

Phase Transition

1 Gibbs free energy and the enthalpy

We start with some revision of thermodynamic concepts.

So far we have considered the total energy U and the Helmholtz free energy F as thermodynamic functions describing a physical system. It is convenient to introduce two more “free energies”, the enthalpy and the Gibbs free energy.

The *enthalpy* is defined as

$$H = U + pV,$$

so that for a thermal system in equilibrium

$$dH = \tau d\sigma + \mu dN + V dp,$$

and the “natural” variables for H are σ , N and p . We then have

$$\left(\frac{\partial H}{\partial \sigma}\right)_{N,p} = \tau, \quad \left(\frac{\partial H}{\partial N}\right)_{\sigma,p} = \mu \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_{\sigma,N} = V.$$

H is sometimes useful as the effective free energy when changes take place in a system at fixed pressure.

The *Gibbs free energy* is defined as

$$G = U + pV - \tau\sigma = F + pV = H - \tau\sigma.$$

This free energy is useful in describing processes where the temperature and pressure of a system are controlled. We have

$$dG = -\sigma d\tau + \mu dN + V dp,$$

so that the natural variables for G are τ , p and N . Its partial derivatives are

$$\left(\frac{\partial G}{\partial \tau}\right)_{p,N} = -\sigma, \quad \left(\frac{\partial G}{\partial N}\right)_{\tau,p} = \mu \quad \text{and} \quad \left(\frac{\partial G}{\partial p}\right)_{\tau,N} = V.$$

Now consider a system where the only extensive variables are U , V and N . Since these variables are all extensive we expect that the microscopic state of the system only depends on ratios of these. For example, any two systems with the same particle concentration and energy per particle will have the same temperature and pressure *etc.* Likewise, specifying the temperature and pressure will completely determine the microscopic condition of the system. This means that we should expect any extensive quantity, such as the Gibbs free energy to be proportional to N for a given pressure and temperature. Thus

$$G = N\phi(p, \tau).$$

But we know that $\phi = \mu$ from above, so that

$$G = N\mu.$$

More generally, when there are many particle species present in a system, we have

$$G = \sum_j N_j \mu_j.$$

In practice, G is often the most useful of the free energies for describing the properties of physical systems. This is because it is easiest to directly control the intensive variables p and τ in an experiment.

2 Why phase transitions?

Consider a fixed number of atoms in a box of fixed volume. It is not uncommon for the interactions between the atoms to cause the entropy, considered as a function of the total energy of the atoms to have kinks in it. At fixed N and V the entropy of an ideal gas varies as $\ln U$, but interactions between the atoms (at lower temperatures) may result in an entropy curve more like:

We consider the behaviour of this system between the points marked A and B , say at the point marked by C . The entropy of the system at this point is $\sigma(U_C)$.

Now construct a different system by taking αN particles ($\alpha < 1$) with total energy αU_A inside a volume αV . Given the extensive behaviour of thermal systems, this system will be in the same state as the particles at A — having the same temperature, pressure, chemical potential *etc.* We combine this with $(1 - \alpha)N$ particles having total energy $(1 - \alpha)U_B$ and occupying a volume $(1 - \alpha)V$, and these particles will be in the same state as those in the original system at B .

The total number of particles in this composite system is just N and its total volume is V . Its total energy is

$$U = \alpha U_A + (1 - \alpha)U_B,$$

which can be made equal to U_C with an appropriate choice for α , *i.e.*

$$\alpha = \frac{U_B - U_C}{U_B - U_A}.$$

Now consider the entropy of the combined system,

$$\sigma' = \alpha \sigma_A + (1 - \alpha) \sigma_B.$$

Graphically, we can find this by drawing a straight line connecting the entropy surface at A and B , and then we have a plot of $\sigma'(U)$. We see that the entropy of the inhomogeneous composite system is higher than the entropy of the homogeneous system at C — and hence it is the mixed system which is the “more stable”.

