Stationary flows in quantum dissipative closed circuits as a challenge to thermodynamics

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Abstract

An experimentally inspired model is constructed and rigorously solved from the Hamiltonian level where a dc circular spontaneous flow exists in absence of a magnetic field, irrespective of presence of dissipation causing otherwise proper relaxation. The flow causes a spontaneous unidirectional transfer of heat from one bath to another one, even against temperature step. This is what is explicitly forbidden by the Clausius form of the Second law of thermodynamics. The unidirectionality of the flow is caused by that of spontaneous processes known to bear this property since their introduction by Einstein. The model slightly improves the previous one (Čapek & Sheehan 2002), describes a realistic plasma system for which experimental results violating the second law were announced, and the result obtained fully supports the experimental conclusions (Sheehan 1995). Analytical proof of the violation is supported by numerical results. All mathematical details are exposed, two fully independent types of mathematical arguments behind starting equations are invoked, and no approximations that could be made responsible for the striking conclusions are used. It shows how the physics beyond the Second law is still little understood.

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I. INTRODUCTION

Challenges to the second law of thermodynamics \[1, 2\] are almost as old as the law itself, dating back at least to the 1870’s with Maxwell’s celebrated demon \[3, 4, 5, 6\]. Most of them have been resolved under close scrutiny \[5, 7, 8\] but some persisted. Anyway, strong belief in old authorities and natural human tendency to organize things and facts into closed logical units and complexes (scientific disciplines etc.) caused that almost nobody doubts about validity of standard thermodynamics, in particular the Second law, in at least the macroworld \[4, 10\]. Absolutistic statements like ‘...No exception to the second law of thermodynamics has ever been found - not even a tiny one...' \[10\] often appear and the second law is almost universally believed to be unquestionable. In our opinion, the situation is (in view of the fast developing situation perhaps at least still) not so clear. The reason is that experiments questioning the second law have been reported since 1995, have since been subject to a public discussion but remain so far unquestioned \[11, 12\]. Some of these experiments have since been even reproduced (compare \[13\] with \[14\]).

In theory, arguments independent of these experiments appeared since 1997 \[15\] saying that in quantum systems with strong or at least intermediate coupling to its surroundings (identical or connected with usual thermodynamic baths) with mutual strong correlations (entanglement), the standard statistical thermodynamics could be violated. This is in particular, but not only, the case of the second law of thermodynamics. One must keep in mind that from first principles (microscopic Hamiltonian dynamics), derivations of the second law are declared to exist just in classical (in the sense of non-quantum) physics \[16\] or, as in standard textbooks, involving assumption of a weak system-bath coupling only. \(^1\) It should be stressed already here that the classical physics is, according to the Bohr correspondence principle, an infinite temperature limit of the (more general) quantum physics. This, inter alia, implies that its application to finite temperatures as in standard thermodynamics is at least open to discussion. The above lack of general derivation of the second law beyond, in particular, the classical regime could also correspond to the fact that so far reported and seemingly classical paradoxes connected with the second law (see, e.g., \[17\]) usually involve

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\(^1\) Gibbs canonical form of the system density matrix compatible with the standard thermodynamics is correct to just the zeroth order in the system-bath coupling. This is an important fact to be realized already here as the effect reported below is of higher order in this coupling.
sufficiently intense processes that are inherently of the quantum character.

In 1999, it was realized that a long lasting call in chemistry for inclusion of self-organizational tendencies into theory of particle-transfer chemical reactions is, from the microscopic point of view, nothing but a call for inclusion of such mechanisms that can turn any (from the thermodynamical point of view) passive bath into an active one, opening thus door to violations of standard thermodynamic principles [18]. Recent review of theoretical models and state-of-art in theory could be found in, e.g., [19, 20]. So far, two main groups of theoretical models of purely quantum open systems violating the second law existed: Those with quantum reaction channels opening or closing in accordance with the instantaneous state of the system (reminding of the Maxwell demon [3] closing and opening gate in a wall separating two compartments with a classical gas), and those where a specific type of interference of different quantum reaction channels exists [19]. In particular this type of systems is relevant as the contradiction with the second law treated in [19] is not only mathematically well justified but can be given even a very simple physical interpretation based on otherwise experimentally well established facts: Exciton diffusion bearing energy and going (as always diffusion does) in the direction of decreasing exciton concentration.

Recently, as a theoretical response to another positively tested experimental system [11], a next model of still another type has been suggested [21] that also allows rigorous solution (exact within a scaling theory) fully confirming experimental doubts about universal validity of the second law. Detailed discussion and solution of a modified (and nearer to reality) version of the model is the subject of the present paper. Here, however, we are already able to support the conclusions by both scaling and non-scaling arguments. What is perhaps universal for all the models challenging thermodynamics is that the system in question must be, during its activity, outside the canonical state [22]. Mechanisms how to achieve and maintain that might be, of course, different. One should understand, however, that this condition is perhaps necessary but by far not sufficient. For other paradoxical systems that could be also classified as above, showing how physics beyond the second law is still little

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2 A comment might be relevant in this connection that outside equilibrium, there is no reason why the thermodynamic entropy (characterizing individual macroscopic body) and the Shannon-von Neumann entropy (characterizing ensemble, i.e. bearing another physical information) should be identical. For validity of the second law in Nature, the former entropy is relevant while only the latter is usually involved in analytical ‘proofs’ of the second law starting from first principles.
understood see, e.g., [17, 23].

II. THEORETICAL MODEL

Physicists are more conservative than mathematicians. For the latter, one unquestioned proof is standardly enough to accept a new statement, theorem etc. Physicist on the other hand require usually more arguments, especially when old truths or dogmas are challenged. That is why we should like to stress already here that:

• The model treated here is by no means unique. It is just a next one in a long series of models behaving, according to a strict microscopic theory, in a way incompatible with standard thermodynamics. Among those, it is exceptional just in the sense of modelling an experimental system tested positively, from the point of view of violability of the second law, already a long time ago.

• Except for model assumptions, we shall use no approximate steps in our reasoning in the main text here. This is to be stressed in order to avoid misunderstandings.

• Mathematics we are going to use in the main text is that one by Davies [26, 27] which forms, for one specific choice of the scaling parameter, mathematical basis of the weak-coupling kinetic relaxation theory confirming, for the weak-coupling limit, validity of the second law. (Another possibility of deriving basic kinetic equations (12) below may be connected with the Tokuyama - Mori identity stemming from the Heisenberg equations of motion for quantum operators - see, for another model, e.g. [20].) We fully rely upon the Davies mathematics and use, for the chosen model (i.e. a specific case) no additional approximations. Hence, rigour of our approach below is that one of the general Davies theory. We only deviate from a subsequent standard application of general Davies theorems to the weak coupling situation by just another, but equally admissable and physically motivated, choice of the scaling parameter. This choice makes the theory physically applicable also beyond the weak coupling limit.

• In order to convince sceptics concerning physical applicability of the scaling ideas, we also present completely independent mathematical non-scaling arguments. Those may be found in the Appendix and are important in particular in the relevant long-time
As we have numerically verified and as it is also argued below, our results well coincide with those of the weak-coupling theories in the overlap region with the weak-coupling regime. We thus have no doubts on the validity of the second law there. However, beyond the weak coupling regime, our results become appreciably different from standard ones. Physically, we have reasons supported by arguments to understand that: This is a deviation from the canonical state of the system caused by its non-negligible coupling to the bath. As far as the underlying mathematics is concerned, it is general (valid for any choice of the scaling parameter) and cannot be consequently sometimes correct and sometimes not. It can be either correct or not in general; no other alternative exists. The first alternative provides solid basis for arguments in favour of correctness of our approach while the second one (that was even never suggested or indicated) deprives even the weak coupling relaxation theory of its mathematical foundation. Rejecting these alternatives would

- either mean to question physical as well as mathematical principles (including the Liouville equation) on which all the existing renown of description of kinetic phenomena via corresponding kinetic equations (depending on the regime in question) relies,

- or to admit that the very principles of quantum mechanics of the open system would have to be complemented by, e.g., some additional requirements not admitting models of the type investigated here.

In view of existing experimental evidence in favour of the quantum theory as well as because of experimental results indicating violations of the second law in experiment [11, 14, 24] (see also [25] for theoretical interpretation of the experimental results reported in [14] as well as previously [13]), both the latter possibilities seem, in our opinion, rather unlikely. In any case, doubts recently appeared about ability of the Davies scaling theory to yield reliable long-time predictions on the relaxation [28]. The exactly solvable model considered was, however, bilinear in creation and annihilation operators. Such models, like that of harmonic phonons, are known on the other hand to be unable to describe diffusion regime underlying, e.g., the effect discussed in [19]. Thus, [28] should be taken only as a warning against thoughtless application of formal conclusions of the Davies theory to, e.g., diffusion flows where no such flows exist. Here, it means another formal argument for supporting conclusions of the (otherwise broadly tested) Davies theory in our main text by independent arguments in the Appendix.
case, the conclusions suggest that there is at least something in physics beyond the second law what is at present still insufficiently understood.

