3.23 Lecture 11

Look at Maxwell relations to find volumetric expansion

$$(\delta V / \delta T)_P = -(\delta S / \delta P)_T$$
$$(\delta V / \delta T)_P = -(\delta S / \delta V)_T (\delta V / \delta P)_T$$

The volumetric expansion is then

$$\alpha_v = \beta_T (\delta S / \delta V)_T$$

The sign depends on whether the entropy goes up with volume. The entropy is a measure of disorder. It is related to the number of accessible macroscopic states. As the volume increases, the number of accessible states increases. Consider a particle in a box. The energy is related to $1 / L^2$. In a large container, a system with a given energy fluctuates over more energy levels. Physically there is entropy from vibrations, and bonds stretch.

In the case of negative thermal expansion, the entropy goes down with volume. Polymers are a classic case of that. There are lots of ways to arrange a polymer in a small volume, and there is only one state when the polymer is completely stretched.

There can be a negative thermal expansion with other materials. The material with the largest negative thermal expansion is ZrW_2O. The property of the material discussed last lecture was magnetic based, and that property would be lost at high temperature.

Polyhedra solids can show negative thermal expansion. There is a network of polyhedra that are connected at vertices. They can rotate and take up entropy. Below is a picture of a wheel that can rotate. Pump in excitation to rotate the wheel and stretch it out. The entropy increases when the volume decreases, so the derivative is negative. We see this same effect in polyhedra solids.
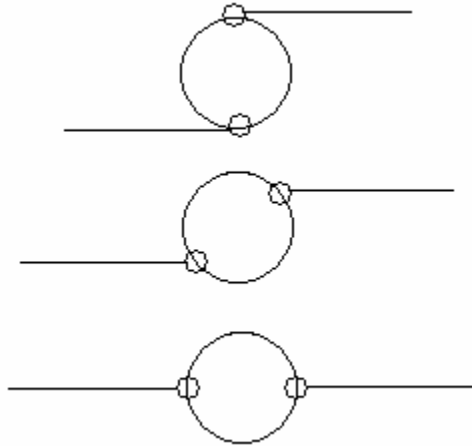
Adiabatic demagnetization

It's not possible to get down to 0 K. An object can't get colder than anything by exchanging heat; the object must release work. Adiabatic demagnetization relies on the following expression being true.

$$(\delta S / \delta H)_{T, P} < 0$$
$$\delta S / \delta H)_{T, P} = (\delta M / \delta T)_H < 0$$

The entropy decreases when there is an applied field. There is less disorder with the alignment of spins. A way to lower the temperature is to exchange entropy between magnetic degrees of freedom and vibrational degrees of freedom. Apply a field isothermally and a system releases heat. Isolate the system, turn off the field, and the system evolves back to $H = 0$. (There was an example shown on the projector). Put the material in a cold environment and do the experiment adiabatically, either insulated or fast.
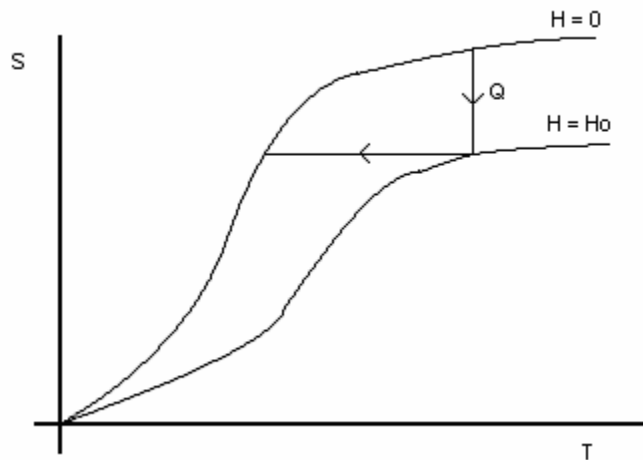
Open systems

$$dU = TdS - pdV + Sum[\mu_i \, dN_i]$$

There is a new intensive variable, which is μ

$$\mu_i = (\delta U / \delta N_i)_{S,V,Nj \neq i}$$

Legendre transforms (one-component systems)

It is possible to make a Legendre transform of any function

Hill function	$L(S, U, \mu) = U - \mu N$
Ray function	$R(S, P, \mu) = H - \mu N$
Granol Function J	$J(T, V, \mu) = F - \mu N$
Guggenheim	$Z(T, P, \mu) = G - \mu N$ (uniquely zero)

Gibbs - Duhem

$$U = TS - PV + Sum[\mu_i \, N_i]$$

$$dU = TdS + SdT - pdV - VdP + Sum[\mu_i \, dN_i] + Sum[N_i \, d\mu_i]$$

The differentials with extensive variables must sum to zero.

$$SdT - VdP + Sum[N_i \, d\mu_i] = 0$$

There is a relationship among the extensive parameters. The extensive variables tell about system size, while the three intensive variables provide slightly less information.

