Computer modelling and design of materials

Lab 1: Bulk modulus of solid argon

1. Introduction

During this lab we will learn how to use molecular dynamics method to predict the mechanical properties of real materials. In particular, we will calculate the bulk modulus, which describes how resistant to compression the considered material is. The system that we will consider in this exercise will be solid argon (again). To describe the interactions of its atoms we will use (again) the Lennard-Jones potential.

2. Bulk modulus

The bulk modulus is a numerical constant that describes the elastic properties of substances. It is defined as the ratio between pressure increase and the resulting decrease in a material’s volume. Together with Young’s modulus, the shear modulus, Poisson’s ratio and Hooke’s law, the bulk modulus describes a materials response to stress or strain.

The bulk modulus $B$ can be formally defined by the equation:

$$ B_X = -V \left( \frac{\partial p}{\partial V} \right)_X. $$

(1)

Here, $V$ denotes volume, while $p$ stands for pressure. Two different bulk moduli can be distinguished, depending on the conditions (parameter $X$, which is kept constant): isothermal bulk modulus ($X = T$) and isentropic bulk modulus ($X = S$). In the first case, the temperature is kept constant.
during the compression. In the latter case, the entropy \( S \) is kept constant. This modulus describes situations, in which the system does not exchange the energy with the environment during the compression.

In this exercise we will calculate the isothermal bulk modulus \( B_T \). Its strict definition looks as follows:

\[
B_T = -V \left( \frac{\partial p}{\partial V} \right)_T. \tag{2}
\]

In general, the bulk modulus depends on the volume, being its function \( B = B(V) \). Typically, one is interested in zero pressure bulk modulus, denoted as \( B_0 = B(V_0) = B(V(p = 0)) \).

In the case of solids the dependence of the pressure \( p \) on the volume \( V \) can be well described using the following two equations of state (EOS):

1. Murnaghan equation of state

\[
p(V) = B_0 \left[ \left( \frac{V}{V_0} \right)^{-B_0'} - 1 \right] \tag{3}
\]

2. Birch-Murnaghan equation of state,

\[
p(V) = \frac{3}{2} B_0 \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} (B_0' - 4) \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} \tag{4}
\]

In both above equations \( B \) denotes bulk modulus, while \( B' \) stands for its derivative with respect to pressure:

\[
B' = \left( \frac{\partial B}{\partial p} \right) \tag{5}
\]

The zero that appears in the lower index informs that parameters \( B \) and \( B' \) should be taken at the equilibrium volume \( V_0 = V(p = 0) \).
3. Exercises

1. Finding the equilibrium volume.
Using LAMMPS program perform a simulation of argon crystal at constant temperature $T = 30$ K and constant pressure $p = 0$ bar ($NpT$ ensemble). Based on it, by performing time averaging calculate the equilibrium volume $V_0$, which corresponds to the zero pressure $p = 0$ atm.

2. Finding the dependence of pressure on volume.
Perform a series of simulations, simulating the behavior of solid argon under constant temperature $T = 30$ K and constant volume $V$ ($NVT$ ensemble). Consider 11 different, equispaced volumes from the range $0.95 V_0 \leq V \leq 1.05 V_0$. For each simulation find the average value and standard deviation of pressure $p$, by performing time averaging. By doing so construct the dependence of pressure on volume $p(V)$.

3. Finding bulk modulus.
Fit the obtained $p = p(V)$ dependence with the Murnagahan equation of state, optimizing its three parameters: $B_0$, $B'_0$ and $V_0$. Express the obtained bulk modulus $B_0$ in GPa and compare it with the available experimental data. Do the same (fit the $p = p(V)$ data) for the Birch-Murnaghan equation of state. Compare parameters ($B_0$, $B'_0$ and $V_0$) obtained for two considered equations of state. Plot the $p = p(V)$ dependence together with the two obtained equations of state.

4. Range of validity.
Discuss the validity of two obtained equations of states (Murnaghan and Birch-Murnaghan). Perform additional simulations to check how the simulated material behaves at higher deformations. Consider the following volumes: $0.85 \, V_0$, $0.875 \, V_0$, $0.90 \, V_0$, $0.925 \, V_0$ and $1.075 \, V_0$, $1.10 \, V_0$, $1.125 \, V_0$, $1.15 \, V_0$. For each volume find the corresponding pressure. Compare the obtained pressures with the pressures calculated from equations of state (previously obtained). For each additional volume calculate the error:

$$e(V) = \left| \frac{\tilde{p}(V) - p(V)}{p(V)} \right| \times 100\%.$$  

Here, $p(V)$ represents the pressure obtained from the simulation (the „exact” result), while $\tilde{p}(V)$ denotes the pressure predicted from the
equation of state (we treat it as approximated result). For two equations of state plot the dependence of error \( e \) on the volume \( V \) and discuss it. Answer the question: which of the two considered equations of states is more general, better describing the behavior of materials at higher deformations?

4. Tips and instructions

1. It is possible to perform simulation under different (than \( NVE \)) conditions, for example under \( NVT \) and \( NpT \) conditions (which are much more close to real – experimental – conditions). In order to perform simulation under these conditions, the \texttt{nve} fix must be replaced with \texttt{nvt} or \texttt{npt} fix.

2. To perform simulation in \( NpT \) ensemble the \texttt{npt} fix must be used. Its syntax looks as follows:

\[
\texttt{fix \ my_npt all npt temp 5.0 5.0 0.1 aniso 0.0 0.0 1.0}
\]

The following parameters must be given: the target temperature (must be specified twice, in the above example it equals 5 K) and the target pressure (also twice, above it equals 0 bar). Two another parameters must be also specified: the damping parameter of the thermostat and the damping parameter of the barostat. In the above example these parameters were set to 0.1 ps (for thermostat) and 1.0 ps (for barostat).

3. To perform simulation in \( NVT \) ensemble the \texttt{nvt} fix must be used. Its syntax is very similar:

\[
\texttt{fix \ my_nvt all nvt temp 5.0 5.0 0.1}
\]

Only parameters that refer to the temperature must be specified (the target temperature – twice – and the thermostat damping parameter).

4. In the case of \( NVE \) ensemble the volume is specified by specifying the initial volume of the simulation box. One may change the volume by changing (adjusting) the lattice constant of the generated crystal.
5. Before fitting the $p = p(V)$ data with the equation of state one needs to initialize its parameters ($V_0$, $B_0$ and $B'_0$). The $V_0$ parameter can be read directly from the $p(V)$ characteristics. The $B_0$ and $B'_0$ parameters can be estimated using finite differences (based on the obtained $p(V)$ characteristics).

6. The values of all other simulation parameters (lengths of equilibration and sampling periods, timestep length, size of the simulated system, cutoff radius, other) should be taken similarly to our previous exercise, in which we calculated specific heat of argon crystal. The input file for this simulation can be found here:

   www.mif.pg.gda.pl/homepages/swinczew/CMDM/simulation.in