High resolution inelastic X Ray measurements on soft matter systems: current results and future perspectives

Alessandro Cunsolo
(NSLS II-Brookhaven National Laboratory)

X-Ray Echo Spectroscopy - Opportunities and Feasibility
APS, September, 8-10 2016

U.S. DEPARTMENT OF ENERGY | Office of Science

BROOKHAVEN NATIONAL LABORATORY | National Synchrotron Light Source II

Outline

- Part I: Polyamorphism (PA) phenomena studied by IXS
  - Introduction
  - The case of amorphous germania (a-GeO_2)
  - Looking ahead
- Part II: Manipulating THz acoustic excitations
  - Phonon propagation on nanoparticle super-lattices.
  - Sound propagation and heat management
  - Preliminary IXS and computational results

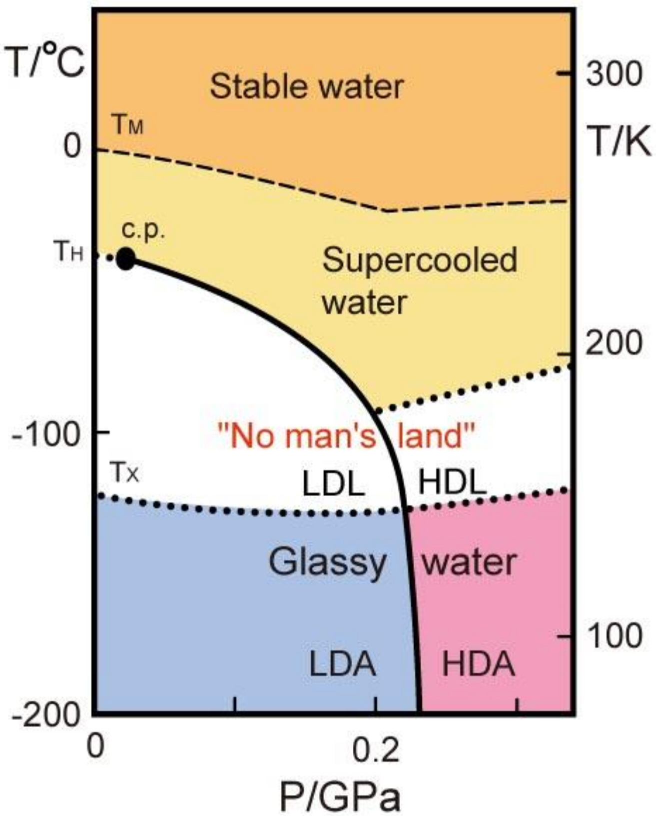
Part I: Polyamorphism (PA) phenomena studied by IXS

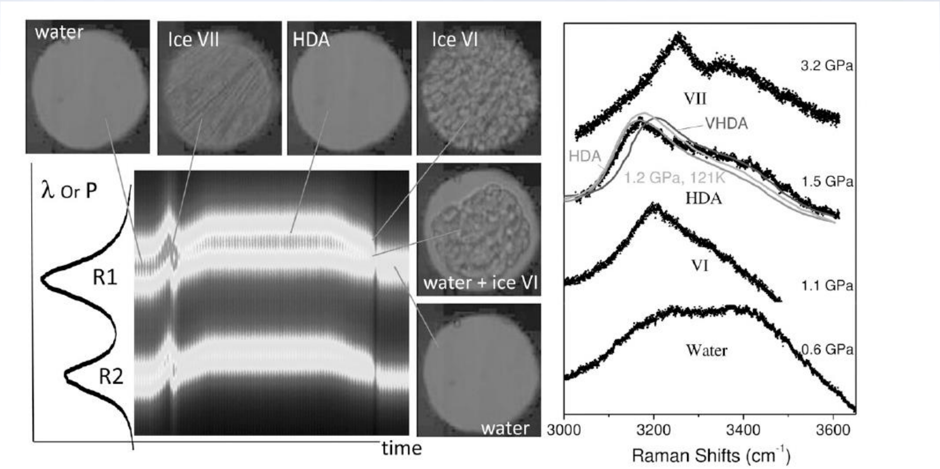
- Polyamorphic (PA) transitions are often difficult to observe. They often happen in metastable thermodynamic regions, where they are overshadowed by competing effects, such as glass transition or crystal nucleation.

- It is commonly believed that ideal candidates to observe PA transitions are systems with an intrinsically open, often tetrahedral, local structure.

Phenomena of polyamorphism in water

J.-Y. Chen and C.-S. Yoo, PNAS **108** 7685–7688 (2011)

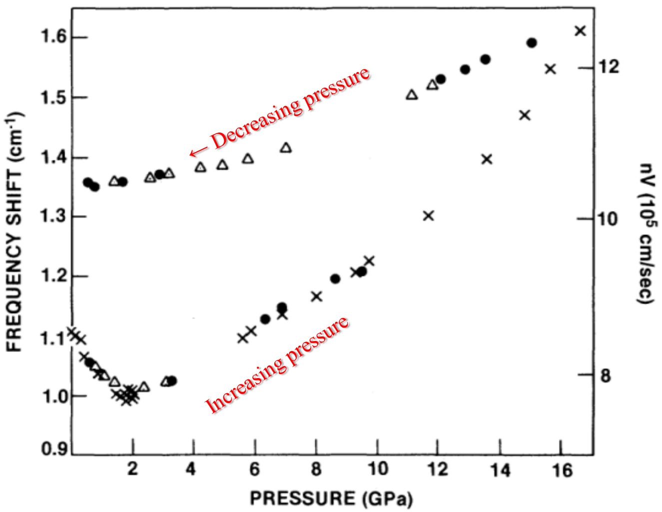




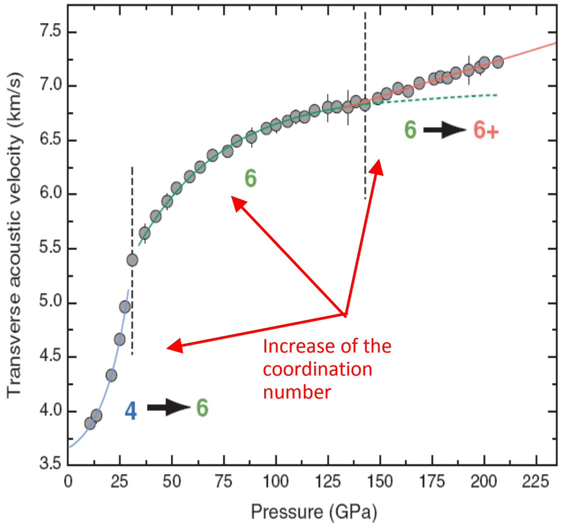
Polymorphic Transitions of Amorphous Materials: Effects on the Dynamics

Amorphous silica (a-SiO_2)

M. Grimsditch, Phys. Rev. Lett. **52**, 2379 (1984)



M. Murakami and J. D. Bass Phys. Rev. Lett.**104**, 025504 (2010)



- PA transition suggest an interplay between structural and dynamic property (sound velocity) at least in the continuum limit probed by Brillouin light scattering.
- IXS can in principle elucidate what is the signature of PA phenomena at mesoscopic scales.

