Unsupervised landmark analysis for jump detection in molecular dynamics simulations

Leonid Kahle,1,∗ Albert Musaelian,1,∗ Nicola Marzari,1 and Boris Kozinsky2

1 Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
2 John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

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Molecular dynamics is a versatile and powerful method to study diffusion in solid-state ionic conductors, requiring minimal prior knowledge of equilibrium or transition states of the system’s free energy surface. However, the analysis of trajectories for relevant but rare events, such as a jump of the diffusing mobile ion, is still rather cumbersome, requiring prior knowledge of the diffusive process in order to get meaningful results. In this work we present a novel approach to detect the relevant events in a diffusive system without assuming prior information regarding the underlying process. We start from a projection of the atomic coordinates into a landmark basis to identify the dominant features in a mobile ion’s environment. Subsequent clustering in landmark space enables a discretization of any trajectory into a sequence of distinct states. As a final step, the use of the Smooth Overlap of Atomic Positions descriptor allows distinguishing between different environments in a straightforward way. We apply this algorithm to ten Li-ionic systems and conduct in-depth analyses of cubic Li7La3Zr2O12, tetragonal Li10GeP2S12, and the β-eucryptite LiAlSiO4.

We compare our results to existing methods, underscoring strong points, weaknesses, and insights into the diffusive behavior of the ionic conduction in the materials investigated.

I. INTRODUCTION

Lithium-ion batteries power an increasingly broad and critical set of technologies.1 Commercially available batteries use organic electrolytes that impose constraints on their safety, power and energy density2 and can introduce chemical instabilities that require the incorporation of fuses and safety vents.3 Solid-state electrolytes are widely considered to be a promising alternative for next-generation batteries: many structural families of promising solid-state ionic conductors have been identified and are under investigation.4 While a good solid-state electrolyte must meet many criteria, such as low electronic mobility, easy device integration, and electrochemical and mechanical stability,5 it must first be a fast Li-ion conductor, and consequently optimizing conductivity and analyzing the mechanisms of Li-ion diffusion has been the focus of a large body of literature.4

Atomistic modeling techniques, in particular molecular dynamics (MD), have been used to study a wide variety of candidates for solid-state electrolytes and the factors that influence their ionic conductivity. Classical/empirical force fields were chosen in several studies6–13 due to their computational efficiency and access to the time and length scales required to characterize ionic transport. Accurate, yet expensive, first-principles simulations have also been employed for selected systems.14–24 The necessary compromise between the transferability of first-principles potential energy surfaces and the computational efficiency of force fields has also motivated the development of novel hybrid quantum/classical approaches25 for modeling lithium-ionic diffusion. The estimate of transport coefficients from the Green-Kubo or Einstein relations using molecular dynamics can be done in a straightforward yet expensive way, though improved methods for obtaining accurate estimates from short trajectories are being developed.26

In addition to computing ionic conductivity, design and characterization of new materials requires detailed understanding of the atomistic mechanisms of ionic transport. The central challenge is to develop automated methods for accurately analyzing the structure and dynamics of
lithium’s local atomic environments and for detecting rare transitions and subtle correlations in large amounts of data.

In many Li-ion conductors, Li ions form a mobile, often disordered, sublattice within a non-diffusive sublattice of other species, which we refer to as the host lattice hereafter. In the jump-diffusion model, the mobile ions spend the majority of their time in the local minima of the potential energy surface and vibrate within such sites for a sufficiently long time to lose memory of their previous locations while intermittently acquiring sufficient kinetic energy to overcome the barrier separating them from a different potential well. This formulation of Li-ion diffusion as occupation of and exchange between well-defined crystallographic sites can be used to model diffusion as a Markov-chain model using kinetic Monte Carlo. Also, using this discrete formulation to understand the microscopic origin of diffusion is a common theme in the literature, and site analysis tools have been used to explore the effects of site volume and anion sublattice structure on ionic conductivity, to identify conduction pathways and rate-limiting steps and correlated diffusion events, and to design new descriptors for conductivity. Ideally, an automated site analysis approach should:

1. automatically identify relevant Li sites;
2. accurately track migration of mobile ions through those sites;
3. require no prior knowledge of the material; and
4. work with the same parameters over a broad range of materials.

Existing methods fall into three classes: distance based, topology based, and density based. Distance-based methods use preexisting knowledge of the equilibrium positions of all Li-ion sites and consider a Li ion to be resident at a site when it comes within a given cutoff distance from the site’s position. Cutoffs can be smooth or discrete, but in both cases they need to be tailored to the structure at hand and are uniform across all sites within it. The positions of sites can also be coupled to the instantaneous positions of nearby host-lattice atoms to decrease sensitivity to thermal noise. Nevertheless, such methods rely on the crystallographic information they are given and also do not account for the varied or non-spherical geometry of sites. Starting from a prior knowledge of the host structure and possible Li sites, mobile ions can also be automatically assigned to sites based on convex-hull analysis of site polyhedra. This topology-based method deals with arbitrary site geometry, eliminates thermal noise and does not require arbitrary distance cutoffs, but does require the site polyhedra to be specified. Density-based methods identify regions of high Li-ion density separated by areas of low Li-ion density, as determined by a threshold, and define each high-density region as a site. These methods thus do not require prior knowledge about the material and can resolve sites with different geometries. In materials with nearby or rapidly exchanging sites, however, choosing a density threshold that can distinguish such sites from one another can be difficult.

In order to overcome some of these challenges, this work introduces an algorithm for accurately and automatically analyzing molecular dynamics trajectories and detecting jumps of the mobile ion through the host lattice with minimal human supervision and no prior knowledge. This algorithm can be combined with the automatic detection of important structural motifs leading to a versatile tool for the unsupervised analysis of trajectories and detection of diffusion events. The algorithm will be discussed in section II; in section III we apply it to three known ionic conductors and to seven non-diffusing materials and discuss the results; some details of the implementation are given in section IV; and our final conclusions are presented in section V.

II. ALGORITHM

Landmarks are persistent local features in an environment and therefore can be used to describe positions in the absence of global information (i.e. real-space coordinates). Landmark-based navigation explains the homing of social insects and has been applied in the field of autonomous navigation and artificial intelligence. Landmark models employ a vector-based description of the environment via a landmark vector \( \mathbf{l} \). Such a vector representation is useful for navigation if the distances between the landmark vectors corresponding to two states or positions \( A \) and \( B \) decrease with reducing distances in real space: \( |\mathbf{r}_A - \mathbf{r}_B| = f(|\mathbf{l}_A - \mathbf{l}_B|) \), where \( f \) is a monotonically increasing function of its input.

When analyzing trajectories, the real-space positions are obviously known beforehand. However, atomic position coordinates are inefficient descriptors for most properties since they are not invariant under rigid translation or rotation of the structure. We will describe the positions of mobile ions as landmarks that encode all the information necessary to detect changes in the ions’ environments and are invariant under these transformations.

