Structure and Dynamics of Glycerol in Gamma-Alumina Nano-pores
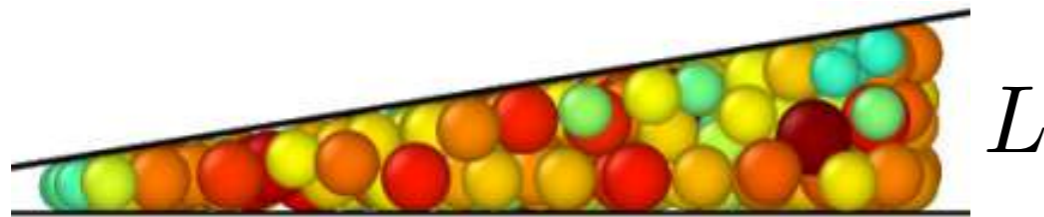
G. Campos-Villalobos

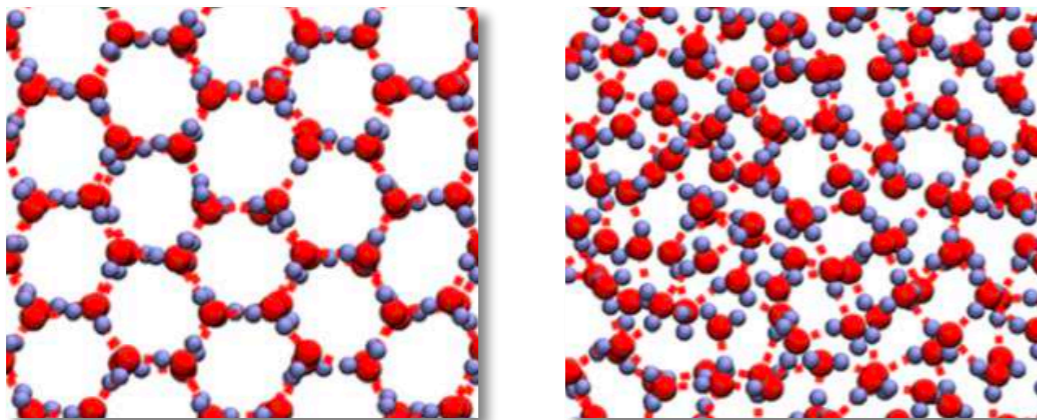# ...or why glycerol can move faster under confinement?

G. Campos-Villalobos

The Classical Picture of Confined Liquids
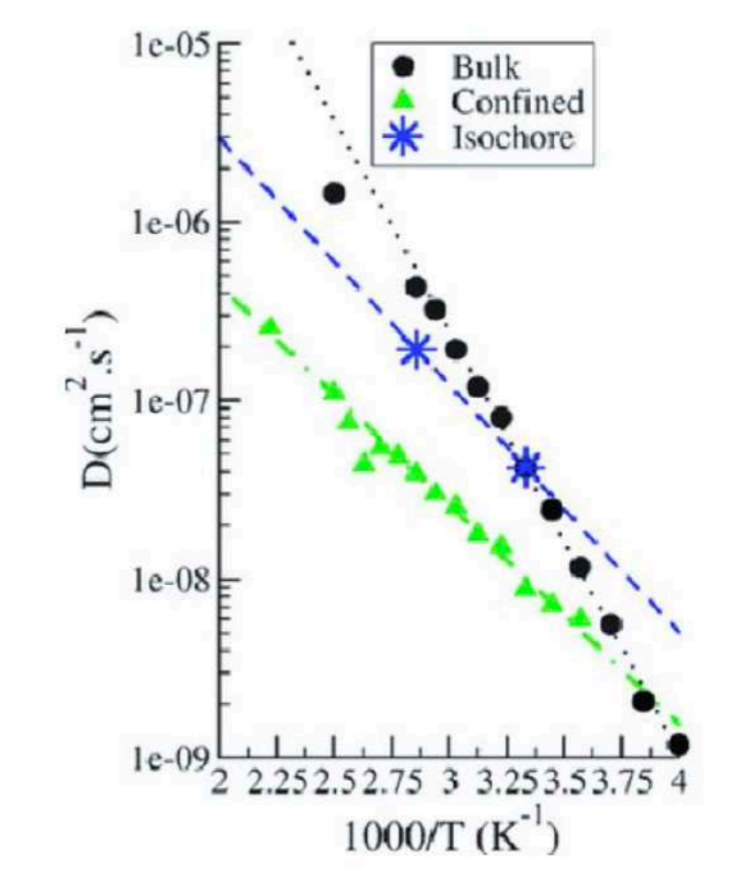
The equilibrium and transport properties of liquids geometrically confined in nano-sized pores are dramatically different to those in the bulk state
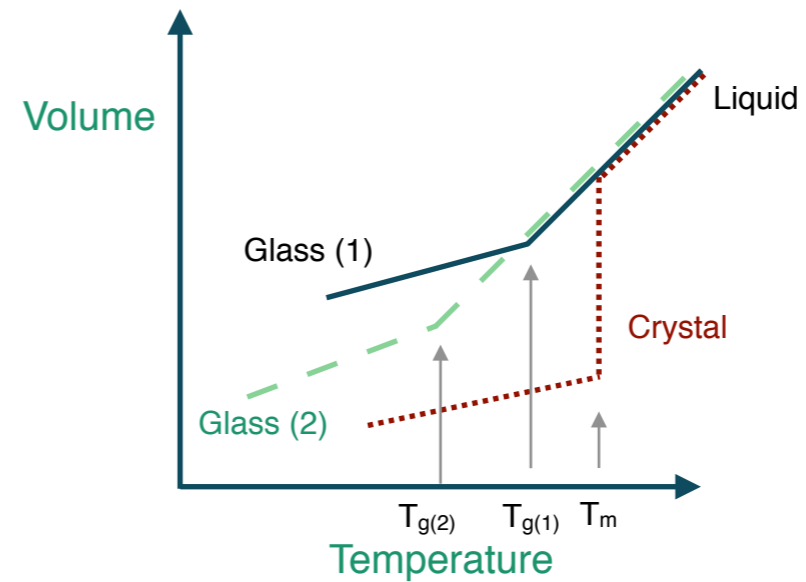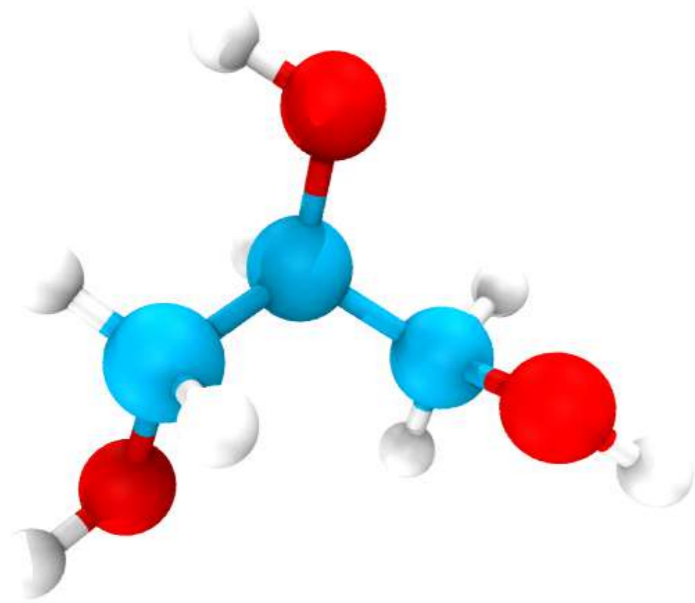

L

Low mobility

Phase Transitions
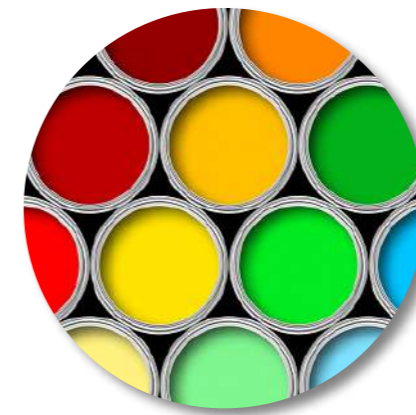
The Curious Case of Glycerol

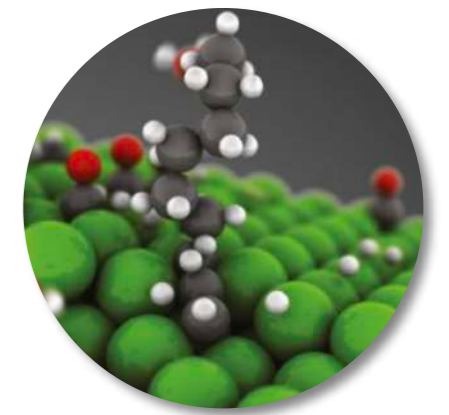Glycerol is a glass-former

Cometics

Bio-Inks

Heterogeneous Catalysis

The Curious Case of Glycerol

Confinement induces both higher free volume and lower molecular mobility in glycerol

