



Full length article

## kMCpy: A python package to simulate transport properties in solids with kinetic Monte Carlo

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### ABSTRACT

Understanding ion transport in functional materials is crucial to unravel complex chemical reactions, improving the rate performance of materials for energy storage and conversion, and optimizing catalysts. To model ion transport, atomistic simulations, including molecular dynamics (MD) and kinetic Monte Carlo (kMC) have been developed and applied. However, kMC simulations are utilized to a lower extent than MDs due to a lack of systematic workflows to construct models for predicting transition rates. Here, we present kMCpy, a lightweight, customizable, and modular python package to compute the ionic transport properties in crystalline materials using kMC. kMCpy is remarkably versatile and user-friendly, making it a powerful code for studying materials' kinetics in crystalline systems. kMCpy can be combined with (local) cluster expansion Hamiltonians derived from first-principles calculations. kMCpy is versatile with respect to any type of crystalline material, bearing any dimensionality, i.e., 1D, 2D, and 3D. kMCpy provides (i) a comprehensive workflow to enumerate all possible migration events in crystalline systems, (ii) to derive transition rates efficiently and at the accuracy of first-principles calculations, and (iii) a robust kMC solver to study kinetic phenomena in materials. The workflow implemented in kMCpy provides a systematic way to compute highly accurate kinetic properties. Hence, kMCpy can be used in high-throughput simulations for the discovery and optimization of novel functional materials.

### 1. Introduction

Quantifying the properties of ion transport in materials is crucial in a wide variety of research fields and applications, such as molecular and protein biology [1–3], energy [4–6], chemical reactions [7,8], and solid mechanics [9–12]. The advancement of computer hardware, theoretical models, and suitable software that scale and parallelize with available computing resources have enabled the evaluation of ionic transport in solid-state materials [13,14]. A widely used atomistic simulation technique to probe kinetic properties is molecular dynamics (MD), [13,15] which propagates the state of a given system as a function of time, where individual particles (atoms) interact via Newton's laws of motion. MD has been implemented in a wide variety of software packages [16–21], where the accuracy of MD is dependent on the accuracy of force evaluations. Forces acting on atoms

in an MD simulation are accessed from accurate (but computationally expensive) first-principles calculations, or inexpensive (and less accurate) interatomic potentials (i.e., force fields). Recently, machine-learning interatomic potentials (MLIPs), including the moment tensor potential (MTP), the spectral neighbor analysis potential (SNAP), the Gaussian approximation potential (GAP), and the atomic energy network (AENET) provide streamlined workflows to construct accurate interatomic potentials leveraging, for example, on *ab initio* molecular dynamics (AIMD) data, which combines the accuracy of first-principles calculations and the computational efficiency of inexpensive classical MD simulations [22–25].

An alternative to MD is kinetic Monte Carlo (kMC, also known as dynamic Monte Carlo) [26–28], which has been applied to study kinetic

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**Table 1**

A qualitative comparison between the capabilities of kinetic Monte Carlo (kMC) and molecular dynamics (MD).

Feature	Kinetic Monte Carlo	Molecular dynamics
Model	Flexible: can use lattice models or simple equations	Force fields (classical MD) or electronic structure (AIMD)
Time scale	Mesoscopic (up to $\mu\text{s}$ or $\text{ms}$ )	Up to a few ns (few hundreds of ps) for classical MD (AIMD)
Length scale	Flexible: atomistic or mesoscopic	Up to a few million (classical MD) or <1000 atoms (AIMD)
Computational efficiency	Transition rates are computed directly for each migration event	Energies and forces of all atoms are evaluated at each timestep
Rare events accessibility	Easy: events propagated randomly based on their transition rates	Hard: long simulations or high temperatures for high barriers
Model construction	Complex: it requires knowledge of all possible transition events	Straightforward: plug & play
Code availability	Limited and often relying on in-house codes	Numerous general purpose codes available

phenomena materials including, rechargeable batteries [29–32], solid-oxide fuel cells [33,34], catalysis [35,36], crystal growth [37], vacancy diffusion in alloys [38,39], thin film growth [40], and fluid dynamics [41]. kMC is particularly useful in quantifying the ion transport in battery materials, as demonstrated by van der Ven et al. in electrode materials, such as  $\text{Li}_x\text{CoO}_2$  [29],  $\text{Li}_x\text{TiS}_2$  [42],  $\text{Li}_{1+x}\text{Ti}_2\text{O}_4$  [43]. Deng et al. [32] recently used kMC simulations to predict the conductivity of Na-ions in solid electrolytes:  $\text{Na}_{1+x}\text{Zr}_2\text{P}_x\text{Si}_{3-x}\text{O}_{12}$ , as a function of Na content and temperature, eventually sampling a vast compositional, spatial, and temporal scale. kMC can also be used to examine the structural evolution of nano-particles as well, as demonstrated by Li et al. [39].

kMC is based on a stochastic algorithm that randomly samples a large number of microstates of a given system, utilizing the ergodic principle to arrive at statistically-averaged transport properties. A comparison between MD and kMC is shown in Table 1 and an example of kMC is presented in Fig. 1. Compared to MD, kMC is a fairly general simulation algorithm that can be applied to coarse grain material properties and contribute to multi-scale modeling efforts [44–46]. Thus, the chief advantage of kMC over MD is the ability of kMC to access “long” timescales ( $\sim\text{ms}$ ) and “large” lengthscales ( $\sim\mu\text{m}$ ) compared to what is usually accessible by MD ( $<\mu\text{s}$ ,  $\sim\text{nm}$ ) [47].

Unlike MD simulations, which require the explicit integration of the equation of motion for all species in the system, kMC selectively propagates transition events based on a simplified model, resulting in significantly improved computational efficiency. Furthermore, MD simulations encounter challenges in effectively describing rare events, such as ion migrations or reaction processes, the former being a crucial aspect in studying ion diffusion for applications, such as rechargeable batteries, fuel cells, and electrolyzers. As shown in Fig. 1, the migration time of Na ions in  $\text{Na}_{1+x}\text{Zr}_2\text{P}_x\text{Si}_{3-x}\text{O}_{12}$  can span a wide time-scale from sub-picoseconds to microseconds, depending on factors, such as temperature and composition. Additionally, other processes, for example, chemical reactions can occur over extended periods, hence presenting clear challenges in the applications of MD methods.

Two main kMC algorithms have been proposed: (i) kMC with rejection (r-kMC) [48] and (ii) rejection-free kMC (rf-kMC) [26]. The former algorithm is similar to the Metropolis algorithm [48] which can select or reject a transition event using a probability estimate. In rf-kMC, a transition event is always executed based on a “list” of probabilities. Thus, rf-kMC is computationally more efficient than r-kMC, especially when transition rates are low (i.e., event rejection rates are high).

There are several software packages to perform kMC simulations [49–60], including codes that target higher efficiency kMC algorithms [61–67], and those that construct novel models to compute accurate transition rates [68–72].

