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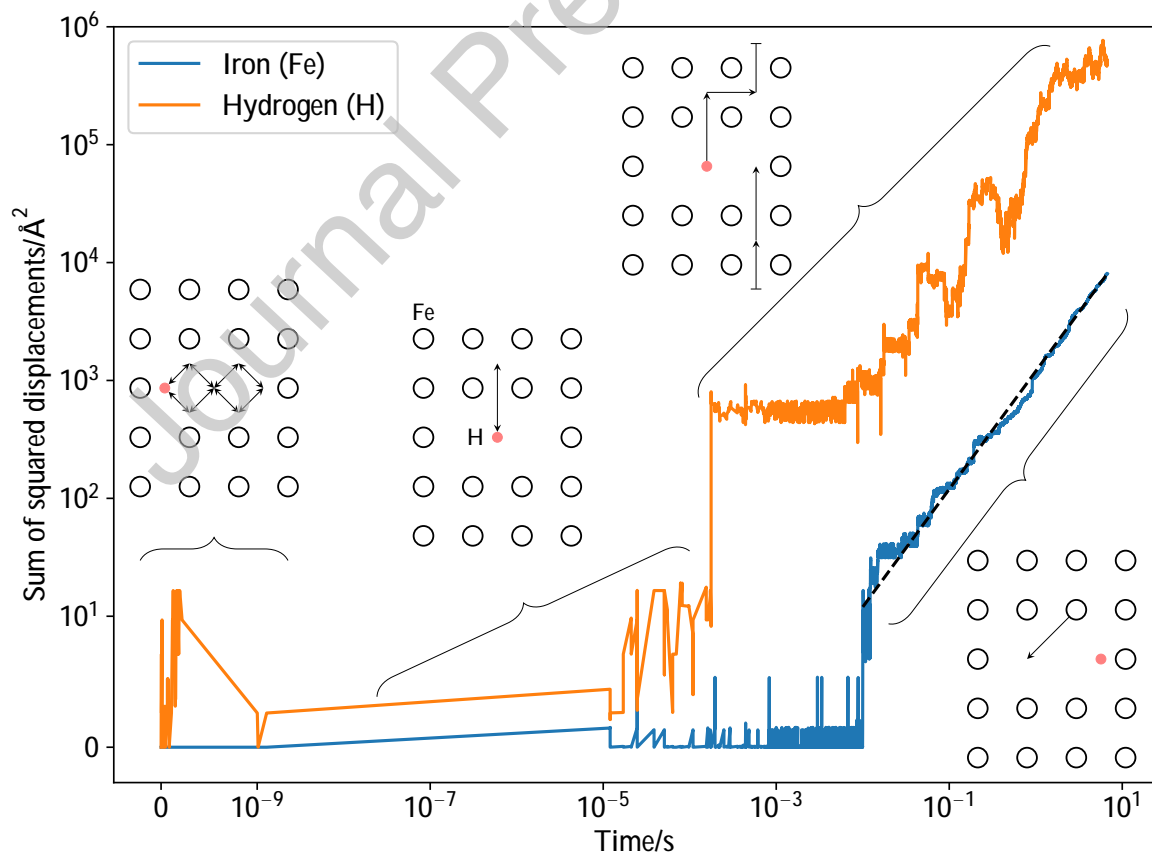
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Graphical Abstract

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Accelerating α -lattice kinetic Monte Carlo simulations to predict hydrogen vacancy-cluster interactions in U -Fe

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Abstract

We present an enhanced α -lattice kinetic Monte Carlo (OLKMC) model, based on a new method for tolerant classification of atomistic local-environments that is invariant under Euclidean-transformations and permutations of atoms. Our method ensures that environments within a norm-based tolerance are classified as equivalent. During OLKMC simulations, our method guarantees to elide the maximum number of redundant saddle-point searches in symmetrically equivalent local-environments. Hence, we are able to study the trapping/detrapping of hydrogen from up to five-vacancy clusters and simultaneously the effect hydrogen has on the diffusivity of these clusters. These processes occur at vastly different timescales at room temperature in body-centred cubic iron. We predict the diffusion pathways of clusters/complexes without *a priori* assumptions of their mechanisms, not only reproducing previously reported mechanisms but also discovering new ones for larger complexes. We detail the hydrogen-induced changes in the clusters' diffusion mechanisms and find evidence that, in contrast to mono-vacancies, the introduction of hydrogen to larger clusters can increase their diffusivity. We compare the effective hydrogen diffusivity to Oriani's classical theory of trapping, finding general agreement and some evidence that hydrogen may not always be in equilibrium with traps, when the traps are mobile. Finally, we compute the *trapping atmosphere* of meta-stable states surrounding non-point traps, opening new avenues to better understand and predict hydrogen embrittlement in complex alloys.

