Isothermal Maxwell daemon and active binding of pairs of particles

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Abstract. An open quantum model of a small system strongly interacting with a thermodynamic bath is suggested which binds cyclically, upon working in isothermal conditions, particles (atoms, molecules or molecular groups) to bound states. The latter may be even energetically disadvantageous. The effect is due to relaxation processes in intermediate states upon combined scattering of the particles on the system and can be viewed as an induced self-organization described here by a linear theory.

1. Introduction

Previously, we have suggested a microscopic quantum model (swing or fish-trap model) whose kinetic behaviour as determined from highly accurate quantum kinetic equations as well as a simple physical reasoning has an unexpected character from the point of view of the standard *macroscopic* thermodynamics [1, 2]. Namely, it was proved that owing to a strong interaction with a bath, microscopic systems are in principle able to transfer, in a cyclic process, particles from a set of particle reservoir states to a more limited set of states with contingently even slightly higher energy. (The particle reservoir is not to be mistaken for the standard thermodynamic bath.) The reverse process (scattering) is very ineffective and, in the most favourite situations, nearly impossible. This strange behaviour of the model seems, at first sight, to be incompatible with standard kinetic approaches. In the latter theories, time development of any system kept in isothermal conditions is, with increasing time and upon assuming weak coupling to the thermodynamic bath, expected to decrease its free energy, i.e. nearly the total energy at low temperatures. Although unexpected, such a type of behaviour is possible, asssuming the interaction with the thermodynamic bath underlying some bath-assisted transversal relaxation processes involved, in energy units, is appreciably stronger (i.e. more effective) than energy splittings caused by some less important terms of the Hamiltonian of the isolated system only. The latter splittings also determine duration of the scattering events of particles on the system in question. In other words, the above tendency to the thermodynamically unexpected asymptotic state of the scattered particles may be due to a proper combination of several features.

  • Long-lasting scattering events (a situation typical of heavy masses of impinging particles).

  • Internal structure of the scatterer (central system) among levels of which there are strong relaxation processes owing to its coupling to the thermodynamic bath. One should

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realize that such strong relaxation processes are omitted *by definition* in usual weak-coupling approaches.

   • A special kind of instability of order of levels of the central system upon accepting the scattered particles which allows the above relaxations in the intermediate scattering states.

   The above behaviour reminds us of the Maxwell daemon, working here, however, in isothermal conditions. The very idea is generalized later to treat processes with joining and mutual coupling of pairs of particles (atoms, molecules etc) with the active role of the open quantum system, i.e. our central system coupled to both the thermodynamic bath and a reservoir of particles. The simultaneous scattering of these pairs on the central system becomes possible at finite particle concentrations and the process then converts to nothing but a kind of chemical reaction stimulated by the central system. Thus we can get a strong catalytic effect of the presence of such a microscopic quantum system in the reservoir of particles in question.

   One should add a comment here concerning both possible applications and basic features of the process to be discussed. In standard investigations of scattering processes, the question of relaxation in intermediate states appears very infrequently as the scattering process itself is usually, or is assumed to be, very fast. On the other hand, all chemical reactions of, for example, heavy organic molecules are in fact a type of scattering process which is, owing to heavy masses of the components, very slow. In such situations, the relaxation processes in intermediate states of the scatterer, in particular in any catalytic system making the chemical reaction in question practically possible, can hardly be ignored.

   Next, heavy (in particular) organic molecules and their complexes are objects which can have a very long lifetime irrespective of the fact that their native states or those of intermediate products during their preparation often do not correspond to quantum-mechanical ground states but rather to excited states of all the complexes in a given situation. If chemical reactions leading to formation of such complexes were usual equilibrium (passive) reactions in, for example, solutions, their yield would be definitely very low. Thus, active elements (enzymes) catalysing such reactions (scattering channels) are needed which, however, need energy to be incorporated in the reaction products as excited states of the complex. In particular, in reactions occurring in solutions, no sufficiently concentrated sources of such energy are available. The present model provides a simple microscopic model showing how, in contrast with the equilibrium thermodynamics, the delocalized thermal energy can serve as a source of the required energy portion in such endothermic reactions. No real contradiction with thermodynamics is expected as the presence of systems modelled here in real solutions simply leads to an increase of the chemical potentials, i.e. the reaction yield of the reaction products.

   Because the problem is technically quite complicated, we shall present its discrete form. This means that we assume two types of particles which can move on a discrete lattice. Designating $m, n, \ldots$ the lattice points, the creation operators of the two types of particles are $c_m^\dagger$ and $g_m^\dagger$; c_m and g_m are the corresponding annihilation operators. Operators corresponding to different types of particles commute. As for the commutational relations of creation and annihilation operators of the same type of particles, we can avoid their specification because they are not needed for the principles of activity of our model. However, in order to be specific, we shall assume them to be Fermi-type anticommutational relations. This automatically does not allow two identical particles to reach the same site. Reserving site 0 for our central system (to be specified later), the reservoir of particles distributed on sites outside the origin can be described by, for example, the Hamiltonian

$$H_{\mathrm{r}} = \sum_{m,n(\neq 0)} [I_{mn} c_m^\dagger c_n + J_{mn} g_m^\dagger g_n] + V \sum_{m(\neq 0)} c_m^\dagger c_m g_m^\dagger g_m. \tag{1}$$

It is worth noting in (1) that we have allowed the c and g particles to interact with the on-site interaction V. For $|V|$ large enough, the resulting bound states of the particles (lying, for $V > 0$ or $V < 0$, above or below the band of scattering states) become well localized. This is meant in the sense of a prevailing probability of finding the c and g particles on the same site though not on one specific site in space; the bound c–g complex can be quite extended in space. That is why we can then roughly say that, for example, $c_m^\dagger g_m^\dagger$ creates (irrespective of the sign of V) a bound c–g state at site m. (1) is thus a Hamiltonian of the famous Hubbard type. We shall, however, not investigate it in detail as it is not our aim here. It is worth mentioning that we have not, for the sake of simplicity, introduced the interaction of particles of the same kind (c–c and g–g coupling).

