Varenna SIF Course 215: Topology and Materials
July 18 2024

From water to colloidal water.... a topological nature of the liquid-liquid transition?

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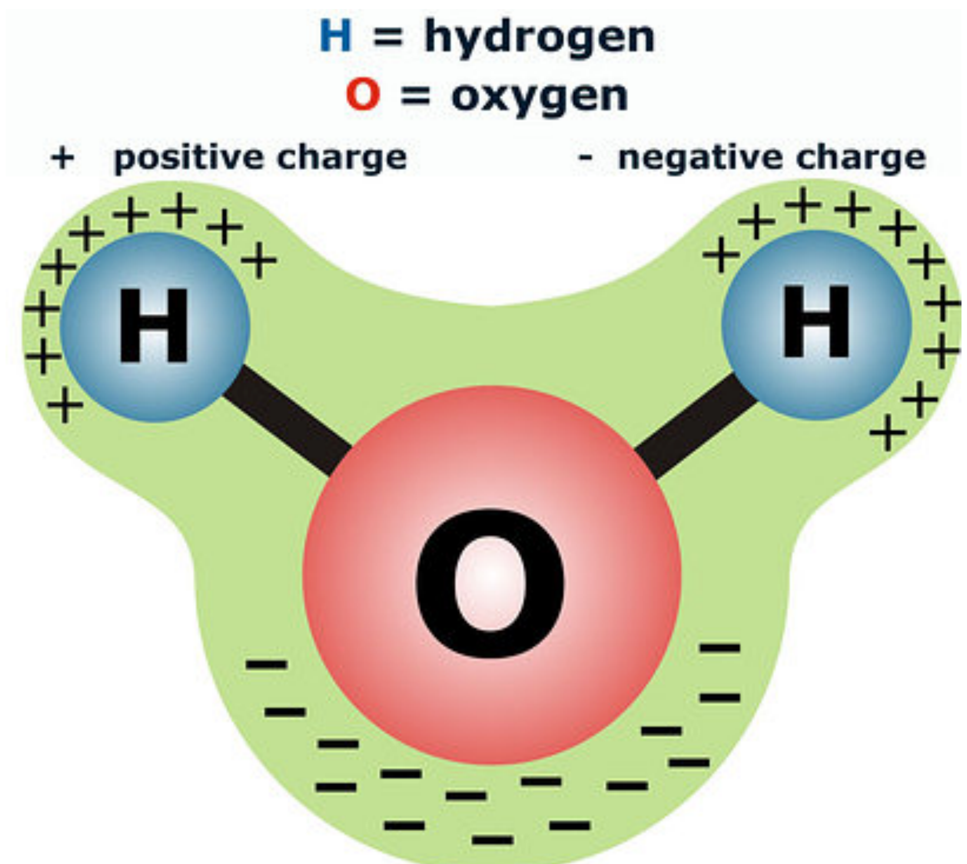
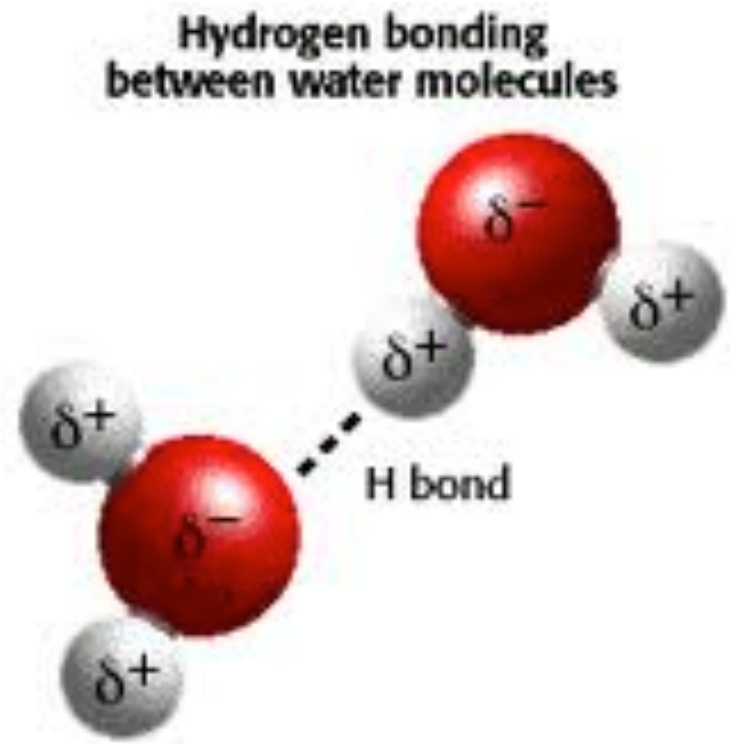
http://www.roma1.infn.it/~sciortif/

SAPIENZA
UNIVERSITÀ DI ROMA

What is special about the water molecule



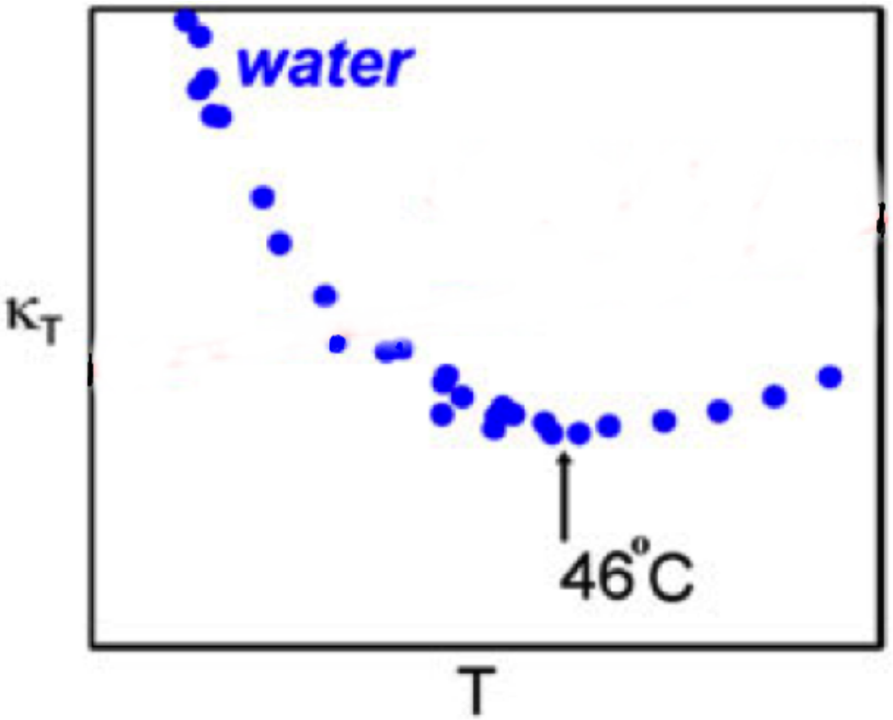


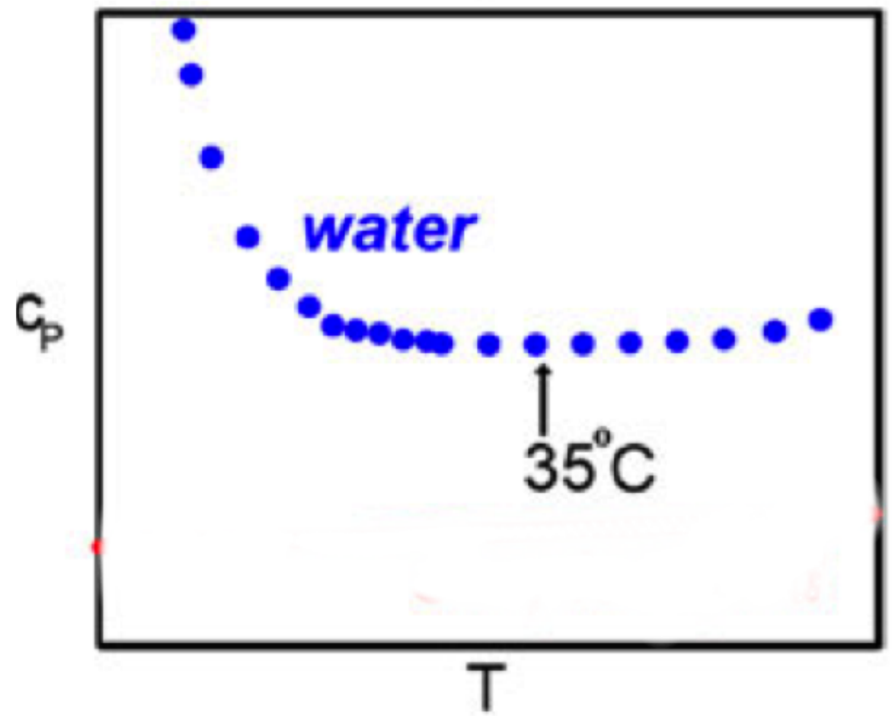
Strong Directional interactions --- Limited number of HB

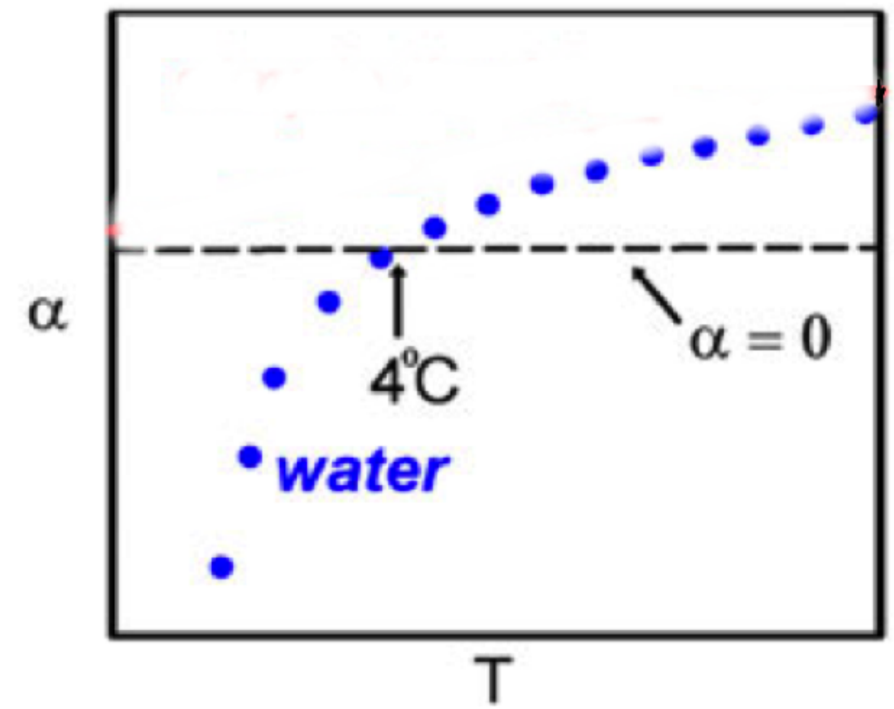
Prone to tetrahedral coordination – Empty liquid !

