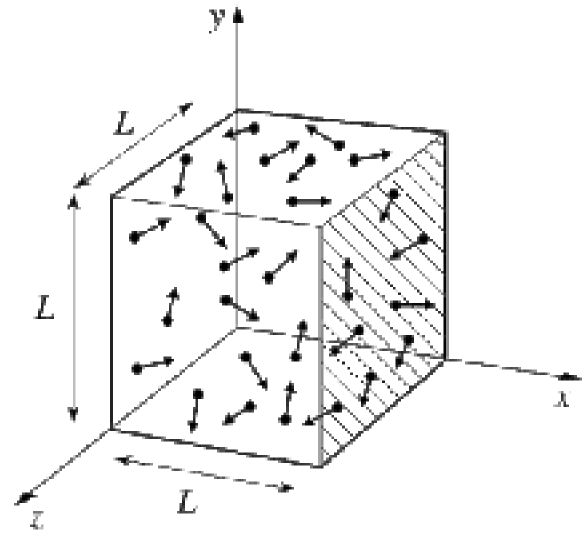
Lecture 21. *Statistical mechanics of an ideal gas*

- Where we apply what we learned in the previous lecture on partition functions and extend that knowledge to the case of the ideal gas

$$Z = \sum_{\alpha} \mathrm{e}^{-\beta E_\alpha}$$



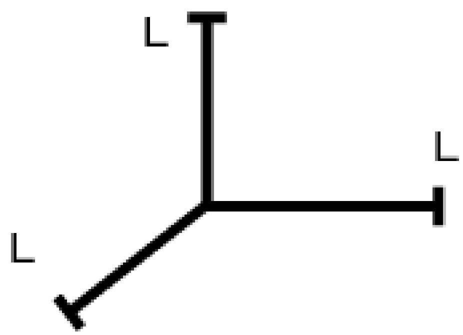
http://www.met.reading.ac.uk/pplato2/h-flap/phys7_5.html

How can we build the partition function in this case?

QM in 1D

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

QM in 3D



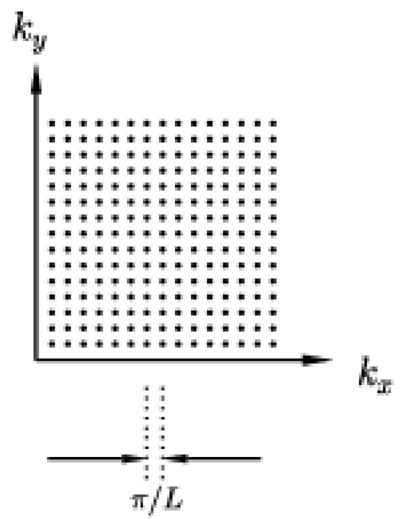
$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right)+\left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right)+\left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right)=E$$

Density of states

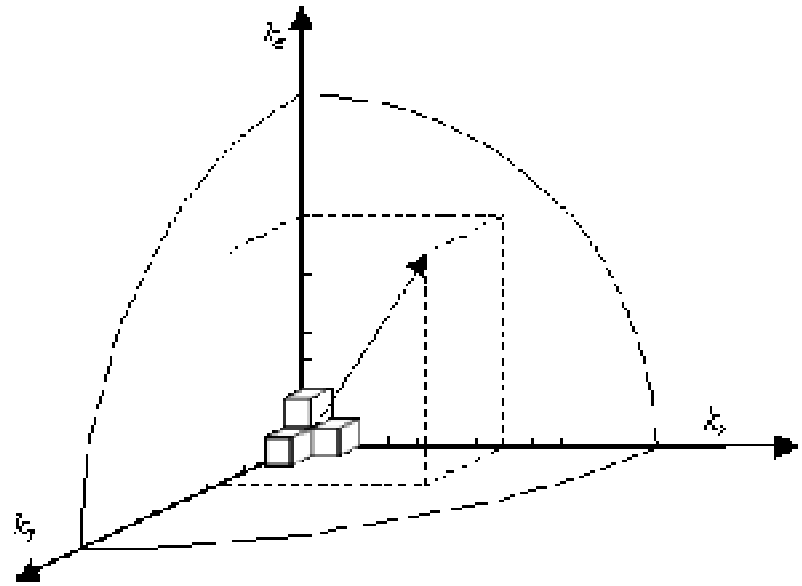
$$k_x = \frac{n_x \pi}{L}, \qquad k_y = \frac{n_y \pi}{L}, \qquad k_z = \frac{n_z \pi}{L}$$

