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Canonical Ensemble and Nonequilibrium States by Molecular Dynamics

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We present a new technique to simulate the contact of a molecular dynamics system with a thermal wall. A canonical ensemble is obtained, and its statistical and thermodynamic fluctuations are studied. The values of the specific heat found by simulation agree with the experimental data. By means of thermal walls at different temperatures, thermal gradients are obtained. The values of the thermal conductivity are consistent with the experimental data.

KEY WORDS: Molecular dynamics; canonical ensemble; transport properties; nonequilibrium states.

1. INTRODUCTION

In this paper we present some new results obtained by introducing stochastic boundary conditions in molecular dynamics (MD) computer experiments. These boundary conditions can be used to simulate thermal walls at a given temperature (that is, the contact with a thermal reservoir), for a MD system. This can be done by using an idea utilized recently by Lebowitz and Spohn to study head transport in a Lorentz gas.(1) We apply this idea to extend the MD technique to the simulation of a canonical ensemble and of stationary thermal nonequilibrium states. It is well known that a canonical ensemble can be simulated by the Monte Carlo method; however, that method does not allow the computation of time-dependent averages. A dynamical simulation of a canonical ensemble has been proposed by Schneider and Stoll(2); their technique is

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computationally cumbersome and restricted to the representation of equilibrium states. As for the stationary nonequilibrium state, the first MD simulation has been performed by Ashurst and Hoover,(3) but their thermalization mechanism is computationally expensive and is not satisfactory from the point of view of statistical mechanics.

A set of atoms confined between thermal walls, all at a given temperature, gives a system with some fixed temperature T, particle number N, and volume V, but with fluctuating total energy E. Thus, a microscopic state of this system is one realization drawn from a canonical ensemble; as the system evolves in time, members of the ensemble are generated, allowing the computation of canonical averages. Furthermore, confining a set of atoms between two thermal walls at different temperatures, one simulates a stationary, nonequilibrium state: a thermal gradient is set up in the system, and the phenomena related to a constant heat flux can be studied.

2. MODEL AND RESULTS

We consider a system of N particles enclosed in a parallelepiped in d dimensions of sides L_i ($i = 1, \dots, d$), interacting through a two-body potential of the Lennard-Jones type. This potential is cut off at a distance $R_c = 3\sigma$. As usual,(4) our units are σ for length, ϵ for energy, and $\tau = (m\sigma^2/48\epsilon)^{1/2}$ for time. For argon, $\sigma = 3.405$ Å, $\epsilon = 119.8k_B$, and $\tau = 3.112 \times 10^{-13}$ sec. The boundary conditions can be either periodic or stochastic (pairs of opposite boundaries being of the same type); the former are well known; the latter are realized by contact with a heat reservoir(1) in the following way. We assume that the moving particle arriving at the wall reenters the box at the same place but with a velocity sampled from a Maxwellian distribution corresponding to the temperature of that wall. Let us call **e** the inward normal unit vector at the surface, and $f_T(\mathbf{p})$ the maxwellian distribution at temperature T. The particle arriving at the stochastic wall therefore reenters with a velocity (independent of its incoming velocity) drawn from a density proportional to

$$\mathbf{e}\cdot\mathbf{p} f_T(\mathbf{p}), \qquad \mathbf{e}\cdot\mathbf{p} > 0$$

As was already noted,(1) this simple mechanism is sufficient to realize the contact with a heat reservoir, at least with respect to thermal phenomena. Note that beyond the stochastic walls there are no "images" of the particles in the box.

To simulate an equilibrium state the stochastic walls must all be at the same temperature. If all the boundaries are stochastic walls, the thermalization is most effective, but due to the finite size of the system, surface effects are important for some thermodynamic properties (for example, the kinetic energy is uniform, while the local values of density and pressure are altered near the stochastic walls). Thus, it may be convenient to use periodic boundary conditions along some directions, and stochastic ones along the others. In this way, one gets translational invariance of the system at least along the periodic directions. On the other hand, to obtain a stationary thermal gradient through the system, one has to put two opposite walls at different temperatures, while the remaining boundaries can be periodic. The thermodynamic analysis of the stationary state must be done by dividing the system into layers parallel to the stochastic walls; the thickness of the layers has to be chosen in such a way that (i) one can assume local equilibrium in the layer and (ii) the number of particles in the layer is sufficiently large. The equations of motion of the particles are generally integrated with the usual central difference algorithm(4); when a particle collides with a stochastic wall, the integration step following this event takes into account the velocity change of that particle. The typical time step in our units is $h = 0.032$.

