Inelastic X-Ray Scattering as a Probe of the Dynamics in Complex and Hybrid Materials

Alessandro Cunsolo
(NSLS II-Brookhaven National Laboratory)

11th Conference on Inelastic X-Ray Scattering-IXS2019
June, 23-28 2019

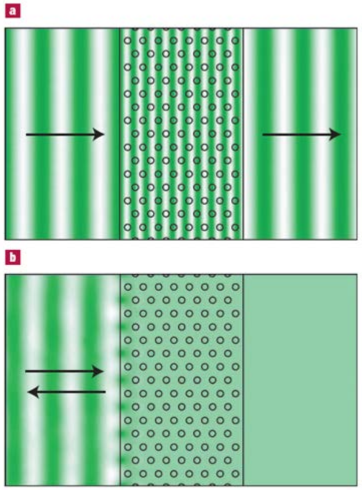
Summary

- A brief introduction to phononics
- The case of diluted NP suspensions
- “Guiding” sound waves in water upon confinement in carbon nanotubes
- Perspectives

What is phononics?

J. Martinez-Sala et al. Nature **378**, 241, (1995).

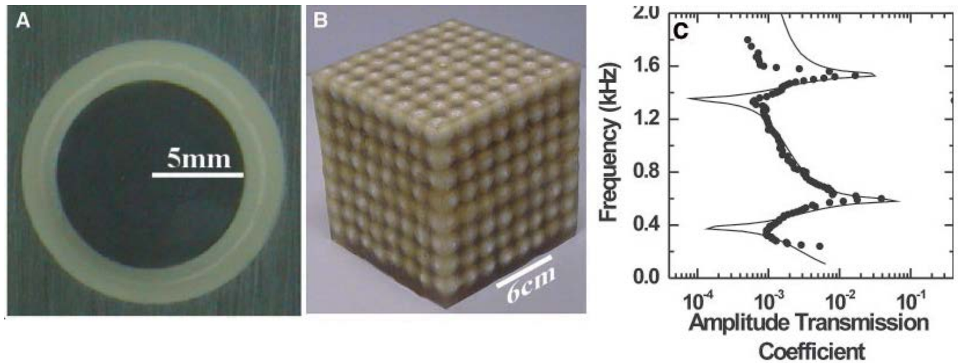
Kinematic Sculpture by Eusebio Sempere
Juan March Foundation Madrid



Phononic crystal have a structural arrangement deeply interfering with acoustic waves (phonons) of certain frequencies which cause the latter to be reflected, trapped, slowed down or even stopped (phononic gaps)

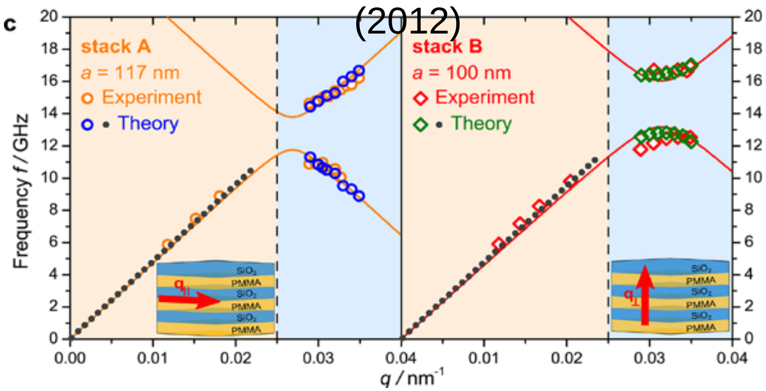
From sonic to hypersonic frequencies

Liu, Z. et alk. *Science*, *289*(5485), 1734 (2000).



The manipulation of **ultrasonic** waves requires assemblies structured at cm scales

D. Schneider et al. Nano Lett. **12**, 3101 (2012)

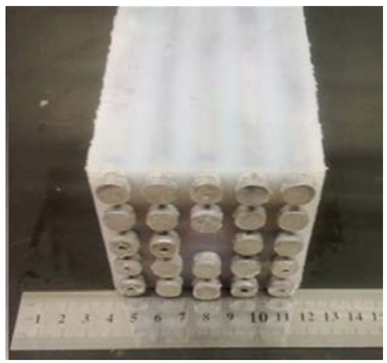


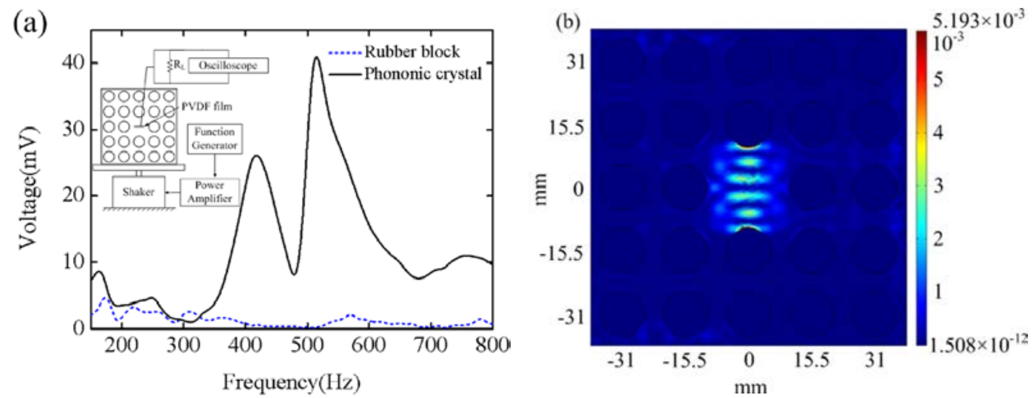
Hypersonic waves can be "stopped" propagation gaps using materials structured in the μm-range

cONTROL OF PHONON PROPAGATION IN COMPOSITE MATERIALS

Hangyuan Lv et al. Appl. Phys. Lett. **102**, 034103 (2013);

Phononic crystals, metamaterials: artificial periodic structures made of two different elastic materials





Maldovan, Nature (2013)

Energy harvesting!!

