

Asymptotics of work distributions in nonequilibrium systems

A. Engel

Institut für Physik, Universität Oldenburg, 26111 Oldenburg, Germany

(Received 25 July 2008; revised manuscript received 24 June 2009; published 21 August 2009)

The asymptotic behavior of the work distribution in driven nonequilibrium systems is determined using the method of optimal fluctuations. For systems described by Langevin dynamics the corresponding Euler-Lagrange equation together with the appropriate boundary conditions and an equation for the leading pre-exponential factor are derived. The method is applied to three representative examples and the results are used to improve the accuracy of free-energy estimates based on the application of the Jarzynski equation.

DOI: [10.1103/PhysRevE.80.021120](https://doi.org/10.1103/PhysRevE.80.021120)

PACS number(s): 05.70.Ln, 05.20.-y, 05.40.-a

I. INTRODUCTION

Recent progress in the statistical mechanics of nonequilibrium systems centered around fluctuation [1,2] and work [3,4] theorems has profound implications for both theory and applications. Rather complementary to the traditional emphasis of statistical mechanics on *typical* behavior of systems these lines of research put the *large deviation* properties of thermodynamic variables such as work or entropy into focus. Of particular interest for many practical applications is the use of the Jarzynski equation [3].

$$e^{-\beta\Delta F} = \langle e^{-\beta W} \rangle \quad (1)$$

to determine the free-energy difference ΔF between two equilibrium states at inverse temperature β from the work distribution $P(W)$ characterizing irreversible transitions between these states. The method works best if ΔF is of the order of the thermal energy, $1/\beta$. Detailed knowledge of free-energy differences in mesoscopic systems is of crucial importance for problems like the conformations of polymers, the decay of metastable states, or the efficiency of molecular motors.

It is very remarkable and particularly attractive for systems with long relaxation times that equilibrium information such as ΔF may be obtained from fast changes of state. The method has been successfully employed in experiments on mesoscopic systems [5–8] as well as in numerical simulations [9,10] where, however, its superiority to other methods is still under debate [11]. The main problems arise from the exponential average in Eq. (1) which is dominated by small values of W from the tail of the distribution $P(W)$. Since these large deviations are rarely sampled the resulting free-energy estimate may be poor. An equivalent observation is [12,13] that the *dominant* trajectories contributing most to the average in the right hand side of Eq. (1) are in general rather different from the typical ones, i.e., from those with the highest probability. Several methods have been put forward to improve the accuracy of free-energy estimates by, e.g., including information from the backward process [4,14–16], using mappings and auxiliary drifts [17–19], or implementing biased path ensembles [20–22].

In the present paper we devise a method to analytically determine the asymptotics of the work distribution $P(W)$ of driven Langevin systems for very small or large values of W . We demonstrate that fitting these asymptotics to the region of

work values that is still sufficiently sampled by experiment or simulation significantly improved estimates of the free-energy difference may be obtained.

The procedure builds on the method of optimal fluctuation which rests on the general assumption of large deviation theory [23,24] that the probability of an unlikely event is dominated by the most probable fluctuation giving rise to it. All other possibilities to bring the same result about are even more unlikely and may be safely neglected. In physical context the method was originally proposed to determine the asymptotic tail of the electronic density of states in random potentials [25–27]. Later applications include the motion of charge density waves in disordered media [28], the velocity distribution in Burgers turbulence [29,30], anomalous optical absorption in disordered semiconductors [31], and the free-energy distribution of a directed polymer in a random medium [32]. Recently there have also been applications to optimal control theory [33] and error correcting codes [34]. In the present example of Langevin dynamics the method corresponds to a saddle-point approximation in a functional integral over stochastic trajectories.

The paper is organized as follows. In Sec. II we outline the general theory. First the optimal path for a work value in the tail of $P(W)$ is determined by the solution of a variational problem, then the contribution from neighboring paths is included. Section III concerns the discussion of three concrete examples. For the first the complete $P(W)$ can be determined analytically so it serves merely as a test of our method. In the second we compare our results with numerical simulations of the Langevin equation whereas the third uses experimental data. Finally, Sec. IV contains some conclusions.

II. GENERAL THEORY

For concreteness we consider a system with overdamped Langevin dynamics described by

$$\dot{x} = -V'(x,t) + \sqrt{2/\beta}\xi(t), \quad (2)$$

where x denotes the degrees of freedom, V is a potential giving rise to a deterministic drift, and $\xi(t)$ is a standard GAUSSIAN white noise source obeying $\langle \xi(t) \rangle \equiv 0$ and $\langle \xi(t)\xi(t') \rangle = \delta(t-t')$. We denote derivatives with respect to x by a prime and those with respect to t by a dot.

