E_3. Ergänzungen zu Kapitel 3

E_3.1 Klassisches ideales Gas im mikrokanonischen Ensemble

Hamiltonfunktion und Γ-Raum des idealen Gases in D Dimensionen

- Hamiltonfunktion $\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}$
- Phasenraum $\Gamma = \mathbb{R}^{ND} \times \{\mathbf{q}^N | 0 \leq q_{ij} \leq L, i = 1, \cdots N, j = 1, 2, 3\}$
- weiters: E, V und N fest

$$S_m = k_{\mathrm{B}} \ln \Omega(E, V, N; \Delta)$$

$$\Omega(E, V, N; \Delta) = \frac{1}{N! h^{ND}} \int_{\Gamma; \mathcal{H}(\mathbf{p}^N, \mathbf{q}^N) \in [E-\Delta, E]} d\mathbf{p}^N d\mathbf{q}^N = \frac{V^N}{N! h^{ND}} (V_E - V_{E-\Delta})$$

wobei V_E und $V_{E-\Delta}$ die Volumina von Kugeln im $\mathbb{R}^{ND}$ mit Radien $\sqrt{2mE}$ und $\sqrt{2m(E-\Delta)}$ sind

somit

$$V_E = \int_{\mathcal{H}\leq E} d\mathbf{p}^N = \int_0^{\sqrt{2mE}} dp\, p^{ND-1} \underbrace{\int_{\Omega_{ND}} d\Omega_{ND}}_{\frac{2\pi^{ND/2}}{\Gamma(ND/2)}}$$

$$\begin{aligned} V_E &= \frac{2\pi^{ND/2}}{\Gamma(ND/2)} \int_0^{\sqrt{2mE}} dp\, p^{ND-1} = \frac{2\pi^{ND/2}}{\Gamma(ND/2)} \left[(2mE)^{ND/2} \frac{1}{ND} \right] \\ &= \frac{2(2m\pi E)^{ND/2}}{ND\ \Gamma(ND/2)} \end{aligned}$$

$$V_{E-\Delta} = \cdots = \frac{2[2m\pi(E-\Delta)]^{ND/2}}{ND\ \Gamma(ND/2)}$$

$$V_E - V_{E-\Delta} = \frac{2(2m\pi E)^{ND/2}}{ND\ \Gamma(ND/2)} \left[1 - \underbrace{\left(\frac{E-\Delta}{E} \right)^{ND/2}}_{\to 0 \text{ fuer } N \text{ gross}} \right] = \frac{2(2m\pi E)^{ND/2}}{ND\ \Gamma(ND/2)}$$

somit

$$\Omega = \frac{V^N}{h^{ND} N!}(V_E - V_{E-\Delta}) = \frac{V^N}{h^{ND} N!} \frac{(2m\pi E)^{ND/2}}{\underbrace{\frac{ND}{2}\,\Gamma(ND/2)}_{\left(\frac{ND}{2}\right)!}}$$

mit $N! \sim \sqrt{2\pi}\mathrm{e}^{-N} N^N N^{1/2}$ und $\left(\frac{ND}{2}\right)! \sim \sqrt{2\pi}\mathrm{e}^{-ND/2}\left(\frac{ND}{2}\right)^{ND/2}\left(\frac{ND}{2}\right)^{1/2}$ erhält man

$$\begin{aligned}\Omega \quad &\sim \quad \frac{V^N}{h^{ND}} \frac{(2m\pi E)^{ND/2}}{\left[\sqrt{2\pi}\mathrm{e}^{-N} N^N N^{1/2}\right]\left[\sqrt{2\pi}\mathrm{e}^{-ND/2}\left(\frac{ND}{2}\right)^{ND/2}\left(\frac{ND}{2}\right)^{1/2}\right]} \\ &= \quad \left[\frac{V^N}{h^{ND}} \frac{1}{N^N}\left(\frac{2m\pi E}{ND/2}\right)^{ND/2} \mathrm{e}^{N+ND/2}\right]\left[\frac{1}{2\pi} N^{-1/2}\left(\frac{ND}{2}\right)^{-1/2}\right]\end{aligned}$$

somit erhält man für die mikrokanonische Entropie S_m

$$S_m = k_\mathrm{B} \ln \Omega = k_\mathrm{B} N \left[\ln \frac{V}{N} + \frac{D}{2} \ln \frac{E}{N} + \frac{D}{2} \ln \left(\frac{4m\pi}{Dh^2} \right) + \left(1 + \frac{D}{2} \right) \right] + \cdots$$

