The Van der Waals Equation of State—C.E. Mungan, Spring 2000

The ideal gas law is

\[ p\nu = RT \]  \hspace{1cm} (1)

where \( \nu \equiv V/n \) is the molar volume. To obtain the van der Waals equation, we need to modify the pressure and volume. Long-range attractive forces between molecules tend to keep them closer together than ideal gas molecules. This has the effect of a compression of the gas and hence a positive term is added to the pressure. You may alternatively wish to note that if you solve Eq. (2) below for the pressure \( p \) on the container walls, it is smaller than it is when \( a \) is zero. On the other hand, short-range repulsive forces keep the molecules from simultaneously occupying the same place and thus the available volume of the gas decreases. The proposed empirical form of the modified equation is

\[ (p + a/\nu^2)(\nu - b) = RT. \]  \hspace{1cm} (2)

In the present note, I remind one of how to roughly derive expressions for the positive constants \( a \) and \( b \) in terms of molecular parameters.

There are \( N(N - 1)/2 \equiv 1/2 \cdot N^2 \) pairs of molecules. Any given pair of molecules cannot lie closer together than \( 2R \) if \( R \) is the molecular radius. Thus, each pair of molecules is excluded from a volume of \( \frac{1}{2}\pi(2R)^3 = 8V_{\text{molecule}} \) and hence the total excluded volume is \( 4N^2V_{\text{molecule}} \). But according to Eq. (2), the excluded volume per molecule is \( nb = Nb/N_A \), where \( N_A \) is Avogadro’s number. Thus the total excluded volume can be alternatively written as \( N^2b/N_A \).

Equating this to the preceding expression for the total excluded volume gives

\[ b = 4N_AV_{\text{molecule}}. \]  \hspace{1cm} (3)

A common approximation uses the fact that in the liquid state the molecules are close but not quite touching, so that \( b \) is roughly equal to the molar volume of the liquid.

Now, from the first law of thermodynamics we have

\[ dE = TdS - pdV \Rightarrow p = -\frac{\partial E}{\partial V}|_S \]  \hspace{1cm} (4)

where the internal PE of the gas (excluding the KE which gives the ideal gas law terms via kinetic theory) is \( E \equiv \frac{1}{2} N^2 \overline{E_{\text{pair}}} \) using the same line of reasoning as above. The standard Lennard-Jones pairwise potential between two molecules is

\[ E_{\text{pair}} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]. \]  \hspace{1cm} (5)

It is easy to show that this has a minimum value of \( -\varepsilon \) at \( r_{\text{min}} = 2^{1/6}\sigma \). The term to the 12th power in this expression is an \textit{ad hoc} approximation to the short-range repulsion between two molecules. It is mathematically simpler to instead model this by an infinite hard-core repulsion at
\( r = 2R \) when the two molecules are in physical contact,

\[
E_{\text{pair}} = \begin{cases} 
\infty & \text{for } r < 2R \\
-E_0 \left( \frac{2R}{r} \right)^6 & \text{for } r > 2R 
\end{cases}
\]  

(6)

where I have retained the \( r^{-6} \) dipole-dipole attractive energy. The origin of this term can be understood as follows. Consider two molecules with no permanent dipole moment separated by a distance \( r \). Because of fluctuations, at some instant in time the first molecule may have a dipole moment \( p_1 \), producing an electric field \( E_1 \propto p_1 / r^3 \) at the location of the second molecule. This will induce a dipole moment in this second molecule of magnitude \( p_2 = \alpha E_1 \propto p_1 / r^3 \) where \( \alpha \) is the molecular polarizability. In turn, this produces an electric field \( E_2 \propto p_2 / r^3 \propto p_1 / r^6 \) back at the location of the first molecule. Hence the interaction energy between these two dipoles is \( p_1 E_2 \propto p_1^2 / r^6 \), which unlike \( p_1 \) does not time average to zero.

If we require Eqs. (5) and (6) to agree at their minima, then we must identify \( 2^{1/6} \sigma = 2R \) and \( \varepsilon = E_0 \). Next, we compute

\[
\overline{E_{\text{pair}}} = \int_{2R}^{\infty} E_{\text{pair}}(r) P(r)dr
\]

(7)

where the probability of finding another molecule at a center-to-center distance of between \( r \) and \( r+dr \) from any given one is approximately

\[
P(r)dr = \frac{4\pi r^2 dr}{V},
\]

(8)

since the molecules are almost free and thus randomly distributed throughout the available volume. Substituting Eqs. (6) and (8) into (7) and performing the integral results in

\[
\overline{E_{\text{pair}}} = 8E_0 \frac{V_{\text{molecule}}}{V}.
\]

(9)

Putting this into Eq. (4) to obtain the extra pressure \( a/v^2 \) in Eq. (2) and using Eq. (3) gives

\[
a = E_0 N_A b.
\]

(10)

Expressing the van der Waals parameters in terms of the Lennard-Jones parameters, we thus have

\[
a = 2^{1/3} \sqrt{2} \pi \sigma^3 N_A^2 \varepsilon \quad \text{and} \quad b = 2^{1/3} \sqrt{2} \pi \sigma^3 N_A.
\]

(11)

If these are checked against the experimental values listed below, ballpark agreement is found.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( a ) (mPa•m⁶/mol³)</th>
<th>( b ) (mL/mol)</th>
<th>( \varepsilon ) (meV)</th>
<th>( \sigma ) (Å)</th>
</tr>
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<tbody>
<tr>
<td>He</td>
<td>3.44</td>
<td>23.6</td>
<td>0.87</td>
<td>2.56</td>
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<tr>
<td>Ne</td>
<td>21.1</td>
<td>16.9</td>
<td>3.1</td>
<td>2.74</td>
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