During the time interval $[0, t_1]$ the potential changes between $V_0(x) = V(x, 0)$ and $V_1(x) = V(x, t_1)$ according to a fixed

protocol. Using prepoint discretization the probability density functional of trajectories starting at $t=0$ at x_0 and ending at $t=t_1$ at x_1 is up to a constant given by

$$p[x(\cdot)|x_0,x_1] \sim \exp\left\{-\beta \int_0^{t_1} dt L[x(t),\dot{x}(t),t]\right\}, \quad (3)$$

with the Lagrangian

$$L(x,\dot{x},t) = \frac{1}{4}[\dot{x} + V'(x,t)]^2. \quad (4)$$

The initial point, x_0 , is sampled from the Gibbs measure corresponding to $V_0(x)$ whereas the final point, x_1 , is free. For the work performed along a particular trajectory $x(t)$ we have [35]

$$W[x(\cdot)] = \int_0^{t_1} dt \dot{V}[x(t),t]. \quad (5)$$

With the initial partition function

$$Z_0 = \int dx e^{-\beta V_0(x)} \quad (6)$$

the probability distribution of the work is given by

$$\begin{aligned} P(W) &= \frac{1}{Z_0} \int dx_0 \exp[-\beta V_0(x_0)] \\ &\times \int dx_1 \int_{x(0)=x_0}^{x(t_1)=x_1} \mathcal{D}x(\cdot) p[x(\cdot)|x_0,x_1] \\ &\times \delta\{W - W[x(\cdot)]\} \end{aligned} \quad (7)$$

Using Eqs. (3)–(5) we then find

$$P(W) = \int \frac{dx_0}{Z_0} \int dx_1 \int \frac{dq}{4\pi/\beta} \int_{x(0)=x_0}^{x(t_1)=x_1} \mathcal{D}x(\cdot) e^{-\beta S[x(\cdot),q]} \quad (8)$$

with the action

$$S[x(\cdot),q] = V_0(x_0) + \frac{1}{2} \int_0^{t_1} dt \left[\frac{1}{2}(\dot{x} + V')^2 + iq\dot{V} \right] - \frac{i}{2}qW. \quad (9)$$

To apply the method of optimal fluctuations in the present context we evaluate the integrals in Eq. (8) for a prescribed value of W by the saddle-point approximation. Formally this corresponds to considering the weak noise limit $\beta \rightarrow \infty$.

A. Optimal trajectory

The determination of the optimal trajectory in Eq. (8) includes the optimal choice of its initial and final point [36]. Introducing the augmented Lagrangian

$$\tilde{L}(x,\dot{x},t) = L(x,\dot{x},t) + i\frac{q}{2}\dot{V}[x(t),t] \quad (10)$$

the corresponding Euler-Lagrange equation (ELE) takes the form

$$\frac{d}{dt} \frac{\partial \tilde{L}}{\partial \dot{x}} - \frac{\partial \tilde{L}}{\partial x} = 0. \quad (11)$$

It is completed by the natural boundary condition

$$\left. \frac{\partial \tilde{L}}{\partial \dot{x}} \right|_{t=t_1} = 0, \quad (12)$$

at the end of the interval and the initial condition

$$\left. \frac{\partial \tilde{L}}{\partial \dot{x}} \right|_{t=0} - V'_0(x_0) = 0, \quad (13)$$

incorporating the sampling of the starting point from the equilibrium distribution at $t=0$. Solving Eqs. (11)–(13) and eliminating the Lagrange parameter q using Eq. (5) we generically find for each value of W exactly one optimal trajectory $\bar{x}(t;W)$. The asymptotic estimate

$$P(W) \sim e^{-\beta S[\bar{x}(\cdot),\bar{q}]} \quad (14)$$

for the distribution of work values becomes the more accurate the larger β is or, equivalently, the more W lies in the tail of $P(W)$.

B. Neighborhood of the optimal trajectory

Although Eq. (14) gives a correct estimate of the asymptotic behavior of $P(W)$ it is often desirable to improve its accuracy by incorporating the dominant pre-exponential factor. This factor has contributions from trajectories in the neighborhood of the optimal one and also accounts for the Jacobian accompanying the transition from $p[x(\cdot)]$ to $P(W)$. It is determined by including the quadratic fluctuations around the saddle-point into the calculation. This can be accomplished by adopting the Gel'fand-Yaglom method [37–39] which yields an ordinary differential equation for the fluctuation determinant to the present problem.

Two points are different from the standard case. First, the free end points of the optimal trajectory contribute to the GAUSSIAN fluctuations and give rise to modified boundary conditions for the fluctuation determinant. Second, the constraint $W[x(\cdot)] = W$ suppresses some fluctuations and gives rise to a correction factor to the free fluctuation determinant. Some details of the explicit calculation necessary to incorporate these two modifications are given in the Appendix.

