APPLICATIONS OF THE MONTE CARLO METHOD IN STATISTICAL PHYSICS

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1. INTRODUCTION

AS is well known, the application of the rigorous methods of statistical physics to classical condensed systems encounters very great difficulties in connection with the necessity of calculating or asymptotically estimating (for $N, V \to \infty$) the configuration integral

$$Q_N = \int \int \ldots \int_{(V)} \exp\{-U_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)/kT\} d\mathbf{r}_1 \ldots d\mathbf{r}_N, \quad (1)$$

where $U_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the interaction energy of the particles of the system, which is assumed to be known, and N is very large. In the type of theory based on the study of integral equations for the correlation functions of groups of particles [1] an equivalent difficulty arises, in the form of the necessity of solving a system of N integro-differential equations for N unknown functions, for $N \to \infty$. In present theories of liquids and dense gases these difficulties are overcome either by an approximate evaluation of Q_N by the method of the free volume,[2] or else by breaking off the chain of equations for the correlation functions by means of the "superposition approximation." [1,3] In both cases the theories obtained are of a very approximate character. Although notable successes have been achieved in such ways, the problem of developing more complete theories remains a very important one.

Kirkwood [4] and Mayer [5,6] have proposed new types of theories based on the method of integral equations for the correlation functions. Although in this case it is in principle possible by solving finite systems of integral equations to get better results than those of the theory based on the

"superposition approximation," still the extraordinary complexity and cumbersomeness of these theories evidently makes them of little practical use. So far there have been no concrete results obtained in this direction.

Essentially new ideas and new results have made their appearance in the last few years in connection with the introduction of methods based on machine calculation, the most important of these being the "Monte Carlo method." The idea of the method as applied to problems of statistical physics was first suggested by J. Mayer (cf. reference 7), and was first applied in references 7 and 8 to highly simplified models of systems of particles; later, after the method had been much improved, it was applied [9,10,11] to more complex and interesting systems.

Generally speaking, the "Monte Carlo method" means a method of numerical calculation in which specifically probabilistic elements are introduced, in contrast to the classical technique of calculation, which consists of successive steps developing completely determined algebraic operations. In recent times different varieties of such methods have already been applied to many problems of physics, technology, and so on. In our case the main point is the calculation of multiple integrals of the type (1) by numerical integration over a random selection of points (subject to certain special rules as to the selection of these points), instead of the usual integration over a regular set of points. A more detailed explanation of the nature of the new method will be given later in this paper.

Although the results obtained so far by the new method are very interesting for statistical physics, they are still rather modest. It must be remembered, however, that the first papers that have

been published have mainly pursued the purpose of checking the usefulness of the method and making improvements in it, and not of obtaining new results. At present it must be granted that the method has fully justified itself, and that after further improvement it can be very promising not only for problems of the theory of liquids, but also for many other problems of statistical physics. In view of the rapid development of the technical means and methods of computational mathematics, these hopes are all the more important and justified. We believe that it is just in this direction that the greatest advances of statistical physics are to be expected in the immediate future, at least in the domain of classical theory. Furthermore, many of the ideas that have arisen in this method (for example, the idea of introducing periodic boundary conditions for a disordered system, to be discussed later) can be useful in statistical physics apart from the method itself.

As developed so far the new method applies only to classical systems, since it makes explicit use of the numerical values of the energy of the system in its various states. In quantum systems the determination of the eigenvalues is itself the main difficulty.

In the present survey we shall give a brief account of the main ideas of the Monte Carlo method and of the results obtained up to the present by applying it to the theory of crystals, liquids, and dense gases. Questions of the foundation of the method are still in need of more careful analysis, and we shall deal with them only in a very cursory way. The last section of the survey is not concerned with the actual Monte Carlo method, but its content is also entirely based on the use of contemporary machine mathematics, and has many points of contact with the contents of the rest of the survey.

2. THE IDEA OF THE METHOD

The basic idea of the new method is that one replaces direct multiple integration in the expression (1), or in analogous integral expressions defining average values of functions of the coordinates,

$$\bar{F} = Q_N^{-1} \int \int \ldots \int_{(V)} F(\mathbf{r}_1, \ldots, \mathbf{r}_N) \\ \times \exp\{-U_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)/kT\} d\mathbf{r}_1 \ldots d\mathbf{r}_N, \quad (2)$$

by averaging over a set of random events (configurations) that form a Markov chain with constant transition probabilities.

Let us consider the 3N-dimensional configuration space of the system in question, and divide it in some discrete way into an arbitrarily large number s of cells that are equal in volume. Let all the

cells be numbered in some definite order. We shall say that the system is in the ith state if its representative point is in the ith cell. In each state we can assign to the system a definite numerical value F_i of any function $F(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ of the coordinates of the system, say by taking the values of $\mathbf{r}_1, \ldots, \mathbf{r}_N$ at the center of the cell. In particular, the interaction energy of the particles of the system is now represented by the set of its possible values $U_i, i = 1, 2, \ldots, s$. It is clear that if s is sufficiently large the replacement of the continuous configuration space by the discrete space has practically no effect on the calculation of the average values of functions of the coordinates. Then instead of Eqs. (1) and (2) we have

$$Q_N \sim Q_N' = \sum_{i=1}^{s} \exp\{-U_i/kT\}, \quad (3)$$

$$\bar{F} = Q_N'^{-1} \sum_{i=1}^{s} F_i \exp\{-U_i/kT\}. \quad (4)$$

Let us now turn to the following formal scheme. We shall regard the manifold of all the s possible states of the system as a set of random events A_i, which form a Markov chain with constant transition probabilities for $A_i \to A_j$; these probabilities are nonnegative, $p_{ij} \geq 0$, and satisfy the normalization condition

$$\sum_{j=1}^{s} p_{ij} = 1, \quad i = 1, 2, \ldots, s. \quad (5)$$

In what follows we shall need some simple results from the theory of homogeneous Markov chains (cf. e. g., reference 12). Let us denote by $p_{ij}^{(n)}$ the probability of the realization of the transition $A_i \to A_j$ after n steps (so that $p_{ij}^{(1)} \equiv p_{ij}$). If all of the A_j, $j = 1, 2, \ldots, s$, form a single ergodic class, i. e., if all the states A_i are nonperiodic, and if from any state A_i any state A_j is attainable by some finite number n of transitions, then there exist limiting probabilities

$$\lim_{n \to \infty} p_{ij}^{(n)} = u_j, \quad j = 1, 2, \ldots, s \quad (6)$$

for all i, and here

$$u_j > 0, \quad \sum_{j=1}^{s} u_j = 1, \quad (7)$$

so that the u_j give a certain probability distribution for the A_j. Moreover, it is proved in the theory of Markov chains that the quantities u_j, as normalized by Eq. (7), are uniquely determined by the values of p_{ij} through the system of linear equations

$$u_j = \sum_{i=1}^{s} u_i p_{ij}, \quad j = 1, 2, \ldots, s \quad (8)$$

and that the distribution defined by the numbers u_j is a stationary probability distribution of the events A_j, that is, a distribution such that if it were taken as the initial distribution it would not change in the course of the Markov process in question. Equations (6) express the approach of the system to a stationary condition, independently of the choice of the initial condition.

