Thermodynamics of Real Gases

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14. Statistical study of a fluid

In a gas, the potential energy of interactions between molecules is small compared to their kinetic energy. At high temperatures and low densities, the regime where the ideal gas approximation is valid, it is even negligible. However as the temperature decreases and/or the density increases the contribution of the interaction energy to the total energy becomes more important and the properties of the gas start to deviate from that of an ideal gas. Finally, when the interaction energy becomes comparable to the kinetic energy, the gas condenses and becomes a liquid.

The Van der Waals model allows to understand this transition from gas to liquid, even though it relies on a rather crude mean field theory and should only be expected to yield qualitative results. This is because it possesses the necessary properties to describe the physical phenomena at play in real gases and liquid-gas phase transitions.

14.1 General case

Consider a mono-atomic^{*} fluid made of $N \gg 1$ identical particles of mass m, contained in a recipient of volume V and kept at temperature T. We can calculate the macroscopic properties of this system using classical mechanics and the partition function:

$$\mathcal{Z} = \frac{1}{N!} \frac{1}{h^{3N}} \int \cdots \int d^3 p_1 \cdots d^3 p_N d^3 r_1 \cdots d^3 r_N \exp\left(-\frac{\mathcal{H}}{k_B T}\right)$$
(14.1)

where

$$\mathcal{H} = \frac{1}{2m} \sum_{i=1}^{N} \vec{p_i}^2 + \mathcal{U}(\vec{r_1}, \cdots, \vec{r_N})$$

^{*}Strictly speaking, the mono-atomic hypothesis is not necessary to derive the EOS of real gases but will simplify our life considerably as it allows us to ignore the internal degrees of freedom and non-spherical shape of molecules that we have previously discussed in the lectures devoted to the statistical mechanics of simple systems.

is the Hamiltonian of the system, complete with its kinetic (first term) and potential (second term) energy parts. The integration over all momenta $\vec{p_i}$, i.e. the kinetic part of \mathcal{Z} , is the same as for the ideal gas, so

$$\mathcal{Z} = \frac{1}{N!} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3N/2} \int \cdots \int d^3 r_1 \cdots d^3 r_N \exp\left(-\frac{\mathcal{U}(\vec{r_1}, \cdots, \vec{r_N})}{k_B T} \right)$$
(14.2)

i.e. when the potential energy \mathcal{U} is negligible in front of $k_B T$, $\int \cdots \int d^3 r_1 \cdots d^3 r_N = V^N$ and \mathcal{Z} is the partition function of the ideal gas. If we want to do better and take into account the interaction between gas particles, we thus have to determine \mathcal{U} .

Suppose that the total interaction energy is the sum of the pairwise interaction energies between particles[†], $u(\|\vec{r_i} - \vec{r_j}\|)$, i.e. that

$$\mathcal{U}(\vec{r_1}, \cdots, \vec{r_N}) = \frac{1}{2} \sum_{i,j}^{i \neq j} u(\|\vec{r_i} - \vec{r_j}\|)$$

where the 1/2 factor arises from the need *not* to double count the interaction energy between particles *i* and *j*. Having made this approximation, we still have to determine u(r). In principle one could calculate it from Quantum Mechanics, but in practice it is a very difficult proposition, especially if the molecules involved are complex. However, one can show that at large distances, *r*, the interaction energy between particles varies like r^{-6} , which corresponds to an attractive "Van der Waals" force that scales like r^{-7} .

 \mathbb{R} The physical origin of these Van der Waals forces is the following: a charge fluctuation in a molecule creates an electric dipole (or more generally multipole) which polarizes a neighbouring molecule. In turn, the dipole (or multipole) induced on this second molecule acts on the polarization of the first. Note that even though we talk about large distances for r, these forces are short-range interactions between neighbouring molecules.

At short distances (when r becomes of the order of the size of the molecules themselves), the molecules exert intense repelling forces upon one another. Essentially this is because the Pauli exclusion principle which rules their electrons prevent molecules from inter-penetrating. This behaviour at short and large distances can be captured by a potential u(r) of the shape given by Fig.14.1, which has two important characteristics: the position r_0 of its minimum, and the value at this minimum $-u_0 < 0$. Their order of magnitude is ~ 1 Å for r_0 and a few 10^{-2} eV for u_0 (i.e. a few 100 K for u_0/k_B).

Practically, one uses empirical analytic forms with the correct shape of u(r). Arguably the most famous one, which we plot in Fig.14.1 is called the *Lennard-Jones* potential:

$$u_{LJ}(r) = u_0 \left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^6 \right]$$
(14.3)

which has only two parameters, u_0 and r_0 and intercepts the x-axis (i.e. $u_{LJ} = 0$) at $r_1 = r_0/2^{1/6} \simeq 0.89 r_0$.

[†]Such an approximation may look natural enough to make, but the main interaction between molecules is caused by the electron motion they induce within one another when they are close, so this could easily be influenced by the presence of a third molecule in the vicinity. In other words, the approximation assumes that three body interactions are weak which is fine for a gas but much less so for a liquid ...



Figure 14.1: The Lennard-Jones potential describing the behaviour of the Van der Waals forces between molecules in a real gas.

14.2 The Van der Waals model

Even with the approximation previously made for the interaction energy, evaluating the volume integral present in the partition function of the system (equation (14.2)) is extremely difficult. So we are going to use a still cruder approximation, albeit one that we have already met before when discussing the statistical mechanics of solid crystals: the mean field approximation.

14.2.1 Mean field approximation

Consider a given molecule. One can say that, at a zeroth order approximation, the $N-1 \gg 1$ other molecules which are almost uniformly distributed in the volume V, are felt by this molecule, as an almost continuous cloud. Neglecting the perturbation of this cloud caused by the presence and motion of the molecule, this latter will have a potential energy $u_{\text{eff}}(\vec{r})$ which will depend only on its position and *not* on the positions of the other N-1 particles anymore. In other words, in this approximation, each particle moves in a mean field created by all the other particles, and the system behaves as an ensemble of *independent* particles, just as the vibrations of atoms in a crystal were turned into an ensemble of independent oscillators.

The total potential energy of the system thus becomes a sum of terms[‡], each of which involves the coordinates of a single particle, i.e.

$$\mathcal{U}(\vec{r_1},\cdots,\vec{r_N}) = \frac{1}{2} \sum_{i=1}^N u_{\text{eff}}(\vec{r_i})$$

and the partition function given by equation (14.2) becomes

$$\mathcal{Z} = \frac{1}{N!} \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3N/2} \left[\int \mathrm{d}^3 r \, \exp\left(-\frac{u_{\mathrm{eff}}(\vec{r})}{2k_B T}\right)\right]^N \tag{14.4}$$

 $[\]overline{\overset{\dagger}{}u_{\text{eff}}(\vec{r})}$ is obtained by averaging $\sum_{i=2}^{N} u(\|\vec{r}-\vec{r_i}\|)$ over the positions $\vec{r_2}, \cdots, \vec{r_N}$ of the N-1 other molecules, so $u(\|\vec{r_i}-\vec{r_j}\|)$ is present in both $u_{\text{eff}}(\vec{r_i})$ and $u_{\text{eff}}(\vec{r_j})$, hence the factor of 1/2 in the following formula for $\mathcal{U}(\vec{r_1}, \cdots, \vec{r_N})$.

