10.40 Thermodynamics **Fall 2003**
Problem Set 8

Problem 10.12 Text

Solution:

For the Sutherland potential, a hard core at $r \leq \sigma$ is superimposed onto a r^{-6} attractive contribution for $r > \sigma$:

$$\Phi_{ij}(r) = \begin{bmatrix} \infty & r \leq \sigma \\ -\varepsilon\,\sigma^6/r^6 & r > \sigma \end{bmatrix}$$

Using Eq. (10-144) to define $|\,\Phi_{ij}\,|$ with $g(r) = 0$ for $r < \sigma$ and $g(r) = 1$ $r \geq \sigma$ (equal weighting)

$$|\,\Phi_{ij}\,|_S = \frac{N}{\underline{V}} \int_\sigma^\infty \left(-\varepsilon \frac{\sigma^6}{r^6} \right) 4\pi r^2 dr \tag{1}$$

$$|\,\Phi_{ij}\,|_S = \frac{-4N\pi\sigma^3\varepsilon}{3\underline{V}} \tag{2}$$

For a vdW fluid, use Eq. (10-146)

$$|\,\Phi_{ij}\,|_{vdW} = \frac{-2aN}{\underline{V}\,N_A^2} \quad \text{(in molar units)} \tag{3}$$

so if $a = 2/3\ \pi\sigma^3\varepsilon N_A^2$ then $|\,\Phi_{ij}\,|_S = |\,\Phi_{ij}\,|_{vdW}$, and with $b = 2/3\ \pi\sigma^3$ then

$$a = b(\varepsilon N_A^2) \tag{4}$$

Now Q_{vdW} using Eq. (10-139) is given as:

$$Q_{vdW} = \frac{q_{int}^N}{N!\Lambda^{3N}} \exp\left[\frac{4/3\pi\sigma^3\varepsilon N}{2\underline{V}kT} \right] (\underline{V}_f)^N \tag{5}$$

where $\underline{V}_f$ is defined as the free volume in the normal way for a vdW fluid. Since the Sutherland potential has a hard-core, this corresponds to the excluded volume being removed:

$$\underline{V}_f = \underline{V} - \underline{V}_{excluded} = \underline{V} - bN/N_A$$

where $b = 2/3\ \pi\sigma^3$ as before for a normal vdW fluid.