Our system, in accordance with the experimental plasma system [11], is assumed to consist of three sites, designated as 1, 2, and 3. The reader is referred to [11] or [21] if he/she is interested in the motivation for construction of the model. The latter is, as compared to [21], only slightly modified here so that it now better corresponds to the experimental system of [11]. Shortly, the above sites correspond to walls of the plasma container, plasma, and the probe. Hamiltonian of the system reads

$$H_S = \sum_{j=2}^{3} \epsilon_j a_j^\dagger a_j + J(a_1^\dagger a_2 + a_2^\dagger a_1) + K(a_2^\dagger a_3 + a_3^\dagger a_2), \quad (1)$$

where the zero of the energy is taken to be at the walls (site 1). Though it is not in principle important, we assume here $\epsilon_3 > \epsilon_2 > 0$. This corresponds to the experimental situation [11]. We assume only one electron in the system that is elastically transferred between sites 1 and 2, and simultaneously between sites 2 and 3. This is in accordance with, e.g., the standard theory of the Richardson-Dushman thermal emission (for the 1 - 2, i.e. wall-plasma transfers) that is based on the idea of prevalingly elastic transfer upon, e.g., electron leaving surface of solids.

The load between the probe and walls in the Sheehan’s experimental set-up [11] is the location at which the electron can inelastically scatter. This means, in our case, phonon-assisted 3 ↔ 1 transitions. The phonons involved are assumed to be those of the load, here designated as bath II. In addition to that, we assume another bath, say bath I, formed by phonons (physically, those from the walls) interacting site-locally with the electron located on site 1. This means that Hamiltonian $H_B$ of the bath of our model reads as

$$H_B = H_B^I + H_B^{II},$$

$$H_B^I = \sum_{\kappa} \hbar \omega_{\kappa} b_{\kappa}^\dagger b_{\kappa}, \quad H_B^{II} = \sum_{\kappa} \hbar \omega_{\kappa} B_{\kappa}^\dagger B_{\kappa}. \quad (2)$$

The electron-bath coupling, $H_{S-B}$, is given by

$$H_{S-B} = H_{S-B}^I + H_{S-B}^{II},$$

$$H_{S-B}^I = \frac{1}{N} \sum_{\kappa_1 \neq \kappa_2} \hbar \sqrt{\omega_{\kappa_1} \omega_{\kappa_2}} g_{\kappa_1,\kappa_2} a_{\kappa_1}^\dagger a_{\kappa_1} (b_{\kappa_1} + b_{\kappa_2}^\dagger)(b_{\kappa_2} + b_{\kappa_2}^\dagger),$$

$$H_{S-B}^{II} = \frac{1}{\sqrt{N}} \sum_{\kappa} \hbar \omega_{\kappa} G_{\kappa} (a_3^\dagger a_1 + a_1^\dagger a_3)(b_{\kappa} + b_{\kappa}^\dagger). \quad (3)$$
(Contingent terms with $\kappa_1 = \kappa_2$ in $H_{S-B}^I$ could be turned below to just a temperature-dependent renormalization of site-energy $\epsilon_1$ of site 1 that we set zero here.) Here the anti-or commutational relations between creation and annihilation operators for electrons and phonons are as usual. Also $N$ designates the number of phonon modes; here it is understood that $N \to +\infty$. Notice that $H_{S-B}^I$ is quadratic in the phonon operators; this is certainly admissable but contrasts with both tradition and the treatment of phonon operators in $H_{S-B}^{II}$. This non-standard assumption is employed to preserve the finite dephasing and local electron heating after the Davies scaling procedure (preserving formally just the lowest-order effects in the scaling parameter) which now follows. Otherwise, we would have to involve higher-order effects in treating the dephasing what could make the theory and the final statements, in eyes of a sceptic reader, rather ambiguous. In any case, we have a freedom to choose the model as above. Concerning $H_{S-B}^I$, one should also notice that the on-site dephasing is here, in contrast to the model from [21], on site 1. This corresponds, in the experimentally tested system of [11], to electron heating inside the walls of the plasma container.

One should first of all realize that the phonon-assisted transfers $3 \leftrightarrow 1$ as provided by $H_{S-B}^{II}$ enable the electron to move in a circle $1 \to 2 \to 3 \to 1$, or vice versa $1 \leftarrow 2 \leftarrow 3 \leftarrow 1$. These two circular motions cannot, however, compensate each other. This is the first of two basic physical observations on which the present model relies. The point is that all the inter-site transfers involved are elastic, i.e. symmetric, except for the $3 \leftrightarrow 1$ one. Such elastic transfers lead to a tendency of equilibration of site occupation probabilities. For instance, assume for a while that we had only a dimer composed of sites 1 and 2, with the coherent (i.e. elastic) hopping term $J(a_1^\dagger a_2 + a_2^\dagger a_1)$ decoupled from any bath. The Hamiltonian reads then $H_S = \epsilon_2^\dagger a_2 + J(a_1^\dagger a_2 + H.C.)$ as above. Stationarity of the solution we are interested in implies $\rho_{12} = \rho_{21}$. Contingently nonzero values of these site-off-diagonal elements are connected with a 1-2 bonding. If we add a mechanism breaking such bonds (but, for simplicity, causing no additional $1 \leftrightarrow 2$ transfer), magnitude of $\rho_{12} = \rho_{21}$ would become suppressed below their maximum value given by positive semi-definiteness of $\rho$. Concerning the site-diagonal elements $\rho_{jj}$, their stationary values can be investigated by generalized master equations where memory functions determine the $1 \leftrightarrow 2$ balance. These memory functions (and also their time integrals whose ratio determines $\rho_{11}(+\infty)/\rho_{22}(+\infty)$) contain two channels [29], sometimes interpreted as phonon- (or bath-) assisted and quasicoherent
The latter channel is, in contrast to the former one, symmetric what is the reason of generally comparable stationary values of $\rho_{11}(+\infty)$ and $\rho_{22}(+\infty)$. Full equilibration $\rho_{11}(+\infty) = \rho_{22}(+\infty)$ then follows from our mathematics below upon full ignoring site 3, as a consequence of elastic character of the $1 \leftrightarrow 2$ transitions. The same applies for dimer 2 and 3 once it is separated from the rest of the system. These facts will be useful below. With that, it is then easy to show that the equality of populations $\rho_{11} \approx \rho_{33}$ stemming from above reasoning based on the elastic character of the $J$- and $K$-induced elastic transfers cannot comply with equilibration of the inelastic phonon-assisted transitions $3 \leftrightarrow 1$ leading $\rho_{11} > \rho_{33}$ or possibly even to $\rho_{11} \gg \rho_{33}$. This fact will be useful to understand the results obtained below. A word of warning is, however, worth already here: What is here now being explained are still just heuristic arguments supported by previous investigations that explain our motivation; true rigorous mathematics comes only below. As it follows from general arguments above as well as the mathematics of the next sections, we do understand why, e.g., the detailed balance conditions could in our system become violated. This is because these conditions do not apply to uphill or downhill transfers caused by elastic mechanisms. We, however, do not raise the question about violations or preserving these conditions here. Our rigorous mathematics below avoids such statements and formulations, and leads directly to the required results and effects investigated here.

For that, let us return to our model (1-3). Between sites 1 and 3, there is an imbalance mechanism owing to spontaneous processes allowed by $H_{S-B}^{II}$ that prefers, because of assumed $\epsilon_3 > 0$, the $3 \rightarrow 1$ transitions to $1 \rightarrow 3$ ones. This is the imbalance (and the only imbalance existing in our system) that makes domination of the circular motion $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ over the $1 \leftarrow 2 \leftarrow 3 \leftarrow 1$ one in fact possible. Owing to the phonon-assisted (prevailing down-hill, i.e. $3 \rightarrow 1$) character of the $3 \leftrightarrow 1$ transfer, this implies heat transfer to bath II. (Each transfer act $3 \rightarrow 1$ is connected, because of the energy conservation law, with emission of a phonon quantum into bath II. Similarly for the back transfer $3 \leftarrow 1$ and phonon absorption. If the former transfers prevail, we get the net heat flow to bath II.) The question is, however, where this heat could come from. The only possible answer is that it is from bath I. Really, dephasing at site 1 means nothing but a continuous emission and absorption of phonons from bath I that can provide the necessary energy transferred by the electron whose energy is not sharp. Simultaneously, this dephasing can break phase relations between amplitude of finding the electron at site 1 and those elsewhere, i.e. it breaks the cor-
responding covalent-type of bonds. Without the sufficiently strong dephasing, the electron distribution in the system (as prescribed by, e.g., the canonical density matrix to which the density matrix usually tends within weak-coupling theories considering coupling to bath as infinitesimally weak) would really contain such and fully developed $J$- and $K$-induced bonds.