Therefore if we consider a chain with an unlimited number of steps, the average value of any function F_i of the state, taken along the chain, will in the limit be given by

$$\bar{F} = \sum_{i=1}^{s} F_i u_i. \tag{9}$$

If we choose

$$u_i = Q_N'^{-1} \exp\{-U_i/kT\}, \tag{10}$$

then the limiting value of the average of F_i along an unlimited Markov chain is equal to the canonical average value of the function F as given by Eq. (4).

The remaining task is to choose the transition probabilities P_{ij} to fit the conditions. It is obvious that this can be done in many ways, since for prescribed u_j the s^2 quantities P_{ij} are not determined uniquely by the $2s$ equations (5) and (8). Therefore in the space of our events there exist many Markov chains possessing the required limiting property given by Eqs. (6) and (10). We note that the relations

$$p_{ij} \exp\{-U_i/kT\} = p_{ji} \exp\{-U_j/kT\}. \tag{11}$$

which obviously express the principle of microscopic reversibility in the system, convert the equations (8) into identities. Therefore in the practical construction of a concrete type of Markov chain with the limiting property we need we can start with the conditions (5) and (11) instead of (5) and (8). Together with Eq. (10) this gives us conditions for the P_{ij} of the form

$$u_i p_{ij} = u_j p_{ji}, \tag{12}$$

Thus a Markov chain in which all the states form a single ergodic class and in which the transition probabilities satisfy the conditions (5) and (12) converges to the Gibbs canonical ensemble in the sense that when the length of the chain is great enough the various states tend to appear with frequencies proportional to the Boltzmann factors $\exp\{-U_i/kT\}$. The convergence does not depend on the choice of the initial state, and averages along the chain of functions of state approach the averages over the canonical ensemble.

Let us now turn to concrete physical systems and examine for them the question as to whether the ergodic requirements are satisfied. For simplicity suppose that the total interaction energy of the particles of the system can be represented as a sum of interactions by pairs,

$$U_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{2} \sum_{\substack{i=1 \\ (i \neq k)}}^{N} \sum_{k=1}^{N} \Phi(r_{ik}), \tag{13}$$

where $\Phi(r)$ is the mutual potential of two particles, and r_{ik} is the distance between the ith and kth particles. If the potential $\Phi(r)$ does not go to $+\infty$ anywhere, then the quantity $\exp\{-U_i/kT\}$ in Eq. (10) does not go to zero anywhere, so that all the u_j in Eq. (6) are also different from zero. Therefore for any transition $A_i \to A_j$ between states in the discrete configuration space there is a nonvanishing probability $p_{ij}^{(n)}$ of its realization for some finite number n of steps. Thus all of the states are attainable from each other, and the entire set of states forms a single ergodic class.[12] In such a case any Markov chain with transition probabilities determined by Eqs. (5) and (12) converges to the canonical ensemble in the sense indicated above.

In applications of statistical physics use is often made of model intermolecular potentials $\Phi(r)$ that go to $+\infty$ at $r = 0$. For example, the power-law potential

$$\Phi(r) = \frac{A}{r^m} - \frac{B}{r^n}, \quad A, B > 0, \quad m > n, \tag{14}$$

which is widely used in the theory of real gases and liquids, is of this type. In this case $\exp\{-U_i/kT\} = 0$ for configurations in which the positions of two particles exactly coincide. Then for these configurations $u_i = 0$. If we exclude the finite number of all these singular states, the Markov chain formed by the transitions between all the other states of the system in the discrete configuration space will again possess the ergodic property. (In the continuous configuration space the set of points where $U_N = +\infty$ has zero measure, and is therefore unimportant.

A difficulty with the ergodic property can arise only if $\Phi(r)$ goes to $+\infty$ in a finite region. For example, in the model of "hard spheres" of diameter a we have

$$\begin{cases} \Phi(r) = +\infty & \text{for } r < a, \\ \Phi(r) = 0 & \text{for } r > a, \end{cases} \tag{15}$$

and the same thing will happen in any model of particles with a "hard" core: for $r < a$ one has the first of the relations (15). At very high densities, close to the maximum density possible for hard particles of the given diameter, interchanges of the particles can become impossible, and then we can

expect the appearance of configurations of the system between which there are no transitions (for example, two configurations that exactly or approximately correspond to the hexagonal and face-centered cubic closest packings of spheres). If this happens, the manifold of all possible states of the system breaks up into isolated ergodic classes without transitions between them, and then the limiting behavior of some definite Markov chain, such as has been described, will depend on which of the ergodic classes contains the initial state of the chain. In such a case the equivalence of the limiting behavior of a Markov chain and the Gibbs canonical ensemble is lost. It must be noted, however, that this possible difficulty is due not to the introduction of the Markov chain into the treatment, but to the properties of the system itself, and is connected with fundamental questions of the foundations of classical statistical physics. In fact, if we go over from the description of states in the configuration space to the dynamic description of the behavior of the system in the complete phase space, the same difficulty is still encountered. The multiple connectivity that has appeared in the configuration space will correspond to a definite multiple connectivity in the phase space also, and a new analysis of the legitimacy of the canonical distribution for and ensemble of such systems is required.

Thus we encounter here the fundamental question of the accessibility of states in statistical physics. These problems call for futher study, and we shall not concern ourselves further with them here. In any case it is clear that difficulties with the ergodic property of the Markov chains of interest to us can arise only for very special forms of the intermolecular potential $\Phi(r)$, and furthermore only for very large densities, corresponding to a highly compressed crystalline state of the system.

We remark in conclusion that the assumption of the two-particle character of the intermolecular forces in Eq. (13) is not a necessary one. The Monte Carlo method as it has been explained here is valid for any law of interaction that depends only on the configuration of the particles, provided that the ergodic requirement is satisfied.

It must also be remarked that if we exclude doubtful cases in which the ergodic condition may possibly be violated, the equivalence of the limiting behavior of the Markov chains studied here to the Gibbs canonical ensemble is an exact one. Therefore the concrete physical results that can be obtained on this basis (with a sufficiently precise practical realization of the method) will contain no lack of exactness except the usual statistical errors. In this the new method explained here differs in principle from, for example, the methods of the free-volume theory or of a theory based on the superposition approximation. Both these theories are essentially approximate, and moreover in such a way that it is even impossible to estimate the degree of approximation in advance.

3. THE REALIZATION OF THE METHOD

The ideas that have been set forth about the reduction of canonical averaging to averaging along a certain Markov chain subject to certain supplementary limitations can be actually realized by the generation of the Markov chains in question with fast computing machines. In papers that have been mentioned [7, 8, 9, 10, 11] such a program has been actually realized for certain simple models of systems.

The first and principal difficulty that arises in this connection is the practical impossibility of making the calculation for a system with a number of particles of the order of Avogadro's number, as would be desirable. If one allows a reasonable amount of machine operation time and requires that the machine generate a chain of sufficient length for the statistical errors to be also within reasonable limits, then the actual possibilities at present do not exceed at the most the treatment of a system with several hundred particles. In a typical case one must confine oneself to still smaller numbers of particles. This can lead to appreciable distortions of the expected results, not only because of inadequacies of the statistics itself, but also because of the large part played by surface effects, especially in condensed states of the system.

