

Real Gases

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1. Introduction

Real gases are not ideal because of molecular interactions. Molecular interactions show up in the *compression factor* Z defined by:

$$Z = \frac{pV_m}{RT} \quad (1)$$

where V_m is the molar volume (V divided by n). An ideal gas has $Z = 1$ at all pressures and temperatures. A graphical picture of Z for several real gases is given in most physical chemistry texts. Pay attention to the horizontal scale. You will note that near 1 atm. the ideal gas law gives the right compression factor to within 1%.

Clearly the ideal gas law is (1) not too bad at or below 1 atm., and (2) not too good above 10 atm. or so.¹ Is there anything better? The answer is yes, there are better equations of state, but they come at a price.

2. Other Equations of State

One often-unnoticed virtue of the ideal gas equation is the fact that it is *independent of the chemical nature of the gas*. According to it any gas with temperature T , volume V , and number of moles n will have the same pressure. It does not matter if the gas is CO_2 or helium. Since it is clear from even a quick look at a graph of Z that real gases show different compression factors, **a more accurate equation of state will have to contain terms that depend upon the kind of gas one is dealing with.**

There are many "better" equations of state. We will talk about some of them here. Why so many? Because each has its strengths and weaknesses. Some are easier to handle mathematically. Others are more accurate at high pressures. Of all of these equations of state, the most famous is the *van der Waals equation*:

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \quad (\text{van der Waals}) \quad (2)$$

in which the constants a and b are different for each chemically different gas. Another often used equation is the *Berthelot equation*:

¹ It is also not too good near the *critical point* or near the *condensation point*.

$$\left(p + \frac{n^2 a}{TV^2}\right)(V - nb) = nRT \quad (\text{Berthelot}) \quad (3)$$

where again a and b are different for each different gas and do *not* have the same values as a and b for the van der Waals equation.

There is also the *Dieterici* equation:

$$p e^{na/VRT} (V - nb) = nRT \quad (\text{Dieterici}) \quad (4)$$

and there is the *Redlich-Kwong* equation:

$$\left(p + \frac{n^2 a}{T^{1/2} V (V + nb)}\right)(V - nb) = nRT \quad (\text{Redlich-Kwong}) \quad (5)$$

In each of these cases a and b are different for each gas and differ from equation to equation. To use these equations, you must find a and b in appropriate tables.

Where do these equations come from? Nowhere. There is no theoretical justification for them. They were dreamed up (rationalized would be a better word) by their authors for one reason or another. Each of them looks like a "corrected" ideal gas equation, and that is what they are. Each of them *is* a corrected ideal gas equation. Don't forget, that for a given amount of gas, as V gets larger and p gets smaller, the gas must behave more and more ideally. For example, it is easy to see that as V increases in the van der Waals equation, the term $n^2 a/V^2$ becomes vanishingly small. Similarly, as V gets large, the nb term in $V - nb$ can be neglected. The result is the ideal gas law.²

On the other hand, for "normal" values of V and p , gases do not behave ideally. Van der Waals' equation can be rationalized as follows: (1) Real gas molecules have a volume. A consequence of this is that *other* gas molecules do not have the volume V to move around in, they actually have a smaller volume. We have to subtract out the volume occupied by the molecules themselves. This is what the $(V - nb)$ term is in van der Waals' equation, a *corrected* volume term. In other words the geometric volume V is too big. The actual volume the molecule "sees" is smaller. The factor b is then in some sense proportional to the molecular volume. (2) Real molecules attract each other. This makes no difference in the bulk of the gas since a given molecule is attracted essentially equally in all directions. But a molecule heading for the wall is pulled back away from the wall since most of the gas molecules are behind it. This results in the measured pressure being *less* than it ideally should be. To correct this the quantity $n^2 a/V^2$ is added to the measured pressure. The factor a is then a measure of the attractive forces between molecules, the larger a , the more they attract each other.

The other equations of state were invented on similar grounds. Berthelot felt that the pressure correction term would fit the data better if it were temperature dependent. Dieterici felt that an exponential correction term would fit the pressure better. And Redlich and Kwong went to an even more complex set of corrections.

² To see if you understand this point, the student should check that each of the other three equations also reduces to the ideal gas equation when V gets large.

3. The Critical Point

The existence of a critical point in real substances is somewhat surprising. To remind the forgetful, the critical point is the temperature and pressure at which a volume of gas becomes indistinguishable from a liquid. The properties of the two merge. Near its critical point, no gas behaves ideally. Thus the properties of a gas at or near the critical point is a strenuous test for any equation of state. The ideal gas equation, of course, fails miserably.

