THEORY OF ACTIVATED RATE PROCESSES: POSITION DEPENDENT FRICTION *

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The non-markoffian generalization of Kramers' theory of activated rate processes is further generalized to the case of position dependent friction in the low-friction limit. A Smoluchowski equation for the action (or energy) of a particle moving in a potential under the influence of position dependent noise and damping Kernel is derived and is used to obtain the escape rate.

1. Introduction

There has recently been a revival of interest in the theory of processes involving thermal activation. Kramers' theory of activated rate processes [1] is often used to describe such processes in many branches of the physical sciences.

In a recent series of articles [2–5] we have generalized Kramers' theory in several directions: We have calculated the escape rate of a particle moving in a potential well under the influence of non-markoffian noise and damping [2,3] and have applied the resulting formalism to the problem of thermal desorption [4]. We have also obtained expressions for the steady-state escape rate valid in the entire friction range (while Kramers' theory yields expressions only for limiting cases) for single [5] and double [6] potential well models. Some generalizations of the Kramers' theory were also provided by other works [7–10].

In this note we further generalize the theory in the low-friction regime to account for the case of position dependent noise and friction. Kramers' work as well as most of the work that followed it use as starting point the Langevin equation

$$\ddot{x} + M^{-1}\mathrm{d}V(x)/\mathrm{d}x + \gamma\dot{x} = M^{-1}R(t), \qquad (1)$$

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$$\langle R(t)\rangle = 0, \quad \langle R(t_1)R(t_2)\rangle = 2\gamma MkT\delta(t_1 - t_2), \qquad (2)$$

or the equivalent Fokker–Planck equation

$$\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial x} - M^{-1}\frac{\mathrm{d}V(x)}{\mathrm{d}x}\frac{\partial P}{\partial v} = \gamma\frac{\partial}{\partial v}\left(\frac{kT}{M}\frac{\partial P}{\partial v} + vP\right), \qquad (3)$$

with the friction γ independent of x. In these equations x and v are the position and velocity of a particle of mass M moving in the potential $V(x)$ under the influence of the random force $R(t)$ and the friction γ (related by the fluctuation–dissipation theorem [2,3]). $P(x, v, t)$ is the probability distribution for the motion of the particle in its phase space, k is the Boltzmann constant and T the temperature.

In many situations the interaction of the particle with its surrounding thermal environment depends on the particle position. This is most clearly the case in desorption of an adatom from a surface [11–13] but is probably true also for isomerization and other chemical reactions in condensed phases where the reaction coordinate may be exposed differently to the thermal environment for different molecular configurations.

In this case eqs. (1) and (2) are replaced by

$$\ddot{x} + M^{-1}\mathrm{d}V(x)/\mathrm{d}x + \gamma(x)\dot{x} = M^{-1}R(x, t), \qquad (4)$$

$$\langle R(t)\rangle = 0, \quad \langle R(t_1)R(t_2)\rangle = 2\gamma(x)MkT\delta(t_1 - t_2), \qquad (5)$$

and lead to eq. (3) with γ replaced by $\gamma(x)$. The functional form and the magnitude of $\gamma(x)$ have been stud-

ied for differential physical cases by d'Agliano et al. [13]. However eq. (3) with $\gamma = \gamma(x)$ has never been solved in any but the high-damping limit, in which case it may be reduced to the Smoluchowski (diffusion) type equation for the probability distribution in the position space

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{1}{\gamma(x)}\left(\frac{kT}{M}\frac{\partial}{\partial x} + M^{-1}\frac{\mathrm{d}V(x)}{\mathrm{d}x}\right)P(x,t)\right]. \quad (6)$$

This leads to the steady-state escape rate

$$r = \omega_0 (kT/2\pi M)^{1/2} \times \left(\int_{-\infty}^{\infty} \mathrm{d}x\, \gamma(x) \exp(-M\omega_B^2 x^2/2kT)\right)^{-1} \times \exp(-E_B/kT), \quad (7)$$

which under the approximations used by Kramers (deep well and parabolic forms of the potential near the bottom and near the barrier top) results in

$$r = (\omega_0 \omega_B / 2\pi\gamma_B)\exp(-E_B/kT), \quad (8)$$

where ω_0 and ω_B are the frequencies associated with the second derivatives of the potential at the bottom and at the barrier top respectively, E_B is the height of the barrier top above the well botton and where $\gamma_B = \gamma(x_B)$, x_B being the position of the barrier top.

