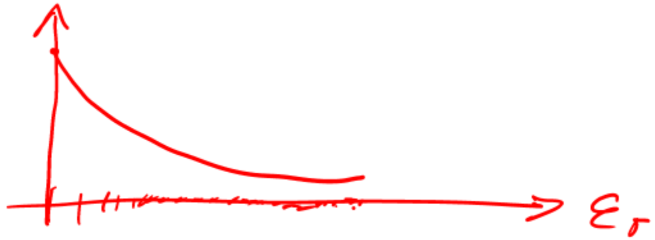
most likely GS

Chapter 3.6: Density of states and velocity distribution



Basis: Boltzmann distribution $P_r = \dfrac{e^{-\beta\varepsilon_r}}{Z}$

Is the probabilty to find a given microstate. But what is probability to find energy ε ?

$P(\varepsilon)$ $\quad \int P(\varepsilon)\, d\varepsilon = 1$

$$\langle\varepsilon\rangle = E = \frac{\int d\Gamma\, e^{-\beta\varepsilon}\varepsilon}{Z} = \int P(\varepsilon)\,\varepsilon\, d\varepsilon$$

idea: change of variables $d\Gamma \to d\varepsilon$

($\times \frac{1}{N!}$ omitted)

$$= \frac{V^N}{Z}\int d\varepsilon\,(2m\varepsilon)^{\frac{3}{2}N-1}\, m\, e^{-\beta\varepsilon}\,\varepsilon$$

2.4-4, 2.4-5: $\varepsilon = \sum_j \frac{p_j^2}{2m}$ ideal gas

$$= \frac{\int \Omega(\varepsilon)\, e^{-\beta\varepsilon}\,\varepsilon\, d\varepsilon}{Z}$$

general:

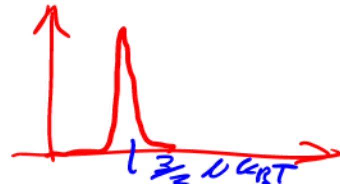
$$P(\varepsilon)\,d\varepsilon = \frac{e^{-\beta\varepsilon}}{Z}\,\Omega(\varepsilon)\, d\varepsilon \quad *$$

$=$ Probability to find $[\varepsilon, \varepsilon + d\varepsilon[$

Maximum $\partial_\varepsilon P(\varepsilon) = 0 = \frac{3}{2}N\varepsilon^{\frac{3}{2}N-1}e^{-\beta\varepsilon} - \beta\varepsilon^{\frac{3}{2}N}e^{-\beta\varepsilon}$

$\Rightarrow \frac{3N}{2\varepsilon} = \beta \qquad \varepsilon = \frac{3}{2}Nk_BT$

ideal gas: $P(\varepsilon) \propto \dfrac{V^N \varepsilon^{\frac{3}{2}N} e^{-\beta\varepsilon}}{Z}$



$Z = \int \Omega(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon$ "Laplace transform"

3.6-2 Density of states and velocity distribution

$P(\varepsilon)d\varepsilon$: Probability for one particle of energy ε

For a single particle: $\langle\varepsilon\rangle = \dfrac{\sum_r e^{-\beta\varepsilon_r}\varepsilon_r}{Z_1} = \int P(\varepsilon)\,\varepsilon\, d\varepsilon = \dfrac{\int e^{-\beta\varepsilon}\varepsilon\, g(\varepsilon)\, d\varepsilon}{Z_1}$

Def. 3.6: The single particle density of states is $g(\varepsilon) = \sum_r \delta(\varepsilon_r - \varepsilon)$

$$P(\varepsilon) = g(\varepsilon)\frac{e^{-\beta\varepsilon}}{Z_1}$$

$$\langle\varepsilon\rangle = \int d\varepsilon\, P(\varepsilon)\,\varepsilon$$

only useful for independent particles (non-interacting)