This situation arises in practice and is the cause of phase transitions.

We have not yet constructed the composite system with the highest possible entropy for N particles having total energy U_C . To do this we must move the points A and B to maximise the entropy of the composite system. It is easy to see that, with A fixed, the entropy will be maximized at C when the straight line AB is tangent to the entropy curve at B . Likewise, with B fixed, the entropy is maximized when the line is tangent at A , so that the overall entropy maximum occurs when the straight line joining A to B is tangent to the entropy curve for the homogeneous system at A and B .

This gives us the general method for constructing the true entropy curve for a thermal system in equilibrium from the entropy curve for the related homogeneous system. We draw a straight line tangent to the entropy curve for the homogeneous system, and if that tangent line lies above the curve everywhere then that point represents the equilibrium state. If the tangent line cuts

the entropy curve elsewhere then we can construct an inhomogeneous system of higher entropy as above. The nett result is that the true entropy curve is found by “rolling” a straight line over the top of the homogeneous entropy curve.

Notice that the slope of the entropy curve gives the temperature:

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_{N,V}.$$

Since the straight line joining A and B is tangent to the entropy curve at A and B the slope of the curve is the same at A and B , so that

$$\tau_A = \tau_B$$

for the two states present during the phase transition. In other words, the two components of the inhomogeneous mixture are in thermal equilibrium with one another during the phase transition. Note that the temperature is also fixed at this same value along the straight line joining A to B , *i.e.* throughout the phase transition.

There is one more important aspect of phase transitions that is readily understood in terms of this treatment. Looking at the diagram of the phase transition more closely

we see that if the homogeneous entropy curve is smooth between A and B , then it must curve upward in some places. If these represented reachable states for the system we see that the temperature decreases as the total energy increases in such a state — the heat capacity of the system would be negative. Adding heat to such a system lowers its temperature, while removing heat will raise it. Such a state is *locally unstable* because the different parts of the system are driven apart in temperature when heat flows from high to low temperature. In practice these states are completely unattainable.

In contrast to this, there are also places (close to the ends of the phase transition region) where the heat capacity remains positive. These represent *metastable* states of the system. They are locally stable, and it is only when some part of the system makes a large excursion from the metastable state that the system will “discover” its higher entropy inhomogeneous state. These regions can be reached by careful heating or cooling of a system. They are referred to as *superheated* or *supercooled* states of the system.

All of this may be generalized in cases where we let other extensive parameters of the system vary too. For example, we can consider the case where N varies. In that case the state of global maximum entropy is found by rolling a *plane* over the homogeneous entropy surface. We can readily see (as above) that when a phase transition occurs we must also have

$$\left(\frac{\partial \sigma}{\partial N} \right)_{U,V} \Big|_A = \left(\frac{\partial \sigma}{\partial N} \right)_{U,V} \Big|_B,$$

so that the chemical potential of the coexistent phases is also the same, *i.e.* the coexistent phases are in thermal and diffusive equilibrium with one another. In the same vein, the pressure of coexistent phases is also the same.

When there are two or more extensive parameters that may vary we also get other phenomena such as triple points and second order phase transitions:

3 The coexistence curve

Typical phase transitions are the melting of a solid and the boiling of a liquid. In melting the solid and liquid phases coexist, while in boiling, liquid and gas phases coexist. We will discuss some features of a phase transition such as this (a first order phase transition) in terms of the boiling of a gas.

As we have established above, during the phase transition there is thermal, mechanical and diffusive equilibrium between the coexisting phases, so that

$$\tau_l = \tau_g, \quad \mu_l = \mu_g \quad \text{and} \quad p_l = p_g,$$

where the subscripts l and g refer to the liquid and gas phases respectively. For a simple system we have $\mu = \mu(p, \tau)$, so that we may summarize these statements by requiring that

$$\mu_l(p, \tau) = \mu_g(p, \tau),$$

where both sides are evaluated at the common temperature and pressure of the system. In general, this equation can only be satisfied along a line in the p, τ plane — the *coexistence curve*.