First, we deduce that the descriptors should only encode local information since the local environment defines the potential energy landscape for the mobile ion, a principle reminiscent of the nearsightedness of electronic matter. In addition, we know from Pauling’s rules in crystal structures that ionic systems minimize their energy by packing into coordination numbers that are determined, among other factors, by the ratio of the radii of the cations and anions. Therefore, possible coordination polyhedra in the local environment are meaningful features. Checking all the possible polyhedra in a crystal is not feasible because of the combinatorial complexity this induces, so we need to restrict the description via a meaningful subset of convex hulls or polyhedra formed.
by the host lattice. A site description and trajectory discretization via pre-selected convex hulls has been previously developed and applied\textsuperscript{10} to study Li-ion diffusion in garnets.

Using polyhedra defined by host-lattice atoms as landmarks relies on the assumption that these atoms fluctuate around equilibrium positions, such that well-defined coordination polyhedra persist throughout the simulation. Equivalently, the host lattice is not changing in a way that causes sites to appear or disappear. Due to this assumption, the present landmark analysis cannot be applied to systems with liquid-like host structure such as polymers, where inter-site hopping happens on a longer time scale than the host motion, and dynamic coordination tracking must be used\textsuperscript{40}. It also cannot be applied to systems with a “paddle-wheel” diffusion mechanism, where the slow rotation of polyatomic anions creates a constantly changing set of local potential minima, such as shown for proton diffusion in CsHSO\textsubscript{4}\textsuperscript{41} or lithium- and sodium-ionic diffusion in the closoborate structures.\textsuperscript{28} On the other hand, the method does not assume that a given site is Markovian, i.e. whether a mobile ion completely loses memory of its past at any site: We define and find a site based on stable and persistent features in the environment of mobile ions, described by the landmark vectors, without considering information in the time domain. Whether the underlying process is Markovian can be determined by analyzing the resulting statistics.

The basic algorithm has three steps:

1. Definition of suitable landmarks.
2. Expression of the coordinates of the mobile ions during their trajectory in the landmark basis.
3. Clustering of the landmark vectors to reveal sites and discretize the trajectory of each mobile atom.

We also implemented, as an option, the possibility to:

4. Merge nearby sites that have high exchange rates and that fulfill some distance criteria.
5. Determine site types based on the geometry and chemistry of the local environment.

While the two last steps are optional and independent from each other, we always apply them in the analysis that we show in section III. Step 4 reduces significantly the noise in the data, and step 5 supplies information on the local geometry and chemistry. In the following we explain each of the steps in greater detail and finish with a discussion on why certain design choices were taken.

A. Step 1: Define Landmarks

The landmark analysis we introduce here is based on the Voronoi tessellation of the equilibrium configuration of the host lattice and its geometric dual, the Delaunay triangulation. Given a set of points in space, termed seeds, a Voronoi tessellation divides space into regions such that all points in each region are closer to the region’s seed than to any other seed.\textsuperscript{42} Formally, the Voronoi region determined by the seed point \( s_i \in \mathbb{R}^n \) is given by:

\[
R_i = \{ x \in \mathbb{R}^n : |x - s_i| \leq |x - s_j| \text{ for all } j \neq i \}
\]

Voronoi regions connect at Voronoi facets, as shown in the schematic in Figure 2. Any point on such a facet is equidistant to the seeds of the adjacent Voronoi regions. Voronoi nodes are, in a space of \( D \) dimensions, points where at least \( D \) facets intersect and therefore are equidistant to at least \( D + 1 \) seed points. It follows that each Voronoi node locally maximizes the distance to its adjacent seed points. The geometric dual of the Voronoi tessellation is the Delaunay triangulation. Such a triangulation or simplicial\textsuperscript{43} decomposition is obtained by connecting seed points that share a Voronoi facet. The Delaunay triangulation has the useful property that the circumcircles of all formed triangles have empty interiors, i.e. there are no seed points inside any circumcircle. It follows from the duality between the two tessellations that every Voronoi node is associated to exactly one Delaunay simplex. The Voronoi node lies at the center of the circumcircle of the associated Delaunay simplex.

In the remainder of the text we will work in three dimensions unless otherwise specified; in three dimensions a Voronoi node is equidistant to four coordinating seeds.

While a Voronoi node is a reasonable guess for a low-energy position since it maximizes the distance to its co-
ordinating seeds, the associated Delaunay simplex cor-
responds to the coordinating polyhedron of the site or a subset thereof. A Voronoi node and its coordinating
host-lattice atoms are together referred to as a landmark.
The coordinating host-lattice atoms of a landmark are
the host-lattice atoms that are vertices of the Delaunay
simplex – dual to the Voronoi node – in the equilibrium
configuration.

B. Step 2: Landmark Vectors

We start from a molecular dynamics trajectory that
gives the real-space positions \( \mathbf{r}_i(t) \in \mathbb{R}^3 \) of each atom
\( i \) at time \( t = N\Delta t_s \), an integer multiple of the sam-
ping timestep \( \Delta t_s \). In the remainder, we will use the
index \( h \) for host-lattice atoms and \( m \) for mobile ions.
First, we calculate the time-averaged positions for host-
lattice atoms \( \bar{\mathbf{r}}_h \), and use these as seed points
for a Voronoi decomposition, resulting in Voronoi nodes
\( \mathbf{R}^N \). The instantaneous position of a mobile particle,
\( \mathbf{r}_m(t) \), is expressed in terms of a proximity or similarity
to any real space position \( \mathbf{r}_m(t) \) can be transformed into a vector
in \( N \)-dimensional landmark space, where \( N \) is the num-
ber of landmarks in the system, equal to the number of Voronoi
nodes and also equal to the number of Delaunay simplices,
due to the duality explained in section II A. We index landmarks
with capital latin characters. For a landmark \( A \), we first define the normalized instantaneous
distance between a mobile particle \( m \) and a host lattice
atom \( h \), where atom \( h \) is one of the coordinating seed
atoms of the landmark \( A \):

\[
d^A_{m,h}(t) = \frac{\| \mathbf{r}_m(t) - \bar{\mathbf{r}}_h(t) \|}{\| \mathbf{R}^A - \bar{\mathbf{r}}_h \|}, \quad h \in A
\]

where \( \bar{\mathbf{r}}_h(t) \) and \( \mathbf{r}_m(t) \) are the instantaneous real-space
positions of host-lattice atom \( h \) and mobile ion \( m \), re-
spectively, \( \mathbf{r}_m \) is the time-averaged position of host-lattice
atom \( h \), and \( \mathbf{R}^A \) is the position of the landmark’s Voronoi
node. The corresponding component of the landmark
vector is then computed as:

\[
l^m_A = \prod_h^{N_{\text{coord}}} \left( f^A_{d^A_{m,h}} \right)^{1/N_{\text{coord}}}, \quad (2)
\]

where \( h \) ranges over the set of \( N_{\text{coord}} \) coordinating host-
lattice atoms and \( f(d) \) is a smooth cutoff function based
on the logistic function \( \sigma(d) \):

\[
f(d; d_0, k) = 1 - \sigma(d; d_0, k) = \frac{1}{1 + e^{k(d - d_0)}} \quad (3)
\]

where \( d_0 \) and \( k \) are the midpoint and the steepness of the
logistic curve, respectively. The function \( f(d) \) varies
smoothly from 1 to 0, reaching \( \frac{1}{2} \) at the set midpoint.
How fast it varies is tuned by the hyperparameter \( k \). As
can be seen from Eq. (2), we normalize \( f^A_{d^A_{m,h}} \) for a
varying \( N_{\text{coord}} \). In three dimensions and in the present
framework, \( N_{\text{coord}} \) is always 4, since we use a simpli-
cial decomposition to determine the landmarks. But the
framework could be changed to include a varying number
of coordinating host-lattice atoms, motivating this nor-
dimization. The cutoff function in Eq. (3) was preferred
due to its continuity and simplicity. Because distances
are normalized to the equilibrium distance between the
Voronoi node and the host atoms, the magnitude of each
landmark vector component depends on neither the vol-
ume nor shape of the corresponding landmark’s polyhe-
dron. This allows landmark analysis to distinguish be-
tween sites whose coordination polyhedra have very dif-
ferent volumes, as well as accurately tracking mobile par-
ticles through highly distorted sites.