Duncan Kilburn[a] and Paul E. Sokol
Indiana University Cyclotron Facility, 2401 Milo B. Sampson Lane, Bloomington, Indiana 47408, USA
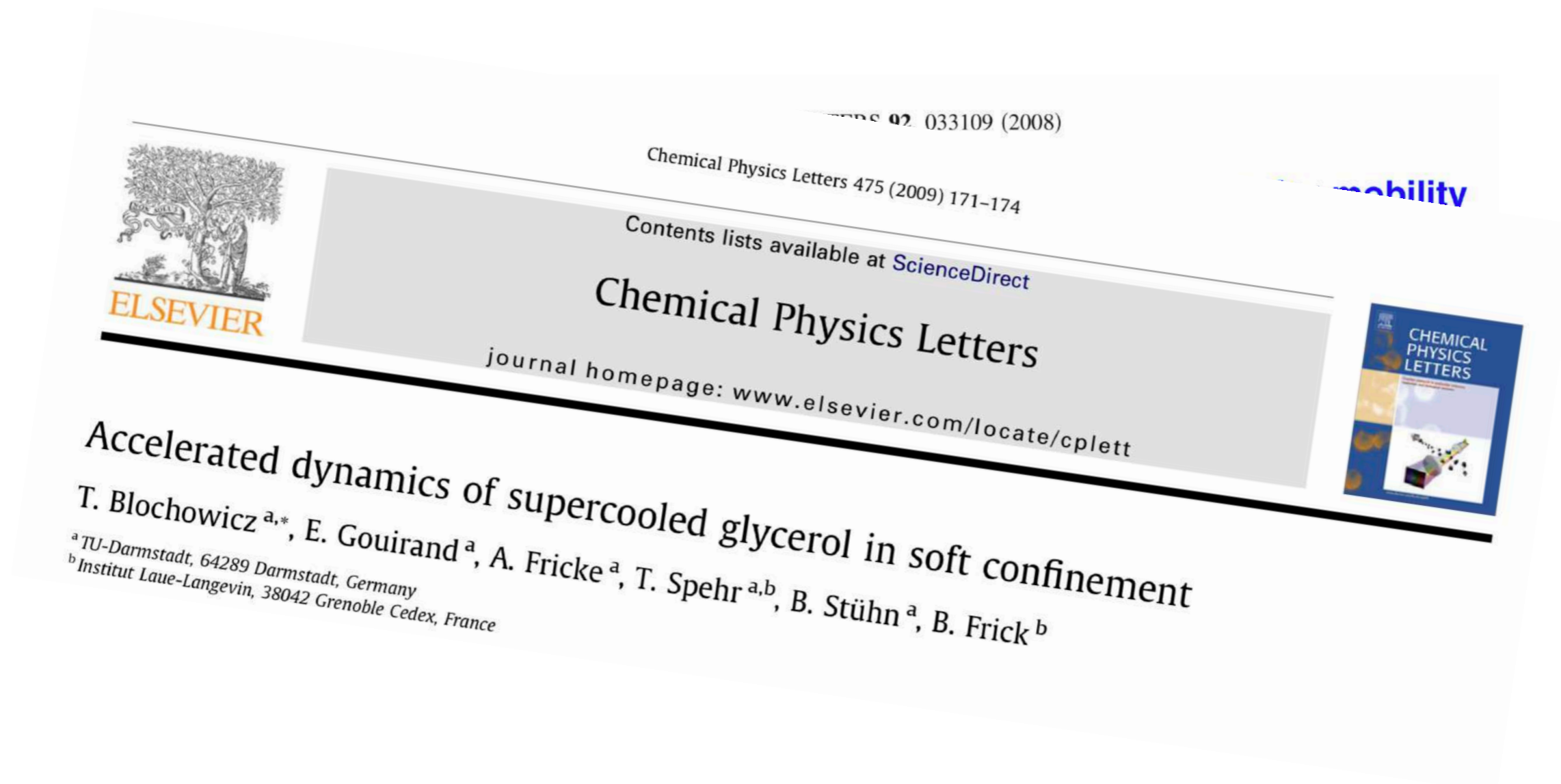
Victoria García Sakai[b]
NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562, USA and Department of Materials Science and Engineering, University of Maryland College Park, Maryland 20742, USA

M. Ashraf Alam
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom
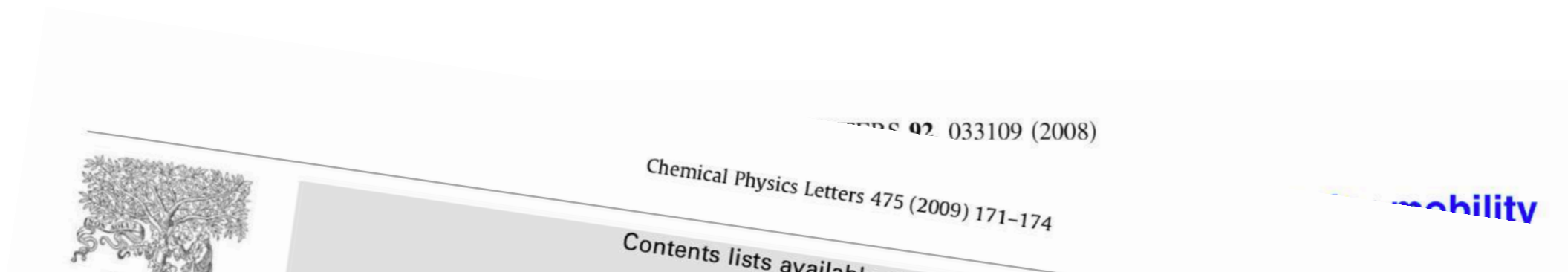
The Curious Case of Glycerol

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Chemical Physics Letters 475 (2009) 171–174

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Accelerated dynamics of supercooled glycerol in soft confinement

T. Blochowicz [a,*], E. Gouirand [a], A. Fricke [a], T. Spehr [a,b], B. Stühn [a], B. Frick [b]

[a] TU-Darmstadt, 64289 Darmstadt, Germany
[b] Institut Laue-Langevin, 38042 Grenoble Cedex, France

The Curious Case of Glycerol

PRS 92 033109 (2008)

Chemical Physics Letters 475 (2009) 171–174

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Hydrogen Bonding Network Disruption in Mesoporous Catalyst Supports Probed by PFG-NMR Diffusometry and NMR Relaxometry

Carmine D'Agostino, Jonathan Mitchell, Lynn F. Gladden, and Mick D. Mantle*

Department of Chemical Engineering & Biotechnology, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, U.K.

The Curious Case of Glycerol

Hydrogen Bonding Netwo... ...Disruption ...Mesoporous Catalyst Supports Probed by PFG-NM... ...etry and NMR Relaxometry

Carmine D'Agostino, Jonathan Mitchell, Lynn F. Gladden, and Mick D. Mantle*

Department of Chemical Engineering & Biotechnology, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, U.K.

