

## CHAPTER 6

### PROPERTIES OF GASES

#### 6.1 *The Ideal Gas Equation*

In 1660, the Honorable Robert Boyle, Father of Chemistry and seventh son of the Earl of Cork, and one of the founders of the Royal Society of London, conducted certain *Experiments Physico-Mechanical Touching the Spring of the Air*. He held a quantity of air in the closed arm of a J-shaped glass tube by means of a column of mercury and he measured the volume of the air as it was subjected to greater and greater pressures. As a result of these experiments he established what is now known as *Boyle's Law*:

*The pressure of a fixed mass of gas held at constant temperature (i.e. in an isothermal process) is inversely proportional to its volume.*

That is, 6.1.1

$$PV = \text{constant.}$$

Later experiments showed that the volume of a fixed mass of gas held at constant pressure increases linearly with temperature. In particular, most gases have about the same volume coefficient of expansion. At 0°C this is about  $0.00366 \text{ } ^\circ\text{C}^{-1}$  or  $1/273 \text{ } ^\circ\text{C}^{-1}$ .

If you extrapolate the volume of a fixed mass of gas held at constant pressure to lower and lower temperatures, the extrapolated volume would fall to zero at  $-273 \text{ } ^\circ\text{C}$ . This is not directly the basis of our belief that no temperatures are possible below  $-273 \text{ } ^\circ\text{C}$ . For one thing, a real gas would liquefy long before that temperature is reached. Nevertheless, for reasons that will be discussed in a much later chapter, we do believe that this is the absolute zero of temperature. In any case:

*The volume of a fixed mass of gas held at constant pressure (i.e. in an isobaric process) is directly proportional to its Kelvin temperature.*

Lastly,

*The pressure of a fixed mass of gas held at constant volume (i.e. in an isochoric process) is directly proportional to its Kelvin temperature.*

If  $P$ ,  $V$  and  $T$  are all allowed to vary, these three laws become

$$PV/T = \text{constant} \tag{6.1.2}$$

The value of the constant depends on how much gas there is; in particular, it is proportional to how many *moles* (hence how many *molecules*) of gas there are. That is

$$PV/T = RN, \tag{6.1.3}$$

where  $N$  is the number of moles and  $R$  is a proportionality constant, which is found to be about the same for most gases.

Of course real gases behave only approximately as described, and only provided experiments are performed over modest ranges of temperature, pressure and volume, and provided the gas is well above the temperature at which it will liquefy. Nevertheless, provided these conditions are satisfied, most gases do conform quite well to equation 6.1.3 with about the same proportionality constant for each.

A gas that obeys the equation

$$PV = NRT \quad 6.1.4$$

exactly is called an *Ideal Gas*, and equation 6.1.4 is called the *Equation of State for an Ideal Gas*. In this equation,  $V$  is the *total volume* of the gas,  $N$  is the number of moles and  $R$  is the *Universal Gas Constant*. The equation can also be written

$$PV = RT. \quad 6.1.5$$

In this case,  $V$  is the *molar volume*. Some authors use different symbols (such as  $V$ ,  $v$  and  $V_m$ ) for total, specific and molar volume. This is probably a good idea, and it is at some risk that I am not going to do this, and I am going to hope that the context will make it clear which volume I am referring to when I use the simple symbol  $V$  in any particular situation. Note that, while total volume is an *extensive* quantity, specific and molar volumes are *intensive*.

It is not impossible to go wrong by a factor of  $10^3$  when using equation 6.1.5. If you are using CGS units,  $P$  will be expressed in dynes per square cm,  $V$  is the volume of a mole (i.e. the volume occupied by  $6.0221 \times 10^{23}$  molecules), and the value of the universal gas constant is  $8.3145 \times 10^7$  erg mole<sup>-1</sup> K<sup>-1</sup>. If you are using SI units,  $P$  will be expressed in pascal (N m<sup>-2</sup>),  $V$  will be the volume of a kilomole (i.e. the volume occupied by  $6.0221 \times 10^{26}$  molecules), and the value of the universal gas constant is  $8.3145 \times 10^3$  J kilomole<sup>-1</sup> K<sup>-1</sup>. If you wish to express pressure in Torr, atm. or bars, and energy in calories, you're on your own.

You can write equation 6.1.4 (with  $V$  = total volume) as  $P = \frac{NN_A}{V} \frac{RT}{N_A}$ , where  $N_A$  is Avogadro's number, which is  $6.0221 \times 10^{23}$  molecules per mole, or  $6.0221 \times 10^{26}$  molecules per kilomole. The first term on the right hand side is the total number of molecules divided by the volume; that is, it is the number of molecules per unit volume,  $n$ . In the second term,  $R/N_A$  is *Boltzmann's constant*,  $k = 1.3807 \times 10^{-23}$  J K<sup>-1</sup>. Hence the equation of state for an ideal gas can be written

$$P = nkT. \quad 6.1.6$$

Divide both sides of equation 6.1.5 by the molar mass ("molecular weight")  $\mu$ . The density  $\rho$  of a sample of gas is equal to the molar mass divided by the molar volume, and hence the equation of state for an ideal gas can also be written

$$P = \frac{\rho RT}{\mu}. \quad 6.1.7$$

In summary, equations 6.1.4, 6.1.5, 6.1.6 and 6.1.7 are all commonly-seen equivalent forms of the equation of state for an ideal gas.

From this point on I shall use  $V$  to mean the *molar volume*, unless stated otherwise, so that I shall use equation 6.1.5 rather than 6.1.4 for the equation of state for an ideal gas. Note that the molar volume (unlike the total volume) is an *intensive* state variable.

In September 2007, the values given for the above-mentioned physical constants on the Website of the National Institute of Science and Technology (<http://physics.nist.gov/cuu/index.html>) were:

Molar Gas Constant  $R = 8314.472 (15) \text{ J kmole}^{-1} \text{ K}^{-1}$ .

Avogadro Constant  $N_A = 6.022\,141\,79 (30) \times 10^{26} \text{ particles kmole}^{-1}$ .

Boltzmann Constant  $k = 1.380\,6504 (24) \times 10^{-23} \text{ J K}^{-1} \text{ per particle}$ .

The number in parentheses is the standard uncertainty in the last two figures.

## 6.2 Real Gases

How well do real gases conform to the equation of state for an ideal gas? The answer is quite well over a large range of  $P$ ,  $V$  and  $T$ , provided that the temperature is well above the critical temperature. We'll have to see shortly what is meant by the critical temperature; for the moment we'll say the ideal gas equation is followed quite well provided that the temperature is well above the temperature at which it can be liquefied merely by compressing it. Air at room temperature obeys the law quite well. Gases in stellar atmospheres also obey the law well, because there is no danger there of the gas liquefying. (In the cores of stars, however, where densities are very large, the gases obey a very different equation of state.)

One measure of how well the law is obeyed by real gases is to measure  $P$ ,  $V$  and  $T$ , and see how close  $\frac{PV}{RT}$  is to 1. The quantity  $\frac{PV}{RT}$  is known as the *compression factor*, and is often given the symbol  $Z$ . For most real gases at very high pressures (a few hundred atmospheres), it is found in fact that  $Z$  is rather greater than 1. As the pressure is lowered,  $Z$  becomes lower, and then, alas, it overshoots and is found to be a little less than 1. Then at yet lower pressures  $Z$  rises again. The exact shape of the  $Z : P$  curve is different from gas to gas, as is the pressure at which  $Z$  is a minimum. Yet, for all gases, *as the pressure approaches zero,  $PV/T$  approaches  $R$  exactly*. For this reason  $R$  is sometimes called the *Universal Gas Constant* as well as the *Ideal Gas Constant*. In the limit of very low pressures, all gases behave very closely to the behaviour of an ideal gas. In Section 6.3 we shall be examining more closely how the compression factor varies with pressure.

Another way to look at how closely real gases obey the ideal gas equation is to plot  $P$  versus  $V$  for a number of different temperatures. That is, we draw a set of *isotherms*. For an ideal gas, these isotherms,  $PV = \text{constant}$ , are rectangular hyperbolas. So they are for real gases at high

temperatures. At lower temperatures, departures from the ideal gas equation are marked. Typical isotherms are sketched in figure VI.1. Alas, my limited skills with this infernal computer in front of me allow me only to sketch these isotherms crudely by hand.

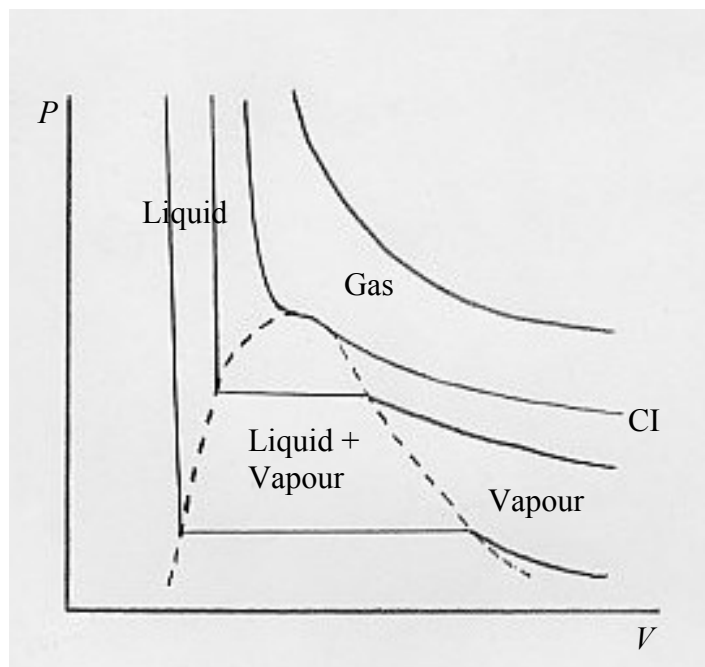


FIGURE VI.1

In the  $PV$  plane of figure VI.1, you will see several areas marked "gas", "liquid", "vapour", "liquid + vapour". You can follow the behaviour at a given temperature by starting at the right hand end of each isotherm, and gradually moving to the left – i.e. increase the pressure and decrease the volume. The hottest isotherm is nearly hyperboloidal. Nothing special happens beyond the volume decreasing as the pressure is increased, according to Boyle's law. At slightly lower temperatures, a kink develops in the isotherm, and at the *critical temperature* the kink develops a local horizontal inflection point. The isotherm for the critical temperature is the *critical isotherm*, marked CI on the sketch. Still nothing special happens other than  $V$  decreasing as  $P$  is increased, though not now according to Boyle's law.

For temperatures below the critical temperature, we refer to the gas as a *vapour*. As you decrease the volume, the pressure gradually increases until you reach the dashed curve. At this point, some of the vapour liquefies, and, as you continue to decrease the volume, more and more of the vapour liquefies, the pressure remaining constant while it does so. That's the horizontal portion of the isotherm. In that region (i.e. outlined by the dashed curve) we have liquid and vapour in equilibrium. Near the right hand end of the horizontal portion, there is just a small amount of liquid; at the left hand end, most of the substance is liquid, with only a small amount of vapour left. After it is all liquid, further increase of pressure barely decreases the volume, because the liquid is hardly at all compressible. The isotherm is then almost vertical.

The temperature of the critical isotherm is the *critical temperature*. The pressure and molar volume at the horizontal inflection point of the critical isotherm are the *critical pressure* and *critical molar volume*. The horizontal inflection point is the *critical point*.

### 6.3 Van der Waals and Other Gases

We have seen that real gases resemble an ideal gas only at low pressures and high temperatures. Various attempts have been made to find an equation that adequately represents the relation between  $P$ ,  $V$  and  $T$  for a real gas – i.e. to find an *Equation of State* for a real gas. Some of these attempts have been purely empirical attempts to fit a mathematical formula to real data. Others are the result of at least an attempt to describe some physical model that would explain the behaviour of real gases. A sample of some of the simpler equations that have been proposed follows:

$$\text{van der Waals' equation:} \quad (P + a/V^2)(V - b) = RT. \quad 6.3.1$$

$$\text{Berthelot's equation:} \quad (P + a/(TV^2))(V - b) = RT. \quad 6.3.2$$

$$\text{Clausius's equation*}: \quad \left( P + \frac{a}{T(V+c)^2} \right) (V - b) = RT. \quad 6.3.3$$

$$\text{Dieterici's equation:} \quad P(V - b)e^{a/(RTV)} = RT. \quad 6.3.4$$

$$\text{Redlich-Kwong:} \quad P = \frac{RT}{V - b} - \frac{a}{bT^{1/2}} \left( \frac{1}{V} - \frac{1}{V + b} \right). \quad 6.3.5$$

$$\text{Virial equation:} \quad PV = A + BP + CP^2 + DP^3 + \dots \quad 6.3.6$$

In the virial equation in general the coefficients  $A$ ,  $B$ ,  $C$ , ... are functions of temperature.

