Problem 1. 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.

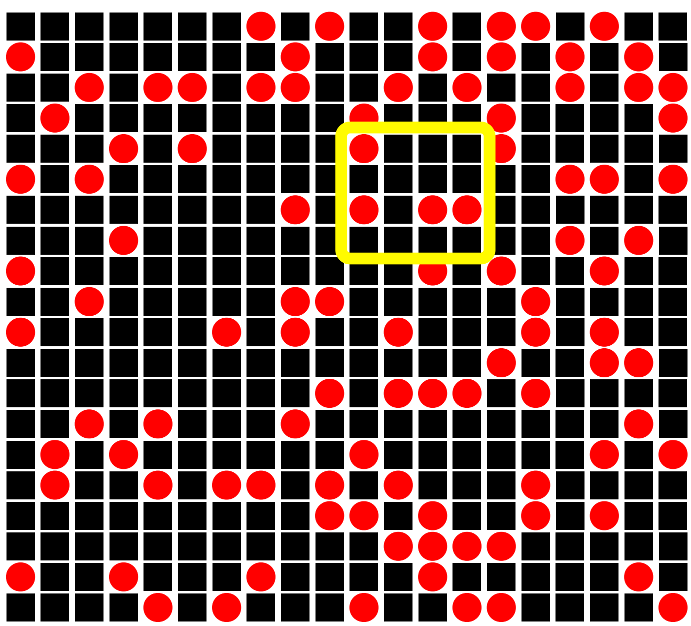
(a) Determine the temperature at which the number of excited atoms reaches $N/4$. You should find $kT = \Delta/\ln 3$.

(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?



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:

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

Thus, the variance is given by:

$$\begin{aligned}
\left\langle (\delta\epsilon)^2 \right\rangle &= \left\langle \epsilon^2 \right\rangle - \langle \epsilon \rangle^2 && (1)\\
&= \frac{\Delta^2}{e^{\beta\Delta}+1}\left(1 - \frac{1}{(e^{\beta\Delta}+1)^2}\right) && (2)\\
&= \frac{\Delta^2 e^{\beta\Delta}}{(e^{\beta\Delta}+1)^2}, && (3)
\end{aligned}$$

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:

$$\left\langle (\delta E)^2 \right\rangle = 16 \left\langle (\delta\epsilon)^2 \right\rangle .$$

Utilizing the identical nature of the atoms, we find:

$$\begin{aligned}
\left\langle E^2 \right\rangle &= \langle E \rangle^2 + \left\langle (\delta E)^2 \right\rangle && (4)\\
&= 16^2 \langle \epsilon \rangle^2 \left(1 + \frac{1}{16}\frac{\left\langle (\delta\epsilon)^2 \right\rangle}{\langle \epsilon \rangle^2}\right), && (5)\\
&= 16^2 \langle \epsilon \rangle^2 \left(1 + \frac{e^{\beta\Delta}}{16}\right) . && (6)
\end{aligned}$$

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

$$\mathrm{d}\mathscr{P} = \frac{1}{\sqrt{2\pi \langle \delta E^2 \rangle}} e^{-(E-\langle E \rangle)^2/2\left\langle \delta E^2 \right\rangle} \mathrm{d}E \tag{7}$$

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

$$\frac{\mathrm{d}\mathscr{P}}{\mathrm{d}E} = P(E) = \frac{1}{\sqrt{2\pi \langle \delta E^2 \rangle}} e^{-(E-\langle E \rangle)^2/2\left\langle \delta E^2 \right\rangle} \tag{8}$$

Problem 2. 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

$$U = \frac{1}{2}m\omega_0^2 x^2 \tag{9}$$

The energy is the kinetic and potential energies and the Hamiltonian[1] is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{10}$$

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 $x+\mathrm{d}x$ and momentum between p and $p+\mathrm{d}p$, i.e. the probability per phase space volume for appropriate constants σ_x and σ_p:

$$\mathrm{d}\mathscr{P}_{x,p} = P(x,p)\,\mathrm{d}x\,\mathrm{d}p\,. \tag{11}$$

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 $x + \mathrm{d}x$ without regards to momentum

$$\mathrm{d}\mathscr{P}_x = P(x)\,\mathrm{d}x \tag{12}$$

(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?

