

## IX

# THE THEORY OF CHEMICAL REACTION RATES\*

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## I. MOTIVATION

The theoretical study of the rates of condensed phase chemical reactions is, by comparison with the gas phase, in an early state of development. However, the last few years have seen renewed interest in the subject, with important new results being obtained, and this in turn has spurred novel experimental activity.

When compared with reactions in the gas phase, the theory of condensed phase processes meets the additional difficulty of having to deal with solvent interactions, but the detailed understanding of their effects is crucial in many

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areas of chemistry, biology, and related sciences. Among the interactions between the reactive species and the solvent, we should distinguish the specific interactions (e.g., electrostatic or those originating from hydrogen bonding) from the stochastic forces generated by the thermal motions of the solvent particles. In this chapter we shall be concerned only with interactions of the latter type and discuss some recent developments.

The strength of the stochastic interactions between the solvent and the reactant may be described (in the Markovian case) by a parameter  $\gamma$ , the damping rate or friction coefficient, which is some measure of the coupling at the microscopic level and is related to the macroscopic viscosity, density, or pressure. Viscosity effects on reaction rates have been known for a long time, but the understanding of the mechanism of these interactions and of the most general form of their effects was very poor. The so-called cage effect is commonly used in discussing the observed viscosity dependence of the reaction rates.<sup>1-3</sup> The motion of the reactant(s) into the reacting position, the "encounter" in the language of collision theory, is hindered by higher viscosities  $\eta$ , and in the diffusive regime the number of these encounters is  $Z \propto \eta^{-1}$ . However, this same factor increases the difficulty for the reactant(s) to move out of position, providing a sort of cage wall, and the time spent inside this cage, or the number of collisions following the initial encounter, is  $n \propto \eta$ . Any reaction rate that is proportional to the total number of collisions,  $Z \times n$ , will be independent of the viscosity. Under certain circumstances, however, the rate will be proportional to  $Z \propto \eta^{-1}$ . One class of processes where this is well known to happen is the quenching of fluorescence, where the chemical process is so fast that the rate is controlled by the diffusion of the quencher to the excited molecule.<sup>4</sup> Similar behavior is observed in very fast proton-transfer reactions.<sup>5</sup> For very high viscosities, the quantity  $n$  will be very large, the chemical reaction will always occur at an early stage of the encounter, and the rate will be proportional to  $Z \propto \eta^{-1}$ . Then, we should expect that the rate of a chemical reaction would always go as  $\eta^{-1}$  for sufficiently high viscosities.

In the other extreme case, when the coupling of the reactant(s) to the solvent is very weak, the reaction rate will also decrease. In fact, once the higher energy molecules have reacted, the replenishment of this top energy layer will be too slow to maintain thermal equilibrium and the rate will slow down.

We shall show that this behavior is predicted in all stochastic theories, the major effort being directed to understanding the conditions when such extreme regimes fail and to predicting the detailed general form of the rate constant.

The most widely used theoretical tool for the understanding of chemical kinetics is still the transition state theory (TST) in its original form,<sup>6</sup> or in

one of its modern versions.<sup>7</sup> Because it is used throughout this chapter as a major reference for comparison of the results obtained with the stochastic theories, it is useful to recall its basic principles and final expression. Conventional transition state theory depends on the following general assumptions (for a detailed discussion of the theory, see, e.g., ref. 8):

1. The rate of a chemical reaction may be calculated by focusing attention on the "transition state," the region near the col or saddle point of the potential energy surface that must be crossed in the process of converting the reactants into products.
2. The transition state is in quasi-thermodynamic equilibrium with the reactants, and the removal of the products does not affect the reactants' equilibrium up to the transition state.
3. In the region around the col, the motion along the reaction coordinate can be treated as free translational motion.

The rate  $k_{\text{TST}}$  is calculated as the product of the population at the transition state and the frequency at which one such species will go into products. The final result may be cast in the form

$$k_{\text{TST}} = \kappa \frac{K_B T}{h} \frac{Q_{\ddagger}}{Q_A} \exp\left(-\frac{E_b}{K_B T}\right) \quad (1)$$

where  $Q_{\ddagger}$  and  $Q_A$  are the partition functions associated with the transition state and the reactant, respectively,  $E_b$  is the activation energy (the potential energy of the col above the ground state of the reactants), and  $h$ ,  $K_B$ , and  $T$  have the usual meaning.  $\kappa$  is the so-called transmission coefficient, an *ad hoc* factor usually taken close to unity, measuring the fraction of the forward moving transition state molecules that actually become products and are not reflected.

If one considers a system with a single degree of freedom,  $Q_{\ddagger} = 1$  and  $Q_A = (1 - \hbar\omega_0/K_B T)^{-1} \approx K_B T/\hbar\omega_0$  (for  $K_B T \gg \hbar\omega_0$ ), the partition function of the harmonic vibration of the reactant, the TST rate is given by

$$K_{\text{TST}} = \frac{\omega_0}{2\pi} \exp\left(-\frac{E_b}{K_B T}\right) \quad (2)$$

if the transmission coefficient is assumed unity. This is the TST rate expression that we will always consider in later sections.

The most interesting applications of transition state theory have been, perhaps, in solution chemistry, and a number of detailed improvements have been made to bring in some of the effects of the solvent. This has been done mostly within the framework of thermodynamics by introducing in Eq. (1)

the solvent dependence of the assumed equilibrium between reactants and transition state. The activation energy is then solvent-dependent, and quantities like activation entropy and activation volume are used in the discussion. (This is thoroughly treated in standard textbooks, for example, in ref. 1.) Other effects originate in the intrinsically dynamic interactions between solvent and solute and are thus not amenable to this kind of thermodynamic treatment. The stochastic theories that have expanded so much in these last few years attempt to deal with these more complicated interactions.

The plan of this chapter is as follows. In Section II, the basic ideas of the method of Kramers are reviewed, and recent generalizations, especially the progress made in bridging the two Kramers limits, are discussed. The remainder of the chapter is devoted to discuss two lines of current development of the theory that seem very promising for the interpretation of chemical rate processes in condensed media. Section III deals with the problem of the interaction of the reactive coordinate with other nonreactive modes and establishes a connection with the field of nonequilibrium nonlinear statistical thermodynamics. The difficulties arising from the breakdown of the hypothesis of time-scale separation (non-Markovian effects) which may be very relevant in condensed phase processes are considered in Section IV. The improved physical interpretation that may be achieved by the general strategy that is the subject of this volume is discussed in Section V. We should note that the three cornerstone techniques of the delta-like strategy proposed in Chapter I are used in Sections III and IV.

## II. THE KRAMERS MODEL AND ITS EXTENSIONS

For our purposes, a chemical reaction is viewed as the passage over a barrier of a particle under the influence of random forces originating in its environment. It was Marcellin<sup>9</sup> who first represented a chemical reaction by the motion of a point in phase space, thus using for the first time the rigorous methods of statistical mechanics. He suggested that the course of a chemical reaction could be followed by the trajectory of a point in the  $2n$ -dimensional space defined by the  $n$  position coordinates necessary to describe the reacting system together with the corresponding conjugate momenta.

Inspired by Christiansen's<sup>10</sup> treatment of a chemical reaction as a diffusional problem, Kramers<sup>11</sup> studied the model of a particle in Brownian motion in a one-dimensional force field and predicted the existence of three fundamental kinetic regimes, depending on the magnitude of the friction. The basic hypothesis and results of this work will be summarized below, as many of the results most recently obtained using more sophisticated models are still best described by reference to Kramers' original model and reduce to Kramers models when the appropriate limits are taken.

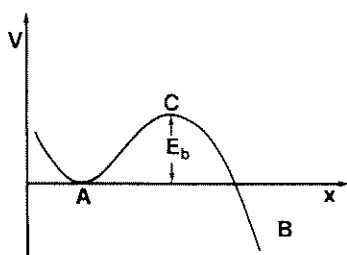


Figure 1. The Kramers potential.

### A. The Kramers Model

Consider an ensemble of noninteracting particles—the reactant—under the influence of (1) a force derived from an external one-dimensional potential  $V(x)$  consisting of a well  $A$  and an adjacent barrier  $C$  (see Fig. 1) and (2) an irregular force resulting from random collisions between the reactant particles and solvent particles at a given temperature  $T$ .

Kramers<sup>11</sup> identified the chemical reaction with the escape over the barrier of the reactant particles initially located in the potential well. The irregular force simulates the interaction with the solvent, which is thus treated as a heat bath.

The motion of a particle (mass  $M$ ) in the Kramers model may be described by the following Langevin equation:

$$\dot{x} = v \quad (3a)$$

$$\dot{v} = -\gamma v - \frac{1}{M} \frac{\partial V}{\partial x} + \frac{1}{M} F(t) \quad (3b)$$

where  $\gamma$  is the friction coefficient (or damping rate) and  $F(t)$  is the irregular force associated with the coupling to the heat bath. This force is assumed to be Markovian, that is, the forces at different times are assumed to be uncorrelated. It may then be defined by

$$\langle F(t) \rangle = 0 \quad (4a)$$

$$\langle F(0)F(t) \rangle = 2\gamma MK_B T \delta(t) \quad (4b)$$

where Eq. (4b) is an expression of the fluctuation-dissipation theorem,<sup>12</sup> which relates the friction  $\gamma$  with the magnitude of the irregular forces acting on the particle.

The Langevin equation (3a, b) is equivalent to the following Fokker-Planck equation which drives the probability distribution in phase space:

$$\frac{\partial}{\partial t} \rho(x, v, t) = \left\{ -v \frac{\partial}{\partial x} + \frac{1}{M} \frac{\partial V}{\partial x} \frac{\partial}{\partial v} + \gamma \left[ \frac{\partial}{\partial v} v + \frac{K_B T}{M} \frac{\partial^2}{\partial v^2} \right] \right\} \rho(x, v, t) \quad (5)$$

In order to obtain simple analytical results from this equation, Kramers assumed further that (3) the potential is parabolic near  $A$ ,  $V(x) = \frac{1}{2}M\omega_0^2x^2$ , and near  $C$ ,  $V(x) = Q - \frac{1}{2}M\omega_b^2(x - x_c)^2$ , and that (4) the height of the barrier is much larger than the thermal energy,  $E_b \gg K_B T$ , so that the reaction process is slow and quasi-stationary. Under these conditions he was able to obtain the following simple expression for the rate of particle flow over the barrier:

$$k_K = \frac{\gamma\omega_0}{4\pi\omega_b} \left[ \left( 1 + \frac{4\omega_b^2}{\gamma^2} \right)^{1/2} - 1 \right] \exp\left( -\frac{E_b}{K_B T} \right) \quad (6)$$

It is important to consider two limiting cases where this general expression may be simplified. For small frictions,  $\gamma \ll 2\omega_b$ , Eq. (6) gives the same expression as that obtained earlier in transition state theory,

$$k_{\text{TST}} = \frac{\omega_0}{2\pi} \exp\left( -\frac{E_b}{K_B T} \right) \quad \gamma \ll 2\omega_b \quad (7)$$

The condition of validity of this expression is easily understood. If the time scale of the damping,  $1/\gamma$ , is much larger than the time scale of the motion atop the barrier,  $1/\omega_b$ , then the particle will have an effectively free motion in its downhill path out of the well. It should be kept in mind that this is exactly one of the fundamental hypotheses of transition state theory. It would be wrong, however, to conclude that there is no lower limit on the friction for the correct applicability of the TST expression. For extremely low frictions, the coupling to the heat bath is no longer able to maintain the quasi-thermodynamic equilibrium in the well, thus invalidating an assumption made by Kramers to derive Eq. (6) and also the underlying conventional TST. For this extreme low-friction region, Kramers<sup>11</sup> was able to calculate the rate by converting the Fokker-Planck equation [Eq. (5)] into a diffusion equation for the energy; the exchange of energy between the heat bath and the particle is the rate-limiting step in these conditions. The following approximate rate equation was obtained:

$$k_{\text{low}} = \gamma \frac{E_b}{K_B T} \exp\left( -\frac{E_b}{K_B T} \right) \quad (8)$$

This energy diffusion process should apply when the characteristic time of damping,  $1/\gamma$ , is much larger than the time of equilibrium escape of a particle from the well,  $1/k_{\text{TST}}$ .

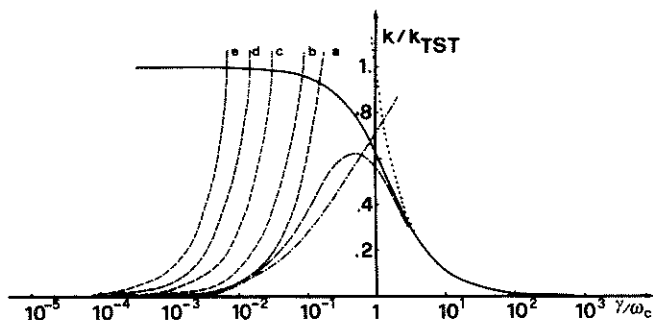


Figure 2. The reaction rate in the Kramers model relative to its transition state value. The low friction rate is plotted for  $(\omega_b/\omega_0)(E_b/K_B T) = 1$  (a), 2 (b), 5 (c), 10 (d), and 20 (e). Also plotted is the interpolated rate of Eq. (13) and that calculated by Buttiker, Harris, and Landauer.<sup>13</sup> (—)  $k_K/k_{TST}$ ; (···)  $k_{high}/k_{TST}$ ; (---)  $k_{low}/k_{TST}$ ; (----)  $k_{int}/k_{TST}$ ; (- - -)  $k_{BHL}/k_{TST}$ .

Kramers<sup>11</sup> suggested that transition state theory should apply in the range of frictions  $(K_B T \omega_0 / 2\pi E_b) \leq \gamma \leq \frac{1}{2} \omega_b$ , the lowest limit corresponding to the point where expressions (7) and (8) give the same rate value.

The general Kramers expression (6) may be simplified in the region of very high friction,  $\gamma \gg 2\omega_b$ , where a purely diffusive regime is attained,

$$k_{high} = \frac{\omega_0 \omega_b}{2\pi \gamma} \exp\left(-\frac{E_b}{K_B T}\right) \quad (9)$$

The plots in Fig. 2 suggest that the limits of validity of transition state theory may be fairly narrow or altogether nonexistent, contrary to the prediction made by Kramers. The nonequilibrium effects duly treated for extremely low friction may start being felt before the TST plateau is approached. This is more likely to occur for the lower barriers and larger ratios  $\omega_0/\omega_b$ .

The following argument may help in understanding the connection between the extreme low-friction regime and the diffusive one. Kramers identified very clearly the two processes that determine the rate of escape: the thermal escape out of the bottom of the well and the actual diffusive crossing of the barrier. The slowest of the two becomes the limiting step and determines the overall rate given by Eqs. (8) and (6), respectively. If we assume that these are successive processes according to the scheme



we can easily calculate a rate expression valid for all frictions. The overall rate of scheme (10) is given by  $k_{\text{int}} = k^d k_r^E / (k_i^E + k^d)$  and the Boltzmann equilibrium requires that  $(k_r^E / k_i^E) = \exp(-E_b / K_B T)$ . The following limits are clearly satisfied:

$$k^d \gg k_i^E \quad k_{\text{int}} = k_i^E \exp\left(-\frac{E_b}{K_B T}\right) = k_{\text{low}} \quad (11)$$

$$k^d \ll k_i^E \quad k_{\text{int}} = k^d \exp\left(-\frac{E_b}{K_B T}\right) = k_K \quad (12)$$

and the general expression for the overall rate may be written as

$$k_{\text{int}}^{-1} = k_{\text{low}}^{-1} + k_K^{-1} \quad (13)$$

The results of this two-step model are also shown in Fig. 2.