At the critical temperature, the $p - V$ curve of a real gas shows a flat spot. This spot occurs at the critical pressure and volume. Experiments show that the curve is *really* flat here. Not only is $(\partial p / \partial V_m)_T$ equal to zero, the *second* derivative is also equal to zero. For a van der Waals gas³ this means that, at the critical point the following three equations are simultaneously true:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (6)$$

$$\left(\frac{\partial p}{\partial V_m} \right)_T = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0 \quad (7)$$

$$\left(\frac{\partial^2 p}{\partial V_m^2} \right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0 \quad (8)$$

Since equations are all simultaneously true at the critical point, they can be solved together to give the molar critical volume V_c , temperature T_c , and pressure p_c in the following way. From Eq. (7)

$$\frac{RT}{(V_m - b)^2} = \frac{2a}{V_m^3} \quad (9)$$

and from Eq. (8)

$$\frac{2RT}{(V_m - b)^3} = \frac{6a}{V_m^4} \quad (10)$$

If Eq. (9) is divided into Eq. (10) the result is simply

$$V_m - b = 2V_m/3 \quad (11)$$

from which, since this is at the critical point:

$$V_c = 3b \quad (12)$$

Using this value in Eq. (9) gives, after some simple algebra:

$$T_c = \frac{8a}{27bR} \quad (13)$$

³ That is, a gas that obeys van der Waals equation.

and then from van der Waals equation itself it is easy to show that:

$$P_c = \frac{a}{27b^2} \quad (14)$$

Thus, if the critical temperature and pressure are known, the van der Waals parameters a and b can be determined. This is often done.

A similar analysis can be done for the other equations of state. The table below lists the results.

Equation	a	b	Z
van der Waals	$\frac{27R^2T_c^2}{64P_c}$	$\frac{RT_c}{8P_c}$	$\frac{3}{8}$
Berthelot	$\frac{27R^2T_c^3}{64P_c}$	$\frac{RT_c}{8P_c}$	$\frac{3}{8}$
Dieterici	$\frac{4R^2T_c^2}{e^2P_c}$	$\frac{RT_c}{e^2P_c}$	$\frac{2}{e^2}$
Redlich-Kwong	$\frac{RT_c^{5/2}}{2.34P_c}$	$\frac{0.260RT_c}{3P_c}$	0.33

Table 1: Critical Constants and the parameters a and b

Note that Z is the compression factor. Real gases have compression factors between (roughly) 0.25 and 0.30. The Dieterici equation predicts $Z = 0.271$. The others are less accurate. However, the others are better in other regions.

4. The Virial Equation

So far we have introduced *five* different equations of state,⁴ and none of them are correct. Each of them offers better than 1% accuracy over a wide range of temperatures and pressures, but none of them are perfect. Is there a perfect equation of state for gases?

So far, nobody has been able to come up with one.⁵ But there is another approach. Assume that we actually know the exact equation of state and we write it with p as a function of T and c in this way:

$$p = f(T, c) \quad (15)$$

where $c = n/V$ is the *concentration* of the gas in moles per liter. In these terms the ideal gas law is simply $p = cRT$. Equations of state for gases can always be written in terms of c , since c is just the reciprocal of the molar volume V_m .

⁴ Counting the ideal gas law.

⁵ And there is very good reason to believe that nobody ever will. See the discussion below on this.

Now, we don't actually know how to write $f(T, c)$ out algebraically. Nevertheless, assuming that p is a continuous function of T and c , $f(T, c)$ does have a Taylor series expansion.⁶ We can write out the Taylor series expansion in powers of the concentration c around the point $c = 0$:

$$p = \left[f(T, c) \right]_{c=0} + \left[\frac{\partial f(T, c)}{\partial c} \right]_{c=0} c + \frac{1}{2!} \left[\frac{\partial^2 f(T, c)}{\partial c^2} \right]_{c=0} c^2 + \dots \quad (16)$$

But this will do us no good unless we can identify the coefficients. Take the first coefficient, $f(T, c)$ evaluated at zero concentration. We *do* know what this has got to be. All gases become ideal at low enough pressures, so as c goes to zero, all terms in Eq. 16 except the first must vanish, and the first must be cRT . So Eq. 16 becomes:

$$p = cRT + \left[\frac{\partial f(T, c)}{\partial c} \right]_{c=0} c + \frac{1}{2!} \left[\frac{\partial^2 f(T, c)}{\partial c^2} \right]_{c=0} c^2 + \dots \quad (17)$$

To make life easier, we divide both sides of Eq. 17 by cRT and rename the right-hand side terms to get:

$$\frac{p}{cRT} = 1 + Bc + Cc^2 + \dots \quad (18)$$

and, to make things clearer, we replace c with n/V to get:

$$\frac{pV}{nRT} = 1 + B\left(\frac{n}{V}\right) + C\left(\frac{n}{V}\right)^2 + \dots \quad (19)$$

But how do we find the coefficients B , C , etc.⁷ There are three ways. One is to calculate them from known equations of state (but this gives us nothing new); another is to measure them experimentally. This has been done. The last is to calculate them from basic theory.

