

Let's 'derive' an equation of state (P-V-T relationship) for real (non-ideal) atoms and molecules in the gas phase, by exploring the simple consequence of the fact that, when they approach each other, they interact by either **repulsion** (at very short distances) or **attraction** (at intermediate distances). For liquids and solids such interatomic and intermolecular interactions are much more complex (covalent, ionic, dipole, quadrupole, ...).

As a most convenient starting point, let's introduce the **compressibility (or compression) factor** that quantifies the deviations from ideal-gas behavior:

$$Z = \frac{PV}{nRT} = PV/(RT)$$

Experience (i.e., experimentation confirmed by many researchers) shows that for some gases $Z > 1$ always, while for others $Z < 1$ at low pressures and $Z > 1$ at high pressures. This agrees with the intuitive notion that repulsive forces are dominant at high pressures (when atoms or molecules are very close to each other), whereas attractive forces may be dominant at low pressures (when they are farther away).

The simplest way to introduce a repulsive force is to recognize the finite size of atoms (and molecules), which means that less than the entire volume V (V minus "excluded volume") is available for their movement and collisions. Therefore, the 'effective' pressure is increased:

$$P = \frac{nRT}{V-V_1}$$

Using geometric arguments (considering elementary particles as hard spheres of radius r and minimum distance $2r$ when they collide), it can be shown that the excluded volume V_1 is 4 times the volume of all the molecules, which allows to estimate b (see order-of magnitude calculation below).

For an attractive force, the simplest assumption (keeping in mind that the 'effective' pressure is reduced as its consequence) is the following:

$$(P+P_1)(V-V_1) = (P +P_1) (V - nb) = RT$$

The functional dependence of this pressure correction term can be understood based on the following arguments:

$$P_1 = \frac{F}{A_1}$$

where F is the force between interacting particles. This force can be expressed in terms of an average force ϕ and a term that depends on the number N of interacting particles: for 1:1 interacting particles $F=\phi$, for 2-2 particles $F=4\phi$, and for 3-3 $F=9\phi$, or, in general,

...

$$F = \left(\frac{N}{2}\right)^2 \phi$$

Now, N can be expressed in terms of the molar volume v of the system:

$$N = nN_A \frac{V_1}{V} = \frac{V_1}{v}.$$

Therefore

$$P_I = \frac{\left(\frac{V_1}{2v}\right)^2 \phi}{A_I} = \frac{a}{v^2}$$

(Note that a depends on the excluded volume and therefore on b !? Is this corroborated by the information provided in Table 1C.3 of the Resource Section?)

Thus, finally,

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

which is one of the many claims to fame of the Dutch scientist Johannes Diderik van der Waals... he proposed this equation in 1873 and was awarded the physics Nobel prize for it in 1910!

Let's now explore the extent of its general applicability by plotting Z vs P .

(See Figures 1C.3 and 1C.8.)

Here is an order-of-magnitude estimation of b (see Table 1C.3):

```
r = 2.1 * 10^-10; (*m, reasonable?*)
vMolecule = 4 / 3 * Pi * r^3; (*m^3/molecule*)
avogadro = 6.022 * 10^23; (*molecules/mol*)
b = 4 vMolecule * avogadro * 10^3 (*L/mol, OK?*)
0.0934431
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