Probability of Second Law Violations in Shearing Steady States

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We propose a new definition of natural invariant measure for trajectory segments of finite duration for a many-particle system. On this basis we give an expression for the probability of fluctuations in the shear stress of a fluid in a nonequilibrium steady state far from equilibrium. In particular we obtain a formula for the ratio that, for a finite time, the shear stress reverses sign, violating the second law of thermodynamics. Computer simulations support this formula.

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Recently some progress has been made in relating macroscopic nonequilibrium properties, such as the transport coefficients of many-particle systems, to the dynamical chaos of their phase space trajectories [1–5]. In particular, the two-dimensional modified Lorentz model has been studied [3–5], using the natural invariant measure for cycle expansions in terms of unstable periodic orbits in a dynamical system [3,4]. Although a rather complete theory has been developed for this system where one particle moves through a periodic triangular array of hard disks, the methods used so far are limited to this very special model. Motivated by these one-dimensional results, we propose in the present paper a generalization of the dynamical measure, as yet not well founded, but potentially very useful for the study of many-particle systems in or far from equilibrium. In particular, we study a nonequilibrium stationary state of a fluid under an external shear and conjecture a natural invariant measure for trajectory segments of this many-particle system [6]. This allows us to derive an expression for the ratio of the probabilities to find the fluid on a phase space trajectory segment of duration τ in a dynamical state with an induced shear stress in the direction of or opposite to, respectively, the externally imposed shear rate. The second case constitutes, for a finite time τ, a violation of the second law of thermodynamics.

The normalized natural invariant measure of a multidimensional system we propose as [6,7]

$$\mu_i(\tau)=\frac{\Lambda_i^{-1}}{\sum_i\Lambda_i^{-1}}=\frac{\exp[-\sum_{n|+}\lambda_{i,n}\tau]}{\sum_i\exp[-\sum_{n|+}\lambda_{i,n}\tau]}\,. \tag{1}$$

Here the index $i=1,\ldots,M$ labels phase space trajectory segments $\Gamma_i(t)$ on each of which the system spends a time τ $(0\le t\le\tau)$. M is, in our simulations, of the order 10^7. Λ_i is the product of expanding eigenvalues of the stability matrix [2,6] of the trajectory segment i and $\{\lambda_{i,n}\}$ the set of corresponding positive local Lyapunov exponents, as indicated by the + signs in the summations over the index n in (1). Equation (1) and all τ-dependent equations in the following, are to be interpreted as specializations for finite τ of the corresponding equations for the entire trajectory, obtained for $\tau\to\infty$.

Using (1), stationary state averages can be computed. If

$$\langle A_i\rangle_\tau=\frac{1}{\tau}\int_0^\tau ds A(\Gamma_i(s)) \tag{2}$$

is a time average of the phase function A over the segment i, then the average of A over all segments i all of duration τ is

$$\langle A\rangle_\tau=\frac{\sum_{i=1}^M\langle A_i\rangle_\tau\Lambda_i^{-1}}{\sum_{i=1}^M\Lambda_i^{-1}}\,. \tag{3}$$

Before applying the measure (1) to a many-particle system in a nonequilibrium stationary state we note that in general the ratio of the probabilities for a trajectory segment i to be in a state i or in a state i^K defined below, for which the signs of the corresponding Lyapunov exponents are reversed, is given by

$$\frac{\mu_i}{\mu_{i^K}}=\frac{\exp[-\sum_{n|+}\lambda_{i,n}\tau]}{\exp[-\sum_{n|+}\lambda_{i^K,n}\tau]}=\frac{\exp[-\sum_{n|+}\lambda_{i,n}\tau]}{\exp[+\sum_{n|-}\lambda_{i,n}\tau]}$$
$$=\exp\left[-\tau\sum_n\lambda_{i,n}\right]=\exp[Nd\langle\alpha_i\rangle_\tau\tau]\,. \tag{4}$$

