Problem 1.   Big numbers and the Shannon entropy

Here $N_A = 6.0 \times 10^{23}$

(a) Consider the approximation

$$e^S = 100000 \, e^{N_A} \simeq e^{N_A} \, . \tag{1}$$

What is the percent error in S made by this approximation?

(b) Consider the approximation

$$e^S = e^{N_A} + e^{1.001 N_A} \simeq e^{1.001 N_A} \, . \tag{2}$$

What is the percent error in S made by this approximation? It may be helpful to recall the Taylor series of the logarithm discussed in previous homework.

(c) Suppose that I have a subsystem which can be in three states, $s = 1, 2, 3$, with probabilities p_s. If I lay down N subsystems drawn from the probability distribution p_s (see Fig. 1 for two concrete examples), then for N large I will have approximately $N_1 \simeq N p_1$ subsystems in state 1, $N_2 \simeq N p_2$ subsystems in state two, and $N_3 \simeq N p_3$ subsystems in state three.

The total number of configurations with specified N_1, N_2 and N_3 that can be generated during this process is Ω. We study its logarithm $S \equiv \ln \Omega$. We showed in class and in prior homework that

$$S \equiv \ln \Omega = \ln \left(\frac{N!}{N_1! N_2! N_3!} \right) \simeq N S_1 \qquad S_1 \equiv \sum_s -p_s \ln p_s \tag{3}$$

where S_1 is known as the Shannon entropy. Thus Ω grows exponentially in the number of subsystems

$$\Omega \simeq e^{N S_1} \tag{4}$$

This formula generalizes straightforwardly to subsystems with more than three states.

  (i) What is the Shannon entropy for the probability distribution leading to Fig. 1(b))? How would this change if my subsystem had two states that are equally likely, or six states that are equally likely?

  (ii) Compute the Shannon entropy for the probability distribution leading to Fig. 1(a)[1]. By comparing Fig. 1(a) and Fig. 1(b) and with no more than a sentence or two, try to qualitatively explain why your result in (ii) is smaller than the case of equal probability discussed in (i).
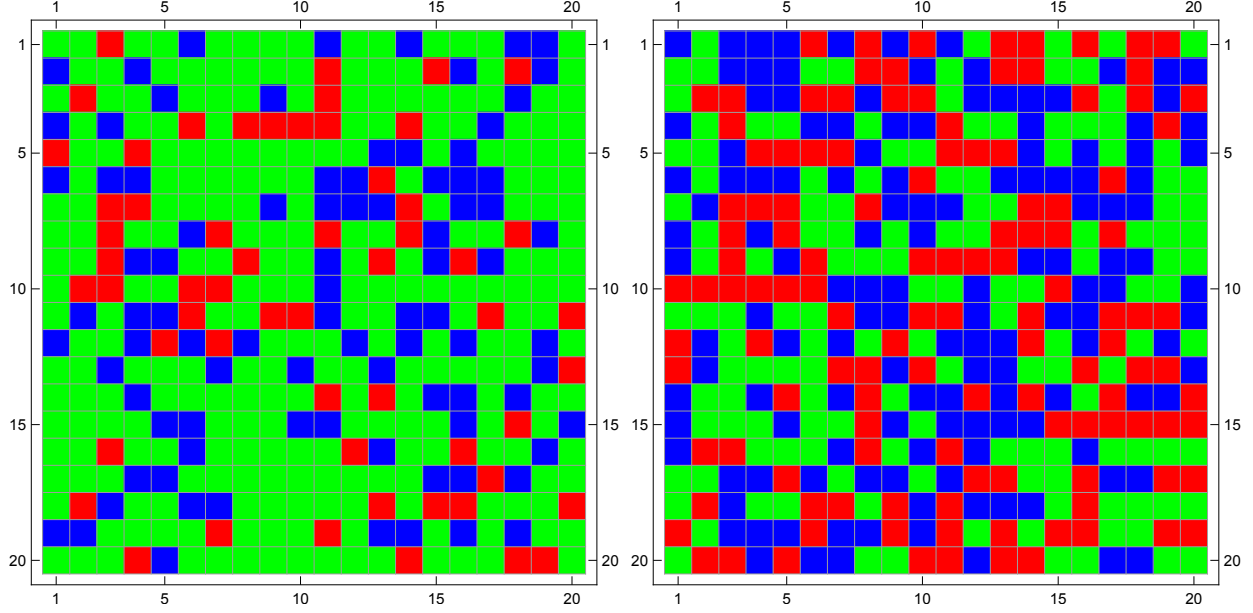
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[1] Answer: 0.9

Figure 1: (a) A configuration generated by laying down 400 subsystems, with probabilities $p_1 = \frac{1}{8}$ (red), $p_2 = \frac{2}{8}$ (blue) and $p_3 = \frac{5}{8}$ (green). $\ln \Omega$ is the number of ways you can shuffle around the red, blue, and green and get a new configuration. (b) A configuration generated by laying down 400 subsystems, with probabilities $p_1 = \frac{1}{3}$ (red), $p_2 = \frac{1}{3}$ (blue) and $p_3 = \frac{1}{3}$ (green).