Thus, it would be stiff enough in the respect that irrespective of the above imbalance, no electron circular motion would finally appear. One can easily verify that by calculating, e.g., the electron flow between any two sites. We always get (by the way, in a correspondence with standard physical reasoning) zero mean flow in the canonical (i.e. zeroth-order in the coupling to the bath) state of the system. From this point of view, lack of on-site amplitude dephasing (or, in other words, that of partial violations of such covalent bonds re-appearing immediately once the system coupling to the bath is re-introduced as a source of corrections to the canonical form of its density matrix) is one of the greatest deficiencies of the weak-coupling kinetic approaches leading to such canonical distributions. For illustration, notice that site off-diagonal elements of the density matrix become, in the weak-coupling kinetic theories, asymptotically independent of the strength of the site-local coupling to the bath even when this type of the coupling causes bath-induced (and on different sites uncorrelated) fluctuations of site energies (see, e.g., formula (28) of [31]). So, even when the model does describe it, its weak-coupling kinetic relaxation formalism is in principle unable to describe the dephasing and breaking of the bonds. Hence, in our case here, we must definitely go beyond the weak coupling kinetic theory in especially the dephasing rate at site 1. This is the second basic and, perhaps, the most important observation connected with the model and the effect we should like to describe here. (One could also pose a question why we should be so keen to describe and include such potentially weak corrections to, e.g. violations of covalent $1-2$ and $2-3$ bonds here. The point is that these violations provide perhaps just small corrections to the canonical density matrix of the system but, simultaneously, these corrections are the very source of the effect we are interested in.) One should add that in our approach involving other than the weak coupling approach below, we also take the limit of the infinitesimal coupling to bath, i.e. infinitesimal dephasing. On the other hand, we simultaneously scale also the hopping (transfer) integrals what makes the ratio of the in-phasing and dephasing constant. This, in contrast to the standard weak coupling scaling, corresponds to reality and allows the above bond breaking. (In the Sheehan experimental plasma system [11], no such $1-2$ or $2-3$ covalent bonding exists). Thus we have a hope,
and really do obtain below the effect expected. So far, of course, all these ideas provide us with at most a physical background of the model, its mathematical treatment, and physics beyond. So, let us now have a look at how these ideas work within a rigorous theory.

III. DAVIES SCALING AND KINETIC EQUATIONS

The scaling procedure we use is based on Davies [26, 27]. (For independent non-scaling arguments fully supporting results obtained here see the Appendix.) We, however, extend our treatment beyond standard weak coupling theory in that we scale not only time and $H_{S-B}$, but also the transfer (overlap, hopping, or resonance) integrals $J$ and $K$, setting

$$t = t' / \lambda^2, \quad H_{S-B} \propto \lambda, \quad J \propto \lambda^2, \quad K \propto \lambda^2$$  \hspace{1cm} (4)

($t'$ playing the role of a new rescaled time.) As usual, we then project off the bath and let $\lambda \to 0$. Such a physical regime where intersite hopping (transfer) integrals determining rates of bath-free transfers inside system get comparable with rates of bath-assisted processes (transfers) can be definitely not that of the weak coupling but rather that of the intermediate or, in a sense, even contingently strong coupling to the bath. Technically, though the mathematics used is completely that by Davies [26], we proceed simultaneously according to [32] where the relevant formulae are rewritten in a physically understandable form.

The Davies formalism starts by writing total Hamiltonian

$$H = H_S + H_B + H_{S-B}$$  \hspace{1cm} (5)

in form

$$H = H_0 + \lambda H_1.$$  \hspace{1cm} (6)

Here, one should add that $\lambda H_1 \propto \lambda$ but that does not exclude the possibility that $\lambda H_1$ includes also higher orders in $\lambda$ ($\lambda^2$ if (4) is accepted). Those who do not like this way of thinking could replace conditions $J \propto \lambda^2, K \propto \lambda^2$ in (4) by $J \propto \lambda, K \propto \lambda$ and proceed as below. The final result is the same.

Next, introduce superoperators

$$\mathcal{L}_0 = \frac{1}{\hbar} [H_0, \ldots], \quad \mathcal{L}_1 = \frac{1}{\hbar} [\lambda H_1, \ldots] \propto \lambda.$$  \hspace{1cm} (7)

Finally, be

$$\mathcal{P} \ldots = \rho^B \otimes \text{Tr}_B (\ldots)$$  \hspace{1cm} (8)
(with \(\text{Tr}_B \rho^B = 1\) implying \(P^2 = P\)) the Argyres-Kelley projector (projection superoperator) in the Liouville space of operators that act in the Hilbert space of the system and bath. Then the message of Davies (see Eq. (1.19) of [26] or Eq. (14) of [32]) is

\[
\lim_{\lambda \to 0} \sup_{0 \leq \lambda^2 t \leq a} ||\rho(t) - e^{-i(\mathcal{L}_0 + (\mathcal{L}_1 + i\lambda^2 \mathcal{K}))t} \rho(0)|| = 0,
\]

\[
\lambda^2 \mathcal{K} = \int_0^{+\infty} dx \text{Tr}_B (e^{i\mathcal{L}_0 x}(-i\mathcal{L}_1)e^{-i\mathcal{L}_0 x}(1 - P)(-i\mathcal{L}_1)(\rho^B \otimes \ldots)),
\]

\[
(\mathcal{L}_1)\ldots = \text{Tr}_B (\rho^B \otimes \mathcal{L}_1\ldots).
\]  

(9)

(Finite constant \(a\) is here arbitrary.) Here \(\rho(t) = \text{Tr}_B \rho^{S+B}(t)\) is the density matrix of the complex ‘system + bath’ with its time-development determined from the exact Liouville equation \(i\frac{d}{dt} \rho^{S+B}(t) = (\mathcal{L}_0 + \mathcal{L}_1)\rho^{S+B}(t)\). The assumptions used were in particular

- that the density matrix of the system and bath \(\rho^{S+B}(t)\) is initially separable, i.e. that

\[
\rho^{S+B}(0) = \rho^B \otimes \rho(0),
\]

(10)

and

- that \(P\mathcal{L}_0 = \mathcal{L}_0 P\). This condition can be, however, well fulfilled as far as, e.g., \(\rho^B = f(H^I_B, H^II_B), [H^I_B, H^II_B] = 0\). This is in particular in our case because we are forced to assume

\[
\rho^B = \frac{\exp(-\beta_I H^I_B - \beta_{II} H^{II}_B)}{\text{Tr}_B \exp(-\beta_I H^I_B - \beta_{II} H^{II}_B)}
\]

(11)

to be able to introduce properly the initial temperatures of baths \(I\) and \(II\) separately.

Suspicious reader with potential objections about applicability of the scaling theories to, in particular, the long-time relaxation phenomena is again referred to the Appendix, in particular its concluding remarks. Here, we should just like to add one comment: Situations are known when (9) cannot be used for finite \(\lambda\)'s (as in Nature). Perhaps the simplest model of this type is that of a single particle on a periodic chain where the system is artificially introduced via a few chosen sites (with the particle or without it), with the rest being the (formal) bath and the system-bath coupling (bringing the particle to or out of the system). Then matrix elements of \(\rho(t)\) between sites of the system decay algebraically [30] while \(e^{-i(\mathcal{L}_0 + (\mathcal{L}_1 + i\lambda^2 \mathcal{K}))t} \rho(0)\) would indicate exponentially dominated decay. The model by Novotný [28] is also of this type. With our real bath known to yield a well-defined relaxation, we
shall for the sake of brevity here postpone discussion of such singular cases with artificially introduced baths to another publication.

Meaning of the mathematically exact statement in the first row of (9) is that time development of \( \rho(t) \) as prescribed by the exact Liouville equation for the density matrix \( \rho^{S+B}(t) \) of the complex ‘system + bath’ is not discernable, in the scaling limit \( \lambda \to 0 \), from that one dictated by the kinetic equation for the density matrix \( \rho(t) \) of just the system

\[
\frac{d}{dt} \rho(t) = (\mathcal{L}_0 + \langle \mathcal{L}_1 \rangle + i\lambda^2 \mathcal{K}) \rho(t). \tag{12}
\]

This general and exact result should now be specified according to the choice of \( H_0 \) and \( \lambda H_1 \) in (3).

Two main possibilities exist.

- Either we accept so called weak-coupling scaling according to van Hove (and often automatically accepted in general situations)

  \[
t = t'/\lambda^2, \quad H_{S-B} \propto \lambda, \quad J = \text{const}, \quad K = \text{const} \tag{13}
\]

  (again with \( \lambda \to 0 \)) which would correspond to the choice

  \[
  H_0 = H_S + H_B, \quad \lambda H_1 = H_{S-B}. \tag{14}
\]

  Then \( \lambda^2 \mathcal{K} \) in (12) is nothing but the weak-coupling relaxation superoperator and (12) reduces to the Redfield equation (before using the Redfield secular approximation) \[33, 34, 35\]. The relaxation is then practically to the canonical state of the system.

