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Long-Time Bath Correlations in the Pollak–Grabert–Hänggi Theory

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We analyze some cases for which the Pollak–Grabert–Hänggi theory on the activated rate processes for generalized Langevin dynamics exhibits unexplained disagreements with numerical results. First we analyze carefully the PGH theory and we show that a kind of Markovian hypothesis implicitly made in the reasoning is sometimes violated. Then we propose modifications of the original theory in order to take into account the possible effects caused by this violation, and we compare the corrected results with simulations.

KEY WORDS: Reaction rate; Brownian motion; generalized Langevin dynamics.

1. INTRODUCTION

Since the famous Kramers's paper[1] on the escape rate of a brownian particle from a potential well, and his calculation of the two limiting formulas for the weak and strong friction cases, a lot of work has been made to provide an unique expression able to describe properly the whole range of friction, and in particular the turnover region where the two curves of Kramers join. In the same time, the extension of the Kramers theory to more complicated brownian dynamics like the Generalized Langevin dynamics, and the calculation of rate reaction in these cases were also a great challenge.[2]

Among the numerous contributions concerning these questions, the paper of Pollak, Grabert and Hänggi[4] (initiated by ref. 3) is without doubt of primordial importance, because this theory (named PGH theory

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in the following)—based on first developments in ref. 5—was the first to be able to give a global answer to the turnover problems, relatively independent from the friction regime as well as from the friction kernel type. Moreover, the validity of the calculations is in this theory can be controlled through non-trivial but easy to evaluate quantities.

Afterwards, this theory has been intensively studied and numerically tested (see refs. 6, 7 and other references in ref. 8), and it appeared that some situations were not well accounted for by the original theory. For most of them, the failure of the PGH theory to produce the correct rate has been well understood: "extreme" dynamics implying extremely long thermalisation time in the bottom of the well, non negligible anharmonic corrections near the saddle, for instance. And for many of them, improvements were proposed.

For instance, in a recent paper,[8] Reese and Tucker analyse certain failure of the PGH theory, and propose an improvement called *curvilinear* PGH theory (or cPGH) which improves the approximation inherent in PGH and broadens its applicability. But they compared their new formulas with very well controlled numerical simulations, and noted that despite this accuracy, some cases still showed some discrepancies, while *all the perturbation parameter were small enough*; moreover they pointed out that this phenomenon was already present in the original PGH paper, because the comparison with the numerics of Straub *et al.*[9] they made showed two cases of unexplained inadequacy.

In this paper, we propose an explanation for this phenomenon, which is generally encountered in situations for which the static friction is weak and the correlation time of the friction kernel is important. After a rapid recall of the PGH theory (we have kept the notations used in the original paper[4] for clarity), we discuss in detail some points and underscore certain subjacent hypothesis implicitly made by PGH. Among other things, we point out that the PGH theory is "markovian" in a certain sense. Underlying that, in some rare cases, these hypothesis are violated, we propose a slight modification of the theory, which is in principle more suitable to describe properly these cases.

2. THE PGH THEORY

We are interested in the rate at which a particle of mass m, mobile in one dimension escapes from a metastable potential well. Let $x(t)$ denote the position of the particle. The main features of the potential $V(x)$ are the height $V^{\ddagger}$ of the barrier, the curvatures at the bottom, $m\omega_0^2$ and at the saddle point $-m\omega^{\ddagger 2}$ (cf. Fig. 1). The particle is in contact with a thermal

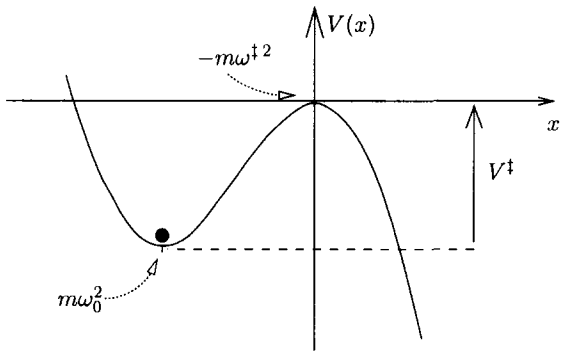

Fig. 1. General form of the potential and related quantities.

bath at a temperature $k_B T \ll V^{\ddagger}$ via a Generalized Langevin dynamics

$$m\ddot{x} + m\int_0^t \gamma(t-u)\,\dot{x}(u)\,du + V'(x) = F(t) \quad \text{with } \langle F(t)\,F(0)\rangle = mk_B T\gamma(t) \tag{1}$$

After a transient, which is negligible if the memory kernel is not too extended, we know that the survival probability decreases proportionnaly to $\exp(-kt)$. By definition, the reaction rate is the parameter k. Our aim is the calculation of its value given the expression of $V(x)$, the temperature and the memory function $\gamma(t)$.

2.1. Zwanzig's Hamiltonian

The PGH theory begins with a description of the stochastic dynamics of the generalized Langevin equation (GLE) using a hamiltonian formalism. As shown by Zwanzig,[10] the dynamics of x can be represented by a bilinear coupling with a number $N \to \infty$ of oscillators q_i through the Hamiltonian

$$\mathcal{H} = \frac{1}{2}m\dot{x}^2 + V(x) + \frac{1}{2}\sum_{i=1}^{N} m_i\left(\dot{q}_i^2 + \omega_i^2\left(q_i + \frac{C_i}{m_i\omega_i^2}x\right)^2\right) \tag{2}$$

where the parameters (m_i, ω_i, C_i) must be chosen such that

$$\gamma(t) = \frac{1}{m}\sum_{i=1}^{N}\frac{C_i^2}{m_i\omega_i^2}\cos(\omega_i t)$$

2.2. Change of Coordinates: Saddle Eigenmodes

Assuming that the potential $V(x)$ is locally inverted parabolic near the saddle, it can be written

$$V(x) = -\tfrac{1}{2}m\omega^{\ddagger 2}x^2 + V_1(x)$$

where $V_1(x)$ is at least cubic near zero. Then it is convenient to separate the quadratic part of $\mathscr{H}$ and write it as

$$\mathscr{H} = \mathscr{H}_q + V_1(x)$$

where $\mathscr{H}_q$ is quadratic in the coordinates (x, q_i).

Following ref. 4, the next step is to diagonalise the quadratic part $\mathscr{H}_q$ using an orthogonal change of the coordinates $(x, q_i) \to (\rho, y_i)$ (this operation preserves the signature of the quadratic form, so that one, and only one, unstable mode ρ corresponds to the unique unstable coordinate x). In these coordinates, $\mathscr{H}_q$ becomes

$$\mathscr{H}_q(\rho, \{y_i\}_{i=1,N}) = \tfrac{1}{2}\dot{\rho}^2 - \tfrac{1}{2}\lambda^{\ddagger 2}\rho^2 + \sum_{i=1}^{N} \tfrac{1}{2}(\dot{y}_i^2 + \lambda_i^2 y_i^2)$$

As x is a linear combination of the new coordinates, it can *a priori* be written as

$$x = \frac{1}{\sqrt{m}}\left(u_{00}\rho + \sum_i u_{i0} y_i\right)$$

Pollak *et al.* showed that, in the limit $N \to \infty$ the quantities of the problem which are actually relevant can be expressed in terms of the initial characteristics of the GLE (1). For instance, $\lambda^{\ddagger}$ becomes the Grote–Hynes frequency given by the implicit relation

$$\lambda^{\ddagger} = \sqrt{\frac{\hat{\gamma}^2(\lambda^{\ddagger})}{4} + \omega^{\ddagger 2}} - \frac{\hat{\gamma}(\lambda^{\ddagger})}{2} \tag{3}$$

