

Lecture #17
Objectives

1. Be able to derive the van der Waals partition function.
2. Be able to identify the salient features of the phase behavior of pure fluids.

1. van der Waals EOS.

Recall the semi-classical partition function:

$$Q = \frac{ZQ_{\text{int}}}{N! \Lambda^{3N}}$$

$$Z = \int \cdots \int \exp[-\beta U(\vec{r}^N)] d\vec{r}^N$$

We derived the ideal gas EOS by setting $U = 0$ and evaluating the configuration integral $Z = V^N$. For the van der Waals equation of state we make some assumptions about the potential and evaluate Z . The $U = 0$ assumption for ideal gas means two things: 1. molecules have zero volume. 2. molecules have no attractive potential.

Let us make the following assumptions instead:

1. Molecules have a hard core of diameter σ that results in an excluded volume of $4\pi\sigma^3/3$ per pair of molecules, or $2\pi\sigma^3/3$ per molecule. Let $b = 2\pi\sigma^3/3$ be the excluded volume per molecule.
2. The pair potential is slowly varying, and can be averaged out to give a “mean field” potential, u_0 ,

$$u_0 = \frac{N}{V} \int_{\sigma}^{\infty} u(r) d\vec{r} = 4\pi \frac{N}{V} \int_{\sigma}^{\infty} u(r) r^2 dr$$

Note the lower limit of integration. u_0 is the potential felt by a pair of molecules. The total mean-field potential is

$$U = \frac{N}{2} u_0$$

If we put this potential into the configuration integral we get

$$Z = \left[4\pi \int_0^{\sigma} e^{-\infty} r^2 dr + 4\pi e^{-\beta u_0/2} \int_{\sigma}^{\infty} r^2 dr \right]^N$$

The second integral is just the free volume of the system,

$$4\pi \int_{\sigma}^{\infty} r^2 dr = V_f = V - Nb$$

So,

$$Z^{\text{vdW}} = V_f^N \exp(-N\beta u_0/2)$$

Now we arrive at the van der Waals partition function,

$$Q^{\text{vdW}} = \frac{Q_{\text{int}} V_f^N}{N! \Lambda^{3N}} \exp(-N\beta u_0/2)$$

Now evaluate Q^{vdW} for the Sutherland potential. We have

$$V_f = V - Nb = V - N \frac{2\pi}{3} \sigma^3$$

$$u_0 = \frac{4\pi N}{V} \int_{\sigma}^{\infty} -\epsilon \left(\frac{\sigma}{r}\right)^6 r^2 dr = -\frac{4\pi N \epsilon \sigma^3}{3V} = -\frac{2aN}{V}$$

where $a = \frac{2\pi}{3} \epsilon \sigma^3 = b\epsilon$.

$$Q_{\text{vdW}} = \frac{Q_{\text{int}} (V - Nb)^N}{N! \Lambda^{3N}} \exp\left(\frac{N^2 a}{V k T}\right)$$

Now find the EOS

$$P = kT \left(\frac{\partial \ln Z}{\partial V} \right)_{N,T}$$

You get

$$P = \frac{NkT}{V - Nb} - \frac{N^2 a}{V^2}$$

2. Phase behavior of pure fluids.

- (a) PVT surface for a pure fluid.
- (b) Vapor-liquid.
- (c) Critical points, supercritical states. The mathematical description of the critical point is given by

$$\left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0$$

This is because the critical point is not only a maximum, but also an inflection point.