Effective diffusion in one-dimensional rough potential-energy landscapes

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Diffusion in spatially rough, confining, one-dimensional continuous energy landscapes is treated using Zwanzig's proposal, which is based on the Smoluchowski equation. We show that Zwanzig's conjecture agrees with Brownian dynamics simulations only in the regime of small roughness. Our correction of Zwanzig's framework corroborates well with numerical results. A numerical simulation scheme based on our coarse-grained Langevin dynamics offers significant reductions in computational time. The mean first-passage time problem in the case of random roughness is treated. Finally, we address the validity of the separation of length scales assumption for the case of polynomial backgrounds and cosine-based roughness. Our results are applicable to hierarchical energy landscapes such as that of a protein's folding and transport processes in disordered media, where there is clear separation of length scale between smooth underlying potential and its rough perturbation.

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I. INTRODUCTION

Diffusion in rough potential energy landscapes has been of interest for many years because its study offers insight into fields from transport processes in disordered media [1–6] to protein folding [7,8] and the study of glassy systems [9–12]. In one dimension, a wide range of behaviors exist, reflecting the many ways in which an energy landscape can be constructed. When working with unbiased potentials, if the energy barriers are of equal height, then the long-time motion is diffusive; if the heights are exponentially distributed, then a transition between diffusive and subdiffusive behavior occurs as the mean height is increased [13,14].

Working in one dimension, Lifson and Jackson derived an expression for the effective diffusion coefficient D^*, which captures the retarding effect of homogeneous energy barriers upon the macroscopic diffusive motion: $\langle x^2 \rangle = 2D^* t$, where $D^* \leqslant D_{\text{free}} = k_{\text{B}}T/\gamma$, the ratio of the thermal energy to the damping coefficient [15]. Their expression has attracted widespread usage and undergone modification so that it can be used to model disordered systems [16]. In particular, the case of Gaussian-distributed amplitudes has received much attention: Zwanzig proposed an expression for the effective diffusion coefficient, $D^* = D_{\text{free}}/e^{(\epsilon/k_{\text{B}}T)^2}$, where ϵ is the root-mean-square roughness [17]. This result has been demonstrated not to hold for the case of motion on a discrete lattice; an even more heavily suppressed diffusion coefficient is obtained [18]. However, when Brownian dynamics simulations are performed on a continuous Gaussian surface good agreement with Zwanzig's unamended expression is observed. This difference is attributed to spatial correlations: their presence brings about a smoothing of the potential energy landscape, removes the deep "Three Site Traps," and thereby leads to the reduction to Zwanzig's result [18]. The case of diffusion in a one-dimensional piecewise-defined energy landscape made up of triangular sections with Gaussian-distributed heights was studied and agreement with Zwanzig's result was obtained in the limit of large thermal energies [19]. In this regime the effect of the presence of three site traps upon the motion will not be significant. These two results appear to show that the meaningful presence of three site traps determines whether or not Zwanzig's result applies.

Returning to lattices, further work built upon the one-dimensional results by considering motion on a d-dimensional lattice with Gaussian disorder. By using an effective medium approximation an expression for the diffusion coefficient was obtained and found to be in good agreement with the results of numerical simulations [20,21]. However, in this work we wish to focus upon the primary thrust of Zwanzig's paper, namely, his attempt to construct a theoretical framework within which diffusion in rough energy landscapes can be treated more directly than is possible with the usual Smoluchowski equation (SE). In particular, rough energy landscapes where the background need not be flat.

Zwanzig's framework has potential application in the study of hierarchical energy landscapes such as that of a protein's potential surface [22–28]. Zwanzig *conjectured* that diffusion in rough energy landscapes can be described by the usual symbolic form of the SE, but with modifications to both the diffusion coefficient and the energy landscape, in order to account for the roughness properly [17]. In this paper, we demonstrate that Zwanzig's proposal works: overdamped Brownian motion in rough energy landscapes *can* be modeled using a

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modified form of the SE, but a different modification to the potential energy landscape is required if the formalism's predications are to agree with the results of numerical simulations.

After recapping Zwanzig's conjecture, we will restrict our focus to confining background energy landscapes with constant roughness and use the configurational partition function to derive the mean potential energy in equilibrium. Numerical simulations reveal disagreement with Zwanzig's proposal but good agreement with our theory's predictions. Comparing the two approaches enables us to suggest a different modification to the energy landscape and bring Zwanzig's proposed formalism into agreement. Using the modified SE to study the approach to equilibrium in a quadratic background, it becomes clear that Zwanzig's modification to the diffusion coefficient is better understood as a modification to the damping γ. Consequently, we propose a modified overdamped Langevin equation (LE), from which we derive a Brownian dynamics simulation scheme. Good agreement between results obtained from this "modified" scheme and the "original" scheme (based upon the unmodified LE) is observed. The modified scheme enable the time step to be *increased* with increasing roughness—in stark contrast to the original scheme where the time step must be *decreased*—thereby affording potentially significant reductions in computational time. We consider the case of piecewise-defined roughness, where the amplitude of each section is taken from a probability distribution. The corresponding modified LE is derived, and the results of numerical simulations for the case of exponentially distributed amplitudes are presented: good agreement is observed over a range of mean amplitudes. Finally, we address the question of when this modified equation can be used and calculate the form of the boundary between validity and invalidity for the case of polynomial backgrounds and cosine-based roughness. This can be reformulated in terms of the characteristic length scales of the smooth background and the superposed roughness. Separation of these length scales, as invoked in Zwanzig's work, is shown to be a looser condition than might first be supposed. Throughout this work we will restrict our attention to cases where the amplitude of the roughness, Q, is not a function of position.