Zustandsgleichungen

- kalorische Zustandsgleichung

$$\left(\frac{\partial S}{\partial E} \right)_V = \frac{1}{T} = k_\mathrm{B} N \frac{D}{2} \frac{1}{E}$$

$$E = k_\mathrm{B} T \frac{ND}{2}$$

- thermische Zustandsgleichung

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{P}{T} = k_\mathrm{B} N \frac{1}{V}$$

$$PV = N k_\mathrm{B} T$$

E_3.2 Klassisches ideales Gas im kanonischen Ensemble

Hamiltonfunktion und Γ-Raum des idealen Gases in D Dimensionen

- Hamiltonfunktion $\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}$
- Phasenraum $\Gamma = \mathbb{R}^{ND} \times \{\mathbf{q}^N | 0 \leq q_{ij} \leq L, i = 1, \cdots N, j = 1, 2, 3\}$
- weiters: V und N fest, Temperatur T vorgegeben

kanonische Entropie, S_k

$$S_k = \beta k_\mathrm{B} \langle E \rangle_k + k_\mathrm{B} \ln Z_k = -\beta k_\mathrm{B} \frac{\partial}{\partial \beta} \ln Z_k + k_\mathrm{B} \ln Z_k$$

$$\begin{aligned} Z_k &= \frac{1}{N! h^{ND}} \int_\Gamma d\mathbf{p}^N d\mathbf{q}^N \exp[-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{q}^N)] \\ &= \frac{V^N}{N! h^{ND}} \int_{\mathbb{R}^{ND}} \underbrace{\Pi_{i=1}^N d\mathbf{p}_i \exp[-\beta \mathbf{p}_i^2/(2m)]}_{\Pi_{i=1}^N \Pi_{j=1}^D dp_{ij} \exp[-\beta p_{ij}^2/(2m)]} = \\ &= \frac{V^N}{N!} \left(\frac{2m\pi}{\beta h^2} \right)^{ND/2} = \frac{V^N}{N!} \frac{1}{\Lambda^{ND}} \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m k_\mathrm{B} T}} \end{aligned}$$

somit

$$S_k = -\beta k_B \underbrace{\frac{\partial}{\partial \beta} \ln \overbrace{\left(\frac{V^N}{N!} \frac{1}{\Lambda^{ND}} \right)}^{Z_k}}_{-(ND)\frac{1}{\Lambda}\frac{\partial \Lambda}{\partial \beta} = -ND\frac{1}{\Lambda}\frac{1}{2}\frac{\Lambda}{\beta}} + k_B \ln \frac{V^N}{N!} - k_B ND \ln \Lambda$$

$$= \beta k_B \frac{ND}{2\beta} + k_B \ln \frac{V^N}{N!} - k_B ND \ln \Lambda$$

$$= k_B N \left[\frac{D}{2} + \frac{1}{N} \ln \frac{V^N}{N!} - D \ln \Lambda \right]$$

wegen $N! \sim \mathrm{e}^{-N} N^N (\sqrt{2\pi} N^{1/2})$ gilt

$$\ln \frac{V^N}{N!} \sim \ln \left(\frac{V^N \mathrm{e}^N}{N^N} \right) = N \ln \frac{V}{N} + N$$

somit erhält man schließlich

$$S_k = k_B N \left[\ln \frac{V}{N} - D \ln \Lambda + \left(1 + \frac{D}{2} \right) \right]$$

Zustandsgleichungen

- kalorische Zustandsgleichung

$$E = -\frac{\partial}{\partial\beta}\ln Z_k = -\frac{\partial}{\partial\beta}\left(-ND\ln\Lambda\right) + 0 = ND\frac{1}{\Lambda}\frac{1}{2}\frac{\Lambda}{\beta} = \frac{D}{2}Nk_{\mathrm{B}}T$$

- thermische Zustandsgleichung:

$$\begin{aligned} F &= -k_{\mathrm{B}}T\ln Z_k = -k_{\mathrm{B}}T\left[\ln\frac{V^N}{N!} - ND\ln\Lambda\right] \\ &\sim -k_{\mathrm{B}}TN\left[\ln\frac{V}{N} - D\ln\Lambda + 1\right] \end{aligned}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_{\mathrm{B}}TN\frac{1}{V}$$

E_3.3 Klassisches ideales Gas im großkanonischen Ensemble

Hamiltonfunktion und Γ-Raum des idealen Gases in D Dimensionen

- Hamiltonfunktion $\mathcal{H} = \sum_i \frac{\mathbf{p}_i^2}{2m}$
- Phasenraum
- weiters: V fest; Temperatur T und chemisches Potential μ vorgegeben

großkanonische Entropie, S_g

$$\begin{aligned} S_g &= -k_\mathrm{B}\langle \ln \rho_g \rangle_g = k_\mathrm{B}\langle \ln Z_g + \beta E - \beta\mu N\rangle_g = \\ &= k_\mathrm{B}\beta\langle E\rangle_g - k_\mathrm{B}\beta\mu\langle N\rangle_g + k_\mathrm{B}\ln Z_g \end{aligned}$$

mit

$$\langle E\rangle_g = -\left(\frac{\partial}{\partial\beta}\ln Z_g\right)_{\mu,V} + \mu\langle N\rangle_g$$

