PC III 24.6.13

8. Anwendungen der statistischen Thermodynamik
8.1 Mittlere Energie

$$\langle E\rangle = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V \quad \text{(N unabhängige Teilchen)}$$

$$\langle E\rangle = \langle E_{trans}\rangle + \langle E_{rot}\rangle + \langle E_{vib}\rangle + \langle E_{elek}\rangle$$

z.B. 2-atomiges ideales Gas: $CO, O_2, \ldots$

$$\langle E_{trans}\rangle = N\cdot\frac{3}{2}kT$$

$$\langle E_{rot}\rangle = NkT\left(\frac{d\ln q_{rot}}{dT}\right) \qquad q_{rot} = \frac{kT}{hcB\sigma}$$

$$\hookrightarrow \langle E_{rot}\rangle = NkT^2\frac{1}{T} = NkT$$

$$\langle E_{vib}\rangle = NkT^2\left(\frac{d\ln q_{vib}}{dT}\right) \qquad q_{vib} = \frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}}$$

$$\ln q_{vib} = -\frac{\Theta_{vib}}{2T} - \ln(1-e^{-\Theta_{vib}/T})$$

$$\left(\frac{d\ln q_{vib}}{dT}\right) = \frac{\Theta_{vib}}{2T^2} + \frac{\Theta_{vib}}{T^2}e^{-\Theta_{vib}/T}\frac{1}{(1-e^{-\Theta_{vib}/T})}$$

$$\hookrightarrow \langle E_{vib}\rangle = NkT^2\left(\frac{\Theta_{vib}}{2T^2} + \frac{\Theta_{vib}}{T^2}\frac{e^{-\Theta_{vib}/T}}{(1-e^{-\Theta_{vib}/T})}\right) = Nk\left(\frac{\Theta_{vib}}{2} + \frac{\Theta_{vib}e^{-\Theta_{vib}/T}}{(1-e^{-\Theta_{vib}/T})}\right)$$

$$= Nk\left(\frac{\Theta_{vib}}{2} + \frac{\Theta_{vib}}{(e^{\Theta_{vib}/T}-1)}\right)$$

$$\langle E_{elek}\rangle = NkT^2\left(\frac{d\ln q_{elek}}{dT}\right) \approx 0 \qquad q_{elek} = g_{e1} + g_{e2}\,e^{-\epsilon_{e2}/kT} + \ldots$$

sehr groß

keine tiefliegenden elektronische Zustände

$$\hookrightarrow \langle E\rangle = U = N\left(\frac{3}{2}kT + kT + \frac{h\nu}{2} + \frac{h\nu}{(e^{h\nu/kT}-1)}\right)$$

hohe Temperatur: $h\nu \ll kT$

$$e^{h\nu/kT} \approx 1 + \frac{h\nu}{kT} + \frac{1}{2!}\left(\frac{h\nu}{kT}\right)^2 + \ldots$$

$$\frac{h\nu}{e^{h\nu/kT}-1} \approx \frac{h\nu}{1+\frac{h\nu}{kT}-1\dots} \approx kT$$

für 1 Mol : $N = N_L$; $N_L k = R$

↳ $U_m = \bar{U} = \underbrace{\frac{3}{2}RT}_{\text{trans}} + \underbrace{RT}_{\text{rot}} + \underbrace{RT}_{\text{vib}} + N_L\frac{h\nu}{2}$ (Innere Energie 2-atomiger Moleküle: hohe Temperatur, keine tiefliegenden elektronischen Zustände)

