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# Measurements of long-range correlations by nonequilibrium molecular dynamics

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Experiments on two-dimensional systems of hard disks have been made in order to measure local fluctuations of thermodynamic quantities and long-range correlations in the presence of a temperature gradient.

## I. INTRODUCTION

The study of local fluctuations in molecular systems in nonequilibrium stationary states and the existence of long-range correlations are the subject of much work, from the theoretical point of view[1] as well as from an experimental one.[2] Theoretical results have been published dealing with the behavior of systems in the presence of temperature gradients; the various methods used range from fluctuating hydrodynamics to kinetic equations. The results provide generalizations to nonequilibrium states of, for example, the well-known Landau-Placzek formula for the (un)equal-time fluctuations. For all these theories, hypotheses have to be made to relate the fluctuations to local parameters like, for example, the temperature and the heat conductivity.

From an experimental point of view, results have been obtained by nonequilibrium molecular dynamics[3] for systems submitted to temperature gradients, which show that the macroscopic laws account quite well for the observed behavior. A linear steady temperature profile is well reproduced although the temperature gradients imposed are extraordinarily large.[4]

Molecular dynamics give us the ideal method to test the existing theories as all parameters are perfectly known for the models considered; this is to be compared to Monte Carlo experiments[5] where evolution is governed by some *ad hoc* transition probability law. However, the influence of boundary conditions on the relatively small systems tractable by today's computers (a few hundred particles), and also the smallness of the effect of the constraints (compared to the fluctuations of quantities of interest already present in equilibrium situations) restrict this "experimental" study to very simple systems. Nevertheless, it should be possible to show the appearance of correlations extending over many intermolecular distances.

To test the validity of the assumptions about local equilibrium, the importance of the boundary conditions, and the relation between the temperature gradient and the correlations, we decided to study molecular assemblies of two-dimensional (2D) particles interacting through a hard-core potential. The system has to be as large as possible if spatial correlations have to be seen. This is, for a given number of molecules, easier to realize in two than in three dimensions. It, however, has to be noted that some of the transport coefficients seem to diverge in two dimensions, which clearly indicates that effects observed for this kind of system cannot immediately be transposed to three-dimensional ones. On the other hand, this approach permits one to follow the system in phase space for times much longer than in 3D, giving much better statistics for the relevant mean quantities.

## II. THE SIMULATIONS

Systems composed of 3000 particles have been studied.

Particles are hard disks disposed initially with a roughly uniform density, in a rectangular box. Periodic boundary conditions are imposed in the $y$ direction, whereas in the $x$ direction two thermal walls are set at given equal or different temperatures. In the direction of the temperature gradient, the system is divided in 21 boxes. Each box is itself subdivided in three cells in the $y$ direction. In each of the boxes, the initial velocities of the particles are chosen at random from a uniform distribution whose mean gives a "local temperature" (defined as the mean kinetic energy per particle of the box) fitting nearly a linear profile from one wall to the other.

The system evolves through collisions between particles and between particles and walls. At collision time between a given particle and a wall, a new velocity for the molecule is chosen from the velocity distribution corresponding to the given temperature.[4] Periodically, the quantities of interest are computed for each of the 63 cells, i.e., mean velocity, momentum, local temperature, local density, together with the averages of products of temperature, density, and mean velocity in a given layer. Each system was followed until a stationary state was established, with a nearly linear temperature profile and a regular density variation along the $x$ axis. For each cell, local equilibrium has been checked using the moments of the velocity distribution function. The pressure has been computed using the virial theorem (within each box) and also from the momentum transfer at the two walls. The system was roughly 220 long (in reduced units by the molecular diameter) and had a width of 60. The density has been chosen to be 0.2 (density at close packing is $2/\sqrt{3}$). Three situations have been studied: equilibrium, and temperature gradients given by $T2=2\,T1$ and $T2=3\,T1$ ($Ti$ reduced temperature at the $i$ wall).

The code written in FORTRAN 77 is standard.

The program has been run on a VAX 11-780 and a CYBER 170-750 at the University of Texas at Austin.

## III. THE RESULTS

### A. System at equilibrium ($T1=T2$)

We show in Fig. 1 the evolution, for the temperature and for the temperature fluctuations, of the precision of the

 

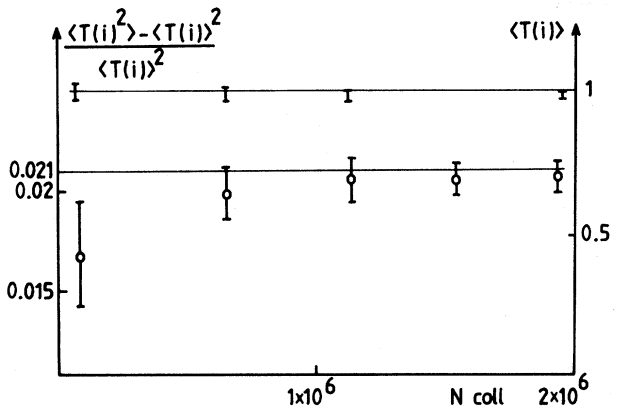


FIG. 1. Mean value and dispersion of the temperature, and temperature fluctuations over different cells as a function of the number of collisions. Solid lines are the theoretical results, $(k_B/c_v)=1/\langle N\rangle$; $\langle\cdots\rangle$ represents the time average.

measurements as a function of the total number of collisions between the particles.