[1] 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

$$V(x) = \alpha|x| \tag{13}$$

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

$$\mathrm{d}\mathscr{P} = P(x)\,\mathrm{d}x \tag{14}$$

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

$$\mathrm{d}\mathscr{P}(x,p) = P(x,p)\mathrm{d}x\mathrm{d}p = Ce^{\mathcal{H}(x,p)/kT}\mathrm{d}x\mathrm{d}p \tag{15}$$

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

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{16}$$

We have

$$\int P(x,p)\mathrm{d}x\mathrm{d}p = 1 \tag{17}$$

The integrals work out as follows:

$$1 = C\int e^{-p^2/2mkT}\mathrm{d}p \int e^{-m\omega_0^2/2kT}\mathrm{d}x \tag{18}$$

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

$$\sigma_p^2 = mkT\,, \tag{19}$$

while the probability in coordinate space is Gaussian with width

$$\sigma_x^2 = kT/m\omega_0^2\,. \tag{20}$$

With this insight we have

$$1 = C\sqrt{2\pi\sigma_p^2}\sqrt{2\pi\sigma_x^2}\,. \tag{21}$$

So the probability distribution is

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

as quoted in the problem statement.

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

$$\mathrm{d}\mathscr{P}_x = \int_p \mathrm{d}\mathscr{P}_{x,p} = \int P(x,p)\mathrm{d}p \tag{23}$$

$$= P(x)\mathrm{d}x \underbrace{\int P(p)\mathrm{d}p}_{=1} \tag{24}$$

$$= \frac{e^{-x^2/2\sigma_x^2}}{\sqrt{2\pi\sigma_x^2}}\mathrm{d}x \tag{25}$$

(c) Then it is straightforward to see that

$$\langle x^2 \rangle = \int P(x,p) x^2 \mathrm{d}x\mathrm{d}p \tag{26}$$

$$= \int P(x) x^2 \mathrm{d}x \cdot \int P(p)\mathrm{d}p \tag{27}$$

$$\langle x^2 \rangle = \int P(x) x^2 \mathrm{d}x \cdot 1 \tag{28}$$

$$= \sigma_x^2 \tag{29}$$

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

$$\langle p^2 \rangle = \int P(x,p) p^2 \mathrm{d}x\mathrm{d}p \tag{30}$$

$$= \int P(x)\mathrm{d}x \cdot \int P(p) p^2 \mathrm{d}p \tag{31}$$

$$\langle p^2 \rangle = 1 \cdot \int P(p) p^2 \mathrm{d}p \tag{32}$$

$$= \sigma_p^2 \tag{33}$$

(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 $\mathcal{H}(x,p)$:

$$\left\langle \frac{p^2}{2m} \right\rangle = \tfrac{1}{2}kT \tag{34}$$

$$\left\langle \frac{1}{2} m\omega_0^2 x^2 \right\rangle = \tfrac{1}{2}kT \tag{35}$$

So we should find

$$\langle p^2 \rangle = mkT \tag{36}$$

while

$$\langle x^2 \rangle = \frac{kT}{m\omega_0^2} \tag{37}$$

This is consistent with part (b).

(e) If the potential is

$$\mathcal{H}(x,p) = \alpha|x| + \frac{p^2}{2m} \tag{38}$$

Then the probability distribution is as before

$$\mathrm{d}\mathscr{P}(x,p) = P(x,p)\,\mathrm{d}x\mathrm{d}p = Ce^{\mathcal{H}(x,p)/kT}\mathrm{d}x\mathrm{d}p \tag{39}$$

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

$$\mathrm{d}\mathscr{P}_{x,p} = P(x)\mathrm{d}x\, P(p)\mathrm{d}p = P(x)\mathrm{d}x\, \frac{e^{-p^2/2\sigma_p^2}}{\sqrt{2\pi\sigma_p^2}}\,. \tag{40}$$

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

$$P(p) \propto e^{-p^2/2mkT} \tag{41}$$

Here the position space probability distribution is

$$P(x)dx = Ce^{-\alpha|x|/kT}dx \tag{42}$$

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

$$\int P(x)dx = \int_{-\infty}^{\infty} Ce^{-\alpha|x|/kT}dx = 1 \tag{43}$$

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

$$1 = 2\int_0^\infty \mathrm{d}x\, Ce^{-\alpha x/kT} = \frac{2kTC}{\alpha} \tag{44}$$

