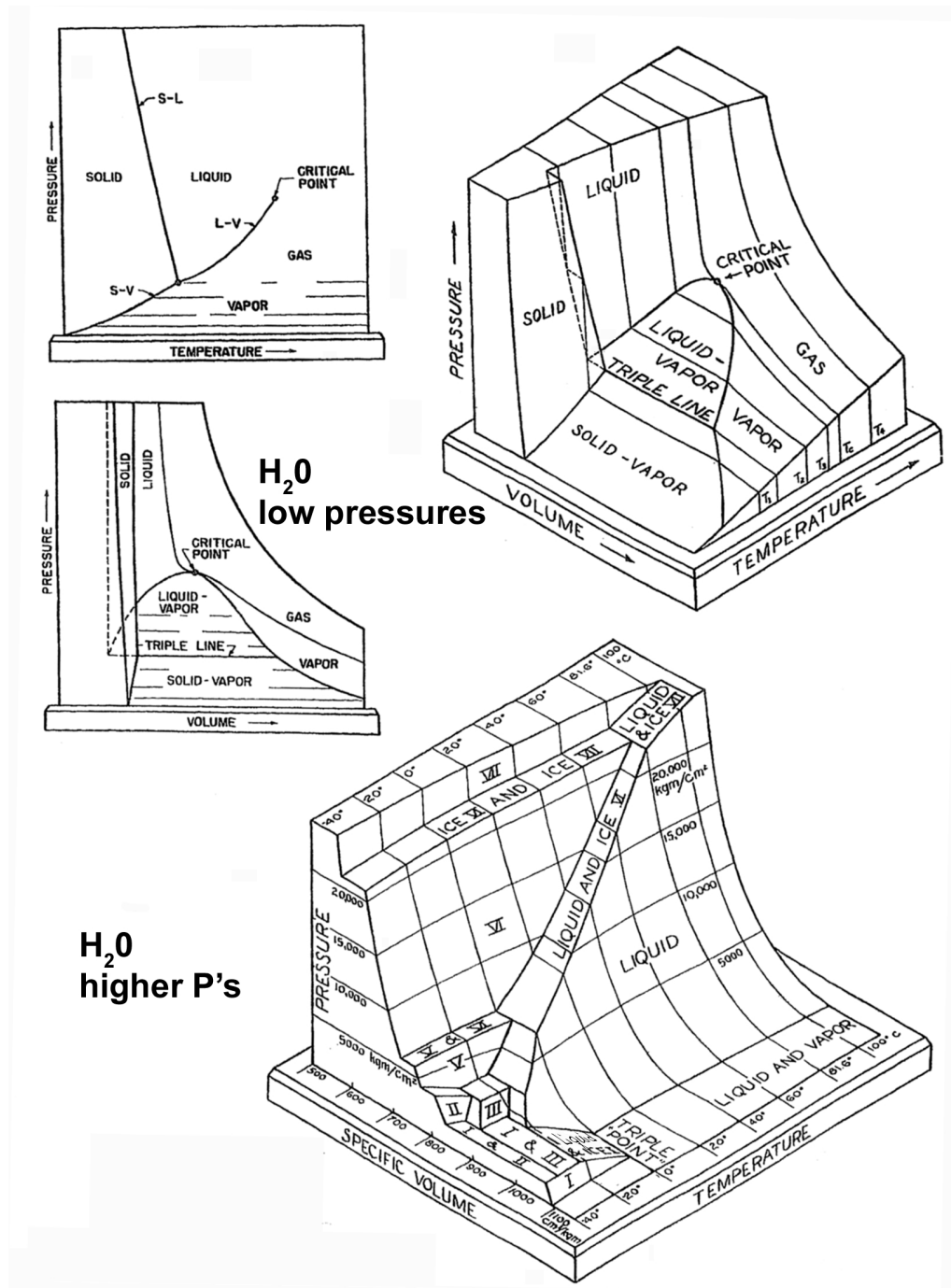


**Lecture TOPIC 13** (Finn: 9.1, 9.2, 9.3)

**Synopsis:** Phases: the  $PVT$  surface and the equilibrium condition for two phases.



Equation of state for water, given any two of P, V, T gives us the third, and the associated phase(s).