Suppose that p_0, τ_0 and $p_0 + dp, \tau_0 + d\tau$ are closely spaced points along the coexistence curve. Then, since $\mu_l = \mu_g$ at both these points we must have

$$\left(\frac{\partial \mu_l}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_l}{\partial \tau}\right)_p d\tau = \left(\frac{\partial \mu_g}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_g}{\partial \tau}\right)_p d\tau,$$

giving

$$\frac{dp}{d\tau} = \frac{\left(\frac{\partial \mu_l}{\partial \tau}\right)_p - \left(\frac{\partial \mu_g}{\partial \tau}\right)_p}{\left(\frac{\partial \mu_g}{\partial p}\right)_\tau - \left(\frac{\partial \mu_l}{\partial p}\right)_\tau}.$$

This is a differential equation for the coexistence curve for the liquid and gas phases.

We can use our results for the Gibbs free energy to rewrite these. We have

$$\left(\frac{\partial G}{\partial p}\right)_{N, \tau} = V = N \left(\frac{\partial \mu}{\partial p}\right)_\tau \quad \text{and} \quad \left(\frac{\partial G}{\partial \tau}\right)_{N, p} = -\sigma = N \left(\frac{\partial \mu}{\partial \tau}\right)_p,$$

so that defining

$$v = \frac{V}{N} \quad \text{and} \quad s = \frac{\sigma}{N},$$

we may write

$$\frac{dp}{d\tau} = \frac{s_g - s_l}{v_g - v_l}.$$

By the definitions, $s_g - s_l$ is the entropy increase and $v_g - v_l$ is the volume increase when one molecule of the liquid goes into the gas phase.

Since the phase change happens at fixed temperature, the heat required to take one molecule from the liquid to the gas phase is $dQ = \tau(s_g - s_l)$, so that

$$L = \tau(s_g - s_l)$$

is the *latent heat of vaporization* for the system (per molecule), a readily accessible quantity. Writing $\Delta v = v_g - v_l$ (also readily accessible), we have the result

$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta v},$$

the *Clausius-Clapeyron equation*. It has been well verified experimentally.

Under normal conditions the specific volume of a vapour (gas) is much greater than ($\sim 1000\times$) that for a liquid or solid. We can then make the (good) approximation

$$\Delta v \simeq v_g = \frac{V_g}{N_g},$$

and assuming that the gas is also ideal we have

$$v_g = \frac{\tau}{p},$$

giving

$$\frac{dp}{d\tau} = \frac{Lp}{\tau^2},$$

which can be used to determine the coexistence curve if we know L . L depends chiefly on the binding energy of molecules to the liquid (or solid) phase, and is fairly weakly dependent on the temperature. Approximating it as a constant, we can integrate this to get

$$p(\tau) = p_0 \exp\left(-\frac{L_0}{\tau}\right).$$

In conventional units this is

$$p(T) = p_0 \exp\left(-\frac{L_0}{RT}\right),$$

where L_0 is now expressed in energy per mole, the gas constant is $R = N_0 k_B$ and N_0 is Avogadro's number. This is why the vapour pressure over a liquid or solid varies approximately exponentially with the temperature.

Recalling the phase diagram of ^4He , below about 1.4 K the coexistence curve for the liquid to solid transition is nearly horizontal. From the Clausius-Clapeyron equation, we see that this means that the entropy per particle in the two phases must be very nearly equal. This is unusual. Even more unusual is the case of ^3He where the solid-liquid coexistence curve is negative at low temperatures ($T \lesssim 0.4$ K), so that the entropy per particle in the solid phase is actually higher than that in the liquid phase. Both occurrences are related to the quantum nature of these liquids - liquid ^3He is behaving like a condensed Fermi gas at these low temperatures.