II. ZWANZIG'S PROPOSAL

Consider a particle diffusing in an energy landscape $U(x) = U_0(x) + U_1(x)$, where $U_0(x)$ is a smooth background of characteristic length scale L_0, and $U_1(x)$ is a rough perturbation of characteristic length scale L_1. Zwanzig *conjectured* that, provided $L_0 \gg L_1$, the behavior is governed by the usual *form* of the SE [17]

$$\frac{\partial \rho}{\partial t} = -\frac{\partial J}{\partial x}, \tag{1}$$

$$J = -D^* e^{-\beta U_Z(x)} \frac{\partial}{\partial x}\left[\rho\, e^{\beta U_Z(x)}\right], \tag{2}$$

where $\beta = 1/k_B T$,

$$D^* = \frac{D_{\text{free}}}{e^{\psi^+} e^{\psi^-}}, \tag{3}$$

is the redefined diffusion coefficient, $D_{\text{free}} = k_B T/\gamma$ is the free diffusion coefficient, $e^{\psi^\pm}$ are given by

$$e^{\psi^\pm} = \left\langle e^{\pm \beta U_1(x)} \right\rangle_x, \tag{4}$$

$\langle(\cdot)\rangle_x = \frac{1}{L_1}\int_0^{L_1} dx\,(\cdot)$ denotes spatial averaging (over the characteristic length scale of the roughness), and

$$U_Z = U_0 - \frac{\psi^-}{\beta} \tag{5}$$

is the redefined potential energy landscape *proposed* by Zwanzig. Since $\psi^\pm$ are independent of x, D^* is independent of position and U_Z is simply U_0 shifted by a constant. Because the energy landscape enters the SE via its gradient, the position-independent offset in Eq. (5) will not affect the motion.

The equilibrium solution to the unmodified SE is the Boltzmann distribution $\rho(x) = e^{-\beta U(x)}/Z$, where the configurational partition function Z is

$$Z = \int dx\, e^{-\beta U_0} e^{-\beta U_1}. \tag{6}$$

Under the assumption of separation of length scales [17], the partition function can be approximated as

$$Z \approx \langle e^{-\beta U_1}\rangle_x \int dx\, e^{-\beta U_0}. \tag{7}$$

This approximation coarse grains the effects of the roughness. Provided that the amplitude of the roughness does not vary with position, the mean potential energy in equilibrium is

$$\langle U_Z\rangle = \int dx\, U_Z(x)\rho(x) \approx \langle U_0\rangle_0 - \frac{\psi^-}{\beta}, \tag{8}$$

where

$$\langle(\cdot)\rangle_0 = \frac{\int dx\, e^{-\beta U_0(x)}(\cdot)}{\int dx\, e^{-\beta U_0(x)}} \tag{9}$$

indicates averaging with respect to the equilibrium distribution in the smooth background U_0.

However, if we consider the mean potential energy in equilibrium $\langle U\rangle = -\partial \ln Z/\partial\beta$, we find that

$$\begin{aligned}\langle U\rangle &\approx -\frac{\partial \psi^-}{\partial \beta} - \frac{\partial}{\partial \beta}\ln\left(\int dx\, e^{-\beta U_0}\right)\\ &= \langle U_0\rangle_0 - \frac{\partial \psi^-}{\partial \beta},\end{aligned} \tag{10}$$

which suggests that the energy landscape should be modified to

$$U^* = U_0 - \frac{\partial \psi^-}{\partial \beta}, \tag{11}$$

with corresponding current density

$$J = -D^* e^{-\beta U^*(x)} \frac{\partial}{\partial x}\left[\rho\, e^{\beta U^*(x)}\right]. \tag{12}$$

III. CONSTANT ROUGHNESS

To test our theory against Zwanzig's proposal, we will consider a sample energy landscape: $U(x) = \frac{\alpha}{m}|x|^m + Q[1 - \cos(n\pi x)]$, where the first and second terms are the confining $(\alpha, m > 0)$ background U_0, and the rough addition U_1, respectively. In this case, it can be shown that $\langle U_0\rangle_0 = \frac{k_B T}{m}$ and $e^{\psi^\pm} = e^{\pm\beta Q} I_0(\beta Q)$, where I_0 is the zeroth-order modified Bessel function of the first kind. Inserting these results into Eqs. (8) and (10) gives the following predictions for the mean