As has already been pointed out, we reserve site 0 for our central system. This system we take as a two-level (molecule, molecular group etc) system with states designated as $|d\rangle$ and $|u\rangle$. The central system is assumed to be joined with the site 0 accessible to both types of particles. The corresponding energies of the above two states $|d\rangle$ and $|u\rangle$ are assumed to be $-\epsilon/2$ and $+\epsilon/2$, respectively, provided that the site 0 contains at most one particle of any of the two types. In the case when both c and g particles appear on site 0, we assume the energies to be reversed. This is the simplest model describing instability, upon adding particles, of the two levels of the central system. The instability can in reality be due to a change of topology of the central system due to appending both c and g particles to it. The corresponding Hamiltonian reads

$$H_{\mathrm{cs}} = \frac{\epsilon}{2}[|u\rangle\langle u| - |d\rangle\langle d|] \otimes [1 - 2c_0^\dagger c_0 g_0^\dagger g_0]. \tag{2}$$

Now, we should append the central system to the reservoir allowing it to accept as well as return particles to it. Once we do this, we introduce scattering processes of the particles on the central system; the c and g particles can scatter individually as a consequence of, for example, the pair forces between the corresponding particle and the central system. These terms are given by the first term in (3) later. However, even when neglecting inhomogeneity in space introduced by the central system, elementary processes coming from, for example, the pair c–g interaction appear where c and g particles hop simultaneously. In (1), we have omitted such processes for technical simplicity. Here, in scattering on the central system, we shall, however, take the (presumably) dominating portion of them into account as they yield the desired effect. In order to justify this, one should also realize that the very amplitude of such processes could, owing to the above inhomogeneity of the space because of the presence of the central system, become dependent on the distance from the central system. Thus, we have the term in the total Hamiltonian describing scattering of particles on the central system in the form

$$H_{\mathrm{r-cs}} = \sum_{m(\neq 0)} [I_m(c_m^\dagger c_0 + c_0^\dagger c_m) + J_m(g_m^\dagger g_0 + g_0^\dagger g_m)] \otimes |d\rangle\langle d|$$

$$+ \sum_{m(\neq 0)} K_m(c_m^\dagger g_m^\dagger g_0 c_0 + c_0^\dagger g_0^\dagger g_m c_m) \otimes |u\rangle\langle u|. \tag{3}$$

One should mention that amplitudes of all the above scattering processes could in principle depend on the state of the central system involved. This is in fact one of the crucial points in our model. One can understand it by realizing that different states of the central system might mean different topology. In particular, in (3), we have assumed that the scattering processes, where the c and g particles scatter on the central system individually, only take place provided that the central system is in its 'down-state' $|d\rangle$. Similarly, we have also assumed that the pair scattering processes only exist when both scattering particles are on the same site and the central system is in the 'up-state' $|u\rangle$.

The important point is that, as usual in statistical thermodynamics, we should divide the whole object investigated into the system and thermodynamic bath. In order to comply with the standard terminology, we define the system as our central system plus the reservoir of particles including their interaction. Thus the Hamiltonian of the system reads as

$$H_S = H_r + H_{cs} + H_{r-cs}. \tag{4}$$

Now, the question concerns the Hamiltonians of the thermodynamic bath H_B and that of the system–bath interaction H_{S-B}. Their details should not be very important provided that the relaxation processes assumed are really present for the model chosen. Thus, we choose the simplest form of H_B,

$$H_B = \sum_k \hbar\omega_k b_k^\dagger b_k \tag{5}$$

and

$$H_{S-B} = \frac{1}{\sqrt{N}} \sum_k \hbar\omega_k \{G_k[|u\rangle\langle d| + |d\rangle\langle u|] + g_k[c_0^\dagger c_0 + g_0^\dagger g_0]\}(b_k + b_{-k}^\dagger). \tag{6}$$

Clearly, this is the model of harmonic phonons representing the bath, with k and $\omega_k = \omega_{-k}$ being the wavevectors and corresponding phonon frequencies. As for H_{S-B}, we assume a form linear in the phonon creation $b_k^\dagger$ and annihilation operators b_k which is able both to cause up- and down-relaxations ($|u\rangle \leftrightarrow |d\rangle$ transitions) in the central system (terms proportional to G_k) and to cause on-site dephasing at site 0, which is important for transversal relaxation (dephasing) processes. Finally, N, $G_k = G_{-k}^*$ and $g_k = g_{-k}^*$ are the number of phonon modes (turning to infinity in the bath thermodynamic limit), the coupling constant of the central system and that of the carriers at site 0 to the bath of phonons, respectively.

2. How the system works

Here, before proceeding to a more detailed theory, we should first of all explain why the central system works as a fish-trap or (in this case isothermal) Maxwell daemon. In order to understand this, we only need a simple physical reasoning combined with the above two main features of the model, namely the following.

• The central system can (as follows from (3) and as it could be in Nature for, for example, topological reasons) accept as well as return both c as well as g particles from and to the reservoir individually (in the uncoupled states) provided that it is in its down-state $|d\rangle$. Similarly, it can accept or return the c as well as g particles by pairs in their bound state only when it is in its up-state $|u\rangle$. In reality, these exclusive possibilities could be replaced by, for example, dominating ones.

• The down-state of the central system (otherwise its ground state) becomes unstable upon accepting, to site 0 joined with the central system, both one c and one g particle. In other words, the up-state $|u\rangle$, with both c and g particles at site 0 appended to the central system, becomes the ground state of the central system. (Here, we have for a while considered the central system with site '0' as switched off from both the particle reservoir and the thermodynamic bath, i.e. we have taken it with Hamiltonian (2).) *Vice versa*, whenever any (or both) of these particles leaves site 0, $|d\rangle$ again becomes the stable ground state.

