



Universitat Autònoma de Barcelona

Facultat de Ciències

Departament de Física

Treball de Fi de Grau en Física

Non-equilibrium statistical mechanics of coupled heat baths

by Pablo Torrón Pérez

directed by Anna Sanpera
& Philipp Strasberg

–15th June 2021–

Abstract

The extended microcanonical master equation is used to study a pair of coupled heat baths out of equilibrium. Their evolution is described using quantum statistical mechanical definitions of concepts such as temperature and entropy, presented earlier in the document.

The equation is solved numerically for many different choices of the free parameters that describe the baths. The results are all consistent with the laws of thermodynamics, and behaviours that differ significantly from the ones that classical models would predict are scarcely found.

Contents

1	Introduction	2
2	Quantum description of coupled heat baths	2
3	Thermodynamics of heat exchanges	3
4	Microscopic definitions of entropy and temperature	5
5	Introducing the quantum master equation	8
5.1	Master equations in probability	8
5.2	The EMME for two coupled heat baths	9
6	Theoretical results and numerical simulations	10
6.1	Non-existence of infinitely oscillating states	10
6.2	Steady-states and equilibrium	10
6.3	Testing the model with simulations	11
6.4	Possibility of heat flowing against the T_{can}^* gradient	12
6.5	Effective temperature vs. Boltzmann temperature	14
6.6	Observational entropy and the 2 nd law	15
7	Conclusions	16
	Acknowledgements	17
A	Equivalence of ensembles	18
B	Relevant details of the derivation of the EMME	20
C	Mathematical proofs	21
C.1	Von Neumann entropy is invariant under unitary evolution	21
C.2	The eigenvalues of W are real	22
C.3	Inequality relating the different definitions of entropy	22
D	Python code	23
	Bibliography	30

1 Introduction

In a time in which nanotechnologies are at the cutting-edge of scientific research and technological advancement, with transistors fighting against Moore's law [1] and nanorobotics being found applications in fields as diverse as ecology [2] and oncology [3], having efficient descriptions of microscopic systems far from equilibrium is becoming increasingly important.

Quantum mechanics and non-equilibrium statistical mechanics are both active fields of research. This work explores a proposal for an equation to describe non-equilibrium quantum systems to check whether its predictions are sensible or, on the contrary, defy any well-known results or break the laws of thermodynamics. More precisely, it is used to study the dynamics of two coupled heat baths.

Section 2 defines what a 'heat bath' is, section 3 reviews a piece of thermodynamics regarding heat exchanges, and section 4 extends the statistical definitions of temperature and entropy to quantum systems out of equilibrium.

In section 5, the equation used to describe the two coupled heat baths is presented and, finally, some results are presented and discussed in section 6. These are both analytic results in the form of proofs, and numerical results obtained via Python simulations.

2 Quantum description of coupled heat baths

A *heat bath* is large system with many energy levels, usually made out of many copies of a same unit: for instance, a sea of coupled spins (a spin bath) or harmonic oscillators (a harmonic bath).

Heat baths are often used to study phenomena such as quantum dissipation, for which a single bath or many baths are all coupled to a small system which we may know how to solve for exactly. In this work, though, the aim is to study the behaviour of two baths coupled to one another.

The Hilbert space of two baths is the tensor product of their individual Hilbert spaces: $\mathcal{H} = \mathcal{H}^L \otimes \mathcal{H}^R$. The Hamiltonian of the two-bath setup is

$$\hat{H} = \hat{H}^L \otimes \hat{\mathbb{1}}^R + \hat{\mathbb{1}}^L \otimes \hat{H}^R + \lambda \hat{H}_{\text{int}} = \hat{H}_0 + \lambda \hat{H}_{\text{int}}. \quad (1)$$

The energy of these heat baths, for the purposes of this work, can only be resolved up to some energy uncertainty δ . They can be described as a set of many coarse-grained energy levels or *energy bands* E_k each with an equivalent degeneracy or *volume term* $\Omega(E_k)$ equal to the sum of the degeneracies of the actual energy levels within the interval $[E_k - \delta/2, E_k + \delta/2]$.

For the two baths to be able to exchange energy without seemingly violating conservation of energy, δ must be the same for both. It makes sense that both baths can have their energy resolved up to the same uncertainty, more so if they are in thermal contact.

The energy of each band can be considered to be $E_k = k\delta$, then, as long as all the energy bands starting from 0 are populated.

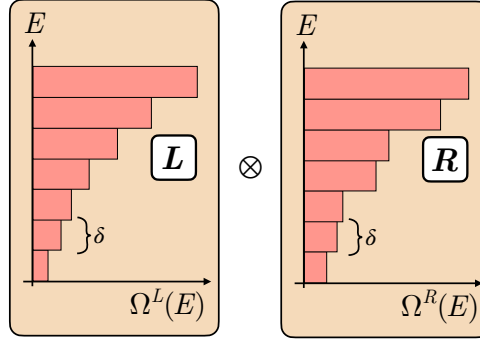


Figure 1: Schematic illustration of the system formed by two baths.

The Hamiltonians for two harmonic baths, for example, would be

$$\hat{H}^{(\ell)} = \sum_{n=1}^N \left(\frac{\hat{p}_n^2}{2m_n} + \frac{1}{2} m_n \omega_n (\hat{x} - \hat{d}_n)^2 \right)$$

for $(\ell) \in \{L, R\}$. The volume term of each energy band would equal all the possible microstates whose energy is less than $\delta/2$ apart from a multiple of δ . A quick calculation using a small N shows that they increase very rapidly with energy.

The interaction Hamiltonian would couple the oscillators in one bath with those of the other bath; and, as seen from the perspective of the coarse-grained energy bands, it would allow one bath to give or take a multiple of δ of energy to or from the other.

With only one harmonic oscillator per bath, solving the dynamics for two coupled harmonic oscillators would lead to endless oscillations in energy and, if there was a way to define it for them, in temperature as well. Of course, one oscillator does not make thermodynamical system as it would not meet the condition of having a negligible standard deviation in its energy.

At the thermodynamical limit of virtually infinitely many oscillators per bath, the temperature would evolve without oscillating at all, at least for a quasistatic process.

Somewhere in the middle, there might be a point at which the collective dynamics of the whole bath can be described using statistical mechanics without those oscillations in temperature having completely gone away. An interesting test for the equation yet to be presented in Section 5 would be to show whether it is able to describe oscillations in energy and temperature.

3 Thermodynamics of heat exchanges

Consider two thermodynamical systems L and R with temperatures T^L and T^R , to be in thermal contact, isolated from their environment and unable to do any work on each other. At equilibrium, any quasistatic change in the entropy of any of them is

$$dS^{(\ell)} = \frac{1}{T^{(\ell)}} dQ^{(\ell)}. \quad (2)$$

for $(\ell) \in \{L, R\}$.

The first law demands $dU^{(\ell)} = dQ^{(\ell)}$ and $dQ^L = -dQ^R$, which makes

$$dS = dS^L + dS^R = \left(\frac{1}{T^L} - \frac{1}{T^R} \right) dQ^L.$$

Given $T^L > T^R$, $dQ^L > 0$ would imply that a decrease in the entropy of the Universe, in contradiction with the second law. Thus, no quasistatic process can behave like that. A quasistatic process between two thermodynamical systems cannot possibly exhibit oscillations in temperature, as these imply a heat flow against the temperature gradient that breaks the 2nd law.

For a non-quasistatic process, Eq. 2 is just a lower bound. Even though global equilibrium is also reached, the systems do not traverse local equilibrium macrostates, and thermodynamics alone is not able to quantitatively describe temperature and entropy.

Describing intensive magnitudes like temperature or pressure out of local equilibrium is not usually a task for thermodynamics, but for statistical mechanics. Despite this, all systems must always obey the laws of thermodynamics whether they are in equilibrium or not, so there must be a sensible way to describe a flow of heat against a temperature gradient even if that temperature is not the one that is usually defined through thermodynamics alone.

Systems out of equilibrium are known to exhibit spontaneous behaviours that may seem to break the 2nd law, even though they are absolutely consistent with it [4, 5].

For example, two gases separated by a mobile piston with unequal pressures, or two springs attached a same one mass with unequal tensions, will oscillate back and forth and slowly dissipate that mechanical energy until mechanical equilibrium (no acceleration of the piston or spring) is reached. These two situations are far from equilibrium, and equilibrium thermodynamics cannot tell where the energy contained in the system initially goes because it does not turn immediately into thermal energy, it turns into kinetic energy.

Similarly, some chemical reactions can oscillate between reactants and products [6], taking place back and forth until chemical equilibrium (no change in concentrations) is eventually reached. Again, this can be explained within the framework of thermodynamics by invoking additional non-equilibrium thermodynamical variables [7].

It is not trivial to know whether thermal equilibrium can exhibit this same oscillating behaviour, as the entropy production of those cases is quite different from the entropy production of a heat exchange, but having heat flow against a non-equilibrium temperature gradient is something we should not dismiss before trying.

For any two systems to oscillate like that, though, it seems like the interaction between them needs to be strong enough in some way. For instance, the gases or springs in the former example must be able to displace the mass that separates them without barely experiencing any friction. Above a critical amount of friction, energy is dissipated into heat faster than oscillations are able to occur. We will not be able to describe a strong coupling between the two heat baths because of the assumptions made to derive the equation in Section 5, but we will be able to describe non-equilibrium evolution, so this oscillating behaviour can still be something to look out to when solving it.

4 Microscopic definitions of entropy and temperature

In classical statistical mechanics, entropy is typically described microscopically using two different definitions.

- *Gibbs entropy*, or *Shannon entropy* in information theory. It depends on the specific probability distribution $\rho(q, p)$ of microstates and the number of particles.

$$S_G(\rho) \equiv -k_B \int \cdots \int_{\Omega} \rho(q, p) \log \rho(q, p) \frac{d^{3N}q d^{3N}p}{h^{3N}}. \quad (3)$$

These p, q are the coordinates of the phase space; in general, the positions and momenta of all the particles in the system.

