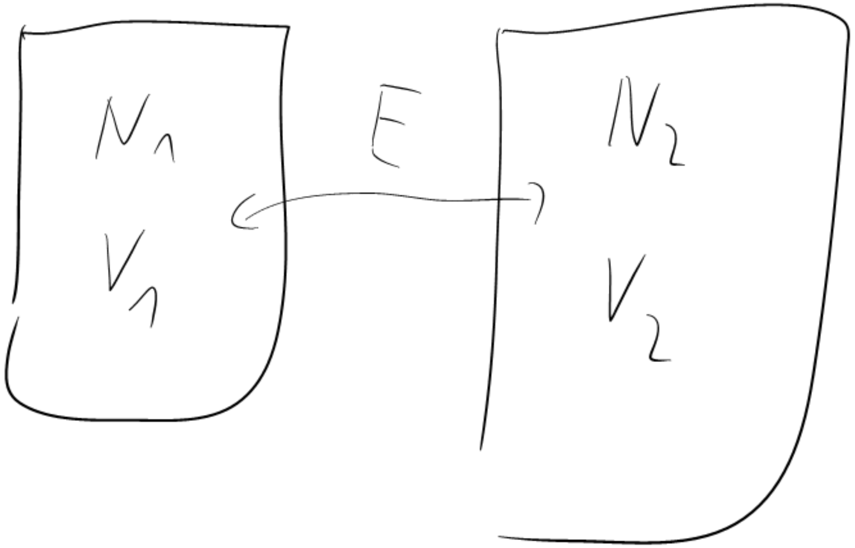
Boltzmann Distribution, Partition Function and Free Energy



we know:

$$\Omega_{tot}(E) = \frac{1}{\Delta E} \int_0^E dE_1 \, \Omega_1(E_1) \, \Omega_2(E - E_2) =$$

$$= \frac{\Delta E}{N_1! \, N_2!} \frac{1}{(2\pi\hbar)^{3(N_1+N_2)}} \int d\Gamma_1 \int d\Gamma_2 \, \delta\left(H_1(\Gamma_1) + H_2(\Gamma_2) - E \right)$$

we want: $\rho(\Gamma_1)\, d\Gamma_1 \equiv$ probability to find the left system near phase space point Γ_1 = ?

we know:

$$\rho(\Gamma_1, \Gamma_2) = \frac{1}{\Omega_{tot}(E)} \frac{1}{N_1!} \frac{1}{N_2!} \frac{1}{(2\pi\hbar)^{3(N_1+N_2)}} \Delta E\, \delta\big(H_1(\Gamma_1) + H_2(\Gamma_2) - E\big)$$

$$\rho(\Gamma_1) = \int d\Gamma_2\, \rho(\Gamma_1, \Gamma_2) = \frac{1}{\Omega_{tot}(E)} \frac{1}{N_1!} \frac{1}{(2\pi\hbar)^{3N_1}} \times$$

$$\times \underline{\frac{1}{N_2!} \frac{\Delta E}{(2\pi\hbar)^{3N_2}} \int d\Gamma_2\, \delta\Big(H_2(\Gamma_2) - \big(E - H_1(\Gamma_1)\big)\Big)} =$$

$$\rho(\Gamma_1) = \frac{1}{N_1!}\frac{1}{(2\pi\hbar)^{3N_1}}\frac{\Omega_2\left(E - H_1(\Gamma_1)\right)}{\Omega_{tot}(E)}$$

ONLY dependence on Γ_1!

Now, $\Omega_2\left(E - H_1(\Gamma_1)\right) =$

$$= \exp\left[S\left(E - H_1(\Gamma_1)\right)\right]$$

Now, let $N_2 \to \infty$, $V_2 \to \infty$, $\frac{N_2}{V_2}$ fixed

$E_2 \to \infty$, $\frac{E_2}{V_2}$ fixed $\to$ infinite reservoir of energy

HEAT BATH

$$S\left(E - H_1(\Gamma_1)\right) = \underbrace{S(E)}_{O(N_2)} - \underbrace{\frac{\partial S}{\partial E}}_{=\beta=\frac{1}{T}} \underbrace{H_1(\Gamma_1)}_{O(N_1)} + \underbrace{\ldots}_{\text{neglect!}}$$