So

$$P(x)\mathrm{d}x = \frac{kT}{2\alpha}e^{-\alpha|x|/kT}\mathrm{d}x \tag{45}$$

(f) The probability takes the form

$$\mathrm{d}\mathscr{P}_{x,p} = P(x)\mathrm{d}x\, P(p)\,\mathrm{d}p \tag{46}$$

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

$$\mathrm{d}\mathscr{P}_x = \int_p \mathrm{d}\mathscr{P}_{x,p} = P(x)dx \int P(p)dp = P(x)\mathrm{d}x \tag{47}$$

with $P(x)$ given in Eq. (45). To make a graph we define a length $\ell_0 \equiv kT/\alpha$, so

$$P(x)\mathrm{d}x = e^{-|x|/\ell_0}\frac{\mathrm{d}x}{\ell_0} \tag{48}$$

where as for the Gaussian we have

$$P(x)\mathrm{d}x = \frac{e^{-x^2/2\sigma^2}}{\sqrt{2\pi}}\frac{\mathrm{d}x}{\sigma_x} \tag{49}$$

The two distributions are shown in Fig. 1

(g) The mean potential energy is

$$\langle PE\rangle = \int P(x)\mathrm{d}x \cdot \alpha|x| \tag{50}$$

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

$$\langle PE\rangle = 2\int_0^\infty \frac{kT}{2\alpha}e^{-\alpha x/kT}\mathrm{d}x \cdot \alpha x \tag{51}$$

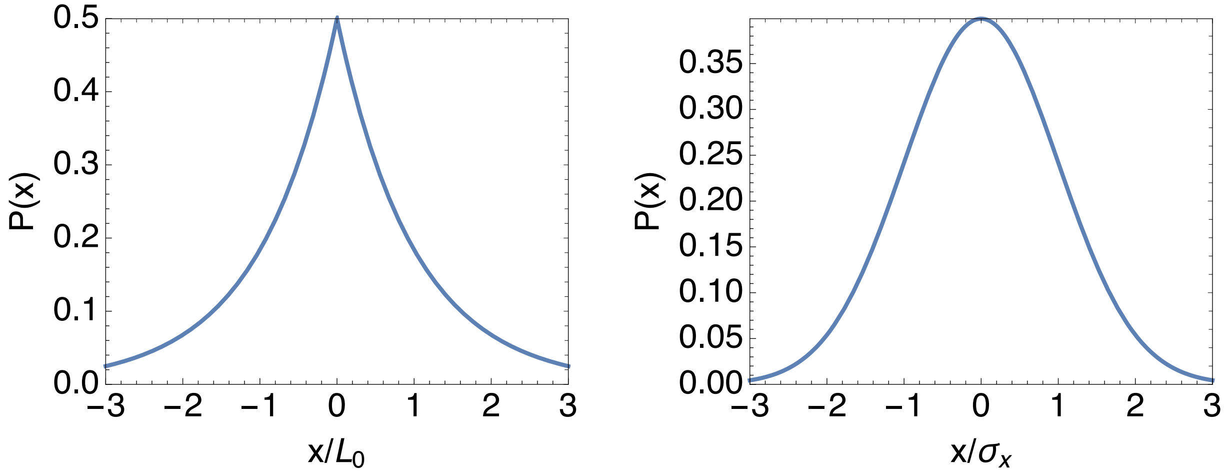


Figure 1: The probability density for two potentials.

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

$$\langle PE\rangle = \alpha\ell_0 \int_0^\infty \frac{\mathrm{d}x}{\ell_0} e^{-x/\ell_0}\, \frac{x}{\ell_0} \tag{52}$$

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

$$\langle PE\rangle = kT \tag{53}$$

The kinetic energy is the same as in the previous item

$$\langle KE\rangle = \tfrac{1}{2}kT \tag{54}$$

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.

Problem 3. Logarithmic Derivatives

The percent change in x is dx/x. Thus it is common to see

$$x\frac{dy}{dx} \tag{55}$$

which is the change in y per *percent* change in x. This is known as a logarithmic derivative with respect to x since

$$x\frac{dy}{dx} = \frac{dy}{d\ln x} \tag{56}$$

Similarly the *percent* change in y per change in x is

$$\frac{1}{y}\frac{dy}{dx} = \frac{d\ln y}{dx} \tag{57}$$

Logarithmic derivatives appear frequently in the course and recognizing this can help.

