A Thought Construction of Working Perpetuum Mobile of the Second Kind

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A previously published model of the isothermal Maxwell demon as one of models of open quantum systems endowed with faculty of selforganization is reconstructed here. It describes an open quantum system interacting with a single thermodynamic bath but otherwise not aided from outside. Its activity is given by the standard linear Liouville equation for the system and bath. Owing to its selforganization property, the model then yields cyclic conversion of heat from the bath into mechanical work without compensation. Hence, it provides an explicit thought construction of perpetuum mobile of the second kind, contradicting thus the Thomson formulation of the second law of thermodynamics. No approximation is involved as a special scaling procedure is used which makes the kinetic equations employed exact.

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1. Introduction

In this letter, we should like to report on a result which can be obtained, for the model in question, without approximations from standard quantum theory of open systems governed by the linear Liouville - von Neumann equation. Irrespective of this, it contradicts the second law of thermodynamics. Leaving details of physical motivation to a next publication, we mention here just the fact that the main inspiration for construction of the model has been taken from biology, namely from topological changes of biologically important molecules upon detecting, at a specific site (receptor), particles (excitations, molecules or molecular groups) to be processed [1].

Previous version of the model has been published in [2]. Detailed treatment of this model [3] as well as other microscopic models of open quantum systems working on analogous principles [4, 5, 6, 7, 8] revealed property of spontaneous (i.e. not induced by external flows) selforganization. This then leads to such unexpected phenomena contradicting basic principles of statistical thermodynamics as, e.g., violation of consequences of the detailed balance (in connection with impossibility of rigorous justification thereof). From this, implicit violations of the second law of thermodynamics could be deduced as mentioned in, e.g., [5, 6]. Here, we reconstruct the model so that it is able to work cyclically and without compensation as a perpetuum mobile of the second kind, in the sense contradicting explicitly the Thomson formulation of the second law of thermodynamics [9].

2. Model

The fully quantum Hamiltonian of our model in its simplest version (see also [10]) can be as usual written as a sum of the Hamiltonians of the (extended) system, thermodynamic bath, and that of the system-bath interaction. Thus,

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

where

$$H_S = J(c_{-1}^\dagger c_0 + c_0^\dagger c_{-1}) \cdot |d\rangle\langle d| + I(c_1^\dagger c_0 + c_0^\dagger c_1) \cdot |u\rangle\langle u| + K(c_1^\dagger c_{-1} + c_{-1}^\dagger c_1)$$
$$+ \frac{\epsilon}{2}[1 - 2c_0^\dagger c_0] \cdot [|u\rangle\langle u| - |d\rangle\langle d|]. \tag{2}$$

As for the Hamiltonians of the bath H_B and that of the system-bath interaction H_{S-B}, they are not important here. Before explaining the symbols used in (2), let us only add that we shall assume H_{S-B} to consist of two additive and non-interfering contributions H'_{S-B} and H''_{S-B}. Here H'_{S-B} causes transitions between states of the central system $|u\rangle$ and $|d\rangle$ (see below) while H''_{S-B} is responsible for a sufficiently intense (and, for the sake of simplicity, equally strong) dephasing of the particle states at all three sites. As an example, one can take a model of the bath consisting of harmonic oscillators $H_B = \sum_k \hbar\omega_k b_k^\dagger b_k$ interacting with the

central system by a linear site-local coupling causing the $|u\rangle \leftrightarrow |d\rangle$ transitions exactly as in [2] but complemented, for our purposes, by, e.g., a non-interfering site-local coupling of the particle to the bath with the same coupling constant at all three sites. This means, e.g., $H_{S-B} = \frac{1}{\sqrt{N}} \sum_k \hbar\omega_k G_k (b_k + b^\dagger_{-k})[|u\rangle\langle d| + |d\rangle\langle u|]$ $+ \frac{1}{N} \sum_{kk'} \hbar\sqrt{\omega_k \omega_{k'}} g_{kk'} (b_k + b^\dagger_{-k})(b_{k'} + b^\dagger_{-k'})(c^\dagger_{-1}c_{-1} + c^\dagger_0 c_0 + c^\dagger_{+1}c_{+1}) \equiv H'_{S-B} + H''_{S-B}$. These specific forms of H_B and H_{S-B} will not be, however, used below.

