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ARTICLES

Ensemble dependence of the transient fluctuation theorem

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The fluctuation theorem gives an analytical expression for the probability of observing second law violating dynamical fluctuations in nonequilibrium systems. At equilibrium, statistical mechanical fluctuations are known to be ensemble dependent. In this paper we generalize the transient and steady-state fluctuation theorems to various nonequilibrium dynamical ensembles. The transient and steady-state fluctuation theorem for an isokinetic ensemble of isokinetic trajectories is tested using nonequilibrium molecular dynamics simulations of shear flow. © 2000 American Institute of Physics. [S0021-9606(00)50433-4]

I. INTRODUCTION

The fluctuation theorem¹⁻³ (FT) gives a general formula for the logarithm of the probability ratio that the time-averaged dissipative flux takes a value, \bar{J}_t , to minus the value, $-\bar{J}_t$, in a nonequilibrium steady state. This formula is an analytic expression that gives the probability, for a finite system and for a finite time, that the dissipative flux flows in the reverse direction to that required by the second law of thermodynamics. For steady-state trajectory segments of length t (i.e., those trajectory segments that are initiated long after the application of a field so that the system has reached a steady state), the steady-state FT (SSFT) is only true in the long time limit. Evans and Searles² have shown that if transient trajectories are considered rather than steady-state trajectories, a transient FT (TFT) that is true at all times can be derived. In the transient experiment the value of \bar{J}_t is obtained by averaging along a trajectory segment that is initially (at $t=0$) sampled from a known distribution (such as an equilibrium distribution), but to which a field is subsequently applied ($t \geq 0$). When the nonequilibrium steady state is unique, one would expect the asymptotic convergence of the transient to the steady-state fluctuation theorem since averages over transient segments should then approach those taken over nonequilibrium steady-state segments. However, there has been some recent discussion^{4,5} of this point and not all parties agree on asymptotic convergence.

The transient FT considers the thermostatted response of an ensemble of systems to an applied dissipative field. The system is thermostatted so that it may reach a steady state after a Maxwell time, τ_M . In the original derivation² it was supposed that the initial ensemble was the microcanonical ensemble and the dynamics was isoenergetic. This initial ensemble was chosen because the probability of observing trajectories originating in a specified phase volume is simply proportional to the measure of that volume. However, it is

straightforward to apply the same procedure to an arbitrary initial ensemble, and an analytical form of the FT that is valid at all times can be obtained. In this paper we demonstrate how the FT can be extended to an arbitrary system, and as an example we derive a transient FT for the isokinetic nonequilibrium response of an initial isokinetic ensemble.

II. TRANSIENT FLUCTUATION THEOREM (TFT)

Consider an N -particle system with coordinates and peculiar momenta, $\{\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N\} \equiv (\mathbf{q}, \mathbf{p}) \equiv \Gamma$. The internal energy of the system is $H_0 \equiv \sum_{i=1}^N p_i^2/2m + \Phi(\mathbf{q}) = K + \Phi$, where $\Phi(\mathbf{q})$ is the interparticle potential energy, which is a function of the coordinates of all the particles, \mathbf{q} and K is the total peculiar kinetic energy. In the presence of an external field F_e , the thermostatted equations of motion are taken to be

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m + \mathbf{C}_i(\Gamma)F_e, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(\mathbf{q}) + \mathbf{D}_i(\Gamma)F_e - \alpha(\Gamma)\mathbf{p}_i, \end{aligned} \quad (1)$$

where $\mathbf{F}_i(\mathbf{q}) = -\partial\Phi(\mathbf{q})/\partial\mathbf{q}_i$, α is the thermostat multiplier, which in this case is applied to the peculiar momenta, and \mathbf{C}_i and \mathbf{D}_i represent the coupling of the system to the field. The dissipative flux is given by J , where $\dot{H}_0^{\text{ad}} \equiv -J(\Gamma)VF_e$.

The probability that a trajectory segment will be observed within an infinitesimal phase space volume of size $\delta V = \lim_{\delta\mathbf{q}, \delta\mathbf{p} \rightarrow 0} \delta q_{x1} \delta q_{y1} \delta q_{z1} \delta q_{x2} \cdots \delta q_{zN} \delta p_{x1} \cdots \delta p_{zN}$ about Γ at time t , $\text{Pr}(\delta V(\Gamma(t), t))$ is given by

$$\text{Pr}(\delta V(\Gamma(t), t)) = f(\Gamma(t), t) \delta V(\Gamma(t), t), \quad (2)$$

where $f(\Gamma(t), t)$ is the normalized phase space distribution function at the point $\Gamma(t)$ at time t . The Lagrangian form of the nonequilibrium Kawasaki distribution function² is given by

$$\begin{aligned} f(\mathbf{\Gamma}(t), t) &= \exp\left(-\int_0^t \Lambda(\mathbf{\Gamma}(s)) ds\right) f(\mathbf{\Gamma}(0), 0) \\ &= \exp\left(-\int_0^t \Lambda(\mathbf{\Gamma}(s)) ds\right) f(\mathbf{\Gamma}(0), 0), \end{aligned} \quad (3)$$

where $\Lambda(\mathbf{\Gamma}) \equiv \dot{\mathbf{\Gamma}} \cdot \partial \mathbf{\Gamma}$ is the phase-space compression factor. Now consider the set of initial phases in the volume element of size $\delta V(\mathbf{\Gamma}(0), 0)$ about $\mathbf{\Gamma}(0)$. At time t , these phases will occupy a volume $\delta V(\mathbf{\Gamma}(t), t)$. Since the number of ensemble members within a comoving phase volume is conserved, (3) can be used to show

$$\delta V(\mathbf{\Gamma}(t), t) = \exp\left(\int_0^t \Lambda(\mathbf{\Gamma}(s)) ds\right) \delta V(\mathbf{\Gamma}(0), 0), \quad (4)$$

which is simply the phase-space volume contraction along the trajectory, from $\mathbf{\Gamma}(0)$ to $\mathbf{\Gamma}(t)$.

