

Insights Regarding the Irreversible Molecule Pulling in Complex Fluid Systems by Means of Molecular Dynamics Simulations

Kalil Bernardino^a (PG), André Farias de Moura^a (PQ)

^a Departamento de Química, Centro de Ciências Exatas e de Tecnologia, Universidade Federal de São Carlos, Rodovia Washington Luiz km 235, CP 676, CEP 13565-905, São Carlos, SP, Brasil.

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INTRODUCTION

Although the Jarzynski equality (JE)¹ provides a way to obtain the equilibrium free energy difference from an ensemble of irreversible amounts of work, its convergence can be very poor, especially if the system is far from equilibrium, since the more negative contributions, although rare, have a greater weight in JE. Instead, if the distributions of irreversible amounts of work can be assumed to be normal, a simple relation emerges from JE relating the free energy to the more easily converging arithmetic average, $\langle w \rangle$, and variance, σ^2 .¹ (Equation 1)

$$\Delta F = \langle w \rangle - \frac{\sigma^2}{2k_B T} \quad (1)$$

This work aims to test this equation and the physical hypotheses behind it in complex fluid systems by calculating ensembles of the irreversible pulling of a surfactant ion from an equilibrated micelle at several pulling speeds.

METHODS

The model systems consisted of a coarse-grained SDS micelle (N=60) in aqueous solution. Starting with structures obtained from equilibrium simulations, several pulling experiments were performed in which a single surfactant ion was removed from the micellar cluster by defining a reaction coordinate between the head of the molecule to be removed and the center of mass of the remaining cluster, forcing the surfactant to move along this reaction coordinate at a constant speed from its initial position to the bulk solution. The integration of the force exerted on the pulling group along the reaction coordinate yielded the irreversible amount of work for the complete removal. This protocol was repeated at several speeds: 120 replicas at 0.01 m/s, 240 at 0.05, 240 at 0.1, 360 at 0.2, 480 at 0.5 and 960 at 1.0 m/s.

RESULTS AND DISCUSSION

The variance varied linearly with the average values calculated for the work ensembles at each pulling speed (Figure 1), as suggested in Eq. 1. However, the slope of the linear regression, (4.3 ± 0.3) kJ/mol, is significantly smaller than the $2k_B T$ value at 300 K (5.0 kJ/mol). Three main effects can explain this discrepancy and are currently being investigated: (1) a feedback control effect induced by the methodology itself, which, if present, should introduce a correction in Eq. 1, (2) The fact that surfactant may start at different positions along the reaction coordinate in the outset of each pulling simulation, due to the flexible nature of the micelle, and (3) small differences from the normal distribution that should also introduce corrections in Eq. 1.

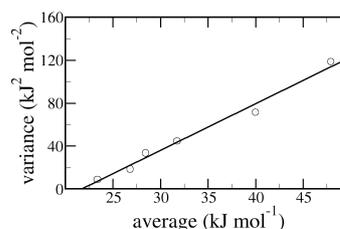


Figure 1. Linear regression of the variance as a function of average values of irreversible work distributions obtained at different pulling speeds.

CONCLUSIONS

Our results should be applicable to other complex fluid systems and suggest corrections in Eq. 1. and those corrections may provide physical insights on the behavior of these systems.

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¹ C. Jarzynski, *Annu. Rev. Condens. Matter Phys.* 2, 329 (2011).