Properties of isolated systems in external fields

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We investigate evolution of an isolated system in an external field, and compare the ensemble averages of the response on successive constant internal energy surfaces to the ensemble averages of steady-state responses constrained to the same energy. We find that the two ensemble averages converge for sufficiently high energies, irrespective of the field strength and the initial energy from which the adiabatic evolution starts. This rule is satisfied for any phase-space distribution on the initial energy surface that can relax to equilibrium. At sufficiently high energies transport coefficients converge to their equilibrium values, because the effect of a constant field on the behavior of a system decreases with its temperature.

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I. INTRODUCTION

In recent years, a lot of research has been devoted to investigation of systems in external fields constrained to a constant internal energy or a constant kinetic energy hypersurface in phase space [1]. Such systems exchange heat with their surroundings in order to compensate for the work done by the field. As a consequence, the initial available phase-space volume on average contracts in time and the phase functions reach a well-defined ''steady state'' after a transient period. Much work has been done on characterizing the evolution of systems towards steady states and the underlying strange attractors that represent them. The approach to a steady state is irreversible even for a system governed by time-reversible equations of motion, and the probabilistic nature of this irreversibility has been linked to the probability of violations of the second law of thermodynamics [1].

If a system is subjected to a constant external field without being allowed to interact with the environment, the work done by the field is converted into its internal energy, which then increases indefinitely. Such ''adiabatic'' processes are very different from constant energy or isothermal nonequilibrium processes. In most cases, the initial phase-space volume does not change, but the trajectories evolve towards hypersurfaces of increasing internal energy. The volume of a constant internal energy surface (i.e., the number of possible microstates it contains) increases with the increase of the value of internal energy. If a field is applied adiabatically to an ensemble of phase-space trajectories of a system initially in equilibrium at the internal energy equal to $E(0)$, the phase-space volume of the initial hypersurface $V_\Gamma[E(0)]$ will be conserved at all times. As trajectories evolve towards higher internal energy states, the ratio of the phase-space volume occupied by the states that evolved from $E(0)$ to the phase-space volume available at the given hypersurface decreases monotonically, approaching zero at the infinite time limit. On the other hand, for dissipative systems in the same external field but confined to different constant internal energy surfaces, the rate of volume contraction decreases with the increase of internal energy, and such a system approaches equilibrium in the infinite energy limit.

Despite their differences, the adiabatic and the isothermal systems show many formal similarities. For hard spheres, the particle trajectories derived from the conservative field-dependent adiabatic Hamiltonian, and then transformed using time scaling or field scaling, are isomorphic to those generated by constant-field thermostated mechanics [2–5]. The fluctuation theorem for adiabatic systems [6], giving the ratio of probabilities of positive to negative time-averaged work done by the external field on the system, has the same formal expression as in thermostated case, although its interpretation is different.

Nevertheless, neither of the above approaches provides a clear answer for the behavior of averages of phase functions in an adiabatic process and their relationship to thermostated averages. The objective of this work is to clarify some properties of the adiabatic evolution by molecular dynamics simulation. We are especially interested in finding some universal properties of adiabatic flows in the long time limit on surfaces of high internal energies. The aim is to relate the ensemble-averaged adiabatic responses on constant internal energy surfaces to the steady-state responses at the same energies, when the evolution is from an equilibrium or nonequilibrium phase-space distribution.

In order to answer these questions, we performed molecular dynamic simulations on the simplest model nonequilibrium system, a system of Weeks-Chandler-Andersen (WCA) [7] particles in a color field [8]. The theoretical background for the equilibrium, constant energy, and adiabatic response of this system is outlined in Sec. II. The technical details of the simulations are given in Sec. III, and we present and discuss the simulation results in Sec. IV. The concluding remarks are given in Sec. V.

II. MODEL AND THEORETICAL BACKGROUND

A. The model

Let us consider a system of N particles interacting through a short-range repulsive WCA pair potential, given as

$$\Phi_{ij}=4\varepsilon[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6}]+\varepsilon, \tag{1}$$

if $r_{ij}\leqslant 2^{1/6}\sigma$ and 0 otherwise. In Eq. (1), r_{ij} is the distance between particle i and particle j, $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$, σ is the particle diameter, and ε is the depth of the potential well. Half of the particles have a color charge of $+1$ and the color

charge of the other half is -1, so that ''color neutrality'' is satisfied. Color charge has no impact on the interparticle forces.

B. Equilibrium

In equilibrium, i.e., with no external forces applied to the system, the particle equations of motion are

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m,$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i, \tag{2}$$

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and the momentum of the particle i, respectively, and $\mathbf{F}_i$ is the total force derived from potential (1) acting upon it. All the particles have equal mass m. Equations (2) can be derived from the equilibrium Hamiltonian

$$H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_i \sum_j \Phi_{ij}. \tag{3}$$

The value of $H_0 = E$ is conserved at all times and represents the internal energy of the system. The phase-space compression factor

$$\lambda = \sum_{i=1}^{N} \left(\mathbf{r}_i \cdot \frac{\partial \dot{\mathbf{r}}_i}{\partial \mathbf{r}_i} + \mathbf{p}_i \frac{\partial \dot{\mathbf{p}}_i}{\partial \mathbf{p}_i} \right), \tag{4}$$

which defines the rate at which the phase-space volume decreases in time, vanishes for Hamiltonian systems. The initial phase-space volume is conserved.

