Lecture #2 - office hour Thursday 2-3

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Note that T, P, μ are all functions of s, v $\Rightarrow$ we can eliminate s, and v to obtain a relation between (T, P, μ) i.e. $\mu(T, P)$

$\Rightarrow$ These cannot be varied independently.

This is called the Gibbs - Duhem relation

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

∂_λ Now, differentiate w.r.t. λ:

$$U(S,V,N) = \frac{\partial U}{\partial(\lambda S)}\bigg|_{\lambda V, \lambda N} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda}$$

$$= T(\lambda S, \lambda V, \lambda N) \cdot S - P(\lambda S, \lambda V, \lambda N) V + \mu(\lambda S, \lambda V, \lambda N) N$$

set $\lambda = 1$

$$\boxed{U = TS - PV + \mu N}$$ (Euler relation)

Divide by N: $U/N \equiv u$ (2)

$$u = Ts - Pv + \mu$$

but, the first law is $dU = TdS - PdV + \mu dN$

take differential of Euler relation:

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

$$dU$$

$$\Rightarrow 0 = SdT - VdP + Nd\mu$$

or $\boxed{d\mu = -s\,dT + v\,dP}$

Gibbs-Duhem relation.

in entropy rep:

$$d\left(\frac{\mu}{T}\right) = u\,d\left(\frac{1}{T}\right) + v\,d\left(\frac{P}{T}\right)$$

Euler $\Rightarrow S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T}$; $dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN + U\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{P}{T}\right) - N\,d\left(\frac{\mu}{T}\right)$

dS, also

$$\cancel{dS} = \cancel{dS} - \cancel{\frac{P}{T}dV} + \cancel{\frac{\mu}{T}dN} + \cancel{\frac{P}{T}dV} - \cancel{\frac{\mu}{T}dN} + U\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{P}{T}\right) - N\,d\left(\frac{\mu}{T}\right) \Rightarrow d\left(\frac{\mu}{T}\right) = v\,d\left(\frac{P}{T}\right) + u\,d\left(\frac{1}{T}\right)$$

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Example: Ideal Gas, $PV = NT$

find the entropy: $s(u,v)$ $(k_B = 1)$

$$dS = \frac{dU}{T} + \frac{P}{T} dV \quad ; \; U = NT\left(\frac{3}{2}\right)$$

$$ds = \frac{du}{T} + \frac{P}{T} dv$$

why? $S = \frac{U}{T} + \frac{P}{T} V - \frac{\mu}{T} N$

$$s = \frac{u}{T} + \frac{P}{T} v - \frac{\mu}{T}$$

derivation

$$ds = \frac{du}{T} + \frac{P}{T} dv + \underbrace{u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right) - d\left(\frac{\mu}{T}\right)}_{\text{vanishes by Gibbs-Duhem relation}}$$

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

Ideal Gas $\Rightarrow = \frac{3}{2} \frac{dT}{T} + \frac{1}{v} dv$ write as a differential!

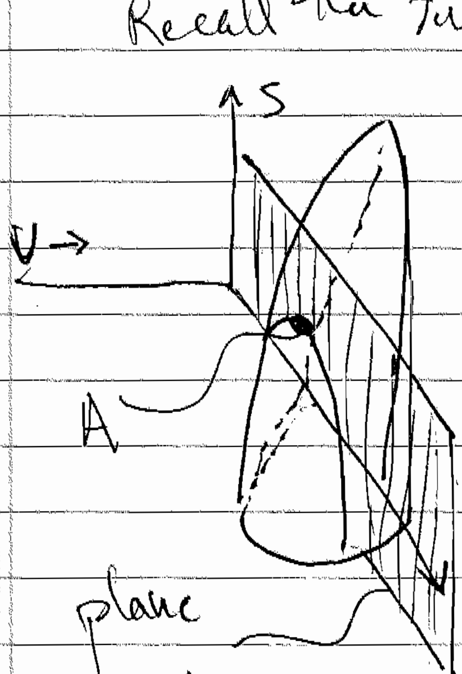
$$= \frac{3}{2} \frac{du}{u} + \frac{1}{v} dv$$

$$ds = \frac{3}{2} d \log u + d \log v = d\left[\log\left(u^{\frac{3}{2}} \cdot v\right)\right]$$

$$\boxed{\therefore \; s = s_0 + \log\left(u^{\frac{3}{2}} \cdot v\right)}$$

[fundamental relation]

