

Tuesday evening lectures:

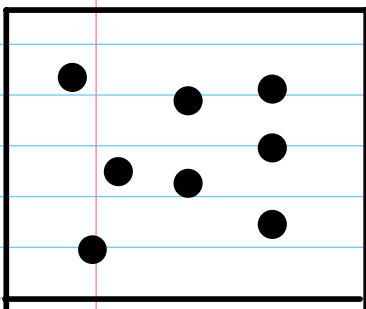
Non-equilibrium thermodynamics of quantum systems

1) Classical Thermodynamics

- Born in the XIX-th century, **thermodynamics** was motivated by the technological progress of the Industrial Revolution.
- At its center is the invention of the **heat engine**, which operates by converting **heat** (energy flow between two systems at \neq temperatures) and **work** (energy flow that generates motion).
- Scientists: **Sadi Carnot** (Heat engine), **James Joule** (nature of heat and work), **Robert Mayer**, **Hermann von Helmholtz**, **Rudolph Clausius**, **Lord Kelvin** (Laws of thermodynamics)...

1.1) The Laws of Thermodynamics

- **Classical thermodynamics** is a theory of energy conversion in macroscopic systems. The prime example is a gas of particles, characterized by macroscopic variables, called **state variables**, such as volume, pressure, temperature or particle number (V, P, T, N).



$$\text{State} = \{V, P, T, N\}.$$

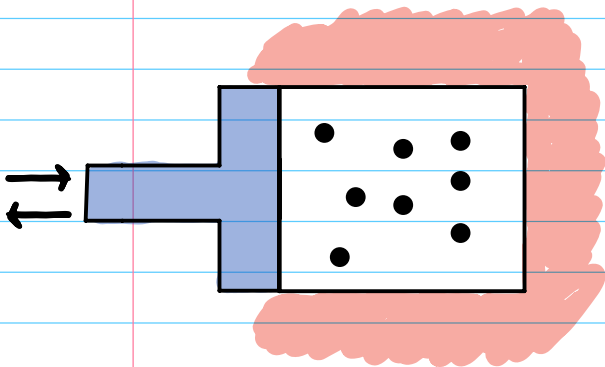
$V \equiv$ Volume

$P \equiv$ Pressure

$T \equiv$ Temperature

$N \equiv$ Number of particles

- The state of the system is changed by changing the state variables, e.g. compressing / expanding the gas with a piston, heating / cooling with a thermal reservoir.
- The energy $E \equiv E(V, P, T, N)$ and entropy $S \equiv S(V, P, T, N)$ are called **state functions** and depend on the state of the system. They change when the state changes:



$$T' = T + \Delta T \quad (\text{Reservoir})$$

$$V' = V + \Delta V \quad (\text{Piston})$$



$$\Delta E \equiv \text{Energy change}$$

$$\Delta S \equiv \text{Entropy change}$$

First law of thermodynamics

The change in energy can be written as:

$$\Delta E = Q + W, \quad Q \equiv \text{Heat}$$

$$W \equiv \text{Work}$$



- We use the convention $Q, W > 0$ for **heat (work)** entering the system. Note that for a **cyclic process** $\Delta E = 0$, since E is state function, but $Q, W \neq 0$. **Heat and work are NOT** state functions.

- It is tempting to interpret the first law as a simple statement of energy conservation. This is not true, because the physical meaning of heat and work are only complete through the second law.

Second law of thermodynamics

The change in entropy of a system in contact with a **Reservoir** at temperature T obeys the inequality:

$$\Delta S \geq Q/T \quad [\text{Clausius inequality, 1865}]$$

or equivalently as an equality:

$$\Delta S = \Sigma + Q/T, \quad \Sigma \geq 0 \quad (\text{Entropy production})$$

Σ is a measure of **irreversibility** of physical processes, with $\Sigma = 0$ for **reversible processes**. ■

- The entropy flow is usually defined as:

$$\Delta S_R = -Q/T \quad (\text{Entropy change in the reservoir}).$$

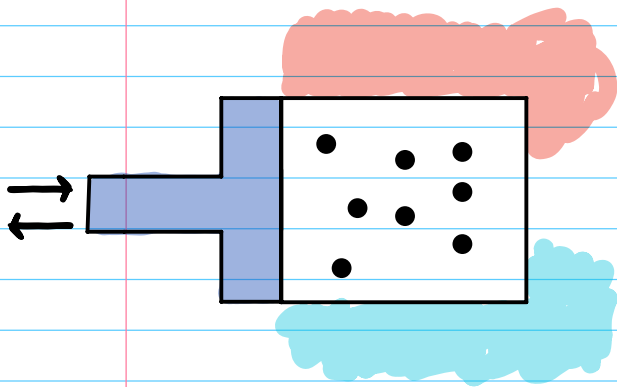
- Therefore, **heat** is that part of the energy associated with an entropy flow. **Work** is what remains and has no entropy flow associated.

