

Chapter 3

Phase transitions

3.1 Introduction

Phase transitions are ubiquitous in Nature. We are all familiar with the different phases of water (vapour, liquid and ice), and with the change from one to the other. Changes of phase are called *phase transitions*. These phenomena are very important not only in natural processes, but also in industry. To name just a few everyday examples: the evaporation of liquids, formation of ice or liquid water sheets on surfaces, construction of different materials in metallurgy...

Here we give an elementary introduction to the subject of phase transitions. This is a vast subject, and a lot of research effort is still being dedicated to phase transitions, both from experimental and theoretical points of view. The first microscopically-based understanding of phase transitions is due to van der Waals, who in 1873 presented a primitive theory of the gas-liquid transition. In his doctoral thesis he presented the van der Waals equation of state, and linked its parameters to a molecular model. Even though it was a first attempt, it laid down the basic ideas on which the modern theoretical understanding is based. Later, Landau (1937) proposed a phenomenological (not fully microscopic) approach that was crucial to understand second-order phase transitions and later developments. Another paramount step forward was given by Wilson (1971) and others, who developed a powerful and unifying set of concepts (basically the idea of scaling close to critical points and the renormalisation group) for second-order phase transitions. First-order transitions are less well understood, and current work relies almost exclusively on mean-field theory, which we shall review and apply in various contexts.

3.2 Thermodynamics of phase transitions

Let us start with the so-called *phase diagram* of a simple substance. A phase diagram is a representation, typically in a plane, of the regions where some substance is stable in a given phase. The axes represent external control variables (intensive parameters), such as pressure, temperature, chemical potential or an external field, or sometimes one extensive variable (volume, magnetisation, etc.) Density is sometimes used in the case of fluids. The different phases are separated by lines, indicating phase transitions, or regions where the system is unstable.

Let us review some of the most important features of the phase diagram of a simple substance. In Fig. 3.1(a) the phase diagram is represented in the pressure-temperature (p - T) plane. The three possible phases (solid, liquid and gas) are separated by *first-order phase transition lines* (continuous lines in the graph) where two phases coexist at the same time (hence the name ‘coexistence lines’). Phases are indicated by their names, and two special points are called T (*triple point*) and C (*critical point*).

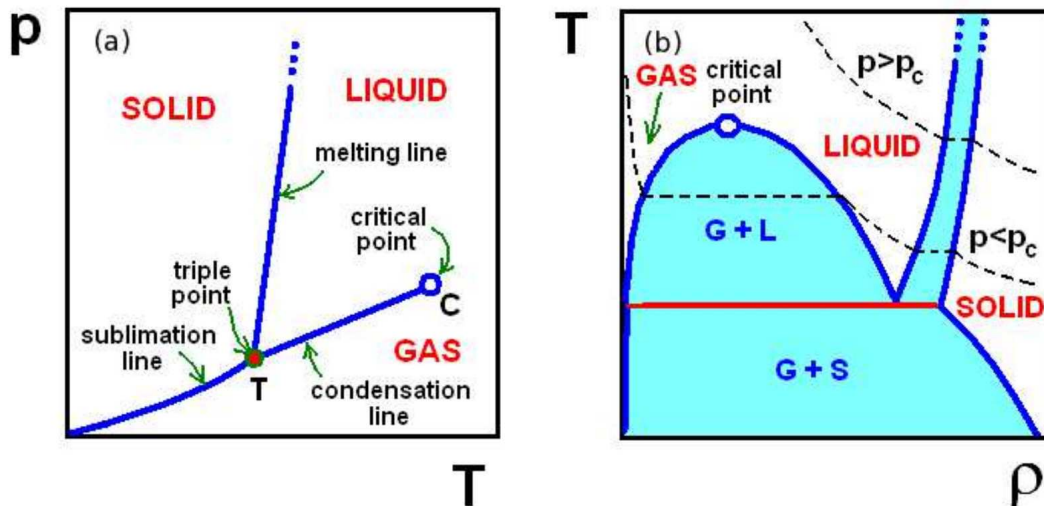


Figure 3.1: (Colour on the Web). Schematic phase diagram in the (a) pressure-temperature, and (b) temperature-density plane.

The three coexistence lines are:

- sublimation line: here the solid coexists with the gas. This line exists from zero temperature up to the triple-point temperature, T_3 . On lowering the temperature at constant pressure starting from the gas side, the gas would reach the sublimation line, at which crystallites would begin to form until the whole system becomes a crystal. Conversely, when crossing the line from the crystal side, gas would begin to sublime from the crystal until the system has passed to gas entirely. Any other trajectory on the diagram would lead to a similar behaviour.
- melting line, also called *fusion line*: here the solid coexists with the liquid. On crossing this line from the liquid side the system would begin to crystallise; conversely, the crystal would melt in the other direction. This line exists from T_3 up to infinite temperature (there is no upper limit in the melting line). This means that one cannot pass from liquid to crystal (or the other way round) without crossing the transition line, a result coming from the essentially different symmetries of these phases (full translational and rotational invariance in the liquid turn into discrete symmetries in the case of the crystal phase).
- condensation line, also called *vapour-pressure line*: here the gas coexists with the liquid. On crossing the line from the gas side the system begins to form droplets of

liquid on the condensation line, which grow and coalesce until all the material has passed to the liquid phase. Conversely, from the liquid side, gas bubbles form at the line, which grow and coalesce until all the material has transformed into gas. This is also called vapour-pressure line because it gives the maximum pressure the system can stand as a gas for a given temperature. The line begins at the triple point and ends at the *critical point*, C , with T_c the critical temperature and p_c the critical pressure. Above this point C there is no distinction between gas and liquid, and one may continually pass from gas to liquid, without ever crossing the transition line, by going into the supercritical region. This indicates that there is basically one fluid phase, which can be understood from the point of view of symmetry since both phases, liquid and gas, have the same symmetries (rotational and translational invariance).

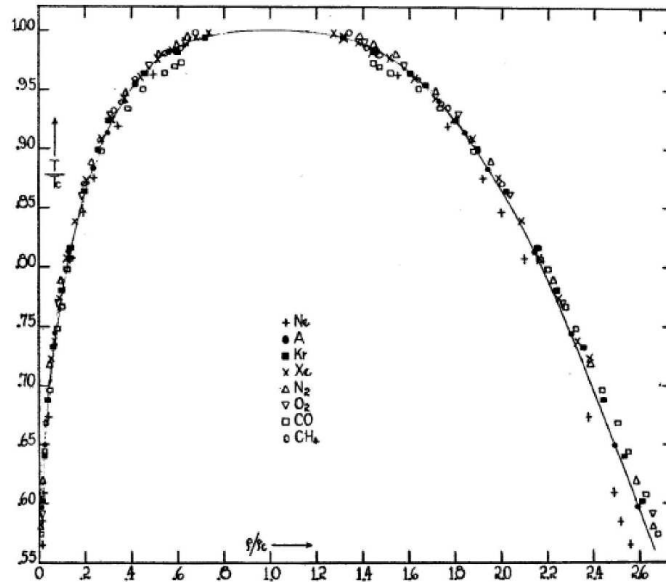


Figure 3.2: Original graph by Guggenheim (1945) where the law of corresponding states was first shown with experimental data on a reduced temperature vs. reduced density phase diagram for a number of substances.

