ON THE BREAKDOWN OF THE KRAMERS THEORY AS A PROBLEM OF CORRECT MODELLING

by

Fabio MARCHESONI

Dublin Institute for Advanced Studies,

10 Burlington Road, DUBLIN-4 (Ireland)

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Permanent address: Dipartimento di Fisica, Universita' di Perugia, I-06100-

PERUGIA (Italy)

1. Introduction

Recently there has been a great revival of theoretical interest in the one-dimensional barrier crossing problem, and its applications to many physical-chemical systems/1-7/. The problem has been modelled essentially by a 'Brownian particle' moving into a double-well potential V. Since the original work of Kramers/8/, a number of investigators have improved and clarified several points. We mention the results for multidimensional systems in the overdamped and under-damped limit/9/, the effects of anharmonicities in the potential form/7/, the role of non-Gaussian white thermal noise/1,10/, the effect of a rate enhancement via parametric fluctuations/11/ and finally the influence due to the non-Markov statistics of the heat bath/2-6/.

At the same time some authors addressed the problem of the derivation of exact Langevin equations(LE), i.e. the LE derived from a Liouville equation, and of their reduction to the mathematically more tractable phenomenological LE employed for modelling real physical-chemical systems/12-15/. Mohanty et al. studied in great detail the time dependence of the momenta of two Brownian particles of mass M interacting with a harmonic potential in a fluid of particle of mass m. Under the conditions $M \gg m$ and $\omega \tau_o < 1$, where ω is the frequency of the Brownian oscillator and τ_o is the relaxation time of the bath particles, very general LE can be derived. Eventhough such conditions have been commonly

assumed at in the quoted literature/1,11/, the structure of these exact LE is

still more complicated than that of the phenomenological LE actually treated.

In particular, the friction coefficients are functions of $x(t)$, where $x(t)$ is

the separation of the oscillator particles, and the noise terms are generalized

(i.e. not purely additive or purely multiplicative), Gaussian and non-stationary.

The various approximations which must be made to reduce the LE derived from

the Liouville equation to the simple one-dimensional LE, so far discussed, are of

three types: (i) The terms which describe the rotation of the oscillator in the

fluid must be neglected; (ii) It is necessary to approximate ad hoc the $x(t)$

dependence of the friction coefficients which arises from the interactions between

the Brownian particles; (iii) The term involving the mean force exerted by the

fluid on the oscillating Brownian particles must be either neglected or approxi-

mated by a linear term in $x(t)-x_o$, where x_o is the equilibrium interparticle

separation of the oscillator.

With a few necessary restrictions, detailed in ref.15, we can finally recover

the phenomenological LE

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

$$\dot{v} = -V'(x) - \lambda_o v - 2\lambda_1 x v - \lambda_2 x^2 v + f(t) + x\,\eta(t) \, , \qquad (1.1)$$

where $f(t)$ and $\eta(t)$ are white Gaussian noises with

$$\langle f(t) \rangle \equiv 0 \, , \qquad \langle f(t)\, f(0) \rangle = 2 D_o\, \delta(t) \, ,$$

$$\langle \eta(t) \rangle \equiv 0 \, , \qquad \langle \eta(t)\, \eta(0) \rangle = 2 D_2\, \delta(t) \, , \qquad (1.2)$$

$$\langle f(t)\, \eta(0) \rangle = 2 D_1\, \delta(t) \, ,$$

and

$$D_i \equiv \lambda_i\, k_B\, T \qquad (k_B \text{ Boltzmann constant}) \qquad (1.3)$$

Here $V(x)$ denotes the harmonic potential $\omega^2 x^2 /2$. These LE have been obtained

first by Lindenberg and Seshadri/14/ by studying explicitly a specialized vers:

of a model Hamiltonian introduced by Zwanzig/13/ for a one-dimensional system

interacting with a heat bath. Such a model admits as a peculiar feature an exac

Langevin equation that can be derived by direct integration. The LE of eq.(1)

be then recovered by employing the Markovian approximation which consists on

assuming that the exact noise terms are delta-correlated Gaussian stochastic

processes.

Although criticism on ref.15 is limited to the problem of the description

oscillating molecules in a fluid via one-dimensional LE with simple noise stru

most arguments introduced by Mohanty et al./15/ and by Lindenberg and Seshadri,

apply also to the problem of modelling the decay of a metastable state. This

problem plays a central role in many areas of science, most notably in chemica

kinetics, electron transport in semiconductors, and nonlinear optics. In the

recent literature detailed experimental work has been carried out by several

groups/16,17/ in order to answer the basic question: To what extent is a one-

-dimensional barrier crossing picture applicable to actual physical-chemical systems? Experimental discrepancies with the fundamental theory of Kramers/8/ have been explained by having recourse to one or more of the correcting mechan

isms quoted above. Memory effects due to the non-Markovian statistics of the heat bath coupled (phenomenologically) to the 'Brownian particle' associated with the reaction coordinate $x(t)$, are pointed out as being the most important cause of the remarkably increased activation rates of a number of chemical reactions in the high friction limit/1-6,17/. The consequence of including such additional mechanism is a 'frequency dependent friction'/2-5/, which is supposed to account for the unclear separation between the heat bath relaxation time scale τ_0 and the 'mechanical' time scales related to the characteristic frequencies of the driving potential $V(x)$.

On the contrary, nobody has heeded the advice, implicit in the exact approaches of ref.12, that friction terms appearing in the LE modelling any single process under investigation may involve a dependance on the reaction coordinate itself which generally will be non-factorizable. The present paper is aimed at extending Lindenberg ans Seshadri's approach to the case when the Brownian particle is driven by a double-well potential in the underdamped and overdamped limit. The x-dependent friction terms are shown to affect the rate of escape over the barrier (i.e. the relaxation process) distinctly in the two regimes. Our main

conclusion is that the specific nature of the coupling between the Brownian particle and the heat bath cannot generally be neglected by substituting the generalized friction term with an effective one ($- \lambda_{eff} \dot{x}(t)$)/14/, somehow proportional to the solvent viscosity (hydrodynamic assumption)/17/.

The organization of this paper is as follows. In Section 2 we discuss, via projection operator techniques, the derivation of the LE (1.1)-(1.3) from Zwanzig's model Hamiltonian. Corrections due to the presence of anharmonicities in the Hamiltonian describing the heat bath and the coupling with the system of interest are accounted for. In Section 3 we adapt the Lindenberg and Seshadri's model to the problem of the decay of a metastable state. The corresponding corrections to the Kramers' activation rates are estimated in the case of small x-dependent friction terms both in the overdamped and underdamped regime. In Section 4 Lindenberg and Seshadri's derivation/14/ of the LE (1.1)-(1.3) is improved by taking into account the effects of non-Markovian statistics of the he bath. Finally, in Section 5 we summarize our findings and discuss their implica tions in the applications to chemical-physical problems.

2. Discussion of the one-dimensional Zwanzig model.

The most general Hamiltonian H for a one-dimensional system coupled to a heat bath can be decomposed in the form

$$H = H_S + H_B + H_{SB} . \qquad (2.1)$$

Here H_S is the system Hamiltonian, H_B is the bath Hamiltonian and H_{SB} is the interaction term between the system and the heat bath. Let us assume that our system is described in the phase-space (x,p) by the classical Hamiltonian

$$H_S = \frac{P^2}{2M} + U(x) . \qquad (2.2)$$

H_S depicts the dynamics of a particle of mass M bounded by a nonlinear potential $U(x)$. The heat bath consists of N independent harmonic oscillators of mass m_ν, canonical coordinates (q_ν, p_ν) and frequency ω_ν ($\nu = 1,\ldots N$). The bath Hamiltonian is thus a diagonal bilinear form:

$$H_B = \sum_\nu \left(\frac{P_\nu^2}{2m_\nu} + \frac{\omega_\nu^2}{2} q_\nu^2 \right) . \qquad (2.3)$$

By following Zwanzig/13/, H_B could be written as

$$H_B = \frac{1}{2} X^T \cdot K \cdot X , \qquad (2.4)$$

where $X = (q_1, \ldots q_N, P_1, \ldots P_N)$, T denotes the transpose and K is a symmetric non-singular 2N×2N matrix. The choice of eq.(2.3) corresponds to diagonalizing Zwanzig's bath Hamiltonian (without any loss of generality) and K reads accordingly:

$$K_{ij} = \delta_{ij} \begin{cases} \omega_j , & j \leq N \\ m_{i-N}^{-1} & i > N \end{cases} \qquad (2.5)$$

As pointed out by Mohanty et al./15/ the assumptions we now make to give H_{BS} a more tractable form can affect dramatically both the potential and the dissipation terms in the final LE. Let us start by assuming the interaction to be linear in the bath coordinates:

$$H_{SB} = H_{SB}^{(0)} \equiv - \sum_\nu \omega_\nu^2 q_\nu a_\nu(x) . \qquad (2.$$

The total Hamiltonian can then be re-written as :

$$H = \frac{P^2}{2M} + V(x) + \frac{1}{2} \sum_\nu \left[\frac{P_\nu^2}{2m_\nu} + \omega_\nu^2 \left(q_\nu - a_\nu(x) \right)^2 \right] , \qquad (2.$$

where

$$\overline{V}(x) = U(x) - \frac{1}{2} \sum_\nu \omega_\nu^2 a_\nu^2(x) . \qquad (2.$$

The choice (2.6) implies that the potential energy of the isolated system will be corrected by including a 'static' portion of the interaction as emerges from the following treatment.

