



General Physics I

Lect.23 Statistical Thermodynamics

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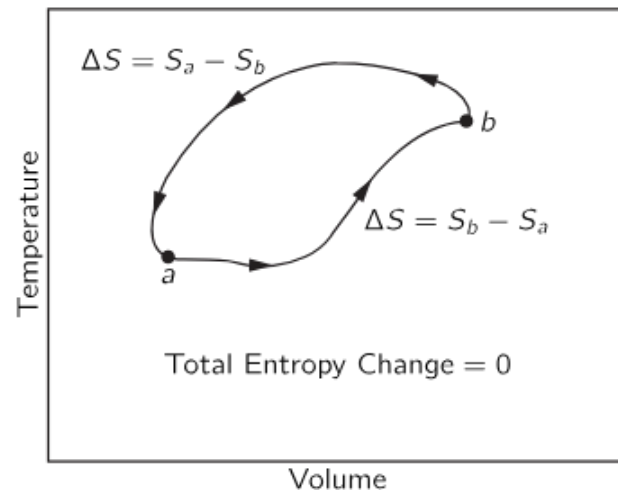
Limitation of thermodynamic entropy

We have a clear microscopic picture of internal energy U , which in ideal gas is directly related to the kinetic energy. Recall in L20 we introduced Clausius' entropy from purely thermodynamic origin.

$$dS = dQ/T.$$

$$S_b - S_a = \int_a^b \frac{dQ}{T}$$

We have a differential expression of entropy, such that we can compare the ΔS of two states. But like every integral, the “zero point” definition of entropy is unclear, nor is its microscopic picture.



Transition from a to b for a substance.

Microstates

- Let's consider an isolated system a lot of particles. The full description of the whole system, is made up by many many small states, called *microstates*.
- Actual explanation for microstates are the eigenstates of the Hamiltonian, i.e. solutions to the time-independent **Schrödinger equation**.

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad (\text{not required for exam})$$

- But imagine for a macroscopic system, the solution of the state has a very large number of degree of freedom, like $\sim 10^{23}$. The energy configuration can be quite complicated to know what each particle is doing, plus small perturbation.
- Moreover, the solution is usually totally uninteresting. Rather, we are interested in the probability, $p(n)$ of the system to sit in each states.

Macrostates

- We will only discuss systems that is in equilibrium, so the energy and momentum in the system has been redistributed among the many particles, and any memory of whatever special initial conditions the system started in has long been lost. The probability distribution is independent of time, thus the macroscopic observables. Defined by such variables, **macrostate** can correspond to many different microstates.
- The 2nd law says that the direction of a change is only a function of the states, and we do not need to consider how you get from state to state. This root from the fact that the time reversibility of laws of physics.
- To begin with, we first discuss the **microcanonical ensemble**, which describes an isolated system with fixed energy, E . Every system in the ensemble must be strictly isolated with its environment without heat and particle exchange, i.e., the total energy (E) and the particle number (N) in each system is fixed.

In modern statistical mechanics, the concept of an ensemble, developed by Josiah Gibbs in the 1870s, is fundamental. An ensemble involves creating multiple identical copies of a system and observing how they behave under different conditions.

1. Microcanonical (NVE) Ensemble: Each system is completely isolated, with no heat or particle exchange. Both energy (E) and particle number (N) are fixed in each system.

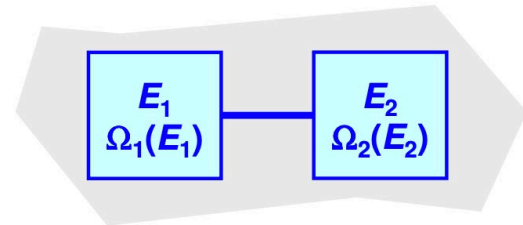
2. Canonical (NVT) Ensemble: The systems can exchange heat, allowing them to reach a common temperature (T). However, each system may have different energy levels, and the particle number (N) remains fixed in each.

