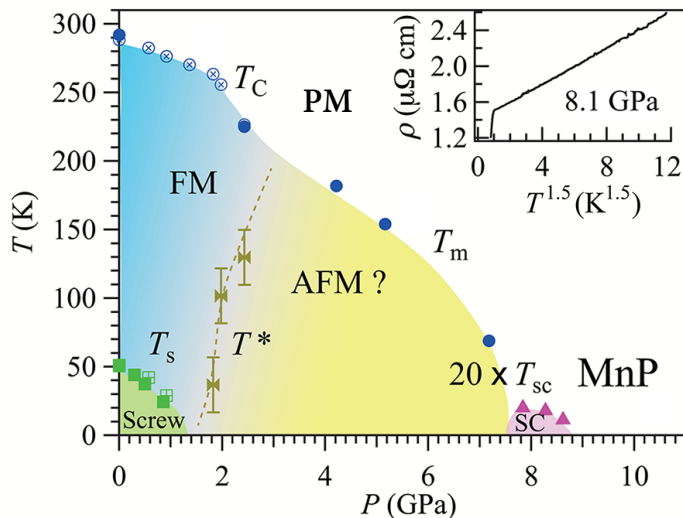
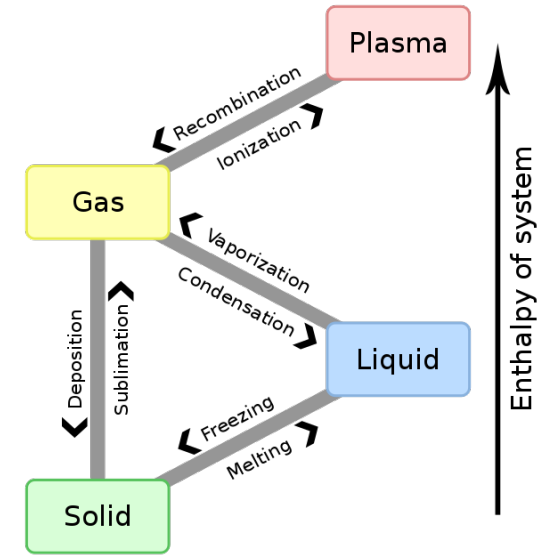


INTRODUCTION to PHASE TRANSITIONS

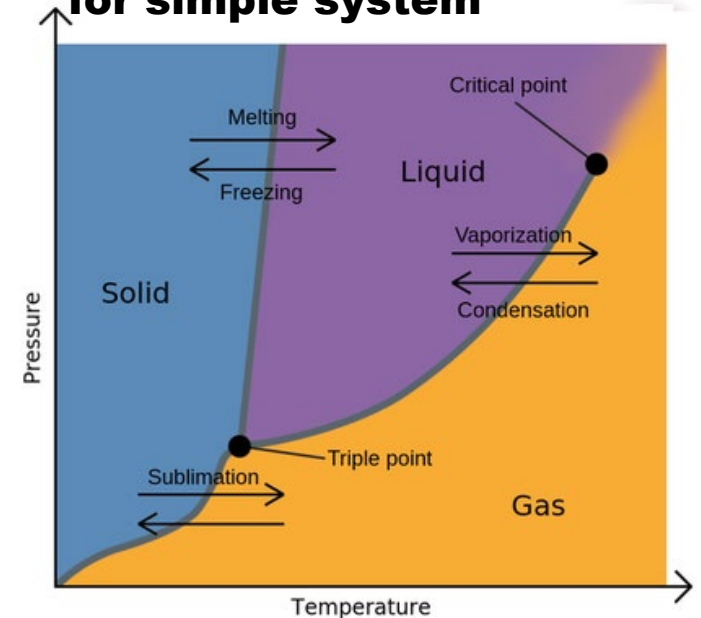
The simplest kinds of phase, and the names given in English to the transitions between them, are shown at right.

