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Origin of sorption hysteresis of micro-porous polymers: an explanation based on hydrogen bonds

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Soft nanoporous matter encompasses man-made materials such as compliant porous solids, intrinsically porous polymers and organic membranes as well as natural materials such as wood, bamboo, cotton and other plantderived materials. These materials can undergo significant deformation during water adsorption because of strong coupling between the adsorption and mechanical properties. In addition, hysteresis is observed in the sorption isotherms of these materials. We find that sorption-induced deformation is the cause of hysteresis and analyze the special role played by the different types of hydrogen bonds.

We prepare three samples of amorphous cellulose as the host material considering its wide presence in nature. Water sorption and deformation are simulated with a hybrid Grand Canonical ensemble (GCMC)/ Molecular Dynamics (MD) method. The sorption isotherms simulated for each of the three samples exhibit significant hysteresis and the simulation results agree well with experimental data on low-crystalline cellulose. Significant hysteresis is observed as also seen in a variety of micro-porous polymers. The volumetric strain is monitored and shows significant swelling strains reaching as high as 36% at the saturation point. We note that, if we eliminate the deforming effect by freezing the cellulose at the dry state or the saturated state and then conduct an additional adsorption or desorption loop, the simulated isotherms significantly deviate from the experiments and the hysteresis disappears. This shows that the hysteretic sorption strongly depends on the deformation of the system.

We explore the mechanism of sorption hysteresis by further interrogating the systems. As amorphous cellulose is a non-cross-linked polymer, hydrogen bonds play a crucial role in both sorption and deformation processes. Hydrogen bonds are analyzed to monitor the interactions inside the system, revealing different configurations during adsorption and desorption. We find that the origin of sorption hysteresis in amorphous cellulose can be attributed to the process of creation of new adsorption sites due to hydrogen bond breaking during swelling. During adsorption process, some cellulose-to-cellulose hydrogen bonds (HBCC) change into cellulose-to-water hydrogen bonds (HBCW). However, the recovery of these new adsorption sites back to HBCC during desorption is less likely since they more likely remain occupied by water molecules. Consequently, the system accommodates the same amount of water molecules distributed over more sorption sites at lower energy state during desorption process, leading to hysteresis in the sorption isotherms observed in both experiments and simulations. Moreover, sorption hysteresis is also shown to have a significant influence on other important properties such as pore size distribution and bulk modulus.

References

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