Hydrogen bond (HB) network of nanometric capillary bridge

Procedure to obatain the HB network:

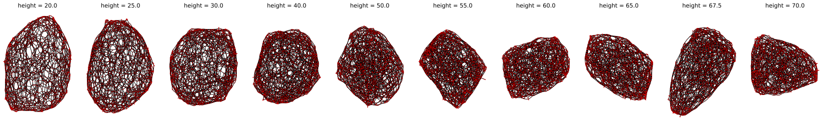
Geometrical criterion:

- $\theta_{\mathrm{OOH}} \leq 30^\circ$
- $d_{\mathrm{OO}} \leq 3.5$Å
- $d_{\mathrm{OH}} \leq 2.4$Å

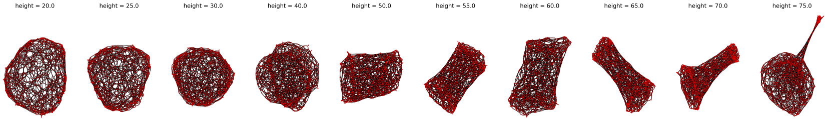
Graph layout:

- Force Atlas 2 algorithm

Hydrophobic Surface $k = 0.0$

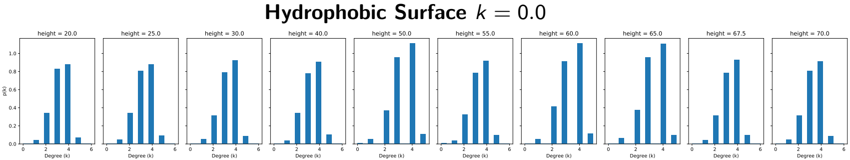


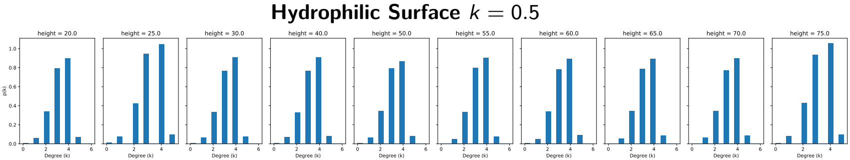
Hydrophilic Surface $k = 0.5$



Node degree histogram

https://mathinsight.org/degree_distribution

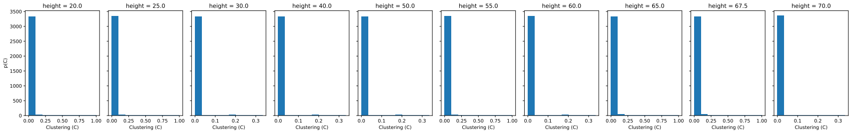




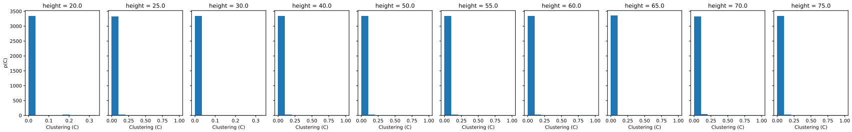
Clustering histogram

https://en.wikipedia.org/wiki/Clustering_coefficient

Hydrophobic Surface $k = 0.0$

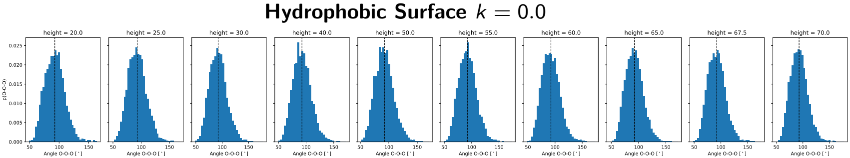


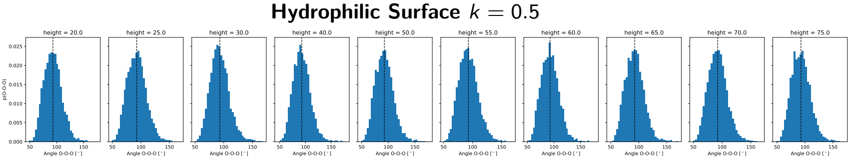
Hydrophilic Surface $k = 0.5$



Oxygen-Oxygen-Oxygen (O-O-O) angles histogram

Angle between the Oxygen atoms of water neighbors.

