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Non-Markoffian Theory of Activated Rate Processes

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The Brownian motion of a general classical anharmonic oscillator is studied in the low-viscosity limit for a general non-Markoffian interaction with a heat bath. Memory effects are shown to have a profound influence on the rate of energy accumulation and relaxation.

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The dynamics of activated rate processes plays a central role in many areas of physics and chemistry. Following Kramers,[1] most studies use as a model a particle moving in a potential well under the influence of a thermal bath and distinguish between three cases: The high-viscosity limit corresponds to a diffusive motion of the overdamped oscillator described by the Smoluchowski equation. The intermediate-viscosity case focuses on the diffusive motion near the potential barrier and yields transition-state theory as the low-viscosity limit. Finally, for very low viscosities, the dynamics of the energy accumulation by the particle becomes important and the rate approaches zero as the viscosity decreases. Obviously, the dynamics of energy accumulation is always important for nonsteady-state processes, e.g., when the kinetics is monitored following a temperature jump.

The starting point in the Kramers model is the Langevin equation $\ddot{x} = -(1/M)\partial V(x)/\partial x - \gamma\dot{x} + (1/M)R(t)$, where x is the coordinate of the particle of mass M moving in the potential $V(x)$ and where γ and R are the damping rate and the (assumed Gaussian) fluctuating force associated with the coupling to the thermal bath [γ and R are related by the fluctuation-dissipation theorem $\langle R(t_1)R(t_2)\rangle = 2\gamma MkT\delta(t_1 - t_2)$, k being the Boltzmann constant and T the temperature]. In many cases the correlation time associated with the bath is longer than the characteristic period of the particle (though still much shorter than the rate of energy exchange).

In this case we use the model described by the generalized Langevin equation

$$\ddot{x} = -(1/M)\partial V(x)/\partial x - \int_0^t d\tau\, Z(t-\tau)\dot{x}(\tau) + (1/M)R(t), \tag{1}$$

where $\langle R\rangle = 0$ and

$$\langle R(t_1)R(t_2)\rangle = Z(t_1 - t_2)MkT; \quad \int_0^\infty dt\, Z(t) = \gamma. \tag{2}$$

The correlation function $Z(t)$ is characterized by the correlation time τ_c. For specificity we shall refer to the simple model

$$Z(t) = (\gamma/\tau_c)\exp(-t/\tau_c). \tag{3}$$

For molecular dynamics problems we usually have (ω is the oscillator frequency)[2]

$$\gamma \ll 1/\tau_c \ll \omega. \tag{4}$$

The existence of these vastly different time scales makes the problem very difficult to solve numerically though such solutions have been obtained using stochastic classical trajectories.[3] In this work we reduce Eq. (1) so as to obtain a Markoffian equation (characterized by a single time scale) for the time evolution of the system energy (or rather the action variable). We thus generalize Kramers's result for this low-viscosity limit to the non-Markoffian case.

Three previous studies are relevant to our problem. Zwanzig[4] has described a procedure for reducing Hamilton's equations of motion to get a result similar to Eq. (21) below. Grote and Hynes[5] have studied non-Markoffian effects on the diffusive dynamics near the barrier top, thus generalizing Kramers's theory for the intermediate-viscosity case. The result obtained here corresponds to the energy pumping stage rather than to the barrier dynamics. Lax[6] has described a reduction procedure which can be used to derive the Fokker-Planck equation corresponding to Eq. (8) below. Lax, however, limits himself to the standard second-order iteration procedure which is not sufficient in our case as discussed below.

Starting from Eq. (2), we assume that the free motion $[\ddot{x}=-(1/M)\partial V(x)/\partial x]$ is known in the sense that $x(t)$ and $v(t)=\dot{x}(t)$ are given as[7]

$$x(t)=\textstyle\sum_n x_n(J)\exp(in\varphi);\qquad v(t)=\textstyle\sum_n v_n(J)\exp(in\varphi) \tag{5}$$

with known coefficients $x_n(J)$ and $v_n(J)=in\omega(J)\times x_n(J)$. J and φ are the action-angle variables whose free equations of motion (EOM's) are $J=\text{const}$ and $\varphi=\varphi_0+\omega(J)t$.

