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A Class of Collision Processes with Memory and Application to Simple Chemical Reactions in a Solvent

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We apply the general formalism of a class of non-Markovian processes which we have studied elsewhere to three simple models of chemical reactions: dissociation, isomerization, and diffusion in a double-well potential. Our method leads to explicitly solvable models and numerical computations. The results are in agreement with numerical simulation and stochastic dynamics studies of other authors.

KEY WORDS: Non-Markovian processes; chemical reactions; bistable potentials.

1. INTRODUCTION

In this work, we define a general class of non-Markovian collision processes (see also Ref. 1) and apply this formalism to study very simple models of chemical reactions in the presence of a surrounding medium. The dynamics combines a deterministic dynamics, which would be the dynamics of the reaction if the reactant molecules were isolated, and a stochastic effect due to the presence of the medium. The existence of non-exponential waiting times causes these processes to be non-Markovian and introduces memory terms in their evolution equation.

We investigate three models: the first two are models with a finite number of regimes and trivial state space and are models of dissociation and isomerization. The third model is the diffusion in a two-well potential. In a sense, this last model is a substitute to the Langevin equation and an amelioration of Kramers' transition state theory, with the advantage that

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we can compute explicitly our model without integrating a partial differential equation of Fokker–Planck type.

A consequence of the combination of deterministic and stochastic dynamics is an oscillating approach to equilibrium, which is confirmed by numerical computations.

2. NON-MARKOVIAN COLLISION PROCESSES

2.1. A General Model

We want to describe a system (a test molecule, a group of molecules, or some abstract degrees of freedom) evolving under the action of external and internal forces. We assume that this evolution go through different phases, which we call regimes, labeled by an index ε taking values from 0 to m. In each regime ε, the state of the system is represented by a point in a state space E_ε and this state space may depend on ε, because in each regime we may be interested by different degrees of freedom (think, for example, of the different steps of a chemical reaction). At time t, the system is described by two random variables $\varepsilon(t)$ and $X(t)$ belonging to $E_{\varepsilon(t)}$. Its probability law is $P_\varepsilon(A, t)$, which is the probability that $\varepsilon(t) = \varepsilon$ and $X(t)$ is in the subset A of $E_{\varepsilon(t)}$.

Our fundamenal hypothesis is that the process keeps no memory of events prior to the beginning of a regime, specified by its initial time and initial state. This is a kind of partial Markov property (this hypothesis was also made by Van Kampen in his composite stochastic processes[2] with more restrictive conditions).

Under regime ε, the evolution is a Markov process with an infinitesimal operator $L_\varepsilon(x)$; we denote by $p_\varepsilon(x, t)$ the densities of its transition probabilities, satisfying

$$\frac{\partial}{\partial t} p_\varepsilon(x, t \mid x_0) = L_\varepsilon(x)\, p_\varepsilon(x, t \mid x_0), \qquad x \in E_\varepsilon$$

Suppose now that we are in regime ε_0; call $T_{\varepsilon\varepsilon_0}$ the stochastic duration of regime ε_0 knowing that the next regime is ε. We denote by $\Lambda_{\varepsilon_0}(t, x_0)$ the conditional probability that $\operatorname{Inf}_\varepsilon T_{\varepsilon\varepsilon_0} > t$ knowing that we have just entered regime ε_0 at time 0 and in state $x_0 \in E_{\varepsilon_0}$, and by $\Gamma_{\varepsilon_1\varepsilon_0}(dt \mid x_0)\, dt$ the conditional probability that the first transition after time 0 occurs within the time interval $(t, t + dt)$ and yields the regime ε_1, knowing that we have just entered regime ε_0 at time 0 and in the initial state $x_0 \in E_{\varepsilon_0}$.

Finally, we denote by $y_{\varepsilon_1\varepsilon_0}(x_1 \mid x_1^-, t_1)\, dx_1$ the conditional probability that $\varepsilon(t_1) = \varepsilon_1$, $X(t_1) \in dx_1 \subset E_{\varepsilon_1}$, knowing that $\varepsilon(t_1 - 0) = \varepsilon_0$, $X(t_1 - 0) = x_1^-$, and a transition $\varepsilon_0 \to \varepsilon_1$ occurs at time t_1.

Our purpose is to find the conditional probability $P_{\varepsilon\varepsilon_0}(dx, t \mid x_0)$ that the system is at time t in regime ε, in $dx \subset E_\varepsilon$, knowing that a transition has occurred at time 0, yielding ε_0 and a state $x_0 \in E_{\varepsilon_0}$.

2.2. The Evolution Equation

We shall use a matrix notation: $\mathbf{P}(dx, t \mid x_0)$ is the matrix $P_{\varepsilon\varepsilon_0}(dx, t \mid x_0)$, ε, $\varepsilon_0 = 1,..., m$; $\mathbf{\Theta}(dx, t \mid x_0)$ is the matrix

$$\Theta_{\varepsilon\varepsilon_0}(dx, t \mid x_0) = \delta_{\varepsilon\varepsilon_0} \Lambda_{\varepsilon_0}(t)\, p_{\varepsilon_0}(dx, t \mid x_0) \tag{2.1}$$

$\boldsymbol{\phi}(dx_1, d\tau \mid x_0)$ is the matrix

$$\phi_{\varepsilon_1\varepsilon_0}(dx, d\tau \mid x_0) = \int_{x_0^- \in E_{\varepsilon_0}} y_{\varepsilon_1\varepsilon_0}(dx_1 \mid x_0^-)\, \Gamma_{\varepsilon_1\varepsilon_0}(d\tau \mid x_0)\, p_\varepsilon(dx_0^-, \tau \mid x_0) \tag{2.2}$$

The general evolution equation is, using matrix products,

$$\begin{aligned} &\mathbf{P}(dx, t \mid x_0) \\ &\quad = \mathbf{\Theta}(dx, t \mid x_0) + \int_{0<\tau<t} \int_{x_1 \in E_{\varepsilon_1}} \mathbf{P}(dx, t-\tau \mid x_1)\, \boldsymbol{\phi}(dx_1, d\tau \mid x_0) \end{aligned} \tag{2.3}$$

which can be treated by Laplace transforms.

Remarks:

(i) We have assumed time homogeneity.

(ii) Equation (2.3) is easily derived by separating the "no-collision events" and the "at least one collision events" (see Ref. 1).

2.3. Case of Exponential and Deterministic Waiting Times

In the Markovian case, it is well known[3] that the waiting times in each regime ε are stochastic and exponentially distributed with the constant λ_ε, so that

$$\Lambda_\varepsilon(t) = \exp(-\lambda_\varepsilon t) \tag{2.4}$$

and

$$\int_0^t \Gamma_{\varepsilon_1\varepsilon_0}(d\tau \mid x_0) = \Gamma_{\varepsilon_1\varepsilon_0}(t \mid x_0) = \mu_{\varepsilon_1\varepsilon_0}[1 - \exp(-\lambda_{\varepsilon_0} t)] \tag{2.5}$$

where $\mu_{\varepsilon_1\varepsilon_0}$ is the transition probability from ε_0 to ε_1.

As a simple modification of this pure Markovian case, we now suppose that in each regime ε_0, another physical process can cause a transition at a deterministic time τ_{ε_0} if the purely Markovian process has not yet produced its own transition before τ_{ε_0}. In case this deterministic process operates, let $v_{\varepsilon_1\varepsilon_0}$ be the transition probability for going from regime ε_0 to regime ε_1. Then the transition laws are given as follows:

(i) If $t < \tau_\varepsilon$,

$$\begin{aligned} \Lambda_\varepsilon(t) &= e^{-\lambda_\varepsilon t} \\ \Gamma_{\varepsilon'\varepsilon}(t) &= \mu_{\varepsilon'\varepsilon}(1 - e^{-\lambda_\varepsilon t}) \end{aligned} \tag{2.6}$$

(ii) If $t \geqslant \tau_\varepsilon$,

$$\begin{aligned} \Lambda_\varepsilon(t) &= 0 \\ \Gamma_{\varepsilon'\varepsilon}(t) &= \mu_{\varepsilon'\varepsilon}(1 - e^{-\lambda_\varepsilon \tau_\varepsilon}) + v_{\varepsilon'\varepsilon}\, e^{-\lambda_\varepsilon \tau_\varepsilon} \end{aligned} \tag{2.7}$$

We will use the Laplace transforms $\hat{\Lambda}_\varepsilon(s)$ and $\hat{\Gamma}_{\varepsilon'\varepsilon}(s)$ of $\Lambda_\varepsilon(t)$ and $\Gamma_{\varepsilon'\varepsilon}(t)$:

$$\begin{aligned} \hat{\Lambda}_\varepsilon(s) &= \frac{1}{s + \lambda_\varepsilon}(1 - e^{-(s+\lambda_\varepsilon)\tau_\varepsilon}) \\ \hat{\Gamma}_{\varepsilon'\varepsilon}(s) &= \mu_{\varepsilon'\varepsilon}\frac{\lambda_\varepsilon}{s(s+\lambda_\varepsilon)}(1 - e^{-(s+\lambda_\varepsilon)\tau_\varepsilon}) + v_{\varepsilon'\varepsilon}\frac{e^{-(s+\lambda_\varepsilon)\tau_\varepsilon}}{s} \end{aligned} \tag{2.8}$$

