

Using Nonequilibrium Fluctuation Theorems to Understand and Correct Errors in Equilibrium and Nonequilibrium Simulations of Discrete Langevin Dynamics

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Subject Area: Classical Probability, Classical Probability, Statistical Mechanics

I. INTRODUCTION

I consider a particle moving in a potential $\mathcal{H}(t)$ under the influence of a time-dependent force $f(t)$ and a friction coefficient γ . The particle's position r and velocity v are coupled to a heat bath at temperature T . The Langevin equation for the particle's motion is

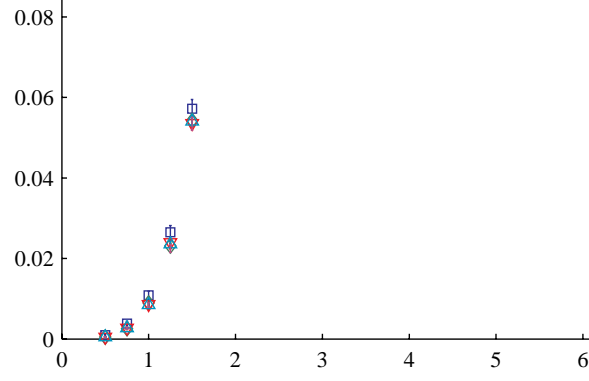
$$dr = v dt, \quad (H)$$

$$dv = \frac{f(t)}{m} dt - \gamma v dt + \sqrt{\frac{2\gamma}{\beta m}} dW(t), \quad (1)$$

where $\mathcal{H}(t) = \frac{1}{2}mv^2 + \mathcal{H}(r, t)$ is the total energy, $\mathcal{H}(r, t)$ is the potential energy, m is the mass, $f(t)$ is the external force, $\beta = 1/k_B T$, k_B is Boltzmann's constant, and T is the temperature. The noise $dW(t)$ is a Wiener process with $\langle dW(t) \rangle = 0$ and $\langle dW(t)^2 \rangle = dt$. The friction coefficient γ is assumed to be constant.

The work done on the particle is $W(t) = \int_0^t f(r) \cdot v dt$. The heat $Q(t)$ is the energy transferred from the heat bath to the particle, $Q(t) = \int_0^t \gamma v^2 dt$. The entropy production $\Sigma(t)$ is the logarithm of the ratio of the probability of a trajectory to the probability of its time-reversed counterpart, $\Sigma(t) = \ln \frac{P(r, v, t)}{P(r, v, 0)}$. The fluctuation theorem states that the probability of observing a certain amount of entropy production is exponentially related to the probability of observing the opposite amount, $\frac{P(\Sigma)}{P(-\Sigma)} = e^{\Sigma}$. This theorem has been used to derive the Jarzynski equality and the Crooks fluctuation theorem.

V. MULTIVARIATE FLUCTUATION THEOREM



$$P(X) = \int \delta(W_1[X] - W_{1c}) \delta(W_2[X] - W_{2c}) e^{-\beta F_c} P(W_1, W_2) dW_1 dW_2$$
 EQ. (4)

$$P[X] = P[X] e^{\beta(W_1[X] + W_2[X] - F_c)} \quad (8)$$

$$\delta(W_1[X] - W_{1c}) \delta(W_2[X] - W_{2c})$$

$$\frac{P(W_{1c}, W_{2c})}{P(-W_{1c}, -W_{2c})} = e^{\beta(W_{1c} + W_{2c} - F_c)} \quad (9)$$

EQ. (9)

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EQ. (9)

VI. RECOVERING EQUILIBRIUM STATISTICS FROM NONEQUILIBRIUM SIMULATIONS

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$$F_c = 11.4 \pm 0.2 k_B T$$

$$F_c / N_{H_2O} k_B T \approx a t^4 \quad (7)$$

EQ. (9)

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EQ. (12)

A \mathbb{R}^n matrix M is G -orthogonal if $M^T G M = G$, where G is a symmetric positive definite matrix. [42,43](#),
 The set of all G -orthogonal matrices is denoted by O_G .
 For a given G -orthogonal matrix M , the matrix $B = M^{-1} G M$ is symmetric and positive definite. The eigenvalues of B are $\lambda_i = \beta_i$, where $\beta_i \in \{-\beta, \beta\}$.

$$\frac{P(W_{i^*} < 0)}{P(W_{i^*} > 0)} \Big/ \langle e^{-\beta W_{i^*}} \rangle_{W_{i^*} > 0}, \quad (15)$$

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$$\langle e^{-\beta W_{i^*}} \rangle_{W_{i^*} > 0} / \langle e^{-\beta W_{i^*}} \rangle_{W_{i^*} > 0} (+)$$

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VIII. EPILOGUE

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