As stated above, we provide here a solution for the escape rate in the other extreme limit – the low-damping limit. Starting with a non-markoffian generalization of eqs. (4) and (5) we derive a Smoluchowski type equation for the action J of the particle (analog of the corresponding equation derived by Kramers in the markoffian constant friction case) and evaluate from it the escape rate as the mean first passage time to reach a given threshold energy. As we have argued before [2,3], this procedure is the classical analog of the master equation (in energy space) approach to chemical kinetics and to desorption processes, which is also valid only in the small damping limit.

2. The model

In contrast to the markoffian case [eqs. (4), (5) and (3)], there is no rigorous statistical mechanical derivation of a non-markoffian equation for brownian motion with position-dependent friction. In what follows we use as starting point the generalized Langevin equation

$$\ddot{x} + M^{-1}\mathrm{d}V(x)/\mathrm{d}x + \int_0^t \mathrm{d}\tau Z(x(t), x(\tau), t-\tau)\dot{x}(\tau) = M^{-1}R(x,t), \quad (9)$$

and require that R and Z be of the forms

$$R(x(t), t) = f(x(t))\rho(t), \quad (10)$$

$$Z(x(t), x(\tau), t-\tau) = f(x(t))f(x(\tau))z(t-\tau), \quad (11)$$

with

$$\langle \rho(t)\rho(\tau)\rangle = MkTz(t-\tau), \quad (12a)$$

and

$$\gamma \equiv \int_0^\infty \mathrm{d}t\, z(t). \quad (12b)$$

While no rigorous derivation of eqs. (9)–(12) from a microscopic theory is available we note that these equations reduce to eqs. (4) and (5) in the markoffian limit [$z(t) = 2\gamma\delta(t)$] with $\gamma(x) = \gamma f^2(x)$. Moreover we demonstrate in the appendix that the non-markoffian form (9) is valid in at least one realistic case.

3. The energy equation

Inserting eqs. (10) and (11) into eq. (9) we get

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

$$\dot{v} = -M^{-1}\mathrm{d}V(x)/\mathrm{d}x - f(x(t))\int_0^t \mathrm{d}\tau\, z(t-\tau)f(x(\tau))v(\tau) + M^{-1}f(x(t))\rho(t). \quad (13)$$

These can be transformed into equations of motion for the action J and the phase ϕ[‡]. This procedure (see appendix A of ref. [3]) leads to

‡ The transformation $(x, v) \to (J, \phi)$ is defined from the hamiltonian associated with the deterministic part of the motion.

$$\dot{J} = M(\partial x/\partial\phi) f(x) \times \left(-\int_0^t \mathrm{d}\tau\, z(t-\tau) f(x(\tau)) v(\tau) + M^{-1}\rho(t) \right),$$

$$\dot{\phi} = \omega(J) - M(\partial x/\partial J) f(x) \times \left(-\int_0^t \mathrm{d}\tau\, z(t-\tau) f(x(\tau)) v(\tau) + M^{-1}\rho(t) \right). \quad (14)$$

Introduce the transformation $x \to G(x)$, where

$$G(x) = \int^x \mathrm{d}x' f(x'), \quad (15)$$

then we have in terms of G

$$(\partial x/\partial\phi) f = \partial G/\partial\phi, \quad (\partial x/\partial J) f = \partial G/\partial J, \quad fv = \dot{G}. \quad (16)$$

Thus eqs. (14) lead to

$$\dot{J} = M(\partial G/\partial\phi) \left(-\int_0^t \mathrm{d}\tau\, z(t-\tau) \dot{G}(\tau) + M^{-1}\rho(t) \right),$$

$$\dot{\phi} = \omega(J) - M(\partial G/\partial J) \left(-\int_0^t \mathrm{d}\tau\, z(t-\tau) \dot{G}(\tau) + M^{-1}\rho(t) \right). \quad (17)$$