In addition, we have the possibility of longitudinal relaxation processes between the up- and down-states of the central system. Attention should be turned to the fact that quantum

mechanical amplitudes for the in- and out-scattering (appending and releasing) processes of the c and g particles on the fixed central system are assumed symmetric. This is a consequence of hermicity of our Hamiltonian (see (3)). The final asymmetry of the process (i.e. production of even energetically less advantageous bound states of c and g particles) is due to a combination of the above specific form of (3) with the $|u\rangle \leftrightarrow |d\rangle$ relaxation asymmetry. The latter is due to spontaneous processes with respect to the thermodynamic bath. Hence, no model treating the thermodynamic bath on a classical level (replacing it by, for example, a stochastic field) can yield the same desired effect. Similarly, switching off the bath immediately stops the process. That is why we call the system an *isothermal* Maxwell daemon having in mind differences as well as similarities with the original Maxwell daemon [3].

Let us now assume an arbitrary initial state of the system (i.e. the central system as well as the particle reservoir). We shall (as later specified quantitatively) limit our attention to the situation with very low values of I_m, J_m and K_m. For simplicity, let us assume that the previous cycle has just finished, i.e. the central system has already returned to its ground state $|d\rangle$ and there is neither a c nor g particle at site 0. Because of H_{r-cs} in (3), the c and g particles can now occasionally appear on site 0, too. Owing to efficient transversal relaxation (processes mediated by terms proportional to g_k in H_{S-B} in (6)), the particle phases are lost very fast, i.e. no additional stabilization of the down-state of the central system, owing to back and forth transitions of the c and g particles between site 0 and reservoir, appears. One must add here that when one (say c) particle already resides on site 0, transfer of the second (g) particle is energetically quite disadvantageous as it requires additional energy $\epsilon > 0$. This in addition to low values of I_m and J_m, is what can make this process relatively slow. However, it does not forbid simultaneous appearance of one c and one g particle at site 0 at all. The point is that no energy conservation requirement enters this process; the transfer in our situation is just virtual (being caused by H_{r-cs}). It is of the same type as that bringing (although with different probabilities) the particle in an arbitrarily asymmetric dimer to both sides whenever there is a transfer (resonance or hopping) term in the Hamiltonian (see in this connection terms proportional to I_m and J_m in H_{r-cs} in (3)) connecting the two dimer sites.

As soon as both particles virtually attach to the central system, the latter becomes energetically unstable and, unless one of the particles leaves site 0 in between which is a very slow process, it turns to the up-state with lower energy $-\epsilon/2$. This, however, makes both the particles unable to leave the central system individually but allows them to leave it simultaneously, by a transfer to the same site (say m). In our situation (owing to high values of $|V|$ in H_r (see (1))), this practically means leaving it in the bound state located at m. Again the transversal relaxation processes break any stabilization of the up-state of the central system by a partial simultaneous presence of the particles on site 0 as well as, already in the bound state, in the reservoir. Leaving site 0 by the pairing of both particles as a consequence of $K_m \neq 0$, making this process possible even at $T = 0$ is again a process which does not conserve energy. Thus, the process must be again looked at as only virtual and treated in a non-trivial manner. For small $|K_m|$, it may take a long time before such a simultaneous hop of our pair of particles appears. Once it really happens, however, the central system again becomes unstable and turns again, with the help of the interaction with the bath, to the down-state. This completes the cycle and the system is ready to accept a new pair of unbound particles from the reservoir. In what follows, we shall try to model this process on a quantitative footing.

3. Asymmetry by perturbational arguments

The $m, n(m \neq n) \leftrightarrow m = n$ transitions in fact form a kind of scattering process with bath-assisted relaxation processes in intermediate states. We want to treat them first by perturbational arguments. Let us assume that we have initially one c particle at site m and one g particle at site n, that the central system is in its down-state (with site 0 empty to be ready to accept particles) and that the reservoir is in its ground state. We calculate the probability of finding, in the final state, the two (c and g) particles in a bound state located at site r and the central system in the same initial state $|d\rangle$, ready to accept a new pair in question and start the cyclic process again. The latter site r we presume empty so as to be able to accept the pair in question. As a perturbation, we take all the terms in the Hamiltonian which may cause particle transfer and relaxation. These are the sum $H_{r-cs} + H_{S-B}$. For simplicity of arguments, we omit explicitly the above dephasing (transversal relaxation) processes, i.e. we put $g_k = 0$ in H_{S-B} in (6). Let us, however, stress here that in the next section, we again need and assume $g_k \neq 0$. This is also so for the discussion of the total energy balance of the cyclic process.

We call the transition just described the forth process. We realize that intermediate steps in this process, which are due to H_{r-cs} only, may be treated by simply solving the coherent back-and-forth oscillations in symmetric or asymmetric dimers. A typical time for bringing the c particle to site 0 first and only then transferring the g particle is then $\hbar/(2|I|) + \hbar/\sqrt{\epsilon^2 + 4J^2}$. (The second step requires the excitation energy ϵ. Here and later, for simplicity we fully disregard the problem of yield of the coherent transfer in the asymmetric dimer.) Similarly, for the reversed order of the elementary steps. Thus, the typical time for the forth transition as a whole reads

$$T_{\text{forth}} \approx \text{Min}\left[\frac{\hbar}{2|I_m|} + \frac{\hbar}{\sqrt{\epsilon^2 + 4J_n^2}}, \frac{\hbar}{2|J_n|} + \frac{\hbar}{\sqrt{\epsilon^2 + 4I_m^2}}\right] + \frac{\hbar}{\sqrt{V^2 + 4K_r^2}} + 2T_\downarrow \tag{7}$$

where

$$T_\downarrow^{-1} \equiv \Gamma_\downarrow \approx \frac{2\pi}{N\hbar} \sum_k |G_k \hbar \omega_k|^2 \delta(\epsilon - \hbar\omega_k)[1 + n_B(\hbar\omega_k)] \tag{8}$$

is the downwards (in energy) relaxation time of the central system in lowest-order perturbation (in H_{S-B}) theory. There are two such times in (7) as there are two downward relaxation processes involved. In (8), $n_B(z) = [\exp(\beta z) - 1]$ is the Bose–Einstein–Planck distribution for phonons. When the temperature $T = (k_B \beta)^{-1}$ turns to zero, $\Gamma_\downarrow$ remains non-zero, i.e. $T_\downarrow$ is finite in our case. In (8) and later, we automatically assume in all formalae of the type $1/N \sum_k \ldots$ that the thermodynamic limit of the bath $N \rightarrow +\infty$ is already performed. This allows us to get rid of the Poincaré cycles [4]. Thus, for small $|I_m|$, $|J_n|$ and $|K_r|$, T_{forth} is practically given by times required for the particle transfer to and from the central system to the respective sites.

