

Internal energy U and entropy S are of the 1st order homogeneous function. We can write the internal energy with the **Euler Equation** :

$$U = TS - PV + \sum_{j=1}^r \mu_j N_j \quad (1)$$

By using the Maxwell relations ... If there are $t + 1$ variables, the second order derivative $\frac{t(t+1)}{2}$.

The differential is

$$dU = TdS - PdV + \mu dN \quad (2)$$

And we defined:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad (3a)$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \quad (3b)$$

By applying these relations we obtain :

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial T}{\partial V}_{S,N} \quad (4)$$

$$\frac{\partial^2 U}{\partial S \partial V} = -\frac{\partial P}{\partial S}_{V,N} \quad (5)$$

It implies that

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \quad (6)$$

1

These are all Maxwell relations.

Let us consider the Helmholtz free energy, that it is obtained by a Legendre transformation

$$dA = -SdT - PdV + \mu dN \quad (7)$$

Let's consider (T, V) , where T is conjugate with S while V with $-P$. From this, we obtain: $-\left(\frac{\partial P}{\partial T}\right)_{V,N} = -\left(\frac{\partial S}{\partial V}\right)_{T,N}$.

Another important concept is the

0.1 Response functions

Any observation is just the perturbation of a system and looking for the response. We consider *fluid system*, *thermal expansion* at $P = \text{const}$ that means $dp = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$, and the other one is the *heat capacity* at constant pressure that means $c_P = \left(\frac{\delta Q}{dT}\right)_P \stackrel{\text{reversible}}{=} T\left(\frac{\partial S}{\partial T}\right)_P$.

Remember that Gibbs's potential is a function of pressure

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

Lecture 2.

Friday 11th

October, 2019.

Compiled:

Saturday 12th

October, 2019.

We insert the last formula in the previous

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

Now, we define the *adiabatic* pressibility

$$k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N} \stackrel{\text{homework}}{=} -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N}$$

The isothermal one is :

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

If we use the maxwell relation $\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$ we obtain:

$$dG = -SdT + VdP \quad (8)$$

And:

$$V\alpha_P = \left(\frac{\partial V}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial P}\right)_{T,N} \quad (9)$$

And

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{\alpha_P}{k_T} \quad (10)$$

Therefore for quasistatic transformations

$$c_V = \left(\frac{\delta Q}{dT}\right)_V = T\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial(-\partial A/\partial T)_{V,N}}{\partial^2 T}\right) \quad (11)$$

Consider (M, H) , a magnetic field

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \stackrel{M=-(\frac{\partial G}{\partial H})_T}{=} -\left(\frac{\partial^2 G}{\partial H^2}\right)_T$$

Consider \vec{M}, \vec{H} :

$$\chi_{\alpha\beta} = \frac{\partial M_\alpha}{\partial H_\beta} = \frac{\partial^2 G}{\partial H_\alpha \partial H_\beta}$$

we have

$$c_V \equiv \left(\frac{\delta Q}{dT}\right)_V \geq 0$$

$$c_P \equiv \left(\frac{\delta Q}{dT}\right)_P \geq 0$$

This means thermal stability.

The isothermal compressibility:

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right) \geq 0$$

Just for the case of the magnetic field in which we have: $c_H \geq 0, c_M \geq 0$ and $\chi_M \geq 0$.

If we take the difference

$$c_P - c_V = \frac{TVdP^2}{k_T} = \frac{1}{Vk_T}T\left(\frac{\partial V}{\partial T}\right)^2$$

$$c_H - c_M = \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T} \right)^2$$

Finally

$$\begin{cases} c_P \geq c_V \geq 0 \\ c_H \geq c_M \geq 0 \end{cases} \quad (12)$$

We have seen the thermodynamics of a phase, the equilibrium state can be described for instance by the maximum of the entropy. We have a given phase and we look for the gibbs function. We want to describe equilibrium system in a given phase. If we have more phases, we want to change between these phases.

Consider a liquid system and we consider the $\frac{G}{N} \equiv g = g(T, P)$. The little g is not anymore a function of N because we have divided for N . We consider α in a given phase that can be *liquid*, *gas*, *solid*. Therefore $g_\alpha(T, P)$. The new value of T and P corresponds to the minimum of g_α

2

We have the g_α and g_β and we are looking for the lower one. There is a moment in which they coexist, the coexistence line is the projection

$$g_\alpha(T, P) = g_\beta(T, P)$$

Now, we fix $P = P^*$, we have $g_\alpha(T, P^*)$: 3 Remember $c_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right) \geq 0$, it is a concave function. 4

At the triple point we have $g_{\text{solid}}(T_a, P^*) = g_{\text{liquid}}(T_a)$ and $g_{\text{liquid}}(T_b) = g_{\text{gas}}(T_b, P^*)$. We see that 5

There are other cases in which we do not have this effect. For example: 6 This is different from the previous situation in which we had a jump. If we look for example at the specific heat: 7 It represent the transition from superconduction.

The critical point is special because there is not a jump, so we can go continuously from gas to liquid. The response function when we plot this point shows that the specific heat diverges. The transitions are classified in the first order transition and continuous transition. The superfluid transition is a transition where the second derivative of the thermodynamic potential diverges. There are many phase transitions that can be classified in different ways.

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) = \frac{1}{V} \left(\frac{\partial^2 A}{\partial V^2} \right)$$

8 We note that at the coexistence line we increase V , but the pressure remains constant. At the coexistence line we see bubbles. It is the density that is changing locally, the bubbles become bigger and bigger and at the V_G , becomes a liquid. Usually critical points are end point of first order transition phases. Why there is no critical point between solid and liquid? Landau point. There is a break of symmetry, for instance the bravais lattice. From gas to liquid you are not breaking any symmetry.

We can have a magnetization different from 0 even when there is no magnetic field. Supposing $P \leftrightarrow H, V \leftrightarrow M$ we have $(P, T) \leftrightarrow (H, T)$. 9 We have two equilibrium states that are connected continuously, this is a first order transition. For instance: 10 At the critical point the magnetization passes through zero. 11