SCIENTIFIC REPORTS

OPEN

Received: 09 July 2015
Accepted: 15 September 2015
Published: 13 October 2015

Signature of a polyamorphic transition in the THz spectrum of vitreous GeO_2

Alessandro Cunsolo[1], Yan Li[2], Chaminda N. Kodituwakku[1], Shibing Wang[3], Daniele Antonangeli[4], Filippo Bencivenga[5], Andrea Battistoni[5,6], Roberto Verbeni[7], Satoshi Tsutsui[8], Alfred Q. R. Baron[8,9], Ho-Kwang Mao[10,11], Dima Bolmatov[1] & Yong Q. Cai[1]

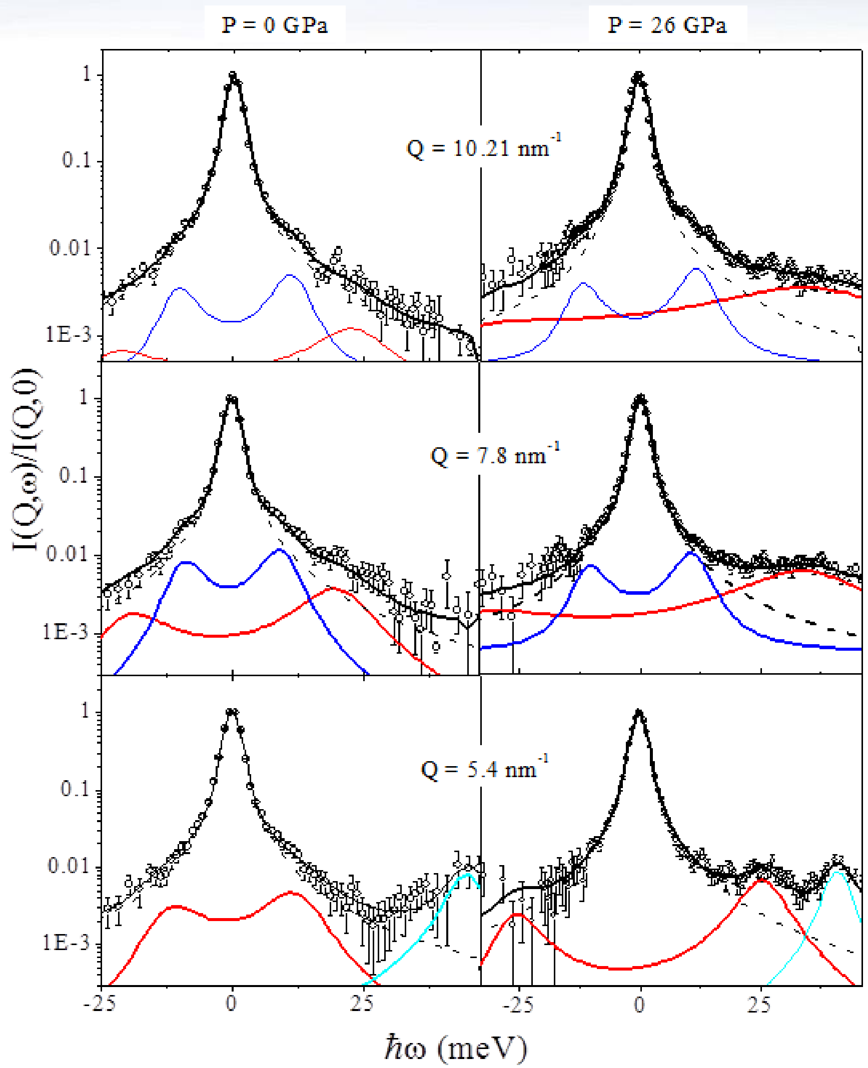
Purpose of the experiment

- Looking for signatures of a PA transition in the THz spectrum of density fluctuations.

