# INTRODUCTION to PHASE TRANSITIONS

Different Thermodynamic Phases in Nature are a consequence of INTERACTIONS.

The simplest kinds of phase, and the names given in English to the transitions between them, are shown at right.
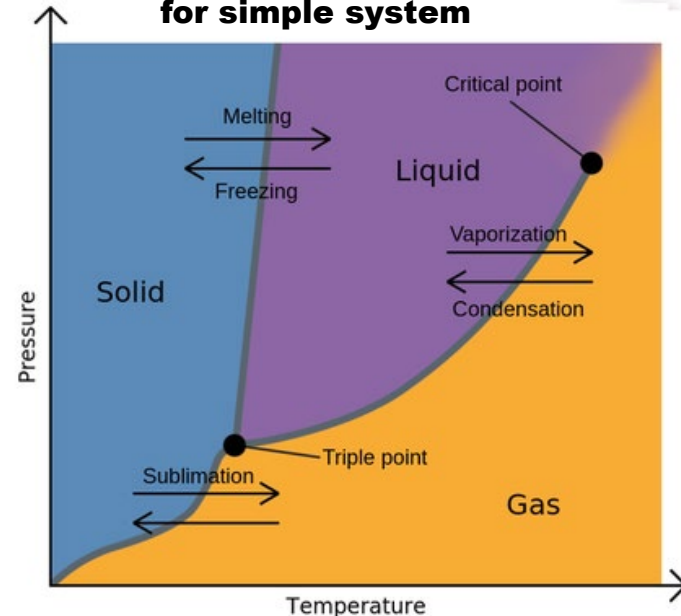
The classic phase transitions are the one between the liquid, solid, and gaseous phases of a system. In this case one can plot the boundaries between these phases in a P,T phase diagram.
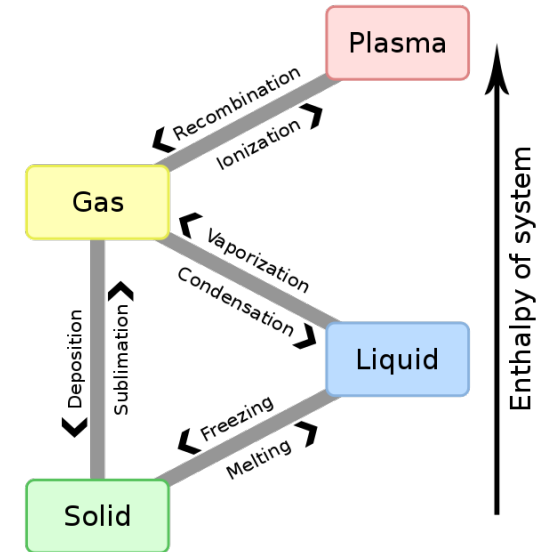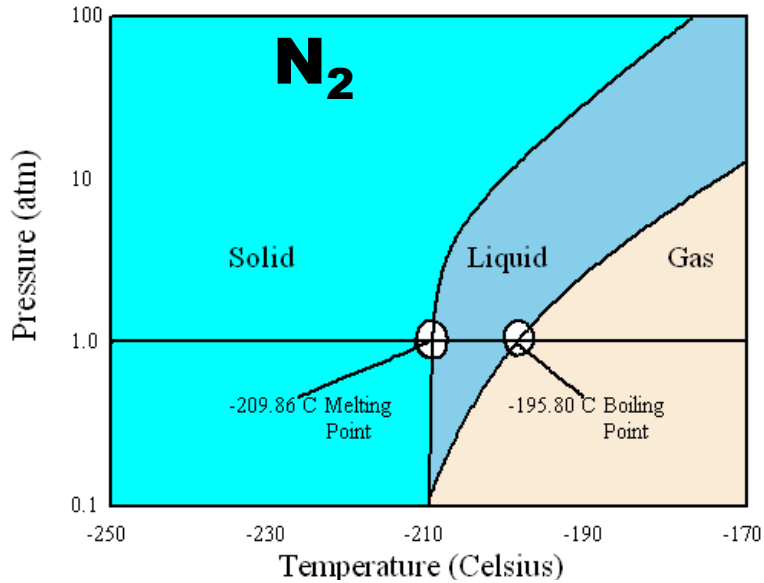

