

# Theoretical study of memory kernel and velocity correlation function for condensed phase isomerization. I. Memory kernel

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A unified memory kernel function is proposed on the basis of molecular dynamics simulations and comparison with experimental data. A frozen-solvent-like friction arises from the near-neighbor solvent cage effect, while the interaction between the system and the disordered heat bath or "broken cage" gives rise to a white-noise friction. On short time scales, the apparent friction is a "series addition" of these two limits, each solute molecule experiencing either an intact cage or a broken cage environment. For longer time scale behavior, the solvent is able to evolve, and some system molecules can experience both types of environments during the course of their own dynamics: the effective friction for these molecules then appears as a "parallel addition" of the same two contributions. This leads to a memory kernel having a simple exponential behavior. As the time scale for the system dynamics becomes still longer, the cage becomes indistinguishable from the heat bath, and a purely Markoffian relaxation with delta-function memory kernel ensues. This unified memory kernel model has been found to be applicable to ultrafast chemical reaction rates and diffusion properties both in molecular dynamics simulations and laboratory experiments.

## I. INTRODUCTION

Recent molecular dynamics (MD) computations,<sup>1-4</sup> theoretical studies,<sup>5,6</sup> and experimental observations<sup>7</sup> on *cis-trans* isomerization have indicated that the functional form of the memory kernel or TDF (the time dependent friction) may depend on the reacting system variables, including the solute/solvent mass ratio and the form of the barrier potential. This dependence is a necessary consequence of nonlinear coupling<sup>1-6</sup> between the "system" and the neighboring solvent. From a practical point of view, it is the cause in experimental work<sup>8</sup> of the inability to carry over a friction formalism from barrierless experiments to isomerization reactions when a barrier is present. Methods for extending the linear theory of Grote and Hynes<sup>9</sup> thus become a challenge for chemical reaction dynamics, since interactions in any real liquid, even among simple Lennard-Jones particles, are nonlinear.

In the *cis-trans* isomerization problem, the *functional form* of the memory kernel may be vastly different for reacting systems with different barrier potentials.<sup>2,3</sup> This effect is of maximal importance for "ultrafast" reactions when the barrier (or well) frequency is high in comparison with the relevant frequencies of the solvent motion. In such cases the MD results show that the TDF can be expressed as a combination of two limits: (1) a delta function, which represents the Brownian white-noise limit; and (2) a near constant, which represents the frozen solvent limit. This type of memory kernel leads to a specific form of the Grote-Hynes<sup>9</sup> or (extended) Kramers equation.<sup>3,7</sup> For many experimentally examined isomerization reactions having an activation barrier, this model has been found to exhibit a realistic behavior.<sup>7</sup>

On the other hand, the MD simulations have shown that the memory kernel for barrierless systems and low solvent viscosities displays an exponential behavior.<sup>2</sup> The exponential version of the memory kernel has been used frequently because of its mathematical simplicity and because of its relevance to Brownian motion theory.<sup>10-12</sup>

The natural extension of past work is to find a generally valid unified form of the memory kernel that is applicable not only to the above two types of problems,<sup>2,3</sup> but to intermediate cases as well. This is the task of this paper (part I). In a forthcoming paper (part II), we propose an analytical model for the relevant angular velocity autocorrelation function (AVACF). These models will then be applied to the discussion of reaction rates and diffusion properties.

## II. MEMORY KERNEL

The computation of the memory function using MD methods has a long history starting with the elegant work of Berne and Harp,<sup>13,14</sup> and also of Levesque and Verlet.<sup>15</sup> According to the TDF model of Levesque and Verlet, the friction is described by a four-parameter formulation, which is based on molecular dynamics simulations of a pure Lennard-Jones fluid.

$$\zeta(t) = \Omega_0^2 e^{-B_0 t^2/2} + A_0 t^4 e^{-\alpha_0 t}. \quad (1)$$

The short-time Gaussian portion represents a collisional contribution, while the long-time portion represents a collective or hydrodynamic part that ultimately leads to Stokes law friction acting on a macroscopic particle in the fluid. This model was modified by Grote, van der Zwan, and Hynes<sup>16</sup> for higher viscosity liquids, and was then applied to the calculation of rate constants for atom-transfer reactions.

