The Van der Waals Equation of State

The van der Waals Equation of State is an equation relating the density of gases and liquids to the pressure, volume, and temperature conditions (i.e., it is a thermodynamic equation of state). It can be viewed as an adjustment to the ideal gas law that takes into account the non-zero volume of gas molecules, which are subject to an inter-particle attraction. It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for this work.

Previously, we saw that for the pair potential

\[ u(r) = \begin{cases} \infty & r \leq \sigma \\ -\frac{C_6}{r^6} & r > \sigma \end{cases} \]

we could write the second virial coefficient as

\[ B_2(T) = \frac{2}{3} \pi N_0 \sigma^3 \left[ 1 - \frac{C_6}{3 k_B T \sigma^6} \right] \]

Let us introduce to simplifying variables

\[
\begin{align}
    b &= \frac{2}{3} \pi N_0 \sigma^3 \\
    a &= \frac{2 \pi N_0^2 C_6}{9 \sigma^3}
\end{align}
\]

in terms of which

\[ B_2(T) = b - \frac{a}{RT} \]

With these definitions, the virial equation of state becomes

\[
\begin{align}
    P &= \frac{nRT}{V} + \frac{n^2}{V^2} RT \left( b - \frac{a}{RT} \right) \\
    &= \frac{nRT}{V} \left( 1 + \frac{nb}{V} \right) - \frac{an^2}{V^2}
\end{align}
\]

If we assume \( nb/V \) is small, then we can also write

\[ 1 + \frac{nb}{V} \approx \frac{1}{1 - \frac{nb}{V}} \]

so that

\[ P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \]

which is known as the van der Waals equation of state. Equation \( \text{ref(Eq7)} \) can also be rewritten as

\[ \left( P + \frac{n^2a}{V^2} \right) (V - nb) = nRT \]

The first term in this equation is easy to motivate. In fact, it looks very much like the equation of state for an ideal gas

\[ PV = nRT \]

however, using \( V - nb \) fort the volume rather than \( V \). This part of the van der Waals equation is due entirely to the hard-wall potential \( u_\sigma(r) \). Essentially, this potential energy term describes a system of “billiard balls” of diameter
\( \sigma \). Figure \( \PageIndex{1} \) shows two of these billiard ball type particles at the point of contact (i.e., the distance of closest approach). At this point, they undergo a collision and separate, so they cannot be closer than that distance.

![Figure \( \PageIndex{1} \): Two hard spheres of diameter \( \sigma \) at closest contact. The distance between their centers is also \( \sigma \). A sphere of radius \( \sigma \) just containing the two particles is shown in cross-section.](image)

At this point, the distance between their centers is also \( \sigma \), as Figure \( \PageIndex{1} \) indicates. Because of this distance of closest approach, the total volume available to the particles is not \( V \) but some volume less than \( V \). This reduction in volume can be calculated as follows: Figure \( \PageIndex{1} \) shows a shaded sphere that just contains the pair of billiard ball particles. The volume of this sphere is the volume excluded from any two particles. The radius of the sphere is \( \sigma \) as the figure shows. Hence, the excluded volume for the two particles is \( 4 \pi \sigma^3/3 \), which is the volume of the shaded sphere. From this, we see that the excluded volume for any one particle is just half of this or \( 2 \pi \sigma^3/3 \). The excluded volume for a mole of such particles is just \( 2 \pi \sigma^3 N_0/3 \), which is the parameter \( b \):

\[
\begin{align*}
\text{Redlich-Kwong Equation of State} \\
&\text{The van der Waals cubic Equation of State had to wait almost 100 years before a real, successful improvement was introduced to it. This progress occurred once researchers committed themselves to finding the empirical temperature dependency of the attraction parameter \( a \) proposed by van der Waals. In contrast, very little attention has been paid to modifying the parameter \( b \) for co-volume. It makes a lot of sense that \( b \) would not be modified by temperature, because it represents the volume of the molecules, which should not be affected by their kinetic energy (measured in terms of temperature). The very first noteworthy successful modification to the attraction parameter came with the publication of the equation of state of Redlich-Kwong in 1949.} \\
&\text{The Redlich–Kwong equation of state is an empirical, algebraic equation that relates temperature, pressure, and volume of gases. It is generally more accurate than the van der Waals equation and the ideal gas equation at temperatures above the critical temperature. It was formulated by Otto Redlich and Joseph Neng Shun Kwong in 1949, who showed that a simple two-parameter, cubic equation of state could well reflect reality in many situations. Redlich and Kwong revised the van der Waals Equation of State (Equation \( \text{ref(Eq7)} \)) and proposed the following expressions:}
\end{align*}
\]

\[
[ b = \dfrac{2}{3} \pi \sigma^3 N_0 ] \\
\text{Given \( n \) moles of gas, the total excluded volume is then \( nb \), so that the total available volume is simply \( V - nb \).} \\
\]
\[
\left( P + \frac{a}{\sqrt{T} \bar{V} (\bar{V} + b)} \right) (\bar{V} - b) = RT \quad \text{(Equation 10.1)}
\]