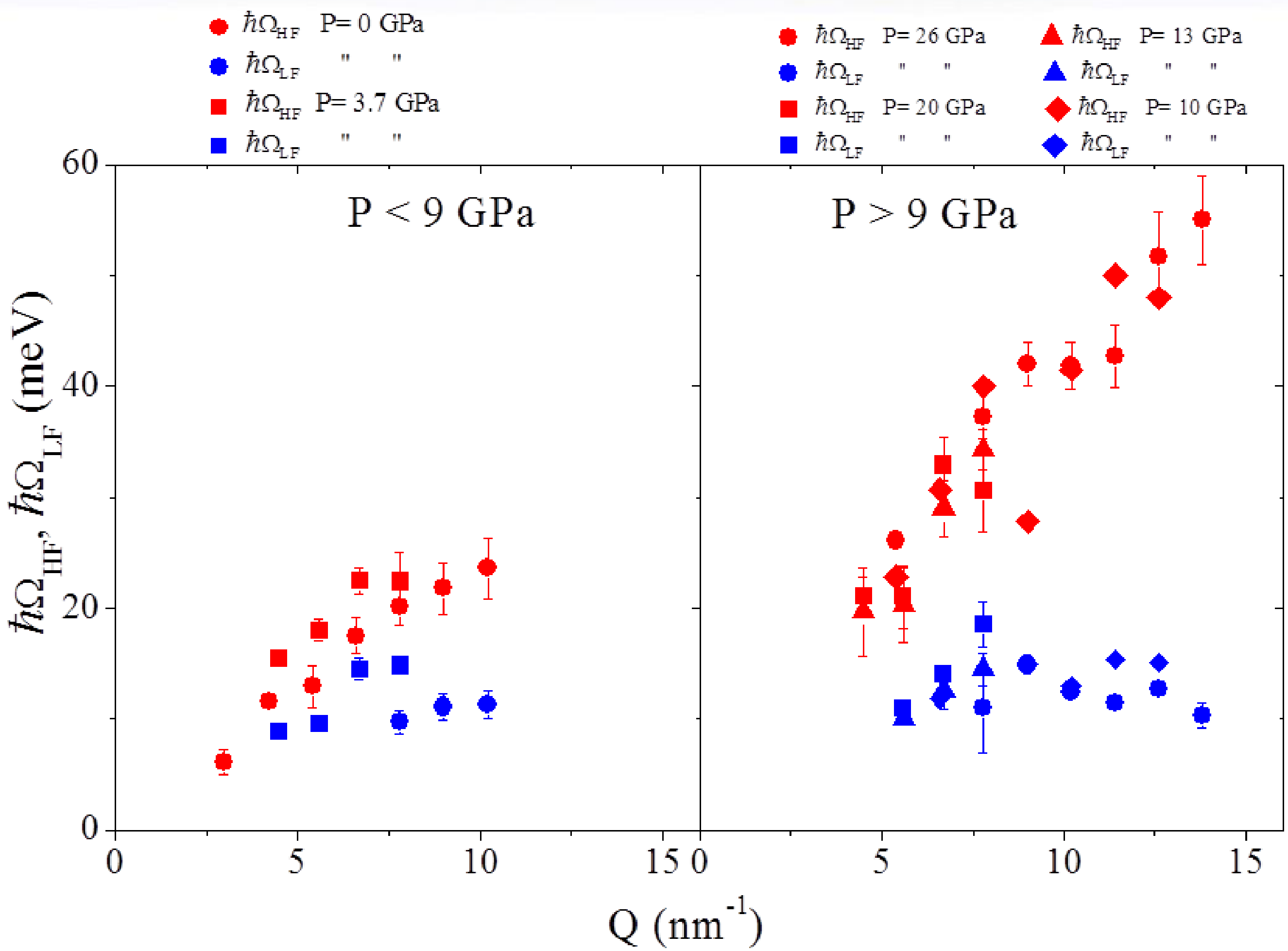
The a-GeO_2 sample

- As compared to its structural analogous (SiO_2) GeO_2 has a larger unit cell, which makes it prone to important structural changes even at moderate pressures.
- Furthermore, the absorption length of GeO_2 roughly matches the typical thickness of samples embedded in Diamond Anvil Cells (DACs).

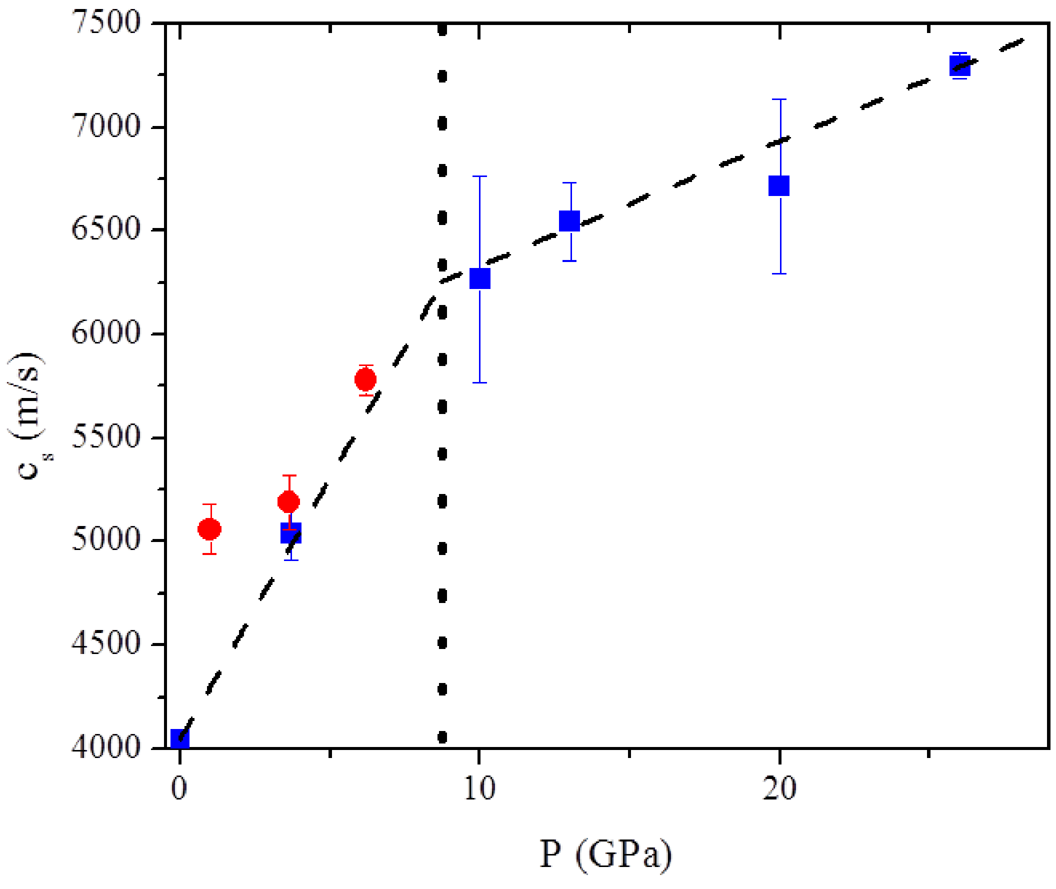
Measurement of the IXS spectra below and above the PA transition