(k_x, k_y, k_z) uniquely labels each state

We can work in "k-space" without loss of information

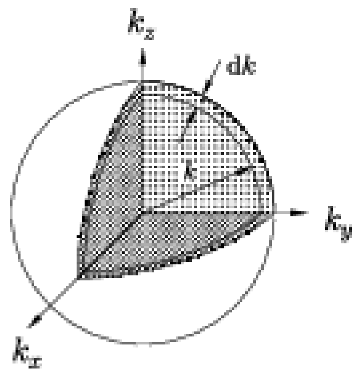


A point in k-space occupies a volume: $(\pi/L)^3$



https://ecee.colorado.edu/~bart/book/book/chapter2/ch2_4.htm

Magnitude of a wave vector



How many states with wave vectors of length between k and $k + dk$?

Volume of the shell: $\frac{1}{8} \times 4\pi k^2 dk$

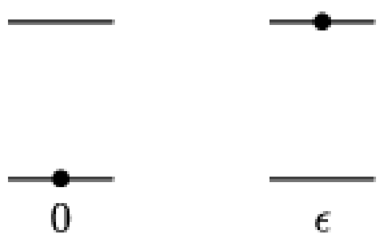
Partition function of the ideal gas

$$Z_1 = \int_0^\infty \mathrm{e}^{-\beta E(k)}\, g(k)\,\mathrm{d}k \quad \text{with} \quad E(k) = \frac{{}^2k^2}{2m}$$

$$\Rightarrow \quad Z_1 = \int_0^\infty \mathrm{e}^{-\beta\ {}^2k^2/2m} \frac{V k^2\,\mathrm{d}k}{2\pi^2} = \frac{V}{{}^3}\left(\frac{mk_\mathrm{B}T}{2\pi}\right)^{3/2}$$

Many-particle states

So far, we have considered single-particle states, what happens for a N-particle state?

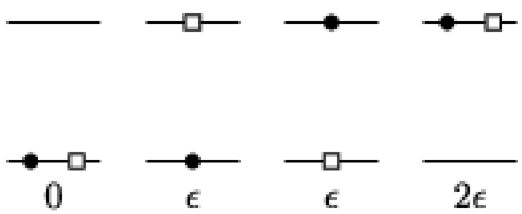


Particles can exist in two states with energy 0 or ϵ

Single-particle partition function is:

$$Z_1 = \mathrm{e}^0 + \mathrm{e}^{-\beta\epsilon} = 1 + \mathrm{e}^{-\beta\epsilon}$$

2 distinguishable particles



$$Z_2 = \mathrm{e}^0 + \mathrm{e}^{-\beta\epsilon} + \mathrm{e}^{-\beta\epsilon} + \mathrm{e}^{-2\beta\epsilon}$$

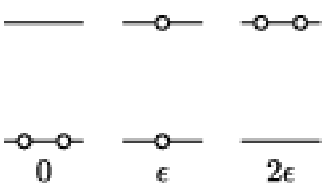
$$Z_2 = (Z_1)^2$$

In general, for N particles:

$$Z_N = (Z_1)^N$$

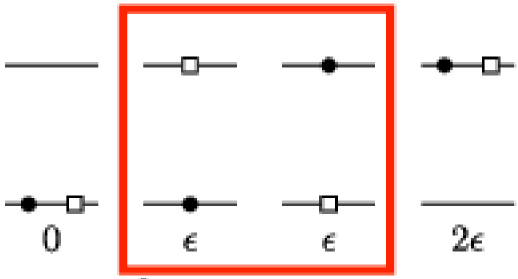
What if the particles *were in*distinguishable?

