Statistical Molecular Thermodynamics

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Video 3.5

van der Waals Equation of State Redux
**A Trial Partition Function**

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

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

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

\[ \langle P \rangle = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,\beta} \]

First, we expand \( \ln Q \),

\[ \ln Q = \frac{3}{2} N \left( \ln 2\pi m - \ln \hbar^2 - \ln \beta \right) + N \ln (V - Nr) + \frac{s\beta N^2}{V} - \ln N! \]
The Associated Equation of State

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

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**

\[
\langle P \rangle = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N\beta}
\]

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

Continuing,

\[
P = \frac{Nk_B T}{V - Nr} - \frac{sN^2}{V^2}
\]

\[
\left( P + \frac{sN^2}{V^2} \right)(V - Nr) = Nk_B T
\]

For \( N = N_A \), and \( a \) and \( b \) expressed in molar units

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

The van der Waals Equation of State