Note Title

V13

9.7.2019

$$q_{mol} = g_{0,el} \cdot \left(\frac{V}{\Lambda^3}\right) \cdot \left(\frac{1}{1-e^{\Theta_{vib}/T}}\right) \cdot \frac{T}{\sigma \cdot \Theta_{rot}}$$

4. Anwendungen zu q_{mol}

(i) Mittlere Energie $\langle \varepsilon \rangle = kT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$

$\langle \varepsilon_{trans} \rangle = 3/2\, kT$, $\langle \varepsilon_{rot} \rangle = 1/2\, kT$ (pro FG)

Schwingung? $\langle \varepsilon_{vib}(T) \rangle$?

$$q_{vib} = \frac{1}{1-e^{-\Theta/T}} \Rightarrow \varepsilon_{vib} = kT^2 \frac{\partial}{\partial T}\left(-\ln\left(1-e^{-\Theta/T}\right)\right) = kT^2 \cdot \left(\frac{1}{1-e^{-\Theta/T}}\right)\left(\frac{\Theta}{T^2}\right)\cdot\left(-e^{-\Theta/T}\right)$$

$$= k\Theta \cdot \frac{e^{-\Theta/T}}{1-e^{-\Theta/T}} \quad / \cdot \frac{e^{\Theta/T}}{e^{\Theta/T}}$$

$$\boxed{\langle \varepsilon_{vib}(T) \rangle = \frac{k\Theta}{e^{\Theta/T}-1}}$$

Grenzfall $T \to \infty$: $\langle \varepsilon_{vib} \rangle \longrightarrow kT$

$(T \gg \Theta_{vib})$

$$\frac{k\Theta}{\left(1+\frac{\Theta/T}{1!}+\dots\right)-1}$$

2-atomig : $$\boxed{\langle \varepsilon_{ges}(T) \rangle = 3/2\, kT + kT + \frac{k\Theta}{e^{\Theta/T}-1}}$$

(ii) N Teilchen?

$$E_{ges} = \sum N_i \varepsilon_i = \sum \left(\frac{N}{q} \cdot e^{-\varepsilon_i/kT}\right) \cdot \varepsilon_i$$

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

$$= N \cdot \frac{\sum \varepsilon_i \cdot e^{-\varepsilon_i/kT}}{\sum e^{-\varepsilon_i/kT}} = \boxed{N \cdot kT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V}$$

$$\Rightarrow E_{ges\,(N=N_A)} = RT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$$

.... Innere Energie: $U = U(0K) + E(T)$

ii) C_V

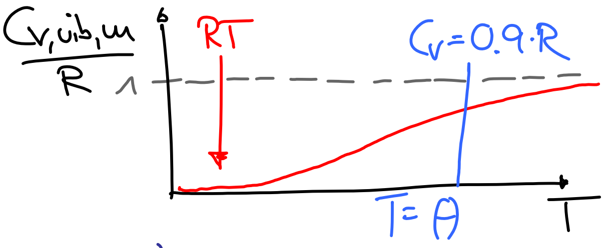
$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(U(0K) + E(T)\right) = \frac{\partial}{\partial T}\left(\underbrace{NRT^2\left(\frac{\partial \ln q}{\partial T}\right)}_{E(T) \text{ bzw. } \langle \varepsilon \rangle}\right)_V}$$

$\Longrightarrow$ $C_{V,\text{trans}} = \frac{3}{2} N \cdot R$, $C_{V,\text{trans},m} = \frac{3}{2} R$

$C_{V,\text{rot}}$ (pro FG) $= \frac{1}{2} NR$

$$C_{V,\text{vib}} = \frac{\partial}{\partial T}\left(\frac{NR\Theta}{e^{\Theta/T}-1}\right) = \frac{-NR\Theta \cdot \left(-\frac{\Theta}{T^2}\right) \cdot e^{\Theta/T}}{\left(e^{\Theta/T}-1\right)^2} = \boxed{NR\left(\frac{\Theta}{T}\right)^2 \cdot \frac{e^{\Theta/T}}{\left(e^{\Theta/T}-1\right)^2}}$$

(2-atomig)



($T \to \infty$: $C_{V,\text{vib},m} \to R$)

($\Longrightarrow$ Festkörper, Debye- bzw. Einstein-Gesetz)

$$\boxed{C_{V,m}(T) = \frac{1}{2} R \cdot \left(3 + f_{\text{rot}} + 2 \cdot \sum_i \left[\left(\frac{\Theta_i}{T}\right)^2 \cdot \frac{e^{\Theta_i/T}}{\left(e^{\Theta_i/T}-1\right)^2}\right]\right)}$$

$f_{\text{rot}} \in \{0; 2; 3\}$

iv) N 2-Niveau

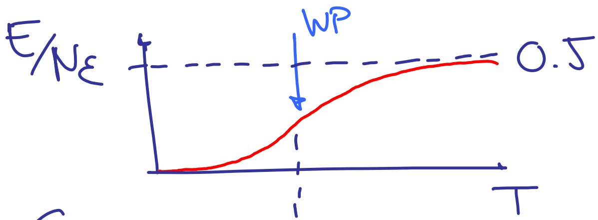
$q_{\text{mol}} = 1 + e^{-\varepsilon/kT}$

$$E = NkT^2 \frac{\partial}{\partial T}\left(\ln\left(1 + e^{-\varepsilon/kT}\right)\right)$$