All these transitions are first-order phase transitions, which are accompanied by a latent heat (the system absorbs or gives energy to the heat bath) and a change in density (or volume). A different phenomenon is the critical point, where no such discontinuities occur. A critical point is an example of a *continuous phase transition*.

In Fig. 3.1(b) the phase diagram is represented in the temperature-density plane. Shaded regions correspond to *coexistence regions* where the system presents two phases at the same time. In dashed line different *isobars* [i.e. the curves $T = T(\rho, p)$ for fixed pressure] at different temperatures are represented. Below the critical pressure p_c the isobars have two horizontal sectors corresponding to the gas-liquid and liquid-solid phase transitions. Above p_c only one plateau (that corresponding to the liquid-solid phase transition at T_c) can occur. Exactly at the critical pressure the isobar develops an instability where the inverse compressibility becomes zero, a behaviour that is reproduced by the simple

statistical-mechanical theories developed so far (extended second-virial coefficient and perturbation theory).

An intriguing feature of the liquid-gas coexistence curve is that it approximately follows the *law of corresponding states*: When the coexistence line $T - \rho$ is plotted in scaled units, using T_c and the critical density ρ_c as units of temperature and density, the experimental data approximately lie on a single universal line. This is followed by a large number of substances, except a few ones (typically very light elements). In Figs. 3.2 and 3.3 the phase diagrams of some noble gases (Ar, Ne, Kr and Xe) are displayed in reduced units, i.e. units scaled by the values of the critical parameters:

$$\rho^* = \frac{\rho}{\rho_c}, \quad T^* = \frac{T}{T_c}, \quad p^* = \frac{p}{p_c}. \quad (3.1)$$

The different data collapse into a single line when plotted in reduced units; therefore the liquid-gas coexistence line becomes ‘universal’. Some other molecular substances also follow this law. The law is rather remarkable considering the disparate values of critical parameters of the substances; some data are given below:

	T_c (K)	p_c (atm)	ρ_c (g cm ³)
H ₂ O	647.5	218.5	0.325
CO ₂	304.2	72.8	0.46
O ₂	154.6	49.7	0.41
Xe	289.8	57.6	1.105
Ar	150.8	48.3	0.53

Gibbs phase rule

Let us now discuss the *coexistence conditions*, i.e. the conditions that two phases have to satisfy in order to coexist on a firstorder transition line and therefore *with the same thermodynamic conditions*. Two coexisting phases have the same thermodynamic Gibbs free energy per particle¹ $\mu = G/N$ at the coexistence line; outside of this line one or the other is the most stable phase. Thermodynamics says that in order for two systems in contact to be in equilibrium (in our case two phases of the same substance) there must be mechanical, thermal and chemical equilibrium. Let us denote by a and b the two phases; then

$$T_a = T_b, \quad p_a = p_b, \quad \mu_a = \mu_b. \quad (3.2)$$

But the chemical potential is a function of (p, T) (remember that according to the Gibbs-Duhem equation, μ , p and T are not independent). Therefore, at two-phase coexistence (i.e. on a coexistence line, for example, the condensation line),

$$\mu_a(p, T) = \mu_b(p, T). \quad (3.3)$$

This gives a relation between p and T , e.g. $p = p(T)$ which is a line on the p - T phase diagram. Is it possible to have three (a , b and c), instead of two, phases coexisting at the same time? We should have

$$\mu_a(p, T) = \mu_b(p, T) = \mu_c(p, T), \quad (3.4)$$

¹Here we should remember that Euler’s theorem applied to the Gibbs free energy gives $G = N\mu$, see Eqn. (1.27).

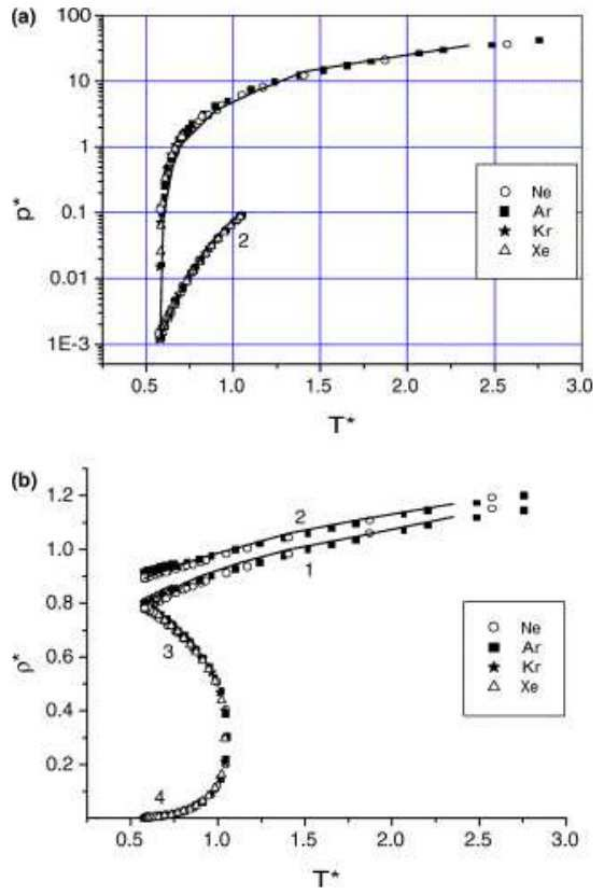


Figure 3.3: (Colour on the Web). (a) Reduced pressure $p = p/p_c$ and (b) equilibrium coexistence densities $\rho = \rho/\rho_c$ versus reduced temperature $T = T/T_c$ along the phase coexistence curves for Ar, Ne, Kr and Xe. Figure taken from Vorobev, Chem. Phys. Lett. **383**, 359 (2004).

which leads to a single point, the triple point, on the phase diagram. We can see that it is not possible to have more than three phases coexisting at the same time for a simple one-component substance, except in very special circumstances.

Let us now consider a more general system, namely a mixture of l components, characterised by the parameters $(N, p, T, x^{(i)})$, where $x^{(i)} = N^{(i)}/N$ [with $N^{(i)}$ the number of particles of species i and N the total number of particles] is the molar fraction or composition of the i -th species. Note that $\sum_i x^{(i)} = 1$ so that only $l - 1$ mole fractions are independent. Let us denote by $\mu^{(i)}$, $i = 1, 2, \dots, l$ the chemical potential of the i -th species. In order to have coexistence between r different phases a_1, a_2, \dots, a_r , we must have

$$\begin{aligned}
 \mu_{a_1}^{(1)}(p, T, \{x^{(i)}\}) &= \mu_{a_2}^{(1)}(p, T, \{x^{(i)}\}) = \dots = \mu_{a_r}^{(1)}(p, T, \{x^{(i)}\}), \\
 \mu_{a_1}^{(2)}(p, T, \{x^{(i)}\}) &= \mu_{a_2}^{(2)}(p, T, \{x^{(i)}\}) = \dots = \mu_{a_r}^{(2)}(p, T, \{x^{(i)}\}), \\
 &\dots \\
 \mu_{a_1}^{(l)}(p, T, \{x^{(i)}\}) &= \mu_{a_2}^{(l)}(p, T, \{x^{(i)}\}) = \dots = \mu_{a_r}^{(l)}(p, T, \{x^{(i)}\}).
 \end{aligned} \tag{3.5}$$

