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On the Asymptotic Convergence of the Transient and Steady-State Fluctuation Theorems

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Nonequilibrium molecular dynamics simulations are used to demonstrate the asymptotic convergence of the transient and steady-state forms of the fluctuation theorem. In the case of planar Poiseuille flow, we find that the transient form, valid for all times, converges to the steady-state predictions on microscopic time scales. Further, we find that the time of convergence for the two theorems coincides with the time required for satisfaction of the asymptotic steady-state fluctuation theorem.

KEY WORDS: Nonequilibrium statistical mechanics; dynamical systems; computer simulation.

The Fluctuation Theorem[(1–5)] (FT) gives a general formula valid in non-equilibrium systems, for the logarithm of the probability ratio that the time averaged dissipative flux $\bar{J}_t \equiv 1/t \int_0^t ds\, J(s)$, takes on a value, $\bar{J}_t$, to minus the value, namely $-\bar{J}_t$. The *Steady State* FT (SSFT)[(1, 5)] is only valid asymptotically ($t \to \infty$), and gives the probability for a finite system that the time averaged dissipative flux flows in the reverse direction to that required by the Second Law of Thermodynamics. Gallavotti and Cohen derived the SSFT using the SRB measure and the Chaotic Hypothesis.[(5)] Evans and Searles[(2–4)] have shown that if transient trajectories are considered which originate from an equilibrium distribution of phases and evolve in time towards the nonequilibrium steady state, then a *Transient* FT (TFT) that is true at all times can be derived.

When the nonequilibrium steady state is unique (i.e., steady state time averages are independent of the initial phase from which a trajectory originates) one would expect the asymptotic convergence of the Transient

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FT towards the Steady State FT. However, there has been some recent discussion[6] of this point and not all parties agree on this asymptotic convergence.

In this paper we will present convincing non-equilibrium molecular dynamics (NEMD) simulation results that demonstrate the asymptotic convergence of the Transient and Steady State Fluctuation Theorems. We will show that the Transient FT holds for all time, and that after a finite time, the two Theorems converge to the *same* predictions for the probability ratios. Not only does TFT approach the SSTF, but the time of convergence for the two Theorems coincides with the corresponding time of convergence for the asymptotic SSTF itself.

The simulation was exactly as described in ref. 7, and we will only very briefly discuss some details here. We simulated planar Poiseuille flow where an atomic fluid obeying Newton's equations of motion is placed between two heat extracting walls. Heat sinks in the walls remove heat at precisely the rate required to make the total energy of the system a constant of the motion. As in ref. 7 we calculated the *Integrated* form of the Transient and Steady State FT's (TIFT and SSIFT respectively), written as

$$p_-(t)/p_+(t) = \phi(t)$$

where

$$\phi(t) \equiv \langle \exp[-3N_W \bar{\alpha}(t)\, t] \rangle_+$$

and p_-/p_+ is the probability of observing an anti-trajectory versus a trajectory, N_W is the number of ergostatting wall particles, $\alpha = -J(\mathbf{\Gamma})\, VF_e/2K_W$ is the thermostat multiplier, $K_W = \sum_{i=1}^{N_W} p_i^2/2m$ is the kinetic energy of the wall particles, F_e is the external field, the dissipative flux, J is defined, $-J(\mathbf{\Gamma})\, V \equiv \int d\mathbf{r}\, n(\mathbf{r})\, u_x(\mathbf{r})$, where $n(\mathbf{r})$ and $u_x(\mathbf{r})$ are the density and flow velocity. The averages, $\langle \cdots \rangle_+$ denote averages over all trajectory segments for which $\bar{\alpha}(t) = 1/t \int_0^t \alpha(s)\, ds > 0$. The notation is identical to ref. 7.

Testing the validity of TIFT and SSIFT with NEMD requires a method of generating either a set of transient trajectories or a single long steady state trajectory. In the transient case, two hundred transient non-equilibrium trajectory segments were generated from a microcanonically distributed ensemble of initial phase configurations, $\{\mathbf{\Gamma}_{eq}\}$. Each transient segment was studied for $t = 10$ (the integration time step was $\delta t = 0.001$). This time is sufficiently long that all time averaged properties have converged to their steady state values.

Each transient was simultaneously subjected to an external field ($F_e = 0.032$) and initialized as a new transient segment time origin. After following the transient segment for $t = 10$, the trajectory was terminated, and a new equilibrium configuration was selected. A TTIFT can then be tested by examining each of the transient segments at equal time intervals from their respective transient time origins.

It is not possible to generate an exact steady state trajectory. This is because within phase space, the measure of any dissipative nonequilibrium steady state is zero. Therefore the probability of selecting initial phase points that lie exactly on the steady state attractor is zero. We can only *approach* the nonequilibrium steady state. We used an *equilibration method* of approaching the steady state: an arbitrary microcanonical phase point was chosen; an $F_e = 0.032$ external field was applied and the system was allowed to equilibrate towards the steady state for a time ($t = 500$). This time is *very much* greater than the decay time of transient time averages ($t = 3 - 4$). Subsequently a $t = 5000$ "steady state" trajectory was generated. The "steady state" trajectory was decomposed into 2.5×10^4 "steady state" subsegments each of duration $t = 0.2$, which could be examined to test the SSIFT with observation times ranging from $t = 0.2$ (with 2.5×10^4 possible samples for $\bar{\alpha}_+(t_1)$), $t = 0.4$ (with 1.25×10^4 possible samples for $\bar{\alpha}_+(t_2)$) to $t = 5000$ (one sample of $\bar{\alpha}_+(t_{5000})$).

