Yet Another Approach to Loschmidt’s Paradox

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Abstract

Time reversal symmetry of microscopic motion is not violated by entropy “growth” of statistical mechanics. Non-equilibrium state is a local minimum of the system entropy: its first-order time derivative is zero \( \dot{S} = 0 \), while the second order derivative is non-negative \( \ddot{S} \geq 0 \).

1 Introduction

According to the Second Law of Thermodynamics, the most probable consequence of an initial non-equilibrium state of a closed system is a steady increase of its entropy\(^1\). This statement is frequently described by inequality \( \dot{S} \geq 0 \) which explicitly distinguishes past and future. Such asymmetry is usually referred to as the irreversibility of thermodynamics and contrasted with perfect time-reversal symmetry of mechanics (both classical or quantum). One of the objections (also known as Loschmidt’s paradox) to Boltzmann’s proof of \( H \)-theorem is based on this conflict: it should not be possible to single out a preferred direction in time from time-symmetric dynamics.

To resolve this difficulty we follow the arguments discussed by Bronstein, Landau\(^2\), and Peierls\(^3\). Consider equilibrium ensemble represented by multiple copies of the same closed system. Time-symmetric equations of motion determine the paths traversed by each realization. Projections of these paths to \((t, S)\) plane are the plots of time-dependent entropy \( s(t) \). Fluctuations are responsible for deviations of \( s(t) \) from equilibrium entropy \( S_{\text{max}} \). The average entropy does not depend on time \( \langle s(t) \rangle = \text{const} \lesssim S_{\text{max}} \).

Now select a sub-ensemble corresponding at \( t = 0 \) to the same entropy \( s(0) = S_0 < S_{\text{max}} \), see Fig.1. These paths represent more or less improbable fluctuations, their projections to \((t, S)\) plane pass through \( S_0 \) at \( t = 0 \). For each path \( p \) (with the entropy \( s(t) \)) there exists a conjugate, time-reversed path \( p^* \) (with the entropy \( s(-t) \) — the entropy itself is invariant under time reversal). The sub-ensemble is time-symmetrical and the probabilities of “forward” and “backward” paths are equal. The average plot is also perfectly symmetric. The conditional average (denoted below as \( \langle \ldots \rangle_{S_0} = \langle \ldots \rangle_{s(0)=S_0} \)) of the entropy is

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Figure 1: "Forward" path $p$ with the entropy $s(t)$, "backward" path $p^*$ with the entropy $s(-t)$, and the "average" entropy $S(t)$.

not a constant any more $S(t) \equiv \langle s(t) \rangle_0 \neq \text{const}$, but it is an even function $S(t) = S(-t)$ and has zero derivative at origin

$$\dot{S}(t) = \langle \dot{s}(0) \rangle_0 = 0.$$  \hspace{1cm} (1)

The Second Law in this picture would imply that the function $S(t)$ has a minimum at $t = 0$. Local time-symmetrical formulation of the Second Law is therefore

$$\ddot{S}(t) = \langle \ddot{s}(0) \rangle_0 \geq 0.$$ \hspace{1cm} (2)

Interestingly, such statement can be analyzed quantitatively.

2 Classical example

Consider a simple thermalization problem: a closed system consists of two subsystems with initially different temperatures $T_1$ and $T_2$. Total Hamiltonian $H(q, p) = H_1(q, p) + H_2(q, p)$ gives conserved total energy and includes the interaction term. Generalized coordinates and momenta for entire system are denoted as $q$ and $p$. Initial partition corresponds to the local equilibrium

$$\rho(q, p) = \frac{\exp(-N(q, p))}{\int \exp(-N(q, p)) dq dp} \equiv Ae^{-N(q, p)},$$

where $A > 0$ is the normalization constant and $N(q, p)$ is the "weighted Hamiltonian"

$$N(q, p) = \frac{H_1(q, p)}{T_1} + \frac{H_2(q, p)}{T_2}.$$  

Similar setup is discussed in the paper[4] by Jarzynski and Wójcik, but they turn the interaction on only temporarily. It is convenient to monitor the variation of
the quantity \(N(q,p)\), in a closed system it uniquely determines the energy (or heat) transfer between subsystems.