Thermodynamic Anomalies ! (Angell, Speedy)

Speedy, R. J.; Angel!, C. A. J. Chem. Phys. **1976**, 65, 851. 98. (Kt)
Angelí, C. A.; Sichina, W. J.; Oguni, M. J. Phys. Chem. **1982**, 86, 998. (Cp)







Thermodynamic Anomalies !

$$< \Delta\rho^2 >$$

$$< \Delta S^2 >$$

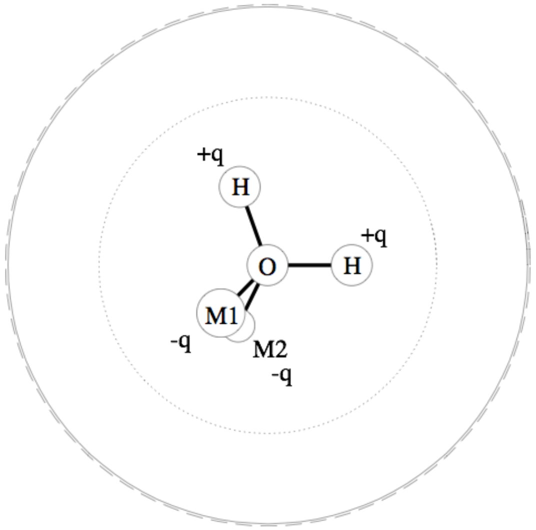
$$< \Delta H^2 >$$

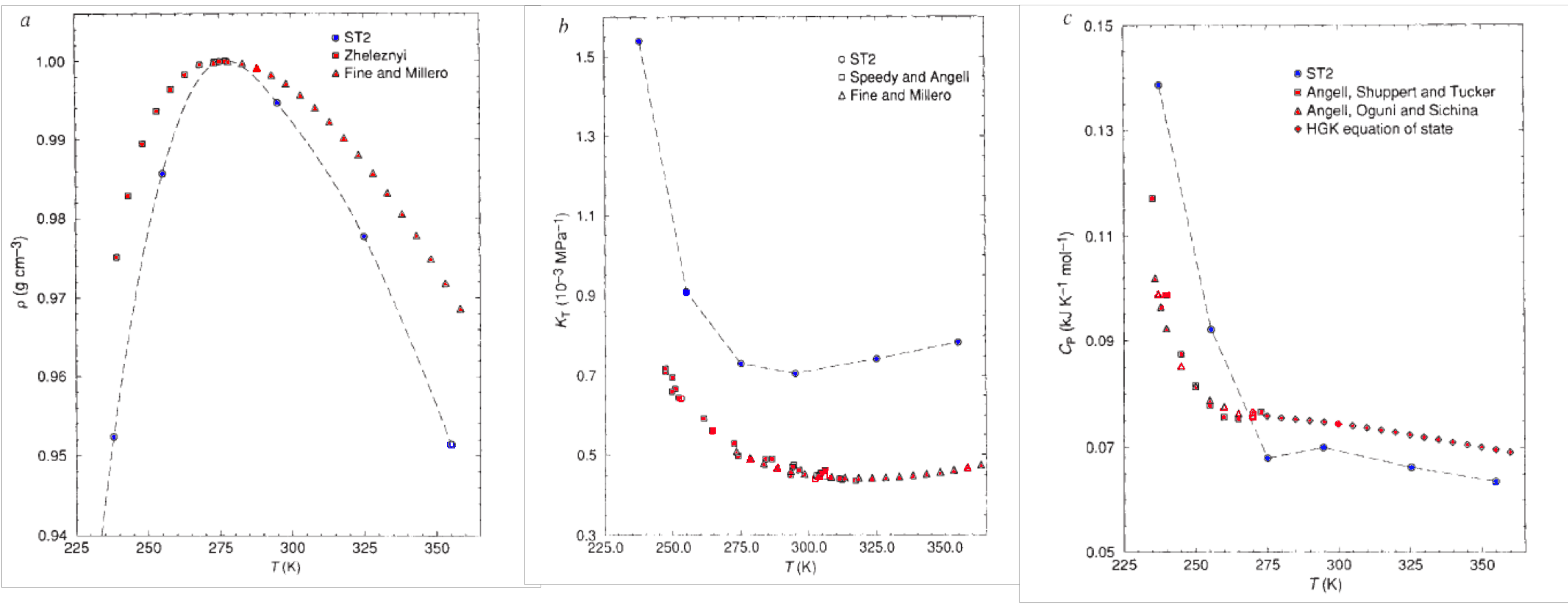
$$< \Delta S \Delta V >$$

Supercooling enhances fluctuations…..

Do response function diverge at lower T ?

Search for the origin of the anomalies via computer simulations (1990)
ST2 model of water



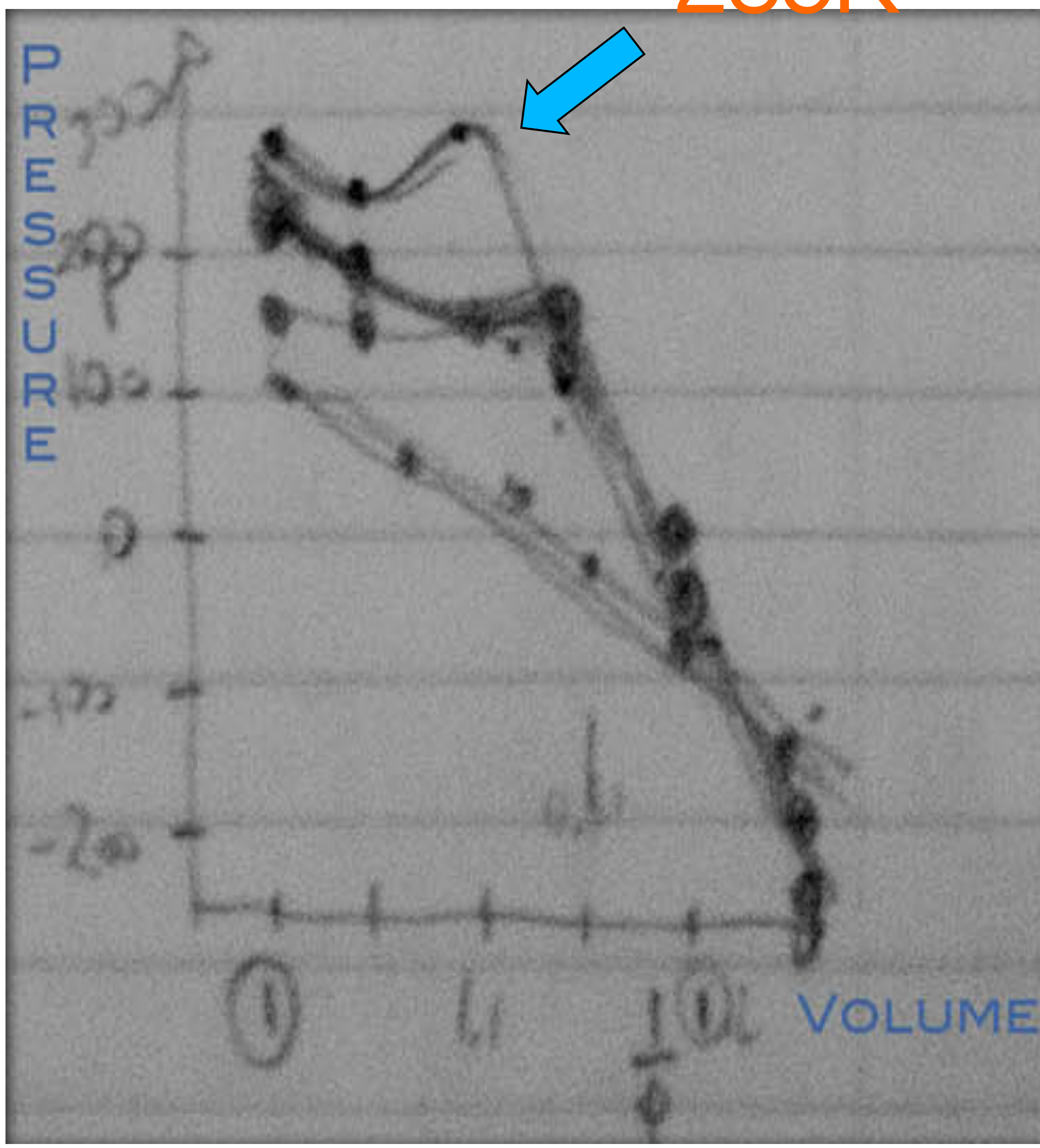


Comparison with applied shift in T (35 K) and P (80 MPa)

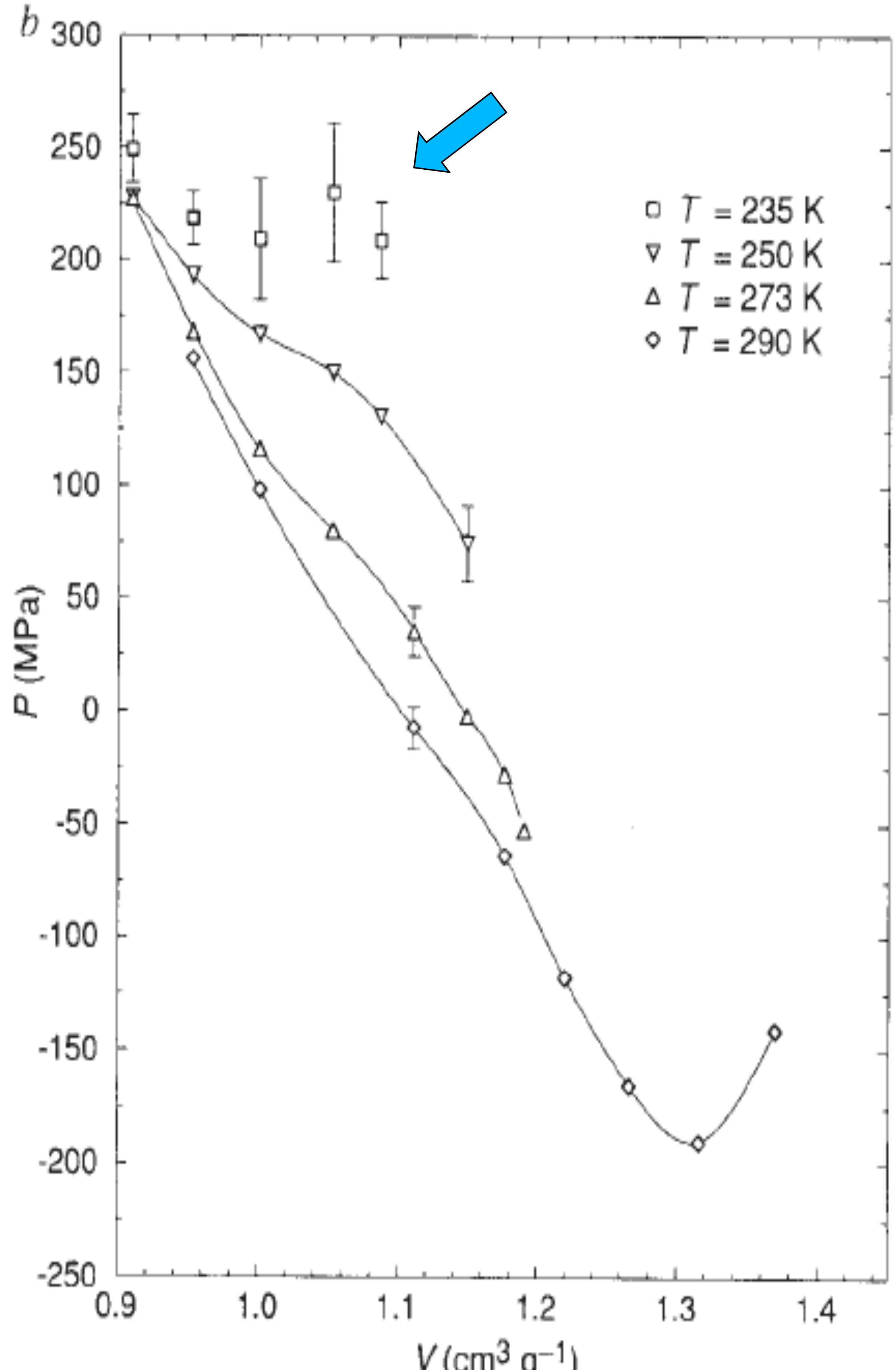
Liquid-Liquid critical point hypothesis: the beginning

