Classical dynamics of a coupled double well oscillator in condensed media[a]

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The influence of a deterministic coupling between the reaction coordinate and a transverse normal mode on the reaction rate is considered within the context of classical (stochastic) dynamics. Our theoretical approach is based on a scheme of elimination of rapidly relaxing (irrelevant) variables. This procedure, perturbational in nature, makes it possible to get corrections of increasing accuracy to the results of the "standard adiabatic method" as perturbation terms of higher and higher order are taken into account. In the large friction case, the very first significant correction to the standard adiabatic scheme is shown to picture the reaction coordinate as being driven by a diffusionlike equation exhibiting instability phenomena. Thus, our approach makes an intriguing link between the activation of a reaction process via excitation of a nonreactive normal mode and noise-induced phase transition phenomena. When the frequency of the nonreactive mode varies slowly with the reaction coordinate, the reaction threshold can be expressed by a simple analytical formula. Results of computer calculations, which allow the exploration of a still wider range of physical conditions, are also discussed.

I. INTRODUCTION

The influence of nonreactive modes on reaction coordinates has recently been discussed from two different points of view.[1-3] Christoffel and Bowman[1] confined their attention to an isomerization process in dilute phase. In their bidimensional model, the reactive motion along a double-well potential is symmetrically coupled to another degree of freedom described as a transverse harmonic oscillator. The interaction between the reactive and nonreactive modes appears because the frequency of the transverse oscillator depends on the actual value of the reaction coordinate. On the other hand, Grote and Hynes,[2,3] completely neglected this kind of interaction while tracing back the dependence of the reaction rate on the nonreactive modes to the influence of the solvent.

The major aim of this paper is to extend Christoffel and Bowman's investigation to the condensed phase or, equivalently, to study the effect of a deterministic coupling between reactive and nonreactive modes within the context of a classical scheme such as that of Grote and Hynes. We shall consider a bidimensional model; the form of the potential used can be written in terms of x, the reaction coordinate, and y, the coordinate of a transverse normal mode, as

$$V(x, y) = \phi(x) + \omega_{\text{eff}}^2(x) y^n , \tag{1.1}$$

$\phi(x)$ is a double-well potential modeling the chemical reaction under study, which we shall assume to be of the following analytical form

$$\phi(x) = \frac{V_0}{a^4} (x^2 - a^2)^2 . \tag{1.2}$$

For simplicity we omitted the exponential terms appearing in the potential used by Christoffel and Bowman.[1] Their potential is a rather refined expression for dealing with the specific problem of ammonia inversion, whereas our main interest is to study a unspecified reaction process taking place in condensed phase. Therefore, we are not rigidly bound to use the same analytical form. Furthermore, we think that the physical effects that we are going to discuss do not significantly depend on the detailed form of the double-well potential. Similar remarks can also be applied to the detailed form of $\omega_{\text{eff}}(x)$, which will be assumed to be given by the following expression

$$\omega_{\text{eff}}(x) = \left[\tfrac{1}{2} \omega_0^2 + \psi(x)\right]^{1/2} , \tag{1.3}$$

where

$$\psi(x) = - \frac{\omega_0^2}{2} \lambda_{\text{int}} \exp(-x^2/r^2) . \tag{1.4}$$

{Christoffel and Bowman used an effective frequency of the form, $\omega_{\text{eff}}(x) = \omega_0 + [2\psi(x)/\omega_0]$.} This prevents us from exploring the case where λ_{int} is larger than 1. The quantity r in Eq. (1.4) can be regarded as the range of the coupling of the transverse mode onto the reactive motion. For the Grote and Hynes' assumption[2,3] on the mode separability in the saddle region to be valid, a fairly large value of r is required.

We shall focus our attention on the following set of equations of motion:

$$\dot{x} = v , \tag{1.5}$$

$$\dot{v} = - \phi'(x) - \gamma v - \psi'(x) y^n + f(t) , \tag{1.5'}$$

$$\dot{y} = w , \tag{1.5''}$$

$$\dot{w} = - \lambda w - n y^{n-1} \psi(x) - y \omega_0^2 + f'(t) . \tag{1.5'''}$$

As far as the stochastic forces $f(t)$ and $f'(t)$ are con-

cerned, we shall assume that they are Gaussian white noises defined by:

$$\langle ff(t)\rangle = 2D\,\delta(t) \ , \tag{1.6}$$

$$\langle ff'(t)\rangle = \langle f'f(t)\rangle = 0 \ , \tag{1.6'}$$

$$\langle f'f'(t)\rangle = 2D'\,\delta(t) \ . \tag{1.6''}$$

This means that the coupling between reactive and non-reactive modes via the solvent is completely neglected. We do not claim this assumption to be realistic. Rather, we want to study a physical condition left completely unexplored by Grote and Hynes.[2,3] They assume, in fact, that reactive and nonreactive modes can only interact via the cross correlation functions $\langle ff'(t)\rangle$ and $\langle f'f(t)\rangle$.

The first step of our approach consists in replacing the set of differential equations (1.5) by the corresponding Fokker–Planck equation using standard techniques:

$$\frac{\partial}{\partial t}\rho(x,y,v,w,t) = \left[-v\,\frac{\partial}{\partial x} + \phi'(x)\,\frac{\partial}{\partial v} + \psi'(x)y^n\,\frac{\partial}{\partial v} \right.$$
$$+ \gamma\left\{ \frac{\partial}{\partial v}v + \langle v^2\rangle\frac{\partial^2}{\partial v^2} \right\} - w\,\frac{\partial}{\partial y} + ny^{n-1}\psi(x)\,\frac{\partial}{\partial w} + y\omega_0^2\,\frac{\partial}{\partial w}$$
$$\left. + \lambda\left\{ \frac{\partial}{\partial w}w + \langle w^2\rangle\frac{\partial^2}{\partial w^2} \right\} \right]\rho(x,y,v,w,t) \ . \tag{1.7}$$

In the applications of this paper, we will focus our attention on the case $n = 2$.

