On asymptotic behavior of work distributions for driven Brownian motion

Viktor Holubec¹, Dominik Lips², Artem Ryabov¹, Petr Chvosta¹, and Philipp Maass²

¹ Charles University in Prague, Faculty of Mathematics and Physics, Department of Macromolecular Physics, V Holešovičká 2, CZ-180 00 Praha, Czech Republic
² Universität Osnabrück, Fachbereich Physik, Barbarastrasse 7, 49076 Osnabrück, Germany

Received: date / Revised version: date

Abstract. We propose a simple conjecture for the functional form of the asymptotic behavior of work distributions for driven overdamped Brownian motion of a particle in confining potentials. This conjecture is motivated by the fact that these functional forms are independent of the velocity of the driving for all potentials and protocols, where explicit analytical solutions for the work distributions have been derived in the literature. To test the conjecture, we use Brownian dynamics simulations and a recent theory developed by Engel and Nickelsen (EN theory), which is based on the contraction principle of large deviation theory. Our tests suggest that the conjecture is valid for potentials with a confinement equal to or weaker than the parabolic one, both for equilibrium and for nonequilibrium distributions of the initial particle position. For potentials with stronger confinement, the conjecture fails and gives a good approximate description only for fast driving. In addition we obtain a new analytical solution for the asymptotic behavior of the work distribution for the V-potential by application of the EN theory, and we extend this theory to nonequilibrated initial particle positions.

PACS. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 05.70.Ln Nonequilibrium and irreversible thermodynamics

1 Introduction

With the ever-improving possibilities to manipulate and control physical systems on the single-molecule level, the analysis of the role of thermodynamic quantities such as work, heat, and entropy, when defined for single system trajectories, has become an important field in nonequilibrium statistical mechanics [1,2]. One of the most intriguing achievements in this field is the discovery of detailed and integral fluctuation theorems [3,4,5,6,7,8], which in general refer to nonequilibrium systems that are externally driven by a protocol \( \lambda(t) \) of control variables during a time interval \([0,T]\). These theorems hold true universally and they can be viewed as a generalization of the second law of thermodynamics.

Among the theorems, the detailed Crooks fluctuation theorem (CFT) [4], and its integral counterpart, the Jarzynski equality (JE) [3] are perhaps the most prominent. They pertain to systems in contact with a heat reservoir at temperature \( T \) and in equilibrium at the initial time \( t_0 = 0 \). The CFT states that work probability distributions (WPD) \( p(w) \) and \( p_R(w) \) for a protocol \( \lambda(t) \) and the associated reversed protocol \( \lambda_R(t) = \lambda(t_f - t) \), respectively, are related according to

\[
p(w)/p_R(-w) = e^{\beta \Delta F} \, .
\]

where \( \Delta F = F_{t_f} - F_0 \) is the difference in equilibrium free energies \( F_{0,f} \) of the macrostates specified by the control variables \( \lambda_{0,f} = \lambda(t_{0,f}) \), and \( \beta = (k_B T)^{-1} \) is the inverse thermal energy (\( k_B \) is the Boltzmann constant and \( T \) is the temperature). The JE states that

\[
\langle e^{-\beta w} \rangle = \int dw \, p(w) e^{-\beta w} = e^{-\beta \Delta F} \, .
\]

It becomes particularly valuable in unidirectional experimental settings, where the work for the reversed protocol can not be measured, and accordingly the Crooks theorem can not be applied [9]. In applications of the JE, measured histograms generally need to be extended to the tail regime, because the average of \( e^{-\beta w} \) in the JE is dominated by rare trajectories with work values \( w \ll \Delta F \). This problem can in principle be resolved by fitting the wings of a measured WPD to theoretical predictions for the asymptotic behavior in the limit \( w \to -\infty \).