Indistinguishable



$$Z_2 = e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} \neq (Z_1)^2$$

Distinguishable case



Z_1^2 overcounted!

For N particles, Z_1^N overcounts states when all N particles are in different states by a factor $N!$

How can we calculate Z_N?

Approximation: why not ignore the states where there are two or more particles in the same energy level?

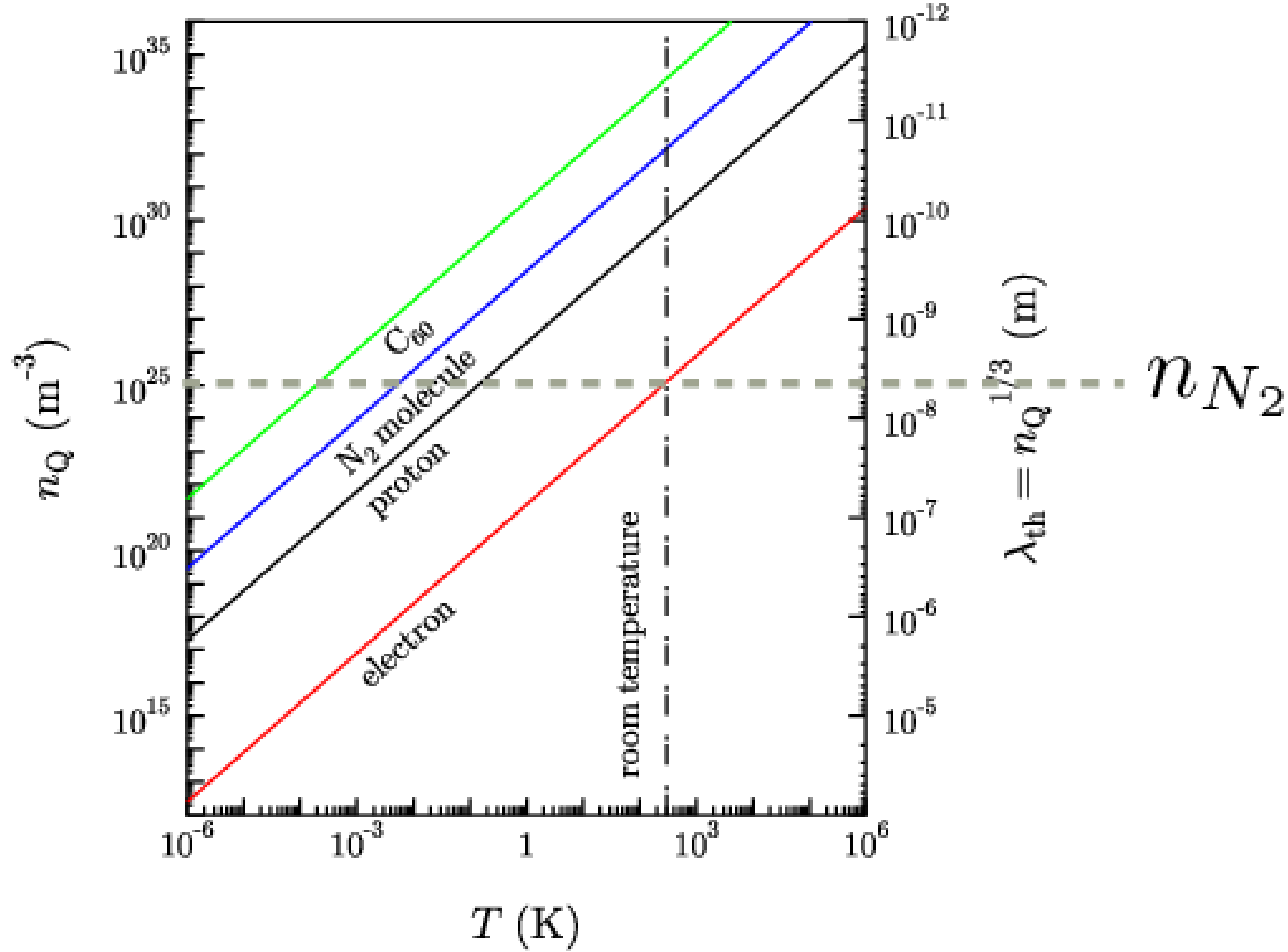
$$Z_N = \frac{(Z_1)^N}{N!}$$

When is it good? If most of the configurations correspond to one particle per level; that is: when the number of levels is much larger than the number of particles.