In a system of colored particles one can define a ''color current density'' as

$$\mathbf{j} = \frac{1}{V}\sum_{i=1}^{N} c_i \dot{\mathbf{r}}_i, \tag{5}$$

where V is the volume of the system. Equilibrium fluctuations of the color current density characterize the color transport in equilibrium. The Green-Kubo relations define the equilibrium ''color conductivity'' σ_0 as [9]

$$\sigma_0 = (\beta V/3)\int_0^\infty dt \langle \mathbf{j}(t)\cdot\mathbf{j}(0)\rangle. \tag{6}$$

In Eq. (6), $\beta = 1/k_B T$, where k_B is the Boltzmann constant, T is the temperature of the system calculated from the equipartition theorem, $(3/2)Nk_BT = \langle \Sigma p_i^2/2m\rangle$, and the angular brackets $\langle\cdots\rangle$ denote the ensemble average. Equilibrium color conductivity is related to the diffusion coefficient D by the relationship

$$\sigma_0 = \beta\rho D, \tag{7}$$

where $\rho = N/V$ is the number density.

C. Adiabatic process

One can apply a ''color-sensitive'' external field to the above system. Such a field acts upon oppositely charged particles in opposite directions. The equations of motion in a color field of magnitude F_c applied in the x direction are

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m,$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \hat{\mathbf{i}} c_i \mathbf{F}_c, \tag{8}$$

where $\hat{\mathbf{i}}$ is the unit vector along the x axis. Equations (8) conserve the color Hamiltonian H

$$H = H_0 + H_c, \tag{9}$$

where H_c is the field-dependent term, given by

$$H_c = -F_c \sum_{i=1}^{N} c_i r_{xi}$$

and r_{xi} is the x component of position of particle i. Since the system is still Hamiltonian, the phase-space volume is conserved.

Since $\dot{H} \equiv 0$, the rate of change of internal energy H_0 is always compensated by the rate of change of the field-dependent term H_c,

$$\dot{H}_0 = -\dot{H}_c = F_c \sum_{i=1}^{N} c_i \dot{r}_{xi} = VF_c j_x, \tag{10}$$

where j_x is the x component of the color current density $\mathbf{j}$ given by Eq. (5). The term $VF_c j_x$ represents the rate at which the external field F_c does work on the system. Equation (10) expresses the fact that all work done by the field is converted into internal energy. There is no dissipation from heat exchange with the surroundings.

In equilibrium, all the directions of current are equally probable. In the presence of a field it is more probable that the current have the direction of the field than opposite to it. Therefore, internal energy, on an average, increases in an external field. However, along a single phase-space trajectory this increase is not generally monotonic in time because of the current fluctuations. This fact is quantified in the fluctuation theorem for adiabatic systems [6]. In its original form, it states that, along a trajectory in phase space starting at internal energy $H_0(0) = E$ at time $t = 0$ when the field is switched on, the ratio of probabilities of observing the quantity $\beta V \overline{(j_x)_t} F$ take a value A and the opposite value $-A$ increases exponentially in time:

$$\ln \frac{P(\beta V \overline{(j_x)_t} F_c = A)}{P(\beta V \overline{(j_x)_t} F_c = -A)} = At. \tag{11}$$

In Eq. (11), P denotes probability and $\beta = 1/k_B T(0)$, where $T(0)$ is the temperature on the initial energy surface E, and $\overline{(j_x)_t}$ is the time average of the current density along the trajectory during time t in the field,

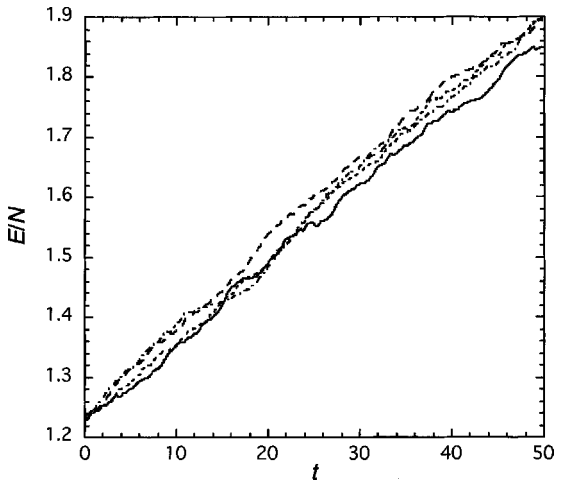

FIG. 1. For a single trajectory, internal energy does not increase monotonically in an adiabatic process. The plot represents the change of internal energy for four trajectories of a system of $N=500$ WCA particles at a reduced density of $\rho^*=\rho\sigma^3=0.6$, starting at initial internal energy per particle $E(0)=1.2$ in a color field $F_c=0.25$.

$$\overline{(j_x)_t}=\frac{1}{t}\int_0^t j_x(s)ds. \tag{12}$$

Using Eqs. (10) and (12),

$$\beta V\overline{(j_x)_t}F_c=\beta\overline{(\dot{H}_0)_t},$$

and the statement of theorem (11) can be reformulated as

$$\ln\frac{\overline{P((\dot{H}_0)_t=A)_t}}{\overline{P((\dot{H}_0)_t=-A)}}=\beta At. \tag{13}$$

The meaning of Eq. (13) is that, as time progresses, it becomes overwhelmingly more probable that the internal energy has increased from its initial value than that it has decreased along any adiabatic trajectory.

