory at low densities. In the intermediate-density region analytical theories for the equation of state have to take into account higher-order correlations between the particles.