## The equilibrium condition for two phases at fixed temperature and pressure

*In thermal equilibrium,  $P$  and  $T$  are constant throughout the system, so  $G$  must be at a minimum.*

Consider a system of two coexisting phases in equilibrium with **specific** (per unit mass) Gibbs free energy  $g_1$  and  $g_2$  and the masses  $M_1$  and  $M_2$ : the total Gibbs free energy for the system is  $G = g_1M_1 + g_2M_2$ . During a phase transition, the proportions of the two phases change, but  $T$  and  $P$  do not.

Conservation of mass:  $dM_1 + dM_2 = 0$ ,

combined with the equilibrium condition that  $dg = g_1dM_1 + g_2dM_2 = vdP - sdT = 0$  (trivially, for  $T$  and  $P$  fixed,  $dT = 0, dP = 0$ ) gives

$$g_1dM_1 + g_2dM_2 = 0 \implies g_1 = g_2$$

Conclusion: when two component phases of a system coexist at constant temperature and pressure, their specific Gibbs functions are equal. If  $g$  for one phase is lower than the other, then only the phase with the lower  $g$  is present. At a given external temperature, coexistence is only possible at one fixed external pressure.

*The phase boundary is a line on  $P$ - $T$  diagram*

With fixed volume boundaries, equilibrium still requires  $P$  and  $T$  to be the same in each phase, and  $g_1 = g_2$ . However the volume constraint  $V = v_1M_1 + v_2M_2$  can be met by adjusting the amounts of the two phases.

*There is an area of phase coexistence on a  $V$ - $T$  diagram (and on  $P$ - $V$ )*

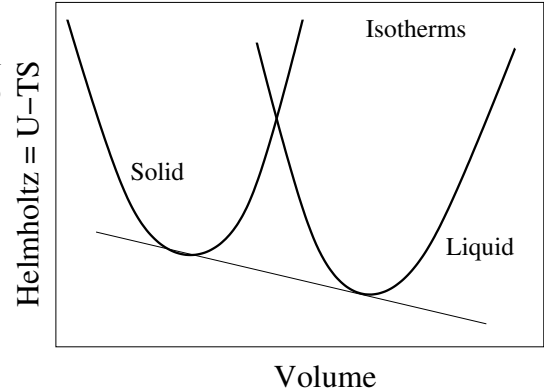
1. **Phase diagram** The projection of the equation of state surface on to the  $PT$  is called a **phase diagram** because it shows which phase is stable for given  $T, P$ . The phase boundaries where coexistence is allowed are lines.
2. **Fixed volume** The projection on to the  $TV$  plane also shows phase boundaries, but this time coexistence at fixed volume occurs for a range of volumes.
3. **PV plane** Used for indicator diagrams, projection onto the  $PV$  plane may allow two solutions (e.g. water at ambient pressure has a density maximum, so there may be two temperatures at which  $P, V$  are the same.  $P$  and  $V$  are conjugate variables, and in some unusual cases specifying both is not enough to uniquely determine the state of the system.
4. **Conjugate variables and positive quantities**  $P, V$  are conjugate (appear together in free energy expressions), if  $\partial P / \partial V > 0$  free energy can be spontaneously reduced by volume collapse, implying the system is not in equilibrium. So negative bulk modulus is not possible in equilibrium. The TS equivalent of this statement (heat capacity must be positive) is another statement of the Second Law.
5. **Triple point** Triple points occur where three phases coexist, this is a unique point on a  $PT$  phase diagram. Heating/work done at the triple point changes the proportion the phases without changing  $P, T$ , so very stable heat/pressure baths at  $T_{TP}, P_{TP}$  can be made accurately. Is useful for defining a standard temperature point for thermometry.
6. **Sublimation** If a substance has liquid-solid-gas triple point, then for  $T < T_{TP}$  or  $P < P_{TP}$  no liquid phase can be formed; the solid transforms directly to vapour (e.g. for  $\text{CO}_2$   $P_{TP} = 5.2\text{atm}$  and  $T_{TP} = 216.6\text{K}$ : hence dry ice).
7. **Critical point** Point at which the liquid-vapour transition vanishes. Dense gas is indistinguishable from liquid, it is usually called a “fluid”.
8. **Phase transitions** The stable phase, or combination of phases, is always the one with the lowest free energy (Helmholtz or Gibbs, depending on boundary conditions).

