TD Potentials

Helmholtz free energy

Relevant for systems at fixed T, V, N

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

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

We want to replace S with T

Legendre transform:

$$F = U - TS$$ (Eliminate S in favor of T)

$F = F(T, V, N)$ ← as much info as in the fundamental relations.

$$F = U - TS$$

$$dF = \underbrace{dU}_{\cancel{TdS} - pdV + \mu dN} - SdT - \cancel{TdS}$$

- $dF = -SdT - pdV + \mu dN$

$$dU = TdS - pdV + \mu dN$$

So $T \leftrightarrow S$ and the sign is switched.

We can read:

From dF:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

From dU:

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

(Different quantites are held const.)

Enthalpy

Replace $V \leftrightarrow P$

Legendre transform; the enthalpy

$$H = U + PV \qquad H = H(S, P, N)$$

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

$$\Rightarrow \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$$

This is interesting in the case where P, N is constant. Because then

$$dH = TdS \quad : \text{change in heat.}$$

Gibbs free energy

Double Legendre transf: $S, V, N \rightarrow T, P, N$

$$G = U - TS + PV \qquad G = G(T, P, N)$$

$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

TD Potentials.

$$U(S,V,N) = U \quad \text{Energy}$$
$$F(T,V,N) = U-TS \quad \text{Helmholtz}$$
$$H(S,P,N) = U+PV \quad \text{Enthalpy}$$
$$G(T,P,N) = U-TS+PV \quad \text{Gibbs}$$
$$?(S,V,\mu) = U-\mu N$$
$$\Omega \to \Phi_g(T,V,\mu) = U-TS-\mu N \quad : \text{Grand potential}$$

Landau pot.

$$?(S,P,\mu) = U+PV-\mu N$$
$$?(T,P,\mu) = U-TS+PV-\mu N$$

Extensivity

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

This does not for all systems. Especially not for those where surface effects are important.

Assume that it holds

Differentiate w.r.t λ and set $\lambda = 1$.

RHS: $\frac{\partial}{\partial \lambda}\left(\lambda S(U,V,N)\right) = S(U,V,N)$

LHS: $\frac{\partial}{\partial \lambda} S(\lambda U, \lambda V, \lambda N)$

$$= \underbrace{\frac{\partial(\lambda U)}{\partial \lambda}}_{U} \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{\frac{1}{T}} + \underbrace{\frac{\partial(\lambda V)}{\partial \lambda}}_{V} \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{P/T} + \underbrace{\frac{\partial(\lambda N)}{\partial \lambda}}_{N} \underbrace{\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{-\frac{\mu}{T}}$$

$$dU = T\,dS - P\,dV + \mu\,dN$$

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

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

Multiply by T and solve for U

$$\boxed{U = TS - PV + \mu N}$$: No differential

Euler equation.

$$dU = \underbrace{TdS - PdV + \mu dN}_{dU} + \underbrace{SdT - VdP + Nd\mu}_{\text{must be } 0}$$

So changes in T, P & μ are not independent for an extensive system

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$$

Gibbs-Duhem relation

TD Potentials and extensivity.

$U = TS - PV + \mu N$ Euler eq. (extensivity)

$F = U - TS = -PV + \mu N$

$H = U + PV = TS + \mu N$

$G = U - TS + PV = \mu N \Rightarrow \mu = \frac{G}{N}$

$\varphi[T, P, \mu] = U - TS + PV - \mu N \underset{\substack{\uparrow \\ \text{Euler eq.}}}{=} 0$

TD identities

Derivatives: What is held constant matters!

Ideal gas: $U = \frac{3}{2} N k_B T$, $PV = N k_B T$

from $dU = TdS - pdV + \mu dN$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_{P,N} = \frac{\partial}{\partial V}\left(\frac{3}{2} PV\right)_{P,N} = \frac{3}{2} P$$

3 different answers
Different quantities were held const.

- Always write explicitly what is held constant.

Standard quantities.

Coeff. of thermal expansion:

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

Isothermal compressibility

$$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

Specific heat at const. pressure

$$c_P = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

Specific heat at const. volume

$$c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N}$$

Heat capacity: $C_P = Nc_P$, $C_V = Nc_V$

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

for constant T & N

$$dG = VdP$$

$$\Rightarrow \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

Compressibility:

$$\left(\frac{\partial V}{\partial P}\right)_{T,N} = \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N}$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N}$$

Maxwell relations

For N const : $dU = TdS - pdV$

dU is an exact differential .

