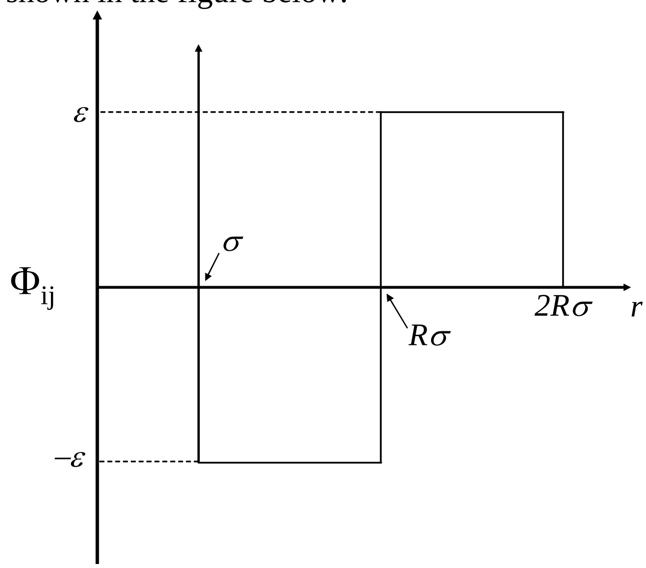
10.40 Thermodynamics **Fall 2003**
Exam 2

Problem 5

5. (20 points) A set of different polyatomic, multi-polar molecules all have similar intermolecular potential functions for their binary interactions, as described approximately by the functional from shown in the figure below.



(a) (10 points) Develop an expression for *B(T)*, the second virial coefficient, for a particular pure component species.

(b) (10 points) Would you expect all pure fluids in this set of compounds to follow the Law of Corresponding States? What are the appropriate scaling parameters to non-dimensionalize *T, P, and V* for each fluid that you could use to test your answer with a set of experimental volumetric data? Briefly explain the rationale behind your choice of scaling parameters.

Solution:

(a) By inspection from the figure:

$$\Phi_{ij} = \begin{Bmatrix} \infty \text{ for } r < \sigma \\ -\varepsilon \text{ for } \sigma < r < R\sigma \\ +\varepsilon \text{ for } \mathrm{R}\sigma < r < 2R\sigma \\ 0 \text{ for } 2\mathrm{R}\sigma < r \end{Bmatrix} \tag{1}$$

The equation that relates Φ_{ij} to B(T) is given in Tester and Modell as:

$$B(T) = -2\pi N_A \int_0^\infty \left[\exp\left(-\beta\Phi\left(r\right)\right) - 1\right] r^2 dr \tag{10-127}$$

Let $B(T) = B_1(T) + B_2(T) + B_3(T) + B_4(T)$ where each $B_i(T)$ is for a part of Φ_{ij}

Plugging (1) into (10-127) and integrating yields,

$$B_1(T) = -2\pi N_A \int_0^\sigma \left[\underbrace{e^{-\infty}}_{=0} - 1\right] r^2 dr = \frac{2}{3}\pi N_A \sigma^3$$

$$B_2(T) = -2\pi N_A \int_\sigma^{R\sigma} \left[e^{-\beta(-\varepsilon)} - 1\right] r^2 dr = \frac{2}{3}\pi N_A \left(1 - e^{\beta\varepsilon}\right)\left(\left(R\sigma\right)^3 - \sigma^3\right)$$

$$B_3(T) = -2\pi N_A \int_{R\sigma}^{2R\sigma} \left[e^{-\beta\varepsilon} - 1\right] r^2 dr = \frac{2}{3}\pi N_A \left(R\sigma\right)^3 \left(1 - e^{-\beta\varepsilon}\right)\left(8 - 1\right)$$

$$B_4(T) = -2\pi N_A \int_{2R\sigma}^{\infty} \left[e^0 - 1\right] r^2 dr = 0$$

$$\boxed{B(T) = \frac{2}{3}\pi N_A \left(\sigma^3 + \left(1 - e^{\beta\varepsilon}\right)\left(\left(R\sigma\right)^3 - \sigma^3\right) + 7\left(R\sigma\right)^3\left(1 - e^{-\beta\varepsilon}\right)\right)}$$

(b)
Since all of the pure fluids in this set of compounds have similar intermolecular potential functions, they should follow the same Law of Corresponding States. We have assumed that value of R for the different fluids is similar, so that the intermolecular potentials will be similar.

From the equation from B(T), temperature always shows up as the product $\beta\varepsilon = \varepsilon/(kT)$, so temperature can be scaled by ε/k. $T^* \equiv \frac{kT}{\varepsilon}$

Volume terms in B(T) are σ^3 and $(R\,\sigma)^3$, so by inspection volume could be scaled by σ^3, the hard sphere radius. $V^* = \frac{V}{\sigma^3}$

To determine the proper scaling for pressure, we start from the relationship between pressure and Z^* given by Tester and Modell

$$P = kT\left(\frac{\partial \ln Z^*}{\partial \underline{V}}\right)_{T,N} = \frac{kT}{Z^*}\left(\frac{\partial Z^*}{\partial \underline{V}}\right)_{T,N} \tag{10-77}$$

In order to determine the proper scaling for P, we need to scale Z^*.

Since $\Phi_{ij} = \varepsilon\Phi'\left[\frac{r_{ij}}{\sigma}\right]$ where Φ' is some function. Then, as shown in Tester and Modell,

$$Z^* = \sigma^{3N} g\left(\frac{kT}{\varepsilon}, \frac{V}{\sigma^3}\right) = \sigma^{3N} g\left(T^*, V^*\right) \tag{2}$$

Plugging (2) into (10-77) and scaling,

$$\frac{P}{\varepsilon} = \left(\frac{kT}{\varepsilon}\right)\frac{1}{\sigma^{3N} g(T^*,V^*)}\left(\frac{\partial\left(\sigma^{3N} g(T^*,V^*)\right)}{\sigma^3 \partial \underline{V}^*}\right)_{T,N} \quad \text{where } \underline{V}^* = \frac{VN}{\sigma^3}$$

$$\frac{P\sigma^3}{\varepsilon} = \left(T^*\right)\frac{1}{g(T^*,V^*)}\left(\frac{\partial\left(g(T^*,V^*)\right)}{\partial \underline{V}^*}\right)_{T,N}$$

Therefore, P should be scaled by ε/σ^3. $P^* \equiv \frac{P\sigma^3}{\varepsilon}$