

# Influence of nanoscale porosity on fluid behavior

D.R. Cole, M.S. Gruszkiewicz, J.M. Simonson, A.A. Chialvo, Y.B. Melnichenko,  
G.D. Wignall, G.W. Lynn, J.S. Lin, A. Habenschuss, B. Gu, K.L. More, T.D. Burchell  
*Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA*

A. Striolo, Y. Leng, P.T. Cummings  
*Vanderbilt University, Nashville, TN 37235 USA*

W.T. Cooper, M. Schilling  
*Florida State University, Tallahassee, FL 32306 USA*

K.E. Gubbins  
*North Carolina State University, Raleigh, NC 27695 USA*

H. Frielinghaus  
*Institut für Festkörperforschung, Jülich, Germany*

**ABSTRACT:** Fluids including hydrocarbons, aqueous solutions, and gaseous species (e.g. CO<sub>2</sub>, CH<sub>4</sub>) can occupy the pores or fractures within solid matrices. The size, distribution and connectivity of these confined geometries, the chemistry of the solid, the chemistry of the fluids and their physical properties collectively dictate how fluids migrate into and through these micro- and nano-environments, wet and ultimately react with the solid surfaces. The purpose of this project is to demonstrate the application of state-of-the-art experimental, analytical and computational tools to assess key features of the fluid-matrix interaction. Our multidisciplinary approach combines neutron and X-ray scattering experiments, FTIR and NMR spectroscopy, molecular dynamics simulations, and thermodynamic measurements to quantitatively assess molecular properties of fluids confined to well-characterized porous media, subjected to a wide range of experimental conditions. These studies are providing a molecular-level understanding of how intrinsically different fluids behave in confined geometries compared to bulk systems.

## 1 INTRODUCTION

Fluids containing inorganic and organic solutes (including hydrocarbons) and gaseous species (e.g. CO<sub>2</sub>, CH<sub>4</sub>) can occupy the pores or fractures of numerous types of complex heterogeneous solids. The porosity (void) volumes within the solids span wide length scales including micro-, meso- and macroporous regimes ( $d/\text{Å} < 20$ ,  $20 < d/\text{Å} < 500$ , and  $d/\text{Å} > 500$ , respectively, as defined by IUPAC). These solid materials include such practical systems as supported catalysts, ceramics and composites, glasses, rock, soil, and bone. A number of factors dictate how fluids, and with them reactants and products of intra-pore transformations, migrate into and through these nano-environments, wet and ultimately adsorb and react with the solid surfaces. These include the size, shape, distribution and interconnectivity of these confined geometries, the chemistry of the solid, the chemistry of the fluids and their physical properties (Cole & Chakraborty, 2001). The dynamical behavior of fluids and gases contained within solids is controlled by processes occurring at the interface between the various phases (e.g. water-water, water-solute, water-solid, solute-solid etc.), as well as the rates of supply and removal of mobile constituents. The richness and complexity of fluid behavior (e.g., phase transitions, molecular orientation and relaxation, diffusion, adsorption,

wetting, capillary condensation, etc.) in confined geometries only underscores the need to adopt a multidisciplinary approach when trying to quantify this behavior regardless of the fluid type or nature of the porous medium. If properly calibrated and scaled, an atomistic or molecular understanding of fluid-solid interaction may provide quantitative insight into the behavior of systems at the macroscopic level.

## 2 APPROACH

There is general agreement that the collective structure and properties of bulk fluids are altered by confinement between two surfaces or in narrow pores due to the interplay of the intrinsic length scales of the fluid and the length scale due to confinement (Idziak & Li, 1998). Also crucial to the molecular behavior of fluids is the geometry of the pore which can include simple planar walls as encountered in micas; slits, cylinders, and spheres; and spheres linked with cylinders as observed in zeolites (Alejandro et al. 1996). Other factors that contribute to the modification of fluid properties include the randomness of the matrix and the connectivity of the pore network (Pitard et al. 1996).