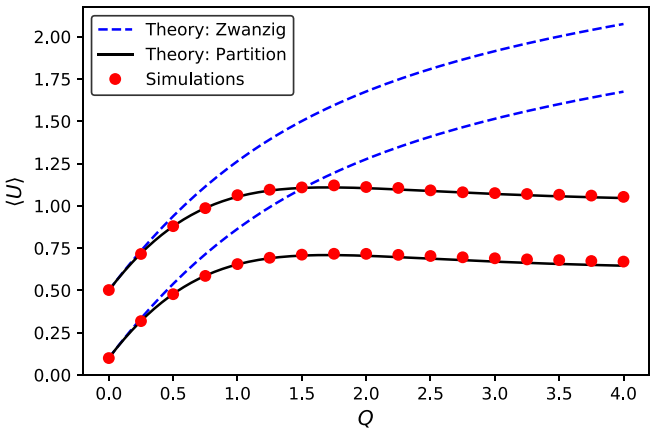

FIG. 1. The mean potential energy in equilibrium is plotted as a function of Q for two background energy landscapes: the uppermost dashed and solid lines represent $m = 2$, while the lowermost represent $m = 10$.

potential energy in equilibrium:

$$Zwanzig: \langle U_Z \rangle = \frac{k_B T}{m} + Q - \frac{\ln(I_0(\beta Q))}{\beta}, \tag{13}$$

$$Partition: \langle U \rangle = \frac{k_B T}{m} + Q\left[1 - \frac{I_0'(\beta Q)}{I_0(\beta Q)}\right]. \tag{14}$$

Brownian dynamics simulations were performed with an ensemble of 10^5 particles and unit values of thermal energy and damping for two backgrounds: $m = 2$ and $m = 10$. The time step was 10^{-4} for $Q \leqslant 2.5$, and 5×10^{-5} thereafter. To a reasonable approximation, the combination $\alpha = 4, n = 4$ satisfied the condition of separation of length scales—a point to which we will return in a later section. Once the system had fully equilibrated, as determined by comparison of the mean-squared displacement to the theoretical value, the mean potential energy was calculated by averaging over the ensemble of particles. Figure 1 shows that the simulation results agree with Zwanzig's proposed formalism for only the smallest values of Q. In contrast, good agreement between the results and our theory is observed for all amplitudes considered. We conclude that Zwanzig's framework is correct provided we use Eqs. (11) and (12) instead of Eqs. (2) and (5).

IV. LANGEVIN DYNAMICS

We will now use the amended formalism to study the approach to equilibrium. The SE can be solved analytically for quadratic ($m = 2$) background energy landscapes: for a system initialised to $x = 0$, the probability distribution ρ evolves as

$$\rho(x,t) = \frac{1}{\sqrt{2\pi f(t)}} \exp\left[\frac{-x^2}{2f(t)}\right], \tag{15}$$

where

$$f(t) = \frac{1}{\alpha\beta}[1 - e^{-2D^*\alpha\beta t}]. \tag{16}$$

The mean-squared displacement is

$$\langle x^2(t) \rangle = \int dx\, x^2 \rho(x,t) = \frac{1}{\alpha\beta}[1 - e^{-2D^*\alpha\beta t}]. \tag{17}$$

We are, in effect, considering diffusion in a smooth quadratic well, a problem that can be addressed with the overdamped LE,

$$\gamma \frac{dx}{dt} = -\frac{dU_0}{dx} + \xi(t), \tag{18}$$

where $\xi(t)$ is the usual thermal noise with zero mean $\langle \xi(t) \rangle = 0$ and covariance $\langle \xi(t)\xi(t') \rangle = 2\gamma k_B T \delta(t - t')$. The mean-squared displacement of a particle initialized to $x = 0$ in the energy landscape $U_0 = \frac{\alpha}{2}x^2$ can be derived from Eq. (18):

$$\langle x^2(t) \rangle = \frac{1}{\alpha\beta}[1 - e^{-2\alpha t/\gamma}]. \tag{19}$$

The same general form of Eqs. (17) and (19) leads us to conclude that the effect of the roughness can be accounted for by modifying the damping γ. This can be seen most easily by using Eq. (3) to rewrite the exponent in Eq. (17) in terms of the damping: $-2\alpha t/(\gamma e^{\psi^+} e^{\psi^-})$. Comparison with Eq. (18) reveals equivalence under

$$\gamma \mapsto \gamma^* = \gamma\, e^{\psi^+} e^{\psi^-}. \tag{20}$$

This expression, in conjunction with the modified energy landscape in Eq. (11), leads us to propose the following: when considering the diffusive motion of Brownian particles in energy landscapes comprising a confining background $U_0(x)$ and a superposed roughness $U_1(x)$, provided that the length scale of the roughness is sufficiently smaller than that of the background ($L_1 \ll L_0$), the dynamics can be described by the modified LE,

$$\gamma^* \frac{dx}{dt} = -\frac{dU^*}{dx} + \xi^*(t), \tag{21}$$

where U^* and γ^* are as before, and ξ^* has zero mean $\langle \xi^*(t) \rangle = 0$ and the following covariance:

$$\langle \xi^*(t)\xi^*(t') \rangle = 2\gamma^* k_B T \delta(t - t'). \tag{22}$$

Modifying the damping coefficient means that the fluctuation-dissipation relationship must also change, as can be seen in Eq. (22). This ensures that the behavior of a free particle in the modified regime is the same as the long-time behavior of a particle navigating a rough energy landscape in the original regime: the diffusion coefficients must agree. The coarse-grained effect of the roughness is captured by the dimensionless number $e^{\psi^+} e^{\psi^-}$.

