

OBLIG 3 FYS2160

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In this oblig, we are dealing with a system consisting of a solid and a gas in equilibrium. We model our system as ideal, which is why we can describe the system by using the chemical potential for both an einstein crystal and ideal gas. Our solid consists of an A number of atoms, where each of these atoms has an energy $-\epsilon_A$.

Problem A

We want to find the partition function for one A atom within the crystal, which is our model for the solid in our system. Each atom is modelled as an harmonic oscillator, which helps us describe the total energy in the system. We know from the assignment text that in bound state, each atom has an energy $-\epsilon_A$. To describe the partition for one atom in the crystal, we use the formula from page 185 in *Elementary Thermal and Statistical Physics Using Python*:

$$Z_A(N, V, T) = Z_A = \sum_{n=0}^{\infty} e^{-n\epsilon_A/kT} = \frac{1}{1 - e^{-\epsilon_A/kT}}$$

Where k is the Boltzmann constant and T is temperature.

Problem B

We use a model for our solid – the Einstein crystal – where each atom is fixed in place in a lattice structure. This is why we consider the atoms within this system to be distinguishable – we can by referring to a specific combination of coordinates specify a specific atom we're interested in, and thereby see what state the atom is in.

We wish to find the partition function for the entire solid, consisting of N_A atoms identical to A. We can do this by using the formula from page 275 in *Elementary Thermal and Statistical Physics Using Python*, the partition function for an Einstein crystal is given:

$$Z = (Z_A)^{N_A} = \left(\frac{1}{1 - e^{-\epsilon_A/kT}} \right)^{N_A}$$

This means that we can easily express the partition function for the entire solid as a function of the partition of a singular atom.

Problem C

We know that Helmholtz free energy is at a minimal when our system is at equilibrium, which is applicable to our system. Furthermore, we know that since we are dealing with N_A identical distinguishable harmonic oscillators. From page 200 in *Elementary Thermal and Statistical Physics Using Python*, we have the expression for the Helmholtz free energy:

$$F_{total} = -kT \ln(Z)$$

There k is Boltzmann's constant, and T is the temperature. In our case, the Helmholtz free energy will be expressed as

$$F_{total} = -kT \ln(Z) = -kT \ln((Z_A)^{N_A}) = -N_A kT \ln(Z_A) = -N_A kT \ln\left(\frac{1}{1 - e^{-\epsilon_A/kT}}\right)$$

Problem D

Gibbs free energy is defined at page 296 in *Elementary Thermal and Statistical Physics Using Python*,

$$G(T, p, N_A) = E - TS + pV = F + pV$$

In our instance, it would be beneficial for us to use the definition $G = F + pV$, because we already found an expression for Helmholtz free energy F . We associate a volume v_A to each particle in the crystal, and insert our function/arguments into the function for Gibbs free energy:

$$G(T, p, N_A, v_A) = F + pV = -N_A kT \ln(Z_A) + pN_A v_A = -N_A kT \ln\left(\frac{1}{1 - e^{-\epsilon_A/kT}}\right) + pN_A v_A$$

We need to take a closer look at the $\ln(Z_A)$;

$$\ln(Z_A) = \ln\left(\frac{1}{1 - e^{-\epsilon_A/kT}}\right) = \ln\left(e^1 - e^{\ln\left(e^{-\frac{\epsilon_A}{kT}}\right)}\right) = \frac{\epsilon_A}{kT}$$

We insert this into our expression for Gibbs free energy:

$$G(T, p, N_A, v_A) = -N_A \epsilon_A + pN_A v_A$$

Problem E

On page 298 in *Elementary Thermal and Statistical Physics Using Python*, we can retrieve a definition of Gibbs free energy that does incorporate the chemical potential:

$$G(T, p, N_A) = N_A \mu_A(T, p)$$

This means we can rewrite our expression:

$$\mu_A(T, p) = \frac{-N_A \epsilon_A + p N_A v_A}{N_A} = -\epsilon_A + p v_A$$

Which is what we wanted to show.

Problem F

In equilibrium we assume that the chemical potentials for both the solid and the gas are the same. $\mu_A(T, p) = \mu_g(T, p) = -\epsilon_A$, after we assume $p v_A \ll \epsilon_A$. For an ideal gas, we have from page 301 in the textbook the expression for μ_g :

$$\mu_g = kT \ln \left(\frac{N/V}{n_Q kT} \right) = kT \ln \left(\frac{p}{n_Q kT} \right) = kT \ln \left(\frac{n}{n_Q} \right) = -\epsilon_A$$

which we know as the formula presented in the assignment text. We're interested in the pressure, so we need to rewrite our formula:

$$-\epsilon_A = kT \ln \left(\frac{p}{n_Q kT} \right) \Rightarrow p(t) = n_Q kT e^{-\epsilon_A/kT}$$

We can insert our value for $n_Q = \left(\frac{2\pi m kT}{h^2} \right)^{3/2}$:

$$p(t) = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} kT e^{-\epsilon_A/kT}$$

