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A Transition-State Model for Diffusive Molecular Dynamics of Interstitial Solutes

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Abstract

Mass transport in crystalline solids originates from thermally activated transitions between metastable atomic configurations on a complex potential energy landscape. In metallic systems containing interstitial solutes, such as hydrogen in magnesium, diffusion kinetics are highly sensitive to the local atomic environment. Capturing these effects over time scales that exceed those accessible to conventional molecular dynamics constitutes a fundamental challenge in atomistic modeling, as it would require the explicit resolution of rare events and thermal fluctuations. Diffusive Molecular Dynamics (DMD) circumvents this limitation by formulating diffusion in terms of smoothly evolving occupation probabilities, thereby eliminating the need to explicitly resolve thermal fluctuations, while retaining atomistic resolution. The predictive capability of DMD, however, critically depends on the physical soundness of the kinetic model governing the evolution of these probabilities. In this work, a transition-state-based formulation of Diffusive Molecular Dynamics is proposed, in which diffusion is explicitly described as a sequence of thermally activated hopping events between neighboring metastable states. The evolution of site occupation probabilities is governed by a discrete master equation, whose transition rates are determined from activation free energies associated with saddle-point configurations, in accordance with transition state theory. This formulation establishes a direct connection between DMD kinetics and the atomistic energy landscape, eliminating the need for phenomenological diffusion coefficients or prescribed mobilities. To enable efficient simulations of large systems,

a mean-field approximation for the activation energies is introduced. Within this approximation, the saddle-point energies are expressed as local, environment-dependent functionals of the evolving atomic configuration, allowing activation barriers to be evaluated on-the-fly during the simulation. This approach retains the essential physics of thermally activated diffusion while avoiding the prohibitive cost of explicit saddle-point searches. The resulting kinetic model is thermodynamically consistent and ensures monotonic dissipation of the system free energy. A key feature of the proposed framework is the intrinsic coupling between mechanical relaxation and diffusion. Since activation barriers depend on the instantaneous atomic configuration, local stress, strain, and coordination directly influence transition rates. This enables the description of stress-assisted diffusion, barrier modulation near defects, and kinetic heterogeneities arising in mechanically non-uniform regions, all within a unified variational setting. The transition-state DMD model is applied to the study of hydrogen diffusion in magnesium, considering both bulk crystalline systems and magnesium-based nanomaterials.

Keywords:

Diffusive Molecular Dynamics Atomistic Model Multiscale Model