2.4. Case of Trivial Phase Spaces

In the first two examples of Sections 3 and 4, there is no phase space in each regime; this means that the state of the system is completely determined by the regime ε. We can apply Eq. (2.3) and obtain the Laplace transform $\hat{\mathbf{P}}(s)$ of $\mathbf{P}(t)$ in matrix notation:

$$\hat{\mathbf{P}}(s) = \hat{\boldsymbol{\theta}}(s)\,\mathbf{A}^{-1}(s) = \hat{\boldsymbol{\theta}}(s)[\mathbf{I} - s\hat{\boldsymbol{\Gamma}}(s)]^{-1} \tag{2.9}$$

with

$$\hat{\theta}_{\varepsilon'\varepsilon}(s) = \delta_{\varepsilon'\varepsilon}\hat{\Lambda}_\varepsilon(s), \qquad \hat{A}_{\varepsilon'\varepsilon}(s) = \delta_{\varepsilon'\varepsilon} - s\hat{\Gamma}_{\varepsilon'\varepsilon}(s) \tag{2.10}$$

Then, the asymptotic probability distribution is

$$P_{\varepsilon\varepsilon_0}(\infty) = P_\varepsilon(\infty) \propto t_\varepsilon q_\varepsilon$$

where

$$t_\varepsilon = \hat{\Lambda}_\varepsilon(0) = \lambda_\varepsilon^{-1}(1 - e^{-\lambda_\varepsilon \tau_\varepsilon})$$

and (q_ε) is the right null vector of $\mathbf{A}(0)$. Here

$$\mathbf{A}(0) = [\mathbf{I} - s\hat{\boldsymbol{\Gamma}}(s)]_{s=0} = \mathbf{I} - \boldsymbol{\mu}[\mathbf{I} - \exp(-\boldsymbol{\lambda}\tau)] - \boldsymbol{\nu}\exp(-\boldsymbol{\lambda}\tau)$$

with obvious matrix notations.

3. A MODEL OF DISSOCIATION

3.1. Description of the Model

The dissociation of a molecule, for instance I_2, and the corresponding recombination have often been taken in the literature as an example of a simple chemical reaction, which allows a test of stochastic methods used to simulate the interaction with the medium.[4–8] Here we consider a very crude model for a dissociation:

$$\mathrm{AB} \rightleftarrows \mathrm{A} + \mathrm{B}$$

Supposing that this reaction may be described by a single reaction coordinate x which is 0 for the molecule AB and infinite when the dissociation is achieved, we can model the internal dissociation potential $V(x)$ by the piecewise constant potential shown in Fig. 1:

$$V(x) = \begin{cases} V_1 < 0 & \text{if } 0 \leqslant x < a \\ V_2 > 0 & \text{if } a \leqslant x < b \\ 0 & \text{if } b \leqslant x \end{cases} \tag{3.1}$$

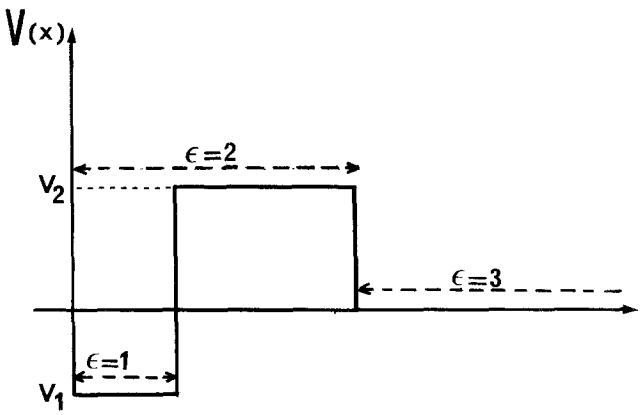


Fig. 1. Simple model of potential for dissociation–recombination of a molecule.

We say that the system (A, B) is in regime 1 (bound state) if its energy E is less than V_2 and if $0 \leqslant x \leqslant a$; in the same manner, we say that it is in regime 2 if $E \geqslant V_2$ and $0 \leqslant x \leqslant b$ (transitory regime) and in regime 3 (dissociated state) if $x \geqslant b$.

Now, if the system is trapped in regime 1, it can only change if a collision with other molecules of the medium gives if enough energy to go to regime 2. We suppose that the waiting time T_1 of such a collision is independent of the past of the system and exponentially distributed with a time constant λ_1,

$$\text{Prob}(T_1 > t) = e^{-\lambda_1 t} \tag{3.2}$$

Once the system is in regime 2, it will pass to regime 3 after a deterministic time τ_2 unless before τ_2 another external collision brings it back into regime 1, which can occur after a stochastic time T_2 exponentially distributed with a time constant λ_2.

Finally, if the system is dissociated (regime 3), it can pass to regime 2 if a collision of A and B occurs with interference of other molecules of the medium so that the velocity and energy conditions are fulfilled; this happens after a stochastic time T_3 exponentially distributed with time constant λ_3.

Although elementary, this model of dissociation presents some interesting features because it allows us to use distinct time constants λ_i, $i = 1, 2, 3$ (in particular, λ_3 should be very different from λ_1 and λ_2), and mainly because it is non-Markovian due to the existence of the noninstantaneous transitory regime 2.

3.2. Applications of the Results of Section 2

We apply the results of Section 2, with $\varepsilon = 1, 2, 3$, $\tau_1 = \tau_3 = +\infty$. We write

$$\rho(s) = e^{-(s+\lambda_2)\tau_2} \tag{3.3}$$

and we obtain, with the notations of Section 2 and of Ref. 1, the following Laplace-transformed matrices:

$$\begin{aligned} \hat{\mathbf{\Theta}}(s) &= \begin{pmatrix} (\lambda_1+s)^{-1} & 0 & 0 \\ 0 & (1-\rho)(\lambda_2+s)^{-1} & 0 \\ 0 & 0 & (\lambda_3+s)^{-1} \end{pmatrix} \\ \mathbf{A}(s) &= \begin{pmatrix} 1 & -\lambda_2(1-\rho)(\lambda_2+s)^{-1} & 0 \\ -\lambda_1(\lambda_1+s)^{-1} & 1 & -\lambda_3(\lambda_3+s)^{-1} \\ 0 & -\rho & 1 \end{pmatrix} \end{aligned} \tag{3.4}$$

Then

$$\det \mathbf{A}(s) = \left[\prod_{i=1}^{3} (\lambda_i + s)\right]^{-1} s[s^2 + (\lambda_1 + \lambda_2 + \lambda_3 - \lambda_3 \rho)\, s + \lambda_3(\lambda_1 + \lambda_2) - [\lambda_3(\lambda_1 + \lambda_2) - \lambda_1 \lambda_2]\rho] \tag{3.5}$$

and $\hat{\mathbf{P}}(s)$ can be easily computed by using Eq. (2.9). But $\mathbf{P}(t)$ cannot be expressed in a simple analytical form.

3.3. Long-Time Behavior of P(*t*)

The results of Section 2 give immediately the asymptotic value $P_\varepsilon(\infty)$ of $P_{\varepsilon\varepsilon_0}(t)$:

$$P_\varepsilon(\infty) \propto \begin{pmatrix} (1-\sigma)\lambda_1^{-1} \\ (1-\sigma)\lambda_2^{-1} \\ \sigma\lambda_3^{-1} \end{pmatrix} \tag{3.6}$$

where

$$\sigma = e^{-\lambda_2 \tau_2}$$

In the case $\tau_2 = \infty$, the system is equivalent to a Markov chain on the two states 1 and 2, and (3.6) yields the classical result

$$P_1(\infty) \propto \lambda_1^{-1}, \qquad P_2(\infty) \propto \lambda_2^{-1}, \qquad P_3(\infty) = 0$$

In order to study the approach to equilibrium, we must determine the nonzero values of s for which $\det A(s)$ given by (3.5) vanishes; they are the roots of

$$f(s) \equiv s^2 + (\lambda_1 + \lambda_2 + \lambda_3 - \lambda_3 \rho)s + \lambda_3(\lambda_1 + \lambda_2)(1-\rho) + \lambda_1 \lambda_2 \rho = 0 \tag{3.7}$$

These values cannot be explicitly calculated, because ρ depends on s by (3.3).

On the other hand, an approximate solution such that $s\tau_2 \ll 1$ is easily found since ρ may be replaced by $\sigma = e^{-\lambda_2 \tau_2}$; the roots of (3.7) in this approximation are

$$s_\pm = -\tfrac{1}{2}[(\lambda_1 + \lambda_2 + \lambda_3 - \lambda_3 \sigma) \pm \delta^{1/2}] \tag{3.8}$$

with

$$\delta = [\lambda_1 + \lambda_2 - \lambda_3(1-\sigma)]^2 - 4\sigma\lambda_1\lambda_2 \tag{3.9}$$

It can be seen that the condition $s_+ \tau_2 \ll 1$ is realized if $\lambda_1 \tau_2 \simeq \lambda_2 \tau_2 \ll 1$ (which implies that $1-\sigma \simeq \lambda_2 \ll 1$), and the approximation (3.8) for the actual roots applies if the deterministic time for dissociation τ_2 is very short compared to the mean time intervals λ_1^{-1} and λ_2^{-1} between the collisions that cause the change of regimes.

It should be noted that the roots $s_\pm$ may be complex, when

$$\lambda_3 \simeq \frac{\lambda_1 + \lambda_2}{1-\sigma} \tag{3.10}$$

(which in turn implies that λ_3 is of order $1/\tau_2$). Under condition (3.10) we have an oscillating approach to equilibrium, which never occurs in a purely Markovian case ($\tau_2 = 0$ or $\tau_2 = \infty$) and is indeed confirmed by numerical computations.

4. A MODEL OF ISOMERIZATION

4.1. Description of the Model

Following Chandler, Berne, and other authors,[8-10] we model the isomerization of a molecule (for example, of butane) as the motion of a particle along a single reaction coordinate x in a double-well potential $V(x)$; the two wells of the potential are associated with the two states of the isomer (for example, the *gauche* and *trans* isomer of butane). The true intramolecular potential (more precisely, the effective potential, which includes the average interaction with the medium[9]) is approximated by a piecewise constant potential, the numerical characteristics of which may be deduced from experimenal data. The potential is schematized in Fig. 2.

