XI School of Neutron Scattering "Francesco Paolo Ricci"

Rosaria Mancinelli

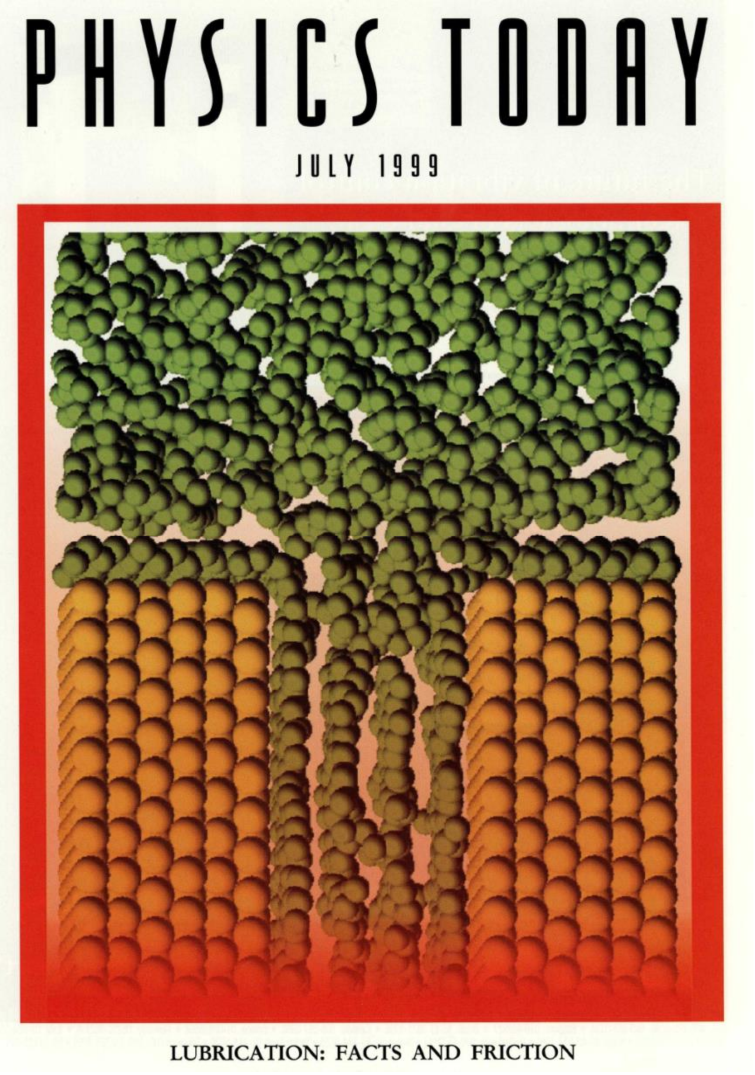
1. An informal and brief introduction to confined fluids

(now)

2. Methods to deal with structure of confining/confined media: the case of water confined in MCM-41

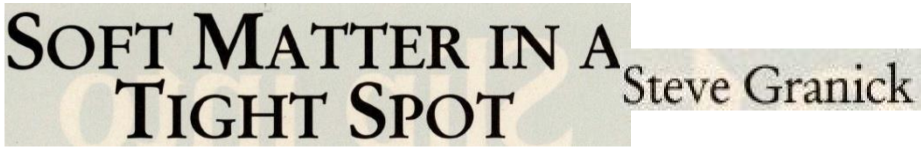
(tomorrow morning)

What is a confined fluid?

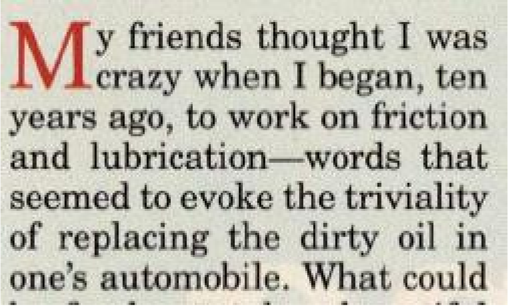

PHYSICS TODAY

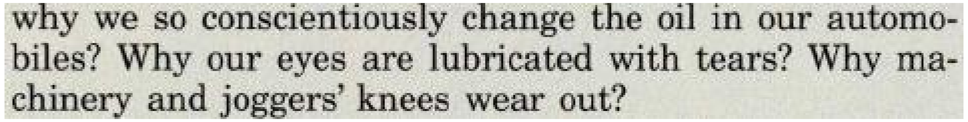
JULY 1999

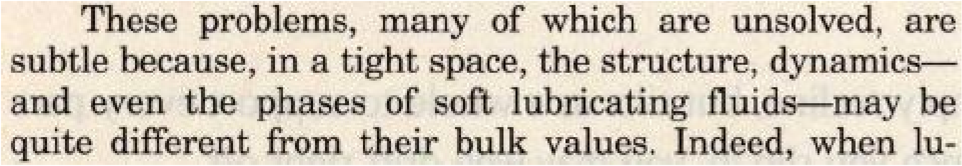
LUBRICATION: FACTS AND FRICTION


SOFT MATTER IN A TIGHT SPOT

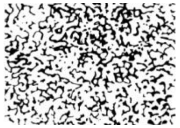
Steve Granick


My friends thought I was crazy when I began, ten years ago, to work on friction and lubrication—words that seemed to evoke the triviality of replacing the dirty oil in one's automobile. What could

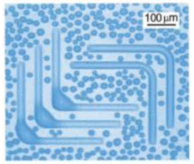

why we so conscientiously change the oil in our automobiles? Why our eyes are lubricated with tears? Why machinery and joggers' knees wear out?

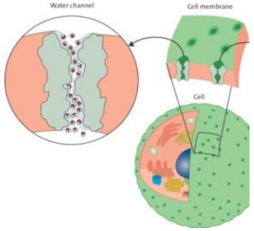

These problems, many of which are unsolved, are subtle because, in a tight space, the structure, dynamics—and even the phases of soft lubricating fluids—may be quite different from their bulk values. Indeed, when lu-

Understanding the behaviour of **fluids in confining geometries** is of great importance not only in tribology but in many other fields such as

- 
geology (*zeolites, clays and minerals*)

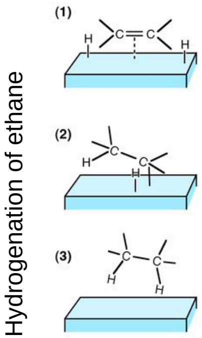
engineering (*ñlab on a chipòand microfluidic technologies*)
H.Gau et al Science 283,1999



- 

- **biology** (*ion channels, membrane pores, intracellular environmenté*): water is never so far from cellular walls!

- **industry** (*heterogeous catalysis):* confinement reduces the entropy of reactans favouring catalysis



LEAST BUT NOT LAST confinement is an ideal tool to investigate on peculiar proprierties of fluids such as **superfluidity and supercooling**

How much do confined fluids look like bulk fluids?

How does it work classical physics?

Index

1. Reology of thin films

2. List of **possible relevant variables** to take into account when dealing with confined fluids

3. Recall the **physics of the capillars** and its extension at nanometric lenghts

4. Reduction of density induced by confinement in terms of **packing fraction**

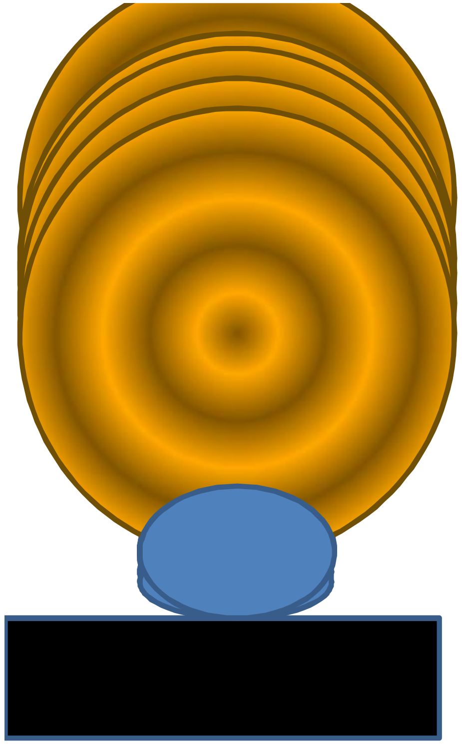
5. How confinement can be considered a reduction of **dimensionality** in scaling laws

6. Confinement as a **tool for theoretical physics**

7. **Summary** of the characteristic behaviour of normal fluids under confinement

