Approach to equilibrium in adiabatically evolving potentials

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For a potential function (in one dimension) which evolves from a specified initial form $V_i(x)$ to a different $V_f(x)$ asymptotically, we study the evolution, in an overdamped dynamics, of an initial probability density to its final equilibrium. There can be unexpected effects that can arise from the time dependence. We choose a time variation of the form $V(x,t)=V_f(x)+(V_i-V_f)e^{-\lambda t}$. For a $V_f(x)$, which is double welled and a $V_i(x)$ which is simple harmonic, we show that, in particular, if the evolution is adiabatic, this results in a *decrease* in the Kramers time characteristic of $V_f(x)$. Thus the time dependence makes diffusion over a barrier more efficient. There can also be interesting resonance effects when $V_i(x)$ and $V_f(x)$ are two harmonic potentials displaced with respect to each other that arise from the coincidence of the intrinsic time scale characterizing the potential variation and the Kramers time. Both these features are illustrated through representative examples.

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I. INTRODUCTION

The pioneering work of Kramers [1] on thermally activated barrier crossing has provided an understanding of the microscopic mechanism underlying the Arrhenius temperature dependence of crossing rates [2]. Several variants of the basic problem have subsequently been studied in the literature. A fair amount of attention has recently been devoted to the study of more complex nonequilibrium systems. These include the cases of diffusion over a barrier in the presence of harmonic force [3–10] and diffusion over a fluctuating barrier [11–17]. The hallmark of the former situation is the phenomenon of stochastic resonance, where the signal-to-noise ratio of the system response to an applied harmonic force displays a local maximum as a function of the diffusion constant or the temperature. In fluctuating barriers, the discovery [12] that the mean first passage time has a minimum as a function of the correlation time characterizing the fluctuation has prompted a wide variety of investigations. The problem of surmounting potential barriers [17–19] has gained importance in other fields of science such as evolutionary computations [20,21] and global optimization [22] as well.

In the present work we consider the situation of barrier crossing of a time-dependent potential which adiabatically evolves from $V_i(x)$ at $t=0$ to the potential $V_f(x)$ as $t\to\infty$. In such a situation there will be an eventual equilibrium distribution given by

$$P_{eq} \sim \exp - \frac{V_f(x)}{\epsilon}, \tag{1}$$

where ϵ is the diffusion constant and the approach to this equilibrium will be governed by a characteristic time, which differs from the corresponding characteristic time for the stationary potential $V(x)=V_f(x)$. We note that the characteristic time is the same as Kramers time where the potential $V_f(x)$ is one with a barrier.

Our main results are given in the following section, where we derive the time-dependent probability distribution for a specific form of the time variation leading from the initial potential $V_i(x)$ to the final $V_f(x)$. Other forms of the time variation can be treated by a simple extension of the techniques outlined there. In Sec. III, two specific examples of evolving potentials are considered. When the time scale of the perturbation matches the Kramers time for the stationary potential $V_f(x)$, there is a *resonance* which delays the onset of equilibrium. This case is treated within the time-dependent perturbation theoretic method of Dirac. The second case we study is one where $V_i(x)$ has a single minimum while $V_f(x)$ is bistable. By reducing to an effective two-state dynamics, we show that the Kramers time for the stationary potential $V_f(x)$ is reduced. The paper concludes with a summary and discussion in Sec. IV. Our result also sheds some light on the global optimization scheme recently introduced by Hunjan, Sarkar, and Ramaswamy (HSR) [21,31].

