Theo 4; Zettel 8; Marc Hauer, Franka Weroncle, Angelo Brade; 03.12.24

Aufgabe 3:

a)

Weitere Freiheitsgrade in Quantenzahlen

$$Z=\underbrace{\int d^3x_1\dots\int d^3x_N}_{V^N}\int\frac{d^3p_1}{(2\pi\hbar)^3}\dots\int\frac{d^3p_N}{(2\pi\hbar)^3}\,e^{-\beta\sum_{n=1}^N\frac{\vec p_n^{\,2}}{2m}}\cdot Z_\alpha \quad\Big|\; Z_\alpha=\sum_{\alpha\in(\alpha_n)_n}e^{-\beta\sum_n^N\varepsilon_{i,n}(\alpha_n)}$$

$(2\pi\hbar)^{3N}$

$(H_{i,n}|i\rangle=\varepsilon_{i,n}|i\rangle)$

aus $H=\sum_{n=1}^N\left(\frac{\vec p_n^{\,2}}{2m}+H_{i,n}\right)$

$$=\left(\frac{V}{(2\pi\hbar)^3}\right)^N\int d^3p_1\dots\int d^3p_N\,e^{-\beta\sum_{n=1}^N\frac{\vec p_n^{\,2}}{2m}}\cdot\sum_{\alpha\in(\alpha_n)_n}e^{-\beta\sum_n^N\varepsilon_{i,n}(\alpha_n)}\quad\Big|\;\beta=\frac{1}{k_BT}$$

$$=\left(\frac{V}{(2\pi\hbar)^3}\right)^N\int d^3p_1\dots\int d^3p_N\,e^{-\beta\sum_{n=1}^N\frac{\vec p_n^{\,2}}{2m}}\cdot\sum_{\alpha\in(\alpha_n)_n}\prod_n^N e^{-\frac{\varepsilon_{i,n}(\alpha_n)}{k_BT}}$$

$$=\left(\frac{V}{(2\pi\hbar)^3}\right)^N\int d^3p_1\dots\int d^3p_N\,e^{-\beta\sum_{n=1}^N\frac{\vec p_n^{\,2}}{2m}}\cdot\prod_n^N\sum_{\alpha_n}e^{-\frac{\varepsilon_{i,n}(\alpha_n)}{k_BT}}$$

b)

$$Z=\left(\frac{V}{(2\pi\hbar)^3}\right)^N\underbrace{\int d^3p_1\dots\int d^3p_N\,e^{-\beta\sum_{n=1}^N\frac{\vec p_n^{\,2}}{2m}}}_{\overset{NR}{=}\sqrt{2mk_BT\pi}^{\,3N}}\cdot\prod_n^N\sum_{\alpha_n}e^{-\frac{\varepsilon_{i,n}(\alpha_n)}{k_BT}}$$

Teilchenindex

Da jedes Teilchen gleich ist, ist $\sum_{\alpha_n}e^{-\frac{\varepsilon_{i,n}(\alpha_n)}{k_BT}}$ für jedes n auch gleich: $\prod_n^N\sum_{\alpha_n}e^{-\frac{\varepsilon_{i,n}(\alpha_n)}{k_BT}}=z_i^N$ mit $z_i=\sum_{\alpha_n}e^{-\frac{\varepsilon_{i,n}(\alpha_n)}{k_BT}}$, wobei $n\in\{1,\dots,N\}$

$$=\left(\frac{V}{\lambda^3}z_i\right)^N \text{ mit } \lambda=\frac{2\sqrt{\pi}\,\hbar}{\sqrt{2mk_BT}}$$

NR:
$$\int d^3p_1\dots\int d^3p_N\,e^{-\beta\sum_{n=1}^N\frac{\vec p_n^{\,2}}{2m}}=\prod_{n=1}^N\int d^3p_n\,e^{-\beta\frac{\vec p_n^{\,2}}{2m}}\quad\Big|\;\vec p_n^{\,2}=p_{n,x}^2+p_{n,y}^2+p_{n,z}^2$$

$$=\prod_{n=1}^N\int d^3p_n\,e^{-\beta\frac{(p_{n,x}^2+p_{n,y}^2+p_{n,z}^2)}{2m}}$$

$$=\prod_{n=1}^N\prod_{i=1}^3\int dp_{n,i}\prod_{i=1}^3 e^{-\beta\frac{p_{n,i}^2}{2m}}\quad\Big|\; p_i \text{ ist unabhängig von } p_j$$

$$=\prod_{n=1}^N\prod_{i=1}^3\underbrace{\int dp_{n,i}\,e^{-\beta\frac{p_{n,i}^2}{2m}}}_{\sqrt{2k_BTm\pi}}\quad\Big|\;\beta=\frac{1}{k_BT}$$

$$=\prod_{n=1}^N\sqrt{2k_BTm\pi}^{\,3}$$

$$=\sqrt{2k_BTm\pi}^{\,3N}$$

c) $Z(V,T,N)$ abhängig von V, T und N => kanonisches Ensemble

$$\Rightarrow F = -k_B T \ln(Z(V,T,N)) \quad | \; Z(V,T,N) = \left(\frac{V}{\lambda^3}\cdot Z_i\right)^N$$

$$= -k_B T N \ln\left(\frac{V}{\lambda^3}\cdot Z_i\right) \quad | \; \ln(x\cdot y) = \ln x + \ln y$$

$$= -k_B T N\left[\ln\frac{V}{\lambda^3} + \ln Z_i\right] \qquad \square$$

d)

