The Equation of State for Real Gases

The kinetic theory of gases has provided a microscopic understanding of the equation of state of an ideal gas,

$$p \cdot V = N \cdot k_B \cdot T \tag{1}$$

a very important law. Here, p is the average pressure, V is the fixed volume of the container enclosing N non-interacting, structureless gas particles, T the constant temperature imposed on the gas from the outside, and k_B is the universal Boltzmann constant. Equation (1) relates the average internal energy content U of the gas, which is due to chaotic motion of the gas particles, to the temperature,

$$U = N \cdot \bar{\varepsilon}_{therm} = N \cdot \frac{3}{2} \cdot k_B \cdot T \tag{2}$$

This internal random-motion energy is also called "thermal energy". For complex particles with more than translational degrees of freedom, such a random thermal energy can be defined also for the other degrees of freedom (*dof*). In thermal equilibrium, the average thermal energy per *dof* is always given by

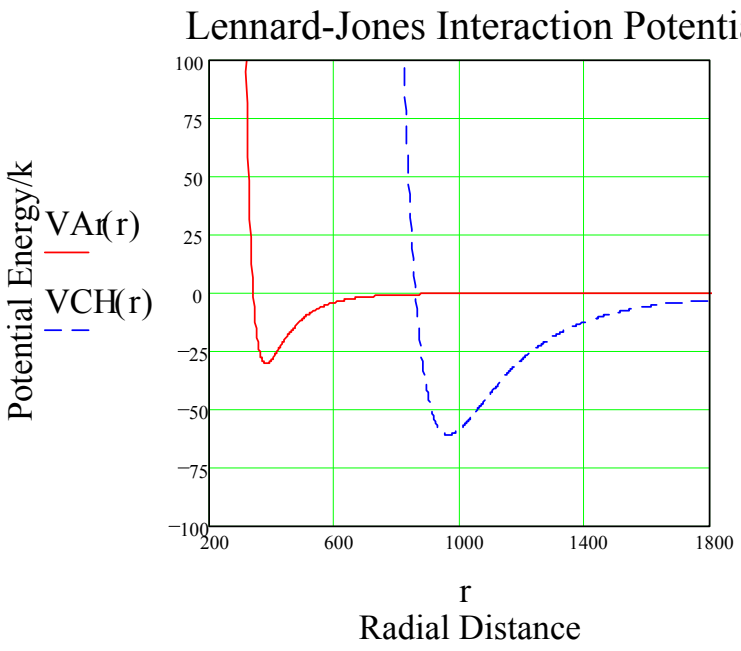
$$U / dof = \bar{\varepsilon}_{therm} / dof = \frac{1}{2} \cdot k_B \cdot T \tag{3}$$

The most stringent precondition for this simple theory to hold is the ***absence of interactions between the gas particles***. This can always be achieved for sufficiently dilute gases of any kind. However, for higher pressures or lower temperatures, deviations from the ideal-gas *EOS* can become substantial and depend very much on the properties of a given gas and the experimental conditions. Departures from ideal-gas *EOS* are usually measured in terms of a ***compressibility factor***

$$Z := pV/Nk_BT \tag{4}$$

which is equal to unity for an ideal gas. The name reflects the fact that for *Z > 1,* one needs to exert a higher pressure than necessary for an ideal gas to enclose the gas in a given volume *V*. The gas is more difficult to compress than an ideal gas, i.e., it has a lower compressibility than an ideal gas.

Experimental measurements give *Z > 1* by a few per cent, for H_2 or *He*, ***while Z < 1 for more complex molecules such as*** NH_3 ***or*** CH_4 indicates a higher compressibility for the latter type of molecule. ***At high enough pressures and/or high temperatures, however, it is seen for all gases that Z > 1, i.e., it becomes more difficult to compress them***. This implies that, ***with increasing pressure, the interaction becomes more repulsive.*** On the other hand, the interactions between complex gas molecules are ***attractive when the pressures (and the densities) are not too high***, i.e., average distances not too small. For smaller distances, a ***repulsive core in the interaction potential*** becomes effective.