This is a set of $(r - 1) \times l$ equations. The number of unknowns is $2 + r \times (l - 1)$, corresponding to p, T and the $l - 1$ mole fractions in each of the r phases. Then we must necessarily have:

$$(r - 1)l \leq 2 + r(l - 1) \rightarrow r \leq l + 2. \quad (3.6)$$

This is the famous *Gibbs phase rule*. For $l = 1$ (one-component system) $r \leq 3$, so that we have at most three phases coexisting at the same time (triple point). For $l = 2$ (binary mixture) we have $r \leq 4$ so that we may have up to a quadruple point where four phases coexist simultaneously, and so on. In general, for l components, the phase diagram has to be plotted in the $l + 1$ -dimensional space $(p, T, x^{(1)}, x^{(2)}, \dots, x^{(l-1)})$ [note that N is not relevant since G , which determines all properties of the system, is simply proportional to N , i.e. $G(N, p, T) = N\mu(p, T)$] and in this diagram we may have subspaces of dimensionality $d = l + 1, l, l - 1, \dots, 2, 1$ and 0 , with $r = l + 2 - d$ phases coexisting in each subspace, corresponding respectively to ‘volumes’ (one stable phase, $r = 1, d = l + 1$), ‘areas’ (two coexisting phases, $r = 2, d = l$), ‘lines’ (three coexisting phases, $r = 3, d = l - 1$), ..., and finally ‘points’ ($r = l + 2$ coexisting phases in subspaces of dimension $d = 0$). The Gibbs phase rule relates phase coexistence to the topology of the phase diagram.

Clausius-Clapeyron equation

This is again a result for first-order phase transitions. Suppose two phases of a one-component system coexist on a coexistence line (e.g. liquid and gas on the condensation line). We have $\mu_a(p, T) = \mu_b(p, T)$. If we move along the coexistence line by differential amounts dp and dT , we will have $\mu_a(p + dp, T + dT) = \mu_b(p + dp, T + dT)$, since we are still at coexistence. Then:

$$\begin{aligned} \mu_a(p, T) + \left(\frac{\partial \mu_a}{\partial p}\right)_T dp + \left(\frac{\partial \mu_a}{\partial T}\right)_p dT &= \mu_b(p, T) + \left(\frac{\partial \mu_b}{\partial p}\right)_T dp + \left(\frac{\partial \mu_b}{\partial T}\right)_p dT, \\ \left(\frac{\partial \mu_a}{\partial p}\right)_T \left(\frac{dp}{dT}\right)_{\text{coex}} + \left(\frac{\partial \mu_a}{\partial T}\right)_p &= \left(\frac{\partial \mu_b}{\partial p}\right)_T \left(\frac{dp}{dT}\right)_{\text{coex}} + \left(\frac{\partial \mu_b}{\partial T}\right)_p. \end{aligned} \quad (3.7)$$

But using the Gibbs-Duhem equation, $Nd\mu - Vdp + SdT = 0$, we have

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{1}{\rho}, \quad \left(\frac{\partial \mu}{\partial T}\right)_p = -\frac{S}{N} \equiv -s \quad (3.8)$$

(where s is the entropy per particle), so that we arrive at the *Clausius-Clapeyron equation*:

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{s_a - s_b}{v_a - v_b} = \frac{s_a - s_b}{V_a - V_b} = \frac{\Delta S}{\Delta V}, \quad (3.9)$$

where $v = 1/\rho = V/N$ is the specific volume (volume per particle), ρ_a and ρ_b the densities of the coexisting phases, and ΔS and ΔV the jumps of the entropy and volume at the transition line at (p, T) . Incidentally, in view of the finite value of the derivative dp/dT at coexistence, the Clausius-Clapeyron equation explains why a first-order phase transition is characterised by discontinuous changes in entropy and volume (or density). ΔS gives

the heat L that is transferred from the system to the environment as $L \equiv \delta Q = T\Delta S$, called the *latent heat*.

We can apply this equation to the liquid-gas coexistence line. The derivative of the coexistence curve at any point is given by (3.9). Since this derivative is positive, ΔS and ΔV must have the same sign. The sign depends on the identification of a and b . Let us associate a with the gas and b with the liquid. Since $V_a > V_b$ (because the gas has a larger volume) we must have $S_a > S_b$: the gas has more entropy, as it should be if we are to identify entropy with disorder. When going from a low-temperature phase to a high-temperature phase entropy always increases, $\Delta S > 0$, because $C_p = T(\partial S/\partial T)_p > 0$. But the sign of ΔV is more uncertain. Generally it is also positive, but in some cases it is negative; a paradigmatic example is that of freezing in water: when going from ice to liquid water $\Delta S > 0$ but $\Delta V < 0$ (since ice is less dense than liquid water at coexistence) which implies that the slope of the freezing line is negative. We see that the Clausius-Clapeyron equation allows us to identify some basic properties of first-order phase transitions on the basis of the slope of the coexistence line.

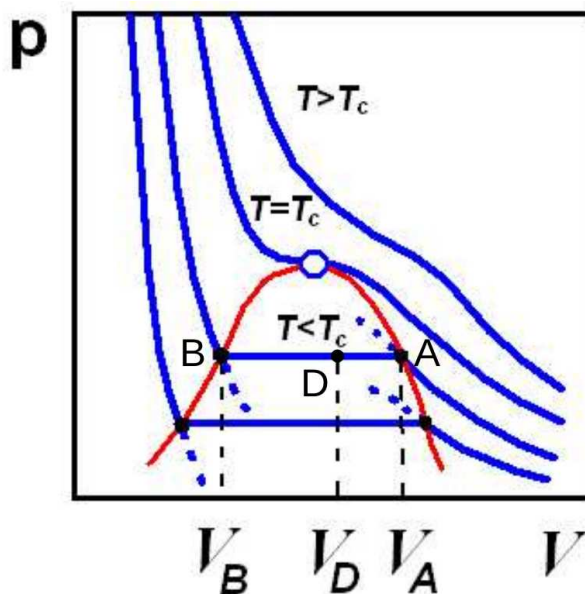


Figure 3.4: (Colour on the Web). Schematic pressure-specific volume phase diagram for different temperatures above, equal to and below the critical temperature T_c . Coexistence conditions are represented by the horizontal lines. The red line is the envelope of coexistence specific volumes. Dashed lines represent metastable states (see later in the chapter).