MANCHESTER
1824

The University of Manchester

Model Systems
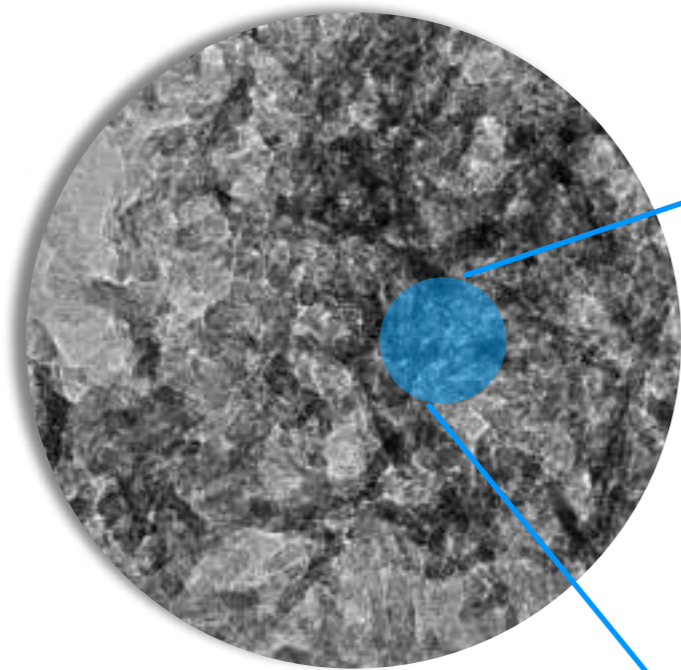
Glycerol in Gamma-Alumina

Gamma-Alumina

{100} hydroxylated facet exposed to the liquid. CLAYFF force-field

l_c

Glycerol

OPLS-AA
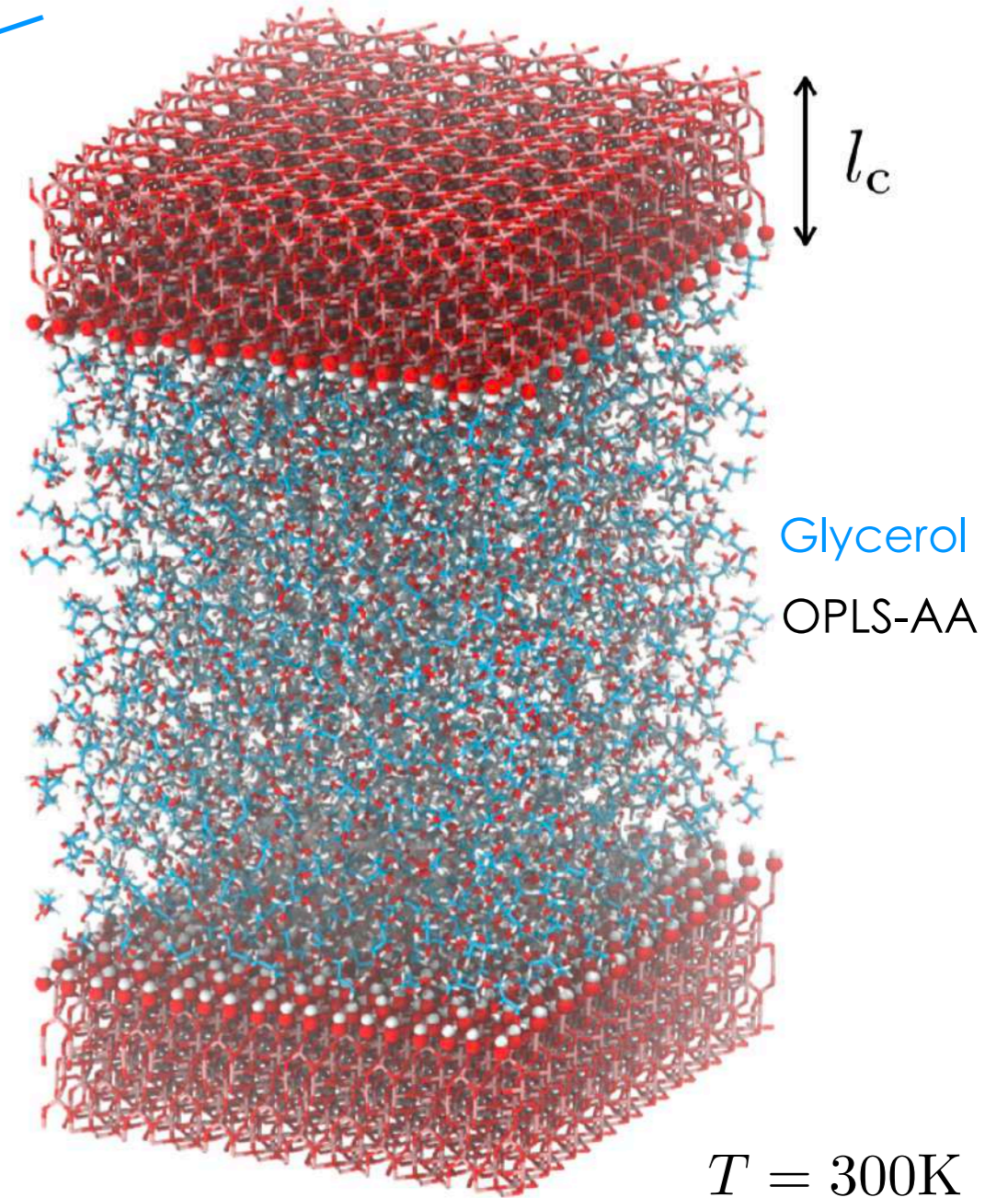
Pore size l_z

$$\rho_{\mathrm{conf}} = \frac{M_{\mathrm{glycerol}}}{V_{\mathrm{pore}}}$$

A measure of the pore saturation

$T = 300\mathrm{K}$
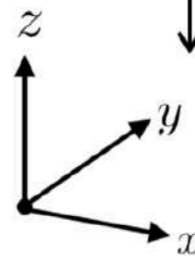
Order and Symmetry Breaking at Interfaces

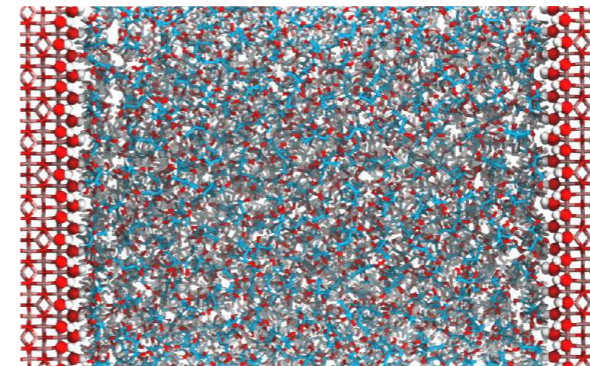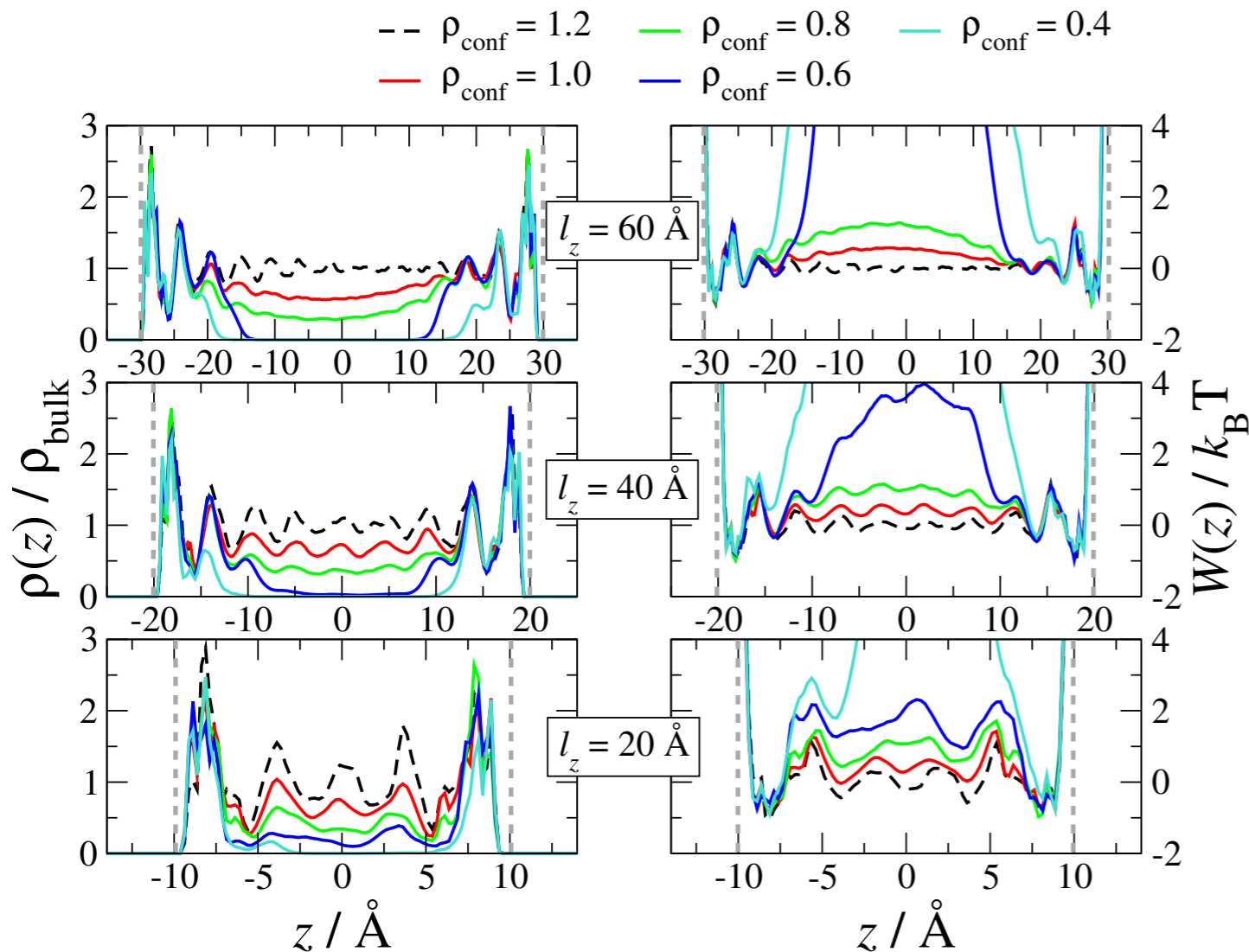Reduction of Pore Saturation ρ_{conf}
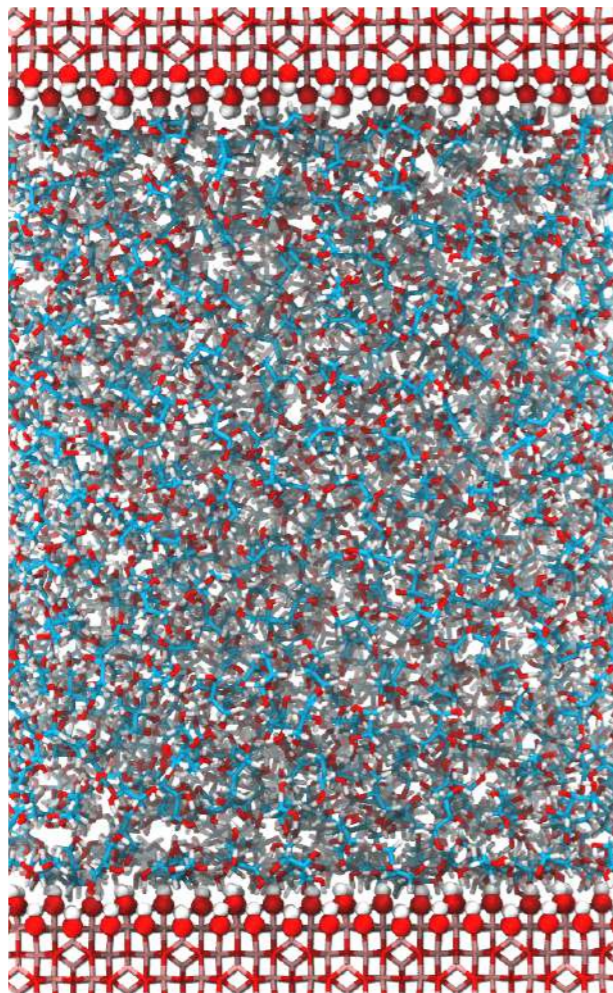
Fully saturated pore
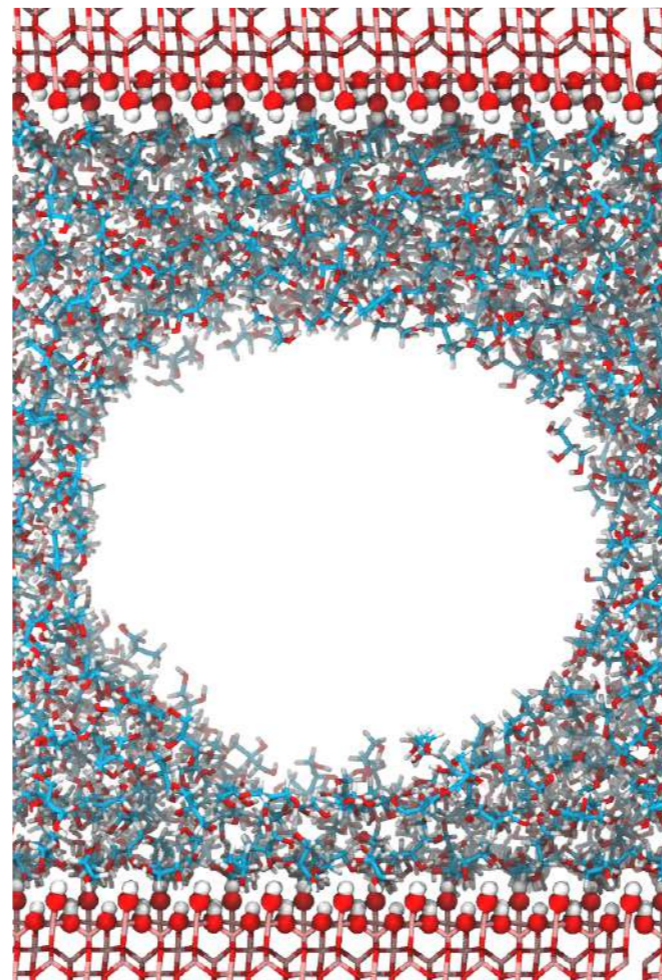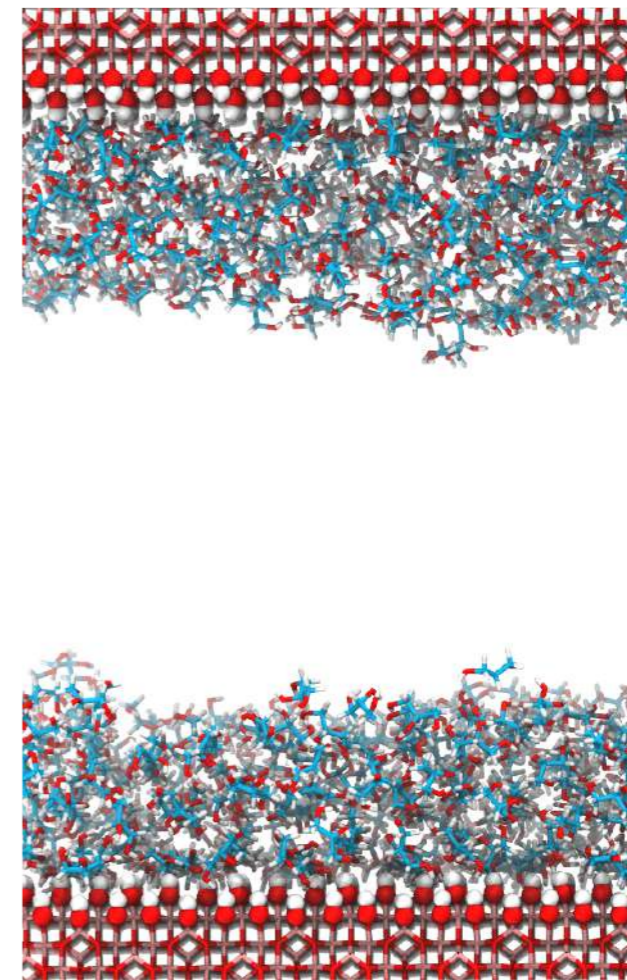
Bubble

