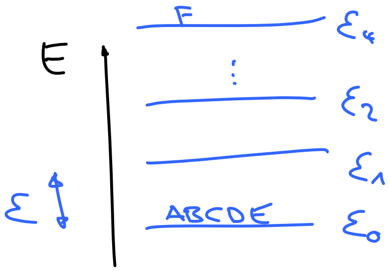
II. Statistische Thermodynamik

1. Klassische Verteilungsfunktionen



$\{5;0;0;0;1\}$, $\boxed{\varepsilon_{ges} = 4\varepsilon,\ N=6}$

$$\Omega = \frac{6!}{5!\cdot 1!} = 6$$

$$\Omega\{2;4;0\ldots\} = \frac{6!}{4!\cdot 2!} = 15 \qquad \Omega\{3;2;1;\ldots\} = 60$$

Gesucht: wahrscheinlichste Konfiguration (für große N)

$$\Rightarrow d\Omega \overset{!}{=} 0 \quad \text{bzw.} \quad \boxed{d\ln\Omega \overset{!}{=} 0}$$

Stirling:
$$\ln N! \sim (N\cdot\ln N) - N$$

$$d\ln\Omega = \sum_i \left(\frac{\partial \ln\Omega}{\partial N_i}\right) dN_i$$

NR:
$$\ln\Omega = \ln N! - \sum_i \ln N_i! = (N\ln N - N) - \sum_i (N_i \ln N_i - N_i)$$

„für N_j" $(i=j)$:
$$\frac{\partial \ln\Omega}{\partial N_j}\Big|_{(i=j)} = -\frac{\partial}{\partial N_j}\left(N_j\ln N_j - N_j\right) = -\left(\ln N_j + \frac{N_j}{N_j} - 1\right) = -\ln N_j$$

Abgeschlossenes System:
(1) $N = \text{const}$, $dN = 0$, $\sum_i dN_i = 0$ $\quad \uparrow \neq 0?$

(2) $E = \text{const}$, $dE = 0$, $\sum \varepsilon_i dN_i = 0$

Lagrange:
$$d\ln\Omega = \sum_i \left[\Big(\underbrace{\frac{\partial \ln\Omega}{\partial N_i} - \alpha - \beta\varepsilon_i}_{\overset{!}{=}0}\Big) dN_i\right] \overset{!}{=} 0$$

$$\hookrightarrow -\ln N_j - \alpha - \varepsilon_j\beta = 0$$

$$\Longleftrightarrow \boxed{N_j = e^{-\alpha}\cdot e^{-\beta\varepsilon_j}} \quad \text{Boltzmann-Verteilung}$$

$$\frac{N_j}{N} = \frac{e^{-\beta\varepsilon_j}}{\sum_i e^{-\beta\varepsilon_i}} = P_j$$

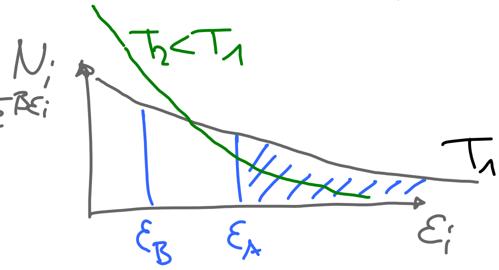
NR: $N = \sum N_i = \sum_i e^{-\alpha} e^{-\beta\varepsilon_i} = e^{-\alpha} \cdot \sum e^{-\beta\varepsilon_i}$

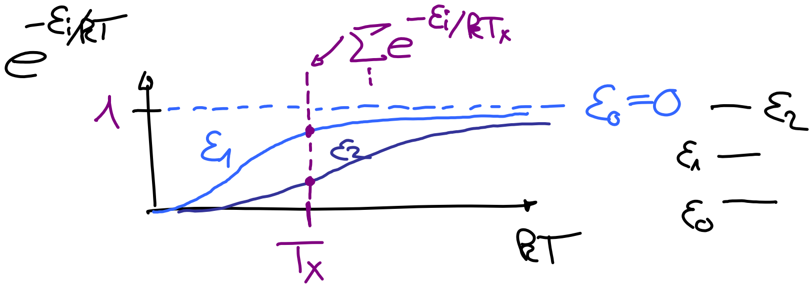
Und β? $[\beta] = \frac{1}{J} \Rightarrow \varepsilon = k_B T$ (s. Gleichverteilungssatz)

$\rightarrow \beta = 1/kT$

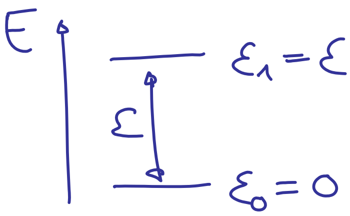
$$\Rightarrow \boxed{N_j/N = \frac{e^{-\varepsilon_j/kT}}{\underbrace{\sum_i e^{-\varepsilon_i/kT}}_{=:q}}} = P_j$$

