

Oppgave I

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

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

$$\begin{aligned} \langle \alpha q_1^2 \rangle &= \frac{\int \alpha q_1^2 e^{-\beta H} dq_1}{\int e^{-\beta H} dq_1} = \frac{\int \alpha q_1^2 e^{-\beta \alpha q_1^2} dq_1}{\int e^{-\beta \alpha q_1^2} dq_1} \\ &= -\frac{2}{\partial \beta} \ln \int e^{-\beta \alpha q_1^2} dq_1 = -\frac{2}{\partial \beta} \ln \left\{ \frac{1}{\sqrt{\beta \alpha}} \int dx e^{-x^2} \right\} \\ &= \frac{1}{2} \frac{\partial}{\partial \beta} \{ \ln \beta + \ln \text{const.} \} \quad \text{uavh. av grenseset} \\ &= \frac{1}{2\beta} = \frac{1}{2}kT \end{aligned}$$

2. Ideell gass.
En atomise molekyl

$$H = \frac{p^2}{2m} \quad U = \frac{3}{2}NkT \quad C_V = \frac{3}{2}Nk$$

To-atomise molek.

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

$$U = \frac{3+2+1+1}{2} NkT = \frac{7}{2}NkT \quad C_V = \frac{7}{2}Nk$$

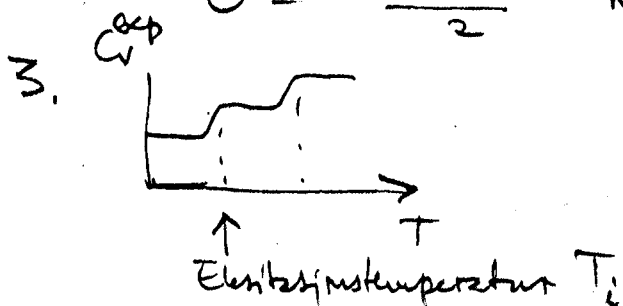
Lineare 3-atomise molekyl

Trans: 3 ledd Rot: 2 ledd

Vib. moder: $\leftarrow O \quad O \quad O \rightarrow, \quad O \leftarrow O \quad O, \quad \uparrow \quad \downarrow \quad \uparrow, \quad \oplus \quad \ominus \quad \oplus$

3. Vib: 4 lin. ledd 4 pot. ledd 2 polariseringer

$$U = \frac{3+2+4+4}{2} NkT \quad C_V = \frac{13}{2}Nk$$



$T_i^{\text{trans}} \approx \text{O}$ (termisk $10^{-14}K$)
 $T_i^{\text{rot}} \sim 50K$
 $T_i^{\text{vib}} \sim 2000K$
 Endelig T_i knesleves av kvantemele.

Oppgave II

$$1. \quad \Xi = \sum_{N \geq 0} \frac{e^{\beta \mu N}}{N! \Lambda^{3N}} \int d\mathbf{p} d\mathbf{q} e^{-\beta H_N(\mathbf{p}, \mathbf{q})}$$

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

$$\Xi = \sum_{N \geq 0} \frac{e^{\beta \mu N}}{N! \Lambda^{3N}} Q_N \quad \Lambda = \frac{h}{\sqrt{2\pi m kT}}; \quad Q_N = \int \dots \int d\vec{q}_1 \dots d\vec{q}_N e^{-\beta U_N}$$

2.

$$\Xi = e^{\beta p V} \quad \beta p = \frac{1}{V} \ln \Xi$$

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

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

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

$$p = \frac{kT}{V} \ln \Xi(\mu, T; V)$$

$$\rho = \frac{\partial p(\mu, T; V)}{\partial \mu}$$

↪ Parameter framstilling ω $p = p(p, T)$, eller for i våre tilfelle $p = p(p, T; V)$.

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

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

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

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

4.

$$\langle N \rangle = \frac{\sum N e^{\beta \mu N} Q_N / N! \Lambda^{3N}}{\sum \text{---} \text{---}} \sqrt{-\beta \frac{\partial \mu}{\partial \mu}}$$

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

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

Visuelt observerbar (kritisk opalescens) nær kritisk punkt der $\left(\partial \rho / \partial \rho \right)_T \rightarrow 0$. [ρ_g korrelasjonslengden blir av størrelsesorden lysets bølgelengde!]]

Oppgave III

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

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

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

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

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

$$= \frac{c}{2} \tanh \frac{\alpha}{2}$$

2.

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

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

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

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

3.

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

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

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

$$\begin{aligned}
M_s &= \frac{1}{\beta} \frac{\partial}{\partial \alpha} \frac{1}{N} \ln Z_s \\
&= \frac{1}{\beta} \frac{\partial}{\partial \alpha} \left\{ \ln \sinh \left[\left(s + \frac{1}{2} \right) \alpha \right] - \ln \sinh \frac{\alpha}{2} \right\} \\
&= \frac{1}{\beta} \left\{ \frac{\cosh \left[\left(s + \frac{1}{2} \right) \alpha \right]}{\sinh \left[\left(s + \frac{1}{2} \right) \alpha \right]} \cdot \left(s + \frac{1}{2} \right) \frac{c}{kT} - \coth \frac{\alpha}{2} \cdot \frac{c}{2kT} \right\} \\
&= c \left\{ \left(s + \frac{1}{2} \right) \coth \left[\left(s + \frac{1}{2} \right) \alpha \right] - \frac{1}{2} \coth \frac{\alpha}{2} \right\}
\end{aligned}$$