An obvious shortcoming of these models, when applied to chemical reaction dynamics in the condensed phase, is that the fitting parameters  $\Omega_0$ ,  $A_0$ ,  $B_0$ , and  $\alpha_0$  are based on the molecular dynamics of the pure solvent. Information is missing about the influence of the solute on the friction, which is particularly important when the solute particle is not too large and is very dissimilar to the solvent particle.

In a recent paper, Straub, Borkovec, and Berne<sup>4</sup> have discussed the dynamic friction on intramolecular degrees of freedom. With the harmonic approximation of the potential barrier and by constraining the reaction coordinate to either the well minimum or the barrier maximum, these authors found that the functional form of the memory kernel changes with increasing solvent mass. They also found that the friction along the reaction coordinate depends on the bond length. However, no explicit functionality was given.

From a large number of MD simulations of reactant-solvent systems,<sup>1-3</sup> we have found that the memory kernel, within the reactivity period for an isomerization reaction, can be successfully fit to a four-parameter empirical function,

$$\xi(t) = \mathcal{A} + \mathcal{B}\delta(t) + \mathcal{C}e^{-\alpha t}; \quad (2a)$$

or in frequency space,

$$\hat{\xi}(s) = \mathcal{A}/s + \mathcal{B} + \frac{\mathcal{C}}{\alpha + s}, \quad (2b)$$

where  $\mathcal{A}$ ,  $\mathcal{B}$ ,  $\mathcal{C}$ , and  $\alpha$  are positive constants, which depend on the relative "time scales," measured by the intrinsic accelerations, of solute and solvent particles. Some examples are given in Figs. 1-3 corresponding to the five systems described in Table I. As the solvent viscosity increases,  $\mathcal{A}$  increases relative to  $\mathcal{B}$ , and, as the barrier height increases, the value of  $\mathcal{C}$  decreases. Thus, the functional form of the friction can change completely with variations in solute/solvent parameters. The following special cases can arise.

Case 1. Low barrier,  $\mathcal{A} = \mathcal{B} = 0$ :

$$\xi(t) = \mathcal{C}e^{-\alpha t}. \quad (3)$$

This case is depicted in Figs. 1 (lower curve) and 2 (also Fig.

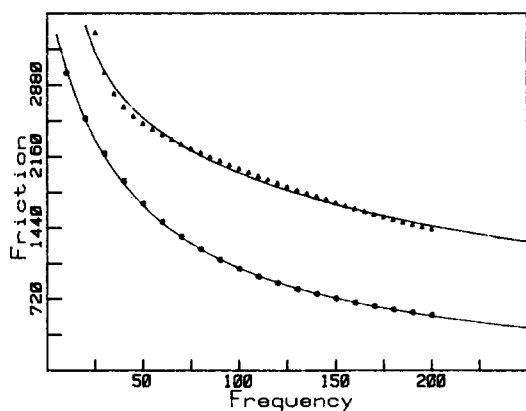


FIG. 1. Memory kernels in frequency space. The symbols represent MD results for system I (lower curve) and system III (upper curve). For both of these systems the barrier height is zero. The solid lines are best fits to the Laplace transform of Eq. (3) and to Eq. (2b), respectively. In all figures, the variables are expressed in conventional Lennard-Jones reduced units.

