

TCM315 Fall 2022: Introduction to Open Quantum Systems

Lecture 3: Work and heat in stochastic thermodynamics

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INTRODUCTION

Our presentation of thermodynamics of Langevin equation draws from [4, 5]. A more advanced reference is [1] and the lecture notes [2].

LANGEVIN DYNAMICS AND IRREVERSIBILITY

Langevin dynamics illustrates Boltzmann's vision of a first principle derivation of thermodynamics from the reversible law of classical mechanics. It is possible to rigorously prove under stricter hypotheses than considered here (see [3] and references therein) that Langevin dynamics models in a certain scaling limit the evolution of a system interacting with an oscillator bath according to the law of classical mechanics. The probability distribution of the Langevin particle obeys the Fokker-Planck equation. The Fokker-Planck equation embodies in this way an example of kinetic theory: a coarse grained master equation governing how the a single particle distribution effectively evolves while interacting with a gas of particles. The phase space of the single particle is the μ space.

We now aim to show that the Fokker-Planck equation satisfies an **H-theorem**. This means that in the absence of external time dependent forces, the evolution of a probability density is compatible with **equilibration** as time elapses. Equilibration of a coarse grained evolution in μ -space was the mechanism suggested by Boltzmann to explain the origin of macroscopic irreversibility. Furthermore, under additional hypotheses [3], the equilibrium state takes the form of a canonical probability distribution. In other words, Langevin dynamics may also be also compatible with **thermalization**.

Equilibration

The Fokker–Planck equation

$$\partial_t \rho_t(\mathbf{y}) + \partial_{\mathbf{y}}^\top \mathbf{b}(\mathbf{y}) \rho_t(\mathbf{y}) = \frac{\beta^{-1}}{2} \text{Tr} \partial_{\mathbf{y}} \otimes \partial_{\mathbf{y}} \mathbb{D}(\mathbf{y}) \rho_t(\mathbf{y}) \quad (1a)$$

$$\rho_0(\mathbf{y}) = \rho(\mathbf{y}) \quad (1b)$$

$$\rho_t(\mathbf{y})|_{\mathbf{y} \in \partial \mathcal{M}} = \text{probability preseving boundary conditions} \quad (1c)$$

describes a μ space density evolution. We now show that at variance with the conservative Liouville evolution, the Fokker–Planck equation is generically compatible with an irreversible evolution towards a steady state. To this goal we consider, two probability densities $\rho_t^{(i)}(\mathbf{x})$ $i = 1, 2$ both evolving according to the same Fokker–Planck equation (1a) and subject to the same boundary conditions (1a) but having **distinct initial data** in (1a). In order to quantify how much the two probability density differ we introduce the **Kullback–Leibler divergence** or **relative entropy between** the two densities

$$K(\rho_t^{(1)} || \rho_t^{(2)}) = \int_{\mathcal{M}} d^{2d} \rho_t^{(1)}(\mathbf{x}) \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \quad (2)$$

The reason why the Kullback–Leibler entropy is an interesting indicator is that it is **positive definite** and vanishes if and only if the two densities coincide.

To prove the claim we observe that the inequality

$$-\ln x \geq 1 - x$$

once applied to the definition of Kullback–Leibler

$$K(\rho_t^{(1)} || \rho_t^{(2)}) = - \int_{\mathcal{M}} d^{2d} \rho_t^{(1)}(\mathbf{x}) \ln \frac{\rho_t^{(2)}(\mathbf{x})}{\rho_t^{(1)}(\mathbf{x})} \geq \int_{\mathcal{M}} d^{2d} \rho_t^{(1)}(\mathbf{x}) \left(1 - \frac{\rho_t^{(2)}(\mathbf{x})}{\rho_t^{(1)}(\mathbf{x})} \right) = 0$$

We then readily verify that

$$K(\rho_t || \rho_t) = 0$$

Finally, for $\rho_t^{(1)}$ fixed the Kullback–Leibler divergence is monotonic in $\rho_t^{(2)}$ hence can vanish only in one point.

