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Experimental insights into the effect of surface roughness on Knudsen diffusivity

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Diffusion in disordered nanoporous media is a complex phenomenon involving different geometrical and physicochemical effects. Even though it has been studied extensively, the overall picture has not yet been fully unveiled, and recent studies continue to reveal new aspects on the importance of confinement effects, such as geometrical surface heterogeneity, in diffusion and catalysis [1]. The internal pore surface of many amorphous mesoporous media is not smooth at the molecular level, as various structural characteristics inherent in the materials and their synthesis methods give rise to roughness that ranges in size from sub-nanometre up to the size of the pore diameter [2]. Surface roughness creates perturbations along the pore walls, which decrease the accessibility of the surface area to diffusing gas molecules and act as molecular traps having an impact on their transport through the pore. In such mesoporous materials, the dominant transport mechanism for gases is often Knudsen diffusion, where the collisions of gas molecules with the pore walls are more frequent than intermolecular collisions making the effect of pore walls in the Knudsen regime even more pronounced.

Analytical and Monte-Carlo simulations [2,3] in 2D and 3D pores with internal fractal surface roughness (within a finite range) modelled by random fractal Koch segments have showed a strong influence on the Knudsen diffusion of gas molecules. In addition, expressions have been derived to correlate the decrease of the Knudsen diffusivity with the fractal surface roughness. However, diffusion in disordered porous media may be more complicated than one can predict, as interactions between molecules or between molecules and pore walls, or other phenomena, such as adsorption, which might not be originally considered, may play a significant, non-trivial role. Therefore, an experimental validation is crucial to connect the theory and computer simulations with the engineering applications and identify any inconsistencies. In this work, the measurement of Knudsen transport and self-diffusivity was studied in a single pore, to eliminate the interference of morphological and topological effects (e.g. pore connectivity). A series of experiments, where a single pore is projected to the macroscale, was performed in a unique Ultra-High Vacuum Setup [4] to maintain diffusion in the Knudsen regime, and a 3D-printed channel with internal fractal roughness. Latest experimental results will be discussed in detail and compared with previous computational and analytical theoretical work.

References

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