



Lecture TOPIC 14 (Finn: 9.3, 9.4, 9.6, 9.7)

Synopsis: Positive Compressibility and Heat Capacity. The Gibbs-Helmholtz and Clausius-Clapeyron equations. The vaporization curve. First order phase changes.

Thermodynamically Impossible Properties

Consider a homogeneous sample at equilibrium, thermally isolated, fixed volume split into two sections V_A and V_B by a light piston. Imagine that section A spontaneously expands isentropically by ΔV (so B contracts by ΔV). This would move the piston, generating work - violating the Kelvin statement of the Second Law.

To see how this works out analytically, consider the total internal energy $U = U_A + U_B$.

$$dU_A = \left(\frac{\partial U}{\partial V}\right)_s \Delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)_s \frac{(\Delta V)^2}{2} + O(V^3)$$

$$dU_B = -\left(\frac{\partial U}{\partial V}\right)_s \Delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)_s \frac{(\Delta V)^2}{2} - O(V^3)$$

$$dU = dU_B + dU_A = \left(\frac{\partial^2 U}{\partial V^2}\right)_s (\Delta V)^2 = -V \left(\frac{\partial P}{\partial V}\right)_s \frac{(\Delta V)^2}{V} = K_P \frac{(\Delta V)^2}{V}$$

Using the result from the Central Equation ($dU = TdS - PdV$) that $\left(\frac{\partial U}{\partial V}\right)_s = -P$

V and $(\Delta V)^2$ are obviously positive. U is minimised at equilibrium, so $dU > 0$. Therefore K_P , the adiabatic bulk modulus must be positive. An exactly similar argument can be applied to splitting into two sections of slightly different entropy, dS but fixed volume. This leads to $C_v > 0$. A negative heat capacity would imply heat would spontaneous flowing from cold to hot, in violation of the Clausius statements. Using H in place of U gives $C_p > 0$, and using F gives positive isothermal bulk modulus (K_T).

Note this works for conjugate variables: there is no similar argument for thermal expansions. ¹

Elastic constants and Poisson Ratio

Bulk modulus is just one elastic constant, relating pressure to volume In a homogenous medium, the shear modulus is another, with conjugate variables shear stress and shear strain. In a crystal, there are potentially 21 different elastic moduli. These can be represented using the full elastic tensor relating stress to strain.

$$U_{elastic} = \sigma_{ij}e_{kl} = \sum_{ijkl} \frac{1}{2} C_{ijkl} e_{ij} e_{kl}$$

The tensor approach (81 components!) overcomplicates the situation. Universal symmetry (i.e. energy is unchanged by rotation and translation) requires that $C_{ijkl} = C_{klij} = C_{jikl} = C_{ijlk}$. For almost all real materials there are additional symmetries simplifying things further. For a homogeneous fluid only bulk and shear modulus remain, and shear modulus is zero.

Note that stress and strain are conjugate variables, BUT energy is a *sum*, so it is possible for some elements of C_{ijkl} to be negative. e.g. Poisson ratio, $\nu = -\frac{de_y}{de_x}$ is normally around 0.3 (if you pull something, it gets thinner). But there is no thermodynamic constraint on this, and values down to -12 have been found in so-called *auxetic* materials.

¹There is an assumption about homogeneous samples: for phase coexistence the bulk modulus is zero. Curious behaviour can be obtained for inhomogeneous metamaterials and self-gravitating clusters

Gibbs-Helmholtz relation for calculating free energy and entropy changes

In an atomistic computer simulation, we can easily evaluate P,V,T,U and H given the position of the atoms and their velocities. However, entropy is not a function of a particular arrangement of atoms (microstate), and so nor are F and G.