A necessary condition for evolution towards a unique steady state is that the Kullback–Leibler divergence must be monotonically decreasing. We now show that this is the case

$$\frac{d}{dt} K(\rho_t^{(1)} || \rho_t^{(2)}) \leq 0$$

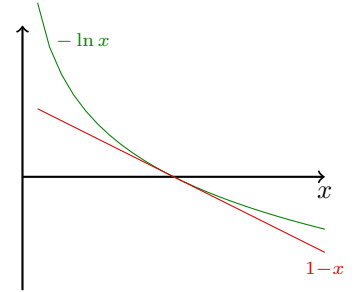
Proof that the Kullback-Leibler is monotonically decreasing with time

The total derivative of the Kullback–Leibler entropy takes then the form

$$\frac{d}{dt} K(\rho_t^{(1)} || \rho_t^{(2)}) = \int_{\mathcal{M}} d^{2d} \mathbf{x} \left((\partial_t \rho_t^{(1)})(\mathbf{x}) \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} + \rho_t^{(1)}(\mathbf{x}) \left(\frac{1}{\rho_t^{(1)}(\mathbf{x})} (\partial_t \rho_t^{(1)})(\mathbf{x}) - \frac{1}{\rho_t^{(2)}(\mathbf{x})} (\partial_t \rho_t^{(2)})(\mathbf{x}) \right) \right)$$

In (1) we assume that the probability density satisfies at the boundary $\partial \mathcal{M}$ of the domain \mathcal{M} conditions ensuring probability conservation. Therefore

$$\int_{\mathcal{M}} d^{2d} \mathbf{x} \partial_t \rho_t^{(1)}(\mathbf{x}) = \partial_t \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t^{(1)}(\mathbf{x}) = 0$$



We therefore obtain

$$\begin{aligned} \frac{d}{dt} K(\rho_t^{(1)} || \rho_t^{(2)}) &= - \int_{\mathcal{M}} d^{2d} \mathbf{x} \left((\partial_{\mathbf{x}}^{\top} \mathbf{b}(\mathbf{x}) \rho_t^{(1)}(\mathbf{x})) \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} - \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \partial_{\mathbf{x}}^{\top} \mathbf{b}(\mathbf{x}) \rho_t^{(2)}(\mathbf{x}) \right) \\ &+ \frac{\beta^{-1}}{2} \int_{\mathcal{M}} d^{2d} \mathbf{x} \left(\text{Tr} (\partial_{\mathbf{x}} \otimes \partial_{\mathbf{x}} \mathbb{D}(\mathbf{x}) \rho_t^{(1)}(\mathbf{x})) \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} - \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \text{Tr} (\partial_{\mathbf{x}} \otimes \partial_{\mathbf{x}} \mathbb{D}(\mathbf{x}) \rho_t^{(2)}(\mathbf{x})) \right) \end{aligned} \quad (3)$$

The first row on the right hand side vanishes. This is because

$$\begin{aligned} &\int_{\mathcal{M}} d^{2d} \mathbf{x} \partial_{\mathbf{x}}^{\top} \left(\mathbf{b}(\mathbf{x}) \rho_t^{(1)}(\mathbf{x}) \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right) \\ &= \int_{\mathcal{M}} d^{2d} \mathbf{x} \left((\partial_{\mathbf{x}}^{\top} \mathbf{b}(\mathbf{x}) \rho_t^{(1)}(\mathbf{x})) \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} + \rho_t^{(2)}(\mathbf{x}) \mathbf{b}^{\top}(\mathbf{x}) \partial_{\mathbf{x}} \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right) \end{aligned}$$

holds true. Furthermore, invoking our hypothesis of probability preserving boundary conditions

$$\int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t^{(2)}(\mathbf{x}) \mathbf{b}^{\top}(\mathbf{x}) \partial_{\mathbf{x}} \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} = - \int_{\mathcal{M}} d^{2d} \mathbf{x} \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \partial_{\mathbf{x}}^{\top} \mathbf{b}(\mathbf{x}) \rho_t^{(2)}(\mathbf{x})$$

we are entitled to conclude that the first row in (3) is indeed a total derivative which must then vanish because of probability conservation.

We turn now to the second row in (3): again assuming that all boundary terms vanish

$$\begin{aligned} &\int_{\mathcal{M}} d^{2d} \mathbf{x} \text{Tr} (\partial_{\mathbf{x}} \otimes \partial_{\mathbf{x}} \mathbb{D}(\mathbf{x}) \rho_t^{(1)}(\mathbf{x})) \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} = - \int_{\mathcal{M}} d^{2d} \mathbf{x} \text{Tr} \left((\partial_{\mathbf{x}} \otimes \mathbb{D}(\mathbf{x}) \rho_t^{(1)}(\mathbf{x})) \partial_{\mathbf{x}} \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right) \\ &= - \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t^{(1)}(\mathbf{x}) \left(\partial_{\mathbf{x}} \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right)^{\top} \mathbb{D}(\mathbf{x}) \left(\partial_{\mathbf{x}} \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right) - \int_{\mathcal{M}} d^{2d} \mathbf{x} \text{Tr} \left((\partial_{\mathbf{x}} \otimes \mathbb{D}(\mathbf{x}) \rho_t^{(2)}(\mathbf{x})) \partial_{\mathbf{x}} \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right) \\ &= - \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t^{(1)}(\mathbf{x}) \left(\partial_{\mathbf{x}} \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right)^{\top} \mathbb{D}(\mathbf{x}) \left(\partial_{\mathbf{x}} \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right) + \int_{\mathcal{M}} d^{2d} \mathbf{x} \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \text{Tr} (\partial_{\mathbf{x}} \otimes \partial_{\mathbf{x}} \mathbb{D}(\mathbf{x}) \rho_t^{(2)}(\mathbf{x})) \end{aligned}$$

