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Monte Carlo Equation of State of Molecules Interacting with the Lennard-Jones Potential. I. A Supercritical Isotherm at about Twice the Critical Temperature*

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Values obtained by Monte Carlo calculations are reported for the compressibility factor, excess internal
energy, excess constant-volume heat capacity, and the radial distribution function of Lennard-Jones (12,6)
molecules at the reduced temperature $kT/\epsilon^*=2.74$, and at thirteen volumes between $v/v^*=0.75$ and 7.5.
(v is the molar volume; $v^*=2^{-\frac{1}{2}}N_0 r^{*3}$; N_0 is Avogadro's number; ϵ^* is the depth, and r^* the radius of the
Lennard-Jones potential well.) The results are compared with the experimental observations of Michels
(~150–2000 atmos) and Bridgman (~2000–15 000 atmos) on argon at 55°C, using Michels' second virial
coefficient values for the potential parameters. Close agreement with Michels is found, but significant dis-
agreement with Bridgman. The Monte Carlo calculations display the fluid-solid transition; the transition
pressure and the volume and enthalpy increments are not precisely determined. The Lennard-Jones-
Devonshire cell theory gives results which disagree throughout the fluid phase, but agree on the solid
branch of the isotherm. Limited comparisons with the Kirkwood-Born-Green results indicate that the
superposition approximation yields useful results at least up to $v/v^*=2.5$.

INTRODUCTION

THE Monte Carlo method for obtaining the
equation of state of a system of interacting
particles was devised by Metropolis et al.[1] and applied
by them to the case of hard spheres in two dimensions
and to hard spheres in three dimensions by Rosenbluth
and Rosenbluth.[2] The latter investigation also presented
qualitative results for Lennard-Jones molecules in two
dimensions. Here we shall present quantitative results
for three-dimensional molecules interacting in pairs
according to the Lennard-Jones (LJ) potential

$$u_{\text{LJ}}(r)=\epsilon^*\left[\left(\frac{r}{r^*}\right)^{-12}-2\left(\frac{r}{r^*}\right)^{-6}\right]; \qquad (1)$$

$u_{\text{LJ}}(r)$ is the potential energy of interaction of two
molecules at the distance r. This paper will discuss an
isotherm at about twice the critical temperature,
specifically one for which the reduced temperature
$\theta=kT/\epsilon^*$ has the value 2.74. The range of the reduced
volume $\tau=v/v^*$ is from 0.75 to 7.5; see the abstract for
the definition of these quantities. Additional results

for the isotherms $\theta=1, 5, 20$, and 100 are being prepared
for publication.

This program, which has been carried out on IBM
type 701 and 704 electronic calculators, was undertaken
in order to establish the feasibility of the Monte Carlo
method for nonsingular potentials such as the Lennard-
Jones potential, as contrasted with the hard-sphere
potential in which there is no long-range interaction.
In addition, two other objectives have determined the
course of our investigation. It is of course desirable to
compare the Monte Carlo results with those of other
theories, such as the Lennard-Jones and Devonshire
cell theory[3] and the Kirkwood-Born-Green theory in
the superposition approximation.[4,5] Also, it seemed of
interest to compare the calculated results with experi-
mental observations of the equation of state of molecules
for which a simple potential would be reasonably
realistic. The Lennard-Jones potential was thought to
be a reasonable compromise, inasmuch as most of the
existing statistical mechanical theories have been

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[1] Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller, J.
Chem. Phys. 21, 1087 (1953).
[2] M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. 22,
881 (1954).

[3] See, e.g., Wentorf, Buehler, Hirschfelder, and Curtiss, J. Chem.
Phys. 18, 1484 (1950). The numerical values used here were
calculated by Dr. Wildon Fickett of this Laboratory (LASL),
from the Lennard-Jones-Devonshire theory as modified by
Wentorf et al.
[4] Kirkwood, Lewinson, and Alder, J. Chem. Phys. 20, 929
(1952).
[5] Zwanzig, Kirkwood, Stripp, and Oppenheim, J. Chem. Phys.
21, 1268 (1953). The values used here include the correction for
the hard core, but not the empirical scale factor c introduced by
Zwanzig et al.

applied to it, and since it is reasonably realistic. In addition, it has the advantage of being inherently faster (as regards calculator time) than some possibly more realistic alternatives such as the exp-six potential.

The most reasonable choices of experimental comparison fluids are clearly the rare gases, of which argon has been the most studied. Since it was our intention to establish internally (insofar as possible) the feasibility of the Monte Carlo method as a valid statistical mechanical procedure for potentials of the LJ type, the comparison with experiment is viewed as being mostly a test of the assumptions regarding the intermolecular potential. This being the case, *we have introduced no adjustable parameters.* The values of the potential constants for argon have been taken throughout as $\epsilon^*/k = 119.76°K$, $r^* = 3.822$ A, $v^* = 23.79$ cm^3/mole, as determined by Michels[6] from second virial coefficient data. Using these values, the reduced temperature $\theta = 2.74$ corresponds to a temperature of 55°C for argon, and was so chosen in order to permit comparison with Bridgman's[7] high pressure data at this temperature. This temperature is also in the region of Michels'[6] medium pressure data.

In the following parts of this paper, we first sketch a somewhat more elaborate proof than given in reference 1 of the equivalence of the general Monte Carlo method and the classical-mechanical petite canonical ensemble of Gibbs, using the theory of Markov chains. Next we discuss the approximations which must be introduced into the Monte Carlo method in order to adapt it to the capabilities of even the fastest modern calculators. Then follow the presentation of the present results and comparisons with the experimental data for argon and with the other theories.

THEORY

The Monte Carlo method (throughout this paper, we will mean by this, the Metropolis-Rosenbluth-Teller method) is a means of estimating the configurational or "excess" contributions to the thermodynamic properties of a classical statistical mechanical system; the momenta make their usual classical contributions. Applied to a system of N such molecules confined in a volume V at temperature T, the method consists in the generation of a Markov chain with constant transition probabilities,[8] in which the states of the chain are points in the $3N$-dimensional configuration space of the system. It is convenient in the theoretical discussion to consider this space to be subdivided into a sufficiently large number S of cells, such that the positions of the N molecules are specified by giving the single number associated with the cell into which its representative point falls. This simplification permits us to utilize the theory of discrete chains; it is physically

[6] Michels, Wijker, and Wijker, Physica 15, 627 (1949).
[7] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 70, 1 (1935).
[8] W. Feller, *Probability Theory and Its Applications* (John Wiley and Sons, Inc., New York, 1950), Chap. 15.

reasonable that a sufficiently fine subdivision of configuration space should give results indistinguishable from a continuum of possible states, and in any case such a subdivision is inherent in numerical calculation, the fineness depending on the number of binary bits used to represent the position coordinates of the molecules. Thus, a single integer $k = 1, 2 \cdots S$ suffices to specify a state in the chain; associated with each such integer are other variables such as U_k, the potential energy of configuration k, etc. In order to avoid circumlocution, we will adopt the usual terminology in which successive states of the chain are said to occur at successive instants of time. It must be emphasized that no *physical* time is involved; there are no molecular velocities involved. The succession of configurations at consecutive instants of "time" is of course intimately related to calculating machine time, as the calculator generates the chain of configuration states one after the other by the procedure to be described.

The object of the Monte Carlo method is to generate a Markov chain in which asymptotically (indefinitely longer chain) each state k recurs with a frequency proportional to the Boltzmann factor $\exp(-U_k/kT)$ for that state. Then the average over the chain of any function of the configuration state, such as U_k, in which each occurrence of any state is given equal weight, will converge to the corresponding petite canonical ensemble average of the same quantity as the chain length increases. In order for a Markov chain to have this property it is sufficient[8] that the fundamental one-step transition probabilities satisfy certain conditions. Let $p_{jk} \equiv p_{jk}^{(1)}$ be the conditional probability that if the system be in state j at time t, it will at time $t+1$ be in state k. This matrix of transition probabilities is independent of the time t, and in conjunction with the specification of the state at $t = 0$ uniquely defines a particular Markov process. The p_{jk} must satisfy the normalization conditions

$$\sum_{k=1}^{S} p_{jk} = 1, \quad j = 1, 2 \cdots S. \tag{2}$$

Higher order, or multistep, transition probabilities can be defined, such as the probability $p_{jk}^{(2)}$ that if the system be in state j at time t, then it will be in state k at time $t+2$; this probability is given by

$$p_{jk}^{(2)} = \sum_{k'=1}^{S} p_{jk'}^{(1)} p_{k'k}^{(1)}; \tag{3}$$

and analogously

$$p_{jk}^{(n)} = \sum_{k'=1}^{S} P_{jk'}^{(n-1)} p_{k'k}^{(1)}, \tag{4}$$

for the probability after n steps. It is the asymptotic behavior of $p_{jk}^{(n)}$ as n increases indefinitely in which we are interested. The following theorem from the theory of Markov chains[8] concerns this limiting behavior. Provided that all states are *ergodic* and in the

same *class*, the limits

$$\lim_{n\to\infty} p_{jk}^{(n)} = u_k, \quad k=1, 2\cdots S \qquad (5)$$

exist for all j and are independent of j; furthermore

$$u_k > 0, \quad k=1, 2\cdots S \qquad (6)$$

and

$$\sum_{k=1}^{S} u_k = 1. \qquad (7)$$

Also, the limits u_k satisfy the system of linear equations

$$u_k = \sum_{j=1}^{S} u_j p_{jk}, \quad k=1, 2\cdots S; \qquad (8)$$

in fact, the limits u_k are uniquely determined by (7) and (8). An ergodic state is a nonperiodic state with finite mean recurrence time (see reference 8 for a complete discussion). For our case in which only a finite number of discrete states is possible, the assumption that all states are members of the same ergodic class will be fulfilled if for any pair j, k there exists a nonvanishing multistep probability of finite order n; that is, there exists a n such that $p_{jk}^{(n)} > 0$. Speaking less formally it is required that any state may follow any other state, not necessarily immediately.