P. H. Poole, F. Sciortino,
U. Essmann and H. E. Stanley,
Phase behavior of metastable water
Nature 360, 324-328, 1992

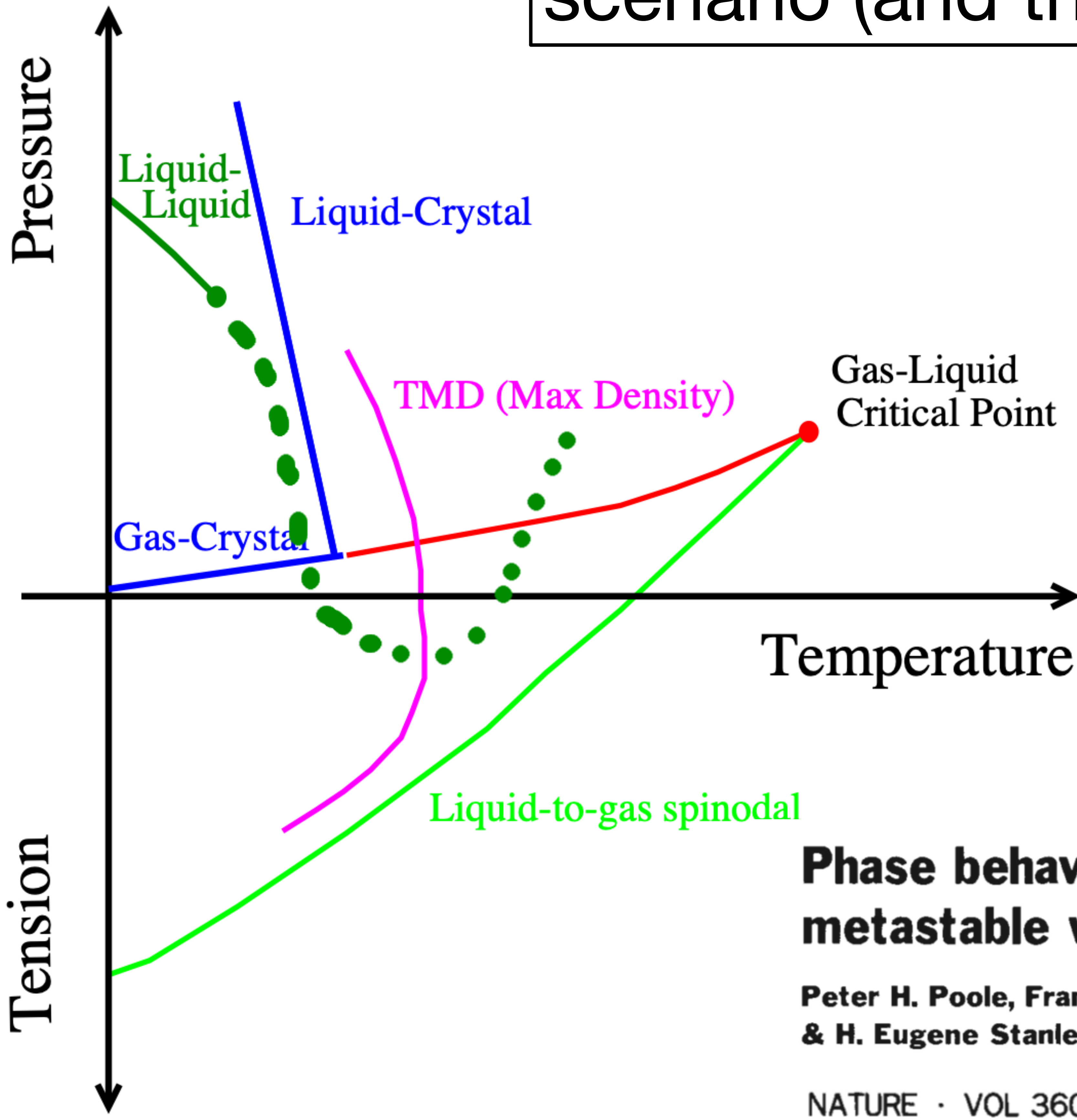
235K



992



The liquid-liquid critical point scenario (and the two-glasses)



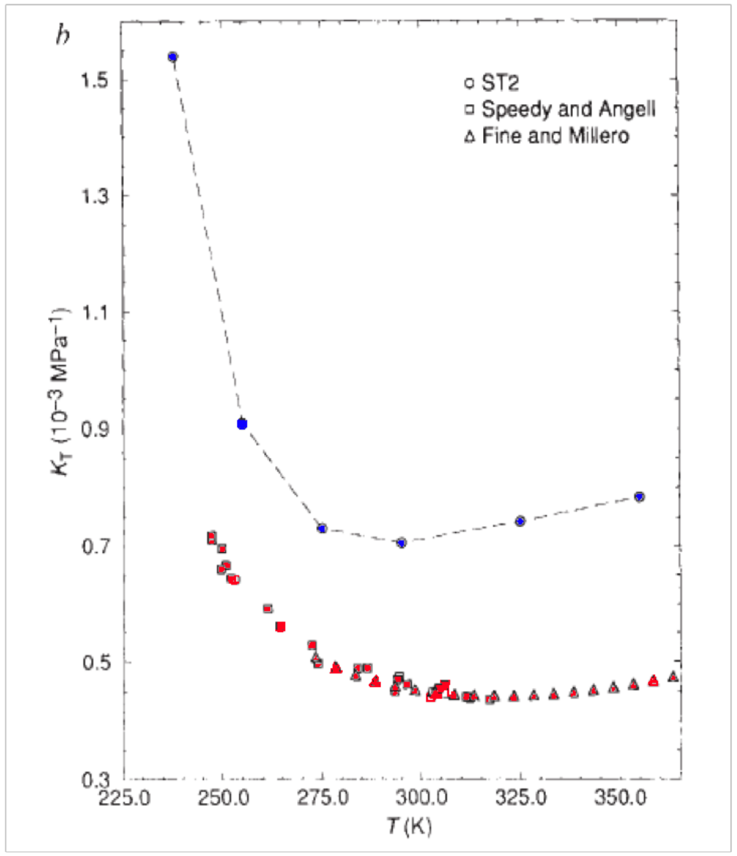
Phase behaviour of metastable water

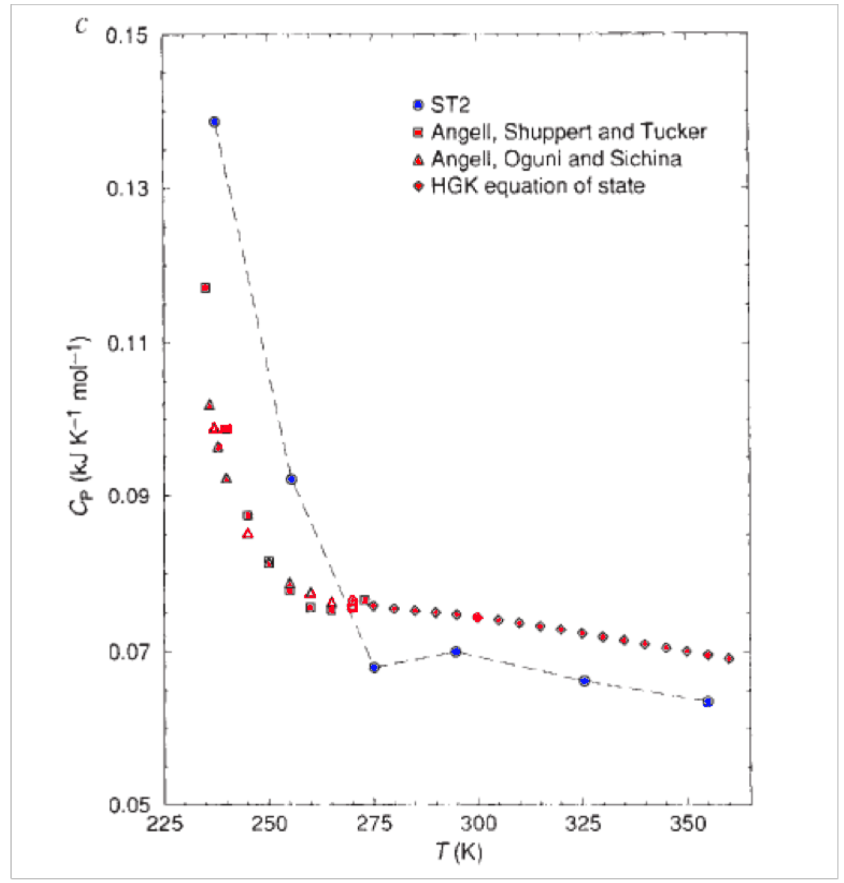
Peter H. Poole, Francesco Sciortino, Ulrich Essmann & H. Eugene Stanley

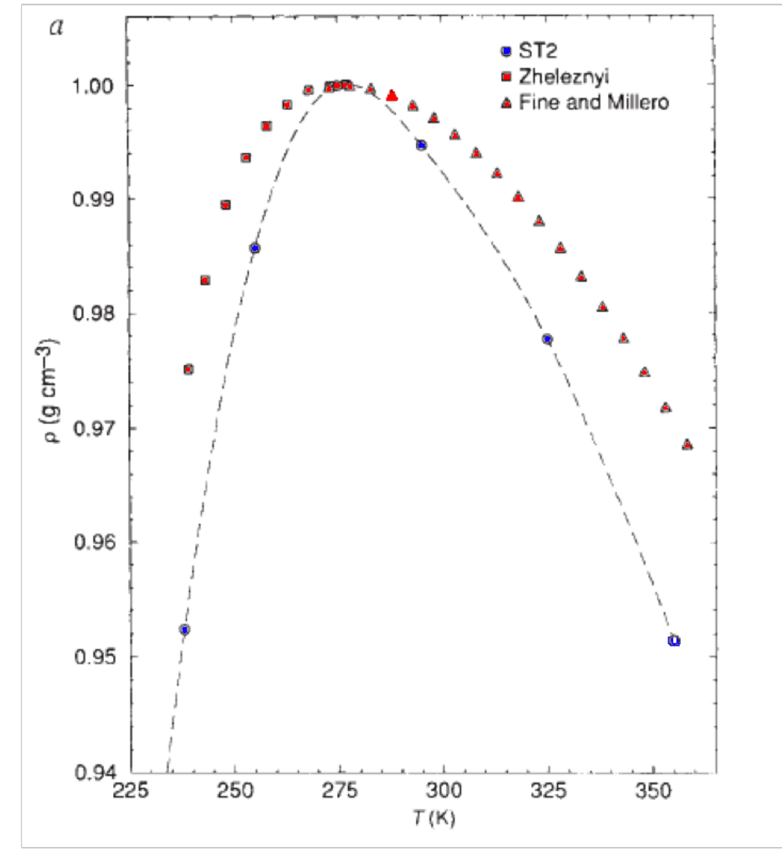
NATURE · VOL 360 · 26 NOVEMBER 1992

Where are we after 30 years

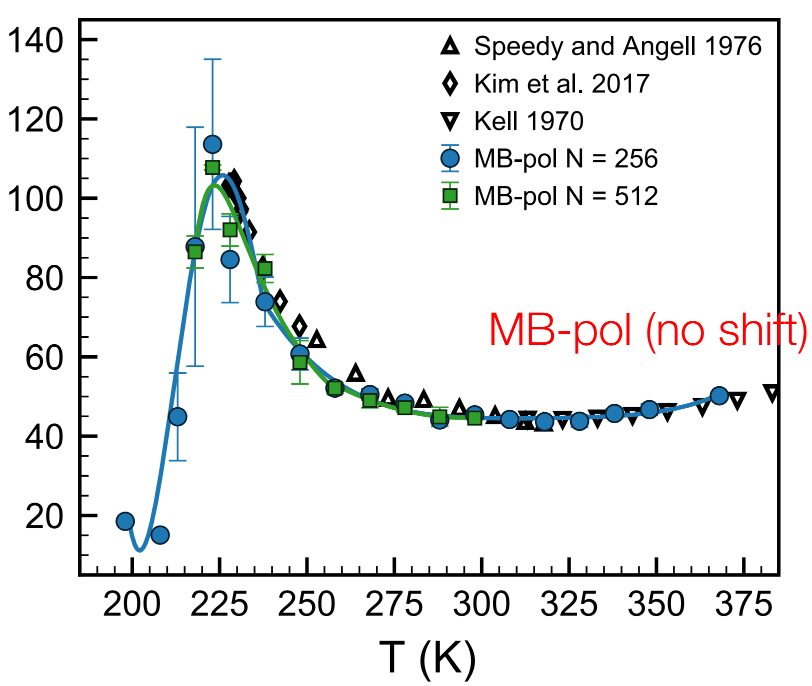
ST2 (shift in 35 K T and 80 Mpa in P)