C. Step 3: Landmark Clustering

The magnitude of each component of the landmark
vector indicates the extent to which a mobile atom’s po-
sition is dominated by that landmark. If, for example,
a mobile atom occupies a tetrahedral site, its landmark
vector would have one large value at the corresponding
landmark’s component and some low-magnitude noise
for neighboring landmarks. During a transition between
sites, there are no dominant contributions, as shown
schematically in two dimensions in Figure 3.

If an atom occupies an octahedral site, however, the
landmark vector will have four major contributions, cor-
responding to the four tetrahedrons resulting from the
Voronoi transform’s tessellation of the octahedron. We
show this schematically for two dimensions in Figure 4.

Because we have chosen a smooth function of position
for the landmark vector components, the landmark vec-
tors are a continuous function of trajectory time. By def-
nition, landmark vectors are invariant under rigid trans-
lations or rotations of the system and as such are ideally
suited as descriptors for dominant recurring features. A
clustering of the landmark vectors can be used to group
similar landmark vectors and therefore discretize our tra-
jectory in landmark space. We use density-based clusters
of landmark vectors, where each cluster is described by a
high-density region in landmark space, corresponding to
a frequent feature in the local environment of the mobile
ion. Therefore, we define sites as clusters in landmark
space.

We use a custom hierarchical clustering algorithm (de-
scribed in more detail in section A) with a simple cosine
similarity metric:

\[
S(l_A, l_B) = \frac{l_A \cdot l_B}{\|l_A\| \|l_B\|}, \quad (4)
\]

where \( l_A \) and \( l_B \) are landmark vectors. The clustering algo-
rithm scales linearly with the number of landmark vec-
tors.
Figure 3. Simplified schematic to illustrate our algorithm: A mobile ion (in violet) is jumping from site A to site B along a straight line. The reaction coordinate of the jump takes a value of 0 when the ion is at the Voronoi node of A and a value of 1 when it is at the Voronoi node of site B. The distance to the neighboring host atoms is marked with a dashed black line. The host-lattice atoms are shown at an instantaneous position (equation of motion of an harmonic oscillator, initialized randomly) and are colored red if they are part of landmark A, blue if part of landmark B, and half red, half blue if they belong to both. We show the Delaunay triangulation based on the equilibrium positions of the host lattice as semi-translucent red and blue triangles. The lower panel shows the landmark vector components of the mobile ion corresponding to A and B in red and blue respectively against the reaction coordinate. The vertical grey lines indicate the three snapshots shown in the top panel. We see that during the transition component A is decreasing while component B is increasing smoothly. At the transition point, the landmark components are approximately equal.

The clustering algorithm is run on the landmark vectors computed from the real-space positions of all mobile atoms every $n$ frames, where $n$ is sufficiently small and corresponds to a time span that is below the jump rate. A mobile atom is said to be occupying site $i$ at time $t$ if its corresponding landmark vector at that time is a member of the $i$-th landmark cluster. If the mobile atom’s landmark vector is not a member of any cluster, the atom is said to be unassigned at that time. The time sequence of such site assignments for a given mobile atom is its discretized trajectory; every change of site in that discretized trajectory is defined as a jump event.

The center of each site is defined as the spatial average of all real-space positions assigned to it over all time.

D. Step 4 (optional): Merge Sites

While one of the main strengths of landmark analysis is its ability to distinguish between very close sites, that level of resolution often identifies multiple sites where only one should exist. This is mainly due to a lack of data for the clustering. This issue is particularly prominent in host lattices containing sites with greater than four-fold coordination whose coordination polyhedra are highly distorted from the corresponding regular polyhedra. To merge such split sites, a post-processing clustering of the sites themselves can be applied, taking into account information from the time domain. We define $M$ as the stochastic matrix observed from the exchanges of ions between sites:

$$[m_{AB}] = \begin{cases} 0 & \text{if } |r_A - r_B| > \text{cutoff} \\ p_{A \rightarrow B} & \text{otherwise} \end{cases}$$

where $r_A$ is the center of site A and $p_{A \rightarrow B}$ is the probability that an ion occupies site B, conditional on the ion’s having occupied site A in the previous frame (for $A \neq B$). For $A = B$ it is the probability that an ion remains at site A until the next frame.

We apply Markov Clustering\textsuperscript{44} to the weighted graph defined by the stochastic matrix $M$, resulting in clusters of highly-connected subgraphs. Sites belonging to the same subgraph are merged (additional details are given in section B).

E. Step 5 (optional): Site Type Analysis

Sites are commonly defined by their Wyckoff points, and symmetry-equivalent sites can be interpreted as one site type. Such analysis depends on preexisting crystallographic data and also neglects that the energetics of a site are defined by the local geometry and chemistry. In line with our goal of making unsupervised site analysis possible, we developed a method for determining the type of the sites identified by the steps described from
section II A to section II D. Different sites whose environments cannot be distinguished are said to be of the same *site type*.

We describe local atomic environments using the Smooth Overlap of Atomic Positions (SOAP)\textsuperscript{45} as implemented in the QUIP molecular dynamics framework.\textsuperscript{46} Briefly, a SOAP descriptor is a vector that describes the local geometry around a point in a rotation-, translation-, and permutation-invariant way. The descriptor changes smoothly with the Cartesian coordinates of the structure. For these reasons, SOAP descriptors have become a powerful tool to express local geometry for machine-learning applications\textsuperscript{34,35} and the detection of structural motifs.\textsuperscript{34,35}

Multiple SOAP vectors must be computed for each site to provide sufficient data density for subsequent clustering. Computing these vectors for a site requires some procedure for sampling the real-space positions of both the site and its surrounding host-lattice atoms. We implemented two sampling schemes:

1. Real-space averaging: the real-space positions of all mobile atoms when they occupy the site are collected, and $n$ average real-space positions are computed for the site, where $n$ is a parameter chosen by the user. SOAP is computed on the averaged sites.

2. SOAP-space averaging: SOAP vectors are computed for all real-space positions with the host-lattice atoms at their corresponding instantaneous positions. Then, $n$ average descriptor vectors are computed in SOAP-space.

After reducing the dimensionality of the SOAP vectors with Principal Component Analysis, we cluster them using density-peak clustering\textsuperscript{48} with a Euclidean distance metric. A simple parameter estimation scheme is used to determine the number of clusters (see section C). Each cluster of descriptor vectors corresponds to a site type. Each site is assigned to the type corresponding to the descriptor cluster to which the majority of its descriptors were assigned. Small majorities (less than 70-80% agreement) typically indicate insufficient data, poorly chosen SOAP parameters, or very similar environments.