\*In Clausius's equation, if we choose  $c = 3b$ , we get a fairly good agreement between the *critical compression factor* of a Clausius gas and of many real gases. The meaning of "critical compression factor", and the calculation of its value for a Clausius gas is described a little later in this section.

There are many others, but by far the best known of these is van der Waals' equation, which I shall describe at some length.

It is not possible for the voice-box of an English speaker correctly to pronounce the name van der Waals, although the W is pronounced more like a V than a W, and, to my ear, the v is somewhat intermediate between a v and an f. To hear it correctly pronounced – especially the vowels – you must ask a native Dutch speaker. The frequent spelling "van der Waal's equation" is merely yet another symptom of the modern lamentable ignorance of the use of the apostrophe so much regretted by Lynne Truss.

The units in which the constants  $a$  and  $b$  should be expressed sometimes cause difficulty, and they depend on whether the symbol  $V$  in the equation is intended to mean the specific or molar volume. The following might be helpful.

If  $V$  is intended to mean the *specific* volume, van der Waals' equation should be written

$$(P + a/V^2)(V - b) = RT/\mu, \text{ where } \mu \text{ is the molar mass ("molecular weight"). In this case}$$

the dimensions and SI units of  $a$  are  $M^{-1}L^5T^{-2}$  and  $\text{Pa m}^6 \text{ kg}^{-2}$

and the dimensions and SI units of  $b$  are  $M^{-1}L^3$  and  $\text{m}^3 \text{ kg}^{-1}$

If  $V$  is intended to mean the *molar* volume, van der Waals' equation should be written in its familiar form

$$(P + a/V^2)(V - b) = RT. \text{ In this case}$$

the dimensions and SI units of  $a$  are  $\text{ML}^5\text{T}^{-2}\text{mole}^{-2}$  and  $\text{Pa m}^6 \text{ kmole}^{-2}$

and the dimensions and SI units of  $b$  are  $\text{L}^3\text{mole}^{-1}$  and  $\text{m}^3 \text{ kmole}^{-1}$

The van der Waals constants, referred to molar volume, of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are approximately:

$$\text{H}_2\text{O}: \quad a = 5.5 \times 10^5 \text{ Pa m}^6 \text{ kmole}^{-2} \quad b = 3.1 \times 10^{-2} \text{ m}^3 \text{ kmole}^{-1}$$

$$\text{CO}_2: \quad a = 3.7 \times 10^5 \text{ Pa m}^6 \text{ kmole}^{-2} \quad b = 4.3 \times 10^{-2} \text{ m}^3 \text{ kmole}^{-1}$$

The van der Waals equation has its origin in at least some attempt to describe a physical model of a real gas. The properties of an ideal gas can be modelled by supposing that a gas consists of a collection of molecules of zero effective size and no forces between them, and pressure is the result of collisions with the walls of the containing vessel. In the van der Waals model, there are supposed to be attractive forces between the molecules. These are known as van der Waals forces and are now understood to arise because when one molecule approaches another, each induces a dipole moment in the other, and the two induced dipoles then attract each other. This attractive force reduces the pressure at the walls, the reduction being proportional to the number of molecules at the walls that are being attracted by the molecules beneath, and to the number of molecules beneath, which are doing the attracting. Both are inversely proportional to  $V$ , so the pressure in the equation of state has to be replaced by the measured pressure  $P$  plus a term that is inversely proportional to  $V^2$ . Further, the molecules themselves occupy a finite volume. This is tantamount to saying that, at very close range, there are *repulsive* forces (now understood to be Coulomb forces) that are greater than the attractive van der Waals forces. Thus the volume in which the molecules are free to roam has to be reduced in the van der Waals equation. For more on the forces between molecules, see Section 6.8.

However convincing or otherwise you find these arguments, they are at least an attempt to describe some physics, they do represent the behaviour of real gases better than the ideal gas equation, and, if nothing else, they give us an opportunity for a little mathematics practice.

We shall see shortly how it is possible to determine the constants  $a$  and  $b$  from measurements of the critical parameters. These constants in turn give us some indication of the strength of the van der Waals forces, and of the size of the molecules.

Van der Waals' equation, equation 6.3.1, can be written

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad 6.3.7$$

A horizontal inflection point occurs where  $\frac{\partial P}{\partial V}$  and  $\frac{\partial^2 P}{\partial V^2}$  are both zero. That is

$$-\frac{RT}{(V - b)^2} + \frac{2a}{V^3} = 0 \quad 6.3.8$$

and

$$\frac{2RT}{(V - b)^3} - \frac{6a}{V^4} = 0. \quad 6.3.9$$

Eliminate  $RT/a$  from these to find the critical molar volume of a van der Waals gas:

$$V_c = 3b. \quad 6.3.10$$

Substitute this into equation 6.3.8 or 6.3.9 (or both, as a check on your algebra) to obtain the critical temperature:

$$T_c = \frac{8a}{27Rb}. \quad 6.3.11$$

Substitute equations 6.3.10 and 6.3.11 into equation 6.3.7 to obtain the critical pressure:

$$P_c = \frac{a}{27b^2}. \quad 6.3.12$$

From these, we readily obtain

$$\frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375. \quad 6.3.13$$

This quantity is often called the *critical compression factor* or *critical compressibility factor*, and we shall denote it by the symbol  $Z_c$ . For many real gases  $Z_c$  is about 0.28; thus the van der Waals

equation, while useful in discussing the properties of gases in a qualitative fashion, does not reproduce the observed critical compression factor particularly well.

Let us now substitute  $p = P/P_c$ ,  $v = V/V_c$ ,  $t = T/T_c$ , and van der Waals' equation, in which the pressure, volume and temperature are expressed in terms of their critical values, becomes

$$(p + 3/v^2)(v - \frac{1}{3}) = \frac{8}{3}t. \quad 6.3.14$$

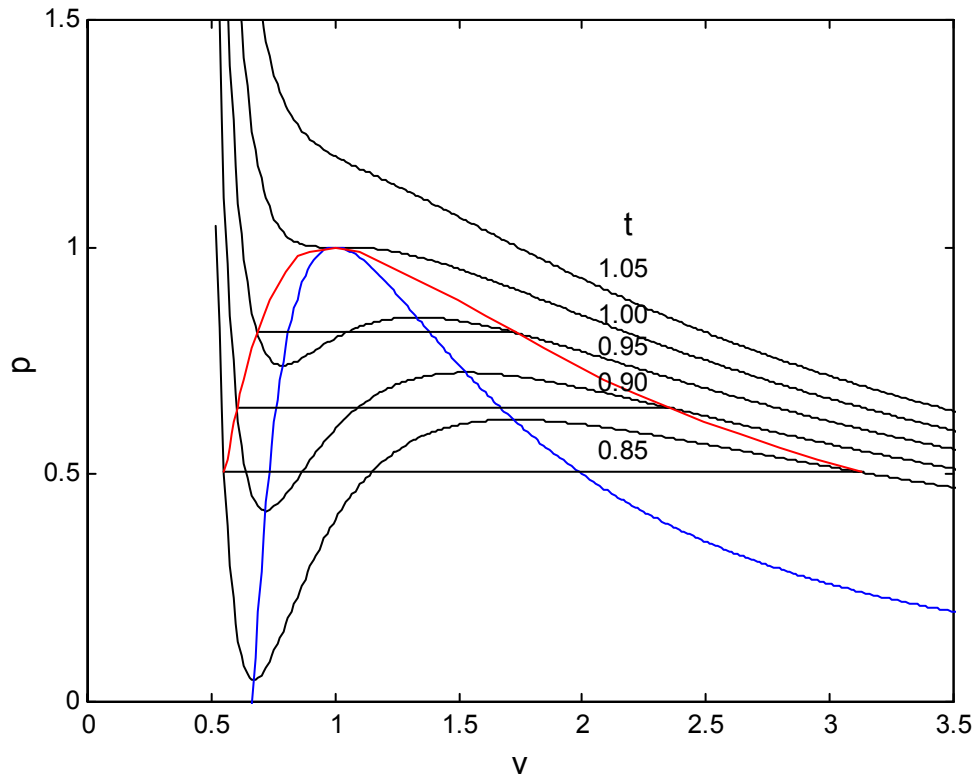
This can also be written  $3pv^3 - (p+8t)v^2 + 9v - 3 = 0. \quad 6.3.15$

For volumes less than a third of the critical volume, this equation does not describe the behaviour of a real gas at all well. Indeed, you can see that  $p = \infty$  when  $v = 1/3$ , which means that you have to exert an infinite pressure to compress a van der Waals gas to a third of its critical volume. You might want to investigate for yourself the behaviour of equations 6.3.14 and 15 for volumes smaller than this. You will find that it goes to infinity at  $v = 0$  and  $1/3$ , and it has a maximum between these two volumes. But the equation is of physical interest only for  $v > 1/3$ , where the variation of pressure, volume and temperature bears at least some similarity to the behaviour of real gases, if by no means exact. In figure VI.2, I show the behaviour of a van der Waals gas for five temperatures – one above the critical temperature, one at the critical temperature, and three below the critical temperature. The locus of maxima and minima is found by eliminating  $t$  between equation 6.3.14 and  $\partial p / \partial v = 0$ . You should try this, and show that the locus of the maxima and minima (which I have shown by a blue line in figure VI.2) is given by

$$p = \frac{3}{v^2} - \frac{2}{v^3} \quad 6.3.16$$



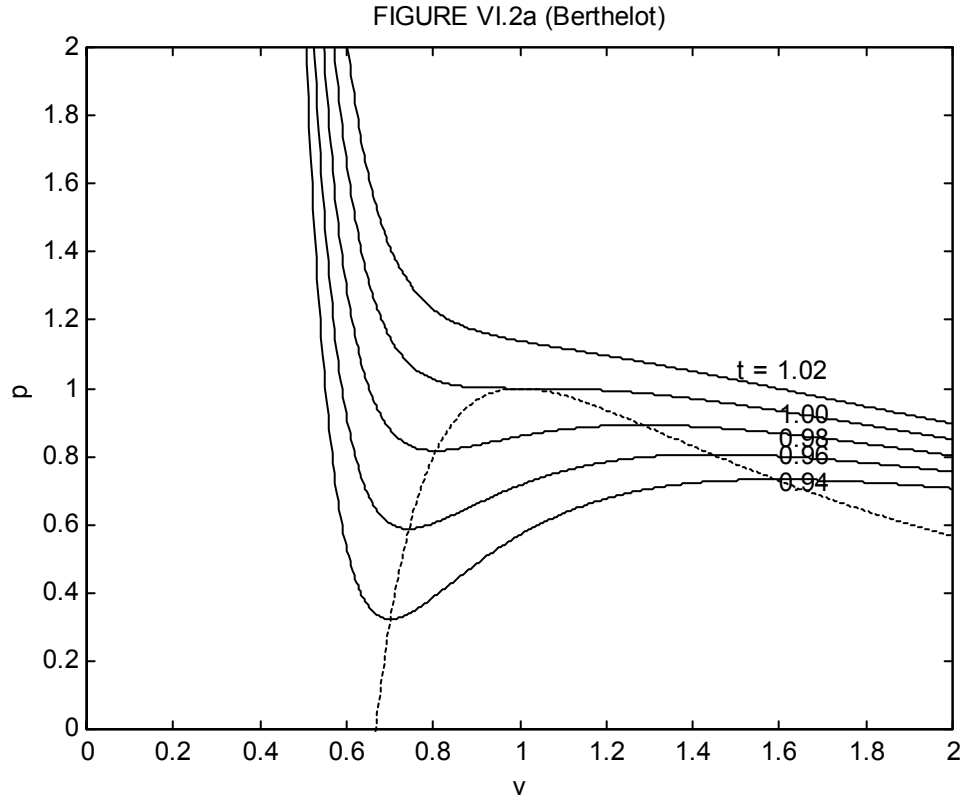
FIGURE VI.2



Don't confuse the **blue** curve in this figure (it shows the locus of maxima and minima) with the dashed curve in figure VI.1 (it shows the boundary between phases.). For the temperatures 0.85, 0.90 and 0.95 I have drawn the constant pressure lines where liquid and vapour are in equilibrium in the real fluid. These are drawn so that they divide the van der Waals curve into two equal areas, above and below. This means that the work done by the real fluid when it changes from liquid to vapour at constant pressure is equal to the work that would be done by its hypothetical van der Waals equivalent along its wiggly path. We shall later see that the placement of the horizontal line is a consequence of the fact that the *Gibbs function* (which we have not yet met) is constant while the liquid and vapour are in equilibrium. The dashed line of figure VI.1 would correspond on figure VI.2 to the locus of the ends of the horizontal lines. I have drawn this locus, which outlines the region where liquid and vapour are in equilibrium, in **red** in figure VI.2. While the van der Waals equation is only a rough approximation to the behaviour of real gases, it is nevertheless true that, if pressures, temperatures and molar volumes are expressed in terms of the critical pressures, temperatures and molar volumes, the actual equations of state of real gases are very similar. Two gases with the same values of  $p$ ,  $v$  and  $t$  are said to be in *corresponding states*, and the observation that the  $p : v : t$  relation is approximately the same for all gases is called the *Law of Corresponding States*. We may think of gases as being composed of particles (molecules) and the only difference between different gases is in the sizes of their molecules (i.e. their different van der Waals  $b$  constants) and their dipole moments or their electrical polarizabilities (i.e. their different van der Waals  $a$  constants). In the dimensionless forms of the equation of state, these van der Waals constants are removed from the equations, and it is not surprising that all gases then conform to the same equation of state.