- Or we assume (11) what means to identify

  \[
  H_0 = H_S|_{J=K=0} + H_B, \quad \lambda H_1 = H_{S-B} + H_S|_{J\neq 0, K\neq 0} - H_S|_{J=K=0}. \tag{15}
\]

  Then several things have to be realized:

  - Though the relaxation superoperator \( \lambda^2 \mathcal{K} \) in (12) [as defined in (9)] involves formally also higher orders in \( \lambda \), application of the rule \( \text{Tr}_B([a_m^\dagger a_n, \ldots]) = [a_m^\dagger a_n, \text{Tr}_B(\ldots)] \) yields that in fact just second order terms in \( \lambda \) survive.

  - Because now \( \mathcal{L}_0 = \frac{1}{\hbar}[H_S|_{J=K=0} + H_B, \ldots] \) and \( H_S|_{J=K=0} \) is site-diagonal, the relaxation is not any more (like in case of the weak-coupling choice (14)) among eigenstates of \( H_S \) but, instead, among those (site-local eigenstates) of \( H_S|_{J=K=0} \). On
the other hand, in (12), terms $\mathcal{L}_0 + \langle \mathcal{L}_1 \rangle$ reproduce $\frac{1}{\hbar}[H_S, \ldots] \equiv \frac{1}{\hbar}[H_S|J\neq0\neqK, \ldots]$ what is a free propagation among eigenstates of the full (site-off-diagonal) $H_S$. This competition between site-local and site off-local tendencies of the time development is what makes the dynamics much richer than in the weak-coupling case.

- The fact that $\lambda^2 K$ describes relaxation in the site-local basis is not owing to neglecting anything or any type of approximation. It is owing to choice of another regime; in our case that one in which $J$- and $K$-induced processes become at most comparable with those caused by the system interaction with the bath.

The physical argument in favour of the form of the relaxation superoperator corresponding to the choice (13) is that we are interested in the regime in which the bath-assisted processes inside the system are at least comparable with, or even dominating over the internal transfer processes inside the system caused, in our case, by the $J$- and $K$-dependent hopping terms in $H_S$ (1). Once we realize that the weak-coupling theory presumes, in the sense of (13), the system-bath coupling to be infinitesimal, i.e. infinitely times weaker than all other relevant competing transfer and relaxation mechanisms, this excludes scaling (13), i.e. the choice (14), in the regime considered here. On the other hand, it allows to use (14), i.e. the choice (15). That is why we shall below stick to this alternative. So, we use $\mathcal{K}$ from (9) with (15) for our model (1-3). This means the Redfield form of $\mathcal{K}$ in the localized basis as a consequence of another (than the weak-coupling) physical regime, i.e. also correspondingly another form of identification of perturbation. So, this form of the Redfield tensor is definitely not consequence of any additional approximation applied to the Redfield form of the relaxation superoperator in the weak-coupling regime (for discussion of such an approximation in the weak-coupling regime see [39]). After some straightforward algebra,
Here, we have used the notation (12) then turns in the site representation to

\[
\begin{pmatrix}
    \rho_{11} \\
    \rho_{22} \\
    \rho_{33} \\
    \rho_{12} \\
    \rho_{21} \\
    \rho_{13} \\
    \rho_{31} \\
    \rho_{23} \\
    \rho_{32}
\end{pmatrix}
= 
\begin{pmatrix}
    \mathcal{A} & \mathcal{B} \\
    \mathcal{B}^T & \mathcal{C}
\end{pmatrix}
\begin{pmatrix}
    \rho_{11} \\
    \rho_{22} \\
    \rho_{33} \\
    \rho_{12} \\
    \rho_{21} \\
    \rho_{13} \\
    \rho_{31} \\
    \rho_{23} \\
    \rho_{32}
\end{pmatrix}
\]

(16)

The sub-matrices \(\mathcal{A}, \mathcal{B}, \mathcal{C}\) (\(\mathcal{B}^T\) is the transpose of \(\mathcal{B}\)) are given as

\[
\mathcal{A} = 
\begin{pmatrix}
    -i\hbar\Gamma_\uparrow & 0 & i\hbar\Gamma_\downarrow & -J & J \\
    0 & 0 & 0 & J & -J \\
    i\hbar\Gamma_\uparrow & 0 & -i\hbar\Gamma_\downarrow & 0 & 0 \\
    -J & J & 0 & -2i\hbar\Gamma - \frac{i\hbar}{2}\Gamma_\uparrow - \epsilon_2 & 0 \\
    J & -J & 0 & -2i\hbar\Gamma - \frac{i\hbar}{2}\Gamma_\uparrow + \epsilon_2 & 0
\end{pmatrix},
\]

\[
\mathcal{B} = 
\begin{pmatrix}
    0 & 0 & 0 & 0 \\
    0 & 0 & -K & K \\
    0 & 0 & K & -K \\
    -K & 0 & 0 & 0 \\
    0 & K & 0 & 0
\end{pmatrix},
\]

\[
\mathcal{C} = 
\begin{pmatrix}
    -2i\hbar\Gamma - \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) - \epsilon_3 & \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) & J & 0 \\
    \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) & -2i\hbar\Gamma - \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) + \epsilon_3 & 0 & -J \\
    J & 0 & -\frac{i\hbar}{2}\Gamma_\downarrow + \epsilon_2 - \epsilon_3 & 0 \\
    0 & -J & 0 & -\frac{i\hbar}{2}\Gamma_\downarrow - \epsilon_2 + \epsilon_3
\end{pmatrix}.
\]

(17)

Here, we have used the notation

\[
\Gamma_\uparrow = \frac{2\pi}{\hbar} \frac{1}{N} \sum_\kappa |h\omega_\kappa|^2 |g_\kappa|^2 n_B(\beta_{11}, h\omega_\kappa) \delta(h\omega_\kappa - \epsilon_3),
\]

14
\[ \Gamma_{\uparrow} \equiv \frac{2\pi}{\hbar} \frac{1}{N} \sum_{\kappa} |\hbar \omega_{\kappa}|^2 |g_{\kappa}|^2 [1 + n_B(\beta_{II}, \hbar \omega_{\kappa})] \delta(\hbar \omega_{\kappa} - \epsilon_3) = \Gamma_{\uparrow} \cdot e^{\beta_{II} \epsilon_3}, \]
\[ 2\Gamma = \frac{2\pi}{\hbar} \frac{1}{N^2} \sum_{\kappa_1, \kappa_2} |g_{\kappa_1, \kappa_2}|^2 (\hbar \omega_{\kappa_1, \kappa_2})^2 n_B(\beta_{I}, \hbar \omega_{\kappa_1}) [1 + n_B(\beta_{I}, \hbar \omega_{\kappa_2})] \delta(\hbar \omega_{\kappa_1} - \hbar \omega_{\kappa_2}), \]
\[ n_B(\beta, z) = \frac{1}{e^{\beta z} - 1}, \quad (18) \]

where \( T_{I(II)} = 1/(k_B \beta_{I(II)}) \) are the initial temperatures of Baths I and II; \( n_B(\beta, z) \) is the Bose-Einstein phonon distribution function. \( \Gamma_{\uparrow} \) and \( \Gamma_{\downarrow} \) are the Golden Rule formulae for transfer rates \( 1 \rightarrow 3 \) and \( 3 \rightarrow 1 \). Note that \( \Gamma_{\uparrow} \) and \( \Gamma_{\downarrow} \) are different solely in that the latter involves a \( 1 + n_B \) term, whereas the former has only \( n_B \). Physically, this corresponds to \( \Gamma_{\uparrow} \) involving only bath-assisted stimulated up-hill transitions (absorption), whereas \( \Gamma_{\downarrow} \) involves both bath-assisted spontaneous and bath-assisted stimulated down-hill transitions (emission). Finally, \( 2\Gamma \) determines the rate of dephasing arising from local electron-energy fluctuations from Bath I, and also the rate of electron heating in the walls (site 1).