At this point we are done with the formal structure of thermodynamics. There is material about stability that could be studied.

Summarize what's in mathematical structure – conceptual review

1) Identify work terms

How does the system exchange energy with the environment? A key term is dU. It is related to a set of differentials, but it can be tough to know.

2) Write down the relevant thermodynamic potential for equilibration
3) Know how to define equilibrium
4) Understand properties that characterize a system
5) Be able to relate properties to each other

Relate the heat capacities and compressibilities under different conditions.

Phase transitions and how to characterize

This involves understanding what state matter takes on. Find the states that are the lowest free energy. This may change with conditions, such as temperature and pressure. Changing *T, P* changes the equilibrium and the states.

Look at how *G* changes with *T* and *P*.

$$dG = -SdT + VdP$$
$$-S = (\delta G / \delta T)_P$$
$$V = (\delta G / \delta P)_T$$
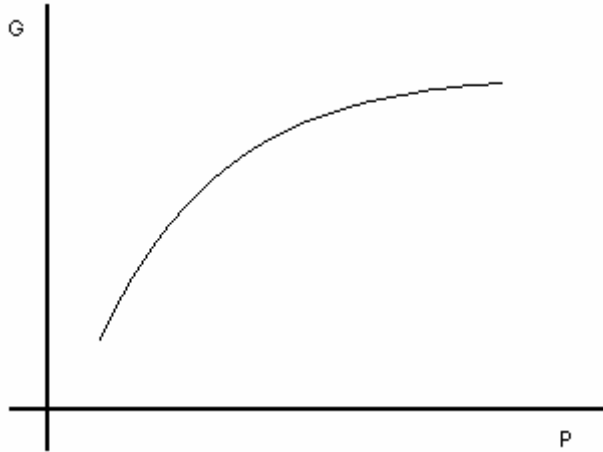
The first derivative of *S* is related to heat capacity

$$\delta^2 G / \delta T^2 = -(\delta S / \delta T)$$
$$\delta^2 G / \delta T^2 = -C_P / T$$
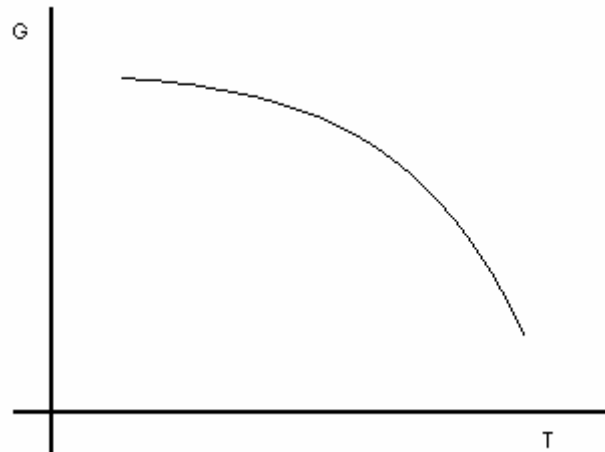
Look at derivatives related to compressibility

$$\delta^2 G / \delta P^2 = -(\delta V / \delta P)$$
$$\delta^2 G / \delta T^2 = -V\beta_T$$

Callen goes through a systematic way of looking at phase diagrams

The solid state and liquid state are a function of G. Find out where each is stable. Find the point of intersection. This is the phase boundary.

