

## Studies in Molecular Dynamics. I. General Method

B. J. Alder and T. E. Wainwright

Citation: *J. Chem. Phys.* **31**, 459 (1959); doi: 10.1063/1.1730376

View online: <http://dx.doi.org/10.1063/1.1730376>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v31/i2>

Published by the American Institute of Physics.

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT

### Instruments for advanced science

#### Gas Analysis



- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

#### Surface Science



- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

#### Plasma Diagnostics



- plasma source characterization
- etch and deposition process
- reaction kinetic studies
- analysis of neutral and radical species

#### Vacuum Analysis



- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

**HIDEN**  
ANALYTICAL

[info@hideninc.com](mailto:info@hideninc.com)  
[www.HidenAnalytical.com](http://www.HidenAnalytical.com)

CLICK to view our product catalogue



For the other compounds measured the spin-orbit coupling constants thus obtained are either unreasonably large or small.

$(\text{CH}_3\text{NH}_3)_2\text{IrCl}_6$ ,  $(\text{C}_5\text{H}_6\text{N})_2\text{IrCl}_6$  and  $(\Phi_4\text{As})_2\text{IrCl}_6$  display a rather peculiar magnetic behavior with moments considerably below the expected values over the whole temperature range investigated. No ex-

planation of this behavior will be attempted in the present paper.

#### ACKNOWLEDGMENTS

The authors wish to thank Research Corporation, University Research Council, and American Viscose Corporation for financial support of this research.

## Studies in Molecular Dynamics. I. General Method\*

B. J. ALDER AND T. E. WAINWRIGHT

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

(Received February 19, 1959)

A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computers are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

### INTRODUCTION

ONE of the great difficulties in the present day theoretical attempts to describe physical and chemical systems is the inadequate mathematical apparatus which has been available to solve the many-body problem. Thus, although the properties of an isolated molecule are well established and the elementary processes which occur when two such molecules interact are described by well-known laws, the behavior of systems of many interacting molecules cannot, in general, be dealt with theoretically in an exact way. Even a three-particle system presents great analytical difficulty. Since these difficulties are not conceptual but mathematical, high-speed computers are well suited to deal with them.

To take explicitly into account the interaction of a fairly large number of particles involves either multi-dimensional integrals or high-order differential equations. These mathematical expressions can be reduced to manageable equations for dilute systems since, in that case, the behavior of the system can be conceived of as a succession of essentially unrelated binary interactions. In the case of nondilute systems, that is, when the range of intermolecular forces is not small compared to the average intermolecular distance, analytical theories have been developed to approximate the many-body problem in various ingenious ways.

The most common scheme is to let a representative particle experience the potential of the rest of the particles held fixed in an average position. This average potential can be obtained from a definite physical model or in a self-consistent way. The next better approximation in such a scheme would be to let two molecules move in the potential of the rest of the system. This procedure and several variations of it have indeed been worked out for various physical models. However, the calculations are so complicated that it is necessary to seek numerical solutions by means of automatic computers. It is interesting to note that to calculate the actual dynamics of the many-particle system is, in some cases, not a greater problem than the calculations required for the models.

One of the aims of the exact numerical solution is to compare the results with these analytical theories. Such comparisons are more clean-cut than comparisons with experiments on natural systems because it is possible to set up artificial many-particle systems with interactions which are both simple and exactly known and for which analytical theories are relatively easy to work out. Furthermore, much more detailed information is available from calculations of this type than it is ever possible to get from real experiments. Since the detailed history of the motion of each particle is accessible, such a calculation makes it possible to check analytical theories at various critical intermediate points. Beyond determining which analytical schemes best approximate many-particle behavior,

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

these numerical calculations could conceivably be used to deduce new generalizations which are not now recognizable because of the mathematical complexities involved.

Another aim of the calculations is to study phenomena which present theories have difficulty describing because, for example, too many molecules have to be considered simultaneously. Some phase transitions fall into this class because of the rather large number of molecules which have to cooperate to form the nucleus of a new phase. The quantitative description of pure liquids also requires the considerations of several distinct representative molecules. Another type of problem for which the dynamical calculation might prove useful is one in which the number of molecules in the system is rather large but not so large that statistical methods can be used with confidence. The nucleation problem is a case in point. The stability and surface tension of the nuclei could, for example, be studied.

Many of the aforementioned advantages of the dynamical calculation also pertain to the Monte Carlo calculations which have been and are being carried out by various workers.<sup>1-3</sup> In the Monte Carlo calculation, however, the moves of the particles are artificial rather than dynamical so that only the average positions of the particles are meaningful. For this reason, only the equilibrium properties can be calculated. The dynamical calculation was, on the other hand, originally designed to study relaxation phenomena and can, in principle, be used to study transport properties generally. This is particularly desirable since the present analytical theories of transport phenomena are considerably less advanced than those dealing with equilibrium phenomena. The early applications of the method are, however, principally concerned with equilibrium situations in order to study the feasibility of the method.<sup>4-6</sup> The Monte Carlo method and also the molecular dynamics scheme are exact but subject to the limitations discussed below when comparison to real systems is made.