Corresponding predictions for this asymptotic behavior are, however, difficult to obtain. WPD depend on details of the experimental setup and only a few generic properties have been reported so far. In the limit of quasi-static driving, the WPD becomes a delta function, \( p(W) = \delta(W - \Delta F) \), and for sufficiently slow driving, close to the quasi-static limit, it can be approximated by a Gaussian distribution in the relevant regime of the integrand in the JE [10]. The JE equality moreover gives the constraint that \( p(w) e^{-\beta w} \) is integrable, which implies that for \( w \to -\infty \), the WPD must decay faster than \( e^{-\beta |w|} \).
For overdamped Brownian motion of a particle in time-varying potentials, a sophisticated theory based on the contraction principle of large deviation theory was recently developed by Engel and Nickelsen (EN theory) \[11,12\]. This allows one to predict the asymptotic behavior of the WPD by solving a system of ordinary differential equations with certain boundary conditions (see Appendix A). Analytical solutions of these equations were given for the harmonic potential \[11,12\], where in the protocol either its minimum is moved (“sliding parabola”) or the stiffness is varied (“breathing parabola”). In the Appendix \[13\] we further derive an analytical solution for the case of a V-potential \[13\] with time-varying slope. However, in general, the explicit functional form of the WPD asymptotic behavior remains unknown and the respective differential equations have to be solved numerically.

In this work we show that the functional form can be often guessed by a simple method, which becomes exact in the limit of infinitely fast driving. It is referred to as the functional form (FF) conjecture in the following. We show in Sec. 2 that for the rare cases of potentials and protocols, where the WPD has been derived analytically, the FF conjecture always provides the correct functional form. This leads to the question whether the FF conjecture can be applied in general to predict the functional form of the WPD asymptotics.

To tackle this problem, one could test the FF conjecture against simulations. However, in corresponding simulations it becomes very difficult to capture the WPD behavior for large negative work values with sufficient statistics. Another possibility is to compare the predictions of the FF conjecture with results obtained from the EN theory. This theory, which relies on the applicability of large deviation theory to the WPD, has been shown to reproduce the exact Gaussian WPD for the sliding parabola \[11,12\] and further results obtained from it for the breathing parabola turned out to agree with an exact treatment \[14\]. Moreover, the EN theory was shown to match simulated data for the asymptotic WPD behavior for several other potentials and protocols \[12,13\].

Using the exact results for the logarithmic-harmonic potential \[14\], we provide in Sec. 2 further severe evidence of the validity of the EN theory. Given this evidence, we then base our evaluation of the FF conjecture on the EN theory. This evaluation is supplemented by WPD data from Brownian dynamics (BD) simulations. In the corresponding analysis of the FF conjecture in Sec. 3, we will consider both “hard potentials” (with stronger confinement than the harmonic one) and “soft potentials” (with weaker confinement than the harmonic one). In Sec. 4 we furthermore generalize both the EN theory and the FF conjecture to the case of a non-equilibrated initial position of the particle.

### 2 FF conjecture and EN theory versus exact results

The time evolution of the particle position \(x\) for overdamped one-dimensional Brownian motion in a time-varying potential \(\dot{U}(x, \lambda(t))\) can be derived exactly (see Appendix B).

\[
\frac{dx}{dt} = -\mu \frac{\partial U(x, \lambda(t))}{\partial x} + \eta(t),
\]

where \(\mu\) is the mobility, \(U(x, \lambda(t))\) is the potential, and \(\eta(t)\) is a Gaussian white noise with zero mean and correlation \(\langle \eta(t)\eta(t') \rangle = 2\mu k_B T \delta(t-t').\) In the following we set \(k_B T\) as our energy unit, and consider \(x\) as dimensionless, which allows to set \((\mu k_B T)^{-1}\) as the time unit \[16\]. The work \(w\) done on the particle along the stochastic trajectory \(x(t)\) during the time interval \([0, t_f]\) is

\[
w = \int_0^{t_f} dt \left. \frac{\partial U(x(t), \lambda(t))}{\partial \lambda} \right| \frac{dx(t)}{dt}.
\]

To keep the treatment simple, we consider potentials that depend monotonically on the protocol \(\lambda(t)\) (the only exception is the sliding parabola potential in the first line in Tab. 1), and we always use monotonic protocols, where both \(\partial U(x(t), \lambda(t))/\partial \lambda\) and \(d\lambda/dt\) do not change sign in \([0, t_f]\).

In the limit of infinitely fast driving, where the protocol \(\lambda(t)\) jumps from its initial value \(\lambda_0 = \lambda(t_0)\) to its final value \(\lambda_f = \lambda(t_f)\) at some time instant in the interval \([0, t_f]\), the WPD is given by

\[
p(w) = \int p_{eq}(x) \delta \left[ w - \Delta U(x) \right] \rho_0(x),
\]

where \(\Delta U(x) = U(x, \lambda(t_f)) - U(x, \lambda(0))\), and \(\rho_0(x)\) is the initial distribution of the position of the particle at time \(t = 0\). In Refs. \[12,17\] it was pointed out that for the breathing parabola the functional form of the WPD asymptotics is the same as that for infinitely fast driving.