($\hat{\gamma}(s)$ being the Laplace transform of $\gamma(t)$). Likewise, u_{00}, which is the weight of the unstable normal mode in x, becomes in the continuum limit

$$u_{00} = \frac{1}{\sqrt{\varepsilon + 1}} \qquad \text{with} \quad \varepsilon = \frac{1}{2}\left(\frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}} + \frac{d\hat{\gamma}}{ds}(\lambda^{\ddagger})\right)$$

What is the interest of such a transformation? In the vanishing ε limit, x and ρ are very similar. Therefore, when x goes from the reactant region

$x<0$ towards the product region $x>0$, the eigenmode ρ evolves from $\rho<0$ to $\rho>0$. However, there is a noticeable difference between these two descriptions, because the future behaviour of a particle at the saddle depends very much on the state of the thermal coordinates q_i and different cases can be observed: sharp crossing, slow diffusion, local oscillations due to a locally trapping effective potential, etc. But for the ρ mode, the vicinity of the separatrix $\rho=0$ is a domain where ρ is decoupled from the y_i because V_1 vanishes near the saddle. Then, Pollak *et al.* noticed that, if the unstable mode approaches the saddle at $\rho\lesssim 0$ with a velocity oriented towards the exit ($\dot\rho>0$), the trajectory becomes ballistic and the crossing is almost certain. The re-crossings are then forbidden, which is the great advantage of this description.

2.3. Statistics of the Unstable Mode

To obtain the reaction rate, one has to know the statistical properties of the ρ mode. It is convenient to follow the approach introduced by Kramers[1] and to consider a fictitious stationary regime obtained by injecting particles at the bottom of the well at constant flow that matches their escape rate. In this regime, the number $\mathcal{N}$ of particles remaining in the metastable region is constant, as well as the distribution function of the unstable mode $P_{\text{meta}}(\rho, \dot\rho)$, which is defined such that, in the metastable region, the proportion of particles being at position $\rho \pm d\rho/2$ and moving with a velocity $\dot\rho \pm d\dot\rho/2$ is $d\mathcal{N}/\mathcal{N} = P_{\text{meta}}(\rho, \dot\rho)\, d\rho\, d\dot\rho$. With this function, the reaction rate is simply

$$k = \int_0^\infty P_{\text{meta}}(\rho=0, \dot\rho)\, \dot\rho\, d\dot\rho$$

Note that this formula already takes into account the absence of re-crossings: $P_{\text{meta}}(0, \dot\rho<0)=0$. We can rewrite it as

$$k = \int_0^\infty P_{\text{meta}}(\rho=0, \sqrt{2E})\, dE \equiv \int_0^\infty f(E)\, dE$$

where $f(E)\, dE\, dt$, defined for $E>0$, can be interpreted as the likelihood for finding the particle between t and $t+dt$ at the saddle with an unstable mode energy (defined *a priori* by $E=\dot\rho^2/2 - \lambda^{\ddagger 2}\rho^2/2$) between E and $E+dE$. PGH define also the analogous quantity for the negative energies: for $E<0$, $f(E)\, dE\, dt$ is the likelihood for finding the particle at a turning point ($\dot\rho=0$) of his trajectory with (potential) energy E; one can see that

here $f(E) = P_{\text{meta}}(-\sqrt{-2E}/\lambda^{\ddagger}, \dot{\rho} = 0)$. This extension to negative energies will be explained in the following.

This description of the ρ process using energy variables is quite natural because the rate limiting process is the energy diffusion from stables modes y_i to the unstable one ρ: as soon as the ρ mode reaches the saddle energy, the reaction occurs with probability one. So, one has to evaluate this $f(E)$ to obtain the rate k. To do that, PGH introduce a master equation, which characterizes the stationarity of the process $\rho(t)$, and also assume the asymptotic form of that distribution. They propose the master equation

$$f(E) = \int_{-V^{\ddagger}}^{0} P(E \mid E')\, f(E')\, dE' \tag{4}$$

where $P(E \mid E')\, dE$ is defined as "the conditional probability that a system leaving the barrier region with energy E' in the ρ mode returns to the barrier with an energy between E and $E + dE$." In the same time they give the following limiting condition: when one considers particles located deep inside the well, having energies notably less than $-k_B T$, $f(E)$ must reach in that region its equilibrium value, i.e., the value that would be implied by an infinitely deep well. This value recalled by PGH is

$$f_{eq}(E) = \frac{\beta\omega_0}{2\pi} \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \exp(-\beta(E + V^{\ddagger}))$$

2.4. Solution for $f(E)$ and Calculation of the Reaction Rate

Writing (4), amounts to substituting an unknown quantity for another one, so we still have to precise $P(E \mid E')$ at least for energies near the saddle energy (far from the saddle $f(E)$ will be imposed by the limiting condition f_{eq}, so that it is sufficient to determine the conditional probability in the vicinity of the saddle region). This calculation, based on the microcanonical structure of the description—trajectories are solutions of the equations derived from the Zwanzig Hamiltonian—leads to[4]

$$P(E \mid E' \sim 0) = (4\pi k_B T \Delta E)^{-1/2} \exp\left(-\frac{(E - E' + \Delta E)^2}{4k_B T \Delta E}\right) \tag{5}$$

During an oscillation in the metastable well, the *typical* behaviour of the unstable mode is to lose a characteristic energy ΔE (always positive) given by[8]

$$\Delta E = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds\, g(s)\, \Re[\hat{K}(is)] \tag{6}$$

In this expression, $\hat{K}(s)$ is

$$\hat{K}(s) = \sum_{i=1}^{N} \frac{u_{i0}^2}{u_{00}^2} \frac{s}{s^2 + \lambda_i^2} \xrightarrow{N \to \infty} \frac{1}{u_{00}^2} \frac{s}{s^2 + s\hat{\gamma}(s) - \omega^{\ddagger 2}} - \frac{s}{s^2 - \lambda^{\ddagger 2}}$$

Moreover, $g(s)$ is given by

$$g(s) = \left| \int_{-\infty}^{\infty} dt\, e^{ist} u_{00} V_1'(u_{00} \rho_{as}(t)) \right|^2$$

where $\rho_{as}(t)$ is the asymptotic solution of

$$\ddot{\rho} - \lambda^{\ddagger 2} \rho = -u_{00} V_1'(u_{00}\rho) \qquad \text{with} \quad \rho(t) \leqslant 0,\ \rho(\pm\infty) = 0,\ \dot{\rho}(\pm\infty) = 0$$

i.e., we consider a trajectory starting at $\rho = 0$ with no initial velocity at time $t \to -\infty$ and coming back to the same state at $t \to +\infty$. Let us mention that it corresponds to a motion in an effective potential $Q(\rho) = V_1(u_{00}\rho/\sqrt{m}) - \lambda^{\ddagger 2}\rho^2/2$ with shape generally similar to that of $V(x)$ and a barrier height denoted by $Q^{\ddagger}$.

Once the kernel $P(E \mid E')$ is known one solves equation (4) taking into account the limiting condition $f(E) \to f_{eq}(E)$ at $E \to -\infty$ using the Wiener–Hopf method.[5] This gives the analytical PGH formula for the rate

$$k = \int_0^{\infty} f(E)\, dE = A \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \frac{\omega_0}{2\pi} e^{-\beta V^{\ddagger}} \tag{7}$$

where

$$A = \exp\left(\frac{2}{\pi} \int_0^{\infty} \frac{dy}{1 + y^2} \ln(1 - e^{-(\beta \Delta E)(1 + y^2)/4}) \right)$$

3. ABOUT THE MASTER EQUATION

In order to go beyond the PGH theory, it is necessary to examine in details its underlying assumptions; in particular, we think that the physical interpretation of Eq. (4) is not as obvious as it can appear.

First, one notes that the conditional probability $P(E \mid E')$ is related to a single isolated event, without any reference to the duration of oscillation, while a naive idea of stationarity should imply $P(E', t + t' \mid E, t) = P(E', t' \mid E, 0)$ instead of this absence of time in the propagator.

