An increase of dynamical heterogeneity with confinement in supercooled water

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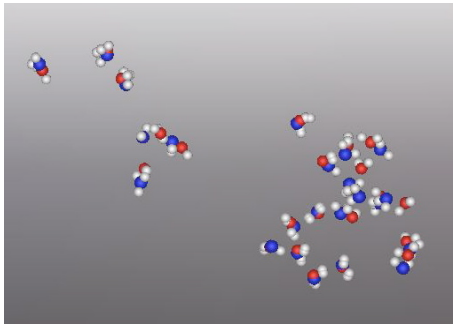
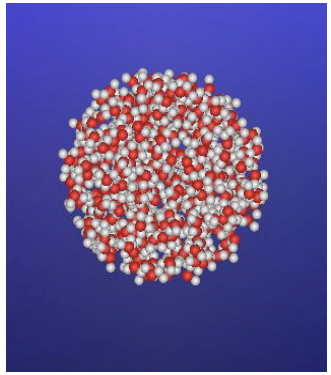


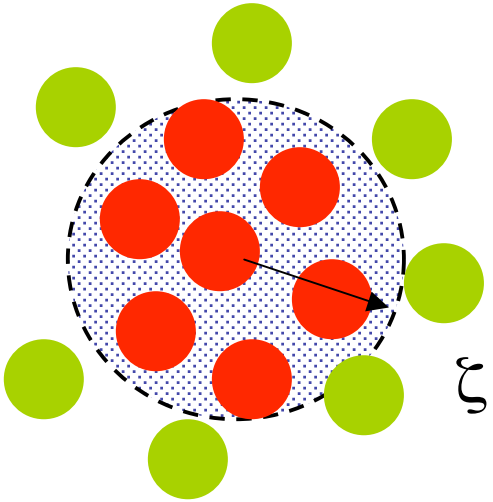


Expected:

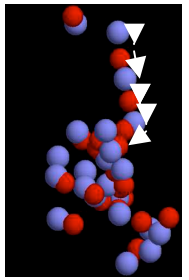
- Cutoff of the cooperative length scales

=> Cutoff of the dynamical heterogeneity

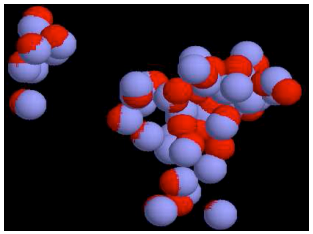
- Acceleration of the dynamics due to this cutoff

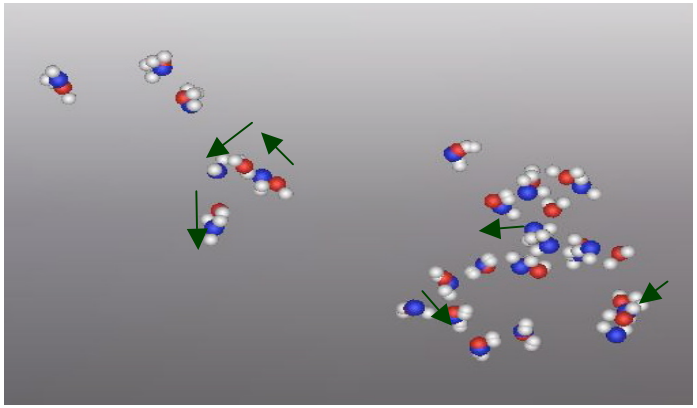


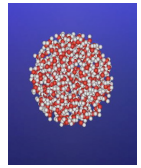
Mobile (string-like motions)



Slow (simple clusters)







