Thermodynamik

HS: $dU = \delta Q - \delta W$, $dS \geq \frac{\delta Q_{rev}}{T}$, $S(T \to 0) = S_0 = 0$

Ideal Gas: $pV = nRT = Nk_BT$

Van der Waals Gas: $(v-b)\left(p + \frac{a}{v^2}\right) = RT$, $T_c = \frac{8}{27}\frac{a}{bR}$

Ausdehnungskoeffizient $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p$

Spannungskoeffizient $\beta = \frac{1}{p}\frac{\partial p}{\partial T}\Big|_V$

Isotherme Kompressibilität $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T$

adiabatische Kompressibilität $\kappa_S = -\frac{1}{V}\frac{\partial V}{\partial T}\Big|_S$

$C_V = \frac{\partial U}{\partial T}\Big|_V = T\frac{\partial S}{\partial T}\Big|_V$, $C_p = \frac{\partial (U+pV)}{\partial T}\Big|_p = T\frac{\partial S}{\partial T}\Big|_p$

$C_p - C_V = R$

Adiabatengleichungen ($\delta Q = 0$):

$pV^{\gamma} = \text{const.}$, $p^{\frac{1-\gamma}{\gamma}}T = \text{const.}$, $V^{\gamma-1}T = \text{const.}$

für monoatomares Gas $\gamma = 5/3$:

$pV^{5/3} = \text{const.}$, $p^{-2/5}T = \text{const.}$, $V^{2/3}T = \text{const.}$

Wirkungsgrad Wärmemaschine: $\eta = \frac{\Delta W}{Q^{\swarrow}} = 1 - \frac{Q^{\nearrow}}{Q^{\swarrow}}$

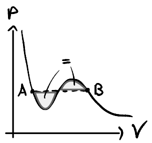
Wärmepumpe: $\eta = \frac{Q^{\swarrow}}{\Delta W} = \frac{1}{1 - Q^{\nearrow}/Q^{\swarrow}}$

Carnotmaschine (Isotherm-Adiabat.) $\frac{Q^{\nearrow}}{Q^{\swarrow}} = \frac{T_{Kl.}}{T_{Gr.}}$

Maxwell-Konstruktion $\int_A^B dV\, p(V) \overset{!}{=} p_S(V_B - V_A)$

Clausius-Clapeyron

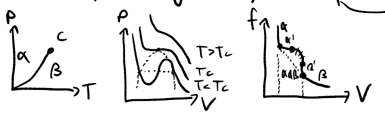
$$\frac{dp_S}{dT} = \frac{\Delta S}{\Delta V} = \frac{\ell}{T\Delta V}$$



Gibbs-Duhem: $0 = SdT - Vdp + nd\mu$

Mean free path: $\ell = \frac{1}{n\sigma}$, σ: Scattering-crosssection

Gibbsche Phasenregel: $f = 2 + r - \nu$ (r: anz. Komponenten, ν: anz. Phasen)



- Innere Energie $U(S,V,n) = TS - pV + \mu n$

$dU = TdS - pdV + \mu dn$ $\quad \frac{\partial T}{\partial V}\Big|_S = -\frac{\partial p}{\partial S}\Big|_V$

$\frac{\partial U}{\partial S}\Big|_{V,n} = T$, $\frac{\partial U}{\partial V}\Big|_{S,n} = -p$, $\frac{\partial U}{\partial n}\Big|_{S,V} = \mu$

- Freie Energie $F(T,V,n) = U - TS = -pV + \mu n$

$dF = -pdV - SdT + \mu dn$ $\quad \frac{\partial S}{\partial V}\Big|_T = \frac{\partial p}{\partial T}\Big|_V$

$\frac{\partial F}{\partial V}\Big|_{T,n} = -p$, $\frac{\partial F}{\partial T}\Big|_{V,n} = -S$, $\frac{\partial F}{\partial n}\Big|_{V,T} = \mu$

- Enthalpie $H(S,p,n) = U + pV = TS + \mu n$

$dH = TdS + Vdp + \mu dn$ $\quad \frac{\partial T}{\partial p}\Big|_S = \frac{\partial V}{\partial S}\Big|_p$