The latent heat for a phase transition is equal to the increase in enthalpy of the substance in the phase transition. This follows from integrating the thermodynamic identity

$$\tau d\sigma = dU + p dV - \mu_g dN_g - \mu_l dN_l,$$

where we have separated the counting of the two phases. The total number of particles in the system is fixed, so that $dN_l = -dN_g$, and we also know that $\mu_g = \mu_l$ during the phase transition. The pressure is also fixed during the phase transition, so that integrating through the phase transition gives

$$L = \tau \Delta\sigma = \Delta U + p \Delta V = \Delta H.$$

Absolute enthalpies are found by integrating the heat capacity at constant pressure:

$$C_p = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_p = \left(\frac{\partial U}{\partial \tau} \right)_p + p \left(\frac{\partial V}{\partial \tau} \right)_p = \left(\frac{\partial H}{\partial \tau} \right)_p,$$

so that

$$H = \int_0^\tau C_p d\tau.$$

4 Example: model system for gas solid coexistence

We model a solid as being made of atoms which act as independent simple harmonic oscillators of frequency ω . We will assume that the binding energy of each atom in the solid in its ground state is $-\epsilon_0$, *i.e.* the energy of an atom in the solid in its ground state is ϵ_0 less than the energy of a stationary free atom.

The partition function for a single atom is

$$Z_s = \sum_n \exp \left(-\frac{n\hbar\omega - \epsilon_0}{\tau} \right) = \frac{\exp \left(\frac{\epsilon_0}{\tau} \right)}{1 - \exp \left(-\frac{\hbar\omega}{\tau} \right)},$$

and the Helmholtz free energy is

$$F_s = -\tau \ln Z_s.$$

The Gibbs free energy per atom is

$$G_s = U - \tau \sigma_s + p v_s = F_s + p v_s = \mu_s.$$

Now the pressure in the gas is equal to the pressure in the solid, and the specific volume in the gas is much greater than that in the solid, so that we see that $p v_g \gg p v_s$. On the other hand, we must have $\mu_g = \mu_s$ in equilibrium. It follows that $p v_s$ must be negligible in the expression for G_s , and hence $F_s \simeq \mu_s$. We therefore have for the absolute activity of the solid phase

$$\lambda_s \simeq \exp \left(\frac{F_s}{\tau} \right) = \frac{1}{Z_s} = \exp \left(-\frac{\epsilon_0}{\tau} \right) \left[1 - \exp \left(-\frac{\hbar\omega}{\tau} \right) \right].$$

If we assume that the gas phase is ideal and that the atoms have spin zero, then for the gas

$$\lambda_g = \frac{n}{n_Q} = \frac{p}{\tau} \left(\frac{2\pi\hbar^2}{M\tau} \right)^{\frac{3}{2}}$$

(using the results for ideal gases). In equilibrium $\lambda_s = \lambda_g$, so that we get

$$p = \left(\frac{M}{2\pi\hbar^2} \right)^{\frac{3}{2}} \tau^{\frac{5}{2}} \exp \left(-\frac{\epsilon_0}{\tau} \right) \left[1 - \exp \left(-\frac{\hbar\omega}{\tau} \right) \right]$$

as the coexistence equation. The lone exponential term will dominate the behaviour of this expression when $\epsilon_0 \gg \tau$.

5 Van der Waals equation of state

Van der Waals modified the ideal gas equation of state,

$$pV = N\tau \quad \text{to} \quad \left(p + \frac{aN^2}{V^2}\right)(V - Nb) = N\tau,$$

where a and b are constants. These changes allow to some degree for the real interaction between the molecules in a gas. We will first consider how this equation comes about.

