Problem 1.   Two State System

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

(a) Calculate the mean energy $\langle\epsilon\rangle$. Sketch $\langle\epsilon\rangle/kT$ as a function of Δ/kT. Explain both the high and low temperature limits qualitatively.

(b) Show that the variance of energy $\langle(\delta\epsilon)^2\rangle$ for an individual atom takes the form

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

Graph $\frac{\langle(\delta\epsilon)^2\rangle}{(kT)^2}$ 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?
Hint: Think about how the central limit theorem applies here.
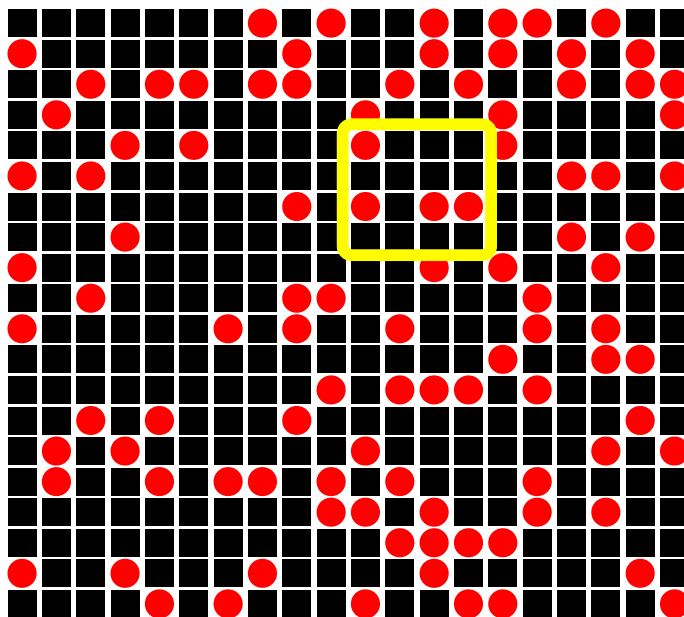
Problem 2.   Classical distribution of two potentials

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

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

1

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

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

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 $dx\,dp$:

$$d\mathscr{P}_{x,p} = P(x, p)\,dx\,dp \tag{3}$$

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.

What is the probability of finding position between x and $x + dx$ without regards to momentum

$$d\mathscr{P}_x = P(x)\,dx \tag{4}$$

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

(c) 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, $m\omega_0^2 x^2/2$. 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?

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

$$V(x) = \alpha|x| \tag{5}$$

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.

What is the probability of finding position between x and $x + dx$ without regards to momentum

$$d\mathscr{P} = P(x)\,dx \tag{6}$$

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

---

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

(e) 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.

Problem 3. Logarithmic Derivatives

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

$$x\frac{dy}{dx} \tag{7}$$

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

$$x\frac{dy}{dx} = \frac{dy}{d\ln x} \tag{8}$$

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

$$\frac{1}{y}\frac{dy}{dx} = \frac{d\ln y}{dx} \tag{9}$$

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

$$\frac{dy}{y} = k\frac{dx}{x} \tag{10}$$

Show also

$$x\frac{\partial}{\partial x} = k\, y\frac{\partial}{\partial y} \tag{11}$$

Briefly answer:

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

$$T\frac{\partial}{\partial T} \quad \text{and} \quad \beta\frac{\partial}{\partial \beta} \tag{12}$$

(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:

$$\frac{1}{Z}\frac{dZ}{dx} = \frac{1}{Z_1}\frac{dZ_1}{dx} + \frac{1}{Z_2}\frac{dZ_2}{dx} \tag{13}$$

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

$$P_r = \frac{1}{Z(\beta)} e^{-\beta \epsilon_r} \tag{14}$$

is correctly normalized

$$\sum_i P_i = 1 \tag{15}$$

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

$$Z_1(\beta) = \int \frac{dx\,dp}{h} e^{-\beta \epsilon} \tag{16}$$

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

$$\langle \epsilon \rangle = -\frac{1}{Z(\beta)} \frac{\partial Z}{\partial \beta} \tag{17}$$

Show also that

$$\langle \epsilon^2 \rangle = \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \left(-\frac{\partial}{\partial \beta} \right) Z = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \tag{18}$$

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. (14). 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 $\ln Z$

$$\langle \epsilon \rangle = -\frac{\partial \ln Z(\beta)}{\partial \beta} \tag{19}$$

$$\langle (\delta \epsilon)^2 \rangle = \frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = -\frac{\partial \langle \epsilon \rangle}{\partial \beta} \tag{20}$$

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

$$C_V = Nk \left[\frac{\langle (\delta \epsilon)^2 \rangle}{(kT)^2} \right] \tag{21}$$

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.

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 x^2 \tag{22}$$

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. (19). Does your answer agree with last week's Homework and the equipartition theorem?

Problem 5.   Working with the speed distribution

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

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

(b) Determine the normalized speed distributions $d\mathscr{P}_v = P(v)dv$ 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 $d\mathscr{P}_{v_x,v_y,v_z}$ in three dimensions and generalize it to two dimensions. Then go through the steps to get from the velocity distribution to the speed distribution $d\mathscr{P}_v$ 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

$$\mathscr{P} \simeq 0.428 \tag{23}$$