We wish to invert the usual process; that is, we inquire what set of probabilities p_{jk} will converge to previously known set of u_k, namely,

$$u_k = c \exp(-U_k/kT), \quad k=1, 2\cdots S, \qquad (9)$$

where c is a normalization constant. As far as (8) is concerned, we note that it will be satisfied identically if the p_{jk} satisfy the condition of microscopic reversibility,

$$u_j p_{jk} = u_k p_{kj}, \quad \text{all } j, k, \qquad (10)$$

provided the normalization condition (2) holds. Therefore, if the p_{jk} satisfy (2) and (10) and also the ergodicity condition, then the Markov chain converges to the petite canonical ensemble, in the sense that the various states tend to occur with the frequencies indicated by the Boltzmann factors. The convergence is ultimately independent of the initial state. These are just the conditions formulated earlier.[1,2]

Equation (10) evidently does not determine a unique set p_{jk}. We now proceed to discuss the transition probabilities which we actually use, and afterwards we will consider the ergodic question. The transition probabilities used in most of the present calculations[9]

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[9] It should be pointed out that this formulation of p_{jk}, which was suggested by Dr. Marshall Rosenbluth, differs from that used in the previous work.[1,2] In the latter investigations r' in Eq. (12) was determined uniquely by the "time" position of configuration j in the chain, according to the relation $r'=t$ modulo N and an initially assigned ordering of the molecules. A few of our chains were also generated by this procedure, which corresponds to a Markov process with time-dependent transition probabilities. We have not studied the corresponding convergence properties except by a few empirical comparisons of chain generated by both methods, which are discussed later.

are given by

$$p_{jk} = A_{jk}, \qquad\qquad \text{if } U_k \leqslant U_j,$$
$$= A_{jk} \exp[-(U_k - U_j)/kT], \text{ if } U_k > U_j, \quad k\neq j, \quad (11)$$

$$p_{jj} = 1 - \sum_{k\neq j} p_{jk},$$

where

$$A_{jk} = \frac{1}{8N\delta^3}, \quad \text{if } x_j^{(\alpha,r)} = x_k^{(\alpha,r)},$$

and

$$|x_j^{(\alpha,r')} - x_k^{(\alpha,r')}| < \delta;$$
$$r=1, 2\cdots r'-1, r'+1, \cdots N; \qquad (12)$$
$$r'=1, 2\cdots N;$$
$$\alpha=1, 2, 3;$$
$$=0, \text{ otherwise.}$$

Here $x_j^{(\alpha,r)}$ is the αth, $\alpha=1, 2, 3$, Cartesian coordinate of molecule r in configuration j, etc. In words, the single-step transition probability is nonzero only for configurations which differ in the position of a single molecule r', which may be any one of the N molecules. Furthermore, the differences of the three coordinates of r' between the two configurations must each be less than the fixed parameter δ. Transition probabilities between configurations satisfying this condition (which is symmetrical in the configurations) are determined in unsymmetrical fashion by their potential energies, according to (11). It is readily seen that (2) and (10) are satisfied independently of the value of δ; thus, the Markov chain averages converge to the petite canonical ensemble averages independently of the value of this parameter. However, the latter will be expected to influence the rate of convergence with increasing chain length, since it in part determines the rate of effective configurational "motion."

There remains to be examined the ergodic character of the Markov chain defined by (11) and (12). In the first place, if the potential energy function is finite for all configurations except possibly for those in which two or more molecules have exactly the same positions, then there will be a nonvanishing probability for moving from any configuration to any other in a finite time; a lower bound for this probability, and a corresponding minimum time, can readily be found by simply moving molecules one at a time from their positions in the first configuration to their positions in the second configuration, in each case by the minimum number of time intervals permitted by the parameter δ. Furthermore, a nonvanishing lower bound for the probability of the same succession of configurations occurring in reverse order can be obtained. Thus we conclude, in the case of potential energy functions of this kind, that the chain defined by (11) and (12) is ergodic, and therefore all requirements are met for equivalence of

the Monte Carlo procedure and the petite canonical ensemble.

For potential energy functions which have infinities over extended regions of phase space, such as is the case for "hard-sphere" or "billiard-ball" molecules, the situation is more complicated. Here it is possible that at sufficiently high densities there may be configurations between which it may be impossible to pass. Even if this is the case we note that if a transition (possibly multistep) is possible from configuration j to configuration k, then the reverse transition from k to j is also possible. Thus the total set of states break up into separate classes, all of which are ergodic, but between which no transitions can occur. If this is the case then the asymptotic behavior will be different for initial states belonging to different ergodic classes. However the corresponding dynamical physical system would presumably have the same compartmentalization of phase space imposed on it, so that this question is really related to the general question of accessibility in statistical mechanics.

The most serious question of this nature then seems to be what we may call the quasi-ergodic problem. That is, the possibility that in some situation of interest configuration space may be divided into two or more regions, all making appreciable contributions to the proper statistical mechanical phase integral, and which are formally members of the same ergodic class, but between which the n-step transition probabilities, though nonzero, are very small except for very large n (the basis of comparison being of course the conveniently attainable chain length). If this situation should arise, the Monte Carlo method will clearly be in danger of giving fallacious results. Clearly this difficulty, if it exists, will tend to be most serious in fairly dense systems. Comparison of the calculated results with experiment can of course be helpful in deciding the question, but the issue will tend to be obscured by uncertainties in the proper potential energy expressions. In addition, the possibility can be tested in a limited way by making perturbations on the initial configuration (see below), and of course by extending the chains to as great lengths as possible.

PERIODIC BOUNDARY CONDITION

Calculator speed seriously limits the number of molecules N which may be considered, as was noted in the earlier work.[1,2] The greater computational complexity of the LJ potential, especially the long-range character of the interaction, has limited the present investigation to systems of 32 and 108 molecules. In order to minimize surface effects with so small a number of molecules, we have used the same periodic boundary condition used in the earlier work.[1,2] This consists in filling three-dimensional space by repetitions of the fundamental cell of volume V, each containing N molecules in the same relative positions as occupied by the fundamental set of N molecules in the fundamental
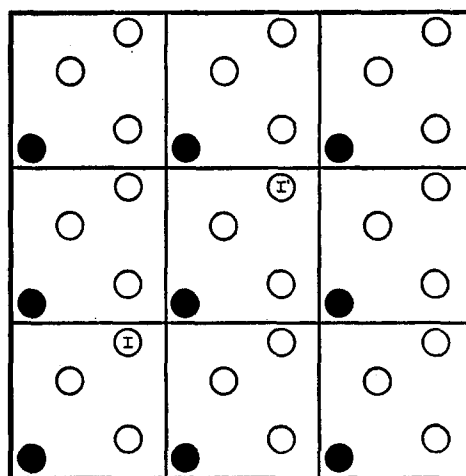

FIG. 1. The periodic boundary condition in two dimensions. The central square represents the fundamental Monte Carlo cell, the others are replicas of it. One of the molecules in the fundamental cell and its eight images are shown as solid circles.

cell in the particular configuration being examined. Figure 1 illustrates this procedure in two dimensions with a system of four molecules. Thus only the motion of the N molecules of the fundamental set need be followed by the calculator, while at the same time the system is somewhat representative of the essentially infinite extent characteristic of ordinary thermodynamic systems. Use of the periodic boundary condition implies that the shape of the Monte Carlo cell of volume V containing the N molecules must be such as to fill space under successive unit translations. This requirement makes the cell similar to the familiar unit cell of crystallography, except the latter is ordinarily chosen to be the smallest of various possible alternatives, which may not be convenient for the Monte Carlo calculation. In the present work this cell is a cube containing 32 or 108 molecules; it may be considered to be made up of cubical arrays of the smallest cubical unit cell, containing 4 molecules, which will generate a face-centered cubic lattice. The most obvious result of imposing the periodic boundary condition is of course the omission of fluctuations in the number of molecules contained in volumes V and greater. A concomitant possibility is a limitation on the ergodic behavior compared to that to be expected from a macroscopic system. Consider, for example, the possibility of two molecules in a quite dense hard sphere system exchanging positions. At close packings this might be impossible when 32 or 108 particles are constrained to be in the fixed volume V. It might occur in a larger system without such a restriction, for instance during a fluctuation in which the number of molecules in the same volume V is reduced.