Our aim is to determine the ratio of probabilities of observing trajectory segments with time-averaged dissipations of equal magnitude, but opposite sign. For any segment with a particular time-averaged dissipative flux, a segment that has an average of the same magnitude but has an opposite sign can be constructed using a mapping, and the probability of observing this trajectory segment from the initial phase space distribution can be determined. We will refer to the trajectory starting at $\mathbf{\Gamma}(0)$ and ending at $\mathbf{\Gamma}(t)$ as $\mathbf{\Gamma}_{(0;t)}$. If we advance time from 0 to $t/2$ using the equations of motion (1), we obtain $\mathbf{\Gamma}(t/2) = \exp(iL(\mathbf{\Gamma}(0), F_e)t/2)\mathbf{\Gamma}(0)$, where the phase Liouvillian, $iL(\mathbf{\Gamma}, F_e)$ is defined as $iL(\mathbf{\Gamma}, F_e) = \dot{\mathbf{q}}(\mathbf{\Gamma}, F) \cdot \partial / \partial \mathbf{q} + \dot{\mathbf{p}}(\mathbf{\Gamma}, F) \cdot \partial / \partial \mathbf{p}$. Continuing to time t gives $\mathbf{\Gamma}(t) = \exp(iL(\mathbf{\Gamma}(t/2), F_e)t/2)\mathbf{\Gamma}(t/2) = \exp(iL(\mathbf{\Gamma}(0), F_e)t)\mathbf{\Gamma}(0)$. As discussed previously,² a time-reversed trajectory segment that is initiated at time zero, and for which $\mathbf{\Gamma}_{(0;t)}^* = M^{(T)}(\mathbf{\Gamma}_{(0;t)})$, where $M^{(T)}$ is the time-reversal mapping, can be constructed by applying a time-reversal mapping at the midpoint of $\mathbf{\Gamma}(t/2)$ and propagating forward and backward in time from this point for a period of $t/2$ in each direction. At time zero, this generates $\mathbf{\Gamma}^*(0) = \exp(-iL(\mathbf{\Gamma}^*(t/2), F_e)t/2)\mathbf{\Gamma}^*(t/2) = M^T \exp(iL(\mathbf{\Gamma}(t/2), F_e)t/2)\mathbf{\Gamma}(t/2) = M^T \mathbf{\Gamma}(t)$. See Ref. 2 for further details. The point $\mathbf{\Gamma}^*(0)$ is related to the point $\mathbf{\Gamma}(t)$ by a time-reversal mapping. This provides us with an algorithm for finding initial phases, which will subsequently generate the conjugate segments. Since the Jacobian of the time-reversal mapping is unity, the phase volume $\delta V(\mathbf{\Gamma}(t), t)$ is equal to the phase volume $\delta V(\mathbf{\Gamma}^*(0), 0)$. The ratio of the probability of observing the two volume elements at time zero is

$$\begin{aligned} \frac{\Pr(\delta V(\mathbf{\Gamma}(0), 0))}{\Pr(\delta V(\mathbf{\Gamma}^*(0), 0))} &= \frac{f(\mathbf{\Gamma}(0), 0) \delta V(\mathbf{\Gamma}(0), 0)}{f(\mathbf{\Gamma}^*(0), 0) \delta V(\mathbf{\Gamma}^*(0), 0)} \\ &= \frac{f(\mathbf{\Gamma}(0), 0)}{f(\mathbf{\Gamma}(t), 0)} \exp\left(-\int_0^t \Lambda(\mathbf{\Gamma}(s)) ds\right), \end{aligned} \quad (5)$$

where we have used the symmetry of the time-reversal mapping and Eq. (4) to obtain the final equality. This TFT is completely general and applies to any ensemble or type of dynamics. If the initial phase-space distribution function is known (regardless of whether it is an equilibrium distribution), we can then obtain an analytical expression for the probability ratio. Note that the phase-space distribution function in the numerator and denominator both refer to that at time zero, therefore it is readily applied to a system that is at equilibrium at time zero but moves away from equilibrium (when the distribution function may be intractable).

For arbitrary initial ensembles and arbitrary dynamics (constant energy, temperature and/or pressure, etc.) it is convenient to define a general dissipation function $\mathcal{B}(\mathbf{\Gamma})$, so that

$$\begin{aligned} \int_0^t ds \mathcal{B}(\mathbf{\Gamma}(s)) &= \ln\left(\frac{f(\mathbf{\Gamma}(0), 0)}{f(\mathbf{\Gamma}(t), 0)}\right) \\ &\quad - \int_0^t \Lambda(\mathbf{\Gamma}(s)) ds, \equiv \bar{\mathcal{B}}_t, \end{aligned} \quad (6)$$

we can obtain a formula for the probability ratio of observing a particular value of $\bar{\mathcal{B}}_t$ and its negative. This is achieved by summing over all appropriate regions of phase and a TFT for the property \mathcal{B} is obtained^{2,6} of the form