### LIMITATIONS

The essential limitations of the method are due to the relatively small number of particles that can be handled. The size of the system of molecules is limited by the

memory capacity and speed of the computing machines. With the best presently available computers, it has been possible to treat up to five hundred molecules. With five hundred molecules it requires about a half-hour to achieve an average of one collision per molecule, so that computing speed presently is the limiting factor rather than memory space. Computers now being planned should be able to handle ten thousand molecules in calculations which do not require very many collisions. Even that number of molecules is still small enough so that the nature of the boundaries has to be critically considered. If it is desired to represent a macroscopic system as nearly as possible with the small number of molecules which can be used, it is probably best to employ periodic boundaries, that is, to let the molecules be in a box with penetrable walls, but constrained in such a way that the number of molecules in the box remains constant. This is accomplished by causing a molecule which leaves the box through one wall to re-enter with unchanged velocity through the opposite wall. The alternative is to let the walls be reflecting. In that case, a relatively large number of the molecules (half of them in the case of a 500-molecule system) are, at any time, next to an artificial barrier, whereas, in the periodic boundary case molecules interact only with other molecules. The periodic boundary condition in molecular dynamics and the Monte Carlo method can be considered as giving rise to an infinite system made up of identical cells of a few hundred particles each, rather than the one or two particles that can be handled analytically. The difference in the virial coefficients between an infinite system and a system consisting of a finite number of molecules,  $N$ , with periodic boundary conditions can be shown theoretically to be of order  $1/N$ . Thus, for a system of a few hundred molecules the pressure can be calculated to better than one percent. For a few hundred particles in a box with hard walls, the difference would be much larger when compared to an infinite system. At high densities no such theory is available. However, in the solid phase the boundaries naturally force a particular crystalline periodic arrangement on the molecules. In the liquid and solid regions empirical tests have to be made by comparing large and small samples to estimate the seriousness of the effect of the boundary. Such studies have shown that the size of the sample in the dense region is of no more serious consequence than in the gas region except in phase transition regions.

In phase transition regions the artificial inhibition of density fluctuations caused by maintaining a constant number of molecules in the box can be serious. In a macroscopic system a transition region is characterized by two phases of different densities which exist together in equilibrium. The volume over which one of these phases extends may contain more than a few hundred molecules. Thus, for example, in a heterogeneous equilibrium between various sized crystallites and the melt, the equilibrium size distribution is seriously

<sup>1</sup> Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller, *J. Chem. Phys.* **21**, 1087 (1953); M. N. Rosenbluth and A. W. Rosenbluth, *ibid.* **22**, 881 (1954).

<sup>2</sup> Alder, Frankel, and Lewinson, *J. Chem. Phys.* **23**, 417 (1955).

<sup>3</sup> W. W. Wood and F. R. Parker, *J. Chem. Phys.* **27**, 720 (1957); W. W. Wood and J. D. Jacobson, *ibid.* **27**, 1207 (1957).

<sup>4</sup> B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957).

<sup>5</sup> T. E. Wainwright and B. J. Alder, *Nuovo cimento* **9**, Suppl. Sec. 10, 116 (1958).

<sup>6</sup> B. J. Alder and T. E. Wainwright, *Proceedings of the I.U.P.A.P. Symposium on Statistical Mechanical Theory of Transport Processes, Brussels, 1956* (Interscience Publishers, Inc., New York, to be published).

distorted since the maximum size a crystallite can have would be, say, 500 particles. Equally serious is the necessity that this 500-particle crystal solidifies not only in a given lattice type but also in a special orientation with respect to the boundary, affecting its probability of appearance. Thus the only way solids formed from a melt can differ is by a translational displacement. Evidence will be presented that in order to examine the properties of a heterogeneous system it is necessary to use many more particles than in the case of a single phase system. In the homogeneous solid region itself various lattice types can be studied to overcome the above mentioned difficulty and the one of lowest free energy determined. Examples of this have been worked out.

Although small systems can represent an infinite system remarkably well, the statistical fluctuations of any property (the pressure, for example) must be examined. From the point of view of making most efficient use of computing time, these statistical fluctuations are best reduced by averaging a large number of calculations with a small system rather than making a smaller number of calculations in a large system.

