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Numerical Investigations of a Simple Model of a One-Dimensional Fluid[1]

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ABSTRACT

Various properties of a one-dimensional fluid with nearest neighbor interactions have been studied with the help of a high-speed computer. Because of the simplicity of the interaction potential employed, it is possible to follow the dynamical evolution of the system and so compute meaningful time averages. At the same time, one can compute the values of the corresponding phase averages and so compare the two results. In computing the phase averages it was necessary to use the Lebowitz-Percus method for relating phase averages calculated with one type of ensemble to those calculated with some other type. This necessity arises because one can compute phase averages for an isobaric canonical ensemble in closed form with the type of forces involved, while one needs phase averages for a microcanonical ensemble in order to compare with the time averages. The results of our investigation very clearly showed the necessity of using the latter ensemble in making this comparison. In one case, using a thousand particle system we found the time average of $\beta = 1/kT$ to be 4.8353. Its value for an isobaric-canonical ensemble was 4.8261 while for a microcanonical ensemble it was 4.8343. In addition to the above equilibrium studies, we have considered the approach to equilibrium of our system starting from a manifestly non-equilibrium state.

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INTRODUCTION

With the advent of high-speed computers the possibility arose of the numerical study of simple N-body systems where $N > 10$. For the most part these calculations were restricted to a determination of equations of state for these systems. Thus, Alder and Wainwright [1] studied the equation of state for a system of hard spheres in three dimensions and found, for certain conditions, that it could exist in two distinct states which they called the solid and liquid phase. Some computations dealing with nonequilibrium configurations with an end to studying the equipartition of energy as the system approached equilibrium were undertaken by Fermi, Pasta, and Ulam [2] and more recently by Northcote and Potts [3]. As a preparatory exercise to the study of a realistic model for a liquid, we undertook the numerical study of a one-dimensional system of hard rods with a short-range linear attractive potential between particles. On the basis of knowledge gained by studying such a system, we are now in the process of investigating the more realistic model of hard discs or spheres with short-range harmonic forces between them. Nevertheless the results of this preliminary study seemed to have enough interest in themselves as they bear on the general problem of N-body machine computations that we felt justified in setting them forth in this paper.

The main advantage of our model is that it allows one to follow the dynamical evolution of the system over relatively long periods of time, and hence to compute meaningful time averages of dynamical variables along a trajectory of the system. In our discussion we shall refer to these averages as the "measured" values of the quantity under consideration. Thus an evaluation of the time average of the mean square velocity yields a measurement of the temperature of the system. These measured values can then be compared with the corresponding theoretical values as determined from statistical mechanics. Since the system considered had a constant volume and energy, phase averages should be calculated using a microcanonical ensemble. However, closed form expressions for phase averages could only be obtained using an isobaric canonical ensemble. These averages were then corrected to first order in $1/N$ to give values for the microcanonical ensemble by a method due to Lebowitz and Percus [4]. The measured values of the temperature were accurate enough to distinguish between the corrected and uncorrected averages and agreed with the corrected values in some cases to 1 part in 10^4.

Our pressure measurements were much less accurate than those of temperature, agreeing with the theoretical values to only about 1 part in 100. This was to be expected since the pressure measurement involved the evaluation of the time average of the momentum transfer to the walls on the system. Within a one-dimensional system, only one particle can interact with each wall. We also measured the pressure of the system indirectly by measuring the pair distribution function for the system and making use of the virial theorem. In general, this latter measurement gave better agreement with theory then did the wall pressure determination.

A second study was related to the accuracy of a machine calculation and involved finding the extent to which a computed trajectory could be time reversed. Starting with a given set of initial data we computed a trajectory up to some point T. The final positions and velocities of the particles were then taken as initial data for a new trajectory, the time-reversed trajectory of the original trajectory, which was also computed up to the point T. We then determined how large T could be (number of collisions) before the final configuration of the time-reversed trajectory deviated significantly from the initial configuration of the original trajectory. Even for the simple system considered where the trajectory between collisions could be determined analytically it was only possible to get coincidence between the two configurations for a time corresponding to about 40–50 collisions per particle. We conclude, therefore, that it would be completely meaningless to use a machine to observe a Poincaré recurrence cycle for any but the simplest few particle systems. The test of reversibility is, of course, the most severe test of accuracy of a calculation of a trajectory. Nevertheless, one should keep in mind that once one passes the reversal point in a given trajectory calculation one is looking not at the pure dynamical evolution of the system but at the dynamical evolution of the system in interaction with what is effectively a thermal bath represented by the random errors introduced into the calculation by rounding (which was always done by truncation) approximations, etc.

