

Motivations

- Exploring and developing rechargeable batteries with lower self-discharge
- Understanding the suitability of new materials to substitute the common batteries materials
- Enhancing the batteries lifetime and power/energy
- Enhancing the batteries performance by modeling and optimizing their thermal, structural, electrical, and chemical properties

Proposed approach and goals

Approach

- Molecular dynamic simulations of LiCoO₂ as the cathode material using LAMMPS
- Implementing Buckingham potential for determining the interactions between the species
- Implementing the Nose-Hoover thermostat to equilibrate the system in a canonical ensemble (NVT)

Goals

- Understanding the thermal transport properties of LiCoO₂ cathode material.
- Understanding the thermal expansion of the system and its effects on the batteries performance.
- Understanding the structural stabilities of the system at high temperatures.
- Understanding the effects of the lattice distortions on the charge transport of the LiCoO₂ cathode material.
- Understanding the diffusion of species and their contributions on the LiCoO₂ batteries performance.

Simulation method

The interaction pair potential between ions *i* and *j* consists of a short-range term, the long-range Coulombic term and van der Waals interactions. These short-range interactions were modeled using the Buckingham potential:

$$V_{ij}(r_{ij}) = A \exp(-r_{ij}/r) - Cr_{ij}^2 \quad Eq.1$$

Where A, F, and C are the Buckingham potential parameters and *r* is the interatomic distance. Figure 1 depicts the supercell as well as the unit cell of a lithium cobalt oxide cathode materials.

