Übung 4 Pg. 1

a) Im Skript II.9.

b) Phasenraumvolumen:

$$\bar{\Omega}(E) = \int \frac{d^N p\, d^N q}{h^N N!} \; \Theta\left(-\sum_i \frac{p_i^2}{2m} + \sum_i \frac{m\omega^2}{2} q_i^2 + E\right)$$

Variablenwechsel: $\Gamma_i = \left\{ \frac{p_i}{\sqrt{2m}}, \sqrt{\frac{m\omega^2}{2}}\, q_i \right\}$

$$= \sqrt{2m}^N \sqrt{\frac{2}{m\omega^2}}^N \int d^{2N}\Gamma_i \; \Theta\left(-\sum_i \Gamma_i^2 + E\right)$$

$$= \left(\frac{2}{\omega}\right)^N \frac{1}{h^N N!} \int_0^{\sqrt{E}} dr_\Gamma \, r_\Gamma^{2N-1} \int d\Omega_{2N}$$

Oberflächenint.

$$= \left(\frac{2}{\omega}\right)^N \frac{1}{h^N N!} \frac{1}{2N} E^N \frac{2\pi^N}{\underbrace{\Gamma(N)}_{=(N-1)!}} = \left(\frac{E}{\hbar\omega}\right)^N \frac{1}{(N!)^2}$$

$$\Rightarrow \quad \bar{\Omega}(E) = \left(\frac{E}{\hbar\omega}\right)^N \frac{1}{(N!)^2} \simeq \left(\frac{E}{N\hbar\omega}\right)^N \frac{1}{N^N} e^{2N}$$

Entropie:

$$S = k \log(\bar{\Omega}(E)) = kN\left[\log\left(\frac{E}{N^2\hbar\omega}\right) + 2\right]$$

Temperatur:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{kN}{E} \Rightarrow \boxed{NkT = E}$$

P4.2

Sackur-Tetrode Glgn:

$$\boxed{S(E,V,N) = k N \left\{ \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\,\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2}\right\}}$$

a) Homogenität

$$S(\lambda E, \lambda V, \lambda N) = \lambda k N \left\{ \ln\left[\frac{\lambda V}{N\lambda}\left(\frac{4\pi m}{3h^2}\,\frac{E\lambda}{N\lambda}\right)^{3/2}\right] + \frac{5}{2}\right\}$$

$$= \lambda\, S(E,V,N)$$

b)

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{S}{N} + \frac{5}{2}k$$

$$T^{-1} = \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{3}{2} k N \frac{1}{E} \Rightarrow \boxed{E = \frac{3}{2} N k T}$$

$$\frac{S(T,V,N)}{N} = k \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\,\frac{3}{2}kT\right)^{3/2} + \frac{5}{2}\right]$$

$$\Rightarrow \boxed{\mu(T,V,N) = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi m}{h^2}kT\right)^{3/2}\right]}$$

c) Freie Energie:

$$F = E - T \cdot S = E - T \cdot S(E, V, N)$$

$$F(T, V, N) = \frac{3}{2} N k T - T \cdot \underbrace{S(T, V, N)}_{= k N \log\left(\frac{V}{N}\left(\frac{2\pi m k T}{h^2}\right)^{3/2} e^{5/2}\right)}$$

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{3}{2} k T - T \left(\frac{\partial S}{\partial N}\right)_{T,V}$$

$$\left(\frac{\partial S}{\partial N}\right)_{T,V} = \frac{S}{N} - k \quad \Rightarrow \quad \left(\frac{\partial F}{\partial N}\right)_{T,V} = - T \frac{S}{N} + \frac{5}{2} k T$$

$$\Rightarrow \mu(T, V, N) = - k T \ln\left[\frac{V}{N}\left(\frac{2\pi m k T}{h^2}\right)^{3/2}\right]$$

wie zuvor!

H4.1

a) $$Z_N(T,V) = \frac{1}{h^{3N} N!} \int d^{3N}x \, d^{3N}p \; e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + mgz_i}$$

$$= \frac{1}{h^{3N} N!} \left[\int_V d^3x \int_{-\infty}^{\infty} d^3p \; e^{-\beta\left(\frac{\vec{p}^{\,2}}{2m} + mgz\right)} \right]^N$$

$$= \frac{1}{N! h^{3N}} \left[A \left(\int_{-\infty}^{\infty} dp \; e^{-\beta p^2/2m} \right)^3 \int_0^h e^{-\beta mgz} \right]^N$$

$$= \frac{A^N}{N!} \frac{(2m\pi)^{\frac{3}{2}N}}{\beta^{\frac{3}{2}N} h^{3N}} \frac{1}{\beta^N (mg)^N} \left(1 - e^{-q}\right)^N \qquad q := \beta mgh$$

$$\Rightarrow \boxed{\ln Z_N = N\left[-\frac{5}{2}\ln\beta + \ln\left(1-e^{-q}\right) + \ln A + \ln\left(\frac{(2m\pi)^{3/2}}{h^3 mg}\right) \right] - \ln N!}$$

b)