Second, much more questionable is the affirmation in ref. 4 that $P(E \mid E')$ obeys the detailed balance equation

$$P(E \mid E') \exp(-\beta E') = P(E' \mid E) \exp(-\beta E)$$

Indeed, the situation which is considered is essentially out of equilibrium, consequently not invariant by time reversal; therefore there is no reason *a priori* for $P(E \mid E')$ to follow the detailed balance equation, which is a statistical signature of the time-reversal symmetry.

To precise these two points of the PGH theory, it is useful to explain in details the underline methodology employed by PGH to extract relevant informations from the process $\rho(t)$, in spite of the complexity of its dynamics, by examining the statistics of the eigenmode ρ. When, at time $t=0$, a particle is placed in the bottom of the well, it is thermalised very quickly in comparison with the mean escape time k^{-1}; then the trajectory of $\rho(t)$ is confined in the $\rho<0$ region during a very long time (with respect to the characteristic times of the dynamics in the well), and exhibits a large number of turning points inside the well. Let us denote by t_n the times at which the velocity $\dot{\rho}$ vanishes and changes its sign. At these points, the (potential) energy in the unstable mode is $E_n \equiv -1/2\lambda^{\ddagger 2}\rho(t_n)^2$. Finally the particle reaches the saddle $\rho=0$ at a time t_f with an energy $E_f>0$ and the reaction occurs. We can then extract from the whole continuous process $\rho(t)$ a discrete series of energies $\{E_n = -1/2\lambda^{\ddagger 2}\rho(t_n)^2\}_n$ constructed with *all* the inner turning points of the trajectory considered plus the energy at the saddle (Fig. 2). This sequence of energies is finite but very long in the $k_B T \ll V^{\ddagger}$ limit. This is also a random process, and it is stationary as well as $\rho(t)$: after a negligible transient, the distribution function $R(E)$ of the E_n

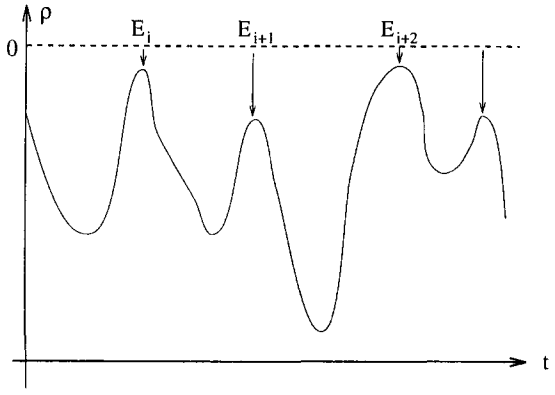

Fig. 2. The turning points of the unstable mode ρ define a discrete sequence of energies.

is independent of time ($R(E)\,dE$ is the probability that, given an "event"—that is, a turning-point or an arrival at the saddle—its energy is comprised in the domain $[E, E+dE]$; notice that $\int R(E)\,dE = 1$ on $[-V^{\ddagger}, \infty]$). On the other hand, it is clear that there are correlations between successive events: the $(n+1)$th event is strongly dependent on the nth one. As a result, the stationarity of the process is formally transcribed by

$$R(E_{n+1}) = \int_{-V^{\ddagger}}^{0} dE_n\, P(E_{n+1} \mid E_n) \frac{R(E_n)}{\mathscr{R}} \tag{8}$$

where

$$\mathscr{R} = \int_{-V^{\ddagger}}^{0} dE\, R(E)$$

In this master equation, the probability $P(E \mid E')$ is now naturally defined without any reference to the time, because it is simply the propagator from a turning point to the *next* event of the process $\{E_n\}$. Notice that this equation is very close to (4), except for the number $\mathscr{R}$, which is the normalisation imposed by the fact that all the particles that remain at a certain time come necessarily from the metastable region of the potential; notice that this normalisation is different from the one of $R(E)$ over the full range $[-V^{\ddagger}, \infty]$ of the energies accessible to the random sequence which is considered. If the well is deep, $\mathscr{R}$ is close to 1 and it is tempting to make this approximation and recover (4). Nevertheless, doing so, this amounts to imposing the unwanted result $\int_0^{\infty} R(E)\,dE = 0$. Then, to recover (4), we are at the same time compelled to make the integral of $R(E)$ divergent by throwing the left limit of the integral toward $-\infty$ ($R(E)$ itself diverges at $-\infty$). We see then that the change $V^{\ddagger} \to \infty$ is not only useful for applying simply the Wiener–Hopf technique, but is also *mandatory* to obtain a non-zero solution of (4). To conclude this paragraph, let us note that with this prescription, we would recover the same equation as PGH, because it is easy to verify that $R(E)$ and $f(E)$ are proportional.

Pollak *et al.* give an astute evaluation of the probability $P(E \mid E')$, which takes advantage of the microcanonical structure of the description, providing that the coupling between ρ and the stable modes y_i would be small enough (that is $\varepsilon \ll 1$): they consider a typical oscillation of the mode ρ, which begins near the saddle and evaluate the energy exchange between ρ and the y_i during this time. This transfer depends on the initial conditions $(y_i(0), \dot{y}_i(0))$ of all the stable modes, which are assumed to be random variables: one describes the initial conditions canonically, whereas the dynamics that follows is studied from the microcanonical point of view.

As a result, the energetic transfer is also a random variable, function of the $(y_i(0), \dot{y}_i(0))$.

Now, one has to give an ansatz for the distribution function of the $(y_i(0), \dot{y}_i(0))$, *knowing the unstable mode energy*. Pollak *et al.* choose an **equilibrium** distribution function independent of the ρ energy, i.e., $P(\{y_i, \dot{y}_i\}) \propto \Pi_i \exp(-\beta(\dot{y}_i^2 + \lambda_i^2 y_i^2)/2)$. This means implicitly that the calculation neglects the retroaction of ρ back on the thermalisation bath. Consequently, from the statistical point of view, the future behaviour of ρ depends only on the initial turning point energy E_1, and not on the previous ones: in other words, the $\{E_i\}$ process is supposed here to be *markovian*. This "weak" equilibrium hypothesis has a second consequence, which gives an answer to the second question we raised above: $P(E_2 \mid E_1)$ must now obey the detailed balance equation. Indeed, at any turning point, the whole system has kept no memory of the past, particularly no remembrance of the out-of-equilibrium situation: locally, i.e., from a turning point to another one, the statistical behaviour of the unstable mode is supposed to be the same as in an equilibrium context. Then it can be noticed that all the non-equilibrium characteristics are entirely contained in the structure of the master equation (through the integration restricted to the domain $E<0$).

4. MODIFIED PGH THEORY FOR STRONG CORRELATIONS

This markovian hypothesis, although never explicited in the original PGH paper, is *a priori* a very good approximation, and the numerical simulations showed often an excellent agreement in a vast range of parameters.[4] But we shall see that a violation of this assumption is possible for some situations that we shall identify, and that the problems previously noted by Reese and Tucker[8] correspond precisely to these situations.

4.1. Bath Correlation Time

Let us imagine that at $t=0$ the unstable mode undergoes a turning point with energy E_1 near the saddle ($E_1 \sim -k_B T$). At this time the stable modes y_i are supposed to have the initial conditions $\{y_i(0), \dot{y}_i(0)\}$. At a certain time later $\tilde{t}$, which actually is not infinite as the asymptotic trajectory ρ_{as} would imply (because E_1 is not strictly zero), the ρ mode undergoes a second turning point. During this time interval, the y_i modes oscillated in a parabolic well with frequency λ_i, each weakly perturbed by ρ. If their oscillation frequency is large in comparison with $1/\tilde{t}$, the y_i have made many oscillations, and therefore a little relative inaccuracy on

$\tilde{t}$ leads to a enormous change of $(y_i(\tilde{t}),\ \dot{y}_i(\tilde{t}))$; for such modes, we expect that correlations between their motion and that of ρ cannot grow. On the other hand, if λ_i is of the same order of magnitude as, or smaller than, $1/\tilde{t}$, the stable mode partly keeps a remembrance of the initial energy after an oscillation; the variables $y_i(\tilde{t})$ and E_1 are then significantly correlated with respect to the distribution of the $\{y_i(0),\ \dot{y}_i(0)\}$.