The phononic spectrum

IXS

MANIPULATION OF SOUND AND HEAT IN A LARGE FREQUENCY SPECTRUM

MAINLY ORDERED, NANOSTRUCTURED
PHONON PROPAGATION INSIDE A HYBRID SYSTEM WITH INELASTIC X RAY SCATTERING

ACS NANO
Cite This: ACS Nano 2019, 13, 8867−8874
www.acsnano.org

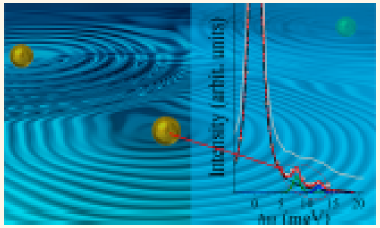
Damping Off Terahertz Sound Modes of a Liquid upon Immersion of Nanoparticles

Alessio De Francesco,[†] Luisa Scaccia,[‡] Marco Maccarini,[§] Ferdinando Formisano,[†] Yugang Zhang,[∥] Oleg Gang,[⊥,#] Dmytro Nykypanchuk,[⊥] Ayman H. Said,[∇] Bogdan M. Leu,[∇,∞] Ahmet Alatas,[∇] Yong Q. Cai,[∥] and Alessandro Cunsolo*[∥]

[†]Consiglio Nazionale delle Ricerche, Istituto Officina dei Materiali c/o OGG Grenoble 38043, France
[‡]Dipartimento di Economia e Diritto, Universita' di Macerata, Via Crescimbeni 20, 62100 Macerata, Italy
[§]Laboratoire TIMC/IMAG UMR CNRS 5525, Université Grenoble-Alpes, Grenoble 38042, France
[∥]National Synchrotron Light Source II and [⊥]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States
[#]Department of Chemical Engineering and Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, United States
[∇]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States
[∞]Department of Physics, Miami University, Oxford, Ohio 45056, United States

Supporting Information

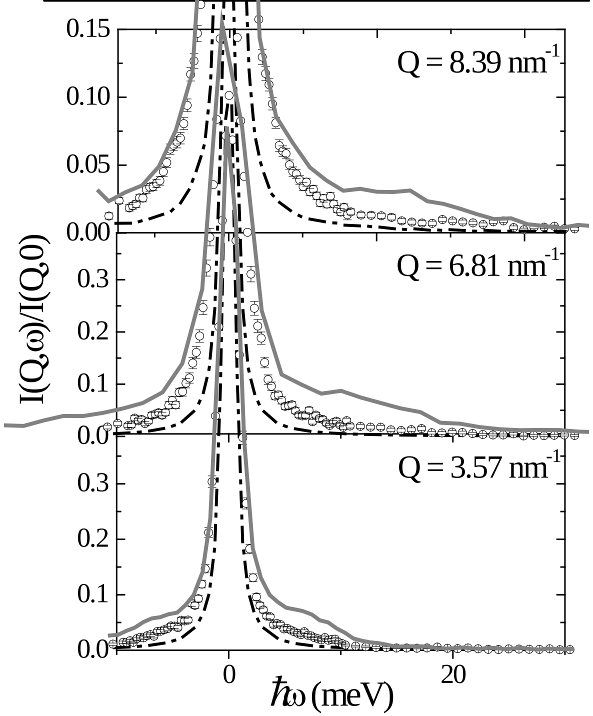
ABSTRACT: The control of phonon propagation in nanoparticle arrays is one of the frontiers of nanotechnology, potentially enabling the discovery of materials with unknown functionalities for potential innovative applications. The exploration of the terahertz window appears quite promising as phonons in this range are the leading carriers of heat transport in insulators and their control is the key to implement devices for heat flow management. Unfortunately, this scientific field is still in its infancy, and even a basic topic such as the influence of floating nanoparticles on the terahertz phonon propagation of a colloidal suspension still eludes a firm answer. Shedding some light on this topic is the main motivation of the present work, which focuses on inelastic X-ray scattering (IXS) measurements on a dilute suspension of Au nanospheres in water. Measured spectra showed a nontrivial shape displaying multiple inelastic features that, based on a Bayesian inference analysis, we assign to phonon modes propagating throughout the nanoparticle interior. Surprisingly, the spectra bear no evidence of propagating modes, which are known to dominate the spectrum of pure water, owing to the scattering that these modes suffer from the sparse nanoparticles in suspension. In perspective, this finding may inspire simple routes to manipulate high-frequency acoustic propagation in hybrid—liquid and solid—materials.



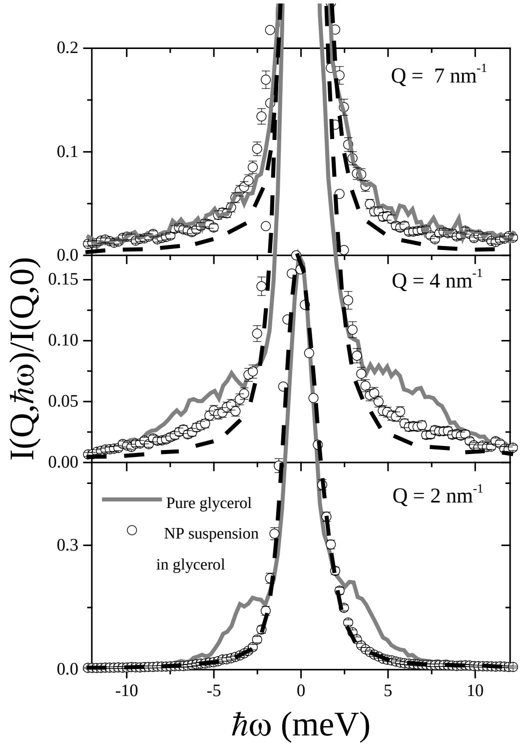
KEYWORDS: *inelastic X-ray scattering, colloidal systems, phonon propagation, water, nanoparticles, Bayesian analysis*