(iii) Suppose that the subsystem actually describes two independent subsystems A and B, $p_s \equiv p_s^{AB}$. For instance, system A can be in states $a = 1, 2$ with probability p_a^A, and system B can be in states $b = 1, 2, 3$ with probability p_b^B. The probability to be in a state labeled by a and b is

$$p_s^{AB} = p_a^A p_b^B \tag{5}$$

where the six possible states labeled by $s \equiv (a, b)$ are

$$s \equiv (a, b) \in \{(1, 1), (1, 2), (1, 3), (2, 1), (2, 2), (2, 3)\} \tag{6}$$

Show that entropy of the total subsystem is the sum of the entropy of A and B

$$S_1^{AB} = S_1^A + S_1^B \tag{7}$$

where

$$S_1^A = \sum_a -p_a^A \ln p_a^A \qquad \text{and} \qquad S_1^B = \sum_b -p_b^B \ln p_b^B \tag{8}$$

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Solution

(a) We have
$$e^S = 100000\, e^{N_A} = e^{11.5} e^{N_A} = e^{11.5+N_A} \simeq e^{N_A}\,. \tag{9}$$

So we have
$$\% \text{ error} = 100.\times \frac{11.5}{N_A} \simeq 1.9\times 10^{-21} \tag{10}$$

(b) We have
$$e^S = e^{N_A} + e^{1.001 N_A} = e^{1.001 N_A}(1 + e^{-0.001 N_A}) \tag{11}$$

So taking the log, noting that $\ln(1+x) \simeq x$
$$S = \ln\left[e^{1.001 N_A}(1 + e^{-0.001 N_A})\right] = 1.001 N_A + \ln(1 + e^{-0.001 N_A}) \simeq 1.001 N_A + e^{-0.001 N_A} \tag{12}$$

Thus the percent error is
$$\% \text{ error} = 100\times \frac{e^{-0.001 N_A}}{1.001 N_A} \simeq e^{-0.001 N_A - 50.} \simeq e^{-0.001 N_A} = 10^{-2.6\times 10^{20}} \tag{13}$$

(c) (i) We have
$$S_1 = \sum_{i=1}^{3} -\frac{1}{3}\ln(\frac{1}{3}) = \ln(3) \simeq 1.099 \tag{14}$$

For two states we have $S_1 = \ln(2)$, while for six states we have $S_1 = \ln(6)$

(ii) For Fig. 1(a) we have
$$S_1 = -\frac{1}{8}\ln\frac{1}{8} - \frac{2}{8}\ln\frac{2}{8} - \frac{5}{8}\ln\frac{5}{8} = 0.900 \tag{15}$$

So the entropy is lower for the figure (a). Intuitively it is visually less random. If I add another green square this will not increase the number of configurations by much – in the limit it is all green adding another green square will still make it just one state. Adding a red square will increase the number of states, but the probability of this is very low.

(iii) We have
$$S_1^{AB} = \sum_{(a,b)} -p_s^{AB}\ln(p_s^{AB}) \tag{16}$$
$$= \sum_a \sum_b -p_a^A p_b^B \ln(p_a^A p_a^B) = \sum_a \sum_b -p_a^A p_b^B \ln(p_a^A) - p_a^A p_b^B \ln(p_b^B) \tag{17}$$
$$= \sum_a -p_a^A \ln(p_a^A) + \sum_b -p_b^B \ln(p_b^B) = S_1^A + S_1^B \tag{18}$$

In passing from the second to third line we have used
$$\sum_b p_b^B \times \text{some fcn of } p_a^A = 1 \times \text{some function of } p_a^A \tag{19}$$

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Problem 2.   Counting

Consider 400 atoms laid out in a row. Each atom can be in one of two states a ground state with energy 0 and an excited state with energy Δ. Assume that 100 of the atoms are excited, so the total energy is $U = 100\,\Delta$.

(a) Show that there are e^{225} configurations, called microstates, for this energy U. One microstate is shown below.

