Non-Markovian 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-Markovian 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 \( \dot{x} = -(1/M)\partial V(x)/\partial x - \gamma \dot{x} + (1/M)R(t) \), where \( x \) is the coordinate of the particle of mass \( M \) moving in the potential \( V(x) \) and where \( \gamma \) and \( R \) are the damping rate and the (assumed Gaussian) fluctuating force associated with the coupling to the thermal bath \( \gamma \) and \( R \) are related by the fluctuation-dissipation theorem \( \langle R(t_1)R(t_2) \rangle = 2\gamma M k T \delta(t_1-t_2) \), \( k \) 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

\[
\dot{x} = -(1/M)\partial V(x)/\partial x - \int_0^t d\tau Z(t-\tau)\xi(\tau) + (1/M)R(t),
\]

where \( \langle R \rangle = 0 \) and

\[
\langle R(t_1)R(t_2) \rangle = Z(t_1-t_2)MkT; \quad \int_0^\infty dt Z(t) = \gamma. \quad (2)
\]

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

\[
Z(t) = (\gamma/\tau_c)\exp(-t/\tau_c). \quad (3)
\]

For molecular dynamics problems we usually have (\( \omega \) is the oscillator frequency)

\[
\gamma \ll 1/\tau_c \ll \omega. \quad (4)
\]

The existence of these vastly different time scales makes the problem very difficult to solve numerically though such solutions have been ob-
tained using stochastic classical trajectories.\textsuperscript{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\textsuperscript{4} has described a procedure
for reducing Hamilton's equations of motion to get a result similar to Eq. (21) below. Grote
and Hynes\textsuperscript{5} have studied non-Markffian 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\textsuperscript{6} has
described a reduction procedure which can be used to derive the Fokker-Planck equation cor-
responding to Eq. (8) below. Lax, however, limits himself to the standard second-order iter-
ation procedure which is not sufficient in our case as discussed below.

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

$$x(t) = \sum_{n} x_{n}(t) \exp(i n \varphi);$$
$$v(t) = \sum_{n} v_{n}(t) \exp(i n \varphi)$$
(5)

with known coefficients $x_{n}(J)$ and $v_{n}(J) = i n \omega(J)$
$\times x_{n}(J)$. $J$ and $\varphi$ are the action-angle variables
whose free equations of motion (EOM's) are $J = \text{const}$ and $\varphi = \varphi_{o} + \omega(J)t$.

Under the influence of the thermal bath the EOM's for $J$ and $\varphi$ become

$$\dot{J}(t) = M(\vartheta \bar{x}/\vartheta \varphi)[\int_{0}^{t} d\tau Z(t - \tau)v(\tau) + (1/M)R(t)],$$
$$\dot{\varphi}(t) = \omega(J) - M(\vartheta \bar{x}/\vartheta \varphi)[\int_{0}^{t} d\tau Z(t - \tau)v(\tau) + (1/M)R(t)].$$
(6)

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

$$\dot{J} = F(J) + i R(t) \sum_{n} x_{n} \exp(i n \varphi),$$
$$\dot{\varphi} = \bar{\omega}(J) - R(t) \sum_{n} x_{n} \exp(i n \varphi),$$
(7)
(8)

with

$$F(J) = -M \omega(J) \sum_{n} n^{2} x_{n}^{2} Z_{n},$$
$$\bar{\omega}(J) = \omega(J) + i M \omega(J) \sum_{n} n x_{n} \times Z_{-n},$$
$$Z_{n} = Z_{n}(\omega(J)) = \int_{0}^{\infty} dt Z(t) \exp[-i n \omega(J)t].$$
(9)
(10)
(11)

Here $x_{n} = d x_{n}/d J$. 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

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

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

Consider, for example, $\Delta J$. The standard procedure is to use

$$\Delta J(t, \tau) = \int_{0}^{\tau} ds \int_{0}^{t+s} dJ' \bar{J}(J, \varphi, t+s, J', \varphi'),$$
(13)

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

$$\Delta J^{(l)}(t, \tau) = \int_{0}^{\tau} ds \int_{0}^{t+s} dJ' \bar{J}(J, \Delta J^{(l-1)}(t+s, \varphi, t+s), \Delta \varphi^{(l-1)}(t+s, \varphi, t+s)).$$
(14)