Here one has used that [2,8]

$$\sum_n\lambda_{i,n}=-Nd\langle\alpha_i\rangle_\tau\,, \tag{5}$$

where N is the number of particles of the system and d is the dimension of space. We emphasize that (4) only involves $\langle\alpha_i\rangle_\tau$, i.e., the sum of *all* Lyapunov exponents associated with the segment i (which is, as will be shown below, related to the dissipation of energy on the trajectory segment i in the nonequilibrium stationary state), not the sum of the positive Lyapunov exponents alone. This enables us to make simple statements on the relative

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weights of any states of the system, even those far from equilibrium. To the best of our knowledge such a formula is not in the literature, where instead of the dynamical weights used here, nonequilibrium distribution functions appear derived from the equilibrium Gibbs distribution, without incorporating a thermostating mechanism to assure the existence of a stationary state [9] [cf. Eqs. (6) below].

Although we would like to test Eq. (1) directly, statistical fluctuations in the value of $\lambda_{i,n}$ amplified by the exponentation in Eq. (1) make a direct numerical test of that equation very difficult. This reduces us at present to a test of Eq. (4). To that end we consider a nonequilibrium stationary state of a fluid driven by an external shear rate $\gamma = \partial u_x/\partial y$, the gradient of the x component of the local fluid velocity $\mathbf{u}$ in the y direction, and coupled to a thermostat to assure a stationary state. The equations of motion of the particles in such a system are the so-called SLLOD equations [8]:

$$\dot{\mathbf{q}}_j = \frac{\mathbf{p}_j}{m} + \mathbf{i}\gamma y_j, \quad \dot{\mathbf{p}}_j = \mathbf{F}_j - \mathbf{i}\gamma p_{yj} - \alpha \mathbf{p}_j . \tag{6}$$

Here $j = 1, \ldots, N$ labels the N particles of mass m of the fluid, $\mathbf{p}_j = m\dot{\mathbf{q}}_j - \mathbf{i} m u_x(\mathbf{q}_j)$ is the peculiar momentum of particle j with respect to the local fluid velocity $u_x(\mathbf{q}_j) = \gamma y_j$, $\mathbf{i}$ is the unit vector in the x direction, and $\mathbf{F}_j$ is the intermolecular force on particle j. α is determined using Gauss' principle of least constraint [8], keeping the internal energy $H_0(\Gamma) = \sum_j p_j^2/2m + \Phi(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ fixed, where $\Gamma = (\mathbf{q}_i, \mathbf{p}_1, \ldots, \mathbf{q}_N, \mathbf{p}_N)$ is the phase of all particles and Φ is the total potential energy of the fluid, leading to

$$dH_0(\Gamma)/dt = -\alpha(\Gamma) \sum_j p_j^2/m - P_{xy}(\Gamma) V\gamma = 0 .$$

Here $P_{xy}(\Gamma)$ is the microscopic pressure tensor

$$P_{xy}(\Gamma) V = \sum_{j=1}^{N} p_{jx} p_{jy}/m - \tfrac{1}{2} \sum_{j \neq j'} x_{jj'} F_{jj',y} ,$$

where $\mathbf{F}_{jj'}$ is the force on j due to j' ($\mathbf{F}_j = \sum_{j'(\neq j)} \mathbf{F}_{jj'}$), $x_{jj'} = q_{j'x} - q_{jx}$, and V is the volume of the fluid. Thus

$$\alpha = \alpha(\Gamma) = -\frac{P_{xy} V\gamma}{\sum_{j=1}^{N} p_j^2/m} , \tag{7}$$

and α_i in Eq. (4) is given by (7) specialized to the trajectory segment i and similarly for $P_{xy,i}$. In Eqs. (6) and (7) and subsequent equations, all quantities are interpreted as dimensionless [2], by scaling them with the particle mass m and the parameters ϵ and σ of the steeply repulsive Weeks-Chandler-Anderson (WCA) potential $\Phi(r)$ [10], used here to compute the interparticle forces $\mathbf{F}_{jj'}$: $\Phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon$ for $r < 2^{1/6}\sigma$ and $\Phi(r) = 0$ for $r > 2^{1/6}\sigma$, where r is the interparticle distance. For this potential the flow is assumed to be hyperbolic, as for a hard sphere fluid.