$N_1 \ll N_2 \qquad \frac{N_1}{N_2} \ll 1$

$\rightarrow$ Taylor expansion in $\frac{N_1}{N_2}$

$$\exp\left[S\left(E - H_1(\Gamma_1)\right)\right] \simeq \exp(S(E)) \underbrace{\exp(-\beta H_1(\Gamma_1))}_{\text{Boltzmann factor}}$$

$p(\Gamma_1) \propto \exp(-\beta H_1(\Gamma_1))$ normalization

$$\Rightarrow \underbrace{p(\Gamma_1) = \frac{1}{Z}\,\frac{1}{N_1!}\,\frac{1}{(2\pi\hbar)^{3N_1}}\,\exp(-\beta H_1(\Gamma_1))}_{\text{Boltzmann distribution}}$$

$$\underbrace{Z = \frac{1}{N_1!}\,\frac{1}{(2\pi\hbar)^{3N_1}} \int d\Gamma_1 \exp(-\beta H_1(\Gamma_1))}_{\text{canonical partition function}}$$

Remark:

$$Z(\beta) = \frac{1}{N_1!} \frac{1}{(2\pi\hbar)^{3N_1}} \int dE_1 \int d\Gamma_1 \; \delta\left(H_1(\Gamma_1) - E_1\right) \exp\left(-\beta E_1\right) =$$

$$= \int dE_1 \, \Omega_1(E_1) \exp(-\beta E_1) \implies$$

$$\Omega_1(E_1) \xrightarrow[\text{transformation}]{\text{Laplace-}} Z(\beta)$$

microcan. part. fct.

canonical part. fct

In terms of potentials

$$dE = T\,dS - P\,dV + \mu\,dN \qquad \Big|\cdot\beta$$

$$F = E - TS \qquad \Big|\cdot(-\beta)$$

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$dS = \beta\,dE + \beta P\,dV - \beta\mu\,dN$$

$$-\beta F = S - \beta E$$

$$d(-\beta F) = -E\,d\beta + \beta P\,dV - \beta\mu\,dN$$

$$S \xrightarrow{\text{legendre tr.}} -\beta F$$

and $\dfrac{\partial(-\beta F)}{\partial\beta} = -E$

on the other hand

$$-\langle E\rangle = \frac{\int d\Gamma \exp(-\beta H(\Gamma))\,(-H(\Gamma))}{\int d\Gamma \exp(-\beta H(\Gamma))} =$$

$$= \frac{\frac{\partial}{\partial\beta}\int d\Gamma \exp(-\beta H(\Gamma))\,\frac{1}{N!}\,\frac{1}{(2\pi\hbar)^{3N}}}{\int d\Gamma \exp(-\beta H(\Gamma))\,\frac{1}{N!}\,\frac{1}{(2\pi\hbar)^{3N}}} =$$

$$= \frac{1}{Z}\frac{\partial}{\partial\beta} Z = \frac{\partial}{\partial\beta}\ln Z$$

So: $-E = \frac{\partial}{\partial\beta}(-\beta F) = \frac{\partial}{\partial\beta}\ln Z$

$\rightarrow$ SUSPICION: $-\beta F = \ln Z$

What about the V derivative? We know

$$\frac{\partial}{\partial V}(-\beta F) = \beta P$$

. on the other hand

$$\frac{\partial}{\partial V}(\ln Z) = \frac{1}{Z}\frac{\partial Z}{\partial V} = \frac{1}{Z}\frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}}\int d\Gamma\, e^{-\beta H(\Gamma)}(-\beta)\frac{\partial H}{\partial V} =$$

$$-\beta \left\langle \frac{\partial H}{\partial V} \right\rangle_{\text{canon.}} \underset{\substack{\uparrow \\ \text{thermodyn.} \\ \text{limit}}}{=} -\beta \left\langle \frac{\partial H}{\partial V} \right\rangle_{\text{microcan.}} =$$

$$= -\beta \left.\frac{\partial E}{\partial V}\right|_S = (-\beta)(-P) = \boxed{\beta P}$$