I leave it to the reader to show that, for a *Berthelot* gas, the critical molar volume, temperature and pressure and the critical compression factor are, respectively,  $3b$ ,  $\sqrt{\frac{8a}{27bR}}$ ,  $\frac{1}{b}\sqrt{\frac{aR}{216b}}$  and 0.375, that the equation of state in terms of the dimensionless variables is

$$p = \frac{8t}{3v-1} - \frac{3}{tv^2}, \quad 6.3.17$$



and that the locus of maxima and minima is

$$p = \frac{1}{v^{1/2}} \left( \frac{4}{v} - \frac{6}{3v-1} \right). \quad 6.3.18$$

These are shown in figure VI.2a. It will be noted that the critical compression factor is the same as (and hence no better than) for a van der Waals gas.

For a *Clausius* gas, the critical molar volume, temperature and pressure and the critical compression factor are, respectively,  $3b+2c$ ,  $\sqrt{\frac{8a}{27(b+c)R}}$ ,  $\frac{1}{(b+c)}\sqrt{\frac{aR}{216(b+c)}}$  and  $\frac{3b+2c}{8(b+c)}$ .

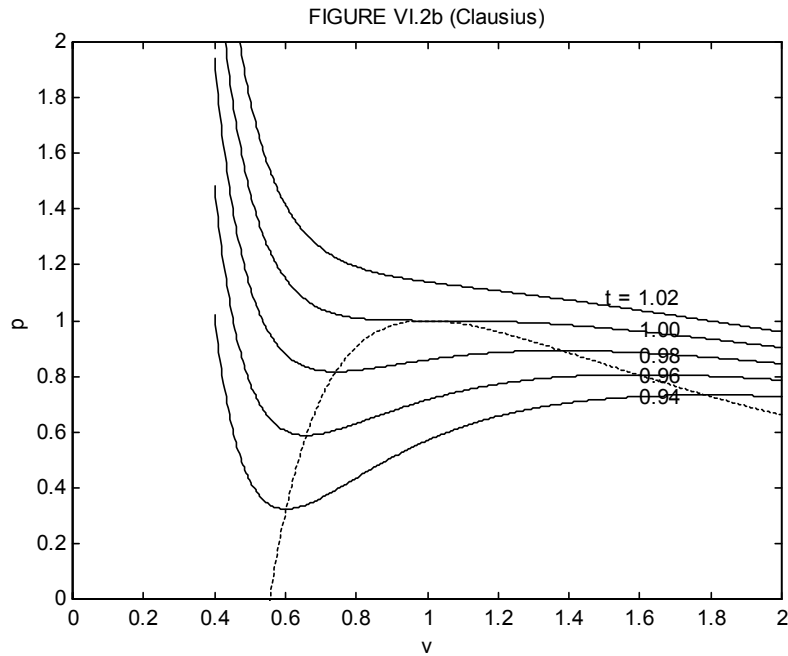
If  $c = 3b$ , these become  $3c$ ,  $\sqrt{\frac{2a}{9cR}}$ ,  $\frac{1}{c}\sqrt{\frac{aR}{512c}}$  and  $\frac{9}{32} = 0.28125$ . I choose  $c = 3b$  because that gives a good agreement with the critical compression factor for many real gases. In dimensionless units, the Clausius equation becomes

$$p = \frac{32t}{9v - 1} - \frac{48}{t(3v + 1)^2}. \quad 6.3.19$$

The locus of maxima and minima is

$$p = \frac{1}{\sqrt{1 + 3v}} \left( \frac{80 - 144v}{1 - 6v - 27v^2} \right) = \frac{16(5 - 9v)}{(1 - 9v)(1 + 3v)^{3/2}}. \quad 6.3.20$$

These are shown in figure VI.2b



The Clausius equation was hard work. *Dieterici's* is a little easier. The critical molar volume, temperature and pressure and the critical compression factor are, respectively,  $2b$ ,  $\frac{a}{4Rb}$ ,  $\frac{a}{4e^2b^2}$  and

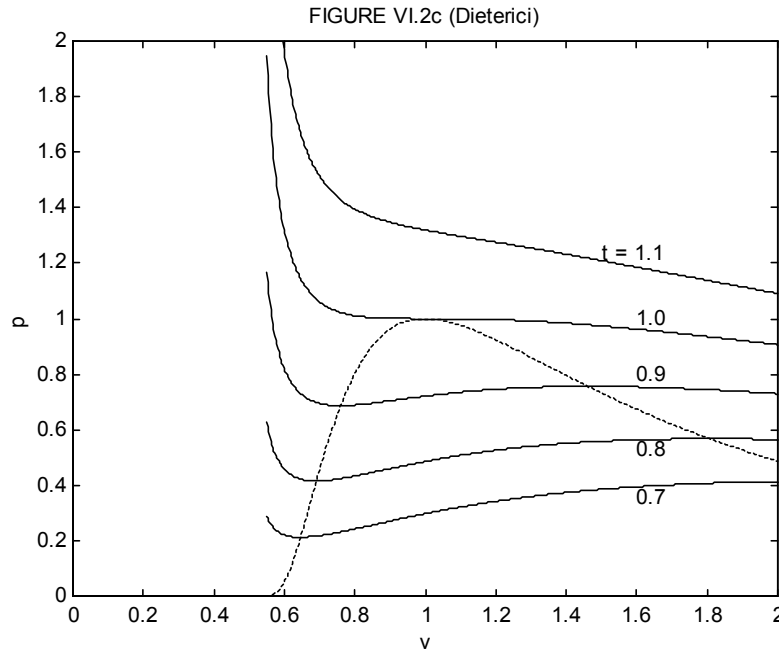
$2/e^2 = 0.271$ . Note that the critical compression factor is much closer to that of many real gases. The dimensionless form of the Dieterici equation is

$$p = \frac{t}{2v - 1} \exp\left(2 - \frac{2}{tv}\right). \quad 6.3.21$$

The locus of maxima and minima is

$$p = \frac{1}{v^2} \exp\left(\frac{2(v-1)}{2v-1}\right). \quad 6.3.22$$

These are shown in figure VI.2c.



The *Redlich-Kwong* equation of state, like those of van der Waals, Bethelot and Dieterici, has just two parameters ( $a$  and  $b$ ). All of them are not too bad at temperatures appreciably above the critical temperature, but, close to the critical temperature, the Redlich-Kwong empirical equation agrees a little better than the van der Waals equation does with what is observed for real gases. Obtaining the critical constants in terms of the parameters is done by exactly the same method as for the van der Waals and other equations, but requires perhaps a little more work and patience. The reader might like (or might not like) to try it. For the critical constants I get

$$V_c = xb, \quad 6.3.23$$

$$T_c = y \left( \frac{a}{bR} \right)^{2/3} \quad 6.3.24$$

and

$$P_c = z \left( \frac{a^2 R}{b^5} \right)^{1/3}, \quad 6.3.25$$

where

$$x = 3.847\,322\,100, \quad 6.3.26$$

$$y = 0.345\,039\,996 \quad 6.3.27$$

and 
$$z = 0.029\,894\,386. \quad 6.3.28$$

The critical compression factor is  $xz/y$ , which is exactly  $1/3$ . This is not as close to the compression factor of many real gases as the Dieterici critical compression factor is.

We can invert these equations to obtain expressions for  $a$  and  $b$  in terms of the critical temperature and pressure (or temperature and volume, or pressure and volume). Thus

$$a = u \left( \frac{R^2 T_c^{5/2}}{P_c} \right) \quad 6.3.29$$

and 
$$b = w \frac{RT_c}{P_c}, \quad 6.3.30$$

where 
$$u = 0.427\,480\,233 \quad 6.3.31$$

and 
$$w = 0.086\,640\,350. \quad 6.3.32$$

(You can also do this for the other equations of state, of course.)

In order to reproduce these results, you'll have to do a little work to see where all the constants come from. It turns out that the value of the constant  $x$  is the positive real root of the equation

$$x^3 - 3x^2 - 3x - 1 = 0. \quad 6.3.33$$

In the above analysis, I obtained all the constants from a numerical solution of equation 6.3.33, but the solution to this equation (and all subsequent constants) can also be written in surds. Thus, with  $f = \sqrt[3]{2} - 1$ ,  $g = \sqrt[3]{4} - 1$ ,  $h = \sqrt[3]{16} - 1$ , the constants can be calculated from

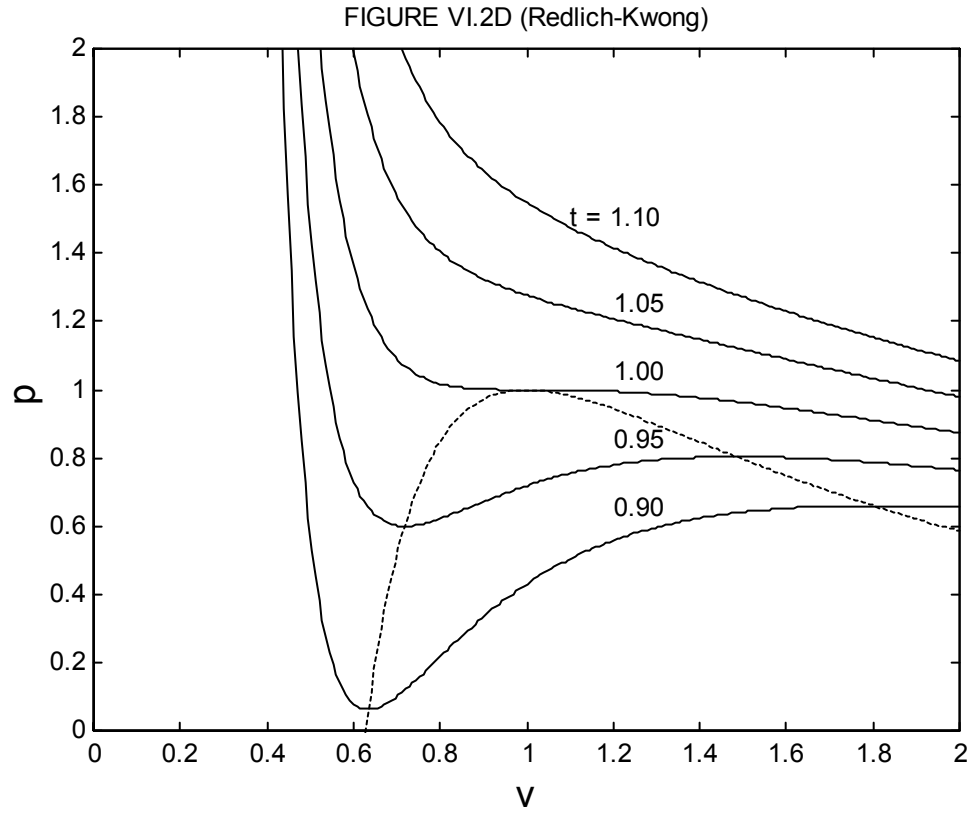
$$x = \frac{1}{f}, \quad y = g^2, \quad z = \frac{3-5g}{g+h}, \quad u = \frac{1}{9f} \quad \text{and} \quad w = \frac{1}{3}f. \quad 6.3.34$$

If we now introduce the dimensionless variables  $p = P/P_c$ ,  $v = V/V_c$ ,  $t = T/T_c$ , and substitute these and equations 6.3.23-25 into equation 6.3.6, we obtain the dimensionless Redlich-Kwong equation

$$p = \frac{lt}{xv-1} - \frac{1}{mt^{1/2}} \left( \frac{1}{xv} - \frac{1}{xv+1} \right), \quad 6.3.35$$

where 
$$l = y/z = 11.541\,96631 \quad \text{and} \quad m = gz = 0.017559994. \quad 6.3.36$$

The dimensionless Redlich-Kwong equation is illustrated in figure VI.2d. I have not tried to find an explicit equation for the locus of maxima, but instead I calculated it numerically, illustrated by the dashed line in figure VI.2d.



