

Abstract Submitted
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Microscopic Theory of Activated Penetrant Diffusion in Liquids and Glasses RUI ZHANG, KENNETH SCHWEIZER, University of Illinois at Urbana-Champaign — We formulate a force-level, self-consistent, nonlinear Langevin equation theory for the long-time diffusivity of a penetrant in molecular and polymeric supercooled liquids and glasses. The theory predicts that for a wide range of penetrant to matrix molecular unit size ratios (R), activated hopping is the dominant transport mechanism. The penetrant diffusivity (D) and jump distance exhibit different R -dependences in three dynamic regimes: $R < 0.5$, $0.5 < R < 1$, $R > 1$, which are physically distinguished by the nature of the matrix motion required to facilitate hopping. The penetrant diffusion constant decreases the fastest with R in the first regime where the matrix behaves as a harmonic amorphous solid. The other two regimes involve larger scale, anharmonic matrix motions. Below and above the matrix glass transition temperature, D exhibits an Arrhenius and supra-Arrhenius temperature dependence, respectively. The reduction of D associated with penetrant-matrix attractive forces has also been studied. Our a priori theoretical calculations agree reasonably well with experiments for both fast transport (e.g., gas permeation) and slow transport (e.g., barrier materials) systems, covering more than 10 orders of magnitude of variation of the diffusion constant.

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