Let $y \propto x^k$ with k a real number. Show that the percent change in y is proportional to the percent change in x

$$\frac{dy}{y} = k\frac{dx}{x} \tag{58}$$

Show also

$$x\frac{\partial}{\partial x} = k\,y\frac{\partial}{\partial y} \tag{59}$$

Briefly answer:

(i) With $\beta = 1/kT$, relate

$$T\frac{\partial}{\partial T} \quad \text{and} \quad \beta\frac{\partial}{\partial \beta} \tag{60}$$

(ii) If $E = p^2/2m$, how is dE/E related to dp/p?

(iii) Show that if $Z(x) = Z_1(x)Z_2(x)$ then the percent change in Z with x is a sum of the percent changes:

$$\frac{1}{Z}\frac{dZ}{dx} = \frac{1}{Z_1}\frac{dZ_1}{dx} + \frac{1}{Z_2}\frac{dZ_2}{dx} \tag{61}$$

Solution

First we have since $y = Cx^k$

$$\mathrm{d}y = kCx^{k-1}\,\mathrm{d}x = ky\,\frac{\mathrm{d}x}{x} \qquad or \qquad \frac{\mathrm{d}y}{y} = k\frac{\mathrm{d}x}{x} \tag{62}$$

Then by the chain rule on an arbitrary function $f(x) \equiv f(y(x))$

$$x\frac{\partial f}{\partial x} = x\frac{\partial f}{\partial y}\,\frac{\partial y}{\partial x} = x\frac{\partial f}{\partial y} \times Ckx^{k-1} = k\,y\,\frac{\partial f}{\partial y} \tag{63}$$

Here f was arbitrary so

$$x\frac{\partial}{\partial x} = k\,y\frac{\partial}{\partial y} \tag{64}$$

In a more intuitive way this is clear using the previous part

$$df = x\frac{\partial f}{\partial x}\,\frac{\mathrm{d}x}{x} = y\frac{\partial f}{\partial y}\,\frac{\mathrm{d}y}{y} \tag{65}$$

Then using $dy/y = k\,\mathrm{d}x/x$ leads to the result

$$y\frac{\partial}{\partial y} = \frac{1}{k}\,x\frac{\partial}{\partial x} \tag{66}$$

(a) $T \propto \beta^{-1}$ so

$$T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial \beta} \tag{67}$$

(b) $E \propto p^2$ so

$$\frac{dE}{E} = 2\frac{dp}{p} \tag{68}$$

(c) This is clear

$$\ln Z(x) = \ln Z_1 + \ln Z_2 \tag{69}$$

differentiating with respect to x leads to the quoted result.

Problem 4. Basics of Partition Functions

Important!

Consider a quantum mechanical system with energy levels ϵ_i with $i = 1, 2, \ldots n$. Recall the definition of the partition function

$$Z(\beta) = \sum_i e^{-\beta\epsilon_i}$$

Z is a the normalization constant so that the probability of being in the r-th state

$$P_r = \frac{1}{Z(\beta)} e^{-\beta\epsilon_r} \tag{70}$$

is correctly normalized

$$\sum_i P_i = 1 \tag{71}$$

The results of this problem also apply to a classical particle where (in 1D for simplicity) the single particle partition function reads

$$Z_1(\beta) = \int \frac{dxdp}{h} e^{-\beta\epsilon} \tag{72}$$

(a) Show that the mean energy can be found if you know $Z(\beta)$ via the formula:

$$\langle\epsilon\rangle = -\frac{1}{Z(\beta)}\frac{\partial Z}{\partial\beta} \tag{73}$$

Show also that

$$\left\langle\epsilon^2\right\rangle = \frac{1}{Z}\left(-\frac{\partial}{\partial\beta}\right)\left(-\frac{\partial}{\partial\beta}\right) Z = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} \tag{74}$$

What is $\langle\epsilon^m\rangle$ in terms of the derivatives of $Z(\beta)$?

From this exercise you should realize that the partition function is essentially the generating function for the probability distribution in Eq. (70). Indeed, the partition function "generates" averages of the form, $\langle\epsilon^m\rangle$, by differentiating m times with respect to the parameter $-\beta$.