As a result, if a large proportion of the stable modes belongs to the first case ($\lambda_i \gg 1/\tilde{t}$), we have a decorrelated situation for which the PGH ansatz is very well adapted. But, if most of the y_i are in the $\lambda_i \lesssim 1/\tilde{t}$ domain, then some discrepancies would possibly be observed. We expect then that the relevant quantity governing the corrections is related to the proportion of low frequency modes in the bath.

4.2. Non Markovian Master Equation

These correlations act on the function $P(E_2 \mid E_1)$. It would be nice if we could calculate this kernel, taking into account explicitly their effect by a self-consistent choice of the stable modes distribution. This task is probably difficult to achieve, and we adopted another line of reasoning.

The PGH master equation is not the unique one adapted to express the stationarity of the process. We can also imagine a more complicated form, which explicits a possible memory: denoting by $R(E_n, E_{n-1},..., E_1)$ the likelihood for observing the turning points $E_1, E_2,..., E_n$ in succession, the stationarity can also be written

$$R(E_n, E_{n-1},..., E_1) = \frac{1}{\mathscr{R}_n} \int_{-V^\ddagger}^{0} dE_0\, P(E_n \mid E_{n-1},..., E_0)\, R(E_{n-1}, E_{n-2},..., E_0)$$

with the normalisation constant $\mathscr{R}_n = \int_{-V^\ddagger}^{0} dE_n \cdots dE_1\, R(E_n,..., E_1)$ (concerning this number, the same remark as for $\mathscr{R}$ above, is also valid here). With this formal equation, we express directly the possible correlations; for instance if we know that $P(E_n \mid E_{n-1},..., E_1)$ depends in fact only on the first two energies E_n and E_{n-1}, we can claim that the PGH is valid in that case. Of course, we first tried the simplest generalisation

$$R(E_2, E_1) = \int_{-\infty}^{0} dE_0\, P(E_2 \mid E_1, E_0)\, R(E_1, E_0)$$

which is well suitable for correlations inefficient beyond two turning points. This equation can also be expressed as

$$R(E_2) = \int_{-\infty}^{0} dE_0\, dE_1\, P(E_2 \mid E_1, E_0)\, P(E_1 \mid E_0)\, R(E_0) \tag{9}$$

which turns it into an implicit equation for the one-variable function $R(E)$. The probability $P(E_1 \mid E_0)$ is formally the same as the kernel in the one-step master equation of PGH (Eq. (4)). Therefore, a good approximation is obtained by choosing for $P(E_1 \mid E_0)$ the PGH formula (5). Moreover, the limiting condition for $R(E)$ is the same as before:

$$R(E) \xrightarrow{E \to \infty} \beta \exp(-\beta E)$$

There is now a new unknown quantity $P(E_2 \mid E_1, E_0)$ that we have calculated following the same method as PGH (cf. Appendix). Consequently, we have the same restrictions concerning the validity of the formula: for instance, we must have $2\Delta E \ll Q^{\ddagger}$ in principle. Moreover, we emphasize that this kernel is still calculated in an equilibrium context, but nevertheless we claim that the result is an improvement of the theory because more informations concerning both the correlations and the out-of-equilibrium situation are given. The result for $P(E_2 \mid E_1, E_0)$ is

$$P(E_2 \mid E_1, E_0) = \frac{1}{\sqrt{4\pi \Delta E k_B T}} \frac{1}{\sqrt{1-\zeta^2}} \times \exp\left\{ -\frac{1}{4k_B T \Delta E} \frac{(E_2 - E_1 + \Delta E - \zeta \times (E_1 - E_0 - \Delta E))^2}{1-\zeta^2} \right\} \tag{10}$$

and shows an additional quantity ζ:

$$\zeta[(t_0 + t_1)/2] = \frac{\int_{-\infty}^{+\infty} ds\, g(s)\, \Re[\hat{K}(is)] \cos[s(t_0 + t_1)/2]}{\int_{-\infty}^{+\infty} ds\, g(s)\, \Re[\hat{K}(is)]} \tag{11}$$

which is in fact a symmetric function of E_0 and E_1 via t_0 and t_1, which are the oscillation times from E_0 to E_1 and from E_1 to E_2 respectively. We can remark that the $\zeta \to 0$ limit corresponds to the PGH theory, so that the value of ζ quantifies the role of the correlations. Moreover, in that function we recover quantitatively the qualitative arguments that we pointed out in the preceding paragraph: its magnitude near the saddle is controlled by the relative proportion of the low frequency modes (in comparison with $1/\tilde{t}$).

But if one looks carefully at ζ, one sees that just at the saddle $E = 0$, the oscillation time is infinite, leading to $\zeta = 0$ because it contains the integral over s of a fast oscillating terms. Then it is tempting to make the approximation $\zeta = 0$, and retrieve the PGH theory. But one should not to do so, because, as the saddle is an unstable equilibrium, the oscillation time varies very much with the initial energy, and falls very quickly down to

rather small values. More precisely, we can write this oscillation time t_0 (function of the initial energy E_0 of the mode) as

$$t_0 \sim \frac{2}{\lambda^\ddagger} \operatorname{arg\,cosh}\left(\sqrt{\frac{E^*}{E_0}}\right) + t_p \overset{E_0 \lesssim 0}{\sim} \frac{1}{\lambda^\ddagger} \ln \frac{4E^*}{E_0}$$

where E^* is the characteristic energy so that the inverted parabolic approximation is no longer valid for energies below it, and t_p is the characteristic time for oscillations in the *bottom* of the well of $Q(\rho)$. So, t_0 diverges logarithmically, then despite $\zeta = 0$ exactly at the saddle, it can possibly reach substantial values for very small values of the initial energy (small in comparison with $k_B T$). This phenomenon can also be viewed noticing that for (E_0, E_1) both very small we have

$$\zeta \sim (E_0 E_1)^\nu$$

where the exponent ν can be much less than one. Finally we expect ζ to be negative near the saddle, due to the positive slope of $g(s)\,\Re[\hat{K}(is)]$ at $s = 0$.

These remarks are illustrated on the Fig. 3, for different cases (the justification of the choice of these particular cases is discussed below) and

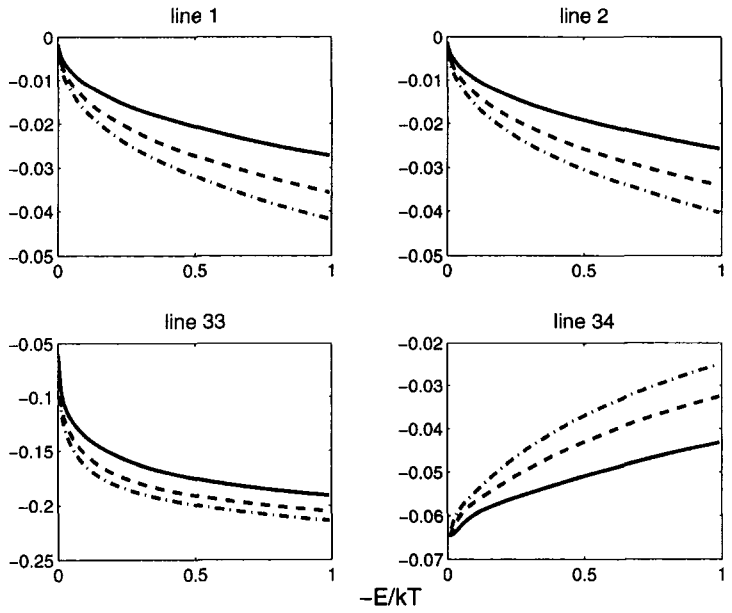

Fig. 3. Shape of $\zeta(E_1, E_0)$ for several lines of the Table I in PGH's paper. For each line one plots the function for several values of E_0: $\beta E_0 = -0.5, -1.0, -1.5$ correspond respectively to the full line, dashed, and dash-dotted lines.

for the model considered by PGH in their paper (Fig. 6 below is analogous for Reese and Tucker's model). One notes also that in the saddle region $E_0, E_1 \sim k_B T$, ζ can be considered raisonnably as constant (except the initial and negligible transient). Assuming the irrelevance of the precise value of ζ far from the saddle, it led us to solve the master equation (9) with a constant ζ.