Although not strictly necessary it is obviously desirable, if we hope to obtain useful results for condensed systems (certainly for crystalline systems), to choose the cell shape and its population N so as to

permit the periodic boundary condition to generate a perfect lattice from a suitably regular arrangement of the N molecules in the fundamental cell. We note that a cell shape and a population N which are appropriate for one lattice (e.g., the face-centered cubic) will not in general generate a lattice of different type (e.g., hexagonal). In this way the imposition of the periodic boundary condition further limits the ergodic character of the resulting molecular system compared to that of a macroscopic system, since one lattice arrangement cannot be generated from the other. Thus, with the presently feasible number of molecules, we cannot expect the method to give a correct account of the relative importance of alternative lattice arrangements in the structure of a condensed phase, at least not at distances greater than the cell dimensions. In principle, independent calculations based on a face-centered cubic lattice on the one hand, and a hexagonal lattice on the other hand, might resolve the question of the relative stability of the two arrangements of LJ molecules; in actuality the differences seem much too small to be resolved from the inherent statistical fluctuations.

It will be noticed also that the introduction of this approximation results in a certain similarity to the cell theories of the fluid state, the distinguishing feature being of course the large number of molecules per cell. It should be remarked that the boundary condition for motion in the adjacent cells is different from that usually introduced in the cell theories. Other ways of characterizing the effects of the periodic boundary condition are as an incomplete elimination of surface effects, distortion of long wavelength lattice vibrations, or distortion of large clusters. In view of the fair success of the simple cell theories, and on intuitive grounds, it seems likely that in spite of such defects the method should produce useful approximations to the thermodynamic properties of systems of LJ molecules. Empirically, one can attempt to assess its effect by comparing the results obtained with different N, as is done below for the cases of 32 and 108 molecules in the previously described cube. A rather limited investigation of the effect of a different cell shape (one appropriate for the hexagonal lattice) has been made on another isotherm, and will be reported in a future paper. Briefly, although significant differences in the outer part of the radial distribution function were found, the thermodynamic functions did not differ within the statistical fluctuations.

EVALUATION OF THE ENERGY SUMMATION

Although use of the periodic boundary condition allows us to approximate the behavior of an infinite sample, further specifications are required concerning the evaluation of the potential energy of any resulting configuration. If the results of the calculation are to be representative of a macroscopic system of Lennard-Jones molecules, the long-range character of the potential (combined with the small size of the systems which can be studied) requires that the energy sum include more than just the interactions of the N fundamental molecules. It is well known that the lattice energy sum for particles interacting according to the inverse sixth power is slowly convergent. For a face-centered cubic lattice, the contributions to the potential energy per molecule of interactions beyond (and not including) neighbors of order n can be expressed in the form

$$U^{(n)}/N = \epsilon^* (A^{(n)} \tau^{-4} - B^{(n)} \tau^{-2}), \qquad (13)$$

with the coefficients given in Table I; the values for $n=0$ are the complete sums including all interactions. The slow convergence of the attractive contribution is evident. For later use and for comparison with these values we also calculate the corresponding potential energy resulting from interaction of each molecule with a uniform distribution *outside* a shell of radius r, which is given by

$$U'(r)/N = 2\pi\sqrt{2}\epsilon^* (\tfrac{1}{9}x^{-9}\tau^{-4} - \tfrac{2}{3}x^{-3}\tau^{-2}), \qquad (14)$$

where $x=r/a$, a being the nearest neighbor separation. This expression is often used for estimating the previ-

TABLE I. Summation coefficients for the Lennard-Jones potential.

n	$A^{(n)}$	$B^{(n)}$	$a^{(n)}$	$b^{(n)}$	$x^{(n)}$
0	6.0659	14.454	...	...	...
1	0.0659	2.454	0.0934	2.700	1.300
2	0.0191	1.704	0.0299	1.847	1.475
3	0.0026	0.815	0.0026	0.816	1.936
4	0.0011	0.627	0.0012	0.638	2.100
5	0.0004	0.435	0.0004	0.444	2.37

ously defined lattice sums by setting $r=r^{(n)}$, where $r^{(n)}$ is chosen to be the radius of a sphere which, if filled at the macroscopic number density, contains as many molecules as are in all shells of the lattice of order n or less. With this correspondence and with

$$\frac{U'(r^{(n)})}{N} = \epsilon^* (a^{(n)} \tau^{-4} - b^{(n)} \tau^{-2}), \qquad (15)$$

we obtain the values shown in Table I. We note that $b^{(n)}$ and $a^{(n)}$ rather quickly become useful approximations to $B^{(n)}$ and $A^{(n)}$. This comparison forms the basis for the method of correction to be described later.

Considerations of machine speed obviously require some limitation on the number of interactions to be included in calculating the potential energy of any configuration. The most severe truncation, which is the fastest method and the one we have used most, is that used in the earlier work.[1,2] It may be characterized as the minimum-image distance method, and consists in considering for inclusion in the sum all pair interactions among the fundamental set of N molecules, but for each pair taking as interaction distance the smallest distance between any images of the two molecules. In the ex-

ample of Fig. 1, the interaction between the solid circle and circle I' in the central square would be computed as that between the solid circle in the central square with circle I in the lower left square. Only one such image interaction is calculated for each of the $\frac{1}{2}N(N-1)$ pairs. If the results from this convention are compared with a complete summation of all interactions without restriction (except for use of the periodic boundary condition), it is readily seen that the minimum image distance method includes all interactions at separations less than one-half the cell edge, but for longer range interactions includes a smaller and smaller fraction, decreasing to none beyond the cell diagonal. In terms of the radial distribution function, at relatively low densities it has its normal appearance in the range of smaller distances, but in the range from 0.5 to 1.73 times the cell edge decreases smoothly from values near one to zero. At higher densities, where the true radial distribution function begins to consist of a series of disconnected peaks, the minimum distance convention gives peaks in the range 0.5 to 1.73 times the cell edge which may be highly asymmetric, and of course much reduced in amplitude. For a face-centered cubic lattice, with 32 molecules the edge of the Monte Carlo unit cell is $2\sqrt{2}a$. Thus the minimum-distance convention begins to distort the true structure at $\sqrt{2}a$, which happens to coincide with the second shell of neighbors. With 108 molecules, the Monte Carlo cell edge is $3\sqrt{2}a$, and distortion begins between the 4th and 5th shells.

Since an appreciable increase in calculating speed can be obtained by excluding interactions which fall in the range of distortion (that is, between 0.5 and 1.73 times the cell edge) and since it seemed possible that excluding them entirely might introduce less error than including some of them in unsymmetrical fashion, the majority of the investigations reported here (speaking of those in which the minimum image distance convention was used) excluded all interactions at distances greater than half the cell edge. A few calculations in which this procedure was compared with inclusion of all minimum image distance interactions showed no significant differences in the radial distribution functions at distances less than half the cell edge. With this convention and a 32-molecule system, the 704 calculator generates about 19 000 configurations per hour. With 108 molecules the rate is about 6500 configurations per hour.

Inspection of Table I will suggest that the problem of estimating the contribution of the excluded interactions can become quite serious for the 32-molecule system, as will be discussed below. We have found that a useful procedure in this connection is a so-called "augmented" summation convention, in which *all* interactions between any molecule of the fundamental cell and all the other molecules and their images are included providing they are at distances less than an appropriately chosen maximum. This procedure was suggested by the fact that it will give correct results

in the extremes of a static lattice on one hand, and a uniform ideal fluid on the other. Test calculations comparing the minimum image distance convention for 108 molecules and this augmented convention for 32 molecules but including all interactions within the "distortionless" range of the larger system yielded radial distribution functions and thermodynamic functions which were not appreciably different. Under these conditions the augmented convention yields about 6300 configurations per hour. This is in some respects an improvement, timewise, over the 108-molecule-minimum-distance method, since a large number of configurations *per molecule* is undoubtedly very desirable in order to sample configuration space well. On the other hand the larger systems have smaller over-all fluctuations, so that the short-term statistical scatter is smaller and the average over a fixed total number of configurations correspondingly better determined. Also as earlier discussed, certain transition probabilities may be smaller than desirable in the smaller system because of the more severe restraints. Thus the augmented convention is useful only as a means of correcting for truncation of the energy summations of the minimum-image-distance 32-molecule chains.