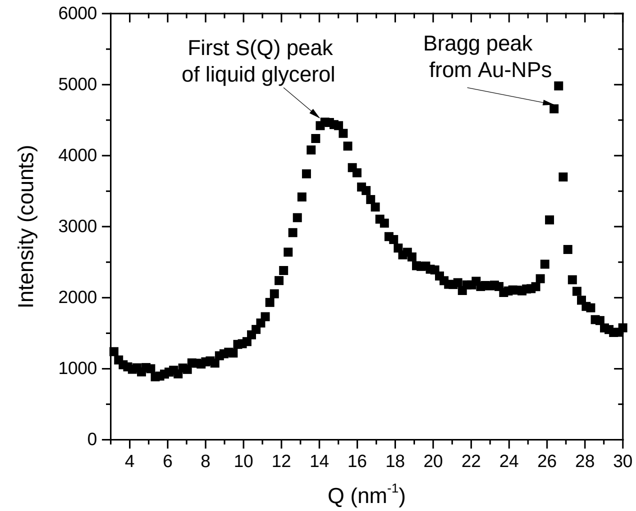
Damping off collective modes of the hosting liquid in very diluted colloidal suspensions

Au nano-rods in water
ϕ=10 nm, l=40 nm
0.05% (volume) concentration



Au nano-spheres in glycerol
ϕ=10 nm 0.05% volume concentration



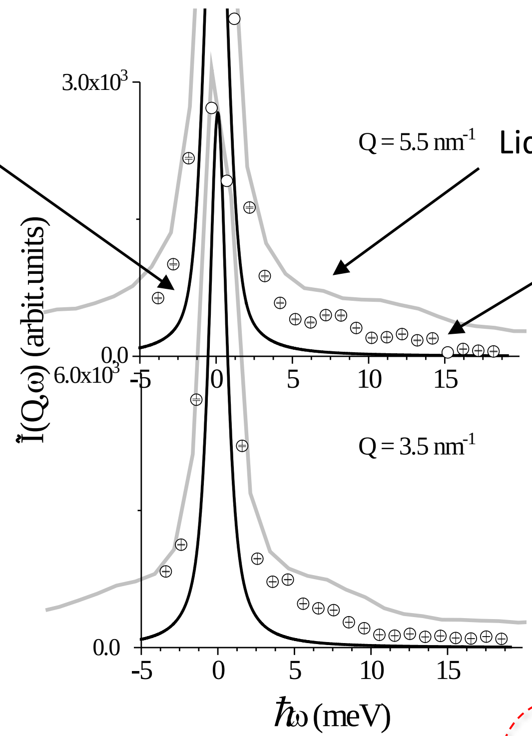


De Francesco et al. submitted to ACS Nano

Suspension of Au nano-spheres crystal (ϕ=50 nm) in liquid water at room T
volume concentration = 0.5 %

Resolution ~1.5 meV

Liquid water



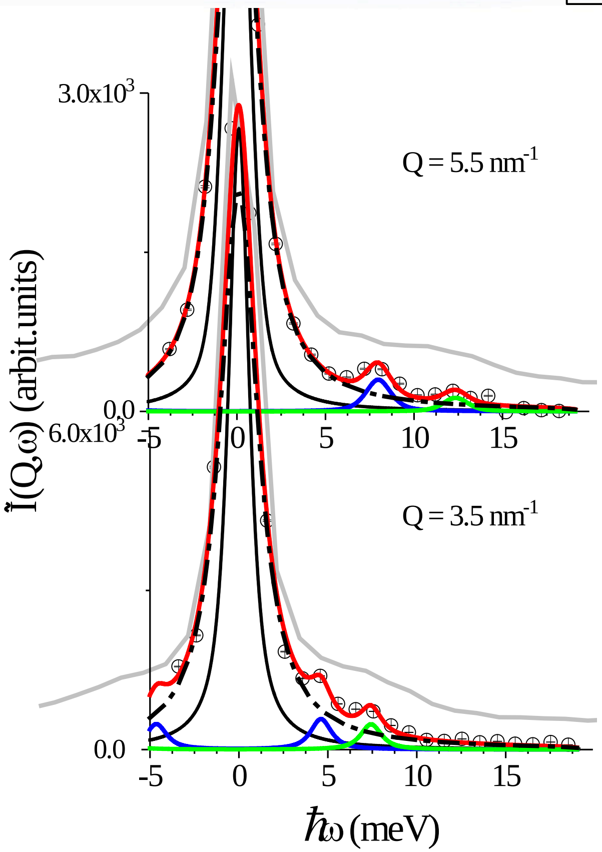
No apparent sign of the liquid collective dynamics