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 different magnetic phases (FM = Ferromagnet, AFM = Antiferromagnet, and PM = paramagnet)



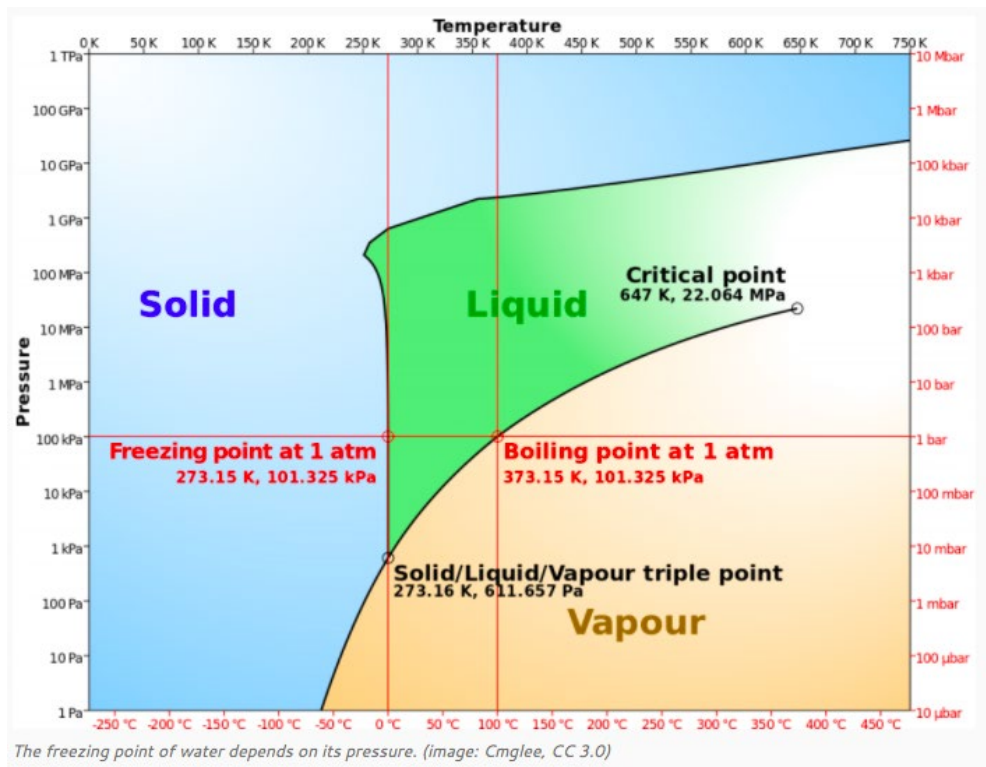
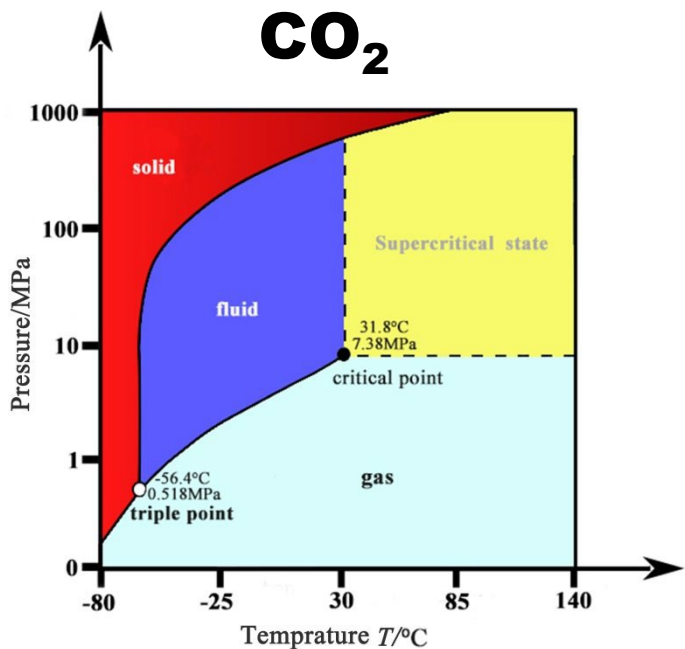
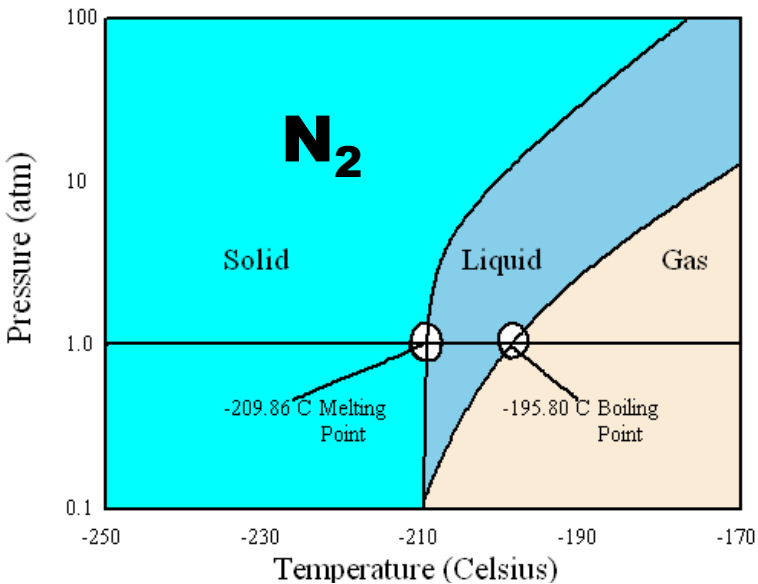
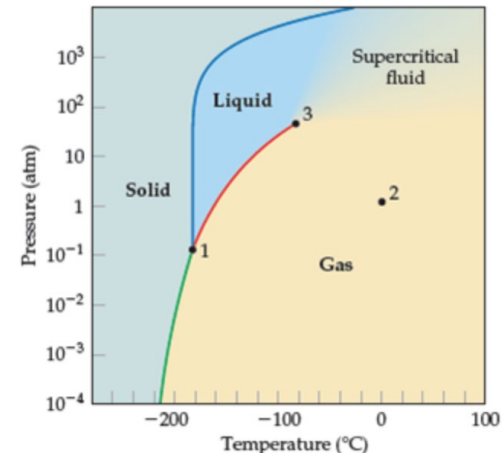
Standard phase diagram for simple system



