

Wdhk • Ensemble sind gleichberechtigt

$$\frac{\langle E^2 \rangle - \langle E \rangle^2}{\langle E \rangle^2} \rightarrow 0$$

$N \rightarrow \infty$
 $V \rightarrow \infty$ } $\frac{N_1}{V} = \text{const}$

• Gleichverteilungssatz

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

• Maxwell-Verteilung

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

• $h_x = -\partial_p h_x z_c$ $p = +\frac{1}{\beta} \partial_v h_x z_c$ kanonisch

$$h = \left(-\partial_p + \frac{1}{\beta} \partial_p \right) h_x z_c$$

$$\left(-\partial_p + \frac{1}{\beta} \partial_p \right) e^{+\beta p \cdot h} f(\beta) = e^{+\beta p \cdot h} (-\partial_p) f(\beta)$$

• HO:

\rightarrow klass. Kont. Bew. $Z_c^{\text{cont}} = \frac{1}{\beta \hbar \omega}$

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

2.3.4. Wärmekapazität von Festkörpern

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

↑
3N-dim. Vektor

$$\left| \begin{array}{ccc} \dots & \dots & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \end{array} \right|$$

$$H_{\text{opt}} = \frac{K}{2} \left[q_1^2 + \sum_{i=1}^{N-1} (q_i - f_{\text{opt}})^2 + q_N^2 \right]$$

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

- V: 3N x 3N Matrix
- symmetrisch (reell)
- positiv definit

Normalen-Trafo:

$$\underline{Q} = \underline{O} \underline{Q} \quad \underline{P} = \underline{O} \underline{P}$$

↑
neue Koordinaten

↑
neue Impulse

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

$$\underline{O}^T \underline{V} \underline{O} = \underline{V}_D = \begin{pmatrix} \omega_1 & & & \\ & \ddots & & \\ & & \omega_{3N} & \\ & & & \omega_{3N} \end{pmatrix}$$

Diagonalmatrix

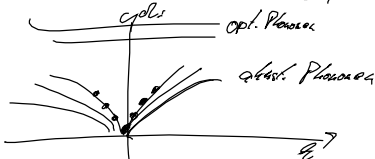
↑
Eigenwerte

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

$$= \frac{1}{2m} \sum_{i=1}^f \underline{P}_i^2 + \frac{1}{2} m \sum_{i=1}^f \omega_i^2 \underline{Q}_i^2$$

opt. Planonen opt. Planonen

$$\omega_i^2 = \omega^2 \cdot \nu_i$$



3N f=3N

a) Klassisch hart. $Z_c = \prod_{i=1}^f Z_i$ $Z_i^{cl} = \frac{1}{\beta \hbar \omega_i}$

$$U = - \partial_{\beta} \ln Z_c = - \sum_{i=1}^f \partial_{\beta} \ln(\beta \hbar \omega_i) = 3M \cdot k_B T$$

$$C_V = \frac{\partial U}{\partial T} = 3M \cdot k_B = 3M \cdot R = M \cdot C_V^{mol} \Rightarrow C_V^{mol} = 3 \cdot R$$

passt für viele Stoffe bei hoher Temp.
aber nicht für tiefe Temp.

$C_V^{mol} = 3 \cdot R$
 Gesetz von Dulong-Petit

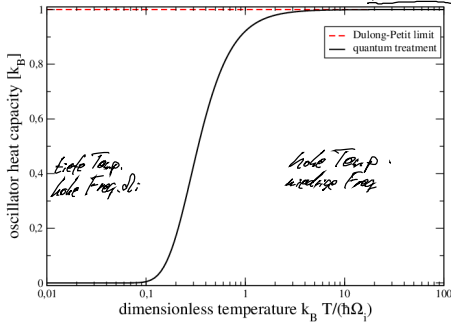
b) diskrete Rechnung $E_{h_i} = \hbar \omega_i (h_i + \frac{1}{2})$

$$Z_c = \sum_{\underline{h}} e^{-\beta E_{\underline{h}}} = \sum_{h_1} \dots \sum_{h_f} e^{-\beta E_{h_1}} \dots e^{-\beta E_{h_f}} = \prod_{i=1}^f Z_i$$

$$\underline{h} = \begin{pmatrix} h_1 \\ \vdots \\ h_f \end{pmatrix} \quad h_i \in \{0, 1, \dots\}$$

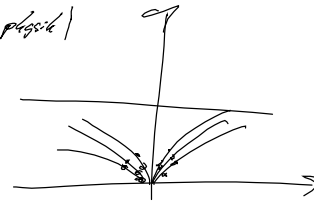
$$U = - \sum_i \partial_{\beta} \ln Z_i = \sum_i \frac{\hbar \omega_i}{2} \coth\left(\frac{\beta \hbar \omega_i}{2}\right)$$

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



$C_V^{mol} \propto T^3$ für $T \rightarrow 0$
(VL Festkörperphysik)

$C_V^{cl} \propto T$



2.3.5. Wärmekapazität harmonischer Gase

ideal: • keine inter-molekularen Kräfte • quantisierte Atome
• intra-molekulare WW sind harmonisch gestört
ohne Sch.