Notice that the fundamental change they introduced was to the functional form of \(\delta P_{\text{attraction}}\) (Equation 7.8). Additionally, they introduced the co-volume “b” into the denominator of this functional form. The important concept here is that the attraction parameter \(a\) of van der Waals needed to be made a function of temperature to do a better job of quantitatively matching experimental data. This was a realization that van der Waal had suggested, but no actual functional dependency had been introduced until the Redlich-Kwong equation.

We know what follows at this point. To come up with an expression for \(a\) and \(b\) of Equation (ref{10.1}), we apply the criticality conditions to this EOS. As we recall, imposing the criticality conditions allows us to relate the coefficients “a” and “b” to the critical properties \((P_c, T_c)\) of the substance. Once we have done that, we obtain the definition of “a” and “b” for the Redlich-Kwong EOS,

\[
a = 0.42780 \frac{R^2 T_c^{2.5}}{P_c} \quad \text{(Equation 10.2a)}
\]

\[
b = 0.086640 \frac{RT_c}{P_c} \quad \text{(Equation 10.2b)}
\]

This EOS radically improved, in a quantitative sense, the predictions of vdW EOS. We now recall that vdW-type equations are cubic because they are cubic polynomials in molar volume and compressibility factor. It comes as no surprise then, that we can transform Equation \(\text{(ref{10.1})}\) into:

\[
\bar{v}^3 - \left( \frac{RT}{P} \right) \bar{v}^2 + \left( \frac{1}{P} \left( \frac{1}{T^{0.5}} - bRT - Pb^2 \right) \right) \bar{v} - \frac{ab}{PT^{0.5}} = 0 \quad \text{(Equation 10.3)}
\]

and, by defining the following parameters,

\[
A = \frac{aP}{R^2T^{2.5}} \quad \text{(Equation 10.3a)}
\]

\[
B = \frac{bP}{RT} \quad \text{(Equation 10.3b)}
\]

and introducing the compressibility factor definition

\[
Z = \frac{P\bar{v}}{RT}
\]

we get:

\[
Z^3 - Z^2 + \left( A - B - B^2 \right) Z - AB = 0 \quad (\text{Equation 10.4})
\]

We may also verify the two-parameter corresponding state theory by introducing Equations \(\text{(ref{10.2a})}\), \(\text{(ref{10.2b})}\), and \(\text{(ref{10.3})}\) into Equation \(\text{(ref{10.4})}\),

\[
Z^3 - Z^2 + \frac{P_r}{T_r} \left( \frac{0.42748}{T_r^{1.5}} - 0.08664 - 0.007506 \frac{P_r}{T_r} \right) Z - 0.03704 \frac{P_r^2}{T_r^{3.5}} = 0 \quad \text{(Equation 10.5)}
\]

In Equation \(\text{(ref{10.5})}\), we can observe the same thing that we saw with vdW EOS: gases at corresponding states have the same properties. Equation \(\text{(ref{10.5})}\) is particularly clear about it: any two different gases at the same \(P_r, T_r\) condition have the same compressibility factor.
Just as any other cubic equation of state, Equations \((\text{ref}(10.1))\) through \((\text{ref}(10.5))\), as they stand, are to be applied to pure substances. For mixtures, however, we apply the same equation, but we impose certain mixing rules to obtain “a” and “b”, which are functions of the properties of the pure components. Strictly speaking, we create a new “pseudo” pure substance that has the average properties of the mixture. Redlich-Kwong preserved the same mixing rules that vdW proposed for his EOS:

\[
\begin{align*}
  a_m &= \sum_i \sum_j y_i y_j a_{ij} \\
  a_{ij} &= \sqrt{a_ia_j} \\
  b_m &= \sum_i y_i b_i
\end{align*}
\]

Naturally, Redlich and Kwong did not have the last word on possible improvements to the vdW Equation fo State. The Redlich-Kwong Equation fo State, as shown here, is no longer used in practical applications. Research continued and brought with it new attempts to improve the RK Equation fo State. After more than two decades, a modified RK EOS with very good potential was developed.

Contributors

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