$\frac{\partial H}{\partial S}\Big|_{p,n} = T$, $\frac{\partial H}{\partial p}\Big|_{S,n} = V$, $\frac{\partial H}{\partial n}\Big|_{S,p} = \mu$

- Gibbs Potential $G(T,p,n) = F + pV = U - TS = \mu n$

$dG = -SdT + Vdp + \mu dn$ $\quad \frac{\partial S}{\partial p}\Big|_T = -\frac{\partial V}{\partial T}\Big|_p$

$\frac{\partial G}{\partial T}\Big|_{p,n} = -S$, $\frac{\partial G}{\partial p}\Big|_{T,n} = V$, $\frac{\partial G}{\partial n}\Big|_{T,p} = \mu$

- Grosses Potential $\Omega(T,V,\mu) = U - TS - \mu n = -pV$

$d\Omega = -SdT - pdV - nd\mu$ $\quad \frac{\partial n}{\partial T}\Big|_\mu = \frac{\partial S}{\partial \mu}\Big|_T$

$\frac{\partial \Omega}{\partial T}\Big|_{V,\mu} = -S$, $\frac{\partial \Omega}{\partial V}\Big|_{T,\mu} = -p$, $\frac{\partial \Omega}{\partial \mu}\Big|_{T,V} = -\mu$

$\frac{\partial U}{\partial V}\Big|_T = T\frac{\partial p}{\partial T}\Big|_V - p$, $\frac{\partial H}{\partial p}\Big|_V = T\frac{\partial S}{\partial p}\Big|_V + V$

Massenwirkungsgesetz:

$K(T,p;\{\nu_i\}) = \exp\left[-\sum_i \nu_i \mu_i(T,p)/RT\right] = \prod_i \left(\frac{n_i}{n}\right)^{\nu_i}$ ($g_i(T,p)$)

Osmotischer Druck: $p_1 = \frac{n_1}{n_0}\frac{RT}{V_0} = n_1\frac{RT}{V}$ (Lösung (Zucker))

Mischungen: $p = \sum_i p_i$, $n = \sum_i n_i$, $V = \sum_i V_i$

$U = \sum_i n_i u_i$, $S = S_0 + R\sum_i n_i \ln(n/n_i)$, $S_0 = \sum_i n_i S_i$

Kinetische Gastheorie

$\dim \Gamma = 6N$

Zustandsraum $\Gamma \ni (p,q) = \{p_1, \dots, p_{3N}; q_1, \dots, q_{3N}\}$

Hamiltonian $\mathcal{H}(p,q) = T + V$; $\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$, $\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$

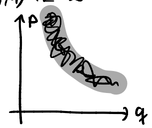
Zeitmittel $\overline{\mathcal{M}}^T = \lim_{T\to\infty}\frac{1}{T}\int_0^T dt\, \mathcal{M}(p(t), q(t))$

Ensemblemittelwert $\langle \mathcal{M} \rangle = \frac{\int d^{3N}p\, d^{3N}q\, \mathcal{M}(p,q)\, \rho(p,q)}{\int d^{3N}p\, d^{3N}q\, \rho(p,q) = N}$

Dichtefkt. $\rho(p,q)\, d^{3N}p\, d^{3N}q$ "Wahrscheinlichkeit das System in $d^{3N}p\, d^{3N}q$ anzufinden"

Im Ggw ($V,N,E,\dots$ fix): $\rho(p,q) = \begin{cases} \text{const.} & E < \mathcal{H}(p,q) < E + \Delta \\ 0, & \text{sonst} \end{cases}$

$\overline{\mathcal{M}}^T = \langle \mathcal{M} \rangle$ "ergodisch"



Einteilchenphasenraum $\mu \ni (\vec{p}, \vec{q})$, $\dim \mu = 6$

Einteilchenverteilungsfkt. $f(\vec{p}, \vec{q}, t)\, d^3p\, d^3q$

"Anzahl Teilchen in $d^3p\, d^3q$ zur Zeit t"

$\int d^3p\, d^3q\, f(\vec{p}, \vec{q}, t) = N$, $\int d^3p\, f(\vec{p}, t) = \frac{N}{V} = n$