II. THE TIME-DEPENDENT DISTRIBUTION

For concreteness, we consider the time-dependent potential

$$V(x,t) = V_f(x) + [V_i(x) - V_f(x)]e^{-\lambda t}, \tag{2}$$

which evolves via homotopy from $V_i(x)$ at $t=0$ to $V_f(x)$ at $t\to\infty$. The Fokker-Planck equation for the probability distribution $P(x,t)$ is

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left(P\frac{\partial V}{\partial x}\right) + \epsilon\frac{\partial^2 P}{\partial x^2}, \tag{3}$$

which, with the substitution [23–25],

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$$P(x,t) = \phi(x,t)\exp - \frac{V(x,t)}{2\epsilon}, \tag{4}$$

reduces to

$$\frac{\partial \phi}{\partial t} = H_0\phi + H_1(t)e^{-\lambda t}\phi, \tag{5}$$

where (primes denoting differentiation with respect to x),

$$H_0 = \epsilon\frac{\partial^2}{\partial x^2} + \frac{1}{2}V_f'' - \frac{1}{4\epsilon}V_f'^2, \tag{6}$$

$$H_1 = \left[\frac{\Delta V''}{2} - \frac{\lambda}{2\epsilon}\Delta V - V_f'\frac{\Delta V'}{2\epsilon}\right] - \frac{(\Delta V')^2}{4\epsilon}e^{-\lambda t}, \tag{7}$$

and

$$\Delta V = V_i(x) - V_f(x). \tag{8}$$

H_0 satisfies the eigenvalue equation

$$H_0\psi_n = -E_n\psi_n(x) \tag{9}$$

with nonpositive eigenvalues. By construction, the ground state has eigenvalue $E_0=0$, with the eigenfunction $\psi_0(x) = A\exp - V_f(x)/2\epsilon$, A being a normalization constant. Denoting the space-independent part of H_1 by $V_0(t)$, the solution of Eq. (3) can be written as

$$\phi(x,t) = \sum c_n(t)\exp^{[-E_n(t)+\int V_0(t')dt']}\psi_n(x). \tag{10}$$

Application of the standard techniques of the Dirac time-dependent perturbation theory leads to

$$\dot{c}_n(t) = \sum_m c_m(t)\langle m|H_2|n\rangle e^{-(E_m-E_n)t}, \tag{11}$$

where

$$H_2 = e^{-\lambda t}(H_1 - V_0). \tag{12}$$

The perturbative expansion for the coefficients in Eq. (10) is in powers of H_2,

$$c_n(t) = \sum_{j=0}^{\infty} c_{nj}(t) \tag{13}$$

with

$$\dot{c}_{n0} = 0, \tag{14}$$

and for $j \geqslant 1$,

$$\dot{c}_{nj}(t) = \sum_m c_{m,j-1}(t)\langle m|H_2|n\rangle e^{-(E_m-E_n)t}. \tag{15}$$

It can be seen immediately that the c_{n0}'s are constants determined by the state of the system at $t=0$. Assuming that the system is in the equilibrium state of the potential $V_i(x)$ at $t=0$, namely,

$$P(x,0) = A_0\exp - \frac{V_i}{\epsilon}, \tag{16}$$

this implies that

$$\phi(x,0) = P(x,0)\exp\frac{V_i}{2\epsilon} = A_0\exp - \frac{V_i}{2\epsilon} \tag{17}$$

with normalization constant A_0. The constants c_{n0} are now determined from the initial condition, as

$$c_{n0} = A_0\int_{-\infty}^{\infty} dx\psi_n(x)\exp - \frac{V_i}{2\epsilon}. \tag{18}$$

Substituting this in Eq. (15), the complete solution to the problem can be obtained using Eqs. (13) and (10).

Note that as $t\to\infty$, $\phi(x,t)$ in Eq. (10) tends to $c_{00}\psi_0(x) = c_{00}\exp - V_f/2\epsilon$, and therefore,

$$P(x,t\to\infty) \to A\exp - \frac{V_f}{\epsilon}, \tag{19}$$

the equilibrium distribution corresponding to $V_f(x)$.

Also note from Eqs. (11) and (12) that since H_2 has the time-dependence $\exp - \lambda t$, there will be a resonance when $E_m - E_n = \lambda$, giving a secular growth of the first-order term, $c_{n1}(t) \propto t$. This is analogous to case of the time-dependent perturbation theory [26,27] in quantum mechanics.

