

Calculation of Dynamic Friction on Intramolecular Degrees of Freedom

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A simple method is presented for determining the dynamic (frequency-dependent) friction experienced by solute intramolecular coordinates due to the solvent molecules. This method is applied to the case of a diatomic molecule dissolved in Lennard-Jonesium.

1. Introduction

In many problems in liquid-state chemistry one degree of freedom, x , plays a special role and is treated by projecting out all of the remaining degrees of freedom of the system. The simplest case occurs in a liquid solution, where x can be any of the three coordinates specifying the position of the molecular center of mass. Using projection operator techniques, it is then a simple matter to derive a generalized Langevin equation for this coordinate^{1,2}

$$m\ddot{x}(t) = - \int_0^t d\tau \zeta(\tau) \dot{x}(t-\tau) + R(t) \quad (1.1)$$

where m is the mass of the molecule, and $\dot{x}(t)$, $\ddot{x}(t)$, $\zeta(t)$, and $R(t)$ are the velocity, acceleration, dynamic friction, and random force, respectively. The second fluctuation dissipation theorem provides a relationship between $\zeta(t)$ and the fluctuating force³

$$\zeta(t) = \frac{1}{kT} \langle F e^{iQLt} F \rangle \quad (1.2)$$

where F is the force acting on the coordinate x , L is the Liouville operator, and Q is the projection operator, $1 - \langle \dots \rangle / \langle \dot{x}^2 \rangle \dot{x}$. It is worth noting that in Brownian motion theory the friction coefficient is given by

$$\zeta_B(t) = \frac{1}{kT} \langle F e^{iL_t} F \rangle \quad (1.3)$$

where e^{iL_t} is the propagator for the total system with the velocity of the Brownian particle constrained to be zero. Clearly the true friction given by eq 1.2 will generally be different from the Brownian friction given by eq 1.3. Deutch and Silbey have shown that for a particle linearly coupled to a harmonic bath these two friction coefficients will be equal.⁴

In the case of the center of mass motion, it is possible to determine $\zeta(t)$ from molecular dynamics. The basic approach is to calculate the velocity autocorrelation function

$$C_v(t) = \frac{\langle \dot{x}(t) \dot{x}(0) \rangle}{\langle \dot{x}^2 \rangle} \quad (1.4)$$

from molecular dynamics trajectories.⁵ Substitution of the calculated $C_v(t)$ into the integral equation

$$m\dot{C}_v(t) = - \int_0^t d\tau \zeta(\tau) C_v(t-\tau) \quad (1.5)$$

followed by numerical integration, gives $\zeta(t)$. Alternatively, one can evaluate the Laplace transform of $C_v(t)$, giving

$$\tilde{C}_v(s) = \frac{1}{[s + \tilde{\zeta}(s)/m]} \quad (1.6)$$

which may be solved for $\tilde{\zeta}(s)$ through Laplace inversion. Here $\tilde{C}_v(s)$ and $\tilde{\zeta}(s)$ are the Laplace transforms of $C_v(t)$ and $\zeta(t)$, respectively. These procedures have been used to determine $\zeta(t)$ in liquids^{3,6} and super cooled liquids.⁷ In the latter, $\zeta(t)$ consists

of a short-time decay, characterizing the duration of strong repulsive collisions with solvent molecules, followed by a long-time decay, characterizing collective or hydrodynamic interactions. It is the aim of modern self-consistent mode-mode coupling theories to predict this behavior.⁸

In the barrier-crossing problems that arise in chemical reaction dynamics, the reaction coordinate is assumed to obey a generalized Langevin equation⁹

$$\mu\ddot{x}(t) = - \frac{\partial W(x)}{\partial x} - \int_0^t d\tau \zeta_r(\tau) \dot{x}(t-\tau) + R(t) \quad (1.7)$$

where the potential of mean force $W(x)$ has wells and barriers and μ is the reduced mass. The reaction coordinate usually involves the relative motions of different groups in the same molecule. Clearly, the dynamic friction $\zeta_r(t)$ acting on the reaction coordinate can be quite different from the dynamic friction experienced by the center of mass of a molecule, since this coordinate can be significantly shielded from the solvent atoms.¹⁰ It is very difficult to determine $\zeta_r(t)$ analytically, and only very simple hydrodynamic models have been invoked.⁸

