Problem 1. 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 below¹

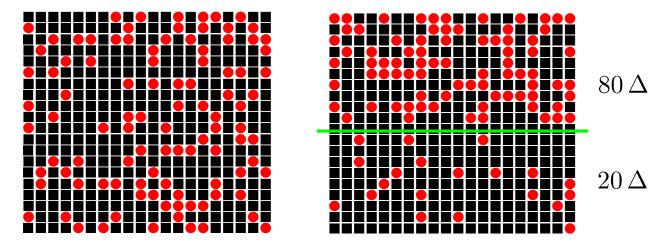


Figure 1: (a) A microstate where the energy is not partitioned. (b) a microstate where the energy is partitioned -80% on the top and 20% on the bottom.

¹Answer: 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:

$$\ln \Omega = \ln \frac{N!}{N_1! N_2!} \simeq -N_1 \ln(N_1/N) - N_2 \ln(N_2/N)$$
 (1)

$$=400\left[-\frac{1}{4}\ln(\frac{1}{4}) - \frac{3}{4}\ln(\frac{3}{4})\right] \tag{2}$$

$$\simeq 225;$$
 (3)

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

$$\ln \Omega_1 = \ln \frac{N!}{N_1! N_2!} \simeq -N_1 \ln(N_1/N) - N_2 \ln(N_2/N)$$
(4)

$$=200\left[-\frac{80}{200}\ln(\frac{80}{200}) - \frac{120}{200}\ln(\frac{120}{200})\right]$$
 (5)

$$\simeq 134.;$$
 (6)

While the bottom half we are selecting 20 out of 200

$$\ln \Omega_1 = \ln \frac{N!}{N_1! N_2!} \simeq -N_1 \ln(N_1/N) - N_2 \ln(N_2/N)$$
 (7)

$$=200\left[-\frac{20}{200}\ln(\frac{20}{200}) - \frac{180}{200}\ln(\frac{180}{200})\right] \tag{8}$$

$$\simeq 65.;$$
 (9)

So the total number of configurations is a product

$$\ln(\Omega_1 \Omega_2) = \ln(\Omega_1) + \ln(\Omega_2) \simeq 199 \tag{10}$$

Problem 2. The Gamma function

The $\Gamma(x)$ function can be defined as²

$$\Gamma(x) = \int_0^\infty du e^{-u} u^{x-1}$$
(11)

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

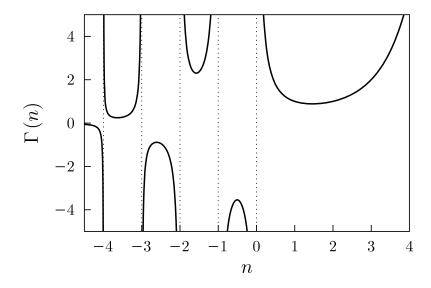


Fig. C.1 The gamma function $\Gamma(n)$ showing the singularities for integer values of $n \leq 0$. For positive, integer n, $\Gamma(n) = (n-1)!$.

Figure 2: 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.

$$\Gamma(x+1) = x\Gamma(x), \qquad (12)$$

or

$$x! = x \cdot (x-1)!, \tag{13}$$

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. (12).

- (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)

$$A_d(r) = \frac{2\pi^{d/2}}{(\frac{d}{2} - 1)!} r^{d-1} = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1}$$
(14)

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

According to the previous problem $\int dx e^{-x} x^{n+1} = \prod (n+1)^{n}$ definition of M(n+1) $\Gamma(1/2) = \int_{-x}^{x} dx e^{-x} x^{1/2}$ $y = \sqrt{x}$ dy = 1 dx or $2\sqrt{x}$ 2 dy = dx So we find oo J'dy e-y2 4 = J dy e-y2 = 1 gaussian integral $\int dx e^{-\frac{1}{2}x^2} = \sqrt{2115^2}$ This $\Gamma(V_2) = \sqrt{\Pi}$ with 02 = 1/2