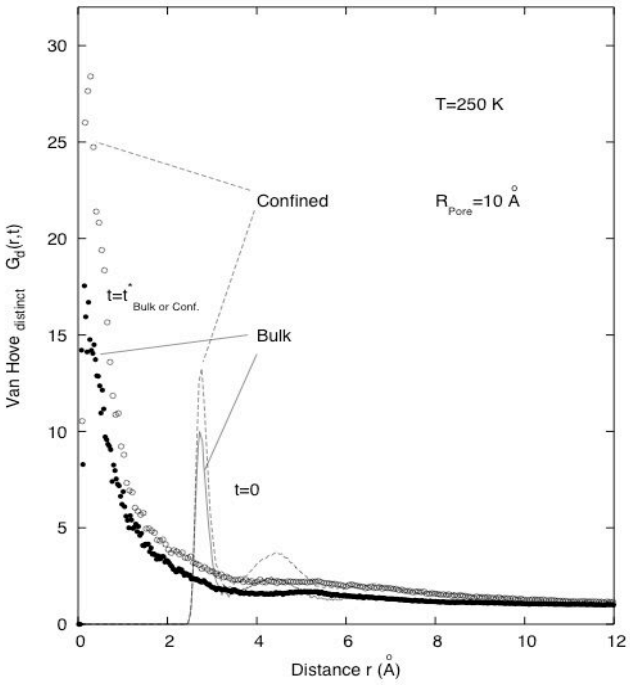
$$G_d(r,t) = \frac{V}{N(N-1)} \sum_{i,j=1}^{N} \delta(r - |\vec{r}_i(t+t_0) - \vec{r}_j(t_0)|)$$

Results:

(The opposite of what was expected)

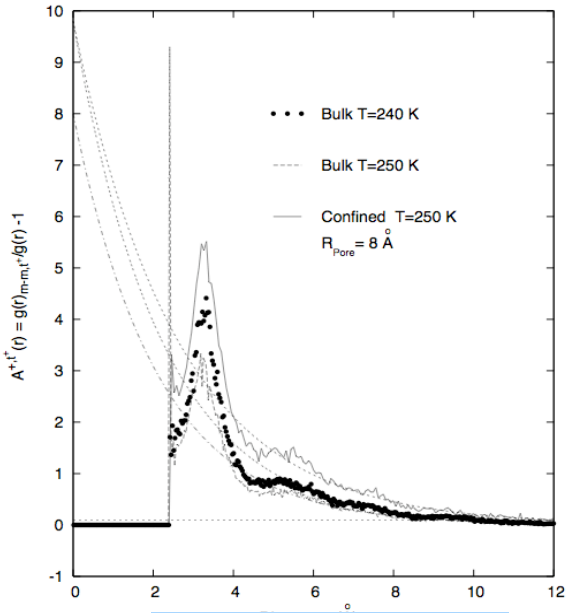
- Increase of the dynamical heterogeneity (clusters of slow and clusters of mobile)
- Increase of the string-like mechanism
- Increase of the size of the clusters (larger than the pore size) in the pore axis direction

- Slow down of the dynamics
- Structure unchanged (in the center of the pore)



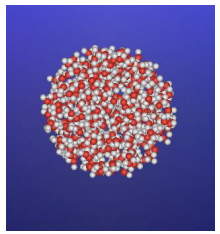
Distance r (Å)

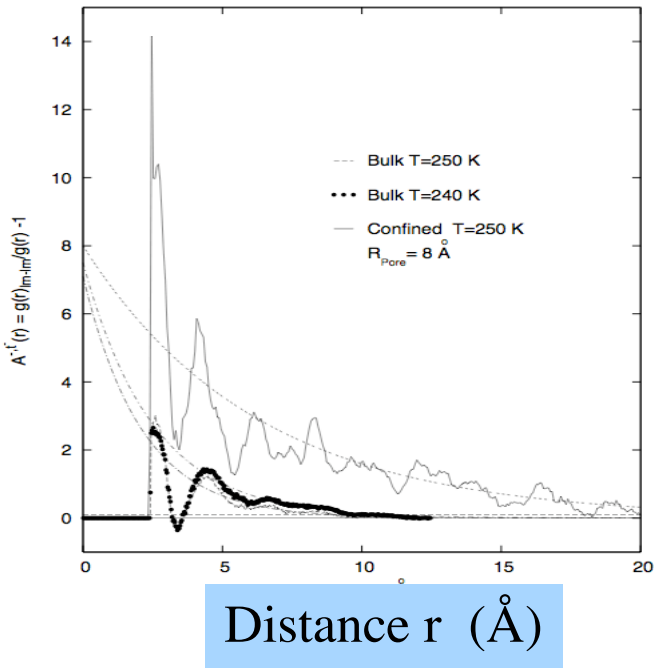
$$A^{+}(r,t) = \frac{g_{mm}(r)}{g(r)} - 1$$



