

A DEEPER LOOK 9 The virial and the virial equation of state

This section shows how the equation of state for a dilute fluid in which the interactions between molecules are isotropic and pairwise (Topic 14C),

$$p = \frac{nRT}{V} - \frac{2\pi}{3} \left(\frac{N}{V} \right)^2 \int_0^\infty v_2(r) g(r) r^2 dr \quad (1a)$$

with the virial $v_2(r)$ given by

$$v_2(r) = r \frac{dV_2}{dr} \quad (1b)$$

results in a virial equation of state from which the van der Waals parameters can be identified.

Step 1 Set up an expression for the potential energy

Consider a potential energy that has a hard core and a shallow rectangular trough (Fig. 1):

$$V_2(r) = \begin{cases} \infty & \text{for } r < R_1 \\ -\varepsilon & \text{for } R_1 \leq r < R_2 \\ 0 & \text{for } r > R_2 \end{cases} \quad (2)$$

Step 2 Evaluate the contribution of the virial

The potential energy has abrupt steps at which the virial is not defined. To proceed, use the physical interpretation that $v_2(r)$ is the work done to move a molecule from r to infinity. In this case, the work done, the interpretation of $r dV_2/dr$ as explained in the text, is ε provided the initial separation is between R_1 and R_2 , and zero beyond R_2 . Equation 1a then becomes

$$p = \frac{nRT}{V - nb} - \frac{2\pi\varepsilon}{3} \left(\frac{N}{V} \right)^2 \int_{R_1}^{R_2} g(r) r^2 dr \quad (3a)$$

The denominator of the first term on the right has been changed from V to $V - nb$ to accommodate the effect of the hard core, which reduces the volume available to the

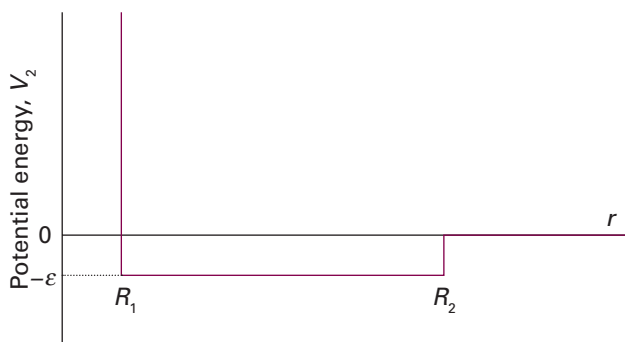


Figure 1 The potential energy considered in this calculation.

molecules. Provided the fluid is dilute in the sense $nb \ll V$, this term can be expanded as follows:

$$\frac{nRT}{V - nb} = \frac{nRT}{V} \left\{ 1 + \frac{nb}{V} + \dots \right\}$$

and eqn 3a becomes

$$p = \frac{nRT}{V} \left\{ 1 + \frac{nb}{V} + \dots \right\} - \frac{2\pi\varepsilon}{3} \left(\frac{N}{V} \right)^2 \int_{R_1}^{R_2} g(r) r^2 dr \quad (3b)$$

Step 3 Evaluate the integral

If the well is so shallow that the particle distribution is uniform, then $g(r) = 1$ and

$$\int_{R_1}^{R_2} g(r) r^2 dr = \frac{1}{3} (R_2^3 - R_1^3) \quad (4)$$

It follows that

$$\begin{aligned} p &= \frac{nRT}{V} \left\{ 1 + \frac{nb}{V} + \dots \right\} - \frac{2\pi\varepsilon}{9} \left(\frac{N}{V} \right)^2 (R_2^3 - R_1^3) \\ &= \frac{nRT}{V} \left\{ 1 + \frac{n}{V} \left[b - \frac{2\pi N_A^2 \varepsilon}{9RT} (R_2^3 - R_1^3) \right] + \dots \right\} \end{aligned} \quad (5)$$

Step 4 Compare this equation of state with the virial equation of state and identify the second virial coefficient

The virial equation of state is

$$p = \frac{nRT}{V} \left\{ 1 + \frac{nB}{V} + \dots \right\} \quad (6)$$

By comparing this expansion with eqn 5, the second virial coefficient B can be identified as

$$B = b - \frac{2\pi N_A^2 \varepsilon}{9RT} (R_2^3 - R_1^3) \quad (7a)$$

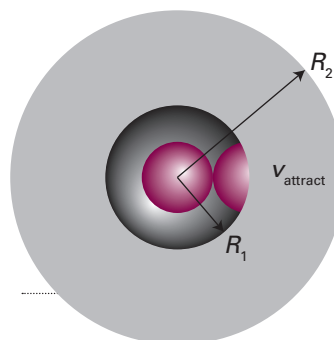


Figure 2 The volume excluded (the central grey cavity) and the volume where attraction takes place (the light grey zone).

The volume enclosed between the radii R_1 and R_2 (Fig. 2) is $v_{\text{attract}} = (4\pi/3)(R_2^3 - R_1^3)$, and its molar value is $v_{\text{attract,m}} = N_A v_{\text{attract}}$, so

$$B = b - \frac{\varepsilon_m v_{\text{attract,m}}}{6RT} \quad (7b)$$

where $\varepsilon_m = N_A \varepsilon$.

Step 5 Identify the van der Waals parameters

The van der Waals equation of state is

$$p = \frac{nRT}{V-nb} - a \frac{n^2}{V^2} \quad (8a)$$

By using the same expansion as above when $nb \ll V$, this equation becomes

$$\begin{aligned} p &= \frac{nRT}{V} \left\{ 1 + \frac{nb}{V} + \dots \right\} - a \frac{n^2}{V^2} \\ &= \frac{nRT}{V} \left\{ 1 + \frac{n}{V} \left(b - \frac{a}{RT} \right) + \dots \right\} \end{aligned} \quad (8b)$$

Finally, by comparing this expansion with eqn 6 it follows that the second virial coefficient is related to the van der Waals parameters by

$$B = b - \frac{a}{RT} \quad (9)$$

and comparison of this relation with eqn 7 shows that the parameter a can be identified as

$$a = \frac{1}{6} \varepsilon_m v_{\text{attract,m}} \quad (10a)$$

The parameter b is related to the volume of each molecule, v_{molecule} , and the corresponding molar molecular volume, $v_{\text{molecule,m}} = N_A v_{\text{molecule}}$. The radius of each molecule is $\frac{1}{2}R_1$, so $v_{\text{molecule}} = (4\pi/3)(R_1/2)^3 = \frac{1}{8}(4\pi/3)R_1^3$ and $v_{\text{molecule,m}} = \frac{1}{8}(4\pi/3)N_A R_1^3$. As the distance of closest approach is R_1 , each molecule excludes a volume $\frac{1}{2}(4\pi/3)R_1^3$ (as depicted in Fig. 2), so $b = \frac{1}{2}(4\pi/3)N_A R_1^3$. Therefore

$$b = 4v_{\text{molecule,m}} \quad (10b)$$

For another illustration of how the potential energy depicted in Fig. 1 plays a role in the formulation of the van der Waals equation, see *A deeper look 7*.