Equation 19 is called the *virial equation*. The coefficient B is known as the *second virial coefficient* and C is called the *third virial coefficient*.

To give an idea of how the second virial coefficient varies with temperature, the experimentally measured second virial coefficient data for argon is given below. The behavior is typical, B is negative at low temperatures, becomes zero at some temperature,⁸ and then becomes (and stays) slightly positive.

⁶ You were warned that calculus was a prerequisite for this course! If you don't remember what a Taylor series is, look it up in your calculus book. Technically, since we will expand around $c = 0$, this is a Maclaurin series expansion, not a Taylor series expansion.

⁷ Don't forget, B , C , etc., are *not* constants. They are functions of T . They are *not* functions of c , since the coefficients are evaluated at $c = 0$.

⁸ This temperature is known as the Boyle point.

T	B
100	-185.5
150	-84.7
200	-47.6
250	-28.0
300	-15.6
400	-0.9
500	7.3
600	12.5

Table 2: Second Virial Coefficient of Argon

The data is from Dymond and Smith, *The Virial Coefficients of Gases*, Oxford, 1969. Note that the temperatures are in Kelvins and B is in *cubic centimeters per mole*.

Third virial coefficients can (and have been) measured experimentally. Beyond this it gets very hard. The deviations from ideality are small and it is very hard to measure gas properties such as pressure to enough precision to enable very small effects to show up.

Virial equation data is very useful, far better than theory, since it represents experimental reality. And in principle, if we could measure enough virial coefficients, the virial equation should lead to excellent results. Right? Unfortunately, this is wrong. And it is easy to see why. At some combinations of temperature and pressure *changes of phase* occur. The gas turns to a liquid or to a solid. This change involves a *discontinuous* change in properties. Volume is a typical example. Can the virial equation show such behavior? No. It is a continuous function. And continuous functions cannot have discontinuities.⁹ So even the virial equation will ultimately, not be the perfect equation of state.

Virial coefficients can be calculated from equations of state. There is absolutely no practical point in doing this, since the equation of state already contains all possible information. But it is interesting to see what the second (and third) virial coefficients look like when derived from common equations of state.¹⁰ The trick is to get the equation of state into a power series in $1/V_m$. For the van der Waals equation we first write the equation of state as:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (20)$$

and then factor out an RT/V_m :

$$p = \frac{RT}{V_m} \left[\frac{1}{1 - b/V_m} - \frac{a}{RTV_m} \right] \quad (21)$$

The next step requires a calculus memory. Back in the days when you looked at power series you found that:¹¹

⁹ Perhaps you studied Fourier series in calculus. If so, do you remember the behavior of the Fourier series in the presence of a discontinuity.

¹⁰ And there is the fact that textbooks sometimes make a lot of this, so it would be good to see an example worked out in detail.

¹¹ If you don't remember, check your calculus book. You did keep your calculus book, didn't you?

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots = \sum_{n=0}^{\infty} x^n \quad |x| < 1 \quad (22)$$

Then:

$$p = \frac{RT}{V_m} \left[1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \dots - \frac{a}{RTV_m} \right] \quad (23)$$

and gathering like terms:

$$p = \frac{RT}{V_m} \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \dots \right] \quad (24)$$

Thus the van der Waals second virial coefficient B is:

$$B = b - \frac{a}{RT} \quad (25)$$

and the third coefficient C is:

$$C = \frac{b^2}{V_m^2} \quad (26)$$

5. Calculation of the Second Virial Coefficient from Basic Theory

It is possible to compute the second virial coefficient if one knows the potential energy between two molecules. The formula is derived in courses in statistical thermodynamics; the derivation is messy but the result is simple.

What do I mean by the "potential energy". Imagine a graph¹² whose horizontal axis is the distance between the centers of two molecules and the vertical axis is the potential energy between them. This potential energy is zero when the two atoms or molecules are far apart. As they get closer together the potential energy becomes negative. This means that it *will take energy* to separate the particles. In other words, they *attract* each other. When the particles get too close, the potential energy becomes positive, indicating that the particles repel each other.¹³ When I speak of "knowing" the potential energy between two molecules, I mean that we know the *equation* for the potential energy curve in the graph.

