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Phase Transitions

Life is pleasant. Death is peaceful. It's the transition that's troublesome.

Isaac Asimov (1920–1992), biochemist, and author of both science fiction and non-fiction books.

One of the most interesting branches of thermal physics is the study of phase transitions. While most of thermodynamics is concerned with the consequences of analyticity in relating different measurable quantities, phase transitions occur at points where analyticity (Section 9.6.4) breaks down.

Examples of phase transitions abound. Water can freeze, going from a liquid to a solid state when the temperature is lowered. Water can also boil, going from a liquid state to a gaseous state when the temperature is raised. Iodine can sublime, going directly from a solid to a gaseous state. In fact, almost all materials can exist in different states, with abrupt transitions between them.

Water boiling and freezing and iodine sublimating are examples of first-order transitions; that is, phase transitions in which the extensive variables change discontinuously.

An example of a second-order transition is given by the magnetization of iron, which goes to zero continuously at a ‘critical’ temperature of 1044 K . The partial derivative of the magnetization with respect to temperature is not only discontinuous, but it diverges as the critical temperature is approached from below.

The classification of phase transitions as first-order or second-order is a hold-over from an early classification scheme due to the Austrian physicist Paul Ehrenfest (1880–1933). Ehrenfest classified phase transitions at which the n -th partial derivative of the free energy was discontinuous as being n -th order. For first-order phase transitions this classification is very useful, but for higher-order transitions it is less so. Phase transitions have turned out to be much more complex and interesting than Ehrenfest thought. In current usage his definition of first-order transitions is retained, but ‘second-order’ generally refers to any transition with some sort of non-analytic behavior, but continuous first partial derivatives of the free energy.

17.1 The van der Waals Fluid

To illustrate some of the basic ideas about phase transitions we will use a model for a fluid of interacting particles that was invented by the Dutch physicist, Johannes Diderik van der Waals (1837–1923), who was awarded the Nobel Prize in 1910.

17.2 Derivation of the van der Waals Equation

There are several ways of deriving the van der Waals equations, but they all begin with making approximations for the changes in the behavior of an ideal gas when the effects of interactions on the properties are included. As discussed in Chapter 7, a typical interaction between two particles has the form shown in Fig. 7.1. For very short distances the interactions between molecules are generally repulsive, while they are attractive at longer distances. In the van der Waals model the effects of the attractive and repulsive parts of the interactions between particles are considered separately. Rather than calculating the properties of the van der Waals fluid directly from a specific interaction potential of the form shown in Fig. 7.1, we will follow the usual procedure of introducing a parameter a for the overall strength of the attractive part of the interaction, and another parameter b for the strength of the repulsive part.

We will start from the Helmholtz free energy for the ideal gas. (X is the usual constant.)

$$F_{IG} = -Nk_B T \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln(k_B T) + X \right]. \quad (17.1)$$

Since an interaction of the form shown in Fig. 7.1 implies that each particle is attracted to the particles in its neighborhood, we would expect the average energy of attraction to be proportional to the density of particles in the neighbor of any given particle, which we will approximate by the average density, N/V . The total energy of attraction for N particles can then be written as $-aN^2/V$, where $a > 0$ is a constant.

Assuming that the most important effect of the repulsive part of the interaction potential is a reduction in the available volume, we subtract a correction term proportional to the number of particles, so that $V \rightarrow V - bN$.

Naturally, the constants a and b will be different for different fluids.

With these two changes in eq. (17.1), we find the Helmholtz free energy for the van der Waals fluid,

$$F_{vdW} = -Nk_B T \left[\ln\left(\frac{V - bN}{N}\right) + \frac{3}{2} \ln(k_B T) + X \right] - a\left(\frac{N^2}{V}\right). \quad (17.2)$$

From eq. (17.2) we can use the usual partial derivatives of F_{vdW} with respect to T and V to find two equations of state,

$$P = \frac{Nk_B T}{V - bN} - \frac{aN^2}{V^2} \quad (17.3)$$

and

$$U = \frac{3}{2}Nk_B T - a\left(\frac{N^2}{V}\right). \quad (17.4)$$

Note that both van der Waals equations of state, eqs. (17.3) and (17.4), are unchanged (invariant) if U , V , and N are multiplied by an arbitrary constant λ , demonstrating that the van der Waals gas is extensive. This is because surfaces and interfaces are completely neglected in this model, and the fluid is assumed to be homogeneous.

17.3 Behavior of the van der Waals Fluid

At very high temperatures, the gas expands, the density is small, and V is large in comparison with the correction term bN . For low density the correction term for the pressure is also small, so that the predictions of the van der Waals equation, eq. (17.3), are very close to those of the equation for an ideal gas.

