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Local equilibrium in stationary states by molecular dynamics

Alexander Tenenbaum
Dipartimento di Fisica, Università degli Studi di Roma, I-00185 Roma, Italy
and Gruppo Nazionale di Struttura delle Materia del Consiglio Nazionale delle Ricerche, Roma, Italy

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I have further developed a molecular-dynamics technique, based on the introduction of stochastic boundary conditions, which had been used previously to simulate stationary nonequilibrium states. By simulating two symmetrical thermal gradients, periodic boundary conditions can be used in all directions. In this way unphysical effects of the thermal walls, existing in the previous version of the technique, have been eliminated. The local equilibrium hypothesis has been verified throughout the whole region of the thermal gradient. The new technique seems suited to study the correlation of dynamical variables in stationary nonequilibrium states.

Recently, noticeable developments have occurred in the theoretical analysis of nonequilibrium stationary states. An important branch of this research[1] has focused on the study of fluctuations of dynamical variables (such as the microscopic densities of mass, momentum, and energy) in a fluid which is in a stationary nonequilibrium state. As a matter of fact, the correlations of these quantities are believed to be long ranged in a nonequilibrium state, thus generating observable effects, for example, in the light scattering. An experimental test of the theory is not easy, and suitable computer experiments could therefore be valuable in this investigation.

The method of molecular dynamics, that is, the full microscopic simulation of a system of interacting particles, has been developed in the last years toward the modeling of nonequilibrium stationary states. In a preceding paper,[2] Ciccotti, Gallico, and I communicated computer experiments in which stationary thermal gradients were set up in a dense fluid; we used our method to check the limit of validity of Fourier's law. The system's boundary conditions in the directions perpendicular to the thermal gradient were the standard ones in molecular-dynamics experiments, that is, they were periodic. On the other hand, two thermal walls at different temperatures were introduced in the direction in which a thermal gradient should set up. The thermal contact of the particles with the walls was obtained through a stochastic mechanism originally proposed by Lebowitz and Spohn[3]: When a particle arrived at a thermal wall, it was reflected inside the box with a velocity sampled from a particular probability density depending only on the temperature of the wall.

It was not possible to use periodic boundary conditions (PBC) in the direction of the gradient because the temperatures of the two opposite walls were different. Therefore the particles inside the box and near these walls had no images of particles beyond the walls to interact with; this "vacuum" influenced the same properties of the system in the region adjacent to the wall, in particular, the microscopic densities of mass and internal energy. A consequence of this fact was the following. When the local temperature and local density were measured in thin layers perpendicular to the thermal gradient, it was found that in the bulk their values verified the equation of state within 2%; the validity of the local equilibrium hypothesis in the bulk could thus be confirmed. On the other hand, the deviation of the local density from the value estimated through the equation of state was much higher near the stochastic walls; for example, in one case reported in Ref. 2 (density $\rho = 0.85$ in reduced Lennard-Jones units) this deviation attained 8% near the "hot" wall. Such an unphysical wall effect did not alter the measure of the thermal conductivity, but it would become a hindrance if one would use this method for studying the correlation of the microscopic densities of mass and energy. Indeed, the region influenced by this effect can be relevant, because of the small size of the simulated system; for example, at $\rho = 0.85$ this region amounts to about a quarter of a system of 256 particles.

In the present report I illustrate an improved version of the stochastic boundary technique which eliminates the unphysical wall effect just described. The basic change consists in simulating two symmetrical gradients, so the PBC can be used in all directions (Fig. 1). The system is contained in a parallelepiped, bounded in the x direction by two thermal walls at the same temperature. Two symmetrical gradients are set up by putting a third wall at a higher temperature in the middle of the box. Differently from the method used in Ref. 2, the thermal walls are not reflecting, but permeable, i.e., a particle is thermalized while passing across a thermal wall. This mechanism of thermal contact is obviously related to the use of PBC in the direction parallel to the thermal gradients.

In Ref. 2 the equations of motion of the particles were integrated by means of the algorithm

$$\vec{r}_i(t+h) = 2\,\vec{r}_i(t) - \vec{r}_i(t-h) + \frac{\vec{f}_i(t)}{m}h^2, \quad i = 1,N \ , \quad (1)$$

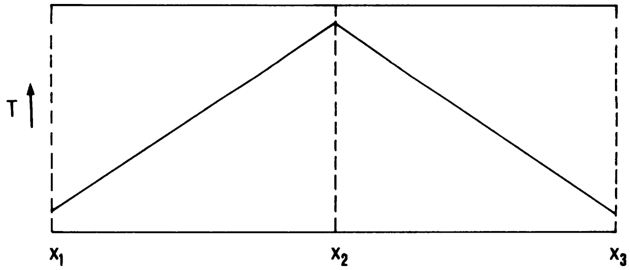

FIG. 1. Two temperature gradients obtained by means of two cold walls (in x_1 and x_3) and a hot wall (in x_2). The thermal walls are permeable and periodic boundary conditions are used.