In order to assess key features of the fluid-matrix interaction at the nanoscale, a multidisciplinary

nary approach was taken that addressed the following areas:

(a) Characterization of the physical nature (e.g. size, shape, fractal geometry, etc.) of the pores using various types of microscopy (SEM; TEM), scattering (small-angle X-ray and neutron), and gas sorption methods, (b) Determine the thermodynamic properties of water in confined geometries using the isopiestic method over a wide ranges of temperature and pressure. (c) Determine the local short-duration dynamics and longer-scale hindered motion of water, CO<sub>2</sub> and hydrocarbons through use of complementary techniques including neutron scattering, NMR, and FTIR spectroscopy, as a function of pressure and temperature. (d) Apply, refine and, where necessary, develop molecular-based simulations methods that describe the properties and structure of confined fluids. Selected aspects of these activities are highlighted below.

### 3 SOLIDS CHARACTERIZATION

The physical characterization of solids is a crucial step that sets the stage for how variations in pore size, roughness, distribution, connectivity, composition (hydrophobic versus hydrophilic), surface charge, and structure (i.e. crystalline versus amorphous) influence molecular behavior of confined fluids. Table 1 summarizes the different porous solids selected for experimentation and/or modeling, their pore shapes and widths, and surface chemistry.

Table 1. Porous solids used in experiments and modeling.

Solid Widths	Surface	Pore Shapes	Pore (nm)
Porous glass	O, Si	Cylinder	2 - 8
Silica sol-gels	O, Si	Cylinder	2.5 - 20
Silica aerogel	O, Si	Irreg. cyl.	6 - 7
Activated C fibers	C (O, H)	Varied	0.4 - 1.0
C nanotubes	C (O, H)	Cylinder	1.0 - 1.6
Na-K Zeolites	K, Na, Si, Al, O	Cylinder, cage	0.3 - 0.8
Montmorillonite	Na, Si, Al, O	Slit, pillars	0.5 - 0.8
Muscovite (2M1)	K, Si, Al, O	Slit	0.6 - 1.0

The solids we selected for study exhibit many of the following characteristics: (a) sparingly soluble at the pressure-temperature-fluid composition conditions of the experiments, (b) suitable for detailed characterization of pore features such as size, shape, distribution, roughness, etc., (c) susceptible to chemical manipulation from hydrophobic to hydrophilic by chemical pretreatments, and (d) limited crystallinity to minimize the impact on small-angle scattering. In addition to the more conventional methods typically used to characterize porous matrices (SEM, TEM), we used a number of scattering and spectroscopic techniques. While not yielding di-

rect imaging information, scattering and diffraction experiments can provide global statistical information about interfaces (e.g. total porosity, pore surface area, pore length scale, skeletal density, fractality) over an enormous range of length scales (Å to μm), represented by reciprocal or Q-space (where  $Q = 4\pi\lambda^{-1}\sin\theta$  is the momentum transfer,  $2\theta$  is the angle of scattering, and  $\lambda$  is the wavelength). The scattering intensity,  $I(Q)$ , is measured as a function of momentum transfer, and exploits the difference in scattering power (contrast) between the solid matrix, and air or fluid occupying the pore space.

An example of results from small-angle neutron scattering (SANS) is shown in Figure 1 for three different porous silica sol-gel glasses. This plot reveals that the correlation peaks (vertical arrows) shift to successively longer distances, which is indicative of variations in the dehydration process designed to produce the different pore sizes. The glass with 75 Å pores yields the minimal excess scattering in the small-angle region, which makes it better suited for studying the influence of confinement on liquid-gas critical behavior. For the most part, the disordered porous silica glasses have rather smooth pores that are uniformly distributed throughout the solid. The porous carbons have more wide-ranging pore sizes, and exhibit varying degrees of crystallinity depending on the temperature of burn-off and its duration used to activate the solid.