$$\begin{aligned} \ln \frac{\Pr(\bar{\mathcal{B}}_t = A)}{\Pr(-\bar{\mathcal{B}}_t = A)} &= \ln \frac{\sum_{i|\bar{\mathcal{B}}_t = A} \Pr(\delta V_i(\mathbf{\Gamma}(0), 0))}{\sum_{i|\bar{\mathcal{B}}_t = -A} \Pr(\delta V_i(\mathbf{\Gamma}(0), 0))} = \ln \frac{\sum_{i|\bar{\mathcal{B}}_t = A} \Pr(\delta V_i(\mathbf{\Gamma}(0), 0))}{\sum_{i|\bar{\mathcal{B}}_t = A} \Pr(\delta V_i(\mathbf{\Gamma}^*(0), 0))} \\ &= \ln \frac{\sum_{i|\bar{\mathcal{B}}_t = A} \Pr(\delta V_i(\mathbf{\Gamma}(0), 0))}{\sum_{i|\bar{\mathcal{B}}_t = A} \frac{f(\mathbf{\Gamma}(t), 0)}{f(\mathbf{\Gamma}(0), 0)} \exp(\int_0^t \Lambda(\mathbf{\Gamma}(s)) ds) \Pr(\delta V_i(\mathbf{\Gamma}(0), 0))} = \ln \frac{\sum_{i|\bar{\mathcal{B}}_t = A} \Pr(\delta V_i(\mathbf{\Gamma}(0), 0))}{\sum_{i|\bar{\mathcal{B}}_t = A} \exp(-\bar{\mathcal{B}}_t) \Pr(\delta V_i(\mathbf{\Gamma}(0), 0))} = \bar{\mathcal{B}}_t, \end{aligned} \quad (7)$$

where the notation $\sum_{i|\bar{\mathcal{B}}_t = A}$ is used to indicate that the sum is carried out over phase volumes for which $\bar{\mathcal{B}}_t = A$. In (7) we carry out the time-reversal mapping to obtain the second equality, then substitute Eqs. (5) and (6). The final equality is

obtained by recognizing that since the summation is only carried out over trajectory segments with particular values of $\bar{\mathcal{B}}_t$, the exponential term can be removed from the summation.

The equation (7) has previously been considered for a system that is initially in a microcanonical ensemble and that undergoes isoenergetic dynamics.^{2,6-8} In this case $\mathcal{B}(\Gamma) = -\Lambda(\Gamma) = -VF_e\beta J(\Gamma)$ and simulations have verified the resulting TFT, that is, $\ln \Pr(\bar{A}_t=A)/\Pr(-\bar{A}_t=A) = -At = -VF_e\beta \bar{J}_t t$, where $\bar{J}_t = A/(VF_e\beta)$.^{1,2,5,6,8} Our purpose in this paper is to derive equations equivalent to (7) for other ensembles and dynamics.

As an example, we consider a system initially in the isokinetic ensemble and undergoing isokinetic dynamics. The isokinetic distribution function is

$$f(\Gamma(0),0) = f_K(\Gamma(0),0) = \frac{\exp(-\beta H_0(\Gamma(0))) \delta(K(\Gamma(0)) - K_0)}{\int d\Gamma \exp(-\beta H_0(\Gamma)) \delta(K(\Gamma) - K_0)}. \quad (8)$$

Substituting into Eq. (5) gives

$$\begin{aligned} \frac{\Pr(\delta V(\Gamma(0),0))}{\Pr(\delta V(\Gamma^*(0),0))} &= \frac{f_K(\Gamma(0),0) \delta V(\Gamma(0),0)}{f_K(\Gamma^*(0),0) \delta V(\Gamma^*(0),0)} \\ &= \frac{\exp(-\beta H_0(\Gamma(0)))}{\exp(-\beta H_0(\Gamma(t)))} \\ &\quad \times \exp\left(-\int_0^t \Lambda(\Gamma(s)) ds\right) \\ &= \exp\left(\beta \int_0^t \dot{\Phi}(\Gamma(s)) ds\right) \\ &\quad \times \exp\left(-\int_0^t \Lambda(\Gamma(s)) ds\right), \quad (9) \end{aligned}$$

where we have used the symmetry of the mapping, $H_0(\Gamma^*(0)) = H_0(\Gamma(t))$, $V(\Gamma^*(0),0) = V(\Gamma(t),t)$, and $K(\Gamma^*(0),0) = K(\Gamma(t),t)$ to obtain the second equality and $H_0(\Gamma(t)) = H_0(\Gamma(0)) + \int_0^t \dot{H}_0(\Gamma(s)) ds = H_0(\Gamma(0)) + \int_0^t \dot{\Phi}(\Gamma(s)) ds$ to obtain the final equality. We see that

$$\mathcal{B}(\Gamma) = \beta \dot{\Phi}(\Gamma) - \Lambda(\Gamma) = -\beta J(\Gamma) VF_e,$$

and from (7) we therefore have

$$\ln \frac{\Pr(\bar{J}_t=A)}{\Pr(\bar{J}_t=-A)} = -AtF_e\beta V. \quad (10)$$

The TFT given by Eq. (10) is true at all times for the isokinetic ensemble when all initial phases are sampled from an equilibrium isokinetic ensemble.

If the system reaches a unique steady state, then at long times the value of J will fluctuate about its steady-state value. A set of nonequilibrium time-averaged currents, $\{\bar{J}_{t,SS}\}$, can be generated by evolving time along a single phase space trajectory that starts at some initial phase, which is consistent with the macroscopic conditions (N, V, T or E, F_e , etc.). One waits for a time that is much longer than the Maxwell time, τ_M , which characterizes the transient response, before one begins to analyze time contiguous ‘‘steady-state’’ trajectory segments and computes, for example, the statistics of the set $\{\bar{J}_{t,SS}\}$.