The fact that the increase of internal energy is not monotonic in time along a single trajectory is illustrated in Fig. 1, where evolution of internal energy for four trajectories originating on the same $H_0=E=1.2N$ surface is shown for the WCA fluid at the reduced density of $\rho^*=0.6$. Fluctuations in the slope can be clearly seen, the slope being sometimes negative for short periods of time. This corresponds to the instantaneous current density j_x being in the direction opposite to the field direction (10). The fluctuations would be much more prominent in a system with a small number of degrees of freedom in a low field [6], where one would observe internal energies lower than the initial energy after longer times t. Because of this nonmonotonicity, a phase-space trajectory can cross each constant H_0 surface more than once as time progresses. The current fluctuations along a single trajectory increase as energy increases, and the probability of negative instantaneous current is larger for higher temperatures. As a consequence, although the phase-space volume is conserved in time in an adiabatic process, it is not conserved on successive infinitesimally thin constant-energy shells. The ensemble averages on one surface shell were calculated from all the states in that shell, even when belonging to different times of passage.

The internal energy has a zero ensemble-averaged rate of change with time at $t=0$ because $\langle j_x\rangle$ vanishes in equilibrium.

The reason why the temperature in β is the initial rather than the current temperature lies in the conservation of the phase-space volume. If an ensemble of adiabatic phase-space trajectories in the field is started from the energy surface E, it will always stay within the phase-space volume of E, even as it traverses the surfaces of increasing internal energy. In this sense, the initial energy is always ''remembered'' and is present in Eqs. (11) and (13). The appearance of β on the right-hand side of Eq. (13) means that the exponential decrease of the ratio of probabilities is slower if the trajectories start from a higher energy surface than if they start from a lower energy surface with the same field. An explanation for this is that the width of the initial equilibrium distribution of j_x (related to the Maxwell-Boltzmann velocity distribution) is smaller if the energy is lower.

D. Ergostat

If the excess energy created by the work of the field on the system is removed, the system will stay at the constant internal energy surface $H_0=E$. This can be achieved by adding a Lagrange multiplier $-\alpha\mathbf{p}_i$ (''ergostat'') to the momentum equations with field (8), which constrains the internal energy to an exact constant according to the Gauss principle [8]. In that case the equations of motion are

$$\dot{\mathbf{r}}_i=\mathbf{p}_i/m,$$

$$\dot{\mathbf{p}}_i=\mathbf{F}_i+\mathbf{i}c_iF_c-\alpha\mathbf{p}_i, \tag{14}$$

where

$$\alpha=F_c\sum_{i=1}^{N}c_ip_{xi}\Big/\sum_{i=1}^{N}p_i^2. \tag{15}$$

In fact, a physically more correct way to constrain the internal energy would be to constrain the quantity

$$\sum_{i=1}^{N}\frac{[p_i-(c_imj_x/2\rho)]^2}{2m}+\frac{1}{2}\sum_i\sum_j\Phi_{ij},$$

i.e., the sum of potential energy and the *peculiar* kinetic energy, defined as the kinetic energy of motion relative to the mean velocity of each type of charge [10]. However, this type of constraint would introduce unnecessary complications in the definition of the initial equilibrium energy surface because of the equilibrium current fluctuations, without contributing anything new to general conclusions.

From the invariance of internal energy, $\dot{H}_0\equiv 0$, and the equations of motion (14), it follows that

$$j_xF_cV=2E_K\alpha, \tag{16}$$

where E_K is the total kinetic energy of the system. The rate at which field does work on the system (left-hand side) exactly matches the dissipation, i.e., heat taken out of the system (right-hand side) at all times.

In such a system the ensemble averages of all phase functions (e.g., pressure, temperature, or color current) reach steady-state values after an initial transient period. The color conductivity is given by the constitutive relationship

$$\sigma_c = \langle j_x \rangle / F_c , \tag{17}$$

where $\langle j_x \rangle$ is the ensemble average of the response current for the applied field strength F_c. For low fields the response becomes linear. In this case, conductivity σ_c obtained from Eq. (17) approaches the equilibrium conductivity σ_0 and current becomes directly proportional to the field.

In a system of constant internal energy E in a field, it is more probable for the response current to be oriented in the field direction than in the direction opposite to it. According to Eq. (16), this is equivalent to saying that it is more probable for heat to be extracted than to be added to the system. The fluctuation theorem (FT) for the systems of constant internal energy in an external field [1],

$$\ln \frac{P(\overline{(j_x)_t} = A)}{P(\overline{(j_x)_t} = -A)} = \frac{VF_c}{k_B T} A t, \tag{18}$$

quantifies this probability. The difference between the adiabatic forms (11) and (18) is that in Eq. (18) T is the (constant) temperature corresponding to energy E. The FT (18) states that it is exponentially more probable for time-averaged current along any trajectory to be oriented in the direction of the field than opposite to it. The probability of negative fluctuations is larger for short times t after the field is switched on, high temperatures, and weak fields.

The color Hamiltonian H changes at the rate

$$\dot{H} = -j_x F_c V = -2 E_K \alpha .$$

The phase-space contraction factor (4) is equal to the rate of change of the color Hamiltonian. Since the ensemble average of the current is positive, the color Hamiltonian decreases, on an average, in time and the phase-space volume contracts continuously to a strange attractor embedded in the constant internal energy surface. This decrease is shown in Fig. 2. The initial slope at $t=0$, when the field is first applied, is equal to zero and decreases to a constant negative value at later times. If the same field is applied at higher and higher energies, the rate of decrease of H changes. Whether the slope would decrease or increase depends on the change of conductivity with temperature. For the WCA system at the reduced density of $\rho^* = 0.6$, conductivity and the slope of H decrease with temperature and internal energy.

