Eksamen 14/12-77 Løsninger ≡ F 12 - Stat.mek. ≐ Teor. fysikk IB

Oppgave I

1. Bidrag på $\overbrace{\tfrac{1}{2}kT}^{\text{til den indre energi}}$ pr. kvadratisk ledd i Hamiltonfunksjonen.

$$H = \alpha q_1^2 + H'(\text{uavhengig av } q_1)$$

$$\langle \alpha q_1^2 \rangle = \frac{\int dp\,dq\, \alpha q_1^2 e^{-\beta H}}{\int dp\,dq\, e^{-\beta H}} = \frac{\int dq_1 \alpha q_1^2 e^{-\beta\alpha q_1^2}}{\int dq_1 e^{-\beta\alpha q_1^2}}$$

$$= -\frac{\partial}{\partial\beta} \ln \underbrace{\int dq_1 e^{-\beta\alpha q_1^2}}_{\sqrt{\frac{\pi}{\beta\alpha}}} = -\frac{\partial}{\partial\beta} \ln\left\{\frac{1}{\sqrt{\beta\alpha}} \int dx\, e^{-x^2}\right\}$$

uavh. av grensene

$$= \frac{1}{2}\frac{\partial}{\partial\beta}\{\ln\beta + \ln \text{const.}\}$$

$$= \frac{1}{2\beta} = \frac{1}{2}kT.$$

2. Ideell gass.

En-atomige molekyler

$$H = \frac{\vec{p}^2}{2m} \qquad U = \frac{3}{2}NkT \qquad C_v = \frac{3}{2}Nk$$

To-atomige molek.

$$H = \frac{\vec{p}^2}{2m} + \text{to kin. rot. ledd} + 1 \text{ kin. vib. ledd} + 1 \text{ pot. vibr. ledd}$$

$$U = \frac{3+2+1+1}{2}NkT = \frac{7}{2}NkT \qquad C_v = \frac{7}{2}Nk.$$

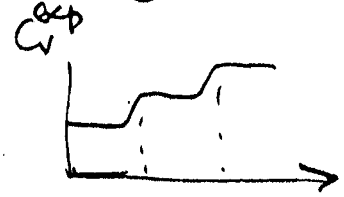
Lineære 3-atomige molekyler

Trans: 3 ledd Rot: 2 ledd.

Vib. moder: ←O O O→ , O→←O O→ , (2 polarisasjoner)

∴ Vib: 4 kin. ledd 4 pot. ledd

$$U = \frac{3+2+4+4}{2}NkT \qquad C_v = \frac{13}{2}Nk$$

3. 

$T_i^{trans} \approx 0$ (teoretisk 10^{-14} K)

$T_i^{rot} \sim 50$ K

$T_i^{vib} \sim 1000$ K

Endelig T_i konsekvens av kvantemek.

Oppgave II

1. $$\Xi = \sum_{N\geq 0} \frac{e^{\beta\mu N}}{N!\,h^{3N}} \int dp\,dq\; e^{-\beta H_N(p,q)}$$

Impintegr.: $$\int\cdots\int d\vec{p}_1\cdots d\vec{p}_N\; e^{-\beta \frac{\vec{p}_i^{\,2}}{2m}} = (2\pi m kT)^{\frac{3N}{2}}$$

$$\Xi = \sum_{N\geq 0} \frac{e^{\beta\mu N}}{N!\,\Lambda^{3N}} Q_N \qquad \Lambda = \frac{h}{\sqrt{2\pi m kT}}\,;\; Q_N = \int\cdots\int dq_1\cdots dq_N\, e^{-\beta U_N}$$

2.
$$\Xi = e^{\beta p V} \qquad \beta p = \frac{1}{V}\ln \Xi$$

$$\langle N\rangle = \frac{\sum N\cdot \frac{e^{\beta\mu N}}{N!\,\Lambda^{3N}}Q_N}{\sum \text{---}\,''\,\text{---}} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi$$

$$= \frac{1}{\beta}\frac{\partial}{\partial\mu}(\beta p V)$$

$$\rho = \frac{\langle N\rangle}{V} = \frac{\partial p}{\partial\mu}$$

$$\boxed{\begin{aligned} p &= \frac{kT}{V}\ln\Xi(\mu,T;V) \\ \rho &= \frac{\partial p(\mu,T;V)}{\partial\mu}\end{aligned}}$$

↳ Parameterframstilling av $p=p(\rho,T)$, eller for å være pirkete $p=p(\rho,T;V)$.