- For a **cyclic process** $\Delta E = \Delta S = 0$ and thus:

$$\sum = -Q/T = W/T \geq 0.$$

The system has to **expel heat** to its exterior in any cyclic process. Moreover, it is **impossible to extract work** from such a process.

- Consider a system connected to **multiple reservoirs**:



T_H : **Hot reservoir**

T_C : **Cold reservoir**

First law : $\Delta E = Q_H + Q_C + W$.

Second law : $\Delta S = \sum + \frac{Q_H}{T_H} + \frac{Q_C}{T_C}$.

If the process is cyclic $\Delta E = \Delta S = 0$, we have:

First law : $Q_C = -W - Q_H$.

Second law : $\sum = -\frac{Q_H}{T_H} - \frac{Q_C}{T_C} =$

$$= -\frac{Q_H}{T_H} - \frac{(-W - Q_H)}{T_C} = Q_H \left(\frac{1}{T_C} - \frac{1}{T_H} \right) + \frac{W}{T_C}$$

Entropy production for a cyclic process between two reservoirs

$$\Sigma = Q_H \left(\frac{1}{T_c} - \frac{1}{T_H} \right) + \frac{W}{T_c} \geq 0 .$$

- This formula has two very important implications:

The efficiency of energy conversion

Suppose I want to extract an amount of work - W from the heat flowing from the hot reservoir into system $Q_H > 0$. I can define the efficiency:

$$\eta \equiv - \frac{W}{Q_H} \quad (\text{Efficiency of heat-to-work conversion}).$$

The entropy production tells me that:

$$\Sigma = Q_H \left(\frac{1}{T_c} - \frac{1}{T_H} \right) + \frac{W}{T_c} = \frac{1}{T_c} \left[Q_H \left(1 - \frac{T_c}{T_H} \right) + W \right]$$

$$= \frac{Q_H}{T_c} \left[\left(1 - \frac{T_c}{T_H} \right) + \frac{W}{Q_H} \right]$$

$$= \frac{Q_H}{T_c} (\eta_c - \eta) \geq 0 .$$

$$\eta_c \equiv 1 - \frac{T_c}{T_H}$$

(Carnot Efficiency).

Thus, the efficiency of energy conversion is limited by Carnot efficiency. Entropy production thus has very practical implications.

The flow of heat

In the absence of work $W = 0$, we have:

First law: $Q_H = -Q_C$

Second law: $\Sigma = Q_H \left(\frac{1}{T_C} - \frac{1}{T_H} \right) \geq 0$.

If $T_C < T_H$, then $Q_H \geq 0 \Leftrightarrow Q_C \leq 0$. In other words: heat flows from hot to cold.

1.2) Statistical Mechanics

- Classical thermodynamics makes no reference to the microscopic state of the system, which would involve specifying the energy, momenta and positions of the particles that compose it.
- Statistical mechanics establishes a bridge between classical mechanics of particles and thermodynamics.

- The central idea is the **statistical ensemble**: a collection of identical systems, each one representing a different microscopic state compatible with the macroscopic state. Each microscopic state (microstate) is assigned a probability.

Gibbs - Shannon Entropy

Consider a system with N different microstates, each with a given energy $\{E_i\}_{i=1}^N$. The Gibbs - Shannon entropy of the system is given by:

$$S = -k_B \sum_{i=1}^N P_i \log P_i \geq 0,$$

where P_i is the probability of microstate i and $\sum_{i=1}^N P_i = 1$. ■

- The **Gibbs - Shannon entropy** is, at first sight, completely disconnected from the thermodynamic entropy we have seen before. It says nothing about energy, heat or temperature.
- It is a purely **informational quantity**, representing the ignorance about the microscopic state; or equivalently, the information gained by knowing the microstate with certainty.

