Molecular dynamics of nonergodic hard parallel squares with a Maxwellian velocity distribution

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(Received 20 December 1979)

Molecular-dynamics calculations were done for hard parallel squares (HPS) at areas relative to close packing of 4.5, 2.0, 1.345, and 1.31. A Maxwellian velocity distribution (which was maintained in time) was used. A phase transition was found at 1.345 which, from these previous results, appears most likely to be a first-order transition. The normalized velocity autocorrelation function for the densities of 4.5 and 2.0 displayed a "long-time" tail whose decay approximates a minus-one power of the time. These results agreed with other molecular-dynamics simulations using a different initial velocity distribution but disagreed with Monte Carlo calculations. Speculation is presented on the ability of certain nonergodic systems such as the HPS to mimic the behavior of an ergodic system with regards to a number of properties.

I. INTRODUCTION

In this paper we conclude our numerical molecular-dynamics investigations of hard parallel squares (HPS) in a square box with periodic boundary conditions. Our interests in studying this system are due, in part, to the fact that this nonergodic system possesses $2N$ extra analytic integrals of the motion. These are the two initial components of the N-particle velocities (momenta). This system is the first nontrivial model for noncentral molecular interactions which seems to bypass the hydrodynamic stage in reaching a final non-Maxwellian velocity distribution if started with a general arbitrary initial velocity distribution. If the initial velocity distribution of the HPS is Maxwellian, it remains Maxwellian. Because of this property, we felt that in order to compare the behavior of the HPS system for various initial velocity distributions, we must also study it for the case of an initial Maxwellian velocity distribution. We shall focus our studies on the ultimately achieved static pressure (and phase transition behavior) and the velocity autocorrelation function.

The existence of a first-order phase transition for hard disks and hard spheres has been established by following the variation of pressure as a function of density along an isotherm. The density (or equivalently the area or volume relative to close packing) at which the transition from a solid to a fluid state occurs is 1.266–1.312 and 1.36–1.50 for hard disks and hard spheres, respectively.[1] These transitions have been found in both Monte Carlo[2] and molecular-dynamics[3] studies. The pressure is obtained in different ways for these two methods. In Monte Carlo calculations one used the "contact" pair-correlation function; in molecular-dynamics simulations, the virial equation is employed. In order for the Monte Carlo ensemble averaged pressure to equal the molecular-dynamics time-averaged pressure, the Monte Carlo results must be scaled by $N/(N-1)$, where N is the number of particles under study.[4]

Similar investigations of phase transition behavior have also been done for two-dimensional hard parallel squares (HPS). The Monte Carlo work of Ree and Ree[5] displayed isotherms which were monotonically increasing functions of the density. Systems containing 25, 64, 100, and 400 HPS were simulated and Monte Carlo runs as long as 8×10^5 trials/particle were generated. Their result was in contradiction to the work of Rudd and Frisch[6] and Carlier and Frisch.[7] Rudd and Frisch[6] found qualitative evidence for the existence of a solid-fluid transition. A detailed study by Carlier and Frisch,[7] using mainly 400 particles and some runs with 900 particles, indicated a first-order phase transition for $1.34<\tau<1.35$ ($\tau=A/A_0$—the area relative to close packing A_0). Here, A_0 is the number of squares times the area of one square. A van der Waals loop was obtained and a Maxwell equal-areas construction predicted the virial at the phase transition to be 5.705. The disagreement between the two methods may be due to the fact that the hard parallel square system is *not* ergodic[8] (in the sense that an arbitrary initial velocity distribution will not relax to a Maxwellian distribution at long times). The Carlier-Frisch study used an initial nonuniform unit-circle velocity distribution. We have examined the use of a Maxwellian velocity distribution in order to probe the effect of the velocity distribution on the behavior of parallel hard squares. In addition, we have studied the behavior of the long-time tail of the velocity autocorrelation function. We will comment on the general significance of these results in the discussion.