The generalized Langevin equation, eq 1.7, cannot be derived in general from classical or quantum dynamics. It is usually assumed to apply without questioning its validity. It is not at all clear that for nonlinear systems this equation is valid even in simple cases. It has been derived for an anharmonic oscillator linearly coupled to a harmonic bath.¹¹ In this case, the dynamical friction has the simple form, for a continuum bath

$$\zeta_r(t) = \int d\omega \frac{J(\omega)}{\omega^2} \cos(\omega t) \quad (1.8)$$

and for a discrete bath

$$\zeta_r(t) = \sum_{\alpha} \frac{g_{\alpha}^2}{m_{\alpha} \omega_{\alpha}^2} \cos(\omega_{\alpha} t) \quad (1.9)$$

Here, g_{α} is the coupling constant of the reaction coordinate to the bath, m_{α} and ω_{α} are the masses and frequencies of the harmonic oscillators in the bath, and $g_{\alpha}^2/m_{\alpha}\omega_{\alpha}^2$ is independent of the bath or solvent masses, m_{α} , because $m_{\alpha}\omega_{\alpha}^2$ is a mass-independent force constant. The only mass dependence arises from the frequency

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factors ω_a , in the cosines, which are proportional to $m_a^{-1/2}$. Thus if the solvent mass is changed, only the time scale will change; that is, there should be no change in the overall functional form of $\zeta_r(t)$. Clearly, there is no dependence of $\zeta_r(t)$ on the reaction coordinate itself. Moreover, because the bath is harmonic⁴ we expect that the dynamic friction is identical with that computed by using eq 1.3.

Recently, it has been shown that if $\zeta_r(t)$ is known, it is possible to calculate the rate constant for barrier crossing in certain limits.^{9,12} The rate constants so obtained can be very sensitive to the model used for $\zeta_r(t)$.¹³ In this paper, we introduce a very simple method for determining $\zeta_r(t)$ for any given reaction coordinate. We apply this method to a model of a liquid-state reaction. $\zeta_r(t)$ for the reaction coordinate is determined and compared with the dynamic friction $\zeta_s(t)$ for the solvent atoms. This provides great insight into dynamic interaction between a reacting molecule and the solvent.

In this paper only the dynamic friction is discussed. The calculation of the rate constant is left for another paper.

2. Method for Determining Dynamic Friction

The potential in eq 1.7 is a nonlinear function of x . It is usually assumed that $\zeta_r(t)$ arises entirely from the fluctuating force on x due to the bath, where the bath consists of all coordinates and momenta other than x and p_x . If this assumption is valid, then $\zeta_r(t)$ should be invariant to the choice of potential $U(x)$. It follows that a good test of this assumption is to compare $\zeta_r(t)$ corresponding to different potentials. If these differ, then the assumption is wrong.

To proceed, we replace the potential function $U(x)$ by a harmonic potential

$$U^{(0)}(x; x_0, \omega) = \frac{1}{2} m \omega^2 (x - x_0) \quad (2.1)$$

with frequency ω , and equilibrium displacement x_0 . In this case, one can derive the generalized Langevin equation using projection operators²

$$\mu \ddot{q}(t) = \mu \tilde{\omega}^2 q(t) - \int_0^t d\tau \zeta_r(\tau) \dot{q}(t - \tau) + R(t) \quad (2.2)$$

where $q(t) \equiv x(t) - \langle x \rangle$ is the deviation of the bond length x from the mean bond length $\langle x \rangle$ in the bath, and $\tilde{\omega}$ is the renormalized frequency given by

$$\tilde{\omega}^2 = [\beta \mu \langle q^2 \rangle]^{-1} \quad (2.3)$$

Both $\langle x \rangle$ and $\langle q^2 \rangle$ depend on x_0 , ω , and the forces exerted by the bath on the reaction coordinate x including centrifugal distortion.