14.2.2 Effective potential

The mean field approximation neglects the correlations between molecules, i.e. it considers that the molecules are uniformly distributed in the recipient volume. In these conditions, the effective potential $u_{\text{eff}}(\vec{r}) = u_{\text{eff},0}$ ought to be constant over the entire volume V. However, we have seen that this approximation breaks down when the distance between molecules approaches the molecule size, r_1 (see Fig.14.1). On these small distances, individual molecules do not feel an average attractive force created by an homogeneous cloud, but a very strong repulsive force from their immediate neighbour. To crudely account for this effect, we will simply consider that a fraction V_0/V of the recipient volume is forbidden to any given molecule, due to the presence of the others. This allows us to calculate the integral in the formula (14.4) as:

$$\int d^3 r \, \exp\left(-\frac{u_{\text{eff}}(\vec{r})}{2k_B T}\right) = (V - V_0) \, \exp\left(-\frac{u_{\text{eff},0}}{2k_B T}\right)$$

Our task now boils down to evaluating the constants V_0 and $u_{\text{eff},0}$.

Let us start by the excluded volume, V_0 . The minimum allowed distance between two particles is almost equal to r_1 , as the interaction potential is extremely steep at smaller distances (for the Lennard-Jones potential it diverges in r^{-12} , see Fig.14.1). So when two molecules approach one another, the volume forbidden to one of them due to the presence of the other is $4\pi r_1^3/3$. As there are N(N-1)/2 possible pairs of molecules, the total volume excluded simply is $N(N-1)/2 \times 4\pi r_1^3/3 \simeq 2\pi N^2 r_1^3/3$, if we assume that $V_0 \ll V$ so that the spheres of exclusion of any pair of molecules almost never intersect. The excluded volume *per particle*, is therefore $V_0 = 2\pi r_1^3/3 \times N \equiv bN$, i.e. V_0 is proportional to N, with a proportionality constant, b, which only depends on the nature of the gas and is of the order of four times the *proper volume*, $v_0 \equiv 4\pi/3 \times (r_1/2)^3$, of a molecule.

Let us now turn to $u_{\text{eff},0}$ and take for origin of our coordinate system the position of a given particle. As previously mentioned, the others are uniformly distributed in space, except that they cannot get closer to the origin than r_1 . The number $n(\vec{r}) d^3r$ of particles contained in an infinitesimal volume d^3r around \vec{r} is therefore:

$$n(\vec{r}) = \begin{cases} 0 & \text{if } r < r_1 \\ \frac{N-1}{V-V_0} \simeq \frac{N}{V} & \text{if } r > r_1 \end{cases}$$

The potential energy of the particle located at the origin of the coordinate system is thus:

$$u_{\text{eff},0} = \int u(\vec{r}) n(\vec{r}) \, \mathrm{d}^3 r = \frac{N}{V} \int_{r_1}^{+\infty} 4\pi r^2 u(r) \, \mathrm{d}r$$

with u(r) < 0 over the entire integration domain (see Fig. 14.1). In other words, $u_{\text{eff},0} < 0$ and independent of \vec{r} , as expected. An order of magnitude for $u_{\text{eff},0}$ is the number of particles times the minimal value of the potential between two particles, $N \times (-u_0)$, times the ratio of the *interaction volume*[§] and the total volume, V. This ratio is of the order of a few v_0/V where "few" depends on the exact model used for u(r). In a general manner, one therefore writes $u_{\text{eff},0} = -2aN/V$ where a > 0 is a constant of order a few u_0v_0 which depends on the nature of the fluid.

R The important point in this calculation is that $u(r) \xrightarrow{r \to \infty} 0$ fast enough for $\int 4\pi r^2 u(r) dr$ to converge. This is obviously true for Van der Waals forces, where $u(r) \propto r^{-6}$ at large distances, but *not* for charged particles where $u(r) \propto r^{-1}$.

[§]This is the volume of a sphere whose radius is equal to the range of the potential u(r).

Exercise 14.1 Calculate $u_{\text{eff},0}$, a and b as a function of u_0 and v_0 in the specific case of the Lennard-Jones potential given by equation (14.3).

Ans: $u_{\text{eff},0} = -64Nu_0v_0/(3V)$, $a = 32u_0v_0/3$ and $b = 4v_0$.

Plugging the general expressions obtained for V_0 and $u_{\text{eff},0}$ in the formula (14.4) for the partition function we finally obtain

$$\mathcal{Z} = \frac{V^N}{N!} \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3N/2} \left[\left(1 - \frac{bN}{V}\right) \exp\left(\frac{aN}{k_B T V}\right) \right]^N \tag{14.5}$$

which is the partition function of the system in the Van der Waals approximation. Note that is is equal to the partition function of the ideal gas, multiplied by a corrective term (in between square brackets and raised to the power N).

14.3 Thermodynamical quantities

Now that we have derived the partition function of the system in the Van der Waals approximation, we can use it to obtain thermodynamical quantities of interest, and in particular the famous Van der Waals equation of state. We therefore start with the calculation of the Helmholtz free energy of the system, F, as we know this is the one which provides the most direct route to the EOS. We have, using expression (14.5) for \mathcal{Z} and Stirling's formula:

$$F = -k_B T \ln \mathcal{Z}$$

= $-Nk_B T \left[\frac{3}{2} \ln \left(\frac{mk_B T}{2\pi\hbar^2} \right) + 1 \right] - Nk_B T \ln \left(\frac{V - bN}{N} \right) - \frac{aN^2}{V}$ (14.6)

where the first term on the right hand side and the $-Nk_BT\ln(V/N)$ part of the second term combine to give the Helmholtz free energy of a mono-atomic ideal gas, and the -bNpart of the second term and the third term are Van der Waals corrections. Note that, as required, F is extensive, F/N only depends on the ratio N/V, not on N and V separately.

To get the EOS, we then calculate the system pressure:

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

which is known as the Van der Waals equation of state, and more commonly written as:

$$\left(p + \frac{aN^2}{V^2}\right)(V - bN) = Nk_BT \tag{14.7}$$

Once again this EOS is similar to that of the ideal gas, with a smaller volume available (V - bN) instead of V to account for the finite size of the molecules, and a reduced pressure (by an amount aN^2/V^2) because of the attraction between molecules at large distances.

The internal energy, is

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{3}{2}Nk_BT - \frac{aN^2}{V}$$
(14.8)

which is, once again, the internal energy of a mono-atomic ideal gas with a correction term (second term on the right hand side) that accounts for the potential energy of the particles in a real gas $(N \times u_{\text{eff},0}/2)$. On the other hand, the heat capacity at constant volume, $C_V = (\partial U/\partial T)_{V,N} = 3Nk_B/2$, is the *same* as that of an ideal gas.

Note that the second term in the internal energy for a Van der Waals gas depends on V and not on T. It is therefore not correct to say that the internal energy of a real gas is a function of T alone, this statement only applies to ideal gases.
What is true for C_V, i.e. it is the same for a Van der Waals gas than for an ideal gas, is not true for C_p (see exercise 14.2)

Exercise 14.2 Calculate C_p for a Van der Waals gas as the sum of C_p for a mono-atomic ideal gas and a corrective term which is a function of T and V. **Ans:** $C_p = 5Nk_B/2 + 2aN^2k_B(V - bN)^2/(k_BTV^3 - 2aN(V - bN)^2)$.

The entropy of the gas reads:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B \left[\frac{3}{2}\ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + \frac{5}{2}\right] + Nk_B \ln\left(\frac{V-bN}{N}\right)$$
(14.9)

which can also be split into the entropy of a classical ideal gas with a correction, -bN in the second right hand side term, which accounts for the reduced volume due to the finite size of the particles. In order words, the entropy of a Van der Waals gas is smaller than that of an ideal gas because the volume really accessible to the particles is smaller.

