

Chapter 2

(Non-)Dissipative Effects?

Before we start discussing possible effects and phenomena we need to be more precise about the meaning of dissipative *versus* non-dissipative aspects. As alluded to already in the abstract that plays in two ways: there will be (1) activity parameters, and (2) important time-symmetric path-variables. In general the activity parameters allow more or bigger changes and transitions in the system; we can think how e.g. temperature or diffusion constants allow the system to rapidly explore more state space. Or how by shaking we can reactivate a cold battery. As examples of time-symmetric variables we can try to observe the sojourn time in a given condition or the undirected traffic between different regions in state space.

The easiest way to be more specific about all those is to refer to the modeling via Markov processes, a common tool in nonequilibrium statistical mechanics. For the moment we miss crucial and interesting physics by ignoring spatial extensions or confinements but some important points can (and should) already be illustrated for continuous time jump processes on a finite state space K without insisting on spatial structure or architecture. The elements of K are called states $x, y, \dots \in K$ and can represent the coarse grained position of particle(s) or a chemical-mechanical configuration of a molecule, or an energy level as derived via Fermi Golden's Rule in quantum mechanics etc. There are transition rates $k(x, y) \geq 0$ for the jump $x \rightarrow y$, and they are supposed to make physical sense of course. In particular here we have in mind that all such transitions are associated with an entropy flux $s(x, y) = -s(y, x)$ in the environment. The environment is taken to be time-independent and consisting possibly of multiple equilibrium reservoirs which are characterized primarily by their (constant) temperature or chemical potential. Their presence in the model is indirect, and the (effective) Markov dynamics should in principle be obtained via some weak coupling limit or other procedures that integrate out the environment. The point is that the entropy fluxes in these reservoirs are entirely given in terms of the changes in the states of the system. (We no longer call it the open (sub)system from now on.) The $s(x, y)$ is the change of the entropy in one of the equilibrium reservoirs in the environment associated to the change $x \rightarrow y$ in the system.

In a deep sense that entropy flux $s(x, y)$ measures the time-asymmetry. The point in general is that we understand our modeling such that the ratio of transition rates for jumps between states x to y satisfies

$$\frac{k(x, y)}{k(y, x)} = e^{s(x, y)} \quad (2.1)$$

where $s(x, y) = -s(y, x)$ is the entropy flux per k_B (Boltzmann's constant) over the transition $x \rightarrow y$. That hypothesis (2.1), which can be derived in the usual Markov approximation when the reservoirs are well separated, is called the condition of local detailed balance and follows from the dynamical reversibility of standard Hamiltonian mechanics; see [3–7]. It is obviously an important indicator of how to model the time-antisymmetric part of the transition rates. Loosely speaking here, dissipative is everything which is expressed in terms of those entropy fluxes or other quantities that are anti-symmetric under time-reflection/reversal. A driving field or force can generate currents with associated entropy fluxes into the various reservoirs in contact with the system. If we specify a trajectory $\omega = (x_s, s \in [0, t])$ of consecutive states in a time-interval $[0, t]$, then the time-antisymmetric sector contains all functions $J(\omega)$ which are anti-symmetric under time-reversal, $J(\theta\omega) = -J(\omega)$ for $(\theta\omega)_s = x_{t-s}$. We could for a moment entertain the idea that the nonequilibrium condition of the system would be entirely determined by giving the interactions between the particles and the values of all observables in the time-antisymmetric sector, or even only by the values of some currents or mean entropy fluxes, together with the intensive parameters of the equilibrium reservoirs making up the environment. Or we could hope that the stationary nonequilibrium distribution is determined by a variational principle involving only the expected entropy production as function of probability laws on K . All that however would be a dissipative dream, at best holding true for some purposes and approximations close-to-equilibrium. Non-dissipative effects bring time-symmetric observables to the fore-ground, like the residence times in states or the unoriented traffic between states. When such observables as the time-symmetric dynamical activity explicitly contribute to the nonequilibrium physics, we will speak of a frenetic contribution.

The rates (and hence the modeling) is of course not determined completely by (2.1). We also have the products $\gamma(x, y) = k(x, y)k(y, x) = \gamma(y, x)$ which each are symmetric between forward and backward jumps. It is like the “width” of the transition. Note also that it enters independently from the entropy flux because over all edges where $\gamma(x, y) = \psi^2(x, y) \neq 0$, we can write

$$k(x, y) = \sqrt{k(x, y)k(y, x)} \sqrt{\frac{k(x, y)}{k(y, x)}} = \psi(x, y) e^{s(x, y)/2} \quad (2.2)$$

We call the $\psi(x, y) = \psi(y, x) \geq 0$ activity parameters; they may depend on the temperature of the reservoir(s) but what is also very important is that they may (as do the $s(x, y)$) depend on the driving fields, like external forces or differences

in reservoir temperatures and chemical potentials. The $\psi(x, y)$ will be determined again from some weak coupling procedure but can also be obtained from Arrhenius and Kramers type formulæ for reaction rates. How they will depend on driving (nonequilibrium) parameters is an important challenge. We count as non-dissipative effect how the $\psi(x, y)$ specify or even determine the nonequilibrium condition, in particular through their variation with the external field. Again we will speak here about a frenetic contribution.

Let us finally compare again with the equilibrium situation. Here we need the dynamics to be undriven in the sense that the stationary distribution when extended in the time-domain is invariant under time-reversal. In other words, when under equilibrium we must have that all expectations $\langle J(\omega) \rangle_{\text{eq}} = 0$ of time-antisymmetric observables $J(\omega)$ vanish. That is of course much more than requiring stationarity, which only says that $\langle f(x_t) - f(x_0) \rangle = 0$ for all times t . Time-reversal invariance in the stationary condition (reversibility or equilibrium, for short) is equivalent with having (2.1) for $s(x, y) = \mathcal{F}(x) - \mathcal{F}(y)$ for some free energy function \mathcal{F} on K . We do not prove that statement here, but the reader then recognizes the typical expressions for transition rates under (global) detailed balance, as

$$k(x, y) = \psi(x, y) \exp[\mathcal{F}(x) - \mathcal{F}(y)]/2, \quad \psi(x, y) = \psi(y, x)$$

with stationary distribution $\rho_{\text{eq}}(x) \propto \exp -\mathcal{F}(x)$ as prescribed by Gibbs. Note that ρ_{eq} does not depend on the activity parameters $\psi(x, y) > 0$; there is no such frenetic contribution in equilibrium.

We start in the next section with non-dissipative effects on the stationary distribution and then we go on with other instances for the current, in response etc. Beyond and above these examples it should be clear however that as such dynamical activity is present as an important time-symmetric background for systems even before perturbations or other changes are applied. In some way we find in it the analogue of a *vis viva* through which typical nonequilibrium phenomena can get realized. Taking now living matter indeed, it has for example become clear in the last decade “that stimulus- or task-evoked activity accounts for only a fraction of the metabolic budget of the brain, and that intrinsic activity, i.e. not stimulus- or task-driven activity, plays a critical role in brain function” [8]. There is also the older “vacuum activity” coined by Konrad Lorenz in the 1930s, for innate patterns of animal behaviour that are there even in the absence of external stimuli. That has nothing to do with “vacuum polarization” or the self-energy of the photon but that in itself is a dynamical activity of the vacuum which is crucial for electrodynamics in the quantum regime and will change under nonequilibrium; see e.g. [9].

Non-Dissipative Effects in Nonequilibrium Systems

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2018, VII, 53 p. 15 illus., 14 illus. in color., Softcover

ISBN: 978-3-319-67779-8