Using $\bar{S} = S[\bar{x}(\cdot),\bar{q}]$, $\bar{V} = V[\bar{x}(t),t]$ and similarly for derivatives of V the final result for the asymptotics of the work distribution is

$$P(W) = \frac{e^{-\beta \bar{S}}}{Z_0 \sqrt{RQ}(t_1)} [1 + \mathcal{O}(1/\beta)] \quad (15)$$

where $Q(t)$ is the solution of the initial value problem

$$0 = \ddot{Q} + 2\bar{V}''\dot{Q} + [(2 - i\bar{q})\bar{V}''' + (\dot{\bar{x}} - \bar{V}')\bar{V}''']Q$$

$$Q(t=0) = 1 \quad \dot{Q}(t=0) = 0 \quad (16)$$

and R is given by

$$R = \int_0^{t_1} dt \int_0^{t_1} dt' \dot{V}'[\bar{x}(t), t] \left[\frac{\delta^2 \bar{S}}{\delta x(t) \delta x(t')} \right]^{-1} \dot{V}'[\bar{x}(t'), t']. \quad (17)$$

III. EXAMPLES

A. Shifted parabola

As a first example we consider a Brownian particle dragged in a parabolic potential, i.e.,

$$V(x, t) = (x - t)^2/2. \quad (18)$$

This system has been analyzed thoroughly both from the theoretical [40–42] as well as from the experimental side [43]. The distribution $P(W)$ is known to be GAUSSIAN [40,41]

$$P(W) = \sqrt{\frac{\beta}{2\pi\sigma_W^2}} \exp\left(-\beta \frac{(W - \sigma_W^2/2)^2}{2\sigma_W^2}\right) \quad (19)$$

with

$$\sigma_W^2 = 2(t_1 - 1 + e^{-t_1}). \quad (20)$$

Since in this example the complete distribution $P(W)$ is known exactly it merely serves as a test of our method.

The ELE Eq. (11) is for Eq. (18) linear and can be solved analytically with the result

$$\bar{x}(t; W) = \frac{1}{2}(2t + e^{-t} - e^{-t_1}) - \frac{W(2 - e^{-t} - e^{-t_1})}{2(t_1 + e^{-t_1} - 1)}.$$

This yields

$$S[\bar{x}(\cdot), \bar{q}] = \frac{(W - (t_1 + e^{-t_1} - 1))^2}{4(t_1 + e^{-t_1} - 1)} \quad (21)$$

which correctly reproduces the exponential factor in Eq. (19). The explicit form $\bar{x}(t; W)$ of the optimal trajectory for different values of W and t_1 characterizes the optimal combination of unlikely initial condition x_0 and rare realization of the noise $\xi(t)$ necessary to bring about large deviations in W .

To determine the prefactor in Eq. (19) we first observe that for Eq. (18) the differential Eq. (16) reduces to

$$\ddot{Q} + 2\dot{Q} = 0, \quad Q(0) = 1, \quad \dot{Q}(0) = 0 \quad (22)$$

with the solution $Q(t) \equiv 1$. Moreover

$$\frac{\delta^2 \bar{S}_N}{\delta x(t) \delta x(t')} = -\frac{1}{2} \delta''(t - t') + \frac{1}{2} \delta(t - t'). \quad (23)$$

Combining this expression with the boundary conditions $\dot{y}(0) = y(0)$ and $\dot{y}(t_1) = -y(t_1)$ for the fluctuations around the optimal path yields

$$\left[\frac{\delta^2 \bar{S}_N}{\delta x(t) \delta x(t')} \right]^{-1} = -2\theta(t - t') \sinh(t - t') + e^{t-t'}. \quad (24)$$

With $\dot{V}' \equiv -1$ we then find

$$R = 2(t_1 - 1 + e^{-t_1}) = \sigma_W^2. \quad (25)$$

Putting all together and using $Z_0 = \sqrt{2\pi/\beta}$ the prefactor of Eq. (19) is also reproduced. In this simple example the asymptotic result hence already gives the complete distribution.

B. Breathing parabola

A more advanced example [36] is given by the breathing parabola [44,45],

$$V(x, t) = \frac{k(t)}{2} x^2 \quad (26)$$

for which the distribution of work is neither GAUSSIAN nor completely accessible analytically. We will consider the case of a monotonously decreasing function $k(t)$ implying $W \leq 0$ and determine the asymptotic form of $P(W)$ for $W \rightarrow -\infty$. The ELE Eq. (11) is given by

$$\ddot{x} + [(1 - iq)\dot{k} - k^2]x = 0 \quad (27)$$

whereas the boundary conditions Eqs. (13) and (12) acquire the form

$$\dot{x}(0) = k(0)x_0 \quad \text{and} \quad \dot{x}(t_1) = -k(t_1)x_1, \quad (28)$$

