

Problem 1. Classical distribution of a harmonic oscillator

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

$$U = \frac{1}{2}m\omega_0^2x^2 \quad (1)$$

The energy is the kinetic and potential energies and the Hamiltonian¹ is

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

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 $dx dp$:

$$d\mathcal{P} = P(x, p) dx dp \quad (3)$$

Your final result for $P(x, p)$ should be a function of ω_0, p, x, m and $k_B T$. 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) Compute the $\langle x^2 \rangle$ and $\langle p^2 \rangle$ by integrating over the probability distribution. (Don't do dimensional integrals.)

You should find $\langle x^2 \rangle = k_B T / m\omega_0^2$ and $\langle p^2 \rangle = mk_B T$.

- (c) The equipartition theorem precisely says that, for a classical system, the average of each quadratic form in the Hamiltonian is $\frac{1}{2}k_B T$. 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?
- (d) (i) For one mole of an ideal diatomic molecule H_2 (treated in a classical approximation), what are the total number of degrees of freedom (in the sense of the equipartition theorem), if translations, rotations, *and* now vibrations are included and treated classically? (ii) What is the energy of the gas for one mole of substance, U^{1ml} ? Express

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

your result in terms of R and T . (iii) As discussed in class the specific heat² at constant pressure C_p is related to the internal energy U . Indeed, $C_p^{1\text{ml}} = (\partial U^{1\text{ml}}/\partial T)_V + R$ for one mole of substance. Is your result for $U^{1\text{ml}}$ consistent with the experimental data on $C_p^{1\text{ml}}$ shown below? Explain.

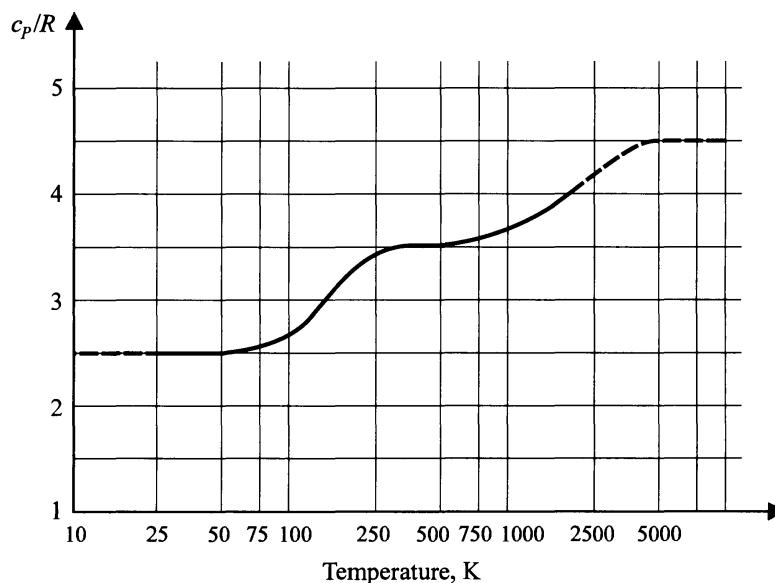


Figure 1: The heat capacity $C_p^{1\text{ml}}$ for one mole of substance.

²Specific Heat are not on the exam.

SHO

a)

$$d\mathcal{P} = C e^{-H/k_B T} dx dp$$

$$= C e^{-p^2/2mk_B T} e^{-\frac{1}{2}m\omega_0^2 x^2/k_B T} dx dp$$

Let $\sigma_x^2 = \frac{k_B T}{m\omega_0^2}$ and $\sigma_p^2 = m k_B T$

So

this is a product: $f_{\text{cn}}(x) = f_{\text{cn}}(p)$

$$d\mathcal{P} = C e^{-x^2/2\sigma_x^2} e^{-p^2/2\sigma_p^2} dx dp$$

We know the normalization of a gaussian:

$$\int du e^{-u^2/2\sigma^2} = (2\pi\sigma^2)^{1/2}$$

Leading to $\int dx dp f_{\text{cn}}(x) f_{\text{cn}}(p) = \int dx f_{\text{cn}}(x) \cdot \int dp f_{\text{cn}}(p)$, or

$$d\mathcal{P} = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} dx dp \quad (\text{see below})$$

$$d\mathcal{P} \equiv P(x) dx P(p) dp$$

Integrating over p , determines $P(x) = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}}$