On the other hand, let us now investigate the reverse process with the bath initially in the ground state of the bath again. Treating it in the same way would, however, yield for the typical transfer time

$$T_{\text{back}} \approx \text{Min}\left[\frac{\hbar}{2|I_m|} + \frac{\hbar}{\sqrt{\epsilon^2 + 4J_n^2}}, \frac{\hbar}{2|J_n|} + \frac{\hbar}{\sqrt{\epsilon^2 + 4I_m^2}}\right] + \frac{\hbar}{\sqrt{V^2 + 4K_r^2}} + 2T_\uparrow \tag{9}$$

where

$$T_\uparrow^{-1} \equiv \Gamma_\uparrow \approx \frac{2\pi}{N\hbar} \sum_k |G_k \hbar \omega_k|^2 \delta(\epsilon - \hbar\omega_k) n_B(\hbar\omega_k) \tag{10}$$

is the upwards (in energy) relaxation time of the central system in lowest-order perturbation (in H_{S-B}) theory. At zero temperature, however, $T_\uparrow$ would turn, according to (10), to infinity, i.e. the process would be fully prohibited. In fact, this is not so but the result shows that the reverse process should be investigated to higher orders of perturbation theory. In this case, we obtain at very low (formally zero) temperature that

$$T_{\text{back}} \approx \text{Min}\left[\frac{\hbar}{2|I_m|} + \frac{\hbar}{\sqrt{\epsilon^2 + 4J_n^2}}, \frac{\hbar}{2|J_n|} + \frac{\hbar}{\sqrt{\epsilon^2 + 4I_m^2}}\right] + T' \qquad (11)$$

where, already in the zero-temperature limit for the thermodynamic bath,

$$(T')^{-1} = \frac{2\pi}{\hbar} \sum_{k,k'} |T^{(3)}|^2 \delta(V - \hbar\omega_k - \hbar\omega_{k'}) \qquad (12)$$

is the lowest (according to the probability amplitude, the third) order perturbational contribution to a typical time of the process starting with the c–g pair of the particles at site r with the central system in state $|d\rangle$ and finishing with both particles at site 0 and the central system in the same state, having the bath initially in its ground state. The corresponding third-order T-matrix element in (12) reads

$$T^{(3)} = \frac{G_k \hbar\omega_k}{\sqrt{N}} \frac{1}{V - \hbar\omega_{k'} + i\eta} K_r \frac{1}{-\epsilon - \hbar\omega_{k'} + i\eta} \frac{G_{k'}\hbar\omega_{k'}}{\sqrt{N}}. \qquad (13)$$

Here η is a positive infinitesimal. From this, we obtain that by the order of magnitude, $(T')^{-1} \approx |G|^2 (K_r/(\epsilon - V))^2 \Gamma_\downarrow|_{T=0}$. Here G is a typical value of G_k. Arguing by the weakness of the coupling to the bath ($|G| \ll 1$) as well as by the smallness of the $|K_r/(\epsilon - V)|$ ratio, one easily obtains that at zero temperature (and correspondingly at low temperatures in general)

$$T_{\text{forth}} \ll T_{\text{back}}. \qquad (14)$$

This fully illustrates the origin and magnitude of the effect of the back–forth asymmetry of the transition (scattering).

4. Kinetic treatment

Having thus illustrated the effect in the formal zero-temperature limit, let us now return to such finite temperatures at which the lowest-order bath-assisted transfer rates in the backward direction have a chance to dominate over the above third-order processes in (12) and (13). So we are justified in omitting the latter processes. The standard Markovian (Pauli-master-equation (PME) [5, 6] like) theory with second-order transfer rates cannot be rigorously used as there are coherent channels in (4) (see (3)) involved. That is why we use the Nakajima–Zwanzig [4, 7–9] form of the time-convolution generalized master equations (TC-GME). In the long-time asymptotics, the theory then turns to a form formally reminiscent of PME, however. We shall, for reasons mentioned later, work with the projector suggested by Peier [10]. In order to make the technique simpler, we assume only two sites (1 and 2) in the particle reservoir and only one c and one g particle. That means that we substitute our Hamiltonian of the system (central system and particle reservoir) H_S in (4) (with (1), (2) and (3)) by

$$H_S = V(c_1^\dagger c_1 g_1^\dagger g_1 + c_2^\dagger c_2 g_2^\dagger g_2) + I(c_1^\dagger c_0 + c_0^\dagger c_1 + c_2^\dagger c_0 + c_0^\dagger c_2) \otimes |d\rangle\langle d|$$
$$+ J(g_1^\dagger g_0 + g_0^\dagger g_1 + g_2^\dagger g_0 + g_0^\dagger g_2) \otimes |d\rangle\langle d|$$
$$+ K(c_1^\dagger c_0 g_1^\dagger g_0 + c_2^\dagger c_0 g_2^\dagger g_0 + c_0^\dagger c_1 g_0^\dagger g_1 + c_0^\dagger c_2 g_0^\dagger g_2) \otimes |u\rangle\langle u|. \qquad (15)$$

We consider other possible terms to be negligible here. Hamiltonian (15), as well as the total Hamiltonian $H = H_S + H_B + H_{S-B}$ (with H_B and H_{S-B} given by (5) and (6)) are symmetric with respect to the $1 \leftrightarrow 2$ interchange. Thus the kinetics in symmetric and antisymmetric c–g states are independent. In fact, there is no kinetics for the antisymmetric states in our simplified model. That is why we shall only treat symmetric states.

