

Chapter 5

Phase transitions

In this last section of the course we will look briefly at the theory of phase transitions such as the liquid-gas transition that occurs on boiling, or the ferromagnetic transition that occurs when the dipoles are aligned in a magnet.

5.1 Introduction

A *phase* is defined as a system (or part of a system) which is homogeneous in chemical composition and physical state, and has definite boundaries. For example the states of matter – gas, liquid and solid are different phases. Transitions between these states are called *phase transitions*. The phase of the system depends on the thermodynamic variables such as pressure and temperature. A phase diagram for a simple substance is shown in Fig. 5.1. The lines represent coexistence between the phases. For most substances the solid-liquid line has a positive gradient. However for water it has a negative gradient, so it is possible by increasing the pressure at fixed temperature to pass from vapour to solid to liquid.

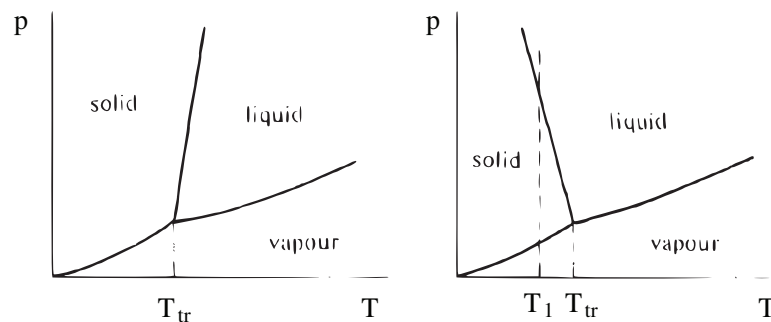


Figure 5.1: (left) A phase diagram for a typical solid-liquid-gas system. (right) A phase diagram for water which expands on freezing.

Phase transitions can be first-order or second order (also called a continuous phase transition). In first-order phase transitions such as the melting of ice there is an abrupt (discontinuous) change in the entropy. We must supply the latent heat of melting in the case of the solid/liquid phase transition of

water. In second order phase transitions, such as the ordering of a magnetic dipoles in a ferromagnet there is a continuous transition and no associated latent heat.

The *order parameter* is a useful tool in characterising a phase transition and provides a measure of order. This is a quantity that is zero in the disordered high temperature phase, and non-zero in the more ordered low temperature phase. For example in the ferromagnetic phase transition the magnetisation is the order parameter, whereas in the liquid-gas transition it is the density difference from the gas state.

Phase transitions can be described approximately using *mean field theory*. Here instead of describing all the interactions between particles in a system we replace them with their average effect acting on one particle. This dramatically simplifies the problem though it does exclude many effects such as the correlation between particles. We will now look at some examples of mean field theory descriptions of phase transitions.

Weiss theory of Ferromagnetic phase transition

We have modelled a spin $\frac{1}{2}$ particle in a magnetic field as a two level system, where the magnetic moment can be either parallel or antiparallel to the magnetic field. If the magnetic moment is of magnitude m_0 and the field strength B then the energy of the system is $U = \pm m_0 B$. The probability of a parallel (\uparrow) or antiparallel (\downarrow) spin can be calculated using the Boltzmann distribution

$$p_{\uparrow} = \frac{e^{m_0 B / (k_B T)}}{Z} \quad (5.1)$$

$$p_{\downarrow} = \frac{e^{-m_0 B / (k_B T)}}{Z} \quad (5.2)$$

$$Z = e^{-m_0 B / (k_B T)} + e^{m_0 B / (k_B T)}. \quad (5.3)$$

The average magnetic moment can be calculated as

$$\langle m \rangle = p_{\uparrow} m_0 - p_{\downarrow} m_0 = m_0 \tanh \frac{m_0 B}{k_B T} \quad (5.4)$$

In a ferromagnet the neighbouring magnetic moments interact with each other, so that as the system is cooled they can align with each other and form a ferromagnet. A mean field model of the ferromagnetic transition can be made by using the average orientation of the magnetic moments on each site, ω as the order parameter, i.e.