FURTHER DETAILS OF CALCULATION

The procedure by which the calculator is caused to develop a chain of configurations in accordance with (11) and (12) is briefly as follows. Let the configuration existing at time t be called configuration j. One of the N molecules is selected at random (but uniformly) by use of pseudo-random numbers generated by the calculator; call this molecule r'. Again, by use of pseudo-random numbers, the molecule r' is given a new position in which each of its coordinates differs randomly and uniformly on the interval $(-\delta,\delta)$ from its value in configuration j. Designate the resulting configuration, which differs from j only in the position of molecule r', as configuration k. The potential energies U_j and U_k are then computed and compared. If U_k is less than U_j the configuration at time $t+1$ is taken to be configuration k, and the process begins over again. If the opposite is the case, the exponential appearing in (11) is calculated and compared with another pseudo-random number uniform on the interval (0,1). If the exponential is the smaller, the configuration at $t+1$ is j; if larger, it is k; in either case, the process then repeats.

In practice it is convenient to take the side of the Monte Carlo cell as unit of length. The desired reduced volume r then determines the magnitude of r^* in these units, while the desired reduced temperature θ becomes a multiplicative factor in the exponential Boltzmann factors, which in practice is absorbed into the scaling of the energy expressions. Little use is made of the floating-point arithmetic operations of the 704. Account must be taken of the indefinite increase of the LJ potential as the separation distance decreases. In the

present work, the potential as given by (1) has been modified as follows:

$$u(r) = \infty, \qquad r < r_1,$$
$$= u_{\mathrm{LJ}}(r), \quad r \geq r_1. \qquad (16)$$

The cutoff point r_1 is set at sufficiently high interaction energies so that their omission cannot be expected to appreciably change the thermodynamic properties of the system. We determined r_1 from the relation

$$u_{\mathrm{LJ}}(r_1) = u_{\mathrm{LJ}}(a) + 40kT. \qquad (17)$$

This has apparently been satisfactory, since when it is used the first few subdivisions of the cumulative distribution function (see below) have always been empty.

The total potential energy of a configuration is taken, using the assumption of additivity of pair potentials, as

$$U = \tfrac{1}{2} \sum_{ij}' u(r_{ij}), \qquad (18)$$

where r_{ij} is the distance between molecules i and j, and where the interpretation of the summation sign has been discussed above. Then the petite ensemble gives the excess molar internal energy E' as

$$E'/RT = \bar{U}/NkT, \qquad (19)$$

the excess (constant-volume) molar heat capacity C_v' as

$$\frac{C_v'}{R} = N\left[\left\langle\left(\frac{U}{NkT}\right)^2\right\rangle_{\mathrm{Av}} - \left(\frac{\bar{U}}{NkT}\right)^2\right], \qquad (20)$$

and the compressibility factor as

$$pv/RT = 1 - \left(\frac{\bar{\phi}}{3NkT}\right), \qquad (21)$$

where

$$\phi = \tfrac{1}{2} \sum_{ij}' r_{ij} \frac{du(r_{ij})}{dr_{ij}}. \qquad (22)$$

The bars in these formulas indicate the petite canonical ensemble averages or by the previously shown equivalence, the Monte Carlo or Markov chain averages. The codes used cause these quantities to be calculated as the Markov chain is developed, except that the earlier codes did not evaluate the heat capacity as given by (20). For convenience in monitoring the problem the calculator produces, in addition to the grand average of U/NkT used in (19), a sequence of subaverages of U/NkT each over a fixed number of consecutive configurations of the chain. The codes also classify each r_{ij} for every configuration into a suitable number of classes or counters in equal intervals Δr_{ij}^2 and maintain a continual count of the number in each counter. Step by step summation of the counters yields, after averaging over a sufficiently large number of configurations, the cumulative radial distribution

function giving the average number $N(r)$ molecules inside a sphere of radius r, excluding the reference molecule at the center. Differentiation of this cumulative distribution function gives the usual radial distribution function:

$$g(r) = \frac{v}{4\pi N_0 r^2} \frac{dN(r)}{dr}. \qquad (23)$$

The required numerical differentiation has usually been done using centered two or four-point difference formulas. There is of course statistical fluctuation in $N(r)$ which is magnified upon differentiation, and in addition we have sometimes not used a sufficient number of counters under the steeply rising inside of the first peak to obtain good detail on this portion of g.

The parameter δ appearing in (12), controlling the maximum difference between successive configurations, as previously mentioned affects the rate of convergence but not the finally convergent results. We have not studied in detail the effect of varying δ. In practice we have chosen δ so that successive configurations in the chain are identical approximately one-half the time. A satisfactory estimate has been the smaller of the two values $(a-r_1)/2$ or the rms amplitude of vibration calculated from the nearest-neighbor, harmonic-oscillator approximation to the Lennard-Jones-Devonshire cell theory. The pseudo-random numbers were obtained as appropriate portions of 70 bit numbers generated by the middle square process.

Except where otherwise mentioned, the initial configuration of the Markov chains has been taken as a regular face-centered cubic lattice arrangement. As discussed before, the convergence of the process should be independent of this choice, but we may reasonably expect to obtain more rapid convergence by omitting from the average the first few early configurations which are closely associated with the initial regular arrangement.

CORRECTION OF RESULTS

As mentioned previously, interactions at distances greater than those included in the Monte Carlo summation contribute importantly to the thermodynamic functions, and corrections for their omission must be applied to the direct results if they are adequately to represent the behavior expected of a macroscopic system of Lennard-Jones molecules. The procedure which we have used is as follows. From the calculated cumulative distribution function we choose the largest distance r_c in the "distortionless" region (r_c less than one-half the cell edge unless the augmented convention is used) at which $N(r_c)$ is equal to the sum of an integral number of neighbor shells of the f.c.c. lattice; for $N=32$ this sum is 12, for $N=108$ it is 54. All interactions at distances greater than r_c are removed from the Monte Carlo averages, by use of the calculated radial distri-

bution function and the relations

$$\frac{E'}{RT} = \frac{2\pi N_0}{vkT} \int u(r)g(r)r^2 dr, \qquad (24)$$

$$\frac{pv}{RT} - 1 = \frac{2\pi N_0}{3vkT} \int \frac{du(r)}{dr} g(r)r^3 dr. \qquad (25)$$

Next, two different estimates are made for the contributions of interactions at distances beyond r_c: one, called the "lattice correction," is calculated from (13) (and the analogous expression for pv/RT); the second, called the "fluid correction," is calculated from (14) (and its analog for pv/RT) with $r=r_c$. The discrepancy between these two values is taken as a measure of the systematic uncertainty in the corrected results, unless the appearance of the radial distribution function clearly indicates a preference for one or the other. The appearance also influences, of course, the decision as to whether to use one or the other pairs of values, or some combination of them, to correct the Monte Carlo results.

When the two estimates of the correction are quite different, and there is no clear preference for one or the other, as happens for the $N=32$ systems at the smaller reduced volumes, we cannot obtain a reliable correction without a better estimate of $g(r)$ for $r>r_c$. In this case we obtain the required information from a corresponding $N=108$ or "augmented" 32 chain, with use of the correction procedure just described based on the larger r_c for these systems. Examples of these various
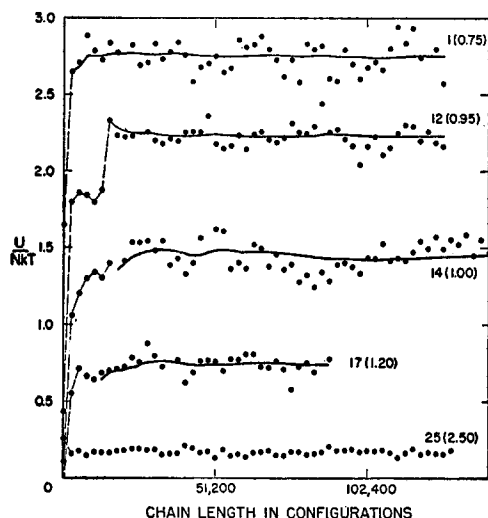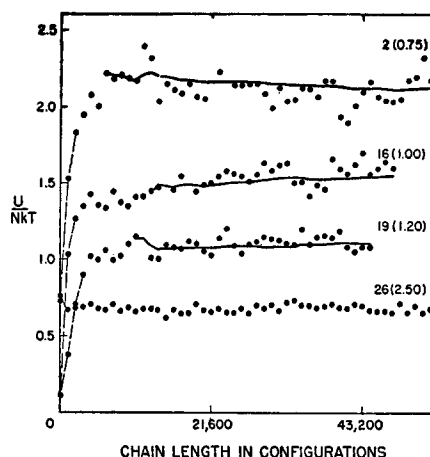

FIG. 3. Typical convergence and fluctuation of the reduced internal energy obtained with 108-molecule Monte Carlo chains at various reduced volumes. See the legend of Fig. 2. The abscissas should be multiplied by 4 for chain 16 and by 2 for chain 19. The origin for the ordinate scale is arbitrary, and different for each volume. For chain 26 the solid curve is omitted to avoid confusion.

methods of correction will be found below. No correction of the calculated C_v'/R values has been attempted, since this would require the triplet correlation function.

