Technische Universität Berlin
Institut für Theoretische Physik
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Exercises: Dr. Christian Carbogno, Henrik Kowalski et al.

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http://www.itp.tu-berlin.de/menue/lehre/lv/ss_2017/pflichtveranstaltungen_masterstudium/theoretische_physik_vi_vertiefung_theoretische_festkoerperphysik_i_ii/

Theoretical Material Science: Exercise Sheet 10

Please hand in solutions by: Tuesday, July 4, start of the exercise class

Exercise 24 (16 points): *Using Molecular Dynamics to Describe Highly Anharmonic Systems*
Often an approximate treatment of lattice anharmonicity via perturbation theory or simple methods such as the quasi-harmonic approximation is not sufficient to achieve a qualitatively correct description of material properties. To overcome this limitation, the full anharmonicity, i.e. the complete parts of the potential-energy surface that are accessible at certain thermodynamic conditions, have to be taken into account in the calculation. This can be achieved via molecular dynamics simulations, in which the classical motion of the nuclei is computed by evaluating the Newtonian equations of motion:

$$\mathbf{F}_I = M_I \mathbf{a}_I \quad . \tag{1}$$

a) To computationally evaluate the forces one can use the so called velocity Verlet algorithm,

$$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \mathbf{v}_I(t)\delta t + \frac{\mathbf{F}_I(t)}{2M_I}\delta t^2 \tag{2}$$

$$\mathbf{v}_I(t+\delta t) = \mathbf{v}_I(t) + \frac{\mathbf{F}_I + \mathbf{F}_I(t+\delta t)}{2M_I}\delta t \tag{3}$$

Derive these equations from expanding the position vector $\mathbf{R}_I(t+\delta t)$ and $\mathbf{R}_I(t-\delta t)$ into a Taylor series up to third order.

b) Before starting the actual calculations you have to find out how long you have to thermalize the system until it is equilibrated and if the chosen runtime is sufficient. For this purpose slowly increase the time for the thermalization and the actual run time. When do you reach convergence?

c) Calculate the temperature dependent volume of silicon using the quasi-harmonic approximation in the second cubic supercell. Next calculate the temperature dependent volume with a molecular dynamics simulations from 200 to 800 K in 100 K steps using the runtimes from part b). Proceed as explained in the computational script. Plot and compare the results.

d) Redo the quasi-harmonic calculation using only classical free-energies. Do they match the results of the molecular dynamics simulation?

e) Take a look at the standard deviation of each trajectory. Do you notice a trend? Can you explain it?

f) Repeat the calculations from parts b) and c), but this time for argon in a temperature range up to 80K. For the molecular dynamics simulation choose a temperature interval from 20 to 80K in 10K steps. Plot and compare the results from the quasi-harmonic approximation to the results from the molecular dynamics simulation.

g) Do you notice any differences in the behavior of silicon and argon? Which material would you consider to display a greater degree of lattice anharmonicity and why?