$$\omega = \frac{\langle m \rangle}{m_0}.$$

The probabilities p_{\uparrow} and p_{\downarrow} can be re-expressed in terms of the order parameter

$$p_{\downarrow} + p_{\uparrow} = 1 \quad \text{and} \quad p_{\uparrow} - p_{\downarrow} = \omega \quad (5.5)$$

$$\Rightarrow p_{\uparrow} = \frac{1 + \omega}{2} \quad (5.6)$$

$$p_{\downarrow} = \frac{1 - \omega}{2} \quad (5.7)$$

If we have two neighbouring spins that are parallel then they have a low energy $-J$. However, if the neighbouring spins are antiparallel then they are higher in energy J . The average energy between two neighbouring spins can be calculated by averaging over the four possibilities $\uparrow\uparrow, \downarrow\downarrow, \uparrow\downarrow$ and $\downarrow\uparrow$. The

probabilities of these four alternatives are

$$p_{\uparrow\uparrow} = \left(\frac{1+\omega}{2}\right)^2 \quad (5.8)$$

$$p_{\downarrow\downarrow} = \left(\frac{1-\omega}{2}\right)^2 \quad (5.9)$$

$$p_{\uparrow\downarrow} = p_{\downarrow\uparrow} = \left(\frac{1-\omega}{2}\right)\left(\frac{1+\omega}{2}\right) \quad (5.10)$$

The average interaction energy for two neighbouring spins is then

$$-J(p_{\uparrow\uparrow} + p_{\downarrow\downarrow}) + 2p_{\uparrow\downarrow}J = -J\omega^2 \quad (5.11)$$

If there are z neighbours for a spin, then it will share z bonds with neighbours. Hence the average energy per spin is

$$\langle E \rangle = -m_0\omega B - \frac{zJ}{2}\omega^2 = -m_0\omega \underbrace{\left(B + \frac{zJ}{2}\omega\right)}_{B_{\text{eff}}} \quad (5.12)$$

where B_{eff} is the effective magnetic field experienced by a spin due to both the external field and the interaction with neighbouring spins. The entropy can be calculated from the Gibbs expression for the entropy

$$S = -k_B \sum_i p_i \ln p_i \quad (5.13)$$

$$= -Nk_B \left[\left(\frac{1+\omega}{2}\right) \ln \left(\frac{1+\omega}{2}\right) + \left(\frac{1-\omega}{2}\right) \ln \left(\frac{1-\omega}{2}\right) \right] \quad (5.14)$$

where we have multiplied the entropy for one site by the number of spins N . The total free energy of the system is

$$F = \underbrace{-Nm_0\omega \left(B + \frac{zJ\omega}{2}\right)}_{\text{Energetic term}} + \underbrace{Nk_B T \left[\left(\frac{1+\omega}{2}\right) \ln \left(\frac{1+\omega}{2}\right) + \left(\frac{1-\omega}{2}\right) \ln \left(\frac{1-\omega}{2}\right) \right]}_{\text{Entropic term}} \quad (5.15)$$

The equilibrium value of ω can be found by minimising this expression over ω . This produces the result

$$\frac{\partial F}{\partial \omega} = -Nm_0B - zJNm_0\omega + k_B T \left(\frac{1}{2} \ln(1+\omega) - \frac{1}{2} \ln(1-\omega) \right) = 0 \quad (5.16)$$

$$\Rightarrow \omega = \tanh \frac{m_0 J \omega}{k_B T} \quad (5.17)$$

where we have set $B = 0$ in the second line (i.e. ignored the effect of the external field). This last non-linear equation can not be solved analytically, but it can be solved graphically. It has solutions $\omega = 0$ for all values of temperature, and an $\omega \neq 0$ solution for $T < T_c = \frac{m_0 J}{k_B}$. Below this temperature it has made a transition to the ferromagnetic state.

Bragg-Williams theory of β -brass ordering transition

β -brass is made up of an equal parts of copper (Cu) and zinc (Zn). At high temperatures it forms a body-centred cubic lattice with Cu and Zn randomly distributed between the lattice sites. At low

temperatures (below around 400°C) an ordering transition occurs. There are two types of sites the atoms can occupy which we shall call A and B . Below the transition temperature T_c the Cu and Zn atoms start ordering so that the Cu are at the centre of the unit cell and the Zn at the corners. As the temperature is lowered crystal becomes ordered until at $T = 0$ all the Cu atoms are at the centre of the unit cell, and the Zn atoms are at the corners of the unit cell. There is an anomaly in the heat capacity of the system at T_c that can be explained by this transition.