The remedy for this was indicated in the very first of these papers,[7] and consists of the imposition of periodic boundary conditions at the boundaries of the small volume that can be treated, with its small number of particles. The entire three-dimensional space is divided into equal cells of volume V with N particles in each cell. We stipulate that one of them is the basic cell, and that the relative configurations and motions of the particles in it are repeated in all the other cells, so that a displacement of the entire system by the length of a side of the basic cell and along this side changes nothing in the total configuration of the system. With this arrangement, if one of the particles of the basic cell is carried out of this cell by its motion through a particular face, then at the same time it in effect enters this same cell through the opposite face (and the same is true for all the cells). Thus although we are considering an unbounded system the computing machine has only to deal with the motion of the N molecules in the basic cell, since along with this motion the motion of the

entire system is then given. Furthermore it is stipulated that the calculation of the energy of any configuration is made by summing the interactions of all the particles of the whole system, and not only the interactions of the particles in the basic cell. In the calculations made up to the present the basic cell has been taken to be a cube containing 32, 108, or 256 particles.

It is clear that the method of periodic boundary conditions takes into account for the system as a whole only a small fraction of all the possible configurations of the particles. Roughly speaking, we can divide all the omitted configurations of the system as a whole into two groups, according to whether the number of particles and the configuration of the particles in each cell are close to or far from the number and configuration in the basic cell. In the former case the statistical weights of the omitted configurations are close to those of the configurations that are used, and thus this group of configurations is actually taken into account approximately. In the second case we have to do with "large-scale" density fluctuations in volumes comparable with or larger than the volume V of the elementary cell, and with amplitudes comparable with or larger than the average density N/V. If the dimensions of the basic cell and the number N of particles in it are not too small, such fluctuations are relatively improbable events (for the system as a whole), and their contribution to the statistical integral and to the estimates of average equilibrium values of physical quantities is negligible. As for the "small-scale" fluctuations, for not too small values of N and V they are taken into account in this method. Therefore it may be supposed that the method of periodic boundary conditions, applied for not very small basic cells and not very small numbers of particles per cell, must lead to sufficiently reliable results. This very interesting question calls for further study.

Preliminary data on this point have been obtained in a paper[13] on a study of the effect of periodic boundary conditions on the properties of a gaseous system. For the second and third virial coefficients the following relations were obtained:

$$B_N = B_\infty (1 - 1/N),$$ (16)

$$C_N = C_\infty (1 + 1/5N - 6/5N^2),$$ (17)

where the indices ∞ and N refer respectively to the ordinary unbounded system and to the same system with periodic boundary conditions and N particles in the basic cell. The question has not been studied for a condensed system.

The necessity of working with a small volume V of the elementary cell and with a small number N of particles in the cell also gives rise to the difficulty that in the case of "hard" particles the possible troubles with the ergodic property that have been discussed earlier can appear at smaller mean densities than in a system of very large dimensions. For example, at a large density of rigid spheres in a small volume shiftings of the spheres past each other may be impossible, although in a large volume with the same average density they would be facilitated because of density fluctuations. If, however, N is not very small, say of the order of a few hundred, even here this difficulty relates only to extremely concentrated crystalline states of the system.

A more serious point is evidently that which is given the name of the "quasiergodic" problem by the authors of reference 9. This is the question of the possibility that in some cases the configuration space of our system may contain two or more regions which make comparable contributions to the complete configuration integral but are such that, although formally they belong to the same ergodic class of states, the probability of transitions between them is very small (at least for a fixed length of the chain). Since any practically realizable Markov chain must be finite, in cases in which this situation exists the Monte Carlo method as we have stated it can lead to false results. If this difficulty indeed exists, it is clear that it also must apply to extremely condensed states of a system, and, most likely, to the case of "hard" particles. Practical measures to remove this possible difficulty are either lengthening the Markov chain, so far as this is possible, or variation of the initial state of the chain within certain limits (by generating a series of chains instead of a single one).

Let us now examine the problem of the concrete construction of the Markov chains in which we are interested. In work done so far the single-step transition probabilities have been chosen in the following way. Let $x_r^{a(i)}$, where

$$\alpha = 1, 2, 3; \quad r = 1, 2, \ldots, N; \quad i = 1, 2, \ldots, s,$$

denote the ath Cartesian coordinate of the rth particle in the ith state (configuration) of the system. The coordinate axes are chosen along the sides of the basic cell. A single step in the Markov chain consists in the displacement of just one particle through a certain distance, so that

$$p_{ij} = 0,$$ (18)

if the configurations i and j differ in the positions of

two or more particles. Furthermore one introduces some arbitrary (but fixed) length δ , much smaller than the side of the basic cell, which limits the magnitude of the possible displacement of the one particle in a single step. Equation (18) holds again if the length of the displacement of the particle for the change of the configuration in a given transition is such that $|x_r^{\alpha(i)} - x_r^{\alpha(j)}| > \delta$.

If, however,

$$\left. \begin{array}{l} |x_r^{\alpha\,(i)} - x_r^{\alpha\,(j)}| \leqslant \delta, \\ x_s^{\beta\,(i)} - x_s^{\beta\,(j)} = 0, \end{array} \right\} \tag{19}$$

with

$$\alpha,\ \beta = 1,\ 2,\ 3;\quad r = 1,\ 2\ \ldots,\ N;$$
$$s = 1,\ 2,\ \ldots,\ r-1,\ r+1,\ \ldots,\ N.$$

then the probability of the single-step transition is taken to be

$$\left. \begin{array}{ll} p_{ij} = C & \text{for} \quad U_j \leqslant U_i, \\ p_{ij} = C\exp\{-(U_j - U_i)/kT\} & \text{for} \quad U_j > U_i, \end{array} \right\} \tag{20}$$

if $j \neq i$, and

$$p_{ii} = 1 - \sum_{\substack{j=1 \\ (j \neq i)}}^{s} p_{ij}, \tag{21}$$

for $j=i$. It is easy to see that the fundamental equations (5) and (12) for P_{ij} are then satisfied identically for any choice of the constant C that does not make $p_{ii} < 0$. Actually the choice of C is taken so that if we were to drop the exponential weight factor in Eq. (20) the expression $p_{ij} = C$, accepted for all i and j, including the case $j = i$ would give with correct normalization equal probabilities for all transitions of any particle within the limits of a cube of volume $(2\delta)^3$ (see further discussion).

This is accomplished practically in the following way. [7,9] Let the ith state of the system be fixed. A special device in the computer makes an arbitrary choice of three independent random quantities ξ^α, $\alpha = 1, 2, 3$. whose values can vary over the range $-1 < \xi^\alpha < 1$, and an arbitrary choice of the number r, which can take the values $r = 1, 2, \ldots, N$. Corresponding to the result of these random events there is a possible displacement of the rth particle to a new position:

$$x_r^{\alpha\,(i)} \longrightarrow x_r^{\alpha\,(j)} = x_r^{\alpha\,(i)} + \xi^\alpha \delta, \tag{22}$$

The energy U_j in this possible position is computed. If $U_j \leqslant U_i$, the new coordinates given by the right member of Eq. (22) are assigned to the th particle, and the system is regarded as having gone into the new state j. If, on the other hand, $U_j > U_i$, then the machine makes an additional arbitrary choice of another random quantity ξ^4, which varies over the range $0 \leqslant \xi^4 \leqslant 1$, and the result of this choice is compared with the quantity $\exp\{-(U_j - U_i)/kT\}$. If $\xi^4 < \exp\{-(U_j - U_i)/kT\}$, then the

transition of the system into the new state A_j is made, but if it turns out that $\xi^4 > \exp\{-(U_j - U_i)/kT\}$, the rth particle remains in its old place, and there is no transition to the state A_j.