One of the attractive features of this choice is the ability to establish explicitly the connection between the fluctuating force in the LE and the form of the interaction in the Hamiltonian. Following Lindenberg and Seshadri restatement of Zwanzig's procedure/14/, we can integrate the Hamiltonian equations for the heat bath and eliminate the bath coordinate from the system equations, which thus read

$$\dot{x} = P/M$$

$$\dot{P} = -V'(x) + \int_0^t d\tau \left\{ \sum_\nu a_\nu'(x(t)) \, a_\nu'(x(t-\tau)) \, \omega_\nu^2 \cdot \cos\left(\frac{\omega_\nu}{\sqrt{m}} \tau \right) \right\} \left\{ P(t-\tau) + \left[\bar{a}'(x(t)) \right]^T \cdot F(t) \right. \qquad (2.$$

where $\bar{a}(x)$ is the 2N-dimensional column vector $(a_1(x), \ldots, a_N(x), 0, \ldots, 0)$. A

detailed derivation of the generalized LE, eq.(2.9), can be found in refs.13 and 14.

$F(t)$ is the initial condition-dependent portion whose statistical properties can

be assimilated to those of a Gaussian noise with zero mean value and auto-correlation

functions

$$\langle F_\nu(t)\, F_\nu^{\mathsf{T}}(t') \rangle = k_B T\, \omega_\nu^2 \cos\left(\frac{\omega_\nu}{m_\nu}(t-t')\right) a_\nu'^{\,2}(x). \qquad (2.10)$$

In order to obtain the LE (1.1)-(1.3) Lindenberg and Seshadri choose a quadratic

form for the coupling components $a_\nu(x)$ and, in addition, introduce the Markovian

approximation so that the random forces $F(t)$ on eq.(2.10) result to be delta-

-correlated.

An alternative procedure consists in employing an equivalent Fokker-Planck

formalism. The corresponding Fokker-Planck(FP) equation can be obtained by means

of an adiabatic elimination procedure/18/ which allows us to eliminate the bath

variables provided that $\omega \tau_0 < 1$, where now $1/\omega$ denotes a suitable mechanical

time scale related to the effective potential $V(x)$. By changing the bath variables

$$P_\nu \rightarrow P_\nu, \qquad q_\nu \rightarrow Q_\nu \equiv q_\nu - a_\nu(x), \qquad (2.11)$$

the Hamiltonian equations corresponding to the total Hamiltonian of eq.(2.7) can

be re-written as

$$\dot{x} = p/M$$
$$\dot{p} = -V'(x) + \sum_\nu \omega_\nu^2 Q_\nu\, a_\nu'(x) \qquad (2.12)$$

$$\dot{Q}_\nu = P_\nu/m_\nu - a_\nu'(x)\, p/M$$
$$\dot{P}_\nu = -\omega_\nu^2 Q_\nu, \qquad \nu = 1, \ldots, N$$

The related Liouvillian operator L defined as $i[H, \ldots]$, where $[\ldots, \ldots]$

denotes the Poisson brakets, can be separated into an unperturbed part (L_o)

and a perturbation part (L_I):

$$L_o = \sum_\nu \left(-\frac{P_\nu}{m_\nu}\frac{\partial}{\partial Q_\nu} + \omega_\nu^2 Q_\nu \frac{\partial}{\partial P_\nu} \right), \qquad (2$$

$$L_I = -\frac{p}{M}\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial p} - \sum_\nu \left(\omega_\nu^2 Q_\nu \frac{\partial}{\partial p} - \frac{p}{M}\frac{\partial}{\partial Q_\nu} \right) a_\nu'(x). \qquad (2$$

For clarity we give further details of our perturbation technique in the Appe

This applies in the presence of a clearcut time scale separation between the heat

bath relaxation process and the mechanical driving by the potential $V(x) - \omega \tau$

in notation of ref.15. Our final result is a FP equation of the type:

$$\frac{\partial}{\partial t}\rho(x, p; t) = \sum_{r=0}^{\infty} \Gamma_r\, \rho(x, p; t) \qquad (2$$

where $\rho(x, p; t)$ is the reduced distribution function in the relevant canonical

coordinates of the system under study and Γ_r are the perturbation terms of

order r-th of the corresponding FP operator. In particular we find,

$$\Gamma_o = -\frac{p}{M}\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial p}, \qquad (2$$

$$\Gamma_1 = \gamma(N, x)\left(k_B T\frac{\partial^2}{\partial p^2} + \frac{1}{M}\frac{\partial}{\partial p} p \right), \qquad (2$$

where

$$\gamma(N,x) \equiv \int_0^\infty d\tau \sum_\nu \omega_\nu^2 a_\nu'^2(x) \cos\left(\frac{\omega_\nu}{\sqrt{\mu_\nu}}\tau\right) \ . \tag{2.18}$$

With the choice of ref.14 for $a_\nu(x)$,

$$a_\nu(x) = \Gamma_\nu x + \beta_\nu x^2/2 \ , \tag{2.19}$$

we readily obtain [*]

$$\gamma(N,x) = \lambda_0 + 2\lambda_1 x + \lambda_2 x^2 \ . \tag{2.20}$$

We remark that the FP equation (2.15)-(2.17) with the friction terms given by

eq.(2.20) corresponds exactly to the LE (1.1)-(1-3). The Markovian assumption is

now implicit in the truncation of the series of eq.(2.15) at r=1.

Before going beyond such an approximation by calculating Γ_2, we briefly

discuss the critical choice (2.6) for the interaction Hamiltonian H_{SB}. Although

a very general choice of H_{SB} makes the model untractable, we can slightly improve

our understanding of its role on assuming that the linear term H_{SB}^0 is perturbed

by nonlinear corrections of the type:

$$H_{SB} - H_{SB}^{(0)} = \sum_\nu Q_\nu^n b_\nu(x) \tag{2.21}$$

for any $n > 1$. The additional interaction modifies the perturbation part $\mathbb{L}_I$ of

the Liouvillian operator as follows:

$$\mathbb{L}_I = \mathbb{L}_I(eq.(2.14)) - \sum_\nu \left[Q_\nu^n b_\nu'(x) - n Q_\nu^{n-1} a_\nu'(x) \right.$$

$$\left. \cdot b_\nu(x) \right] \frac{\partial}{\partial P} - \sum_\nu n Q_\nu^{n-1} b_\nu(x) \frac{\partial}{\partial P_\nu} \ . \tag{2.22}$$

The third term on the r.h.s. of eq.(2.22) does not contribute to our FP equation

(see Appendix). Without loss of generality we assume for instance n even so that

$\mathbb{L}_I$ can conveniently re-written as:

$$\mathbb{L}_I = -\frac{P}{M}\frac{\partial}{\partial x} + \left(V'(x) - \sum_\nu Q_\nu^n b_\nu'(x) \right)\frac{\partial}{\partial P} -$$

$$- \sum_\nu \left[Q_\nu\left(\omega_\nu^2 - n Q_\nu^{n-2} b_\nu(x) \right)\frac{\partial}{\partial P} - \frac{P}{M}\frac{\partial}{\partial Q_\nu} \right] a_\nu'(x) \ . \tag{2.2}$$

On applying the perturbation technique outlined in the Appendix we find for Γ_0

and Γ_1 the same formal expression of eqs.(2.16) and (2.17) respectively,

where V(x) now reads

$$\overline{V}(x) = U(x) - \frac{1}{2}\sum_\nu \omega_\nu^2 a_\nu^2(x) - \sum_\nu (n-1)!! \left(\frac{k_B T}{\omega_\nu^2}\right)^{\frac{n}{2}} b_\nu(x) \tag{2.2}$$

and $\gamma(N,x)$ exhibits an explicit dependence on $k_B T$. The explicit dependence on the

temperature is due to the averages $\langle Q_\nu^m \rangle$ taken over the umperturbed equilibriu

bath distribution (see Appendix).

