



Figure 2: The Gibbs free energy of a droplet as a function of its radius.

Abrupt phase transitions

Phase transitions can be grouped into two classes: *abrupt phase transitions*, where the order parameter has a discontinuity, and *continuous phase transitions*, where the order parameter has a singularity but still continuous.

Abrupt phase transitions are sometimes called first order, and the continuous one as second order. This terminology originates from Ehrenfest's classification, which considered the lowest derivative of the free energy that is discontinuous at the transition. Ehrenfest's approach is no longer used, as it turned out that different higher order phase transitions are not fundamentally different, some even do not fit in (eg. divergent derivatives).

First let us consider abrupt phase transition, and our example will be water held at fixed T and p . As illustrated on Fig. 1, if we change the parameters (T and p) on a path which crosses a phase coexistence curve, a sudden jump in properties occur, which can be captured by the order parameter, the density ρ .

What underlies of an abrupt phase transition is that in the parameter space one crosses from a domain A where the free energy of phase A is lower to domain B where that of phase B is lower.

When the coexistence curve (of equal free energies) is crossed, the system does not necessarily recognise immediately that some other state would be lower in free energy: this happens via fluctuations. Suppose that by fluctuations a small sphere of radius R of the lower free energy phase is formed. To fix notation let us consider cooling down a gas to form liquid at fixed pressure. Then the Gibbs free energy of the small liquid droplet is

$$G_{\text{droplet}}(R) = c_1 R^2 - c_2 R^3 \Delta T,$$

see Fig. 2. The first term corresponds to surface tension: it costs free energy to create an interface between the two phases. This is positive and quadratic in R , dominating the expression for small R . The origin of the second term is the difference between the bulk free energies: this is proportional to the volume of the droplet ($\sim R^3$). The prefactor is proportional to ΔT (the difference between the coexistence temperature and the actual temperature), as the bulk free energies are smooth functions of the temperature, therefore their difference can be approximated to be linear in ΔT . This term is negative, and dominates at large R .

The free energy of a large droplet is negative, therefore this is the thermodynamically stable state. However, the system needs to