

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

The ideal gas law is

$$pv = RT \quad (1)$$

where $v \equiv V/n$ 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

$$(p + a/v^2)(v - b) = RT. \quad (2)$$

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 $N(N-1)/2 \cong \frac{1}{2}N^2$ 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 $\frac{4}{3}\pi(2R)^3 = 8V_{\text{molecule}}$ 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

$$b = 4N_A V_{\text{molecule}}. \quad (3)$$

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

$$dE = TdS - pdV \quad \Rightarrow \quad p = -\left.\frac{\partial E}{\partial V}\right|_S \quad (4)$$

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

$$E_{\text{pair}} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]. \quad (5)$$

It is easy to show that this has a minimum value of $-\epsilon$ at $r_{\text{min}} = 2^{1/6}\sigma$. The term to the 12th power in this expression is an *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,

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

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 α 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 \mathbf{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

$$\overline{E_{\text{pair}}} = \int_{2R}^{\infty} E_{\text{pair}}(r) P(r) dr \quad (7)$$

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

$$P(r) dr = \frac{4\pi r^2 dr}{V}, \quad (8)$$

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

$$\overline{E_{\text{pair}}} = 8E_0 \frac{V_{\text{molecule}}}{V}. \quad (9)$$

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

$$a = E_0 N_A b. \quad (10)$$

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

$$a = \frac{2}{3} \sqrt{2} \pi \sigma^3 N_A^2 \varepsilon \quad \text{and} \quad b = \frac{2}{3} \sqrt{2} \pi \sigma^3 N_A. \quad (11)$$

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

Gas	a (mPa•m ⁶ /mol ²)	b (mL/mol)	ε (meV)	σ (Å)
He	3.44	23.6	0.87	2.56
Ne	21.1	16.9	3.1	2.74