Multiplying eq 2.2 by $\dot{q}(0)$, averaging over a canonical ensemble, and remembering that $\langle R(t) \dot{q}(0) \rangle = 0$, gives an equation for the velocity autocorrelation function $C_v(t)$

$$\dot{C}_v(t) = - \int_0^t d\tau K(\tau) C_v(t - \tau) \quad (2.4)$$

where the memory function is

$$K(t) = \tilde{\omega}^2 + \frac{\zeta_r(t)}{\mu} \quad (2.5)$$

These quantities depend parametrically on x_0 and ω . $C_v(t)$ is now determined by molecular dynamics on the liquid system with $U(x)$ replaced by the harmonic reference potential $U^{(0)}(x; x_0, \omega)$, and $K(t)$ can be determined by the method of Berne and Harp.³ If, furthermore, $\langle x \rangle$ and $\langle q^2 \rangle$ are determined in the same simulation, $\tilde{\omega}^2$ can be calculated.

Substitution of $K(t)$ and $\tilde{\omega}$ into eq 2.5 yields $\zeta_r(t)$. This can be repeated for different values of ω for a given x_0 , and for different values of x_0 . Writing

$$\zeta_r(t) = \zeta_r(t; x_0, \omega) \quad (2.6)$$

TABLE I: Summary of Simulation Runs^a

ω	x_0	m_A/m_A	$\tilde{\omega}^2$	$\langle q \rangle$	$\zeta(t=0)$	$\zeta(0)$
15.0	1.25	1.0	143	-0.060	419	21.2
20.0	1.25	1.0	312	-0.027	427	22.2
25.0	1.25	1.0	542	-0.018	433	19.4
19.2	1.25	1.0	294	-0.036	426	21.5
25.0	0.75	1.0	597	-0.097	319	13.1
19.2	1.25	1.0	294	-0.036	426	21.5
22.5	1.75	1.0	554	-0.030	502	28.8
40.0	1.25	4.0	1360	-0.037	454	42.2
19.2	1.25	1.0	294	-0.036	426	21.5
17.5	1.25	0.1	304	-0.0029	435	8.15
		1.0			960	38.0

^a The fourth line is the average of the first three lines. The last line is for the single particle friction.

to indicate the parametric dependence of the friction on x_0 and ω , $\zeta_r(t)$ will be compared with the dynamical friction $\zeta_s(t)$ of a single solvent atom.

3. Molecular Dynamics

The physical system consists of N solvent atoms A and one diatomic molecule A_2^* where the solvent-solvent interaction is given by

$$\varphi_{AA}(r) = 4\epsilon_{AA} \left[\left(\frac{\sigma_{AA}}{r} \right)^{12} - \left(\frac{\sigma_{AA}}{r} \right)^6 \right] \quad (3.1)$$

The diatomic molecule interacts with the solvent through a site-site Lennard-Jones potential of the same form as the solvent-solvent interaction

$$\varphi_{AA^*}(r) = 4\epsilon_{AA} \left[\left(\frac{\sigma_{AA}}{r} \right)^{12} - \left(\frac{\sigma_{AA}}{r} \right)^6 \right] \quad (3.2)$$

The diatomic intramolecular potential

$$\begin{aligned} \varphi_{A^*A^*}(r) &= Q(1 - \lambda^2 y^2) \quad \text{for } |y| < y_1 \\ &= Q(y - y_0)^2 \quad \text{for } |y| > y_1 \end{aligned} \quad (3.3)$$

is a symmetric bistable piecewise continuous potential with parabolic barrier and harmonic wells where y is defined by $r = a + (4Q/\omega_0^2)^{1/2} y$, a is the position of the barrier maximum, Q is the barrier height, and ω_0 and ω_B are the harmonic well and barrier frequencies, respectively. The well and barrier regions of $\varphi_{A^*A^*}(r)$ are joined continuously at y_1 and the well minima are located at $y = \pm y_0$ where $y_1^2 \lambda_2 [\lambda(1 + \lambda^2)] = 1$, $y_0 = y_1(1 + \lambda^2)$, and $\lambda = \omega_B/\omega_0$. The Lennard-Jones reduced units are defined such that $m_{A^*} = \sigma_{AA} = \epsilon_{AA} = k_B = 1$ and $(m_{A^*} \sigma_{AA} / \epsilon_{AA})^{1/2}$ is the unit of time. In all our calculations, the barrier $Q = 25$ is positioned at $r = a = 1.25$, with $\omega_B = \omega_0 = 30$ placing the positions of the wells at approximately $r = 0.75$ and 1.75 . The reduced temperature $\hat{T} = (k_B T / \epsilon_{AA}) = 2.5$ and the reduced density $\hat{\rho} = n_A \sigma_{AA}^3 = 1.05$.

