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Phonon mode cooperating with a particle serving as a Maxwell gate and rectifier

V Čápek¹ and T Maňcal^{1,2}

¹ Institute of Physics of Charles University, Faculty of Mathematics and Physics,
Charles University, Ke Karlovu 3-5, CZ-121 16 Prague 2, Czech Republic

² Institut für Physik, Humboldt Universität zu Berlin, Hausvogteiplatz 5-7, D-10117 Berlin,
Germany

E-mail: capek@karlov.mff.cuni.cz and mancal@physik.hu-berlin.de

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Abstract

A fully standard quantum model of a particle interacting with a single-mode phonon system under the influence of a thermodynamic bath is considered. Numerically exact solution shows that, for very specific values of parameters involved, the phonon mode cooperating with the particle becomes able to respond to particle hops and thus to suppress the back particle transfer. The particle becomes free at the end of the process, during which it can be transferred prevailing in one direction only, even going uphill in energy, at the cost of just the thermal energy of the single bath. This behaviour is due to the fact that both the particle and the particle + oscillator density matrices differ, in the stationary situations and for at least intermediate oscillator coupling to the bath, from the respective canonical forms.

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1. Introduction

Basic knowledge acquired from, for example, biology is that general systems can appreciably profit from their capability to check the state of their surroundings as well as themselves and to decide, on the grounds of the results thus obtained, about their next steps or activities. This is the basis for activity of real biomolecules [1]. One can call such a type of behaviour active. Except for some general rules and rather phenomenologically described examples discussed by synergetics, no really microscopic open quantum systems defined by explicit Hamiltonians and able to behave actively in the above sense have, however, been known and investigated until recently. The point is that the system–bath interaction has so far, almost exclusively, been treated by perturbation theory in the system–bath coupling only, which may, for technical reasons, be only approximate beyond some finite orders and in the case

of weak coupling to the reservoir. Finite orders appreciably distort, however, any contingent correlations between the state of the system and that of its surroundings which underlie the effect investigated here³.

The active systems of the type we are going to investigate here always consist of a central system (particle) cooperating with the active part of the system. Under the assumption that rates describing this cooperation are commensurable with, or greater than, relaxation rates caused by the interaction with the bath (this and only this is the regime we call the intermediate- or strong-coupling regime), one can expect unusual phenomena as already discussed [3,4]. Deviations from standard statistical physics as represented by the usual canonical ensemble are due to the fact that the density matrix of the system deviates in such situations from its canonical form. This is due to the fact that our system does, as usual, properly relax in stationary conditions to a stationary state. This state is, however, never the truly standard thermal equilibrium one. (Here, one should realize that the canonical form of the density matrix results in just the zeroth order in the system–bath coupling, which is insufficient in the above intermediate- or strong-coupling regimes.) In our case, as in [3,4], the system is represented by a single particle. Then the one-way particle transfer obtained may be viewed as a slow scattering of the transferred particles on a central or active part of the system with an instability and ensuing reorganization of the latter in its intermediate states including the particle in question. If the reorganization of the central system (necessary to block back-particle-transfer reaction channels) following this instability is to be among two characteristic configurations, then this does not necessarily imply that the quantum variable associated with this reorganization must be only dichotomic. We have in mind the possibility of a usual oscillator mode having infinitely many excited states and working, together with the particle, on an infinite bath representing a macroscopic body. This then ensures the irreversible character of the dynamics. This oscillator mode has a tendency of relaxing, at finite temperatures, to two different canonical states: dressed versus undressed, or deformed versus undeformed in the polaron language, according to whether the transferred particle happens to appear at a specific site—receptor or not. For the first time, such a model has been reported in [5] and [3]; this paper provides a detailed form of the theory as well as more extended results than preliminarily reported there.

The above behaviour is nothing but the particle–oscillator entanglement and all that is possible provided that the particle is kept for a while fixed or is slow enough. The latter assumption is, of course, not exactly but in principle well fulfilled when the particle can move. This is then what provides us, upon sufficiently slow particle motion, with the possibility of the oscillator responding dynamically to the presence of the particle by a sufficiently fast re-relaxation to another state of the mode in question, as a result of the particle detection at the specific site. The re-relaxation or reorganization can then block the back-particle-transfer channel, i.e. allow effectively just one-way particle transfer. The point is that, for example, the deformed canonical state of the mode may mean carrying the receptor with the transferred particle away in space from the site the particle came from and, on the other hand, joining it with another, previously disconnected site.

The importance of such particle behaviour for, *inter alia*, endothermic chemical reactions can be hardly overestimated [6]. We should like to add right here that though our system (our particle on three sites + the oscillator) is microscopic, the ‘system + bath’ complex is macroscopic in its standard sense (it even becomes infinite with the infinite number of degrees

³ Technically, this observation implies the necessity to treat at least a part of the coupling to the surroundings as exactly as possible. This why we, starting from [2], in many ensuing works as well as here, include part of the surroundings (our oscillator below) of the real system of interest (transferred particles) in our system, utilizing the fact that, in specific cases, Hamiltonians of such systems still remain relatively simple and solvable. Hence, the crucial correlations can be properly included well. The rest of the surroundings is then treated as a bath in the usual sense.

of freedom in the thermodynamic limit of the bath). Applications of the mechanism discussed here to more realistic situations will, however, be discussed elsewhere.

The paper is organized as follows. In the next section, the Hamiltonian of the model system, its coupling to the bath and the corresponding equations of motion are introduced. In section 3, heuristic arguments based on an analysis of the model are given in order to elucidate the effect to be expected. Numerical results confirming the arguments of section 3 are given in section 4. The rigorous derivation of the equations of motion as well as further comments on the results obtained can be found in the appendices.

2. Model

Having thus defined the aim of this work, let us start with introducing the model formally. As usual in the nonequilibrium statistical mechanics, the quantum Hamiltonian can be split as

$$H = H_S + H_B + H_{S-B}. \quad (1)$$

Here H_S designates the Hamiltonian of our system consisting, for simplicity, of a single particle hopping among three sites available, and a single branch of harmonic vibrations (phonons) interacting with the particle in a special but fully standard way. The Hamiltonian is standard. What is in fact special is just very specific values of the parameters involved and the numerically exact solution presented below (see also [3]). In order to be specific, we choose H_S as

$$H_S = J(c_{-1}^\dagger c_0 + c_0^\dagger c_{-1}) \cdot [b + b^\dagger + 2\gamma] + I(c_0^\dagger c_1 + c_1^\dagger c_0) \cdot [b + b^\dagger] \\ + \delta\epsilon c_1^\dagger c_1 + \hbar\omega(b^\dagger + \gamma c_0^\dagger c_0)(b + \gamma c_0^\dagger c_0). \quad (2)$$

Here c_{-1} , c_0 and c_1 (or c_{-1}^\dagger , c_0^\dagger and c_1^\dagger) are the annihilation (or creation) operators of the particle at the above three sites -1 , 0 and 1 . Next, b (b^\dagger) designates the phonon annihilation (creation) operator while $\hbar\omega$ is the phonon energy. Commutational relations between b and b^\dagger are Bose–Einstein-like. More complicated models are easily at hand and can be investigated as below. The spin variables, if any, and the (anti)commutational relations among the particle creation and annihilation operators become irrelevant as we have just one particle here. The latter, whenever located at the -1 , 0 or 1 site, has site energy equal to 0 , 0 or $\delta\epsilon$, respectively. Therefore, if $\delta\epsilon > 0$ and the particle initially located outside site 1 is, at the very end of the process, transferred to this site, the transfer is then up in energy (against the potential force responsible for the site energy differences and acting on the particle). As for γ , this is a so far arbitrary real parameter with the meaning of the relative strength of the site-local particle coupling to the phonon mode *as well as* that of the rigid-lattice hopping integral for the ‘ -1 ’ \leftrightarrow ‘ 0 ’ particle transitions $2\gamma J$ with respect to the corresponding phonon-assisted amplitude J in (2). This double-role of γ is one of the features of the model that condition the effect to be reported below. As for I , this is the corresponding phonon-assisted hopping amplitude for the ‘ 0 ’ \leftrightarrow ‘ $+1$ ’ particle transfers. Other Hamiltonians of the same type can be easily constructed as well.

Such Hamiltonians as (2) have been, in different notations and context, used many times in different branches of, for example, solid-state or molecular physics. Except for the greater number of sites involved, this type of Hamiltonian corresponds to, for example, [7]. (The coordinate of our oscillator mode then, or in general in the chemical context, represents the solvent coordinate.) On a more general level, Hamiltonians of this type belong to a class of so-called models of quantum dissipative systems of the type of the spin-boson model Hamiltonian (with, of course, an explicit form of the bath and coupling to it, which still remains to be specified here)—see [8, 9] and papers cited therein. Essential differences as compared with these works consist here only in investigation of one specific regime (definitely outside the

weak-coupling one) for very specific values of parameters and application of an analytical method allowing us to derive starting equations by a rigorous method of scaling and in the above specific regime. These are solved numerically. The similarity to, and correspondence with, all the older works is what makes our conclusions obtained here so surprising and, simultaneously, so challenging.

