

## Understanding the Key Concepts from the Lecture

### Exercise 1 What is the Partition Function Q? Mathematical Meaning

The goal of this exercise is to understand the partition function  $Q$  from a mathematical point of view. Consider a coin toss, where the outcome can either be heads (H) or tails (T). Furthermore, we know that the probabilities of the two states are in a ratio of 3:5, which means that we can almost write

$$P(H) \stackrel{?}{=} 3 \quad P(T) \stackrel{?}{=} 5 \quad (1)$$

This, of course, is not entirely correct. We know that for probabilities, the sum over all possible states

$$\sum_x P(x) = 1 \quad (2)$$

needs to be equal to one. There is a simple way to fix this, namely by setting

$$P(H) = \frac{3}{8} = \frac{3}{Q} \quad P(T) = \frac{5}{8} = \frac{5}{Q}, \quad (3)$$

where we defined the normalization constant  $Q = 8$ , which is also called **partition function** in statistical mechanics. This is now a correct probability distribution, since  $P(H) + P(T) = 1$ . Note that we obtained it by calculating  $Q = 3 + 5$ , since this is simply the sum of the weights for the two states H and T.

- Consider an atom that can be in two states 1 and 2 with energies  $E_1$  and  $E_2$ . We know that the probabilities  $P(1)$  and  $P(2)$  are in a ratio of 4:7. Calculate the partition function  $Q$ , the probabilities  $P(1)$  and  $P(2)$  of the two states and the mean energy  $\langle E \rangle = P(1)E_1 + P(2)E_2$ .
- Repeat the same exercise, but now for three states with energies  $E_1, E_2$  and  $E_3$ , where the corresponding probabilities are in a ratio of 1 : 2 : 3.

The same idea can also be used for continuous distributions. Consider the Gaussian function  $f(x) = e^{-\frac{x^2}{2a}}$  for some  $a > 0$ . We want to define a probability

$$P(x) \propto e^{-\frac{x^2}{2a}} = f(x) \quad (4)$$

, where the symbol “ $\propto$ ” means “proportional to” or “equal up to a constant”. In this form, this is not a probability distribution, since

$$\int_{-\infty}^{\infty} f(x) dx = \int_{-\infty}^{\infty} e^{-\frac{x^2}{2a}} dx = \sqrt{2\pi a} \neq 1, \quad (5)$$

at least in general (unless  $a = 1/\sqrt{2\pi}$ ). Also in this case, we define the  $Q = \sqrt{2\pi a} = \int_{-\infty}^{\infty} f(x) dx$ . Then,

$$P(x) = \frac{1}{Q} f(x) = \frac{1}{\sqrt{2\pi a}} e^{-\frac{x^2}{2a}} \quad (6)$$

satisfies  $\int_{-\infty}^{\infty} P(x) dx = 1$  and thus is a correctly normalized probability distribution (also called **probability measure**). The idea behind this trick is that  $Q$  measured by how much the integral of  $f$  is too big. If it is too big by a factor of 3, we can divide by 3 to turn  $f$  into a probability distribution etc.

- (c) Consider the function  $f$  defined on the interval  $[0, \infty)$  and given by  $f(x) = x^2 e^{-x}$ . Calculate an appropriate partition function  $Q$  for this function and turn it into a valid probability distribution. *Hint:* You can use that  $\int_0^\infty x^2 e^{-x} dx = 2$ .

## Exercise 2 What is the Partition Function $Q$ ? Connection to Materials Science

In this exercise, we will discuss the most important mathematical trick that is used to do calculations in all of statistical mechanics. It was already discussed in the lecture, but since it is so important (also for the exam), we will guide you through a step by step derivation to help you really understand why the trick works.

For simplicity, we use the letter  $x$  for the microstate of a material, and let  $E(x)$  be the energy in state  $x$ . Then, the **canonical probability distribution** (also called **canonical probability measure**) for the temperature  $T$  is defined up to a constant by

$$P(x) \propto e^{-\beta E(x)} = e^{-\frac{E(x)}{k_B T}}, \quad (7)$$

where  $\beta = \frac{1}{k_B T}$  is the inverse temperature of the system. We then define the **canonical partition function**

$$Q = \sum_x e^{-\beta E(x)} \quad (8)$$

which can be used to define the correctly normalized probability measure

$$P(x) = \frac{1}{Q} e^{-\beta E(x)} = \frac{e^{-\beta E(x)}}{\sum_x e^{-\beta E(x)}}. \quad (9)$$

Once we know  $Q$ , we have fully specified the probability measure  $P$ , and are now able to calculate material properties such as the internal energy

$$\langle E \rangle = \sum_x P(x) E(x) \quad (10)$$

from which we can compute experimentally measurable quantities like the heat capacity  $C = \frac{\partial E}{\partial T}$ .

