ON ESCAPE RATES IN SYSTEMS WITH MEMORY EFFECTS

Peter HÄNGGI
Department of Physics, Polytechnic Institute of New York, 333 Jay Street, Brooklyn, NY 11201, USA

We note that the result of the thermal activation rate in presence of non-markovian damping, given in a recent treatment by Guardia, Marchesoni and San Miguel, is generally not uniquely defined. We also clarify the connection with previous work and show that the modelling of the memory kernel used by Guardia et al. is subjected to restrictions which are generally not met.

The study of non-markovian effects on the escape rates in equilibrium systems has attracted attention among various research groups [1–5]. The approach to the activated escape rate is based on the model of the non-markovian equilibrium dynamics of a brownian particle in a potential field $U(x)$. With a unit mass, the linearized dynamics around the barrier top $x = x_b \equiv 0$, $U(x) = U(0) - \frac{1}{2}\omega_b^2 x^2 + ...$, is thus consistently given by [1–3]

$$\ddot{x} = \omega_b^2 x - \int_0^t \varphi(t-\tau)\dot{x}(\tau)\,d\tau + \xi(t), \qquad (1)$$

where $\xi(t)$ is a stationary, non-white gaussian random force of zero mean obeying the fluctuation–dissipation theorem

$$\langle \xi(t)\,\xi(s)\rangle = k_B T \varphi(t-s). \qquad (2)$$

In a recent study to the same problem [5], the uniform memory in (1) has been modelled by use of an enlarged markovian phase-space description of the heat bath coupling. Unfortunately, the advocates of ref. [5] have misrepresented the content and some of the results of the previous work in this field [1–4]. Grote and Hynes [1] and Hänggi and Mojtabai [2,3] have treated the non-markovian escape problem associated with the barrier dynamics; i.e. the rate determining step is controlled by the diffusion at the top of the potential barrier. This is also the situation considered in ref. [5]. In the weak noise limit, the activation rate r has then the form [1–3]:

$$\mu = (\lambda_0/\omega_b)(\omega_0/2\pi)\exp(-E_b/k_B T). \qquad (3)$$

Hereby, E_b denotes the barrier height, ω_0 is the angular frequency in the bottom of the potential well and $\omega_b > 0$ is the angular frequency at the barrier top. The effective frequency λ_0 is determined solely by the angular frequency ω_b and the memory kernel $\varphi(t)$; i.e. within the harmonic barrier and harmonic well approximation, λ_0 is not an explicit function of the temperature T. In the derivation of Hänggi and Mojtabai the form of the memory kernel $\varphi(t)$, which might exhibit a non-exponential arbitrary slow long-time decay, has not been restricted. It has been shown in refs. [2,3] (see also the appendix of ref. [4]) that λ_0 in (3) is unique and equals the *largest, real and positive pole*, $z = \lambda_0 > 0$ of a function $\hat{\rho}(z)$

$$\hat{\rho}(z) = [z^2 - \omega_b^2 + z\hat{\varphi}(z)]^{-1}, \qquad (4a)$$

where $\hat{\varphi}(z)$ denotes the Laplace transform of $\varphi(t)$. Clearly, this is equivalent with λ_0 being the *largest, positive and real solution* of

$$\lambda_0 = \omega_b^2/[\lambda_0 + \hat{\varphi}(\lambda_0)]. \qquad (4b)$$

In proving this assertion, it has been assumed [2] that $\hat{\varphi}(z)$ has a representation as a meromorphic function (including a slight generalization thereof [2]). Eq. (4b) is known as the Grote–Hynes relation [1]. However, those authors did not specify λ_0 as being the physically relevant solution among possibly several positive solutions of (4b); nor did the authors of ref. [5] which rederived (4b) by use of a special form of the heat bath coupling consistent with eqs. (2) and (3). In ref. [5] it was assumed that $\hat{\varphi}(z)$ admits the continued fraction representation

$$\hat{\varphi}(z) = \frac{\Delta_1^2}{z+\gamma_1 +} \frac{\Delta_2^2}{z+\gamma_2 +} \cdots \frac{\Delta_n^2}{z+\gamma_n} . \tag{5}$$

This form implies of course that $\hat{\varphi}(z)$ has a representation as a meromorphic function ($[n-1/n]$-Padé-approximant) and thus this case is contained in the treatment of ref. [2]. More importantly, due to the special choice of the markovian modelling of the memory function in ref. [5], obtained by introducing a certain coupling to additional bath variables, it follows from the equilibrium potential of the extended markovian heat bath description (see eq. (8) in ref. [5]) together with the markovian fluctuation–dissipation relations in eq. (6) of ref. [5] that the parameters occurring in (5) are actually *subjected to the restrictions*

$$\Delta_i^2 > 0, \quad i = 1, ..., n, \qquad \gamma_i \geqslant 0, \quad i = 1, ..., n. \tag{6}$$