Here are some phase diagrams for some simple Systems

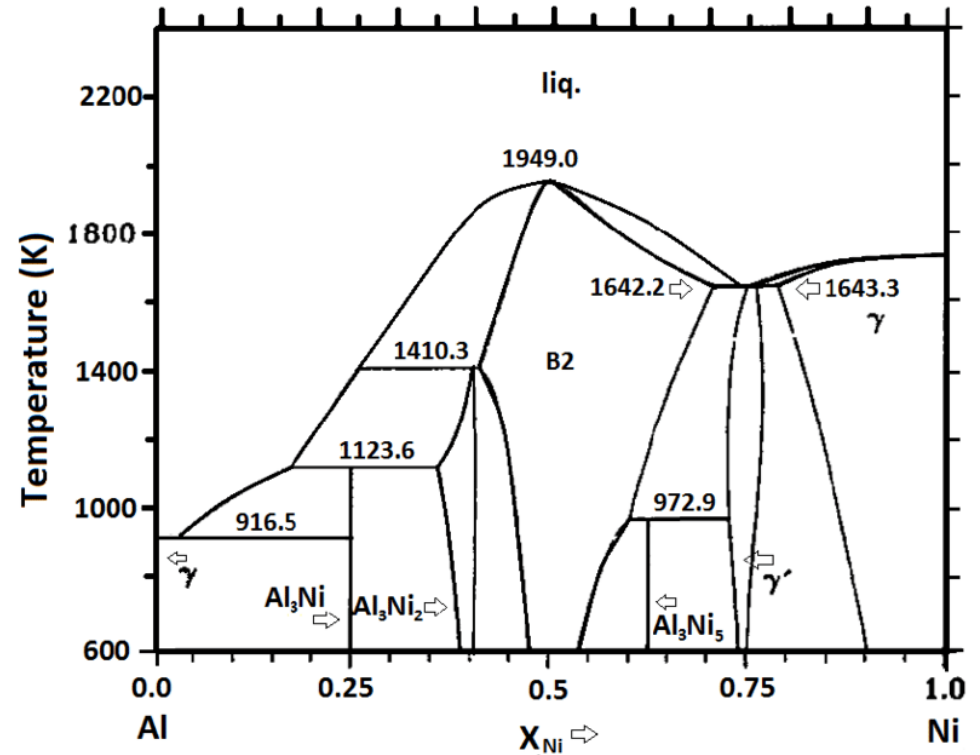
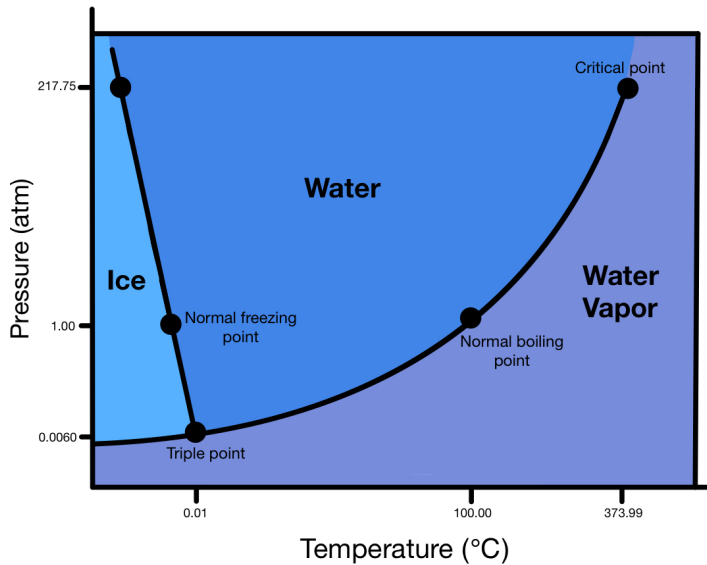
(NB: note logarithmic pressure scales)