A few comments are worth mentioning already here. First, notice that temperature \( T_I \) of bath I enters (16) only via the dephasing (and simultaneously heating) rate \( 2\Gamma \). This rate depends, however, also on strength and details of the electron coupling to bath I. Thus, moderate changes of \( T_I \) may be well compensated by those of the coupling and vice versa. As there are no abrupt qualitative changes expected with moderate changes of the coupling, only continuous changes of, e.g., the electron \( 1 \rightarrow 2 \rightarrow 3 \) flow are expected when (the initial) temperature \( T_I \) of bath I sinks below that (i.e. \( T_{II} \)) of bath II. This is important for interpretation of the result to be obtained below. Finally, concerning (the initial) temperature \( T_{II} \) of bath II: We shall assume here the inequality
\[ k_B T_{II} \lesssim \epsilon_3. \quad (19) \]

The opposite inequality would imply high-temperature regime in which the spontaneous \( 3 \rightarrow 1 \) processes would become negligible with respect to stimulated ones. So, asymptotically, \( \Gamma_{\uparrow}/\Gamma_{\downarrow} \) would turn to unity and the driving force in the circle \( 1 \rightarrow 2 \rightarrow 3 \rightarrow 1 \) would disappear implying disappearance of the electron flow. This means that also the contradiction with the second law we aim at would disappear, in a full correspondence with the Bohr correspondence principle and the Martynov proof of validity of the second law in classical statistical mechanics [16]. On the other hand, the low-temperature limitation (19) is not severe. With, e.g., \( \epsilon_3 \approx 1\text{eV} \), temperatures \( T_{II} \) appreciably higher than room temperatures are viable.
IV. ANALYTICAL SOLUTION AND STEADY-STATE HEAT-FLOW

Let us henceforth investigate the stationary situation. Then the left hand side of (16) equals zero so that we have a homogeneous set of 9 linear algebraic equations for the stationary values of the electron density matrix. The matrix rank is, however, only 8 since the sum of its first three rows is zero. Thus, the set can (and must) be complemented by the normalization condition

\[ \rho_{11} + \rho_{22} + \rho_{33} = 1. \]  

This provides us with a complete inhomogeneous set of 9 linear algebraic equations for 9 elements of the particle density matrix. The site-diagonal matrix elements \( \rho_{jj} \) give the probabilities of finding the electron at site \( j \). Full algebraic solution of this set of equations is possible but unwieldy. That is why the set will be solved numerically below. First, however, we shall analytically prove that there is always, for nonzero temperatures \( T_I \) and \( T_{II} \), a positive electron flow \( 1 \rightarrow 2 \rightarrow 3 \rightarrow 1 \) implying, for \( T_I < T_{II} \), violation of the second law of thermodynamics in its Clausius formulation. The proof is made by logical contradiction. We stress from the outset that the mathematical derivation of our starting equations (16), including scaling, involves no approximation; therefore, aside from the model assumptions, our treatment here is fully rigorous, in the full mathematical meaning of the word.

Cyclic mean electron flow in the system (taken as positive in the direction \( 1 \rightarrow 2 \rightarrow 3 \rightarrow 1 \)) can be written, on grounds of physical meaning of \( \Gamma_\uparrow \) and \( \Gamma_\downarrow \) in (18), as

\[ \mathcal{J} = \Gamma_\downarrow \rho_{33} - \Gamma_\uparrow \rho_{11}. \]  

From the first and second equations of (13) one also has

\[ \mathcal{J} = \frac{i}{\hbar} J(\rho_{21} - \rho_{12}) = \frac{i}{\hbar} K(\rho_{32} - \rho_{23}). \]  

These formulae can be also easily derived from elementary quantum mechanics. Assume now that no heat flows directly from bath I to bath II and vice versa. So, only the electron-mediated heat flow from I to II may appear. Since the \( 3 \leftrightarrow 1 \) phonon-assisted transitions are associated with influx or efflux of energy (heat) to or from Bath II (proportionally to the magnitude of \( \epsilon_3 \)), the total mean heat flow from Bath I to Bath II may be written as

\[ Q = \epsilon_3 \mathcal{J}. \]
This is the main quantity we are interested in.

Let us now assume, in accord with our strategy of proof by contradiction, that there is no heat flow between the baths, i.e.

$$Q = 0.$$  \hfill (24)

Since \(\epsilon_3 > 0\), this implies, via (21) and (23), that

$$\Gamma_\downarrow \rho_{33} - \Gamma_\uparrow \rho_{11} = 0.$$  \hfill (25)

The reader could easily recognize that (25) is nothing but a detailed balance condition for inelastic phonon-assisted 1 \(\leftrightarrow\) 3 direct transitions. Because of (22) this also implies that

$$\rho_{21} = \rho_{12}, \quad \rho_{32} = \rho_{23}.$$  \hfill (26)

Now, summing the fourth and fifth equations of (16) with zero left hand side, we get

$$0 = \frac{K}{\hbar} (\rho_{31} - \rho_{13}) + (-2i\Gamma - \frac{i}{2} \Gamma_\uparrow) (\rho_{12} + \rho_{21}) + \frac{\epsilon_2}{\hbar} (\rho_{21} - \rho_{12}).$$  \hfill (27)

Similarly, from the sixth and seventh equation, and also from the eighth and ninth equation of (16) (always with zero left hand side), we get

$$0 = \frac{K}{\hbar} (\rho_{21} - \rho_{12}) - 2i\Gamma (\rho_{13} + \rho_{31}) + \frac{\epsilon_3}{\hbar} (\rho_{31} - \rho_{13}) + \frac{J}{\hbar} (\rho_{23} - \rho_{32})$$  \hfill (28)

and

$$0 = \frac{J}{\hbar} (\rho_{13} - \rho_{31}) + \frac{\epsilon_2 - \epsilon_3}{\hbar} (\rho_{23} - \rho_{32}) - \frac{i}{2} \Gamma_\downarrow (\rho_{23} + \rho_{32}).$$  \hfill (29)

In combination with (24), Eqs. (27-29) give

$$\rho_{12} = \rho_{21} = \frac{K}{\hbar} \frac{\bar{\rho}_{31}}{2\Gamma + \frac{1}{2} \Gamma_\uparrow} \Im \rho_{31},$$  \hfill (30)

$$\Re \rho_{31} = \frac{\epsilon_3}{2\hbar \Gamma} \Im \rho_{31},$$  \hfill (31)

and

$$\rho_{23} = \rho_{32} = -\frac{2J}{\hbar \Gamma_\downarrow} \Im \rho_{31}. $$  \hfill (32)

Let us now take difference of the fourth and sixth equation in (16) in the stationary state. Owing to (30-31), it gives

$$0 = -\frac{J}{\hbar} (\rho_{11} - \rho_{22}) + \left\{ -\frac{\epsilon_2}{\hbar} \frac{2K}{\hbar \Gamma + \frac{1}{2} \Gamma_\uparrow} - \frac{K}{\hbar \Gamma} \frac{\epsilon_3}{\hbar \Gamma} \right\} \Im \rho_{31}.$$  \hfill (33)
Similarly, from the difference of the sixth and seventh equation and taking into account (27), (31) and (32), we obtain
\[
0 = \left[ \left( \frac{K}{\hbar} \right)^2 \frac{1}{\Gamma + \frac{1}{4} \Gamma_{\uparrow}} + \left( \frac{J}{\hbar} \right)^2 \frac{4}{\Gamma_{\downarrow}} + \left( \frac{\epsilon_3}{\hbar} \right)^2 \frac{1}{\Gamma} + 2(2\Gamma + \Gamma_{\uparrow} + \Gamma_{\downarrow}) \right] \Im m \rho_{31}. \tag{34}
\]
As the expression in the square brackets is always positive, this implies that
\[
\Im m \rho_{31} = 0, \tag{35}
\]
i.e. using (27-29)
\[
\rho_{13} = \rho_{31} = \rho_{12} = \rho_{21} = \rho_{23} = \rho_{32} = 0. \tag{36}
\]
On the other hand, from (33) and (35), we get that in the stationary state
\[
\rho_{11} = \rho_{22}. \tag{37}
\]
One should realize that conditions (37) and \(\rho_{12} = \rho_{21}\) (see (36)) obtained so far fully correspond to what has been said above about no-flow equilibrium inside the dimer ‘1 - 2’.

The eighth or ninth equation of (16) yield, in the stationary state and with the help of (36),
\[
\rho_{22} - \rho_{33} = 0. \tag{38}
\]
Together with (20) and (25), it provides an inhomogeneous set of three linear algebraic equations determining the site occupation probabilities (all the time provided that the no-flow condition (24) used above applies). The solution reads
\[
\rho_{11} = \frac{\Gamma_{\downarrow}}{\Gamma_{\downarrow} + 2\Gamma_{\uparrow}}, \quad \rho_{22} = \rho_{33} = \frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow} + 2\Gamma_{\uparrow}}. \tag{39}
\]
This result, on the other hand, contradicts (37). This is the required contradiction implying that (24) cannot be correct. One can also ask what is the reason for the contradiction. Clearly, (37) would be satisfied by (38) if there were \(\Gamma_{\downarrow} - \Gamma_{\uparrow} = 0\). That would, however, mean to disregard the spontaneous processes that are responsible for the difference on the left hand side. The spontaneous processes are, however, purely quantum. Similarly, one can easily observe that (38) becomes fully compatible with (37) in the limit of the infinite temperature \(T_{II} \to +\infty\). The infinite temperature limit means, however, the classical limit (the Bohr correspondence principle). All that is why we can understand the violation of the second law we arrive at below (as well as in other models yielding such a striking conclusion - see above) as a consequence of quantum effects.
So, there is always an electron circular flow in the system implying (not in general but) in our specific situation nonzero heat transfer $Q$ (as given by (23) and (21) or (22)) between baths I and II. The last questions to be solved before we resort to a numerical study are what is its orientation and how the conclusion contradicts the second law.