Finally, the chemical potential of the Van der Waals gas can be calculated from:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_B T \left[\frac{3}{2}\ln\left(\frac{mk_B T}{2\pi\hbar^2}\right) + 1\right] - k_B T \ln\left(\frac{V - bN}{N}\right) + \frac{k_B T V}{V - bN} - \frac{2aN}{V}$$
(14.10)

which differs from that of an ideal gas by the -bN part in the second and third terms on the right hand side, as well as the presence of the last term. We can easily rewrite this expression for μ as:

$$\mu = \frac{F}{N} + \frac{k_B T V}{V - bN} - \frac{aN}{V} = \frac{1}{N} (F + pV) \equiv \frac{G}{N}$$
(14.11)

where we have used the equation of state (14.7) to obtain the last equality, and ultimately the definition of the Gibbs free energy, G. This relation between μ and G is a general result for a fluid characterised by three external parameters, i.e. it holds for real and ideal gases.

15. Gas-liquid phase transition

Even though the Van der Waals model for real gases derived in the previous chapter involves rather crude approximations, it still proves very useful as it contains the basic physical ingredients necessary to understand the phase transition between liquid and vapour observed to take place in real fluids. This will be the subject of this chapter.

15.1 Van der Waals isotherms

Isotherms for an ideal gas are monotonic hyperbolae. That is to say, for a given value of T, $p \propto 1/V$. Van der Waals isotherms generally have a similar shape, except that for some values of T, the extra terms contributing to the pressure and volume become significant and extrema appear. Indeed, differentiating the Van der Waals equation of state (14.7), one obtains:

$$\left(\frac{\partial p}{\partial V}\right)_{T,N} = -\frac{Nk_BT}{(V-bN)^2} + 2a\frac{N^2}{V^3}$$
(15.1)

This expression is equal to zero when:

$$V - bN = \left(\frac{k_B T}{2aN}\right)^{1/2} V^{3/2}$$
(15.2)

Plotting both left-hand $(y_0 = V - bN)$ and right-hand $(y_i = \sqrt{k_B T_i/(2aN)}V^{3/2})$, with $i \in \mathbb{N}^+$ and $T_1 < T_2 < \cdots < T_n$ side terms of the previous equation onto a single graph in Fig.15.1 for various temperatures T_i , one realises that either these two curves intersect in two places (at low temperatures), or not at all (high temperatures). Moreover, from the same figure, it is quite clear that there must exist a *critical temperature*, $T_i \equiv T_c$, for which the two curves are tangent to one another, i.e.

$$\left(\frac{\partial y_0}{\partial V}\right)_{T,N} = \left(\frac{\partial y_i}{\partial V}\right)_{T_i,N} \quad \Leftrightarrow \quad 1 = \left(\frac{9k_B T_c}{8aN}\right)^{1/2} V^{1/2} \tag{15.3}$$



Figure 15.1: Graphical solution of equation (15.2). The cyan solid line represents $y_0 = V - bN$ whereas the orange curve indicates $y_2 = y_c$, for which $T_2 = T_c$ and y_0 is a tangent in V_c . y_1 (green curve) and y_3 (red curve) correspond to temperatures $T_1 = 3T_c/4$ and $T_3 = 3T_c/2$ respectively lower and higher than T_c . Note that the only curves to intersect y_0 twice are those with $T_i < T_c$.

This yields an expression for the *critical volume*, $V_c = 8aN/(9k_BT_c)$, which, when injected into $y_0 = y_i$ at the point of tangency gives $T_c = 8a/(27k_Bb)$, and thus $V_c = 3bN$. Finally, plugging these expressions into the Van der Waals equation of state, one obtains the *critical pressure*, $p_c = a/(27b^2)$. Also note that $(\partial p/\partial V)_{T,N}$ is always negative (the first term in equation (15.1) always dominates), except between the two extrema when they exist, and that these extrema are located further and further apart as the temperature of the isotherm decreases. All these considerations lead to the isotherms for a Van der Waals gas plotted on Fig. 15.2.

Let us pick a specific isotherm with temperature T. For high values of the volume V, pressure is a slowly decreasing function of V which corresponds to a high compressibility (a small increase of pressure changes the volume considerably) typical of a gas. On the other hand, for low values of V the pressure is a rapidly decreasing function of V. In other words, one needs a large change of pressure to reduce the volume by a small amount so the fluid is almost incompressible: it is a liquid.

R In this latter domain (small values of V) the Van der Waals approximation is poorly justified, but it qualitatively captures the behaviour of the liquid because it takes into account the main characteristic of the interaction between molecules, namely that their potential energy becomes comparable to their kinetic energy.

For intermediate values of $V \sim V_c$ things are more complicated. Looking at the isotherm graph (Fig.15.2) there clearly exist two domains of temperature:

- At high temperature $(T > T_c)$, p remains a decreasing function of V for all values of the volume. When one follows such an isotherm, i.e. when one increases V at constant T, one *continuously* moves from a weak compressibility regime (liquid) to a high compressibility regime (gas). The system remains *homogeneous* during the transformation, and we call the fluid *supercritical*.
- At low temperature $(T < T_c)$, there exists a range of values of V where $(\partial p/\partial V)_{T,N} > 0$, i.e. a range of *negative* compressibility. This means that the system becomes *unstable* in these conditions (the fluid wants to expand as one compresses it) and the isotherm *cannot* be an equilibrium state for the fluid. A more detailed analysis of



Figure 15.2: Examples of Van der Waals isotherms in the three different temperature regimes, $T_3(=3T_c/2) > T_c$ (red curve), $T_2 = T_c$ (orange curve) and $T_1(=3T_c/4) < T_c$ (green curve). Note that the green curve intersects the x-axis, p = 0, at $V_c/2$ and V_c , and possesses both a minimum and a maximum, as indicated on the figure. The horizontal blue line corresponds to the equilibrium pressure of the system when it splits into two phases, liquid and gas (see example 15.2 for detail on how it is calculated).

what happens to the system is required and we will devote the rest of this chapter to it.

R For low enough values of the temperature (e.g. $T_i = 3/4T_c$ in Fig.15.2), p itself becomes negative, a sure sign that everything is going to hell in a handbasket!

The isotherm corresponding to $T_i = T_c$, which separates the two temperature domains previously described is called the *critical isotherm*. The ratio $p_c V_c / (Nk_B T_c)$, sometimes called "compression factor at the critical point", is a dimensionless quantity and is independent of the parameters a and b used in the Van der Waals approximation, i.e. it has the same value for *all* fluids $(p_c V_c / (Nk_B T_c) = 3/8 = 0.375)$. Typical experimental values for real fluids show that this is indeed the case, but with values closer to 0.3, and even lower for so-called polar fluids like water.

Example 15.1 — Experimental values for real fluids. Helium (He) has $T_c = 5.2$ K, $V_c = 57.8 \text{ cm}^3 \text{mol}^{-1}$, $p_c = 2.26$ atm and $p_c V_c / (Nk_B T_c) = 0.3$; Nitrogen (N₂) has $T_c = 126.1$ K, $V_c = 90.1 \text{ cm}^3 \text{mol}^{-1}$, $p_c = 33.5$ atm and $p_c V_c / (Nk_B T_c) = 0.29$; Water (H₂O) has $T_c = 647.4$ K, $V_c = 56.3 \text{ cm}^3 \text{mol}^{-1}$, $p_c = 218.3$ atm and $p_c V_c / (Nk_B T_c) = 0.23$.