The impact of a field of constant strength F_c on the particle trajectories decreases with the increase in temperature. This is a general rule that can be derived exactly for hard spheres [11–13], where deviation of free flight in the field from free flight in equilibrium scales as $F_c / \langle p \rangle$, where $\langle p \rangle$ is the average particle momentum. Therefore, we expect an ergostated system in color field to approach the linear limit with the increase in kinetic or total internal energy, irrespective of the field strength. The steady-state conductivities (17) would in this case converge towards equilibrium conductivities. In an ergostated system in a field there would still be a finite current at a finite field, even as $E \to \infty$. It is not so easy to anticipate what would happen with the adiabatic conductivities at successively higher internal energy surfaces.

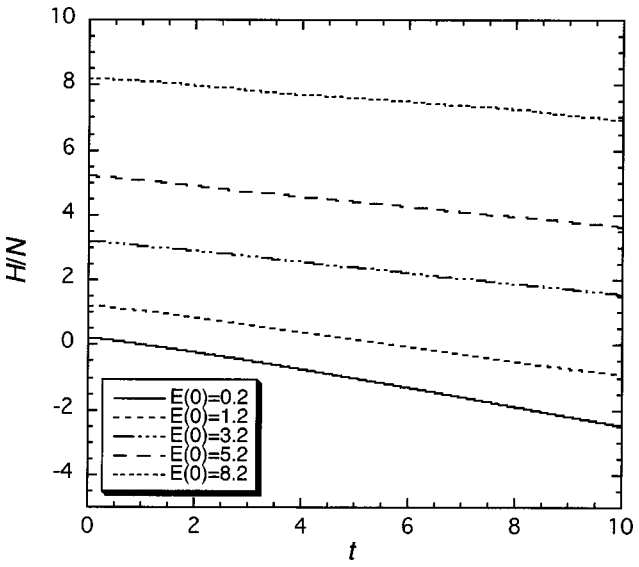

FIG. 2. Decrease of the value of the color Hamiltonian per particle, H/N, in an ergostated system because of the phase-space contraction. The ensemble average is a line with slope equal to $-\langle J_x \rangle F_c / \rho^*$. The plot was obtained from trajectories starting from different initial energies $E(0)$ in a system of $N=500$ WCA particles at a reduced density of $\rho^* = \rho\sigma^3 = 0.6$ in a color field $F_c = 1.0$.

III. TECHNICAL DETAILS

Let us first point out some symmetries of the color Hamiltonian H (9) in periodic boundary conditions. Because of the charge neutrality, H is invariant to translation of all particle positions by the same arbitrary vector $\mathbf{R}$. In other words, its value is independent of the origin of the reference frame.

If all the particles are within the periodic cell, its equilibrium value on a constant internal energy surface $H_0 = E$ will most probably be very close to E. This corresponds to distribution of particles of each charge spread uniformly over the cell. It will not generally be equal to E for each configuration, but its ensemble average $\langle H \rangle$ on the surface will be exactly equal to E because of the ''mirror symmetry'' in equilibrium: if all x coordinates of particle positions x_i are changed to $-x_i$, such a microstate will have the same internal energy H_0 and the same equilibrium probability, but the opposite value of H_c.

The value of H for a phase point $\{\mathbf{r}_i, \mathbf{p}_i, i = 1,...,N\}$ in the periodic cell represents a class of values of H obtained for any configuration obtained from it by a transformation $\mathbf{r}_i \to \mathbf{r}_i + \mathbf{n}_i L$, where $\mathbf{n}_i$ is an arbitrary triplet of integers, in general, different for every particle i, and L is the side of the periodic box. In a simulation with periodic boundary condi-

tions, the adiabatic equations of motion (8) conserve the color Hamiltonian H only if one applies the minimum image convention [14] without ever moving the particles back inside the periodic box.

All simulations were done on a system of $N=500$ WCA particles. In equilibrium simulations, we calculate the equilibrium diffusion coefficient from the Green-Kubo relations using the integral of the velocity autocorrelation function [14], since this is equivalent to Eq. (6), but more efficient. We use Eq. (7) to relate the diffusion coefficient to color conductivity. Each value of D was obtained from two runs of 10^7 time steps. The time window for evaluation of the Green-Kubo integrals was ten Lennard-Jones reduced time units [14].

For adiabatic simulations starting from equilibrium states on a constant-energy surface, the evolution of an equilibrium trajectory (2) was followed in time. For every 1000 time steps, the field was switched on adiabatically, Eq. (8), and produced a nonequilibrium trajectory. The resulting nonequilibrium trajectories were followed for the number of time steps necessary for the system to gain the desired final internal energy. The averages of the response current and other properties were collected after equal times and on energy shells of width of 0.001 reduced units. The averages were calculated from a total of 20 000 nonequilibrium trajectories.

As discussed in Sec. II, conservation of energy and phase-space volume are very important for equilibrium and adiabatic systems. Therefore for these simulations we used the Sanz-Serna integrator [15], which has the same symplectic properties as the Hamiltonian equations of motion (2) and (8). Being a fourth-order method, it has smaller discretization errors than the second-order symplectic methods such as ''velocity'' Verlet (or Störmer) [14] and superior Hamiltonian and phase-space volume conservation. With this method we used the time step of 0.005 time units.