¹² Or, if you can't, look at Figure 1 on the next page.

¹³ Actually, if U is the potential energy, the force between the molecules is $F = -dU/dr$, so that the molecules attract when the slope is positive and repel when it is negative.

An example of a potential energy graph is given in Figure 1:

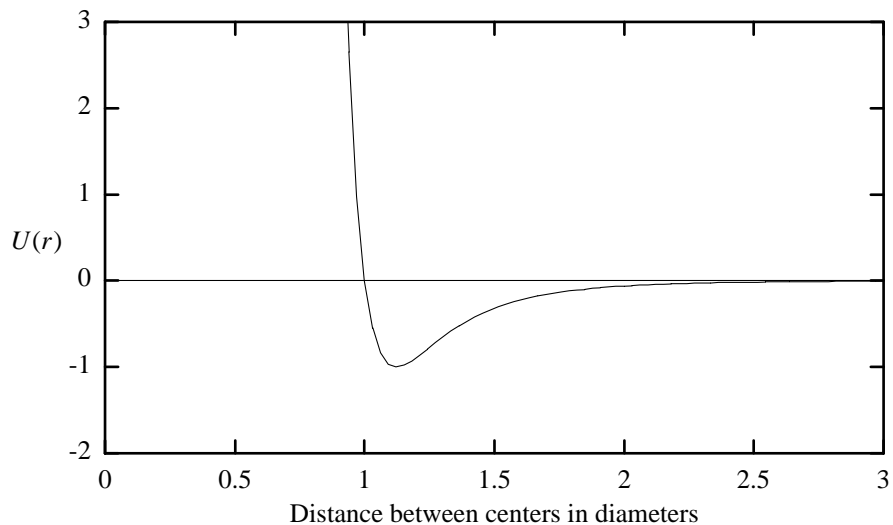


Figure 1: Potential Energy vs. Particle Separation

Life is much simpler if we deal only with spherically symmetric molecules.¹⁴ If the potential energy between two molecules is given by $U(r)$, where r is the distance between the centers of the two molecules, then the second virial coefficient B is given by:

$$B(T) = 2\pi N_o \int_0^{\infty} (1 - e^{-U(r)/kT}) r^2 dr \quad (27)$$

where N_o is Avogadro's number. The second virial coefficient B is generally a function of temperature, and so is sometimes written $B(T)$, as in Eq. 27.

The simplest case is the ideal gas. This is simple because *there is no potential energy between molecules*. Thus $U(r) = 0$ and B is identically zero.

The next simplest case is called the **Hard Sphere Approximation**. Here molecules are considered to be hard spheres but to have no other interaction. If the diameter of a molecule is σ , then the *hard sphere potential* is given by:

$$U(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (28)$$

¹⁴ That means a triple integration is reduced to a single integration.

This potential energy "equation" is shown in Figure 2:

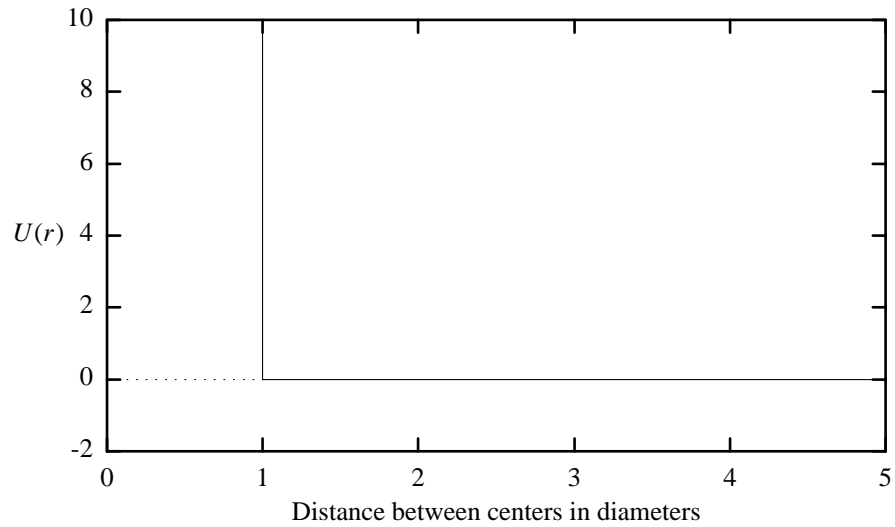


Figure 2: Hard Sphere Potential vs. Separation Distance

Now how does one do an integral with a two part formula? Why, by breaking the integral into two parts. The first part runs from 0 to σ with $U(r) = \infty$. This gives:

$$\int_0^{\sigma} (1 - e^{-\infty}) r^2 dr = \int_0^{\sigma} r^2 dr = \frac{\sigma^3}{3} \quad (29)$$

The second runs from σ to ∞ with $U(r) = 0$. This gives:

$$\int_{\sigma}^{\infty} (1 - e^0) r^2 dr = 0 \quad (30)$$

So B is simply

$$B = \frac{2\pi N_0 \sigma^3}{3} \quad (31)$$

The second virial coefficient for a gas made up of hard spheres is *independent of temperature*.