Then $\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad , \quad -p = \left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_{S,N} = \left(\frac{\partial(-p)}{\partial S}\right)_{V,N}$$

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$: Maxwell relation.

$$\frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial S}\right)_{V,N}\right]_{S,N}$$

$$\left(\frac{\partial T}{\partial P}\right)_{S,\mu} = \left(\frac{\partial\ ?}{\partial\ ?}\right)_{?,\mu}$$

TD potential with variables P, S, μ

$$d\,\underbrace{\text{Noname}}_{J}(P,S,\mu) = T\,dS + V\,dP - N\,d\mu$$

$$T = \left(\frac{\partial J}{\partial S}\right)_{P,\mu}$$

with μ const

$$dJ = T\,dS + V\,dP$$

$$V = \left(\frac{\partial J}{\partial P}\right)_{S,\mu}$$

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_{S,\mu} = \left(\frac{\partial V}{\partial S}\right)_{P,\mu}$$

Partial derivatives as Jacobians.

Jacobian: $$\frac{\partial(u,v)}{\partial(x,y)} \equiv \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$ ← determinant

$$= \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}$$

Can be extended to any number of vars.
(more rows & columns)

Properties:

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} = \frac{\partial(v,u)}{\partial(y,x)} = -\frac{\partial(u,v)}{\partial(y,x)}$$

$$\frac{\partial(u,v,w)}{\partial(x,y,z)} = -\frac{\partial(u,w,v)}{\partial(x,y,z)}$$ etc...

Partial derivatives & Jacobians:

$$\frac{\partial(u,y)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \underbrace{\frac{\partial y}{\partial x}}_{=0} & \underbrace{\frac{\partial y}{\partial y}}_{=1} \end{vmatrix} = \left(\frac{\partial u}{\partial x}\right)_y$$

so

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{\partial(F,V,N)}{\partial(T,\underbrace{V,N}_{\text{quantities held const.}})}$$

Chain rule:

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(r,s)}\,\frac{\partial(r,s)}{\partial(x,y)}$$

$u_r \equiv \frac{\partial u}{\partial r}$

$$= \begin{vmatrix} u_r & u_s \\ v_r & v_s \end{vmatrix} \cdot \begin{vmatrix} r_x & r_y \\ s_x & s_y \end{vmatrix}$$

$$= \begin{vmatrix} u_r r_x + u_s s_x & u_r r_y + u_s s_y \\ v_r r_x + v_s s_x & v_r r_y + v_s s_y \end{vmatrix}$$

$$= \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial(u,v)}{\partial(x,y)}$$

An identity:

$$\frac{\partial(u,v)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(c,d)} = \frac{\partial(u,v)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(x,y)}$$

Proof: chain rule

$$\frac{\partial(u,v)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(c,d)} = \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(c,d)}$$

$$= \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)}$$

$$= \frac{\partial(u,v)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(x,y)} \quad \checkmark$$

Reciprocals:

$$\frac{\partial(u,v)}{\partial(u,v)} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 1$$

chain rule

$$1 = \frac{\partial(u,v)}{\partial(u,v)} \overset{\downarrow}{=} \frac{\partial(u,v)}{\partial(x,y)} \frac{\partial(x,y)}{\partial(u,v)}$$

$$\Rightarrow \quad \frac{\partial(u,v)}{\partial(x,y)} = \frac{1}{\dfrac{\partial(x,y)}{\partial(u,v)}}$$

$$\left(\text{SO} \quad \left(\frac{\partial V}{\partial S}\right)_{T,N}^{-1} = \left(\frac{\partial S}{\partial V}\right)_{T,N} \right)$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(P,V,N)}{\partial(P,T,N)} \frac{\partial(P,T,N)}{\partial(T,V,N)}$$

$$= \frac{\partial(V,P,N)}{\partial(T,P,N)} \left(- \frac{\partial(P,T,N)}{\partial(V,T,N)}\right)$$

$$= -\left(\frac{\partial V}{\partial T}\right)_{P,N} \cdot \left(\frac{\partial P}{\partial V}\right)_{T,N}$$