R Another approximation than Van der Waals for real gases, the Dietericci approximation that you will encounter in one of the problem sheets, yields a value of this ratio of 0.29, in better agreement with the experimental measures.

15.2 The law of corresponding states

This property of the compression factor at the critical point lead us to go further and define reduced coordinates as the following dimensionless quantities: $\tilde{T} \equiv T/T_c$, $\tilde{V} \equiv V/V_c$ and

 $\tilde{p} \equiv p/p_c$. We can then rewrite the Van der Waals equation of state as:

$$\left(\tilde{p} + \frac{3}{\tilde{V}^2}\right) \left(3\tilde{V} - 1\right) = 8\tilde{T}$$
(15.4)

This reduced equation is independent of the Van der Waals parameters a and b, i.e. it is the same for all Van der Waals fluids! One thus says that two different fluids (as in fluids with different values of T_c , V_c and p_c) verify the law of "corresponding states". This means that if we fix their \tilde{T} and \tilde{V} at the same values, then their value for \tilde{p} is also the same.

15.3 Helmholtz free energy

R

To gain some insight into the unstable region previously uncovered by looking at the Van der Waals isotherms, let us examine how the Helmholtz free energy of the system, F, varies as a function of V, at constant T.

R Although this is a natural choice since we have seen in the lecture on availability that a system at fixed T and V will spontaneously evolve towards an equilibrium for which F is a minimum, most other textbooks prefer to use the Gibbs free energy, G, which is minimal for a system in equilibrium at fixed T and p, to discuss phase transitions. As repeatedly mentioned in these lectures, F is more directly linked to the equation of state of thermodynamical systems than G, so we will stick to it.

Speaking in general terms, as p must remain a positive quantity, $(\partial F/\partial V)_{T,N} = -p$ should always be negative. In other words, at fixed T, F should be a decreasing function of V. Furthermore, we expect this decrease to be fast at small V (high pressure) and slow at large V (low pressure). As we have seen previously, when $T > T_c$, p itself, as for an ideal gas, is everywhere a decreasing function of V, so that $(\partial p/\partial V)_{T,N} < 0$ and $(\partial^2 F/\partial V^2)_{T,N} = -(\partial p/\partial V)_{T,N} > 0$. Mathematically, this last statement means that for Fto be a true, stable minimum for the system, F(V) needs to be *convex* (i.e. at each point V of F(V), the tangent is below the curve).

Let us now consider the case of a Van der Waals isotherm with $T < T_c$ (see Fig.15.2). We realise that F(V) will then present two inflection points (change of concavity) corresponding to the two extrema of the isotherm, since $(\partial p/\partial V)_{T,N}$ — and thus $(\partial^2 F/\partial V^2)_{T,N}$ — changes sign at these extrema. Given that F is convex both at very small and very large V, it will be *concave* between the extrema, and the stability condition $(\partial p/\partial V)_{T,N} < 0$ will not be satisfied. As a consequence, F(V) as sketched in Fig.15.3 *cannot* represent the Helmholtz free energy of a system in equilibrium in this volume range.

So what went wrong? Why can't there exist an equilibrium solution for the system in this volume range? Well, we have only considered *homogeneous* systems so far, and we know that two fluid states (liquid and gas) exist *separately* from one another. So, in principle, nothing prevents our system from spontaneously separating into two sub-systems, each of them homogeneous, but corresponding to these two different macroscopic states. When such a separation occurs, we say that the system is composed of two *phases* in equilibrium.

Nothing guarantees a priori that the two phases can co-exist. We know from the previous lectures on basic thermodynamics that two systems are in mechanical and thermal equilibrium if they have the same pressure and temperature respectively, but this is already the case here because the two phases are located on the same isotherm and we consider a unique value of p on that isotherm. So we are left with only one requirement, which arises because our two sub-systems can exchange particles: they



Figure 15.3: Sketch of the Helmholtz free energy (green solid curve) corresponding to the Van der Waals isotherm $T = 3T_c/4$ plotted in Fig.15.2. The blue line represents the bi-tangent to F derived in equation (15.5), with V_{liq} and V_{gas} calculated in example 15.2. The pink shaded region indicates the range of volume values where F is concave and therefore *cannot* be the free energy of a system in equilibrium. This latter must split into two phases and follow the bi-tangent instead.

must be in *diffusive* (also called "chemical" sometimes) equilibrium, i.e. their chemical potential must be the same ($\mu_{gas} = \mu_{liq}$). We will prove this latter equality later on, but for the moment note that the three equilibrium conditions involve *intensive* variables.

How do we decide how many particles are in the liquid and gas phases? Well, we know that at fixed T and V, the equilibrium state of a system must minimise the Helmholtz free energy. This means that our two phase solution will only be preferred by the system if its resulting Helmholtz free energy, which is the sum of the Helmholtz free energy of the two phases (F is additive), is smaller than the Helmholtz free energy of the homogeneous system. Pushing this argument a bit further, we conclude that of *all* possible separations in two phases, the one with the lowest Helmholtz free energy will constitute the equilibrium state of the system.

We now turn to the task of calculating this minimal Helmholtz free energy. Let us call $F_{\text{liq}} \equiv F(V_{\text{liq}}, T, N)$, the Helmholtz free energy of the homogeneous system of N molecules at temperature T when it is in the liquid phase, and $F_{\text{gas}} \equiv F(V_{\text{gas}}, T, N)$, the Helmholtz free energy of the homogeneous system when it is in the gas phase. If we build a two phase system with N_{liq} molecules in the liquid phase and $N_{\text{gas}} = N - N_{\text{liq}}$ molecules in the gas phase, the volume occupied by this system will simply be $V_{2\text{ph}} \equiv V = V_{\text{liq}} \times N_{\text{liq}}/N + V_{\text{gas}} \times N_{\text{gas}}/N$, and its Helmholtz free energy $F_{2\text{ph}} = F_{\text{liq}} \times N_{\text{liq}}/N + F_{\text{gas}} \times N_{\text{gas}}/N$. Eliminating $N_{\text{liq}}/N = 1 - N_{\text{gas}}/N$ from this latter expression, we can rewrite F as:

$$F_{\rm 2ph} = F_{\rm liq} + \frac{V - V_{\rm liq}}{V_{\rm gas} - V_{\rm liq}} \times (F_{\rm gas} - F_{\rm liq})$$

$$\tag{15.5}$$

where V is a volume point located between V_{liq} and V_{gas} . This is the equation of the straight line joining the points $(V_{\text{liq}}, F_{\text{liq}})$ and $(V_{\text{gas}}, F_{\text{gas}})$ in Fig.15.3.

R When $T > T_c$, $F_{2ph}(V) > F(V)$, as F is always convex in that case. In other words, the straight line (chord) $F_{2ph}(V)$ is always above the curve F(V) and the system remains homogenous in a single phase over all the volume range since this corresponds to a smaller F.

To obtain the values of V_{liq} and V_{gas} geometrically, i.e. to determine which of all the possible straight lines $F_{2\text{ph}}$ follows, we require the equilibrium condition $p(V_{\text{liq}}) = p(V_{\text{gas}})$ on the isotherm, that is to say we require that the pressure be the same for the two homogeneous phases which mark the beginning and the end of the system phase transition. This is a "natural limit" requirement since the two phases must constitute an equilibrium for the system when they co-exist, no matter how many particles are in which phase. Mathematically, this means that $(\partial F/\partial V)_{T,N}(V_{\text{liq}}) = (\partial F/\partial V)_{T,N}(V_{\text{gas}})$, i.e. $F_{2\text{ph}}(V)$ must be tangent to F(V) at both volume values V_{liq} and V_{gas} .

