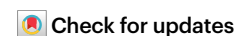


A solid-state electrolyte with liquid-like vibrational character

Claudio Cazorla



Solid-state electrolytes with high ionic conductivity are promising candidates for battery applications. Experiments in one of these materials now reveal a mechanism that mediates ionic diffusivity and mirrors the vibrational properties of liquids.

Solid-state electrolytes (SSEs) with high ionic conductivity are pivotal for the development of transformative green-energy technologies such as fuel cells, electrocatalysts and batteries. SSEs are complex materials with widely varying compositions, structures, and ionic mobilities, making it challenging to understand them at a fundamental level. For example, understanding the mechanism of ion diffusion and its coupling with phonons – quanta of lattice vibrations – remains an open problem. Now, writing in *Nature Physics*, Jingxuan Ding and colleagues employ a combined approach, comprising inelastic and quasi-elastic neutron scattering experiments and machine-learned molecular dynamics simulations, to address these fundamental questions¹.

Phonons, which originate from lattice vibrations in crystals, play a crucial role in governing a range of physical phenomena, including thermal transport² and electrical conductivity³. The frequency spectrum associated with lattice vibrations is usually characterized by a quantity known as the vibrational density of states (VDOS). Depending on the material, VDOS exhibits various characteristic features as the frequency of vibration goes to zero. For example, in crystalline materials, the VDOS has a quadratic dependence on the frequency at very low values. This behaviour is well reproduced by the Debye model of lattice dynamics⁴. Furthermore, for crystals with no ionic conductivity, the VDOS vanishes at zero frequency.

Collective atomic vibrations with a frequency spectrum and defined VDOS also occur in disordered condensed-matter systems such as liquids. In the case of liquids, it was first theoretically predicted⁵ and later experimentally demonstrated⁶ that in the zero-frequency limit, the VDOS is proportional to the vibration frequency. Moreover, the VDOS of liquids also vanishes at zero frequency⁵.

SSEs have traditionally been described as hybrids between liquids and solids, owing to their characteristic ionic diffusivity within a vibrating crystalline matrix (Fig. 1a). However, considering the vibrational properties, it remained unclear whether SSEs more closely resemble a liquid or a crystal, if either.

The investigation of the influence of phonons on ionic transport has recently emerged as an active area of research^{7,8}. The focus is to understand whether atomic vibrations could either promote or inhibit fast ionic diffusivity. Similarly, the vibrational properties of crystals, which are relatively easy to measure in the laboratory and to simulate using computers, could potentially serve as a means of screening new

