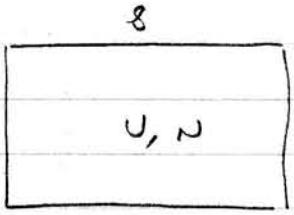
Lecture 5

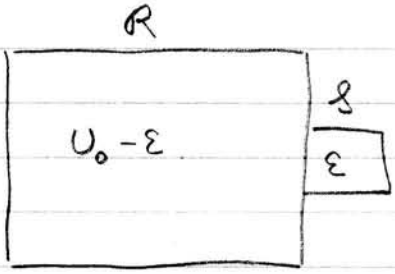
So far we've worked with an isolated system S and fixed the total energy U. This statistical ensemble is called the "microcanonical ensemble"



"Microcanonical ensemble"

We showed that likeliest macrostate maximizes entropy $S_S(U, N)$

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



"canonical ensemble"

The total system $S + R$ is isolated

so $U_0 = U_R + \mathcal{E} =$ fixed

$\therefore U_R = U_0 - \mathcal{E}$

This situation is so common it is called the canonical ensemble

Here, we again assume the # of particles in S N_S is fixed. If we allow particles to transfer between $R + S$ we call it the grand canonical ensemble, which we'll come back to later

What are the properties of the canonical ensemble?

If 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 Ω_{R+S} of the total system $R+S$

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

$$\Omega_{R+S} = \Omega_R(U_0 - \varepsilon_i)\,\underbrace{\Omega_S(\varepsilon_i)}_{1 \text{ since its a single state}}$$

Let's take the ratio of prob. for two systems S with energy ε_1 and ε_2

$$\frac{p(\varepsilon_1)}{p(\varepsilon_2)} = \frac{\Omega_R(U_0-\varepsilon_1)}{\Omega_R(U_0-\varepsilon_2)} = \frac{e^{S_R(U_0-\varepsilon_1)/k_B}}{e^{S_R(U_0-\varepsilon_2)/k_B}} \qquad \text{since } S = k_B \ln \Omega$$

$$= \exp\left[S_R(U_0-\varepsilon_1) - S_R(U_0-\varepsilon_2)\right]/k_B$$

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

$$S_R(U_0-\varepsilon_i) = S_R(U_0) - \left.\frac{\partial S_R}{\partial U}\right|_{U_0} \varepsilon_i + \cdots$$

$$\approx S_R(U_0) - \frac{1}{T}\varepsilon_i$$

$$\therefore\ S_R(U_0-\varepsilon_1) - S_R(U_0-\varepsilon_2) \approx \frac{1}{T}(\varepsilon_1 - \varepsilon_2)$$

Note that $T = T_R = T_S$ at equilibrium

$$\therefore \quad \frac{p(\varepsilon_1)}{p(\varepsilon_2)} = \exp -\frac{(\varepsilon_1 - \varepsilon_2)}{k_B T}$$

How do we get $p(\varepsilon_i)$?

Normalization $\sum_i p(\varepsilon_i) = 1$

$$\therefore \quad \boxed{p(\varepsilon_i) = \frac{e^{-\varepsilon_i / k_B T}}{\sum_i e^{-\varepsilon_i / k_B T}}} \leftarrow \text{the "Boltzmann factor"}$$

If we define the partition function Z as

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

Then $$p(\varepsilon_i) = \frac{1}{Z(T)} e^{-\varepsilon_i / k_B T}$$

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

To recap:
Fundamental assumption says each microstate of total isolated system $R+S$ is equally likely, but probability for system S goes as Boltzmann factor

If $\varepsilon_1 > \varepsilon_2$ then for R $U_0 - \varepsilon_1 < U_0 - \varepsilon_2$

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

and $\Omega_{R+S} = \Omega_R(U_0 - \varepsilon_1) \ll \Omega_R(U_0 - \varepsilon_2)$ so more likely microstate for S is with $\varepsilon_2 < \varepsilon_1$