Equation (21) is analogous to Zwanzig's modified SE. One of the most significant implications of this modified framework is found in the numerical simulation of motion in rough energy landscapes. Consider the following two discretized expressions—one for the original LE, one for the modified LE—which give the change in a particle's position at each time step of its simulated motion:

$$\Delta x_O = -\frac{d[U_0(x) + U_1(x)]}{dx}\frac{\Delta t}{\gamma} + \sqrt{\frac{2k_B T}{\gamma}\Delta t}\,\mathcal{N}(0,1) \tag{23}$$

TABLE I. The ratio of the time steps for the original "O" and modified "M" simulation schemes is given as a function of the amplitude of the roughness Q for the case $U_1(x) = Q(1 - \cos(n\pi x))$. The thermal energy $k_B T = 1$.

Q	$\frac{\Delta t_M}{\Delta t_O} = I_0^2(\beta Q)$
1	1.6
2	5.2
5	740
10	7.9×10^6

and

$$\Delta x_M = -\frac{dU_0(x)}{dx}\frac{\Delta t}{\gamma e^{\psi^+}e^{\psi^-}} + \sqrt{\frac{2k_B T}{\gamma}\frac{\Delta t}{e^{\psi^+}e^{\psi^-}}}\,\mathcal{N}(0,1), \tag{24}$$

where the subscripts "O" and "M" refer to the "original" and "modified" LEs, respectively, Δt is the time step, and $\mathcal{N}(0, 1)$ is a normal distribution with zero mean and unit variance sampled at each time step.

In order for the simulation schemes to work well, Δt must be small enough to resolve motion on the smallest length scale present in the system. The original scheme contains both the background U_0 and the roughness U_1, while the modified scheme contains only U_0. Taken with the requirement for separation of length scales, this implies that a larger time step can be used in the modified scheme than in the original scheme. Depending upon the form of the roughness (specified by Q and n in the above case), this factor can be between 50- and 100-fold.

Note also that $e^{\psi^+}e^{\psi^-}$ is an increasing function of the amplitude of the roughness, often rapidly so. In the modified scheme the ratio $\Delta t/e^{\psi^+}e^{\psi^-}$ decreases with increasing amplitude, thereby increasing the accuracy of the simulations. Conversely, one could increase the time step in line with $e^{\psi^+}e^{\psi^-}$ without losing accuracy. Combining these two factors, the possibility of significant increases in simulation speed becomes apparent. For large amplitudes of roughness, where equilibrium is established only very slowly, and the original scheme requires a yet-smaller-still time step to counterbalance the increase in amplitude, the modified approach represents a significant improvement.

Table I illustrates the scale of improvements possible when the roughness is given by $U_1(x) = Q(1 - \cos(n\pi x))$. Figure 2 shows good agreement between the trajectories produced by the original and modified simulation schemes. It is important to note that the modified scheme is *not* valid on the shortest timescales. This can be seen most easily from its failure to follow the original scheme's mean potential energy trajectory upwards from zero, starting instead at $Q[1 - I_0'(\beta Q)/I_0(\beta Q)]$. However, this failure is not unexpected: in the modified scheme, the effects of the roughness are manifest through its spatial average. Physically, this averaging is the spreading out of the particle ensemble into minima adjacent to the global minimum. Only when a sufficient fraction of the ensemble has made this jump does the modified scheme become valid. This takes some time, hence the discrepancy at the start of the motion.

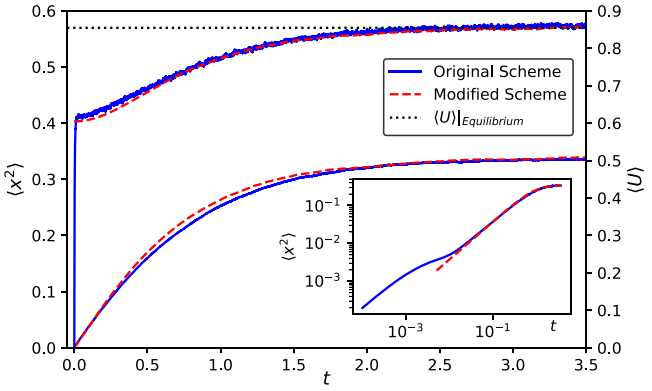

FIG. 2. The equilibration of an ensemble of 10^5 particles in a quartic background ($\alpha = 4$, $n = 4.3$, $Q = 2$) is simulated using the original and modified schemes with $k_B T = \gamma = 1$. $\Delta t_O = 10^{-4}$ and $\Delta t_M = 5 \times 10^{-3}$. The uppermost lines are the mean potential energy; the lowermost the mean-squared displacement. The inset presents the approach to equilibrium of the mean-squared displacement on logarithmic scales so that the differing short-time behavior of the simulation schemes can be appreciated.

The inset of Fig. 2 hints at underoptimization of the modified scheme: the red, dashed line extends to the left of the point at which the two schemes first coincide. A further doubling of the time step used in the modified simulations ought to be possible, giving an overall 100-fold increase in simulation speed.

V. RANDOM ROUGHNESS

Let us now turn to the case of piecewise-defined roughness, where the amplitude of each section is taken from a probability distribution. Zwanzig developed his formalism by considering the mean first-passage time from one point in an energy landscape to another. By relating the mean first-passage times in the presence and absence of roughness with a multiplicative factor, he deduced Eq. (3), the effect of the roughness upon the diffusion coefficient.