\Rightarrow für sehr große Temp: $U = \frac{f_{trans}}{2} k_B T + f_{rot} \cdot k_B T$

Bsp: 2-Atome $\left\{ \begin{array}{l} \text{Schwanz} \\ \text{O} \end{array} \right.$

a) $H_{trans} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$

\rightarrow klass. Behandlung OK für große V

QM: $E_{rot} = \frac{\hbar^2 \vec{L}^2}{2I} = \frac{\hbar^2}{2I} (L_x^2 + L_y^2 + L_z^2)$
OK $I = V^{1/3}$

b) $\int_{\Omega} \dots G \dots$ $H_{rot} = \frac{L_x^2 + L_y^2}{2I}$ $E_{rot} = \frac{\hbar^2 l(l+1)}{2I}$ $l \in \{0, 1, \dots\}$

bei sehr tiefen Temp. "eingefroren"
 Moleküleigenschaft
 Quantisierung muss berücksichtigt werden für tiefe Temp.
 Moleküleigenschaft

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

$\Rightarrow C_V^{mol} = \frac{3}{2} R + \frac{2}{2} R + \frac{2}{2} R \rightarrow \frac{7}{2} R$
 3x Translation 2x Rotation 1x Vibration $C_P^{mol} = \frac{9}{2} \rightarrow \gamma = \frac{9}{7}$

2.3.6 Die N. kanon. Entwicklung

N id. Teilchen Volumen V konvergente Struktur
 hohe Temp. μ \rightarrow kan. Beh. der ZS $f = 3N$

$Z_0 = \frac{1}{N!} \int e^{-\beta H(x)} d\Gamma(x)$ $d\Gamma = \frac{1}{i^{3N}} \frac{d^3 p_i}{h^3} \frac{d^3 q_i}{h^3}$

$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{3N} U_{rot}(q_i, q_j)$
 $U_{rot}(q_1, \dots, q_N)$

Z_0 kann nicht exakt ausgew. werden
 $Z_0 = \frac{1}{N!} \frac{1}{h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{3N/2} Z_N$
 $Z_N = \int_V e^{-\beta U_{rot}(\dots)} \frac{dq_1 \dots dq_N}{d^3 q_1 \dots d^3 q_N}$

$\langle U_{rot} \rangle = - \partial_{\beta} \ln Z_N$
 $\lim_{\beta \rightarrow 0} Z_N = V^N$
 $\int_{\beta} d\beta [\dots]$

$\ln Z_N(\beta) - \ln Z_N(0) = - \int_0^{\beta} \langle U_{rot}(\beta') \rangle d\beta'$
 $N \cdot \ln V$ $N \rightarrow 1$

$\langle U_{rot}(\beta) \rangle = \frac{N(N-1)}{2} \langle u \rangle \approx \frac{N^2}{2} \langle u \rangle$
 mittlere Energie pro Teilchenpaar

Wenig Drücken: $\frac{N}{V}$ sehr klein
 $\langle u \rangle = \frac{\int_V e^{-\beta u} d^3 q}{\int_V e^{-\beta u} d^3 q} = - \partial_{\beta} \ln \int_V e^{-\beta u} d^3 q$

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

$$I(\beta) = \int (e^{-\beta u} - 1) d^3q \xrightarrow{\text{Kugelkoordinaten}} \int_0^\infty (e^{-\beta u(r)} - 1) \cdot 4\pi r^2 dr \quad (I(0) = 0)$$

u hängt nur vom Abstand ab

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

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

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

$$P = \frac{1}{\beta} \partial_r \ln Z_k$$

$$\beta P = \partial_r \ln Z_k = \frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I(\beta) + \dots = \frac{P}{k_B T} = C_1(T) \frac{N}{V} + C_2(T) \left(\frac{N}{V} \right)^2 + \dots$$

Virialgleichung

• id. Gas $C_1(T) = 1$ $C_2(T) = 0$

• reales Gas $C_1(T) = 1$ $C_2(T) = -\frac{1}{2} \int_0^\infty 4\pi r^2 (e^{-\beta u(r)} - 1) dr$
Virialkoeffizient