V. VIOLATION OF THE SECOND LAW

In order to infer what is the orientation of the mean heat flow, let us turn to above formulae (21) and (23). From (23) we get that signs of $Q$ and $J$ coincide ($\epsilon_3 > 0$). As for the latter, we remind that $\rho_{33}$ is always (as a site occupation probability) positive and that $\Gamma^\uparrow$ disappears for $T_{II} \to 0$. Thus, from (21), we get that $J$ is, in the low temperature limit of bath II but arbitrary nonzero $T_I$, always positive. This is, by the way, also what our numerical results show.

Let us now increase $T_{II}$. One should realize that $Q$ is a continuous function of $T_{II}$ and never turns to zero. (For that, see the above proof.) So it should remain positive even when $T_{II}$ becomes greater than $T_I$. (In fact, owing to intermixture of $T_I$ with details of coupling to bath I in $H_{S-B}$ inside $\Gamma$, nothing can happen at the moment when $T_{II}$ passes $T_I$. This fact was also confirmed numerically.) Positive values of $Q$ mean, however, a positive rate of heat transfer from bath I to bath II which thus goes, for $T_I < T_{II}$, against temperature step. As the heat transfer is spontaneous (there is no external expenditure of energy or whatever else conditioning this transfer), this conclusion explicitly contradicts the Clausius form of the second law [2] stating that such processes are impossible. On the other hand, the conclusion obtained analytically here (and verified numerically below) that the second law is in our system really violated fully corresponds to conclusions of [11] where, for an experimental plasma system corresponding to the above model, the universal validity of the second law was first seriously challenged.

VI. NUMERICAL RESULTS

In order to verify the above conclusions, we have solved the set (16) and (20) numerically. There was also a secondary reason for this numerical study: Analytically, we were unable to prove that the heat transfer really turns to zero in the limit of zero temperature $T_I$ of
bath I. This is what must be expected physically because in such a limit, there is no heat available in bath I to be transferred to bath II. In just other words: There is no dephasing in this limit between sites 1 and 2. So, the covalent bond 1-2 should become perfect, making thus the electron (and consequently also the heat) flow impossible.

Fig. 1 shows typical results. We designate $\gamma_0 = \Gamma_{\uparrow} e^{\beta_{II} - 1}$. Three things are worth noticing:

- In accordance with the above analytical arguments, the mean heat flow $Q$ is always positive (i.e. going from bath I to bath II).

- With decreasing dephasing rate $2\Gamma$ corresponding to decreasing temperature $T_I$, $Q$ turns apparently to zero.

- For constant rate $2\Gamma$, $Q$ is only very little dependent on temperature $T_{II}$ of bath II. Slight increase as well as decrease with $T_{II}$ are both possible. This may be interpreted as a result of two competing tendencies:
  
  - Increasing $T_{II}$ increases also the rate of dephasing between sites 2 and 3 caused by nonzero and $T_{II}$-dependent terms $-i\hbar/2 \Gamma_{\downarrow}$ in 3-3 and 4-4 elements of block $C$ in (16). Similarly the terms $-i\hbar/2 \Gamma_{\uparrow}$ in 4-4 and 5-5 elements of block $A$ in (16) contributing to dephasing of sites 1 and 2. This leads to greater violations of the 2-3 and 1-2 bonds, i.e. to increase of $Q$.
  
  - Increasing $T_{II}$ on the other hand implies relatively decreasing role of the spontaneous processes in $3 \rightarrow 1$ transitions what means suppression of $Q$.

Dependence of $Q$ on $T_{II}$ is, however, always very small.

VII. CONCLUSION

We have obtained a spontaneous heat flow between two macroscopic baths that is owing to a specific activity of our microscopic single-electron system not aided from outside. So, starting from rigorous mathematics of the quantum theory of open systems, a contradiction with the second law of thermodynamics has been obtained for the model in question. Remind that except for model assumptions, no approximations were made that could be
made responsible for the effect, and that the model corresponds to an experimental system positively tested in [11]. This indicates that one should choose between just two alternatives:

- There is still something hidden in physics beyond the second law what is at present not fully understood. This possibility might also mean complementing contemporary quantum mechanics and present philosophy of quantum-mechanical modelling in order to reconcile the quantum theory with (presumably) universally valid thermodynamics.

- The second alternative is to refrain from the so far universally assumed validity of thermodynamics in the macroworld. One should realize that though our system is microscopic, appending the macroscopic reservoirs turn the physics to the macroscopic one.

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IX. APPENDIX: DERIVATION OF THE STARTING EQUATIONS BY NON-SCALING ARGUMENTS

Arguments in favour of violation of the second law as reported above critically depend on the existence of the heat flow from bath I to bath II, i.e. on the existence of the electron mean circular flow $\mathcal{J}$. Existence of the flow has been above proved using scaling which does not belong to a generally accepted weaponry in kinetic theories. Moreover, though standard practice confirms such a possibility, one could ask about justification to use such a (as well as any other) kinetic approach beyond (time) limits of the kinetic regime. (Notice, e.g., that constant $a$ in $\sup_{0\leq \lambda^2 t \leq a} \ldots$ in (3) is always finite.) That is why we present another treatment below that is non-scaling but fully confirms the above conclusions. This treatment is then fully resistive even against such objections as it assumes, as experiments
require, taking first (though after the thermodynamic limit of the bath) the dc, i.e. the
infinite time limit. Only then (if at all) discussion based on smallness of individual terms in
the Hamiltonian (coupling constants etc.) comes into question.

For reasons connected with unreliability of the finite-order approximations in convolution
theories discussed in [40], we refrain from convolution theories of the Nakajima-Zwanzig
[41, 42] type. Instead, we adopt the formalism based on the time-convolutionless (i.e. time-
local) Generalized master equations (TCL-GME). These were first suggested by Fuliński and
Kramarczyk [43, 44] but more operative (and in fact equivalent [45]) are those by Shibata,
Hashitsume, Takahashi, and Shingu [46, 47]. The starting Shibata, Hashitsume, Takahashi,
and Shingu identity (derived as a direct consequence of the Liouville equation) reads

$$\frac{d}{dt} \rho^{S+B}(t) = -iP \mathcal{L}[1 + i \int_0^t \exp\{-i(1 - P)\mathcal{L}\tau\}(1 - P)\mathcal{L}P \exp\{i\mathcal{L}\tau\} d\tau]^{-1}$$

\[ \cdot \exp\{-i(1 - P)\mathcal{L}t\}(1 - P)\rho^{S+B}(0) + P \rho^{S+B}(t) \]  (40)

Now we make two steps. First we take for $P$ the Argyres-Kelley projector (8), and assume
the initial condition (10). Let us now split our Hamiltonian as in (6) and introduce $\mathcal{L}_0$ and
$\lambda \mathcal{L}_1$ as in (7). This reduces, for both the weak coupling (14) and our identifi-
cation (15), equation (40) to

$$\frac{d}{dt}\rho(t) = (-i \mathcal{L}_0 - i \langle \mathcal{L}_1 \rangle + \lambda^2 \mathcal{L}^{TCL-GME}(t))\rho(t).$$  (41)

Here, because $P \mathcal{L}_0 = \mathcal{L}_0 P$,

$$\lambda^2 \mathcal{L}^{TCL-GME}(t) \ldots = -Tr_B \left( \mathcal{L}_1[1 + i \int_0^t \exp\{-i(1 - P)\mathcal{L}\tau\}(1 - P)\mathcal{L}_1P \exp\{i\mathcal{L}\tau\} d\tau]^{-1} \right.$$  

\[ \cdot \int_0^t \exp\{-i(1 - P)\mathcal{L}\tau\}(1 - P)\mathcal{L}_1P \exp\{i\mathcal{L}\tau\} d\tau (\rho^B \otimes \ldots) \right) \]  (42)

Notice that the relaxation superoperator $\lambda^2 \mathcal{L}^{TCL-GME}(t)$ still involves also higher-than-
second order terms in $\lambda$. It is also time-dependent. This time dependence is determined
by the decay-to-zero of the integrand (after the implicit but everywhere assumed thermo-
dynamic limit of the bath). The characteristic times are given by dephasing in the bath.
Once we disregard a transient (and for our purposes fully unimportant) initial time period,
we may turn time $t$ in (42) to infinity.