If the steady state is unique, the statistics of the set $\{\bar{J}_{t,SS}\}$ is independent of the original initial phases. Since the

steady state is unique we can also gather the statistical information on $\{\bar{J}_{t,SS}\}$ by studying the response of an ensemble of initial phases, provided we wait several Maxwell times before gathering ‘‘steady-state’’ data. After the transient response time, the instantaneous system properties will be characteristic of the steady state. The set $\{\bar{J}_{t,T}\}$ averaged over transient trajectory segments, starting from an equilibrium ensemble of phases will approach the (unique) steady-state set $\{\bar{J}_{t,SS}\}$ with $\{\bar{J}_{t,T}\} = \{\bar{J}_{t,SS}\} + O(\tau_M/t)$.

The transient flux, $\bar{J}_{t,T} = \bar{J}_{t,SS} + O(\tau_M/t)$, can be expanded using a Taylor series analysis and because at sufficiently long times the deviation of $\bar{J}_{t,SS}$ from its mean value decreases as $O(t^{-1/2})$, Eq. (10) can be written as

$$\begin{aligned} \ln \frac{\Pr(\bar{J}_{t,T}=A)}{\Pr(\bar{J}_{t,T}=-A)} &= \ln \frac{\Pr(\bar{J}_{t,SS}=A)}{\Pr(\bar{J}_{t,SS}=-A)} + \ln(O(\tau_M/t)t) \\ &= -AtF_e\beta V. \quad (11) \end{aligned}$$

Therefore since t_M is finite, provided t is sufficiently long and the steady state is unique, we expect

$$\lim_{t \rightarrow \infty} \frac{1}{t} \ln \frac{\Pr(\bar{J}_{t,SS}=A)}{\Pr(\bar{J}_{t,SS}=-A)} = -AF_e\beta V. \quad (12)$$

Although there is some contention regarding this point,^{4,5} the numerical tests presented below support the possibility of this convergence.

In Table I we give transient FTs for various ergodically consistent ensembles,⁷ that is, for systems where the zero field dynamics preserves the initial ensemble: $\partial f(\Gamma,0)/\partial t|_{F_e=0} = 0$. We also give the exact form of the steady-state FT derived from the transient FT by assuming the steady state is unique.

The steady-state FT, proposed and tested by Evans, Cohen, and Morriss¹ and proven by Gallavotti and Cohen referred to particular conditions (that the dynamics is dissipative, isoenergetic,⁹ reversible, and chaotic) and may be expressed by the formula⁴

$$\lim_{t \rightarrow \infty} \frac{1}{t} \ln \frac{\Pr(\bar{\Lambda}_t=A)}{\Pr(\bar{\Lambda}_t=-A)} = -A. \quad (13)$$

In a Gaussian isoenergetic system the phase-space contraction rate is instantaneously proportional to both the entropy production rate per unit volume and the dissipative flux, and the fluctuations in these three properties will be directly related. Alternative forms of the FT for the isoenergetic system in terms of the fluctuations of the dissipative flux or the entropy production rate per unit volume are therefore trivially obtained. In the original work of Gallavotti and Cohen, for example, the FT was expressed in terms of the entropy production rate per unit volume.³ For a system undergoing *isokinetic* dynamics the dissipative flux is no longer instan-

TABLE I. Transient fluctuation formula in various ergodically consistent ensembles.^{a,b}

Isokinetic dynamics	$\ln \frac{\Pr(\bar{J}_t)}{\Pr(-\bar{J}_t)} = -\bar{J}_t F_e \beta V$	$-J F_e V = \frac{dH_0^{\text{ad}}}{dt}$
Isobaric–isothermal	$\ln \frac{\Pr(\bar{J}_t)}{\Pr(-\bar{J}_t)} = -\bar{J}_t F_e \beta V$	$-J F_e V = \frac{dI_0^{\text{ad}}}{dt}$
Isoenergetic	$\ln \frac{\Pr(\overline{J\beta}_t)}{\Pr(-\overline{J\beta}_t)} = -\overline{J\beta}_t F_e V$	$-J F_e V = \frac{dH_0^{\text{ad}}}{dt}$
	or $\ln \frac{\Pr(\bar{\Lambda}_t)}{\Pr(-\bar{\Lambda}_t)} = -\bar{\Lambda}_t$	
Isoenergetic boundary-driven flow	$\ln \frac{\Pr(\bar{\Lambda}_t)}{\Pr(-\bar{\Lambda}_t)} = -\bar{\Lambda}_t$	
Nosé–Hoover (canonical) dynamics	$\ln \frac{\Pr(\bar{J}_t)}{\Pr(-\bar{J}_t)} = -\bar{J}_t F_e \beta V$	$-J F_e V = \frac{dH_0^{\text{ad}}}{dt}$
Wall ergostatted field-driven flow ^c	$\ln \frac{\Pr(\overline{J\beta}_{\text{wall } t})}{\Pr(-\overline{J\beta}_{\text{wall } t})} = -\overline{J\beta}_{\text{wall } t} F_e V$	$-J F_e V = \frac{dH_0^{\text{ad}}}{dt}$
	or $\ln \frac{\Pr(\bar{\Lambda}_t)}{\Pr(-\bar{\Lambda}_t)} = -\bar{\Lambda}_t$	
Wall thermostatted field-driven flow ^c	$\ln \frac{\Pr(\bar{J}_t)}{\Pr(-\bar{J}_t)} = -\bar{J}_t F_e \beta V$	$-J F_e V = \frac{dH_0^{\text{ad}}}{dt}$
	$-\ln(\langle \exp[\bar{\Lambda}_t(1 - \beta_{\text{system}}/\beta_{\text{wall}})] \rangle_{\bar{J}_t})$	
Steady-state isoenergetic dynamics. ^d	$\ln \frac{\Pr(\overline{J\beta}_t)}{\Pr(-\overline{J\beta}_t)} = -\overline{J\beta}_t F_e V$	$-J F_e V = \frac{dH_0^{\text{ad}}}{dt}$
$\bar{J}_t = 1/t \int_{t_0}^{t_0+t} J(s) ds$, where $t_0 \gg \tau_M$	$-\ln \left\{ \exp \left[F_e V \left\langle \int_0^{t_0} J(s) \beta(s) ds \right. \right. \right. \right.$	
	$\left. \left. \left. + \int_{t_0+t}^{2t_0+t} J(s) \beta(s) ds \right] \right\} \right\}_{\bar{J}_t}$	
	$\lim_{t \rightarrow \infty} \frac{1}{t} \ln \frac{\Pr(\overline{J\beta}_t)}{\Pr(-\overline{J\beta}_t)} = -\overline{J\beta}_t F_e V$	

