

Lecture 34 - Van der Waals equation

What's Important:

- B_2 for hard spheres
- B_2 for attraction and repulsion
- van der Waals equation

Text: Reif

Second virial coefficient

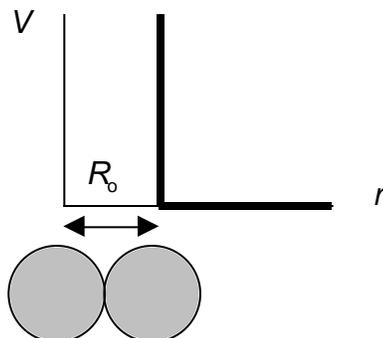
At the end of the previous lecture, we established that the second virial coefficient in the equation of state of a non-ideal gas is:

$$B_2 = -\frac{1}{2} \int_0^\infty (e^{-\beta u} - 1) d^3r \quad (34.1)$$

where u is a two-body interaction potential. In this lecture, we obtain an expression for B_2 for a hard-sphere gas in terms of microscopic parameters. This then permits us to relate the van der Waals parameters to the size of the gas particles.

Hard sphere gas

In the hard sphere problem, the interparticle potential looks like



Note that R_0 is the sphere diameter, not the sphere radius.

With the definition (34.1), the second virial coefficient becomes

$$\begin{aligned} B_2 &= -\frac{1}{2} \int_0^{R_0} (-1) d^3r + \int_{R_0}^\infty (1-1) d^3r \\ &= +\frac{1}{2} \cdot \frac{4}{3} R_0^3 \\ &= \frac{1}{2} \cdot [\text{excluded volume}] \end{aligned}$$

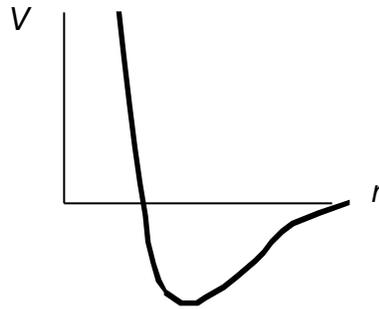
Note that B_2 is independent of temperature. Because it is positive, its effect in

$$\beta\bar{p} = n + B_2n^2 + B_3n^3 + \dots$$

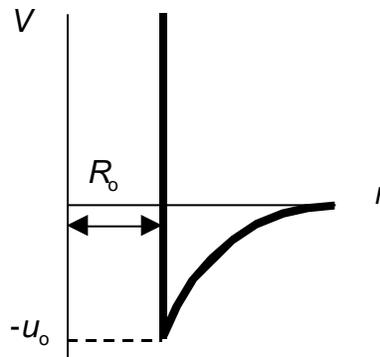
is to increase the pressure compared to the ideal gas value.

Attraction and repulsion

More generally, the interparticle potential for atoms looks like



which, for simplicity, we will approximate as



with the functional form

$$\begin{aligned} u(r) &= -u_0 & r < R_0 \\ u(r) &= -u_0(R_0/r)^s & r > R_0 \end{aligned}$$

For example, the power s is equal to 6 for the Lennard-Jones interaction.

The calculation of the virial coefficient starts off as with the hard-sphere potential

$$\begin{aligned} B_2 &= -\frac{1}{2} \int_0^{R_0} (-1)d^3r + \int_{R_0}^{\infty} (e^{-\beta u} - 1)d^3r \\ &= -\frac{1}{2} \left[-\frac{4}{3} R_0^3 + 4 \int_{R_0}^{\infty} (e^{+\beta u_0 (R_0/r)^s} - 1)r^2 dr \right] \end{aligned}$$

Now, if the temperature is high enough with respect to u , then βu is small and the exponential can be approximated by

$$e^{+\beta u} \sim 1 + \beta u,$$

Thus,

$$B_2 = +\frac{2}{3} R_0^3 - 2 \beta u_0 R_0^s \int_{R_0} r^{2-s} dr$$

The integral has the usual polynomial form

$$\int_{R_0} r^{2-s} dr = \frac{1}{3-s} R_0^{3-s}$$

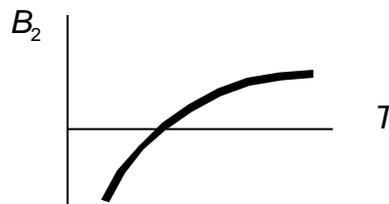
where we have assumed $s > 3$ for convergence. Then, B_2 becomes

$$\begin{aligned} B_2 &= \frac{2}{3} R_0^3 - 2 \beta u_0 R_0^s \frac{R_0^{3-s}}{3-s} \\ &= \frac{2}{3} R_0^3 \left(1 - \frac{3}{s-3} \frac{u_0}{k_B T} \right) \end{aligned}$$

The signs have been arranged so that the second term is clearly negative when $s > 3$, as it is with the Lennard-Jones potential. Further, B_2 now depends on temperature:

$$\begin{array}{ll} k_B T > \frac{3}{s-3} u_0 & B_2 > 0 \\ k_B T < \frac{3}{s-3} u_0 & B_2 < 0 \end{array}$$

as in



van der Waals equation

We can massage our expression for B_2 into the usual van der Waals form with a little work.

Define

$$B_2 = b' - \frac{a'}{k_B T} \quad b' = \frac{2}{3} R_0^3 \quad a' = \frac{3}{s-3} b' u_0$$

Substituting into the expression for the pressure

$$\beta \bar{p} = n + b' n^2 - \frac{a'}{k_B T} n^2 + \text{other terms}$$

Dropping higher order terms in n , this becomes

$$\bar{p} = nk_B T + (b' k_B T - a') n^2$$

or

$$\bar{p} + a'n^2 = nk_B T(1 + b'n)$$

$$\frac{\bar{p} + a'n^2}{1 + b'n} = nk_B T$$

$$(\bar{p} + a'n^2) \cdot (1 - b'n) = nk_B T$$

where the last line follows from the approximation $(1+x)^{-1} \sim 1-x$.

Dividing by n

$$(\bar{p} + a'n^2) \cdot \frac{1}{n} - b' = k_B T$$

Now, the density is inversely proportional to the volume, so this equation has the van der Waals form

$$\bar{p} + \frac{a}{v_m^2} (v_m - b) = RT$$

(where v_m is the molar volume) if we make the identifications

$$a = N_o^2 a' \quad b = N_o b'$$

whence

$$a = N_o^2 \frac{3}{s-3} \frac{2}{3} R_o^3 u_o$$

$$b = N_o \frac{2}{3} R_o^3$$

Thus, the macroscopic measured values of a and b in a van der Waals fit to data can be related to the microscopic parameters R_o , u_o and s (one of which must be fixed by other means).