☐ Freie Energie: $F = -kT \ln Z_N$

c) Innere Energie:

$$\mathcal{U} = \langle H \rangle = -\frac{\partial}{\partial\beta} \ln Z_N(T,V) = \frac{5}{2}\frac{N}{\beta} - N\frac{\partial}{\partial\beta}\ln(1-e^{-q\ldots})$$

$$= \frac{5}{2}\frac{N}{\beta} + Nmgh\,\frac{-e^{-qh}}{1-e^{-qh}} = N\varkappa T\left[\frac{5}{2} - \frac{q}{e^{q}-1}\right]$$

$$q = \frac{mgh}{\varkappa T}$$

Grenzfälle:

$$\mathcal{U} \approx \begin{cases} \frac{5}{2} N\varkappa T & q \gg 1 \\ \frac{3}{2} N\varkappa T & q \ll 1 \end{cases} \quad \leftarrow \text{ideales Gas}$$

Wärmekapazität:

$$C_V = \left(\frac{\partial \mathcal{U}}{\partial T}\right)_V = N\varkappa\left[\frac{5}{2} - \frac{q}{e^{q}-1}\right] - N\varkappa T\frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta}\frac{q}{e^{q}-1}$$

$$T\frac{\partial\beta}{\partial T} = -\beta \,, \qquad \frac{\partial}{\partial\beta}\frac{q}{e^{q}-1} = \underbrace{\frac{\partial q}{\partial\beta}}_{mgh}\underbrace{\frac{\partial}{\partial q}\frac{q}{e^{q}-1}}_{\frac{1}{e^{q}-1} - \frac{q\,e^{q}}{(e^{q}-1)^2}}$$

$$\Rightarrow \; C_V = Nk\left[\frac{5}{2} - \frac{q}{e^q-1} + q\left(\frac{1}{e^q-1} - \frac{q e^q}{(e^q-1)^2}\right)\right]$$

$$\boxed{C_V = Nk\left[\frac{5}{2} + \frac{q^2}{(1-e^q)(1-e^{-q})}\right]}$$

$$C_V \approx \begin{cases} \frac{5}{2} Nk & q \gg 1 \\ \frac{3}{2} Nk & q \ll 1 \end{cases} \qquad \square$$

d) Druck:

$$p = kT \frac{\partial \ln Z_N}{\partial V} = \frac{kT}{A}\frac{\partial \ln Z_N}{\partial h} = \frac{kT}{A}\frac{\partial q}{\partial h}\frac{\partial}{\partial q}\ln(1-e^{-q})$$

$$= \frac{mg}{A}\frac{e^{-q}}{1-e^{-q}} = \frac{mg}{A}\frac{1}{e^q-1} = \frac{mg}{A}\frac{1}{e^{\beta mgh}-1}$$

$$\Rightarrow \; \boxed{p = \frac{NkT}{V}\frac{q}{e^q-1}}$$

für $q \ll 1$ wird hieraus wieder das ideale Gasgesetz.

H4.2

$$\langle n(\vec{x})\rangle = \sum_{i=1}^{N} \langle \delta^{(3)}(\vec{x}-\vec{x}_i)\rangle = N \cdot \langle \delta(\vec{x}-\vec{x}_1)\rangle$$

$$= N \cdot \frac{\int d^3x_1 d^3p_1 \, \delta^{(3)}(\vec{x}-\vec{x}_1)\, e^{-\beta\left(\vec{p}_1^{\,2}/2m + mgz_1\right)}}{\int d^3x_1\, d^3p_1\, e^{-\beta \vec{p}_1^{\,2}/2m - \beta mgz_1}}$$

$$= N \cdot \frac{e^{-\beta mgz}}{A\int_0^h dz\, e^{-\beta mgz}} \quad \Theta(h-z)$$

$$= \frac{N\beta mg}{A}\frac{e^{-\beta mgz}}{1-e^{-a}} \sim \text{const} \cdot e^{-\beta mgz}$$

Druck in der Höhe z: $(h\to\infty)$

$$P(z) := \int_z^\infty dz' \, \langle n(\vec{x}')\rangle \, mg$$

$$= \frac{N\beta mg}{A}\int_z^\infty dz'\, e^{-\beta mgz'} \, mg = \frac{Nmg}{A}\, e^{-\beta mgz}$$

"P_0" Barometrische Höhenformel

H4.3

1) Keine Wechselwirkungen zwischen den Molekülen:

$$Z_N(T,V) = \frac{1}{h^{6N}(2N)!} \left\{ \int \cdots \int d^3p_1\, d^3p_2\, d^3r_1\, d^3r_2\, e^{-\beta H_0} \right\}^N .$$