There are just five symmetric c–g particle states forming a basis in our particle Hilbert space:

$$|1\rangle = \frac{1}{\sqrt{2}}[c_1^\dagger g_2^\dagger + c_2^\dagger g_1^\dagger]|\text{vac}\rangle$$

$$|2\rangle = \frac{1}{\sqrt{2}}[c_1^\dagger g_1^\dagger + c_2^\dagger g_2^\dagger]|\text{vac}\rangle$$

$$|3\rangle = \frac{1}{\sqrt{2}}[c_1^\dagger + c_2^\dagger]g_0^\dagger|\text{vac}\rangle$$

$$|4\rangle = \frac{1}{\sqrt{2}}[g_1^\dagger + g_2^\dagger]c_0^\dagger|\text{vac}\rangle$$

$$|5\rangle = c_0^\dagger g_0^\dagger|\text{vac}\rangle. \tag{16}$$

Here $|\text{vac}\rangle$ is the vacuum state of the particles. As for the central system, we have $|u\rangle$ and $|d\rangle$ states only, i.e. together we have ten states of our system (central system and reservoir of particles) $|j, u\rangle = |j\rangle \otimes |u\rangle$ and $|j, d\rangle = |j\rangle \otimes |d\rangle$, $j = 1, 2, \ldots, 5$. Working with the total density matrix of the system $\rho(t)$ with the Argyres–Kelley projector [11] but otherwise as below would thus lead to a set of ($10^2 =$) 100 linear integrodifferential equations for a total of 100 elements of $\rho(t)$. With the time-convolutionless formalism as (for a slightly different model and problem) in [2], that would again yield the set of 100 linear equations, although this time only differential equations. The problem would require the calculation (by hand) of 10^4 coefficients of the set as functions of time. Together with technical reasons connected with the scope of this paper, this is why we refrain from using this formulation here (although it contains more information) and work in the formalism and with the Peier projector ([10]) mentioned previously. This leads us to the set of ten TC-GME of the form

$$\frac{d}{dt}P_{ip}(t) = \sum_{jq(\neq ip)} \int_0^{t-t_0} [w_{ip,jq}(\tau)P_{jq}(t-\tau) - w_{jq,ip}(\tau)P_{ip}(t-\tau)]\,d\tau + J_{ip}(t, t_0)$$

$$i, j = 1, 2, \ldots, 5, \ p, q = u \text{ or } d. \tag{17}$$

Here $P_{ip}(t) = \rho_{ip,ip}(t) = \sum_\lambda \rho_{ip\lambda,ip\lambda}^{S+B}(t)$ is the probability of finding, at time t, the system in state ip (i.e. the c and g particles in state i and the central system in state $p = u$ or d), with the thermodynamic bath being in its arbitrary state. ρ^{S+B} is the density matrix of the system (central system plus particles) as well as bath and summation over Greek indices designates henceforth that over the states of the thermodynamic bath. As for the memory functions $w_{\ldots}(\tau)$ and the initial condition term $J_{ip}(t, t_0)$, we have exact formulae ([9]):

$$w_{ip,jq}(\tau) = -\sum_{\lambda\mu\nu}[\mathcal{L}e^{-i(1-\mathcal{P})\mathcal{L}\tau}(1-\mathcal{P})\mathcal{L}]_{ip\lambda,ip\lambda,jq\mu,jq\nu}\rho_{\mu\nu}^0$$

$$J_{ip}(t, t_0) = -i\sum_\lambda[\mathcal{L}e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)}(1-\mathcal{P})\rho^{S+B}(t_0)]_{ip\lambda,ip\lambda}. \tag{18}$$

Here $\mathcal{P}$ is the Peier projector defined as

$$[\mathcal{P}\ldots]_{ip\mu,jq\nu} = \delta_{ip,jq}\rho_{\mu\nu}^0 \sum_\lambda [\ldots]_{ip\lambda,ip\lambda} \tag{19}$$

with ρ^0 being an arbitrary matrix with indices of states of the bath except for the idempotency condition

$$\sum_{\mu} \rho^0_{\mu\mu} = 1. \tag{20}$$

For simplicity, we shall as usual limit ourselves to such a class of initial conditions that ρ^{S+B} is initially separable, i.e. $(\rho^{S+B})_{ip\mu,jq\nu}(t_0) = \rho^0_{\mu\nu}\rho_{ip,jq}(t_0)$ where $\rho^0_{...}$ (the initial density matrix of the bath) is identical with that in (19) and (20) and $\rho_{ip,jq}(t_0)$ (the initial density matrix of the system) is diagonal, $\rho_{ip,jq}(t_0) = P_{ip}(t_0)\delta_{ip,jq}$. Then $(1 - \mathcal{P})\rho^{S+B}(t_0) = 0$, i.e. the initial condition term disappears $J_{ip}(t, t_0) = 0$. This simplifies the analysis.

As for the memory functions $w_{ip,jq}(\tau)$, we can start expanding them in the perturbation series in those terms in the Hamiltonian $H = H_S + H_B + H_{S+B}$ (i.e. in H_S in (15) and H_{S+B} in (6)) which cause transitions among the above states. To finite order, many of the memory functions then turn to zero. We shall keep only those which are non-zero already in second-order perturbation theory. These are first of all

$$w_{ju,jd}(\tau) \approx w_{5d,5u}(\tau) \approx \frac{2}{N} \sum_k |G_k|^2 \omega_k^2 \left\{ n_B(\hbar\omega_k) \cos\left(\left(\frac{\epsilon}{\hbar} - \omega_k\right)t\right) \right.$$

$$\left. + [1 + n_B(\hbar\omega_k)] \cos\left(\left(\frac{\epsilon}{\hbar} + \omega_k\right)t\right) \right\} \qquad j = 1, 2, \ldots, 4$$

$$w_{jd,ju}(\tau) \approx w_{5u,5d}(\tau) \approx \frac{2}{N} \sum_k |G_k|^2 \omega_k^2 \left\{ n_B(\hbar\omega_k) \cos\left(\left(\frac{\epsilon}{\hbar} + \omega_k\right)t\right) \right.$$

$$\left. + [1 + n_B(\hbar\omega_k)] \cos\left(\left(\frac{\epsilon}{\hbar} - \omega_k\right)t\right) \right\} \qquad j = 1, 2, \ldots, 4. \tag{21}$$