Under the influence of the thermal bath the EOM's for J and φ become

$$\begin{aligned}\dot{J}(t)&=M(\partial x/\partial\varphi)\left[-\int_0^t d\tau\, Z(t-\tau)v(\tau)+(1/M)R(t)\right],\\ \dot{\varphi}(t)&=\omega(J)-M(\partial x/\partial J)\left[-\int_0^t d\tau\, Z(t-\tau)v(\tau)+(1/M)R(t)\right].\end{aligned} \tag{6}$$

Using (4) and (5) and invoking the rotating-wave approximation by disregarding deterministic terms containing $\exp(in\varphi)$ with $n\neq 0$,[8] we can approximate (6) by

$$\dot{J}=F(J)+iR(t)\textstyle\sum_n nx_n\exp(in\varphi), \tag{7}$$

$$\dot{\varphi}=\bar{\omega}(J)-R(t)\textstyle\sum_n x_n'\exp(in\varphi), \tag{8}$$

with

$$F(J)=-M\omega(J)\textstyle\sum_n n^2|x_n|^2 Z_n, \tag{9}$$

$$\bar{\omega}(J)=\omega(J)+iM\omega(J)\textstyle\sum_n nx_n'x_{-n}Z_{-n}, \tag{10}$$

$$Z_n=Z_n(\omega(J))=\int_0^\infty dt\, Z(t)\exp[-in\omega(J)t]. \tag{11}$$

Here $x_n'=dx_n/dJ$. Despite their appearance, Eqs. (7) and (8) are not Markoffian. The time evolution of the probability distribution $P(J,\varphi,t)$ is determined by the equation

$$\frac{\partial P}{\partial t}=\lim_{\tau\to 0+}\left\{\frac{1}{\tau}\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\sum_{\substack{m,k=0\\ m+k=n}}^{\infty}\left(\frac{\partial}{\partial J}\right)^m\left(\frac{\partial}{\partial\varphi}\right)^k\left[\langle(\Delta J)^m(\Delta\varphi)^k\rangle P\right]\right\}, \tag{12}$$

where $\Delta W=\Delta W(t,\tau)=W(t+\tau)-W(t)$ (W is J or φ). The limit in Eq. (12) should be understood as taking $\tau\ll\gamma^{-1}$. However, τ is kept larger than τ_c (and ω^{-1}) in order to yield a coarse-grained Markoffian equation.

Consider, for example, ΔJ. The standard procedure is to use

$$\Delta J(t,\tau)=\int_0^\tau ds\,\dot{J}(J(t+s),\varphi(t+s),t+s), \tag{13}$$

where $\dot{J}(J,\varphi,t)$ is given by Eq. (7), as a basis for iteration in the form

$$\Delta J^{(l)}(t,\tau)=\int_0^\tau ds\,\dot{J}(J(t)+\Delta J^{(l-1)}(t,s),\varphi(t)+\Delta\varphi^{(l-1)}(t,s),t+s). \tag{14}$$

Here (l) denotes the lth iteration stage. In the Markoffian case (where τ_c is the shortest time scale) it is usually found that (a) moments $\langle(\Delta J)^m(\Delta\varphi)^k\rangle$ with $m+k>2$ are of order τ^n, $n\geqslant 2$, and do not contribute to (12), and (b) all the relevant terms (of order τ) of the necessary first and second moments ($m+k=1$ or 2) are obtained at the second iteration stage. This leads to the standard Fokker-Planck equation.

