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Twilight of a Dogma of Statistical Thermodynamics

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Twilight of a Dogma of Statistical Thermodynamics

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In very specific situations, processes are possible where particles get transferred from one subsystem to another one, even uphill in energy and at the cost of thermal energy of the bath only. This means that expected grandcanonical equilibrium is not achieved in the course of the time development what imposes limitations on so far supposed universal validity of the standard statistical thermodynamics.

Keywords: Pump; correlations; statistical thermodynamics

1. INTRODUCTION

The present author has had a long, fruitful and very pleasant collaboration with Prof. E. A. Silinsh (to whose memory the present volume is devoted) in the field of molecular organic crystals, in particular their polarization and transport properties (see [1] and papers cited therein). The last joint activity of both the authors was connected with an interplay of these properties, namely with dynamic formation of electronic polarization [2] in organic molecular condensates. Electron (Toyozawa) polaron[3,1] in molecular condensates is a specific example where strong particle-particle correlations may appreciably influence macroscopic properties of matter. It was also this activity on specific types of the particle-particle correlations in connection with the particle transport which brought the present author to ideas scrutinizing the very basic principles of statistical thermodynamics. Prof. Silinsh has not taken part in the latest development of such ideas. He followed it, however, and his continuing interest was highly stimulating.

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The present paper is not intended as a presentation of any detailed theory. It uses ideas previously published by us (though in very specific contexts) elsewhere. The aim of this work is, however, to use these results in much more general form and situations, and to scrutinize, in such a way, basic axioms of the statistical thermodynamics. Let us start with the situation where the usual derivation of the grand-canonical ensemble begins. We let upon the reader to verify that similar reasoning as below can in principle be used to scrutinize also standard introduction of the canonical ensemble. Thus, we have two subsystems designated as '1' and '2' which are in a contact enabling mutual exchange of particles and energy. (For the sake of simplicity, we assume one type of particles only.) Both the subsystems form together a system under investigation and can interact with their surroundings which may be considered to be appreciably greater than both the subsystems. Thus, it forms a thermodynamic bath in the usual sense. We assume the complex 'system + bath' to be isolated from the rest of universe for us to be able to describe it via standard quantum statistical mechanics with the Schrödinger or Liouville equations. Before increasing time, however, we must let the bath (so far not the system) to increase to infinity. This procedure is called the thermodynamic limit of the bath. In such a way, we introduce irreversibility and avoid appearance of the Poincaré recurrencies (cycles) [4].

After the thermodynamic limit of the bath has been taken, assume now that we wait sufficiently long so that a stationary situation in the system gets established. Standardly, one speaks about equilibrium. We should, however, like to avoid this word as it is usually being connected with such features of the state which we should like to scrutinize here and, under very specific conditions, even to question. If both the subsystems are sufficiently great and if the interactions between (or among) particles are sufficiently short-ranged, one can, as usual and again in standard situations, neglect a contribution of the interaction between the subsystems to the total energy. This is conditioned by the fact that fluctuations of energies of the subsystems and energy flows between the subsystems get, in such stationary situations, negligible. Let us immediately stress that, upon establishing the stationary situation, this interaction is, on the other hand, highly important. Similarly and in the above (already established) stationary situation, we also neglect contribution of the system-bath interaction to the total energy. On grounds of arguments of sufficient magnitude of the subsystems, one can also, in the above stationary situations, neglect fluctuations of particle numbers. Then one usually infers that

- in the bases of eigenstates of the Hamiltonians of both the subsystems (with density matrices ρ_1 and ρ_2) characterized by sharp values of particle numbers, and that one resulting from direct product of the latter bases (for the

density matrix ρ_{1+2} of the total system), all the density matrices are diagonal, and

