

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, $PV = \text{constant.}$ 6.1.1

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 inversely 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 inversely proportional to its Kelvin temperature.

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

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

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

$$PV/T = RN, \quad \text{6.1.3}$$

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 volume of the gas, N is the number of moles and R is the *Universal Gas Constant*. The equation can also be written

$$PV_0 = RT, \quad 6.1.5$$

where V_0 is the volume of a mole of the gas, or the *molar volume*.

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_0 is the volume of a mole (i.e. the volume occupied by 6.0222×10^{23} molecules), and the value of the universal gas constant is 8.3143×10^7 erg mole⁻¹ K⁻¹. If you are using SI units, P will be expressed in pascal (N m⁻²), V_0 will be the volume of a kilomole (i.e. the volume occupied by 6.0222×10^{26} molecules), and the value of the universal gas constant is 8.3143×10^3 J kilomole⁻¹ K⁻¹. 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 as $P = \frac{NN_0}{V} \cdot \frac{RT}{N_0}$, where N_0 is Avogadro's number, which is 6.0222×10^{23} molecules per mole, or 6.0222×10^{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_0 is *Boltzmann's constant*, $k = 1.3806 \times 10^{-23}$ J K⁻¹. 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") μ . The density ρ 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.

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_0 and T , and see how close PV_0/T is to R . For most real gases at very high pressures (a few hundred atmospheres), it is found in fact that PV_0/T is rather greater than R . As the pressure is lowered, PV_0/T becomes lower, and then, alas, it overshoots and is found to be a little less than R . Then at yet lower pressures PV_0/T rises again. The exact shape of the $PV_0/T : P$ curve is different from gas to gas, as is the pressure at which PV_0/T is a minimum. Yet, for all gases, *as the pressure approaches zero, PV_0/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.

Another way to look at how closely real gases obey the ideal gas equation is to plot P versus V_0 for a number of different temperatures. That is, we draw a set of *isotherms*. For an ideal gas, these isotherms, $PV_0 = \text{constant}$, 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.

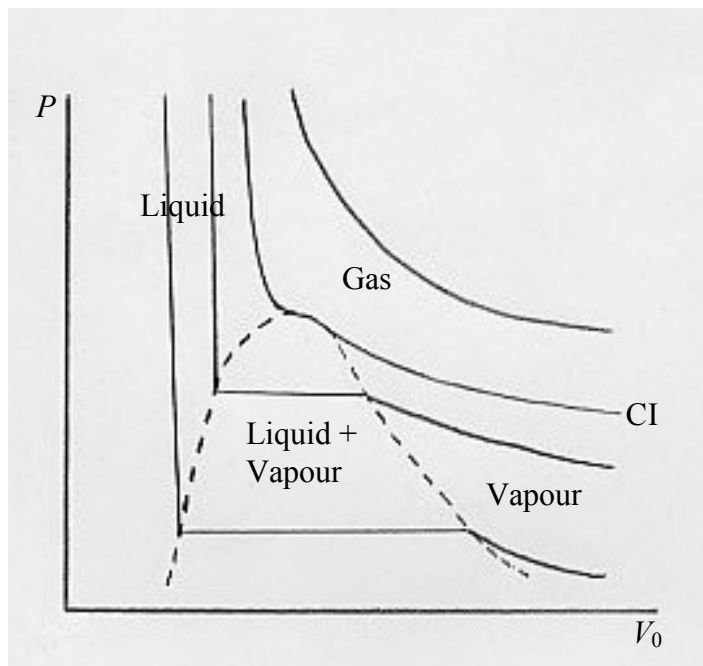


FIGURE VI.1

In the PV_0 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_0 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 increase the pressure, the volume gradually decreases until you reach the dashed curve. Then, quite suddenly, there is a large and discontinuous reduction in volume – the vapour liquefies! 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_0 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:

$$\text{van der Waals' equation:} \quad (P + a/V_0^2)(V_0 - b) = RT. \quad 6.3.1$$

$$\text{Clausius' equation:} \quad \left(P + \frac{a}{T(V_0 + c)^2} \right) (V_0 - b) = RT. \quad 6.3.2$$

$$\text{Dieterici's equation:} \quad P(V_0 - b)e^{a/(RTV_0)} = RT. \quad 6.3.3$$

$$\text{Virial equation:} \quad PV_0 = A + \frac{B}{V_0} + \frac{C}{V_0^2} + \frac{D}{V_0^3} + \dots \quad 6.3.4$$

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.