(b) Consider the two state system with energy 0 and Δ discussed two homeworks ago. Compute the partition function, and then compute $\langle\epsilon\rangle$ and $\langle\epsilon^2\rangle$ using the methods of this problem, and compare with the methods of the previous homework.

(c) Although it is not obvious at this level, it is generally better to work with the logarithm of $Z(\beta)$, i.e. $\ln Z(\beta)$. Show that the mean and variance of the energy are determined by the derivatives of $\ln Z$

$$\langle\epsilon\rangle = -\frac{\partial \ln Z(\beta)}{\partial\beta} \tag{75}$$

$$\left\langle(\delta\epsilon)^2\right\rangle = \frac{\partial^2 \ln Z(\beta)}{\partial\beta^2} = -\frac{\partial\langle\epsilon\rangle}{\partial\beta} \tag{76}$$

In particular note, that the mean $\langle\epsilon\rangle$ determines the variance.

(d) Now consider a hunk of material consisting of N two level atoms with energy levels 0 and Δ. Find the total energy $U(T)$ of the system at temperature T. Use the results of this problem to show quite generally that the specific heat C_V of the material is related to the variance in the energy of an individual atom

$$C_V = Nk \left[\frac{\langle (\delta\epsilon)^2 \rangle}{(kT)^2} \right] \tag{77}$$

Sketch C_V/R for one mole of substance, versus Δ/kT and comment in comparison to last weeks homework.

(e) Finally consider a classical particle in a harmonic potential from last week.

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2 \tag{78}$$

Compute the partition function recognizing the similarities with part (a) of the problem from last week. Compute the average energy $\langle \epsilon \rangle$ using Eq. (75). Does your answer agree with last week's Homework and the equipartition theorem?

Partition Fcn Basics

We have

$$Z = \sum_s e^{-\beta \varepsilon_s}$$

So

$$-\frac{\partial Z}{\partial \beta} = \sum_s -\frac{\partial}{\partial \beta} e^{-\beta \varepsilon_s} = \sum_s e^{-\beta \varepsilon_s} \varepsilon_s$$

This repeats

$$\left(-\frac{\partial}{\partial \beta}\right)^2 Z = -\frac{\partial}{\partial \beta}\left(\sum_s e^{-\beta \varepsilon_s} \varepsilon_s\right) = \sum_s e^{-\beta \varepsilon_s} \varepsilon_s^2$$

So

$$\boxed{\langle \varepsilon \rangle = \frac{\sum_s e^{-\beta \varepsilon_s} \varepsilon_s}{\sum_s e^{-\beta \varepsilon_s}} = \frac{1}{Z} \frac{-\partial Z}{\partial \beta}}$$

and

$$\boxed{\langle \varepsilon^2 \rangle = \frac{\sum_s e^{-\beta \varepsilon_s} \varepsilon_s^2}{\sum_s e^{-\beta \varepsilon_s}} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}}$$

b) We had $Z(\beta) = \sum_s e^{-\beta \varepsilon_s} = e^{-\beta 0} + e^{-\beta \Delta} = 1 + e^{-\beta \Delta}$

Then $\langle \varepsilon \rangle = \frac{-1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{(1+e^{-\beta \Delta})} \Delta e^{-\beta \Delta}$ ✓

Similarly

$$\langle \varepsilon^2 \rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{(1+e^{-\beta\Delta})} \Delta^2 e^{-\beta\Delta}$$ ✓

c) $$\boxed{\langle \varepsilon \rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{1}{Z}\left(-\frac{\partial Z}{\partial \beta}\right) = \text{same as before}}$$

Similarly

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\,\frac{\partial Z}{\partial\beta}\right) = \underbrace{\frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}} - \underbrace{\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2}$$

$$= \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \langle \delta\varepsilon^2 \rangle$$