- owing to the presumed statistical independence of the subsystems, ρ_{1+2} is factorizable as

$$\rho_{1+2} = \rho_1 \otimes \rho_2. \tag{1}$$

- Diagonal form of the density matrices follows from the Liouville theorem in our stationary situation.* Designating then these diagonal elements as probabilities $w...(E..., N...)$, we have the famous equation

$$w_{1+2}(E_1 + E_2, N_1 + N_2) = w_1(E_1, N_1) \cdot w_2(E_2, N_2). \tag{2}$$

We stress here that, in contrast to standard reasoning, we still distinguish among functions w_{1+2}, w_1, and w_2. Standard way to proceed is

- to identify functions $w_{1+2}(E, N)$, $w_1(E, N)$, and $w_2(E, N)$, designating them by, e.g., a joint symbol $w(E, N)$, and
- to assume that $w(E, N)$ is a continuous function of both its arguments.

This then implies that

$$w(E, N) = \mathrm{e}^{\alpha - \beta(E - \mu N)}. \tag{3}$$

(Here α is, however, additive.) Eq. (3) may be then easily recognized to represent nothing but the grand-canonical distribution. Then $\alpha = \beta\Omega$ where Ω is the Gibbs potential, $\beta = 1/(k_B T)$ is the reciprocal temperature in energy units, and μ is the chemical potential. Clearly, from (2), it follows that the latter two quantities are the same in subsystems '1' and '2'.

If we want to question this procedure, we should immediately specify the point in the above reasoning which is, according to our opinion, in general not universally valid. This is, as we are going to argue now, the point where we set that functions $w_{1+2}(E_1 + E_2, N_1 + N_2)$, $w_1(E_1, N_1)$, and $w_2(E_2, N_2)$ are the same (differing by just their arguments). This identification is sometimes considered as a principle whose justification stems from the fact that it depends just on our choice which of, e.g. the subsystems will be next considered. It is also connected with the tacitly anticipated fact that channels connecting subsystems '1' and '2' are in a way symmetric, preferring neither '1'→'2' nor '2'→'1' direction of the particle (energy etc.) transfer. Asymmetric channels (which we shall henceforth call also pumps) have until recently been known in microscopic treatments just when they were aided from outside. This fully corresponds to the picture developed by biologists concerning, e.g., active membrane pumps aided by the

* The density matrices can, in stationary situations, be expressed as functions of preserving quantities only. These are, in our situation and up to negligible fluctuations, just energy and number of particles.

ATP→ADT splitting. On the other hand, in connection with microscopic systems showing effect of the so called isothermal Maxwell demon [5–10], such unidirectional pumps, this time *not* aided from outside and working from just the thermal energy of the bath, have already been theoretically suggested. Their exceptional activity has also been explained and proven by theoretical quantum statistical arguments [5–10]. Below, we shall briefly discuss one, perhaps the simplest of such pumps, which provides a simple generalization of that one from [7] to, in our situation, many-body systems.

2. SIMPLE UNIDIRECTIONAL PUMP AND ITS ACTIVITY

Let us for simplicity assume that our subsystems '1' and '2' consist of particles of one sort, distributed on localized states called sites henceforth and designated by index n. This index may take on values of either negative or positive integers for subsystems '1' and '2', respectively. Site '0' has a special coupling to both subsystems and also to another special two-level system. The latter system forms, by its special coupling to the particles, a pump driving, by its instability and utilizing its coupling to the bath as well as the particles, the particles mostly in one direction only. We shall see that site '0' serves as a receptor needed by the pump to recognize that the particle to be transferred is at our disposal. Hence, the Hamiltonian of the system is assumed in form

$$
\begin{aligned}
H_S &= H_{S_1} + H_{S_2} + H_{pump},\\
H_{S_1} &= \sum_{m,n=-\infty}^{-1} [\varepsilon_m \delta_{m,n} + J_{mn}(1-\delta_{m,n})] a_m^\dagger a_n,\\
H_{S_2} &= \sum_{m,n=+1}^{+\infty} [\varepsilon_m \delta_{m,n} + J_{mn}(1-\delta_{m,n})] a_m^\dagger a_n,\\
H_{pump} &= \frac{\epsilon}{2}[1 - 2a_0^\dagger a_0][|u\rangle\langle u| - |d\rangle\langle d|]\\
&\quad + J(a_{-1}^\dagger a_0 + a_0^\dagger a_{-1})|d\rangle\langle d| + I(a_1^\dagger a_0 + a_0^\dagger a_1)|u\rangle\langle u|. \qquad (4)
\end{aligned}
$$