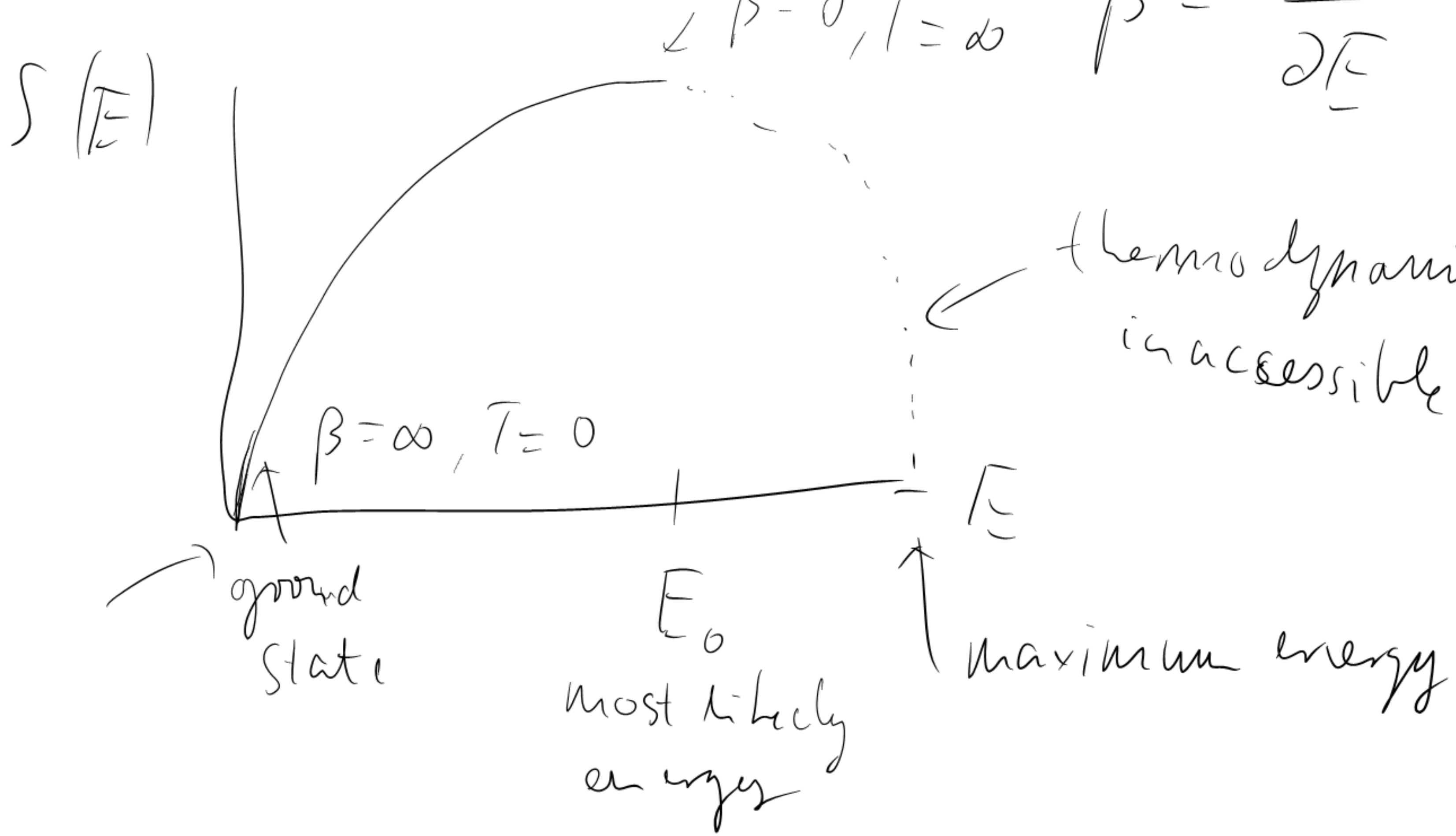
$$dE = T\,dS - P\,dV + \mu\,dN$$

$$\Rightarrow \boxed{\frac{\partial}{\partial V}(-\beta F) = \frac{\partial}{\partial V} \ln Z} \Rightarrow -\beta F = \ln Z + \underbrace{\text{const.}}_{= 0 \ \underline{\text{why?}}}$$