■ Example 15.2 — Calculation of V_{liq} and V_{gas} for the Van der Waals isotherm $I = 3/4 T_c$. For this isotherm, $T = 2a/(9k_Bb)$. Together with $p(V_{\text{liq}}) = p(V_{\text{gas}})$, $\mu(V_{\text{liq}}) = \mu(V_{\text{gas}})$ yields a system of transcendental equations, as can easily be seen from the expression of the chemical potential in the Van der Waals model (equation 14.10). In general such a system must be solved numerically, but one can assume $V_{\text{gas}} \gg V_{\text{liq}}$ for this particular isotherm and $V_{\text{liq}} \approx 3bN/2^*$ to eliminate the V_{liq} terms and obtain a simplified transcendental equation: $-\ln(X/2) + 7X - 4 = 0$, which is accurate to first order in $X \equiv bN/V_{\text{gas}}$. Solving this equation yields $V_{\text{gas}} \simeq 19bN \gg V_{\text{liq}}$, as initially assumed. Plugging this value of V_{gas} into the pressure equilibrium constraint, we get $p(V_{\text{liq}}) = p(V_{\text{gas}}) \simeq a/(104b^2)$, so that the Van der Waals EOS turns into the following cubic equation for $V_{\text{liq}} : V_{\text{liq}}^3 - (217/9)bNV_{\text{liq}}^2 + 104b^2N^2V_{\text{liq}} - 104b^3N^3 = 0$, whose root $V_{\text{liq}} \simeq 1.47bN$ is the one compatible with our initial assumption for V_{liq}^{\dagger} .

Note that F_{2ph} is also a function of the temperature T, both *explicitly* because of the expressions of F_{liq} and F_{gas} we derived in the previous chapter (see equation 14.6) but also *implicitly* as the values of V_{liq} and V_{gas} depend on the Van der Waals isotherm considered.

^{*}We know that for the two phases to be able to achieve pressure equilibrium, the exact value of V_{liq} must be very close to that which cancels the pressure as p is a very steep function of V for a liquid, see Fig.15.2.

[†]Normally one would need to iterate the procedure, i.e. inject this new value of V_{liq} back into the diffuse equilibrium constraint to get a new value of V_{gas} , and so on and so forth until convergence of both V_{liq} and V_{gas} to a pre-defined level of accuracy is achieved, but our initial guess is already accurate to the level of a few percent, so we stop here.

15.4 Liquid-vapour equilibrium



Figure 15.4: Typical three dimensional phase diagram representing surfaces of equilibrium of a pure substance which contracts upon freezing (contrary to e.g. water), borrowed from J. Carstensen (University of Kiel). Bold numbers in between brackets indicate the number of phases of the substance which co-exist in the region. Note that the liquid-vapour co-existence curve which joins together all the values of $V_{\text{lig}}(T)$ and $V_{\text{gas}}(T)$ (and is labelled 'saturated liquid line' and 'saturated vapor line' on the diagram) is not planar. The critical point is denoted by the letter 'K'. Note that even though the solid phase (and its interface with the liquid and gas phases) is missing from our analysis because the Van der Waals model is a poor one for solids, you can intuitively understand what is happening in the different regions of the diagram. For instance, the 'sublimation line' and 'sublimation region' where solid and vapour co-exist, the 'melting line' and 'melting region' where solid and liquid co-exist and the 'triple line' (in green) where all three phases co-exist. Two interesting isobaric paths are marked on the figure (A to F in red, and G to J in green). On both of these paths you heat the system to go progressively from the pure solid to the pure gas phase, following the arrows, and see how the (specific) volume of the system changes. Notice that from B to C (in the 'melting region'), even though you continue heating the system, its temperature does not change: the heat simply converts the solid into a liquid, and similarly from D to E in the 'wet steam region', heat turns the liquid into vapour. We will come back to this concept of *latent heat* later in this chapter, but it should not surprise you: if the two phases co-exist in thermal equilibrium, their temperature must stay the same as long as they co-exist. The same reasoning applies on the 'triple line' (from H to I), where the three phases co-exist in equilibrium. Note that the specific volume increases sharply (discontinuity) when such phase transitions occur, but that otherwise it varies very little (especially in the pure solid and liquid phases, from A to B or C to D or G to H).

Looking back at Fig.15.2, it is now easy to describe the behaviour of the system at equilibrium for $T < T_c$. Let us consider an isotherm at temperature T below the critical

temperature and increase the volume slowly enough so that the system goes through a series of equilibrium states. As long as $V < V_{\text{liq}}(T)$, the system is an homogeneous liquid phase. When V becomes greater than V_{liq} and until it reaches a value of V_{gas} , the system splits into two phases: a liquid phase with the characteristics of an homogeneous system occupying a volume of V_{liq}/N per molecule, and a gaseous phase (also called *vapour*) with the characteristics of an homogenous system occupying a volume of V_{gas}/N per molecule. The number of particles in the liquid phase is $N_{\text{liq}} = N(V_{\text{gas}} - V)/(V_{\text{gas}} - V_{\text{liq}})$, and the number of particles in the vapour phase is $N_{\text{gas}} = N(V - V_{\text{liq}})/(V_{\text{gas}} - V_{\text{liq}})$.

R The ratio $N_{\text{liq}}/N_{\text{gas}} = (V_{\text{gas}}-V)/(V-V_{\text{liq}})$ can be read directly on the isotherm (Figure 15.2): the number of particles in a phase is inversely proportional to the distance which separates the volume V of the system from the volume of the homogeneous phase in question (V_{liq} or V_{gas}). This is the so-called "lever rule".

The Helmholtz free energy of the system is then $F_{2ph}(V)$, which is a linear function of V (see equation (15.5)), so that the pressure $p = -(\partial F_{2ph}/\partial V)_{T,N}$ is a constant as long as the two phases are present. It is called the *saturation vapour pressure*, and is a function of T only. In other words, between volumes V_{liq} and V_{gas} on Fig.15.2, the system does not follow the green Van der Waals isotherm, but the horizontal blue segment. For $V > V_{\text{gas}}(T)$, the system becomes homogeneous again, but in a gas phase this time around. Finally, as T increases, the volumes V_{liq} and V_{gas} get closer together, until they superimpose at a value of V_c for $T = T_c$. For temperatures above T_c , the distinction between liquid and vapour does not make much sense anymore. All this information can be summarised in a three dimensional phase diagram, an example of which is plotted in Fig.15.4.

As indicated by the front red arrow on Fig.15.4, the equilibrium surfaces of this three dimensional phase diagram can be projected onto the (p, V) plane that we have used to study the Van der Waals isotherms.



Figure 15.5: Two dimensional phase diagram representing projected surfaces of equilibrium of the Van der Waals fluid onto the (p, V) plane (corresponding to, from top to bottom, isotherms with $T = 1.5T_c$ (red), $T = T_c$ (orange), $T = 0.9T_c$ (blueish-green), $T = 0.75T_c$ (green) and $T = 0.6T_c$ (blue)). Note the existence of *meta-stable* states of the system sandwiched between the co-existence curve (solid black line) and the *spinodial* curve (dotted black line) which links together all the pressure extrema of the Van der Waals isotherms (see Fig. 15.2). We will discuss their meaning shortly.

