COMPUTATIONAL MECHANICS 2021
36th conference with international participation
Srní
November 8 - 10, 2021

Study of anharmonic vibrational properties in 3D crystals using molecular dynamics simulations

J. Očenášek[a]

[a] *New Technologies - Research Centre, University of West Bohemia in Pilsen, Univerzitní 8, 301 00 Plzeň, Czech Republic*

In classical theory, solids are elastic objects that obey Hooke's law, according to which the deformation (strain) of an object is proportional to the stress applied to it. However, if the deformations have wavelengths of the magnitude comparable to the interatomic distances, classical continuum elasticity fails quantitatively. A correct prediction of these nanoscale deformations can only be obtained by considering the atomic vibrations in the crystal lattice. A unit (quantum) of vibrational energy in crystal lattice is called phonon. In this paper, we present one of the few possible numerical approaches to phonon spectra estimation that is very general and allows the study of specific anharmonic features such as phonon softening.

The linear mass-spring chain model is a classical model of a one-dimensional crystal lattice with the potential to reveal the main principles of lattice dynamics, i.e., vibrational waves propagating through the lattice, where the isolated masses represent atoms. In this contribution, a linear mass-spring model is introduced and extended to provide an accurate 3D model of a ferroelectric barium titanate (BTO) crystal, with a perovskite structure, see Fig. 1.

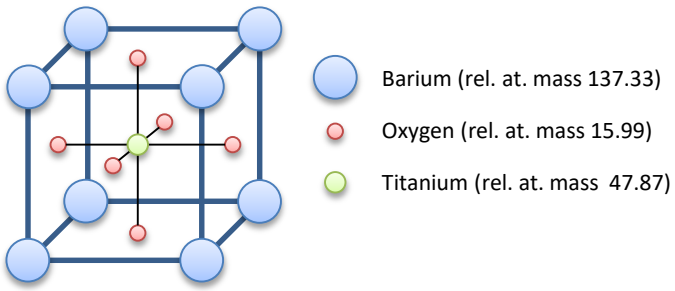

Fig. 1. Unite cell structure of barium titanate

Atomic forces in the BTO lattice were modelled by means of a shell model, which is a simple method for adding polarizability to the system. The shell model treats an atom as two coupled particles connected by a spring: (i) a core with positive charge, which holds the atomic mass of the atom, and (ii) a massless shell with negative charge. All cores and shells interact by Coulomb forces except the core and shell of the same atom. A short-range atomic pair interaction is set only between the shell particles. The short-range interaction was implemented as Born potential. The interaction scheme is given in Fig. 2, and model parameters were optimized in [3].

In order to correctly represent the possible states of the mechanical system at absolute temperature, a canonical ensemble NVT was set and thermalized by means of the Nosé–Hoover thermostat algorithm. This provides approximation of a system in thermal equilibrium with a Maxwell-Boltzmann statistics of the particles energy states.

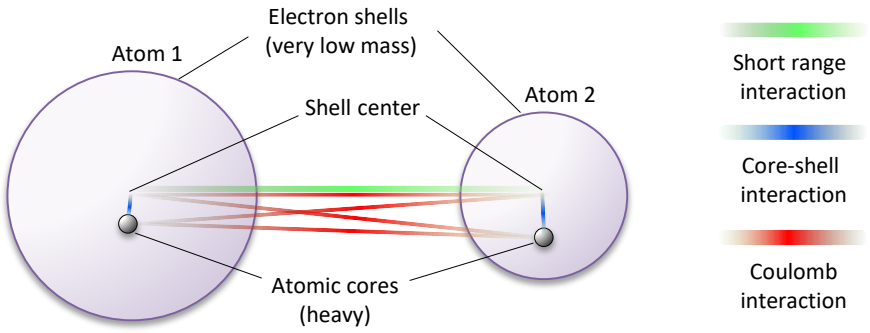

Fig. 2. Schematic representation of the core-shell model

This model, together with the classical molecular dynamics method (based on Newton´s equations of motion), is employed to numerically solve the trajectories of the atoms at a given temperature. Computer simulations were done using LAMMPS code [2]. Calculated atomic trajectories were then used to analyze the lattice vibrational properties and construct the phonon dispersion, i.e. to determine the wave frequencies present, the corresponding wavelength and the direction of propagation. The mathematical procedure involves autocorrelation of the Fourier transformed atomic velocities, details can be seen in [1]. Resulting phonon spectra for a selection of wave vectors (set of points at brillouin zone symmetry lines between [000] [001] and [½ ½ 0] wave vectors) is given in the Fig. 3. This method allows identification of all 12 optical modes and 3 acoustic modes of the spectra.

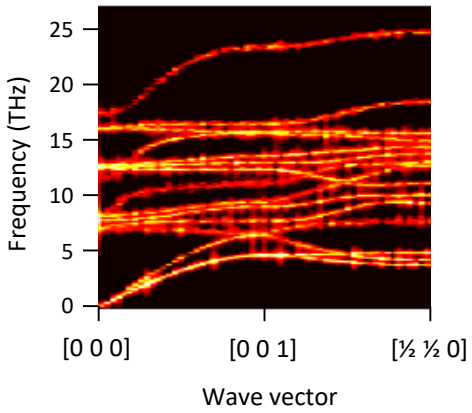

Fig. 3. Calculated phonon spectra at the low temperature (rhombohedral) BTO phase

Finally, specific anharmonic effects such as soft phonons, which are related to the phase transformation of the BTO crystal lattice at elevated temperatures, are discussed.

Acknowledgements

This work by was supported by The Ministry of Education, Youth and Sports under grant CEDAMNF CZ.02.1.01/0.0/0.0/15_003/0000358 (Czech Republic).

References

[1] Koukaras, E.N., Kalosakas, G., Galiotis, C., Papagelis, K., Phonon properties of graphene derived from molecular dynamics simulations, Scientific Reports 5 (2015) 12923.
[2] Plimpton, S., Fast parallel algorithms for short-range molecular dynamics, Journal of Computational Physics 117 (1995) 1-19.
[3] Vielma, J.M., Schneider, G., Shell model of $BaTiO_3$ derived from ab-initio total energy calculations, Journal of Applied Physics 114 (2013) 174108.