Aggregation of the most mobiles water molecules

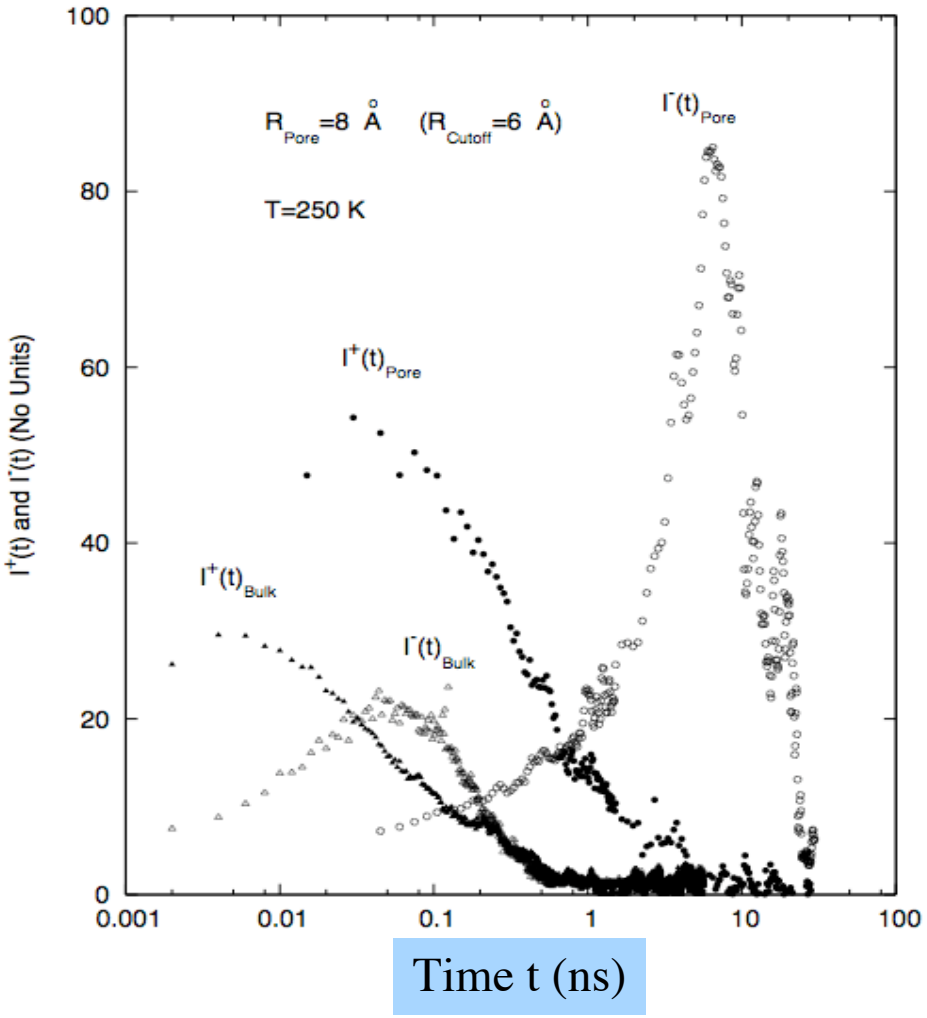
$$A^{-}(r,t) = \frac{g_{lm}(r)}{g(r)} - 1$$