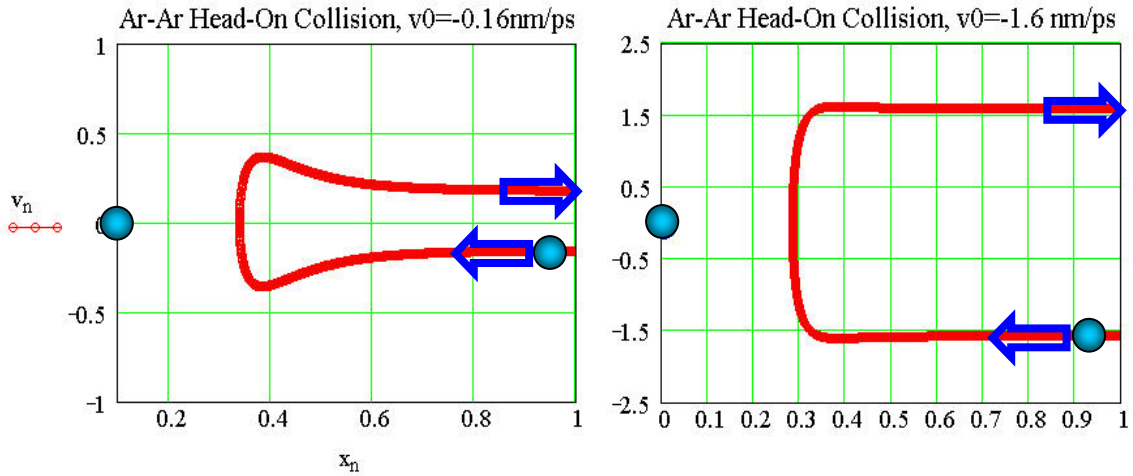


The quantitatively different behavior of simple and complex gases can be understood in terms of the actual interaction potentials, which can be modeled in terms of the radial (***r***) dependence of the ***Lennard-Jones*** potential

$$V(r) = \varepsilon \cdot \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \qquad (5)$$

Here, ε is the strength parameter, and σ is the zero of the potential. The figure compares the potentials for *Ar* (VAR) and C_6H_6 (VCH) with one another. The potential energies have been divided by k (= k_B) and are expressed in temperature units (degrees *K*), the distance is given in units of *pm* ($10^{-12}m$). Obviously, the repulsive, ***hard core*** of the potential for the larger molecule reaches out to larger distances than for the smaller argon particles. Consequently, the deviations of C_6H_6 from the ideal-gas behavior occur already for larger distances and associated lower pressures.

In order to understand the dependence on temperature and pressure of the average interaction felt by the particles in a gas, it is instructive to inspect typical trajectories of the particles in the gas. The figures below show numerically calculated projectile trajectories $\{x_n=x(t_n),\ v_n=v(t_n)\}$, the velocity of the projectile atom at time t_n *vs.* its distance from the target atom. The calculations were done with a simple Molecular Dynamics code. The collisions are central ("head-on") Ar-Ar collisions at two initial relative velocities, v_0 = -0.16nm/ps (left panel) and v_0 = -1.6nm/ps (right panel). These velocities are typical (average) for *T=30K* and *T=3000K*, respectively. The target Ar atom is indicated at rest, at the left of each plot.



In each case, the projectile approaches the target with an initial velocity $v_0<0$ at $x_0=1$, determined by the temperature T chosen. In the approach phase, the projectile is first accelerated towards the target, until it reaches the equilibrium distance, the minimum of the potential. After that, the projectile is slowed down by the repulsive part of the potential, until it reaches the distance of closest approach, where $v=0$. Thereafter, the projectile is accelerated back with increasing velocity. After the projectile has passed the potential minimum on its way out, it is decelerated by the attractive part of the potential.