Here, $n_B(z) = [\exp(\beta z) - 1]^{-1}$ ($\beta = 1/(k_B T)$) is the Bose–Einstein distribution for phonons. These expressions are pleasant in the sense that they decay to zero with increasing time (yielding well integrable functions) after taking the thermodynamic limit of the bath $N \to +\infty$. As for other memories which are non-zero to second order, these are $w_{1d,3d}(\tau) \propto J^2$, $w_{3d,1d}(\tau) \propto J^2$, $w_{1d,4d}(\tau) \propto I^2$, $w_{4d,1d}(\tau) \propto I^2$, $w_{2d,3d}(\tau) \propto J^2$, $w_{3d,2d}(\tau) \propto J^2$, $w_{2d,4d}(\tau) \propto I^2$, $w_{4d,2d}(\tau) \propto I^2$, $w_{2u,5u}(\tau) \propto K^2$, $w_{5u,2u}(\tau) \propto K^2$, $w_{3d,5d}(\tau) \propto I^2$, $w_{5d,3d}(\tau) \propto I^2$, $w_{4d,5d}(\tau) \propto J^2$ and $w_{5d,4d}(\tau) \propto J^2$. Their second-order explicit expressions are simple. One must, however, note that the latter do not properly decay to zero. The proper decay is restored only if one includes higher-order contributions partially summed up to infinity [12]. Even including only those intermediate states which are identical with the initial and final states indicated by indices of the memories (for example, $|4d\rangle$ and $|5d\rangle$ states upon calculating $w_{5d,4d}(\tau)$), i.e. working as in a dimer, is not a simple task [13, 14]. (For that, on the other hand, one needs justification to be able to work so. That is the point where the dephasing owing to $g_k \neq 0$ again enters the game, destroying phase relations among individual states $|j, d\rangle$ and $|j, u\rangle$ existing in eigenstates of H_S.) We shall assume that the above memories were calculated in this manner but utilize the fact that we do not, on the other hand, need explicit expressions for such memories.

Therefore one can solve (17) using some of the mathematical techniques available. Here, our problem is to discuss the long-time asymptotics of the solution only. Taking the limit $t \to +\infty$ in (17) analytically, one obtains the set of linear algebraic equations

$$0 = \sum_{jq(\neq ip)} [W_{ip,jq} P_{jq}(+\infty) - W_{jq,ip} P_{ip}(+\infty)]$$

$$W_{ip,jq} = \int_0^{+\infty} w_{ip,jq}(\tau) \, d\tau \qquad i, j = 1, 2, \ldots, 5, \ p, q = u \text{ or } d. \tag{22}$$

The rank of the system of 10 equations (22) equals nine. Together with the condition

$$\sum_{j=1}^{5} \sum_{q=u,d} P_{jq}(+\infty) = 1 \tag{23}$$

(22) provides the set of 10 linearly independent equations determining the asymptotic state of the system. An explicit form of some of the $W_{ip,jq}$ coefficients is easy to find from the above formulae. In particular, within the above accuracy,

$$\Gamma_{\uparrow} \equiv W_{ju,jd} = \int_0^{+\infty} w_{5d,5u}(\tau)\,d\tau$$

$$= \frac{2\pi}{\hbar N} \sum_k |G_k|^2 (\hbar\omega_k)^2 n_{\mathrm{B}}(\hbar\omega_k) \delta(\epsilon - \hbar\omega_k) \qquad j = 1, 2, \ldots, 4$$

$$\Gamma_{\downarrow} \equiv W_{jd,ju} = \int_0^{+\infty} w_{5u,5d}(\tau)\,d\tau$$

$$= \frac{2\pi}{N\hbar} \sum_k |G_k|^2 (\hbar\omega_k)^2 [1 + n_{\mathrm{B}}(\hbar\omega_k)] \delta(\epsilon - \hbar\omega_k) \qquad j = 1, 2, \ldots, 4. \tag{24}$$

These memories well fulfill (to second order) the unrenormalized detailed balance condition (DBC)

$$\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}} = e^{-\beta\epsilon}. \tag{25}$$

As for other coefficients $W_{ip,jq} = \int_0^{+\infty} w_{ip,jq}(\tau)\,d\tau$ which is non-zero here, we do not need the above higher-order expressions for memories $w_{ip,jq}(\tau)$. We only parametrize the result as

$$\begin{array}{lllll}
W_{1d,3d} = P & W_{3d,1d} = P' & W_{1d,4d} = Q & W_{4d,1d} = Q' & W_{2d,3d} = S \\
W_{3d,2d} = S' & W_{2d,4d} = T & W_{4d,2d} = T' & W_{2u,5u} = F & W_{5u,2u} = F' \\
W_{3d,5d} = G & W_{5d,3d} = G' & W_{4d,5d} = H & W_{5d,4d} = H'.
\end{array} \tag{26}$$

All these quantities should be (as probability rates in the Markovian limit) positive. On the other hand, they need *not* fulfil any simple DBC. The reason is that they are *not* due to bath-assisted transitions but rather due to simple constant overlap (hopping or transfer) integrals in the Hamiltonian. This may be easily shown in an asymmetric dimer case [15]; as a consequence, the ratios P/P', Q/Q' etc (as well as the values P, P' etc) remain definitely finite and non-zero in the zero-temperature limit. Therefore, one can write (22) explicitly. Instead, in order to avoid (for our qualitative reasoning) useless clumsy expressions, we shall first specify our regime.