Here is a summary of the results for the two-parameter equations of state:

	$P_c$	$V_c$	$T_c$	$Z_c$	$a$	$b$
Van der Waals	$\frac{a}{27b^2}$	$3b$	$\frac{8a}{27Rb}$	$\frac{3}{8}$	$\frac{27R^2T_c^2}{64P_c}$	$\frac{RT_c}{8P_c}$
Berthelot	$\frac{1}{b} \sqrt{\frac{aR}{216b}}$	$3b$	$\sqrt{\frac{8a}{27bR}}$	$\frac{3}{8}$	$\frac{27R^2T_c^3}{64P_c}$	$\frac{RT_c}{8P_c}$
Dieterici	$\frac{a}{4e^2b^2}$	$2b$	$\frac{a}{4Rb}$	$2e^{-2}$	$\frac{RT_c}{e^2P_c}$	$\frac{4R^2T_c^2}{e^2P_c}$
Redlich-Kwong	$z \left( \frac{a^2R}{b^5} \right)^{1/3}$	$xb$	$y \left( \frac{a}{bR} \right)^{2/3}$	$\frac{1}{3}$	$u \left( \frac{R^2T_c^{5/2}}{P_c} \right)$	$w \frac{RT_c}{P_c}$
	$z = 0.0299$	$x = 3.85$	$y = 0.345$		$u = 0.427$	$w = 0.0866$

The reader can try to reproduce these (let me know ([jtatum@uvic.ca](mailto:jtatum@uvic.ca)) if you find any mistakes!) or at least (a useful exercise) verify their dimensions.

We mentioned in Section 6.2 that a useful way of indicating how the behaviour of a real gas differs from that of an ideal gas is by plotting the compression factor  $Z = \frac{PV}{RT}$  versus pressure. As the pressure approaches zero, the compression factor approaches 1. This is because the molecules are then so far apart that there are no appreciable forces (attractive or repulsive) between them. As the pressure is increased from zero, the compression factor generally at first drops a little below 1, and then rises above 1 as the pressure is increased. It will be interesting to see how the compression factor is expected to vary with pressure for the various “theoretical” gases that we have been discussing. I’ll do it just for a van der Waals gas, and I’ll use the dimensionless form of van der Waals’ equation, which was first given as equation 6.3.14:

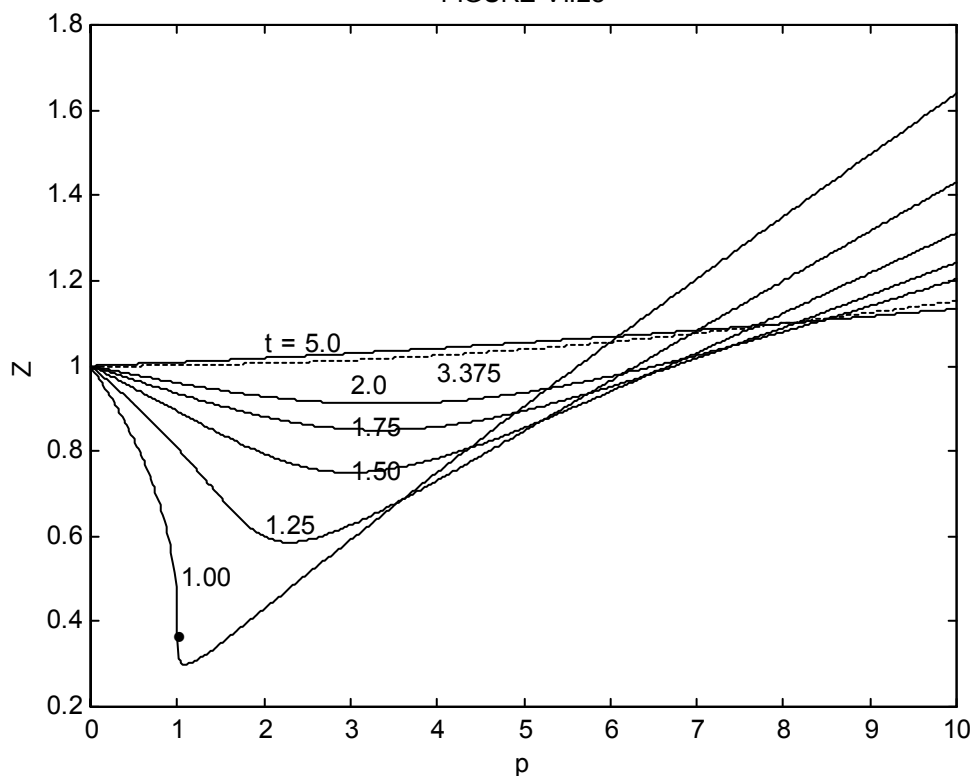
$$(p + 3/v^2)(v - \frac{1}{3}) = \frac{8}{3}t. \quad 6.3.37$$

The compression factor is  $Z = \frac{PV}{RT}$  and the critical compression factor is  $Z_c = \frac{P_c V_c}{RT_c}$ . From this,

we see that  $Z = \frac{pv}{t} Z_c$ . For a van der Waals gas,  $Z_c = \frac{3}{8}$ , so that  $Z = \frac{3pv}{8t}$ . Unfortunately, in

order to plot  $Z$  versus  $p$  for a given  $t$ , we have to be able to express  $v$  in terms of  $p$ , which means solving equation 6.3.37, which is a cubic equation in  $v$  [ $3pv^3 - (p+8t)v^2 + 9v - 3 = 0$ ]. I have done this numerically, and I show the resulting graphs of  $Z$  versus  $p$  for several temperatures, in figure VI.2e. Notice that at  $p = 1$  and  $t = 1$ , (i.e. at the critical point), the compression factor is 0.375. The  $Z$  versus  $p$  curves for real gases have the same general shape, but the precise agreement in numerical detail is not quite so good. Where  $Z > 1$ , the pressure is greater than that of an ideal gas, the  $b$  (repulsive) part of the van der Waals equation being more important than the  $a$  (attractive) part. Where  $Z < 1$ , the pressure is less than that of an ideal gas, the  $a$  (attractive) part of the van der Waals equation being more important than the  $b$  (repulsive) part. I haven’t investigated whether the other “theoretical” equations of state do appreciably better. Why not have a go yourself?!

FIGURE VI.2e



**Figure VI.2e.** The compression factor  $Z = PV/RT$  versus  $p$  (pressure in units of the critical pressure for a van der Waals gas, for several values of  $t$  (temperature in units of the critical temperature.) For a van der Waals gas the compression factor is greater than 1 for all temperatures greater than  $t = 27/8 = 3.375$ . At this temperature, the compression factor is close to 1 up to  $p$  equals approximately 2, and this temperature is known as the *Boyle temperature*. At the Boyle temperature, the  $Z : p$  curve is flat and close to 1 for a fairly large range of pressures. Thus, at the Boyle temperature, even a non-ideal gas obeys Boyle's law fairly closely. For a van der Waals gas, the critical temperature is  $8a/(27Rb)$ , so the Boyle temperature for a van der Waals is  $a/(Rb)$ . The reader should calculate this for  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , using the values of the van der Waals constants given in this Chapter. The dot on the  $t = 1.00$  isotherm at  $p = 1$  and  $Z = 0.375$  corresponds to the critical point. Anyone who feels in need of more mental exercise might like to ask: For what value of  $p$  (other than zero) is  $Z = 1$ . For example, can you show that, for  $t = 1$ ,  $Z = 1$  for  $p = 152/27 = 5.630$ ?

The last proposed empirical equation of state that we mentioned is the virial equation, equation 6.3.6:  $PV = A + BP + CP^2 + DP^3 + \dots$ . This is sometimes written in the form

$$PV = A + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \dots, \text{ but in these notes we'll use the form of equation 6.3.6.}$$

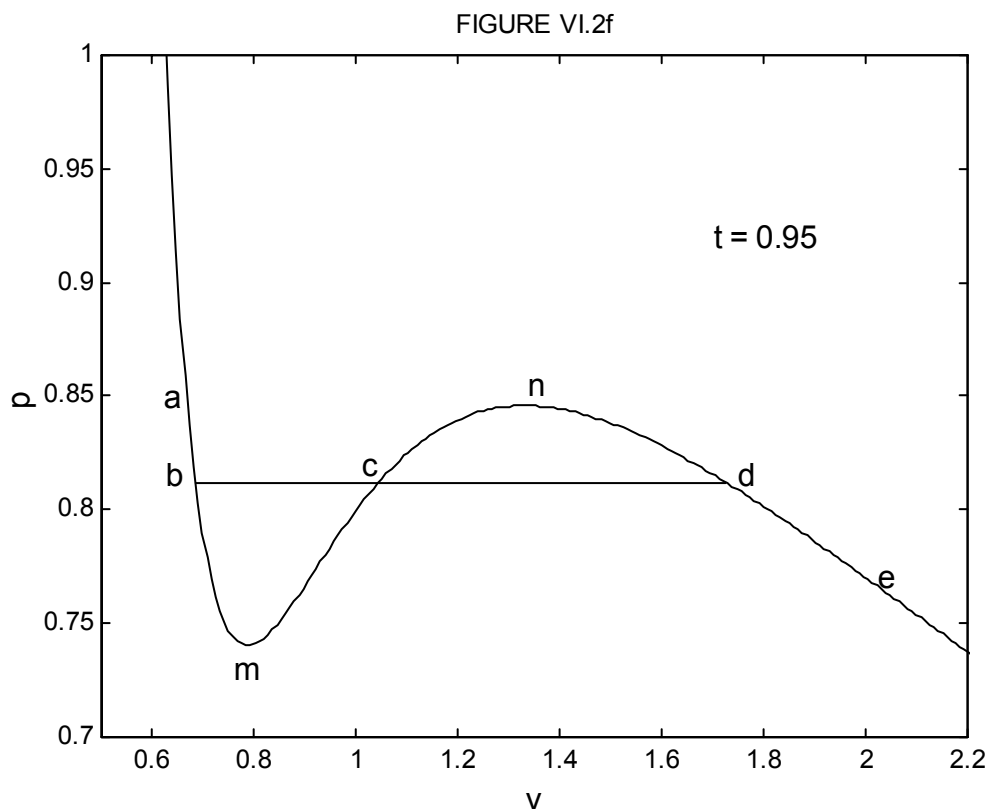
The coefficients  $A, B$ , etc are called the *virial coefficients* and are functions of temperature. The first coefficient,  $A$ , is just  $RT$ . We can also write the virial equation as



$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots$$

We could measure the coefficient  $B'$  for a real gas by plotting  $Z$  as a function of pressure in a similar manner to figure VI.2e. The initial slope  $\left(\frac{\partial Z}{\partial P}\right)_T$  extrapolated to zero pressure gives the value of  $B'$ . At low temperatures  $B'$  is negative; at high temperatures  $B'$  is positive. At the *Boyle temperature*  $B'$  is zero, and at that temperature the compression factor is unity for a large range in pressures, and the gas accordingly closely conforms to Boyle's law. The coefficient  $C'$  is small, so the term  $C'P^2$  comes into play only at higher pressures. At higher pressures,  $Z$  increases, showing that  $C'$  is a positive coefficient. The coefficient  $D'$  is smaller still than  $C'$ .

All the mathematically “well-behaved” equations of state below the critical temperature have a maximum and a minimum – i.e. the curve shows a “wiggle”. I illustrate this in figure VI.2f. This is the van der Waals isotherm for  $t = 0.95$  in dimensionless variables. It is the same as one of the curves shown in figure VI.2, drawn to a different scale so as to emphasize the “wiggle”.