respectively. These equations constitute a Sturm-Liouville eigenvalue problem which for the special choice

$$k(t) = \frac{1}{1+t} \quad (29)$$

can be solved analytically. The result is

$$\begin{aligned} \bar{x}(t; W) = & \pm \frac{\sqrt{-W}}{\sqrt{g(\mu)}} \sqrt{1 + t} \{ 2\mu \cos[\mu \ln(1+t)] \\ & + \sin[\mu \ln(1+t)] \} \end{aligned} \quad (30)$$

where

$$g(\mu) = \frac{1}{2} \left[\left(\mu - \frac{1}{4\mu} \right) \sin \nu - \cos \nu + 1 + \nu \left(\mu + \frac{1}{4\mu} \right) \right] > 0, \quad (31)$$

and $\mu = \sqrt{iq - 9/4}$ is a solution of

$$(4\mu^2 - 3) \sin \frac{\nu}{2} - 8\mu \cos \frac{\nu}{2} = 0 \quad (32)$$

with $\nu = 2\mu \ln(1+t_1)$.

There are hence infinitely many discrete values $\bar{q}_0, \bar{q}_1, \dots$ of q each associated with two trajectories $\bar{x}^{n+}(t; W)$ and $\bar{x}^{n-}(t; W)$ related to each other by the inversion symmetry $x \rightarrow -x$ of the problem. All $\bar{x}^{n\pm}(t; W)$ are local maxima of $p[x(\cdot)]$. However, it can be proved that $p[\bar{x}^{0\pm}(\cdot)] > p[\bar{x}^{n\pm}(\cdot)]$ for all $n > 0$, i.e., the maxima at $\bar{x}^{0\pm}(t; W)$ are the dominant ones. This is in accordance with intuition since large absolute values of W are realized by trajectories which are most of the time far from the minimum of the potential. On the other hand it is known from the

general theory of Sturm-Liouville problems that the $\bar{x}^{n\pm}(t; W)$ have n zeros in the interval $(0, t_1)$. It is hence not surprising that the “ground-state” solutions $\bar{x}^{0\pm}(t; W)$ dominate the asymptotics of $P(W)$.

Neglecting contributions from the subdominant maxima we hence find from Eqs. (9), (26), and (30) for the exponential term in the asymptotic work distribution

$$P(W) \sim e^{-\beta S[\bar{x}^{0\pm}(\cdot, \bar{q}_0)]} = e^{\beta h(\mu_0)W} \quad (33)$$

where

$$h(\mu) = \frac{1}{8g(\mu)} \left[(8\mu^2 - 6)\cos \nu - \left(2\mu^3 - 11\mu + \frac{9}{8\mu} \right) \sin \nu + 8\mu^2 + 6 + \nu \left(2\mu^3 + 5\mu + \frac{9}{8\mu} \right) \right]. \quad (34)$$

Using Eq. (31) one can show that $h(\mu) > 1$ as is necessary for the existence of the Jarzynski average Eq. (1). Note also that in the present case different values of W do not correspond to different values of \bar{q} since the latter is fixed. As shown by Eq. (30) different values of W are realized by different initial conditions of $\bar{x}^{0\pm}(t; W)$.

In the determination of the pre-exponential factor to the asymptotic we concentrate on its dependence on W . From Eq. (16) we find using Eq. (26)

$$0 = \ddot{Q} + 2k(t)\dot{Q} + (2 - i\bar{q}_0)\dot{k}(t)Q \quad (35)$$

and therefore $Q(t_1)$ is independent of W . Likewise

$$\frac{\delta^2 \bar{S}_N}{\delta x(t) \delta x(t')} = -\frac{1}{2} \delta''(t-t') + \frac{1}{2} [k^2 - (1 - \bar{q}_0)\dot{k}] \delta(t-t') \quad (36)$$

does not depend on W and hence neither does its inverse. On the other hand $\dot{V}' = \dot{k}\bar{x}^{0\pm}$ is proportional to $\sqrt{-W}$ as follows from Eq. (30). This implies $R \sim \sqrt{-W}$ and we get the asymptotic result

$$P(W) \sim \frac{e^{\beta h(\mu_0)W}}{\sqrt{-W}}. \quad (37)$$

It is instructive to check this result against numerical simulations of the Langevin dynamics [36]. Figure 1 shows a histogram of work values obtained from such simulations together with the asymptotics Eq. (37). Figure 2 provides a logarithmic blowup of the small- W region. To determine the prefactor in Eq. (37) a breakpoint W^* is chosen and the area under the asymptotic form of $P(W)$ for $W < W^*$ is set equal to the total weight $\Phi_{<}$ of the histogram for $W < W^*$ (gray bars in Fig. 1). The value of W^* has to be chosen such that on the one hand $P(W)$ is already well approximated by its asymptotic form Eq. (37) and on the other hand the region around W^* is still sufficiently sampled by the histogram. As shown by Fig. 2 in the present case there is a whole window of admissible values of W^* extending from roughly -1.5 down to around -5 .

