Barrier Crossing Coupled to a Small Set of Oscillators†

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This paper presents a study of the behavior of a one-dimensional system, with two potential minima separated by a barrier, coupled to a small set of harmonic oscillators. The time correlation function of equilibrium fluctuations in particle number (number correlation function) is found by computer simulation. An analogue of Kramers turnover in the barrier crossing rate is observed. The Grote−Hynes theory of non-Markovian rate processes provides a reasonable estimate for the rate constant at intermediate frictions. However, at high friction, the number correlation function becomes nonexponential, and the decay is much slower than expected from the Grote−Hynes theory. The model shows that close coupling to a small heat bath provides a mechanism for "internal friction".

We report numerical experiments on the barrier crossing of a one-dimensional system interacting with a small harmonic oscillator heat bath. The experiments had two quite different motivations. We were curious to see how well a small harmonic oscillator heat bath could effectively imitate the friction and noise of conventional Brownian motion. And we were curious to see if it could provide an "internal friction" that might affect the rates of unimolecular rearrangements of a group of atoms inside a protein. The experiments used molecular dynamics to follow the time dependent decay of a number correlation function.

We found that in the particular system studied here, a small heat bath (10, 20, or 30 oscillators) leads to a decaying number correlation function. In some instances, the decay is approximately exponential, but in others it is more complex. The results do not follow the conventional Kramers−Grote−Hynes picture.

Kramers' classic theory of Brownian motion over a potential barrier is often used to account for the rate of rearrangement of a molecule in a viscous medium. The surrounding fluid provides friction and random noise. Conventionally, the friction is assumed to be Markovian and the noise is Gaussian and white. In an extension of Kramers' theory, Grote and Hynes[1] showed how to deal with non-Markovian friction. Hanggi et al.[2] give a historical review of the subject.

It is well-known that a frictional environment can be modeled by the bilinear interaction of a system with a harmonic oscillator heat bath.[3] Pollak[4] showed that when multidimensional transition state theory is applied to this model, one immediately obtains the rate constant predicted by the Grote−Hynes (G−H) theory.

Conventionally, one assumes that the oscillator heat bath contains an infinite number of oscillators, with a continuous spectrum. This allows for the construction of any kind of non-Markovian memory function. However, it appears that Pollak's theory should still be applicable if the heat bath contains a small number of oscillators because the exact nature of the frequency spectrum does not appear in the derivation. A more decisive requirement is that transition state theory is applicable in the first place. We note that because of this requirement, the G−H theory does not predict the Kramers turnover and is appropriate for intermediate to high friction. One goal of these numerical experiments was to see how well Pollak's version of G−H theory works when the heat bath is small.

The other interest motivating this work came originally from experiments on the rearrangement of proteins in solution.[5] In the high friction limit, Kramers' rate theory predicts that the rate constants are inversely proportional to the friction, which is usually attributed to the solvent viscosity. However, to fit experimental data using Kramers' theory, some additional "internal friction" is required.[6] (In polymer literature,[7] this is called "internal viscosity"). It seems possible that this internal friction can come from a bath of oscillators that are part of the molecule rather than an external environment.

We start by reviewing some familiar material about Langevin equations.[3] The system is described by a coordinate x and its conjugate momentum p. The system Hamiltonian H_S is

$$H_S = \frac{p^2}{2} + U(x) \tag{1}$$

In the numerical experiments, all masses have been set equal to 1. The heat bath is described by a set of coordinates $\{q_j\}$ and their conjugate momenta $\{p_j\}$. The heat bath Hamiltonian, for given x, is

$$H_B = \sum_{j=1}^{N}\left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2\left(q_j - \frac{\gamma_j}{\omega_j^2}x\right)^2\right) \tag{2}$$

in which ω_j is the frequency of the j-th oscillator, and γ_j measures the strength of coupling of the system to the j-th oscillator. Note the bilinear coupling of the system to the bath. The combined Hamiltonians of system and bath lead to the generalized Langevin equation

$$\frac{dp(t)}{dt} = -U'(x(t)) - \int_0^t dsK(s)p(t-s) + F_p(t) \tag{3}$$

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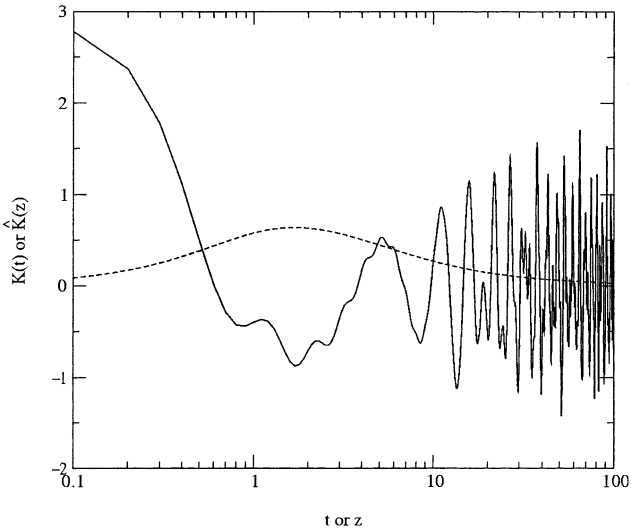

Figure 1. Memory function $K(t)$ (solid curve) and its Laplace transform (dashed curve).