On the other hand, as the temperature is reduced, the deviations from ideal-gas behavior become pronounced. If the temperature is below a certain critical temperature, T_c , the deviations from the ideal-gas law are not only large, but the behavior is qualitatively different.

Below T_c , a plot of $P(V)$ vs. V looks qualitatively like Fig. 17.1, while above T_c the slope is negative everywhere. The value of the critical temperature, T_c , can be found from the condition that $P(V)$ has an inflection point at which both

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = 0, \quad (17.5)$$

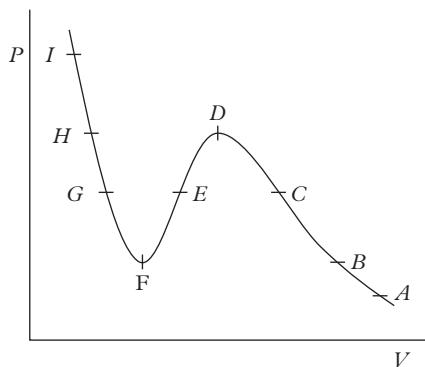


Fig. 17.1 Schematic $P - V$ plot of an isotherm (constant temperature) for the van der Waals equation at a low temperature. The marked points are used to illustrate the calculation of the location of the phase transition. They are the same points as those marked in Fig. 17.2

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,N} = 0. \quad (17.6)$$

With a little algebra, eqs. (17.5) and (17.6) can be solved for the critical values for the volume, pressure, and temperature,

$$V_c = 3bN \quad (17.7)$$

$$P_c = \frac{a}{27b^2} \quad (17.8)$$

$$k_B T_c = \frac{8a}{27b}. \quad (17.9)$$

A very interesting feature of the van der Waals equation is that although it contains only two arbitrary constants, a and b , it predicts the three critical values, V_c , P_c , and T_c . This means that the three values cannot be independent. Indeed, they can be combined to make a non-trivial prediction for the ratio

$$\frac{P_c V_c}{N k_B T_c} = \frac{3}{8} = 0.375. \quad (17.10)$$

The measured values of this ratio vary for different materials, but not as much as might be guessed from such a simple theory. For example, the experimental values of $P_c V_c / N k_B T_c$ for helium, water, and mercury are, respectively, 0.327, 0.233, and 0.909.

If we define the reduced values $\tilde{V} = V/V_c$, $\tilde{P} = P/P_c$, and $\tilde{T} = T/T_c$, we can write the van der Waals equation in dimensionless form as

$$\tilde{P} = \frac{8\tilde{T}}{3\tilde{V} - 1} - \frac{3}{\tilde{V}^2}, \quad (17.11)$$

or

$$(\tilde{P} + 3\tilde{V}^{-2})(3\tilde{V} - 1) = 8\tilde{T}. \quad (17.12)$$

17.4 Instabilities

The qualitative differences between the PV plot for the low-temperature van der Waals gas and for an ideal gas are dramatic. The PV plot for an ideal gas is simply an hyperbola ($PV = Nk_B T$). The plot of a low-temperature isotherm for the van der Waals gas, shown in Fig. 17.1, has the striking feature that the slope is positive in the region between points F and D ,

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} > 0. \quad (17.13)$$

This is surprising, because we know from Chapter 16 (see eq. (16.19)) that the derivative in eq. (17.13) must be negative for stability. Therefore, the region of the van der Waals plot from points *F* to *D* in Fig. 17.1 must be unstable.

We noted that the van der Waals equation was derived under the assumption that the system was homogeneous. The violation of the stability condition in the region between points *F* and *D* marks where this assumption breaks down. This part of the curve must represent unphysical states.

More insight into the unusual features of the van der Waals equation can be seen if the axes of Fig. 17.1 are flipped, as shown in Fig. 17.2.