Grigolini and co-workers[4–7] developed a computational algorithm (henceforth referred to as the continued-fraction algorithm) which has been proven successful, especially for dealing with nonlinear Fokker–Planck equations. However, the case of four variables represents a region where that algorithm, when applied to evaluating the rate of escape from a potential well, still has unsolved convergence problems. The case of three variables[8] is the maximum computational success achieved so far.

In order to simplify the problem, we shall use an adiabatic reduction technique of the type discussed in detail in Ref. 7, which produces corrections to the standard procedure.[1] A formalism of adiabatic reduction is developed in Sec. II to derive the general equation of motion of a projected probability distribution, Eq. (2.16). In Sec. III, the influence of the transverse normal mode on the reaction rate is discussed; to clarify the nature of our approach, two major limiting cases are considered: (I) the low friction case and (II) the diffusional case. This section also includes some analytical results aimed at providing a qualitative understanding of the role played by the mode interaction on the chemical reaction rate. Section IV contains some final remarks about the critical importance of the coupling.

II. GENERAL THEORY

Let us consider a system described by the following equation of motion

$$\frac{\partial}{\partial t}\rho(a,b,t) = L\rho(a,b,t) \tag{2.1}$$

$$= (L_0 + L_1)\rho(a,b,t) \ , \tag{2.2}$$

where

$$L_0 = L_a + L_b \tag{2.3}$$

and (a,b) are two sets of stochastic variables. L is a Fokker–Planck operator with a component L_a acting on variables a, a component L_b acting on variables b and an interaction part L_1 acting both on variables a and on variables b. Throughout this paper, it is assumed that a identifies the slow, "relevant" variables and b the fast, "irrelevant" ones.

It has been shown earlier[7,8] that the interaction picture is convenient to apply Zwanzig[9] projection procedure. For a Lagrangian separated in two parts,

$$L = L^0 + L' \tag{2.4}$$

and the interaction picture defined by

$$\bar{\rho}(t) = e^{-L^0 t}\rho(t) \ , \tag{2.5}$$

$$L'(t) = e^{-L^0 t}L'e^{L^0 t} \ , \tag{2.6}$$

the time evolution of a projected part may be written[8]

$$\frac{\partial}{\partial t}P\bar{\rho}(t) = PL'(t)P\bar{\rho}(t) + PL'(t)(1-P)G(t,0)(1-P)\bar{\rho}(0)$$
$$+ \int_0^t d\tau\,PL'(t)(1-P)G(t,\tau)(1-P)L'(\tau)P\bar{\rho}(\tau) \ , \tag{2.7}$$

where

$$G(t,\tau) = \overleftarrow{\exp}\int_\tau^t ds(1-P)L'(s) \tag{2.8}$$

and the arrow denotes the chronological ordering operator.[9] The second term in the right-hand side of Eq. (2.7) may be disregarded if we assume[8] that the fast variables are in equilibrium in the initial prepared state. In this work we shall assume that there is a clear separation between the time scales of the slow, relevant variables a and the fast variables b. The distribution of the slow variables is described by the projected probability density $P\rho(t)$, with the projection operator P defined by

$$P\rho(t) = P\rho(a,b,t)$$

$$= \rho_{eq}(b)\int db\,\rho(a,b,t), \tag{2.9}$$

where $\rho_{eq}(b)$ is the equilibrium canonical distribution on the space of variables b.

We define now an interaction picture such that the fast time variation induced upon $\rho(a,b,t)$ by L_b is separated out,

$$\bar{\rho}(a,b,t) = e^{-L_b t}\rho(a,b,t) \ , \tag{2.10}$$

$$L'(t) = e^{-L_b t}(L_a + L_1)e^{L_b t} \tag{2.11}$$

$$= L_a + L_1(t) \ . \tag{2.12}$$

In Eq. (2.12) we took into consideration the commutation of L_a and L_b. Below, we shall also use the commutation property of L_a with the projection operator P defined by Eq. (2.9) and with its complement $(1-P)$.

Substitution of Eq. (2.12) into Eq. (2.7) leads to

$$\frac{\partial}{\partial t} P\tilde{p}(t) = L_a P\tilde{p}(t) + PL_1(t) P\tilde{p}(t) + \int_0^t d\tau\, PL_1(t)(1-P)$$

$$\times \exp[L_a(t-\tau)]\, G(t,\tau)(1-P)L_1(\tau)P\tilde{p}(\tau)\ , \quad (2.13)$$

where $G(t,\tau)$ is given by Eq. (2.8) with $L_1(s)$ substituted for $L'(s)$.