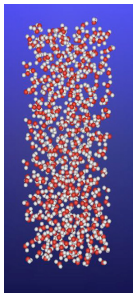


Aggregation of the least mobiles water molecules

$$I^{+/-}(t) = \frac{N}{V}\int_0^{\infty} A^{+/-}(r,t).4\pi r^2 dr$$



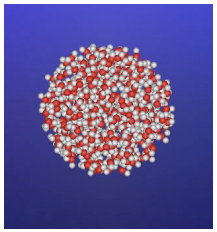
The 'intensity' I(t) of the LMM aggregation increases much more sharply with the confinement than the MMM aggregation.



Notations:

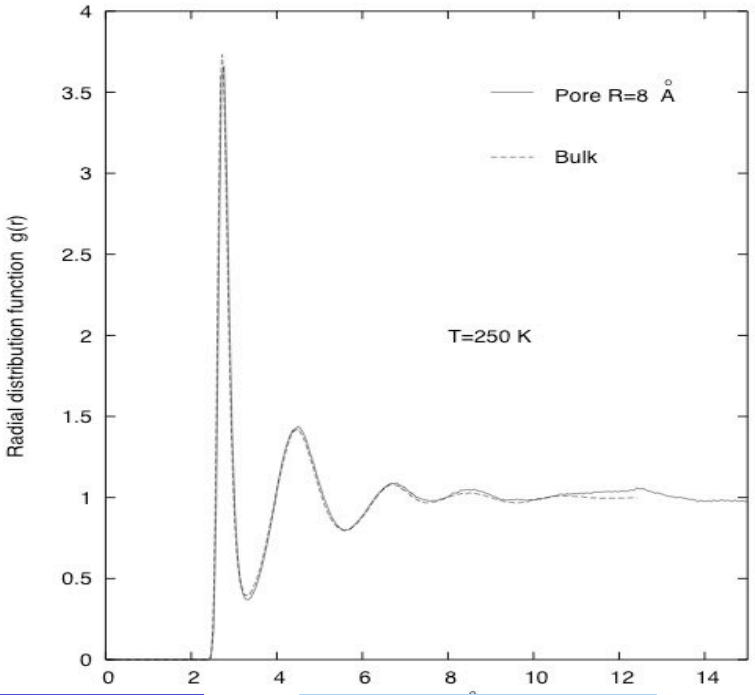
-: LMM (least mobile molecules)

+: MMM (most mobile molecules)