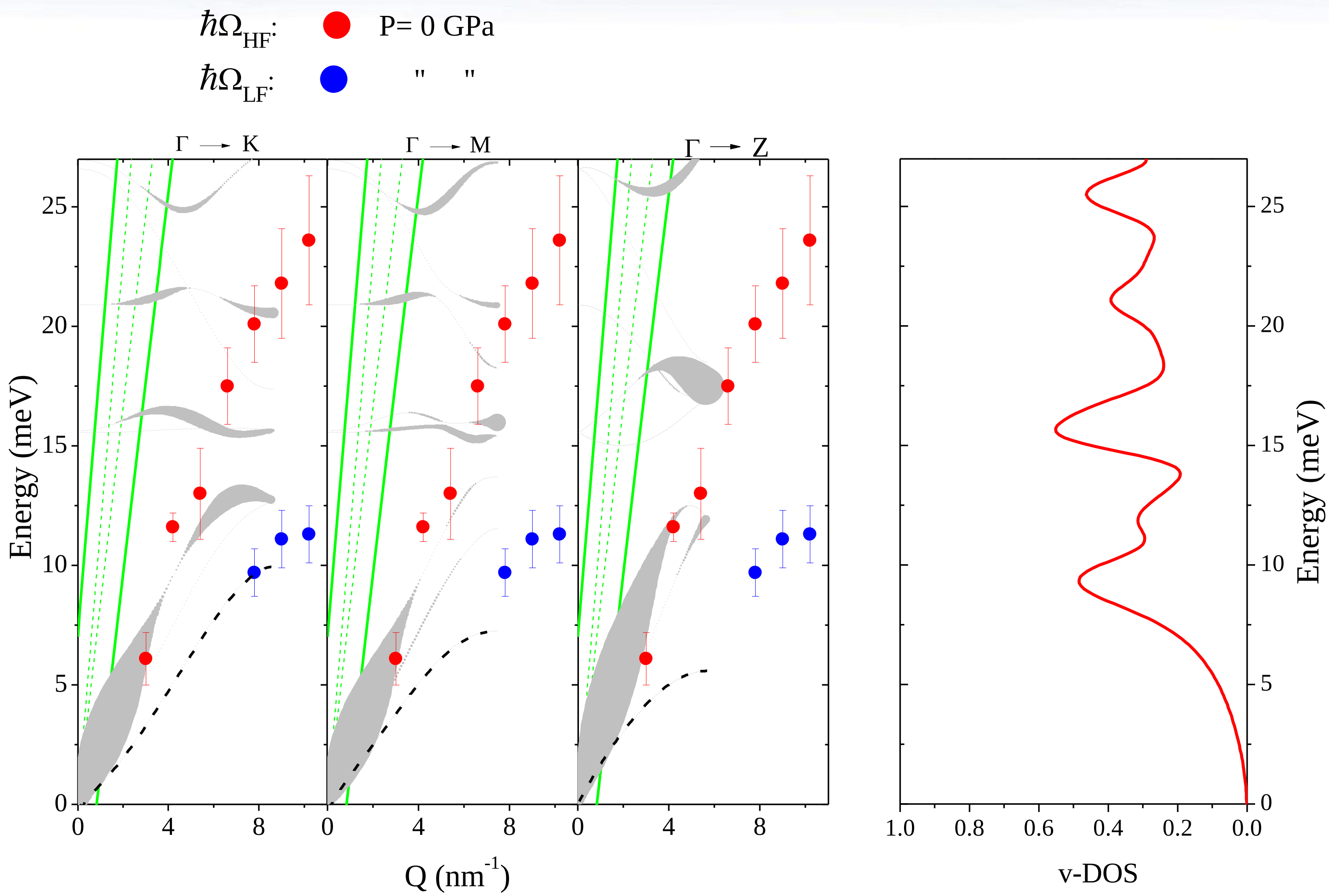
The dispersive behavior of the high frequency (HF) and low frequency (LF) modes below and above the PA transition



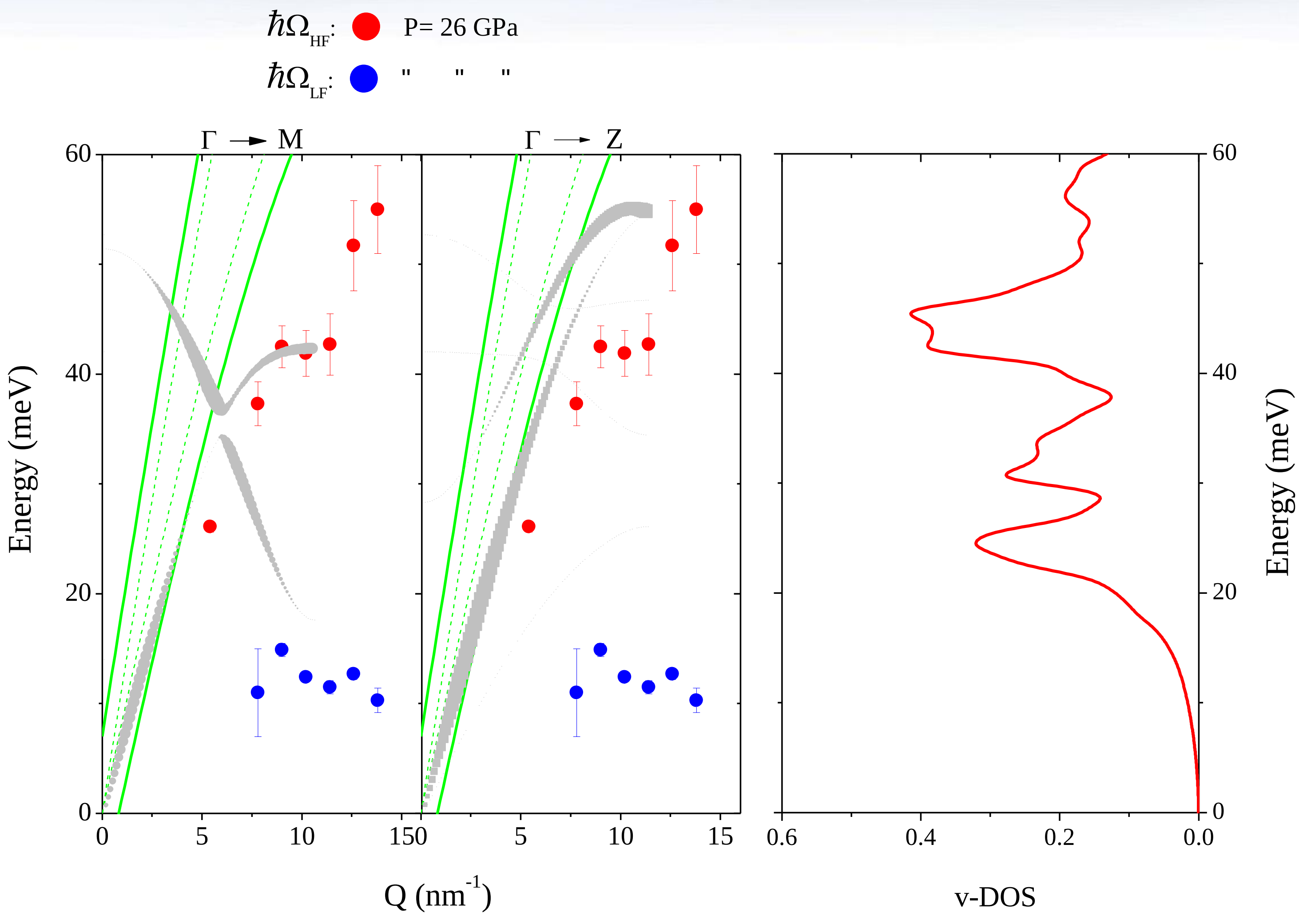
The slope of dispersion curves: cusp-like behavior of the longitudinal sound velocity