4.3. Numerical Resolution of the Master Equation and Results

Knowing $P(E_2 \mid E_1, E_0)$ from Eq. (10), the master equation (9) is completely defined. As discussed previously, it is reasonable to consider ζ as a constant which already brings a significant simplification. However, this approximation is not sufficient to allow us to solve Eq. (9) analytically because the integral equation is no longer of the Wiener–Hopf type. The kernel is indeed now

$$K(E_2, E_0) \equiv \int_{-\infty}^{0} dE_1 \, P(E_2 \mid E_1, E_0) \, P(E_1 \mid E_0)$$

$$= \frac{1}{2\sqrt{8\pi k_B T \Delta E(1+\zeta)}} \exp\left(-\frac{(E_2 - E_0 + 2\Delta E(1+\zeta))^2}{8 k_B T \Delta E(1+\zeta)} \right)$$

$$\times \operatorname{erfc}\left(\frac{E_2 + E_0 + 2\Delta E\zeta}{\sqrt{8 k_B T \Delta E(1-\zeta)}} \right)$$

and is clearly not of the form $K(E_2 - E_0)$. So we solved it numerically by successive iterations. This procedure gives good numerical convergence if the kernel is first symmetrised and if the asymptotic divergence of the solution is expressed apart. Figure 4 shows how the prefactor A of the reaction rate in Eq. (7) is modified with increasing $|\zeta|$. The combined role of correlations and out of equilibrium situation that bias the energy distribution toward lower values tend to reduce the mean energy exchange with the bath when successive turning points are considered (ΔE replaced by $\Delta E_{\text{eff}} = \Delta E(1 + 2\zeta)$). The leading consequence is a decrease of reaction rate as one could qualitatively retrieve from the PGH expression with a reduced ΔE.

With these results, we are now able to analyse the possible role played by the correlations in the examples studied in the papers of refs. 4 and 8.

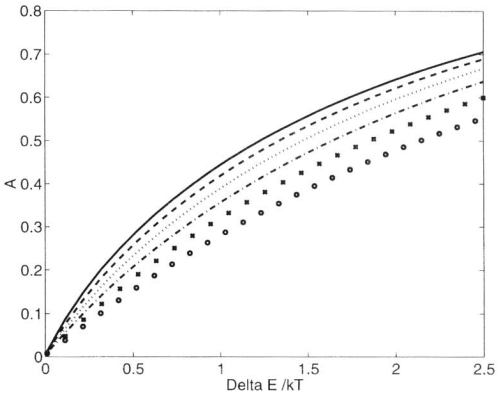

Fig. 4. Variation of the prefactor $A(\beta\Delta E)$ with respect to ζ; $\zeta = 0$ (plain), $\zeta = -0.1$ (dashed), $\zeta = -0.2$ (dotted), $\zeta = -0.3$ (dash-dotted), $\zeta = -0.4$ (stars), $\zeta = -0.5$ (circles).

4.3.1. Numerical Results for the PGH Examples. The kernel considered by these authors is the exponential $\gamma(t) = \alpha^{-1} \exp(-t/\alpha\gamma)$. This function corresponds to a density of modes[8]

$$\Re[\hat{K}(is)] \propto \frac{s^2}{(\omega^{\ddagger 2} + s^2)^2 + \gamma^2 s^2 (1 - \alpha(\omega^{\ddagger 2} + s^2))^2}$$

The potential used was piecewise parabolic and imposes the function $g(s)$:

$$g(s) \propto \frac{1}{(\lambda_0^2 - s^2)^2} \left(\frac{\lambda_0^2}{s} \sin(st_p/2) - \lambda^{\ddagger} \cos(st_p/2) \right)^2$$

where $\lambda_0^2 = u_{00}^2(\omega_0^2 + \omega^{\ddagger 2}) - \lambda^{\ddagger 2}$ and $\lambda_0 t_p = \pi + \arccos[(\lambda_0^2 - \lambda^{\ddagger 2})/(\lambda_0^2 + \lambda^{\ddagger 2})]$ (this example was previously numerically studied by Straub *et al.*[9]).

Among the 36 different cases gathered in the Table I of the PGH paper (p. 4083), two of them are of particular interest because they present discrepancies between the theoretical and numerical results which are not at all expected. They are the cases labeled 33 and 34. Indeed the perturbation parameter ε is very small in these cases ($4.2\ 10^{-3}$ and $7.8\ 10^{-4}$ respectively), and moreover the energy transfer is small enough in comparison with $Q^{\ddagger}$ (0.6 and 0.1 to be compared with 20). Consequently these discrepancies were originally ascribed by Pollak *et al.* to mistakes in the numerics.

But Reese and Tucker also met such failures in an other model, for situations very similar to the 33 and 34th cases of PGH (and first suggested that they were probably not due to numerical inaccuracies): all

of them correspond to a weak static friction $\int \gamma(t)\,dt$ and a long persistence time $\alpha\gamma$ of the kernel. We show now that the explanation of these failures lies in the existence of non-negligible correlations in the sequence $\{E_i\}$:

For the line 33, the PGH theory overestimates the rate with a factor between 1.17 and 1.59. On the other hand, from Fig. 3, we see that the appropriate value for ζ is ~ -0.2 for this case. We find a correction factor $A_{\zeta=0}/A_{\zeta=-0.2} = 1.19$, which is in the proper range [1.1754, 1.5909] though close to the minimum.

The case 34 is not so accurate: the overestimation factor of PGH is large, between [1.45,1.85]. But the corresponding ζ is only -0.05 much too less to correct the rate enough, giving a factor 1.07 only. Why is it so? Let us remember the hypothesis of quite short correlations (not extended beyond two correlations) that we made and let us look at the characteristic times of the kernels in both cases: for line 33, $\alpha\gamma = 2.5/\omega^\ddagger$, and the typical oscillation time is $1/\lambda^\ddagger \sim 1/\omega^\ddagger$; here our hypothesis is rather well verified. But the case 34 corresponds to a time extension of $\gamma(t)$ *ten times larger*, for a same geometry. It is then clear now why the result based on $P(E_2 \mid E_1, E_0)$ only is here so inaccurate: we would need much more than two steps of correlations to retrieve the overestimation factor quantitatively.