3. Ideell gass: $Q_N = V^N$

$$e^{\beta p V} = \Xi = \sum_{N\geq 0}\frac{e^{\beta\mu N}}{N!\,\Lambda^{3N}}V^N = \exp\left\{V\frac{e^{\beta\mu}}{\Lambda^3}\right\}$$

$$\beta p = \frac{e^{\beta\mu}}{\Lambda^3} \quad\Rightarrow\quad \frac{\mu}{kT} = \ln\frac{p}{kT} + 3\ln\Lambda$$

$$\mu = kT\ln p - \frac{5}{2}kT\ln T + kT\ln\frac{h^3}{k^{5/2}(2\pi m)^{3/2}}$$

4. $$\langle N\rangle = \frac{\sum N\, e^{\beta\mu N} Q_N / N!\,\Lambda^{3N}}{\sum \text{—— " ——}} \;\left[= \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi\right] = V\frac{\partial p}{\partial \mu}$$

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\ln\Xi = \frac{1}{\beta}\frac{\partial}{\partial\mu}\langle N\rangle = \frac{1}{\beta}V\left(\frac{\partial\rho}{\partial\mu}\right)_T$$

$$= kT\,V\left(\frac{\partial\rho}{\partial p}\right)_T\left(\frac{\partial p}{\partial\mu}\right)_T = V\,kT\left(\frac{\partial\rho}{\partial p}\right)_T\rho$$

$$\boxed{\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle^2} = \frac{1}{\langle N\rangle}\,\frac{kT}{(\partial p/\partial\rho)_T}}$$

Visuelt observerbar (kritisk opalescens) nær kritisk punkt der $(\partial p/\partial\rho)_T \to 0$. [Og korrelasjonslengden blir av størrelsesorden lysets bølgelengde!]

Opgave III

1. $$Z_{\frac{1}{2}} = \sum_{s_z^{(i)}=\pm\frac{1}{2}} \prod_{i=1}^{N} e^{\beta c s_z^{(i)} \mathcal{H}} = \left[e^{\frac{1}{2}\beta c \mathcal{H}} + e^{-\frac{1}{2}\beta c \mathcal{H}} \right]^N$$

$$= \left[2 \cosh \frac{\alpha}{2} \right]^N ; \qquad \alpha \equiv \frac{c\mathcal{H}}{kT}$$

$$M_{\frac{1}{2}} = c \langle s_z^{(i)} \rangle = c \, \frac{\sum_{s_z^{i}=\pm\frac{1}{2}} s_z^{(i)} e^{\beta c s_z^{(i)} \mathcal{H}}}{\sum_{s_z^{i}=\pm\frac{1}{2}} e^{\beta c s_z^{(i)} \mathcal{H}}}$$

$$= \frac{1}{\beta} \frac{\partial \frac{1}{N} \ln Z_{\frac{1}{2}}}{\partial \mathcal{H}} = \frac{1}{\beta} \frac{\partial}{\partial \mathcal{H}} \left[\ln 2 + \ln \cosh \frac{\alpha}{2} \right]$$

$$= \frac{1}{\beta} \cdot \frac{\sinh \frac{\alpha}{2}}{\cosh \frac{\alpha}{2}} \cdot \frac{c}{2kT}$$

$$= \frac{c}{2} \operatorname{tgh} \frac{\alpha}{2}$$

2. $$S_{\frac{1}{2}} = \frac{1}{N} \frac{\partial}{\partial T} \left(kT \ln Z_{\frac{1}{2}} \right)$$

$$= \frac{\partial}{\partial T} \left[kT \left(\ln 2 + \ln \cosh \frac{\alpha}{2} \right) \right]$$

$$= k \left\{ \ln 2 + \ln \cosh \frac{\alpha}{2} + T \, \frac{\sinh \frac{\alpha}{2}}{\cosh \frac{\alpha}{2}} \cdot \left(-\frac{\alpha}{2T} \right) \right\}$$

$$= k \left\{ \ln 2 + \ln \cosh \frac{\alpha}{2} - \frac{\alpha}{2} \operatorname{tgh} \frac{\alpha}{2} \right\}$$

