Wdh: • Ensembles sind gleichberechtigt

$$\left.\begin{array}{l} N \to \infty \\ V \to \infty \end{array}\right\} \frac{N}{V} = \text{const} \qquad \frac{\langle E^2\rangle - \langle E\rangle^2}{\langle E\rangle^2} \longrightarrow 0$$

• Gleichverteilungssatz

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{2} k_B T$$

• Maxwell-Verteilung

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left\{-\frac{m \cdot v^2}{2 k_B T}\right\}$$

• $u = -\partial_\beta \ln Z_c \qquad P = +\frac{1}{\beta}\partial_V \ln Z_c$ kanonisch

$$u = \left(-\partial_\beta + \frac{\mu}{\beta}\partial_\mu\right) \ln Z_{gk}$$

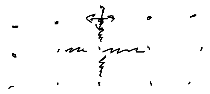
$$\left(-\partial_\beta + \frac{\mu}{\beta}\partial_\mu\right) e^{+\beta\mu N} f(\beta) = e^{+\beta\mu N}(-\partial_\beta) f(\beta)$$

• HO:

$\rightsquigarrow$ klass. kont. Besch. $\quad Z_c^{\text{cont}} = \frac{1}{\beta\hbar\omega}$

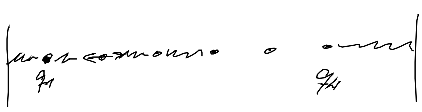
diskret " $\quad Z_c = \frac{1}{e^{+\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} \xrightarrow{\beta \to 0} \frac{1}{\beta\hbar\omega} + \mathcal{O}(\beta\hbar\omega)^2$

2.3.4. Wärmekapazität von Festkörpern



$$H = \frac{1}{2m} \underline{p}^T \cdot \underline{p} + \frac{1}{2} m \cdot \omega^2 \underline{q}^T \underline{\underline{V}} \underline{q}$$

3N-dim. Vektor



$$U_{pot} = \frac{K}{2}\left[q_1^2 + \sum_{i=1}^{N-1}(q_i - q_{i+1})^2 + q_N^2\right]$$

$$\underline{\underline{V}} \propto \begin{pmatrix} +1 & -1 & & & \\ -1 & +2 & \ddots & & \\ & \ddots & \ddots & \ddots & \\ & & \ddots & +2 & -1 \\ & & & -1 & +1 \end{pmatrix}$$

• V: 3N×3N Matrix
• symmetrisch (reell)
• positiv definit

Normalmoden-Trafo:

$$\underline{q} = \underline{\underline{O}}\, \underline{Q} \qquad \underline{p} = \underline{\underline{O}}\, \underline{P}$$

neue Koordinaten $\qquad$ neue Impulse

$$\underline{\underline{O}}^T \underline{\underline{O}} = \mathbb{1}$$

Diagonalmatrix

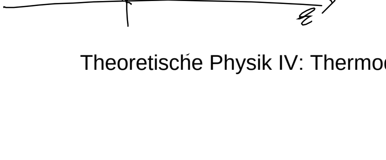
$$\underline{\underline{O}}^T \underline{\underline{V}}\, \underline{\underline{O}} = \underline{\underline{V}}_D = \begin{pmatrix} v_1 & & \\ & \ddots & \\ & & v_f \end{pmatrix}$$

Eigenwerte

$$\Omega_i^2 = \omega^2 \cdot v_i$$

$$H = \frac{1}{2m} \underline{P}^T \cdot \underline{P} + \frac{1}{2} m\omega^2 \underline{Q}^T \cdot \underline{\underline{V}}_D \underline{Q},$$

$$= \frac{1}{2m}\sum_{i=1}^{f} P_i^2 + \frac{1}{2} m \sum_{i=1}^{f} \Omega_i^2 \cdot Q_i^2$$



3N $\qquad f = 3N$

a) klassisch behandelt. $\quad Z_c = \prod_{i=1}^{f} Z_i \qquad Z_i^{cont} = \frac{1}{\beta\hbar\Omega_i}$

$$U = -\partial_\beta \ln Z_c = \sum_{i=1}^{3N} \partial_\beta \ln\left(\beta\hbar\Omega_i\right) = 3N\cdot k_B T$$

$$C_V = \frac{\partial U}{\partial T} = 3N\cdot k_B = 3n\cdot R = n\cdot C_V^{mol} \implies \boxed{C_V^{mol} = 3\cdot R}$$

Gesetz von Dulong-Petit

- passt für viele Stoffe bei hohen Temp.
- aber nicht für tiefe Temp.