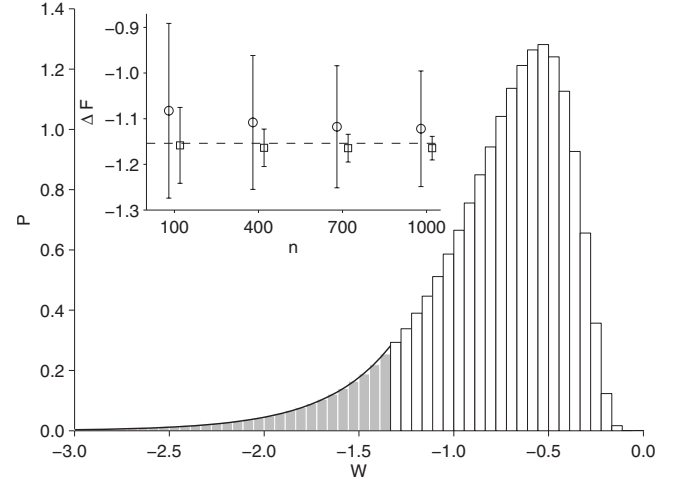


FIG. 1. Histogram of work values as obtained from 10^7 simulations of the Langevin Eq. (2) with $\beta=2$, $t_1=100$, and $V(x, t)$ given by Eqs. (26) and (29). The full line is the asymptotic form of the work distribution as derived in Eq. (37). The inset shows two estimates for the free-energy difference ΔF together with their standard deviation as function of the sample size n . Circles are the standard estimate Eq. (38), squares give the improved one Eq. (39) incorporating the asymptotic behavior of $P(W)$ with $W^* = -4/3$. The dashed line is the exact result.

The asymptotic form of $P(W)$ can be utilized to improve the estimate Eq. (1) for the free-energy difference ΔF . To show this we have subdivided the 10^7 work values W_i obtained in the simulations into 10^4 runs. Using $n=10^2 \dots 10^3$ values from each run we have then determined the standard Jarzynski estimate

$$\Delta F^{\text{st}} = -\frac{1}{\beta} \ln \left(\frac{1}{n} \sum_{i=1}^n e^{-\beta W_i} \right) \quad (38)$$

as well as an improved one

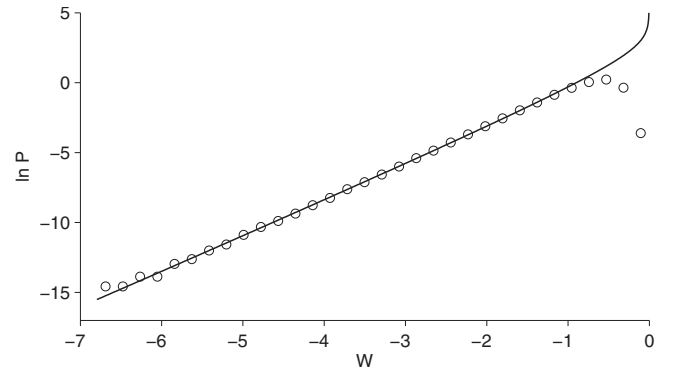


FIG. 2. Comparison of the simulation results (circles) for $P(W)$ shown in Fig. 1 and the asymptotic behavior Eq. (37) (full line) on a logarithmic scale.

$$\Delta F^{\text{im}} = -\frac{1}{\beta} \ln \left(c \int_{-\infty}^{W^*} \frac{e^{(h-1)\beta W}}{\sqrt{-W}} dW + \frac{1}{n} \sum_{W_i \geq W^*} e^{-\beta W_i} \right) \quad (39)$$

using the asymptotic form of $P(W)$ for $W < W^*$. Here the constant c is determined from the normalization condition

$$\Phi_{<} = c \int_{-\infty}^{W^*} \frac{e^{h\beta W}}{\sqrt{-W}} dW. \quad (40)$$

The inset in Fig. 1 shows both estimates together with their standard deviation for different values of n as well as the exact result $\Delta F^{\text{exact}} = -\ln(1+t_1)/(2\beta)$. As is clearly seen both the bias and the standard deviation are significantly reduced when combining the histogram with the asymptotic form of $P(W)$ as given by Eq. (37).

C. Driven Brownian particle near a wall

We finally demonstrate the applicability of our method to the analysis of experimental data. In [7] a charged colloidal particle near a wall was subjected to a time-dependent anharmonic potential $V(x, t)$ generated by optical tweezers. Measuring the distance of the particle from the wall the distribution of work performed during one cycle of the potential modulation was determined (histogram in Fig. 4 in [7]). Since $V_0(x) = V_1(x)$ this case is characterized by $\Delta F = 0$.