(b) Suppose that we make a partition of the energy so that the first 200 atoms have an energy of $80\,\Delta$, and the next 200 atoms have an energy of $20\,\Delta$ (see below). The terminology here is that we have specified the "macrostate" (i.e. the 80/20 split), leaving the microstates (exactly which atoms are up are down) to be further specified. How many microstates are there with this macrostate? One microstate for this 80/20 split macrostate is shown below[2]
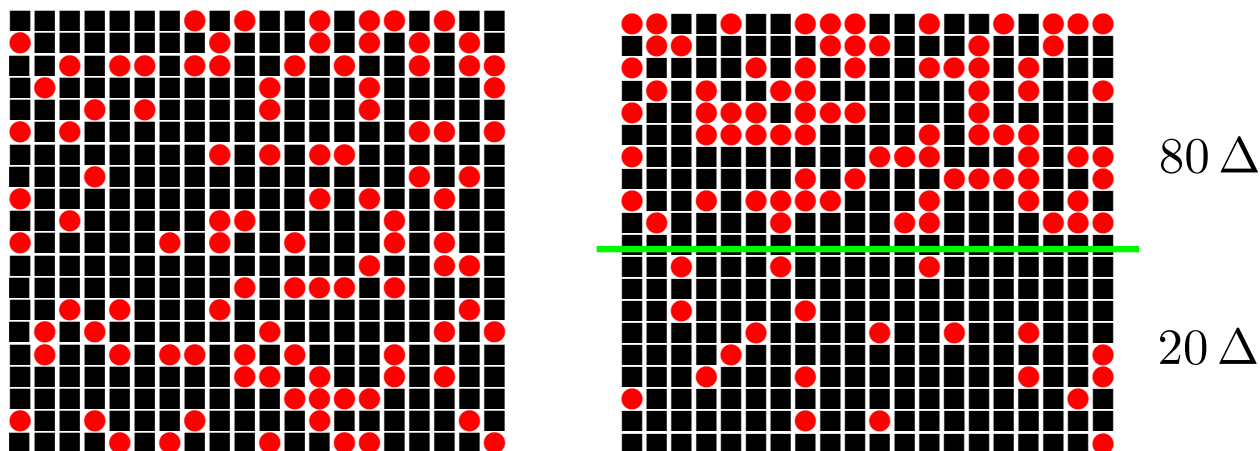

Figure 2: (a) A microstate where the energy is not partitioned. (b) a microstate where the energy is partitioned – 80% on the top and 20% on the bottom.

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[2]Answer: e^{200}.

Solution:

(a) We are making a selection of $N_1 \simeq 100$ atoms out of $N = 400$ to be excited, with $N_2 = 300$ not excited:

$$\ln \Omega = \ln \frac{N!}{N_1! N_2!} \simeq -N_1 \ln(N_1/N) - N_2 \ln(N_2/N) \tag{20}$$

$$= 400 \left[-\frac{1}{4} \ln(\frac{1}{4}) - \frac{3}{4} \ln(\frac{3}{4}) \right] \tag{21}$$

$$\simeq 225; \tag{22}$$

Thus there e^{225} microstates.

(b) The reasoning is similar for top half, we are selecting 80 out of 200. So for the first half

$$\ln \Omega_1 = \ln \frac{N!}{N_1! N_2!} \simeq -N_1 \ln(N_1/N) - N_2 \ln(N_2/N) \tag{23}$$

$$= 200 \left[-\frac{80}{200} \ln(\frac{80}{200}) - \frac{120}{200} \ln(\frac{120}{200}) \right] \tag{24}$$

$$\simeq 135.; \tag{25}$$

While the bottom half we are selecting 20 out of 200

$$\ln \Omega_1 = \ln \frac{N!}{N_1! N_2!} \simeq -N_1 \ln(N_1/N) - N_2 \ln(N_2/N) \tag{26}$$

$$= 200 \left[-\frac{20}{200} \ln(\frac{20}{200}) - \frac{180}{200} \ln(\frac{180}{200}) \right] \tag{27}$$

$$\simeq 65.; \tag{28}$$

So the total number of configurations is a product

$$\ln(\Omega_1 \Omega_2) = \ln(\Omega_1) + \ln(\Omega_2) \simeq 200. \tag{29}$$

Problem 3.   The Gamma function

The $\Gamma(x)$ function can be defined as[3]

$$\Gamma(x) \equiv \int_0^\infty \mathrm{d}u\, e^{-u} u^{x-1} = \int_0^\infty \frac{\mathrm{d}u}{u} e^{-u} u^x$$

(30)

A plot of $\Gamma(x)$ is shown below. $\Gamma(n)$ provides a unique generalization of $(n-1)!$ when n is not an integer and even negative or complex. It will come up a number of times in this course and is good to know.
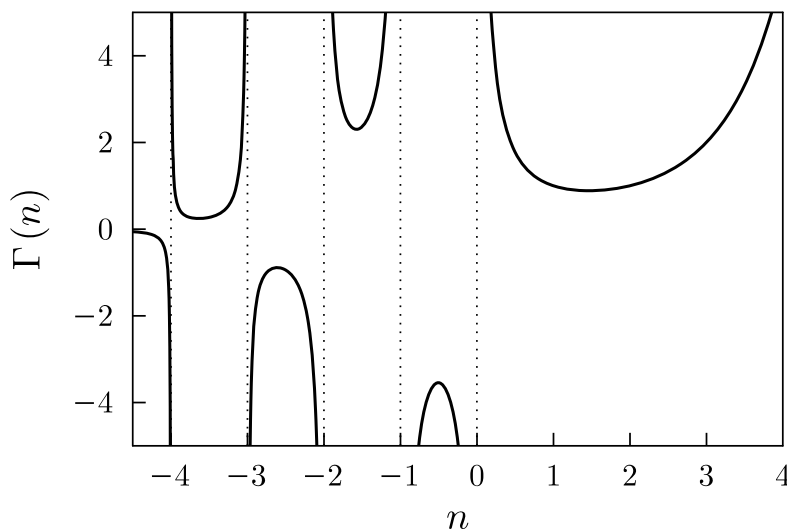

Fig. C.1 The gamma function $\Gamma(n)$ showing the singularities for integer values of $n \le 0$. For positive, integer n, $\Gamma(n) = (n-1)!$.