CH₄



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

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.

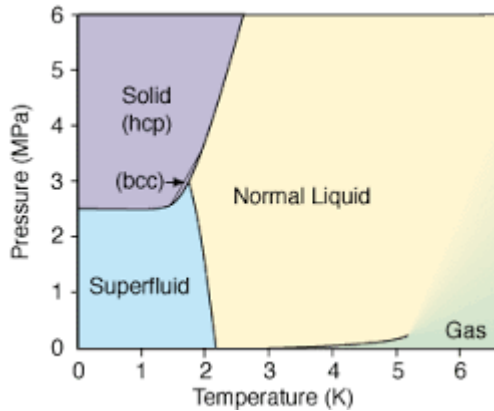
These properties can be explained by looking at the “cage-like” structure of the solid on the atomic scale.

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

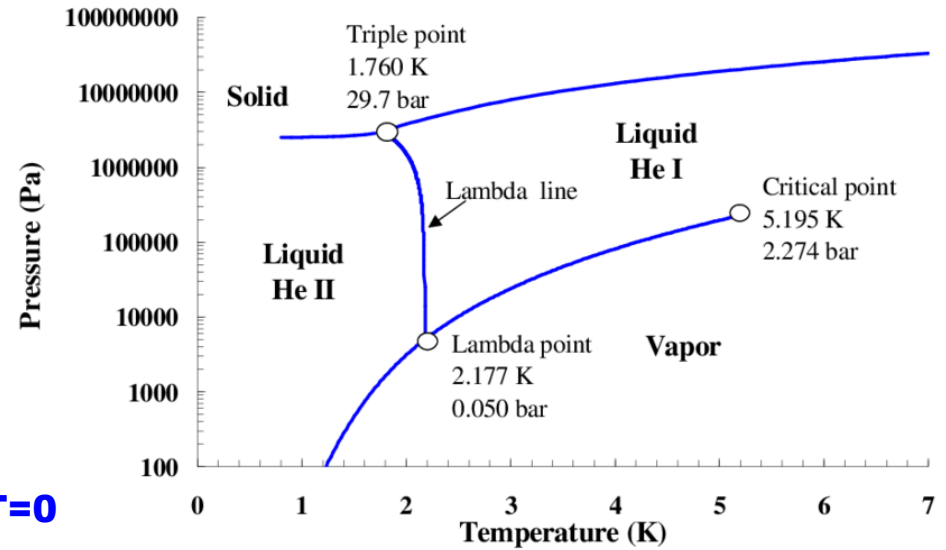
The understanding of these has been a crucial part of the development of early technology and tools.