Eqs. (17) are identical in form to the equations (ref. [3], eqs. (III.1)) that constitute the starting point of the reduction procedure used in the constant friction case, the difference being that $G(x)$ and $\dot{G}(x)$ replace x and v. The reduction procedure that leads to a diffusion equation for the energy is carried out by first introducing the transformation $G(x) \to G(J, \phi)$, $\dot{G}(x, \dot{x}) \to \dot{G}(J, \phi)$ according to *

$$G(J, \phi) = \sum_{n=-\infty}^{\infty} G_n(J) \exp(\mathrm{i}n\phi), \quad (18)$$

$$\dot{G}(J, \phi) = \sum_{n=-\infty}^{\infty} \mathrm{i}n\omega(J) G_n(J) \exp(\mathrm{i}n\phi) \quad (19)$$

and then following exactly the same steps as described in the constant friction case [2,3]. This leads to a diffusion equation for the probability $P(J)$ to find the particle with the action J of the same form as in that case

$$\partial P(J, t)/\partial t = (\partial/\partial J) [\epsilon(J) (kT\, \partial/\partial J + \omega(J)) P(J, t)], \quad (20)$$

where the function $\epsilon(J)$ is given by

$$\epsilon(J) = 2M \sum_{n=1}^{\infty} n^2 |G_n(J)|^2 \hat{z}_n^{\mathrm{c}}(\omega(J)), \quad (21)$$

where

$$\hat{z}_n^{\mathrm{c}}(\omega) = \int_0^{\infty} \mathrm{d}t\, z(t) \cos(n\omega t). \quad (22)$$

Eq. (20) is equivalent to the energy diffusion equation (using $\mathrm{d}E = \omega(J)\,\mathrm{d}J$)

$$\partial P(E, t)/\partial t = (\partial/\partial E) [D(E) (kT\partial/\partial E + 1) \omega(E) P(E, t)], \quad (23)$$

where

$$P(E) = P(J)/\omega(E) \quad (24)$$

and

$$D(E) = \epsilon(J)\, \omega(J). \quad (25)$$

4. Discussion

The diffusion equations (20) and (23) are identical in form to those obtained in the constant friction case. The difference enters in the definition of $\epsilon(J)$, eq. (21) where the functions $G_n(J)$ replace $x_n(J)$. Obviously, for constant friction $f(x) = 1$ and $G(x) = x$ so the present results reduce to those obtained before. [Note that G is defined only up to an additive constant which however does not contribute to $\epsilon(J)$.]

In the markoffian case $z(t) = 2\gamma\delta(t)$ and $\hat{z}_n^{\mathrm{c}}(\omega) = \gamma$. Eq. (21) then reduces to

$$\epsilon(J) = 2M\gamma \sum_{n=1}^{\infty} n^2 |G_n|^2. \quad (26)$$

In the constant friction case $G_n = x_n$ and using the identity [3] $J = 2M\omega\Sigma_{n=1}^{\infty} n^2 |x_n|^2$, we get

$$\epsilon(J) = \gamma J/\omega(J), \quad (27)$$

which is the original Kramers result.

It is interesting to note that all these different cases

* The expansions (18) and (19) rely on the assumption that $G(x)$ is an analytic function of x.

are characterized by the same form of diffusion equation, with different functions $\epsilon(J)$. This can be understood by realizing that in the low-friction limit there is only one rate of interest: the average (over a period) rate of energy (or action) loss. Using the loss term in eq. (13),

$$(\dot{v})_{\text{loss}} = -f(x(t)) \int_0^t \mathrm{d}\tau\, z(t-\tau) f(x(\tau))\, v(\tau)\,. \tag{28}$$

to evaluate $(\bar{\dot{E}})_{\text{loss}} = \overline{Mv(\dot{v})}_{\text{loss}}$ (the bar denotes averages over a period leads to (using eqs. (15) and (19) and some of the principles inherent in the reduction procedure) [2]

$$(\bar{\dot{E}})_{\text{loss}} = -\epsilon(J)\,\omega^2(J)\,. \tag{29}$$

$\epsilon(J)$ may be obtained in this way and the rest of the structure of eqs. (20) and (23) may be guessed from the principle of detailed balance.

Finally we note that the procedures described previously to obtain the function $\epsilon(J)$ in the constant friction case may be extended also to the present case. This includes the direct calculation of the functions $x_n(J)$ (which is feasible e.g. for the Morse oscillator) [2,3] which may be then used to obtain $G_n(J)$, or running deterministic trajectories at a given energy and evaluating $\epsilon(J)$ numerically from [4]

$$\epsilon(J) = [M/\omega^2(J)] \int_0^\infty \mathrm{d}t\, z(t)\, \overline{\dot{G}(0)\,\dot{G}(t)}\,, \tag{30}$$

where the bar again denotes average over the initial phase.