From Fig. 17.2 it can be seen that the van der Waals equation actually predicts that the volume is a triple-valued function of the pressure in the region between points *B* and *H*. The possibility of three solutions can also be seen directly from the form of the van der Waals equation. If eq. (17.3) is rewritten as

$$(PV^2 + aN^2)(V - bN) = Nk_B TV^2, \quad (17.14)$$

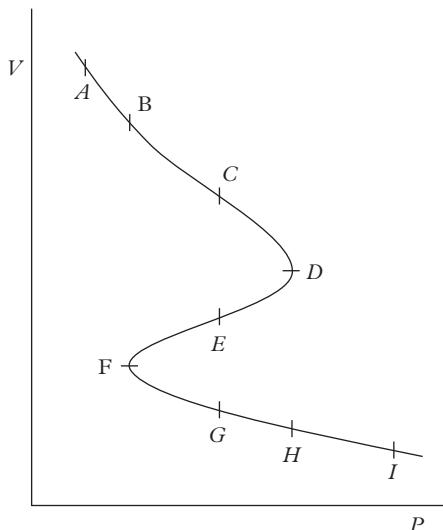


Fig. 17.2 Schematic $V - P$ plot of an isotherm (constant temperature) for the van der Waals equation at a low temperature. This is a plot of the same function as in Fig. 17.1, but the axes have been flipped. The marked points are used to illustrate the calculation of the location of the phase transition. They are the same points as those marked in Fig. 17.1

and the left side of eq. (17.14) is expanded, the van der Waals equation is seen to be a cubic equation in V for fixed P . It can therefore have either one or three real solutions, which is consistent with Fig. 17.2.

To find the stable states predicted by the van der Waals equation we must eliminate the section of the curve between points D and F on the basis of instability, but we still have to choose between the two remaining solutions. This will be done in the next section.

17.5 The Liquid–Gas Phase Transition

To resolve the problem of multiple solutions of the van der Waals equation, we need to go back to Chapter 16 and investigate the stability of the high- and low-density states in Fig. 17.2. For the stable state, the Gibbs free energy at constant temperature and pressure should be a minimum. Note that this criterion is not restricted to infinitesimal variations; it is also valid for the large differences in the volume between the states on the upper and lower branches in Fig. 17.2.

To use the stability condition on the Gibbs free energy, G , we must be able to calculate it. Since this is an extensive system, we know two very helpful things.

First, as shown in eq. (13.27) of Chapter 13,

$$G = U - TS + PV = \mu N, \quad (17.15)$$

so that the condition that G be a minimum is the same as the condition that μ be a minimum.

Next, the Gibbs–Duhem equation, given in eq. (13.11),

$$d\mu = -\left(\frac{S}{N}\right)dT + \left(\frac{V}{N}\right)dP, \quad (17.16)$$

is valid for the van der Waals fluid. Since Fig. 17.2 is an isotherm (constant temperature), we can set $dT = 0$ in eq. (17.16) and integrate it to find G or μ as a function of P ,

$$G = \mu N = \int V dP. \quad (17.17)$$

Starting with point A in Fig. 17.2 and integrating eq. (17.17) to point D , we find the increasing part of the curve shown in Fig. 17.3. Note that the curvature of this part of the plot is negative because the integrand (V) is decreasing. As we continue to integrate along the curve in Fig. 17.2 from point D to point F , we are moving in the negative P -direction, so the contributions of the integral are negative, and the value of $G = \mu N$ decreases. When we reach point F and continue to point I , we are again integrating in the positive P -direction and the value of $G = \mu N$ increases.

The integration of the van der Waals equation of state in Fig. 17.2, using eq. (17.17), is peculiar for at least two reasons. First, since the function $V = V(P)$ is multivalued, the integration must proceed in three stages: initially in the positive P -direction, then in the negative P -direction, and finally in the positive P -direction again. The more problematic feature is that we have already established that the states corresponding to the part of the function that lies between points D and F in Figs. 17.1 and 17.2 are unstable. They could only be regarded as equilibrium states if they somehow were subject to an added constraint that they remain homogeneous. However, since we only need the van der Waals equation in the unstable region for the formal integral, and that part of the curve is an analytic continuation of the van der Waals isotherm, the procedure is valid—strange, but valid.

The parts of the curve in Fig. 17.3 corresponding to equilibrium states are the two sections from point A to C and from point G to I , which have the minimum Gibbs free energy. Note that although the points C and G are distinct in Figs. 17.1 and 17.2, they have the same Gibbs free energy and occupy the same location in Fig. 17.3.

There are two kinds of instability that occur along the unstable parts of the curve. First, we have already noted that states corresponding to points between D and F are unstable to small perturbations because $\partial P/\partial V > 0$ in that region. On the other hand, $\partial P/\partial V < 0$ in the regions C to D and F to G , so that the corresponding states are stable to small perturbations. Nevertheless, they are still not equilibrium states, because there exist states with lower Gibbs free energy. They are unstable in a second sense: they are