We now apply the ratio (4) to determine the probability of occurrence of two dynamical states of segment i, denoted by i and i^K, which have a given value of the pressure tensor $\langle P_{xy,i}\rangle_\tau$ and its opposite, $\langle P_{xy,i^K}\rangle_\tau = -\langle P_{xy,i}\rangle_\tau$, respectively. We note that the state i^K seen in the computer simulations is not the time reversed state i^T of i which has $\langle P_{xy,i^T}\rangle_\tau = \langle P_{xy,i}\rangle_\tau$ [since $P_{xy}(\Gamma)$ is an even function of $\mathbf{p}$] but also $-\gamma$ instead of γ, as $M^T(\mathbf{q},\mathbf{p},\gamma) = (\mathbf{q}, -\mathbf{p}, -\gamma)$, where M^T is the time reversal operator. The observed state i^K with $-\langle P_{xy,i}\rangle_\tau$ and γ is obtained from the state i by the transformation $M^K = M^T \cdot M^Y$, where $M^Y(\mathbf{q},\mathbf{p},\gamma) = (x, -y, z, p_x, -p_y, p_z, -\gamma)$ [8], which leaves the SLLOD equations as well as γ invariant. This state i^K has Lyapunov exponents opposite to those of the state i, since M^T (but not M^Y) changes their signs; i.e., $\lambda_{i^K,n} = -\lambda_{i,2Nd-n+1}$. Therefore we can apply (4) to compute the ratio of probabilities to find a segment i with a value of the pressure tensor $\langle P_{xy,i}\rangle_\tau$ equal to a given value $P_{xy\tau}$ or to its opposite $-P_{xy\tau}$, respectively, as

$$\frac{p(P_{xy\tau})}{p(-P_{xy\tau})} = \exp\left\{ \sum_i{}^* [Nd\langle\alpha_i\rangle_\tau \tau] \Big/ \sum_i{}^* 1 \right\} , \tag{8}$$

where $\sum^*$ indicates that in the exponent only those dynamical states i for which $\langle P_{xy,i}\rangle_\tau = P_{xy\tau}$ should be taken into account. Equation (8) states that the probability of seeing an i^K state with $P_{xy\tau} > 0$ lasting a time τ is exponentially smaller than that of seeing the corresponding i state with $P_{xy\tau} < 0$ of segment i. The exponent is proportional to $Nd\langle\alpha_i\rangle_\tau$, a generalized rate of entropy production during τ in the segment i (see below).

The molecular dynamics simulations were carried out for $N = 56$ disks, in $d = 2$, interacting with a WCA potential, using Lees-Edwards periodic boundary conditions [8], for an internal energy per particle $H_0/N = 1.56032$, a number density $n = N\sigma^2/V = 0.8$, shear rates $\gamma = 0.1$ and