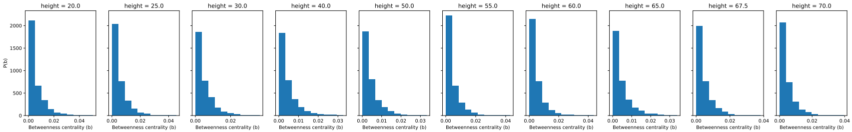




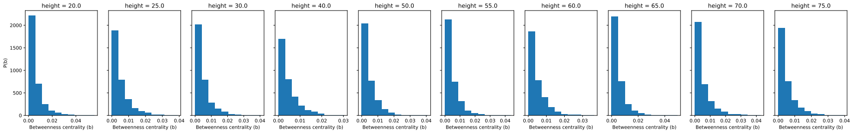
Betweenness centrality histogram

https://en.wikipedia.org/wiki/Betweenness_centrality

Hydrophobic Surface $k = 0.0$



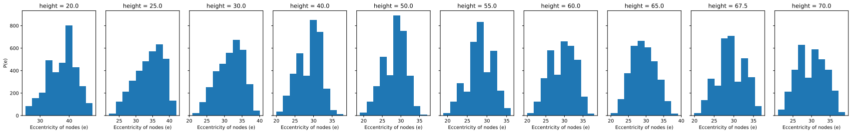
Hydrophilic Surface $k = 0.5$



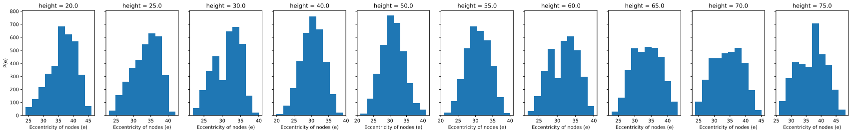
Eccentricity histogram

http://mathworld.wolfram.com/GraphEccentricity.html

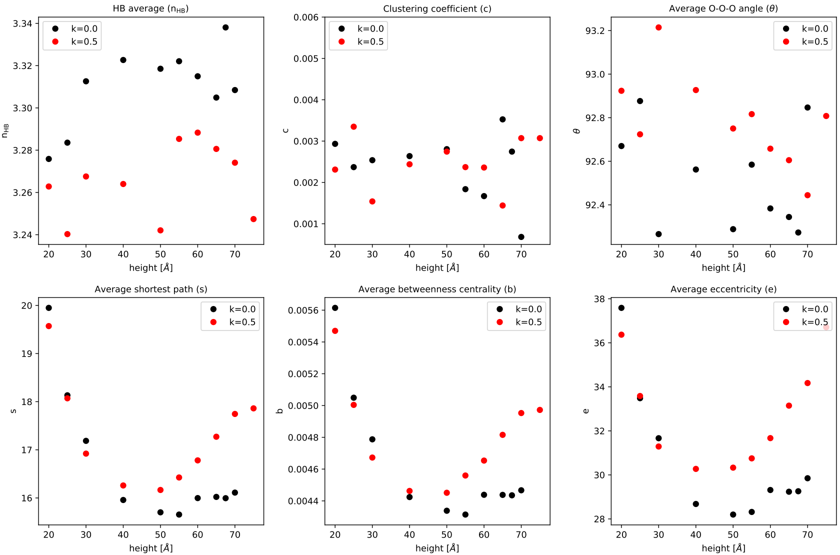
Hydrophobic Surface $k = 0.0$



Hydrophilic Surface $k = 0.5$



Averages of graph measures

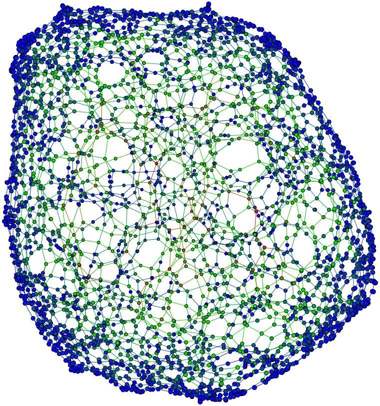


Network analysis on Gephi

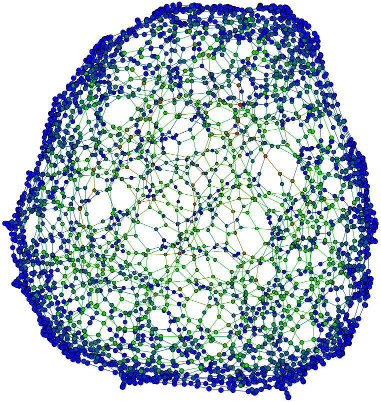
Betweenness centrality (node colors) and Eccentricity (node size)