Although there are numerous advantages to employing kMC to investigate ion transport in solid-state materials, it is important to mention that in kMC, all transition events must be known *a priori*, and a model is typically required to efficiently compute transition rates between different microstates. Constructing such a model is often a nontrivial task, and it requires additional expertise and significant effort. Consequently, researchers often resort to developing in-house codes to address this challenge, leading to much slower progress in the advancement of this field compared to “plug-and-play” MD simulations. Hence, it is essential to develop kMC workflows that are flexible

and can be “tailored” to any given system. These kMC workflows should potentially include modules for generating all possible transition events, comprehensive models for the swift and accurate computation of transition rates for each event. These workflows should also include robust kMC solvers.

Here, we present our python-based code `kMCpy`<sup>1</sup> to simulate the kinetic properties of materials, with inputs from first principles calculations. Specifically, we implement a local cluster expansion (LCE) model [29,30] to compute migration barriers in crystalline materials (within the transition state theory framework), where the model is fitted to calculated barriers from accurate first-principles calculations. `kMCpy` contains a rf-kMC solver and related python classes to extract ion transport properties, such as diffusivities, conductivities, etc. In addition, `kMCpy` includes the following features:

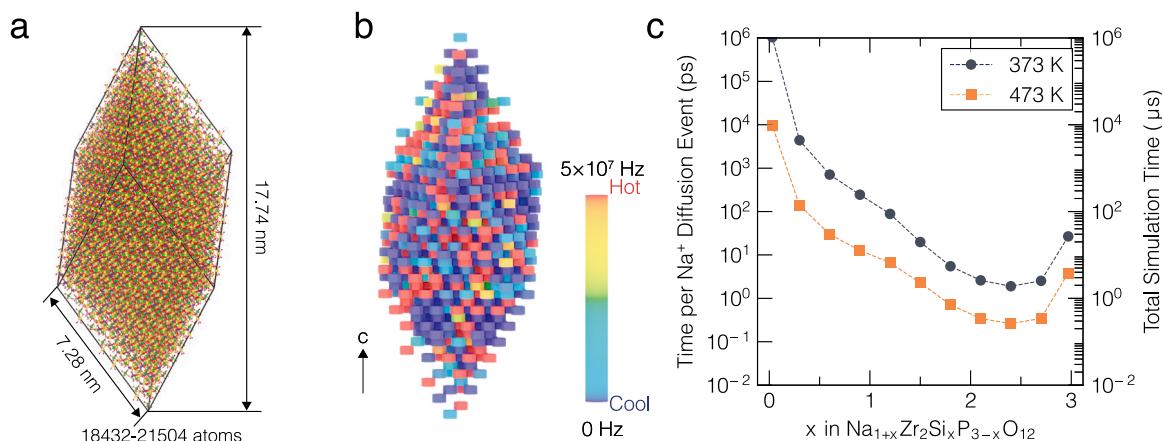
- `kMCpy` is fully developed using python [73,74]. It is compatible with packages that are widely used in computational materials science, such as `Pymatgen` [75]. `kMCpy` is highly flexible and is easy to be adapted to any materials system.
- Cross Platform: `kMCpy` supports most “mainstream” operating systems, such as Windows, macOS, and Linux/UNIX, in both x86/64 and ARM architectures. Therefore, `kMCpy` is POSIX compliant.
- Modular Code Structure: `kMCpy` is written as modulus, which can be easily modified and ported/integrated into any specific application.
- Ease of Use: All input and output data are supplied using human-readable JSON format, which can be easily parsed and generated by computers.
- Performance: The computationally-intensive routines of `kMCpy` are translated into optimized machine code at runtime using `Numba` [76], which is a just-in-time (JIT) compiler designed to increase computational performance of python codes.

The paper is structured as follows: Section 2 deals with the theoretical background to compute transport properties in crystalline materials, Section 3 provides an overview of the `kMCpy` code, Section 5 describes the performance of `kMCpy`, and Section 6 compiles our concluding remarks and possible future developments of `kMCpy`. All nomenclature used throughout the manuscript is listed in the Appendix. `kMCpy` is highly flexible and easy to use, making it exceptionally useful for investigating kinetic phenomena in crystalline materials.

## 2. Theoretical background

Ionic transport in solids is a stochastic process, occurring through a series of correlated/non-correlated migration events (or ionic “hops”), which can be effectively modeled using the kMC formalism. The local energy landscape around the migrating ion determines the ease of migration within the solid. Quantifying macroscopic ionic transport of a given chemical species in a given material is usually done in terms of ionic diffusivities and/or ionic conductivities (see below), both of which can be evaluated using kMC [29].

<sup>1</sup> `kMCpy` is an open-source code developed under the MIT license and can be accessed at: <https://github.com/caneparesearch/kMCpy>



**Fig. 1.** Length scale and time scale of kMC simulations: Panel **a** shows the length scale of a kMC simulation of an example:  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  with periodic boundary condition, ranging from 18,432 to 21,504 atoms depending on the value of  $x$ . Panel **b** depicts a snapshot of kMC simulation colored with Na-ion hopping probability from 0 Hz (blue) to  $5 \times 10^7$  Hz (red) at 573 K, at composition  $x = 1.5$ . Panel **c** presents the average time costs for each Na-ion hop, as well as the total simulation time for this material. Each data point in panel **c** consists of an average of 50 kMC simulations and each kMC simulation included 2,048,000 equilibration steps, followed by 12,288,000 production steps for statistical analysis. Each step is a Na-ion migration.

Before understanding how a typical kMC simulation progresses, we briefly overview some of the fundamentals of ion transport in solids. The macroscopic measure of mobility of a migrating species is determined by the chemical diffusivity ( $D_c$ ), which relates to the flux and conductivity of the species through Fick's law [77,78], as stated in Eq. (1).

$$J = -D_c \nabla C \quad (1)$$

where  $J$  is the flux of the migrating species, and  $C$  is the composition of the mobile species defined as the number of migrating ions per unit volume. The chemical diffusivity of the migrating ion relates to the jump diffusivity ( $D_J$ ) through the thermodynamic factor  $\Theta$  of Eq. (2).

$$D_c = D_J \Theta \quad (2)$$

$\Theta$  measures the deviation of the interaction between migrating ions from ideal behavior and is given in Eq. (3)

$$\Theta = \frac{\partial \left( \frac{\mu}{k_B T} \right)}{\partial \ln x} \quad (3)$$

where  $\mu$  is the chemical potential,  $k_B$  is the Boltzmann constant, and  $x$  is the mole fraction of the migrating species.

$D_J$  of Eq. (2) is proportional to the mean squared displacement of the center of mass of the mobile species, as mathematically described in Eq. (4).

$$D_J = \frac{(\sum_i \bar{r}_i)^2}{2dNt} \quad (4)$$

where  $d$  is the dimensionality of the diffusion process,  $N$  is the number of diffusing species, and  $t$  is the time taken for diffusion. Furthermore, from the square of displacements of the migrating ions, one can also calculate the tracer diffusivity ( $D^*$ , Eq. (5)), which excludes cross-correlation effects between the migrating ion [30].

$$D^* = \frac{\sum_i \bar{r}_i^2}{2dNt} \quad (5)$$

The ionic conductivity  $\sigma$  can be then computed via the Nernst–Einstein relationship:

$$\sigma = \frac{e^2 C D_J}{k_B T} \quad (6)$$

where  $C$  is the number of migrating species per unit volume.