   We assume that, owing to the previously assumed small values of $|I|$, $|J|$ and $|K|$,

$$\Gamma \equiv \Gamma_{\downarrow} \gg F \gg P, P', Q, Q', S, S', T, T', F', G, G', H, H' \gg \Gamma_{\uparrow}. \tag{27}$$

The first inequality together with the last ensures that F determines the transfer rate $5d \to 5u \to 2u \to 2d$ which is due to the existence of our central system. As we shall see later, the second inequality ensures effectiveness of the latter. In particular, it helps us to make the transfer channel $3d$ (and similarly $4d$) $\xrightarrow{G'} 5d \xrightarrow{\Gamma} 5u \xrightarrow{F} 2u \xrightarrow{\Gamma} 2d$ dominate over the direct one mediated by S, i.e. $3d \xrightarrow{S} 2d$ (and similarly T)—see (26). In other words, it helps us to make the effect of the presence of our 'daemon' sufficiently pronounced. The third inequality is, for given constant values of $|I|$, $|J|$ and $|K|$, a limitation to low temperatures. We use here the fact that $\Gamma_{\uparrow}$ gives the relaxation rate owing to absorption

of bath excitations which disappear in the zero-temperature limit (compare with (25)). We easily obtain from (22) by setting formally $\Gamma_\uparrow = 0$ that

$$P_{1u}(+\infty) = P_{3u}(+\infty) = P_{4u}(+\infty) = 0. \tag{28}$$

The remaining seven equations of (22) read

$$
\begin{pmatrix}
-P' - Q' & 0 & 0 & P & Q & 0 & 0 \\
0 & -\Gamma - F' & 0 & 0 & 0 & F & 0 \\
0 & \Gamma & -S' - T' & S & T & 0 & 0 \\
P' & 0 & S' & -P - S - G' & 0 & 0 & G \\
Q' & 0 & T' & 0 & -Q - T - H' & 0 & H \\
0 & F' & 0 & 0 & 0 & -F & \Gamma \\
0 & 0 & 0 & G' & H' & 0 & \Gamma - G - H
\end{pmatrix}
$$
$$
\cdot
\begin{pmatrix}
P_{1d}(+\infty) \\
P_{2u}(+\infty) \\
P_{2d}(+\infty) \\
P_{3d}(+\infty) \\
P_{4d}(+\infty) \\
P_{5u}(+\infty) \\
P_{5d}(+\infty)
\end{pmatrix}
= 0. \tag{29}
$$

Owing to (27), the matrix A of (29) splits well into $A = A_0 + A_1$ where the 'big' matrix A_0 has all elements zero except for $-A_{22} = A_{32} = A_{67} = -A_{77} = \Gamma$. Correspondingly, the 'small' matrix A_1 has only zero or small elements $P, P', Q, \ldots, H$. Looking for the solution X of the problem $(A_0 + A_1)X = 0$ (X is the column of asymptotic probabilities $P_{...}(+\infty)$ in (29)) in the form of $X = X_0 + X_1 + X_2 + \cdots$ with $X_1 \propto A_1$, $X_2 \propto A_1^2$ etc, we find the set

$$A_0 X_0 = 0 \qquad A_1 X_0 = -A_0 X_1 \qquad \ldots. \tag{30}$$

From the first equation of (30), we obtain

$$
X_0 \approx
\begin{pmatrix}
P_{1d}(+\infty) \\
P_{2u}(+\infty) \\
P_{2d}(+\infty) \\
P_{3d}(+\infty) \\
P_{4d}(+\infty) \\
P_{5u}(+\infty) \\
P_{5d}(+\infty)
\end{pmatrix}
=
\begin{pmatrix}
a \\
0 \\
b \\
c \\
d \\
e \\
0
\end{pmatrix}. \tag{31}
$$

Here a, b, c, d and e are still arbitrary. The remaining equations can be obtained by multiplying the second equation of (30) from the left by five different left-eigenvectors of A_0. This yields four independent equations:

$$
\begin{pmatrix}
-P' - Q' & 0 & P & Q & 0 \\
0 & -S' - T' & S & T & F \\
P' & S' & -P - S - G' & 0 & 0 \\
Q' & T' & 0 & -Q - T - H' & 0
\end{pmatrix}
\begin{pmatrix}
a \\
b \\
c \\
d \\
e
\end{pmatrix}
= 0. \tag{32}
$$

Therefore,

$$a \equiv P_{1d}(+\infty) = K \cdot F[QT'(P + S + G') + PS'(Q + T + H')]$$
$$b \equiv P_{2d}(+\infty) = K \cdot F[P'(Q + T + H')(S + G') + Q'(P + S + G')(T + H')]$$
$$c \equiv P_{3d}(+\infty) = K \cdot F[S'(T + H')(P' + Q') + P'Q(S' + T')]$$

$$d \equiv P_{4d}(+\infty) = K \cdot F[T'(S + G')(P' + Q') + PQ'(T' + S')]$$
$$e \equiv P_{5u}(+\infty) = K \cdot (P' + Q')[G'S(T + H') + T'H'(S + G')]$$
$$+ (S' + T')[G'P'Q + H'Q'P]. \tag{33}$$

The multiplicative positive constant K (depending on F) in (33) enters all constants $a, \ldots, e$ and its value is determined by the normalization condition (23). This means, with our approximations and regime (27), $a + b + c + d + e = 1$.

We mention the different role played by the above transfer rate F for different coefficients in (33). For $F = 0$, we, for instance, find that $P_{5u}(+\infty) = 1$ with all other asymptotic probabilities equal to zero. This is, however, not the case we discuss here. Instead, let us assume that F is sufficiently large (in the sense of the second inequality in (27)). Then owing to the increase of K with increasing F, $e \equiv P_{5u}(+\infty)$ turns to zero and we get

$$a \equiv P_{1d}(+\infty) = K' \cdot [QT'(P + S + G') + PS'(Q + T + H')]$$
$$b \equiv P_{2d}(+\infty) = K' \cdot [P'(Q + T + H')(S + G') + Q'(P + S + G')(T + H')]$$
$$c \equiv P_{3d}(+\infty) = K' \cdot [S'(T + H')(P' + Q') + P'Q(S' + T')]$$
$$d \equiv P_{4d}(+\infty) = K' \cdot [T'(S + G')(P' + Q') + PQ'(T' + S')] \tag{34}$$

where the (F-independent) constant K' is determined by the normalization condition

$$a + b + c + d \equiv P_{1d}(+\infty) + P_{2d}(+\infty) + P_{3d}(+\infty) + P_{4d}(+\infty) = 1 \tag{35}$$

with all other asymptotic probabilities turning almost to zero in the above regime (27). With that, we could already discuss the effect of the existence of our central system. We find it, however, simpler to note that (34) is a solution (normalized to unity as in (35)) of the set of equations

$$\begin{pmatrix} -P' - Q' & 0 & P & Q \\ 0 & -S' - T' & S + G' & T + H' \\ P' & S' & -P - S - G' & 0 \\ Q' & T' & 0 & -Q - T - H' \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = 0. \tag{36}$$

One could also have derived these equations directly from (32). A proper normalization condition (35), necessary for comparison with the limiting case, can be, however, deduced only in the above limiting case of dominating F (see the second inequality of (27)).