$$\langle N\rangle_g = k_\mathrm{B} T\frac{\partial}{\partial\mu}\ln Z_g$$

für das ideale Gas gilt $Z_g = \exp\left[\frac{zV}{\Lambda^3}\right]$ mit $z = \exp[\beta\mu]$
somit

$$\langle E\rangle_g = \bar{E} = -\frac{\partial}{\partial\beta}\left(\frac{zV}{\Lambda^D}\right) + \mu\bar{N}$$

$$= -\mu\frac{zV}{\Lambda^D} - \frac{zV}{\Lambda^{D+1}}(-D)\underbrace{\left(\frac{\partial\Lambda}{\partial\beta}\right)}_{\frac{1}{2}\frac{\Lambda}{\beta}} + \mu\underbrace{\bar{N}}_{\frac{zV}{\Lambda^D}} = \frac{D}{2}\bar{N}k_\mathrm{B}T$$

$$\langle N\rangle_g = \bar{N} = k_\mathrm{B}T\frac{\partial}{\partial\mu}\left(\frac{zV}{\Lambda^D}\right) = \frac{zV}{\Lambda^D} = \ln Z_g$$

$$S_g = k_\mathrm{B}\beta\bar{E} - k_\mathrm{B}\mu\beta\bar{N} + k_\mathrm{B}\ln Z_g = \frac{1}{T}\frac{D}{2}\bar{N}k_\mathrm{B}T - \frac{\mu}{T}\bar{N} + k_\mathrm{B}\bar{N}$$

$$= k_\mathrm{B}\bar{N}\left[\left(1+\frac{D}{2}\right) - \frac{\mu}{k_\mathrm{B}T}\right] = (\mathrm{mit}\ \exp[\mu/(k_\mathrm{B}/T)] = \frac{\bar{N}}{V}\Lambda^D)$$

$$= k_\mathrm{B}\bar{N}\left[\ln\frac{V}{\bar{N}} - D\ln\Lambda + \left(1+\frac{D}{2}\right)\right]$$

Zustandsgleichungen

- $\langle N \rangle_g = \bar{N} = k_{\mathrm{B}} T \frac{\partial}{\partial \mu} \ln Z_g \Rightarrow \bar{N} = \bar{N}(T, V, \mu)$
  Invertieren dieser Beziehung führt zu $\mu = \mu(T, V, \bar{N})$

$$\langle N \rangle_g = \ln Z_g = \frac{zV}{\Lambda^D}$$

also

$$\mu = \mu(T, V, \bar{N}) = \frac{1}{\beta} \ln \frac{\bar{N}\Lambda^D}{V} \quad \text{bzw.} \quad z = \frac{\bar{N}\Lambda^D}{V}$$

- thermische Zustandsgleichung

$$\frac{PV}{k_{\mathrm{B}} T} = \ln Z_g[T, V, \mu(T, V, \bar{N})] = z\frac{V}{\Lambda^D} = \frac{\bar{N}\Lambda^D}{V}\frac{V}{\Lambda^D} = \bar{N}$$

- kalorische Zustandsgleichung

$$E = -\left(\frac{\partial}{\partial \beta} \ln Z_g\right)_{\mu, V} + \mu\bar{N} = -\frac{\partial}{\partial \beta}\left(\mathrm{e}^{\beta\mu}\frac{V}{\Lambda^D}\right)_{\mu, V} + \mu\bar{N} = \frac{D}{2}\bar{N} k_{\mathrm{B}} T$$

E_3.4 Entropie des idealen Gases ($D = 3$)

$$
\begin{aligned}
S_m &= k_\mathrm{B} N \left[\underline{\frac{3}{2} \ln \frac{E}{N}} + \underset{\sim\sim\sim}{\ln \frac{V}{N}} + \frac{3}{2} \ln \frac{4\pi m}{3h^2} + \frac{5}{2} \right] \\
S_k &= k_\mathrm{B} N \left[\ln \frac{V}{N} - 3 \ln \Lambda + \frac{5}{2} \right] \\
&= k_\mathrm{B} N \left[\underline{\frac{3}{2} \ln k_\mathrm{B} T} + \underset{\sim\sim\sim}{\ln \frac{V}{N}} + \frac{3}{2} \ln \frac{2\pi m}{h^2} + \frac{5}{2} \right] \\
S_g &= k_\mathrm{B} \langle N \rangle_g \left[\ln \frac{V}{\langle N \rangle_g} - 3 \ln \Lambda + \frac{5}{2} \right] \\
&= k_\mathrm{B} \langle N \rangle_g \left[\underline{\frac{3}{2} \ln k_\mathrm{B} T} + \underset{\sim\sim\sim}{\ln \frac{V}{\langle N \rangle_g}} + \frac{3}{2} \ln \frac{2\pi m}{h^2} + \frac{5}{2} \right]
\end{aligned}
$$

mit

$$
\Lambda = \left(\frac{h^2}{2\pi m k_\mathrm{B} T} \right)^{1/2}
$$