The van der Waals equation (that is to say, 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 (that is to say, 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_0 , 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_0^2 . 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.

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

$$P = \frac{RT}{V_0 - b} - \frac{a}{V_0^2}. \quad 6.3.5$$

A horizontal inflection point occurs where $\frac{\partial P}{\partial V_0}$ and $\frac{\partial^2 P}{\partial V_0^2}$ are both zero. That is

$$-\frac{RT}{(V_0 - b)^2} + \frac{2a}{V_0^3} = 0 \quad 6.3.6$$

and

$$\frac{2RT}{(V_0 - b)^3} - \frac{6a}{V_0^4} = 0. \quad 6.3.7$$

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

$$V_c = 3b. \quad 6.3.8$$

Substitute this into equation 6.3.6 or 6.3.7 (or both, as a check on your algebra) to obtain the critical temperature:

$$T_c = \frac{8a}{27Rb}. \quad 6.3.9$$

Substitute equations 6.3.8 and 6.3.9 into equation 6.3.5 to obtain the critical pressure:

$$P_c = \frac{a}{27b^2}. \quad 6.3.10$$

From these, we readily obtain

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.667. \quad 6.3.11$$

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

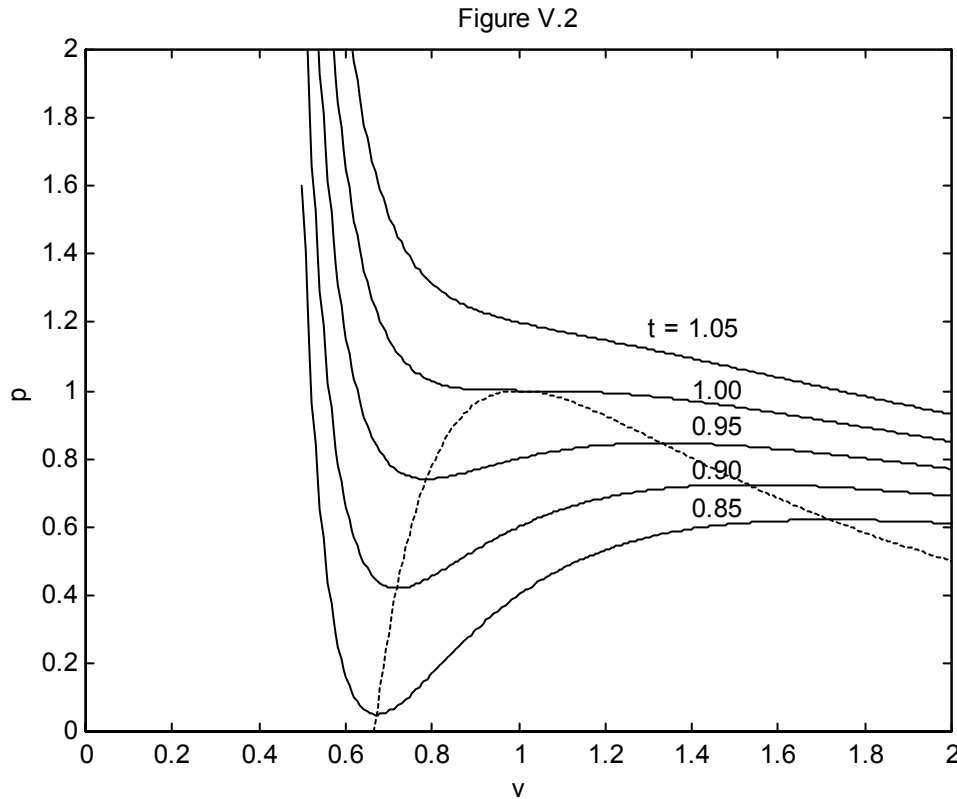
$$(p + 3/v^2)(3v - 1) = 8t. \quad 6.3.12$$