Another common kind of phase diagram involves magnetic phases (FM = Ferromagnet, AFM = Antiferromagnet, and PM = paramagnet)
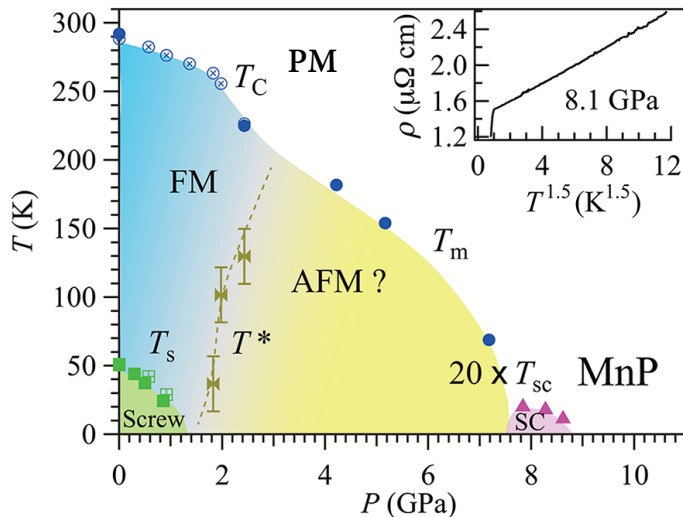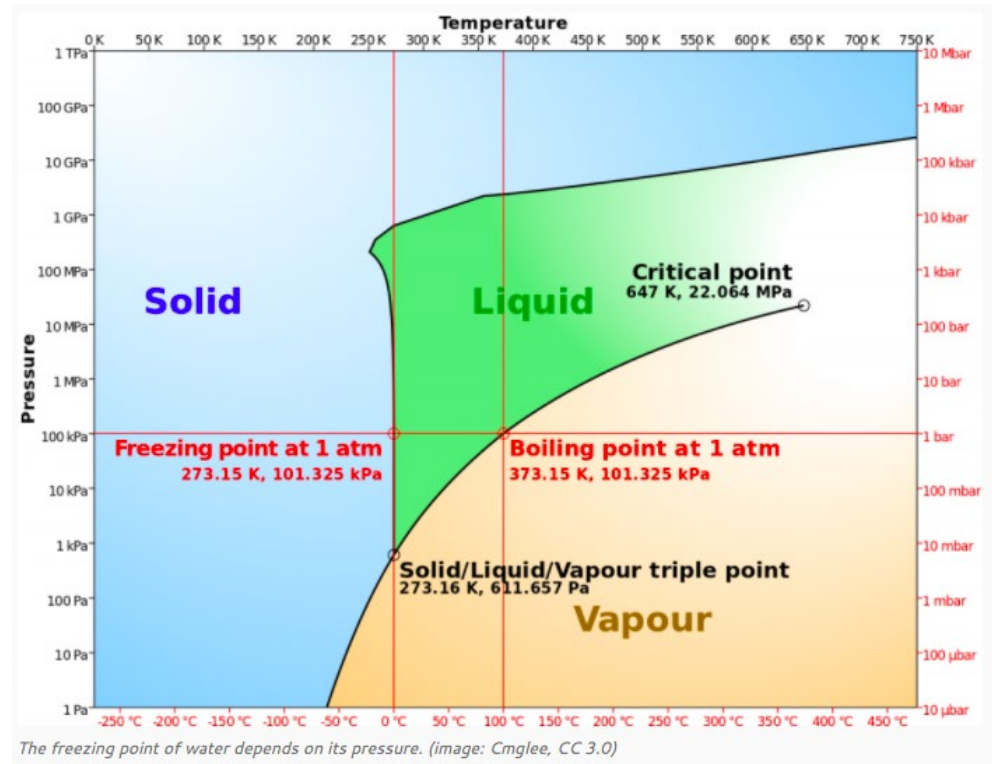