Both the Monte Carlo method and the dynamical method can have difficulty due to the slow convergence of the system to the equilibrium configuration. In the dynamical method, with presently available machines, it is practical to follow a small system of molecules for only about one millimicrosecond at low temperature (the order of a few hundred thousand collisions for a 32-particle system). It is sometimes a worry whether a system is in equilibrium or whether it is in a metastable state. This question can usually be resolved by starting the system in various initial configurations and observing whether the same final state is reached.

Still another limitation on the method which is connected with the smallness of the system, is that molecules with long-range potentials cannot be adequately studied since the field of one molecule would extend outside the periodic box. This limitation could be probably overcome by introducing approximations similar to those used in analytical theories. That is, the particles could interact properly at short range but the long-range interactions could be replaced by an average potential. A direct numerical solution of the quantum-mechanical many-body problem has not been attempted. The present calculation is restricted, in its application to real systems, to those for which perturbation theory from the classical equations is adequate.

#### DESCRIPTION OF THE METHOD

In order to follow the dynamics of a many-particle system with any sort of interaction potential, one could at any instant calculate the force on each particle by considering the influence of each of its neighbors. The trajectories could then be traced by allowing the particles to move under a constant force for a short-

time interval and then by recalculating a new force to apply for the next short-time interval, and so on. This method could also handle particles with anisotropic potentials and with rotational and other degrees of freedom, provided that classical description is adequate. The accuracy of such calculations would depend on the length of the time interval. Since it was desired in the present work to make no approximations in the calculations, a simple potential was chosen for which the force is truly constant (zero) for short-time intervals during which the particles are allowed to move. Although it is feasible to deal with realistic potentials, it entails a considerable slowing down of the calculation and involves the problem of having to cope with repulsive collisions where the forces the particles experience change very rapidly.

The most general interaction potential which has so far been used is the square-well potential,  $V$ ,

$$\begin{aligned} V &= \infty & r < \sigma_1 \\ V &= V_0 & \sigma_1 < r < \sigma_2 \\ V &= 0 & r > \sigma_2, \end{aligned}$$

where  $r$  is the magnitude of the separation of the centers of a pair of molecules and  $\sigma_1$ ,  $\sigma_2$ , and  $V_0$  are constants. The hard sphere potential is a special case. This interaction potential allows the sequence of events in a many-body system to be described by a series of two-body collisions. That is, since a particle does not experience any change in velocity except at the instant when it is separated from another particle by  $\sigma_1$  or  $\sigma_2$ , there will never, in a finite system, be more than two particles at a time whose velocities are changing. This potential has the qualitative features of a real molecular potential and still some elements of simplicity which make the analytical theories relatively easy to apply. Furthermore, it is possible to make theoretical extensions of the results to more realistic potentials by perturbation techniques. It is important to develop such perturbation techniques in order to overcome one of the most severe limitations of numerical schemes, namely, that they are only valid for the specific case solved.

In the dynamical calculation the molecules are all given initial velocities and positions. From then on, of course, the future behavior of the system is determined. Various initial conditions have been used but most frequently the molecules have been given equal initial kinetic energies with a random selection of the three direction cosines of the velocity and initial positions corresponding to a face-centered cubic lattice. For such a lattice the number of molecules will be multiples of 4 which is the number of lattice sites in a basic cube. The box at whose sides the periodic boundary conditions are applied has usually been taken to be a cube with edges of unit length so that the number of molecules typically used have been 32, 108, 256, and 500; that is,  $4n^3$ . The specific volume of the system,  $v$ , compared to the close-packed specific volume,  $v_0$ , is