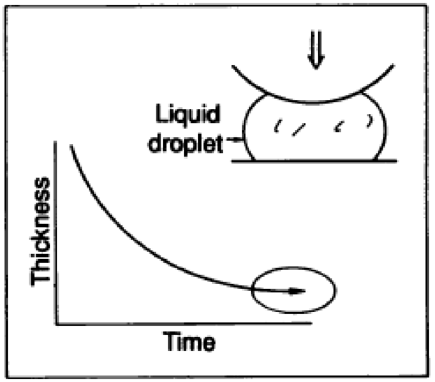
8. The anomalous behaviour of **water**
    - reology of water
    - hydrogen bond and 1° order transitions in glass formation
    - breakdown of Stokes-Einstein equation

1.Rheology of thin films



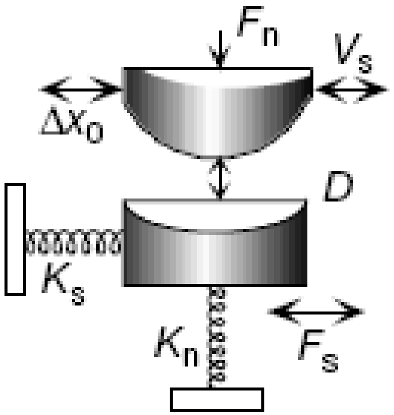
ñThe Armchair effectò: enhanced normal resistance

A ball falls on a liquid droplet, pushing it but not beyond a certain thickness.

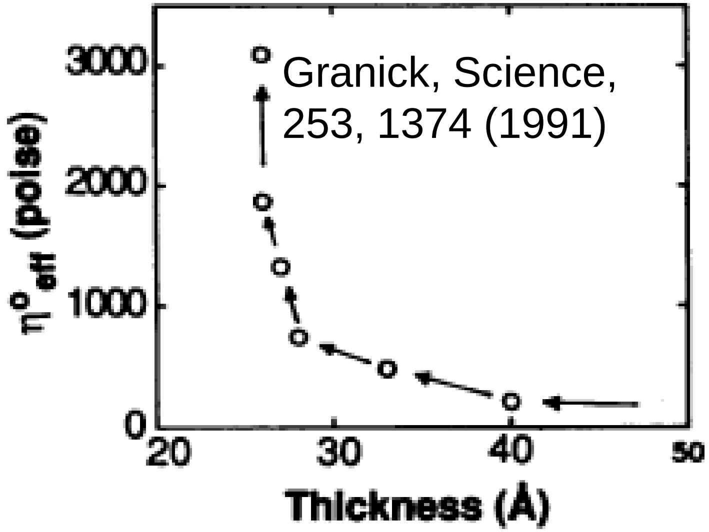


Why liquid cannot be compressed any more?

Atomic force spectroscopy allows to study how normal or tangential force propagates into a medium.



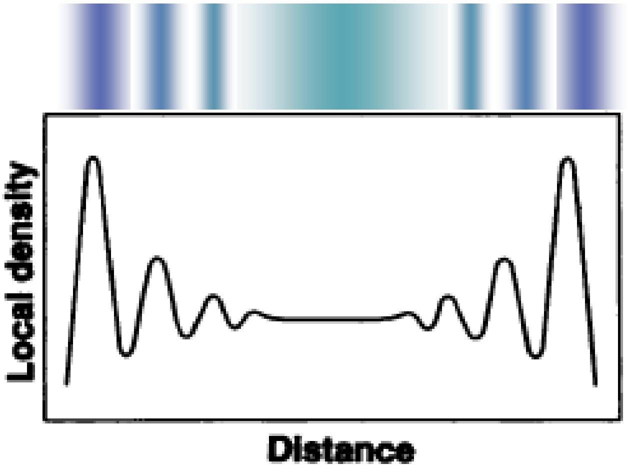
Enhanced <u>tangential</u> resistance (viscosity)



Granick, Science, 253, 1374 (1991)

The resistance to flow can increase by several orders of magnitude in films approaching molecular nanoscale dimensions

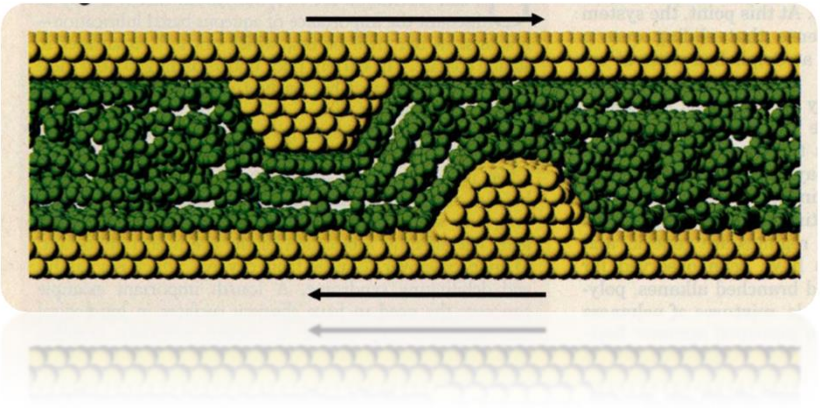
Explanation



These phenomena are manifestation of the inhomogeneous density profile, indicating the granular nature of matter.

Molecules slightly accumulate close to the surface of the substrates. This layer forms a hard wall to liquid so a second layer may form and so on.

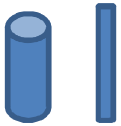
Liquid ordering induced by confinement (which is a sort of transition to solid state) between two solid surface leads the so called **layering**, which is a very stable phenomenum as it persists also in dynamical situations or in presence of not flat walls.



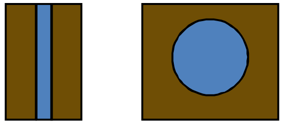
2. List of relevant variables

To understand how much classical physics works in confined media,
it is necessary to consider at least :

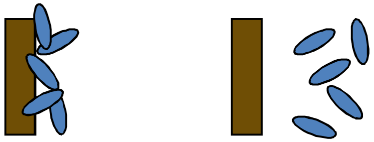
confinement size



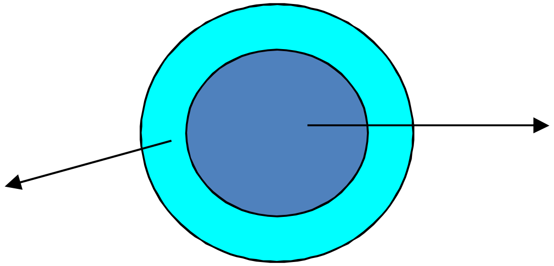
confinement shape



fluid-wall interaction



é and distinguish, if possible, at least two relevant zones



Surface layers

Inner core
(not directly influenced by the wall)

as suggested by the classical studies on macroscopically confined systems,
i.e. *fluids in capillars*

which obviously represent our starting point.

3. Adsorption theory: dependence of fluid-wall interaction

In presence of a fluid, solid walls can be

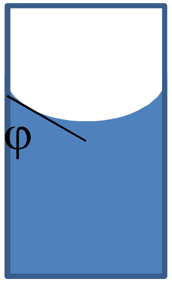
wet

Attraction between fluid and wall

dry

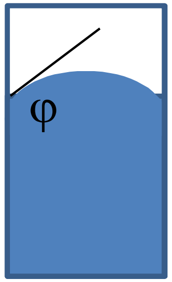
Repulsion between fluid and wall

A good indicator of the wetting is the **wetting angle**



ű is acute

If the liquid wets the container, fluid tends to be thermodynamically favoured.



ű is obtuse

In the case of dry walls, fluid tends to leave the pore (evaporation) or to aggregate (turns into a solid)

3. Gibbs Thomson equation: dependence on size

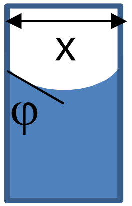
The phenomenum just described is well known as capillary melting / condensation.