where $\vec{f}_i$ is the force acting on the ith particle due to the presence of the other particles, m is the mass, and h is the time step. In the new technique the same algorithm is used, but $\vec{f}_i$ is computed taking into account also the images of particles generated by the use of PBC in the direction parallel to the thermal gradient. Algorithm (1) is used as long as particles move inside the box. When a particle (j) at time t has just crossed a stochastic wall, passing during a time step h from $\vec{r}_j(t-h)$ to $\vec{r}_j(t)$, the following procedure is started (Fig. 2):

(i) A new velocity $\vec{v}$ is sampled from the probability density described below.

(ii) The position at time $t-h$ is updated as $\vec{r}_j(t-h) = \vec{r}_j(t) - \vec{v}h$.

(iii) The positions of the particles which have not crossed a thermal wall are not affected.

(iv) Algorithm (1) is used again for all particles.

The probability density used to draw the velocity components v_y and v_z perpendicular to the thermal gradient is a Maxwellian distribution at the temperature of the thermal wall. The componet v_x is sampled from the probability density

$$\phi(v_x) = \frac{m}{k_B T} v_x \exp\left(-\frac{m v_x^2}{2 k_B T}\right) ,$$

where v_x must have the same sign as the x component of the incoming velocity. This condition realizes the permeability of the thermal walls used here, in contrast to the reflecting property of those used in Ref. 2. The thermalization mechanism just described is simpler than the one adopted in Ref. 2; moreover, it has a purely kinetic character because the potential energy of the system does not change during the thermalization procedure. The numerical implementation has thus precisely the property of the ideal mechanism proposed by Lebowitz and Spohn.[3]

The efficiency of the thermal contact between wall and liquid realized by the new mechanism is similar to that of the mechanism used in Ref. 2. This has been tested by repeating the runs with the highest gradients at $\rho = 0.85$. For the highest gradient simulated at that density I have performed, as in Ref. 2, a comparison between the computed local density and its experimental value, estimated at the pressure of the system and at the local temperature. For this purpose, a system of 512 particles has been placed in a box, the side of which, in the x direction, was twice the side in the other directions; this way, each of the halves had the same size as the box used for the analogous computer experiment in Ref. 2. The box has been divided in 16 layers of equal thickness, perpendicular to the thermal gradient. In each layer the local density and the local temperature have been computed, in the way described in Ref. 2. The comparison between the expected and the computed densities shows that the difference does not exceed 2.5% in any layer, with an average deviation of 1% in absolute value. This result indicates that the two-gradients technique eliminates the undesirable effects due to the thermal walls, maintaining their real physical influence. The result also indicates that the local equilibrium hypothesis is valid in all points of a system subject to a very high thermal gradient: If the parameters of the Lennard-Jones potential used in this simulation are given the values corresponding to argon, the thermal gradient mentioned above is of the order of 1.7×10^8 K/cm.

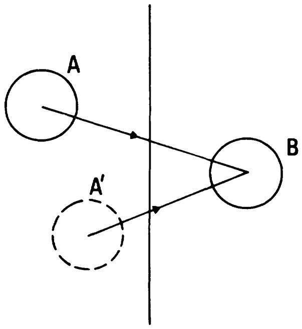

FIG. 2. Thermalization mechanism at the thermal wall. A particle in A at time $t-h$ crosses the wall and goes to B at time t. The thermalization is performed by changing the position at time $t-h$ to A'. A' is determined by the condition that the particle endowed with the (new) thermal velocity would have gone from A' to B in the same time step.

The need for a system twice as large as the system used with the previous technique is compensated by the gain in statistics. The latter is indeed larger than a factor of 2 because the introduction of PBC makes the whole system useful for the microscopic analysis, whereas the layers nearer to the thermal walls are unusable if a single gradient is simulated. In conclusion, this new technique seems promising for the microscopic study of nonequilibrium stationary states.

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[1] I. Procaccia, D. Ronis, M. A. Collins, J. Ross, and I. Oppenheim, Phys. Rev. A 19, 1290 (1979); A.-M. S. Tremblay, M. Arai, and E. D. Siggia, *ibid.* 23, 1451 (1981); T. R. Kirkpatrick, E. G. D. Cohen, and J. R. Dorfman, *ibid.* 26, 950 (1982).

[2] A. Tenenbaum, G. Ciccotti, and R. Gallico, Phys. Rev. A 25, 2778 (1982).

[3] J. L. Lebowtiz and H. Spohn, J. Stat. Phys. 19, 633 (1978).