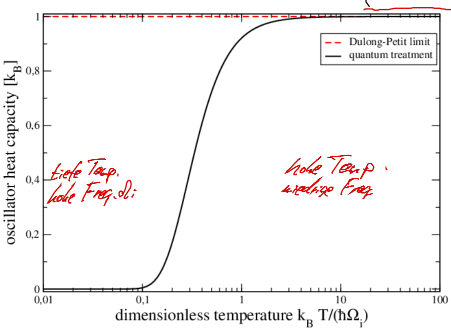
b) diskrete Rechnung $\qquad E_{n_i} = \hbar\Omega_i\left(n_i + 1/2\right)$

$$Z_c = \sum_{\underline{n}} e^{-\beta E_{\underline{n}}} = \sum_{n_1} \cdot \ldots \cdot \sum_{n_f} e^{-\beta E_{n_1}} \cdot \ldots \cdot e^{-\beta E_{n_f}} = \prod_{i=1}^{f} Z_i$$

$$\underline{n} = \begin{pmatrix} n_1 \\ \vdots \\ n_f \end{pmatrix} \qquad n_i \in \{0, 1, \ldots\}$$

$$U = -\sum_i \partial_\beta \ln Z_i = \sum_i \frac{\hbar\Omega_i}{2} \coth\left(\frac{\beta\hbar\Omega_i}{2}\right)$$

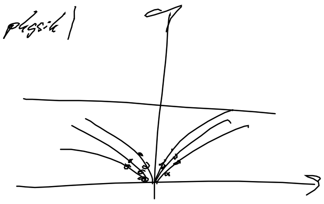
$$C_V = n\cdot C_V^{mol} = \left(\frac{\partial U}{\partial T}\right) = k_B \sum_{i=1}^{f} \frac{\left(\beta\hbar\Omega_i\right)^2}{\left(e^{+\beta\hbar\Omega_i/2} - e^{-\beta\hbar\Omega_i/2}\right)^2} = \sum_{i=1}^{f} C_V^{(i)}$$



$C_V^{mol} \propto T^3$ für $T \to 0$

(VL Festkörperphysik)

$C_V^{el} \propto T$



2.3.5. Wärmekapazität mehratomiger idealer Gase

ideal:
- keine inter-molekularen WW
- intra-molekulare WW wird harmonisch genähert

∘ punktförmige Atome

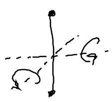
ohne Schw.

$\implies$ für sehr große Temp.: $\quad U = \frac{f_{non\text{-}vib}}{2} k_B T + f_{vib.}\cdot k_B T$

Bsp.: 2-Atome $\qquad$ Schwerpunkt

a) $H_{trans} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \qquad$ QM: $E_{\underline{k}} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$, $\quad L = V^{1/3}$

$\longrightarrow$ klass. Behandlung OK für große V

b.)  $H_{rot} = \frac{L_x^2+L_y^2}{2\Theta}$ $\qquad E^l_{rot} = \frac{\hbar^2 l(l+1)}{2\Theta} \qquad l \in \{0,1,\dots\}$

Moleküleigenschaft

bei sehr tiefen Temp. "eingefroren"

c.)  $H_{vib} = \frac{1}{2}m\omega^2 q^2 + \frac{\tilde{p}^2}{2m}$

Moleküleigenschaft

Quantisierung muss berücks. werden für tiefe Temp.