Standard phase diagram for simple system
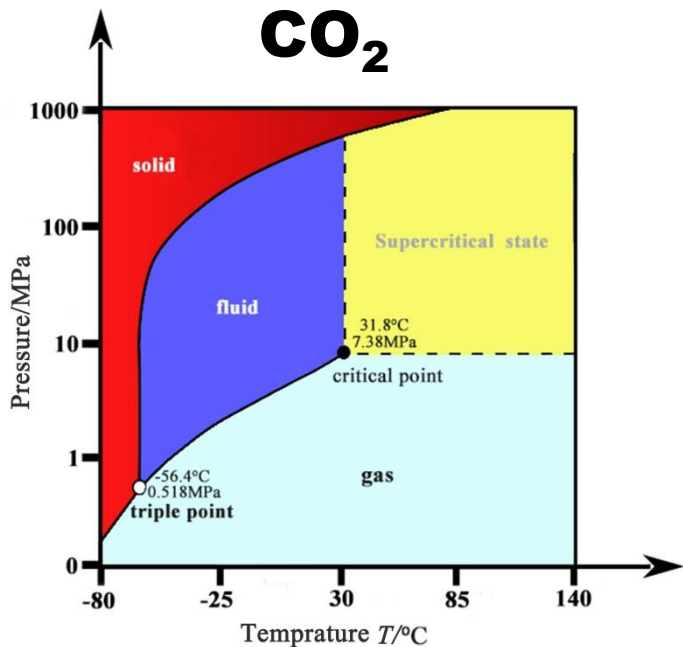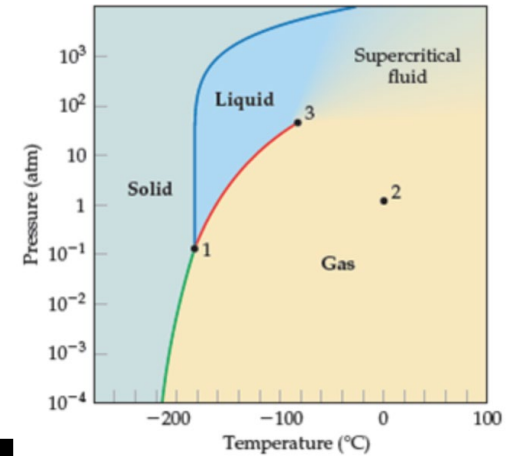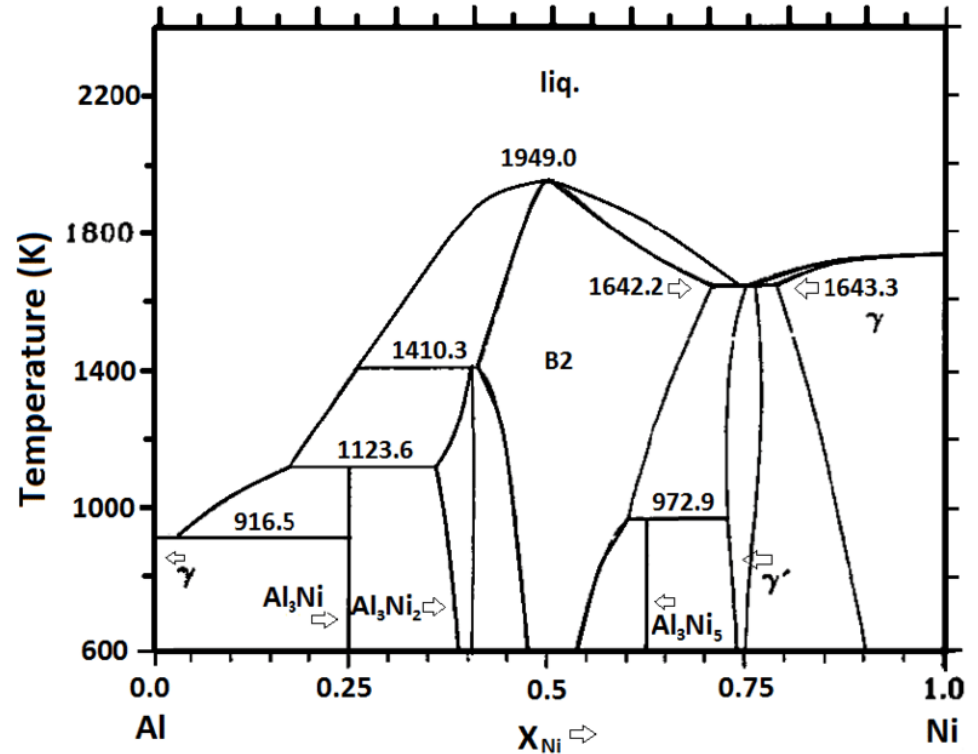
EXAMPLES of SIMPLE PHASE DIAGRAMS

N$_2$

Here are some phase diagrams for some simple Systems

(NB: note logarithmic pressure scales)

CH$_4$

CO$_2$

The freezing point of water depends on its pressure. (image: Cmglee, CC 3.0)

MORE COMPLICATED PHASE DIAGRAMS

Phase Diagram of Water
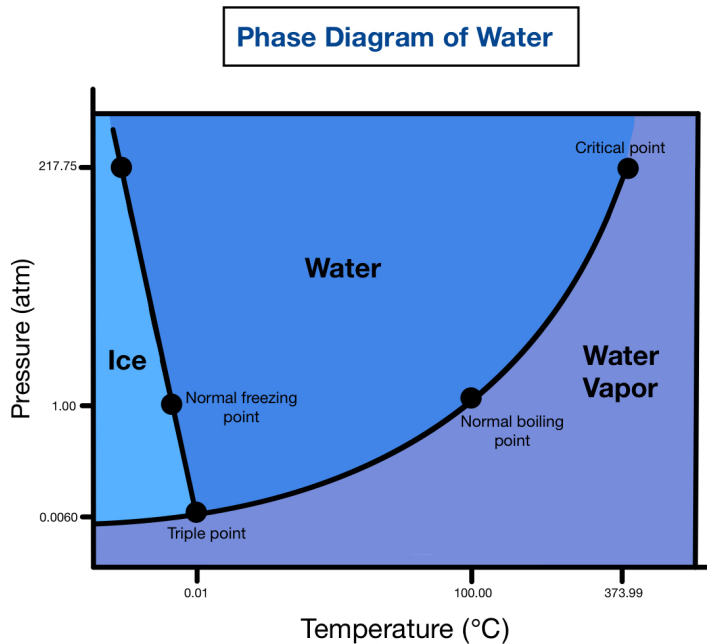
Water is not such a simple system. The liquid-ice transition temperature actually goes down in T as P increases; and the liquid is denser than the solid.

These properties can be explained by looking at the "cage-like" structure of the solid on the atomic scale.

Alloys have very complex phase diagrams as a function of the concentration of the relevant constituents. The example of the phase dagram for Al-Ni alloys gives a hint of this complexity.

The understanding of these has been a crucial part of the development of early technology and tools.

