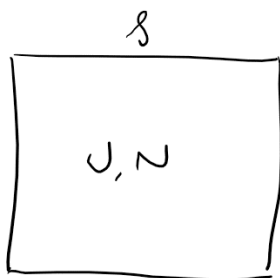
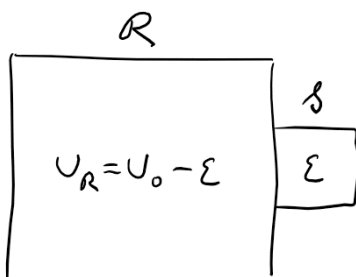


Lecture 5 – Canonical ensemble



LAST TIME: So far we've worked with a closed system \mathcal{S} and fixed total energy U . The likeliest macrostate is the one that maximizes entropy.

This statistical ensemble is called the microcanonical ensemble



TODAY: A more common situation is when the system \mathcal{S} is in thermal contact with a large reservoir \mathcal{R} at temperature T . Here the system energy ϵ is not fixed but T is (we showed this for a system in equilibrium with a reservoir).

The total system $\mathcal{R} + \mathcal{S}$ is closed so $U_0 = U_{\mathcal{R}} + \epsilon$ is fixed

This situation is so common it is called the canonical ensemble

(Note: Here we again assume the number of particles in \mathcal{S} $N_{\mathcal{S}}$ is fixed. If we allow particles to be exchanged between $\mathcal{R} + \mathcal{S}$ we call it the grand canonical ensemble, which we'll return to later.)

What are the properties of the canonical ensemble?

KEY CONCEPT: the Boltzmann distribution

If \mathcal{S} is in a single quantum state i with energy ϵ_i , what is the probability of being in that state?

From fundamental assumption, the probability is proportional to the multiplicity $\Omega_{\mathcal{R}+\mathcal{S}}$ of the total system $\mathcal{R} + \mathcal{S}$

$$p(\epsilon_i) = \frac{\Omega_{\mathcal{R}+\mathcal{S}}(\epsilon_i)}{\sum_{\text{All } \epsilon_i} \Omega_{\mathcal{R}+\mathcal{S}}(\epsilon_i)}$$

but $\Omega_{\mathcal{R}+\mathcal{S}} = \Omega_{\mathcal{R}}(U_0 - \epsilon_i) \underbrace{\Omega_{\mathcal{S}}(\epsilon_i)}_1 = \Omega_{\mathcal{R}}(U_0 - \epsilon_i)$ since \mathcal{S} is in a single quantum state

Let's take the ratio of probs. for two systems with energy ϵ_1 and ϵ_2 in equilibrium with \mathcal{R}

$$\begin{aligned} \frac{p(\epsilon_1)}{p(\epsilon_2)} &= \frac{\Omega_{\mathcal{R}}(U_0 - \epsilon_1)}{\Omega_{\mathcal{R}}(U_0 - \epsilon_2)} = \frac{e^{S_{\mathcal{R}}(U_0 - \epsilon_1)/k_B}}{e^{S_{\mathcal{R}}(U_0 - \epsilon_2)/k_B}} \\ &= \exp[S_{\mathcal{R}}(U_0 - \epsilon_1) - S_{\mathcal{R}}(U_0 - \epsilon_2)]/k_B \end{aligned}$$

Now, we showed for a reservoir \mathcal{R} that $U_0 \gg \varepsilon_1$ or ε_2 , so we can expand about U_0

$$S_{\mathcal{R}}(U_0 - \varepsilon_i) = S_{\mathcal{R}}(U_0) - \left. \frac{\partial S_{\mathcal{R}}}{\partial U} \right|_{U_0} \varepsilon_i + \dots \approx S_{\mathcal{R}}(U_0) - \frac{\varepsilon_i}{T}$$

$$\text{so } S_{\mathcal{R}}(U_0 - \varepsilon_1) - S_{\mathcal{R}}(U_0 - \varepsilon_2) \approx -\frac{\varepsilon_1 - \varepsilon_2}{T}$$

(Note that $T_{\mathcal{R}} = T_{\mathcal{S}} = T$ at equilibrium)

It follows that:

$$\frac{p(\varepsilon_1)}{p(\varepsilon_2)} = e^{-(\varepsilon_1 - \varepsilon_2)/k_B T}$$