In the latter case, however, it is recorded that there has been a step $A_i \to A_i$ in the Markov chain, with the probability P_{ii} . After this the entire procedure starts again, beginning from the new state A_j if the transition to it has occurred.

The set of possible values of the parameters $\xi^\alpha (\alpha = 1, 2, 3)$ is discrete, and the density of these values determines the number s of the divisions of the entire configuration space of the system into discrete cells, which was described in the first section. As for the choice of the constant parameter δ , it is arbitrary, since the transition probabilities (18)--(21) satisfy the fundamental equations (5) and (12), independently of the concrete value of δ . A practically successful choice of δ is very important, however, since too small a value of δ leads to very small steps and the necessity of generating very long chains, and for large values of δ and a pre- scribes set of possible values of the ξ^α many states of the system may be left out.

4. RESULTS OF CALCULATIONS FOR A SYSTEM WITH A LENNARD-JONES POTENTIAL

A study by the Monte Carlo method of a real system for which one chooses the potential of the intermolecular forces in the Lennard-Jones form

$$\Phi(r) = \varepsilon\left\{ \left(\frac{a}{r}\right)^{12} - 2\left(\frac{a}{r}\right)^{6} \right\} \tag{23}$$

is of great interest because of its "realistic" char- acter, and was made for the two-dimensional case in one of the early papers.[7] The more interesting three-dimensional case has been studied in refer- ences 9 and 11. To make possible a comparison of the results of the calculations with experimental data the constants ϵ and a in Eq. (23) were taken to have the values

$$\varepsilon = 1.653 \cdot 10^{-14} \ erg \quad a = 3.822 \cdot 10^{-8} \ cm \tag{24}$$

which are found from studies of the second virial coefficient for argon.[14] Comparisons with the data for the other noble gases can be made by the prin- ciple of corresponding states.[2] We remark that the length a in Eq. (23) is obviously the distance to the minimum of $\Phi(r)$, and not the "diameter" of the molecule.

In references 9 and 11 the Markov chains were studied for systems with 32 and 108 molecules in the fundamental cell. All of the calculations were made for just one isotherm, $T = 328^\circ$ K, which

corresponds approximately to twice the critical temperature of argon, and in the range of reduced volumes from $v/v* = 0.75$ to $v/v* = 7.5$. Here v is the volume per particle in the system and $v* = 2^{1/2}a^3$ represents the volume per particle in a close-packed system of spheres of diameter a. In all 31 Markov chains were generated for 13 values of the reduced volume. The chain lengths for the various cases ranged from about thirty thousand to almost half a million transitions. In thirteen cases the length of the chain exceeded a hundred thousand transitions. Seven chains corresponded to 108 particles in the basic cell, and the others to 32 particles in the cell.

The greatest difficulty, and one which is also of importance in principle, was found in the calculation of the total interaction energy by Eqs. (13) and (23). If one calculates the interaction energy of one molecule with all the others, beginning with the nearest neighbors and then going on to the more distant particles, because of the presence of the term in r^{-6} in Eq. (23) the sum will converge very slowly. The finite speed of the computing machine and the necessity of making the whole calculation of the chain in not too excessive a time seriously limits the accuracy of the calculation of these sums, which have to be calculated all over again for each transition in the chain. In practice these sums were broken off at a small number of terms, including the interactions of a few layers of nearest neighbors of each particle (in the various cases this meant the computation of from 12 to 54 interactions for one particle), and then various sorts of corrections were introduced to improve the result. More detailed information about this is given in the original paper.[9] We remark only that the summation of the interactions was extended not only to the particles of the basic cell, but included the neighbors of each particle that were in adjacent cells.

A knowledge of the interaction energy of the particles in each configuration makes it possible to determine all of the thermodynamic characteristics of the system. The mean molar internal energy of the system is obtained directly from Eq.(13) in the form

$$E = N_A \left\{ \frac{3}{2}kT + \frac{1}{2N} \overline{\sum_{\substack{i=1 \\ (k \neq i)}}^{N} \sum_{k=1}^{\infty} \Phi(r_{ik})} \right\} ,$$ (25)

where N_a is Avogadro's number, N is the number of particles in the basic cell, and the bar denotes averaging along the chain. The first term in Eq. (25) is due to the kinetic energy of the particles. The molar specific heat c_v can be determined from the well known fluctuation formula

$$c_v = \frac{3}{2}R + \frac{1}{kT^2} \left\{ \overline{U_{N_A}^2} - \left(E - \frac{3}{2}RT \right)^2 \right\} ,$$ (26)

where $\overline{U_{N_A}^2}$ is the average along the chain of the square of the interaction energy (13) of the particles in a calculation for N_A particles, and R is the gas constant, $R = N_A k$. The pressure in the system can be calculated from the equation

$$pv = kT - \frac{1}{6N} \overline{\sum_{\substack{i=1 \\ (k \neq i)}}^{N} \sum_{k=1}^{\infty}} r_{ik} \frac{d\Phi(r_{ik})}{dr_{ik}} .$$ (27)

which follows from the virial theorem. In practice, as we have already said, the infinite sums in Eqs. (25), (26) and (27) were computed approximately, by the use of a small number of terms and the introduction of supplementary corrections.

For each configuration of the system a computation was also made of the total number $N_i(r)$ of particles contained in a sphere of prescribed radius r around each particle i, and the average integral distribution of particle numbers

$$N(r) = \frac{1}{N} \sum_{i=1}^{N} N_i(r).$$ (28)

was constructed. These calculations were made for a dense set of values of r from zero to several times a. The ordinary radial distribution function $g(r)$ for the particles is obtained from this by differentiation:

$$g(r) = \frac{v}{4\pi r^2} \frac{dN(r)}{dr} .$$ (29)

In the case of a gas or liquid the functions $N(r)$ and $g(r)$ give a complete knowledge of the molecular structure of the system.

Knowledge of the functions $\Phi(r)$ and $g(r)$ enables us to determine the energy E and pressure p in the system in an independent way from equations well known from the theory of liquids.[1,3] A comparison of the results of the two methods of calculation makes it possible to introduce additional corrections in the course of the calculations, in particular in the computation of the sum of the interaction energies of the particles.