For every initial microstate of an adiabatic trajectory, three additional microstates were created in order to preserve the inherent symmetries of the equilibrium distribution and reduce the systematic error in nonequilibrium averages. One of them was a ''mirror image'' of the initial state, with changed signs of all x coordinates of particle positions. This ensured that the average of the color Hamiltonian was equal to the initial internal energy at all times. The other two were the time-reversed initial state and its mirror image, obtained by reversing all momenta. This ensured that the ensemble-averaged equilibrium initial current j_x was identically equal to zero.

The symplectic integrators such as velocity Verlet and Sanz-Serna have superior accuracy only when used for solving systems of differential equations with symplectic properties. Constant internal energy equations of motion in field (14) are neither Hamiltonian nor symplectic. For this system, the Verlet algorithm would be cumbersome because of the explicit velocity dependence of the ergostat multiplier, and the Sanz-Serna integrator would be inefficient because it needs four force evaluations per time step, without improving the accuracy. We chose the fifth-order Gear predictor-corrector scheme [14] for the ergostated system because of its efficiency. A time step of 0.001 was needed in order to obtain the same level of energy conservation as in equilibrium and adiabatic simulations. The system was first equilibrated for 10^5 time steps, and then brought to a steady state during subsequent 10^5 time steps of simulation with the field and the ergostat. Finally, the steady-state averages were collected during 10^7 time steps.

Calculation of adiabatic evolution of a system in a field from a nonequilibrium distribution on a constant internal energy surface was done using a combination of the two methods. Nonequilibrium ergostated steady-state trajectories were integrated with the Gear predictor-corrector method and a time step of 0.001. For every 2500 time steps, an adiabatic trajectory was started by switching off the ergostat, and was integrated using the Sanz-Serna method with the time step of 0.005. The length of adiabatic runs depended on the approximate time needed to achieve the desired final value of internal energy. There are no symmetries of initial conditions in this case. The averages in adiabatic runs were calculated in the same way as in the case of an equilibrium initial state.

IV. RESULTS AND DISCUSSION

Let us consider two systems in equilibrium on different energy surfaces $E_1(0)<E_2(0)$. At $t=0$ we apply the same field to both systems. Evidently, the ensemble averages of currents generated in the two systems will always differ if compared at the same time because the phase-space trajectories are at different energies. We investigate the relationship between the ensemble averages of currents on the same energy surfaces if they are reached from E_1 and E_2.

In Fig. 3(a), the full and the dotted-line curves, respectively, represent simulation results of the WCA system at the reduced density of $\rho^*=0.6$ in the field $F_c=1.0$ for the initial equilibrium energies of $E_1=0.2N$ and $E_2=3.2N$. The equilibrium properties of the two systems are very different. At energy E_1, the motion is very slow and there is almost no interaction between particles. The energy is too low to allow for more than the barest overlap and the potential energy per particle is negligible. The behavior of this system is very close to a hard sphere fluid. The particle velocity (Maxwell-Boltzmann) distribution has a narrow peak around the most probable magnitude. At higher energy E_2, the repulsive interactions are considerable, which is evidenced in the ensemble-averaged value of potential energy per particle of 0.662, i.e., 20% of the total energy. The velocity distribution has a much larger spread and a lower peak. Finally, the volume of the available phase space on the lower energy shell is much smaller than the volume of the higher energy shell. Therefore, we expect to see different current distributions as the trajectories from the two surfaces evolve towards higher energies.

This is what can be observed in Fig. 3(a) in the initial stages of evolution of the states from E_1 and E_2 towards higher energies. The conductivities shown on the ordinate, calculated from Eq. (17), are numerically equal to current densities. The first difference between the two evolutions is in the ensemble average on the initial energy surface. In equilibrium, the ensemble average of the current density vanishes. According to the adiabatic version of FT (11), if the