Lever rule

Let us reconsider the liquid-gas phase transition which will allow us to introduce a few new concepts. Fig. 3.4 illustrates the phase diagram in the $p - V$ plane. Again we have drawn isotherms for $T < T_c$, $T = T_c$ and $T > T_c$, but let us focus on the first. The coexistence line is represented by a heavy line. The dotted sectors of the gas and liquid branches rep-

resent the metastable states, i.e. mechanically stable (with positive compressibility) but thermodynamically unstable states (since it is more favourable energetically to proceed with the phase transition); in fact it is possible to prepare metastable states in very pure substances by special procedures. We will comment on these states later. What happens as we compress the gas at fixed temperature below the critical temperature? The pressure follows the isotherm until it reaches point A; here liquid droplets begin to form in the system. As the system is further compressed, it moves along the horizontal line AB (at constant pressure) until the whole amount of gas has condensed into liquid at B. From there on the system follows the same isotherm with increasing values of the pressure. At all points between A and B the system is a mixture of gas and liquid. Take point D, with global density ρ_D (the density of the liquid regions will be ρ_A and that of the gas regions will be ρ_B). Take $v_D = 1/\rho_D$ to be the total specific volume, and $v_A = 1/\rho_A$ and $v_B = 1/\rho_B$ the specific volumes of gas and liquid. Then

$$v_D = \frac{N_A}{N}v_A + \frac{N_B}{N}v_B = x_A v_A + x_B v_B, \quad (3.10)$$

where N_A , N_B are the number of molecules in the gas and liquid regions, respectively, x_A , x_B the mole fractions, and $N = N_A + N_B$ the total number of molecules. Since $x_A + x_B = 1$, multiplying:

$$(x_A + x_B)v_D = x_A v_A + x_B v_B \quad \rightarrow \quad \frac{x_A}{x_B} = \frac{v_B - v_D}{v_D - v_A}. \quad (3.11)$$

This is the so-called *lever rule*: the ratio of mole fractions is equal to the inverse ratio of the distance between the specific volumes of the phases to the global specific volumes.

Behaviour of thermodynamic potentials: types of phase transitions

In discussing phase transitions it is convenient to use the Gibbs free energy, $G = G(N, p, T)$ since it depends on two intensive variables, (p, T) , which are the same for the two phases that coexist at a first-order phase transition line. G satisfies the stability criterion $d^2G > 0$ which, as explained in Chapter 1, leads to a number of stability conditions on the response functions. For example:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2} \right)_T > 0, \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p > 0. \quad (3.12)$$

These conditions, together with the relations

$$V = \left(\frac{\partial G}{\partial p} \right)_T, \quad S = - \left(\frac{\partial G}{\partial T} \right)_p, \quad (3.13)$$

are sufficient to obtain some conclusion as to the form of the function $G/N = \mu = \mu(p, T)$ as a function of p and T .

In Fig. 3.5 the volume vs. pressure is plotted in a region where there is no phase transition. In part (a) the volume V (which of course is positive) is plotted, as a monotonically decreasing function of pressure p , as it should be in view of the stability condition $\kappa_T > 0$;

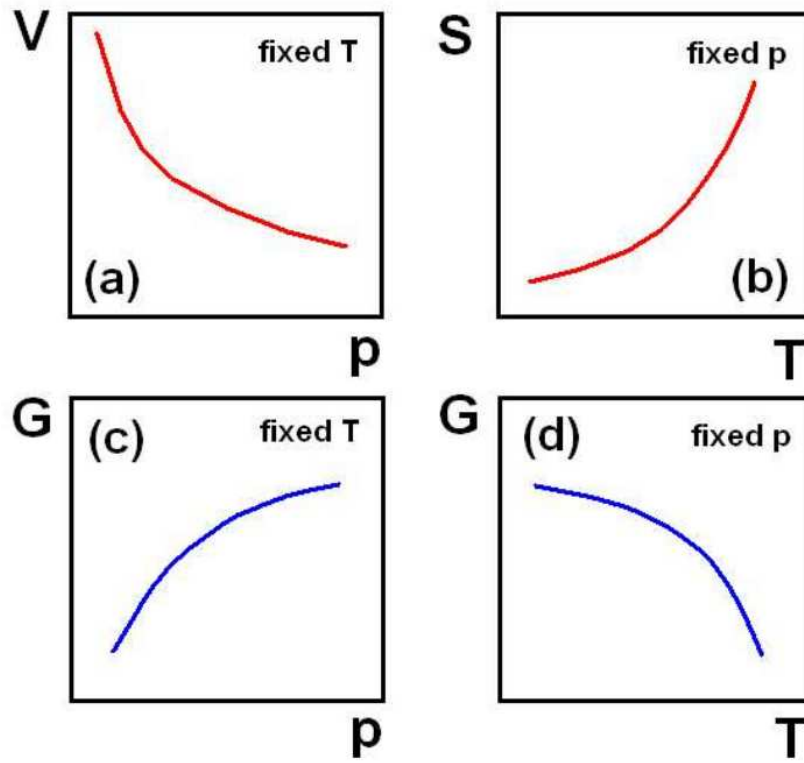


Figure 3.5: (Colour on the Web). Behaviour of Gibbs free energy $G(N, p, T)$ and its first derivatives V and S for fixed N with respect to p [at fixed T], (a) and (c), and with respect to T [at fixed p], (b) and (d), when there is no phase transition.

these two facts allow one to plot the function $\mu(p, T)$ for fixed T in part (b) as a monotonically increasing function of p , but with negative second derivative (that is, as a concave function). In panels (c) and (d) the dependence of $\mu(p, T)$ with T is discussed; note that $S > 0$, that $C_p > 0$ suggests that S increases monotonically with T and finally that $\mu(p, T)$ is also a concave function with respect to T at fixed p . Note that μ (and therefore G) is always continuous.

When a first-order transition is present, the situation changes. We have seen that there is an associated latent heat at the transition, so that the entropy must be discontinuous. Also, the volume is discontinuous. This is reflected in Fig. 3.6. The effect of all this on μ is the existence of a ‘kink’ at the transition, both with respect to p and T . Again G (but *not* its first derivatives, reflecting jumps in entropy and volume) is a continuous function of its variables.

A similar analysis can be made based on the Helmholtz free energy $F = F(N, V, T)$. But here p is replaced by V , which is discontinuous at the transition. Also, one expects $p > 0$ so that $\partial F / \partial V < 0$, and

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(\frac{\partial p}{\partial V} \right)_T = \frac{1}{V} \left(\frac{\partial^2 F}{\partial V^2} \right)_T > 0, \quad (3.14)$$