$h = 20$

Hydrophobic Surface $k = 0.0$



Hydrophilic Surface $k = 0.5$

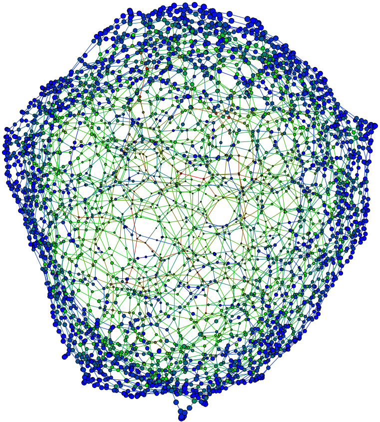


Network analysis on Gephi

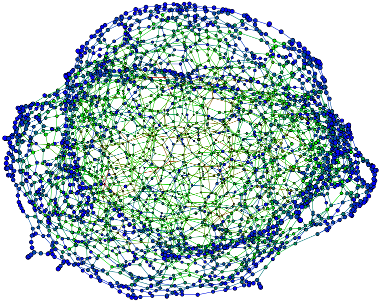
Betweenness centrality (node colors) and Eccentricity (node size)

$h = 40$

Hydrophobic Surface $k = 0.0$

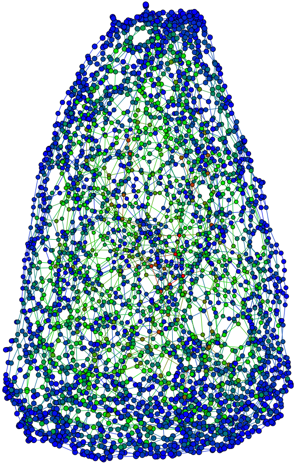


Hydrophilic Surface $k = 0.5$

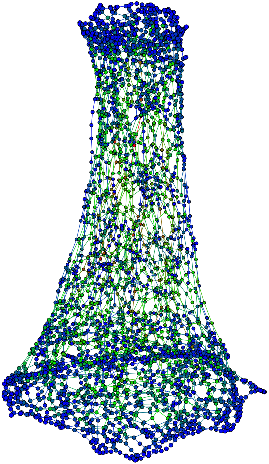


$h = 70$

Hydrophobic Surface $k = 0.0$

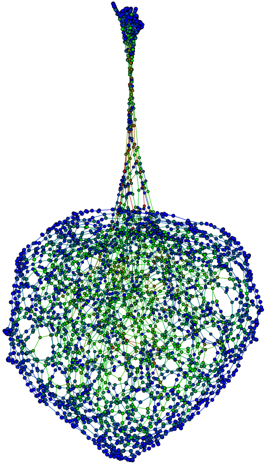


Hydrophilic Surface $k = 0.5$



$h = 75$

Hydrophilic Surface $k = 0.5$



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ChemNetworks: A Complex Network Analysis Tool for Chemical Systems

Abdullah Ozkanlar* and Aurora E. Clark*

Many intermolecular chemical interactions persist across length and timescales and can be considered to form a "network" or "graph." Obvious examples include the hydrogen bond networks formed by polar solvents such as water or alcohols. In fact, there are many similarities between intermolecular chemical networks like those formed by hydrogen bonding and the complex and distributed networks found in computer science. Contemporary network analyses are able to dissect the complex local and global changes that occur within the network over multiple time and length scales. This work discusses the *ChemNetworks* software, whose purpose is to process Cartesian coordinates of chemical systems into a network/graph formalism and apply topological network analyses that include network neighborhood, the determination of geodesic paths, the degree census, direct structural searches, and the distribution of defect states of network. These properties can help to understand the network patterns and organization that may influence physical properties and chemical reactivity. The focus of *ChemNetworks* is to quantitatively describe intermolecular chemical networks of entire systems at both the local and global levels and as a function of time. The code is highly general, capable of converting a wide variety of systems into a chemical network formalism, including complex solutions, liquid interfaces, or even self-assemblies.