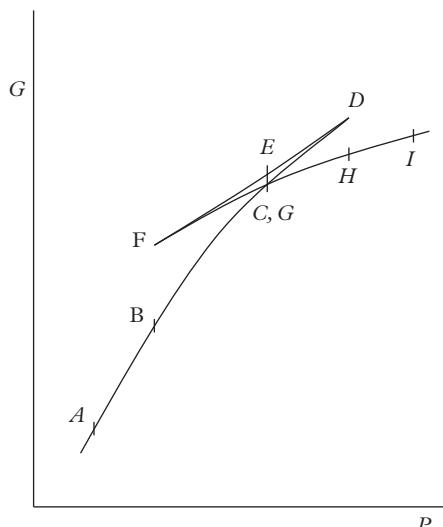


Fig. 17.3 Schematic $G - P$ plot for the van der Waals fluid at a low temperature. The function $G = G(P)$ is obtained by performing the integral in eq. (17.17) on the van der Waals equation of state shown in Fig. 17.2

'globally' unstable with respect to a large change. The term for such states is 'metastable'. Because they are stable to small perturbations, metastable states can exist for a long time. However, eventually a large fluctuation will occur and the system will make a transition to the true equilibrium state, which will lower the Gibbs free energy.

17.6 Maxwell Construction

The integration of the van der Waals equation of state in Fig. 17.2, using eq. (17.17), includes a positive contribution from point C to D , followed by a smaller negative contribution from D to E . The sum of these two contributions gives a net positive contribution to the Gibbs free energy. The magnitude of this net positive contribution is the shaded area under the curve EDC in Fig. 17.4.

The integral from E to F gives a negative contribution, and it is followed by a smaller positive contribution from F to G , giving a net negative contribution. The magnitude of this contribution is the shaded area above the curve EFG in Fig. 17.4.

Since the total integral from the point C to the point G must vanish (C and G have the same Gibbs free energy), the two shaded regions in Fig. 17.4 must have equal areas. The procedure of adjusting the position of the line CG until the two areas are equal is known as the Maxwell construction, first noted by the Scottish physicist James Clerk Maxwell (1831–1879).

17.7 Coexistent Phases

The points C and G in Figs. 17.1, 17.2, 17.3, or 17.4 indicate distinct phases that are in equilibrium with each other at the same temperature and pressure. The fact that they are in equilibrium with each other is demonstrated by their having the same Gibbs free

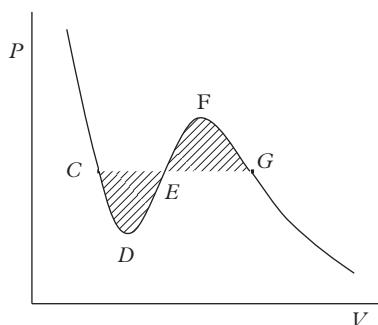


Fig. 17.4 Schematic $P - V$ plot of an isotherm (constant temperature) for the van der Waals equation at a low temperature. The labeled points coincide with those in Fig. 17.1. By the Maxwell construction, the two shaded areas must have equal areas when the horizontal line bounding them is at the correct pressure to have equilibrium between the liquid and gas phases

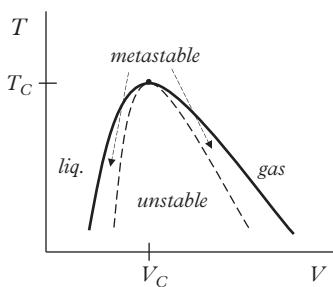


Fig. 17.5 Schematic $T - V$ plot of the coexistence diagram for the van der Waals fluid. The solid line indicates the liquid and gas phase volumes at each temperature. The dot at the top of the curve indicates the critical point. The dashed curves indicate the spinodals, which correspond to the points D and F in Figs. 17.1 through 17.4. Regions of liquid and gas phases are indicated, as well as regions of unstable and metastable states

energy in Fig. 17.3. That they are distinct phases is clear because of the difference in their volumes.

The phase corresponding to point C in the figures corresponds to a small volume and a high density. We will call it the liquid phase to distinguish it from the gas phase corresponding to point G, which has a large volume and small density.

For each temperature, we can draw an isotherm and perform the Maxwell construction to determine the pressure at which the liquid and gas phases are in equilibrium with each other, as well as the volumes of the liquid and gas phases.

Fig. 17.5 shows a qualitative plot of the relationship between the liquid and gas volumes at coexistence and the temperature. The area under the solid curve is known as the coexistence region, because those temperatures and volumes can only be achieved by having distinct liquid and gas phases coexisting next to each other. The dot at the top of the coexistence curve indicates the critical point, with the critical temperature T_c and the critical volume V_c . As the temperature increases toward T_c from below, the volumes of the liquid and gas phases approach each other. Above T_c , there is no distinction between liquid and gas—only a single fluid phase.