Using the little cylinder and piston to the right of the graph, try and imagine what happens to the enclosed liquid or vapour as you move the piston in and out at constant temperature, moving from  $a$  to  $e$  and back again on the graph. Start at  $e$ . The cylinder is filled with vapour. Move the piston inwards, going from  $e$  to  $d$ ; the pressure increases and the volume

decreases. Now a real gas doesn't follow the van der Waals function all the way. At  $d$ , something different happens. Actually it *is* possible to take a vapour a little way past  $d$  towards (but not beyond)  $n$ . That would be a *supercooled vapour*, such as is used in a cloud chamber. It will condense immediately into a line of liquid droplets as soon as a charged particle flies through the vapour. However, what usually happens is that some of the vapour starts to condense as liquid, and we move horizontally from  $d$  to  $b$ . As we move the piston down at constant temperature, the volume of course decreases, and more and more liquid condenses in such a manner that the pressure remains constant. In the portion  $db$ , we have liquid and vapour existing together in the piston, in thermodynamic equilibrium. Near to the  $d$  end there is only a little liquid; near to the  $b$  end it is nearly all liquid, with only a little vapour left. Beyond  $b$ , towards  $a$ , the space is completely filled with liquid. We can push and push, increasing the pressure greatly, but there is very little change in volume, because the liquid is almost (though not quite) incompressible. The isotherm is very steep there. It is actually possible to take the liquid a little way from  $b$  towards (but not beyond)  $m$  without any of it vaporizing. This would be a *superheated liquid*, such as is used in a bubble chamber. It will vaporize immediately into a line of bubbles as soon as a charged particle flies through the liquid.

There will be further important material concerning change of state in Chapters 9 and 14. At present, though, I want to ask: At what pressure does condensation commence? Putting it another way, what is the height of the line  $bd$  in figure VI.2f? I have heard it argued that the height of  $bd$ , (the pressure at which condensation occurs) must be such that the area  $bmc$  is equal to the area  $cnd$ . I am not sure that I fully understand the arguments leading to this conclusion. After all, a real gas doesn't conform exactly to a van der Waals equation or any of the other theoretical/empirical equations that we have discussed. But perhaps it is not unreasonable to draw  $bd$  such that the areas above and below it are equal, and in any case it makes for an interesting (and challenging) computational exercise. The van der Waals equation, in dimensionless variables, is given as equation 6.3.14. Can you calculate the pressure such that the area  $bmc$  below  $bd$  is equal to the area  $cnd$  above it? I make it  $p = 0.812$ , which is the height where I have drawn it in the figure. I haven't done the calculation for the other equations. I leave that to you!

#### 6.4 Gas, Vapour, Liquid and Solid

Our description of the behaviour of a real substance in section 6.2 was incomplete in many ways, not least because it made no mention of the solid state. At very low temperatures or at very high pressures, most substances will solidify

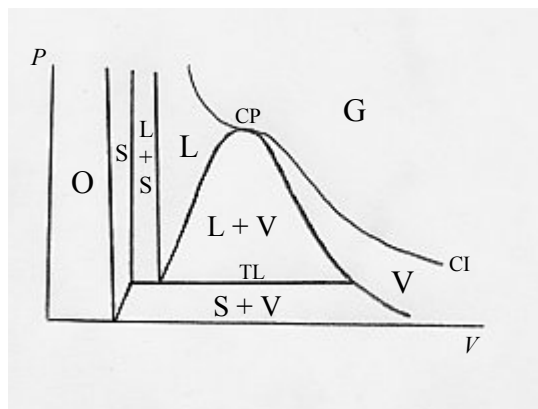


FIGURE VI.3

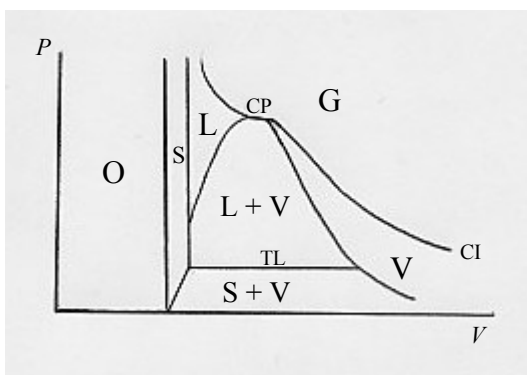


FIGURE VI.4

In figures VI.3 and 4 I have sketched schematically, by hand, the several regions in the  $PV$ -plane in which a substance exists in its several stages. Unlike in Figure VI.1 and VI.2, I have not drawn *isotherms*. The various lines are intended to represent the boundaries between phases, and are therefore more akin to the dashed curves in figures VI.1 and VI.2. The one exception is the critical isotherm, CI, which is indeed the curve that separates gas from vapour or liquid, but which is also, of course, an isotherm. The difference between figures VI.3 and VI.4 is that figure VI.3 represents a substance that expands when it melts from solid to liquid, while figure VI.4 represents a substance that contracts when it melts from solid to liquid (that is, the solid is less dense than the liquid, and will float upon it.) Most substances expand upon melting, but we have to include those exceptional substances that contract upon melting, because one such substance is one of the most important of all – water.

You can try to understand the figures a little by moving along a horizontal line (isobar) or along a vertical line (isochor) and noticing where phase changes take place. Can you see, for example, where a solid will change to a vapour without going through a liquid phase (sublimation)?

You will note, in the figures, the *critical isotherm* CI, that separates gas from liquid or vapour, and you will note that, at temperatures above the critical temperature, the only phase possible is *gas*, and the substance cannot be liquefied merely by compression. You will note also the *critical point* CP. You will also see the *triple line* TL, along which solid, liquid and vapour co-exist together. What of the region marked O? The substance cannot exist here in solid, liquid or gaseous phase. To that extent, we see that the van der Waals equation may be a little bit better than we thought it was, because you will remember that it went up to infinity at a third of the critical volume. All that this means is that by then the molecules are so tightly jammed together that you simply cannot compress them any further. Although a substance cannot exist in an ordinary solid, liquid or gas phase in the region marked O, if the matter is *degenerate* it will be in this region. The electron structure of the atoms breaks down, so that it then does become possible to jam the atoms closer together. This may mean something to those of you who are familiar with the concept of degenerate matter. If you have not heard of it, do not worry; you are unlikely to come across it unless you visit a white dwarf star, or the core of a massive star, or have to take an examination in astrophysics. For the time being, we shall look the other way and pretend it doesn't exist.

We can get a little more insight by looking at the  $PT$ -plane. Figure VI.5 shows a substance that expands on melting, and figure VI.6 shows a substance (such as water) that expands on freezing. In the  $PT$ -plane, the *triple point* (where solid, liquid and vapour) are in equilibrium with each other, appears as the *triple point*, TP. (In  $PVT$ -space it is a *line*, although the critical point CP remains a genuine point in  $PVT$ -space.) The line separating liquid from vapour terminates at the critical point, and the line is often drawn as though it were somehow left hanging in mid-air, so that one is uncertain whether a given point near the critical point represents a gas, a vapour or a liquid. But in the  $PT$ -plane, the critical isotherm is a vertical line (shown as dashed in the figures), and the liquid/vapour boundary terminates at the critical isotherm, and there is no question what phase is represented by a point near to the critical point. To the right of the critical isotherm, we have a gas. To the left, we have either a liquid or a vapour, depending on whether we are above or below the liquid/vapour boundary. As we cross the solid/vapour boundary, below the critical temperature and below the critical pressure (on Mars!) we have a phase change directly from solid to vapour or vapour to solid – i.e. sublimation.

(I have often heard that, below the triple point, a solid will "sublime". I think I prefer the verb "to sublime".)

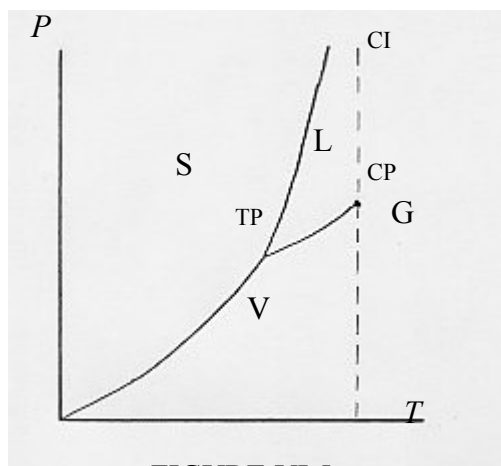


FIGURE VI.5

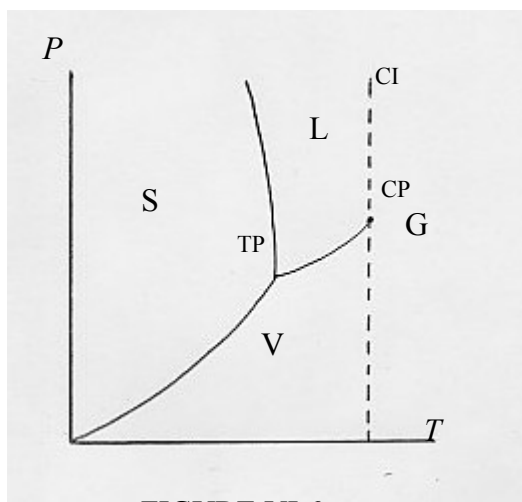


FIGURE VI.6

Really to appreciate these diagrams you need to see and to handle a three-dimensional model in 3-space. My skills at making drawings with my computer are nowhere near good enough yet for me to attempt a three-dimensional drawing, but Mr Charles Card of the University of Victoria was kind enough to photograph for me a model from the University's collection, and I reproduce these below as figures VI 7,8 and 9.