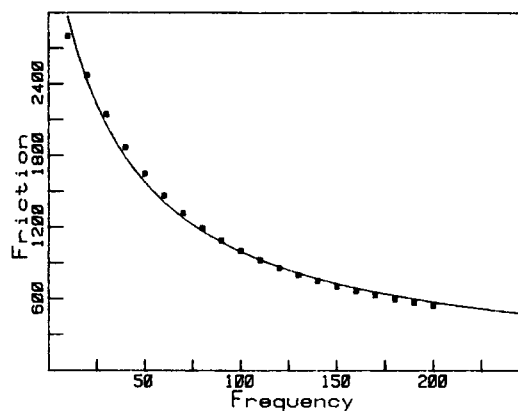


FIG. 2. Memory kernel in frequency space. The symbols represent MD results for system II. The barrier height is only  $3kT$ , the system masses are equal to the solvent masses, and thus the barrier frequency  $\omega_b$  is relatively low for this system. The solid line is a best fit using the Laplace transform of the "barrierless" memory kernel in Eq. (3).

2 of Ref. 2). If the mass of the reacting system with zero barrier is comparable to or greater than that of solvent molecules, this formalism provides a reasonable description of rotational diffusion.<sup>17</sup> In fact, Fig. 2 illustrates that when the reacting particle is similar in size and mass to the solvent particle, Eq. (3) may still be a good description of the memory kernel even though the barrier frequency does not equal to zero.

Case 2. High barrier,  $\mathcal{C} = 0$ :

$$\xi(t) = \mathcal{A} + \mathcal{B}\delta(t). \quad (4)$$

Equation (4) is particularly important for liquid phase isomerizations, having been investigated in detail in previous papers.<sup>2,3</sup> Examples are depicted in Fig. 3. As the viscosity increases, the first term starts to dominate the second, until a

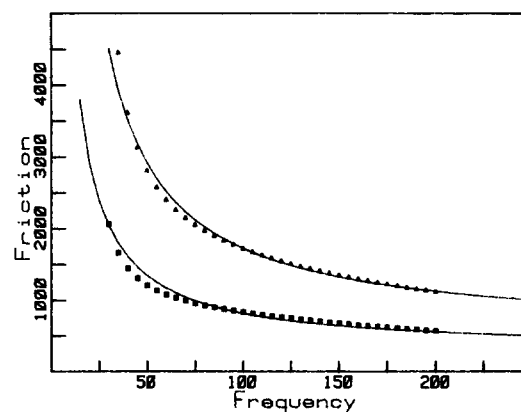


FIG. 3. Memory kernels in frequency space. The symbols represent MD results for systems IV ( $\times$ ) (upper curve) and V (lower curve). For both of these nonzero barrier cases, the system masses are small compared with the solvent masses. Thus, the barrier frequencies  $\omega_b$  are relatively high, and the time scale for system motions is short compared to that for solvent motions. The best fits of  $\hat{\xi}(s)$  (shown as solid lines) over this relevant frequency range are given by the Laplace transform of Eq. (4). As indicated already in Ref. 2, the "knees" in these curves near reduced frequencies of 75 are poorly represented by the barrierless form of the memory kernel.

TABLE I. Input data and fitting parameters.

System <sup>a</sup>	<i>M/m</i>	<i>V<sub>0</sub>/kT</i>	<i>ω<sub>b</sub></i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>α</i>
I	1	0	0	0	0	135.8	33.47
II	1	3	18.05	0	0	134.7	35.39
III	1/16	0	0	215.76	0	5581.77	213.76
IV	1/16	3	72.186	901.84	7.40	0	0
V	1/16	5	93.19	1194.56	5.28	0	0

<sup>a</sup>In reduced units, the Lennard-Jones parameters  $\sigma$  and  $\epsilon$  have the value unity for all solvent and solute particles. The best fitting parameters are in arbitrary units. The standard deviations are in the range from 1.9% to 3.5%.

virtually constant TDF is reached. This is the frozen solvent or matrix isolation limit.

Case 3. High barrier, low viscosity,  $A \approx 0$ ,  $C = 0$ :

$$\xi(t) \approx B\delta(t). \quad (5)$$

In this case, the memory kernel becomes approximately Markoffian.