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

$$= e^{-u} \times | + \int_{0}^{\infty} e^{-u} \times u^{\times -1}$$

$$= 0.+ \times \int_{0}^{\infty} e^{-u} u^{\chi-1}$$

[d) So if
$$\Gamma(7/2) = 5\Gamma(5) = 5.3\Gamma(3)$$

$$= \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, \frac{\Gamma(\frac{1}{2})}{2}$$

$$= 15 \sqrt{\pi} \approx 3.3$$

$$2! < 15 \sqrt{11} < 3!$$
 or $2 < 3.3 < 6$

$$A_3 = 2 \pi^{3/2} r^2 = 2\pi^{3/2} r^2$$

$$\frac{1}{\Gamma(3)} \Gamma(1/2)$$

using [1/2] = To we have &

Problem 3. Two State System

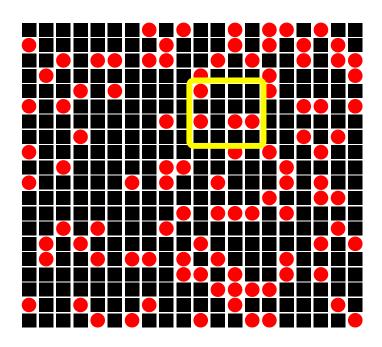
Consider an array of N atoms forming a medium at temperature T, with each atom possessing two energy states: a ground state with energy 0 and an excited state with energy Δ .

- (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:

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

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?



(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:

$$\left\langle (\delta \epsilon)^2 \right\rangle = \left\langle \epsilon^2 \right\rangle - \left\langle \epsilon \right\rangle^2 \tag{15}$$

$$= \frac{\Delta^2}{e^{\beta\Delta} + 1} \left(1 - \frac{1}{(e^{\beta\Delta} + 1)^2} \right) \tag{16}$$

$$=\frac{\Delta^2 e^{\beta \Delta}}{(e^{\beta \Delta} + 1)^2},\tag{17}$$

which matches the problem statement after simplification.

(c) The energy is a sum:

$$E = \epsilon_1 + \dots \epsilon_{16}$$
.

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:

$$\langle E^2 \rangle = \langle E \rangle^2 + \langle (\delta E)^2 \rangle$$
 (18)

$$=16^{2} \langle \epsilon \rangle^{2} \left(1 + \frac{1}{16} \frac{\langle (\delta \epsilon)^{2} \rangle}{\langle \epsilon \rangle^{2}}\right). \tag{19}$$

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

Problem 4. 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

$$U = \frac{1}{2}m\omega_0^2 x^2 \tag{20}$$

The energy is the kinetic and potential energies and the Hamiltonian³ is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{21}$$

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 volume⁴

$$d\mathscr{P}_{x,p} = P(x,p) \, dx \, dp \tag{23}$$

Your final result for P(x, p) should be a function of ω_0, p, x, m and kT. 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

$$d\mathscr{P}_x = P(x) dx \tag{24}$$

(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 $\langle p^2 \rangle = mkT$.

$$d\mathscr{P}_{x,p} = \frac{e^{-x^2/2\sigma_x^2}}{\sqrt{2\pi\sigma_x^2}} \frac{e^{-p^2/2\sigma_p^2}}{\sqrt{2\pi\sigma_p^2}} dx dp$$
 (22)

for appropriate constants σ_x and σ_p

³The Hamiltonian is the energy as a function of x and p.

⁴You should find that the probability takes the form

- (d) The equipartition theorem precisely says that, for a classical system, the average of each quadratic form in the Hamiltonian is $\frac{1}{2}kT$. The quadratic forms here are the kinetic energy $p^2/2m$, and the potential energy, $m\omega_0^2x^2/2$. Are your results of the part (b) consistent with the equipartition theorem. What is the average total energy of the oscillator and the number of "degrees of freedom" of the oscillator?
- (e) Now consider a classical particle of mass m in a potential of the form

$$V(x) = \alpha |x| \tag{25}$$

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 + dx without regards to momentum

$$d\mathscr{P} = P(x) dx \tag{26}$$

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

$$d\mathscr{P}(x,p) = P(x,p)dxdp = Ce^{\mathcal{H}(x,p)/kT}dxdp$$
(27)

where C is a normalization. So since the Hamiltonian is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2$$
 (28)

We have

$$\int P(x,p)\mathrm{d}x\mathrm{d}p = 1 \tag{29}$$

The integrals work out as follows

$$1 = C \int e^{-p^2/2mkT} dp \int e^{-m\omega_0^2/2kT} dx$$
(30)