We also investigated the problem of the approach to equilibrium of our system when its initial configuration is manifestly not an equilibrium configuration. The problem here, of course, is to characterize an equilibrium configuration for a closed system. We have examined various criteria for this purpose. Among others, we took the deviation of the velocity distribution from a Gaussian distribution, as measured by a

χ^2-test, as a measure of the deviation from equilibrium. In many regards this test appears to be a rather sensitive test, and it is possible to observe the decrease in χ^2 from an initially large value corresponding to an initial nonequilibrium configuration to a final low value which one would expect corresponding to a Gaussian distribution. However, there are initial configurations, e.g. velocities Gaussianly distributed with all the particles filling only a portion of the available volume, for which the χ^2-test gives a poor indication of the deviation from equilibrium. We also looked at the change in the coarse-grained entropy of the system as a measure of the deviation from equilibrium. While it tended to increase, as one approached a Gaussian velocity distribution, it did not change percentage-wise nearly as rapidly as did χ^2. Furthermore, one had to choose the size of the velocity cells with some care in computing this quantity before meaningful results could be obtained.

I. Description of the Model

The system we undertook to study consisted of N rods of unit length and unit mass confined to a box of length $L > N$. A short range attractive potential was assumed to exist between neighboring rods of such a nature that the attractive force was constant inside this range and zero outside. Thus, if r_i represents the distance between the centers of the ith and $(i-1)$th rod measured in units of the rod length, $V(r_i)$ has the form of a hard core plus triangular well:

$$V(r_i) = \begin{cases} \infty, & r_i < 1 \\ V_0(r_i - 2), & 1 < r_i < 2 \\ 0, & 2 < r_i \end{cases} \tag{1}$$

where V_0 is a constant. While this potential is too simple to approximate a real molecular potential [one would have liked to use at least a parabolic attractive potential in the interval (1,2)], it has the great advantage that the motion of the system can be described in terms of known simple linear and quadratic functions of the time between collisions. As a consequence, the main purpose of a computer is to keep track of the momentum changes, which are of course known exactly, during collisions.

The solution of the equations of motion for an N-body system with

interparticle potential (1) is, of course, quite simple. Consider a clump of N particles such that all particles in the clump are closer together than 2 units, so that they are all interacting. Only two cases need be considered. An interior particle sees no forces acting on it between collisions and hence moves as a free particle. The end particles see a constant attractive force and again their equations of motion can be easily integrated between collisions. Thus, we have the following solutions for the ith particle position x_i:

(i) particle i is an interior particle in a clump or not part of a clump

$$x_i(t) = x_i^0 + v_i^0 t \tag{2a}$$

(ii) particle i is an end particle in a clump

$$x_i(t) = \pm \tfrac{1}{2} V_0 t^2 + v_i^0 t + x_i^0 \tag{2b}$$

for particles of unit mass. The $\pm$ is according to whether the particle is in the left or right end of a clump. In both cases x_i^0 and v_i^0 are the values of position and velocity, respectively, at time t_0, and x_i is measured from the left wall of the container.

The potential $V(r)$ has two singular points, one at the hard core where $r = 1$ and one at the end of its range where $r = 2$. In the former case the two particles collide and exchange momentum while in the latter case the forces on the particles change. In both cases one must change the analytic solution of the two particles involved. During a collision both energy and momentum are conserved so that, if their velocities before collision were v_i^- and v_{i+1}^- they will be $v_i^+ = v_{i+1}^-$ and $v_{i+1}^+ = v_i^-$ after the collision. Thus one must use either (i) or (ii) to compute v_i^- and v_{i+1}^- at the time of collision and replace v_i^0 and v_{i+1}^0 in these solutions by v_i^+ and v_{i+1}^+ to obtain the solutions after collision. In the case of a separation or a joining, i.e., where $r_i = 2$, the forces on the particles involved change, and so at these singular points one must replace solution (i) by (ii) or vice versa for the particles involved.

II. Method of Calculation

There are essentially two different methods of computing the over-all trajectory of the system starting from a set of initial data. One could determine the time at which the first singular event occurs by finding

all of the times for which each $r_i = 1$ and 2, and then finding the smallest of these times. One would then make the necessary changes in velocities or trajectory equations as outlined above and recompute the times for the occurrence of singular events. The smallest of these recomputed times would then determine the next singular event and so on. Proceeding from one singular event one could determine the configuration of the system at any time. However, for many purposes it is desirable to know the configuration of the system at regularly spaced time intervals during the evolution of the system. While this information could be obtained from the above method of computation, we found that an alternate method of computation was more convenient for this purpose and also more efficient.