The results of the calculations are presented in references 9 and 11 in the form of tables and curves. As an illustration we show in Fig. 1, taken from reference 11, three theoretical radial distribution functions for the value $v/v* = 2.5$ of the reduced volume. Experimental radial distribution functions for argon in this region of temperatures $(T = 328°K)$ and densities do not exist. One of the three curves shown was found by Kirkwood and his coworkers[15] on the basis of the superposition approximation for a system with the modified Lennard-Jones potential:

$$\Phi*(r) = +\infty \quad \text{for} \quad r < 2^{-1/6}a,$$
$$\Phi*(r) = \varepsilon \left\{ \left(\frac{a}{r} \right)^{12} - 2\left(\frac{a}{r} \right)^{6} \right\} \quad \text{for} \quad r > 2^{-1/6}a.$$ (30)
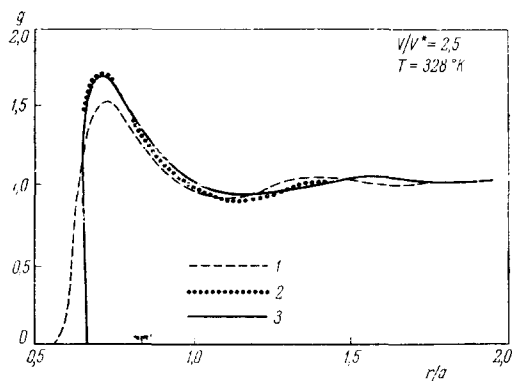
FIG. 1. Theoretical radial distribution functions. 1--Monte Carlo method, potential (23); 2--Monte Carlo method, potential (30); 3--superposition approximation,[15] potential (30).

The other two curves were obtained by the Monte Carlo method for this same modified potential and for the potential (23). It can be seen from the diagram that the introduction of a hard "core" of the molecule considerably changes the behavior of the radial distribution function. For the same intermolecular potential the results of the theory constructed on the superposition approximation deviate somewhat from those of the theory we are discussing, which must be regarded as more rigorous. The data of Fig. 1 are for a system with comparatively small density. From the other curves in reference 9 it can be seen that with increase of the density this difference between the results of the two theories gets larger and larger.

To make possible a comparison of theory with experiment a special Monte Carlo calculation was made[11] with 32 particles in the basic cell to obtain the radial distribution function for a system with the potential (23)--(24) at $T = 126.7°$ K and $v/v* = 1.528$. Figure 2 shows a comparison of the results of these calculations with the experimental radial distribution function for liquid argon at the same values of the thermodynamic parpmeters, as obtained in reference 16. As can be seen from the diagram, there is quite satisfactory qualitative agreement of these results. The authors of reference 11 explain the deviations in the details of the two curves mainly in terms of the crudeness of the practical Fourier transformation of the experimental curve of the angular intensity distribution of the scattering of x-rays by the liquid, by which one gets the radial distribution function of the particles. The remaining, evidently smaller, part of the difference between the curves of Fig. 2 is due to the inaccuracy of the Lennard-Jones potential and the statistical errors of the monte Carlo method.

Among the thermodynamic results, let us give our attention to the equation of state of the system

in question. Figure 3, taken from reference 9, shows the results of calculations of the equation of state at $T = 328°K$ according to the method we are discussing, according to the free-volume theory, and according to the theory based on the superposition approximation. It also shows experimental results for argon taken from references 14 and 7. At the same time the diagram illustrates the size of the statistical errors of the Monte Carlo method. These errors were very different in different cases on account of the differences in the lengths of the Markov chains. For sufficiently long chains these errors are very small. As can be seen from the diagram, in the range of volumes larger than $1.5 v*$ the agreement of the results of the Monte Carlo method with the experimental data from reference 14 is very good. For smaller volumes the agreement with the experimental data from reference 17 is not so good. It is possible that the results of this older paper[17] need reexamination. Comparison of the three theoretical results with each other shows the inadequacy of the theory of the free volume at intermediate and large specific volumes of the system, and of the superposition approximation for small volumes.

The most interesting peculiarity of the results of the Monte Carlo method shown in Fig. 3 is the appearance of a break in the pressure isotherm in the region between $v/v* = 0.90$ and 0.95. There is a similar peculiarity also in the isotherm of the internal energy of the system.[9] This must be interpreted as an indication of a phase transition from a dense-gas to a crystalline state. Although unfortunately a closer study of the behavior of the pressure isotherm in the neighborhood of the transition region has not been made, it is impossible to doubt the existence of a phase transition. This is further confirmed by a comparison of the radial distribution functions for states on the two sides of the transition region. In one case these functions have the typical "crystalline" form, with sharp peaks separated by deep minima, and in the
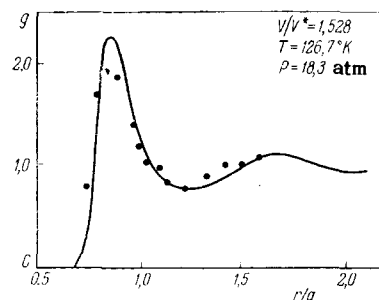

FIG. 2. Radial distribution function for argon, as found experimentally (points) and theoretically by the Monte Carlo method (solid line).
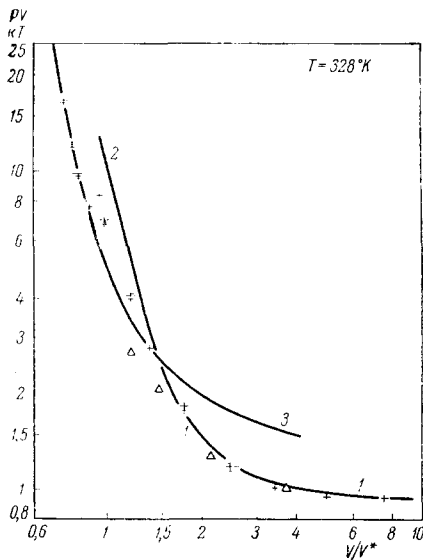
FIG. 3. The equation of state of argon. 1--experimental data from reference 14; 2--experimental data from reference 17; 3--free-volume theory. The horizontal cross marks give the results of the Monte Carlo method (the short marks for 108 and the long ones for 32 particles in the cell). The vertical cross marks show the probable errors of the Monte Carlo method.

other case they have the typical "liquid" form, with diffuse and poorly separated peaks (cf. reference 9). Besides this, a special analysis of the configurations of the particles of the system along the Markov chains on both sides of the transition region showed that to the right of the break in the isotherm of Fig. 3 there is well developed self diffusion of the particles, whereas to the left of the break there is practically no self diffusion.

Thus for a model of a real system the Monte Carlo method has given for the first time, and quite clearly, a demonstration of a liquid-to-crystal transition contained in Gibbsian statistical physics, and a simultaneous description of both phases.

Figure 4 shows the isotherm of the "potential" part of the specific heat of the system, as calculated by the use of the second term of the right member of Eq. (26). It can be seen that there is good agreement of the calculated values with the experimental
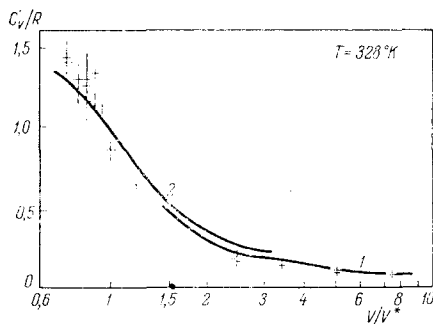

FIG. 4. "Potential" part of the specific heat of argon. 1--experimental data from reference 14; 2--free-volume theory; the crosses are calculated by the Monte Carlo method, as in Fig. 3.

data where the latter exist, and that there is a large spread of the values of the specific heat in the transition region.