What happens is a competition between superficial and volumic terms, being the former relevant when the confining media is thin :

Substrate-liquid interfacial energy

$$\Delta T = -\frac{4\sigma\cdot T_m}{x\cdot\Delta H\cdot\rho_{solid}}\cos(\varphi)$$

Free energy of fusion



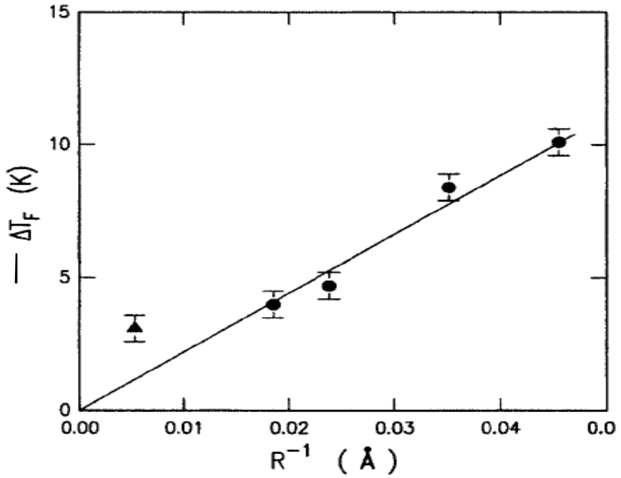
So the smaller the pore, the bigger the shift, which is a reduction in case of wet walls, a increase in case of dry walls.

$$x\downarrow \quad\Rightarrow\quad \Delta T\uparrow$$

$$\cos(\varphi)<0 \quad\Rightarrow\quad \Delta T>0$$

This formula holds also for fluids confined in mesoscopic hydrophilic pores (see figure) and it is consistent with the formation of layers in case of dry thin walls which occurs also at ambient T, as seen in tribology.

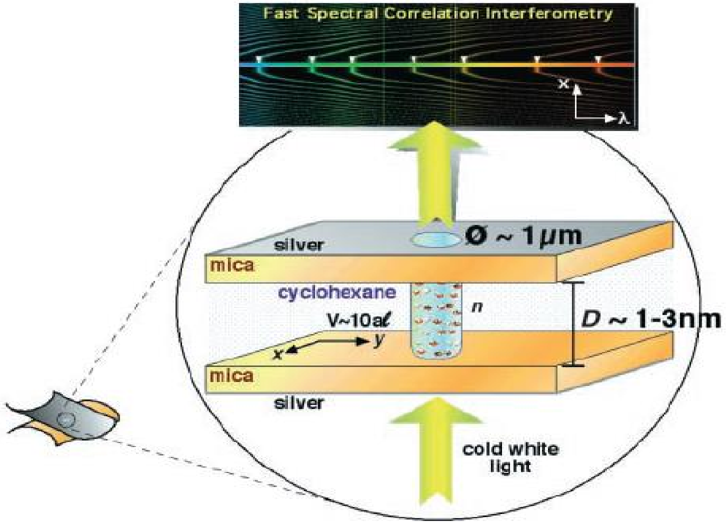
Oxygen in xerogel cylindrical pores



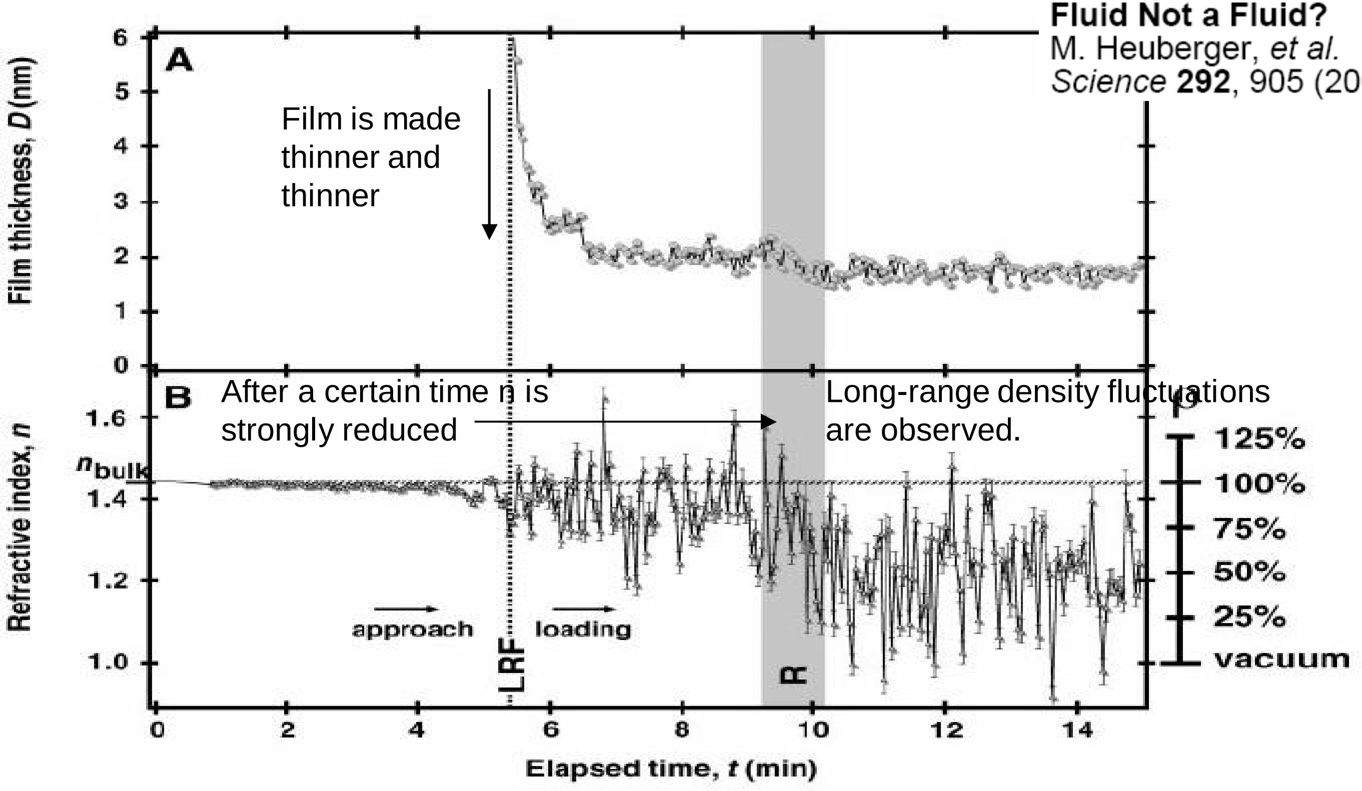
Deviations for Thomson-Gibbs law are often observed for the smallest pore sizes: where the enthalpy of fusion associated with melting in confinement has in general been found to be reduced compared to bulk and the smaller the pores the greater the reduction.

4. Reduction of density

The interference fringes position depends on the optical distance, Ω=Dn (being D the film thickness, n the refractive index). When the film thickness is changed, the condition for constructive interference is altered, and the wavelength shift of interference fringes can be measured. Odd- and even-ordered fringes shift differently as a function of n, an effect that allows D and n to be independently determined.



Density Fluctuations Under Confinement: When Is a Fluid Not a Fluid?
M. Heuberger, *et al.*
Science **292**, 905 (2001);



Film is made thinner and thinner

After a certain time n is strongly reduced

Long-range density fluctuations are observed.

With decreasing pore width, cyclohexane is found to undergo a drastic transition from a three-dimensional bulk fluid to a two-dimensional adsorbate with strikingly different properties.

4. Density reduction in case of dry walls and packing fraction

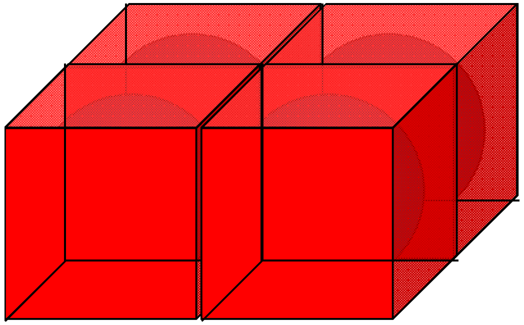
Density reduction is often observed in confined media.