Therefore, the cross-correlation between migrating ions can be quantified from the ratio of  $D^*$  and  $D_J$ , which is called the Haven's ratio ( $H_R$ ) [79]. Note that  $H_R$  does not measure the correlation between

subsequent hops of a single ion that is migrating, i.e., the deviation of the trajectory of a single migrating ion from a fully random walk. This deviation from a fully random walk is measured by the correlation factor ( $f$ ) of Eq. (7).

$$f = \frac{\sum_i \bar{r}_i^2}{Nna^2} \quad (7)$$

where  $\bar{r}_i$  is the net displacement of a migrating ion after  $n$  hops, while  $a$  is the average distance for a single hop. Therefore, an accurate calculation of the ionic transport properties requires the sampling of a large enough number of migration events, which requires that all mobile species are tracked during the simulation.

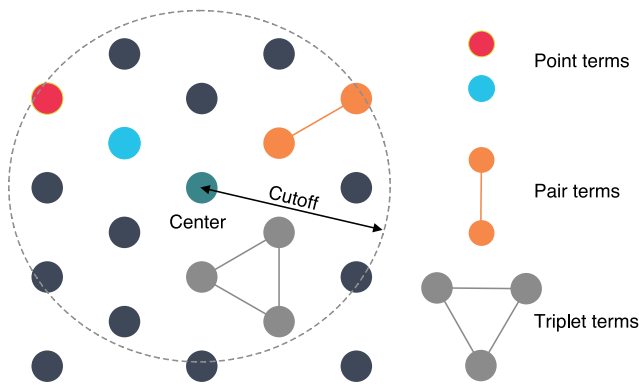
One of the important parameters required by a kMC simulation is the migration barriers ( $E_b$ s), which are the energy barriers that the mobile ion must overcome to complete a successful hop.  $E_b$  ultimately determines the probability of occurrence of a given ionic hop. Typically,  $E_b$ s are evaluated using the nudged elastic band (NEB) method in combination with density functional theory (DFT) [80,81]. In an NEB calculation, one performs a constrained relaxation of a specific number of virtually connected "images", between the initial and final positions of a migration event, along a guessed minimum energy pathway (MEP). The relaxation is constrained to maintain a uniform spacing between the images (i.e., as uniform as possible), through the addition of fictitious spring forces. Other tools, such as force fields and machine-learned interatomic potentials, can also be used to determine  $E_b$  instead of DFT, and kMCPy is also compatible with such tools.

Note that  $E_b$  in solids not only depends on the local environment of the migrating ion but also the direction of the hop. Hence, to remove any direction-dependence of a hop, we resort to the so-called kinetically resolved activation barrier ( $E_{\text{KRA}}$ ) of Eq. (8) proposed by van der Ven et al. [29].

$$E_{\text{KRA}} = E_b[i \rightarrow j] - \frac{1}{2} \Delta E_{\text{end}} \quad (8)$$

where  $E_b[i \rightarrow j]$  is the calculated  $E_b$  (e.g., with NEB) for a site  $i$  to site  $j$  hop and  $\Delta E_{\text{end}}$  is the absolute difference between the computed DFT total energies of the initial and final positions (i.e., the endpoints).

In principle, the  $E_{\text{KRA}}$  has to be calculated for all possible migration events that can occur in a solid (as the local bonding/coordination environment changes for example). However, calculating  $E_b$  for all possible hops via NEB calculations is computationally intensive and often impractical. One strategy to circumvent the computational obstacles of NEB calculations is that of the LCE approach. An LCE is normally used to construct a simplified lattice Hamiltonian, which can



**Fig. 2.** Example of clusters that are typically encountered in a cluster expansion overlaid over a representative lattice. Within a cutoff distance from the center of a given lattice site, local orbits are drawn which extract the different interactions, such as point (red and blue dots), pair (orange dots), and triplet (gray dots). For each lattice, only the symmetrically-unique clusters are used to construct the cluster expansion.

generate approximate  $E_b$  quickly (by estimating a  $E_{\text{KRA}}$ ), based on the local configuration(s) of the moving and nonmoving species, which is defined in Eq. (9) [29,82].

$$E_{\text{KRA}} = V_0 + \sum_{\alpha} V_{\text{orbit}} \phi_{\text{orbit}} \quad (9)$$

where

$$\phi_{\text{orbit}} = \prod_{i \in \text{orbit}} \sigma_i \quad (10)$$

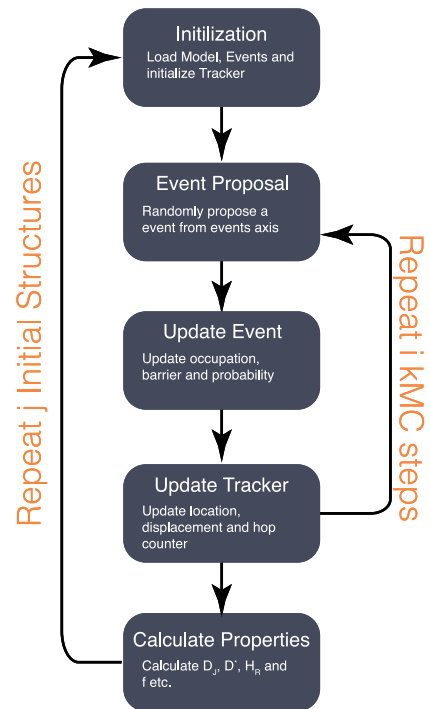
Here, an orbit implies a cluster of sites, which for example, can be a point, a pair, or a triplet, or higher-order terms, as depicted in Fig. 2.  $\sigma$  is the occupation variable of a given site within a cluster, whose value depends on the basis set used. For example,  $\sigma$  can take the value of  $-1$  or  $+1$  to indicate the presence or absence of an atom at a given site. To account for local interactions, orbits are usually truncated at finite distances from a given site. In Eq. (9), the terms  $V_0$  and  $V_{\text{orbit}}$  are the kinetic effective cluster interactions (KECIs). The values of the KECIs are determined by fitting Eq. (9) a set of NEB-calculated  $E_{\text{KRA}}$ . Note that instead of an LCE, surface models, thin-film models, or coarse grain models [44,45] can also be used for estimating  $E_b$ .

After determining  $V_{\text{orbit}}$  and  $V_0$  in Eq. (9), one proceeds with kMC simulations, whose workflow is shown schematically in Fig. 3(a). In kMCPy, we have implemented the rf-kMC method, also known as the Bortz–Kalos–Lebowitz (BKL) algorithm [26]. Specifically, we list the set of all possible migration events in a given solid and their corresponding probabilities, amongst which one migration event is selected. Once a hop is selected, the hop is always executed, and subsequently, the list of possible migration events is updated.