As discussed in [7] the dynamics of the particle may be approximately modeled by an overdamped Langevin equation. Due to the vicinity of the wall the friction coefficient and the noise intensity now depend on the state x . Moreover, in order to retain the Gibbs measure as stationary distribution of the stochastic process an additional drift term has to be added [46]. Using Itô convention the resulting equation is [36]

$$\dot{x} = -D(x)V'(x, t) + D'(x) + \sqrt{2D(x)}\xi(t), \quad (41)$$

with potential

$$V(x, t) = A e^{-\kappa(x-a)} + B(t)(x-a) \quad (42)$$

and state dependent diffusion coefficient [47]

$$D(x) = \frac{D_0}{1 + \frac{R}{x}}. \quad (43)$$

The values for D_0 , the radius R of the particle, the parameters A , κ , and a of $V(x, t)$, and the protocol function $B(t)$ are taken from the experiment [48]. Instead of Eq. (4) we now have

$$L(x, \dot{x}, t) = \frac{1}{4D(x)} [\dot{x} + D(x)V'(x, t) - D'(x)]^2. \quad (44)$$

The corresponding ELE

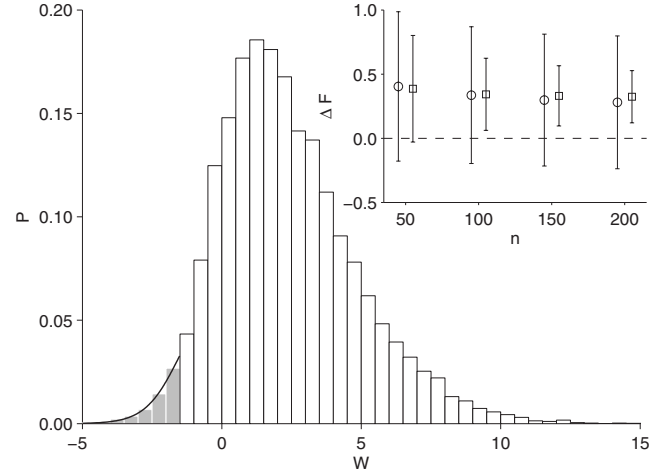


FIG. 3. Histogram of 16200 work values obtained experimentally in [7] together with the asymptotic form (full line) derived from Eqs. (41)–(43). The inset shows the standard (circles) and the improved (squares) estimate for the free-energy difference. The exact result is $\Delta F = 0$ (dashed line).

$$0 = \ddot{x} - \frac{D'}{2D} \dot{x}^2 + (1 - iq)D\dot{V}' + (D' - DV') \left(DV'' - D'' + \frac{1}{2}D'V' + \frac{D'^2}{2D} \right) \quad (45)$$

can no longer be solved analytically but its numerical solution does not pose any specific problems [36]. Solving Eq. (45) for a wide range of q values and using the solution in Eq. (5) to establish the relation between q and W the extremal action \bar{S} can be determined. The calculation of the pre-exponential factor is now much more involved since the differential equation for $Q(t)$ is more complicated and both $Q(t_1)$ and R will depend on W in a nontrivial way. We leave this problem for further investigations and use for the present example only the asymptotic behavior of $P(W)$ resulting from Eq. (14). It is shown in Fig. 3 together with the histogram of experimental results. The inset gives again a comparison of the estimates for ΔF determined analogously to Eqs. (38) and (39) with $W^* = -3/2$.

While the asymptotic form of $P(W)$ seems to be well captured the improvement in the free-energy estimates is less distinctive than in Fig. 1. The reason may be that $P(W)$ decreases rather rapidly for small W which makes the matching between histogram and asymptotics more difficult, in particular since the pre-exponential factor is not available. On the other hand, Eq. (41) is already an approximation to the experimental situation and the asymptotic form of $P(W)$ derived from it may therefore differ from the true one.

IV. CONCLUSION

We have shown that the method of optimal fluctuations allows to analytically characterize the asymptotic form of the work distribution in driven Langevin systems. This information may be combined with histograms of work values as obtained in experiments or numerical simulations to improve

the accuracy of free-energy estimates exploiting the Jarzynski equation. The method will work best in situations where an overlap region in W values exists which is sufficiently sampled by the histogram and at the same time well described by the asymptotic behavior.

Our method builds on a saddle-point calculation of a functional integral over stochastic trajectories constrained to a specific value of the performed work W . Although similar techniques have been used in the context of nonequilibrium work and fluctuation theorems (see, e.g., [49–51]) our emphasis is on the application to constrained problems aiming at the *asymptotic* behavior of the work distribution. It will be interesting to generalize the method to higher-dimensional situations.