The second method of computation used by us was to compute the final configuration of the system after some fixed interval of time Δt, but neglecting singular events. Then in general several of the r_i will be less than 1 indicating that the corresponding particles actually collided sometime in the interval Δt. One finds the times at which these collisions occurred, makes the necessary changes and recomputes the final positions and velocities for these colliding particles. Likewise, one can develope criteria for when a split or a joining should have occured, again go back to these times, make the necessary changes for such an occurrence, and again recompute the final positions and velocites for the particles involved. In this way one gets the final corrected configuration of the system at the end of the interval. If Δt is not too large only a few readjustments need be made. The final configuration is now taken as the initial configuration for the next interval. Proceeding in this way, one obtains a step-wise description of the evolution of the system together with a set of configurations.

Using an IBM 7090 to carry out the above-outlined calculations we were able to calculate for a 100-particle system at the rate of about 20 collisions per second of machine time, using double precision. For 1000 particles in a comparable situation, this rate was cut to 10 collisions per second. We might compare this rate with that attained by Potts (personal communication) for calculations on a linear system of harmonically bound hard rods. For a 31-particle system he was able to calculate 100 collisions per particle in 70 minutes or 44 collisions per minute. Thus the change from a linear to an harmonic force, even neglecting separations and joinings, changes the computing rate by an order of magnitude.

III. Statistical Mechanics Predictions

Since we are dealing with a system in one dimension with nearest neighbor interactions it is possible to evaluate the partition function as well as the distribution functions for the system and hence make a direct comparison between the results of equilibrium statistical mechanics [5] and those obtained from the calculation of the detailed dynamics of system.

We consider our particles as being enclosed in a one-dimensional box of length L with interparticle interactions given by Eq. (1). The wall potential $V_w(r)$ is given by

$$V_w(r) = \begin{cases} \infty, & r \leq \frac{1}{2} \\ 0, & r > \frac{1}{2} \end{cases}$$

where r is the distance between the wall and the particle nearest it. Then, for a canonical ensemble, the partition function for an N-particle system is given by

$$Z(L, \beta) = \int_0^{\infty} \cdots^{(N+1)} \int \exp\left[-\beta \left\{ V_w(r_1) + \sum_{i=2}^{N} V(r_i) + V_w(r_{N+1}) \right\} \right] \cdot \delta\left(L - \sum_{i=0}^{N+1} r_i \right) \prod_{i=1}^{N+1} dr_i. \tag{3}$$

In general one cannot evaluate the integrals appearing in the expression for $Z(L, \beta)$. However, by going over from the canonical ensemble (fixed L and β) to an isobaric ensemble (fixed p, β) by means of a Legendre transformation, it is possible to evaluate the partition function for this ensemble. Thus defining

$$W(p\beta, \beta) \equiv \int_0^{\infty} Z(L, \beta) \exp(-p\beta L)\, dL$$

one finds that

$$W(p\beta, \beta) = f_0^2(p\beta, \beta) f^{N-1}(p\beta, \beta)$$

where here

$$f_0(p\beta, \beta) = \frac{\exp(-\frac{1}{2} p\beta)}{p\beta}$$

and

$$f(p\beta, \beta) = \frac{\exp(-p\beta + \beta V_0) - \exp(-2p\beta)}{\beta V_0 + p\beta} + \frac{\exp(-2p\beta)}{\beta p}$$

$$= \exp(2\beta V_0) \frac{\exp(-\beta\{V_0 + p\} - \exp(-2\beta\{V_0 + p\}}{\beta V_0 + p\beta}$$

$$+ \exp(2\beta V_0) \frac{\exp(-2\beta\{p + V_0\}}{p\beta}.$$

For this ensemble we can calculate average values of L and E:

$$\bar{L}(p\beta, \beta) = -\frac{\partial \ln W}{\partial p\beta} \tag{4}$$

and

$$\bar{E}(p\beta, \beta) = -\frac{\partial \ln W}{\partial \beta} \tag{5}$$

The only trouble with the above procedure is that we are not observing an isobaric ensemble but rather time averages of a system with constant L and E. According to the fundamental assumption of statistical mechanics, these averages are equal to ensemble averages of a microcanonical system. Consequently, in order to make a comparison between our observed averages of β and $p\beta$ we must relate average values in the two ensembles. Since the two averages differ only by terms $\sim 1/N$ where N is the number of particles in the system, we can make use of the approximation procedure developed by Lebowitz and Percus [4] to relate the two averages. By expanding the average value in one ensemble about the corresponding average value in the other one obtains the result that if $\langle\ \rangle$ denotes microcanonical average,

$$\langle Q(\bar{L}, \bar{E})\rangle = \left\{1 - \frac{1}{2}\frac{\partial \bar{L}}{\partial(p\beta)}\frac{\partial^2}{\partial \bar{L}^2} - \frac{1}{2}\left(\frac{\partial \bar{E}}{\partial(p\beta)} + \frac{\partial \bar{V}}{\partial \beta}\right)\frac{\partial^2}{\partial \bar{L}\partial \bar{E}}\right.$$