The corrections to the isolated nonlinear potential U(x) are the exact couter-

part of the mean force exerted by the fluid on the melecular oscillator as it

appears in the LE obrained by Mohanty et al./15/. If $a_\nu(x)$ and $b_\nu(x)$ are chosen

to be polynomials in x, $\gamma(N,x)$ assumes a form still resembling that of eq.(2.20):

$$\gamma(N,x) = \sum_{k=0} \lambda_k(T) x^k \ . \tag{2.2}$$

It is noteworthy that the same kind of corrections to eqs.(2.16) and (2.17) can be determined also on assuming that the heat bath consists of nonlinear oscillators provided that nonlinearities can be treated perturbatively. If we add a nonlinear perturbation term to H_B in eq.(2.3) and change variables as in eq.(2.11), such a result follows immediately from our perturbation approach. We conclude that the T-dependence exhibited by both the phenomenological potential $V(x)$ and the friction terms $\gamma(\Pi,x)$ - see eqs.(2.24) and (2.25) - is general in its nature and should be traced back to the intrinsic nonlinear features of the total system and namely of the Hamiltonians H_B and H_{SB}. In Section 5 we discuss the physical relevance of such a dependence for applications to chemical-physical systems. For the purposes of Sections 3 and 4 however nonlinear corrections to H_B+H_{SB} can be disregarded without loss of generality.

With the choices of eqs.(2.3) and (2.6) for H_B and H_{SB}, we can easily compute Γ_2 of eq.(2.15). On employing our adiabatic elimination technique we readily find

$$
\Gamma_2 = - S_1(\Pi,x) \frac{\partial}{\partial P}\left[k_B T + \frac{P}{M} \right]\left[-\frac{P}{M}\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial P} \right] +
$$

$$
+ S_2(\Pi,x) \frac{\partial}{\partial P}\left[-\frac{P}{M}\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial P} \right]\left[k_B T \frac{\partial}{\partial P} + \frac{P}{M} \right] - \tag{2.26}
$$

$$
- S_3(\Pi,x) \frac{\partial}{\partial P}\frac{P}{M}\left[k_B T \frac{\partial}{\partial P} + \frac{P}{M} \right] ,
$$

where

$$
S_1(\Pi,x) = \frac{1}{2}\int_0^{\alpha} ds_o \int_0^{s_o} \sum_\nu a_\nu'^2(x)\ \omega_\nu^2 \cos\left(\frac{\omega_\nu}{m_\nu} s_o\right) ds_1 , \tag{2.}
$$

$$
S_2(\Pi,x) = \frac{1}{2}\int_0^{\infty} ds_o \int_0^{s_o} \sum_\nu a_\nu'^2(x)\ \omega_\nu^2 \cos\left[\frac{\omega_\nu}{m_\nu}(s_o-s_1)\right] ds_1 , \tag{2.}
$$

$$
S_3(\Pi,x) = \frac{1}{2}\int_0^{\infty} ds_o \int_0^{s_o} \sum_\nu a_\nu'(x)\ a_\nu''(x)\ \omega_\nu^2 \cos\left[\frac{\omega_\nu}{m_\nu}(s_o-s_1)\right] ds_1 . \tag{2.}
$$

The structure of Γ_2 is rather complicated. On following the procedure adopted for Γ_1, by choosing an explicit form for $a_\nu(x)$ and assuming the convergence of th integrals in eqs.(2.27), S_1, S_2 and S_3 can be given the form of polynomials in x: eight new parameters (three from S_1 and S_2 each and two from S_3) contro the non-Markovian corrections at the lowest perturbation order. In Section 4 we shall study numerically the role of the non-Markovian statistics of the heat bath under some stronger assumptions in order to gain a deeper comprehension of the underlying dynamics.

3. Activation rates in the Markovian limit.

In Section 2 we discussed under which assumptions the phenomenological LE (1.1) can be employed as a sensible description of a chemical reaction. Apart from the possible T-dependence of both the effective potential $V(x)$ and the friction terms arising from the inevitable nonlinearities of $H_S + H_{SB}$, the Markovian statistics of the heat bath are understood in the system of eqs.(1.1) as the main assumption. In the present Section we estimate the quantitative corrections to the rate of escape due to the multiplicative friction terms in λ_1 and λ_2 provided that these can be regarded as small in comparison with the usual dissipation term $-\lambda_0 v$ of the Kramers theory. Our treatment applies also to more general choices for $V(x)$ and $\gamma(N,x)$ as those on eqs.(2.24) and (2.25) respectively.

a) the overdamped limit

We study first the limit most discussed in the literature/2-8/ of high viscosity and large activation energy. For simplicity we assume our effective potential to be modelled as

$$V(x) = -a x^2/2 + b x^4/4 . \qquad (3.1)$$

It represents a symmetric double-well potential with two stable fixed points, $x_\pm = \pm(a/b)^{\frac{1}{2}}$, an instable fixed point in $x=0$ and activation energy defined as

$$\Delta V = V(0) - V(x_\pm) = a^2/4b . \qquad (3.2)$$

The height of the barrier ΔV is assumed large compared to the thermal energy $k_B T$. Furthermore the characteristic mechanical time scale mentioned in Section 2 is now given by $\sqrt{a}$, being $V''(0)=a$ and $V''(x_\pm)=2a$. Here high viscosity means that $\lambda_0 \gg \sqrt{a}$, since we chose to consider the x-dependent friction terms as comparative small. This is the well known overdamped limit of our system.

We proceed further by applying the standard analysis/1,3,7/ which consists in eliminating the variable velocity perturbatively. We employ again the perturbation technique in the Appendix.

The FP operator corresponding to the LE (1.1)-(1.3) can be divided into a perturbation part Γ_I and an umperturbed part Γ_0 such as:

$$\Gamma_0 = \lambda_0 \left(\frac{\partial}{\partial v} v + k_B T \frac{\partial^2}{\partial v^2} \right) , \qquad (3.3)$$

$$\Gamma_I = -v \frac{\partial}{\partial x} + V'(x) \frac{\partial}{\partial v} + \left(\lambda_2 x^2 + 2\lambda_1 x \right) \cdot \left[\frac{\partial}{\partial v} v + k_B T \frac{\partial^2}{\partial v^2} \right] . \qquad (3.4)$$

The result of our projection technique can be finally written as follows:

$$\frac{\partial}{\partial t} p(x;t) = \frac{1}{\lambda_0} \frac{\partial}{\partial x} D(x) \hat{j}(x) p(x;t) + \frac{1}{\lambda_0^3} \left[\frac{\partial}{\partial x} \hat{j}(x) \frac{\partial}{\partial x} \hat{j}(x) - \frac{\partial^2}{\partial x^2} \hat{j}^2(x) \right] p(x;t) \qquad (3.5)$$

where

$$\hat{j}(x) = V'(x) + k_B T \frac{\partial}{\partial x} , \qquad (3.6)$$

and

$$D(x) = \left[1 - \frac{2\lambda_1}{\lambda_0}x + \left(\frac{4\lambda_1^2}{\lambda_0^2} - \frac{\lambda_2}{\lambda_0}\right)x^2 + \frac{4\lambda_1\lambda_2}{\lambda_0^2}x^3 - \frac{\lambda_2^2}{\lambda_0^2}x^4\right]. \qquad (3.6')$$

Further details about this kind of calculation have been reported in refs.18 and 25.