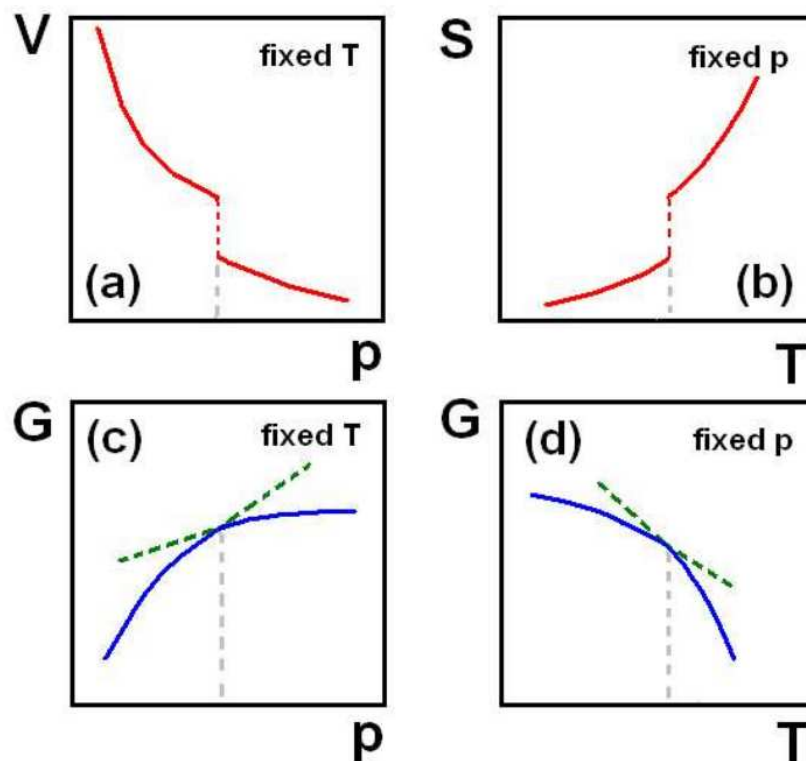


Figure 3.6: (Colour on the Web). Same as Fig. 3.5 but when there is a first-order phase transition. The discontinuity of G at the transition is indicated by plotting in dashed lines the tangents on both sides of the transition.

so that F is an overall convex function of V . With this proviso the dependence of F on V at constant temperature T when a phase transition is present can be plotted as in Fig. 3.7. Note the linear sector joining the two coexisting states, along which the phase transition takes place (i.e. the two phases exist at the same time in varying proportions).

But there are other types of phase transitions. Older classification schemes (e.g. that due to Ehrenfest) have been revised and nowadays all transitions not being of first order are called second-order or (preferably) continuous phase transitions. Here not only G but also its first derivatives are continuous functions (therefore there is no latent heat or volume discontinuities); it is the second derivatives of G (i.e. the response functions) that may exhibit anomalies. The anomalies may be of two types: either discontinuities, or divergencies (logarithmic, power-law or otherwise). For example, Fig. 3.8 shows the divergence of the constant-pressure heat capacity of a sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, which is a high- T_c superconductor, at the superconductor phase transition.

3.3 Mean-field theory: van der Waals theory

From now on we consider the problem of phase transitions from the point of view of statistical mechanics, seeking an explanation in terms of microscopic properties. We have already obtained van der Waals equation essentially by two methods: calculation of virial

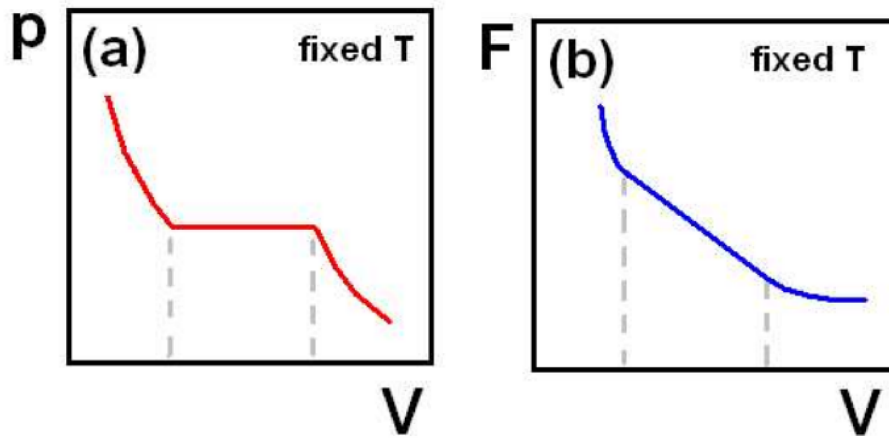


Figure 3.7: (Colour on the Web). Behaviour of F when there is a first-order phase transition. The horizontal sector in the $p = p(V)$ curve is transformed into a linear sector in $F = F(V)$. In the case when there is no phase transition this linear sector is absent.

equation of state up to second order and resummation of the hard-sphere contribution to the pressure (Clausius equation) and direct use of perturbation theory. There is yet a third way, which is more general in the sense that it contains the idea of a *mean field* which pervades the field of statistical mechanics. Also, we will study the instability predicted by van der Waals theory in more detail, which will help us get acquainted with many of the basic features of phase transitions.

Consider the configurational partition function of a classical simple fluid:

$$Z_N = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)}. \quad (3.15)$$

Suppose that the effect of particles on a given one can be represented by means of an effective one-particle potential ϕ acting on each particle separately but being otherwise identical for all the particles:

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \phi(\mathbf{r}_i). \quad (3.16)$$

The configurational partition function can then be factorised:

$$Z_N = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N e^{-\beta \sum_i \phi(\mathbf{r}_i)} = \left[\int_V d\mathbf{r} e^{-\beta \phi(\mathbf{r})} \right]^N. \quad (3.17)$$

This is the general expression of the *mean-field approximation* for a classical fluid. Different choices for $\phi(\mathbf{r})$ give different implementations of the theory. In essence, the mean-field approach is an ideal approximation in the sense that it apparently decouples the degrees of freedom. But there is more than meets the eye: the mean field is meant to contain not only the contribution of any external field but also, indirectly and in an average way, the effect on a given particle of the remaining ones.

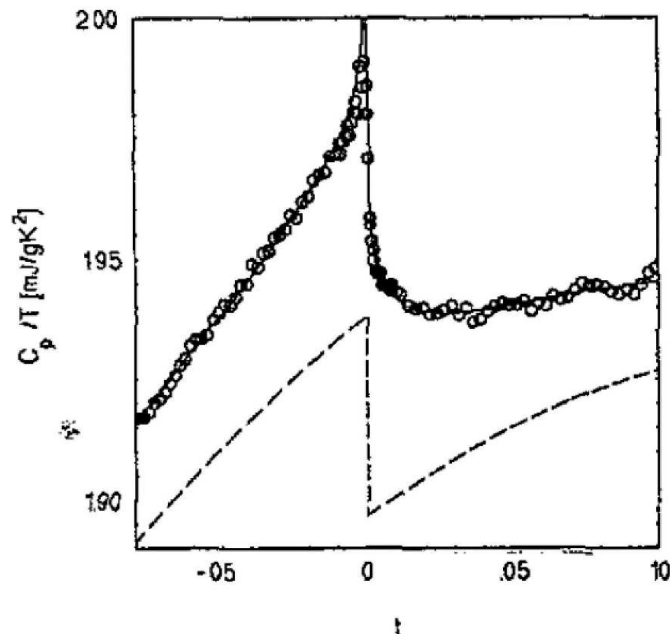


Figure 3.8: Constant-pressure heat capacity divided by temperature, c_p/T , of a sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at the superconductor phase transition. In this case the divergence is logarithmic. More details to be found in Regan et al., *J. Phys.: Condens. Matter* **3**, 9245 (1991). The temperature axis is $t \equiv (T - T_c)/T_c$.