a-GeO_2 at ambient conditions: comparison with DFT calculations for an α-quartz crystal structure



a-GeO_2 at 26 GPa: comparison with DFT calculations for a rutile crystal structure

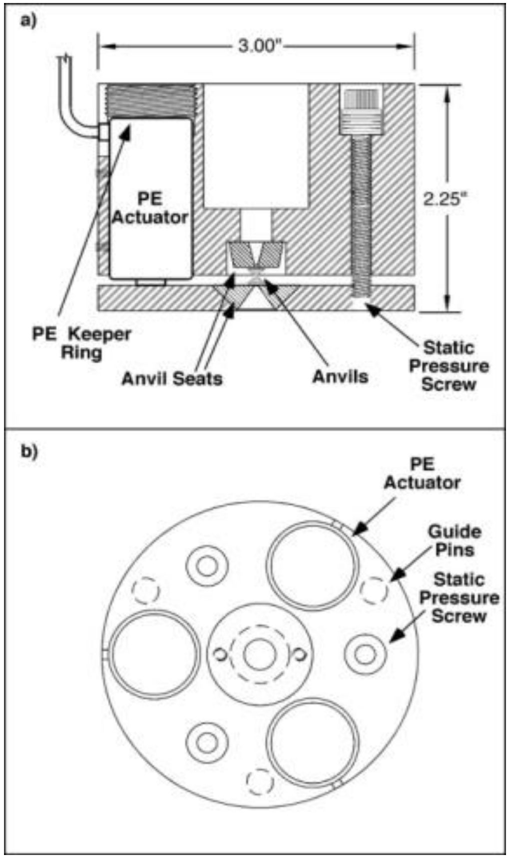


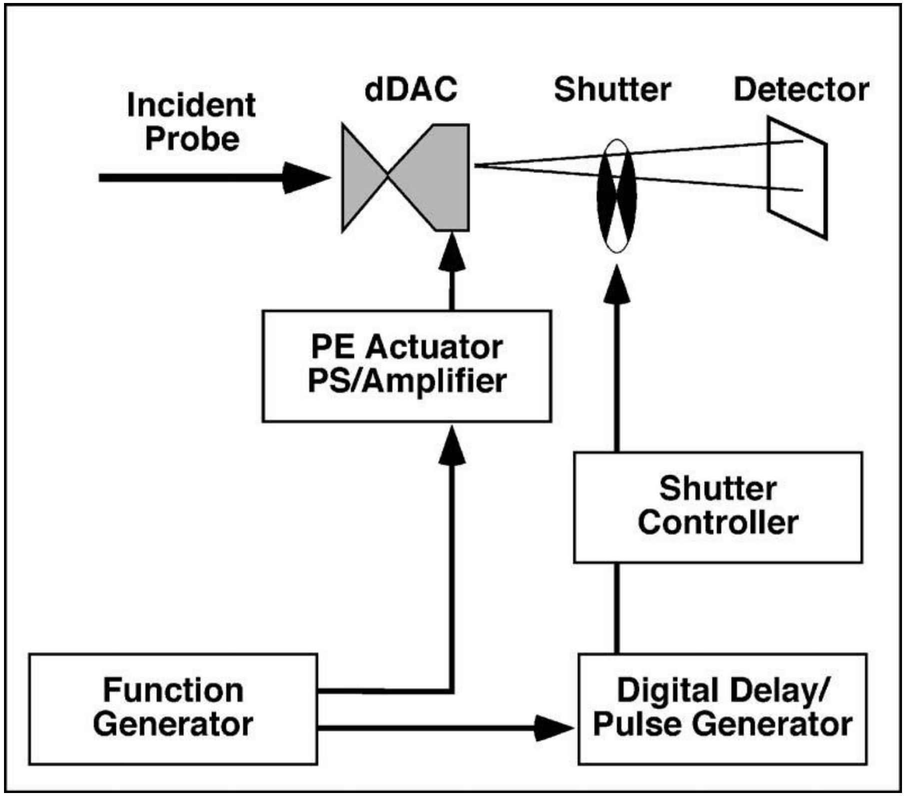
Conclusions

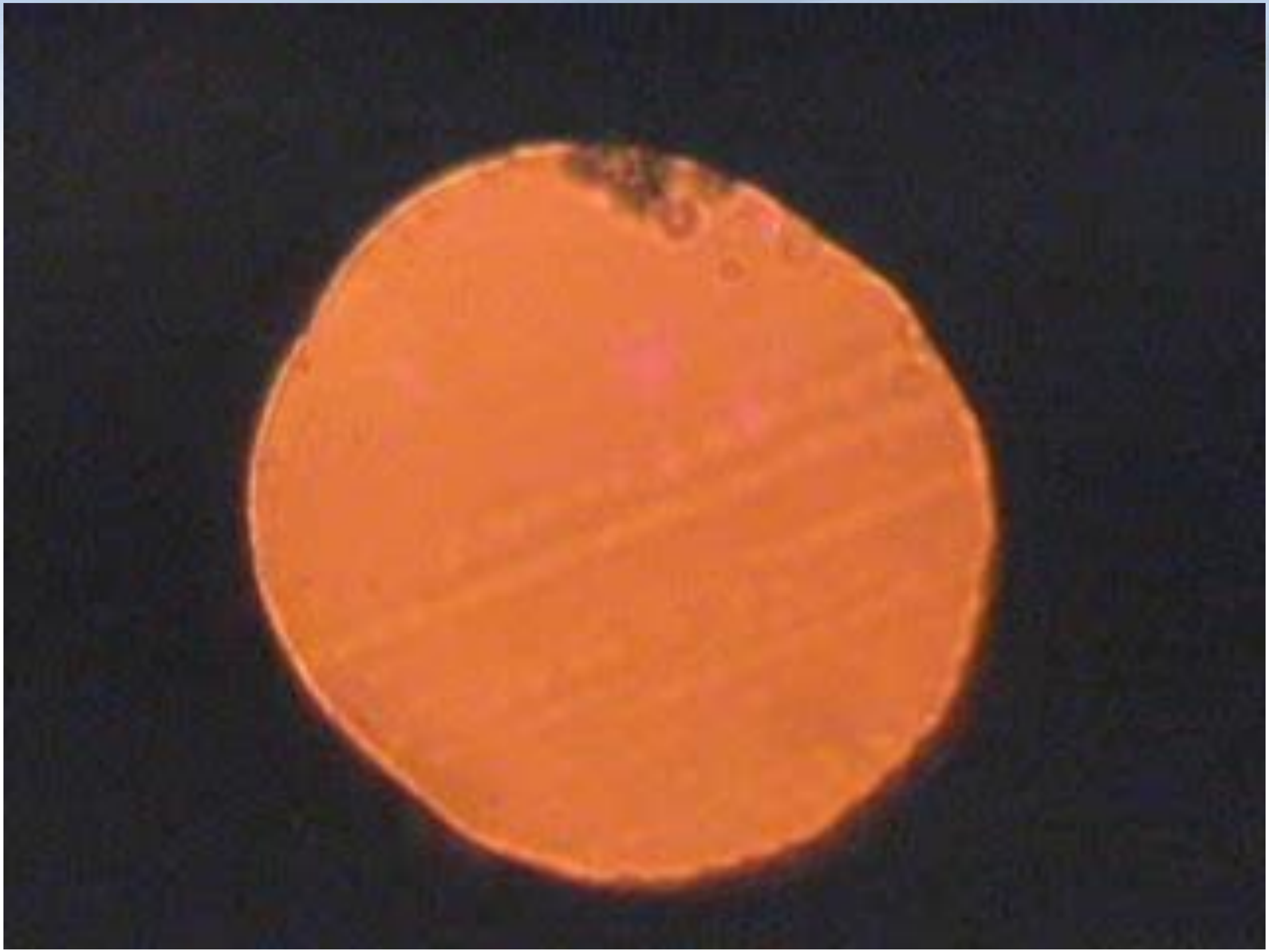
- Signatures of a PA transition on the sound dispersion behavior can be detected in the form of a cusp in the P-dependence of the longitudinal sound velocity.
- Overall, presented results demonstrate that a PA transition leaves a clear footprint on the phonon dispersion.
- Looking ahead, what is the possible contribution of a X Ray Echo spectrometer?

Performing time dependent measurement with a d-DAC

W. J. Evans et al., Rev. Sci. Inst. **78**, 073904 (2007)







Part II: Manipulating THz acoustic excitations

Inelastic X-ray Scattering determination of the inter- and intra-particle dynamics of nanoparticle superlattices: key to the development of THz phononic crystals

Alessandro Cunsolo[1] (PI), Yong Q. Cai[1] (co-PI), and Oleg Gang[2] (co-PI),
1) Photon Sciences, BNL 2) CFN, BNL