Büttiker, Harris, and Landauer<sup>13</sup> refined the Kramers treatment of the low-friction case, allowing for a nonzero density of particles at the energy of the barrier, and obtained an expression for the rate  $k_{\text{BHL}}$  which may be cast in the form

$$k_{\text{BHL}} = \frac{[1 + 4k_{\text{TST}}/k_{\text{low}}]^{1/2} - 1}{[1 + 4k_{\text{TST}}/k_{\text{low}}]^{1/2} + 1} k_{\text{low}} \quad (14)$$

This expression converges to  $k_{\text{TST}}$  for high friction and starts correcting  $k_{\text{low}}$  according to

$$k_{\text{BHL}} \sim \left\{ 1 - \left(\frac{k_{\text{low}}}{k_{\text{TST}}}\right)^{1/2} + \frac{1}{2} \left(\frac{k_{\text{low}}}{k_{\text{TST}}}\right) - \frac{1}{8} \left(\frac{k_{\text{low}}}{k_{\text{TST}}}\right)^{3/2} + \frac{1}{8} \left(\frac{k_{\text{low}}}{k_{\text{TST}}}\right)^2 \dots \right\} k_{\text{low}} \quad (15)$$

while Eq. (13) introduces a correction of the form

$$k_{\text{int}} \sim \left\{ 1 - \left(\frac{k_{\text{low}}}{k_K}\right) + \left(\frac{k_{\text{low}}}{k_K}\right)^2 \dots \right\} k_{\text{low}} \quad (16)$$

As may be seen by comparing Eqs. (15) and (16) and also by inspection of the plots in Fig. 2, our interpolating expression gives a rate higher than that calculated by the method of Büttiker, Harris, and Landauer<sup>13</sup>, but for higher frictions it approaches the Kramers function in the correct way. (See Section II.B for further discussion of this point.)



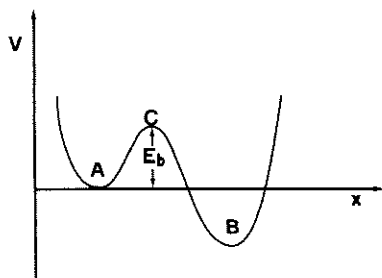


Figure 3. The unidimensional bistable potential.

### B. The Bistable Model and Other Generalizations of the Kramers Method

In the model studied by Kramers,<sup>11</sup> the particles are assumed to be initially at the well around *A* and to be lost as they escape above the barrier. Many physical processes, however, are more realistically modeled by a bistable potential (see Fig. 3), namely when two states *A* and *B* may be interconverted. In the original Kramers model no back-crossings from *B* to *A* were considered; the particles were somehow absorbed as they arrived at *B*.



It should be noted that states *A* and *B* are not well-defined states but rather probability distributions around the potential minima *A* and *B*. For high barriers like those assumed originally by Kramers, there should be no ambiguities, but one should be careful when dealing with small barriers. One way to deal with this problem rigorously is to work with the eigenvalues of the operator driving the probability distribution in time. For simplicity, consider the case of a symmetric potential, and let  $\varphi_n(x)$  be the eigenfunctions associated with eigenvalues  $\lambda_n$ . The following interpretation emerges from an interesting paper by van Kampen<sup>14</sup>:  $\varphi_0(x)$  ( $\lambda_0 = 0$ ) is the equilibrium distribution; the lowest nonzero eigenvalue,  $\lambda_1$ , is usually the one defining the chemical relaxation rate, as it corresponds to the slowest time scale, and its associated eigenfunction  $\varphi_1(x)$  is antisymmetric. To this first level of approximation, the probability distribution is given by  $\varphi_0(x) + \varphi_1(x)\exp(-\lambda_1 t)$  and describes the evolution from  $t = 0$ , when the two functions may cancel each other in the right-hand well, up to the final equilibrium distribution  $\varphi_0(x)$ . It is easy to see that  $\lambda_1 = k_r + k_l$ , and the individual one-way rate constants may be determined if the equilibrium constant is known as well. Other methods of avoiding this ambiguity consist

of calculating the expectation value of the position,  $\langle x \rangle$ , (see, e.g., ref. 15) or the total population in a well defined by  $n_A(t) = \int_{-\infty}^{x_c} dx \rho(x, t)$  (see, e.g., ref. 16) and look for the time evolution of these variables.

Brinkman<sup>17</sup> considered the bistable potential problem and showed that the diffusive, very-high-friction regime of Kramers was still correct,

$$k_{\text{high}}^r = \frac{\omega_A \omega_c}{2\pi\gamma} \exp\left(-\frac{V_c - V_A}{K_B T}\right) \quad (18)$$

$$k_{\text{high}}^l = \frac{\omega_B \omega_c}{2\pi\gamma} \exp\left(-\frac{V_c - V_B}{K_B T}\right) \quad (19)$$

Instead of the quasi-stationary state assumption of Kramers, he assumed only that the density of particles in the vicinity of the top of the barrier was essentially constant. Visscher<sup>18</sup> included in the Fokker-Planck equation a source term to account for the injection of particles so as to compensate those escaping and evaluated the rate constant in the extreme low-friction limit. Blomberg<sup>19</sup> considered a symmetric, piecewise parabolic bistable potential and obtained a partial solution of the Fokker-Planck equation in terms of tabulated functions; by requiring this piecewise analytical solution to be continuous, the rate constant is obtained. The result differs from that of Kramers only when the potential has a sharp, nonharmonic barrier.

Brinkman,<sup>17</sup> Landauer and Swanson,<sup>20</sup> and Donnelly and Roberts<sup>21</sup> made important progress in extending Kramers' method to models with several spatial dimensions. For the relatively simple models that were worked out, the major conclusions attained by Kramers do hold well. (A more detailed discussion of this point is given in the next section.)

Van Kampen<sup>14</sup> presented a detailed analysis of a specialized one-dimensional, symmetric double-well potential and obtained expressions for the eigenfunctions and eigenvalues of the associated Smoluchowski equation. He was able to reproduce and correct the Kramers result in the diffusional limit and clarified the various relaxation processes that occur in the different time scales of a reaction process with a high barrier. Taking as initial distribution a delta-like function placed at the bottom of one well, which is equivalent to considering a linear combination of infinitely many excited states, he showed that a quasi-equilibrium is attained after an initial fast relaxation process; this quasi-equilibrium consists of an equally weighted linear combination of the ground state (the equilibrium distribution) and the first excited state. The eigenvalue of the first excited state corresponds to the Kramers rate of escape. This shows how the Kramers theory gives a satisfactory description of the slow escape process, while an accurate picture of the faster processes, consisting mainly in the initial relaxation inside the well, would require the evaluation of an overwhelming number of excited states.

Larson and Kostin<sup>22</sup> considered a symmetric double-well potential and solved the Fokker-Planck equation driving the probability distribution in phase space, assuming the barrier to be high. Three cases were considered: the diffusional limit, where the Smoluchowski equation may be used; an intermediate range of the friction coefficient  $\gamma$ ; and the limit of very low friction. A variational approach was used to calculate the eigenvalues, and the eigenfunctions were obtained by a perturbational technique. For high and intermediate values of the friction, asymptotic formulas for the rate are given, their accuracy being tested against numerical calculations. Starting from the limit  $\gamma \rightarrow 0$ , they proposed a semiempirical expression apparently valid for all frictions and suggested that the lower limit of validity of TST would be far higher than predicted by Kramers.<sup>11</sup> (See also the discussion at the end of Section II.A.)

Several other attempts have been made to derive general expressions for the chemical rate, valid from the extreme low-friction regime to the moderate and high friction ones. Earlier, Visscher<sup>23</sup> had performed numerical calculations in the transition region between low and intermediate friction regimes and fitted a one-parameter expression which appeared to cover the entire range of frictions. Skinner and Wolynes<sup>16</sup> constructed a sequence of Padé approximants from the analytical results known for small friction and large friction; although some theoretical difficulties may arise with this use of the approximants, the results obtained seem very satisfactory. The same technique was applied very recently by Garrity and Skinner.<sup>24</sup> Montgomery, Chandler, and Berne<sup>25</sup> used a stochastic dynamics trajectory method to solve the bistable either piecewise harmonic or piecewise constant potential and found that the actual rate was always below 50% of the TST value. (For comparison with Fig. 2, we note that the parameters taken correspond to  $E_b/K_B T = 4.9$  and, for the piecewise harmonic potential,  $\omega_0/\omega_b = 3.05$ .)

Büttiker, Harris, and Landauer<sup>13</sup> extended the treatment made by Kramers<sup>11</sup> for the extreme low-friction regime to take into account the effect that the flow of particles out of the well has on their distribution inside the well. They obtained the rate expression of Eq. (14), valid from the extreme low-friction region up to intermediate friction but converging to the TST value (see Fig. 2). Carmeli and Nitzan<sup>26</sup> proposed a new approach based on a division of the particle phase space into two overlapping regions. In the first, for the lower energies deep inside the wells, the variation of phase is assumed to be much faster than that of the energy, and a diffusion equation for the energy will hold. The second corresponds to the higher energy region near the top of the barrier, where a spatial diffusion of the particles may be assumed. The final expression for the rate,  $k_{CN}$ , may be written in the form

$$k_{CN}^{-1} = \tau_1 + s k_K^{-1} \quad (20)$$

where  $\tau_1$  is the mean first passage time for the particle to reach the boundary between the two regions referred above,  $k_K$  is the Kramers rate given by Eq. (6), and  $s$  is a complicated factor assuming values between  $\frac{1}{2}$  (for  $\gamma \rightarrow 0$ ) and 1 (for large  $\gamma$ ). This method and the final result, Eq. (20), should be compared with the very simplistic two-step model discussed at the end of Section II.A. The factor  $s$  now introduced makes the rate  $k_{\text{CN}}$  always larger than  $k_{\text{int}}$  but closely related to it. Moving away from the smallest frictions, the corrections introduced are of the form

$$k_{\text{CN}} \sim \left\{ 1 - s \left( \frac{k_{\text{low}}}{k_K} \right) + s^2 \left( \frac{k_{\text{low}}}{k_K} \right)^2 \dots \right\} k_{\text{low}} \quad (21)$$

if we identify  $\tau_1^{-1} \approx k_{\text{low}}$ . As the factor  $s$  is close to  $\frac{1}{2}$  in this region, it is clear how  $k_{\text{CN}}$  is closer to  $k_{\text{low}}$  (or more rigorously, to  $\tau_1^{-1}$ ) than  $k_{\text{int}}$ . A factor  $s = \frac{1}{2}$  for the first-order correction in the form of Eq. (21) had been proposed earlier by Visscher<sup>23</sup> to fit the numerical results of a Kramers-type model that includes a source term. This should be contrasted with the refined Kramers treatment of Büttiker, Harris, and Landauer,<sup>13</sup> which over-corrects  $k_{\text{low}}$  by comparison with the two-step model. [See Eqs. (14) and (15) and Fig. 2.] The approach of Carmeli and Nitzan has been generalized by the same authors to the non-Markovian case, but this is the subject of Section IV.

Very recently, Lavenda<sup>27</sup> devised an interesting method of solution of the Kramers problem in the extreme low-friction limit. He was able to show that it could be reduced to a formal Schrödinger equation for the radial part of the hydrogen atom and thus be solved exactly. One particular form of the long-time behavior of the rigorous rate equation coincides with that obtained by Kramers with the quasi-stationary hypothesis and may thus clarify the implications of this hypothesis. The method of Lavenda is reminiscent of that used by van Kampen<sup>14</sup> but applied to a Smoluchowski equation for the diffusion of the energy.

### III. MULTIMODAL THEORIES

In the Kramers<sup>11</sup> model, the reaction process is described by the motion of a particle along a single coordinate. This is what in the jargon of chemical kinetics is called the reaction coordinate, a concept lacking rigorous definition in most cases. In actual problems of chemical interest, the barrier may be fairly wide near the saddle point and, besides, the normal mode separation may break down in that region. Real systems do usually require a many-coordinate description, and the coupling among these modes may play

an important role in the rate process. Landauer and Swanson<sup>20</sup> extended Kramers' work to the general multidimensional case to find that in the diffusive regime (high friction) the rate expression showed the same deviation from the TST value as that found in one dimension. In the other extreme case, for very low frictions, however, there appeared to be an effect of dimensionality. It is the aim of this section to evaluate the results obtained with multimodal theories, and we start by discussing in Section III.A two interesting attempts to deal with more detailed models, one to bring in the effects of the solvent, the other to deal directly with a two-dimensional coupled system. Later, in Section III.B, another detailed model is presented which aims to supplement the results of these two works.

### A. Two Detailed Models

The two particular models of mode coupling that we shall briefly discuss in this subsection are illuminating about the many different mechanisms that are involved and the difficulty in establishing a general simple pattern.

Grote and Hynes<sup>28</sup> studied a model for an exchange reaction in solution,



assuming that the motion in the saddle region is separable into reactive and nonreactive normal modes. The solvent dynamics act on the motion on each mode and may also induce a dynamical coupling among them. In the particular case of Eq. (22), the reactive mode is the antisymmetric stretch of the molecular system ABC. For example, it is easy to see that the solvent reaction forces upon the translational mode (one of the nonreactive normal modes) will couple this one into the reactive mode. This coupling may have three sources: (1) the different masses of the atoms, (2) the different friction on the central atom relative to the more exposed external atoms, and (3) the cross correlation between the atomic forces. Grote and Hynes described the motion on each coordinate  $q_i$  by a generalized Langevin equation of the type

$$\ddot{q}_i(t) = -\omega_i^2 q_i(t) - \sum_j \int_0^t d\tau \gamma_{ij}(\tau) \dot{q}_j(t-\tau) + F_i(t) \quad (23)$$

where the frequency  $\omega_i$  is imaginary for the reactive mode. They found that, except for the limiting cases of very high and very low friction, the rate of the reaction would depend very markedly on the assumed friction kernels  $\gamma_{ij}(\tau)$ . [It should be kept in mind that these are related to the correlation functions of the solvent forces,  $\gamma_{ij}(\tau) = \langle F_i(0)F_j(\tau) \rangle / K_B T$ .] Moreover, the mode coupling reduced the effective friction that was "felt" on the reactive mode. This shows how important and complex may be the role played by the solvent in determining the reaction rate.

Another source of coupling between the reactive and the other modes may result from the shape of the potential of the (solvent free) reacting system. A particular case of this class was studied by Christoffel and Bowman,<sup>29</sup> who considered a two-dimensional potential based on that of ammonia,

$$V(x, y) = \left[ \frac{1}{2}ax^2 + \frac{1}{2}bx^4 + V_0\exp(-cx^2) \right] + \frac{1}{2}m[\omega_y(x)]^2 y^2 \quad (24a)$$

with

$$\omega_y(x) = \omega_0[1 - \lambda\exp(-\alpha x^2)] \quad (24b)$$

This has the form of a double-well oscillator coupled to a transverse harmonic mode. The adiabatic approximation was discussed in great detail from a number of quantum-mechanical calculations, and it was shown how the two-dimensional problem could be reduced to a one-dimensional model with an effective potential where the barrier top is lowered and a third well is created at the center as more energy is pumped into the transverse mode. From this change in the reactive potential follows a marked increase in the reaction rate. Classical trajectory calculations were also performed to identify certain specifically quantal effects. For the higher energies, both classical and quantum calculations give parallel results.