- In greater detail:

$$\int d\mathcal{P} = C \int e^{-x^2/2\sigma_x^2} dx \int e^{-p^2/2\sigma_p^2} dp = 1$$

$$= C (2\pi\sigma_x^2)^{1/2} (2\pi\sigma_p^2)^{1/2} = 1$$

$$C = \frac{1}{(2\pi\sigma_x^2)^{1/2}} \frac{1}{(2\pi\sigma_p^2)^{1/2}}$$

- Since the probability density factorizes, it is helpful to note that the probability to find x , without regard to p , is found by summing all possible values of p (leaving x fixed)

$$\begin{aligned} d\mathcal{P}_x &= \int_p d\mathcal{P}_{x,p} = \int_p \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} dx dp \\ &= \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} dx \underbrace{\int_{-\infty}^{\infty} \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} dp}_{=1} \end{aligned}$$

$$d\mathcal{P}_x = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} dx \equiv P(x) dx$$

- Similarly a small calculation shows that:

$$d\mathcal{P}_p = \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} dp \equiv P(p) dp$$

So

$$\underline{b)} \quad \langle x^2 \rangle = \int_{-\infty}^{\infty} dx \, x^2 P(x)$$

$$\text{Here } dP_x = P(x) dx = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} dx$$

So

$$\boxed{\langle x^2 \rangle} = \int_{-\infty}^{\infty} dx \, x^2 \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}}$$

$$= \sigma_x^2 \int_{-\infty}^{\infty} du \, u^2 \frac{e^{-u^2/2}}{\sqrt{2\pi}} = \boxed{\sigma_x^2 = \frac{k_B T}{m\omega_0^2}}$$

Similarly

$$\boxed{\langle p^2 \rangle} = \int_{-\infty}^{\infty} dp \, p^2 \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} = \sigma_p^2 = \boxed{m k_B T}$$

the integral is the same as the x-case

c) Note

$$\langle K \rangle = \left\langle \frac{p^2}{2m} \right\rangle = \frac{1}{2m} \langle p^2 \rangle = \frac{1}{2m} m k T = \frac{1}{2} k T \quad \checkmark$$

Similarly

$$\langle U \rangle = \frac{1}{2} m \omega_0^2 \langle x^2 \rangle = \frac{1}{2} m \omega_0^2 \left(\frac{kT}{m \omega_0^2} \right) = \frac{1}{2} kT$$

The h

$$\langle E \rangle = \langle U \rangle + \langle K \rangle = kT$$

Thus each oscillator consists of two dof.

$$2 \times \frac{1}{2} kT = kT$$

d) The energy is

$$U = N \left(\underset{\substack{\uparrow \\ \text{translations}}}{3 \times \frac{1}{2} k_B T} + 2 \underset{\substack{\uparrow \\ \text{rotations}}}{\frac{1}{2} k_B T} + 2 \times \underset{\substack{\uparrow \\ \text{vibrations}}}{\frac{1}{2} k_B T} \right) \dots$$

$$= N \frac{7}{2} k_B T$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{7}{2} N k_B$$

$$C_P = C_V + N k_B = \frac{9}{2} N k_B$$

So for one mole

$$C_p^{\text{int}} = N_A \frac{9}{2} k_B = \frac{9}{2} R$$

So at the highest temperature it agrees.

Problem 2. Partition function of two state system

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

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

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

$$P_r = \frac{1}{Z(\beta)} e^{-\beta\epsilon_r} \quad (4)$$

is correctly normalized

$$\sum_i P_i = 1 \quad (5)$$

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

$$\langle \epsilon \rangle = -\frac{1}{Z(\beta)} \frac{\partial Z}{\partial \beta} \quad (6)$$

Show also that

$$\langle \epsilon^2 \rangle = \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \left(-\frac{\partial}{\partial \beta} \right) Z = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (7)$$

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. (4). Indeed, the partition function “generates” averages of the form, $\langle \epsilon^m \rangle$, by differentiating m times with respect to the parameter $-\beta$.