DISCUSSION OF RESULTS

The thermodynamic results obtained from the 31 chains calculated on this isotherm are shown in Table II. The extreme values given in columns 5, 6, and 7 are given primarily as indications of the over-all trend of the cumulative averages, and also as relatively crude measures of the statistical reliability of the reported results. On the whole, the agreement of the results from different chains tends to be compatible with the tabulated extremes. At all except the lowest densities, the average giving the excess heat capacity converges very slowly; this may indicate a comparatively slow convergence of the triplet correlation function, or may simply be due to the usual difficulty in estimating a variance by sampling techniques. The convergence of most of the 108-molecule chains is poor, due in part to the longer time required, and in part to our tendency to regard these chains as useful mostly for their radial distribution functions between $x=1.3$ and 2.1. In this region of the radial distribution function, convergence seems to be quite rapid; it is the first peak which equilibrates rather slowly. The two longest 108-molecule chains, at reduced volumes 1.0 and 0.85, show a slight tendency to give higher values of energy and pressure than the corresponding 32-molecule chains, but the differences cannot be said to be significant.

The best empirical comparison of the results of the two types of Markov processes[9] is among the four chains at reduced volume 1.00, where the agreement is seen to be quite good.

Graphs showing the convergence of the average

FIG. 2. Typical convergence and fluctuation of the reduced internal energy obtained with 32-molecule Monte Carlo chains at various reduced volumes. The first number in the label for each curve is the chain number from Table II; the second number, in parentheses, is the reduced volume. The solid curves show the variation of the cumulative average with increasing chain length. The circles represent the average over only those configurations generated since the preceding circle. The abscissa should be multiplied by 4 for chain 12. The origin for the ordinates is arbitrary and different for each volume. For chain 25 the solid curve is omitted to avoid confusion.

TABLE II. Equation of state results obtained by Monte Carlo calculation on the Lennard-Jones isotherm $kT/\epsilon^* = 2.74$.

Chain number[a]	Reduced volume v/v^*	Number of molecules[b] N	Number of configurations in averages[c] (in thousands; approx)	Reduced excess internal energy (corrected)[d] $\dfrac{E'}{RT}$	Compressibility factor (corrected)[d] $\dfrac{pv}{RT}$	Reduced excess heat capacity[d] $\dfrac{C_c'}{R}$	x_c	Corrections[e] $\dfrac{E'}{RT}$	$\dfrac{pv}{RT}$
1 (R)	0.75	32	128	−1.04(−0.01+0.04)	16.47(−0.04+0.13)	1.42(−0.04+0.12)	1.211	−1.55(−1.52;−1.96)	−2.91(−2.88;−3.51)
2 (R)		108	49	−0.97(−0.01+0.05)	16.77(−0.05+0.19)	1.40(−0.25+0.14)	2.102	LF(−0.41;−0.41)	LF(−0.81;−0.82)
3 (R)	0.80	32	256	−1.54(−0.01+0.00)	12.31(−0.03+0.02)	1.25(−0.07+0.14)	1.215	−1.38(−1.34;−1.73)	−2.61(−2.56;−3.16)
4 (R)		32 (A)	77	−1.51(−0.04+0.01)	12.44(−0.16+0.04)	1.28(−0.00+0.14)	2.103	LF(−0.36;−0.36)	LF(−0.71;−0.72)
5 (R)	0.85	32	256	−1.78(−0.00+0.05)	9.57(−0.00+0.22)	1.17(−0.04+0.05)	1.221	−1.24(−1.19;−1.53)	−2.36(−2.30;−2.83)
6 (R)		32 (A)	77	−1.75(−0.01+0.03)	9.72(−0.04+0.13)	1.24(−0.03+0.13)	2.101	LF(−0.32;−0.32)	LF(−0.63;−0.64)
7 (R)		32 (0.96)	204	−1.78(−0.01+0.01)	9.56(−0.04+0.06)	1.28(−0.11+0.02)	1.221	−1.24(−1.19;−1.53)	−2.36(−2.30;−2.83)
8 (R)		32 (0.92)	204	−1.76(−0.01+0.00)	9.68(−0.04+0.03)	1.21(−0.01+0.20)	1.221	−1.24(−1.19;−1.53)	−2.36(−2.30;−2.83)
9 (R)		108	186	−1.73(−0.00+0.03)	9.84(−0.00+0.16)	1.26(−0.03+0.23)	2.094	LF(−0.32;−0.32)	LF(−0.63;−0.64)
10 (R)	0.90	32	261	−1.86(−0.01+0.02)	7.81(−0.03+0.11)	1.30(−0.06+0.02)	1.229	−1.12(−1.07;−1.35)	−2.13(−2.06;−2.53)
11 (R)		32 (A)	77	−1.90(−0.00+0.01)	7.70(−0.02+0.04)	1.11(−0.07+0.06)	2.099	LF(−0.28;−0.29)	F(−0.56;−0.57)
12 (R)	0.95	32	463	−1.50(−0.00+0.02)	8.47(−0.01+0.09)	1.10(−0.03+0.03)	1.262	−1.01(−0.96;−1.14)	−1.96(−1.87;−2.17)
13 (S)	1.00	32	55	−1.60(−0.01+0.06)	7.03(−0.05+0.30)	...	...	...	...
14 (R)		32	128 (15)	−1.60(−0.02+0.04)	6.97(−0.12+0.19)	...	1.270	−0.92(−0.87;−1.01)	−1.78(−1.70;−1.94)
15 (R)		32 (0.95)	46	−1.62(−0.02+0.05)	6.90(−0.10+0.22)	0.85(−0.00+0.13)	1.270	−0.92(−0.87;−1.01)	−1.78(−1.70;−1.94)
16 (S)		108	140 (41)	−1.59(−0.03+0.01)	7.06(−0.18+0.06)	...	2.092	LF(−0.23;−0.24)	LF(−0.46;−0.47)
17 (S)	1.20	32	78 (13)	−1.57(−0.00+0.02)	4.08(−0.01+0.13)	...	1.290	−0.65(−0.61;−0.68)	−1.28(−1.20;−1.33)
18 (S)		32 (0.95)	49	−1.58(−0.00+0.02)	4.04(−0.01+0.13)	0.64(−0.01+0.05)	1.290	−0.65(−0.61;−0.68)	−1.28(−1.20;−1.33)
19 (S)		108	69 (22)	−1.59(−0.03+0.01)	4.01(−0.17+0.03)	...	2.101	F(−0.16;−0.16)	F(−0.32;−0.32)
20 (R)	1.40	32	58 (13)	−1.46(−0.01+0.01)	2.66(−0.02+0.07)	...	1.294	F(−0.45;−0.50)	F(−0.89;−0.98)
21 (R)	1.80	32	66 (13)	−1.17(−0.01+0.00)	1.64(−0.03+0.01)	...	1.302	F(−0.27;−0.30)	F(−0.54;−0.59)
22 (S)		108	58 (22)	−1.16(−0.02+0.00)	1.76(−0.13+0.00)	...	2.102	F(−0.07;−0.07)	F(−0.14;−0.14)
23 (R)	2.50	32	96 (53)	−0.86(−0.00+0.00)	1.13(−0.06+0.01)	0.21(−0.03+0.01)	1.296	F(−0.14;−0.16)	F(−0.28;−0.31)
24 (R)		32	29	−0.85(−0.01+0.00)	1.20(−0.08+0.00)	0.18(−0.04+0.00)	1.296	F(−0.14;−0.16)	F(−0.28;−0.31)
25 (R)		32	128	−0.85(−0.00+0.01)	1.18(−0.00+0.03)	0.19(−0.02+0.00)	1.294	F(−0.14;−0.16)	F(−0.28;−0.32)
26 (R)		108	54	−0.87(−0.01+0.00)	1.16(−0.09+0.01)	0.19(−0.04+0.00)	1.933	F(−0.05;−0.05)	F(−0.10;−0.10)
27[f](R)		32	64	−0.98(−0.01+0.00)	1.46(−0.02+0.01)	0.03(−0.00+0.01)	1.298	F(−0.14;−0.16)	F(−0.28;−0.31)
28 (R)	3.50	32	115	−0.61(−0.01+0.00)	1.03(−0.01+0.01)	0.14(−0.00+0.01)	1.287	F(−0.07;−0.08)	F(−0.14;−0.16)
29 (R)	5.00	32	38	−0.43(−0.00+0.01)	0.98(−0.01+0.01)	0.10(−0.00+0.00)	1.282	F(−0.04;−0.04)	F(−0.07;−0.08)
30 (R)		108	27	−0.44(−0.00+0.01)	0.98(−0.00+0.02)	0.11(−0.01+0.00)	2.100	F(−0.01;−0.01)	F(−0.02;−0.02)
31 (R)	7.00	32	115	−0.29(−0.00+0.00)	0.97(−0.01+0.00)	0.08(−0.00+0.01)	1.280	F(−0.02;−0.02)	F(−0.04;−0.04)

[a] The chain numbers are used for reference in the figures. The letters in parentheses refer to the method of generating the chain: R indicates that successive configurations are generated by a random choice of the molecule to be moved, as indicated in Eq. (12). S indicates that the molecules were moved sequentially, according to an initially assigned ordering, as in the earlier calculations of references 1 and 2.