In fact, the partition function  $Q$  is so useful that we can obtain  $\langle E \rangle$  without even having to calculate the expectation value, namely by using

$$\langle E \rangle = -\frac{\partial \log Q}{\partial \beta} \quad (11)$$

The goal of this exercise is to understand why this trick works.

- (a) Starting from the definition of  $Q$ , show that

$$-\frac{\partial Q}{\partial \beta} = \sum_x E(x) e^{-\beta E(x)} \quad (12)$$

- (b) Use the chain rule to show that

$$-\frac{\partial \log Q}{\partial \beta} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} \quad (13)$$

and combine this with the previous part to show that  $\langle E \rangle = \sum_x P(x) E(x)$ . *Hint:* What was the explicit formula for  $P(x)$ ?

(c) Similarly to part (a), show that the second derivative

$$\frac{\partial^2 Q}{\partial \beta^2} = \sum_x E(x)^2 e^{-\beta E(x)} \quad (14)$$

and conclude that  $\langle E^2 \rangle = \frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2}$ . This trick was used in the lecture to show that the variance  $\text{Var}[E] = \langle E^2 \rangle - \langle E \rangle^2$  of the energy is related to the heat capacity  $C_V$  of the system via  $\text{Var}[E] = k_B T^2 C_V$ .

(d) This trick is not restricted to derivatives with respect to  $\beta$ . Consider the probability measure

$$P(x) \propto e^{-\alpha N(x) - \gamma M(x)}, \quad (15)$$

where  $N(x)$  and  $M(x)$  are some material properties for the state  $x$  of the material, and  $\alpha, \gamma$  are some parameters whose meaning is not so important for now. Define an appropriate partition function  $Q$  for this probability measure and show that

$$\langle N \rangle = -\frac{\partial \log Q}{\partial \alpha}, \quad \langle M \rangle = -\frac{\partial \log Q}{\partial \gamma} \quad (16)$$

The last part shows that we can essentially get any material property by taking appropriate derivatives of partition functions. This is why this differentiation trick is so powerful and important!

In fact, it is known in thermodynamics that we can get all material properties by taking derivatives of thermodynamic potentials with respect to suitable variables. Since we can also get all material properties from  $\log Q$ , this suggests that there is a connection between  $\log Q$  and thermodynamic potentials. . . In this case, we will see that the Helmholtz free energy  $A = -k_B T \log Q$ , which provides a connection between thermodynamics and statistical mechanics!

## Application: Einstein Model of Solids

Now that we have discussed how important the partition function  $Q$  is, it is time to practice calculating it with many examples. We will do so with one of the first successful mathematical models to describe the properties of solids which was proposed by Albert Einstein in 1907, which also was very important for the discovery of quantum mechanics!

Einstein imagined that the atoms in a solid oscillate around their equilibrium position with a frequency  $\omega$ . A material is thus a collection of many oscillators.

We begin in Exercise 3 by studying the thermal properties of a single harmonic oscillator, and compare the results obtained using classical mechanics against quantum mechanics. Together, these provide us with one example each for a continuous and discrete probability measure. We then move on to Exercise 4, where we study the properties of real solids by considering a collection of many oscillators.

### Exercise 3 Statistical Mechanics of Single Harmonic Oscillator

In classical physics, the energy of a harmonic oscillator as a function of the position  $q$  and momentum  $p = mv$  is given by

$$E(p, q) = E_{\text{kin}}(p) + V(q) = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 q^2, \quad (17)$$

where  $\omega$  is the angular frequency ( $\omega = \sqrt{k/m}$  for a spring). You might only have seen this in the form  $E = \frac{1}{2}mv^2 + \frac{1}{2}kq^2$ , but you should convince yourself that the two expressions are the same.

In quantum mechanics, on the other hand, a harmonic oscillator has discrete energy levels

$$E(n) = \hbar\omega \left( n + \frac{1}{2} \right) \equiv \hbar\omega n \quad (+\text{const.}), \quad (18)$$

where  $n = 0, 1, 2, \dots$  and we have ignored the extra term of  $\frac{1}{2}\hbar\omega$  in the last equation since it is only a constant shift in the energy that does not affect experimentally measurable quantities.

We start calculating the thermodynamic properties for the quantum mechanical version, since the math is slightly simpler. We thus have

$$P_{\text{QM}}(n) \propto e^{-\beta E(n)} = e^{-\beta \hbar \omega n} \quad (19)$$

for  $n = 0, 1, 2, \dots$

(a) Calculate  $Q_{\text{QM}}$ . Hint: use the geometric series  $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ .

(b) Conclude that the probability of being in the  $n$ -th energy level is equal to

$$P_{\text{QM}}(n) = \left( 1 - e^{-\beta \hbar \omega} \right) e^{-\beta \hbar \omega n} \quad (20)$$

(c) Calculate  $\langle E \rangle$

We now compare this with the results from classical mechanics. Here, the probability measure  $P(q, p)$  depends on two variables (the position and momentum) and is given by

$$P_{\text{CM}}(q, p) \propto e^{-\frac{\beta}{2m}p^2 - \frac{\beta m \omega^2}{2}q^2} \quad (21)$$

(d) Calculate  $Q_{\text{CM}}$ . Hint: You will need to evaluate a double integral, but using  $e^{x+y} = e^x e^y$ , you should be able to split it into two single integrals of Gaussians.

- (e) Conclude that the probability density for a particle to have position  $q$  and momentum  $p$  is given by

$$P_{CM}(q, p) = \frac{\omega\beta}{2\pi} e^{-\frac{\beta}{2m}p^2 - \frac{\beta m\omega^2}{2}q^2} \quad (22)$$

- (f) Calculate  $\langle E \rangle$

- (g) Show that the heat capacity  $C_V = \frac{\partial E}{\partial T} = k_B$  (which is just a constant!).

As mentioned in the introduction, this model of oscillators played a key role in the discovery of quantum mechanics.

In fact, even to this day, statistical mechanics provides us one of the best ways to understand the relation between classical and quantum physics. Roughly speaking, classical mechanics is the “high temperature limit” of quantum mechanics. The colder the temperature of a system, the more quantum it behaves. This is why everyone who is developing quantum computers works at very low temperatures on the order of a few Kelvins or even milli-Kelvins.

- (h) Show that for high temperatures  $T \rightarrow \infty$ , the quantum partition function asymptotically approaches the classical one up to a factor of  $h$  (the Planck constant), i.e.  $Q_{QM} \rightarrow \frac{1}{h} \cdot Q_{CM}$ . *Hint:* Instead of  $T \rightarrow \infty$ , use  $\beta \rightarrow 0$  and combine this with  $e^x \sim 1 + x$  for small  $x$ .

#### Exercise 4 From Single Oscillators to Real Materials

In a solid with  $N$  particles, each particle can oscillate in the  $x$ ,  $y$ , and  $z$ -directions, leading to  $3N$  oscillator modes in total. Thus, if we let  $q_1, \dots, q_{3N}$  be the  $3N$  position coordinates and  $p_1, \dots, p_{3N}$  the corresponding momenta, the classical energy can be written as

$$E(p_1, \dots, p_{3N}, q_1, \dots, q_{3N}) = \sum_{i=1}^{3N} \frac{1}{2m} p_i^2 + \frac{1}{2} m \omega^2 q_i^2. \quad (23)$$

In the quantum case, the energy of each of the  $3N$  oscillator modes needs to be specified by a separate quantum number  $n_1, n_2, \dots, n_{3N}$ . The total energy (ignoring the  $+\frac{1}{2}\hbar\omega$  contributions) then is

$$E(n_1, n_2, \dots, n_{3N}) = \sum_{i=1}^{3N} \hbar\omega n_i, \quad n_i \in \{0, 1, 2, \dots\}. \quad (24)$$

- (a) Begin with a quantum system consisting of two oscillators, so

$$E(n_1, n_2) = \hbar\omega n_1 + \hbar\omega n_2 \quad (25)$$

Show that the quantum mechanical 2-oscillator partition function  $Q_{QM,2}$  is related to the single-oscillator partition function  $Q_{QM,1}$  by

$$Q_{QM,2} = Q_{QM,1}^2 \quad (26)$$

- (b) By extending the argument, show that for a 3D material consisting of  $N$  atoms and thus having  $3N$  oscillator modes, the total partition function  $Q$  is given by

$$Q_{QM,Material} = Q_{QM,1}^{3N} \quad (27)$$

- (c) Show that  $\log Q_{QM,Material}$  is extensive, and in fact simply  $3N$  times the original  $\log Q$  for a single oscillator. In particular, conclude that the energy  $\langle E \rangle$ , heat capacity  $C_V$  etc. of the material are simply  $3N$  times the values you calculated for a single oscillator in the previous exercise.
- (d) Make sure that you can also perform the same arguments as in parts (a) and (b) using classical mechanics, and show that the heat capacity is equal to  $C_V = 3Nk_B$ , which is the famous Dulong-Petit law!