$$\left. - \frac{1}{2}\frac{\partial \bar{E}}{\partial \beta}\frac{\partial^2}{\partial \bar{E}^2} + \cdots\right\} \bar{Q}(p\beta, \beta),$$

where $\bar{L}$, $\bar{E}$ and $p\beta$, β are related by Eqs. (4) and (5). In particular, if Q is taken to be $p\beta$, then

$$\langle p\beta(\bar{L}, \bar{E})\rangle = p\beta - \frac{1}{2}\frac{\partial}{\partial(p\beta)}\left(\Delta^{-1}\frac{\partial \bar{E}}{\partial \beta}\right) + \frac{1}{2}\frac{\partial}{\partial \beta}\left(\Delta^{-1}\frac{\partial \bar{L}}{\partial \beta}\right) + \cdots \tag{6}$$

while for $Q = \beta$

$$\langle \beta(\bar{L},\bar{E}) \rangle = \beta + \frac{1}{2} \frac{\partial}{\partial(p\beta)} \left(\Delta^{-1} \frac{\partial \bar{E}}{\partial(p\beta)} \right) - \frac{1}{2} \frac{\partial}{\partial \beta} \left(\Delta^{-1} \frac{\partial \bar{L}}{\partial(p\beta)} \right) + \ldots \tag{7}$$

where

$$\Delta = \begin{vmatrix} \partial \bar{L}/\partial p\beta & \partial \bar{L}/\partial \beta \\ \partial \bar{E}/\partial p\beta & \partial \bar{E}/\partial \beta \end{vmatrix}$$

In applying these formulas one uses values of $p\beta$ and β in evaluating the right-hand sides that yield the values $\bar{E}$ and $\bar{L}$ when substituted into the right-hand sides of Eqs. (4) and (5).

IV. Determination of Time Averages

In order to check the predictions of statistical mechanics, we compared the time averages of β and $p\beta$ with the ensemble averages of these quantites obtained from Eqs. (6) and (7). The time average of β is obatined by computing the time average of $1/N \sum v_i^2$ and taking its reciprocal. What was done was to compute this quantity after each ΔT interval and average these values over a large number of such intervals.

The calculation of the time average of $p\beta$ for our model is more difficult than that for β. We used two different methods of computation. The pressure in the system can be gotten directly by calculating the total change in momentum at a wall during the interval ΔT, dividing by ΔT, and then averaging over a large number of intervals. The chief difficulty with this method of calculation is that the wall-pressure in a one-dimensional system suffers rather large fluctuations since it involves only the end particles. The other method of "measuring" the pressure in the system is to make use of the pair distribution function $g(r)$. If $N^{(2)}(r)\, dr$ is the number of pairs of particles with a separation between r and $r + dr$, then $g(r)$ is defined by the relation

$$N^{(2)}(r)\, dr = \frac{N^2}{L} g(r)\, dr. \tag{8}$$

The pressure can then be obtained in terms of $g(r)$ by means of the virial theorem. One has that

$$\bar{K} = \sum_{i=1}^{N} \overline{(p_i^2/2m)} = \tfrac{1}{2} pL - \tfrac{1}{2} \sum_{i=1}^{N} \overline{(\mathbf{r}_i \cdot \mathbf{F}_i)}.$$

Consequently

$$pL = N/\beta - \sum_i \overline{r_i F_i}$$

$$= N/\beta - \frac{N^2}{L} \int_0^\infty g(r) \frac{d\varphi}{dr} r \, dr,$$

where φ is the interparticle potential. For the potential of our model, with $V_0 = 1$,

$$\int_0^\infty g(r) \frac{d\varphi}{dr} r \, dr = \int_1^2 g(r) r \, dr - \frac{1}{\beta} g(1),$$

so that finally

$$p\beta = \frac{N}{L} + \left(\frac{N}{L}\right)^2 g(1) - \left(\frac{N}{L}\right)^2 \beta \int_1^2 g(r) r \, dr. \tag{9}$$

While the value of the integral can be gotten directly from the measured values of $g(r)$, it is necessary to extrapolate these values to obtain $g(1)$. This extrapolation was accomplished by fitting a straight line to $\ln g(r)$ since, in a one dimensional system, the effect of all other particles on two neighboring particles can be replaced by an effective pressure. One can also take this effective pressure to be a measure of the pressure of the system.

V. Comparison of Theory and Experiment

The main results of our work are exhibited in Table I. In all cases the time averages are computed from the end portions of longer runs so that, for these portions, we can expect an equipartition between kinetic and potential energy. This expectation was born out by observing the change in the time average of v^2 toward the end of a run. This change has been indicated by the $\pm$ values attached to the experimental values of $(kT)^{-1}$. Likewise, we have indicated the change in the time average of the wall pressure at the end of the run by a $\pm$ value attached to this time average. We see from the table that the theoretical and experimental values of these quantities agree within experimental error, and that the errors in the values of the wall pressure are much larger than those in the temperature. We have also indicated in our table the running time on the IBM 7094 machine used for the calculations. The long run-

ning times are due, in part, to the use of double precision which was found to be necesssary.