We should like to stress that

- turning $t$ to infinity in $\lambda^2 \mathcal{L}^{TCL-GME}(t)$ still does not mean treating just the final result
  of the finished process of relaxation;
• the long-time limit taken in (42) is dictated by the experimental situation (we are not interested in short-time transient relaxation effects) and time $t$ could be, beyond some bath dephasing time, well taken arbitrarily large, in accordance with the experiment.

• This is unlike the situation with the value of $\lambda$. In Nature, this coupling constant is determined, for a given experiment, once for ever and cannot be arbitrarily changed.

That is why one should expand, if at all, in powers of $\lambda$ only after the long time limit $t \to +\infty$ in $\lambda^2 K^{TCL-GME}(t)$. That is what we do here. If we take $t \to +\infty$ in (42) and then limit our attention to the lowest nonvanishing (i.e. the second) order in $\lambda$, (42) then turns to

$$\lambda^2 K^{TCL-GME}(t) \ldots$$

$$= -Tr_B \left( L_1 \int_0^{+\infty} \exp\{-iL_0\tau\}(1 - \mathcal{P})L_1\mathcal{P} \exp\{iL_0\tau\} d\tau (\rho^B \otimes \ldots) \right) + O(\lambda^4). \quad (43)$$

The first term on the right hand side of (43) should now be compared with that of $\lambda^2 K$ in (4). The point is that if identity of these two expressions for the relaxation superoperator is established, the TCL-GME (41) becomes, for both the standard weak coupling choice (14) and that one by Čápek and Barvík (15), fully equivalent to (12).

At the first sight, there is a similarity but no identity observed. In order to discuss the point in detail, let us make several physically motivated and justifiable steps. First, the integrations, in both $\lambda^2 K$ in (4) and $\lambda^2 K^{TCL-GME}(t)$ in (42), lead (upon explicit introduction of the matrix elements involved) to distributions $\lim_{\delta \to 0^+} \frac{-ih}{\Delta E - i\delta}$ that we approximate as $\pi \hbar \delta(\Delta E)$ ($\Delta E$ being relevant differences of eigenenergies of $H_0$). This step amounts to neglect term v.p. $\frac{-ih}{\Delta E}$ (here v.p. means the fraction in the Cauchy sense); such imaginary terms are standardly interpreted as just renormalizations of transfer (hopping or resonance) integrals. (In this connection, notice the imaginary unit $i$ in the $(-iL_0 - i\langle L_1 \rangle)$ term on the right hand side of (41) or (4).) Doing so, the $mn$-matrix element of $\lambda^2 K \ldots$ in (4) turns to

$$(\lambda^2 K \ldots)_{mn} = -\frac{1}{\hbar} \sum_{\mu} \sum_{s\sigma} \sum_{q\kappa} \{ \langle m\mu|\lambda H_1|s\sigma\rangle\langle s\sigma|\lambda H_1|q\kappa\rangle\langle q\kappa|\rho^B \otimes \ldots |n\mu\rangle \pi \delta(E_{s\sigma} - E_{m\mu})$$

$$-\langle m\mu|\lambda H_1|s\sigma\rangle\langle s\sigma|\rho^B \otimes \ldots |q\kappa\rangle\langle q\kappa|\lambda H_1|n\mu\rangle \pi \delta(E_{s\sigma} - E_{m\mu})$$

$$-\langle m\mu|\lambda H_1|q\kappa\rangle\langle q\kappa|\rho^B \otimes \ldots |s\sigma\rangle\langle s\sigma|\lambda H_1|n\mu\rangle \pi \delta(E_{n\mu} - E_{s\sigma})$$

$$+\langle m\mu|\rho^B \otimes \ldots |q\kappa\rangle\langle q\kappa|\lambda H_1|s\sigma\rangle\langle s\sigma|\lambda H_1|n\mu\rangle \pi \delta(E_{n\mu} - E_{s\sigma}) \}$$

23
\begin{align*}
+ \left( \lambda^2 \Delta K \ldots \right)_{mn}. \tag{44}
\end{align*}

Here, we have used the notation $|m\mu\rangle = |m\rangle \otimes |\mu\rangle$ etc. where $|m\rangle$ and $|\mu\rangle$ are respectively eigenstates of $H_0 - H_B$ and $H_B$; $E_{m\mu} = E_m + E_\mu$ are the corresponding eigenenergies. In the same way, disregarding already the transient time-dependence and higher-than-second order terms (by the definition absent in \ref{eq:3})

\begin{align*}
\left( \lambda^2 K^{TCL-GME \ldots} \right)_{mn} &= -\frac{1}{\hbar} \sum_{\mu} \sum_{s\sigma} \sum_{q\kappa} \left\{ \langle m\mu|\lambda H_1|s\sigma\rangle \langle s\sigma|\lambda H_1|q\kappa\rangle \langle q\kappa|\rho^B \otimes \ldots |n\mu\rangle \pi \delta(E_{s\sigma} - E_{q\kappa}) \\
&\quad - \langle m\mu|\lambda H_1|s\sigma\rangle \langle s\sigma|\rho^B \otimes \ldots |q\kappa\rangle \langle q\kappa|\lambda H_1|n\mu\rangle \pi \delta(E_{q\kappa} - E_{n\mu}) \\
&\quad - \langle m\mu|\lambda H_1|q\kappa\rangle \langle q\kappa|\rho^B \otimes \ldots |s\sigma\rangle \langle s\sigma|\lambda H_1|n\mu\rangle \pi \delta(E_{m\mu} - E_{q\kappa}) \\
&\quad + \langle m\mu|\rho^B \otimes \ldots |q\kappa\rangle \langle q\kappa|\lambda H_1|s\sigma\rangle \langle s\sigma|\lambda H_1|n\mu\rangle \pi \delta(E_{q\kappa} - E_{s\sigma}) \right\} \\
&\quad + \left( \lambda^2 \Delta K^{TCL-GME \ldots} \right)_{mn}. \tag{45}
\end{align*}

Obviously, the second and third terms from \ref{eq:44} equal respectively to the third and second terms in \ref{eq:45}. As for the remaining terms, there are differences between the Davies \ref{eq:14} and TCL-GME \ref{eq:15} results that may become important when, e.g., different matrix elements of the coupling to phonons interfere.

In order to show that this is not our case for the above model and the regime investigated, let us make several specifications and observations.

- First, assume that

$$\langle \mu|\rho^B|\nu\rangle = \delta_{\mu,\nu} p_\mu. \tag{46}$$

This is consistent with assumptions od both the scrutinized approaches.

- Realize that for the model specified by \ref{eq:13}, the two terms in the system-bath coupling then do not interfere. For the site-local coupling, it is trivial to see the equivalence of the first and the fourth terms in \ref{eq:44} and \ref{eq:15}. So, we turn our attention to just the site off-local coupling term $H^I_{S-B}$ in \ref{eq:3}.

- We specify our reasoning here to the regime corresponding to our choice \ref{eq:15}. Then $H_S|_{J=K=0}$ is site-diagonal, i.e. the Latin summation indices in \ref{eq:44} and \ref{eq:15} are sites.

Because of the last point, equivalence between the first rows of \ref{eq:44} and \ref{eq:15} and, similarly, between the fourth rows of \ref{eq:44} and \ref{eq:15}, is then for the site off-local coupling easily seen.
[For example, with $\lambda H_1$ being in the first row of (14) and (13) substituted by $H_{S-B}^{II}$ from (3), the form of $H_{S-B}^{II}$ implies that nonzero contribution appears just for $m = q$. Because of (16), only terms with $\kappa = \mu$ contribute what makes the equivalence between the first rows of (14) and (13) explicit.] As for the last terms in (14) and (15) ignored so far, we get

$$
(\lambda^2 \Delta \mathcal{K} \ldots)_{mn} = \int_0^{+\infty} dx T_{\tau B} \left( e^{i\mathcal{L}_C x} \mathcal{L}_1 e^{-i\mathcal{L}_C x} \mathcal{P} \mathcal{L}_1 (\rho^B \otimes \ldots) \right)
$$

$$
= \frac{1}{\hbar} \sum_{\mu \alpha} \sum_a \left\{ \langle m\mu|\lambda H_1|a\alpha\rangle \langle \alpha|\rho^B|\mu\rangle \langle \alpha|e^{iH_B x/\hbar} \rho^B e^{iH_B x/\hbar}|\mu\rangle \right\}
$$

$$
- \langle \mu| [\lambda H_1, \rho^B \otimes \ldots]|a\nu\rangle \langle \alpha|\rho^B|\alpha\rangle \langle a\nu|\lambda H_1|n\mu\rangle \pi \delta(E_{n\mu} - E_{a\alpha}) \right\}.
$$