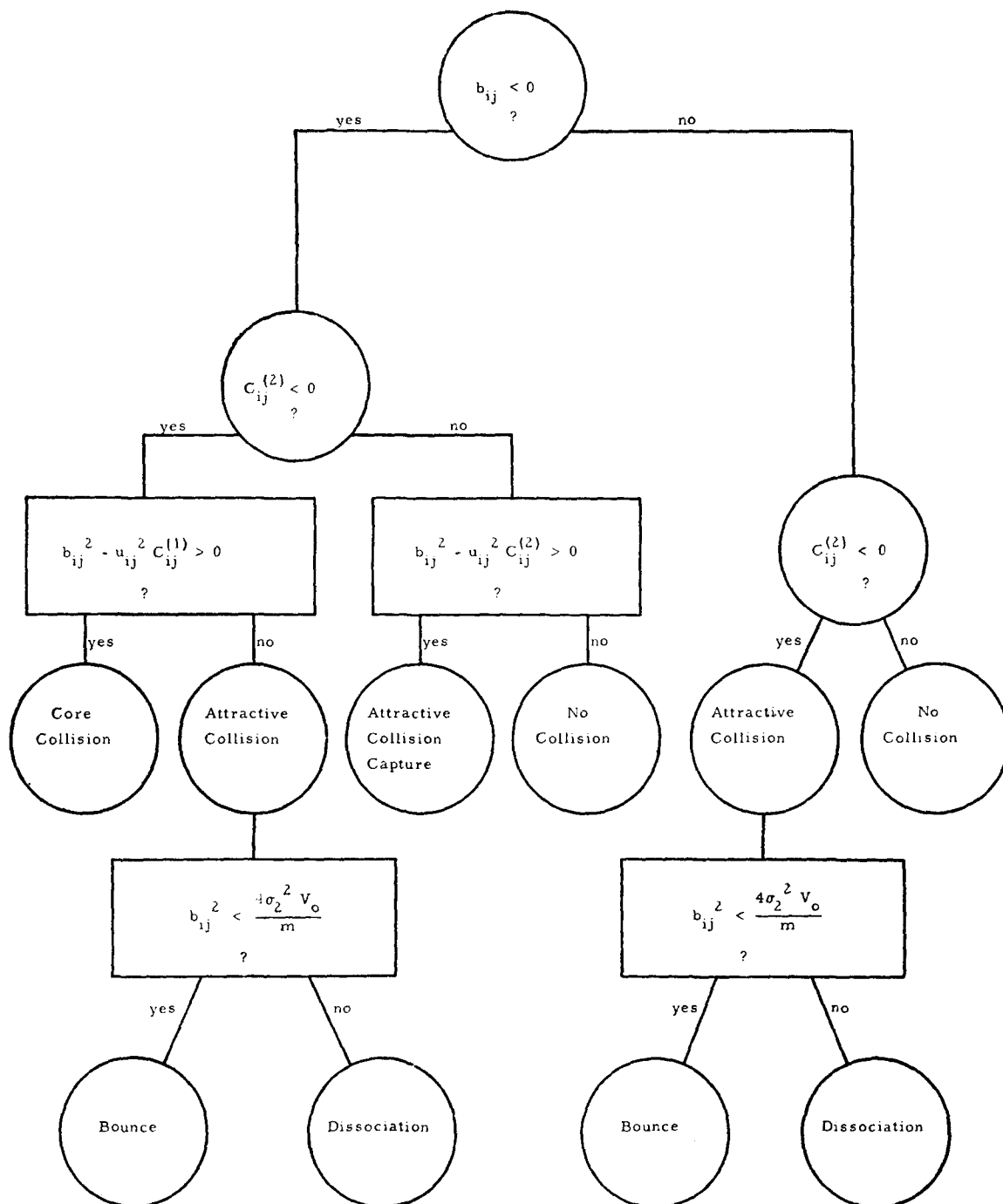


FIG. 1. Schematic diagram of the logical sequence of the calculations.

$v/v_0 = \sqrt{2}/N\sigma_1^3$ , where  $N$  is the number of molecules in the system.  $\sigma_1$  is adjusted to produce the desired specific volume for the system. For other lattice types the basic cell may be more complicated, but as long as it is possible to construct a rectangular parallelepiped with a whole number of cells, the same type of periodic boundary conditions can be used.

Once the initial configuration is set up the machine

is made to calculate exactly, to the number of significant figures carried (9), the time at which the first collision occurs in the system. The word "collision" is used to mean either an attractive or repulsive encounter between two molecules. The collision time is obtained by evaluating, for each pair in the system, the time required for the projected paths to reach a separation of  $\sigma_1$  or  $\sigma_2$ . If two molecules,  $i$  and  $j$ , have

initial positions  $\mathbf{r}_{i0}$  and  $\mathbf{r}_{j0}$  and velocities  $\mathbf{u}_i$  and  $\mathbf{u}_j$ , then at a later time,  $t$ , the square of the separation of the molecules will be

$$(\mathbf{r}_i - \mathbf{r}_j)^2 = (\mathbf{r}_{i0} - \mathbf{r}_{j0})^2 + 2t(\mathbf{r}_{i0} - \mathbf{r}_{j0}) \cdot (\mathbf{u}_i - \mathbf{u}_j) + t^2(\mathbf{u}_i - \mathbf{u}_j)^2.$$

Thus the time required for a repulsive or attractive collision is

$$t_{ij}^{(\alpha)} = \frac{-b_{ij} \pm (b_{ij}^2 - u_{ij}^2 C_{ij}^{(\alpha)})^{\frac{1}{2}}}{u_{ij}^2},$$

where

$$\begin{aligned} \mathbf{r}_{ij} &= \mathbf{r}_{i0} - \mathbf{r}_{j0} & b_{ij} &= \mathbf{r}_{ij} \cdot \mathbf{u}_{ij} \\ \mathbf{u}_{ij} &= \mathbf{u}_i - \mathbf{u}_j & C_{ij}^{(\alpha)} &= r_{ij}^2 - \sigma_\alpha^2. \end{aligned}$$

$t_{ij}^{(1)}$  is the time required for a repulsive collision and  $t_{ij}^{(2)}$  is the time required for an attractive collision. It is clear that  $C_{ij}^{(1)}$  must be positive, otherwise the two hard cores overlap. If  $C_{ij}^{(1)}$  is negative, an error has been made and the machine is made to stop. (Another insurance against machine errors in the calculation is a check of the total energy which must remain constant.)  $C_{ij}^{(2)}$ , however, can be either positive or negative depending on whether or not the separation of molecules  $i$  and  $j$  is within the range of the attractive potential.