[b] The letter A indicates that the augmented summation convention described in the text was used. Where a fraction f is given in parentheses, the initial f.c.c. lattice was slightly compressed into one corner of the Monte Carlo cell so as to reduce the intermolecular distances to f times their uncompressed values.

[c] The numbers in parentheses give the number of configurations (in thousands) utilized in determining the radial distribution function, in those cases where it differs from the number utilized in obtaining the thermodynamic quantities.

[d] The numbers in parentheses give the extreme values (with reference to the quoted average) of the Monte Carlo averages over the last three-fourths of the chain.

[e] Beyond the reduced cutoff distance $x_c = r_c/a$, the contributions to E'/RT and pv/RT were estimated by approximate radial distribution functions. The first number in parentheses corresponds to a perfect lattice, the second to the ideal fluid ($g=1$). LF (or F) preceding the parentheses indicates that the unweighted average of these two extremes was used (or the fluid value). Where numbers precede the parentheses, they are the corrections obtained from the radial distributions calculated from the chains at the same reduced volume, but with either 108 molecules or with the augmented summation convention. For chain 12 the corrections were obtained by weighted interpolation between the extreme values, the weight factors being themselves interpolated from their values at the adjacent volumes, as determined from the chains with larger N. For chain 13, for which no radial distribution function was calculated, the corrections were estimated from chains 14 and 15.

[f] Chain 27 was calculated using the modified Lennard-Jones potential of reference 4.

internal energy, as well as giving a qualitative picture of the fluctuation of successive averages over a small fixed number of configurations, are given in Fig. 2 for representative 32-molecule chains, and in Fig. 3 for 108-molecule chains. The behavior of chain 1 in Fig. 2 is representative of the other chains at reduced volumes less than 0.95. Except for the greater fluctuation, corresponding to the expected greater excess heat capacity, it will be noticed that the behavior is qualitatively similar to that at the larger volumes, exemplified by chains 17 and 25. The sudden jump occurring in the energy of chain 12 (Fig. 2), after it apparently began to level off at a lower value, was our first indication of the apparent transition to be discussed below. Previous

to obtaining this result, we had been accustomed to terminate the chains at about the point where the jump occurs in chain 12 (note that in Fig. 2 the abscissas are to be multiplied by 4 for this chain). When we observed this jump we lengthened chain 12 to the extent shown; since there seems to be no tendency to return to the low initial level, the low-lying first configurations were omitted from the reported averages. Furthermore, in order to guard against missing similar jumps at other volumes, the other chain lengths were also appreciably increased. At the slightly higher reduced volume 1.00, we have chain 14 (Fig. 2), which displays a more gradual buildup period followed by a

rather long period oscillation with more rapid fluctuations superimposed.

The 108-molecule chains in Fig. 3 show less stabilized averages, as expected from both their generally somewhat shorter absolute chain lengths, and the much shorter length in terms of configurations per molecule. This lack of convergence is particularly evident for chains 2 and 16. The lack of a long period oscillation in chain 16 (whose reduced volume is the same as that of chain 14) is possibly significant in terms of the absolute lengths of both chains, but not if the relevant comparison is in terms of chain length per molecule, as may well be the case.

Columns 8–10 of Table II concern the corrections mentioned earlier. Besides giving the actual corrections which were applied to the directly calculated results to obtain the values reported in columns 6–8, the extreme values obtained from a perfect lattice arrangement of the distant molecules on the one hand, and a uniform distribution on the other, are also displayed. It will be noticed that over the whole range of reduced volumes reported here, the two extreme estimates are essentially identical for the 108-molecule chains, well within the statistical precision of the directly calculated contributions. Furthermore, for the 108-molecule chains the tabulated value of $x_c = r_c/a$, obtained as described earlier, in each case agrees closely with the corre-

FIG. 5. Reduced excess internal energy *versus* reduced volume. See the legend for Fig. 4. The solid curve represents Michels' experimental results; the dashed curve, the Lennard-Jones-Devonshire cell theory.

sponding value in Table I.[10] These observations indicate that there should be little systematic error in the corrections applied to these chains. Thus we believe that the 108-molecule results have as principal source of uncertainty their relatively short length and correspondingly poorer statistical convergence.

For the 32-molecule chains, where the directly calculated contributions are used only through the first shell of 12 neighbors, Table II shows that the necessary correction is poorly bracketed by the two extremes at the higher densities. Here, therefore, we have followed the previously described procedure of estimating the necessary corrections from chains having a longer range of intermolecular interaction. It is believed that this procedure is quite reliable as an estimate of the excluded interactions. It is to be emphasized, of course, that these corrections cannot be expected to result in complete agreement between 32-molecule and 108-molecule chains. They are concerned with the gross effects of truncating the energy sums, and simply supply estimates of the omitted interactions. They cannot account for the likelihood that inclusion of the missing contributions would alter to some extent the distribution of the directly calculated interactions. The reasonably good agreement shown in Table II encourages us to believe that such effects are reasonably small.

In Figs. 4, 5, and 6 the values of the thermodynamic functions are compared with the experimental p-v-T data for argon obtained by Michels[6] and Bridgman,[7] as well as the thermodynamic functions derived from Michels' data. In both cases 55°C isotherms were used, and conversion to reduced volume v/v^* as independent variable was made with use of the previously mentioned value of v^*. In the figures comparison is also made with the two theoretical equations of state mentioned earlier, the Lennard-Jones-Devonshire cell theory[3] and the
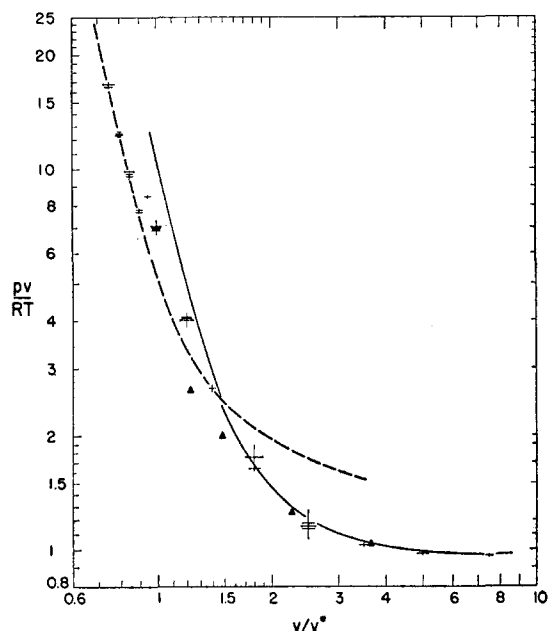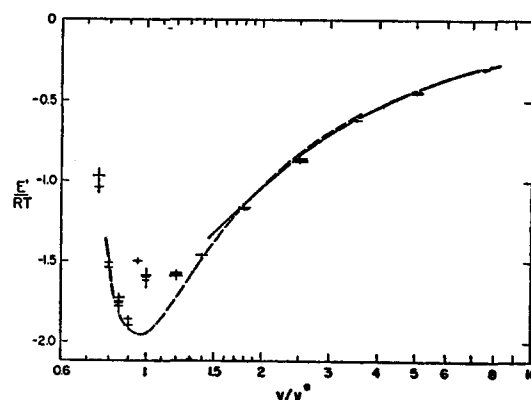
FIG. 4. Compressibility factor *versus* reduced volume. The horizontal bars represent the positions of the Monte Carlo averages; those bearing the small dots at their ends represent results from 108-molecule systems. The vertical extent of the symbols covers the range obtained by subtracting from and adding to each average the difference of largest magnitude shown for it in column 6 of Table II. The upper solid curve represents Bridgman's measurements on argon; the lower one, Michels' measurements. The dashed curve is the Lennard-Jones-Devonshire cell theory isotherm. The triangles are the superposition integral equation results of reference 5.

[10] The value of x_c shown in Table II for chain 26 corresponds to a cumulative distribution function equal to 42 (three complete f.c.c. shells), and also agrees well with the corresponding value in Table I.
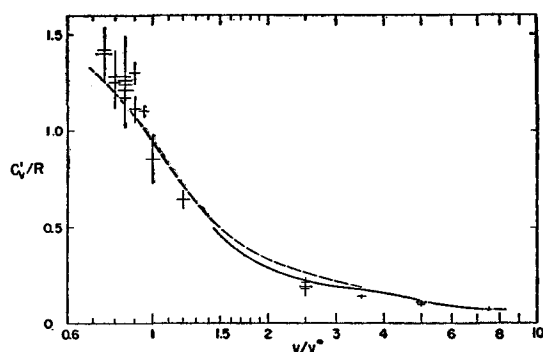
FIG. 6. Reduced excess constant-volume heat capacity *versus* reduced volume. See the legend for Fig. 4. The solid curve represents Michels' experimental results; the dashed curve, the values obtained from the Lennard-Jones-Devonshire cell theory.

