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Detailed balance in micro- and macrokinetics and micro-distinguishability of macro-processes

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ABSTRACT

We develop a general framework for the discussion of detailed balance and analyse its microscopic background. We find that there should be two additions to the well-known *T*- or *PT*-invariance of the microscopic laws of motion:

1. Equilibrium should not spontaneously break the relevant *T*- or *PT*-symmetry.
2. The macroscopic processes should be microscopically distinguishable to guarantee persistence of detailed balance in the model reduction from micro- to macrokinetics.

We briefly discuss examples of the violation of these rules and the corresponding violation of detailed balance.

1. The history of detailed balance in brief

> VERY deep is the well of the past. . . .For the deeper we sound, the further down into the lower world of the past we probe and press, the more do we find that the earliest foundation of humanity, its history and culture, reveal themselves unfathomable.
>
> T. Mann [1]

Detailed balance as a consequence of the reversibility of collisions (*at equilibrium, each collision is equilibrated by the reverse collision*, Fig. 1) was introduced by Boltzmann for the Boltzmann equation and used in the proof of the *H*-theorem [2] (Boltzmann's arguments were analysed by Tolman [3]). Five years earlier, Maxwell used the principle of detailed balance for gas kinetics with the reference to the *principle of sufficient reason* [4]. He analysed equilibration in cycles of collisions and in the pairs of mutually reverse collisions and mentioned "Now it is impossible to assign a reason why the successive velocities of a molecule should be arranged in this cycle, rather than in the reverse order."

In 1901, Wegscheider introduced detailed balance for chemical kinetics on the basis of classical thermodynamics [5]. He used the assumption that each elementary reaction is reversible and should respect thermodynamics (i.e. entropy production in this reaction should be always non-negative). Onsager used this work of Wegsheider in his famous paper [6]. Instead of direct citation he wrote: "Here, however, the chemists are accustomed to impose a very interesting additional restriction, namely: when the equilibrium is reached each individual reaction must balance itself." Einstein used detailed balance as a basic assumption in his theory of radiation [7]. In 1925, Lewis recognized the principle of detailed balance as a new general principle of equilibrium [8]. The limit of the detailed balance for systems which include some irreversible elementary processes (without reverse processes) was recently studied in detail [9,10].

In this paper, we develop a general formal framework for discussion of detailed balance, analyse its microscopic background and persistence in the model reduction from micro- to macrokinetics.

2. Sampling of events, *T*-invariance and detailed balance

2.1. How detailed balance follows from microreversibility

In the sequel, we omit some technical details assuming that all the operations are possible, all the distributions are regular and finite Borel (Radon) measures, and all the integrals (sums) exist.

The basic notations and notions:

- Ω – a space of states of a system (a locally compact metric space).
- Ensemble ν – a non-negative distribution on Ω.
- Elementary process has a form $\alpha \to \beta$ (Fig. 2), where α, β are non-negative distributions.

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- Complex – an input or output distribution of an elementary process.
- Υ – the set of *all* complexes participating in elementary processes. It is equipped with the weak topology and is a closed and locally compact set of distributions.
- The reaction rate r is a measure defined on $\Upsilon^2 = \{(\alpha, \beta)\}$. It describes the rates of all elementary processes $\alpha \to \beta$.
- The support of r, $\mathrm{supp}\, r \subset \Upsilon^2$, is the *mechanism* of the process, i.e. it is the set of pairs (α, β), each pair represents an elementary process $\alpha \to \beta$. (Usually, $\mathrm{supp}\, r \subsetneq \Upsilon^2$.)
- The rate of the whole kinetic process is a distribution W on Ω (the following integral should exist):

$$W = \frac{1}{2} \int_{(\alpha,\beta)\in\Upsilon^2} (\beta - \alpha) \mathrm{d}[r(\alpha, \beta) - r(\beta, \alpha)].$$

The distribution v depends on time t. For systems with continuous time, $\dot{v} = W$. For systems with discrete time, $v(t + \tau) - v(t) = W$, where τ is the time step. To create the closed kinetic equation (the associated *nonlinear Markov process* [11]) we have to define the map $v \mapsto r$ that puts the reaction rate r (a Radon measure on Υ^2) in correspondence with a non-negative distribution v on Ω (the *closure problem*). In this definition, some additional restrictions on v may be needed. For example, one can expect that v is absolutely continuous with respect to a special (equilibrium) measure. There are many standard examples of kinetic systems: mass action law for chemical kinetics [12,13], stochastic models of chemical kinetics [18], the Boltzmann equation [14] in quasichemical representation [15] for space-uniform distributions, the lattice Boltzmann models [16], which represent the space motion as elementary discrete jumps (discrete time), and the quasichemical models of diffusion [17].

We consider interrelations between two important properties of the measure $r(\alpha, \beta)$:

(EQ) $W = 0$ (equilibrium condition);

(DB) $r(\alpha, \beta) \equiv r(\beta, \alpha)$ (detailed balance condition).

It is possible to avoid the difficult closure question about the map $v \mapsto r$ in discussion of T-invariance and relations between EQ and DB conditions.