Figure 3: Appendix C.2 of our book

(a) Explain briefly why $\Gamma(n) = (n-1)!$ for n integer.

(b) Prove that $\Gamma(\frac{1}{2}) = \sqrt{\pi}$. *Hint:* try a substitution $y = \sqrt{u}$.

The following identity is needed below.

$$\Gamma(x+1) = x\Gamma(x)\,,$$

(31)

or

$$x! = x \cdot (x-1)!\,,$$

(32)

but now x is a real number, and $x!$ is defined by $\Gamma(x+1)$.

(c) (Optional. Dont turn in) Use integration by parts to prove the identity in Eq. (31).

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[3] I like to write $\Gamma(x) = \int_0^\infty \frac{\mathrm{d}u}{u} e^{-u} u^x$, which makes the x is more explicit. Also the measure du/u is invariant under a homogeneous rescaling, e.g. under change of variables $u \to u' = \lambda u$ we have $du'/u' = du/u$.

(d) Use the results of this problem to show that $\Gamma(\frac{7}{2}) = 15\sqrt{\pi}/8$. What is the result numerically? $7/2$ is between two integers. Show that $\Gamma(7/2)$ is between the appropriate factorials related to those two integers?

(e) The "area" (i.e. circumference) of a "sphere" in two dimensions (i.e. the circle) is $2\pi r$. The area of a sphere in three dimensions is $4\pi r^2$. A general formula for the area of the sphere in d dimensions is derived in the book is (the proof is simple, using what we know)

$$A_d(r) = \frac{2\pi^{d/2}}{(\frac{d}{2} - 1)!}r^{d-1} = \frac{2\pi^{d/2}}{\Gamma(d/2)}r^{d-1} \tag{33}$$

Show that this formula gives the familiar result for $d = 2$ and $d = 3$.

Gamma Fcn

(a)   According to the previous problem

$$n! = \int_0^\infty dx \, e^{-x} \, x^n$$

$$= \int_0^\infty \frac{dx}{x} \, e^{-x} \cdot x^{n+1} = \Gamma(n+1)$$

$$\underbrace{}$$

(b)   So   definition of $\Gamma(n+1)$

$$\Gamma(1/2) = \int_0^\infty \frac{dx}{x} \, e^{-x} \, x^{1/2}$$

- writing $y = \sqrt{x}$, $dy = \frac{1}{2} \frac{dx}{\sqrt{x}}$, or

$$\frac{2 \, dy}{y} = \frac{dx}{x}$$

- So we find

$$\Gamma(1/2) = 2 \int_0^\infty \frac{dy}{\cancel{y}} \, e^{-y^2} \cancel{y} = \int_{-\infty}^\infty dy \, e^{-y^2} = \sqrt{}$$

- This is a gaussian integral $\int_{-\infty}^\infty dx \, e^{-\frac{1}{2} \frac{x^2}{\sigma^2}} = \sqrt{2\pi\sigma^2}$,

with $\sigma^2 = 1/2$, so $\boxed{\Gamma(1/2) = \sqrt{\pi}}$

- Then (this is optional):

c) $$\Gamma(x) = \int_0^\infty \frac{du}{u} e^{-u} u^{x+1}$$

$$\Gamma(x+1) = \int_0^\infty du \, e^{-u} u^x$$

$$= \int_0^\infty - de^{-u} u^x$$

$$= e^{-u} u^x \Big|_0^\infty + \int_0^\infty e^{-u} x u^{x-1}$$

$$= 0 + x \int_0^\infty e^{-u} u^{x-1}$$

$$= x \, \Gamma(x)$$

d) So if $\Gamma(7/2) = \frac{5}{2} \Gamma\left(\frac{5}{2}\right) = \frac{5}{2} \cdot \frac{3}{2} \Gamma\left(\frac{3}{2}\right)$

$$= \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \Gamma\left(\frac{1}{2}\right)$$

$$= \frac{15}{8} \sqrt{\pi} \simeq 3.3$$

Now $3 < \frac{7}{2} < 4$ So we expect (and find)

$$2! < \frac{15\sqrt{\pi}}{8} < 3! \qquad \text{or} \qquad 2 < 3.3 < 6$$

e) $\quad A_2 = \dfrac{2\pi^{2/2}}{\Gamma(1)} r = 2\pi r$

$\quad A_3 = \dfrac{2\pi^{d/2}}{\Gamma(\frac{3}{2})} r^2 = \dfrac{2\pi^{3/2}}{\frac{1}{2}\Gamma(1/2)} r^2$

using $\Gamma(1/2) = \sqrt{\pi}$ we have:

$\quad A_3 = 4\pi r^2$

Problem 4.   Two State System

Consider an array of N atoms forming a medium at temperature T, with each atom possessing two energy states: a ground state with energy 0 and an excited state with energy Δ.