In case of **dry** walls, neglecting all but geometrical factor, this reduction can be explained in terms different packing fraction

http://en.wikipedia.org/wiki/Sphere_packing

Maximum density of this arrangement is $\frac{\pi}{\sqrt{18}} \approx 0.74$

But in a single layer, molecules are more similar to spheres confined in a box



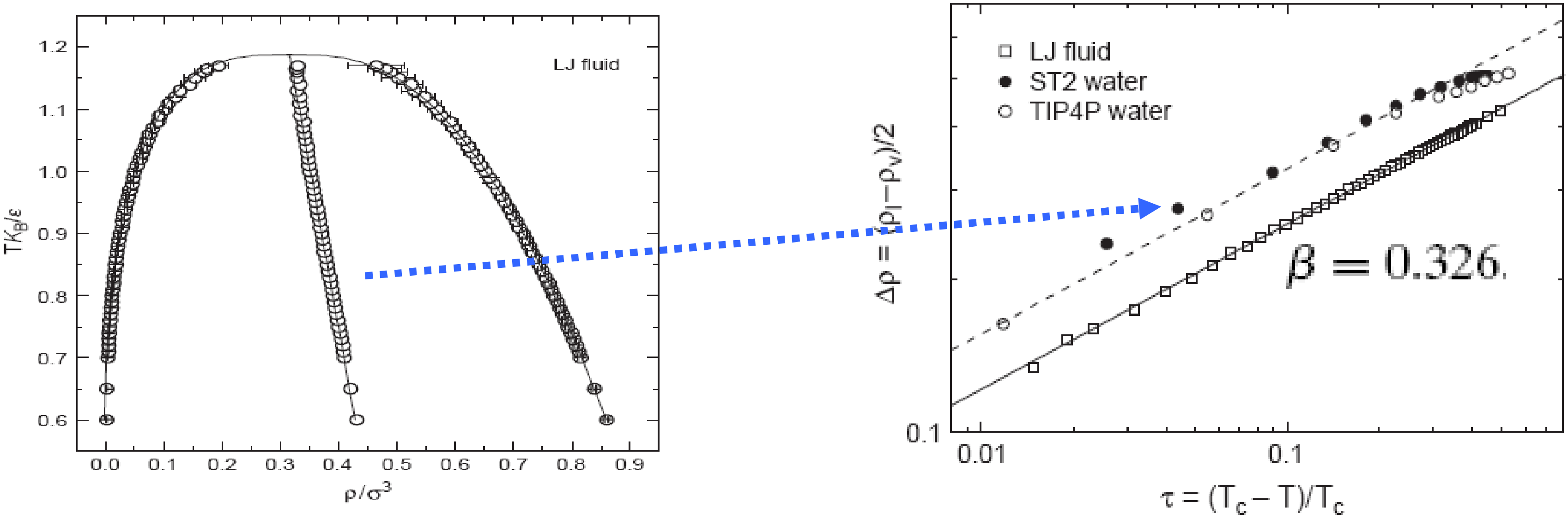
Density of this arrangement is $\frac{\pi}{6} \approx 0.52$

In a n-layer arrangement, density is always smaller than in bulk (recovering it in the limit n→∞)

5. Scaling law in liquid vapour transitions

As you know, the order parameter $$\Delta\rho = \rho_l - \rho_v \approx \left(\frac{T_C - T}{T_C}\right)^{\beta}$$

is determined by a scaling power law (belonging to the universality class of Ising model

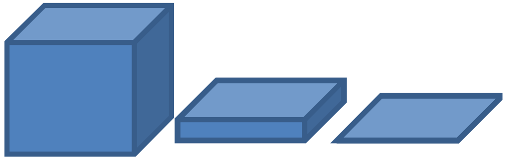


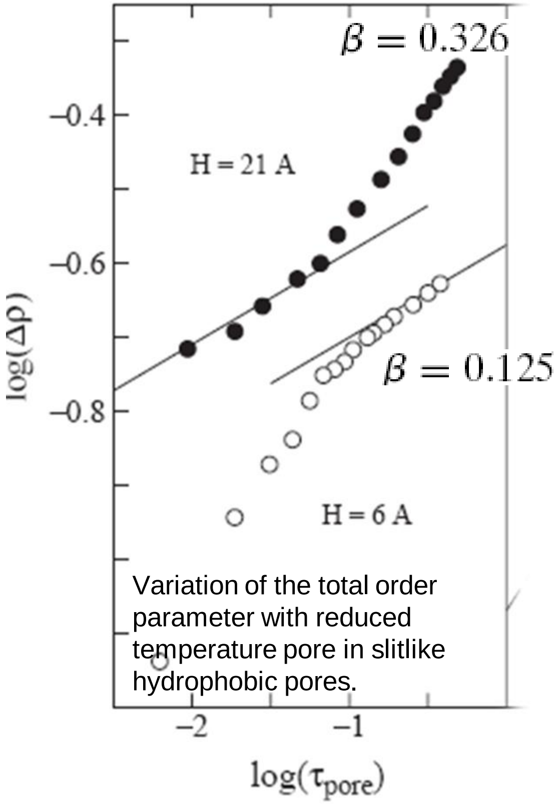
(I.Brovchenko, A. Oleinikova Molecular Organization of Gases and Liquids at Solid Surfaces in *Handbook of Theoretical and Computational Nanotechnology)*

The critical exponent is related to the dimensionality of the system

5. Scaling laws and dependence of the pore shape

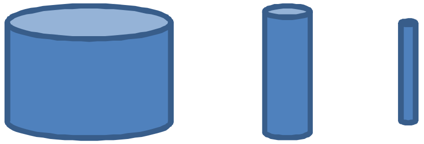
In a **slit**, when the thickness approaches the molecular size, a crossover from 3D to the 2D critical behaviour occurs.

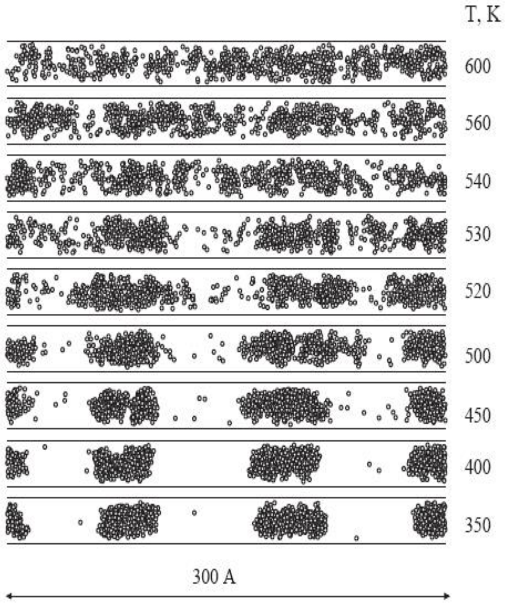




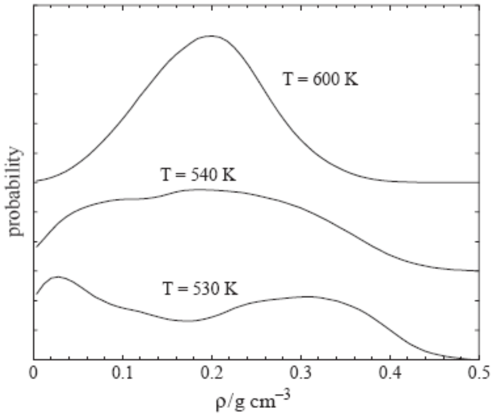
Variation of the total order parameter with reduced temperature pore in slitlike hydrophobic pores.

For **cylindrical pore** as cross sectional area decreases, a 1° order phase transition appears. Infact in a 1D system a true liquid-vapour transition does not occur



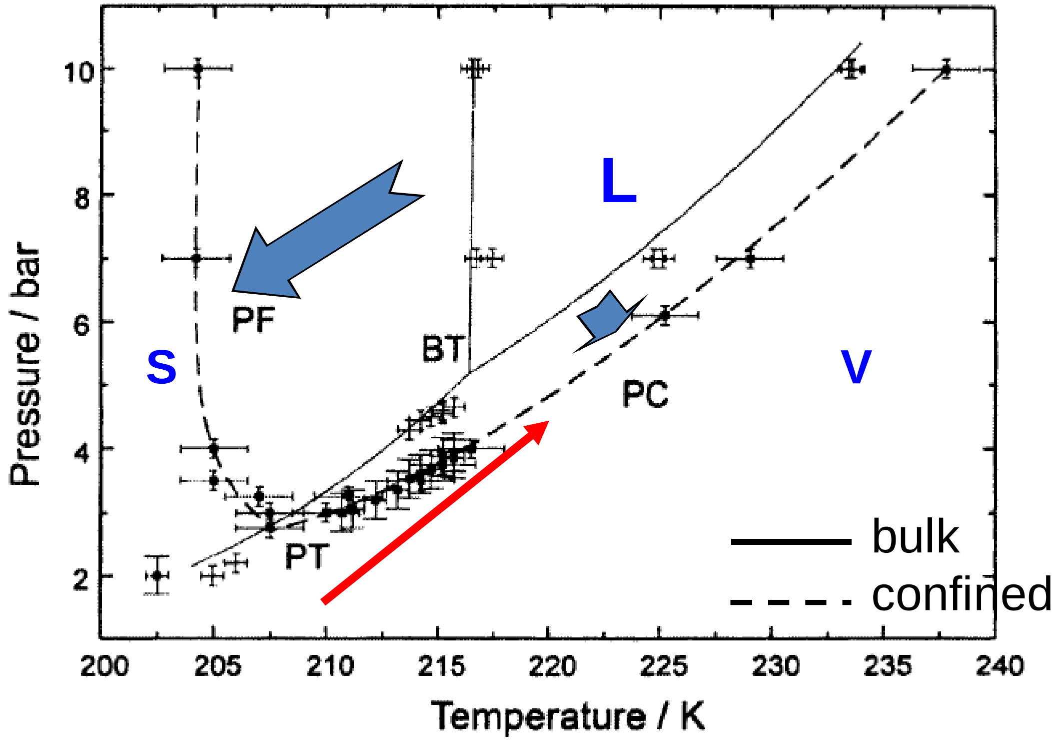


This corresponds to the gradual disappearance of a coesistence phase (two maxima in density distribution) with increasing temperature



6. Modified phase diagram

Looking at the change induced by confinement in the phase diagram of CO_2 in Vycor (pore diam 4nm), itôevident that **liquid phase** is favoured by confinement.