Recall the Fundamental Relation $S(U, V, N, \dots)$



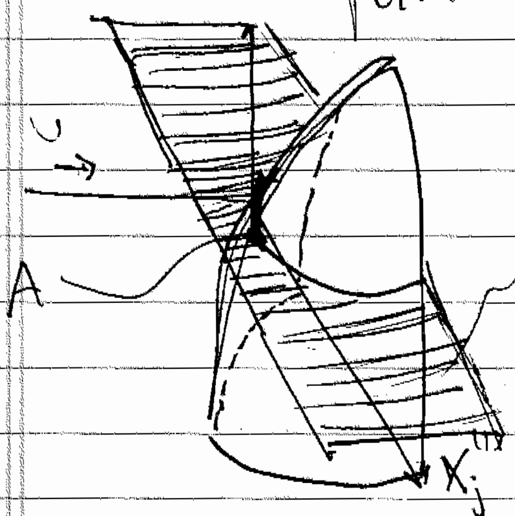
Extensive parameters of the composite system: $(U, V, N_?)$

$U = U^{(1)} + U^{(2)}$

$V = V^{(1)} + V^{(2)}$; $N = N^{(1)} + N^{(2)}$

$X_j^{(1)} = \{ U^{(1)}, V^{(1)}, N_j^{(1)}, \dots \}$

point A Maximizes S for constant U



plane $S = S_0$

point A Minimizes U for constant S

pt. A is Equilibrium state

$S = S^{(1)} + S^{(2)} = f(U, U^{(1)}, X_j, X_j^{(1)} \dots)$

Entropy Maximum Principle: Equilibrium value of any unconstrained internal parameter is such so as to maximize the entropy for the given value of total internal energy.

$$\Rightarrow \left.\frac{\partial S}{\partial X^{(1)}}\right|_U = 0, \quad \left.\frac{\partial^2 S}{\partial X^{(1)2}}\right|_U < 0$$

Link to statement of energy Minimum.

$$dS = \left.\frac{\partial S}{\partial U}\right|_{X^{(1)}} dU + \left.\frac{\partial S}{\partial X^{(1)}}\right|_{U} dX^{(1)}$$

$$\therefore \left.\frac{\partial U}{\partial X^{(1)}}\right|_{S} = -\left.\frac{\partial S}{\partial X^{(1)}}\right|_{U} \Big/ \left.\frac{\partial S}{\partial U}\right|_{X^{(1)}} = -T\left.\frac{\partial S}{\partial X^{(1)}}\right|_{U}$$

$$\therefore \left.\frac{\partial U}{\partial X^{(1)}}\right|_{S} = 0 \quad \text{because} \quad \left.\frac{\partial S}{\partial X^{(1)}}\right|_{U} = 0$$

Same argument w/ $\left.\frac{\partial U}{\partial X^{(1)}}\right|_{S}$ as a function of $U, X^{(1)}$

$$d\left[\left.\frac{\partial U}{\partial X^{(1)}}\right|_{S}\right] = \frac{\partial}{\partial U}\left[\left.\frac{\partial U}{\partial X^{(1)}}\right|_{S}\right]_{X^{(1)}} dU + \frac{\partial}{\partial X^{(1)}}\left[\left.\frac{\partial U}{\partial X^{(1)}}\right|_{S}\right]_{U} dX^{(1)}$$

$$\therefore \left.\frac{\partial^2 U}{\partial X^{(1)2}}\right|_{S} = \frac{\partial}{\partial X^{(1)}}\left[\left.\frac{\partial U}{\partial X^{(1)}}\right|_{S}\right]_{U} + \frac{\partial}{\partial U}\left[\left.\frac{\partial U}{\partial X^{(1)}}\right|_{S}\right] \overbrace{\cancel{\left.\frac{\partial U}{\partial X^{(1)}}\right|_{S}}}^{0}$$

$$= \frac{\partial}{\partial X^{(1)}}\left[-\frac{\partial S/\partial X^{(1)}|_{U}}{\partial S/\partial U|_{X^{(1)}}}\right]_{U}$$

entropy Max

$$= -\frac{\left(\partial^2 S/\partial X^{(1)2}\right)|_{U}}{\partial S/\partial U|_{X^{(1)}}} + \frac{\overbrace{\cancel{\left.\frac{\partial S}{\partial X^{(1)}}\right|_{U}}}^{0}\ \frac{\partial}{\partial X^{(1)}}\left[\frac{\partial S}{\partial U}\right]_{X^{(1)}\,U}}{\left[\left.\frac{\partial S}{\partial U}\right|_{X^{(1)}}\right]^2}$$

$$= -T\left.\frac{\partial^2 S}{\partial X^{(1)2}}\right|_{U} > 0$$

$$\therefore \quad \left.\frac{\partial U}{\partial X^{(1)}}\right|_S = 0, \quad \left.\frac{\partial^2 U}{\partial X^{(1)2}}\right|_S > 0$$

$\Rightarrow$ Equilibrium value of any unconstrained internal parameters is such so as to ~~maximize the~~ minimize the energy for a given value of entropy.