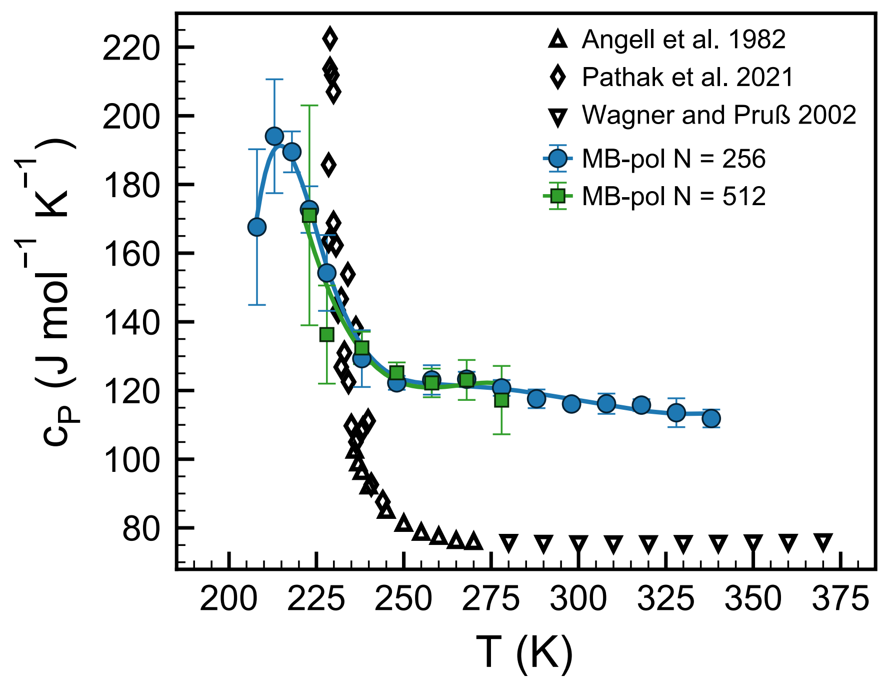




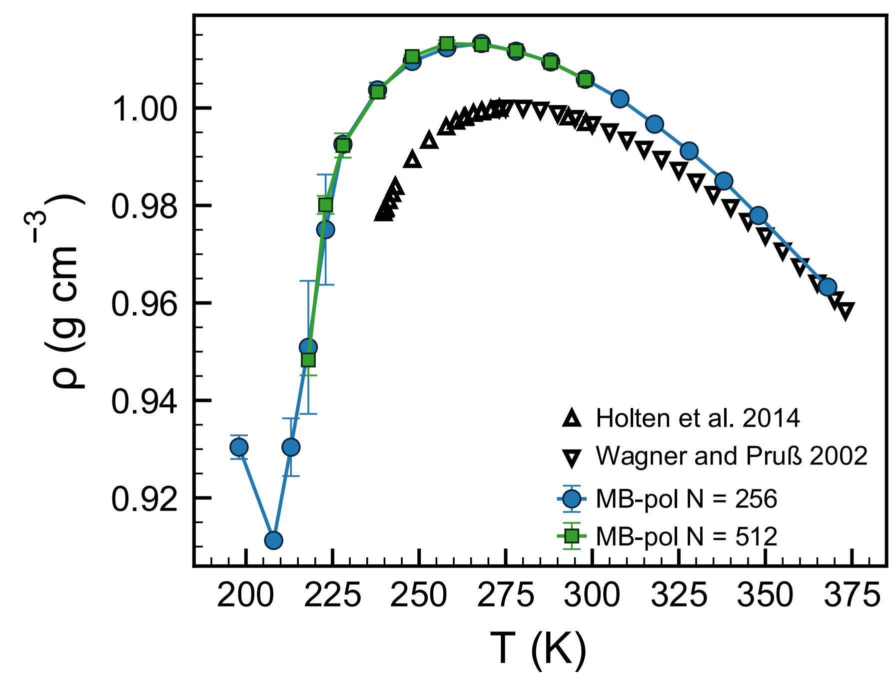
isothermal compressibility



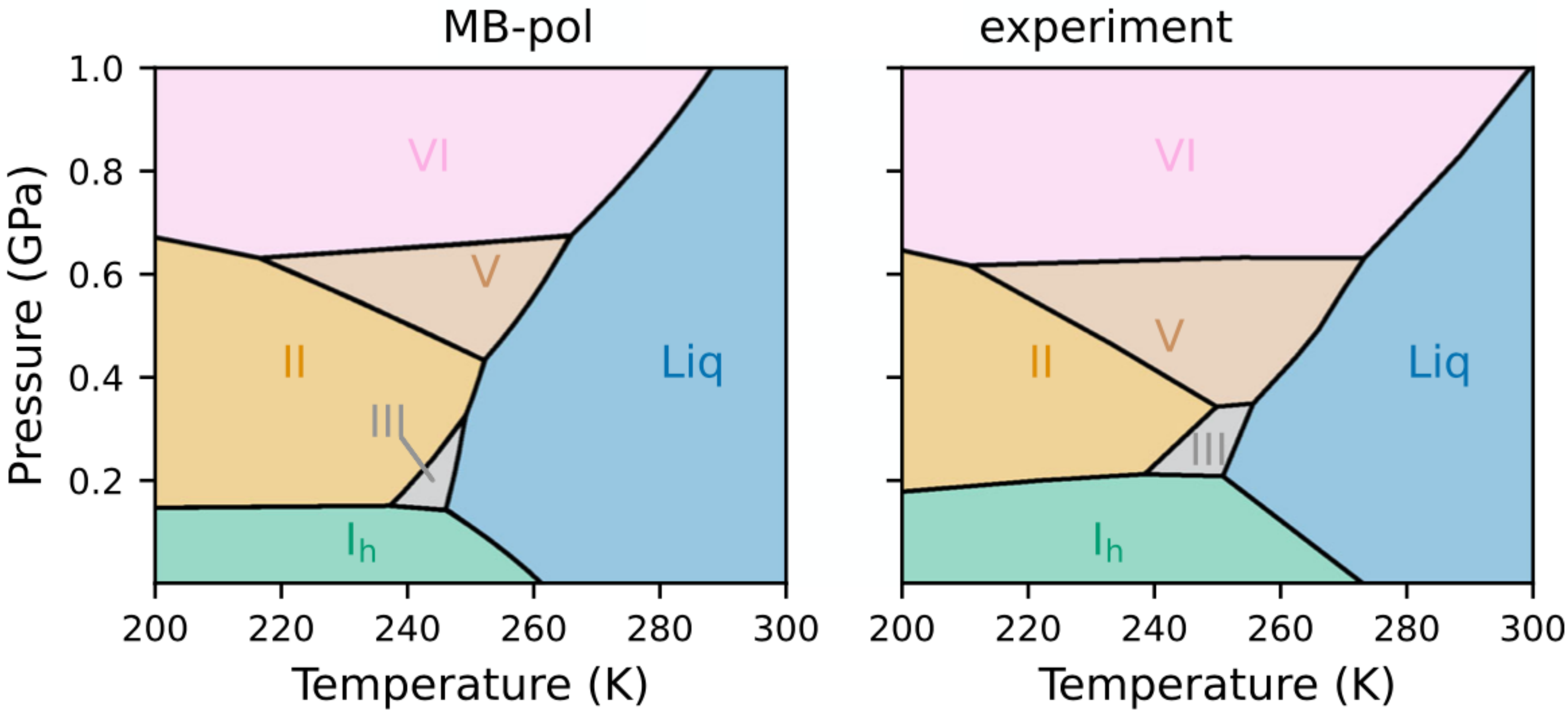
heat capacity



density



Gartner III, Hunter, Lambros, Caruso, Riera, Medders, Panagiotopoulos, Debenedetti, Paesani, J. Phys. Chem. Lett. 13*, 3652 (2022)*

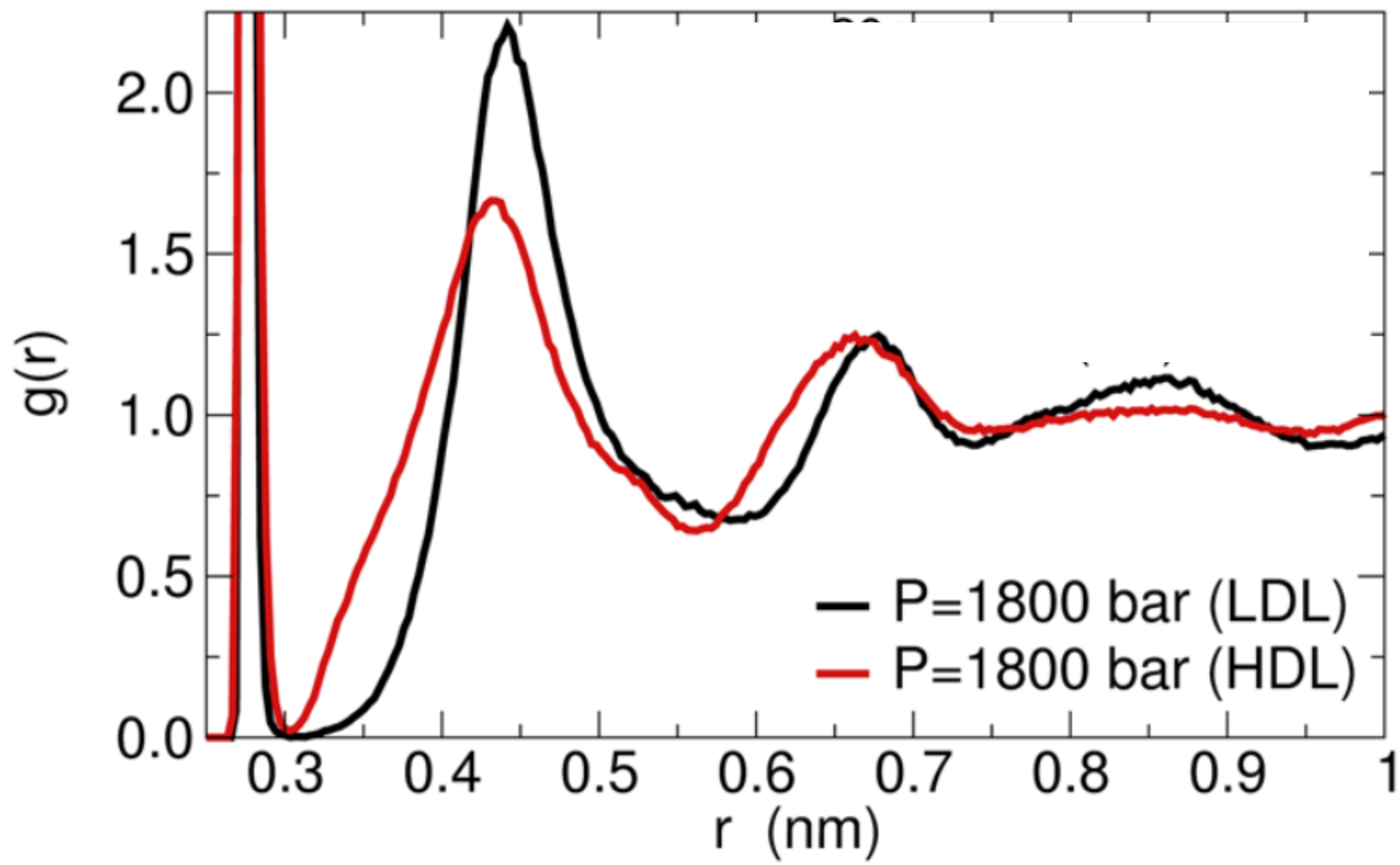


Realistic Phase Diagram of Water from “First Principles” Data-Driven Quantum Simulations

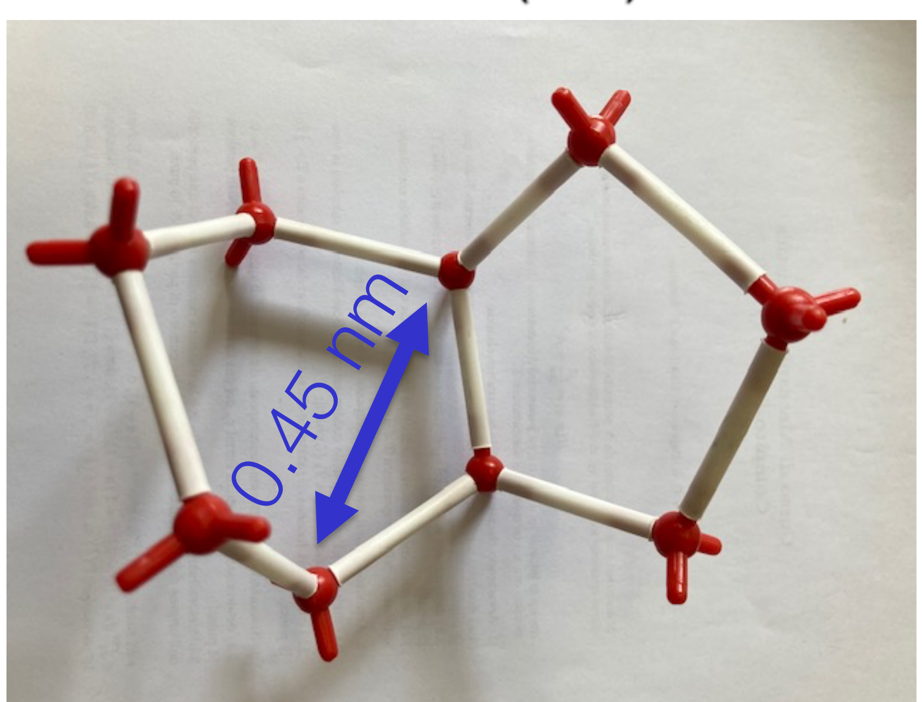
Sigbjørn Løland Bore[1] and Francesco Paesani[1,2,3,4*]

