This exam contains five problems. Work any three of the five problems. All problems count equally although some are harder than others. Do all the work you want graded in the separate exam books. *Indicate clearly which three problems you have worked and want graded.* I will only grade three problems. If you hand in more than three problems without indicating which three are to be graded, I will grade the first three, only!

Write legibly. If I can’t read it, it doesn’t count!

Put your name on all exam books that you hand in. (Only one should be necessary!!!) On the first exam book, rewrite and sign the honor pledge: *I pledge my honor that I have not violated the Honor Code during this examination.*
Physical Constants and Conversion Factors

\[ c = 2.998 \times 10^{10} \text{ cm s}^{-1}, \]
\[ h = 1.054 \times 10^{-27} \text{ erg s}, \]
\[ k = 1.380 \times 10^{-16} \text{ erg K}^{-1}, \]
\[ e = 4.803 \times 10^{-10} \text{ statcoulomb}, \]
\[ N_0 = 6.025 \times 10^{23} \text{ molecules mole}^{-1}, \]
\[ m_{\text{electron}} = 9.108 \times 10^{-28} \text{ g}, \]
\[ m_{\text{proton}} = 1.672 \times 10^{-24} \text{ g}, \]
\[ m_{\text{neutron}} = 1.675 \times 10^{-24} \text{ g}, \]
\[ m_{\text{amu}} = 1.660 \times 10^{-24} \text{ g}, \]
\[ \mu_B = 9.273 \times 10^{-21} \text{ erg Gauss}^{-1}, \]
\[ G = 6.673 \times 10^{-8} \text{ cm}^3 \text{ s}^{-2} \text{ g}^{-1}. \]

1 atm = 1.013 \times 10^6 \text{ dyn cm}^{-2},
1 eV = 1.602 \times 10^{-12} \text{ erg},
1 cal = 4.186 \times 10^7 \text{ erg}.
1. Two identical objects, A and B, are thermally and mechanically isolated from the rest of the world. Their initial temperatures are $\tau_A > \tau_B$. Each object has heat capacity $C$ (the same for both objects) which is independent of temperature.

(a) Suppose the objects are placed in thermal contact and allowed to come to thermal equilibrium. What is their final temperature? How much entropy is created in this process? How much work is done on the outside world in this process?

Solution

No work is done—the objects are just in thermal contact. If energy $dQ$ is transferred from object A to B and the objects are allowed to come to equilibrium, the temperature change of object A is $d\tau_A = -dQ/C$ and the temperature change of object B is $d\tau_B = +dQ/C$. In other words, the temperatures of objects A and B change by equal and opposite amounts, so the final temperature is $\tau_f = (\tau_A + \tau_B)/2$. The change in entropy of the system is

$$\Delta \sigma = \int_{\tau_A}^{\tau_f} \frac{C}{\tau} d\tau + \int_{\tau_B}^{\tau_f} \frac{C}{\tau} d\tau$$

$$= C \log \left( \frac{\tau_f^2}{\tau_A \tau_B} \right)$$

$$= C \log \left( \frac{(\tau_A + \tau_B)^2}{4 \tau_A \tau_B} \right).$$

End Solution
(b) Instead, suppose objects A (temperature $\tau_A$) and B (temperature $\tau_B < \tau_A$) are used as the high and low temperature heat reservoirs of a heat engine. The engine extracts energy from object A (lowering its temperature), does work on the outside world, and dumps waste heat to object B (raising its temperature). When the temperatures of A and B are the same, the heat engine is in the same state as it started and the process is finished. Suppose this heat engine is the most efficient heat engine possible. In other words, it performs the maximum work possible. What is the final temperature of the objects? How much entropy is created in this process? How much work is done on the outside world in this process?