### B. The Coupled Double-Well Oscillator

In this subsection we extend Christoffel and Bowman's investigation to the condensed phase. This is done within a classical context reminiscent of the work of Grote and Hynes,<sup>28</sup> and we make extensive use of both AEP and CFP (see the first four chapters of this volume). A more detailed account is given by Fonseca et al.<sup>30</sup>

Consider a bidimensional model potential,

$$V(x, y) = \phi(x) + \omega_{\text{eff}}^2(x) y^2 \quad (25)$$

where  $x$  is the reaction coordinate and  $y$  is some transverse normal mode,  $\phi(x)$  is a symmetric double-well potential modeling the chemical reaction, and

$$\omega_{\text{eff}}(x) = \left[ \frac{1}{2}\omega_0^2 + \psi(x) \right]^{1/2} \quad (26)$$

with

$$\psi(x) = -\frac{\omega_0^2}{2}\lambda_{\text{int}}\exp\left(-\frac{x^2}{r^2}\right) \quad (27)$$

$\lambda_{\text{int}}$  and  $r$  may be regarded as measures of the intensity and the range, respectively, of the coupling of the transverse mode onto the reactive motion. For Grote and Hynes' assumption on the mode separability in the saddle region to be valid, a fairly large value of  $r$  is required. In fact, when  $r \gg a$  ( $2a$  is the distance between the two minima of the reactive potential), the effect of the deterministic coupling can be viewed as a simple upward translation of the double-well potential on the energy axis; for  $r \ll a$ , however, the reaction coordinate is driven by an effective potential which has a smaller barrier and, in some cases, a third well, an effect already found in Christoffel and Bowman's work.

The classical motion of a stochastic particle in the potential defined by Eq. (25) may be described by the following set of equations:

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\phi'(x) - \gamma v - \psi'(x)y^2 + f(t) \\ \dot{y} &= w \\ \dot{w} &= -\lambda w - \omega_0^2 y - 2y\psi(x) + f'(t)\end{aligned}\tag{28}$$

The stochastic forces  $f(t)$  and  $f'(t)$  are assumed to be of the form of Gaussian white noises and to be statistically uncorrelated; this means that the coupling between reactive and nonreactive modes via the solvent is completely neglected. However, the noise affecting the nonreactive mode is transmitted into the reactive one originating the appearance of multiplicative noise effects. Although the Fokker-Planck equation corresponding to the set of Eqs. (28) may be written straightforwardly, its explicit solution involves some technical difficulties. In order to avoid these difficulties we shall make a set of assumptions similar to those of Christoffel and Bowman. The pair of variables  $(y, w)$  is assumed to be much faster than the pair  $(x, v)$ ; if this condition applies, the AEP can be applied to obtain a simpler Fokker-Planck equation depending only on the slow variables, and the CFP can be used to determine the time evolution of the observables driven by that equation. This kind of approach allows us to determine the rate constant for the chemical process under investigation in the following two different physical situations:

1. *System in Thermal Equilibrium.* The two modes have available the same thermal energy, and in this case, we study the whole range of values of the friction  $\gamma$  on the reactive mode.
2. *System Being Excited.* We assume that the nonreactive mode can be continuously heated by an external source without affecting the reactive one, thereby creating a physical situation where a canonical equilibrium does not exist.

In both of these physical situations we assume the nonreactive mode to be overdamped, with the friction  $\lambda$  so large (with respect to  $\omega_0$ ) as to allow the set of Eqs. (28) to be replaced by

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\phi'(x) - \gamma v - \psi'(x)y^2 + f(t) \\ \dot{y} &= -\frac{\omega_0^2}{\lambda}y - \frac{2}{\lambda}\psi(x)y + \frac{f'(t)}{\lambda}\end{aligned}\quad (29)$$

The AEP is applied to the set of Eqs. (29) in order to obtain from its equivalent Fokker-Planck equation,

$$\begin{aligned}\frac{\partial}{\partial t}\rho(x, v, y, t) &= \left\{ -v\frac{\partial}{\partial x} + \phi'(x)\frac{\partial}{\partial v} + \psi'(x)y^2\frac{\partial}{\partial v} \right. \\ &\quad + \gamma\left[\frac{\partial}{\partial v}v + \langle v^2 \rangle\frac{\partial^2}{\partial v^2}\right] + \frac{2}{\lambda}\psi(x)\frac{\partial}{\partial y} \\ &\quad \left. + \frac{\omega_0^2}{\lambda}\left[\frac{\partial}{\partial y}y + \langle y^2 \rangle\frac{\partial^2}{\partial y^2}\right]\right\}\rho(x, v, y, t)\end{aligned}\quad (30)$$

the one describing the time evolution of the probability distribution of the slow variables,  $\sigma(x, v, t)$ :

$$\begin{aligned}\frac{\partial}{\partial t}\sigma(x, v, t) &= \left\{ -v\frac{\partial}{\partial x} + \frac{\partial}{\partial v}\phi'(x) + \gamma\frac{\partial}{\partial v}v \right. \\ &\quad + \frac{\partial}{\partial v}\psi'(x)\langle y^2 \rangle - \frac{2}{\omega_0^2}\frac{\partial}{\partial v}\langle y^2 \rangle\psi'(x)\psi(x) \\ &\quad \left. + \gamma\langle v^2 \rangle\frac{\partial^2}{\partial v^2} + \frac{\partial^2}{\partial v^2}\langle y^2 \rangle^2\frac{\lambda}{\omega_0^2}[\psi'(x)]^2\right\}\sigma(x, v, t)\end{aligned}\quad (31)$$

(This result is obtained by using corrections up to the second perturbational order; for a detailed discussion of how the perturbation parameter is defined, see Chapter I.)

It is illuminating to briefly discuss the significance and importance of each term in Eq. (31). The first three terms are trivial, as they are nothing but a description of the deterministic evolution in the reactive mode in the absence of coupling with the nonreactive mode; the sixth term is also trivial and is a diffusional term corresponding to the effect of the stochastic force



$f(t)$  over the reactive mode. More interesting are the remaining terms: in fact, the fourth term is equivalent to the standard adiabatic correction to the reactive potential found by Christoffel and Bowman and arises as a consequence of the deterministic coupling of the reactive mode to the nonreactive mode. When one applies the AEP to the set of Eqs. (29), this term appears as the first-order correction. The fifth and seventh terms appear as the second-order correction provided by the AEP; the fifth is a nonstandard adiabatic correction to the reactive potential, and the seventh is a multiplicative diffusional term that transmits to the reactive mode the effect of the thermal fluctuations acting on the nonreactive mode. It can also be proved that higher order corrections provided by the AEP will generate the true effective potential "felt" by the reactive mode.

Equation (31) is valid when the characteristic times of the position  $x$  and velocity  $v$  are similar; when both  $v$  and  $y$  are assumed to be fast variables, the AEP applied to the set of Eqs. (29) leads to

$$\begin{aligned} \frac{\partial}{\partial t} \sigma(x, t) = & \left\{ \frac{1}{\gamma} \frac{\partial}{\partial x} \left[ \phi'(x) + \langle y^2 \rangle \psi'(x) \right. \right. \\ & \left. \left. - 2 \frac{\langle y^2 \rangle}{\omega_0^2} \psi'(x) \psi(x) - \frac{\langle y^2 \rangle^2}{\gamma^2 R_1} \psi'(x) \psi''(x) \right] \right. \\ & + \frac{1}{\gamma} \frac{\partial^2}{\partial x^2} \left[ \langle v^2 \rangle + \frac{\langle y^2 \rangle^2}{\gamma^2 R_1} [\psi'(x)]^2 \right] \\ & + \frac{1}{\gamma} \frac{\partial}{\partial x} \left[ \frac{2 \langle y^2 \rangle^2}{\gamma^2 (1 + 2 R_1)} \psi'(x) \psi''(x) \right. \\ & \left. \left. + 4 \frac{\langle y^2 \rangle}{(\omega_0^2)^2} \psi'(x) \psi(x)^2 \right] \right\} \sigma(x, t) \end{aligned} \quad (32)$$

where  $R_1 = (\omega_0^2/\lambda)/\gamma \equiv \tau_v/\tau_y$ . This equation was obtained taking into account corrections up to the fourth order on the AEP and considering  $v$  as a fast variable but not infinitely fast when compared to  $x$ . It must be noted that the last term in this equation is, with respect to Eq. (31), the next nonstandard adiabatic correction to the reactive potential. It is interesting to study how Eq. (32) behaves with  $\gamma$  or more directly with  $R_1$ ; when  $R_1$  assumes large values, which is equivalent to taking small values of  $\gamma$  and

therefore making the system more inertial, the fourth and seventh terms of Eq. (32) cancel each other out, and the resulting equation is equivalent to that obtained starting from Eq. (31) and eliminating (with the AEP) the velocity  $v$ . When  $R_1$  tends to zero,  $\gamma$  tends to infinity, and the diffusional limit is approached; in this limit, Eq. (32) can be rewritten as

$$\begin{aligned} \frac{\partial}{\partial t} \sigma(x, t) = & \left\{ \frac{1}{\gamma} \frac{\partial}{\partial x} \left[ \phi'(x) + \psi'(x) \langle y^2 \rangle \right. \right. \\ & \left. \left. - 2 \frac{\langle y^2 \rangle}{\omega_0^2} \psi'(x) \psi(x) + 4 \frac{\langle y^2 \rangle}{(\omega_0^2)^2} \psi'(x) \psi(x)^2 \right] \right. \\ & \left. - \frac{1}{\gamma} \frac{\partial}{\partial x} \frac{\langle y^2 \rangle^2}{\gamma^2 R_1} \psi'(x) \psi''(x) \right. \\ & \left. + \frac{1}{\gamma} \frac{\partial^2}{\partial x^2} \left[ \langle v^2 \rangle + \frac{\langle y^2 \rangle^2}{\gamma^2 R_1} [\psi'(x)]^2 \right] \right\} \sigma(x, t) \quad (33) \end{aligned}$$

This same equation can be obtained from the set of Eqs. (29) assuming  $v$  infinitely faster than  $x$ . This touches the Itô-Stratonovich controversy discussed by Faetti et al. in Chapter X (note that  $R_1$  is to be identified with their parameter  $R^{-1}$ ). In line with their remarks, we are led to the conclusion that when the system becomes inertial the Itô description is valid [see Eq. (31)] and that when inertia is completely absent [see Eq. (33)] the Stratonovich description is attained.

The results obtained considering that the system is thermalized can be summarized in Fig. 4, where the chemical reaction rate  $k$  is displayed as a function of  $R_1$  ( $= \tau_v/\tau_y$ ).  $\tau_y$  was kept constant, and therefore this figure exhibits the same kind of  $k$  dependence on  $\gamma$  ( $\gamma$  is the friction acting on the reactive mode) as that already discussed in Section II.A. Note, however, that new effects originating from the coupling between reactive and nonreactive modes appear in this case, as will be discussed later on. When  $R_1 \rightarrow 0$ , the high-friction region is attained and a linear dependence of  $k$  on  $1/\gamma$  is obtained, in agreement with the classical Kramers result. As  $R_1$  increases, the system becomes more inertial, and it is also interesting to note that as  $\lambda_{\text{int}}$  increases, straight lines of increasing slope are obtained. This is a manifestation of the role played by inertia: the sensitivity of the reaction rate  $k$  to the intensity of the coupling increases as the reactive system becomes more iner-

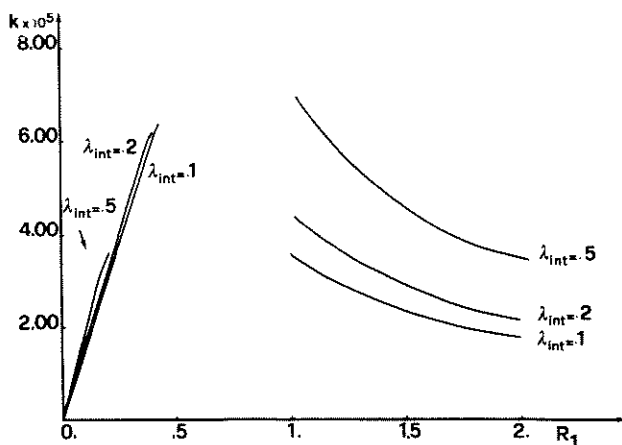


Figure 4. Synergism of inertia and multiplicative fluctuation. Variation of the reaction rate  $k$  throughout the whole range of values of the friction  $\gamma$  [ $R_1 = (\omega_0^2/\lambda)/\gamma$ , and  $\omega_0^2/\lambda$  was kept constant]. The curves on the left-hand side were obtained using the CFP, and  $k$  was identified with the inverse (at the origin) of the Laplace transform describing the time evolution of the average value of the position  $\langle x \rangle$ . Those on the right-hand side were obtained by the first-passage time technique, and  $k$  was identified with the inverse of that time. The parameters were given the values  $E_b = 2 \times 10^{-7}$ ,  $a = 0.5$ ,  $r = 2a$ , and  $\langle y^2 \rangle \omega_0^2 = \langle v^2 \rangle = 10^{-7}$ . Atomic units are used throughout. [Taken from T. Fonseca et al., *J. Chem. Phys.*, **80**, 1826 (1984).]

tial. Above a certain value of  $R_1$ , the lines start bending down, a sign that the intermediate friction regime is being approached (see introduction). Unfortunately, we had difficulty with the convergence of the CFP in this region, and therefore there is little reliance to be placed on results provided by those computer calculations.

As  $R_1$  tends to infinity, the energy-controlled regime is approached and the important role played by the interaction between reactive and nonreactive modes can be assessed by some remarks on Eq. (31). Let us consider the case where  $\langle y^2 \rangle = 0$ . If  $\gamma \langle v^2 \rangle$  is also assumed to vanish, Eq. (31) describes a purely deterministic process, and the overcoming of the barrier is rigorously forbidden when the total energy of the reactant is lower than the barrier height. However, when the coupling between reactive and nonreactive modes is restored, the reactant undergoes the influence of the fluctuations acting on the nonreactive mode, and this can supply enough energy for the reactant to overcome the barrier. Fluctuations become ineffective near the top of the barrier, where their intensity vanishes as implied by  $\psi'(0) = 0$ . This means that inertia is absolutely necessary for the barrier to be really overcome. As a result of such a synergism between inertia and multiplicative fluctuations, the chemical reaction can take place even when Kramers' the-

ory predicts vanishingly small rates. This is an interesting property, a quantitative discussion of which requires a point of view completely different from the one considered until now. To derive a Fokker-Planck equation for the energy, we follow Lindenberg and Seshadri,<sup>31</sup> who used energy and displacement as independent variables. We define the energy as

$$E = \frac{v^2}{2} + \Theta(x) \quad (34a)$$

$$\Theta(x) = \phi(x) + \psi(x)\langle y^2 \rangle - [\psi(x)]^2 \frac{\langle y^2 \rangle}{\omega_0^2} \quad (34b)$$

In the absence of the additive and multiplicative stochastic forces,  $E$  would be a constant of motion, rigorously independent of time. Under the influence of these fluctuations,  $E$  becomes time-dependent, but its dynamics will certainly be very slow compared to the dynamics of the variable  $x$ , thus allowing us to also eliminate the space variable. Starting from Eq. (31), we rewrite it in terms of the new pair of variables,  $x$  and  $E$ , and after eliminating  $x$  with a procedure introduced by Stratonovich,<sup>32</sup> the following final equation is obtained:

$$\begin{aligned} \frac{\partial}{\partial t} \sigma(E, t) = & \left\{ -\frac{\partial}{\partial E} \left[ -\gamma \frac{\varphi(E)}{\varphi'(E)} + \gamma \langle v^2 \rangle + \frac{\lambda_{\text{int}}^2 \langle y^2 \rangle^2 \lambda}{r^4 \omega_0^2} \frac{\chi'(E)}{\varphi'(E)} \right] \right. \\ & \left. + \frac{1}{2} \frac{\partial^2}{\partial E^2} \left[ 2\gamma \langle v^2 \rangle \frac{\varphi(E)}{\varphi'(E)} + 2 \frac{\lambda_{\text{int}}^2 \langle y^2 \rangle^2 \lambda}{r^4 \omega_0^2} \frac{\chi(E)}{\varphi'(E)} \right] \right\} \sigma(E, t) \end{aligned} \quad (35)$$

where

$$\varphi(E) = \int dx [E - \Theta(x)]^{1/2} \quad (36a)$$

$$\chi(E) = \int dx x^2 e^{-x^2/r^2} [E - \Theta(x)]^{1/2} \quad (36b)$$

with the integration extending over a domain that includes all values of  $x$  for which  $E \geq \Theta(x)$ .