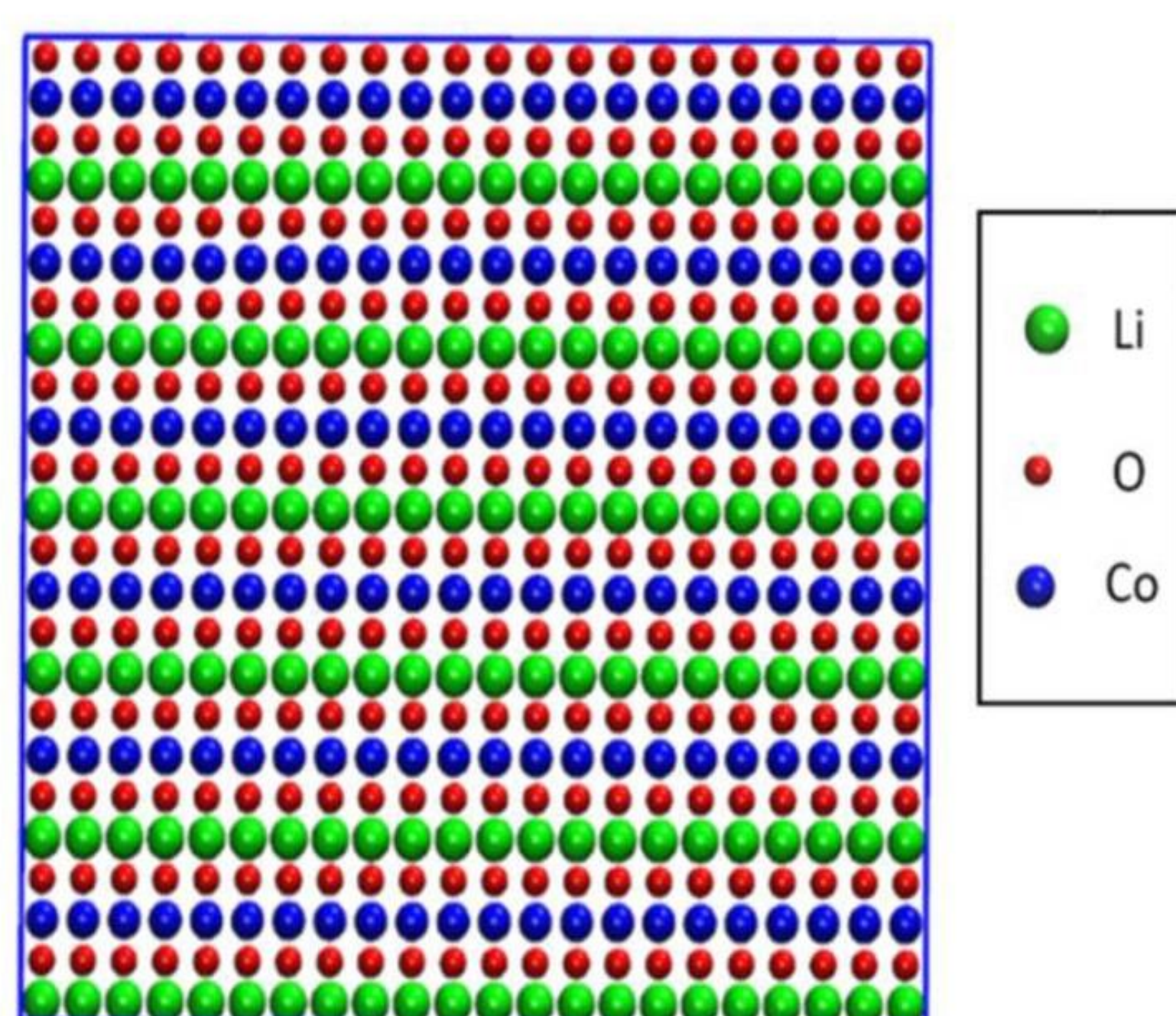


Figure 1. Lithium cobalt oxide crystal, a) supercell, b) unit cell.

Results and discussion

Structural parameters

The structure of LiCoO₂ at the equilibrium state was measured by the radial distribution function (RDF).

- These peaks are sharp at low temperatures and become broad at higher temperatures which is due to thermal motion.
- The height of the first peak decreases as the temperature increases because ions move away from equilibrium lattice positions at high temperatures and the crystalline volume expansion.