We notice that generally the x-dependent friction coefficients ($2\lambda_1 x$ and $\lambda_2 x^2$)

are to be taken large in comparison with $\sqrt{a}$ (even if small with respect to λ_0).

This implies that the second term on the r.h.s. of eq.(3.5) can be neglected. It is

noteworthy that at any perturbation order the stationary distribution $\bar{p}(x)$ mantains

its canonical form/18/:

$$\bar{p}(x) = \mathcal{N} \exp\left(-\bar{V}(x)/k_B T\right) \qquad (3.7)$$

where $\mathcal{N}$ is a normalization constant.

A useful estimate of the activation rate for this type of problem is introduced

in refs.5 and 19. If T_0 denotes the mean first-passage time(MFPT) to reach the barrier

top, the activation rate μ is defined as:

$$\mu = 1/T_0. \qquad (3.8)$$

The first term on the r.h.s. of eq.(3.5) can be re-written as

$$\frac{\partial}{\partial t}p(x;t) = \left[\frac{\partial}{\partial x}\bar{W}(x) + k_B T\frac{\partial^2}{\partial x^2}D(x)\right]p(x;t) \qquad (3.9)$$

where

$$\bar{W}(x) = \bar{V}'(x)D(x) - k_B T D'(x). \qquad (3.10)$$

Under the mentioned assumptions the diffusion coefficient $k_B TD(x)$ is positive within

the bistable region $[x_-,x_+]$ so that the MFPT can be readily evaluated. If $x = \pm\infty$

are our natural reflecting boundaries and $x = 0$ an absorbing state, one finds for   (3

the MFPT/5,19/:

$$T_0 = \frac{1}{k_B T} \int_{-\infty}^{+\infty} \frac{dx}{D(x)\bar{p}(x)} \int_{-\infty}^{x} \bar{p}(z)\,dz .$$

In eq.(3.11) the symmetry of both V(x) and $\bar{p}(x)$ are taken into account.

In the case of a large barrier, i.e. $\Delta V/k_B T \gg 1$, we can evaluate (3.11) by

use of the method of steepest descendent. We readily obtain the following expression   (3

for μ, (3.8):

$$\mu(\lambda_i) = \mu(\lambda_0) / H\left(\frac{\lambda_1}{\lambda_2}, \frac{\lambda_2}{\lambda_3}\right) ,$$

where $\mu(\lambda_0)$ is the well-known rate of escape calculated by Kramers/8/ in the

overdamped limit   (3

$$\mu(\lambda_0) = \frac{a}{\pi\sqrt{2}} \frac{1}{\lambda_0} \exp\left(-\Delta V/k_B T\right) ,$$

and $H(\frac{\lambda_1}{\lambda_0}, \frac{\lambda_2}{\lambda_0})$ contains the corrections we are looking for: (3

$$H\left(\frac{\lambda_1}{\lambda_0}, \frac{\lambda_2}{\lambda_0}\right) = \left[1 + \left(\frac{4\lambda_1^2}{\lambda_0^2} - \frac{\lambda_2}{\lambda_0}\right)\frac{k_B T}{a} - \frac{\lambda_2^2}{\lambda_0^2}\left(\frac{k_B T}{a}\right)^2\right] . \qquad (3.$$

We note that the contribution from the terms of the diffusion $k_B TD(x)$ which are

odd in x vanish exactly for symmetric potentials.

We make now two relevant remarks:

(i) The restrictions under which our perturbation technique is valid can be determined

from eq.(3.14). The assumption of a definitive positive diffusion $k_B T D(x)$ within

the bistable region is satisfied when

$$\frac{\lambda_2}{\lambda_0} \frac{k_B T}{a} \ , \ \frac{\lambda_1}{\lambda_0} \left(\frac{k_B T}{a} \right)^{\frac{1}{2}} \ll 1 \ . \tag{3.15}$$

Such an inequality corresponds to impose that the x-dependent friction terms are

small compared to $-\lambda_0 v$ /14/.

(ii) The effects of the internal multiplicative noise (λ_1, $\lambda_2 \neq 0$) on the activation

rate are determined by the prefactor $H(\frac{\lambda_1}{\lambda_0}, \frac{\lambda_2}{\lambda_0})^{-1}$: The dependence on the temperature

is no lomger controlled by the Arrhenius factor in eq.(3.13) solely even assuming

that λ_0, λ_1 and λ_2 constant; the rate of escape increases or decreases depending

on whether λ_1^2 is smaller than $\lambda_0 \lambda_2$ or not. In Section 5 we shall discuss some

consequences of the main results of the present Section for application to practical

chemical-physical problems.

b) the underdamped limit

Let us now face the problem of 'small' friction terms and large activation

energies. Following Stratonovitch/20/ and adopting notation of ref.14, we describe

the system by LE for the deplacement x and the energy envelope E,

$$E \equiv \underline{v^2} + \overline{V}(x) \ , \tag{3.16}$$

The energy envelope technique is based on the assumption that the average energy

envelope $\langle E(t) \rangle$ varies slowly compared to the average displacement $\langle x(t) \rangle$

This condition places two restrictions on the parameter values for which the

technique is valid: the damping must be weak in comparison with the characteristic

mechanical frequencies, and the variations in the average energy envelope must be

slow in comparison with the average period of oscillation inside a single potentia

well. We shall justify the application of such a technique to our problem at the e

On changing variables

$$X \rightarrow X \ , \ V \rightarrow E \ ,$$

the FP equation corresponding to the LE (1.1)-(1.3) reads/14/:

$$\frac{\partial}{\partial t} P(x,E;t) = \left\{ -\frac{\partial}{\partial x} \left\{ 2\left[E - V(x) \right] \right\}^{\frac{1}{2}} + 2\left(\lambda_0 + 2\lambda_1 x + \lambda_2 x^2 \right) \cdot \right.$$
$$\cdot \frac{\partial}{\partial E} \left[E - V(x) \right] - \left(D_0 + 2D_1 x + D_2 x^2 \right) \frac{\partial}{\partial E} + 2\left(D_0 - 2D_1 x + \right.$$
$$\left. D_2 x^2 \right) \frac{\partial^2}{\partial E^2} \left[E - V(x) \right] \right\} P(x,E;t) \ ,$$

where the probability density $P(x,E;t)$ is related to $\rho(x,v;t)$ occurring in (2.1

by

$$P(x,E;t) \, dx \, dE = \rho(x,v;t) \, dx \, dv \ .$$

$P(x,E;t)$ can be exactly written as the product/20/

$$P(x,E;t) = w\left(x,t \,\middle|\, E \right) P_E(E;t) \ ,$$

where $w(x,t \,|\, E)$ is the probability density that the displacement at time t is x

conditional on its energy envelope being E (and also conditional on the initial

conditions). The method of Stratonovitch is based on the assumption that, in-

dependently of the initial condition $(x(0),E(0))$, $w(x,t\,|\,E)$ is proportional to the

time that the system -with energy envelope E- spends at x. The time spent at x is

in turn inversely proportional to the velocity at x, i.e. to $v(t)$. Thus we obtain

$$ w(x,t\,|\,E) = \left\{ 2\,\phi'(E)\,[\,E-V(x)\,]^{\frac{1}{2}} \right\} \tag{3.21}$$

where

$$ \phi(E) \equiv \int_R [\,E-\overline{V}(x)\,]^{\frac{1}{2}}\,dx \;, \tag{3.22}$$

and the prime denotes a derivative with respect to E. The region of integration R

in (3.22) defines the domain of x for which $E \geqslant V(x)$. On substituting eqs.(3.20) and

(3.21) into eq.(3.18) and integrating over x, we find an approximate FP equation for

the reduced probability density $p_E(E;t)$/14/:

$$ \frac{\partial}{\partial t} p_E(E,t) = \left\{ \frac{\partial}{\partial E}\left[\lambda_0\,\frac{\phi(E)}{\phi'(E)} - D_0 + \frac{\lambda_2\,\psi(E) - D_2\,\psi'(E)}{\phi'(E)} \right] + \right. $$
$$ \left. + \frac{\partial^2}{\partial E^2}\left[\frac{D_0\,\phi(E) + D_2\,\psi(E)}{\phi'(E)} \right] \right\} p_E(E;t) \;, \tag{3.23}$$

where

$$ \psi(E) \equiv \int_R x^2\,[\,E-\overline{V}(x)\,]^{\frac{1}{2}}\,dx \;. \tag{3.24}$$

Note that in this approximation the contributions of the terms proportional to λ_1

vanish.