In order to find the time of the first collision in the system it is necessary to calculate a collision time for each pair of particles. In calculating a collision time for molecules  $i$  and  $j$ , the computing machine goes through the following sequence of tests and classification (see also Fig. 1).

I  $b_{ij} < 0$  (Centers are approaching.)

(a)  $C_{ij}^{(2)} < 0$  ( $\mathbf{r}_{ij}$  is within the attractive range.)

(1)  $b_{ij}^2 - u_{ij}^2 C_{ij}^{(1)} > 0$  (Cores collide.)

$$t_{ij}^{(1)} = \frac{-b_{ij} + (b_{ij}^2 - u_{ij}^2 C_{ij}^{(1)})^{\frac{1}{2}}}{u_{ij}^2}.$$

(2)  $b_{ij}^2 - u_{ij}^2 C_{ij}^{(1)} < 0$  (Cores do not collide. Attractive collision takes place.)

$$t_{ij}^{(2)} = \frac{-b_{ij} + (b_{ij}^2 - u_{ij}^2 C_{ij}^{(2)})^{\frac{1}{2}}}{u_{ij}^2}.$$

(b)  $C_{ij}^{(2)} > 0$  ( $\mathbf{r}_{ij}$  is outside the attractive range.)

(1)  $b_{ij}^2 - u_{ij}^2 C_{ij}^{(2)} > 0$  (Attractive collision takes place; capture.)

$$t_{ij}^{(2)} = \frac{-b_{ij} - (b_{ij}^2 - u_{ij}^2 C_{ij}^{(2)})^{\frac{1}{2}}}{u_{ij}^2}.$$

(2)  $b_{ij}^2 - u_{ij}^2 C_{ij}^{(2)} < 0$  (No collision takes place.)

II  $b_{ij} > 0$  (Centers recede.)

(a)  $C_{ij}^{(2)} < 0$  ( $\mathbf{r}_{ij}$  is within attractive range. Attractive collision takes place.)

$$t_{ij}^{(2)} = \frac{-b_{ij} + (b_{ij}^2 - u_{ij}^2 C_{ij}^{(2)})^{\frac{1}{2}}}{u_{ij}^2}.$$

(b)  $C_{ij}^{(2)} > 0$  ( $\mathbf{r}_{ij}$  is outside the attractive range. No collision takes place.)

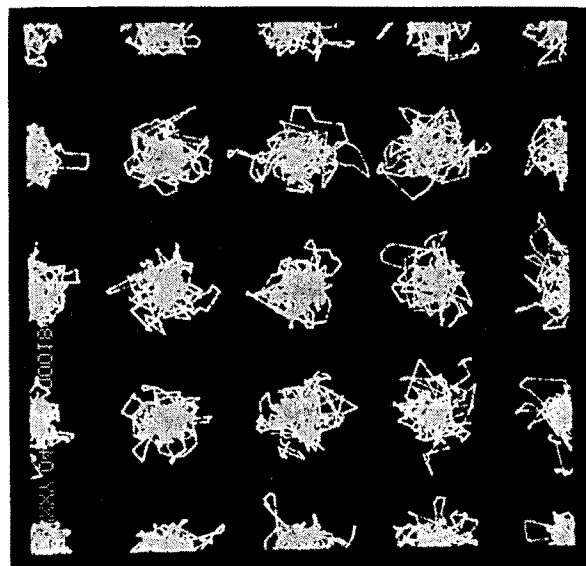


Fig. 2. The traces of 32 hard sphere particles in the periodic boundary conditions in the solid phase for about 3000 collisions.