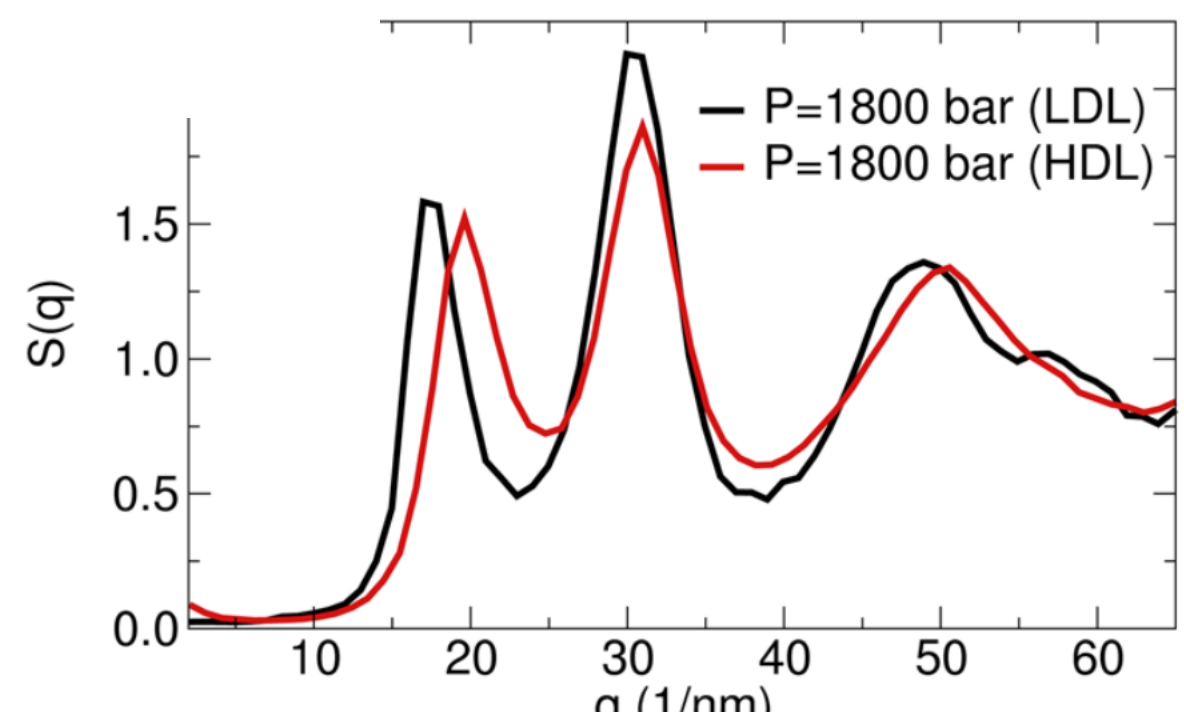
Nature Communications | (2023)14:3349

What are the difference between the two liquids ?



The density:
0.92 – 1.1 g/cm^3

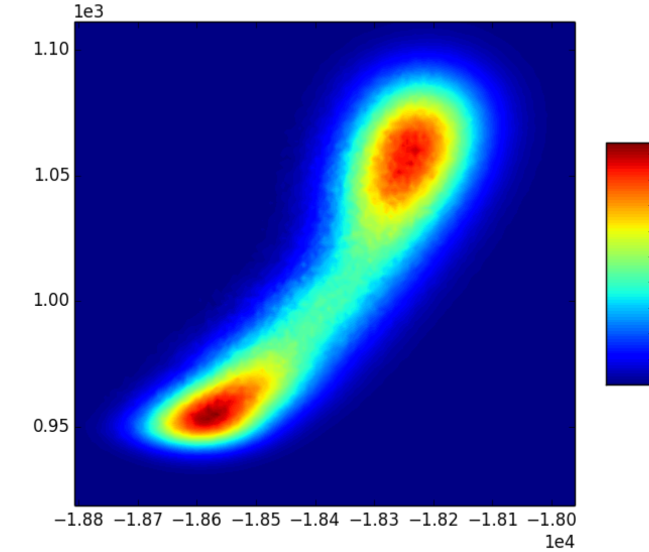


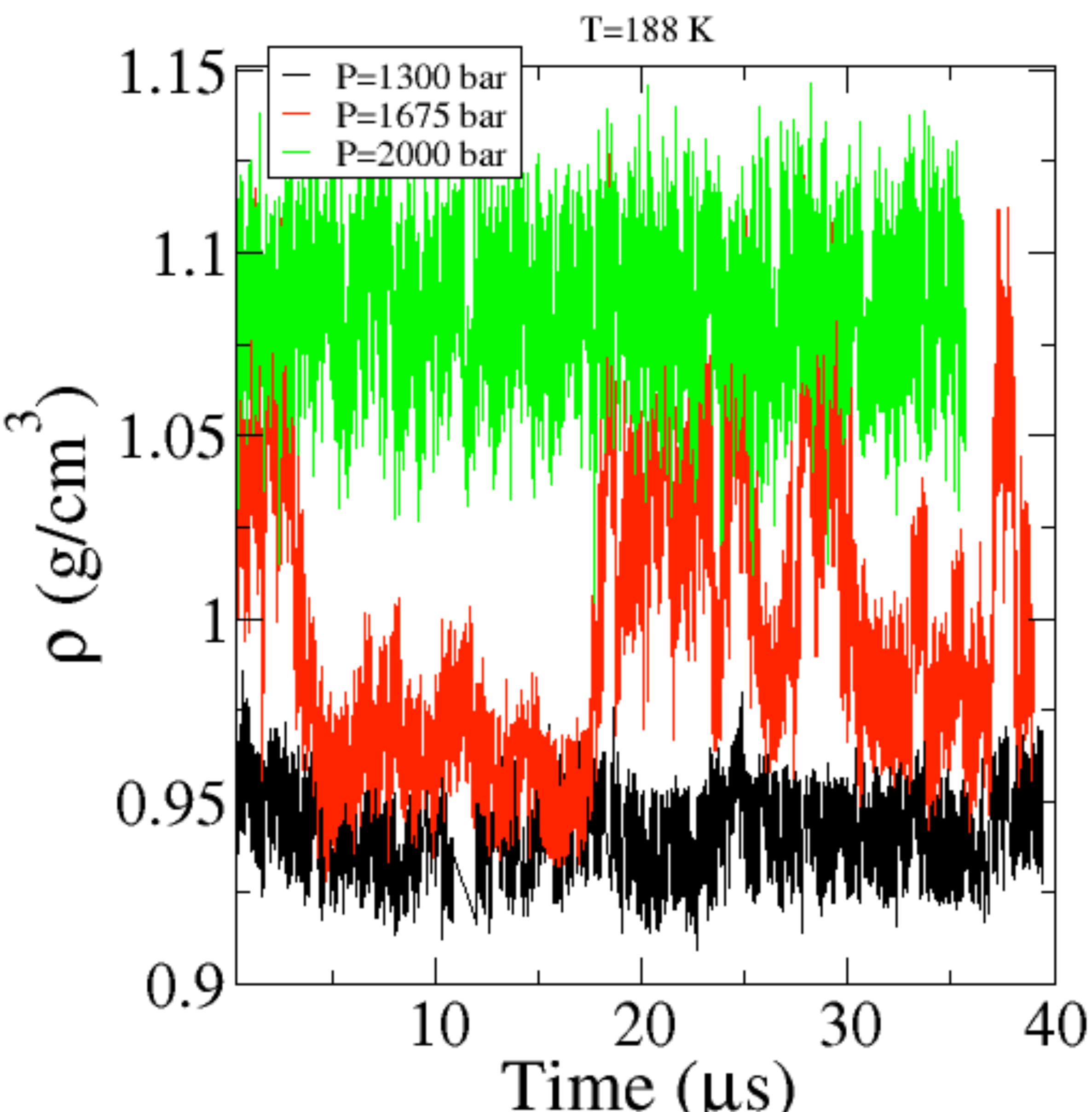


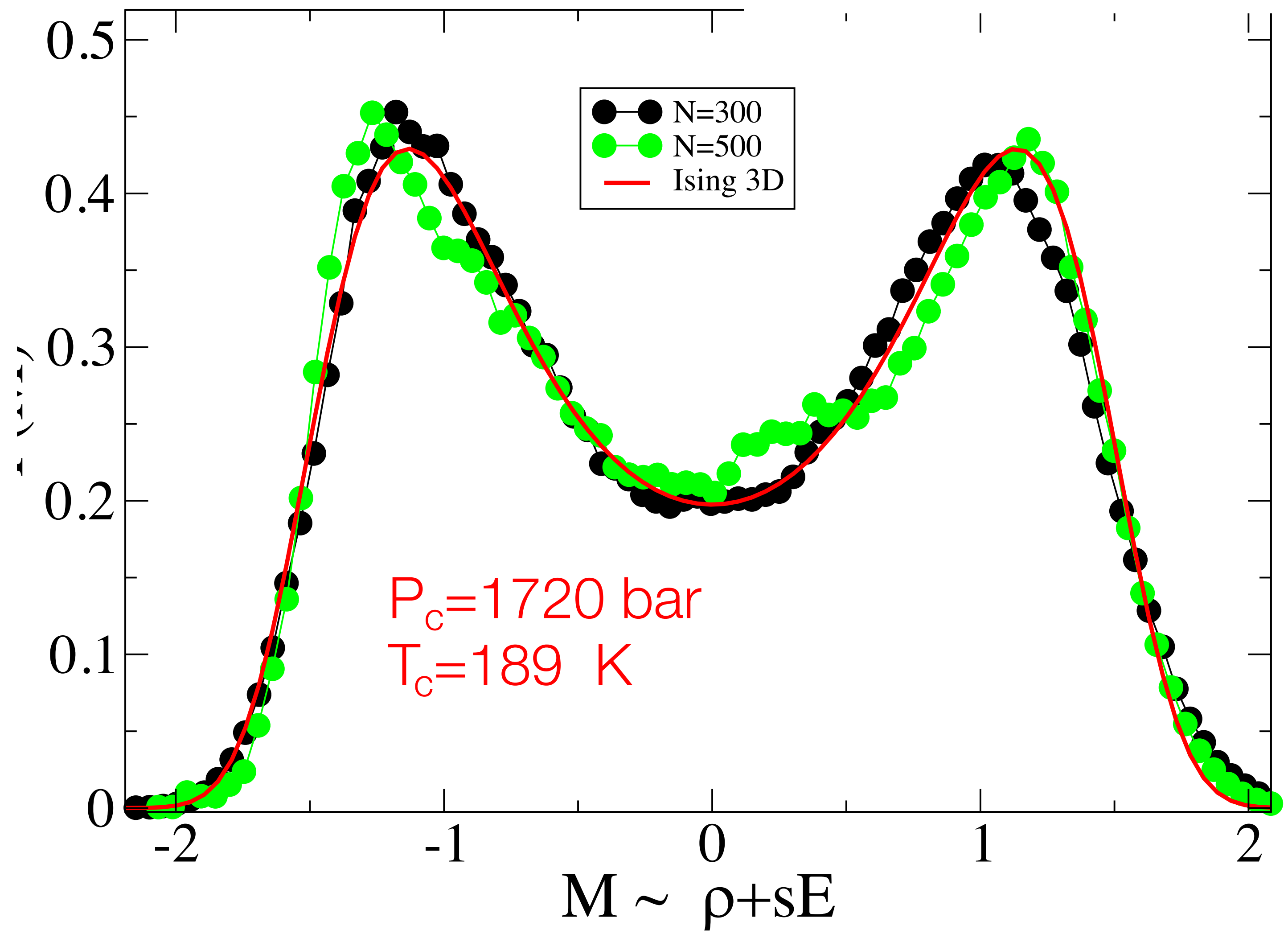
Is the LL transition observed in other models ?

