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Impulsive stochastic models of molecular relaxation and isomerization reactions

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We discuss several aspects of the problem of modeling the effect of collisions on isomerization reactions. We show how to generate stochastic dynamics for systems which suffer more than one type of collision, and derive the appropriate master equation for the phase space distribution function. We discuss a variety of different collision models and sketch how one might deduce the form and parameters of the model from experiment and molecular dynamics. Finally, we examine a one-dimensional model of an isomerization reaction in the presence of two types of collisions, finding that the reaction rate varies nonlinearly with the various collision rates.

INTRODUCTION

Isomerization dynamics can often be described by a single reaction coordinate. It is then equivalent to the motion of a particle in a multistable potential. When the energy barriers of this potential are large compared to thermal energies, passage over the barriers is infrequent. Several studies¹⁻⁴ indicate that the solvent plays a fundamental role in the dynamics. The packing of solvent molecules can drastically affect the potential energy associated with the reaction coordinate, and "collisions" with the solvent enable the system to gain sufficient energy to traverse the energy barriers, and to lose energy and relax into one of the potential wells. In addition, at high collision rates, the Newtonian motion of the system can be so strongly perturbed as to make the motion Brownian.

The complicated many-body dynamics encourages one to invoke a stochastic model. Kramers was the first to do this.¹ Implicit in his model was the notion that the momentum conjugate to the reaction coordinate could change only by very small increments, and furthermore that these small increments occurred very frequently. This model is thus very specific about the dynamics and leads to a definite prediction about the dependence of the rate constants on the "momentum correlation time," τ_p , or friction constant. This model has provided great insight into the underlying reaction dynamics, and its high friction limit (small step diffusion model) is often adopted as the canonical model for the process.

It is important to determine to what degree the results of stochastic modeling are dependent on the particular stochastic model. If there is great sensitivity to the model one must be careful to define a stochastic model appropriate to the particular system. Skinner and Wolynes³ and Montgomery *et al.*⁴ have studied a stochastic model in which large impulsive momentum

changes are involved. The dependence of rate constants on τ_p for this BGK model⁵ is significantly different from that exhibited by Kramers' model. Skinner and Wolynes, and Berne have independently discussed even more general stochastic models for which the differences are still more marked.⁶ All of these models predict that the rate constant first rises linearly with τ_p^{-1} (with a model dependent slope), reaches a maximum, and then falls off at high collision rates, eventually reaching the same asymptotic small step behavior proportional to τ_p . The maximum value of the rate constant falls well below the transition state theory prediction.

The above comparisons were made for stochastic motion in one dimension. These models can be generalized to higher dimensionality. Analytic approaches become progressively more cumbersome as the dimensionality increases. Here the simulation of stochastic dynamics on a computer has significant advantages. The work of Montgomery *et al.*⁴ shows how impulsive stochastic models can be simulated. The simulation of such models requires far less computer time than does full molecular dynamics. The rich variety of stochastic models (and the sensitivity of the results to the model) makes it necessary to examine carefully the correspondence between any particular system and a model. The parameters describing a model must be independently determined. The kinetic theory of dense polyatomic fluids, still in its infancy, might eventually be used to determine appropriate stochastic models. Nevertheless, at this stage, we must depend on experiment or molecular dynamics for this information.

In this paper we address several issues relating to the stochastic modeling of real systems. We show how to model systems in which there are several different kinds of collisions. For example, we have in mind the case of molecules like the *n*-alkanes where the atoms can each experience a collision with a solvent molecule. Some parts of the molecule will be shielded from collisions with the solvent by other parts of the molecule, and this will lead to different collision frequencies, or indeed, models for the various atomic sites. Still an-

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other example is that of a fluid, where the forces on the reaction coordinate can often be decomposed into a long range soft force and a short range repulsive force. The reaction coordinate can then be thought to suffer two kinds of collisions (hard and soft) with different collision frequencies. Rice and Allnatt⁷ used a similar model to describe transport in simple fluids, finding that the hard forces were the main contribution to the friction constant. In charged systems, soft forces can be a major contributor to friction.⁸ In addition, long range forces can provide coupling to high frequency motions in the solvent which can compete as an effective energy loss channel. One might also imagine modeling the interaction of the reaction coordinate with other degrees of freedom in the same molecule, by an effective collisional picture distinct from collisions with the bath. Below we show how such a variety of models can be simulated by effective dynamics. We then study a particular example in some detail. An interesting result is that the addition of only a small fraction of collisions of one kind can perturb the rate constant dramatically. Finally we suggest ways to parametrize collision models using molecular dynamics information.

II. IMPULSIVE STOCHASTIC DYNAMICS

As an alternative to Langevin dynamics in which the molecules experience continuous dissipative terms (frictional forces), one can consider impulsive stochastic schemes in which particles follow ordinary classical trajectories on a potential energy surface (Hamiltonian flow) except for certain instants when they suffer collisions of zero duration.