In order to understand why the behaviour reported below is, in a way, so exceptional and difficult to find, one should realize that, for example, three site Hamiltonians with site-local as well as nonlocal linear coupling to a single harmonic phonon mode needed here are characterized by 13 parameters (three site energies, three hopping integrals, three site-local and three site-nonlocal coupling strengths and the phonon frequency). Two of them can be taken as irrelevant owing to possible energy shifts and rescaling. We should, on the other hand, also add temperature in energy units $k_B T$. Thus, we have a space of 12 model parameters. In only a very limited part of the latter, however, can the effect reported below be expected and really found. Moreover, we should (as already stressed above) take the above couplings inside the system (particle and the phonon mode) as generally intermediate or rather strong, i.e. we should avoid perturbational arguments of any type. Concerning the form of H_S in (2), one should realize that in addition to other terms, it also includes the site-diagonal particle–phonon coupling

$$H_{part-ph}^{site-diag} = \gamma \hbar \omega c_0^\dagger c_0 (b + b^\dagger). \quad (3)$$

This coupling is of vital importance as will be argued below. With (2) and corresponding forms of H_B and H_{S-B} , our problem then consists in solving the linear Schrödinger or Liouville–von Neumann equations or equations derived from them, which are, however, *always linear*. Irrespective of that, spontaneous self-organization (known otherwise in nonlinear and rather phenomenological models) surprisingly appears even without, for example, persistent external flows.

Now, the question is which form of the Hamiltonian of the bath H_B and the system–bath coupling H_{S-B} we shall use. Let us stress that we are interested in neither the precise details (dynamics) of the bath nor the role of specific forms of H_{S-B} . This is why we only assume the following points.

- The bath is assumed to be connected to the system by just its coupling to the above oscillator. Thus, for particle relaxation, our oscillator plays the role of a bottle-neck. The simplest form of H_{S-B} (and H_B) compatible with this assumption as well as that below concerning the Landau–Teller kinetics (11)–(13) is, for example,

$$H_{S-B} + H_B = \frac{1}{\sqrt{N}} \sum_k \hbar \Omega_k G_k (b^\dagger B_k + B_k^\dagger b) + \sum_k \hbar \Omega_k B_k^\dagger B_k. \quad (4)$$

This is nothing but the coordinate–coordinate coupling of the oscillator of the system with those from the bath, in the rotating wave approximation (the latter can also be easily omitted). Here N is the number of bath oscillators (designated by k), which should be taken to grow to infinity in the thermodynamic limit of the bath.

- We do not, in our numerically exact calculations below, require that J and I must necessarily be very small (as compared with rates of the bath-assisted relaxations). In any case, the regime of small J and I is the simplest one to comprehend analytically. In this regime of very small values of J and I (small parameters of the problem), the oscillator relaxation is assumed to go as usual to the canonical state in the representation of eigenstates of H_S when $J = I \approx 0$ (no particle transfer possible): this means to

$$\rho_{osc}^{can} = [1 - e^{-\beta \hbar \omega}] \sum_{v=0}^{\infty} |v\rangle e^{-\beta v \hbar \omega} \langle v| \equiv \rho_{osc}^{(1)} \quad (5)$$

when the particle is at sites -1 or 1 , or to

$$\rho_{osc}^{can} = [1 - e^{-\beta\hbar\omega}] \sum_{v=0}^{\infty} |v'\rangle e^{-\beta v\hbar\omega} \langle v'| \equiv \rho_{osc}^{(0)} \quad (6)$$

when the particle is at site 0 . Here

$$|v\rangle = \frac{1}{\sqrt{v!}} (b^\dagger)^v |0\rangle \quad |v'\rangle = \frac{1}{\sqrt{v!}} (b^\dagger + \gamma)^v |0'\rangle \quad (7)$$

and $|0\rangle$ and $|0'\rangle$ are the corresponding oscillator ground states defined by $b|0\rangle = 0$ and $(b + \gamma)|0'\rangle = 0$. Clearly, $|0'\rangle = \exp(\gamma(b - b^\dagger))|0\rangle$. Finally, $\beta = (k_B T)^{-1}$ is the reciprocal temperature in the energy units. One should add that relaxation to the above canonical states may be not necessarily (as usually assumed) due to a weak coupling, in the usual sense, of our oscillator to the bath (see a discussion of this point below).

- In particular when J and I are assumed to be very small, the particle transfer (which is the problem addressed here) is slow, i.e. details of the (relatively) fast oscillator relaxation are unimportant. This is why we, in this study, do not need details of H_B and H_{S-B} determining this fast relaxation and assume the latter in a simple form known for more than 50 years. This form, suggested by Landau and Teller [10], which is compatible with (4), yields a simple exponential oscillator relaxation if the oscillator is split off from the particle, or if the particle transferred is fully immobile. The relaxation is assumed according to the standard Landau–Teller formula for transition rates among oscillator states (see (13) below) in the corresponding oscillator bases (according to the position of the particle) mentioned above. Derivation of the exponential relaxation can be found, including discussion of its validity, in many textbooks (see e.g. [11]).

With this, we can specify the above model in terms of formulae as follows. Let the Latin indices $m, n, \dots = -1, 0$ or 1 designate the position of the particle and let the Greek indices $\mu, \nu, \dots = 0, 1, 2, \dots$ be the quantum numbers of our central oscillator (phonon occupation numbers). Let $\bar{\rho}(t) = Tr_{bath} \rho^{sys+bath}(t)$ be the density matrix of the ‘particle + oscillator’ system, i.e. $\rho_{m\mu, n\nu}(t)$ its matrix in the representation of the states $|m\mu\rangle = |m\rangle \otimes |\mu\rangle$. ($\rho^{sys+bath}(t)$ designates here the full density matrix of the system and bath.) Then the Liouville equation determining the time development of $\bar{\rho}(t)$ reads

$$i \frac{d}{dt} \rho_{m\mu, n\nu}(t) = \sum_{p\pi, q\kappa} \mathcal{L}_{m\mu, n\nu, p\pi, q\kappa} \rho_{p\pi, q\kappa}(t). \quad (8)$$

For (8) to include no inhomogeneous term, we only need the condition that there are no initial correlations between our system and the bath. In (8), $\mathcal{L}_{m\mu, n\nu, p\pi, q\kappa}$ is the four-(double-)index matrix of the Liouville superoperator \mathcal{L} [11] consisting of two parts as

$$\mathcal{L} = \mathcal{L}_S + \mathcal{L}^{rel}. \quad (9)$$

Here $\mathcal{L}_S \dots = [H_S, \dots]/\hbar$, i.e.

$$(\mathcal{L}_S)_{m\mu, n\nu, p\pi, q\kappa} = \frac{1}{\hbar} \{ (H_S)_{m\mu, p\pi} \delta_{q\kappa, n\nu} - (H_S)_{q\kappa, n\nu} \delta_{m\mu, p\pi} \}. \quad (10)$$

As for the oscillator relaxation part of the Liouvillian \mathcal{L}^{rel} , it should describe the Landau–Teller relaxation to ρ_{osc}^{can} , which should, according to (6) or (5), be different if the particle resides at site 0 or outside. Thus,

$$\begin{aligned} \mathcal{L}_{m\mu, n\nu, p\pi, q\kappa}^{rel} = & \delta_{mp} \delta_{nq} \cdot \{ (1 - \delta_{m,0})(1 - \delta_{n,0}) \mathcal{K}_{\mu, \nu, \pi, \kappa} \\ & + \frac{1}{2} [(1 - \delta_{m,0}) \delta_{n,0} + \delta_{m,0} (1 - \delta_{n,0})] [\mathcal{K}_{\mu, \nu, \pi, \kappa} + \mathcal{K}'_{\mu, \nu, \pi, \kappa}] + \delta_{m,0} \delta_{n,0} \mathcal{K}'_{\mu, \nu, \pi, \kappa} \}. \end{aligned} \quad (11)$$

Describing the Landau–Teller relaxation in terms of the generalized stochastic Liouville equation model [12–14] in the parametrization of the Haken–Strobl–Reineker [15, 16] type, we obtain $\mathcal{K}_{\mu,v,\pi,\kappa}$ in the form [17–19]

$$\mathcal{K}_{\mu,v,\pi,\kappa} = i \left(2\delta_{\mu,v}\delta_{\pi,\kappa} \left[\gamma_{\mu\pi} - \delta_{\mu\pi} \sum_{\lambda} \gamma_{\lambda,\mu} \right] - (1 - \delta_{\mu,v})\delta_{\mu,\pi}\delta_{v,\kappa} \sum_{\lambda} [\gamma_{\lambda,\mu} + \gamma_{\lambda,v}] + 2(1 - \delta_{\mu,v})\delta_{\mu,\kappa}\delta_{v,\pi}\bar{\gamma}_{\mu,v} \right) \quad (12)$$

with the Landau–Teller [10] formula for the relaxation rate

$$\gamma_{\mu,v} = \tilde{k}[(\mu + 1)\delta_{v,\mu+1} + \mu \exp(-\beta\hbar\omega)\delta_{v,\mu-1}]. \quad (13)$$