So all we are left to do is choosing an adequate effective potential $\phi(\mathbf{r})$. A simple choice can be made if we bear in mind that the real pair potential has repulsive and attractive contributions: in the integral over \mathbf{r} (the positions of a given particle, all the others being equivalent) only the regions where there is no particle overlap contribute. So we subtract the volume excluded to a given particle by the remaining $N - 1$ particles, V_{exc} , coming from the repulsive (exclusion) interactions, and leave a constant (attractive) contribution $u_0 < 0$ (constant in the sense that it does not depend on the positions of the other particles but in an average way). Then

$$Z_N = \left[(V - V_{\text{exc}}) e^{-\beta u_0} \right]^N, \quad (3.18)$$

and

$$Q = \frac{Z_N}{N! \Lambda^{3N}} = \frac{\left[(V - V_{\text{exc}}) e^{-\beta u_0} \right]^N}{N! \Lambda^{3N}}. \quad (3.19)$$

The Helmholtz free energy is then:

$$F = kT \log (N! \Lambda^{3N}) - NkT [\log (V - V_{\text{exc}}) - \beta u_0]. \quad (3.20)$$

The pressure is

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{NkT}{V - V_{\text{exc}}} - N \left(\frac{\partial u_0}{\partial V} \right)_T. \quad (3.21)$$

Since it is reasonable to assume that u_0 be proportional to the density (i.e. to the number of particles), $u_0 = a\rho$, and that there will be a contribution to V_{exc} from each of the $N - 1$ particles, $V_{\text{exc}} = bN$ (we take $N - 1 \simeq N$), we obtain

$$p = \frac{\rho kT}{1 - b\rho} - a\rho^2, \quad (3.22)$$

which is van der Waals' equation of state. Connection of the energy constant a and the volume constant b with molecular parameters of a particular model, the squarewell fluid, is given in section 2.3.2, where we found $b = 2\pi\sigma^3/3$ and $a = 2\pi\lambda\sigma^3/3$, with σ the hard-sphere diameter, and ϵ the well depth; λ is related to the breadth of the well δ by Eqn. (2.32). This identification is not crucial at the moment and we will keep on using a and b as the system constants.

We already made the observation that the second term in the righthand side of (3.22) can make the compressibility to be negative. To see this more explicitly, let us calculate the derivative $(\partial p/\partial\rho)_{N,T}$:

$$(kT)^{-1} \left(\frac{\partial p}{\partial\rho} \right)_{N,T} = \frac{\partial}{\partial\rho} \left\{ \frac{\rho}{1 - b\rho} - \frac{a\rho^2}{kT} \right\} = \frac{1}{(1 - b\rho)^2} - \frac{2a\rho}{kT}. \quad (3.23)$$

From here the inverse compressibility is

$$\left(\frac{\kappa_T}{\kappa_T^0} \right)^{-1} = \frac{1}{(1 - b\rho)^2} - \frac{2a\rho}{kT}. \quad (3.24)$$

There will be an instability (i.e. $\kappa_T^{-1} = 0$) when

$$\frac{1}{(1 - b\rho)^2} - \frac{2a\rho}{kT} = 0. \quad (3.25)$$

In Fig. 3.9 the function

$$g(\rho) \equiv \left(\frac{\kappa_T}{\kappa_T^0} \right)^{-1} = \frac{1}{(1 - b\rho)^2} - \frac{2a\rho}{kT} \quad (3.26)$$

is represented for different values of T (for simplicity we have set some particular values for the constants a , b and k in the figure since the actual values of ρ and $g(\rho)$ are not important for the argument). Note that the excess of $g(\rho)$ over unity reflects the contribution of interactions to the inverse compressibility. The function $g(\rho)$ has a root for the first time at some temperature T_c , called *critical temperature*, and it is a double root (a minimum). The values of T_c and the critical density ρ_c follow by calculating the location of the minimum, searching for the condition that the minimum is zero, i.e.

$$\left(\frac{\partial p}{\partial\rho} \right)_{\rho_c, T_c} = 0, \quad \left(\frac{\partial^2 p}{\partial\rho^2} \right)_{\rho_c, T_c} = 0. \quad (3.27)$$

Differentiating $g(\rho)$ [which is equivalent to calculating the second derivative $(\partial^2 p/\partial\rho^2)$] and equating to zero:

$$g'(\rho) = 2 \left[\frac{b}{(1 - b\rho)^3} - \frac{a}{kT} \right] = 0, \quad (3.28)$$

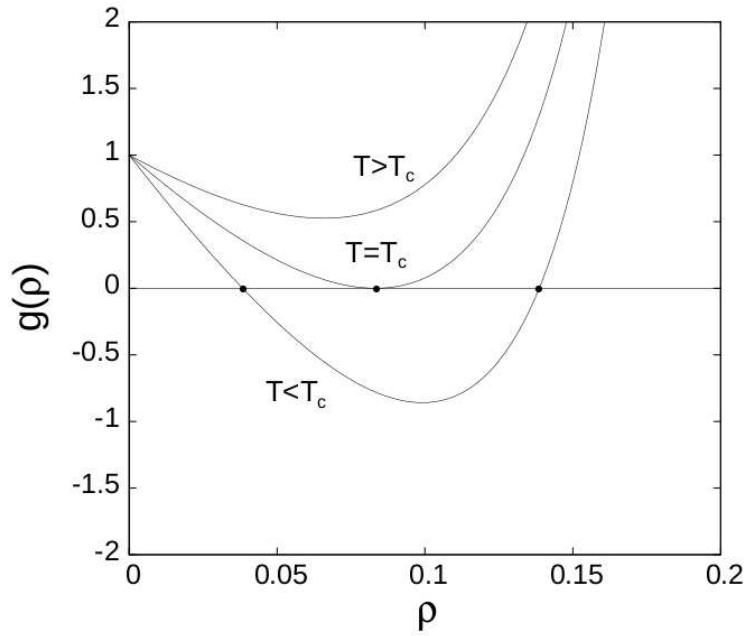


Figure 3.9: The function $g(\rho)$ (inverse compressibility normalised by same function for ideal-gas, defined by Eqn. (3.26) for three different values of T .

from which the minimum is at

$$\rho = \frac{1}{b} \left[1 - \left(\frac{kTb}{a} \right)^{1/3} \right]. \quad (3.29)$$

Substituting, the value of $g(\rho)$ at the minimum is

$$g(\rho) = 3 \left(\frac{a}{kTb} \right)^{2/3} - 2 \left(\frac{a}{kTb} \right), \quad (3.30)$$

which is zero at a temperature T_c such that

$$g(\rho) = 3 \left(\frac{a}{kTb} \right)^{2/3} - 2 \left(\frac{a}{kTb} \right) = 0 \quad \rightarrow \quad kT_c = \frac{8a}{27b}, \quad (3.31)$$

From here the critical density is

$$\rho_c = \frac{1}{b} \left[1 - \left(\frac{kT_c b}{a} \right)^{1/3} \right] = \frac{1}{3b}, \quad (3.32)$$

and the critical pressure

$$p_c = \frac{\rho_c k T_c}{1 - b \rho_c} - a \rho_c^2 = \frac{a}{27b^2}. \quad (3.33)$$