To get $p(\varepsilon_i)$, we use the normalization condition for probabilities: $\sum_i p(\varepsilon_i) = 1$:

$$\sum_j \frac{p(\varepsilon_j)}{p(\varepsilon_i)} = \sum_j e^{-(\varepsilon_j - \varepsilon_i)/k_B T}, \text{ so } \frac{1}{p(\varepsilon_i)} = e^{+\varepsilon_i/k_B T} \sum_j e^{-\varepsilon_j/k_B T} \text{ and}$$

$$p(\varepsilon_i) = \frac{e^{-\varepsilon_i/k_B T}}{\sum_j e^{-\varepsilon_j/k_B T}}, \quad \text{the Boltzmann distribution}$$

This is the most useful formula in statistical mechanics. Memorize it!

Each factor of the form $e^{-\varepsilon_i/k_B T}$ is known as a Boltzmann factor

It is also useful to define the partition function $Z(T)$:

$$Z(T) = \sum_i e^{-\varepsilon_i/k_B T}$$

$$\text{so } p(\varepsilon_i) = \frac{e^{-\varepsilon_i/k_B T}}{Z(T)}$$

Important note: the sum is taken over microstates of the system \mathcal{S} only – states of the reservoir \mathcal{R} don't factor at all.

To recap:

- Fundamental assumption states that each microstate of total closed system $\mathcal{R} + \mathcal{S}$ is equally likely, but probability of microstate of system \mathcal{S} goes as Boltzmann factor. Why?

If $\varepsilon_1 > \varepsilon_2$ for \mathcal{S} then $U_0 - \varepsilon_1 < U_0 - \varepsilon_2$ for \mathcal{R}

then $S_{\mathcal{R}+\mathcal{S}} = S_{\mathcal{R}}(U_0 - \varepsilon_1) < S_{\mathcal{R}}(U_0 - \varepsilon_2)$, according to T^*

and $\Omega_{\mathcal{R}+\mathcal{S}} = \Omega_{\mathcal{R}}(U_0 - \varepsilon_1) \ll \Omega_{\mathcal{R}}(U_0 - \varepsilon_2)$

Therefore, more likely microstate of \mathcal{S} is with lower energy $\varepsilon_2 < \varepsilon_1$!

*Assuming $T > 0$. For $T < 0$, inequalities get reversed

Mean values:

$$U = \langle \varepsilon \rangle = \sum_i \varepsilon_i p(\varepsilon_i) = \frac{\sum_i \varepsilon_i e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}}$$

Here's a useful math trick. Define $\beta \equiv 1/k_B T$:

$$U = -\frac{\partial}{\partial \beta} \ln \underbrace{\sum_i e^{-\beta \varepsilon_i}}_{Z(T)}$$

$$\text{so } U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z \quad \text{or} \quad U = k_B T^2 \frac{\partial}{\partial T} \ln Z = \frac{k_B T^2}{Z} \frac{\partial}{\partial T} Z$$

Can get many things from Z – incredibly useful quantity

Question 1: Determine a) the partition function for a spin- $\frac{1}{2}$ particle in a magnetic field (i.e. a paramagnet) and b) its average energy.

a) Each spin- $\frac{1}{2}$ particle can be in one of two states, aligned or anti-aligned, so

$$Z_1 = e^{\mu B/k_B T} + e^{-\mu B/k_B T} = 2 \cosh \frac{\mu B}{k_B T}$$

b) The average energy U is

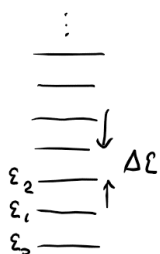
$$U = \langle \varepsilon \rangle = \frac{-\mu B e^{\mu B/k_B T} + \mu B e^{-\mu B/k_B T}}{Z_1} = -\mu B \frac{\sinh(\mu B/k_B T)}{\cosh(\mu B/k_B T)} = -\mu B \tanh \frac{\mu B}{k_B T}$$

Alternately, we can use the math trick

$$U = -\frac{\partial}{\partial \beta} \ln(2 \cosh \beta \mu B) = -\mu B \frac{\sinh \beta \mu B}{\cosh \beta \mu B} = -\mu B \tanh \beta \mu B$$

KEY CONCEPT: the partition function $Z(T)$ and its properties

Z in canonical ensemble is analogous to Ω in microcanonical ensemble. Z counts microstates of system like Ω , but weighs each one by a Boltzmann factor according to its energy and the temperature of the system set by the reservoir.