- *Boltzmann entropy*. It depends on the number of microstates Ω compatible with the observed macrostate (U, N, \dots) that are accessible to the system:

$$S_{\text{mic}}(U, N, \dots) \equiv k_B \log \Omega(U, N, \dots). \quad (4)$$

These U, N, \dots are the extensive macroscopic magnitudes of the system (besides entropy itself): energy, number of particles, volume...

For microcanonical ensemble states, Gibbs entropy equals Boltzmann's. For canonical ensemble states, it is

$$S_{\text{can}}(T, N, \dots) \equiv k_B \log \mathcal{Z}(T, N, \dots) + \frac{U(T, N, \dots)}{T}. \quad (5)$$

with $\mathcal{Z}(T, N, \dots)$ being the canonical partition function.

Gibbs entropy is not necessarily more general than Boltzmann's, both are well-defined for any state, microcanonical or not. The definition of S_{can} , however, only makes sense for canonical states, in a strict sense. The reasons why both definitions are commonly used in statistical mechanics are mainly historical [8, 9]: the former comes from Gibbs' approach of analysing whole ensembles, whereas the latter comes from Boltzmann's approach to statistical mechanics of analysing a single multiparticle system.

Before generalising temperature and entropy for systems out of equilibrium, though, we shall generalise them for quantum systems. In quantum mechanics, Gibbs entropy turns into¹ von Neumann entropy times k_B , whose definition [10] is

$$S_{\text{vN}}(\hat{\rho}) \equiv \text{tr}\{\hat{\rho} \log \hat{\rho}\}, \quad (6)$$

with $\hat{\rho}$ the density operator of the system.

The density operator is a trace-1 positive-semidefinite operator that describes the state of an ensemble. The density matrix of a *pure state* $|\psi\rangle$ is just $|\psi\rangle\langle\psi|$, and the one of an arbitrary ensemble or *mixed state* $\{p_i, |\psi_i\rangle\}$ is just

$$\sum_i p_i |\psi_i\rangle\langle\psi_i|.$$

¹Through the correspondence principle; the density operator is the analogue of the probability distribution, and the trace is the analogue of the summation or the integral over all phase space.

As it was stated in Section 2, the Hilbert space of a system made up of k non-identical subsystems can be described as the tensor product of the Hilbert space of each system, so $\mathcal{H} = \mathcal{H}_1 \otimes \cdots \otimes \mathcal{H}_k$. The marginal density operators for any given subspace can be computed by “tracing out” the remaining ones, for instance

$$\hat{\rho}_1 = \text{tr}_2\{\cdots \text{tr}_k\{\hat{\rho}\}\cdots\}.$$

When $\hat{\rho} = \hat{\rho}_1 \otimes \cdots \otimes \hat{\rho}_k$, the subsystems are *decorrelated*. Otherwise, the whole is said to be *correlated*, either clasically or quantumly, what is known as entanglement.

Von Neumann entropy is useful not only on its own, but also to define many meaningful quantities [10] such as the *relative entropy* of two states

$$\mathcal{D}(\hat{\rho} \parallel \hat{\rho}') \equiv S_{\text{vN}}(\hat{\rho}) - \text{tr}\{\hat{\rho} \log(\hat{\rho}')\} = \text{tr}\{\hat{\rho} (\log \hat{\rho} - \log \hat{\rho}')\}, \quad (7)$$

which measures how different the $\hat{\rho}'$ is with respect to $\hat{\rho}$; and the *mutual information* between two subsystems A, B

$$\mathcal{I}^{A:B}(\hat{\rho}) \equiv S_{\text{vN}}(\hat{\rho}_A) + S_{\text{vN}}(\hat{\rho}_B) - S_{\text{vN}}(\hat{\rho}) = \mathcal{D}(\hat{\rho} \parallel \hat{\rho}_A \otimes \hat{\rho}_B), \quad (8)$$

which measures how correlated A and B are.

On the other hand, Boltzmann entropy $S_{\text{mic}}(E)$ can be computed for quantum systems as the von Neumann entropy of a microcanonical state with the energy of the system.

Microcanonical ensemble states are defined through their energy. One such quantum state with energy E will be measured, with equal probability and phase, in any eigenstate with E . Its density operator can be expressed as

$$\hat{\omega}(E) \equiv \frac{1}{\Omega(E)} \hat{\Pi}_E = \frac{1}{\Omega(E)} \sum_k |E, k\rangle \langle E, k|, \quad (9)$$

with $\hat{\Pi}_E$ the projector onto the subspace of energy E , and $\Omega(E) \equiv \text{tr}\{\hat{\Pi}_E\}$ the number of eigenstates or *degeneracy* of E .

Conversely, canonical ensembles states are defined through their temperature. For any T_{can} , the density operator of the corresponding canonical ensemble state is

$$\hat{\pi}(T_{\text{can}}) \equiv \frac{1}{\mathcal{Z}(T_{\text{can}})} e^{-\hat{H}/k_B T_{\text{can}}} \quad (10)$$

with $\mathcal{Z}(T_{\text{can}}) \equiv \text{tr}\{e^{-\hat{H}/k_B T_{\text{can}}}\}$ being the *canonical partition function*, the normalisation factor that makes it a well-defined density operator.

T_{can} only makes sense for those states, but a sensible microscopic temperature can actually be defined by applying the thermodynamic relation between E and T to $S_{\text{mic}}(E)$:

$$T_{\text{mic}} = \frac{\partial E}{\partial S_{\text{mic}}} = \left(k_B \frac{\partial}{\partial E} \log \Omega(E) \right)^{-1} = \frac{\Omega(E)}{k_B} \left(\frac{\partial \Omega}{\partial E} \right)^{-1} \quad (11)$$

This temperature can be called the *microcanonical* or *Boltzmann temperature*.

T_{can} can be generalised to apply to any quantum state as well. Given any $\hat{\rho}$ with energy $E = \text{tr}\{\hat{\rho}\hat{H}\}$, there is one T_{can}^* , and only one, that makes

$$\text{tr}\{\hat{\rho}\hat{H}\} = \text{tr}\{\hat{\pi}(T_{\text{can}}^*)\hat{H}\}.$$

Whenever $\hat{\rho} \neq \hat{\pi}(T_{\text{can}}^*)$, this T_{can}^* is called its *effective (canonical) temperature*.

Both definitions of temperature depend solely on energy and apply even to states out of local equilibrium. Notwithstanding that, they exhibit quite different behaviours, especially regarding negative temperatures. For a system to have negative T_{can}^* , it needs finitely many energy levels and population inversion; whereas, a negative T_{mic} only requires one of the system's energy levels to have a smaller Ω than the one before it.

This two definitions should coincide at the thermodynamical limit by virtue of *equivalence of ensembles*, the idea that the thermodynamic variables of a system should not depend on the ensemble chosen to describe it (discussion and sketch of a proof in Appendix A). The description of our heat baths will stay far from that limit, so we should expect those two temperatures to be quite different.

As per the entropies, Gibbs-von Neumann entropy is invariant under Hamiltonian evolution (as proven in Appendix C.1), which does not make a good candidate for thermodynamical entropy. Moreover, we cannot compute the von Neumann entropy if the most we know about our baths is the value of coarse-grained probabilities and not the whole $\hat{\rho}$.

Boltzmann entropy, even though it can change over time, might do so discontinuously even for continuous processes [11], so it does not make a perfect candidate either.

Our choice for this middle-grounded entropy is the *observational entropy* relative to the coarse-grained energies [12], whose definition is

$$S_{\text{obs}}(\hat{\rho}) = k_B \sum_k p(E_k) \log \left(\frac{\Omega(E_k)}{p(E_k)} \right). \quad (12)$$

with E_k the coarse-grained energies of the respective bath, and $p(E_k)$ the probability of the energy being measured to be E_k . It is only symbolically applied to $\hat{\rho}$, we need not know the entire density operator to compute it.

Ideally, there would be a microscopic definition of entropy more finer than Boltzmann's—so it can be continuous—, but not as coarse-grained as von Neumann's—so it can lose track of some information and increase over time—. It treats different energy bands like von Neumann's would, but it treats the microstates within each band like Boltzmann's would.

Relative entropy and mutual information can be adapted to the coarse-graining as well for them to be compatible with the observational entropy, like so:

$$\mathcal{D}_{\text{cg}}(\hat{\rho} \parallel \hat{\rho}') = k_B \sum_k p(E_k) \log \left(\frac{p(E_k)}{p'(E_k)} \right), \quad \mathcal{J}_{\text{cg}}^{L:R} = \mathcal{D}_{\text{cg}}(\hat{\rho} \parallel \hat{\rho}^L \otimes \hat{\rho}^R). \quad (13)$$

Just like thermodynamical entropy, thermodynamical temperature is an emergent property. Different microscopic descriptions yield different definitions of temperature.

5 Introducing the quantum master equation

Solving the von Neumann equation—the Schrödinger equation for density operators—with a Hamiltonian such as the one in Eq. 1 will often be impossible analytically and take too much time to compute numerically.

Under certain assumptions and approximations, though, the von Neumann equation is simplified into a quantum master equation, an equation that is more likely to be solvable by ordinary means. These come from the statistical physics concept of a master equation, which is discussed before as an introduction.

5.1 Master equations in probability

A *master equation* is a linear system of differential equations for the probability of any given system being in each of its possible states under some process. That process is said to be Markovian when its evolution does not depend on its past states, for which it is sufficient to have a time-independent matrix for the system of ODEs.