If the width of each section of the roughness is L, then the mean first-passage time to move from $x = 0$ to $x = NL$, i.e., across N full sections, is given by [29]

$$\tau = \frac{1}{D}\int_0^{NL} dy\, e^{\beta U} \int_0^y dz\, e^{-\beta U}, \tag{25}$$

which, upon breaking up the integrals into their component parts across each section of the energy landscape, can be written as

$$\tau = \frac{1}{D}\sum_{i=1}^{N}\int_{(i-1)L}^{iL} dy\, e^{\beta U_0}e^{\beta U_{1,i}} \int_{(i-1)L}^{y} dz\, e^{-\beta U_0}e^{-\beta U_{1,i}} + \frac{1}{D}\sum_{i=2}^{N}\sum_{j=1}^{N-1}\int_{(i-1)L}^{iL} dy\, e^{\beta U_0}e^{\beta U_{1,i}} \int_{(j-1)L}^{jL} dz\, e^{-\beta U_0}e^{-\beta U_{1,j}}. \tag{26}$$

Assuming separation of length scales, we can replace the terms involving the rough part of the energy landscape by their spatial average and hence remove them from within the

integrals. Doing so, we find

$$\tau = \frac{1}{D}\sum_{i=1}^{N} e^{\psi_i^+} e^{\psi_i^-} \int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(i-1)L}^{y} dz\, e^{-\beta U_0} + \frac{1}{D}\sum_{i=2}^{N}\sum_{j=1}^{N-1} e^{\psi_i^+} e^{\psi_j^-} \int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(j-1)L}^{jL} dz\, e^{-\beta U_0}. \tag{27}$$

The amplitudes characterizing the roughness are distributed according to a probability distribution $p(Q)$, which means that the averaged mean first-passage time is given by

$$\overline{\tau} = \int dQ_1 \cdots dQ_N\, p(Q_1, \ldots, Q_N)\tau(Q_1, \ldots, Q_N). \tag{28}$$

The separability of the joint probability distribution $p(Q_1, \ldots, Q_N)$ into a product of individual probability distributions $p(Q_1)\ldots p(Q_N)$ means that Eq. (28) can be rearranged into the following form:

$$\begin{aligned}\overline{\tau} = {} & \frac{1}{D}\sum_{i=1}^{N}\left[\int dQ_i p(Q_i) e^{\psi_i^+} e^{\psi_i^-}\right] \times \int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(i-1)L}^{y} dz\, e^{-\beta U_0} \\ & + \frac{1}{D}\sum_{i=2}^{N}\sum_{j=1}^{N-1}\left[\int dQ_i p(Q_i) e^{\psi_i^+}\right]\left[\int dQ_j p(Q_j) e^{\psi_j^-}\right] \times \int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(j-1)L}^{jL} dz\, e^{-\beta U_0}.\end{aligned} \tag{29}$$

Finally, by denoting the three integrals involving the probability distribution as follows:

$$\int dQ_i p(Q_i) e^{\psi_i^+} e^{\psi_i^-} = \overline{e^{\psi^+} e^{\psi^-}}, \qquad \int dQ_i p(Q_i) e^{\psi_i^\pm} = \overline{e^{\psi^\pm}}, \tag{30}$$

we are able to rewrite the expression for the averaged mean first-passage time more compactly as

$$\overline{\tau} = \frac{\overline{e^{\psi^+} e^{\psi^-}}}{D}\sum_{i=1}^{N}\int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(i-1)L}^{y} dz\, e^{-\beta U_0} + \frac{\overline{e^{\psi^+}} \times \overline{e^{\psi^-}}}{D}\sum_{i=2}^{N}\sum_{j=1}^{N-1}\int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(j-1)L}^{jL} dz\, e^{-\beta U_0}. \tag{31}$$

The mean first-passage time from $x = 0$ to $x = NL$ in the smooth background U_0 alone is given by

$$\tau_0 = \frac{1}{D}\int_0^{NL} dy\, e^{\beta U_0} \int_0^{y} dz\, e^{-\beta U_0}, \tag{32}$$

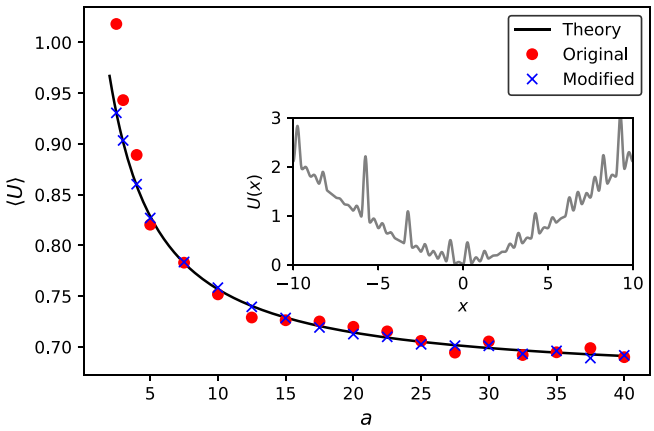

FIG. 3. The mean potential energy in equilibrium is plotted as a function of a. Good agreement between numerical simulations based upon the "original" LE and our theory is observed for $a > 5$. The inset shows an example energy landscape ($a = 8$) in which the ensemble equilibrated.