The order parameter here can be written as the difference in the concentration of Cu atoms on the sites of type A , and sites of type B .

$$\omega = \frac{n_A - n_B}{n_A + n_B} \quad (5.18)$$

where n_A denotes the concentration of Cu atoms on A sites, and n_B denotes the concentration of Cu atoms on B sites. If we have N sites in total, then $n_A + n_B = N/2$. The remaining sites are filled with the Zn atoms. Note we can write n_A and n_B in terms of ω which will be useful later

$$n_A = \frac{N}{4}(1 + \omega) \quad (5.19)$$

$$n_B = \frac{N}{4}(1 - \omega) \quad (5.20)$$

When the system is totally disordered $n_A = n_B$, i.e. we have an equal number of Cu atoms on the A and B sites, hence $\omega = 0$. When the system is completely ordered then $n_A = 1$ and $n_B = 0$, so $\omega = 1$. When there is partial ordering on the sites $0 < \omega < 1$.

To make a mean field model we will need the following probabilities

$$\text{Prob. Cu on } A \text{ site: } \frac{n_A}{N/2} = \frac{1 + \omega}{2} \quad (5.21)$$

$$\text{Prob. Cu on } B \text{ site: } \frac{n_B}{N/2} = \frac{1 - \omega}{2} \quad (5.22)$$

$$\text{Prob. Zn on } A \text{ site: } \frac{N/2 - n_A}{N/2} = \frac{1 - \omega}{2} \quad (5.23)$$

$$\text{Prob. Zn on } B \text{ site: } \frac{N/2 - n_B}{N/2} = \frac{1 + \omega}{2} \quad (5.24)$$

A mean field model of the system can be made by considering a pair of neighbouring sites – one A and one B . The interaction energy of the sites can be summarised as follows If we sum together all

Site occupants (A-B)	Interaction energy	Probability
Cu-Cu	u_{cc}	$\left(\frac{1+\omega}{2}\right)\left(\frac{1-\omega}{2}\right)$
Cu-Zn	u_{cz}	$\left(\frac{1+\omega}{2}\right)^2$
Zn-Cu	u_{cz}	$\left(\frac{1-\omega}{2}\right)^2$
Zn-Zn	u_{zz}	$\left(\frac{1+\omega}{2}\right)\left(\frac{1-\omega}{2}\right)$

these contributions then we can calculate the average energy of a pair of sites

$$\langle u \rangle = \left(\frac{1+\omega}{2} \right)^2 u_{cz} + \left(\frac{1-\omega}{2} \right)^2 u_{cz} + \left(\frac{1+\omega}{2} \right) \left(\frac{1-\omega}{2} \right) (u_{cc} + u_{zz}) \quad (5.25)$$

$$= \frac{\omega^2}{4} (2u_{cz} - u_{cc} - u_{zz}) + \frac{1}{4} (2u_{cz} + u_{cc} + u_{zz}) \quad (5.26)$$

We will denote $\Delta = -\frac{(2u_{cz} - u_{cc} - u_{zz})}{4}$. Note $\Delta > 0$ if a Cu-Zn pair has a lower energy when adjacent than the average of Cu-Cu and Zn-Zn. The other term in the average energy is simply a constant, so we will discard it. Hence our average energy of interaction per pair of particles is

$$\langle u \rangle = -\Delta\omega^2. \quad (5.27)$$

The entropy of the system can be calculated using Boltzmann's expression for the entropy. We will consider each set of sites at a time for the A sites we have $N/2$ sites, and n_A of these are Cu atoms, and $\frac{N}{2} - n_A$ are Zn atoms. Hence there are

$$W = \frac{(N/2)!}{n_A!(N/2 - n_A)!} = \frac{(N/2)!}{n_A!n_B!} \quad (5.28)$$

corresponding microstates. The expression for the B sites is exactly the same, so the entropy of the system is

$$S = k_B \ln \left(\frac{(N/2)!}{n_A!n_B!} \right)^2 \quad (5.29)$$

If we expand this expression using Stirling's approximation we obtain

$$S = 2k_B \left(\frac{N}{2} \ln \frac{N}{2} - n_A \ln n_A - n_B \ln n_B \right) \quad (5.30)$$

or in terms of the order parameter ω

$$S = Nk_B \left[\ln 2 - \frac{1}{2}(1+\omega) \ln(1+\omega) - \frac{1}{2}(1-\omega) \ln(1-\omega) \right] \quad (5.31)$$

