Isothermal Maxwell demon as a quantum ''sewing machine''

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(Received 2 April 1997; revised manuscript received 18 July 1997)

A model of an open microscopic quantum system interacting with an isothermal bath and able to bind actively particles from a reservoir to their even excited bound states at the cost of the bath energy is presented. The binding (potentially important in, e.g., chain reactions—hence ''sewing'') is due to dynamic processes in a central part of the system accompanying the particle transfer. The outcome thus challenges the second law of thermodynamics. [S1063-651X(98)00304-3]

PACS number(s): 05.30.−d, 82.20.Mj, 82.40.−g

I. INTRODUCTION

In an attempt to model some vital processes in biological cells, we have found a model exhibiting a strange behavior. Before mentioning the physical motivation in more detail, let us start with introducing the model formally. As is usual in the nonequilibrium statistical mechanics, the quantum Hamiltonian can be split as

$$H=H_S+H_B+H_{S-B}. \tag{1}$$

Here we choose the Hamiltonian H_S of the system under consideration as a sum

$$H_S=H_{cen\ sys}+H_{part}+H_{cs\ part}. \tag{2}$$

$H_{cen\ sys}$ describes a central system (molecule), which we assume to have just two eigenstates $|u\rangle$ and $|d\rangle$ with energies $\pm\epsilon/2$. Thus

$$H_{cen\ sys}=\frac{\epsilon}{2}[|u\rangle\langle u|-|d\rangle\langle d|]. \tag{3}$$

As for the particle Hamiltonian, we assume two types of particles with creation (annihilation) operators $c_m^\dagger$ and $g_m^\dagger$ (c_m and g_m). The c operators commute with g operators as usual. As for the (anti)commutational c vs c or g vs g relations, however, these will be unimportant as we shall assume only one c and one g particle for the sake of simplicity here; assuming the above creation and annihilation operators of both types to be of the Fermi or Bose type makes no difference. Though generalization to greater particle reservoirs (as well as a greater number of particles) is straightforward, we shall for simplicity deal here just with a particle reservoir consisting of only two sites (labeled 1 and 2). So we have

$$H_{part}=J(g_1^\dagger g_2+g_2^\dagger g_1+c_1^\dagger c_2+c_2^\dagger c_1)+V(c_1^\dagger c_1 g_1^\dagger g_1+c_2^\dagger c_2 g_2^\dagger g_2). \tag{4}$$

We shall always assume the c-g interaction $V>0$ (though practically all the formulas apply also to the opposite case; the reason is that there is perhaps no doubt that the inelastic scattering on the central system can bring the particles down in energy, i.e., to their bound state at $V<0$, even at very low temperatures). As for the interaction Hamiltonian between the central system and reservoir of particles, we assume it to consist of two terms, i.e.,

$$H_{cs\ part}=H'_{cs\ part}+H''_{cs\ part},\qquad H'_{cs\ part}=\epsilon[|d\rangle\langle d|-|u\rangle\langle u|]c_0^\dagger c_0 g_0^\dagger g_0. \tag{5}$$

In connection with that, one should mention that we assume our model to contain also the third site (labeled 0, with creation operators of particles $c_0^\dagger$ and $g_0^\dagger$), which we do not ascribe, however, to the particle reservoir but assume it to be tightly connected with the central system. The form $H'_{cs\ part}$ is chosen in such a way that whenever the site 0 accepts both one c and one g particle, the central system with the Hamiltonian $H_{cen\ sys}+H'_{cs\ part}$ becomes unstable in the sense that the states $|u\rangle$ and $|d\rangle$ having originally eigenenergies $\pm\epsilon/2$ acquire energies $\mp\epsilon/2$. (We shall always assume below that $\epsilon>0$.) In reality, this may easily happen as a change of a stable molecular configuration upon accepting a pair of particles. As for the $H''_{cs\ part}$ term in Eq. (5) (part of the interaction between the central system and particle reservoir transferring the particles between them), it will be specified below.

At this point, we should not only explain our motivation and physical ideas but we could also say something about possible applications of the systems of the above type in nature. The first point is the above instability of the central system upon accepting the c-g pair to our site 0. In the world of macromolecules, we know such examples when the molecules change their topology upon accepting (getting bound with) additional ions, molecular groups, etc. In the language of, e.g., biology, site 0 would in such a case designate a receptor(s) for the species in question. Our idea hidden beyond our Hamiltonian is twofold.