The law of corresponding states can be explained by van der Waals equation. If we scale ρ , p and T with the corresponding critical values, it is easy to arrive at

$$p^* = \frac{8\rho^* k T^*}{3 - \rho^*} - 3\rho^{*2}. \quad (3.34)$$

van der Waals theory then provides a universal equation of state and in fact it gives plausibility to the law, but the universal equation provided by van der Waals theory is not the correct one. For example, the so-called *compressibility factor*, defined by $Z = pv/kT$ (a non-dimensional number), adopts a more or less universal value at the critical point, a value which experimentally is observed to be $Z_c = p_c v_c / kT_c \simeq 0.29$ for a wide range of substances, whereas van der Waals theory predicts

$$Z_c = \frac{p_c v_c}{kT_c} = \frac{p_c}{\rho_c kT_c} = \frac{3}{8} = 0.375. \quad (3.35)$$

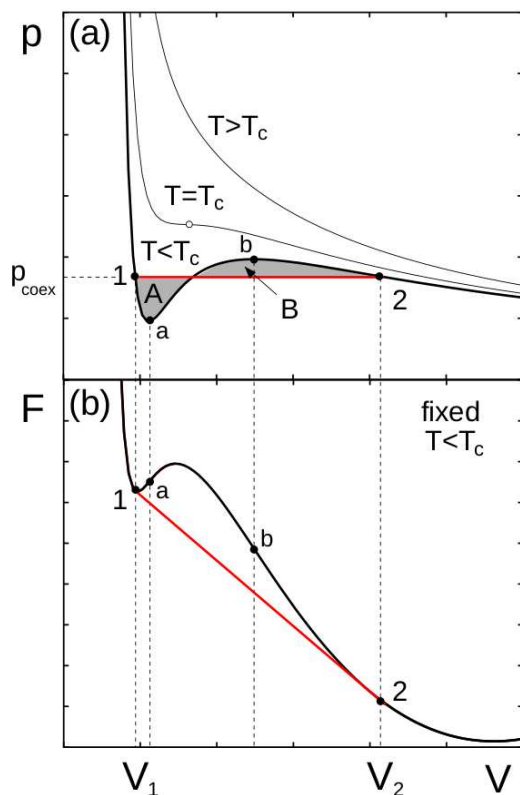


Figure 3.10: (Colour on the Web). (a) Pressure-volume curves for different temperatures. The one for $T < T_c$ shows a loop with extrema at ‘a’ and ‘b’. The true thermodynamic phase transition is indicated by the red horizontal line at pressure p_{coex} . 1 and 2 are the coexisting liquid and vapour phases, respectively. Shaded regions A and B have the same area according to Maxwell’s construction. In (b), a linear term in the volume has been added to better visualise the loop (this does not affect the calculation of the coexistence parameters, as can be easily checked).

In Fig. 3.10(a) three isotherms of the scaled van der Waals equation are represented for temperatures $T > T_c$, $T = T_c$ and $T < T_c$ (scales in axes are not given as they are irrelevant for the present discussion). The first two isotherms are as expected. But that for $T < T_c$ (thick black line) looks peculiar: it does not predict a horizontal sector signalling coexistence between the gas and the liquid, but a ‘loop’ with a maximum and a minimum, denoted in the figure by ‘a’ and ‘b’. This is strange because at these extrema $\kappa_T^{-1} = 0$, so

they are a kind of critical points: they define the *spinodal line*, more visible in a $T - V$ phase diagram, Fig. 3.11(a) [in this case the extensive variable has been chosen as density ρ]. Inside the spinodal line the fluid is unstable, since $\kappa_T^{-1} < 0$, which implies $\partial p / \partial V > 0$, which is not possible for a stable material. If we disregard these unstable states (between ‘a’ and ‘b’), predicted by the theory, we are left with the gas and liquid branches, from small volumes up to ‘a’, and from large volumes up to ‘b’ (i.e. the regions where $\kappa_T > 0$). But still we have to explain the phase transition. The correct interpretation is that:

- the phase transition occurs at some pressure p_{coex} , i.e. at some horizontal line connecting the two outer branches at points 1 and 2, as experimentally observed [see for example Fig. 3.5(a)]
- the remaining parts of the two branches, between 1 and ‘a’ and between 2 and ‘b’, represent *metastable* (i.e. mechanically stable but thermodynamically unstable) states. The existence of metastable states is a genuine (but in fact not 100 % correct) prediction of van der Waals theory (actually of *any* mean-field theory)

In order for this interpretation to be operational, we must somehow be able to calculate p_{coex} . The way the transition pressure is calculated is based on the Maxwell construction. We proceed as follows: Using the relation

$$F(N, V, T) = - \int^V p(N, V, T) dV \quad (3.36)$$

(we are of course assuming that N is fixed and constant) we can obtain the free energy as a function of V for fixed T , Fig. 3.10(b). The analytical expression is:

$$F(N, V, T) = NkT \left[\log(\rho\Lambda^3) - 1 \right] - NkT \left[\log(1 - b\rho) + \frac{a\rho}{kT} \right]. \quad (3.37)$$

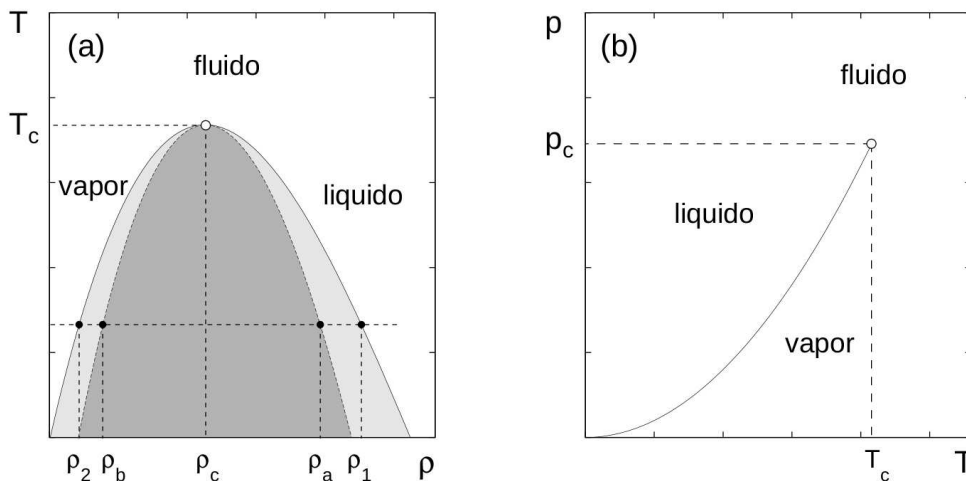


Figure 3.11: Schematic phase diagrams $V - T$ (a) and $p - T$ (b) of the van der Waals model.

The loop visible in $F = F(V)$ is traced back to the loop in the equation of state $p = p(V)$.