Alternatively, one can project these surfaces onto the (p, T) plane as indicated by the

right hand side red arrow on Fig.15.4:



Figure 15.6: Two dimensional phase diagram representing projected surfaces of equilibrium of the Van der Waals fluid onto the (p, T) plane. The solid blue curve which separates the homogeneous liquid phase (blank region above the curve) from its gaseous counterpart (blank region below the curve) is called the *vaporization curve*. The two phases only co-exist along that curve, which is bounded by the critical point at the top, and the *triple point* at the bottom. This latter is not represented on the diagram as it corresponds to the existence of a *solid* phase at low T (see Fig.15.4), that the Van der Waals approximation fails to account for. The shaded light blue region marks the domain where the distinction between liquid and vapour makes little sense and one only talks about a Van der Waals fluid.

15.5 Characteristics of the transition

The liquid-vapour transition we have just studied presents three fundamental properties which pertain to a whole class of phase transitions called *first order* phase transitions.

15.5.1 Co-existence of the two phases

If $T < T_c$, we have seen that the liquid and vapour phases co-exist in thermal and mechanical equilibrium for all values of V between V_{liq} and V_{gas} . This means that if the vaporization (or liquefaction) happens at fixed pressure (temperature), the temperature (pressure) remains constant all along the process. We will now demonstrate that the associated thermodynamics potential, namely the Gibbs free energy, G, stays constant as well during the process[‡]. Indeed, during the co-existence regime, we have $G_{2\text{ph}} = F_{2\text{ph}} + pV$, where $F_{2\text{ph}}$ is given by equation (15.5) and $p = -(\partial F_{2\text{ph}}/\partial V)_{T,N}$ so that:

$$G_{2\text{ph}} = F_{\text{liq}} + \frac{V - V_{\text{liq}}}{V_{\text{gas}} - V_{\text{liq}}} \times (F_{\text{gas}} - F_{\text{liq}}) - V \frac{F_{\text{gas}} - F_{\text{liq}}}{V_{\text{gas}} - V_{\text{liq}}}$$
$$= \frac{F_{\text{liq}}V_{\text{gas}} - F_{\text{gas}}V_{\text{liq}}}{V_{\text{gas}} - V_{\text{liq}}}$$
(15.6)

and since, as we have seen previously, V_{liq} and V_{gas} are functions of temperature alone and so are F_{liq} and F_{gas} and by extension $G_{2\text{ph}}$. As the temperature is constant during the phase transition process, $G_{2\text{ph}}$ is therefore a constant. From this result, one deduces that at equilibrium between the phases, the Gibbs energy per particle of each homogeneous phase,

[‡]We have already used this result to calculate V_{liq} and V_{gas} on the specific isotherm $T = 3T_c/4$ in a previous example, but here we establish why this was a legitimate thing to do.

a.k.a. the chemical potentials of the two phases, $\mu_{\text{liq}} \equiv G_{\text{liq}}/N$ and $\mu_{\text{gas}} \equiv G_{\text{gas}}/N$, are equal. Indeed, proceeding as we previously did for F, we can call $G_{\text{lig}}(p,T,N)$ and $G_{\text{gas}}(p,T,N)$ the Gibbs free energies of the homogeneous system when all its N particles are in the liquid and vapour phases respectively. We then have $G_{2\text{ph}} = G_{\text{liq}} \times N_{\text{liq}}/N + G_{\text{gas}} \times N_{\text{gas}}/N$. As we have just demonstrated that G_{2ph} is a constant and given that p, T and N are fixed, we can differentiate this expression to obtain $dG_{2ph} = G_{liq}/N \times dN_{liq} + G_{gas}/N \times dN_{gas} = 0$ so that $(\mu_{\text{liq}} - \mu_{\text{gas}}) dN_{\text{liq}} = 0$ and the equality between chemical potentials immediately follows. As previously mentioned, this form $\mu_{liq} = \mu_{gas}$ is often used to characterise the diffusive equilibrium between two phases, in direct analogy with $p_{\text{liq}} = p_{\text{gas}}$ and $T_{\text{liq}} = T_{\text{gas}}$ for the mechanical and thermal equilibria respectively.

15.5.2 Entropy variation during the phase transition

When n molecules out of N go (at constant T and p) from the liquid state to the vapour state, the entropy of the system, S, increases by:

$$\Delta S \equiv \frac{n}{N} (S_{\text{gas}} - S_{\text{liq}}) = nk_B \ln \left(\frac{V_{\text{gas}} - bN}{V_{\text{liq}} - bN} \right)$$
(15.7)

given equation (14.9) and using the same notation for the entropies S_{lig} and S_{gas} as previously used for the Helmholtz and Gibbs free energies. This increase is positive since $V_{\text{gas}} > V_{\text{liq}} > bN$ and proportional to the number of particles vaporized, n. This entropy variation must be accompanied by a heat exchange of the system with its surroundings. Indeed, since G = U - TS + pV stays constant during the vaporization, as do T and p, we must have $\Delta G = \Delta U - T\Delta S + p\Delta V = 0$. Defining W and Q as the work and heat given to the system during the vaporization process, the first law of thermodynamics yields $\Delta U = W + Q$, and since the transformation is *reversible* (the system stays in thermal, mechanical and diffusive equilibrium throughout), $W = -p\Delta V$ and $Q = T\Delta S$. We thus conclude that Q > 0, i.e. heat must be given to the system for ΔG to cancel: this is an endothermic process. This heat needed to change the state of the system from the liquid to the vapour phase is called *latent heat* of vaporization and is usually defined per mole:

$$L = \frac{\mathcal{N}_A}{n} T \Delta S = RT \ln \left(\frac{V_{\text{gas}} - bN}{V_{\text{liq}} - bN} \right)$$
(15.8)

Note that this is completely intuitive: you have to keep on heating liquid water when it starts boiling to turn all of it into water vapour at the same temperature! As the simple exercise given below shows, this latent heat is large when compared to the amount of heat required to raise the temperature of each different homogeneous phase by tens of degrees.

Exercise 15.1 Take a litre of water at 10°C and vaporize it to 160°C at constant standard pressure $p = 10^5$ Pa. How much heat Q, do you need? [The specific heat capacities of water in its liquid and vapour phases are $c_p^{\text{liq}} = 4200$ J kg⁻¹K⁻¹ and $c_p^{\text{gas}} = 1900$ J kg⁻¹K⁻¹ respectively, and its specific latent heat of vaporization at 100°C $L_V = 2.3 \times 10^6$ J kg⁻¹.] **Ans:** $Q = 2.8 \times 10^6$ J.

- As V_{liq} and V_{gas} are functions of T alone, so is L.
 L = 0 when T = T_c as V_{liq} = V_{gas} for that particular isotherm.
 S(T) will exhibit a discontinuity when the phase transition occurs, as ΔS > 0 but

the temperature does not change. This jump in the value of S will be of order L/T. • The reverse process also exists: vapour can condense into a liquid. This is an *exothermic* process where the latent heat is given to the surroundings of the system.

15.5.3 Meta-stable states

Let us come back to the Van der Waals isotherms in Fig.15.2. Between point $p(V_{\text{liq}})$ and the minimum of p as well as between the maximum of p and $p(V_{\text{gas}})$, p still is a decreasing function of V, and thus the compressibility of the system is positive. Of course we have shown that the true equilibrium state of the system does not follow the Van der Waals isotherms between $p(V_{\text{liq}})$ and $p(V_{\text{gas}})$, but the points in the two regions previously defined can still be reached by the system: they are called *meta-stable* states.

