

# Liquids confined in nanopores; Novel ice structures - Pressure Enhancement Effects

MALGORZATA SLIWINSKA-BARTKOWIAK<sup>1</sup>, KAMILA DOMIN<sup>1</sup>, KWONG-YU CHAN<sup>1</sup>

YUN LONG<sup>3</sup> and KEITH E. GUBBINS<sup>4</sup>

<sup>1</sup> Faculty of Physics, Adam Mickiewicz University, Poznan 61-614, Poland  
msb@amu.edu.pl

<sup>2</sup> Department of Chemistry, Hong-Kong University, Pokfulam Road, Hong Kong

<sup>3</sup> Department of Chemical & Biomolecular Engineering, National University of Singapore, Singapore 117585

<sup>4</sup> Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, USA

## ABSTRACT

Phenomena that occur only at very high pressures in the bulk phase are often observed to occur in the confined phase at normal pressures (the pressure of the bulk phase in equilibrium with the confined phase). Abundant experimental evidence suggests that adsorbates confined in nanoporous materials exhibit high pressures, such as high pressure crystal structures, high pressure chemical reactions, and the deformation of pore walls due to the adsorbate. Also molecular simulation studies of the pressure tensor for simple adsorbates in carbon nanopores of slit, cylindrical and spherical geometries show that for modest bulk phase pressures, the pressure normal to the wall is of the order of hundreds of MPa, and can be positive or negative depending on the pore size [1]. The ice structures experimentally observed in nanopores are typical for high pressures ice.

We report X-ray diffraction studies of water and carbon tetrachloride adsorbed in nanoporous activated carbon fibres (ACFs) and CMK-3 carbon mesopores of different pore sizes. The fibres are built of turbostratic nanoparticles separated by quasi two-dimensional voids, forming narrow slit-shaped pores; CMK-3 are the reverse carbon replica of silica SBA-15 porous matrices. In order to determine the structure of water within the pores and its influence on the fibres' structure, mean interatomic and intermolecular distances have been estimated from the positions of the maxima of the normalized angular distribution functions obtained by X-ray diffraction [1]. We observe significant changes in the interlayer distance of the carbon nanoparticles; the results suggest that very high pressures arise within the pores, about a few hundred MPa, as has been observed in molecular simulations [1,2]. Such a results are confirmed by observation of high pressure forms of ice in cylindrical nanocarbons, using neutron and X-ray diffraction methods [3]. For water in multiwalled carbon nanotubes (MWCN), below the pore melting point the existence of cubic ice was observed. This kind of ice structure can be obtained during re-crystallisation from high pressure phases at low temperatures for bulk water. For CMK-3 mesopores we observe the existence of a stacking-disordered ice [4,5],  $I_{sd}$ . This metastable ice is neither cubic nor hexagonal, and is not a simple mixture of the two, but a combination of cubic sequences intertwined with hexagonal sequences. Moreover, the stacking disorder may vary in complexity depending on the way the ice is formed and on the prevailing thermal conditions during this process. The analysis of the kind of  $I_{sd}$  formed in CMK-3 of different pore size will be presented. These crystal forms, which occur in bulk water only at temperatures below 180 K in the case of cubic ice, and at pressures of hundreds or thousands MPa are stabilized by the confinement.

## References

- [1] M.Sliwinska-Bartkowiak, M.Drozdowski, M.Jazdzewska, Y.Long, J.Palmer, K.E.Gubbins, *Phys. Chem. Chem. Phys.*, **14**, 7145, (2012)
- [2] Y. Long, J.Palmer, B.Coasne, M.Sliwinska-Bartkowiak, K.E.Gubbins, *Phys. Chem. Chem. Phys.*, **13**, 17163 (2011) 17163; Y. Long at al, *Microporous and Mesoporous Materials* **154**, 19-23 (2013).
- [3] M.Jazdzewska, M. Sliwinska-Bartkowiak, A.I. Beskrovnyy, S.G. Vasilovskiy, S.W. Ting, K.Y. Chan, L.L. Huang, K.E. Gubbins, *Phys. Chem. Chem. Phys.*, **13**, 9008 (2011).
- [4] Malkin, T. L., Murray, B. J., Salzmann, C., Molinero, V., Pickering, S. J., & Whale, T. F. *Phys. Chem. Chem. Phys.*, **17**, 60-76 (2014).
- [5] K. Domin, M.Sliwinska – Bartkowiak, K. Y. Chan, Hoi Yung, K.E.Gubbins, M. Jarek; *in press*.