TIP4P (Ice and 2005)

A potential model for the study of ices and amorphous water: TIP4P/Ice
JLF Abascal, E Sanz… - The Journal of …, 2005 - aip.scitation.org
… Head-Gordon. more... May 2004. High precision determination of the melting points of water **TIP4P/2005** and water TIP4P/Ice models by the direct coexistence technique MM Conde, M. Rovere, and P. Gallo. more... Dec 2017 …
☆ 99 Citato da 671 Articoli correlati Tutte e 15 le versioni »







Real time (computer time) - 1 year

2 Sizes
40 state points
Several tenth of μs
Constant pressure
Histogram reweighting

Second critical point in two realistic models of water

Pablo G. Debenedetti[1]*†, Francesco Sciortino[2]†, Gül H. Zerze[1]†

Science **369**, 289–292 (2020)

PHYSICAL REVIEW LETTERS **129,** 255702 (2022)

Editors' Suggestion | Featured in Physics

Liquid-Liquid Transition in Water from First Principles

Thomas E. Gartner III,[1,‡] Pablo M. Piaggi,[1] Roberto Car,[1,2,3,4]
Athanassios Z. Panagiotopoulos,[5,†] and Pablo G. Debenedetti[5,*]

PHYSICAL REVIEW LETTERS **129,** 255702 (2022)

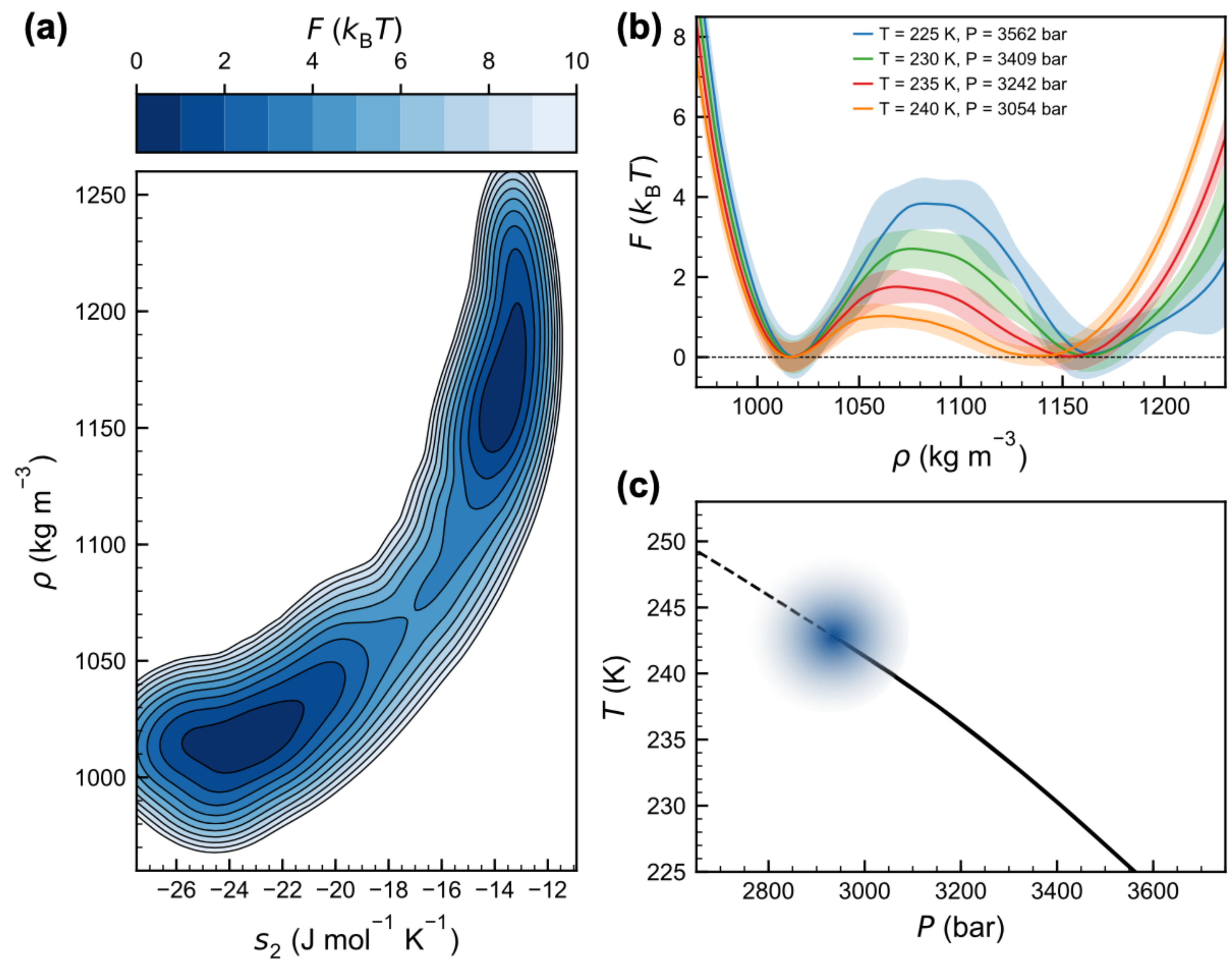
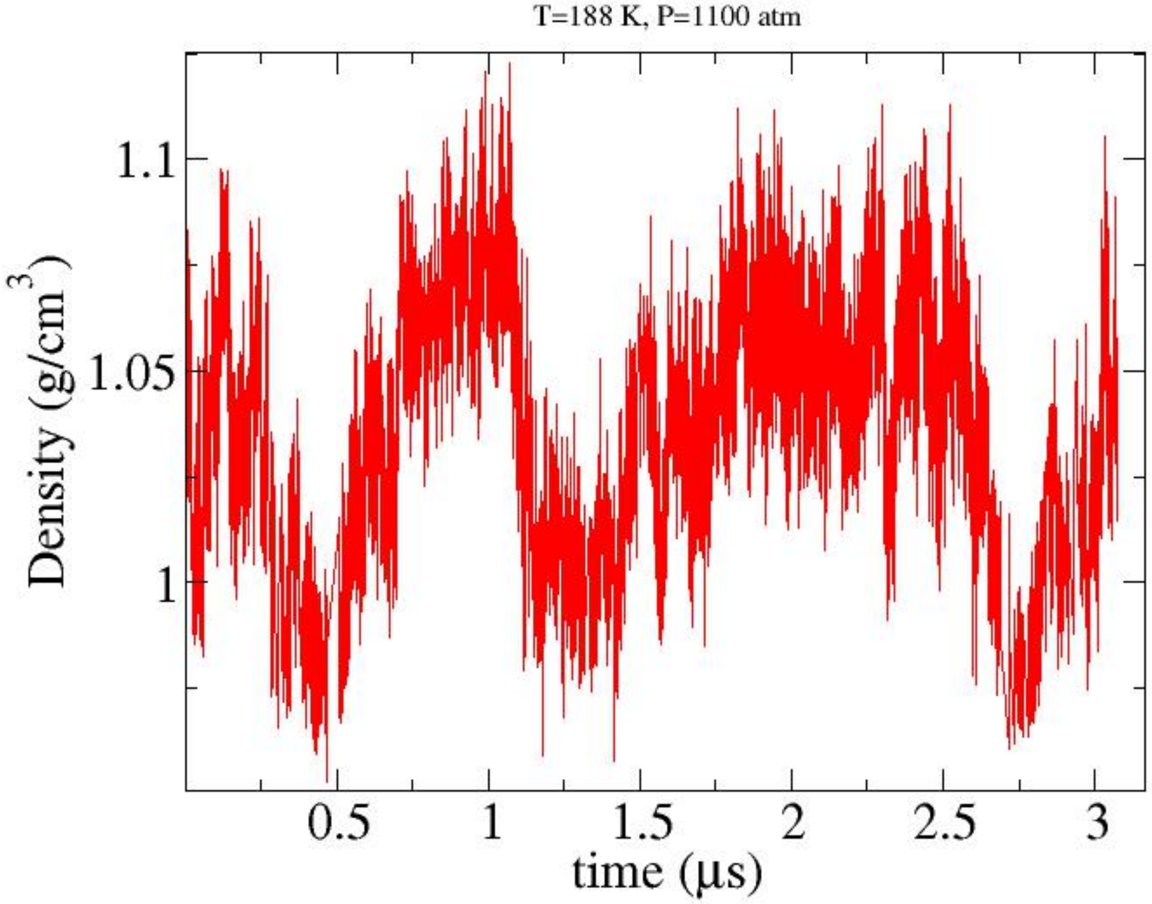
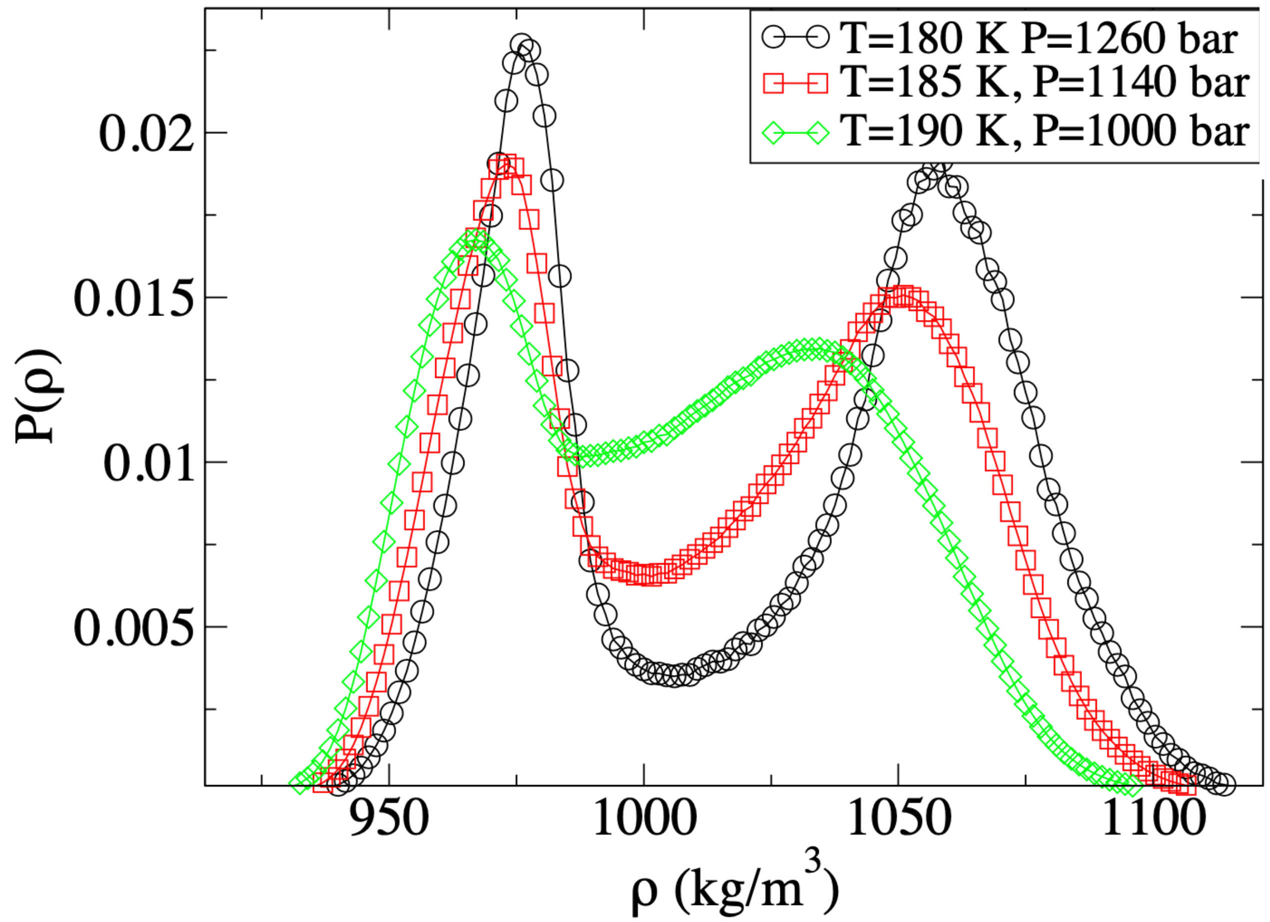
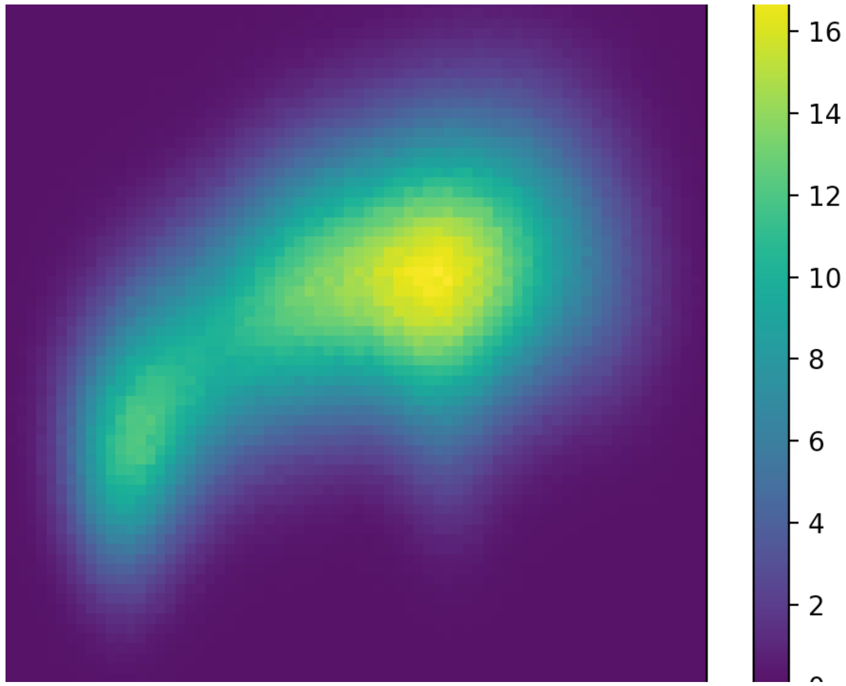


FIG. 3. Phase coexistence from multithermal-multibaric (MTMB) simulations. (a) Free energy (F) as a function of ρ and s_2 from MTMB simulations with $N = 192$ molecules at $T = 225$ K and $P = 3525$ bar. (b) F vs ρ at various T and P as marked. Shaded regions represent 95% confidence intervals. (c) Liquid-liquid binodal (solid black line), approximate critical point location (shaded blue region), and line of maximum isothermal compressibility (dashed black line) in the T-P plane.