To confirm this analysis, we calculated the probability $P(E_3 \mid E_2, E_1, E_0)$ following the same procedure as for $P(E_2 \mid E_1, E_0)$, which is valid near the saddle and for energy transfers such that $3\Delta E \ll Q^\ddagger$ (this is very well fulfilled in this case 34 where $\Delta E \sim 0.1$ and $Q^\ddagger \sim 20$). The result (to first order in ζ) is

$$P(E_3 \mid E_2, E_1, E_0) = \frac{1}{\sqrt{4\pi\Delta E k_B T}} \times \exp\left\{ -\frac{(E_3 - E_2 + \Delta E - \zeta \times (E_2 - E_1 - \Delta E) - \tilde{\zeta} \times (E_1 - E_0 - \Delta E))^2}{4k_B T \Delta E} \right\}$$

with $\tilde{\zeta} = \zeta[(t_0 + 2t_1 + t_2)/2] \sim \zeta[2\tilde{t}]$. This result is interesting, because it shows that this probability is not necessarily of second order in ζ with respect to the preceding one, but gives instead a new parameter $\tilde{\zeta}$, which is not necessarily negligible in comparison with ζ. And indeed, in the case 34 for instance, the function $\zeta(t)$ (cf. Eq. (11) and Fig. 5) tends very very slowly to zero and stays for a very long time around -0.05. For a particle starting at the energy $E = -k_B T/2$, the oscillation time $\tilde{t}$ is approximately $(1 + \ln(160))/\lambda^\ddagger \sim 6/\lambda^\ddagger$ and one verifies on Fig. 5 that $\zeta \equiv \zeta(\tilde{t}) \approx \tilde{\zeta} \equiv \zeta(2\tilde{t}) \approx \zeta(3\tilde{t}) \approx -0.05$. It confirms that in that case the correlations extend very far (at least half a dozen turning points or so). As a result, if we would like to

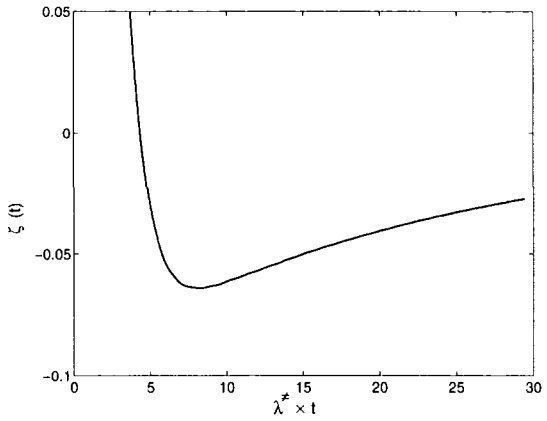

Fig. 5. Shape of $\zeta(t)$ for line 34 of Table I in PGH.

calculate the rate to a good accuracy here, we would have to solve a master equation with a great number of correlation steps explicitly expressed, a complicated task indeed. Nevertheless one still remarks that the 3-steps correlation theory induces a change of the mean energy transfer $\Delta E \to (1+2(\zeta+\tilde{\zeta}))\times \Delta E$, which shows that this second correction is again in the right direction (this qualitative argument is however quite rough, because the width of the gaussian in P is not renormalised; in particular, it forbids an approximate resolution of the master equation based on such an ansatz).

So, it is interesting to note that $\zeta \approx \zeta(\tilde{t})$ is not the right quantity to characterise the effects of correlations, but rather the sum

$$\mathscr{S} = \sum_{n \geqslant 1} \zeta(n\tilde{t})$$

The cases 33 and 34 correspond to two different situations where this sum is not negligible: in one case, the friction is weak and the correlation time is not too extended, leading to a substantial value of $\mathscr{S}$ made by only a few terms. In the other case, the friction is stronger, which reduces *a priori* the strength of correlations (and then each $\zeta(n\tilde{t})$), but these are much further extended, implying a significant value of $\mathscr{S}$, despite the little individual contribution of each term of the sum.

We have analysed here some cases for which the PGH theory fails. It is suitable to discuss also the reason why it does work in many cases. For instance it can be seen from Fig. 3 that for the lines 1 and 2 of Table I in PGH, the value of ζ is minute; according to our approach we expect a good validity of the PGH theory. This is indeed what they observed.

The common feature of the cases 3 and 7 is the great mean energy loss $\beta\Delta E$: 13.98 and 17.22 respectively. In these cases, the Grote–Hynes formula $k = \lambda^{\ddagger}\omega_0/(2\pi\omega^{\ddagger}) \exp(-\beta V^{\ddagger})$ gives the correct result (as well as the PGH formula for $A \sim 1$), because a particle starting from the top of the barrier transfers its energy very efficiently to the y_i in the bottom. Then we do not expect the correlations between two turning points occurring in the neighbourhood of the saddle to be present (but it would be perhaps possible to imagine "strange" memory kernels for which we could have both $\beta\Delta E \gg 1$ and efficient correlations nevertheless). Anyway, the correction presented here is not appropriate in these cases, because the approximation we used for the conditional probability imposes a small ΔE.

Lines 14 and 15 in PGH table give a ζ completely negligible ($\sim 10^{-3}$), due to the fact that the oscillation time near the saddle t_0 is dominated by the oscillation time in the bottom, $t_p \propto 1/\lambda_0$, which is huge. But there are noticeable discrepancies between simulation and theory, with a prediction *too* slow in comparison with the experiment. As a result, these inaccuracies are not an evidence for the presence of correlations; the explanation lies probably rather in the neglected anharmonicity of the potential (the barrier are in these cases almost "cusp-shaped").

We have not considered the other lines because the remaining cases have a renormalised barrier height $Q^{\ddagger}$ very different from the original barrier height $V^{\ddagger}$, and Reese and Tucker showed that the trajectory $\rho_{as}(t)$ is a bad ansatz for the effective typical asymptotic trajectory and in these cases we should use their theory cPGH to calculate $g(s)$ properly.

4.3.2. Numerical Results from Reese and Tucker's Example. In ref. 8, Reese and Tucker compared their theory with numerical simulations made with a ϕ^3 potential and with the same exponential kernel as PGH. For this geometry

$$g(s) \propto \left(\frac{(s/\lambda^{\ddagger})[(s/\lambda^{\ddagger})^2 + 1]}{\sinh(\pi s/\lambda^{\ddagger})} \right)^2$$

Moreover, the oscillation time in the renormalised potential $Q(\rho)$ is an elliptic integral, with, as before, a logarithmically divergent behaviour at the saddle:

$$t(E) \sim \frac{2}{\lambda^{\ddagger}} \log \frac{16\lambda^{\ddagger 3}}{u_{00}^3 \sqrt{-2E}}$$

(we recall that E is the energy at the onset of the oscillation, with the convention that the saddle is at $E = 0$). The calculation of ζ is made with these

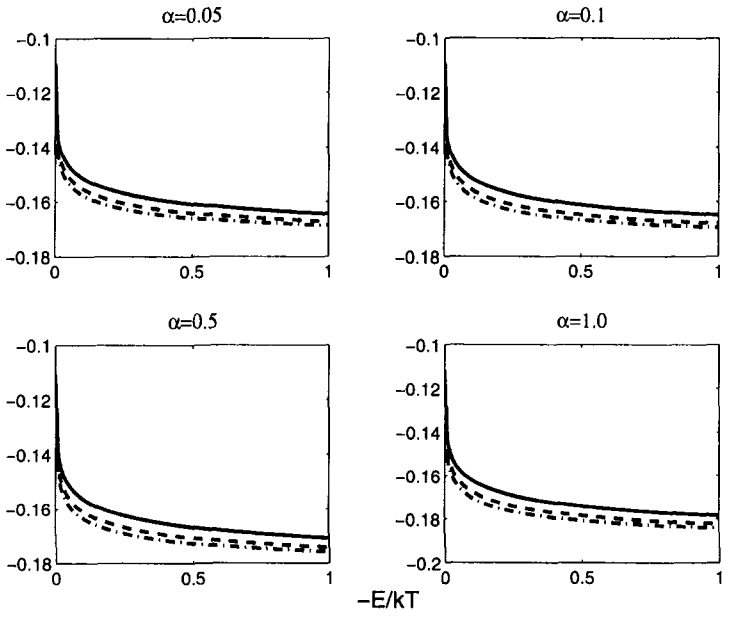

Fig. 6. Shape of $\zeta(E_1, E_0)$ for the four first lines of the Table I in the Reese and Tucker's paper.[8] For each line one plots the function for several values of E_0: $\beta E_0 = -0.5, -1.0, -1.5$ correspond respectively to the full line, dashed, and dash-dotted lines.

functions, and the results are plotted in Fig. 6 (we have not considered the cases $\gamma \geqslant 7$, because in these situations the renormalised barrier height $Q^{\ddagger}$ is less than $k_B T$, and we should imperatively take into account the cPGH corrections). $|\zeta|$ is clearly always greater than 0.15, a piece of evidence for existing correlations.