which can be separated in exactly the same way as Eq. (26) to give

$$\tau_0 = \frac{1}{D}\sum_{i=1}^{N}\int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(i-1)L}^{y} dz\, e^{-\beta U_0} + \frac{1}{D}\sum_{i=2}^{N}\sum_{j=1}^{N-1}\int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(j-1)L}^{jL} dz\, e^{-\beta U_0}. \tag{33}$$

Isolating the second term in the above and substituting it into Eq. (31) produces the following expression for the averaged mean first-passage time:

$$\overline{\tau} = \overline{e^{\psi^+}} \times \overline{e^{\psi^-}}\tau_0 + \frac{1}{D}[\overline{e^{\psi^+} e^{\psi^-}} - \overline{e^{\psi^+}} \times \overline{e^{\psi^-}}] \times \sum_{i=1}^{N}\int_{(i-1)L}^{iL} dy\, e^{\beta U_0} \int_{(i-1)L}^{y} dz\, e^{-\beta U_0}, \tag{34}$$

which now contains τ_0. Unlike the case of constant-amplitude roughness, the *averaged* mean first-passage time cannot in general be related to the mean first-passage time in the absence of roughness τ_0 by a multiplicative factor.

In the limit of large N the first term in Eq. (34) dominates the averaged mean first-passage time because the number of terms in the formula for τ_0 grows as N^2. This enables us to make the following approximation:

$$\overline{\tau} \approx \overline{e^{\psi^+}} \times \overline{e^{\psi^-}}\tau_0. \tag{35}$$

For a physical system, this limit corresponds to a sufficiently short length scale of roughness when compared to the smooth background for the effect of the roughness upon the smooth background to be felt in many sections. An example of what is meant by this can be seen in the inset of Fig. 3, where rough features are observed some distance away from the global minimum. If we use this approximate relationship as our starting point, then, by following Zwanzig's reasoning, the equivalent of Eq. (20) for the case of random roughness is

$$\gamma \mapsto \overline{\gamma} = \gamma\, \overline{e^{\psi^+}} \times \overline{e^{\psi^-}}. \tag{36}$$

In order to create a modified LE, we must specify the modified energy landscape. For the case of constant roughness, we found that $U^* = U_0 - \partial\psi^-/\partial\beta$ gives a mean potential energy in equilibrium consistent with simulation results. Let us propose, therefore, that

$$\overline{U^*} = \int dQ\, p(Q) U^* = U_0 - \int dQ\, p(Q) \frac{\partial \psi^-}{\partial \beta} \tag{37}$$

and

$$\langle \overline{\xi}(t)\overline{\xi}(t')\rangle = 2\overline{\gamma} k_B T \delta(t - t') \tag{38}$$

is the correct form. Equations (36) and (37) define the modified LE for random roughness,

$$\overline{\gamma}\frac{dx}{dt} = -\frac{d\overline{U^*}}{dx} + \overline{\xi}(t). \tag{39}$$

When each section of the roughness has the form $Q[1 - \cos(n\pi x)]$, and the amplitudes are distributed exponentially $p(Q) = a\beta e^{-a\beta Q}$, we find

$$\overline{\gamma} = \gamma \frac{a^2}{\sqrt{(a-1)^2 - 1}\sqrt{(a+1)^2 - 1}} \tag{40}$$

and

$$\overline{U^*} = U_0 + a\int_0^\infty d(\beta Q)\, e^{-a\beta Q}\left[1 - \frac{I_0'(\beta Q)}{I_0(\beta Q)}\right]. \tag{41}$$

To test our hypotheses, Brownian dynamics simulations were performed using an ensemble of 10^4 particles and unit values of the thermal energy and damping. The background energy landscape and roughness are described by $m = 1.5$, $\alpha = 0.1$, and $n = 4.0$, respectively. Motion was simulated for a range of values of a (one energy landscape for each value), and good agreement between the mean potential energy in equilibrium and Eq. (46) was found for $a \gtrsim 5$. The discrepancy for $a \lesssim 5$ is due to the breakdown of the assumptions that allowed us to write Eq. (35).

VI. VALIDITY

We have so far focused upon the implications of the modified LE and neglected the important matter of its validity. It is this topic to which we now turn. In moving from Eq. (6) to Eq. (7) we assumed that the term involving the roughness could be replaced by its spatial average and hence removed from within the integral. Validity is thus a question of when the difference between quantities derived from the exact and approximate partition functions is deemed acceptably small. This makes it hard to address in a satisfactory manner because the question is one of degree, not one of an absolute. Nonetheless, by studying the mean-squared displacement in equilibrium we hope to illustrate one way in which this element of the work might be addressed.