The latest member of the certified LLCP family: DNN@MB-pol

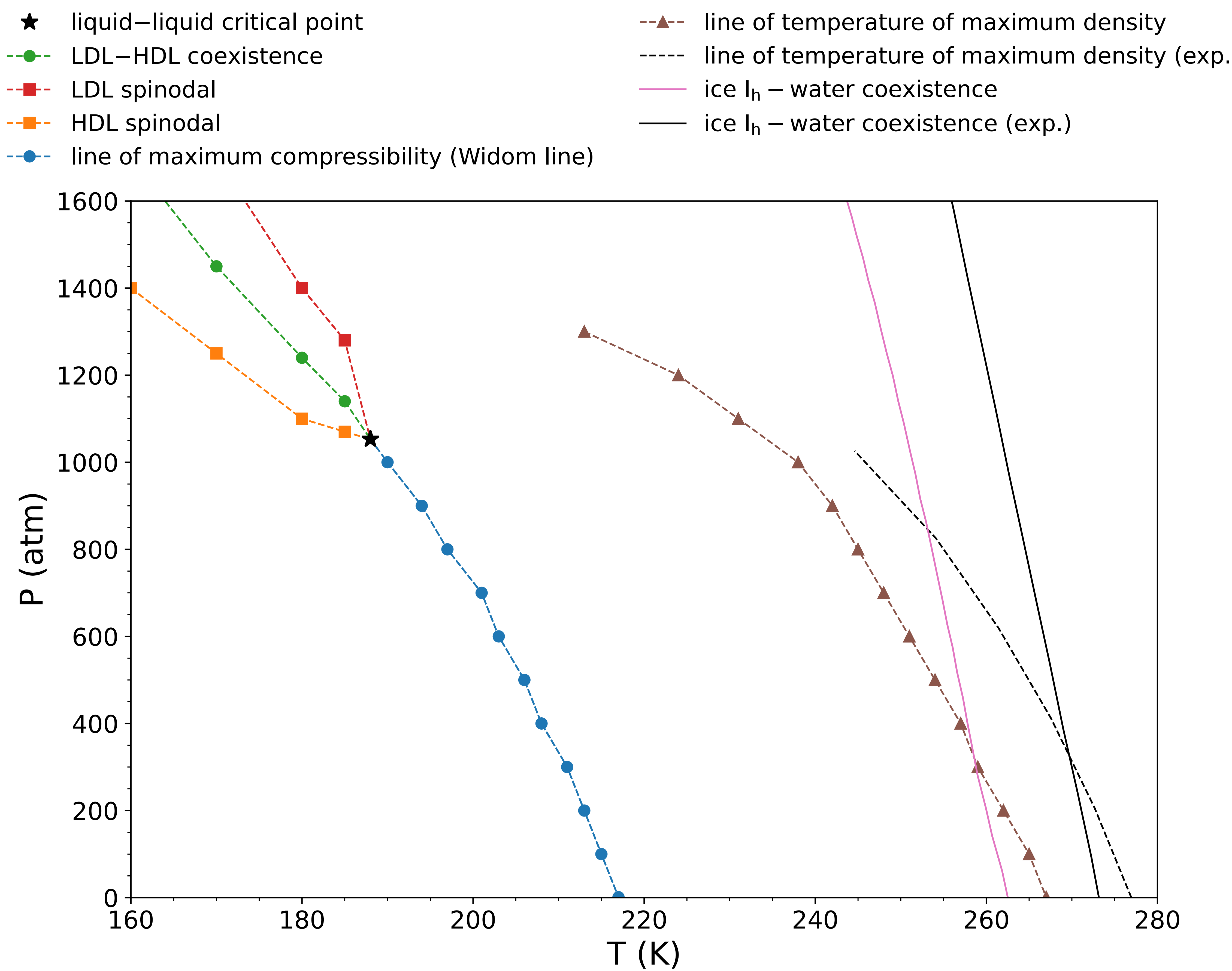






Pinpointing the Location of the Elusive Liquid-Liquid Critical Point in Water

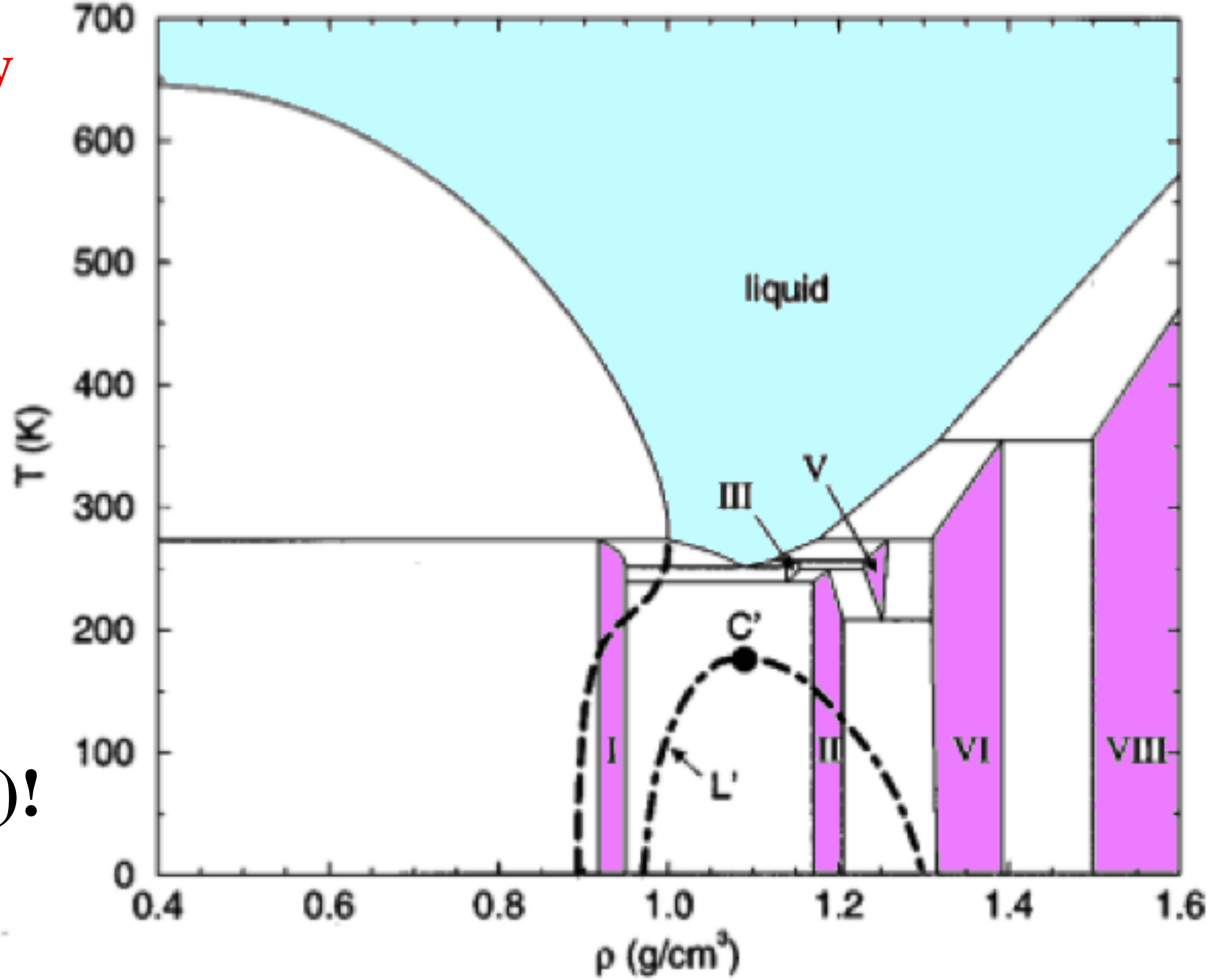
F **Sciortino**, Y Zhai, SL Bore, F **Paesani** - 2024 - chemrxiv.org



Pinpointing the Location of the Elusive Liquid-Liquid Critical Point in Water

F **Sciortino**, Y Zhai, SL Bore, F **Paesani** - 2024 - chemrxiv.org

Can we experimentally observe the LL CP ?



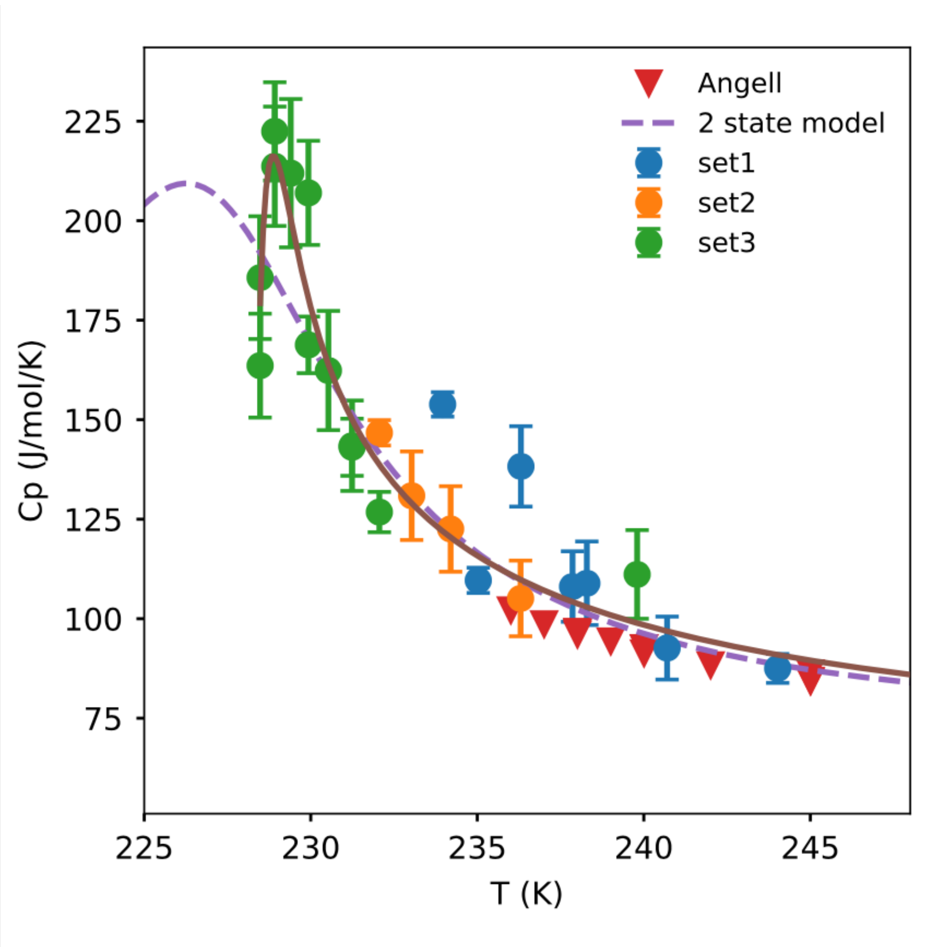
Bulk samples crystallize (μs time scales)!