↳ im Einklang mit klassischem Gleichverteilungssatz

mittlere Energie $\frac{1}{2}RT$ pro quadratischem Term

$$E_{vib} = \quad + \frac{1}{2}kq^2$$

$$\frac{1}{2}RT + \frac{1}{2}RT = RT$$

8.2 Wärmekapazität

$$C_V = \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_V$$

z.B. 1-atomiges ideales Gas

$$U_m = \frac{3}{2}RT$$

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_V = \frac{3}{2}R$$

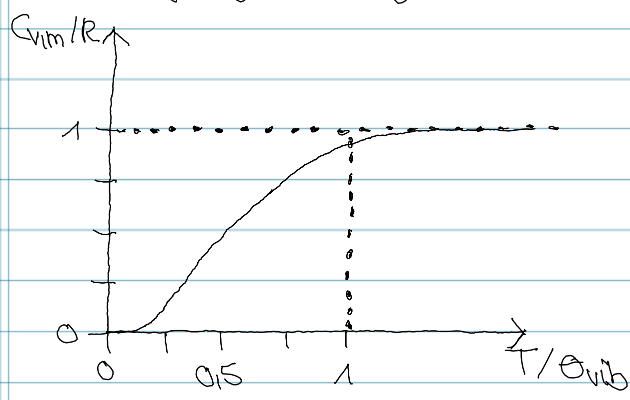
z.B. 2-atomiges ideales Gas

$$C_{V,m} = \frac{3}{2}R + R + N_A h\nu \frac{d}{dT}\left(\frac{1}{e^{h\nu/kT}-1}\right)$$

$$= \frac{5}{2}R + N_A h\nu\left(\frac{h\nu}{kT^2}\right) e^{h\nu/kT} \frac{1}{(e^{h\nu/kT}-1)^2}$$

$$= \frac{5}{2}R + R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} = \frac{5}{2}R + R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})}$$

Schwingungsbeitrag zur Wärmekapazität: T-Abhängigkeit

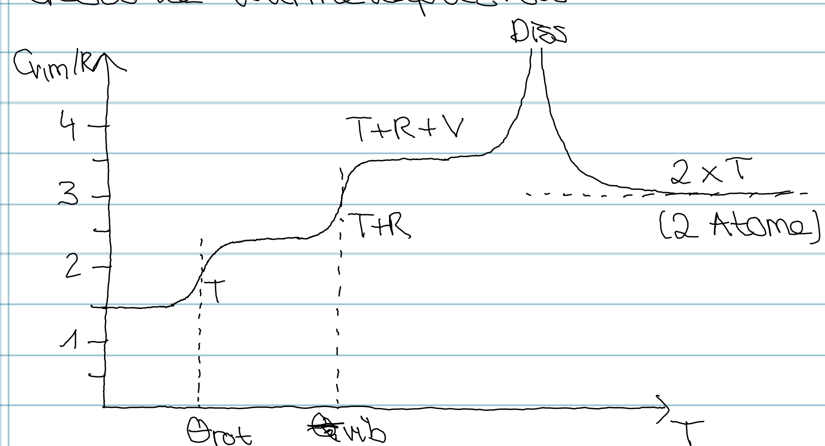


	Θ_{rot}/K	Θ_{vib}/K
Br_2	0,12	465
Cl_2	0,35	805
O_2	2,08	2274
N_2	2,88	3393
CO	2,78	3122

$$\Theta_{rot} = \frac{hcB_0}{k} \qquad B \propto \frac{1}{I}$$

$$\Theta_{vib} = \frac{h\nu}{k} \qquad 2\pi\nu = \sqrt{\frac{k}{\mu}}$$

Gesamte Wärmekapazität

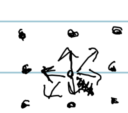


z.B. Festkörper

Einstein-Modell: – atomarer Kristall

– Atome schwingen mit derselben Frequenz ν

– N Atome schwingen um Gitterpositionen



↳ 3 N unabhängige harmonische Oszillatoren

$$q_{ho}(T) = \sum_{v=0}^{\infty} e^{-h\nu(v+\frac{1}{2})/kT} = e^{-\frac{1}{2}\frac{h\nu}{kT}} \sum_{v=0} e^{-h\nu v/kT}$$

$$= \frac{e^{-\frac{1}{2}\frac{h\nu}{kT}}}{1-e^{-h\nu/kT}}$$

$$Q = e^{-U_0/kT}\left(\frac{e^{-\frac{1}{2}\frac{h\nu}{kT}}}{1-e^{-h\nu/kT}}\right)^{3N}$$