ACKNOWLEDGMENTS

I would like to thank Sascha von Egan-Krieger for the fruitful collaboration on the issues discussed in this paper. I have also benefited from interesting discussions with Daniel Grieser, Aljoscha Hahn, Peter Reimann, and Holger Then. Thanks are due to Valentin Blickle for sending us the detailed parameters and relevant results of his experiments.

APPENDIX

In this we give some details on the calculation of the GAUSSIAN fluctuations around the saddle point in the integral Eq. (8). Using $\epsilon = t_1/N$, $t_j = \epsilon j$, $V_j = V(\bar{x}(t_j), t_j)$, and similar for the derivatives of $V(\bar{x}(t), t)$ the time-sliced version of this integral reads

$$P(W) = \lim_{N \rightarrow \infty} \frac{\beta}{4\pi Z_0} \left(\frac{\beta}{4\pi\epsilon} \right)^{N/2} \int dq \int \prod_{j=0}^N dx_j e^{-\beta S_N(\{x_j\}, q)} \quad (\text{A1})$$

with the discretized action defined by

$$S_N(\{x_j\}, q) = V_0 + \frac{\epsilon}{2} \sum_{j=0}^{N-1} \left[\frac{1}{2} \left(\frac{x_{j+1} - x_j}{\epsilon} + V'_j \right)^2 + iq \dot{V}_j \right] - \frac{i}{2} q W. \quad (\text{A2})$$

Denoting the saddle-point values of x_j and q by an overbar, using $\bar{S}_N = S_N(\{\bar{x}_j\}, \bar{q})$ and expanding the exponent to second order in $x_j - \bar{x}_j$ and $q - \bar{q}$ we find

$$P(W) = \lim_{N \rightarrow \infty} \frac{\epsilon}{Z_0} \frac{e^{-\bar{S}_N}}{\sqrt{\det M}} [1 + \mathcal{O}(1/\beta)] \quad (\text{A3})$$

where the symmetric matrix M is given by

$$M_{kl} = 2\epsilon \frac{\partial^2 S_N}{\partial x_k \partial x_l} =: A_{kl} \quad \text{for } k, l = 0, \dots, N$$

$$M_{kN+1} = 2\epsilon \frac{\partial^2 S_N}{\partial x_k \partial q} = i\epsilon^2 \dot{V}'_k \quad \text{for } k = 0, \dots, N$$

$$M_{N+1N+1} = 2\epsilon \frac{\partial^2 S_N}{\partial q \partial q} = 0.$$

Here A_{kl} is a tridiagonal fluctuation matrix of the usual form [37–39]. Its determinant can be obtained from a recursion relation which for $\epsilon \rightarrow 0$ turns into a differential equation. Analogous to the standard Gel'fand-Yaglom procedure we find $\det A = Q(t_1)$ where $Q(t)$ is the solution of the initial value problem Eq. (16).

In order to reduce the calculation of $\det M$ to that of $\det A$ we multiply the first $N+1$ rows of M by $-i\epsilon^2(\dot{V}')^T A^{-1}$ and add this to the last row. The resulting matrix has then in the last row all zeros except for the last entry which reads

$$R_N := \epsilon^4 \sum_{k,l} \dot{V}'_k (A^{-1})_{kl} \dot{V}'_l. \quad (\text{A4})$$

Consequently $\det M = R_N \det A$. This result is in fact quite intuitive. Assume for simplicity that the constraint $W[x(\cdot)] = W$ is orthogonal to one eigenvector \mathbf{e}_n of A with eigenvalue λ_n . Then $\{\dot{V}'_k\}$ which is the gradient of the constraint is parallel to \mathbf{e}_n and R_N is proportional to $1/\lambda_n$. It hence cancels exactly that eigenvalue of the unconstrained fluctuation matrix A describing fluctuations perpendicular to the constraint which are forbidden.

Using

$$\lim_{N \rightarrow \infty} R_N = \epsilon^2 R \quad (\text{A5})$$

with R given by Eq. (17) we finally end up with Eq. (15).

-
- [1] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
 [2] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
 [3] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
 [4] G. E. Crooks, Phys. Rev. E **61**, 2361 (2000).
 [5] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, Jr., and C. Bustamante, Science **296**, 1832 (2002).
 [6] F. Douarche, S. Ciliberto, A. Petrosyan, and I. Rabbiosi, Europhys. Lett. **70**, 593 (2005).
 [7] V. Blickle, T. Speck, L. Helden, U. Seifert, and C. Bechinger,

- Phys. Rev. Lett. **96**, 070603 (2006).
 [8] N. C. Harris, Y. Song, and C.-H. Kiang, Phys. Rev. Lett. **99**, 068101 (2007).
 [9] D. A. Hendrix and C. Jarzynski, J. Chem. Phys. **114**, 5974 (2001).
 [10] S. Park and K. Schulten, J. Chem. Phys. **120**, 5946 (2004).
 [11] W. Lechner and C. Dellago, J. Stat. Mech. (2007), P04001.
 [12] F. Ritort, J. Stat. Mech. (2004), P10016.
 [13] C. Jarzynski, Phys. Rev. E **73**, 046105 (2006).
 [14] C. H. Bennett, J. Comput. Phys. **22**, 245 (1976).
 [15] M. R. Shirts, E. Bair, G. Hooker, and V. S. Pande, Phys. Rev.