Let $P_a(t)$ be the probability of a system being in its a th state at time t , and W_{ba} be the transition rate from the a th to the b th states. Then, the following equation holds

$$\frac{d}{dt}P_a(t) = \sum_{b \neq a} W_{ab}P_b(t) - \sum_{b \neq a} W_{ba}P_a(t),$$

which is called the *master equation* of the system. The probability in the second summation does not depend on said sum, so we can define

$$W_{aa} = - \sum_{b \neq a} W_{ba} \quad (14)$$

and the master equation takes on the simpler form

$$\frac{d}{dt}P_a(t) = \sum_b W_{ab}P_b(t). \quad (15)$$

The sum of all probabilities must equal 1 at all times, so the sum of all time-derivatives must equal 0 at all times: probability is conserved. The definition of W_{aa} above—as the rate at which the system stays in each state—is consistent with this, as

$$\frac{d}{dt} \sum_a P_a(t) = \sum_a \frac{d}{dt} P_a(t) = \sum_a \sum_b W_{ab}P_b(t) = \sum_b P_b(t) \sum_a W_{ab} \stackrel{(14)}{=} 0.$$

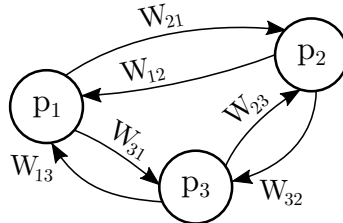


Figure 2: Heuristic representation of a Markov process with three possible states.

5.2 The EMME for two coupled heat baths

A *quantum master equation* is a system of linear differential equations which describes the time-evolution of some system A in contact with one bath B or many, B_1, B_2, \dots , whose detailed evolution is, to some degree, unknown.

Many different quantum master equations can be derived by simplifying the von Neumann equation under different assumptions [13]. A well-known and commonly used one is the BMS master equation, which assumes B to be a heat reservoir weakly coupled to A that does not cool down or heat up.

Instead, the extended microcanonical master equation, or EMME, is used in this work. It also assumes weak coupling between A and B ², but also allows for a coarse-grained description of the dynamics of B as well and has proven to be more accurate than the BMS [14]. For the purposes of this work, A and B will be the L and R baths, so A will also be described up to a similar coarse-graining (see Appendix B for details).

The EMME turns the evolution of $L \otimes R$ described by the von Neumann equation into a Markovian ODE for the coarse-grained probabilities $p(E^L, E^R)$, whose matrix is

$$W = \bigoplus_E W(E), \quad W_{ab}(E) = \begin{cases} \frac{\mathfrak{S}_{ab}(E)}{\Omega^L(E_b)\Omega^R(E-E_b)} & a \neq b, \\ -\sum_{\ell \neq k} W_{\ell a}(E) & a = b. \end{cases} \quad (16)$$

$\mathfrak{S}_{kq}(E)$ is a symmetric matrix determined by the interaction Hamiltonian, and Ω^L, Ω^R are just the volume terms for every energy band of each bath, respectively. The E in $\mathfrak{S}_{kq}(E)$ and $W_{kq}(E)$ is the sum of E^L and E^R , and their indices represent the energy band of the L bath, which are labelled with whole numbers between 0 and E/δ if all the bands can be populated (if they have a non-zero volume term).

The direct sum over E signifies the probabilities forming independent Markovian processes according to their total energy,

$$\frac{d}{dt} p(E_a, E - E_a; t) = \sum_b W_{ab}(E) p(E_b, E - E_b; t), \quad (17)$$

which implies energy is always conserved. Due to the fact that the indices in $\mathfrak{S}_{ab}(E)$ are symmetric, the transition rates satisfy

$$\begin{aligned} \frac{W_{ab}(E)}{W_{ba}(E)} &= \frac{\Omega^L(E_a)\Omega^R(E-E_a)}{\Omega^L(E_b)\Omega^R(E-E_b)} \\ \implies k_B \log \left(\frac{W_{ab}(E)}{W_{ba}(E)} \right) &= \Delta S_{\text{mic}} \end{aligned} \quad (18)$$

with ΔS_{mic} = the change in Boltzmann entropy of going from the state $p(E_b, E - E_b) = 1$ to $p(E_a, E - E_a) = 1$. This is known as the *local detailed balance* condition, and it implies that the dynamics maximise entropy at each t .

²It also assumes that the $\mathfrak{S}_{ab}(E)$ terms are time-independent, something called the Markov approximation as it turns the master equation into a Markovian one, as well as the so-called secular approximation. The BMS master equation also assumes these two approximations. See Appendix B.

6 Theoretical results and numerical simulations

6.1 Non-existence of infinitely oscillating states

The differential equation for a Markov process is a linear system of differential equations; therefore, the exponential of the W matrix will always be a solution. As long as W is diagonalisable, the solutions are characterised by its eigenvalues:

- *real* non-0 eigenvalues lead to real exponential solutions,
- *complex* non-0 ones lead to complex exponential solutions (expns. and sines),
- eigenvalues equal to 0 lead to constant solutions.

If all eigenvalues are real, no solution can be infinitely oscillating; therefore, if temperature crossings are possible, there will at most be finitely many.

For any interaction Hamiltonian, W equals a symmetric matrix times a diagonal one:

$$W = \mathfrak{S}D, \quad \mathfrak{S}_{ab}(E) \text{ is symmetric, and } D_{ab}(E) = \frac{\delta_{ab}}{\Omega^L(E_b)\Omega^R(E - E_b)} \text{ is diagonal.}$$

Such matrices only have real eigenvalues (as proven in Appendix C.2).

6.2 Steady-states and equilibrium

For every energy E , we can prove

$$\lim_{t \rightarrow \infty} p(E_k, E - E_k; t) = \Omega^L(E_k)\Omega^L(E - E_k)\alpha_E$$

with α_E a constant. It follows from Eq. 17 that this limiting state is a steady-state, as

$$\frac{d}{dt} p(E_k, E - E_k; t) = \dots = \alpha_E \left(\sum_q S_{kq} - \sum_q S_{qk} \right) = 0.$$

It is a sensible choice to pick a canonical ensemble state as the initial one. The density matrix of the whole is be a single tensor product³ at this point—there is no correlation between the two baths, their mutual information is null—, which implies

$$p(E_k, E - E_k) = \Omega^L(E_k) \frac{e^{-E_k/k_B T_0^L}}{\mathcal{Z}(T_0^L)} \Omega^R(E - E_k) \frac{e^{-(E-E_k)/k_B T_0^R}}{\mathcal{Z}(T_0^R)}. \quad (19)$$

If their initial temperatures are equal, their initial Boltzmann factors must be as well, thereby making all probabilities follow the following expression, independent of k ,

$$p(E_k, E - E_k) = \Omega^L(E_k)\Omega^R(E - E_k) \frac{e^{-E/k_B T}}{\mathcal{Z}(T)}, \quad (20)$$

which is a steady-state. Microcanonical ensemble states are also steady-states.

³This is not always the case, which is why the whole density operator $\hat{\rho}$ is impossible to recover from all the probabilities.

6.3 Testing the model with simulations

It would be interesting to see if both baths reach a steady-state with the same temperature at different initial temperatures, and whether the correlations among them vanish or not. To see this, it will be better to first solve the EMME for many different examples, and draw conclusion from that data.

All the solutions used throughout this section have been computed using the Python code found in Appendix D. It asks for a specific N , $\mathfrak{S}_{ab}(E)$, $\Omega^L(E)$, $\Omega^R(E)$ and the initial state of each bath, and then it uses 4th order Runge-Kutta to solve the EMME.

From the solution, the code computes the effective temperature T_{can}^* at every instant t by finding the only such β that makes

$$\underbrace{\sum_k E_k p(E_k; t)}_{E(t)} - \sum_k E_k \frac{\Omega(E_k) e^{-\beta E_k}}{\mathcal{Z}(1/k_B \beta)} = 0 \quad (21)$$

for each bath using the Newton-Raphson iterative method, taking the previous temperature as the initial temperature with which to iterate. $T_{\text{can}}^*(t)$ is just the multiplicative inverse of the β found at t . It also computes the total observational entropy

$$S_{\text{obs}}(t) = S_{\text{obs}}^L(t) + S_{\text{obs}}^R(t) - \mathcal{J}_{\text{cg}}^{L,R}(t),$$

according the definitions of observational entropy itself and the coarse-grained mutual information, in Eq. 12 and Eq. 13 respectively.

The total entropy of two canonical ensemble states with the same temperatures,

$$S_{\text{can}}(t) = S_{\text{can}}(T_{\text{can}}^{*L}(t)) + S_{\text{can}}(T_{\text{can}}^{*R}(t)),$$

is also computed for comparison.

The two baths are assumed to be made up of many different small systems. Thus, $\Omega(E)$ is expected to increase with E and to do so quite fast—but not exponentially or faster, as that would make $\mathcal{Z}(T)$ diverge—. Their ground state is taken to have a volume term of 1 so that the lowest entropy, the entropy at 0 temperature, equals 0; furthermore, this would be the case for a harmonic bath, a spin bath or a bath made out of any quantum system whose ground state is not degenerate.

For any possible setup and initial condition, the hotter bath always gets colder and, the colder one, hotter. However, their final effective temperature are exactly equal only when Ω^L and Ω^R all differ by the same multiplicative factor, $\Omega^L(E) \equiv k\Omega^R(E)$.

Making both Ω^L and Ω^R increase polynomially, even if the exact polynomials are different, usually makes the difference in the final effective temperatures negligible, anyway, see Fig. 3.

Changing the values of $\mathfrak{S}_{ab}(E)$ does not change the final temperature (as long as none is taken to be 0), but it does change the speed at which that temperature is reached. If they take on different values, the evolution may even be observed to happen in steps.