Zustandssumme





2-Niveau-System



$$\Rightarrow q = \sum_1^2 e^{-\varepsilon_i/kT} = \boxed{1 + e^{-\varepsilon/kT}}$$

$T \to 0$: $q \to 1$

$T \to \infty$: $q \to 2$

$$N_j/N = \frac{e^{-\varepsilon_j/kT}}{q} = P_j$$

für $\varepsilon_0 = 0$: $P_0 = \frac{1}{1 + e^{-\varepsilon/kT}}$

für $\varepsilon_1 = \varepsilon$: $P_1 = \frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}}$

$T \to 0$	$T \to \infty$
1	1/2
0	1/2
1	1

Allg.: $q = \sum_i g_i \cdot e^{-\varepsilon_i/kT}$

g_i: Entartung

und damit: $P_j = \frac{g_j \cdot e^{-\varepsilon_j/kT}}{q}$ Boltzmann

$\varepsilon_A/\varepsilon_B \Rightarrow N_A/N_B = \frac{g_A}{g_B} \cdot e^{-\underbrace{(\varepsilon_A - \varepsilon_B)}_{\Delta\varepsilon}/kT}$

Zustandssumme Translation

$$\varepsilon_n = n^2 \frac{h^2}{8 m x^2}, \quad \text{Kasten Länge } x$$

$$\Rightarrow q = \sum_{n=1}^{\infty} g_n \cdot e^{-(n^2-1)\varepsilon/kT}$$

$$↯\ \varepsilon_{n=1} \neq 0 \Rightarrow \varepsilon_n = (n^2-1) \cdot \underbrace{\frac{h^2}{8 m x^2}}_{\varepsilon}$$

Überlegung: $\Delta\varepsilon(n=1, n=2;\ {}^1H,\ x = 0.1\,m) = 10^{-38}\,J$

Vergleich: $k_B T_{(300K)} = 4 \cdot 10^{-21}\,J$

$$q = \int_1^{\infty} e^{-(n^2-1)\varepsilon/kT}\, dT \approx \int_0^{\infty} e^{\underbrace{-n^2\varepsilon/kT}_{=a^2}}\, dn \qquad \int_{-\infty}^{+\infty} e^{-a^2}\, da = \sqrt{\pi}$$

$$\left(a^2 = n^2 \varepsilon \beta,\quad da/dn = \sqrt{\varepsilon\beta}\right) \qquad \boxed{\beta = \frac{1}{kT}}$$

$$= \int_0^{\infty} e^{-a^2}\, da \cdot \frac{1}{\sqrt{\varepsilon\beta}} = \frac{1}{2}\sqrt{\frac{\pi}{\beta\varepsilon}} = \frac{1}{2}\left(\frac{kT \cdot 8\pi m x^2}{h^2}\right)^{1/2}$$

$$\Rightarrow \boxed{q_{trans,1D} = \left(\frac{2\pi m kT}{h^2}\right)^{1/2} \cdot x}$$

O_2, 298K, $x = 0.1\,m$

$q \sim 10^{10}$

Translation in 3D: $\varepsilon_{trans,3D} = \frac{h^2}{8m}\left(\frac{n_x^2}{x^2} + \frac{n_y^2}{y^2} + \frac{n_z^2}{z^2}\right) = \varepsilon_x + \varepsilon_y + \varepsilon_z$

$$q_{trans,3D} = \sum_{(n_x,n_y,n_z)} e^{-(\varepsilon_x+\varepsilon_y+\varepsilon_z)/kT} = \underbrace{\sum e^{-\varepsilon_x/kT}}_{q_{trans,1Dx}} \cdot \underbrace{\sum e^{-\varepsilon_y/kT}}_{q_{trans,1Dy}} \cdot \underbrace{\sum e^{-\varepsilon_z/kT}}_{q_{trans,1Dz}}$$

$$\boxed{q_{trans,3D} = \frac{(2\pi m kT)^{3/2}}{h^3} V}$$

$(298K, O_2, V = 1\,l)$ $q_{trans,3D} = 1.8 \cdot 10^{29}$

$N_{(O_2,g)} = 2.7 \cdot 10^{22}$

$\frac{N}{q} \sim 10^{-7} \Rightarrow \boxed{\text{Boltzmann OK}}$

$\varepsilon_{ges} = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib}$

$\Rightarrow q_{ges} = q_{trans} \cdot q_{rot} \cdot q_{vib}$

$\boxed{q_{mol}}$