3. Grandcanonical (μ VT) Ensemble: Systems can exchange both heat and particles. Neither energy nor particle number is fixed, leading to both thermal and chemical equilibriums. All systems share the same temperature (T) and chemical potential (μ).

We can define other ensembles with fixed state variables, like (P, N, T).

Temperature: The division of energy

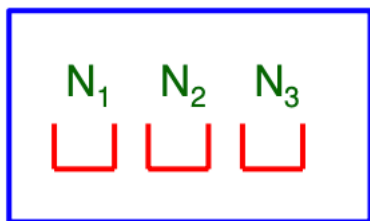
- Consider an **isolated system** (fixed energy and fixed number of particles). There are many, equally likely, microstates of the system with energy and particles arranged in different ways. The system can move from one microstate to another (thermodynamics applies to systems in flux) while keeping the same energy and no of particles.
- We can split an isolated system into 2 sub-systems in thermal contact. For a particular ‘macrostate’ in which the sub-systems have energies E_1 and E_2 , the atoms and the way that energy is stored within each sub-system can be rearranged in many ways (Ω_1 and Ω_2 microstates respectively) without changing E_1 and E_2 , giving a total number of corresponding microstates of the whole system, $\Omega = \Omega_1 \times \Omega_2$.
- The most likely ‘macrostate’ (here = division of energy between E_1 and E_2) is the one with the most corresponding microstates.



Example of Ω : three harmonic oscillators

Consider a box containing $M=3$ distinct simple harmonic oscillators each with energy $E = \hbar\omega(1/2+N)$ that are weakly interacting so quanta can flow from one to another, but the nature of the states is not affected by the interactions.

Now consider the different ways (macrostates) to put N quanta into the three boxes. For each value of N there are a number of ways of arranging the energy where $N_1 + N_2 + N_3 = N$



$$N=0 \quad \Omega=1 \quad (000)$$

$$N=1 \quad \Omega=3 \quad (100) (010) (001)$$

$$N=2 \quad \Omega=6 \quad (200) (020) (002) (110) (101) (011)$$

$$N=3 \quad \Omega=10 \quad (300) (030) (003) (210) (201) (120) (021) (102) (012) (111)$$

As N rises Ω rises rapidly.

of ways to arrange $N+M-1$ objects

$$\Omega = \frac{(N + M - 1)!}{N! (M - 1)!}$$

of ways to arrange identical objects

QQW $QQQQ$ WQ WW QQQ W QQQ W Q
 $N_1=2$ $N_2=4$ $N_3=1$ $N_4=3$ $N_5=3$ $N_6=1$
 $N_4=0$

Temperature in statistical thermodynamics

- Assume we have two connected macrostates: Ω_A and Ω_B , with corresponding energy in each state E_A and $E_B = E - E_A$ (the total energy E of the two system is fixed)
- To look for a condition on E and Ω that can be related to the classical thermodynamics concept of temperature, maximize $\Omega = \Omega_A \Omega_B$ w.r.t. E_A :

$$0 = \frac{d}{dE_A} (\Omega_A(E_A) \Omega_B(E - E_A)) = \Omega_A' \Omega_B - \Omega_A \Omega_B'$$
$$\Rightarrow \frac{\Omega_A'}{\Omega_A} = \frac{\Omega_B'}{\Omega_B} \Rightarrow \frac{d \ln \Omega_A}{dE_A} = \frac{d \ln \Omega_B}{dE_B}$$

- The most likely macrostate (distribution of internal energy between the two states) is the one with the max value of $\Omega = \Omega_A \Omega_B$, and thus is the condition when $T_A = T_B$ (the 0th law). β is a common factor shared by all the systems Ω at thermal equilibrium, and Ω must relate to the classical thermodynamics concept of temperature by:

$$\beta = \frac{d \ln \Omega}{dE} = \frac{1}{k_B T}$$

Entropy: the statistical definition

Boltzmann provided a probability interpretation of entropy,

$$S = k_B \ln \Omega \quad \boxed{k_B = 1.381 \times 10^{-23} \text{ J/K}}$$

Immediately, We can derive $\frac{\partial S}{\partial E} = 1/T$, which hints on the 0th law of temperature (see previous slide). Also, suppose we bring together two systems at slightly different temperatures $T_1 > T_2$:

$$\begin{aligned} \delta S &= \frac{\partial S_1(E_1)}{\partial E} \delta E_1 + \frac{\partial S_2(E_2)}{\partial E} \delta E_2 \\ &= \left(\frac{\partial S_1(E_1)}{\partial E} - \frac{\partial S_2(E_2)}{\partial E} \right) \delta E_1 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1 \end{aligned} \quad \boxed{S > 0 \Leftrightarrow E_1 < 0}$$



Ludwig Boltzmann (1844-1906)

“ $S = k \log W$ ” is inscribed on Boltzmann’s tombstone.

Unfortunately, his theory was not widely accepted by the community before his death.

Example: Two State System (microcanonical)

Consider a system of N non-interacting particles. Each particle is fixed in position and can sit in one of two possible states which, for convenience, we can call them “spin up” and “spin down”. The energy of the two states are:

$$E_{\downarrow} = 0 \quad , \quad E_{\uparrow} = \epsilon$$

which means that the spins want to be down; you pay an energy cost of ϵ for each spin which points up. The energy of the system is $E = N_{\uparrow}\epsilon$, and the number in the spin-down state is $N_{\downarrow} = N - N_{\uparrow}$

For a microcanonical system, the number of states $\Omega(E)$ of the total system which have energy E .

$$\Omega(E) = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!}$$

The entropy is given by

$$S(E) = k_B \log \left(\frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!} \right)$$

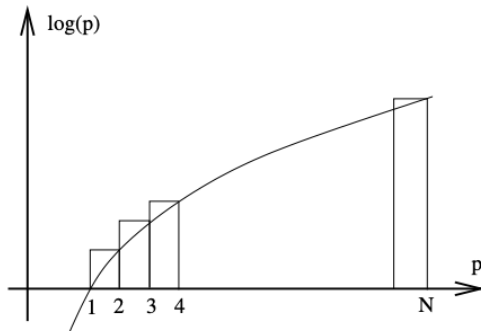
Stirling's Formula

To calculate $\log(N!)$ for large N , there is a remarkably accurate approximation, known as Stirling's formula, we shall prove it in the homework.

$$\log N! = N \log N - N + \frac{1}{2} \log 2\pi N + \mathcal{O}(1/N)$$

However, a less accurate but easier prove comes from the simplification, where we have approximated the sum by the integral as shown in the figure:

$$\log N! = \sum_{p=1}^N \log p \approx \int_1^N dp \log p = N \log N - N + 1$$



Entropy of a two state system

The Boltzmann's definition gives the entropy of a two state system (spin-up: $\epsilon = \epsilon$, spin-down $\epsilon=0$):

$$S(E) = k_B \log \left(\frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!} \right)$$

Using the math from last slide:

$$\begin{aligned} S(E) &= k_B [N \log N - N - N_{\uparrow} \log N_{\uparrow} + N_{\uparrow} - (N - N_{\uparrow}) \log(N - N_{\uparrow}) + (N - N_{\uparrow})] \\ &= -k_B \left[(N - N_{\uparrow}) \log \left(\frac{N - N_{\uparrow}}{N} \right) + N_{\uparrow} \log \left(\frac{N_{\uparrow}}{N} \right) \right] \\ &= -k_B N \left[\left(1 - \frac{E}{N\epsilon} \right) \log \left(1 - \frac{E}{N\epsilon} \right) + \frac{E}{N\epsilon} \log \left(\frac{E}{N\epsilon} \right) \right] \end{aligned}$$

The temperature:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\epsilon} \log \left(\frac{N\epsilon}{E} - 1 \right)$$

Distribution:

$$\frac{N_{\uparrow}}{N} = \frac{E}{N\epsilon} = \frac{1}{e^{\epsilon/k_B T} + 1}$$