The equilibrium distribution $\overline{p}_E(E)$ of the FP equation (3.23) can be readily

calculated ($\mathcal{N}$ is a normalization constant):

$$ \overline{p}_E(E) = \mathcal{N}\,\phi'(E)\,\exp\left(-E/k_B T \right) \;. $$

We propose the following definition of activation time T_E in the underdamped

limit: T_E coincides with the average time needed for the energy envelope $\langle E(t) \rangle$

to reach the value of the activation energy ΔV starting from its mean value E_0

$$ T_E(E_0) = \int_{E_0}^{\Delta V} \frac{dE}{\overline{p}_E(E)\,D(E)} \int_0^E \overline{p}_E(E')\,dE' \;, $$

where $D(E)$ is the diffusion coefficient on eq.(3.23):

$$ D(E) = \left(D_0\,\phi(E) + D_2\,\psi(E) \right) \Big/ \phi'(E) \;. $$

The expression (3.26) is the counterpart of eq.(3.11) and has been obtained by sol

the corresponding MFPT problem as outlined in ref.20.

In order to estimate E_0 we must calculate explicitly $\phi(E)$ on eq.(3.22). Tha

integral involves complete elliptic integrals of first and second kind. In the lim

of high activation energies however we can suitably avoid the difficulty approxim

ting $V(x)$ by two upright branches of parabola intersecting in x=0. The height of the

barrier is kept equal to ΔV and the frequencies of such parabolas are as those

obtained by linearly expanding the potential $V(x)$ around x_+ and x_- respectively.

Thus we find an approximated expression for $\phi(E)$:

$$\phi(E) \simeq \phi_0(E) \equiv 2 \int_R \sqrt{E - ax^2} \, dx = \frac{\pi}{\sqrt{a}} E , \qquad (3.28)$$

and analogously for $\psi(E)$:

$$\psi_0(E) = \frac{\pi}{\sqrt{a}} \frac{E^2}{4a} . \qquad (3.29)$$

It is noteworthy to remark that such an estimate works fairly well in the limit

$\Delta V/k_B T \gg 1$ and that the first corrections to $\phi(E)$ are proportional to $\phi_0(E) \left(\frac{E}{\Delta V} \right)^{\frac{1}{2}}$.

On substituting $\phi_0(E)$ into eq.(3.25), we determine

$$E_0 = k_B T \qquad (3.30)$$

We are now in a position to work out eq.(3.26). Substituting eqs.(3.25) and (3.27)

with eqs.(3.28) and (3.29) into eq.(3.26) yields:

$$T_E(k_B T) = \left(\frac{k_B T}{\lambda_0} \right)^{-1} \int_{k_B T}^{\Delta V} \frac{e^{E/k_B T}}{\phi_0(E) + (\lambda_2/\lambda_0) \psi_0(E)} dE \int_0^E \phi_0'(E') e^{-E/k_B T} dE' . \qquad (3.31)$$

On integrating by parts the integral on the right , we obtain

$$T_E(k_B T) = \left(\frac{k_B T}{\lambda_0} \right)^{-2} \int_{k_B T}^{\Delta V} \frac{e^{E/k_B T}}{\phi_0(E) + (\lambda_2/\lambda_0) \psi_0(E)} dE \int_0^E \phi_0(E') e^{-E'/k_B T} dE' \qquad (3.32)$$

where terms $\mathcal{O}\left(\frac{\Delta V}{k_B T} \right)$ will be negligible compared to terms $\mathcal{O}\left(e^{\Delta V/k_B T} \right)$ from (3.32).

We can now separate $T_E(k_B T)$ into two parts as follows:

$$T_E(k_B T) \equiv \langle \tau \rangle + \delta \langle \tau \rangle$$

where

$$\langle \tau \rangle \equiv \left(\frac{k_B T}{\lambda_0} \right)^{-2} \int_{k_B T}^{\Delta V} \frac{e^{E/k_B T}}{\phi_0(E)} dE \int_0^E \phi_0(E') e^{-E'/k_B T} dE' ,$$

and

$$\delta \langle \tau \rangle = - (k_B T)^{-2} \frac{\lambda_2}{\lambda_0} \int_{k_B T}^{\Delta V} \frac{\phi_0(E) e^{E/k_B T}}{\lambda_0 \phi_0(E) + \lambda_2 \psi_0(E)} dE \int_0^E \phi_0(E') e^{-E'/k_B T} dE'$$

Here $\langle \tau \rangle$ denotes the limit of $T_E(k_B T)$ for $\lambda_2 \to 0$, while $\delta \langle \tau \rangle$ is the correcti

due to the x-dependent friction terms.

The integrals on eqs.(3.34) and (3.35) can be calculated explicitly by substit

eqs.(3.28) and (3.29):

$$\langle \tau \rangle = \frac{1}{\lambda_0} \left[Ei \left(\frac{\Delta V}{k_B T} \right) - Ei(1) \right] ,$$

$$\delta \langle \tau \rangle = - \frac{1}{\lambda_0} \left[Ei \left(\frac{\Delta V}{k_B T} + \frac{1}{\beta k_B T} \right) - Ei \left(1 + \frac{1}{\beta k_B T} \right) \right] \cdot e^{-\frac{1}{\beta k_B T}}$$

where $\beta \equiv \lambda_2/4a\lambda_0$ and Ei(x) denotes the exponential-integral function/21/,

which can be expanded as:

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We are now in a position to work out eq.(3.26). Substituting eqs.(3.25) and (3.27) with eqs.(3.28) and (3.29) into eq.(3.26) yields:

$$T_E(k_B T) = \left(\frac{k_B T}{\lambda_0}\right)^{-1} \int_{k_B T}^{\Delta V} \frac{e^{E/k_B T}}{\phi_0(E) + (\lambda_z/\lambda_0) \psi_0(E)} dE \int_0^E \phi_0'(E') e^{-E/k_B T} dE' \, . \qquad (3.31)$$

On integrating by parts the integral on the right, we obtain

$$T_E(k_B T) = \left(\frac{k_B T}{\lambda_0}\right)^{-2} \int_{k_B T}^{\Delta V} \frac{e^{E/k_B T}}{\phi_0(E) + (\lambda_z/\lambda_0) \psi_0(E)} dE \int_0^E \phi_0(E') e^{-E'/k_B T} dE' \qquad (3.32)$$

where terms $\mathcal{O}\left(\frac{\Delta V}{k_B T}\right)$ will be negligible compared to terms $\mathcal{O}\left(e^{\Delta V/k_B T}\right)$ from (3.32).

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$$T_E(k_B T) \equiv \langle \tau \rangle + \delta \langle \tau \rangle \qquad ($$

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and

$$\delta \langle \tau \rangle = -\left(k_B T\right)^{-2} \frac{\lambda_z}{\lambda_0} \int_{k_B T}^{\Delta V} \frac{\phi_0(E) e^{E/k_B T}}{\lambda_0 \phi_0(E) + \lambda_z \psi_0(E)} dE \int_0^E \phi_0(E') e^{-E'/k_B T} dE' \qquad ($$

Here $\langle \tau \rangle$ denotes the limit of $T_E(k_B T)$ for $\lambda_2 \to 0$, while $\delta \langle \tau \rangle$ is the correction due to the x-dependent friction terms.

The integrals on eqs.(3.34) and (3.35) can be calculated explicitly by substituting eqs.(3.28) and (3.29):

$$\langle \tau \rangle = \frac{1}{\lambda_0} \left[Ei\left(\frac{\Delta V}{k_B T}\right) - Ei(1) \right] \, , \qquad ($$

$$\delta \langle \tau \rangle = -\frac{1}{\lambda_0} \left[Ei\left(\frac{\Delta V}{k_B T} + \frac{1}{\beta k_B T}\right) - Ei\left(1 + \frac{1}{\beta k_B T}\right) \right] \cdot e^{-\frac{1}{\beta k_B T}} \, , \qquad ($$

where $\beta \equiv \lambda_2/4a\lambda_0$ and $Ei(x)$ denotes the exponential-integral function/21/, which can be expanded as:

$$Ei(x) = e^x \sum_{k=1}^{\infty} \frac{(k-1)!}{x^k} \quad . \tag{3.38}$$

On employing eq.(3.38), we can determine the leading term on eq.(3.36):

$$\langle \tau \rangle = \frac{1}{\lambda_0} \frac{k_B T}{\Delta V} \cdot \exp\left(\Delta V / k_B T \right) \quad . \tag{3.39}$$

In view of the approximations introduced in eqs.(3.28) and (3.29), contributions proportional to $\langle \tau \rangle \left(\frac{k_B T}{\Delta V} \right)^k$, $k > 1$, are meaningless. The inverse of $\langle \tau \rangle$ on eq.(3.39) coincides exactly with the well-known rate of escape found by Kramers/8/ in the underdamped limit. This result makes us more confident of our approach based on the energy envelope technique and on the definition (3.26) of activation time.