Let us, on the other hand, switch off our central system from our reservoir of particles from the very beginning. This means we set $G', H' \to 0$ after neglecting $\Gamma_\uparrow$ in (22) (we again use the notation (26)). Then all the asymptotic probabilities turn to zero except for those in (35). Those which remain non-zero fulfill (in addition to (35)) the set of equations to which (22) reduces, i.e.

$$\begin{pmatrix} -P' - Q' & 0 & P & Q \\ 0 & -S' - T' & S & T \\ P' & S' & -P - S' & 0 \\ Q' & T' & 0 & -Q - T \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = 0. \tag{37}$$

Direct comparison of (36) with (37) shows that the presence of the central system means an effective increase of transfer rates S (for the transfer $3d \to 2d$) and T (for the transfer $4d \to 2d$) to $S + G'$ and $T + H'$. Even without analysing our result (34) for G' and H' non-zero as compared with that for G' and H' equal to zero, this is easily seen to increase the asymptotic population $b \equiv P_{2d}(+\infty)$. This increase may be (when $G' \gg S$ and $H' \gg T$) even appreciable. (In this connection, one should note that when the second inequality of (27) applies, our central system works very fast, i.e. the rate of transfer of the

pairs of particles to the bound state is given by the transfer rates of bringing the c and g particles to it. The latter are nothing but G' and H'.)

One should also mention the following important facts following from (33).

• $P_{2d}(+\infty)$ is always positive, owing to positive values of $P, P', Q, \ldots, H'$. This fact already follows from the structure of (22) as far as the relevant probabilities are initially non-negative.

• $P_{2d}(+\infty)$ remains finite in the zero-temperature limit $T \to 0$, owing to non-zero low-temperature limits of $P, P', Q, \ldots, H'$.

5. Discussion

Thus, we have found that at low temperatures the occupation probability for the state $|2d\rangle$ becomes temperature insensitive, in contrast to the prediction of the standard Boltzmann equilibrium statistics

$$P_{2d}|_{\text{equi}} \propto e^{-\beta V} \tag{38}$$

and (possibly even appreciably) enhanced by the presence of our central system working as indicated. At intermediate temperatures limited from below, one can, on the one hand, prove from (37) in the same way as in [15] that (38) applies well when $|I_m|$, $|J_m|$ and $|K_m|$ are small enough (in this case, state $|2\rangle$ above becomes a real localized eigenstate of the particles) and $G' = H' = 0$. On the other hand, as follows from the above treatment, our 'daemon' investigated here works with the rate which may be appreciable and is only slightly temperature dependent and remains finite even at $T = 0$. This proves that our central system may really play an active and important role in increasing appreciably the population of the bound state (state $|2\rangle$) of our c and g particles. (For $V > 0$, this state is energetically unfavourable.) This opens at least two important questions.

• To which extent does this favourable situation change in the case of an infinite reservoir of particles?

• Which is the source of energy needed to create, for $V > 0$, a bound and energetically unfavourable state of our particles?

To answer these questions, let us return to our original Hamiltonian $H = H_S + H_B + H_{S-B}$ with (4)–(6). With the infinite reservoir of the c and g particles, i.e. an infinite number of sites accessible, the presence of one single central system only should not change the population ratio of the bound or scattering c–g states. This is irrespective of non-zero flow, through states joined with the central system, to the manifold of the bound states. It is easy to see that this is true because, in particular, the bath-assisted de-excitation processes omitted here are connected with each site in the reservoir. Thus, they should integrally certainly dominate over one, though perhaps strong, channel investigated above and which 'sews' the particles together. Including excitation and de-excitation processes assisted by the thermodynamic bath and also running on each site in the particle reservoir then allows the restoration of the temperature-activated form of populations (38). On the other hand, even in an infinite reservoir of particles we have a non-zero effect of the presence of the systems of the type of our central system, provided that their concentration (number relative to the number of sites accessible for particles) remains finite. This is the way in which, according to the above results, central systems of our type may, at their finite concentrations c_{sys}, appreciably influence the amount of bound c and g particles.

As for the second question posed above, let us remember that, according to the above arguments, the process of sewing the c and g particles together may, at $V > 0$, go up in particle energy. The only source of energy accessible to compensate this particle-energy

increase is the bath. One cycle of sewing is, roughly speaking and at low temperatures, connected with two acts of the spontaneous emission of the bath excitations (phonons). This would seemingly make the process prohibited by energy conservation law arguments. On the other hand, we have already argued that we in fact need sufficiently fast dephasing in our process destroying phase relations among our localized states $|j, u\rangle$ and $|j, d\rangle$. This is possible due to the active and sufficiently strong interaction with the bath when $g_k \neq 0$. This interaction, however, implies multiple and intense absorption and emission of phonons from the bath, which finally make the whole cycle energetically possible. As for the rate of kinetics, the above mechanism also certainly yields additional acceleration of the natural down-in-energy, bath-assisted processes whenever $V < 0$. This is what may make the above mechanism important as a source of unusual catalytic properties, even allowing reactions which would be otherwise, in simple situations, on usual time scales and at finite temperatures, hardly possible. Owing to the one-way and possibly cyclic character of the process, the present mechanism of sewing particles together might have applications in chain processes in biological systems.

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