By developing $G(t,\tau)$ into a Taylor power series, Eq. (2.13) may be recast into

$$\frac{\partial}{\partial t} P\tilde{p}(t) = L_a P\tilde{p}(t) + PL_1(t) P\tilde{p}(t) + \sum_{k=1}^{\infty} \int_0^t ds\, D_k(t,s)\tilde{p}(s)\ ,$$
$$(2.14)$$

where

$$D_1(t,s) = PL_1(t)(1-P)\exp[L_a(t-s)]\,L_1(s)P\ , \quad (2.15)$$

$$D_k(t,s) = \int_s^t ds_1 \int_s^{s_1} ds_2 \cdots \int_s^{s_{k-2}} ds_{k-1}$$

$$\times PL_1(t)(1-P)\exp[L_a(t-s)]L_1(s_1)\cdots(1-P)L_1(s_{k-1})$$

$$\times (1-P)L_1(s)P,\ k \geq 2\ . \quad (2.15')$$

The kernels $D_k(t,s)$ in Eq. (2.14) are functions of the time lapse $(t-s)$ only and decay to zero on the time scale of the fast variables, characteristic time τ_b. We are looking for the time evolution of $P\tilde{p}(t)$ on the time scale of the slow variables, characteristic time τ_a. Therefore, $P\tilde{p}(s)$ in the integrands of Eq. (2.14) does not change appreciably in times of the order of $\tau_b \ll \tau_a$ and the quantity $P\tilde{p}(t)$ may be substituted for it. Moreover, the exponential factors $\exp[L_a(t-s)]$ that appear in the $D_k(t,s)$ of Eqs. (2.15) may be disregarded as they would introduce corrections of the order of (τ_b/τ_a).

In this work we shall only use the lowest order term in the summation in the right-hand side of Eq. (2.14) with the final result

$$\frac{\partial}{\partial t} P\tilde{p}(t) = L_a P\tilde{p}(t) + PL_1(t) P\tilde{p}(t)$$

$$+ \int_0^t ds\, PL_1(t)(1-P)L_1(s)P\tilde{p}(t)\ . \quad (2.16)$$

This is the equation to be used in all the applications of this theory that are discussed in the next section. The criteria used to establish the order of magnitude of terms to be kept in Eq. (2.16) need some further clarification. As discussed above, the memory kernels $D_k(t,s)$ have a memory time of the order of τ_b; the order of magnitude of the interaction operator L_1, $(1/\tau_1)$ is assumed to be much smaller than $(1/\tau_b)$. The kernel D_k, of order of magnitude $(1/\tau_1)^{k+1}$, is integrated k times giving a contribution to Eq. (2.14) of order $(1/\tau_1)$ $\times (\tau_b/\tau_1)^k$. Therefore, the terms disregarded in writing Eq. (2.16) are smaller than those preserved there by a factor of at least (τ_b/τ_1) which is assumed to be very small.

III. THE INFLUENCE OF THE TRANSVERSE NORMAL MODE ON THE REACTION RATE

When dealing with the problem discussed in Sec. I, two major limiting cases are especially suited for making available straightforward analytical or numerical

treatments of certain applications, namely, (I) the low friction case and (II) the diffusional case. To discuss these two physical conditions, let us recall which are the parameters determining the rate of change of the variables x, v, y, and w. The velocity w of the transverse mode may be regarded as changing much faster than y when[10]

$$\lambda \gg 2\omega_0\ . \quad (3.1)$$

As far as the variables x and v are concerned, the counterpoint of ω_0 is provided by

$$\omega_0' = \sqrt{4V_0/a^2}\ , \quad (3.2)$$

which corresponds to the harmonic expansion of the potential ϕ, Eq. (1.2), around $x = 0$. We shall consider x as being very much slower than v when condition

$$\gamma \gg 2\omega_0' \quad (3.3)$$

is satisfied.

Following Christoffel and Bowman,[1] we shall always consider the pair of variables (y, w) as being much faster than the pair (x, v); this is true, provided

$$\omega_0' \ll \omega_0\ , \quad (3.3')$$

an assumption that we will always make.

If condition (3.3) is not satisfied, we are forced to define a and b as follows:

$$\text{Limiting case (I)}\ \begin{cases} a \equiv (x, v)\ , & (3.4) \\ b \equiv (y, w)\ . & (3.4') \end{cases}$$

This is the low-friction case.

When Eq. (3.3) is satisfied, we can define a and b as follows:

$$\text{Limiting case (II)}\ \begin{cases} a \equiv x\ , & (3.5) \\ b \equiv (v, y, w)\ . & (3.5') \end{cases}$$

This is the diffusional case.

A. Low-friction limit (case I)

We consider first the low-friction limit where condition (3.3') is satisfied and the separation of variables displayed in Eqs. (3.4) is adopted. The corresponding unperturbed Liouville operators are

$$L_a \equiv -v\frac{\partial}{\partial x} + \phi'(x)\frac{\partial}{\partial v} + \gamma\left\{\frac{\partial}{\partial v}v + \langle v^2 \rangle \frac{\partial^2}{\partial v^2}\right\}, \quad (3.6)$$

$$L_b \equiv \lambda\left\{\frac{\partial}{\partial w}w + \langle w^2 \rangle \frac{\partial^2}{\partial w^2}\right\} + \omega_0^2 y\frac{\partial}{\partial w} - w\frac{\partial}{\partial y}, \quad (3.6')$$

with the perturbation (remaining) part

$$L_1 = \psi'(x)y^n\frac{\partial}{\partial v} + ny^{n-1}\psi(x)\frac{\partial}{\partial w}\ . \quad (3.7)$$