We have shown that for an ideal gas

$$F_{\text{ideal}} = -N\tau \left[\ln \left(\frac{nQ}{n} \right) + 1 \right].$$

Van der Waals first approximation is to treat the gas molecules as “billiard balls” — having hard surfaces, so that each molecule excludes the others from some volume surrounding itself. This is quite a reasonable model for the steep repulsive core in molecular interaction potentials. In this simple model a volume of space Nb , b constant, is excluded by the presence of the molecules, so that we replace V by $V - Nb$ in the expression for F ,

$$F = -N\tau \left[\ln \left\{ \frac{nQ(V - Nb)}{N} \right\} + 1 \right].$$

We also want to add a correction for the attractive interaction between molecules at moderate distances. For this we use the *mean field method*. The idea is to take the time average of the interaction potential between a molecule and its neighbours. We assume that the interaction has a negligible effect on the mean concentration of neighbours close to a molecule, so that the mean number within a volume dV is $n dV$. This ignores all effects of the molecule-molecule interactions on the mean particle concentration.

If $\phi(r)$ is the molecular interaction potential between two molecules separated by a distance r , then the mean interaction energy between one molecule and the rest of the gas is

$$\int_b^\infty \phi(r)n dV = n \int_b^\infty \phi(r) dV = -2na,$$

where this defines a ,

$$a = -\frac{1}{2} \int_b^\infty \phi(r) dV.$$

The total interaction energy is then

$$\Delta F = \frac{1}{2}N(-2na) = -\frac{N^2a}{V},$$

where we have been careful not to count the interaction energy twice.

We add this to the free energy, so that

$$F_{\text{vdW}} = -N\tau \left[\ln \left\{ \frac{nQ(V - Nb)}{N} \right\} + 1 \right] - \frac{aN^2}{V}.$$

We then have the pressure as

$$p = - \left(\frac{\partial F}{\partial V} \right)_{\tau, N} = \frac{N\tau}{V - Nb} - \frac{aN^2}{V^2},$$

which is the van der Waals equation of state stated above.

6 Critical point for the van der Waals gas

Depending on the value for τ , the pressure for a van der Waals gas can be a monotonically decreasing function of the volume, or it can have two turning points. Defining

$$\tau_c = \frac{8a}{27b},$$

for $\tau < \tau_c$ the above equation for the pressure has two turning points, while for $\tau > \tau_c$ it has none. When $\tau = \tau_c$, there is a point of inflection where the slope of the curve for p is zero, this occurs at

$$V_c = 3Nb \quad \text{and} \quad p_c = \frac{a}{27b^2}.$$

It is convenient to rewrite the equation in terms of

$$\hat{p} = \frac{p}{p_c}; \quad \hat{V} = \frac{V}{V_c} \quad \text{and} \quad \hat{\tau} = \frac{\tau}{\tau_c},$$

giving

$$\hat{p} = \frac{8\hat{\tau}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2}.$$

We see that the equation of state of all gases obeying the van der Waals equation is the same in terms of these variables - the *law of corresponding states*.

The following diagram shows $\hat{p}$ as a function of $\hat{V}$ for temperatures close to the critical temperature.

Values for a and b are usually determined empirically. Real gases only obey this equation approximately.

For $\tau < \tau_c$ (i.e. $\hat{\tau} < 1$),

$$\left(\frac{\partial \hat{p}}{\partial \hat{V}} \right)_{\tau, N} > 0$$

over a range of $\hat{V}$, which includes 1. This is physically unreasonable, since the pressure of the gas would decrease as it was compressed and increase as it expanded. In fact, such states are unstable and not really reachable. Instead, the van der Waals gas undergoes a phase transition starting from points at the same pressure outside this region.