At constant pressure, change the temperature and plot the energy. When changing phases, there can be a discontinuity in volume. For instance, water expands when freezing. There is also a discontinuity of $\delta G / \delta T$. The value of entropy is different on both sides. The discontinuity is related to the latent heat.

$$\Delta H = T \Delta S$$
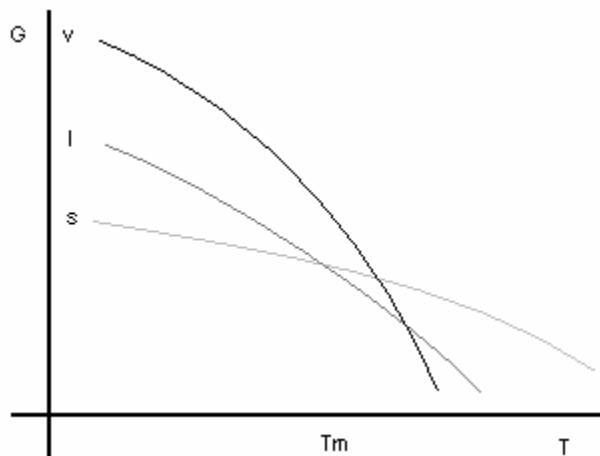
Higher entropy means that there is a greater slope downward. The liquid state is at a higher energy initially, and it intersects the solid curve. The vapor is associated with higher entropy than the liquid, and the vapor curve is steeper than the liquid curve. The point of intersection is the boiling point. There are metastable points. When heating a solid very fast, for instance, it is possible to reach a metastable point.

The point of intersection in some materials is before the intersection of the liquid and solid curve, and this is the point of sublimation.   When there is an applied pressure, the points of intersection move with respect to each other.
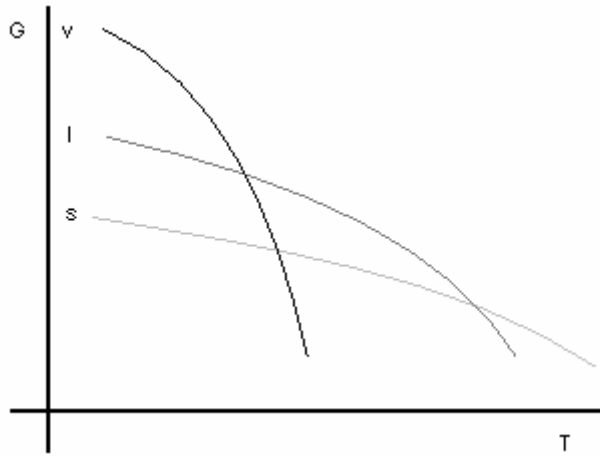
The curves are not linear, but the difference of curves can be approximated as such. Linearize the free energy difference between liquid and water.

$$\Delta G = \Delta H - T\Delta S$$

Both ΔH and ΔS are functions of T. The expression is linearized when we say ΔH and ΔS are not a function of T. At room temperature, look at where ΔG =0. Below is data taken from 293 K. Extrapolate the boiling point of water by linearizing.

$$\Delta H = 44.17 \text{ kJ / mol}$$
$$\Delta S = 119.5 \text{ J / mol K}$$
$$T_B = \Delta H / \Delta S$$
$$T_B = 37°\text{K}$$

Differences are fairly linear, and what is we are saying is that ΔH is not a function of temperature.

$$\Delta H \neq f(T)$$
$$\Delta S \neq f(T)$$
$$\Delta C_P = 0$$

The heat capacities of vapor and liquid are approximated as the same.

$$(\delta \Delta H / \delta T)_P = \Delta C_P$$

Entropy falls out

$$(\delta \Delta S / \delta T)_P = \Delta C_P / T$$

The heat capacities do not swing by orders of magnitude. This is a point where linearizing is useful. Usually one knows ΔH_m, which is the latent heat. This occurs at the transition where $\Delta G = 0$. If ΔH is known, than ΔS can be found.

$$\Delta H = T_{PT} \, \Delta S_{PT}$$

The energy difference is given by the expression below

$$\Delta G = G_\beta - G_\alpha$$

where $\Delta G(T) = \Delta H - T\Delta S$. The terms ΔH and ΔS are constant and taken at the phase transition.

$$\Delta G(T) = \Delta H_{PT} \, (1 - T / T_{PT})$$

Often need free energy difference between two phases. Linearize free energy differences. This works up to about 100° away from the phase transition.

Classification of phase transition

When the nth derivative of TD potential is discontinuous, the transition is called an nth order phase transition.