This suggests the following FF conjecture: If the position of the Brownian particle is initially in equilibrium with distribution \(p_{eq}(x) = \exp[-\beta U(x, \lambda(0))] / Z_0\), the functional form of the WPD asymptotic behavior is given by

\[
p(w) = \int p_{eq}(x) \delta \left[ w - \Delta U(x) \right] / Z_0, \quad w \to \pm \infty.
\]
the resulting expression after performing the integration, all coefficients depending on $\lambda(t_f)$ or $\lambda(0)$ are considered as unknown parameters. For example, inserting the potential $U(x, \lambda(t)) = \kappa[x - \lambda(t)]^2/2$ from the first line of Tab. 1 into Eq. (3), one obtains $p(w) = \exp[-(2w - \kappa\Delta\lambda^2)/8\kappa]\exp(\kappa\Delta\lambda)]$ after integration, where $\Delta\lambda = \lambda(t_f) - \lambda(0)$. The constants containing $\Delta\lambda$ are considered as unknown numbers, and marked by $A$, $B$ and $C$ in the table, giving $p(w) = A \exp[-(Bw - C)^2]$. Another example is the potential $U(x, \lambda(t)) = \lambda(t)x^2/2$ from the second line of Tab. 1. In this case one obtains from Eq. (3) $p(w) = \exp[-\beta\lambda(0)x^2/2\Delta\lambda]$. The resulting functional form is $p(w) = A\exp[-(Bw - C)^2]$, because the exponent $-1/2$ does not depend on the driving $\Delta\lambda$.

The first three potentials in Tab. 1 refer to those, where exact analytical results for the complete WPD have been derived, namely (i) the sliding parabola $\exp(-t_f)$, (ii) the breathing parabola $\exp(-t_f)$, and (iii) the logarithmic-harmonic potential $\exp(-t_f)$. As a fourth example we added the V-potential, where the asymptotic behavior predicted by the EN theory could be derived analytically (see Appendix). For all these potentials, where the asymptotic behavior of the WPD is known analytically, the FF conjecture on the functional form is correct.

Let us note that in Eq. (3) we assumed that $\Delta U(x)$ is different from zero, which always is the case for a monotonous protocol $d\lambda(t)/dt$ strictly positive or negative in $[0, t_f])$. Moreover, in Eq. (3) we not only refer to the asymptotic behavior for $w \to +\infty$ (relevant for the JE), but also to the limit $w \to -\infty$. The WPD asymptotic behavior in the latter limit is also in agreement with all analytically known results. The surprising agreement suggests that the functional form of WPD asymptotic behavior does not depend on the velocity of the driving and gives us the motivation to further test the FF conjecture.

The EN theory is exact in the weak noise limit, i.e., up to the first order in thermal energy $k_B T$ [see Eq. (8) in Appendix A]. The thermal energy determines the free diffusion coefficient $D_0 \propto k_B T$ and thus the weak noise regime means that the internal dynamics of the system is slow. For driven systems, the slowness should be compared with the speed of the driving. In this respect, a slowly driven system can be obtained by either fixing the driving speed and increasing the temperature or vice versa.

As discussed in the Introduction, we first provide further compelling evidence that EN theory is indeed valid also for slowly driven systems. We find this necessary, because (i) confirmation of this theory by analytical results has so far been done only for the harmonic potential, where the propagator for the dynamics is Gaussian, and (ii) the EN theory for other potentials has been tested by BD simulations, which, however, are restricted to relatively fast driving, where the tails of the WPD can be determined with sufficient statistics. For slow driving, the essential part of the WPD is always well described by a Gaussian distribution $\exp(-t_f)$, while the asymptotic behavior shows up only when going to extremely large $|w|$ values.

