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Intrawell Relaxation Time: The Limit of the Adiabatic Approximation

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We consider the overdamped motion of a Brownian particle in a potential well and examine the relaxation of its probability distribution. We give a new definition, based on the mean first passage time, for the *intrawell relaxation time*, which characterizes the relaxation process in the entire well and can be expressed analytically for an arbitrary potential. Further, we show how it can be approximated by other simple quantities in most cases. If the characteristic time scale of some modulation of the potential is much longer than this intrawell relaxation time, the particle's probability distribution can be considered to be *adiabatically adjusted* to the potential at every instant. [S0031-9007(99)08815-8]

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The relaxation of (the probability distribution of) an overdamped Brownian particle in a potential well is crucial in many physical, chemical, and biological systems, where the potential of the particle is subject to change (e.g., due to some chemical transition, external fluctuation, or oscillation). When the particle is placed into a new potential well, or its potential well suddenly changes, it takes some time for the particle's probability distribution to adjust to the new circumstances. This *intrawell relaxation time* (IRT) is of great importance because it separates two different regimes of the system's behavior. If the characteristic time scale of the change of the potential is much longer than the IRT, the particle's probability distribution can be considered to be adjusted to the potential at any instant, otherwise the adiabatic approximation may fail and a more detailed analysis of the Brownian motion is required.

There is no obvious quantitative definition for the IRT. The relaxation is not exponential and proceeds differently at different points of the well. One natural choice for the IRT is the inverse of the smallest nonvanishing eigenvalue of the corresponding Fokker-Planck equation, λ_1^{-1} . Another possibility is the correlation time (τ_{corr}) defined as the area $\int_0^\infty C(t)/C(0) dt$ under the curve of the normalized autocorrelation function of the particle's position $x(t)$, where $C(t) = \langle x(0)x(t) \rangle - \langle x(0) \rangle^2$ is the autocorrelation function and the symbol $\langle \dots \rangle$ designates the equilibrium ensemble average [1].

The shortcoming of the above two choices is that in most cases these quantities characterize the relaxation only near the bottom of the well, where the majority of the probability can be found. However, there are very important situations (such as escape over a barrier or chemical transition which is allowed only near the top of a barrier) when the relaxation of the probability density in the *entire well* is crucial.

In this paper we give a new definition for the IRT that overcomes these shortcomings, can be expressed analytically for an arbitrary potential, and can be well approximated by other simple quantities in the most relevant cases. We also elaborate on the difference between the IRT for reflecting and absorbing boundaries, and give some examples when the IRT plays an important role.

The time evolution of the probability density $P(x, t)$ of an overdamped Brownian particle in a potential $U(x)$ is described by the Fokker-Planck equation (FPE)

$$\dot{P}(x, t) = -J'(x, t), \quad (1)$$

where

$$J(x, t) = -U'(x)P(x, t)/\gamma - DP'(x, t) \quad (2)$$

is the particle's probability current. The diffusion coefficient D and viscous drag coefficient γ are connected by the Einstein relation $D = k_B T/\gamma$, where k_B denotes the Boltzmann constant and T is the absolute temperature. In the following we denote the expectation value

$\int f(x)P(x) dx$ of an arbitrary function $f(x)$ averaged over the particle's probability density $P(x)$ by $f[P(x)]$.

A central quantity of our paper is the mean first passage time (MFPT), defined as the average time needed for a particle moving in the interval $[A, C]$ to reach the position x ($A \leq x \leq C$) from the initial position x_0 ($A \leq x_0 \leq C$), given that there is a reflecting boundary at the opposite end point (A if $x_0 < x$ and C if $x < x_0$) of the interval. A general formula for the MFPT is given in Ref. [2] and in Sec. 5.2.7 of Ref. [3],

$$\mathcal{F}_A[x_0 \rightarrow x] = \frac{1}{D} \int_{x_0}^x \int_A^y e^{[U(y)-U(z)]/k_B T} dz dy$$

if $x_0 \leq x$,

(3)

$$\mathcal{F}_C[x_0 \rightarrow x] = \frac{1}{D} \int_x^{x_0} \int_y^C e^{[U(y)-U(z)]/k_B T} dz dy$$

if $x \leq x_0$.

