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CHE 528
TEST 2

1) Consider a binary mixture of 2 species where species 1 contains N_1 particles and species 2 contains N_2 particles. Given the potential energy, Φ , derive a formula for the second virial coefficient $B_2(T,x)$.

$$\Phi = \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} u_{11}(r_{aa'}) + \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} u_{22}(r_{bb'}) + \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} u_{12}(r_{ab})$$

The ideal gas equation approximates atomic interactions in a dilute system. At low densities, particles are so far apart that their interactions are negligible. To mimic increasing density, or lower temperature states, a virial expansion is used to provide the first correction to an ideal gas equation of state by incorporating intermolecular interactions.

$$\frac{pV}{(N_1+N_2)k_BT} = 1 + \frac{B_2(T,x)}{V}$$

In this case we neglect higher order terms in order to solve for the second virial coefficient.

$$p = k_BT \frac{\partial}{\partial V} \ln \int_0^\infty d\tilde{r}\, e^{-\beta\Phi}$$

To solve for the configurational integral, $\int_0^\infty d\vec{r}\, e^{-\beta\Phi}$, one must employ the Mayer function. Where the Mayer function, $f_{ij}+1$ can be substituted for $e^{-\beta\Phi}$.

$$e^{-\beta U(r_{ij})} = f_{ij}(r) + 1$$

Therefore, for a particular system with species 1 and 2, there are 3 possible modes of interaction in which only particles from substance 1 interact with each other (aa'), only particles from substance 2 interact with each other (bb'), and particles from species 1 and 2 interact with each other (ab). Let $f(r_{ij}) = f_{ij}$.

$$\begin{aligned} f_{aa'} &= e^{-\beta u_{11}(r_{aa'})} - 1 \\ f_{bb'} &= e^{-\beta u_{22}(r_{bb'})} - 1 \\ f_{ab} &= e^{-\beta u_{12}(r_{ab})} - 1 \end{aligned}$$

In general, for a low density mixture the configuration integral, Q, may be written

$$\begin{aligned} Q(N,V,T) &= \int_V dr^N e^{-\beta\Phi_N}(r^N) \\ &= \int_V dr^N \prod_{i<j}^{N}[1+f(r_{ij})] \\ &= \int_V dr^N \left[1+\sum_{i<j} f(r_{ij})+...\right] \end{aligned}$$

for each of our Mayer functions which are summed over all particles in the species. So, for a pairwise additive potential, Φ

$$\begin{aligned} Q(N,V,T) &= \int_0^\infty d\vec{r2} \prod_i \prod_{i<j}[1+f_{ij}] \\ &= \int_0^\infty d\vec{r2} \left(1+\sum_{a=1}^{N_1}\sum_{a'=a+1}^{N_1} f_{aa'}\right)\left(1+\sum_{b=N_1+1}^{N_1+N_2}\sum_{b'=b+1}^{N_1+N_2} f_{bb'}\right)\left(1+\sum_{a=1}^{N_1}\sum_{b=N_1+1}^{N_1+N_2} f_{ab}\right) \end{aligned}$$

Considering two unique species, where N is the number of species, we perform the integral over each species explicitly. After distributing the Mayer function the configuration integral becomes

$$\begin{aligned} Q(N,V,T) = \int_0^\infty d\vec{r_1}\int_0^\infty d\vec{r_2} & \left(1+\sum_{a=1}^{N_1}\sum_{a'=a+1}^{N_1} f_{aa'}+\sum_{b=N_1+1}^{N_1+N_2}\sum_{b'=b+1}^{N_1+N_2} f_{bb'}+\sum_{a=1}^{N_1}\sum_{b=N_1+1}^{N_1+N_2} f_{ab}\right)+... \\ ...+&\left(\sum_{a=1}^{N_1}\sum_{a'=a+1}^{N_1} f_{aa'}\sum_{b=N_1+1}^{N_1+N_2}\sum_{b'=b+1}^{N_1+N_2} f_{bb'}\right)+... \\ ...+&\left(\sum_{a=1}^{N_1}\sum_{a'=a+1}^{N_1} f_{aa'}\sum_{a=1}^{N_1}\sum_{b=N_1+1}^{N_1+N_2} f_{ab}\right)+... \\ ...+&\left(\sum_{b=N_1+1}^{N_1+N_2}\sum_{b'=b+1}^{N_1+N_2} f_{bb'}\sum_{a=1}^{N_1}\sum_{b=N_1+1}^{N_1+N_2} f_{ab}\right)+... \\ ...+&\left(\sum_{a=1}^{N_1}\sum_{a'=a+1}^{N_1} f_{aa'}\sum_{b=N_1+1}^{N_1+N_2}\sum_{b'=b+1}^{N_1+N_2} f_{bb'}\sum_{a=1}^{N_1}\sum_{b=N_1+1}^{N_1+N_2} f_{ab}\right) \end{aligned}$$