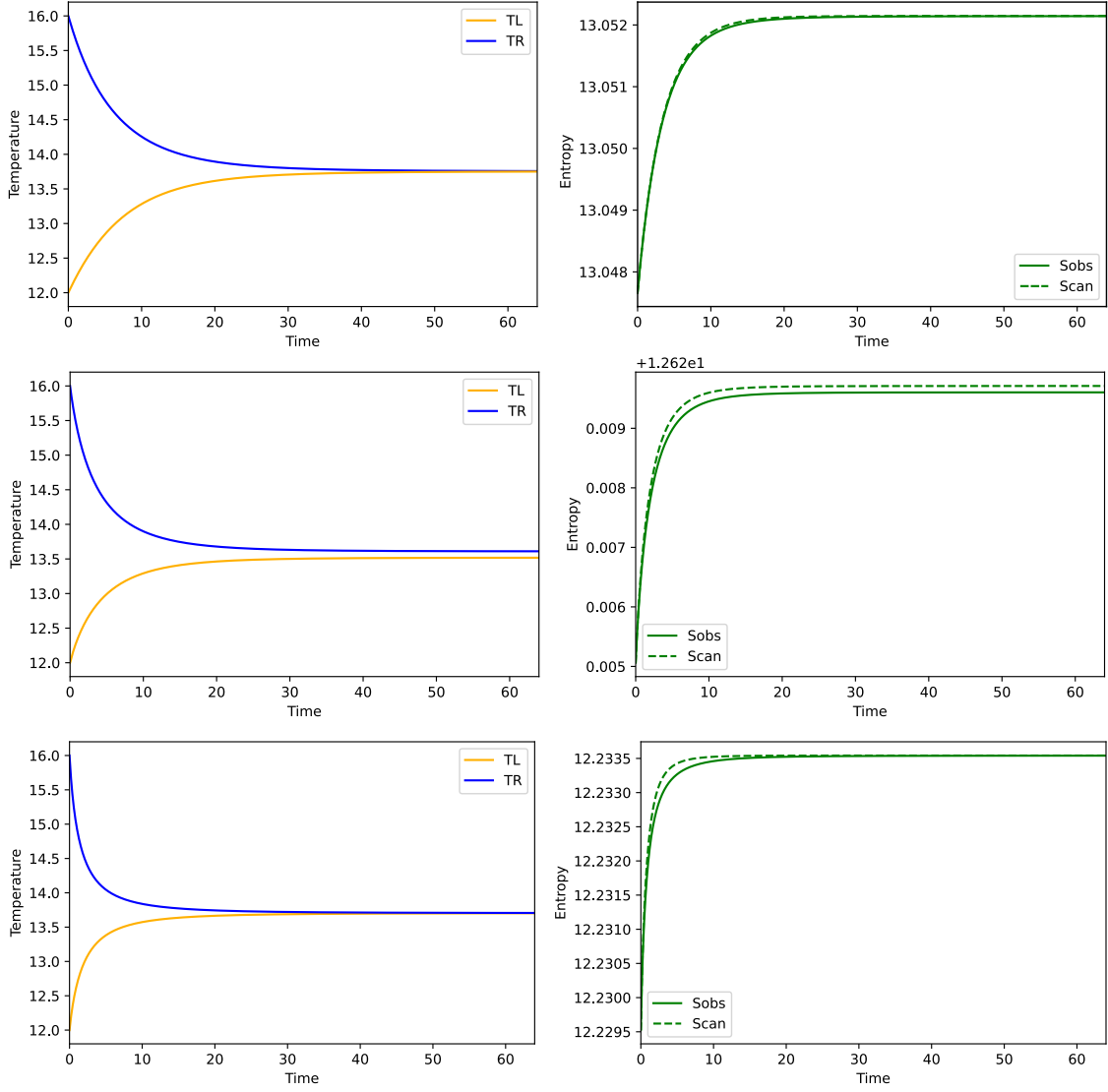


Figure 3: Plots for $N = 16$, $\delta = 1$ and all $\mathfrak{S}_{ab}(E)$ equal to 8; time-steps of $\Delta t = 2^{-7}$.

From top to bottom, each row shows the following cases: all Ω s equal to 24; all Ω s equal to a random integer between 1 and 50; and $\Omega^L(E_k) = \lceil (3k^2 + 1)/2 \rceil$, $\Omega^R(E_k) = 2k^2 + k + 1$.

As the simulation uses $\hbar = k_B = 1$, $T_{\text{can}}^* = 1$ is already quite a high temperature—think Plank temperature for illustration—. As the states for temperatures > 1 up to $+\infty$ are all almost identical, the entropy changes are quite small. These temperatures worked best because the code broke with temperatures < 1 due to carrying too many decimals.

6.4 Possibility of heat flowing against the T_{can}^* gradient

Despite trying many different setups and initial temperatures, in no case did the effective temperatures cross past each other a single time before approaching equilibrium. As this could only happen if the effective temperatures—and, therefore, the energies—presented local extremes, I thought of attempting to prove that the EMME cannot possibly lead the derivative of $E^L(t)$ or $E^R(t) = E - E^L(t)$ being 0 unless it is 0 everywhere.

Before looking for a proof, to be absolutely sure, I tweaked the code slightly to check for a specially crafted extreme case.

Consider two baths with three energy levels, uneven transition rates and —this is the part that required to change the code— uneven differences between the energies of each band. It can also be thought as two baths with many fine bands, all of which have 0 volume terms except for those three. See Fig. 4.



Figure 4: Schematic representation of two hypothetical baths with only 3 energy bands. the vertical axis represents energy, and each line stands for a whole band. The initial state is a canonical state really close to the microcanonical state in which only the non-dotted lines are populated. The transition rate in red taken to be negligible.

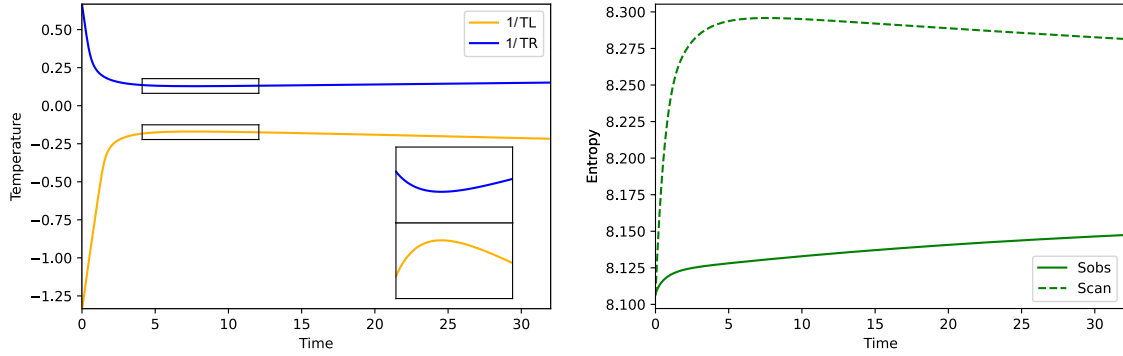


Figure 5: Plots for the system in Fig. 4. $1/T_{\text{can}}^*$ is plotted instead of T_{can}^* to avoid infinite temperatures.

Fig. 5 shows how temperatures do present one local extreme. This rules out the hypothesis of the EMME not being able to describe any evolution that makes the effective temperatures present a local extreme, but it is nothing like the temperature oscillations we would expect from a harmonic bath. In fact, the temperatures do not even get to cross past each other, nor do they end up with a same temperature.

Not only that, but the middle bands are all considered to be δ apart evenly, these local extremes vanish. Moving the middle energy band as showcased in Fig. 4 is necessary for this to happen.

As per the entropies, the observational entropy grows very slowly, and mostly because of the build-up of correlations between the two baths. The entropy of two canonical ensemble states with the same temperature grows much more and experiences a local maximum when the temperatures start diverging, unlike the observable entropy, which grows monotonically.

6.5 Effective temperature vs. Boltzmann temperature

Boltzmann entropy and temperature have been computed for all the examples above, but the behaviour of the effective temperature and observational entropy is far better. The definition from Eq. 11 cannot be directly applied, as the derivative of $\Omega(E)$ has to be discretised, so

$$T_{\text{mic}} = \frac{\Omega(E_{\text{cg}})}{k_B} \frac{2\delta}{\Omega(E_{\text{cg}} + \delta) - \Omega(E_{\text{cg}} - \delta)}.$$

with E_{cg} being the energy rounded to the nearest whole multiple of δ . Something similar must be done to the Boltzmann entropy,

$$S_{\text{mic}} = \log \Omega(E_{\text{cg}}).$$

For small N (~ 10), Boltzmann's is too coarse-grained to be useful: it remains constant at all times except for one or two discrete jumps which may increase or even decrease its value. Boltzmann temperatures reduce their difference as the baths evolve, but for small enough N the smallest difference they can have can be quite big in comparison with the initial difference.

For a larger N , the final Boltzmann entropy seems to be larger than the initial one every time. The two Boltzmann temperatures are pretty much equal and always lie close to the average of the initial temperatures. Their values differ significantly from the values observational entropy and effective temperatures have. See Fig. 6.