The results obtained above may be generalized [14] to the case where the random force R and friction kernel Z of eq. (9) are given by the expansions

$$R(t) = \sum_\alpha f_\alpha(x(t))\,\rho_\alpha(t)\,,$$

(with $\langle \rho_\alpha \rangle = 0$ and $\langle \rho_\alpha(t)\,\rho_\beta(\tau)\rangle = MkT z_{\alpha\beta}(t-\tau)$) and

$$Z = \sum_\alpha \sum_\beta f_\alpha(x(t)) z_{\alpha\beta}(t-\tau) f_\beta(x(\tau))\,,$$

where $\{f\}$ is a complete orthonormal set of functions on the relevant x domain. In this case eq. (20) is still valid with $\epsilon(J)$ given by [14]

$$\epsilon(J) = 2M \sum_{n=1}^\infty n^2 \sum_\alpha \sum_\beta G_{\alpha,-n}(J)\, \hat{z}^{\mathrm{c}}_{\alpha\beta,n}(\omega(J)) G_{\beta n}(J),$$

where $G_\alpha(x) = \int^x \mathrm{d}x' f(x')$ and $G_{\alpha,n}(J)$ and $z^{\mathrm{c}}_{\alpha\beta,n}(\omega(J))$ are obtained from $G_\alpha(x)$ and $z_{\alpha\beta}(t)$ by equations similar to (18) and (22).

5. The escape rate

Eq. (23) implies the following expression for the mean first passage time to reach a particular energy E starting from a lower energy E_0:

$$\tau_{\text{MFP}}(E_0 \to E) = \frac{1}{kT} \int_{E_0}^{E} \mathrm{d}E_1\, \frac{\exp(E_1/kT)}{D(E_1)} \int_0^{E_1} \mathrm{d}E_2\, \frac{\exp(-E_2/kT)}{\omega(E_2)}\,. \tag{31}$$

For deep enough wells this time is insensitive to the choice of E_0 provided the latter is not taken too close to E. In the low-friction limit $\tau^{-1}_{\text{MFP}}(E_0 \to E_{\text{B}})$ may be identified as the steady-state escape rate out of the well. This identification relies on the assumption (usually involved in energy master equation theories of rate processes) that reaching the threshold energy is a sufficient condition for the process to occur. This assumption is expected to be valid for very low friction (see refs. [2,3] for a further discussion of this point).

For very deep wells, i.e. $E_{\text{B}} \gg kT$ the integrals in eq. (31) with $E = E_{\text{B}}$ may be evaluated approximately by replacing the upper limit in the E_2 integral by ∞ and by pulling $\omega(E_2) \approx \omega_0$ and $D(E_1) \approx D(E_{\text{B}})$ out of the integrals. This leads to

$$r = \tau^{-1}_{\text{MFP}}(E_0 \to E_{\text{B}}) = [\omega_0 D(E_{\text{B}})/kT] \exp(-E_{\text{B}}/kT). \tag{32}$$

In the constant friction case $D(E_{\text{B}}) = \gamma J_{\text{B}}$ where J_{B} is the action at the barrier. In that case eq. (32) is identical to the result of Kramers for this limit. In the present situation $D(E_{\text{B}})$ should be calculated from eqs. (21) and (25). Note that in both cases there are no non-markoffian effects in the very deep wells limit since $\epsilon(J)$, eq. (21) is calculated at $\omega(J_{\text{B}}) = 0$.