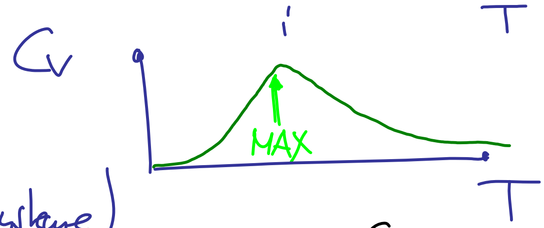
$$= NkT^2 \frac{1}{\left(1 + e^{-\varepsilon/kT}\right)} \cdot \left(\frac{\varepsilon}{kT^2}\right) \cdot e^{-\varepsilon/kT} \quad \Big/ \cdot \frac{e^{\varepsilon/kT}}{e^{\varepsilon/kT}}$$

$$\boxed{E = \frac{N\varepsilon}{1 + e^{\varepsilon/kT}}}$$

$(E_{\text{ges}} = N_0 \cdot \varepsilon_0 + N_1 \cdot \varepsilon_1) \Longrightarrow$ für $T \to \infty$: $E \to \frac{1}{2} N\varepsilon$



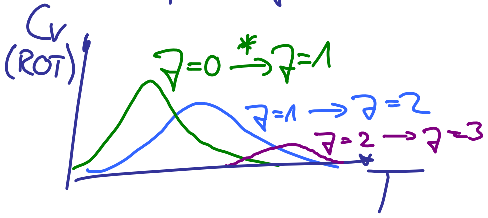
$$C_V = \frac{\partial}{\partial T}\left(\frac{N\varepsilon}{\left(1 + e^{\varepsilon/kT}\right)}\right) \ldots$$



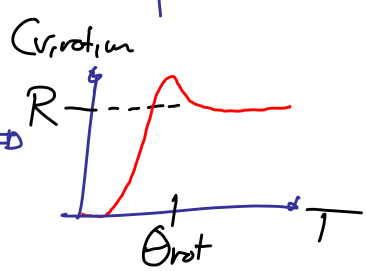
$\Longrightarrow$ C_V als "Energiespeicher"

$\Longrightarrow$ Schottky-Anomalie (Spin-Systeme)

$\Longrightarrow$ Rotations-C_V



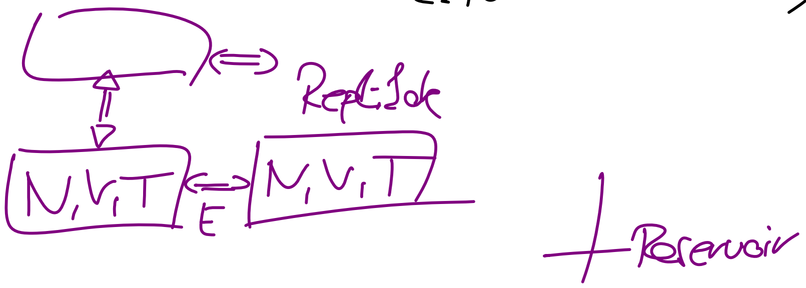
$\Longrightarrow$



5. Kanonische Gesamtheit (Gibbs'scher Gedankenexp. 2. Postulat der TD)

Forderung: WW zw. Teilchen

System ≡



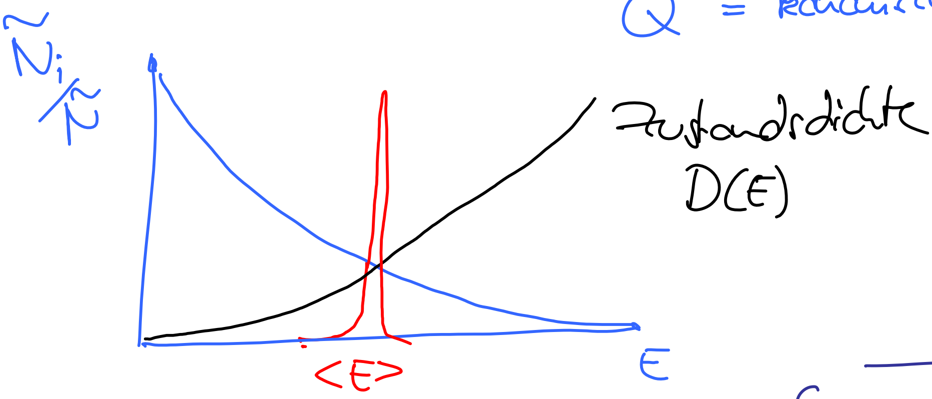
gesucht: $\langle E\rangle$

⇒ Wahrsch. Verteilung $\tilde N_i$ auf $\tilde E_i$ $(\tilde\psi_i)$

Statistisch: $\tilde N$ Replikate, $\tilde N_i$ in jew. $\tilde E_i$, fordern: $\tilde E = \text{const}$, $\tilde N = \text{const}$