Now let us assume that the memory kernel $\varphi(t)$ admits a Taylor series expansion

$$\varphi(t) = \varphi(0) + \frac{\varphi'(0)}{1!} t + \frac{\varphi''(0)}{2!} t^2 + ... \tag{7}$$

Then, the corresponding high-frequency series of $\hat{\varphi}(z)$ can be recast into a continued fraction representation of generally infinite order of the form in (5) [6]. However, the set of coefficients $\{\Delta_i^2, \gamma_i\}$ are generally not all positive (including zero) [6]. A particularly simple counter-example is given by the two term exponentially decaying memory

$$\varphi(-t) = \varphi(t) = \exp(-t) + \exp(-2t), \quad t \geqslant 0, \tag{8a}$$

which has the Laplace transform

$$\hat{\varphi}(z) = \frac{2}{z+3/2 +} \frac{-1/4}{z+3/2} , \tag{8b}$$

where $\Delta_2^2 = -\frac{1}{4} < 0$. Actually, most of the relaxation functions of the type in (8) will not satisfy the restrictions in (6). Therefore, the approach put forward in ref. [5] does not have its broad applicability as has been claimed originally.

We should also point out here that the result in (3) fails if the rate determining step is given by the energy accumulation process in the potential well. For the extremely underdamped case, i.e. $\hat{\varphi}(z=0) \to 0$, the rate r can be identified with the inverse mean first passage time $\tau(E_b)$, $r = 1/\tau(E_b)$, to reach the barrier top [7,8]. Based on a recent refinement [9], which extends Kramers' original approach [10] (limit of white gaussian noise) of the extremely underdamped case to the full underdamped regime, the non-markovian rate within this full underdamped regime has been investigated in ref. [11]. For weak noise, which is equivalent to a deep potential well, one obtains

$$r = \left\{ \frac{[1+4(k_B T)^2/D(E_b)]^{1/2} - 1}{[1+4(k_B T)^2/D(E_b)]^{1/2} + 1} \right\} \frac{D(E_b)}{(k_B T)^2} \frac{\omega_0}{2\pi} \times \exp(-E_b/k_B T). \tag{9}$$

$D(E_b)$ denotes the energy-diffusion coefficient of the non-markovian dynamics [7,8,11]. In terms of the action variable $J(E_b)$ at energy E_b of the undamped, deterministic motion one obtains for the case of a *smooth* barrier region [4,8,11]

$$D(E_b) \approx k_B T J(E_b)\, \hat{\varphi}(z=0), \tag{10a}$$

whereas for a *cusped-shaped* barrier region [11]

$$D(E_b) \approx k_B T J(E_b)\, \mathrm{Re}\,\{\hat{\varphi}(z = \mathrm{i}\omega_0/2\pi)\}, \tag{10b}$$

where Re denotes the real part. In contrast to the result in (3), valid for moderate-large damping, the rate in (9), valid in the underdamped regime, incorporates via $J(E_b)$ information of the global potential shape.

[1] R.F. Grote and J.T. Hynes, J. Chem. Phys. 73 (1980) 2715.
[2] P. Hänggi and F. Mojtabai, Phys. Rev. A26 (1982) 1168 Rap. Commun.; J. Stat. Phys. 30 (1983) 401.
[3] P. Hänggi, in: Proc. 4th Intern. Conf. on Physico-chemical hydrodynamics (New York, June 1982), Ann. N.Y. Acad. Sci. 404 (1983) 198.
[4] B. Carmeli and A. Nitzan, Phys. Rev. A29 (1984) 1481.
[5] E. Guardia, F. Marchesoni and M. San Miguel, Phys. Lett. 100A (1984) 15.
[6] P. Hänggi, F. Roesel and D. Trautmann, Z. Naturforsch. 33A (1978) 402;
P. Hänggi and H. Thomas, Phys. Rep. 88 (1982) 207; sect. 5.3.
[7] B. Carmeli and A. Nitzan, Phys. Rev. Lett. 49 (1982) 423; J. Chem. Phys. 79 (1983) 393.
[8] R.F. Grote and J.T. Hynes, J. Chem. Phys. 77 (1982) 3736.
[9] M. Büttiker, E.P. Harris and R. Landauer, Phys. Rev. B28 (1983) 1268.
[10] H.A. Kramers, Physica 7 (1940) 284.
[11] P. Hänggi and U. Weiss, Phys. Rev. A29 (May 1984), to be published.