In this scheme it is necessary to specify the times at which the impulsive collisions take place. For simplicity we assume that the collisions are statistically independent events of zero duration. In any real dense system the collisions are correlated, but such correlations are at the present time rather difficult to model. Let us assume that the molecule can experience several different kinds of impulsive collisions, and let $\alpha_j^{-1} = \tau_j$ be the mean time between collisions of type j . Given the statistical independence of the collisions, it follows that the probability of a molecule experiencing n_j collisions of type j in the time t is

$$P_{n_j}^{(j)}(t) = \frac{1}{n_j!} (\alpha_j t)^{n_j} e^{-\alpha_j t}. \quad (2.1)$$

It follows from this that the probability of a molecule experiencing n_1, n_2, n_3, \dots collisions of types 1, 2, 3, ... in the time t is

$$P_{n_1, n_2, \dots, n_j}(t) = \prod_j P_{n_j}^{(j)}(t). \quad (2.2)$$

The Hamiltonian flow of the molecule between these collisions of zero duration can be described by the propagator

$$\hat{G}_0(t) = e^{-iL_0 t}, \quad (2.3)$$

where the Liouville operator L_0 is given by

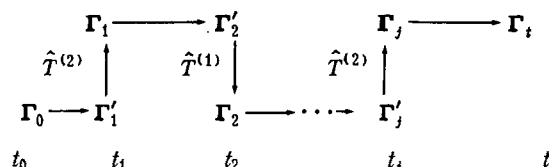
$$iL_0 = \sum_k \left(\frac{\mathbf{p}_k}{m_k} \cdot \frac{\partial}{\partial \mathbf{r}_k} + \mathbf{F}_k \cdot \frac{\partial}{\partial \mathbf{p}_k} \right), \quad (2.4)$$

where $\{\mathbf{r}_k, \mathbf{p}_k\}$ are the positions and momenta specifying the state Γ of the free molecule, and $\{\mathbf{F}_k\}$ are the forces arising from the intramolecular potential (as well as any external forces present).

When a collision occurs the state of the molecule $\Gamma' = \{\mathbf{r}_k', \mathbf{p}_k'\}$ changes instantaneously to a new state $\Gamma = \{\mathbf{r}_k, \mathbf{p}_k\}$. The precise outcome of the collision depends not only on the initial state of the molecule, but also on the state of the bath particle with which it collides. Since we are not concerned with a complete specification of the bath, we must provide a statistical definition of the collision process. To this end we define a conditional probability distribution $T^{(j)}(\Gamma|\Gamma')$, such that $T^{(j)}(\Gamma|\Gamma') d\Gamma'$ gives the probability that a molecule in state Γ' (in $d\Gamma'$) prior to collision of type j will be found in state Γ after collision. Thus the effect of a collision is represented as an integral operator

$$\hat{T}^{(j)} A(\Gamma) = \int d\Gamma' T^{(j)}(\Gamma|\Gamma') A(\Gamma'). \quad (2.5)$$

A typical stochastic trajectory can be represented schematically by



Here the molecule initially in state Γ_0 evolves freely (collisionlessly) on its potential surface until at time t_1 , when it is in state Γ'_1 , it suffers a collision of type 2 and then instantaneously changes state to Γ_1 whereupon it evolves freely to state Γ'_2 at time t_2 , suffers a collision of type 1, etc.

The propagator for this particular trajectory is

$$\hat{G}(t) = \hat{G}_0(t - t_j) \hat{T}^{(2)} \dots \hat{G}_0(t_3 - t_2) \hat{T}^{(1)} \hat{G}_0(t_2 - t_1) \hat{T}^{(2)} \hat{G}_0(t_1). \quad (2.6)$$

Starting from Γ_0 , there are many trajectories each having quite different sequences of collisions, and different collision times. Let us define $\langle G(t) \rangle_{\{n_j\}}$ as the "average" propagator characterizing all those trajectories in which there is a given number of collisions of each type $\{n_j\}$ in the time t irrespective of the precise times of these collisions. Simple considerations enable us to derive an expression for this average propagator. Suppose that at time τ , we know the quantity $\langle G(\tau) \rangle_{n_1, n_2, \dots, n_{j-1}}$. Now a collision of type j can occur between τ and $\tau + d\tau$ with probability $\alpha_j d\tau$. Suppose no other collision occurs between τ and t so that the system propagates freely. This will occur with probability $P_{\{0\}}(t - \tau)$.