Analogously, expanding eq.(3.37) at the first order in $k_B T / \Delta V$, we find :

$$\delta \langle \tau \rangle = - \frac{k_B T}{\lambda_0} \left(\Delta V + \frac{1}{\beta} \right)^{-1} \exp\left(\Delta V / k_B T \right) \quad , \tag{3.40}$$

On putting eqs.(3.39) and (3.40) together, we conclude:

$$T_E (k_B T) \simeq \langle \tau \rangle \left(1 - \frac{\beta \Delta V}{1 + \beta \Delta V} \right) \quad , \tag{3.41}$$

We make now some relevant remarks:

(i) The activation rate in the underdamped limit,

$$\mu_E (\lambda_0, \lambda_2) = T_E^{-1} (k_B T) \quad , \tag{3.42}$$

is an increasing function of λ_2. In the frame of the Stratonovitch method, eqs.(3.? and (3.27) prove this immediately. In the limit of high activation energies - see eqs.(3.28) and (3.29)- from eq.(3.41) we obtain:

$$\mu_E (\lambda_0, \lambda_2) = \langle \tau \rangle^{-1} \left(1 + \beta \Delta V \right) = \mu_E (\lambda_0) \left(1 + \frac{\lambda_2}{\lambda_0} \frac{a}{16b} \right), \tag{3.$$

where $\mu_E (\lambda_0)$ is the inverse of the Kramers escape time for $\lambda_0 / \sqrt{a} \to 0$ given in eq.(3.39). If we compare this result to that of eqs.(3.12)-(3.14) for the overdamped limit we conclude that the x-dependent friction terms play a different role in the two viscosity regimes.

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$$T_E(k_B T) \simeq \langle \tau \rangle \left(1 - \frac{\beta \Delta V}{1 + \beta \Delta V} \right) \,, \tag{3.41}$$

We make now some relevant remarks:

(i) The activation rate in the underdamped limit,

$$\mu_E(\lambda_0, \lambda_2) = T_E^{-1}(k_B T) \,, \tag{3.42}$$

is an increasing function of λ_2. In the frame of the Stratonovitch method, eqs.(3.?) and (3.27) prove this immediately. In the limit of high activation energies - see eqs.(3.28) and (3.29)- from eq.(3.41) we obtain:

$$\mu_E(\lambda_0, \lambda_2) = \langle \tau \rangle^{-1} \left(1 + \beta \Delta V \right) = \mu_E(\lambda_0) \left(1 + \frac{\lambda_2}{\lambda_0} \frac{a}{16 b} \right) \,, \tag{3.?}$$

where $\mu_E(\lambda_0)$ is the inverse of the Kramers escape time for $\lambda_0 / \sqrt{a} \to 0$ given in eq.(3.39). If we compare this result to that of eqs.(3.12)-(3.14) for the overdamped limit we conclude that the x-dependent friction terms play a different role in the two viscosity regimes.

(ii) The restrictions under which eq.(3.32) for T_E is valid can be summarized

as follows:

$$\Delta \overline{V}/k_B T \gg 1 \qquad \text{(high activation energy)}, \qquad (3.44)$$

$$\lambda_o \left(1 + \frac{\lambda_2}{\lambda_o} \frac{a}{16 b} \right) \ll \sqrt{a} \qquad \text{(small friction)}. \qquad (3.45)$$

The second inequality can be justified by noting that its first term plays the

role of an 'effective' friction constant in $\mu_E(\lambda_0, \lambda_2)$ -see eq.(3.43)-

and that $\mu_E(\lambda_0)$ has been obtained in the limit $\lambda_0 \ll \sqrt{a}$. The same conclusion

can be reached by supposing that the 'effective' friction constant $\lambda_o - \lambda_2 \left\langle \dfrac{\psi_o(E)}{\phi_o(E)} \right\rangle_E$

in the denominator of the first integral on eq.(3.32) is very small compared to

$\sqrt{a}$ /14/. $\langle ... \rangle_E$ denotes the average with respect to the energy equilibrium

distribution (3.25). When $\beta \Delta V$ (i.e. λ_2) is small then (3.45) reduces to

simply Stratonovitch's original weak damping condition $\lambda_0 \ll \sqrt{a}$. On the other

hand, when $\beta \Delta V$ is large, relation (3.45) restricts the range of values of λ_0

and λ_2 to

$$(3.46)$$

(iii) Eq.(3.46) implies that there are ranges of parameter values in which the

multiplicative fluctuations and the corresponding damping can have very strong

dynamical effects. In such a range the condition that the energy envelope

variations are slow compared to the average period of oscillation inside a single

potential well is certainly satisfied- note that $\Delta V/k_B T \gg 1$. In order to adopt

eq.(3.43) as a reliable estimate of the activation rate in the underdamped limit,

we must further impose the restriction that contributions proportional to β

are larger than the inaccuracies implied by the approximations on eqs.(3.28) and

(3.29). Since the larger corrections are proportional to $\mu_E(\lambda_0)(k_B T/\Delta V)^{\frac{1}{2}}$,

we must require that the following inequality is satisfied (beside $\lambda_0 \ll \sqrt{a}$):

$$\frac{\lambda_o}{\lambda_2} \frac{b}{16 a} \ll \left(\frac{\Delta V}{k_B T} \right)^{\frac{1}{2}} \qquad (3.47)$$

In other words, our analytical expression for $\mu_E(\lambda_0, \lambda_2)$ is of practical

use only if the value of λ_2 is not too small.

4. Activation rates in the presence of memory effects.

This subject has been treated by many authors[2-6] on using different approaches. In the present Section we study a particular case of the first-order correction to the Markovian limit analyzed in refs.14 and 15. A completely general derivation has been studied in Section 2, however eqs.(2.26) and (2.27) are of no use for practical purposes due to the presence of too many unknown parameters. Since we are interested in a qualitative description of the effects of the non--Markovian statistics of the heat bath, we can simplify our problem as follows.

Let us assume that $a_\nu(x) \equiv a(x)$ for any $\nu = 1, \ldots, N$. In this case eqs.(2.9) can be re-written as:

$$\dot{x} = v$$
$$\dot{v} = -V'(x) + a'(x) \int_0^\infty d\tau \, \varphi(t-\tau) \left\{ a'(x(\tau)) v(\tau) \right\} +$$
$$+ a'(x) f(t) , \qquad (4.1)$$

where M has been chosen unit and

$$\varphi(t) \equiv \sum_\nu \omega_\nu^2 \cos\left(\frac{\omega_\nu}{\sqrt{m}_\nu} t\right) . \qquad (4.2)$$

Eq.(4.1) is a generalized Langevin equation and the function $\varphi(t)$ defined on eq.(4.2) plays the role of memory-kernel. Generalizing the technique expounded in ref.3 we make the problem (4.1)-(4.2) Markovian by introducing enough additional variables. In our case the Laplace transform $\hat{\varphi}(z)$ of $\varphi(t)$ admits a continued

fraction expansion[12c]:

$$\hat{\varphi}(z) = \frac{\Delta_1^2}{z+} \quad \frac{\Delta_2^2}{z+} \quad \ldots \quad \frac{\Delta_n^2}{z+\gamma_n} . \qquad (4.3)$$

Eqs.(4.1)-(4.3) are then equivalent to a set of n+2 Markovian equations:

$$\dot{x} = v$$
$$\dot{v} = -V'(x) + a'(x) \xi_1$$
$$\dot{\xi}_1 = -\gamma_1 \xi_1 - \Delta_1^2 b(x) v + \xi_2$$
$$\dot{\xi}_2 = -\gamma_2 \xi_2 - \Delta_2^2 \xi_1 + \xi_3 \qquad (4.4)$$
$$- - - - - - - - - - - - - - - - - -$$
$$\dot{\xi}_n = -\gamma_n \xi_n - \Delta_n^2 \xi_{n-1} + \eta(t)$$

where the random force $\eta(t)$ is a Gaussian white noise of zero mean and correla

$$\langle \eta(t) \eta(0) \rangle = 2 k_B T \gamma_n \Delta_1^2 \ldots \Delta_n^2 \delta(t), \qquad (4.5)$$

and the function $b(x)$ is suitably related to $a(x)$:

$$b(x) = \gamma_1 a'(x) / \Delta_1^2 . \qquad (4.6)$$

We assume that $\varphi(t)$ is approximated by means of an exponential function, $\exp(-\gamma_1 t)$, which corrects the Markovian limit $\varphi(t) = \delta(t)$ on ref.14: this implies that n is chosen equal 1.