Now we have quantum fluctuations, as well as thermal fluctuations, playing a role
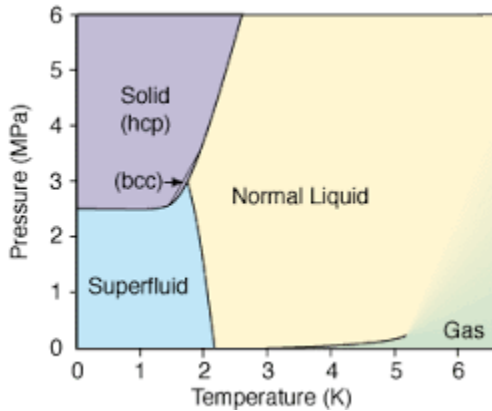
The He-4 phase diagram is a simple example – the low-pressure phase at T=0 is superfluid
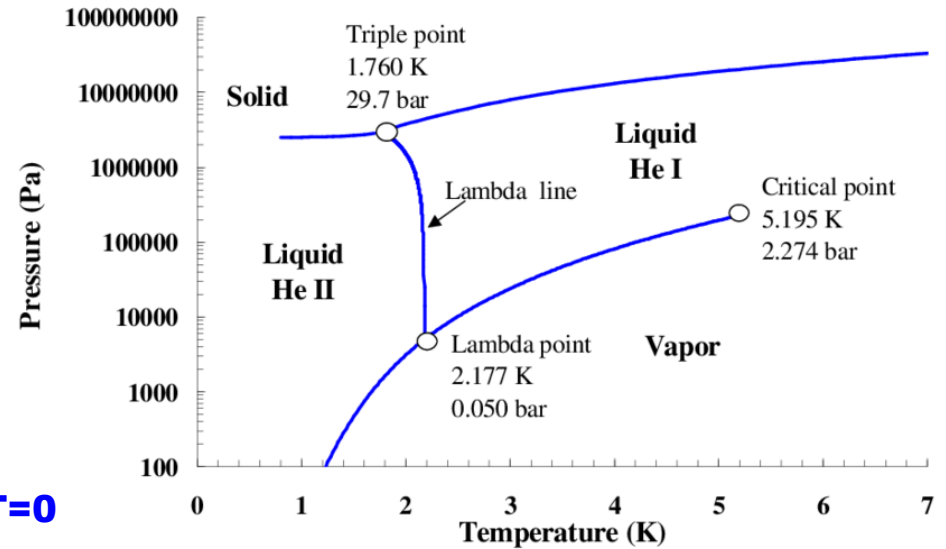
The He-3 phase diagram is much more complex, because the He-3 atoms have a spin, and are fermions (and can form Cooper pairs to give superluid phases. The spin makes the system magnetic

EHRENFEST CLASSIFICATION for PHASE TRANSITIONS

This starts by asking how the thermodynamic state functions (here the Gibbs free energy **G**) vary as we pass through the transition. A 1st order transition has a kink, & its derivative is discontinuous. A 2nd order transition has a kink in the derivative; and so on.

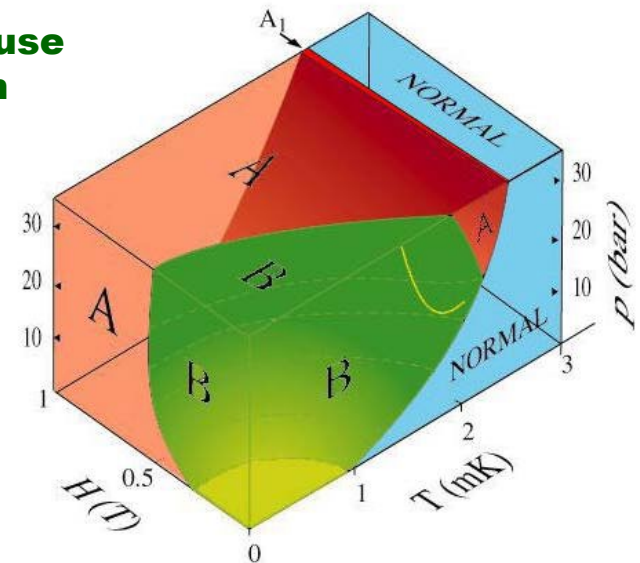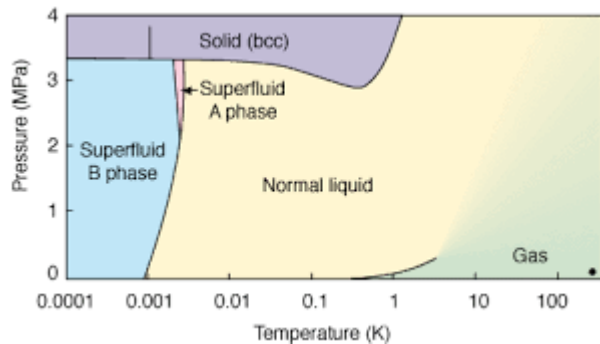One then gets the characteristic features shown. Here the parameter being varied to take us through the transition is temperature **T**. But it could be many other things (**B**, **p**, concentration, etc).