Adsorbed liquid films

Order and Symmetry Breaking at Interfaces

Formation of discrete molecular layers close to the surface
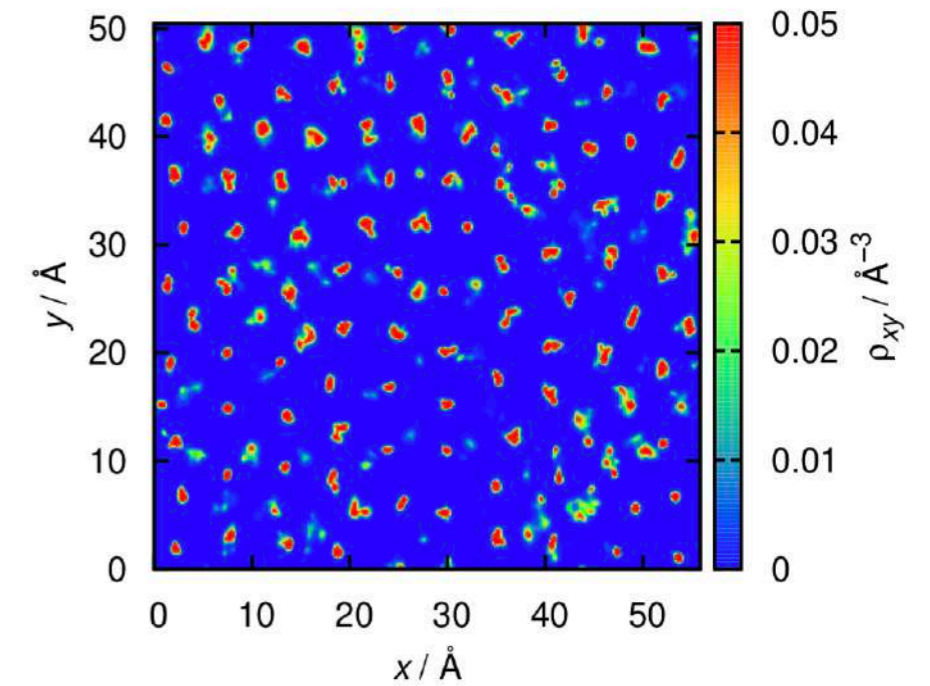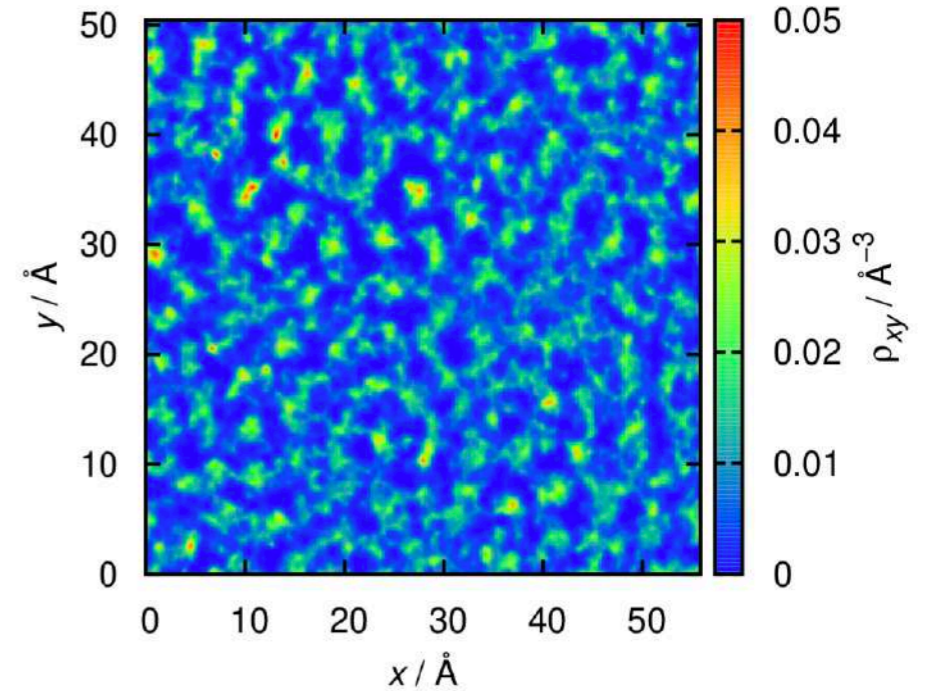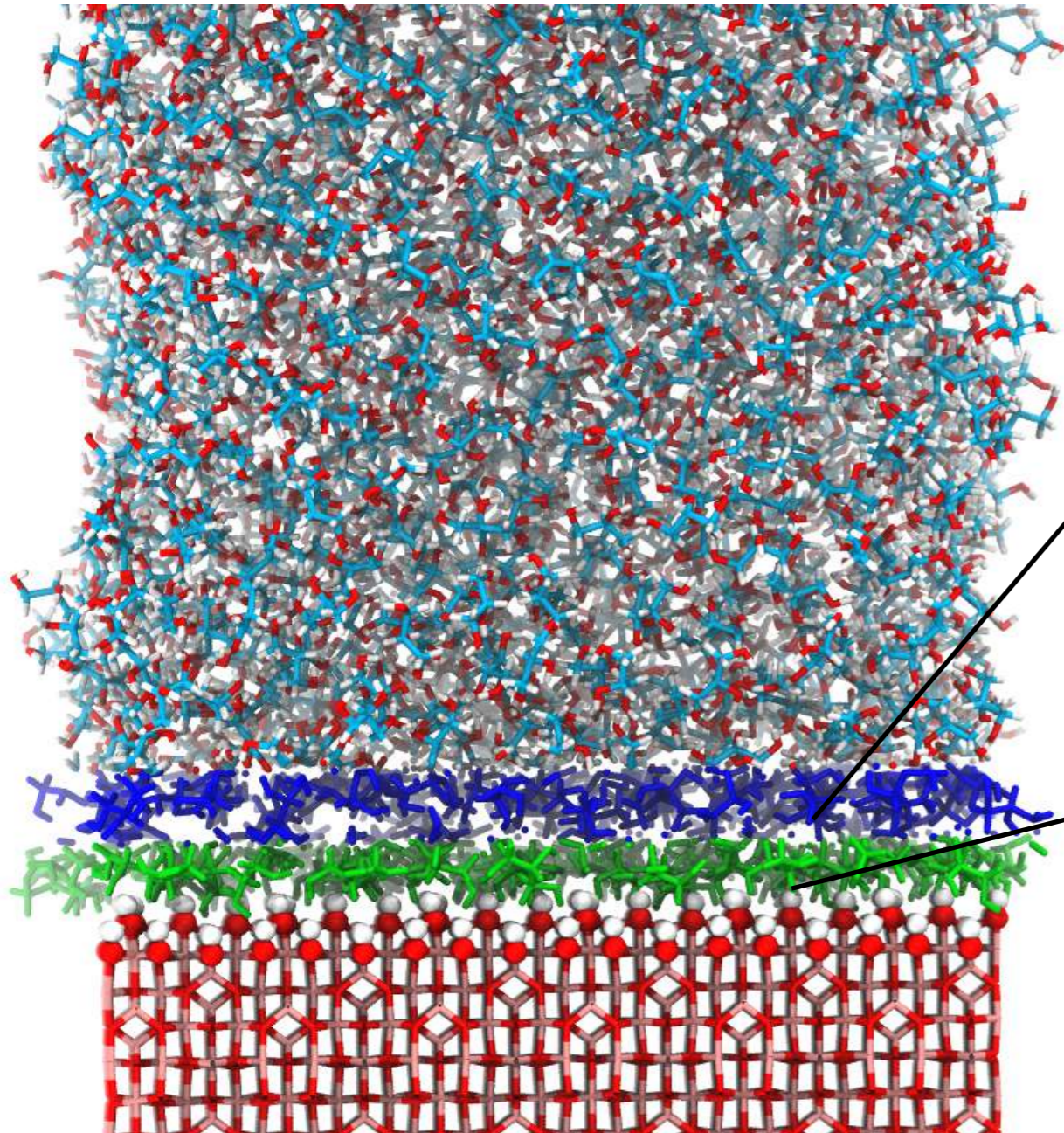