In calculating these collision times, the periodic boundary conditions are allowed for as follows. Each pair of molecules,  $i$  and  $j$ , represents an infinite set of pairs whose separations can be generated by adding integers to the  $x$ ,  $y$ , and  $z$  components of  $\mathbf{r}_{ij}$ . (The dimensions of the periodic box are taken to be unity.) In calculating  $t_{ij}^{(\alpha)}$  only the closest of all the possible pairs is considered. This means that some possible collisions are ignored but all of them are among pairs of molecules, each component of whose separations is greater than  $\frac{1}{2}$ . A maximum time,  $t_m$ , is assigned which is too short to allow any two molecules to change their separation by as much as  $(\frac{1}{2} - \sigma_2)$  and any  $t_{ij}^{(\alpha)}$  which is greater than  $t_m$  is rejected. If, as may happen in a dilute system, no  $t_{ij}^{(\alpha)}$  is found which is less than  $t_m$ , all the molecules are allowed to move at constant velocity for a time equal to  $t_m$  and another try is made to find an acceptable  $t_{ij}^{(\alpha)}$ . When all the  $t_{ij}^{(\alpha)}$  which are less than  $t_m$  have been found, the machine has finished what is called a "long cycle." All the molecules are now allowed to move at constant velocity for a time which is equal to the shortest  $t_{ij}^{(\alpha)}$  found. Now one pair of molecules has a separation of  $\sigma_1$  or  $\sigma_2$  so that their velocities must be changed. In all the calculations so far made the molecules are assumed to have equal masses so that the members of a colliding pair will experience equal and opposite velocity changes. The velocity change,  $\Delta \mathbf{v}$ , depends upon the type of collision as follows†:

(1) core collision

$$\Delta \mathbf{v}_i = -\Delta \mathbf{v}_j = \frac{-\mathbf{r}_{ij} b_{ij}}{\sigma_1^2}$$

† These formulas result from conservation of momentum and energy of the classical two-body problem for square-well molecules.

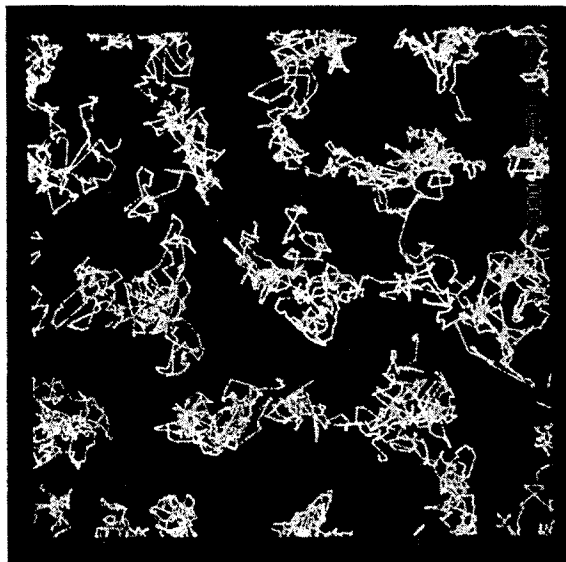


Fig. 3. The traces of the same system as in Fig. 2 after it has transformed to the fluid phase also for 3000 collisions.

(2) attractive collision

(a)  $C_{ij}^{(2)} > 0\frac{1}{2}$

“Capture”

$$\Delta \mathbf{v}_i = -\Delta \mathbf{v}_j = \frac{-\mathbf{r}_{ij}}{2\sigma_2^2} \left[ \left( \frac{4\sigma_2^2 V_0}{m} + b_{ij}^2 \right)^{\frac{1}{2}} + b_{ij} \right]$$

(b)  $C_{ij}^{(2)} < 0\frac{1}{2}$

(i)  $b_{ij}^2 > \frac{4\sigma_2^2 V_0}{m}$

“Dissociation”

$$\Delta \mathbf{v}_i = -\Delta \mathbf{v}_j = -\frac{\mathbf{r}_{ij}}{2\sigma_2^2} \left[ -\left( \frac{4\sigma_2^2 V_0}{m} + b_{ij}^2 \right)^{\frac{1}{2}} + b_{ij} \right]$$

(ii)  $b_{ij}^2 < \frac{4\sigma_2^2 V_0}{m}$

“Bounce”

$$\Delta \mathbf{v}_i = -\Delta \mathbf{v}_j = -\frac{\mathbf{r}_{ij} b_{ij}}{\sigma_2^2}$$

At this point the machine could start another long cycle and proceed indefinitely. A great saving in computing time is made, however, by utilizing the rest of the  $t_{ij}^{(a)}$  calculated in the long cycle just completed. The difference between the shortest  $t_{ij}^{(a)}$  which has just elapsed and the next larger  $t_{ij}^{(a)}$  is the additional time required for the next collision unless one of the molecules which was involved in the first collision is immediately involved in a second collision. It is necessary then only to re-examine all possible collisions which can be made by the two molecules whose velocities have just been changed. This is called a short

cycle. All the  $t_{ij}^{(a)}$  in the previously compiled list are diminished by the shortest  $t_{ij}^{(a)}$  which has already elapsed. Those  $t_{ij}^{(a)}$  in the list which pertain to molecules whose velocities have been changed are eliminated since they have been based on the erroneous presumption that the two were not going to collide. (With each time that is stored in the memory, the identity of the two particles to which it pertains are also saved.) The new  $t_{ij}^{(a)}$  which were calculated in the short cycle are added to the list if they are less than the largest  $t_{ij}^{(a)}$  present on the list. The number of pairs which must be examined in a short cycle is only  $2N-3$ , whereas, in a long cycle  $N(N-1)/2$  pairs must be examined so that in a large system the saving in computing time is very great.