Gibbs - Boltzmann distribution

Suppose we know the average energy of the system

$$\langle E \rangle = \sum_{i=1}^N P_i E_i \quad (\text{Macroscopic constraint}).$$

Then the distribution $\{P_i\}_{i=1}^N$ that maximizes the Gibbs-Shannon entropy under the constraint of average energy is:

$$P_i = Z^{-1} e^{-\beta E_i} \quad (\text{Gibbs - Boltzmann distribution}).$$

$$\text{with } \beta = 1/(k_B T) \text{ and } Z = \sum_{i=1}^N e^{-\beta E_i}. \quad \blacksquare$$

- This distribution represents a system in **thermal equilibrium** at temperature T , about which we know only its average energy. Since its entropy is maximal, we have maximum ignorance about its microscopic state. In this sense, the thermal state is maximally random.
- So far, we have only dealt with system in thermal equilibrium. In order to describe the **evolution** of the system (**dynamics**) as it exchanges heat and work, we need equations of motion for the system itself. **Quantum physics** provides these equations, allowing us to **non-equilibrium thermodynamics**.

2) Quantum Physics

- **Quantum physics** was developed from 1900 - 1930s to explain the properties of energy and matter that cannot be explained by classical reasoning.
- At its core is the following idea: **energy and matter** (particles) **cannot be described by specific microscopic states** (position, energy, momentum), but instead by a **superpositions** of such microstates.
- **Superpositions are physical**: we have to assume that they exist in order to explain the properties of matter and energy. However, they are never directly observed in experiments: we always observe a specific microstate. This gives rise to interesting questions in **quantum foundations**.
- **Quantum entanglement** is a specific type of **superposition** between two or more quantum systems. Its application lead to **quantum information science**, with Nobel Prizes awarded in 2022.

2.1) Quantum Statistical Mechanics

Density operator

- We consider a **complex Hilbert space** \mathcal{H} and linear operators acting on that space. The **quantum state** is generally described by a **density operator**:

$$\rho = \sum_{\alpha=1}^M P_{\alpha} |t_{\alpha}\rangle \langle t_{\alpha}| \quad , \quad \sum_{\alpha=1}^M P_{\alpha} = 1 .$$

- The **density operator** is the quantum generalization of the classical ensemble (**quantum statistical ensemble**), where M is the dimension of the ensemble.
- The set $\{ |\psi_a\rangle\langle\psi_a| \}_{a=1}^M$ are called projectors. They simply mean this: **each state vector** $|\psi_a\rangle \in \mathcal{H}$ (sometimes called the wavefunction) **occurs with probability** P_a .
- $\rho \geq 0$ (Positive eigenvalues)
 $\text{Tr}[\rho] = 1$ (Sum of eigenvalues is 1) } Density operator is a (quantum) probability distribution.
- $\text{Tr}[\rho^2] \leq 1$. The equality holds if and only if $\rho = |\psi\rangle\langle\psi|$ (**pure state**). Otherwise, the state is called a **mixed state**.

Observables

- An **observable** is a linear operator A obeying $A^\dagger = A$, i.e. with **real eigenvalues**. They represent the **physical properties** of a quantum system.

$$\langle A \rangle = \text{Tr}[A\rho] \quad , \quad \text{Average value of } A \text{ in the quantum state } \rho.$$

- **Energy operator / Hamiltonian**

$$H|i\rangle = E_i|i\rangle \quad , \quad \{|i\rangle\}_{i=1}^N : \text{energy eigenstates (microstates)}$$

$$\{E_i\}_{i=1}^N : \text{energies of each state.}$$

Dynamics - von Neumann equation

- The time-evolution of the density operator is given by the von-Neumann equation.

von Neumann equation

An isolated/closed quantum system evolves according to

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar} [H(t), \rho(t)] \quad (\text{von Neumann equation}),$$

where $H(t)$ is the Hamiltonian of the system at time t and $[\cdot, \cdot]$ is the commutator. The solution is:

$$\rho(t) = U(t, t_0) \rho(t_0) U^\dagger(t, t_0) \quad (\text{Unitary evolution})$$

$$U(t, t_0) = T \exp \left[-\frac{i}{\hbar} \int_{t_0}^t H(t') dt' \right].$$

where $U(t, t_0)$ is the unitary evolution operator obeying $U(t, t_0) U^\dagger(t, t_0) = U^\dagger(t, t_0) U(t, t_0) = \mathbb{1}$ and T is the time-ordering operator.