P: pore B:bulk F:freezing C:condensation T: triple point

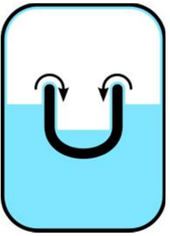
In some way, confined liquid behaves like a hotter and compressed bulk liquid.

Roughly speaking, this is due to the disorder and attraction induced by walls.

This expanded stability of liquid phase can be used to deeply investigate on peculiar phenomena such as

superfluidity

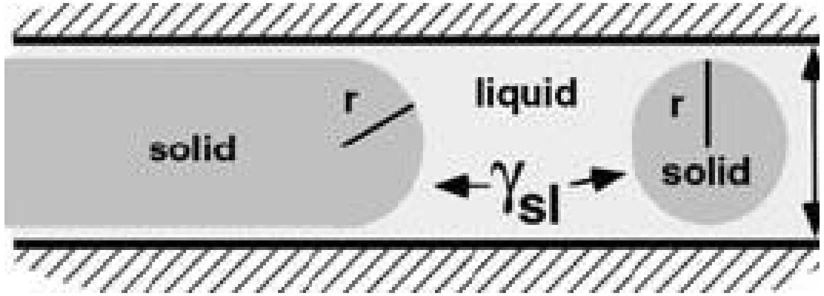
Helium confined to 6 nm pores in Vycor glass remained superfluid at temperatures and pressures which would lead to solidification in bulk .



supercooling

6. Supercooling

In confinement solid-solid interface contacts are energetically not convient, so the **homogeneous nucleation can happen in the center of the pore**.




Christenson

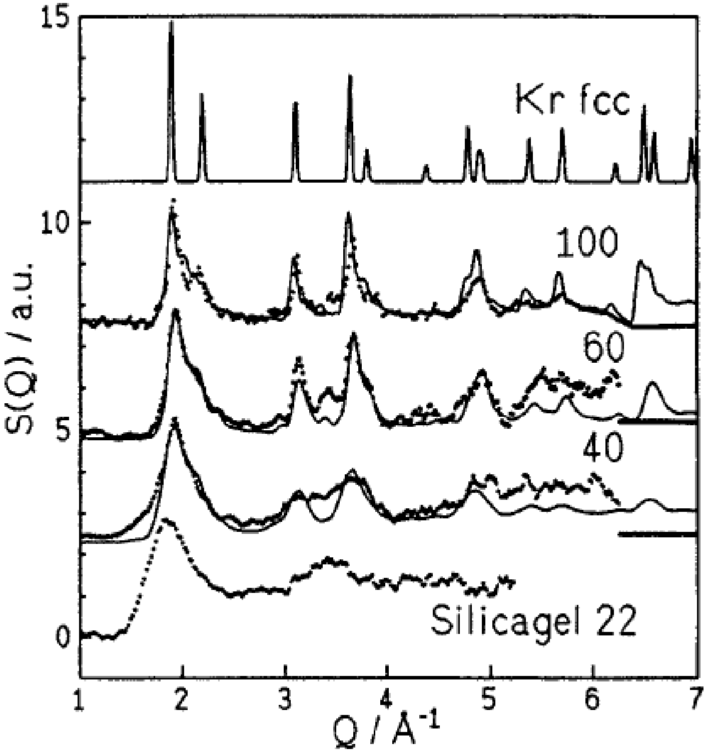
Confinement effects on freezing and melting

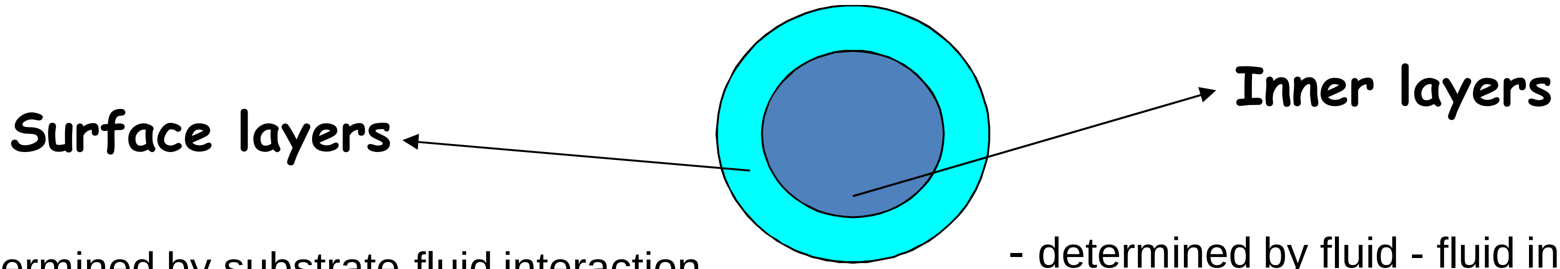
J. Phys.: Condens. Matter 13 (2001) R95–R133

Freezing will not occur at all when the pore is so small that cannot accomodate the minimum-size stable solid nucleus.

Looking at kripton in silica gel of various pore diameter in Å at 119K, itôs visible that it freezes easily in larger pores.
In the smallest pores the transition is not so clear.

Pore geometry, more than kinetic factors such as nucleation rates, controlls freezing in the confined system.





Surface layers

- determined by substrate-fluid interaction
- structure not dependent on pore size & T but on wettability of surface (calorimetry scans and various diffraction measurements are consistent with the presence of a non-freezing, or amorphous layer on the pore walls)
- The viscosity can be very high and, in general, dynamics is slowing down.
- itôs almost impossible to define a thermodynamics

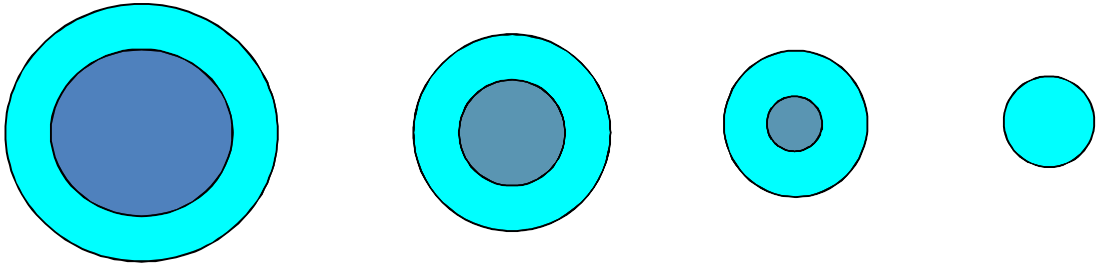
Inner layers

- determined by fluid - fluid interaction
- structure strongly dependent on confinement size; a frozen core or a bulk droplet eventually exists
- The viscosity can be lower than the bulk one
- It makes sense to define a thermodynamics

$$\Delta\rho \approx |T - T_c|^{\beta}$$

$$\Delta T \approx -\frac{\cos(\varphi)}{x}$$

Of course when the confinement lenght is extremely reduced



only surface layers survive and the classical laws of physics totally fail!

7. Summarizing

An average fluid molecule in a confining matrix feels
the same sensation of a human in a bus.

ubr0001 www.fotosearch.it

In the same space the bus can host less people than an open space (**density reduction**).

The rows have to fit to the available space in size and shape (**difficulty to crystallize near the walls**).

People can feel hot and oppressed by the presence of the walls (**shift of diagram phase**).

It is difficult to move (**enhanced viscosity**).

Is it always so?