The compelling evidence is obtained by utilizing the exact analytical results for the logarithmic-harmonic potential $U(x, \lambda(t)) = -g \log(|x|) + \lambda(t)x^2/2$, see third line in Tab. 1 because in the presence of the logarithmic part ($g \neq 0$) the propagator for the dynamics is no longer Gaussian, and the pre-exponential factor depends sensitively on the strength $g$ of the logarithmic part and the inverse temperature $\beta$. For slow driving, the asymptotic regime is expected to occur at very large negative work values with extremely small $p(w)$ values beyond a possible physical realization, while the main part of the WPD can be well described by a Gaussian. According to the
reasons given above, we deliberately want to test the EN theory in this situation. For this test we first calculate numerically the WPD asymptotic behavior using the EN theory (the numerical method used for solving the EN equations is described in Appendix [20]) and fit the form predicted in Tab. II to these data. Then we compare the fitted coefficients \(\nu\) with the results predicted in [14]. Results for the protocol

\[
\lambda(t) = \frac{k}{1 + rt} \quad (4)
\]

with \(k = 1, r = 1, \) and \(t_f = 1\) are shown in Fig. [11] for three different \(g\) values. They strongly suggest that the EN theory is correct even for slow driving. The parameters \(\nu\) and \(B\), determined from fits in the \(w\) interval \([-350, w_+]\), are shown in the insets as functions of the upper bound \(w_+\) of the fit interval. As can be seen from these graphs, \(\nu\) and \(B\) converge to the predicted values with decreasing \(w_+\). It becomes clear also that the convergence to the exact asymptotic functional form occurs at very large negative work values, where \(p(w)\) attains extremely small values of order \(10^{-300}\). Irrespective of this slow convergence to the asymptotic functional form, it should be noted that the data from the EN theory are very close to the exact solution of the complete WPD in the whole \(w\) interval shown in Fig. [11].

In the following we now assume the EN theory to be valid. The FF conjecture is tested against it and against BD simulations, which have been carried out by numerical integration of the Langevin equation [11] with the Heun algorithm [20]. WPD determined from the BD simulations have been calculated from typically \(10^8\) simulated trajectories.

3 FF conjecture versus EN theory for equilibrium initial condition

As mentioned in the Introduction, an analytical solution of the differential equations of the EN theory can be obtained for the V-shaped potential, which for any monotonic protocol \(\lambda(t)\) gives the WPD asymptotic behavior. If \(d\lambda(t)/dt > 0, p(w)\) has support only for \(w > 0\), and \(p(w) \sim \exp(-Bw)\) for \(w \to +\infty\), while for \(d\lambda(t)/dt < 0, p(w)\) has support only for \(w < 0\), and \(p(w) \sim \exp(|B|w)\) for \(w \to -\infty\), where \(B = \beta\lambda_0/(\lambda_f - \lambda_0)\). This functional form is predicted by the FF conjecture, where, quite surprisingly, in this case also the parameter \(B\) is correctly given. We have tested these results against BD simulations (data not shown).

Further tests of the FF conjecture have been performed by us for various potentials, the potentials [5] and [6] given below, the double-well potential \(x^4 + \lambda(t)x^2\), various potentials of the form \(\lambda(t)|x|^n\), and the potential \(\lambda(t)\log(1 + x^2)\). These tests were carried out for different protocols, the one given in Eq. (4), the linear protocol \(\lambda(t) = k + rt\) and the exponential protocol \(\lambda(t) = k\exp(-rt)\). Our findings suggest that for “hard potentials”, with stronger confinement than the harmonic one, the FF conjecture fails in general, and gives, as expected, only a good approximate description for sufficiently fast driving.

For “soft potentials”, with weaker confinement than the harmonic one, there is evidence that the FF conjecture always predicts correctly the main \(|w| \to \infty\) asymptotics of the WPD (exponential part), and in some cases even the pre-exponential factor. This is true for all examples in Tab. II which refer either to soft potentials or the harmonic one. It is possible, however, that the pre-exponential factor is not correctly captured by the FF conjecture.

In the following we exemplify these findings for one hard and one soft potential, namely

\[
U(x, \lambda(t)) = \lambda(t)x^4, \quad (5)
\]

and

\[
U(x, \lambda(t)) = \lambda(t)|x| + |x|^{3/2}, \quad (6)
\]

with the protocol \(\lambda(t)\) given in Eq. (4).