For the ideal gas, we want many more states than particles for this to work out!

That happens when n (**number density of molecules**) << n_Q

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^N$$



10^{35}
10^{30}
10^{25}
10^{20}
10^{15}
$n_Q\ (m^{-3})$
10^{-12}
10^{-11}
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
$\lambda_{th} = n_Q^{1/3}$ (m)
C_{60}
N_2 molecule
proton
electron
room temperature
10^{-6}
10^{-3}
1
10^{3}
10^{6}
T (K)
n_{N_2}

Functions of state of the ideal gas

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_{\mathrm{th}}^3}\right)^N \propto (VT^{3/2})^N$$

$$\Rightarrow$$

$$\ln Z_N = N \ln V + \frac{3N}{2}\ln T + \text{constants.}$$

$$\begin{aligned}\ln Z_N &= N\ln V - 3N\ln\lambda_{\mathrm{th}} - N\ln N + N \\ &= N\ln\left(\frac{V\mathrm{e}}{N\lambda_{\mathrm{th}}^3}\right),\end{aligned}$$

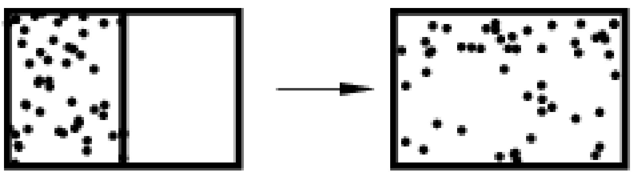
Gibbs paradox

$$S = Nk_\mathrm{B}\left[\frac{5}{2} - \ln\left(n\lambda_\mathrm{th}^3\right)\right]$$

Sackur-Tetrode equation

Joule expansion

(a)



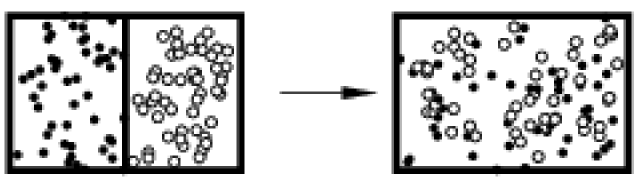
$\Delta S = Nk_B \ln 2$

$$\begin{aligned}\Delta S &= S_{\text{final}} - S_{\text{initial}} \\ &= Nk_B\left[\frac{5}{2} - \ln\left(\frac{n}{2}\lambda_{\text{th}}^3\right)\right] - Nk_B\left[\frac{5}{2} - \ln(n\lambda_{\text{th}}^3)\right] \\ &= Nk_B \ln 2,\end{aligned}$$

"one uncertainty bit per molecule"

(b)

Distinct molecules

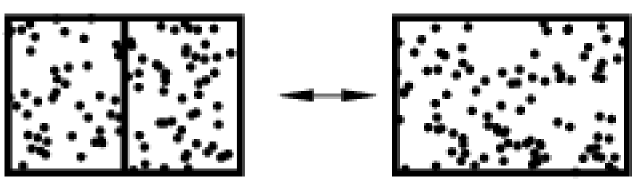


$\Delta S = 2Nk_B \ln 2$

Also an irreversible process

(c)

Same molecules



$\Delta S = 0$

A reversible process!

Paradox?

Paradox resolution

There is a fundamental difference between the two cases!

We do not lose information (e.g., on where a molecule of gas is located) in the second case!

Gibbs resolved this paradox by realizing that indistinguishability was fundamental and that ***all states of the system that differ only by a permutation of identical molecules should be considered as the same state.***

Failure to do this results in an expression for the entropy that is not extensive!