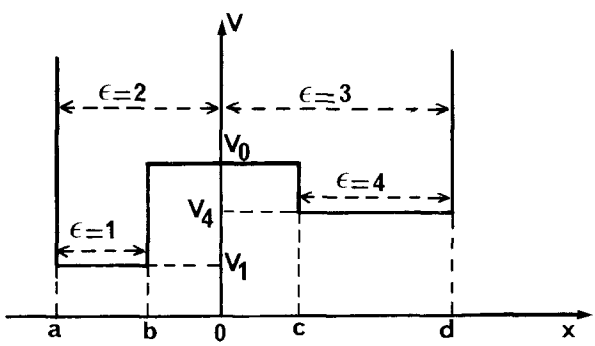


Fig. 2. Simple model of potential for isomerization.

Supposing that the origin of the x coordinate is the middle point of the top of the barrier potential, we define the following regimes for the reacting molecule:

$$\begin{array}{lll} \text{regime 1:} & a \leqslant x \leqslant b & \text{and energy} < V_0 \quad (\textit{trans}\text{ isomer}) \\ \text{regime 2:} & x < 0 & \text{and energy} > V_0 \\ \text{regime 3:} & x > 0 & \text{and energy} > V_0 \quad \Big\} \text{ (transition states)} \\ \text{regime 4:} & c \leqslant x \leqslant d & \text{and energy} < V_0 \quad (\textit{gauche}\text{ isomer}) \end{array}$$

We suppose that random collisions with the solvent molecules may induce the transitions $1 \to 2$, $2 \to 1$, $3 \to 4$, and $4 \to 3$ with the respective stochastic times T_1, T_2, T_3, and T_4, each T_i being exponentially distributed with time constant λ_i^{-1}, independently of the past events.

On the other hand, the molecules can go from 2 to 3 and 3 to 2 after a purely deterministic time τ if no collision has occurred before; τ results from the deterministic motion in $V(x)$ and the internal energy of the molecule (which we take to be the mean value at thermodynamic equilibrium at temperature T); the deterministic motion in $V(x)$ is an undamped oscillation between a and d.

4.2. Applications of the Results of Section 2

We summarize the preceding description of this model in the formalism developed in Section 2; the matrices $\boldsymbol{\mu}$ and $\mathbf{v}$ which give the possible stochastic and deterministic transitions are

$$\boldsymbol{\mu} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \qquad \mathbf{v} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{4.1}$$

The matrix $\mathbf{A}(s)$ and its determinant are computed in Appendix A.

Using the results of Section 1, one obtains the asymptotic value $P_\varepsilon(\infty)$ of $P_{\varepsilon\varepsilon_0}(t)$ as

$$p_\varepsilon(\infty)) \propto \begin{pmatrix} \sigma_3(1-\sigma_2)\lambda_1^{-1} \\ \sigma_3(1-\sigma_2)\lambda_2^{-1} \\ \sigma_2(1-\sigma_3)\lambda_3^{-1} \\ \sigma_2(1-\sigma_3)\lambda_4^{-1} \end{pmatrix} \tag{4.2}$$

with

$$\sigma_i = e^{-\lambda_i \tau}$$

The approach to equilibrium is characterized by

$$\mathbf{P}(t)-\mathbf{P}(\infty) \propto e^{st}$$

where s is the nonzero root of $\det \mathbf{A}(s)=0$ that has the smallest absolute value. This last equation can be written as

$$s(s+\lambda_1+\lambda_2)(s+\lambda_3+\lambda_4)(1-\rho_2\rho_3)+\lambda_1\lambda_2\rho_2(1-\rho_3)(s+\lambda_3+\lambda_4)$$
$$+\lambda_3\lambda_4\rho_3(1-\rho_2)(s+\lambda_1+\lambda_2)=0 \tag{4.3}$$

where $\rho_i=e^{-\tau(\lambda_i+s)}$ (see Appendix A for details).

When $s\tau \ll 1$, ρ_2 and ρ_3 can be replaced by the constants σ_2 and σ_3 with $\sigma_i=e^{-\lambda_i\tau}$, and the solution s of (4.3) is the solution of a third-degree equation.

It can be shown analytically and numerically that the root s_0 of smallest absolute value can be complex, which indicates an oscillating approach to equilibrium: the complete rigorous discussion is given in Appendix A and is rather delicate in this case of the model of isomerization (see Appendix A for the range of values of parameters λ_i and τ such that this occurs). A purely dissipative mechanism would give an exponential nonoscillating decrease of the deviation from equilibrium; a deterministic dynamics would lead to undamped oscillations; here, as in the example of dissociation, we have a mixing of these behaviors. This phenomenon has been predicted by a numerical simulation by Chandler *et al.*[9,10] It is also obtained in the simulation by Adelman *et al.*[7,8]

5. A MODEL OF DIFFUSION BETWEEN TWO POTENTIAL WELLS

5.1. General Description and Motivation

This model is an improvement of the crude model of isomerization previously studied and may also be used for any reaction from stable state A to another stable state B described by a reaction coordinate x. The state A is observed when the system is trapped in the left well of the intramoleclar potential $0 \leqslant x < a$; the state B is observed when the system is in the other well $L \leqslant x \leqslant L+b$ (see Fig. 3).

Both states A and B are represented by one regime; their excited forms A* and B* are also represented by one regime. The difference between this model and the isomerization model of the preceding section is that the behavior of the reacting system near the top of the barrier is investigated more carefully by introducing a fifth regime in which the "spatial" motion

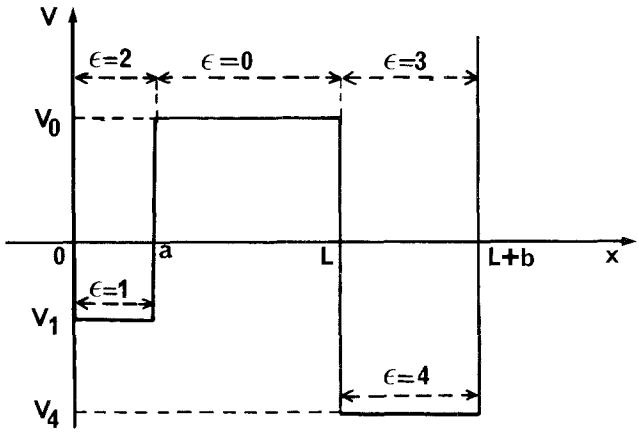
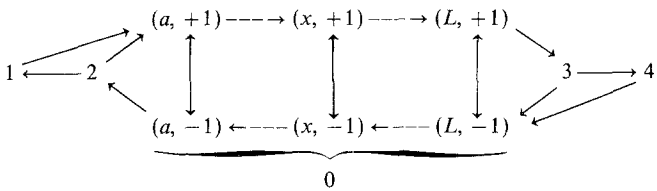


Fig. 3. Simple double-well potential. The diagram given below shows symbolically the allowed transitions between the different regimes in our model; a line with an arrow indicates an allowed transition in the sense of the arrow:



is explicitly taken into account in a simplified way. This point is of interest since the reactive flux $k(t)$ at short times (see Section 5.6) depends on the behavior of the system near the top of the barrier.[9,12] On the other hand, the introduction of a spatial state in this intermediary regime makes the calculations much more complicated. However, it will be seen that the model can be solved explicitly and in particular the reactive flux can be investigated completely.

5.2. Mathematical Description of the Model

We shall adopt the more general language introduced in Section 2 in the case of the diffusion of a "particle" between two potential wells of respective depths E_2 and E_3 (see Fig. 3). The model has five regimes, denoted $\varepsilon = 0, 1, 2, 3, 4$, with the following specifications:

Regime $\epsilon = 1$. The particle is trapped in the potential well $[0, a]$. Its state space in that regime is the trivial space with one point. After an exponential waiting time T_1 with law $\text{Prob}(T_1 > t) = e^{-\lambda_1 t}$, the particle is activated and goes to regime $\varepsilon = 0$ at point a with speed $+v$.

Regime $\epsilon = 4$. The particle is trapped in the potential well $[L, L+b]$; T_4 is the exponential waiting time with constant λ_4; at T_4 the particle is activated and goes to regime $\varepsilon = 0$ at point L with speed $-v$.

Regime $\epsilon = 0$. The particle wanders on the top of the barier, its deterministic motion being perturbed by random collisions that change the sign of its velocity without changing the absolute value v of the velocity.

The state space is the Cartesian product $[a, L] \times \{+1, -1\}$ giving the position $x \in [a, L]$ and the sign $\alpha = \pm 1$ of its velocity v. Denote $\tau_+(x) = (L-x)/v$, $\tau_-(x) = (x-a)/v$: these are the times to go from x to L with speed $+v$ and from x to a with speed $-v$. Let T_0 be an exponential waiting time of constant λ_0. Suppose that the particle is in state (x, α) either just after entering regime 0 or just after a collision has occurred in regime 0. Then, if $T_0 > \tau_\alpha(x)$, the particle goes from (x, α) to regime $\varepsilon = 3$ if $\alpha = 1$, or $\varepsilon = 2$ if $\alpha = -1$ in time $\tau_\alpha(x)$; if $T_0 < \tau_\alpha(x)$, the particle goes from (x, α) to $(x', -\alpha)$ at time T_0 with velocity αv and $x' = x + \alpha v$, changes the sign of its velocity at T_0, and continues independently according to this rule.