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 equation 6.3.12 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 6.3.2 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 dashed line in figure VI.2) is given by

$$p = \frac{3}{v^2} - \frac{2}{v^3}. \quad 6.3.13$$

One last point of interest before leaving the van der Waals gas. You know that, for an ideal gas, $\frac{PV_0}{RT} = 1$. You might like to show that, for a van der Waals gas,

$$\frac{PV_0}{RT} = 1 + \frac{1}{8t} \left(p - \frac{9}{v} + \frac{3}{v^2} \right). \quad 6.3.14$$



I leave it to the reader, if he or she wishes, to perform a similar analysis for a Clausius or a Dieterici gas.

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.

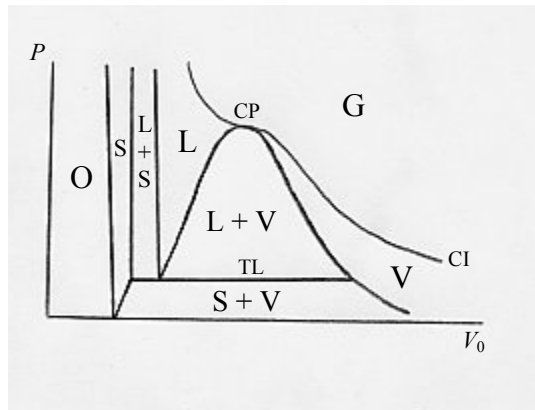


FIGURE VI.3

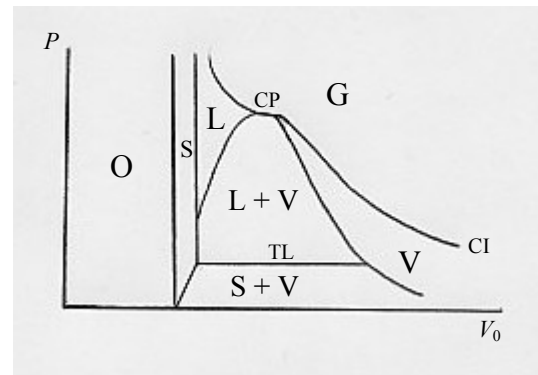


FIGURE VI.4

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* TP, 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 V.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".

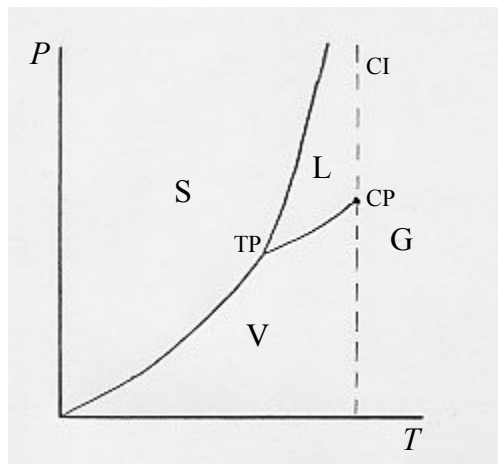


FIGURE VI.5

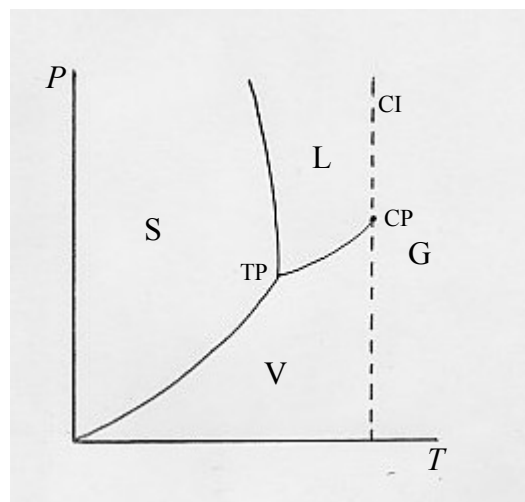


FIGURE VI.6

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.