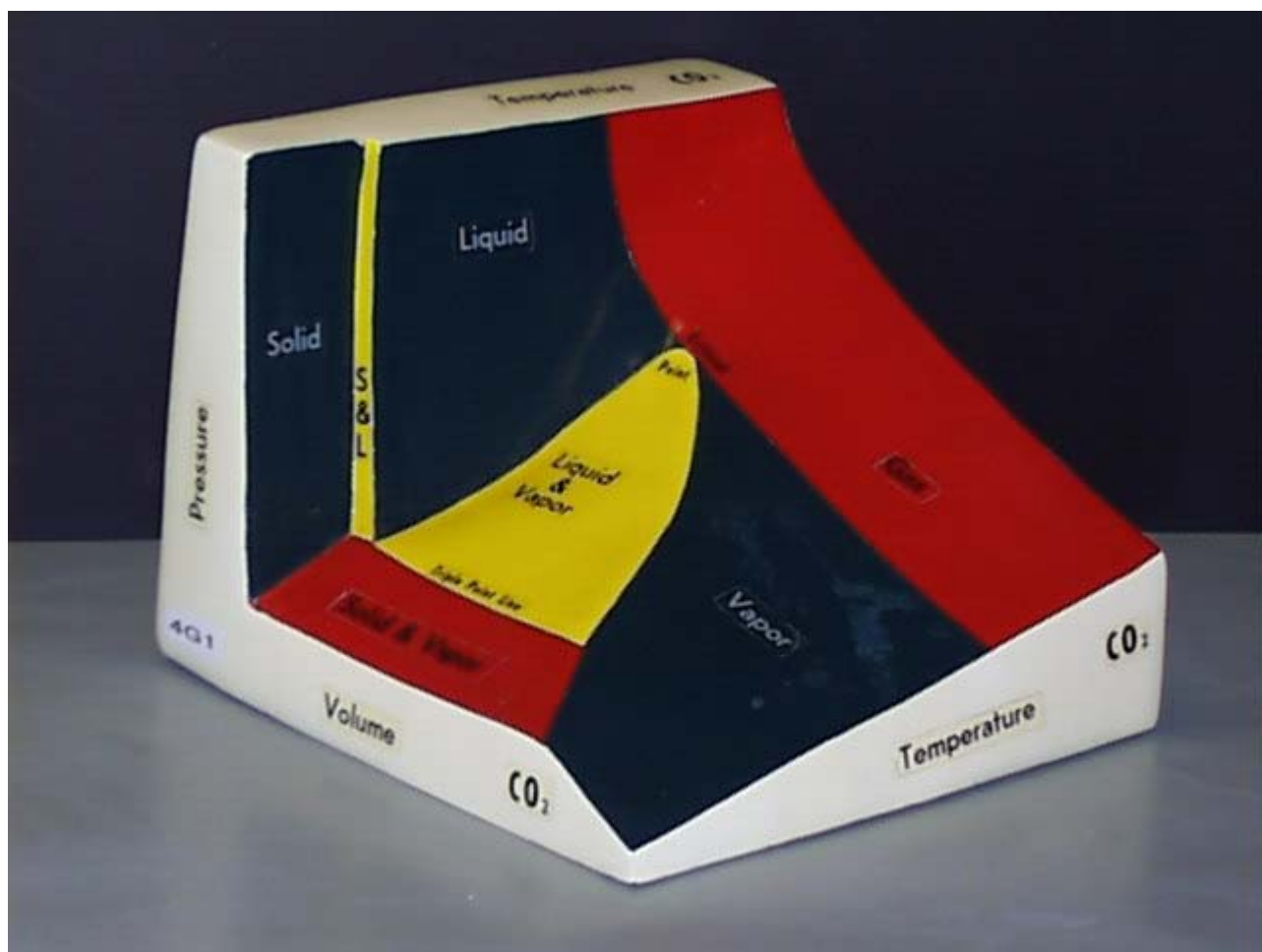


FIGURE VI.7



FIGURE VI.8

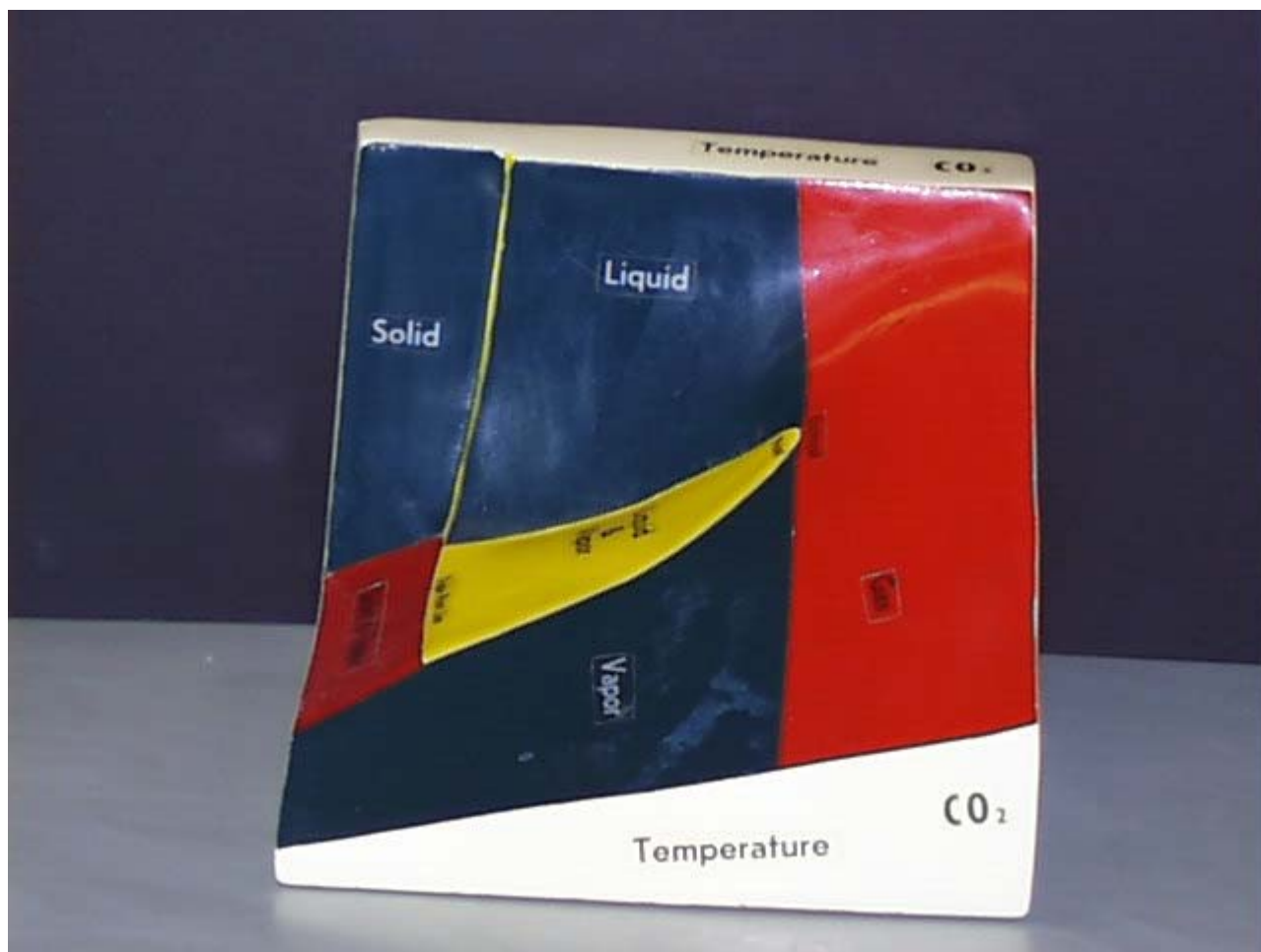


FIGURE VI.9

I now give some numerical values for the critical temperature and pressure, the compression factor, and the temperature and pressure of the triple point for  $\text{H}_2\text{O}$  and for  $\text{CO}_2$ . These are not intended as definitive values. I looked them up in a number of sources and I found a surprisingly wide range of the numbers quoted. They are given here merely to give the reader a rough idea of what the values are for these two substances. The temperature quoted for the triple point of  $\text{H}_2\text{O}$  is, of course, exact, being one of the fixed points of the Kelvin scale. Recall that one atmospheric pressure is about  $1.01 \times 10^5 \text{ Pa}$ .

	$T_c \text{ (K)}$	$P_c \text{ (Pa)}$	$Z$	$T_3 \text{ (K)}$	$P_3 \text{ (Pa)}$
$\text{H}_2\text{O}$	647	$2.1 \times 10^7$	0.234	273.16	$6.1 \times 10^2$
$\text{CO}_2$	304	$7.3 \times 10^6$	0.276	217	$5.1 \times 10^5$

The reader might like to see whether these numbers are compatible with the numbers I gave for the van der Waals constants in Section 6.3. Exact agreement is not to be expected, because the figures I quote are only approximate and are gleaned from a variety of sources and also, of course, neither gas can be expected to obey van der Waals' equation exactly. If the numbers seem to be wildly discrepant, please let me know.

*Some idle thoughts on vapours.* There is a question of how to spell "vapour". In the United States, "vapor" is usual, and in the United Kingdom "vapour" is usual. "Vaporize" is a bit trickier. The spelling "vaporize" is usual in the United States, but what to do in the United Kingdom? Is it vapourize, vapourise, vaporize or vaporise? Is there a u or no u? Is it z or s? To answer the first question: In the United Kingdom, the u, as in the United States, is omitted. Only weak spellers and those who would try to be "more English than the English" would try to insert a u. As for s or z, either seems to be used in the United Kingdom. Etymologically, z would be the better choice, so the spelling "vaporize" is perfectly acceptable on both sides of the Atlantic Ocean.

*More idle thoughts on vapours.* Is a "vapour" a "gas"? What is a "fluid"? And is glass a liquid? Some authors treat "gas" and "vapour" as though they were quite different things: a gas is not a vapour, and a vapour is not a gas. Others regard a "vapour" as being a sort of gas – namely a gas whose temperature is below the critical temperature and which can be liquefied by increasing the pressure. In that case, what do you call a gas that is above the critical temperature? The term *permanent gas* is often used. Thus a vapour is a gas below its critical temperature, and a permanent gas is a gas above its critical temperature.

A *fluid* is something that flows. Thus liquids and gases (including vapours) are fluids. There is, you would imagine, always a clear distinction between a liquid and a gas. But is the distinction always so clear? I admit that I have never actually seen the phenomenon that I am about to describe, but it is described so often that I presume someone has seen it! Consider a closed container with a liquid in equilibrium with its vapour. The liquid and vapour are separated by a sharp, horizontal boundary. That is to say, the system is on the line separating liquid and vapour in figures VI.5 and 6. This line can be regarded, if you like, as a graph of boiling point versus temperature, or equally of vapour pressure versus temperature. If you raise the pressure, the boiling point increases; or if you increase the temperature, the vapour pressure increases. More liquid will enter the vapour state, and, as the pressure of the vapour increases, so does its density. The liquid, on the other hand, is almost incompressible, and, because of thermal expansion, its density decreases. As we move up the line separating liquid from vapour in the  $P:T$  plane, the density of the vapour increases and the density of the liquid decreases. Their densities become more and more equal until, as we approach the critical point, the boundary between liquid and vapour becomes less and less distinct, and less constrained by gravity to be horizontal, until eventually, at the critical point, the distinction between liquid and vapour blurs and ultimately disappears. So – what have you got then? It is certainly a *fluid*, but are you going to call it a gas, a vapour or a liquid? Since none of these words would seem to have a stronger claim than either of the others, some authors refer to the substance when a little above and to the right of the critical point in the  $P:T$  plane as a *supercritical fluid*.

There is also the question as to whether glass is a solid or a liquid. A famous radio personality many years ago, on a "Brains Trust" programme broadcast by the British Broadcasting Corporation, Professor C. E. M. Joad, was famous for his sentence: "It all depends on what you mean by..." So I suppose the question as to whether glass is a liquid or a solid depends on what you mean by a liquid or a solid. The moment when I drop a tumbler and it shatters into many viciously sharp fragments is not a good moment to convince me that glass is a liquid. Those who assert that glass is a liquid say that it has not got a solid crystalline structure, and that it *flows*, albeit very slowly. It has a very large viscosity. We are told that windows in ancient mediaeval cathedrals are thicker at the bottom than at the top, as a result of the viscous liquid flow over the centuries. I don't know if any of the many people who have told me that have actually personally measured the thickness of a cathedral window.

At any rate, before you started this chapter, you had a very clear idea in your mind about the differences between a solid, liquid and a gas. Now that I have painstakingly explained it all, you are completely confused, and are no longer at all sure that you know the difference.



### 6.5 Kinetic Theory of Gases: Pressure

There will be more about *macroscopic PVT* relations for gases when we go further into thermodynamics. In this section, we deal with *microscopic* properties, and how pressure and temperature are related to the number density of molecules and their speed.

We shall consider an ideal gas, containing  $n$  molecules per unit volume, each of mass  $m$ , held in a cubical box of side  $l$ . The velocity of a particular molecule is to be denoted by  $\mathbf{c} = u\mathbf{i} + v\mathbf{j} + w\mathbf{k}$ . Here  $u, v, w$  are the components of the velocity parallel to the sides of the box. As ever, I shall use the word *velocity* to mean "velocity" and the word *speed* to mean "speed". Thus the velocity of the molecule is  $\mathbf{c}$  and its speed is  $c$ . We are going to start by calculating the pressure on the walls, assumed to be caused by the collisions of millions of molecules repeatedly colliding with the walls.

("Why do you keep banging your head against the wall?" "Because it feels so good when I stop.")

Consider the  $x$ -motion. Assuming that collisions are elastic, we note that the change of the  $x$ -component of momentum when a molecule bounces off a  $yz$ -wall is  $2mu$ . The time taken to cross to the other side of the cube and back again is  $2l/u$ . The number of collisions that this molecule makes with one  $yz$ -wall per unit time is  $u/(2l)$ . The rate of change of momentum of that molecule at that wall is therefore  $2mu \times u/(2l) = mu^2/l$ . The rate of change of the  $x$ -component of the momentum at that wall of all the  $nl^3$  molecules in the box is  $nl^3 \times mu^2/l = nml^2\overline{u^2}$ . That is, the force on that wall is  $nml^2\overline{u^2}$ , and so the pressure on the wall is  $nml\overline{u^2}$ . But  $\overline{u^2} = \overline{v^2} = \overline{w^2}$  (that's assuming that the velocities are isotropic and there's no wind) and  $\overline{u^2} + \overline{v^2} + \overline{w^2} = \overline{c^2}$  (that's Pythagoras's theorem), and therefore  $\overline{u^2} = \frac{1}{3}\overline{c^2}$ . So the pressure is

$$P = \frac{1}{3}nmc^2 = \frac{1}{3}\rho\overline{c^2}. \quad 6.5.1$$

Here  $\rho$  is the density = mass  $\div$  volume = molar mass  $\div$  molar volume =  $\mu/V$ , (here  $V$  = molar volume) and therefore

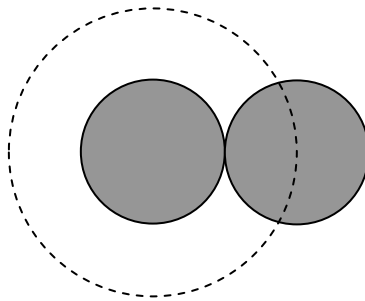
$$PV = \frac{1}{3}\mu\overline{c^2}. \quad 6.5.2$$

But  $\frac{1}{3}\mu\overline{c^2}$  is  $\frac{2}{3}$  of the translational kinetic energy of a mole of gas, and we already know that  $PV = RT$ , so that we deduce that the *translational kinetic energy of the molecules in a mole of gas* is equal to  $\frac{3}{2}RT$ . That is to say the mean translational kinetic energy per molecule is  $\frac{3}{2}kT$ , where  $k$  is Boltzmann's constant (see Section 6.1).