Regime $\epsilon = 2$. The state space is a trivial space with one point. In this regime we consider that the particle is above the well $[0, a]$ with an energy higher than the barrier and absolute velocity $v_2 = (v^2 + 2E_2/m)^{1/2}$. We denote by $\tau_2 = 2a/v_2$ the deterministic sojourn time in regime $\varepsilon = 2$. If the particle comes from $\varepsilon = 0$, it enters $\varepsilon = 2$, say at time t, and then if $\tau_2 > T_2$ (T_2 is the exponential time of constant λ_2), it becomes desactivated at time $T_2 + t$ and goes to regime $\varepsilon = 1$ at that time. On the other hand, if $\tau_2 < T_2$, it comes back to regime $\varepsilon = 0$ at time $\tau_2 + t$, into state $(a, +1)$.

Regime $\epsilon = 3$. This regime is similar to $\varepsilon = 2$: the particle is above the well $[L, L+b]$ with an energy higher than the barrier and absolute velocity $v_3 = (v^2 + 2E_3/m)^{1/2}$. Let $\tau_3 = 2b/v_3$; if the particle comes from regime $\varepsilon = 0$ at time t, it enters $\varepsilon = 3$, and then if $\tau_3 < T_3$, it becomes desactivated and goes to regime $\varepsilon = 4$ at time $T_3 + t$; if $\tau_3 < T_3$, it comes back to regime $\varepsilon = 0$ at time $\tau_3 + t$, into state $(L, -1)$.

For $\varepsilon, \varepsilon' = 1, 2, 3, 4$, the state spaces of these regimes are one-point spaces and $P_{\varepsilon'\varepsilon}(t)$ is the transition probability for going from regime ε to regime ε' in time t knowing that at time 0 the particle has just entered regime ε.

For $\varepsilon = 1, 2, 3, 4$, we denote by $P_{0\varepsilon}(x, \alpha, t)$ the transition probability for going from regime ε to regime 0 at point $(x, \alpha) \in [a, L] \times \{-1, +1\}$ in time t, knowing that at time 0 the particle has just entered regime ε. We also denote by $P_{\varepsilon 0}(t \mid x, \alpha)$ the transition probability for going from state (x, α) in regime 0 to regime ε in time t, knowing that at time 0 the particle

has just entered regime 0 or has just suffered a collision that has inverted its velocity.

Our purpose is to find expressions for these transition probabilities; in particular, we are interested in computing $P_{10}(t \mid L, \pm 1)$ because $P_{10}(\infty \mid L, \pm 1)$ is connected with the flux across the potential barrier separating the two wells, as discussed in Section 5.7.

5.3. Evolution Equations for $P_{1\epsilon}$

We shall apply the general formalism developped in Ref. 1 to write down the evolution equation for $P_{1\varepsilon}$. We denote

$$\eta(\tau) = \begin{cases} 1 & \text{if} \quad \tau > 0 \\ 0 & \text{if} \quad \tau < 0 \end{cases}$$

$$t \wedge t' = \min(t, t')$$

Then the transition probabilities $P_{1\varepsilon}$ satisfy the system of integral equations [for convenience the equations are enumerated by $(5.\varepsilon)$ for $P_{1\varepsilon}$]

$$P_{11}(t) = e^{-\lambda_1 t} + \int_0^t d\tau\, \lambda_1 e^{-\lambda_1 t} P_{10}(t-\tau \mid a, +1)\, d\tau \tag{5.1}$$

$$\begin{aligned} P_{12}(t) = &\int_0^{t \wedge \tau_2} d\tau\, \lambda_2 e^{-\lambda_2 \tau} P_{11}(t-\tau)\, d\tau \\ &+ \eta(t-\tau_2) e^{-\lambda_2 \tau_2} P_{10}(t-\tau_2 \mid a, +1) \end{aligned} \tag{5.2}$$

$$\begin{aligned} P_{10}(t \mid x, \alpha) = &\int_0^{t \wedge \tau_\alpha(x)} d\tau\, \lambda_0 e^{-\lambda_0 \tau} P_{10}(t-\tau \mid x + \alpha\tau, -\alpha) \\ &+ \delta_{\alpha,+1} \eta(t-\tau_\alpha(x)) e^{-\lambda_0 \tau_\alpha(x)} P_{13}(t-\tau_\alpha(x)) \\ &+ \delta_{\alpha,-1} \eta(t-\tau_\alpha(x)) e^{-\lambda_0 \tau_\alpha(x)} P_{12}(t-\tau_\alpha(x)) \end{aligned} \tag{5.0}$$

$$\begin{aligned} P_{13}(t) = &\int_0^{t \wedge \tau_3} d\tau\, \lambda_3 e^{-\lambda_3 \tau} P_{14}(t-\tau)\, d\tau \\ &+ \eta(t-\tau_3) e^{-\lambda_3 \tau_3} P_{10}(t-\tau_3 \mid L, -1) \end{aligned} \tag{5.3}$$

$$P_{14}(t) = \int_0^t d\tau\, \lambda_4 e^{-\lambda_4 \tau} P_{10}(t-\tau \mid L, -1)\, d\tau \tag{5.4}$$

We now perform a Laplace transformation in this system; we denote by s the Laplace variable, writing, as previously,

$$\hat{f}(s) = \int_0^{+\infty} e^{-st} f(t)\, dt$$

and in particular we define $\hat{P}_{\varepsilon'\varepsilon}(s)$, $\hat{P}_{\varepsilon 0}(s\,|\,x, \alpha)$. Using the formulas of Appendix B, we finally obtained the Laplace transform of the above system of equations:

$$\hat{P}_{11}(s) = \frac{1}{\lambda_1 + s} + \frac{\lambda_1}{\lambda_1 + s} P_{10}(s\,|\,a, +1) \tag{5.1}$$

$$\hat{P}_{12}(s) = \frac{\lambda_2}{\lambda_2 + s}(1 - e^{-(\lambda_2 + s)\tau_2})\,\hat{P}_{11}(s) + e^{-(\lambda_2 + s)\tau_2}\,\hat{P}_{10}(s\,|\,a, +1) \tag{5.2}$$

$$\begin{aligned}\hat{P}_{10}(s\,|\,x, \alpha) = \int_a^L dx'\,\hat{P}_{10}(s\,|\,x', -\alpha) \\ \times \frac{\lambda_0}{v}\left\{\exp\left[-\alpha(\lambda_0 + s)\frac{x' - x}{v}\right]\right\}\eta(\alpha(x' - x)) \\ + \delta_{\alpha,+1}\{\exp[-(\lambda_0 + s)\,\tau_\alpha(x)]\}\,\hat{P}_{13}(s) \\ + \delta_{\alpha,-1}\{\exp[-(\lambda_0 + s)\,\tau_\alpha(x)]\}\,\hat{P}_{10}(s\,|\,L, -1)\end{aligned} \tag{5.0}$$

$$\hat{P}_{13}(s) = \frac{\lambda_3}{\lambda_3 + s}(1 - e^{-(\lambda_3 + s)\tau_3})\,\hat{P}_{14}(s) + e^{-(\lambda_3 + s)\tau_3}\,\hat{P}_{13}(s\,|\,L, -1) \tag{5.3}$$

$$\hat{P}_{14}(s) = \frac{\lambda_4}{\lambda_4 + s}\,\hat{P}_{13}(s\,|\,L, -1) \tag{5.4}$$

5.4. Solution of the System of Laplace-Transformed Equations

The solutions of the system of Eqs. $\widehat{(5.\varepsilon)}$ are obtained by eliminating $\hat{P}_{11}$, $\hat{P}_{12}$, $\hat{P}_{13}$, $\hat{P}_{14}$ among Eqs. $\widehat{(5.\varepsilon)}$; then $\widehat{(5.0)}$ yields a system of two integral equations in x for $\hat{P}_{10}(s\,|\,x, \pm 1)$, which can be differentiated in x and gives a system of two equations of first order,

$$\begin{aligned}\frac{\partial \hat{P}_{10}(s\,|\,x, +1)}{\partial x} &= -\frac{\lambda_0}{v}\,\hat{P}_{10}(s\,|\,x, -1) + \frac{\lambda_0 + s}{v}\,\hat{P}_{10}(s\,|\,x, +1) \\ \frac{\partial \hat{P}_{10}(s\,|\,x, -1)}{\partial x} &= \frac{\lambda_0}{v}\,\hat{P}_{10}(s\,|\,x, +1) - \frac{\lambda_0 + s}{v}\,\hat{P}_{10}(s\,|\,x, -1)\end{aligned} \tag{5.5}$$

with boundary conditions at $x = a$ and L

$$\begin{aligned}\hat{P}_{10}(s\,|\,L, +1) &= C(s)\,\hat{P}_{10}(s\,|\,L, -1) \\ \hat{P}_{10}(s\,|\,a, -1) &= A(s) + B(s)\,\hat{P}_{10}(s\,|\,a, +1)\end{aligned} \tag{5.6}$$

with

$$A(s)=\frac{\lambda_2}{(\lambda_1+s)(\lambda_2+s)}(1-e^{-(\lambda_2+s)\tau_2})$$

$$B(s)=e^{-(\lambda_2+s)\tau_2}+\frac{\lambda_1\lambda_2}{(\lambda_1+s)(\lambda_2+s)}(1-e^{-(\lambda_2+s)\tau_2}) \tag{5.7}$$

$$C(s)=e^{-(\lambda_3+s)\tau_3}+\frac{\lambda_3\lambda_4}{(\lambda_3+s)(\lambda_4+s)}(1-e^{-(\lambda_3+s)\tau_3})$$

The solutions of this system are

$$\begin{aligned}\hat{P}_{10}(s\,|\,x,\,+1)&=\lambda_0 Ee^{-\xi_0 x}+\lambda_0 Fe^{-\xi_0(L-x)}\\ \hat{P}_{10}(s\,|\,x,\,-1)&=\mu_- Ee^{-\xi_0 x}+\mu_+ Fe^{-\xi_0(L-x)}\end{aligned} \tag{5.8}$$

where $\xi_0=[(2\lambda_0+s)s]^{1/2}/v$.