(a) Determine the temperature at which the number of excited atoms reaches $N/4$. You should find $kT = \Delta/\ln 3$.

(b) Calculate both the mean energy $\langle \epsilon \rangle$ and the variance of energy $\langle (\delta\epsilon)^2 \rangle$ for an individual atom. Your results should take the following form:

$$\langle (\delta\epsilon)^2 \rangle = \frac{\Delta^2 e^{-\beta\Delta}}{(1 + e^{-\beta\Delta})^2}$$

Additionally, create a graph depicting $\frac{\langle (\delta\epsilon)^2 \rangle}{(kT)^2}$ as a function of $\frac{\Delta}{kT}$.

(c) Suppose you have a collection of 16 such atoms (shown below). Calculate the average values of $\langle E \rangle$, $\langle (\delta E)^2 \rangle$ and $\langle E^2 \rangle$, where E represents the total energy of all 16 atoms. What approximately is the probability distribution for the energy E?
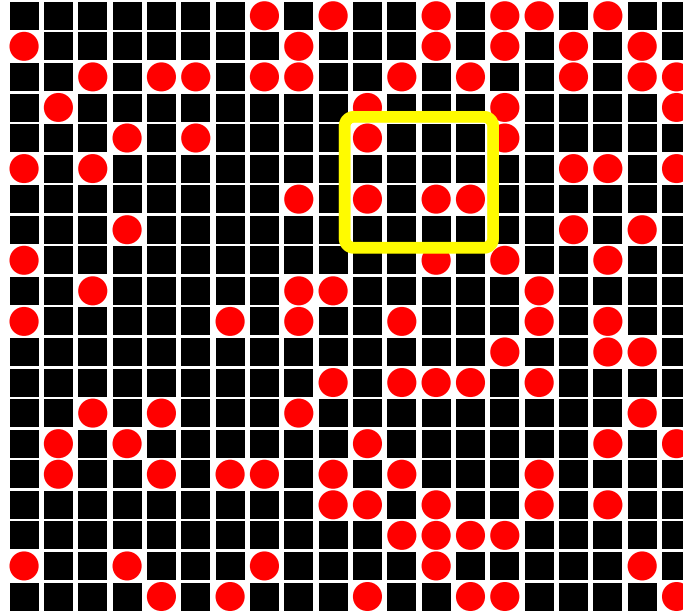
Solution

(a) The probability of being excited is (see lecture):

$$P_1 = \frac{e^{-\beta\Delta}}{Z} = \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} = \frac{1}{e^{\beta\Delta} + 1}.$$

We want to find T (or $\beta = 1/kT$) when $P_1 = \frac{1}{4}$. Simple algebra yields:

$$e^{\beta\Delta} + 1 = 4 \quad \Rightarrow \quad kT = \frac{\Delta}{\ln(3)}.$$

(b) The mean energy is:

$$\langle \epsilon \rangle = P_0 \cdot 0 + P_1 \cdot \Delta = P_1 \Delta = \frac{\Delta}{e^{\beta\Delta} + 1}.$$

The mean energy squared is:

$$\langle \epsilon^2 \rangle = P_0 \cdot 0^2 + P_1 \cdot \Delta^2 = P_1 \Delta^2 = \frac{\Delta^2}{e^{\beta\Delta} + 1}.$$

Thus, the variance is given by:

$$\langle (\delta\epsilon)^2 \rangle = \langle \epsilon^2 \rangle - \langle \epsilon \rangle^2 \tag{34}$$

$$= \frac{\Delta^2}{e^{\beta\Delta} + 1} \left(1 - \frac{1}{(e^{\beta\Delta} + 1)^2} \right) \tag{35}$$

$$= \frac{\Delta^2 e^{\beta\Delta}}{(e^{\beta\Delta} + 1)^2}, \tag{36}$$

which matches the problem statement after simplification.

(c) The energy is a sum:
$$E = \epsilon_1 + \ldots \epsilon_{16}.$$

The total energy behaves like a random walk, with each atom having $\epsilon = 0$ or $\epsilon = \Delta$. Since the atoms are identical:
$$\langle E \rangle = 16 \langle \epsilon \rangle.$$

Similarly, for a sum of statistically independent terms. The variance of a sum is the sum of the variances:
$$\langle (\delta E)^2 \rangle = 16 \langle (\delta\epsilon)^2 \rangle.$$

Utilizing the identical nature of the atoms, we find:

$$\langle E^2 \rangle = \langle E \rangle^2 + \langle (\delta E)^2 \rangle \tag{37}$$

$$= 16^2 \langle \epsilon \rangle^2 \left(1 + \frac{1}{16} \frac{\langle (\delta\epsilon)^2 \rangle}{\langle \epsilon \rangle^2} \right), \tag{38}$$

$$= 16^2 \langle \epsilon \rangle^2 \left(1 + \frac{e^{\beta\Delta}}{16} \right). \tag{39}$$

In the limit that 16 is very large the second term can often be neglected.