From now on we follow the perturbation approach described in Section 2. The FP operator corresponding to the set of eqs.(4.4) with n=1, must be separated into a an unperturbed part,

$$\Gamma_0 = \gamma_1 \left[\frac{\partial}{\partial \xi_1} \xi_1 + \langle \xi_1^2 \rangle \frac{\partial^2}{\partial \xi_1^2} \right] , \qquad (4.7)$$

and a perturbation part

$$\Gamma_I = -v\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial v} - a'(x)\xi_1\frac{\partial}{\partial v} + \Delta_1^2 b(x)v\frac{\partial}{\partial\xi_1},$$ (4.8)

where $\langle\xi_1^2\rangle = \gamma_1 k_B T$ (see eq.(4.5)). The perturbation expansion is supposed to

converge for $\gamma_1 \gg$ ia (see ref.25). In Mohanty et al./15/ notation this corresponds

to $\omega_0\tau \ll 1$ (see Section 1).

calculations are straightforward. The operator Γ_2 on eq.(2.26) should be

now replaced by (M=1):

$$\Gamma_2 = \frac{a'(x)^2}{\gamma_1^2}\frac{\partial}{\partial v}\left(-v\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial v}\right)a'(x)\left(k_B T\frac{\partial}{\partial v} + v\right) -$$

$$-\frac{a'(x)^2}{\gamma_1}\frac{\partial}{\partial v}\left(k_B T\frac{\partial}{\partial v} + v\right)\left(-v\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial v}\right).$$ (4.9)

The FP equation for the reduced probability $\rho(x,v;t)$ corrected up to the first-

-order in γ_1^{-1}, can be re-written in a more compact manner as follows:

$$\frac{\partial}{\partial t}\rho(x,v;t) = \left\{-\frac{\partial}{\partial x}j(v) + \left(1 - \frac{a'^2(x)}{\gamma_1}\right)\frac{\partial}{\partial v}j(x) + \right.$$

$$\left. + \frac{\partial}{\partial v}\left(a'^2(x) + a(x)a''(x)\right)\frac{v}{\gamma_1}\right\}\rho(x,v;t),$$ (4.10)

where j(x) is defined on eq.(3.6) and

$$j(v) = k_B T\frac{\partial}{\partial v} + v.$$ (4.11)

On adopting for a(x) the choice of eq.(2.19), i.e. $\Gamma x + \beta x^2/2$, we write

$$a'(x)^2 = \lambda_2 x^2 + 2\lambda_1 x + \lambda_0, \quad \lambda_1^2 = \lambda_0\lambda_2,$$ (4.12)

$$a'(x)a''(x) = \lambda_2 x + \lambda_1.$$

Therefore the parameter controling the relevance of the non-Markovian corrections

is γ_1. For $\gamma_1 \to \infty$ the Markovian limit is recovered.

Following the prescription of refs.3 and 18 we define the escape time from

the reactant well, e.g. x_-, to the product well, e.g. x_+, as the area below the

curve $\langle x(t)\rangle/\langle x(0)\rangle$. For fairly high values of the barrier ΔV, this curve

is mostly an exponential throughout the whole time dominion but a narrow region

close to t=0. This fast relaxation significantly depends on the starting point

distribution, $\rho(x,v,0)/22/$. Let us assume $\rho(x,v;0)$ to be given by $\delta(x-x_-)$.

This choice possibly enhances the effect of the short time relaxation on our

definition of rate of escape:

$$\mu' \equiv \hat\Phi(0)^{-1}$$ (4.13

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 $\Delta V/k_B T$, μ' can be relied on as a suitable

estimate of the activation rate of the process. Definition (4.13) is especially

suited for computational purposes.

To apply the analytical approach of the foregoing Section to the FP equation

(4.10) would be cumbersome and of no practical use. For that reason we chose to

to employ a numerical algorithm which has been shown to give excellent perform-

ances in such computations/22,23/. This algorithm(CFP), based on a continued

fraction expansion a la Mori/12/, is now reviewed in ref.23. Fig.1 displays our

results. The most remarkable effect of the non-Markovian corrections is the

increase of μ' as the heat bath relaxation time γ_1^{-1} increases. Curve 1 refers

to the choice $a(x)=\Gamma x$, i.e. $\lambda_1 = \lambda_2 = 0$. The small discrepancy with the

Markovian limit $\mu(\lambda_0)$ of eq.(3.13) is to be accounted for as an effect of the

interplay of inertia and anharmonicities in the potential form/7/. These have

been disregarded when we worked out eqs.(3.9) and (3.11) using the steepest descendent

method in the Smoluchowski approximation. The more accurate values of Larson and

Kostin/7/ are reproduced with a precision of some percent.

Curve 2 refers to the case $\lambda_0 = \lambda_1 = \lambda_2 = 1$ -see eq.(4.12). In the Markovian

limit, $\gamma_1 \to \infty$, the smaller rate of escape confirms the predictions of eqs.(3.12)

and (3.14) provided that $\mu(\lambda_0)$ of eq.(3.13) is substituted with the Larson

and Kostin's rate/7/. The dependence of the activation rate on the parameter γ_1

for λ_1 and $\lambda_2 \neq 0$ is the main finding of the present Section. Curve 1 closely

reproduces results already obtained in ref.3. In the forthcoming Section we shall

discuss the relevance of these results in view of applications to chemical-phy

sical problems.

5. Summary and conclusions.

concluding remarks.

In this Section we wish to draw some conclusions about the relevance of the

phenomenological LE to applications to chemical-physical systems.

In Section 2 we reviewed Lindenberg and Seshadri/14/ derivation of the LE (1.1)

starting from Zwanzig's model Hamiltonian/13/ which describes a nonlinear one-

-dimensional system coupled with a heat bath of harmonic oscillators. If small non-

linearities are included in the interaction term - or in the heat bath Hamiltonian

a formally identical set of LE,(1.1)-(1.3), can be recovered where both the effecti

potential V(x) and the friction coefficients λ_i now depend on the system tempera

ture T. In Section 3 we determined quantitatively the effects of x-dependent

friction terms on the activation rate of a process modelled as the escape of a

Brownian particle from a well (the reactant well) to another one (the product well)

Corrections to the Kramers theory in the overdamped limit are shown to depend on th

relative magnitude of λ_1^2 and $\lambda_0 \lambda_2$. In Section 4 the effects due to the non-

-Markovian statistics of the heat bath are accounted for in a simplified case where

the relevance of such a property is regulated by means of one new parameter only,

$\gamma_1^{-1} \equiv \tau_0$. A finite heat bath correlation time τ_0 is proved to increase the rate

of escape of the Brownian particle over the barrier. The main analytical tool emplo

throughout this paper is the perturbation technique of adiabatic elimination of

fast relaxing variables described in the Appendix.

When in refs.16 and 17 experimenters claim that the Kramers theory fails in describing a number of chemical-physical processes, they usually refers to the phenomenological model (1.1) with $\lambda_1 = \lambda_2 = 0$ (Wang-Uhlenbeck LE/24/) and to the corresponding rate of escape which for high friction constants coincides with Kramers' rate $\mu(\lambda_0)$ on eq.(3.13). Theorists improved/1-9/ such an estimate on accounting for a variety of additional effects all of which, however, assume the Wang-Uhlenbeck model as a starting point or as the zero-order approximation of their perturbation approaches. The description obtained first by Lindenberg and Seshadri/14/ and discussed in detail by Mohanty et al./15/ is to be regarded as a more realistic basic picture for real chemical-physical systems. This can be reduced to the well--known Wang-Uhlenbeck model under some restrictions and approximations/15/.