Then we have a contribution

$$P_{\{0\}}(t - \tau) \hat{G}_0(t - \tau) (\alpha_j d\tau) \hat{T}^{(j)} \langle G(\tau) \rangle_{n_1 \dots n_{j-1}} \dots \quad (2.7)$$

If this result is summed over all kinds of collisions j and integrated over all times $\tau = (0, t)$ for this last collision we arrive at the result

$$\begin{aligned} \langle G(t) \rangle_{n_1 \dots n_j} = & \sum_j \alpha_j \int_0^t d\tau P_{\{0\}}(t - \tau) \\ & \times \hat{G}_0(t - \tau) \hat{T}^{(j)} \langle G(\tau) \rangle_{n_1 \dots n_{j-1}}. \end{aligned} \quad (2.8)$$

The propagator

$$\langle G(t) \rangle \equiv \sum_{\{n_j\}} \langle G(t) \rangle_{\{n_j\}} \quad (2.9)$$

represents the effect of all possible sequences of collisions occurring between 0 and t , properly weighted by the frequency of these collisions. Remembering that $\langle G(t) \rangle_{\{0\}} = P_{\{0\}}(t) \hat{G}_0(t)$ we can sum the terms in Eq. (2.9) and by taking the derivative show that

$$\left(\frac{\partial}{\partial t} + iL_0 \right) \langle G(t) \rangle = - \sum_j \alpha_j (1 - \hat{T}^{(j)}) \langle G(t) \rangle. \quad (2.10)$$

This is readily turned into an equation for $f(\Gamma, t)$, the probability distribution of the state Γ , at time t . Since

$$f(\Gamma, t) = \langle G(t) \rangle f(\Gamma, 0), \quad (2.11)$$

operation on $f(\Gamma, 0)$ from the left with Eq. (2.11) gives

$$\left(\frac{\partial}{\partial t} + iL_0 \right) f(\Gamma, t) = + \sum_j \alpha_j \int d\Gamma' \{ T^{(j)}(\Gamma | \Gamma') f(\Gamma', t) - T^{(j)}(\Gamma' | \Gamma) f(\Gamma, t) \}, \quad (2.12)$$

where we have inserted Eq. (2.5) into Eq. (2.10) and used the property of the conditional probability that

$$\int d\Gamma' T^{(j)}(\Gamma' | \Gamma) = 1. \quad (2.13)$$

The preceding approach shows how the underlying impulsive stochastic dynamics leads to the master equation. If the transition probability for each collision satisfies detailed balance, that is, if

$$T^{(j)}(\Gamma' | \Gamma) e^{-\beta H_0(\Gamma)} = T^{(j)}(\Gamma | \Gamma') e^{-\beta H_0(\Gamma')}, \quad (2.14)$$

then, as is well known, an H theorem can be demonstrated and the distribution function will approach the equilibrium distribution function, $e^{-\beta H_0(\Gamma)}$. Therefore we require that the $\{T^{(j)}(\Gamma | \Gamma')\}$ satisfy Eq. (2.14).

To solve Eq. (2.12) subject to an initial distribution $f(\Gamma, 0)$ we merely have to simulate an effective dynamics in the following way:

(a) Sample a set of initial states from $f(\Gamma, 0)$.

(b) For each initial state sample a sequence of collision times. This is done by sampling a set of times for each kind of collision j from

$$P_{0j}(t) = e^{-\alpha_j t}, \quad (2.15)$$

and then ordering these times. Thus each initial state will have a sequence of collisions each at a stated time.

(c) For each initial state (together with its set of collision times) we generate an effective trajectory by the following method. Solve the Hamiltonian equations for H_0 until the first collision occurs. At the instant of this collision which is of known kind (say, j), sample a new state from $T^{(j)}$, then continue the free motion subject to this new state until the next collision occurs. This is repeated until time t .

(d) Step (c) generates an ensemble of trajectories. We can thus determine the distribution of states at any time t given the initial distribution. This distribution is the solution of Eq. (2.12).

In the case of a molecule containing multiple collision sites there are several kinds of models. We mention one in particular. Suppose each site can experience only one kind of collision. Then the index j designates the j th site and $T^{(j)}(\Gamma | \Gamma')$ designates the collision dynamics for this site and can be taken as

$$T^{(j)}(\Gamma | \Gamma') = \delta(\mathbf{r}_j, \mathbf{p}_j | \mathbf{r}'_j, \mathbf{p}'_j) \times \prod_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r}'_i) \delta(\mathbf{p}_i - \mathbf{p}'_i). \quad (2.16)$$

This simply means that during a collision with site j only the state (position and momentum) of site j changes, and this kind of collision occurs with frequency α_j . If the collisions are instantaneous, then during a collision of type j only the momentum of this site can change and we can express

$$T^{(j)}(\mathbf{r}_j, \mathbf{p}_j | \mathbf{r}', \mathbf{p}'_j) = \tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j) \delta(\mathbf{r}_j - \mathbf{r}'). \quad (2.17)$$

For $T^{(j)}(\Gamma | \Gamma')$ to be normalized and to satisfy detailed balance it follows that

$$\int d\mathbf{p}_j \tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j) = 1, \quad (2.18)$$

$$\frac{\tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j)}{\tau^{(j)}(\mathbf{p}'_j | \mathbf{p}_j)} = \frac{\phi_0(\mathbf{p}_j)}{\phi_0(\mathbf{p}'_j)}, \quad (2.19)$$

where $\phi_0(\mathbf{p}_j)$ is the Maxwell distribution function.