As for H_S in (2), we have chosen the simplest model with only three particle states, i.e. sites ($m = -1, 0$ and $+1$). Operators $c^\dagger_m$ and c_m, $m = -1, 0$, or $+1$ designate the particle creation and annihilation operators at site m. For simplicity, we shall assume only one particle in the system. This is why we do not need the commutational (anticommutational) relations of the particle creation and annihilation operators. In (2), I, J and K are transfer (hopping or resonance) integrals connecting the sites involved. Worth noticing is that in (2), the forth and back transfers in any pair of the sites are always with the same amplitude as a consequence of the hermicity of H_S. The one-directional character of the process reported here is not owing to a contingent difference between these amplitudes but results exclusively (as it will become clear later on) from the existence of spontaneous processes. Site '0' is understood to be attached to a central system representing, e.g., a specific molecule or molecular group (e.g. tail connecting site '0' with either site '-1' or '+1' but not both simultaneously). This central system is assumed to have (in a given range of energies of interest) two levels with energies $\pm\epsilon/2$ (with corresponding states $|d\rangle$ and $|u\rangle$; we assume $\epsilon > 0$). At the moment when the particle is transferred to site '0' attached to the central system, the relative order (on the energy axis) of the two levels of the central system gets interchanged. (This of course causes instability of the central system with respect to the $|d\rangle \rightarrow |u\rangle$ transition which is the same effect as additional-load-induced instability of a ship in water.) Asymmetry in transfer rates $|u\rangle \leftrightarrow |d\rangle$ is ensured by the above spontaneous processes with respect to the bath. Conversion of this up-and-down asymmetry into the left-and-right one is then owing to the above special form of the first two terms on the right hand side of (2) discussed below. Technically, this imbalancing is due to the fourth term on the right hand side of (2) proportional to $1 - 2c^\dagger_0 c_0$ and may be in reality due to correlation effects as the particle transferred may, upon its transition to site 0, change the topology (originally stable conformation may become energetically disadvantageous) or orientation of the central system in space. (Such changes condition activity of many biologically important molecules in living organisms [1].)

3. Equations of motion

In our theory, we shall closely follow [3] but shall be interested in just a stationary situation. That is why we can apply any proper kinetic method yielding time derivatives of matrix elements of the density matrix of our extended system (particle + the central two-level system), and to set these time derivatives zero. In order to avoid unnecessary technical complications, we have avoided time-convolution meth-

ods. From mutually equivalent time-convolutionless methods, we have chosen (like in [3]) that of Tokuyama and Mori [11]. In order to avoid unnecessary discussions about role of approximations, we have employed one of the scaling procedures turning, in the limiting sense, Tokuyama-Mori equations into exact kinetic equations. This means the following steps:

- We formally introduce a joint small parameter, say g, of both H_{S-B} and all the hopping integrals I, J, and K in the sense of setting $H_{S-B} \propto g$ but I, J, $K \propto g^2$. Right here, let us remind the reader of the fact that this scaling of some parameters from H_S is what distinguishes our approach from scaling standardly used in weak coupling theories (inapplicable to our presumably intermediate or rather strong coupling situation discussed here) [12].

- We introduce new time unit $\tau \propto g^2$, i.e. introduce new time $t' = t/\tau_0$. This step formally disappears as far as we are, like here, interested in just the stationary (long-time) asymptotics.

- We divide our general Tokuyama-Mori kinetic equations by g^2 and perform the limit $g \to 0$.

The reader can easily see that this method preserves just the lowest order (in g^2) terms which can be calculated exactly. The result can be reported as follows (for details see a next extended publication):

First, we arrange all the 36 matrix elements $\rho_{\alpha\gamma}(t)$ of the density matrix of our extended system (α, β... $= md$ or mu with $m = 0$ or ± 1 while d or u designate the states of the central system) in groups of nine designating