III. APPLICATIONS

A. Case I

Consider first a case where the initial and final potential have the same number of minima. Specifically, we take $V_i = (x-a)^2$ and $V_f(x) = x^2$, namely, harmonic potentials that are spatially displaced. This leads to

$$\Delta V = a^2 - 2ax, \tag{20}$$

$$H_1 = \left[-\frac{\lambda(a^2-2ax)}{2\epsilon} + \frac{2ax}{\epsilon}\right] - \frac{a^2e^{-\lambda t}}{\epsilon}, \tag{21}$$

which has the space-independent part

$$V_0(t) = -\frac{\lambda a^2}{2\epsilon} - \frac{a^2e^{-\lambda t}}{\epsilon}, \tag{22}$$

giving

$$H_2(x,t) = \frac{ax}{\epsilon}(\lambda+2)e^{-\lambda t}. \tag{23}$$

The leading term in the expansion, namely,

$$H_0 = \epsilon\frac{\partial^2}{\partial x^2} + 1 - \frac{x^2}{\epsilon} \tag{24}$$

has the eigenvalue spectrum $E_n = 2n$ $(n=0,1,2,\ldots)$ with eigenfunctions

$$\psi_n(x) = [2^n n!\sqrt{\epsilon\pi}]^{-1/2}\mathcal{H}_n(x/\sqrt{\epsilon})\exp -\frac{x^2}{2\epsilon}, \quad (25)$$

where $\mathcal{H}_n(y)$ are the usual Hermite polynomials. The time-dependent probability is therefore

$$P(x,t) = \phi(x,t)\exp\left[-\frac{x^2}{2\epsilon} - \frac{(a^2-2ax)}{2\epsilon}e^{-\lambda t}\right], \quad (26)$$

giving, for $\phi(x,t)$, the expansion [cf. Eq. (10)]

$$\phi(x,t) = \sum_n c_n(t)\exp\left[-2nt - \frac{a^2}{2\epsilon}(1-e^{-\lambda t})\right]\psi_n(x). \quad (27)$$

To first order in the perturbation expansion, we find

$$c_n(t=0) = \left[\frac{a}{2\epsilon^{1/2}}\right]^n \frac{e^{-a^2/2\epsilon}}{[2^n n!]^{1/2}}. \quad (28)$$

At the lowest order of perturbation theory, only the c_{n0}'s, which are given by Eq. (28) matter. Straightforward algebra now shows that

$$P(x,t) = \left[\frac{1}{\pi\epsilon}\right]^{1/2}\exp -\frac{x^2+a^2}{\epsilon} + \frac{2axe^{-2t}}{\epsilon}\exp\frac{ax(e^{-\lambda t})-e^{-2t}}{\epsilon} + O(c_{n1}). \quad (29)$$

Since all terms to first order have not been included in the perturbation, the equilibrium distribution is not properly normalized as $t\to\infty$ and has the extraneous factor $\exp(-a^2/\epsilon)$. After computation of c_{n1} from Eq. (15) we find, after taking the appropriate matrix elements and carrying out the integration over time, that

$$c_{n1}(t) = \frac{a}{\epsilon}\left(\frac{n+1}{2}\right)^{1/2}[1-e^{-\lambda t}]c_{n+1}(0) + \left(\frac{\lambda+2}{\lambda-2}\right)\frac{a}{\epsilon}\left(\frac{n}{2}\right)^{1/2}[1-e^{-(\lambda-2)t}]c_{n-1}(0). \quad (30)$$

The coefficients $c_{n\pm1}(0)$ are known from Eq. (28) and after some amount of algebra we get, correct to first order in the perturbing "Hamiltonian,"

$$P(x,t) = \left(\frac{1}{\pi\epsilon}\right)^{1/2}e^{-x^2/\epsilon}\left[1 + \frac{2axe^{-\lambda t}}{\epsilon} + \frac{4ax(e^{-2t}-e^{-\lambda t})}{(\lambda-2)\epsilon} + \cdots\right]. \quad (31)$$