There are clearly many possible models, and we list only a few below:

$$\tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j) = \phi_0(\mathbf{p}_j), \quad (2.20)$$

$$\tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j) = \delta(|\mathbf{p}_j| - |\mathbf{p}'_j|) / 4\pi p_j^2, \quad (2.21)$$

$$\tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j) = [2\pi m_j kT(1 - \psi_j^2)]^{-3/2} \times \exp - [(\mathbf{p}_j - \psi_j \mathbf{p}'_j)^2 / 2m_j kT(1 - \psi_j^2)]. \quad (2.22)$$

In the first model [Eq. (2.20)], the collision thermalizes the momentum, that is, the new momentum \mathbf{p}_j is totally uncorrelated with the old momentum \mathbf{p}'_j , and is sampled from a Maxwell distribution. This is the BKG model.⁵ In the second model [Eq. (2.21)], the collision does not change the magnitude of the momentum, but randomizes its direction. These two models are similar in spirit to the J and M diffusion models used to describe rotational diffusion.⁹ The third, more general, model contains a parameter ψ_j which specifies how the momentum \mathbf{p}_j after a collision is correlated with the old momentum \mathbf{p}'_j ,

$$-1 \leq \frac{\langle \mathbf{p}_j \cdot \mathbf{p}'_j \rangle}{\langle p_j^2 \rangle} = \psi_j \leq 1. \quad (2.23)$$

ψ_j is just the value of the average velocity correlation function after one impulsive event. Three limiting cases of interest are as follows: when $\psi_j \approx 1$, only small momentum changes of the test particle can occur and the Brownian motion limit of Kramers is recovered; when $\psi_j = 0$, there is no correlation and the situation is described by Eqs. (2.20) and (2.21); and when $\psi_j \approx -1$, the momentum is nearly reversed upon collision. In one dimension, an approximate treatment^{6a} of hard sphere scattering¹⁰ leads to a transition probability of the form,

Eq. (2.22), with

$$\psi_j = (1 - \gamma_j)/(1 + \gamma_j), \quad (2.24)$$

where γ_j (in the exact theory¹⁰) is the mass ratio

$$\gamma_j = m_{\text{solvent}}/m_j. \quad (2.25)$$

In this one-dimensional approximation, the three limits discussed above occur respectively when $\gamma_j \approx 0$ (Rayleigh limit), $\gamma_j = 1$ (BGK), and $\gamma_j \approx \infty$ (Lorentz limit). This one-dimensional kernel was first used by Widom in a study of the rough circle model.¹¹

Another kind of model that should not be difficult to develop is one in which a collision affects the different components of the momentum of particle j differently. For example, if \mathbf{u}_{ji} denotes the direction of a chemical bond pointing from atom i to atom j and p_{\parallel} and p_{\perp} denote the components of the momentum of j parallel and perpendicular to this bond, then it is possible to define a collision model

$$\tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j) = \tau_1(p_{\parallel} | p'_{\parallel}) \tau_2(p_{\perp} | p'_{\perp}), \quad (2.26)$$

where τ_1 , τ_2 define the outcome of the collisions.

A quite different collisional model is one in which during a collision all the atoms suffer changes in the momenta, albeit with different outcomes. Then the sum over j reduces to one term, but

$$T(\mathbf{\Gamma} | \mathbf{\Gamma}') = \prod_{j=1}^n \tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j) \delta(\mathbf{r}_j - \mathbf{r}'_j), \quad (2.27)$$

where each $\tau^{(j)}(\mathbf{p}_j | \mathbf{p}'_j)$ can be different. For example, atoms buried on the inside of molecules may feel only the long range forces and may thus experience only small momentum changes, whereas those on the surface may experience strong momentum changes. One can be more general and again have the molecule suffer different kinds of collisions as a whole. For example, one can imagine a collision as occurring now near one side of the molecule and then near another. Then atoms near the collision sites suffer different momentum changes than those far from it. Each $T^{(j)}(\mathbf{\Gamma} | \mathbf{\Gamma}')$ corresponds to a collision site on the surface of the molecular. It is clear that one can invent many imaginative models for impulsive stochastic trajectories.