No! There is an anomalous guy that behaves differentlyé

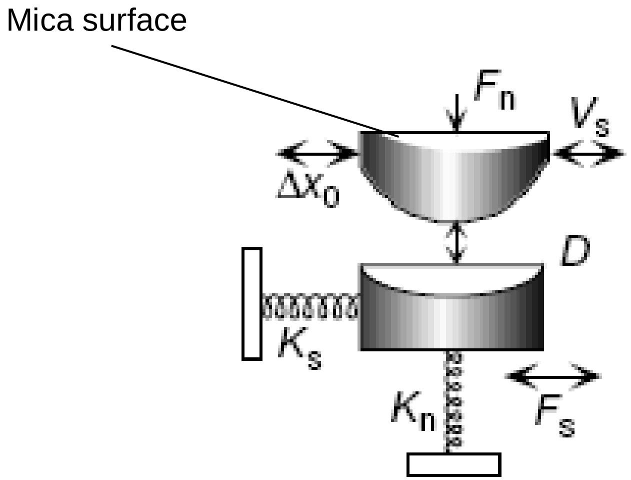
K. HOKUSAI (1790–1849)/BRIDGEMAN

WATER

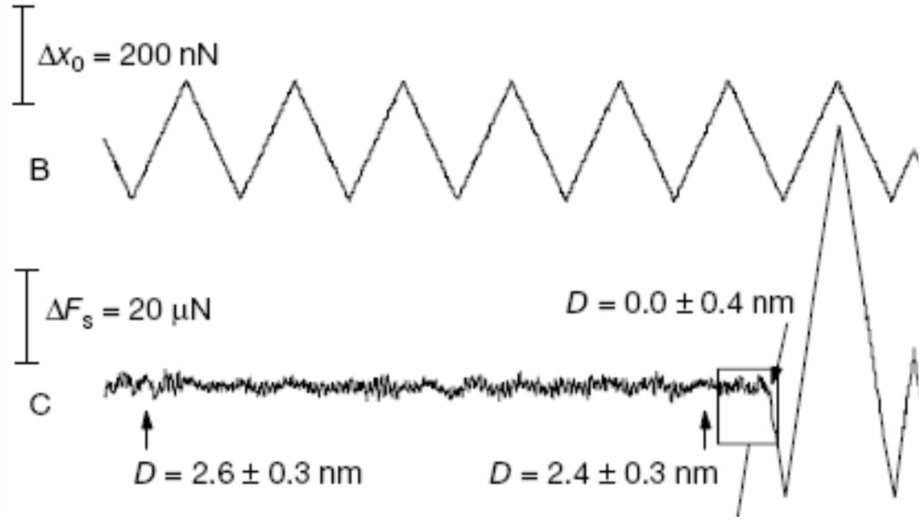
ñWater is a profoundly unusual liquid, and its peculiarities may make it uniquely suited to act as life's matrix. Even if this were not so, however, we should expect the effects of nanometre-scale confinement and inhomogeneities owing to surface effects to alter the liquid's properties in the cell relative to those in the bulk. Whether water's unusually high degree of local structure makes such influences even more marked than for 'normalóliquids remains an open question with potentially important consequences for biomolecular interactions.ò
Philp Ball, *Cellular and Molecular Biology* **47(5)**, 717-720 (2001)

8. Reology of water

Viscosity does not increase by decreasing the thickness of the slit
U.Raviv et al. Nature 413, 51 (2001)



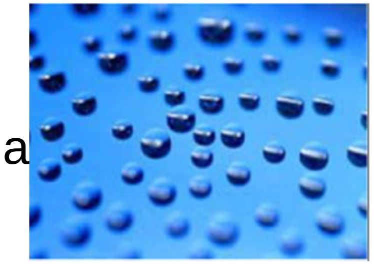
back-and-forth lateral motion as surfaces drift towards each other



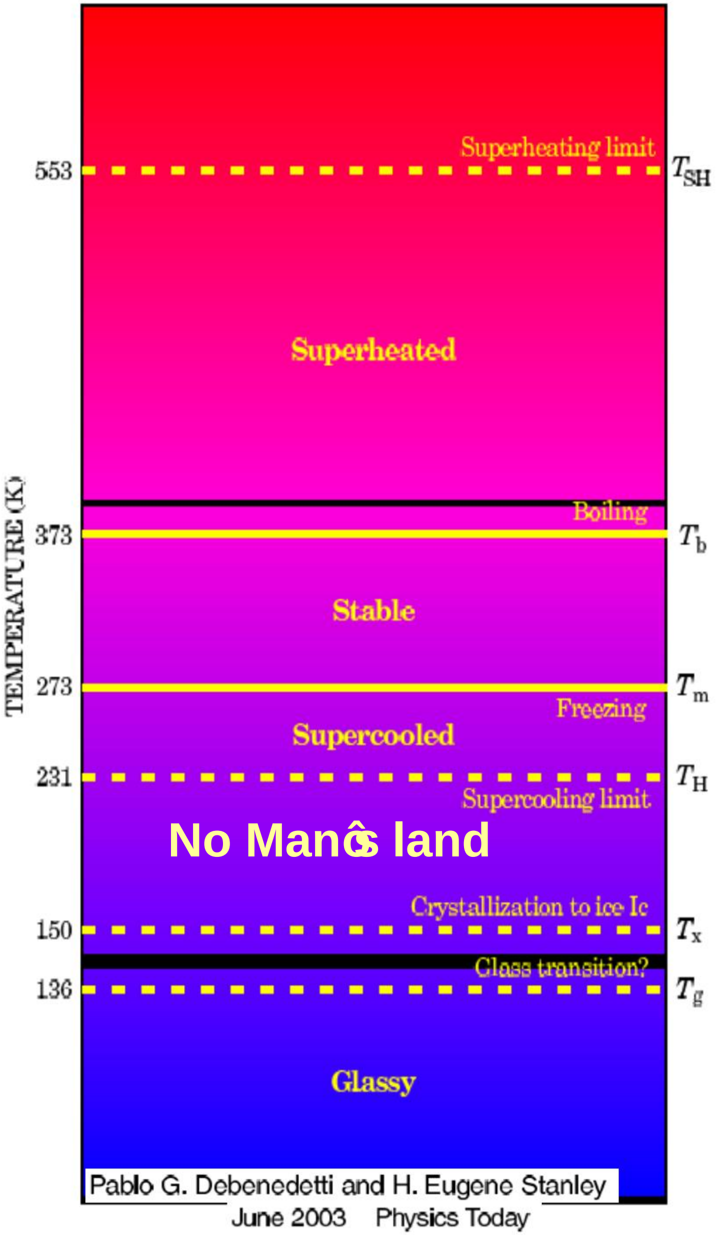
The corresponding shear force Fs transmitted between the surfaces, indistinguishable from the noise until adhesive contact

Pressure-like effects due to the presence of surface → Distorsion of HB → Solid transition is inhibited

Usually liquid confined water behaves like a gel,
but a very curious behaviour has been found, i.e. water can respond according to the allignement of rows of atoms in mica sheets, which like a ñegg cartonòmay force a ordering of eggs (Zhu et al.PRL 87 (2001)).

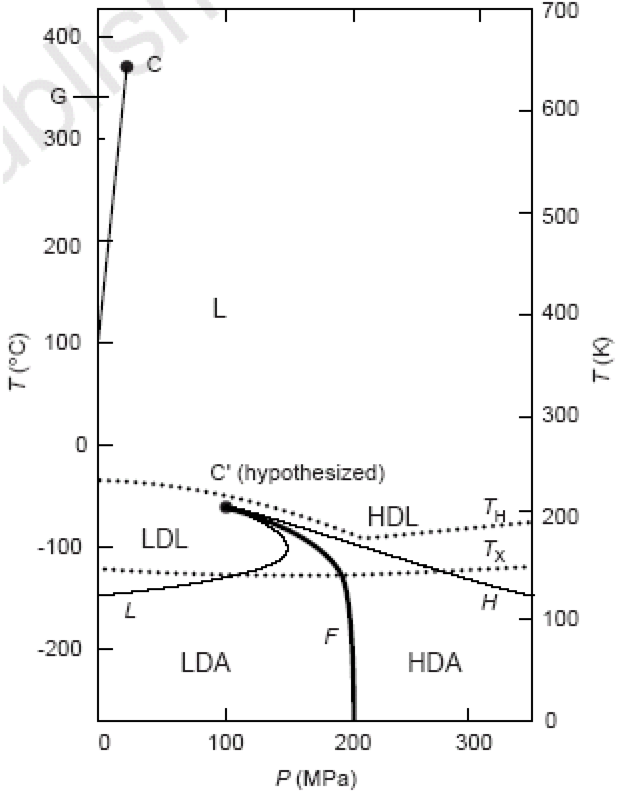


8. Inside the no manôs land



Liquid water can exist in a metastable form for T ranging from 231 K to 553 K.