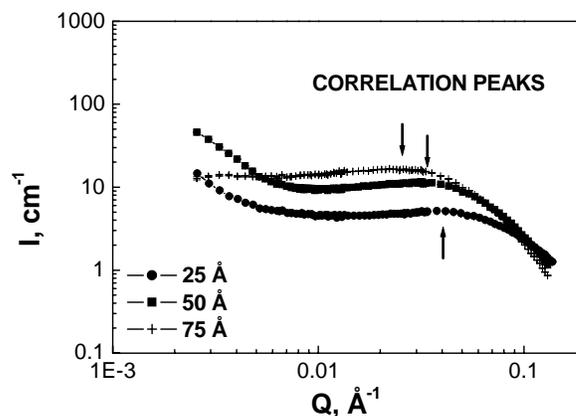


Figure 1. SANS from various silica sol-gel glasses.

### 4 WATER SORPTION

The total adsorption capacity of a porous or fractured solid matrix depends on the total exposed solid surface area, the shape and size distribution of voids in the matrix, and the nature of the interaction between fluid molecules and the solid surface, and between the molecules themselves. The competition between liquid-solid and liquid-liquid interactions leads to monolayer and cluster formation at low pressure, and capillary condensation at high pressures. In order to understand these effects in a fluid with strong intermolecular interactions, adsorp-

tion/desorption isotherms of water were measured for 15 solid samples (e.g., porous silica, carbon monoliths, zeolites, clay) at 105, 150, and 200°C from vacuum to saturated vapor pressure in an isopiestic apparatus. This apparatus is unique in its capability for precise weighing of samples at elevated temperature and pressure between vacuum and 4 MPa. This gravimetric method, in contrast to the more common volumetric techniques, allows for continuous monitoring of the changes of the adsorbent itself due to degassing, oxidation, or decomposition (Gruszkiewicz et al. 2001).

Figure 2 shows representative water sorption results at 105°C from vacuum to saturated vapor pressure (0.121 MPa) for several of the porous solids. At low pressure the isotherms reflect competition between liquid-solid and liquid-liquid interactions (forming the monolayer and subsequent clusters or layers, pore filling). The behavior at higher pressures reflects the impact pore size and structure have on capillary condensation and possible hysteresis.

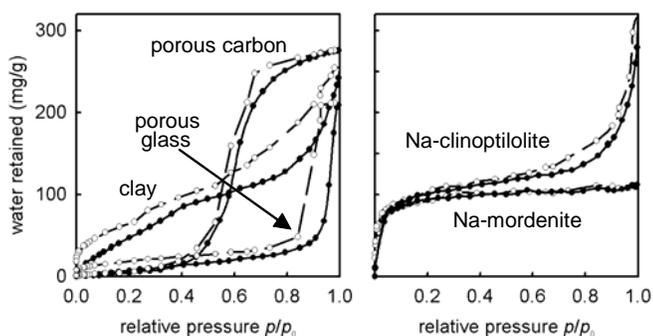


Figure 2. Adsorption (solid) and desorption (dashed) isotherms of water measured for a variety of porous solids at 105°C.

Both zeolites exhibit very steep isotherms at low pressure followed by relatively flat trends at moderate to high pressures. This behavior is indicative of strong water-solid intermolecular interaction dominated by mono-layering. The porous carbon and silica glass have rather flat slopes at low pressure followed by steep trajectories indicating weak water-solid interaction and capillary pore filling. The montmorillonite exhibits a steady increase in water uptake suggestive of multi-layering characteristic of dipolar electrostatic interaction. Results such as these can form the basis of testing various MD simulation schemes.

## 5 FLUID STRUCTURE AND DYNAMICS

Confinement in porous media leads to perturbation of structures and motion of molecules such as water. Properties affected include vibrational, rotational and translational motion, adsorption/condensation, phase equilibria, critical phenomena, and hydrogen bonding. Because molecular motion and structure

occur over widely different time and length scales, respectively, we used a number of complementary techniques to address molecular behavior in a variety of systems: (a) water and electrolytes (LiCl, CaCl<sub>2</sub>, NdCl<sub>3</sub>) in porous silica glass using QENS, (b) water, chloroform and soil organic matter in porous silica glass with NMR, (c) CO<sub>2</sub> phase behavior and critical phenomena in silica aerogel using SANS, (d) and water and aniline in montmorillonite with FTIR. One example of this effort is discussed below.