To evaluate the chemical reaction rate via Eq. (35), we adopt the first-passage time method,<sup>32,33</sup> identifying  $k$  with the inverse of the mean first-passage time. The results are displayed on the right-hand side of Fig. 4 and in Fig. 5.

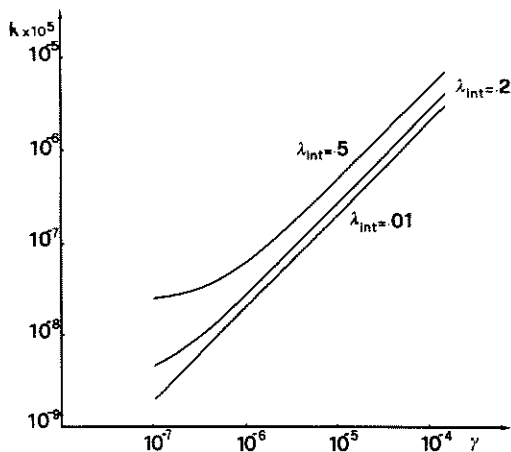


Figure 5. Variation of the reaction rate in the low-friction region,  $\gamma \rightarrow 0$ . These results were obtained using the first-passage time technique. Parameters were given the same values as in Fig. 4. [Taken from T. Fonseca et al., *J. Chem. Phys.*, **80**, 1826 (1984).]

The results illustrated on the right-hand side of Fig. 4 show that in this region the increase of  $k$  is much more sensitive to the increases in  $\lambda_{\text{int}}$  than it is in the high-friction region, thereby corroborating our statements about the role of inertia. This trend is especially emphasized in the limit  $\gamma \rightarrow 0$  and is better seen in Fig. 5. As remarked above, the reaction rate stays finite in this zero-friction limit, counter to Kramers' prediction.

Until now we have limited ourselves to study the thermalized system, that in physical condition (1) cited at the very beginning of this subsection. When we assume that the nonreactive mode may be continuously heated by an external source, the system ceases to be thermalized, and interesting new effects can occur as a consequence of the coupling between reactive and nonreactive modes. Returning to Eq. (32) we can guess what really happens when  $\omega_0^2 \langle y^2 \rangle$  is increased: on the one side, the deterministic effect over the reactive potential increases and consists of lowering the barrier to be overcome. However, and in addition to this effect, the intensity of the multiplicative fluctuations is increased with respect to the intensity of the additive fluctuations; this creates a gradient of temperature inside the reactant well that pushes the reactant particles to the region near the barrier while supplying them with energy. This effect vanishes at  $x = 0$  (the barrier top), but due to the presence of the additive fluctuations the reaction occurs with a velocity that is much faster than in the absence of this effect. If we continue to increase the energy of the nonreactive mode, a threshold region is attained when the deterministic counterpart of the multiplicative diffusional term

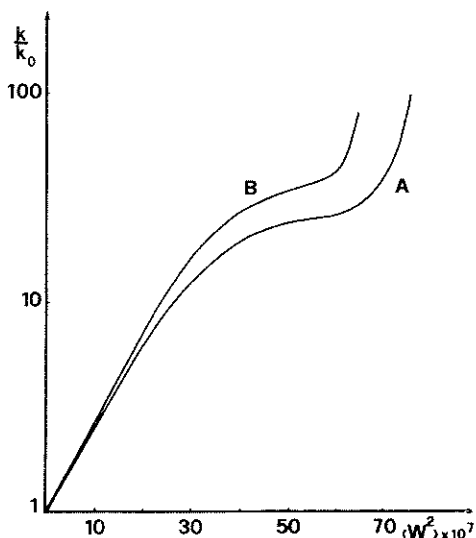


Figure 6. Variation of the reaction rate while increasing the energy in the nonreactive mode. Curve *A* corresponds to results obtained when the role of inertia was completely neglected. Curve *B*, in turn, corresponds to results obtained when these effects were present. The parameters were given the values  $\lambda_{\text{int}} = 0.5$ ,  $E_b = 2 \times 10^{-7}$ ,  $\langle v^2 \rangle = 1 \times 10^{-7}$ ,  $R_1 = \frac{1}{3}$ ,  $a = 0.5$ , and  $r = 2a$ .  $k_0 = 1.2 \times 10^{-5}$  is the  $k$  value when  $\langle v^2 \rangle = \langle w^2 \rangle$ . [Taken from T. Fonseca et al., *J. Chem. Phys.*, **80**, 1826 (1984).]

equals the frequency corresponding to the harmonic expansion of the effective potential around the top of the barrier. In the absence of additive fluctuations, it is well known after the work of Schenzle et al.<sup>34,35</sup> that this threshold corresponds to centering the probability distribution at the top of the barrier, and in chemical language we can roughly identify this with an activation process. When the threshold is passed and we continue to pump energy into the nonreactive mode, the probability distribution tends to become still more concentrated on the top of the barrier, rendering the chemical reaction even faster. The results obtained in this particular physical condition are displayed in Fig. 6.

Curve *A* was obtained using Eq. (33), that is, completely neglecting the role of inertia; curve *B* was obtained using Eq. (32), where these effects are present. The increase in the reaction rate is very clear; the threshold region corresponds to the plateau, and the increase of  $k$  after this region is much more marked. Once again the role of inertia is to speed up the chemical reaction, and this seems to imply that the threshold condition would be attained at lower values of the energy given to the nonreactive mode.

#### IV. NON-MARKOVIAN EFFECTS ON THE RATE

In this section we shall explore a different kind of generalization of the Kramers theory to take into account the problems resulting from the breakdown of the time-scale separation between the reactive mode and its thermal bath. This problem may also be found in the multimodal theories in Section III when the nonreactive modes are not much faster than the motion along the reaction coordinate.

Computer simulations of the molecular dynamics of the liquid state<sup>36-39</sup> (see also Chapter VI) clearly show that the correlation function of the velocity variable is not exponential; rather it usually exhibits a sort of damped oscillatory behavior. This means that the Markovian assumption is often invalid. This makes it necessary, when studying a chemical reaction in a liquid phase, to replace the standard Kramers condition [see Eq. (4b)] with a more realistic correlation function having a finite lifetime. Recall the rate expression obtained by Kramers for moderate to high frictions, Eq. (6). This may be cast into the form  $k_K = k_{\text{TST}}f(\omega_b, \gamma)$ , where  $k_{\text{TST}}$ , given by Eq. (7), is essentially an equilibrium property depending on the thermodynamic equilibrium inside the well. As a canonical equilibrium property, it is not affected by whether or not the system is Markovian. The calculation of the factor  $f(\omega_b, \gamma)$  depends, however, on the dynamics of the system and will thus be modified when non-Markovian behavior is allowed for.

Another problem of interest concerns the effect of external radiation fields. In the overdamped regime this will be shown to be reminiscent of the effect of the nonreactive modes. These problems will be the major topics of the present section.

This section is organized as follows: in subsection A the approaches based on the assumption of heat bath statistical equilibrium and those which use the generalized Langevin equation are reviewed for the case of a bounded one-dimensional Brownian particle. A detailed analysis of the activation dynamics in both schemes is carried out by adopting AEP and CFP techniques. In subsection B we shall consider a case where the non-Markovian character of the variable velocity stems from the finite duration of the coherence time of the light used to activate the chemical reaction process itself.

##### A. Noise-Activated Escape Rate in the Presence of Memory Effects

To discuss the idea of noise-activated reactions we begin by noting that the random forces which occur in the Langevin equation related with the process under investigation may have quite different origins. In an ordinary microscopic derivation of a Langevin equation (or the corresponding Fokker-Planck equation), the random term is interpreted as associated with

the thermal fluctuations of the system. This thermal or internal noise scales with the size of the system (except near instability points).<sup>40-43</sup> A different interpretation of such a contribution to a Langevin equation is necessary, however, when this is thought to model what can be defined as an external noise. In this latter case, one considers a system which experiences fluctuations that are not “self-originating.” These fluctuations can be due to a fluctuating environment or can be the result of an externally applied random force. The mathematical modeling of these fluctuations is done by considering a deterministic equation appropriate in the absence of external fluctuations and then considering the external parameter which undergoes fluctuations to be a stochastic variable. The noise term of the stochastic differential equation so obtained is usually multiplicative in nature, that is, it depends on the instantaneous value of the variable of the system. It does not scale with the system size and is not necessarily small. We can regard the external noise as an external force field which drives the system, always maintaining its statistical equilibrium. Among the experimental situations in the presence of external noises so far considered, the example of illuminated chemical reactions<sup>43</sup> may be of particular interest for our readers.

In Chapters I, X, and XI it is stressed that the “microscopic” derivation of equations such as some of those used here should be discussed carefully. This is to avoid some ambiguous features of a purely phenomenological treatment. However, as these are widely used in the literature of stochastic processes, we shall show how to approach the problem of their solution while avoiding those difficulties by using a more rigorously founded “microscopic” derivation (see Chapters X and XI).

### 1. *Examples of Non-Markovian External Noises*

Let us focus on the one-dimensional dynamics of an order parameter  $x$  exhibiting bistability, that is,

$$\dot{x} = f(x, \mathbf{a}) \quad (37)$$

where  $\mathbf{a}$  denotes an external control parameter. The flow  $f(x, \mathbf{a})$  is assumed to possess three real roots  $\{x_1, x_u, x_2\}$ . We choose  $x_1 < x_2$ , where  $x_1$  and  $x_2$  denote locally stable steady states and  $x_u$  is an intermediate, locally unstable, steady state. In the presence of a fluctuating control parameter  $\mathbf{a}$ , the deterministic flow in Eq. (37) should be replaced by a stochastic one:

$$\dot{x} = f(x, \mathbf{a}) + g(x)\xi(t) \quad (38)$$

where the multiplicative noise (state-dependent coupling) represents the linear coupling of  $\mathbf{a}$  to the order parameter  $x$  in the dynamical flow, Eq. (37). A common example of Eq. (38) is provided by the Smoluchowski approximation of the random walk of a Brownian particle bounded into a symmet-



rical double-well potential,

$$V(x) = -\frac{ax^2}{2} + \frac{bx^4}{4} \quad (39)$$

In such a case  $g(x)$  is assumed to be 1,  $x_u = 0$ , and  $x_{1,2} = \pm(a/b)^{1/2}$ .

The problem may be formulated as follows. Given random noises  $\xi(t)$  with different correlation parameters  $\tau_1$  and  $\tau_2$  but possessing identical spectral densities  $S_\xi(\omega = 0)$  at zero frequency, that is,

$$S_\xi(0) = \int \langle \xi_1(t)\xi_1(0) \rangle dt = \int \langle \xi_2(t)\xi_2(0) \rangle dt = 2D \quad (40)$$

what is the relationship between the corresponding activation rates of the metastable states?

Hänggi and Riseborough<sup>44</sup> carried out an exact calculation of the activation rates for the bistable flow of Eq. (38) for the case when the noise of the control parameter can be modeled by a telegraphic noise of vanishing mean,

$$\xi(t) = d(-1)^{n(t)} \quad (41a)$$

$$\langle \xi(t)\xi(s) \rangle = \frac{D}{\tau} \exp\left(-\frac{|t-s|}{\tau}\right) \quad (41b)$$

where  $n(t)$  is a Poisson counting process with parameter  $(2\tau)^{-1}$  and  $d$  denotes a random step with density

$$\rho_d = \frac{1}{2} \left\{ \delta \left[ d - \left( \frac{D}{\tau} \right)^{1/2} \right] + \delta \left[ d + \left( \frac{D}{\tau} \right)^{1/2} \right] \right\}. \quad (42)$$

We may now elaborate on the problem posed above: the system with a smaller correlation time  $\tau$  is subject to random forces with larger amplitude (see Fig. 7), and this might lead to the conclusion that the rate was enhanced.

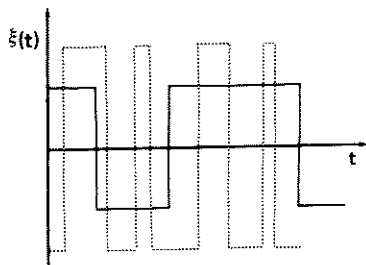


Figure 7. Sketch of possible realizations of a telegraphic noise,  $\xi(t)$ , for differing correlation times  $\tau$ , Eq. (41). The solid curve is for  $\tau_1$  and the dashed curve for  $\tau_2$ , where  $\tau_2 < \tau_1$ . [Taken from P. Hänggi and P. Riseborough, *Phys. Rev.*, **A27**, 3329 (1983).]

However, the time interval over which the force is constant decreases; since the random force changes sign more rapidly, one might now expect that the system did not have enough time to reach the point of instability, and consequently the rate would be suppressed for a smaller correlation time. Thus, it is not obvious a priori which of the two random forces,  $\xi_1(t)$  or  $\xi_2(t)$ , yields a smaller rate, that is, a larger escape time.

The analysis made in ref. 44 is based on the discussion of the related exact non-Markovian master equation<sup>45,46</sup> and allows us to conclude that when the noise intensity  $S_\xi(0)$ , Eq. (40), is constant the rates are exponentially enhanced with decreasing correlation time  $\tau$  and this is independent of the specific form of the nonlinear bistable flow  $f(x, \mathbf{a})$  and also of whether the random noise is additive or multiplicative. [The only condition imposed is  $g(x) \neq 0$  in  $\{x_1, x_u, x_2\}$ .]

