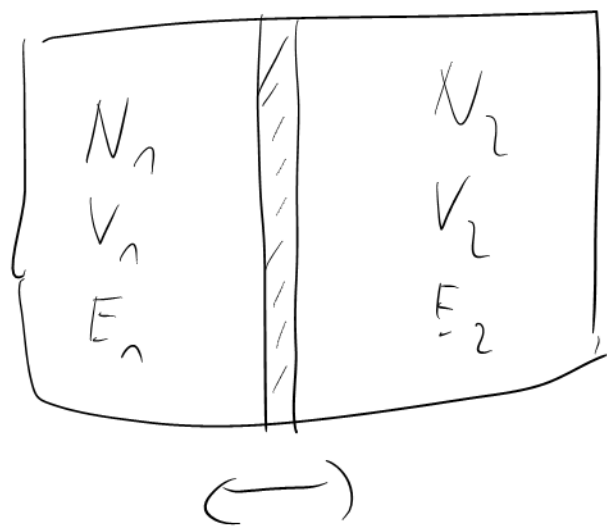


→ temperature

N_1, N_2 fixed

$$V_1 + V_2 = V$$

$$E_1 + E_2 = E$$



$$\Omega_{\text{tot}}(E, V) = \frac{1}{\Delta E \Delta V} \int_0^E dE_1 \int_0^V dV_1 \Omega_1(E_1, V_1) \Omega_2(E - E_1, V - V_1)$$

small ΔE and ΔV
 normalization volume
 analogous to ΔE

Maximize $\Omega_1(E_1, V_1) \Omega_2(E - E_1, V - V_1)$ wrt.

both energy and volume $\rightarrow \bar{E}_1, \bar{V}_1$

$$S_{\text{tot}} = S_1(\bar{E}_1, \bar{V}_1) + S_2(E - \bar{E}_1, V - \bar{V}_1)$$

$\Rightarrow \left. \frac{\partial S}{\partial E} \right|_V$ must be the same in both systems, AND

$\left. \frac{\partial S}{\partial V} \right|_E$ " " " " " " " " " " " "

Define: Pressure

$$P = T \frac{\partial S}{\partial V}$$

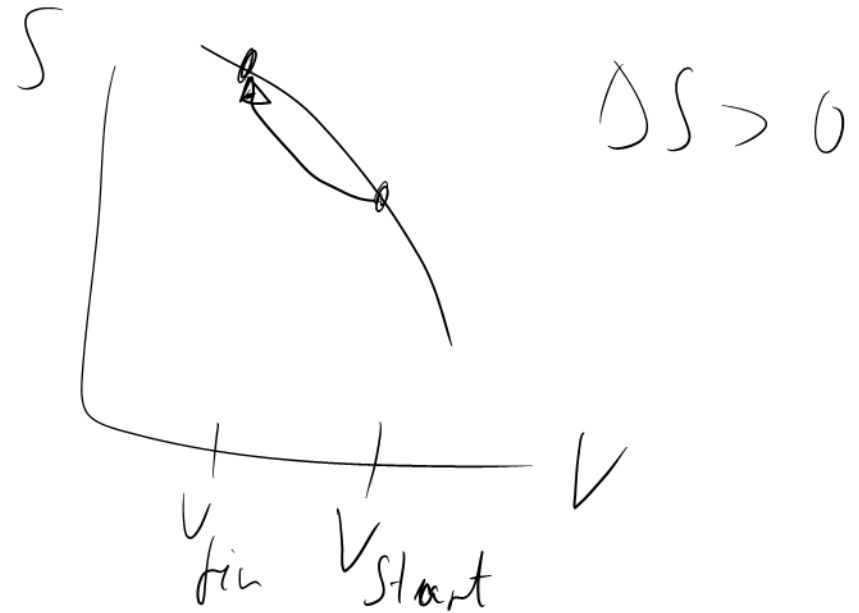
- intensive, units: energy/volume

ideal gas: $S = N \ln V + \text{terms independent of } V$

$$P = T N \frac{1}{V} \quad \Rightarrow \quad \boxed{PV = TN} \quad \begin{array}{l} \text{equation of state of} \\ \text{an ideal gas} \end{array}$$

Claim: $P > 0$. Proof: Assume $P < 0$

$$\Rightarrow \frac{\partial S}{\partial V} < 0 \quad (T > 0)$$



System would collapse!

