# Transport mechanism of solid-state electrolytes via machine learning potentials at hybrid DFT level

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Lithium ortho-thiophosphate ($Li_3PS_4$) is a promising solid-state electrolyte for batteries, yet the microscopic mechanisms governing Li-ion transport within it remain unclear.
Moreover, computational works have yet to compute the thermal conductivity at the DFT level. In this talk, I will show how we build machine learning potentials trained over state-of-the-art DFT references (PBEsol, SCAN, and PBE0) to study the electrical [1] and thermal conductivity [2] of all the known phases of $Li_3PS_4$ (α, β and γ), for large system sizes and timescales. I will discuss the physical origin of the observed superionic behaviour of $Li_3PS_4$, where the $PS_4$ flipping drives a structural phase transition to a highly conductive phase, characterised by an enhancement of Li-site availability and by a drastic reduction in the activation energy of Li-ion diffusion. I will show the effect of the phase transition on both the electrical and thermal conductivity. We elucidate the role of inter-ionic dynamical correlations in charge transport by highlighting the failure of the Nernst-Einstein approximation to estimate the electrical conductivity. Then, we will discuss how thermal conductivity presents two distinct behaviours: low and constant with temperature for the α and β phases and a phonon-like behaviour for the γ phase. In the last part of the presentation, we will focus on our latest results on surfaces of $Li_3PS_4$, showing how the rotation of the $PS_4$ tetrahedra affects surface reconstruction.

## Figures

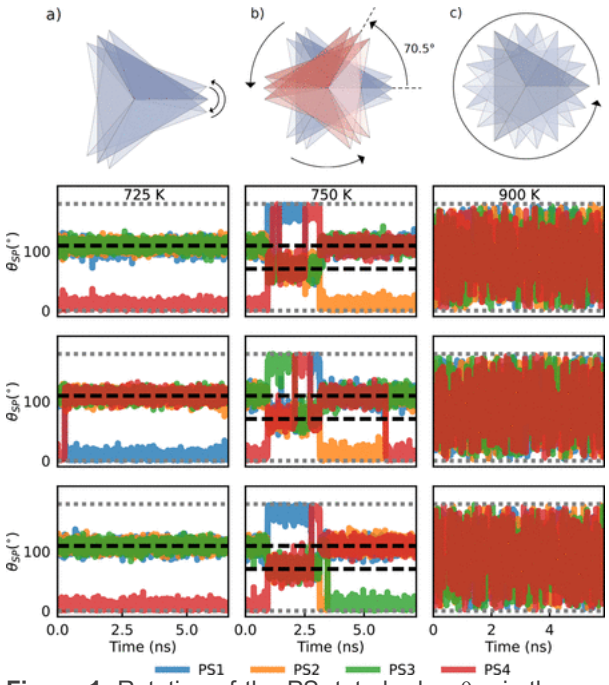


**Figure 1.** Rotation of the $PS_4$ tetrahedra. $\theta_{SP}$ is the angle between the PS bound and the *x*-axis. We can identify three regimes: at low temperatures, the tetrahedra oscillate around their equilibrium position; around 750K, the tetrahedra start to flip; at very high temperatures, the tetrahedra rotate freely.

## References

[1] L. Gigli, D. Tisi, F. Grasselli and M. Ceriotti, *Chem. Mater.,* **2024**, 36, 1482−1496
[2] D. Tisi, F. Grasselli, L. Gigli and M. Ceriotti, *Phys. Rev. Materials*, **2024,** 8, 065403