PHYS 521: Statistical Mechanics

Homework #4

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1. Consider an $N-$dimensional sphere.

   (a) If a point is chosen at random in an $N-$ dimensional unit sphere, what is the probability of it falling inside the sphere of radius 0.99999999?

   Solution:

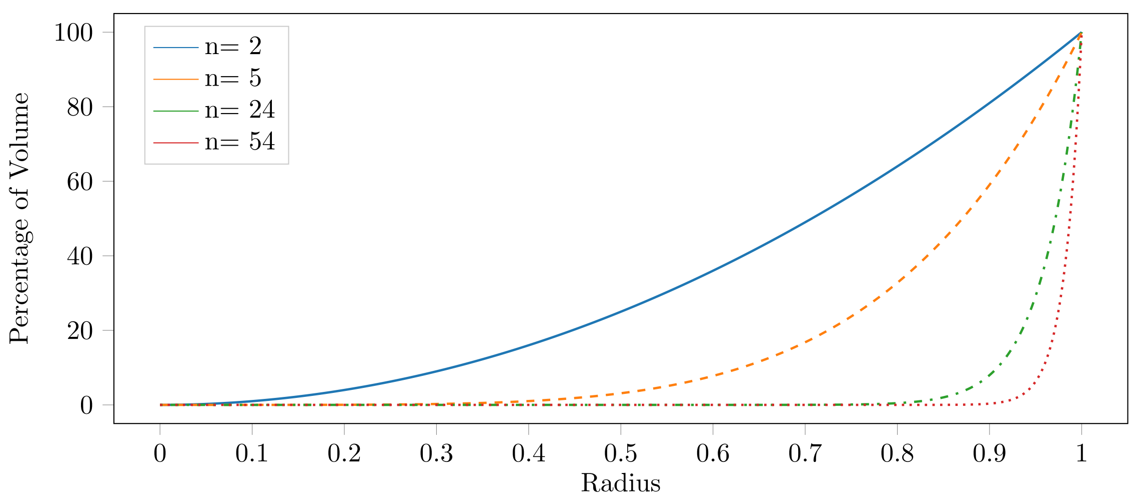
   The probability of a point falling inside a volume of radius r within a sphere of radius R is given by

$$p = \frac{V(r)}{V(R)} \tag{1}$$

   where $V(x)$ is the volume of sphere of radius x. The volume of N dimensional sphere of radius x is

$$V(x) = \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)} x^n$$

   The progression of volume for different radius.



   Using this in (1) we obtain

$$p = \left(\frac{r}{R}\right)^n \tag{2}$$

   This gives the probability of a particle falling within a radius r in a Ndimensional sphere of radius R. □

   (b) Evaluate your answer for $N = 3$ and $N = N_A$(the Avogadro Number)

   Solution:

   For $r = 0.999999$ and $N = 3$ and $N = N_A = 6.023 \times 10^{23}$ we get

$$p_3 = \left(\frac{0.999999}{1}\right)^3 = 0.999997000003 \qquad p_{N_A} = \left(\frac{0.999999}{1}\right)^{6.023\times10^{23}} = 0.0000000000000$$

The probability of a particle falling within the radius nearly 1 in higher two-dimensional sphere is vanishningly small. □

(c) What do these results say about the equivalence of the definitions of entropy in terms of either of the total phase space volume of the volume of outermost energy shell?
Solution:
Considering a phase space volume bounded by $E + \Delta$ where $\Delta \ll E$. The entropy of system bounded by the $E + \Delta$ and the outermost shell $\Sigma(E + \Delta) - \Sigma(E)$,

$$S_E = k \ln \left(\frac{\Sigma(E + \Delta)}{h^{3N}} \right), \qquad S_\Delta = k \ln \left(\frac{\Sigma(E + \Delta) - \Sigma(E)}{h^{3N}} \right)$$

Subtracting to see the differnce we get

$$S_E - S_\Delta = k \ln \left(1 - \frac{\Sigma(E)}{\Sigma(E + \Delta)} \right) \leq -\frac{\Sigma(E)}{\Sigma(E + \Delta)}$$

But for large dimension, the ration $\frac{\Sigma(E)}{\Sigma(E+\Delta)} \ll 0$. So we obtain

$$S_E - S_\Delta \approxeq 0 \qquad S_e \approxeq S_\Delta$$

This shows that the entropy interms of outrmost shell volume and the entire volume are almost the same. □

2. A harmonic oscillator has a Hamiltonian energy H related to its momentum P and its displacement q by the equation

$$p^2 + (M\omega q)^2 = 2MH$$

When $H = U$, a constant energy, sketch the path of the system in two-dimensional phase space.
Solution:
The phase space trajectory can be rearranged into

$$\frac{p^2}{\left(\sqrt{2MH}\right)^2} + \frac{q^2}{\left(\frac{1}{\omega}\sqrt{\frac{2H}{M}}\right)^2} = 1$$

This represents an ellipse in the phase space with semi major axis $a = \sqrt{2MH}$ and the semi minor axis $b = \frac{1}{\omega}\frac{2H}{M}$.