- (b) (Optional) Explicitly work out the relation between the generating function as we defined previously and $Z(\beta)$. *Hint:* Show that $Z(\beta + \delta\beta)/Z(\beta)$ is the generating function³, $\langle e^{-\delta\beta\epsilon} \rangle$, for the probability distribution, $P_r = e^{-\beta\epsilon_r}/Z(\beta)$.
- (c) 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. Show that the variance in energy is

$$\langle (\delta\epsilon)^2 \rangle = \Delta^2 \left[\frac{e^{-\beta\Delta}}{(1 + e^{-\beta\Delta})^2} \right] \quad (9)$$

What is the variance in the high temperature limit $k_B T \gg \Delta$. Explain the result qualitatively.

³In our previous notation the generating function was $\langle e^{a\epsilon} \rangle$, where the average is over the probability distribution of ϵ . The parameter of the generating function was called a instead of $-\delta\beta$ as it is here. Somewhat pedantically then:

$$\langle \epsilon \rangle = \frac{\partial \langle e^{a\epsilon} \rangle}{\partial a} \Big|_{a=0} = -\frac{\partial \langle e^{-\delta\beta\epsilon} \rangle}{\partial \delta\beta} \Big|_{\delta\beta=0} = -\frac{1}{Z(\beta)} \frac{\partial Z(\beta')}{\partial \beta'} \Big|_{\beta'=\beta} \quad (8)$$

Two State

Then

$$Z = \sum_n e^{-\beta E_n}$$

$$-\frac{\partial Z}{\partial \beta} = \sum_n E_n e^{-\beta E_n}$$

$$-\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \langle E_n \rangle$$

• $Z = 1 + e^{-\beta \Delta}$

$$-\frac{\partial Z}{\partial \beta} = e^{-\beta \Delta} \Delta \quad \text{and} \quad \langle E \rangle = \frac{\Delta e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})}$$

Problem 3. Partition function of three level system

Consider an ensemble at temperature T of N independent “atoms”, each of which have the three energy levels shown below.

$$\text{————— } E_2 = 5\Delta$$

$$\text{————— } E_1 = \Delta$$

$$\text{————— } E_0 = 0$$

- (a) Determine the partition function and mean energy of an atom as a function of temperature.
- (b) Determine the probabilities to be in the first excited and second excited states, P_1 and P_2 , and qualitatively sketch these probabilities versus temperature on the same graph, from very low to very high temperatures:
 - (i) Explain the qualitative features of your graph by pointing to specific terms in your equations.
 - (ii) Determine the approximate value P_2 at high temperatures, and explain the result physically. Taking $\Delta = 0.1 \text{ eV}$, estimate the temperature (in Kelvin) when your result becomes approximately valid.

Problem 2

a) $Z = \sum_n e^{-E_n/kT}$

(8 ~~pts~~ points)

$$Z = 1 + e^{-\Delta/kT} + e^{-5\Delta/kT}$$

4 + 4 points

$$\langle E \rangle = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\Delta e^{-\Delta/kT} + 5\Delta e^{-5\Delta/kT}}{(1 + e^{-\Delta/kT} + e^{-5\Delta/kT})}$$

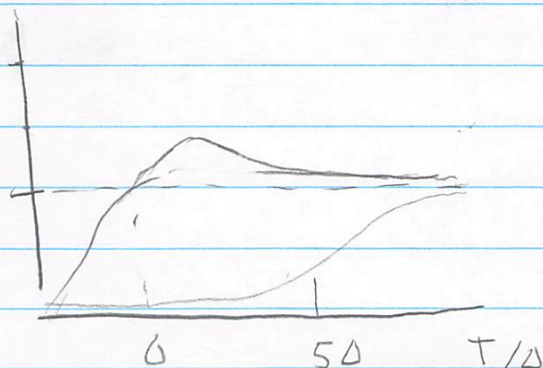
b) $P_1 = \frac{e^{-\Delta/kT}}{(1 + e^{-\Delta/kT} + e^{-5\Delta/kT})}$