Problem G

N_A atoms of type B gets dissolved in our crystal. This means that there will be one possible position of a B atom for each A atom, as described in the assignment text. To study the mixing entropy, we first need to use this information to find the number of microstates in our new system. This we do easily by

$$\Omega = \binom{N_A}{N_B} = \frac{N_A!}{N_B! (N_A - N_B)!}$$

We use the formula for entropy on the page 139 in the textbook to describe the entropy in our system:

$$S = k \ln(\Omega) = k \ln\left(\frac{N_A!}{N_B! (N_A - N_B)!}\right) = k(\ln(N_A!) - \ln(N_B!) - \ln(N_A - N_B!))$$

We use Stirling's approximation for a large number, N : $\ln(N!) \approx (N \ln(N) - N)$

$$\begin{aligned} S &= k((N_A \ln(N_A) - N_A) - (N_B \ln(N_B) - N_B) - ((N_A - N_B) \ln((N_A - N_B)) - (N_A - N_B))) \\ &= k(N_A \ln(N_A) - N_B \ln(N_B) - N_A \ln(N_A) + N_A \ln(N_B) + N_B \ln(N_A) - N_B \ln(N_B) + N_B) \\ &= N_B k \left(-\ln\left(\frac{N_A}{N_B}\right) - \frac{N_A - N_B}{N_B} \ln\left(\frac{N_A - N_B}{N_B}\right) + 1 \right) = N_B k \left(\ln\left(\frac{N_A}{N_B}\right) + 1 \right) \end{aligned}$$

Which is what we wanted to show.

Problem H

We want to find Gibbs free energy for this new system. We know that the A-atoms have a chemical potential $-\epsilon_A$, and the B-atoms have a bound state energy $-\epsilon_B$. We have from the formula on page 296 in the textbook, that we the total Gibbs energy in our system:

$$G_{tot} = E - TS + pV$$

In this case we have a total energy $E = \epsilon_A N_A + \epsilon_B N_B$ from the atoms, and an S already calculated. Since we have approximated the atoms B to have no volume, $pV = pN_A v_A$. Therefore, the expression for Gibbs free energy in our new system is:

$$G_{tot} = \epsilon_A N_A + \epsilon_B N_B - T N_B k \left(\ln\left(\frac{N_A}{N_B}\right) + 1 \right) + p N_A v_A$$

Previously, we did assume that $p v_A \ll \epsilon_A$, so

$$G_{tot} = -\epsilon_A N_A - \epsilon_B N_B - T N_B k \left(\ln\left(\frac{N_A}{N_B}\right) + 1 \right)$$

We can also express Gibbs free energy of an ideal mixture, which is what our system is, by the formula on page 317 in our textbook:

$$G = \sum_{i=1}^k G_i^0 + NkT \sum_{i=1}^k x_i \ln x_i = \sum_{i=1}^k G_i^0 - TS$$

Where $x_i = N_i/N$, and S is the mixing entropy. In our instance, this expression can be rewritten to

$$G = G_A + G_B - kT \left(N_A \ln \left(\frac{N_A}{N_A + N_B} \right) + N_B \ln \left(\frac{N_B}{N_A + N_B} \right) \right)$$

Problem I

We use the formula for chemical potential of individual species in an ideal mixture presented at page 318 in the textbook:

$$\mu_i = \mu_i^0 + kT \ln(x_i)$$

We know that $x_i = \frac{N_i}{N} = \frac{N_B}{N_A + N_B}$, which, since $N_B \ll N_A$, we can set $x_i = \frac{N_i}{N} \simeq \frac{N_B}{N_A}$, which we can approximate by using $\ln(1-x) \simeq -x$.

$$\mu_A = \mu_A^0 - kT \frac{N_B}{N_A}$$

μ_A^0 is the μ_A in our original state, which equals to $-\epsilon_A$, so

$$\mu_A = -\epsilon_A - kT \frac{N_B}{N_A}$$

which is what we wanted to show.

Problem J

The vapor pressure for the A-atoms as a function of $\frac{N_B}{N_A}$ can be described by the same formula as explained previously

$$p(t) = n_Q kT e^{\mu_A/kT}$$

We want to express it in terms of $\frac{N_B}{N_A}$, which we can do by inserting $\mu_A = -\epsilon_A - kT \frac{N_B}{N_A}$ to

$$\Rightarrow p_A(t) = n_Q kT e^{(-\epsilon_A - kT \frac{N_B}{N_A})/kT} = n_Q kT e^{(-\epsilon_A/kT - \frac{N_B}{N_A})}$$

Problem K

Our results for the problems throughout the assignment are cohesive and makes sense. We expressed the vapor pressure as a function of $\frac{N_B}{N_A}$, and we can compare the expression we found for vapor pressure from A-atoms before and after the B atoms were inserted into the crystal:

$$p_{before}(t) = n_Q kT e^{-\epsilon_A/kT}$$

$$p_{after}(t) = n_Q kT e^{\left(-\epsilon_A/kT - \frac{N_B}{N_A}\right)}$$

We see that the vapor pressure expression changes by the factor $-\frac{N_B}{N_A}$ in the exponent. We see that when there's a presence of B-atoms in the crystal, they have a dampening effect on the vapor pressure from A-atoms. The larger amount of B-atoms within our system, the larger this dampening effect will be. This does make sense, since one would expect the distribution of the total pressure to shift when the distribution of atoms changes.