In our model, the exponent n equals 2 and the terms in the right-hand side of Eq. (2.16) may be written explicitly as

$$PL_1(t)P = \psi'(x)\langle y^2 \rangle\frac{\partial}{\partial v} \quad (3.8)$$

and

$$\lim_{t \to \infty} \int_0^t ds\, P L_1(t)(1-P) L_1(s) P = \psi'(x)^2 \frac{\partial^2}{\partial v^2} \left\{ -\frac{\cos^4 \tau \langle q_1^2 \rangle}{\epsilon_1} - \frac{\sin^4 \tau \langle q_2^2 \rangle}{\epsilon_2} - \frac{4 \sin^2 \tau \cos^2 \tau \langle q_1^2 \rangle \langle q_2^2 \rangle}{\epsilon_1 + \epsilon_2} \right\}$$

$$+ 2 \frac{i}{\omega_0} \psi(x)\, \psi'(x) \frac{\partial}{\partial v} \left\{ -\frac{\cos^3 \tau \sin \tau \langle q_1^2 \rangle}{\epsilon_1} + \frac{\cos \tau \sin^3 \tau \langle q_2^2 \rangle}{\epsilon_2} - \frac{2 \sin \tau \cos \tau}{\epsilon_1 + \epsilon_2} [\sin^2 \tau \langle q_2^2 \rangle - \cos^2 \tau \langle q_1^2 \rangle] \right\} , \qquad (3.9)$$

where the quantities $\cos \tau$, $\sin \tau$, q_1, q_2, ϵ_1, and ϵ_2 are completely specified in the Appendix. The calculation of the limit $t \to \infty$ in Eq. (3.9) introduces important simplifications in this expression by eliminating fluctuations in a time scale τ_b; its substitution into Eq. (2.16) amounts to the use of an averaged operator [acting on $\bar{p}(t)$] smoothened to the time scale of that equation, i.e., τ_a. No new approximations or hypothesis are implied by this operation.

The contribution originated from Eq. (3.9) when replaced into Eq. (2.16) is unimportant in the extreme limit of very large ω_0 (compared with ω_0'), and will be disregarded. The final form of Eq. (2.16) (for this case I) is obtained using operators (3.6) and (3.8) and it was solved using the continued-fraction algorithm.[4-7] The progress of the reaction is measured by some function of the time, normalized to lie in the interval $(1,0)$ such as the average value of the position $\langle x \rangle$ (or the population at one well). Its Laplace transform at the origin gives an estimate of the time duration of the reaction process and the inverse of this quantity K, shall be used as a measure of the reaction rate. The larger the potential barrier, the better is this measure of the rate.

The results are displayed in Fig. 1. In agreement with the quantum-mechanical calculation by Christoffel and Bowman,[1] we obtain a significant increase of the reaction rate as $\langle y^2 \rangle$ increases. This can easily be interpreted as being the result of the modification of $\phi(x)$ into an effective potential,

$$V'_{eff} = \phi'(x) + \psi'(x) \langle y^2 \rangle . \qquad (3.10)$$

We see that, in this low friction limit, the effect of giving more energy to the transverse mode (larger $\langle y^2 \rangle$) is equivalent to deepening the valley that the coupling creates at the center of the barrier in a way resembling the effect found by Christoffel and Bowman.[1] This modification of the potential has a direct effect on the reaction rate as shown in Fig. 1. [It should be noted that an increase in λ_{int} is equivalent to an increase in $\langle y^2 \rangle$ due to Eqs. (3.10) and (1.4).]

In the next subsection, we shall evaluate corrections to the standard adiabatic approximation which will be shown to become of increased significance as the absolute value of (ω_0/ω_0') decreases. A single stochastic variable will be used, which makes the numerical calculations based on the continued-fraction algorithm a lot easier.

B. Diffusional limit (case II)

In the diffusional case the method of calculation consists in regarding x as being the only variable of interest

among those appearing in the set of Eqs. (1.5). This, of course, requires that γ as well as ω_0 be fairly large (compared with ω_0').

In this case [cf. Eqs. (3.5)] we have

$$a \equiv x , \qquad (3.11)$$

$$L_a \equiv 0 , \qquad (3.12)$$

$$L_b = -w \frac{\partial}{\partial y} + \lambda \left\{ \frac{\partial}{\partial w} w + \langle w^2 \rangle \frac{\partial^2}{\partial w^2} \right\}$$

$$+ y \omega_0^2 \frac{\partial}{\partial w} + \gamma \left\{ \frac{\partial}{\partial v} v + \langle v^2 \rangle \frac{\partial^2}{\partial v^2} \right\} , \qquad (3.12')$$

$$L_1 = \left\{ \phi'(x) + \psi'(x) y^n \right\} \frac{\partial}{\partial v} + n y^{n-1} \psi(x) \frac{\partial}{\partial w} - v \frac{\partial}{\partial x} . \qquad (3.13)$$

From now on this will be called the *first scheme* of calculation. In our model the exponent n equals 2. When operators (3.12) and (3.13) are substituted into Eq. (2.16), it is not difficult to see that the first and second terms on the right-hand side vanish; the third
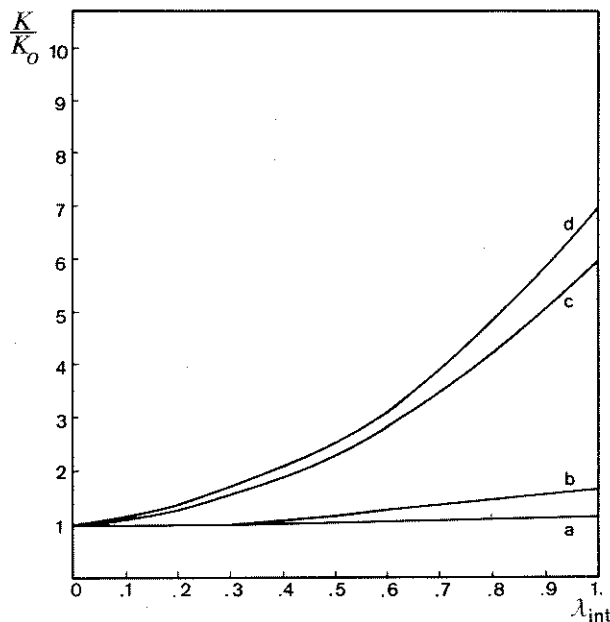