(i) The change in the topology could bring the c-g pair together, forcing the particles to form a bound state by overcoming the contingent potential barrier or even the potential step due to, e.g., repulsive forces between the particles. For instance, the central molecule, being originally, e.g., rodlike, could bend or screw upon accepting the pair. For this to happen irrespective of, e.g., the repulsive forces between the g and c particles, the central molecule must be sufficiently stiff in its (tendency to the) new topology. In other words, ϵ

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should exceed the potential step as well as the barrier above [compare, e.g., Eq. (22) below]. This is the reasoning that formed the original motivation of the present work.

(ii) Such a process seems to require, however, a corresponding portion of energy. Though one could postpone the discussion of this point, it is preferable to discuss this important point here so as not to lose the trust of the reader. If we simply take the lacking energy from the bath, the process would become energy activated as a bath-assisted process. This would make it ineffective except at very high temperatures when all the states of the system would become, at long times, more or less equally populated. This would make the problem uninteresting. However, in the microworld governed by laws of strict quantum dynamics, processes are allowed that seemingly contradict the energy conservation law. Tunneling is one such example, but this is not our situation here. We rather have in mind the fact that localization of any particle may increase, due to the quantum uncertainty relations, its kinetic energy T, i.e., also the total energy $E=T+U$. As a textbook example, one can take the zero-point energy in, e.g., the quantum oscillator. The latter energy lies above the minimum of the potential and the wave function has a Gaussian form around the potential-energy minimum. This is so because further localization of the particle at the potential-energy minimum would still lower the mean potential energy, but it would also appreciably increase the mean kinetic, i.e., also the total energy, which should on the other hand, be minimal in the ground state of the system. Hence, as long as there are terms in the Hamiltonian H_S allowing delocalization (these terms will in our case be provided by $H''_{cs\ part}$ to be specified below), the eigenstates of H_S (in any finite system as in our case) will certainly, also according to the variational principle of the quantum mechanics, be at least partially delocalized. Thus, if we compile the eigenstates into a time-dependent solution of the Schrödinger equation for the particles in the isolated system $i\hbar d|\Psi(t)\rangle/dt=H_S|\Psi(t)\rangle$ and if we initially put our particles outside site 0, we get from the solution that with a nonzero probability, they will definitely appear later (separately as well as simultaneously) at site 0 too. This is a purely quantum process that may bring both the c and the g particles to site 0, irrespective of how much site energy it costs. Notice that for this process, no energy from the reservoir (bath) is needed as the bath was completely split off in the above Schrödinger equation. The bath energy and the very interaction with the bath enters the process only at the moment of turning it from the virtual-type to the real-type process as discussed below. This change of the character of the process after bringing both particles to site 0 without requiring the bath energy will be connected with the above instability of the central system upon accepting both the c and the g particle [see the form of $H'_{cs\ part}$ and the discussion following Eq. (5)] and the form of $H''_{cs\ part}$ to be introduced below. We have in mind the dynamic closing of back-reaction channels (forbidding the particles to leave site 0 individually in the same way as they arrived there) once the central system reorganizes on account of the above instability. So, not the above bringing the particles to site 0 but the ensuing ''closing the gate behind them'' and opening of a new reaction channel for the particles to proceed in their bound state requires the interaction (i.e., the energy exchange) with the bath. As also argued below, however, no activation energy is needed for this closing and opening the reaction channels as these are (as reorganization processes owing to the central system instability) mostly spontaneous (down-in-energy) processes with respect to the bath.

These two points mentioned immediately suggest the kind of processes to which our system may lead: Our system, working as a real molecular machine, could serve as an active catalyst of reactions that would otherwise be completely impossible. By the word ''active'' we mean a catalytic property that is not reducible to just lowering the potential barriers. We mean an active collecting of the thermal energy (if needed or at least borrowing it for a while for virtual processes) from the bath in order to make some specified, e.g., endothermic reactions (binding particles in our case) even possible. In order to convince the reader that such systems could really exist and work, we should continue with the construction of our Hamiltonian.

