

Diffusion in a rough potential

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ABSTRACT Diffusion in a spatially rough one-dimensional potential is treated by analysis of the mean first passage time. A general expression is found for the effective diffusion coefficient, which can become very small at low temperatures.

This paper deals with diffusion in a rough potential. The work was motivated in part by ideas of Frauenfelder and co-workers concerning the dynamical behavior of proteins (for a good summary with figures, see ref. 1). They suggest that the potential surface of a protein might have a hierarchical structure, with potential minima within potential minima, etc. That is, the potential surface might be rough.

The treatment reported here of diffusion in a rough potential is restricted to one-dimensional systems and may not have any immediate relevance to multidimensional protein dynamics. However, the one-dimensional results seem interesting in themselves. In particular, the roughness of a potential gives rise to a dramatic slowing down of diffusion at low temperatures, especially when fluctuations in the potential have a Gaussian distribution.

An example of what is meant by “rough” is shown in Fig. 1. This particular one-dimensional potential was constructed from the arbitrarily chosen function

$$U(x) = x^2 + 0.02(\cos 167x + \sin 73x). \quad [1]$$

The general parabolic shape of the first term is clearly visible, but superimposed on it are many small potential barriers distributed in a more or less random way. The amplitude $\epsilon = 0.02$ of the second term is a measure of the “roughness” of the potential, a term which will be used here generally to denote the characteristic energy scale ϵ of the potential barriers.

One expects that at very high temperatures, compared with ϵ , diffusion is essentially unaffected by the many small barriers. But at temperatures that are small compared with ϵ , diffusion will be seriously hampered by having to cross over the barriers. This is an important point made by Frauenfelder and co-workers.

A rough potential $U(x)$ has in general a smooth background $U_0(x)$ on which a rapidly, and perhaps randomly, oscillating perturbation $U_1(x)$ is superimposed. The perturbation has a typical amplitude ϵ and a typical length scale Δx . When $U(x)$ is spatially averaged over Δx , the perturbation is eliminated and only the smooth background remains. In the given example, the length scale Δx is of the order of 0.1.

We are concerned only with diffusion on a much larger length scale than Δx . This separation of the length scale of roughness and the length scale of observed motion is essential to the following discussion. The results make sense only if many fluctuations in roughness take place in the distance of interest.

Brownian motion or diffusion of a system in a potential $U(x)$ is described by the Smoluchowski equation. This equa-

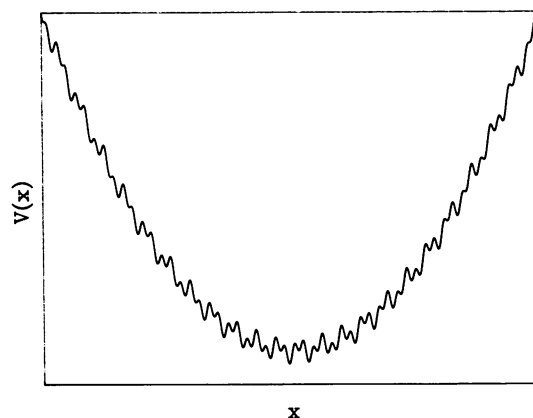


FIG. 1. An example of a rough potential is shown. The potential is given in Eq. 1 of the text.

tion determines the time (t) dependence of the probability distribution $\rho(x, t)$. It has the form

$$\partial \rho / \partial t = -\partial J / \partial x, \quad [2]$$

$$J = -D e^{-\beta U(x)} \partial / \partial x e^{\beta U(x)} \rho \quad [3]$$

in which J is a current density, D is a diffusion coefficient, and $\beta = 1/k_B T$, where T is the temperature.

When the potential U is smooth, solution of the Smoluchowski equation is straightforward (although numerical methods may be required). But when the potential is rough, standard procedures are not so useful. This paper presents an approximate treatment of diffusion in a rough one-dimensional potential. The approach taken is an extension of some old work of Lifson and Jackson (2). It makes use of an analytic expression for the mean first passage time (mfpt) to move from one position to another. The main result is that the original diffusion coefficient D is replaced by an effective diffusion coefficient D^* , and the original potential $U(x)$ is replaced by an effective smooth potential $U^*(x)$. D^* and U^* may depend very strongly on temperature, and D^* may be very much smaller than D . Illustrations will be given later.