* I've assumed $T > 0$. For $T < 0$, inequalities get reversed

Mean values:

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

Here's a useful math trick. Define $\beta \equiv \frac{1}{k_B T}$

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

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

Can get everything from Z - incredibly useful quantity

Z in canonical ensemble is analogous to Ω in microcanonical ensemble. It counts microstates like Ω, but weights each one by Boltzmann factor according to its energy

Z for independent particles

Let's say you have N independent particles, so

$$E_{tot} = E_1 + E_2 + \cdots E_N$$

(No interaction means no terms like E_{12} etc...)

$$Z_{tot} = \sum_{E_1, E_2 \cdots E_N} e^{-\beta E_{tot}} = \left(\sum_{E_1} e^{-\beta E_1} \right) \left(\sum_{E_2} e^{-\beta E_2} \right) \cdots \left(\sum_{E_N} e^{-\beta E_N} \right)$$

↑ Sum over all states of all particles

↑ Sum over all states of single particle

$$\therefore \quad Z_{tot} = Z_1 \cdot Z_2 \cdot \cdots Z_N$$

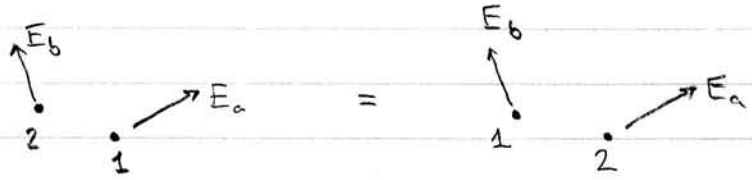
This is convenient. As long as sums are independent, I can treat them separately and multiply Z's to get Z_{tot}

Consider N independent identical (indistinguishable) particles

$$Z_N \neq Z_1^N$$

This overcounts states because particles are indistinguishable

Ex: 2 particles



If $Z_2 = \sum_{E_1} e^{-\beta E_1} \sum_{E_2} e^{-\beta E_2}$

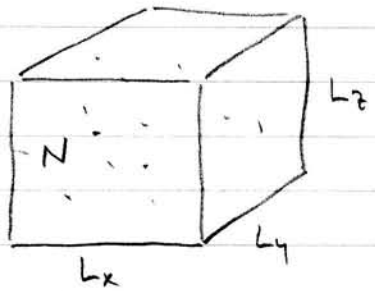
we'd get terms like $e^{-\beta E_{1a}} e^{-\beta E_{2b}} + e^{-\beta E_{1b}} e^{-\beta E_{2a}}$

but these are the same state so we have to divide by 2

For N indistinguishable particles:

$$\boxed{Z_N = \frac{Z_1^N}{N!}}$$

Ideal gas (revisited)

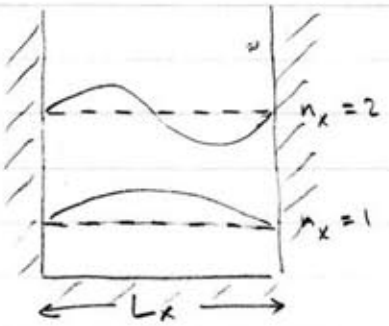


N particles in a box of $V = L_x L_y L_z$

All we need is single particle Z_1 and the rest will follow

Again treat these as particles in a box

In K+K, they use boundary conditions where wavefunction $\psi = 0$ at boundaries



$$k_x = \frac{n_x \pi}{L_x} \qquad n_x = 1, 2, 3 \cdots$$

(same for k_y, k_z)

$$E_1 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

$$= E_x + E_y + E_z$$

$$\therefore \; Z_1 = \sum_{n_x, n_y, n_z} e^{-\beta E_1} = \left(\sum_{n_x=1}^{\infty} e^{-\beta E_x}\right)\left(\sum_{n_y=1}^{\infty} e^{-\beta E_y}\right)\left(\sum_{n_z=1}^{\infty} e^{-\beta E_z}\right)$$