The equilibrium probability distribution is given by $\rho(x) = e^{-\beta U_0} e^{-\beta U_1}/Z$. Hence, the exact expression for the mean-squared displacement in equilibrium is

$$\langle x^2\rangle = \frac{\int dx\, x^2 e^{-\beta U_0} e^{-\beta U_1}}{\int dx\, e^{-\beta U_0} e^{-\beta U_1}}, \tag{42}$$

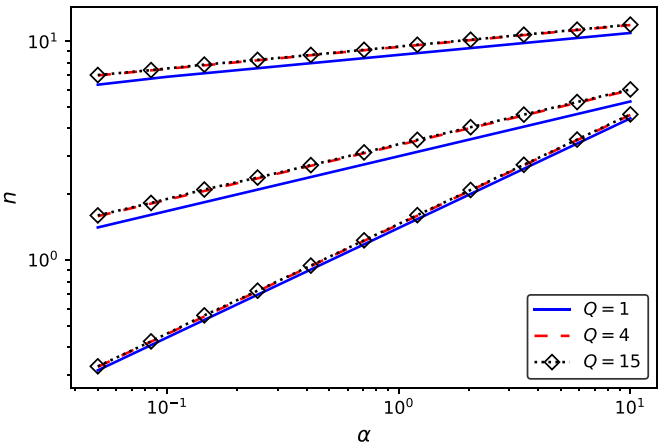

FIG. 4. A phase space showing the boundaries between validity and invalidity. The top three curves are for $m = 10$; the middle three for $m = 4$; the bottom three for $m = 2$.

while the approximate expression—obtained by invoking separation of length scales—is

$$\langle x^2\rangle \approx \frac{\langle e^{-\beta U_1}\rangle_x \int dx\, x^2 e^{-\beta U_0}}{\langle e^{-\beta U_1}\rangle_x \int dx\, e^{-\beta U_0}} = \frac{\int dx\, x^2 e^{-\beta U_0}}{\int dx\, e^{-\beta U_0}}. \tag{43}$$

We decided that, for a given background energy landscape and roughness, Zwanzig's approach—and hence the modified LE—would be deemed valid if the percentage difference between the mean-squared displacement in equilibrium calculated using Eqs. (42) and (43) is less than 0.1%. Although this threshold is essentially arbitrary, it is strict, which we believe is a plus.

To study validity we used the same model energy landscape as before, $U(x) = \frac{\alpha}{m}|x|^m + Q(1 - \cos(n\pi x))$, and focused upon three smooth backgrounds, $m = 2$, 4, and 10. For each background, we selected an amplitude Q and a series of values of α for which we sought to establish the value of n beyond which the modified LE is deemed valid. In this way, a "boundary" between validity and invalidity was established: n as a function of α.

Figure 4 shows the behavior of these boundaries for each background for three different amplitudes of roughness ($Q =$ 1, 4, and 15), over a range of values of α. In each case the boundary is well described by

$$n(\alpha, m, Q) = \mathcal{C}(Q, m)\alpha^{1/m}, \tag{44}$$

where $\mathcal{C}$ is a constant for a given amplitude of roughness Q and characteristic power m.

For the same values of α and Q, larger values of m require larger values of n in order to reach the same threshold of validity. Furthermore, for a given background energy landscape (α, m), larger amplitudes of roughness Q also demand larger values of n: in other words $\mathcal{C}(Q, m)$ is an increasing function of Q. However, note that this is an effect which diminishes with Q—the lines representing $Q = 4$ and $Q = 15$ lie almost atop one another—but which does so less rapidly for larger values of m. When $m = 2$ all three lines lie almost on top of each other, but for both $m = 4$ and $m = 10$, there is clear separation between the line for $Q = 1$ and the lines for $Q = 4$, 15.

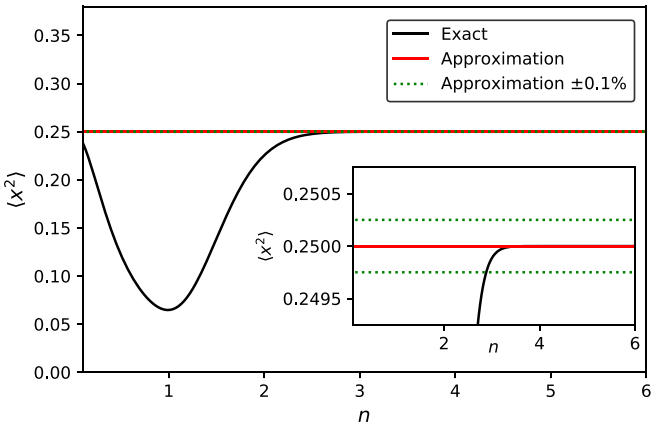

FIG. 5. The exact mean-squared displacement is calculated as a function of n for a quadratic background energy landscape. $Q = 2, m = 2, \alpha = 4$.

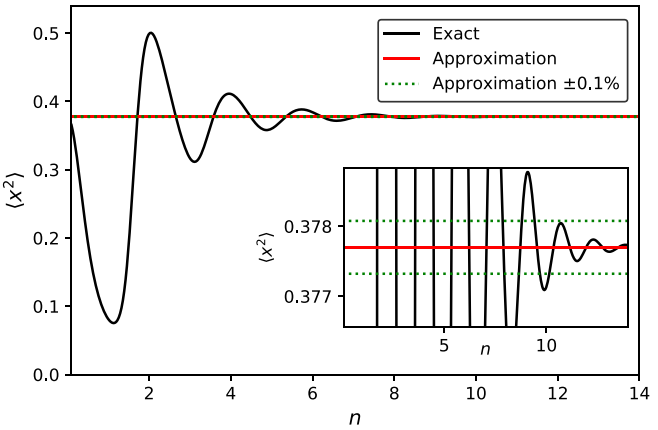

FIG. 7. The exact mean-squared displacement is calculated as a function of n for a 10th-power background energy landscape. $Q = 2, m = 10, \alpha = 4$.