The $\mu_\pm$ and E and F are given in Appendix B by formulas (B.11) and (B.14).

The solutions are then given by (5.8), and the other functions $\hat{P}_{1\varepsilon}(s)$, $\varepsilon=1, 2, 3, 4$, are given by formulas (B.5) and (B.6) of Appendix B for $\hat{P}_{12}$ and $\hat{P}_{13}$, namely

$$\begin{aligned}\hat{P}_{12}(s)&=A(s)+B(s)\,\hat{P}_{10}(s\,|\,a,\,+1)\\ \hat{P}_{13}(s)&=C(s)\,\hat{P}_{10}(s\,|\,L,\,-1)\end{aligned} \tag{5.9}$$

and by Eqs. $\widehat{(5.1)}$ and $\widehat{(5.4)}$ themselves for $\hat{P}_{11}$ and $\hat{P}_{14}$. As a result, the solution of the system (5.ε) is determined analytically by the Laplace transforms of the transitions probabilities.

5.5. Transition Rates $P_{10}(t|L, \pm 1)$ at Large Times

The asymptotic value of $P_{10}(t\,|\,L,\,\pm 1)$ is given by the limiting behavior for $s\to 0^+$ of $\hat{P}_{10}(s\,|\,L,\,\pm 1)$. We refer to Appendix C to obtain

$$\begin{aligned}\hat{P}_{10}(s\,|\,L,\,-1)&=N(s)/D(s)\\ \hat{P}_{10}(s\,|\,L,\,+1)&=N(s)\,C(s)/D(s)\end{aligned} \tag{5.10}$$

where $N(s)$ and $D(s)$ are defined by formula (C.1) and $C(s)$ by formula (B.7).

After some calculations given in Appendix C it is found that for $s\to 0^+$

$$s\hat{P}_{10}(s\,|\,L,\,-1)=\alpha+\beta_- s+O(s^2)$$

$$s\hat{P}_{10}(s\,|\,L,\,+1)=\alpha+\beta_+ s+O(s^2)$$

with, by formulas (C.10)–(C.13),

$$\alpha = \frac{a}{c} \equiv \lambda_1^{-1}(1 - e^{-\lambda_2 \tau_2}) \left[2\frac{L-a}{v} + (1 - e^{-\lambda_2 \tau_2})(\lambda_1^{-1} + \lambda_2^{-1}) + (1 - e^{-\lambda_3 \tau_3})(\lambda_3^{-1} + \lambda_4^{-1}) \right]^{-1} \tag{5.11}$$

$$\beta_- = \frac{a}{c}\left(\frac{b}{a} - \frac{d}{c}\right)$$

$$\beta_+ = \beta_- - \alpha(1 - e^{-\lambda_3 \tau_3})(\lambda_3^{-1} + \lambda_4^{-1})$$

In particular, the asymptotic value of $P_{10}(t \mid L, \pm 1)$ is

$$P_{10}(\infty \mid L, \pm 1) = \alpha$$

As an example we have, in the case of a symmetric potential $\lambda_1 = \lambda_4$, $\lambda_2 = \lambda_3$, $\tau_2 = \tau_3 = 2\,a/v_2$ and $a = b$; then

$$\alpha = \frac{1}{2}\left[1 + \frac{\lambda_1}{\lambda_2} + \lambda_1 \frac{L-a}{v}(1 - e^{-2\lambda_2 a/v_2})^{-1} \right]^{-1}$$

5.6. The Particular Case $\lambda_1 = \lambda_4 = 0$

This particular case means that once the particle is in the regime $\varepsilon = 1$ or $\varepsilon = 4$, it is trapped there forever. It is also the limiting case for very large relaxation time (see Section 5.7). In that case we can obtain the following simplified results:

$$A(s) = \frac{\lambda_2}{s(\lambda_2 + s)}(1 - \rho_2), \qquad B(s) = \rho_2, \qquad C(s) = \rho_3$$

$$s\hat{P}_{10}(s \mid L, -1) = \frac{\lambda_2(\lambda_2 + s)^{-1}(1 - \rho_2)s^{1/2}(2\lambda_0)(2\lambda_0 + s)^{1/2}}{D(s)} \tag{5.12}$$

where, as usual,

$$\rho_i = e^{-(\lambda_i + s)}, \qquad i = 2, 3$$

λ_0 is the collision frequency in regime ε_0; $D(s)$, given in Appendix C, depends on ρ_2, ρ_3, and λ_0.

We can now perform two kinds of limits:

(i) We fix λ_0 and expand in powers of $\sigma = (s/\lambda_0)^{1/2}$ to obtain

$$s\hat{P}_{10}(s \mid L, -1) = \frac{1 - \rho_2}{1 - \rho_2\rho_3 + (1 - \rho_2)(1 - \rho_3)\,\lambda_0(L-a)/v} + O(\sigma) \tag{5.13}$$

In this expansion, we are interested in the case $\lambda_1 = \lambda_4 = 0$ and $s/\lambda_0 \equiv \sigma$ small, which means that we look for the asymptotic behavior of $P_{10}(s \mid L, -1)$ for a scale of time large with respect to the scale of the relaxation time on the top of the barrier and very small with respect to the activation time when the particle is in the bottom of the wells (which is really infinite).

(ii) We first let λ_0 tend to zero in (5.12), which leads to

$$\lim_{\lambda_0 \to 0} s\hat{P}_{10}(s \mid L, -1) = \frac{\lambda_2(\lambda_2 + s)^{-1}(1 - \rho_2)}{e^{[(L-a)/v]s} + \rho_3 \rho_2 \, e^{-[(L-a)/v]s}} \tag{5.14}$$

When $s \to 0$ this expression tends to

$$\frac{1 - \rho_2}{1 - \rho_2 \rho_3 + 2\rho_3 (L - a)/v} \tag{5.15}$$

This is the asymptotic value for $t \to \infty$ of the conditional probability if there is no collision when the system is on the top of the barrier.

It is clear by (5.12) and (4.14) that it differs from the asymptotic value of case (i).

5.7. Application to Reaction Dynamics

We apply these results to study the dynamics of systems similar to models of Hynes et al.[6, 12] and Chandler et al.[9, 10] We consider that the particle is in state A if it is in regime 1 or 2 and in state B if it is regime 3 or 4. Let $N_A(t)$ and $N_B(t)$ be the numbers of particles in states A and B at time t and $\delta N_A(t)$ and $\delta N_B(t)$ their fluctuations. The correlation function is

$$C(t) = \langle \delta N_A(0) \, \delta N_B(t) \rangle \tag{5.16}$$

where $\langle \cdots \rangle$ is an equilibrium average over initial conditions. The reactive flux from B to A is

$$k(t) = \frac{1}{N} \frac{dC}{dt} \tag{5.17}$$

and so in our case, following Chandler,[9] we obviously have from (5.16) and (5.17)

$$k(t) = \langle \eta(x(0) - L) \, v(t) \, \delta(x(t) - a) \rangle \tag{5.18}$$

with η the Heaviside function, δ the Dirac function, and $x(0)$ and $v(0)$ the

initial position and velocity of the particle, respectively. In our model the equilibrium probability is

$$P(x, \pm) = \frac{1}{2Q} \exp\left(-\frac{U(x)}{kT}\right) \quad \left(\text{velocities } \pm v \text{ with probability } \frac{1}{2}\right)$$

where

$$Q = \int_L^{L+b} dx \exp\left(-\frac{U(x)}{kT}\right)$$

and U is the internal potential of the system. Then $k(t)$ takes the form

$$k(t) = k_{\mathrm{TST}}[P_{A0}(t \mid L, +1) - P_{A0}(t \mid L, -1)] \tag{5.19}$$

where

$$P_{A0}(t \mid L, \pm 1) = P_{10}(t \mid L, \pm 1) + P_{20}(t \mid L, \pm 1) \tag{5.20}$$

and

$$k_{\mathrm{TST}} = \frac{1}{2} \frac{v}{Q} \exp\left(-\frac{U(L)}{kT}\right) \tag{5.21}$$

Here k_{TST} is the reactive flux resulting from the transition state theory,[9] which neglects all possible returns from A to B.

Now, it is clear that $k(t) \to 0$ if $t \to +\infty$, since the asymptotic values of the conditional probabilities do not depend on the initial states; this property can also be verified in our model by direct calculations using formulas previously derived.

Now, we want to look at $k(t)/k_{\mathrm{TST}}$ for a scale of time t_0 such that

$$t_{\mathrm{mol}} \ll t_0 \ll t_{\mathrm{rel}} \tag{5.22}$$

where t_{mol} is the molecular time of order λ_0^{-1} (or λ_2^{-1} or λ_3^{-1}, which are about of the same order and are related to the free mean path of our reacting system in the surrounding medium) and t_{rel} is the chemical relaxation time, which is of order λ_1^{-1} or λ_4^{-1} and is much greater than t_{mol}; this means that we consider the reactive flux at a scale of time much larger than the time of absorption in the wells, but much less than the reactivation time t_{rel}. Now, at that scale of time, we obtain

$$P_{20}(t_0 \mid L, \pm 1) \simeq 0$$

and so we have

$$\frac{k(t_0)}{k_{\mathrm{TST}}} = \lim_{t_{\mathrm{mol}} \ll t_0 \ll t_{\mathrm{rel}}} [P_{10}(t_0 \mid L, +1) - P_{10}(t_0 \mid L, -1)] \tag{5.23}$$

Let us pause to note that we cannot take simply the limit $t_0 \to +\infty$ in the preceding formula, because this would mean that we would take

$$\lim_{s \to 0} s[\hat{P}_{10}(s \mid L, +1) - \hat{P}_{10}(s \mid L, -1)]$$

but this is zero because $\hat{P}_{10}(s \mid L, +1) = C(s)\, \hat{P}_{10}(s \mid L, -1)$, where $C(s) \sim 1$ if $s \to 0$ [which confirms what we said, namely $k(t) \to 0$ if $t \to +\infty$].