In general the full Eq. (2) must be used to map reaction processes in an intermediate regime. This is illustrated by the upper curve in Fig. 1. Comparing this curve with the curve in Fig. 2, we notice that the form of  $\hat{\zeta}(s)$  and thus  $\zeta(t)$  is governed by the relative time scales of the reactive motion and the solvent motion. The former is described by the barrier frequency (determined by mass of reactive particles, height of barrier). The latter depends on the solvent viscosity. Although systems II and IV possess the same barrier height, system II represents a "slow" motion [exponential version of  $\zeta(t)$ ] because of the similarity in mass and size of the reactive particles to the solvent particles. System IV, because of its much lighter reactive mass, presents a "fast" solute motion, and its  $\zeta(t)$  is thus described more accurately by Eq. (4). System III, though barrierless (small "chemical" forces) but with a very light system mass, belongs to the intermediate case. Its TDF must therefore be described by the full expression (2a). The best fitting parameters for these five systems are listed in Table I.

### III. PHYSICAL PICTURE

To see how these cases and the general case in Eq. (2) may arise, we consider the following. By the fluctuation-dissipation theorem, the TDF is equal to the normalized random force autocorrelation function.<sup>18</sup> The TDF, according to the Wiener-Khintchine theorem,<sup>19</sup> can furthermore be expressed in terms of the cosine transform of the power spectrum  $D(\omega)$  of fluctuations in the random force.

$$\xi(t) = \frac{1}{2\pi} \int_0^\infty D(\omega) \cos \omega t d\omega. \quad (6)$$

This approach to chemical reaction dynamics was recently rekindled by Pollak.<sup>20</sup> More recently it was pointed out by ourselves,<sup>2</sup> and also by Zwanzig,<sup>21</sup> that the calculation (MD) or estimation of such power spectra would provide an alternate approach to the determination of the memory kernel for real systems. This is certainly true in the bilinear system/bath coupling regime,<sup>20</sup> but the approach may also be applicable to certain nonlinear problems, as already evi-

dent from the work of Lindenberg and her co-workers<sup>5</sup> and of Grigolini.<sup>6</sup>

It is easiest to visualize the desired connections using frequency-space friction  $\hat{\zeta}(s)$ . The Laplace transform of Eq. (6) yields,

$$\hat{\zeta}(s) = \frac{1}{2\pi} \int_0^\infty D(\omega) \frac{s}{s^2 + \omega^2} d\omega. \quad (7)$$

Now consider a simple spectral density function that is white (constant in  $\omega$ ) at low frequencies but has a cutoff  $\omega_0$ ,

$$D(\omega) = 4\kappa \quad 0 \leq \omega \leq \omega_0,$$

$$D(\omega) = 0 \quad \omega > \omega_0,$$

where  $\kappa$  is a constant. In this model,

$$\hat{\zeta}(s) = \frac{2\kappa}{\pi} \tan^{-1} \frac{\omega_0}{s}, \quad (8)$$

which leads, for small  $\omega_0/s$ , to,

$$\hat{\zeta}(s) = \frac{2\kappa}{\pi} \left[ \frac{\omega_0}{s} - \frac{1}{3} \left( \frac{\omega_0}{s} \right)^3 + \dots \right] \approx \frac{2\kappa}{\pi} \frac{\omega_0}{s};$$

and for large  $\omega_0/s$ , to,

$$\hat{\zeta}(s) = \frac{2\kappa}{\pi} \left[ \frac{\pi}{2} - \frac{s}{\omega_0} + \dots \right] \approx \kappa.$$

Each of the first two terms of Eq. (2b) have one of these forms, indicating perhaps that the spectral density in MD or experimental systems can be approximated as having a low frequency branch  $\omega_0^{(-)}$  and a high frequency branch  $\omega_0^{(+)}$  relative to relevant frequencies  $s$  of the solute.

In time space, the TDF of Eq. (8) has the form  $(2\kappa/\pi)t \sin \omega_0 t$ , which decays at short times like, but a bit faster than,  $(2\kappa\omega_0/\pi) \exp[-\omega_0^2 t^2/6]$ . Thus, the connection between our proposed TDF for ultrafast reactions and that proposed by Levesque and Verlet in Eq. (1) for pure fluids is not so different as it might at first appear.