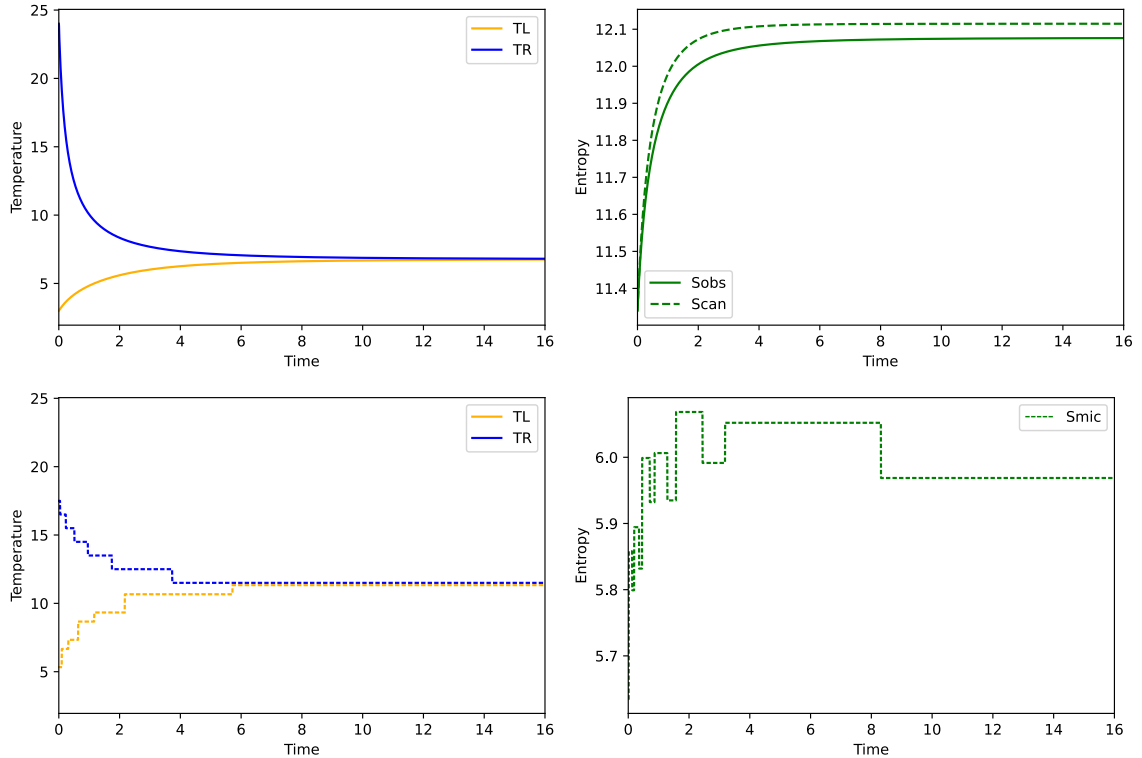


Figure 6: Plots for $N = 30$, $\delta = 1$, $\Omega^L(E_k) \equiv \lceil (3k^2 + 1)/2 \rceil$, $\Omega^R(E_k) \equiv k^2 + k + 1$ and all the $\mathfrak{S}_{ab}(E)$ terms equal to 8; time-steps of $\Delta t = 2^{-9}$. Dashed lines in the left-hand plots stand for T_{mic} instead of T_{can}^* .

Instead of using canonical ensemble states as the initial states, microcanonical ensemble states could be used. T_{mic} is better-behaved in this case, as temperature exchanges occur simultaneously for both baths. Moreover, $S_{\text{obs}}(t)$ is now closer to $S_{\text{mic}}(t)$. See Fig. 7.

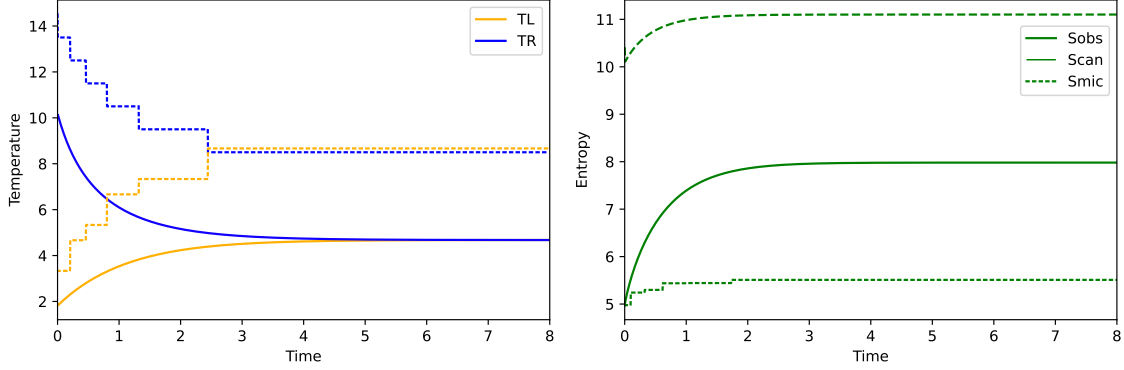


Figure 7: Plots for $N = 30$, $\delta = 1$, $\Omega^L(E_k) \equiv \lceil (3k^2 + 1)/2 \rceil$, $\Omega^R(E_k) \equiv k^2 + k + 1$ and all $\mathfrak{S}_{ab}(E)$ equal to 8; time-steps of $\Delta t = 2^{-9}$. The initial state, unlike in the other figures, is not a canonical state, but the microcanonical state $p(3\delta, 14\delta) = 1$.

6.6 Observational entropy and the 2nd law

In Section 4, observational entropy was introduced as a way to have a sensible definition for entropy that allows for a coarse-graining finer than the one assumed by Boltzmann entropy, but not as fine as the one assumed by von Neumann entropy.

Boltzmann entropy can also be computed from the coarse-grained energies of the baths by using the volume terms, though, it is only von Neumann's that we cannot compute, as we lack the exact $\hat{\rho}(t)$ of the whole system.

After all the simulations run on the EMME and all the results obtained from them, the following observations are worth making.

- $S_{\text{mic}}(t)$ is discontinuous. For large enough values of N or distinct enough temperatures, its final value is larger than its initial value, but it may increase or decrease in the process.
- $S_{\text{can}}(t)$ is always continuous. As it depends solely on the two effective temperatures, it will only decrease in the event that heat flows against the T_{can}^* gradient.
- $S_{\text{obs}}(t)$ has proven to be monotonically increasing even when under non-equilibrium situations in which we would expect $S_{\text{mic}}(t)$ and $S_{\text{can}}(t)$ not to be.
- In most situations, the following inequality holds.

$$S_{\text{can}}(t) \geq S_{\text{obs}}(t) \geq S_{\text{mic}}(t). \quad (22)$$

Only when the probabilities follow a canonical ensemble distribution is the former inequality saturated, whereas the latter is not saturated exclusively when they follow a microcanonical ensemble one. See Appendix C.3.

- Correlations between the two baths begin at 0 at the initial state, whether the two baths are in a canonical or microcanonical ensemble states, they grow quickly and sharply when they exchange the most heat, and finally go down slowly as the two baths reach the same final temperature.

In the event that they don't reach a final temperature, the correlations usually stay above 0 even in the asymptotic future.

7 Conclusions

This work studied the dynamics of two coupled heat baths using the extended microcanonical master equation, the EMME. Out of the research that has been conducted and the results that have been obtained from the simulations that were run to solve it, the following conclusions have been reached.

The EMME allows for a description of coupled heat baths consistent with the laws of thermodynamics. Two baths with different initial temperatures and no initial correlations evolve towards having equal temperatures by steadily exchanging heat from hot to cold. Throughout this process, the sum of their energies is conserved and their entropy always increases.

Studying this has been more complex than it was originally thought, as thermodynamical concepts like temperature and entropy do not have an unique and obvious generalisation to quantum statistical mechanics. For the analysis conducted in this work, observational entropy has been found to be the microscopic definition of entropy that works best. As for temperature, both microcanonical temperature and effective canonical temperature make sense. The former evolves continuously and could take on any sensible value for the temperature of a heat bath, whereas the latter evolved in such a way, that the final temperatures of the coupled baths were as close as they could be to the average of their initial temperatures; each has its pros and cons.

It was interesting to see if this equation was able to describe, under any circumstance, a heat flow going against a temperature gradient—an effective canonical temperature gradient—. This was inspired by the fact that a harmonic bath with few oscillators would, if solved exactly, exhibit oscillations in temperature.

The model could only describe such a flow under very specific and special conditions, and it looked nothing like it would for damped oscillations. Not only that, the model had to be tweaked quite a lot to allow for this, even though the effect was minuscule.

Nonetheless, the study of the EMME has proven to be interesting, and is likely to pave the way towards a solid theory able to describe non-equilibrium quantum matter.

The reader is encouraged to apply the EMME to any specific system, and compare its behaviour to the one predicted by classical statistical mechanics and thermodynamics. After all, what makes this one or any other physical model useful is its predictive power, which only be proven through experimentation. Appendix B discusses other ways in which this work could be expanded upon, by making changes to the EMME either by making the coupling strong or by dropping the Markovian approximation.

Acknowledgements

I would really like to thank, with every fiber of my being, my directors Philipp Strasberg and Anna Sanpera. Not only have they guided me through the process of choosing the topic for my TFG and helping me get something out of it, but they have also taught me a lot about statistical mechanics and quantum physics. They have been the nicest to me despite my —at times— little competence.

I would also like to thank Miquel Saucedo for helping me out with some of the math I had to know for this project; as well as my boyfriend Rubén and my friend Jokin for dealing with me during the breakdowns I have had while working on it.

Appendices

A Equivalence of ensembles

The description of a thermodynamical system in equilibrium is often done under certain assumptions on the state of said system. These assumptions define the different kinds of *ensemble*, each associated to some probability density function on the phase space (in Classical Mechanics) or the Hilbert space (in Quantum Mechanics) of states.

The thermodynamic description of the system, though, is expected to be independent of the chosen ensemble, so we are usually free to work with the one that is most convenient and the thermodynamic limit—if it can be taken—will work out the rest.

Proving that the fundamental thermodynamic equations—either $S_{\text{mic}}(U, N, V \dots)$ or a Legendre transform of it—obtained with each ensemble limit each other under the thermodynamic limit is not hard, a sketch of it is presented below, but the details of the proof and the conditions under which it works are not trivial at all.

The energy distribution $p(E) dE$ for a canonical ensemble at temperature T follows

$$p_{\text{can}}(E, N \dots) \equiv \frac{\Omega(E, N \dots) e^{-E/k_B T}}{\mathcal{Z}(T_{\text{can}}, N \dots)};$$

whereas a microcanonical ensemble follows

$$p_{\text{mic}}(E, N \dots) \equiv \delta(E - U(T_{\text{mic}}, N \dots))$$

with $T_{\text{mic}}(U, N \dots)$ a caloric equation that is derived from the fundamental equation $S_{\text{mic}}(U, N \dots)$. It can be computed, as Eq. 11 shows, with

$$T_{\text{mic}}(E, N \dots) \equiv \frac{\Omega(E, N \dots)}{k_B} \left(\frac{\partial \Omega}{\partial E}(E, N \dots) \right)^{-1} \Big|_{E=U},$$

Maximising $p_{\text{can}}(E, N \dots)$ shows that it peaks at $E = U(T_{\text{mic}}, N \dots)$, where the bump of the Dirac delta lies. Indeed, equating its derivative to 0, we find

$$\begin{aligned} 0 &\stackrel{!}{=} \frac{\partial}{\partial E} p_{\text{can}}(E) \equiv \left(\frac{\partial \Omega}{\partial E}(E, N \dots) - \frac{1}{k_B T} \Omega(E, N \dots) \right) \frac{e^{-E/k_B T}}{\mathcal{Z}(T_{\text{can}}, N \dots)} \\ \Rightarrow 0 &= \frac{\partial \Omega}{\partial E}(E, N \dots) - \frac{1}{k_B T} \Omega(E, N \dots) \Rightarrow T = T_{\text{mic}}(E, N \dots). \end{aligned}$$

Although the average energy of a microcanonical ensemble and a canonical ensemble do not coincide for $T_{\text{can}} = T_{\text{mic}}$, their median energies do coincide.