Indeed, considering our F_{2ph} formulation as a linear function of V (equation (15.5)), one clearly sees that any "local" straight line connecting two points located either between point F_{liq} and the first inflection point of F(V) or between its second inflection point and point F_{gas} will be above F(V) (see Fig.15.3). Conversely, only straight lines joining a point between point F_{liq} and the first inflection point of F(V) to another point between its second inflection point and point F_{gas} are below F(V). This tells us that if somehow the system manages, one way of another, to find itself trapped between F_{liq} and the first inflection point of F(V) or between its second inflection point and F_{gas} , fluctuations of small amplitude will not be able to move it away from this point: the system is locally stable. However, a fluctuation with a large enough amplitude will "see" that there exists a possibility of realizing a more stable state by separating into two phases. As the probability of fluctuations goes down rapidly when their amplitude increases, a meta-stable state can therefore be maintained for quite a long time.

In practice, when we slowly increase the volume available to the liquid at constant T, the system can remain homogeneous beyond point F_{liq} , in a state called *superheated* liquid, but not beyond the first inflection point of F(V) when it becomes violently unstable (negative compressibility). In a similar manner, if we slowly reduce the volume available to the vapour at fixed T, we will be able to keep it in a homogeneous phase beyond point F_{gas} (but not beyond the second inflection point of F(V)), in a meta-stable state called supercooled vapour. Important perturbations (like a drop of liquid in supercooled vapour, or a vapour bubble in a superheated liquid, impurities, or a simple shock) will trigger an evolution of the system towards its true equilibrium: the two-phase state. The meta-stable domain is bounded by the two phase co-existence curve on one side, and the curve linking the extrema of the different Van der Waals isotherms (or equivalently the inflection points of the different corresponding F(V)) as T varies. Such a curve is called a spinodial curve and is represented on Fig.15.5.

15.6 The Clausius-Clapeyron equation

Let us now examine the other two dimensional phase diagram, the one obtained when projecting in the (p, T) plane (see Fig.15.6). The line in this diagram defines the region where the two phases co-exist. In other words, if we are in the homogeneous gas phase on the line (i.e. $T < T_c$) and p increases slightly, we will jump to the homogeneous liquid phase immediately. This will appear as a volume discontinuity and is a characteristic of the liquid-vapour phase transition.

On either side of the line, all N particles are either in the gas or the liquid phase. As we have previously shown, the Gibbs free energy (at fixed p and T) of these two phases are equal: $G_{\text{liq}} = G_{\text{gas}}$. This means that G is continuous as we cross the phase transition line. Let us then sit on this line and move upwards along it by an infinitesimal amount. As the total number of particles, N, is constant, the change in G caused by this displacement for each phase is given by:

$$dG_{\text{liq}} = -S_{\text{liq}}dT + V_{\text{liq}}dp$$

$$dG_{\text{gas}} = -S_{\text{gas}}dT + V_{\text{gas}}dp$$
(15.9)

Equating these two expressions to enforce the continuity of G across the phase transition line at the new position yields:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_{\mathrm{gas}} - S_{\mathrm{liq}}}{V_{\mathrm{gas}} - V_{\mathrm{liq}}} = \frac{L}{T(V_{\mathrm{gas}} - V_{\mathrm{liq}})}$$
(15.10)

where the last equality arises from the definition of latent heat $(L = T\Delta S)$. This relation which defines the slope of the phase transition line as the ratio of the latent heat released by the phase transition and the discontinuity in volume between the phases is known as the *Clausius-Clapeyron equation*.

Exercise 15.2 Find an approximated solution, p(T), to the Clausius-Clapeyron equation. [Assume that L is independent of T, $V_{\text{gas}} \gg V_{\text{liq}}$ and that the gas EOS is that of an ideal gas.]

Ans: $p = p_0 \exp(-L/(k_B T)).$

15.7 Classification of phase transitions

The liquid-gas phase transition that we have just studied is not the only kind of phase transition that exists in nature. Ehrenfest thus proposed to classify phase transitions based on whether the derivatives of the thermodynamical potential (usually F or G) of a system are continuous. This means that if the n^{th} derivative of this potential is discontinuous, we will say that we have a n^{th} order phase transition. In the case of the liquid-gas phase transition, as we have seen, latent heat is released/absorbed, so $S = -(\partial F/\partial T)_{V,N}$ is discontinuous, as is $V = (\partial G/\partial p)_{T,N}$. So we are dealing with a first order phase transition.

In practice, phase transitions of order greater than two are rare, and the thermodynamical limit tends to break down at phase transition (fluctuations are large), so the thermodynamic potentials are not well defined. For these reasons, the modern classification is more simple than that originally advocated by Ehrenfest: if latent heat is present, the phase transition is first order; if not, the phase transition is called *continuous*.

Note that when T → T_c, the amplitude of the discontinuity diminishes as S_{liq} → S_{gas}, and that for T ≥ T_c we do get a *continuous* phase transition.
For most simple materials, the liquid-gas phase transition is part of a larger phase transition which includes a solid phase at smaller T or higher p, as illustrated on Fig.15.4.

16. Cooling of real gases

The purpose of these final lectures is to close the loop. Recall the Basic Thermodynamics part of the course at the beginning of the year, where we studied the thermal behaviour of ideal gas under certain practical transformations (adiabatic, isothermal expansions, etc ...). We will now see how real gases behave during similar transformations and what practical consequences this has.

16.1 Joule expansion revisited

Remember the Joule expansion for ideal gases (section 5.6.2). No heat enters or leaves the system as the containers are thermally insulated, no work is done either by or on the gas as it expands in a vacuum, so its internal energy, U, is unchanged according to the first law. For an ideal gas, U is a function of T alone, so $\Delta U = 0 \implies \Delta T = 0$.

We can reformulate this statement using the *Joule coefficient*, $\mu_J \equiv (\partial T/\partial V)_U$, i.e. the change of temperature induced by a change in volume at constant internal energy, which is the relevant constraint in the case of a Joule expansion. Using the reciprocity and reciprocal theorems, we can re-write the Joule coefficient as $\mu_J = -(\partial T/\partial U)_V (\partial U/\partial V)_T =$ $-1/C_V (\partial U/\partial V)_T$. From the first law of Thermodynamics, dU = TdS - pdV, so that $(\partial U/\partial V)_T = T(\partial S/\partial V)_T - p$, and using the Maxwell relation for F (equation (6.3)), one gets $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$, therefore

$$\mu_J = -\frac{1}{C_V} \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right]$$
(16.1)

As we have just recalled, for a mole of an ideal gas with EOS p = RT/V, $\mu_J = 0$. Now for a real gas, we have seen than the pressure is always lower than for an ideal gas because of the presence of an attractive long-range force between molecules. This means that since $C_V > 0$, $\mu_J < 0$ for a real gas. Indeed, as U is not changing in a Joule expansion (Q = W = 0), and the potential energy of the gas becomes less negative as it expands (the distance between

gas molecules increases and the intermolecular attraction becomes weaker), then the kinetic energy of the gas must also decrease and the real gas must thus cool.

Let us calculate by how much. That is where μ_J becomes handy. Indeed, during a Joule expansion, the change of T is simply:

$$\Delta T = \int_{V_i}^{V_f} \mu_J \, \mathrm{d}V = -\int_{V_i}^{V_f} \frac{1}{C_V} \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] \mathrm{d}V \tag{16.2}$$

Take the Van der Waals EOS. For one mole of gas, it yields $p = RT/(V-b) - a/V^2$ so $(\partial p/\partial T)_V = R/(V-b)$ and $\mu_J = -a/(C_V V^2)$. As $V_i < V_f$, we deduce that $\Delta T = -a/C_V \times (1/V_i - 1/V_f) < 0$ for a Van der Waals gas: as expected, it cools.

