Identification of asymmetric current fluctuations in small systems

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Abstract—Theories of stochastic dynamics often used to model the behavior of mesoscopic and nanoscale systems predict temporal asymmetry in fluctuations of their properties when such systems are out of equilibrium. For example, in a system where a fluctuating current is produced, the way the current rises is different to the way in which it falls. Since mesoscopic systems can be considered as a collection of microscopic systems, we are led to ask: is this a fictitious effect of stochastic models, or does this asymmetry in the fluctuations even occur in more fundamental molecular level models, which are deterministic and reversible? Here we provide clear numerical evidence that asymmetric fluctuations do occur in nonequilibrium steady state molecular dynamics. In previous work, we observed fluctuations with asymmetric behavior in a microscopic system of particles undergoing Couette flow. We now extend our observations to a microscopic system of particles subject to color field, to verify that the presence of asymmetry in fluctuations holds more generally for reversible microscopic samples of matter out of equilibrium.

Keywords; *molecular dynamics simulations, fluctuations, Onsager-Machlup theory, microscopic systems, nanoscale systems, transient time correlation function.*

I. INTRODUCTION

Fluctuations of properties become more and more important as the size of a system decreases, yet due to the relatively recent growth of interest of nanoscale systems, the science behind these fluctuations is still being developed. This paper aims to contribute to nanoscience so that ultimately fluctuations can be utilised (or avoided) in nanotechnological applications.

Stochastic models such as Langevin dynamics are commonly used to study mesoscopic (nanoscale) systems, and often provide an effective description of them. It is proven that certain stochastic models exhibit a break of symmetry in the fluctuations of their thermodynamic properties out of equilibrium [1] [2]. That is, it can be shown that for properties that fluctuate, there will be a different time-dependence as the property rises to a peak value, than there is as it departs from this value. This is referred to as time-asymmetry, or temporal asymmetry. The theories that describe the behaviour of these systems are based on the extension of

the Onsager-Machlup fluctuation theory [3] to the nonequilibrium and non-linear domain. Stochastically perturbed electrical circuit have been used as analogues of a form of Brownian motion in a force field with weak white noise, and have provided experimental evidence of asymmetric fluctuations [4]. The following question should therefore be asked: would asymmetry in fluctuations of thermodynamic properties occur in models for microscopic systems, which are reversible and deterministic? In our previous paper [5], we were able to show that this is the case in systems undergoing Couette flow produced by homogeneous, nonequilibrium molecular dynamics simulations, indicating that this phenomenon occurs in deterministic, reversible systems, made of a small number of particles.

In the last 20 years a number of advances have been made that show how thermodynamic irreversibility emerges from reversible dynamics (see for example [6]). The results of [5] and this paper also demonstrate for the first time that a new type of irreversibility can be observed. The implications of these results need to be explored from both theoretical and practical perspectives. In particular, it will be of interest to examine how this behavior can be dealt with, and eventually exploited, in the development of nanoscale technologies.

In our earlier work on homogeneous Couette flow, it was necessary to use time dependent periodic boundary conditions. This introduces periodic fluctuations to the properties, and their influence needs to be carefully removed [5]. Furthermore the geometry of this system might be thought to introduce artificial asymmetry. For these reasons we decided to consider a somewhat simpler system: that which involves the flow of colored particles caused by color field. In order to monitor the fluctuations nonequilibrium steady state molecular dynamics simulations were carried out. These allow us to compute the properties of physical systems as a function of time by simulating the dynamics of their molecules.

Figure 1. Pictorial representations of the physical systems that are modelled by the simulations. The simulations model a small homogeneous region far from boundaries, as represented in the zoomed images. (A) Shows shear flow with a velocity profile imposed on a liquid by the different velocities of two walls; (B) Shows color diffusion where molecules of opposite charges are forced in opposite directions by an applied field. In a physical system, heat developed from the imposed motion would be extracted by a large source in constant thermal equilibrium with the liquid, and this is modelled by homogeneous thermostats in our simulations.

II. DETAILS OF THE MOLECULAR DYNAMICS MODEL

Our previous numerical experiments were conducted on the SLLOD model of homogeneous shear flow with Lees-Edwards periodic boundary conditions [5,7]. In this work, we consider the well-established algorithm for the simulation of steady state color diffusion [7,8]. This models the flow of particles of opposite 'color' charge, interacting with each other according to an interaction potential, that are pushed in opposite direction by a field that drives the system out of equilibrium. The field does work on the system so, to prevent it from heating, a reversible thermostat is applied. The system is similar to a thermostatted system of charged particles to which a field is applied, except that the particles are not influenced by the charges on other particles. The system is in 2 Cartesian dimensions with a square unit cell and periodic boundary conditions [9]. In both [5] and this work the interaction potential is the Weeks-Chandler-Andersen potential [10] and a Gaussian isokinetic thermostat is used. Pictorial representations of the SLLOD and color field dynamics are given in Figure 1.