The dashed lines in Fig. 17.5 correspond to the points D and F in Figs. 17.1 through 17.4. They are known as ‘spinodals’ and represent the boundaries of the metastable regions. All states under the dashed lines are unstable.

17.8 Phase Diagram

Equilibrium between liquid and gas phases occurs at a specific pressure for any given temperature, as determined by the Maxwell construction. The locus of the coexistence points on a $P - T$ diagram is plotted schematically in Fig. 17.6.

The curve in Fig. 17.6 is known as the ‘coexistence curve’ and separates regions of liquid and gas. At points along the curve, the liquid and gas phases coexist. The curve

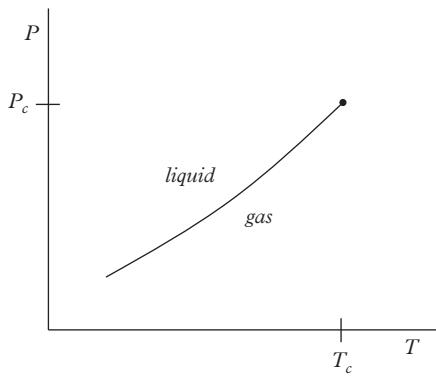


Fig. 17.6 Schematic $P - T$ plot of the phase diagram of the van der Waals fluid. The solid line separates the liquid and gas phase regions. The dot at the end of the curve indicates the critical point

ends in a critical point with, logically enough, critical values of the temperature, T_c , and pressure, P_c .

At temperatures or pressures above the critical point, there is no distinction between liquid and gas; there is only a fluid. This has the curious consequence that, at least in some sense, liquid and gas phases are different aspects of the same phase.

Consider a process that starts with a gas on the coexistence curve (or infinitesimally below it) at a temperature T_o and pressure P_o . Raise the temperature of the gas at constant pressure. When the temperature is above T_c , the pressure is increased until it is above P_c . At this point, the temperature is again lowered until it is at the original value at T_o . Now lower the pressure until the original value of P_o is reached. The system has now returned to the original temperature and pressure, *but on the other side of the coexistence curve*. It is now in the liquid phase.

Since the coexistence curve was not crossed anywhere in the entire process, the fluid was taken smoothly from the gas to the liquid phase without undergoing a phase transition. The initial (gas) and final (liquid) phases must, in some sense, represent the same phase. Considering how obvious it seems that water and steam are different, it might be regarded as rather surprising to discover that they are not fundamentally different after all.

17.9 Helmholtz Free Energy

The graph of the Helmholtz free energy F as a function of the volume V for constant temperature T is qualitatively different than the graph of G as a function of P shown in Fig. 17.3. The essential difference is that in Fig. 17.3 the independent variable, P , was intensive, so that the phase transition occurred at a point. In Fig. 17.7 the independent variable is extensive, so that it takes on different values in the two phases at a first-order transition.

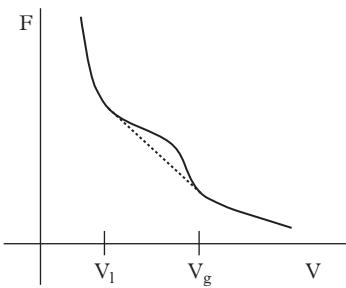


Fig. 17.7 Schematic $F - V$ plot for the van der Waals fluid at a fixed temperature $T < T_c$. The straight dashed line indicates the coexistence region in which part of the system is liquid in equilibrium with the rest of the system in the gas phase. (The true plot has the same features as shown here, but it is more difficult to see them clearly without magnification due to their relative magnitudes. Generating the true plot is left to the exercises.)

The first partial derivative of F with respect to V is the negative of the pressure, so it is negative:

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P < 0. \quad (17.18)$$

The second partial derivative of F with respect to V is related to the isothermal compressibility, so it is positive:

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial P}{\partial V}\right)_{T,N} = \frac{V}{\kappa_T} > 0. \quad (17.19)$$

We know from the previous discussion of the $P - V$ diagram of the van der Waals gas that the model predicts an unstable region. In Fig. 17.1 this was found between the points D and F and identified by the positive slope in this region, which would imply a negative compressibility. This violates a stability condition.

In terms of the Helmholtz free energy, the unstable region is signaled by a negative curvature, which violates the inequality in eq. (17.19). As a consequence, the schematic $F - V$ plot exhibits a region of negative curvature between two inflection points, as shown in Fig. 17.7.