Phase transitions can be significantly modified by confinement and disorder. The liquid-vapor behavior in porous systems with quench disorder, such as aerogels, is of particular interest because it may provide an experimental test of which theoretical model best describes critical phenomena in confined fluids. Currently, there are two competing theoretical models – the Random Field Ising model and the “single pore” model (Melnichenko et al, in press). The experimental efforts to verify the validity of the models for confined binary liquid solutions have been obscured by experimental complications caused by the local composition gradients in pores as well as sluggish kinetics in the liquid-liquid region. SANS is particularly well suited to study the critical phenomena in small pores due to a short wavelength of neutron radiation (~ several Å), which allows for extracting information on the correlation length of the order of a nanometer and higher. In our experiments silica aerogel (~96% porosity) was filled with CO<sub>2</sub> at different temperatures and pressures appropriate for bracketing the critical region. SANS measurements (Fig. 3) of the correlation length of the density fluctuations ( $\xi$ ) indicate that quench disorder works to suppress density fluctuations in the critical region. The correlation length does not exceed the characteristic pore size which provides strong evidence in favor of the single pore model (Melnichenko et al., in press).

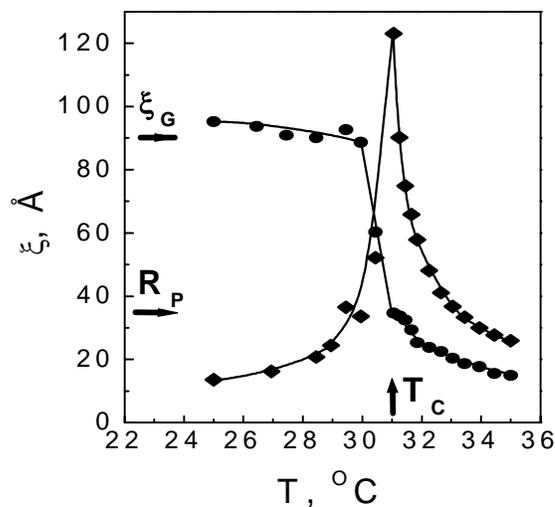


Figure 3. Correlation length of density fluctuations of CO<sub>2</sub> for bulk (♦) and confinement (●).  $R_p$  = pore radius,  $\xi_G$  = aerogel correlation length,  $T_c$  = critical temperature.

## 6 SIMULATION STUDIES

Experimental information determined from characterization of the porous media, adsorption-desorption isotherms, and scattering and spectroscopic assessments of fluids at different length and time scales provide crucial synergistic input to molecular-based simulations. Our efforts have focused on the behavior of water in two very different solids, porous carbons and muscovite. In the former we used the SPC/E model for water, whereas in the latter we used TIP4P. The grand canonical Monte Carlo method (GCMC) was used to simulate water in carbon-slit pores with widths of 0.6, 1.0 and 1.6 nm and in single-walled carbon nanotubes with diameters of 1.36 and 1.63 nm in the temperature range 298-530K. A comparison of experimental sorption results (Fig. 2) and the simulations (Fig. 4) indicates that because of a competition between strong water-water and weak water-carbon interactions, adsorption isotherms are characterized by negligible uptake at low pressures, by pore filling following a capillary-like condensation mechanism, and by adsorption/desorption hysteresis loops. As temperature increases, the relative pressure at which pore filling occurs increases and the size of the hysteresis loops decreases.