Upon inserting the result in (3) a further integration by parts shows that

$$\frac{d}{dt} K(\rho_t^{(1)} || \rho_t^{(2)}) = - \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t^{(1)}(\mathbf{x}) \left(\partial_{\mathbf{x}} \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right)^{\top} \mathbb{D}(\mathbf{x}) \left(\partial_{\mathbf{x}} \ln \frac{\rho_t^{(1)}(\mathbf{x})}{\rho_t^{(2)}(\mathbf{x})} \right) \leq 0$$

as claimed.

The result proves that any pair of densities evolves towards a constant value of the of the Kullback–Leibler divergence.

Steady state equation

Proving the uniqueness of the steady state ultimately requires proving that the equation

$$\partial_{\mathbf{x}}^{\top} \mathbf{b}(\mathbf{x}) \rho_{eq}(\mathbf{x}) = \frac{\beta^{-1}}{2} \text{Tr} \partial_{\mathbf{x}} \otimes \partial_{\mathbf{x}} \mathbb{D}(\mathbf{x}) \rho_{eq}(\mathbf{x})$$

admits a unique **positive definite**

$$\rho_{eq}(\mathbf{x}) \geq 0$$

and **normalizable**

$$\int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_{eq}(\mathbf{x}) < \infty$$

solution.

Einstein relation and thermalization

Thermalization consists in proving that the steady state is embodied by a probability distribution compatible with equilibrium statistical mechanics. This is a stronger requirement on a dissipative dynamics, so it should not come as a surprise that thermalization is attained under more restrictive hypotheses concerning the form of the vector field \mathbf{b} . We require that

$$\mathbf{b}(\mathbf{x}) = \mathbb{J}(\partial H)(\mathbf{x}) - \frac{1}{2}\mathbb{D}(\mathbf{x})(\partial H)(\mathbf{x}) + \frac{\beta^{-1}}{2}\partial_{\mathbf{x}}^{\top}\mathbb{D}(\mathbf{x}) \quad (4)$$

The requirement (4) corresponds to imposing that (1a) satisfies **Einstein relation**:

$$\partial_t \rho_t(\mathbf{x}) + \partial_{\mathbf{x}}^{\top} \left(\mathbb{J}(\partial H)(\mathbf{x}) - \frac{1}{2}\mathbb{D}(\mathbf{x})(\partial H)(\mathbf{x}) \right) \rho_t(\mathbf{x}) = \frac{\beta^{-1}}{2} \partial_{\mathbf{x}}^{\top} \mathbb{D}(\mathbf{x})(\partial \rho_t)(\mathbf{x}) \quad (5)$$

Consequences of the Einstein relation

More explicitly this means that the Fokker–Planck equation is amenable to the form

$$\partial_t \rho_t(\mathbf{x}) + \mathbf{v}_H^{\top}(\mathbf{x})(\partial \rho_t)(\mathbf{x}) = \frac{1}{2} \partial_{\mathbf{x}}^{\top} \mathbb{D}(\mathbf{x}) \mathbf{j}_t(\mathbf{x}) \quad (6)$$

where

$$\mathbf{v}_H(\mathbf{x}) = \mathbb{J}(\partial H)(\mathbf{x})$$

is the Hamiltonian, hence divergence-free, vector field governing the evolution of the system in the absence of interaction with the environment. Thus the terms on the left hand side of (6) coincide with those appearing in the Liouville equation governing the closed system evolution. Einstein relation ensures that the source term on the right hand side of (6) is sustained by the probability current

$$\mathbf{j}_t(\mathbf{x}) = (\partial H)(\mathbf{x}) \rho_t(\mathbf{x}) + \beta^{-1}(\partial \rho_t)(\mathbf{x}) \quad (7)$$