$$
\begin{aligned}
(\rho_{uu})^T &= \Big(\rho_{-1u,-1u},\ \rho_{0u,0u},\ \rho_{1u,1u},\ \rho_{-1u,0u},\ \rho_{-1u,1u},\ \rho_{0u,-1u},\ \rho_{0u,1u},\ \rho_{1u,-1u},\ \rho_{1u,0u}\Big),\\
(\rho_{dd})^T &= \Big(\rho_{-1d,-1d},\ \rho_{0d,0d},\ \rho_{1d,1d},\ \rho_{-1d,0d},\ \rho_{-1d,1d},\ \rho_{0d,-1d},\ \rho_{0d,1d},\ \rho_{1d,-1d},\ \rho_{1d,0d}\Big),\\
(\rho_{ud})^T &= \Big(\rho_{-1u,-1d},\ \rho_{0u,0d},\ \rho_{1u,1d},\ \rho_{-1u,0d},\ \rho_{-1u,1d},\ \rho_{0u,-1d},\ \rho_{0u,1d},\ \rho_{1u,-1d},\ \rho_{1u,0d}\Big)
\end{aligned}
\tag{3}
$$

and similarly for ρ_{du}. Superscript $\cdots^T$ designates transposition. Then the above kinetic equations in the asymptotic time domain (and after the above scaling) read as

$$
\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \mathcal{A} & \mathcal{B} & \mathbf{0} & \mathbf{0} \\ \mathcal{C} & \mathcal{D} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \cdots & \cdots \\ \mathbf{0} & \mathbf{0} & \cdots & \cdots \end{pmatrix} . \begin{pmatrix} \rho_{uu} \\ \rho_{dd} \\ \rho_{ud} \\ \rho_{du} \end{pmatrix} .
\tag{4}
$$

Here, in the square matrix, all the elements are in fact blocks 9×9. Hence, the whole set splits into two independent sets of 18 equations each; we shall be interested just in that one for ρ_{uu} and ρ_{dd}. This reads as in (4) with typical forms of the block 9×9 matrices $\mathcal{A},\mathcal{B},\mathcal{C}$ and $\mathcal{D}$. Here

$$\mathcal{A}=$$

$$\begin{pmatrix}
-\Gamma_\downarrow & 0 & 0 & 0 & iK/\hbar & 0 & 0 & -iK/\hbar & 0\\
0 & -\Gamma_\uparrow & 0 & 0 & 0 & 0 & iI/\hbar & 0 & -iI/\hbar\\
0 & 0 & -\Gamma_\downarrow & 0 & -iK/\hbar & 0 & -iI/\hbar & iK/\hbar & iI/\hbar\\
0 & 0 & 0 & k-2\Gamma & iI/\hbar & 0 & 0 & 0 & -iK/\hbar\\
iK/\hbar & 0 & -iK/\hbar & iI/\hbar & -\Gamma_\downarrow-2\Gamma & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & k^*-2\Gamma & iK/\hbar & -iI/\hbar & 0\\
0 & iI/\hbar & -iI/\hbar & 0 & 0 & iK/\hbar & k^*-2\Gamma & 0 & 0\\
-iK/\hbar & 0 & iK/\hbar & 0 & 0 & -iI/\hbar & 0 & -\Gamma_\downarrow-2\Gamma & 0\\
0 & -iI/\hbar & iI/\hbar & -iK/\hbar & 0 & 0 & 0 & 0 & k-2\Gamma
\end{pmatrix}. \tag{5}$$

Here $k=-i\epsilon/\hbar-0.5(\Gamma_\uparrow+\Gamma_\downarrow)$ and $\cdots^*$ designates complex conjugation. $\Gamma_\uparrow$ and $\Gamma_\downarrow$ designate bath-assisted uphill and downhill transfer rates in our two-level system calculated as if, formally (owing to the above scaling) $I=J=K=0$. Let us mention that via $\Gamma_\uparrow$ and $\Gamma_\downarrow$, the (initial) bath temperature T enters the game. These rates are known from the usual Pauli Master Equation approach to general kinetic problems and, consequently, are related to each other by the detailed balance condition $\Gamma_\uparrow=\Gamma_\downarrow \mathrm{e}^{-\beta\epsilon}$, $\beta=1/(k_BT)$. In general, however, owing to intermixture of coherent and incoherent transfer channels, the detailed balance condition does not apply to our particle transfer problem. Finally, 2Γ is the dephasing rate determined by H''_{S-B}. As for the block $\mathcal{B}$, it is fully diagonal with diagonal elements $\mathcal{B}_{11},\ldots,\mathcal{B}_{99}$ equal to $\Gamma_\uparrow$, $\Gamma_\downarrow$, $\Gamma_\uparrow$, $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, $\Gamma_\uparrow$, $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, $\Gamma_\uparrow$ and $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, respectively. Next,