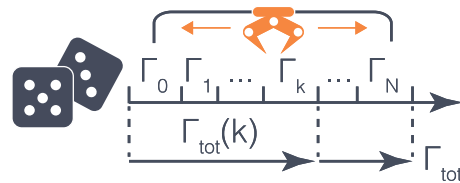
The typical procedure for the BKL method is summarized in the text below and Fig. 3. Note that Fig. 3 does not include the equilibration process.

- 1. Initialization:** In this step, a representative structure is generated, which contains a fixed concentration of mobile ions and vacancies (assuming a vacancy-mediated migration mechanism). These structures can be obtained from canonical Monte Carlo (CMC), grand-canonical Monte Carlo (GCMC) [83] simulations, random structure generators [38], or other structural enumeration techniques. During the initialization, a tracker is also set, which keeps track of the migration observables, such as the mean squared displacement (MSD) of the diffusing species, the location of the center of mass,  $D_j$ , and  $f$ .
- 2. Event proposal:** A list of probabilities ( $\Gamma_m$ ) is generated for all possible migrating paths ( $m$ ) available for all mobile ions in the simulation box. This list also includes hops that may not

## a Rejection-free Kinetic Monte Carlo



## b Event Proposal



**Fig. 3.** a Flow chart of the kMC process.  $i$  kMC steps are repeated with each kMC simulation starting from a different initial structure (i.e.,  $j$  initial structures in total). b All migration events are listed on a hypothetical axis, with the solid line representing their hopping probabilities ( $\Gamma$ ). An event no.  $k$  is then randomly proposed based on a random number  $\rho$ .  $\Gamma_{\text{tot}}(k)$  is a cumulative sum of events from no. 0 to no.  $k$  (i.e.,  $\Gamma_{\text{tot}}(k) = \sum_{m=0}^k \Gamma_m$ ).  $\Gamma_{\text{tot}}$  is the sum of the hopping probabilities of all migration events.

be feasible. For example, if both the initial and final sites of a migration event (path) are occupied by an atom (instead of one of the sites being vacant), the value of  $\Gamma_m$  is set to 0. The hopping probability ( $\Gamma$ ) for each migration event is calculated using the transition state theory [84] via Eq. (11).

$$\Gamma = \nu^* \exp\left(\frac{-E_b}{k_B T}\right) \quad (11)$$

From Eqs. (8) and (9), it is possible to quickly generate  $E_b$  for every possible hop.  $\nu^*$  is the prefactor and is usually assumed to be of the order of  $10^{11}$  to  $10^{13}$  Hz [29,85].  $T$  is the simulation temperature.

Following the generation of the probability list, a migration event ( $k$ ) is chosen based on a random number ( $0 < \rho < 1$ ), such that it satisfies Eq. (12).

$$\frac{1}{\Gamma_{\text{tot}}} \sum_{m=1}^{k-1} \Gamma_m < \rho \leq \frac{1}{\Gamma_{\text{tot}}} \sum_{m=1}^k \Gamma_m \quad (12)$$

where  $\Gamma_{\text{tot}}$  is the sum of all the individual probabilities of all migration events. This step is shown schematically in Fig. 3(b).

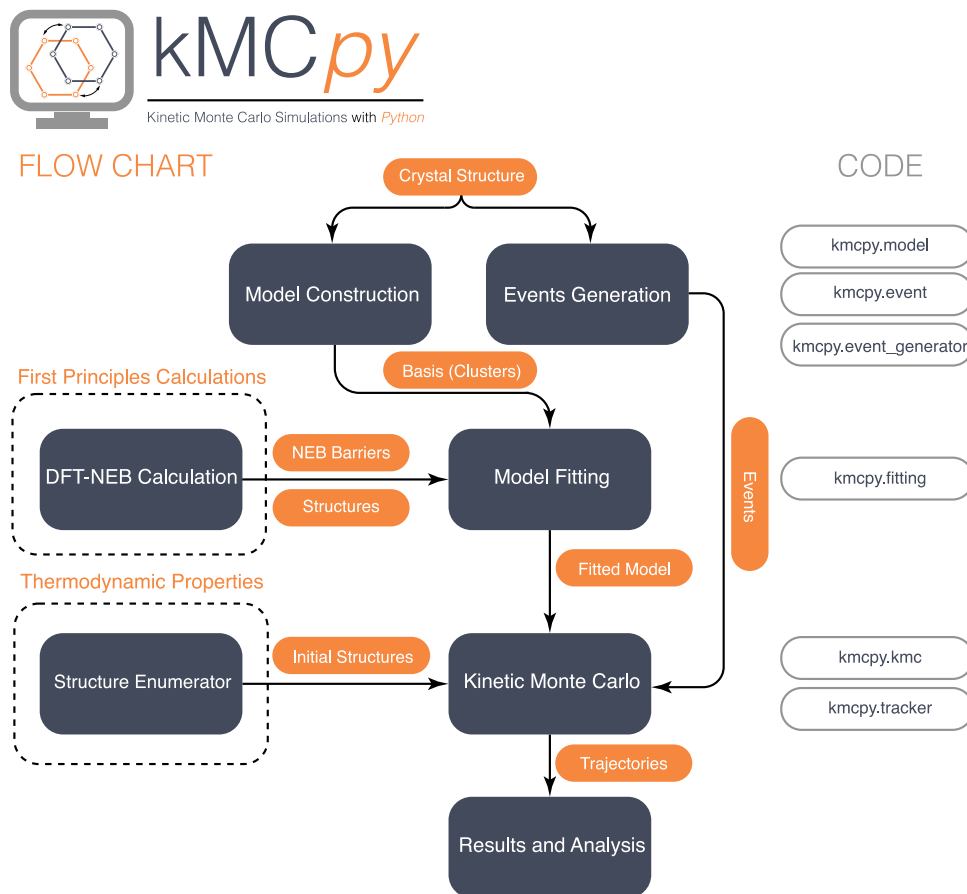


Fig. 4. Left Workflow of kMCpy package. Right python classes of kMCpy used for each stage of execution. Note that the initial structures for running kMC simulations are obtained from a structure enumerator. Migration barriers are computed from DFT-NEB calculations (dashed boxes), or even from MLIP-NEB calculations. In the current version, only the LCE model has been implemented.

3. *Update event and tracker*: After an event is chosen and executed, the time step ( $\delta t$ ) is updated by drawing another random number ( $0 < \zeta < 1$ ) as shown in Eq. (13).

$$\delta t = -\frac{1}{\Gamma_{\text{tot}}} \ln \zeta \quad (13)$$

Subsequently, the occupation vector, the new event list, and their corresponding probabilities, the displacement vector(s), the location ( $s$ ) of the mobile ions, the location of the center of mass, and the hop counter are updated.

A single kMC pass includes repeating the event proposal, updating the event, and updating tracker steps the same number of times as the number of mobile ions in the initialized structure. Generally, a large number of kMC passes are required to accurately predict transport properties. For example, Deng et al., undertook  $\approx 10^6$  kMC passes to simulate Na-transport in superionic conductors over a millisecond scale [32]. After running a sufficiently large number of kMC passes, properties, such as  $D_j$ ,  $D^*$ ,  $H_{R^*}$ , and  $f$  are estimated. Thus, a collection of kMC passes for a single initial structure is referred to as a kMC run. To get a better estimate of the transport properties at a given composition, kMCpy also calculates the properties as the initial structure is varied  $j$  times (i.e.,  $j$  kMC runs). This ensures that the transport properties calculated represent a statistical estimate that is observed in experiments.