From the definition $dG = Vdp - SdT$, we have $\left(\frac{\partial G}{\partial T}\right)_p = -S$. Now consider the quantity:

$$\left(\frac{\partial G/T}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{(G+TS)}{T^2} = -\frac{H}{T^2}$$

This gives us a recipe for calculating changes in G if we know the properties of a series of microstates:

$$\frac{G_2}{T_2} - \frac{G_1}{T_1} = - \int_{T_1}^{T_2} \frac{\langle H \rangle}{T^2} dT$$

This is known as the Gibbs-Helmholtz relation. Once G is known, calculating S is straightforward. The integral on the right hand side is path independent and straightforward to calculate, e.g. in a molecular dynamics simulation, once any reference value G_1 is chosen, G_2 can be directly calculated. There is no need to evaluate all possible “Ways” as in $k_B \log(W)$.

The Clausius-Clapeyron equation for “first-order” phase changes

We next apply the Gibbs condition to study the mathematical properties of a phase boundary across which there is a discontinuous change of state variables S and V (a first order transition). A first order phase change is accompanied by a latent heat ($T\Delta s$), and a specific volume change (Δv).

For two adjacent points A and B on the phase transition line,

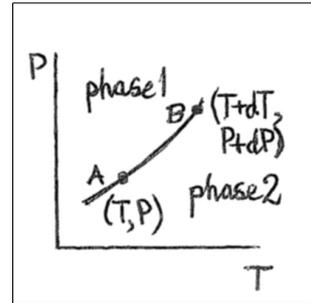
$$\text{at A } g_1(T,P) = g_2(T,P)$$

$$\text{at B } g_1(T+dT, P+dP) = g_2(T+dT, P+dP)$$

To get information on specific volumes and, via entropy, latent heat use:

$$dg = vdP - sdT$$

Moving along the phase line $g_1(P,T) = g_2(P,T)$ at each (P,T) point



Using a Taylor expansion for g for each phase about point A, and then equating the g 's at the neighbouring point $B \equiv (P+dP, T+dT)$ which also lies on the phase transition line:

$$\begin{aligned} \text{at B } g_1(T_A, P_A) + \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP + \text{higher order terms} \\ = g_2(T_A, P_A) + \left(\frac{\partial g_2}{\partial T}\right)_P dT + \left(\frac{\partial g_2}{\partial P}\right)_T dP + \text{higher order terms} \end{aligned}$$

from which, neglecting the higher order terms and rearranging

$$\left[\left(\frac{\partial g_1}{\partial T}\right)_P - \left(\frac{\partial g_2}{\partial T}\right)_P \right] dT = \left[\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T \right] dP$$

The partial derivatives can be identified with the entropies and volumes of each phase yielding $[(-s_1) - (-s_2)]dT = [s_2 - s_1]dT = [v_2 - v_1]dP$ as previously. Rearranging:

$$\boxed{\left(\frac{dP}{dT}\right)_{\text{pb}} = \frac{s_2 - s_1}{v_2 - v_1}}$$

Where the suffix pb means we are constrained to moving along the phase boundary. Note: this implies $s_2 - s_1$ and $v_2 - v_1$ per Kg, but the same equation can be used with units per mole or per arbitrary mass because the unit of normalisation cancels between the numerator and denominator.

Latent heat

For a phase change at temperature T from phase 1 to 2,

$$\text{latent heat} = l = T(s_2 - s_1)$$

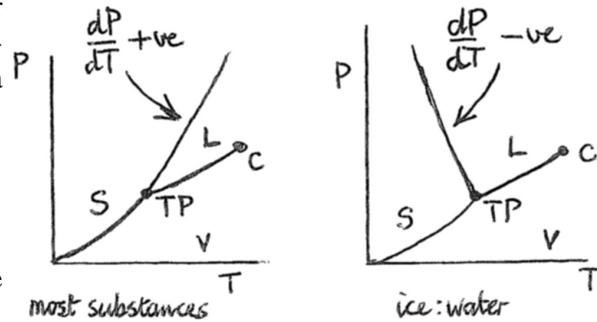
If $s_2 > s_1$, l is positive and heat must be put INTO the system (eg water at 100°C changing to water vapour at 100°C).