### F. Discussion of design choices

The main motivation for a landmark based approach was its ability to significantly reduce noise resulting from thermal vibrations in the system while reducing the dimensionality and discretizing the trajectory of the mobile ions. The design described in this section was driven by physical intuition and trial-and-error. While developing our method, we attempted and discarded a number of approaches due to poor performance in our trial systems:

- Directly clustering the Cartesian coordinates of the mobile ions (the density-based approach discussed in section I) was found to work poorly in some systems. We show this in more detail in section III A.

- An analysis based on the $N$ nearest neighbors of the mobile atom was tried but discarded, since we could not determine $N$ without relying on knowledge of...
the structure under investigation, in particular the expected size of the coordination shell of Li.

- We tried various landmark representations, the most simple being the distance to each host-lattice atom, therefore taking the instantaneous positions of host-lattice atoms as landmarks. The results for different systems were not satisfactory.

- We implemented a cosine-based cutoff function in Eq. (3), but found that it could not be normalized and remain smooth. Our tests indicated, however, that the choice of cutoff function has only a minor effect on the performance of the algorithm as long as the chosen function behaves roughly as the chosen function.

We conclude this section by pointing out that passing from Cartesian coordinates to landmark vectors was found to significantly reduce the noise that comes mostly from thermal vibrations in the system. Different formulations of landmarks can be envisioned, and while the present framework performs well for Li-ionic diffusion, a different landmark framework might be needed to describe, for example, a Groththus-like proton diffusion in superprotonic CsHSO$_4$.41

III. RESULTS AND DISCUSSION

We apply the algorithms above to 10 representative materials, Li$_7$La$_3$Z$_2$O$_{12}$, LiAlSiO$_4$, Li$_{10}$GeP$_2$S$_{12}$, Li$_3$Al$_6$Bi$_6$O$_{64}$, Li$_{24}$Sc$_8$B$_{16}$O$_{48}$, Li$_{24}$Ba$_{16}$Ta$_8$N$_{32}$, Li$_{24}$Re$_4$N$_{16}$, Li$_{12}$Rb$_8$B$_4$P$_{16}$O$_{56}$, Li$_6$Zn$_6$As$_6$O$_{24}$ and Li$_{24}$Zn$_4$O$_{16}$. For the subsequent analysis, we also calculate radial distribution functions, mean-square displacements, and ionic densities. The mobile-ion densities $n_M(r)$ are calculated from molecular dynamics trajectories as:

$$n_M(r) = \left\langle \frac{1}{N_M} \sum^M_m \delta(r - r_m(t)) \right\rangle_t,$$

where the index $m$ runs over all mobile ions $M$ and the angular brackets $\langle \cdot \rangle_t$ indicate a time average over the trajectory, which is equal to an ensemble average under the assumption of ergodicity. In practice, the delta function in Eq. (5) is replaced by a Gaussian with a standard deviation of 0.3Å, and the summation is performed on a grid of 10 points per Å in every direction. The tracer diffusion coefficient of the mobile species $D^M_{tr}$ is computed from the mean-square displacement of the mobile ions as a function of time:

$$D^M_{tr} = \lim_{\tau \to \infty} \frac{1}{6\tau^2} \frac{1}{N_M} \sum^M_m \langle (r_m(\tau + t) - r_m(t))^2 \rangle_t,$$

where $r_m(t)$ is the position of the mobile ion at time $t$. In practice, we fit a line to the mean-square displacement in the diffusive regime. An estimate of the error of the tracer diffusion coefficients is obtained via a block analysis.49 The radial distribution function $g(r)_{M-S}$ of the mobile ions $M$ with species $S$ is calculated as:

$$g_{M-S}(r) = \frac{\rho(r)}{f(r)} = \frac{1}{\langle f(r) \rangle N_M} \sum^M_m \sum^S_s (\delta(r - |r_m(t) - r_s(t)|))_t,$$

where $f(r)$ is the ideal-gas average number density at the same overall density. In addition, we integrate the average number density $\rho(r)$ to give the average coordination number as a function of distance.

A. Analysis of Li$_7$La$_3$Z$_2$O$_{12}$

Garnet-type structures were proposed as lithium-ionic conductors by Thangadurai et al.50 The general formula of garnets is Li$_7$La$_3$M$_2$O$_{12}$ (M = Ta, Nb),51 but aliovalent substitutions of $M$ can change the lithium content. Xie et al.52 studied in more detail the distribution of Li$^+$ in garnets. Their results indicate that increasing the lithium concentration in garnets leads to an increase in occupation of octahedral sites, which is confirmed by simulations10 and also in experiments.53 It has been established7,54,55 for the garnet structure that Li ions can occupy tetragonal 24d sites, octahedral 48g sites and 96h distorted octahedral sites. The latter stem from a site splitting of the 48g sites to increase the Li-Li distances and occur at higher lithium concentrations. In this work, we studied the Li-ion distribution of Zr-based cubic garnets with the stochiometric formula Li$_7$La$_3$Z$_2$O$_{12}$, referred to as LLZO in the remainder.

The dynamics in the cell of 192 atoms are sampled in the canonical ensemble via a GLE thermostat56 at a temperature of 500K, using a lattice constant of 12.9872 Å, and a polarizable force-field. The parameters of the force-field were taken from the work by Mottet et al.57 which was shown to accurately reproduce the kinetics of the diffusing process in LLZO. The simulations for LLZO were performed with the LAAMPS58 code.

The estimate of the diffusion coefficient via Eq. (6) reveal that Li-ions indeed are diffusive in LLZO, with a tracer diffusion coefficient of $D^L_{tr} = 2.4 \times 10^{-7}$ cm$^2$s$^{-1}$. Application of the Nernst-Einstein equation gives the ionic conductivity $\sigma$:

$$\sigma = \frac{Z^2e^2N}{kB T} D_{tr},$$

where $H$ is the Haven ratio, $(Z e)$ the carrier’s charge, $N$ the carrier density, $k_B$ the Boltzmann constant and $T$ the absolute temperature. We find a $\sigma = 0.23$ Scm$^{-1}$, assuming a Haven ratio of 1. This value is one order of magnitude larger than the values reported by Murugan et al.59 which is within the acceptable range, especially for
Figure 5. The Li-ion density in LLZO is shown above as 3 isosurfaces going from green (low density) to yellow (high density). The equilibrium positions of lanthanum are shown in blue, of zirconium in turquoise, and of oxygen in red. The Li-ion densities reveal the 3D percolation pathways in this material.

Figure 6. Upper panel: Radial distribution $g(r)$ as a function of distance $r$ for lithium to lithium (blue), to oxygen (orange), to zirconium (green) and to lanthanum (red). The integral, representing the coordination as a function of distance, is plotted against the right axis using dashed lines and the same color encoding. Lower panel: Radial distribution function for lithium-oxygen pairs for the two distinct site types we found. The red lines correspond to site type 0, the green lines to site type 1, and the integrals are shown with dashed lines and the same color encoding.