A bit of thermodynamics

$$\underbrace{[N = \text{const.}]}_{\text{1st law}} \quad S = S(E, V)$$

$$dS = \left. \frac{\partial S}{\partial E} \right|_V dE + \left. \frac{\partial S}{\partial V} \right|_E dV = \frac{1}{T} dE + \frac{P}{T} dV$$

$$dE = TdS - PdV$$

(standard form of the
1st law)

$$P = - \left. \frac{\partial E}{\partial V} \right|_S$$

Legendre transformation:

S as natural variable for E

→ T " " " " F (Helmholtz
free energy)

$$dF = \dots dT - P dV$$

$$\boxed{\dots = ? \quad F = ?}$$

$$d(TS) = T dS + S dT$$

$$dE = T dS - P dV$$

$$d \underbrace{(E - TS)}_{\bar{F}} = \underbrace{-S dT - P dV}$$

$$\bar{F} = E - TS \quad d\bar{F} = -S dT - P dV$$

$$\Rightarrow \underbrace{P = - \left. \frac{\partial \bar{F}}{\partial V} \right|_T}$$

"Differential swapping" between P and V

$$- dE = T dS - P dV$$

$$- dH = T dS + V dP$$

$$- d(PV) = V dP + P dV$$

$$d(E + PV) = T dS + V dP$$

$$\Rightarrow \boxed{H = E + PV}$$

$H = ?$ enthalpy

T & S conjugate

P & V "

$$H = H(S, P)$$

$$T = \left. \frac{\partial H}{\partial S} \right|_P \quad V = \left. \frac{\partial H}{\partial P} \right|_S$$

\bar{E} , \bar{F} , H are called thermodynamic potentials; they are all related by Legendre transformations!

$$dE = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$

$$\rightarrow H = \bar{E} + PV$$

$$\rightarrow \bar{F} = \bar{E} - TS$$

Still missing:

Gibbs potential or
(Gibbs) free enthalpy

Starting from \mathbb{E} : $G = E - TS + PV$

$$dG = \cancel{TdS} - \cancel{PdV} - \cancel{TdS} - SdT + \cancel{PdV} + VdP$$

$$= -SdT + VdP$$

$$G = F + PV = H - TS$$

Natural variables of G : T, P Intensive !!

$G = G(T, P)$ BUT G IS EXTENSIVE!

HOW? Answer: 3rd argument N (particle #)