The four first lines of the Table I in the R&T paper show discrepancies between the PGH theory and the simulations, characterised by the factors 2, 1.55, 1.29, 1.12 respectively. The resolution of the 2-steps master equation with the corresponding ζ's gives correction factors 1.6, 1.27, 1.18, 1.07, which are better, but quantitatively not very satisfactorily (we should have 1 instead!). The explanation lies as well as before in the fact that the extension of $\gamma(t)$ is here chosen to be of order 10, whereas the characteristic oscillation lasts about π: this involves efficient correlations till probably the fourth step in the sequence. The other lines were not investigated because for these cases, the barrier height is strongly renormalised, what imposes *a priori* to take into account the curvilinear corrections calculated by Reese and Tucker.

5. CONCLUSION

We showed that the few situations for which the PGH theory seems not to hold and predicts incorrect rates contradict the implicit hypothesis made by Pollak *et al.*: we can call it "weak markovian" hypothesis because the calculation of $P(E \mid E')$ assuming the equilibrium of the bath *plus* the unstable mode is equivalent to assume that the discrete sequence of turning point energies is markovian. Although this condition is almost always fulfilled, the discrepancies observed, which correspond to a small static friction but large time extension of the friction kernel (with respect to a mean duration of an oscillation beginning in the vicinity of the saddle, say with energy $\sim -k_B T$) exhibits precisely such anomalous long correlations.

We proposed a slight modification of the PGH theory in order to treat properly these cases, by substituting to the PGH master equation another equation, formally equivalent but including explicitly more information about the correlations (and consequently more complicated).

The numerical resolution of this new equation becomes very arduous when the required number of correlations increases and we were able to calculate the correction implied by only one additional correlation step. Unfortunately, we noticed that the correction induced by this 2-steps theory is generally quite smaller than the observed deviations, due to the fact that substantial deviations are obtained with intensive correlations, for which the 2-steps approximation is generally not sufficient. Furthermore, we noticed that some "extreme" situations correspond to locally weak correlations extending over a great amount of turning points. Such ones are naturally described by master equations involving a large number of successive steps, and are therefore almost impossible to treat. But the physical relevance of such extraordinary bath correlation times is questionable, insofar as usually the memory of the bath does not exceed too much the typical times of the dynamics of the brownian particle.

On the other hand, the situations for which the characteristic times of the potential $V(x)$ and that of the memory kernel are of the same order, leading to possible non-markovian behaviour, are certainly of physical interest and could be encountered in biological environments for which reactions sometimes occur on small sites located on large biological molecules or walls, who act on the dynamics of the reaction like coloured noise with a time extension at most of the same order than the characteristic time of the particle in its well.

APPENDIX: CALCULATION OF $P(E_2 \mid E_1, E_0)$ IN THE LIMIT $\epsilon \ll 1$

In the following, we assume that the condition $\varepsilon \ll 1$ is fulfilled.

We want to calculate the conditional probability, knowing that at $t = 0$ the unstable mode ρ undergoes a turning point with energy E_0 *and*

that the one just afterwards occurs with an energy E_1 (after a time denoted t_0 but not imposed), that the third event occur with energy E_2 ($E_2 < 0$ corresponds to a turning point, $E_2 > 0$ corresponds to a crossing over). The time of this latter is denoted $t_0 + t_1$. Let us stress that these times does not represent any constraint in the probability, the only one being that the three events occur successively.

What is the dynamics of the degrees of freedom in our system? The description is microcanonical, so that the evolution equations derive simply from the Zwanzig's Hamiltonian (2):

$$\ddot{\rho} - \lambda^{\ddagger 2}\rho = -u_{00} W$$

$$\ddot{y}_i + \lambda_i^2 y_i = -u_{i0} W$$

with

$$W = \frac{1}{\sqrt{m}} V_1' \left[\left(u_{00}\rho + \sum_{i=1}^{N} u_{i0} y_i \right) \Big/ \sqrt{m} \right]$$

As u_{i0}/u_{00} is of order $\sqrt{\varepsilon/N}$, at the lower order we have

$$W \approx \frac{1}{\sqrt{m}} V_1'(u_{00}\rho/\sqrt{m})$$

So, the dynamical equations are

$$\ddot{\rho} - \lambda^{\ddagger 2}\rho = -\frac{u_{00}}{\sqrt{m}} V_1'(u_{00}\rho/\sqrt{m}) \tag{12}$$

$$\ddot{y}_i + \lambda_i^2 y_i = -\frac{u_{i0}}{\sqrt{m}} V_1'(u_{00}\rho/\sqrt{m}) \tag{13}$$

We notice that Eq. (12) for ρ is decoupled from the stable modes and corresponds to the free oscillation of ρ in the effective potential $Q(\rho)$ already mentioned. We call $\rho(E_0, t)$ the solution for a mode starting at $t = 0$ with a zero velocity at the point ρ_0 defined by $E_0 = -1/2\lambda^{\ddagger 2}\rho_0^2$. We stress that this energy E_0 is not the one associated with the conserved quantity $1/2\dot{\rho}^2 + Q(\rho)$, but the part of the global hamiltonian $\mathcal{H}$ related to the unstable mode: $E_\rho = 1/2\dot{\rho}^2 - 1/2\lambda^{\ddagger 2}\rho^2$. The duration t_0 of the oscillation is a function of E_0. With this notation, the asymptotic trajectory $\rho_{as}(t)$ defined above corresponds to $\rho(E = 0, t)$ (the corresponding t_0 being here infinite).

As, in this approximation, the ρ mode comes back to its starting point after an oscillation, it seems that its energy remains unchanged. But (12) is only used to calculate the trajectory $\rho(t)$; to get the energy loss of the mode, we have to solve the equations (13) for the modes y_i. They are very simple (forced oscillators) and we have[4]

$$y_i(t) = y_i(0)\cos(\lambda_i t) + \dot{y}_i(0)\frac{\sin(\lambda_i t)}{\lambda_i} + \int_0^t dt' \frac{\sin[\lambda_i(t-t')]}{\lambda_i} g_i F(E_0, t')$$

$$= y_i(0)\cos(\lambda_i t) + \dot{y}_i(0)\frac{\sin(\lambda_i t)}{\lambda_i} + \frac{1}{\lambda_i}\eta_i(E_0, t)\sin(\lambda_i t/2)$$

$$-(g_i/\lambda_i)\cos(\lambda_i t/2)\int_{-t/2}^{t/2} dt' \sin(\lambda_i t')\, F(E_0, t' + t/2) \tag{14}$$

$$\dot{y}_i(t) = -\lambda_i y_i(0)\sin(\lambda_i t) + \dot{y}_i(0)\cos(\lambda_i t) + \int_0^t dt' \cos[\lambda_i(t-t')]\, g_i F(E_0, t')$$

$$= -\lambda_i y_i(0)\sin(\lambda_i t) + \dot{y}_i(0)\cos(\lambda_i t) + \eta_i(E_0, t)\cos(\lambda_i t/2)$$

$$+ g_i \sin(\lambda_i t/2)\int_{-t/2}^{t/2} dt' \sin(\lambda_i t')\, F(E_0, t' + t/2) \tag{15}$$

In this equations we have defined

$$F(E_0, t) = -\frac{u_{00}}{\sqrt{m}} V_1'(u_{00}\rho(E_0, t)/\sqrt{m})$$

$$g_i = u_{i0}/u_{00} \sim \sqrt{\varepsilon/N}$$

$$\eta_i(E_0, t) = g_i \int_{-t/2}^{t/2} dt' \cos(\lambda_i t')\, F(E_0, t' + t/2)$$

Let us also note that the last integrals of (14) and (14) are zero if time t is the time t_0 of the next turning point; moreover, the variation of $\eta_i(E_0, t_0)$ with respect to E_0 is slow in a large interval around the saddle, so that we will use its asymptotic value $\eta_i \equiv \eta(E=0, t=\infty)$ in the following.