$$\begin{aligned}
S_s &= \frac{1}{N} \frac{\partial}{\partial T} (kT \ln Z_s) = \frac{\partial}{\partial T} [kT (\ln \sinh [\alpha(s + \frac{1}{2})] - \ln \sinh \frac{\alpha}{2})] \\
&= k \left\{ \ln \sinh \left[\left(s + \frac{1}{2} \right) \alpha \right] - \ln \sinh \frac{\alpha}{2} \right. \\
&\quad \left. + T \coth [\alpha(s + \frac{1}{2})] \cdot \left(s + \frac{1}{2} \right) \left(-\frac{\alpha}{T} \right) - T \coth \frac{\alpha}{2} \cdot \left(-\frac{\alpha}{2T} \right) \right\} \\
&= k \left\{ \ln \sinh \left[\left(s + \frac{1}{2} \right) \alpha \right] - \ln \sinh \frac{\alpha}{2} \right. \\
&\quad \left. - \left(s + \frac{1}{2} \right) \alpha \coth \left[\left(s + \frac{1}{2} \right) \alpha \right] + \frac{\alpha}{2} \coth \frac{\alpha}{2} \right\}
\end{aligned}$$

Kontroll

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

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

$$= \frac{c}{2} \tanh \frac{\alpha}{2} \quad \text{OK}$$

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

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

(Formeln ~~bevorzugt~~ ~~leicht~~ für $\sinh$ & $\coth$ til den dobbelte vinkel
bevorzugt ~~leicht~~ ~~avvikle~~, eller finnes i Rottmann)

$$4. \lim\{c \rightarrow 0, \lambda \rightarrow \infty, cs = c_0\}$$

$$M_\infty = c_0 \left\{ \coth \alpha_0 - \frac{1}{\alpha_0} \right\} \quad \alpha_0 = \frac{c_0 \lambda}{kT} \quad (\text{Langevin's formula})$$

$$\bar{S}_\lambda = S_\lambda - k \ln \frac{2s+1}{4\pi}$$

$$\stackrel{\substack{A \gg 1 \\ AC \gg c_0}}{\approx} k \left\{ \ln \sinh \alpha_0 - \ln \frac{c_0 \lambda}{2kT} - \alpha_0 \coth \alpha_0 + 1 - \ln \frac{2s+1}{4\pi} \right\}$$

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

Vi må "renormalisere" entropien med konstanten $-k \ln \frac{2s+1}{4\pi}$ for å få det klassiske resultatet for en dipol.

kvantemekan. tilstander $= 2s+1 \rightarrow \infty$, mens "# klassiske tilstander" settes konvensjonelt likt fasevolumet, her $\int d\Omega = 4\pi$. Går en uten slik renormalisering, til den "klassiske grensen" blir entropien alltid ∞ !

$$5. a) \lambda = 0$$

$$\underline{s = \frac{1}{2}}: \alpha = 0 \quad S_{\frac{1}{2}}(\alpha=0) = k \ln 2$$

uendelig temperatur!

$$\underline{s = \infty}, \lambda c = c_0, \alpha_0 \rightarrow \infty \quad \bar{S}_\infty(\alpha_0 \rightarrow \infty) = k \ln 4\pi$$

$$b) \lambda \neq 0, T \rightarrow 0 \Rightarrow \alpha \rightarrow \infty, \alpha_0 \rightarrow \infty$$

$$\underline{s = \frac{1}{2}} \quad S_{\frac{1}{2}}(\alpha \rightarrow \infty) \approx k \left\{ \ln 2 + \ln \frac{1}{2} e^{\frac{\alpha}{2}} (1 + e^{-\alpha}) - \frac{\alpha}{2} \frac{(1 + e^{-\alpha})}{1 + e^{-\alpha}} \right\}$$

$$\approx e^{-\frac{\alpha}{2}} - \frac{\alpha}{2} (-2e^{-\alpha} \dots)$$

$$\approx \alpha e^{-\alpha} \rightarrow 0$$

$$\underline{s = \infty} \quad \lambda c = c_0 \quad \bar{S}_\infty(\alpha_0 \rightarrow \infty) \approx k \left\{ \ln 4\pi e + \ln \frac{1}{2} e^{\alpha_0} (1 + e^{-2\alpha_0}) - \ln \frac{c_0 \lambda}{kT} - \alpha_0 \frac{1 + e^{-2\alpha_0}}{1 + e^{-2\alpha_0}} \right\}$$

$$\begin{aligned}\bar{S}_\infty &\approx k \left\{ \ln \frac{2\pi e k}{c_0 \mathcal{K}} + \ln T - e^{-2\alpha_0} \dots - 2\alpha_0 e^{-2\alpha_0} \dots \right\} \\ &\approx k \left\{ \ln T - \ln \frac{c_0 \mathcal{K}}{2\pi e k} \dots \right\} \rightarrow -\infty.\end{aligned}$$

Med konvensjonelt definerte nullpunkt, vil kvantemekanikk gi $S(T \rightarrow 0) = k \ln g_0$ der g_0 er degenerasjonsgraden.

For $s = \frac{1}{2}$ er $g_0 = 2$ i null felt, $g_0 = 1$ for $\mathcal{K} \neq 0$. Stemmer.

Klemte vil $S(T \rightarrow 0) \rightarrow k \ln T \rightarrow -\infty$ med konvensjonelt nullpunkt dersom en ikke har for mye "degenerasjon". Ved $\mathcal{K} = 0$, fullt kaos i virkel rommet antar $T \Rightarrow \bar{S}_\infty = k \ln 4\pi$.