If we then work out how all the thermodynamic functions vary with whatever parameter is being varied, we get the typical results shown below (varying with **T**)
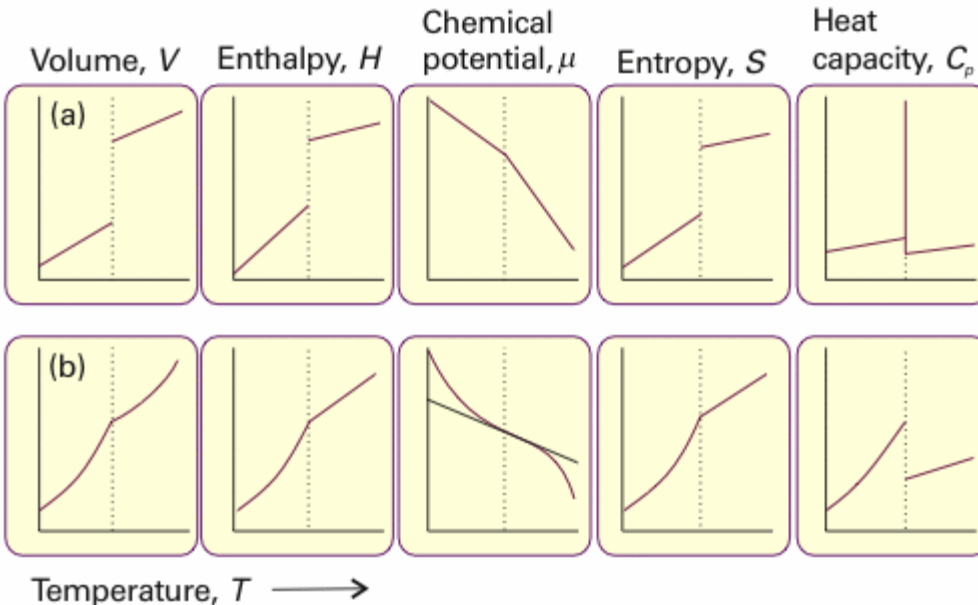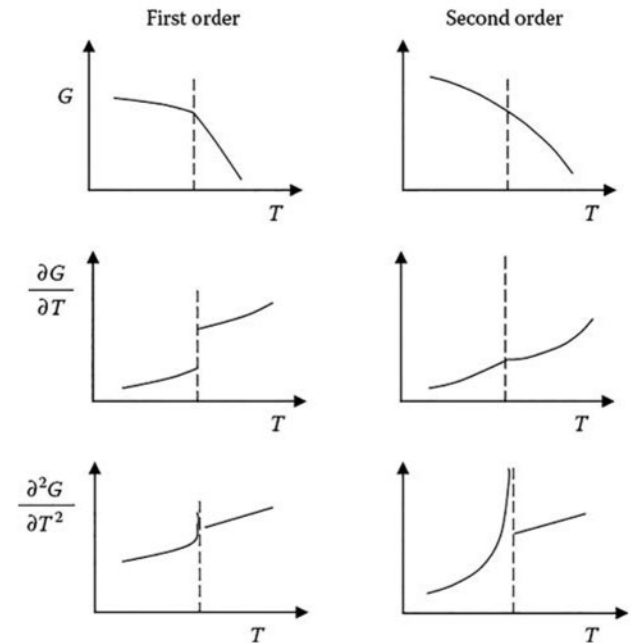
(a) 1st-order transition: kinks in G(T), μ(T); jumps in V, H, S; & a delta-function in $C_p(T)$

(b) 2nd-order transition: kinks in 1st derivatives of G(T), μ(T); kinks in V, H, S; & a jump in $C_p(T)$

1st ORDER PHASE TRANSITIONS

In a 1st order phase transition, the chemical potentials of the 2 phases cross (as do the free energies, etc.). Thus we can have the 2 phases in equilibrium with each other at the transition, which is thus defined by the condition

$$\mu_1 = \mu_2 \quad \text{(phase eqlbm)}$$

Suppose, eg., we deal with a gas, so that the phase eqlbm. condition can be written as

$$\mu_1(p,T) = \mu_2(p,T)$$

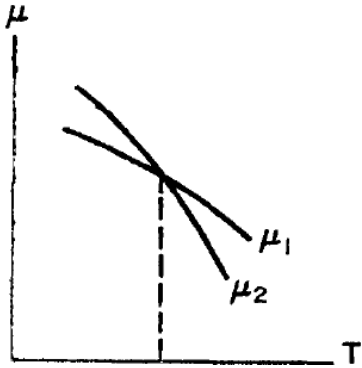We can then define the phase diagram by differentiating this expression with respect to, eg., T, to get

$$\frac{\partial \mu_1}{\partial T} + \frac{\partial \mu_1}{\partial P} \frac{dP}{dT} = \frac{\partial \mu_2}{\partial T} + \frac{\partial \mu_2}{\partial P} \frac{dP}{dT}$$

However, we know from elementary thermodynamics that

$$(\partial \mu / \partial T)_P = -s \qquad (\partial \mu / \partial P)_T = v \qquad \text{(per unit volume)}$$

so that the phase line is defined by

$$\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2}$$

Moreover, it is clear that the "latent heat" developed in going from the higher entropy to the lower entropy state is just

$$q = T(s_2 - s_1) \quad \text{from which we get} \qquad \frac{dP}{dT} = \frac{q}{T(v_2 - v_1)} \quad \text{(Clausius-Clapeyron)}$$