Applying this to the above relation for $(dP/dT)_{pb}$ gives the Clausius-Clapeyron equation for the slope of a phase boundary on a phase diagram.

$$\left(\frac{dP}{dT}\right)_{pb} = \frac{l}{T(v_2 - v_1)} = \frac{L}{T(V_2 - V_1)}$$

where pb reminds us that it is the slope of the phase boundary.

l is always positive going from low T (solid) to high T phase (liquid). For $v_L > v_S$ (solid expands on melting), dP/dT is positive. For $v_L < v_S$ (solid – like ice – contracts on melting) dP/dT is negative.



The equation of the vaporization curve

At least for making order of magnitude calculations, the equation for a vaporization curve can be obtained quickly from the Clausius-Clapeyron equation. Replace v_2 and v_1 by v_V and v_L , the specific volumes of vapour and liquid respectively. Then for $v_V \gg v_L$, use the ideal gas approximation for the vapour to get:

$$\left(\frac{dP}{dT}\right)_{pb} \approx \left(\frac{l}{T}\right) \left(\frac{P}{RT}\right)$$

Assuming l is constant, integration along the phase boundary leads to the approximate formula:

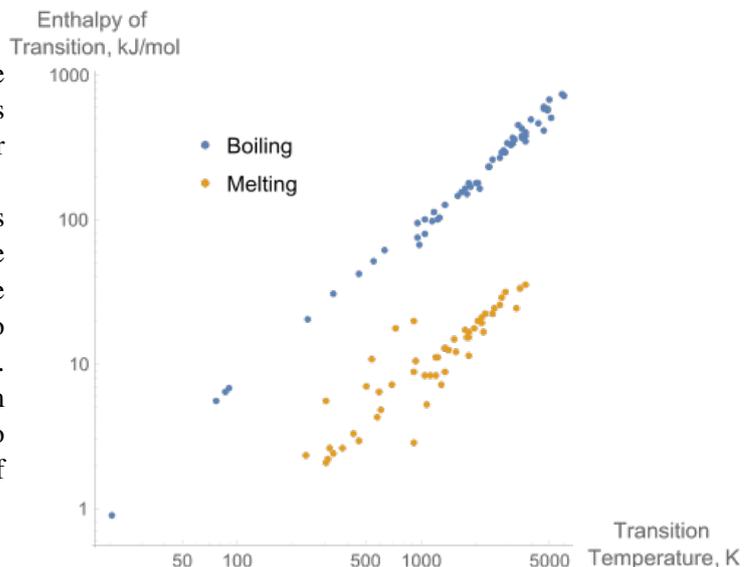
$$\ln P = \int \frac{l}{RT^2} dT = -\frac{l}{RT} + \text{constant}$$

be careful that the latent heat l may not be constant over the range of integration. e.g. at the critical point it must be zero.

Trouton's rule

If the structure of all liquids was the same and the (lack of) structure of all gases was also the same, then the amount of disorder in each would be the same.

Trouton's "Rule" $\Delta S_{vap} = 10.5R$ applies reasonably well to large molecules (see figure) which don't have much structure to the liquid (i.e. not water). According to the rule the molar latent heat is $10.5RT_{vap}$. Notice the need to eliminate *mass* from the expressions. The number of ways to arrange atoms is virtually independent of their mass.



Changes to state variables crossing first-order transitions

The phase diagram can be related to the behaviour of the coordinates s (entropy), v (specific volume) and g (the Gibbs function) – **for first order phase transitions**.