2.1. The temperature is estimated by $T_\tau = 2\bar{K}/dNk_B$, where $\bar{K}$ is the average of the kinetic energy of the system over a time τ. As τ is not infinite, we expect T_τ to differ from T (temperature of the bath). The statistical error entailed by this finite time averaging is $\eta = (2n/Nd\mathcal{N}_c)^{1/2}$, where n is the mean number of time steps between thermally independent configurations and $\mathcal{N}_c$ is the number of time steps in the stationary state (typically 3000). A rough estimate of n can be obtained by equating η to the actual relative deviation $\delta = |T - T_\tau|/T$. For the different systems described in the first five columns of Table I, the estimated values of n are reported in column 6. As expected, n increases when the number of thermal walls decreases; for systems having the same number of stochastic walls, n increases with N, the thermalization being a surface effect. It turns out that n is much larger than the time between independent configurations in the microcanonical case (about 30 time steps); this is due to the fact that the thermal relaxation of the system to the thermal walls is much slower than the dynamical relaxation of the kinetic energy.

If $\tau \simeq nh$, T_τ would represent a typical fluctuation of the temperature near its equilibrium value T. The variation coefficient μ of these thermodynamic fluctuations, which are important when the system is small, is given by the Einstein formula(5)

$$\mu \equiv \langle(\Delta T)^2\rangle^{1/2}/T = (NC)^{-1/2} \tag{1}$$

where C is the specific heat per particle at constant volume. When $\tau > nh$, T_τ should differ from T by less than μT. And indeed δ is almost always smaller than μ, the latter being estimated by formula (1), where we use the experimental value for C when $d = 3$ and the value computed in the microcanonical ensemble when $d = 2$ (see Table I). The only exception is the two-dimensional case, in which δ is slightly larger than μ; this is not surprising, because in this case n is of the order of $\mathcal{N}_c$. Thus, the results show that the thermalization obtained with our mechanism is satisfactory.

Table I. Energy Fluctuations and Specific Heat per Particle C[a]

d	s	N	ρ	T	n	C_{mc}	C_{c}	C_{ex}(a)	C_{ex}(b)
3	6	256	0.85	0.763	100	2.86	2.23	2.87	2.62
3	2	256	0.85	0.763	900	2.81	2.67	2.87	2.62
3	6	864	0.85	0.776	500	2.48	2.73	2.88	2.63
2	4	1296	0.712	1.177	2500	1.33	1.27	—	—

[a] d, number of dimensions; s, number of stochastic walls; N, number of particles; ρ, number density; T, temperature of the system; n, number of time steps between thermally uncorrelated configurations; C, specific heat per particle, in k_{B} units. The subscript mc (c) refers to the microcanonical (canonical) case; the experimental values C_{ex} are taken from Ref. 6 (set a) and from Ref. 7 (set b) for argon at density ρ and temperature T.

2.2. In the microcanonical ensemble the specific heat per particle C is related to the fluctuation of the kinetic energy$^{(8)}$:

$$\langle (K - \langle K \rangle_{\mathrm{mc}})^2 \rangle_{\mathrm{mc}} = (d/2) N k_{\mathrm{B}}{}^2 T^2 (1 - d k_{\mathrm{B}}/2C)$$

$\langle \cdot \rangle_{\mathrm{mc}}$ represents the microcanonical ensemble average. $C = C_k + C_i$, where $C_k = \frac{1}{2} d k_{\mathrm{B}}$ is the kinetic component of the specific heat, and C_i is the potential component. In the canonical ensemble, the specific heat is related to the fluctuation of the total energy:

$$\langle (H - \langle H \rangle_{\mathrm{c}})^2 \rangle_{\mathrm{c}} = N k_{\mathrm{B}} T^2 (C_k + C_i)$$

In general

$$\begin{aligned} \langle (H - \langle H \rangle_{\mathrm{c}})^2 \rangle_{\mathrm{c}} &= \langle (K - \langle K \rangle_{\mathrm{c}})^2 \rangle_{\mathrm{c}} + \langle (U - \langle U \rangle_{\mathrm{c}})^2 \rangle_{\mathrm{c}} \\ &\quad + 2 \langle (K - \langle K \rangle_{\mathrm{c}})(U - \langle U \rangle_{\mathrm{c}}) \rangle_{\mathrm{c}} \end{aligned}$$

In principle, the first term on the right-hand side is equal to $(d/2) N k_{\mathrm{B}}{}^2 T^2$ and the last is zero. Thus, only the fluctuation of the potential energy has to be explicitly computed. Therefore, we obtained C by

$$C_i = \overline{(U - \bar{U})^2} / N k_{\mathrm{B}} T^2$$

and $C_k = \frac{1}{2} d k_{\mathrm{B}}$. The values of the specific heat computed in various cases are reported in Table I. The values C_{mc} for $d = 3$ can be compared to the value 2.74 given in Ref. 8 for a simulation at $\rho = 0.85$ and $T = 0.88$. Nearly all the values of C_{mc} and C_{c} are in the range of the experimental data. In particular, the more reliable simulation of the canonical ensemble seems to be that of the systems $N = 864$, $s = 6$ and $N = 256$, $s = 2$, i.e., the systems that are less affected by surface effects.

