

Theoretical Material Science: Exercise Sheet 9

Please hand in solutions by: **Tuesday, June 27**, start of the exercise class

Exercise 22 (6 points): *Everything moves*

In the previous task you learned how to perform basic phonon calculation using *ab-initio* simulations. However also other properties such as the vibrational free energy and the specific heat can be obtained for these calculations. Both of them are heavily influenced by quantum nuclear effects. In this task you will see that those effects can determine the vibrational behavior of solids over a large temperature range.

- a) As bosonic quasi-particles phonons obey the Bose-Einstein statistic $n_s^{\text{B-E}}(\mathbf{q}) = \frac{1}{e^{\frac{\hbar\omega_s(\mathbf{q})}{k_{\text{B}}T} - 1}}$. Show that for high (classical) temperature and low energies it reduces to the Rayleigh-Jeans law $n_s^{\text{R-J}}(\mathbf{q}) = \frac{k_{\text{B}}T}{\hbar\omega_s(\mathbf{q})}$
- b) Starting from the quantum nuclear partition function derive an expression for the free-energy $F^{\text{vib}} = -k_{\text{B}}T \ln(Z)$. Which terms cannot occur in classical physics and why? Similar to part a recover the free-energy in the classical limit.
- c) Calculate the vibrational free energy quantum mechanical and classical using the *ab-initio* simulations in the second cubic supercell from exercise 21. Compare and plot both free energies.
- d) Derive an expression for the heat capacity at constant volume $C_V = -T \left(\frac{\partial^2 F^{\text{vib}}}{\partial T^2} \right)_V$. Show that the mode specific heat (before taking the integral) does not depend on the temperature in the **classical** limit.
- e) Calculate the heat capacity at constant volume quantum mechanical and classical, using the *ab-initio* simulations in the second cubic supercell from exercise 21. Compare and plot both heat capacities. At which temperature quantum nuclear effects can be neglected?

Exercise 23 (6 points): *Quasi-harmonic approximation*

Despite its usefulness the harmonic approximation is clearly limited in reach. Particularly it fails to predict anharmonic quantities such as the thermal expansion of solids. In this exercise you will see how we can overcome this limitation by explicitly assuming volume dependent second order force constants.

- a) Starting from the microscopic expression for the pressure

$$P = -\frac{\partial}{\partial V} (E^{\text{eq}} + \sum_{s,\mathbf{q}} \frac{1}{2} \hbar\omega_s(\mathbf{q})) + \sum_{s,\mathbf{q}} \left(-\frac{\partial\omega_s(\mathbf{q})}{\partial V} \right) \frac{1}{e^{\beta\hbar\omega_s(\mathbf{q})} - 1}, \quad (1)$$

derive an expression for the thermal expansion

$$\alpha = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

in terms of the overall Grüneisen parameter.

You might find the following relations useful

i The thermal expansion $\alpha = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{3B_0} \left(\frac{\partial P}{\partial T} \right)_V$

ii The mode Grüneisen parameter $\gamma_s(\mathbf{q}) = -\frac{V}{\omega_s(\mathbf{q})} \frac{\partial\omega_s(\mathbf{q})}{\partial V}$

iii The overall Grüneisen parameter $\gamma = \frac{\sum_{s,\mathbf{q}} \gamma_s(\mathbf{q}) c_s(\mathbf{q})}{\sum_{s,\mathbf{q}} c_s(\mathbf{q})}$. Here $c_s(\mathbf{q})$ is the mode specific heat.

- b) Calculate the thermal expansion coefficient for diamond silicon and plot it. Do you notice anything odd and can you explain it?
- c) Take a closer look at the calculated lattice constant at 0 K. Compare it to the static case and explain the difference.