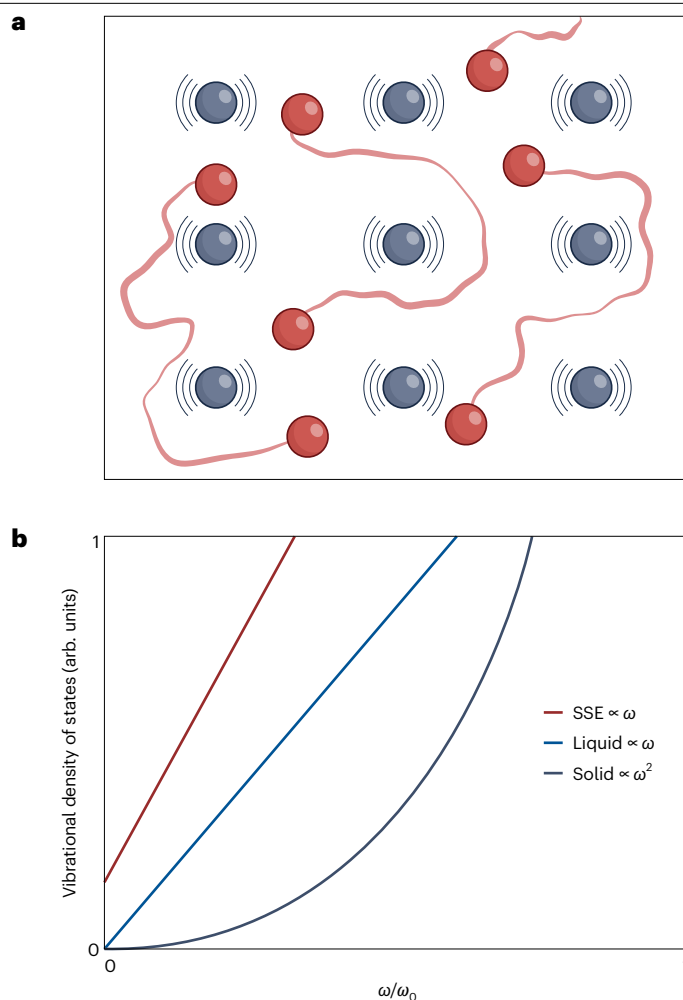


Fig. 1 | Vibrational properties of a solid-state electrolyte (SSE) in the vibrational zero-frequency limit. **a**, Sketch of a superionic material in which mobile ions (red spheres) diffuse over time through a solid matrix formed by vibrating atoms (blue spheres). **b**, VDOS of an SSE in the limit of zero frequency compared to that of a non-superionic solid and a liquid. Here, ω denotes the vibrational phonon frequency of the system and ω_0 denotes the characteristic vibrational phonon frequency of the system.

and improved SSEs^{7,8}. It is now accepted that low-frequency phonons can significantly affect the ionic hopping barrier and ionic diffusion pre-factors in SSEs⁷⁻⁹. However, the specific atomistic mechanisms by which the couplings between lattice dynamics and mobile atoms impact fast ionic diffusion remain controversial¹⁰.

Through a combination of inelastic and quasi-elastic neutron scattering measurements and molecular dynamics simulations based on machine learning potentials, Ding and co-workers have advanced the understanding of SSEs by addressing several of the open questions.

Specifically, by focusing on the archetypal superionic compound $\text{Li}_6\text{PS}_3\text{Cl}$, the authors demonstrated that the fast lithium ions' hopping results in a linear frequency dependence, rather than the quadratic Debye VDOS expected for solids. This behaviour resembles what occurs in liquids (Fig. 1b), along with an extreme damping and breakdown of low-frequency anharmonic phonons.

Furthermore, the team found a non-vanishing VDOS at the zero-frequency limit, in contrast to what occurs in non-superionic solids and liquids (Fig. 1b). This observation matches well with the theoretical expectations¹.

Importantly, Ding and colleagues also established an intrinsic connection between low-frequency vibrational modes and diffusive dynamics. Their machine-learned molecular dynamics simulations demonstrated a phonon-induced enhancement of lithium diffusivity by an order of magnitude at ambient temperature. Specifically, vibrations of the anionic PS_3 units were critical in opening the structural paths through which the lithium ions diffuse in the crystal. Conversely, they observed little influence of PS_3 rotations on ionic diffusivity, in contrast to a previously proposed ionic transport enhancement mechanism¹⁰.

The experiments and simulations conducted by the team established valuable connections between ionic diffusivity and lattice dynamics in fast ion conductors, surpassing previous simple descriptors based on quasi-harmonic approximations and averaged lithium vibrational frequencies⁷. They showed that the Debye model for phonons does not apply to SSEs in the zero-frequency limit, which agrees with the behaviour observed in orientationally disordered molecular crystals⁴. Additionally, the results demonstrate that a substantial coupling between ionic transport and low-frequency phonons is possible through atomistic mechanisms other than anionic unit rotations.

Implementing this wealth of new fundamental information to improve the selection and design of technologically relevant SSEs is

not a straightforward task. For example, it is not yet clear whether the same vibrational principles discovered in $\text{Li}_6\text{PS}_3\text{Cl}$ (ref. 1) would apply to other SSEs with significantly different structures, compositions and stoichiometries. In this regard, future works should systematically address the influence of defects and composition on the VDOS properties of SSEs.

Furthermore, precisely accessing the vibrational properties of various SSE families, especially in the zero-frequency limit, poses significant challenges both experimentally and theoretically. Researchers could benefit from investigating other related properties of SSEs, such as heat capacity, phase transition entropy, and thermal conductivity, which are readily measurable in the laboratory. Further studies in this direction may provide significant advances with regard to applications, bridging the gap between fundamental understanding and practical uses of SSEs.

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Published online: 6 January 2025

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Competing interests

The author declares no competing interests.