### 3. Overview of kmcpy

#### 3.1. Workflow

The workflow of kMCpy is shown in Fig. 4. Note, the NEB (Nudged Elastic Band) barriers and initial structures, as shown in the dashed boxes of Fig. 4 are inputs for kMCpy. The specific python classes for each action are shown as gray boxes on the right-hand side of Fig. 4. kMCpy contains functions to analyze crystal structures, construct an LCE model, and generate a list of possible migration events (see Sections 3.2 and 3.3). Starting from a list of DFT-NEB (or even MLIP-NEB) computed barriers, kMCpy fits an LCE model (see Section 3.4). The constructed model and events are then used to run kMC simulations with input structures that are either the thermodynamic ground state(s) or any other user-defined structures (Section 3.5). The trajectory of each mobile species is stored and analyzed with a Tracker class as implemented in kMCpy (Section 3.6). Examples of input and output files are provided in Section 3.7. All python classes mentioned in the following sections can be stored in a human-readable JSON format and can be re-initialized after each stage.

#### 3.2. Model construction

Before running a kMC simulation, a representative lattice model must be constructed to compute the barriers efficiently for any local

environment, and the current version of kMCpy uses the LCE framework. However, the modular nature of kMCpy is such that other lattice models can also be used and integrated.

The LCE is implemented in the `LocalClusterExpansion` class in `kMCpy.model`. The local environment in the LCE model is described using a migration unit (`MigrationUnit`), which is defined as a representative collection of sites centered around a given activated state (AS), where possible migration events can take place. The migration unit is generated using the user-specified cutoff radius. As a result, when a local environment is imported, an “occupation vector” (see Appendix) will be constructed based on the atomic species at each site.

Subsequently, all clusters within a migration unit are found by enumerating all points, pairs, triplets, etc. via a cutoff radius (specified by the user) for each type of cluster. All symmetrically equivalent clusters are then grouped as orbits, which become elements in the “correlation vector” (see Appendix). Clusters and orbits are coded into the `kMCpy.model` as the `Cluster` and the `Orbit` classes. In addition to the species and the atomic coordinates, `Cluster` and `Orbit` both have functions to compute “correlation” (see Appendix) for a given orbit based on the occupation of sites.

### 3.3. Events' generation

A kMC simulation needs a list of all possible migration events within a given simulation cell before its execution. Therefore, in kMCpy, we handle migration events using the `Event` class in `kMCpy.event`. `Event` stores the indices of two sites (e.g., initial and final sites) involved in the migration event and the indices of all sites within the surrounding migration unit, i.e., local environment indices. `Event` also has built-in functions to compute the correlation vector, the migration barrier, and the hopping probability after an occupation vector has been assigned.

kMCpy enumerates all `Event` objects, before the kMC run. This is done via a wrapper function, `EventGenerator` class as implemented in `kMCpy.event_generator`, which receives the `LocalClusterExpansion` as input and loops through all migration units in the whole simulation cell to generate all possible events. From a given identifier of mobile species (i.e., the `mobile_ion_identifier` parameter), two site indices involved in the migration event, namely, sites that the ion hops from and hops into, are identified. Subsequently, the indices of all sites in the current migration unit are stored for calculating the migration barrier.

### 3.4. Model fitting

To fit DFT-NEB barriers using the LCE model, we have implemented the `Fitting` class in `kMCpy.fitting`. This function performs fitting by interfacing with the python package `scikit-learn` [86]. kMCpy also stores fitted results (i.e., the KECIs) in a portable JSON format. The current implementation of kMCpy uses the “LASSO” regression [87] to perform the fitting. Indeed, LASSO limits the selection of orbits in the fit to the most important ones. LASSO requires a user-specified  $\alpha$  parameter to reduce the total number of selected orbits. The `Fitting` class stores the fitting history, e.g.  $\alpha$  and weights used during LASSO regression, for keeping a record and fine-tuning the LCE.

Note that an LCE typically fits the  $E_{\text{KRA}}$  that is obtained from NEB calculations. Therefore, the  $\Delta E_{\text{end}}$  term in Eq. (8) can be computed either from CMC (e.g., by interfacing other codes, such as CASM [88], smol [89], and CLEASE [90] or by fitting a separate LCE model. kMCpy has the flexibility to adopt either approaches to determine  $E_{\text{end}}$ . In the case an LCE is used for fitting values of  $E_{\text{end}}$  too, then the  $E_{\text{end}}$  data extracted from NEB calculations is used as an input for the fitting process.

### 3.5. Kinetic Monte Carlo

The KMC class in `kMCpy.kmc` can be used to perform kMC simulations. Multiple (e.g., 50) kMC runs should be done to eliminate the dependency of the results on the starting configurations. Initial structures of kMC runs are taken either from the thermodynamic ground state(s) (e.g., from CMC or GCMC simulations), or from a structure enumerator (see Fig. 4). Auxiliary tools are provided in `kMCpy.tools.gather_mc_data` to extract the occupation vectors from a structure in the crystallographic information file (CIF) format.

The general process of rf-kMC is described in Fig. 3, and an example of a standard output of both the initialization and the execution processes of kMC is shown in Fig. 5a and b. The KMC class is first initialized using a size specification of the simulation (super)cell, the initial occupations, the fitted model, the generated events, and a reference crystal structure. When the LCE model is used, information about clusters, orbits, and the KECIs is provided. kMCpy then “walks” through all available migration events and evaluates the occupations, correlation vectors, and hopping frequencies, given a simulation temperature and a  $v^*$ .

Upon initialization of the kMC, the `KMC.run()` function is called to perform the kMC simulation by supplying the total number of equilibration and sampling steps, respectively. The equilibration steps are not explicitly shown in Fig. 3a. A `Tracker` object is initialized once the equilibration process is complete (see Section 3.6). As shown in Fig. 3b, for each kMC step, an event  $k$  is randomly proposed using `KMC.propose()`, based on Eq. (12).

After the proposed event is executed, the related occupations, correlations, and hopping frequencies are updated. Since a given site may be involved in multiple migration events, all events with sites associated with the proposed event are updated. The number of events that require update after a proposed event is defined as the coupling strength of events, which can influence the computational performance of kMC (see Section 5). We use a pre-computed table (`event_kernel`) to quickly identify all events that need to be updated.

### 3.6. Tracking diffusion

To follow the displacements of all mobile species with respect to their original positions and to count the number of hops of each mobile ion, kMCpy uses a `Tracker` class in `kMCpy.tracker`. This class is activated only after the equilibration is complete. The `Tracker` is initialized with the initial occupation vectors, a reference crystal structure of the simulation cell, the formal charge on migrating species, the dimensionality of the overall diffusion process, the average hopping distances (in Å), the simulation temperature, and  $v^*$ . The initial location of each migrating species is recorded and their displacement vectors and counters are set to zero during initialization. During each kMC step, `Tracker.update()` updates the displacement vector (taking into account periodic boundary conditions) and the hopping counter of the migrating species involved in a proposed event.