3. $$Z_s = \left[\sum_{s_z=-s,\dots,+s} e^{\beta c s_z \mathcal{H}} \right]^N$$

$$= \left[\frac{e^{-\beta c s \mathcal{H}} - e^{+\beta c (s+1) \mathcal{H}}}{1 - e^{\beta c \mathcal{H}}} \right]^N = \left\{ \frac{e^{+\frac{\alpha}{2}} \left[e^{-\alpha(s+\frac{1}{2})} - e^{\alpha(s+\frac{1}{2})} \right]}{e^{\frac{\alpha}{2}} \left[e^{-\frac{\alpha}{2}} - e^{\frac{\alpha}{2}} \right]} \right\}^N$$

$$= \left\{ \frac{\sinh\left[\alpha \left(s + \frac{1}{2} \right) \right]}{\sinh \frac{\alpha}{2}} \right\}^N$$

$$M_s = \frac{1}{\beta}\frac{\partial}{\partial x}\,\frac{1}{N}\ln Z_s$$

$$= \frac{1}{\beta}\frac{\partial}{\partial x}\left\{\ln\sinh\left[\left(s+\tfrac{1}{2}\right)\alpha\right] - \ln\sinh\frac{\alpha}{2}\right\}$$

$$= \frac{1}{\beta}\left\{\frac{\cosh\left[\left(s+\frac{1}{2}\right)\alpha\right]}{\sinh\left[\left(s+\frac{1}{2}\right)\alpha\right]}\cdot\left(s+\tfrac{1}{2}\right)\frac{c}{kT} - \coth\frac{\alpha}{2}\cdot\frac{c}{2kT}\right\}$$

$$= c\left\{\left(s+\tfrac{1}{2}\right)\coth\left[\left(s+\tfrac{1}{2}\right)\alpha\right] - \tfrac{1}{2}\coth\frac{\alpha}{2}\right\}$$

$$S_s = \frac{1}{N}\frac{\partial}{\partial T}\left(kT\ln Z_s\right) = \frac{\partial}{\partial T}\left[kT\left(\ln\sinh\left[\alpha\left(s+\tfrac{1}{2}\right)\right] - \ln\sinh\frac{\alpha}{2}\right)\right]$$

$$= k\left\{\ln\sinh\left[\left(s+\tfrac{1}{2}\right)\alpha\right] - \ln\sinh\frac{\alpha}{2}\right.$$
$$\left. + T\coth\left[\alpha\left(s+\tfrac{1}{2}\right)\right]\cdot\left(s+\tfrac{1}{2}\right)\left(-\frac{\alpha}{T}\right) - T\coth\frac{\alpha}{2}\cdot\left(-\frac{\alpha}{2T}\right)\right\}$$

$$= k\left\{\ln\sinh\left[\left(s+\tfrac{1}{2}\right)\alpha\right] - \ln\sinh\frac{\alpha}{2}\right.$$
$$\left. - \left(s+\tfrac{1}{2}\right)\alpha\coth\left[\left(s+\tfrac{1}{2}\right)\alpha\right] + \frac{\alpha}{2}\coth\frac{\alpha}{2}\right\}$$

Kontroll

$$Z_{\frac{1}{2}} = \left(\frac{\sinh\alpha}{\sinh\frac{\alpha}{2}}\right)^N = \left(\frac{2\sinh\frac{\alpha}{2}\cosh\frac{\alpha}{2}}{\sinh\frac{\alpha}{2}}\right)^N = \left(2\cosh\frac{\alpha}{2}\right)^N \qquad \text{ok.}$$

$$M_{\frac{1}{2}} = c\left\{\coth\alpha - \tfrac{1}{2}\coth\frac{\alpha}{2}\right\} = c\left\{\frac{\coth^2\frac{\alpha}{2}+1}{2\coth\frac{\alpha}{2}} - \tfrac{1}{2}\coth\frac{\alpha}{2}\right\}$$

$$= \frac{c}{2}\tanh\frac{\alpha}{2} \qquad \text{ok}$$

$$S_{\frac{1}{2}} = k\left\{\ln\frac{\sinh\alpha}{\sinh\frac{\alpha}{2}} - \alpha\coth\alpha + \frac{\alpha}{2}\coth\frac{\alpha}{2}\right\}$$

$$= k\left\{\ln 2 + \ln\cosh\frac{\alpha}{2} - \frac{\alpha}{2}\tanh\frac{\alpha}{2}\right\} \qquad \text{ok.}$$