Kontinuitätsgl. (N const.): $\partial_t f + \dot{\vec{q}} \cdot \vec{\nabla}_q f + \dot{\vec{p}} \cdot \vec{\nabla}_p f = 0$

Boltzmann-Transport Gleichung:

$$\underbrace{\partial_t f + \dot{\vec{q}}\, \vec{\nabla}_q f + \dot{\vec{p}}\, \vec{\nabla}_p f}_{\mathcal{D}f} = \frac{\partial f}{\partial t}\Big|_{\text{Stösse}}$$

Streurate $W_{\vec{p}', \vec{p}} \approx \dots = W_{\vec{p}, \vec{p}'}$ "wie oft pro Sekunde wird aus $\vec{p} \to \vec{p}'$?"

T-D (erhält N, E; $\cancel{P}$) $\frac{\partial f}{\partial t}\Big|_{\text{Stösse}} = -\int d^3p\, W_{\vec{p}\vec{p}'}(f(\vec{p}) - f(\vec{p}'))$

T-T (erhält N, E, P):

$\frac{\partial f}{\partial t}\Big|_{\text{Stösse}} = -\int d^3p'\, d^3p_1\, d^3p_1'\, W_{\vec{p}',\vec{p}_1';\vec{p},\vec{p}_1}\left[f(\vec{p})f(\vec{p}_1) - f(\vec{p}')f(\vec{p}_1')\right]$

T-M (erhält N; $\cancel{E}, \cancel{P}$): $\frac{\partial f}{\partial t}\Big|_{\text{Stösse}} = \dots$

Für $\Phi(\vec{p}, f(\vec{p}, \vec{q})) = 1, \vec{p}, \vec{p}^2$

und Dichte $S_\Phi(\vec{q}, t) = \int d^3p\, \Phi(\vec{p}, f) f(\vec{p}, \vec{q}, t)$

$\partial_t \Phi|_{\text{Stösse}} = 0 \Rightarrow$ Teilchendichte ($\Phi = 1$), Impulsdichte ($\Phi = \vec{p}$), Energiedichte ($\Phi = \vec{p}^2$) sind erhalten!

Für $\Phi = \ln f$: $S_{\ln f} = \int d^3p\, f \ln f = H(t)$ (Entropie)

$\hookrightarrow \partial_t H|_{\text{Stösse}} = -\frac{1}{4}\int d^3p\, d^3p_1\, d^3p'\, d^3p_1'\, W_{\vec{p}\vec{p}_1\vec{p}'\vec{p}_1'} \underbrace{(ff_1 - f'f_1')\ln\frac{ff_1}{f'f_1'}}_{(x-y)\ln(x/y) \geq 0}$

$\Rightarrow \partial_t H|_{\text{Stösse}} \leq 0$

Entropiedichte $s(\vec{q}, t) = -k_B \int d^3p\, f \ln f \Rightarrow \partial_t s|_{\text{Stösse}} \geq 0$

Im Gleichgewicht: $\ln f_0$, $1, \vec{p}, \vec{p}^2 = 2mE$ erhalten

$\ln f_0 = A1 + \vec{B} \cdot \vec{p} - C E$

Normierung n, Konvektiver Strom $\vec{p}_0$, Gas Gl. $pV = nRT$

Maxwell-Boltzmann Verteilung:

$$f_0(\vec{p}) = n\left(\frac{1}{2\pi m k_B T}\right)^{3/2} e^{-\frac{(\vec{p} - \vec{p}_0)^2}{2mk_BT}}$$

De Broglie Wellenlänge $\lambda^2 = \frac{2\pi\hbar^2}{mk_BT}$

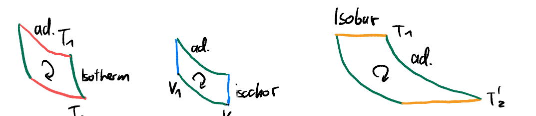
Mittlere Energie $\langle \varepsilon \rangle = \frac{3}{2}k_BT$

Wahrscheinlichste Geschwindigkeit $\bar{v} = \sqrt{\frac{2k_BT}{m}}$

mittlere Geschwindigkeit $\langle v^2 \rangle^{1/2} = \sqrt{\frac{3k_BT}{m}} > \bar{v}$

