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## LECTURE 14: LEGENDRE TRANSFORMATIONS

Friday, February 14, 2020

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Recall from last lecture that we defined the Legendre transformation:

$$g(p) = \min_x \{f(x) - xp\} \quad (\text{Legendre Transformation})$$

$$f(x) = \max_p \{g(p) + px\} \quad (\text{Inverse Legendre Transformation})$$

where

$$\begin{aligned} f'(x) &= p & \text{or} & & df &= p dx \\ g'(p) &= -x & \text{or} & & dg &= -x dp \end{aligned}$$

The plus and minus in the transform and its inverse can be switched with no effect to the validity of the transformation.

### 0.1 Helmholtz Free Energy

We start with the entropy  $S(U, V, N)$  which we know is monotonically increasing in  $U$  since  $\frac{\partial S}{\partial U} = \frac{1}{T}$ . We know it's also concave in  $U$ . We can solve this for  $U(S, V, N)$  (we don't care about  $V$  and  $N$  right now, they're just coming along for the ride). The same information is contained in both equations, so this is still a thermodynamic potential.

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

Because  $S(U)$  is concave,  $U(S)$  is convex (and still monotonically increasing).  $S$  is an awkward variable. Let's change it to  $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ . We can do this with a Legendre transform:

$$F(T, V, N) = \min_S \{U(S, V, N) - TS\} \quad (\text{Helmholtz Free Energy})$$

This function  $F$  is the Helmholtz free energy. We could choose either a minus or plus sign, but minus is conventionally used. In order to turn  $T dS$  into  $-S dT$ , we need a minus sign. Say we would like to calculate  $dF$ :

$$\begin{aligned} dF &= d(U - TS) \\ &= dU - (T dS + S dT) \\ &= T dS - P dV + \mu dN - T dS - S dT \\ &= -S dT - P dV + \mu dN \end{aligned}$$

If we had chosen a  $+$  here, the  $T dS$  terms would not have canceled nicely. This will turn out differently for other situations. With this function, we now have some additional definitions for the entropy, pressure, and chemical potential:

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

Notice that we now have a function  $S(T, V, N)$ , which is *not* a thermic potential.

Consider a system at constant  $T$  and  $N$  such that  $dT = dN = 0$ :

$$dF = -P dV = dW$$

The maximum amount of work that can be extracted from a system at fixed  $T$  and  $N$  is equal to the free energy difference between the initial and final states. Note the distinction between the energy and free energy. If you let a system do work and want to see how much work was done, you can't just use the difference in energies  $\Delta U$ , you have to use the difference in the Helmholtz free energies  $\Delta F$ . We can do this by replacing other variables other than  $S$  with  $T$ .

## 0.2 Enthalpy

Instead of replacing  $S$  with  $T$ , replace  $V$  with  $P$ . The result is called the enthalpy:

$$H(S, P, N) = \min_V \{U(S, V, N) + PV\} \quad (\text{Enthalpy})$$

We need the transformation to have a different sign because  $dU$  has a  $-P dV$  term.

$$dH = T dS + V dP + \mu dN$$

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

Let's look at a system with constant  $P$  and  $N$  (imagine a liquid in a test tube, if the tube is open, the pressure is just 1atm and the number of particles is not changing):

$$dH = T dS = dQ$$

The change in heat under these conditions is the change in enthalpy.

## 0.3 Gibbs Free Energy (Free Enthalpy)

What if we exchanged both  $S$  for  $T$  and  $V$  for  $P$ ?

$$G(T, P, N) = \min_{S,V} \{U(S, V, N) - TS + PV\} \quad (\text{Gibbs Free Energy})$$

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

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

For a system with constant  $T$  and  $P$ ,

$$dG = \mu dN$$

The change in the Gibbs free energy when adding one particle is the chemical potential.

## 0.4 Grand Potential

Now let's exchange  $S$  for  $T$  and  $N$  for  $\mu$ :

$$\Omega(T, V, \mu) = \min_{S,N} \{U(S, V, N) - TS - \mu N\} \quad (\text{Grand Potential})$$

$$d\Omega = -S dT - P dV - N d\mu$$

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

This potential is useful when the number of particles is not fixed, and turns out to be very helpful in quantum statistics.

### One Final Trick

The expressions

$$\min_{S,\dots} \{U(S, V, N) - TS \pm \dots\}$$

and

$$\min_{U,\dots} \{U - TS(U, V, N) \pm \dots\}$$

are equivalent! We are just running over the same set of  $U$ ,  $V$ , and  $N$ , but labeling  $U$  and  $S$  differently.