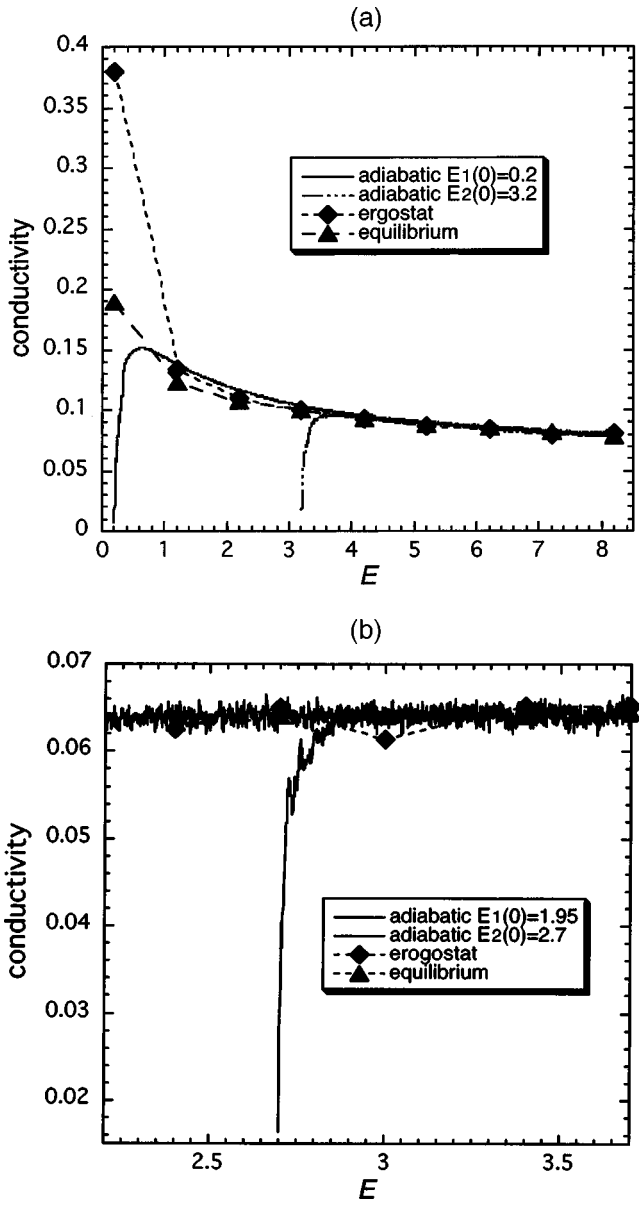

FIG. 3. Dependence of the ensemble-averaged color conductivity on internal energy, for two adiabatic processes starting from equilibrium distributions on different initial energy surfaces $E_1(0)$ and $E_2(0)$ and in a color field applied at a constant energy for the system at (a) $\rho^*=0.6$ in the field $F_c=1.0$ and (b) $\rho^*=0.8$ in the field $F_c=0.5$. For energies $E \gg E_1(0)$, $E_2(0)$, all the averages converge to the same value, despite the fact that their energy dependence is very different.

ratio of the field to the initial temperature is as high as it is in the case of the lower initial energy E_1, the probability of energy decreasing even for a short initial time interval and of multiple crossings of the initial energy surface is very small, and we observe a very low ensemble average of current density on the E_1 surface. When the ratio of the field to the initial temperature is lower, the probability of multiple crossings of the initial energy surface increases, and the ensemble average of the current density on the initial energy surface is much larger.

Nevertheless, when the two systems reach high-enough energies $E \gg E_2 > E_1$, the currents converge to the values obtained by applying the same field and an ergostat to the system at energy E. At high energies, the corresponding transport coefficients (17) converge to the equilibrium values as expected. For sufficiently high energies the response of any system becomes linear for any field strength. This rule holds irrespective of whether current decreases [Fig. 3(a)] or increases [Fig. 3(b)] with internal energy.

There are two mechanisms that determine how equilibrium conductivity would change with temperature. The impact of the field on particle trajectories decreases with the increase in temperature, and therefore with the increase in internal energy. This causes the response current and conductivity to decrease with temperature. Indeed, in a hard sphere system, where the increase in temperature (or internal energy) is equivalent to time scaling, diffusion coefficient increases with temperature as $T^{1/2}$, and the equilibrium color conductivity (7) decreases as $T^{-1/2}$ [Fig. 3(a)].

On the other hand, in systems with ''soft'' interaction potentials, particles become effectively smaller with the increase in internal energy and can, therefore, move more easily. This effect takes over at high densities, where conductivity slowly increases with temperature [Fig. 3(b)].

One consequence of the linearity of response at high energies is that if one applies adiabatically two different fields F_{c1} and F_{c2} to the same equilibrium system, then for all energies sufficiently larger than the initial energy the ratio of the ensemble-averaged currents will be equal to the ratio of the fields [Fig. 4(a)], while the corresponding conductivities converge to the same values, equal to the equilibrium conductivities at given energies [Fig. 4(b)].

Finally, we investigated whether the same convergence to the equilibrium conductivity and the ergostated current at high energies holds if the field is applied adiabatically to a nonequilibrium phase-space distribution on the initial energy surface. A nonequilibrium constant-energy distribution was realized on two different internal energy surfaces, $E_1(0)/N=1.2$ and $E_2(0)/N=3.2$, by applying a color field of $F_c=1.0$ with an ergostat (14) to the equilibrium state. At time $t=0$, the ergostat was turned off and averages were collected at successive energies. The obtained current averages were compared to the averages resulting from the evolution of the initial equilibrium distributions and to the steady-state averages obtained with the ergostat (Fig. 5). We first observe that, surprisingly, ensemble-averaged currents at high energies $E \gg E_2(0) > E_1(0)$ still converge to the currents obtained from the evolution of the equilibrium initial distribution and to ergostated values.

Another surprising result that can be observed in Fig. 5 is that the current averages on the initial surface with nonequilibrium distribution are now *lower* than the averages obtained with the ergostat. An explanation is that the probability of inverse current and recrossing of the initial energy surface increases when the ergostat is turned off.

The convergence of the adiabatic ensemble-averaged currents to the ergostated averages at high-enough energy for any field strength is surprising when we look at the different mechanisms in the phase space governing the approach and different phase-space volume properties in the two cases. It