Innere Energie $U = N\varepsilon = \frac{3}{2}k_BT = \frac{3}{2}n_{mol}RT$, $C_V = \frac{3}{2}Nk_B$

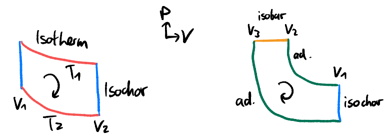
Entropie $S = Nk_B \ln T^{3/2} V$



Carnot $\eta = 1 - \frac{T_1}{T_2}$

Otto $\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}$

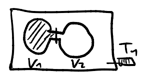
Escher-Wyss $\eta = 1 - \frac{T_2'}{T_1}$



$r = \frac{V_1}{V_2}$, $r_2 = \frac{V_3}{V_1}$

Stirling $\eta = \frac{1 - T_1/T_2}{1 + \frac{1 - T_1/T_2}{\log(V_2/V_1)} \cdot \frac{C_V}{nR}}$

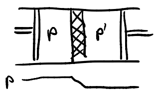
Diesel $\eta = 1 - r^{1-\gamma}\frac{r_2^{\gamma} - 1}{\gamma(r_2 - 1)}$



Gay-Lussac

$\delta Q = 0$, $\delta W = 0$

$\Rightarrow U = U(T)$



Joule-Kelvin

$\delta Q = 0$

Enthalpie erhalten

Hydrodynamik

Gleichungen: Dichte $\vec{n}(\vec{r},t)$, Konvektie Strömung $\vec{u}(\vec{r},t)$, Temperatur $T(\vec{r},t)$

lokale Maxwell-Boltzmann Verteilung:

$$f(\vec{v};\vec{r},t)=f_{\ell 0}=n(\vec{r},t)\left(\frac{1}{2\pi m k_B T(\vec{r},t)}\right)^{3/2}\exp\left[-\frac{m(\vec{v}-\vec{u}(\vec{r},t))^2}{2k_B T(\vec{r},t)}\right]$$

$\Phi=1,\vec{p},\vec{p}^2$ in $\int d^3p\, \mathcal{D}f_0\,\Phi=0$ einsetzen:

$\Phi=1$ (Kontinuität) $\quad \partial_t n+\partial_i j_i=0$

$\Phi=\vec{p}$ (Treiber) $\quad \partial_t j_k+\frac{1}{m}\partial_i\Pi_{ik}=\frac{n}{m}F_k$

$\Phi=\vec{p}$ (Energie) $\quad \partial_t e+\partial_i\varepsilon_i=\underbrace{j_iF_i}_{\text{Leistung}}$

Dichte $\quad n=\int d^3p\, f$

Stromdichte $\quad j_k=\int d^3p\, v_k f$

Energie $\quad e=\int d^3p\,\frac{p^2}{2m}f$

Impulsstromdichte $\quad \Pi_{ik}=m\int d^3p\, v_i v_k f$

Energiestromdichte $\quad \varepsilon_k=\int d^3p\,\frac{p^2}{2m}v_k f$

Eulergleichungen (0. Ordnung, $f=f_{\ell 0}$)

$D_t=\partial_t+u_i\partial_i$

$$D_t n+n\vec{\nabla}\cdot\vec{u}=0$$
$$mnD_t\vec{u}+\vec{\nabla}(nk_BT)=n\vec{F}$$
$$\frac{3}{2}D_tT+T\vec{\nabla}\cdot\vec{u}=0$$

Navier-Stokes (1. Ordnung, $f=f_{\ell 0}-\tau\mathcal{D}f_{\ell 0}$)

$$D_t n+n\vec{\nabla}\cdot\vec{u}=0$$
$$mnD_t\vec{u}+\vec{\nabla}(nk_BT)=n\vec{F}-\vec{\nabla}(\eta\hat{P})$$
$$nk_B\left[\frac{3}{2}D_tT+T\vec{\nabla}\cdot\vec{u}\right]=\vec{\nabla}\cdot(\kappa\vec{\nabla}T)-(\eta\hat{P}\cdot\vec{\nabla})\cdot\vec{u}$$

Stationäre Navier-Stokes Gl.

$$(\vec{v}\cdot\vec{\nabla})\vec{v}=-\frac{\vec{\nabla}\vec{P}}{\rho}+\frac{\eta}{\rho}\Delta\vec{v}$$

Reynolds nr. $\quad Re\ll 1\to$ laminar

$\quad Re>1\to$ turbulen

Statistische Physik $\quad \mathcal{H}\xrightarrow{*}Z_N\xrightarrow{\checkmark}\text{Pot.}\xrightarrow{\partial}$ Zst-Gl.