The Gibbs free energy for the van der Waals gas is

$$G = F + pV = \frac{N\tau V}{V - Nb} - \frac{2aN^2}{V} - N\tau \ln \left[\frac{n_Q(V - Nb)}{N} \right] - N\tau,$$

which gives G as a function of (V, τ, N) , rather than in terms of the natural variables (p, τ, N) . We would like to have G in terms of the natural variables, since $G = \mu N$, and we would then be able to determine the coexistence curve by solving for $\mu_l(\tau, p) = \mu_g(\tau, p)$. Although the equation for p can

be inverted analytically to get $V(p)$ the result is very messy, so that we rely on numerical solution anyway. The following figure shows results for G versus p for the two cases $\tau = \tau_c$ and $\tau = 0.95\tau_c$.

At any given pressure and temperature it is the state with the lowest Gibbs free energy which is stable, so that the upper part of the curve represents the states which are bypassed in the phase transition. The curves for G versus τ at fixed p behave similarly (see Kittel & Kroemer).

Consider an isotherm in the p - V diagram for the van der Waals gas. If the phase transition occurs between V_1 and V_2 , then for $V < V_1$ the fluid is a liquid and for $V > V_2$ it is a gas. Between these two volumes is the region of the phase transition where the liquid and gas can coexist. Now for fixed τ and N we have

$$N d\mu = dG = -\sigma d\tau + V dp + \mu dN = V dp,$$

since the other terms are zero. If we integrate this through the region of the phase transition (following the curve for the homogeneous gas) we get

$$(\mu_g - \mu_l)N = \int_{V_1}^{V_2} p dV,$$

But the chemical potential must be the same in the coexisting phases, so that the integral must come to zero. It is easy to see that this is just the difference in the two areas marked in the figure, so that these are equal. This is the condition which governs the location of the actual transition pressure in the p - V diagram.

We have already discussed supercooling (*etc.*). One way that this comes about is due to the effect of surface energy on small droplets. The surface energy (or surface tension) γ of a liquid is the energy per unit area of free surface (due to dangling bonds *etc.*). If we consider the transfer of molecules from the gas phase into a small droplet of liquid the change in free energy is

$$\Delta G = G_l - G_g = \frac{4\pi}{3}R^3 n_l(\mu_l - \mu_g) + 4\pi R^2 \gamma,$$

where R is the radius of the droplet and n_l is the concentration of the liquid. The system moves towards the state of lowest Gibbs free energy, so that the droplet will grow provided that ΔG decreases as R increases, *i.e.* provided that

$$\frac{d\Delta G}{dR} = 4\pi R^2 n_l(\mu_l - \mu_g) + 8\pi R \gamma < 0.$$

This is always positive unless $\mu_g > \mu_l$ and R is sufficiently large, *i.e.* $R > R_c$, where the *critical radius for nucleation* is

$$R_c = \frac{2\gamma}{n_l \Delta\mu}$$

and $\Delta\mu = \mu_g - \mu_l$. In order to get the phase transition to start in a pure vapour contained in a clean and smooth vessel, it is necessary for the gas to be cooled slightly below the actual transition temperature so that $\mu_g > \mu_l$.

Assuming that the vapour behaves as an ideal gas,

$$\Delta\mu = \tau \ln \left(\frac{p}{p_{\text{eq}}} \right),$$

where p_{eq} is the equilibrium vapour pressure for the liquid. Taking $\gamma = 0.072 \text{ J m}^{-2}$, appropriate for water, $T = 300 \text{ K}$ and $p = 1.1p_{\text{eq}}$, we get $R_c \simeq 1.1 \times 10^{-8} \text{ m}$ (a critical droplet contains about 3×10^4 water molecules).

7 A model for ferromagnetism

Another use for the mean field approximation is to model ferromagnetism, where a substance spontaneously develops a magnetic moment. For this model we assume that when a material has a magnetization M , each atom within it experiences an effective magnetic field

$$B_E = \lambda M$$

(we ignore any external field).

Now we have shown that a system containing n atoms per unit volume, each having spin $\frac{1}{2}$ and magnetic moment μ , develops a magnetic moment

$$M = n\mu \tanh \left(\frac{\mu B}{\tau} \right)$$

in the presence of an external field B . If this is just the mean field of the other atoms, then this equation becomes

$$M = n\mu \tanh \left(\frac{\mu \lambda M}{\tau} \right),$$

a transcendental equation for the magnetic moment.