Using Eqs. (2)–(7) in Section 2, `Tracker` computes transport properties, such as MSD,  $D_J$ ,  $D^*$ ,  $\sigma$ ,  $f$ , and  $H_R$  from the displacements of all migrating ions. The chemical diffusivity,  $D_c$  (Eq. (2)) can be computed once  $\theta$  is identified for systems with variable compositions, such as electrodes [30]. `Tracker.summary()` and `Tracker.write_results()` routines print and save the simulation results, respectively.

### 3.7. Input and output files

The inputs required by kMCpy (Fig. 4a) can be prepared in JSON format, through the use of Jupyter notebooks for instance. Sample input files are provided in the `input_example` folder of our GitHub repository (<https://github.com/caneparesearch/kMCpy>). Further, a command line wrapper executes kMCpy from the command line, which can be

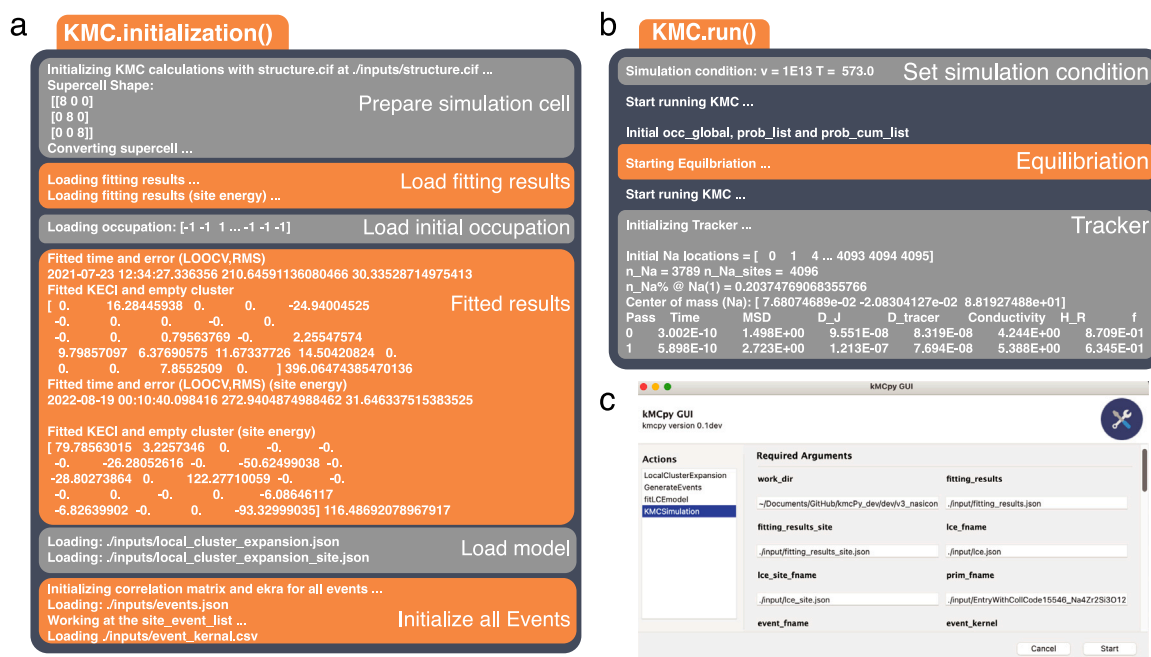


Fig. 5. Screenshots of initialization (`KMC.initialization()`, in a) and execution (`KMC.run()`, in b) of `kMCpy`. `KMC.initialization()` prints the input parameters and `KMC.run()` shows the computed results. A Tracker object is initialized and subsequently called at the end of `KMC.run()`. c shows the graphic user interface (GUI) of `kMCpy` relying on the python library Gooley.

found in `kMCpy.executable.wrapper`. Users can also customize their workflow by importing specific modules described in the previous sub-sections.

An example of a standard output of `KMC.initialization()` and `KMC.run()` is shown in Fig. 5a and b. `kMCpy` prints the information imported from the JSON input files and sets the parameters described in Sections 3.5, 3.6, and Fig. 3.

`kMCpy.executable.gui_wrapper` offers a graphical user interface (GUI) as shown in Fig. 5c, which builds upon the python library Gooley [91]. This GUI covers all required and optional arguments for each step, providing a convenient way to test different parameters and for educational/demonstration purposes as well.

A required task in the Actions box must be chosen in the GUI interface, following the descriptions in Sections 3.2 to 3.5. Next, all essential input parameters required for this task must be provided. For example, if `KMCSimulation` is chosen, one must provide: the working directory, the initial occupation, the original crystal structure, the fitted LCE model, the generated events, a value of  $\nu^*$ , and the simulation temperature. The documentation is available via a website (<https://kMCpy.readthedocs.io>) with details on all input parameters to run `kMCpy`. By clicking the “Start” button, `kMCpy` will perform the selected task with the standard output of the simulation (similar to the command line output of Fig. 5a and b) displayed in a separate pop-up window.

#### 4. Practical tips on using `kMCpy` and data analysis

Although `kMC` is conceptually straightforward, several considerations must be taken into account when applying this method in practice. These are:

1. During the construction of the model, the selection of an appropriate cutoff value is paramount to ensure that the model captures most of the diffusion properties of the relevant chemical species.
2. Identifying minimal sizes of the basis set that can accurately represent the NEB barriers is another important consideration. The choice of cutoffs for clusters determines the size of the basis

- set, with larger cutoffs including more clusters in the model. However, regularization techniques must be employed to select only the most representative clusters, with the regularization process, for example, controlled by the “ $\alpha$ ” parameter in the LASSO procedure. In addition, as shown in Fig. 6c, an extremely large basis set may worsen the performance of `kMC` simulations.
3. In the fitting process, it is important to minimize the fitting error and ensure that the number of non-zero KECl does not exceed the number of NEB barriers.
4. As a rule of thumb, it is important to limit the root mean square (RMS) error of fitted barriers below  $\pm 60$  meV, as this ensures an acceptable level of accuracy corresponding to an order of magnitude error in diffusivity [92].

By adhering to these guidelines, users can improve significantly the reliability and accuracy of the `kMC` method in practical applications.