Example

- Consider a **time-independent Hamiltonian** H and an initial state given by:

$$\rho(t_0) = \sum_{\alpha} P_{\alpha} |\psi_{\alpha}(t_0)\rangle \langle \psi_{\alpha}(t_0)| .$$

- We expand $|\psi_{\alpha}(t_0)\rangle$ in the eigenbasis of H :

$$|\psi_{\alpha}(t_0)\rangle = \sum_i c_i^{\alpha}(t_0) |i\rangle , \text{ where } c_i^{\alpha}(t_0) \in \mathbb{C} \text{ are}$$

complex coefficients. Each state vector is therefore a **superposition of energy eigenstates** (microstates). The density operator is then:

$$\begin{aligned} \rho(t_0) &= \sum_{\alpha} \sum_{i,i'} (c_i^{\alpha})^* c_{i'}^{\alpha} P_{\alpha} |i'\rangle \langle i| = \\ &= \sum_{i,i'} \left[\sum_{\alpha} (c_i^{\alpha})^* c_{i'}^{\alpha} P_{\alpha} \right] |i'\rangle \langle i| = \\ &= \sum_{i,i'} \rho_{i'i}(t_0) |i'\rangle \langle i| , \text{ where:} \end{aligned}$$

$$\rho_{i'i}(t_0) \equiv \sum_{\alpha} (c_i^{\alpha})^* c_{i'}^{\alpha} P_{\alpha} \left. \vphantom{\sum_{\alpha}} \right\} \text{Matrix elements of the density operator}$$

- The evolution can then be computed by using:

$$U(t, t_0) |i'\rangle = e^{-\frac{i}{\hbar} H(t-t_0)} |i'\rangle = e^{-\frac{i}{\hbar} E_{i'}(t-t_0)} |i'\rangle .$$

$$\rho(t) = \sum_{i,i'} c_{ii}(t) |i'\rangle\langle i|, \text{ where:}$$

$$c_{ii}(t) = e^{\frac{-i(E_{i'} - E_i)(t-t_0)}{\hbar}} c_{ii}(t_0).$$

- The **diagonal elements** $i = i'$ represent **probabilities** to find the system in a given energy microstate. They do not evolve in time.
- The **off-diagonal elements** $i \neq i'$ represent **superpositions** and have no classical analog: they are purely quantum in nature and evolve in time; a.k.a. **coherences**.

von Neumann entropy

- The only ingredient left is a notion of **entropy** for quantum states. This is achieved through the von Neumann entropy:

Entropy of a quantum state

The generalization of the Gibbs-Shannon entropy to quantum systems is given by the **von Neumann entropy**

$$S(\rho) = -k_B \text{Tr}[\rho \log \rho] \geq 0.$$

- 1) $S(\rho)$ is **invariant under unitary evolution**.
- 2) $S(\rho) = 0$ if ρ is a pure state.
- 3) $S(\rho)$ is equivalent to G-S entropy if ρ is diagonal in the energy eigenbasis. ■

- Just like the Gibbs-Shannon entropy, the von Neumann entropy is a **purely informational quantity**: it represents the lack of knowledge about the actual quantum state.
- The entropy of a quantum system does not change under **unitary evolution**, which is totally **reversible**. This does not mean, however, that there are no irreversible processes happening.

Quantum Relative Entropy

- Consider the difference between the von Neumann entropy of two density operators ρ and σ .

$$\begin{aligned}
 S[\rho] - S[\sigma] &= -k_B \text{Tr} [\rho \log \rho] + k_B \text{Tr} [\sigma \log \sigma] \\
 &= -k_B \text{Tr} [\rho \log \rho - \sigma \log \sigma - \underbrace{\rho \log \sigma + \sigma \log \rho}_0] \\
 &= -k_B \text{Tr} [\rho (\log \rho - \log \sigma) - (\sigma - \rho) \log \sigma] \\
 &= -D[\rho|\sigma] - k_B \text{Tr} [(\sigma - \rho) \log \sigma] \quad \text{Thus:}
 \end{aligned}$$

$$\begin{aligned}
 S[\rho] - S[\sigma] &= \\
 &= -D[\rho|\sigma] - k_B \text{Tr} [(\sigma - \rho) \log \sigma], \quad \text{where:}
 \end{aligned}$$

Quantum relative entropy

$$D[\rho|\sigma] = k_B \text{Tr} [\rho (\log \rho - \log \sigma)] \geq 0$$

- The relative entropy can be shown to always be **non-negative** and vanishes if $\rho = \sigma$. It is a good candidate for **entropy production** as we will see.