For simplicity, we shall always assume the $1\leftrightarrow 2$ symmetry of our Hamiltonian. That is why we can limit our considerations to just symmetric states. The symmetric eigenstates of our particle Hamiltonian and the corresponding eigenenergies read

$$
\begin{aligned}
|\phi_1\rangle &= \frac{1}{\sqrt{[V+\sqrt{V^2+16J^2}]^2+16J^2}} \\
&\quad\times\left[[V+\sqrt{V^2+16J^2}]\,\frac{1}{\sqrt{2}}\,(c_1^\dagger g_1^\dagger+c_2^\dagger g_2^\dagger)|\mathrm{vac}\rangle\right. \\
&\quad\left.+4J\,\frac{1}{\sqrt{2}}\,(c_1^\dagger g_2^\dagger+c_2^\dagger g_1^\dagger)|\mathrm{vac}\rangle\right], \\
E_1^{part} &= \frac{1}{2}\,[V+\sqrt{V^2+16J^2}], \\
|\phi_2\rangle &= \frac{1}{\sqrt{[V+\sqrt{V^2+16J^2}]^2+16J^2}} \\
&\quad\times\left[-4J\,\frac{1}{\sqrt{2}}\,(c_1^\dagger g_1^\dagger+c_2^\dagger g_2^\dagger)|\mathrm{vac}\rangle\right. \\
&\quad\left.+[V+\sqrt{V^2+16J^2}]\,\frac{1}{\sqrt{2}}\,(c_1^\dagger g_2^\dagger+c_2^\dagger g_1^\dagger)|\mathrm{vac}\rangle\right], \\
E_2^{part} &= -\frac{8J^2}{V+\sqrt{V^2+16J^2}}, \\
|\phi_3\rangle &= \frac{1}{\sqrt{2}}\,[c_1^\dagger+c_2^\dagger]g_0^\dagger|\mathrm{vac}\rangle, \\
|\phi_4\rangle &= \frac{1}{\sqrt{2}}\,[g_1^\dagger+g_2^\dagger]c_0^\dagger|\mathrm{vac}\rangle, \\
E_3^{part} &= E_4^{part}=J, \\
|\phi_5\rangle &= c_0^\dagger g_0^\dagger|\mathrm{vac}\rangle, \\
E_5^{part} &= 0.
\end{aligned}
\tag{6}
$$

Thus, ignoring the antisymmetric states, H_{part} can be rewritten as

$$H_{part}=\sum_{i=1}^{5}|\phi_i\rangle E_i^{part}\langle\phi_i|. \tag{7}$$

With that, we can now rewrite $H'_{cs\ part}$ as

$$H'_{cs\ part}=\epsilon[|d\rangle\langle d|-|u\rangle\langle u|]\otimes|\phi_5\rangle\langle\phi_5| \tag{8}$$

and specify $H''_{cs\ part}$ as

$$H''_{cs\ part}=P([|\phi_2\rangle+|\phi_5\rangle][\langle\phi_3|+\langle\phi_4|]+\text{H.c.})\otimes|d\rangle\langle d| + Q(|\phi_5\rangle\langle\phi_1|+\text{H.c.})\otimes|u\rangle\langle u|. \tag{9}$$

(Here H.c. means the Hermitian conjugate.) In words, we assume that the central system allows different types of particle transitions (channels of the particle scattering) in different physical configurations. The detailed form of Eq. (9) is chosen in our model in the simplest version yielding the desired effect.

With that, we have already specified the Hamiltonian of our system in the form required above. As for the thermodynamic bath, its detailed form is (except that it cannot be dispersionless) in fact unimportant. We only need that, in connection with the system-bath coupling, it yields the desired and sufficiently fast transitions among different states of the central system. The simplest version is that of noninteracting bosons (e.g., phonons)

$$H_B=\sum_k \hbar\omega_k b_k^\dagger b_k. \tag{10}$$

Here $\hbar\omega_k$ are energies of the bath excitations and $b_k^\dagger$ (b_k) is the corresponding creation (annihilation) operator, which we assume to be bosonlike. The same applies to the system-bath interaction. Its simplest form causing relaxation between states of the central system can be chosen as

$$H_{S-B}=\frac{1}{\sqrt{N}}\sum_k \hbar\omega_k(b_k+b_{-k}^\dagger)\{G_k[|u\rangle\langle d|+|d\rangle\langle u|] + g_k|\phi_5\rangle\langle\phi_5|\}. \tag{11}$$