TABLE I

No. of particles	999	999	999
Length of container	1201	1500	2500
Energy	116.24	456.43	612.92
$(kT)^{-1}$ (experimental)	.54626±.0003	.48353±.0002	.54319±.0003
$(kT)^{-1}$ (theoretical microcanonical)	.54618	.48349	.54263
$(kT)^{-1}$ (theoretical canonical, isobaric)	.54511	.48261	.54173
Pressure, wall	8.28±.13	3.40±.07	1.29±.12
Pressure, effective	7.94	3.53	1.08
Pressure, virial	7.88	3.55	1.08
Pressure, theoretical	8.21	3.58	1.09
No. of time intervals	28	48	50
No. of collisions	106,953	84,168	33,445
Running time in hours	1.63	1.2	.91
$\lim_{r\to\infty} N^{(2)}(r)\,dr$ (experimental)	41.00	33.07	19.89
$\lim_{r\to\infty} N^{(2)}(r)\,dr$ (theoretical)	41.58	33.27	19.96

The calculations of the effective and the virial pressure in Table I were carried out with the help of the measured pair distribution functions. A typical pair distribution function is shown in Fig. 1 for the case of 999 particles, container of length 2500, energy 612.92 and $dr = .05$. We see that it appears to be approaching an asymptotic value which was determined to be 19.89. A theoretical value for this value can be obtained by noting that

$$\lim_{r\to\infty} g(r) \simeq 1 + \frac{1}{L^2}\frac{\partial L}{\partial p\beta}.$$

For the system under consideration the $1/L^2\,(\partial L/\partial p\beta)$ correction term is approximately -4.3×10^{-4}. Thus, using Eq. (8) we obtain a theoretical value for the asymptote of 19.96. Theoretical and experimental values of $\lim_{r\to\infty} N^{(2)}(r)\,dr$ are given in Table I.

One can derive an expression for $g(r)$ in the region $1 < r < 2$ directly from a knowledge of the partition function (3). Alternately, one can obtain this expression heuristically by assuming that, in addition

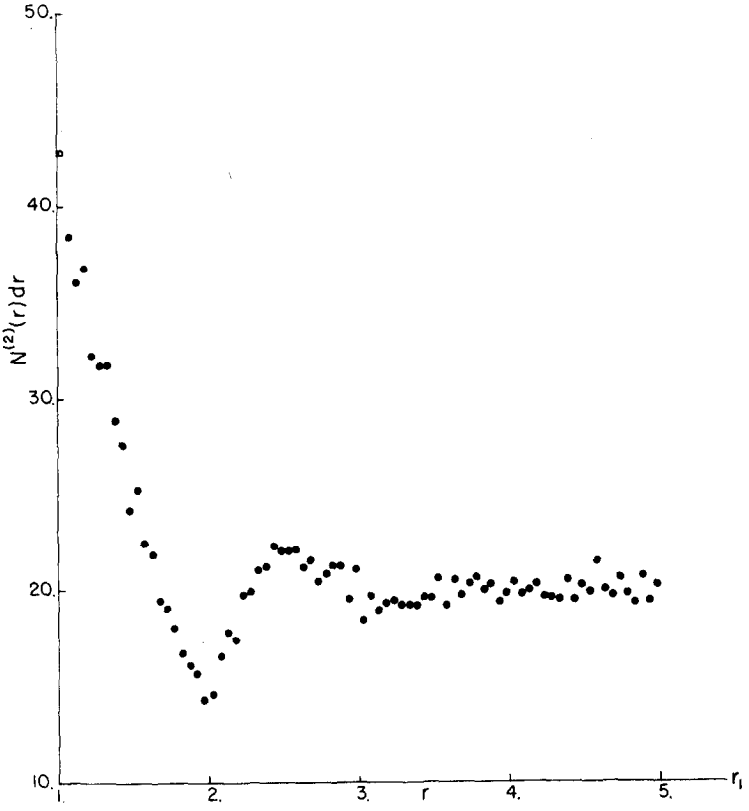

FIG. 1. Typical averaged pair distribution function for a 1000-particle system of hard rods with short-range attractive forces. $N^{(2)}(r)\,dr$ is the number of pairs with a separation between centers lying between r and $r + dr$ with $dr = 0.05$.

to the direct force between two neighboring particles, there is an effective pressure force acting on them due to the other particles in the system. Consequently, in this region (again choosing $V_0 = 1$)

$$g(r) = g_1(r) = C \exp(-\beta\{pr + (r - 2)\}),$$

where C is determined by the normalization condition $\int_0^\infty g_1(r)\,dr = L/N$, corresponding to $1/L \int_{-L/2}^{L/2} g(r)\,dr = 1 + 0(1)$. The experimen-

tally determined slope of $\ln g_1(r)$, obtained by fitting a straight line to the experimental points by means of a least squares fit, then yields what we have called the effective pressure. In Fig. 2 we have plotted the experimental values of $\ln \{N(r)\, dr\}$ together with the curve $\ln \{(N^2/\bar{L})\, g_1(r)\, dr\}$ using the theoretically determined value of p.