Many interesting phenomena could happen in the so called No manôs land, such as the existence of a second critical point

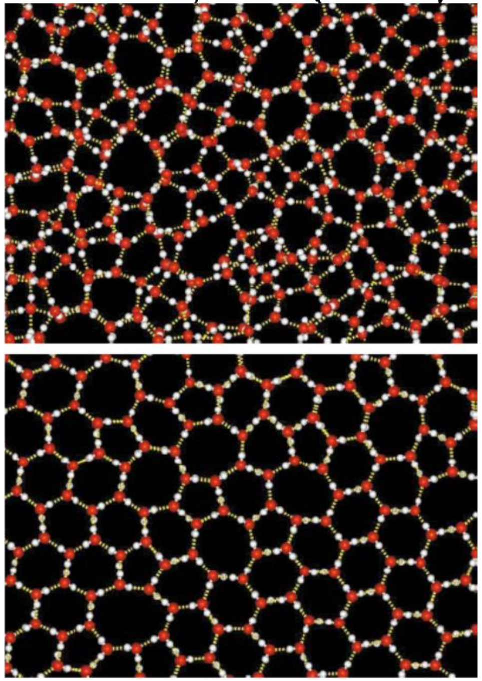


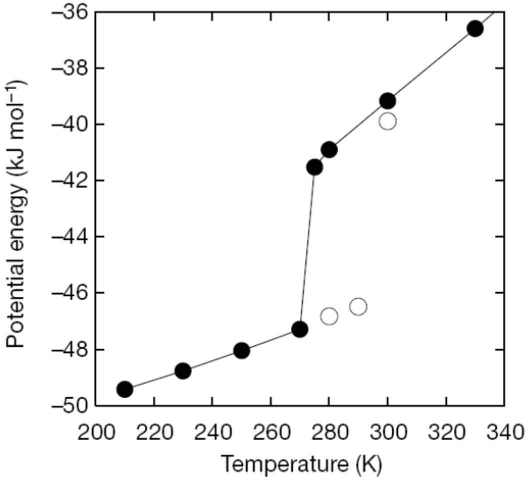
But homogeneous nucleation limit can be **bypassed** by confining water in sufficiently small pores

★ 8.First order transition in bilayer water between HDL and LDA

K.Koga et al Nature 408, 564 (2000)

On cooling, the extremely confined water, which has an imperfect random hydrogen-bonded network, transforms into a bilayer amorphous phase with a perfect network (owing to the formation of various hydrogen-bonded polygons) but no long-range order.





The sharp changes in energy and the hysteresis suggest a strong first-order phase transition.

Moreover, the diffusion constants calculated before and after the transition differ by four orders of magnitude, indicating the transition to a viscous glassy state.

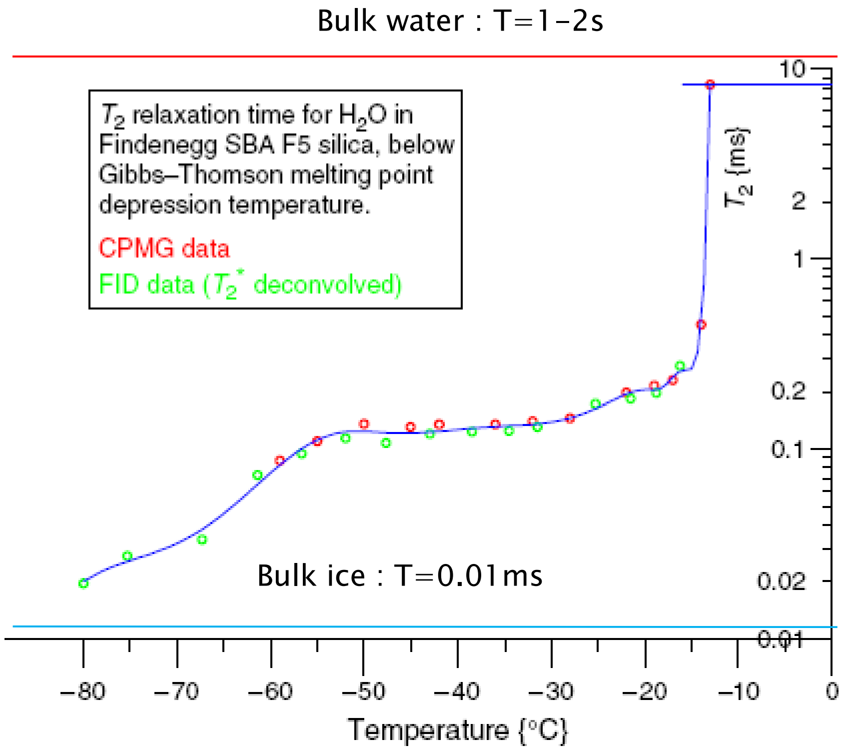
8. Changes in Nuclear Magnetic relaxation time say that

the transition to the glassy state is gradual

- The relaxation time of water in the pore is reduced due to the magnetization exhange between the protons and the surface

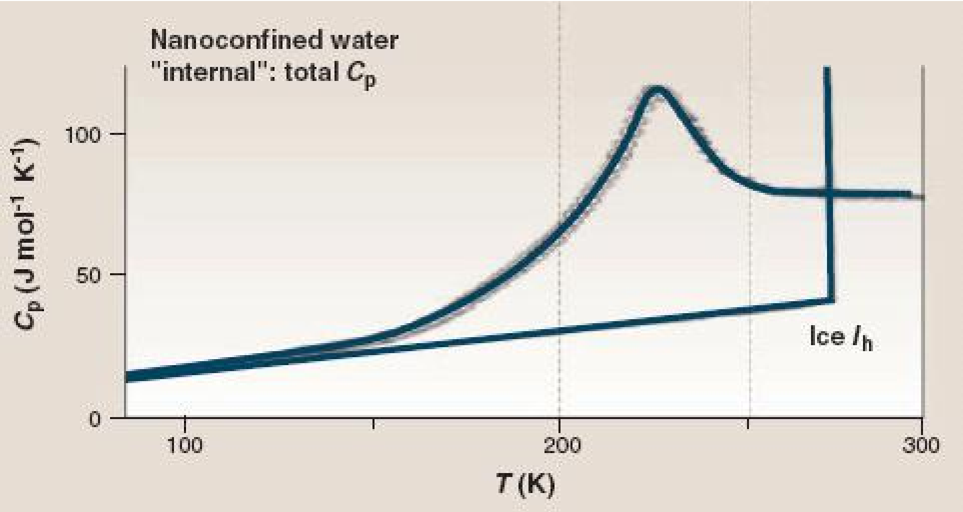
- The relaxation time of glass formed in the pores is increased over the value for bulk ice to an increased proton mobility (due to local defect or disorder in the solid state)

(B.Weber, J.Dore J. Phys.: Condens. Matter 16 (2004) S5449ï S5470)



Different glass formation mechanism (Angell, Science 319 (2008))

Glass is normally generated by a rapid cooling: its thermodynamic signature is a rapid drop of the heat capacity (as traslational, rotational degrees of freedom are frozen out).