FIG. 1. Comparison between the decay rates K (relative to K_0, the decay rate of $\langle x \rangle$ without interaction $\lambda_{int} = 0$) as calculated in the two limiting cases, the low friction limit with $\langle v^2 \rangle = 0.5 \times 10^{-7}$ (a) or $\langle v^2 \rangle = 2.0 \times 10^{-7}$ (b) and the diffusional limit (second scheme of calculation) with $\langle v^2 \rangle = 0.5 \times 10^{-7}$ (c) or $\langle v^2 \rangle = 2.0 \times 10^{-7}$ (d). Other parameters were given the values $V_0 = 3.3 \times 10^{-7}$, $a = 0.365$, $r = 0.167$, $\gamma = 1.0 \times 10^{-2}$ and $\langle y^2 \rangle \omega_0^2 = \langle w^2 \rangle = \langle v^2 \rangle$. The absolute decay rate K_0 takes the values of 75.0×10^{-6} and 0.55×10^{-6} for the assumed average square velocities $\langle v^2 \rangle = 2.0 \times 10^{-7}$ and 0.5×10^{-7}, respectively. Atomic units are used throughout.

term may be computed following the technique used to derive Eq. (3.9). The final result may be written in the form

$$\frac{\partial}{\partial t} f(x,t) = \left\{ \frac{1}{\gamma} \frac{\partial}{\partial x} \left[\phi'(x) + \psi'(x) \langle y^2 \rangle \right] + \frac{\langle v^2 \rangle}{\gamma} \frac{\partial^2}{\partial x^2} \right\} f(x,t) ,$$

(3.14)

where

$$f(x,t) = \int dv\, dy\, dw\, \bar{\rho}(x,v,y,w,t) .$$

(3.15)

Higher-order contributions [$k \geq 2$ in Eq. (2.14)] can easily be evaluated by following the normal mode method of the Appendix. However, these results are so cumbersome as to make it difficult to apply the computational algorithm. On the other hand, the result expressed by Eq. (3.14) is trivial in that this is nothing but the result obtained in Sec. III A in the diffusional limit, with potential (3.10), that is the standard result of the adiabatic elimination procedure.[11] Mori and co-workers[12,13] stressed that significant corrections can result from higher-order contributions. Thus, it becomes vital to solve the problem of evaluating such corrections.

To bypass the above mentioned computational difficulty we envisaged a *second scheme* of calculation, whose first step consists in replacing Eqs. (1.5) with

$$\dot{x} = -\frac{\phi'(x)}{\gamma} - \frac{\psi'(x)}{\gamma} y^2 + \frac{f(t)}{\gamma} ,$$

(3.16)

$$\dot{y} = -2y \frac{\psi(x)}{\lambda} - \frac{y \omega_0^2}{\lambda} + \frac{f'(t)}{\lambda} .$$

(3.16')

This means that we assumed γ and λ to be so large as to make the diffusional assumption to be possible in both cases. The variable of interest is still x. A measure of the time scale of the changes of this variable can easily be obtained from the harmonic expansion of the potential ϕ around $x = 0$ and $x = \pm a$. In the absence of the coupling with the transverse normal mode the short time dynamics of $\langle x^2(t) \rangle$ is easily proven to be

$$\langle x^2(t) \rangle = \langle x^2(0) \rangle \exp(2\Gamma_x t)$$

(3.17)

for a starting point distribution mainly concentrated around $x = 0$, and

$$\langle x^2(t) \rangle = \langle x^2(0) \rangle \exp(-2\Gamma_x' t)$$

(3.18)

for a starting point distribution mainly concentrated around one of the minima $x = \pm a$ with the damping parameters given by

$$\Gamma_x' = 2\Gamma_x ,$$

(3.19)

$$\Gamma_x = \frac{\omega_0'^2}{\gamma} .$$

(3.19')

The time scale for variable y, on the other hand, depends on the damping parameter

$$\Gamma_y = \frac{\omega_0^2}{\lambda} .$$

(3.20)

We shall assume that the order of magnitude of λ is the same as that of γ. This, together with condition (3.3'), allows us to regard y as being a fast variable

when compared to x. Under these assumptions, the second scheme of calculation leads to

$$L_a = \frac{\partial}{\partial x} \frac{\phi'(x)}{\gamma} + \frac{\langle v^2 \rangle}{\gamma} \frac{\partial^2}{\partial x^2} ,$$

(3.21)

$$L_b = \frac{\omega_0^2}{\lambda} \frac{\partial}{\partial y} y + \frac{\langle w^2 \rangle}{\lambda} \frac{\partial^2}{\partial y^2} ,$$

(3.21')

$$L_1 = 2 \frac{\psi(x)}{\lambda} \frac{\partial}{\partial y} y + \frac{y^2}{\gamma} \frac{\partial}{\partial x} \psi'(x) .$$

(3.22)

Applying now the perturbation procedure of Sec. II up to the second order in L_1, i.e., Eq. (2.16), we obtain the new equation of motion

$$\frac{\partial}{\partial t} f(x,t) = \left\{ \frac{1}{\gamma} \frac{\partial}{\partial x} \phi'(x) + \frac{\langle y^2 \rangle}{\gamma} \frac{\partial}{\partial x} \psi'(x) + \frac{\lambda}{\omega_0^2} \frac{\langle y^2 \rangle}{\gamma} \frac{\partial}{\partial x} \psi'(x) \right.$$

$$\left. \times \left[\frac{\langle y^2 \rangle}{\gamma} \frac{\partial}{\partial x} \psi'(x) - \frac{2}{\lambda} \psi(x) \right] + \frac{\langle v^2 \rangle}{\gamma} \frac{\partial^2}{\partial x^2} \right\} f(x,t) .$$