$$\mathcal{D}=$$

$$\begin{pmatrix}
-\Gamma_\uparrow & 0 & 0 & iJ/\hbar & iK/\hbar & -iJ/\hbar & 0 & -iK/\hbar & 0\\
0 & -\Gamma_\downarrow & 0 & -iJ/\hbar & 0 & iJ/\hbar & 0 & 0 & 0\\
0 & 0 & -\Gamma_\uparrow & 0 & -iK/\hbar & 0 & 0 & iK/\hbar & 0\\
iJ/\hbar & -iJ/\hbar & 0 & k^*-2\Gamma & 0 & 0 & 0 & 0 & -iK/\hbar\\
iK/\hbar & 0 & -iK/\hbar & 0 & -\Gamma_\uparrow-2\Gamma & 0 & -iJ/\hbar & 0 & 0\\
-iJ/\hbar & iJ/\hbar & 0 & 0 & 0 & k-2\Gamma & iK/\hbar & 0 & 0\\
0 & 0 & 0 & 0 & -iJ/\hbar & iK/\hbar & k-2\Gamma & 0 & 0\\
-iK/\hbar & 0 & iK/\hbar & 0 & 0 & 0 & 0 & -\Gamma_\uparrow-2\Gamma & iJ/\hbar\\
0 & 0 & 0 & -iK/\hbar & 0 & 0 & 0 & iJ/\hbar & k^*-2\Gamma
\end{pmatrix}. \tag{6}$$

As for the block $\mathcal{C}$, it reads as $\mathcal{B}$ except for the interchange $\Gamma_\uparrow\leftrightarrow\Gamma_\downarrow$. The form of all the matrices in (4) is *exactly* the same as, e.g., that one which we would get from

the stochastic Liouville equation SLE [13] provided, however, that H_{S-B} is replaced by a proper stochastic (e.g. Gaussian delta-correlated) potential field acting on the central system. The only difference between our form of the $\mathcal{A}-\mathcal{D}$ blocks and that of the same matrices in the corresponding SLE theory is dictated by physics of the problem: Namely, in contrast to the SLE approach, spontaneous processes with respect to the bath naturally appear in our fully quantum model (H_{S-B} is, in our case, a coupling to a genuine *quantum* bath). Thus, $\Gamma_\uparrow <$ or even $\ll \Gamma_\downarrow$ in our case. As SLE is quite standard and well understood, this comment will hopefully turn attention of suspicious readers from potential speculations about correctness of our approach to the form of our Hamiltonian. It is the latter what is responsible for the striking conclusions obtained.

4. Stationary flow and power output.

Upper half of (4) provides a set of 18 linear algebraic homogeneous equations for 18 components of the density matrix ρ_{uu} and ρ_{dd} (remaining components becoming decoupled and irrelevant in what follows) of the rank 17. So, it should be complemented by the normalization condition

$$\sum_{m=-1}^{+1}[\rho_{mu,mu}+\rho_{md,md}]=1. \tag{7}$$

Then this set and (7) determine the relevant components of the density matrix uniquely. From the physical meaning of the transfer rates, one can then determine the flow '-1'→'0'→'+1'→'-1' as

$$\mathcal{J}=\Gamma_\downarrow\rho_{0d,0d}-\Gamma_\uparrow\rho_{0u,0u}. \tag{8}$$

Calculated flow is, as simple inspection or numerical solution shows, always nonzero. Already this implies, owing to the persistent character of the flow, important consequences. We are, however, here interested rather in the possibility of converting the heat from the bath into a usable work. For that, we connect the particle running through our system organized as a circle of three sites (as '-1→0→+1→-1') with a screw (with its axis perpendicular to the plane of our three sites '-1', '0' and '+1'). The above persistent flow could then drive the screw at the cost of just the thermal energy of the bath, converting thus the latter directly to the mechanical work. So the existence or nonexistence of the stationary flow according to the above definitions converts to a question of a direct violation of the 2nd law of thermodynamics as applied to our system in the sense of the existence or nonexistence of the perpetuum mobile of the second kind. The problem can be easily solved numerically in our model. The idea is to provide the system with potential steps the particle (and the screw) must overcome when passing from '-1' to '0', from '0' to '+1' or from '+1' to '-1'. (When passing virtually in the opposite directions, the potential steps as felt by the particle would get the opposite sign.) We have chosen these steps equal, designating their value as $\Delta/3$. Hence $\Delta>0$ is the mechanical work the particle exerts