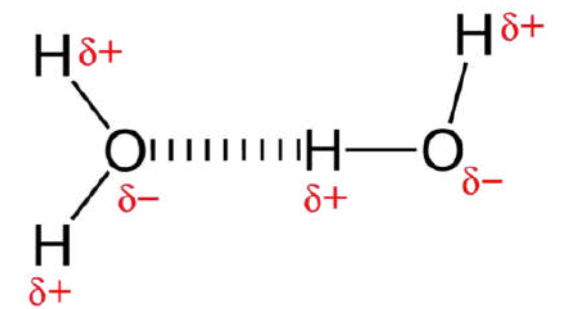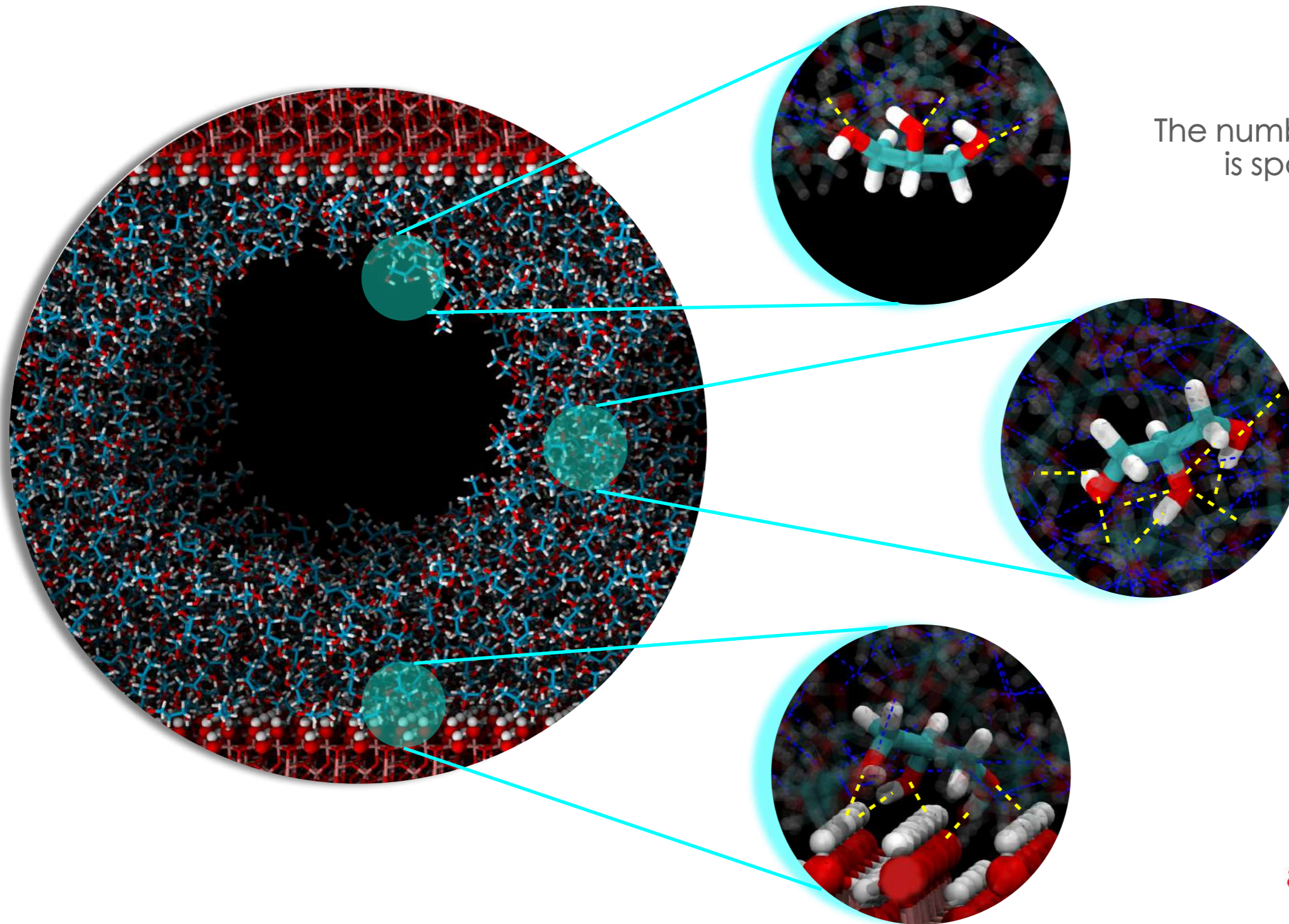Fully saturated pore
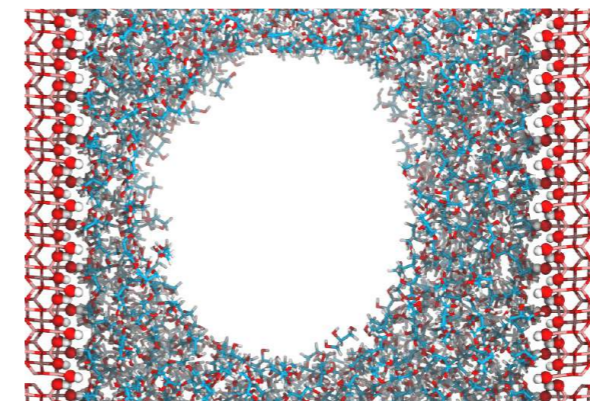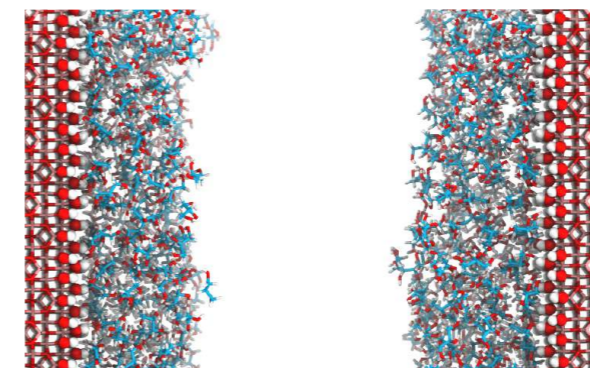
Bubble