Because we want to consider the behavior of $k(t_0)/k_{\mathrm{TST}}$ in (5.23) for $t_0 \ll t_{\mathrm{rel}}$, we can take $\lambda_1 = \lambda_4 = 0$ and apply the results of Section 5.6. But since we want $t_{\mathrm{mol}} \ll t$, this means that the parameter $\sigma = (s/\lambda_0)^{1/2}$ is small and we can apply the first expansion (5.14). Let us take $\lambda_2 = \lambda_3 = \lambda_0 \equiv \alpha$, a symmetric potential, so that $\tau_2 = \tau_3 = \tau$ and $a = b$; by (5.14) we obtain

$$\begin{aligned} s\hat{P}_{10}(s \mid L, -1) &= \frac{1 - e^{-\alpha\tau}}{1 - e^{-2\alpha\tau} + \alpha[(L-a)/v](1 - e^{-\alpha\tau})^2} + O(\sigma) \\ &= \left[1 + e^{-\alpha\tau} + \alpha\left(\frac{L-a}{v}\right)(1 - e^{-\alpha\tau})\right]^{-1} + O(\sigma) \end{aligned}$$

But, by Section 5.4, we know that if $\lambda_4 = 0$,

$$C(s) = e^{-(\lambda_3 + s)\tau_3}$$

Thus

$$C(s) \sim e^{-\alpha\tau} + O(\sigma)$$

and

$$s\hat{P}_{10}(s \mid L, +1) = C(s)\, s\hat{P}_{10}(s \mid L, -1)$$

so that for $t_{\mathrm{mol}} \ll t \ll t_{\mathrm{rel}}$, we obtain from (5.23) and the preceding asymptotics

$$\frac{k(t_0)}{k_{\mathrm{TST}}} \sim -\frac{1 - e^{-\alpha\tau}}{1 + e^{-\alpha\tau} + \alpha[(L-a)/v](1 - e^{-\alpha\tau})} \tag{5.24}$$

Here τ is twice the time needed for a return over the potential well, so that it is

$$\tau \propto 2a/v_2 = 2a(v^2 + 2E/m)^{1/2}$$

where E is the barrier potential [we observe that the sign in (5.24) is negative due to the fact that we have computed the reactive flux coming from the right of the barrier potential].

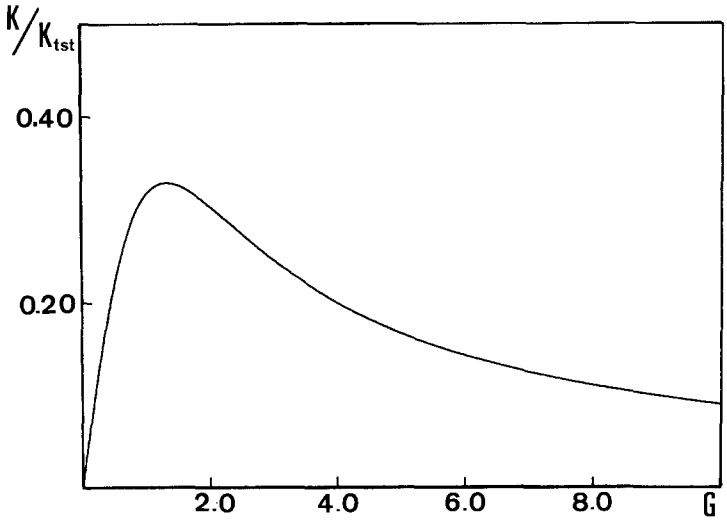


Fig. 4. Chemical rate constant for a symmetric double-well potential as a function of the dimensionless collision frequency $G = \alpha(L-a)/v$ [formula (5.24), with $\tau v/(L-a) = 1$].

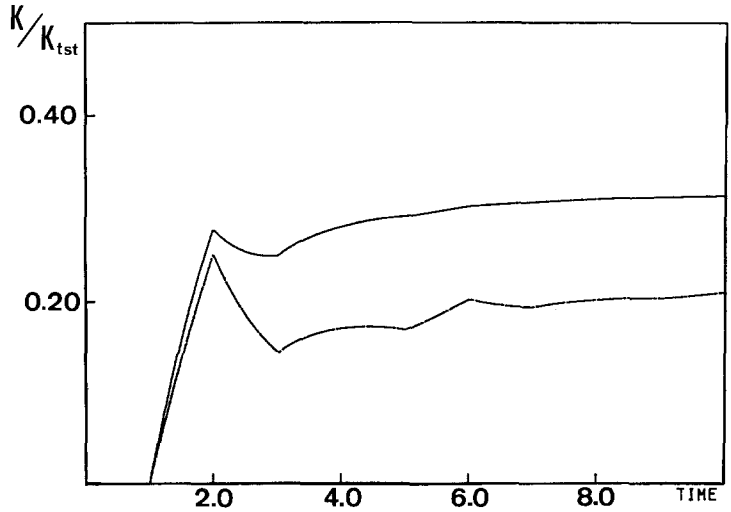


Fig. 5. Time-dependent rate constant $k(t)$ for a symmetric double-well potential: (—) $G = \alpha(L-a)/v = 1$, $S = \tau v/(L-a) = 1$; (– –) $G = 0.5$, $S = 1$.

Now, we can take in (5.24) the limits for $\alpha \to +\infty$ (high viscosity) or $\alpha \to 0$ (small viscosity) to obtain

$$|k(t_0)/k_{\mathrm{TST}}| \sim v/\alpha(L-a) \qquad \alpha \to +\infty$$

$$|k(t_0)/k_{\mathrm{TST}}| \sim \tfrac{1}{2}\tau\alpha \qquad \alpha \to 0$$

in agreement with the standard results of the Kramers theory.[4,9,12,13]

Numerical computations and graphs are given in Figs. 4 and 5.

6. CONCLUSION

We have applied the general formalism developed in Ref. 2 and in the previous paper[1] to three models: two models with finite state space, and a model of diffusion in a two-well potential with continuous state space. In the first two models we obtained an approach to equilibrium either by decreasing exponentials or by decreasing oscillating exponentials, depending on the values of the parameters; this last behavior is due to the combination of a deterministic and a stochastic dynamics with different time scales. In the more elaborate models, we have found that our results are in agreement with numerical simulations and experimental data for the reactive flux at an intermediate scale of time. Moreover, our approach is entirely analytical and rigorous and the new phenomena that we have found by our analysis confirm numerical simulations done by previous authors.

We note also that we have not used the full power of the general processes that we defined in the beginning of the second reaction and in Ref. 1, since all stochastic times are exponential. In particular, the non-Markovian character of the evolution is very mild and occurs only because of the deterministic times introduced to distinguish several phases of the evolution (in the potential wells, on the top of the barrier). Moreover, this cannot be used for a very dense medium. In further work in progress, we will treat more complicated processes with more realistic approximations of a dense environment (in particular, of the cage effect), by introducing convenient nonexponential random times to obtain memory effects.

The advantage of this kind of model is that they are simple enough to be solved exactly while preserving the main features of the dynamics, whereas the Fokker–Planck approach leads a partial differential equation which in general is not exactly solvable and does not always give a suitable approximation of the evolution (see, for example, another model of chemical reaction in Ref. 15).

APPENDIX A

In this appendix, we give detailed computations for Section 4. The matrix $\mathbf{A}(s)$ defined by (2.8), (2.9), and (4.1) is

$$\mathbf{A}(s)=\begin{pmatrix} 1 & \lambda_2(\lambda_2+s)^{-1}(\rho_2-1) & 0 & 0 \\ -\lambda_1(\lambda_1+s)^{-1} & 1 & -\rho_3 & 0 \\ 0 & -\rho_2 & 1 & -\lambda_4(\lambda_4+s)^{-1} \\ 0 & 0 & \lambda_3(\lambda_3+s)^{-1}(\rho_3-1) & 1 \end{pmatrix}$$

with

$$\rho_i=e^{-(\lambda_i+s)\tau}$$

According to the general theory, the matrix $\hat{\mathbf{P}}(s)$ is

$$\hat{\mathbf{P}}(s)=\hat{\boldsymbol{\theta}}(s)\,\mathbf{A}^{-1}(s)$$

where $\hat{\boldsymbol{\theta}}(s)$, defined by (2.10), is

$$\hat{\boldsymbol{\theta}}(s)=\begin{pmatrix} (\lambda_1+s)^{-1} & 0 & 0 & 0 \\ 0 & (\lambda_2+s)^{-1} & 0 & 0 \\ 0 & 0 & (\lambda_3+s)^{-1} & 0 \\ 0 & 0 & 0 & (\lambda_4+s)^{-1} \end{pmatrix}$$

The asymptotic value of $P(t)$ is

$$P_{\varepsilon\varepsilon_0}(\infty)=P_\varepsilon(\infty)\propto t_\varepsilon q_\varepsilon$$

where

$$t_1=\lambda_1^{-1},\qquad t_2=(1-\sigma_2)\lambda_2^{-1},\qquad t_3=(1-\sigma_3)\lambda_3^{-1},\qquad t_4=\lambda_4^{-1}$$

with

$$\sigma_i=e^{-\lambda_i\tau_i},\qquad i=2,3$$

(q_ε) is the right null-vector of $A(0)$:

$$q_1=\sigma_3(1-\sigma_2),\qquad q_2=\sigma_2,\qquad q_3=\sigma_3,\qquad q_4=\sigma_2(1-\sigma_3)$$

which leads to formula (4.2) for $\mathbf{P}(\infty)$.