The machine continues executing short cycles until all of the  $t_{ij}^{(a)}$  have been used up and then goes through another long cycle to repeat the process. Except in very dilute systems, the time spent in long cycles is relatively small so that the average calculating time per collision is roughly proportional to  $N$ . For example, for 500 particles in the liquid region, the machine spends about five minutes in a long cycle and does not need to prepare another list of times for the next three hours of calculating.

The calculation was first set up for the Univac computer. The small capacity of the high-speed memory of this machine limited the system which could be efficiently handled to about 100 rigid spheres. With this number of molecules, roughly 100 collisions (that is, two mean collision times) could be calculated in one hour. The IBM 704 calculator handles about 2000 collisions per hour for 100 molecules and about 500 collisions per hour for 500 molecules. As can be seen, the number of collisions that can be calculated per hour depends in these denser systems about

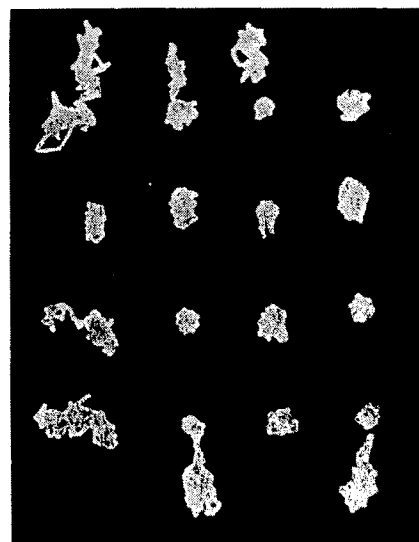


Fig. 4. The traces of 32 particles with free boundaries for about 5000 collisions.

†  $C_{ij}^{(2)}$  is calculated before the particles are moved into the contact position.

linearly on the number of molecules. However, the average number of collisions per molecule per hour is proportional to the square of the number of molecules. The 704 machine can calculate 40 collisions per molecule per hour for a 100-molecule system and only 2 collisions per molecule per hour for a 500-molecule system. Hence it is more economical to work with small rather than large samples as long as boundary effects are not serious. The effects of inherent fluctuations can be removed by calculating a large number of collisions per molecule.

It is clearly desirable to speed the calculation up even further for equilibrium calculations. The Monte Carlo method is calculationally simpler so that many more moves can be made per unit calculating time. But practical experience so far has shown that both methods are about equally efficient in arriving at equilibrium configurations. For small systems, major improvements can only come through increased calculator speed. The smallest system that can be studied with a hope that the boundary effects might not be serious contains 32 particles. Below that number in a cube, even the nearest neighbors of a given particle are not all independent particles. Since a practical limit for the calculating time on a single problem is about 40 hours, a 32-particle system at liquid densities can now be followed for only about  $10^{-9}$  second and, with presently planned machines, for about  $10^{-7}$  second if the present code is used. For larger systems this time will be even less. Machines with very large memories, however, will make it possible to arrange the calculations in such a way that the computing time per collision per molecule will approximately be proportional to  $N$  rather than  $N^2$ . The principle of this scheme is to consider only collisions between close particles. The cube of unit dimensions is divided up into a grid of smaller cubes. Collisions are considered only between particles in neighboring cubes of the grid. This calculation eliminates the calculation of collision times for particles which are far apart and hence are very likely to be deflected before they collide. This would be done at the expense of keeping track of particles which are in neighboring cubes of the grid. New times have to be calculated as before when particles collide and, furthermore, as particles cross the grid, new times have to be also calculated for them since their set of neighboring cubes has partially changed. At high densities and with a good choice of the grid, however, few particles will cross grid lines.

