Lecture 18 Thermodynamic potentials + Maxwell relations

Some lectures ago we introduced the Helmholtz free energy $F = U - TS$ when discussing the canonical ensemble: F is minimized for a system S maintain at constant T by its environment (reservoir) R

What does F really represent?
Let's say you could create a system S from nothing, in an environment at constant T. How much work does this cost?

You have to provide energy U, but S can extract heat Q from R for free ($Q = T\Delta S$. As long as $\Delta S_{R+S} \geq 0$, can transfer from R to S).

So, actual cost to you is $U - TS = F$ ($S = \Delta S$ = entropy of syst. S)

F = work provided to create S
(conversely F = work you can extract if you annihilate S. You can't take the entropy because R would be left with less)

To see this explicitly, look at change in F at constant T

$$\Delta F = \underbrace{\Delta U}_{Q + W} - T\Delta S = Q + W - T\Delta S \qquad \therefore \quad \Delta F = W$$

True for a reversible process. If there is irreversibility recall $T\Delta S > Q$

so $\boxed{W \geq \Delta F}$ in general.

at constant T

Now consider an environment at constant pressure P
(ex: the classroom $p = 1$ atm)

Now not only do you account for energy to create $\delta(U)$ but also work to displace the atmosphere around $\delta(PV)$. This is called the enthalpy:

$$H \equiv U + PV$$

$-PV$ is work done automatically by the atmosphere surrounding δ so work you must provide to create δ at constant p is

$$G = U + PV - TS$$

where again we subtracted the heat $q = TS$ we get for free.
You saw this quantity before in your homework, it's called the Gibbs free energy

Explicitly, consider a change in G at constant p

$$\Delta G = \Delta U + P\Delta V - T\Delta S = q + W + P\Delta V - T\Delta S$$
$$= W + P\Delta V$$

Define W' as work other than that automatically done by atmosphere $W' = W - (-P\Delta V)$. (ex: electrical work). Like before:

$$\boxed{W' \geq \Delta G} \qquad \text{at constant } p, T$$

(W' is the work you can extract from annihilating system δ at constant p)

These 4 quantities are called the 4 thermodynamic potentials

Energy : $U = U(S,V)$ $\quad dU = TdS - pdV$ from thermo. identity

Helmholtz free energy :

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

once you've fixed T, V you've set F .

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= TdS - pdV - TdS - SdT \\ &= -SdT - pdV \end{aligned}$$

Enthalpy : $H = H(p,S) \equiv U + PV$

$$\begin{aligned} dH &= dU + PdV + Vdp \\ &= TdS - pdV + pdV + Vdp \\ &= TdS + Vdp \end{aligned}$$

Gibbs free energy :

$$G = G(p,T) \equiv U + PV - TS = H - TS$$

$$\begin{aligned} dG &= dU + pdV + Vdp - TdS - SdT \\ &= TdS - pdV + pdV + Vdp - TdS - SdT \\ &= -SdT + Vdp \end{aligned}$$

Notes: F is useful in situations where T, V are constant (ex: many systems in condensed matter physics)

- G is used where p, T are constant (ex: chemical reactions, biology = V can change)

Maxwell relations

Notice all 4 potentials are functions of two independent variables:
S or T, p or V (one extensive, one intensive)

In general for a function $f(x,y)$:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

derivative with respect to x, keeping y fixed

Also: $$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial y}\frac{\partial f}{\partial x}$$

This general property leads to useful expressions called Maxwell relations

$dU = TdS - pdV \quad \therefore \quad T = \left(\frac{\partial U}{\partial S}\right)_V \qquad p = -\left(\frac{\partial U}{\partial V}\right)_S$

and $$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V} \quad (1)$$

$dF = -SdT - pdV \quad \therefore \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V} \quad (2)$$

$dH = TdS + Vdp \quad \therefore \quad T = \left(\frac{\partial H}{\partial S}\right)_p \qquad V = \left(\frac{\partial H}{\partial p}\right)_S$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p} \quad (3)$$

$dG = -SdT + Vdp \qquad S = -\left(\frac{\partial G}{\partial T}\right)_p \qquad V = \left(\frac{\partial G}{\partial p}\right)_T$

$$\boxed{\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p} \quad (4)$$

All of these relations come about, ultimately, from $S = S(U,V)$ and the equation:

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U$$

that we introduced in an early lecture

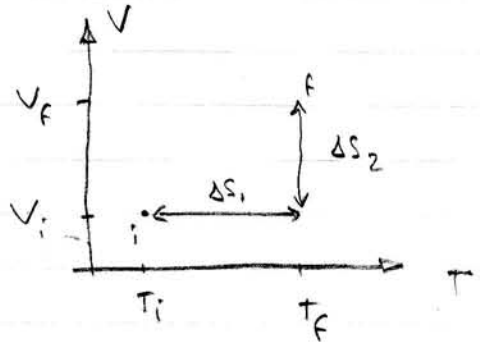
What are the Maxwell relations used for?

Ex 1: Let's say we measure T, V of a gas and want to get S. Natural variables for S are U, V, but we want $S(T,V)$

$$dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{\frac{C_V}{T}}\,dT + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial P}{\partial T}\right)_V}\,dV \qquad \text{Maxwell relation (2)}$$

C_V is something we can measure, so is $P(T,V)$ (this is the equation of state)

∴ From S at T_i, V_i, can get S at T_f, V_f



Step 1 $\quad \Delta S_1 = \int_{T_i}^{T_f} C_V(T, V_i)\,\frac{dT}{T}$

Step 2 $\quad \Delta S_2 = \int_{V_i}^{V_f} \frac{\partial P}{\partial T}(T_f, V)\,dV$

$$S(T_f, V_f) = S(T_i, V_i) + \Delta S_1 + \Delta S_2$$

Path doesn't matter S only depends on the state f

Ex 2: suppose we want heat capacity at <u>constant pressure</u> C_p, rather than C_V

$$TdS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{from before}$$

$$\therefore \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

Note $C_p = \left(\frac{dQ}{dT}\right)_p$

and $C_V = \left(\frac{dQ}{dT}\right)_V$

For ideal gas eq'n of state is $PV = N k_B T$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{N k_B}{V} \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{N k_B}{P}$$

$$\therefore \quad \boxed{C_p = C_V + N k_B}$$

Makes sense: $C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial (U+PV)}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$

PV term accounts for energy lost as work against constant p

so $C_p > C_V$

Generalizations of Maxwell relations

We ignored situation in which particle # N can vary
If we include it we now have for example $F = F(T,V,N)$

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

$$\qquad \quad \parallel \qquad\qquad\qquad \parallel \qquad\qquad\qquad \parallel$$

$$\qquad -S \qquad\qquad\quad -p \qquad\qquad\quad \mu \text{ chemical potential}$$

and we have new Maxwell relations:

$$-\left(\frac{\partial S}{\partial N}\right)_{T,V} = \frac{\partial^2 F}{\partial N \partial T} = \left(\frac{\partial \mu}{\partial T}\right)_{N,V} \qquad \text{etc} \ldots$$

Ex: how much heat is transfered changing N, but keeping T, V constant?

$$dq = T dS = T\left(\frac{\partial S}{\partial N}\right)_{T,V} dN + T\left(\frac{\partial S}{\partial T}\right)_{N,V} \cancel{dT}^{\to 0} + T\left(\frac{\partial S}{\partial V}\right)_{N,T} \cancel{dV}^{\to 0}$$

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