We now summary the properties exhibited by the model of eqs.(1.1)-(1.3) in comparison with the naive Wang-Uhlenbeck picture.

dependence on the temperature. If the viscosity is kept constant in the overdamped limit the activation rate is supposed to depend on T by the Arrhenius law - see eq.(3.13). In view of the findings of Sections 2 and 3, we suggest however that deviations from that fundamental rule could be revealed by means of detailed measurements. The physical origin of such corrections is twofold. First, when we approximated the Liouville description of the global system through a set of LE we pointed out that

the potential of the isolated Brownian particle $U(x)$ was to be replaced by an 'effective' potential $V(x)$, (2.8). This is the potential whose parameters (activation energy, characteristic frequencies, etc.) can be obtained from the experimental data of any single process. The inevitable anharmonicities of the real heat bath ($H_{SB} + H_B$) determine the T-dependence of $V(x)$, (2.24), and of λ_i, (2.25). Second, even if we neglect this kind of dependence and we refer to the 'zero-order approximation', eqs.(1.1)-(1.3), the x-dependent friction terms imply that a more reliable expression for the activation rate would be now $\mu(\lambda_i)$ on eq.(3.12), where the tempe enters into the correction prefactor $H(\frac{\lambda_1}{\lambda_0}, \frac{\lambda_2}{\lambda_0})$ as well. Slight deviations from the Arrhenius law have been measured recently for instance in ref.17: a more detail analysis should be of great interest.

dependence on viscosity. When the experimental results for the dependence of the activation rate on dissipation are compared with Kramers' predictions (i.e. with the Wang-Uhlenbeck model), it is common/16,17/ to assume a sort of hydrodynamical model for λ_0 in which

$$\lambda_0 \propto \eta$$ (5.

where η_s is the solvent viscosity. If we adopt the LE (1.1)-(1.3) as an alternative phenomenological model, a new difficulty arises. Since we cannot fit too many parameters to the experimental data, one could think to take η proportional to an 'effective' or 'average' damping/14/. Unfortunately this choice is inconsistent wit

our results of Section 3 where we showed the x-dependent friction terms play a distinct role in correcting the activation time in the overdamped and underdamped limit. In eq.(3.12) we should define λ as $\lambda_0 H(\frac{\lambda_1}{\lambda_0}, \frac{\lambda_2}{\lambda_0})$ while in eq.(3.43) λ would be read $\lambda_0(1+\beta\Delta V)$. Therefore it is no surprise that many experimental papers conclude claiming the breakdown of the Kramers theory because of an incorrect prediction of the viscosity dependence of the activation rates/16,17/.

dependence on heat bath relaxation time. This is an example of the additional mechanisms introduced/1-6/ to account for the discrepancies in the η-dependence mentioned above. These improvements are no doubt well founded from a physical point of view, but are still to be regarded as perturbation corrections to the Wang-Uhlenbeck model. When we tried to apply one of those approaches/3/ to the phenomenological LE (1.1)-(1.3), we found that the well-known increase of the activation rate with $\tau_0 = \gamma_1^{-1}$ depends dramatically on the choice of the friction parameters λ_i -see fig.1.

We conclude remarking that the LE (1.1)-(1.3) are just an example of a generalized version of the Wang-Uhlenbeck model and therefore, before using one-dimensional phenomenological LE of this type, one would be well advised to check under what assumptions these equations are valid descriptions of the dynamics of the specific chemical-physical system under investigation.

Appendix

This Appendix is aimed at giving some technical rules for applying the AEP (adiabatic elimination procedure) of ref.25 to the system of eqs.(2.12).

We found it easier to carry out our projection procedure by using a new set of heat bath variables:

$$\eta_{1\nu} = \frac{p_\nu}{\sqrt{m_\nu}} + i\,\omega_\nu\,Q_\nu \qquad (\nu = 1, \cdots, N) \tag{A.1}$$

$$\eta_{2\nu} = \frac{p_\nu}{\sqrt{m_\nu}} - i\,\omega_\nu\,Q_\nu \tag{A.2}$$

The canonical equilibrium distribution ρ_{eq} is defined as:

$$L_0\,\rho_{eq} \equiv 0 \tag{A.3}$$

In the (p_ν, Q_ν) frame ρ_{eq} reads:

$$\rho_{eq}(p_\nu, Q_\nu) = \mathcal{N} \exp\left[-\frac{1}{k_B T}\sum_\nu\left(\frac{p_\nu^2}{2m_\nu} + \frac{\omega_\nu^2 Q_\nu^2}{2}\right)\right], \tag{A.4}$$

while in the new one, (A.1) and (A.2),

$$\rho_{eq}(\eta_{1\nu}, \eta_{2\nu}) \equiv \mathcal{N} \exp\left(-\frac{1}{2k_B T}\sum_\nu \eta_{1\nu}\eta_{2\nu}\right), \tag{A.5}$$

with $\mathcal{N}$ a suitable normalization constant.

In the new variables $(\eta_{1\nu}, \eta_{2\nu})$ the unperturbed, (2.13), and perturbation part, (2.14), of the FP operator can be re-written as:

$$L_0 = -2\sum_\nu \frac{i\,\omega_\nu}{\sqrt{m_\nu}}\left(\eta_{1\nu}\frac{\partial}{\partial\eta_{1\nu}} - \eta_{2\nu}\frac{\partial}{\partial\eta_{2\nu}}\right), \tag{A.6}$$

$$L_I = -\frac{p}{M}\frac{\partial}{\partial x} + V'(x)\frac{\partial}{\partial p} - \sum_\nu i\omega_\nu a_\nu'(x)\left[\frac{p}{M}\left(\frac{\partial}{\partial \eta_{1\nu}} - \frac{\partial}{\partial \eta_{2\nu}}\right)^+\right.$$

$$+ \left.\frac{\partial}{\partial p}(\eta_{1\nu} - \eta_{2\nu})\right],$$

(A.7)

respectively.

Two basic rules of our AEP (see ref.25, Section 3) are then to be recast as follows:

$$P e^{L_0 t} = P e^{-\gamma_{i\nu} t}$$

(A.8)

$$P e^{L_0 t}\frac{\partial}{\partial \eta_{i\nu}} = P e^{-\gamma_{i\nu} t}\frac{\partial}{\partial \eta_{i\nu}}$$

$$P e^{L_0 t}\eta_{i\nu} = P e^{-\gamma_{i\nu} t}\eta_{i\nu},$$

(A.9)

where i=1,2 and

$$\gamma_{i\nu} = (-1)^{i-1}\frac{2 i \omega_\nu}{m_\nu}.$$

(A.10)

Here we used notation as in ref.25. In particular P is the projection operator on to the relevant variables (x,p) subspace. Finally, eq.(A.5) yields:

$$\langle(\eta_{1\nu} - \eta_{2\nu})^2\rangle = -k_B T,$$

(A.11)

and $\langle\eta_{1\nu}^2=\eta_{2\nu}^2\rangle=0$. We are now in a position to apply straightforwardly the perturbation technique described in many details in ref. 25 : eqs.(2.16)-(2.18) and (2.26)-(2.27) are readily recovered.

The treatment of the perturbation (nonlinear) corrections to $H_{SB}^{(0)}$ is based on the counting rule expounded in ref.25 (Section 3): Since $\rho_{eq}(p_\nu,Q_\nu)$ is a Gaussian function in the variables Q_ν, the integral-product of terms from L_I whose global

power in Q_ν (for any ν) is odd vanish. On employing this rule results as in eqs.(2

and (2.25) are easily determined.

FOOT-NOTES

pag. $\vee$

Discrepancies between our formulas (2.8),(2.10) and (2.18) and the corresponding
ones of ref.14 are due to some minor mistakes therein.

pag. $\vee$

It is not our purpose here to establish the conditions under which the convergence
of integral (2.18) can be proved. The assumption is appropriate for instance, if
N is large and $\omega_\nu/\tilde{\omega}_\nu$ are to each other as irrational numbers. $\vee$

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