Solution

If we have the most efficient engine possible, it must be a reversible engine which means that the entropy created is zero. Any entropy extracted from object A must wind up in object B. This means

$$d\sigma = 0 = \frac{C\, d\tau_a}{\tau_a} + \frac{C\, d\tau_b}{\tau_b},$$

where $\tau_a$ and $\tau_b$ are the temperatures of object A and B. Integrating gives

$$\log \tau_a + \log \tau_b = \log (\tau_a \tau_b) = \text{Constant},$$

so $\tau_a \tau_b$ is constant in this process. Thus, $\tau_f = \sqrt{\tau_A \tau_B}$. When $\tau_a$ changes by $d\tau_a$, the work done on the outside world is

$$dW = -C\, d\tau_a - C\, d\tau_b = -C \left(1 - \frac{\tau_b}{\tau_a}\right) d\tau_a.$$

We could integrate this expression to find the total work done, but it’s much easier to use the initial and final temperatures

$$W = C \left(\tau_A - \tau_f\right) - C \left(\tau_f - \tau_B\right)$$

$$= C \left(\tau_A + \tau_B - 2\sqrt{\tau_A \tau_B}\right).$$

An interesting point to notice: if we plug $\tau_f = \sqrt{\tau_A \tau_B}$ into the expression for the entropy created that was derived in part (a), we find $d\sigma = 0$, as we should.

End Solution
2. Consider waves on a liquid surface where the restoring force is produced by surface tension. Assume there is a single polarization and the dispersion relation is

\[ \omega^2 = \frac{\gamma}{\rho} k^3, \]

where \( \gamma \) is the surface tension of the liquid, \( \rho \) is its density, \( \omega \) is the frequency of the waves and \( k \) is the wavenumber of the waves. Our goal is to find the contribution of these waves to the low temperature heat capacity of the liquid.

(a) If the surface is in equilibrium at temperature \( \tau \), what is the average energy of a wave with frequency \( \omega \)? (Ignore the \( \hbar \omega/2 \) zero point energy.)

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Solution

The thermal average occupancy of a mode is \( 1/(\exp(\hbar \omega/\tau) - 1) \), and the energy in the mode is just the energy per surface “phonon” times the occupancy. So

\[ \langle \epsilon(\omega) \rangle = \frac{\hbar \omega}{e^{\hbar \omega/\tau} - 1}. \]

Note: if you forgot the occupancy expression, it only takes a couple of lines to work it out from the partition function:

\[
Z = \sum_{n=0}^{\infty} e^{-n\hbar \omega/\tau} = \frac{1}{1 - e^{-\hbar \omega/\tau}}.
\]

\[
\langle n \rangle = \frac{1}{Z} \sum_{n=0}^{\infty} ne^{-n\hbar \omega/\tau} = -\frac{\tau}{\hbar} \frac{\partial \log Z}{\partial \omega}.
\]

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(b) Suppose the surface is a square of side \( L \) and area \( A = L^2 \). How many modes are there with wavenumbers between \( k \) and \( k + dk \)?

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Solution

We will need standing waves which means an integer number of half wavelengths must fit in the square. This requires

\[ k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L}. \]

We see that the “volume” of a mode is

\[ dk_x dk_y = \frac{\pi^2}{L^2}. \]
The "volume" contained between $k$ and $k + dk$ is the area of a quarter annulus of radius $k$ and thickness $dk$. This is $\pi k dk / 2$. Then the number of modes between $k$ and $k + dk$ is

$$N(k) \, dk = \frac{\pi k \, dk / 2}{\pi^2 / L^2} = \frac{L^2}{2\pi} k \, dk = \frac{A}{2\pi} k \, dk.$$ 

(c) At low temperatures what are the energy and heat capacity of these surface waves? You will come up with an integral that can’t be done easily. Explain why it’s OK to set the upper limit to $\infty$. Having done this, convert the integral to dimensionless form and call its value $I$.

To get the energy, we need to add up the energy per mode times the number of modes. From the dispersion relation, we find

$$k \, dk = \frac{2}{3} \left( \frac{\rho}{\gamma} \right)^{2/3} \omega^{1/3} d\omega.$$ 

Then

$$U = \int_0^{\omega_{\text{max}}} \frac{\hbar \omega}{e^{\hbar \omega / \tau} - 1} \frac{A}{2\pi} \frac{2}{3} \left( \frac{\rho}{\gamma} \right)^{2/3} \omega^{1/3} d\omega,$$

where $\omega_{\text{max}}$ indicates that there aren’t an infinite number of modes. The number of modes must be the same as the number of molecules in the surface. However, at very low temperatures, the higher energy modes are not excited (they are killed by the exponential in the denominator), so we make negligible error if we extend the integral to infinite frequency. To make the integral dimensionless, change variables to $x = \hbar \omega / \tau$. Then

$$U = \frac{A}{2\pi} \frac{2}{3} \left( \frac{\rho}{\gamma} \right)^{2/3} \frac{\tau^{7/3}}{\hbar^{1/3}} \int_0^\infty \frac{x^{4/3} \, dx}{e^x - 1},$$

$$= \frac{AI}{3\pi} \left( \frac{\rho^2 \tau^7}{\gamma^2 \hbar^4} \right)^{1/3}.$$