It will now be proven that the fundamental equation describing any thermodynamical system ($U(S, N, V \dots)$ or a Legendre transform of it) predicted by microcanonical and canonical ensembles coincide at the thermodynamical limit. To achieve this, the difference between $F_{\text{mic}}(T, N, V \dots)$ and $F_{\text{can}}(T, N, V \dots)$ will be shown to vanish.

The thermodynamical limit takes all extensive variables to infinity, so $N \rightarrow \infty$, $V \rightarrow \infty$ and so on, while keeping intensive variables constant.

$F_{\text{mic}}(T, N, V \dots)$ is the Legendre transform of $S_{\text{mic}}(U, N \dots)$, which we know to be

$$S_{\text{mic}}(U, N \dots) \equiv k_B \log(\Omega(U, N \dots)),$$

using $U_{\text{mic}}(T, N \dots)$ to get the relation between U and its conjugated variable T —well, actually, its conjugated variable is $\beta = 1/k_B T$, but we will use T —. We get

$$F_{\text{mic}}(T, N \dots) \equiv U(T, N \dots) - T S_{\text{mic}}(U(T, N \dots), N \dots).$$

Interestingly, we get the same if we leave both U, T as free variables and choose the U that makes F_{mic} minimal. $F_{\text{can}}(T, N \dots)$ can be directly computed as

$$F_{\text{can}}(T, N \dots) \equiv -k_B T \log(\mathcal{Z}(T, N \dots)).$$

Now we have both, we have to find a way to compare them. Let us begin by solving for $\mathcal{Z}(T, N \dots)$ in the latter equation and substituting it by its definition. We find

$$\begin{aligned} e^{-F_{\text{mic}}(T, N \dots)/k_B T} &= \int_0^\infty \Omega(E, N \dots) e^{-E/k_B T} dE = \int_0^\infty e^{S_{\text{mic}}(E, N \dots)/k_B} e^{-E/k_B T} dE = \\ &= \int_0^\infty e^{-(E - T S_{\text{mic}}(E, N \dots))/k_B T} dE = \dots \end{aligned}$$

By introducing the perturbative parameter δE with

$$E = U(T, N \dots) + \delta E,$$

the function that relates U to the microcanonical temperature with $T_{\text{mic}} = T$. We can rewrite

$$\begin{aligned} E - T S_{\text{mic}} &= U_{\text{mic}} - T S_{\text{mic}} + \delta E - \cancel{T \frac{1}{T} \delta E} + \frac{1}{2T} \frac{\partial T}{\partial E} \delta E^2 + O(\delta E^3) \\ &= F_{\text{mic}} + \frac{\delta E^2}{2T C_V} + O(\delta E^3) \end{aligned}$$

which makes the integral

$$\dots = \int_0^\infty e^{-F_{\text{mic}}(T, N \dots)/k_B T} \exp\left\{-\frac{\delta E^2}{2k_B T^2 C_V}\right\} d(\delta E).$$

Rearranging, we have

$$e^{-(F_{\text{can}}(T, N \dots) - F_{\text{mic}})/k_B T} = \int_0^\infty \exp\left\{-\frac{x^2}{2k_B T^2 C_V}\right\} dx;$$

and, finally, solving the Gaußian integral, we get

$$F_{\text{can}} - F_{\text{mic}} = -k_B T \log\left\{\sqrt{2\pi k_B T^2 C_V}\right\} = -\frac{k_B T}{2} \log\{2\pi k_B T^2 C_V\} \sim \log N.$$

Their difference grows as $\log N$, as the only extensive quantity it depends in, C_V , is only found once, inside the logarithm. Thus, we see that

$$\frac{F_{\text{can}} - F_{\text{mic}}}{F_{\text{can}}} \sim \frac{\log N}{N} \implies \lim_{N \rightarrow \infty} \left\{ \frac{F_{\text{can}} - F_{\text{mic}}}{F_{\text{can}}} \right\} = \lim_{N \rightarrow \infty} \left\{ \frac{\log N}{N} \right\} = 0.$$

B Relevant details of the derivation of the EMME

The EMME is presented without much justification. We shall see, here, a sketch of how the von Neumann equation turns into the EMME, in its most generality, and how the specifics of the case presented in this work (two baths in thermal contact) leads to the version of the EMME that is actually used thereafter.

Let $\hat{\rho}_A$ be the marginal density operator of the system, E be the energy of the bath (there would be independent $E_1, E_2 \dots$ if we had many baths) and let

$$\hat{H}_{\text{int}} = \sum_k \hat{A}_k \otimes \hat{B}_k;$$

then, the EMME [14] can be written like

$$\frac{d}{dt} \hat{\rho}_A(E; t) = -\frac{i}{\hbar} [\hat{H}'_S(E), \hat{\rho}_A(E; t)] + \mathcal{D}(E) \hat{\rho}_A(t). \quad (23)$$

On the left, there is the time derivative of $\hat{\rho}_A(E; t)$, the marginal density operator for A with B having energy E (so $\text{tr}\{\hat{\rho}_A(E; t)\}$ is the probability of B having energy E at t), and on the right, there are two different terms.

The former represents unitary evolution with $\hat{H}'_S(E)$, which is a modified Hamiltonian of A , different for each energy of B , which commutes with the actual \hat{H}_S . The latter,

$$\begin{aligned} \mathcal{D}(E) \hat{\rho}_A = \sum_{\alpha\beta} \sum_{\omega} \left(\frac{\gamma_{\alpha\beta}(E, E + \hbar\omega)}{\Omega_B(E + \hbar\omega)} \hat{\mathcal{A}}_{\alpha}(-\omega) \hat{\rho}_A(E + \hbar\omega) \hat{\mathcal{A}}_{\beta}^{\dagger}(-\omega) \right. \\ \left. - \frac{\gamma_{\alpha\beta}(E + \hbar\omega, E)}{2\Omega_B(E)} \{ \hat{\rho}_A(E), \hat{\mathcal{A}}_{\beta}^{\dagger}(\omega) \hat{\mathcal{A}}_{\alpha}(\omega) \} \right), \end{aligned}$$

is a dissipative term, and represents non-unitarity evolution. All the terms in it depend on the interaction hamiltonian, as

$$\hat{\mathcal{A}}_{\alpha}(\omega) = \sum_k \sum_q \langle k | \hat{A}_{\alpha} | q \rangle | k \rangle \langle q | \delta_{\epsilon_q - \epsilon_k, \hbar\omega}$$

and

$$\gamma_{\alpha\beta}(E, E') \delta_{E', E + \hbar\omega} = \int_{-\infty}^{\infty} \text{tr}_B \left\{ e^{-i\hat{H}_0\tau} \hat{B}_{\alpha}^{\dagger} e^{i\hat{H}_0\tau} \hat{\Pi}_E \hat{B}_{\beta} \hat{\Pi}_{E'} \right\} e^{i\omega\tau} d\tau.$$

Computing these $\gamma_{\alpha\beta}(E, E')$ can be hard, even for simple interaction Hamiltonians. In the II.C section of [14], some ways to work around that are presented. In fact, [14] even shows how the EMME looks without dropping their time-dependence, something that is justified as the so-called Markovian approximation, a very fitting name for the approximation responsible for turning the EMME into a Markovian ODE. That version also drops the secular approximation, the one responsible for making all the terms with mixed ω s vanish.

To get the version of the EMME used in this document to describe the interaction between two baths, let us consider A to be the L bath and B to be the R baths. Then, we have $p(E_L, E_R; t) = \text{tr}\{\hat{\rho}_A(E_L; t) \hat{\Pi}_{E_L}\}$.

The EMME can be used to find the time-derivative of this $p(E_L, E_R; t)$, proceeding in a similar way to the one depicted in Section III of [14]. It is found that

$$\begin{aligned} \frac{d}{dt} p(\varepsilon_k, E - \varepsilon_k; t) = \sum_{q \neq k} \left(\frac{\mathfrak{S}_{kq}(E)}{\Omega_L(\varepsilon_q) \Omega_R(E - \varepsilon_q)} p(\varepsilon_q, E - \varepsilon_q; t) \right. \\ \left. - \frac{\mathfrak{S}_{qk}(E)}{\Omega_L(\varepsilon_k) \Omega_R(E - \varepsilon_k)} p(\varepsilon_k, E - \varepsilon_k; t) \right), \end{aligned} \quad (24)$$

which looks identical to Eq. 17, after defining these $\mathfrak{S}_{kq}(E)$ to be

$$\mathfrak{S}_{kq}(E) \equiv \sum_{\alpha} \sum_{\beta} \gamma_{\alpha\beta}(E - \varepsilon_k, E - \varepsilon_q) \text{tr}\{\hat{A}_{\alpha} \hat{\Pi}_{\varepsilon_q} \hat{A}_{\beta} \hat{\Pi}_{\varepsilon_k}\} \quad (25)$$

for any $k \neq q$. It is immediate to prove they are symmetric and non-negative from this very definition. These $\gamma_{\alpha\beta}$ terms should be time-dependent, which would make the transition rates time-dependent and, thus, would make the ODE no longer describe a Markovian process, but it is actually the Markov approximation mentioned before the one that eliminates that time dependence.