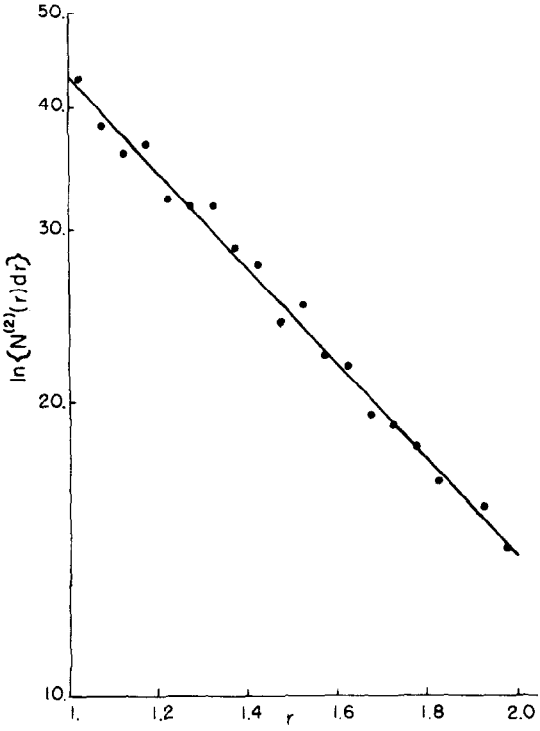

FIG. 2. Logarithmic plot of averaged pair distribution of Fig. 1 in interval $1 < r < 2$.

VI. REVERSIBILITY OF SYSTEM AND ROUNDING ERRORS

The main sources of error in our calculations were the rounding errors involved in computing the times at which a collision occurred and when a discontinuity in the interparticle force was reached. This in turn resulted in errors in computing the positions and velocities of the particles involved in such an event. There are a number of ways of estimating the effect of these errors on the calculation. By noting the change in the energy of the system, which should be a constant of the motion,

we can get a measure of the accuracy of the measured time averages for the system. In all cases the energy was observed to fluctuate by less than one part in 10^6 during a run when double precision methods were employed. Double precision was necessary since the energy was found to vary appreciably during a run when only single precision was employed. Single precision with a statistical rounding off method gave only slightly better results than without the rounding method. From the constancy of the energy over a given run, it is reasonable to conclude that the computed time averages were close to those that would have been computed without roundoff errors.

A much more rigorous test of the accuracy of our method of calculation was obtained by comparing a given trajectory with its time reversed counterpart. This latter trajectory was obtained by using the final state of the original trajectory with all velocities reversed as a new initial state. We then determined the interval over which the two trajectories coincided. In making this determination, we took the point of divergence to be whenever a coordinate or velocity differed by more than 1% on the two trajectories. For a system of 100 particles typical trajectories were observed to coincide for about 50 collisions per particle. Similar results hold for systems of 10 and 1000 particles, as might be expected from the method of calculation.

With such an elaborate calculation it was comforting that we were able to get reversibility for as long an interval as we did. On the basis of these observations, we concluded that our metohd of calculation and the associated code used for the calculation were without error. However, these observations also showed that even for simple systems one cannot hope to compute trajectories for long periods with any accuracy. Moreover, in our case, the trajectories could be given by analytic expressions between collisions, or between discontinuities in the forces between particles. From these results, it appears that the determination of parameters associated with large portions of a trajectory, e.g., recurrence times, cannot be accurately determined by means of a computer. It would, for instance, be impossible to observe a Poincaré cycle. The effect of the errors that lead to the nonreversibility of trajectories will be small, however, when we compute averages over a trajectory, as the constancy of the energy of our system showed.

VII. Approach to Equilibrium

Strictly speaking, it is meaningless to talk about the approach to equilibrium of an isolated finite system, since there will exist a finite recurrence time corresponding to any chosen accuracy of recurrence. The term "equilibrium" can properly refer only to a set of states, an infinite system, or one to which stochastic forces are applied. Although the extent to which the last possibility has been avoided in our computations is questionable, a single state with well-defined initial conditions will still be macroscopically indistinguishable from an equilibrium situation over most of its lifetime. The criterion for deciding when a system has reached such a configuration is hardly unique, so that the study of the approach to equilibrium of an isolated system is beset with a good deal of arbitrariness.

