

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots \quad 6.40$$

The result of the advanced derivation is that each virial coefficient can be expressed exactly as an integral over the intermolecular interactions characterized by the potential function. Even at the introductory level we can illustrate this approach for the second virial coefficient. Comparing the virial equation at low-density, $Z = 1 + B\rho$, with Eqn. 6.29, we can see that the second virial coefficient is related to the radial distribution function at low density. Inserting the low-density form of the radial distribution function as given by Eqn. 6.34, and subsequently integrating by parts (the topic of homework problem 6.23), we find

$$B = 2\pi N_A \int_0^\infty \left(1 - \exp\left(-\frac{u}{kT}\right)\right) r^2 dr \quad 6.41$$

This relationship is particularly valuable, because experimental virial coefficient data may be used to obtain parameter values for pair potentials.

The van der Waals Equation of State

As we discussed in previous sections, the predecessor of modern cubic equations of state is the equation of van der Waals. The beauty of his argument is that detailed knowledge of the radial distribution function is not necessary, only the kind of general knowledge of its existence as described in the preceding section. Van der Waals started with the pressure equation and reasoned that the integral could be broken into two parts: a repulsive part and an attractive part.

$$\frac{P}{\rho RT} = 1 - \frac{\rho N_A^2}{6RT} \int_0^\sigma r \left(\frac{du}{dr}\right) g(r) 4\pi r^2 dr - \frac{\rho N_A^2}{6RT} \int_\sigma^\infty r \left(\frac{du}{dr}\right) g(r) 4\pi r^2 dr \quad 6.42$$

Each integral can now be analyzed separately. Mathematically, analysis of the first integral is difficult because the number of atoms in the range 0 to σ is zero except at $r = \sigma$, and the derivative of the potential is zero except at $r = \sigma$, where it is basically equal to infinity. The proper mathematical analysis is presented in Appendix C. The result of that analysis is that the only quantity of interest in the repulsive range is the value of the radial distribution function at $r = \sigma$, i.e., the “contact value” of the radial distribution function with the conclusion,

$$\frac{P^{HS}}{\rho RT} = 1 + 4b\rho g^{HS}(\sigma) \quad 6.43$$

Technically, the contact value of the radial distribution function depends on the strength of the attractive forces, as well as the repulsive forces. But we can identify the repulsive contribution to the contact value as the part that remains when the temperature approaches infinity. The attractive forces have no impact on the fluid structure in that limit. Then, we can treat the first part of the integral just as if it was simply for the hard-sphere potential. Considering the low-density limit as outlined above, the value of the radial distribution function at contact must approach unity at low densities. The high-density limiting value for the radial distribution function at contact must diverge at the close-packing limit, for the same reasons that the pressure diverges. The only way to

characterize this divergence is to perform computer simulations based on the hard-sphere potential. This has been done¹ and the result is:

$$g(\sigma) \sim 1/(1 - 1.5b\rho) \text{ (high density limit for hard spheres)} \quad 6.44$$

Unfortunately, this result was about 100 years too late for van der Waals' benefit. Even so, the approximate reasoning applied by van der Waals has turned out to be remarkably accurate. He missed the precise values of the close-packed density and the second virial coefficient for hard-sphere fluids, but the qualitative trends were correct. The fact that the van der Waals equation still provides the basis of modern engineering equations of state is a testimonial to the utility of simple physical reasoning in engineering analysis. With a little effort, you can learn from van der Waals' example. Making the substitution into Eqn. 6.43, we have:

$$\frac{-\rho N_A^2}{6RT} \int_0^\sigma r \left(\frac{du}{dr} \right) g(r) 4\pi r^2 dr \approx 4b\rho g(\sigma) = \frac{4b\rho}{(1-1.5b\rho)} \sim \frac{b\rho}{(1-b\rho)} \quad 6.45$$

As for the second integral of Eqn. 6.42, this basically represents the attractive contribution to the pressure. Consider, for example, what happens to this integral when u is given by the Sutherland potential. Then,

$$\frac{\rho N_A^2}{6RT} \int_\sigma^\infty r \left(\frac{du}{dr} \right) g(r) 4\pi r^2 = \frac{\rho N_A^2 \sigma^3 \epsilon}{6RT} \int_1^\infty x \left(\frac{d(u/\epsilon)}{dx} \right) g(x) 4\pi x^2 dx \text{ where } x \equiv r/\sigma \quad 6.46$$

The integral on the right hand side is independent of the particular substance of interest because the only way of distinguishing different substances in the Sutherland potential is by different values of σ and ϵ . By factoring the σ^3 and ϵ out of the integral, we obtain an integral which can be applied universally to any substance. Van der Waals did not have information available about $g(r)$; therefore, he made the approximation that the value of this integral was some universal constant independent of T and ρ . This may seem somewhat crude since we know that $g(r)$ changes significantly with respect to density, but the way that $g(r)$ oscillates about unity leads to a weak density dependence for the integral. When this universal constant is factored in with σ^3 and ϵ , a single, substance-dependent constant is obtained,

$$a \equiv \frac{4\pi N_A \sigma^3 N_A \epsilon}{6} \left\{ \frac{(g(\sigma) - g^{HS}(\sigma))}{N_A \epsilon} + \int_1^\infty x \left(\frac{du/\epsilon}{dx} \right) g(x) x^2 dx \right\} \quad 6.47$$

The resulting equation of state is:

$$\boxed{Z = 1 + \frac{b\rho}{(1-b\rho)} - \frac{a\rho}{RT} = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}} \quad 6.48$$

This is the equation presented in Section 6.5. At the present time, we can use molecular simulations to investigate the inaccuracies of the attractive term as well as the repulsive term. These simulations show that the temperature and density dependence of the attractive part of the van der Waals equation of state are actually quite accurate. The primary sources of inaccuracy are in the repulsive term as discussed above.

1. Tobochnik, J., Chapin, P.M., J. Chem. Phys., 88:5824 (1988).