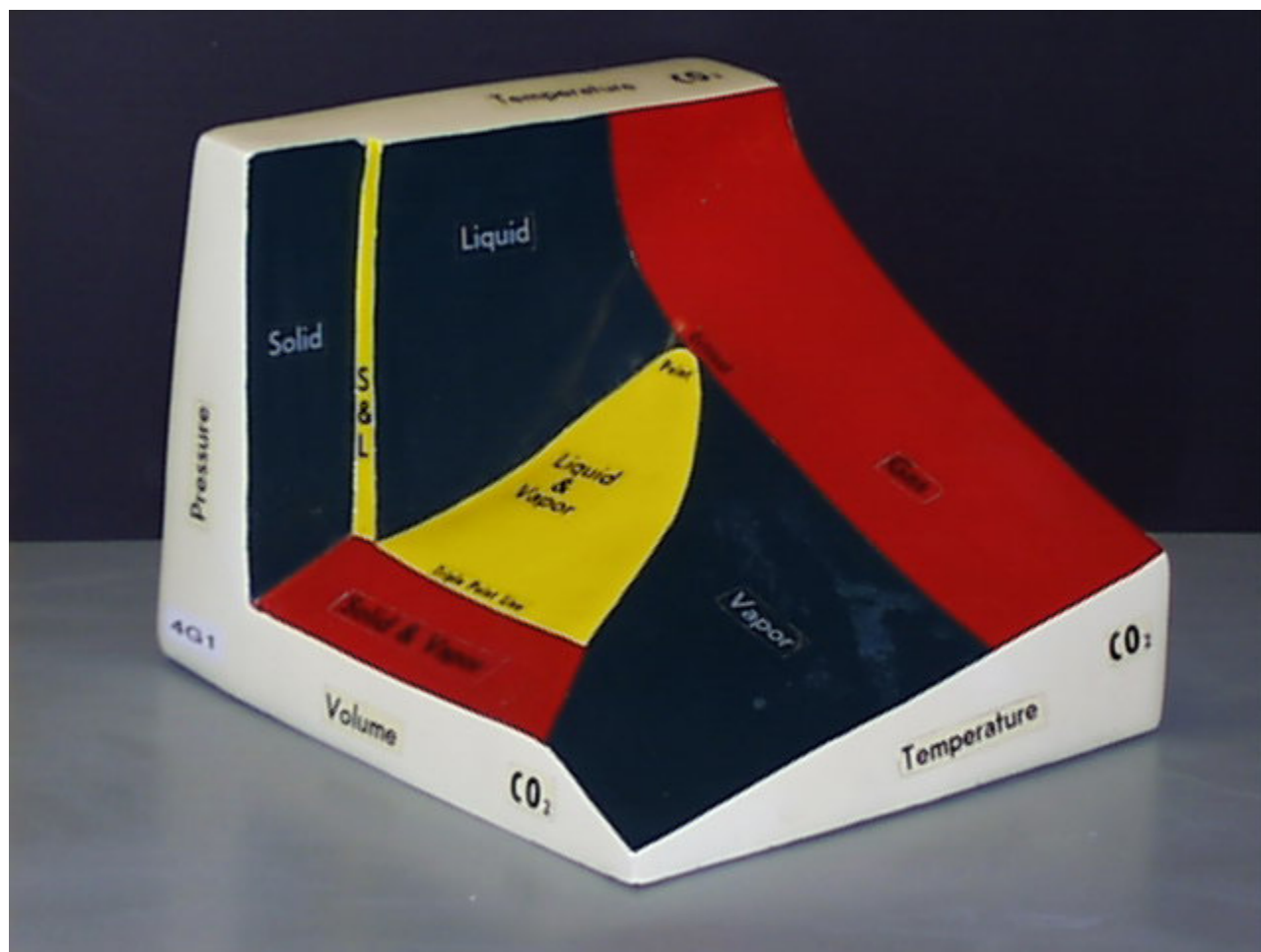


FIGURE VI.7

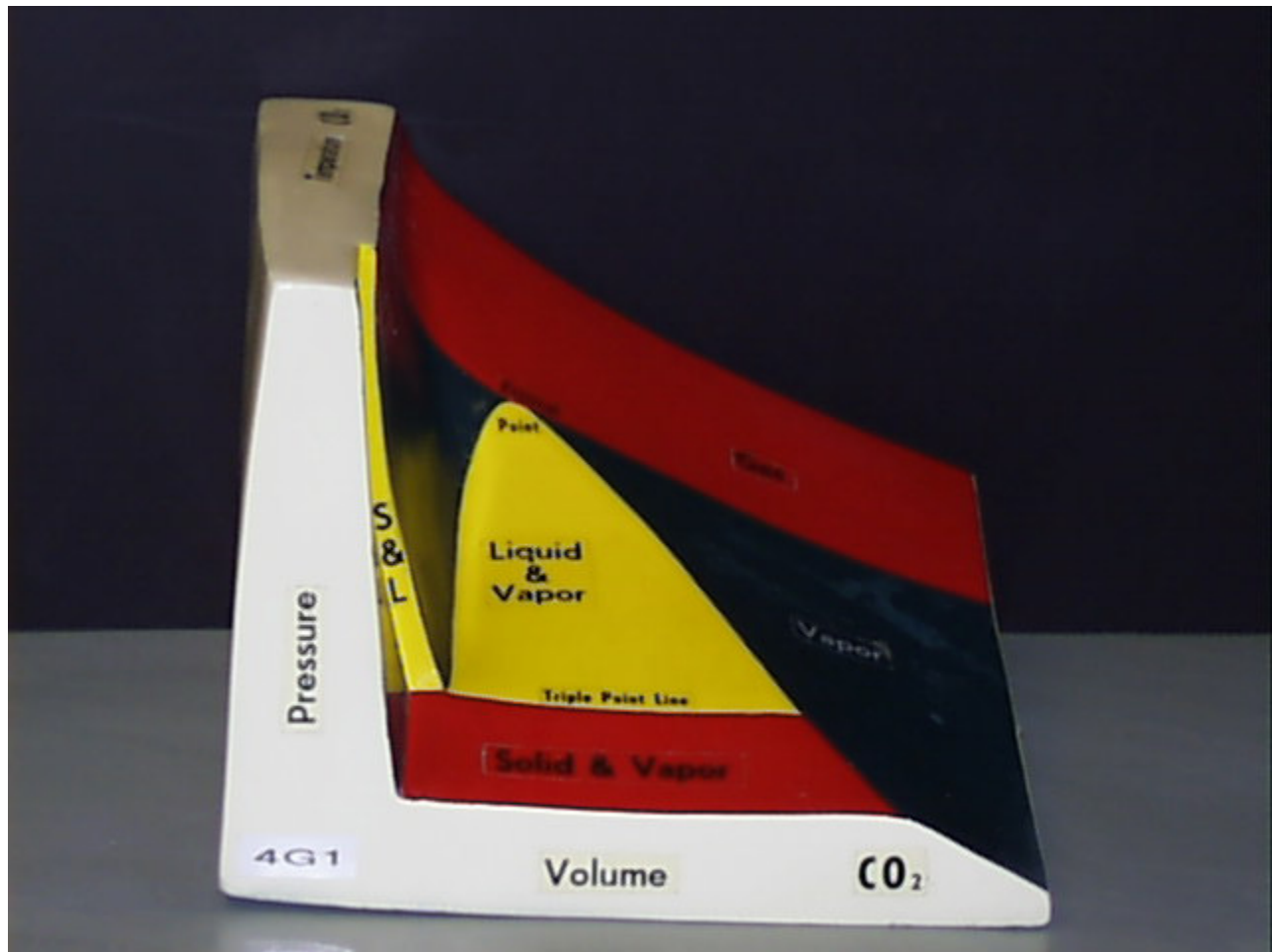


FIGURE VI.8

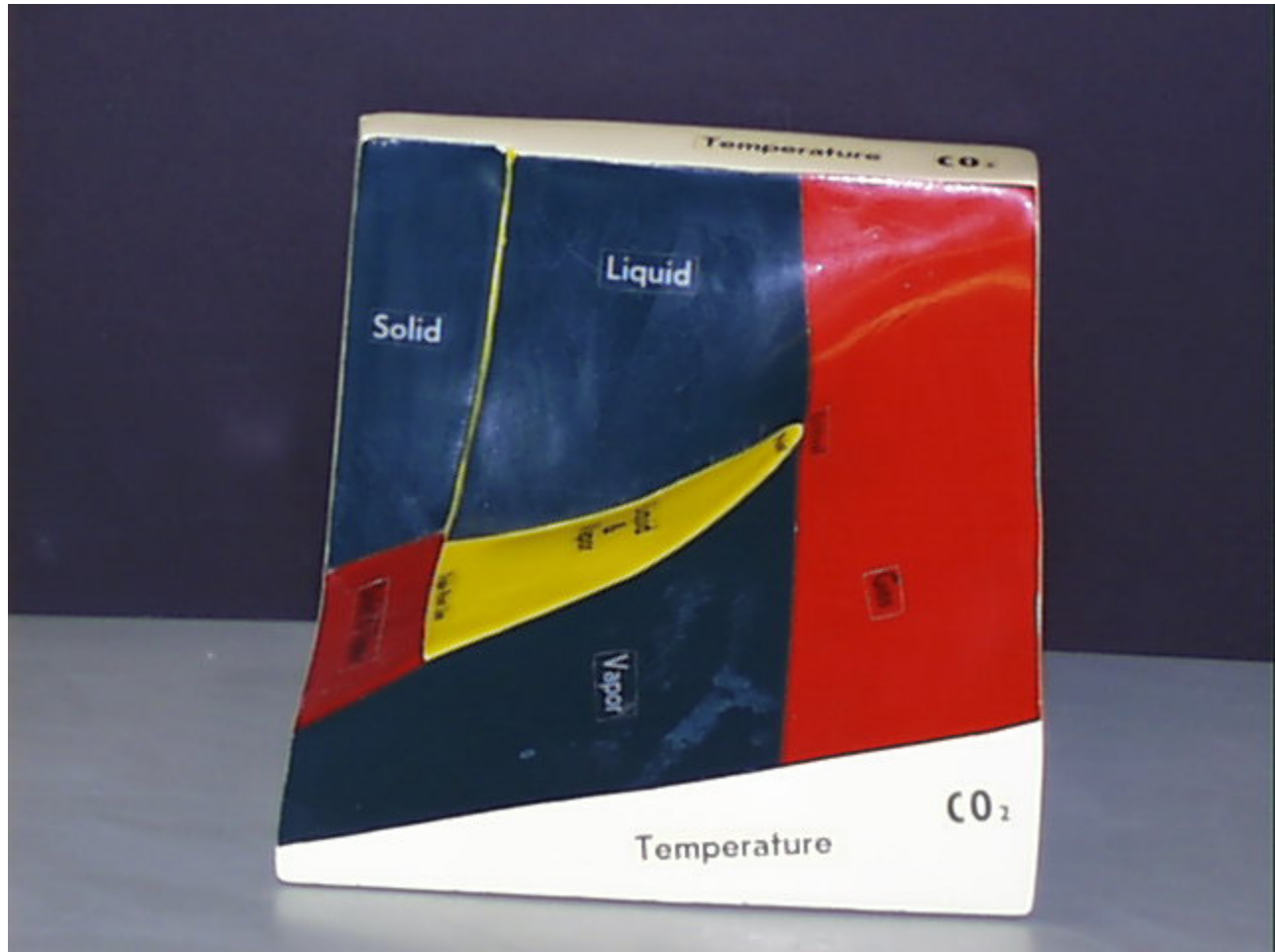


FIGURE VI.9

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 $\overline{u^2} = \overline{v^2} = \overline{w^2}$ and $\overline{u^2} + \overline{v^2} + \overline{w^2} = \overline{c^2}$, and so the pressure is

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

Here ρ is the density = mass/ volume = molar mass/ molar volume = μ/V_0 , and therefore

$$PV_0 = \frac{1}{3}\mu\overline{c^2}. \quad 6.5.2$$

But $\frac{1}{3}\mu\overline{c^2}$ is $\frac{2}{3}$ of the kinetic translational kinetic energy of a mole of gas, and we already know that $PV_0 = RT$, 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 πd^2 .