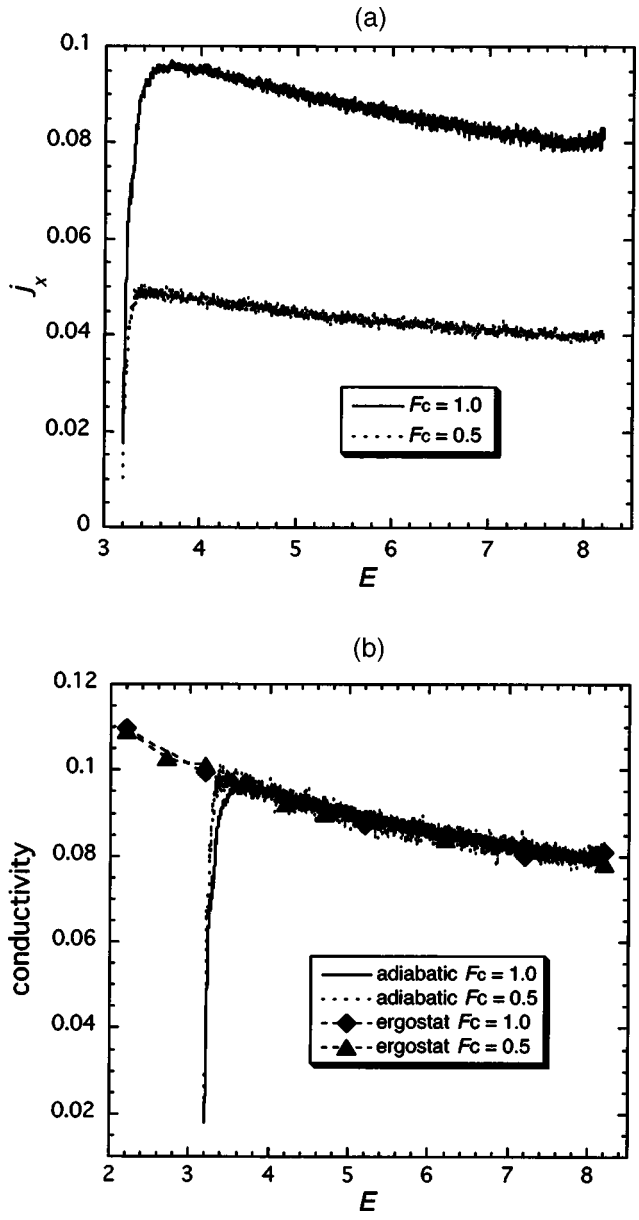

FIG. 4. Dependence of the ensemble-averaged adiabatic color current (a) and conductivity (b) on internal energy when trajectories evolve in two different fields, $F_c=1.0$ and $F_c=0.5$ from the same initial internal energy surface $E(0)/N=3.2$, for the system at the reduced density $\rho^*=0.6$. Conductivities converge to the equilibrium conductivity as the two systems approach the linear limit, while the ratio of currents on the high energy surfaces becomes equal to the ratio of fields.

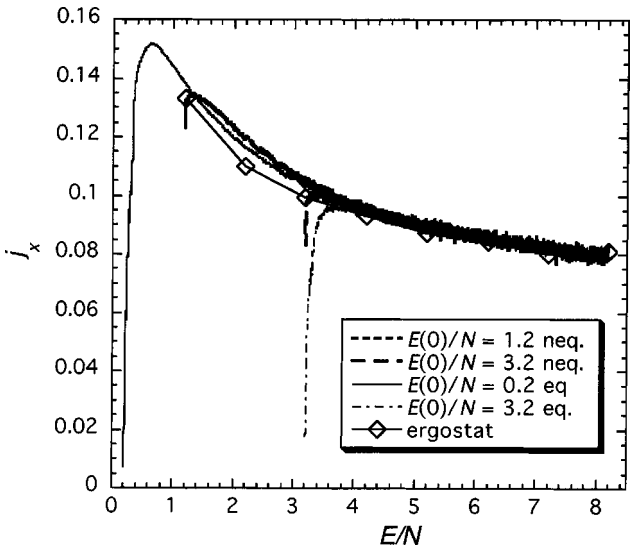

FIG. 5. Dependence of the ensemble-averaged adiabatic color current on internal energy when trajectories evolve from a nonequilibrium distribution on initial internal energy surface. Color field $F_c=1.0$ is applied to the system of reduced density $\rho^*=0.6$ first with an ergostat in order to prepare a nonequilibrium distribution, and later adiabatically. Bold lines represent ensemble averages in systems with nonequilibrium initial distributions. Short-dashed line—initial energy per particle of $E(0)/N=1.2$ and long-dashed line—$E(0)/N=3.2$. Thin full and dash-dotted lines represent systems with equilibrium initial distributions at $E(0)/N=0.2$ and $E(0)/N=3.2$, respectively. Diamonds are the steady-state ensemble averages obtained in the same field with an ergostat.

is not so surprising if we consider it in terms of relaxation times. If the field is very weak, the ergostat term (15) is very small and the ergostated and the adiabatic phase-space trajectories are quite close for some short period of time τ_1. The response current is small and in the adiabatic case energy increases slowly, so that the adiabatic system stays in the same thin energy shell between E and $E+\Delta E$ for some time τ_2. If these two times are longer than the relaxation time τ_R needed for the system to get to the steady state at this energy and field, then the ensemble-averaged adiabatic and the ergostated responses will match. The relaxation can be obtained not only from equilibrium, but also from any nonequilibrium state at the same energy. At energy E the effect of field on the particle trajectories, and therefore the relaxation time τ_R, increases with field strength and decreases with energy. When the field is very strong, the time spent in one energy shell τ_1 might be short but the effects of the field and the relaxation time decrease as the energy increases. There is always a sufficiently high energy E_0 for which $\tau_R < \tau_1$, so that the adiabatic response converges to the ergostated response for $E>E_0$.