Here N and G_k are the number of bath modes (numerated by index k taken as a wave vector here) and set of interaction constants. In the thermodynamic limit of the bath, N tends to infinity and the sums $(1/N)\Sigma_k\cdots$ turn to the usual integrals. As Eq. (11) allows $|u\rangle\leftrightarrow|d\rangle$ relaxation, our problem can be viewed also as a slow combined particle scattering on a central system with relaxation between its (and special type of instability of the) intermediate states. Special attention should also be devoted to the term in Eq. (11) that is proportional to g_k. This term is the simplest one causing (in reality very strong) transversal relaxation (dephasing) processes. In order to understand the important role of the dephasing, one should realize that with Eq. (6), one can easily diagonalize the whole Hamiltonian of the system H_S [Eq. (2)]. If the dephasing (transversal relaxation) were fully omitted, one would get transitions among the corresponding eigenstates of H_S as the only effect of the coupling to the bath. This is the way submitted by the weak-coupling (second order in H_{S-B}) theories yielding a transition to the canonical state. That means relaxation to practically the ground state at low enough temperatures. The ground state of H_S, however, is not the desired asymptotic state here. It contains components with our particles outside site 0 as well as at this site, with definite phase relations among these components. These relations are due to $H''_{cs\ part}$ in Eq. (9), which must be taken, in the weak coupling (to the bath) theories, as dominating over H_{S-B} in Eq. (11). In our model, however, we assume the opposite relation between the roles of $H''_{cs\ part}$ and H_{S-B}. This means that higher orders in H_{S-B} also become effective, which causes, in addition to transitions, also the transversal relaxation. Physically, the meaning of the sufficiently strong transversal relaxation (dephasing) consists in destroying the above tough phase relations among individual components of the eigenstates of H_S, i.e., turning the above transitions to those that are between the two eigenstates $|u\rangle$ and $|d\rangle$ of Eq. (3) (instead of those among eigenstates of H_S) as already suggested by the form of the first term in Eq. (11) proportional to G_k. As already mentioned, such a dephasing would be provided already by higher-order terms in G_k, in particular when these coupling constants (i.e., the whole H_{S-B}) are sufficiently strong. In order to see this effect explicitly, one would need, however, a detailed higher-order theory, while the term proportional to g_k in Eq. (11) yields such dephasing processes immediately. Technically, the importance of such terms in H_{S-B} in Eq. (11) proportional to g_k becomes clear, realizing that with such a dephasing, the memory functions to be invoked below become more strongly decaying functions of time, i.e., their time integrals become better convergent. From the point of the energy conservation law, the importance of these terms becomes clear from the observation that our asymptotic state of the system (to be obtained below) lies in energy well above the ground state of H_S. Thus, in order to make our process of the active binding of our particles really effective, we need an intense energy exchange with the bath (which is the only source of energy at our disposal for our endothermic process investigated). This means a strong absorption as well as emission of boson excitations in our bath. These processes are effectively provided by, in particular, the second term in H_{S-B} in Eq. (11) proportional to g_k.

Before going to the solution of the dynamic problem connected with the above Hamiltonian, let us briefly mention the problem of the order of energies of the Hamiltonian of the system H_S. This is a very important question in connection with the weak-coupling (in H_{S-B}) kinetic theories. In such approaches, the relaxation certainly goes mostly (and at low temperatures exclusively) to the ground state of H_S. Our theory here, however, is definitely not the weak-coupling theory of such a type. Rather than the strength of the system-bath coupling, the parameters P and Q in $H''_{cs\ part}$ in Eq. (9) play the role of the small parameters, though no real expansion in powers of P and Q is used. (As for the real regime assumed see below.) Anyway, it is worth mentioning, as we will argue below, that $|\phi_1\rangle\otimes|d\rangle$ is actually the asymptotic state of the system (i.e., the particle bound state $|\phi_1\rangle$ is practically the asymptotic state of the particles). This state is one of the eigenstates of H_S at $P=Q=0$ and remains approxi-

mately so at low (but still finite) values of P and Q. In this connection, one should realize that the corresponding particle energy E_1 is appreciably above all other particle energies E_i, $i=2,\ldots,5$ in Eq. (6) whenever $V \gg |J| > 0$. In connection with the solution presented below, this is what we contend makes our model so challenging.

