350c Configurational Diffusion of Small Molecules through Nano-Confined Polymers

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Configurational diffusion in glassy, amorphous polymers is dictated by the structure and dynamics of the polymer since the penetrant has to travel through a tortuous pathway afforded by the free volume within the polymer while being in close contact with the polymer matrix. Confinement of the polymer to nanometer length scales can thus be expected to have an effect on permeation of penetrant molecules. Experimental studies have shown that altering the local structure of the polymer by confining it to a pore [1] or by adding nanoparticles to it [2] results in improved separation (permeability and selectivity) properties. The goal of this work is to use molecular dynamics (MD) simulations to understand the effect of nano-confinement on the permeation of small gas molecules through polymers.

MD simulations were carried out on a fully atomistic model of glassy, amorphous atactic polypropylene (aPP) confined to a slit shaped pore. The polymer structure was generated by using a method by Kotelyanskii et al. [3] modified for a slit pore. Mirror boundary conditions were used at the pore walls (z direction) while regular periodic boundary conditions were used in the x and y directions. Simulations were carried out for two different penetrants, namely helium and methane at two temperatures, 233 K and 296 K (one below and the other above the glass transition temperature of aPP). MD trajectories were simulated for 10 nanoseconds.

Polymer density was found to be higher near the pore wall than in bulk. The penetrant diffusivities for the confined polymer were larger than that for diffusion through bulk polymer under same conditions of temperature and pressure (results for bulk polymers obtained from [4]). Methane did not reach the Fickian diffusion regime during the time scale of simulation, but the diffusivity could be estimated using analysis of jump maps. The results are used to interpret recent reports of enhancement of selectivity in nanocomposite membranes [1,2].

References:

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