At this time $t = t_0$, (14) and (15) can be rewritten in a condensed and practical manner: if one defines

$$\vec{Y}(t_0) = {}^t(\lambda_1 y_1(t_0),\ \dot{y}_1(t_0),\ \lambda_2 y_2(t_0),\ \dot{y}_2(t_0),\ldots,\ \lambda_N y_N(t_0),\ \dot{y}_N(t_0))$$

and

$$\vec{\chi}(t) = {}^t(\eta_1 \sin\lambda_1 t/2,\ \eta_1 \cos\lambda_1 t/2,\ldots,\ \eta_N \sin\lambda_N t/2,\ \eta_N \cos\lambda_N t/2)$$

we have

$$\vec{Y}(t_0) = U(t_0)\ \vec{Y}(0) + \vec{\chi}(t_0) \tag{16}$$

where $U(t)$ is an orthogonal evolution matrix, block diagonal with the 2×2 matrices

$$\begin{pmatrix} \cos(\lambda_i t) & \sin(\lambda_i t) \\ -\sin(\lambda_i t) & \cos(\lambda_i t) \end{pmatrix}_i$$

in the diagonal. It verifies the properties $U(t_0 + t_1) = U(t_0)\ U(t_1)$ and ${}^tU(t) = U(t)^{-1} = U(-t)$. We have also the relation $U(t)\ \vec{\chi}(t') = \vec{\chi}(2t + t')$.

With these notations, the initial conditions of the thermal modes are simply $\vec{Y}(0)$ and the energy at time t of all these modes $E_{\text{modes}}(t) = \sum_i (\dot{y}_i^2 + \lambda_i^2 y_i^2)/2$ is just $\| \vec{Y}(t) \|^2/2$. Likewise, we have that $2\Delta E = \| \vec{\chi}(t_0) \|^2 = \sum_i \eta_i^2$, where ΔE is the PGH formula (6).

Then, if one considers the norms in Eq. (16), one finds

$$E_{\text{modes}}(t_0) = E_{\text{modes}}(0) + \Delta E + \vec{\chi}(-t_0).\vec{Y}(0)$$

(This is only a condensed rewriting of Eq. (3.21) in ref. 4). On the other hand, we know that the entire energy $\mathscr{H} = E_\rho + E_{\text{modes}} + V_1$ is preserved. It follows that, if the energy of ρ is E_0 at the onset of the oscillation (at $t = 0$) and the corresponding energy at the end of the same oscillation is labeled by E_1 (at $t = t_0$), we have

$$E_1 = E_0 - \Delta E - \vec{\chi}(-t_0).\vec{Y}(0) - \{ V_1(x(t = t_0)) - V_1(x(t = 0)) \} \tag{17}$$

For an oscillation beginning in the very neighbouring of the saddle, and ending also in that region, the interaction term (with V_1) does not contribute; that is the reason why the authors of PGH theory neglected it; we will also neglect it for clarity (it would correspond to a anharmonicity correction). We mention that we could in principle handle the calculation with that term, because in the limit $\varepsilon \ll 1$, it becomes linear with respect to the y_i:

$$V_1(x(t = t_0)) - V_1(x(t = 0)) \approx \frac{1}{\sqrt{m}} \left(\sum_i u_{i0}(y_i(t_0) - y_i(0)) \right) V_1'(u_{00}\rho(E_0)/\sqrt{m})$$

So, at $t = 0$, the unstable mode leaves the saddle with the energy E_0, comes back at time t_0 with energy E_1 given by the expression above. If the

mode leaves again for a next journey in the depth of the well, it is easy to see that its energy of *second* turning point E_2 is related to E_1 in a similar way as (17), that is

$$E_2 = E_1 - \Delta E - \vec{\chi}(-t_1).\vec{Y}(t_0) - \{V_1(x(t=t_1)) - V_1(x(t=t_0))\}$$
$$\sim E_1 - \Delta E - \vec{\chi}(-t_1).\vec{Y}(t_0)$$

where $t_1(E_1)$ is the duration of the second trip. Equation (16) leads to

$$E_2 = E_1 - \Delta E - \vec{\chi}(-t_1).\vec{\chi}(t_0) - \vec{\chi}(-2t_0 - t_1).\vec{Y}(0)$$

Let us note that the characteristic energy transfer ΔE is here the same as for the first oscillation, which is consistent in the approximations: $\varepsilon \ll 1$ and $\Delta E \sim$ constant in the saddle region.

The energy E_2 is then a random variable which depends linearly dependent on the $y_i(0)$ and $\dot{y}_i(0)$ assumed to be at the equilibrium at the initial time, namely $\lambda_i^2 \langle y_i^2(0) \rangle = \langle \dot{y}_i^2(0) \rangle = k_B T$ and $\langle y_i(0) \rangle = \langle \dot{y}_i(0) \rangle = \langle y_i(0)\, \dot{y}_i(0) \rangle = 0$. But these random variables are constrained in the calculation of the probability over E_2 we look for, because we must take into account the imposed energies E_0 and E_1. So a particular sample of the modes $(y_i(0), \dot{y}_i(0))$ (or of the vector $\vec{Y}(0)$) must fulfill the constraint (17), which is an information considered as known.

As a result, $P(E_2 \mid E_1, E_0)$ is given by a measure over a subspace of the entire phase space imposed by these constraints:

$$P(E_2 \mid E_1, E_0) = \frac{\int d\vec{Y}\, e^{-\beta(\vec{Y}.\vec{Y})/2}\, \delta(w_0 - \vec{\chi}(-t_0).\vec{Y})\, \delta(w_1 - \vec{\chi}(-2t_0 - t_1).\vec{Y})}{\int d\vec{Y}\, e^{-\beta(\vec{Y}.\vec{Y})/2}\, \delta(w_0 - \vec{\chi}(-t_0).\vec{Y})} \tag{18}$$

with the definitions $w_0 = E_0 - E_1 - \Delta E$ and $w_1 = E_1 - E_2 - \Delta E_1 - \vec{\chi}(-t_1).\vec{\chi}(t_0)$.

This integral is gaussian and then can be explicitly evaluated; by means of

$$\vec{\chi}(-t_0).\vec{\chi}(-2t_0 - t_1) = \sum_i \eta_i^2 \cos\left(\lambda_i \frac{t_0 + t_1}{2}\right)$$

we have finally

$$P(E_2 \mid E_1, E_0) = \frac{1}{\sqrt{4\pi \Delta E k_B T}} \frac{1}{\sqrt{1 - \zeta^2}}$$
$$\times \exp\left\{ -\frac{1}{4k_B T \Delta E} \frac{(E_2 - E_1 + \Delta E - \zeta \times (E_1 - E_0 - \Delta E))^2}{1 - \zeta^2} \right\}$$

where

$$\zeta = \sum_i \eta_i^2 \cos\left(\lambda_i \frac{t_0 + t_1}{2}\right) \Big/ \sum_i \eta_i^2$$

This ζ becomes (11) when $N \to \infty$.

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