Exceptions to this rule are the initial nonequilibrium states that do not relax either to equilibrium or to a steady state with field and ergostat, i.e., the states for which $\tau_R \to \infty$. One such exception is illustrated in Fig. 6. When a nonequilibrium steady-state phase-space distribution is created by application of a field of $F_c=1.0$ to the system of reduced density $\rho^*=0.6$ at energy $E(0)/N=0.2$ with an ergostat and allowed to evolve adiabatically afterwards (Fig. 6), the current increases steadily on successive energy surfaces (full line) and does not ever converge to lower values obtained with an ergostat at higher energies (diamonds). The reason for this is that at such low density and high ratio of the field to the average particle kinetic energy, the steady state is characterized by particles moving only along the x axis in the direction determined by the field and the charge without any interaction. In this state, y and z components of the current density are identically zero, and j_x is the maximum current

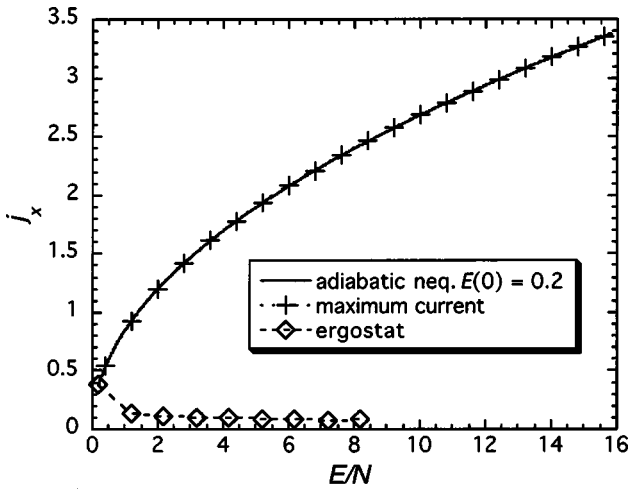

FIG. 6. Full line represents the dependence of the ensemble-averaged adiabatic color current on internal energy when trajectories evolve from a nonequilibrium distribution on initial internal energy surface $E(0)/N=0.2$ of the system of reduced density $\rho^*=0.6$. The initial nonequilibrium distribution is obtained by application of the color field $F_c=1.0$ with an ergostat. This state is characterized by the absence of interactions and the maximum current allowed by the ergostat. The maximum current (crosses) is realized on all subsequent energy surfaces as energy rises when the ergostat is turned off. There is no convergence to ergostated steady-state currents (diamonds).

allowed by ergostat (15) when the total internal energy is equal to the kinetic energy:

$$j_x=\frac{N}{mV}\sqrt{2mE/N}.$$

When the ergostat is removed, they continue to move in the x direction with increasing kinetic energy without any interactions, and the current increases to the maximum value (crosses) determined by the higher energy. At such low densities, for every initial energy $E(0)$ there exists a limiting color field F such that this type of ordering results for all $F_c>F$ [13].

These ordered states are examples of nonergodic initial states with extremely low equilibrium probability. Their contribution to equilibrium ensemble averages is negligible, but the phase-space trajectories that start from them can never escape this region. The infinite-time averages of phase functions on such trajectories are very different from the equilibrium phase-space averages. Although highly improbable in equilibrium, such states can be reached by application of a suitable external field at low energies and densities, causing the system to undergo an ordering phase transition. Because of their nonmixing character in equilibrium, these states may evolve differently from the rest of the phase space when subjected to an adiabatic external field.

V. CONCLUSION

We have investigated evolution of an isolated system in an external field to the states of increasing internal energies using molecular dynamic simulations.

Because the increase of internal energy is not monotonic along a single phase-space trajectory, the initial phase-space volume is not conserved on each energy surface, although it is conserved in time. The probability of multiple crossings of an energy surface would increase with its energy while the system proceeds, with increasing fluctuations, in the general direction of equilibrium where the probability of an instantaneous negative current becomes larger [11]. The volume of accessible phase space on surfaces of increasing internal energy is not constant but grows with energy. It is not straightforward to determine the rate of this growth, and whether the fraction of the available phase space occupied by the attractor is the same for the ergostated system at the initial energy and the adiabatic system at infinite energy, as claimed in Eq. (11).

For the energies close to the initial energy, the ensemble averages of the response depend on the initial energy of the system when the field was applied. For the energies sufficiently higher than the initial energy, all the ensemble-averaged adiabatic responses in the same field converge to the ergostated responses at the same energies. In the high-energy limit, the ergostated response to any field becomes linear and, consequently, both the adiabatic and ergostated transport coefficients converge to their equilibrium values. For sufficiently high energies, the ensemble averages of adiabatic responses to different fields have the same ratio as the field magnitudes.

A plausible explanation of this apparently universal rule is in terms of decreasing relaxation times as energy increases. However, a theory providing a rigorous proof of this convergence and the exact conditions for it to occur is still needed, although the results are intuitively acceptable. The fluctuation theorem for adiabatic systems [6] gives only the probability relationship for the average change of energy during a time interval t after the field is turned on, but says nothing about the average value of the response after time t or on a given energy surface $E>E(0)$, or about its time-dependent or energy-dependent distributions.

This limiting behavior holds for both equilibrium and nonequilibrium initial phase-space distributions, provided that the initial states are sufficiently mixing. If the adiabatic field trajectories are started from the initial states that are not sufficiently mixing to be ergodic in equilibrium, it is possible that they stay nonmixing as they evolve to higher energies, and violate this general limit. This is, in particular, true if the steady-state distribution created by the ergostated field is nonmixing and nonergodic in equilibrium, and the adiabatic trajectories are started from this distribution.

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