The asymptotic behavior of $\mathbf{P}(t)-\mathbf{P}(\infty)$ is determined by the poles of $\hat{\mathbf{P}}(s)$, which are the nonzero roots of $\det A(s)=0$. It is found that

$$\det\ \mathbf{A}(s)=sD(s)\prod_{i=1}^{4}(\lambda_i+s)^{-1}$$

with

$$D(s) = s(s+\lambda_1+\lambda_2)(s+\lambda_3+\lambda_4)(1-\rho_2\rho_3)$$
$$+ \lambda_1\lambda_2\rho_2(1-\rho_3)(s+\lambda_1+\lambda_2) + \lambda_3\lambda_4\rho_3(1-\rho_2)(s+\lambda_3+\lambda_4)$$

The zeros of $D(s)$ cannot be found analytically, since $\rho_i = \sigma_i e^{-s\tau_i}$. However, if $s\tau \ll 1$, ρ_i may be replaced by the constant σ_i and $D(s)$ becomes a polynomial $\bar{D}(s)$ of order three in s. It can be shown that it has two complex roots for convenient values of the λ_i.

Proof. Writing

$$\lambda_1 + \lambda_2 = a(1+\theta)$$
$$\lambda_3 + \lambda_4 = a(1-\theta)$$
$$\lambda_1\lambda_2\sigma_2(1-\sigma_3) = \alpha_2 a^2(1+\theta)^2/4$$
$$\lambda_3\lambda_4\sigma_3(1-\sigma_2) = \alpha_3 a^2(1-\theta)^2/4$$

It is easily seen that $|\theta| < 1$ and $\alpha_2 + \alpha_3 < 1$.

As a particular case, take $\alpha_2 = \alpha_3 = \alpha < 1/2$. Then the equation $\bar{D}(s) = 0$ implies, for $u = s/a$,

$$F(u) \equiv (u+1)(u^2+u+\alpha/2) - \theta^2(u(1-\alpha/2)+\alpha/2) = 0$$

or

$$y(u) \equiv u^2 + u + \alpha/2 = \theta^2 \frac{u(1-\alpha/2)+\alpha/2}{u+1} \equiv z(u)$$

For $u < -1$, this equation admits one real root and only one, since the left-hand side decreases from $+\infty$ to $\alpha/2$, and the right-hand side increases from $\theta^2(1-\alpha/2)$ to $+\infty$ when u increases from $-\infty$ to -1.

For $u > -1$, the right-hand side $z(u)$ vanishes for $u = -(\alpha/2)(1-\alpha/2)^{-1} = u_0$ and

$$z(u) \leqslant \frac{dz}{du}(u_0)\cdot(u-u_0) = \theta^2 \frac{1-\alpha/2}{1-\alpha}\left[u\left(1-\frac{\alpha}{2}\right)+\frac{\alpha}{2}\right]$$

Thus

$$F(u) \equiv y(u) - z(u)$$
$$\geqslant u^2 + u\left(1-\theta^2\frac{(1-\alpha/2)^2}{1-\alpha}\right) + \frac{\alpha}{2}\left(1-\theta^2\frac{1-\alpha/2}{1-\alpha}\right) \equiv G(u)$$

The discriminant Δ of $G(u)$ is found to be

$$\Delta = \left(\theta^2 \frac{(1-\alpha/2)^2}{1-\alpha} - \frac{1-3\alpha/2}{1-\alpha/2}\right)^2 - \frac{\alpha^3/2}{(1-\alpha/2)^2}$$

which is negative if $\alpha > 0$ and

$$\theta^2 \simeq \frac{(1-\alpha)(1-3\alpha/2)}{(1-\alpha/2)^3} \quad (<1 \text{ if } \alpha < 1/2)$$

For these values of θ, $G(u)$ is positive for any u, and

$$F(u) \geqslant G(u) > 0 \qquad \text{for} \quad u > -1$$

Then $F(u) = 0$ has only one real root and two complex roots.

APPENDIX B

This appendix gives the details of the calculations of Section 5.3. We denote by $\mathscr{L}$ the operator of Laplace transform, namely

$$(\mathscr{L}f)(s) = \hat{f}(s)$$

We need the following preliminary calculations:

$$\mathscr{L}\left(\int_0^t f(\tau)\, g(t-\tau)\, d\tau\right) = \mathscr{L}f \cdot \mathscr{L}g$$

$$\mathscr{L}\left(\int_0^{t \wedge S} \lambda e^{-\lambda\tau} P(t-\tau)\, d\tau = \frac{\lambda}{\lambda+s}(1-e^{-(\lambda+s)S})\, \mathscr{L}(P)\right. \tag{B.1}$$

$$\mathscr{L}(\eta(t-S)\, P(t-S)) = e^{-sS}\, \mathscr{L}(P)$$

We have to compute

$$\mathscr{L}\left(\int_0^{t \wedge \tau_\alpha(x)} \lambda_0 e^{-\lambda_0\tau} P_{10}(t-\tau \mid x+\alpha v\tau, -\alpha)\, d\tau\right)$$

$$= \int_a^L dx_1\, \mathscr{L}\left(\int_0^{t \wedge \tau_\alpha(x)} \lambda_0 e^{-\lambda_0\tau} P_{10}(t-\tau \mid x_1, -\alpha)\, \delta(x_1 - x - \alpha v\tau)\, d\tau\right)$$

and using (1), we obtain:

$$= \int_a^L dx_1\, \mathscr{L}(\eta(\tau)\, \eta(\tau_\alpha(x)-\tau)\, \lambda_0 e^{-\lambda_0\tau}\, \delta(x_1 - x - \alpha v\tau))$$

$$\times \mathscr{L}(P_{10}(\tau \mid x_1, -\alpha))$$

But we have

$$\mathscr{L}(\eta(\tau)\,\eta(\tau_\alpha(x)-\tau)\,\lambda_0 e^{-\lambda_0\tau}\,\delta(x_1-x-\alpha v\tau))(s)$$
$$=\begin{cases}\dfrac{\lambda_0}{v}\,e^{-(\lambda_0+s)(x_1-x)/v}\,\eta(x_1-x) & \text{if} \quad \alpha=+1\\[2ex] \dfrac{\lambda_0}{v}\,e^{(\lambda_0+s)(x_1-x)/v}\,\eta(x-x_1) & \text{if} \quad \alpha=-1\end{cases}$$

so that

$$\mathscr{L}\left(\int_0^{t\wedge\tau_\alpha(x)}\lambda_0 e^{-\lambda_0\tau}\,P_{10}(t-\tau\,|\,x+\alpha v\tau,\,-\alpha)\,d\tau\right)(s)$$
$$=\int_a^L dx'\,\hat{P}_{10}(s\,|\,x',\,-\alpha)\,\frac{\lambda_0}{v}\,e^{-\alpha(\lambda_0+s)(x'-x)/v}\,\eta(\alpha(x'-x)) \qquad \text{(B.2)}$$

Using these formulas, it is easy to derive the Laplace-transformed system $\widehat{(5.0)}$–$\widehat{(5.4)}$ from (5.0)–(5.4). We want to solve this system.

This system can be written as

$$\hat{P}_{12}(s)=A(s)+B(s)\,\hat{P}_{10}(s\,|\,a,\,+1) \qquad \text{(B.5)}$$
$$\hat{P}_{13}(s)=C(s)\,\hat{P}_{10}(s\,|\,L,\,-1) \qquad \text{(B.6)}$$

with

$$A(s)=\frac{\lambda_2}{(\lambda_1+s)(\lambda_2+s)}\,(1-e^{-(\lambda_2+s)\tau_2})$$
$$B(s)=e^{-(\lambda_2+s)\tau_2}+\frac{\lambda_1\lambda_2}{(\lambda_1+s)(\lambda_2+s)}\,(1-e^{-(\lambda_2+s)\tau_2}) \qquad \text{(B.7)}$$
$$C(s)=e^{-(\lambda_3+s)\tau_3}+\frac{\lambda_3\lambda_4}{(\lambda_3+s)(\lambda_4+s)}\,(1-e^{-(\lambda_3+s)\tau_3})$$

We now use Eqs. (B.5) and (B.6) in $\widehat{(5.0)}$, to obtain

$$\hat{P}_{10}(s\,|\,x,\,+1)=\int_x^L dx'\,\hat{P}_{10}(s\,|\,x',\,-1)\,\frac{\lambda_0}{v}\,e^{-(\lambda_0+s)(x'-x)/v}$$
$$+\,e^{-(\lambda_0+s)\,\tau_+(x)}\,C(s)\;\hat{P}_{10}(s\,|\,L,\,-1)$$
$$\hat{P}_{10}(s\,|\,x,\,-1)=\int_a^x dx'\,\hat{P}_{10}(s\,|\,x',\,+1)\,\frac{\lambda_0}{v}\,e^{+(\lambda_0+s)(x'-x)/v} \qquad \text{(B.8)}$$
$$+\,e^{-(\lambda_0+s)\,\tau_-(x)}[A(s)+B(s)\,\hat{P}_{10}(s\,|\,x,\,+1)]$$