We note that

$$\boxed{\langle \delta\varepsilon^2 \rangle = -\frac{\partial}{\partial\beta}\langle \varepsilon \rangle = \frac{\partial^2 \ln Z}{\partial\beta^2}}$$

d) Then

$$U(T) = N\langle \varepsilon \rangle$$

Now recall since at fixed volume $dU_v = dQ_v = C_V\,dT$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = N\frac{\partial}{\partial T}\langle \varepsilon \rangle = \frac{N}{T}\,T\frac{\partial\langle \varepsilon \rangle}{\partial T} = \frac{N}{T}\,-\beta\frac{\partial}{\partial\beta}\langle \varepsilon \rangle$$

use $T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial\beta}$

see problem on log derivs

So

$$C_V = Nk\,\beta^2\left(-\frac{\partial\langle\varepsilon\rangle}{\partial\beta}\right) = Nk\,\beta^2\langle\delta\varepsilon^2\rangle$$

use previous item

$$\boxed{C_V = Nk\left[\frac{\langle\delta\varepsilon^2\rangle}{(kT)^2}\right]}$$

Now we find

$$\langle\delta\varepsilon^2\rangle = \frac{\partial^2\ln Z}{\partial\beta^2} = -\frac{\partial}{\partial\beta}\frac{\Delta e^{-\beta\Delta}}{(1+e^{-\beta\Delta})} = -\frac{\partial}{\partial\beta}\frac{\Delta}{(e^{\beta\Delta}+1)}$$

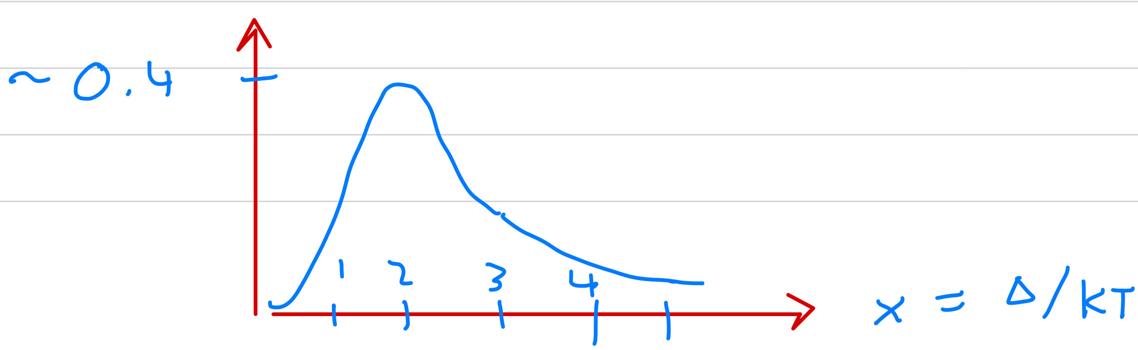
$$= \Delta^2\frac{e^{\beta\Delta}}{(e^{\beta\Delta}+1)^2} = \frac{\Delta^2 e^{-\beta\Delta}}{(1+e^{-\beta\Delta})^2}$$

So

$$\boxed{\frac{C_V}{Nk} = \beta^2\langle\delta\varepsilon^2\rangle = (\beta\Delta)^2\frac{e^{-\beta\Delta}}{(1+e^{-\beta\Delta})^2}}$$

A sketch is shown below, we are plotting

$$\frac{x^2 e^{-x}}{(1+e^{-x})^2} \quad \text{with } x = \beta\Delta = \Delta/kT$$



e)

$$Z = \int \frac{dx\,dp}{h} e^{-\beta(p^2/2m + \frac{1}{2}m\omega_0^2 x^2)}$$

The integrals factorize and are gaussians

$$Z = \frac{1}{h}\int dx\; e^{-\frac{1}{2}x^2/\sigma_x^2} \cdot \int dp\; e^{-p^2/2\sigma_p^2}$$

where

$$\sigma_x^2 \equiv \frac{1}{\beta m \omega_0^2} \quad \text{and} \quad \sigma_p^2 \equiv \frac{m}{\beta}$$

So

$$Z = \frac{(2\pi\sigma_x^2)^{1/2}(2\pi\sigma_p^2)^{1/2}}{h} = \frac{2\pi}{h}\left(\frac{1}{\beta m\omega_0^2}\,\frac{m}{\beta}\right)^{1/2} = \frac{2\pi}{\beta h\omega_0} = \frac{1}{\beta\hbar\omega_0}$$

$$\boxed{Z = \frac{1}{\beta\hbar\omega_0}} \propto \frac{1}{\beta} \Leftarrow$$

Note we will differentiate $\ln Z$ with β. Follow this algebra the constants don't matter, Just $Z \propto \beta^{-1}$!