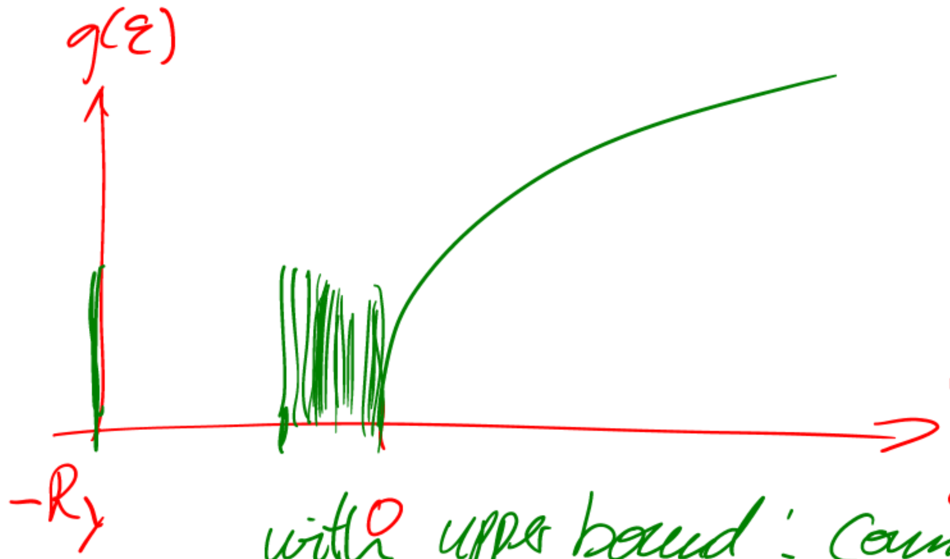
The single particle density of states $g(\varepsilon)$, determines the probability $P(\varepsilon)d\varepsilon = g(\varepsilon)e^{-\beta\varepsilon}d\varepsilon / Z_1$ for energies in the interval $[\varepsilon, \varepsilon + d\varepsilon[$ for each independent particle.

$g(\varepsilon)$ may in many cases increase

but also cases where GS remains most probable

but many particle $\Omega(\varepsilon)$ increases

Atom



with upper bound: counter example: Exercise 6c

Example: Single particle density of states for a free classical particle

→ change of variables

$$\varepsilon = \frac{p^2}{2m} \qquad p = \sqrt{2m\varepsilon} \qquad dp = \sqrt{\frac{m}{2\varepsilon}}\, d\varepsilon \quad *$$

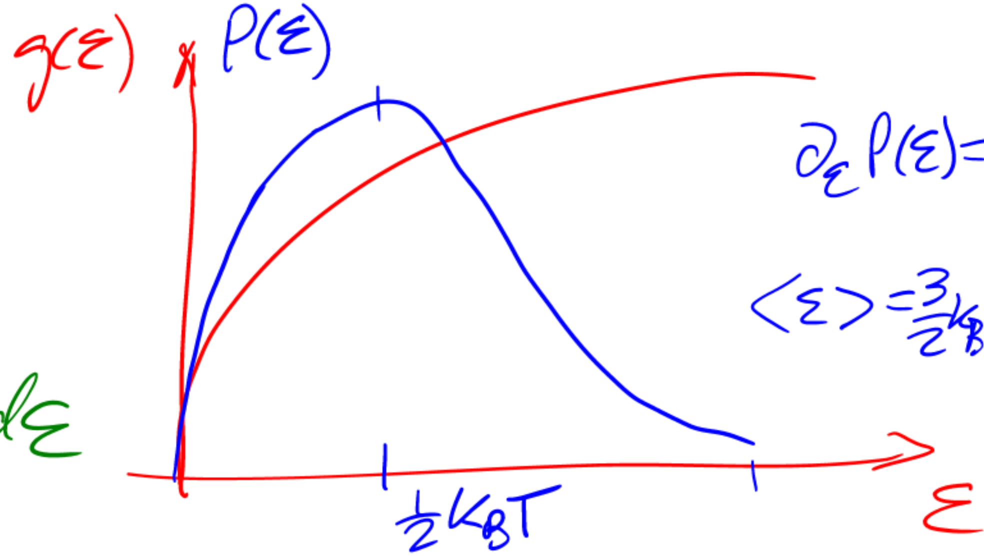
$$\langle \varepsilon \rangle = \frac{\int d\varepsilon\, g(\varepsilon) e^{-\beta\varepsilon}\varepsilon}{Z_1} = \frac{\int d^3\vec{r} d^3\vec{p}\; e^{-\beta\varepsilon}\varepsilon}{Z_1} = \frac{V}{Z_1}\int 4\pi p^2 dp\; e^{-\beta\frac{p^2}{2m}} \frac{p^2}{2m}$$