Here $(l)$ denotes the $l$th iteration stage. In the Markovian case (where $\tau_{c}$ 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 $\tau^{m}$, $n \geq 2$, and do not con-
tribute to (12), and (b) all the relevant terms (of order $\tau$) 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 $\tau$ are found at all orders. For example, the integral
\[ I_n^{(N)} = \int_0^\tau ds_0 \int_0^{s_0} ds_1 \cdots \int_0^{s_{N-1}} ds_N \exp[i\omega t(s_0 - s_N)] Z(s_0 - s_N), \tag{15} \]
encountered in the $N$th order iteration of $(\Delta J)$, satisfies
\[ I_n^{(N)} = \frac{\tau}{(in)^{N-1}(N-1)!} \left( d/d\omega \right)^{N-1} Z_n(\omega) + O(\tau^2/\tau), \tag{16} \]
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 $d^N Z_n(\omega)/d\omega^N$, $N \gg 1$. The two non-negligible contributions which do not have analogs in the Markovian case appear in the calculations of $(\Delta J)$ and $(\Delta \phi)$ in the third order of the iteration procedures. There we get terms containing $(d\omega/d\tau) I_n^{(0)}$ which lead to results containing $dZ_n/d\omega$ rather than $dZ_n/d\omega$. The final results for the moments which contribute to (12) are
\[
\begin{align*}
\frac{\langle \Delta J \rangle}{\tau} &= -2M \omega \sum_{n=1}^\infty n^2 |x_n|^2 Z_n^c + 2MkT \frac{d}{dJ} \left( \sum_{n=1}^\infty n^2 |x_n|^2 Z_n^c \right), \\
\frac{\langle \Delta \phi \rangle}{\tau} &= \frac{\omega + M \omega \sum_{n=1}^\infty d|x_n|^2}{dJ} Z_n^a - M kT \frac{d}{dJ} \left( \sum_{n=1}^\infty n^2 \frac{d|x_n|^2}{dJ} \right) Z_n^a, \\
\frac{\langle (\Delta J)^2 \rangle}{\tau} &= 4MkT \sum_{n=1}^\infty n^2 |x_n|^2 Z_n^c, \quad \frac{\langle (\Delta \phi)^2 \rangle}{\tau} = 4MkT \sum_{n=1}^\infty \frac{dx_n}{dJ} \cdot \frac{d}{dJ} \left( Z_n^c \right),
\end{align*}
\tag{17}
\]
(with corrections of order $\tau^2$, where $Z_n^c = \text{Re} Z_n^c(\omega)$ and $Z_n^a = -\text{Im} Z_n^a(\omega)$).

From Eqs. (12) and (17) we get a Fokker-Planck equation for $P(J, \phi, t)$. For our purpose it is sufficient to consider the situation where $P = P(J, \phi, t)$ is independent of $\phi$. We get
\[
\frac{\partial}{\partial t} P(J, t) = \frac{\partial}{\partial J} \left[ \epsilon(J) \left( \omega^2(J) + kT \frac{\partial}{\partial J} \right) P(J, t) \right], \tag{18}
\]
where
\[
\epsilon(J) = 2M \sum_{n=1}^\infty n^2 |x_n|^2 Z_n^c. \tag{19}
\]

Equations (18) and (19) constitute our final result. Equation (18) [and Eq. (22) below] have been previously derived by Zwanzig.\textsuperscript{4} We next study their behavior in some simple limits. At equilibrium, $\partial P/\partial t = 0$, we obtain the Boltzmann distribution
\[
P_{eq}(J) \sim \exp[-H(J)/kT], \tag{20}
\]
where $H(J) = \int J^2 d\phi J' \omega(J')$ is the energy. In the Markovian limit $Z(\ell) = 2\gamma \delta(\ell)$ and $Z_n = \gamma$ we get
\[
\epsilon(J) = 2M \sum_{n=1}^\infty n^2 |x_n|^2 = \gamma J/\omega(J), \tag{21}
\]
where
\[
\tau_{\text{MFP}}(J, J_B) = \frac{1}{kT} \int_J^{J_B} dx \exp[H(x)/kT] \int_0^x dy \exp[-H(y)/kT], \tag{23}
\]
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 $\tau_{\text{MFP}}(0, J_B)$ for $H(J_B) = 2.5kT$ for a
Morse oscillator and the model (3) as a function of $\tau_c$. 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 $J_z$ corresponds to the dissociation threshold where the low-viscosity condition $\omega \gg \gamma$ does not apply. We also see that $\tau_c$ has a profound effect on the rate obtained in the non-Markoffian Kramers model.

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\[1\] H. A. Kramers, Physica (Utrecht) 7, 284 (1940).
\[2\] Actually the left inequality in (4) may be replaced by the less stringent condition $|Z(\omega)| \ll \tau_c^{-1} |Z(\omega)|$ defined by (11).
\[7\] Unless states otherwise $\Sigma_i$ denotes a sum from $-\infty$ to $\infty$.
\[8\] One can proceed without invoking the rotating-wave approximation, at the cost of more tedious algebra, to arrive at the same final result.

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, desorbed, and sputtered 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-