Kirkwood-Born-Green theory.[4] With the cell theory, we have of course used the same Lennard-Jones potential as in the Monte Carlo calculations reported here. The Kirkwood-Born-Green equations were solved[4] for a modified Lennard-Jones potential which satisfies (15) with $r_1 = 2^{-1/6} r^*$, the hard core beginning at the cross-over point of the ordinary LJ potential. Zwanzig *et al.*[5] attempted a rough correction to make the results applicable to the LJ potential; these are the points shown in Fig. 4.

In discussing Figs. 4–6 it is convenient to distinguish three reduced volume intervals according to the available experimental information. In the range 1.5 to 10, we have Michels' extensive *p-v-T* data and the derived thermodynamic functions. Between 0.95 and 1.5 we have Bridgman's *p-v* values, but no thermodynamic functions. In the range 0.75 to 0.95 there is no experimental information. Throughout Michels' region the Monte Carlo compressibility factors (Fig. 4) are in essential agreement with the experimental values. At the largest volumes there is a tendency for the calculated values to be slightly low, by a percent or so. In the higher density portion of Michels' range the deviations are larger, about 5%, but the scatter in the Monte Carlo results is quite comparable. The *pv/RT* values of Zwanzig *et al.*[5] are seen to approach the experimental results at low density, but tend to become too low as the density increases. Those of the cell theory are of course quite poor in this region. The excess internal energy (Fig. 5) obtained from the Monte Carlo calculations tends to be slightly low by amounts close to the limits of significance at Michels' high density limit, the agreement improving as the density decreases. Such agreement is not extremely significant, since even rather crude approximations such as the cell theory give quite reasonable values of the energy in this range in which their errors in pressure are very large. Thus the divergent trend at higher densities may very well be significant. The Monte Carlo and experimental heat capacities shown in Fig. 6 are also in reasonably good agreement. Here again, however, so crude a treatment

as the ordinary cell theory gives comparably good results.

Bridgman's experimental results begin where those of Michels' end, with a small discontinuity of about 5% in the compressibility factor; there is also a noticeable discontinuity in the slopes of the two curves at this point. In the range of Bridgman's volumes, the Monte Carlo results give much lower values of *pv/RT*, amounting to 30% and more at the highest pressures. We do not wish to minimize this disagreement, since it is perfectly possible that either the LJ pair potential itself or the assumption of additivity of pair potentials may be responsible. However, two points may be worth mentioning. First, the Monte Carlo points seem to represent the more natural continuation of Michels' curve. Secondly, comparison of more recent *p-v-T* data[11,12] for nitrogen with those of Bridgman reported in the same paper[7] as his argon data shows comparable differences. Benedict's data was obtained in Bridgman's laboratory, and Professor Bridgman[13] has stated that he believes this more recent data to be better, and that the argon data may well be no more reliable than the earlier results for nitrogen. Thus, the significance of the disagreement in this region remains an open question, until the *p-v-T* behavior of argon is carefully reinvestigated. In this region of volumes (0.95 to 1.5 in v/v^*), the cell theory gives too small values for *pv/RT*. No experimental values of internal energy and heat capacity are available in the Bridgman region. The Monte Carlo energies in this region deviate strongly from those of the cell theory, passing through a smaller (in absolute value) minimum at a larger volume than the latter. The heat capacity results are quite scant, and begin to show large scatter, but are compatible with the apparent trend of Michels' data as are those of the cell theory also.

At still smaller volumes than reached by Bridgman we observed the very interesting behavior shown in Figs. 4 and 5, where the points for reduced volumes 0.90 and less are seen to lie on an essentially different curve from those at the larger volumes. A number of considerations have led us to identify the region of the break in the curve with the first-order transition between fluid and solid (crystalline) phases; the qualitative appearance of Figs. 4 and 5 corresponds to this behavior. To discuss first the corresponding behavior of argon molecules, the melting curve has been investigated by Bridgman[7] and by Robinson,[14] but has not been carried up to the temperature of our isotherm. Extrapolation of Robinson's results by means of the empirical Simon relation between *p* and *T* along the coexistence line indicates that the freezing pressure of argon at this temperature should be about 13 500 atmos. Bridgman's measurements are the only ones

[11] M. Benedict, J. Am. Chem. Soc. **59**, 2233 (1937).
[12] D. S. Tsiklis, Doklady Akad. Nauk USSR **79**, 289 (1951).
[13] P. W. Bridgman (private communication).
[14] D. W. Robinson, Proc. Roy Soc. (London) **A225**, 393 (1954).

giving the volume change upon fusion. A rough extrapolation suggests a volume increment of somewhat less than 0.8 cm³/mole, which would be an increment of about 0.03 on our reduced volume scale. Over the range of roughly 1000 to 6000 atmos, Bridgman obtained (from his p, v, T measurements by use of the Clapeyron equation) an essentially constant enthalpy of fusion of about 260 cal/mole. If the same value obtains at 328°K, $\Delta H/RT$ would be approximately 0.40.

Turning to the Monte Carlo results in the vicinity of the apparent transition, several observations are in order. First and foremost, the small number of molecules, the periodic boundary condition, and the formal equivalence of the Monte Carlo method to the *petite* canonical ensemble, will all have an effect on the results to be expected across a first-order phase transition.[15] Secondly, we may very well expect the Monte Carlo process to be slowly convergent, with possible appearance of metastable plateaus of long chain length, in such a transition region (chain 12). Thus a detailed investigation of such a region might well be extraordinarily time consuming, particularly since it would undoubtedly be essential to investigate the dependence of the results on the number of molecules. Thirdly, we have too few points to permit even a Maxwell equal-area determination of the coexistent phases of the 32-molecule Monte Carlo system. Thus, although the existence of an apparently first-order transition seems indicated by our results, the parameters characterizing it are very crudely determined. Furthermore, the dependence of the transition on the number of molecules has not been investigated as well as would be desirable, since little confidence could be placed on anything but chains much longer than any obtained to date with 108 molecules. Thus, it has not seemed worthwhile to generate 108-molecule chains at the two points on the apparent boundary of the transition region ($v/v^*=0.90$ and 0.95). At the two next adjacent volumes (0.85 and 1.0) we do have our two longest 108-molecule investigations. In both cases the resulting pressures and energies are slightly higher than the corresponding 32-molecule results, but the convergence of the larger systems in both cases leaves something to be desired, and we hestitate to attribute significance to the differences. In any case, the qualitative nature of our results is not changed. It should be pointed out that the existence of a break in the curves would be indicated even if the results at $v/v^*=0.90$ and 0.95 were ignored, especially in the case of the internal energy curve. In order to check the stability of our results in this vicinity with respect to perturbation of the initial configurations, we generated chains 7, 8, 15, and 18, in which the ordinary regular initial array was slightly compressed into one corner of the Monte Carlo cell. In the case of chain 8 this compression was sufficient to raise the initial potential energy noticeably above

the average value. In all cases the results are in essential agreement with the normally started chains. Thus, the transition behavior seems not to be an artifact introduced by any of the approximations which we can investigate. It is to be noted, as far as the ergodic question is concerned, that the usual regular initial configuration and the compressed one just mentioned obviously are members of the same class, so that such agreement as obtained should be expected.

With due regard for the limitations mentioned in the previous paragraph, it is still of interest to compare the rough values of the transition parameters obtained by Monte Carlo with those to be expected for argon. The values of pv^*/RT are 8.6 at $v/v^*=0.90$, and 8.9 at $v/v^*=0.95$. Thus, we have an apparent region of mechanical instability, but on the borderline of statistical significance. If the previously mentioned parameters for argon are used to convert to the physical pressure scale, these two points correspond to a pressure of about 10 000 atmos, rather lower than the expected freezing pressure for argon at this temperature. The difference of 0.05 in the reduced volumes is somewhat larger than the value 0.03 estimated from Bridgman's data. The difference in melting pressures may be significant; another way of stating it is that Robinson's data indicate quite clearly that under a pressure of 10 000 atmos argon should melt at about 270°K.

If the difference in E'/RT at $v/v^*=0.90$ and 0.95 is taken as $\Delta E/RT$ for the transition, and the values $p=10\,000$ atmos and $\Delta v/v^*=0.05$ are used, we find $\Delta H/RT=1.0$. This is two and one-half times the value extrapolated from Bridgman's measurements at 6000 atmos. The interpretation of these differences in melting parameters is not clear, if they really represent convergent behavior of the 32-molecule system. They could possibly be due to the small number of molecules used in our calculations. But they could well be due to departures of the argon potential energy from the additive Lennard-Jones form; it may be expected that high-pressure melting phenomena will be quite sensitive to the details of the repulsive potential.