To see how one might estimate the parameters of a particular model from, for example, an experimental knowledge of the diffusion constant, let us first inspect the momentum relaxation in the various models. Letting

$$\langle \mathbf{p}_i(t) \rangle_0 = \int d\mathbf{\Gamma} \mathbf{p}_i f(\mathbf{\Gamma}, t) \quad (2.28)$$

be the average momentum of particle i given that the initial distribution is $f(\mathbf{\Gamma}, 0)$, we can easily derive an equation of motion for these averages. The results are

$$\frac{\partial}{\partial t} \langle \mathbf{p}_i(t) \rangle_0 = \langle \mathbf{F}_i(t) \rangle_0 - \beta_i \langle \mathbf{p}_i(t) \rangle, \quad (2.29)$$

where $\langle \mathbf{F}_i(t) \rangle_0$ is the average intramolecular force acting on particle i at time t given that the initial distribution is $f(\mathbf{\Gamma}, 0)$ and where β_i has different definitions depending on whether each collision affects one and only one site at a time (the first class of collision models) or each col-

lision affects all the sites at the same time. In the one site models

$$\beta_i = \alpha(1 - \psi_i), \quad (2.30a)$$

whereas in the many site models

$$\beta_i = \alpha(1 - \psi_i). \quad (2.30b)$$

Here α_i is the collision rate for site i , whereas α is the collision rate for the whole molecule. Of course, ψ_i can still be different for the different sites.

In the simplest models all sites are assumed to have the same value $\beta_i = \beta_0$. The relaxation of the COM momentum, $\mathbf{p} \equiv \sum_i \mathbf{p}_i$ can then be found by summing Eq. (2.29) over i and noting that $\langle \sum_i \mathbf{F}_i(t) \rangle_0 = 0$. Then

$$\frac{\partial}{\partial t} \langle \mathbf{p}(t) \rangle_0 = -\beta_0 \langle \mathbf{p}(t) \rangle_0, \quad (2.31)$$

and the COM momentum correlation function is

$$\langle \mathbf{p}(t) \cdot \mathbf{p}(0) \rangle = \left(3 \sum_i m_i kT \right) e^{-\beta_0 t}. \quad (2.32)$$

Thus from the Kubo relation one finds that the diffusion coefficient is

$$D = kT/M\beta_0, \quad M = \sum_i m_i, \quad (2.33)$$

where of course β_0 will be different for the different models. Nevertheless, experimental values for D enable us to choose β_0 . When the β_i 's are different this is no longer possible.

III. ONE-DIMENSIONAL MODEL

As an example of a simple system which undergoes complex interactions with the solvent, we explore the reaction dynamics of a one-dimensional model in which a particle of mass m moves on the potential energy curve presented in Fig. 1. It is assumed that the particle can experience two different kinds of collisions ($j=1, 2$) described by the transition probabilities given by the one-dimensional analogues of Eq. (2.22):

$$\tau^{(j)}(p | p') = [2\pi kTm(1 - \psi_j^2)]^{-1/2} \exp - \left(\frac{(p - \psi_j p')^2}{2mkT(1 - \psi_j^2)} \right). \quad (3.1)$$

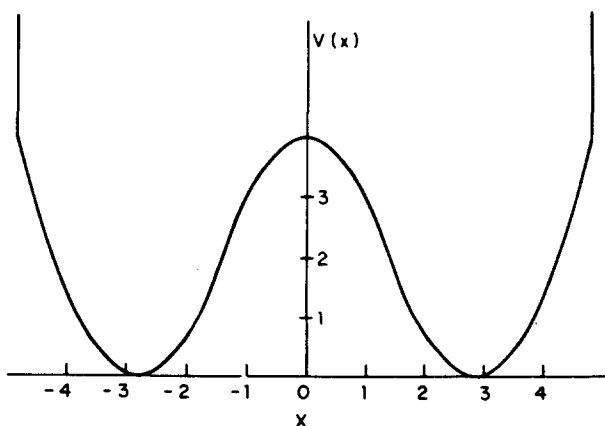


FIG. 1. The symmetric piecewise quadratic potential for which the calculations are carried in Sec. III. Energy is measured in units of kT , and distance in units of $(2kT/m)^{1/2} \omega_0^{-1}$.

The kinetic equation for the one-dimensional system [obtained from Eq. (2.12)] is

$$\left(\frac{\partial}{\partial t} + \frac{p}{m} \frac{\partial}{\partial x} - \frac{\partial U}{\partial x} \frac{\partial}{\partial p}\right) f(x, p, t) = -L_c f(x, p, t), \quad (3.2)$$

where

$$L_c f(x, p, t) = \int dp' [\kappa(p'|p) f(x, p, t) - \kappa(p|p') f(x, p', t)], \quad (3.3)$$

and

$$\kappa(p|p') = \alpha_1 \tau^{(1)}(p|p') + \alpha_2 \tau^{(2)}(p|p'). \quad (3.4)$$

The collision operator L_c is characterized by its eigenfunctions and eigenvalues^{6a}

$$\phi_n(p) = \phi_0(p) H_n \left(\frac{p}{\sqrt{2mkT}} \right), \quad (3.5)$$

$$\epsilon_n = \epsilon_n^{(1)} + \epsilon_n^{(2)}, \quad \text{where } \epsilon_n^{(j)} = \alpha_j (1 - \psi_j^n), \quad (3.6)$$

and H_n are the Hermite polynomials. The first nonzero eigenvalue ϵ_1 is simply the reciprocal momentum correlation time τ_p^{-1} . Similarly, ϵ_2 is related to the kinetic energy correlation time.