6. Example

As an example to the procedure described above we calculate the low-friction escape rate (inverse

mean first passage time) for a particle in a Morse potential well,

$$V(x) = D\{1 - \exp[-(x - x_0)/a]\}^2 , \quad (33)$$

for which

$$\omega(J) = \omega_0(1 - \omega_0 J/2D) , \quad (34)$$

$$x(J, \phi) = x_0 + a \ln\{[1 - (1 - \lambda^2)^{1/2}\cos\phi]/\lambda^2\} , \quad (35)$$

where

$$\lambda = 1 - \omega_0 J/2D \quad (36)$$

and where ω_0 is the bottom frequency

$$\omega_0 = (2D/Ma^2)^{1/2} . \quad (37)$$

For the function $f(x)$ we choose

$$f(x) = \frac{1 + A}{\exp(x/a) + A} , \quad (38)$$

which, for $A > 0$ is a monotonously decreasing function in $x \geqslant 0$. The functions $V(x)$ and $f(x)$ are shown in fig. 1. Eqs. (15) and (35) lead to

$$G(J, \phi) = a \frac{1+A}{A} \ln\left(\frac{1 - (1 - \lambda^2)^{1/2}\cos\phi}{1 + B\lambda^2 - (1 - \lambda^2)^{1/2}\cos\phi}\right) \quad (39)$$

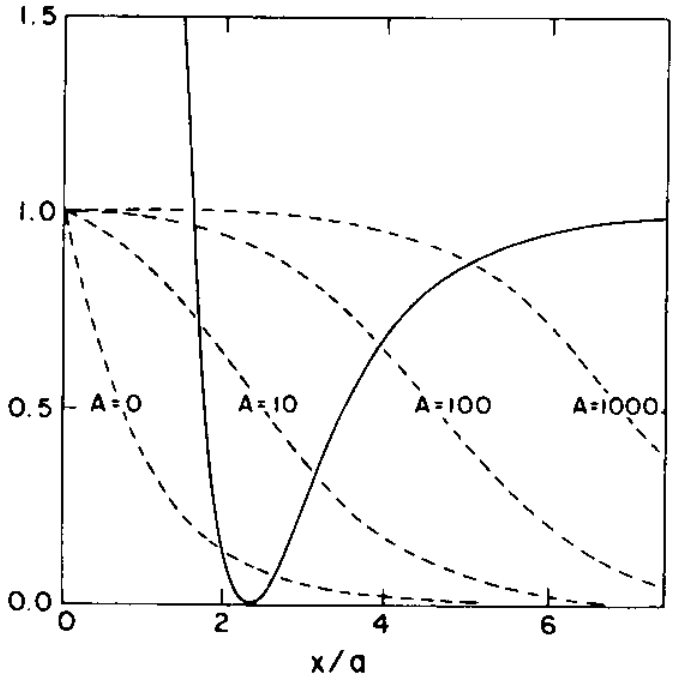

Fig. 1. A schematic representation of the potential $V(x)$ and the function $f(x)$ used in the present work. Full line, Morse potential $V(x)/D = \{1 - \exp[-(x - x_0)/a]\}^2$ versus x/a where $x_0/a = \ln(10)$. Dashed lines, $f(x) = (1 + A)/[\exp(x/a) + A]$ versus x/a for several values of A.

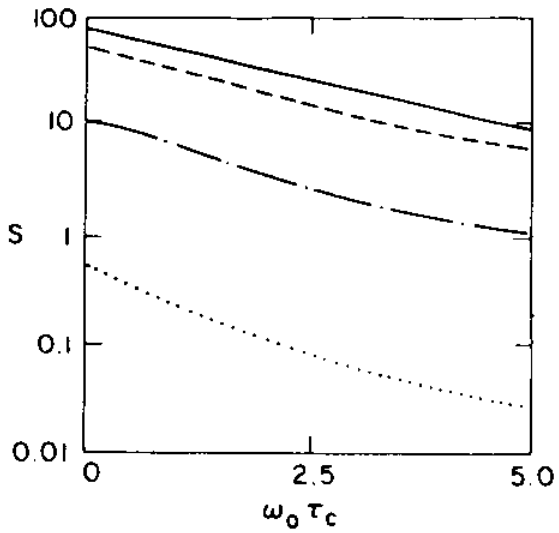

Fig. 2. The parameter S ($=K\omega_0/\gamma$) versus the bath correlation time for several values of A. Solid, dashed, dot-dashed and dotted lines correspond to cases of A = 1000, 100, 10 and zero respectively.