(With (4), we would obtain $\tilde{k} \approx \frac{2\pi}{N}(1 - \exp(-\beta\hbar\omega))^{-1} \sum_k (G_k \Omega_k)^2 \delta(\omega - \Omega_k)$.) Notice that, in contrast to the original stochastic Liouville equation model [15, 16, 20], the transfer rates $2\gamma_{\mu,v}$ are in general asymmetric here because of inclusion of spontaneous (with respect to the quantum bath) transfer processes $v \rightarrow \mu$. The constant \tilde{k} is the only one reflecting the strength of the oscillator coupling to the bath. It need not be small as compared with, for example, $|J|/\hbar$ or $|I|/\hbar$. For simplicity, we set as usual $\bar{\gamma}_{\dots} = 0$ here. As for $\mathcal{K}'_{\mu,v,\pi,\kappa}$, it describes the same relaxation but with the particle present at site 0. Thus, this relaxation is no longer to ρ_{osc}^{can} in (5). Instead, the oscillator relaxation should go to the canonical state in the lattice deformed (owing to the coupling $H_{part-ph}^{site-diag}$ in (3)) by the polaron effect once the particle resides at site 0, i.e. to ρ_{osc}^{can} in (6). Thus, in the basis of the deformed (polaron) states $|v'\rangle$, the form of \mathcal{K}' should be the same as that of \mathcal{K} in the basis of the undeformed states $|v\rangle$. In other words

$$\mathcal{K}'_{\mu,v,\pi,\kappa} = \sum_{\zeta,\eta,\iota,\lambda} \langle \mu | \zeta' \rangle \langle \eta' | v \rangle \langle \iota' | \pi \rangle \langle \kappa | \lambda' \rangle \mathcal{K}_{\zeta,\eta,\iota,\lambda}. \quad (14)$$

As for the products such as $\langle \mu | \zeta' \rangle = \langle \zeta' | \mu \rangle^*$, we obtain from (7) that

$$\langle \mu | \zeta' \rangle = \frac{\sqrt{\zeta! \cdot \mu!}}{\max(\mu, \zeta)!} e^{-\gamma^2/2} \gamma^{|\mu-\zeta|} (-1)^{\mu-\min(\mu,\zeta)} L_{\min(\mu,\zeta)}^{|\mu-\zeta|}(\gamma^2). \quad (15)$$

Here

$$L_p^\alpha(z) = \frac{e^z z^{-\alpha}}{p!} \frac{d^p}{dz^p} (e^{-z} z^{p+\alpha}) = \sum_{r=0}^p (-1)^r \frac{\Gamma(p+\alpha+1)}{r!(p-r)!\Gamma(r+\alpha+1)} z^r \quad (16)$$

is the associated Laguerre polynomial.

Let us add here that, at the early stage of the work, we have also tested another form of (11). The result confirmed that as far as such variations include, in the corresponding situations, sufficiently fast relaxation to either (5) or (6), and also include proper dephasing, the effect reported here must always be, in the corresponding region of the parameter space, qualitatively reproduced.

As for the term $\propto \frac{1}{2}[(1 - \delta_{m,0})\delta_{n,0} + \delta_{m,0}(1 - \delta_{n,0})]$ in (11) (and the coefficient $\frac{1}{2}$ in this term itself), its form fully corresponds to what is known about structure of $\mathcal{L}_{m\mu,nv,p\pi,q\kappa}^{rel}$ in both the stochastic Liouville equation model and its quantum generalizations (see, for example, [14, 16]) provided that only those mechanisms of the transversal relaxation (damping of the off-diagonal elements of $\rho_{m\mu,nv}(t)$) exist that also lead to the longitudinal one (transitions among different states). In other words, we assume the form of H_{S-B} for which the γ_0 parameters of Haken, Strobl and Reineker [15, 16] are equal to zero. In view of the explanation of the effect expected in section 4 below, we expect that complementing H_{S-B} by terms yielding the transversal relaxation also without contributing to the longitudinal one could, perhaps, slow the particle transfer-and-relaxation process but would definitely make the final effect

even more pronounced. A final comment worth making here is that we have seemingly fully disregarded the possible influence of finite values of J and I on the structure of $\mathcal{K}_{\mu,\nu,\pi,\kappa}$ and $\mathcal{K}'_{\mu,\nu,\pi,\kappa}$ in \mathcal{L}^{rel} in (11), (12), though we take the first-order (in J and I) terms into account in \mathcal{L}_S in (9) and (10). For $I = J = 0$, the structure of (12) can be well justified [21]. At $I \neq 0 \neq J$, however, the corresponding corrections, if introduced by hand, would be small not only due to presumably small values of J and I but also because of the presumed weakness of the oscillator coupling to the bath. Scaling arguments where, in contrast to the usual weak-coupling situation, not only a time-unit and the system–bath coupling but also the hopping (transfer) integrals J and I are scaled show this unambiguously—see the appendix. Here, we state that, in fact, formal omission of I and J from the relaxation part of the Liouvillian is not an approximation at all but is dictated, according to the physical regime chosen, by the exact scaling mathematics. Physically, one can comprehend this by saying that I, J, \tilde{k} etc are in fact scaled not with respect to each other but with respect to the reciprocal of a new time unit τ , $\tau^{-1} \propto \lambda^2$ (λ being a scaling parameter). So, for example, I -dependent (I being $\propto \lambda^2$) corrections to $\tilde{k} \propto \lambda^2$ scale out as λ^4 terms even when I or J are comparable to or even greater than (but still commensurable with) \tilde{k} .

3. Effect to be expected

One could already guess on the grounds of what has been said above what might be the effects expected here. In order to comprehend the situation physically, let us add some heuristic arguments in favour of them. Genuine proof that these rather vague arguments are in fact correct and that our effect really does exist is provided only by the numerical calculations below. The reader should also realize in what follows that, as we shall argue and show below, the rectification effect with the particle even going against the acting external forces appears here whenever the re-relaxation processes between states of the oscillator (5) and (6) are sufficiently fast (the particle is slow). This fully corresponds to the original motivation from microbiology: real biomolecules [1] respond to the presence of a processed particle (molecule, molecular group) at a receptor *before* it has a chance to escape somewhere else. This also corresponds to the style of work in which the original Maxwell demon was supposed to open and close the gate between two compartments [22,23]. One should add here that such biomolecules are definitely microscopic but, because they collaborate with (what we call here) a macroscopic bath, the result of such an activity is definitely macroscopic.

Initially, before the (presumably) slow particle leaves site ‘−1’, the oscillator relaxes to (or starts at $t = 0$ from) the canonical state (5). This means that the mean value of the first term on the right-hand side of (2) with respect to the oscillator state is equal to $2\gamma J(c_{-1}^\dagger c_0 + c_0^\dagger c_{-1})$. In other words, the particle is well allowed to come to site ‘0’ and return back to ‘−1’ unless something happens with the oscillator in between. On the other hand, the mean value (with respect to the oscillator) of the second term on the right-hand side of (2) is zero, indicating that the particle cannot (on average) immediately proceed to site ‘+1’ once it appears at site ‘0’. Assume, however, that the particle really partially appeared at site ‘0’. Fast dephasing processes leading to the transversal relaxation in the system caused by the transfer processes among states of our oscillator as above allow us to treat the particle as deprived of any phase relations with site ‘−1’. This means that the particle is localized separately at just site ‘−1’ or site ‘0’. (In other words, the $\rho_{-1,0}$ and $\rho_{0,-1}$ elements of the particle density matrix become highly suppressed.) If the particle happens to appear at site ‘−1’, the story starts as from the beginning. Assume therefore that, at a time $t > 0$, the particle is localized at site ‘0’ only. Then, according to the above picture, the oscillator quickly re-relaxes to the canonical state (6). This implies that the mean value of $b + b^\dagger$ with respect to the canonical oscillator state (6)

becomes equal to -2γ . Hence, the mean values with respect to the oscillator of the first and second terms on the right-hand side of (2) become 0 and $2\gamma I(c_0^\dagger c_1 + c_1^\dagger c_0)$, respectively. This implies that the particle practically cannot return to site ‘-1’ but can freely proceed to site ‘+1’. Once this happens, however, the oscillator again re-relaxes to the canonical state (5). Hence the return channel of the particle to site ‘0’ is closed and the particle is forced to remain at site ‘+1’.