Scientific impact:

➢ Programmable super-lattices of nanoparticles can be used as chemical sensors, optical enhancer, etc. (e.g. particle shape, linkage strength).

➢ Phonon propagation determine heat transport, it is then crucial to implement heat management based upon structure engineering. This is particularly true for THz phonons, which are the leading carriers of heat transfer.

➢ The production of phononic crystals efficient in this dynamic range, requires the syntesis of NP superlattices with nm-size NP and lattice parameter.

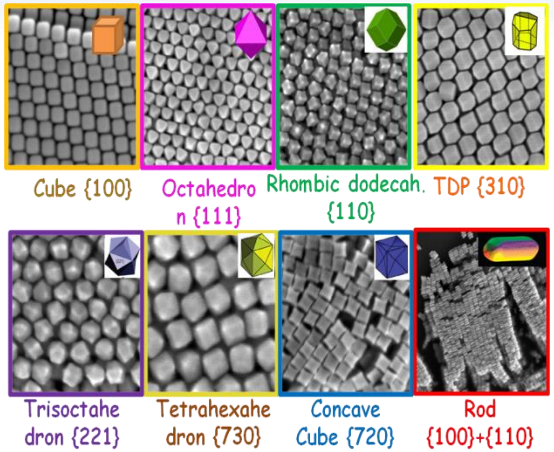
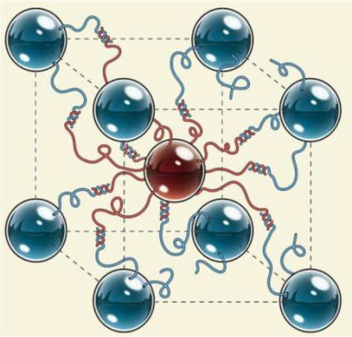


Fig 3:ure. Preliminary results on fabrication of shaped particles (Au) with low- and high- index surfaces using specific adsorbents.

Appproach:

➢ We foresee synthesis of hybrid (liquid-solid) metamaterials.taking advantage the current capabilities offered by O.Gang group at CFN.

➢ The use of the high resolution Inelastic X Ray Scattering (IXS) will allow to study the phonon dynamics of this new generation of materials with unprecedented resolution and spectral contrast.



What is a phononic crystal?