In this simple model we correct the ideal gas eqtn of state with terms which account for (i) the volume of the gas particles (modelled as hard spheres) and (ii) their interactions; we have

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = NkT$$

Increasing T

C

van der Waals isotherms

N·b
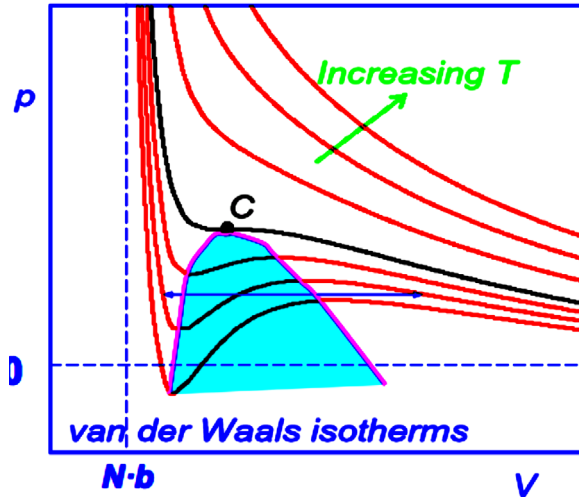
It is then an interesting exercise to plot the "isotherms" directly from this equation, which give the relation between p and V for this model of a liquid-gas system. These are shown at left.

At high T we see only weak deviations from the ideal gas law (for which p = NkT/V). As we lower T the pressure is lowered for a given V, as compared to the ideal gas, and eventually we get an instability - for a given V one has 2 values of p.

Maxwell dealt with this ambiguity using the "Maxwell construction", in which the horizontal line indicates we can have some fraction of one phase coexisting with the other, each having its own respective molar volume.

P

$P_{vap}(T_1)$

V_{liq} V_{gas} V
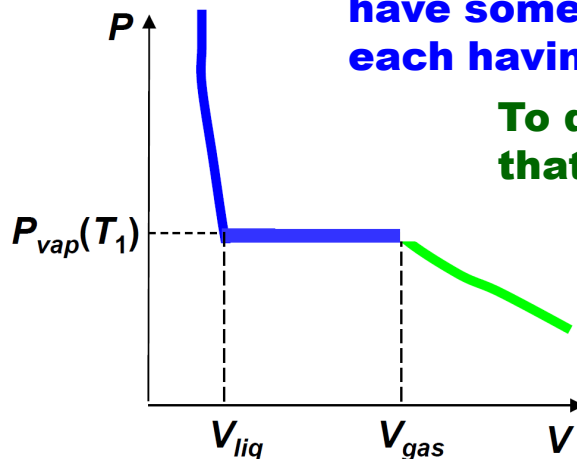
To decide where to draw the line, note that between he 2 end-points we have

$$\int_1^2 d\mu = 0 \quad \text{so that} \quad \int_1^2 V \, dP = 0$$

Thus the shaded regions shown at right have equal area.
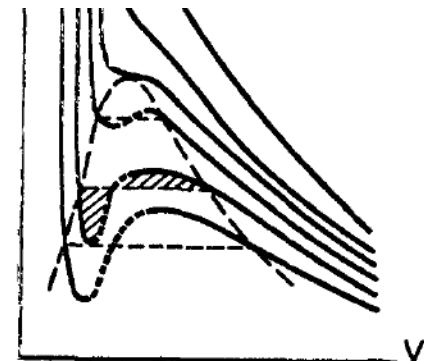
KINETICS of 1st ORDER PHASE TRANSITIONS

There is a famous model for the kinematics and dynamics of 1st order phase transitions, sometimes called the droplet model for reasons that will become obvious. Suppose we have a simple problem in which 2 phases A and B have different bulk free energies. Phase B with the lowest free energy is thermodynamically favoured – but if we start with A, we have to find a way of growing or "nucleating" a region of phase B inside it.

The idea is that this can happen anywhere – but to create the "bubble" of new phase, we need to create a transition regime, in the form if a surface of finite thickness, between them. This surface has a finite energy per unit area, which we call the surface energy – it is responsible for the "surface tension".
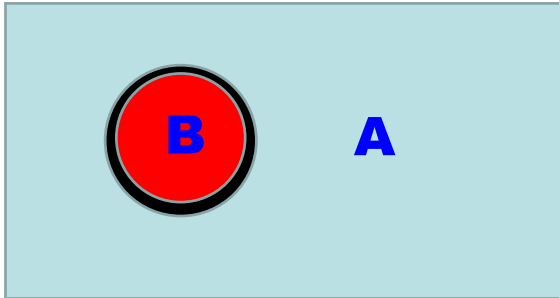
Example: gas-liquid interface