and

$$
(\lambda^2 \Delta \mathcal{K}_{TCL-GME} \ldots)_{mn} = \int_0^{+\infty} d\tau T_{\tau B} \left( \mathcal{L}_1 e^{-i\mathcal{L}_C \tau} \mathcal{P} \mathcal{L}_1 \mathcal{P} e^{i\mathcal{L}_C \tau} (\rho^B \otimes \ldots) \right) + O(\lambda^4)
$$

$$
= \frac{1}{\hbar} \int_0^{+\infty} dx \sum_{\mu \alpha \beta} \sum_{a b} \left\{ \langle m\mu|\lambda H_1|a\alpha\rangle \langle \alpha|e^{-iH_B x/\hbar} \rho^B e^{iH_B x/\hbar}|\mu\rangle \right\}
$$

$$
\times \left\{ -\frac{-i\langle \alpha|e^{iH_B x/\hbar} \rho^B e^{iH_B x/\hbar}|\mu\rangle}{E_{m\nu} - E_{b\beta} - i0+} + \frac{i\langle \alpha|e^{iH_B x/\hbar} \rho^B e^{iH_B x/\hbar}|\mu\rangle}{E_{b\beta} - E_{m\nu} - i0+} \right\}
$$

$$
- \left\{ \frac{-i\langle \alpha|e^{iH_B x/\hbar} \rho^B e^{iH_B x/\hbar}|\mu\rangle}{E_{m\nu} - E_{b\beta} - i0+} + \frac{i\langle \alpha|e^{iH_B x/\hbar} \rho^B e^{iH_B x/\hbar}|\mu\rangle}{E_{b\beta} - E_{m\nu} - i0+} \right\}
$$

$$
\cdot \langle \mu|e^{-iH_B x/\hbar} \rho^B e^{iH_B x/\hbar}|\alpha\rangle \langle a\alpha|\lambda H_1|n\mu\rangle + O(\lambda^4).
$$

(47)

Clearly, expressions (47) and (48) are discernibly different even when we omit the renormalization terms. Fortunately, with (16) and the fact that both the terms in $H_{S-B}$ in (3) are off-diagonal in the phonon indices, both (47) and (48) are in fact exactly zero. This makes the proof of full equivalency, for our model and to the lowest perturbational order, of the relaxation superoperator $\mathcal{K}$ as derived from the scaling Davies theory with that one derived by the non-scaling time-convolutionless Generalized Master Equation theory complete. The latter theory thus provides independent non-scaling way to our above equation (16) with (17) forming basis of the above discussion. The important point is that we have here, after taking the thermodynamic limit of the bath, first turned the real physical time behind dephasing time of the bath, i.e. potentially even to infinity. Only then we have discussed the form of the relaxation tensor determining the relaxation process up to infinite times as valid for small couplings. Hence, unlike the scaling theories, strength of the coupling never comes into any competition with time limitations of the theory so that no objections can be raised that the kinetic theory used is inapplicable behind some long critical times.
[1] W. Thomson, Trans. Roy. Soc. Edinburgh **16**, 541 (1849).
[2] R. Clausius, Ann. Phys. Chem. **79**, 368 (1850).
[3] J. C. Maxwell, *Theory of Heat*. (Longmans, Green and Co, London, 1871.)
[4] J. Loschmidt, Akademie der Wissenschaften, Wien. Mathematisch-Naturwissenschaftliche Klasse, Sitzungsberichte **59**, Abth. 2, 395 (1869).
[5] L. Szilard, Z. Physik **52**, 840 (1929).
[6] H. S. Leff and A. F. Rex, *Maxwell’s demon. Entropy, Information, Computing*. (Hilger and Inst. of Physics Publishing, Bristol, 1990.)
[7] R. P. Feynman, R. B. Leighton, M. Sands, The Feynman Lectures on Physics, Vol. 2. (Addison-Wesley, Reading, Massachusetts, 1966.)
[8] G. Muser, Scientific American **280**, 13 (1999).
[9] E. H. Lieb and J. Yngvason, Physics Reports **310**, 1 (1999).
[10] E. H. Lieb and J. Yngvason, Physics Today **53**, April issue, 32 (2000).
[11] D. P. Sheehan, Phys. Plasmas **2**, 1893 (1995).
[12] A. V. Nikulov, [http://xxx.lanl.gov/abs/physics/9912023](http://xxx.lanl.gov/abs/physics/9912023).
[13] A. V. Nikulov and I. N. Zhilyaev, J. Low Temp. Phys. 112 (1998) 227.
[14] S. V. Dubonos, V. I. Kuznetsov, and A. V. Nikulov, [http://xxx.lanl.gov/abs/physics/0105054](http://xxx.lanl.gov/abs/physics/0105054).
[15] V. Čapek, Czech. J. Phys. **47**, 845 (1997).
[16] G. A. Martynov, *Classical Statistical Mechanics*. Fundamental Theories of Physics, Vol. 89. (Kluver Academic Publishers, Dordrecht - Boston - London, 1997).
[17] D.P. Sheehan, J. Scient. Exploration **12**, 303 (1998).
[18] V. Čapek and H. Tributsch, J. Phys. Chem. **B 103**, 3711 (1999).
[19] V. Čapek, [http://xxx.lanl.gov/abs/cond-mat/0012056](http://xxx.lanl.gov/abs/cond-mat/0012056). Europ. Phys. J. B 25 (2002) 101.
[20] V. Čapek, J. Bok, Physica **A 290**, 379 (2001).
[21] V. Čapek, D. P. Sheehan, Physica **A 304**, 461 (2002).
[22] A. E. Allahverdyan and Th. M. Nieuwenhuizen, [http://xxx.lanl.gov/abs/cond-mat/0110422](http://xxx.lanl.gov/abs/cond-mat/0110422).
[23] L. G. M. Gordon, Foundations of Physics **13**, 989 (1983).
[24] D. P. Sheehan, J. D. Means, Phys. Plasmas **5**, 2469 (1998).
[25] A. V. Nikulov, [http://xxx.lanl.gov/abs/physics/0104073](http://xxx.lanl.gov/abs/physics/0104073), Phys. Rev. **B 64**, 012505 (2001).

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[26] E. B. Davies, Math. Annalen 219, 147 (1976).
[27] E. B. Davies, Quantum Theory of Open Systems. (Academy Press, London, 1976.)
[28] T. Novotný, http://xxx.lanl.gov/abs/cond-mat/0204302
[29] V. Čápek, Z. Physik 99, 261 (1996).
[30] V. M. Kenkre, in Exciton Dynamics in Molecular Crystals and Aggregates. Springer Tracts in Modern Physics 94, Ed. G. Höhler. (Springer, Berlin - Heidelberg - New York, 1982.)
[31] V. Čápek, Physica A 203, 520 (1994).
[32] V. Čápek and I. Barvík, Physica A 294, 388 (2001).
[33] A. G. Redfield, IBM J. Res. Develop. 1, 19 (1957).
[34] A. G. Redfield, in Advances in Magnetic Resonance (Ed. J. S. Waugh, Vol. 1. Academic Press, New York - London, 1965, p. 1).
[35] G. Mahler and V. A. Weberuš, Quantum Networks. Dynamics of Open Nanostructures (Springer, Berlin - Heidelberg - New York, 1995).
[36] E. B. Davies, Commun. math. Phys. 39, 91 (1974).
[37] I. Barvík, V. Čápek, and P. Heřman, J. Luminescence 83-84, 105 (1999).
[38] V. Čápek, I. Barvík, and P. Heřman, Chem. Phys. 270, 141 (2001).
[39] U. Kleinekathöfer, I. Kondov, and M. Schreiber, Chem. Phys. 268, 121 (2001).
[40] V. Čápek, Physica A 203, 495 (1994).
[41] S. Nakajima, Progr. Theor. Phys. 20, 948 (1958).
[42] R. Zwanzig, Physica 30, 1109 (1964).
[43] A. Fuliński, Phys. Letters A 25, 13 (1967).
[44] A. Fuliński and W. J. Kramarczyk, Physica 39, 575 (1968).
[45] H. Gzyl, J. Stat. Phys. 26, 679 (1981).
[46] N. Hashitsume, F. Shibata, and M. Shingu, J. Stat. Phys. 17, 155 (1977).
[47] F. Shibata, Y. Takahashi, and N. Hashitsume, J. Stat. Phys. 17, 171 (1977).
Figure captions

Figure 1: Spontaneous energy flow $Q$ in units $4K^2/h$ from bath I to bath II as a function of temperature $T_{II} = 1/(k_B\beta_{II})$ of bath II. We set $J = K = 0.5$ eV, $\epsilon_2/K = 4$, $\epsilon_3/K = 2$, $\hbar\gamma_0/K = 0.02$, and $\hbar\Gamma/K = 10^{-2}, 10^{-3}$ and $10^{-4}$ (decreasing dephasing rate, i.e. also heating, at site 1) for curves a), b), and c), respectively. Notice that $2\Gamma$ incorporates also temperature $T_I$ of bath I.