Figure [2] shows the results of the EN theory (circles) and BD simulations (squares) for the hard potential (5), which coincides in the asymptotic regime \(w \ll |\Delta F|\). The FF conjecture predicts the asymptotic behavior of WPD \(p(w) \sim |w|^{-3/4} \exp(-B|w|)\). Fits of this functional form to the EN data for three fitting intervals with different upper bounds \(w_+\) are depicted by the lines. As the \(B\) factor, shown in the inset of Fig. 2, shows no tendency to converge to a constant with decreasing upper limit \(w_+\) of the fit interval \([-120, w_+]\) (see also the non-overlapping of the three lines in the main part of the figure), we conclude that the FF conjecture fails in this case.
exp (the overlapping of the three lines in the main part of the factors from the fits clearly tend to constants, see also extensive BD simulations and found always a good agree-

Figure 3 shows the results of the EN theory (circles) and BD simulations (squares) for the soft potential, which again coincide in the asymptotic regime \( w \ll \Delta F \). The FF conjecture predicts the asymptotic behavior \( p(w) \sim \exp(-Bw - C|w|^{3/2}) \) to the EN data for different fitting intervals \([-36, w_+]\) with upper bounds \( w_+ = -25.3, -14.5, \) and \(-37\). The insets show the fitting parameters \( B \) and \( C \) as functions of \( w_+ \). The errors bars given in the insets, which are smaller than or comparable to the size of the symbols, mark 95% confidence bounds of fitting parameters. The free energy difference reads \( \Delta F \approx -0.24 \).

To sum up, the FF conjecture for the non-equilibrium initial distribution suggests that for wide initial conditions the weights of the trajectories corresponding to large \( |w| \) values are determined solely by the initial distribution and the potential. On the other hand, for narrow initial conditions the FF conjecture suggests that these weights are determined rather by the evolved distribution at some time \( t_{\star} > 0 \) in the interval \([0, t_f]\). If the propagator of the dynamics of the position is known, one can calculate the WPD analytically for this one-step protocol by replacing \( \rho_{\star}(x) \) by the position distribution \( \rho(x, t_{\star}) \) at time \( t_{\star} \) in Eq. (4). Investigating potentials with explicit solutions of the underlying Smoluchowski equation, we indeed found that for wide \( \rho_{\star}(x) \) the results were in agreement with Eq. (4), while for narrow \( \rho_{\star}(x) \) the results were in agreement with Eq. (6).

4 FF conjecture versus EN theory for nonequilibrium initial condition

The generalization of the EN theory to a nonequilibrium initial distribution \( \rho_0(x) \) is presented in the Appendix. We compared the predicted asymptotic behavior from the generalized EN theory for various initial distributions against extensive BD simulations and found always a good agreement, both for hard and soft potentials in the sense intro-

duced above (comparison of the confinement with respect to the harmonic potential).

Based on the findings in the previous section, an extension of the FF conjecture to nonequilibrium initial distributions is considered for soft potentials only. A straightforward extension is to replace the \( \rho_{eq}(x) \) in Eq. (3) by \( \rho_{0}(x) \), i.e.,

\[
p(w) = \int \! dx \delta [w - \Delta U(x)] \rho_0(x), \quad w \to \pm \infty. \tag{7}
\]

When testing this ansatz, we indeed found functional forms predicted by Eq. (7) to fit the data of the EN theory. However, this support of Eq. (7) was only obtained, if \( \rho_{0}(x) \) is “wide” compared to the equilibrium distribution \( \rho_{eq}(x) \) in the sense that \( \lim_{|x| \to \infty} \rho_{0}(x)/\rho_{eq}(x) = \infty \). If \( \rho_{0}(x) \) is “narrow” compared to the equilibrium distribution \( \rho_{eq}(x) \), meaning \( \lim_{|x| \to \infty} \rho_{0}(x)/\rho_{eq}(x) < \infty \), our tests showed that Eq. (3) rather than Eq. (7) fits the results of the EN theory. From a consideration of protocols with infinitely fast driving, this can be understood by studying a one-step protocol, where, when starting from the distribution \( \rho_{0}(x) \), the potential is suddenly changed by \( \Delta U(x) \) at some time instant \( t_{\star} > 0 \) in the interval \([0, t_f]\). If the propagator of the dynamics of the position is known, one can calculate the WPD analytically for this one-step protocol by replacing \( \rho_{\star}(x) \) by the position distribution \( \rho(x, t_{\star}) \) at time \( t_{\star} \) in Eq. (4). Investigating potentials with explicit solutions of the underlying Smoluchowski equation, we indeed found that for wide \( \rho_{\star}(x) \) the results were in agreement with Eq. (4), while for narrow \( \rho_{\star}(x) \) the results were in agreement with Eq. (6).
that the three fitting lines in the main parts of Fig. 4(a) and (b) can hardly be distinguished on the scale of the graphs, which gives further support that the FF conjecture predicts correctly the main $|w| \to \infty$ asymptotics of WPD. Also in this case we have tested the predicted pre-exponential factors $|w|^{1/2}$ by fitting the generalized formula $p(w) \sim |w|^{1/2} \exp(-B|w|)$ to the numerical data. The results suggest that in the case of narrow initial condition the factor $C$ from the corresponding fit shows no tendency to converge to $-1/2$ [see Fig. 5(a)]. On the other hand, for the wide initial condition the factor $C$ from the corresponding fit clearly converges to $1/2$ with decreasing $w_+$ [see Fig. 5(c)]. We hence can conclude that the FF conjecture fails to predict the pre-exponential factor for the narrow initial condition, while its prediction is precise for the wide initial condition.