The extensive variables are discontinuous in first-order phase transitions. These are physical changes that are impossible to miss. This is the case in the 1st order phase transitions.
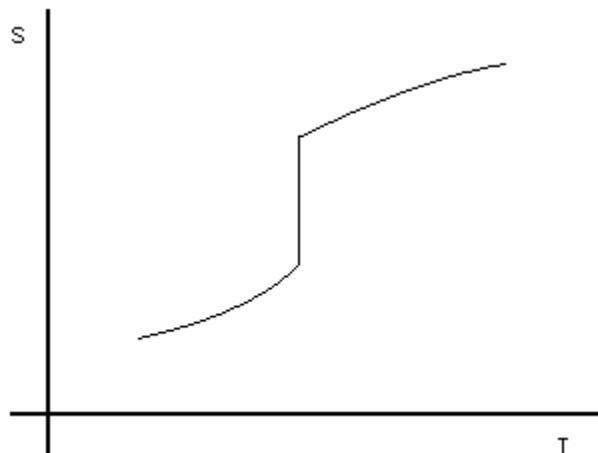
Second-order phase transitions are continuous in the first-order. There is no ΔS or ΔV. What is discontinuous in a second-order phase transition? There is a discontinuity in ΔC_P and $\Delta \beta_T$.

When looking at data from a real experiment, finding the differences between a first order phase transition and second order transition is difficult. The second-order phase transition can be the point where thermodynamics fails. There can be a logarithmic singularity on a heat capacity curve. Macroscopic fluctuations become macroscopic in size. Usually, there is no relationship between the interactions of two elements in the bulk material.
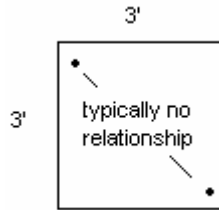

There is linearity when things do not interact. When there is an interaction, there is quadratic behavior. In a second order phase transition, the fluctuations become macroscopic in size. Extensivity is not true. Typical second-order transitions are magnetic (curie point, ferroelectric transitions). For a transition to be possibly 2nd order, conditions must be satisfied. There is a symmetry classification scheme.

The glass transition temperature is a point where degrees of freedom are frozen.
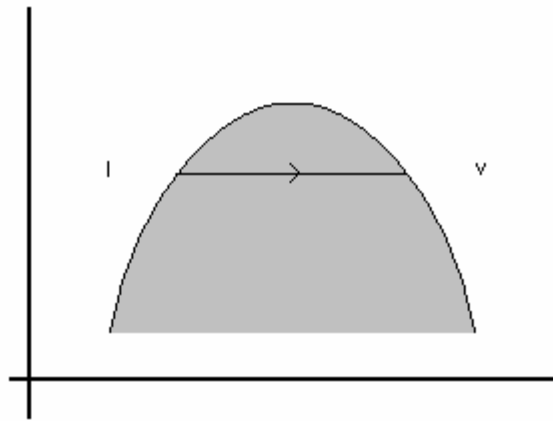
Plot stable phase as a function of intensive variables

Below is a picture of a phase diagram. Phase boundaries are where the free energy surface interact. This is where the properties are discontinuous. Discontinuities occur at one point.
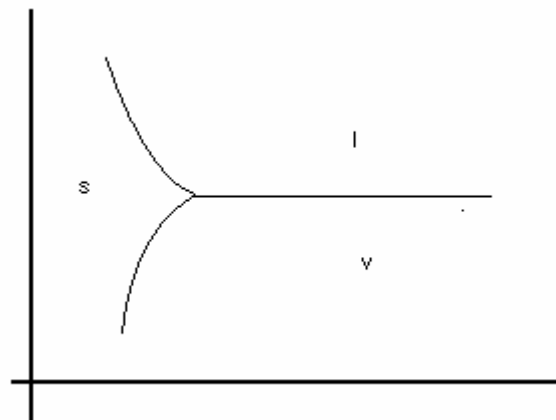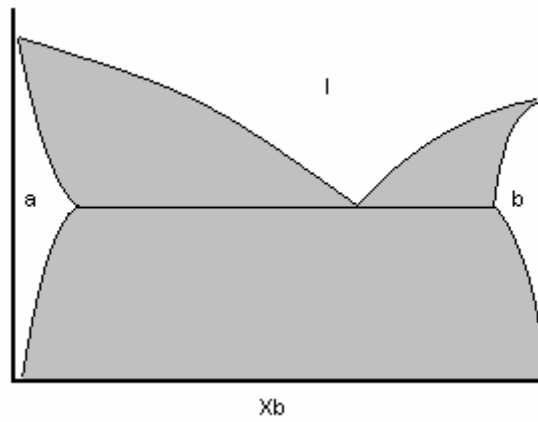

Below is a plot in partly extensive variables. When plotting versus extensive variables, a discontinuity appears.

In two-phase phase diagrams, there is a nonexistence region. There are certain combinations that are not allowed.

Discontinuities can collapse if the phase diagram is a plot versus intensive variables