We can solve this graphically by setting

$$x = \frac{\mu \lambda M}{\tau},$$

so that the equation becomes

$$\frac{\tau}{n\mu^2\lambda} x = \tanh x.$$

If we plot $\tanh x$ and Ax on the same diagram, we see that for $A > 1$ the only solution for x is at $x = 0$, but for $A < 1$ this equation has solutions at finite x . The solutions correspond to the spontaneously magnetized ferromagnetic state. They occur when

$$\tau < \tau_c = n\mu^2\lambda,$$

where τ_c is known as the *Curie temperature*.

We can also use this to construct the magnetization curve for a ferromagnet, and the results roughly fit the data. The two most significant features of this curve are: 1) that the magnetization rapidly saturates as τ decreases below τ_c ; and 2) near to τ_c the magnetization behaves as

$$M \propto \sqrt{1 - \frac{\tau}{\tau_c}}.$$

8 Landau theory

There is a substantial body of physics involved in the study of phase transitions. The language that it uses is derived in large part from the terms introduced by Landau for a general discussion of phase transitions in systems described by a mean field theory.

We consider systems at fixed volume and τ , so that the Helmholtz free energy $F = U - \tau\sigma$ is minimized for systems in equilibrium. The minimization is completely general, but often it is useful to consider the minimization with respect to a single variable which is called the *order parameter* and denoted by ξ . Typical examples are the magnetization for a ferromagnet, the polarization for a ferroelectric substance or the fraction of superconducting electrons in a superconductor. (It is difficult to cleanly identify an order parameter in liquid to gas phase transitions).

The order parameter has an equilibrium value $\xi_0(\tau)$, which is the value which minimizes F . In order that F can be minimized with respect to ξ we must be able to specify

$$F_L(\xi, \tau) = U(\xi, \tau) - \tau\sigma(\xi, \tau)$$

in some neighbourhood of the equilibrium at $\xi = \xi_0$. We then have

$$F(\tau) = F_L(\xi_0, \tau) \leq F_L(\xi, \tau),$$

for any value of ξ for which this is meaningful. F_L may have other local minima, but the global minimum is the one which gives the equilibrium state of the system.

For convenience we will also assume that F is an even function of ξ when there are no external fields, and that it can be expanded in a power series in ξ :

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4 + \frac{1}{6}g_6(\tau)\xi^6 + \dots$$

The coefficients g_0, g_2, g_4, g_6 depend on the physical system of interest. Their values govern the shape of the surface which is the plot of $F_L(\xi, \tau)$, and it is this which determines the types of phase transition that can occur.

The first case that we will consider is that of a second order phase transition. This occurs when the coefficient g_2 changes sign at some temperature τ_0 . We can model this behaviour by assuming that

$$g_2(\tau) \simeq \alpha(\tau - \tau_0)$$

close to $\tau = \tau_0$. We ignore the coefficients of higher order than g_4 , so that this must be positive (so that F has a minimum). We then have

$$F_L(\xi, \tau) \simeq g_0(\tau) + \frac{1}{2}\alpha(\tau - \tau_0)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4.$$

This looks like:

The extrema of F are given as the roots of

$$\left(\frac{\partial F_L}{\partial \xi}\right)_\tau = \alpha(\tau - \tau_0)\xi + g_4\xi^3 = 0,$$

i.e.

$$\xi = 0 \quad \text{or} \quad \xi^2 = -\frac{(\tau - \tau_0)\alpha}{g_4}.$$

If $\alpha > 0$, then for $\tau > \tau_0$ the minimum of F_L occurs at $\xi = 0$. For $\tau < \tau_0$ the other root(s) give the minimum for F_L . This means that ξ_0 is zero for $\tau > \tau_0$ and

$$\xi_0 \propto \pm\sqrt{\tau_0 - \tau},$$

for $\tau < \tau_0$.