We have used, as one measure of how close a configuration is to an equilibrium configuration, the deviation of the velocity distribution from Gaussian. The measure of this deviation was taken to be $\chi^2 = \sum_i (n_i - x_i)^2/n_i$, where the sum is over the velocity intervals $(v_i, v_i + \Delta v_i)$, n_i is the expected number of particles with velocities in this interval for Gaussianly distributed velocities, and x_i is the observed number. The intervals were so chosen that the n_i were all equal. Finally, the velocity domain was broken into 20 intervals so that, in the language of probability theory we had a system of 19 "degrees of freedom." For such a system the probability that a normal distribution in each interval centered around n_i has a given χ^2 or greater has been tabulated. For $\chi^2 = 30$, $P = .05$, for $\chi^2 = 12.4$, $P = .90$.

In one instance we measured χ^2 as a function of time for a system of 999 particles with the initial distances between particles uniform and initial velocities chosen randomly to have the values ± 1. At $t = 0$, $\chi^2 = 9000$. At $t = 10$, $\chi^2 = 291$; at $t = 60$, $\chi^2 = 18$; and thereafter χ^2 fluctuated around the value 15. One can conclude therefore that the system "thermalized" in about 60 time intervals. On the other hand, we observed a system with random initial positions and velocities distributed according to a double-peaked Gaussian with the velocity of the second peak five times that of the first. At $t = 815$ (corresponding to 44 hours of machine time) the system had still not thermalized.

In addition to studies of velocity thermalization, we investigated position thermalization, again using a χ^2 criterion. We started wity a system with velocites gaussianly distributed and the initial positions between

particles all equal to 2.1. Since the total available volume is 2500 and the system contained 999 particles the initial configuration corresponded to a "bunching together" of the particles. In the course of time the system expanded to fill the box. However, position thermalization occurred very slowly, taking 235 time intervals or about 166 collisions per particle. Undoubtedly the slow approach to equilibrium in this and other cases is due to the fact that we are dealing with a one-dimensional system.

VIII. Conclusions

We have seen that it is possible to reproduce the phase space averages of equilibrium statistical mechanics to very high accuracy by studying the long time dynamic behavior of a model many-body system. The accuracy was sufficient to distinguish as well between isobaric and isovolume, canonical and microcanonical distributions. We have also seen how the approach to equilibrium may be assessed and have given examples of its dependence upon initial conditions. However, by means of reversibility tests, we have shown as well that the exact dynamics can be followed for only an embarrassingly short time through efficient use of a high-speed digital computer, so that detailed dynamical questions are not amenable to analysis at this level.

Appendix

The Code

The appendix outlines our method of computation in determining the trajectories of the N-body system considered here. The flow chart diagram of Fig. 3 is a quick survey of this method.

Since the problems solved in the computing code were those that revolved about distances between particles, the basic variables used in the code were r_i, vr_i, and a_i, denoting respectively the relative position, the relative velocity and the relative force between the ith and the $(i-1)$th particles. Thus, instead of Eqs. (2a) and (2b), we used