In the `kMC` process, properties such as  $D_J$ ,  $D^*$ ,  $H_R$ , and  $f$  are efficiently computed with `kMCpy`. However, when it comes to calculating the mean square displacement (MSD), used to compute values of diffusivities, multiple approaches can be invoked. A widely used approach is the so-called *direct method*:

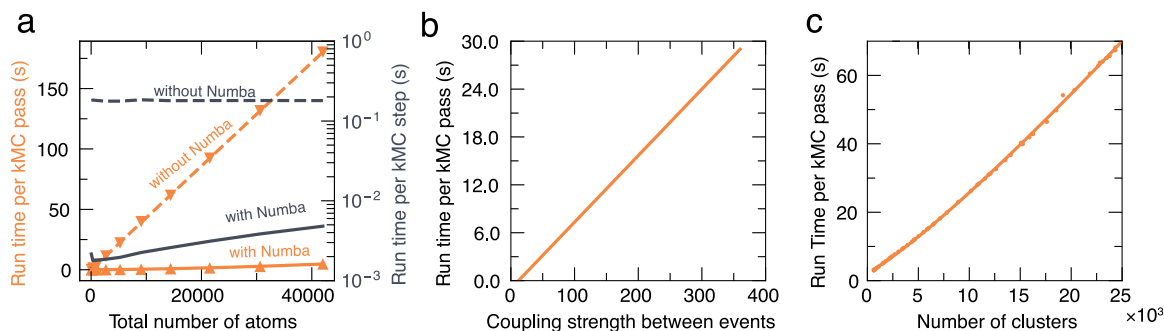
$$\text{MSD}(t) = \frac{1}{N} \sum_{i=1}^N (\vec{r}_i(t) - \vec{r}_i(0))^2 \quad (14)$$

where  $N$  is the total number of particles.

Another approach is the *window average method*, which offers an alternative way of calculating the MSD:

$$\text{MSD}(\tau) = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_{\text{steps}} - \tau} \sum_{k=0}^{N_{\text{steps}} - \tau - 1} (\vec{r}_i(k + \tau) - \vec{r}_i(k))^2 \quad (15)$$

where  $\tau$  is the window size in time steps, and  $N_{\text{steps}}$  is the total number of time frames. This method, represented by Eq. (15), involves computing an average of the MSD across all possible window lengths  $\tau$  employed throughout the simulation. By considering various window lengths, this method provides a broader perspective on particle displacement, enabling a comprehensive understanding of diffusivity. However, it is worth noting that the window average method can be computationally intensive, especially when dealing with large datasets.



**Fig. 6.** **a** shows the average computing time, per kMC pass (left y-axis, orange lines) and per kMC step (right y-axis, black lines), as a function of the total number of atoms for kMC simulations of  $\text{Na}_{1+x}\text{Zr}_2\text{P}_x\text{Si}_{3-x}\text{O}_{12}$ , scaling from  $1 \times 1 \times 1$  (42 atoms) to  $10 \times 10 \times 10$  supercells (42,000 atoms). The details of this model can be found in Ref. [32]. Solid and dashed lines refer to the time consumption with and without Numba, respectively. The LCE model contains 19 unique orbits and 212 possible clusters, with a coupling strength of 12. **b** shows the relationship between the time consumption and coupling strength between events (defined in Appendix) performed on an  $8 \times 8 \times 8$  supercell lattice. **c** describes the effect of basis set size (number of clusters/orbits in LCE model) on simulation time, using the  $8 \times 8 \times 8$  supercell.

To mitigate this computational burden, an efficient approach is to implement the Fast Fourier Transform (FFT) algorithm, which can significantly accelerate the calculations involved in the window average method.

Presently, the implementation of kMCPy uses primarily the direct method for computing the MSDs. However, future versions will include the window average method.

## 5. Performance of kMCPy

kMCPy has been developed in python, a high-level, human-interpretable language that combines flexibility and ease of programming. Since python is one of the most widely used programming languages [73,74] both in the fields of materials informatics and data science, it provides a set of readily available tools and libraries that can be used to accelerate the development of new codes and libraries. Among them, we utilize a JIT compiler, Numba [76], to increase the computational performance of kMCPy. Specifically, Numba translates the most numerically demanding part of kMCPy into optimized machine code.

We emphasize that kMCPy is a serial code, i.e., a single kMC run is executed on a single CPU core. However, multiple kMC runs can be executed simultaneously on a multi-core platform, such as a high-performance computing server or on the cloud. For example, different initial structures can be generated for a system and a kMC run for each initial structure can be run in parallel, thus reducing compute time.

Computationally, the intensive part of kMCPy is evaluating the correlation vector for each Event. Therefore, the size of the basis set (i.e., number of clusters and orbits), the total number of events, and the coupling strengths between different events (see Appendix) can crucially influence the determination of the correlation vector and the computational performance. For example, the basis-set size controls the computational cost of updating the correlation vector of a single event, whereas the total number of unique events and the coupling strengths between events set the total number of events to be updated during each kMC step. These quantities are usually coupled with each other, i.e., larger cutoff radii usually lead to larger basis sets, and in turn, stronger coupling between events, resulting in an increased computational cost of the kMC run.

We benchmarked,<sup>2</sup> the computational performance of kMCPy with the data compiled in Table 2, which shows the time required to prepare

**Table 2**

Time (in s) distribution for bootstrapping and running a kMC simulation of a test model. Details of hardware information and input model to perform these benchmarks are mentioned in footnotes 2 and 3.

Action	Time elapsed (s)
Model Generation (212 clusters)	2.10
Model Fitting (19 orbits)	2.60
Events Generation (6144 events)	1.31
kMC simulation (100 passes/51,200 steps)	168.00

inputs and run a very short simulation on a test system.<sup>3</sup> The process of input preparation includes the construction of the model, fitting of the model, and events generation, which in total takes less than 10 s. 100 kMC passes (51,200 steps per pass) on this model takes ~3 min, indicating that the time required for preparing the input is generally marginal compared to the kMC simulation itself.

Eq. (16) shows fitted dependencies between the simulation time and the three major factors:

$$t \propto f_{\text{Numba}}(N_{\text{cell}}) \times N_{\text{cluster}}^{1.16} \times N_{\text{cell}}^{1.01} \times N_{\text{coupling}}^{1.10} \quad (16)$$

where  $N_{\text{cluster}}$ ,  $N_{\text{cell}}$ ,  $N_{\text{coupling}}$  are the number of clusters, the size of the supercell, and the coupling strength, respectively.  $f_{\text{Numba}}$  denotes the acceleration effect using the Numba routines on the computational time. The benchmark results are shown in Fig. 6.

The average simulation time using different cell sizes (indicated by the total number of atoms per simulation box) is depicted in Fig. 6a. Without Numba, the elapsed time per kMC step remains approximately constant  $\sim 10^{-1}$  s (dashed black line). Numba accelerates significantly the kMC simulation by factor of  $\sim 2$  ( $10^{-3}$  s, solid black line). The speedup by Numba is weakened when the simulation cell becomes larger. Therefore, Numba can enable access to longer and larger scale simulations with kMCPy [32]. As 1 kMC pass is just the total number of available sites within the simulation cell, the run time per kMC pass grows linearly when the cell size (i.e., the number of atoms) becomes larger. Figs. 6b and 6c demonstrate the effect of the coupling strength between events, and the basis set size, which also contributes to a quasi-linear increase towards the run time of each kMC pass. These results show that the time complexity of the implemented kMC algorithm is  $O(\sim N)$ .

<sup>3</sup> A LCE model for Na ion migration was built with a  $\sim 6$  Å cutoff radius for point, pair and triplet clusters on  $\text{Na}_{1+x}\text{Zr}_2\text{P}_x\text{Si}_{3-x}\text{O}_{12}$  yielding a total of 19 unique orbits and 212 possible clusters. The LCE model was fitted with data from DFT-NEB calculations. 6144 distinct Na-ion hopping events were generated in a  $8 \times 8 \times 8$  supercell lattice.