In such a phase transition the equilibrium state changes continuously, and the entropy is also continuous. Since the entropy is continuous, there is no latent heat required to take a system through such a phase transition. This type of transition is known as a *second order phase transition*. The Curie point for a ferromagnet is an example of a second order phase transition, as is the onset of superconductivity.

8.1 Example: ferromagnetism

We can show directly that the onset of ferromagnetism is a second order phase transition under the mean field model. The interaction energy in a ferromagnet is

$$U(M) = -\frac{1}{2}MB = -\frac{1}{2}\lambda M^2,$$

where the half eliminates double counting of the interaction energy. The entropy can be shown to have the form

$$\sigma(M) = \text{constant} - \frac{M^2}{2n\mu^2},$$

for small M , so that the free energy is

$$F_L(M) = \text{constant} - \frac{1}{2}M^2 \left(\lambda - \frac{\tau}{n\mu^2} \right) + \dots$$

According to the discussion above this puts the transition at

$$\tau_0 = n\mu^2\lambda,$$

as we found before.

9 First order phase transitions

When the free energy considered as a function of the order parameter has more than one local minimum, the global minimum in the free energy can flip between two of these minima at some temperature:

When this happens there is a discontinuous change in the equilibrium value of the order parameter and we get a *first order phase transition* (such as melting or boiling). Because the equilibrium

state of the system changes discontinuously at such a phase transition, so does the entropy, with the result that there is a finite latent heat required to make the transition.

We can model this in terms of our expansion for F_L with some additional conditions on the coefficients.

$$F_L = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4 + \frac{1}{6}g_6(\tau)\xi^6 + \dots$$

has extremes where

$$\left(\frac{\partial F_L}{\partial \xi}\right)_\tau \simeq g_2\xi + g_4\xi^3 + g_6\xi^5 = 0,$$

i.e. for $\xi = 0$ or at

$$\xi^2 = \frac{-g_4 \pm \sqrt{g_4^2 - 4g_6g_2}}{2g_6}.$$

Now F_L must increase at large ξ , since otherwise it would not have any global minimum, so that $g_6 > 0$. Unless both of the non-zero roots for ξ^2 are real and positive, F_L will have only one local minimum (at $\xi = 0$ if there is no other real root, and at the non-zero root if there is only one). We therefore require

$$g_4^2 > 4g_2g_6, \quad g_2 > 0 \quad \text{and} \quad g_4 < 0,$$

in which case F_L has local minima at $\xi = 0$ and at

$$\xi_1^2 = \frac{-g_4 + \sqrt{g_4^2 - 4g_6g_2}}{2g_6}.$$

A little further algebra shows that, under these conditions, the minimum at $\pm\xi_1$ is the global minimum whenever

$$g_4^2 > \frac{16}{3}g_2g_6,$$

while that at $\xi = 0$ is the global minimum otherwise.

For the sake of demonstration, we will assume that $g_4 < 0$ and $g_6 > 0$ are fixed, and that $g_2 = \alpha(\tau - \tau_0)$ again. In that case, for

$$\tau - \tau_0 \geq \frac{g_4^2}{4\alpha g_6}$$

the only local minimum in F_L is the one at $\xi = 0$ and this is the global minimum. For

$$\frac{3g_4^2}{16\alpha g_6} < \tau - \tau_0 < \frac{g_4^2}{4\alpha g_6},$$

there is a second local minimum at $\xi_1 > 0$, but the global minimum remains at $\xi = 0$. There is a first order phase transition at

$$\tau - \tau_0 = \frac{3g_4^2}{16\alpha g_6},$$

when the global minimum in F_L flips to $\xi_1(\tau)$, and this remains the stable state at lower temperatures.

Assignment: 1, 4, 7