Since E is a *sum* of many (i.e. 16) *independent and identical* objects, we have that its probability distribution will tend to a Gaussian. This is the Central Limit Theorem. The probability of having energy between E and $E + \mathrm{d}E$ is

$$\mathrm{d}\mathscr{P} = \frac{1}{\sqrt{2\pi \langle \delta E^2 \rangle}} e^{-(E - \langle E \rangle)^2 / 2\langle \delta E^2 \rangle} \mathrm{d}E \tag{40}$$

where $\langle \delta E^2 \rangle$ and $\langle E \rangle$ were given above. In the notation we have adopted, the probability density is

$$\frac{\mathrm{d}\mathscr{P}}{\mathrm{d}E} = P(E) = \frac{1}{\sqrt{2\pi \langle \delta E^2 \rangle}} e^{-(E - \langle E \rangle)^2 / 2\langle \delta E^2 \rangle} \tag{41}$$

Problem 5. Classical distribution of two potentials

Consider a classical harmonic oscillator in one dimension interacting with a thermal environment. This could be for example a single atom attached to a large molecule in a gas.

The potential energy is $U = \frac{1}{2}kx^2$. At some point in physics we stop using the spring constant k (for some unknown reason) and start expressing k in terms of the oscillation frequency $\omega_0 = \sqrt{k/m}$. Thus, I will (usually) write the potential as

$$U = \frac{1}{2}m\omega_0^2 x^2 \tag{42}$$

The energy is the kinetic and potential energies and the Hamiltonian[4] is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{43}$$

The oscillator is in equilibrium with an environment at temperature T.

(a) What is the normalized probability density $P(x,p)$ to find the harmonic oscillator with position between x and $x+dx$ and momentum between p and $p+dp$, i.e. the probability per phase space volume for appropriate constants σ_x and σ_p:

$$d\mathscr{P}_{x,p} = P(x,p)\, dx\, dp. \tag{44}$$

Your final result for $P(x,p)$ should be a function of ω_0, p, x, m and kT, and should factorize into a Gaussian of x times a Gaussian of p with corresponding widths σ_x and σ_p. You can check your result by doing part (b). Check that your result for $P(x,p)$ is dimensionally correct.

Hint: Change variables to $u_1 = x/\sigma_x$ and $u_2 = p/\sigma_p$ before doing any integrals. You need to look at the integrand (like the exponent) and decide what the appropriate length scale, σ_x, and momentum scale, σ_p, are.

(b) What is the probability of finding position between x and $x + dx$ without regards to momentum
$$d\mathscr{P}_x = P(x)\, dx \tag{45}$$

(c) Compute the $\langle x^2 \rangle$ and $\langle p^2 \rangle$ by integrating over the probability distribution. (Don't do dimensionful integrals.)

You should find $\langle x^2 \rangle = kT/m\omega_0^2$ and $\langle p^2 \rangle = mkT$.

(d) The equipartition theorem precisely says that, for a classical system, the average of each quadratic form in the Hamiltonian is $\frac{1}{2}kT$. Are your results of the part (b) consistent with the equipartition theorem? Explain which quadratic forms you are talking about and how they determine $\langle x^2 \rangle$ and $\langle p^2 \rangle$. What is the average total energy of the oscillator and the number of "degrees of freedom" of the oscillator?

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[4]The Hamiltonian is the energy *as a function of* x and p.

(e) Now consider a classical particle of mass m in a potential of the form

$$V(x) = \alpha|x| \tag{46}$$

at temperature T.

Write down the Hamiltonian and determine the normalized probability density $P(x,p)$. You can check your result by doing the next part.

(f) What is the probability of finding position between x and $x + \mathrm{d}x$ without regards to momentum

$$\mathrm{d}\mathscr{P} = P(x)\,\mathrm{d}x \tag{47}$$

Sketch the $P(x)$ from part (a) and the $P(x)$ from (d).

(g) Determine the mean potential energy and mean kinetic energy of the particle in the potential by integrating over the coordinates and momenta. Does the equipartition theorem apply here? Explain.

You should find that the average potential energy and average kinetic energy are kT and $\frac{1}{2}kT$ respectively.