Here we recognize that we are dealing with two Gaussians. The probability in momentum space is a gaussian with width

$$\sigma_p^2 = mkT \tag{31}$$

while the probability in coordinate space is gaussian with with

$$\sigma_x^2 = kT/m\omega_0^2 \tag{32}$$

With this insight we have

$$1 = C\sqrt{2\pi\sigma_p^2}\sqrt{2\pi\sigma_x^2} \tag{33}$$

So the probability distribution is

$$d\mathscr{P}_{x,p} = \frac{e^{-x^2/2\sigma_x^2}}{\sqrt{2\pi\sigma_x^2}} \frac{e^{-p^2/2\sigma_p^2}}{\sqrt{2\pi\sigma_p^2}} dx dp \equiv P(x) dx P(p) dp$$
(34)

as quoted in the problem statement.

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

$$d\mathscr{P}_x = \int_p d\mathscr{P}_{x,p} = \int P(x,p)dp \tag{35}$$

$$=P(x)dx \underbrace{\int P(p)dp}_{=1}$$

$$=\frac{e^{-x^2/2\sigma_x^2}}{\sqrt{2\pi\sigma_x^2}}dx$$
(36)

$$=\frac{e^{-x^2/2\sigma_x^2}}{\sqrt{2\pi\sigma_x^2}}\mathrm{d}x\tag{37}$$

(c) Then it is straightforward to see that

$$\langle x^2 \rangle = \int P(x, p) x^2 dx dp$$
 (38)

$$= \int P(x)x^2 dx \cdot \int P(p)dp \tag{39}$$

$$\langle x^2 \rangle = \int P(x)x^2 dx \cdot 1 \tag{40}$$

$$=\sigma_x^2 \tag{41}$$

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

$$\langle p^2 \rangle = \sigma_p^2 \tag{42}$$

(d) The equipartition theorem says that the mean of every quadratic form in the classical Energy (Hamiltonian) is $\frac{1}{2}kT$. So

$$\left\langle \frac{p^2}{2m} \right\rangle = \frac{1}{2}kT \tag{43}$$

$$\left\langle \frac{1}{2}m\omega_0^2 x^2 \right\rangle = \frac{1}{2}kT \tag{44}$$

So we should find

$$\langle p^2 \rangle = mkT \tag{45}$$

while

$$\left\langle x^2 \right\rangle = \frac{kT}{m\omega_0^2} \tag{46}$$

This is consistent with part (b).

(e) If the potential is

$$\mathcal{H}(x,p) = \alpha|x| + \frac{p^2}{2m} \tag{47}$$

Then the probability distribution is as before

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

Since Hamiltonian is a sum into a part that depends only on x and a part that depends only p. Let us anticipate that the probability takes the form

$$d\mathscr{P}_{x,p} = P(x)dx P(p)dp = P(x)dx \frac{e^{-p^2/2\sigma_p^2}}{\sqrt{2\pi\sigma_p^2}}$$
(49)

where we have recognized that the momentum space part of the previous item is the same here, i.e. the same probability distribution

$$P(p) \propto e^{-p^2/2mkT} \tag{50}$$

Here the position space probability distribution is

$$P(x)dx = Ce^{-\alpha|x|/kT}dx (51)$$

The normalization constant can be determined from

$$\int P(x)dx = \int_{-\infty}^{\infty} Ce^{-\alpha|x|/kT}dx = 1$$
 (52)

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

$$1 = 2 \int_0^\infty dx \, C e^{-\alpha x/kT} = \frac{2kTC}{\alpha} \tag{53}$$

So

$$P(x)dx = \frac{kT}{2\alpha}e^{-\alpha|x|/kT}$$
(54)

(f) The probability takes the form

$$d\mathscr{P}_{x,p} = P(x)dx P(p) dp \tag{55}$$

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

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

with P(x) given in Eq. (54)

(g) The mean potential energy is

$$\langle PE \rangle = \int P(x) dx \cdot \alpha |x|$$
 (57)

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

$$\langle PE \rangle = 2 \int_0^\infty \frac{kT}{2\alpha} e^{-\alpha x/kT} dx \cdot \alpha x$$
 (58)

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

$$\langle PE \rangle = \alpha \ell_0 \int_0^\infty \frac{\mathrm{d}x}{\ell_0} e^{-x/\ell_0} \mathrm{d}x \frac{x}{\ell_0}$$
 (59)

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

$$\langle PE \rangle = kT \tag{60}$$

The kinetic energy is the same as in the previous item

$$\langle KE \rangle = \frac{1}{2}kT \tag{61}$$

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 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 $\langle PE \rangle = \frac{1}{2}kT$, which is not accurate.