Energetics: The total Gibbs free energy for a bubble
of radius R is

$$G(R) \; = \; g_L M_L(R) \; + \; g_g M_g(R) \; + \; 4\pi\gamma R^2$$

$$= \; \frac{4\pi}{3}\rho_L \, \Delta g \, R^3 \; + \; 4\pi\gamma R^2 \; + \; const$$

where we define $\Delta g \; = \; (g_L - g_g)$
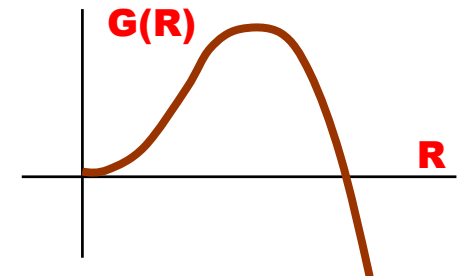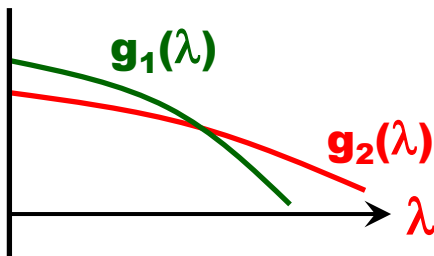
The thermodynamic phase transition is where the 2 free energy lines cross. Here λ = p,T,V,H, etc.. is some control parameter (which could be T or p for the gas-liquid system).

Note if we are growing a bubble of gas in the liquid (so the liquid is unstable), then $\Delta g > 0$ (this is the case of boiling or even superheating, where gas bubbles grow in the liquid). On the other hand if the liquid bubble is growing in the gas (ie, we have condensation of the liquid, or even supercooling), then $\Delta g < 0$.

Dynamics: The top of this energy barrier caused by surface tension is defined by

$$\frac{dG}{dR} = 4\pi(\rho_L \Delta g\, R^2 + 2\gamma R)$$

giving a 'critical radius' $R_c = \dfrac{-2\gamma}{\rho_L \Delta g}$, & barrier height $U_c = G(R_c) = \dfrac{16\pi}{3}\dfrac{\gamma^3}{(\rho_L \Delta g)^2}$

Because of this energy barrier, one can in principle go well into the unstable phase, to give either superheating or supercooling.
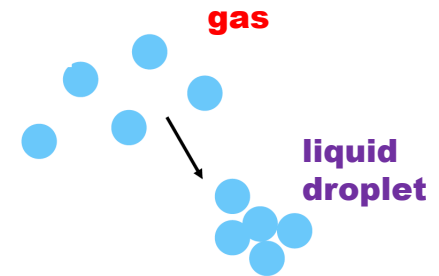
The analysis so far has been thermodynamic. One can also analyse it microscopically, by looking at how gaseous clusters of particles (the incipient liquid) can form or dissociate into a gas.

gas

liquid droplet

Let's suppose that the gas dynamics is diffusive, implying that the rate of change of mass of the liquid droplet will go like

$$\Gamma \equiv \frac{dm_L}{dt} = -D_o \nabla \rho_g(\mathbf{r}) \quad \text{Fick's law (diffusion)}$$

which leads to $\quad \Gamma = -4\pi r^2 D_o \dfrac{d\rho_g}{dr}$

and integrating: $\quad \Gamma \displaystyle\int_{R_c}^{\infty} \frac{dr}{r^2} = -4\pi D_o \int_{R_c}^{\infty} d\rho_g(r)$

so finally we get $\quad \Gamma = 4\pi R_c D_o \left[\rho_g(R_c) - \rho_g^{(\infty)}\right]$

or, using the ideal gas law $\quad \Gamma = 4\pi R_c D_o \dfrac{m}{kT}\left[p_g(R_c) - p_g^{(\infty)}\right]$

The point here is that the gas pressure must be higher at the bubble surface than at infinity. This can be seen from the remark that energy is associated with the surface curvature (NB: this is not obvious from this derivation).

Now let's look at all this in another way

ANOTHER WAY of looking at REACTION RATES

Obviously the topic of reaction rates is an important one in physics, chemistry & biology. So it is worth asking how else we can approach it.

Now the transitions of the system out of the potential well can go in one of 2 ways, viz.,

(1) by direct tunneling from the ground state (n = M), or by thermal activation from the ground state to some level n, followed by tunneling from level n

(3) by thermal activation to states above the barrier (at which point the system is no longer bound).

Let's ignore process (2) for the moment, and focus on (1). Then we can write that the rate of barrier traversal will be

$$\Gamma(T) = \sum_n p_T(E_n)\Gamma_o(E_n)$$

which multiplies the probability that the system is in the n-th level, by the tunneling rate through the barrier from that level (whose energy is E_n).

Obviously we have

$$p_T(E) \propto \exp[-E/kT]$$

The WKB tunneling rate is

$$\Gamma_o(E) = \Omega_o \exp[-\frac{1}{\hbar}\int_{x_1}^{x_2} dx\sqrt{2m(V(x)-E)}]$$

where **V(x)** is the barrier potential, m is the effective mass of the object, x_1 and x_2 are entry and exit points through this potential, and Ωo is an 'attempt frequency'

For an inverted parabolic potential one has

$$\Gamma_o(E_n) \propto \exp[\Delta_o(E_n - E_m)]$$

The exponential increase with E of Γ_o fights against the exponential decrease of $p_T(E)$, with a crossover between the two when Δ_o kT ~ 1 .