U_0 = Sublimationsenergie bei 0 K

Zustandssumme Einstein-Modell

$C_{V,m}$?

$$\langle E \rangle = U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_N$$

$$\ln Q = -\frac{U_0}{kT} + 3N\left(-\frac{1}{2}\frac{h\nu}{kT} - \ln(1-e^{-h\nu/kT}\right)$$

$$\left(\frac{d\ln Q}{dT}\right) = \frac{U^0}{kT^2} + 3N\left(\frac{1}{2}\frac{h\nu}{kT^2} + \frac{h\nu}{kT^2}e^{-h\nu/kT}\frac{1}{(1-e^{-h\nu/kT})}\right)$$

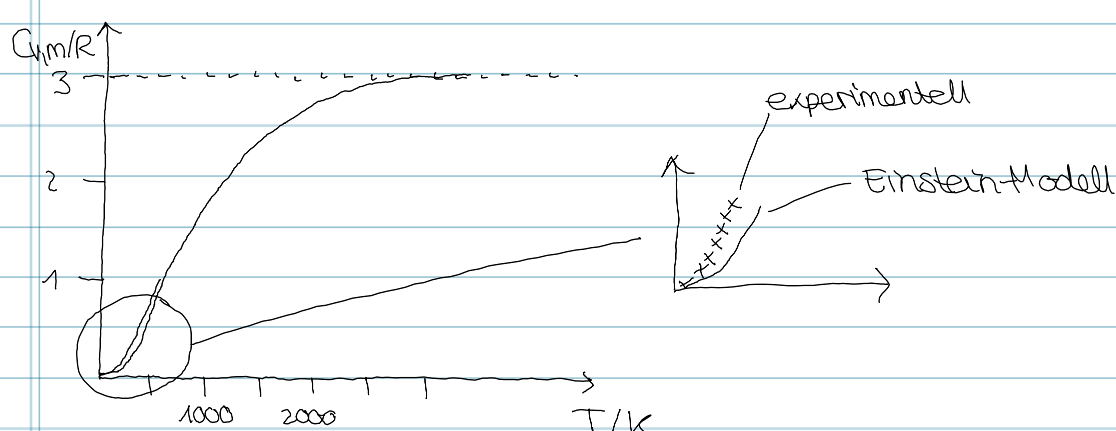
$$U = U_0 + 3N\left(\frac{1}{2}h\nu + \frac{h\nu e^{-h\nu/kT}}{(1-e^{-h\nu/kT})}\right)$$

$$C_{V,m} = 3N_A\frac{(h\nu)^2}{kT^2}e^{-h\nu/kT}\frac{1}{(1-e^{-h\nu/kT})^2}$$

$$\boxed{C_{V,m} = 3R\left(\frac{h\nu}{kT}\right)^2\frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}}$$

↳ vgl. Theorie mit Experiment: ν einziger anpassbarer Parameter

↳ Diamant: $\nu = 2{,}75 \cdot 10^{13}\ \frac{1}{s}$



hohe Temperatur: $h\nu \ll kT$

$$\frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2} \approx \frac{1-\frac{h\nu}{kT}\cdots}{(1-\frac{h\nu}{kT}+1\ldots)^2} \approx \frac{1}{\left(\frac{h\nu}{kT}\right)^2}$$

$$C_{V,m} = 3R\left(\frac{h\nu}{kT}\right)^2\left(\frac{kT}{h\nu}\right)^2 \approx 3R$$

$$C_{V,m} \approx 3R = 24{,}9\ J/molK$$

↳ im Einklang mit Dulong-Petit-Gesetz für atomare Festkörper