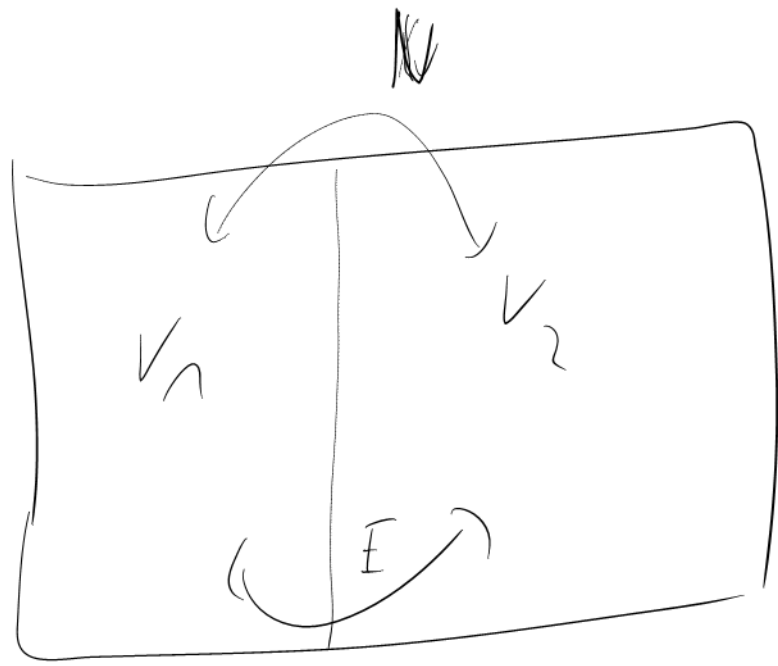
$$G = G(T, P, N)$$

only ONE extensive variable left

$$\left. \frac{\partial G}{\partial N} \right|_{T, P} = \frac{G}{N}$$

$$G = G(T, P, N) = N g(T, P)$$

L), intensive L) also intensive



permeable
membrane

V_1 fixed

V_2 "

$$N_1 + N_2 = N$$

$$E_1 + E_2 = E$$

now the particles are INDISTINGUISHABLE

recall $\Omega^{\text{naive}} = \Omega$ where Indist. is disregarded

$$\Omega_{\text{tot}}^{\text{naive}}(E, N) =$$

$$= \sum_{N_1=0}^N \frac{1}{\Delta E} \int_0^E dE_1 \underbrace{\Omega_1^{\text{naive}}(E_1, N_1)}_{\text{wavy}} \underbrace{\Omega_2^{\text{naive}}(E - E_1, N - N_1)}_{\text{wavy}} \times$$

$N!$

$N_1!$ $(N - N_1)!$

wavy wavy

$$\Rightarrow \Omega_{\text{tot}}(\bar{E}, N) = \frac{1}{\Delta E} \sum_{N_n=0}^N \int dE_n$$

$$\Omega_1(E_n, N_n) \Omega_2(E - E_n, N - N_n)$$

$$S_{\text{tot}} = S_1(\bar{E}_n, \bar{N}_n) + S_2(E - \bar{E}_n, N - \bar{N}_n)$$

\bar{E}_n, \bar{N}_n via maximization w.r.t. to both

E_n, N_n

$\frac{\partial S}{\partial E}$ must be the same in both systems

$\frac{\partial S}{\partial N}$ must be the same in both systems

define

$$\mu = -T \left. \frac{\partial S}{\partial N} \right|_{V, E}$$

chemical potential

$$V = \text{const.} \quad \Rightarrow \quad dV = 0$$

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial N} dN = \frac{1}{T} dE - \frac{\mu}{T} dN$$

$$dE = T dS + \mu dN$$

Dependence on ALL variables:

$$dE = TdS - PdV + \mu dN$$

1st law
with
extended
form 1

$$\Rightarrow dF = -SdT - PdV + \mu dN$$

$$dH = TdS + VdP + \mu dN$$

$$dG = -SdT + VdP + \mu dN$$

Gibbs-Duhem
relation

$$G = Ng(T, P) \Rightarrow g \equiv \mu \Rightarrow \boxed{G = N\mu}$$

μ - N differential swapping

$$d\bar{F} = -SdT - PdV + \mu dN$$

$$d(\mu N) = \mu dN + N d\mu$$

$$\left(d(\bar{F} - \mu N) = -SdT - PdV - N d\mu \right)$$



$\bar{\Phi}$ grand-canonical potential

$$\bar{\Phi} = \bar{\Phi}(T, V, \mu)$$

Energy exchange
particle exchange at $V = \text{const.}$

An ensemble where $DNLL$ intensive variables occur as natural variables can't occur.

The case of $E = \text{const.}$ / $H = \text{const.}$ at fluctuating N is in principle possible,

BUT experimentally difficult.

recall : $\zeta(T, P, N) = N g(T, P) = N \mu$

now $\bar{\Phi}(T, \mu, V) = V \varphi(T, \mu)$

$$\frac{\bar{\Phi}}{V} = \frac{\partial \bar{\Phi}}{\partial V} = -P$$

$$d\bar{\Phi} = -SdT - Nd\mu - PdV$$

$$\boxed{\bar{\Phi} = -PV}$$