As mentioned in section 2, the dynamic memory function is determined from a long molecular dynamics run. The bond velocity correlation function for the solute molecule with a harmonic reference potential, eq 2.1, is determined in the standard way from runs of length 2×10^6 time steps. The method of Berne and Harp³ is used to determine the corresponding memory function and eq 2.5 gives $\zeta_r(t)$. The time step was 2×10^{-3} and an average run required 4 h of CPU time on an FPS 264 attached processor. The simulation included 30 solvent atoms and the reacting diatomic molecule. The small size of our system was dictated by the fact that we perform a phase space average for a single impurity. To check for size dependence, we compared our results for 62 solvent atoms with a simulation including 106 solvent atoms and found good agreement.

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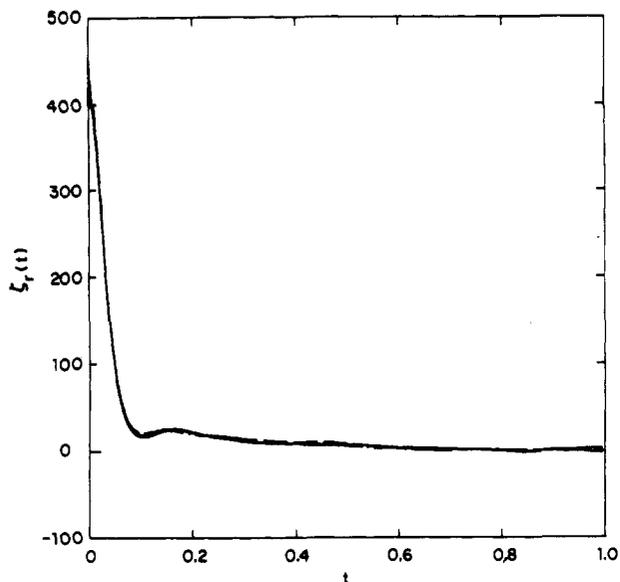


Figure 1. The friction kernel $\zeta_r(t) = \zeta_r(t; x_0, \omega)$ shown as a function of time for three values of the harmonic frequency for the confining potential: $\omega = 15$ (—), $\omega = 20$ (---), and $\omega = 25$ (-·-·-) for $x_0 = 1.25$.

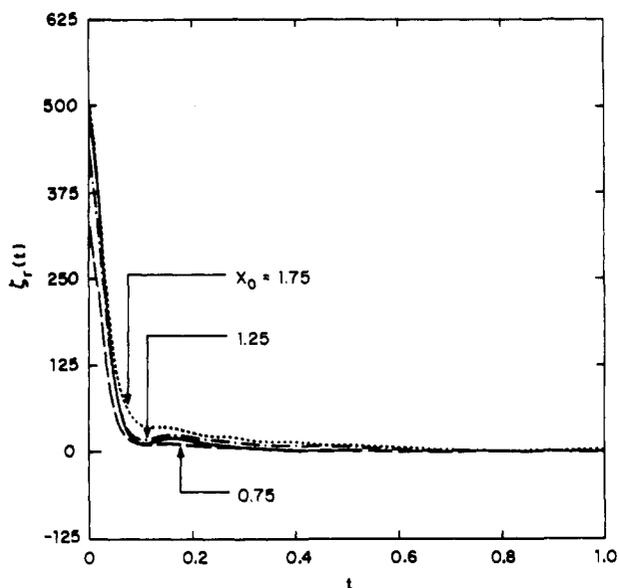


Figure 2. The friction kernel $\zeta_r(t) = \zeta_r(t; x_0)$ shown as a function of time for three values of the minimum of the confining potential: $x_0 = 0.75$ (-·-·-), $x_0 = 1.25$ (---), and $x_0 = 1.75$ (·····). Also displayed is $\zeta_s(t)/2$, which is one-half of the friction for a single solvent atom (—).