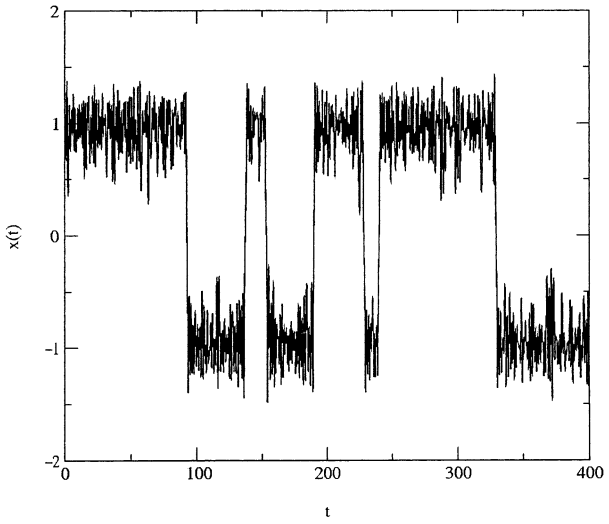

Figure 2. Time dependence of the position of the barrier crossing particle in a short trajectory.

The memory function is

$$K(t) = \sum_{j=1}^{N} \frac{\gamma_j^2}{\omega_j^2} \cos \omega_j t \tag{4}$$

and the noise, which is a linear combination of heat bath initial conditions, has a Gaussian distribution with the second moment

$$\langle F_p(t) F_p(t') \rangle = kTK(t - t') \tag{5}$$

Although formally correct, this Langevin equation is useful as a practical matter only if there is a clear separation of time scales, so that the system is slow and the heat bath is fast.

The possible choices for the system potential energy, the oscillator spectrum, and the coupling constants, are limitless. Here, some arbitrary choices are made. The potential energy is quartic

$$U(x) = U_0(x^2 - 1)^2 \tag{6}$$

The frequencies of the heat bath Hamiltonian are arbitrarily chosen to be

$$\omega_j^2 = cj, \; 1 \le j \le N \tag{7}$$

The coefficient c is unity for $N = 10$, and for other N, it is determined by

$$c = \sum_{1}^{N} (1/j) / \sum_{1}^{10} (1/j) \tag{8}$$

The coupling constants γ_j are all equal to γ. This has the consequence that the initial value of the memory function does not change as N is varied. The memory function is a sum of cosines

$$K(t) = \gamma^2 \sum_{1}^{N} \frac{1}{cj} \cos(\sqrt{cj}\, t) \tag{9}$$

Figure 1 shows the early time behavior of $K(t)$ for $N = 30$ and $\gamma = 1$. It does not resemble any familiar memory function, and at long times, it appears quite random. For many purposes, however, its Laplace transform $\hat{K}(z)$, also shown in Figure 1, is more useful. Note that the transform is considerably smoother, but unlike familiar memory functions, it vanishes at small z. This is a consequence of using a small number of oscillators. (In normal applications, $\hat{K}(0)$ does not vanish.)

The simulation involves solving Hamilton's equations for the coupled system and oscillator bath. The main goal was to find the number correlation function (time correlation function of equilibrium fluctuations in particle number) $C(t)$, defined by

$$C(t) = 2\langle H[x(t)] H[x(0)] \rangle - 1 \tag{10}$$

where $H(x)$ is the unit step function. The barrier height is $U_0 = 2$. Note that this is small enough that barrier crossing is not a rare event. Except for one microcanonical run, the system was prepared by choosing oscillator initial conditions from a canonical ensemble distribution with $k_B T = 1$ (referred to as "canonical runs"). In typical runs, 5000 trajectories were started from the right side of the quartic potential, and the averaged number correlation function was calculated. Figure 2 shows a small piece of one trajectory; it is evident that the system jumps back and forth between regions where $x < 0$ and $x > 0$.

A single very long microcanonical run, where $N = 30$ and the total constant energy is equal to the average energy of the canonical runs, reproduces the averaged behavior of the canonical runs.

Figure 3 shows the decay of $C(t)$ when the number of oscillators N was either 10, 20, or 30. and the coupling strength γ was set equal to 1. For $N = 10$, $C(t)$ does not appear to decay to zero, probably because some initial states did not have enough total energy to cross the barrier. For $N = 30$, the decay is approximately exponential, and is fit reasonably well by $\exp(-t/7.62)$.

In Figure 4, we show $C(t)$ when the coupling constant was decreased to $\gamma^2 = 0.1$ and 0.01. Note that there is a substantial slowing down of the decay as γ^2 decreases below 1. Figure 4 also shows that there is substantial slowing down in the decay of $C(t)$ when γ^2 is increased past 1. (That the fastest decay comes at γ^2 near 1 is an accidental result of the particular choice of spectrum.) Because the memory function or "friction" is proportional to γ^2, this behavior is reminiscent of the Kramers turnover. Note that at $\gamma^2 = 10$, $C(t)$ has an initial oscillatory decay which is followed by a very slow decay.