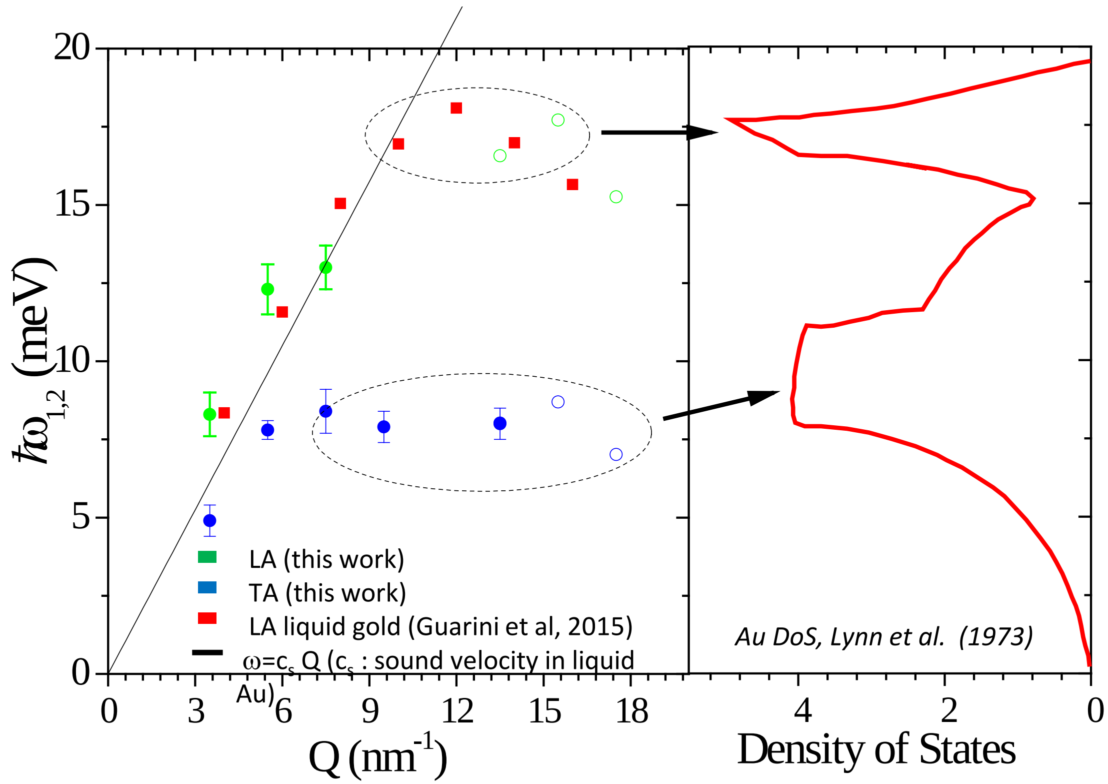
Small peaks emerge

$$\tilde{S}(Q,E) = A_e(Q)\delta(E) + [n(E)+1]\left\{L_{A_0,z_0}(Q,E) + \sum_{j=1}^{k} A_j(Q)\delta_j(E \pm \bar{E}_j)\right\}$$

Bayesian inference based hypothesis test
on the number of modes k

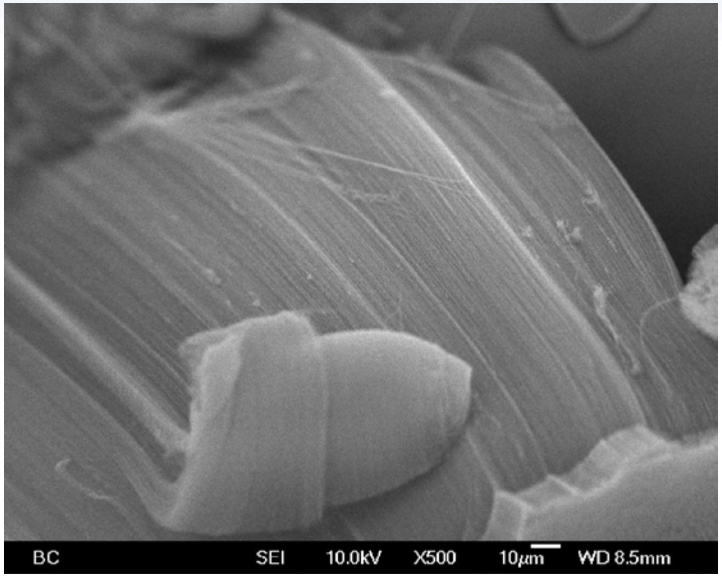
DISPERSION CURVES

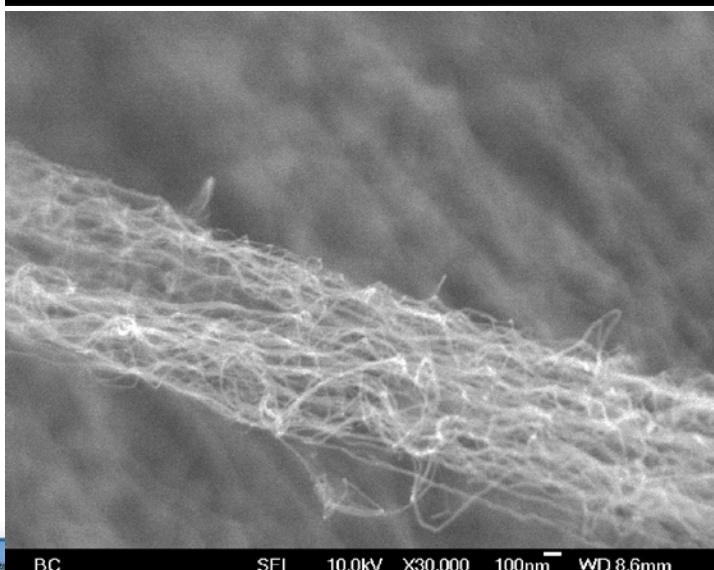




The experiment can only probe the ongitudinal and transverse collective dynamics from Au NPs
Water dynamics damped by NP-induced scattering of phonons with Au NP ?