We shall not discuss here the other thermodynamic results obtained by the application of the Monte Carlo method to this system; they are contained in references 9 and 11. We note only the interesting and rather unexpected fact that there is almost no difference between the results obtained with 32 and with 108 molecules in the basic cell.

5. RESULTS OF CALCULATIONS FOR A SYSTEM OF HARD SPHERES

A large place in the theory of liquids and gases is occupied by studies of the simplest possible model of a system--the system of hard noninteracting spheres, described by the intermolecular potential (15). Therefore also in the Monte Carlo method it was natural to turn to the study of such a system. This was done already in the first paper[7] for the two-dimensional case, and in later papers[8,10,11] for the more interesting three-dimensional case. In reference 8 a study was made of a system with $N = 256$ spheres in the basic cell. With such a comparatively large N one could have expected that results of very high accuracy would be obtained. It is easy to see, however, that to get reliable results a resort to large N must be accompanied by a great increase of the length of the Markov chain. This was not done in reference 8, and because of the insufficient length of the Markov chains that were constructed the results where not altogether accurate. In particular, no phase transition between ordered and disordered phases was found. The other papers,[10,11] on which we shall rely for the most part, used a basic cell containing only 32 particles, but the greater care used in the calculations led to more reliable and more interesting results. We note, by the way, that the problem of hard noninteracting spheres by its very nature permits the obtaining of more accurate results by the Monte Carlo method, since in it one does not have the complicated problem of getting a reliable summation over the interactions in the system.

Since now in Eq. (20) we have $\exp\{-(U_j - U_i)/kT\}$ equal to either 0 or 1 for all U_i and U_j, all the transitions given by Eqs. (19) and (22) are equally probable, provided only they do not lead to an overlapping of the spherical particles, and otherwise are forbidden. Therefore the construction of the Markov chains is decidedly simplified: for any choice of the random quantities r and ξ^α, $\alpha = 1, 2, 3$ that does not lead to overlapping of particles the transition (22) is made, and in the opposite case the rth particle is

returned to its old place (see Sec. 3). With the same machines and the same computing time as for the preceding problem this allows the construction of much longer Markov chains. In references 10 and 11 many of the chains reached lengths of a million or even several million transitions.

In all of the papers mentioned the radial distribution functions were first calculated as described in Sec. 4, and then the pressure was found from the well known equation [1,3]

$$\frac{pv}{kT} = 1 + \frac{2\pi\sqrt{2}}{3}\frac{v_0}{v}g(a), \tag{31}$$

where $v_0 = a^3/2^{1/2}$ is the volume per particle in a close-packed array of spheres of diameter a and $g(a) = g(a+0)$ is the limiting value of the radial distribution function as the distance approaches the diameter of a particle through larger distances. In all of the papers all of the Markov chains had as their initial states an ordered face-centered cubic distribution of the particles, or a state that arises from this by a slight disturbance (in the case of control chains).

Figure 5, taken from references 10 and 11, shows equations of state of a system of hard spheres according to various theories and according to the Monte Carlo method. The crosses show the results of the dynamical calculation described in the next section, and the two heavier curves in the diagram are also from this work. It is clear that the results of the free-volume theory and the theory based on the superposition approximation differ decidedly from the more accurate results of the Monte Carlo method as used in references 10 and 11. At large volumes the five-term virial equation of state found in reference 8 is more accurate than the superposition approximation and the free-volume theory. The excellent accuracy at very small volumes that the five-term virial equation of state seems from the drawing to possess is illusory, as we shall see in what follows.

The most remarkable feature of Fig. 5 is the appearance of two branches of the isotherm with a break between them, which undoubtedly indicates a phase transition of the system. Just as in the case of particles with a Lennard-Jones potential, an examination of the form of the radial distribution functions and the self diffusion of the particles on the two sides of the transition region gives evidence of a transition from a dense gas to a crystal. As can be seen from the diagram, the free-volume theory and the five-term virial equation of state do not give even a hint of a phase transition, and this is their main shortcoming. It is also clear from this that the good results of the five-term virial equation of state are purely accidental, since the

meaning of this equation lies only in its use for a gas, and the close agreement of the values of the pressure is in the crystalline region. In contrast to this, although it also gives too low values of the pressure, the superposition approximation in the theory of liquids correctly predicts the existence of a limit of the stability of the liquid or gaseous phase. According to this theory the limit of the stability of a homogeneous phase in a hard-sphere system occurs at a volume per particle that is twice the actual volume of a particle.[3,18] In the notation used in Fig. 5 this corresponds to the value $v/v_0 = 1.48$, which agrees fairly well with the results of the Monte Carlo method, although it is somewhat too small. According to reference 11 the transition region between the phases in the system of noninteracting spheres lies on both sides of the value $v/v_0 = 1.55$.

It is interesting to emphasize that Fig. 5 leaves no doubt that the transition between the ordered and disordered phases in the system of hard noninteracting spheres is an ordinary phase transition of the first kind. "Superheated" and "undercooled" states are clearly visible in the diagram. There have been suggestions in the literature that this transition may be only a transition of the second kind, since because there is no interaction between the particles there must also be no latent heat of the
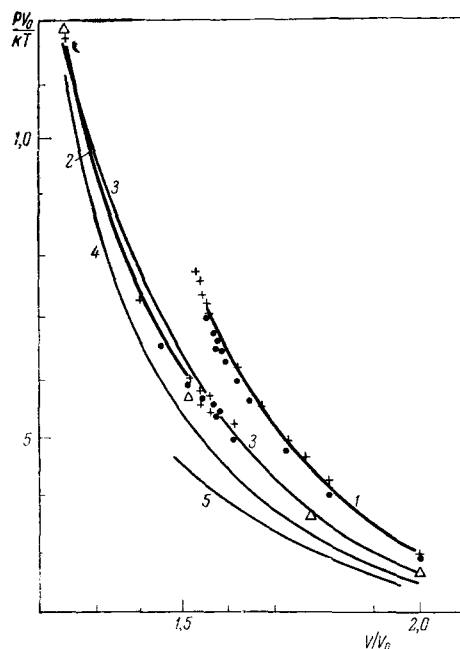

FIG. 5. Equation of state of a system of hard spheres. 1 and 2 -- results of molecular-dynamics computations[19,20] for 108 particles in a cell; crosses -- the same for 32 particles in cell; 3 -- five-term virial equation of state; 4 -- free-volume theory; 5 -- superposition approximation[18] $\triangle$ -- Monte Carlo method, reference 8; • -- Monte Carlo method, references 10, 11.

transition.[18] The erroneousness of such a conclusion has already been explained in an earlier paper, where the possibility was pointed out that a latent heat of a transition can be a purely entropic effect, and not an energetic effect. Then well known thermodynamic arguments necessarily lead to the appearance also of a discontinuity of the density (the specific volume) in the transition. Figure 5 confirms this.