(4)

The subscript of the MFPT always indicates the position of the relevant reflecting boundary. Note that the MFPT is additive in the following sense: $\mathcal{F}_A[x_0 \rightarrow x_1] + \mathcal{F}_A[x_1 \rightarrow x_2] = \mathcal{F}_A[x_0 \rightarrow x_2]$ if $A \leq x_0 \leq x_1 \leq x_2 \leq C$.

First consider an arbitrary potential segment on the interval $[A, C]$ with reflecting boundaries at both end points. The equilibrium distribution of the particle's position in this interval is the Boltzmann distribution $B(x)$ with the normalization factor Z ,

$$B(x) = \frac{1}{Z} e^{-U(x)/k_B T}, \quad Z = \int_A^C e^{-U(x)/k_B T} dx.$$
(5)

By some algebraic manipulation of the integrals, remarkably one can show that the average MFPT from a position x_0 to a final position x averaged over the Boltzmann distribution $\mathcal{F}_{A,C}[x_0 \rightarrow B(x)] \equiv \tau_r$ is independent of initial position x_0 and can be written as

$$\tau_r = \frac{1}{DZ} \int_A^C \int_x^C \int_y^C e^{[-U(x)+U(y)-U(z)]/k_B T} dz dy dx.$$
(6)

Note that in $\mathcal{F}_{A,C}[x_0 \rightarrow B(x)]$ the order of x_0 and x is not defined if $A < x_0 < C$; therefore both reflecting end points of interval must be indicated in the subscript.

The time τ_r can be interpreted as the average time that is necessary for the required amount of probability [which is proportional to the $B(x)$] to get to every position x from position x_0 to reach equilibrium. Since τ_r is independent of x_0 , any deviation from the equilibrium distribution vanishes during this time. Thus, τ_r truly is the IRT in an interval with reflecting boundaries.

Let us further investigate the physical meaning of τ_r . Since it is independent of the starting position, τ_r is also equivalent to $\mathcal{F}_{A,C}[B(x_0) \rightarrow B(x)]$ which can be interpreted as the average time of the redistribution of the particle's equilibrium distribution.

If the starting position is at the bottom of the potential well, the MFPT to a position x increases exponentially with the potential energy at x , but the Boltzmann factor $B(x)$ decreases exponentially. Thus, each point of the well has a similar contribution to τ_r , and not only the points near the bottom.

Another argument for our definition is as follows [4]. Consider the MFPT from A to C . Since C is the farthest point from A , the probability density (starting from a delta function at A) relaxes at C last. Therefore, the MFPT from A to C can be divided into two parts corresponding to two hardly overlapping processes: the relaxation in the well and the passage from the equilibrium distribution to C . Thus, the IRT can be given as the difference between the MFPT from A to C ($\mathcal{F}_A[A \rightarrow C]$) and the MFPT from a Boltzmann distributed position x to C ($\mathcal{F}_A[B(x) \rightarrow C]$). Using the additivity of the MFPT, this can be written as $\mathcal{F}_A[A \rightarrow B(x)]$, which coincides with τ_r .

The above argument indicates that τ_r characterizes the slowest possible relaxation process in a closed interval, namely, the relaxation of the probability density at one end point of the interval starting from a delta function at the other end point. Therefore, in many cases τ_r is significantly larger than either λ_1^{-1} or τ_{corr} . The reason for this is that if the eigenvalues of the FPE are close to one another, the linear combination of the corresponding exponential functions (at positions far from the bottom of the well) can result in a function characterized by a time much larger than the inverse of the smallest eigenvalue. Consider a particle on a linear potential (for which the FPE can be solved analytically) with slope F , reflecting boundaries at $x = 0$ and $x = L$, and starting position at $x_0 = 0$. Then, if $FL \gg k_B T$, our definition for the IRT gives $\tau_r \approx \gamma L/F$ (in perfect agreement with the analytical result for the relaxation time at $x = L$). In stark contradiction, $\lambda_1^{-1} \approx \tau_{\text{corr}} \approx 2\gamma k_B T/F^2$ is independent of L and proportional to T , indicating that λ_1^{-1} and τ_{corr} describe the relaxation only at the diffusion dominated bottom region.