(Formlene ~~bevises lett~~ for sinh og coth til den dobbelte vinkel bevises lett direkte, eller finnes i Rottmann)

4. $\lim\{c\to 0, s\to\infty, \quad cs=c_0\}$:

$$M_\infty = c_0\left\{\coth\alpha_0 - \frac{1}{\alpha_0}\right\} \qquad \alpha_0=\frac{c_0\mathcal{H}}{kT} \qquad \text{(Langevins formel)}$$

$$\bar{S}_s = S_s - k\ln\frac{2s+1}{4\pi}$$

$$\underset{\substack{s\gg 1\\ sc=c_0}}{\simeq} k\left\{\ln\sinh\alpha_0 - \ln\frac{\frac{c_0\mathcal{H}}{s}}{2kT} - \alpha_0\coth\alpha_0 + 1 - \ln\frac{2s+1}{4\pi}\right\}$$

$$\bar{S}_\infty = k\left\{\ln 4\pi e + \ln\sinh\alpha_0 - \ln\alpha_0 - \alpha_0\coth\alpha_0\right\}$$

Vi må "renormalisere" entropien med konstanten $-k\ln\frac{2s+1}{4\pi}$ for å få det klassiske resultatet for en dipol. # kvantemek. tilstander $=2s+1\to\infty$, mens "# klassiske tilstander" settes konvensjonelt like fasevolumet, her $\int d\Omega=4\pi$. Gir en uten slik renormalisering til den "klassiske grensen" blir entropien <u>alltid</u> ∞!

5. a) $\mathcal{H}=0$

<u>$s=\frac{1}{2}$</u> : $\alpha=0$ $\quad S_{\frac{1}{2}}(\alpha=0) = k\ln 2$

uansett temperatur!

<u>$s=\infty$</u>, $sc=c_0, \alpha_0=0$ $\quad \bar{S}_\infty(\alpha_0=0) = k\ln 4\pi$

b) $\mathcal{H}\neq 0$, $T\to 0 \Rightarrow \alpha\to\infty, \alpha_0\to\infty$

<u>$s=\frac{1}{2}$</u> $\quad S_{\frac{1}{2}}(\alpha\to\infty) \simeq k\left\{\ln 2 + \ln\frac{1}{2}e^{\frac{\alpha}{2}}(1+e^{-\alpha}) - \frac{\alpha}{2}\frac{(1-e^{-\alpha})}{1+e^{-\alpha}}\right\}$

$$\simeq e^{-\alpha} - \frac{\alpha}{2}\left(-2e^{-\alpha}\dots\right)$$

$$\simeq \alpha e^{-\alpha} \longrightarrow 0.$$

<u>$s=\infty$</u> $\quad sc=s_0$

$$\bar{S}_\infty(\alpha_0\to\infty) \simeq k\left\{\ln 4\pi e + \ln\frac{1}{2}e^{\alpha_0}(1-e^{-2\alpha_0}) - \ln\frac{c_0\mathcal{H}}{kT} - \alpha_0\frac{1+e^{-2\alpha_0}}{1-e^{-2\alpha_0}}\right\}$$

$$\bar{S}_\infty \simeq k\left\{\ln \frac{2\pi e k}{c_0 \mathcal{H}} + \ln T \div e^{-2\alpha_0} \cdots - 2\alpha_0 e^{-2\alpha_0} \cdots \right\}$$

$$\simeq k\left\{\ln T - \ln \frac{c_0 \mathcal{H}}{2\pi e k} \cdots \right\} \longrightarrow -\infty .$$

Med konvensjonelle definerte nullpunkt, vil kvantemekanikk gi $S(T \to 0) = k \ln g_0$, der g_0 er degenerasjonsgraden. For $s = \frac{1}{2}$ er $g_0 = 2$ i null felt, $g_0 = 1$ for $\mathcal{H} \neq 0$. Stemmer. Klassisk vil $S(T \to 0) \to k \ln T \to -\infty$ med konvensjonelt nullpkt dersom en ikke har for mye "degenerasjon". Ved $\mathcal{H} = 0$, fullt kaos i vinkelrommet uansett $T \Rightarrow \bar{S}_\infty = k \ln 4\pi$.