We now test the applicability of the G−H theory to the present system under intermediate and high friction. The first

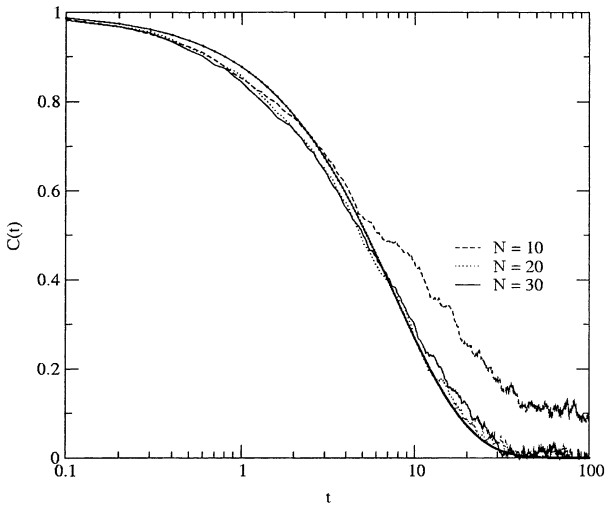

Figure 3. Number correlation function for $\gamma = 1$ and $N = 10$, 20, and 30. The smooth solid curve is a fit of the $N = 30$ data to the exponential $\exp(-t/7.62)$.

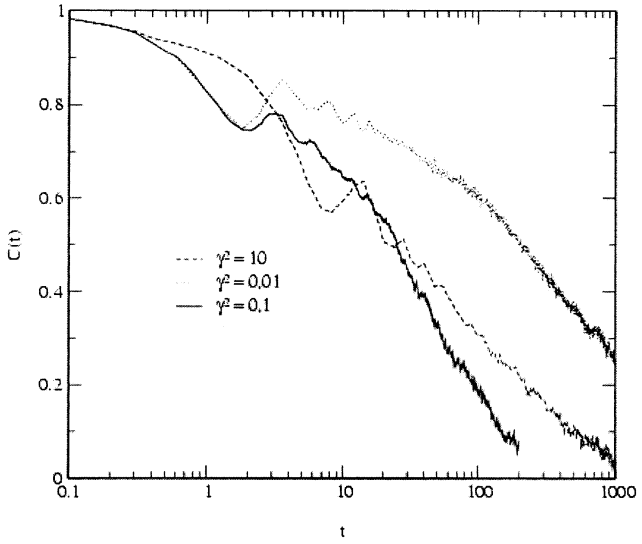

Figure 4. Number correlation function $\gamma^2 = 0.1$, 0.01, and 10 and $N = 30$.

stage is to find the conventional transition state theory rate. This is determined by the initial decay of the number correlation function.[3,8] For $U_0 = 2$, the TST decay time is $\tau = 6.5$ (calculated using the full potential rather than its harmonic approximation). The result is independent of the coupling to the heat bath; however, it is close to the decay time 7.6 that was found in the simulation runs where $\gamma^2 = 1$.

The next stage is to find the Laplace transform of the memory function

$$\hat{K}(z) = \int_0^\infty dt e^{-zt} K(t) = \gamma^2 \sum_{j=1}^{N} \frac{1}{cj} \frac{z}{z^2 + cj} \tag{11}$$

The curvature at the barrier is characterized by the frequency $\omega_b = 2\sqrt{U_0}$. Then one solves the equation

$$z^* = \frac{{\omega_b}^2}{z^* + \hat{K}(z^*)} \tag{12}$$

The G−H rate is given by

$$k_{\mathrm{G-H}} = \frac{z^*}{\omega_b} k_{\mathrm{TST}} \tag{13}$$

For the coupling constant $\gamma^2 = 1$, this leads to the decay time 7.3, which is closer than the TST time to the observed time 7.6.

However, the G−H approach does not appear to work so well in the limit of large coupling. For example, when $\gamma^2 = 10$, the predicted decay time is 18, which is much shorter than what is seen in the simulations. The root z^* is small, and for small z, the memory function is proportional to z; for $N = 30$, it is

$$\hat{K}(z) \rightarrow 0.866 z\gamma^2 \tag{14}$$

and the root of the G−H condition is

$$z^* \approx \frac{\omega_b}{(1 + 0.866\gamma^2)^{1/2}} \approx 1.074 \frac{\omega_b}{\gamma} \tag{15}$$

For large γ, the decay time is predicted to be proportional to the first power of γ, in distinction to the familiar G−H theory, where it is proportional to γ^2. Neither dependence on γ is what one sees from the simulation, where the decay time increases much more rapidly as the coupling strength increases.

We see that a small oscillator heat bath can lead to barrier crossing events. Further, the decay of the number correlation function suggests that it may be reasonable to speak of some kind of "internal friction" in the system. However, this does not behave like the friction that appears in conventional Brownian motion theory, and small oscillator heat baths do not appear to be useful mimics of that friction.

After writing this paper, we became aware of a paper[9] by Plyukhin and Schofield that dealt with the effects of a finite oscillator heat bath in a different context.

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