- μ-kanonisch $\quad E,V,N$ fix

$$\rho(p,q)=\frac{1}{h^{3N}N!}\quad \text{für } E<\mathcal{H}(p,q)<E+\Delta,\ \text{sonst } 0$$

$$\Gamma(E)=\int d^{3N}p\,d^{3N}q\,\rho(p,q),$$

$$\Sigma(E)=\int_{\mathcal{H}(p,q)<E}d^{3N}p\,d^{3N}q\,\frac{1}{h^{3N}N!}$$

$$S=k_B\ln\Gamma(E)\approx k_B\ln\Sigma(E)$$

- Kanonisch $\overset{Ⓡ}{T},V,N$ fix, $\quad \beta=\frac{1}{k_BT}$

$$\rho(p,q)=\frac{1}{h^{3N}N!}e^{-\beta\mathcal{H}(p,q)}$$

$$Z_N(T,V)=\int d^{3N}p\,d^{3N}q\,\rho(p,q)$$

$$F=-k_BT\ln Z_N$$

- Gross-Kanonisch $\overset{Ⓡ}{T},V,\overset{Ⓡ}{\mu}$ fix, $\quad z=e^{-\beta\mu}$ "fugazität"

$$\rho(p,q)=\frac{1}{h^{3N}N!}e^{-\beta(\mathcal{H}(p,q)-\mu N+pV)}$$

$$\mathcal{Z}=\sum_N z^NZ_N=\sum_N\int\frac{d^{3N}p\,d^{3N}q}{h^{3N}N!}e^{-\beta(\mathcal{H}(p,q)+pV)}$$

$$\Omega=-k_BT\ln\mathcal{Z}=-pV$$

Mittlere Energie: $\langle\mathcal{H}\rangle=U=\sum_N\int d^{3N}p\,d^{3N}q\,\mathcal{H}(p,q)\,\rho(p,q,N)$

Mittlere Teilchenzahl: $\langle N\rangle=\sum_N\int d^{3N}p\,d^{3N}q\,N\rho(p,q,N)$

$$=\frac{1}{\mathcal{Z}}\sum_N Nz^NZ_N$$

Äquipartitionsprinzip $\left\langle x_i\frac{\partial\mathcal{H}}{\partial x_i}\right\rangle=\delta_{ij}k_BT,\quad x_i=p_i,q_i$

für $\mathcal{H}=\sum\frac{p_i}{2m}\quad\left\langle\frac{p_i^2}{2m}\right\rangle=\frac{k_BT}{2}$

Variationsprinzip $\mathcal{H}=\mathcal{H}_0+\mathcal{H}',\ F\overset{\le}{=}F_0+\langle H'\rangle_0$

Kumulantenentw. $F=F_0+\langle H'\rangle_0-\frac{1}{2k_BT}\left[\langle H'^2\rangle_0-\langle H'\rangle_0^2\right]+\cdots$

$\langle A\rangle_0=\int d\varphi\,A\,e^{-\beta\mathcal{H}_0(\varphi)}$ (kanonisches ensemble)

Ising Modell: $\mathcal{H}(\{S_i\})=\underbrace{-\frac{J}{2}\sum_{\langle i,j\rangle}S_iS_j}_{\mathcal{H}_I}\underbrace{-\mu h\sum_i S_i}_{\mathcal{H}^{ext}}$

