Applicability of optimal protocols and the Jarzynski equality

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Received 4 February 2014
Accepted for publication 6 February 2014
Published 11 March 2014

Abstract

The Jarzynski equality is a well-known and widely used identity, relating the free energy difference between two states of a system to the work done over some arbitrary, nonequilibrium transformation between the two states. Despite being valid for both stochastic and deterministic systems, we show that the optimal transformation protocol for the deterministic case seems to differ from that predicated from an analysis of the stochastic dynamics. In addition, it is shown that for certain situations, more dissipative processes can sometimes lead to better numerical results for the free energy differences.

Keywords: free energy, molecular dynamics, fluctuation relations

Some figures may appear in colour only in the online journal

1. Introduction

The fluctuation relations developed in the past 20 years have opened a new perspective on small driven and relaxing systems [1–9]. In particular, the relation known as the Jarzynski equality (JE) [10, 11] has become popular in various fields, biophysics in particular. It relates the work $W$ done on a collection of systems driven away from a canonical equilibrium state characterized by a parameter $\lambda(0) = A$, according to a given protocol $\lambda(t)$ which ends at $\lambda(\tau) = B$, to the free energy difference between the initial state and the one to which the systems may eventually relax:

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta [F(B) - F(A)]},$$

where $\beta = 1/k_B T$, $\langle \ldots \rangle$ is the average with respect to the initial ensemble, $[F(B) - F(A)]$ is the free-energy difference between the initial equilibrium state with $\lambda = A$ and the equilibrium state corresponding to $\lambda = B$. Sufficient conditions for equation (1) to hold are that the dynamics are reversible, that the system exhibits a type of ergodic consistency [12]. If these conditions are met, equation (1) will hold arbitrarily far from equilibrium (arbitrarily large $d\lambda/dt$).

The process always begins in the same macroscopic state, the equilibrium state with $\lambda = A$, but in different microscopic states. This is why the measured work varies, unless the protocol is quasi-static: if the protocol is fast enough, the different initial conditions will result in different interactions with the driving environment, hence in different amounts of work done. At time $\tau$, when the protocol stops, the system will not in general be in equilibrium. Obviously, these quantities of work are path functions since they depend on the initial microstate—but they are nevertheless measurable quantities [13].

To build the statistics of the work done, the same protocol must be repeated very many times. Indeed, the left hand side of equation (1) can be hard to compute precisely in some cases because of its exponential form and the fact that large contributions to that average can sometimes be given by rare, large negative values of $W$ [14]. Therefore, the question of protocols that optimally achieve the best estimate for the free-energy difference has been investigated intensely. In order to obtain mathematical results, most investigations have focused on stochastic processes, for which numerous techniques are available. In particular, the works by Schmeidl
and Seifert [15] and by Aurell et al [16] consider Langevin models such as
\[
\dot{\xi}_i = -\frac{1}{\tau} \partial_{\xi_i} V(\xi_i, t) + \frac{2}{\tau \beta} \dot{\xi}_i.
\] (2)

Reference [15] comes to the conclusion that the optimal protocols at fixed finite \( \tau \) are not continuous but are characterized by sudden jumps at the beginning and at the end of the process\(^7\). This is consistent with the overdamped nature of the evolution equation, but these jumps will disappear for protocols where there is some form of resistance to rapid change in the system [18]. The question of the range of applicability of the optimal protocols obtained from Langevin-type processes is whether these situations are realizable in practice and, if so, how common they are.

To investigate this question in the case of particle systems, it seems appropriate to consider deterministic models, such as those of molecular dynamics, rather than other stochastic processes, which are based on the same assumptions of the Langevin models. In particular, molecular dynamics models can interrogate the wide separation between microscopic scales concerning the constituents of heat baths and systems of interest and the mesoscopic scales, which is assumed by the stochastic description. In this sense, the deterministic description complements the stochastic one [19].

Here, we consider the problem of fast expansion or compression of a gas by means of an adiabatic piston. The gas is initially in equilibrium at a given temperature \( T \). It is then isolated from the outer environment, and the piston starts to move according to a specified protocol. Multiple molecular dynamics simulations were completed with various piston velocities. Each simulation modelled a 16-particle system in a three-dimensional box, with one moving wall. The equations of motion for the particles in the system as they move between walls are
\[
\dot{q}_i = \frac{p_i}{m} \quad \dot{p}_i = F_i - S_i \alpha p_i,
\] (3)

where \( q_i \) and \( p_i \) are the coordinates and momenta of the \( i \)th particle, \( F_i \) is the interparticle force on a particle, obtained from a Weeks–Chandler–Anderson short-ranged repulsive pair potential [20], and \( S_i \) is a switch to determine whether or not a thermostat is applied. The thermostat multiplier \( \alpha \) is a Nosé–Hoover thermostat [21]
\[
\alpha = Q_s \left( \frac{2K}{3Nk_b} - T \right),
\] (4)

