Problem 1

N lattice sites where gos molecules can bind. Each site has an energy -E when a molecule does bind, we have an ideal gas flowing over the surface at temperature T.

Let's solve this problem in three different ensembles, thinking about constraints as we go along.

(c) Find the fractional coverage $\theta = \frac{M}{N}$ in the MCE.

Constraints: $Z(\#\text{ particles }, V, E)$
- M is the # particles adsorbed on the lattice, which we will hold fixed as we apply the MCE.
- We also have a fixed lattice with N sites.

Note: this is like the two-state model of Section 3.4

$$Z(E, N) = \frac{N!}{(N-M)! M!} \quad \text{This is the number of ways of arranging M molecules on a lattice with N sites.}$$

$$\frac{S}{k_B} = k_B \ln Z$$

$$\beta = \frac{\partial S}{\partial E}$$

$$\beta = -\frac{1}{E} \left( \frac{\partial (N!)}{\partial E} \right)$$

$$= -\frac{1}{E} \left( \frac{N!}{\partial (N-M)!} \right)$$

Apply the Sterling approximation.

$$-\beta E = \ln \left( \frac{N!}{(N-M)!} \right)$$

What does this mean? That at each temperature there will be a given fractional coverage $\theta$. As $\beta \to 0$ ($T \to \infty$) $\theta \to 1/2$.

Thus, at high temperatures we have the state with the highest energy, and as $\beta \to 0$ ($T \to \infty$), if $E > 0$ (intended) then $\theta = 1$.

That is, as $T \to 0$ we should see $\theta = 0$, which is true only if the lattice is entirely filled or empty (depends on sign of $E$).
Next let us use the canonical ensemble. We still have a fixed number of particles but now allow the energy to vary.

Constraints: \( E(N, M, V, T) \)

But if we allow \( E \) to vary, that means we must also allow the number of adsorbed particles to vary, because \( E = M(-E) \). Thus, we should hold fixed the number of lattice sites, while allowing the number of adsorbed particles \( M \) to vary. Again, when we apply the NCE, we kept fixed \( M \), but when we apply the CE we keep fixed \( N \).

Note: this is like the application of the 1-state model in section 3.4.

\[
\Omega(E, M) = \sum_{M_1, M_2} \exp \left( -\beta \frac{E}{N} \right) \]

where \( \Omega \) refers to whether a particle is adsorbed on a lattice site or not.

\[
\Omega = \left( \frac{1}{e^{\beta E}} + 1 \right)^N
\]

Now, \( -\beta A = N E \ln \left( 1 + e^{\beta E} \right) \)

\[
\Theta = \frac{M}{N} = \frac{\langle E \rangle}{N}
\]

\[
\langle E \rangle = -\frac{N E}{1 + e^{\beta E}}
\]

\[
\Theta = \frac{1}{1 + e^{\beta E}}
\]

We get the same answer as when we apply the NCE! Just as in section 3.4, this happens because when we apply the NCE we are looking at one \( M \) value at a time, and that \( M \) value determines the energy (because it determines \( E \)), which in turn is related to the temperature. When we apply the CE we are looking at all the possible values of the \( \langle E \rangle \) (and hence \( M \)) at once, holding the lattice free constant. But the underlying physics are the same.
Here's another way of solving the problem in the CE that may help clear things up.

\[ Q = \sum_{m=0}^{N_1} \frac{N_1!}{m!(N_1-m)!} e^{-\beta(E-m)} \]

Here we are summing over \( m \) (really the energy, \( \langle E \rangle \)) and counting the number of states with each energy \( \frac{N_1}{m!(N_1-m)!} \).

Again, we are counting over all the states of the system, constrained by fixed \( T \) and fixed \( N_1 \).

\[ Q = \sum_{m=0}^{N_1} \frac{N_1!}{m!(N_1-m)!} e^{\beta E_m} = \left( 1 + e^{\beta E} \right)^{N_1} \]

Next,

\[ \langle M \rangle = \sum_{m=0}^{N_1} \frac{m N_1!}{m!(N_1-m)!} e^{\beta E_m} \]

\[ \langle M \rangle = \frac{e^{\beta E} (1 + e^{\beta E})^{N_1}}{(1 + e^{\beta E})^{N_1} - 1} \]

\[ \langle M^2 \rangle = \frac{e^{\beta E} (1 + e^{\beta E})^{N_1+1}}{(1 + e^{\beta E})^{N_1} - 1} \]

\[ \theta = \frac{1}{1 + e^{-\beta E}} \]

we can count in more than one way and get the same result, so long as we are treating the same set of energy-weighted states!

The limiting behavior for the CE for \( \beta \to 00 \) and \( \beta \to 0 \) is the same as for the true CE.
Finally, let's solve the problem in the GCE.