One should easily see that these arguments apply just ‘on average’. A possible objection is that the gates between sites ‘-1’ and ‘0’, or ‘0’ and ‘+1’, are never fully closed due to fluctuations of the oscillator coordinate $\propto b + b^\dagger$ around its mean values and its finite relaxation rate. In any case, one should expect, at least for slow particle transfers, negligible oscillator-coordinate fluctuations around the corresponding mean values, and, for a sufficiently fast oscillator relaxation, an appreciable increase of population of site ‘+1’ with respect to equilibrium values provided by quantum mechanics and statistical physics in simple three-site models. One should notice one very important aspect of the above argument: increase of the site occupation probability $\rho_{+1,+1} \equiv P_{+1}(t)$ is just on account of the above dynamic behaviour of the oscillator and is *not* influenced by a site energy of the particle at, for example, site ‘+1’. Hence, the mechanism can increase the site occupation probability $P_{+1}(t)$ even if the transfer to site ‘+1’ is connected with an appreciable increase of the (site) energy of the particle transferred (i.e. when $\delta\epsilon$ in (2) is taken as positive). As there is no site-diagonal coupling of the particle at site ‘+1’ to the oscillator, the above increase of $P_{+1}(t)$ cannot be explained as a polaron shift down in (site) energy of the particle at site ‘+1’. Hence, the transferred particle is unbound (free) and its acquired potential energy may be optionally used in, for example, further chemical reactions, for emission of a photon (in connection with, e.g., the particle return to site ‘-1’) to be absorbed by hotter bodies etc, as again argued below. The possibility of such a cyclic work of the system when the back particle transfer ‘+1 \rightarrow -1’ could be accompanied by a deposition of the acquired site energy somewhere else is, of course, not trivial. For more about this see below or, for another model, in [4]. The last comment to be placed here is that we speak in the above arguments about canonical states which the oscillator in our system is, by its presumably sufficiently strong interaction with the bath, driven to. We should stress right here that this is just the situation as approximately viewed by the oscillator. The whole ‘particle + oscillator’ system is driven, by the bath-assisted transitions in the oscillator, out of any canonical state. As argued in detail in the appendix, neither can the whole ‘system + bath’ complex in general be, in the stationary asymptotic situation, in the corresponding canonical thermal equilibrium (i.e. Gibbs) state.

4. Calculation and results

We have performed calculations of, in particular, all the site occupation probabilities $P_n(t) \equiv \rho_{nn}(t) = \sum_{\mu} \rho_{m\mu,m\mu}(t)$ for times ranging between $t = 0$ (when the particle is localized at site ‘-1’) and those values where a full transition to a stationary state is observed. Details of the method are in the appendix. Our calculations clearly confirmed the existence of the above effect. Numerical values used (see figure captions) range between the strong-coupling regime $|J|/\hbar \approx |I|/\hbar \ll \tilde{k}$ and the weak-coupling one $|J|/\hbar \approx |I|/\hbar \gg \tilde{k}$, where a continuous transition to the weak-coupling solution according to the van Hove scheme (see the appendix) with the usual order of site populations is observed (see figure 3). On the other hand, with our identification of what is to be considered as a perturbation but still within the exact mathematics by Davies (see the appendix), our results in the intermediate- and strong-coupling regimes naturally deviate from those of the van Hove–Davies weak-coupling scheme (again figure 3). One should add right here that criteria of the above regimes do *not* involve site energies,

oscillator frequency, time or temperature. This is why our numerical data *do* correspond to the above regimes irrespective of the fact that formally, in the scaling procedure used in the appendix to derive starting equations (8)–(12), the joint parameter of both the system–bath coupling and the particle hopping integrals is sent to zero. The point is that the decisive competition between, or relative rates of, the particle transfer and bath-assisted relaxation (that distinguishes the above strong- and weak-coupling regimes) is preserved. As for the decreasing strength of the relaxation as well as particle transfer processes when the scaling parameter goes to zero, it is compensated by increasing the time units (λ^2 in $\dots \sup_{0 \leq \lambda^2 t \leq a}$ in (31) has the meaning of a reciprocal time unit). This is the physical spirit of the scaling procedure, independent of what is identified, during the scaling procedure, as H_0 and H_1 . For those who still feel any distrust of the type of derivation of (8)–(12), another way of justifying the resulting asymptotic values of site occupation probabilities is sketched in appendix C.

Figure 1 shows probabilities of finding the particle at sites ‘0’ and ‘+1’ (lower and upper clusters of curves), for different values of the energy-uphill step $\delta\epsilon$. The rather intermediate temperatures used here meant that the convergence of the results with increasing number of phonon mode vibrational states was, in contrast to other pictures presented below, rather slow. With our finite computer memory, a full convergence with respect to the number of oscillator levels was not achieved in all situations. Namely, with 20 unshifted and ten shifted oscillator levels, the full convergence has still not been achieved, in contrast to other cases reported below, in figure 1. Increasing the number of phonon levels still further, however, has always been found to yield qualitatively the same picture as well as making the effect reported more and more pronounced. Hence, no complications are expected⁴. As also just small corrections are expected upon increasing the number of phonon states to infinity, reliable conclusions can be drawn as for the full oscillator. One should add that full convergence in (24) (as a function of the number of $\tilde{L}_k(t)$ functions really used) has been achieved. The most remarkable results are as follows:

- In all cases, the resulting long-time (stationary) values of $P_{+1}(t)$ well exceed values predicted by the standard equilibrium statistical thermodynamics. The latter could not, of course, be expected to apply. The point is that our system is all the time driven out of the standard thermal equilibrium because of the bath-assisted oscillator relaxation rates exceeding particle transfer rates inside the system. As our results show, the stationary situation is on the other hand established. However, neither can the whole ‘system + bath’ complex then be found in a canonical Gibbs state (see the appendix).
- The effect becomes, after the energy-uphill step $\delta\epsilon$ exceeds some critical value, even more pronounced with increasing $\delta\epsilon$. So far, however, for purely technical reasons, we have data for just $\delta\epsilon < \hbar\omega$, though the above heuristic arguments do not indicate any change in such behaviour even for $\delta\epsilon \gtrsim \hbar\omega$.
- With increasing $\delta\epsilon$, on the other hand, the relaxation to the stationary situation becomes slower.

In the remaining pictures, full convergence both in the number of phonon states and in the number of expansion functions in (24) has been achieved. Thus, the results are really computer exact. Figure 2 shows the same results as figure 1, except that the temperature has been now taken lower. The most remarkable effects of lowering the temperature are:

- that the dynamics of the relaxation to a stationary distribution becomes slightly faster, and
- that the effect becomes less pronounced.

⁴ Understanding the above limitations concerning the number of oscillator levels used as a model assumption, figure 1 reproduces computer-exact results for the thus specified model.

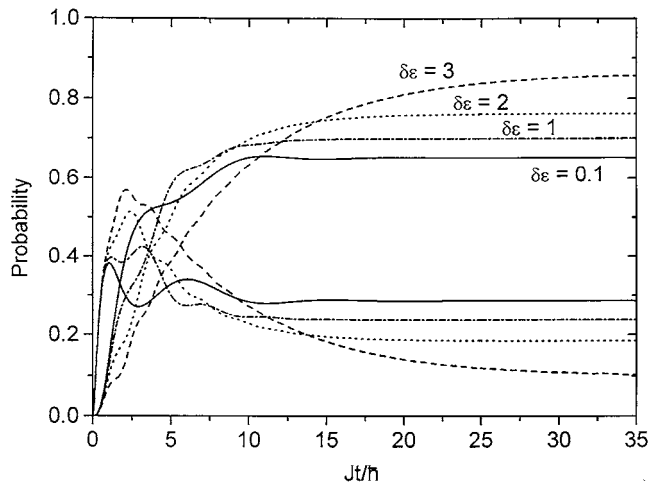


Figure 1. Probabilities of finding the particle at sites ‘0’ (lower cluster of curves) and ‘+1’ (upper cluster of curves) as functions of the dimensionless time $t = \hbar/J$, $I = J > 0$. Initially, the particle is located at site ‘-1’ and the oscillator is in the corresponding canonical state (5). Parameters $\hbar\omega = 5J$, $k_B T = J$, $\gamma = 1$, $\tilde{k} = 3J/\hbar$, $\delta\epsilon = 0.1J$, J , $2J$ and $3J$ (full, dash-dotted, dotted and dashed curves, respectively).

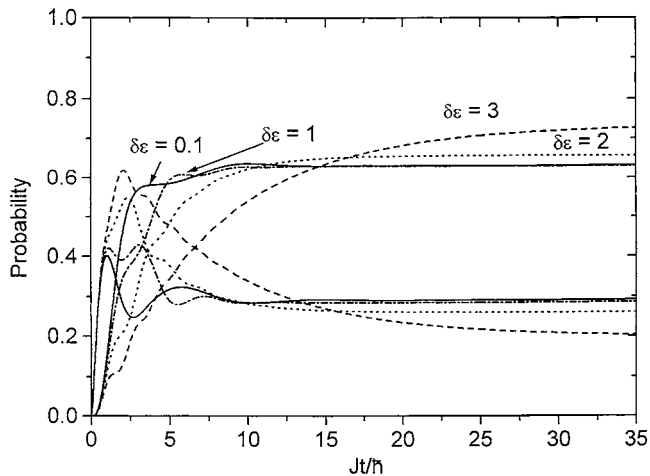


Figure 2. The same as figure 1 but with lower temperatures $k_B T = 0.2J$.