Describing two baths with an equation meant to describe a system and a bath might seem to be little rigorous, even though it can be made completely rigorous.

Another approach, though, could be to describe a system coupled to two baths, so that the system itself describes the means by which the two baths can exchange heat. When deriving the EMME, instead of assuming weak coupling, singular coupling could be assumed instead, see Section XX of [13]. This means, roughly speaking, that the system is taken to be small instead of the coupling strength, which might allow the two baths to interact in ways that are more similar to those described in Section III.

Deriving the corresponding EMME, however, would have been complicated enough as to not be worth trying given the time and resources that we had.

C Mathematical proofs

C.1 Von Neumann entropy is invariant under unitary evolution

$S_{\text{vN}}(\hat{U} \hat{\rho} \hat{U}^{\dagger}) = S_{\text{vN}}(\hat{\rho})$ will now be proven, with $S_{\text{vN}}(\hat{\rho}) \equiv \text{tr}\{\hat{\rho} \log \hat{\rho}\}$ as defined in Eq. 6.

The logarithm of an operator is defined to be the inverse operation to the exponentiation of an operator,

$$\log(e^{\hat{A}}) = \hat{A}, \quad e^{\hat{A}} \equiv \sum_{n=0}^{\infty} \frac{\hat{A}^n}{n!}.$$

It is easy to check that $(\hat{U}^{\dagger} \hat{A} \hat{U})^n = \hat{U}^{\dagger} \hat{A}^n \hat{U}$, as the product of n times $\hat{U}^{\dagger} \hat{A} \hat{U}$ would lead to cancellations of all the $\hat{U}^{\dagger} \hat{U}$ groups in between the \hat{A} s.

This implies $e^{\hat{U}^{\dagger} \hat{A} \hat{U}} = \hat{U}^{\dagger} e^{\hat{A}} \hat{U}$, which in turn implies $\log(\hat{U}^{\dagger} \hat{A} \hat{U}) = \hat{U}^{\dagger} \log(\hat{A}) \hat{U}$ as

$$\log(\hat{U}^{\dagger} e^{\hat{A}} \hat{U}) = \log(e^{\hat{U}^{\dagger} \hat{A} \hat{U}}) = \hat{U}^{\dagger} \hat{A} \hat{U} = \hat{U}^{\dagger} \log(e^{\hat{A}}) \hat{U}.$$

Thus, if an operator evolves unitarily, its logarithm also evolves unitarily. This makes

$$S_{\text{vN}}(\hat{U}\hat{\rho}\hat{U}^\dagger) = \text{tr}\{\hat{U}^\dagger\hat{\rho}\hat{U}\hat{U}^\dagger \log \hat{\rho}\hat{U}\} = \text{tr}\{\hat{\rho} \log \hat{\rho}\} = S_{\text{vN}}(\hat{\rho}),$$

by virtue of the cyclic property of the trace, which completes the proof. \blacksquare

The analogous proof for Gibbs entropy would change the Hilbert space for the phase space, and consequently, $\hat{\rho}$ for $\rho(q, p)$ and unitary transformations for volume-preserving canonical transformations. The result that is reached is the same one.

C.2 The eigenvalues of W are real

It will now be proven that any endomorphism $M = \mathfrak{S} \circ D$ over a finite space, with \mathfrak{S} symmetric and D positive definite, only has real eigenvalues.

As D can be diagonalised and all its eigenvalues are ≥ 0 —this is directly implied from the positive definite condition—, it has a canonical square root, namely, the endomorphism whose eigenvalues are the square root of D 's in any basis D is diagonal.

The characteristic polynomial of M is

$$\begin{aligned} p_M(\lambda) &= \det(\mathbb{I} - \lambda M) = \det(\mathbb{I} - \mathfrak{S}D) = \det(\mathbb{I} - \mathfrak{S}D) \sqrt{\frac{\det(D)}{\det(D)}} = \\ &= \det(D^{1/2}) \det(\mathbb{I} - \mathfrak{S}D) \det(D^{-1/2}) = \det(\mathbb{I} - D^{1/2} \mathfrak{S} D^{1/2}); \end{aligned}$$

hence, it equals the characteristic polynomial of $D^{1/2} \mathfrak{S} D^{1/2}$. As it is symmetric, all its eigenvalues are real by virtue of the spectral theorem. \blacksquare

C.3 Inequality relating the different definitions of entropy

As stated in Eq. 21, the simulations run on the EMME seem to imply that

$$S_{\text{can}}(t) \geq S_{\text{obs}}(t), \text{ and } S_{\text{obs}}(t) \geq S_{\text{mic}}(t)$$

are inequalities that hold for most, if not all, possible states.

The former inequality is actually true, it can be proven from the fact that only a canonical ensemble state makes S_{obs} maximal for each bath, so S_{can} is actually defined to be the greatest possible observational entropy for a given energy (*).

The latter, though, is not true for *every* possible state. Experimenting with the formulae for S_{obs} and S_{mic} show that the situations in which Boltzmann entropy is greater are very few, as their values coincide for microcanonical ensemble states and S_{obs} is locally decreasing before them and increasing after them, whereas S_{mic} is locally constant around them. Proving this would be challenging, unfortunately.

The statement marked as (*) will now be proven. The function of (p_1, \dots, p_n)

$$S_{\text{obs}}(E_1, \dots, E_n) \equiv k_B \sum_k p_k \log \left(\frac{\Omega(E_k)}{p_k} \right)$$

with respect to, respectively, the constraints of unitarity and energy conservation, which ought to be given the Lagrange multipliers λ and ξ ,

$$\sum_k p_k \stackrel{!}{=} 1, \quad \sum_k p_k E_k \stackrel{!}{=} U(T, N, \dots).$$

Now, proceeding as usual,

$$0 \stackrel{!}{=} \sum_k \frac{\partial}{\partial p_k} \left[k_B p_k \log \left(\frac{\Omega(E_k)}{p_k} \right) + \lambda p_k + \xi p_k E_k \right].$$

The equality must be fulfilled term by term, so we can write

$$\begin{aligned} 0 &\stackrel{!}{=} \frac{\partial}{\partial p_k} p_k \left[k_B \log \left(\frac{\Omega(E_k)}{p_k} \right) + \lambda + \xi E_k \right] \implies k_B = k_B \log \left(\frac{\Omega(E_k)}{p_k^*} \right) + \lambda + \xi E_k \\ \implies \frac{\Omega(E_k)}{p_k^*} &= e^{1 - (\lambda + \xi E_k)/k_B} \implies p_k^* = \Omega(E_k) e^{\lambda/k_B - 1} e^{\xi E_k/k_B}. \end{aligned}$$

The Lagrange multiplier λ can be directly determined from the unitarity condition, as

$$1/e^{\lambda/k_B - 1} = \sum_k \Omega(E_k) e^{\xi E_k/k_B}$$

which I claim to be equal to $\mathcal{Z}(T_{\text{can}}, \dots)$. With these p_k^* , the maximal observational entropy for a given energy U looks like

$$\begin{aligned} S_{\text{obs}}(p_1, \dots, p_n) &\equiv \sum_k \frac{\Omega(E_k) e^{-\xi E_k/k_B}}{\mathcal{Z}(T_{\text{can}}, \dots)} [k_B \log \mathcal{Z}(T_{\text{can}}, \dots) - \xi E_k] \\ &= k_B \log \mathcal{Z}(T_{\text{can}}, \dots) - \xi U \end{aligned}$$

Applying the following thermodynamical identity, we can determine ξ in terms of $\beta = 1/k_B T_{\text{can}}$,

$$\beta = \frac{1}{k_B} \frac{\partial S_{\text{obs}}}{\partial U} = -\frac{\xi}{k_B},$$

which justifies the choice of notation for $\mathcal{Z}(T_{\text{can}}, \dots)$.

As a final note, to sum everything up, it has been found that the probability distribution that makes the observational entropy of any one bath maximal, for a given energy U , are canonical ensemble probabilities,

$$p_k^* = \frac{\Omega(E_k) e^{-\beta E_k}}{\mathcal{Z}(T_{\text{can}}, \dots)}.$$

As S_{can} is defined to be precisely the observational entropy of these states, $S_{\text{can}} \geq S_{\text{obs}}$ for a same T_{can}^* .

D Python code

This code implements Runge-Kutta 4 to solve the EMME. It uses Runge-Kutta 4 instead of Euler implicit because it is meant to be ready to allow the transition rates to depend on time (and, thus, not represent a Markovian process anymore).

The implementation is done manually and not with the library *SciPy* because I would have to turn a matrix with variable dimensions into a single vector and back :(

(All of this is Python v. 3)

```
import math
import time
import numpy as np
import matplotlib.pyplot as plt

Ne = 24      # Number of energy bands in each bath
delta = 1    # Bandwidth of energy of each band.

Nt = 2**13   # Number of time-steps.
Tt = 2**6    # Total time.

dt = Tt/Nt   # Duration of a time-step.

Time = np.zeros(Nt)
for t in range(Nt):
    Time[t] = t*dt

H = [delta*x for x in range(Ne)] # Coarse-grained Hamiltonian.
V = np.ones((2, Ne))            # Degeneracies.

for i in range(Ne):
    V[0][i] = math.ceil((3*(i**1) + 1)/2)
    V[1][i] = math.ceil(2*(i**1 + i + 1)/2)

p = np.zeros((Nt, Ne, Ne))
S = 12

TL = 12 # Initial temperatures.
TR = 16

# Thermodynamics. Temperature is computed via Newton-Raphson.

def pi(b, syst):
    Z = 0
    R = []
    for i in range(Ne):
        Z += V[syst][i]*np.exp(-b*H[i])

    for i in range(Ne):
        R.append(V[syst][i]*np.exp(-b*H[i])/Z)

    return(R)
```

```

def temp(E, syst, b0):
    b = b0
    for i in range(4):
        num = 0
        den = 0
        for j in range(Ne):
            num += H[j]*pi(b, syst)[j]
            den += (H[j]**2)*pi(b, syst)[j]
        b += - (E-num)/den
    if b == 0: return(float('inf'))
    else: return(b)

# Defining the ODE.

W = []
for i in range(2*Ne-1):
    if i < Ne:
        W.append(S*np.ones((1 + i, 1 + i)))
    else:
        W.append(S*np.ones((2*Ne - 1 - i, 2*Ne - 1 - i)))

for i in range(2*Ne-1):
    for j in range(len(W[i][0])):
        W[i][j][j] = 0
        for k in range(len(W[i][0])):
            if k != j:
                mnm = 0
                if i > Ne - 1:
                    mnm = i - Ne + 1
                W[i][k][j] *= 1/(V[0][i-j-mnm]*V[1][j+mnm])
                W[i][j][j] += -W[i][k][j]

def ODE(y):
    out = np.zeros((Ne, Ne))
    for i in range(Ne):
        for j in range(Ne):
            mnm = 0
            if i + j > Ne - 1:
                mnm = i + j - Ne + 1
            for k in range(mnm, mnm + len(W[i+j][0])):
                s = i + j
                d = i + j - k
                out[i][j] += W[s][j-mnm][k-mnm] * y[d][k]

    return(out)

