extra problems for chapter 14 of *Statistical Thermodynamics* by Iwao Teraoka

6. The mean-field approximation was used in section 14.1.1 because of the difficulty of calculating $Z$, equation 14.1, exactly. This problem explores the difficulties by calculating $Z$ exactly for a few particles on a small lattice. The seven-site lattice is drawn at right. Let $N_A=2$ and $N_B=5$.

1. Calculate the number of configurations. (Equation 14.6 works.)
2. Six-fold rotational symmetry of the lattice makes configurations degenerate. There is also non-symmetry degeneracy. All configurations have one of three energies. (Energy is $E_k$ in equation 14.2). Let $g_k$ be the degeneracy of $E_k$. By counting bonds, write formulas for $E_1$, $E_2$, and $E_3$. State the values of $g_1$, $g_2$, and $g_3$.
3. Let $\varepsilon_{AA}=\varepsilon_{BB}=0$. Write the formula for $Z$.
4. Evaluate $Z$ at $\beta=1/\varepsilon_{AB}$.
5. The lattice has 12 bonds and 7 sites, so the average coordination number $\zeta=24/7$. Use that $\zeta$ to calculate the mean-field $Z$, equation 14.7. As before, let $\varepsilon_{AA}=\varepsilon_{BB}=0$ and $\beta=1/\varepsilon_{AB}$.
6. Calculate the percent difference between $Z$ and the mean-field $Z$.

7. Mixing parameter $\chi$ is defined in equation 14.12; equation 14.15 shows $\chi$ in the Helmholtz free energy of mixing. Throughout this problem assume that $\zeta$, $\varepsilon_{AB}$, $\varepsilon_{AA}$, and $\varepsilon_{BB}$ are constant; they do not depend on temperature. Recall the thermodynamic relations

$$\Delta S = \left(\frac{\partial \Delta F}{\partial T}\right)_{N,V} \quad \text{and} \quad \Delta U = \left(\frac{\partial \Delta F}{\partial \frac{1}{T}}\right)_{N,V}.$$  

1. Assuming that $\chi$ has only the T-dependence that is explicit in equation 14.12, is $\chi x_A x_B$ energetic or entropic?
2. Let $\chi = A + \frac{B}{T}$, where $A$ and $B$ are constants [Michael Rubinstein and Ralph Colby, *Polymer Physics*, Oxford U Press, 2003, equation 4.31]. Identify $A$ as entropic or energetic. Likewise, $B$.
3. Here is a particular case: $A=-18.843$ and $B=8105$ K. [Lin and Huang, *Int. J. Pharmaceutics*, 2020, 399:109-115] In this case, does the energy of mixing, $\Delta U$, favor mixing? Does the non-ideal part of the entropy of mixing, the entropic part of $N k_B \chi x_A x_B$, favor mixing?
8. Consider the role of lattice connectivity, ζ, in a mixture of A and B atoms on a lattice. There are two systems, system I and system II. Both have the same temperature. For both, \( N_B/N_A = 3 \). For both systems, 
\[
\left[ \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \right] = \frac{3}{4} kT.
\]
For system I, ζ = 4. For system II, ζ = 6.
(1) Is system I stable, metastable, or unstable?
(2) Is system II stable, metastable, or unstable?

9. Consider the unequal-size binary liquid mixture that was analyzed in section 2 of chapter 10. \( N_B = 2 \) (there are two B-B molecules). \( N_A = 2 \).
The N=6 sites are evenly distributed on a sphere, as sketched at right. ζ = 4. Nearest-neighbor noncovalent interaction energies are, as usual, \( \epsilon_{AA} \), \( \epsilon_{AB} \), and \( \epsilon_{BB} \). For this problem do not use mean-field theory; use the actual numbers of possible arrangements and, for each arrangement, the number of A-A, A-B, and B-B noncovalent interactions. The numbers of arrangements are in the table.

<table>
<thead>
<tr>
<th>arrangement</th>
<th>two B²'s are</th>
<th>equatorial</th>
<th>non-equatorial</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of arrangements</td>
<td>6</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>number of non-covalent contacts</td>
<td>A-A</td>
<td>A-B</td>
<td>B-B</td>
</tr>
</tbody>
</table>

(1) Count the number of non-covalent interactions for the equatorial arrangement and for the non-equatorial arrangement. Write the interaction energy of each arrangement.
(2) Write the formula for the partition function \( Z \) in terms of \( \beta \) and the interaction energies.
(3) From \( Z \), derive a formula for the average energy, \( U \). \( U \) will depend on \( \beta \) (or \( kT \)) and the interaction energies. Note that \( U \), not \( \Delta U_{mix} \), is wanted.
**10.** Consider the mixture of N\textsubscript{A} A atoms and N\textsubscript{B} B\textsubscript{2} molecules. From equation 14.33, the free energy of mixing is as follows:

\[
\Delta F = Nk_B T \left[ \frac{X_B}{2} \ln x_B + \left( 1-x_B \right) \ln(1-x_B) + x_B (1-x_B) \right]
\]

Write N, x\textsubscript{B}, and (1-x\textsubscript{B}) in terms of N\textsubscript{A} and N\textsubscript{B}. Then derive the formula for \(\Delta \mu\) by applying the definition: \(\mu = \left( \frac{\partial F}{\partial N_A} \right)_{N_B,T}\). (Constant V is not indicated because lattice volume is not an independent variable.) \(\Delta \mu\) means the chemical potential of mixing, \(\mu - \mu^*\), where \(\mu^*\) is the chemical potential of A in pure liquid A, before mixing. The result should be as follows:

\[
\frac{\Delta \mu_A}{k_B T} = \frac{1}{2} x_B + \ln(1-x_B) + x_B^2
\]

**11.** Consider the mixture of N\textsubscript{A} A atoms and N\textsubscript{B} B\textsubscript{2} molecules. A is solvent, B is solute. The osmotic pressure is \(\Pi\). N is the number of lattice sites. V is volume and equals \(Nv_{site}\cdot \frac{\Pi V}{Nk_B T} = -\frac{\Delta \mu_A}{k_B T}\). The change in the chemical potential of A upon mixing is

\[
\Delta \mu_A = k_B T \left[ \frac{1}{2} x_B + \ln(1-x_B) + x_B^2 \right]
\]

The osmotic virial series is

\[
\frac{\Pi V}{Nk_B T} = \frac{1}{2} x_B + B_2 x_B^2 + B_3 x_B^3 + \cdots
\]

where \(B_2\) and \(B_3\) are the second and third osmotic virial coefficients.

1. Expand \(\Delta \mu_A\) in a power series in \(x_B\), keeping terms to order \(x_B^3\).
2. By comparing, write formulas for the second osmotic virial coefficient, \(B_2\), and the third osmotic virial coefficient, \(B_3\).
3. At the "theta" condition, \(B_2 = 0\). What value of \(\chi\) corresponds to the theta condition?