Now, let us consider a potential well with reflecting boundaries at $x = 0$ and $x = L$ (as illustrated in Fig. 1a),

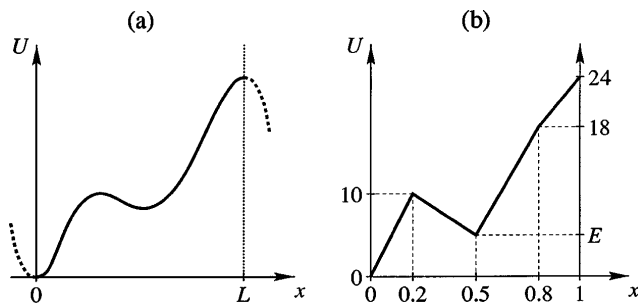


FIG. 1. (a) Schematic picture of a potential well with reflecting boundaries at $x = 0$ and $x = L$, and (b) a four-segment piecewise linear potential for the illustration of our results.

and see how the IRT can be approximated by other simple quantities in most cases. If the potential well is deep enough (compared to $k_B T$) and it has a sufficiently steep slope all the way from $x = 0$ to L , the IRT (which can be written as $\mathcal{F}_L[L \rightarrow B(x)]$) can be approximated by $\mathcal{F}_L[L \rightarrow 0]$, which can be further estimated by the *deterministic sliding down time* from the top of the barrier to the bottom of the well [4,5]. If the potential well is deep enough and contains an additional deep local minimum, the IRT can be approximated by the *equilibration time between the two subwells*, i.e., by the inverse of the sum of the rate constants between the two subwells.

To illustrate our definition we solved the FPE numerically for the potential well depicted in Fig. 1b for different values of the parameter E that allowed us to explore a number of qualitatively different important situations over a wide range of time scales. The probability density was initially set to a delta function at $x = 0$, and the units were chosen such that $L = \gamma = k_B T = 1$. We measured the relaxation time of the probability density at $L = 1$ (estimated as the time that is needed to reach the $1 - e^{-1}$ portion of the equilibrium value). Since the probability density equilibrates at position $L = 1$ last, the relaxation time there properly describes the relaxation in the entire well. The results of the numerical evaluation (indicated by circles in Fig. 2) agree with our definition for the IRT (solid line) extremely well. The IRT can be approximated by $\mathcal{F}_L[L \rightarrow 0]$ (dashed line) when $E > 3$, i.e., when the Boltzmann distribution is dominated at 0. For $E < 10$ and $E > 18$ there is an additional local minimum, and the IRT can be well approximated by the relaxation time between the two subwells (dotted line and dashed line with long dashes) when the local minimum is deep enough ($E < 7$ or $E > 21$). For $12 < E < 16$ the slope of the well is steep enough and the IRT can be approximated by the deterministic sliding down time (dash-dotted line).

The situation with absorbing boundaries is problematic. The system is open, the probability is continuously flowing out at the absorbing boundaries, and there is no stationary probability distribution to which the particle's distribution would converge. τ_{corr} cannot be defined either, and the smallest eigenvalue λ_0 of the FPE (which is zero for closed systems) becomes nonzero. However, if the barriers of a potential well are sufficiently high, the outflow during

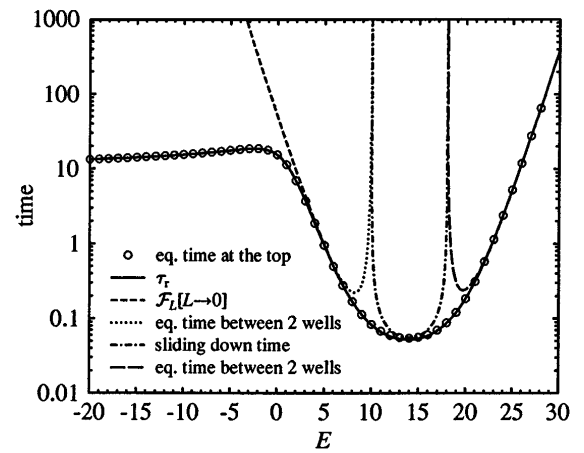


FIG. 2. The numerical results for the relaxation time of the probability density at the top of the potential of Fig. 1(b) (circles) agree perfectly with our definition for the IRT (solid line) for any value of the parameter E . The other lines are approximations for the IRT (see the text for details).

the “relaxation” can be neglected, and the IRT can be approximated by that for reflecting barriers.

