

The van der Waals Model

To understand phase transformations more deeply, a good approach is to introduce a specific mathematical model. For liquid-gas systems, the most famous model is the **van der Waals equation**,

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT, \quad (5.49)$$

proposed by Johannes van der Waals in 1873. This is a modification of the ideal gas law that takes molecular interactions into account in an approximate way. (Any proposed relation among P , V , and T , like the ideal gas law or the van der Waals equation, is called an **equation of state**.)

The van der Waals equation makes two modifications to the ideal gas law: adding aN^2/V^2 to P and subtracting Nb from V . The second modification is easier to understand: A fluid can't be compressed all the way down to zero volume, so we've limited the volume to a minimum value of Nb , at which the pressure goes to infinity. The constant b then represents the minimum volume occupied by a molecule, when it's "touching" all its neighbors. The first modification, adding aN^2/V^2 to P , accounts for the short-range attractive forces between molecules when they're not touching (see Figure 5.19). Imagine freezing all the molecules in place, so that the only type of energy present is the negative potential energy due to molecular attraction. If we were to double the density of the system, each molecule would then have twice as many neighbors as before, so the potential energy due to all its interactions with neighbors would double. In other words, the potential energy associated with a single molecule's interactions with all its neighbors is proportional to the density of particles, or to N/V . The *total* potential energy associated with all molecules' interactions must then be proportional to N^2/V , since there are N molecules:

$$\text{total potential energy} = -\frac{aN^2}{V}, \quad (5.50)$$

where a is some positive constant of proportionality that depends on the type of molecules. To calculate the pressure, imagine varying the volume slightly while holding the entropy fixed (which isn't a problem if we've frozen all thermal motion); then by the thermodynamic identity, $dU = -PdV$ or $P = -(\partial U/\partial V)_S$. The contribution to the pressure from just the potential energy is therefore

$$P_{\text{due to p.e.}} = -\frac{d}{dV} \left(-\frac{aN^2}{V} \right) = \frac{aN^2}{V^2}. \quad (5.51)$$

If we add this negative pressure to the pressure that the fluid would have in the



Figure 5.19. When two molecules come very close together they repel each other strongly. When they are a short distance apart they attract each other.

absence of attractive forces (namely, $NkT/(V - Nb)$), we obtain the van der Waals equation,

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}. \quad (5.52)$$

While the van der Waals equation has the right properties to account for the qualitative behavior of real fluids, I need to emphasize that it is nowhere near exact. In "deriving" it I've neglected a number of effects, most notably the fact that as a gas becomes more dense it can become inhomogeneous on the microscopic scale: Clusters of molecules can begin to form, violating my assertion that the number of neighbors a molecule has will be directly proportional to N/V . So throughout this section, please keep in mind that we won't be making any accurate quantitative predictions. What we're after is qualitative understanding, which can provide a starting point if you later decide to study liquid-gas phase transformations in more depth.

The constants a and b will have different values for different substances, and (since the model isn't exact) will even vary somewhat for the same substance under different conditions. For small molecules like N_2 and H_2O , a good value of b is about $6 \times 10^{-29} \text{ m}^3 \approx (4 \text{ \AA})^3$, roughly the cube of the average width of the molecule. The constant a is much more variable, because some types of molecules attract each other much more strongly than others. For N_2 , a good value of a is about $4 \times 10^{-49} \text{ J}\cdot\text{m}^3$, or $2.5 \text{ eV}\cdot\text{\AA}^3$. If we think of a as being roughly the product of the average interaction energy times the volume over which the interaction can act, then this value is fairly sensible: a small fraction of an electron-volt times a few tens of cubic ångströms. The value of a for H_2O is about four times as large, because of the molecule's permanent electric polarization. Helium is at the other extreme, with interactions so weak that its value of a is 40 times less than that of nitrogen.

Now let us investigate the consequences of the van der Waals model. A good way to start is by plotting the predicted pressure as a function of volume for a variety of different temperatures (see Figure 5.20). At volumes much greater than Nb the isotherms are concave-up, like those of an ideal gas. At sufficiently high

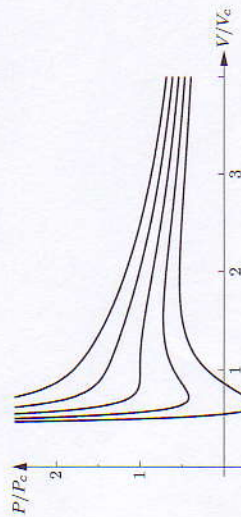


Figure 5.20. Isotherms (lines of constant temperature) for a van der Waals fluid. From bottom to top, the lines are for 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c , the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point; in these units the minimum volume (Nb) is $1/3$.

temperatures, reducing the volume causes the pressure to rise smoothly, eventually approaching infinity as the volume goes to Nb . At lower temperatures, however, the behavior is much more complicated: As V decreases the isotherm rises, falls, and then rises again, seeming to imply that for some states, compressing the fluid can cause its pressure to decrease. Real fluids don't behave like this. But a more careful analysis shows that the van der Waals model doesn't predict this, either.