In the rigorous theory we would have to expect that there would be a horizontal section of the pressure isotherm in the region of the phase transition. This was not obtained in references 10, 11. The reason for this is the very slow convergence of the Markov chains near the transition region. An idea of this is given by Fig. 6, which we have taken from reference 11, and which shows the average number N_1 of molecules in a thin spherical layer immediately surrounding some arbitrarily chosen molecule, in the various configurations of the system, for two Markov chains with $v/v_0 = 1.55$. Qualitatively speaking, according to Eq. (31) we have an approximate correspondence between the quantity N_1 and the pressure in the system, since N_1 is proportional to $g(a)$. It can be seen that all the values of N_1 group themselves near two levels, which correspond to the two branches of the isotherm in Fig. 5. In the case of the shorter chain with one and one-half million transitions, the values of N_1 that occur oscillate rather stably around the lower level of values, except for one jump up to the upper level, which was observed during about 10^5 transitions of the chain. In the second, longer, chain with more than three million transitions, values of N_1 near the upper and lower levels (predominantly near the upper level) were observed by turns, with three jumps between the levels. It is clear that averaging over the shorter chain leads rather accurately to a value of the pressure at $v/v_0 = 1.55$ that is in the crystalline phase of the system, but averaging over the longer chain leads to a result that will differ very strongly both from the pressures in each of the two metastable phases for $v/v_0 = 1.55$ and from the value of the pressure in the quilibrium two-phase system. The chain is too long to give one of the former results, and too short to give the latter. A calculation of the pressure in the equilibrium two-phase system, for which averaging over the two groups of levels is needed, would require the generation of a chain at least ten times as long as the longer of the chains shown in the diagram. At present, however, this is quite impractical, if we note that the longer chain in Fig. 6 was generated by about 40 hour operation of a very modern machine.
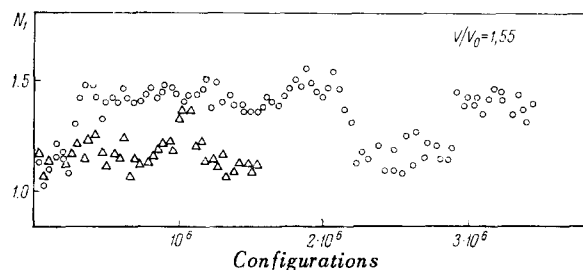

FIG. 6. Convergence of two Markov chains (triangles and circles) in the transition region.

The data shown in Fig. 5 for the pressure in the neighborhood of $v/v_0 = 1.55$ were found by the authors of references 10 and 11 by averaging over only single groups of levels of N_1, which made it possible to distinguish each of the metastable phases in pure form, and to continue them right up to the point $v/v_0 = 1.55$. With this method of calculation the section inside the transition region, where each of the phases separately is absolutely unstable, did not appear. (It is possible that the hard-sphere system is an exception to the usual thermodynamic rules, and that here such a section actually should not appear.)

6. MOLECULAR-DYNAMICS COMPUTATIONS FOR THE HARD-SPHERE SYSTEM

In this section we shall examine briefly the results of two very interesting papers,[19, 20] in which fast computers were used to integrate the classical equations of motion for a system of many particles treated as hard noninteracting spheres. The Monte Carlo method was not used here, but we decided to include this material in this survey because of its exceptional interest for statistical physics, and also because of the close connection of the results thus obtained with those of the Monte Carlo method. Besides this, both methods owe their existence to the use of modern fast computers and the use of the idea of the introduction of periodic boundary conditions in many-body problems. The close relation between the two types of work is also emphasized in references 10 and 11.

As in the Monte Carlo method, one considers systems of N spherical particles contained in a cubical volume with periodic boundary conditions at its faces, so that actually unbounded systems are dealt with. At small mean densities the cases $N = 32$ and 100 were studied, and at large densities, the cases with $N = 32$, 108, 256, and 500 particles in the basic cell, i.e., the cases $N = 4n^3$ which allow face-centered cubic closest packing of the spheres in the cube. In addition, in some cases at large densities there were studies of a system with 96 particles in a basic cell which had the shape of a

rectangular parallelopiped with a ratio of sides permitting hexagonal close packing of spheres. The results in these latter cases do not differ from the others. Just as in the Monte Carlo method, the requirements of a reasonable machine operating time and the securing of a sufficient statistics by the end of such a time at present leads to a preference for systems with small values of N in the basic cell. The most reliable results were obtained in the cases $N = 32$, 100, and 108; furthermore control computations showed that the results relating to the statistical characteristics of the system as a whole obtained in the case $N = 32$ do not differ very appreciably from the results in the case $N = 108$.

At the initial instant for each system all the particles of the basic cell were placed at the sites of a face-centered cubic lattice (or hexagonal close pack in the case of $N = 96$) that extended uniformly over the entire volume of the cell, and they all had velocities equal in magnitude but in various directions. The distribution in direction of the initial velocities of the particles was a random one. The integration of the equations of motion for later times was accomplished by letting the particles move uniformly in straight lines in the direction of their initial velocities up to the occurrence of the first collision of a pair of particles of the system. Then the laws of elastic collision of rigid spheres were used to calculate the velocities of this pair of particles after the collision, and all of the particles were again moved uniformly in straight lines with their new velocities until the next collision of some pair of particles, and so on. Calculations of the motion were made in this way for a large number of systems, with 24 values of the mean density of the particles, and for many of them the results were computed repeatedly with different values of N. In all cases the motion was studied for a long time, and in many cases the number of collisions in the basic cell was half a million or more.

For each system the values of the coordinates and velocities of the particles of the basic cell were stored in the memory of the machine throughout the entire motion (i.e., for all the collisions), and then the statistical characteristics of the system were calculated from these data. Thus a large number of both the kinetic and the equilibrium-statistical properties of the system of spheres were studied.

We shall give only brief attention here to the kinetic properties of the system. First of all, although the initial distribution of the velocities was far from the equilibrium distribution, the equilibrium Maxwell distribution was reached very quickly and then remained unchanged. The corresponding relaxation time was very short--of the order of the average time for a given particle to have from two to four collisions, depending on the mean density of the system in question. The same result is obtained from a study of the time variation of the Boltzman H function. In all cases the H function decreased monotonically, and after two to four collisions per particle reached a constant value, around which it made only very weak oscillations, owing to the smallness of the number of particles in the system. For the same reason the Maxwell distribution of the velocities was attained only in the region of small and intermediate speeds. During the short operating time of the machine and with the small number of particles in the basic cell the "tail" of the Maxwell distribution for very large speeds could naturally not be observed.

Calculations were also made of the autocorrelation function for the speeds:

$$\varrho(\tau) \sim \overline{(u(t) - \bar{u})(u(t+\tau) - \bar{u})}, \tag{32}$$

where $\bar{u}$ is the mean speed. For small densities $\rho(\tau)$ has the exponential form well known from the theory of gases,

$$\varrho(\tau) = e^{-\beta\tau}, \tag{33}$$

where $1/\beta$ is the relaxation time for the speeds. At large densities, however, there are marked deviations of the autocorrelation function from the simple exponential form, owing to the existence of an appreciable correlation between the present and past states of a particle, which is brought about through the neighboring particles.