2.3. We have already discussed the method we used to create a stationary thermal gradient. In such a system there is a stationary heat current, related to the thermal gradient by Fourier's law in the linear region:

$$\mathbf{J}^q = -\lambda \nabla T \tag{2}$$

The microscopic expression for the heat current has been given by Irving and Kirkwood.(9) In the center-of-mass reference frame $\mathbf{J}^q$ equals the energy current $\mathbf{J}^E$. We were interested in the computation of the average value of $\mathbf{J}^E$. Due to the nonequilibrium state of our system, we preferred to measure this time average in each of the layers in which the box is divided, as explained before. As expected, in the stationary state the time-averaged heat current in all layers is uniform within the noise; the noise is easily measured by computing the heat current in the directions perpendicular to ∇T. Moreover, the temperature profile is linear through the system, with the exception of the layers next to the walls (Fig. 1). We computed the thermal conductivity λ from (2), where $\mathbf{J}^q$ is the heat current averaged through the layers, and, due to the linearity of the profile, $|\nabla T| = (T_2 - T_1)/L$. Here T_2 (T_1) is the temperature of the hot (cold) wall as it results from the linear least square extrapolation of the temperature profile, and L is the distance between the walls. The results are shown in Fig. 2 together with experimental data at the same density.(7) The gradients involved in the simulation ranged from the one shown in Fig. 1 to a value twice as high. A further study of the thermal transport has shown that λ does not depend on $|\nabla T|$ up to values of the gradient much higher than the ones reported here. The agreement between our results and the available experimental values is satisfactory (within 20%). Therefore, the above method for simulating a thermal stationary state seems reliable, and permits the study of physical properties in a nonequilibrium state; the results obtained by systematic study of thermal transport and local equilibrium in a stationary nonequilibrium state will be presented elsewhere.

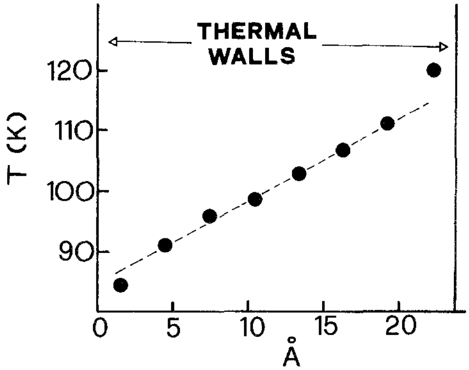

Fig. 1. Thermal gradient by MD, values converted for argon. $N = 864$, $\rho = 1.26\ \mathrm{g\,cm^{-3}}$ ($\rho = 0.75$ in LJ units). The temperatures are measured over 4000 time steps. The dashed line stresses the linear profile of T in the bulk. The left wall is at 34 K; the right wall is at 184 K.

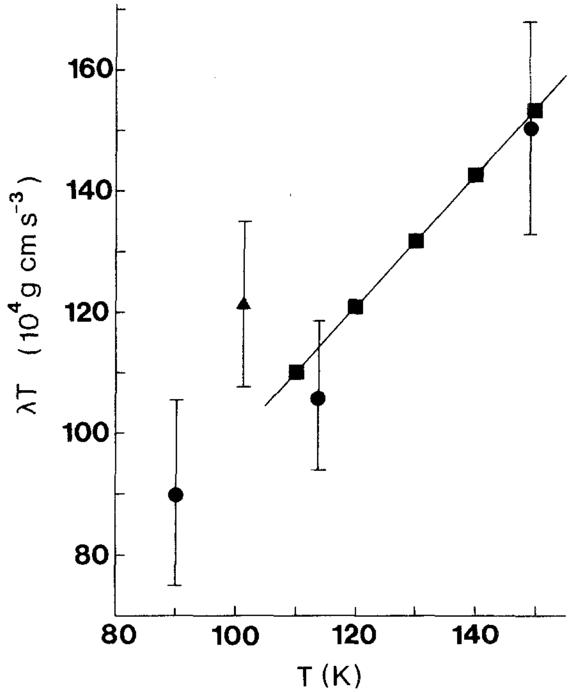

Fig. 2. Thermal conductivity λ, values for argon. T is the temperature averaged through the layers. $\rho = 1.26$ g cm^{-3}. (■) experimental values (see Ref. 7). (●) MD simulation, $N = 256$, 5000 time steps. (▲) MD simulation, $N = 864$, 4000 time steps. The errors on λT are given by the combined errors on ∇T and $\mathbf{J}^E$.

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