Both these features can be comprehended by noticing that small polarons become more self-localized (less mobile) with increasing temperature [14]. Thus, with increasing temperature, our dynamic gate leading to the observed prevailing particle localization at site ‘+1’ also becomes less and less penetrable for the particle back-escape from site ‘+1’ to ‘0’ and ‘-1’.

Figure 3 shows the role and effect of increasing oscillator relaxation rate. One should realize that, after any particle hop, it is this phonon (re-)relaxation which provides closing of our dynamic gate, hindering the back-particle flow (escape) from site ‘+1’. Really, increasing the phonon relaxation rate makes the effect, as seen in figure 3, more and more pronounced. Worth noticing is that at low values of the oscillator relaxation rate ($\tilde{k} = 0.5J/\hbar$ in figure 3)

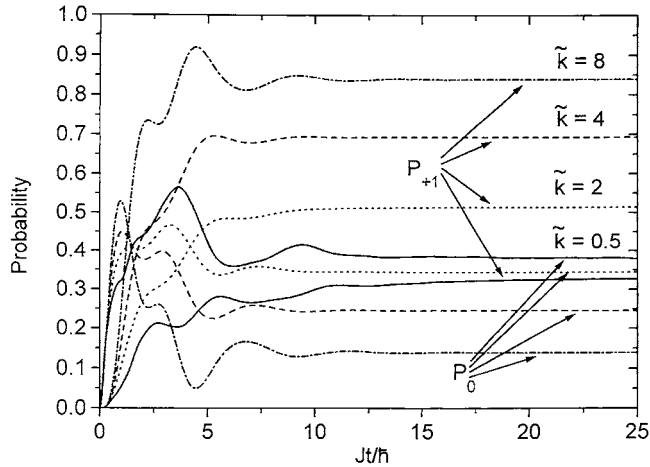


Figure 3. The same probabilities for $\hbar\omega = 5J$, $k_B T = 0.2J$, $\gamma = 1$, $\delta\epsilon = J$ and $\tilde{k} = 0.5J/\hbar$, $2J/\hbar$, $4J/\hbar$ and $8J/\hbar$ (full, dotted, dashed and dash-dotted curves, respectively). For the same parameters but with the density matrix of the system taken in the canonical form, $P_{+1} = 0.056$.

the relative order of the asymptotic populations $P_{+1}(t \rightarrow +\infty)$ and $P_0(t \rightarrow +\infty)$ becomes as usual (population of the higher level is less and *vice versa*), i.e. the effect disappears.

Hence, though our model is nothing but a special case of a general interacting particle–phonon Hamiltonian, we have verified that it is able to yield an active (or intelligent) behaviour in the sense specified above. The contingent increase of the particle energy upon the ‘ -1 ’ \rightarrow ‘ $+1$ ’ transfer is fully at the cost of the bath energy only, as already discussed in, for example, [24, 25]. (Owing to complications mentioned in [26], we avoid here discussion of entropy.) This type of behaviour should be confronted with, for example, detailed balance conditions of the usual equilibrium statistical thermodynamics [27]. If it could be transferred to the macroworld and implemented into analogous but cyclically working systems, it would mean implications for validity of the Planck–Thomson formulation of the second law [28].

5. Discussion and conclusions

One should add that we have solved, for a few situations, the set (8) as it stands, i.e. as a set of (a high number of) differential equations by the Runge–Kutta method. Within numerical accuracy, the result was the same as with our method (see the appendix). As the derivation of starting equation (8) is in the analytical scaling sense also rigorous (involving no approximation at all), our results are reliable and attention should be turned to their interpretation.

The careful reader could immediately try to confront the obtained behaviour of our system with the second law, following reasoning known from, for example, [4]. Two objections in favour of the second law can, however, be still raised. First, one might object that we have still a long way to any challenge of the second law as our system is microscopic while the second law applies to macroscopic systems only. In this connection, one should, however, realize several facts.

- Our system, i.e. the particle on three sites complemented by the central oscillator, is definitely microscopic. So was, however, the original Maxwell demon. Let us cite from [22]: ‘... if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being ... would be able to do what is at present

impossible to us. . .'. Then description of the demon follows, that it must be able to make just detection followed by a binary decision. This is what our system as well as, for example, molecular machines in biological systems really do.

- So as to violate the second law, this being our central system must of course work on a macroscopic body. Our system *complemented by the bath* does, however, form a macroscopic body (system).

In the original Maxwell system (gas in a vessel), however, there was a second portion where the 'warmer' molecules were deposited. In our case, in order to obtain a possibility of a continuous (periodic) activity of the model, we would correspondingly need necessarily something, for example some other macroscopic system or second bath, where the gained energy would be deposited in a useful form. If so, we would *not need to treat these macroscopic bodies and the total energy balance* in detail to discuss violability of the macroscopic thermodynamics; calculation of the energy flow between the two baths through our microscopic system would be enough. For another system, this programme was accomplished in [4]. For our microscopic system treated here and complemented by two macroscopic baths, the results will be published elsewhere. At the present stage, however, the persistent lack of this second bath serving as a collector of the gained energy is connected with the inability of our system to work cyclically. This is the second objection against raising the above behaviour of our model against the second law. At present, therefore, though the behaviour of our system obtained above is challenging, it still cannot be used against the second law of thermodynamics. In any case, the real effect indicated is in a way macroscopic. Just for purposes of illustration: assume that the deposition (to the second macroscopic bath) of the gained energy connected with the back '+1' \rightarrow '-1' transfer, if it is possible in principle as in [4], is faster than our uphill particle transfer. Let $J \approx I \approx 0.01$ eV determine, by the order of magnitude, the transfer frequency $\approx |J|/\hbar$, and let $\delta\epsilon \approx 0.1$ eV. Then we would obtain, ignoring possible losses, the energy gain from *only one* such single microscopic system collaborating with a macroscopic body (our bath, which is understood, in a limiting sense, to even be infinite here) $\approx |J| \cdot \delta\epsilon/\hbar \approx 1$ erg s⁻¹. Even without presuming a finite concentration of such independently working systems, we obtain that already this effect of our microscopic central system (as measured by the heat transferred from a macroscopic bath) collaborating with the macroscopic reservoir is really macroscopic.

Hence, summarizing, we have the following.

- On the grounds of the present model, we still cannot question the second law of thermodynamics.
- The results obtained (skew asymptotic particle distribution), however, do not comply with such standard results of statistical thermodynamics as the detailed balance condition.
- Mechanisms violating the detailed balance can, however, be used to construct dissipative systems (in contact with thermodynamic baths) with persistent flows [27]. Such flows generally also transfer energy, which can be directly connected with the possibility to scrutinize principles upon which thermodynamics rests. All this shows how little the physics beyond basic principles of nonequilibrium statistical thermodynamics is still understood.

Acknowledgments

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Appendix

A.1. Generalized master equations and their solution

Already before solving (8) with (9)–(14), one should notice that for really dominating \tilde{k} , one never obtains the asymptotic (with time increasing to infinity) solution in the form of the canonical density matrix of the system $\bar{\rho} \propto \exp(-\beta H_S)$. The point is that $\bar{\rho}$ would then result, according to (9)–(14) and in contrast to its canonical form, diagonal in the above basis $|m\mu\rangle$. This is why really new effects should be expected.

The way of solving (8) consists of two steps. First, we convert (8) into a set of nine (time-convolution) generalized master (i.e. integro-differential) equations

$$\frac{d}{dt}\rho_{mn}(t) = \sum_{p,q=-1}^{+1} [u_{mn,pq}\rho_{pq}(t) + \int_0^t w_{mn,pq}(t-\tau)\rho_{pq}(\tau) d\tau] + I_{mn}(t) \quad (17)$$

for matrix elements of the particle density matrix $\rho_{mn}(t) = \sum_v \rho_{mv,nv}(t)$. Let us recall that the diagonal elements $\rho_{nn}(t)$ are equal to probabilities $P_n(t)$ of finding the particle at site $n = -1, 0$ or 1 in the system, irrespective of the state of the environment (oscillator and the bath). In the second step, we solve (17) by a special method, converting it to a set of linear algebraic equations.