where \( Q_s \) is a factor that controls the oscillations in the kinetic energy, \( N \) is the number of particles in the system, \( k_b \) is Boltzmann’s constant, \( K \) is the instantaneous kinetic energy of the system and \( T \) is the Nosé–Hoover target temperature. In this work, in order to generate initial phase points from a Nosé–Hoover canonical distribution [21], \( S_i = 1 \) for all particles during the equilibration period. In order to carry out an adiabatic expansion/contraction, \( S_i = 0 \) for all particles when the piston is moving. Particle–wall interactions reversed the momentum perpendicular to the walls, while particle–piston interactions changed the momentum such that \( v'_{z,i} = 2v_z - v_{z,i} \), where \( z \) is the axis parallel to the piston velocity \( v_p \), and \( v_{z,i} \) and \( v'_{z,i} \) are the projections on the \( z \)-direction of the velocity of particle \( i \) before and after the collision, respectively. All results are given in Lennard-Jones reduced units. The driving protocol consists of either an adiabatic expansion from density \( \rho(0) = 0.1 \) to \( \rho(\tau) = 0.05 \), or the opposite (a compression) [22]. The protocol involves varying the volume of the box by varying the position of the piston in time. If this process took place quasi-statically, and the object was macroscopic, the final equilibrium state would be that of a system in an adiabatic container of given volume and energy.

Because no heat is exchanged with the environment, the work carried out over the period \( \tau \) for each trajectory for this system, appearing in equation (1), is
\[
W = H(q(t), p(t); \lambda = B) - H(q(0), p(0); \lambda = A),
\] (5)

where \( H \) is the internal energy of the system of particles. This is different from the situation described by the Langevin equation where the bath is always exchanging energy with the system of interest. It is a similar situation to that considered by Bena et al [23], although they consider a deterministic hard sphere system so the change in the internal energy is solely due to collisions with the piston.

The JE [10, 24] and the maximum likelihood estimator (MLE) [25, 26] have here been used to calculate the free-energy differences due to expansion and contraction of a system similar to that considered in [22]. In the MLE, the free energy \( \Delta F \) is determined iteratively through solution of the equation
\[
\sum_{i=1}^{N_f} \left( 1 + \frac{N_f}{N_b} \exp(\beta(W_i - \Delta F)) \right)^{-1} = \sum_{i=1}^{N_b} \left( 1 + \frac{N_b}{N_f} \exp(\beta(W_{i,b} + \Delta F)) \right)^{-1},
\]

where the summations are over the \( N_f \) forward and \( N_b \) backward trajectories that transform the system between the two states at temperature \( T = (k_b \beta)^{-1} \) with work \( W_{i,f} \) or \( W_{i,b} \). Nine different protocols \( \lambda(t), t \in [0, \tau] \), were considered, as illustrated in figure 1(a). The value of \( \lambda(t) = L_z(t)/(L_z(\tau) - L_z(0)) \) varies between 0 and 1, where \( L_z(t) \) is the position of the piston. Changing from 9 to 1, these protocols provide a better and better approximation to the discontinuous jumps described by Schmiedl and Seifert [15]. Each run was repeated \( 1.5 \times 10^5 \) times for a given simulation length, and the results for the computed free-energy difference \( \Delta F \) have been averaged over ten groups of \( 1.5 \times 10^4 \) samples, and reported in figure 1(b), where the standard error represents their reproducibility, not the error in convergence. As expected for quasi-static (sufficiently slow) transformations, \( \Delta F \) does not depend on the protocol. Consequently, the black curve gives a good numerical estimate of \( \exp(-\beta W) \) in all cases. However, if the protocol is fast the optimal protocol appears to be number 5, i.e. the smoothest of all, at variance with the results of Schmiedl and Seifert [15]. This provides one simple example in which the predictions for the most efficient protocol obtained using some stochastic approach
Figure 1. (a) Graphical description of the transformation algorithms. In protocols 1–4, the piston velocity is faster at the beginning and end; and in 6–9 the piston is faster in the middle. Protocol 5 corresponds to a constant piston velocity. (b) MLE value of $\Delta F$ for the nine different protocols. The curves represent results for $1.5 \times 10^5$ simulation runs with $\tau = 5000$, 10000 or 80000 reduced-time units. The standard errors obtained were determined from averaging over ten groups of $1.5 \times 10^4$ forward and reverse runs and are smaller than the symbols.

Figure 2. Comparison of (a) dissipation and (b) free-energy differences for expansion and compression protocols. Despite the dissipation associated with the expansion process being less than that associated with the compression process, the compression simulations return more accurate free-energy differences.

for these same transformations, and compares them to the slow-change result. The negative of the compression free-energy change is shown for ease of comparison. Despite the significantly lower dissipation obtained from the expansion simulations, the compression simulations produce more accurate free-energy calculations. When only considering a one-directional transformation, the algorithm which minimizes dissipation also produces the most accurate free-energy differences. Out of the expansion protocols, the one with the greatest dissipation provides the best estimate of the $\Delta F$. Thus, because the free-energy difference between two states can be calculated in either direction, this demonstrates that a more dissipative transformation path can produce more accurate free energies than a less dissipative one.