As we saw earlier in this chapter, below T_c the homogeneous solution to the van der Waals equations is not stable between two values of the volume corresponding to the liquid (V_l) and the gas (V_g). In this region, the Helmholtz free energy is lower for coexisting liquid and gas states. The values of F in this coexistence region are indicated by the straight dashed line in Fig. 17.7. The line is found as the common tangent to the van der Waals curve at the values V_l and V_g .

It is useful to compare the plot of G vs. P in Fig. 17.3 and the plot of F vs. V in Fig. 17.7. The former has an *intensive* variable on the horizontal axis, and the phase transition occurs at a single value of P . The latter has an *extensive* variable on the horizontal axis, and the phase transition occurs over a range of values of V . There are many diagrams of thermodynamic potentials as functions of various quantities, but they all fall into one of these two categories.

17.10 Latent Heat

We all know that it takes heat to boil water. More generally, to cross the coexistence curve in Fig. 17.6 requires adding energy to the liquid. If we add a small amount of heat dQ to a system, its entropy changes by an amount $dS = dQ/T$. Therefore, there will be a difference in the entropy between the liquid state corresponding to point G and the gas state corresponding to the point C in Fig. 17.1.

To calculate the difference in entropy, ΔS , between the liquid and gas phases, consider a process by which we integrate the equation

$$dS = \left(\frac{\partial S}{\partial V} \right)_{T,N} dV \quad (17.20)$$

along the isotherm in Fig. 17.1 from point G to point C . Since the process is isothermal, the total heat needed to go from the liquid to the gas phase will be $T\Delta S$.

To find the partial derivative in eq. (17.20) we can use a Maxwell relation associated with the differential form of the fundamental relation $dF = -SdT - PdV + \mu dN$,

$$\left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{V,N}. \quad (17.21)$$

With this Maxwell relation, the change in entropy is given by the integral

$$\Delta S = \int_G^C \left(\frac{\partial P}{\partial T} \right)_{V,N} dV. \quad (17.22)$$

Since the partial derivative in eq. (17.22) can be calculated from the van der Waals equation of state in eq. (17.3), evaluating the integral is straightforward.

The energy per particle needed to make a first-order phase transition is called the latent heat, denoted by ℓ ,

$$\ell = \frac{T\Delta S}{N}. \quad (17.23)$$

It is also quite common to denote the energy needed to make a first-order phase transition for a complete system of N particles as the heat capacity, L ,

$$L = N\ell = T\Delta S. \quad (17.24)$$

17.11 The Clausius–Clapeyron Equation

It might be supposed that the coexistence curve in the phase diagram in Fig. 17.6 merely separates the phases and is of no particular significance in itself. However, the German physicist Rudolf Clausius, whom we have already encountered as a founder of thermodynamics, and the French physicist Benoît Paul Émile Clapeyron (1799–1864) found a remarkable equation that links the slope of the coexistence curve with the change in volume across the transition and the value of the latent heat.

Consider two points along the coexistence curve. Denote the liquid phase at the first point by X and the gas phase at the same temperature and pressure by X' . Similarly denote the liquid and gas phases by Y and Y' at the other point. At each of these points, let the sample contain N particles. Assume that the points are very close together, so that the difference in temperature, $dT = T_Y - T_X = T_{Y'} - T_{X'}$, and the difference in pressure, $dP = P_Y - P_X = P_{Y'} - P_{X'}$, are both small.

Since the liquid and gas phases are in equilibrium, we must have

$$\mu_X = \mu_{X'}, \quad (17.25)$$

and

$$\mu_Y = \mu_{Y'}, \quad (17.26)$$

which implies that

$$\mu_Y - \mu_X = \mu_{Y'} - \mu_{X'}. \quad (17.27)$$

On the other hand, we know from the Gibbs–Duhem equation from eq. (13.11) in Section 13.2, that if we have the same number of particles on both sides of the transition, then,

$$\mu_Y - \mu_X = -\left(\frac{S}{N}\right)dT + \left(\frac{V}{N}\right)dP, \quad (17.28)$$

and

$$\mu_{Y'} - \mu_{X'} = -\left(\frac{S'}{N}\right)dT + \left(\frac{V'}{N}\right)dP. \quad (17.29)$$

Combining these equations, we see that

$$\frac{dP}{dT} = \frac{S' - S}{V' - V} = \frac{\Delta S}{\Delta V}. \quad (17.30)$$

Comparing eq. (17.30) with the definition of the latent heat in eq. (17.23), we find the Clausius–Clapeyron equation,

$$\frac{dP}{dT} = \frac{\ell N}{T \Delta V} = \frac{L}{T \Delta V}. \quad (17.31)$$

Note that the latent heat is positive by definition, and most materials expand when they melt or boil, $\Delta V > 0$. The slopes of *almost* all coexistence curves are positive, as is the coexistence curve for the van der Waals gas, shown schematically in Fig. 17.6.

