

Diffusion of He in Frozen Polypropylene Structures: Polymer Density & Simulation Size Effects

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Abstract

Molecular simulations of penetrant diffusion in glassy polymers show a regime of anomalous diffusion between ballistic motion and Fickian diffusion. Various investigations attribute this effect to the tortuous diffusion pathway topology and correlated motion of the polymeric structure in which the penetrants diffuse.¹ The turnover from anomalous to Fickian diffusion is also known to depend on the simulation box size,³ which can lead to erroneous calculations of the diffusivity. This work aims at decoupling the effect of the polymer topology and motion on the molecular diffusion of small molecule penetrants in atactic, glassy polypropylene. United atom polypropylene structures of different sizes and densities are created using the Gaussian Lattice algorithm of Kotelyanskii et al.² Penetrant gas diffusion is studied by direct molecular dynamics simulations in frozen polymer structures and compared to results of simulations in which the polymer is allowed thermal motion.⁴ The diffusion mechanism and simulation size effects are studied by analysis of the self-part of the Van-Hove space-time autocorrelation function for penetrant diffusion. For the frozen matrix, the diffusion is no longer an activated process. Comparisons with fully mobile matrix simulations demonstrate the influence of polymer motion on the mechanism of molecular diffusion in glassy polymers and are in qualitative agreement with previous studies¹. Furthermore, the anomalous diffusion regime is identified to be a consequence of the tortuosity in the percolated diffusion pathways in the polymer structure, which itself is connected to the correlation length in the polymer glass. System size effects are studied by simulating polymeric structures with central linear dimensions ranging from approximately 25 to 60 Å. The turnover from anomalous to Fickian diffusion shows a marked simulation size dependence not seen in the results in which the polymer is allowed thermal motion.

References

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