From the shape of the trajectories, one observes that the projectile spends a larger fraction of its trajectory within the attractive potential when it has a low initial velocity. A fast projectile traverses the attractive ($V<0$) potential very rapidly and runs high up the repulsive ($V>0$) core of the potential. For the two cases pictured above, the numerical integration along the trajectories yields average effective potentials of $<V>=-13\ k_BK$ and $<V>=+79k_BK$, for the low and high incident velocities, respectively. This behavior implies that at low temperatures, the effective pressures of a real gas are lower than those of an ideal gas. At high temperatures, the situation is reversed. In the latter case, the real gas seems to be less compressible than an ideal gas. There is obviously a classically forbidden space around each atom which is inaccessible by the other particles. Because of the very steep repulsive core of the potential, the radius of this excluded "co-volume" does not depend noticeably on the particle velocities, i.e., it is not strongly dependent of temperature of the gas.

In order to account for these non-ideal effects, one devises an effective equation of state (EOS). For example, one may add to the ideal-gas *EOS* (1) higher-order terms in pressure p or density ρ. One then arrives at a ***virial expansion*** in p,

$$p\cdot V = Nk_BT + B(T)\cdot p + C(T)\cdot p^2 + \ldots. \qquad (6)$$

which depends on the first, second, etc., ***virial coefficient 1, B, C,*** etc. Analogously, one could expand the product *pV* in powers of the density ρ:

$$p \cdot V = N k_B T + B'(T) \cdot \rho + C'(T) \cdot \rho^2 + \ldots. \qquad (7)$$

with corresponding virial coefficients *1, B′, C′,* etc.

A first qualitative understanding of the modified ***equation of state of real gases*** was achieved by ***van der Waals*** (1837-1923) taking account of the finite volume of the gas molecules themselves, the so-called ***covolume b***, which prevents the total collapse of the volume at $T = 0$. The available volume is strictly not equal to the container volume $V = V_{ideal}$, but is reduced by the covolume appropriate for the number *N* of gas particles:

$$V_{ideal} \rightarrow V_{ideal} = V_{real} - Nb \qquad (8)$$

At normal temperatures and pressures, this volume correction is relatively small, at most of the order of 10^{-4}. However, in many industrial applications, where pressures of 100 *atm* to several1000 *atm* are employed, the covolume is no longer negligible.

Furthermore, the interactions neglected in the ideal-gas model are expected to also modify the pressure. For low temperatures, the average interaction between the particles of a real gas is attractive. Hence, particles are effectively retained by the potential, and the pressure which they exert on the container walls is reduced. For room temperatures, or higher, the opposite is true. To account for this pressure effect in theoretical descriptions, one should add a pressure correction term to the actual pressure. To obtain an estimate, one realizes that the frequency of particle-particle interactions or 'collisions' scales with the probability to find two particles at roughly the same position. This, in turn, scales with the square of the gas particle density, $\rho = N/V$. Consequently, the pressure is expected to change with the second power in the particle density, ρ^2:

$$p_{ideal} \rightarrow p_{ideal} = p_{real} + a{\cdot}\rho^2 \qquad (9)$$

Depending on whether the effective interaction is attractive or repulsive, the parameter ***a*** is negative or positive, respectively. Since the effect of the interaction depends on the energy of the particles, i.e., on the temperature *T*, one expects the quantities *a* and *b* to be functions of T. However, if these corrections are relatively small, one may instead try to take *a* and *b* as constants and expects the corrected EOS to be valid in certain limited regions of temperature, pressure, and density.

Approximately then, one expects a real gas to follow an *EOS* equivalent in form to the ideal-gas *EOS*, but with the effective pressure and the effective volume discussed above:

$$\left(p + a\left(\frac{N}{V}\right)^2\right) \cdot (V - Nb) = Nk_BT \qquad (10)$$

This is the ***van der Waals Equation***. Here, the quantities *a* and *b* are constants characteristic of the material. The correction terms in Equ. (10) are often small compared to the main terms, such that the quantity *N/V* ***in these terms*** can be approximated by the ideal-gas expression $N/V \approx p/k_BT$. Then, one derives from Equ. (10) the relation