Again consider that spacing between energy levels is much much smaller than total energy (<u>high-temperature limit</u>).

$$\therefore \sum_{n_x=1}^{\infty} \longrightarrow \int_0^{\infty} dn_x$$

↑
Notice we start from 0

$$\int_0^\infty dn_x \exp\left(-\frac{\hbar^2\pi^2 n_x^2}{2mL_x^2 k_B T}\right) = \sqrt{\frac{2mk_BT}{\hbar^2\pi^2}}\, L_x \int_0^\infty du\, e^{-u^2}$$

$u \equiv \sqrt{\frac{\hbar^2\pi^2}{2mL_x^2k_BT}}\, n_x$

and similarly for n_y n_z

$$\therefore \quad z_1 = \left(\frac{2mk_BT}{\hbar^2\pi^2}\right)^{3/2} L_xL_yL_z \left(\int_0^\infty du\, e^{-u^2}\right)^3$$

$$= \frac{\sqrt{\pi}}{2}$$

$$z_1 = \left(\frac{2mk_BT}{\hbar^2\pi^2}\right)^{3/2} V \frac{\pi^{3/2}}{8} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} V$$

↑

z is a number so this must have units of $1/V$

Quantum density $n_Q \equiv \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}$

$\lambda_T \equiv \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$ "thermal de Broglie wavelength"
de Broglie wavelength of particle with kinetic energy $\sim k_BT$

$n_Q = \frac{1}{\lambda_T^3}$ $1/$cube of side λ_T

$\therefore \quad z_1 = n_Q V = n_Q/n$ $\quad n = 1/V$ the density of particles

n_Q will come back over and over in class
When $n \sim n_Q$ wavefunctions overlap and quantum effects are important. Limit $n \ll n_Q$ is called <u>classical regime</u>

Ex: He at room T (~ 300 K) atmospheric p
$n_Q = 0.8 \times 10^{25}$ cm^{-3} ($\sim$1 atom / (0.5 Å)^3)
$n = 2.5 \times 10^{19}$ cm^{-3} ($\sim$1 atom / (34 Å)^3) so $n \ll n_Q$

$\therefore \quad Z_1 = n_Q V \gg 1$ In classical regime

$Z_N = \dfrac{(n_Q V)^N}{N!}$ N-particle partition function

$U = \langle E \rangle = -\dfrac{\partial \ln Z_N}{\partial \beta}$ only n_Q depends on $\beta = 1/k_B T$

$n_Q \propto \beta^{-3/2}$

$= -N \dfrac{\partial}{\partial \beta} \ln n_Q$

$= \dfrac{3}{2} N \dfrac{1}{\beta} = \dfrac{3}{2} N k_B T$ like before

Another point on classical regime $n_Q V \gg 1$

Result for U says energy per particle $E_1 \sim k_B T$ (ignoring factors of order 1)

How does this compare to spacing between energy levels?

$\Delta E = \dfrac{\hbar^2}{m} k \Delta k$

$\Delta k = \dfrac{\pi}{L}$, $k = \sqrt{\dfrac{2mE}{\hbar^2}} \sim \sqrt{\dfrac{m k_B T}{\hbar^2}}$

$\therefore \Delta E \sim \sqrt{k_B T \dfrac{\hbar^2 \pi^2}{m L^2}}$ or $\dfrac{\Delta E}{k_B T} \sim \sqrt{\dfrac{\hbar^2 \pi^2}{m k_B T L^2}}$

But $n_Q V = \left(\dfrac{L}{\lambda_T}\right)^3 \gg 1$ so $\dfrac{\lambda_T}{L} = \sqrt{\dfrac{2\pi \hbar^2}{m k_B T L^2}} \ll 1$

$\therefore \dfrac{\Delta E}{k_B T} \ll 1$

Classical regime justifies treating energy levels as a continuum and replacing Σ with $\int$