Exercise 16.1 What is the temperature change when one Joule expands 1 mole of Helium enclosed in a $(0.1 \text{ m})^3$ container into a $(0.2 \text{ m})^3$ container? [Use the Van der Waals EOS with $a = 0.00346 \text{ J m}^3 \text{ mol}^2$ and the *molar heat capacity*^a of Helium, $C_V = 12.48 \text{ J K}^{-1} \text{ mol}^{-1}$.]

Ans: $\Delta T = -0.243$ K.

^aThis is the specific heat of Helium times its molar mass (4g).

16.2 Joule-Kelvin expansion

The Joule expansion is interesting conceptually, but of little practical use. As we have seen, the gas cools a bit when it expands but then "so what"? What you would want in practice is a kind of "cooling machine" where you feed in warm gas and get out cold liquid! As it turns out, James Joule and William Thomson (a.k.a. Lord Kelvin) discovered the process such a machine could be based on. Note that this process, similarly to the Joule expansion, is inherently *irreversible*.



Figure 16.1: Schematic diagram of a Joule-Kelvin expansion.

Consider a highly pressurized gas at pressure p_i enclosed in a thermally insulated container of volume V_i , which is forced through a porous plug (see Fig. 16.1). It might be helpful to pretend it is pushed by a piston^{*}. The internal energy of this gas is U_i and the work done by the piston is p_iV_i . This gas expands as it goes through the plug and occupies another thermally insulated container of volume $V_f > V_i$. It also has to do work to push another piston which exerts a lower pressure $p_f < p_i$ at the back of the container[†]. This

^{*}In reality, this piston could be "virtual" and it would then be the inflowing gas behind the gas that is enclosed in volume V_i that is doing the pushing.

[†]Again, in reality, the expanding gas could be pushing the lower pressure gas in front of it instead of the piston, as long as any change in the bulk kinetic energy of the gas flow can be considered negligible throughout the process.

work is $p_f V_f$. The temperature of the gas may change in the process, so we will denote its internal energy by U_f .

The first law tells us that since there is no heat exchange, the change of energy $\Delta U = U_f - U_i$ must be equal to the amount of work done on the gas to get it through the plug, minus the amount of work done by the gas as it comes out of it. Mathematically, $\Delta U = p_i V_i - p_f V_f$, i.e $U_i + p_i V_i = U_f + p_f V_f$ or $H_i = H_f$, that is to say the process conserves the enthalpy of the gas. As in the Joule expansion we want to know how much the temperature of the gas has changed during the process, so we define the *Joule-Kelvin coefficient*, $\mu_{JK} \equiv (\partial T/\partial p)_H$, which measures the temperature change of the gas as we reduce its pressure at constant enthalpy. In a similar fashion as what we did for μ_J , we can use the reciprocity and reciprocal theorems, coupled to the definition of C_p^{\dagger} to re-write this coefficient as $\mu_{JK} = -(\partial T/\partial H)_p (\partial H/\partial p)_T = -1/C_p (\partial H/\partial p)_T$. Again from the first law of Thermodynamics, dU = TdS - pdV, so that dH = TdS + Vdp and $(\partial H/\partial p)_T = -T(\partial S/\partial p)_T + V$, and using the Maxwell relation for G (equation (6.4)), one gets $(\partial H/\partial p)_T = -T(\partial V/\partial T)_p + V$, therefore

$$\mu_{JK} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right]$$
(16.3)

As for μ_J , for a mole of an ideal gas with EOS V = RT/p, $\mu_{JK} = 0$, and thus the change in temperature during a Joule-Kelvin expansion,

$$\Delta T = \int_{p_i}^{p_f} \mu_{JK} \, \mathrm{d}p = \int_{p_i}^{p_f} \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] \mathrm{d}p \tag{16.4}$$

is also nil. But what about a real gas? Will ΔT be positive or negative? Well, it depends on the sign of μ_{JK} , which can, contrary to μ_J , be positive or negative; and since $C_p > 0$, it ultimately depends on the sign of $T(\partial V/\partial T)_p - V$.

R The change in entropy during a Joule-Kelvin expansion can be calculated quite straightforwardly. As the enthalpy is constant, we have dH = TdS + Vdp = 0, so that dS = -V/Tdp, and thus

$$\Delta S = -\int_{p_i}^{p_f} \frac{V}{T} \, \mathrm{d}p$$

which for a mole of ideal gas with EOS V/T = R/p yields $\Delta S = R \ln(p_i/p_f) > 0$, in line with what we expect for an irreversible process.

Therefore, the equation

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}$$

(16.5)

defines the so called *inversion curve* in the T-p plane, i.e. the locus where the Joule-Kelvin expansion switches from cooling the gas to heating it (see Fig.16.2).

Example 16.1 — Calculation of the inversion curve for a Van der Waals gas. Starting from the Van der Waals EOS in the form $p = Nk_BT/(V - bN) - aN^2/V^2$, we calculate

[‡]At constant p we have dH = dU + pdV, as we used in equation (3.1).

 $(\partial T/\partial V)_p$, take its inverse, multiply it by T and substract V from the result to obtain equation (16.5) in the form $(V - bN)/(1 - \xi) - V = 0$, with $\xi = 2aN(V - bN)^2/(k_BTV^3)$. This yields $\xi = bN/V \iff (V - bN)^2 = bk_bTV^2/(2a)^{\$}$. As V, (V - bN), T, a and b are all positive, we can take the square root of this last equation to get $V = bN/(1 - \sqrt{bk_BT/2a})$. Injecting this expression for V in the Van der Waals EOS then yields the following explicit form of the inversion curve:

$$p = \frac{1}{b^2} \left(-\frac{3bk_B}{2}T + \sqrt{8abk_B}T^{1/2} - a \right)$$

The (quadratic) equation p = 0 has two roots, $T_+ = 2a/(bk_B) = 27T_c/4$ and $T_- = 2a/(9bk_B) = 3T_c/4$, and a maximum pressure $p_{\text{max}} = 9p_c$, achieved when dp/dT = 0, i.e. for $T = 8a/(9bk_B) = 3T_c$. This curve is plotted in Fig.16.2.



Figure 16.2: Joule-Kelvin expansion inversion curve (in solid red) for a Van der Waals gas, as calculated in example 16.1. The inversion curve separates a light blue shaded domain where $\mu_{JK} < 0$ which means that the Joule-Kelvin expansion is cooling the gas, from a blank region where $\mu_{JK} > 0$ and the Joule-Kelvin expansion heats the gas. Note that the inversion curve also crosses the co-existence curve (in solid blue), which makes it very interesting a process to liquefy gases!

 T_+ , as calculated in example 16.1 for the Van der Waals gas, is called the *maximum* inversion temperature, as it is clear that above this temperature the Joule-Kelvin expansion can only heat the gas, regardless of its pressure. Note that this maximum temperature can be quite low. For instance, ⁴He has $T_+ = 43$ K. This means that to cool Helium using the Joule-Kelvin process, one needs to cool it below 43 K first! Finally, let us mention that the Joule-Kelvin process is very useful to liquefy gases (intersection with the co-existence curve: see Fig.16.2), and one can show that a liquefier needs to work on the inversion curve for maximal efficiency.

[§]Rigorously speaking, this solution is only valid for $\xi \neq 1$, but in the case $\xi = 1$, we have $(\partial T/\partial V)_p = 0$ so T independent of V and the solution to the inversion curve equation is V = 0, which we can rightfully discard.