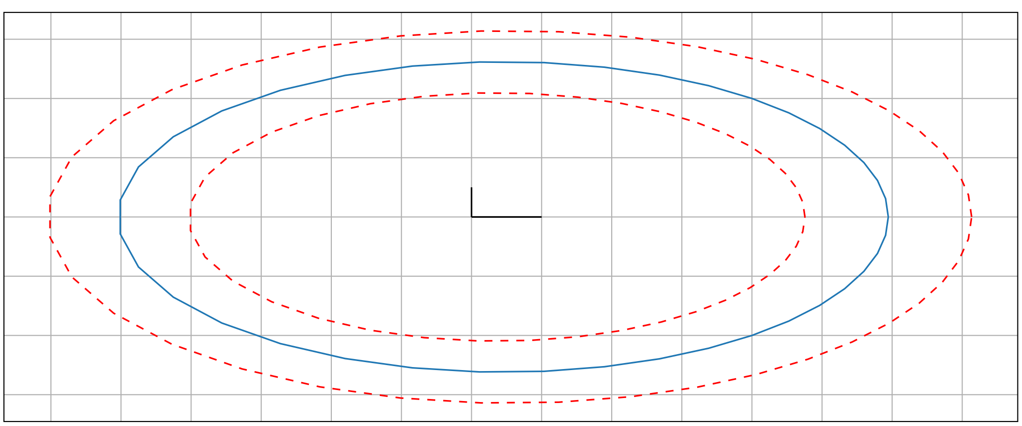


Figure 1: Phase plot of the system.

The volume of this 'volume' in phase space for constant energy $H = U$ is the area of ellipse which is

$$V = \pi ab = \pi\sqrt{2MU} \cdot \frac{1}{\omega}\sqrt{\frac{2U}{M}} = \frac{2\pi U}{\omega}$$

This gives the required phase space 'volume'. □

What volume of phase space does it enclose? In the case of N similar oscillators, which have the total energy U given by

$$\sum_{j=1}^{N} p^2 + \sum_{j=1}^{N} (M\omega q)^2 = 2MU$$

with additional coupling terms, too small to be included but large enough to ensure equipartition of energy, what is the nature of the path traversed by the system point?

(a) Show that the volume of the phase space "enclosed" by this path is $\frac{1}{N!}\left(\frac{2\pi U}{\omega}\right)^N$.
Solution:
Lets assume that the phase space volume of n harmonic oscillators which form a $2n$ dimensional ellipsoid be $C_n a^n b^n$ The coefficient can be found by usual method to be

$$C_n = \frac{\pi^n}{\Gamma(n+1)}$$

Noting that for this problem $a = \sqrt{2MU}$ and $b = \frac{1}{\omega}\sqrt{\frac{2U}{M}}$. The phase space volume becomes

$$\Sigma(U) = \frac{\pi^n}{\Gamma(n+1)} \left(\sqrt{2MU}\right)^n \left(\frac{1}{\omega}\sqrt{\frac{2U}{M}}\right)^n = \frac{1}{n!}\left(\frac{2\pi U}{\omega}\right)^n$$

This gives the required phase space volume. □

(b) Use the final result of (2a) to show that the entropy of N distinguishable harmonic oscillators, according to microcannonical ensemble is

$$S = Nk\left[1 + \ln\left(\frac{k}{\hbar\omega}\right)\right]$$

Solution:
The entropy of system by definition is

$$S = k\ln\left(\frac{\Sigma(U)}{h^n}\right) = k\ln\left(\frac{1}{n!}\left(\frac{2\pi U}{h\omega}\right)^n\right) = k\ln\left(\frac{1}{n!}\right) + nk\ln\left(\frac{U}{\hbar\omega}\right)$$

Using Sterling's approximation for we get

$$\ln\left(\frac{1}{n!}\right) = -n\ln n + n$$

Susbtuting this back in the entropy equation gives

$$S = nk - nk\ln n + nk\ln\left(\frac{U}{\hbar\omega}\right) = nk\left[1 + \ln\left(\frac{U}{n\hbar\omega}\right)\right]$$

But for the simpile harmonic oscillator the energy $U = nkT$ using this gives

$$S = nk\left[1 + \ln\left(\frac{kT}{\hbar\omega}\right)\right]$$

This is the require expression for the entropy of the system. □

3. Consider a system fo N particles in which the energy of each particle can assume two and only two distinct values 0 and $E(>0)$. Denote by n_0 and n_1 the occupation numbers of energy level 0 and E, respectively. The total energy of the system is U.