(10 points)

$$P_2 = \frac{e^{-5\Delta/kT}}{(1 + e^{-\Delta/kT} + e^{-5\Delta/kT})}$$

4 points

i) So at low temperature $P_1 + P_2$ are zero, while at high temperature $P_0 = P_1 = P_2 = \frac{1}{3}$, all states are equally likely. The P_1 curve reaches its high temperature limit sooner



6 points

- We can estimate what high temperature means.
We want

$$5\beta\Delta \rightarrow 0$$

So

$$P_2 \approx \frac{1}{(1+1+1)} \approx \frac{1}{3}$$

So the high temperature limit is when

$$5\beta\Delta \ll 1 \quad \text{or} \quad \frac{5\Delta}{k_B T} \ll 1 \quad \text{or} \quad T \gg \frac{5\Delta}{k_B}$$

Substituting

$$T \gg 5 \cdot \left(\frac{0.1 \text{ eV}}{0.025 \text{ eV}} \right) \left(\frac{300^\circ \text{K}}{1} \right)$$

or

$$T \gg 6000^\circ \text{K}$$

Problem 4. Balls in baskets

Consider N “atoms” with total energy E . The total energy consists of q units of vibrational quanta of energy $E \equiv q\hbar\omega_0$, where q is an integer. We want to count the number of ways (also called states) that the atoms can share the q units energy.

- (a) For four atoms and three quanta of energy ($N = 4$ and $q = 3$) show that there are 20 ways for the oscillators to share the energy. For instance, the first atom could have the three quanta and the rest none. That is one possible state out of 20.
- (b) Show in general that there are

$$\Omega(q) = \frac{(N + q - 1)!}{q!(N - 1)!} \quad (10)$$

ways to distribute q units of energy amongst the N atoms. Verify that this expression reproduces the results of part (a)

Hint: Consider each oscillator to be a bin, and each bit of energy to be a ball. We are asking for the number of ways to put q balls in N bins.

Take seven balls (units of energy) and five bins (oscillators), $N = 5$ and $q = 7$. Lay out the 7 balls (solid circles) between the dashed lines.



To partition the 7 balls amongst the five bins, I need four dividers, shown by the solid lines. In the figure below, I have placed the four dividers in one possible way, partitioning the energy so that the first bin has 2 units, the second bin has none, the third bin has 3, the fourth has two, and the fifth has none. The total number of objects, ball or divider, is $q + (N - 1) = 11$. Use this logic and the number of ways of choosing q of these objects to be balls to explain Eq. (10).

- (c) Using the Stirling approximation, show that for $N = 400$ oscillators and $q = 400$ quanta the number of states is approximately

$$e^{2N \ln 2} = e^{555} \quad (11)$$

Ways to partition energy amongst N SHO

a) $\begin{array}{cccc} & 0 & & \\ & 0 & & \\ \hline & 0 & - & - & - \end{array}$ 4 configs like this

$\begin{array}{cccc} & 0 & & \\ \hline 0 & 0 & - & - \end{array}$ 12 configs like this

$\begin{array}{cccc} 0 & 0 & 0 & - \\ \hline & & & \end{array}$ 4 configs like this

b) There are $\frac{4}{20}$ configs with one particle having all the energy

c) The $(N+q-1)$ objects we choose q of them to be balls $N-1$ to be dividers. The combinatorics of choosing says there are

$${}^{N+q-1}C_q = \frac{(N+q-1)!}{q!(N-1)!} \text{ ways to do this}$$

d) Using the stirling approximation for large N and large q but $\bar{n} = \frac{q}{N}$ fixed, we have (dropping the 1) and using that $N! \approx (N/e)^N$

$$\Omega(q) = \left(\frac{N+q}{e}\right)^{N+q} \frac{1}{\left(\frac{q}{e}\right)^q} \frac{1}{\left(\frac{N}{e}\right)^N} = \frac{N^{N+q}}{N^{N+q}} \frac{(1+\bar{n})^{N+q}}{\bar{n}^q}$$

- Now in the current question

$$N = 400 \quad q = 400 \quad \text{and} \quad \bar{n} = q/N = 1$$

So

$$\Omega = \frac{(1+1)^{2N}}{1^N} = 2^{2N} = e^{2N \ln 2} \approx \underline{e^{555}}$$