PHASE DIAGRAMS for QUANTUM LIQUIDS/SOLIDS

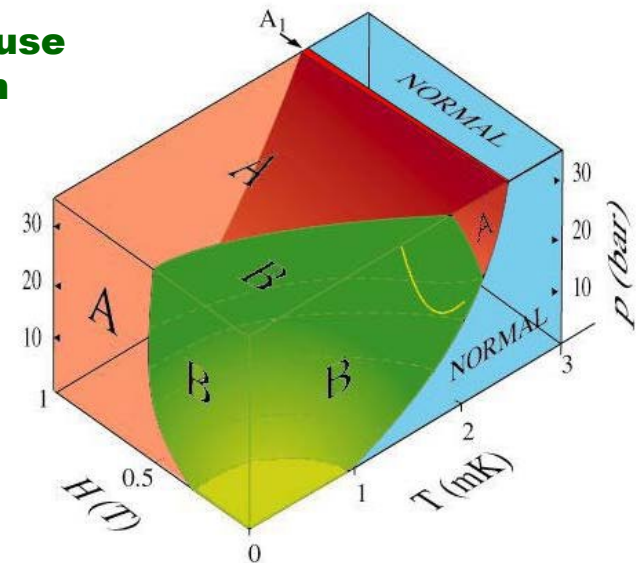
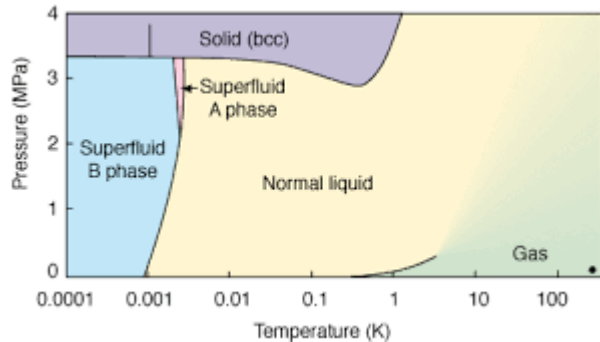
Now we have quantum fluctuations, as well as thermal fluctuations, playing a role



The He-4 phase diagram is a simple example – the low-pressure phase at $T=0$ is superfluid



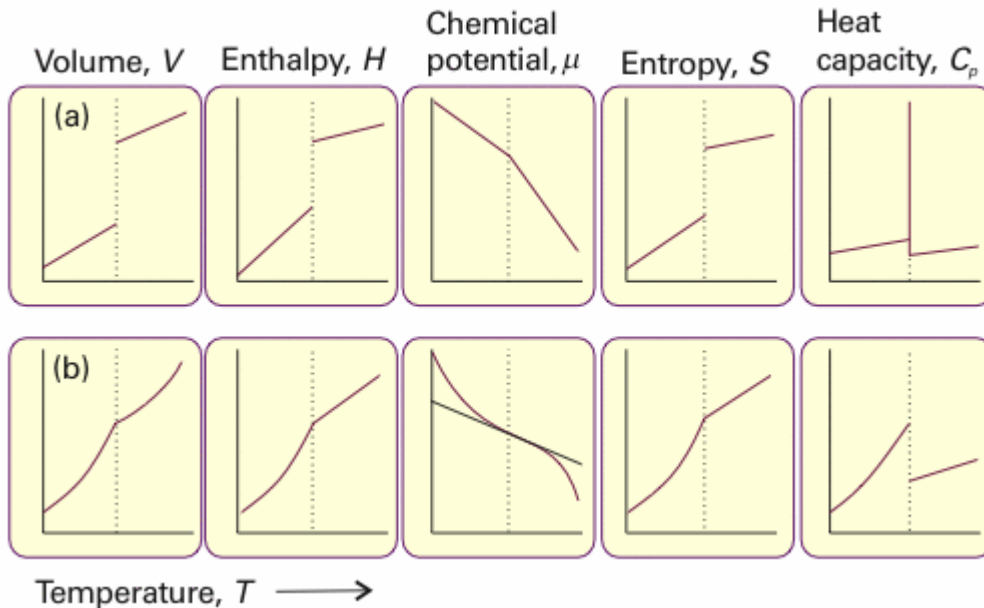
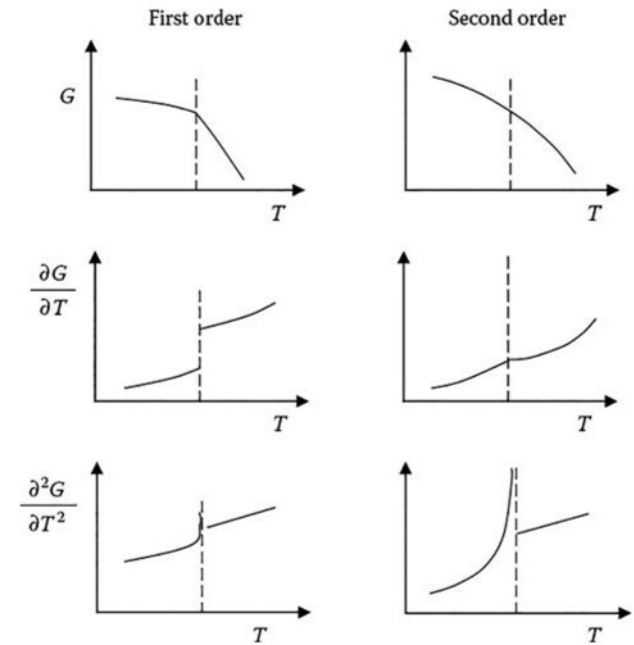
The He-3 phase diagram is much more complex, because the He-3 atoms have a spin, and are fermions (and can form Cooper pairs to give superfluid phases). The spin makes the system magnetic