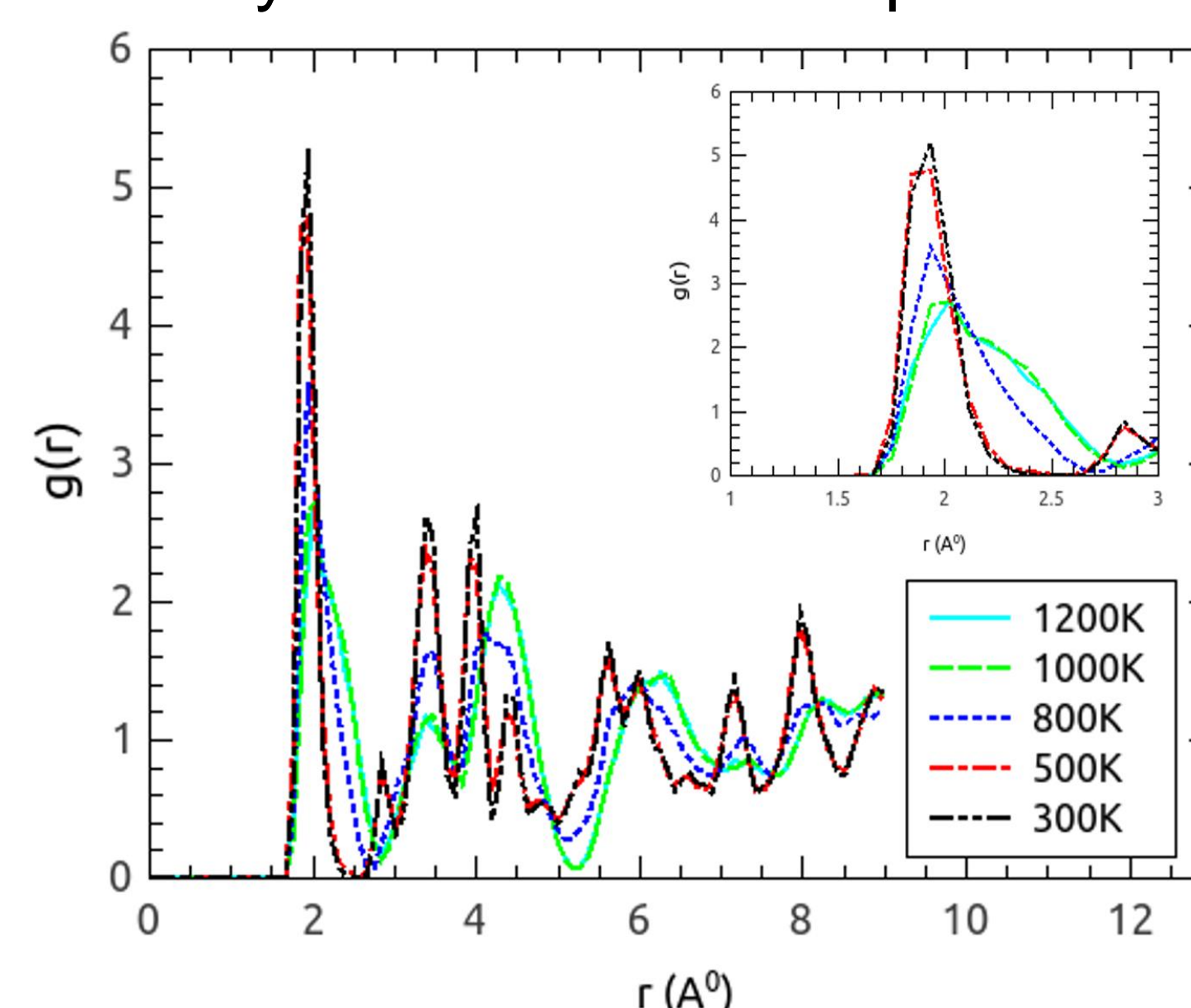


Figure 2. Radial distribution functions of Li-O at various temperatures

- Ions with lower cohesive energies are more stable compared with those of containing higher cohesive energies.
- Li-Li has the highest peak indicating lithium ions are unstable than other sorts of ions in the LiCoO₂ crystal.