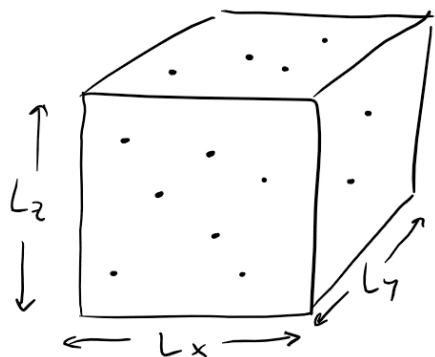


Consider system with energy levels $\varepsilon_0 < \varepsilon_1 < \varepsilon_2 \dots$

$$Z(T) = \sum_i e^{-\varepsilon_i/k_B T} = e^{-\varepsilon_0/k_B T} + e^{-\varepsilon_1/k_B T} + e^{-\varepsilon_2/k_B T} \dots$$

Each term in Z gets progressively smaller. If $k_B T < \Delta \varepsilon$, the average spacing between energy levels, then only first few terms contribute significantly to sum. If $k_B T \gg \Delta \varepsilon$, then many terms contribute.

Ideal gas (revisited)



N atoms in a 3-D box of volume $V = L_x L_y L_z$

All we need to determine is the single-particle partition function $Z_1(T)$ and the rest will follow

Again treat gas as particles in a box:

$$k_x = \frac{\pi n_x}{L_x}, k_y = \frac{\pi n_y}{L_y}, k_z = \frac{\pi n_z}{L_z}, \text{ with } n_{x,y,z} = 1, 2, 3, \dots$$

and the single-particle energy is

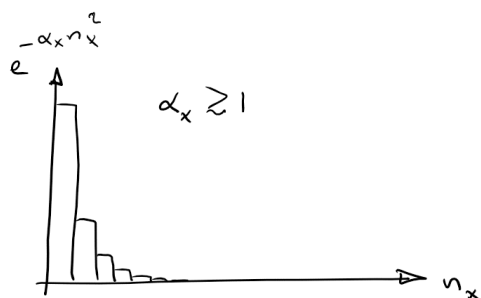
$$\varepsilon_1 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

How do we evaluate the single-particle partition function?

$$Z_1(T) = \sum_{\text{All states}} e^{-\varepsilon_1/k_B T} = \sum_{n_x, n_y, n_z} e^{-\varepsilon_1(n_x, n_y, n_z)/k_B T}$$

The sum is over the triplet $\{n_x, n_y, n_z\}$. Note that the x , y , and z terms are independent so

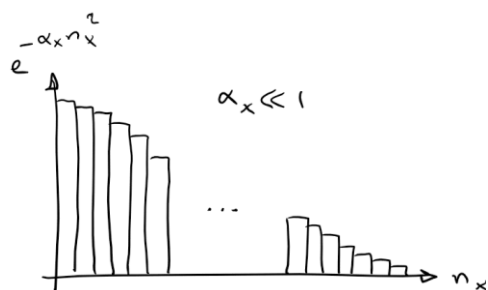
$$Z_1(T) = \sum_{n_x=1}^{\infty} e^{-\hbar^2 \pi^2 n_x^2 / 2m L_x^2 k_B T} \sum_{n_y=1}^{\infty} e^{-\hbar^2 \pi^2 n_y^2 / 2m L_y^2 k_B T} \sum_{n_z=1}^{\infty} e^{-\hbar^2 \pi^2 n_z^2 / 2m L_z^2 k_B T}$$



Taking one of these sums:

$$\sum_{n_x=1}^{\infty} e^{-\alpha_x n_x^2}, \text{ with } \alpha_x = \frac{\hbar^2 \pi^2}{2m L_x^2 k_B T}$$

If $\alpha_x \gtrsim 1$ only the first few terms of sum contribute because the exponents increase rapidly with n_x .