II. SOLUTION

We assume the notation for states of our system $|im\rangle = |\phi_i\rangle \otimes |m\rangle$, $i=1,\ldots,5$, $m=u$ or d. Then for probabilities $P_{im}(t)$ of finding, at time t, our system (central system plus particles) in state $|im\rangle$, one can write Nakajima-Zwanzig generalized master equations [1,2] with the Peier type of projector $\mathcal{P}$ [3] as

$$\frac{d}{dt}P_{im}(t) = \sum_{jn\ (\neq im)} \int_0^t [w_{im,jn}(\tau)P_{jn}(t-\tau) - w_{jn,im}(\tau)P_{im}(t-\tau)]d\tau. \tag{12}$$

We have already omitted the initial condition term as a consequence of special initial conditions assumed [2,3], namely,

$$\rho_{tot}(0) = |2m\rangle\langle 2m| \times \rho^B, \quad m=u \text{ or } d, \tag{13}$$

provided the initial density matrix of the bath $\rho^B = \exp(-\beta H_B)/\mathrm{Tr}_B \exp(-\beta H_B)$ is used in the projector $\mathcal{P}$ [3]. This introduces the initial bath temperature $T = 1/k_B\beta$ into the memory functions

$$w_{im,jn}(\tau) = -\sum_{\mu,\nu,\lambda} [\mathcal{L}e^{-i(1-\mathcal{P})\mathcal{L}\tau} \times (1-\mathcal{P})\mathcal{L}]_{im\mu,im\mu,jn\nu,jn\lambda}\rho^B_{\nu\lambda} \tag{14}$$

(see [3]). (Here the summation over greek indices is that one over states of the bath; $\mathcal{L}$ is the Liouville superoperator and the algebra of four-index matrices is introduced as usual [2–4].) For other initial conditions, one may argue that the initial condition (inhomogeneous) term in Eq. (12) decays fast with increasing time.

We shall not try to calculate our memory functions (14) exactly. Going even beyond the lowest order of the perturbation theory provides here a difficult task. Instead, we shall only argue that [as seen from a comparison of different memory functions and corresponding matrix elements of, in particular, $H''_{cs\ part}$ in Eq. (9)]

$$\begin{aligned} &w_{2d,3d}(t) = w_{2d,4d}(t), \quad w_{3d,2d}(t) = w_{4d,2d}(t), \\ &w_{3d,5d}(t) = 2_{4d,5d}(t), \quad w_{5d,3d}(t) = w_{5d,4d}(t), \\ &w_{jd,ju}(t) = w_{5u,5d}(t), \quad j=1,\ldots,4 \\ &w_{ju,jd}(t) = w_{5d,5u}(t), \quad j=1,\ldots,4. \end{aligned} \tag{15}$$

Except for $w_{1u,5u}(t)$ and $w_{5u,1u}(t)$, other memory functions turn to zero in the lowest order in $H_{S-B}+H''_{cs\ part}$ (part of the total Hamiltonian causing transitions) and for simplicity shall be fully disregarded as unimportant here. A detailed analysis of nonzero higher-order memory functions that are zero in the second order shows that a sufficient justification for that at, e.g., low and intermediate temperatures $T \ll \epsilon/k_B$ can be provided by the inequality

$$|G|^2[Q/(\epsilon - V)]^2 \ll 1 \tag{16}$$

(here G is a typical value of G_k). Let us add only that omission of the above memory functions that disappear in the second order is in principle not necessary and can be avoided. Here we proceed in this way just for technical simplicity of the solution and final formulas.