The present case is different: Terms of order τ are found at all orders. For example, the integral

$$I_n^{(N)}=\int_0^\tau ds_0\int_0^{s_0}ds_1\cdots\int_0^{s_{N-1}}ds_N\exp[i\omega n(s_0-s_N)]Z(s_0-s_N), \tag{15}$$

encountered in the Nth order iteration of $\langle\Delta J\rangle$, satisfies

$$I_n^{(N)}=\frac{\tau}{(in)^{N-1}(N-1)!}(d/d\omega)^{N-1}Z_{-n}(\omega)+O(\tau_c/\tau), \tag{16}$$

so that such terms contribute in principle to (12). A careful examination of such higher-order contributions reveals that all but two are negligibly small, being of order $d^N Z_n(\omega)/d\omega^N$, $N\geqslant 1$. The two nonnegligible contributions which do not have analogs in the Markoffian case appear in the calculations of $\langle\Delta J\rangle$ and $\langle\Delta\varphi\rangle$ in the third order of the iteration procedures. There we get terms containing $(d\omega/dJ)I_n^{(1)}$ which lead to results containing dZ_n/dJ rather than $dZ_n/d\omega$. The final results for the moments which contribute to (12) are

$$\begin{gathered}\frac{\langle\Delta J\rangle}{\tau}=-2M\omega\sum_{n=1}^{\infty}n^2|x_n|^2Z_n{}^c+2MkT\frac{d}{dJ}\Big(\sum_{n=1}^{\infty}n^2|x_n|^2Z_n{}^c\Big),\\ \frac{\langle\Delta\varphi\rangle}{\tau}=\omega+M\omega\sum_{n=1}^{\infty}n\frac{d|x_n|^2}{dJ}Z_n{}^s-MkT\frac{d}{dJ}\left(\sum_{n=1}^{\infty}n\frac{d|x_n|^2}{dJ}Z_n{}^s\right),\\ \frac{\langle(\Delta J)^2\rangle}{\tau}=4MkT\sum_{n=1}^{\infty}n^2|x_n|^2Z_n{}^c,\quad\frac{\langle(\Delta\varphi)^2\rangle}{\tau}=4MkT\sum_{n=1}^{\infty}\left|\frac{dx_n}{dJ}\right|^2Z_n{}^c,\quad\langle\Delta J\cdot\Delta\varphi\rangle/\tau=0\end{gathered} \tag{17}$$

(with corrections of order τ), where $Z_n{}^c=\mathrm{Re}Z_n(\omega)$ and $Z_n{}^s=-\mathrm{Im}Z_n(\omega)$.

From Eqs. (12) and (17) we get a Fokker-Planck equation for $P(J,\varphi,t)$. For our purpose it is sufficient to consider the situation where $P=P(J,t)$ is independent of φ. We get

$$\frac{\partial}{\partial t}P(J,t)=\frac{\partial}{\partial J}\left\{\epsilon(J)\left[\omega(J)+kT\frac{\partial}{\partial J}\right]P(J,t)\right\}, \tag{18}$$

where

$$\epsilon(J)=2M\sum_{n=1}^{\infty}n^2|x_n|^2Z_n{}^c. \tag{19}$$

Equations (18) and (19) constitute our final result. Equation (18) [and Eq. (22) below] have been previously derived by Zwanzig.[4] We next study their behavior in some simple limits. At equilibrium, $\partial P/\partial t=0$, we obtain the Boltzmann distribution

$$P_{\mathrm{eq}}(J)\sim\exp[-H(J)/kT], \tag{20}$$

where $H(J)=\int^J dJ'\omega(J')$ is the energy. In the Markoffian limit $Z(t)=2\gamma\delta(t)$ and $Z_n=\gamma$ we get

$$\epsilon(J)=2\gamma M\sum_{n=1}^{\infty}n^2|x_n|^2=\gamma J/\omega(J), \tag{21}$$

where the last identity may be derived from $J=M\oint v\,dx$ by use of Eq. (5). Equations (18) and (21) lead to the result derived by Kramers for the low-viscosity limit. Finally, for a harmonic oscillator $x_n=0$ for $|n|\neq 1$ and $x_1(J)=x_{-1}(J)=(J/2M\omega)^{1/2}$. In this case $\epsilon(J)=Z_1{}^c(\omega)J/\omega$ and

$$\frac{\partial P}{\partial t}=Z_1{}^c(\omega)\frac{\partial}{\partial J}\left[\frac{J}{\omega}\left(\omega+kT\frac{\partial}{\partial J}\right)P\right]. \tag{22}$$

This result clearly shows the effect of finite time correlations on the rate: The time is scaled with $Z_1{}^c(\omega)$ in exactly the same way as it is with γ in the absence of correlations.