A classical force-field, and not of concern since the focus of this work is the analysis method. The diffusive pathways can be illustrated by the Li-ionic densities, shown for 3 isosurfaces in Figure 5. By visual inspection, the densities look similar to those presented by Adams and Rao in their computational study. The splitting of 48g sites into 96h sites cannot be seen from the isosurfaces at any isovalues, which is consistent with the conclusions drawn by Chen et al., that density-based clustering of real-space positions cannot resolve the two distinct 96h sites in LLZO from the 48g site. The radial distribution function $g(r)$ shown in the upper panel of Figure 6 shows how the Li ions in our simulation are, as expected, coordinated closest by oxygen and then by other Li ions.

The site analysis presented is used to discretize the trajectory of lithium ions into meaningful states, as illustrated for one lithium ion in Figure 7. The subsequent SOAP analysis produces two clearly resolvable clusters, which are detected by the clustering algorithm. We show the first two principal components in Figure 8, with a color encoding representing the cluster detected. It is evident that the SOAP descriptor produces data that clusters well in this projection and that the clustering algorithm correctly assigns the clusters. The algorithm detects 24 sites of one kind (type 1) and 83 of another (type 0). We attribute the tetrahedral environment to the former, and the octahedral environment to the latter, since the expected values are 24 sites for the tetrahedral environment and 96 for the octahedral one. The under-prediction of the number of octahedral sites is due to the merging, in some cases, of octahedral sites into a single site. The proximity and fast ion exchange between the octahedral sites explains why our algorithm does not give the correct answer, but it is remarkably close to the correct result, without any encoding of prior information about possible site splitting.

To ensure that the analysis of LLZO provides reasonable and expected results, we calculate the radial distribution function $g(r)$ separately for each site type; these are shown in the bottom panel of Figure 6. For clarity, we only show the lithium-oxygen pair distribution function. Li ions attributed to sites of type 1 have an environment characterized by a distinct nearest-neighbor peak stemming from four-fold coordination of lithium with oxygen, as evidenced by the integral plateauing at a value of four. The first peak for type 0, shown in red, has a shape compatible with a distorted octahedron, due to the appearance of a shoulder, and the weak, but distinguishable, plateau of the integral at a value of approximately 6. This is further evidence that the site types have been correctly attributed to the tetrahedral and octahedral site environments of LLZO, and that the SOAP descriptor
Figure 7. Site trajectory in LLZO at 500K for a representative mobile lithium ion over 1000 frames. For every frame, we determine the most likely site the ion is occupying. We plot the ion’s occupation over time, where discontinuities are interpreted as jumps. The site index on the y-axis is arbitrary, and the distances are not reflective of the actual jump distances.

Figure 8. SOAP descriptor clustering for LLZO. Each point is an average SOAP vector and is colored according to its assigned cluster (site type). The first and second principal components are plotted along the X and Y axes respectively.

Figure 9. Li-ion density in LLZO is shown above for the same isovalue (0.1) for Type 0 (octahedral environment) in green and Type 1 (tetrahedral environment) in bordeaux.

Figure 10. We show the jump lag or residence time in LLZO, which is the time an ion spends in site A before jumping to site B, averaged over sites of the same type. The color encodes the residence time, with no color (white) meaning that no jump has been observed. The time is given in multiples of the interval between frames.

Can be used to cluster site types correctly. Additionally, we resolve the Li-ion density by site type in Figure 9. The isosurfaces are compatible, by visual inspection, with reported work.

We also calculate the jump lag, which is the average residence time at a site A before jumping to a site B. If we average over all sites belonging to the same type, as shown in Figure 10, we see that jumps between the octahedral sites are fastest. From the site splitting of the 48g into 96h sites follows that two sites are present inside each octahedron, and that there is a potential energy barrier between. Our results are therefore in agreement with ab initio calculations, that show that the minima in the Li-ion potential energy surface are displaced from the original central site in the octahedral site. The presence of two distinct but very close sites manifests in very high exchange rates.

LLZO also displays fast jumps from the octahedral into the tetrahedral environment, whereas the reverse jump takes three to four times longer. No jumps between tetrahedral environments were observed, as expected, since an ion needs to traverse octahedral sites to reach a different tetrahedral site. While the jump probabilities, or lag times, are non-symmetric, the fluxes are symmetric, which is necessary to observe local detailed balance.

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Figure 11. The diffusive pathways in LLZO at 500K. The centers of sites of type 0 (octahedral environment) and type 1 (tetrahedral environment) are shown as crosses and plusses respectively. The color of the sites encodes the average residence time. Edges connect sites that have exchanged mobile ions, with the edge width related linearly to the observed flux of particles. The equilibrium host lattice positions of oxygen (red), lanthanum (grey) and zirconium (light grey) are shown as small spheres. The entire network of diffusion has one connected component.

are shown in Figure 11. The connectivity analysis reveals the existence of a single dominant pathway that allows mobile ions to diffuse through the entire simulation cell. The edge widths in the figure are proportional to the observed flux of particles, and we see that, where the octahedral site splitting is correctly determined, there is a large flux of ions between split octahedral sites compared to the smaller flux between the tetrahedral and octahedral environments.

Summarizing our results for this material, our site analysis finds the splitting of the $48g$ to $96h$ sites, which sets it apart from any density-based analysis. An analysis based on distance criteria to crystallographic sites would have worked as well or better, but obviously requires prior knowledge.

B. Analysis of LiAlSiO$_4$

The structure of the beta-encryphte LiAlSiO$_4$ referred to as LASO hereafter, is taken from the COD entry 9000368. The structure has been studied for its anisotropic expansion coefficient and its ionic conductivity. The structure can be described as an ordered $\beta$-quartz solid solution, with alternating aluminum and silicon planes. Location and occupation of the sites for lithium have been contested. In the original reference, the difficulties in determining the lithium sites in previous and in the same work are explained very well. For example, earlier work concluded that the Li sites are coplanar with the Al sites, while Pillars and Peacor show that the lithium sites are also present in the Si plane. Later work also shows that both sites are available to lithium and establishes the unidimensional chain of these sites as the mechanism for ionic diffusion in this material. There is now a better understanding of this structure and the sites available to lithium, but the original CIF-file in the COD originating from the experiments by Pillars and Peacor does not list all sites. Any analysis that relies on this knowledge would therefore have failed. Our molecular dynamics simulations and subsequent site analysis yield results that are compatible with the latest literature regarding the ionic transport in this material.

The structure is simulated starting from the reported CIF-file, which is Li$_{12}$Al$_{12}$Si$_{12}$O$_{48}$. A full atomic and cell optimization resulted in a volume increase of 3.6% without changing the cell angles in a significant way. The subsequent dynamical simulations were performed using Born-Oppenheimer ab-initio molecular dynamics in the canonical ensemble at a temperature of 750K, with further details given in section D. In total, 291 ps of simulation were performed.

We show in Figure 12 the Li-ionic densities sampled during the dynamics. The unidimensional chains of ionic diffusion are compatible with published results. The diffusion coefficient is hard to converge for the short dynamics we obtained for this system, and so quantifying the diffusion coefficient and its error cannot be done
Figure 13. Upper panel: radial distribution function $g(r)$ as a function of distance $r$ for lithium to oxygen (green), silicon (blue), aluminum (orange) and lithium (red). The integral of the average number density is plotted against the right axis as dashed lines in the same color. Lower panel: $g(r)$ for lithium to oxygen, silicon and aluminum by the site type that lithium is occupying in blue, green, and red respectively. Site type 0 is shown as a solid line and site type 1 as a dash-dotted line.

