10.40 Thermodynamics **Fall 2003**
Problem Set 8

Problem 10.11 Text

Solution:

The second virial coefficient in molar units is given by Eq. (10-114)

$$B(T) = -2\pi N_A \int_0^\infty \left[\exp\left[\frac{-\Phi(r)}{kT} \right] - 1 \right] r^2 dr \qquad (1)$$

For a hard-sphere fluid

$$\Phi(r) = \infty \qquad r \leq \sigma$$
$$\Phi(r) = 0 \qquad r > \sigma$$

Substituting into Eq. (1)

$$B^{HS} = -2\pi N_A \left[\int_0^{\sigma} (-1)\, r^2 dr + \int_{\sigma}^{\infty} (0)\, r^2 dr \right]$$

$$B^{HS} = \frac{2}{3}\pi N_A\, \sigma^3 \neq f(T) \qquad (2)$$

For a square-well fluid

$$\Phi(r) = \infty \quad r \leq \sigma$$
$$\Phi(r) = -\varepsilon \quad \sigma < r \leq R\sigma$$
$$\Phi(r) = 0 \quad r > R\sigma$$

Substituting again into Eq. (1)

$$B^{SW}(T) = -2\pi N_A \left[\int_0^{\sigma} (-1) r^2 dr + \int_{\sigma}^{R\sigma} (\exp\,(+\varepsilon/kT) - 1) r^2 dr + \int_{R\sigma}^{\infty} (0) r^2 dr \right]$$

$$B^{SW}(T) = \frac{2\pi N_A \sigma^3}{3}\left[1 + (1 - \exp(\varepsilon/kT))(R^3 - 1)\right] = B^{HS}\, g(T) \qquad (3)$$

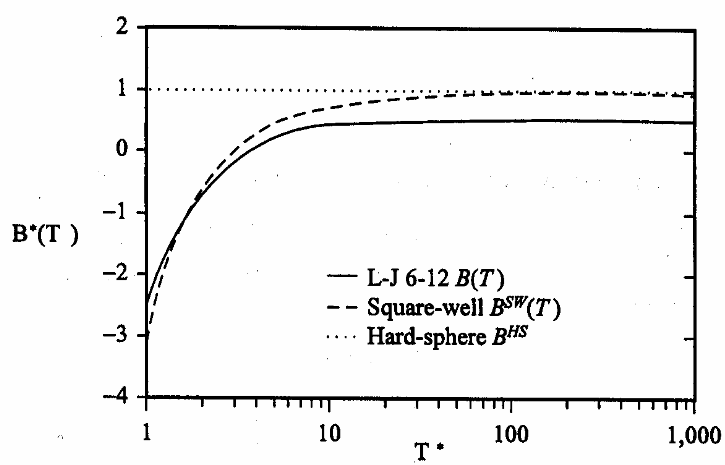
With R = 1.5

$$B^{SW}(T) = B^{HS}\left[1 + (1 - \exp(\varepsilon/kT))((3/2)^3 - 1)\right] = B^{HS}\left[\frac{1}{8}(27 - 19\exp(\varepsilon/kT))\right] \qquad (4)$$

Defining

$$T^* \equiv kT/\varepsilon \quad \text{and} \quad B^*(T) \equiv B(T)/B^{HS}$$

The following figure shows the dimensionless $B(T)$ for these potentials scaled to the temperature independent hard-sphere B^{HS}



The Leonard Jones 6-12 potential is a special case of the Kihara potential, when $a^* = 0$, so we expect the Kihara potentials to behave similarly to the LJ 6-12 potential.

At T* =1000: $B^*_{HS} = B^*_{SW} = 1$, $B^*_{L\text{-}J\ 6\text{-}12} = 0.29$. At T^*= infinity: $B^*_{HS} = B^*_{SW} = 1$, $B^*_{L\text{-}J\ 6\text{-}12} = 0$.

At T^*= infinity, the Kihara potential will go to values slightly greater than 0 depending on the value of a^*.