We obtain equations (8)–(17) using the time-independent projection formalism of Nakajima and Zwanzig [29–31]. The exact form of the coefficients $u_{mn,pq}$, memories $w_{mn,pq}(t)$ and initial condition term $I_{mn}(t)$ is

$$\begin{aligned} u_{mn,pq} &= -i \sum_{\mu,\nu,\lambda} \mathcal{L}_{m\mu,n\mu,p\nu,q\lambda} \mathcal{Q}_{\nu,\lambda}^R \\ w_{mn,pq}(t) &= - \sum_{\mu,\nu,\lambda} [\mathcal{L}e^{-i(1-\mathcal{P})\mathcal{L}t} (1-\mathcal{P})\mathcal{L}]_{m\mu,n\mu,p\nu,q\lambda} \mathcal{Q}_{\nu,\lambda}^R \end{aligned} \quad (18)$$

and

$$I_{mn}(t) = -i \sum_{\mu} [\mathcal{L}e^{-i(1-\mathcal{P})\mathcal{L}t} (1-\mathcal{P})\bar{\rho}(0)]_{m\mu,n\mu}. \quad (19)$$

Here $\bar{\rho}(0)$ is the initial density matrix of the complex ‘particle + oscillator mode’ $\bar{\rho}(t)$ (with matrix elements $\rho_{m\mu,n\nu}(t)$). In our formulation, the bath is already projected off, being reflected just in the \mathcal{L}^{rel} matrix entering (9) above. As for \mathcal{P} , this is the Argyres–Kelley [32] projector (superoperator) defined by its matrix elements

$$\mathcal{P}_{m\mu,n\nu,p\pi,q\kappa} = \delta_{mp}\delta_{nq}\mathcal{Q}_{\mu,\nu}^R\delta_{\pi,\kappa} \quad (20)$$

with $\mathcal{Q}_{\mu,\nu}^R$ so far arbitrary but fulfilling the normalization condition $\sum_u \mathcal{Q}_{\mu,\mu}^R = 1$ ensuring that $\mathcal{P}^2 = \mathcal{P}$ (idempotency condition).

Let us return to the initial density matrix $\bar{\rho}(0)$. We shall specify the problem assuming the following.

- Initially, the oscillator and the particle were statistically independent, i.e.

$$\bar{\rho}(0) = \rho(0) \otimes \rho^{osc}(0) \quad (21)$$

where $\rho(t) = Tr_{osc}\bar{\rho}(t)$ and $\rho^{osc}(t) = Tr_{part}\bar{\rho}(t)$ are the density matrices of the particle and the oscillator, respectively.

- The initial density matrix of the oscillator ρ_{osc} coincides with ϱ^R , i.e.

$$\rho_{\mu\nu}^{osc}(0) = \varrho_{\mu\nu}^R \quad (22)$$

(choice of ϱ^R in (20)).

Then $(1 - \mathcal{P})\rho(0) = 0$, i.e. the initial condition term $I_{mn}(t) = 0$. In fact, we shall assume here that $\rho^{osc} = \rho_{osc}^{can}$ in (5). This introduces the initial oscillator temperature (equal to that of the bath in (13)) into (17). Further, we assume that $\rho_{mn}(0) = \delta_{mn}\delta_{n,-1}$, i.e. that the particle is initially at site ‘-1’ (on the left).

For the solution of (17) we use an older method by Skála and Bílek [33–35] recently proved to be operative by Menšík [17, 18]. Instead of using modified Bessel functions as in [17, 18], we shall involve functions directly related to the above Laguerre polynomials (16) as suggested by Skála (unpublished, see also the application of the method in [19, 36, 37] for another model). In connection with working with the set of equations (17) (instead of just one scalar integro-differential equation as in [17, 18]), this allows us to extend the time interval investigated up to the end of the relaxation process. The exact method used is based on several important steps. First, let us introduce the (modified Laguerre) functions

$$\bar{L}_p(z) = e^{-az} L_p^0(z) \quad (23)$$

where a is a so far arbitrary real parameter. These functions (forming a complete set) are then used to express the required density matrix elements $\rho_{mn}(t)$ as well as the memory functions $w_{mn,pq}(t)$ as series

$$\begin{aligned} \rho_{mn}(t) &= \sum_{k=0}^{+\infty} \rho_{mn}^k \bar{L}_k(t) \\ w_{mn,pq}(t) &= \sum_{k=0}^{+\infty} w_{mn,pq}^k \bar{L}_k(t). \end{aligned} \quad (24)$$

Owing to well known properties of the Laguerre polynomials with respect to convolutions and differentiation [38, 39], one can easily show that

$$\begin{aligned} \int_0^t \bar{L}_m(\tau) \bar{L}_n(t - \tau) d\tau &= \bar{L}_{m+n}(t) - \bar{L}_{m+n+1}(t) \\ \frac{d}{dt} \bar{L}_n(t) &= - \sum_{m=0}^{n-1} \bar{L}_m(t) - a \bar{L}_n(t). \end{aligned} \quad (25)$$

Thus, the set of integro-differential (generalized master) equations (17) to be solved, supplemented by the above initial condition, becomes the algebraic set of equations

$$\begin{aligned} \delta_{m,-1} \delta_{n,-1} &= \sum_{p,q=-1}^{+1} M_{mn,pq} \rho_{pq}^0 \\ \delta_{m,-1} \delta_{n,-1} - \sum_{j=0}^{k-1} \left[\rho_{mn}^j + \sum_{p,q=-1}^{+1} \{w_{mn,pq}^{k-j} - w_{mn,pq}^{k-j-1}\} \rho_{pq}^j \right] &= \sum_{p,q=-1}^{+1} M_{mn,pq} \rho_{pq}^k \end{aligned} \quad (26)$$

$k = 1, 2, 3, \dots$. The specific forms of the left-hand sides of both the equations here are due to the above initial condition used. Further

$$M_{mn,pq} = (1 - a) \delta_{m,p} \delta_{n,q} - u_{mn,pq} - w_{mn,pq}^0. \quad (27)$$

Therefore, in order to determine the expansion coefficients ρ_{mn}^i , $i = 0, 1, 2, \dots$ of the solution, one must first know the coefficients, i.e. $w_{mn,pq}^i$, $i = 0, 1, 2, \dots$. As for the $u_{mn,pq}$ coefficients, they are fully determined by their definition in (18).

From (23) and definition of the Laguerre polynomials (16), one can easily obtain that the modified Laguerre functions (23) are orthonormal with respect to the scalar product $(f, g) = \int_0^{+\infty} \exp((-1+2a)x) f(x)g(x) dx$, i.e. that

$$\int_0^{+\infty} e^{(-1+2a)x} \bar{L}_m(x) \bar{L}_n(x) dx = \delta_{mn}. \quad (28)$$

Thus, from the second equation of (24), we obtain that

$$w_{mn,pq}^k = \int_0^{+\infty} e^{(-1+2a)t} w_{mn,pq}(t) \bar{L}_k(t) dt. \quad (29)$$

An important observation on which the present method relies is now that this time integral can be calculated exactly. It yields after introducing here the definition of the memory function from (18) that

$$\begin{aligned} w_{mn,pq}^k &= - \sum_{\mu\nu\lambda} [\mathcal{L}\{i(1-\mathcal{P})\mathcal{L} - a\}^k \{i(1-\mathcal{P})\mathcal{L} + 1 - a\}^{-k-1} (1-\mathcal{P})\mathcal{L}]_{m\mu,n\mu,p\nu,q\lambda} \mathcal{Q}_{\nu\lambda} \\ &= - \sum_{\mu\nu\lambda} [\mathcal{L}(1-\mathcal{P})\mathcal{L}\mathcal{A}^{-1}(1-\mathcal{A}^{-1})^{k+1}]_{m\mu,n\mu,p\nu,q\lambda} \mathcal{Q}_{\nu\lambda} \\ \mathcal{A} &= i(1-\mathcal{P})\mathcal{L} + (1-a). \end{aligned} \quad (30)$$

As all the matrices are defined above, calculation of all the coefficients $w_{mn,pq}^k$, $k = 0, 1, 2, \dots$, as well as $u_{mn,pq}$, and, finally, solution of (26) for ρ_{mn}^k is just a matter of a straightforward algebra. Results obtained are, apart from some limitations imposed by requirement of non-negative eigenvalues of \mathcal{A} , insensitive to the choice of parameter a . We have always taken $a = 0.3$.

A.2. Derivation of starting equations

Projection methods by Nakajima and Zwanzig [29–31] start from the Liouville–von Neumann equation for the density matrix of the system and bath. This equation automatically implies that, for example, energy of the ‘system + bath’ complex is preserved. (The energy of just the system, i.e. our particle and the oscillator, cannot be conserved owing to relaxation processes in the system.) Applying the Argyres–Kelley projector [32] to the so called Nakajima–Zwanzig [29–31] identity leads to time-convolution generalized equations (TC-GMEs) for the density matrix $\bar{\rho}(t)$ for our system, i.e. the complex ‘particle + oscillator mode’ [32, 40]. An alternative method leading to time-convolutionless generalized master equations (TCL-GMEs) for $\bar{\rho}(t)$ is provided by application of the same projector in the formalisms by Fuliński and Kramarczyk, or Shibata, Hashitsume, Takahashi and Shingu [41–45]⁵. By mathematically well established methods [46, 47], both TC-GMEs and TCL-GMEs may be then turned to equations of quantum dynamical semigroups of the form (8)–(10). There is no space for speculations here. So, the only problem regards the form of \mathcal{L}^{rel} in (11) above.