For a detailed analysis let us consider the relaxation in a sufficiently deep well (as shown in Fig. 1a) with absorbing boundary at $x = L$ (and reflecting one at $x = 0$). Since the outflow at L is very slow, one can make the system closed by putting the probability that would flow out of the system back to the position $x = 0$, without altering the “quasistationary” probability distribution too much. For this system the stationary distribution $S(x)$ can easily be derived from the FPEs (1) and (2),

$$S(x) = \frac{1}{Y} \int_x^L e^{[-U(x)+U(y)]/k_B T} dy, \quad (7)$$

where

$$Y = \int_0^L \int_x^L e^{[-U(x)+U(y)]/k_B T} dy dx \quad (8)$$

is the normalization factor. Similar to the situation with reflecting boundaries, we can define the IRT as $\mathcal{F}_0[0 \rightarrow S(x)]$, i.e., the difference between the MFPT from 0 to L and the MFPT from a stationary distributed position x to L . By some algebraic manipulation one can show that this quantity can be written as

$$\tau_a = \frac{1}{DY} \int_0^L \int_x^L \int_y^L \int_z^L e^{[-U(x)+U(y)-U(z)+U(v)]/k_B T} dv dz dy dx, \quad (9)$$

which is identical with $I[L \leftrightarrow S(x)]$, the mean instanton time (MIT) between L and a stationary distributed position x .

The MIT between L and x is defined as the average duration of the travel (instanton) from L to x (or from

x to L) after the particle has touched its initial position L (or x) for the last time. Amazingly, the MIT is independent of the direction of the travel. From Sec. 9.1.5 of Ref. [3] one can express the MIT between L and x as

$$I[L \leftrightarrow x] = \frac{1}{DZ_{[x,L]}^*} \int_x^L \int_y^L \int_z^L e^{[U(y)-U(z)+U(v)]/k_B T} dv dz dy = \mathcal{F}_L[L \rightarrow x] - \mathcal{W}_x[L], \quad (10)$$

where

$$\mathcal{W}_x[L] = \frac{1}{DZ_{[x,L]}^*} \int_x^L \int_y^L \int_x^z e^{[U(y)-U(z)+U(v)]/k_B T} dv dz dy = \mathcal{F}_x^*[B_{[x,L]}^*(y) \rightarrow L] \quad (11)$$

is the mean wiggling time (MWT) at the end point L of the interval $[x, L]$. The relation $\mathcal{F}_L[L \rightarrow x] = I[L \leftrightarrow x] + \mathcal{W}_x[L]$ reflects that the mean first passage from L to x (with reflecting boundary at L) can be viewed as a wiggling process at L , during which the particle hits the boundary L (infinitely) many times, followed by a travel from L to x after the particle has touched L for the last time. The superscript $*$ on any quantity indicates that the inverted potential, $-U(x)$, should be considered, and the subscript $[x, L]$ indicates that both the Boltzmann distribution $B_{[x,L]}^*(y) = \exp\{U(y)/(k_B T)\}/Z_{[x,L]}^*$ and its normalization factor $Z_{[x,L]}^* = \int_x^L \exp\{U(y)/(k_B T)\} dy$ are defined on the interval $[x, L]$.

Since the potential well has been chosen to be sufficiently deep, the distributions $B(x)$ and $S(x)$ are very similar to each other and both are dominated at the bottom of the well. Therefore, based on the relation between the MFPT and the MIT, $\tau_a = I[L \leftrightarrow S(x)]$ can be well approximated by $\mathcal{F}_L[L \rightarrow B(x)] - \mathcal{W}_0[L]$, leading to the approximate relation that the IRT for the absorbing barrier is shorter than that for the reflecting barrier by about the MWT at the top,