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

$$= -\left(\frac{\partial(F+TS)}{\partial V}\right)_{N,T}$$

$$= \frac{k_B T N \lambda^3}{V}\cdot\frac{1}{\lambda^3}$$

$$\Rightarrow pV = N k_B T$$

e)

$$S = -\frac{\partial F}{\partial T}$$

offensichtlich (habe ich es nachgerechnet [trust me bro]) (I)

$$= k_B N\left[\ln\frac{V}{\lambda^3} + \ln Z_i + \underbrace{T\frac{\partial}{\partial T}\ln\frac{V}{\lambda^3}}_{=\frac{3}{2}} + T\frac{\partial \ln Z_i}{\partial T}\right]$$

$$= k_B N\left[\ln\frac{V}{\lambda^3} + \ln Z_i + \frac{3}{2} + T\frac{\partial\ln Z_i}{\partial T}\right]$$

$$E = F + TS$$

$$= -k_B T N\left[\cancel{\ln\frac{V}{\lambda^3}} + \cancel{\ln Z_i}\right] + T k_B N\left[\cancel{\ln\frac{V}{\lambda^3}} + \cancel{\ln Z_i} + \frac{3}{2} + T\frac{\partial \ln Z_i}{\partial T}\right]$$

$$= T k_B N\left[\frac{3}{2} + T\frac{\partial\ln Z_i}{\partial T}\right]$$

I: $$\frac{\partial \ln\frac{V}{\lambda^3}}{\partial T} = \underbrace{\frac{\lambda^3}{V}\left(-3\frac{V}{\lambda^4}\right)\left(\frac{2\sqrt{\pi}\hbar}{\sqrt{2\pi m k_B}}\cdot\frac{-1}{2}\cdot\frac{1}{\sqrt{T}^3}\right)}$$

$$= \frac{3}{\lambda}\cdot\frac{\sqrt{\pi}\hbar}{2\pi m k_B}\cdot\frac{1}{\sqrt{T}}\cdot\frac{1}{T} = \frac{3}{2}\frac{1}{T}$$

f)

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$$

$$= T\frac{\partial}{\partial T} k_B N \left[\ln\frac{V}{\lambda^3} + \ln z_i + \frac{3}{2} + T\frac{\partial \ln z_i}{\partial T}\right]$$

$$= k_B N\left[\frac{3}{2} + T\frac{\partial \ln z_i}{\partial T} + \frac{\partial \ln z_i}{\partial T} + T\frac{\partial^2 \ln z_i}{\partial T^2}\right]$$

$$= k_B N\left[\frac{3}{2} + \frac{\partial}{\partial T}(T\ln z_i) - \ln z_i + \cancel{\frac{\partial}{\partial T} z_i} + \frac{\partial}{\partial T}\left(T\frac{\partial \ln z_i}{\partial T}\right) - \cancel{\frac{\partial}{\partial T} z_i}\right]$$

$$= k_B N\left[\frac{3}{2} + \frac{\partial}{\partial T}\left(T\left(\ln z_i + \frac{\partial \ln z_i}{\partial T}\right)\right)\right]$$

$$= k_B N\left[\frac{3}{2} + \frac{\partial}{\partial T}\left(T\frac{\partial}{\partial T}(T\ln z_i)\right)\right] \quad \Bigg| \quad \frac{\partial \ln z_i}{\partial T} = \frac{\partial \ln z_i}{\partial \beta}\cdot\frac{\partial \beta}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial \ln z_i}{\partial \beta}$$

Von hier aus weiß ich nicht weiter :C

$$\frac{\partial}{\partial T}(T\ln z_i) = \ln z_i + \frac{\partial \beta}{\partial T}\frac{\partial \ln z_i}{\partial \beta}$$

g)

$$z_{vib} = \exp\frac{-\sum_n \omega\hbar(n+\frac{1}{2})}{k_B T} = \exp\left[-\Theta_{vib}\beta k_B \sum_n (n+\tfrac{1}{2})\right] \text{ mit } \Theta_{vib} = \frac{\hbar\omega}{k_B} \text{ und } \beta = \frac{1}{k_B T}$$

h)

$$\langle E\rangle = \sum_n \varepsilon_{n,vib} W_{vib}(n)$$

$$= \sum_n \Theta_{vib} k_B (n+\tfrac{1}{2}) \frac{e^{-\frac{\Theta_{vib}}{T}(n+\frac{1}{2})}}{z_{vib}}$$

$$= -k_B T\frac{\partial}{\partial \beta}\ln(z_{vib})$$

i)

$$C_V^{vib} = -N k_B \frac{\partial}{\partial T}\left(\frac{1}{k_B}\frac{\partial \ln z_{vib}}{\partial \beta}\right)$$

$$= -N k_B \frac{\partial}{\partial T}\left(\frac{1}{k_B}\left(-\Theta_{vib} k_B \sum_n (n+\tfrac{1}{2}) \exp\left[-\Theta_{vib}\beta k_B \sum_n (n+\tfrac{1}{2})\right]\right)\right)$$

$$= N k_B \Theta_{vib} \sum_n (n+\tfrac{1}{2}) \frac{\partial \beta}{\partial T}\left(\frac{\partial}{\partial \beta}\exp\left[-\Theta_{vib}\beta k_B \sum_n (n+\tfrac{1}{2})\right]\right)$$

$$= \frac{N}{T^2}\Theta_{vib}^2\left(\sum_n (n+\tfrac{1}{2})\right)^2 k_B z_{vib}$$

$$= N k_B\left(\frac{\Theta_{vib}\sum_n (n+\frac{1}{2})}{T}\right)^2 z_{vib}$$