Consider a system with (T,P) boundary conditions along the isobar XY.

$$\left(\frac{\partial g}{\partial T}\right)_P = -s < 0$$

Since entropy, s , is positive, all g versus T curves have negative slope. In addition, their gradient become steeper with increasing T . This last feature follows from

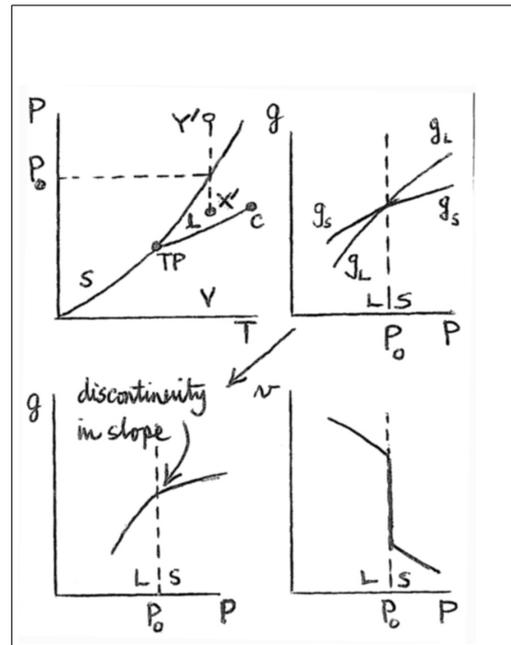
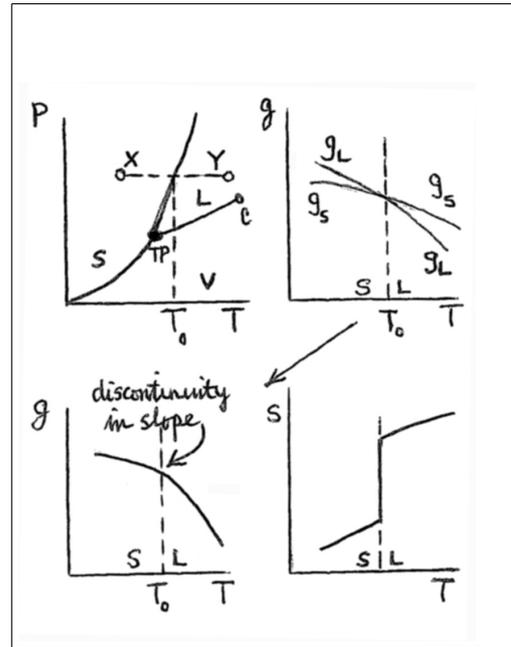
$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{c_P}{T} < 0$$

At the phase transition temperature (T_0), the Gibbs functions g_L and g_S are equal. For $T < T_0$, the solid phase is stable and so must correspond to the lower curve (for $T < T_0$) for the Gibbs function. Meanwhile, for $T > T_0$, $g_L < g_S$

The discontinuity in the slope at T_0 corresponds to a finite change in entropy $\Delta s = -\Delta(\partial g/\partial T)_P$ at the phase transition. The liquid has higher entropy.

If s is discontinuous, its derivative, the Heat Capacity $T\left(\frac{\partial s}{\partial T}\right)_P$ is infinite.

An equivalent discussion for the traverse $X'Y'$ – note that this time it is from liquid to solid – correlates the discontinuity in the gradient of the Gibbs function with respect to pressure, at P_0 , with the change in specific volume (density). In the figure the liquid has the larger value of v , ie is less dense than the solid, and therefore has a larger slope $(\partial g/\partial T)_P$. The solid must therefore have the lower value of g at high pressure. This is consistent with the +ve slope of the phase line. For ice/water - water expands on freezing - ice has the larger $(\partial g/\partial T)_P$ and water must be the higher pressure phase, consistent with a negative slope for the ice-water phase line.



Discontinuities at Phase Transitions

Process	New phase	Divergence
Increasing pressure	→ smaller volume	infinite compressibility
Increasing temperature	→ higher entropy	infinite heat capacity

In an experiment, “infinite specific heat” means supplying finite heat energy with no change in T (i.e. latent heat). “infinite compressibility” means doing finite work ($-PdV$) with no change in pressure.

Finally, consider a triple point. The three phases (A,B,C) have different densities, so an isobar cannot go $(A \rightarrow B \rightarrow C \rightarrow A)$, because that would mean A was simultaneously denser *and* less dense than B and C, which makes no sense. The same argument applies for entropies, or any other linear combination of s and v . Taken together, it means that no segment between lines at a triple point can be more than 180° .