The effect of time dependence in the potential can be seen by contrasting the above result, Eq. (31) with the sudden limit, when the potential is instantaneously changed from $V_i(x)$ to $V_f(x)$. The initial probability distribution corresponding to $V_i(x)$ is $(1/\pi\epsilon)^{1/2}e^{-(x-a)^2/\epsilon}$ and this approaches the equilibrium distribution corresponding to $V_f(x)$ as

$$P(x,t) = \left(\frac{1}{\pi\epsilon}\right)^{1/2}e^{-x^2/\epsilon}\left[1 + \frac{2axe^{-2t}}{\epsilon}\right]. \quad (32)$$

The coefficient $2ax/\epsilon$ of e^{-2t} has the extra factor $[1+2/(\lambda-2)]$. Note that the time-dependent perturbation effectively keeps the system from attaining equilibrium by always managing to cause transition to neighboring states. The approach to equilibrium depends on the value of the adiabaticity parameter λ and there are three different regimes of interest.

(1) When $\lambda > 2$, the approach to equilibrium is governed by e^{-2t} but the coefficient of this term is significantly increased.

(2) If $\lambda < 2$, the approach is controlled by $e^{-\lambda t}$ and in the long time limit

$$P(x,t) \sim \frac{1}{(\pi\epsilon)^{1/2}}e^{-x^2/\epsilon}\left[1 + \left(\frac{4ax/\epsilon}{2-\lambda}\right)e^{-\lambda t}\right]. \quad (33)$$

(3) Finally, we have the extremely interesting situation of $\lambda \simeq 2$, in which case

$$P(x,t) = \frac{1}{(\pi\epsilon)^{1/2}}e^{-x^2/\epsilon}\left(1 + \frac{4axt}{\epsilon}e^{-2t} + \cdots\right). \quad (34)$$

This is the resonance that we have discussed already, which shows up as the coefficient of the usual correction to $P_{eq}(x)$ diverging with time.

This divergence of the coefficient of e^{-2t} in Eq. (34) would eventually get transferred to the argument of the exponential function as is usual in such cases. This can be explicitly verified in this case, because an exact solution for harmonic potentials has been written down by Hänggi and Thomas [28]. The answer for $P(x,t)$, adapting the work of Hänggi and Thomas to this situation is

$$P(x,t) = \left[\frac{1}{\pi\epsilon(1-e^{-4t})}\right]^{1/2} \times\exp\left[-\frac{(x-ae^{-2t}[1+2(1-e^{-(\lambda-2)t})/(\lambda-2)])^2}{\epsilon(1-e^{-4t})}\right]. \quad (35)$$

If we expand the exponential in powers of a all the three cases cited above are exactly reproduced. This shows that the method of quantum mechanical time-dependent perturbation theory that we have adopted here is capable of yielding the correct results.

B. Case II

We now turn to a situation where an initially single well structure $V_i = x^2$ crosses over to a double well structure $V_f = -x^2/2 + x^4/4$ as $t\to\infty$. The approach to equilibrium in double well potential is governed by the Kramers time, the long time scale coming from the possibility of noise induced hopping. Following the procedure outlined in Eqs. (4) and (5), we get

$$H_0 = -\epsilon\frac{d^2}{dx^2} + \frac{(x^3-x)^2}{4\epsilon} - \frac{1+3x^2}{2}, \quad (36)$$

$$H_1 = \frac{3}{2}(1-x^2) - \frac{1}{4\epsilon}x^2(3-x^2)(1-x^2) - \frac{\lambda}{8\epsilon}x^2(6-x^2) + \frac{1}{4\epsilon}x^2(3-x^2)^2(1-e^{-\lambda t}). \quad (37)$$