Water confined in nanotubes: few hints from existing literature



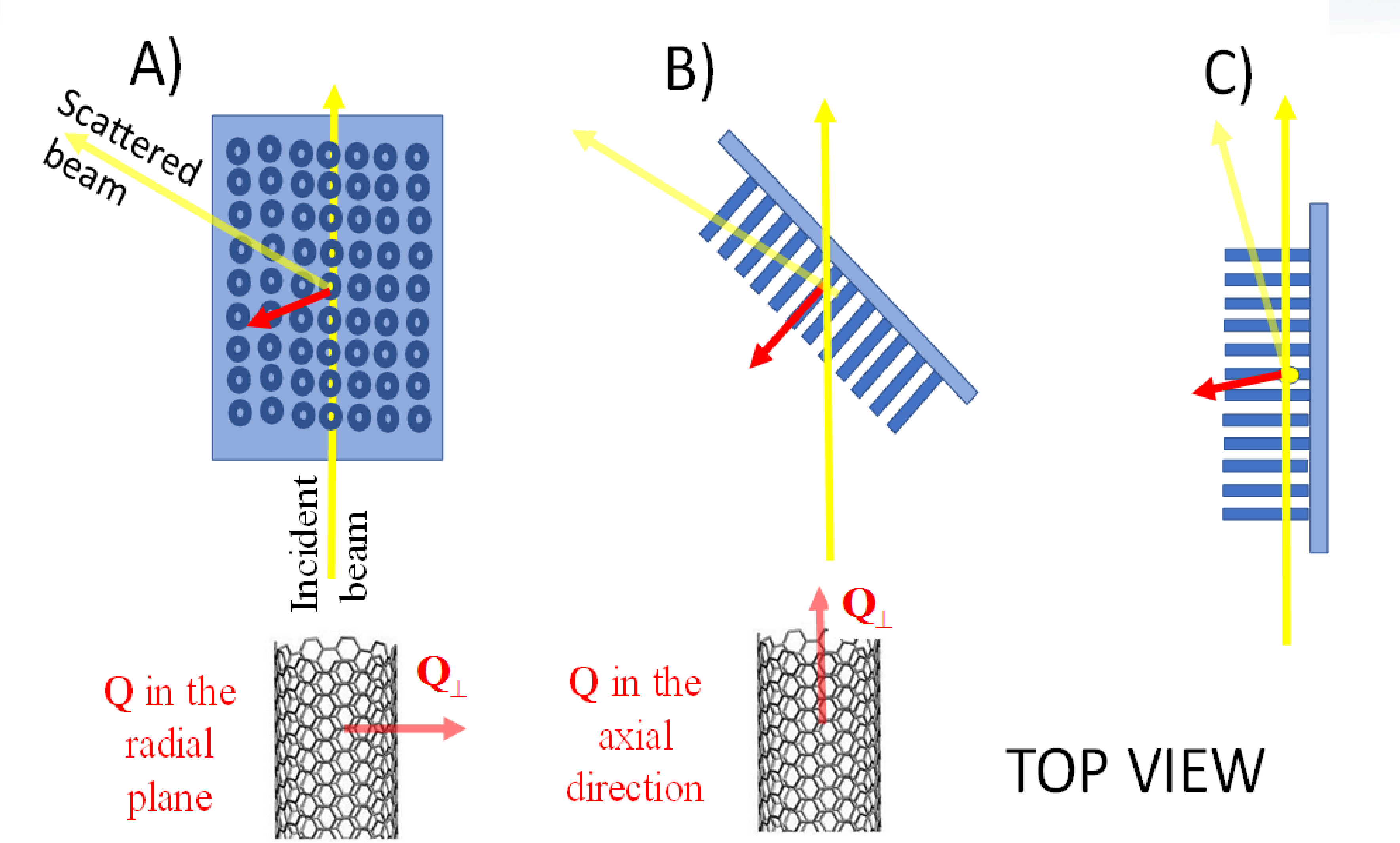


Two main evidences emerging from the large body of literature results:

- The confinement in CNTs induces a layered structure on water which favours diffusive flow in the axial direction.

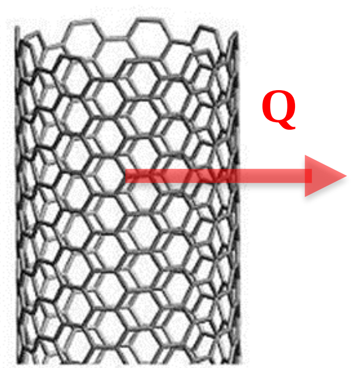
- Although this unidimensional confinement reduces the number of hydrogen bonds it makes them more directional and preferentially directed along the CNTs axis.

The two scattering geometries considered



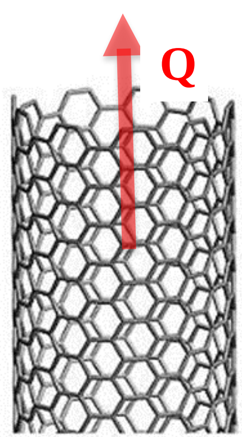
A scheme of the *a priori* expected outcome

Q in the radial plane



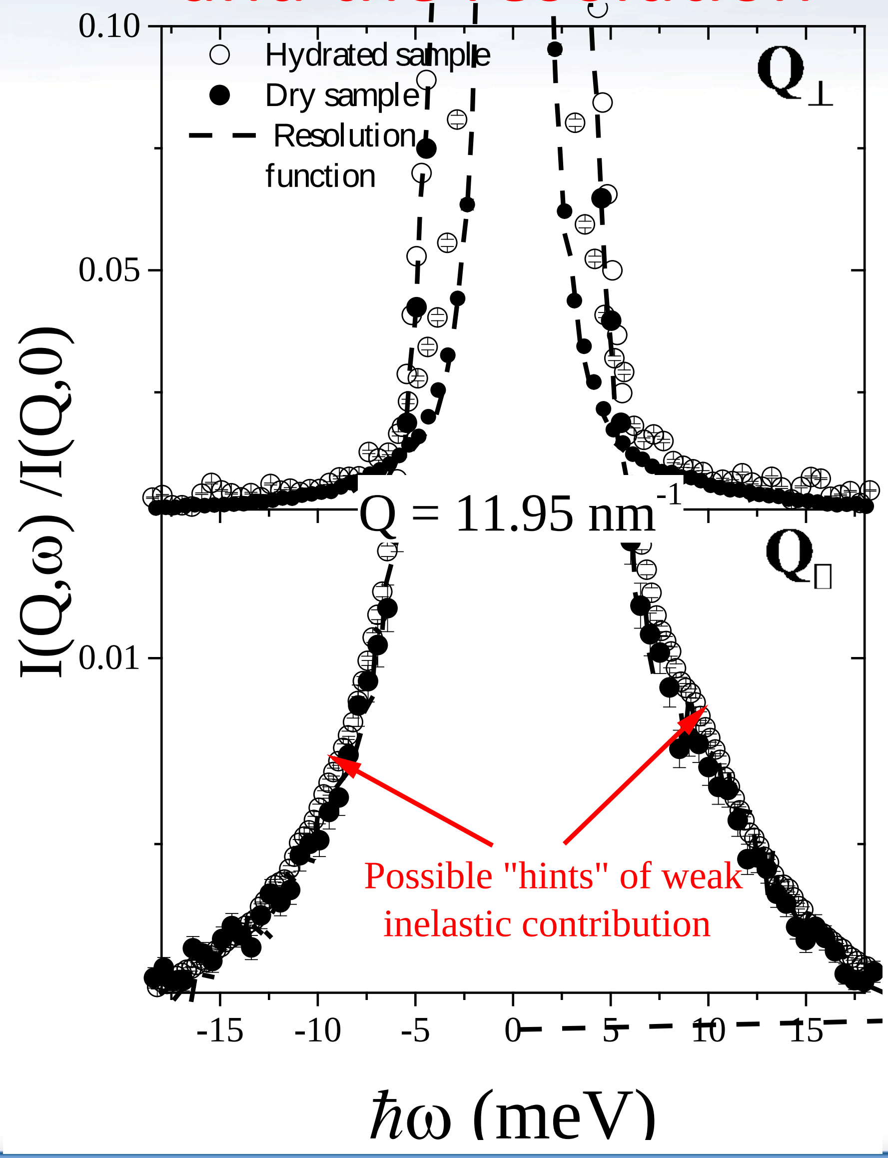
Only **transverse** modes of watercan propagate in the basal plane (⊥ **Q)**