To summarize, the main $|w| \to \infty$ asymptotic behavior predicted by the generalized EN theory agrees well with simulated data, and there is good evidence that the FF conjecture for nonequilibrium initial distributions holds for soft potentials. The pre-exponential behavior predicted by the FF conjecture may be incorrect.

5 Summary and perspectives

We have shown that the functional form of the WPD asymptotic behavior for overdamped Brownian motion in confining potentials can be obtained often from a simple conjecture, in which it is assumed that the respective form is independent of the driving velocity. This conjecture was motivated by the fact that it is valid for all potentials and protocols, where analytical solutions for the WPD have been obtained in the literature. In fact, these potentials are either the harmonic one or they belong to what we classified as soft potentials, with weaker confinement than the harmonic potential.

Tests of the FF conjecture have been performed against the predictions of the EN theory. With respect to that theory, (i) we gave further evidence of its validity, in particular in the case of slow driving, by a comparison of results with the exact WPD for the logarithmic-harmonic potential, (ii) we have obtained an analytical solution for the V-potential in addition to the formerly known parabolic potentials, and (iii) we have extended the theory to the case of nonequilibrium initial distributions of the particle position.

The tests of the FF conjecture indeed showed good agreement for soft potentials. For hard potentials, with stronger confinement than the harmonic potential, our results strongly indicate that the FF conjecture is not valid both for equilibrium and nonequilibrium distributions of the initial particle position. In the nonequilibrium case for soft potentials, the tests were most convincing for wide initial distributions, which decay slower than the equilibrium one. However, also for narrow initial distributions, decaying faster than the equilibrium one, our results indicate...
the FF conjecture to hold true. All our new findings were also checked by BD simulations whenever it was possible. It is surprising that for all analytically known cases the FF conjecture is valid. Whether this is a mere coincidence or has a deeper reasoning needs to be clarified. To this end, theoretical insight should be gained, why the FF conjecture fails for hard potentials.

With respect to applications, the FF conjecture can be useful to guess reasonable functional forms for the WPD asymptotic behavior, which, as pointed out in the Introduction, are needed, when measured WPD data have to be extended to the tail regime for use of the JE. A quite general form of the WPD asymptotic behavior was suggested in [12] and, based on it, a “Jarzynski estimator” for better determination of free energy differences in experiments was proposed. In cases where it is possible to guess functional forms of the driving potential, the FF conjecture can be more specific and utilized to develop improved Jarzynski estimators, or to choose a most appropriate one among the possible driving potentials. If an appropriate potential is found, a modeling of the process by BD simulations and an application of the EN theory can be used to identify the parameters in this potential.

In our work here we considered overdamped Brownian motion in one dimension under monotonic protocols. It would be interesting to check in future studies, whether extensions of the FF conjecture (and also of the EN theory) to non-monotonic protocols, to Brownian motion in higher dimensions, and to the underdamped case are possible. In fact, the FF conjecture has been seen to be valid also for a specific case of underdamped diffusion in a breathing parabola [17].

Support by the Ministry of Education of the Czech Republic (project no. 7AMB14DE003), and by the Deutsche Akademische Austauschdienst (DAAD, project no. 57066299) is gratefully acknowledged.

**Author contribution statement**

V.H. proposed to study the FF conjecture and together with A.R. tested its validity using the EN theory. V.H. also derived the results for the V-potential and generalized the EN theory for the case of nonequilibrium initial distributions of the particle position. D.L. performed all computer simulations used in the manuscript. P.M. supervised the work at every stage, proposed to perform the tests of the FF conjecture using the EN theory and to test the EN theory against the results obtained for the log-harmonic potential. P.C.H. supervised the work at every stage and proposed to study work distributions for driven Brownian motion.