(Here, we as usual write, e.g., $a_m^\dagger a_n$ instead of $a_m^\dagger a_n \otimes \mathbf{1}$ where $\mathbf{1}$ designates unity operator in the Hilbert space spanned on two states $|u\rangle$ and $|d\rangle$ of our two-level system connected with our receptor – site '0' – and forming an inherent part of the pump. Similarly, we have for simplicity omitted the symbol $\otimes$ in H_{pump} what should cause no problem.) For simplicity, we take $J_{mn}= 0$ once $m{\cdot}n <$ 0. Hence, the only way for particles from subsystem '1' to '2' or *vice versa* is via the pump. Below, we shall for simplicity also assume that $\varepsilon_m = 0$ for $m < 0$ (subsystem '1') and $\varepsilon_m = \delta\in$ for $m > 0$ (subsystem '2'). This means homogeneity of

the subsystems and mutual shift of the particle site-energies in these subsystems. Similarly, we can put J_{mn} nonzero just between, e.g., nearest neighbours. As for the Hamiltonian of the bath, we assume it in its simplest form as, e.g., the set of noninteracting bosons (phonons)

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

For the system-bath coupling, we need two different couplings at least without which our pump would not act as assumed.

- We need coupling of the two-level system (the driving pump) to the bath in order to make transitions between its states $|u\rangle \leftrightarrow |d\rangle$ possible. These transitions then provide dynamic closing and opening of the gate for particles transferred. Worth noticing is that the first term in H_{pump} in (4) causes interchange of order of the energy levels of the pump (as calculated for $J = I = 0$) whenever site '0' (receptor) gets occupied by the transferred particle. The type of the coupling of the two-level system to the bath considered makes the required transitions $|u\rangle \leftrightarrow |d\rangle$ really possible. One should notice that, owing to the quantum character of the bath assumed, transitions downhill in energy always dominate over uphill ones. This causes the proper dynamic opening and closing of the gates for the particle just being transferred and thus the left-right asymmetry for the particle transfer rates.
- We also need a sort of coupling (to the bath) of particles inside both our subsystems '1' and '2'. The point is that we should allow violation of contingent phase relations among neighbouring sites inside the subsystems or the subsystems and site '0' (breaking of valence bonds). These phase relations would otherwise make the one-by-one transfer (provided by our pump as argued below) impossible. Our numerical studies [11] indicate this fact unambiguously. As for the coupling of the particle at site '0' directly to the bath, it only helps the above dephasing.

Thus, the simplest form of the system-bath coupling enabling the desired activity of our pump is

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

Everywhere, a_m ($a_m^\dagger$) and b_k ($b_k^\dagger$) are annihilation (creation) operators of the transferred particles at individual sites and annihilation (creation) operators of the bosons (phonons) forming the bath. We have used notation as if k designates,

e.g., a plane wave vector characterizing one (of totally N) states (modes) of the bosons. The transferred particles can be, e.g., fermions.

3. PUMP ACTIVITY

We shall not present the detailed theory here. The point is that for one particle transferred, it has been done in detail elsewhere [7] (or, in a simple modification implying even violation of the Second law of thermodynamics, in [11]). The one-particle theory of [7] well includes all the difficult aspects of the transfer process. Generalization of [7] to many-particle systems is technically very clumsy but physically straightforward. It will be published elsewhere. Here, we shall concentrate mostly on two points:

- Discussion of approximations always accompanying kinetic theories of the particle transfer, and
- explanation, in physical terms, how the pump works and what is the result of its activity.