(a) Find the entropy of such a system.
Solution:
Since there are $N = n_0 + n_1$ particles the total ways in which n_0 particle can go into 0 energy level is given by

$$\Omega = {}^N C_{n_0} = \frac{N!}{n_0! n_1!}$$

So the entropy of system is

$$S = k \ln \Omega = k \ln \left(\frac{N!}{n_0! n_1!} \right) = k \ln N! - k \ln n_0! - k \ln n_1!$$

For large N this can be simplified by using Sterling's approximation as

$$S = k(N \ln N - N + n_0 - n_0 \ln n_0 + n_1 - n_1 \ln n_1) = kN \left[\ln \left(\frac{N}{n_0} \right) + \frac{n_1}{N} \ln \left(\frac{n_0}{n_1} \right) \right]$$

This can be rearranged to obtain

$$S = -k \left[n_0 \ln \left(\frac{n_0}{N} \right) + n_1 \ln \left(\frac{n_1}{N} \right) \right]$$

This is the required entropy of the system. □

(b) Find the most probable value of the n_0 and n_1 and find the mean square fluctuations of these quantities.
Solution:
For this system, the energy constraint is

$$n_0 \cdot 0 + n_1 \cdot E = U$$

And the total number constraint is

$$N = n_0 + n_1$$

We have to maximize the function

$$\frac{S'}{k} = S - \alpha(n_0 + n_1 - N) + \beta \left(n_0 \cdot 0 + n_1 \cdot E - U \right)$$

Differentiating with respect to each occupation number n_0 and n_1 and α and β. We get

$$\ln n_1 + \alpha = 0$$
$$\ln n_1 + \alpha + E = 0$$

Solving these the only possible value of n_1 is

$$n_1 = \frac{U}{E} \qquad n_0 = N - n_1 = N - \frac{U}{E}$$

These are the possible values of n_0 and n_1 the occupation numbers.

□

(c) What happens when a system of negative temperature is allowed to exchange heat with a system of positive temperature?
Solution:
When the system of negative temperature is allowed to exchange energy with the system of positive energy the energy flows from the system of negative temperature to the system of positive temperature. □

4. **(Huang 6.4)** Using the corrected entropy formula, work out the entropy of mixing for the case of different gases for the case of identical gases, thus showing explicitly that there is no Gibbs paradox any more. Find also internal energy, U, and chemical potential, μ, using the corrected entropy formula and corrected entropy formula. The latter is called 'Sackur-Tetrode equation'.

Solution:
By using gibbs correction the phase space volume should be divided by $N!$

$$\Sigma(E) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N C_{3N}R^{3N} = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N\left(\frac{2}{3N}\right)\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}(\sqrt{2ME})^{3N}$$

so the entropy function really becomes

$$S = k\ln\left((E)\right) = -N\ln N + N + Nk\ln\left[\frac{V}{h^3}R^3\right] + k\ln C_{3N}$$

Since N is a very large number we can make the better approximation of the Sterling approximation

$$\ln C_n = \ln\left(\frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)}\right) \approx \frac{n}{2}\ln\left(\frac{2\pi e}{n}\right)$$

Which yields us

$$\begin{aligned} S &= k\left[\frac{3N}{2}\ln\left(\frac{2\pi e}{3N}\right) + N\ln\left(\frac{V}{Nh^3} + \frac{3}{2}N\ln(2mE)\right)\right] \\ &= Nk\left[\ln\left(\frac{4\pi mE}{3}\right)^{3/2} + \ln\left(\frac{V}{Nh^3}\right)\right] + \frac{3Nk}{2} \\ &= Nk\ln\left(\frac{V}{N}u^{3/2}\right) + \frac{3}{2}Nk\left[\frac{5}{3} + \ln\left(\frac{4\pi m}{3h^2}\right)\right] \end{aligned}$$

This is the fundamental equation of the system shich can be always inverted to find our intensive parameters. So the internal energy becomes

$$U = \left(\frac{3}{4}\frac{N\hbar^2}{\pi mV}\right)^{3/2}\exp\left(\frac{2S-5}{3Nk}\right)$$

□