In order to avoid discussions due to inaccurate description of mathematical steps leading to (8), let us cite from mathematical literature: the exact formula (1.18) of [48] rewritten in physical terms reads

$$\lim_{\lambda \rightarrow 0} \sup_{0 \leq \lambda^2 t \leq a} \|\bar{\rho}^{exact}(t) - e^{-i(\mathcal{L}_0 + \lambda(\mathcal{L}_1) + i\lambda^2 \gamma t)} \bar{\rho}(0)\| = 0 \quad (31)$$

⁵ Neither this TCL-GME nor the TC-GME of the previous sentence should be mistaken for the generalized master equations of appendix A.1. In the present section, we speak about projecting off (all the information concerning) the bath, reducing the treatment to just $\bar{\rho}$. On the other hand, in appendix A.1, we mean to start from $\bar{\rho}$ and to project off the oscillator mode, arriving at a set of equations for the density matrix of just the particle.

where (see formulae (1.19) and (1.12) of [48])

$$\begin{aligned}\mathcal{H} \dots &= \int_0^{+\infty} dx \operatorname{Tr}_B (e^{i\mathcal{L}_0 x} (-i\mathcal{L}_1) e^{-i\mathcal{L}_0 x} (1 - \mathcal{P}) (-i\mathcal{L}_1) (\dots \otimes \rho^B)) \\ \langle \mathcal{L}_1 \rangle \dots &= \operatorname{Tr}_B (\mathcal{L}_1 \dots \otimes \rho^B).\end{aligned}\quad (32)$$

(Finite constant a is here arbitrary, $\mathcal{P} \dots = (\operatorname{Tr}_B \dots) \times \rho^B$ is the Argyres–Kelley projector and ρ^B is the initial density matrix of the bath assumed in the canonical form.) In (31), $\bar{\rho}^{exact}(t)$ is the exact density matrix of the system (particle + oscillator in our case) with its time dependence determined from the Liouville equation for the whole ‘system + bath’ complex, subsequently taking the trace over the bath, while

$$\bar{\rho}(t) = e^{-i(\mathcal{L}_0 + \lambda \langle \mathcal{L}_1 \rangle + i\lambda^2 \mathcal{H})t} \bar{\rho}(0) \quad (33)$$

is the same quantity where its time dependence is given, as follows from (33), by

$$i \frac{d}{dt} \bar{\rho}(t) = (\mathcal{L}_0 + \lambda \langle \mathcal{L}_1 \rangle + i\lambda^2 \mathcal{H}) \bar{\rho}(t). \quad (34)$$

Here $H = H_0 + \lambda H_1$ is a formal way of splitting the Hamiltonian H of our system and bath into an arbitrary unperturbed part H_0 and a corresponding correction λH_1 , and $\mathcal{L}_j \dots = [H_j, \dots]/\hbar$, $j = 0, 1$. Incidentally, prescription (32) is not the only one; formula (1.33) of [48] proves that (in fact infinitely many) other (and, in the scaling limit, equivalent) forms exist. One should in particular mention the form with

$$\mathcal{H} \rightarrow \mathcal{H}^\natural = \lim_{t \rightarrow +\infty} \frac{1}{2t} \int_{-t}^{+t} e^{-i\mathcal{L}_S(\lambda=0)x} \mathcal{H} e^{i\mathcal{L}_S(\lambda=0)x} dx \quad (35)$$

(see also [49]), where the correspondence with (11) is direct. In any case, (31) proves the general validity of (34), exactly in the scaling sense.

Now, as long as we identify $H_0 = H_S + H_B$ and $\lambda H_1 = H_{S+B}$, terms $\mathcal{L}_0 \bar{\rho}(t)$, $\lambda \langle \mathcal{L}_1 \rangle \bar{\rho}(t)$ and $+i\lambda^2 \mathcal{H} \bar{\rho}(t)$ give the term in (8) resulting from \mathcal{L}_S in (9), its possible temperature-dependent renormalization due to the system–bath coupling (there is even no such term with our choice (4) and canonical form of ρ^B) and the terms in (8) resulting from \mathcal{L}^{rel} in (9), respectively. Notice that owing to the definition of H_0 involving the whole Hamiltonian of the system H_S , the relaxation (as described by (32)) is among eigenstates of H_S and goes to a canonical form of $\bar{\rho}(t)$ when $t \rightarrow +\infty$ [50]. This is the usual weak-coupling scheme according to the van Hove scheme.

On the other hand, our scheme is based on putting formally J , $I \propto \lambda^2$ (implying that $H_S(\lambda)$ becomes λ dependent) and identification $H_0 = H_S(\lambda = 0) + H_B$, $\lambda H_1 = H_{S+B} + H_S(\lambda \neq 0) - H_S(\lambda = 0) \equiv H_{S+B} + \Delta H_S$. Then $\mathcal{L}_0 \bar{\rho}(t)$ in (34) gives only $\mathcal{L}_S(\lambda = 0)$ in (8). On the other hand, the sum $(\mathcal{L}_0 + \lambda \langle \mathcal{L}_1 \rangle) \bar{\rho}(t)$ reproduces, up to the same renormalization terms as in the weak-coupling alternative, all the term $\mathcal{L}_S \bar{\rho}(t) \equiv \mathcal{L}_S(\lambda \neq 0) \bar{\rho}(t)$ in (8). Finally, H_0 now involves only $H_S(\lambda = 0)$, i.e. the I - and J -dependent terms ΔH_S do not contribute to \mathcal{H} via \mathcal{L}_0 in (32). Moreover, by algebraic properties of \mathcal{P} and $\operatorname{Tr}_B \dots$ ($\operatorname{Tr}_B [H_B, \dots] = 0$, $\mathcal{P}(1 - \mathcal{P}) = (1 - \mathcal{P})\mathcal{P} = 0$, $\mathcal{P}[\Delta H_S, \dots] = [\Delta H_S, \mathcal{P} \dots]$), all $[\Delta H_S, \dots]$ terms from \mathcal{L}_1 fall out from \mathcal{H} . Hence, \mathcal{H} turns out to be completely I and J independent. In other words, the relaxation is now completely due to the system–bath coupling and proceeds exclusively among eigenstates of $H_S(\lambda = 0)$. Because of the fact that our bath interacts in our system just with the oscillator, this means relaxation among just oscillator eigenstates.

Both the above alternatives are mathematically equally justified. One cannot accept either one of them and automatically exclude the other one. The identification of H_0 and H_1 is dictated just by the chosen physical regime. In the weak-coupling case when the bath-assisted processes are appreciably slower than all the transfer processes inside the system, the weak-coupling identification and theory is fully legitimate. The same applies, however, to the second

alternative, i.e. our choice of theory in the case when the bath-assisted processes become comparable to (or even faster than but still commensurable with) the particle transfer inside the system. About (and only about) the latter situation we speak here.

A.3. Another justification of the results

Those who still feel a kind of mistrust of the above derivation of (8)–(12), as presented by the Davies type of scaling described above, might feel more satisfied by another procedure which we are going to sketch here and which is just based on a standard stationary perturbation theory. The method is based on deriving, by, for example, the methods of Nakajima and Zwanzig [29–31] with the Argyres–Kelley projector \mathcal{P} [32,40], the system of exact TC-GMEs

$$\frac{d}{dt}\rho_{m\mu,n\nu}(t) = -\frac{i}{\hbar}(\text{Tr}_B[H, \bar{\rho}(t) \otimes \rho^B])_{m\mu,n\nu} + \sum_{p\pi,q\kappa} \int_0^t d\tau w_{m\mu,n\nu,p\pi,q\kappa}(\tau) \rho_{p\pi,q\kappa}(t-\tau). \quad (36)$$

Taking the thermodynamic limit of the bath and turning $t \rightarrow +\infty$ yields

$$0 = -\frac{i}{\hbar}(\text{Tr}_B[H, \bar{\rho}(+\infty) \otimes \rho^B])_{m\mu,n\nu} + \sum_{p\pi,q\kappa} \int_0^{+\infty} d\tau w_{m\mu,n\nu,p\pi,q\kappa}(\tau) \cdot \rho_{p\pi,q\kappa}(+\infty). \quad (37)$$

Expanding now the time integrals $\int_0^{+\infty} d\tau \dots$ of the memory functions $w_{m\mu,n\nu,p\pi,q\kappa}(\tau)$ in powers of H_{S-B} reproduces fully the weak-coupling scheme of van Hove–Davies applicable in the regime where bath-assisted relaxation is much (and in the mathematical sense, infinitely) slower than the particle transfer processes inside the system. We instead here assume the physical regime where the particle hopping rates are commensurable with the bath-assisted relaxation. Based on this, we must identify as a perturbation $\lambda H_1 = H_{S-B} + H_S(\lambda \neq 0) - H_S(\lambda = 0)$ as above. Then (37) reduces, after some straightforward but tiring algebra, to the long-time limit of (8)–(12), thus reproducing completely the above results. The latter are therefore not tributary to just the above modification of the Davies scaling procedure.