An important property of the telegraphic noise, Eq. (41), is the approach to a Gaussian white noise in the limit  $\tau \rightarrow 0$ .<sup>47</sup> With

$$\lim_{\tau \rightarrow 0} \frac{1}{2\tau} e^{-|t|/\tau} = \delta(t)$$

Eq. (41) reduces to

$$\langle \xi(t)\xi(s) \rangle = 2D\delta(t-s) \quad (43)$$

From now on we consider the stochastic differential equation (38) with  $\xi(t)$  a random force associated with a zero-mean Gaussian process and an autocorrelation function given by Eq. (41). This system has been thoroughly investigated by Sancho et al.<sup>48-50</sup> The use of such Gaussian noises is justified by the central limit theorem.<sup>11b,41</sup> For a Gaussian noise with exponential autocorrelation, Eq. (41), the so-called Ornstein-Uhlenbeck noise, one is unable to derive exact expressions for activation rates.<sup>48a,50,51</sup> In ref. 50 an approximate Fokker-Planck equation is obtained for the probability distribution of the variable  $x$  by applying functional methods. These methods provide an alternative to the more often used cumulant techniques<sup>49,52,53</sup> and may be shown to lead to consistent results.<sup>49,50</sup> The same approximate Fokker-Planck equation, however, can be recovered with the AEP technique. The AEP can be applied by introducing an equivalent formulation of the process under investigation, Eq. (38):

$$\begin{aligned} \dot{x} &= f(x, \mathbf{a}) + g(x)\xi \\ \dot{\xi} &= -\frac{1}{\tau}\xi + \eta(t) \end{aligned} \quad (44)$$

The exact equivalence of these formulations may be proved,<sup>54</sup> for the case

where:

1.  $\eta(t)$  is a white Gaussian noise with

$$\langle \eta(t) \rangle = 0 \quad \text{and} \quad \langle \eta(t)\eta(s) \rangle = \frac{2D}{\tau^2} \delta(t-s) \quad (45)$$

2. A fluctuation-dissipation relationship for the auxiliary variable  $\xi$  is understood, and it is initially prepared at its Gaussian equilibrium with

$$\langle \xi^2(0) \rangle = \langle \xi^2 \rangle_{\text{eq}} = \frac{D}{\tau} \quad (46)$$

The perturbation reduction of the corresponding Markovian Fokker-Planck equation for the two-variable process  $(x(t), \xi(t))$  to an approximate one in  $x(t)$  has been carried out in Section V.A of Chapter II. For brevity we report only the approximate time-evolution equation for  $\sigma(x, t)$  up to order  $D$ ;

$$\frac{\partial}{\partial t} \sigma(x, t) = \left\{ -\frac{\partial}{\partial x} f(x, \mathbf{a}) + D \frac{\partial}{\partial x} g(x) \frac{\partial}{\partial x} [g(x) - \tau M(x)] \right\} \sigma(x, t) \quad (47a)$$

where

$$M(x) = f(x)g'(x) - f'(x)g(x) \quad (47b)$$

where the prime denotes the derivative. [The reader can find a detailed discussion of some technical properties of Eq. (47) in Chapter II.]

The problem we are addressing now is the same one posed in ref. 44 for a case of a non-Markovian telegraphic noise: Given Gaussian noises with different autocorrelation times  $\tau_1$  and  $\tau_2$  but identical intensities  $2D$ , Eq. (40), which of them will provide a smaller rate (larger escape time)? Since detailed balance does not hold for Eq. (44), the standard methods<sup>11a,20,55</sup> fail in evaluating the activation rate of the non-Markovian process under investigation, and the more general method of refs. 56 and 57 is rather cumbersome because the stationary probability  $\sigma_{\text{st}}(x, \xi)$  should first be determined perturbatively. If  $T$  denotes the mean first passage time<sup>32,33</sup> to reach the barrier top, the activation rate can be estimated as

$$K = \frac{1}{2} T^{-1} \quad (48)$$

where the factor  $\frac{1}{2}$  takes into account that the random walker has equal chance to either continue to the adjacent stable state or return to the old one. Without loss of generality, we consider the particular case of the Smoluchowski approximation of the random walk of a Brownian particle bound into a symmetrical double-well potential, that is,

$$f(x, \mathbf{a}) = V'(x) \quad \text{and} \quad g(x) = 1$$

where  $V(x)$  is given in Eq. (39). The chemical meaning of this model has been discussed at length in the preceding sections. If  $x = -\infty$  is a natural reflecting boundary and  $x = x_u = 0$  an absorbing state, one finds,<sup>32,58</sup> for the mean first passage time  $T(x)$  of a walker which started out at  $x(0) = x_{st} < 0$ ,

$$T(x) = \int_{x_{st}}^0 \frac{dy}{\sigma_{st}(y)D(y)} \int_{-\infty}^y \sigma_{st}(z) dz \quad (49)$$

$\sigma_{st}(x)$  denotes the stationary probability of the approximate Fokker-Planck equation, Eq. (47).  $D(x)$  is the corresponding diffusion coefficient, that is,  $D(x) = D(1 - \tau M(x))$ . With the assumptions of (1) small enough autocorrelation time  $\tau$  and (2) weak noise such that  $D < a^2/b$ , we can evaluate  $T(x)$  by applying the method of steepest descent to Eq. (49). From Eqs. (47) and (39), we obtain

$$T(x) = \frac{\pi}{a\sqrt{2}} \left( \frac{1+2a\tau}{1-a\tau} \right)^{1/2} \exp\left(\frac{\Delta\phi}{D}\right) \quad (50)$$

with

$$\Delta\phi = \int_0^{x_1} \frac{f(y, \mathbf{a})}{1 + \tau f(y, \mathbf{a})} dy = \frac{a^2}{4b} \left( 1 - \frac{a^2\tau^2}{2} \right) + O(\tau^3) \quad (51)$$

Since Eq. (49) takes into account only the term of order  $D\tau$ , the term of order  $\tau^2$  in Eq. (51) is meaningless and the term linear in  $\tau$  in  $\Delta\phi$  vanishes exactly. For  $\tau = 0$ , our result equals the well-known Smoluchowski rate.<sup>11a</sup>

The main conclusion we can draw is that the activation rates for non-Markovian processes like Eq. (44) decrease as  $\tau$  increases; the exact result of ref. 44 can thus be extended to the case of Gaussian random forces of finite correlation time as well. However, if we take Eq. (50) seriously, we obtain an Arrhenius factor,  $\exp(\Delta\phi/D)$ , of  $T(x)$  which does not exhibit a dependence on  $\tau$ . This is in contrast to the result found for telegraphic noises, where the Arrhenius factor increases with increasing autocorrelation time  $\tau$  (see ref. 44). The result of a numerical simulation for  $T(x)$  based on the bi-

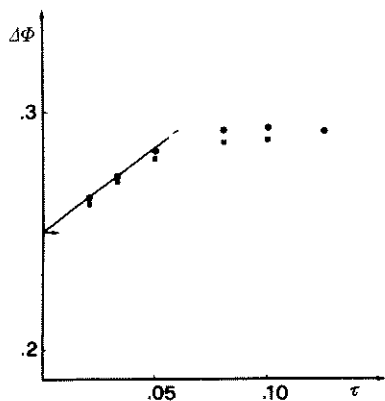


Figure 8.  $\Delta\Phi$ , defined in Eq. (51), versus the noise autocorrelation time  $\tau$ . The computer simulation of Eqs. (44) has been carried out by applying the numerical algorithm of ref. 50 with an integration step of 0.01. The values of the parameters are  $a = b = 1$ ,  $D = 0.1$  (●) and  $D = 0.05$  (■).  $T$  is the average over 1000 first passage times considering the initial conditions (46) for  $\xi$  and  $\sigma(x, 0) = \delta(x - x_1)$  for  $x$ . The maximum error bar in our numerical simulation is estimated to be about 10%. The arrow denotes the white noise limit  $\Delta\Phi(\tau = 0)$ . [Taken from P. Hänggi et al., *Z. Phys.* **B56**, 333 (1985).]

stable flow is given in Fig. 8. In contrast with our prediction in Eq. (50),  $\Delta\phi$  increases with increasing autocorrelation time  $\tau$ . The increase is proportional to the first order in  $\tau$  and is not dependent on the small noise parameter  $D$ . The origin of the disagreement must be ascribed to the expansion in a Taylor series of  $\exp\{\mathcal{L}_a s\}$  appearing in the memory kernel of Eq. (3.15) of Chapter II. This expansion is proven<sup>60</sup> virtually equivalent to considering only  $\mathcal{L}_b$  (see Chapter II) as being the unperturbed part of the total operator  $\mathcal{L}$ . When  $\mathcal{L}_a$  is replaced with an equivalent linear operator so as to avoid this perturbative expansion, then a complete agreement with the predictions of the master equation method<sup>59</sup> is recovered.<sup>60,61</sup>

## 2. Chemical Reactions Driven by Bona Fide Non-Markovian Fluctuation-Dissipation Processes

When the chemical reaction process takes place in condensed phase (for example, in a liquid), a reliable description of it seems to be achieved<sup>49</sup> simply by replacing Eqs. (3) with

$$\dot{x} = v \quad (52a)$$

$$\dot{v} = -\frac{1}{M} V'(x) - \int_0^t \varphi(t-\tau) v(\tau) d\tau + f(t) \quad (52b)$$

where the kernel  $\varphi(t)$  and the stochastic force are related to each other via

$$\langle v^2 \rangle \varphi(t) = \langle f(0) f(t) \rangle \quad (53)$$

This takes into account the fact that the stochastic force  $f(t)$  can have a finite

correlation time, for example,

$$\varphi(t) = \frac{\gamma}{\tau_c} \exp\left(-\frac{t}{\tau_c}\right) \quad (54)$$

In the absence of the external potential  $V$ , Eqs. (52) can be given a rigorous derivation from a microscopic Liouville equation (see Chapter I). We make the naive assumption that when an external potential driving the reaction coordinate is present, the two contributions (the deterministic motion resulting from the external potential and the fluctuation-dissipation process described by the standard generalized Langevin equation) can simply be added to each other.

A more realistic and more general treatment would presumably lead to a set of equations like Eqs. (52), with the potential  $V(x)$  fluctuating as a consequence of couplings with nonreactive modes (see Section III). For the sake of simplicity, we study separately the two different aspects. While Section III was devoted to pointing out the role of multiplicative fluctuations (derived from nonlinear microscopic Liouvillians) in the presence of additive white noise, this subsection is focused on the effects of a non-Markovian fluctuation-dissipation process (with a time convolution term provided by a rigorous derivation from a hypothetical microscopic Liouvillian) in the presence of a time-independent external potential.

A more general expression for  $\varphi(t)$  can be derived from the continued fraction expansion, ref.<sup>62</sup>

$$\hat{\varphi}(z) = \frac{\Delta_1^2}{z + \lambda_1 + \frac{\Delta_2^2}{z + \lambda_2 + \frac{\Delta_3^2}{\ddots + \frac{\Delta_n^2}{z + \hat{\varphi}_n(z)}}}} \quad (55)$$

defining its Laplace transform. In the explicit calculations presented in this subsection, we shall limit ourselves to considering the case of Eq. (54) which corresponds to truncating Eq. (55) at the first order ( $\Delta_2^2 = 0$ ) while assuming  $\lambda_1 = 1/\tau_c$  and  $\Delta_1^2 = \gamma/\tau_c$ . A truly rigorous derivation from a microscopic Liouvillian would lead to  $\lambda_i = 0$  unless coherent oscillatory motions have to

be simulated (in that case  $\lambda_i$  would be purely imaginary numbers). The chain of Eq. (55) is often truncated at the  $n$ th order by assuming  $\hat{\phi}_n(z) = \gamma_n$ . When this is done, the dissipative term  $\gamma_n$  simulates the infinite remainder of the chain. In most cases (see, for example, Grote and Hynes<sup>28a,37</sup>)  $\varphi(t)$  is given a certain analytical expression without taking into account the formal constraints provided by the derivation from a hypothetical microscopic Liouvillian. In such a case the parameters  $\lambda_i$  can be real numbers. If we adopt the basic ideas of the RMT (which in the present linear case to which the standard generalized Langevin equation applies is virtually equivalent to the methods described by Ferrario and Grigolini<sup>63</sup>), we find that the set of Eqs. (52) is equivalent to

$$\dot{x} = v \quad (56a)$$

$$\dot{v} = -V'(x) + A_1 \quad (56b)$$

$$\dot{A}_1 = -\Delta_1^2 v - \lambda_1 A_1 + A_2 + \xi_1(t) \quad (56c)$$

$$\dot{A}_2 = -\Delta_2^2 A_1 - \lambda_2 A_2 + A_3 + \xi_2(t) \quad (56d)$$

$$\vdots$$

$$\dot{A}_n(t) = -\Delta_n^2 A_{n-1} - \lambda_n A_n + \xi_n(t) \quad (56n)$$

The random forces  $\xi_1(t), \dots, \xi_n(t)$  are Gaussian white noises of zero mean and correlations

$$\langle \xi_i(t) \xi_j(s) \rangle = 2\delta_{ij} K_B T \lambda_i (\Delta_1^2 \cdots \Delta_i^2) \delta(t-s) \quad (57)$$

These forces are introduced<sup>64</sup> so as to supplement the frictions  $\lambda_i$  with the corresponding noise term and guarantee the attainment of a canonical equilibrium. The Fokker-Planck equation associated with the set of Eqs. (56) can be written as

$$\frac{\partial}{\partial t} \rho(q, t) = \frac{\partial}{\partial q_\mu} D_{\mu\nu} \left[ (K_B T)^{-1} \left( \frac{\partial}{\partial q_\nu} U(q) \right) + \frac{\partial}{\partial q_\nu} \right] \rho(q, t) \quad (58)$$

where a summation over repeated indices is implicit,  $\mu, \nu = 1, \dots, n+2$ , and  $q = x, v, A_1, \dots, A_n$ . The generalized potential  $U$  is

$$U(q) = \frac{V(x)}{M} + \frac{v^2}{2} + \frac{A_1^2}{2\Delta_1^2} + \cdots + \frac{A_n^2}{2\Delta_1^2 \cdots \Delta_n^2} \quad (59)$$

and the kinetic matrix  $D_{\mu\nu}$  is

$$D_{\mu\nu} = K_B T \begin{bmatrix} 0 & -1 & 0 & 0 & \cdots & \cdots & 0 \\ 1 & 0 & -\Delta_1^2 & 0 & \cdots & \cdots & 0 \\ 0 & \Delta_1^2 & \lambda_1 \Delta_1^2 & -\Delta_1^2 \Delta_2^2 & \cdots & \cdots & 0 \\ 0 & 0 & \Delta_1^2 \Delta_2^2 & \cdots & \cdots & \cdots & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & -\Delta_1^2 \cdots \Delta_n^2 \\ 0 & & & & & & \Delta_1^2 \cdots \Delta_n^2 \quad \lambda_n \Delta_1^2 \cdots \Delta_n^2 \end{bmatrix} \quad (60)$$

The equilibrium stationary solution of Eq. (58) is

$$\rho_{st}(q) = N \exp \left[ -\frac{U(q)}{K_B T} \right] \quad (61)$$

where  $N$  is a normalization constant.

