



COLLEGE OF ARTS AND SCIENCES

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The UNIVERSITY *of* OKLAHOMA

Statistical Mechanics

PHYS 5163 HOMEWORK ASSIGNMENT 2

PROBLEMS: {1,2,3,4}

Due: February 4, 2022 at 6:00 PM

STUDENT

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PROFESSOR

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Problem 1:

This problem serves as a refresher of thermodynamics: it utilizes the concepts of thermal and mechanical equilibrium as well as expressions for the temperature and the pressure in terms of the entropy.

Some substance has the entropy function

$$S = \lambda V^{1/2} (NE)^{1/4}, \quad (1)$$

where N is in moles, λ is a constant with appropriate units, and E and V denote energy and volume, respectively. A cylinder is separated by a partition into two halves, each of volume 1 m^3 . One mole of the substance with an energy of 200 J is placed in the left half, while two moles of the substance with an energy of 400 J is placed in the right half.

- (a) Assuming that the partition is fixed but conducts heat, what will be the distribution of the energy between the left and right halves at equilibrium?

"At equilibrium" means at the same temperature. Given that we have an entropy function we can calculate the temperature with

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}$$

Where the above can be inverted and solved for T . We now want to see how much will be in A vs. in B. Mathematically this looks like

$$\begin{aligned} A &\Rightarrow \text{Left} \\ B &\Rightarrow \text{Right} \end{aligned} \quad \frac{1}{T_A} = \frac{1}{T_B} \Rightarrow \left(\frac{\partial S_A}{\partial E_A} \right)_{N,V} = \left(\frac{\partial S_B}{\partial E_B} \right)_{N,V}.$$

The entropy functions are then

$$S_A = \lambda V_A^{1/2} (N_A E_A)^{1/4}, \quad S_B = \lambda V_B^{1/2} (N_B E_B)^{1/4}$$

We now calculate the inverse temperature,

$$\left(\frac{\partial S_A}{\partial E_A} \right)_{N,V} = \frac{1}{4} \lambda V_A^{1/2} (N_A)^{1/4} E_A^{-3/4}, \quad \left(\frac{\partial S_B}{\partial E_B} \right)_{N,V} = \frac{1}{4} \lambda V_B^{1/2} (N_B)^{1/4} E_B^{-3/4}$$

Equating these two

$$\frac{1}{4} \lambda V_A^{1/2} (N_A)^{1/4} E_A^{-3/4} = \frac{1}{4} \lambda V_B^{1/2} (N_B)^{1/4} E_B^{-3/4}, \quad V_A^{1/2} N_A^{1/4} E_A^{-3/4} = V_B^{1/2} N_B^{1/4} E_B^{-3/4}$$

$$E_A = \left(\left(\frac{V_A}{V_B} \right)^{1/2} \left(\frac{N_A}{N_B} \right)^{1/4} E_B^{3/4} \right)^{4/3}$$

We now put in our values

$$E_A = \left(\left(\frac{1}{2} \right)^{1/2} \left(\frac{1}{2} \right)^{1/4} \right)^{4/3} E_B = \left(\frac{1}{2} \right)^{1/3} E_B \quad \therefore \quad E_A = \frac{E_B}{2^{1/3}}$$

Problem 1: Continued

From this we can see that the distribution of energy will be

$$E_B = 2^{1/3} E_A \Rightarrow E_A = 265.5 \text{ J}, E_B = 334.5 \text{ J}$$

- (b) Does your result from part (a) make sense? If so, provide an intuitive explanation of your result. If not, explain why your result does not make sense.

Yes this makes sense. The particles may be at equilibrium but this does not mean that there is an equal amount of particles on each side. Since the left hand side has less particles than the right, we should expect the left side to have less energy which we do from (a).

- (c) Assuming that the partition moves freely and also conducts heat, what will be the volumes and energies of the samples in both sides at equilibrium?

Since we are still at equilibrium, this means $T_A = T_B$. We can calculate the volumes by

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N}$$

using the above, we do a similar procedure as in (a),

$$T = \frac{P}{\left(\frac{\partial S}{\partial V} \right)_{E,N}}, \quad T_A = T_B \quad \therefore \quad \frac{P_A}{\left(\frac{\partial S_A}{\partial V_A} \right)_{E_A, N_A}} = \frac{P_B}{\left(\frac{\partial S_B}{\partial V_B} \right)_{E_B, N_B}}, \quad P_A = P_B$$

Calculating these we have

$$\left(\frac{\partial S_A}{\partial V_A} \right)_{E_A, N_A} = \frac{1}{2} \lambda V_A^{-1/2} (N_A E_A)^{1/4}, \quad \left(\frac{\partial S_B}{\partial V_B} \right)_{E_B, N_B} = \frac{1}{2} \lambda V_B^{-1/2} (N_B E_B)^{1/4}$$

Setting these two equal we have

$$P_A V_A^{-1/2} (N_A E_A)^{1/4} = P_B V_B^{-1/2} (N_B E_B)^{1/4}, \quad V_A^{-1/2} = V_B^{-1/2} (N_A E_A)^{1/4} (N_B E_B)^{-1/4}$$

Continuing we have

$$\left(\frac{V_A}{V_B} \right)^{-1/2} = \left(\frac{N_A E_A}{N_B E_B} \right)^{1/4} \Rightarrow \left(\frac{V_A}{V_B} \right)^{-1} = \left(\frac{200 \text{ J}}{800 \text{ J}} \right)^{1/2} \quad \therefore \quad V_A = \frac{V_B}{2}$$

$$V_B = 2 V_A$$

We know from the problem statement $V_A + V_B = 2 \text{ m}^3 \quad \therefore$

$$V_A = \frac{2 \text{ m}^3 - V_A}{2} \Rightarrow 2V_A + V_A = 2 \text{ m}^3 \quad \therefore \quad V_A = \frac{2}{3} \text{ m}^3 \Rightarrow V_B = \frac{4}{3} \text{ m}^3$$

Problem 1: Continued

$$V_B = 2V_A, V_A = \frac{2}{3}m^3, V_B = \frac{4}{3}m^3, E_A = 200J, E_B = 400J$$

- (d) Does your result from part (c) make sense? If so, provide an intuitive explanation of your result. If not, explain why your result does not make sense.

Yes this result makes sense. Since more of the particles reside on the right hand side we should expect its values to be greater than A's. In fact, there is a two to one ratio of molecules and this translates to volume.

Problem 1: Review

Procedure:

- We are going to use the inverse temperature equation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}$$

for two separate systems

- Proceed to use the above equation and calculate $\frac{1}{T_{A,B}}$
- Set the inverse temperatures equal to one another
- Solve for E_B in terms of E_A
- – Consider the number of particles on each side and what you would expect the energy to be on each
- – We are going to calculate pressure using

$$P = T \left(\frac{\partial S}{\partial V} \right)_{E,N}$$

for each separate system

- Set T_A and T_B equal to one another and solve for a relationship of V_B in terms of V_A
- Use the statement for the total volume to determine values of V and E
- – Consider again the number of particles on each side

Key Concepts:

- When a system like this is in equilibrium it means that the temperatures are equal
- Because the left hand side has less particles on its side we can expect its energy to be less
- Once again when a system is in equilibrium it means that the temperatures are equal
- Because one side has more particles in it, it makes sense that the volumes and energies are of different value

Variations:

- We of course can be given a different entropy function
 - * This would change the functions that we take derivatives of and what not but not the over all procedure
- The values for the volume and energy can be different
 - * This would change the final answers but not how the final answer was calculated
- Since this is qualitative it cannot really change
- We essentially could be presented with the same changes as in part (a)
 - * We then would apply the same methodology to deal with those changes
- Once again this is qualitative and can't be changed unless a different question is asked

Problem 2:

Suppose that the Hamiltonian \mathcal{H} contains a term that is linear in the parameter λ ,

$$\mathcal{H}(\vec{p}, \vec{q}) = \mathcal{H}_0(\vec{p}, \vec{q}) + \lambda h(\vec{p}, \vec{q}). \quad (2)$$

There are many physical situations that can be described by this type of Hamiltonian. For example, if we consider N particles in an external gravitational field, then the parameter λ can be identified as the gravitational acceleration g and the function h would take the form

$$h = m \sum_{i=1}^N z_i. \quad (3)$$

For the purpose of this problem, we will leave λ and h unspecified. Show that the microcanonical average of the observable $h(\vec{p}, \vec{q})$ is given by

$$\langle h \rangle = -T \frac{dS}{d\lambda}. \quad (4)$$

The following will be helpful:

$$\frac{d}{d\lambda} \log f = \frac{df}{f} \quad \text{and} \quad \frac{d}{d\lambda} \theta(E - \mathcal{H}_0 - \lambda h) = -h \delta(E - \mathcal{H}_0 - \lambda h). \quad (5)$$

For the microcanonical ensemble, the entropy can be calculated by

$$S = k \log (\Sigma(E))$$

where we can calculate $\Sigma(E)$ with

$$\Sigma(E) = \frac{1}{h^{3N}} \int_{H < E} d^{3N}p d^{3N}q = \frac{1}{h^{3N}} \int_{\text{All space}} \Theta(E - H) d^{3N}p d^{3N}q$$

Applying our definition for H we see that,

$$\Sigma(E) = \frac{1}{h^{3N}} \int_{\text{All space}} \Theta(E - H_0 - \lambda h) d^{3N}p d^{3N}q$$

We now have an integral that can be solved. For the microcanonical ensemble we know the average expected value of the Hamiltonian is the total energy.

We now start evaluating $-T \frac{dS}{d\lambda}$,

$$-T \frac{dS}{d\lambda} = -kT \frac{d}{d\lambda} \log (\Sigma(E)) = \frac{-kT}{\Sigma(E)} \frac{d\Sigma(E)}{d\lambda} \quad (*)$$

We choose to solve for T ,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}, \quad \frac{1}{T} = k \cdot \frac{\partial \Sigma(E)}{\partial E} \cdot \frac{1}{\Sigma(E)} \quad \therefore T = \frac{\Sigma(E)}{k} \left(\frac{\partial E}{\partial \Sigma(E)} \right)_{V,N}$$

Problem 2: Continued

Putting this back into (*) we see that

$$-T \frac{dS}{d\lambda} = -\frac{K}{\sum(E)} \frac{\sum(E)}{K} \left(\frac{\partial E}{\partial \sum(E)} \right)_{V,N} \frac{d\sum(E)}{d\lambda} = -\frac{\partial E}{\partial \lambda}$$

We use the fact that $E = \langle H \rangle$, $H = H_0 - \lambda h$

$$-T \frac{dS}{d\lambda} = -\frac{\partial}{\partial \lambda} \langle H \rangle = -\frac{\partial}{\partial \lambda} \langle H_0 - \lambda h \rangle = -\cancel{\frac{\partial H_0}{\partial \lambda}} + \cancel{\frac{\partial}{\partial \lambda}} \lambda \langle h \rangle = \langle h \rangle \checkmark$$



Problem 2: Review

Procedure:

- To prove this we first use the equation for entropy

$$S = k \log (\Sigma(E))$$

where we can calculate the number of microstates with

$$\Sigma(E) = \frac{1}{(N!)h^{3N}} \int_{\mathcal{H} < E} d^{3N}p d^{3N}q = \frac{1}{(N!)h^{3N}} \int_{\tau} \int_{\tau} \Theta(E - \mathcal{H}) d^{3N}p d^{3N}q$$

- Use equation (4)

$$\langle h \rangle = -T \frac{dS}{d\lambda}$$

where S is calculated from the first equation

- Use the fact that $\langle \mathcal{H} \rangle = E$ and the equation can be proven

Key Concepts:

- Since we are in the microcanonical ensemble we can calculate the entropy with the first equation
- Using equation (4) and the fact that the average value of the Hamiltonian is the Energy and the equation can be proven

Variations:

- We could be given a completely different identity to prove
 - * We then would have to use different equations and what not to prove the relation

Problem 3:

Mathematically, there are quite a few similarities between the system considered here and the ideal gas system considered in class.

The position of a two-dimensional diatomic molecule with fixed distance between the two atoms can be described by the three co-ordinates (x, y, θ) , where x and y are the Cartesian co-ordinates of the center-of-mass of the molecule and θ gives the orientation of the molecular axis with respect to the x -axis. The conjugate momenta are denoted by (p_x, p_y, p_θ) . Physically, p_x and p_y are the linear center-of-mass momenta and p_θ is the angular momentum of the molecule about its center-of-mass. The energy ϵ of the molecule is

$$\epsilon = \frac{p_x^2 + p_y^2}{2m} + \frac{p_\theta^2}{2I}, \quad (6)$$

where I is the moment of inertia about the center-of-mass.

- (a) For a system of N non-interacting two-dimensional diatomic molecules confined to a two-dimensional area \mathcal{A} , use the microcanonical ensemble to calculate the entropy $S(N, E, \mathcal{A})$.

We know that for the microcanonical ensemble the entropy for our system is

$$S = k \log(\Sigma(E))$$

here the number of microstates is calculated with

$$\Sigma(E) = \frac{1}{N! h^{3N}} \int_{H \leq E} d^{3N} p d^{3N} q = \frac{1}{N! h^{3N}} \int_{\text{All sp.}} \int_{\text{All gd.}} \Theta(E - H) d^{3N} p d^{3N} q$$

Since our system is non interacting, this tells us that $E \rightarrow H$. Knowing this we can write the Hamiltonian as

$$H = \sum_i^N \frac{p_{x,i}^2}{2m} + \frac{p_{y,i}^2}{2m} + \frac{p_{\theta,i}^2}{2I} \quad (*)$$

We now wish to put $(*)$ into $\Sigma(E)$,

$$\Sigma(E) = \frac{1}{N! h^{3N}} \int d^{3N} q \int \Theta\left(E - \left(\sum_i^N \frac{p_{x,i}^2}{2m} + \frac{p_{y,i}^2}{2m} + \frac{p_{\theta,i}^2}{2I}\right)\right) d^{3N} p$$

We can make a transformation of variables to make our lives easier,

$$p_x = \sqrt{2m} u_x, \quad p_y = \sqrt{2m} u_y, \quad p_\theta = \sqrt{2I} u_\theta$$

$$d^N p_x = (2m)^{N/2} d^N u_x, \quad d^N p_y = (2m)^{N/2} d^N u_y, \quad d^N p_\theta = (2I)^{N/2} d^N u_\theta$$

Substituting this the equation for $\Sigma(E)$ becomes

$$\Sigma(E) = \frac{(2\pi\lambda)^N}{N! h^{3N}} \int \Theta\left(E - \left(\sum_i^N u_{x,i}^2 + u_{y,i}^2 + u_{\theta,i}^2\right)\right) d^{3N} p$$

Problem 3: Continued

We now make the substitution,

$$R_E^2 = \sum_i u_{x,i}^2 + u_{y,i}^2 + u_{z,i}^2$$

This simplifies to

$$\Sigma(E) = \frac{(2\pi A)^N}{N! h^{3N}} \int \Theta(E - R_E^2) R_E^{3N-1} dR_E$$

Evaluating this integral we find

$$\begin{aligned} \Sigma(E) &= \frac{(2\pi A)^N}{N! h^{3N}} \int \Theta(E - R_E^2) R_E^{3N-1} dR_E = \frac{(2\pi A)^N}{N! h^{3N}} \cdot E^{N/2} \frac{\pi^{3N/2}}{\Gamma(\frac{3N+1}{2})} \\ &= \frac{(2\pi A \sqrt{8m^2})^N}{N! h^{3N}} E^{N/2} C_{3N} \end{aligned}$$

Finally, the entropy for this system will be

$$S(N, E, A) = k \log \left(\frac{(2\pi A \sqrt{8m^2})^N}{N! h^{3N}} E^{N/2} C_{3N} \right)$$

- (b) Using the entropy, derive the equations of state of the system, i.e., the equations that give the pressure and the energy per particle as functions of the temperature and density.

We do this by using the equation

$$P = T \left(\frac{\partial S}{\partial A} \right)_{E,N}$$

We do this mathematically by

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

Therefore we have

$$\frac{\partial S}{\partial E} = \frac{3Nk}{\theta} \cdot \frac{1}{E}, \quad E = \left(\frac{N! h^{3N}}{(2\pi A \sqrt{8m^2})^N C_{3N}} \right)^{2/3N} e^{\theta S / 3Nk}, \quad \frac{\partial E}{\partial A} = \frac{2}{3} \frac{E}{A}$$

Problem 3: Continued

Therefore Pressure is

$$P = \frac{NkT}{A}$$

The temperature is

$$T = \left(\frac{\partial E}{\partial S} \right)_{V,N} = \frac{2}{3Nk} E \Rightarrow \frac{E}{N} = \frac{3}{2} kT$$

Therefore the energy per particle is

$$\frac{E}{N} = \frac{3}{2} kT$$

(c) Calculate the constant volume (actually, it is better to say constant area) specific heat per particle, defined through

$$C_V = \frac{1}{N} \left(\frac{\partial E(N, T, A)}{\partial T} \right)_{N,A} . \quad (7)$$

Note for part (b): In two dimensions, "pressure" is "force per unit length that is required to confine the particles to an area A ". It is given by a formula analogous to the three-dimensional formula, namely

$$P = T \left(\frac{\partial S}{\partial A} \right)_{N,E} . \quad (8)$$

Looking at part b.) , we know our energy to be

$$E(N, T, A) = \frac{3}{2} NkT$$

Calculating the Constant area specific heat we have,

$$C_A = \frac{1}{N} \left(\frac{\partial E(N, T, A)}{\partial T} \right)_{N,A} = \frac{1}{N} \left(\frac{\partial}{\partial T} \right)_{N,A} \frac{3}{2} NkT = \frac{1}{N} \cdot \frac{3}{2} Nk = \frac{3}{2} k \checkmark$$

Therefore we finally have,

$$C_A = \frac{3}{2} k$$

Problem 3: Review

Procedure:

- Since we are in the microcanonical ensemble we will calculate the entropy in the normal way with the micro state equation being

$$\Sigma(E) = \frac{1}{(N!)h^{3N}} \int_{\tau} \int_{\tau} \Theta(E - \mathcal{H}) d^{3N}p d^{3N}q$$

- Proceed to calculate the number of microstates by inserting the Hamiltonian

$$\mathcal{H} = \sum_i^N \frac{p_{x,i}^2}{2m} + \frac{p_{y,i}^2}{2m} + \frac{p_{\theta,i}^2}{2I}$$

into the above equation for $\Sigma(E)$

- Put $\Sigma(E)$ into S to find the entropy function
- Calculate the pressure with

$$P = T \left(\frac{\partial S}{\partial A} \right)_{E,N}$$

where we use A since we are working in 2D

- Calculate the energy per particle by first calculating the temperature with

$$\frac{1}{T} = \left(\frac{\partial E}{\partial S} \right)_{A,N}$$

and solve for E/N

- Proceed to calculate the constant volume specific heat with equation (7)

Key Concepts:

- Using the common definition for entropy we can calculate it by solving for the number of microstates $\Sigma(E)$
- We can calculate the pressure and energy per particle with the above equations
- The specific heat is calculated with equation (7)

Variations:

- We can be given a different Hamiltonian
 - * This would change how the integral evaluates for the number of microstates but would not change the procedure for finding S
- We could be asked to find a different value
 - * We then would use a different set of equations
- Same as part (b)

Problem 4:

For a system of N one-dimensional massless particles in a “one-dimensional box” of length L , calculate the entropy $S(N, E, L)$ of the system. Start by thinking about the energy of a single *massless* particle.

To evaluate the required N -dimensional integral, you might consider a recursive approach. Alternatively, you might look explicitly at $N = 1, 2, \dots$ to deduce a pattern.

The entropy for our system is

$$S = k \log(\Sigma(E))$$

We must calculate what $\Sigma(E)$ is with

$$\Sigma(E) = \frac{1}{N! h^N} \int \int \Theta(E - H) d^N p d^N q = \frac{L^N}{N! h^N} \int \Theta(E - H) d^N p$$

Putting the Hamiltonian into this we see ($H = \sum_i \epsilon_i p_i$)

$$\Sigma(E) = \frac{L^N}{N! h^N} \int \Theta(E - \sum_i \epsilon_i p_i) d^N p \quad \text{with } \epsilon_i = \epsilon(p_i)$$

This changes to

$$\Sigma(E) = \frac{L^N}{N! (ch)^N} \int \Theta(E - \sum_i \epsilon_i) d^N \epsilon = \frac{L^N}{N! (ch)^N} \int \dots \int \Theta(E - \epsilon_1 - \epsilon_2 - \dots) d\epsilon_1 d\epsilon_2 \dots$$

Using a prior solution for this integral we find

$$\int \Theta(E - \sum_i \epsilon_i) d^N \epsilon = \frac{E^N}{N!}$$

Using this the entropy will be

$$S = k \log \left(\left(\frac{\partial E L}{c h} \right)^N \frac{1}{(N!)^2} \right) = k \left[N \log \left(\frac{\partial E L}{c h} \right) + 2N(\log(N) - 1) \right]$$

So, our entropy finally is

$$S = k \left[N \log \left(\frac{\partial E L}{c h} \right) + 2N(\log(N) - 1) \right]$$

Problem 4: Review

Procedure:

- We calculate the entropy with the standard definition and number of microstates with

$$\Sigma(E) = \frac{1}{(N!)h^N} \int_{\tau} \int_{\tau} \Theta(E - \mathcal{H}) d^N p d^N q$$

for the 1D system

- Insert the Hamiltonian

$$\mathcal{H} = \sum_i c |p_i|$$

into the microstates equation

- This integral will simplify to

$$\Sigma(E) = \frac{L^N}{(N!)(hc)^N} \int_{\tau} \Theta(E - \sum_i \epsilon_i) d^N \epsilon$$

where the above integral evaluates to

$$\int_{\tau} \Theta(E - \sum_i \epsilon_i) d^N \epsilon = \frac{E^N}{N!}$$

- Using the above result for $\Sigma(E)$, put this into the entropy equation

Key Concepts:

- Because we are in 1D the microstates equation will have the q integral evaluate to L
- Because our particles are massless that is why $E = pc$
- After inserting the Hamiltonian into the microstates equation we can see that we have to use the common integral to evaluate the infinite sum

Variations:

- We can be given a different system where we are in 2D or 3D
 - * This would change what the Hamiltonian is and what the microstates equation will evaluate to