Assume that we work (as indicated) to the above lowest order but include in a proper way partially higher-order terms up to infinity in order to get the decay of memories and convergent memory integrals $\int_0^{+\infty} w\ldots(t)dt$ (see, e.g., [4]). The necessity of at least a partial summation to infinity to obtain a decay of the memory functions to zero was stressed by Silbey [5]. One should also mention that our above dephasing processes appearing for $g_k \neq 0$ are, in addition to higher-order processes, the main reason for a proper decay of the memory functions. With that, taking the long-time limit of Eq. (12) and designating

$$\begin{aligned} &\int_0^{+\infty} w_{2d,3d}(t)dt = A', \quad \int_0^{+\infty} w_{3d,2d}(t)dt = A, \\ &\int_0^{+\infty} w_{3d,5d}(t)dt = B', \quad \int_0^{+\infty} w_{5d,3d}(t)dt = B, \\ &\int_0^{+\infty} w_{1u,5u}(t)dt = C', \quad \int_0^{+\infty} w_{5u,1u}(t)dt = C, \\ &\int_0^{+\infty} w_{1u,1d}(t)dt = \Gamma_\uparrow \equiv \frac{2\pi}{\hbar}\frac{1}{N}\sum_k |G_k|^2(\hbar\omega_k)^2 \times \delta(\epsilon - \hbar\omega_k)n_B(\hbar\omega_k) + O(|G|^4), \\ &\int_0^{+\infty} w_{1d,1u}(t)dt = \Gamma_\downarrow \equiv \frac{2\pi}{\hbar}\frac{1}{N}\sum_k |G_k|^2(\hbar\omega_k)^2\delta(\epsilon - \hbar\omega_k) \times [1 + n_B(\hbar\omega_k)] + O(|G|^4), \end{aligned} \tag{17}$$

we obtain from Eq. (12)

$$0 = \begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{C} & \mathcal{D} \end{pmatrix} \begin{pmatrix} P_{1u}(+\infty) \\ P_{1d}(+\infty) \\ P_{2u}(+\infty) \\ P_{2d}(+\infty) \\ P_{3u}(+\infty) \\ P_{3d}(+\infty) \\ P_{4u}(+\infty) \\ P_{4d}(+\infty) \\ P_{5u}(+\infty) \\ P_{5d}(+\infty) \end{pmatrix} = 0. \tag{18}$$

[In the explicit formulas for $\Gamma_\uparrow$ and $\Gamma_\downarrow$, we have for a while set $g_k=0$. With g_k nonzero, the δ functions $\delta(\epsilon\pm\hbar\omega_k)$ ensuring the energy conservation would become simply broadened.] The 5×5 blocks $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, and $\mathcal{D}$ are given as

$$\mathcal{A}=\begin{pmatrix} -\Gamma_\downarrow-C & \Gamma_\uparrow & 0 & 0 & 0 \\ \Gamma_\downarrow & -\Gamma_\uparrow & 0 & 0 & 0 \\ 0 & 0 & -\Gamma_\downarrow & \Gamma_\uparrow & 0 \\ 0 & 0 & \Gamma_\downarrow & -\Gamma_\uparrow-2A & 0 \\ 0 & 0 & 0 & 0 & -\Gamma_\downarrow \end{pmatrix},$$

$$\mathcal{B}=\begin{pmatrix} 0 & 0 & 0 & C' & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ A' & 0 & A' & 0 & 0 \\ \Gamma_\uparrow & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathcal{C}=\begin{pmatrix} 0 & 0 & 0 & A & \Gamma_\downarrow \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & A & 0 \\ C & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathcal{D}=\begin{pmatrix} -\Gamma_\uparrow-A'-B & 0 & 0 & 0 & B' \\ 0 & -\Gamma_\downarrow & \Gamma_\uparrow & 0 & 0 \\ 0 & \Gamma_\downarrow & -\Gamma_\uparrow-A'-B & 0 & B' \\ 0 & 0 & 0 & -\Gamma_\uparrow-C' & \Gamma_\downarrow \\ B & 0 & B & \Gamma_\uparrow & -\Gamma_\downarrow-2B' \end{pmatrix}. \tag{19}$$

Clearly, the lowest (in $|G|^2$) order terms in $\Gamma_\downarrow$ and $\Gamma_\uparrow$ represent the standard golden-rule results for the down- and up-relaxation rates of the central system. At $k_BT\ll\epsilon$, it is easy to see that

$$\frac{\Gamma_\uparrow}{\Gamma_\downarrow}\approx e^{-\beta\epsilon}. \tag{20}$$