Solution

(a) The probability is

$$\mathrm{d}\mathscr{P}(x,p) = P(x,p)\mathrm{d}x\mathrm{d}p = Ce^{\mathcal{H}(x,p)/kT}\mathrm{d}x\mathrm{d}p \tag{48}$$

where C is a normalization constant. So since the Hamiltonian is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{49}$$

We have

$$\int P(x,p)\mathrm{d}x\mathrm{d}p = 1 \tag{50}$$

The integrals work out as follows:

$$1 = C\int e^{-p^2/2mkT}\mathrm{d}p \int e^{-m\omega_0^2/2kT}\mathrm{d}x \tag{51}$$

Here we recognize that we are dealing with two Gaussians one in x and one in p. The probability in momentum space is a Gaussian with width

$$\sigma_p^2 = mkT\,, \tag{52}$$

while the probability in coordinate space is Gaussian with width

$$\sigma_x^2 = kT/m\omega_0^2\,. \tag{53}$$

With this insight we have

$$1 = C\sqrt{2\pi\sigma_p^2}\sqrt{2\pi\sigma_x^2}\,. \tag{54}$$

So the probability distribution is

$$\mathrm{d}\mathscr{P}_{x,p} = \frac{e^{-x^2/2\sigma_x^2}}{\sqrt{2\pi\sigma_x^2}}\frac{e^{-p^2/2\sigma_p^2}}{\sqrt{2\pi\sigma_p^2}}\mathrm{d}x\,\mathrm{d}p \equiv P(x)\mathrm{d}x\,P(p)\mathrm{d}p \tag{55}$$

as quoted in the problem statement.

(b) Then if we do not care about momentum we make integrate over p

$$\mathrm{d}\mathscr{P}_x = \int_p \mathrm{d}\mathscr{P}_{x,p} = \int P(x,p)\mathrm{d}p \tag{56}$$

$$= P(x)\mathrm{d}x \underbrace{\int P(p)\mathrm{d}p}_{=1} \tag{57}$$

$$= \frac{e^{-x^2/2\sigma_x^2}}{\sqrt{2\pi\sigma_x^2}}\mathrm{d}x \tag{58}$$

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(c) Then it is straightforward to see that

$$\langle x^2 \rangle = \int P(x,p) x^2 \mathrm{d}x \mathrm{d}p \tag{59}$$

$$= \int P(x) x^2 \mathrm{d}x \cdot \int P(p) \mathrm{d}p \tag{60}$$

$$\langle x^2 \rangle = \int P(x) x^2 \mathrm{d}x \cdot 1 \tag{61}$$

$$= \sigma_x^2 \tag{62}$$

where in the last step we used the property of Gaussians proved in an earlier homework. Similarly

$$\langle p^2 \rangle = \int P(x,p) p^2 \mathrm{d}x \mathrm{d}p \tag{63}$$

$$= \int P(x) \mathrm{d}x \cdot \int P(p) p^2 \mathrm{d}p \tag{64}$$

$$\langle p^2 \rangle = 1 \cdot \int P(p) p^2 \mathrm{d}p \tag{65}$$

$$= \sigma_p^2 \tag{66}$$

(d) The equipartition theorem says that the mean of every quadratic form in the classical Energy (Hamiltonian) is $\frac{1}{2}kT$. So we see two quadratic forms in $\mathcal{H}(x,p)$:

$$\left\langle \frac{p^2}{2m} \right\rangle = \tfrac{1}{2}kT \tag{67}$$

$$\left\langle \frac{1}{2}m\omega_0^2 x^2 \right\rangle = \tfrac{1}{2}kT \tag{68}$$

So we should find

$$\langle p^2 \rangle = mkT \tag{69}$$

while

$$\langle x^2 \rangle = \frac{kT}{m\omega_0^2} \tag{70}$$

This is consistent with part (b).

(e) If the potential is

$$\mathcal{H}(x,p) = \alpha|x| + \frac{p^2}{2m} \tag{71}$$

Then the probability distribution is as before

$$\mathrm{d}\mathscr{P}(x,p) = P(x,p)\,\mathrm{d}x\mathrm{d}p = Ce^{\mathcal{H}(x,p)/kT}\mathrm{d}x\mathrm{d}p \tag{72}$$

Since Hamiltonian is a sum of two parts – a part that depends only on x, and a part that depends only p – let us anticipate that the probability takes the form

$$\mathrm{d}\mathscr{P}_{x,p} = P(x)\mathrm{d}x\, P(p)\mathrm{d}p = P(x)\mathrm{d}x\, \frac{e^{-p^2/2\sigma_p^2}}{\sqrt{2\pi\sigma_p^2}} \cdot \tag{73}$$