^aIt is assumed that the limit of a large system has been taken so that $O(1/N)$ effects can be neglected. In the Nosé–Hoover dynamics, it is also assumed that the mass associated with the heat bath is an extensive variable.

^b H_0 is the equilibrium internal energy and I_0 is the equilibrium enthalpy.

^cIn these wall ergostatted/thermostatted systems, it is assumed that the energy/temperature of the full system (wall and fluid) is fixed.

^dSimilar steady-state formula can be obtained for other ensembles. τ_M is the Maxwell time that characterizes the time required for relaxation of the nonequilibrium system into a steady state.

taneously proportional to the phase-space contraction rate [although the time-averaged values are proportional in the limit $t \rightarrow \infty$ since $\bar{\Lambda}_t(\Gamma) = V F_e \beta \bar{J}_t(\Gamma) + O(1/t)$], and it is therefore of interest to consider (13) for the isokinetic dynamics.

III. NUMERICAL RESULTS FOR TRANSIENT AND STEADY-STATE SYSTEMS

We test Eqs. (10), (12), and (13) for systems consisting of $N = 32$ WCA particles in two Cartesian dimensions undergoing isokinetic shear flow in two Cartesian dimensions using the SLLOD equations of motion for planar Couette flow.⁷ The equations of motion are

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m_i + \mathbf{i}\gamma y_i, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{i}\gamma p_{yi} - \alpha \mathbf{p}_i, \end{aligned} \quad (14)$$

where γ is the applied strain rate, and α is the Gaussian isokinetic thermostat multiplier:

$$\alpha = \frac{\sum_{i=1}^N \mathbf{F}_i \cdot \mathbf{p}_i - \gamma p_{xi} p_{yi}}{\sum_{i=1}^N \mathbf{p}_i \cdot \mathbf{p}_i}. \quad (15)$$

In this case the dissipative flux J is equal to P_{xy} , the xy element of the pressure tensor and $\Lambda(\Gamma) = -2N\alpha(\Gamma) + O(1)$. All results below are presented in reduced units. The simulations are carried out for systems under two conditions. In the first case a temperature of $T = 1.0$, a particle density of $n = 0.8$ and an applied strain rate of $F_e = \gamma = 0.5$ are employed. This applied strain rate is sufficiently high that we are in the nonlinear regime and the shear thinning is approximately 12%. In the second case a temperature of $T = 1.0$, a particle density of $n = 0.4$ and an applied strain rate of $F_e = \gamma = 0.01$ are employed and the system is in the linear regime.

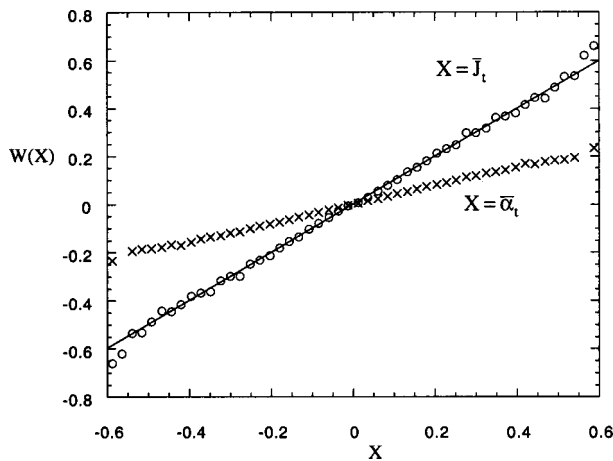


FIG. 1. The normalized logarithmic probability ratio $W(X)$ for the fluctuations in a transient response numerical experiment with $T=1.0$, $n=0.8$, $N=32$, $\gamma=0.5$, and a transient trajectory segment of length $t=0.6$. The circles are a test of the transient FT given by Eq. (11) and the crosses show that the limiting expression given by Eq. (13) is not applicable, at least at this value of t . The straight line is the expected result from Eqs. (11) and (13).

For both sets of conditions, transient trajectories and steady-state trajectory segments are considered. The transient trajectories of length t are initiated from an isokinetic equilibrium ensemble and the time-averaged value of the thermostat multiplier and the dissipative flux is calculated for each trajectory. The steady-state trajectory segments are initiated at equally spaced time origins along a single steady-state trajectory. In this case the thermostat multiplier and the dissipative flux are calculated for each trajectory segment of length t .