## The Helmholtz function as an indicator of equilibrium in fixed volume

The key property of the Helmholtz function  $F=U-TS$  is that it has a minimum value for a system in equilibrium at constant  $T$  and  $V$ . This makes it ideally suited to treating a mixture of two phases of a single substance, such as ice and water. The equilibrium condition becomes

$$dF = -PdV - SdT = 0$$

An isotherm on a plot of  $F$  vs  $V$  typically comprises multiple sections, one for each phase.



$F$  may be minimised by a mixture of phases. These can be linked by a common tangent, the slope of which is the phase transition pressure.

$$\left(\frac{\partial F}{\partial V}\right)_T = P(T)$$

The phases have different specific volumes, so relative amounts of the two phases must give the externally specified volume  $V = N_1 v_1 + N_2 v_2$ ; where  $N_1$  and  $N_2$  are the number of moles of each phase, which can change spontaneously subject to  $dN_1 = -dN_2$  and  $v_1, v_2$  the molar volumes. This is sometimes known as the lever rule. Note that the Helmholtz free energies  $f_1$  and  $f_2$  are not equal at equilibrium, and the pressure and temperature remain constant as the two phase mixture is compressed, provided it remains at equilibrium.

### Isotherms of a Van der Waals fluid

The Van der Waals, equation of state yields more interesting isotherms than for an Ideal gas. The equation can be rewritten in the form:

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0$$

where  $v = V/n$ ,  $n$  being the number of moles of molecules in the sample.

In general, for given  $a$  and  $b$  (ie a given gas) for each  $P, T$  there can be three possible values of  $v$ . Two of these are stable “phases”, the third is unstable.

The three “roots” of the equation coincide for a unique set of values of  $P$ ,  $v$  and  $T$  defining a “critical point”, with coordinates ( $P_c = \frac{a}{27b^2}$ ,  $v_c = 3b$ ,  $RT_c = \frac{8a}{27b}$ ).

- The Van der Waals equation can be rewritten with  $a$  and  $b$  replaced with  $P_c, T_c, v_c$
- For  $T > T_c$ , the equation has only one real root: there is only one phase (“fluid”).
- For  $T < T_c$ , the equation has three roots, two are minima of  $g$ : two phases (“liquid” and “gas”).
- The “Boyle temperature”  $T_B = a/(Rb) = 27T_c/8$  is where the real gas behaves “most like” an ideal gas. At higher  $T$  volume exclusion ( $b$ ) is important, and  $PV$  increases with pressure. At lower  $T$  bonding effects ( $a$ ) are important, and  $PV$  decreases with pressure. Most real gases have  $T_b \approx 2.75T_c$
- Considering a power law expansion for the van der Waals fluid in the small quantity  $1/v$ ,

$$\begin{aligned} \frac{Pv}{RT} &= 1 + B_2 \left(\frac{1}{v}\right) + B_3 \left(\frac{1}{v}\right)^2 + \dots \\ \frac{Pv}{RT} &= 1 + C_2 P + B_3 P^2 + \dots \end{aligned}$$

$B_i, C_i$  are all functions of  $T$ , and at the Boyle Temperature  $B_2 = b - \frac{a}{RT} = 0$ .