Q in the axial direction

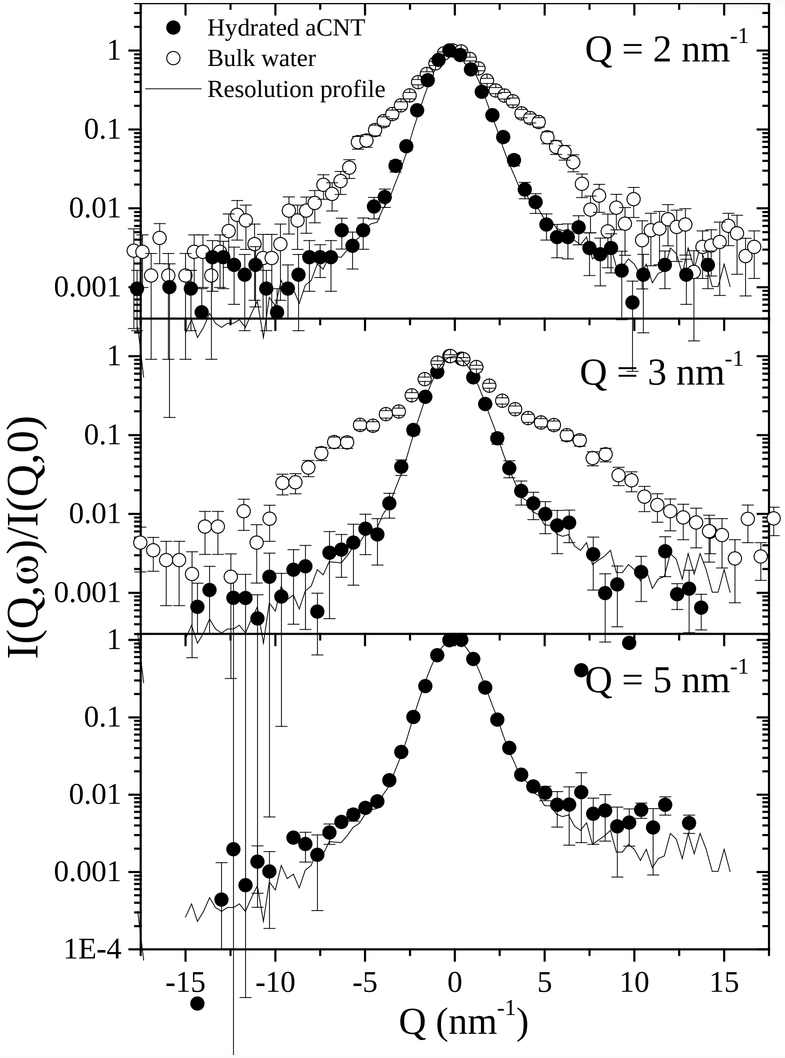


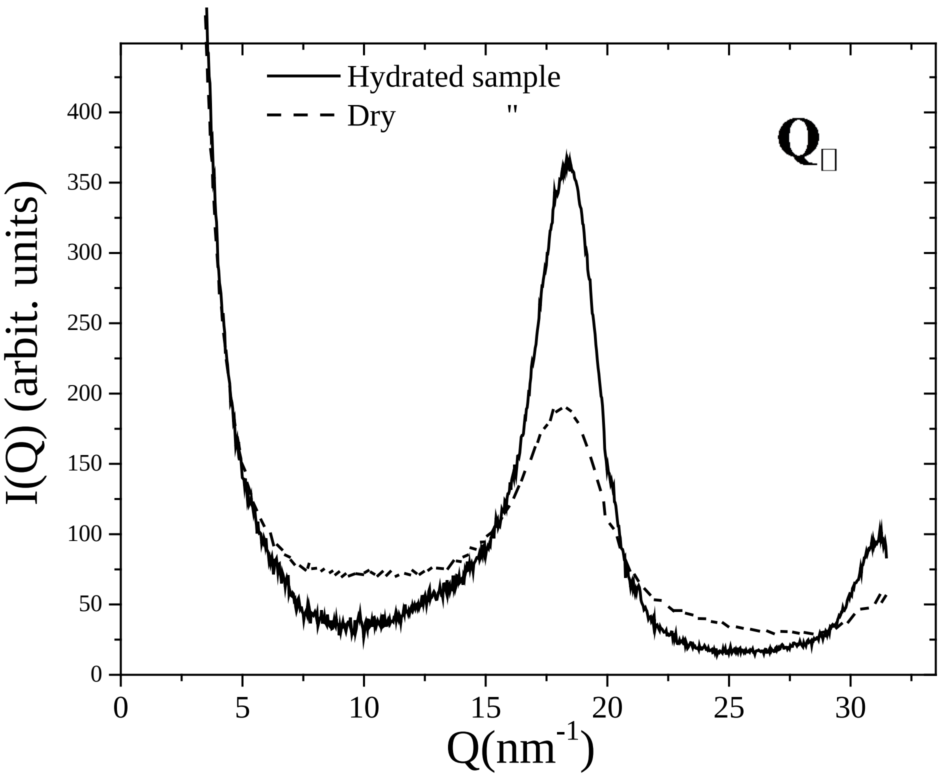
Only **longitudinal** modes of water can propagate along the CNT axis (|| **Q)**