Results for transient trajectories are shown in Figs. 1 and 2. In Fig. 1, transient trajectory segments of length $t=0.6$ are considered. The value of $W_J(t) \equiv -\ln(\text{Pr}(\bar{J}_t)/\text{Pr}(-\bar{J}_t))/(t\gamma\beta V)$ is plotted as a function of \bar{J}_t to test Eq. (10), and $W_\alpha(t) \equiv \ln(\text{Pr}(\bar{\alpha}_t)/\text{Pr}(-\bar{\alpha}_t))/(2Nt)$ is plotted as a function of $\bar{\alpha}_t$ to test Eq. (13). If the equations are valid, a straight line of unit slope is obtained. As expected, the results indicate that Eq. (10) is valid, whereas Eq. (13) is clearly *not* valid for an averaging time $t=0.6$. In Fig. 2 we show how the slopes of the lines formed from a plot of $W_J(t)$ vs \bar{J}_t and $W_\alpha(t)$ vs $\bar{\alpha}_t$ vary with averaging time, t . We denote the slopes of these lines $S_J(t)$ and $S_\alpha(t)$, respectively. This figure demonstrates that the transient FT derived in this paper for a isokinetic systems and given by (10) is valid at all times, but that Eq. (13) is not valid at the times considered. The behavior of $S_\alpha(t)$ is consistent with a $1/\sqrt{t}$ convergence to 1 for the system where $F_e=0.5$: this is the same rate at which the standard deviation of the distribution of the value of $\bar{\alpha}_t$ goes to zero, however, it can also be fitted to other functional forms. The data for the system where $F_e=0.01$ do not appear to converge to a slope of 1, although it has clearly not reached its limiting behavior at the times considered.

In Fig. 3, we test the FT for *steady-state* simulations where neither Eq. (10) nor (13) is true instantaneously, but we expect (10) to be true for times greater than a several Maxwell times ($\tau_M=0.084$ for $T=1.0$, $n=0.8$, $\gamma=0.5$) [i.e.,

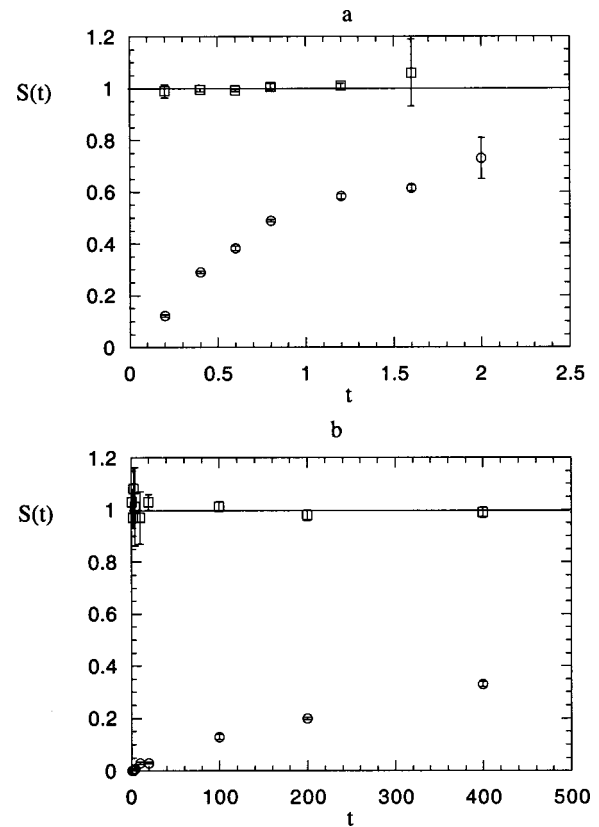


FIG. 2. The squares show the slope of a straight line fitted through a plot of $W_J(t)$ vs \bar{J}_t , as a function of t for the transient response of a two-dimensional system of 32 particles at (a) $T=1.0$, $n=0.8$, and $\gamma=0.5$ and (b) $T=1.0$, $n=0.4$, and $\gamma=0.01$. Equation (10) tests the TFT for this system and predicts a slope of 1 at all times, which is indeed observed. The circles show the slope of a straight line fitted through a plot of $W_\alpha(t)$ vs $\bar{\alpha}_t$, as a function of t for the same system. Equation (13) says the slope will be 1 in the limit of long times. $O(1/N)$ effects have been accounted for.

we expect that the steady-state FT given by Eq. (12) is true]. The steady-state trajectory segment averages are obtained from a single trajectory, sampled at different points along the trajectory, and consider the same state points as examined for the transient simulations. Clearly, convergence to the limiting behavior predicted by Eq. (12) is observed. In contrast, the limiting behavior predicted by Eq. (13) has not been realized, even at the longest times considered. The data indicate that *if* convergence does occur, it is very slow compared to its convergence in an isoenergetic system [note that the $n=0.8$ state point is quite similar to that studied by Evans, Cohen, and Morriss,¹ where convergence to within the error bars of the data (3%) was observed when the averaging time was 0.5 and $\gamma=0.5$].

The values of $S_\alpha(t)$ determined in the transient experiments are also shown in Fig. 3 to demonstrate the convergence of the distribution of the averages over transient trajectories to those over steady-state trajectory segments with time. Although (13) is not valid at the times considered, the values of $S_\alpha(t)$ obtained from the transient experiments agree with those obtained from the steady-state trajectory segments at sufficiently long times. Furthermore, the $S_J(t)$ for the transient and steady-state segments agree, and the TFT given by Eq. (10) and the steady-state expression given