Note that there is an instability region where F is concave (between ‘a’ and ‘b’); this corresponds to the unstable sector in $p(V)$ [positive derivative $p(V)$]. Now, searching for the horizontal ($p = p_{\text{coex}}$) sector associated with the phase transition in $p(V)$ is equivalent to searching for the straight line in $F(V)$, joining points 1 and 2 (i.e. the two coexisting phases), that corresponds to the true, thermodynamically permissible trajectory followed by the fluid, represented in Fig. 3.10(b) in red. This sector is linear in the graph $F = F(V)$ since, in this region, $\partial F/\partial V = p_{\text{coex}}$. In order to identify the points 1 and 2 (i.e. the volumes of the coexisting gas and liquid, V_1 and V_2), we first note that they must have the same pressure [i.e. same slope in the $F(V)$ graph], so that

$$\left(\frac{\partial F}{\partial V}\right)_1 = \left(\frac{\partial F}{\partial V}\right)_2 \quad (3.38)$$

Also, the straight line must have a common tangent at 1 and 2, which implies

$$\left(\frac{\partial F}{\partial V}\right)_1 = \left(\frac{\partial F}{\partial V}\right)_2 = \frac{F_1 - F_2}{V_1 - V_2}, \quad (3.39)$$

In fact this condition can be written

$$p_1(V_2 - V_1) = F_1 - F_2 = \int_{V_1}^{V_2} p dV. \quad (3.40)$$

The integral is the area under the curve $p = p(V)$ between 1 and 2. This equation implies that the areas of A and B in the graph of $p(V)$ must be equal. This graphical criterion fixes the pressure $p_1 = p_2 = p_{\text{coex}}$ at the transition, and we have Maxwells construction. Note that the condition (3.39) reflects in fact the equality of chemical potentials, since

$$G = \mu N = F + pV = F - \left(\frac{\partial F}{\partial V}\right) V, \quad (3.41)$$

and from (3.39) we have, rearranging terms:

$$F_1 - \left(\frac{\partial F_1}{\partial V}\right)_1 V_1 = F_2 - \left(\frac{\partial F_2}{\partial V}\right)_2 V_2. \quad (3.42)$$

Therefore, an equivalent statement of the Maxwell construction is

$$p(\rho_1, T) = p(\rho_2, T), \quad \mu(\rho_1, T) = \mu(\rho_2, T), \quad (3.43)$$

as we should have expected since this is a phase transition problem where two phases, at 1 and 2, coexist in equilibrium at the same temperature.

Finally, in Fig. 3.11(b), a schematic p - T phase diagram for the van der Waals model is depicted. It only contains a liquid-vapour coexisting line, since the transitions involving the solid cannot be described by the theory.

Critical exponents

One of the most interesting and important topics in the field of phase transitions is critical

points. A critical point exhibits very peculiar properties; for instance, we already know that compressibility becomes infinite, which means that the material does yield when an arbitrarily small pressure is exerted on it. This and in fact all properties of critical points are due to the so-called *scale invariance* of critical phases. According to this hypothesis, thermodynamic properties of the system exhibit divergencies or become zero according to very simple mathematical functions, usually power laws with well-defined exponents, called *critical exponents*. The remarkable thing is that the values of critical exponents are the same for a large class of very different experimental systems, depending only on very general properties, such as dimensionality, and not on specific details of the interactions. This is because in the vicinity of a critical point there are fluctuations of all length scales. Systems sharing the same values of critical exponents are said to belong to the same *universality class*. In this section we will simply calculate the critical exponents of the van der Waals model for the liquid-vapour phase transition. The subject will be covered more deeply in a later chapter.

We begin with the isothermal compressibility obtained from the scaled van der Waals equation (we omit the superscripts ‘*’ for the sake of brevity in notation):

$$p = \frac{8\rho T}{3-\rho} - 3\rho^2 \quad \rightarrow \quad \kappa_T^{-1} = \rho \left(\frac{\partial p}{\partial \rho} \right)_T = \frac{24\rho T}{(3-\rho)^2} - 6\rho^2. \quad (3.44)$$

At the critical density $\rho_c = 1$ (but for general T) and since the critical temperature is $T_c = 1$:

$$\kappa_T^{-1} = 6(T-1) \quad \rightarrow \quad \kappa_T \sim (T-T_c)^{-\gamma}, \quad (3.45)$$

where γ is the critical exponent associated with the compressibility. The compressibility diverges as a power law, as indeed observed experimentally in the liquid-vapour transition, and van der Waals theory predicts the exponent to be $\gamma = 1$.

Let us now examine the heat capacity at constant volume. Experimentally $C_V \sim |T - T_c|^{-\alpha}$. To see the value of α predicted by van der Waals theory we first calculate the energy. Using (3.37):

$$E = -T^2 \left(\frac{\partial F/T}{\partial T} \right)_V = \frac{3}{2}MkT - Na\rho. \quad (3.46)$$

Therefore

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2}Nk \sim |T - T_c|^0, \quad (3.47)$$

so that van der Waals theory predicts $\alpha = 0$.

Another critical exponent is δ , defined as

$$\frac{p}{kT_c} \sim \text{const.} + \text{const.}(\rho - \rho_c)^\delta, \quad T = T_c, \quad (3.48)$$

i.e. it says how the pressure tends to its critical value at the critical temperature. Setting $T = 1$ and expanding about $\rho = \rho_c = 1$:

$$p = \frac{8\rho}{3-\rho} - 3\rho^2 = 1 + \frac{3}{2}(\rho-1)^3 + \dots \quad (3.49)$$

exponent	value vdW (mean field)	experimental value
α	0	0.1
β	0.5	0.33
γ	1	1.35
δ	3	4.2

so that $\delta = 3$. Finally, another very important exponent is the β exponent, associated with the variation of the density difference between the coexisting liquid and vapour $\Delta = \rho_1 - \rho_2$ below T_c :

$$\Delta\rho \sim (T - T_c)^\beta, \quad T < T_c. \quad (3.50)$$

It can be shown that van der Waals predicts $\beta = 1/2$.

Table 3.3 summarises the values of the exponents predicted by van der Waals theory. In fact, all mean-field theories give the same values for the exponents, and these values are called classical exponents. The differences with respect to the real (experimental) values come from the neglect of fluctuations inherent to mean-field theories. Inclusion of fluctuations is crucial to improve the theory of critical phenomena beyond mean field.

3.4 Lattice models

The statistical mechanics of simple liquids and gases of interacting particles is extremely difficult. Sometimes severe approximations are necessary. It is therefore useful to consider crude models that are amenable to analytical treatment, and for which sometimes even exact solutions can be obtained. By considering these models much can be learned on the effect of interactions and on the nature of phase transitions. These models are typically *lattice models*, where microscopic variables are discretised and translational coordinates are frozen, normally on a crystalline lattice. Analysis of lattice models has led in many cases to a deep understanding of quite general concepts in the theory of phase transitions.

An important model is the so-called *lattice gas*: a system of N atoms restricted to lie on the sites of a D -dimensional lattice, with the condition that there is at most one atom on each site. Typically only nearest-neighbour interactions are considered. The model is appropriate for understanding real problems, such as the liquid-vapour transition, adsorption phenomena, etc. We will have more to say about this model later.

In fact, the lattice gas can be shown to be isomorphic to another discrete model, the *Ising model*, which was proposed to understand the phenomenon of ferromagnetism. We turn to discuss this model in some detail in the next few sections. First, let us define the Hamiltonian.

The model is defined on a one-, two-, three- (or more) dimensional lattice, on each node of which there lies a spin with discrete orientations. For example, for a spin-1/2 Ising model, the i -th spin could point up or down, and this is accounted for by a spin variable