$$r_i(t) = r_i^0 + vr_i^0 t + a_i t^2/2 \tag{10a}$$

$$vr_i(t) = vr_i^0 + a_i t, \tag{10b}$$

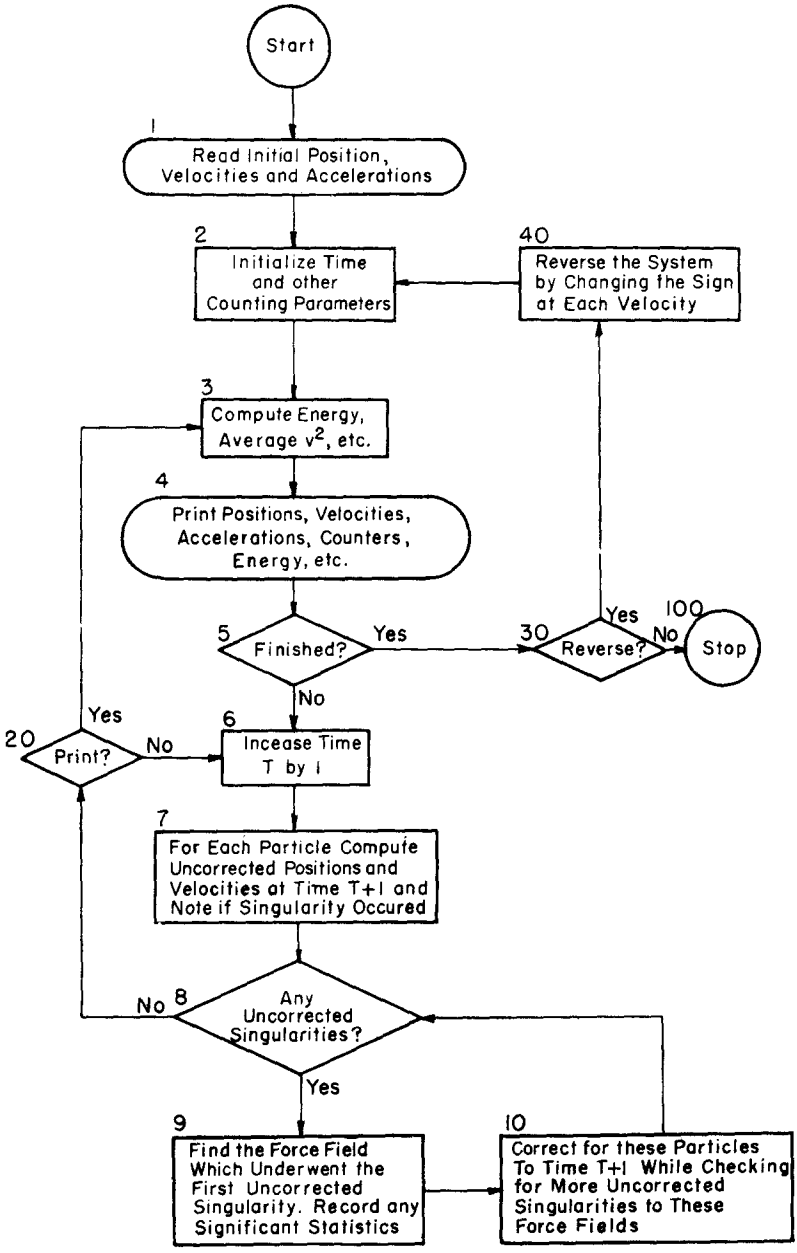

FIG. 3. Flow chart for computation of trajectories.

where r_i^0 and vr_i^0 are the values at time t_0 and $r_i(t)$ and $vr_i(t)$ are the values at time $t_0 + t$. For convenience $i = 1$ and $i = N + 1$ were taken respectively to be the subscripts for the left wall and the first particle and for the Nth particle and the right wall.

Starting with a set of values at time t_0, Eqs. (10a) and (10b) with $t = 1$ were used to compute the values $r_i(1)$ and $vr_i(1)$ for the time $t_1 = t_0 + 1$, as though no singularity existed in the force fields of the particles. While uptating each r_i^0 and vr_i^0 we checked for the first occurrence of a singularity in the ith force field during the time interval from t_0 to t_1. (Boxes 6 and 7 in Fig. 3.) This required testing Eq. (10a) for each i, $i = 1, 2, \ldots, N + 1$, to find if a t existed in the time interval for which $r_i(t) = 2$ or $r_i(t) = 1$. If a_i is zero, then $r_i(t)$ is a linear function of t. This means that a simple comparison of $r_i(1)$ with r_i^0 will tell if a situation with $r_i(t) = 2$ or $r_i(t) = 1$ has occurred. If a_i is not zero, then $r_i(t)$ is a quadratic function of t, and a mere comparison of $r_i(1)$ with r_i^0 will not be sufficient. In this case we would test Eq. (10a) first for the existence of a solution of $r_i(t) = 2$. If none existed and if the particles were in an attractive force field, we would compare $r_i(1)$ with 1 to find if a collision had occurred. If a singularity did occur, the time from the singularity to time t_1, denoted dt_i, was computed and saved along with the information of how the relative velocities or force fields should have been changed.

Next we ordered the dt_i. The largest dt_i, to which we assign the subscript k, located the first of our uncorrected singularities. After collecting any pertinent statistics from the occurrence at time $t_1 - dt_k$, the $r_j(1)$ and $vr_j(1)$, $j = k - 1, k, k + 1$, were recomputed while checking for a singularity in the force field of each during the time interval from $t_1 - dt_k$ to t_1, as above. If a collision had occurred to the $(k - 1)$st and kth particles, i.e., $r_k(1 - dt_k) = 1$, this recomputation was done on the basis of $vr_k(t)$ changing direction, but not magnitude, at time $t_1 - dt_k$. If a particle collided with a wall, $k - 1$ could be disregarded if $k = 1$, and $k + 1$ could be disregarded if $k = N + 1$. If a change in force field occurred, the changes were made on the basis of corrections in a_{k-1}, a_k, a_{k+1}. Again the dt_i were ordered, the first one corrected, and so on until there were no uncorrected singularities in the time interval from t_0 to t_1 (boxes 8, 9, and 10 in Fig. 3).

Then, unless we wanted to print our most recent statistics, we computed from the values at time t_1 for the values at $t_2 = t_i + 1$, etc. When our calculation had run for as many time intervals as we desired, we then

reversed the system by reversing the signs of the velocities and initializing the time and other counting parameters. (Boxes 30, 40, and 2.)

References

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