If $\alpha_x \ll 1$, then many terms contribute and are each of comparable magnitude – the sum can be approximated by an integral:

$$\sum_{n_x=1}^{\infty} e^{-\alpha_x n_x^2} \approx \int_0^{\infty} dn_x e^{-\alpha_x n_x^2} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha_x}}$$

(Notice lower limit is approximated as 0)

$$Z_1(T) \approx \int_0^\infty dn_x e^{-\alpha_x n_x^2} \int_0^\infty dn_y e^{-\alpha_y n_y^2} \int_0^\infty dn_z e^{-\alpha_z n_z^2} = \frac{\pi^{3/2}}{2^3 (\alpha_x \alpha_y \alpha_z)^{1/2}}$$

$$= \frac{\pi^{3/2}}{2^3} \left(\frac{2mk_B T}{\pi^2 \hbar^2} \right)^{3/2} L_x L_y L_z = \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} V$$

valid in the limit $\alpha_x, \alpha_y, \alpha_z \ll 1$ which corresponds to $k_B T \gg \frac{\hbar^2 \pi^2}{2mL_x^2}, \frac{\hbar^2 \pi^2}{2mL_y^2}, \frac{\hbar^2 \pi^2}{2mL_z^2}$, i.e. when $k_B T$ is much larger than the average spacing between energy levels $\Delta \varepsilon = \hbar^2 \pi^2 / 2mV^{2/3}$.

This is true in almost all real physical situations ($\Delta \varepsilon / k_B \sim 10^{-15} \text{ K}$) and it justifies approximating energy levels as a continuum of states and turning the sums in Z to integrals.

Note that this limit also means $\left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} V \gg 1$; makes sense, Z_1 counts many, many states.

Note: This is exactly the same approximation we used when we calculated Ω in Lect. 4.

Using $k_x = \frac{\pi n_x}{L_x}$ etc. and $\varepsilon_1 = \frac{\hbar^2 k^2}{2m}$

$$\int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z e^{-(\alpha_x n_x^2 + \alpha_y n_y^2 + \alpha_z n_z^2)} = \frac{V}{\pi^3} \int_0^\infty dk_x \int_0^\infty dk_y \int_0^\infty dk_z e^{-\hbar^2 (k_x^2 + k_y^2 + k_z^2) / 2mk_B T}$$

$$= \frac{V}{\pi^3} \frac{4\pi}{8} \int_0^\infty dk k^2 e^{-\hbar^2 k^2 / 2mk_B T} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon_1 \varepsilon_1^{1/2} e^{-\varepsilon_1 / k_B T}$$

Evaluating the integrals all give the same answer.

Question 3: Determine the average energy U for an ideal gas of N indistinguishable particles.

The total partition function is $Z_{tot} = Z_1^N / N!$, with $Z_1 = \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} V$.

Again, it's easiest to use the math trick

$$U = -\frac{\partial}{\partial \beta} \ln Z_{tot} = -N \frac{\partial}{\partial \beta} \ln Z_1 = -N \frac{\partial}{\partial \beta} (\ln \beta^{-3/2} + \text{terms independent of } \beta)$$

$$= \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T \quad \text{as expected.}$$

KEY CONCEPT: Quantum density

$$Z_1(T) = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} V$$

↑

Z is unitless so this factor must be a density

Define quantum density $n_Q(T) \equiv \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}$ so that $Z_1(T) = n_Q(T)V$

Quantum mechanics tells us that particles behave as waves with deBroglie wavelength $\lambda = h/p$, where p is the particle momentum. For an ideal gas, each particle has average energy

$$\langle \varepsilon \rangle = \left\langle \frac{p^2}{2m} \right\rangle = \frac{3}{2} k_B T, \text{ so its average deBroglie wavelength is } \langle \lambda \rangle \approx \frac{h}{\sqrt{2m\langle \varepsilon \rangle}} = \sqrt{\frac{4\pi^2 \hbar^2}{3mk_B T}}.$$

So, $n_Q(T)$ = density of one particle in a cube of side $\sqrt{\frac{2\pi\hbar^2}{mk_B T}}$, which (ignoring factors of order unity) is the deBroglie wavelength of the particle at temperature T .

$n_Q(T)$ will reappear many times in class. When particle density $n \sim n_Q$ wavefunctions overlap and quantum effects are important. Limit that $n \ll n_Q$ is called classical regime.

Ex: He at room temperature ($T = 300\text{K}$) and atmospheric pressure

$$n_Q(T) = 0.8 \times 10^{25} \text{ cm}^{-3} \rightarrow 1 \text{ atom per } (0.5 \text{ \AA})^3$$

$$n = 2.5 \times 10^{19} \text{ cm}^{-3} \rightarrow 1 \text{ atom per } (34 \text{ \AA})^3$$

so $n \ll n_Q$.