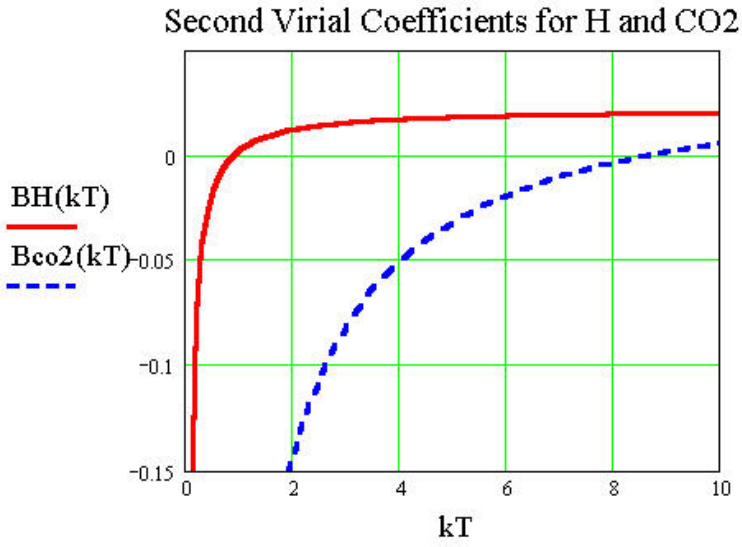
$$p(1 + \frac{ap}{p^2} \cdot \frac{N^2}{V^2})(V - Nb) = Nk_BT \qquad (11)$$

and

$$pV = \frac{Nk_BT}{1 + \frac{a \cdot p}{(k_BT)^2}} + b \cdot Np \qquad (12)$$

which is equivalent to the ***van der Waals*** equation to first order. An expansion of Equ. (12) in terms of powers of the small parameter $a{\cdot}p/(k_BT)^2 \ll 1$ yields a series of the form

$$p{\cdot}\, V = Nk_BT + N[b - a/(k_BT)]p + \ldots. \qquad (13)$$



This series is of the kind of the virial expansion of Equ. (7), with the first virial coefficient

$$B(T) = N[b - a/(k_B T)]$$

The figure illustrates this temperature dependence for the ***2nd virial coefficients*** *B(T)* ***of hydrogen*** (***H_2***) ***and CO_2***, BH and Bco2, respectively, ***per particle***.