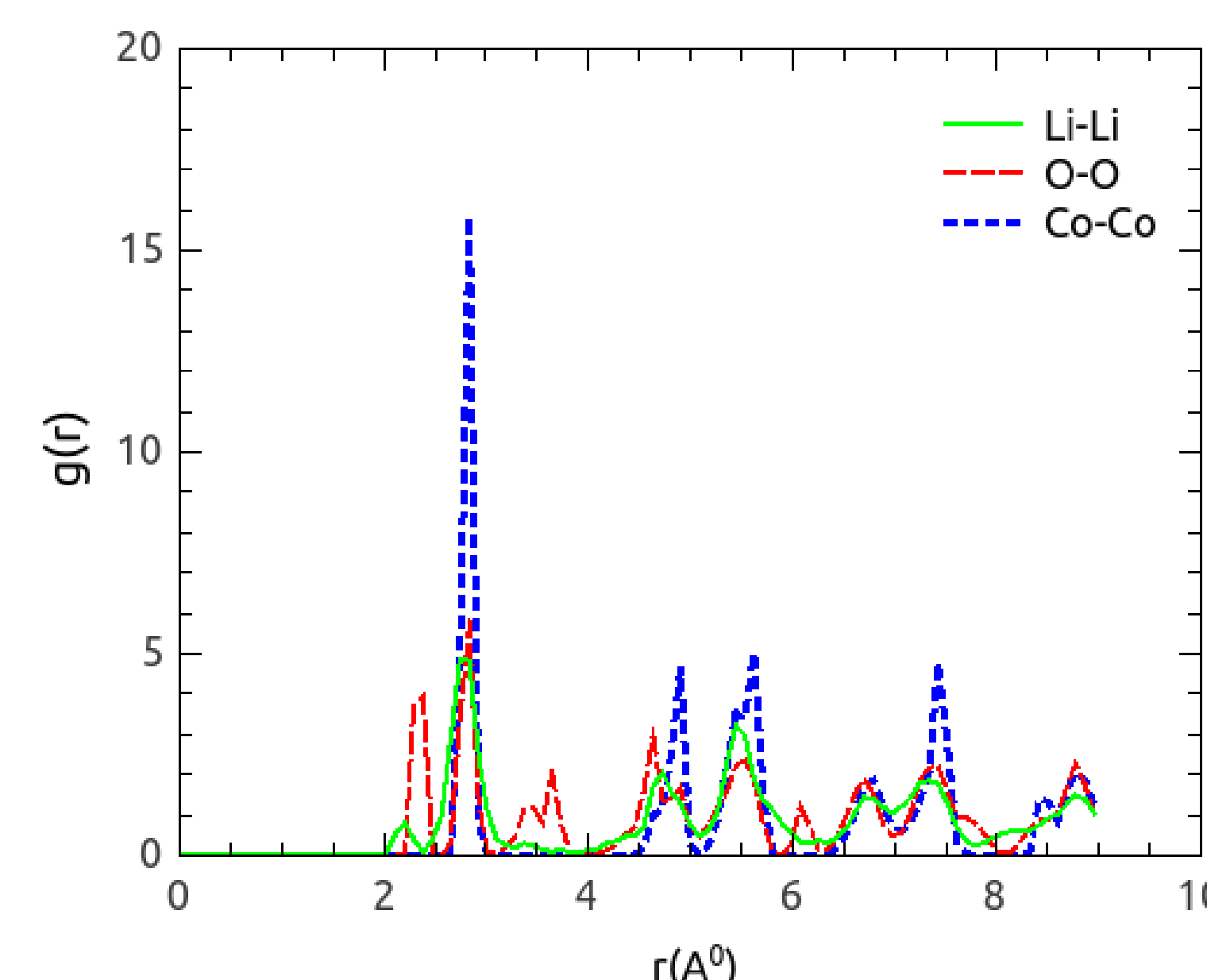
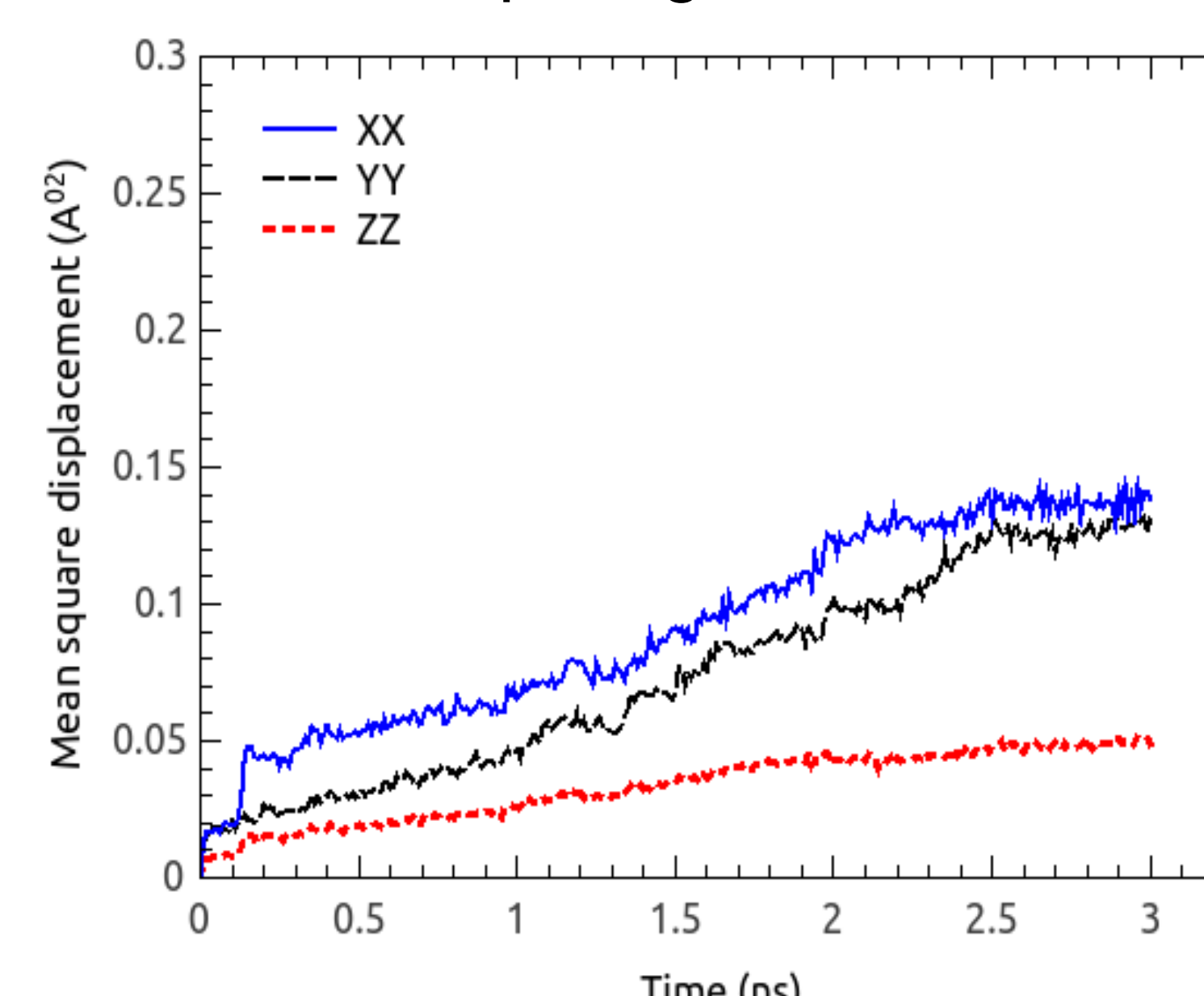


Figure 3. Radial distribution functions of Li-Li, O-O and Co-Co at room temperature

Table 1. Cohesive energies of ions

	Lithium	Oxygen	Cobalt
Cohesive energy (eV)	-7.1277	-25.5091	-25.1613

Figure 4. Mean square displacement of lithium ion for: XX-, YY- and ZZ- directions.



