Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 3.5

van der Waals Equation of State Redux

A Trial Partition Function

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!} \qquad q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

We've established that the above partition functions are consistent with the ideal gas equation of state (by solving for the pressure as a function of the partition function Q)

Let's now consider a *different* partition function Q

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2} (V - Nr)^N e^{s\beta N^2/V}$$

where r and s are positive constants

The Associated Equation of State

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}(V - Nr)^N e^{s\beta N^2/V}$$

$$\langle P \rangle = k_{\mathrm{B}}T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

First, we expand $\ln Q$,

$$\ln Q = \frac{3}{2}N\left(\ln 2\pi m - \ln h^2 - \ln \beta\right) + N\ln(V - Nr) + \frac{s\beta N^2}{V} - \ln N!$$

The Associated Equation of State

$$\ln Q = \frac{3}{2}N\left(\ln 2\pi m - \ln h^2 - \ln\beta\right) + N\ln\left(V - Nr\right) + \frac{s\beta N^2}{V} - \ln N!$$

Now, we differentiate with respect to V

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V - Nr} - \frac{s\beta N^2}{V^2}$$

With this in hand, we can finish solving for pressure

The Associated Equation of State

$$\langle P \rangle = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} \qquad \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} = \frac{N}{V - Nr} - \frac{s\beta N^2}{V^2}$$

Continuing,

$$P = \frac{N k_B T}{V - Nr} - \frac{s N^2}{V^2}$$

$$\left(P + \frac{s N^2}{V^2} \right) (V - Nr) = N k_B T$$

For $N = N_A$, and *a* and *b* expressed in molar units

$$\left(P + \frac{a}{\overline{V}^2} \right) (\overline{V} - b) = RT$$

The van der Waals Equation of State