Die Impulsintegrationen lassen sich unmittelbar ausführen (1.137):

$$\int d^3p \exp\left(-\beta \frac{\mathbf{p}^2}{2m}\right) = (2\pi\, m\, k_B T)^{3/2}.$$

Es bleibt für die Zustandssumme zu berechnen:

$$Z_N(T,V) = \frac{(2\pi\, m\, k_B T)^{3N}}{h^{6N}(2N)!}\, Q_\alpha^N(T),$$

$$Q_\alpha(T) = \iint d^3r_1\, d^3r_2 \exp\left(-\beta\frac{\alpha}{2}\,|\,\mathbf{r}_1 - \mathbf{r}_2\,|^2\right).$$

Schwerpunkt- und Relativkoordinaten:

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2); \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2,$$

$$dr_x\, dR_x = \frac{\partial(r_x, R_x)}{\partial(r_{1x}, r_{2x})}\, dr_{1x}\, dr_{2x} = \begin{vmatrix} 1 & -1 \\ \frac{1}{2} & \frac{1}{2} \end{vmatrix}\, dr_{1x}\, dr_{2x}.$$

Analog die anderen Komponenten:

$$d^3r\, d^3R = d^3r_1\, d^3r_2$$

$$\Longrightarrow\ Q_\alpha(T) = \iint d^3R\, d^3r \exp\left(-\beta\frac{\alpha}{2}r^2\right) = V\,4\pi \int_0^\infty dr\, r^2 \exp\left(-\beta\frac{\alpha}{2}r^2\right) =$$

$$= 4\pi\, V \left(\frac{z}{\beta\,\alpha}\right)^{3/2} \frac{1}{2}\Gamma\left(\frac{3}{2}\right) = V\left(\frac{2}{\beta\,\alpha}\right)^{3/2} \pi^{3/2}.$$

Zustandssumme:

$$Z_N(T,V) = \frac{(2\pi\, m\, k_B T)^{3N}}{h^{6N}(2N)!}\, V^N \left(\frac{2\pi\, k_B T}{\alpha}\right)^{3N/2} =$$

$$= c_N\, V^N\, (k_B T)^{9N/2}.$$

2) Freie Energie:

$$F(T,V,N) = -k_B T \ln Z_N(T,V) =$$

$$= -k_B T\left(\ln c_N + N \ln V + \frac{9N}{2} \ln k_B T\right).$$

Druck:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T\, \frac{N}{V}.$$

$\Longrightarrow$ Zustandsgleichung des idealen Gases:

$$p\,V = N\,k_B T.$$

3) Innere Energie:

$$U = -\frac{\partial}{\partial\beta}\ln Z_N(T,V) = -\frac{\partial}{\partial\beta}\left(\ln c_N + N\,\ln V - \frac{9N}{2}\,\ln\beta\right) =$$
$$= \frac{9N}{2}\,\frac{1}{\beta} = \frac{9N}{2}k_B T.$$

Wärmekapazität:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{9}{2}N\,k_B T.$$

4)

$$\langle\,|\,\mathbf{r}_1 - \mathbf{r}_2\,|^{\,2}\,\rangle = \frac{\iint d^3r_1\,d^3r_2\,|\,\mathbf{r}_1 - \mathbf{r}_2\,|^{\,2}\,\exp\left(-\beta\frac{\alpha}{2}\,|\,\mathbf{r}_1 - \mathbf{r}_2\,|^{\,2}\right)}{\iint d^3r_1\,d^3r_2\,\exp\left(-\beta\frac{\alpha}{2}\,|\,\mathbf{r}_1 - \mathbf{r}_2\,|^{\,2}\right)}.$$

Alle anderen Faktoren kürzen sich heraus!

$$\Longrightarrow\ \langle\,r^2\,\rangle = -\frac{2}{\alpha}\,\frac{\partial}{\partial\beta}\,\ln\left[\iint d^3r_1\,d^3r_2\,\exp\left(-\beta\frac{\alpha}{2}\,|\,\mathbf{r}_1 - \mathbf{r}_2\,|^{\,2}\right)\right] \overset{(\alpha)}{=} -\frac{2}{\alpha}\,\frac{\partial}{\partial\beta}\,\ln Q_\alpha(T) =$$
$$= -\frac{2}{\alpha}\,\frac{\partial}{\partial\beta}\,\ln\left[V\left(\frac{2}{\beta\alpha}\right)^{3/2}\pi^{3/2}\right] = -\frac{2}{\alpha}\left(-\frac{3}{2}\right)\frac{1}{\beta}$$

$$\Longrightarrow\ \langle\,r^2\,\rangle = \frac{3}{\alpha}\,k_B T.$$