

16.5: The Second Virial Coefficient

The second virial coefficient describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules, and so on and so forth.

Introduction

As the density is increased the interactions between gas molecules become non-negligible. Deviations from the ideal gas law have been described in a large number of equations of state. The *virial equation of state* expresses the deviation from ideality in terms of a power series in the density:

$$\frac{P}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

- $B_2(T)$ is the second virial coefficient,
- $B_3(T)$ is called the third virial coefficient, etc.

The j^{th} virial coefficient can be calculated in terms of the interaction of j molecules in a volume V . The second and third virial coefficients give most of the deviation from ideal (P/rkT) up to 100 atm.

The **second virial coefficient** is usually written as B or as B_2 . The second virial coefficient represents the initial departure from ideal-gas behavior. The second virial coefficient, in three dimensions, is given by:

$$B_2(T) = -\frac{1}{2} \int \left(\exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right) - 1 \right) 4\pi r^2 dr$$

where $\Phi_{12}(\mathbf{r})$ is the intermolecular pair potential, T is the temperature, and k_B is the Boltzmann constant. Notice that the expression within the parenthesis of the integral is the *Mayer f -function*. In practice, the integral is often *very hard* to integrate analytically for anything other than, say, the hard sphere model, thus one numerically evaluates:

$$B_2(T) = -\frac{1}{2} \int \left(\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right) \right\rangle - 1 \right) 4\pi r^2 dr$$

calculating:

$$\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right) \right\rangle$$

for each r using the numerical integration scheme proposed by Harold Conroy ^{[1][2]}.

Calculation of virial coefficients

The configuration integrals for Z_1 , Z_2 , and Z_3 are:

- $Z_1 = \int d\mathbf{r}_1 = V$
- $Z_2 = \int e^{-U_2/kT} d\mathbf{r}_1 d\mathbf{r}_2$
- $Z_3 = \int e^{-U_3/kT} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$

The series method allows the calculation of a number of virial coefficients. Recall that the second and third virial coefficient can account for the properties of gases up to hundreds of atmospheres. We will discuss the calculation of the second virial coefficient for a monatomic gas to illustrate the procedure. To calculate $B_2(T)$ we need U_2 . For monatomic particles it is reasonable to assume that the potential depends only on the separation of the two particles so $U_2 = u(r_{12})$, where $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$. Using a change of variables we can write this integral $r_{12} = r_2 - r_1$ and after integration over r_1 we can transform variables from $d\mathbf{r}_{12}$ to $4\pi r^2 dr$. The result is:

$$B_2(T) = -2\pi \int [e^{-\beta u(r)} - 1] r^2 dr$$

This expression can be used to obtain parameters from experiment. The second virial coefficient is tabulated for a number of gases. For a hard-sphere potential there is an infinite repulsive wall at a particle radius σ . There is no attractive part.

$$B_2(T) = -2\pi \int_0^\sigma [-1] r^2 dr \\ = \frac{2\pi\sigma^3}{3}$$

The Lennard-Jones potential cannot be calculated analytically, but the integral can be computed numerically. The second virial coefficient was a useful starting point for obtaining Lennard-Jones parameters that were used in simulations.

Isihara-Hadwiger Formula

The Isihara-Hadwiger formula was discovered simultaneously and independently by Isihara and the Swiss mathematician Hadwiger in 1950. The second virial coefficient for any hard convex body is given by the exact relation:

$$B_2 = RS + V$$

or:

$$\frac{B_2}{V} = 1 + 3\alpha$$

where:

$$\alpha = \frac{RS}{3V}$$

where V is the volume, S , the surface area, and R the mean radius of curvature.

Hard spheres

For the hard sphere model one has:^[9]

$$B_2(T) = -\frac{1}{2} \int_0^\sigma (\langle 0 \rangle - 1) 4\pi r^2 dr \\ \text{leading to} \\ B_2 = \frac{2\pi\sigma^3}{3}$$

Note that B_2 for the hard sphere is independent of temperature.

Van der Waals equation of state

For the Van der Waals equation of state one has:

$$B_2(T) = b - \frac{a}{RT}$$

Excluded volume

The second virial coefficient can be computed from the expression:

$$B_2 = \frac{1}{2} \iint v_{\text{excluded}}(\Omega, \Omega') f(\Omega) f(\Omega') d\Omega d\Omega'$$

where v_{excluded} is the excluded volume.

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Related reading

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