Adsorbed liquid films

Order and Symmetry Breaking at Interfaces

In-plane ordering

Interfacial Effects

The number of HB per molecule is spatially-dependent
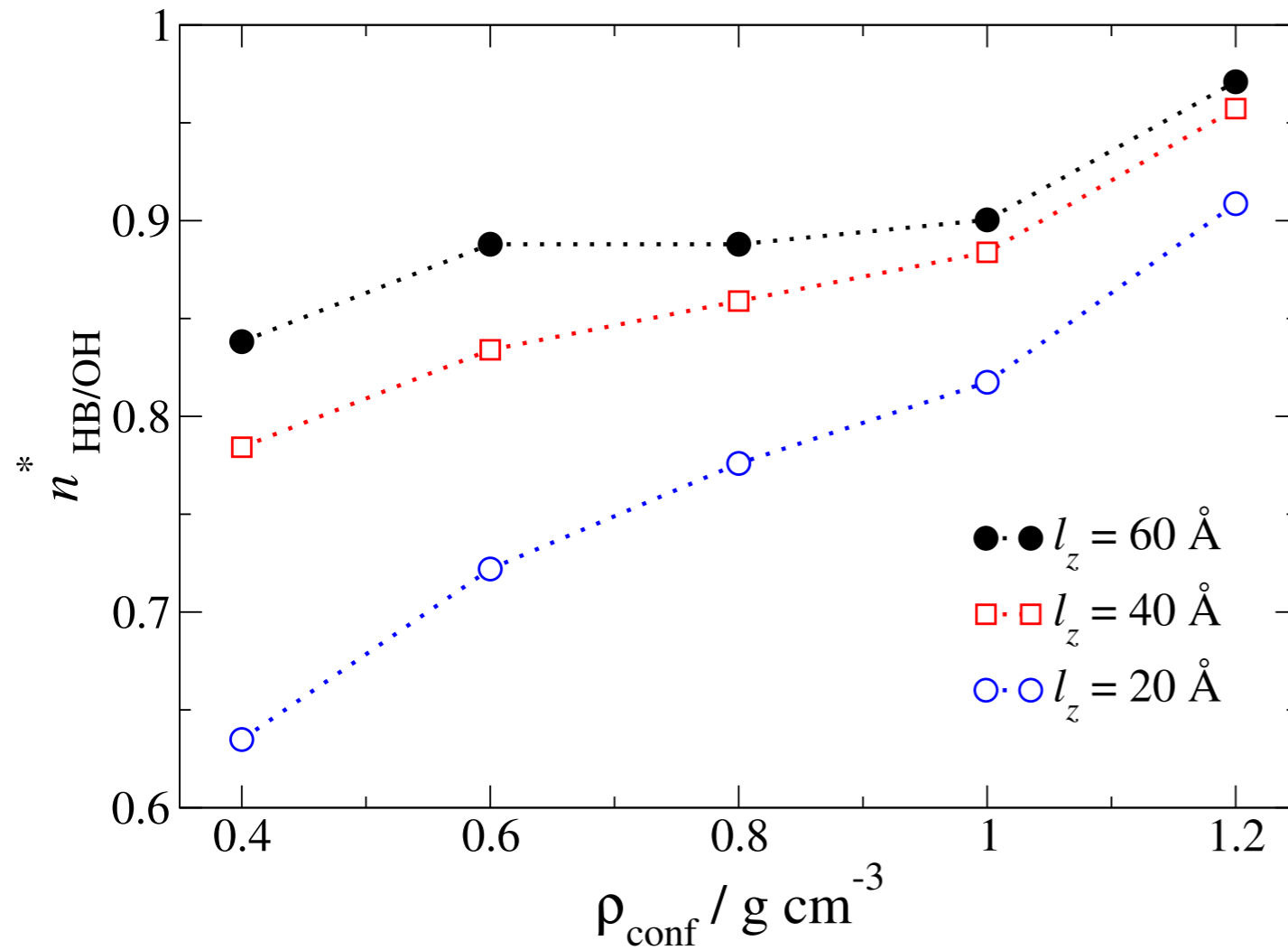
Interfacial Effects

HB change with confinement length and density
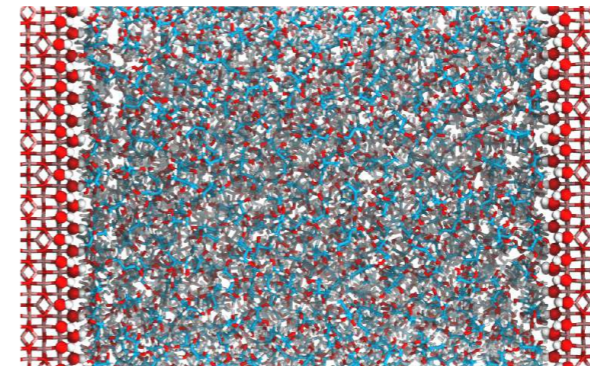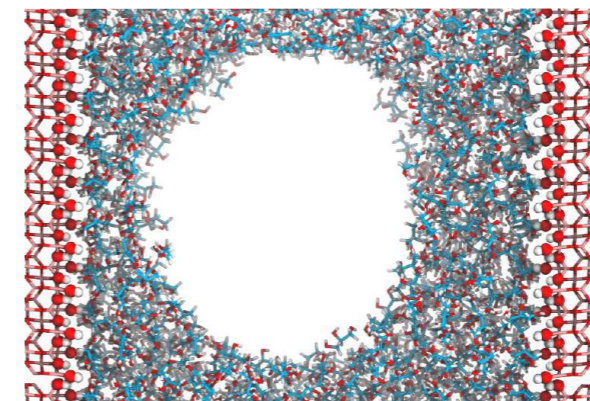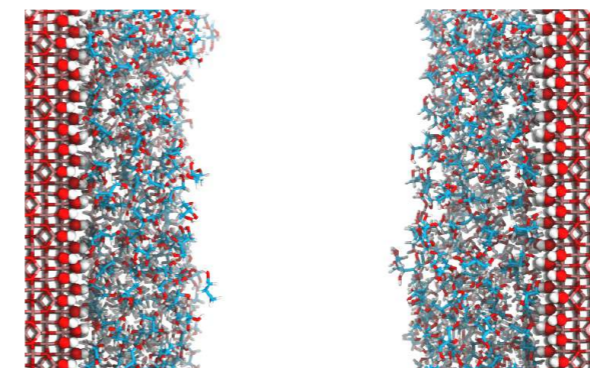
Consequences on the Dynamics: HB Networks

