13 A two–level system: prototype of a heat storage

Aim: This exercise serves you to repeat the basic concepts of statistical physics, namely how to derive thermodynamic properties from a canonical partition sum. Basic conepts such as in/distinguishability, non–interacting particles, specific heat (heat storage) and pressure, will be discussed. Some mathematical knowledge about series is required!

Time: 2-3 hours (if the knowledge of the lecture is there!)

Given is a system of volume V of N not interacting particles, which can be in two energy states $\epsilon_1 = 0$ and $\epsilon_2 = \epsilon > 0$. Exchange of energy with a heat bath is possible. Our aim is to derive thermodynamic properties via the partition sum $Z(T, N, V)$ for distinguishable (**I**) and indistinguishable (**II**) particles. We start with distinguishable particles. First we have to ask the question how to count states.

1. What is the partition sum for one particle ($N = 1$)?
2. Calculate for a fixed number of excited states n [1] the Hamilton function (energy).
3. How many configurations with exactly this energy are there for distinguishable and indistinguishable particles?
4. Now calculate the total partition sum for distinguishable (**I**) without restriction of the number of excited states, only the total particle number N is fixed.
   Hint: binomial formula $(a + b)^N$.
5. How does the partition sum of indistinguishable particles look like? Calculate it.
   Hint: Geometric series.

The following steps have to be performed for distinguishable (**I**) and indistinguishable (**II**) particles.

6. What is the probability to find n particles in the excited energy level?
7. What is the average particle number in the excited energy level? Sketch this quantity depending on the temperature T.
   Hint (**I**): Write out the binomial coefficient and rewrite it.
   Hint (**II**): Use a derivative.
8. What is the average internal energy U in the system?[2] What can we say about energy fluctuations in this system? (look into the lecture notes) Quantify them.
9. Calculate the thermodynamic potential, derive the entropy S and make the connection to the internal energy U.
10. Calculate and sketch the specific heat depending on the the temperature T. Hint: hyperbolic functions

[1] Subset n of N particles, which are in the excited state (state 2)
[2] Use the fact that we have a non–interacting system.

11. When is this system best suited as heat storage?
    (You may search a local maximum (if it exists), simplify the terms as far as possible, solve numerically or graphically)
    In which case (**I** or **II**) can we have a higher specific heat?

12. Now assume that the higher energy level depends from the volume:

$$\epsilon = \frac{1}{V}.$$

13. Calculate the pressure of the system depending on the temperature and the volume.
    Try to establish a connection between pressure and internal energy.

14 Einstein solid

Aim: Application of statistical tools to derive the specific heat of crystals. You may need differentiation rules for hyperbolic functions

Time: 1 hour (after having solved 13 this should be easy)

The Einstein solid is a rather simple model for a solid based on the following assumptions (we consider a total of N atoms in contact with a thermal bath):

- Each of the atoms has the same mass m
- Each of the atoms in the solid is an independent 3D quantum harmonic oscillator
- All atoms oscillate with the same frequency[3]

The Hamiltonian of a 3D harmonic oscillator is (we have a total of $3N$ degrees of freedom):

$$H = \sum_{i=1}^{3N} \frac{1}{2} m(\dot{q}_i^2 + \omega^2 q_i^2) \tag{1}$$

1. Remember from your quantum mechanics course: What are the eigenstates ε_n of such a single quantum mechanical harmonic oscillator?
2. Calculate the partition sum for one oscillator. You should end up with some hyperbolic function. (assume an infinite number of possible eigenstates).
3. Calculate the partition sum for N particles.
   Hint: You may use the fact, that the oscillators are independent. $Z(N,T) = Z(1,T)^N$
4. Calculate the thermodynamic potential
5. Calculate the entropy
6. Calculate the internal energy

[3] This constraint is simple but not always correct. The Debye model represents a more accurate description of a solid with variable frequencies.

7. Calculate the specific heat
8. How does the specific heat behaves in the low and high temperature limit? Which behaviour is in agreement with the physical laws (name them, what do they say)?

\+ (half a bonus point) Proof that a 3D harmonic oscillator is equivalent to 3 1D oscillators by working with quantizations in 3 dimensions $n = n_x + n_y + n_z$. Find out the degeneracy for a fixed energy characterized by the integer quantum number n and calculate the partition sum. Show that this is equivalent to $Z(1,T)^3$ in one dimensions.

Interludium: Non–interacting systems

The following points can help you to better understand the concept of non–interacting particles. You are not supposed to prepare those tasks for the exercise.

1. Which property of a Hamilton operator must be given to be able to speek from a interaction–free system? State an Hamilton which is interacting and proof that this property is violated.
2. Proof that the canonical partition sum of a non–interacting (bosonic or fermionic) system can be expressed via the partition sum of a single particle (degree of freedom).

   To do so start with the sum over all quantum numbers $\{n_1, n_2, \ldots, n_N\}$[4], split the Hamilton function according to those quantum numbers and conclude the factorizability.
3. Since the summands in the (grand)canonical ensemble depend only on the energy of the states we look at another important transformation:
   Energy representation: We do not sum over states but over energies and take into account how many states with the same energy occur (degeneracy). This number of states per energy is called **density of states**. Perform this step formally also for interacting systems.
4. Derive the mean occupation of the k^{th} fermionic or bosonic[5] energy state. Use the eigenenergies ϵ_i and the occupation numbers n_i: $H = \sum_i \epsilon_i n_i$.