In order to solve Eq. (18) we have to evaluate $\epsilon(J)$. This may be done numerically by truncating the infinite series in (19), provided the deterministic motion [i.e., the functions $x_n(J)$ and $\omega(J)$] is known. For a Morse oscillator, $V(x)=D[\exp(-2x/a)-2\exp(-x/a)]$, we get $x_n(J)=(a/n)[\omega_0 J/(4D-\omega_0 J)]^{n/2}$ where $\omega_0=(2D/Ma^2)^{1/2}$ is the bottom frequency ($\omega_0 J\leqslant 2D$). The series in (22) thus converges rapidly for $H(J)<D$.

Equation (21) may be used to obtain an expression for the mean first-passage time for energy accumulation in the oscillator. The result is[9]

$$\tau_{\mathrm{MFP}}(J,J_B)=\frac{1}{kT}\int_J^{J_B}dx\,\frac{\exp[H(x)/kT]}{\epsilon(x)}\int_0^x dy\,\exp[-H(y)/kT], \tag{23}$$

where J is the initial action and J_B is the action corresponding to the specified energy threshold. This result may be used to obtain the rate of activated processes in the low-friction limit where energy accumulation becomes the rate determining step. In Fig. 1 we plot $\tau_{\mathrm{MFP}}(0,J_B)$ for $H(J_B)=2.5kT$ for a

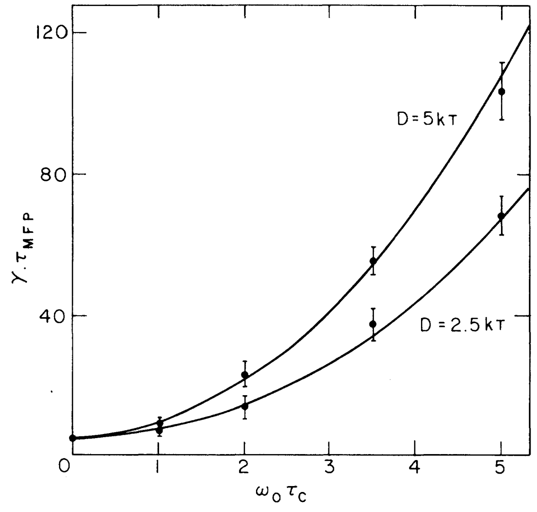

FIG. 1. $\gamma\tau_{MFP}$ vs $\omega_0\tau_c$ for a Morse oscillator from Eq. (23) (lines) and from stochastic classical trajectories (points with error bars). $\gamma/\omega_0 = 0.04$.

Morse oscillator and the model (3) as a function of τ_c. For $D=2.5kT$ and $5kT$ we compare results calculated from Eqs. (1)–(3) using stochastic classical trajectories to those obtained from Eq. (23). The agreement is good even when J_B corresponds to the dissociation threshold where the low-viscosity condition $\omega \gg \gamma$ does not apply. We also see that τ_c has a profound effect on the rate obtained in the non-Markoffian Kramers model.

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Infinite Conical Well: An Analytic Model for Quantum Mechanical Hindered Rotors

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The rotational quantum mechanics of a new analytic model for a hindered rotor is presented, and rotational-state distributions of the hindered rotor are given in terms of unhindered rotor states.

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The role played by the rotational degrees of freedom of diatomic molecules which are dynamically coupled to solid surfaces has been the focus of several recent experiments in which the observed rotational-state distributions of diatomic molecules scattered,[1] desorbed,[2] and sputtered[3] from surfaces bear no obvious relationship to equilibrium state distributions inferred from surface temperatures. In this communication we present the main features and illustrative numer-