Problem 2: Thermodynamic properties of Mo under pressure

In this exercise we want to study ab-initio the thermodynamic properties of Molibdenum. Molibdenum is a bcc crystal with one atom per unit cell. The experimental cubic lattice constant is $a_0 = 3.147$ Å.

1. Compute the total energy of Molibdenum as a function of the lattice constant using the Density functional theory method. You can use the pseudopotential `Mo.pz-spn-kjpaw_psl.1.0.0.UPF` from `pslibrary` for the LDA functional.

2. Fit the energy with a Murnaghan equation and determine the theoretical lattice constant at the minimum energy. Plot the pressure as function of the volume.

3. At the equilibrium volume compute the phonon dispersions along a few high symmetry lines of the Brillouin zone. Compare with the experimental phonon dispersions that you find in the literature.

4. Interpolating the dynamical matrices on a thick grid, compute the vibrational energy, free energy, entropy, and constant volume heat capacity.

5. Using the pressure versus volume curve determined at point 2, find the lattice constant that is needed to have pressures of 50 Kbar, 500 Kbar, and 2000 Kbar.

6. Recompute the phonon dispersions for these three volumes. Evaluate the effect of pressure on the vibrational energy, free energy, entropy, and constant volume heat capacity.

7. Redo the exercise using the PBE functional using the pseudopotential `Mo.pbe-spn-kjpaw_psl.1.0.0.UPF`. Discuss the effect of the exchange and correlation functional on the thermodynamic properties of Mo.

In all cases check your results with respect to the computational parameters: kinetic energy cut-offs, number of **k**-points, smearing parameter. Some of these calculations are reported in Physical Review B **85**, 214121 (2012). Compare with your results when possible.