EHRENFEST CLASSIFICATION for PHASE TRANSITIONS

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

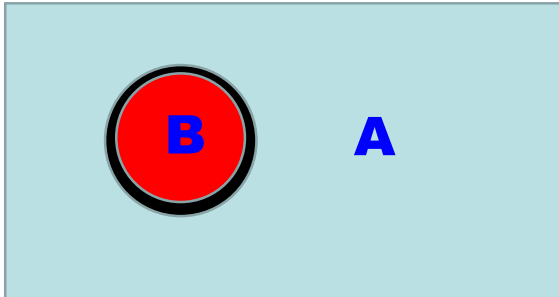
One then gets the characteristic features shown. Note that I am showing here that the parameter that is being varied to take us through the transition is temperature **T**. But it could be many other things (**H**, **p**, concentration, etc).



If we then work out how all the different interesting thermodynamic functions vary with the key parameter that is being varied, we get the typical results shown at left.

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 of 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”.

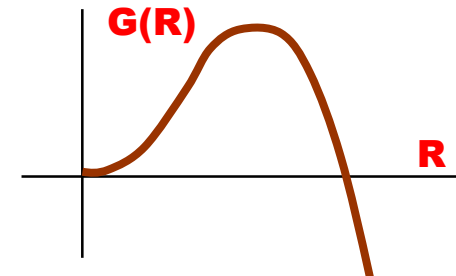
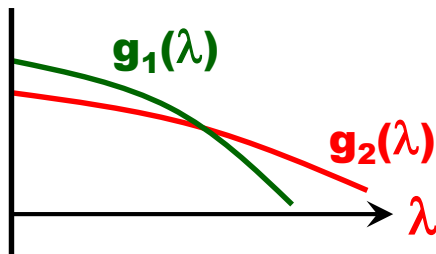
Example: gas-liquid interface

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 $\lambda = p, T, V, H$, 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 $\Delta g < 0$.

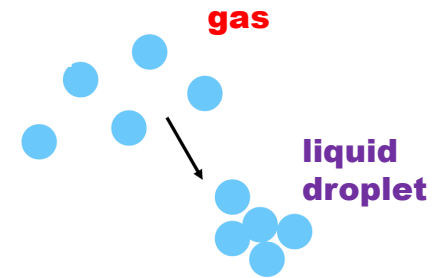
Dynamics: The top of this energy barrier caused by surface tension is defined by

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

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

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.



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 $\Gamma = -4\pi r^2 D_o \frac{d\rho_g}{dr}$

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

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

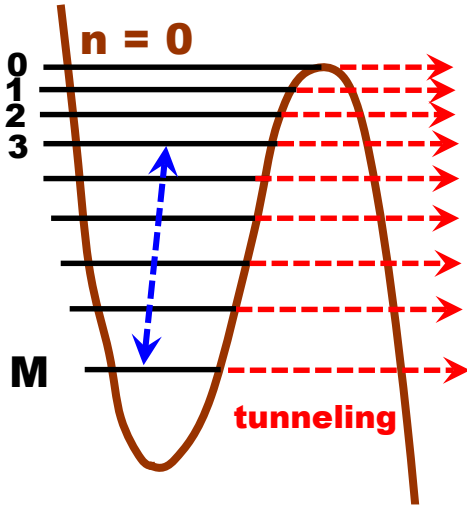
or, using the ideal gas law $\Gamma = 4\pi R_c D_o \frac{m}{kT} [p_g(R_c) - p_g^{(\infty)}]$

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

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

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 Ω_o 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 $\Delta_o kT \sim 1$.

The growth & nucleation of a critical bubble is a special case of this analysis. At low T we have "quantum nucleation"