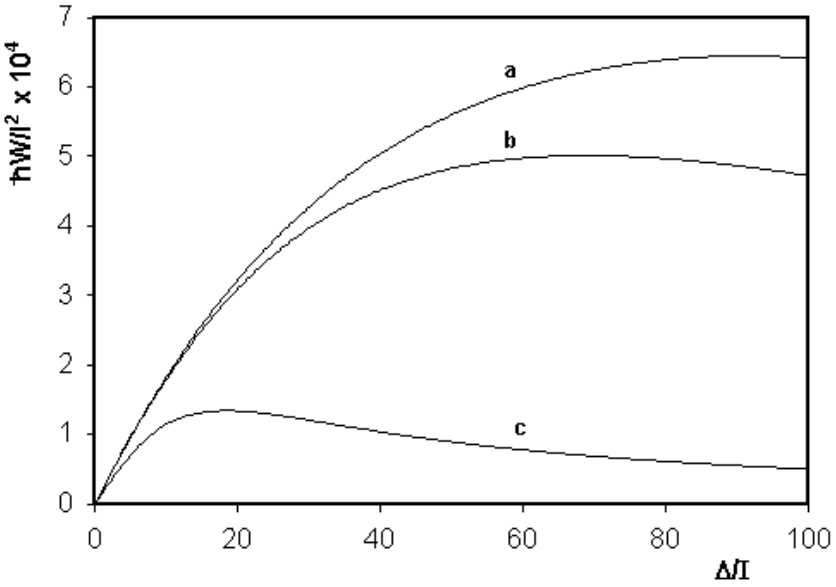

Figure 1: Thermal-to-mechanical energy conversion power-output W in units $I^2/\hbar$ (as determined by (10)) as a function of Δ; $I = J > 0$, $\epsilon = 50I$, $\Gamma_\uparrow = 0$, $\Gamma_\downarrow = 10I/\hbar$, $2\Gamma = 3I/\hbar$. Parameter $K = 0.1I$, $0.05I$ and $0.01I$ for curves a, b, and c, respectively.

on the screw during one turn in the above direction. One should realize that taking these steps as those of the potential energy of the screw connected with the particle, the latter potential energy is not unique as a function of the particle position on the above triangle of the sites. Instead, it is unique as a function of the rotation angle ϕ of the particle (or screw). In other words, when the particle performs one turn '-1'→'0'→'+1'→'-1', $\phi \to \phi + 2\pi$, the potential ascribed to the particle connected with the screw increases by Δ though the particle formally returns to the same site.

Technically, inclusion of the above potential steps is simple. As it follows from the above formalism or already even from the Liouville equation for the whole complex of the system and the bath, it only means to add to block matrices $\mathcal{A}$ and $\mathcal{D}$ above the 9×9 block $\mathcal{E}$ with all matrix elements equal to zero except for $\mathcal{E}_{44} = \mathcal{E}_{77} = \mathcal{E}_{88} = -\mathcal{E}_{55} = -\mathcal{E}_{66} = -\mathcal{E}_{99} = i\Delta/(3\hbar)$.

From the solution to

$$0 = \begin{pmatrix} \mathcal{A}+\mathcal{E} & \mathcal{B} \\ \mathcal{C} & \mathcal{D}+\mathcal{E} \end{pmatrix} \cdot \begin{pmatrix} \rho_{uu} \\ \rho_{dd} \end{pmatrix}. \tag{9}$$

and (7), one can then determine the mechanical energy power output (as measured on the screw), i.e. the thermal-to-mechanical energy conversion power output (per

second)

$$W = \mathcal{J} \cdot \Delta. \tag{10}$$

Fig.1 then unambiguously illustrates the positive result of our test whether the conversion of the thermal energy of our single bath to the mechanical work is, in our model, possible or not. One should realize the fact that the mechanical output is, as Fig. 1 shows, really positive. Hence, the system produces, owing to its selforganizational properties and properly timed opening and closing of the particle transfer channel across site '0', positive mechanical work. This work can, because of the construction of the model, be at the cost of just heat of the thermodynamic bath. Hence, we have a direct 'heat → mechanical work' conversion. As we have just one bath, there is no compensation possible. Thus, our system working cyclically provides an example of perpetuum mobile of the second kind, violating thus the second law of thermodynamics in its Thomson form.

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