However, ice contracts when it melts, so that $\Delta V < 0$ and $dP/dT < 0$ along the ice–water coexistence curve. The negative slope required by the thermodynamics analysis presented here is confirmed qualitatively and quantitatively by experiment.

17.12 Gibbs' Phase Rule

Phase diagrams in a general system can be considerably more complicated than Fig. (17.6). However, there is a limitation on the structure of these diagrams that is called ‘Gibbs’ phase rule’.

To derive Gibbs’ phase rule, consider a general thermodynamic system with K components; that is, K different kinds of molecules. Let the number of distinct phases in equilibrium with each other be denoted by ϕ . The variables describing this system are T and P , plus the concentrations of each type of particle in each phase. For the j -th phase, $\{x_k^{(j)} = N_k^{(j)} / N^{(j)} | k = 1, \dots, K\}$, where $N_k^{(j)}$ gives the number of type k particles in the j -th phase. Since the total number of particles in the j -th phase is $N^{(j)} = \sum_{k=1}^K N_k^{(j)}$, the sum of the concentrations is unity, $1 = \sum_{k=1}^K x_k^{(j)}$, and there are only $K - 1$ independent concentration variables for each of the ϕ phases. The total number of variables is then $2 + \phi(K - 1)$.

However, the equilibrium conditions on the chemical potentials limit the number of independent variables, since the chemical potential of a given component must take on the same value for every phase. Letting $\mu_k^{(j)}$ denote the chemical potential of the k -th component in the j -th phase, we have

$$\mu_k^{(1)} = \mu_k^{(2)} = \dots = \mu_k^{(\phi)}. \quad (17.32)$$

Since there are K components, this gives a total of $K(\phi - 1)$ conditions on the variables describing the system.

Putting these two results together, the total number F of independent variables for a general system with K components and ϕ phases is

$$F = 2 + \phi(K - 1) - K(\phi - 1), \quad (17.33)$$

or

$$F = 2 + K - \phi. \quad (17.34)$$

This is Gibbs' phase rule.

As an example, consider the case of a simple system containing only a single kind of molecule, so that $K = 1$. If we consider the boundary between normal ice and liquid water ($\phi = 2$), we see that the number of independent variables is $F = 2 + 1 - 2 = 1$. This means that we have one free parameter to describe the boundary between solid and liquid. In other words, the two phases will be separated by a line in a phase diagram (a plot of P vs. T), and the one parameter will tell us where the system is on that line. The same is true for the boundaries between the liquid and vapor phases and the solid and vapor phases.

As a second example, consider the triple point of water, at which three phases come together ($\phi = 3$). In this case, the number of independent variables is $F = 2 + 1 - 3 = 0$, so that there are no free parameters; coexistence of the three phases can occur only at a single point.

The phase diagram of ice is actually quite complicated, and there are at least ten distinct crystal structures at various temperatures and pressures. Gibbs' phase rule tells us that two different forms of ice can be separated in the phase diagram by a line and three phases can coexist at a point, but we cannot have *four* phases coexisting at a point. And, in fact, four phases do not coexist at any point in the experimental phase diagram.

17.13 Problems

PROBLEM 17.1

Properties of the van der Waals gas

1. Just for practice, starting from the expression for the Helmholtz free energy, derive the pressure, $P = P(T, V, N)$.
2. Again starting from the expression for the Helmholtz free energy for the van der Waals fluid, derive the energy as a function of temperature, volume, and number of particles,

$$U = U(T, V, N).$$

3. Using the conditions for the critical point,

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = 0$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,N} = 0$$

derive expressions for P_c , T_c , and V_c as functions of a and b .

4. Derive the value of the ratio

$$\frac{P_c V_c}{Nk_B T_c}$$

as a pure number, independent of the values of a and b .

PROBLEM 17.2

Properties of the van der Waals gas by computation

I suggest doing the following calculations as functions of the van der Waals parameters a and b . However, make the plots in terms of the reduced quantities T/T_c , V/V_c , and P/P_c .

1. Write a program to compute and plot P as a function of V at constant T for the van der Waals gas.
2. Modify your program to include a comparison curve for the ideal gas law at the same temperature.
3. Make plots for values of T that are at, above, and below T_c .
4. For some values of temperature, the plots will have a peculiar feature. What is it?
5. Make plots of T as a function of V for values of P above, below, and at P_c .
6. Make a plot of the chemical potential μ as a function of P . You might want to include a plot of V vs. P for comparison.