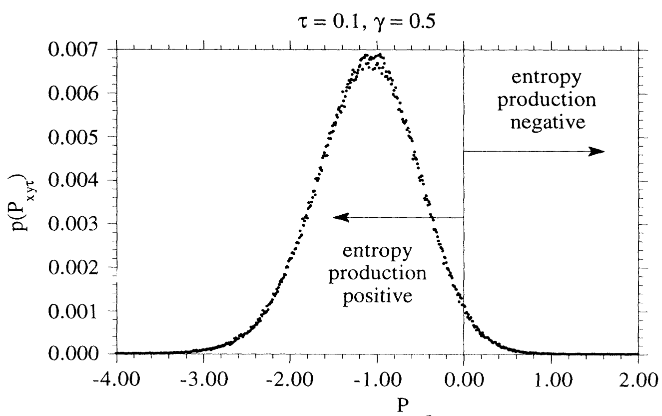

FIG. 1. The probability distribution of segment averages, $\langle P_{xy,i}\rangle_\tau$, of the xy element of the pressure tensor for 56 WCA disks at $H_0/N = 1.56032$, $n = 0.8$, a shear rate $\gamma = 0.5$, and a segment time $\tau = 0.1$. For those states where $\langle P_{xy,i}\rangle_\tau = P_{xy\tau}$ is positive the entropy production is negative for a period of time τ, counter to the second law of thermodynamics.

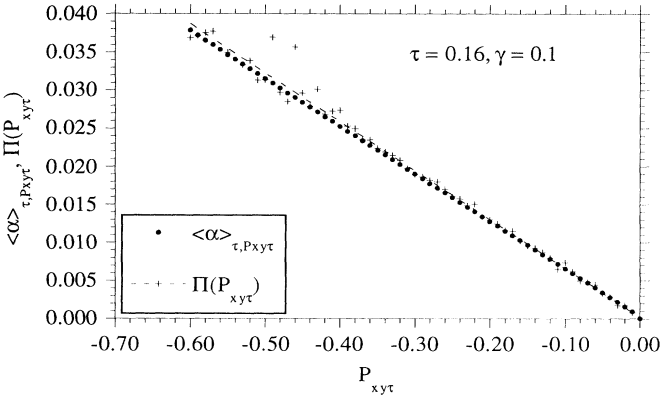

FIG. 2. The logarithmic probability ratio $\Pi(P_{xy\tau})$ and $\langle\alpha\rangle_{\tau,P_{xy\tau}}$ as a function of the segment averaged shear stress $P_{xy\tau}=\langle P_{xy,i}\rangle_\tau$ for $\tau=0.16$ and $\gamma=0.1$. As can be seen the two curves are essentially linear [11], with very nearly equal slopes. The agreement between the two slopes becomes progressively better as τ increases. The straight line shows the results of a weighted linear least-squares fit to the logarithmic probability ratio data.

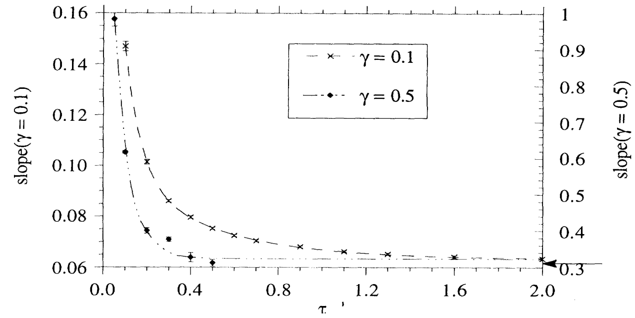

FIG. 3. The slope obtained from the probability ratio Π as a function of τ for $\gamma=0.1$ and 0.5. The error bars are for most of the data smaller than the plotting symbols. The smooth curves show weighted least-squares exponential fits. For $\gamma=0.1$ the asymptotic fitted slope, namely, -0.0633 ± 0.001, agrees within estimated statistical uncertainties with the slope of -0.06259 ± 0.00003, predicted from the $\langle\alpha\rangle_{\tau,P_{xy\tau}}$ data using (8) (and indicated by the arrow). For $\gamma=0.5$ the corresponding slopes are -0.313 ± 0.01 and -0.3137 ± 0.0003 (indicated by the same arrow), respectively, consistent with the proportionality of α and γ.

0.5, and various times τ ranging from 0 to 2. The solutions to the equations (6) and (7) for $\mathbf{q}_i(t),\mathbf{p}_i(t)$ allow an evaluation of $\langle\alpha_i\rangle_\tau$, by using (7) to compute a time average over the trajectory segment i.