```

```

# Setting up and solving. The ODE is solved via RK-4.

K = np.zeros((4, Ne, Ne))

def solve(Tl, Tr):
    for i in range(Ne):
        for j in range(Ne):
            p[0][i][j] = pi(1/Tl, 0)[i] * pi(1/Tr, 1)[j]

    for t in range(Nt-1):
        K[0] = ODE(p[t])
        K[1] = ODE(p[t] + (dt/2)*K[0])
        K[2] = ODE(p[t] + (dt/2)*K[1])
        K[3] = ODE(p[t] + dt*K[2])

        for i in range(Ne):
            for j in range(Ne):
                p[t+1][i][j] =
                    p[t][i][j]+(dt/6)*(K[0][i][j]
                        +2*K[1][i][j]+2*K[2][i][j]+K[3][i][j])

    if t%64 == 0: time.sleep(0.05)

solve(TL, TR)

print('simulation finished')

# Energies, temperatures and entropies.
# First, energies are computed into Q, and the inverse temperatures
# are computed into B.

QL = np.zeros((Nt))
QR = np.zeros((Nt))

BL = np.zeros((Nt))
BR = np.zeros((Nt))
BL[-1] = 1/TL
BR[-1] = 1/TR

for t in range(Nt):
    for i in range(Ne):
        for j in range(Ne):
            QL[t] += H[i]*p[t][i][j]
            QR[t] += H[j]*p[t][i][j]

```

```

BL[t] = temp(QL[t], 0, BL[t-1])
BR[t] = temp(QR[t], 1, BR[t-1])

if t%64 == 0: time.sleep(0.05)

print('energies computed')

# Now, entropies are computed into S.

SL = np.zeros((3,Nt)) # 0 observacional, 1 Gibbs.
SR = np.zeros((3,Nt))
I = np.zeros((Nt))

trL = np.zeros((Nt, Ne)) # These are the marginal probabilites.
trR = np.zeros((Nt, Ne))

for t in range(Nt):
    for i in range(Ne):
        for j in range(Ne):
            trR[t][i] += p[t][i][j]
            trL[t][j] += p[t][i][j]

for t in range(Nt):
    argL = 0
    argR = 0
    for i in range(Ne):
        if trR[t][i] != 0:
            SL[0][t] += trR[t][i] * np.log(V[0][i]/trR[t][i])
        if trL[t][i] != 0:
            SR[0][t] += trL[t][i] * np.log(V[1][i]/trL[t][i])

    argL += V[0][i]*np.exp(-H[i]*BL[t])
    argR += V[1][i]*np.exp(-H[i]*BR[t])

    for j in range(Ne):
        if p[t][i][j] != 0:
            I[t] += p[t][i][j] * np.log(p[t][i][j]/(trR[t][i]
            * trL[t][j]))

    SL[1][t] += np.log(argL) + (BL[t])*QL[t]
    SR[1][t] += np.log(argR) + (BR[t])*QR[t]

print('entropies computed')

```

```

# Plotting functions. "probs" plots the probs. with the most populated
# subspace of states that add up to a same energy. "energy", "temp" and "b"
# plot energy, temperature and Boltzmann factor of both baths. "entropy"
# plots canonical, Boltzmann and observational entropies, and
# "corr" plots the mutual information.

def plot_probs():
    plt.xlim(0, Nt*dt)
    for i in range(Ne):
        plt.plot(Time, [p[i][Ne-1-i] for p in p])

def plot_energy():
    plt.xlim(0, Nt*dt)

    plt.plot(Time, QL, color = 'r', label = 'EL')
    plt.plot(Time, QR, color = 'b', label = 'ER')
    plt.xlabel('Time')
    plt.ylabel('Energy')
    plt.legend()

def plot_temp():
    plt.xlim(0, Nt*dt)

    plt.plot(Time, 1/BL, color = 'r', label = 'TL')
    plt.plot(Time, 1/BR, color = 'b', label = 'TR')
    plt.xlabel('Time')
    plt.ylabel('Temperature')

    plt.plot(Time, [V[0][int(QL[t]/delta)]*2*delta/(V[0][int(QL[t]/delta)
        +1]-V[0][int(QL[t]/delta)-1]) for t in range(Nt)], color = 'r')
    plt.plot(Time, [V[1][int(QR[t]/delta)]*2*delta/(V[1][int(QR[t]/delta)
        +1]-V[1][int(QR[t]/delta)-1]) for t in range(Nt)], color = 'b')
    plt.legend()

    print(TL, TR, ((1/BL[-1])+(1/BR[-1]))/2, (1/(BL[-1])-(1/BR[-1]))/2)

def plot_b():
    plt.xlim(0, Nt*dt)

    plt.plot(Time, BL, color = 'r')
    plt.plot(Time, BR, color = 'b')
    plt.xlabel('Time')
    plt.ylabel('Boltzmann factor')

    print(1/TL, 1/TR, (BL[-1]+BR[-1])/2, (BL[-1]-BR[-1])/2)

```

```

def plot_entropy():
    plt.xlim(0, Nt*dt)

    plt.plot(Time, [SL[0][t]+SR[0][t]-I[t] for t in range(Nt)],
             color = 'g', label = 'Sobs')
    plt.plot(Time, [SL[1][t]+SR[1][t] for t in range(Nt)],
             color = 'r', linestyle = 'dashed', label = 'Scan')
    plt.xlabel('Time')
    plt.ylabel('Entropy')

    plt.plot(Time, [np.log(V[0][int(QL[t]/delta)])+np.log(V[1][int(QR[t]/delta)])
                    for t in range(Nt)], color = 'b')
    plt.legend()

def plot_corr():
    plt.xlim(0, Nt*dt)
    plt.ylim(0, max(I))
    plt.xlabel('Time')
    plt.ylabel('Mutual information')

    plt.plot(Time, I, color = 'yellow')

def plot_dif():
    plt.xlim(0, Nt*dt)

    plt.plot(Time, [0]+[SL[0][t]+SR[0][t]-I[t]-SL[0][t-1]
                       -SR[0][t-1]+I[t-1] for t in range(1, Nt)], color = 'g')

```

Bibliography

- [1] Derek Muller and Andrea Morello. *Transistors & the End of Moore's Law*. Video on youtu.be/rtI5wRyHpTg, 2013.
- [2] Diana Vilela et al. *Graphene-Based Microbots for Toxic Heavy Metal Removal and Recovery from Water*. 2016. DOI: [10.1021/acs.nanolett.6b00768](https://doi.org/10.1021/acs.nanolett.6b00768).
- [3] Suping Li et al. *A DNA nanorobot functions as a cancer therapeutic in response to a molecular trigger in vivo*. 2018. DOI: [10.1038/nbt.4071](https://doi.org/10.1038/nbt.4071).
- [4] Joel L. Lebowitz. *Boltzmann's entropy and time's arrow*. 1993. DOI: [10.1063/1.881363](https://doi.org/10.1063/1.881363).
- [5] *Entropy Production in Oscillating Chemical Systems*. 1985. DOI: [10.1515/zna-1985-0903](https://doi.org/10.1515/zna-1985-0903).
- [6] Manuel A. Gracia-Naval et al. *Probing the oscillating Belousov-Zhabotinskii reaction with micrometer-sized electrodes: the effect of C, Pt, and Au*. 2019. DOI: [10.20964/2019.08.89](https://doi.org/10.20964/2019.08.89).
- [7] Juan Miguel Rubí and Antonio Pérez-Madrid. *Inertial Effects in Non-Equilibrium Thermodynamics*. 1998. arXiv: [cond-mat/9807284](https://arxiv.org/abs/cond-mat/9807284).
- [8] Joel L. Lebowitz. *Boltzmann's entropy and time's arrow*. 1993. DOI: [10.1063/1.881363](https://doi.org/10.1063/1.881363).
- [9] Jonathan Bain. *Boltzmann Entropy, Gibbs Entropy, Shannon Information*. 2020.
- [10] Emili Bagan. *Notes d'Informació i Computació Quàntiques*. 2007.
- [11] Dominik Šafránek, Anthony Aguirre, and J. M. Deutsch. *Classical dynamic coarse-grained entropy and comparison with the quantum version*. 2019. arXiv: [1905.03841](https://arxiv.org/abs/1905.03841).
- [12] Philipp Strasberg and Andreas Winter. *Entropy production in quantum systems: a unifying picture*. 2020. arXiv: [2002.08817](https://arxiv.org/abs/2002.08817).
- [13] Heinz-Peter Breuer and Francesco Petruccione. *The Theory of Open Quantum Systems*. Addison-Wesley Professional, 2002.
- [14] Andreu Riera-Campenya, Anna Sanpera, and Philipp Strasberg. *Quantum systems correlated with a finite bath: nonequilibrium dynamics & thermodynamics*. 2020. arXiv: [2008.02184](https://arxiv.org/abs/2008.02184).