**A EN theory**

According to [11,12], the WPD asymptotic behavior for overdamped Brownian motion of a particle in a time-dependent confining potential \( U(x, \lambda(t)) \) [Eq. (1)], for the initial particle position in equilibrium with distribution \( \rho_{eq}(x) = \exp[-\beta U(x, 0)]/Z_{eq} \), reads

\[
p(w) = \frac{\sqrt{2N}}{Z_{eq}} \frac{\exp(-\beta S)}{\sqrt{(\det A)(V'|A^{-1}|V')}} (1 + O(\beta^{-1})) , \quad (8)
\]

where

\[
N = \exp\left(\frac{1}{2} \int_0^{t_f} dt V''_t \right) , \quad (9)
\]

\[
\det A = 2(V''_t \chi_{tt} + \chi_{tt}) , \quad (10)
\]

\[
(V''|A^{-1}|V') = \int_0^{t_f} dt \psi_t V'_t , \quad (11)
\]

and

\[
S = V_0 + \int_0^{t_f} dt \left[ \frac{1}{4} (\dot{y}_t + V')^2 + \frac{q}{2} \dot{V} - \frac{q}{2} w \right] , \quad (12)
\]

where \( y_t \) stands for the most probable trajectory which yields the work value \( w = \dot{y}_t/\dot{V} \). In all the above formulas the mobility \( \mu \) [cf. Eq. (1)] was set to unity, and we have abbreviated the time dependence by the lower index. The function \( V_t \) is defined as \( V_t = U(y_t, \lambda(t)) \), \( \dot{V}_t = \partial U(x, \lambda(t))/\partial x \big|_{x=y_t} \), \( V''_t = \partial^2 U(x, \lambda(t))/\partial x^2 \big|_{x=y_t} \), and analogously for higher derivatives.

The “optimal trajectory” \( y_t \) minimizing the action \( S \) and the auxiliary functions \( \psi_t \) and \( \chi_t \) are obtained from the following system of three second-order ordinary differential equations

\[
\ddot{y}_t = (q-1)\dot{V}'_t + \dot{V}'_t V''_t , \quad (13a)
\]

\[
\ddot{\psi}_t = (V'''_t + V''_t V''_t - (1-q)\dot{V}''_t)\psi_t - \dot{V}'_t , \quad (13b)
\]

\[
\ddot{\chi}_t = (V'''_t + V''_t V''_t - (1-q)\dot{V}''_t)\chi_t , \quad (13c)
\]

with the boundary conditions

\[
\dot{y}_0 = V'_0 , \quad \dot{y}_t = -\dot{V}'_t , \quad (14a)
\]

\[
\dot{\psi}_0 = V''_0 \psi_0 , \quad \dot{\psi}_t = -V''_t \psi_t , \quad (14b)
\]

\[
\chi_0 = 1 , \quad \dot{\chi}_0 = V''_0 . \quad (14c)
\]

The constraint

\[
w = \int_0^{t_f} dt \dot{V}_t \quad (15)
\]

fixes the \( q \) value in Eqs. (12), (13b), and (13c).

**B EN theory applied to V-potential**

For the potential \( U(x, \lambda(t)) = \lambda(t)|x| \) the right hand side of Eq. (3) can be calculated analytically. As we show below, for large enough values of \( |w| \) the optimal trajectories \( y_t \) never crosses the origin. Since we are interested in the tail behavior \( |w| \to \infty \), this means that the non-analytical nature of \( |x| \) at the origin does not influence the asymptotic behavior of the WPD and in the Eqs. (9)-(14), one can safely assume that \( V''_t = V'''_t = 0 \) etc. for
all $x$. Then the differential equations for the functions $\psi_t$ and $\chi_t$, which determine the pre-exponential factor in (8), become independent of $yt$ and thus of $w$ also.