Figures 5–7 show the behavior of the mean-squared displacement calculated using the exact expression [Eq. (42)] as a function of n for each of the different background energy landscapes under study: $m = 2,\ 4$, and 10.

The inset of each plot shows the same information as the main plot, albeit with the range of mean-squared displacements severely restricted to the region on immediately either side of the value obtained using the approximate form of the partition function [Eq. (43)]. Our condition for validity—a difference of no more than 0.1% between the exact and approximate values of the mean-squared displacement—and the approach towards it now becomes clearer. Note that for $m > 2$ the exact result enters and leaves the $\pm 0.1\%$ region multiple times before settling to coincide with the approximate result (see Figs. 6 and 7). Consequently care must be taken to ensure that the search for validity finds the correct value of n. For some potential energy landscapes it could be better to search back-to-front by starting with very large values of n and looking for the value of n below which disagreement exceeds 0.1%. These figures provide useful context for the boundaries in Fig. 4 by showing how the approach to validity differs from one background energy landscape to the next.

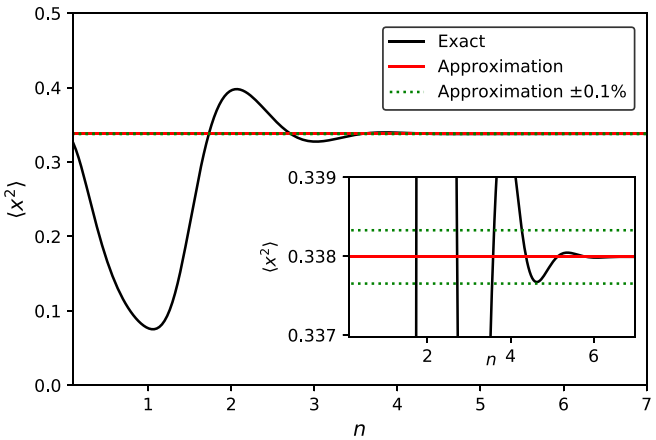

FIG. 6. The exact mean-squared displacement is calculated as a function of n for a quartic background energy landscape. $Q = 2, m = 4, \alpha = 4$.

In establishing Eq. (44) as a good model for the boundary between validity and invalidity we are in a position to understand better what is meant by the separation of the length-scale condition. Multiplying the expression for the potential energy landscape by β to render it dimensionless and rewriting the resulting expression in terms of constants with the dimensions of length gives

$$\beta U(x) = \left|\frac{x}{L_0}\right|^m + \beta Q\left[1 - \cos\left(\frac{2\pi x}{L_1}\right)\right], \tag{45}$$

where $L_0 = (\beta\alpha/m)^{-1/m}$ and $L_1 = 2/n$. Inserting these expressions into Eq. (44) we find

$$\frac{L_0}{L_1} = \frac{\mathcal{C}(Q,m)}{2}\left(\frac{m}{\beta}\right)^{\frac{1}{m}}. \tag{46}$$

Evaluating Eq. (46) for $Q = 1$, $\beta = 1$ for each of the three values of m for which boundaries were calculated ($m = 2, 4, 10$) gives the following constants: 2.5, 3.0, and 5.5, respectively. If we can interpret L_0 and L_1 as characteristic length scales of the background and the roughness, respectively, then it is possible to pass comment upon the previously invoked separation of the length-scale condition. Following Zwanzig's work [17] we wrote this condition as $L_0 \gg L_1$. However, the constants obtained from Eq. (46) reveal that a high degree of validity can be obtained for length scales rather closer to one another than might be inferred from this form of the condition. Perhaps all this serves to illustrate the difficulties associated with making concrete statements on a topic which is by definition a matter of degree. We nonetheless hope that this discussion has offered some insights into how the question of validity might be addressed. Likely the most important result is that the shape of the boundary [Eq. (44)] is closely related to the shape of the background energy landscape.

VII. CONCLUSIONS

Zwanzig proposed a formalism for modeling diffusion in rough potential energy landscapes based upon a modified

version of the Smoluchowski equation. We tested Zwanzig's proposal and found that its predictions disagreed with the results of numerical simulations for all but the smallest amplitudes of roughness. Using the configurational partition function, we derived an alternative amendment to the energy landscape, which brought Zwanzig's formalism into agreement with simulations. We proposed a modified version of the overdamped Langevin equation, which coarse grained the effects of the roughness, from which we constructed a simulation scheme. Peculiarities of the scheme lead to potentially significant reductions in computational time. We extended our findings to the case of roughness with randomly distributed amplitudes. We again proposed a modified Langevin equation and observed good agreement with simulations for the case of exponentially distributed amplitudes. Finally, the question of when this scheme is valid was then addressed by studying how the discrepancy between the mean-squared displacement in equilibrium calculated using the exact and approximate formulas changes as a function of the properties of the potential energy landscape. Requiring a discrepancy of less than 0.1% enabled a boundary between validity and invalidity to be drawn, which was then reinterpreted in terms of characteristic length scales. Zwanzig's separation of length scales condition for validity was then examined and found to be satisfied more readily than might first be supposed.

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Correction: A footnote indicating the corresponding author's email address has been inserted.