(3.23)

Figure 1 shows the important role played by this correction in L_1^2. In this figure, results for the low-friction limit are compared with results from the second scheme of calculation for the diffusional limit. We use a very large friction for both limits in such a way that the difference between the results for the low-friction limit and for the diffusional limit cannot be traced back to inertia effects. This discrepancy depends mainly on the correction to the standard adiabatic approximation. We were able to show that, in fact, when the third term on the right-hand side of Eq. (3.23) is neglected one obtains a curve coinciding with that corresponding to the low-friction limit when the terms of Eq. (3.9) are neglected. Since λ_{int} plays the role of the perturbation parameter, our perturbation expansion ceases to be valid when λ_{int} is close to 1. This could be a further contribution to the large discrepancy between the two limits, which, otherwise, has to be assumed to come from the corrections to the adiabatic approximation. In any case, this difference is a clear indication that such corrections tend to increase the rate of the chemical reaction under study.

In Fig. 2, the variation of the reaction rate with the range r of the coupling [Eq. (1.4)] is studied. The maximum enhancement of the reaction rate is obtained for ranges of about 40% of a (the half-distance between the potential minima). We also notice that the effect of the coupling disappears as $r \to \infty$, what seems to agree with Grote and Hynes[2,3] assumption of limiting the effect of the transverse mode to the saddle point. However, even in this limit, $r \to \infty$, large values of $\langle y^2 \rangle$ may produce a sizeable effect as can be shown by the analytical study that follows.

Consider the case

$$r \gg a .$$

(3.24)

Equation (3.23) can be given the following form:

$$\frac{\partial}{\partial t} f(x,t) = -\frac{\partial}{\partial x} \left[dx - bx^3 + \tfrac{1}{2} Qx \right] f(x,t)$$

$$+ \left[\frac{Q}{2} \frac{\partial^2}{\partial x^2} x^2 + \epsilon \frac{\partial^2}{\partial x^2} \right] f(x,t) ,$$
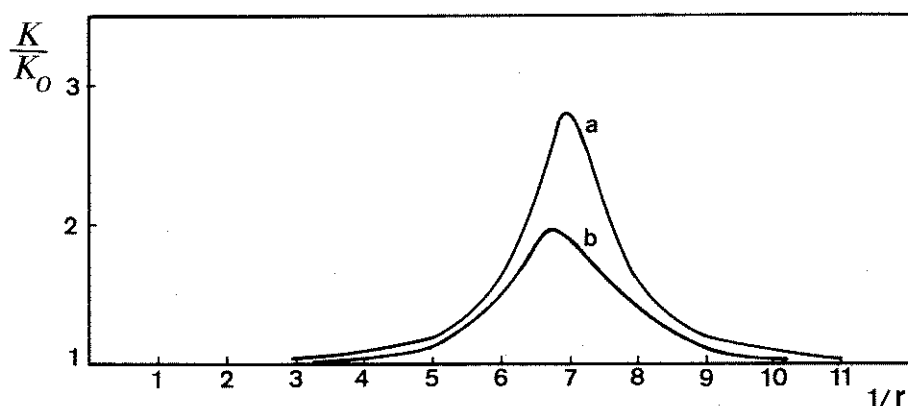
(3.25)

$$\frac{K}{K_0}$$

FIG. 2. Variation of the reaction rate with the inverse of the range r of the interaction potential: (a) low friction limit with $\lambda_{int} = 1.0$; (b) diffusional limit (second scheme of calculation) with $\lambda_{int} = 0.2$. Other parameters were given the same values as in Fig. 1 with $\langle v^2 \rangle = 2.0 \times 10^{-7}$.

where

$$d = 2\omega_0'^2/\gamma - s \frac{\omega_0^2}{\gamma} (\lambda_{int}^2 + \lambda_{int}) , \qquad (3.26)$$

$$b = 2\omega_0'^2/(\gamma a^2) , \qquad (3.26')$$

$$Q = 2p \frac{\omega_0^2}{\gamma} s^2 \lambda_{int}^2 , \qquad (3.26'')$$

$$\epsilon = \langle v^2 \rangle/\gamma , \qquad (3.26''')$$

$$p = \lambda/\gamma , \qquad (3.26'''')$$

$$s = \langle y^2 \rangle/r^2 . \qquad (3.26''''')$$

For the particular case $\epsilon = 0$ (i. e., vanishing additive fluctuations), Eq. (3.25) above belongs to the class of equations studied by Schenzle and Brand,[14] what allows us to apply their interesting remarks about the equilibrium distribution to our problem,

$$f_{eq}(x) = N x^{-1+2d/Q} \exp\left(-\frac{b}{Q} x^2\right) . \qquad (3.27)$$

When Q is small, this distribution is basically a Gaussian function placed at the bottom of a well which may be considered as the reactant well. When Q is increased, the distribution shifts towards $x = 0$ and broadens until a threshold is reached at

$$Q = 2d . \qquad (3.28)$$

If Q is increased further the distribution diverges at $x = 0$.

When $\langle y^2 \rangle$ is increased, d decreases and Q increases. As a consequence the excitation of the transverse normal mode makes the system tend towards the "catastrophic" condition of Eq. (3.28). In this situation the population is distributed around the top of the barrier, what may be likened to the result of an activation process. In the presence of an additive stochastic force (even of weak intensity), this activation process leads to a significant increase of the reaction rate.

