Response Funktionen (Antwort Fkt)

- Halte eine Größe fest und beobachte Antwort des Systems
- man kann beliebige Potentiale einführen $\Phi(H, B)$...

Maxwellrelationen

- Fundamentalbeziehung $dU = TdS - PdV + \mu dN$

$$U(S,V,N) \Rightarrow dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N}}_{-P} dV + \underbrace{\left(\frac{\partial U}{\partial N}\right)_{S,V}}_{\mu} dN$$

- $$\left(\frac{\partial^2 U}{\partial S \partial V}\right)_N = \left(\frac{\partial^2 U}{\partial V \partial S}\right)_N \Rightarrow \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \quad \text{Maxwellrelation}$$

Großkanonisches Potential

$$\Omega(T,V,\mu) \Rightarrow d\Omega = -SdT - PdV - Nd\mu$$

$$\Rightarrow \left(\frac{\partial P}{\partial \mu}\right)_T = \left(\frac{\partial N}{\partial V}\right)_T \quad \text{für} \quad \left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{N^2}{V} k_T$$

$$F(T,V) \Rightarrow dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \qquad -S = \left(\frac{\partial F}{\partial T}\right)_V, \; -P = \left(\frac{\partial F}{\partial V}\right)_T$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Relation zwischen den Response-Funktionen

$$c_p - c_v = TV\frac{\alpha^2}{k_T}$$

$$c_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad S(T,V),\; V(T,P) \Rightarrow S(T,V(T,P)) \text{ oder } S(T,P)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

oder

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$= \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p\right] dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP$$

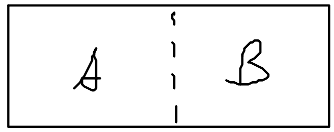
$$\Rightarrow c_p = T\left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p\right]$$

$$c_p - c_v = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \overset{\text{Maxwell}}{=} T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_p \frac{\left(\frac{\partial V}{\partial T}\right)_p}{\underbrace{\left(\frac{\partial V}{\partial P}\right)_T}_{-Vk_T}} = TV\frac{\alpha^2}{k_T}$$

Stabilität

Gedankenexp.:



thermisch leitend
bewegliche
durchlässige Wand

Gleichgewicht: $dU=0$, $dS=0$

$\Rightarrow dU_A=-dU_B$, $dV_A=-dV_B$, $dN_A=-dN_B$

$S(U,V,N)$

$$dS=\underbrace{\left(\frac{\partial S_A}{\partial U_A}\right)_{V_A,N_A}}_{\frac{1}{T_A}}dU_A+\underbrace{\left(\frac{\partial S_B}{\partial U_B}\right)_{V_B,N_B}}_{\frac{1}{T_B}}dU_B+\underbrace{\left(\frac{\partial S_A}{\partial V_A}\right)_{U_A,N_A}}_{\frac{p_A}{T_A}}dV_A+\dots dV_B+\dots dN_A+dN_B$$

aus $dS=\frac{1}{T}dU+\frac{p}{T}dV-\frac{\mu}{T}dN$ (Fundamentalbeziehung)

folgt $dS=\left(\frac{1}{T_A}-\frac{1}{T_B}\right)dU_A+\left(\frac{p_A}{T_A}-\frac{p_B}{T_A}\right)dV_A-\left(\frac{\mu_A}{T_A}-\frac{\mu_B}{T_B}\right)dN_A\overset{!}{=}0$

Mischungsentropie und Gibb'sches Paradoxon

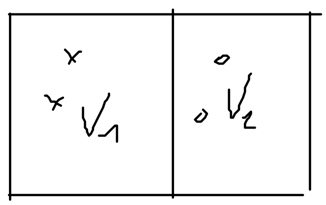
ideales Gas: $S(U,V,N)=Ns_0+Nk\ln\left(\frac{V}{N}\left(\frac{U}{N}\right)^{\frac{f}{2}}\right)$

$=Ns_0+Nk\ln\left(\frac{V}{N}\right)+Nk\frac{f}{2}\ln\left(\frac{U}{N}\right)$

$\left(\frac{\partial S}{\partial V}\right)_{U,N}=\frac{p}{T}=Nk\frac{N}{V}\frac{1}{N}\Rightarrow pV=NkT$

$\left(\frac{\partial S}{\partial U}\right)_{V,N}=Nk\frac{f}{2}\frac{\cancel{N}}{U}\frac{1}{\cancel{N}}\Rightarrow U=\frac{f}{2}NkT$

- Gedankenexperiment:
  - Expansionsentropie
  - Mischungsentropie



Entferne Trennwand

- **Mischungsentropie** $\Delta S=S(\text{„nach"})-S(\text{„vor"})$

$$\left.\begin{array}{l}N=N_1+N_2\\U=U_1+U_2\\V=V_1+V_2\end{array}\right\}\Delta S=0$$

$=S(U,V,N)-S(U_1,V_1,N_1)-S(U_2,V_2,N_2)$

$=Ns_0+Nk\ln\left(\frac{V}{N}\right)+Nk\frac{f}{2}\ln\left(\frac{U}{N}\right)$

$-N_1s_0-N_1k\ln\left(\frac{V_1}{N_1}\right)-N_1k\frac{f}{2}\ln\left(\frac{U_1}{N_1}\right)$

$-N_2s_0-N_2\ln\left(\frac{V_2}{N_2}\right)-N_2k\frac{f}{2}\ln\left(\frac{U_2}{N_2}\right)$

Problem nicht mit klass. Physik erklärbar

QM Korrektur für Ideales Gas

Wahrscheinlichkeitstheorie

- Charakteristische Funktion $\phi(k) = \langle e^{ikx} \rangle = \int dx\, e^{ikx} \rho(x)$
- Wahrscheinlichkeitsverteilung

  $\rho(x) = \int \frac{dk}{2\pi} e^{-ikx} \phi(k)$ Entwickle $\phi(k) = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle$

  $\langle x^n \rangle = \sum_i x_i^n \rho_i = \int dx\, x^n \rho(x)$
- Umgekehrt: n-tes Moment $\langle x^n \rangle = \frac{1}{i^n} \frac{d^n \phi(k)}{dk^n} \Big|_{k=0}$
- Erwartungswert $\langle n \rangle$
- Standardabweichung : $\frac{\sigma_N}{\langle N \rangle}$ $\sigma_N = \sqrt{\langle n^2 \rangle - \langle n \rangle^2}$

Verteilungsfunktionen

- Binomialverteilung
- Gaußverteilung : aus Binom. für große N, pN, qN
  (kontinuierlich)
- Poisson-Verteilung ($N \to \infty$, $p \to 0 \Rightarrow a = Np$ aus Binomial.)

es gibt auch Gaußverteilung für mehrere Variablen