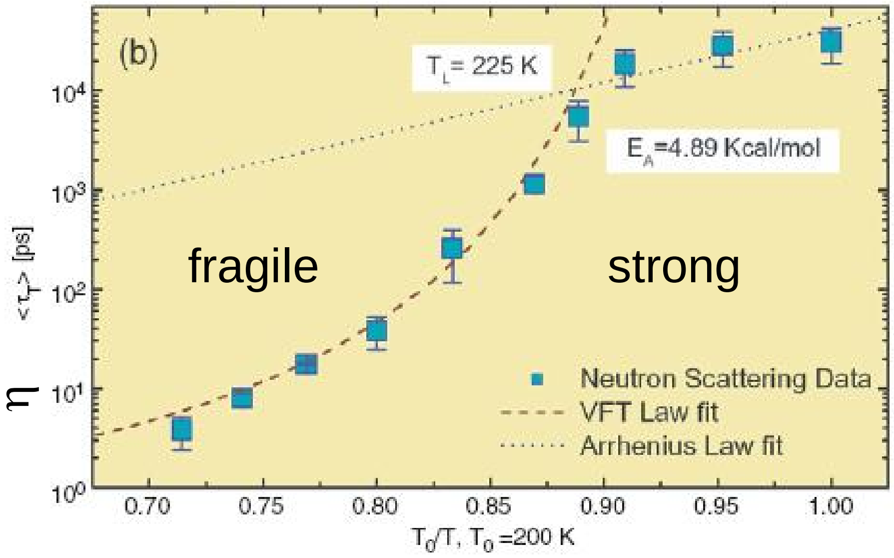


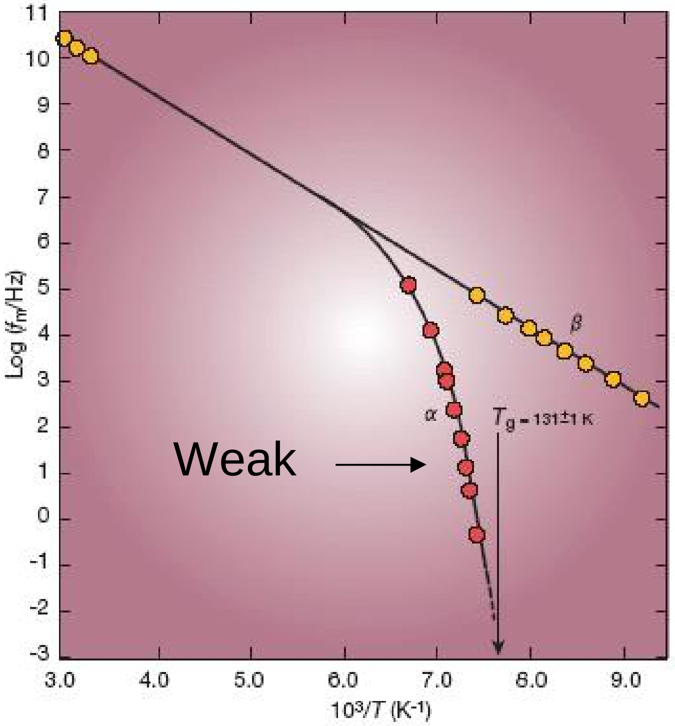
Water is a weak glass former, but crystallization can be avoided by confining water in small pores.

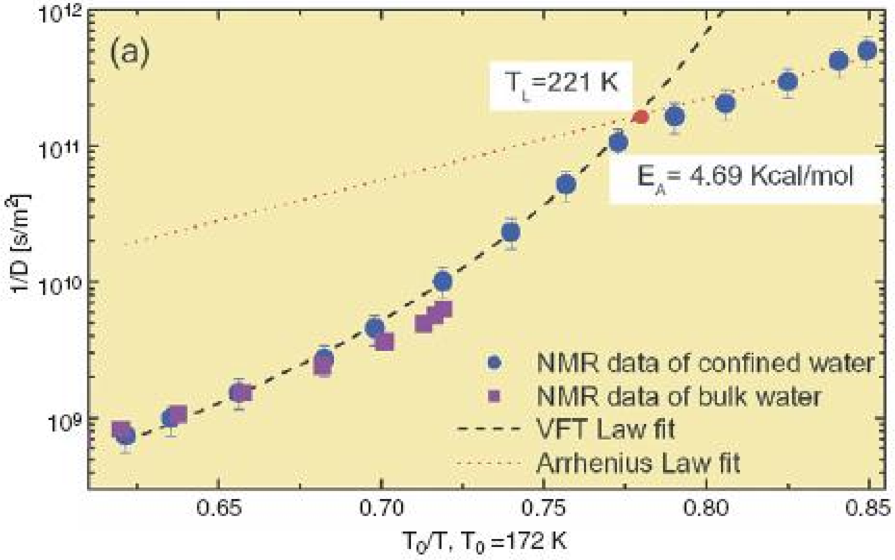
Confinement seems to act as a pressure and a **first order ñorder-disorderò transition** occurs at about 225K, as the transition is gradual.

At 225K confined water has also a **fragile-to-strong liquid transition**

What happens is a decoupling of rotational and translational diffusion, with the result that a single relaxation regime splits into two components the slowest of which (non-Arrhenius, rotational) disappears at 225K.





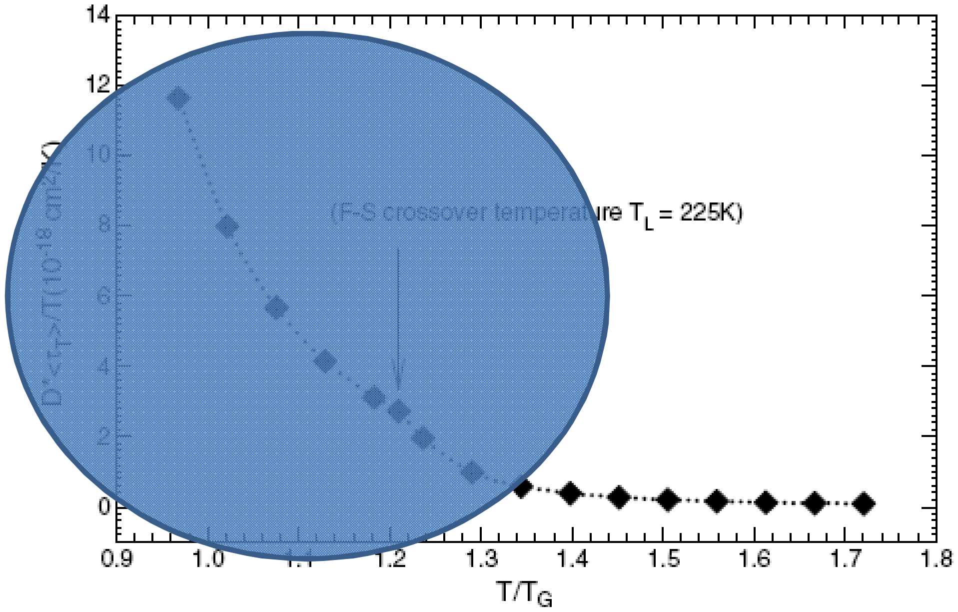


(Faraone et al J.Chem.Phys. 22 (2004), F.Mallamace et al. J. Phys.: Condens. Matter 18 (2006))

Violation of Stokes-Einstein equation

But there is also a decoupling between translational diffusion D and viscosity η which is proportional to the translational relaxation time ***Ű***

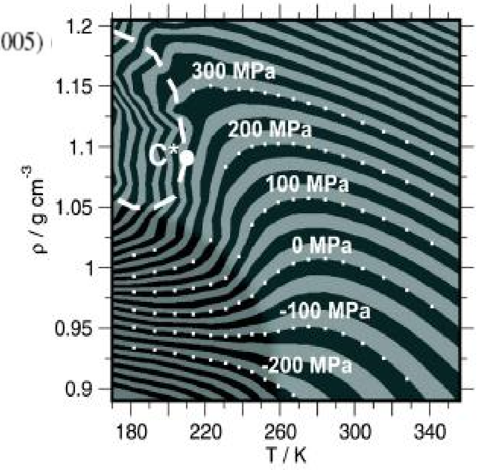
This implies that Stokesï Einstein equation relating the self-diffusion constant *D,* viscosity ɖ and temperature T : D ~ T/ɖ, i.e. DŰ/T ~ const. is violated.

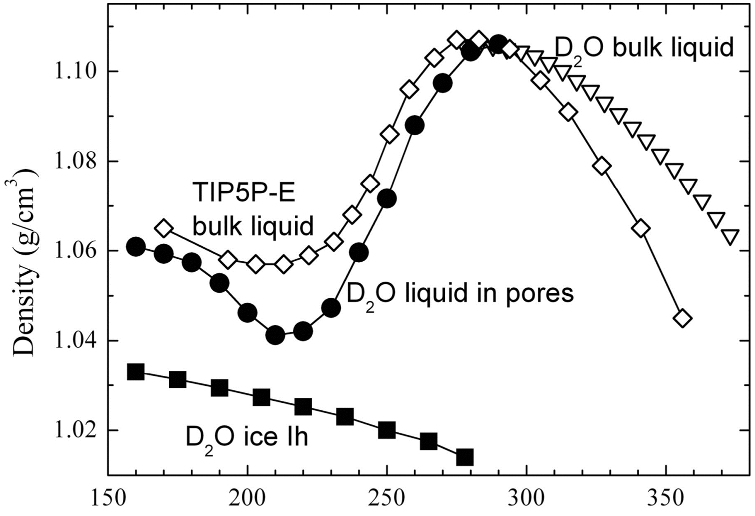


Existence of a density minimum in deeply supercooled confined water

Numerical studies have predicted the existence of a density minimum in deeply supercooled water

PRL 94, 217802 (2005)





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Recently SANS measures performed using confined water in naporous materials, have confirmed this prediction.

What happens at **microscopic structure**?