IXS spectra from the hydrated sample, the dry sample and the resolution

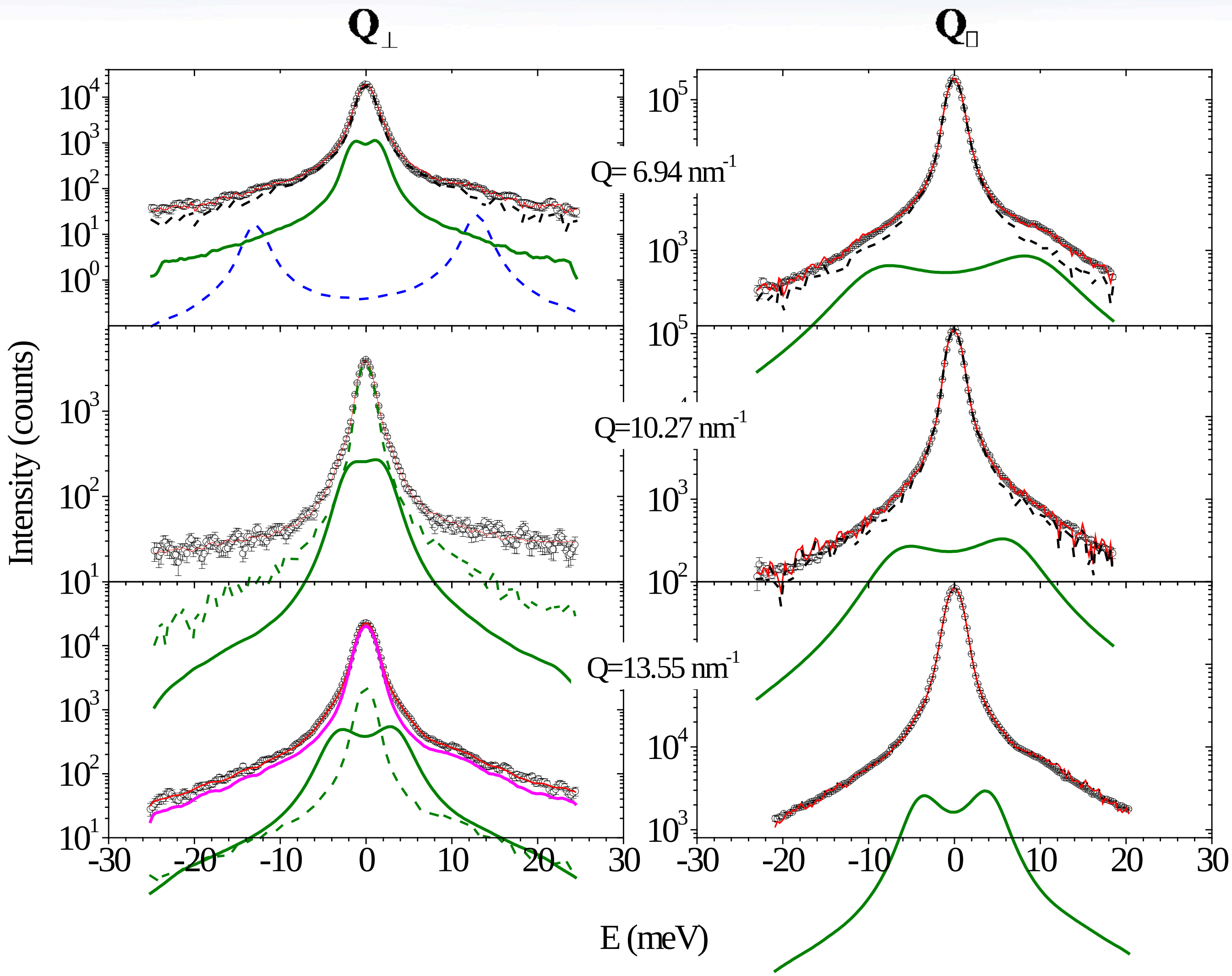


The IXS and GISAXS measurements at NSLS II

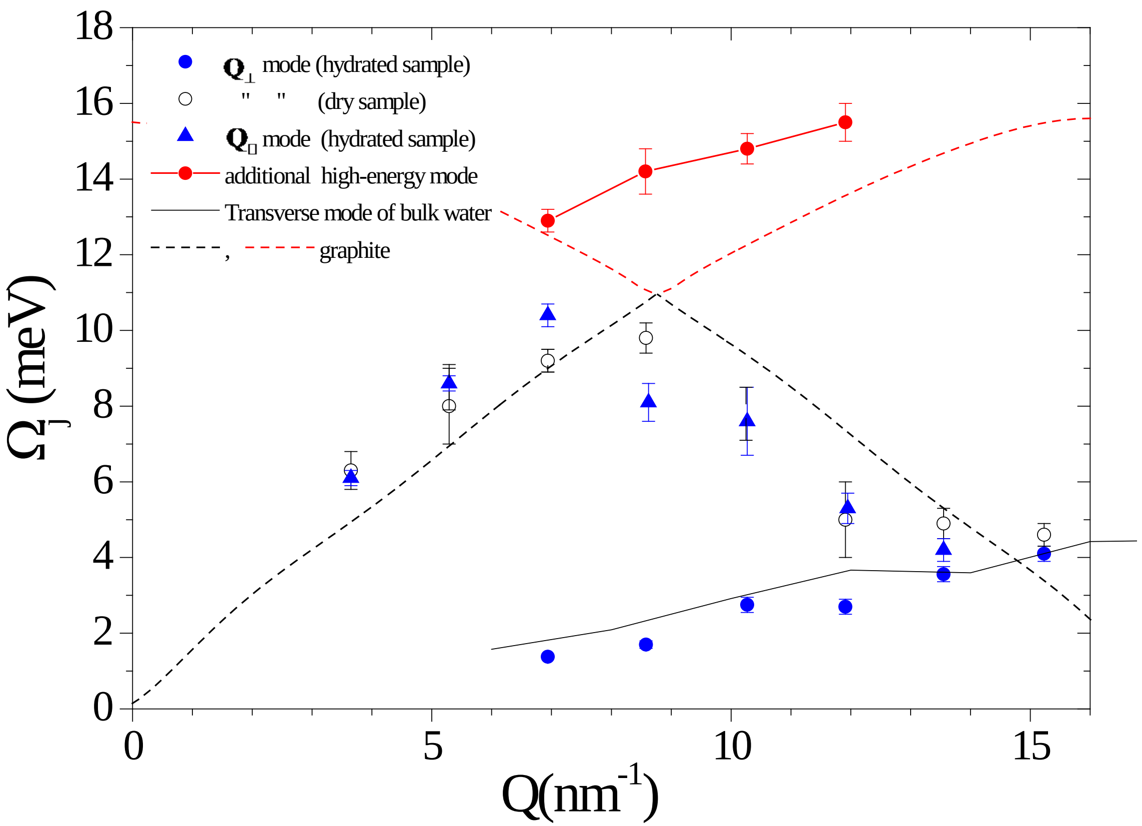




Multiple DHOs+δ(ω) modelling of the lineshape



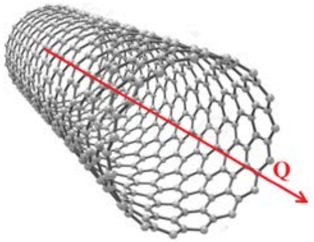
The sound dispersion curves



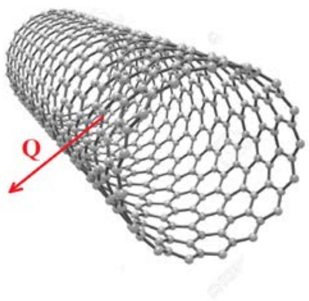
Conclusion (I)

- **The immersion of limited amount of nanoparticles appears a remarkably efficient method to damp off collective excitations in liquids !**

Conclusion (II)



1) Axial (Out of plane) orientation of **Q** $\Rightarrow$ The hydrated array behaves as a nearly perfect **acoustic damper** for confined water, the only inelastic features surviving in the spectrum from hydrated aCNTs are phonons of the carbon matrix.



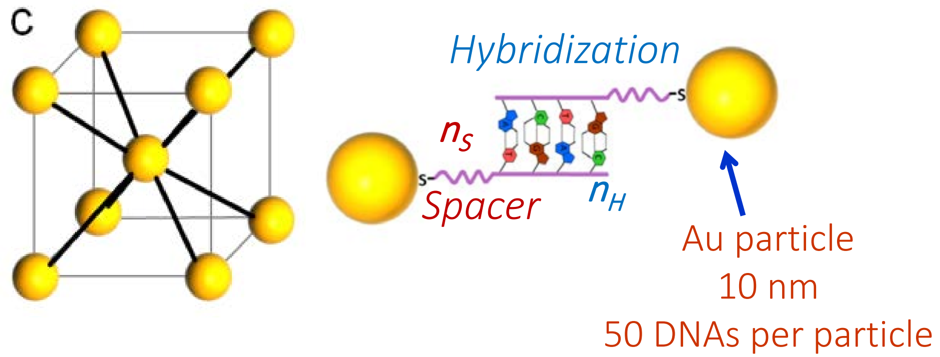
2) Radial (In-plane) orientation of **Q** $\Rightarrow$ only the **transverse mode** is allowed to propagate through the CNTs. The hydrated array behaves as a polarization filter for acoustic excitations in water.

Looking ahead

Simple method to manipulate heat transport through a slight perturbation of the liquid structure: new avenues in the emerging field of phononics ?

I: ice, other liquids, different NP and sizes, T, ……

II: Phonons propagation when the floating assembly is ordered: INS/IXS measurements on superlattice of NP suspended in water.
Tunable structural parameters (bond strengths, distance), shape and size.