Problem 5. Distribution of energies

The speed distribution is

$$d\mathscr{P} = P(v) \, dv \tag{62}$$

where $P(v) = (m/2\pi kT)^{3/2} e^{-mv^2/2kT} 4\pi v^2$.

(a) Show that the probability distribution of energies $\epsilon = \frac{1}{2}mv^2$ is

$$d\mathscr{P} = P(\epsilon) d\epsilon \tag{63}$$

where

$$P(\epsilon) = \frac{2}{\sqrt{\pi}} \beta^{3/2} e^{-\beta \epsilon} \epsilon^{1/2} \tag{64}$$

Note: that the distribution of energies is independent of the mass, and recall $\beta = 1/kT$.

(b) Compute the variance in energy using $P(\epsilon)$. Express all integrals in terms $\Gamma(x)$ (as given in the previous homework) – it is helpful to change to a dimensionless energy $u = \beta \epsilon$. You should find (after evaluating these Γ functions as in the previous homework) that

$$\left\langle (\delta \epsilon)^2 \right\rangle = \frac{3}{2} (k_B T)^2 \tag{65}$$

$$P(V) dV = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mV^2/2kT} 4\pi V^2 dV$$

$$V = \frac{2E}{2}$$

$$dV = 1$$

$$2(\frac{2E}{m})^{1/2} m \cdot (2mE)^{1/2}$$

· So

$$P(\varepsilon) d\varepsilon = 4\pi / m$$

$$\frac{3}{2\pi kT} e^{-\varepsilon/kT} 2 \varepsilon d\varepsilon$$

$$\sqrt{2\pi kT} e^{-\varepsilon/kT} 2 \varepsilon d\varepsilon$$

$$= 2\pi \frac{2^{3/2}}{2^{3/2}} \frac{m^{3/2}}{m^{3/2}} \frac{E^{\frac{1}{2}} dE}{(k_B T)^{3/2}} \frac{1}{\pi^{3/2}} e^{-E/kT}$$

$$P(\varepsilon) d\varepsilon = \frac{2}{\sqrt{\pi}} \beta^{3/2} e^{-\beta \varepsilon} \varepsilon^{1/2} d\varepsilon$$

$$= \int_{\alpha}^{2} \frac{2}{\sqrt{\pi}} \beta^{3/2} e^{-\beta \epsilon} \epsilon^{1/2} d\epsilon \times \epsilon$$

Change vars
$$u = \beta \epsilon$$

$$\langle \epsilon \rangle = 1 \int_{0}^{\infty} \frac{2}{\sqrt{11}} e^{-u} u^{3/2} du$$

$$\langle \varepsilon \rangle = \frac{1}{\beta} \frac{2}{\sqrt{\pi}} \frac{\Gamma(5/2)}{\beta \sqrt{\pi}} = \frac{2}{\beta} \frac{3}{\sqrt{\pi}} \frac{\Gamma(\frac{3}{2})}{\beta}$$

Similarly
$$= \frac{1}{3} \cdot \frac{2}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} = \frac{3}{2} k_3 T$$

$$\langle \xi^2 \rangle = \frac{1}{\beta^2} \int_0^2 \frac{2}{\sqrt{\pi}} e^{-4} u^{5/2} du$$

$$(E^2) = \frac{1}{\beta^2} \sqrt{\pi} \frac{2}{\sqrt{\pi}} \frac{\Gamma(7/2)}{\pi}$$

$$\langle \xi^2 \rangle = 1 \cdot 2 \cdot 5 \cdot 3 \cdot 1 \cdot \Gamma(1/2)$$

$$\beta^2 \sqrt{\pi}^2 \cdot 2 \cdot 2 \cdot 2$$

$$= \frac{1}{\beta^2} \frac{2.5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} = \frac{1}{\beta^2} \frac{15}{4}$$

$$\frac{S_0}{\langle \epsilon^2 \rangle} - \langle \epsilon^3 \rangle^2 = \frac{1}{\beta^2} \left(\frac{15}{4} - \frac{9}{4} \right) = \frac{3}{2} \left(\frac{15}{15} \right)^2$$