The intriguing acoustic properties of Eusebio Sempere's sculpture Madrid, Spain

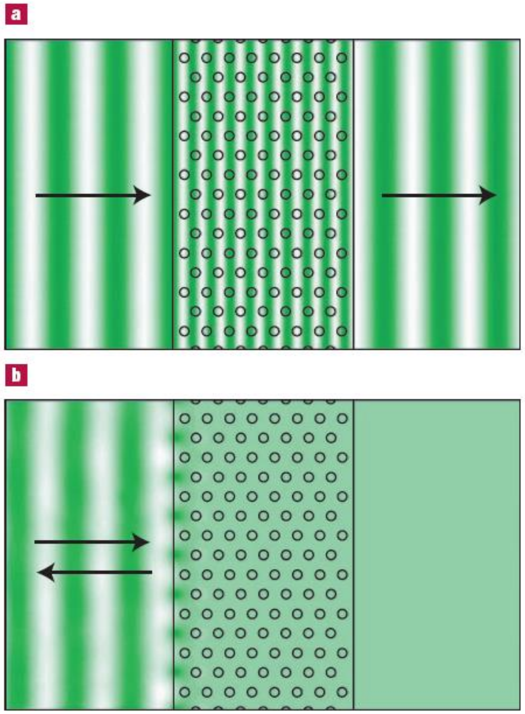
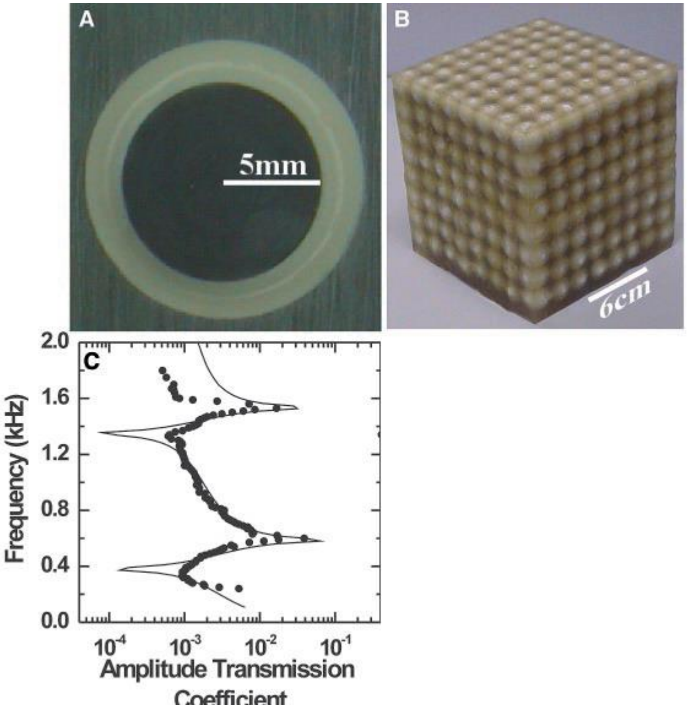


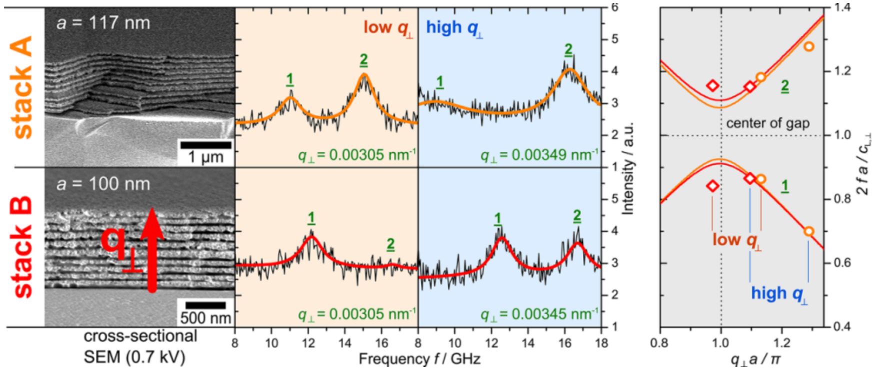
Figure 1 Phononic bandgaps. **a**, A sound wave is incident on the surface of a two-dimensional phononic crystal made of cylinders arranged in a triangular lattice. As the frequency of the incoming wave is not inside the phononic bandgap, the wave is transmitted through the structure. **b**, The sound wave now has a frequency within the gap. The propagation of the wave is not permitted within the phononic crystal and is reflected backwards.

R. Martinez-Sala, et al Nature (London) 378, 241 (1995)

From ultrasonic to hypersonic frequencies

By reducing the lattice size one can move the frequency gaps to higher frequencies…..



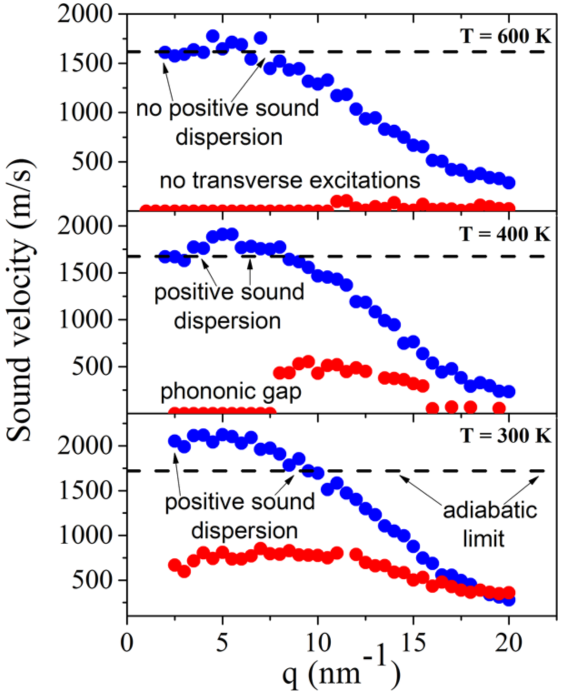


Recent results

The Journal of Physical Chemistry Letters
Letter
pubs.acs.org/JPCL

Revealing the Mechanism of the Viscous-to-Elastic Crossover in Liquids

Dima Bolmatov,*[†] Mikhail Zhernenkov,[†] Dmitry Zav'yalov,[‡] Stanislav Stoupin,[¶] Yong Q. Cai,[†] and Alessandro Cunsolo*[†]