Finally, the self-diffusion coefficient in the system of hard spheres was calculated at the various densities. The calculation was made simultaneously by several different methods, and a critical comparison was made between the results of the different procedures, and also between these results and those of the theory of real gases.

In reference 20 all the results that have been mentioned on the nonequilibrium properties of the system of spheres are presented in the form of tables and curves. The reader must refer to that paper for further details. We shall now go on to the results obtained in references 19 and 20 that relate to the equilibrium properties of the systems in question.

For all these systems the pressure was calculated by two methods: by means of the radial distribution function, in accordance with Eq. (31), and by the virial theorem, with a "virial" in which the

forces acting between the particles are replaced by the changes of momentum of the colliding particles. To the accuracy that could be attained in the calculations the results of the two methods agreed in all cases. The equation of state so obtained for a system of hard noninteracting spheres is shown in Fig. 5 as the two heavy curves, for the case of the system with 108 particles in the basic cell, and by the crosses for the system with 32 particles in the basic cell. As can be seen from the diagram, there is good agreement between these results and the results of the Monte Carlo method for the same system of particles. The existence of a phase transition of the first kind, of the type of crystallization and melting, is fully confirmed also in the method we are now discussing. The identification of the type of the transition is quite unambigous if we bring in the data on the values of the self-diffusion coefficient on the two sides of the transition region.

According to references 19 and 20 the transition region between the phases extends from $v/v_0 = 1.525$ to about $v/v_0 = 1.7$. The very fact of the existence of two phases and a transition region between them manifested itself in this dynamical method in just about the same way as in the Monte Carlo method: at the densities in question the system alternated in the course of time between two conditions. Changes from one condition to the other occurred rather rarely, and when the evolution of the system was followed for finite times, averaging over the whole times did not lead to any definite and reasonable values of the pressure. Just as in the Monte Carlo method, one had in every case to separate the two types of condition from each other and carry out the averaging for each condition separately. The data for the transition region that are shown in Fig. 5 were obtained in this way.

Thus because of the very small number of particles in the basic cell ($N = 32$ or 108) the phase transition between dense gas and crystal was observed not in the form of the simultaneous existence of two phases, but in the form of fluctuations back and forth between these phases. The authors of reference 20 believe, however, that already at $N = 500$ it would be possible to realize in each cell the two phases existing simultaneously, with a transition layer between them.

To get a graphic illustration of the motion of the particles in the system, a many-beam oscilloscope was connected to the computing machine, and the x and y coordinates of 16 of the particles were simultaneously projected on the screen. Figures 7 and 8 give an idea of the results so obtained. Both pictures are for a system with 32 particles in the basic
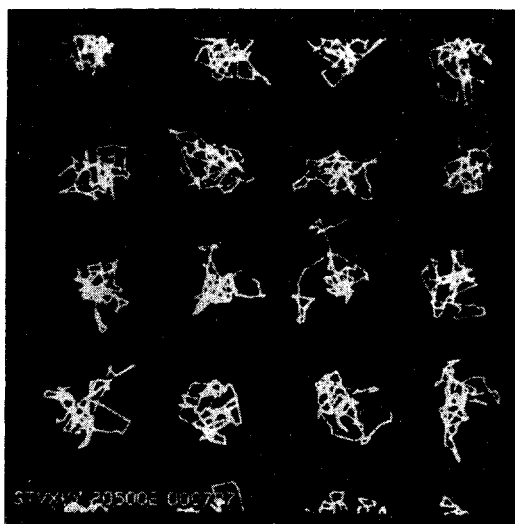

FIG. 7. Plane projection of the motion[20] of 16 particles in a system with 32 particles in the cell, for $v/v_0 = 1.525$. The motion shown corresponds to 1000 collisions per cell, during which time the system "melted."

cell, at $v/v_0 = 1.525$. Figure 7 shows the projection of the tracks of the particles during 1000 collisions (in the whole cell). During this time the system "melted," i.e., passed from the ordered to the disordered phase. Figure 8 shows the projection of the tracks of the particles during the next 3000 collisions, when the system was in the "liquid" state. Reference 20 contains many other photographs of this kind, some of which relate to the pure "crystalline" phase, in which the track of each particle forms a small tangle sharply separated from the similar tangles of the tracks of the other particles.

Figure 8 is in many respects very interesting for the theory of liquids. First of all, the kinetics of the molecular motion in a liquid can be clearly seen in this picture. In full agreement with ideas about the thermal motion of molecules in a liquid, the picture clearly shows the irregular vibrations that the particles execute with great frequency within the limits of their "free volumes," and the rarer jumps of the particles from some quasi-equilibrium positions to others. It is quite obvious that in this example of hard noninteracting particles the activation energy corresponding to these jumps is entirely of an antropic and not an energetic origin.

Figure 8 also gives a good illustration of present views on the nature of the short-range order in a liquid. If we abstract from the traces of long-range order that are present here, owing to the high mean density and the small number in a small volume, it can be seen clearly that we must distinguish between an instantaneous and an average short-range order. The relative positions of the
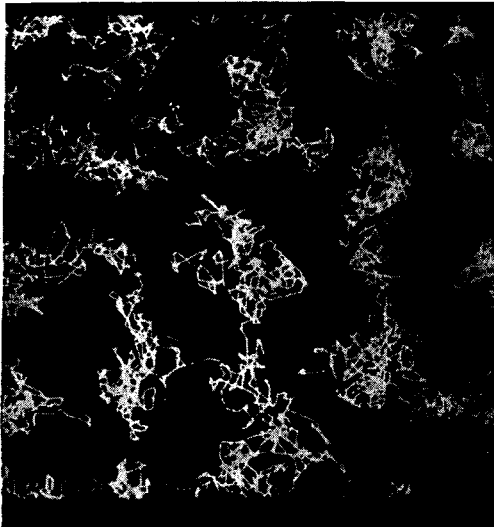
FIG. 8. The same as in Fig. 7, but during the next 3000 collisions in the cell. The system is in the "liquid" state.

average volumes of the vibrations of the particles are comparatively highly ordered. This is precisely the average short-range order in a liquid that is evidenced by the experimentally obtained radial distribution functions $g(r)$. It can also be clearly seen, however, that the average amplitudes of the irregular vibrations of the particles around their quasi-equilibrium positions are of approximately the same length as the distances between the particles, so that there is no ordering of the instantaneous positions of the particles, even in the smallest group of particles. Moreover it must be noted that Fig. 8 applies directly to the melting point, where, according to the ideas of short-range order in a liquid, we should expect the most decidedly "quasi-crystalline" behavior. If we go beyond the melting point, the absence of order in the instantaneous positions of the particles becomes even more marked, although the order in the relative positions of the nearest volumes of vibration is to some extent preserved.

The question of the difference between the instantaneous and average order of the particles in a liquid is of importance in principle for the theory of the electrical properties of electronic conductors and semiconductors. For example, in virtue of the well known adiabatic conditions associated with the slowness of the motions of the atoms, the important thing for the motion of an electron in a liquid is the instantaneous distribution of the particles, not the average distribution.

From this survey of the early work done so far on the application of modern machine-mathematics methods to statistical physics it can be seen how

fruitful and effective these methods are. It may be hoped that their further development will lead to great results.

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Translated by W. H. Furry