

## 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<sup>1</sup>

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

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

1. Remember from your quantum mechanics course: What are the eigenstates  $\varepsilon_n$  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
  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.

<sup>1</sup>This constraint is simple but not always correct. The Debye model represents a more accurate description of a solid with variable frequencies.

## 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 speak 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  $\{n_1, n_2, \dots, n_N\}$ <sup>2</sup>, 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  $k^{\text{th}}$  fermionic or bosonic<sup>3</sup> energy state. Use the eigenenergies  $\epsilon_i$  and the occupation numbers  $n_i$ :  $H = \sum_i \epsilon_i n_i$ .

## 15 Debye Modell

**Aim:** In this problem we improve 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:

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

with the eigenenergies

$$E_j = \hbar\omega_j \left( n_j + \frac{1}{2} \right), \quad n_j = 0, 1, 2, \dots$$

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

<sup>2</sup>The energies are given as functions of those quantum numbers  $n_j$ :  $E_j = f(n_j)$ .

<sup>3</sup>Recall: Each fermionic energy level can only be occupied once, each bosonic energy level can be occupied arbitrarily.

1. Write down the partition sum for fixed  $\omega_j$ , and arbitrary quantum numbers  $n_j = 1, 2, 3, \dots$  in der canonical ensemble. Derive a partition sum that depends on  $\omega_j$  as product over all  $j = 1, \dots, N$  (Perform the summation 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

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

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  $\omega$  scales in 3D like  $\omega^2$ . 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  $\omega_D$  up to which the density is nonzero.

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

- 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  $\sum_{j=1}^{3N}$ .

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

$$C = \frac{9N}{\omega_D^3}$$

- Using the linear isotropic disperions relation  $\mathbf{k} = c_S \boldsymbol{\omega}$  with the speed of sound in the crystal  $c_S$  we can relate the angular frequency  $\omega$  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  $\mathbf{k}$  and assume that those are distributed equally in the reciprocal space<sup>4</sup>.
- Given the dimensions of the crystal by  $V = L \cdot L \cdot L$  we can estimate the minimal possible wave length  $\lambda$  and wave vector  $k = \frac{2\pi}{\lambda}$  by  $k_{\min} = \frac{2\pi}{L} \approx 0$ . This corresponds to the minimal reciprocal volume  $\Delta\mathbf{k} = \frac{(2\pi)^3}{V}$  an oscillation takes in reciprocal space. The maximal wave vector is given by the minimal wavelength  $|\mathbf{k}|_{\max} = \frac{3\sqrt{N}\pi}{L}$
- The total number of modes can be calculated in reciprocal space by an integral

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

<sup>4</sup>Each grid point corresponds to one oscillation.

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

$$\frac{N\pi^3}{V} = \frac{1}{8}4\pi^2 \int_0^{\omega_D} \omega^2 d\omega$$

$$\omega_D = \sqrt[3]{\frac{6N\pi^2}{V}} c_S$$

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

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

## 16 Ising 1D [Bonus task, 1P]

Given is a linear chain consisting of  $N$  atoms with magnetic dipole moments atomic spins. This so-called spin chain is called Ising model in 1D without magnetic field. Each magnetic moment can be in the states  $\pm 1$  corresponding to a spin parallel or antiparallel to the  $z$ -axis. The state is determined by the spin operator  $S_i^z$ :

$$S_i^z |\sigma_1 \sigma_2 \dots \sigma_N\rangle = \sigma_i |\sigma_1 \sigma_2 \dots \sigma_N\rangle; \quad \sigma_i = \pm 1.$$

Since the spins are fixed in space (crystal lattice) they are distinguishable. Between neighbouring spins there is an interaction (think of a spring model), which is given by the Hamilton operator:

$$H = - \sum_{i=1}^{N-1} J_i S_i^z S_{i+1}^z \quad J_i > 0 : \text{interaction constant.}$$

- Consider two spins (sites). State all possible (micro)states! How many microstates are there and how would you describe (count) them. For which configuration is the energy of the system minimized? Which term of the theory of magnetism can be used to describe this lowest energy state?
- Now consider  $N$  sites / spins. How many spin configurations  $|\sigma_1 \dots \sigma_N\rangle$  are there? State the canonical partition sum  $Z_N$  using the spin values  $\sigma_i$ ! This means to sum over all possibilities of each spin adding the Boltzmann factor according to the total energy of each configuration. If you look at this sum, what are the difficulties in processing this sum? Explain in your own words.

- Although the sum looks tough, we will use a trick to solve it: a recursion! To do this, add one link to the chain ( $N \rightarrow N + 1$ ) and derive the recursion formula <sup>5</sup>:

$$Z_{N+1}(T) = 2Z_N(T) \cosh\left(\frac{1}{4}\beta J_N\right).$$

- Consider only one site ( $N = 1$ ) and argue why the canonical partition sum has the form:

$$Z_1(T) = 2.$$

Calculate the partition sum depending on the temperature  $Z_N(T)$ .

From now on we simplify the setup by assuming a homogeneous interaction constant  $J_i = J$  for all sites  $i$ .

- Calculate the correlation function<sup>6</sup>

$$\langle S_i^z S_{i+1}^z \rangle.$$

Hint: Associate the  $S_i^z S_{i+1}^z$  operator with a derivative of the Hamilton function.

- Now we calculate the correlation function as a function of the distance  $j$ :

$$\langle S_i^z S_{i+j}^z \rangle.$$

Trick: insert the identity  $I = 4 S_{i+k} S_{i+k}$ ,  $k \in \{1 \dots j - 1\}$  in between two exponentials and identify again derivatives. Plot the correlation as a function of distance  $j$ .

- Calculate the inner energy  $U$  (remember how this works in the canonical ensemble) and the specific heat  $c_V(T)$  and sketch this function. Is the behaviour for low and high temperature in agreement with physical laws?
- Calculate the chemical potential  $\mu$ .



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<sup>5</sup> $\beta$  represents the inverse temperature.

<sup>6</sup>Remember the definition of an expectation value  $\langle A \rangle$ .