Concerning the approximations necessarily involved, one should immediately stress that the regime in which the above pump is expected to work as indicated in [7] is definitely *not* the weak coupling one but rather the intermediate or even strong-coupling one. Hence, none of the weak coupling theories (describing the kinetic development as just perturbational lowest-order transitions among eigenstates of H_S) can be used. Our regime must necessarily, in addition to bath-assisted transfers inside the system (longitudinal relaxation), involve also intense dephasing (transversal relaxation) among sites involved. This is to prepare, before any act of transition, the proper initial state as *not* an eigenstate of H_S but as a state properly described by the particle density matrix which is well site-diagonal to describe the transfer process as a transition in space. Weak-coupling theories, in their turn, can be well justified by the weak-coupling scaling in which time unit τ is increased to infinity upon decreasing the coupling constant g of $H_{S\text{-}B}$ to zero but keeping the product $g^2\tau$ constant [12,13] (van Hove limit). Here, if we want to use the scaling arguments at all, one should also scale J, I, and J_{mn} (responsible for dynamical building up of phase relations among sites), say as g^2. It is then a matter of simple algebra to show that those processes kept (omitted) in [7] are exactly those processes which survive (disappear) upon such a generalized type of scaling.

Next point is the explanation, in physical terms, how the pump works. Imagine that a particle (always understood as quantum species) in subsystem '1' got to the site connected to the pump (site '-1'). As far as such a particle transport in our

subsystem '1' is (by its Hamiltonian) allowed, this will certainly happen with nonzero probability owing to, e.g., uncertainty relations. Owing to the above assumed dephasing among different sites (see the role of the first term in (6)), the particle state at site '-1' gets at least partly statistically independent of other sites, i.e. its state at site '-1' can be taken as an initial state for next transitions. As for the state of the pump, in particular of the two-level system and occupation of site '0', we shall now argue that either owing to initial conditions (if such conditions are presumed) or owing to the time development as described by the Liouville equation, the site '0' gets mostly (and at temperatures $k_BT \ll \in$ completely) empty and the two-level system is practically completely (with corrections $\propto \exp(-\beta\in)$) turned to state $|d\rangle$. For this situation to become more pronounced, it is advantageous (though not in principle necessary) to assume that J, I, and J_{mn} get appreciably less than $\hbar(\Gamma\uparrow + \Gamma\downarrow)$ where $\Gamma\uparrow$ and $\Gamma\downarrow$ are bath assisted uphill and downhill transfer rates in our two-level system induced by the second term in (6). Let us only add that these conditions are compatible with the above generalized scaling.

Hence, owing to the second term in H_{pump} in (4), the particle can be transferred to site '0' (receptor). Once it happens, however, the state $|d\rangle$ of the two-level system becomes unstable. If the particle does not succeed to escape back to site '-1' (which would just repeat the process anew), the two-level system turns practically (and at $k_BT \ll \in$ completely) to state $|u\rangle$. This means that the back transfer of the particle is blocked (compare the projection term $|d\rangle\langle d|$ in the second term in H_{pump} in (4)). On the other hand, the channel for the particle transfer to site '1' (i.e. to subsystem '2') gets open (compare the third term in H_{pump} in (4)). The question is whether the particle can use this possibility or not.