As mentioned above, in the explicit calculations of this subsection we shall consider  $\lambda_0 = 0$ ,  $\lambda_1 \neq 0$ ,  $\Delta_2^2 = 0$ . This is the simplest case satisfying the requirements of a rigorous derivation from a microscopic Liouvillian. Of course, for the non-Markovian nature of the variable velocity  $v$  to result in observable effects, the effective friction term

$$\gamma_{\text{eff}} \equiv \left[ \int_0^\infty \langle v(0)v(t) \rangle dt \right]^{-1}$$

cannot be infinitely large compared with the frequency  $\omega_0$ , the harmonic approximation around the bottom of the reactant well. This means that inertial effects cannot be disregarded. An interesting discussion of the influence of inertia on the escape over the potential barrier (variational in nature) can be found in a paper by Larson and Kostin.<sup>22b</sup> Their results are valid in the limit of white noise and provide a reliable check of our approach. Furthermore, in an earlier paper,<sup>22a</sup> the same authors improved the Kramers result for the diffusional case by evaluating corrections to the linearization of the Brownian motion within the barrier region. Such an assumption is usually<sup>28a,37,65</sup> at the basis of any approximate analytical calculation of the activation rates. However, as shown by Fonseca et al., when using the CFP this approximation can be avoided. Therefore we shall apply the CFP in the most advanced form reviewed by Grosso and Pastori in Chapter III to the Fokker-Planck equation [Eq. (58)] with  $n=1$  and  $\lambda_1 \neq 0$ , which hopefully should account also for the corrections of ref. 22b.



In Larson and Kostin<sup>22b</sup> notation we change variables as follows:

$$\begin{aligned} x &\rightarrow x\tilde{a} \\ v &\rightarrow v\gamma\tilde{a} \\ t &\rightarrow \gamma^2\tilde{a}^2\frac{t}{q} \\ A_1 &\rightarrow A_1\Delta_1^2\tilde{a} \end{aligned} \quad (62)$$

where

$$\tilde{a} = \left(\frac{a}{b}\right)^{1/2} \quad \gamma = \frac{\Delta_1^2}{\lambda_1} \quad q = \frac{\gamma}{\langle v^2 \rangle} \quad (63)$$

The reduced Fokker-Planck equation now reads

$$\begin{aligned} \frac{\partial}{\partial t}\sigma(x, v, A_1, t) = & \left[ -\alpha v \frac{\partial}{\partial x} + 4c(x^3 - x) \frac{\partial}{\partial v} - \alpha' A_1 \frac{\partial}{\partial v} \right. \\ & \left. + \alpha v \frac{\partial}{\partial A_1} + \alpha' \frac{\partial}{\partial A_1} A_1 + \frac{\partial^2}{\partial A_1^2} \right] \sigma(x, v, A_1, t) \end{aligned} \quad (64)$$

where

$$\begin{aligned} \alpha &= \gamma^3 \frac{\tilde{a}^2}{q} & \alpha' &= \lambda_1 \gamma^2 \frac{\tilde{a}^2}{q} \\ c &= \frac{\gamma}{V_0} & V_0 &= \frac{a^2}{4b} \end{aligned} \quad (65)$$

Let us note that in these dimensionless variables  $c$  plays the role of barrier height, while  $\gamma = \Delta_1^2/\lambda_1$  is the effective friction constant. This can be shown by following the heuristic argument of Section I of Chapter II. Let us assume that  $A_1$  relaxes so fast that  $\dot{A}_1$ , Eq. (56c), is approximately zero; the system of Eqs. (3) will be recovered provided  $\gamma = \Delta_1^2/\lambda_1$ . Moreover, in Section V.C of Chapter II it is shown that the AEP corrections to the trivial Markovian approximation of Eq. (58),  $n=1$ , are perturbation terms in the parameter

$$g = 2 \left( \frac{\alpha}{\alpha'} \right)^{1/2} = \frac{2\Delta_1}{\gamma} \quad (66)$$

In other words, if we keep  $\gamma$  fixed and vary  $g$ , we explore situations with

different "memory strength." Following the prescription of ref. 66, we define the escape time from the reactant well to the product well as the area below the curve  $\langle x(t) \rangle / \langle x(0) \rangle$ . For fairly high values of the barrier  $c$ , this curve is mostly one exponential throughout the entire time range but for a narrow region close to  $t = 0$ . This fast relaxation depends significantly on the starting point distribution,  $\sigma(x, 0)$ .<sup>15a</sup> Let us assume  $\sigma(x, 0)$  to be given by a delta of Dirac placed at the bottom of one well. This choice may enhance the effect of the short time relaxation on our definition of escape time,

$$\tau_K \equiv \hat{\Phi}(0) \quad (67)$$

where  $\hat{\Phi}(0)$  is the Laplace transform of  $\langle x(t) \rangle / \langle x(0) \rangle$  at zero frequency. However, for large enough values of  $c$ ,  $k = \tau_K^{-1}$  can be relied on as a sensible estimate of the activation rate of the process.

Figure 9 describes the results obtained by applying the CFP. The most remarkable feature of these results, is the increase in the rate  $k$  as the parameter  $g$  increases. A further remarkable finding is that for  $g \rightarrow 0$  (Markovian limit) the accurate value of Larson and Kostin<sup>22b</sup> is attained within a precision of a few percent.

Figure 9 is the main result of the present discussion. However, we can attempt to arrive at an analytical expression for the rate of escape over the

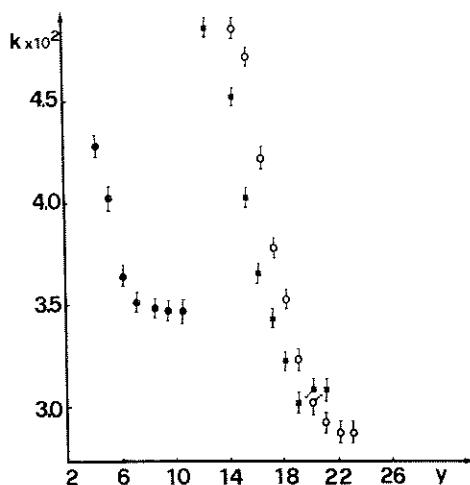


Figure 9. The escape rate  $k$  [see Eq. (67)] as a function of  $y = 4/g^2 = \alpha'/\alpha$  when  $c = 5$ . The approach used to calculate  $k$  is the "exact" one described in Chapter II of this volume. The values of the parameter  $\alpha$  are as follows: (O)  $\alpha = 10$ , (■)  $\alpha = 12$ , and (●)  $\alpha = 20$ . [Taken from F. Marcheroni and P. Grigolini, *J. Chem. Phys.*, **78**, 6287 (1983).]

barrier by using the generalization of Kramers' ideas to systems with many variables.<sup>20,55,67,68,69</sup> Let us come back to the multidimensional potential  $U(q)$ , Eq. (59): It has two metastable minima at  $q_{1,2} = (x_{1,2}, 0, \dots, 0)$  and a saddle point  $q_0 = (x_0, 0, \dots, 0)$ . This generalization essentially consists in the following. One first looks for a quasi-stationary state of Eq. (58). In this state there exists a nonvanishing probability current from one metastable minimum to the other. The nonequilibrium stationary state and the probability current are calculated by linearizing around the saddle point  $q_0$ . The escape rate is given by the flux of probability current through a surface containing the point  $q_0$ . The calculation of  $k$  has been discussed in detail by Langer<sup>20</sup> for a general Fokker-Planck equation with the form of Eq. (58). The final result is

$$k = \frac{|\kappa|}{2\pi} \left( \frac{\det M^1}{|\det M^0|} \right)^{1/2} \exp\left(-\frac{\Delta U}{K_B T}\right) \quad (68a)$$

where

$$\Delta U = U(q_0) - U(q_1) \quad M_{\mu\nu}^0 = \left. \frac{\partial^2 U}{\partial q_\mu \partial q_\nu} \right|_{q=q_0} \quad M_{\mu\nu}^1 = \left. \frac{\partial^2 U}{\partial q_\mu \partial q_\nu} \right|_{q=q_1} \quad (68b)$$

Note that  $\det M^0$  is taken in absolute value in Eq. (68). This corresponds to replacing the negative eigenvalue  $M_{11}^0$ , which indicates the single direction of instability, by its absolute value. The dynamical factor  $\kappa$  is defined as the negative eigenvalue of the matrix  $M^0 D / K_B T$ . It is important to note that the dynamics of the system only enters into Eq. (68) through  $\kappa$ . This factor depends on the kinetic coefficients  $D_{\mu\nu}$ , Eq. (60), while the remaining terms in Eq. (68) are completely determined by the potential  $U$  of the stationary solution. For the case under study, Eqs. (58) and (59), Eq. (68) reduces to

$$k = \frac{|\kappa|}{2\pi} \left( \frac{U''(x_1)}{|U''(x_0)|} \right)^{1/2} \exp\left[-\frac{U(x_0) - U(x_1)}{K_B T}\right] \quad (69)$$

In this particular case,

$$\frac{M^0 D}{K_B T} = \begin{bmatrix} 0 & -U''(x_0) & 0 & \cdots & \vdots & 0 \\ 1 & 0 & -\Delta_1^2 & 0 & \vdots & 0 \\ 0 & 1 & \lambda_1 & -\Delta_2^2 & \vdots & 0 \\ 0 & 0 & 1 & \lambda_2 & \vdots & \\ \cdots & \cdots & \cdots & \cdots & \vdots & \cdots \\ 0 & \cdots & \cdots & \cdots & \vdots & -\Delta_n^2 \\ 0 & \cdots & \cdots & \cdots & \vdots & 1 \quad \lambda_n \end{bmatrix} \quad (70)$$

The eigenvalues of this matrix admit a continued fraction expansion

$$-\kappa = -\frac{U''(x_0)}{-\kappa + \dots} \frac{\Delta_1^2}{-\kappa + \lambda_1 + \dots} \dots \frac{\Delta_n^2}{-\kappa + \lambda_n} \quad (71)$$

From this expression it is clear that  $\kappa$  is the negative solution of the implicit relation

$$-\kappa = \frac{-U''(x_0)}{-\kappa + \hat{\phi}(-\kappa)} \quad (72)$$

Equation (72) coincides with the analytical result of Grote and Hynes.<sup>37</sup> In the Markovian limit,  $\hat{\phi}(t) = 2\gamma\delta(t)$ ,

$$\kappa = \frac{\gamma}{2} - \left( \frac{\gamma^2}{4} - U''(x_0) \right)^{1/2}$$

and we recover the Kramers result, Eq. (6).

The whole effect of the non-Markovian dynamics is contained in  $\kappa$ . As long as the fluctuation-dissipation relation, Eq. (57), is satisfied, the existence of the non-Markovian kernel modifies the dynamics but not the equilibrium solution, Eq. (61), and, on the other hand, a change in the dynamics of the system only changes the value of  $\kappa$  in Eq. (69). The general form of the non-Markovian effects on  $\kappa$  have also been obtained by Hänggi and Mojtabai.<sup>65</sup> Their elegant derivation is based on a non-Markovian master equation first established by Adelman<sup>70</sup> for the probability density of the process which is solved by using the main basic assumption of Kramers. Their results are again proven to agree with those of Grote and Hynes.<sup>37</sup>

As a particular example of Eq. (72) we can consider the case of an Ornstein-Uhlenbeck noise,<sup>37,65</sup> where  $n=1$ ,  $\lambda_1 = \tau_c^{-1}$  and  $\Delta_1^2 = \gamma/\tau_c$ . In this case  $\kappa$  is the negative solution of

$$-\kappa^3 - \lambda_1\kappa^2 - [\Delta_1^2 + U''(x_0)]\kappa + U''(x_0)\lambda_1 = 0 \quad (73)$$

The Markovian limit corresponds to  $\lambda_1 \rightarrow \infty$ . By solving Eq. (73) to the lowest order in  $\lambda_1^{-1}$  it is easy to see that in this case the non-Markovian dynamics leads to an enhancement of the decay rate  $k$ . In the notation of ref. 22b, an approximate expression for Eq. (69) may then be written as

$$k = k(g=0) \left[ 1 - \frac{4c}{\alpha} \left( 1 - \frac{g^2}{4} \right) \right] \quad (74)$$

where  $k(g=0)$  is the Kramers escape rate (in the diffusional limit) and  $g$  is the parameter of "memory strength" defined in Eq. (66). The same result has been obtained in ref. 66 by adopting the variational method of ref. 22b. Equation (74) is the analytical counterpart of the exact results reported in Fig. 9: As shown in ref. 66, the agreement with numerical results is only qualitative. Before concluding this subsection, we would like to mention a further way to explore the effects of non-Markovian statistics on the rate of escape from a well. This consists in applying the AEP of Chapter II to the Fokker-Planck equation, Eq. (58), so as to build up a reduced diffusion-like equation for the variable  $x$  alone. As the chance of proper simulating these effects relies on a faithful simulation of inertia, we quote here the interesting result of Gardiner,<sup>71</sup> which shows that this actually happens. He considered a corrected Smoluchowski equation which is a particular case of the more general reduced equation mentioned above. By using a first-passage time technique he could explore the whole region going from low- to high-friction regime and obtained results in agreement with those of a computer simulation. It therefore seems possible to explore also the effects of a non-white noise by applying the same procedure to the more general reduced equation mentioned above.

### B. Activation of a Chemical Reaction Process via Electromagnetic Excitation

The subject of this subsection is closely related to that of Section III. Indeed, we shall show that the effect of a radiation field on an overdamped reacting system produces activated states which are reminiscent and formally similar to those arrived at by the coupling between reactive and non-reactive modes.

Hänggi<sup>72</sup> studied the model potential

$$V(x) = -\frac{d(t)}{2}x^2 + \frac{b}{4}x^4 \quad (75)$$

where the frequency  $d(t)$  is a stochastic parameter such as

$$d(t) = d + \eta(t) \quad (76)$$

and  $\eta(t)$  is a Gaussian white noise. The main result of this study is that the presence of a multiplicative coupling with the heat bath makes the activation rate increase with respect to that in the Kramers model, where a purely additive noise is considered. In the following we give a detailed discussion of the interplay of additive and multiplicative noises on the basis of a phenomenological model for a photoactivated chemical reaction. De Kepper and

Horsthemke<sup>43</sup> have already used a radiation field as a source of noise. As in refs. 73 and 74, we model the action of a radiation field  $h(t)$  with a finite coherence time  $1/\lambda$ , in terms of the following set of stochastic differential equations:

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -V'(x) - \gamma v + E(x)h(t) + f(t)\end{aligned}\quad (77)$$

where  $f(t)$  is a Gaussian white noise with zero mean and autocorrelation function

$$\langle f(t)f(0) \rangle = 2D\delta(t) \equiv 2\gamma \langle v^2 \rangle \delta(t) \quad (78)$$

$V(x)$  is assumed to be the usual symmetrical double-well potential [ $V(x) = -\delta x^2/2 + \beta x^4/4$ ]; the third term on the right-hand side of Eq. (77) is the coupling between the Brownian particle and the external radiation field, which is characterized through its autocorrelation function

$$\langle h(t)h(0) \rangle = 2 \langle w^2 \rangle \exp(-\lambda t) \cos \omega t \quad (79)$$

Equation (79) has the physical meaning that the coherence of the electromagnetic field is lost in a time  $1/\lambda$ . Models of this kind are frequently used to depict laser light.<sup>75</sup> The electrical dipole of the system interacting with the external field is assumed to have the simple form

$$E(x) = \mu(x - x_0)^n \quad (80)$$

In order to relate the system of Eqs. (77) to a time-independent Fokker-Planck formalism, we replace that set of stochastic differential equations with the equivalent one,

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -V'(x) - \gamma v + E(x)(y + z) + f(t) \\ \dot{y} &= -i\omega y - \lambda y + \eta_y(t) \\ \dot{z} &= i\omega z - \lambda z + \eta_z(t)\end{aligned}\quad (81)$$

The AEP allows us to simplify the discussion of this model provided that we can choose a (slowly relaxing) variable of interest. For that reason we shall focus on an electromagnetic field of frequency comparable to the frequency

corresponding to the harmonic expansion of the reactant well,  $\omega_0$ . The diffusional assumption implies  $\gamma \gg 2\omega_0$ . Furthermore, we shall assume that our experimental apparatus allows us to observe only long-time regions corresponding to  $t \geq \gamma/\omega_0^2$  so that the dynamics induced by the radiation field belongs to the short-time region if  $\lambda \gg 2\omega_0$ . When it is further assumed that the stochastic forces  $\eta_y(t)$  and  $\eta_z(t)$  are independent of each other and related to the field intensity by

$$\begin{aligned}\langle \eta_y(t) \eta_y(0) \rangle &= 2D_y \delta(t) \\ \langle \eta_z(t) \eta_z(0) \rangle &= 2D_z \delta(t)\end{aligned}\quad (82)$$

where

$$D_y = D_z^* = (\lambda + i\omega) \langle w^2 \rangle \equiv \xi \langle w^2 \rangle \quad (83)$$

the current problem takes a form resembling that of the model studied in Section V.C of Chapter II. Let us focus our attention on the case  $\gamma \gg \lambda$ , that is, one in which non-Markovian effects due to light statistics are more relevant than inertial corrections. The perturbation expansion of Eq. (5.31) of Chapter II can then be rewritten as

$$\begin{aligned}\frac{\partial}{\partial t} \sigma(x, t) &= \left\{ \frac{1}{\gamma} \frac{\partial}{\partial x} j(x) + \frac{\langle w^2 \rangle}{\gamma^2(\gamma + \xi)} \frac{\partial^2}{\partial x^2} E^2(x) \right. \\ &\quad \left. + \frac{\langle w^2 \rangle}{\xi(\gamma + \xi)\gamma} \frac{\partial}{\partial x} E(x) \frac{\partial}{\partial x} E(x) + \text{c.c.} \right\} \sigma(x, t)\end{aligned}\quad (84)$$

where  $j(x) = \langle v^2 \rangle \partial / \partial x + V'(x)$  and  $\gamma^{-3}$  or higher order terms have been neglected.