HB lifetime
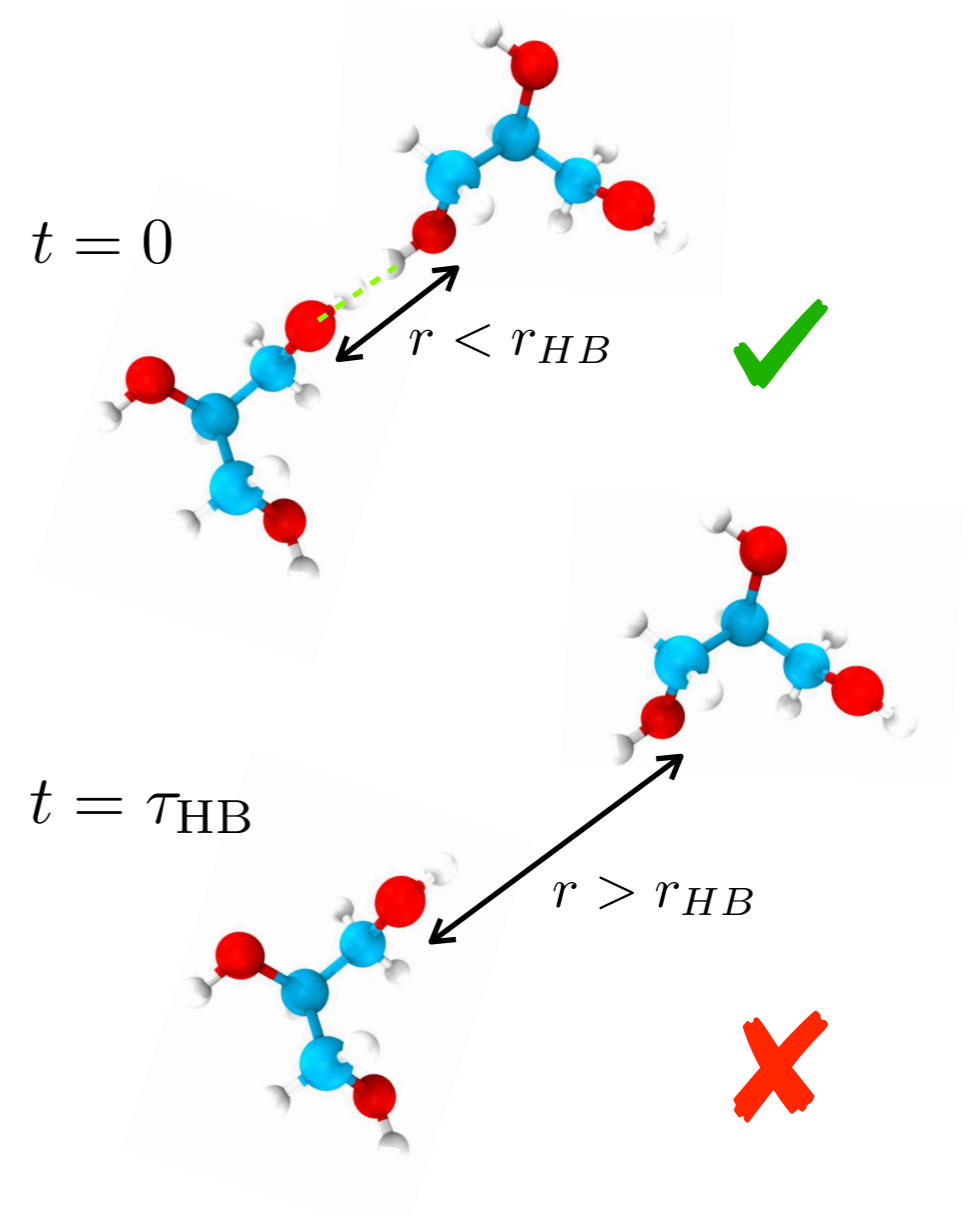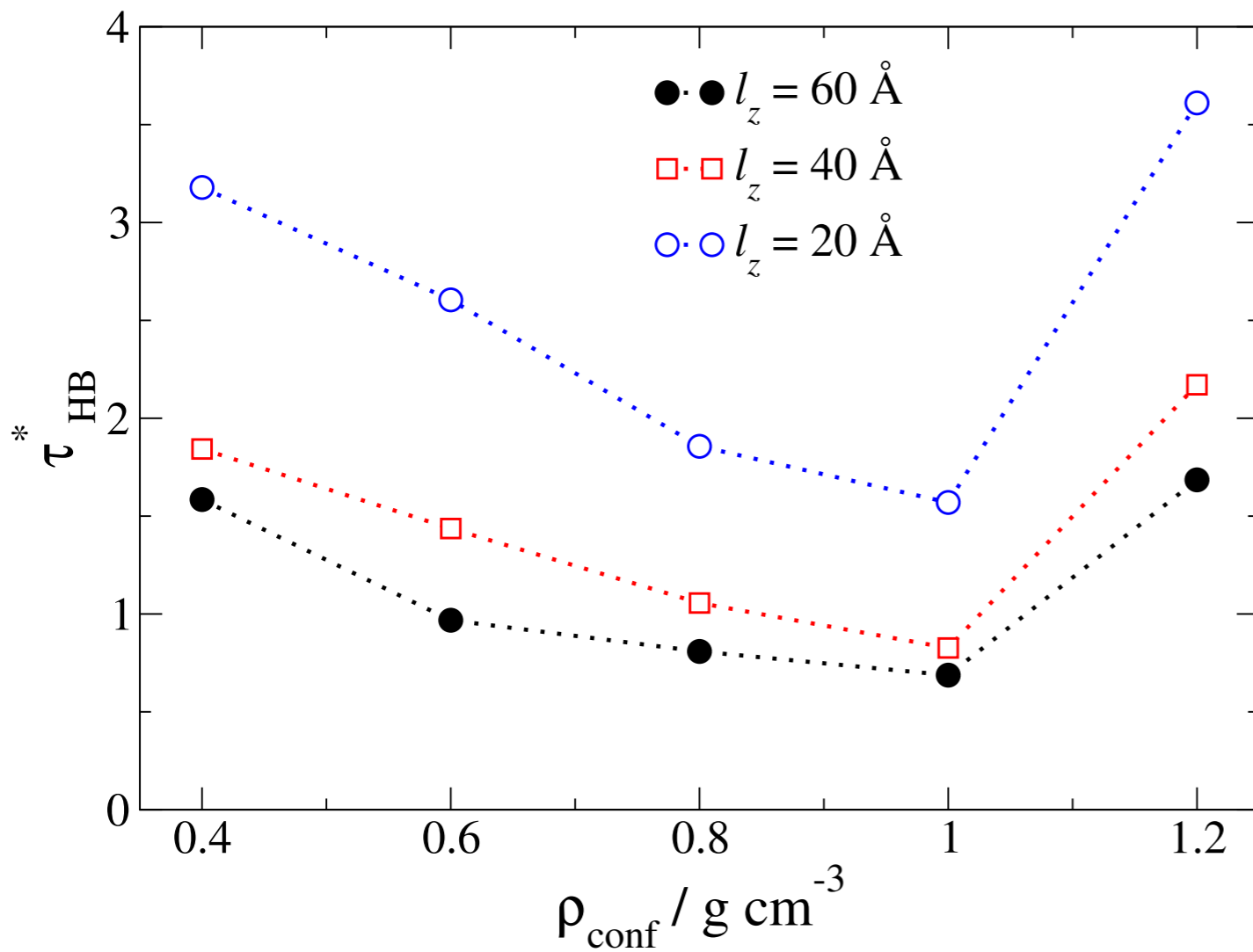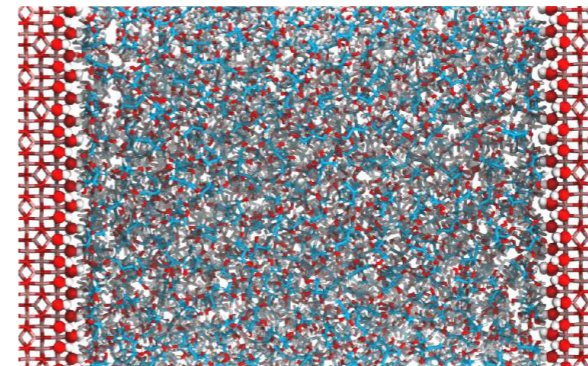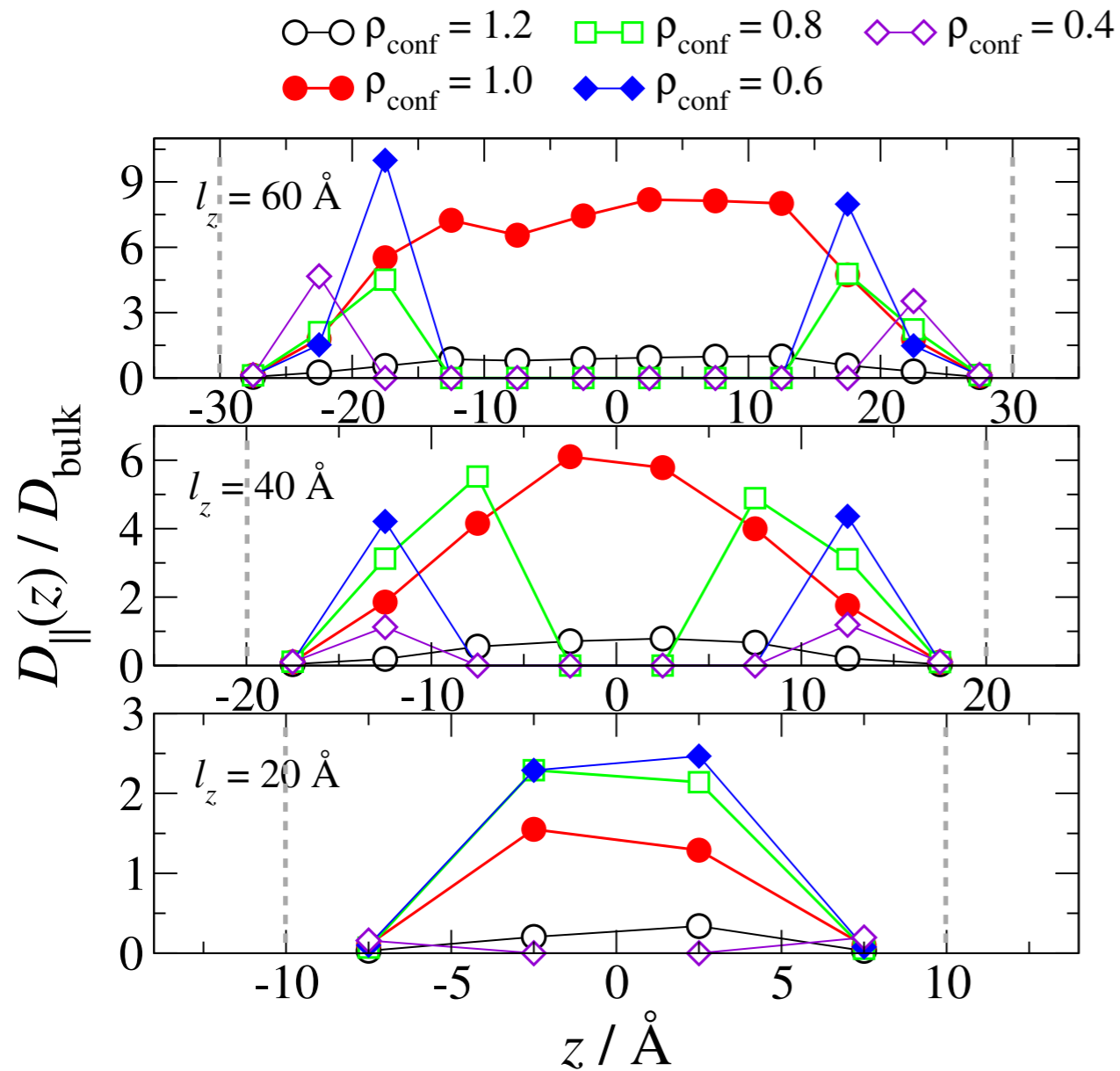
Legend:
- $l_z = 60$ Å (filled black circles)
- $l_z = 40$ Å (red squares)
- $l_z = 20$ Å (blue open circles)