Constants: $E_m(T,V)$

Now we need to think about the particle and lattice size constants again. In the MCE we held the value of $M$ (and $N$) constant. In the DE we had to let the energy vary, which also meant allowing the value of $M$ to vary (though not the value of $N$). In the case of the GCE we can let the value of $M$ vary because we constrain the chemical potential. This implies the energy will also vary.

$$\bar{E}(\mu,T,V) = \sum \frac{e^{\mu - \mu_0 - \mu_0 N}}{\exp \left( \frac{\mu_0 - \mu_0 N}{k_B T} \right) - 1}$$

$$\bar{E}(\mu, T, V) = \left[ 1 + e^{(\mu_0 - \mu_0 N)/k_B T} \right]^{-N}$$

$$\langle N \rangle = \frac{m}{k_B T} \cdot \frac{d}{dE_m} \ln \left[ \frac{dE_m}{dN} \right]_{TV}$$

$$\langle N \rangle = \frac{\partial}{\partial \mu} \frac{N}{k_B T} \cdot e^{\mu - \mu_0 - \mu_0 N}$$

$$\langle N \rangle = \frac{1}{1 + e^{-\mu_0 - \mu_0 N/k_B T}}$$

$$\Theta = \frac{1}{1 + e^{-\mu_0 - \mu_0 N/k_B T}}$$

The only difference here is that we also have a $\mu$ in this expression.

What about the limiting behavior?

Again, one can see that it is the same as before, provided that $\langle E_m \rangle$ is positive.

Physically, at low temperature there is no energy available to move the particles on the lattice. At high temperature, the energy of each particle is so high that the energy reduction that comes from adsorbing on the lattice is negligible, and we find the particles driven off the surface into the gas phase. This is what we expect: particles will adsorb from a surface as the temperature is increased.
Problem 3.

At 25°C the saturation pressure of ethane is 42.07 bar, and the saturation pressure of water is 0.0316 bar.

(a) The ideal version of Raoult's law is:

\[ x_i P_{sat} = P_i \]

where \( P_i \) is the partial pressure of component \( i \) (ethane in our case).

For 1 bar ethane, \( x_i = \frac{P_i}{P_{sat}} = 0.0238 \)

For 35 bar ethane, \( x_i = \frac{35}{42.07} = 0.8319 \)

(b) At 25°C and \( P = 1 \) bar the actual value is \( x_i = 0.83 \times 10^{-4} \)

also,

\[ \beta = 1 - 7.63 \times 10^{-7} P - 7.22 \times 10^{-5} P^2 \]

The "grown up" version of Raoult's law is:

\[ \beta x_i P_{sat} = P_i \]

What is \( x_i \) when \( P_i = 35 \) bar? \( \beta \) is fugacity coefficient of ethane in liquid water.

What is \( x_i \) when \( P_i = 35 \) bar? \( \beta \) is fugacity coefficient of ethane in the gas phase.

This is our reference state at 25°C and \( P = 1 \) bar, let \( \beta = 1 \) of these conditions:

\[ \frac{\beta_i}{x_i} = \frac{2.38}{0.0238} = 172.03 \]

Assume that because we are dealing with a very small range of \( x_i \) values, \( \beta \) will not change.

Calculate the new value of the fugacity coefficient.

\[ \delta \beta = \int_{\beta_i}^{\beta_f} \frac{d\beta}{\beta} = \int_{1}^{0.7400} \left( \frac{7.63 \times 10^{-7}}{\beta} - 7.22 \times 10^{-5} \beta \right) d\beta = -0.301 \]

\[ \beta_f = 0.7400 \]

\[ x_i = \frac{(0.74) (65)}{(72.03) (42.07)} = 8.34 \times 10^{-4} \]

CORRECTION: To find the fugacity coefficient we should be integrating over the total pressure, not the partial pressure of ethane only. In this case we can assume that the presence of water will not affect the result because the partial pressure of water is so low. In other words, the gas phase is composed almost entirely of ethane.
3) Programming assignment for regular solution theory.

See the web for code.

Here are the formulas for the energies and other quantities requested.

\[
\overline{E} = Nz \left[ \frac{1}{2} \varepsilon_{AA}x_A^2 + \frac{1}{2} \varepsilon_{BB}x_B^2 + \varepsilon_{AB}x_Ax_B \right]
\]

\[
Q = \frac{N!}{(N x_A)(N x_B)} \exp \left( \frac{\overline{E}}{k_B T} \right)
\]

\(Q\) is defined for a fixed number of particles. Note that we don’t take into account the fact that each arrangement of particles may have a different energy, because we assume that on average the arrangements will contain roughly the same number of AA, BB, and AB contacts.

\[
\frac{\Delta A}{N} = \left[ -k_B T \left( x_A \ln x_A + x_B \ln x_B \right) + z \left( \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} - \varepsilon_{AB} \right) x_Ax_B \right] / N
\]

What happens when we vary \(T\) and the values for the \(\varepsilon\)’s and \(x\)’s? Last week we showed that a stability criteria is violated for \(\chi > 2\) and compositions near 0.5. Note that \(\chi\) is dependent on temperature. Also note that we can’t actually see the phase separation occur because we are just calculating a value of \(\Delta A/N\), and aren’t solving for the compositions that will actually exist at equilibrium. Note how sensitive these values are to changes in the \(\varepsilon\)’s and \(x\)’s.