To understand further the physical meaning of this friction model, it is illuminating to divide the surrounding solvent into two parts: (1) the inner core (or "cage"), which is comprised of nearest solvent neighbors; and (2) the outer core (or heat bath), which is made up from the remainder of the solvent. This picture is qualitatively similar to the one proposed some time ago by Adelman,<sup>22</sup> and in a different context by Zwanzig.<sup>23</sup> On short time scales, the cage is relatively stable and the forces are slowly varying. This corresponds to the frozen-solvent-like friction. Both the "stiffness" of the cage and the number of solvent molecules comprising the inner core are related to the solvent viscosity. In this picture, the resultant potential field inside the cage does not grow infinitely with increasing solvent viscosity. Only the number of molecules contained in the cage becomes larger, and the temporal persistence of the cage becomes greater. Thus, at high viscosities, the influence from outer core molecules is diminished and the local effective friction displays the "saturation effect" mentioned in Refs. 2 and 3.

Interactions between the reacting system and the rapidly fluctuating outer core solvent molecules conform to a white-noise model. This Markoffian contribution is most important when the solvent viscosity is so low that the cage is not sufficiently rigid to "screen" solute motions from the

continually disruptive influence of the outer core. At low viscosities, one can say that a limit is being approached where the local solvent *interchange time* is fast compared with the reaction time. When this limit is reached, the cage effectively disappears, and a purely white-noise contribution remains. Typically, however, in ultrafast reaction kinetics, some intermediate case will apply.

#### IV. UNIFIED FRICTION

All dynamical time scales of the solute can be taken into account if it is assumed that the solute can be divided into a fraction  $\Omega_2$  undergoing "sufficiently fast" time scale dynamics and another fraction  $(1 - \Omega_2)$  undergoing "slow" time scale dynamics. As suggested above, the solvent time scale here refers to a solvent interchange time at the reaction interface, or equivalently to the lifetime of the solvent cage. This view will be seen to be consistent with the time scale arguments used here. As the reactive mass of the solute is decreased relative to the solvent mass and the barrier forces are increased,  $\Omega_2 \rightarrow 1$ .

It can also be assumed that at any given instant of time, the solvent environment neighboring a solute is either an intact cage with weight  $\Omega_1$  or a broken cage with weight  $(1 - \Omega_1)$ . As the solvent viscosity increases,  $\Omega_1 \rightarrow 1$ .

For the  $\Omega_2$  fraction of solute molecules undergoing fast time scale dynamics, an initially existing solvent state cannot change during the solute dynamics. For some solute molecules, this is an intact cage with friction  $\hat{\zeta}_c$ ; for others it is a broken cage, with white-noise friction  $\hat{\zeta}_w$ . Thus, for fast time scale solute reactions, the dynamics appears as a weighted average<sup>3</sup> of the dynamics corresponding to the intact cage environment and the broken cage environment. The friction is a weighted sum, as in a series electrical resistance circuit.<sup>3</sup>

The remaining solute fraction  $(1 - \Omega_2)$  comprises those solute molecules having slow time scale dynamics relative to the solvent motions. Such solute molecules are subjected to an environment that changes between intact cage and broken cage during their reactive excursions, the dynamical path being dominated by the one having lowest friction as in a parallel resistance circuit<sup>3</sup>:

$$\hat{\zeta}_{cw}^{-1} = \Omega_1 \hat{\zeta}_c^{-1} + (1 - \Omega_1) \hat{\zeta}_w^{-1}.$$