The heat capacity (at constant area) is

$$C_A = \frac{\partial U}{\partial \tau} = \frac{7AI}{9\pi} \left( \frac{\rho^2 \tau^4}{\gamma^2 \hbar^4} \right)^{1/3}.$$

Note that what we’ve done is very similar to the derivation of the Debye theory for the low temperature heat capacity of solids. We find that $C \propto \tau^{4/3}$ instead of $\tau^3$. Part of the difference comes from the fact that we are considering a two dimensional rather than a three dimensional system. (This would have given $\tau^2$.) The other cause of the difference is the strange dispersion relation. Finally, as a point of interest, $I = 1.68$. 

End Solution
3. The normal boiling point (that is, at $p = 1$ atm) of mercury is $T = 630$ K. At this pressure and temperature, mercury vapor may be treated as a monatomic ideal gas. The latent heat of vaporization is $L = 5.93 \times 10^{11} \text{ erg mole}^{-1}$. The atomic weight of mercury is 200.6 amu.

(a) Suppose that the latent heat of vaporization is constant, that mercury vapor may be treated as an ideal gas over the range of interest, and that the specific volume of liquid mercury is negligible compared with the specific volume of mercury vapor. Estimate the vapor pressure of mercury at $T = 300$ K (roughly room temperature).

Solution

This is a problem for Clausius-Clapeyron. Recall that along the melting curve,

$$\frac{dp}{d\tau} = \frac{\Delta \sigma}{\Delta V},$$

where $\Delta \sigma$ is the change in specific entropy between the liquid and vapor and $\Delta V$ is the change in volume. Since we can ignore the volume of the liquid, $\Delta V = V_{\text{vapor}} = \tau/p$ for one mole. The change in entropy is just the latent heat divided by the temperature, so

$$\frac{dp}{d\tau} = \frac{pL}{\tau^2}.$$

We can integrate and get

$$\log \frac{p_2}{p_1} = -L \left( \frac{1}{\tau_2} - \frac{1}{\tau_1} \right),$$

or

$$p_2 = p_1 e^{-\left(\frac{L}{N_0}\right)(1/kT_2 - 1/kT_1)}.$$

At this point, we just plug in the numbers to get

$$p(300 \text{ K}) = 3.9 \times 10^{-6} \text{ atm}.$$

As a point of interest, the CRC handbook gives the vapor pressure as $2.9 \times 10^{-6} \text{ atm}$, so our estimate is not bad!

End Solution

(b) What is the entropy of the liquid at 630 K? Hint: You may need to know the entropy of the vapor. In case you don’t remember the expression, you might want to work it out. Remember that the number of states in $d^3r$ and $d^3p$ is $dn = d^3r d^3p/(2\pi\hbar)^3$. You should also remember that for large $N$, $\log N! \to N \log N - N$. 

If we know the entropy of the gas, we can get the entropy of the liquid by subtracting $L/\tau$. So we need to know the entropy of the gas. The appropriate expression is the Sackur-Tetrode formula which is not something that I would use brain cells to memorize. We can work it out. The one particle partition function is found from

$$Z_1 = \int \int \frac{d^3r}{(2\pi \hbar)^3} \frac{d^3p}{(2\pi \hbar)^3} e^{-\left(p_x^2 + p_y^2 + p_z^2\right)/2m\tau} = V \left(\frac{m\tau}{2\pi \hbar^2}\right)^{3/2} = n_Q V.$$  