4. Results

In Figure 1, $\zeta_r(t; x_0, \omega)$ is presented for $x_0 = 1.25$, corresponding to the barrier position, for three different frequencies $\omega = 15, 20$, and 25 . This figure clearly shows that $\zeta_r(t; x_0, \omega)$ is independent of the harmonic frequency.

The data in Table I show that the initial time value of $\zeta_r(t)$ for different values of ω are within 2% of their mean while the approximate values of the zero frequency friction $\zeta_r(0)$ are within 10% of their mean. [Each run indicated in Table I is the average of one to three simulation runs. Therefore, in computing averages they are not necessarily equally weighted.]

In Figure 2, the dependence of the dynamic friction $\zeta_r(t; x_0)$ on the equilibrium bond length x_0 is presented for $x_0 = 0.75, 1.25$, and 1.75 corresponding to the left well, the barrier, and the right well of the bistable potential. The initial value $\zeta_r(0; x_0)$ increases approximately linearly ($\zeta_r(0; x_0) = 209(q) + 172$) with the average bond length (q) as does the overall dynamic friction $\zeta_r(t; x_0)$. For comparison the dynamic friction experienced by a single solvent atom $\zeta_s(t)$ in the neat fluid at the same temperature and pressure is also shown.

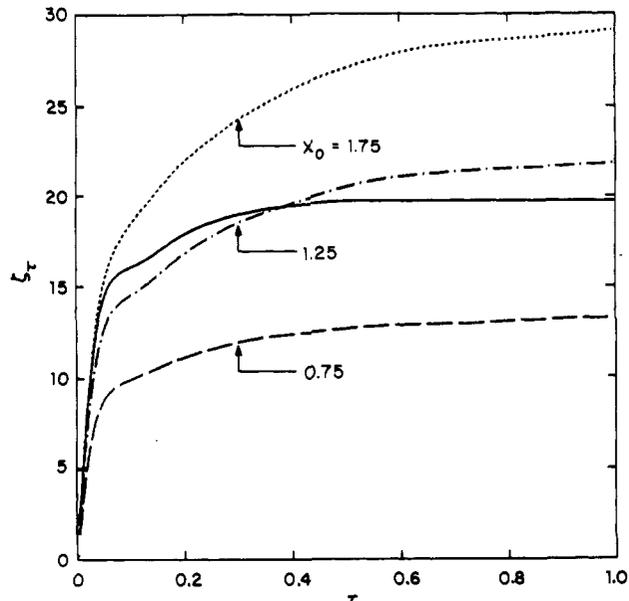


Figure 3. The time-integrated friction kernel $\zeta_\tau = \zeta_\tau(x_0)$, eq 4.1, shown as a function of the endpoint of integration, τ , for the four friction kernels discussed in Figure 2.

The x_0 dependence of the dynamic friction $\zeta_r(t; x_0)$ is magnified by consideration of the integral

$$\zeta_\tau(x_0) = \int_0^\tau dt \zeta_r(t; x_0) \quad (4.1)$$

as a function of τ shown in Figure 3. The static friction constant is given by

$$\zeta_r(x_0) = \lim_{\tau \rightarrow \infty} \zeta_\tau(x_0) = \int_0^\infty dt \zeta_r(t; x_0) \quad (4.2)$$

Figures 2 and 3 show how sensitive the dynamic and static friction constants are to equilibrium bond lengths. The data permit only ball park estimates to be made of the static friction $\zeta_r(x_0)$ because the integrals have not reached clear plateau values. Nevertheless, we tabulate $\zeta_r(0; x_0)$ and $\zeta_r(x_0)$ as a function of x_0 in Table I.