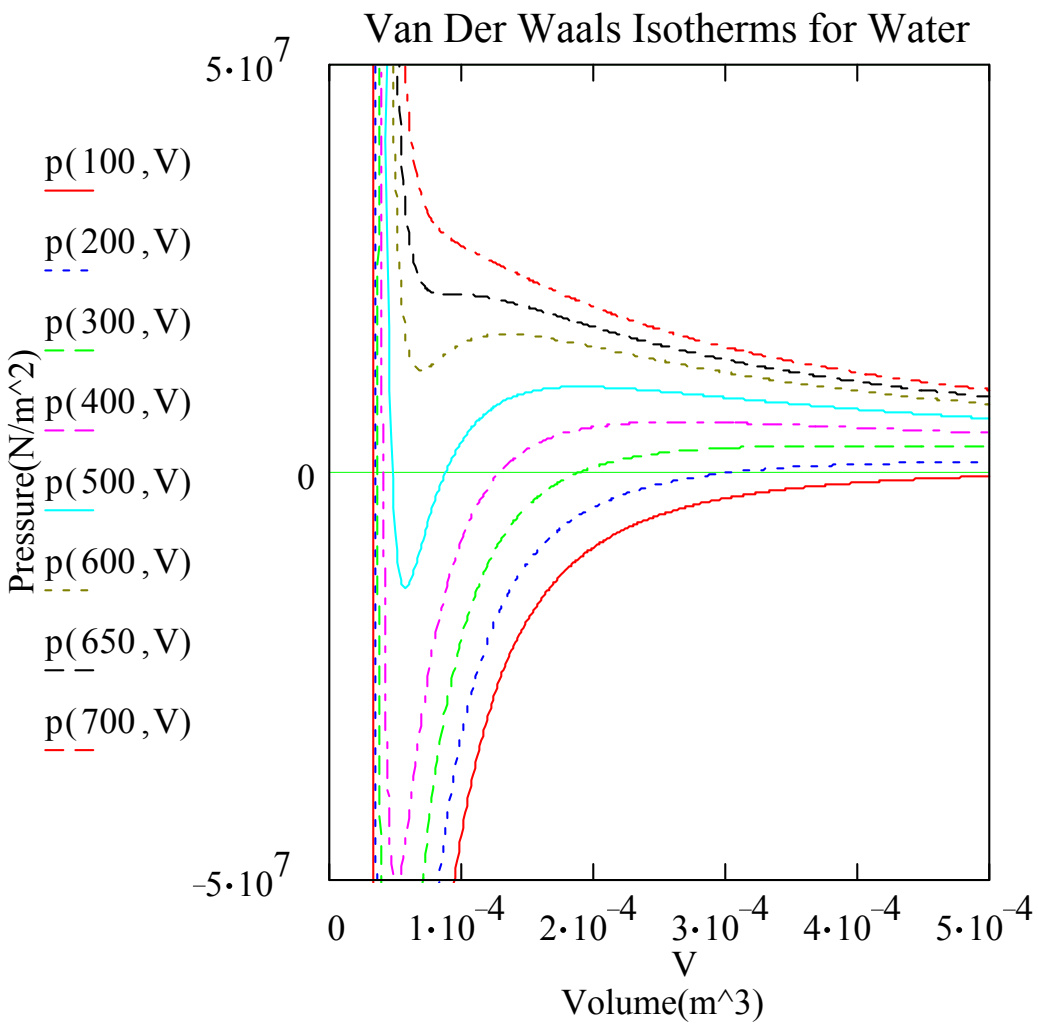
The virial expansion of the ***van der Waals*** equation given by Equ.(10) has been fitted to experimental data. Therefore, the curves in the figure for *H_2 and CO_2* represent accurately the experimental facts.

From the figure, one observes that for low temperatures, the virial coefficient *B* is negative, as expected for an attractive interaction. Because of an effectively attractive interaction, the pressure measured for a real gas is smaller than for an ideal gas. For the reasons mentioned previously, the effect is stronger for *CO_2* than for hydrogen. For very high temperatures, the virial coefficient *B* approaches the value of the ***covolume (per particle) b***. Here, the attractive part of the interaction does not play a major role. The main effect is due to the repulsive core, which decreases the volume available to the particles. The ***van der Waals*** equation also provides expressions for the higher virial coefficients.

Inspecting the ***van der Waals*** equation (10) closely, one notices some inconsistencies: As an illustration, the figure below displays the ***van der Waals*** isotherms *p(T,V)* for water with the parameters *$a=0.56539\ Pa\ m^6\ mol^{-2}$* and *$b = 3.1 \cdot 10^{-5} m^3\ mol^{-1}$* de-

rived from experimental data. Shown are calculated curves for *T = 100-700 K*.

The isotherms $p(V,T=\text{const.})$ for the very high temperatures look almost like the hyperbolas of an ideal gas. But for *T = 650K,* the real-gas isotherm develops a deflection point, and for *T < 650K,* these isotherms have an oscillatory behavior: With increasing volume, the pressure decreases, increases, and decreases again. ***For small temperatures and a range of volumes, the pressure even becomes negative for any sizeable volume***. This would require the system to collapse, an effect which is not observed experimentally. Even the predicted ***decrease in pressure with decreasing volume is unphysical***. Such a system would also not be stable under compression.



One must, therefore, conclude that the mathematical form of Equ. (10) is ***unrealistic for a real substance, at least for a range of temperatures and volumes or pressures***. The answer to this problem lies in the fact that, for this range of temperatures and volumes, the system is no longer a gas. ***It has undergone, partially or totally, a phase transition***. The liquid phase has become energetically more favorable than the gas phase. This will be discussed in detail in another section.