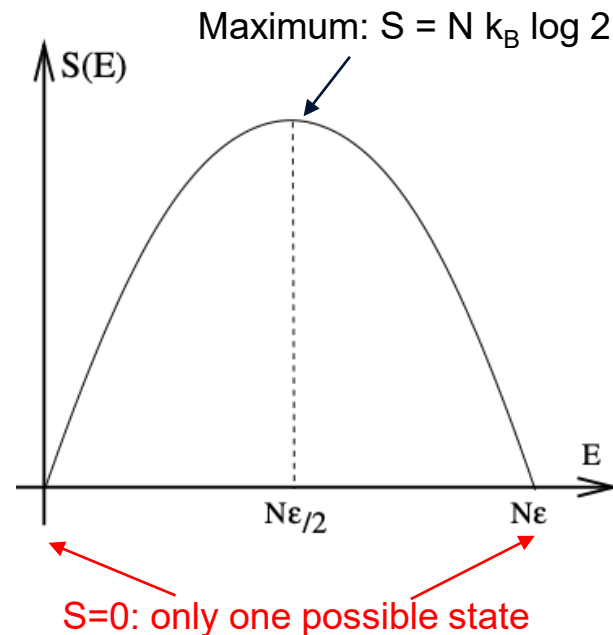
Maximum entropy and negative temperatures

$$S(E) = -k_B N \left[\left(1 - \frac{E}{N\epsilon}\right) \log \left(1 - \frac{E}{N\epsilon}\right) + \frac{E}{N\epsilon} \log \left(\frac{E}{N\epsilon}\right) \right]$$

Temperature of the system:

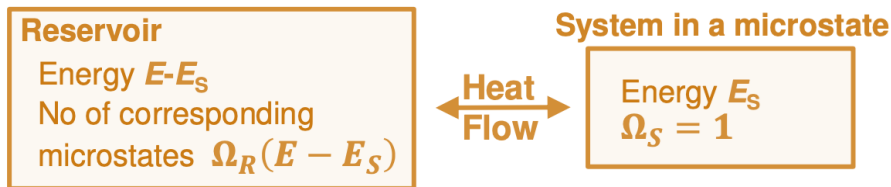
$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\epsilon} \log \left(\frac{N\epsilon}{E} - 1 \right)$$

- For $E > N\epsilon/2$, we have negative temperatures. This should be thought of as hotter than infinity!
- Systems with negative temperatures have the property that the number of microstates decreases as we add energy. They can be realized in laboratories, at least temporarily, by instantaneously flipping all the spins in a system.



The Boltzmann Factor

A typical thermodynamics ‘thought’ experiment is a system in contact with a thermal reservoir (a ‘heat bath’) of such a high heat capacity that its temperature does not change when you transfer (small) amounts of heat in/out of it. If the system is kept at a constant temperature, it satisfies the definition of **canonical ensemble**



Set the probability to 1 for a microstate of the system with its lowest energy $E_S=0$ (a ‘ground state’), with all the available energy (E) stored in the reservoir. The relative probability $P_r(E_S)$ that the system will be in a ‘excited’ microstate of energy E_S is given by:

$$P_r(E_S) = \frac{\Omega_R(E - E_S)}{\Omega_R(E)}$$

The Boltzmann Factor (cont)

Now relate probability $P_r(E_S)$ to $\beta = d \ln \Omega / dE$, using Taylor expansion:

$$\begin{aligned} \ln \Omega_R(E_R) &= \ln \Omega_R(E - E_S) \approx \ln \Omega_R(E) - E_S \frac{d \ln \Omega_R}{dE} \\ &= \ln \Omega_R(E) - E_S \beta \end{aligned}$$

$$\text{Hence: } \ln \Omega_R(E - E_S) - \ln \Omega_R(E) = -E_S \beta$$

Therefore, relative chance of the system being in a microstate with energy E_S :

$$P_r(E_S) = \frac{\Omega_R(E - E_S)}{\Omega_R(E)} = e^{-\beta E_S}$$

- Boltzmann factor is independent of the nature of the reservoir, same temperature = same β .
- The most likely system microstate is the ground state ($E_S=0$).