In time t , a molecule moving with speed c sweeps out a cylinder of volume $\pi d^2 ct$. 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 $\pi d^2 ctn$. But this isn't quite right, because we have not taken into account the fact that the molecules in the mentioned cylinder are moving. It is not as though the 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 the relative speed when the relative velocities of two molecules make an angle of 45° to each other; that is $\sqrt{2}\overline{c}$. Thus the number of collisions per second per unit time that our molecule will experience is $\sqrt{2}\pi d^2 \overline{c}n$, and hence the mean time between collisions is

$$\tau = \frac{1}{\sqrt{2}\pi d^2 \overline{c}n}, \quad 6.6.1$$

and the mean distance between collisions – the *mean free path* – is \bar{c} times this, or

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n}. \quad 6.6.2$$

Now we have seen that the one molecule whose career we have been following experiences $\sqrt{2}\pi d^2 \bar{c} n$ collisions per unit volume per unit time, and, since there are n molecules per unit volume, the total number of collisions experienced by all molecules per unit volume per unit time would seem to be n times this. But it takes two to make a collision, so, in order to avoid counting each collision twice (i.e. we don't want to count A collides with B and B collides with A as two separate collisions), the total *number of collisions per unit volume per unit time* is really $\frac{1}{2}n$ times $\sqrt{2}\pi d^2 \bar{c} n$. That is,

$$Z = \frac{1}{2}\sqrt{2}\pi d^2 \bar{c} n^2. \quad 6.6.3$$

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

$$\frac{1}{4}n\bar{c}. \quad 6.6.4$$

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 $f(u)f(v)f(w) du dv dw$. 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.

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

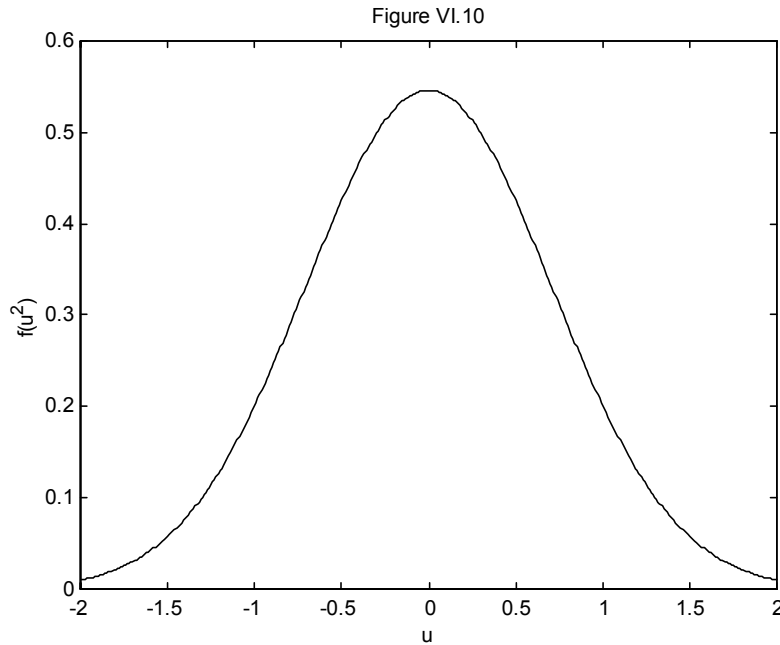
it follows that
$$A = \frac{1}{c_m \sqrt{\pi}}. \quad 6.7.8$$