Convergence of the TIFT and SSIFT can be tested by exploiting the near exponential decay of $p_-(t)/p_+(t)$ and $\phi(t)$ [see Fig. 2 inset] and calculating the ratios $Y(t)$, $Z_p(t)$ and $Z_\phi(t)$ defined as:

$$Ln[p_-(t)/p_+(t)]/Ln[\phi(t)] = Y(t), \qquad \lim_{t \to \infty} Y(t) = 1$$

$$Ln[p_-(t)/p_+(t)]_{SS}/Ln[p_-(t)/p_+(t)]_T = Z_p(t), \qquad \lim_{t \to \infty} Z_p(t) = 1$$

$$Ln[\phi(t)]_{SS}/Ln[\phi(t)]_T = Z_\phi(t), \qquad \lim_{t \to \infty} Z_\phi(t) = 1$$

$Y(t)$ is an identity in the transient case, $Y_T(t) = 1$, $\forall t$, in the steady state (SS), $Y_{SS}(t)$ is only 1 asymptotically (for $t > \sim 4$). Once $Y_T(t)$ and $Y_{SS}(t)$ have converged, we can then examine the convergence of the corresponding transient and steady state *fluctuations* through $Z_p(t)$ and $Z_\phi(t)$. In Fig. 1 we show $Y_T(t)$ (transient) and $Y_{SS}(t)$ (steady state) and as expected, $Y_T(t) = 1$, $\forall t$, and $Y_{SS}(t)$ is only 1 asymptotically (for $t > \sim 4$). Convergence of the transient and steady state fluctuations themselves are shown in Fig. 2 where both $Z_p(t)$ and $Z_\phi(t)$ converge to 1 by a time $t \sim 4$. This test shows that at long times, the *fluctuations* in the transient states converge to the *fluctuations* of the steady states. We note that $Z_p(t)$, $Z_\phi(t)$, and $Y_{SS}(t)$ converge to unity in approximately the same time.

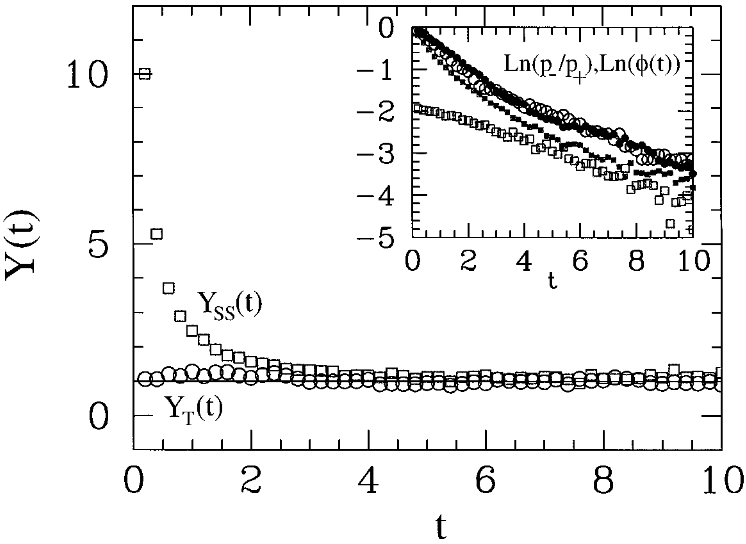

Fig. 1. A plot of $Y_T(t)$ for Transient (circles) and $Y_{SS}(t)$ for Steady States (squares) IFT for $F_e = 0.032$. The inset shows the corresponding $Ln(p_-(t)/p_+(t))$ (open symbol) and $Ln(\phi(t))$ (shaded symbol).

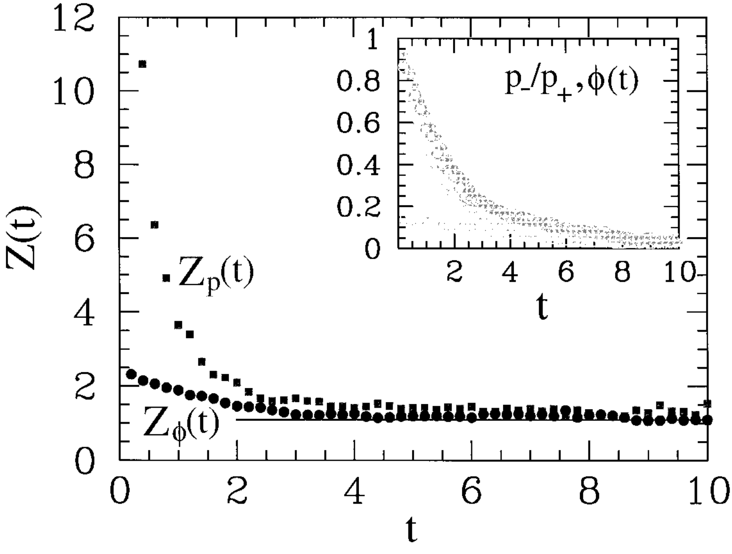

Fig. 2. A plot of $Z_p(t)$ (squares) and $Z_\phi(t)$ (circles) for IFT with $F_e = 0.032$. The inset shows the corresponding $p_-(t)/p_+(t)$ (open symbol) and $\phi(t)$ (shaded symbol).

From examining the Transient and Steady State Fluctuation Theorems for a Poiseuille flow system we find strong numerical evidence that, as expected, when the nonequilibrium steady state is unique, the Transient FT asymptotically converges to the Steady State FT at long times. Further, the time scale for this convergence is the same as the time required for the satisfaction of the Steady State FT itself. For our system, convergence of the two Theorems occurs on a microscopic time scale. These results confirm the assumptions of refs. 2–4. we note that the assumption of a unique nonequilibrium steady state is implicit in all linear and nonlinear response theory. Finally, we have recently shown that for stochastic systems the Transient and Steady State FT's show an analogous asymptotic convergence at long times.[8]

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