

A DEEPER LOOK 7 The van der Waals equation of state

In this section, the connection is traced between the van der Waals equation and the parameters defining the shallow, hard-centred potential energy shown in Figure 1. It is assumed that the potential is isotropic and that the N molecules are confined in a spherical container of radius R_3 . The attractive region is shallow in the sense $\beta\epsilon \ll 1$.

Four key equations need to be assembled:

The canonical partition function:

$$Q = \frac{Z}{\Lambda^{3N}}, \quad \Lambda = \frac{h}{(2\pi m/\beta)^{1/2}} \quad (1)$$

The configuration integral:

$$Z = \frac{1}{N!} \int e^{-\beta E_p} d\tau_1 d\tau_2 \cdots d\tau_N \quad (2)$$

The Helmholtz energy:

$$A = -kT \ln Q \quad (3)$$

The statistical pressure:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T \quad (4)$$

Step 1 Identify the van der Waals parameters

The first combination to note (with $\beta = 1/kT$, and recognizing that Λ is independent of volume) is

$$p = \frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial V}\right)_T = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V}\right)_T \quad (5)$$

The outcome of eqn 5 is then compared with the van der Waals equation

$$p = \frac{nRT}{V-nb} - a\frac{n^2}{V^2} \quad (6)$$

However, the calculation will be confined to pairwise interactions, which implies that when eqn 6 is expressed as a virial equation of state, the comparison must be made with the second virial coefficient (B) in

$$p = \frac{nRT}{V} \left\{ 1 + \frac{nB}{V} + \cdots \right\}$$

because that coefficient arises from pairwise interactions. When eqn 6 is expanded it becomes

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

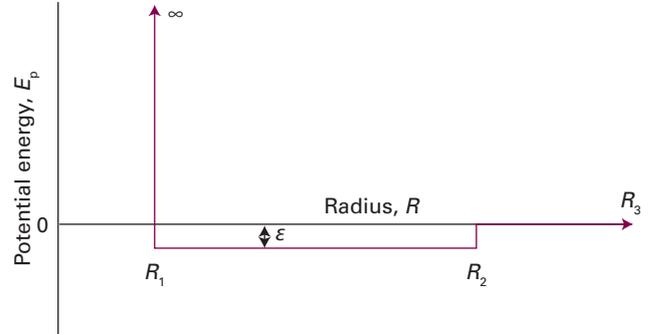


Figure 1 A shallow, hard-centred potential energy function.

which implies that

$$B = b - \frac{a}{RT} \quad (7)$$

Step 2 Simplify the configuration integral for weak pairwise interactions

Now consider the configuration integral, with

$$E_p = \sum_{i=2}^N E_{1,i} \quad (8)$$

for the potential energy of particle 1.

That the potential energy is positively infinite for $r_{12} < R_1$ implies that all the volume integrations must be outside that region: that constraint will be indicated by a prime on the integral sign. Next note that

$$Z = \frac{V^N}{N!} \times \frac{1}{V^N} \int' e^{-\beta E_p} d\tau_1 d\tau_2 \cdots d\tau_N$$

and therefore that

$$\begin{aligned} \ln Z &= \ln \frac{V^N}{N!} + \ln \frac{1}{V^N} \int' e^{-\beta E_p} d\tau_1 d\tau_2 \cdots d\tau_N \\ &= \ln Z^\circ + \ln \frac{1}{V^N} \int' e^{-\beta E_p} d\tau_1 d\tau_2 \cdots d\tau_N \end{aligned}$$

Step 3 Analyse the 'perfect' contribution

The 'perfect' term (Z°) is so-called because it results in the perfect gas law:

$$\begin{aligned} p^\circ &= \frac{1}{\beta} \left(\frac{\partial \ln Z^\circ}{\partial V}\right)_T = \frac{1}{\beta Z^\circ} \left(\frac{\partial Z^\circ}{\partial V}\right)_T \\ &= \frac{1}{\beta(V^N/N!)} \frac{NV^{N-1}}{N!} = \frac{N}{\beta V} = \frac{NkT}{V} = \frac{nRT}{V} \end{aligned}$$

Step 4 Evaluate the contribution of the interaction integral

Now consider the second contribution to the configuration integral:

$$\begin{aligned}
 \ln Z' &= \ln \frac{1}{V^N} \int' e^{-\beta E_i} d\tau_1 d\tau_2 \cdots d\tau_N \\
 &= \ln \frac{1}{V^N} \int' e^{-\beta(E_{i_2} + E_{i_3} + \cdots + E_{i_N})} d\tau_1 d\tau_2 \cdots d\tau_N \\
 &= \ln \frac{1}{V^N} \int' e^{-N\beta E_{i_2}} d\tau_1 \int' e^{-N\beta E_{i_3}} d\tau_2 \cdots \int' e^{-N\beta E_{i_N}} d\tau_N \\
 &= \ln \frac{1}{V^N} \left(\int' e^{-N\beta E_{i_2}} d\tau_1 \right)^{N-1} \approx \ln \frac{1}{V^N} \left(\int' e^{-N\beta E_{i_2}} d\tau_1 \right)^N \\
 &= N \ln \frac{1}{V} \int' e^{-N\beta E_{i_2}} d\tau_1
 \end{aligned}$$