⇒ stat. Gewicht: $$\frac{\tilde N_i}{\tilde N} = \frac{e^{-\tilde E_i/kT}}{\underbrace{\sum e^{-\tilde E_i/kT}}_{Q}}$$

Q = kanonische ZS / System-ZS



$$\langle E\rangle = \frac{\tilde N_i}{\tilde N}\cdot D(E)$$

Scharmittel $$\langle E\rangle = \frac{\tilde E}{\tilde N}$$

⇒ Ergodenhypothese

$$\langle E\rangle = \sum_i D(E)\cdot \tilde E_i$$

Zeitmittel

$$\frac{\Delta\langle E\rangle}{\langle E\rangle} = \frac{1}{\sqrt{\tilde N}}$$

Berechnung von Q?

System in $\tilde E_s$: $$\tilde E_s = \varepsilon_s^{(1)} + \varepsilon_s^{(2)} + \dots \varepsilon_s^{(N)}$$

$$\tilde E_{ges} = \sum_i \left(\varepsilon_i^{(1)} + \varepsilon_i^{(2)} \dots \varepsilon_i^{(N)}\right) = \sum_i \left(\varepsilon_i^{(1)}\right) + \sum \left(\varepsilon_i^{(2)}\right) + \dots$$

$$Q = \sum_i e^{-E_i/kT} = \underbrace{\sum \exp\left(-\tfrac{1}{kT}\cdot\left(\varepsilon_i^{(1)}\right.\right.}_{} + \varepsilon_i^{(2)} + \dots \varepsilon_i^{(N)}))$$

$$= q_{mol}^{(1)} \cdot q_{mol}^{(2)} \cdot \dots q_{mol}^{(N)}$$

$$\boxed{Q = q_{mol}^N}$$ unterscheidbar (Kristall), alle Teilchen gleiche E-Niveau

nicht-unterscheidbare Teilchen? (Gase)

$$\boxed{Q = q_{mol}^N / N!}$$

$$\Longrightarrow \boxed{U = U(0) + kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V}$$

$Q = q_{mol}^N$

$$\boxed{U = U(0) + NkT^2 \left(\frac{\partial \ln q_{mol}}{\partial T}\right)_V}$$

$Q = q_{mol}^N / N!$

$$U = U(0) + kT^2 \frac{\partial}{\partial T}\left(N \ln q_{mol} - \ln N!\right)$$

6. Entropie (und L. Boltzmann)

TD : $S \longrightarrow \max \overset{?}{\Longleftrightarrow}$ statTD : $\Omega \longrightarrow \max$

$$U = U(0) + E(T) = U(0) + \sum N_i \varepsilon_i$$

$$\Longrightarrow \underset{(dV=0)}{dU} = \underbrace{dU(0)}_{=0} + \sum dN_i \varepsilon_i + \underbrace{\sum N_i d\varepsilon_i}_{=0}$$

Aus TD: $dU = p\,dV + dq_{rev} = T\,dS$

$$\hookrightarrow dS = \frac{1}{T} \cdot \left(\sum dN_i \varepsilon_i\right) = k \sum \beta \varepsilon_i \cdot dN_i \qquad // \; \beta = 1/kT$$

MB/Lagrange!

$$\frac{\partial \ln \Omega}{\partial N_i} - \alpha - \beta \varepsilon_i = 0$$

$$dS = k \sum \left(\frac{\partial \ln \Omega}{\partial N_i} - \alpha\right) dN_i$$

$$= \underbrace{k \sum \frac{\partial \ln \Omega}{\partial N_i} dN_i}_{d \ln \Omega} - \underbrace{k\alpha \sum dN_i}_{=0}$$

$$\boxed{S = k \cdot \ln \Omega} \Longrightarrow S \mathrel{\hat{=}} \text{Anzahl der erreichbaren Mikrozustände}$$

$S(Q)$, $\quad \Omega = \dfrac{N!}{\prod N_i!}$

$$S = k \ln \frac{N!}{\prod N_i!} = k \left(N \ln N - N - \sum (N_i \ln N_i - N_i)\right)$$

$$= k \left(N \ln N - \sum N_i \ln N_i\right) = k \sum N_i \ln \frac{N}{N_i} \qquad // \; \frac{N_j}{N} = \frac{e^{-\varepsilon_j / kT}}{q}$$

$N \ln N = \sum N_i$

$$= k\sum N_i\left(\varepsilon_i/kT + \ln q\right) = \frac{1}{T}\underbrace{\sum N_i\varepsilon_i}_{=E(T)=U-U(0K)} + kN\ln q$$

$$\boxed{\begin{aligned} S(q) &= \frac{1}{T}\left(U-U(0K)\right) + Nk\ln q \\ S(Q) &= \frac{1}{T}\left(kT^2\frac{\partial \ln Q}{\partial T}\right)_V + k\ln Q \end{aligned}}$$