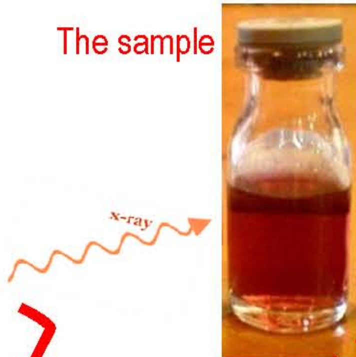


III: Development of new, programmable super-lattice assemblies of nanoparticles functioning as phononic crystals: Using the most advanced nanotechnology we aiming at searching new hybrid metamaterials to implement acoustic manipulation based upon structural engineering

- Extension of phononics to the unexplored THz realm → implementation of heat flow management based upon the design of nanostructure

The outcome of experiments: what can **we learn** from phonon propagation in programmable nanoparticle assemblies?

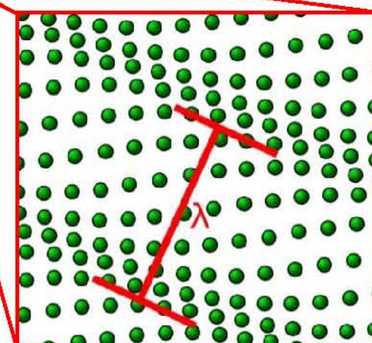
The sample



- Inter-particle phonons: insight on the (tunable) strength of particle linkage
- How phonons are linked to the particle shape and the size? A completely unexplored field....
- How does the damping of phonon relates to macroscopic viscosity of the system? The importance of parallel rheology measurements

Intermediate scale

Probing inter-particle phonons



- The physics of nm-sized elements is very peculiar and still full of mysteries (different thermodynamics, size-driven metal-to insulator transition, etc....)
- How do intra-particle phonons depend on the particle shape and size? Are they coupled with normal vibrational mode at the particle interface?
- At the highest Qs (ballistic regime) the single particle velocity can be probed, providing insight on the local microscopic viscosity.

Smaller scales

Probing intra-particle phonons