## 6.6 Collisions

In this section, we are going to ask: What is the mean time between intermolecular collisions? What is the mean free path between collisions? How many intermolecular collisions are there per unit volume per unit time? How many collisions with the walls of a containing vessel are there per unit area per unit time? Since I know little chemistry, I shall assume that molecules are hard spheres of diameter  $d$ . This may not be too bad for monatomic gases such as the rare gases. For others, the assumption is tantamount to assuming that molecules repel each other when their centres of mass approach within a distance  $d$ . In any case, we shall assume that the *collision cross-section* is of area  $\pi d^2$ .

Notice, from the sketch below, that two equal spheres collide when their centres are separated by their *diameter*  $d$ , and consequently the collision cross section (shown as a dashed circle) is of area  $\pi d^2$ .



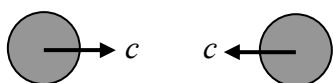
In fact in what follows, I'm just going to call the area of the collision cross section  $\sigma$ ; in doing that, I don't even have to assume that its shape is circular.

In time  $t$ , a molecule moving with speed  $c$  sweeps out a cylinder of volume  $\sigma ct$ . If there are  $n$  molecules per unit volume, the number of collisions that that particular molecule will experience in time  $t$  would appear to be  $\sigma ctn$ , which is to say that the number of collisions it experiences in unit time is  $\sigma cn$ . Thus the mean time  $\tau$  between collisions would appear to be  $\tau = 1/(\sigma cn)$ , and the mean free path  $\lambda$  between collisions is  $\lambda = 1/(\sigma n)$ .

But this isn't quite right, because we have not taken into account the fact that all the molecules in the above-mentioned cylinder are moving. It is not as though our hero molecule were colliding with a set of stationary molecules. The relevant speed to use in this analysis is the *mean relative speed* between molecules, and this is a little greater than the speed  $c$  of each. Let's see if we can do a little better.

Let's start by supposing that all of the molecules are moving with speed  $c$ . There are two extreme sorts of collision:

The "head on" collision:



For such a collision, the relative speed between the molecules is  $2c$ .

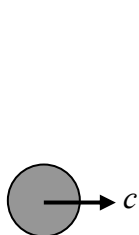
Then there is the sort of collision in which one molecule barely catches up with another one:



In that case the relative speed is zero.

The average relative speed is evidently somewhere between 0 and  $2c$ .

These are extreme cases. The “average” situation is somewhat in between. We may argue that the “average” situation is for the two molecules to be travelling in perpendicular paths:

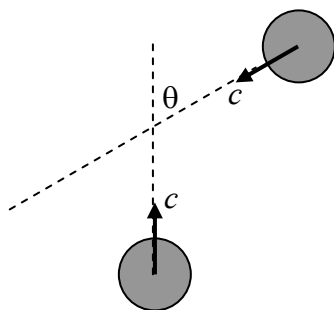


If we think of this as the “average” situation, then we may argue that the “average” relative speed between two molecules is  $\sqrt{2}c$ . In that case, we may conclude that the mean time between collisions is  $\tau = 1/(\sqrt{2}\sigma cn)$ , and the mean free path is  $\lambda = 1/(\sqrt{2}\sigma n)$ .

This argument may or may not be completely convincing, but it is probably closer to the mark than our previous effort.

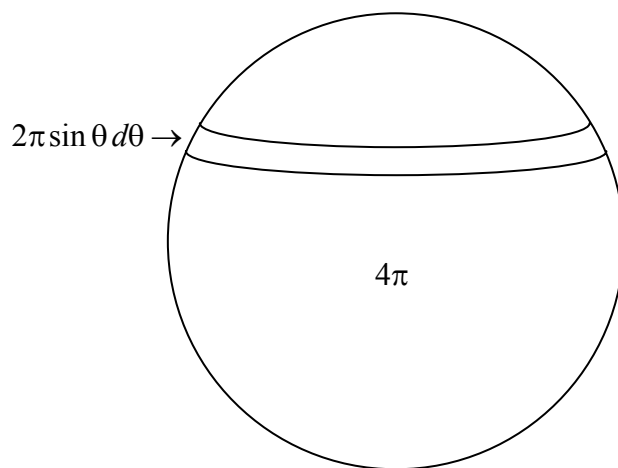
Let's see if we can make a further improvement. As before, we'll suppose that each molecule is moving with speed  $c$ .

Suppose our hero molecule to be moving upward with speed  $c$ , and another molecule approaches at an angle  $\theta$ , as in the sketch below.



By vector addition of velocities, it will be seen (a little thought will be needed) that the relative speed of approach between the two molecules is  $\sqrt{2}c(1 + \cos\theta)^{1/2}$ .

Now the fraction of molecules approaching from angles between  $\theta$  and  $\theta + d\theta$  is  $\frac{1}{2} \sin\theta d\theta$ . This is because the area of an elemental zone of a sphere of unit radius between  $\theta$  and  $\theta + d\theta$  is  $2\pi \sin\theta d\theta$ , and the total area of the sphere is  $4\pi$  - see the sketch below:



Thus the mean relative speed of all the molecules is  $\int_0^\pi \sqrt{2}c(1 + \cos\theta)^{1/2} \times \frac{1}{2} \sin\theta d\theta$ , which works out to be  $\frac{4}{3}c$ .

In this model, then, the mean time between collisions would be  $\tau = \frac{1}{\frac{4}{3}cn}$ , and the mean free path would be  $\lambda = \frac{1}{\frac{4}{3}n}$ .

However, we have still assumed that all the molecules are moving at the same speed. I am told (but I have not verified it myself) that, if you take account of the Maxwell-Boltzmann distribution of speeds (see Section 6.7), the mean relative speed of collision is  $\sqrt{2}\bar{c}$ , where  $\bar{c}$  is the mean speed of

the Maxwell-Boltzmann distribution (equal to  $\sqrt{\frac{8kT}{\pi m}}$ .) If that is so, then we obtain

$$\tau = \frac{1}{\sqrt{2}\sigma\bar{c}n} \quad \text{and} \quad \lambda = \frac{1}{\sqrt{2}\sigma n}.$$

In any case, since molecules are not hard spheres (they are neither spheres nor hard) and the details of a “collision” depend on the shape of the molecules and the force law between them, it may not be meaningful to try to obtain an extremely precise formula for the mean free path, but instead settle for  $\tau = \frac{1}{b\sigma\bar{c}n}$  and  $\lambda = \frac{1}{b\sigma n}$ , and if you wish to take  $b \approx \sqrt{2}$ , you won’t be far out.

Of more interest would be to calculate the mean time between collisions for various pressures and temperatures, and ask how does this compare, for example, with the mean lifetime of an atom in an excited atomic level, or a metastable level. Or to compare the mean free path between collisions with the mean nearest-neighbour distance between molecules in a gas. I think under typical familiar conditions, you’ll find that the mean free path is rather longer than the mean nearest-neighbour distance.

Also of interest is the number of collisions per unit volume per unit time. If we suppose that a single molecule experiences  $b\sigma\bar{c}n$  collisions per unit time, and there are  $n$  molecules per unit volume, then the number of collisions per unit volume per unit time is

$$Z = \frac{1}{2} b\sigma\bar{c}n^2.$$

The factor of  $\frac{1}{2}$  is necessary so that we don’t count collisions of A with B and of B with A as two different collisions.

Another useful result is that the number of molecules striking the walls of a containing vessel per unit area per unit time is

$$\frac{1}{4} n\bar{c}.$$

To avoid repetition, I don’t derive this here, but you will find a derivation in Chapter 1 Section 1.17 of *Stellar Atmospheres*, where I do the derivation with photons rather than with molecules. The only difference is that, in the case of the photons, all are moving at the same speed  $c$  (the speed of light), whereas here we have a distribution of speeds, and we use  $\bar{c}$ , the mean speed of the molecules.

### 6.7 Distribution of Speeds

I am tempted to start by saying "Let  $f(u)du$  be the fraction of molecules of which the  $x$ -component of their velocities is between  $u$  and  $u + du$ ." But we can go a little further than this with the realization that this distribution must be symmetric about  $u = 0$ , and therefore, whatever the function is, it must contain only even powers of  $u$ . So we can start with:

Let  $f(u^2)du$  be the fraction of molecules of which the  $x$ -component of their velocities is between  $u$  and  $u + du$ . Then, unless there is a systematic flow on the  $x$ -direction or the  $x$ -direction is somehow special, the fraction of molecules with  $y$  velocity components between  $v$  and  $v + dv$  is  $f(v^2)dv$ , and the fraction of molecules with  $z$  velocity components between  $w$  and  $w + dw$  is  $f(w^2)dw$ . The fraction of molecules in a box  $du dv dw$  of velocity space is  $f(u^2)f(v^2)f(w^2)du dv dw$ . Since the distribution of velocity components is independent of direction, this product must be of the form

$$f(u^2)f(v^2)f(w^2) = F(c^2), \quad 6.7.1$$

$$\text{or} \quad f(u^2)f(v^2)f(w^2) = F(u^2 + v^2 + w^2). \quad 6.7.2$$

(*Question:* Dimensions of  $f$ ? Of  $F$ ?)

It is easy to see that this is satisfied by

$$f(u^2) = Ae^{\pm u^2/c_m^2}, \quad 6.7.3$$

where  $A$  and  $c_m$  are constants to be determined. It should also be clear that, of the two possible solutions represented by equation 6.7.3, we must choose the one with the minus sign.

$$\text{Since we must have} \quad \int_{-\infty}^{\infty} f(u^2) du = 1, \quad 6.7.4$$

$$\text{it follows that} \quad A = \frac{1}{c_m \sqrt{\pi}}. \quad 6.7.8$$

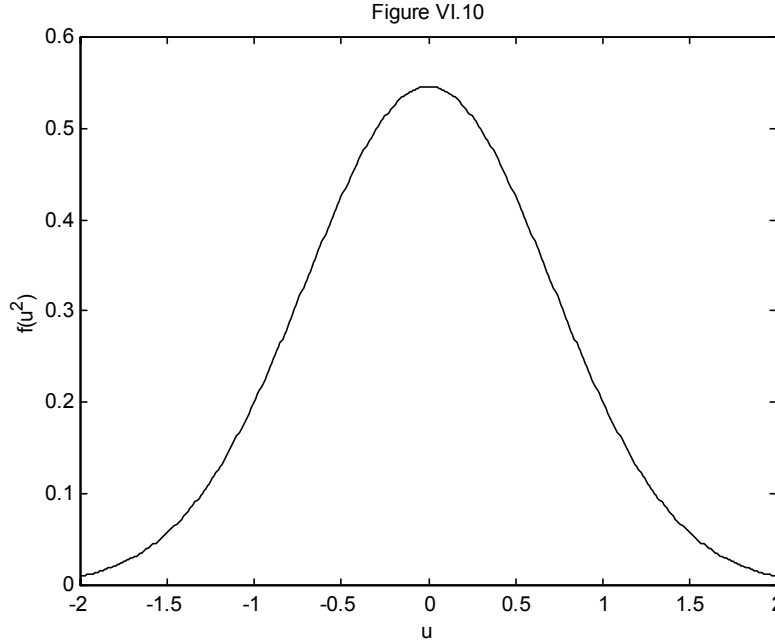
(To see this, you have to know that  $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$ .)

$$\text{Thus we now have} \quad f(u^2) = \frac{1}{c_m \sqrt{\pi}} e^{-u^2/c_m^2}. \quad 6.7.9$$

This is the *gaussian* distribution of a velocity component. We shall shortly find a physical interpretation for the constant  $c_m$ .

The area under the curve represented by equation 6.7.9 is, of course, unity; the maximum value of  $f(u^2)$  is  $1/(c_m \sqrt{\pi})$ .

Figure VI.10 illustrates this distribution. In this figure, the unit of speed is  $c_m$ . The area under the curve is 1. The maximum (at  $u = 0$ ) is  $1/\sqrt{\pi} = 0.564$ . *Exercise:* Show that the FWHM (full width at half maximum) is  $2\sqrt{\ln 2}c_m = 1.665c_m$ . This gives one physical interpretation of  $c_m$ ; we shall soon give another one, which will explain the use of  $m$  as a subscript.