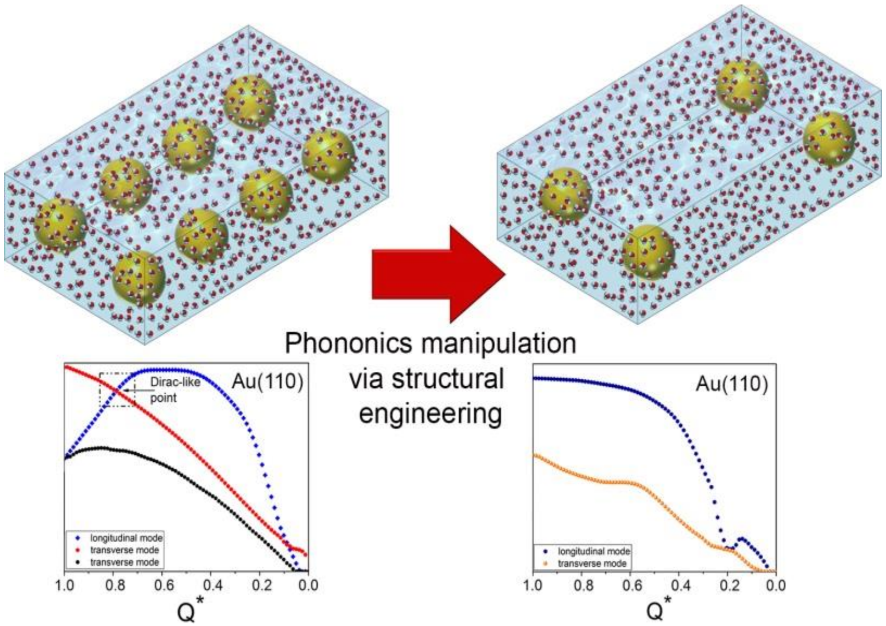


Viscoelasticity and shear waves propagation are universal properties of liquids, which disappear when the extreme T compressed gas phase is reached.

The Journal of Physical Chemistry C
Article
pubs.acs.org/JPCC

Terasonic Excitations in 2D Gold Nanoparticle Arrays in a Water Matrix as Revealed by Atomistic Simulations

Dima Bolmatov,*[†] Mikhail Zhernenkov,[†] Dmitry Zav'yalov,[‡] Yong Q. Cai,[†] and Alessandro Cunsolo[†]



Phonon propagation through the various atomic species presents exceptionally complex features which can be drastically modified by changing the geometry of NP arrangement

What can **we learn** from phonon propagation in programmable nanoparticle assemblies?

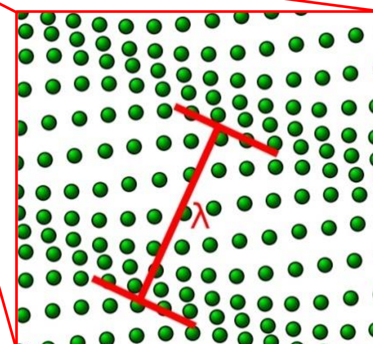
The sample

Increasing Q values

- Interparticle phonons: insight on the programmable interaction strength
- Possible dependence on the shape and on the size: a completely unexplored field….

Intermediate scale

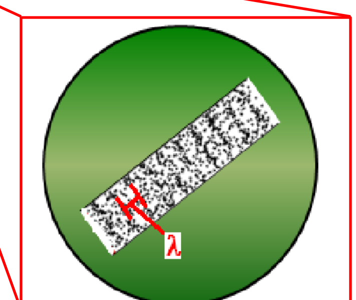
Probing inter-particle phonons



- The physics of nm-sized elements is very peculiar and still full of mysteries (very different thermodynamics, occurrence of a metal-to insulator transition, etc….)
- At the highest Qs (ballistic regime) the single particle dynamics can be probed, gaining insight on microscopic viscosity effects.

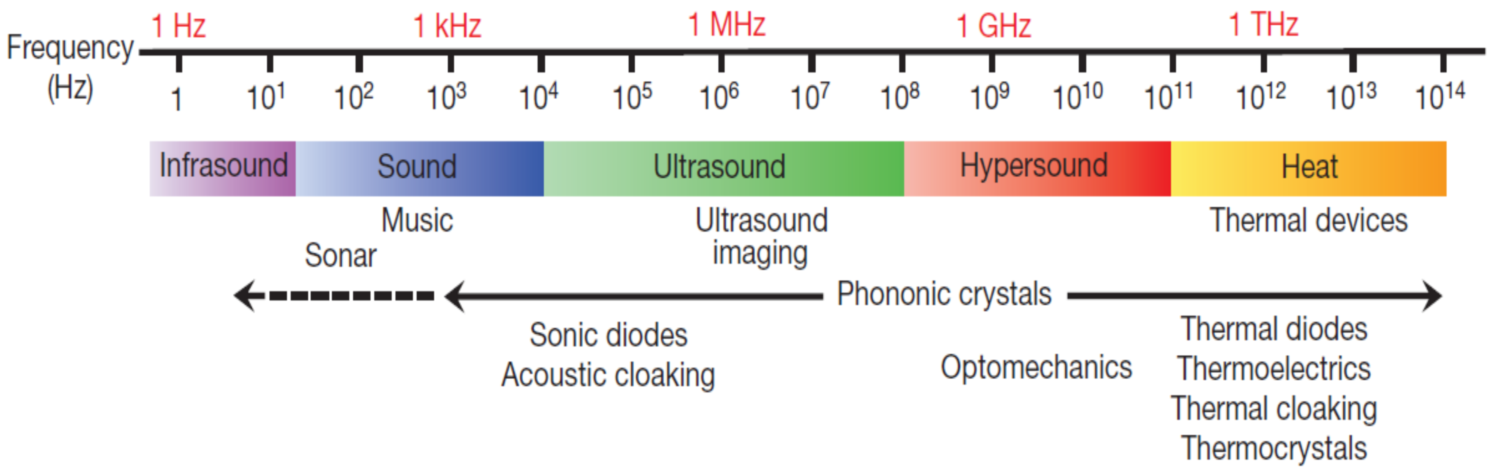
Smaller scales

Probing inter-particle phonons



The "phononic spectrum"

(Why it is important to develop phononic crystal in the THz region)



Heat conduction in insulators uses phonons as a carriers. The ability of manipulating phonon propagation is crucial to implement heat flow management based upon structure engineering.....

The benefit of the X Ray echo technique

Limiting the exposition time provides an invaluable advantage when dealing with DNA-linked super-lattices of nanoparticles, which are particularly exposed to radiation damage.

Thank you!