Thermal state

The equilibrium state must satisfy the stationary Fokker–Planck equation. When Einstein’s relation holds, the stationary Fokker–Planck equation becomes

$$\mathbf{v}_H^{\top}(\mathbf{x})(\partial \rho_{eq})(\mathbf{x}) = \frac{1}{2} \partial_{\mathbf{x}}^{\top} \mathbb{D}(\mathbf{x}) \mathbf{j}_{eq}(\mathbf{x}) \quad (8)$$

The Hamiltonian is by construction a constant of motion of time autonomous Hamiltonian vector fields. Hence the left hand side of (8) vanishes identically for any probability density of the form

$$\rho_{eq}(\mathbf{x}) = F(H(\mathbf{x}))$$

For this reason Einstein relation implies that a sufficient condition equilibrium reduces to

$$\mathbf{j}_{eq}(\mathbf{x}) = 0$$

The explicit expression of the probability current (7) shows that the canonical distribution

$$\rho_{eq}(\mathbf{x}) = \frac{1}{Z} e^{-\beta H(\mathbf{x})} \quad (9)$$

satisfies the stationary Fokker–Planck equation. A further technical analysis shows that when (9) is **normalizable** is also the unique solution.

CLASSICAL STOCHASTIC THERMODYNAMICS.

We showed that a Fokker–Planck evolution satisfying with Einstein relation may relax to a canonical equilibrium distribution (9) with the same temperature β^{-1} of the bath. This fact epitomizes the **zeroth law** of thermodynamics for a system in contact with a fluctuating environment.

We now turn to inquire the validity of the first and second law of thermodynamics. To this goal we suppose that

1. the Hamiltonian includes an explicit time dependence. We need this hypothesis to take into account external work done on the system.
2. The diffusion amplitude \mathbb{D} is constant. This is a mere simplifying assumption.

First Law of thermodynamics

We identify the Hamiltonian with the internal energy of the system. Then the Stratonovich differential yields

$$dH_t(\boldsymbol{\chi}_t) = \partial_t H_t(\boldsymbol{\chi}_t) dt + (\boldsymbol{\partial} H_t)^\top(\boldsymbol{\chi}_t) \circ d\boldsymbol{\chi}_t \quad (10)$$

We interpret this relation as the **first law of stochastic thermodynamics**. Namely on the left hand side we have an exact differential: for any $t_2 \geq t_1$

$$H_{t_2}(\boldsymbol{\chi}_{t_2}) - H_{t_1}(\boldsymbol{\chi}_{t_1}) = \int_{t_1}^{t_2} dH_t(\boldsymbol{\chi}_t) \quad (11)$$

On the right hand side we identify the **work done on the system**

$$\mathcal{W}_{t_2, t_1} = \int_{t_1}^{t_2} dt \partial_t H_t(\boldsymbol{\chi}_t) \quad (12)$$

and the **heat released by the system**

$$\mathcal{Q}_{t_2, t_1} = - \int_{t_1}^{t_2} (\boldsymbol{\partial} H_t)^\top(\boldsymbol{\chi}_t) \circ d\boldsymbol{\chi}_t \quad (13)$$

We therefore write

$$H_{t_2}(\boldsymbol{\chi}_{t_2}) - H_{t_1}(\boldsymbol{\chi}_{t_1}) = \mathcal{W}_{t_2, t_1} - \mathcal{Q}_{t_2, t_1}$$

Consistently with macroscopic thermodynamics work and heat over a finite interval are **not** integral over exact differentials.

Second Law of thermodynamics

We want now to show that the total entropy of the system **and** of the environment grows **on average** during a thermodynamic transition. To this goals we consider the heat functional

$$\mathcal{Q}_{t_2, t_1} = - \int_{t_1}^{t_2} dt (\boldsymbol{\partial} H_t)^\top(\boldsymbol{\chi}_t) \left(\mathbb{J}(\boldsymbol{\partial} H_t)(\boldsymbol{\chi}_t) - \frac{1}{2} \mathbb{D}(\boldsymbol{\partial} H_t)(\boldsymbol{\chi}_t) \right) - \beta^{-1/2} \int_{t_1}^{t_2} (\boldsymbol{\partial} H_t)^\top(\boldsymbol{\chi}_t) \circ \mathbb{D}^{1/2} d\boldsymbol{w}_t$$

The average yields

$$\mathbb{E} \mathcal{Q}_{t_2, t_1} = \frac{1}{2} \int_{t_1}^{t_2} dt \int_{\mathcal{M}} d^{2d} \boldsymbol{x} \rho_t(\boldsymbol{x}) \left((\boldsymbol{\partial} H_t)^\top(\boldsymbol{x}) \mathbb{D}(\boldsymbol{\partial} H_t)(\boldsymbol{x}) - \beta^{-1} \text{Tr}(\mathbb{D} \boldsymbol{\partial} \otimes \boldsymbol{\partial} H_t)(\boldsymbol{x}) \right)$$