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

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

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

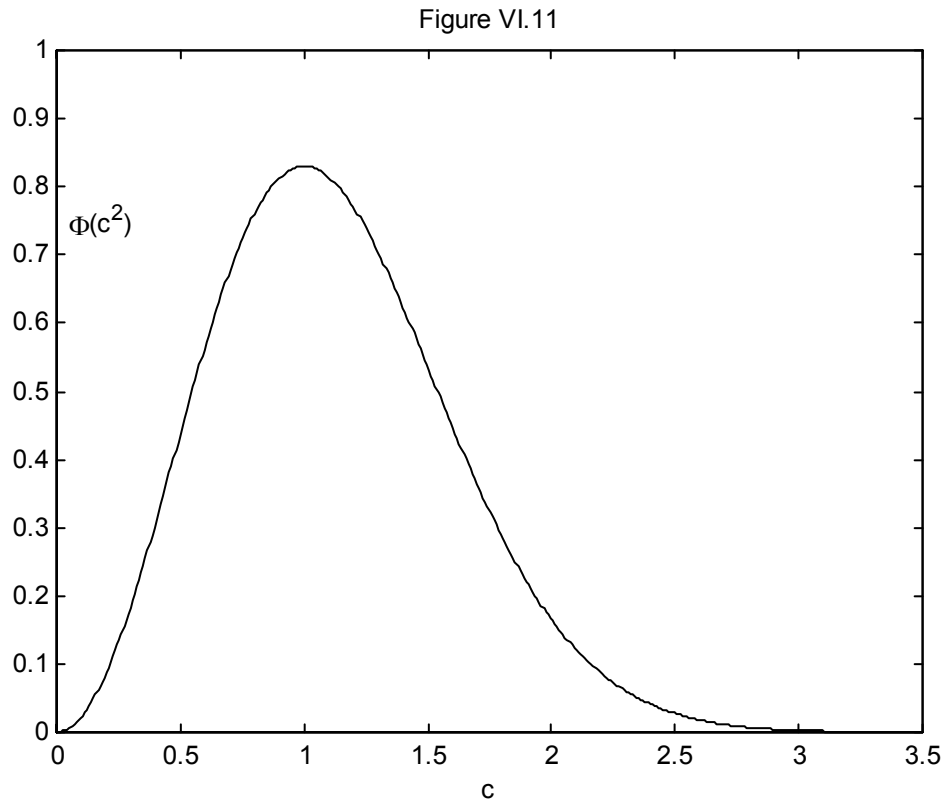
Figure VI.10 illustrates this distribution. In this figure, the unit of speed is c_m . The area under the curve is 1. The maximum (at $u = 0$) is $1/\sqrt{\pi} = 0.564$. *Exercise:* Show that the FWHM (full width at half maximum) is $2\sqrt{2} c_m$. This gives one physical interpretation of c_m ; we 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 $c = c_m$. This provides another interpretation of the constant c_m . The speed at which the maximum of the distribution occurs is called the *mode* or 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_{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_{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, $\frac{1}{2}mc^2$, is equal to $\frac{3}{2}kT$, so now let's bring it all together:

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

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

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

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 $c_{1/2} = 1.08765 c_m$.