For $N$ particles

$$Z_N = \frac{Z_1^N}{N!} = \left(\frac{n_Q V}{N!}\right)^N.$$  

Note the factor of $N!$. The free energy is

$$F = -\tau \log Z_N = -\tau N \left(\log \frac{n_Q}{n} + 1\right).$$  

The entropy is

$$\sigma = -\frac{\partial F}{\partial \tau} = N \left(\log \frac{n_Q}{n} + \frac{5}{2}\right),$$  

which is the Sackur-Tetrode expression. From this, we must subtract the entropy added by the heat of vaporization. We have for the entropy of the liquid

$$\sigma_{\text{liquid}} = N_0 \left(\log \frac{n_Q}{n} + \frac{5}{2}\right) - \frac{L}{\tau},$$  

where the number of molecules has been set to the number in one mole. To get the entropy in conventional units, we also need to multiply by $k$, so we have

$$S_{\text{liquid}} = N_0 k \left(\log \left(\frac{m k T}{2\pi \hbar^2}\right)^{3/2} \frac{k T}{p} + \frac{5}{2}\right) - \frac{L}{T},$$

$$= (6.025 \times 10^{23})(1.380 \times 10^{-16}) \times \left(\log \left(\frac{200.6(1.660 \times 10^{-24})(1.380 \times 10^{-16})630}{2\pi(1.054 \times 10^{-27})^2}\right)^{3/2} \frac{(1.380 \times 10^{-16})630}{1.013 \times 10^6} + \frac{5}{2}\right)$$

$$- \frac{5.93 \times 10^{11}}{630},$$

$$= (8.315 \times 10^7)(20.40 + 2.50) - 9.413 \times 10^8 = 19.042 \times 10^8 - 9.413 \times 10^8,$$

$$= 9.629 \times 10^8 \text{ erg K}^{-1} \text{ mole}^{-1},$$

or

$$\sigma = S/k = 6.98 \times 10^{24} \text{ mole}^{-1}.$$  

Actually, this is what is determined for the entropy of the liquid by starting from near absolute 0 and keeping track of the heat and entropy added to get to the boiling point. This is another way that the Sackur-Tetrode expression has been confirmed!
4. Consider a line of $N + 1$ atoms. Each atom interacts only with its nearest neighbors, so there are $N$ interactions. $N$ is very large—we can always neglect 1 when compared to $N$. Also, $\log N! \approx N \log N - N$. There are two kinds of atoms on the line, type $A$ and type $B$. The interaction energy for an $AA$ pair is $-\epsilon$; for a $BB$ pair, $-\epsilon$; and for an $AB$ pair, $-\epsilon/2$, where $\epsilon > 0$. In other words, when the two atoms in a bond are the same, they are twice as strongly bound as when they are different. The whole line of atoms is in equilibrium at temperature $\tau$. Exchanging energy with the heat bath means that atoms must change positions. For example, if there is a configuration, $ABAB$, then the three bonds in this configuration have a total energy $-3\epsilon/2$. If the inner two atoms swap positions to give $AABB$, the three bonds have a total energy of $-5\epsilon/2$ and energy $\epsilon$ was given to the heat bath.

Let $x$ denote the fraction of $B$ atoms, so if there are $N_A$ and $N_B$ atoms of types $A$ and $B$, respectively, then $N_A = (1 - x)N$ and $N_B = xN$, and $0 \leq x \leq 1$.

(a) Suppose the temperature is high enough that the atoms of each type are randomly and independently distributed along the line (in other words, it is a homogeneous mixture). Obtain expressions for the energy, the entropy, and the Helmholtz free energy as a function of $\epsilon$, $\tau$, $N$ and $x$. Be sure to use the fact that $N$ is large to simplify your answers.

--- Solution ---

A number of you tried to do this part via the partition function. I don’t know how to calculate the partition function for this situation—the problem is counting the configurations correctly. None of the partition function solutions solved the problem. If I use this problem again, I will give a hint that the partition function is too hard to do! (Sorry!)

Since the atoms are randomly distributed, if we pick an atom at random, it’s an $A$ atom with probability $1 - x$ and a $B$ atom with probability $x$. Thus there are $N(1 - x)^2$ $AA$ pairs, $Nx(1 - x)$ $AB$ pairs, $N(1 - x)x$ $BA$ pairs, and $Nx^2$ $BB$ pairs, so the total energy is

$$U = -N\epsilon((1 - x)^2 + (1 - x)x/2 + x(1 - x)/2 + x^2) = -N\epsilon(1 - x - x^2) = -N\epsilon + Nx(1 - x)\epsilon.$$  

There are $N!/(N_A!N_B!)$ ways to distribute $N_A$ and $N_B$ atoms to $N$ sites. The entropy is the logarithm of this number, so

$$\sigma = \log N! - \log N_A! - \log N_B! = N \log N - N - N_A \log N_A + N_A - N_B \log N_B + N_B$$

$$= N \log N - N(1 - x) \log N(1 - x) - Nx \log Nx = -N ((1 - x) \log(1 - x) + x \log x)$$

Finally, the free energy is

$$F = U - \tau \sigma = N (-\epsilon + x(1 - x)\epsilon + \tau ((1 - x) \log(1 - x) + x \log x)).$$

--- End Solution ---
(b) Suppose the temperature is zero! What is the configuration of atoms in this case? What is the ground state energy? What is the entropy? What is the free energy? Once again, use the fact that \( N \) is very large to simplify your answer.

Solution

If the temperature is zero, the system minimizes its free energy by minimizing the energy, in other words by going to the ground state. \( AA \) or \( BB \) bonds represent the least energy, while it takes energy to create an \( AB \) bond. We want the fewest possible \( AB \) bonds. The minimum we can have is 1. All the \( A \) atoms are on the left of the line while all the \( B \) atoms are on the right of the line, or vice-versa. The ground state energy is thus

\[ U = -(N - 1)\epsilon - \epsilon/2 \approx -N\epsilon. \]

There are two ground states, so \( \sigma = \log 2 \approx 0. \) And, the free energy is just the energy in this case, \( F = -N\epsilon. \)

End Solution

(c) In general, the system may be a homogeneous mixture like that in part (a) or it may be more like the configuration in part (b). Suppose \( x = 1/2 \) and determine the transition temperature which separates the (b) like state from the (a) like state. Hint: consider, for the homogeneous mixture case, the plot of free energy versus \( x \) at a given temperature.

Solution

It’s clear that if the free energy is plotted against \( x \) at a given temperature, the curve is symmetric about \( x = 1/2. \) This means \( x = 1/2 \) will be a local maximum or a local minimum. If it’s a local maximum, then the system can lower its free energy by separating into a mostly \( A \) phase containing some \( B \) and a mostly \( B \) phase containing some \( A, \) in other words a configuration similar to part (b). If it’s a local minimum, then a homogeneous mixture, as in part (a) is the equilibrium phase. So we need to find the temperature at which the curve goes from concave down to concave up. In other words, at what temperature is the second derivative with respect to \( x \) 0?

\[
F = N \left( -\epsilon + x(1-x)\epsilon + \tau \left( (1-x) \log(1-x) + x \log x \right) \right)
\]

\[
\frac{dF}{dx} = N \left( (1-2x)\epsilon + \tau (-\log(1-x) + \log x) \right)
\]

\[
\frac{d^2F}{dx^2} = N \left( -2\epsilon + \tau \left( \frac{1}{1-x} + \frac{1}{x} \right) \right),
\]

Inserting \( x = 1/2 \) and setting the second derivative to 0 gives \( \tau = \epsilon/2. \)

End Solution
5. Recall that a definition for the entropy is

\[ \sigma = - \sum_i p_i \log p_i , \]

where \( p_i \) is the probability that the system is in state \( i \) and the sum is over all states which satisfy whatever constraints are placed on the system. Note that this definition handles zero probability states and also produces an additive entropy when two non-interacting systems are combined. In all cases, suppose the volume of the system is fixed. The number of particles in each state is \( N_i \) and the energy of each state is \( E_i \).

(a) Suppose the number of particles in the system is fixed and the energy is fixed. What are the probabilities that maximize the entropy. Of course, the sum will be include only those states which have the correct number of particles and energy. (Or, equivalently, the probability for a state with the wrong number of particles or energy or both is 0.) In this and subsequent parts, you may have to introduce some auxiliary “constants.” Be sure to identify or give a physical interpretation for each such constant. Hint: be sure to use the fact that the system is in some state: \( \sum_i p_i = 1 \).

Solution

This case corresponds to the micro-canonical ensemble. We want to maximize the entropy subject to the constraint that the probabilities sum to 1. Also, we only include states with the correct number of particles and energy. We use a Lagrange multiplier and maximize

\[ f_1 = \sum_i -p_i \log p_i + \lambda_1 \left( 1 - \sum_i p_i \right) . \]

Taking the derivative with respect to a particular \( p_i \) gives

\[ \frac{\partial f_1}{\partial p_i} = -\log p_i - 1 - \lambda_1 . \]

Setting the derivative to zero gives

\[ p_i = e^{1 - \lambda_1} , \]

so all the probabilities (for the states with the correct numbers of particle and the correct energy) are the same. If there are \( M \) such states, the constraint that the probabilities sum to 1 gives

\[ 1 = \sum_i e^{1 - \lambda_1} = M e^{1 - \lambda_1} ; \quad \lambda_1 = 1 - \log M ; \quad p_i = \frac{1}{M} . \]

So, \( \lambda_1 \) is 1 minus the entropy; it also plays a role in normalizing the probabilities.

End Solution
(b) Now suppose the number of particles is fixed, but the system is in equilibrium with a heat bath such that its average energy is $E$. What are the probabilities that maximize the entropy? As before, be sure to identify or give a physical interpretation for any constants you introduce.

Solution

This case corresponds to the canonical ensemble. In this case, we want to maximize

$$f_2 = \sum_i -p_i \log p_i + \lambda_1 \left(1 - \sum_i p_i \right) + \lambda_2 \left(E - \sum_i p_i E_i \right).$$

Differentiating with respect to a given $p_i$ gives

$$\frac{\partial f_2}{\partial p_i} = -\log p_i - 1 - \lambda_1 - \lambda_2 E_i.$$

Setting the derivative to 0, we have

$$p_i = e^{-1 - \lambda_1 - \lambda_2 E_i},$$

so the probabilities are proportional to an exponential function of the energy of a state. This is just a Boltzmann factor and we identify $\lambda_2 = 1/\tau$, where $\tau$ is the temperature. Furthermore, we see that

$$\sum_i p_i = 1 = e^{-1 - \lambda_1} \sum_i e^{-E_i/\tau} = e^{-1 - \lambda_1} Z,$$

where $Z$ is the partition function. In this case, $\lambda_1 = \log Z - 1$ and again, $\lambda_1$ has to do with normalizing the probabilities.

End Solution
(c) Now suppose the system is in equilibrium with a heat bath and a “particle bath” (a reservoir with which it can exchange particles) such that the average energy is $E$ and the average number of particles in the system is $N$. Now what are the probabilities that maximize the entropy? As before, be sure to identify or give a physical interpretation for any constants you introduce.

Solution

This case corresponds to the grand canonical ensemble. In this case, we want to maximize

$$f_3 = \sum_i -p_i \log p_i + \lambda_1 \left( 1 - \sum_i p_i \right) + \lambda_2 \left( E - \sum_i p_i E_i \right) + \lambda_3 \left( N - \sum_i p_i N_i \right).$$

Differentiating with respect to a given $p_i$ gives

$$\frac{\partial f_3}{\partial p_i} = -\log p_i - 1 - \lambda_1 - \lambda_2 E_i - \lambda_3 N_i.$$

Setting the derivative to 0, we have

$$p_i = e^{-1 - \lambda_1 - \lambda_2 E_i - \lambda_3 N_i},$$

so the probabilities are proportional to an exponential function of the energy of a state times an exponential function of the number of particles in the state. This is just a Gibbs factor and we identify $\lambda_2 = 1/\tau$ and $\lambda_3 = -\mu/\tau$, where $\tau$ is the temperature and $\mu$ is the chemical potential. Furthermore, we see that

$$\sum_i p_i = 1 = e^{-1 - \lambda_1} \sum_i e^{(\mu N_i - E_i)/\tau} = e^{-1 - \lambda_1 Z},$$

where $Z$ is the grand partition function. In this case, $\lambda_1 = \log Z - 1$ and again, $\lambda_1$ has to do with normalizing the probabilities.

End Solution
The grade distributions are shown in the figure. The maximum for the homework is 174 and the maximum for the final is 60. The total score is calculated as

\[ 50 \left( \frac{\text{Homework}}{174} + \frac{\text{Final}}{60} \right). \]