Let us consider the most difficult situation with $\delta\in > 0$. This means that the transfer process bringing the particles from subsystem '1' to subsystem '2' goes *against* the acting forces. The classical particle not aided from the side of our bath would stay at site '0'. (Notice that in our model, there are, in the lowest order, no such terms which would allow the bath-assisted '0'→'1' transition*.) This would stop the process. Quantum particle, upon conditions fixed by our Hamiltonian and the generalized scaling, has also no such possibility as far as the bath-assisted processes are concerned. If we allowed only such transitions, this would yield the relative population of sites of our subsystem '2' $\propto \exp(-\beta \cdot \delta\in)$. This would yield standard picture and all our above endeavour connected with the construction of the above model would be in vain. Fortunately, however, there is another type of the transfer process which allows the intersite '0'→'1' transfer sufficiently effectively even at temperatures $T \lesssim \delta\in/k_B << \in/k_B$. We

* Higher-order processes die out in the above generalized scaling.

have in mind a process which allows the particle to get to site '1' without any active role of the bath. This is tunnelling caused by the term $\propto I$ in (4). This process is definitely not $\propto \exp(-\beta\cdot\delta\in)$, i.e. temperature gets here ineffective.

Assume that the particle got, by the tunnelling, to site '1'. The situation then repeats again. The point is that state $|u\rangle$ of the two-level system gets, after a fast dephasing, again unstable. The particle can, with nonzero probability, succeed in returning to site '0' before the two-level system re-relaxes. This would just return the situation to the previous step and the transfer '0'→'1' would start again as before. In the opposite case, the particle does not succeed to return from site '1' to '0' before the two-level system re-relaxes to state $|d\rangle$, blocking thus the back particle transfer. In between, the internal dynamics in our subsystem '1' allows to bring another particle to site '-1'. Our particle at site '1' which has just now been transferred gets a possibility to propagate elsewhere but only inside subsystem '2', letting site '1' empty. This is, except for the just described transfer, again the starting situation, i.e. the whole process goes on cyclically till a kind of a stationary situation becomes established.

4. STATIONARY STATE

In the stationary situation, certain balance of all the processes must appear in order to make the density matrix (matrices) time-independent. This means, we have to estimate the relative strength of all the processes involved, leading to particle transfer processes between our subsystems '1' and '2' in order to estimate, e.g., the relative population of individual sites in subsystems '1' and '2'. Let us first again mention our assumption made on the particle-bath interaction as a part of $H_{S\text{-}B}$ in (6): We assume that the particle-bath interaction is non-zero in order to allow breaking of phase relations among (particle probability amplitudes at different) sites. This still does not prohibit speaking, at least approximately, of energy, entropy etc. of our system and the subsystems. Under these conditions, let us estimate the rates of the forward ('1'→'2') and backward ('2'→'1') transfer processes. At very low temperatures ($k_BT << \in$), the backward processes do exist but just in higher orders of the perturbation theory. Detailed estimate for the above model yields [7]

$$\frac{\Gamma_{1\leftarrow 2}}{\Gamma_{1\rightarrow 2}} \approx |G|^2 \frac{\hbar\Gamma_{\downarrow}|J|}{(\epsilon-\delta\epsilon)^2}. \tag{7}$$

Thus, in the above situation with small but nonzero $|J|$ and small G(=typical value of G_k in (6)), $\Gamma_{1\leftarrow 2} << \Gamma_{1\rightarrow 2}$. If we, in accordance with the above mentioned generalized scaling, fully neglect higher order processes disappearing

upon such scaling, the above rate ratio turns even to zero. This means that sites in the subsystem '1' get empty as long as, in case that the particles are fermions, there are enough sites left in subsystem '2' to accept all the particles transferred from subsystem '1'. Hence, chemical potential of the particles in subsystem '1' (μ_1) gets appreciably lower than that in the subsystem '2' (μ_2). In the above limiting case of neglecting the higher-order reverse processes, μ_1 would even turn to $-\infty$. Let us stress here that this fact still does not in principle challenge the presumed statistical independence of our two subsystems '1' and '2'. Equation (2) may still be well, except for negligible fluctuations, applicable. The above observation questions, however, the next step, i.e. identification of $w_1(E, N)$ and $w_2(E, N)$. This questions the ensuing derivation, i.e. also universal applicability of the grand-canonical distribution (3). At least the equality $\mu_1 = \mu_2$ becomes violated. Similar reasoning may be used to question, in exceptional cases like above, the applicability of the canonical ensemble, too.