Heat capacity of a diatomic gas

Sum of 3 translations, 2 rotations, two vibrations; for 7 modes

Equipartition theorem: mean energy per molecule is $7/2k_BT$ at high temperature

The modes are independent and

$$Z = Z_{\rm trans} Z_{\rm vib} Z_{\rm rot}$$

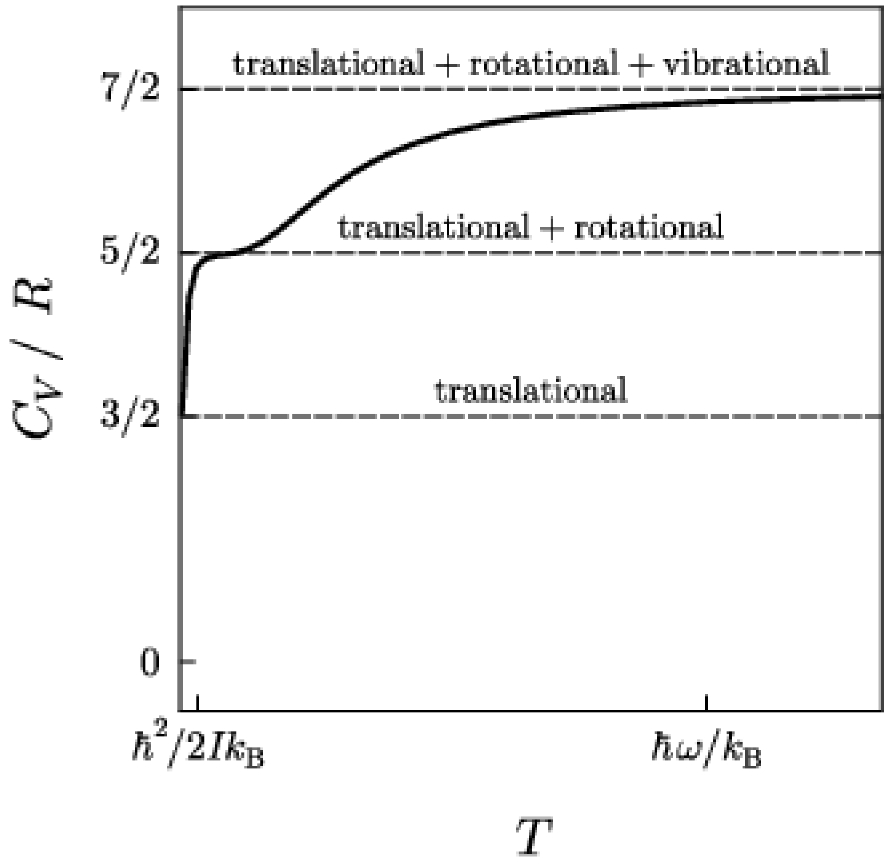
Internal energy is thus the sum of each contribution

C_V is also a <u>sum</u> of each contribution!

$$Z_{\rm trans} = V/\lambda_{\rm th}^3$$

$$Z_{\rm vib} = {\rm e}^{-\frac{1}{2}\beta\hbar\omega}/(1-{\rm e}^{-\beta\hbar\omega})$$

$$Z_{\rm rot} = \sum_\alpha {\rm e}^{-\beta E_\alpha} = \sum_{J=0}^{\infty}(2J+1){\rm e}^{-\beta\hbar^2 J(J+1)/2I}$$



Where should C_V go at T=0? Why?

$$Z_{\mathrm{trans}} = V/\lambda_{\mathrm{th}}^3$$

$$Z_{\mathrm{vib}} = \mathrm{e}^{-\frac{1}{2}\beta\ \omega}/(1-\mathrm{e}^{-\beta\ \omega})$$

$$Z_{\mathrm{rot}} = \sum_{\alpha} \mathrm{e}^{-\beta E_\alpha} = \sum_{J=0}^{\infty}(2J+1)\mathrm{e}^{-\beta\hbar^2 J(J+1)/2I}$$

Summary

For an ideal gas, the partition function can be written

$$Z = V/\lambda_{\rm th}^3$$

where is the thermal wavelength.

The quantum concentration

The -particle partition function is given by

for indistinguishable particles in the low-density case when so that