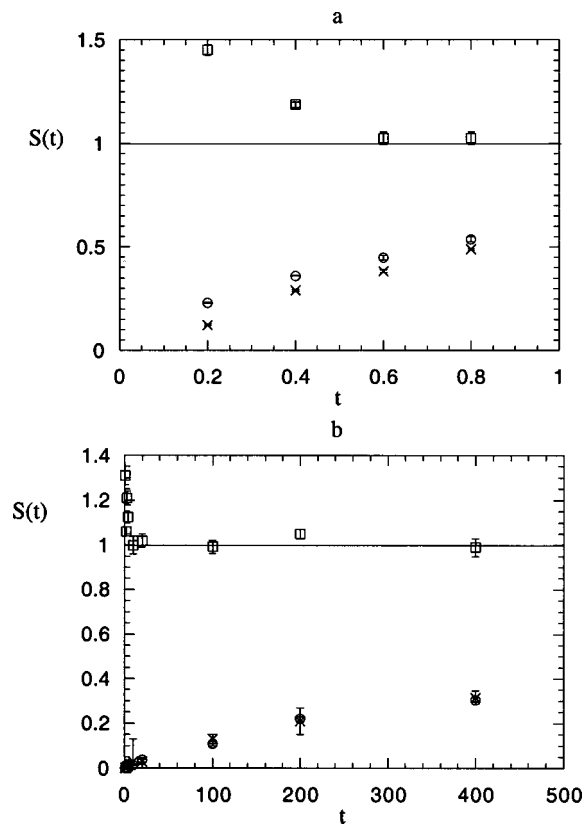


FIG. 3. The squares show the slope of straight line fitted through a plot of $W_j(t)$ vs \bar{J}_t , as a function of t for a steady-state simulation of a two-dimensional system of 32 particles at (a) $T=1.0$, $n=0.8$ and $\gamma=0.5$ and (b) $T=1.0$, $n=0.4$, and $\gamma=0.01$. Equation (10) is the steady-state expression corresponding to the TFT for this system and predicts a slope of 1 in the long time limit, which is consistent with the results. The circles show the slope of a straight line fitted through a plot of $W_\alpha(t)$ vs $\bar{\alpha}_t$, as a function of t for the same system. The crosses show how the slope of a straight line fitted through a plot of $W_\alpha(t)$ vs $\bar{\alpha}_t$ varies with t using data for a transient experiment (as also shown in Fig. 2). Convergence of the transient and steady-state results is observed. $O(1/N)$ effects have been accounted for.

by Eq. (12) are verified for the transient and steady-state systems, respectively. These observations support the possibility that the steady-state relationships are correctly predicted from the limiting behavior of the TFT expressions. It implies that not only does the form of the TFT change when isokinetic dynamics replaces isoenergetic dynamics, but that a corresponding new SSFT is obtained that is given by Eq. (12).

At equilibrium, Eq. (13) is clearly false for isokinetic dynamics for any finite t . In this case the probability of observing positive and negative fluctuations in $\bar{\Lambda}_t$ must be equal, and therefore $S_\alpha(t)=0$ for all finite times. Equation (13) incorrectly suggests that the logarithm of the probability ratio is proportional to the fluctuation, and that $S_\alpha(t)=1$. The falsity of Eq. (13) at equilibrium is consistent with the results in Fig. 3, where the calculated value of $S_\alpha(t)$ is less than unity for the times considered and the departure is greater for the system which is subject to a smaller field. It seems to indicate that either the convergence time becomes infinite as the field goes to zero or that $S_\alpha(t)$ converges to a value less than unity. The behavior of the fluctuations in \bar{J}_t is correctly predicted by Eq. (10), which becomes trivial. The

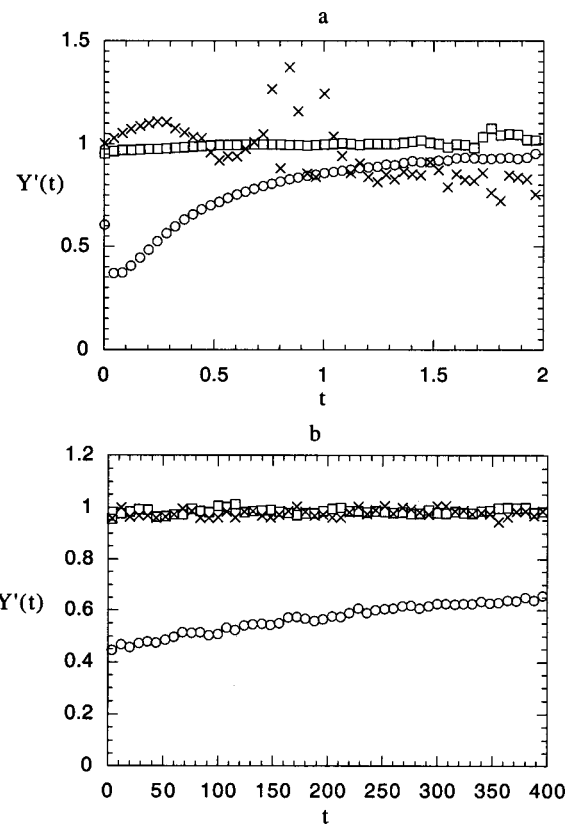


FIG. 4. Tests of the integrated fluctuation formulas given by Eqs. (16)–(18) for a two-dimensional system of 32 particles at (a) $T=1.0$, $n=0.8$, and $\gamma=0.5$ and (b) $T=1.0$, $n=0.4$, and $\gamma=0.01$. The squares show $Y'_j(t)$, which is predicted to be unity at all times by Eq. (16). If Eq. (17) is correct, then $Y'_\alpha(t)$, shown by the circles, should approach unity at long times. The crosses show $\tilde{Y}'_\alpha(t)$, which will equal unity at all times if (18) is valid. Large numerical errors in $\tilde{Y}'_\alpha(t)$ are observed for the system at a large field, as expected.¹⁰

observation that Eq. (13) is not valid for an isokinetic system at equilibrium is not in conflict with Gallavotti and Cohen⁴ because the equilibrium system is both nondissipative and nonisoenergetic,⁹ as is required.

We note that it is difficult to test the FT in nonequilibrium systems for long averaging times, large fields, or large systems, since in these limits the variance of the distributions approach zero. Therefore, the fluctuations become so narrow that by the time the formula has converged to its asymptotic behavior, it is not possible to observe the second law violating trajectory segments either in a computer simulation or experimentally. This highlights the utility of a transient rather than the steady-state FT. Tests of the asymptotic steady-state FT can, of course, *only* be carried out for long averaging times. The transient FT, on the other hand, can be tested for arbitrarily short averaging times, where the probability of spontaneous second law violations is much greater, approaching 0.5 as $t \rightarrow 0$.