In this scheme, the overall frequency-dependent friction, which takes into consideration an ensemble of variously behaving solute molecules, would be given by,

$$\hat{\zeta} = \Omega_1 \Omega_2 \hat{\zeta}_c + (1 - \Omega_1) \Omega_2 \hat{\zeta}_w + (1 - \Omega_2) \hat{\zeta}_{cw}, \quad (9)$$

where, referring to Eq. (8),  $\hat{\zeta}_c \approx 2\pi^{-1} \kappa^{(-)} \omega_0^{(-)}$  and  $\hat{\zeta}_w \approx \kappa^{(+)}$ . Equation (9) incorporates the fact that, as the time scale of the reactive particles becomes fast compared with the time scale of the solvent, both  $\Omega_1$  and  $\Omega_2$  tend toward unity. Because of the form of the Grote-Hynes dynamical equations for barrier crossing, summing the three contributions to the friction, as in Eq. (9), is equivalent to averaging over the barrier crossing dynamics of the variously behaving solute molecules. Of course, if the solute dynamics is sufficiently fast and the instrumental detection capabilities in a laboratory experiment are good enough, the average here may not be appropriate. The dynamics of sets of individually

behaving reacting molecules may be resolvable. This situation would result in a nonexponential decay.

Equation (9) is exactly equal to the four-parameter empirical expression of Eq. (2) if the following connections are made,

$$\mathcal{A} = 2\pi^{-1} \Omega_1 \Omega_2 \kappa^{(-)} \omega_0^{(-)},$$

$$\mathcal{B} = (1 - \Omega_1) \Omega_2 \kappa^{(+)},$$

$$\mathcal{C} = 2\pi^{-1} \kappa^{(-)} \omega_0^{(-)} (1 - \Omega_2) / \Omega_1,$$

$$\alpha = 2\pi^{-1} \kappa^{(-)} / \kappa^{(+)} \omega_0^{(-)} (1 - \Omega_1) / \Omega_1.$$

The four independent parameters are now  $2\pi^{-1} \kappa^{(-)} \omega_0^{(-)}$ ,  $\Omega_1$ ,  $\Omega_2$ , and  $\kappa^{(+)}$ . Using these relationships in Eq. (2b) shows that, for any value of  $\Omega_2$ ; purely "cage friction" is obtained in the high viscosity limit,  $\Omega_1 \rightarrow 1$ , and purely "white-noise friction" arises in the low viscosity extreme,  $\Omega_1 \rightarrow 0$ .

#### V. SUMMARY

To probe more deeply into the fundamental physical characteristics of condensed phase reaction dynamics, we propose an intuitive model in which the "bath" is divided into solvent molecules in an "inner" region and an "outer" region. On time scales short with respect to the solvent "motion," the inner and outer regions remain intact. The inner region, which is stiff and stable on these time scales, provides a frozen-solvent-like friction. The interaction between the solute and outer-region solvent gives rise to a white-noise friction of the Markoffian type. The overall friction felt by the system, in the case where the cage lifetime is long compared with the reaction time, is a weighted sum of these two limiting components. When a slow reaction is considered, the cage concept is no longer applicable, since the cage and the remainder of the heat bath are changing roles on a time-scale faster than the reaction time. The apparent friction is determined by a parallel addition of the same two friction components, giving rise to an exponentially decaying memory kernel.<sup>3</sup>

These results seem to be telling us that even when nonlinearities and non-Brownian time scales are present in the reaction dynamics, it is still possible to use a *phenomenological* generalized Langevin equation, and thus the Grote-Hynes<sup>9</sup> (or extended Kramers<sup>7</sup>) reaction rate formalism, *providing the form of the friction is adjusted for each situation*. This paper suggests a possible form for this friction. In fact, this form of the friction has already been seen to work very well for laboratory experiments<sup>7</sup>; and, in this paper, it is seen to be a reasonable model for MD data as well.

In a future paper (II), we will utilize the above friction model to extend the Grote and Hynes<sup>9</sup> description of activated chemical rate processes. Assuming the potential is harmonic and a generalized Langevin equation is applicable to the reaction process of interest, we will be able to calculate angular velocity autocorrelation functions for the systems listed in Table I and compare them with the AVACFs from MD calculations on these systems. Since the AVACFs sample different regions of the reaction coordinate than the friction, and the models investigated here are nonlinear, the usual connections between these two functions have to be

considered with great care. An AVACF averaged over all system trajectories should not be related in any simple way to the friction near the barrier top.

## ACKNOWLEDGMENTS

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