We start with a familiar expression (2, 3) for the mean time required for a system starting out at x_0 to reach x for the first time. This is the mfpt and is denoted by $\langle t, x \rangle$. For technical reasons that are not relevant to the present discussion, we assume that there is a reflecting barrier at some location $x = a$. For convenience we consider only $a < x_0 < x$. The argument that follows does not depend critically on the values x_0 , x , and a as long as all distances involved are large compared with the length scale of the roughness. The mfpt is found by solving the differential equation

$$e^{\beta U(x)} \partial / \partial x D e^{-\beta U(x)} \partial / \partial x \langle t, x \rangle = -1 \quad [4]$$

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Abbreviation: mfpt, mean first passage time.

with an absorbing boundary condition at $x = x_0$. The solution is

$$\langle t, x \rangle = \int_{x_0}^x dy e^{\beta U(y)} (1/D) \int_a^y dz e^{-\beta U(z)}. \quad [5]$$

Observe that the integrations in this formula have the effect of spatial averages. That is, the integral over a small distance Δx may be approximated by

$$\int dz e^{-\beta U(z)} \cong \int dz e^{-\beta U_0(z)} \langle e^{-\beta U_1(z)} \rangle \quad [6]$$

in which $\langle \rangle$ denotes the spatial average used to smooth the potential. The average of the exponential can still be a function of the coordinate z , if the amplitude of the fluctuations in U_1 varies with z . For this reason, we denote the average by

$$\langle e^{-\beta U_1(z)} \rangle = e^{\psi^-(z)}. \quad [7]$$

Exactly the same approximation may be applied to the integration over y , with the definition

$$\langle e^{+\beta U_1(y)} \rangle \cong e^{\psi^+(y)}. \quad [8]$$

The result of the smoothing is the modified mfpt given by

$$\langle t, x \rangle \cong \int_{x_0}^x dy e^{\beta U_0(y) + \psi^+(y)} (1/D) \int_a^y dz e^{-\beta U_0(z) + \psi^-(z)}. \quad [9]$$

But by working backwards, we can see that this result is actually the mfpt for Brownian motion in the effective potential

$$U^*(x) = U_0(x) - \psi^-(x)/\beta, \quad [10]$$

with the effective diffusion coefficient given by

$$1/D^*(x) = e^{\psi^+(x)} (1/D) e^{\psi^-(x)}. \quad [11]$$

The corresponding effective Smoluchowski equation, valid only for distances much larger than the characteristic length scale of the fluctuations in U , is expected to be

$$\partial \rho / \partial t = -\partial J / \partial x, \quad [12]$$

$$J = -D^*(x) e^{-\beta U^*(x)} \partial / \partial x e^{\beta U^*(x)} \rho. \quad [13]$$

However, this is only a conjecture; there is no direct derivation of the effective Smoluchowski equation for a rough potential. All that we can say is that the mfpt predicted by this effective Smoluchowski equation agrees with the mfpt obtained by the spatial averaging process. (Actually, a similar argument can be made for higher moments of the first passage time distribution. They also are determined by D^* and U^* . So the conjecture is likely to be true.)

If the amplitude of the roughness does not depend on the coordinate, then U^* is U_0 shifted by an irrelevant constant

amount ψ^-/β . Also, the effective diffusion coefficient is independent of coordinate, $D^* = D e^{-\psi^+} e^{-\psi^-}$.

If, for example, the perturbation is simply $U_1(x) = \epsilon \cos(qx)$, then by integration over one period we obtain

$$e^{\psi^+} = e^{\psi^-} = I_0(\beta \epsilon) \quad [14]$$

in which $I_0(\beta \epsilon)$ is the modified Bessel function. This leads to a well-known result (4) in the case where the background potential is completely flat. At low temperatures, where $\epsilon/k_B T$ is very large, the Bessel function grows exponentially, so that D^* is proportional to $\exp(-2\epsilon/k_B T)$. This Arrhenius behavior is due to slow hopping between the many minima in the rough potential.

In another quite interesting example, suppose that the amplitude of the roughness is random and independent of x . In particular, suppose that it has a Gaussian distribution, with a probability proportional to $\exp(-U_1^2/2\epsilon^2)$ in which ϵ is the root-mean-squared roughness, $\epsilon^2 = \langle U_1^2 \rangle$. Then by direct integration one finds

$$e^{\psi^+} = e^{\psi^-} = e^{\beta^2 \epsilon^2 / 2}, \quad [15]$$

and the effective diffusion coefficient is

$$D^* = D \exp[-(\epsilon/k_B T)^2]. \quad [16]$$

This quadratic temperature dependence is significantly stronger than in the case of periodic roughness.

All of the preceding discussion was for one-dimensional diffusion. Unfortunately, there seems to be no generalization to higher dimensionalities of the approach used here (however, see ref. 5 for an attempt in this direction). This is especially sad because the potential surface of a protein molecule is surely multidimensional. One may conjecture that something like what is seen in one dimension will also be seen in higher dimensions; but this calls for further theoretical treatment.

The procedure followed here is a simple extension of the one used by Lifson and Jackson (2). A treatment due to De Gennes (6) of diffusion in a particular kind of random potential is similar to this one.

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