Recall that $\tau_+(x) = (L-x)/v$, $\tau_-(x) = (x-a)/v$ and differentiate with respect to x; finally we obtain the folowing first-order differential system:

$$\begin{aligned} \frac{\partial \hat{P}_{10}(s\,|\,x,\,+1)}{\partial x} &= -\frac{\lambda_0}{v}\,\hat{P}_{10}(s\,|\,x,\,-1) + \frac{\lambda_0+s}{v}\,\hat{P}_{10}(s\,|\,x,\,+1) \\ \frac{\partial \hat{P}_{10}(s\,|\,x,\,-1)}{\partial x} &= \frac{\lambda_0}{v}\,\hat{P}_{10}(s\,|\,x,\,+1) - \frac{\lambda_0+s}{v}\,\hat{P}_{10}(s\,|\,x,\,-1) \end{aligned} \tag{B.9}$$

with the two limit conditions at a and L, which can be derived from (B.8),

$$\begin{aligned} \hat{P}_{10}(s\,|\,L,\,+1) &= C(s)\,\hat{P}_{10}(s\,|\,L,\,-1) \\ \hat{P}_{10}(s\,|\,a,\,-1) &= A(s) + B(s)\,\hat{P}_{10}(s\,|\,a,\,+1) \end{aligned} \tag{B.10}$$

The eigenvalues of the linear system (B.9) we

$$\pm\xi_0 = \pm[(2\lambda_0+s)s/v^2]^{1/2}$$

and the corresponding eigenvectors are

$$\begin{aligned} V_- &\equiv \begin{pmatrix} \lambda_0 \\ \mu_- \end{pmatrix} \equiv \begin{pmatrix} \lambda_0 \\ \lambda_0+s+[(2\lambda_0+s)s]^{1/2} \end{pmatrix} \\ V_+ &\equiv \begin{pmatrix} \lambda_0 \\ \mu_+ \end{pmatrix} \equiv \begin{pmatrix} \lambda_0 \\ \lambda_0+s-[(2\lambda_0+s)s]^{1/2} \end{pmatrix} \end{aligned} \tag{B.11}$$

Then the solutions of system (B.9) are found to be

$$\begin{aligned} \hat{P}_{10}(s\,|\,x,\,+1) &= \lambda_0 E e^{-\xi_0 x} + \lambda_0 F e^{-\xi_0(L-x)} \\ \hat{P}_{10}(s\,|\,x,\,-1) &= \mu_- E e^{-\xi_0 x} + \mu_+ F e^{-\xi_0(L-x)} \end{aligned} \tag{B.12}$$

with

$$\begin{aligned} E = {} & A(s)\,e^{\xi_0 L}[\lambda_0 - C(s)\mu_+] \\ & \times \{[\mu_- - B(s)\,\lambda_0][\lambda_0 - C(s)\mu_+]\,e^{(L-a)\xi_0} \\ & - [\mu_+ - B(s)\lambda_0][\lambda_0 - C(s)\mu_-]\,e^{-\xi_0(L-a)}\}^{-1} \\ F = {} & -A(s)[\lambda_0 - C(s)\mu_-] \\ & \times \{[\mu_- - B(s)\lambda_0][\lambda_0 - C(s)\mu_+]\,e^{(L-a)\xi_0} \\ & - [\mu_+ - B(s)\lambda_0][\lambda_0 - C(s)\mu_-]\,e^{-\xi_0(L-a)}\}^{-1} \end{aligned} \tag{B.13}$$

The solution of our system is determined first by Eq. (B.12), then by Eqs. (B.5) and (B.6), and finally by Eqs. (5.1) and (5.4).

APPENDIX C

We obtain by Eqs. (B.12) and (B.13) of Appendix B and Sections (5.3) and (5.4)

$$\begin{aligned}\hat{P}_{10}(s\,|\,L,-1) = A(s)\,\lambda_0(\mu_- - \mu_+) \\ \times\{[\mu_- - B(s)\lambda_0][\lambda_0 - C(s)\mu_+]\,e^{(L-a)\xi_0} \\ - [\mu_+ - B(s)\lambda_0][\lambda_0 - C(s)\mu_-]\,e^{-(L-a)\xi_0}\}^{-1}\end{aligned} \tag{C.1}$$

where $N(s)$ and $D(s)$ are the numerator and denominator of Eq. (C.1) and also

$$\hat{P}_{10}(s\,|\,L,+1) = \hat{P}_{10}(s\,|\,L,-1)\,C(s) \tag{C.2}$$

We want to find the asymptotic behavior for $s \to 0^+$ of these quantities.

C1. Preliminary Computations

It is found that

$$A(s) = \frac{1}{\lambda_1}(1 - e^{-\lambda_2\tau_2}) + s[\lambda_1^{-1}e^{-\lambda_2\tau_2}\tau_2 - \lambda_1^{-1}(\lambda_1^{-1} + \lambda_2^{-1})(1 - e^{-\lambda_2\tau_2})] + \cdots \tag{C.3}$$

$$B(s) = 1 - \alpha_2 s - \beta_2 s^2 + \cdots \tag{C.4}$$

with

$$\begin{aligned}\alpha_2 &= (1 - e^{-\lambda_2\tau_2})(\lambda_1^{-1} + \lambda_2^{-1}) \\ \beta_2 &= [\lambda_1^{-2} + \lambda_2^{-2} - (\lambda_1\lambda_2)^{-1}](1 - e^{-\lambda_2\tau_2}) + e^{-\lambda_2\tau_2}\tau_2(\lambda_1^{-1} + \lambda_2^{-1})\end{aligned} \tag{C.5}$$

$$C(s) = 1 - \alpha_4 s - \beta_4 s^2 + \cdots \tag{C.6}$$

with

$$\begin{aligned}\alpha_4 &= (1 - e^{-\lambda_3\tau_3})(\lambda_4^{-1} + \lambda_3^{-1}) \\ \beta_4 &= [\lambda_3^{-2} + \lambda_4^{-2} - (\lambda_3\lambda_4)^{-1}](1 - e^{-\lambda_3\tau_3}) + e^{-\lambda_3\tau_3}\tau_3(\lambda_3^{-1} + \lambda_4^{-1})\end{aligned} \tag{C.7}$$

C2. Expansion of $\hat{P}_{10}(s|L,-1)$

We have by (C.1) up to (C.7)

$$s\hat{P}_{10}(s\,|\,L,-1) = \frac{a + bs + \cdots}{c + ds + \cdots} = \frac{a}{c}\left[1 + s\left(\frac{b}{a} - \frac{d}{c}\right)\right] + O(s^2)$$

and so we obtain

$$\lim_{s \to 0} \frac{1}{s}\left[s\hat{P}_{10}(s \mid L, -1) - \frac{a}{c}\right] = \left(\frac{b}{a} - \frac{d}{c}\right)\frac{a}{c} \tag{C.8}$$

with

$$\frac{a}{c} = \frac{\lambda_1(1 - e^{-\lambda_2 \tau_2})}{2(L-a)/v + \alpha_2 + \alpha_4}$$

$$d = (\alpha_2 + \alpha_4)\left[(4\lambda_0)^{-1} - \frac{L-a}{v} + \frac{(L-a)^2}{v^2}\lambda_0\right]$$

$$+ \alpha_2\alpha_4\left(\lambda_0 \frac{L-a}{v} - 1\right) + (2\lambda_0)^{-1}\frac{L-a}{v} + \beta_2 + \beta_4 \tag{C.9}$$

and

$$\frac{b}{a} - \frac{d}{c} = \frac{(4\lambda_0)^{-1} - \alpha_2 + e^{-\lambda_2\tau_2}\tau_2}{1 - e^{-\lambda_2\tau_2}} - \frac{d}{2(L-a)/v + \alpha_2 + \alpha_4} \tag{C.10}$$

C3. Expansion of $\hat{P}_{10}(s \mid L, +1)$

We use (C2) and (C.6),

$$s\hat{P}_{10}(s \mid L, +1) = s\hat{P}_{10}(s \mid L, -1)\, C(s)$$

$$= \frac{a}{c} + s\left[\left(\frac{b}{a} - \frac{d}{c}\right)\frac{a}{c} - \alpha_4 \frac{a}{c}\right] + O(s^2) \tag{C.11}$$

In particular, we can compute

$$s\hat{P}_{10}(s \mid L, +1) - s\hat{P}_{10}(s \mid L, -1) = -s\alpha_4 \frac{a}{c} + O(s^2)$$

and so

$$\lim_{s \to 0} [\hat{P}_{10}(s \mid L, +1) - \hat{P}_{10}(s \mid L, -1)] = -\alpha_4 \frac{a}{c} \tag{C.12}$$

where α_4 is given by (C.7) and a/c by (C.9).

REFERENCES

1. B. Gaveau and M. Moreau, *Lett. Math. Phys* . **9**:213 (1985).
2. N. G. Van Kampen, *Physica* **96A**:435 (1979).
3. J. L. Doob, *Stochastic Processes* (Wiley, New York, 1967).

4. E. W. Montroll and K. E. Shuler, *Adv. Chem. Phys.* **1**:361 (1958).
5. A. Bak and J. L. Lebowitz, *Phys. Rev.* **131**:1138 (1963).
6. J. T. Hynes, R. Kapral, and G. M. Torrie, *J. Chem. Phys.* **72**:177 (1980).
7. C. L. Brooks III, M. Berkowitz, and S. A. Adelman, *J. Chem. Phys.* **73**:4353 (1980).
8. M. Balk, C. L. Brooks III, and S. A. Adelman, *J. Chem. Phys.* **79**:804 (1983).
9. D. Chandler, *J. Chem. Phys.* **68**:2959 (1978).
10. J. A. Montgomery, Jr., D. Chandler, and B. J. Berne, *J. Chem. Phys.* **70**:4056 (1979).
11. B. J. Berne, J. L. Skinner, and P. G. Wolynes, *J. Chem. Phys.* **73**:4314 (1980).
12. S. H. Northrup and J. T. Hynes, *J. Chem. Phys.* **73**:2700 (1980).
13. J. L. Skinner and P. G. Wolynes, *J. Chem. Phys.* **69**:2143 (1978).
14. H. A. Kramers, *Physica* **7**:284 (1940).
15. D. Borgis and M. Moreau, *Mol. Phys.* **57**:33 (1986).