Energy Minimum principle

$S(U, V, N)$ (fundamental relation)

contains complete thermodynamic information, but you actually measure T, P, μ with instruments.

Unfortunately, solving for S in terms of T, V, N from $T(S, V, N)$ and substituting to obtain $U(T, V, N)$ will NOT give the fundamental (a) relation

Example: $U = S^3/VN$; then $T = \left.\frac{\partial U}{\partial S}\right|_{V,N}$

$$T = \frac{3S^2}{VN} \Rightarrow U = (NV)^{\frac{1}{2}}\left(\frac{T}{3}\right)^{3/2}$$

Now, try to invert to obtain $U(S, V, N)$

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N} = 3U^{2/3}(NV)^{-1/3}$$

$$\int dS \Rightarrow \left[U^{-\frac{2}{3}} \frac{\partial U}{\partial S}\Big|_{V,N} = 3\,(NV)^{-\frac{1}{3}} \right]$$ (7)

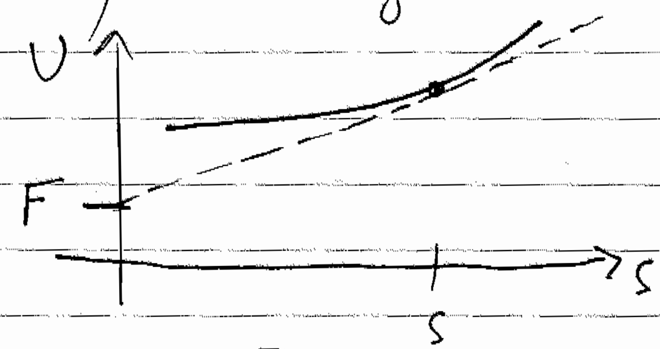
$$3U^{\frac{1}{3}} = 3S(NV)^{-\frac{1}{3}} + C(V,N)(NV)^{-\frac{1}{3}}$$

$$\Rightarrow \quad U = \left[S + \left(\frac{C}{3}\right) \right]^3 \Big/ (VN)$$

Therefor $U(S,V,N)$ is not unique.

[Constant c of integration]

To fix this constant c, we must also specify the tangent to $U(S,V,N)$ at $S=0$



$$\frac{\partial U}{\partial S}(S) = \frac{U-F}{S-0} = \text{slope} \Rightarrow U - F = S \cdot T$$

$$\therefore \boxed{F = U - TS}$$

$$F(T,V,N) \Rightarrow dF = \frac{\partial F}{\partial T}\Big|_{V,N} dT + \frac{\partial F}{\partial V}\Big|_{T,N} dV + \frac{\partial F}{\partial N}\Big|_{T,V} dN$$

But

$$dF = dU - TdS - (dT)S$$

$$= \cancel{TdS} - PdV + \mu dN - \cancel{TdS} - SdT$$

$\therefore\ dF = -P\,dV - S\,dT + \mu\,dN$

$$\therefore\ \left.\frac{\partial F}{\partial V}\right|_{T,N} = -P, \quad \left.\frac{\partial F}{\partial T}\right|_{V,N} = -S, \quad \left.\frac{\partial F}{\partial N}\right|_{V,T} = \mu$$

Now, can we recover $U(S,V,N)$ from $F(T,V,N)$

Yes! Solve for $S(T,N,V) = -\left.\frac{\partial F}{\partial T}\right|_{V,N}$ for T

and substitute into $U = F(T,N,V) + TS$

N.B. We never integrated $\Rightarrow$ no integration constant.

This is called a Legendre Transform.

You've seen it in mechanics $L(q,\dot{q})$

$$-H = L - p\dot{q} = -H(q,p)$$

$$p = \left.\frac{\partial L}{\partial \dot{q}}\right|_{q} \Longleftrightarrow T = \left.\frac{\partial U}{\partial S}\right|_{V,N}$$

$$\Longleftrightarrow F = U - TS = F(T,V,N)$$