A few additional comments are still worth adding: first, the method used justifies our starting equation (8) just in its long-time limit. Thus, the result yields (8)–(12) in the stationary case when the time derivative on the left-hand side of (8) disappears. It is, however, not difficult to verify that the same reasoning may be used to justify (8)–(12) together with $i\frac{d}{dt}\rho_{m\mu,n\nu}(t)$ on the left-hand side provided we only assume time greater than the decay time of the memory functions involved in the time-convolution GME formalism. Second, equally well as from the Nakajima–Zwanzig formalism, one can start from the time-convolutionless formalisms of Fuliński and Kramarczyk, or Shibata, Hashitsume, Takahashi and Shingu [41–45]. We again recover (8) with just, due to a different form of what is considered as a perturbation, another form of \mathcal{L}^{rel} than usual. In general, for each derivation of (8) with a standard (weak-coupling) form of \mathcal{L}^{rel} , there exists a corresponding derivation of (8) with our form of \mathcal{L}^{rel} and *vice versa*. In other words, there is a one-to-one correspondence between the corresponding proofs. Therefore, the only doubt that could, in our opinion, survive, is connected with the possibility of writing down (8) for any form of \mathcal{L}^{rel} . This task has, however, been solved many times and equations (8) now have a broad application in, for example, the energy and particle transfer problem. Mathematically oriented readers may again be referred to, for example, [46,47].

A.4. More about deviation from standard equilibrium statistical thermodynamics

An attempt might still appear to reconcile our conclusions above with the standard equilibrium statistical thermodynamics. The conjecture might be that owing to the strong correlation effects

between the particle and its surroundings, perhaps not the system itself but the whole ‘system + bath’ complex could be, in the stationary situation, in a canonical state in the usual sense. This would then justify attempts to explain or disprove the above skewing of the particle distribution to one side by methods of standard statistical physics. Arguments exist, however, that even such a general conjecture is not true.

In order to make the discussion as simple as possible, let us put $J = 0$ in (2) with the initial condition that the particle is initially distributed arbitrarily but just at sites ‘0’ and ‘+1’. With (4), we thus have

$$H_{S+B} = I(c_0^\dagger c_1 + c_1^\dagger c_0) \cdot [b + b^\dagger] + \hbar\omega(b^\dagger + \gamma c_0^\dagger c_0)(b + \gamma c_0^\dagger c_0) + \frac{1}{\sqrt{N}} \sum_k \hbar\Omega_k G_k (b^\dagger B_k + B_k^\dagger b) + \sum_k \hbar\Omega_k B_k^\dagger B_k. \quad (38)$$

For simplicity, we set everywhere here $\delta\epsilon = 0$. The stationary situation (independent of details of such initial conditions) achieved after some transient period is then again of the type above, i.e. the (long-time) asymptotic site occupation probabilities $P_0 \equiv P_0(t \rightarrow +\infty)$ and $P_1 \equiv P_1(t \rightarrow +\infty)$ fulfill

$$P_0 < P_1. \quad (39)$$

One should stress mainly two points here.

- In the small- I limit, I in (38) determines just the dynamics of the $0 \leftrightarrow 1$ dynamics but not the long-time asymptotics of site occupation probabilities P_0 and P_1 . This may be most easily seen by standard projecting off the bath and the oscillator mode in the Liouville equation for the system + bath density matrix with Hamiltonian (38). Using the projector

$$\mathcal{P} \dots = |0\rangle\langle 0| \text{Tr}_B \text{Tr}_{osc} \dots |0\rangle\langle 0| \otimes \rho_{osc}^{(0)} \otimes \rho^B + |1\rangle\langle 1| \text{Tr}_B \text{Tr}_{osc} \dots |1\rangle\langle 1| \otimes \rho_{osc}^{(1)} \otimes \rho^B \quad (40)$$

and assuming, for example, the initial condition

$$\rho^{sys+bath}(t=0) = |0\rangle\langle 0| \otimes \rho_{osc}^{(0)} \otimes \rho^B \quad (41)$$

(ρ^B being the initial density matrix of the bath) yields from the resulting generalized master equations [29–31]

$$\lim_{I \rightarrow 0} \frac{P_1}{P_0} = \frac{\int_0^{+\infty} w_{1 \leftarrow 0}^{(2)}(t) dt}{\int_0^{+\infty} w_{0 \leftarrow 1}^{(2)}(t) dt}. \quad (42)$$

Here $w_{\dots}^{(2)}(t)$ are the corresponding memory functions in the lowest (second) order in I . Thus the ratio P_1/P_0 is, for low I as a ratio of two terms $\propto I^2$, I independent. Because $P_0 + P_1 = 1$, the same applies to the long-time asymptotics P_0 as well as P_1 separately. Because of the difference between $\rho_{osc}^{(1)}$ and $\rho_{osc}^{(0)}$, the memory functions $w_{0 \leftarrow 1}^{(2)}$ and $w_{1 \leftarrow 0}^{(2)}$ turn out to be structurally (as well as in their values) appreciably different. This is why the ratio (42) differs from unity.

- Even if this were not true and if P_1 and P_0 in (39) fulfilled, for example, $P_1 - P_0 = \mathcal{O}(I^2)$ (making the long-time asymptotics P_1 and P_0 practically equal for very small though finite I), a contradiction with formula (47) to be derived below would still appear. Here, another interesting point is that the right-hand side of (42) becomes $\propto \gamma^2$ for $\gamma \gg 1$, which shows that then in fact $P_1 \gg P_0$.

Let now

$$H_{S+B}^{(0)} = \langle 0|H_{S+B}|0\rangle \quad H_{S+B}^{(1)} = \langle 1|H_{S+B}|1\rangle \quad (43)$$

be effective Hamiltonians of the system oscillator interacting with the bath but with the particle fixed at sites '0' and '+1'. It is not difficult to see that

$$e^S H_{S+B}^{(0)} e^{-S} = H_{S+B}^{(1)} - \gamma^2 \frac{\hbar\omega(1/N) \sum_k \hbar\Omega_k G_k^2}{\hbar\omega - (1/N) \sum_k \hbar\Omega_k G_k^2} \quad (44)$$

where

$$S = \Gamma(b - b^\dagger) + \sum_k \Delta_k (B_k - B_k^\dagger) \quad (45)$$

$$\Delta_k = -\frac{1}{\sqrt{N}} G_k \Gamma \quad \Gamma = -\frac{\hbar\omega\gamma}{\hbar\omega - (1/N) \sum_k \hbar\Omega_k G_k^2}.$$

Assume now that the stationary form of the density matrix of the 'system + bath' complex can be, according to Gibbs, written as

$$\rho^{sys+bath} = f(H_{S+B}) \quad (46)$$

where $f(x)$ is a decreasing holomorphic function of x . For $f(x) \propto \exp(-x)$, it would mean a canonical distribution. Then

$$P_1 = \text{Tr}_B \text{Tr}_{osc} \langle 1 | f(H_{S+B}) | 1 \rangle = \text{Tr}_B \text{Tr}_{osc} f(H_{S+B}^{(1)}) + \mathcal{O}(I^2)$$

$$P_0 = \text{Tr}_B \text{Tr}_{osc} \langle 0 | f(H_{S+B}) | 0 \rangle = \text{Tr}_B \text{Tr}_{osc} f(H_{S+B}^{(0)}) + \mathcal{O}(I^2)$$

$$= \text{Tr}_B \text{Tr}_{osc} f(e^{-S} e^S H_{S+B}^{(0)} e^S) + \mathcal{O}(I^2) = \text{Tr}_B \text{Tr}_{osc} f(e^S H_{S+B}^{(0)} e^{-S}) + \mathcal{O}(I^2)$$

$$= \text{Tr}_B \text{Tr}_{osc} f\left(H_{S+B}^{(1)} - \gamma^2 \frac{\hbar\omega(1/N) \sum_k \hbar\Omega_k G_k^2}{\hbar\omega - (1/N) \sum_k \hbar\Omega_k G_k^2}\right) + \mathcal{O}(I^2). \quad (47)$$

For the decreasing function $f(x)$ and for the particular case of, for example, $\hbar\omega > (1/N) \sum_k \hbar\Omega_k G_k^2$, these results for P_0 and P_1 (implying that P_0 remains greater than P_1 even in the limit of extremely small I) are incompatible with (39). Hence (46) cannot be true for the asymptotic density matrix of the 'system + bath' complex. This clearly makes the validity of (46)—the assumption forming one of basic pillars of the equilibrium Gibbs statistical mechanics—only conditional. In particular, in our situation, this means that our 'system + bath' complex cannot in general be, in the stationary asymptotic situation, in the thermal equilibrium canonical state.

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