Here we have recognized that the momentum space part $\propto e^{-p^2/2mkT}$ is the same as in the previous parts, i.e. the same probability distribution

$$P(p) \propto e^{-p^2/2mkT} \tag{74}$$

Here the position space probability distribution is

$$P(x)dx = Ce^{-\alpha|x|/kT}dx \tag{75}$$

with C to be determined. The normalization constant can be determined from

$$\int P(x)dx = \int_{-\infty}^{\infty} Ce^{-\alpha|x|/kT}dx = 1 \tag{76}$$

We can do this integral by integrating from $x \in [0,\infty]$ so

$$1 = 2\int_0^{\infty} dx\, Ce^{-\alpha x/kT} = \frac{2kTC}{\alpha} \tag{77}$$

So

$$P(x)dx = \frac{kT}{2\alpha}e^{-\alpha|x|/kT}dx \tag{78}$$

(f) The probability takes the form

$$d\mathscr{P}_{x,p} = P(x)dx\, P(p)\, dp \tag{79}$$

So to find the probability of x by itself we integrate over momentum

$$d\mathscr{P}_x = \int_p d\mathscr{P}_{x,p} = P(x)dx \int P(p)dp = P(x)dx \tag{80}$$

with $P(x)$ given in Eq. (78). To make a graph we define a length $\ell_0 \equiv kT/\alpha$, so

$$P(x)dx = e^{-|x|/\ell_0}\frac{dx}{\ell_0} \tag{81}$$

where as for the Gaussian we have

$$P(x)dx = \frac{e^{-x^2/2\sigma^2}}{\sqrt{2\pi}}\frac{dx}{\sigma_x} \tag{82}$$

The two distributions are shown in Fig. 4

(g) The mean potential energy is

$$\langle PE \rangle = \int P(x)dx \cdot \alpha|x| \tag{83}$$

Again to evaluate the integral we integrate for $x \in [0,\infty]$ yielding

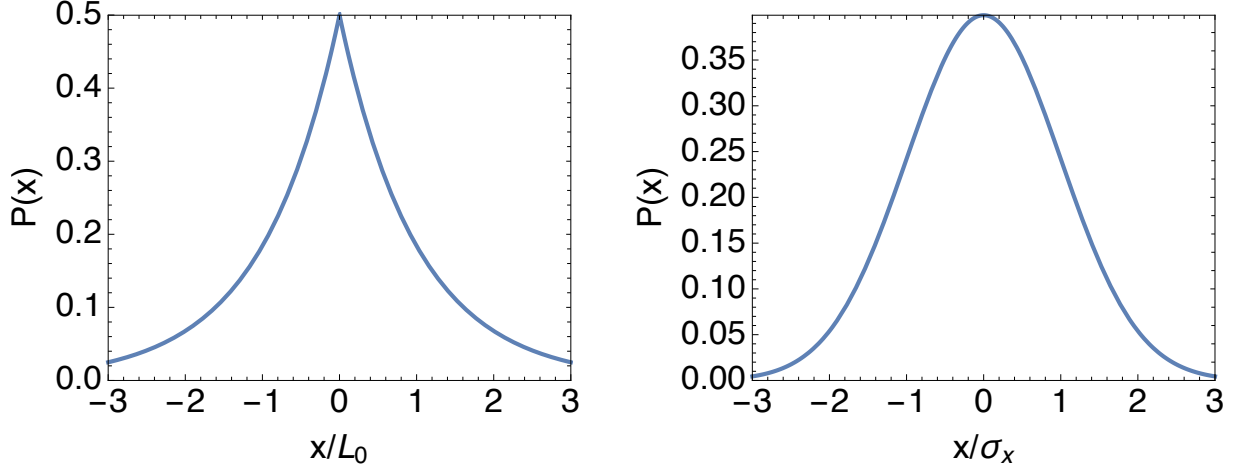$$\langle PE \rangle = 2\int_0^{\infty} \frac{kT}{2\alpha}e^{-\alpha x/kT}dx \cdot \alpha x \tag{84}$$

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Figure 4: The probability density for two potentials.

Now we should change to a dimensionless x, $u = x/\ell_0$ for some ℓ_0. Looking at the exponent we identify a characteristic length scale $\ell_0 \equiv kT/\alpha$. Then the integral takes the form

$$\langle PE \rangle = \alpha \ell_0 \int_0^\infty \frac{\mathrm{d}x}{\ell_0} e^{-x/\ell_0} \frac{x}{\ell_0} \tag{85}$$

Now we use $\int_0^\infty du\, e^u u^n = n!$, yielding finally

$$\langle PE \rangle = kT \tag{86}$$

The kinetic energy is the same as in the previous item

$$\langle KE \rangle = \tfrac{1}{2} kT \tag{87}$$

Discussion: The kinetic energy is a quadratic form in the Hamiltonian, $p^2/2m$. If the dynamics are classical, the equipartition theory states that the average of each quadratic form in the Hamiltonian is $\frac{1}{2} kT$. Thus, $\langle KE \rangle = \frac{1}{2} kT$. The potential energy $\alpha |x|$ is not a quadratic form, so the equipartition theory doesn't apply to it. We have found that $\langle PE \rangle$ is proportional to kT, while a misguided use of the equipartition theorem would incorrectly give $\langle PE \rangle = \frac{1}{2} kT$. Nevertheless the equipartition gives a reasonable order of magnitude estimate for the average of independent terms in a classical Hamiltonian (like $\langle PE \rangle$). The equipartition theorem can be very wrong (i.e. not even a good estimate) if the dynamics is not classical.