Figure 14. Similarly to Figure 10 we show the average residence time before a jump for the two distinct site types in LASO. White corresponds to no jump occurring.

The total RDF distribution in the upper image of Figure 13 hints at the fact that the Li ions prefer to occupy type 1 sites where the Si ions are closer than the Al ions. From the site analysis of our simulation, we calculate the mean occupation ratio to be 77% for site type 1 and 23% for site type 0. Literature reports\textsuperscript{71} give occupancies of 68% and 22% respectively, or a 3:1 ratio.\textsuperscript{65} In Figure 14 we show the jump lag between the type sites. Jumps from type 1 to type 0 are about 3.5 times faster, which is necessary to preserve detailed balance. We observe no

rigorously. For the interested reader, we plot the coordinates of Li ions as a function of time (see Figure 21 in the supplementary material) to show that motion along the z-coordinate is observed during the simulation, compatible with long-range diffusion. The RDF of Li with all present species, shown in the upper panel of Figure 13, display a first coordination shell composed by 4 oxygen ions, compatible with literature findings. A second and third shell are composed of silicon and aluminum, with the amplitude of Si being stronger in the second shell, and Al in the third shell. This hints that Li ions prefer sites in the Si plane to those in the Al plane.

After running the site analysis, we find 24 sites of two different types, 12 of type 0 and 12 of type 1, compatible with the latest literature results. The parameters were as given in section F, except for cutoff-midpoint of 1.3 instead of 1.5, which was more robust with respect to the total number of sites obtained. The clustering analysis in Figure 24 of the Supplementary Materials shows that the types can be distinguished easily. An analysis of the RDF for the individual site types, shown in the bottom image of Figure 13, reveals that the discriminant is the different coordination of Al and Si, which is detected by the SOAP descriptor. For type 0, the second shell is composed of two aluminum atoms; four silicon atoms are in the third shell. For type 1, the numbers are the same, but silicon is replaced by aluminum and vice versa.

Figure 15. The diffusive pathways in LASO at 750K. Type 0 sites are shown as crosses and type 1 sites are shown as plusses. Edges are drawn between sites that exchange ions, similar to Figure 11. Unlike LLZO, this diffusion network has four disconnected components, indicated by different colored edges. The channels in LASO do not exchange ions in our simulations.
jumps within the site types, which is expected since the sites’ types are alternating along the diffusion channels.

We can thus show with first-principles molecular dynamics and an unsupervised analysis that the lithium ions occupy two different site types in LASO. This was done without any knowledge of the possible sites, since in the original CIF file only 12 sites (for 12 lithium ions) were given. This highlights the problems of algorithms that rely on prior knowledge of crystallographic sites. Such information might be missing or wrong, for example, because of the difficulties of resolving low occupancy sites for light elements when using XRD or neutron diffraction, or because of simulation conditions like temperature differing from an experimental setup. Relying on all the sites being known can obviously be problematic in some cases. An unsupervised approach requiring minimal knowledge of the structures should be preferred in such cases. Unlike in LLZO, a density-based clustering on the lithium-ion positions would very likely also have given the same results, as can be conjectured from the lithium-ion densities in Figure 12, where the highest isovalue clearly shows disconnected regions of high ionic density.

C. Analysis of tetragonal Li₁₀GeP₂S₁₂

The superionic conductor Li₁₀GeP₂S₁₂ (LGPS) in its tetragonal phase was first reported by Kamaya et al. Its unprecedented ionic conductivity at room temperature motivated studies of its diffusion mechanisms using atomistic simulation techniques. The original paper reports three site types in the unit cell: tetrahedrally coordinated 16h, tetrahedrally coordinated 8f, and octahedrally coordinated 4d sites, all coordinated with sulphur, with only the latter possessing full occupancy. The 16h and 8f sites denote edge-sharing Li₄ tetrahedra that form one-dimensional channels along the c-axis, the main diffusive pathways. Adams and Rao found evidence for an additional four-fold coordinated site – termed 4c – using classical simulations, which was validated in subsequent experiments by Kuhn et al.

We analyzed the first-principles molecular dynamics trajectories for LGPS that were produced and analyzed for a recent work discussing the failure of the Nernst-Einstein relation in this structure. We refer to the reference for computational details, and state only that the trajectories were run with the cp.x code of the Quantum ESPRESSO distribution with a PBE-exchange correlation functional. Using a unit cell of 50 atoms, 428 picoseconds of dynamics were obtained in the microcanonical ensemble, after an equilibration run at a target temperature of 500K. We find ionic densities (Figure 16) that are compatible with literature results on the unidimensional ion-conducting channels of LGPS. We should note that – to our knowledge – no

![Figure 16. Li-ion density in LGPS is shown above as 3 isosurfaces from violet (low density) to sky blue (high density). The equilibrium positions of sulphur are shown in yellow, of phosphorus in orange, and of germanium in green. The Li-ion densities reveal the unidimensional ion-conducting channels in this material.](image)

compatible with literature results: For example, Kuhn et al. report a value of the lithium-ion tracer diffusion coefficient of $D_{\text{tr}}^{\text{Li}} \approx 10^{-6} \text{cm}^2\text{s}^{-1}$ at 500K, which is close to our estimate and certainly within the likely error bounds of FPMD that stem from, among other factors, short simulations in small unit cells.

The presented analysis is applied to the equilibrated trajectory to determine statistics. We treated germanium and phosphorus atoms as one species since the 4d tetrahedral site is occupied by both species to avoid identifying extraneous site types due to the arbitrary choice of occupation of these sites. We will refer to both phosphorus and germanium as the species phosphorus hereafter. After site detection and SOAP clustering (shown in Figure 23 of the supplementary material) we find 30 sites of type 0, 24 sites of type 1, and 4 sites of type 2. We see that type 2 corresponds to the octahedral environment of the 4d site. A visual depiction of where the sites are located is shown in Figure 18. To understand the difference between the different site types, we calculate the RDF for every site type, shown in the middle and bottom panels of Figure 17 for sulphur and phosphorus.

In the RDFs between lithium and phosphorus, key differences appear between the different site types. While site type 1 is compatible with four-fold coordination with sulphur, site types 0 and 2 tend to plateau towards a coordination with 6 sulphur atoms, which is expected only for the latter site type. There is no evidence for a six-fold coordinated site type inside the ion-conducting channel of LGPS. We should note that – to our knowledge – no
The classification via SOAP vectors can yield different results than the Wyckoff symbols resulting from symmetry analysis. Different Wyckoff positions can be classified as the same site type if their chemical and geometric environments are too similar to differentiate. Further, as a result of symmetry breaking during molecular dynamics, two sites with the same Wyckoff position can be classified as different types, especially in non-ergodic simulations. This is not necessarily a weakness of the analysis, only something to be aware of. It should be noted that despite the obvious difficulties in detecting sites and site types reported in the literature, our analysis found four off-channel four-fold coordinated sites, which were termed 4c sites by Adams and Rao. These sites had been missed in earlier FPMD simulations since they were not reported by preceding experiments. Thus an unsupervised and unbiased analysis can help when experimental data is lacking or incomplete.