Let us study in detail the case where the particle dipole  $E(x)$ , Eq. (80), is given by

$$E(x) = \mu x \quad (85)$$

Equation (84) can be put in a simpler form:

$$\frac{\partial}{\partial t} \sigma(x, t) = \left\{ -\frac{\partial}{\partial x} (-d_Q x + bx^3) + D \frac{\partial^2}{\partial x^2} + Q \frac{\partial}{\partial x} x \frac{\partial}{\partial x} x \right\} \sigma(x, t) \quad (86)$$

where

$$D = \frac{\langle v^2 \rangle}{\gamma} \quad (87)$$

$$d = \frac{\delta}{\gamma} \quad b = \frac{\beta}{\gamma} \quad (88)$$

$$Q = \frac{2\langle w^2 \rangle}{\gamma^2 \lambda (1 + \omega^2 / \lambda^2)} \quad (89)$$

$$d_Q = d - Q \frac{1 + \lambda / \gamma + \omega^2 / \lambda \gamma}{(1 + \lambda / \gamma)^2 + \omega^2 / \lambda \gamma} \quad (90)$$

As a result of AEP, the initial system of the set of Eqs. (81) is reduced to the equation describing the diffusional motion of a Brownian particle which undergoes the action of an additive and a multiplicative noise (with intensities  $D$  and  $Q$ , respectively) in the presence of a renormalized bounding potential, Eq. (90). The Markovian limit corresponds to  $\lambda \rightarrow \infty$ . If we take such a limit at a fixed value of  $\gamma$ ,  $d_Q = d$ , and the case studied by Hänggi<sup>72</sup> is recovered. Of course, having neglected the condition  $\lambda \ll \gamma$  we have reduced the problem to a trivial diffusional (lowest-order) approximation.

The escape rate for the process described by the Fokker-Planck equation, Eq. (86), has been studied in ref. 73. We choose  $\Phi(t) = \langle x(t) \rangle / \langle x(0) \rangle$  as the observable of interest,  $\langle x(\infty) \rangle = 0$ . Then we apply the approach described in the Section IV.A to evaluate the escape rate  $k$  as the area below the curve  $\Phi(t)$ :  $k = \hat{\Phi}(0)^{-1}$ , where  $\hat{\Phi}(0)$  is the Laplace transform of  $\Phi(t)$  at zero frequency. To make the convergence of the computer calculations faster, the CFP algorithm has been applied by taking

$$\sigma(x, 0) = N |x|^{-1 + d_Q/Q} \exp\left(-\frac{d_Q}{2Q} x^2\right) \quad (91)$$

as the initial distribution ( $N$  is a normalization constant). This is the stationary distribution in the absence of additive noise. The most remarkable results are reported in Fig. 10. When  $Q = 0$ ,  $k$  exactly coincides with the corresponding result of Larson and Kostin.<sup>22b</sup> For small values of  $Q$ ,  $k$  is a linear function of  $Q$ . A first change in the slope of  $k(Q)$  is exhibited at those values of  $Q$  corresponding to the onset of the continuum in the spectrum of the purely multiplicative Fokker-Planck operator,<sup>34,35</sup> that is, the Fokker-Planck operator of Eq. (51) with  $D = 0$ . A second is found when the threshold of the phase transition (see ref. 34) is reached. The main conclusion is that



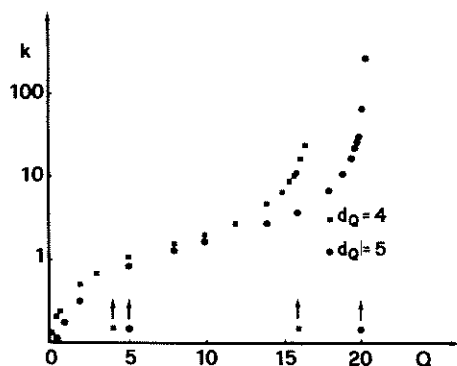


Figure 10.  $k$  as a function of the intensity of the multiplicative noise.  $k$  is defined as  $\hat{\Phi}(0)^{-1}$  with  $\Phi(t) = \langle x(t) \rangle / \langle x(0) \rangle$ . The two arrows on the left denote the point where the discrete branch of the eigenvalue spectrum disappears (see Schenzle and Brand<sup>34</sup>). The two arrows on the right denote the phase transition threshold. [Taken from S. Faetti et al., *Z. Phys.*, **B47**, 353 (1982).]

the cooperative presence of a multiplicative noise produces a marked increase of the thermal (i.e., additive) activation rate.

The question raised at the beginning of the present section is still unanswered. A simple argument, however, can provide information on the role played by non-Markovian dynamics in the problem under investigation. When  $\lambda < \infty$ ,  $d_Q < d$ , so that at a fixed value of  $Q$  the rate of escape will be larger than in the Markovian limit, making  $k(Q, d_Q)$  a decreasing function of  $d_Q$  (see Fig. 10). We are in the presence of a striking effect due to the synergism of different—and statistically unrelated—noise sources, nonlinearity and inertia. We showed in the preceding subsection that the effect of an external additive noise, non-Markovian in its nature, would be to lessen the activation rate of the process with respect to the Markovian case first studied by Kramers. Furthermore, it has been found,<sup>50</sup> by means of a numerical simulation, that the non-Markovian dynamics affects the diffusional relaxation in the presence of external multiplicative noises in a similar way. Contrary to these findings, our major conclusion in this subsection is that when both additive and multiplicative external noises act on the system, a finite correlation time of the multiplicative noise determines an increase of the activation rate. This subject is discussed further in Chapter X.

## V. DISCUSSION AND GENERAL PERSPECTIVE

In order to get a satisfactory perspective of the state of the art in the limited sector of the theory of chemical reactions which is explored in this chapter, we shall devote this final section to the following basic aspects:

1. The relation between current theories and selected experiments and discussion of the extent to which the details of theoretical predictions have been confirmed so far.

2. The relation between chemical reaction rate theories and some recent advances in the field of nonequilibrium statistical thermodynamics.

### A. Supporting Experimental Evidence

Experimental confirmation of the theoretical predictions discussed in this chapter is still far from completely satisfactory. It may be expected that in the near future fresh experimental results will come to motivate new developments in the theory and greatly improve the understanding of the actual experimental conditions where the theoretically predicted effects are relevant. The aim of this subsection is not that of giving a comprehensive review of the already very sizable mass of relevant experimental studies (for more comprehensive reviews see refs. 7b and 76); we shall draw attention to certain difficulties in the interpretation of experimental results in relation to the theory developed here and refer to a few representative pieces of experimental work.

One difficulty of connecting theory and experiment arises from the fact that the relation between the microscopic coupling parameter between the reaction coordinate and the medium (the friction coefficient) and the macroscopic observables is not well understood. The usual rule of thumb follows Stokes's law and states that the friction is proportional to the macroscopic bulk viscosity; however, this may be grossly incorrect. It would be advantageous to use a local viscosity obtained from the measurement of some sort of molecular relaxation phenomenon, but this is not always available.

An alternative strategy is to look at the activation volumes  $V^\ddagger$  related to the pressure dependence of the rate constant by the thermodynamic relation

$$V^\ddagger = -K_B T \left( \frac{\partial \ln k}{\partial P} \right)_T \quad (92)$$

The volume of activation should be formed by an equilibrium (quasi-thermodynamic) part related to the TST rate,  $V_{\text{TST}}^\ddagger$ , plus an extra part,  $V_D^\ddagger$ , originating from the dynamic interaction with the solvent.  $V_{\text{TST}}^\ddagger$  may be estimated with reasonable assumptions about the transition-state conformation, and thus access is gained to  $V_D^\ddagger$ , that is, the pressure dependence of  $k/k_{\text{TST}}$ . This pressure dependence is felt through the friction,

$$V_D^\ddagger = -K_B T \left[ \frac{d}{d\gamma} \frac{K}{K_{\text{TST}}} \right] \left( \frac{\partial \gamma}{\partial P} \right)_T \quad (93)$$

This method was proposed by Montgomery, Chandler, and Berne,<sup>25</sup> who suggested that  $(\partial \gamma / \partial P)_T$  could be estimated from the equation of state of the solvent, together with a hard-sphere collision expression, and thus the friction dependence of  $k/k_{\text{TST}}$  could be assessed.

One would like to know what experimental conditions lead to the energy transfer controlled regime or to the diffusive regime and whether the plateau of transition between these two regimes approaches the TST rate. The experimental evidence to answer this sort of question is still very fragmentary. The first series of very interesting experiments appearing to cover the whole range of friction-dependent kinetic regimes has only very recently been performed. Hasha, Eguchi, and Jonas<sup>77</sup> did a high-pressure NMR study of the conformational isomerization of cyclohexane in several solvents so as to cover a viscosity range of about 50 times. They found a clear transition from the rate-increasing low-friction regime to the rate-decreasing high-friction region, but this decrease does not exceed 7.5% of the maximum for a friction 10 times higher.

Fleming et al.,<sup>78</sup> in a series of studies of the solvent viscosity dependence of the rate of isomerization of several organic molecules (e.g., diphenylbutadiene) in alkane and alcohol solvents, found a similar deviation: For the higher viscosities, the observed rate is lower than that predicted by a fitted Kramers expression. This effect has been explained as coming from the non-Markovian nature of the coupling to the heat bath by Velsko, Waldek, and Fleming;<sup>78c</sup> by Bagchi and Oxtoby,<sup>79</sup> using Grote and Hynes<sup>28</sup> formalism; and also by Carmeli and Nitzan<sup>26b</sup> within their generalized theory.

Other reactions have been studied that appear to also require consideration of non-Markovian effects. For example, in a recent study of the photoisomerization of *trans*-stilbene and *trans*-1,1'-biindanylidene, Rothenberger, Negus, and Hochstrasser<sup>80</sup> found deviations from the Kramers rate in the case of *trans*-stilbene. These discrepancies were tentatively related to the larger flexibility of this molecule but appeared to be well simulated by the non-Markovian theory of Grote and Hynes.<sup>28</sup>

The fitting of the theoretical models to experimental data does normally require adjustment of the frequency parameters ( $\omega_0, \omega_b$ ) related to the molecular potential, since the latter is frequently unknown. It has been noted by several authors<sup>26b,80</sup> that the values obtained appeared to be unrealistic, which sheds doubt as to the validity of the interpretation given to the data.

An explanation of the enhancement and other anomalies of the catalytic reaction rates on metals and certain insulators associated with the large fluctuations of the internal degrees of freedom that occur near a phase transition or by alloying has been attempted by d'Agliano, Schaich, Kumar, and Suhl<sup>81</sup> within the framework of stochastic theories.

To sum up the current position of the experimental evidence on the viscosity effect on condensed phase reaction rates, we may say that the most commonly observed effect is the inverse proportionality associated with the diffusive (high-friction) regime. In some cases, deviations are observed for lower viscosities which fit well with Kramers intermediate friction regime

predictions. (See, for example, the analysis made by McCaskill and Gilbert<sup>82</sup> of data of Shank et al.<sup>83</sup> for the optically induced conformational changes in 1,1'-binaphthyl in several solvents.) Furthermore, there is now enough experimental evidence to show that in more particular conditions the energy transfer controlled (very low friction) regime will set in and may be accompanied by a wealth of finer effects that are discussed in this chapter.

Some of the theoretical results discussed here may also be checked by analogous computer simulation, a topic discussed by Faetti et al. in Chapter X.

### B. Settled and Unsettled Problems in the Field of Chemical Reaction Rate Theory

The current attempts at generalizing the Kramers theory of chemical reactions touch two major problems: The fluctuations of the potential driving the reaction coordinate, including the fluctuations driven by external radiation fields, and the non-Markovian character of the relaxation process affecting the velocity variable associated to the reaction coordinate. When the second problem is dealt with within the context of the celebrated generalized Langevin equation

$$\dot{v} = - \int_0^t \varphi(t - \tau) v(\tau) d\tau + f(t) \quad (94)$$

supplemented by the fluctuation-dissipation relationship

$$\varphi(t) = \frac{\langle f(0)f(t) \rangle_{\text{eq}}}{\langle v^2 \rangle_{\text{eq}}} \quad (95)$$

these topics seem now to be at a fully developed level of understanding. As already illustrated in the foregoing sections, the chemical relaxation process is then described by

$$\dot{v} = - \frac{\partial V}{\partial x} - \int_0^t \varphi(t - \tau) v(\tau) d\tau + f(t) \quad (96)$$

where  $V$  is the external potential driving the reaction coordinate  $x$ .

Carmeli and Nitzan<sup>84</sup> have provided a complete treatment of this problem. They assumed the memory kernel  $\varphi$  to be given the following analytical expression:

$$\varphi(t) = \Omega^2 \exp(-\Gamma t) \quad (97)$$

As already stressed in the foregoing sections, the standard case studied by Kramers is recovered by assuming  $\Gamma$  to be infinitely large. In such a case,  $\varphi(t)$  can be replaced by

$$\varphi(t) = 2\gamma\delta(t) \equiv 2\frac{\Omega^2}{\Gamma}\delta(t) \quad (98)$$

which, when replaced into Eq. (96), results in the standard set of equations studied by Kramers [see Eq. (6)].

The parameter

$$\gamma = \frac{\Omega^2}{\Gamma} \quad (99)$$

can be thought of as a measurement of the friction intensity in the strong memory region also.

