

# Ionic Transport in Anisotropic Oxide Lattices: in-depth Analysis of Molecular Dynamics Data and Selected Experimental Results

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**Abstract.** The present work is focused on the analysis of oxygen migration processes in layered oxide materials, employing molecular dynamics (MD) simulations validated by various experimental results. In addition to standard MD approaches, a new technique was developed to explore anisotropic diffusion by analyzing transfer between special sites – ion trajectory nodes determined without using crystallographic information on the ideal anion positions. Applicability of this approach was demonstrated by the simulations of anisotropic oxygen transport in  $\text{La}_2\text{NiO}_{4+\delta}$

**Key words:** molecular dynamics, ionic transport, diffusion, anisotropic lattice.

## I. INTRODUCTION

Molecular dynamics (MD) is one of the most effective tools for simulation of the condensed matter. Its development started in 1970s when necessary computing resources became accessible. However, only after introduction desktop multicore CPUs in middle of the 2000s MD got a chance to turn to general use instrument for the analysis of such phenomena as diffusion, interactions of the point defects and lattice transformations in solids. These subjects are of special interest for solid state ionics and electrochemistry. The standard MD tools for lattice simulation and analysis have, however, quite important limitations and typically include calculations of the global lattice properties, radial distribution functions and diffusion coefficients. The goal of the present work is to introduce other techniques for deep lattice analysis based on MD simulation results, which does not rely on definite MD codes and potential models. Whilst the basic approach was originally elaborated for DL\_POLY software [1] and phenomenological potentials, it can be easily adjusted for other cases.

## II. BACKGROUND

Standard MD codes cannot provide an explicit control over origin of the migrating particles (atoms or ions) with respect to sublattice of the initial lattice. In case of simple structures like perovskite or fluorite, this situation does not lead to substantial difficulties in further data analysis.

However, for more complicated lattices (e.g. tetragonal  $\text{K}_2\text{NiF}_4$  – like structure of  $\text{La}_2\text{NiO}_4$  with three oxygen positions), ascribing the particles to definite sublattices in MD simulation results becomes a non-trivial problem due to their migration and large deviations from ideal location. For fast ionic conductors, about 10-20% species constituting their lattices are typically involved in the diffusion processes and can migrate from one sublattice to another, hampering any pre-assignment of the mobile ions to any sort or sublattice. The situation becomes even more complicated when strong point-defect interactions, local distortions and cooperative movements take place. Then trajectories of the migrating particle look like as a sequence of smeared clouds (Fig. 1A).

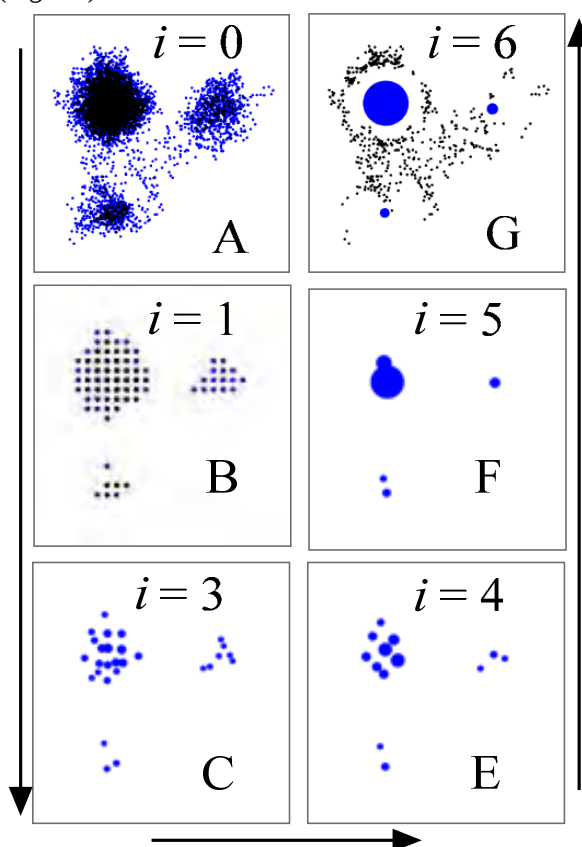


Fig. 1. Evolution of the aggregate of the atoms positions in the course of the refinement. Arrows show the direction of evolution. G is the final aggregate (3 large circles) with “lost” positions shown by small circles;  $i$  is the number of iterations.