The low-lying part of the eigenvalue spectrum of H_0 is characterized by a set of close doublets with exponentially small separations, while the gap between two doublets is of $O(1)$. The ground state $E_0=0$, while the first excited state is the ground state of the supersymmetric partner of

$$\frac{(V_f')^2}{4\epsilon} - \frac{V_f''}{2}, \quad (38)$$

and is exponentially small [29,30]. The next excited state has eigenvalue approximately 2, and hence we can treat the dynamics of the low-lying states as that of a two level system. Denoting the two states by ϕ_0 and ϕ_1, with eigenvalues 0 and δ, then

$$\phi(x,t) = c_0(t)\phi_0(x) + c_1(t)e^{-\delta t}\phi_1(x). \quad (39)$$

The dynamics of c_0 and c_1 is governed by

$$\dot{c}_0 = \langle\phi_0|H_1|\phi_0\rangle e^{-\lambda t}c_0(t) + \langle\phi_0|H_1|\phi_1\rangle c_1(t)e^{-(\lambda+\delta)t}, \quad (40)$$

$$\dot{c}_1 = \langle\phi_1|H_1|\phi_0\rangle e^{-(\lambda-\delta)t}c_0(t) + \langle\phi_1|H_1|\phi_1\rangle e^{-\lambda t}c_1(t). \quad (41)$$

Since the perturbation H_1 is even, $\langle\phi_1|H_1|\phi_0\rangle=0$, decoupling c_0 and c_1. Integrating Eq. (41) and dropping terms like $e^{-2\lambda t}$ which are unimportant for $t>\lambda^{-1}$, we find

$$\dot{c}_1 = c_1\langle\phi_1|\widetilde{H_1}|\phi_1\rangle e^{-\lambda t}, \quad (42)$$

where

$$\widetilde{H_1} = \frac{3}{2}(1-x^2) + \frac{1}{2\epsilon}x^2(3-x^2)(1-x^2) - \frac{\lambda}{8\epsilon}x^2(6-x^2). \quad (43)$$

The primary contribution to $\langle\phi_1|\widetilde{H_1}|\phi_1\rangle$ comes from the vicinity of $x=1$ since ϕ_1 is an antisymmetric wave function strongly peaked near $x\pm1$. Since $\langle\phi_1|\widetilde{H_1}|\phi_1\rangle \simeq -5\lambda/4\epsilon$, we have

$$c_1(t) = B\frac{1-e^{-\lambda t}}{\lambda}\exp - \frac{5\lambda}{4\epsilon} \quad (44)$$

with B a constant of integration. From Eq. (39) we find, after a series of standard manipulations, that

$$\phi(x,t) \simeq N\phi_0(x)\left[1 + \frac{\phi_1(x)}{\phi_0(x)}e^{-\delta t - \frac{3(1-e^{-\lambda t})\alpha}{2\lambda}}\right] \equiv N\phi_0(x)[1 + f(x)e^{-\delta_{\rm eff}t}]. \quad (45)$$

In the above α is a measure of the strength of the ground state wave function at the origin, and where

$$\delta_{\rm eff} = \delta + \frac{3(1-e^{-\lambda t})\alpha}{2\lambda t}. \quad (46)$$

The inverse of $\delta_{\rm eff}$ gives the effective Kramers time for the system and is shorter than the scale for the time-independent system. This speeding up is most effect in the adiabatic limit, namely, for $\lambda \ll 1$.

IV. DISCUSSION AND SUMMARY

The above result is a simple analog of the global optimization principle on an evolving energy landscape. In this case one is interested in finding the minima of a multidimensional potential energy surface which constitutes the energy landscape in problems such as protein folding or finding the ground state configuration of atomic or molecular clusters. The observation of HSR [21,31] that continuously and adiabatically varying potentials assist approach to the desired configuration at $t\to\infty$ by avoiding trapping in local minima. We have shown in a model system, a similar time dependence, the decrease of Kramers time makes escape from a trapping potential easier.

The above demonstration of a reduced Kramers time is for a one-dimensional system. The extension to two dimensions is reasonably straightforward following the technique in Ref. [30] when a well defined tunneling path exists between the two minima. Extensions to more general situations and to three dimensions is being investigated. We have also seen that this technique of dealing with time-dependent perturbations can model the stochastic resonance as a kind of parametric resonance. With the emerging importance of stochastic resonance in biological systems [10] it is possible that yet another way of looking at stochastic resonance can yield new insights.

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