The Jarzynski free-energy estimator from the Random Energy Model

Matteo Palassini* and Felix Ritort
Departament de Física Fonamental, Universitat de Barcelona, Diagonal 647, E–08028 Barcelona, Spain.

Jarzynski's nonequilibrium work theorem[1] is a general result that connects nonequilibrium dynamics to equilibrium thermodynamics. It states that the difference in free energy ΔF between two equilibrium states of a system, kept at inverse temperature $\beta = 1/k_BT$ and at two given values Λ_0 and Λ_1 of an external control parameter Λ, satisfies the relation $e^{-\beta\Delta F} = \langle e^{-\beta\mathcal{W}}\rangle$. $\mathcal{W}$ is the work performed on the system in a nonequilibrium process in which Λ is varied according to an arbitrary but fixed protocol $\{\Lambda(t),\ 0 \leq t \leq \tau\}$, with $\Lambda(0) = \Lambda_0$ and $\Lambda(\tau) = \Lambda_1$, and the average is over all possible trajectories compatible with the protocol. This provides a recipe for estimating free-energy changes in small systems, which has been tested in several experimental and numerical studies[3]. Given N measurements $\mathcal{W}_i$ following the protocol $\Lambda(t)$, the Jarzynski estimator (JE)

$$\Delta F_N \equiv -\frac{1}{\beta}\log\sum_{i=1}^{N} e^{-\beta\mathcal{W}_i} \tag{1}$$

tends to ΔF with probability one for $N \to \infty$. For finite N, ΔF_N is biased because the exponential average is dominated by rare events with $\mathcal{W} < 0$. Controlling analytically how the bias depends on N and the distribution of $\mathcal{W}$ would be important for practical applications, but is a difficult mathematical problem.

We derive a scaling limit for the JE based on a mapping to Derrida's Random Energy Model[2] (REM) (Fig. 1) and we obtain analytic estimates of the expected bias $\langle\Delta F_N\rangle - \Delta F$ in three different regimes of the scaling parameter $x = (\log N)/\mu$, where $\mu = \langle\mathcal{W}\rangle - \Delta F$ is the mean dissipated work, for a generic work distributions that decays as $p(\mathcal{W}) \sim |\mathcal{W}|^{-\alpha}\exp -(|\mathcal{W}|/\sigma)^\delta$ for $\mathcal{W} \to -\infty$, where $\alpha > 0$, $\delta > 1$ and and $\sigma > 0$ is the width of the left tail of the distribution. The analytical estimates are based on a vector replica symmetry breaking scheme (VRSB in Fig.2) for $x >> 1$ on the asymptotic theory of extreme value statistics for $x << 1$ (EV), and for $x \sim 1$ on a generalization of the method used in Ref. 4 to compute the finite-size corrections of the REM (CD).

The combination of these three analytic approaches agrees well with the expectation value of the bias computed from Monte Carlo generated work values for a wide range of values of μ and N, ranging from $N = 1$ to large N, and for different work distributions. Fig. 2 shows an example of our results for a Gaussian distribution of the work and two different values of μ.

Based on these results, we discuss improved free-energy estimators and the application to the analysis of experimental data.

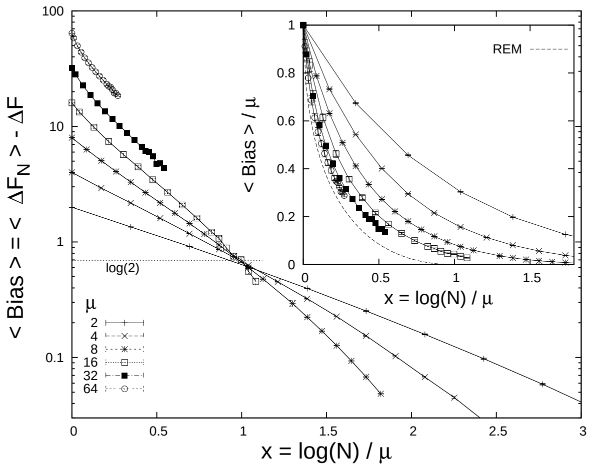

Figura 1. Scaling of the expectation value of the bias of the JE v.s. $\log(N)/\mu$, for a Gaussian distribution of the dissipated work and several values of the mean dissipated work μ. The bias and μ are in units of k_BT. The data points are computed by generating work values by Monte Carlo, the continuous lines are a guide to the eye. Our analytical calculation predicts the data must cross at $x = 1$ and take the value log(2) (horizontal line in the main figure). The dashed line in the inset represents the scaling limit which corresponds to the thermodynamic limit of the Random Energy Model.

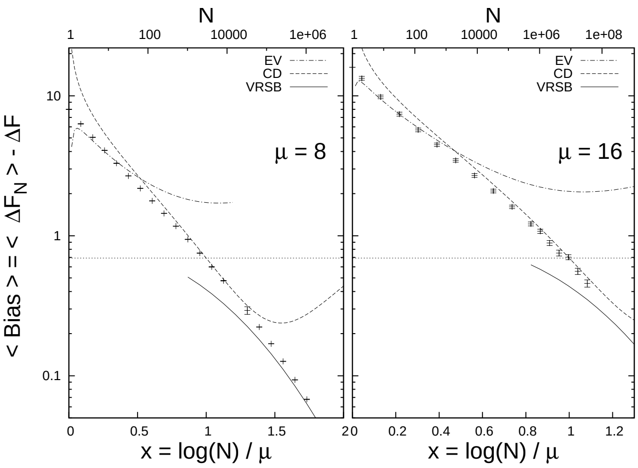

Figura 2. Comparison of the analytical estimates of the bias for two values of μ. The data points represents the same Monte Carlo data as in Fig.1. The lines display the analytical estimates in three different regimes of x (see main text).

---

* palassini@ub.edu
[1] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[2] B. Derrida, Phys. Rev. Lett. **45**, 79 (1980).
[3] See e.g. Liphardt et al., Science **296**, 1832 (2002).
[4] J. Cook and B. Derrida, J. Stat. Phys. **63** (1991).