Obviously, such a trajectory should be treated as jumps between three positions in the lattice. The positions can be refined and associated with relevant crystallographic sites by iterative convergent process (Fig. 1). To generate the initial

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distribution, the individual trajectory can be decomposed in a 3D histogram. The size of the uniform elements is to be chosen from the lattice parameters; the values of 0.15-0.3 Å were found effective enough for oxide compounds. Then the filled bins in the histogram can be used to calculate average density of atomic positions in the trajectory, effective volume:

$$d_{\text{eff}} = \frac{N_{\text{bins}} V_{\text{bin}}}{N_{\text{pos}}} \quad V_{\text{eff}} = N_{\text{bins}} V_{\text{bin}} \quad (1)$$

and effective radius  $R_{\text{eff}}$  of each position:

$$R_{\text{eff}} = \sqrt[3]{\frac{3V_{\text{eff}}}{4\pi N_{\text{bins}}}} \quad (2)$$

where  $N_{\text{bins}}$  is the number of non-empty bins, and  $N_{\text{pos}}$  is the number of positions in one trajectory. The coordinates of the bin centers where the density is higher than average, can be used as initial approach for further iterative refinement of the nodes (Fig. 1B). This initial aggregate was then sorted out to start iterative refinement from the nodes with higher density:

1. Separation of the nodes depending on the presence of neighbors closer than  $R_{\text{eff}}$ .
2. Formation of the new aggregate including all nodes without neighbors and new nodes, which coordinates are derived by averaging between the nodes near initial aggregate.
3. Recalculation of  $R_{\text{eff}}$  for the new aggregate.
4. Calculation of the weight for each position  $W_{\text{pos}}$  in the trajectory with respect to the aggregate. If the coordinates do not fit  $R_{\text{eff}}$  for any node, the position weight is assigned as zero; otherwise it is equal to the number of neighboring nodes.
5. Refinement of the node coordinates vs. trajectory, accounting for the position weight. Also weights are calculated for each node, including one equal to the formal number of positions associated with the given node  $W$ , and weighted number of associated positions,

$$W_{\text{eff}} = \sum_i \frac{1}{W_{\text{pos}}}, \text{ where } N_R \text{ is the number of positions in the vicinity of the node under consideration.}$$

6. Control of the convergence. If the size of the final aggregate after two iterations is found equal to size of the initial aggregate, the refinement is treated as converged and the iteration loop terminates; otherwise the whole cycle is to be repeated from Step 1.

When the sublattices recovery succeeds, the particle trajectories may be replaced with the aggregate of the key positions or nodes (Fig. 1, G). If trajectories of the migrating particles can be presented as a sequence of the jumps from one node to another, the diffusion process may be described more minutely compared to the mean square displacements. The equation [2]

$$D = \frac{1}{6} r^2 \Gamma \quad (3)$$

where  $r$  is the distance of the jumps,  $\Gamma$  is their frequency, and  $D$  is the diffusion coefficient, can be transformed into

$$D = \frac{1}{6} \frac{1}{N_{\text{ens}} \tau} \sum_i^N r_i^2 \quad (4)$$

where  $N_{\text{ens}}$  is the number of particles in ensemble,  $\tau$  is the observation time, and  $N$  is the number of detected jumps. This approach makes it possible to segregate all jumps by “starting position – destination” pairs and, as result, to calculate partial diffusion coefficients related to arbitrary lattice zones (e.g. sublattices), exchange between the lattice elements and migration in crystallographic layers.

### III. EXAMPLES: OXYGEN DIFFUSION IN RUDDLESDEN-POPPER TYPE COMPOUNDS

These formal approaches were validated by the simulations of anisotropic oxygen transport in Ruddlesden-Popper type compounds promising for high-temperature electrochemical applications, primarily  $\text{La}_2\text{NiO}_{4+\delta}$  and  $\text{Sr}_3\text{LaFe}_3\text{O}_{10-\delta}$  where the ionic conductivity and diffusion coefficients were derived from the data on total conductivity and steady-state oxygen permeation fluxes vs. oxygen partial pressure, temperature, membrane thickness and equilibrium nonstoichiometry. As an example, Fig. 2 presents the calculated partial diffusion coefficients between different oxygen positions in the  $\text{K}_2\text{NiF}_4$ -type structure of  $\text{La}_2\text{NiO}_{4+\delta}$ , compared to the average coefficient calculated from the mean squares displacement of oxygen anions. The results provide a clear evidence of the dominant role of complex migration mechanism involving interstitial O3 positions and apical O2 sites in the perovskite-like layers [3].

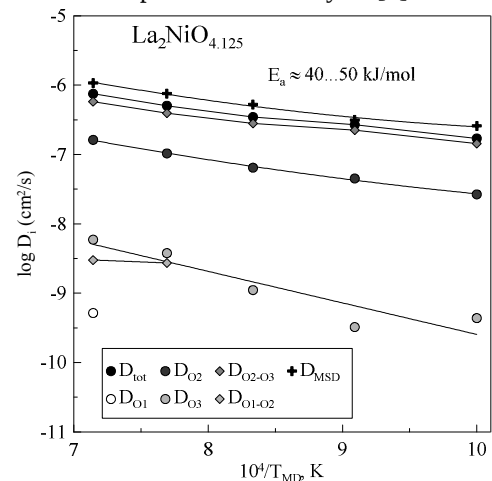


Fig. 2. Calculated diffusion coefficients in  $\text{La}_2\text{NiO}_{4+\delta}$ .  $D_{\text{MSD}}$  is the anion diffusion coefficient derived from mean square displacements [3]; the partial diffusion coefficients are calculated by Eq.4.

### ACKNOWLEDGMENT

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