- Lett. **91**, 140601 (2003).
- [16] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco, and C. Bustamante, *Nature (London)* **437**, 231 (2005).
- [17] C. Jarzynski, *Phys. Rev. E* **65**, 046122 (2002).
- [18] S. Vaikuntanathan and C. Jarzynski, *Phys. Rev. Lett.* **100**, 190601 (2008).
- [19] A. M. Hahn and H. Then, *Phys. Rev. E* **79**, 011113 (2009).
- [20] S. X. Sun, *J. Chem. Phys.* **118**, 5769 (2003).
- [21] F. M. Ytreberg and D. M. Zuckerman, *J. Chem. Phys.* **120**, 10876 (2004).
- [22] H. Oberhofer and C. Dellago, *Comput. Phys. Commun.* **179**, 41 (2008).
- [23] M. I. Freidlin and A. D. Wentzell, *Random Perturbations of Dynamical Systems* (Springer, New York, 1998).
- [24] H. Touchette, *Phys. Rep.* **478**, 1 (2009).
- [25] I. M. Lifshitz, *Sov. Phys. Usp.* **7**, 549 (1965).
- [26] B. I. Halperin and M. Lax, *Phys. Rev.* **148**, 722 (1966).
- [27] J. Zittartz and J. S. Langer, *Phys. Rev.* **148**, 741 (1966).
- [28] M. V. Feigel'man, *Sov. Phys. JETP* **52**, 555 (1980).
- [29] G. Falkovich, I. Kolokolov, V. Lebedev, and A. Migdal, *Phys. Rev. E* **54**, 4896 (1996).
- [30] E. Balkovsky, G. Falkovich, I. Kolokolov, and V. Lebedev, *Phys. Rev. Lett.* **78**, 1452 (1997).
- [31] M. Mostovoy, F. Antonsen, and J. Knoester, *Phys. Rev. B* **65**, 155210 (2002).
- [32] I. V. Kolokolov and S. E. Korshunov, *Phys. Rev. B* **75**, 140201(R) (2007).
- [33] B. E. Vugmeister and H. Rabitz, *Phys. Rev. E* **55**, 2522 (1997).
- [34] V. Chernyak, M. Chertkov, M. G. Stepanov, and B. Vasic, *Phys. Rev. Lett.* **93**, 198702 (2004).
- [35] K. Sekimoto, *Prog. Theor. Phys.* **130**, 17 (1998).
- [36] S. von Egan-Krieger, Diploma thesis, University of Oldenburg, 2009 (unpublished).
- [37] E. W. Montroll, *Commun. Pure Appl. Math.* **5**, 415 (1952).
- [38] I. M. Gel'fand and A. M. Yaglom, *J. Math. Phys.* **1**, 48 (1960).
- [39] M. Chaichian and A. Demichev, *Path integrals in Physics* (IOP Publishing, London, 2001).
- [40] O. Mazonka and C. Jarzynski, e-print arXiv:cond-mat/9912121.
- [41] R. van Zon and E. G. D. Cohen, *Phys. Rev. E* **67**, 046102 (2003); *Phys. Rev. E* **69**, 056121 (2004).
- [42] E. G. D. Cohen, *J. Stat. Mech.* (2008), P07014.
- [43] G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, *Phys. Rev. Lett.* **89**, 050601 (2002).
- [44] C. Jarzynski, *Phys. Rev. E* **56**, 5018 (1997).
- [45] D. M. Carberry, J. C. Reid, G. M. Wang, E. M. Sevick, D. J. Searles, and D. J. Evans, *Phys. Rev. Lett.* **92**, 140601 (2004).
- [46] A. W. C. Lau and T. C. Lubensky, *Phys. Rev. E* **76**, 011123 (2007).
- [47] H. Brenner, *Chem. Eng. Sci.* **16**, 242 (1961).
- [48] V. Blickle (private communication).
- [49] T. Taniguchi and E. G. D. Cohen, *J. Stat. Phys.* **126**, 1 (2007).
- [50] A. Baule and E. G. D. Cohen, *Phys. Rev. E* **79**, 030103(R) (2009).
- [51] D. D. L. Minh and A. B. Adib, *Phys. Rev. E* **79**, 021122 (2009).