But neither of these cases is "real". We can find the "real" second virial coefficient if we know the "real" intermolecular potential. Alas, we do not know it. We have good approximations, but that's all. Among the best approximations is the Lennard-Jones potential:¹⁵

¹⁵ Lennard-Jones is one person.

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (32)$$

where σ is essentially (but not exactly) the diameter of the molecule and ϵ is the "well-depth". Figure 1 above is actually a graph of the Lennard-Jones potential.

Equation 27, with the Lennard-Jones potential plugged into it can actually be solved, but not as an algebraic formula. One gets an infinite series instead.¹⁶ But it is a rapidly converging series, and values of the second virial coefficient for the Lennard-Jones potential are available.

We can go one step further. The **Square Well Potential** is a rough approximation of a realistic potential. It looks like this:

$$U(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon & \sigma \leq r < w\sigma \\ 0 & r \geq w\sigma \end{cases} \quad (33)$$

where σ is the distance of closest possible approach. In the range where the separation between the particles lies between σ and $w\sigma$, it will *take* energy to separate the molecules. Beyond $w\sigma$ there is no interaction energy between the molecules at all.

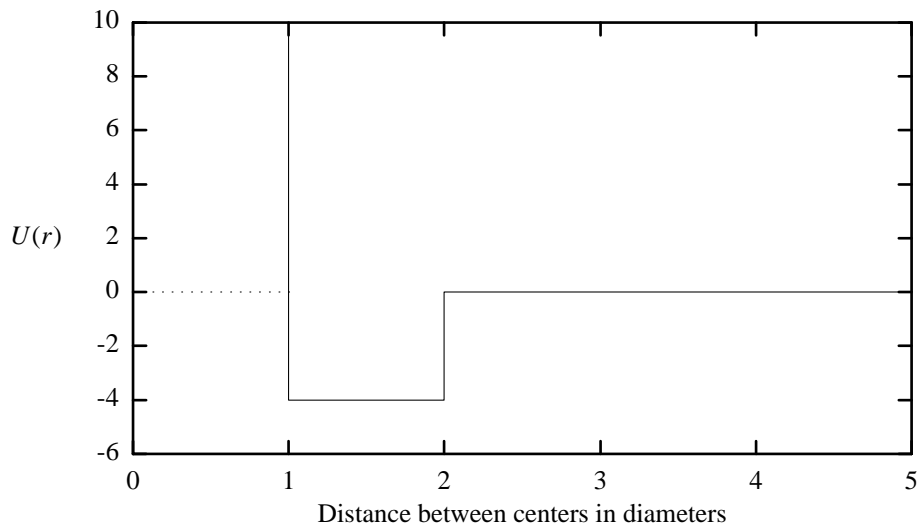


Figure 3: Square Well Potential vs. Separation Distance

This potential can also easily be plugged into Eq. 27. The integral now breaks up into *three* parts. The result is:

¹⁶ By the way, this is a non-trivial mathematical problem. I'll give one hint: you have to expand the formula as an appropriate series *before* you do the integration.

$$B(T) = \frac{2\pi N_0 \sigma^3}{3} \left[e^{\varepsilon/RT} (1 - w^3) + w^3 \right] \quad (34)$$

where ε and R must be in the same units. Of course w is just a pure number and σ is often given in centimeters. Be careful of this when using second virial coefficients.

The interesting thing about *this* second virial coefficient is that it is a function of temperature. At high temperatures the exponential goes to zero and $B(T)$ becomes basically the hard-sphere second virial coefficient. That makes sense because at high T the particles have so much kinetic energy that a little bit of attraction means nothing. At low temperatures however, $B(T)$ is negative because w must be greater than 1. This mimics the behavior of real second virial coefficients which are also negative at low temperatures and positive at higher ones.

We've now gone far enough.¹⁷ I am sorry if this has seemed long, but as you can see there is much to the story of real gases. You can go further, indeed I encourage you to do so, but we must part company here.

¹⁷ Too far, most of you will say.