Step 5 Evaluate the integral

Bear in mind that the integration excludes the regions occupied by the hard core of each molecule. If each molecule of radius $\frac{1}{2}R_1$ occupies a volume ν_{molecule} , the volume excluded by each one is $\frac{1}{2}(4\pi/3)R_1^3 = 4\nu_{\text{molecule}}$. Provided that region is avoided and the attractive interaction is weak (and equal to $-\varepsilon$ up to $r_{12} = R_2$, and zero thereafter),

$$\begin{aligned}
 \int' e^{-N\beta E_{i_2}} d\tau_1 &= \int' (1 - N\beta \overbrace{E_{i_2}}^{-\varepsilon}) \overbrace{d\tau_1}^{4\pi r^2 dr} \\
 &= \underbrace{V - 4N\nu_{\text{mol}}}_{\text{from the 1}} + \underbrace{\frac{4\pi}{3}N\beta\varepsilon(R_2^3 - R_1^3)}_{\text{from the } -N\beta E_{i_2}} \\
 &= V - 4N\nu_{\text{mol}} + N\beta\varepsilon\nu_{\text{range}}
 \end{aligned}$$

where ν_{range} is the volume spanned by the attractive zone of the potential energy (Fig. 2).

Step 6 Evaluate the 'imperfect' contribution to the pressure

At this point

$$\ln Z' = N \ln \left(1 - \frac{4N\nu_{\text{mol}} - N\beta\varepsilon\nu_{\text{range}}}{V} \right)$$

Provided $(4N\nu_{\text{mol}} - N\beta\varepsilon\nu_{\text{range}})/V \ll 1$,

$$\ln Z' = -\frac{N}{V} (4N\nu_{\text{mol}} - N\beta\varepsilon\nu_{\text{range}})$$

and the contribution to the pressure is

$$p' = \frac{N}{\beta V^2} (4N\nu_{\text{mol}} - N\beta\varepsilon\nu_{\text{range}})$$

Step 7 Identify the second virial coefficient

The total pressure, $p = p^\circ + p'$, is

$$\begin{aligned}
 p &= \frac{N}{\beta V} + \frac{N}{\beta V^2} (4N\nu_{\text{mol}} - N\beta\varepsilon\nu_{\text{range}}) \\
 &= \frac{N}{\beta V} \left\{ 1 + (4\nu_{\text{mol}} - \beta\varepsilon\nu_{\text{range}}) \frac{N}{V} \right\} \\
 &= \frac{nN_A}{\beta V} \left\{ 1 + (4\nu_{\text{mol}} - \beta\varepsilon\nu_{\text{range}}) \frac{nN_A}{V} \right\}
 \end{aligned}$$

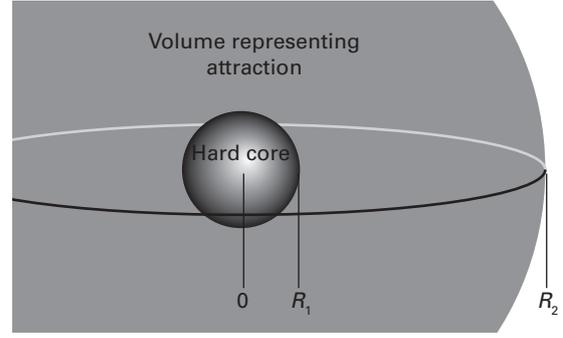


Figure 2 A representation of the volume spanned by the attractive zone of the potential energy function shown in Fig. 1.

and therefore

$$p = \frac{nRT}{V} \left\{ 1 + \left(4N_A\nu_{\text{mol}} - \frac{\varepsilon N_A\nu_{\text{range}}}{RT} \right) \frac{n}{V} \right\}$$

It follows that

$$b = 4N_A\nu_{\text{mol}} \quad a = N_A\varepsilon\nu_{\text{range}}$$

It now follows from the thermodynamic equation of state

$$\pi_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

with $\pi_T = (\partial U / \partial V)_T$, and

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{nR}{V} \left\{ 1 + \frac{4N_A\nu_{\text{mol}}n}{V} \right\}$$

that

$$\begin{aligned}
 \pi_T &= \frac{nRT}{V} \left\{ 1 + \frac{4N_A\nu_{\text{mol}}n}{V} \right\} \\
 &\quad - \frac{nRT}{V} \left\{ 1 + \left(4N_A\nu_{\text{mol}} - \frac{\varepsilon N_A\nu_{\text{range}}}{RT} \right) \frac{n}{V} \right\} \\
 &= \frac{n^2\varepsilon RTN_A\nu_{\text{range}}}{RTV^2} = \frac{n^2\varepsilon N_A\nu_{\text{range}}}{V^2} = \frac{n^2a}{V^2}
 \end{aligned}$$

as claimed in the text.