Note that to compute the average we convert the Stratonovich differential in its equivalent Itô form. We now manipulate the result to exhibit the emergence of the second law. To this goal we observe that

1. the heat released from the system to the environment describes the change of entropy of the environment:

2. the change of entropy of the system is described by the change of the Gibbs-Shannon entropy

$$S_t = - \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t(\mathbf{x}) \ln \rho_t(\mathbf{x})$$

The statement that we want to prove is that the average **total** change of entropy is positive definite

$$\mathbb{E} \mathcal{Q}_{t_2, t_1} + \beta^{-1} (S_{t_2} - S_{t_1}) \geq 0$$

Proof of the second law

As always, we integrate by parts under the working hypothesis of probability preserving boundary conditions:

$$\int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t(\mathbf{x}) \text{Tr}(\mathbb{D} \boldsymbol{\partial} \otimes \boldsymbol{\partial} H_t)(\mathbf{x}) = - \int_{t_1}^{t_2} dt \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t(\mathbf{x}) (\boldsymbol{\partial} \ln \rho_t)^\top(\mathbf{x}) \mathbb{D}(\boldsymbol{\partial} H_t)(\mathbf{x})$$

whence

$$\mathbb{E} \mathcal{Q}_{t_2, t_1} = \frac{1}{2} \int_{t_1}^{t_2} dt \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t(\mathbf{x}) \left((\boldsymbol{\partial} H_t)(\mathbf{x}) + \beta^{-1} (\boldsymbol{\partial} \ln \rho_t)(\mathbf{x}) \right)^\top \mathbb{D}(\boldsymbol{\partial} H_t)(\mathbf{x})$$

To interpret the meaning of this average we recall that the time derivative of the Gibbs-Shannon entropy is

$$\begin{aligned} \partial_t S_t &= - \int_{\mathcal{M}} d^{2d} \mathbf{x} \ln \rho_t(\mathbf{x}) (\partial_t \rho_t)(\mathbf{x}) \\ &= \int_{\mathcal{M}} d^{2d} \mathbf{x} \ln \rho_t(\mathbf{x}) \boldsymbol{\partial}_x^\top \left(\mathbb{J}(\boldsymbol{\partial} H_t)(\mathbf{x}) - \frac{1}{2} \mathbb{D}(\boldsymbol{\partial} H_t)(\mathbf{x}) \right) \rho_t(\mathbf{x}) - \frac{\beta^{-1}}{2} \int_{\mathcal{M}} d^{2d} \mathbf{x} \ln \rho_t(\mathbf{x}) \text{Tr} \mathbb{D} \boldsymbol{\partial}_x \boldsymbol{\partial}_x \rho_t(\mathbf{x}) \end{aligned}$$

and therefore

$$\partial_t S_t = \frac{1}{2} \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t(\mathbf{x}) (\boldsymbol{\partial}^\top \ln \rho_t)(\mathbf{x}) \left(\mathbb{D}(\boldsymbol{\partial} H_t)(\mathbf{x}) + \beta^{-1} \mathbb{D}(\boldsymbol{\partial} \ln \rho_t)(\mathbf{x}) \right)$$

Contrasting with the expression of the heat we conclude that

$$\begin{aligned} \mathbb{E} \mathcal{Q}_{t_2, t_1} + \beta^{-1} (S_{t_2} - S_{t_1}) &= \\ \frac{1}{2} \int_{t_1}^{t_2} dt \int_{\mathcal{M}} d^{2d} \mathbf{x} \rho_t(\mathbf{x}) \left((\boldsymbol{\partial} H_t)(\mathbf{x}) + \beta^{-1} (\boldsymbol{\partial} \ln \rho_t)(\mathbf{x}) \right)^\top \mathbb{D} \left((\boldsymbol{\partial} H_t)(\mathbf{x}) + \beta^{-1} (\boldsymbol{\partial} \ln \rho_t)(\mathbf{x}) \right) &\geq 0 \end{aligned}$$

This is the expression of the second law of thermodynamics: the heat release describes the change of entropy in the environment whereas the Gibbs-Shannon entropy the change in the system. The sum of the two quantities is positive definite and vanishes if we set

$$\rho_t(\mathbf{x}) = \rho_{eq}(\mathbf{x}) = \frac{1}{Z} e^{-\beta H(\mathbf{x})}$$

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