## Phase coexistence for the Van der Waals equation of state

**Van der Waals equation** can conveniently be written in terms of reduced parameters  $v/v_c$ ,  $T/T_c$ ,  $P/P_c$  where  $P_c, T_c, v_c$  are the values of  $P, T, v$  at the critical point (Not to be confused with the triple point):

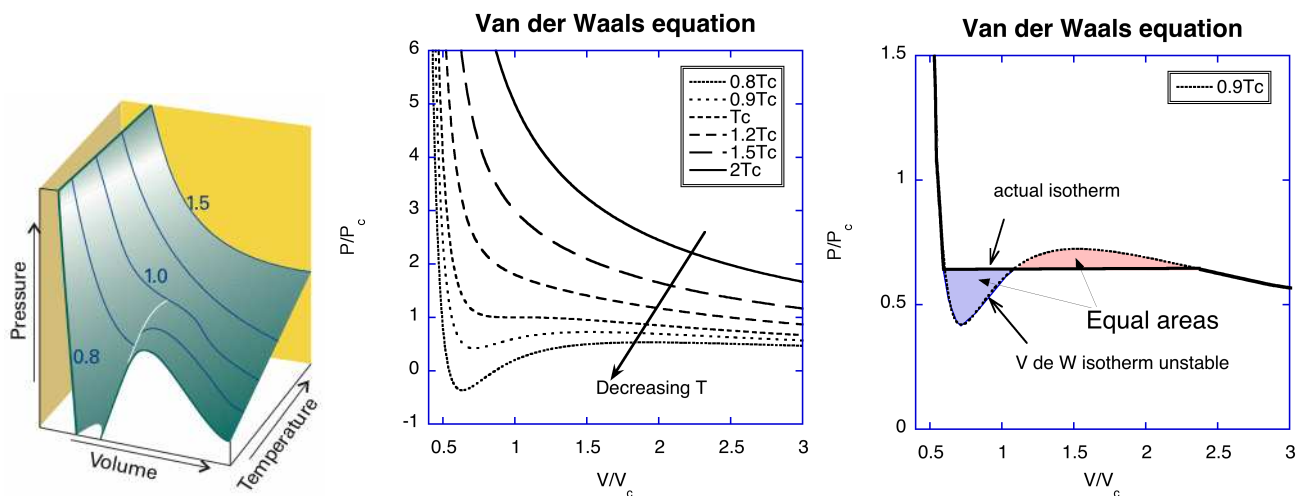
$$\left( \frac{P}{P_c} + \frac{3}{(v/v_c)^2} \right) \left( 3 \frac{v}{v_c} - 1 \right) = 8 \frac{T}{T_c} \quad \text{vdW's Eqn of state}$$

$$\text{with} \quad v_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb}$$

This equation gives a mechanically unstable solution (ie negative bulk modulus,  $-v(dP/dv)_T < 0$ ) for  $T < T_c$  over a range of molar (specific) volumes. The fluid therefore must break up into two phases with different densities which in equilibrium (same  $P, T$ ) must have equal Gibbs Free energies. Since the boundary condition is fixed total volume, the system minimises its Helmholtz free energy.

This leads to the construction shown in the third figure. The ‘real’ isotherm representing phase coexistence is the horizontal line is drawn connecting the denser phase (liquid) at the left and less dense phase (vapour) on the right. The curve from the actual Van der Waals equation represents an out-of-equilibrium single phase.

- The change in Gibbs free energy between the two end points is zero.  $dG = (\partial G/\partial P)_T dP = V dP$
- On the ‘real’ isotherm this is trivial, since  $P$  is constant.
- $G$  is a state variable, so integrating along the vdW line for the same isotherm must also give  $dG = 0$
- Maxwell’s *equal area construction* ensures that  $dG = 0$ .
- Solving the equal area requirement sets the value for  $P$  on the ‘real’ isotherm.



## Phase and the $PVT$ surface

Real substances have similar  $PVT$  surfaces to the van der Waals fluid, with a critical point and critical isotherm. However, because it is homogeneous, the vdW fluid cannot have solid crystalline phases.

An equilibrium thermodynamic process follows a line on the phase diagram, which may traverse several phases. A real substance compressed slowly at constant temperature might pass through a succession of equilibrium states including a vapour-to-liquid transition, following the “easy” compression of the vapour. Then on further compression it may be transformed into successive solid phases at increasing pressure.

A *shock wave* take the system to a state on a line on a phase diagram called a Hugoniot, fully determined by conservation of mass, momentum, and energy, typically reaching very high  $P$  and  $T$ . The final state behind the shock is close to equilibrium, before that the system is out of equilibrium.