#### APPLICATIONS

As the calculation of the motions of the many particle system proceeds, the history of each particle is recorded on magnetic tape. A separate process later analyzes this very detailed data for various desired quantities. The reason for such a two-step procedure is that the size of the computing machine's memory does not allow the analysis to take place at the same

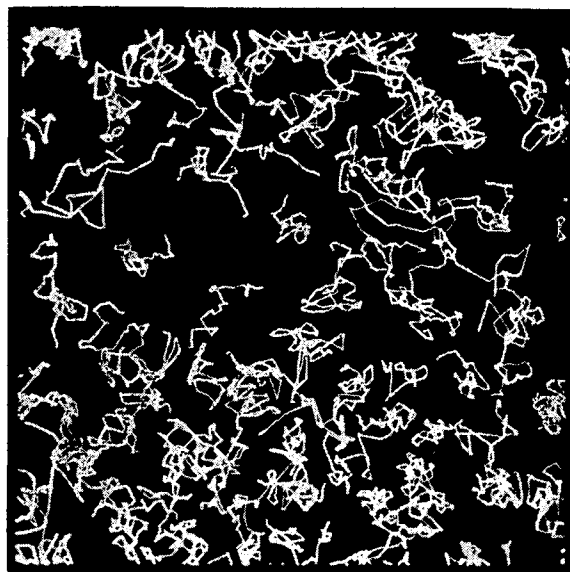


Fig. 5. The traces of 108 particles with periodic boundary conditions for about 3000 collisions in the liquid-vapor region.

time the motions are being calculated. However, a few easily calculated quantities such as the pressure, collision rate, and potential energy are obtained during the first phase of the calculation. This makes it possible to judge when the system has reached equilibrium. To conserve tape the positions and velocities of all the particles are put on tape only infrequently, but for each collision the positions and velocities of the two colliding particles are written on the tape.

The calculation can also be monitored by means of a cathode-ray tube which is attached to the computer and which forms a picture of the system after each time step. On the face of this tube are plotted in plane-projection the positions of the centers of the particles. A camera focused on the face of the tube for a large number of time steps will record the trajectory of each particle as a succession of dots. A slightly different monitoring routine projects an identifying symbol at the position of each molecule so that the beginnings and ends of molecule migrations can be located. Since these photographs have proved very useful in visualizing what is happening in the system, some examples are given in Figs. 2 to 5. Figures 2 and 3 show the difference in molecular motions between a fluid and a solid made up of 32 rigid spheres. Each picture follows the system for 3000 collisions. The solid in Fig. 2 also demonstrates well the periodic boundaries. The molecules near the side of the box sometimes wander over the boundary and reappear at the opposite side. Only 16 traces can be distinguished in this picture because in the plane-projection, half the molecules are almost directly behind other molecules in the lattice. A free boundary is illustrated in Fig. 4, which shows an isolated crystal-lite made up of 32 molecules with attractive potentials. The enhanced motions of particles near the surface is



easily recognized. Figure 5 demonstrates a liquid-vapor phase separation for 108 molecules with attractive potentials.

These pictures are, however, only of qualitative significance; quantitative information can be obtained by direct calculation of both the equilibrium and nonequilibrium properties. In order to average out the statistical fluctuations in the approach to equilibrium, the analysis is averaged over problems which have been restarted several times with slightly different initial conditions. Averages for equilibrium properties can be obtained by running the problem a long time. The amount of averaging depends on the fluctuations which are encountered. Rigid sphere problems in general do not have to run as long as problems involving attractive potentials because, in the former, there are no potential energy fluctuations and also equilibrium is reached more quickly.

Among the properties of systems which have been analyzed before equilibrium is reached, is the behavior of the Boltzmann  $H$  function. In order to do this the distribution in kinetic energy of the particles as a function of time is required, and this is of interest in itself. For example, in a problem in which all the particles have the same initial kinetic energy, it is desirable to ascertain how much time is necessary to produce particles of many times the initial kinetic energy. The analysis also allows one to determine how the kinetic energy is distributed in space. This would be of interest, for example, in the study of the equilibration of a system which initially has a nonuniform temperature distribution. Also the distribution in the components of the velocity can be calculated. This could be of

interest when, for example, a temperature or velocity gradient is impressed on the sample. In a calculation where all the molecules are initially bunched up in a small region of the box, the spacial distribution of the particles themselves is of interest in determining how quickly a subsequent "explosion" fills the container.

At equilibrium, besides the pressure and energy which are calculated as the problem is generated, the mean free path, the self-diffusion coefficient, and the pair and triplet spacial distribution functions of the particles can be calculated. Further analysis can be made of the distribution of cluster sizes, the distribution of diffusion distances about the mean, and of the distribution of the energies of colliding particles in the center-of-mass frame.

The above list is only a partial one to illustrate the range of problems which can be studied. Most of these calculations have been tried out in a few cases which will be subjects of future publications. Some of the analysis, namely, the pair and particularly the triplet distribution functions, are heavy time consumers. However, they do not need to be evaluated in every instance.

A rather large amount of calculation has been devoted to thermodynamic properties. The system of rigid spheres has been made a test case and various boundary conditions, lattice types, and system sizes have been investigated. Two-dimensional hard-disk particles, as well as mixtures of different sizes of spheres, have been investigated too. These calculations, which show the general feasibility of this approach to the many-body problem, will be published soon.