II. METHOD

Initially 400 parallel hard squares of side length σ were placed on a two-dimensional periodic lattice and given a Maxwellian velocity distribution. At first, we sampled the Maxwellian velocity distribution with a rejection technique[9] but found that the resulting numerical fit to the Maxwellian distribution was not sufficiently good for our purposes. Hence, we developed the following sampling method. Since the Maxwellian distribution is an even function, we need consider only the positive velocity region. For a system of 400 particles, the area of this region $\frac{1}{2}$, is partitioned into 200 equal-area strips. A velocity is selected from each strip so that the area of the strip is divided in half. Hence, for the first strip,

$$\frac{1}{2}\left(\frac{1}{2(200)}\right)=\int_0^{v_1} f(v_x)dv_x\,, \tag{1a}$$

where $f(v_x)$ is the x component of the Maxwellian distribution. The second strip gives

$$\frac{1}{2}\left(\frac{1}{200}\right)=\int_{v_1}^{v_2} f(v_x)dv_x\,, \tag{1b}$$

where two half strips contribute to the area. The integrals are error functions which are easily calculated. The other 198 velocities are determined in a similar way. These 200 positive velocities are then reflected to give 200 negative velocities so that there are 400 velocities whose average is zero. The same set of 400 velocities is used for the y components of the velocity.

Each of the 400 particles is randomly assigned independently a unique x and y velocity component. The final velocities are scaled so that the temperature is 1.00 in reduced units.

The dynamics of this system is obtained via the Alder-Wainwright scheme.[10] The initial conditions determine the collision times for all colliding pairs. The shortest collision time is selected from the list of collision times, and all particles are moved for this time to their new positions. At this time, particles i and j collide. Since hard collisions take place, the equal-mass particles exchange the velocity components which are perpendicular to the sides in contact. The collision time is subtracted from all the other listed times. It is then necessary to recompute the collision times involving the pair which has just collided, since they now have new velocities. If these new times are longer than the longest one on the list, they are discarded; otherwise they replace their old values. The next shortest time is selected from the list and the process is repeated until all the tabulated times are exhausted. The positions and velocities of all the particles are placed on magnetic tape after every 5 collisions.

The virial PA/NkT is obtained from the virial theorem

$$\frac{PA}{NkT}=1+\frac{m}{NkT}\frac{dz}{dt}\,;\quad z=\sum_{\substack{\text{all}\\ \text{collisions}}} V_{ij}\,, \tag{2}$$

where P is the pressure, A, the area, N, the number of particles, k, Boltzmann's constant, T, the temperature, m, the particle mass, z, the "momentum sum" for all pairs i and j which collide, and V_{ij} is the difference between the velocities of i and j. The data were segmented into batches of 100 points (representing 500 collisions) and dz/dt was determined by a linear least-squares fit of z vs time for each batch. The normalized velocity autocorrelation function $\psi(t)$ was calculated from

$$\psi(t)=\frac{1}{N_p}\frac{1}{N_0}\sum_j^{N_p}\sum_i^{N_0}\vec{V}_j(t+i)\cdot\vec{V}_j(i)\Big/\frac{1}{N_p}\frac{1}{N_0}\sum_j^{N_p}\sum_i^{N_0}V_j^2(i)\,, \tag{3}$$

where $N_p=400$ (the number of particles), N_0 is the number of time origins the data are averaged over, and $\vec{V}_j(i)$ is the velocity vector of particle j at time i. The velocities are spaced 100 collisions apart in the $\psi(t)$ calculation. In all calculations, reduced units were employed for which m, k, and σ were set equal to 1.

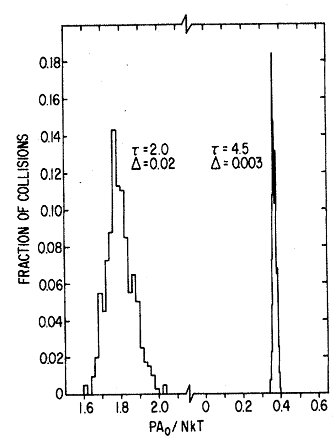

FIG. 1. Histogram of the fraction of collisions with a certain virial. $\tau=4.5$; $\Delta=0.003$. Δ is the interval of the virial $\tau=2.0$; $\Delta=0.02$.