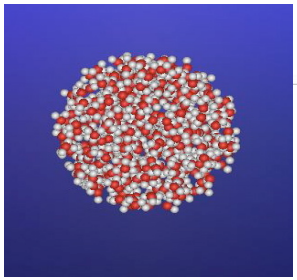


$$g(r) = \frac{V}{N(N-1)} \sum_{i,j=1}^{N} \delta(r - |\vec{r}_i - \vec{r}_j|)$$

Corrected from excluded volumes



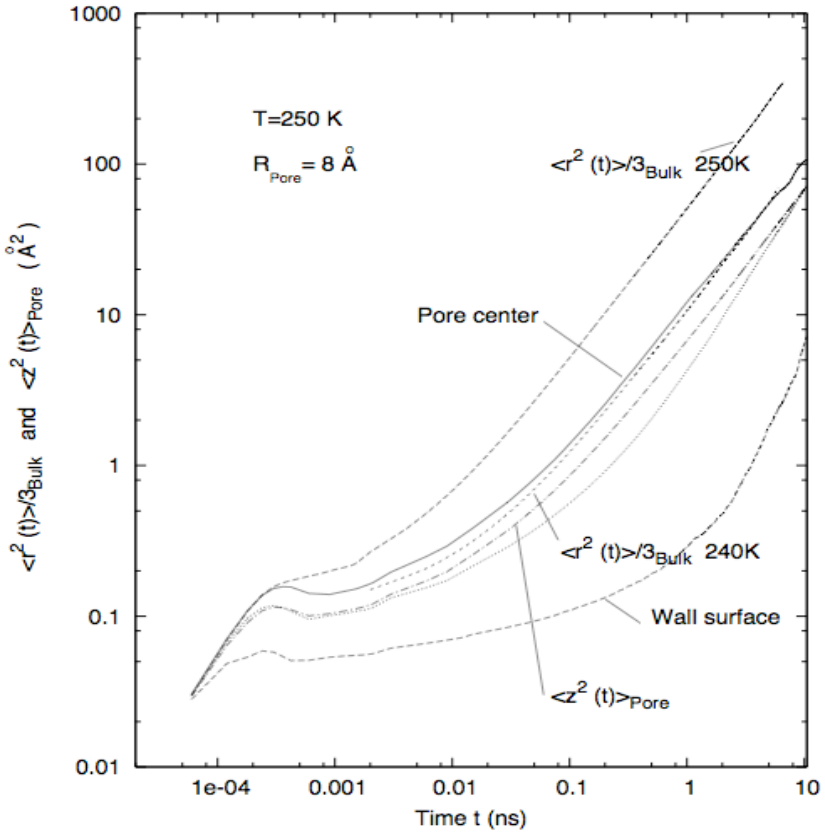
Distance r (Å)



Structure unchanged

(pore center)

$<Z^2(t)>$



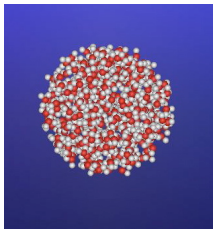
Time t (ns)

Slowing down of the dynamics

Abstract: Large scale ***molecular dynamics simulations*** are used to investigate the ***structural and dynamical modifications*** of supercooled water when confined inside an ***hydrophilic nanopore***. We then investigate the evolution of the ***auto-organization of the most and the least mobile molecules (dynamical heterogeneity and string-like cooperative motions)*** when supercooled water is confined. Our calculations use the recent TIP5P intermolecular potential for water. We observe a ***strong slowing down*** of the dynamical properties when the liquid is confined, although the ***liquid structure is found to remain unchanged*** when corrected from the pore geometry. We then study cooperative motions inside supercooled confined water in comparison with bulk water. We observe strong modifications of the cooperative motions when the liquid is confined. We observe that ***dynamical heterogeneities and the associated correlation lengths are strongly increased as well as string-like motions in the confined liquid.*** This result, which is ***in opposition with the expected limitation of the correlation length by the confinement procedure***, may explain (or be explained by) the slowing down of the dynamics. However the comparison of the dynamical heterogeneities at constant diffusion coefficient shows that ***the slowing down of the dynamics is not sufficient to explain the increase of the correlation lengths***.

References:

Cooperative length scales:
G. Adam, J.H. Gibbs, 1965, *J. Chem. Phys.* **43**, 139
Dynamical heterogeneity (review):
M.D. Ediger, 2000, *Annu. Rev. Phys. Chem.* **51**, 99
H. Sillescu, 1999, *J. Non-Crystal. Sol.* **243**, 81
Dynamical heterogeneity in water:
N. Giovambattista, S.V. Buldyrev, F.W. Starr, H.E. Stanley, 2003, *Phys. Rev. Lett.,* **90**, 085506
M.G. Mazza, N. Giovambattista, F.W. Starr, H.E. Stanley, 2006, *Phys. Rev. Lett.,* **96**, 057803
V. Teboul, A. Monteil, L. C. Fai, A. Kerrache, S. Maabou, 2004, *Eur. Phys. J. B* **40**, 49
V. Teboul, ArXiv: cond-mat/0702551



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