The integrated form of the fluctuation formula (IFT) also provides a means of reducing the statistical error when testing the FT for long periods of time.⁸ The IFT corresponding to Eq. (11) is

$$\frac{p(\bar{J}_t < 0)}{p(\bar{J}_t > 0)} = \langle \exp(\bar{J}_t F_e \beta V) \rangle_{\bar{J}_t > 0}^{-1} = \langle \exp(\bar{J}_t F_e \beta V) \rangle_{\bar{J}_t < 0}^{-1}, \quad (16)$$

where $p(\bar{J}_t > 0)$ and $p(\bar{J}_t < 0)$ refer to the probabilities of observing trajectory segments with positive or negative values of \bar{J}_t , respectively, and the notations $\langle \cdots \rangle_{\bar{J}_t > 0}$ and $\langle \cdots \rangle_{\bar{J}_t < 0}$ refer to ensemble averages over trajectories with positive or negative values of \bar{J}_t , respectively. We define $Y'_j(t) \equiv (\ln(p(\bar{J}_t > 0)/p(\bar{J}_t < 0)) - 1) / (\ln(\langle \exp(\bar{J}_t F_e \beta V) \rangle_{\bar{J}_t < 0} - 1))$ and in Fig. 4 it is verified that $Y'_j(t) = 1$ at all times, in agreement with (16). [Note that subtraction of 1 in the numerator and denominator is carried out to circumvent large statistical errors when the probabilities are almost equal. This property therefore differs from $Y(t)$ used to measure convergence of the IFT in Ref. 5.] The time that can be considered in the IFT is still limited, particularly at high fields.

By defining $Y'_\alpha(t) \equiv (\ln(p(\bar{\alpha}_t < 0)/p(\bar{\alpha}_t > 0)) - 1) / (\ln(\langle \exp(-2N\bar{\alpha}_t) \rangle_{\bar{\alpha}_t > 0} - 1))$ an IFT corresponding to (13) is

$$\lim_{t \rightarrow \infty} Y'_\alpha(t) = \lim_{t \rightarrow \infty} ((\ln(p(\bar{\alpha}_t < 0)/p(\bar{\alpha}_t > 0)) - 1) / (\ln(\langle \exp(-2N\bar{\alpha}_t) \rangle_{\bar{\alpha}_t > 0} - 1))) = 1. \quad (17)$$

The behavior of $Y'_\alpha(t)$ for the nonequilibrium systems examined above is shown in Fig. 4. Convergence to the limiting behavior indicated by (17) has not occurred at the longest times considered. An IFT, valid at all times and for arbitrary field strengths, is

$$\frac{p(\bar{\alpha}_t > 0)}{p(\bar{\alpha}_t < 0)} = \langle \exp(\bar{J}_t F_e \beta V) \rangle_{\bar{\alpha}_t > 0}^{-1}. \quad (18)$$

This relation predicts that $\tilde{Y}'_\alpha(t) \equiv (\ln(p(\bar{\alpha}_t < 0)/p(\bar{\alpha}_t > 0)) - 1) / (\ln(\langle \exp(\bar{J}_t F_e \beta V) \rangle_{\bar{\alpha}_t > 0} - 1))$ is unity at all times. Note that in a numerical test of Eq. (18) the large contribution of rarely observed events (when \bar{J}_t is highly positive) to the ensemble average is problematic.¹⁰ This is observed in the data presented in Fig. 4.

IV. CONCLUSION

In this paper we have shown how the transient FT, which was originally derived for the isoenergetic nonequilibrium response of an equilibrium microcanonical ensemble, may be generalized to cases where the response is observed for different ensembles with different types of thermostats. The form of the FT may change with ensemble, as shown in Table I. This should come as no surprise since even at equilibrium fluctuation formulas are generally ensemble dependent.

We have presented numerical results for the response of the isokinetic ensemble to isokinetic shear flow for a system

far from equilibrium in the nonlinear regime and for a system in the linear regime. We find that the transient FT derived here and given by Eq. (10) for this ensemble/dynamics combination is satisfied for all averaging times. From this transient FT we obtain a corresponding steady-state FT given by Eq. (12) for this system. It is observed that the form of the steady-state FT derived from the transient FT also varies with ensemble. In the limit of long averaging times the computational results again support the validity of the proposed steady-state FT for this combination of ensemble and dynamics.

The major consequences of the TFT are that it explains the second law of thermodynamics from a microscopic basis and that it provides a very general but simple derivation^{1,2(d)} of Green–Kubo and Einstein relations for linear transport coefficients. The theorem is more general than the Green–Kubo relations because, in part, it applies outside the near equilibrium regime required for Green–Kubo and Einstein relations to be valid. Recently the fluctuation theorem has been shown to be valid for a wide class of stochastic systems.⁶ Because fluctuations by their very nature are generally small and therefore hard to observe, a recently proposed *local* fluctuation theorem⁸ that applies to small subregions of a larger system, may be amenable to an experimental test using light scattering techniques.

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- ¹⁰In a numerical test of Eq. (18) the large contribution of rarely observed events (when \bar{J}_t is highly positive) to the ensemble average results in large statistical errors. This was also evident in the evaluation of the Kawasaki normalization factor.² No difficulty is caused by highly negative values of \bar{J}_t since these terms do not have a strong contribution to the average. Similarly, no difficulty is observed in testing Eqs. (16) and (17), where the rarely observed events allowed in the ensemble averages only have small contributions to the average.