good definition for classical case

$$\overset{*}{=} \frac{V}{Z_1}\int 4\pi\, 2m\varepsilon \sqrt{\frac{m}{2\varepsilon}}\, d\varepsilon\; e^{-\beta\varepsilon}\varepsilon$$

$$P(\varepsilon) = \frac{g(\varepsilon)e^{-\beta\varepsilon}}{Z_1} = 2\sqrt{\frac{\beta^3\varepsilon}{\pi}}\, e^{-\beta\varepsilon} \Rightarrow$$

$$g(\varepsilon) = V \cdot 4\pi\, m^{\frac{3}{2}} \sqrt{2\varepsilon} \propto \sqrt{\varepsilon}$$



$\partial_\varepsilon P(\varepsilon) = 0$

$\langle \varepsilon \rangle = \frac{3}{2} k_B T$

Normalization of g(ε) depends on the normalization of Z_1

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

Distribution for general expectation values: Λ

what is the probability $P(\lambda)d\lambda$ to measure Λ in $[\lambda, \lambda + d\lambda[$?

$$\langle \Lambda \rangle = \frac{\sum_r e^{-\beta\varepsilon_r} \langle r|\Lambda|r\rangle}{Z_1} = \int P(\lambda)\, \lambda\, d\lambda$$

Classical example: velocity in x-direction

by change variable v_x

$$\langle v_x \rangle = \int dv_x\, P(v_x) v_x = \frac{\int d^3\vec{r} d^3\vec{p}\, e^{-\beta\varepsilon} v_x}{Z_1} = \frac{V}{Z_1} \int dp_x\, e^{-\beta \frac{p_x^2}{2m}} v_x \int dp_y\, e^{-\beta \frac{p_y^2}{2m}} \int dp_z\, e^{-\beta \frac{p_z^2}{2m}}$$

$$Z_1 = V\left(\int dp\, e^{-\beta \frac{p^2}{2m}}\right)^3 = V\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$= \sqrt{\frac{\beta}{2\pi m}} \int dp_x\, e^{-\beta \frac{p_x^2}{2m}} v_x$$

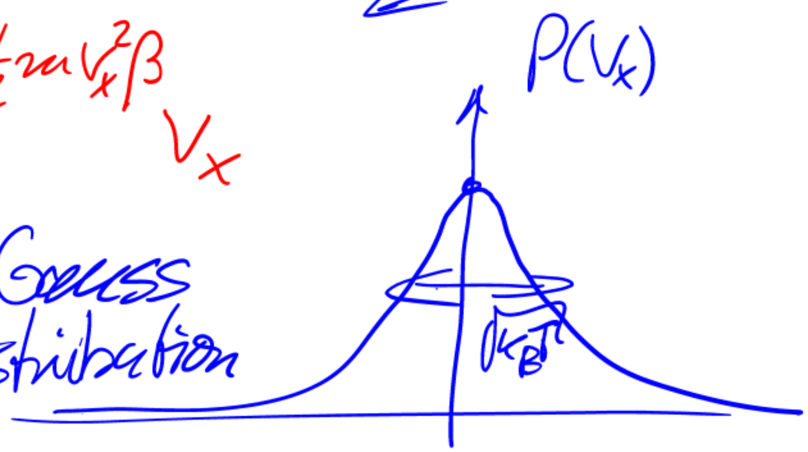
$p_x = m v_x$

$$= \sqrt{\frac{\beta m}{2\pi}} \int dv_x\, e^{-\frac{1}{2} m v_x^2 \beta} v_x$$

$$P(v_x) = \sqrt{\frac{\beta m}{2\pi}}\, e^{-\frac{1}{2} m v_x^2 \beta}$$

$$\int P(v_x)\, dv_x = 1$$

Gauss distribution



Maxwell's velocity distribution

$$\langle v \rangle = \int dv\, P(v) v = \frac{\int d^3\vec{r} d^3\vec{p}\; e^{-\beta\varepsilon} v}{Z_1}$$

Def. 3.7: Maxwell's velocity distribution

$$P(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\beta m v^2/2} dv$$

is the probability for a particle-velocity in the interval $[v, v+dv[$

3.6-6 Density of states and velocity distribution

Mean, most probable and RMS values

$$P(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\beta m v^2/2} dv$$