Axes: τ^*_{HB} vs ρ_{conf} / g cm^{-3}

$t = 0$, $r < r_{HB}$ ✔

$t = \tau_{HB}$, $r > r_{HB}$ ✘

Consequences on the Dynamics: Diffusion
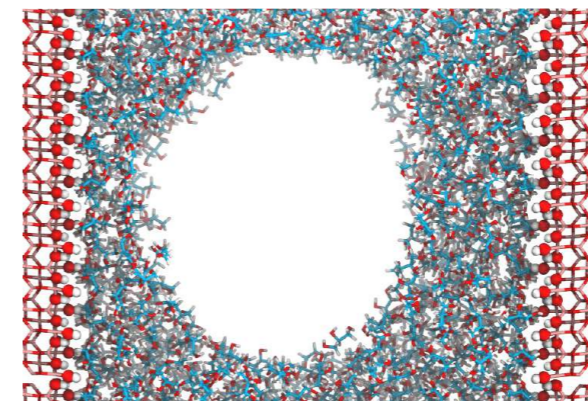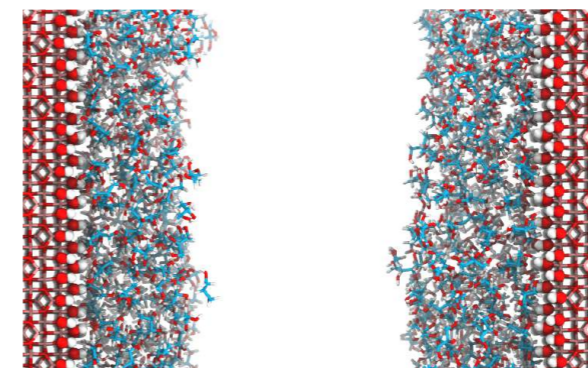
Local diffusion coefficient

Consequences on the Dynamics: Diffusion

Local diffusion coefficient
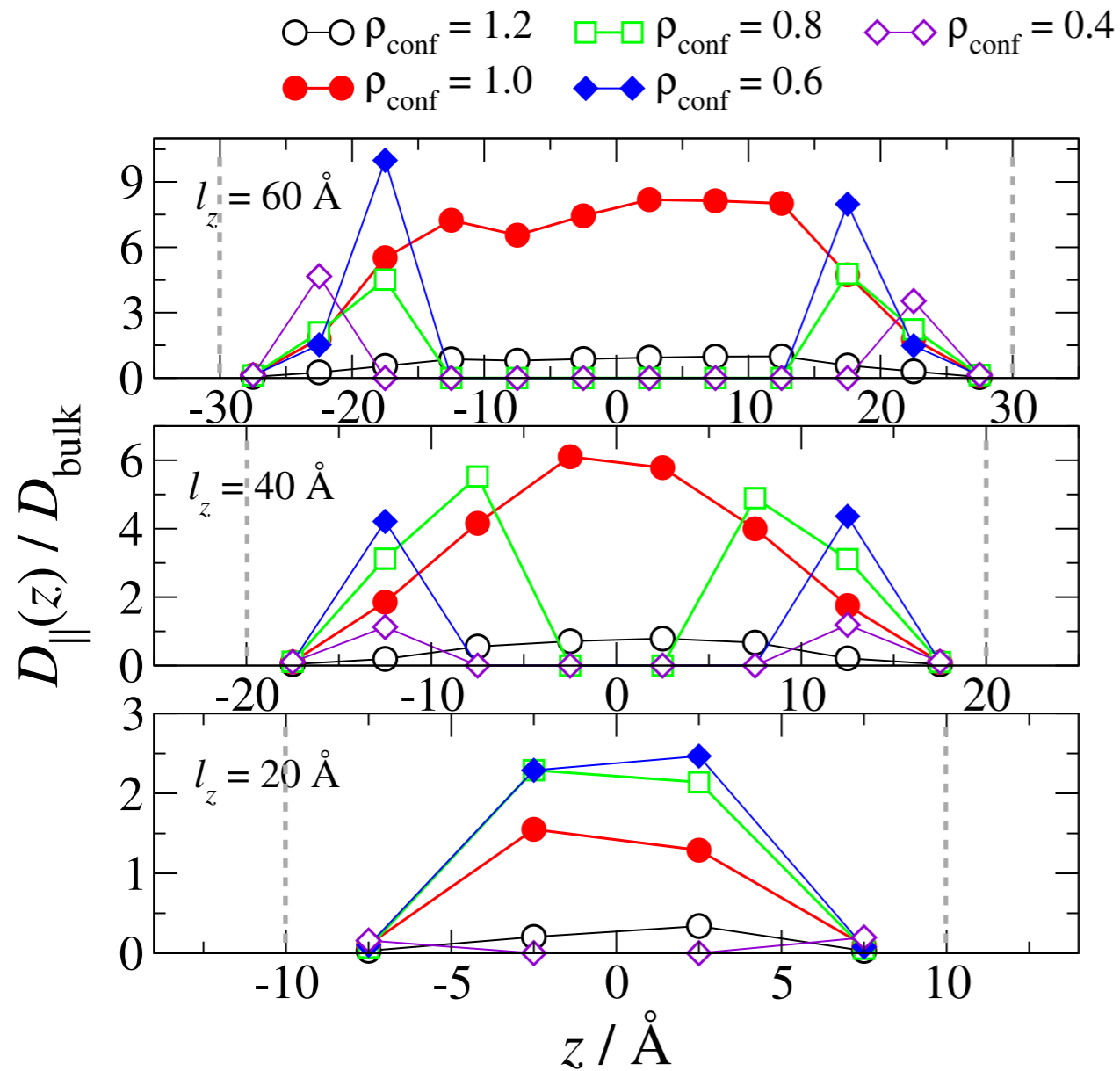
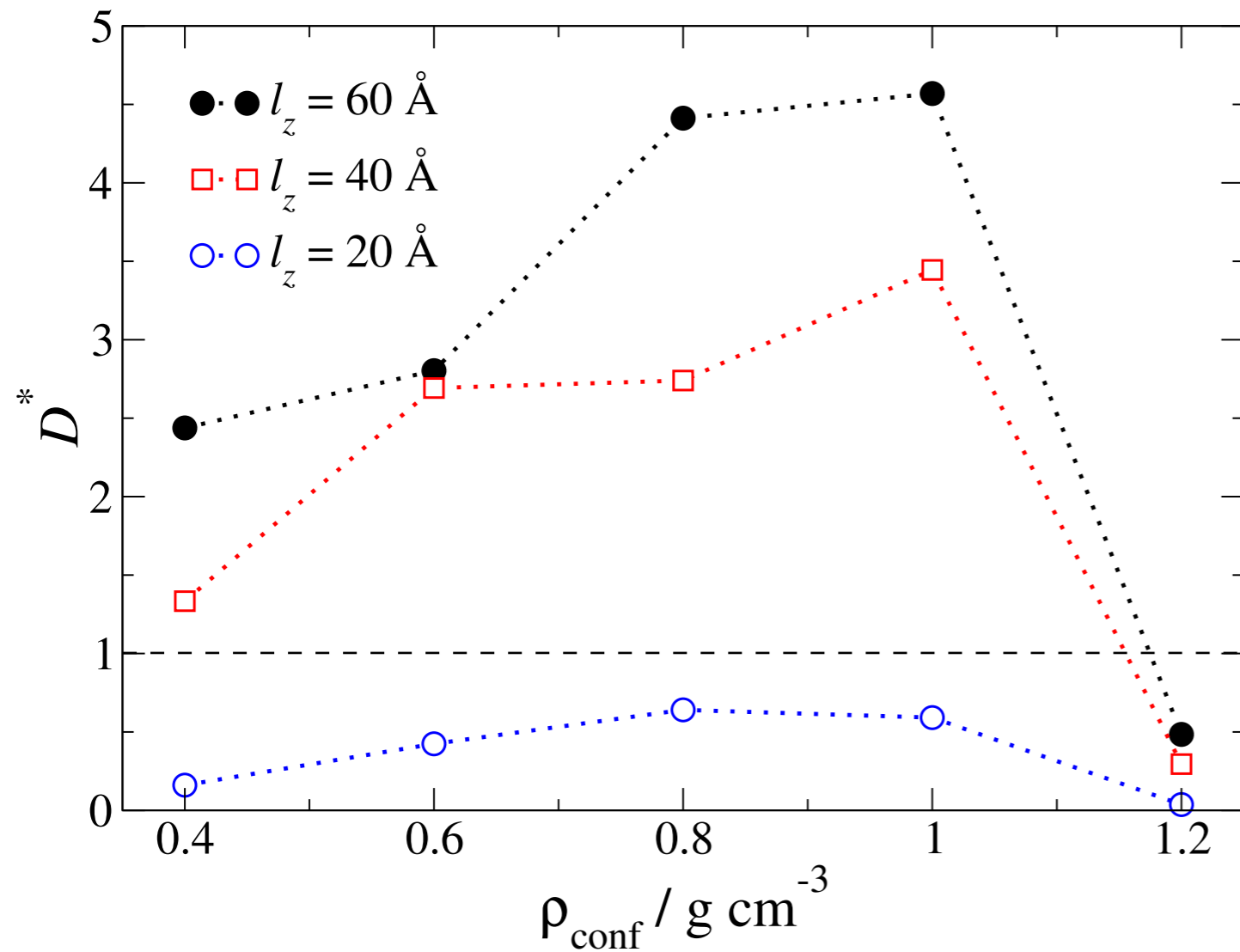$$D_{\mathrm{conf}} = \left\langle D_{\parallel}(z) \right\rangle = \frac{\int_{l_z} D_{\parallel}(z)\, \rho(z)\, dz}{\int_{l_z} \rho(z)\, dz}$$

Consequences on the Dynamics: Diffusion

Global diffusion coefficient

Enhanced molecular self-diffusion in confinement

Outlook

1
The solid imposes a heterogeneity in the liquid, causing the structural and dynamical properties to acquire a spatial dependence

2
The formation of interfaces with the solid and vacuum regions is found profoundly affect the kinetics of breaking and re-formation of hydrogen bonds

3
A necessary condition for the enhancement in the molecular diffusion is the partial saturation of the pores

Acknowledgements

- Alessandro Patti
- Flor R. Siperstein
- Carmine D'Agostino

THANK YOU!