D. Non-diffusive structures

To further validate our method, we additionally studied seven non-conductive structures. The structures were selected from an ongoing screening effort intended to find new solid-state electrolytes. The structures were selected from the least conductive systems in our set that had two site types in their CIF file. For every structure, a molecular dynamics simulation was run at a temperature of 1000 K, with simulation lengths long enough to estimate the diffusivity of the material. All other simulation parameters are the same as those presented for LASO in section III B; details can be found in section D.

Figure 17. Upper panel: RDF for lithium to sulphur (green), germanium (orange), phosphorus (blue) and lithium (red). The Li-Li curve displays the expected liquid-like lack of structure. Center and bottom panels show the RDF of lithium to sulphur and phosphorus respectively. In both images, the RDF is shown separately for lithium occupying sites of type 0 in red, type 1 in green, and type 2 in blue.

Figure 18. The diffusive pathways in LGPS at 500K. Type 0 sites are shown as crosses, type 1 sites are shown as plusses, and type 2 sites as triangles. Unlike LASO, the ion-conducting channels do exchange ions, leading to a single connected component, illustrated by one color for the entire network.
Table I. Comparison between the presented landmark analysis and the sites listed in CIF files taken from structural databases. A checkmark indicates structures where the sites in the CIF file and the results of the unsupervised analysis agree, both in number of site types and number of sites of each type. This is the case in all but two structures, Li$_{20}$Re$_4$N$_{16}$ and Li$_{24}$Zn$_4$O$_{16}$, which are discussed in the text.

mark analysis was run on every second frame of the trajectory (about every 60fs). The same default landmark analysis parameters were used for all of the materials, with further details given in section F.

The results of a full landmark analysis can be seen for each of the seven materials in Table I. For all but two materials, the landmark analysis produces the same number of sites and the same division of those sites into types as given in the corresponding CIF files. For these materials, unlike LGPS, the Wyckoff analysis and the SOAP analysis coincide. In Li$_{20}$Re$_4$N$_{16}$ and Li$_{24}$Zn$_4$O$_{16}$, however – like in LiAlSiO$_4$ – unsupervised landmark analysis identifies sites that are not present in the CIF files from ICSD (see Figure 19). In Li$_{20}$Re$_4$N$_{16}$, these four sites complete the planar connected components in the material; they are transitional sites with low occupancy and residence time. Their existence is confirmed by an analysis of the Li-ion densities observed in the trajectories. In Li$_{24}$Zn$_4$O$_{16}$, Li-ions from neighboring sites occasionally and briefly jump to the additional sites and then back. The additional sites again have low occupancy and residence time and are confirmed by a density analysis of the real-space coordinates.

IV. IMPLEMENTATION

The landmark analysis presented here is implemented as a component of sitator, a modular, extensible, open-source Python framework for analyzing networks of sites in molecular dynamics simulations of solid-state materials.

sitator provides two fundamental data structures: SiteNetwork, which represents possible sites for some mobile atoms in a host lattice and SiteTrajectory, which stores discretized trajectories for those mobile atoms. A SiteNetwork can also store arbitrary site and edge attributes.

sitator includes an optimized implementation of landmark analysis as well as pre-processing utilities for trajectories and tools for analyzing and visualizing the results of site analyses.

V. CONCLUSIONS

We presented a novel method to perform a site analysis of molecular dynamics trajectories to analyze ionic diffusion in solid-state structures. The method is robust and can run over a large range of materials with a minimal set of parameters and little human intervention. As we have shown, our landmark analysis performs very well where other methods fail, whether because of very high exchange rates and/or close proximity between sites (as in LLZO), or because needed prior information is missing (as in LASO, Li$_{20}$Re$_4$N$_{16}$, and Li$_{24}$Zn$_4$O$_{16}$ where several sites that were occupied during our simulations are not given in the experimental CIF file). As became evident
in LGPS, superionic conductors with a liquid-like, highly disordered lithium sublattice are hard to analyze with our tool. The signals from the analysis need to be studied in further detail in subsequent work. A suggestion for subsequent work is automatically computing the configurational entropy descriptor $S$ described by Kweon et al.\textsuperscript{28} While the method presented in this work will not necessarily outperform carefully chosen analysis tools with parameters specific to the system under investigation, it has advantages when studying different systems for comparison and in high-throughput applications such as the search for microscopic descriptors for ionic diffusion in the solid state.

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**AUTHOR CONTRIBUTIONS**

Leonid Kahle started this work with Dr. Boris Kozinsky. The work was further extended by Leonid Kahle, Albert Musaelian, and Dr. Boris Kozinsky. Albert Musaelian is credited with the creation and efficient implementation of sitator. The analysis of LLZO, LGPS and LASO was done by Leonid Kahle. The analysis of the seven non-diffusive structures was done by Albert Musaelian. All simulations except for LGPS were run by Leonid Kahle. All authors contributed to the discussion and revision of the manuscript.
Appendix A: Landmark vector clustering algorithm

When determining the landmarks in a system, we use the efficient implementation of the Voronoi decomposition from Zeo++.78,79 which accounts for periodic boundary conditions.

A custom hierarchical agglomerative algorithm is used to cluster the landmark vectors. The algorithm is designed for “streaming”: no pairwise distance matrix is ever computed or stored, and the landmark vectors can be streamed from disk in the order they were written, avoiding random access.

Clusters are represented by their average landmark vectors, called “centers.” At each iteration clusters whose centers are sufficiently similar are merged. After a small number of iterations, a steady state is reached when no clusters can be merged; this is taken as the final clustering. The original landmark vectors are then each assigned to the cluster whose center they are most similar to.

Two parameters control the characteristics of the landmark clustering: the clustering threshold, which determines how aggressively new clusters (sites) should be added, and the minimum cluster size, which filters out sites whose occupancy is extremely low (such clusters likely represent thermal noise or transitional states). These parameters allow the user to tune spatial and temporal resolution.

Specifically:

1. Set the initial cluster centers $c_i$ to the landmark vectors. The order of the landmark vectors does affect the clustering, but in practice we have found the effect to be minimal. We process the landmark vectors in the order they were generated: chronologically and in whatever order the mobile ions were numbered.

2. Take the first existing cluster center $c_0$ as the first new cluster center $c_0'$. Then, for each remaining cluster center $c_i, i \in [1, N)$:
   (a) Find the new cluster center $c_j'$ to which the old cluster center $c_i$ is most similar:

   \[
   j = \arg \max_{j \in [0, N')} S(c_i, c_j')
   \]

   where $N'$ is the current number of new cluster centers and $S(\cdot, \cdot)$ is the normalized cosine metric:

   \[
   S(c_i, c_j') = \frac{c_i \cdot c_j'}{|c_i||c_j'|}
   \]

   (b) If

   \[
   S(c_i, c_j') > \text{clustering threshold}
   \]

   then merge the old cluster $c_i$ into the new cluster $c_j'$:

   \[
   c_j' = \frac{nc_j' + c_i}{n + 1}
   \]

   where $n$ is the total number of old clusters that have been merged to form $c_j'$ so far.

