Transient Violation of Le Chatelier’s Principle for a Network of Water Molecules

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For a process in a small chemical system observed for short periods of time, the probability that it proceeds in the opposite direction to that found in the thermodynamic limit can be significant. We demonstrate this using simulations of a hydrogen-bonded network of water molecules whose temperature is changed from 300 K to 310 K. It is shown that for this system, and finite periods (up to tenths of picoseconds), the change during an individual observation period might be in either direction which satisfies the transient fluctuation theorem for a temperature change (Journal of Chemical Physics, 131, 214503 (2009)).

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INTRODUCTION

Fluctuation theorems (FT’s) are analytic relations that express the relative probability of observing values of a certain property with opposite signs, in non-equilibrium systems. One of the most important outcomes of these theorems is that when the property considered is the entropy production, it allows a molecular level derivation of the Second Law Inequality. The first FT was obtained in 1993 when Evans, Cohen and Morriss [1] showed that for an ergostatted dissipative system, the ratio of the probability that the irreversible entropy production, $\Sigma$, has a positive value in the range $A \pm dA$ (represented by $P(\Sigma = A)$) to the probability it has a negative value $-A \pm dA$ (represented by $P(\Sigma = -A)$) satisfies the following relationship [1]:

$$\frac{P(\Sigma = A)}{P(\Sigma = -A)} = \exp(A)$$

(1)

Subsequently, several FT’s and related expressions were developed. FT’s of Evans-Searles [2] and Gallavotti-Cohen [3], the Jarzynski equality [4] and the Crooks FT [5] are results of these quests. These theorems can be considered in two general groups. The first of these includes the Evans-Searles and Gallavotti-Cohen FT’s which generalize the second law of thermodynamics so that it applies to small systems including those far from equilibrium. The second group, the work relations (WRs), includes the Jarzynski equality and the Crooks FT, and provide a method of predicting equilibrium free energy differences using path integrals of the work performed along all possible non-equilibrium paths that dynamically connect the two different equilibrium states. While traditional thermodynamics concepts are limited in application to large systems, referred as the “thermodynamic limit” where the second law always holds [6], these theorems lift the size restriction, allowing thermodynamic concepts to be applied to small systems such as those of importance in nano- and biosystems. FT’s have
been tested against computer simulations and proved in laboratory experiments [7-11]. Here we focus on the Evans-Searles transient fluctuation theorem (TFT).

As in laboratory experiments, to sample specific ensembles or to treat non-equilibrium dissipative systems that are maintained at a constant temperature in a simulation, some form of thermostating mechanism must be employed [12-15]. In simulations these thermostats are artificial algorithms irrelevant to the validity of FT’s [12]. In experiments to verify these relations in the laboratory, the thermal bath would be remote from the system of interest and large enough to effectively remain in equilibrium. In a simulation, this can also be done, however for simplicity in this work, where we are mainly interested in verifying the predictions of the FT for a temperature change and Le Chatelier’s principle, we apply a homogeneous thermostat.

FT’s were originally developed for systems subject to some mechanical field or force. More recently thermal systems have been studied which are driven away from equilibrium by reservoirs whose temperatures change [16-19]. As such changes are important in many natural and artificial applications including physiochemistry, biology and nanotechnology, FT’s can provide valuable information on their response to thermal changes [20]. One remarkable example of this is seen in nanomachines and nanomotors operating and rectifying thermal fluctuations to work [21,22].

An extension of the Evans-Searles TFT to small systems has previously been developed by the authors in collaboration with Evans and Williams [20], and that work also provided the first molecular proof of Le Chatelier’s principle. The FT was validated using simulations of the unfolding a polypeptide [20]. However, due to the slow relaxation of that system and its complexity, the simulation times over which the FT could be validated (0.1 ps) was insufficient for this system to relax to a new equilibrium state. In this paper we carry out further simulations to demonstrate the validity of the FT for liquid water which relaxes more quickly to its new equilibrium, in response to a temperature change.

The organization of this paper is as follows: in section 2, we review the derivation of the TFT; computational details for numerical simulations are discussed in section 3; and section 4 provides some concluding remarks.

THEORETICAL BACKGROUND

Central to the TFT is the time-integral of the dissipation function Ω, which is defined as:

\[ \Omega_r(\Gamma) = \int_0^\tau \Omega(\Gamma(t)) \, dt = \int_0^\tau \left( \ln \left( \frac{f(\Gamma(0), 0)}{f(\Gamma(t), 0)} \right) - \int_0^t \Lambda(\Gamma(t)) \, dt \right) \]

and can be considered as a generalized spontaneous entropy production [20,23]. In this equation, \( f(\Gamma(t), 0) \) is the phase space distribution function at the phase space point \( \Gamma(t) \) at time 0, \( \Gamma(q, p) \) is the phase space vector and \( \Lambda(\Gamma(t)) = \frac{\partial}{\partial t} \Gamma(t) \) is the phase space expansion rate due to the dynamics. The TFT then specifies that the ratio of probabilities of observing trajectories of duration \( \tau \) for which the dissipation function takes the values \( A \pm dA \) and \( -A \pm dA \) is:

\[ \frac{P(\Omega_r = A)}{P(\Omega_r = -A)} = e^{\Delta S}. \]

By relating the dissipation function to the extensive entropy production, Eq. (3) can be seen to express the ratio of probability of observing trajectories with positive entropy production and satisfying the second law, to trajectories with negative entropy production, or violating the second law of thermodynamics. Note that \( \Omega_r \) is an extensive property.

Equation (3) can also be written in an intensive, time averaged form, \( \frac{P(\Omega_r/(N\tau) = A)}{P(\Omega_r/(N\tau) = -A)} = e^{\Delta S}. \) This ratio increases exponentially with increased time of observation, \( \tau \), or with system size and approaches infinity in the classical limit, in accord with the second law of thermodynamics [6].

By considering the appropriate phase space distribution functions, and the equations of motion for the dynamics of the system, one can obtain a specific dissipation function and TFT for certain system of interest. Here we summarize the derivation of the TFT due to a temperature change that was presented in [20].

Consider an ensemble of trajectories, sampled from a canonical distribution with temperature \( T \). To achieve sampling from a canonical ensemble in a molecular dynamics simulation one selects points from a trajectory generated by Nosé-Hoover thermostatted dynamics. The Nosé-Hoover distribution function is: