PHYS 521: Statistical Mechanics

Homework #4

Prakash Gautam

May 29, 2018

1. (a) A system is composed of two harmonic osicllators, each of natural frequency ω_0 and each having permissible energies $\left(n+\frac{1}{2}\right)\hbar\omega_0$, where n is any non-negative integer. How many microstates are availabel to the system? What is the netropy of the system.

Solution:

Let the first oscillator be in n_1 and the second be in n_2 state. The total energy of the system then is the sum of the energies of each one

$$\left(n_1+\frac{1}{2}\right)\hbar\omega_0+\left(n_2+\frac{1}{2}\right)\hbar\omega_0=n'\hbar\omega_0 \qquad \Rightarrow n_1+n_2+1=n'$$

The first of these oscillators can go to any one of n' states, but the second one is constrained to be in $n_2=n'-n_1-1$ state. So there is freedom of only one choice among n' states. So the total number of microstates is just

$$\Omega=\binom{n'}{1}=\frac{n'!}{1!(n'-1)!}=n'$$

So the entropy of the system is

$$S=k\ln(n')$$

In terms of energy of the system $E'=n'\hbar\omega_0$, the entropy becomes

$$S=k\ln\left(\frac{E'}{\hbar\omega_0}\right)$$

This is the required entropy of the system. □

(b) A second system is also composed of two harmonic oscillators, wach of natural frequencey $2\omega_0$. The total energy fo the system is $E''=n''\hbar\omega_0$, where n'' is even integer. How many microstates are available in the system? What is the entropy of the system?

Solution:

Let the first oscillator be in n_1 and the second be in n_2 state. The total energy of the system then is the sum of the energies of each one

$$\left(n_1+\frac{1}{2}\right)2\hbar\omega_0+\left(n_2+\frac{1}{2}\right)2\hbar\omega_0=n''\hbar\omega_0 \qquad \Rightarrow n_1+n_2+1=n''/2$$

Since n'' is even integer the number $m=n''/2$ is another integer. The first of these oscillators can go to any one of m states, but the second one is constrained to be in $n_2=m-n_1-1$ state. So the total number of microstates is just

$$\Omega=\binom{m}{1}=\frac{m!}{1!(m-1)!}=m=\frac{n''}{2}$$

So the entropy of the system is

$$S = k \ln \left(\frac{n''}{2} \right)$$

In terms of energy of the system $E'' = n''\hbar\omega_0$, the entropy becomes

$$S = k \ln \left(\frac{E''}{2\hbar\omega_0} \right)$$

This is the required entropy of the system. □

(c) What is the entropy fo the sytem composed of te two preceeding sybsystems (separated and enclosed bya totally restrictive wall)? Express the entropy as a function of E'' and E'.
Solution:
The total entropy of the system is just the sum of individual entropies so

$$S = S_1 + S_2 = k \ln \left(\frac{E}{\hbar\omega_0} \right) + k \ln \left(\frac{E''}{2\hbar\omega_0} \right) = k \ln \left(\frac{E'E''}{2\hbar^2\omega_0^2} \right)$$

This gives the total entropy of the system composed of two given subsystems. □

2. A system consists of three distinguishable molecules at rest, each of which has a quantized magnetic moment, which can have its z-component $+M, 0$ and $-M$. Show that there are 27 different possible states of the system; list them all, giving the total $z-$component M_i of the magnetic moment for each. Compute the entropy $S = -k \sum_i f_i \ln f_i$ of the system for the following priori porbabilities:

A:	-M	-M	-M	-M	-M	-M	-M	-M	-M	M	M	M	M	M	M	M	M	M	0	0	0	0	0	0	0	0	0
B:	-M	-M	-M	M	M	M	0	0	0	-M	-M	-M	M	M	M	0	0	0	-M	-M	-M	M	M	M	0	0	0
C:	-M	M	0	-M	M	0	-M	M	0	-M	M	0	-M	M	0	-M	M	0	-M	M	0	-M	M	0	-M	M	0
Sum:	-3M	-M	-2M	-M	M	0	-2M	0	-M	-M	M	0	M	3M	2M	0	2M	M	-2M	0	-M	0	2M	M	-M	M	0

(a) All 27 states are equally likely.
Solution:
If all states are equally likely then the probability of each state is $f_i = \frac{1}{27}$. So the total entropy of system is

$$S = -k \sum_i f_i \ln f_i = \sum_{i=1}^{27} \frac{1}{27} \ln \left(\frac{1}{27} \right) = k \ln 27$$

□

(b) Each state is equally likely for which the z-component M_z of the total magnetic moment is zero; $f_i = 0$ for all other states.
Solution:
There are six states where the total moment is zero. So the if all them are equally likely and the rest has probability $f_i = 0$ then we have

$$S = -k \sum_i f_i \ln f_i = \sum_{i=1}^{6} \frac{1}{6} \ln \left(\frac{1}{6} \right) = k \ln 6$$

This gives the required entropy. □

(c) Each state is equally likely for which $M_z = M$; $f_i = 0$ fro all other states.
Solution:
There are seven states where the total moment is M. So the if all them are equally likely and the rest has probability $f_i = 0$ then we have

$$S = -k\sum_i f_i \ln f_i = \sum_{i=1}^{7} \frac{1}{7}\ln\left(\frac{1}{7}\right) = k\ln 7$$

This gives the required entropy. □

(d) Each state is equally likely for which $M_2 = 3M$ $f_i = 0$ for all other states.
Solution:
There is just one state where the total moment is 3M. So the if all them are equally likely and the rest has probability $f_i = 0$ then we have

$$S = -k\sum_i f_i \ln f_i = \sum_{i=1}^{1} \frac{1}{1}\ln\left(\frac{1}{1}\right) = k\ln 1 = 0$$

This gives the required entropy. □

(e) The distribution for which S is maximum subject to the requirement that $\sum f_i = 1$ and the mean component $\sum_i f_i M_i = \gamma M$. Show that for this distribution

$$f_i = \frac{e^{(3M-M_i)\alpha}}{(1+x+x^2)^3}$$

where $x = e^{\alpha M}$(α begin Lagrange multiplier) and where the value fo x is determined by equation $\gamma = \frac{3(1-x^)2}{1+x+x^2}$. Compute x and S for $\gamma = 3$ and compare your answers.
Solution:
The entropy of the system is $S = -k\sum f_i \ln f_i$. We have to maximize this function subject to the constraints $\sum_i f_i = 1$ and $\sum_i f_i M_i = \gamma M$. Using lagranges multiplier technique the function to maximize the function $\frac{S}{k}$ is

$$F = \sum_i f_i \ln f_i - \alpha'\left(\sum_i f_i - 1\right) - \beta\left(\sum_i f_i M_i - \gamma M\right)$$

Differentiating with respect to f_j and setting equal to 0 we get

$$\begin{aligned}
\frac{\partial F}{\partial f_j} &= \sum_i \left[\frac{\partial f_i}{\partial f_j}\ln f_i + f_i \frac{\partial \ln f_i}{\partial f_j}\right] - \alpha'\sum_i \frac{\partial f_i}{\partial f_j} - \beta\sum M_i \frac{\partial f_i}{\partial f_j} \\
&= \sum_i \left[\delta_{ij}\ln f_i + f_i \frac{1}{f_j}\delta_{ij}\right] - \alpha'\sum_i \delta_{ij} - \beta\sum_i M_i\delta_{ij} \\
&= \ln f_j + \underbrace{1-\alpha'}_{\alpha} - \beta M_j
\end{aligned}$$

For maximum the derivative has to vanish, setting this derivative equal to zero we have

$$\ln f_i + \alpha - \beta M_j = 0 \qquad \Rightarrow f_i = e^{-\alpha+\beta M_i} \tag{1}$$

The sum of probability constraint and the average constraint are

$$\sum_i f_i = \sum_i e^{-\alpha+\beta M_i} = 1 \qquad \Rightarrow \qquad e^{\alpha} = \sum_i e^{\beta M_i}$$

The last expression on the right can be written as the sum over all the total moments M_i with multiplicity $g(M_i)$ as

$$e^{\alpha} = \sum_{M_i} g(M_i) e^{\beta M_i}$$

Looking at the configuration table we have that the multiplicity for each states is

$$g(3M) = g(-3M) = 1 \qquad g(-2M) = g(2M) = 3 \qquad g(-M) = g(M) = 6 \qquad g(0) = 7$$

Denoting $x = e^{\beta M}$ we have

$$\begin{aligned} e^{\alpha} &= g(-3M)x^{-3} + g(-2M)x^{-2} + g(-M)x^{-1} + g(0)x^0 + g(M)x + g(2M)x^2 + g(3M)x^3 \\ &= x^{-3} + 3x^{-2} + 6x^{-1} + 7 + 6x + 3x^2 + x^3 \\ &= x^{-3}\left(1 + 3x + 6x^2 + 7x^3 + 6x^4 + 3x^5 + x^6\right) \\ &= \frac{\left(1 + x + x^2\right)^3}{x^3} \end{aligned} \tag{2}$$

Substuting this back into (1) we get

$$f_i = \frac{x^3 e^{\beta M_i}}{\left(1 + x + x^2\right)^3} = \frac{e^{3\beta M + \beta M_i}}{\left(1 + x + x^2\right)^3} = \frac{e^{(3M + M_i)\beta}}{\left(1 + x + x^2\right)^3}$$

Now invoking the average moment constraint we get

$$\sum_i f_i M_i = \gamma M \qquad \Rightarrow \sum_i \frac{x^3 e^{(M_i)\beta}}{\left(1 + x + x^2\right)^3} M_i = \gamma M$$

Using $e^{\alpha} = \sum_i e^{\beta M_i}$ the expression becomes

$$\frac{x^3}{\left(1 + x + x^2\right)^3} \frac{\partial}{\partial \beta}\left[\sum_i e^{\beta M_i}\right] = \gamma M \qquad \Rightarrow \qquad \frac{x^3}{\left(1 + x + x^2\right)^3} \frac{\partial e^{\alpha}}{\partial \beta} = \gamma M$$

Since we have $x = e^{\beta M}$, this can be differentiated to get, $\frac{\mathrm{d}x}{\mathrm{d}\beta} = Mx$. And substuting e^{α} from (2) the above expression becomes

$$\begin{aligned} \frac{x^3}{\left(1 + x + x^2\right)^3} \frac{\partial}{\partial x}\left[\frac{\left(1 + x + x^2\right)^3}{x^3}\right] \frac{\partial x}{\partial \beta} &= \gamma M \\ \frac{x^3}{\left(1 + x + x^2\right)^3}\left[\frac{3(x^2 - 1)\left(1 + x + x^2\right)^2}{x^4}\right] Mx &= \gamma M \\ \frac{3(x^2 - 1)}{1 + x + x^2} &= \gamma \end{aligned}$$

Solving this equation for various values of γ we get a quadratic equation.

$$(\gamma - 3)x^2 + \gamma x + (\gamma + 3) = 0 \qquad \Rightarrow x = \frac{\gamma \pm \sqrt{3(12 - \gamma^2)}}{2(3 - \gamma)}$$

Specifically for $3 \geq \gamma \geq 0$ we have to choose the positive sign so

$$x = \frac{\gamma + \sqrt{3(12 - \gamma^2)}}{2(3 - \gamma)}$$

For the various values computed are

γ	x	S
0.0	1.0	-3.29584
1.0	1.69	-3.04037
3.0	-2.0	∞

This gives the various values of entropy for the given values of γ. □

3. Prove that for a system in cannonical ensemble

$$\left\langle \Delta E^3 \right\rangle = k^2 \left[T^4 \left(\frac{\partial C_v}{\partial T} \right)_V + 2T^3 C_v \right]$$

in particular, for ideal gas

$$\left\langle \left(\frac{\Delta E}{U} \right)^2 \right\rangle = \frac{2}{3N} \qquad \text{and} \left\langle \left(\frac{\Delta E}{U} \right)^3 \right\rangle = \frac{8}{9N^2}$$

Solution:
The expectation value of cube of fluctation of E from mean value can be written as

$$\begin{aligned} \left\langle \Delta E^3 \right\rangle = \left\langle (E - \langle E \rangle)^3 \right\rangle = \left\langle E^3 - 3E^2 \langle E \rangle + 3E \langle E \rangle^2 - \langle E \rangle^3 \right\rangle \\ = \left\langle E^2 \right\rangle - 3 \left\langle E^2 \right\rangle \langle E \rangle + 3 \langle E \rangle \left\langle E^2 \right\rangle - \langle E \rangle^3 \\ \left\langle \Delta E^3 \right\rangle = \left\langle E^2 \right\rangle - 3 \left\langle E^2 \right\rangle \langle E \rangle + 2 \langle E \rangle^3 \end{aligned} \tag{3}$$

In light of (3) The average energy of the system can be written as

$$U = \langle E \rangle = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} \tag{4}$$

Differentiating (3) with respect to β we get

$$\begin{aligned} \frac{\partial U}{\partial \beta} &= -\frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}} + \left[-\sum E_i e^{-\beta E_i} \frac{\sum E_i e^{-\beta E_i}}{-\left(\sum e^{-\beta E_i}\right)^2} \right] \\ &= -\frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}} + \left[\frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} \right]^2 \\ &= -\frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}} + U^2 \equiv \left\langle E^2 \right\rangle - \langle E \rangle^2 \end{aligned} \tag{5}$$

Differentiating (5) again with respect to β we get

$$\begin{aligned} \frac{\partial^2 U}{\partial \beta^2} &= \frac{\sum E_i^3 e^{-\beta E_i}}{\sum e^{-\beta E_i}} - \left[\frac{\sum E_i^2 e^{-\beta E_i}}{-\left(\sum e^{-\beta E_i}\right)^2} \cdot \sum -E_i e^{-\beta E_i} \right] + 2U \frac{\partial U}{\partial \beta} \\ &= \frac{\sum E_i^3 e^{-\beta E_i}}{\sum e^{-\beta E_i}} - \left[\frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}} \cdot \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} \right] + 2 \langle E \rangle \left[- \left\langle E^2 \right\rangle + \langle E \rangle^2 \right] \\ &= \left\langle E^3 \right\rangle - \left[\left\langle E^2 \right\rangle \langle E \rangle \right] - 2 \langle E \rangle \left\langle E^2 \right\rangle + 2 \langle E \rangle^3 \\ &= \left\langle E^3 \right\rangle - 3 \left\langle E^2 \right\rangle \langle E \rangle + 2 \langle E \rangle^3 \end{aligned} \tag{6}$$

Comparing (3) and (6) we get

$$\left\langle \Delta E^3 \right\rangle = \frac{\partial^2 U}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(\frac{\partial U}{\partial T} \frac{\partial T}{\partial \beta} \right) = \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial T} \frac{\partial T}{\partial \beta} \right) \frac{\partial T}{\partial \beta}$$

Since $\beta = \frac{1}{kT}$ the derivative $\frac{\partial T}{\partial \beta} = -kT^2$ and recocniging that $\frac{\partial U}{\partial T} = C_v$ we get

$$\left\langle \Delta E^3 \right\rangle = \frac{\partial}{\partial T} \left(-kT^2 C_v \right) \left(-kT^2 \right) = \left(kT^2 \frac{\partial C_v}{\partial T} + 2kTC_v \right) \left(kT^2 \right) = k^2 T^3 \left(T \frac{\partial C_v}{\partial T} + 2C_v \right)$$

This is the required expression for $\left\langle \Delta E^3 \right\rangle$. Using $U = 3NkT; U^2 = 9N^2 K^2 T^2$ and with $C_v = 3NK$, $\frac{\partial C_v}{\partial T} = 0$ and substutig back in the expression we get

$$\left\langle \left(\frac{\Delta E}{U} \right)^2 \right\rangle = \frac{2}{3N} \qquad \text{and} \left\langle \left(\frac{\Delta E}{U} \right)^3 \right\rangle = \frac{8}{9N^2}$$

These are the required values for ideal gas. □

4. Verify that, for ideal gas,

$$\frac{S}{Nk} = \ln\left(\frac{Q_1}{N}\right) + T\left(\frac{\partial \ln Q_1}{\partial T}\right)_P$$

Solution:
For an ideal gas, we assume that each molecule is free and so they dont exert force on each other, so the potential is zero. Also they have same momemtum in all directions which leads to the hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

The partition function for a single molecule is

$$Q_1 = \frac{1}{h^3}\int e^{-\beta H} d^3q d^3p = \frac{1}{h^3}\left[\int_V d^3q\right] \cdot \left[\int_{-\infty}^{\infty} e^{-\beta H} d^3p\right]$$

The integration of the space coordinates q_i just makes gives the volume of the system as it is independent of the momentum coordinates

$$Q_1 = \frac{V}{h^3}\int_{\infty}^{\infty} \exp\left[-\frac{1}{\beta}\left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}\right)\right] dp_x dp_y dp_z$$

Since the momentum in each direction can be considered to be the same and the parameter $\beta = \frac{1}{kT}$ we get

$$Q_1 = \frac{V}{h^3}\int_{\infty}^{\infty} \exp\left[-\frac{1}{kT}\left(\frac{p^2}{2m} + \frac{p^2}{2m} + \frac{p^2}{2m}\right)\right] dpdpdp = \frac{V}{h^3}\left[2\int_0^{\infty} \exp\left(-\frac{p^2}{2mkT}\right) dp\right]^3$$

This integral is just the gamma function and the integral is easily computed to be $\sqrt{\frac{mkT}{2}} \cdot \sqrt{\pi}$. So the partitiion function becomes

$$Q_1 = \frac{V}{h^3}\left[\sqrt{2mkT} \cdot \sqrt{\pi}\right]^3 = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

Also for ideal gas the relation $PV = NKT$ takig the various derivatives of the partition function we get

$$\ln\left(\frac{Q_1}{N}\right) = \ln\left[\frac{KT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

$$\left(\frac{\partial \ln Q_1}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\ln(NKT) - \ln P + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)\right]_P = \left[\frac{1}{T} - 0 + \frac{3}{2}\frac{1}{T}\right] = \frac{5}{2T}$$

Combining these two we get

$$\ln\left(\frac{Q_1}{N}\right) + T\left(\frac{\partial \ln Q_1}{\partial T}\right) = \ln\left[\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + \frac{5}{2}$$

The expression on the right is just $\frac{S}{Nk}$ □