On the asymptotic behavior of distributions of work performed on diffusion particles in time-varying potentials

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For single molecule experiments, the role of thermodynamic quantities such as work, heat, and entropy, when defined on the level of stochastic trajectories, has become an important field in non-equilibrium statistical mechanics [1]. A main achievement in this field is the discovery of detailed and integral fluctuation theorems. These theorems hold true universally and they can be viewed as a generalization of the second law of thermodynamics. The Jarzynski equality (JE) is perhaps the most prominent. It pertains to systems in contact with a heat reservoir at temperature T, which are initially in equilibrium and then are driven out of equilibrium by a change of control variable $\lambda(t)$ during a time interval $[0, t_{\mathrm{f}}]$. The JE states that $< e^{-w/k_{\mathrm{B}}T} > = \int p(w) e^{-w/k_{\mathrm{B}}T} \mathrm{d}w = e^{-\Delta F/k_{\mathrm{B}}T}$, where w is the stochastic work done on the system during one realization (trajectory) of the process, $p(w)$ is the distribution of work values, and $\Delta F = F(\lambda(t_{\mathrm{f}})) - F(\lambda(0))$ is the free energy difference between the macrostates belonging to the initial and final values of the control variable. The JE becomes particularly valuable in unidirectional experimental settings, where the work for the reversed protocol can not be measured, and accordingly other theorems, as, e.g., the Crooks theorem can not be applied.

For applications of the JE measured histograms generally need to be extended to the tail regime, because the average of $< e^{-w/k_{\mathrm{B}}T} >$ in the JE is dominated by rare trajectories with work values $w \ll \Delta F$. If theoretical predictions for the asymptotic behavior for $w \to -\infty$ are available, this problem can be resolved by fitting the wings of a measured WPD to these predictions. Corresponding predictions for this asymptotic behavior are, however, difficult to obtain. WPDs depend on details of the experimental setup and only a few generic properties have been reported so far.

Here we analyze functional forms of the asymptotic behavior of the work distributions for the diffusive motion of a Brownian particle in a time-varying potential. This analysis is performed based on analytical results [2], Monte-Carlo simulations and the theory in [3], which is based on the contraction principle of large deviation theory.

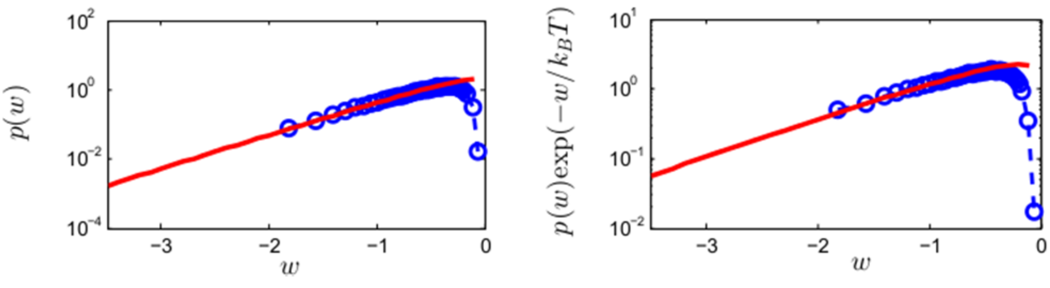

Figure 1: Demonstration of the extension (solid line) of simulated data (symbols) to the tail regime for the work distribution $p(w)$ and the Jarzynski integrand $p(w)e^{-w/k_{\mathrm{B}}T}$ for overdamped Brownian motion in a log-harmonic potential $V(x,t) = -\log|x| + k(t)x^2$ with the protocol $k(t) = 1/(1+t)$ for $t \in [0,1]$. The extension was done based on the theories in [2] and [3].

References

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