Show that the constant is zero

Special system: Energy is bounded, system has a finite # of states

$$\beta = \frac{\partial S}{\partial E} = \frac{1}{T}$$



$$\Omega(E_0) = e^{S(E_0)} \simeq \# \text{ of ALL states in the system}$$

$$\beta = 0 \longrightarrow E = E_0 , \quad S(\beta = 0) = \ln \Omega(E_0)$$
$$\hat{=} \ln(\# \text{ of all states})$$

on the other hand:

$$-\beta F = S - \beta E \xrightarrow{\beta \to 0}$$

$$\longrightarrow S(\beta = 0) - 0 \cdot E_0 = S(\beta = 0)$$
$$= \ln(\# \text{ of all states})$$

finally:

$$\ln Z(\beta \to 0) = \ln \underbrace{\frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}} \int d\Gamma \, 1}_{\#\text{ of all states}} =$$

$$= \ln(\#\text{ of all states}) = S(\beta = 0)$$

$$\Rightarrow \text{const.} = 0, \quad -\beta F = \ln Z$$

$$\boxed{F = -T \ln Z} \quad !$$

The Canonical Partition Function

$$Z = \left(\prod_k \frac{1}{N_k!}\right) \frac{1}{(2\pi\hbar)^{3N}} \int d\Gamma \; e^{-\beta H}$$

species

Cartesian coordinates

$$d\Gamma = d^3\vec{p}_1 \, d^3\vec{p}_2 \ldots d^3\vec{p}_N \; d^3\vec{r}_1 \ldots d^3\vec{r}_N$$

$$H = \sum_i \frac{1}{2m_i} \vec{p}_i^{\,2} + U(\{\vec{r}_i\})$$

$d^3\vec{p}_1 = dp_{1x} \, dp_{1y} \, dp_{1z}$

$$e^{-\beta H} = \exp\left(-\beta \frac{p_{1x}^2}{2m_1}\right) \exp\left(-\beta \frac{p_{1y}^2}{2m_1}\right) \ldots \exp\left(-\beta \frac{p_{Nz}^2}{2m_N}\right) e^{-\beta U}$$

Gaussian integrals $\Rightarrow$

$$Z_{coord.} = \left(\prod_{\nu} \frac{1}{N_{\nu}!}\right) \int d^3\vec{r}_1 \dots \int d^3\vec{r}_N \, e^{-\beta U}$$

$$Z = \frac{1}{(2\pi\hbar)^{3N}} \, Z_{momenta} \, Z_{coord.}$$

$$Z_{momenta} = \int d^3\vec{p}_1 \, e^{-\beta \frac{\vec{p}_1^{\,2}}{2m_1}} \dots \int d^3\vec{p}_N \, e^{-\beta \frac{\vec{p}_N^{\,2}}{2m_N}}$$

$$= \sqrt{2\pi m_1 T}^{\,3} \dots \sqrt{2\pi m_N T}^{\,3} \quad (3N \text{ roots})$$

Define: $$\frac{\sqrt{2\pi m_i T}}{2\pi\hbar} =: \frac{1}{\lambda_i}$$

λ_i "thermal deBroglie wavelength" of particle i

$$Z = Z_{coord} \cdot \prod_i \frac{1}{\lambda_i^3}$$

for ideal gas: $\quad Z = \left(\prod_k \frac{1}{N_k!} \right) \left(\prod_i \frac{1}{\lambda_i^3} \right) V^N$

$\Rightarrow F = -T \ln Z = -T N \ln V$ + terms indep. of V

$$P = -\left.\frac{\partial F}{\partial V}\right|_T = +TN\frac{1}{V} \Rightarrow \boxed{PV = TN}$$

probability for the velocity of particle i:

$$P(\vec{v}_i) = \frac{1}{\sqrt{2\pi \frac{T}{m_i}}^{\,3}} \exp\left[-\beta \frac{m_i}{2} \vec{v}_i^{\,2}\right]$$

Maxwell velocity distribution

$$\langle v_{ix}^2 \rangle = \langle v_{iy}^2 \rangle = \langle v_{iz}^2 \rangle = \frac{T}{m_i}$$

$$\frac{m_i}{2} \langle v_{ix}^2 \rangle = \frac{T}{2}$$ equipartition theorem:

$T/2$ per "quadratic" degree of freedom