15 Debye Modell

Aim: In this problem we improof the Einstein model by taking different oscillation frequencies into account.

Time: 0.5 - 1 hour

The harmonic oscillator of N independent (not interacting) quantum mechanical particles is given by the following Hamilton operator:

$$H = \sum_{j=1}^{3N} \left[\frac{p_j^2}{2m} + \frac{m\omega_j^2}{2} r_j^2 \right],$$

[4]The energies are given as functions of those quantum numbers n_j: $E_j = f(n_j)$.

[5]Recall: Each fermionic energy level can only be occupied once, each bosonic energy level can be occupied arbitrarily.

with the eigenenergies

$$E_j = \hbar\omega_j(n_j + \frac{1}{2}), \qquad n_j = 0, 1, 2, \ldots$$

The energies of each degree of freedom j (in total $3N$ degrees of freedom) is now only dependent from the oscillation frequency ω_j and the excitation (quantum state) n_j (in contrast to the previously discussed Einstein model where all oscillators had the same frequency).

1. Write down the partition sum for fixed ω_j, and arbitrary quantum numbers $n_j = 1, 2, 3, \ldots$ in der canonical ensemble. Derive a partition sum that depends on ω_j as product over all $j = 1, \ldots, N$ (Perform the summatrion over all n_j).
   Hint: Geometric series; try to express the final expression with hyperbolic functions.

   Derive the free energy F and the internal energy U. You should end up with

$$U(T, N) = \sum_j \frac{\hbar\omega_j}{2} \coth \frac{\beta\hbar\omega_j}{2}. \tag{2}$$

What we need now is a distribution of the angular frequencies $D(\omega)$ (density of states) to replace the sum by an integral. The following bullets indicate how the Debye model can be derived (just for information):

- The number of oscillations with a given an angular frequency ω scales in 3D like ω^2. Therefore the assumed density of angular frequency has the form

$$D(\omega) = C\omega^2.$$

- We assume that there is a maximal frequency, the Debye frequency ω_D up to which the density is nonzero.

$$D(\omega) = \begin{cases} C\omega^2 & \omega \le \omega_D \\ 0 & \omega > \omega_D \end{cases}$$

- Normalization: The integral of the density of angular momentum should be equal to the the number of degrees of freedom since it will be used in a sum over those $\sum_{j=1}^{3N}$.

$$\int_0^{\omega_D} D(\omega) d\omega = \frac{C\omega_D^3}{3} \overset{!}{=} 3N$$
$$C = \frac{9N}{\omega_D^3}$$

- Using the linear isotropic disperions relation $\boldsymbol{k} = c_S\boldsymbol{\omega}$ with the speed of sound in the crystal c_S we can relate the angular frequency ω to the oscillations possible in the crystal.

- In order to count the number of oscillations in the crystal, we characterize an oscillation (the mode) by its wave vector $\boldsymbol{k}$ and assume that those are distributed equally in the reciprocal space[6].

[6] Each grid point corresponds to one oscillation.

- Given the dimensions of the crystal by $V = L \cdot L \cdot L$ we can estimate the minimal possible wave length λ and wave vector $k = \frac{2\pi}{\lambda}$ by $k_{\text{min}} = \frac{2\pi}{L} \approx 0$. This corresponds to the minimal reciprocal volume $\Delta \boldsymbol{k} = \frac{(2\pi)^3}{V}$ an oscillation takes in reciprocal space. The maximal wave vector is given by the minimal wavelength $|\boldsymbol{k}|_{\text{max}} = \frac{\sqrt[3]{N}\pi}{L}$
- The total number of modes can be calculated in reciprocal space by an integral

$$\sum_{k_x} \sum_{k_y} \sum_{k_z} 1 \approx \left(\int_{\frac{2\pi}{L} \approx 0}^{\sqrt[3]{N}\pi/L} dk \right)^3 = \frac{N\pi^3}{V}.$$

- We approximate this integral of the reciprocal space by the eighth of a spherical integral using ω_D as maximal radius. This yields for the Debye angular frequency ω_D:

$$\frac{N\pi^3}{V} = \frac{1}{8} 4\pi^2 \int_0^{\omega_D} \omega^2 d\omega$$
$$\omega_D = \sqrt[3]{\frac{6N\pi^2}{V}} c_S$$

Your task now is to calculate the heat capacity:

2. Use the density for the angular frequency $D(\omega)$ to give a representation of the internal energy [Eq. (2)] as an integral. Calculate and sketch the specific heat for high and low temperatures. Use the Debye temperature $\Theta_D = \hbar\omega_D / k_B$ as reference and check if the behaviour of the specific heat is in correspondance with the physical laws. Compare those results to the results of the Einstein model and discuss for which temperature range which model is better suited.

   Useful hint for the approximation of the integral:

   Go back to exponential functions and expand the integrand in a series. Only consider leading polynoms for the approximation and use

$$\int_0^\infty \frac{e^x x^4}{(e^x - 1)^2} dx = \frac{4}{15}\pi^4.$$