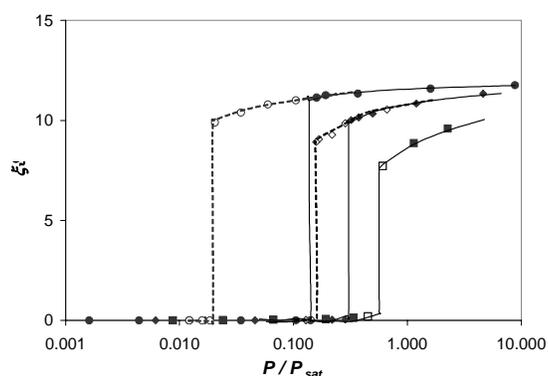


Figure 4. GCMC results for SPC/E water in 1.0 nm wide slit-carbon pores. The number of adsorbed water molecules per  $\text{nm}^2$  of porous surface,  $\xi$ , is plotted as a function of reduced water,  $P/P_{\text{sat}}$ . Circles: 298K, diamonds: 373K, squares: 473K, solid: adsorption, open: desorption. (Striolo et al., in press).

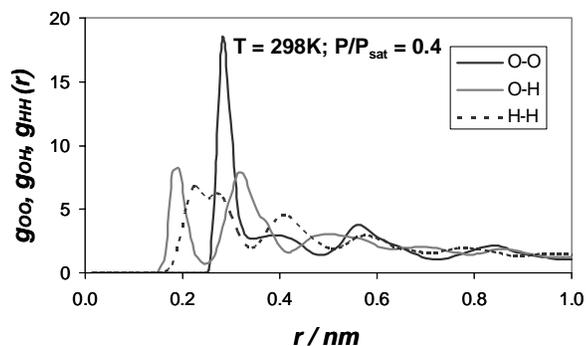


Figure 5. In-plane O-O, O-H, and H-H radial distribution functions (RDF) for SPC/E water in 0.8nm carbon slit-pores.

Differences between simulated and experimental results are primarily due to heterogeneous chemical composition (O, H in C fibers), pore connectivity, and non-uniform pore-size distribution, which are not accounted for in the simulation models. Water confined to 0.8-1nm slit pores undergoes a disorder-to-order transition at  $P$  lower than saturation at 298K. The in-plane RDFs (Fig. 5) suggest the formation of a peculiar structure characterized by long-range spatial correlations.

## 7 SUMMARY

A multidisciplinary, multi-institutional effort has addressed a number of key issues relevant to water/solid interaction at the nanoscale. Contributions have been made in the characterization of numerous complex nanoporous solids with a variety of techniques including neutron scattering. Advanced sorption, scattering and spectroscopic methods have documented the behavior of water and  $\text{CO}_2$  in confined geometries. MD simulations have provided the theoretical underpinning of the experimental results.

## 8 REFERENCES

- Alejandre, J., Lozada-Cassou, M. & Degreve, L. 1996. Effect of pore geometry on a confined hard sphere fluid. *Molec. Phys.* **88**: 1317-1336.
- Cole, D. R. & Chakraborty, S. 2001. Rates and mechanisms of isotopic exchange. In J. W. Valley, J. W. and D. R. Cole (eds), *Stable Isotope Geochemistry, Rev. Min. Geochem.* **44**: 84-223.
- Gruszkiewicz, M. S., Horita, J., Simonson, J. M., Mesmer, R. E. & Hulen, J. B. 2001. Water adsorption at high temperature on core samples from the Geysers geothermal field, California, USA. *Geothermics* **30**: 269-302.
- Idziak, S. H. J & Li, Y. 1998. Scattering studies of complex fluids in confinement. *Curr. Opin. Colloid Interface Sci.* 293-298.
- Melnichenko, Y. B., Wignall, G. D., Cole, D. R., & Frielinghaus, H. in press. Density fluctuations near the liquid-gas critical point of a confined fluid. *Phys. Rev. E*.
- Pitard, E., Rosinberg, M. L. & Tarjus, G. 1996. Thermodynamics of fluids in disordered porous materials. *Molec. Sim.* **17**: 399-419.
- Striolo, A., Gubbins, K. E., Gruszkiewicz, Cole. D. R., Simonson, J. M., Chialvo, A. A., Cummings, P. T., Burchell, T. D. & More, K. L. in press. Effect of temperature on water adsorption in porous carbons. *Fluid Phase Equil.*

Sponsored by Laboratory Directed Research and Development Program (ORNL) and the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U. S. DOE under contract DE-AC05-00OR22725, Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.