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ChemNetworks

Deconstructing the Confinement Effect upon the Organization and Dynamics of Water in Hydrophobic Nanoporous Materials: Lessons Learned from Zeolites

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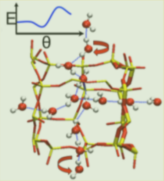
Supporting Information

ABSTRACT: The properties of confined water are relevant to many chemical, geological, and biological phenomena, where they underpin essential changes to molecular scale reactivity—perturbing both the energetic and configurational landscape. Though much prior literature has focused on hydrophilic confinement, the hydrophobic confinement of water is less well understood. Here, we use molecular dynamics simulations to investigate the structures and dynamics of water in hydrophobic all-silica zeolites that have sequentially smaller pore dimensions. Of special interest is the role that pure geometric restriction imparts, relative to the rugged potential energy landscape for water interacting with the atomistic pore surface. These two effects were studied via the hydrogen bond dynamics, specifically the rates and mechanisms of hydrogen bond breakage and formation. Measuring the dynamic features as a function of scaling the water:zeolite interaction energy revealed that geometric restriction is responsible for 67%−86% of the total perturbations to water upon confinement in MFI (depending on the property) while the water:surface interactions are responsible for 14%−33%. The relative magnitude of the interaction of water with the pore surface was confirmed by second order Møller−Plesset perturbation theory. Thus, in a highly confined environment, the weak water-surface interaction should not be neglected—even in hydrophobic adsorbents to which zeolites and other materials like carbon nanotubes belong.



Molecular Dynamics Simulations of Water Confined in Calcite Slit Pores: An NMR Spin Relaxation and Hydrogen Bond Analysis

Sylvia M. Mutisya,[†] Alexsandro Kirch,[‡] James M. de Almeida,[†] Verónica M. Sánchez,[†,§] and Caetano R. Miranda*,[‡]

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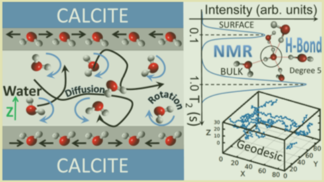

ABSTRACT: We study water confined in calcite (104) slit pores from 6 to 1 nm by molecular dynamics. By determining NMR parameters combined with hydrogen bond network analysis, we provide an important contribution to the understanding of the dynamics of water confined. The water dynamics was found uncorrelated upon confinement within calcite, with the translational dynamics highly dependent on the local density variations and the rotational dynamics varying with local hydrogen bond connectivity. A water layered structuring is observed, and the layer by layer analysis reveals that translational dynamics are the main contribution to spin relaxation of near surface water molecules. The T_2 relaxation time for water molecules directly hydrogen bonded to the surface is short and pore size independent; however, a bulk-like spin relaxation is observed at the center of pores larger than 3 nm. The hydrogen bond network of confined water has a more continuous path topology that results in the slightly longer rotational correlation time for water located up to 2 nm from the surface. Moreover, the number of tetrahedral geometric patterns which are associated with bulk water is reduced upon confinement. The confinement effects are enhanced mainly in the 1 nm pore due to overlap of surface effects.

ChemNetworks

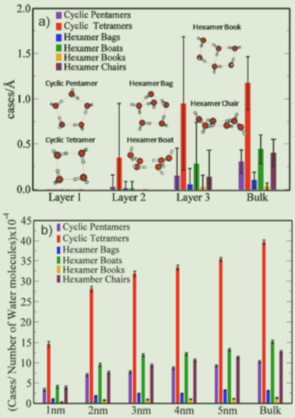

Figure 8. (a) Geometric pattern distribution within each layer for 1 nm water confinement. (The geometric pattern illustrations are adopted from ref 51.) Similar results were obtained for all the pores analyzed in this work. (b) Geometric pattern distribution in each pore in comparison to bulk water. The 6 nm pore system was not investigated because of the computational cost, but a similar trend is expected. Error bars represent standard errors.