The free energy can be calculated by combining our results

$$F = \underbrace{-\frac{N}{2}\omega^2\Delta}_{\text{Energy term}} - \underbrace{Nk_B T \left[\ln 2 - \frac{1}{2}(1+\omega) \ln(1+\omega) - \frac{1}{2}(1-\omega) \ln(1-\omega) \right]}_{\text{Entropic term}} \quad (5.32)$$

The order parameter ω takes a value that minimises this free energy at a particular temperature i.e.

$$\frac{\partial F}{\partial \omega} = 0.$$

If we minimise it with respect to ω we obtain the result

$$0 = -\omega\Delta - k_B T \left[-\frac{1}{2} \ln(1+\omega) + \frac{1}{2} \ln(1-\omega) \right] \quad (5.33)$$

$$\Rightarrow \omega = \tanh \frac{\omega\Delta}{k_B T} \quad (5.34)$$

where the last expression is obtained by exponentiating the previous line and rewriting using the hyperbolic tangent function. This equation is non-linear and cannot be solved analytically for ω . It can be solved graphically by plotting $y = \omega$ and $y = \tanh \frac{\omega\Delta}{k_B T}$. It can be seen that there is always a

solution $\omega = 0$. However if $\frac{\Delta}{k_B T} > 1$ we have an additional non-zero solution for ω . Hence below a critical temperature of $T_c = \frac{\Delta}{k_B}$ there is a transition to an ordered state. By using a Taylor series of the tanh function it can be shown that

$$\omega \approx \sqrt{3 \left(1 - \frac{T}{T_c}\right)} \quad (5.35)$$

for $T < T_c$. There is also a jump in the heat capacity when we cool below the transition temperature. The jump in the heat capacity from the ordering (ignoring the usual heat capacity components from phonons and electrons etc.) is

$$C_P = T \frac{\partial S}{\partial T} = T \frac{\partial S}{\partial \omega} \frac{\partial \omega}{\partial T} \approx \frac{3}{2} N k_B \quad (5.36)$$

5.2 Landau theory

Mean field theories such as the examples considered in this chapter can be generalised for any order parameter. The Helmholtz free energy F can be written down as a power series expansion on the relevant order parameter m . The terms in the power series must have suitable symmetry. For example consider a magnetic system with order parameter, m given by the component of the magnetic dipole in the z direction. If this system has mirror symmetry around the z axis then the terms in the power series should be invariant when $m \rightarrow -m$, i.e. they must be even powers of m

$$F(m) = F_0 + \frac{a}{2} m^2 + \frac{b}{4} m^4 + \dots \quad (5.37)$$

In Landau theory we assume that we are near the transition so the order parameter is small, and a power series expansion is justified. The quantity $a(T)$ is small near the critical temperature. By minimising this free energy with respect to m we can find the equilibrium of the system

$$\frac{dF}{dm} = m(a + bm^2) = 0 \quad (5.38)$$

Hence we have solutions

$$m = 0 \quad \text{or} \quad m = \pm \sqrt{\frac{a}{b}} \quad (5.39)$$

In the second order transition $b > 0$ and

$$a(T) = \alpha(T - T_c) \quad (5.40)$$

hence for $T > T_c$ the $m = 0$ solution is the only one possible, where as for $T < T_c$ there is a new stable solution with $m = \pm \sqrt{\frac{a}{b}}$. The entropy of the system can be calculated from the usual differential relation

$$S = -\frac{\partial F}{\partial T} = \begin{cases} -\frac{\alpha^2(T_c - T)}{2b} & T < T_c \\ 0 & T > T_c \end{cases} \quad (5.41)$$

Hence there is a discontinuity in the specific heat at the transition temperature of

$$\Delta C = -\frac{\alpha^2}{2b}. \quad (5.42)$$

A link to the previous non-linear calculations can be made by making a Taylor series expansion of the free energy. For example if we expand the β -brass free energy of Eq. (5.32) close to $\omega = 0$ we find

$$F \approx \frac{1}{2} N k_B \left(T - \frac{\Delta}{k_B}\right) \omega^2 + \frac{1}{12} k_B N T \omega^4 + \dots \quad (5.43)$$

which has exactly the same form as the power series expansion of Landau theory.