In our work we also obtained the distributions of $W$ for the rapid expansion and compression, which vary quantitatively and qualitatively with the protocol.

As shown in figure 3(a), the distributions for the rapid expansion possess two separate peaks, with the narrower one centred close to zero, corresponding to transformations without any particle–piston interactions. This causes a
significant sampling problem that is different to the stochastic case, since for a very fast expansion almost no particles will be moving fast enough in the deterministic simulation to interact with the piston in each trajectory, and the work obtained will be close to zero for almost all trajectories. This results in a substantial number of very small work values observed in the work distribution, giving a value for the average work that is closer to zero than is obtained with a slow change. Furthermore, if insufficient trajectories are used for the numerical calculations, the sampling of larger negative values of the work will be poor, resulting in free-energy differences (calculated via the finite-sample version of equation (1)) that differ from the correct $\Delta F$. We emphasize that this is a sampling problem, not a theoretical problem with equation (1) (see [30] for a discussion).

Figure 3(b) shows the work distributions from rapid compression. Protocol 1 leads to a very irregular distribution, while protocol 5 gives a quite regularly shaped distribution, and the slow protocol yields a distribution that is sharp initially, and then smooth. However, the results obtained using protocol 1 for compression are noticeably more accurate than those obtained from the expansion work data using the reverse protocol. This is because phase space has been sampled more completely in areas of the distribution that contribute significantly to the ensemble average in equation (1). The peaks in the work distribution for a system undergoing rapid compression are due to particle–piston interactions, as each particle–piston interaction will amount to a significant contribution to the total work. In fact, in the limit of an infinitely fast piston, the average number of particle–piston interactions will become a function solely of the ratio of the pre- and post-compression system lengths. High-speed compressions may significantly increase the mean work (due to the high-energy piston–particle interactions), however the exponentially weighted mean is much less sensitive to these trajectories. Therefore, although the compression results in significantly more dissipation, the convergence of the free-energy determined by the JE is better.

Our work, which was performed with a system of only 16 particles, highlights the sampling issues that can result when thermodynamic properties are determined as ensemble averages of mechanistic experiments. In cases of few degrees of freedom, elements of the mechanics can dominate the behaviour expected with many particles. For example, the initial microscopic conditions are taken from the canonical distribution, but the speed of the protocol affects the final set of states: as the expansion protocol becomes faster, the final state is reached with less and less work on average being done on the piston. As noted, what we do is different to the case described by the Langevin equation because no bath is acting. However, if we introduce a Nosé–Hoover thermostat, our results, and particular the optimal protocol, do not seem to change qualitatively.

We can compare the work distributions with those obtained by Bena et al [23] for deterministic hard sphere systems. They obtained analytical results for a Jepsen gas and compared them with numerical simulations of a dilute hard sphere gas. The rate of expansion/contraction was kept constant in all cases, and they compared the work distributions for different rates. Like in the current work, asymmetry of the work distributions for the compression and expansion protocols is observed and the distributions become less Gaussian as the rate is increased. By comparing the analytical results for the infinite systems with the numerical results they also observed effects due to the use of a finite number of particles in the simulations, which would be even more pronounced in our systems which are two orders of magnitude smaller than those of Bena et al [23]. In contrast with our results which are for particles interaction via soft repulsive potentials, the particles are non-interacting and this will also have some effects on the result e.g. [31–33]. However, the implications of this asymmetry of the distributions on the JE are discussed and are consistent with our observations. Therefore, should a study of the optimal protocol for this system be undertaken like in our current work, we would expect similar results which are unlike the results predicted for the stochastic systems.

We have performed molecular dynamics simulations to calculate the free energy associated with adiabatic expansions and compressions of a low density gas, complementing

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Note that $W$ is the work done by the system in [23], whereas it is work done on the system in our case, so the signs are reversed.
existing results already obtained using stochastic simulation techniques. We observe an optimal protocol for obtaining free-energy estimates using the JE that differs substantially from the protocol observed for stochastic models, even those allowing accelerations. We also note a remarkable and unusual feature of our results, that the better free-energy estimates can be associated with more highly dissipative processes. Finally, the distinction between our scenario and that of the stochastic approach is reinforced by papers such as [17] that show beyond the Langevin framework, the impact of the separation of scales assumed in the stochastic approach is not necessarily verified in small deterministic systems.

Acknowledgments

The authors would like to thank the Australian Research Council for support of this project through a Discovery Project. Computational resources used in this work were provided by Griffith University, University of Queensland, an Australian Research Council LIEF grant and the Queensland Cyber Infrastructure Foundation. LR acknowledges support from the European Research Council under FP7/2007–2013 Framework Programme, ERC grant agreement no. 202680. The EC is not liable for any use that can be made on the information contained herein.

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