A question that often arises in reaction rate theory is: How is the rate constant for barrier crossing affected by the correlation times of the bath? When the characteristic relaxation times of the bath become long compared to the time spent by the reaction coordinate in the vicinity of the barrier, as measured by the inverse barrier frequency ω_B^{-1} , Hynes and co-workers have persuasively argued⁹ that the effective damping of the reaction coordinate should diminish with the consequence that because there will be fewer solvent-induced rapid recrossings of the barrier than predicted by Kramers' theory¹⁴ the rate constant should be closer to transition-state theory.

To test these ideas, it is necessary to determine $\zeta_r(t)$ for a slow solvent. In the foregoing we studied the case when $m_{A^*} = m_A$. Although the non-Markovian nature of $\zeta_r(t)$ in that case is manifested by a "hydrodynamic" long-time decay of the dynamic friction, the time scales are not so far apart that very large non-Markovian effects are found. However, if m_A is increased for fixed $m_{A^*} = 1$, the solvent modes will become slower and one should expect a large separation of time scales in reaction dynamics.

A series of simulations were undertaken to determine how the dynamic friction depends on the solvent mass m_A . The dependence of $\zeta_r(t; x_0 = 1.25)$ and $\zeta_r(x_0 = 1.25)$, at the barrier, $x_0 = 1.25$, on the solvent mass m_A is presented in Figures 4 and 5 as a function of the time in units of the solute Lennard-Jones time scale ($(m_A \sigma_{AA}^2 / \epsilon_{AA})^{1/2} = 1$). It should be clear from these figures that the dynamic and static friction acting on the reaction coordinate

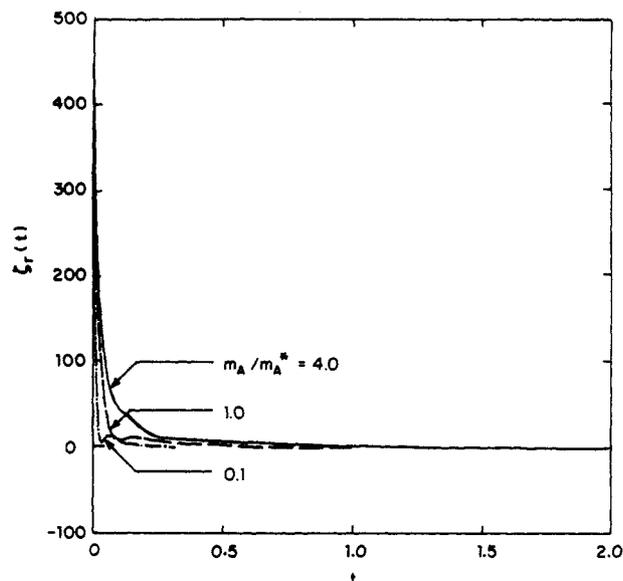


Figure 4. The friction kernel $\zeta_r(t)$ shown as a function of time for three different solvent/solute mass ratios: $m_A/m_{A^*} = 4.0$ (—), $m_A/m_{A^*} = 1.0$ (---), and $m_A/m_{A^*} = 0.1$ (-·-) for $x_0 = 1.25$. The units of time are those of the solute, i.e., $((m_A\sigma_{AA}^2/\epsilon_{AA}))^{1/2} = 1$.

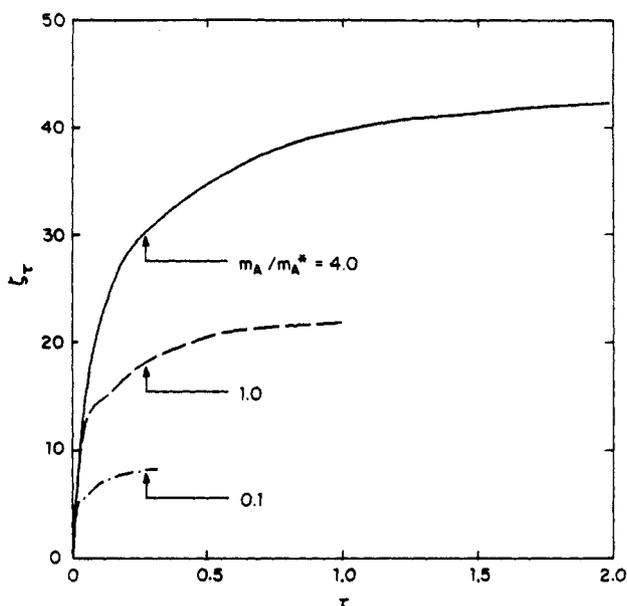


Figure 5. The time-integrated friction kernel ζ_τ , eq 4.1, shown as a function of the endpoint of integration, τ , for the three friction kernels discussed in Figure 4.

is strongly dependent on the solvent mass.