   Otherwise, keep $c_i$ as the center of its own cluster:

   \[
   c_{N'} = c_i
   \]

   \[
   N' = N' + 1
   \]

3. Repeat the previous step until no further clusters can be merged; the $c_i, i \in [0, N)$ are the final clusters.

4. Assign the landmark vectors to clusters. The assignment threshold controls how dissimilar a landmark vector can be to its cluster’s center before it is marked as unassigned. This parameter controls the trade-off between spatial accuracy and the proportion of unassigned mobile atom positions: high values will give greater spatial precision, while lower values will ensure that almost all mobile atoms are assigned to sites at all times.

For each landmark vector $l$:

(a) Find the most similar cluster center:

\[
 s = \max_{j \in [0, N)} S(l, c_j)
\]

(b) If $s > \text{assignment threshold}$, then mark $l$ as a member of the corresponding cluster with confidence $s$.

Otherwise, mark $l$ as unassigned.

5. Remove clusters smaller than the minimum cluster size.

6. Repeat step 4 with the remaining clusters, yielding the final cluster assignments.

Appendix B: Markov clustering

We apply Markov Clustering,44 to the matrix $M$ to simulate biased random walks through a graph, giving preference to high-probability routes. Once the process converges, a set of internally highly connected subgraphs remains. The sites in each resulting subgraph, if there are more than one, are merged into a single site. Their real-space positions are averaged, and the mobile ions
that occupied any of the merged sites now occupy the new site.

We use typical Markov Clustering parameters of 2.0 for both expansion and inflation. We do not add artificial self loops to the graph since \( M \) already contains appropriate nonzero values on the diagonal.

Appendix C: Parameter estimation for Density-Peak clustering

Density-peak clustering\(^{48}\) defines the number of clusters as the number of data points with extreme outlier values of \( \rho \) (density) and \( \delta \) (distance to nearest neighbor with larger \( \rho \)), as determined by a user-specified threshold. Rodriguez and Laio\(^ {48}\) suggest a simple heuristic for determining this threshold that we adopt and automate. First, we compute the values \( \gamma_i = \rho_i \delta_i \) and sort them into decreasing order. In a well behaved clustering problem, a plot of \( \gamma \) then has a recognizable “elbow,” and the points before the elbow – before the curve rapidly flattens out – are the outliers. Thus the problem of determining the thresholds is equivalent to finding the elbow of this curve.

We use a simplified version of the knee-finding algorithm presented by Satopaa et al.\(^ {80}\) A straight line is taken between \( (0, \gamma_0) \) and \( (n, \gamma_n) \), and the point \( (i, \gamma_i) \) with the maximum distance to that line is taken as the elbow. The \( \rho \) and \( \delta \) values corresponding to that point are then used as the thresholds for the density-peak clustering.

Appendix D: Molecular dynamics parameters

The simulations for LASO and the 7 non-diffusive structures were performed with the pw.x module in the Quantum ESPRESSO distribution,\(^ {74}\) using pseudopotentials and cutoffs from the SSSP library 1.0. Efficiency.\(^ {81}\) The exchange-correlation used in the DFT is PBE.\(^ {75}\) The materials informatics platform AiiDA\(^ {82}\) was used to ensure full reproducibility of the results and achieve a high degree of automation.

The vc-relaxation was always performed for the respective unit cell, with a uniform k-point grid of 0.2\( \AA \)^{-1} and no smearing since we consider only electronic insulators. The energy and force convergence thresholds were 0.5 \( \cdot 10^{-4} \) and 0.25 \( \cdot 10^{-5} \) in atomic units, respectively. The pressure had to converge to below 0.5kbar. A meta-convergence threshold on the volume, which specifies the relative volume change between subsequent vc-relaxations, had to converge to below 0.01.

Supercells were created with the criterion that the minimal distance between opposite faces of the supercell is always above 6.5\( \AA \). The molecular dynamics were run with a stochastic velocity rescaling thermostat\(^ {83}\) which was implemented by us into Quantum ESPRESSO, with a characteristic time of the thermostat set to 0.2\( ps \) at constant volume and number of particles (NVT ensemble). The timestep was set to 30 Rydberg atomic units, which corresponds to 1.45\( fs \). Snapshots of the trajectory were taken every 20 timesteps.

The origin of the non-diffusive structures is given in Table II, together with reached simulation length. The structures were either taken from the Inorganic Crystallography Open Database (ICSD)\(^ {84}\) or the Open Crystallography database (COD).\(^ {63}\)

Appendix E: Site analysis parameters

Unless otherwise indicated, landmark analysis used a cutoff midpoint of \( d_0 = 1.5 \) and steepness of \( k = 30 \), a minimum site occupancy of 1%, and landmark clustering and assignment thresholds of 0.9. For computing SOAP descriptors, unless otherwise specified, we used a Gaussian width of 0.5\( \AA \) on the atomic positions, a cutoff transition width of 0.5\( \AA \), and spherical harmonics up to \( n_{max} = l_{max} = 6 \). The radial cutoff is set to always include the nearest neighbor shell of all other species (excluding the mobile species). We calculate SOAP vectors for mobile ions every 10\( th \) frame, and average every 10 SOAP vectors to reduce noise. The principal components of the averaged SOAP vectors are extracted using Principal Component Analysis (PCA) to retain at least 95% of the variance, and the clustering is performed in this reduced space.

| Structure | \( T_{sim} \) (ps) | DB  | DB-ID |
|-----------|-------------------|-----|-------|
| Li\(_{20}\)Al\(_{16}\)B\(_{16}\)O\(_{64}\) | 72    | ICSD | 50612 |
| Li\(_{24}\)Sc\(_{8}\)B\(_{16}\)O\(_{48}\) | 218   | COD  | 2218562 |
| Li\(_{24}\)B\(_{4}\)Ta\(_{8}\)N\(_{32}\) | 58    | ICSD | 75031 |
| Li\(_{20}\)Re\(_{4}\)N\(_{16}\) | 159   | ICSD | 92468 |
| Li\(_{12}\)Rb\(_{8}\)B\(_{4}\)P\(_{16}\)O\(_{56}\) | 116   | ICSD | 424352 |
| Li\(_{6}\)Zn\(_{6}\)As\(_{6}\)O\(_{24}\) | 226   | ICSD | 86184 |
| Li\(_{24}\)Zn\(_{4}\)O\(_{16}\) | 407   | ICSD | 62137 |
Appendix F: Additional information

Figure 20. The mean squared displacement of lithium in LLZO as a function of time, shown in violet, is compatible with diffusive behavior. Thin straight lines are from individual blocks, while the straight thick line denotes the average. Linear fits to the individual blocks of the MSD between 400 and 800ps are shown as dashed lines, and the diffusion coefficient extracted from the linear fit is given in the legend. Oxygen (shown in red), in contrast, is not diffusive in the system.

Figure 21. The x- and y-coordinates of Li in LASO are plotted in the top panel in green and blue, respectively, as a function of simulation time. In the bottom panel, we show the z-coordinate in red, which is the direction along which the lithium ions jump.

Figure 22. Similar to Figure 20, we show the mean squared displacement of Li in LGPS (in violet) as a function of time. Lithium displays diffusive behavior. Sulphur in contrast, shown in yellow, is not diffusive in the system. Again the extracted diffusion coefficients are shown in the legend. Four blocks are used due to the smaller trajectory length.

Figure 23. Clustering of SOAP vectors in the analysis of LGPS. The first two principal components are shown.
Figure 24. Clustering of SOAP vectors in the analysis of LASO. The first two principal components are shown.