

# Phase Transition for a Hard Sphere System

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

The conjecture<sup>1</sup> 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 calculations<sup>1</sup> will also be investigated.

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

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

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

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

<sup>4</sup> 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.

<sup>5</sup> 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.<sup>1,2</sup> The method has been used also to calculate equilibrium properties, particularly the equation of state of hard spheres where differences with previous Monte Carlo<sup>3</sup> results appeared.

The calculation treats a system of particles in a rectangular box with periodic boundary conditions.<sup>4</sup> Initially, the particles are in an ordered lattice with velocities of equal magnitude but with random orientations. After a very short initial run<sup>1,2</sup> 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.<sup>1,2</sup> The pressure has also been evaluated from the radial distribution function.<sup>5</sup> 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 paper<sup>6</sup> 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

reason these jumps occur rather than the system's taking on some mean pressure is that it is not possible to have the two states simultaneously in equilibrium in such a small sample. The fact that the 108 and 32 particles systems give identical branches indicates that the effect of the periodic boundary is not serious even for 32 particles. It can be shown that the first few virial coefficients for a finite system of  $N$  particles with periodic boundary conditions have corrections of order  $1/N$ .

Clearly, it is presently impossible to connect these two branches, though it may be possible to do this with a faster machine by averaging the pressure over a very long run which includes many jumps instead of averaging the branches separately. In the transition region the effect of the number of particles might appear in the average time the system spends in each branch, such that for an infinite system a horizontal line might appear, characteristic of the first-order transition which is strongly indicated by the present results. Such a transition was suggested earlier by the superposition theory at a  $v/v_0 = 1.48$ .

We gratefully acknowledge Mrs. Shirley Campbell's and Mary Shephard's help with the coding problems.

<sup>1</sup> Proceedings of the International Union of Pure and Applied Physics on "Statistical mechanical theory of transport properties," Brussels (1956).

<sup>2</sup> Symposium on the "Many body problem" in New York (1957).

<sup>3</sup> M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.* **22**, 881 (1954).

<sup>4</sup> Alder, Frankel, and Levinson, *J. Chem. Phys.* **23**, 417 (1955).

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

<sup>6</sup> W. W. Wood and J. D. Jacobson, *J. Chem. Phys.* **27**, 1207 (1957).

## Excitation of Nitric Oxide by Active Nitrogen

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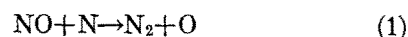
(Received August 5, 1957)

THE nitrogen afterglow and the composition of active nitrogen continue to engage the interest of many investigators. Recent mass-spectrometer studies<sup>1,2</sup> have suggested a reasonable explanation of the origin of the glow and have shown ground-state <sup>4</sup>S atoms to be the major though not the only reactive species.<sup>3</sup> It has long been known that the addition of a little nitric oxide to active nitrogen produces a pronounced change in the emission spectrum and brings about a change of colors from orange yellow through pink and purplish blue to colorless and then to the greenish-yellow air afterglow as increasing amounts of NO are added to the active nitrogen. In the pink and blue stages the NO- $\beta$ - and  $\gamma$ -band systems are emitted strongly.<sup>4</sup>

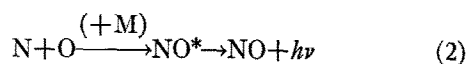
The question of the source of excited NO molecules is of some interest. If the added NO is raised to the  $A^2\Sigma$

and  $B^2\Pi$  states from which it emits the  $\beta$  and  $\gamma$  systems it seems surprising that the pink or blue color is present immediately at the point of mixing active  $N_2$  and NO, but persists over a long distance in a moderately fast flow system as does the nitrogen afterglow. Since addition of a somewhat greater amount of NO extinguishes the glow altogether it seems reasonable to assume that in the blue stage some active  $N_2$  is still present. But then the presence of NO and active  $N_2$  together for a considerable time seems puzzling.

Alternately one may assume NO to react very rapidly with active  $N_2$ , mostly via



and to be completely destroyed as long as active  $N_2$  is in excess. The NO emission would then arise from recombination processes such as



and the steady-state concentration of ground state NO could be quite small.

To decide which explanation is correct, NO-emission spectra were obtained from active  $N_2$  with added  $N^{14}O$  and with added  $N^{15}O$ . The gas streams were mixed just before entry into a 10-cm quartz cell and the radiation focused on the slit of a Leeds & Northrup recording grating spectrometer which has a resolution of about 60 000 in the second order in the uv.  $N^{15}O$  was prepared from  $KN^{15}O_3$  by the standard nitrometer method. Active nitrogen was produced by an electrodeless microwave discharge (Raytheon Microtherm Model CMD-4) of 2400 mc frequency and about 50 to 100 w microwave power output. Purified Matheson nitrogen was used. Calibration runs of the emission spectra of discharges in  $N^{14}O$  and  $N^{15}O$  showed the second positive system of  $N_2$ , the  $\gamma$  system of NO, and the  $N_2^+$  system strongly. The isotope shifts of the band heads were measured and calculated.<sup>5</sup> Agreement to 0.1 Å was consistently obtained. The  $N^{15}O$  was of high isotopic purity (>95%  $N^{15}$ , Isomet Corporation) and  $N^{14}O$  bands were not observed in its discharge.

In the critical experiment, light from the  $N_2$  discharge was carefully shielded from the spectrometer and only the weak glow in the cell was focused on the slit. The spectra resulting from addition of  $N^{15}O$  downstream from the discharge were due to  $N^{14}O$  in every case. NO- $\beta$  bands were observed for the transitions 0-4, 1-5, 0-5, 1-6, 0-6, 0-7, 0-8, 0-9, and 0-10 as were NO- $\gamma$  bands 0-0, 0-1, 0-2, 0-3, 0-4, and 0-5. In the case of the strong  $\beta$  0-8 and 0-9 bands, the  $N^{15}O$  band heads would have been shifted 25 to 30 Å. The absence of these  $N^{15}O$  bands provided an upper limit for the relative amount of excited  $N^{15}O$  that might have been present but whose emission spectrum might have been too weak to be observed.  $N^{15}O$  bands of 1/10 to 1/20 the intensity of the  $N^{14}O$  bands should