

Preliminary Results from a Recalculation of the Monte Carlo Equation of State of Hard Spheres

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the early adsorption of CO on W is a cooperative phenomenon.

Figure 2 also shows the work function as a function of coverage. Φ is seen to go through a maximum for $N_m \approx N_w$ and changes only slightly for coverages greater than N_w . We can compute an effective electric dipole moment, μ , for the adsorbed CO molecule from the formula $\Delta\Phi = 4\pi\mu N_m$. For N_m less than N_w we find $\mu \approx 0.72$ Debye units (1 D.U. = 10^{-18} esu cm) with the positive charge toward the W surface. For greater coverages μ has the opposite sign and appears to be less than 0.1 D.U., approximately. The permanent electric dipole moment of a free CO molecule has been found³ to be 0.10 D.U.

The maximum number of CO molecules that could be chemisorbed was 7.5×10^{14} cm⁻², or about $2N_w$. The corresponding value of Φ is approximately 5.4 eV and Φ for the clean surface is 4.54 eV.

These experiments will be discussed in greater detail in a forthcoming publication. We wish to thank Mr. L. V. Medford for his help in obtaining these results.

¹ J. A. Becker and C. D. Hartman, *J. Phys. Chem.* **57**, 157 (1953).

² J. Eisinger (previous letter).

³ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

Preliminary Results from a Recalculation of the Monte Carlo Equation of State of Hard Spheres*

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THE disagreement between the hard sphere equation of state obtained by Rosenbluth and Rosenbluth¹ using the Monte Carlo method² and that reported in the accompanying paper by Alder and Wainwright³ using detailed molecular dynamics led us to repeat the Monte Carlo investigation. Preliminary results for 32 molecules with cubical periodic boundary conditions^{1,2} are shown in Fig. 1 along with Alder and Wainwright's³ results with which there is rather good agreement. The previous Monte Carlo calculations¹ at reduced volumes v/v_0 (v_0 = close-packed volume) from about 1.5 to 2.0 are in error due to inadequate chain length to detect the behavior described below; the difficulty was aggravated by the concentration of effort on the system of 256 molecules, which requires considerably longer computing time.

The present calculations have been made on IBM Type 704 calculators and use the same method as the earlier work^{1,2} except that the molecules are "moved" in random rather than ordered sequence.⁴

The equation of state is given by $pv/kT = 1 - 2\pi\sqrt{2}v_0g(\sigma)/3v$, where $g(\sigma)$ is the radial distribution function at the collision diameter σ . For v/v_0 between

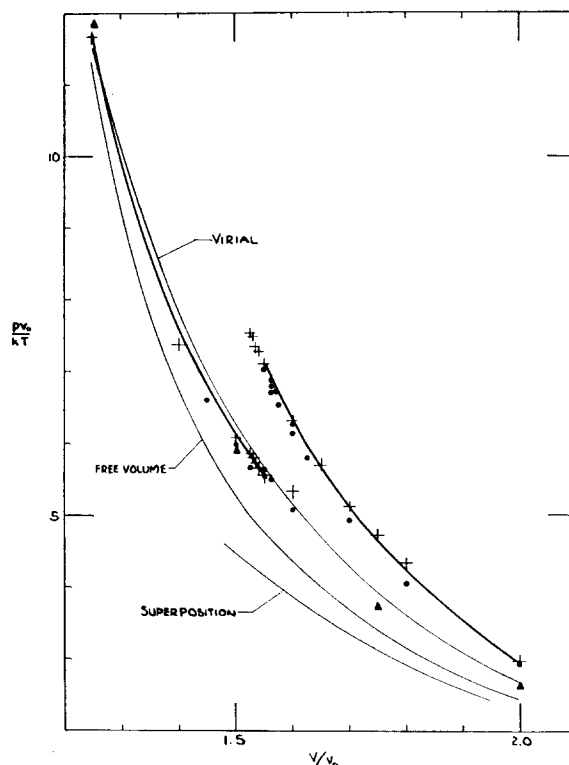


FIG. 1. The equation of state of hard spheres. The heavy solid curve represents Alder and Wainwright's³ 108 molecule results; +, their 32 molecule results. ● and ▲ represent the present and previous¹ Monte Carlo results. Virial = five term virial expression.¹ Superposition = reference 5.

1.55 and 1.6 the Markov chains developed by the Monte Carlo method indicate that the set of configuration states is divided into two classes characterized by different central values of $g(\sigma)$. Transitions between classes take place only rarely; the Markov chains display configurational relaxation. A typical chain started from a regular f.c.c. lattice fluctuates for a variable length of time (which tends to increase with density) in the low $g(\sigma)$ class, then jumps rather suddenly to the high $g(\sigma)$ class. Calculator periods as long as 10–30 hours may sample only 0–3 such interclass transitions, so that the over-all canonical average is very poorly estimated. As a consequence we have averaged the low and high $g(\sigma)$ classes separately to obtain two values of pv_0/kT at each v/v_0 in this range, as shown in Fig. 1. The presence of only two classes of states is indicated by agreement of $g(\sigma)$ values obtained from different chains at the same v/v_0 , and also those obtained when a single chain re-enters a class; furthermore, the pv_0/kT values attributed to the two classes in Fig. 1 vary reasonably smoothly with v/v_0 .