$$\Rightarrow C_V^{mol} = \frac{3}{2}R + \frac{2}{2}R + \frac{2}{2}R \to \frac{7}{2}R$$

nur Translation $\qquad$ 2x Rotation $\qquad$ 1x Vibration $\qquad C_p^{mol} = \frac{9}{2} \to \gamma = \frac{9}{7}$

2.3.6 Die Virialentwicklung

N id. Teilchen, Volumen V, hohe Temp., Masse m $\Big\}$ keine innere Struktur, kont. Bes. der ZS $\qquad f = 3N$

$$Z_c = \frac{1}{N!}\int e^{-\beta H(x)}\, d\Gamma(x) \qquad d\Gamma = \prod_{i=1}^{f}\frac{dp_i\, dq_i}{h}$$

$$H = \sum_{i=1}^{N}\frac{\underline{p}_i^2}{2m} + \underbrace{\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}} U_{pot}(\underline{q}_i, \underline{q}_j)}_{U_{pot}(q_1,\dots,q_f)}$$

Z_C kann nicht exakt ausgew. werden

$$Z_C = \frac{1}{N!}\frac{1}{h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{3N/2} Z_u \qquad Z_u = \int_V e^{-\beta U_{pot}(\dots)}\, \underbrace{dq_1\dots dq_f}_{d^3q_{(1)}\dots d^3q_{(N)}}$$

$$\langle U_{pot}\rangle = -\partial_\beta \ln Z_u$$

$$\boxed{\lim_{\beta\to 0} Z_u \overset{!}{=} V^N}$$

$$\int^{\beta} d\beta\,[\dots]$$

$$\ln Z_u(\beta) - \underbrace{\ln Z_u(0)}_{N\cdot\ln V} = -\int_0^\beta \langle U_{pot}(\beta')\rangle\, d\beta'$$

$$\langle U_{pot}(\beta)\rangle = \frac{N(N-1)}{2}\langle u\rangle \overset{N\gg 1}{\approx} \frac{N^2}{2}\langle u\rangle$$

mittlere pot. Energie pro Teilchenpaar

kleine Dichten: $\frac{N}{V}$ sehr klein

$$\langle u\rangle \approx \frac{\int_V u\, e^{-\beta u}\, d^3q}{\int_V e^{-\beta u}\, d^3q} = -\partial_\beta \ln\int_V e^{-\beta u}\, d^3q$$

$$\int_V e^{-\beta u} d^3q = \int \left[1+\left(e^{-\beta u}-1\right)\right] d^3q = V\left[1+\frac{I(\beta)}{V}\right]$$

$$I(\beta) = \int \left(e^{-\beta u}-1\right) d^3q = \int_0^\infty \left(e^{-\beta u(r)}-1\right)\cdot 4\pi r^2 dr \qquad \left(I(0)=0\right)$$

u hängt nur vom Abstand ab

r

$$\langle u\rangle = -\partial_\beta \ln\left[V\cdot\left[1+\frac{I(\beta)}{V}\right]\right] = -\partial_\beta \ln\left[1+\underbrace{\frac{I(\beta)}{V}}_{\text{klein}}\right]$$

$$\approx -\frac{1}{V}\frac{\partial I(\beta)}{\partial\beta}$$

$$\Rightarrow \ln Z_K(\beta) = N\cdot\ln V + \frac{N^2}{2}\,\frac{1}{V}\cdot I(\beta)$$

$$P = \frac{1}{\beta}\,\partial_V \ln Z_C$$

$$\beta P = \partial_V \ln Z_K = \boxed{\frac{N}{V} - \frac{1}{2}\frac{N^2}{V^2} I(\beta) + \ldots = \frac{P}{k_B T}} = \underbrace{C_1(T)}_{=1}\frac{N}{V} + C_2(T)\left(\frac{N}{V}\right)^2 + \ldots$$

Virialgleichung

- id. Gas $C_1(T)=1$ $\quad C_{i\geq 2}=0$
- reales Gas $C_1(T)=1$ $\quad C_2(T) = -\frac{1}{2}\int_0^\infty 4\pi r^2\left(e^{-\beta u(r)}-1\right) dr$

Virialkoeffizient