All that makes it easy to find and interpret the solution to Eq. (18) as well as the long-time limit of normalizing condition $\Sigma_{j,m}P_{jm}(t)=1$. The solution reads

$$P_{1d}(+\infty)=\left[1+\frac{\Gamma_\uparrow}{\Gamma_\downarrow}\left(1+\frac{C}{C'}\right)+\left(\frac{\Gamma_\uparrow}{\Gamma_\downarrow}\right)^2\frac{C}{C'}\left(1+2\frac{B'}{B}+\frac{A'B'}{AB}\right)+\left(\frac{\Gamma_\uparrow}{\Gamma_\downarrow}\right)^3\frac{B'C}{BC'}\left(2+\frac{A'}{A}\right)\right]^{-1},$$

$$P_{1u}(+\infty)=\frac{C'}{C}P_{5u}(+\infty)=\frac{\Gamma_\uparrow}{\Gamma_\downarrow}P_{1d}(+\infty),$$

$$\frac{ABC'}{A'B'C}P_{2d}(+\infty)=\frac{BC'}{B'C}P_{3d}(+\infty)=\frac{BC'}{B'C}P_{4d}(+\infty)=\frac{C'}{C}P_{5d}(+\infty)=\left(\frac{\Gamma_\uparrow}{\Gamma_\downarrow}\right)^2P_{1d}(+\infty),$$

$$\frac{A}{A'}P_{2u}(+\infty)=P_{3u}(+\infty)=P_{4u}(+\infty)=\frac{B'C}{BC'}\left(\frac{\Gamma_\uparrow}{\Gamma_\downarrow}\right)^3P_{1d}(+\infty). \tag{21}$$

(In the case that the time integrals of the memory functions turn to zero, the ratios of the corresponding integrals should be understood here as, e.g., $C'/C\equiv\lim_{\varepsilon\to0+}\int_0^{+\infty}w_{1u,5u}e^{-\varepsilon t}dt/\int_0^{+\infty}w_{5u,1u}e^{-\varepsilon t}dt$.)

Now let us assume that we deal in general with transitions between states that are not eigenstates of H_S. That means that there are nonzero transfer integrals connecting these states in H_S. Then proper inclusion of higher-order terms (again summed up partially to the infinite order) is under some approximations able to reintroduce the standard detailed balance conditions (DBCs) for ratios of back and forth transition rates. For at least site-local coupling to the bath where sufficiently reliable higher-order formulas exist, these approximations mean, however, neglecting transfer integrals as compared to typical differences $\Delta\epsilon$ of site energies and assuming a high-temperature domain with $k_BT\gg\Delta\epsilon$ [6]. Let us recall that DBCs also provide a cornerstone of the lowest-order Pauli master (PME) theory. One should mention, however, the following.

(i) The standard derivation of DBCs as in the PME is based on the analysis of bath-assisted transfer rates (owing to site nonlocal coupling to the bath) between true eigenstates of the Hamiltonian of the system. This is the case of rates $\Gamma_\uparrow$ and $\Gamma_\downarrow$ provided we can (upon their calculation, as we also did above) neglect coupling of the relevant sites to other sites not involved in the transitions (i.e., to set there $P=Q=0$). No wonder then that also Eq. (20) represent nothing but the DBCs.

(ii) This, however, is not our situation here with the transfer rates A, A', B, B', C, and C'; these transfer rates as defined in Eq. (17) are nonzero just for $P\neq0\neq Q$. The point is that they represent transfer rates between states that are not eigenstates of the Hamiltonian of the system (they become so just in the limit $P,Q\to0$ when, on the other hand, these

transfer rates turn to zero). Then the corresponding DBCs are at most very approximate and definitely break down in the low-temperature domain. In the high-temperature domain, on the other hand, even DBCs lead to an almost-temperature-insensitive ratio of the back and forth transition rates.

The invalidity of DBCs for transfer rates between states that are not eigenstates of H_S may be most easily seen on, e.g., a dimer with a nonzero transfer integral. The mixing property of the latter means that even in the ground state (i.e., equilibrium at zero temperature), the particle is distributed on both sites involved. Simple balance equations then give that as long as any transfer rate between sites is nonzero, both rates must be nonzero. The reader is referred to [6] for detailed formulas or to, e.g., [7] for a detailed form of such wave functions in a simple model. With that, we can now easily discuss our solution (21).