Distributing the integrals $d\vec{r_1}$ and $d\vec{r_2}$ inside the sums, the configuration integral for two species becomes

$$\begin{aligned}
Q(N,V,T) = & \left(\int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2} + \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\, f_{aa'} + \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\, f_{bb'} \right) + ... \\
& ... + \left(\sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\, f_{ab} \right) + ... \\
& ... + \left(\sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\, f_{aa'} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\, f_{bb'} \right) + ... \\
& ... + \left(\sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\, f_{aa'} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\, f_{ab} \right) + ... \\
& ... + \left(\sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\, f_{bb'} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\, f_{ab} \right) + ... \\
& ... + \left(\sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\, f_{aa'} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\, f_{bb'} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\, f_{ab} \right)
\end{aligned}$$

where the volume of each species is

$$\begin{aligned}
\int_0^\infty d\vec{r_1} &= \int d^3\vec{r_a} \int d^3\vec{r_{a'}} ... \int d^3\vec{r_N} &= V_1^N \\
\int_0^\infty d\vec{r_2} &= \int d^3\vec{r_b} \int d^3\vec{r_{b'}} ... \int d^3\vec{r_N} &= V_2^N
\end{aligned}$$

Now recall the equation of state

$$p = k_B T \frac{\partial}{\partial V} \ln Q(N,V,T)$$

Plugging in $Q(N,V,T)$ for the configuration integral $\int_0^\infty d\vec{r}\, e^{-\beta\Phi}$

$$p = k_B T \frac{\partial}{\partial V} \ln \left(V_1^N V_2^N + \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\ f_{aa'} + \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\ f_{bb'} + \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\ f_{ab} \right)$$

$$... + \left(\sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\ f_{aa'} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\ f_{bb'} \right) + ...$$

$$... + \left(\sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\ f_{aa'} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\ f_{ab} \right) + ...$$

$$... + \left(\sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\ f_{bb'} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\ f_{ab} \right) + ...$$

$$... + \left(\sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_1}\ f_{aa'} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_2}\ f_{bb'} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_1} \int_0^\infty d\vec{r_2}\ f_{ab} \right)$$

Integrating over all particles in the species

$$p = k_B T \frac{\partial}{\partial V} \ln \left(V_1^N V_2^N + V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_{a'}}\ f_{aa'} \right) + ...$$

$$... + \left(V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}}\ f_{bb'} \right) + ...$$

$$... + \left(V_1^{N_1-2} V_2^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \int_0^\infty d\vec{r_b} d\vec{r_{b'}}\ f_{ab} \right) + ...$$

$$... + \left(V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_{a'}}\ f_{aa'} \ \cdot\ V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}}\ f_{bb'} \right) + ...$$

$$... + \left(V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_a}\ f_{aa'} \ \cdot\ V_1^{N_1-2} V_1^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_a} \int_0^\infty d\vec{r_b} d\vec{r_b}\ f_{ab} \right) + ...$$

$$... + \left(V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}}\ f_{bb'} \ \cdot\ V_1^{N_1-2} V_2^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \int_0^\infty d\vec{r_b} d\vec{r_{b'}}\ f_{ab} \right) + ...$$

$$... + \left(V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_{a'}}\ f_{aa'} \ \cdot\ V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}}\ f_{bb'} \right) \cdot\ ...$$

$$...\ \cdot \left(V_1^{N_1-2} V_2^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \int_0^\infty d\vec{r_b} d\vec{r_{b'}}\ f_{ab} \right)$$

$$p = k_B T \frac{\partial}{\partial V} \ln \left(V_1^N V_2^N + V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \; f_{aa'} \right) + ...$$

$$... + \left(V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}} \; f_{bb'} \right) + ...$$

$$... + \left(V_1^{N_1-2} V_2^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \int_0^\infty d\vec{r_b} d\vec{r_{b'}} \; f_{ab} \right) + ...$$

$$... + \left(V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \; f_{aa'} \;\cdot\; V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}} \; f_{bb'} \right) + ...$$

$$... + \left(V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_a} \; f_{aa'} \;\cdot\; V_1^{N_1-2} V_1^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_a} \int_0^\infty d\vec{r_b} d\vec{r_b} \; f_{ab} \right) + ...$$

$$... + \left(V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}} \; f_{bb'} \;\cdot\; V_1^{N_1-2} V_2^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \int_0^\infty d\vec{r_b} d\vec{r_{b'}} \; f_{ab} \right) + ...$$

$$... + \left(V_1^{N_1-2} \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \; f_{aa'} \;\cdot\; V_2^{N_2-2} \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} \int_0^\infty d\vec{r_b} d\vec{r_{b'}} \; f_{bb'} \right) \cdot \; ...$$

$$... \;\cdot \left(V_1^{N_1-2} V_2^{N_2-2} \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} \int_0^\infty d\vec{r_a} d\vec{r_{a'}} \int_0^\infty d\vec{r_b} d\vec{r_{b'}} \; f_{ab} \right)$$

Allow the sum of pairwise-additive interactions to be expressed in terms of number of particles. This method accounts for different volumes of species 1 and species 2 and reflects this in the following manner

$$\begin{aligned} \Phi &= \sum_{a=1}^{N_1} \sum_{a'=a+1}^{N_1} u_{11}(r_{aa'}) + \sum_{b=N_1+1}^{N_1+N_2} \sum_{b'=b+1}^{N_1+N_2} u_{22}(r_{bb'}) + \sum_{a=1}^{N_1} \sum_{b=N_1+1}^{N_1+N_2} u_{12}(r_{ab}) \\ &= \left(\frac{N_1(N_1-1)}{2} \right) u_{11}(r_{aa'}) + \left(\frac{(N_1+N_2)(N_1+N_2-1)}{2} \right) u_{22}(r_{bb'}) + (N_1(N_2-1))\, u_{12}(r_{ab}) \end{aligned}$$