[where $B = A\exp(-x_0/a)$], which may be used to get the functions $G_n(J)$. We get

$$|G_n(J)|^2 = \left(\frac{a(1+A)}{nA}\right)^2 \left[\left(\frac{(1-\lambda^2)^{1/2}}{1+\lambda}\right)^n - \left(\frac{(1-\lambda^2)^{1/2}}{1 + B\lambda^2 + \lambda(1 + 2B + B^2\lambda^2)^{1/2}}\right)^n\right]^2 . \quad (40)$$

Eq. (26) then yields $\epsilon(J)$ which is used to evaluate the mean first passage time, eq. (31). The transmission coefficient $K = r/r_{TST}$ (where $r = \tau_{MFP}^{-1}$ and $r_{TST} = (\omega_0/2\pi)\exp(-D/kT)$, the latter being the transition state theory rate) is proportional to the friction γ in the low-friction limit considered here. In fig. 2 we plot $S \equiv K\omega_0/\gamma$ versus $\omega_0\tau_c$ for several values of A. The parameters of the Morse function (33) were taken to be $D = 10kT$ and $x_0/a = \ln(10)$.

The case $A \to \infty$ corresponds to $f(x) = 1$ (position-independent friction). Smaller values of A correspond to lower effective friction (i.e. the cycle averaged rate of energy loss) and to smaller escape rates as seen from fig. 2. The dependence of the escape rate on the bath correlation time τ_c is in accord with the results obtained and discussed in refs. [2,3].

Appendix

Consider a particle (mass M, position x, velocity v)

coupled to a bath made of harmonic oscillators (masses m_i, position measured from equilibrium y_i, velcoity U_i, frequency ω_i). The hamiltonian is

$$H = \tfrac{1}{2}Mv^2 + V(x) + \tfrac{1}{2}\sum_i m_i u_i^2 + U(x,\{y_i\}) ,$$

where $U = \tfrac{1}{2}\Sigma_i m_i\omega_i^2 [y_i - G(x)]^2$. Thus the coupling is represented by an x-dependent change in the equilibrium positions of the bath particles. The equations of motion are

$$\ddot{x} = M^{-1}\left(\frac{dV(x)}{dx} + \sum_i m_i\omega_i^2 \frac{dG(x)}{dx}(G(x) - y_i)\right), \tag{A.1}$$

$$\ddot{y}_i = -\omega_i^2 [y_i - G(x)] . \tag{A.2}$$

The solution to eq. (A.2) is given by

$$y_i(t) = y_i(0)\cos(\omega_i t) + \omega_i^{-1}\dot{y}_i(0)\sin(\omega_i t) + \omega_i \int_0^t d\tau\, G(x(\tau))\sin[\omega_i(t-\tau)] . \tag{A.3}$$

Inserting this into (A.1) and integrating by parts yields

$$\ddot{x} = -M^{-1}\frac{dV(x)}{dx} - \int_0^t d\tau\, Z(x(t),x(\tau),t-\tau)\dot{x}(\tau) + M^{-1}R(x,t) - M^{-1}\frac{dG(x)}{dx}G(x(0))\sum_i m_i\omega_i^2\cos(\omega_i t), \tag{A.4}$$

where $R(x, t) = (dG/dx)\rho(t)$ and

$$\rho(t) = \sum_i m_i\omega_i^2 [y_i(0)\cos(\omega_i t) + \omega_i^{-1}\dot{y}_i(0)\sin(\omega_i t)] , \tag{A.5}$$

and where

$$Z(x(t),x(\tau),t-\tau) = (dG/dx)_{x=x(t)}(dG/dx)_{x=x(\tau)} z(t-\tau) ,$$

$$z(t-\tau) = M^{-1}\sum_i m_i\omega_i^2\cos[\omega_i(t-\tau)] . \tag{A.6}$$

As in other calculations of this kind [15] we take $y_i(0)$ and $\dot{y}_i(0)$ to be gaussian random variables satisfying

$$\langle y_i(0)\rangle = \langle\dot{y}_i(0)\rangle = \langle y_i(0)\dot{y}_i(0)\rangle = 0 ,$$

$$\langle y_i^2(0)\rangle = kT/m_i\omega_i^2 , \quad \langle\dot{y}_i^2(0)\rangle = kT/m_i . \tag{A.7}$$

Then it is easy to show that

$$\langle\rho(t)\,\rho(\tau)\rangle = MkTz(t-\tau) . \tag{A.8}$$

Finally we notice that for a continuum of modes i the last term in eq. (A.4) is a transient that may be disregarded. Eqs. (A.4)–(A.6) and (A.8) are of the form discussed in this paper.

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