An additional check on our method involves examining the initial time value $\zeta_r(0)$ as the ratio of solute to solvent mass is varied. One expects that the initial value of the memory function $K(t)$, eq 2.5, equal to the mean square force divided by the mean square momentum, should vary as the inverse of the reduced mass while $\zeta_r(0)$ should be mass-independent. Comparing the values of $\zeta_r(0)$ in Table I for the three ratios of solute to solvent mass we find that the initial value is independent of mass to within 7% of the mean.

The dependence of the static friction on the solvent mass is displayed in Table I. In all cases the dynamic friction consists of a rapid short-time decay reflecting the duration of collisions experienced by the reaction coordinate and a long-time decay that has been attributed to the coupling of the reaction coordinate to

hydrodynamic modes of the solvent. In the case where $m_{A^*} = m_A$, there is a well-defined separation of time scales for these two processes. However, when $m_A = 4m_{A^*}$ it appears that the duration of the collision becomes long enough that a clear temporal separation is not apparent. Nevertheless, there are at least two very different time constants characterizing the short- and long-time decay. In the opposite case when $m_A = 0.1m_{A^*}$, $\zeta_r(t)$ relaxes relatively quickly and approaches the Markovian limit.

5. Conclusion

In summary, we have presented an accurate method for the calculation of time-dependent friction kernels for a reactive degree of freedom as a function of the reaction coordinate position. Recently, generalized Langevin equation theories for calculating the rate of chemical reactions as a function of the dynamic properties of the solvent have been developed. This method should prove extremely useful in testing the accuracy and applicability of these theories.

The reaction coordinate may be constrained to the well minimum and the resulting $\zeta_r(t)$ may be used to calculate the energy activation rate. It has been suggested that energy transfer between the reaction coordinate and resonant degrees of freedom in the bath could play an important role in accelerating energy activation.¹⁵ Our method allows one to investigate how the friction on the reaction coordinate depends on the intramolecular frequencies of the solvent, allowing, potentially, for the examination of the detailed coupling of the bath degrees of freedom to the reaction coordinate through the intermolecular potential.

The reaction coordinate may be constrained to the barrier maximum for the calculation of $\zeta_r(t)$. Knowing the frequency dependence of the friction at the barrier allows for accurate calculation of the Grote-Hynes rate constant for saddle crossing.¹⁶ Our results show a strong dependence of $\zeta_r(t)$ on both the particular value of the reaction coordinate position and the solute/solvent mass ratio, indicating that the convenient assumption that the single particle memory function, $\zeta_s(t)$, can be assumed a good estimate for the reaction coordinate friction, $\zeta_r(t)$, may be a bad one in some cases. In fact Bergsma et al.¹⁷ have recently used eq 1.3 to approximate the friction experienced by the reaction coordinate in an S_N2 reaction in rare gas and water.

An important conclusion that can be drawn from the observed dependence of $\zeta_r(t)$ on the solvent mass is that the simple harmonic bath model of the friction, given by eq 1.9, is not even remotely applicable. This model predicts that increasing the solvent mass will lead simply to a rescaling in time of $\zeta_r(t)$ and not a change in its functional form. We observe, however, that the functional form changes. Furthermore, the simple model does not predict the bond length dependence of $\zeta_r(t)$. This can be incorporated by building a bond length dependence into the coupling constants, g_α , but it is highly probable that the friction of the generalized Langevin equation of eq 1.7 should be replaced by a friction that is nonlocal in space as well as in time.¹² In the case of strong bond length dependence of $\zeta_r(t)$, it can be concluded that the GLE (eq 1.7) is not valid for the complete description of the dynamics of the reaction coordinate.

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