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ABSTRACT:

A Unified Understanding of the Effects of Mobile Interstitials on Vacancy Diffusion

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Mobile interstitials can redistribute as vacancies migrate, making their effects on vacancy diffusion difficult to predict and leading to apparently contradictory reports of both enhancement and suppression. Here we present a unified thermodynamic framework for understanding the effects of mobile interstitials on vacancy diffusion. We formulate vacancy migration in a grand-canonical ensemble at fixed interstitial chemical potential and define the free-energy landscape along the migration pathway together with the corresponding activation free energy. These quantities are computed using two complementary approaches: hyperplane-constrained thermodynamic integration based on a mean-force relation, and a two-state chemical-potential integration. The latter requires sampling only the initial and transition states, so a single chemical-potential integration yields activation free energies over a wide range of interstitial chemical potentials, enabling rapid mapping across temperature and chemical potential. We apply this framework to vacancy diffusion in FCC, BCC, and HCP metals containing H, including in-plane and out-of-plane diffusion in Zr, as well as to vacancy diffusion in BCC W containing He. The two free-energy approaches give consistent results and agree with diffusion coefficients obtained from mean-square displacements in molecular dynamics simulations. The resulting maps identify regimes in which mobile interstitials suppress or enhance vacancy diffusion. A site-occupancy analysis further links barrier shifts to state-dependent changes in the accessible site spectrum and to transferable interstitial-interaction terms.