At a given temperature and pressure, the true equilibrium state of a system is determined by its Gibbs free energy. To calculate G for a van der Waals fluid, let's start with the thermodynamic identity for G :

$$dG = -SdT + VdP + \mu dN. \quad (5.53)$$

For a fixed amount of material at a given, fixed temperature, this equation reduces to $dG = VdP$. Dividing both sides by dV then gives

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{N,T}. \quad (5.54)$$

The right-hand side can be computed directly from the van der Waals equation (5.52), yielding

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}. \quad (5.55)$$

To integrate the right-hand side, write the V in the numerator of the first term as $(V-Nb) + (Nb)$, then integrate each of these two pieces separately. The result is

$$G = -NkT \ln(V-Nb) + \frac{(NkT)(Nb)}{V-Nb} - \frac{2aN^2}{V} + c(T), \quad (5.56)$$

where the integration constant, $c(T)$, can be different for different temperatures but is unimportant for our purposes. This equation allows us to plot the Gibbs free energy for any fixed T .

Instead of plotting G as a function of volume, it's more useful to plot G vertically and P horizontally, calculating each as a function of the parameter V . Figure 5.21 shows an example, for the temperature whose isotherm is shown alongside. Although the van der Waals equation associates some pressures with more than one volume, the thermodynamically stable state is that with the lowest Gibbs free energy; thus the triangular loop in the graph of G (points 2-3-4-5-6) corresponds to unstable states. As the pressure is gradually increased, the system will go straight from point 2 to point 6, with an abrupt decrease in volume: a phase transformation. At point 2 we should call the fluid a gas, because its volume decreases rapidly with increasing pressure. At point 6 we should call the fluid a liquid, because its volume decreases only slightly under a large increase in pressure. At intermediate volumes between these points, the thermodynamically stable state is actually a combination of part gas and part liquid, still at the transition pressure, as indicated by the straight horizontal line on the PV diagram. The curved portion of the isotherm that is cut off by this straight line correctly indicates what the allowed states *would* be if the fluid were homogeneous; but these homogeneous states are unstable, since

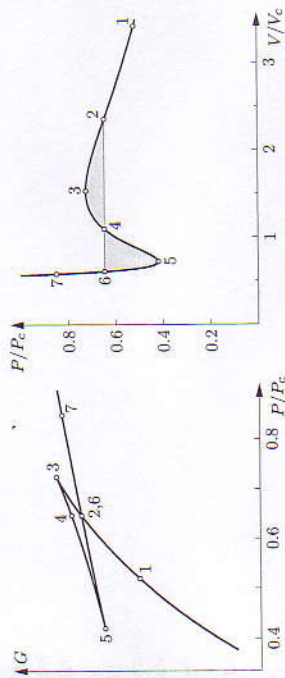


Figure 5.21. Gibbs free energy as a function of pressure for a van der Waals fluid at $T = 0.97c$. The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable.

there is always another state (gas or liquid) at the same pressure with a lower Gibbs free energy.

The pressure at the phase transformation is easy enough to determine from the graph of G , but there is a clever method of reading it straight off the PV diagram, without plotting G at all. To derive this method, note that the net change in G as we go around the triangular loop (2-3-4-5-6) is zero:

$$0 = \int_{\text{loop}} dG = \int_{\text{loop}} \left(\frac{\partial G}{\partial P}\right)_T dP = \int_{\text{loop}} V dP. \quad (5.57)$$

Written in this last form, the integral can be computed from the PV diagram, though it's easier to turn the diagram sideways (see Figure 5.22). The integral from point 2 to point 3 gives the entire area under this segment, but the integral from point 3 to point 4 cancels out all but the shaded region A . The integral from 4 to 5 gives minus the area under that segment, but then the integral from 5 to 6 adds back all but the shaded region B . Thus the entire integral equals the area

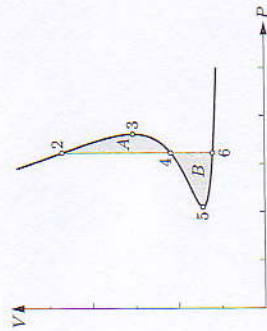


Figure 5.22. The same isotherm as in Figure 5.21, plotted sideways. Regions A and B have equal areas.

of A minus the area of B , and if this is to equal zero, we conclude that the two shaded regions must have equal areas. Drawing the straight line so as to enclose equal areas in this way is called the **Maxwell construction**, after James Clerk Maxwell.