The equations of motion used for color diffusion are:

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{i}c_i F_c - \zeta(\mathbf{p}_i - \mathbf{i}c_i J_x) \\ \zeta &= \frac{\sum \mathbf{F}_i \cdot (\mathbf{p}_i - \mathbf{i}c_i J_x)}{\sum \mathbf{p}_i \cdot (\mathbf{p}_i - \mathbf{i}c_i J_x)}\end{aligned}\quad (1)$$

where $\mathbf{q}_i$ and $\mathbf{p}_i$ are the position and momentum of particle i , $\mathbf{F}_i$ is the force acting on it, $c_i = (-1)^i$ is the color charge, F_c is the color field, ζ is the thermostat multiplier and $J_x = \sum_{i=1}^N c_i p_{xi} / N$ is the color current. These equations are time reversal invariant.

III. FLUCTUATION PATHS

Our aim is to compare the rise (/fall) of a property to its maximum (/minimum) value with its relaxation towards its mean value, for exceptional peaks (/troughs) and for a determined amount of time, τ . In order to select exceptional peaks, a high threshold value is chosen. We refer to the approach and departure to the threshold value as a 'Fluctuation Path' (FP). A typical FP and its construction are shown in Figure 2. There are many other ways that could have been used to define a FP (see [5]), however provided asymmetry is not artificially introduced, they are all valid. The 'average' fluctuation paths are constructed as the conditional average of the peaks and troughs that pass through a selected threshold value. To measure the average asymmetry of property B , we define the asymmetry coefficient α_τ of the FP as:

$$\alpha_\tau = \left\langle \frac{1}{\tau} \int_0^\tau (B(t) - B(-t)) dt \right\rangle \quad (2)$$

where $\langle \dots \rangle$ represents the conditional ensemble average.

Figure 1. (A) Sample of the values of shear stress P_{xy} out of equilibrium; (B) Illustration of the construction of the FP.

IV. NUMERICAL RESULTS

The FPs of the current J_x and pressure, P have been considered for color diffusion. J_x is odd under time reversal, whereas the pressure is even. Lennard-Jones reduced units [9] will be used throughout this work. Two-dimensional molecular dynamics simulations have been carried on a primitive cell containing 8 particles with kinetic temperature fixed at 1 and time step of 10^{-3} . This small system ensures that it will be possible to observe fluctuations in the instantaneous values of the properties. We consider an equilibrium system as well as a range of nonequilibrium systems with color field ranging from 1 to 5, extending from the linear regime to well into the nonlinear regime. The results here presented are obtained with thresholds set to $\mu \pm 2.5\sigma$, where μ is the mean of the property of interest, and σ is its standard deviation. Figure 3 displays the average FP of J_x for various fields, with error bars shown. We note that at equilibrium α_τ is equal to zero to within numerical errors at all times. This is consistent with the fact that the peaks should be perfectly symmetric at equilibrium, in accordance with both equilibrium reversible deterministic dynamics and with the Onsager-Machlup theory for equilibrium systems [3], and confirms the adequacy of our model. Out of equilibrium, asymmetry is observed, in agreement with the results obtained for Couette flow [5]. We

note that α_τ vanishes at $\tau = 0$ (simply due to its definition (2)), it then departs from zero indicating asymmetry, and subsequently returns to zero since the tails of the FP are uncorrelated at large τ . Since α_τ is a time average, at sufficiently long τ , we expect its to approach zero as $1/\tau$, and this is confirmed by the numerical results.

Because they are both proportional to the dissipative flux, we can compare in more detail the color current in color diffusion, and the shear stress in Couette flow. We find that whereas the departure of J_x from the average value to the peak is preferentially less steep than the relaxation, the opposite is true for the shear stress in SLLOD [5].

Figure 4 displays the corresponding average pressure peaks. Again α_τ of the equilibrium peak is zero to within numerical error at all times, while out of equilibrium the departure of pressure from the average value to the peak is preferentially steeper than the relaxation.

Figure 3. (A) Average FP of J_x ; (B) Measure of asymmetry, α_τ , of average FP of J_x . Error bars are shown and obtained as the standard error of the mean.

Figure 4. (A) Average FP of pressure; (B) Measure of asymmetry, α_τ , of average FP of pressure. Error bars are shown and obtained as the standard error of the mean.

V. CONCLUSIONS

The departure from zero of the value of the measure of asymmetry α , as a function of τ is a numerical demonstration of the asymmetry of fluctuation paths for microscopic reversible systems away from equilibrium. This provides evidence that such behavior occurs in generic nonequilibrium systems such those undergoing steady state color diffusion. While this has been observed in shear flow previously, the color diffusion system is free of the complication of time-dependent boundary conditions, which made the analysis of

shear flow more complicated and left the possibility that the observed asymmetry might have been a result of the boundary conditions, or of our analysis. The system here confirms that this was not the case, and that temporal asymmetries are observed in a wide range of reversible, deterministic nonequilibrium steady state dynamics.

The development of a sound theory to justify and characterize such phenomenon is currently being carried out. In order to do this we are examining the link between the asymmetry of fluctuation paths and that of correlation functions. Using this approach we hope to be able confirm theoretically as well as numerically that the asymmetries of fluctuation paths are not an artifact of the stochastic representation, but an intrinsic property of deterministic and reversible thermodynamic systems. We note that the effects that we observe here and in [5] are real, but small (quadratic in the field at low field). It will be of interest to examine if the system size effects and other parameters result in enhanced asymmetry that are of importance in the development of nanoscale devices.

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