$$g(\varepsilon) = \sum_r \delta(\varepsilon - \varepsilon_r)$$

Chapter 3.7 Quantized particle in a box

Some aspects of quantum mechanical systems (vs. classical ones)

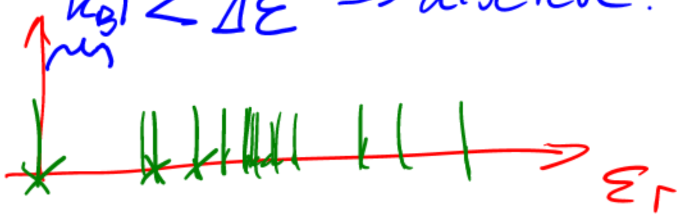
1.) States are generally in a superposition

Specify states as vector in Hilbert space → density matrix $\hat{\varrho}$

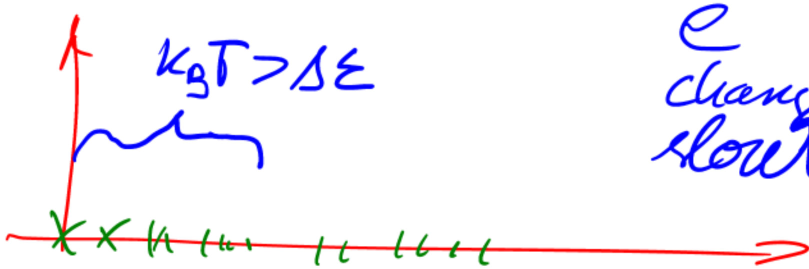
expectation value: sum/trace

2.) Energy levels are quantized

$k_BT < \Delta E$ → discrete!



$k_BT > \Delta E$



$e^{-\varepsilon/k_BT}$ changes slowly

→ sum approx. as integral

3.) Indistinguishable particles are not independent

Fermions: Pauli principle, antisymmetric wavefct under exchange

Bosons: symm. exchange; more multiple occupancy

→ statistical repulsion/attractions → treated later

not relevant for "single particle" → DOS → partition function

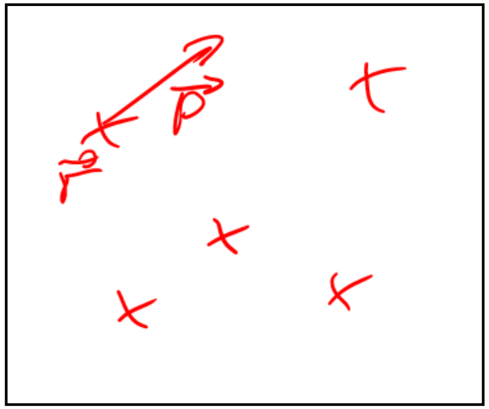
Single particle density of states for quantized particles in a box $\varepsilon = \dfrac{\vec{p}^{\,2}}{2m} = \dfrac{\hbar^2 k^2}{2m} = \dfrac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$

$k_x = \dfrac{2\pi}{\lambda_x} \ldots$

$$g(\varepsilon) = \sum_r \delta(\varepsilon_r - \varepsilon) \qquad Z_1 = \sum_r e^{-\beta\varepsilon_r}$$

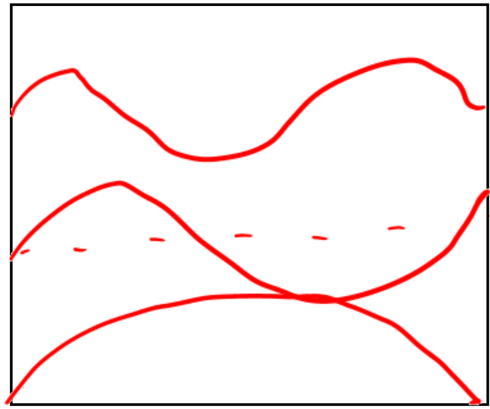
Classical

ideal gas



Quantum

particle in box



standing waves

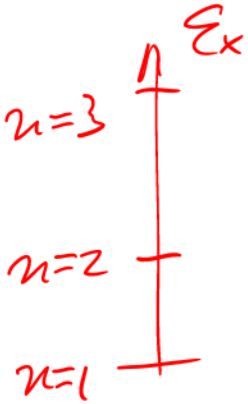
$n_x \dfrac{\lambda_x}{2} = L_x$

in each direction quantum #s

$$Z_1 = \int d^3\vec{r}\, d^3\vec{p}\, e^{-\beta\varepsilon} = V\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}$$

$$k_x = \frac{2\pi}{\lambda_x} = n_x \frac{\pi}{L}$$

n_x, n_y, n_z



$$\varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z$$

$$\varepsilon_x = \frac{\hbar^2}{2m}\frac{\pi^2}{L_x^2} n_x^2$$

$$Z_1 = \sum_{n_x, n_y, n_z = 1}^{\infty} e^{-\beta(\varepsilon_x + \varepsilon_y + \varepsilon_z)} = Z_x Z_y Z_z$$

Quantum partition function of a single particle in a box

$$Z_1 = \sum_r e^{-\beta \varepsilon_r} = Z_x Z_y Z_z$$

$$Z_x = \sum_{n_x=1}^{\infty} \exp(-\beta n_x^2 \frac{\hbar^2 \pi^2}{2mL_x^2}) = \sum_{n=1}^{\infty} e^{-n^2 \pi \alpha}$$

$$\alpha = \left(\frac{\lambda_T}{2L_x}\right)^2$$

Thermal wave-length

$$\lambda_T^2 = 2\frac{\hbar^2 \pi \beta}{m}$$

$$= \frac{1}{2}\sum_{n=-\infty}^{\infty} e^{-n^2 \pi \alpha} - \frac{1}{2}$$

Poisson resummation

$$\sum_{n=-\infty}^{\infty} e^{-n^2 \pi \alpha} = \alpha^{-\frac{1}{2}} \sum_{m=-\infty}^{\infty} e^{-m^2 \pi / \alpha}$$

Jacobi Theta function

$$\Theta_3(z, e^{-\pi\alpha}) = \sum_{n=-\infty}^{\infty} e^{-n^2 \pi \alpha} e^{i2nz}$$

if $\alpha \ll 1$

$$Z_x \simeq \frac{1}{2}\alpha^{-\frac{1}{2}} = \frac{L_x}{\lambda_T}$$

+ exp. small corrections

Def. 3.8: The thermal wave length of a particle is defined as

$$\lambda_T = \hbar\sqrt{\frac{2\pi}{mk_BT}} = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$$

at 298K: H_2 $\lambda_T \approx 7.1228 \times 10^{-11}$ m

O_2 $\lambda_T \approx 1.7878 \times 10^{-11}$ m

4K: H_2 $\lambda_T \approx 6.15 \times 10^{-10}$ m

$a_0 = 0.52 \times 10^{-10}$ m

$\rightarrow \alpha = \left(\frac{\lambda_T}{2L}\right)^2 \ll 1$

for atomic / molecular gases

Maybe for $\bar{e}$ in nanostructures quantization is relevant

$$\langle p \rangle = m\langle v \rangle = \sqrt{\frac{8}{\pi} m k_B T} = \frac{4\hbar}{\lambda_T}$$

$\lambda_T \sim$ average DeBroglie wavelength in thermal equilibrium

The single particle partition function for a quantized particle in a 3D box is

$$Z_1 = \sum_r e^{-\beta \varepsilon_r} = Z_x Z_y Z_z \approx \frac{V}{\lambda_T^3}$$

Single particle density of states

$$g(\varepsilon) = \sum_r \delta(\varepsilon_r - \varepsilon)$$