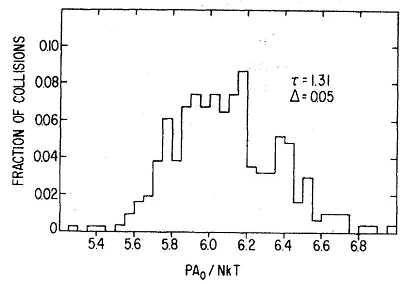

FIG. 2. Histogram of the fraction of collisions with a certain virial. $\tau = 1.31$; $\Delta = 0.05$. Δ is the interval of the virial.

III. RESULTS

Four values of τ have been studied: 4.5, 2.0, 1.345, and 1.31. The virial should remain constant unless there is a phase transition causing the system to randomly move between the virials of the two phases. The virials of the data batches were collected into histograms showing the fraction of batches having a certain virial. At $\tau = 4.5$ and 2.0, the histogram is sharp, indicating single phase behavior. At $\tau = 1.31$, the histogram is broad, indicating the possible onset of the transition. At $\tau = 1.345$, there are two significant peaks which correspond to the transition region observed by Carlier and Frisch. Figures 1, 2, and 3 display the histograms. The numerical value of the virial is taken as the position of the maximum peak; the error in this determination is taken to be the half width of the maximum peak. The results are listed in Table I. They are essentially numerically equal to those obtained by Carlier and Frisch[7] using a different velocity distribution.

Figures 4 and 5 present the $\psi(t)$ results for $\tau = 4.5$ and 2.0. The long-time tail is expected to decay as t^{-1} from studies of hard disks and analytic theories.[11] The data obey that decay law as was also found by Carlier and Frisch.[7] However, as can be seen from Table II, the coefficients are not the same.

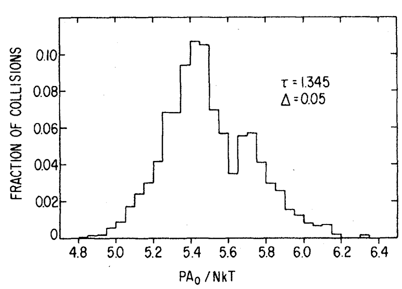

FIG. 3. Histogram of the fraction of collisions with a certain virial. $\tau = 1.345$; $\Delta = 0.05$. Δ is the interval of the virial.

TABLE I. The virials of this work compared to those of Ref. 7 for different areas relative to close packing τ. NT is total number of collisions.

τ	PA_0/NkT	$PA_0/NkT^{(7)}$	NT
4.5	0.362 ± 0.003	0.365 ± 0.003	39 600
1.345	5.45 ± 0.17	5.46 ± 0.04	70 000
	5.70 ± 0.14	5.95 ± 0.25	
1.31	6.0 ± 0.3	6.01 ± 0.03	31 000
2.00	1.77 ± 0.02	1.78 ± 0.02	39 500

IV. DISCUSSION

We have shown numerically (see Refs. 6–8 and this paper) that both the simplest static properties (mechanical equation of state and those "thermodynamic" properties which can be derived from it) and the simplest dynamical property, the velocity autocorrelation function, for two very different initial velocity distributions of HPS (a) resemble each other and (b) resemble the qualitative behavior of the ergodic hard-disk system. Moreover, we have already shown[7] that the low-pressure branch of the equation of state is in excellent agreement with the free-volume theory and the high-pressure branch with the ($P3$, 4) Pade approximant of the virial expansion derived from conventional statistical mechanics based on the assumption of ergodicity for the justification of the equal *a priori* probability principle of equilibrium ensemble theory. Qualitatively, furthermore, the velocity autocorrelation functions of the HPS for both initial distributions resemble (remarkably) each other and that derived for the ergodic hard-disk system. On the other hand, we have conclusively demonstrated numerically nonergodic behavior in that the one-particle velocity distribution does not, in general, relax to a Maxwellian[8] for an arbitrary initial velocity distribution (see specifically the Carlier-Frisch