The kind of process described above is usually called "noise-induced phase transition." Faetti et al.[7] showed that no slowing down is exhibited in the threshold region; this means that the time required to activate the chemical reaction process is finite. The excitation of the transverse normal mode, therefore, can really in-

crease the rate of the chemical reaction process under study.

In our case the phase transition occurs when $\lambda_{int} = \lambda_c$,

$$\lambda_c = r^2 \left\{ -1 \pm \left[1 + 8\left(\frac{\omega_0'}{\omega_0}\right)^2 \left(1 + \frac{r^2}{\langle y^2 \rangle}\right)\right]^{1/2} \right\} \Big/ 2(\langle y^2 \rangle + r^2) \qquad (3.29)$$

in the case $p = 1$.

In Fig. 3, we study how the reaction rate varies with the coupling parameter λ_{int}. We are still using, of course, the second scheme of calculation for the diffusional limit and the figure shows that the reaction rate attains a plateau value which is maintained until the coupling parameter λ_{int} approaches the threshold value λ_c; around this value, there is a very marked increase. This agrees with our remarks concerning the noise-induced phase transition phenomenon, even though $\lambda_c \cong 0.55$ (the threshold value of λ_{int}) is not small enough to completely satisfy the basic requirement of our perturbation approach.

To clarify further the implications of the results in Fig. 3, we point out the following.

(i) We are dealing with an activation process where the thermalization assumption $\langle y^2 \rangle \omega_0^2 = \langle v^2 \rangle$ does not apply. (This assumption was made in the cases treated in Figs. 1 and 2.) The energy on the reactive mode (measured by $\langle v^2 \rangle/2$) is kept always smaller than the potential barrier height, while the transverse mode is given a very large energy from a suitable external source (e. g., an electromagnetic field). In this situation the threshold condition (3.28) may be attained by an appropriate tuning of the coupling parameter λ_{int}.

(ii) Equation (3.25) is valid in the limit $r \gg a$, i. e., on the left-hand side tail of Fig. 2. The new results in Fig. 3 show how an enhancement of the reaction rate is obtained in this region, originating from multiplicative terms while the standard adiabatic corrections are ineffective.

IV. CONCLUDING REMARKS

A major result of this paper is given by Eq. (3.29). This means that the role of the coupling with the transverse mode can be catastrophic in that this is the re-
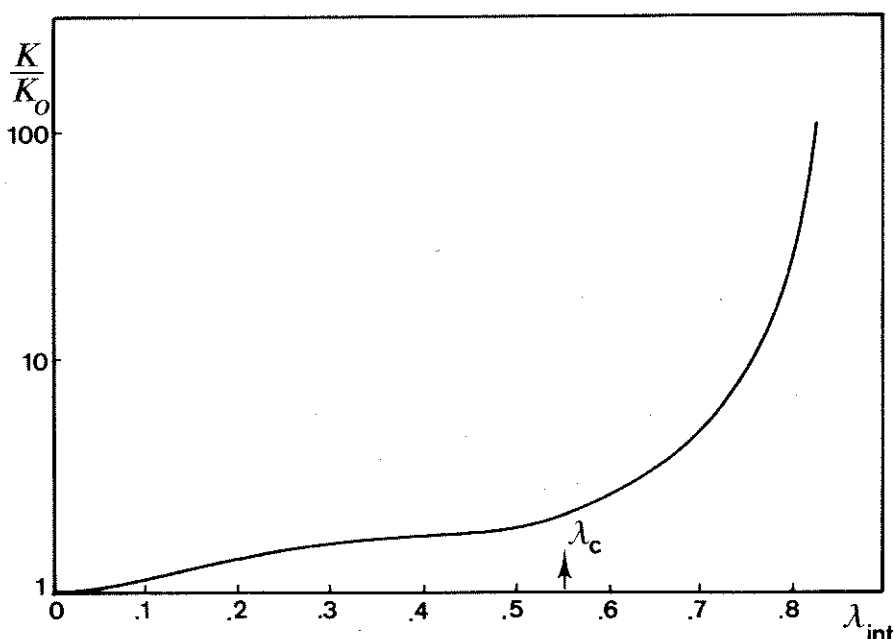
FIG. 3. Variation of the reaction rate with the coupling parameter λ_{int} using the second scheme of calculation in the diffusional limit. The decay rate in the absence of interaction is $K_0 = 30.0 \times 10^{-5}$. The threshold value of λ_{int} is $\lambda_c \approx 0.55$. Other parameters were given the values $V_0 = 3.3 \times 10^{-7}$, $a = 0.183$, $r = 0.366$, $\langle v^2 \rangle = 2.0 \times 10^{-7}$, $\gamma = 1.0 \times 10^{-2}$, and $\langle y^2 \rangle \omega_0^2 = 85 \times V_0$.

quired condition for the noise-induced phase transition of Refs. 7 and 14 to take place. This relationship has been obtained by completely neglecting the additive stochastic force. However, its role may be easily understood. Schenzle and Brand[14] pointed out that no significant change in their analysis is to be expected from additive stochastic forces of small intensity. Additive stochastic forces of strong intensity, on the other hand, make the problem void of interest as a fast chemical reaction process is obtained even in the absence of interaction with the transverse mode.