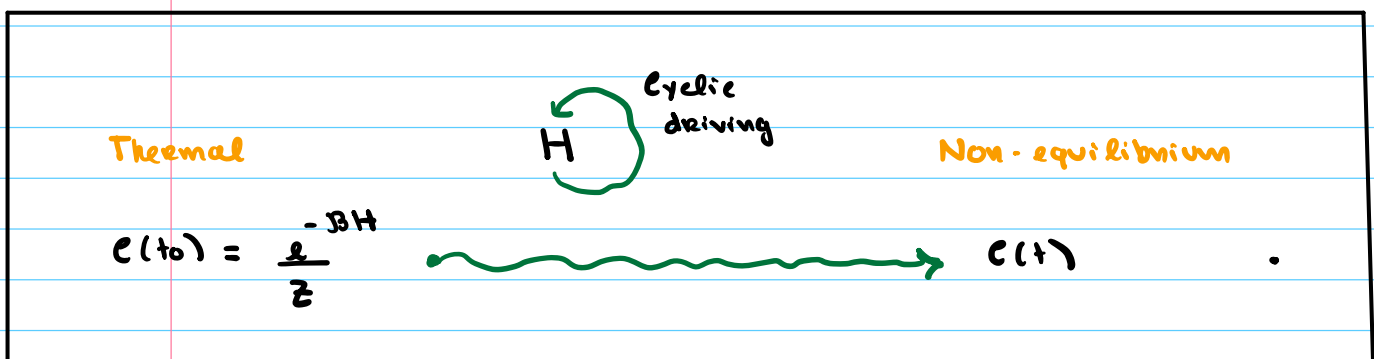
Driving a thermal system out of equilibrium

Suppose we prepare a quantum system at time t_0 in a **thermal state** given by:

$$\rho(t_0) = Z^{-1} e^{-\beta H}, \quad \text{where } H \text{ is the Hamiltonian}$$

This Hamiltonian is then changed in time according to:

$$H(t) = \begin{cases} H, & t \geq t_0 + z \\ \text{arbitrary}, & t_0 + z > t > t_0 \\ H, & t \leq t_0 \end{cases}, \quad z \equiv \text{Driving period.}$$



The change in energy of the system after the driving period z is given by:

$$\Delta E = \text{Tr}[H \rho(t)] - \text{Tr}[H \rho(t_0)]$$

$$= \text{Tr} [H (\rho(t) - \rho(t_0))] .$$

The change in von Neumann entropy is 0 because the evolution is unitary.

$$\Delta S = S [\rho(t)] - S [\rho(t_0)] = 0 .$$

However:

$$\Delta S = - D [\rho(t) | \rho(t_0)] - k_B \text{Tr} [(\rho(t) - \rho(t_0)) \log \rho(t_0)] .$$

Noting that:

$$\log \rho(t_0) = \log \left[\frac{e^{-\beta H}}{Z} \right] = \log \left[e^{-\beta H - \log Z} \right] =$$

$$= -\beta H - \log Z , \quad \text{we have:}$$

$$\text{Tr} [(\rho(t) - \rho(t_0)) \log \rho(t_0)] =$$

$$- \log Z \text{Tr} [\rho(t) - \rho(t_0)] - \beta \text{Tr} [H (\rho(t) - \rho(t_0))]$$

$$= -\beta \Delta E . \quad \text{Therefore:}$$

$$\Delta S = - D [\rho(t) | \rho(t_0)] + \frac{\Delta E}{T} = 0 \Rightarrow$$

$$\Delta E = T D [\rho(t) | \rho(t_0)]$$

$$= k_B T \text{Tr} [\rho(t) (\log \rho(t) - \log \rho(t_0))] \geq 0 .$$

- It is impossible to extract energy from a (closed) thermal state using a finite driving.
- A finite driving, where the initial and final Hamiltonian are the same, is the quantum equivalent of a cyclic process. There is however a crucial distinction: the final state of the system $\rho(t)$ is a non-equilibrium state!
- The energy change ΔE induced by time-dependent driving is associated with work, since there is no reservoir present during the evolution (no entropy flow).

$W \equiv \Delta E > 0$ Impossible to extract work from a thermal state in a cyclic process.

2.2) Open Quantum Systems

- A quantum system is, in practice, open to its environment. The environment is usually too complicated to describe microscopically and we are only interested in the system.
- The theory of open quantum system describes how a quantum system evolves when it interacts w/ the environment. The evolution is not unitary, but is given by a quantum dynamical map.