Let us for concreteness specify our reasoning to, e.g., the regime

$$k_B T \ll \epsilon, \quad 0 < P, Q \lesssim V \ll \epsilon. \tag{22}$$

Thus, for the transfer rates $3d \leftrightarrow 5d$ and $4d \leftrightarrow 5d$ as well as $5u \leftrightarrow 1u$, we definitely have the low-temperature regime for the ratios B'/B and C/C'. Hence both of them should be taken as temperature insensitive. As for the A'/A ratio, its temperature dependence should only be weak as the corresponding transitions are not induced by the bath. Consequently, taking [together with Eq. (20)]

$$\frac{A'}{A} \approx \text{const}, \quad \frac{B'}{B} = \text{const}, \quad \frac{C}{C'} = \text{const} \tag{23}$$

(instead of $B'/B \approx e^{\beta\epsilon}$ and $C/C' \approx e^{\beta(\epsilon+V)}$ as it would follow from the naive and unjustified application of DBCs), we get from Eq. (21) that with an exponential error (proportional to $e^{-\beta\epsilon}$),

$$P_{1d}(+\infty) \approx 1 \tag{24}$$

with all other asymptotic probabilities being practically zero. Thus the particles become, owing to the action of our central system, coupled (in a bound state) with the latter system prepared to start the action on another pair (if any; this is of course beyond our model here working with just one c and one g particle). Combined with the above explanations in connection with the Hamiltonian H_S [see Eqs. (2)–(5) and the ensuing text there], it yields the following picture of the process investigated.

(i) By the mechanism mentioned above, the unbound c and g particles can appear simultaneously at site 0 joined with the central system.

(ii) This leads to the instability of the central system leading to, e.g., the change of topology of the latter. (Already this may bring the particles together, i.e., may lead to a formation of their bound state.)

(iii) Because of the new topology (and as assumed in our Hamiltonian), the particles can then leave site 0 just as a bound pair.

(iv) Once it happens, the central system again becomes unstable, returns to its original topology, and waits for another c-g pair to be bound.

(More details about the above types of activity of the central part of the system can be found in [8], where a less advanced model of this type was discussed. As for a simple version of the model transferring single particles only, see also [9,10].) All that is why the present system in particular could play the role of a quantum microscopic ''sewing machine'' in especially chain processes (reactions). Let us keep in mind that our asymptotic state does not differ from the usual equilibrium state due to some lacking transitions from excited states to the equilibrium one. This may be verified by complementing the model by any transitions possible. Nor can any type of energy renormalization (shifting contingently our asymptotic state sufficiently down in energy and thus reconciling the result with the standard statistical thermodynamics) be found. The difference is really because of the active role of the central system, which is because of a proper combination of its two properties: (i) The instability of the intermediate state of the central system (scatterer) during the transition (scattering of the pair) and (ii) the strong dependence, owing to the matrix elements involved, of the scattering channels on the state of the central system. Our simple result contradicting the usual (of course macroscopic) thermodynamics means an up-in-energy transition at the cost of the thermal energy of the thermodynamic bath. Thus the model and process described reminds us of the Maxwell demon [11,12] working here, however, in isothermal conditions. Splitting the central system from the bath immediately interrupts the process.

III. CONCLUSION

Let us define the intelligent system (machine) as a system that is able to check, at any moment, whether previous steps (particle transfers, etc.) have really been performed and to decide, on grounds of this check, about the next steps to be performed. Then we can see that our system is a model of such an intelligent molecular open system working on the particles from the particle reservoir and governed (together with the bath) by the linear Liouville equation. The resulting particle binding (self-organization) at the cost of the thermal energy of the reservoir and going thus against the standard second law of thermodynamics is then a result of the check whether both the c- and the g-type particle appeared simultaneously at site 0 and of an immediate response of the central system to the positive result of the check. This type of self-organization has nothing to do with persistent external flows as in standard self-organization theories.

ACKNOWLEDGMENTS

Support of the present research by Komerční Banka, Praha, is gratefully acknowledged. The author would also like to thank Professor M. Wagner, University of Stuttgart, and Max-Planck Institute in Stuttgart for their kind invitation and hospitality during the author's stay in Germany. Finally, priceless discussions with Dr. L. Pivec, Czech Academy of Sciences, on possible applications of the above ideas are also gratefully acknowledged.

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