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Coupling of host-framework flexibility and entry-length effects in finite-size nanoporous membranes

Zuluaga-Bedoya C. C.[1]*, Bhatia S.K.[1]

[1]The University of Queensland, Brisbane, Australia
*c.zuluagabedoya@uq.edu.au

The effect of host-framework flexibility on the adsorption and transport properties of nanomaterials is a significant concern, receiving much attention in simulations; however, the predictions are largely dependent on the accuracy of the force field parameters. Existing host-host force field parameters supply a limited representation of the actual frameworks, and structural parameters such as pore diameters and pore void fraction accurately match experimental values in just a few cases. Part of this mismatch is due to a combined contribution of the bond and angle force constants and the partial charges representing the electrostatic interactions, which can create too stiff lattices and reorientate the atoms of the pore windows, obtaining anomalous structures. While several adsorption studies suggest that host-framework flexibility does not affect the adsorbed quantity, it is known that other inherently structural effects (e.g. transitions, swelling, gate opening) are noticeable at high loadings, in both experiments and simulations. Accurate prediction of these effects is highly dependent on the reliability of the force field.

Diffusion as a time-varying phenomenon is influenced by the host-framework flexibility, dependent on the window opening and the pore topology of the solid, but there is insufficient understanding of the behaviour of the diffusion coefficient other than the "window effect", triggered by variation of the atomic position of the framework; partly due to the lack of accuracy/transferability of the host-host force field parameters. This variability affects the diffusion coefficient dramatically, as small biasing in window size leads to multiple orders of magnitude changes in the diffusivity. In addition, there is a non-uniformity of the diffusion coefficient in finite nanoscale crystals, and an excess internal resistance spread over an entry region of developing flow, that is inherently correlated with the external fluid properties. Studies in rigid systems have shown there are transport barriers linked to this entry region, but the significance of these effects in flexible systems is unknown.

Here we investigate the effect of host-framework flexibility on guest transport, by comparing the diffusion coefficient in a fully flexible system with its respective rigid-average structure of equivalent window size, in order to provide a new reference for the analysis of thermal, collision-derived, and entry length-related effects. Equilibrium Molecular Dynamics (EMD) simulations were conducted using the light gases CH_4, C_2H_4 and C_2H_6 in siliceous TON (Theta-1) zeolite nanosheets, and H_2, CO_2 in ZIF-8 nanosheets, to measure the diffusion coefficient in both bulk and finite crystals.

Our investigation reveals that the flexibility effect has three main contributions, one based on the window size oscillations allowing larger number of inter-cage hops, another related to thermal resistance arising from increased kinetic energy of guest molecules when mutual thermalization dominates, and another related to the decrease in the Maxwell-reflection coefficient (i.e. the momentum accommodation of the guest molecules) on wall collision. These effects coexist with the entry-length effect characterized by decrease of the diffusion coefficient for small crystal thicknesses, more severely in flexible systems. We find that in flexible frameworks, where no fluid thermostat is applied, the guest molecules increase in temperature, resulting in a higher diffusivity and an apparent higher number of fluid-wall collisions when compared to the rigid-average framework. However, this effect is overshadowed by the entry-length effect, as diffusivity profiles highlight the decrease in the entry length in a flexible large crystal compared to its rigid-average structure, but for a small flexible crystal the diffusivity is more strongly attenuated at the centre of the solid, compared to the reduction in the rigid-average framework, explained by the reduced Maxwell-reflection coefficient for the flexible case.

Our findings show that the entry length effects are weakened but still preserved for flexible nanosheets, although the thermal effect and the "window effect" increase the diffusivity. These results are crucial for the design of ultrathin membranes with high selectivity and catalysis applications.