Now

$$\langle \varepsilon \rangle = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\left(\ln\frac{1}{\beta\hbar\omega_0}\right) = -\frac{\partial}{\partial\beta}\underbrace{\left[\ln\frac{1}{\beta} + \text{const}\right]}$$

$$= \frac{\partial}{\partial\beta}\ln\beta = \frac{1}{\beta} = kT$$

see how constants don't matter. This greatly simplifies algebra going forward.

Problem 5. Working with the speed distribution

Consider the Maxwell speed distribution, $\mathrm{d}\mathscr{P}_v = P(v)\mathrm{d}v$.

(a) In three dimensions, evaluate the most probable speed v_*. You should find $v_* = (2kT/m)^{1/2}$.

(b) Determine the normalized speed distributions $\mathrm{d}\mathscr{P}_v = P(v)\mathrm{d}v$ in two spatial dimensions, and sketch it.

  (i) Show that $\langle v \rangle = (kT/m)^{1/2}\sqrt{\pi/2}$.

  (ii) By switching to dimensionless variables, show that $\langle v^n \rangle = (kT/m)^{n/2} \times$ constant, and express the constant as a dimensionless integral. Show that the integral is $2^{n/2}\Gamma(n/2+1)$ where $\Gamma(x)$ is the gamma-function introduced last week and that this expression gives the right numerical number for (i).

  Hint: Go through the derivation of the velocity distribution $\mathrm{d}\mathscr{P}_{v_x,v_y,v_z}$ in three dimensions and generalize it to two dimensions. Then go through the steps to get from the velocity distribution to the speed distribution $\mathrm{d}\mathscr{P}_v$ and generalize these steps to two dimensions.

(c) (Optional) Return to three dimensions, determine the probability of having $v < v_*$. Follow the following steps:

  (i) Write down the appropriate integral.

  (ii) Change variables to an appropriate dimensionless speed u, writing the probability as a dimensionless integral to be done numerically.

  (iii) Write a short program (in any language) to evaluate the dimensionless integral, by (for example) dividing up the interval into 200 bins, and evaluates the integral with Riemann sums. You should find

$$\mathscr{P} \simeq 0.428 \tag{79}$$

Speed Distribution

So

a) $$P(v)\,dv = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv$$

- Maximizing $P(v)$ we have

$$P(v) = C\, e^{-v^2/2\sigma^2}\, v^2 \quad \text{with} \quad \sigma \equiv \left(\frac{kT}{m}\right)^{1/2}$$

$$P' = C e^{v^2/2\sigma^2}\left(\frac{v^3}{\sigma^2} + 2v\right)$$

- So P is maximized when $P'(v) = 0$ or

$$v^2 = 2\sigma^2 \implies \boxed{v_* = \sqrt{\frac{2kT}{m}}}$$

For the 2d results see below

b) $$\mathcal{P} = \int_{v_*}^{2v_*} \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv$$

- Substituting

$$u = \frac{v}{(kT/m)^{1/2}} \quad \text{this becomes}$$

$$\mathcal{P} = \int_{\sqrt{2}}^{2\sqrt{2}} \frac{1}{(2\pi)^{3/2}} 4\pi\, e^{-u^2/2} u^2\, du$$

- So

$$\mathcal{P} = \sqrt{\frac{2}{\pi}} \int_{\sqrt{2}}^{2\sqrt{2}} e^{-u^2/2} u^2\, du$$

$$\simeq 0.53$$

See program

In two dimensions the speed distribution is

$$P(v) = \frac{m}{2\pi kT} e^{-\frac{1}{2}mv^2/kT} 2\pi v = Ce^{-v^2/2\sigma^2} v$$

where $\sigma = \sqrt{kT/m}$. Differentiating to find the maximum (where $P'(v) = 0$) we have

$$P'(v) = Ce^{-v^2/2\sigma^2} \left(-\frac{v^2}{\sigma^2} + 1\right) = 0$$

Leading to $v_* = \sigma = \sqrt{kT/m}$.

```
from math import *

xmin = sqrt(2.)
xmax = sqrt(2.)*2.

n = 1000
dx = (xmax - xmin)/n

s = 0.
for i in range(0, n):
    x = i * dx + xmin
    s = s + dx * sqrt(2./pi) * exp(-x*x/2.) * x * x
    print(s)
```