In Fig. 1, the observed probability distribution function of $\langle P_{xy,i}\rangle_\tau$ over the segments $i=1,\ldots,M$ is plotted. The distribution is approximately Gaussian with a mean of about -1.116. The right hand tail of the distribution function, where $\langle P_{xy,i}\rangle_\tau>0$, is due to segments i^K, where for a time τ, the second law of thermodynamics is violated. With increasing τ these violations decrease and for $\tau\to\infty$, the second law requires that $P_{xy\tau}<0$ and $\langle\alpha\rangle_\tau>0$ (cf. Fig. 3).

In Fig. 2 the ratio of the probabilities of observing segments i and i^K in states characterized by the values $P_{xy\tau}=\langle P_{xy,i}\rangle_\tau$ and $-P_{xy\tau}$, respectively, are considered. Plotted are $\Pi(P_{xy\tau})\equiv\ln[p(P_{xy\tau})/p(-P_{xy\tau})]/2N\tau$ as well as $\langle\alpha\rangle_{\tau,P_{xy\tau}}$ (the average $\langle\alpha\rangle_\tau$ of $\langle\alpha_i\rangle_\tau$ over all segments i, at given $\langle P_{xy,i}\rangle_\tau=P_{xy\tau}$) as a function of $P_{xy\tau}$, for $\gamma=0.1$ and $\tau=0.16$. As can be seen both functions are essentially linear in $P_{xy\tau}$ and have very nearly identical slopes [11]. The dashed line is a weighted least-squares fit. For increasing τ both functions remain linear, but the slope of $\Pi(P_{xy\tau})$ becomes progressively less negative, while that of α remains constant. Equation (8) implies that the two slopes should become identical for $\tau\to\infty$. This is shown in Fig. 3, where the slope of $\Pi(P_{xy\tau})$ is plotted as a function of τ for $\gamma=0.1$ and $\gamma=0.5$. In determining the slope, a weighted least-squares fit of the data was used. One sees that for $\tau\to\infty$, the slopes indeed approach the corresponding τ-independent slopes of $\langle\alpha\rangle_{\tau,P_{xy\tau}}$ for $\tau\to\infty$, indicated by the arrow. The agreement with Eq. (8) is very good. While this result is a check of Eq. (4) rather than Eq. (1), it can nevertheless be considered as an indirect check of our conjectured dynamically generated natural measure Eq. (1). We remark that the segments i must be large enough for their measures μ_i to be essentially independent of each other, but small enough that fluctuations $P_{xy\tau}$ and $-P_{xy\tau}$ can be observed.

In the limit $\tau\to\infty$, when the segment i becomes the entire phase space trajectory and for large N, $Nd\langle\alpha_i\rangle_\tau/k_B$ (k_B is Boltzmann's constant) can be considered as a generalized rate of entropy production of the system [12]. This follows from Eq. (7), if one identifies the temperature T of the system with the kinetic temperature $\langle\sum_{j=1}^N p_j^2/2m\rangle/Ndk_B$, where the average is a time average over the entire trajectory. Thus the measure (1) can be considered as a dynamical replacement of the Gibbs distribution function [9] applicable also to nonequilibrium stationary states of realistic many-particle systems, possibly very far from equilibrium, suggesting the usefulness of the dynamical weight method in nonequilibrium statistical mechanics.

We hope that these equations will be tested on other problems in statistical mechanics as well.

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[11] In fact it is easy to show that, for instance, in two dimensions in the limit $\gamma \to 0$, $\langle \alpha \rangle_{\tau, P_{xy\tau}} = P_{xy\tau}\gamma/2nk_BT$, i.e., is *precisely* linear in $P_{xy\tau}$ and equals the rate of entropy production per degree of freedom as given by irreversible thermodynamics.

[12] In the linear regime $\gamma \to 0^+$ and for $\tau \to \infty$, Eq. (8) can be obtained from the Green-Kubo expression for the viscosity and the assumption of a Gaussian distribution of $p(P_{xy\tau})$.