In the absence of external forces, the total diffusion constant would be

$$D = kT/\zeta, \quad \zeta = m\epsilon_1 = m(\epsilon_1^{(1)} + \epsilon_1^{(2)}). \quad (3.7)$$

From Eq. (3.6) we can write

$$1/D = 1/D_1 + 1/D_2, \quad (3.8)$$

that is, the reciprocal diffusion constant is the sum of the reciprocal diffusion constants for the individual collision processes ($D_j^{-1} = m\epsilon_1^{(j)}/kT$).

We are interested in calculating the rate constants which occur in the phenomenological rate equation

$$\partial N_a / \partial t = -k_{ab} N_a + k_{ba} N_b, \quad (3.9)$$

where N_a and N_b are the populations of the left and right wells, respectively. The most useful quantity to examine is the kinetic relaxation rate of the system

$$\tau^{-1} = k_{ab} + k_{ba}. \quad (3.10)$$

The form of Eq. (3.8) raises an important question: To what extent does such a behavior hold for the chemical relaxation rate τ^{-1} ? For very high collisions rates, τ^{-1} is proportional to D , so

$$1/\tau^{-1} = 1/\tau_1^{-1} + 1/\tau_2^{-1}, \quad (3.11)$$

that is, the reciprocal rate constant is the sum of the reciprocal rate constants, τ_1^{-1} and τ_2^{-1} , corresponding to the individual collision processes. On the other hand, for small collision rates we would expect simply to add the rates for each process, leaving

$$\tau^{-1} = \tau_1^{-1} + \tau_2^{-1}. \quad (3.12)$$

Thus in general we expect that there is no simple relation for calculating the rate when there are several collision channels for relaxation.

To study the effect of two different kinds of collisions on the relaxation rate for the reaction in which the par-

ticle moves from the left well to the right well in Fig. 1, it is possible to simulate the effective dynamics of the last section much as was done by Montgomery *et al.* for the BGK model.⁴ In one dimension, Skinner and Wolynes have found the relaxation rate from the kinetic equation analytically, using the method of Pade approximants, and numerically, with a close coupling scheme.^{6a} Since the generalization to a one-dimensional system with two types of collisions is straightforward, we use that method here.

In the following we investigate a model in which collisions of type 2 represent very hard collisions in which p is almost always reversed, that is, $\gamma_2 \rightarrow \infty$ [see Eq. (2.25)], $\psi_2 \rightarrow -1$, and collisions of type 1 are due to rapidly fluctuating weak soft forces, arising from the long range part of the heat bath force, or from coupling of the reaction coordinate to internal molecular degrees of freedom. These type 1 collisions are characterized by the parameter ψ_1 that differs very little from 1 ($\gamma_1 \rightarrow 0$) so that [cf. Eq. (3.6)]

$$\epsilon_n^{(1)} \approx 2\alpha_1 \gamma_1 n \equiv n\zeta_1/m. \quad (3.13)$$

$\zeta_1 = 2\alpha_1 \gamma_1 m$ is the friction constant resulting from type 1 collisions. It is worth noting that in the limit ($\gamma_1 \rightarrow 0$ such that $\alpha_1 \gamma_1$ is constant), $\alpha_1 \tau^{(1)}(p|p')$ reduces to the Fokker-Planck kernel of Brownian motion theory.

To characterize the effect of the two types of collisions it is useful to define a parameter χ which is the fraction of the total drag on the particle resulting from type 1 collisions

$$\chi = \frac{\epsilon_1^{(1)}}{\epsilon_1^{(1)} + \epsilon_1^{(2)}}. \quad (3.14)$$

The effect on the relaxation rate of mixing together different "amounts" of collisions of types 1 and 2 are shown in Figs. 2 and 3, respectively, for $\gamma_2 = 128$ and $\gamma_2 = 14$. In these figures the ordinate is the ratio of the kinetic relaxation rate τ^{-1} to the transition state theory rate

$$\tau_{\text{TST}}^{-1} = \frac{\omega_0}{\pi} e^{-E_0/kT}, \quad (3.15)$$

where E_0 is the barrier height and ω_0 is the harmonic frequency of either well (and in this case, the imaginary frequency at the barrier as well). The abscissa is ϵ_1/ω_0 , where ϵ_1 is, as before, the total momentum relaxation rate. We show both the analytical and the numerical results for different values of χ . The curve for $\chi = 1$ corresponds to pure Brownian motion (the Kramers-Fokker-Planck model), whereas the curve for $\chi = 0$ corresponds to the pure hard collision model (for $\gamma_2 = 128$ and 14, respectively, in Figs. 2 and 3). Both values of γ_2 give almost complete momentum reversal, but $\gamma_2 = 14$ corresponds to what would be expected to happen in a collision between a CH_3 group in butane and a CCl_4 molecule.⁴