Obviously, DB⇒EQ. There exists a trivial case when EQ⇒DB (a sort of linear independence of the vectors $\gamma = \beta - \alpha$ for elementary processes joined in pairs with their reverse processes): if

$$\int_{(\alpha,\beta)\in \mathrm{supp}\, r} (\beta - \alpha) \mathrm{d}\mu(\alpha, \beta) = 0 \Rightarrow \mu = 0$$

for every antisymmetric measure μ on Υ^2 ($\mu(\alpha, \beta) = -\mu(\beta, \alpha)$), then EQ⇒DB.

There is a much more general reason for detailed balance, T-invariance. Assume that the kinetics give a coarse-grained description of an ensemble of interacting microsystems and this interaction of microsystems obeys a reversible in time equation: if we look on the dynamics backward in time (*operation T*) we will observe the solution of the same dynamic equations. For T-invariant microscopic dynamics, T maps an equilibrium ensemble into an equilibrium ensemble. Assuming uniqueness of the equilibrium under given values of the conservation laws, one can just postulate the *invariance of equilibria with respect to the time reversal transformation* or T-invariance of equilibria: if we observe an equilibrium ensemble backward in time, nothing will change.

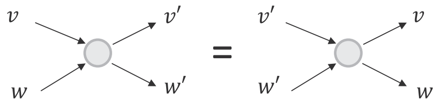

Fig. 1. Schematic representation of detailed balance for collisions: at equilibrium, each collision is equilibrated by the reverse collision.

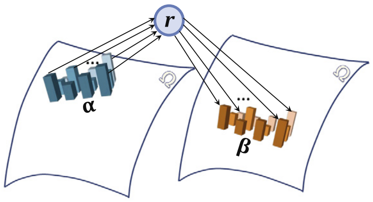

Fig. 2. Schematic representation of an elementary process. Input (α) and output (β) distributions are represented by column histograms.

Let the complexes remain unchanged under the action of T. In this case, the time reversal transformation for collisions (Fig. 1) leads to the reversal of arrow: the direct collision is transformed into the reverse collision. The same observation is valid for inelastic collisions. Following this hint, we can accept that the reversal of time T transforms every elementary process $\alpha \to \beta$ into its reverse process $\beta \to \alpha$. This can be considered as a restriction on the definition of direct and reverse processes in the modelling (a "model engineering" restriction): the direct process is an ensemble of microscopic events and the reverse process is the ensemble of the time reversed events.

Under this assumption, T transforms $r(\alpha, \beta)$ into $r(\beta, \alpha)$. If the rates of elementary processes may be observed (for example, by the counting of microscopic events in the ensemble) then T-invariance of equilibrium gives DB: at equilibrium, $r(\alpha, \beta) = r(\beta, \alpha)$, i.e. EQ⇒DB under the hypothesis of T-invariance.

The assumption that the complexes are invariant under the action of T may be violated: for example, in Boltzmann's collisions (Fig. 2) the input measure is $\alpha = \delta_v + \delta_w$ and the output measure is $\beta = \delta_{v'} + \delta_{w'}$. Under time reversal, $\delta_v \overset{T}{\mapsto} \delta_{-v}$. Therefore $\alpha \overset{T}{\mapsto} \delta_{-v} + \delta_{-w}$ and $\beta \overset{T}{\mapsto} \delta_{-v'} + \delta_{-w'}$. We need an additional invariance, the space inversion invariance (transformation P) to prove the detailed balance (Fig. 1). Therefore, the detailed balance condition for the Boltzmann equation (Fig. 1) follows not from T-invariance alone but from PT-invariance because for Boltzmann's kinetics

$$\{\alpha \to \beta\} \overset{PT}{\mapsto} \{\beta \to \alpha\}.$$

In any case, the microscopic reasons for the detailed balance condition include existence of a symmetry transformation $\mathfrak{T}$ such that

$$\{\alpha \to \beta\} \overset{\mathfrak{T}}{\mapsto} \{\beta \to \alpha\} \tag{1}$$

and the microscopic dynamics is invariant with respect to $\mathfrak{T}$. In this case, one can conclude that (i) the equilibrium is transformed by $\mathfrak{T}$ into the same equilibrium (it is, presumably, unique) and (ii) the reaction rate $r(\alpha, \beta)$ is transformed into $r(\beta, \alpha)$ and does not change because nothing observable can change (equilibrium is the same). Finally, at equilibrium $r(\alpha, \beta) \equiv r(\beta, \alpha)$ and EQ⇒DB.

There remain two questions:

1. We are sure that $\mathfrak{T}$ transforms the equilibrium state into an equilibrium state but is it necessarily the same equilibrium? Is it forbidden that the equilibrium is degenerate and $\mathfrak{T}$ acts non-trivially on the set of equilibria?
2. We assume that the rates of different elementary processes are physical observables and the ensemble with different values of these rates may be distinguished experimentally. Is it always true?

The answer to both questions is "no". The principle of detailed balance can be violated even if the physical laws are T, P and PT