$h\leftrightarrow p,\ m\leftrightarrow V$ $\quad$ Nächste Nachbarn

$$Z_N(T,h)=\sum_{\{S_i\}}\exp\left[-\frac{\mathcal{H}(\{S_i\})}{k_BT}\right]=\sum_{S_1=\pm S}\cdots\sum_{S_i=\pm S}e^{-\frac{\mathcal{H}(S_1)}{k_BT}}\cdots e^{-\frac{\mathcal{H}(S_N)}{k_BT}}$$

$$G(T,h,N)=k_BT\log Z_N(T,h)$$

$$S=-\frac{\partial G}{\partial T}\bigg|_{h,N},\quad M=\frac{\partial G}{\partial h}\bigg|_{T,N},\quad h=\frac{1}{V}\frac{\partial F}{\partial m}$$

$$\chi=\frac{\partial m}{\partial h}=-\frac{1}{V}\frac{\partial^2G}{\partial h^2},\quad \chi^{-1}=\frac{1}{V}\frac{\partial^2F}{\partial m^2}$$

$$F=G+Mh,\quad C_H=T\frac{\partial S}{\partial T}\bigg|_H=-T\frac{\partial^2G}{\partial T^2}$$

Mean field: $\mathcal{H}=-\frac{J}{2}zN\langle S\rangle^2-\mu h'\sum_i S_i$

(z: anz. nächster Nachbarn)

Landau exponents, $|\tau|=1-T/T_c$:

$C_V|_{h=0}\propto\tau^{\alpha=0},\quad \Phi|_{h=0}\propto\tau^{\beta=1/2},\quad \chi|_{h=0}\propto\frac{1}{\tau^{\gamma=1}},\quad \Phi|_{T=T_c}\propto h^{1/\delta=3}$

Φ: order parameter, $m(T)$; $m(h)$; for Ising

for $f(T,\Phi)$ the conjugate field is $h=\frac{\partial f}{\partial\Phi}\big|_T$ (Equation of state)

Clausius: "Wärme kann nicht von selbst aus einem niederen zu einem höheren Temperatur niveau übergehen"

Kelvin: "Es ist unmöglich fortlaufend Arbeit zu erzeugen durch blosse Abkühlung eines einzelnen Körpers."

Math n'Stuff

Gauss $\quad \int_{-\infty}^{\infty}dx\,e^{-\frac{x^2}{\sigma}}=\sqrt{\sigma\pi}$

$$\int_0^\infty dx\,x^{2n}e^{-\alpha x^2}=\frac{(2n)!}{2^{2n+1}n!}\alpha^{-\frac{(2n+1)}{2}}\sqrt{\pi}\overset{n=0}{=}\frac{1}{2}\alpha^{-\frac{1}{2}}\sqrt{\pi}$$

$$\int_0^\infty dx\,x^{2n+1}e^{-\alpha x^2}=\frac{n!}{2\alpha^{n+1}}\overset{n=0}{=}\frac{1}{2\alpha}$$

Stirling: $\Gamma(z+1)=z^Ne^{-z}\sqrt{2\pi z}\,(1+r(z)),\ 0<r(z)<\frac{1}{12z}+\ldots$

$\log(n!)=\log(\Gamma(n+1))\approx n(\log n-1)$

Kettenregel $\quad \frac{\partial x}{\partial y}\Big|_z\frac{\partial z}{\partial x}\Big|_y\frac{\partial y}{\partial z}\Big|_x=-1$

Schwarz $\quad \frac{\partial}{\partial x_i}\left(\frac{\partial\Phi}{\partial x_j}\right)=\frac{\partial}{\partial x_j}\left(\frac{\partial\Phi}{\partial x_i}\right)$

Legendretrans. $f^*(p)=\sup_x[xp-f(x)],\quad f^{**}=f$

Konvexität $f(\lambda x_1+(1-\lambda)x_2)\le\lambda f(x_1)+(1-\lambda)f(x_2)\ \forall\lambda\in[0,1]$

Taylor expansion

$$f_a(x)=\sum_{n=0}^\infty\frac{f^{(n)}(a)}{n!}(x-a)^n=f(a)+\frac{f'(a)}{1!}(x-a)+\frac{f''(a)}{2!}(x-a)^2+\cdots$$

Polarkoordinaten

$x=r\sin\vartheta\cos\varphi,$
$y=r\sin\vartheta\sin\varphi,$
$z=r\cos\vartheta$

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}f(r,\vartheta,\varphi)\,r^2\sin\vartheta\,dr\,d\vartheta\,d\varphi$$

$1\,\text{Å}=10^{-10}\,m,\quad \omega=2\pi f,\quad \lambda f=c$