Figure 2 shows clearly that when only 5% of the drag results from weak collisions (Fokker-Planck), the rate constant is drastically changed from the pure Lorentz case (momentum reversal, $\chi = 0$). When 20% of the drag is due to the weak collisions the results are much closer to the pure Fokker-Planck model than to the Lorentz

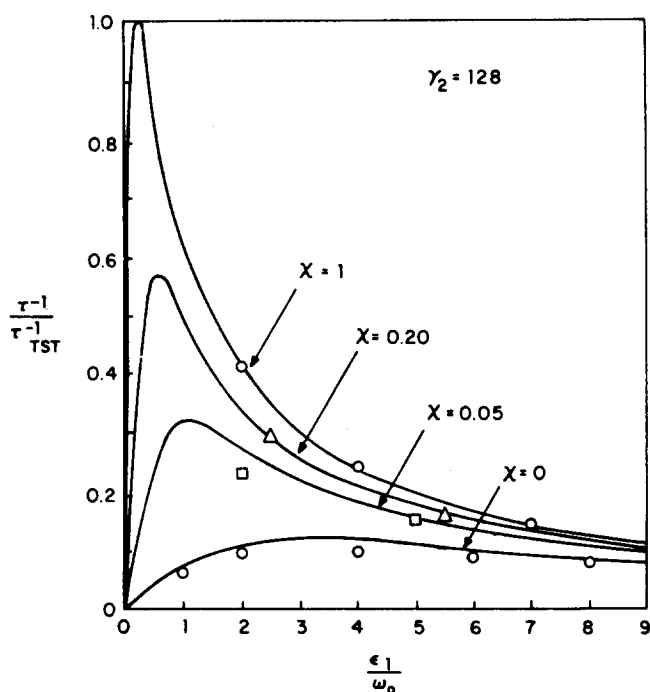


FIG. 2. The relaxation rate as a function ϵ_1 for $\gamma_2=128$, and different mixtures of the two kinds of collisions [cf. Eq. (3.14)]. —, (6,5) Padé approximant; o, Δ , \square , numerical results.

model. The effects are somewhat weaker for $\gamma_2=14$. Thus we see that for a given drag ϵ_1 , the rate constant is a highly nonlinear function of χ .

These results can be explained on the basis of the eigenvalue spectrum of the different collision operators. First we remember that $\epsilon_1^{(j)}$ and $\epsilon_2^{(j)}$ respectively give the contribution to the momentum relaxation and the energy relaxation for collisions of type j . Table I gives these values for small γ_1 and for large γ_2 .

From Table I we see that in the Fokker-Planck model both momentum and energy relax on the same time scale, whereas in the Lorentz model, as $\gamma_2 \rightarrow \infty$, energy relaxation becomes much less efficient than momentum relaxation. Therefore incorporating an amount of type 1 collisions which increases the drag only slightly can increase the rate of energy relaxation substantially. In a chemical relaxation process, for small ϵ_1 , energy activation is the rate limiting mechanism. Therefore it is no surprise that the relaxation rate is such a highly nonlinear function of χ , particularly for small ϵ_1 .

We conclude this section with a discussion of how one might determine which sorts of collision models are most appropriate for a particular site or particular coordinate in a real molecule. A convenient way to characterize a collision model is by examining the first few eigenvalues. For example, in the Fokker-Planck model ϵ_2 is twice ϵ_1 , in the BGK model $\epsilon_2 = \epsilon_1$, whereas in the Lorentz model they may differ by an order of magnitude or more. Below we sketch a method for deducing some information about the eigenvalue spectrum from a full molecular dynamics run. A simpler but similar scheme has been used previously by McCammon *et al.* to find collision rates.¹²

TABLE I.

| | Type 1 (Fokker-Planck) | Type 2 (Lorentz) |
|--------------------------------|---------------------------|----------------------|
| ϵ_1 (Momentum relax.) | ξ_1/m | $2\alpha_2$ |
| ϵ_2 (Energy relax.) | $2\xi_1/m$ | $4\alpha_2/\gamma_2$ |

Suppose for instance that we are interested in idealizing a real system by a particle moving on a one-dimensional potential curve, assuming that the phase space distribution function obeys the kinetic equation Eq. (3.2) with a *single* collision model, i.e., $\alpha_2=0$. A complete specification of the model would then depend on the values of the parameters α_1 and ψ_1 . We focus our attention on a local minimum in this one-dimensional potential of mean force, where

$$U = \frac{1}{2} B x^2. \quad (3.16)$$

Defining the averages for an arbitrary variable A as in Eq. (2.28),

$$\langle A(t) \rangle_0 = \int d\Gamma A f(\Gamma, t), \quad (3.17)$$

we can derive the following equations of motion for these averages:

$$\left. \begin{aligned} \frac{\partial}{\partial t} \langle p(t) \rangle_0 &= -B \langle x(t) \rangle_0 - \epsilon_1 \langle p(t) \rangle_0, \\ \frac{\partial}{\partial t} \langle x(t) \rangle_0 &= \frac{\langle p(t) \rangle_0}{m}, \end{aligned} \right\} \quad (3.18a)$$