Vibrational phonon Density of States

The Fourier transform of the velocity-velocity autocorrelation function from the trajectory of each atom provides phonon density of state in molecular dynamics simulations.

$$D(\omega) = \int e^{i\omega t} \frac{\langle v(0)v(t) \rangle}{\langle v(0)v(0) \rangle} dt \quad Eq.2$$

- For all orientations, the lithium ions have higher phonon DOS.
- As the phonon frequency increases, the phonon DOS decreases.

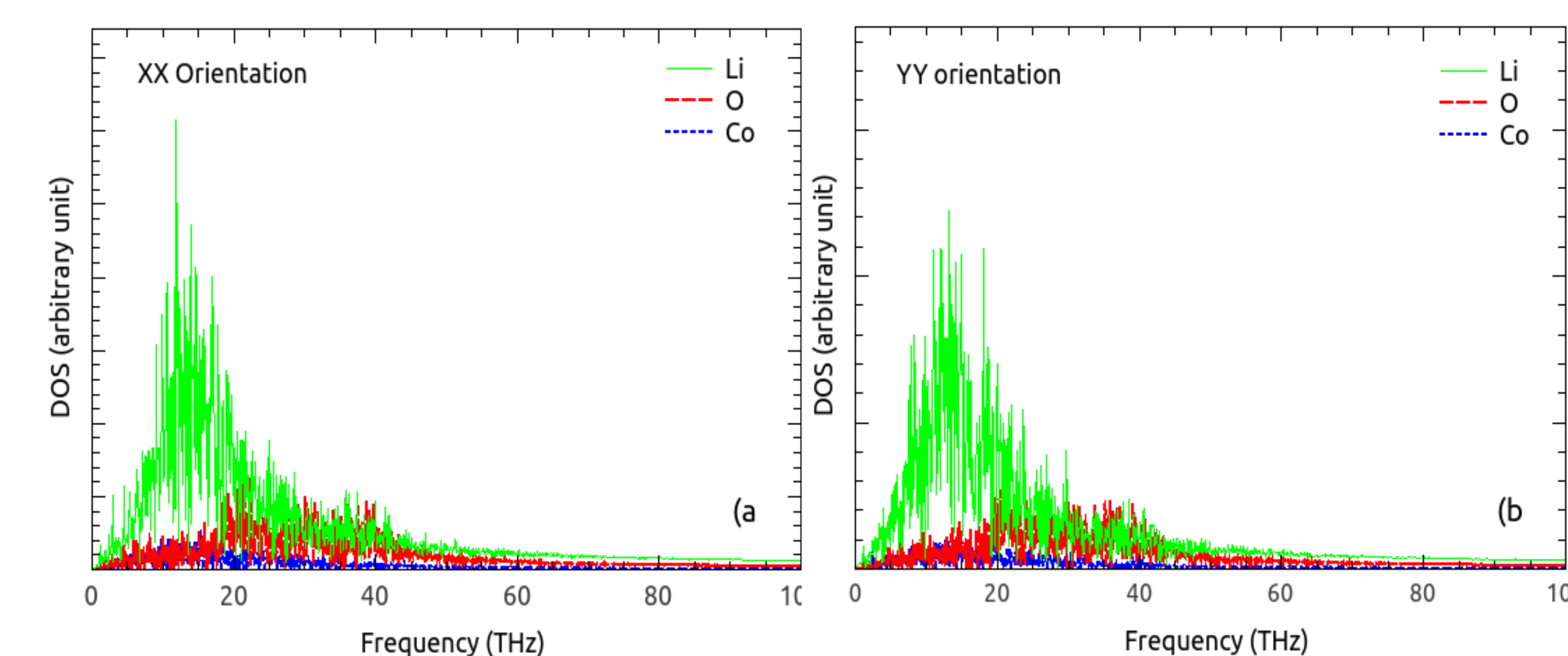


Figure 5. Partial phonon density of states of various ions for: a) XX, b) YY, and c) ZZ orientations at room temperature.

Conclusion

- Lithium ions are more thermally activated comparing to those of oxygen and cobalt ions.
- Lithium ions have higher MSD comparing to those of oxygen and cobalt ions.
- Radial distribution function of different ions shows as the temperature increases, the degree of disorder in the crystalline lattice increases especially at higher temperatures.
- Higher lattice distortion and expansion causes the reduction of thermal transport at higher temperatures.
- Using partial phonon density of states, the contributions of the various species on the phonon DOS were differentiated showing that lithium ions have more vibrations in all different directions rather than oxygen and cobalt ions.

References

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- [4] L. T. Kong, "Phonon dispersion measured directly from molecular dynamics simulations," *Computer Physics Communications*, vol. 182, no. 10, pp. 2201-2207, 2011.