The heat capacity results in this region are too scattered to allow much interpretation; there is a slight tendency to lie above the cell theory curve. There is no sign of the separated high segment of the curve to be expected in the coexistence region,[16] but this can hardly be surprising in view of uncertainty as to the exact position of this region, as well as the unanswered questions involving the necessary length of chain, etc.

The sudden improvement in agreement of the cell theory with our Monte Carlo results on the solid side of the transition is very striking. This may be associated with another striking observation, which increases our confidence in the reality of the observed transition. The calculator codes used do not study in detail the

[15] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Appendix 9.

[16] See, for example, the experimental measurements by A. Michels and J. Strijland, Physica 18, 613 (1952), of C_v for CO_2 in the liquid-vapor coexistence region.
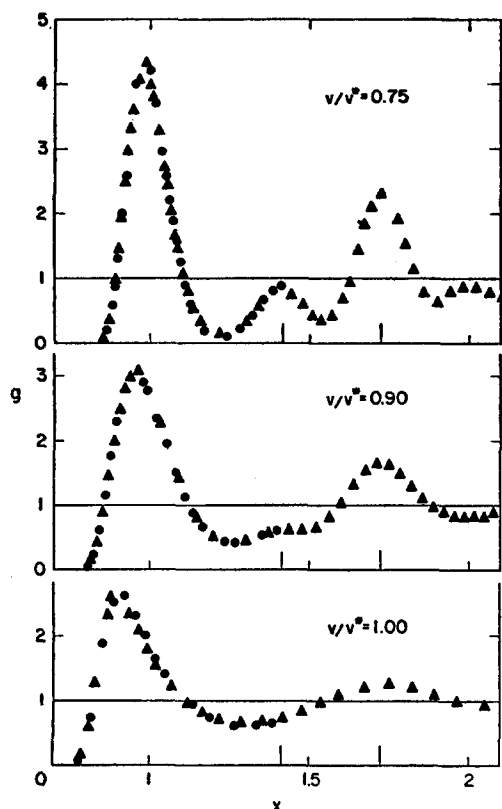
FIG. 7. The radial distribution function g versus the reduced distance $x=r/a$, in the neighborhood of the apparent transition. The circles were obtained from the 32-molecule chains 1, 10, and 15; the triangles, from the 108-molecule (or "augmented" 32) chains 2, 11, and 16.

diffusion of the molecules through the Monte Carlo cell. However, we compared the positions and arrangements of the molecules in the final configurations of chains 1, 3, 5, 10, 12, and 14 with the original regular lattice structures. For the chains on the solid branch (volume 0.90 and less), the relative positions of all the molecules with respect to one another were the same as at the start except for more or less haphazard displacements from a regular lattice small compared to the distance between nearest neighbors. (All molecules had in some cases moved through the cell essentially in unison, subject to the periodic boundary condition, as might be expected if the system as a whole is describing a sort of symmetric random walk, all molecules being essentially in step in formation.) This is in great contrast with the observations at volumes 0.95 and 1.0, where the final arrangement was in both cases completely disordered with molecules appearing in random fashion at positions well removed from where they began.

The appearance of the radial distribution functions on the two sides of the transition region is shown in Fig. 7.[17] There seems to be no abrupt change in their

[17] A set of tables of the cumulative distribution functions obtained from 29 of the 31 chains is available in limited number

qualitative appearance as the transition region is crossed, the peaks simply becoming increasingly well defined as the density increases. Radial distribution functions at larger volumes are shown in Fig. 8, where they are also compared in two instances with the results of the Kirkwood-Born-Green[4] theory. It must again be emphasized, however, that the latters' radial distribution functions correspond to the previously mentioned modified LJ potential. In order to determine how much of the discrepancy is due to this difference in the intermolecular potential, and how much to introduction of the superposition approximation, chain 27 was generated in which we used the same modified potential in a Monte Carlo calculation. In Fig. 9 these Monte Carlo and superposition radial distribution functions are compared; much of the discrepancy has been removed by using the same potential function. The superposition values for E'/RT and pv/RT are, respectively, -0.99 and 1.31. Thus there is essential agreement in the values of the energy, and a residual difference of about 10% in the compressibility factor, some of which however may be due to uncertainty in the precision of our single Monte Carlo chain for these conditions. Thus at this fairly large volume the superposition approximation is seen to give fairly good results.
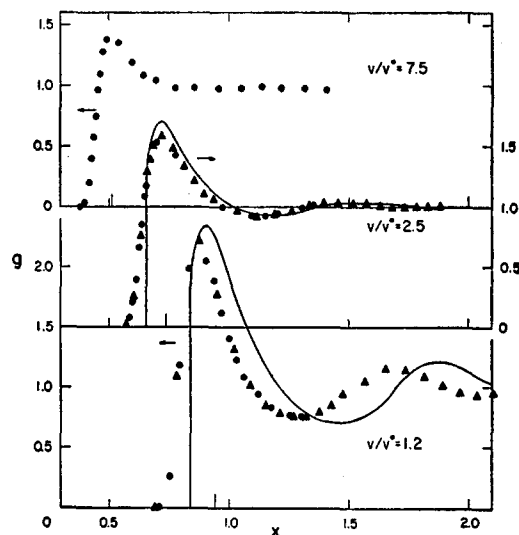

FIG. 8. The radial distribution function g versus the reduced distance $x=r/a$, in the fluid region. The circles are from the 32-molecule chains 31, 25, and 18; the triangles, from 108-molecule chains 26 and 19. The curves are the superposition integral equation results for the modified Lennard-Jones potential (reference 4).

from one of the authors (W. W. Wood). They may also be obtained as Document No. 5330 upon remitting $5.00 for a photoprint or $2.25 for a 35-mm microfilm copy to Chief, Photoduplication Service, ADI Auxiliary Publications Project, Library of Congress, Washington 25, D. C. The tabulations consist of values of $N(x)$ at mostly equally spaced intervals in x^2.
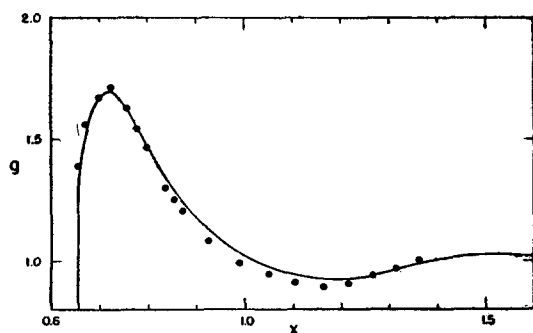
FIG. 9. Comparison of Monte Carlo and superposition-integral equation radial distribution functions for the same modified Lennard-Jones potential. The points are from chain 27; the curve from the tabulations of reference 4. The reduced volume v/v^* is 2.5.

CONCLUSIONS

The essential agreement of our calculations with Michels' data suggests that in this region effects of deviations from the Lennard-Jones pair potential and additivity of pair potentials are fairly small. A reinvestigation of the experimental behavior of argon in the Bridgman region would be very useful for a further assessment of the magnitude of these effects. At volumes removed from the transition region our 32-molecule chains are intentionally much longer (by perhaps a factor of 3 or 4) than needed to obtain useful results, in order to establish with some certainty that the unusual behavior observed is really peculiar to that region. On the other hand, it seems likely that even the 32-molecule chains cannot practically be made long enough to study the detailed behavior in the transition region, and a study of the effect of the number of molecules seems completely out of question. Thus, we shall await the availability of calculators of considerably higher speed before undertaking these investigations. Even outside the transition region, except at the lowest densities, it would be desirable to have 108-molecule chains several times longer than those reported here in order to make a precise assessment of the effect of the number of molecules. The present results are, however, certainly compatible with the hypothesis that these are small.

The simple cell theory seems to be unsatisfactory in the entire fluid region, but is surprisingly good in the crystalline region. The present results should be useful in assessing the effect of various elaborations of the cell theory in the fluid region. The superposition approximation used with the (otherwise rigorous) Kirkwood-Born-Green theory seems likely to be useful on this isotherm at least for volumes greater than 2.5.

As this material was being prepared for publication, we learned of the results for the equation of state of hard spheres obtained by Alder and Wainwright[18] from a numerical integration of the elementary equations of motion. In the range of reduced volumes from 1.5 to 2.0, Alder and Wainwright found substantial discrepancies between their results and the Monte Carlo results reported by the Rosenbluths.[2] We are currently repeating the Monte Carlo investigation, and have already found the earlier Monte Carlo results in the region in question to be wrong, apparently because of insufficient chain length. This investigation, as well as the other Lennard-Jones isotherms previously mentioned, will be the subject of further papers.

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[18] B. J. Alder and T. Wainwright, Proc. I.U.P.A.P. Symposium on Statistical Mechanical Theory of Transport Processes, Brussels, 1956 (to be published).