After two million collisions the dispersion of the temperature over the different cells is less than 1%; for temperature fluctuations it is approximately 8%. The measured temperature is slightly lower than the imposed temperature at the walls, in agreement with previous observations.[6] The agreement is good between our results and theoretical values for the fluctuations.[7]

### B. Systems out of equilibrium

The approximately linear profile for temperature has been maintained together with the appearance of a density variation along the $x$ axis matching the equation of state for each subsystem.[8] The pressure appears to be constant throughout the system. The moments of the velocity distribution functions for each box, indicate a very good agreement (to within 1%) with a Gaussian distribution, which seems to indicate the existence of local thermodynamic equilibrium; this is the case for the two temperature gradients studied. It should be noted (Fig. 2) that a similar simulation performed for a system of 500 particles at the same density gives a nearly perfect linear variation of temperature along the direction of the gradient but no spatial correlations have been observed (see below). The computed temperature from the equation of state,[8] using the observed density, agrees for each subsystem with the measured value. No correlations have been detected between density and velocity fluctuations in different cells (this effect should be of first order in the gradient.[1]). Correlations have been measured for the temperature-temperature fluctuations. Both the spatial dependence and the gradient dependence agree with the theoretical predictions of Nicolis and Malek-Mansour,[9] who studied a case where the fluctuations propagate through the diffusive thermal mode; they are proportional to $(k_B/C_v)(\vec{\nabla}T)^2$ and decrease linearly with the distance ($C_v$ being the heat capacity at constant volume). These correlations are displayed in Fig. 3; their decay may seem to differ from the linear law at large distances, but the statistics for these points is poorer than for the others; moreover, they are more affected by boundary effects. If we discard the points corresponding to a relative distance larger than 15 cell lengths, the ratio of the slopes corresponding to the two different gradients, as determined by a least-squares fit, is 4.1 as compared to the theoretical result 4.0 (ratio of the gradients values squared).

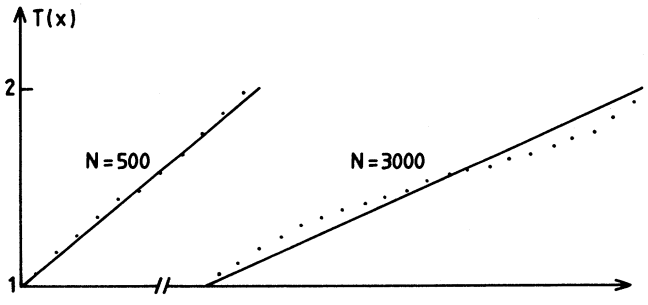


FIG. 2. Displacement between measured temperature and the linear profile for different sizes. $\Delta T/T1=1.0$; the systems were followed during 1300 mean free times.

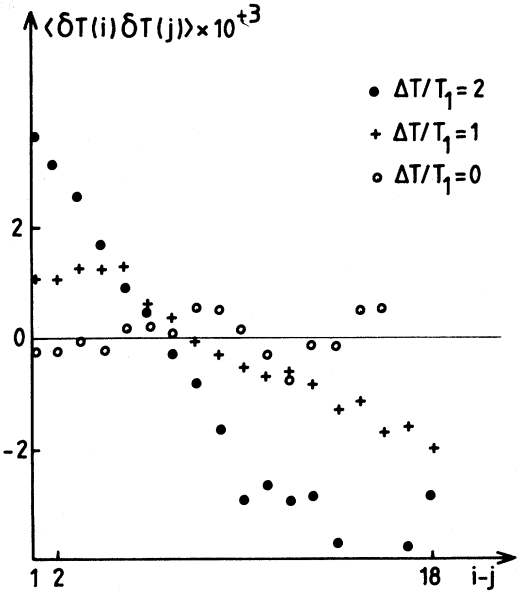


FIG. 3. Experimental observed linear dependence of $\langle T(i)T(j)\rangle-\langle T(i)\rangle\langle T(j)\rangle$ as a function of distance between cells $i$ and $j$; the average over all cells for a given distance has been taken.

The fact that no correlations between density and velocity fluctuations have been observed can be traced to the influence of the boundaries. Indeed these correlations appear because there are more sound waves traveling along the heat flux than opposite to it. A boundary which reflects the sound waves will then annihilate this asymmetry provided the attenuation length of the sound waves is larger than the sample length.[10] This is precisely the case in the present simulation; particles are instantaneously reflected at the thermal walls, and so are the density fluctuations.

## IV. CONCLUSION

The simulations performed for these two-dimensional systems confirm the existence of local equilibrium. Spatial temperature and density variations agree with previously published results, and appear to obey, within each box, the equation of state. Long-distance correlations between temperature and temperature fluctuations which agree with theoretical predictions have been observed. To measure other long-range correlations, the boundary conditions have to be modified. This can probably be done by "absorbing" momentarily incident particles at the walls and reinjecting them at a later moment, in order to dephase the incident and reflected sound waves. Work is in progress in that direction.

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