As we have already discussed, further parameters of interest are the frequencies  $\omega_0$  and  $\omega_b$  deriving from the harmonic approximation at the bottom of the reactant well and the top of the barrier, respectively. Carmeli and Nitzan<sup>84a</sup> evaluated the reaction rate throughout the entire friction dominion ranging from the low-friction regime ( $\omega_b \gg \gamma$ ) to the high-friction regime. (This has also been commented on in Section II.B.) They also studied the dependence of the reaction rate on the correlation time

$$\tau_c = \frac{1}{\Gamma} \quad (100)$$

Their interesting results are shown in Figs. 11 and 12. We learn from these

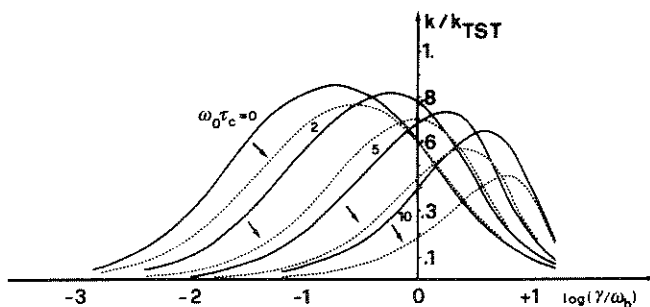


Figure 11. Dependence of the reaction rate on the correlation time  $\tau_c$ . A comparison is made between the analytical results provided by (---) the two-step model [Eq. (13)], and (—) those obtained by Carmeli and Nitzan.<sup>84a</sup> The results of the two-step model were obtained using an effective friction in order to simulate the non-Markovian character of the chemical process [see Eqs. (116) and (124)].  $\omega_0/\omega_b = 5$ .

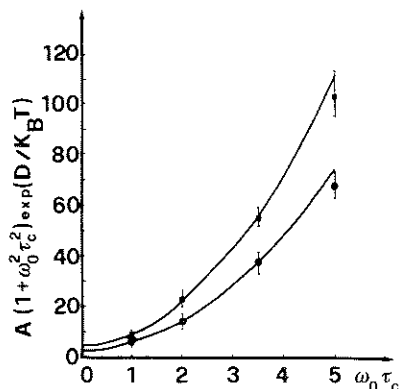


Figure 12. Numerical results provided by Carmeli and Nitzan.<sup>84b</sup> (■)  $E_b = 5K_B T$ ; (●)  $E_b = 2.5K_B T$ . These numerical results were reproduced by the analytical result provided by Eq. (117) using  $A = K_B T / \gamma E_b$  as a fitting parameter. (■)  $A = 0.0292$  for  $E_b = 5K_B T$ ; (●)  $A = 0.236$  for  $E_b = 2.5K_B T$ .

results that the effect of increasing the correlation time  $\tau_c$  is equivalent to shifting the curve corresponding to the case of white noise to the right. The height of the curves also changes as  $\tau_c$  is varied, the form of this change depending on the ratio  $\omega_0/\omega_b$ .

These results are of very special interest, as they provide a definite answer to questions such as: (1) Can the rate be increased beyond any limit by adjusting the value of  $\tau_c$ ? (2) On another region of the friction, can an increase in  $\tau_c$  make the reaction time infinitely large? By inspection of Carmeli and Nitzan's results, we conclude that an unbounded growth of  $\tau_c$  makes the reaction rate vanishingly small; however, when an initial increase in the rate (as a consequence of the growth of  $\tau_c$ ) is observed, it is bound to reach a maximum value and then decrease to a vanishing rate for  $\tau_c \rightarrow \infty$ . This is not merely a problem of academic interest. Considerable attention is currently being devoted to enzyme chemistry,<sup>85</sup> where the enigma to be solved concerns how the activation process takes place. Enzymes succeed in increasing the reaction rates by about six orders of magnitude. A possible mechanism could be the presence of cooperative effects which make  $\tau_c$  tend to infinity. However, Carmeli and Nitzan's results<sup>84</sup> show that in the case of a barrier as high as  $18K_B T$ , the effect of increasing  $\tau_c$  cannot produce an increase in the chemical reaction rate larger than one order of magnitude. This suggests that the enigma of enzyme chemistry has to be solved by other mechanisms—for example, the interaction with nonreactive modes. This is another aspect concerning the generalization of Kramers theory and it touches problems which seem to be still the subject of controversy, such as the validity of the AEP itself.

Concerning the first aspect, on the other hand, we are already in a position to get a fairly definite view, which is clearly illustrated by the results of Carmeli and Nitzan (see Figs. 11 and 12).

What about the role played within this context by the general strategy of this book (as symbolized by the delta-like diagram of Chapter I)? We shall devote a large part of this final section to showing how this strategy may contribute to clarifying the physical meaning of these results. A calculation completely satisfactory from a quantitative point of view should, however, rely largely on the methods developed by other authors (those of Carmeli and Nitzan seem to be of special interest). For the sake of clarity we shall recall some of the key results of the foregoing sections.

When considering the special case studied by Carmeli and Nitzan, the RMT replaces Eq. (96) with

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\frac{\partial V}{\partial x} + w \\ \dot{w} &= -\Omega^2 v + \Gamma w + F(t)\end{aligned}\tag{101}$$

where  $F(t)$  is a white Gaussian noise defined by

$$\begin{aligned}\langle F(t) \rangle &= 0 \\ \langle F(0)F(t) \rangle &= 2\Gamma \langle w^2 \rangle_{\text{eq}} \delta(t)\end{aligned}\tag{102}$$

The physical meaning of Eq. (101) has already been discussed in the foregoing sections, as well as in Chapter I.

First of all we shall apply Eq. (101) to study the low-friction regime:

$$\gamma \ll \omega_0\tag{103}$$

and we assume  $\omega_0$  and  $\omega_b$  to be of the same order of magnitude. The standard Kramers theory corresponds to

$$\Omega \ll \omega_0 \ll \Gamma\tag{104}$$

To take into account the fact that  $f(t)$  of Eq. (94) is not rigorously white, we should explore also the region where

$$\Omega \ll \Gamma \ll \omega_0\tag{105}$$

which is precisely that explored by Carmeli and Nitzan.<sup>84b</sup> Their latest results,<sup>84a</sup> however, seem to apply also to

$$\Gamma \lesssim \Omega \ll \omega_0\tag{106}$$

Since, in the low-friction regime, the escape is largely determined by the behavior of the Brownian particle in the well, we shall focus our attention on that. When considering barriers of large intensity, we are allowed to replace Eq. (101) with its harmonic approximation

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\omega_0^2 x + w \\ \dot{w} &= -\Omega^2 v - \Gamma w + F(t)\end{aligned}\tag{107}$$

We assumed the origin of the space coordinate to be at the bottom of the reactant well. By adopting the method of the stochastic normal modes (see Chapter II), Eq. (107) is replaced by

$$\begin{aligned}\dot{\xi}_+ &= -\Lambda_+ \xi_+ + F_+(t) \\ \dot{\xi}_- &= -\Lambda_- \xi_- + F_-(t) \\ \dot{\xi}_0 &= -\Lambda_0 \xi_0 + F_0(t)\end{aligned}\tag{108}$$

To determine these normal modes one has to diagonalize the matrix

$$A = \begin{bmatrix} 0 & i\omega_0 & 0 \\ -i\omega_0 & 0 & i\Omega \\ 0 & -i\Omega & -\Gamma \end{bmatrix}\tag{109}$$

This antisymmetric form can easily be derived from Eq. (107) by multiplying the variables  $v$  and  $w$  by suitable constants. Note the similarity of this matrix with that of ref. 39.

We may exploit the fact that  $\omega_0$  is much larger than the other parameters,  $\Gamma$  and  $\Omega$ . First of all, let us rewrite the matrix  $A$  in the basis set, where it can be given the form

$$A = \begin{bmatrix} i\omega_0 & 0 & \frac{i\Omega}{\sqrt{2}} \\ 0 & -i\omega_0 & -\frac{i\Omega}{\sqrt{2}} \\ -\frac{i\Omega}{\sqrt{2}} & \frac{i\Omega}{\sqrt{2}} & -\Gamma \end{bmatrix}\tag{110}$$



Then, by a perturbation calculation, we obtain

$$\begin{aligned}\Lambda_+ &\cong i\omega_0 + \frac{\Omega^2}{2(i\omega_0 + \Gamma)} \\ \Lambda_- &\cong -i\omega_0 + \frac{\Omega^2}{2(i\omega_0 - \Gamma)} \\ \Lambda_0 &\cong -\Gamma\end{aligned}\quad (111)$$

This means that the normal modes  $\xi_+$  and  $\xi_-$  are characterized by frequencies  $\Omega_+$  and  $\Omega_-$  given by

$$\begin{aligned}i\Omega_+ &= i \left[ \omega_0 + \frac{\Omega^2\omega_0}{2(\omega_0^2 + \Gamma^2)} \right] \\ i\Omega_- &= -i \left[ \omega_0 - \frac{\Omega^2\omega_0}{2(\omega_0^2 + \Gamma^2)} \right]\end{aligned}\quad (112)$$

both with the same damping,

$$\frac{\Gamma_{\text{eff}}}{2} = \frac{\Omega^2\Gamma}{2(\omega_0^2 + \Gamma^2)} = \frac{\gamma}{2(1 + \omega_0^2\tau_c^2)}\quad (113)$$

If we focus our attention on the damping while neglecting the less important effect on the frequencies, we have that the same result could be obtained from the Markovian system

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\omega_0^2x - \Gamma_{\text{eff}}v + f^*(t)\end{aligned}\quad (114)$$

with the Gaussian white stochastic force  $f^*(t)$  defined by

$$\langle f^*(0)f^*(t) \rangle = 2\Gamma_{\text{eff}}\langle v^2 \rangle_{\text{eq}}\delta(t)\quad (115)$$

Note that in the non-Markovian case ( $\omega_0\tau_c \gg 1$ ) the effective damping

$$\Gamma_{\text{eff}} = \frac{\gamma}{1 + \omega_0^2\tau_c^2}\quad (116)$$

turns out to be much smaller than the damping in the absence of the external field. This is a well-understood effect, discussed at length by Grigolini.<sup>86</sup>

A strong external field acting on a non-Markovian system tends to decouple that system from its thermal bath, thereby rendering smaller its effective damping.

In other words, if we are exploring the low-friction regime, the interplay of non-Markovian statistics and external field renders the system still more inertial, thereby widening the range of validity of the formula provided by Kramers for the low-friction regime provided that  $\gamma$  be replaced by  $\gamma/(1 + \omega_0^2\tau_c^2)$ .

Figure 12 shows that this simple expression agrees fairly well with both the theory of Carmeli and Nitzan and the result of their purely numerical calculations. The plots in Fig. 12 show how well the non-Markovian effects on the rate may be simulated by a simple multiplicative factor  $(1 + \omega_0^2\tau_c^2)^{-1}$ . For the sake of comparison, we fitted an expression with this factor to Carmeli and Nitzan's results so as to include their accurate Markovian rate.

Using Eq. (113), the Markovian low-friction expression of Kramers [Eq. (8)] may be generalized to the non-Markovian case,

$$k_{\text{Low}}(\tau_c) = \frac{\gamma}{1 + \omega_0^2\tau_c^2} \left( \frac{E_b}{K_B T} \right) \exp\left( - \frac{E_b}{K_B T} \right) \quad (117)$$

The discrepancies between the rate given by this expression and that calculated by Carmeli and Nitzan are mostly due to their improved Markovian part.

We believe that the arguments above should convince the reader that the interesting phenomenon detected by Carmeli and Nitzan is another manifestation of the decoupling effect, well understood at least since 1976 (see ref. 86). The only physical systems, the dissipative properties of which are completely independent of whether or not an external field is present, are the purely ideal Markovian ones. Non-Markovian systems in the presence of a strong external field provoking them to exhibit fast oscillations are characterized by field-dependent dissipation properties. These decoupling effects have also been found in the field of molecular dynamics in the liquid state studied via computer simulation (see Evans, Chapter V in this volume).

The region ranging from  $\gamma = \infty$  to  $\gamma \sim \omega_b$  can also be explored using the RMT. In Section IV we showed that the basic ideas of the RMT supplemented by the generalization of the Kramers theory to the multidimensional case allows us to recover the simple expression first derived by Grote and Hynes.<sup>37</sup> This quite interesting formula reads

$$k_H = k_{\text{TST}} \frac{\lambda_r}{\omega_b} \quad (118)$$

where

$$k_{\text{TST}} = \frac{\omega_0}{2\pi} \exp\left(\frac{-E_b}{K_B T}\right)$$

and

$$\lambda_r = \frac{\omega_b^2}{\lambda_r + \hat{\phi}(\lambda_r)} \quad (119)$$

with

$$\hat{\phi}(\lambda_r) = \int_0^\infty dt \exp(-\lambda_r t) \varphi(t) \quad (120)$$

In the case considered by Carmeli and Nitzan,<sup>84b</sup> we obtain

$$\lambda_r = \frac{\omega_b^2}{\lambda_r + \Omega^2/(\lambda_r + \Gamma)} \quad (121)$$

In the high-friction region when the additive noise is almost white, we have

$$\frac{\omega_b^2}{\gamma} \ll \omega_b \ll \gamma \ll \Gamma \quad (122)$$

This means that  $\omega_b^2/\gamma$  can be disregarded compared to both  $\Gamma$  and  $\Omega^2/\Gamma = \gamma$ . In other words,

$$\lambda_r = \frac{\omega_b^2}{\gamma} \quad (123)$$

which is the Kramers high-friction result.

As  $\Gamma$  decreases, this simple formula results in an increase of  $\lambda_r$  in qualitative agreement with Fig. 11 from the Carmeli and Nitzan work.

We are thus in a position to state that the RMT provides quite simple formulas which give a clear and simple picture of the chemical reaction rate as a function of  $\omega_b\tau_c$  (or  $\omega_0\tau_c$ ). The two-step model introduced in Section II.A naturally leads to

$$k_{\text{int}}^{-1}(\tau_c) = k_{\text{high}}^{-1}(\tau_c) + k_{\text{low}}^{-1}(\tau_c) \quad (124)$$

This expression gives a useful semiquantitative description of chemical rate in the most general case, Markovian or non-Markovian and in any range of

friction. Figure 11 illustrates the corresponding results, which are qualitatively the same as those of Carmeli and Nitzan.

The generalization of the Kramers theory involving the problem of multiplicative fluctuations is still an open field of investigation. A large part of the discrepancies between the AEP and the other approaches do certainly derive from the fact that this theory is applied to a set of differential equations, the formal expression of which seems to be not completely legitimate. For instance, a rigorous microscopic derivation certainly cannot result in formal expressions such as those of Eqs. (38) and (44).

The physical reasons for the acceleration of the chemical reaction rate as a result of a coupling with nonreactive modes is the subject of interesting investigations which seem to support the point of view according to which the AEP can successfully be applied to the study of transient dynamics even when failing in reproducing the correct equilibrium distributions which are attained at a much larger time scale. The results of Chapter X show that when the time necessary to get the final equilibrium state (of Gaussian type) is virtually infinitely large, a quasi-equilibrium state is predicted by the AEP which is found to be in surprisingly good agreement with the results of analog simulation. This opens a fertile new field of investigation, which could be of significant relevance for the theory of chemical reactions and especially that of enzyme chemistry.

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