$$\tau_a \approx \tau_r - \mathcal{W}_0[L]. \quad (12)$$

This relationship has a nice physical interpretation. τ_a is not only the IRT of the probability density for the absorbing barrier, but also the relaxation time of the probability current leading to the top of the barrier. Thus, for the reflecting barrier a probability current leading to the top also relaxes during the time τ_a , but due to the reflecting boundary condition the probability that has reached the top is not absorbed, but spends about the MWT at the top before flowing back to the bottom. Therefore, to build up the equilibrium distribution at the top takes about the sum of τ_a and $\mathcal{W}_0[L]$. In most cases $\mathcal{W}_0[L]$ is much smaller than τ_r , in agreement with our expectations that the IRT for the absorbing barrier can usually be well approximated by the IRT for the reflecting barrier.

Finally, let us consider an example when the IRT clearly separates the adiabatic and nonadiabatic regimes. The subject of our examination is the MFPT over a fluctuating barrier [4,6,7]. Let us use again the potential well depicted in Fig. 1b, for a fixed parameter $E = 1$, and apply a dichotomously fluctuating force between $+F$ and $-F$ with amplitude $F = 0.5$ and flipping rate ν . The MFPT from the bottom to the top can be calculated analytically (for any dichotomously fluctuating piecewise linear potential [6]) and is plotted in Fig. 3 (solid line) as a function of the flipping rate. The MFPT in the adiabatic limit can also be calculated from Kramers' rate theory. The result for our potential well (dotted line) starts to deviate from

the exact solution at around $\nu = 10^{-1}$, which coincides with the inverse of the IRT (left vertical bar), confirming our expectation that the adiabatic approximation is valid only when the modulation of the potential is much slower than the inverse of the IRT. Since our potential well contains an additional local minimum, we can make a further check. Let us consider the two subwells separately and apply the rate theory for a system with two states. Now the result (dashed line) starts to deviate from the exact solution at a much larger flipping rate (around $\nu = 10^2$) that corresponds to the maximum of the IRTs in the two subwells (right vertical bar).

We have presented a consistent picture of the intrawell relaxation based on the MFPT. Our new definition for the IRT represents the slowest relaxation within an interval because it incorporates passage from the end points of the interval through the intervening terrain. Thus, this quantity is appropriate for describing the equilibration of the probability distribution in the entire potential; i.e., after this time the probability distribution can safely be considered to be equilibrated at every position irrespective of the initial condition. As a consequence, our definition for IRT gives the correct criterion for the applicability of Kramers' rate theory. Other quantities such as λ_1^{-1} and τ_{corr} provide better estimates of the relaxation of faster processes, such as equilibration near the bottom of the potential, but may severely underestimate the relaxation time at the rarely visited places.

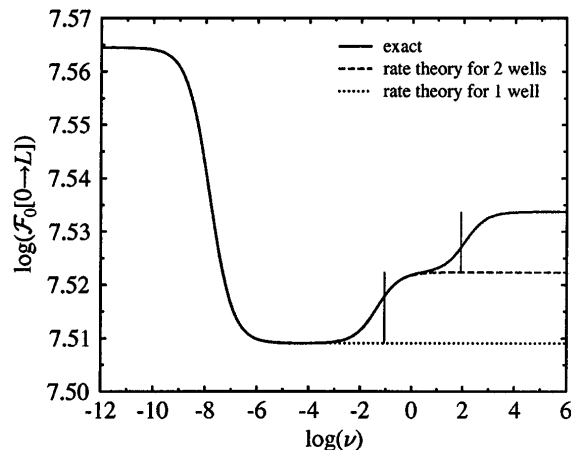


FIG. 3. Log-log plot of the MFPT from the bottom to the top of the potential of Fig. 1(b) (for $E = 1$) as a function of the flipping rate ν of an applied dichotomously fluctuating force between $+F$ and $-F$ with amplitude $F = 0.5$. The adiabatic approximations (dashed and dotted lines) start to deviate from the exact solution (solid line) at the inverse of the corresponding IRTs (vertical bars).

We expect that our result will be important for a number of systems where potential change or fluctuation is involved, such as for Brownian ratchets [8], where the characteristic frequency of the fluctuation should be large enough to achieve fast transport, but not larger than the inverse of the IRT, above which the system “feels” the average potential and the transport vanishes.

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