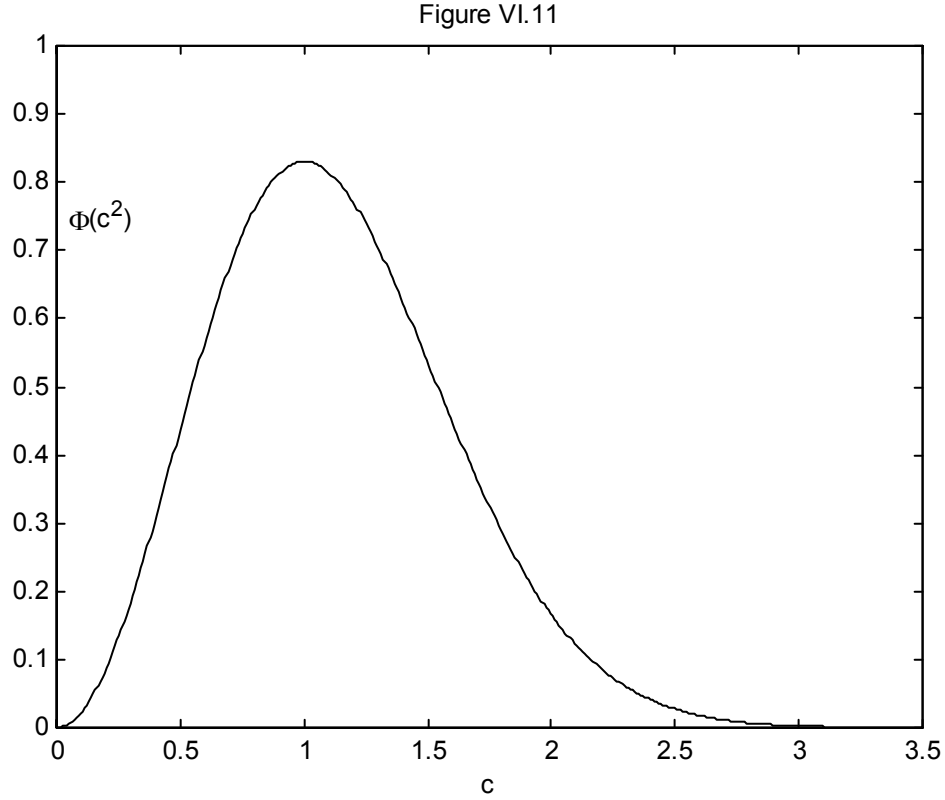


The gaussian distribution deals with *velocity components*. We deal now with *speeds*. The fraction of molecules having speeds between  $c$  and  $c + dc$  is  $F(c^2)$  times the volume of a spherical shell in velocity space of radii  $c$  and  $c + dc$ . (Some readers may recall a similar argument in the Schrödinger equation for the hydrogen atom, in which the probability of the electron's being at a distance between  $r$  and  $r + dr$  is the probability density  $\psi\psi^*$  times the volume of a spherical shell. You'll notice that physics becomes easier and easier, because you have seen it all before in different contexts. In the present context,  $F$  is akin to the  $\psi\psi^*$  of wave mechanics, and it could be considered to be a "speed density".) Thus the fraction of molecules having speeds between  $c$  and  $c + dc$  is

$$\Phi(c^2)dc = \frac{4c^2}{c_m^3\sqrt{\pi}} e^{-c^2/c_m^2} dc. \quad 6.7.10$$

I shall leave it to those who are skilled at calculus to show that  $\int_0^\infty \Phi(c^2)dc = 1$ , and also to show that the *maximum* of this distribution occurs for a speed of  $c = c_m$  and that the maximum value of  $\Phi(c^2)$  is  $4/(c_m e\sqrt{\pi})$ . This provides another interpretation of the constant  $c_m$ . The speed at which

the maximum of the distribution occurs is called the *mode* of the distribution, or the *modal speed* – hence the subscript m. Equation 6.7.10 is the *Maxwell-Boltzmann* distribution of speeds. It is shown in figure VI.7, in which the unit of speed is  $c_m$ . The area is 1, and the maximum is  $4/(e\sqrt{\pi}) = 0.830$ .



The *mean* speed  $\bar{c}$  is found from  $\int_0^\infty c\Phi(c^2)dc$  and the *root mean square* speed  $c_{\text{RMS}}$  is found from  $c_{\text{RMS}}^2 = \int_0^\infty c^2\Phi(c^2)dc$ . If you have not encountered integrals of this type before, you may find that the first of them is easier than the second. If you can do these integrals, you will find that

$$\bar{c} = \frac{2}{\sqrt{\pi}}c_m \quad \text{and} \quad c_{\text{RMS}} = \sqrt{\frac{3}{2}}c_m. \quad 6.7.11$$

The root mean square (RMS) speed, for which I am here using the symbol  $c_{\text{RMS}}$ , is of course the square root of  $\overline{c^2}$ . We have seen from Section 6.5 that the mean kinetic energy per molecule,  $\frac{1}{2}m\overline{c^2}$ , is equal to  $\frac{3}{2}kT$ , so now let's bring it all together:

$$c_m = \frac{\sqrt{\pi}}{2}\bar{c} = 0.886\bar{c} = \sqrt{\frac{2}{3}}c_{\text{RMS}} = 0.816c_{\text{RMS}} = \sqrt{\frac{2kT}{m}} = 1.414\sqrt{\frac{kT}{m}} \quad 6.7.12$$

$$\bar{c} = \frac{2}{\sqrt{\pi}}c_m = 1.128c_m = \sqrt{\frac{8}{3\pi}}c_{\text{RMS}} = 0.921c_{\text{RMS}} = \sqrt{\frac{8kT}{\pi m}} = 1.596\sqrt{\frac{kT}{m}} \quad 6.7.13$$



$$c_{\text{RMS}} = \sqrt{\frac{3}{2}} c_m = 1.225 c_m = \sqrt{\frac{3\pi}{8}} \bar{c} = 1.085 \bar{c} = \sqrt{\frac{3kT}{m}} = 1.732 \sqrt{\frac{kT}{m}} \quad 6.7.14$$

Gauss: 
$$f(u^2) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mu^2}{2kT}}. \quad 6.7.15$$

Maxwell-Boltzmann: 
$$\Phi(c^2) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}}. \quad 6.7.16$$

One last thing occurs to me before we leave this section. Can we calculate the *median* speed  $c_{1/2}$  of the Maxwell-Boltzmann distribution? This is the speed such that half of the molecules are moving slower than  $c_{1/2}$ , and half are moving faster. It is the speed that divides the area under the curve in half. If we express speeds in units of  $c_m$ , we have to find  $c_{1/2}$  such that

$$\frac{4}{\sqrt{\pi}} \int_0^{c_{1/2}} c^2 e^{-c^2} dc = \frac{1}{2}, \quad 6.7.17$$

or 
$$\int_0^{c_{1/2}} c^2 e^{-c^2} dc = \frac{\sqrt{\pi}}{8} = 0.2215567314. \quad 6.7.18$$

That should keep your computer busy for a while. Mine made the answer  $c_{1/2} = 1.08765 c_m$ .

## 6.8 Forces Between Molecules

We described in a qualitative manner in Section 6.3 the forces between molecules – the long-range attractive van der Waals forces caused by induced-dipole/induced-dipole interaction, and the short-range repulsive Coulomb forces as the molecules approach each other closely, and how these intermolecular forces give rise to deviations from the “Boyle’s Law” expectations for the equation of state for an ideal gas. Presumably, if we knew the exact equation for the force law as a function of intermolecular distance, we could in principle calculate the equation of state; conversely, if we knew, through measurement, the form of the equation of state, we could deduce the form of the intermolecular forces. I have not actually done this myself; an early reference worthwhile to look up would be Lennard-Jones, Proc. Roy. Soc. **A112**, 214, (1926).

Qualitatively, the force law for the interaction between molecules would show a repulsive force rapidly falling off with distance when the molecules are very close (the molecules are “hard”) and a longer-range attractive force at larger distances. Two of the simpler equations that have been used to describe this are the Lennard-Jones potential:

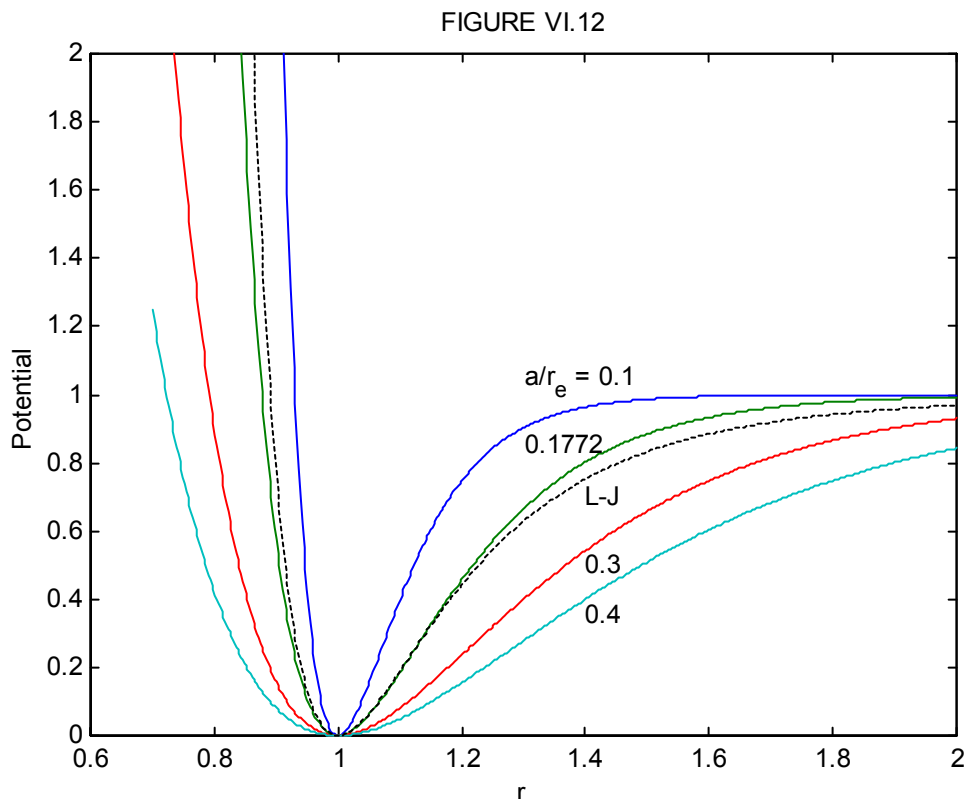
$$V = D \left[ 1 + \left( \frac{r_e}{r} \right)^{12} - 2 \left( \frac{r_e}{r} \right)^6 \right] \quad 6.8.1$$

and the Morse potential:

$$V = D \left( 1 - e^{-(r-r_e)/a} \right)^2. \quad 6.8.2$$

Each of these goes to  $V \rightarrow D$  as  $r \rightarrow \infty$ , and  $V = 0$  when  $r = r_e$ . The Lennard-Jones potential (but not the Morse potential) goes to  $\infty$  as  $r \rightarrow 0$ .

These expressions cannot be “derived” in the usual sense; they are merely expressions that are useful for discussion in that they describe qualitatively the shape of the potential function that you would expect. The Lennard-Jones expression is often used in discussions of the van der Waals force: if the van der Waals attractive force is due mostly to induced-dipole/induced-dipole interaction, an  $r^{-6}$  term is about right. The Morse potential is used more often in discussion of the force between atoms in a bound molecule. If the Morse potential is put into the Schrödinger equation for an anharmonic oscillating diatomic molecule, it results in a simple solution for the eigenfunctions and eigenvalues, with the energy levels being given as quadratic (and no higher) in  $v + \frac{1}{2}$ .



The parameter  $a$  in the Morse expression determines how narrow or how broad the minimum is. It is left as an exercise for the reader to show that the FWHm (full width at half minimum) of the Morse expression is the same as for the Lennard-Jones potential for

$$a = \frac{(2 + \sqrt{2})^{1/6} - (2 - \sqrt{2})^{1/6}}{\ln(3 + \sqrt{8})} = 0.177212908. \quad 6.8.3$$

In figure VI.12, I show, as continuous curves, the Morse potentials (in order of increasing width) for  $a/r_e = 0.1, 0.1772, 0.3$  and  $0.4$ , and the Lennard-Jones potential as a dashed curve. Further comparisons between these two potential functions can be found in T.-C. Lim, *Z. Naturforschung*, **58a**, 615, (2003).