The dynamics of \(N\) in the vicinity of the initial state (so that \(T_1\) and \(T_2\) are constant) should be identified with the entropy production, in agreement with its rate at origin is zero:

\[
\dot{S} = \langle \dot{\mathcal{S}} \rangle_0 = \langle \dot{\mathcal{S}}_1 + \dot{\mathcal{S}}_2 \rangle_0 = \left\langle \frac{\dot{\mathcal{H}}_1}{T_1} + \frac{\dot{\mathcal{H}}_2}{T_2} \right\rangle_0 = \int \dot{\mathcal{N}} \rho \, dq \, dp = A \int \dot{\mathcal{N}} e^{-\mathcal{N}} \, dq \, dp = 0. \tag{3}
\]

As expected from the Second Law \(2\), the second derivative turns out to be non-negative

\[
\langle \dddot{\mathcal{N}} \rangle_0 = \int \dddot{\mathcal{N}} \rho \, dq \, dp = A \int \dddot{\mathcal{N}} e^{-\mathcal{N}} \, dq \, dp = -A \int \frac{d}{dt} e^{-\mathcal{N}} \, dq \, dp = A \int \left( \dot{\mathcal{N}} \right)^2 e^{-\mathcal{N}} \, dq \, dp \geq 0. \tag{4}
\]

3 Quantum-mechanical example

Similar results can be obtained for quantum-mechanical evolution. Hamiltonians of two subsystems are both Hermitian, their sum is the total Hamiltonian \(\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2\). The density matrix of the initial state again corresponds to the local equilibrium with temperatures \(T_1\) and \(T_2\)

\[
\hat{\rho} = \frac{\exp(-\hat{\mathcal{N}})}{\text{Tr} \exp(-\hat{\mathcal{N}})} \equiv A e^{-\hat{\mathcal{N}}},
\]

where \(\hat{\mathcal{N}} = \hat{\mathcal{H}}_1/T_1 + \hat{\mathcal{H}}_2/T_2\). Note, that due to interaction \([\mathcal{H}_1, \mathcal{H}_2] \neq 0\) and the density matrix can not be factorized

\[
e^{-\hat{\mathcal{N}}} \neq e^{-\hat{\mathcal{H}}_1/T_1} e^{-\hat{\mathcal{H}}_2/T_2}.
\]

The operator \(\hat{\mathcal{N}}\) is also Hermitian and has a complete set of eigenvectors, they are also eigenvectors for the density matrix:

\[
\hat{\mathcal{N}} |n\rangle = n |n\rangle , \quad \hat{\rho} |n\rangle = A e^{-n} |n\rangle .
\]

We again start with a check that the time-reversal symmetry is not violated by the first derivative:

\[
\langle \dddot{\mathcal{N}} \rangle_0 = \text{Tr} \hat{\rho} \dddot{\mathcal{N}} = i \text{Tr} \hat{\rho} [\mathcal{H}, \hat{\mathcal{N}}] = i \text{Tr} \left( \hat{\rho} \mathcal{H} \dddot{\mathcal{N}} - \dddot{\mathcal{N}} \mathcal{H} \hat{\rho} \right) = 0. \tag{5}
\]
Averaging of the second derivative is slightly more complicated (here we designate $H_{nn'} = \langle n| \hat{H} |n'\rangle$):

$$\langle \hat{\hat{N}} \rangle = \text{Tr} \hat{\hat{N}} = - \text{Tr} \hat{H} \frac{\partial}{\partial \hat{H}} \left[ \text{Tr} \hat{\hat{N}} \right] =$$

$$= - \text{Tr} \left( \hat{H} \hat{\hat{N}} \hat{\hat{H}} - \hat{\hat{N}} \hat{\hat{H}} \hat{\hat{H}} + \hat{\hat{N}} \hat{\hat{H}} \hat{\hat{H}} \right) =$$

$$= - A \sum_{nn'} (H_{nn'} e^{-n'} H_{n'n} - e^{-n} H_{nn'} e^{-n'} H_{n'n}) =$$

$$= - A \sum_{nn'} |H_{nn'}|^2 (n' - n) (e^{-n'} - e^{-n}) \geq 0. \quad (6)$$

This implies that the non-equilibrium state we consider is the local minimum of the entropy: it originates, on average, from a state with higher entropy and evolves, on average, into a state with higher entropy. In other words, at $t \gtrsim 0$ the energy, on average, flows from the hotter subsystem to the colder one.

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