Boltzmann distribution and canonical ensemble

- As shown previously, the probability that the system sits in state $|n\rangle$ is just the ratio of this number of states to the total number of states,

$$p(n) = \frac{e^{-E_n/k_B T}}{\sum_m e^{-E_m/k_B T}} = \frac{e^{-\beta E_n}}{Z}$$

- We usually write the normalization factor as Z , where $Z = \sum_n e^{-\beta E_n}$, which is the most

important quantity in statistical mechanics, **the partition function**.

- In the canonical ensemble, total energy is not fixed. However, we can compute the average energy,

$$\langle E \rangle = \sum_n p(n) E_n = \sum_n \frac{E_n e^{-\beta E_n}}{Z}$$

- Or more succinctly

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z$$

Energy spread

We can also look at the spread of energies about the mean — in other words, about fluctuations in the probability distribution. As usual, this spread is captured by the variance,

$$\Delta E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

This too can be written neatly in terms of the partition function,

$$\Delta E^2 = \frac{\partial^2}{\partial \beta^2} \log Z = - \frac{\partial \langle E \rangle}{\partial \beta}$$

In the canonical ensemble, where the energy is not fixed, the heat capacity is

$$C_V = \left. \frac{\partial \langle E \rangle}{\partial T} \right|_V$$

So we have the important relation

$$\Delta E^2 = k_B T^2 C_V$$

LHS=probabilistic fluctuations in the energy of the system. RHS=the heat capacity C_V describes the ability of the system to absorb energy. If C_V is large, the system can take in a lot of energy without raising its temperature too much.

Example: Two State System (canonical)

Consider a system of N non-interacting particles. We can rederive our previous results for the two state system using the canonical ensemble. For a single particle with two energy levels, 0 and ϵ , the partition function is given by

$$Z_1 = \sum_n e^{-\beta E_n} = 1 + e^{-\beta\epsilon} = 2e^{-\beta\epsilon/2} \cosh(\beta\epsilon/2)$$

We simply need to multiply the N partition functions together ($Z = Z_1 Z_2 \dots$). We then have

$$Z = 2^N e^{-N\beta\epsilon/2} \cosh^N(\beta\epsilon/2)$$

which has the same result as the microcanonical ensemble

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z = \frac{N\epsilon}{2} (1 - \tanh(\beta\epsilon/2))$$

Entropy for canonical ensemble

- Suppose that we have a large number, W , of identical copies. Each system lives in a particular state $|n\rangle$. If W is large enough, the number of systems that sit in state $|n\rangle$ must be simply $p(n)W$.
- Using Boltzmann's definition of entropy, we have

$$\Omega = \frac{W!}{\prod_n (p(n)W)!}$$

- So the entropy for W copies becomes

$$S = k_B \log \Omega = -k_B W \sum_n p(n) \log p(n)$$

- While we know entropy is additive, hence for each copy, Gibbs found that

$$S = -k_B \sum_n p(n) \log p(n)$$

This was rediscovered some decades later in the context of information theory where it goes by the name of Shannon entropy for classical systems or von Neumann entropy for quantum systems.

Free energy

Previously, we have derived the formula

$$S = -k_B \sum_n p(n) \log p(n)$$

Previously, we have derived the formula

$$S = -k \sum p_i \ln p_i = -k \sum p_i \left(-\frac{E_i}{kT} - \ln Z \right) \quad (p_i = e^{-\frac{E_i}{kT}}/Z)$$

$$S = \frac{1}{T} \sum p_i E_i + k \ln Z \sum p_i = \frac{U}{T} + k \ln Z \quad (U = \sum p_i E_i)$$

Hence:

$$\boxed{F = U - TS = -kT \ln Z}$$

F is a thermodynamic potential with very accessible natural variables, T and V. This means that the partition function, Z, takes a central place in statistical thermodynamics.