Keywords: Atomistic modelling, α -lattice kinetic Monte Carlo, Point defects, Hydrogen embrittlement, Diffusion mechanism

1. Introduction

It has been known for over 100 years [1, 2] that the presence of hydrogen (H) in metals – particularly steels – can severely reduce ductility, leading to catastrophic failure below the yield-stress. The processes that cause these effects are collectively termed *hydrogen embrittlement* (HE). Despite a century of research, the core mechanisms of HE have yet to be fully understood and are still a topic of active research/debate [3]. The difficulty in understanding HE stems from its multi-scale nature; a full description of HE requires understanding of H-adsorption, H-diffusion/transport, and (most crucially) H interaction/influence with/on crystal defects. These processes span many orders

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of length/time scales, which presents challenges when isolating/connecting the impact of H at the atomistic scale to the macroscopic results.

A breadth of mechanisms for HE have been proposed, most of them revolve around the interactions between H and crystal defects. For a more complete description see Ref. 4 and Ref. 3. A few of the most prominent mechanisms are: Hydrogen-induced decohesion (HID) [5–7], Adsorption-induced decohesion (AIDE) [8], Hydrogen-enhanced localised plasticity (HELP) [9–13] and Hydrogen-enhanced strain-induced vacancy (HESIV) formation [14–16]. Many of these mechanisms are supported by bodies of experimental work. As few are orthogonal to each other, it is likely that a full description of HE contains a combination of two/three of these mechanisms (alongside some yet undiscovered).

Theoretical and computational modelling play a crucial role in the study of the Fe-H system due to the inherent difficulty in experimental observations of atomic H [17]. The low solubility and high diffusivity [18] of H in body-centred cubic (BCC) iron (Fe), combined with the small ‘nucleus’ and low electron density, make direct experimental observations extremely challenging. Instead, techniques such as thermal desorption analysis (TDA) [19], electro-permeation (EP) experiments [20] and atom probe tomography (APT) [21] are employed. Many of these methods (with the notable exception of APT) are unable to directly investigate H diffusion and trapping behaviour within metals on the atomic scale thus, we must fall back to computation/theory to unravel the atomic mechanisms that cause HE.

Different computational modelling techniques have been used to investigate HE over varied assumptions and time/length scales. On the smallest length-scales, density functional theory (DFT) is used to study H binding sites [22–24] and occasionally combined with molecular dynamic (MD) in *ab initio* MD to study H diffusion at the highest accuracy [25]. Additionally, work has been done using path-integral MD [26, 27] to explore H diffusion in iron while incorporating quantum effects, which are known to be important at low temperatures [26]. Nevertheless, progress has been made modelling much-larger systems using classical approaches, the most popular of these is MD and its accelerated-variants using semi-empirical potentials. This has enabled the study of H-defect kinetics, such as grain-boundaries [28, 29] and dislocations [30, 31]. Molecular dynamics simulations must resolve atomic vibrations in order to accurately track the dynamics of atom-scale systems. This imposes a significant computational effort as the integration time-step must be of-the-order of these vibrations. Hence, even using today’s computers, MD simulation timescales rarely exceed $\sim 100\mu\text{s}$. Continuing to the longest/largest scales, Monte-Carlo (MC) [32] and kinetic Monte-Carlo (KMC) [33] methods overcome this barrier by ignoring the explicit phase-space trajectory, instead focusing on state-to-state transitions. This can significantly accelerate simulations. However, these methods are confined to discrete representation and require knowledge of mechanisms *a priori*.

On-lattice¹ kinetic Monte Carlo (OLKMC) [34], an extended KMC method, is a general and unbiased tool (discovering mechanisms without any *a priori* input) being successfully applied to study the kinetics of various systems, e.g. Fe/Cu/Al, BCC/FCC, disordered systems, extended defects, point defects, etc. [35–42]. On-lattice KMC automatically discovers the mechanisms available – using saddle-point (SP) searches to locate the transition states – and then applies the KM algorithm [33, 43] to advance the system state/time. On-lattice KMC allows for the exploration of continuous systems, at previously inaccessible timescales, at atomic fidelity. As such, it is the

¹Also known as: “adaptive”, “on-the-fly”, “self-learning” and “self-evolving”.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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