$$(3.18b)$$

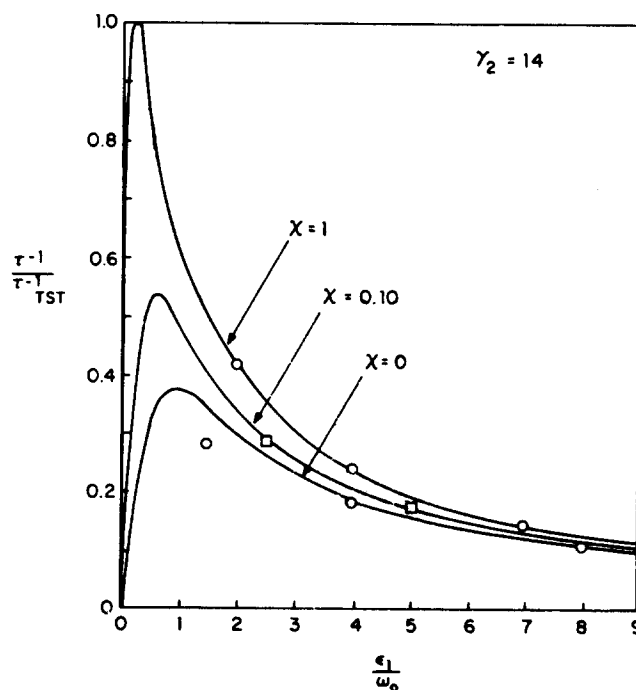


FIG. 3. The relaxation rate as a function of ϵ_1 for $\gamma_2=14$, and different mixtures of the two kinds of collisions [cf. Eq. (3.14)]. —, (6,5) Padé approximant; o, Δ , \square , numerical results.

$$\left. \begin{aligned} \frac{\partial}{\partial t} \langle p(t)^2 - kTm \rangle_0 &= -2B \langle p(t)x(t) \rangle_0 \\ &\quad - \epsilon_2 \langle p(t)^2 - kTm \rangle_0, \end{aligned} \right\} \quad (3.19a)$$

$$\left. \begin{aligned} \frac{\partial}{\partial t} \langle p(t)x(t) \rangle_0 &= \frac{\langle p(t)^2 - kTm \rangle_0}{m} \\ &\quad - B \left\langle x(t)^2 - \frac{kT}{B} \right\rangle_0 - \epsilon_1 \langle p(t)x(t) \rangle_0, \end{aligned} \right\} \quad (3.19b)$$

$$\left. \frac{\partial}{\partial t} \left\langle x(t)^2 - \frac{kT}{B} \right\rangle_0 = \frac{2 \langle p(t)x(t) \rangle_0}{m} \right\} \quad (3.19c)$$

Each bracketed group of equations forms a coupled but closed set, so we can solve for the time dependence of any average in either set, for example, $\langle x(t) \rangle_0$ and $\langle x(t)^2 - kT/B \rangle_0$. From a full molecular dynamics run we could easily find the correlation functions $\langle x(0)x(t) \rangle$ and $\langle (x(0)^2 - kT/B)(x(t)^2 - kT/B) \rangle$ near the potential minimum. Since the time dependence of the equilibrium correlation functions is identical to that of the nonequilibrium averages, we can fit the former to the latter to find ϵ_1 and ϵ_2 , which in turn uniquely determine α_1 and ψ_1 . In conclusion, we envision using full molecular dynamics to find the potential of mean force and the nature of the appropriate stochastic kernel, at which point a stochastic simulation or other method may be used to probe the detailed reaction dynamics of the system.

IV. SUMMARY

In this paper we discuss several aspects of the problem of modeling the effect of collisional contributions from the solvent on isomerization reactions. Given the assumptions of impulsive uncorrelated collisions we show how to generate stochastic dynamics for systems with more than one type of collision, each with its own collision frequency. We then derive a master equation for the phase space distribution function. We discuss several different collision models which describe how a single site in a molecule is affected by collisions. These models range from one with weak but numerous collisions leading to the Brownian motion picture, to one with strong collisions which reverse the momentum of the test particle. We then briefly discuss more elaborate models for complex molecules. We also discuss how, neglecting hydrodynamic interactions and assuming each atom in a molecule feels the same type and number of

collisions, we can estimate the friction constant and hence the collision frequency per site from the experimental diffusion constant.

In Sec. III we discuss a one-dimensional model of an isomerization reaction in which the particle suffers two kinds of collisions: weak but numerous collisions (Fokker-Planck), and strong collisions (Lorentz). We calculate the chemical relaxation rate for this system for various collision rates and "amounts" (measured in the fraction of the total drag, χ) of each type of collision. We find that the rate is a highly nonlinear function of χ , and that the rate constant is very sensitive to the collision model. Finally, we suggest how one might deduce the form and parameters of the collision model from a molecular dynamics simulation.

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