The manner in which complete canonical averaging would connect the two separate, overlapping branches of the equation of state is at present undetermined. A first-order phase transition is, however, strongly suggested. Of some interest in this connection is the fact that the high $g(\sigma)$ states seem to be characterized by

relatively free diffusion, while in the low $g(\sigma)$ states diffusion is much restricted.

The conjecture¹ that some high-order virial coefficients might be negative is not necessarily supported by the present results, since only to the left of the apparent transition do the latter give lower pressures than the five-term virial expression.

Some further investigation for both 32 molecule and larger systems will be made on the present calculators, but a satisfactory determination of the detailed behavior in the apparent transition region will require higher speed equipment. The possibility that a similar phenomenon for hard spheres in two dimensions may have been missed in the original Monte Carlo calculations¹ will also be investigated.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

¹ M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.* **22**, 881 (1954).

² Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller, *J. Chem. Phys.* **21**, 1087 (1953).

³ B. J. Alder and T. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957).

⁴ W. W. Wood and F. R. Parker, *J. Chem. Phys.* **27**, 720 (1957). This paper discusses the Monte Carlo method in some detail, as well as giving computational results for Lennard-Jones molecules.

⁵ Kirkwood, Maun, and Alder, *J. Chem. Phys.* **18**, 1040 (1950).

Phase Transition for a Hard Sphere System

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A CALCULATION of molecular dynamic motion has been designed principally to study the relaxations accompanying various nonequilibrium phenomena. The method consists of solving exactly (to the number of significant figures carried) the simultaneous classical equations of motion of several hundred particles by means of fast electronic computers. Some of the details as they relate to hard spheres and to particles having square well potentials of attraction have been described.^{1,2} The method has been used also to calculate equilibrium properties, particularly the equation of state of hard spheres where differences with previous Monte Carlo³ results appeared.

The calculation treats a system of particles in a rectangular box with periodic boundary conditions.⁴ Initially, the particles are in an ordered lattice with velocities of equal magnitude but with random orientations. After a very short initial run^{1,2} the system reached the Maxwell-Boltzmann velocity distribution so that the pressure could thereafter be evaluated directly by means of the virial theorem, that is by the rate of change of the momentum of the colliding particles.^{1,2} The pressure has also been evaluated from the radial distribution function.⁵ Agreement between the two methods is within the accuracy of the calculation.

A 32-particle system in a cube and initially in a face-centered cubic lattice proceeded at about 300 collisions an hour on the UNIVAC. For comparison a 96-particle system in a rectangular box and initially in a hexagonal arrangement has been calculated, however only at high densities so far. No differences in the pressures can be detected. It became apparent that some long runs were necessary at intermediate densities, accordingly the IBM-704 was utilized where, for 32 particles, an hour is required for 7000 collisions. Larger systems of 108, 256, and 500 particles can also conveniently be handled; in an hour 2000, 1000, and 500 collisions, respectively, can be calculated. The results for 256 and 500 particles are not now presented due to inadequate statistics.

The equation of state shown in Fig. 1 of the accompanying paper⁶ for 32 and 108 particles is for the intermediate region of density, where disagreement was found with the previous Monte Carlo results. The volume, v , is given relative to the volume of close packing, v_0 . Plotted also are the more extended Monte Carlo results; the agreement between these three systems is within the present accuracy of the pressure determination. This agreement provides an interesting confirmation of the postulates of statistical mechanics for this system.

Figure 1 of the accompanying paper shows two separate and overlapping branches. In the overlapping region the system can, at a given density, exist in two states with considerably different pressures. As the calculation proceeds the pressure is seen to jump suddenly from one level to the other. A study of the positions of the particles reveals that as long as the system stays on the lower branch of the curve the particles are all confined to the narrow region in space determined by their neighbors, while on the upper branch of the curve the particles have acquired enough freedom to exchange with the surrounding particles. Since the spheres are originally in ordered positions, the system starts out on the lower branch; the first jump to the upper branch can require very many collisions. The trend, as expected, is that at higher densities more collisions are necessary for the first transition, however, there are large deviations. At $v/v_0=1.60$, 5000 collisions were required; at 1.55, 25 000; while at 1.54 only 400; at 1.535, 7000; at 1.53, 75 000; and at 1.525, 95 000. Runs in excess of 200 000 collisions at v/v_0 of 1.55 and 1.53 have not shown any return to the lower branch, while at 1.525 the system has returned several times, however only for relatively few collisions. The lowest density at which the system did not jump to the upper curve is at 1.50, however the run extends only to 50 000 collisions and at that density it might take very many collisions before the appropriate fluctuation occurs for a molecule to escape from its neighborhood. For comparison, the first jump for 108 particles occurred for $v/v_0=1.55$ and 1.60 at about 2000 collisions. This is fewer collisions per particle than for the smaller system and is indicative of larger possible density fluctuations in larger systems. Apparently, the