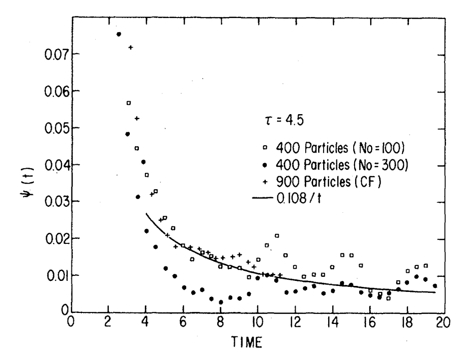

FIG. 4. The normalized velocity autocorrelation, $\psi(t)$ vs time (in collision times) for $\tau = 4.5$. The CF results refer to Ref. 7. Note the decreased oscillations when a larger system was studied.

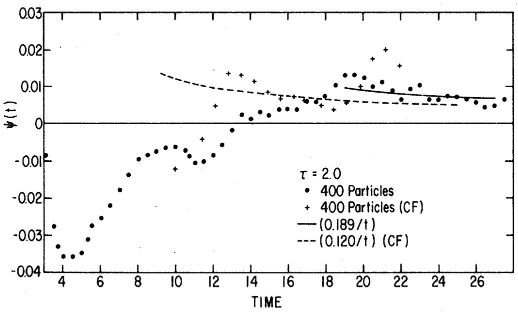

FIG. 5. The normalized velocity autocorrelation, $\psi(t)$ vs time (in collision times) for $\tau = 2.0$. The CF results refer to Ref. 7.

TABLE II. The coefficient C of the t^{-1} decay of the velocity autocorrelation function. $C^{(7)}$ are the results of Ref. 7. ND is the number of collisions discarded and N_0 is the number of time blocks averaged over where the spacing is 100 collisions apart. τ is the area relative to close packing.

τ	ND	N_0	C of C/T	$C^{(7)}$
4.5	1500	100	0.108	0.108
2.0	8000	150	0.189	0.120

distribution[7,8]). Static, final properties such as the virial of the system are numerically (essentially) the same no matter which initial velocity distribution has been employed, providing the particles have the same mean kinetic energy. The coefficients of the asymptotic t^{-1} behavior of $\psi(t)$ reflect the different initial velocity distributions employed. This is expected (see, e.g., Dorfman and Cohen[12]), since the ring-sum operator of the Liouville equation involves averages over the one-particle velocity distribution which will give different numerical values for the different velocity distributions that are finally attained in HPS systems started with different initial velocity distributions. The qualitative dynamic behavior of the nonergodic HPS, like the final static behavior, mimics extremely well the behavior of a similar ergodic system, the hard-disk system.

This raises a number of interesting fundamental questions which cannot be answered by numerical computer experiments: (1) Under what general conditions (nature of the Hamiltonian, container, initial dynamical conditions, etc.) will a truly nonergodic system mimic the behavior of a system described by conventional statistical mechanical ensemble theory whose justification is currently attributed to some kind of ergodicity of the dynamical system studied? (2) Are there real physical systems which are not ergodic but mimic ergodic systems in a fashion similar, but not identical to, that displayed by our HPS system? (3) Is this mimicry simply a consequence of the kind of molecular chaos assumption which ultimately randomly redistributes among the particles any analytically conserved integral of the motion; which is the case for the conserved velocity components of the HPS system? (4) Finally, we ask about the status of the conjecture made in footnote 10 of Ref. 8 which concerns the thermodynamic limit.

Clearly, our studies cannot answer the question of why Monte Carlo investigations[5] do not exhibit an apparent first-order phase transition for HPS at $\tau \sim 1.34-1.35$. Should analytical studies ultimately demonstrate the existence of such a transition for hard disks (or HPS), one can ask if all convex hard particles exhibit such a transition and does there exist a comparison theorem for bounds on the reduced density location of the respective transitions.

ACKNOWLEDGMENTS

This research was supported in part by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank the S.U.N.Y. Albany computer center for generous grants of computer time.

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