To stress the difference between the noise-induced phase transition and the increase in the chemical reaction rate coming from the standard adiabatic approach, we note the following. In the present case the adiabatic approximation is equivalent to substituting the effective potential of Eq. (3.10) for the real one $\phi(x)$. When $r \gg a$, the increase in $\langle y^2 \rangle$, results in a mere decrease of the barrier height. The noise-induced phase transition, on the contrary, is the result of the synergic behavior of both the deterministic contribution $(\partial/\partial x)\frac{1}{2} Qx$ and the diffusional one $(\partial^2/\partial x^2)\frac{1}{2} Qx^2$ [see Eq. (3.25)]. As a matter of fact, when condition (3.29) is attained, the linear part of the effective potential appearing in Eq. (3.25) does not vanish. By expanding the square root appearing in Eq. (3.29) we obtain

$$d = 4 \frac{\omega_0'^2}{\gamma} \left(\frac{\omega_0'}{\omega_0}\right)^2 + 16 \frac{\omega_0'^2}{\gamma} \left(\frac{\omega_0'}{\omega_0}\right)^4 \frac{s+1}{s^2}$$
$$- 16 \frac{\omega_0'^2}{\gamma} \left(\frac{\omega_0'}{\omega_0}\right)^6 \frac{(s+1)^2}{s^3} + \cdots . \qquad (4.1)$$

This means that for $(\omega_0'/\omega_0) \to 0$ the standard adiabatic approach is basically correct. In fact, in this case, the catastrophic behavior depends only on the actual disappearance of the effective barrier. When ω_0'/ω_0 increases, the catastrophic behavior depends on the cooperation between the standard adiabatic effect mentioned above and the novel effect founded in this work.

The role of this latter effect becomes larger and larger as ω_0'/ω_0 increases. The method used here has been proved reliable for the evaluation of this important new contribution.

Our remarks on the strong effect of the transverse normal mode have been limited to the case of large friction. The scheme of Sec. III A shows how to deal with the case of low friction. We believe that a careful study along this direction can allow one to extend the catastrophic behavior of the large friction case to this region.

APPENDIX

Let us consider the linear contribution to the last pair of Eqs. (1.5); we obtain the following two-dimensional matrix:

$$\Gamma \equiv \begin{bmatrix} 0 & 1 \\ -\omega_0^2 & -\lambda \end{bmatrix} . \qquad (A1)$$

This matrix can be made symmetrical by using the simple change of variables

$$y' = y , \qquad (A2)$$
$$w' = w/(i\omega_0) . \qquad (A2')$$

By diagonalizing the matrix Γ we arrive at the following normal modes:

$$q_1 = y \cos \tau + \frac{w}{i\omega_0} \sin \tau , \qquad (A3)$$
$$q_2 = -y \sin \tau + \frac{w}{i\omega_0} \cos \tau , \qquad (A3')$$

where $\sin(2\tau) = 2i\omega_0/\lambda$, corresponding to the eigenvalues

$$\epsilon_1 = -\frac{\lambda}{2} [1 - (1 - 4\omega_0^2/\lambda^2)^{1/2}] , \qquad (A4)$$
$$\epsilon_2 = -\frac{\lambda}{2} [1 + (1 - 4\omega_0^2/\lambda^2)^{1/2}] . \qquad (A4')$$

This result is valid both in the oscillatory $(2\omega_0 > \lambda)$ and in the overdamped $(2\omega_0 < \lambda)$ regimes. It is useful to express coordinates and corresponding derivatives in terms of normal modes. This is achieved by the following relationships:

$$\frac{\partial}{\partial w} = -\frac{i}{\omega_0}\left\{\sin\tau\,\frac{\partial}{\partial q_1} + \cos\tau\,\frac{\partial}{\partial q_2}\right\}\,, \tag{A5}$$

$$\frac{\partial}{\partial y} = \cos\tau\,\frac{\partial}{\partial q_1} - \sin\tau\,\frac{\partial}{\partial q_2}\,, \tag{A5'}$$

$$y = \cos\tau\,q_1 - \sin\tau\,q_2\,, \tag{A6}$$

$$w = i\omega_0\left\{\sin\tau\,q_1 + \cos\tau\,q_2\right\}\,. \tag{A6'}$$

The advantages coming from using normal modes are expressed by

$$e^{-L_0 t}\,\frac{\partial}{\partial q_i}\,e^{L_0 t} = e^{-\epsilon_i t}\,\frac{\partial}{\partial q_i} \tag{A7}$$

and

$$L_0^+ q_i = \epsilon_i q_i\,. \tag{A7'}$$

The latter equation allows us to express q_i as follows

$$q_i = \langle q_i^2\rangle^{1/2}\left\{\sum_n |n+1, i\rangle(n+1)\langle n, i| + \sum_n |n-1, i\rangle\langle n, i|\right\}\,, \tag{A8}$$

where

$$L_0|n, i\rangle = n\epsilon_i |n, i\rangle\,. \tag{A9}$$

Note that

$$|n, i\rangle = \frac{(a_i^+)^n}{[(n!)]^{1/2}}|eq\rangle \tag{A10}$$

and

$$L_0|eq\rangle = 0\,. \tag{A11}$$

We can also express $(\partial/\partial q_i)$ as

$$\frac{\partial}{\partial q_i} = -\frac{1}{\langle q_i^2\rangle^{1/2}}\sum_n |n+1, i\rangle(n+1)\langle n, i|\,. \tag{A12}$$

Defining the creation and annihilation operators

$$a^+ = \sum_n |n+1, i\rangle(n+1)\langle n, i| \tag{A13}$$

$$a^- = \sum_n |n-1, i\rangle\langle n, i|\,, \tag{A13'}$$

we can write that

$$q_i = \langle q_i^2\rangle^{1/2}\left\{a^+ + a^-\right\} \tag{A14}$$

and

$$\frac{\partial}{\partial q_i} = -\frac{1}{\langle q_i^2\rangle^{1/2}}\,a^+\,. \tag{A15}$$

Now it is easy to evaluate the necessary contributions to Eq. (2.16).

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