The growth & nucleation of a critical bubble is a special case of this analysis. At low **T** we have "quantum nucleation"
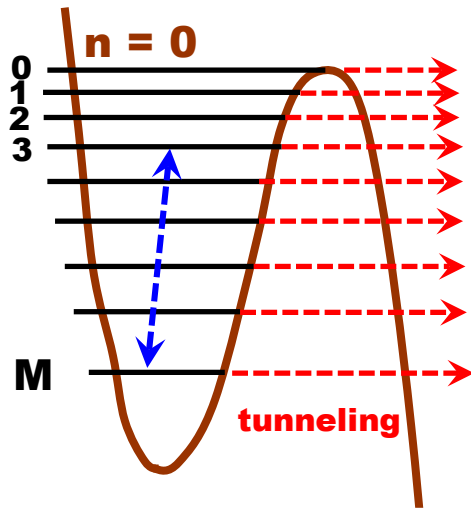
2ⁿᵈ ORDER PHASE TRANSITIONS

In a 2ⁿᵈ-order phase transition, thermodynamic quantities like the entropy **S** or volume **V** vary continuously – only their derivatives, like the specific heat $C_V(T)$ have junps or other discontinuities. To describe these Landau (starting in 1937) introduced the idea of an "order parameter", and wrote the free energy as

$$F(T) = \int d^3x \, f(\psi, T)$$

where $\psi(x, T)$ is the order parameter. Consider the example of magnetization density m(x,T), and write

$$f(m, T) = f_o(T) + \alpha(T)m^2 + \frac{1}{2}\beta(T)m^4 + \gamma(T)\vec{\nabla}m \cdot \vec{\nabla}m$$

where by symmetry of **F** under **m → -m**, we only have even powers. Minimizing F gives an eqlbm (uniform) magnetization according to

$$\alpha\bar{m} + \beta\bar{m}^3 = 0.$$

so that $\bar{m} = \pm\sqrt{-\alpha/\beta}$ for $\alpha < 0$

$$= 0 \quad \text{for} \quad \alpha > 0.$$

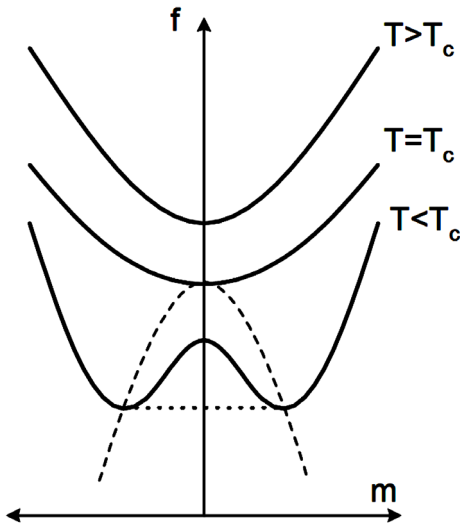Let's then write: $\alpha(T) \simeq a(T - T_c) + \cdots$

$$\beta(T) \simeq b + \cdots$$

$$\gamma(T) \simeq \gamma + \cdots$$

We then have $f \simeq f_o(T) + a(T - T_c)m^2 + \frac{1}{2}bm^4 + \gamma(\vec{\nabla}m)^2$

and the magnetization goes like $\bar{m} \simeq \left(\frac{a}{b}\right)^{1/2} (T_c - T)^{1/2}$ for $T < T_c$

$$0 \qquad \text{for } (T > Tc)$$

If we add an external field B we get a new free energy density going like

$$f(m, T, B) = f_0(T) + a(T - T_c)m^2 + \frac{1}{2}bm^4 + \gamma(\vec{\nabla}m)^2 - mB.$$

and we now find that $\quad m = \left(\frac{1}{2b}\right)^{1/3} B^{1/3}$

as well as recovering the Curie susceptibility $\quad \chi = \left.\frac{\bar{m}}{B}\right|_{B=0} = \frac{1}{2a}(T - T_c)^{-1}$

SUPERFLUIDS & SUPERCONDUCTORS

What about systems like He-4 superfluid, or a superconductor? The Ginzburg-Landau theory (1950) and the later Gross-Pitaevskii theory (1961) generalized the Landau theory to these systems.

For a charged superfluid (where the bosons that condense are formed by "Cooper pairs" of electrons), the Ginzburg Landau Free energy density is

$$f \simeq f_o(T) + \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m^*}|(-i\hbar\nabla - e^*\mathbf{A})\psi|^2 + \frac{|\mathbf{B}|^2}{2\mu_0}$$

and we see that the generalization involves the following features:

  (i) the order parameter is now a complex function ψ **(x,t; T)** which is related to the macroscopic wave-function we previously encountered;

  (ii) we use the "covariant derivative" $|(-i\hbar\nabla - e^*\mathbf{A})$ instead of the simple gradient term, since the electrons couple to the EM field; and we add the Maxwell field energy to the free energy density; and

  (iii) we have effective mass **m*** and an effective charge **e*** for the charge carriers (the Cooper pairs).

The incredible predictive success of these theories, along with that of the Landau Fermi liquid theory and the Landau theory of superfluidity, convinced the world that these "effective field" theories were here to stay.