Repeating the Maxwell construction for a variety of temperatures yields the results shown in Figure 5.23. For each temperature there is a well-defined pressure, called the **vapor pressure**, at which the liquid-gas transformation takes place; plotting this pressure vs. temperature gives us a prediction for the entire liquid-gas phase boundary. Meanwhile, the straight segments of the isotherms on the PV diagram fill a region in which the stable state is a combination of gas and liquid, indicated by the shaded area.

But what about the *high-temperature* isotherms, which rise monotonically as V decreases? For these temperatures there is no abrupt transition from low-density states to high-density states: no phase transformation. The phase boundary therefore disappears above a certain temperature, called the **critical temperature**, T_c . The vapor pressure just at T_c is called the **critical pressure**, P_c , while the corresponding volume is called the **critical volume**, V_c . These values define the **critical point**, where the properties of the liquid and gas become identical.

I find it remarkable that a model as simple as the van der Waals equation predicts *all* of the important qualitative properties of real fluids: the liquid-gas phase transformation, the general shape of the phase boundary curve, and even the critical point. Unfortunately, the model fails when it comes to numbers. For example, the experimental phase boundary for H_2O falls more steeply from the critical point than does the predicted boundary shown above; at $T/T_c = 0.8$, the measured vapor pressure is only about $0.2P_c$, instead of $0.4P_c$, as predicted. More

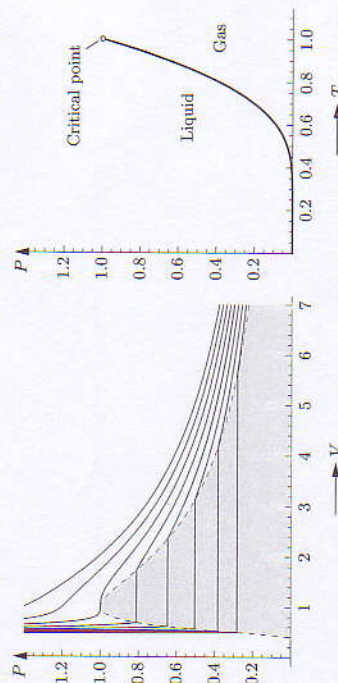


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values.

accurate models of the behavior of dense fluids are beyond the scope of this book,* but at least we've taken a first step toward understanding the liquid-gas phase transformation.

Problem 5.48. As you can see from Figure 5.20, the critical point is the unique point on the original van der Waals isotherms (before the Maxwell construction) where both the first and second derivatives of P with respect to V (at fixed T) are zero. Use this fact to show that

$$V_c = 3Nb, \quad P_c = \frac{1}{27} \frac{a}{b^2}, \quad \text{and} \quad kT_c = \frac{8}{27} \frac{a}{b}.$$

Problem 5.49. Use the result of the previous problem and the approximate values of a and b given in the text to estimate T_c , P_c , and V_c/N for N_2 , H_2O , and He. (Tabulated values of a and b are often determined by working backward from the measured critical temperature and pressure.)

Problem 5.50. The **compression factor** of a fluid is defined as the ratio PV/NkT ; the deviation of this quantity from 1 is a measure of how much the fluid differs from an ideal gas. Calculate the compression factor of a van der Waals fluid at the critical point, and note that the value is independent of a and b . (Experimental values of compression factors at the critical point are generally lower than the van der Waals prediction, for instance, 0.227 for H_2O , 0.274 for CO_2 , 0.305 for He.)

Problem 5.51. When plotting graphs and performing numerical calculations, it is convenient to work in terms of **reduced variables**,

$$t \equiv T/T_c, \quad p \equiv P/P_c, \quad v \equiv V/V_c.$$

Rewrite the van der Waals equation in terms of these variables, and notice that the constants a and b disappear.

Problem 5.52. Plot the van der Waals isotherm for $T/T_c = 0.95$, working in terms of reduced variables. Perform the Maxwell construction (either graphically or numerically) to obtain the vapor pressure. Then plot the Gibbs free energy (in units of NkT_c) as a function of pressure for this same temperature and check that this graph predicts the same value for the vapor pressure.

Problem 5.53. Repeat the preceding problem for $T/T_c = 0.8$.

Problem 5.54. Calculate the Helmholtz free energy of a van der Waals fluid, up to an undetermined function of temperature as in equation 5.56. Using reduced variables, carefully plot the Helmholtz free energy (in units of NkT_c) as a function of volume for $T/T_c = 0.8$. Identify the two points on the graph corresponding to the liquid and gas at the vapor pressure. (If you haven't worked the preceding problem, just read the appropriate values off Figure 5.23.) Then prove that the Helmholtz free energy of a combination of these two states (part liquid, part gas) can be represented by a straight line connecting these two points on the graph. Explain why the combination is more stable, at a given volume, than the homogeneous state represented by the original curve, and describe how you could have determined the two transition volumes directly from the graph of F .

*Chapter 8 introduces an accurate approximation for treating *weakly* interacting gases, as well as the more general technique of Monte Carlo simulation, which can be applied to dense fluids.