Due to the symmetry of the problem, for each work value $w$ two optimal trajectories $yt$ symmetric relative to the origin exist. In the following, we will solve the equations presented in the preceding section assuming that $yt > 0$. The trajectories $yt < 0$ can be incorporated simply by including the factor 2 in the prefactor of the WPD. The optimal trajectory $yt$ follows from the equation

$$
\ddot{y}_t = (q - 1)\dot{\lambda}_t,
$$

which can be easily solved. The two unknown integration constants together with the auxiliary variable $q$ are determined from the formulas

$$
y_0 = \lambda_0, \quad \dot{y}_t = -\dot{\lambda}_t, \quad \int_0^t dt \dot{V}_t = w.
$$

The solution is (for monotonic driving, where $\lambda_t \neq \lambda_0$)

$$
y_t = f_t + \frac{1}{\lambda_t - \lambda_0} w, \quad q = -\frac{2\lambda_0}{\lambda_t - \lambda_0},
$$

where $f_t$ is a function independent of $w$. Due to the work definition (2), the term $w/(\lambda_t - \lambda_0)$ is for a monotonic driving always positive. The function $f_t$ is finite and thus there always exists some $|w|$ large enough that the whole function $y_t$ is positive for an arbitrary $t$. The action (12) can be rewritten as (13)

$$
S = -\frac{w}{2} + \frac{1}{2}(V_t + V_0) - \frac{1}{4}(y_t V_t' + y_0 V_0')
+ \frac{1}{4} \int_0^t dt V_t'(V_t'' - y_t V_t''' + y_0 V_0''') + \frac{1 - q}{4} \int_0^t dt y_t V_t'.'
$$

After inserting the optimal trajectory (16) into this formula one obtains

$$
S = -\frac{w}{2} + \frac{1}{4}(\lambda_t y_t + \lambda_0 y_0) + \frac{1}{4} \int_0^t dt \dot{\lambda}_t^2 + \frac{1 - q}{4} w
= h_{t} + \frac{\lambda_0}{\lambda_t - \lambda_0} w,
$$

where $h_t$ is another function independent of $w$. Accordingly, the WPD fulfills the asymptotic relation

$$
p(w) \sim \begin{cases} 
\exp \left( -\frac{2\lambda_0}{\lambda_t - \lambda_0} w \right), & w \to +\infty, \quad \dot{\lambda}_t > 0, \\
\exp \left( +\frac{2\lambda_0}{\lambda_t - \lambda_0} w \right), & w \to -\infty, \quad \dot{\lambda}_t < 0.
\end{cases}
$$

The EN theory (11) can be generalized to a nonequilibrium initial condition $\rho_0(x) = \exp[-\beta F(x)]Z_0$ of the particle position. The derivation is straightforward and we present only the results here.

**D Numerical procedure used for solving EN equations**

In order to solve the EN equations (Appendices A and C), we have adopted the numerical procedure “bvp4c” implemented in MATLAB and previously used by Nickelsen [15]. Bvp4c is a finite difference code, which solves two-point boundary value problems for ordinary differential equations with possible further unknown parameters. It implements the three-stage Lobatto IIIa formula [21]. This is a collocation formula and the collocation polynomial provides a continuous solution with continuous first derivative that is fourth order accurate uniformly in $[a,b]$. Mesh selection and error control are based on the residual of the continuous solution.

In the code, an initial guess of the solution is used to iteratively find the correct solution. In our implementation we guessed the solution for some small absolute value of $w$, and use the corresponding solution as the initial guess for a new, slightly changed, work value. The corresponding solution is then again used as the guess for another work value and so on until a given final value of $w$ is reached. Problems arise when the solutions of EN equations for two close work values differ significantly. Then the numerical procedure collapses, because it is not able to converge from a distant initial guess to the solution. In our analysis we have encountered such numerical problems when using very soft potentials such as $U(x, \lambda(t)) = \lambda(t) \ln(1 + x^2)$.

**References**

1. U. Seifert, Reports on Progress in Physics 75(12), 126001 (2012)
2. F. Ritort, Adv. Chem. Phys. 137, 31 (2008)
3. C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997)
4. G.E. Crooks, Phys. Rev. E 60, 2721 (1999)
5. U. Seifert, Phys. Rev. Lett. 95, 040602 (2005)
6. M. Esposito, C. Van den Broeck, Phys. Rev. E 82, 011143 (2010)
7. C. Van den Broeck, M. Esposito, Phys. Rev. E 82, 011144 (2010)
16. With the potential are generally associated characteristic length scales, which could be used to define an appropriate length unit in the problem. Because we will consider different potentials, we refrain to introduce them here. One could alternatively introduce a laboratory length scale as length unit. Then the time unit would be given by $\frac{\mu k_B T}{\xi^2}$.