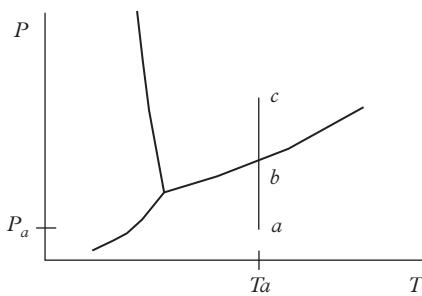
What does the plot of μ vs. P look like at, above, and below T_c ?

The data you need to do a numerical integration of the Gibbs-Duhem relation is the same as you've already calculated for the first plot in this assignment. You just have to multiply the volume times the change in P and add it to the running sum to calculate μ vs. P .

PROBLEM 17.3

Helmholtz free energy near a phase transition

Consider a material described by the phase diagram. A quantity of this material is placed in a cylinder that is in contact with a thermal reservoir at temperature T_a . The temperature is held constant, and the pressure is increased as shown on the phase diagram, through the point b (on the coexistence curve) to the point c .



1. Make a qualitative sketch of the pressure P as following a function of volume V during the process that takes the system from the state a , through the state b , to the state c . Label the points on the phase diagram corresponding to states a , b , and c . Label the phases. Explain the signs and relative magnitudes of the slopes of the lines you draw. Explain any discontinuities in the function or its slope.
2. Sketch the Helmholtz free energy F as a function of the volume V for this process. Again label the phases and the points corresponding to states a , b , and c . Explain the relative magnitudes of the slopes and curvatures of the lines you draw. Explain any discontinuities in the function or its slope.

PROBLEM 17.4

Numerical evaluation of κ_T , α , and c_P as functions of P for the van der Waals gas – PART 1

As we'll see in this problem and the next one, the numerical evaluation of the properties of the van der Waals gas is much easier than finding an analytic solution. In this assignment you will derive the equations needed to write a computer program, which will be your next assignment.

We will use the volume V to parameterize the functions $P(V, T)$, etc. This will enable us to make plots of κ_T , α , and c_P as function of P , without actually solving the equations for $c_P(P, T)$ and $\kappa_T(P, T)$.

For the van der Waals gas:

1. Find an equation for κ_T as a function of P , T , and V by taking the derivative of the van der Waals equation of state with respect to V . You may find it convenient to express your result as $1/\kappa_T$.
2. Find an equation for α as a function of P , T , and V by taking the derivative of the van der Waals equation of state with respect to T .

Hint: it is much easier to find an equation for α if you use a thermodynamic identity for

$$\left(\frac{\partial P}{\partial T}\right)_{V,N}.$$

3. Find c_V as a function of P , T , and V from the van der Waals equation for the energy U .
4. Find equations for c_P from a cleverly chosen thermodynamic identity, as a function of P , T , and V , AND α , AND κ_T , which you have already calculated.

PROBLEM 17.5

Numerical evaluation of κ_T , α , and c_P as functions of P for the van der Waals gas – PART 2

Now use the results of the previous assignment to do a numerical evaluation of the properties of the van der Waals gas.

Use the volume V to parameterize the functions $P(V, T)$, etc. Make plots of κ_T , α , and c_P as function of P . Note that you do not actually have to solve the equations for $\kappa_T(P, T)$, $\alpha(P, T)$, and $c_P(P, T)$.

1. Write a program to plot κ_T , α , and c_P as functions of P AND their reciprocals as functions of P .

Use V to first calculate P , and then use the values of V , P , and T to find $1/\kappa_T$, $1/\alpha$, and $1/c_P$ from the equations derived in the previous assignment.

Make plots for $T > T_c$ and values of P that range from below P_c to above P_c .

2. What happens when you use different values of T above T_c ?
3. What happens at $T = T_c$?
4. What happens when $T < T_c$?

PROBLEM 17.6

Clausius–Clapeyron relation

The slope of a phase boundary in a $P - T$ phase diagram is not arbitrary. The Clausius–Clapeyron equation connects it directly to the latent heat and the change in volume at the transition.

The change in volume between the liquid and the gas, $V_{\text{gas}} - V_{\text{liquid}}$ can be approximated by noting that the liquid is much denser than the gas if you are not too close to the critical point. We can also approximate the latent heat by a constant under the same assumption.

Find an analytic approximation for the function $P(T)$ along the liquid–gas phase boundary. Sketch your answer and compare it to a phase diagram of water that you can find on the Web.