5. CONSEQUENCES AND CONCLUSIONS

Our above discussed example is in a way exceptional. By this, we do not mean that the above model is the only one yielding the unidirectional pumping at the cost of just the (thermal) energy of the thermodynamic bath. More models of this type exist [6–9]. Recently, it has been even found that standard interacting particle-phonon systems may, under very specific conditions leading to constructive interference of different particle-phonon scattering channels, behave in a similar way [10,14–15]. The above exceptionality of our model consists in the fact that, like in all similar cases known so far and behaving in a similar way, strong and very specific correlations between particle positions and state of their surroundings play a decisive role. This is unlike standard models of kinetic and relaxation phenomena. These correlations are then responsible for self-organizational effects not induced by, e.g., external flows. Behaviour of our two-level system illustrates the role of these correlations. These correlations, however, exist and act in a similar way even in models where no similar specialized two-level system as in our model (4–6) exists [10,14–15].

On the other hand, we do not mean that such cases should in Nature appear quite often. At least almost universal applicability of the standard equilibrium statistical physics as observed in Nature supports this statement. (For some doubts and evidence provided by recent experiments as compared to the latest development of phenomenological description involving selforganization upon particle transfer see, e.g., [16].) So, importance of the above type of, perhaps, exceptional systems consists in at least two facts.

- It shows limitations imposed by axioms or arguments of the usual equilibrium statistical thermodynamics. We should turn readers' attention to the fact that our above pump, working autonomously and increasing (for $\delta \in > 0$) the particle energy just at the cost of the thermal energy of the bath, produces selforganization in our system. Such a selforganization is usually believed to exist just in nonlinear systems and under presence of external flows. Our linear system (as described by the usual linear Liouville equation) leads to such a selforganization even without such flows.
- It shows that analysing data from, e.g., experiments, one should always take principles of the contemporary quantum statistical physics as a hint but not necessarily as eternal truths. The point is that already some experimental data from reaction kinetics seem to indicate limitations of standard theories [16].

Natural question appears about physical explanation of existence of the above type of processes. For the particular model discussed above, we have explained it in detail. In order to convince the reader that a much broader class of such unusual processes should be tested against similar effects, however, let us realize that the above particle transfer process is based on an interplay of two processes going on simultaneously: Particle intersite transfer $'\text{-m}' \rightarrow '\text{-1}' \rightarrow '0' \rightarrow '1' \rightarrow '\text{n}'$, m, $n > 0$, and relaxation of our two-level system. As the latter system forms, together with receptor '0', the scatterer, we can speak of (re-)relaxation processes in virtual states (of, e.g., the scatterer) which interfere with the particle scattering. One can then immediately realize that there should be a much broader class of phenomena connected with mutual interference of two simultaneously going processes (see, e.g. [6,8] as an example). Thus, such processes may in principle open a new and more advanced field worth investigating.

Final comment is here to list a few direct consequences which our above mechanism of the particle transfer combined with selforganization could have. Let us remind first of similarity in action (though certainly not in principles) with the original model of the Maxwell demon [17,18]. Worth mentioning is also a similar contribution to the field by J. Loschmidt [19] who suggested principles (though no realization) reminding of the Maxwell demon as well as the above system. Having thus shown that, in strictly quantum systems, such a strange behaviour challenging standard understanding of macroscopic phenomena can, under some very specific condition, really exist, we are naturally led to the following minimal list of potential consequences and applications:

- violation of the detailed balance conditions (chemical reactions etc.),
- spontaneously going one-directional processes,
- molecular rectification,

- potential violation (if Nature really behaves as the quantum theory of open systems suggests) of the Second law of thermodynamics [11] etc.

Let us only add that molecular systems (rather than other ones) are, owing to the necessary cooperative character of simultaneously going processes, certainly better candidates for verification that similar processes can exist not only at the level of the quantum theory of open systems but also in our real world.

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