<sup>2</sup> All benchmarks were performed on a 2020-year model 13-inch Apple MacBook Pro with a M1 chipset (8 core CPU + 8 core GPU) and 16 GB of RAM.



## 6. Conclusion

In summary, we presented kMCpy, a lightweight open-source python package to perform kMC simulations of ionic transport in crystalline solids, with inputs from DFT calculations. kMCpy and its implemented workflow provide a framework for the scientific community to predict the transport properties of any crystalline solid with high accuracy and performance. The design of kMCpy should facilitate its use on most available computational platforms from standard laptops to high-performance supercomputers. The modular framework makes it highly customizable and easily programmable. By utilizing the JIT compiler –Numba, kMCpy achieves high computational performance. Both the input and the output files of kMCpy rely on the human-readable JSON format, which is easy to distribute.

Future developments of kMCpy include: (i) the use of GPU-based acceleration for improved computational performance, (ii) the development of a thermodynamic (CMC/GCMC) module and a built-in structure enumerator, (iii) more fitting approaches for cluster expansion in the form of modularized Fitting objects, and (iv) additional models for the evaluation of  $E_{\text{KRA}}$  that are alternative to LCE. We hope that we can achieve a fully self-consistent, highly robust, and high-performance framework for simulating materials' kinetics using the kMC approach without sacrificing the user-friendliness of kMCpy. In conclusion, kMCpy exhibits a combination of flexibility and user-friendliness, making it useful for investigating the materials' kinetics of crystalline systems.

### CRediT authorship contribution statement

**Zeyu Deng:** Conceptualization of the study, Methodology, Software development, Writing the initial draft. **Tara P. Mishra:** Software development, Writing the initial draft. **Weihang Xie:** Software development, Writing the initial draft. **Daanyal Ahmed Saeed:** Software development, Writing the initial draft. **Gopalakrishnan Sai Gautam:** Methodology, Writing the initial draft. **Pieremanuele Canepa:** Conceptualization of the study, Methodology, Project management, Procurement of funding, Writing the initial draft.

### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Pieremanuele Canepa reports financial support was provided by National Research Foundation.

### Data availability

Data will be made available on request.

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## Appendix. Nomenclature

- **Site:**  $i \in \{0, 1, \dots, N-1\}$  is a site in a simulation cell with  $N$  sites.  $i$  is a unique global index of a site.
- **Occupation:** in a Chebyshev basis  $\sigma_i$  has a value of  $\pm 1$  for site  $i$ , e.g., occupied ( $-1$ ) or unoccupied ( $+1$ ), or species A ( $-1$ ) and species B ( $+1$ ).
- **Occupation Vector:**  $\vec{\sigma} = [\sigma_0, \sigma_1, \dots, \sigma_{N-1}]$  is a vector of occupations in a simulation cell.
- **Migration unit:**  $M = [i_0, i_1, \dots, i_m]$  is a collection of all sites within a specific cutoff radius around the center of a migration unit, where  $m$  is the total number of sites within that migration unit. There are multiple migration units in the simulation cell.
- **Sublattice Site:**  $i \in \{0, 1, \dots, n-1\}$  is a site within a migration unit with  $n$  sites.
- **Distance Matrix: D:** Distance matrix of a migration unit is a  $m \times m$  matrix where  $m$  has been defined above. Matrix elements  $d_{ij}$  are the Cartesian distances between site  $i$  and  $j$  within a migration unit.
- **Cluster:**  $[i_0, i_1, \dots, i_n]$  is a collection of sublattice sites ( $i$ ) within a migration unit with a length of  $n$ . Presently there are four types of clusters implemented in the code:  
Point: a cluster containing 1 site,  $n = 1$ ;  
Pair: a cluster containing 2 sites,  $n = 2$ ;  
Triplet: a cluster containing 3 sites,  $n = 3$ ;  
Quadruplet: a cluster containing 4 sites,  $n = 4$ ;  
Note, the order size of these clusters can be easily extended beyond 4.
- **Cluster Function:**  $\phi_\alpha(\vec{\sigma}) = \prod_{i \in \alpha} \sigma_i$  is a product of all occupations of all sites that belong to a cluster.
- **Orbit,**  $[\alpha[0], \alpha[1], \dots, \alpha[m]]$  is a collection of symmetrically equivalent clusters with a multiplicity of  $m$  within a migration unit.
- **Correlation:**  $\phi_O(\vec{\sigma}) = \sum_{\alpha \in O} \phi_\alpha(\vec{\sigma})$  is the summation of cluster functions of all symmetrically equivalent clusters within a migration unit that belongs to an orbit.
- **Correlation Vector:**

$$\vec{\phi}(\vec{\sigma}) = [\phi_{O[0]}(\vec{\sigma}), \phi_{O[1]}(\vec{\sigma}), \dots, \phi_{O[m]}(\vec{\sigma})] \quad (17)$$

is a collection of all correlations for each orbit within a migration unit with a length of  $n$ . This is also the basis-set size.

- **Cluster Expansion Model:**

$$E(\vec{\sigma}) = V_0 + \sum_{\alpha} V_{\alpha} \phi_{\alpha}(\vec{\sigma}) \quad (18)$$

where  $E$  is the total energy (typically the DFT total energy), and  $V_0$  and  $V_{\alpha}$  are called effective cluster interactions (ECIs) for each cluster, which are fitted from first-principles calculations. The summation polynomials are usually truncated to specific cluster sizes (e.g., quadruplet, quintuplet, etc.). All clusters belonging to the same orbit share the same  $V_{\alpha}$ .

- **Local Cluster Expansion Model** uses a local cluster expansion model,

$$E_{\text{KRA}}(\vec{\sigma}) = K_0 + \sum_{\alpha} K_{\alpha} \phi_{\alpha}(\vec{\sigma}) \quad (19)$$

where  $E_{\text{KRA}}$  is the kinetic resolved activation energy barrier which is independent of migration directions.  $K_0$  and  $K_{\alpha}$  are called kinetic effective cluster interactions (KECIs), which are fitted from first-principles NEB calculations. The directional dependent activation energy can further be recovered using

$$E_b = E_{\text{KRA}}(\vec{\sigma}_{AS}) + \frac{1}{2} \Delta E_{\text{end}} \quad (20)$$

where  $\vec{\sigma}_{AS}$  is the occupation vector at the activated state and  $E_b$  is the activation energy barrier from initial to final images.  $\Delta E_{\text{end}}$  is the total energy difference between the final and initial images, respectively:

$$\Delta E_{\text{end}} = E(\vec{\sigma}_{\text{final}}) - E(\vec{\sigma}_{\text{initial}}) \quad (21)$$

- **Event** is a swap of occupation values between two hopping sites.
- **Pass** is defined as the total number of mutable sites in the simulation cell.
- **Coupling Strength Between Events** is the total number of events that need to be updated after an event has been executed.

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