PHYSICAL REVIEW E VOLUME 55, NUMBER 1 JANUARY 1997

Line of compressibility maxima in the phase diagram of supercooled water

Francesco Sciortino,[1,2] Peter H. Poole,[1,3] Ulrich Essmann,[1,*] and H. E. Stanley[1]

Recent experimental data..
Maxima in supercooled water at ambient pressure



Enhancement and maximum in the isobaric specific-heat capacity measurements of deeply supercooled water using ultrafast calorimetry

Harshad Pathak[a], Alexander Späh[a], Niloofar Esmaeildoost[b], Jonas A. Sellberg[b], Kyung Hwan Kim[c], Fivos Perakis[a], Katrin Amann-Winkel[a], Marjorie Ladd-Parada[a], Jayanath Koliyadu[b], Thomas J. Lane[d], Cheolhee Yang[c], Henrik Till Lemke[e], Alexander Roland Oggenfuss[e], Philip J. M. Johnson[e], Yunpei Deng[e], Serhane Zerdane[e], Roman Mankowsky[e], Paul Beaud[e], and Anders Nilsson[a,1]

[a]Department of Physics, AlbaNova University Center, Stockholm University, SE-10691 Stockholm, Sweden; [b]Biomedical and X-Ray Physics, Department of Applied Physics, KTH Royal Institute of Technology, AlbaNova University Center, SE-10691 Stockholm, Sweden; [c]Department of Chemistry, Pohang University of Science and Technology, Pohang 37673, Republic of Korea; [d]SLAC National Accelerator Laboratory, Linac Coherent Light Source, Menlo Park, CA 94025; and [e]SwissFEL, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

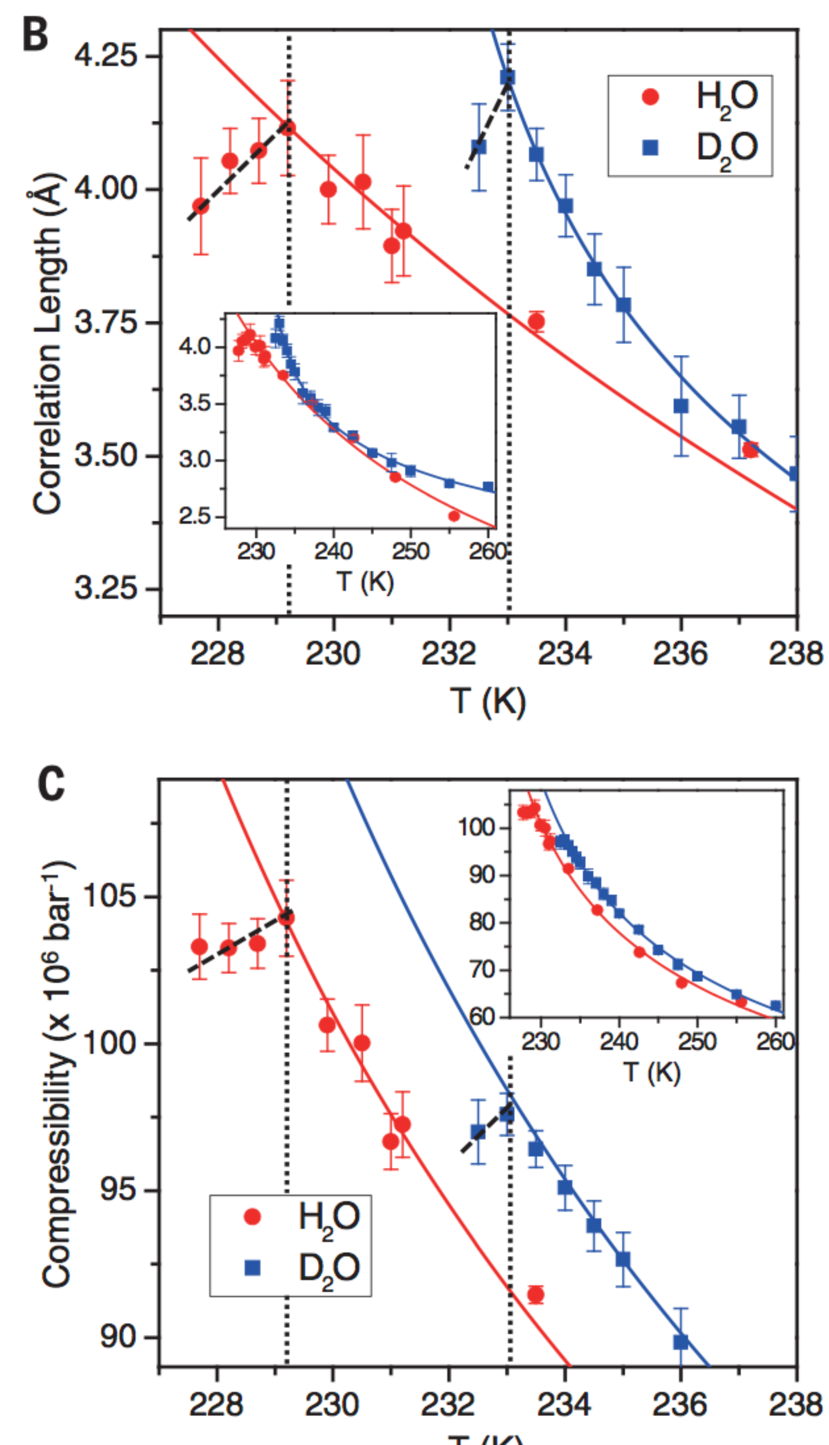
eived for review September 1, 2020)

PNAS 2021 Vol. 118 No. 6 e2018379118

WATER THERMODYNAMICS

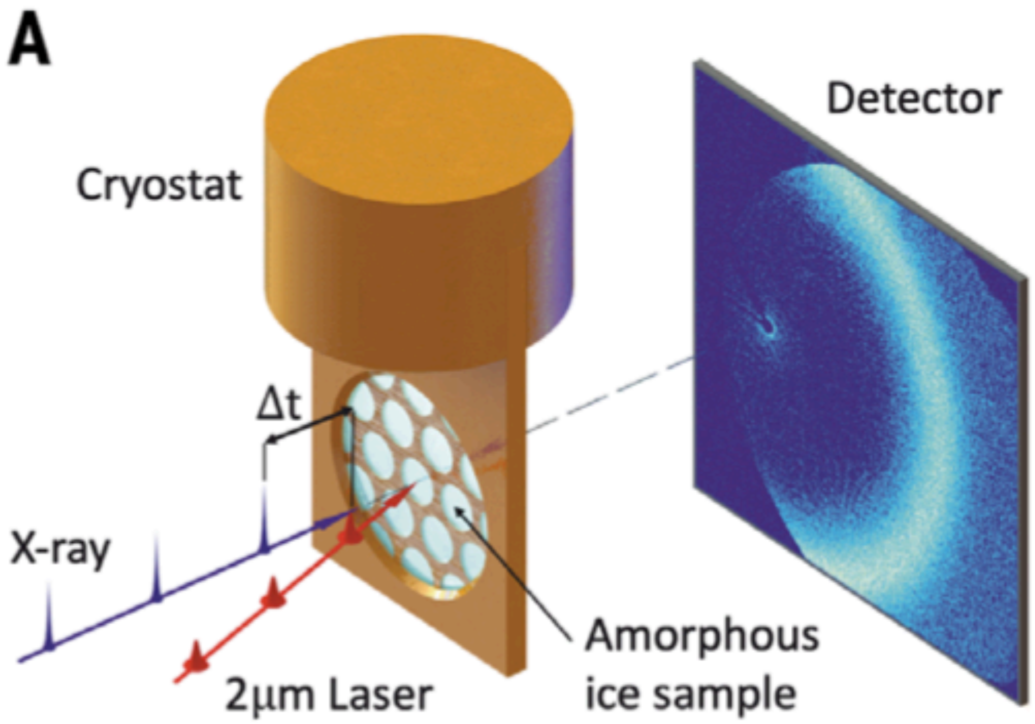
Maxima in the thermodynamic response and correlation functions of deeply supercooled water

Kyung Hwan Kim,[1*] Alexander Späh,[1*] Harshad Pathak,[1] Fivos Perakis,[1] Daniel Mariedahl,[1] Katrin Amann-Winkel,[1] Jonas A. Sellberg,[2] Jae Hyuk Lee,[3] Sangsoo Kim,[3] Jaehyun Park,[3] Ki Hyun Nam,[3] Tetsuo Katayama,[4] Anders Nilsson[1]†



A beautiful recent experiment:

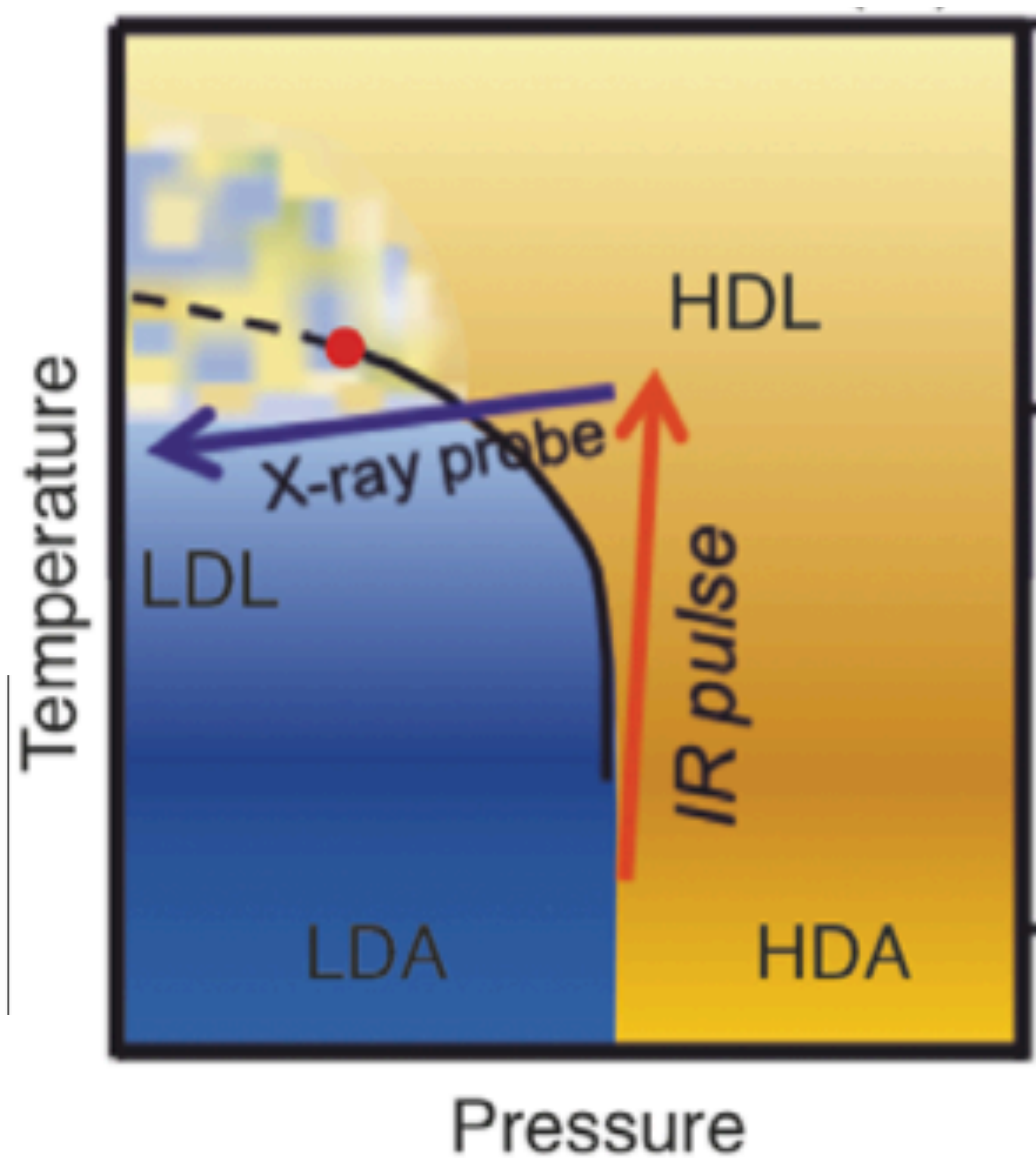
Kim *et al.*, *Science* **370**, 978–982 (2020) 20 November 2020



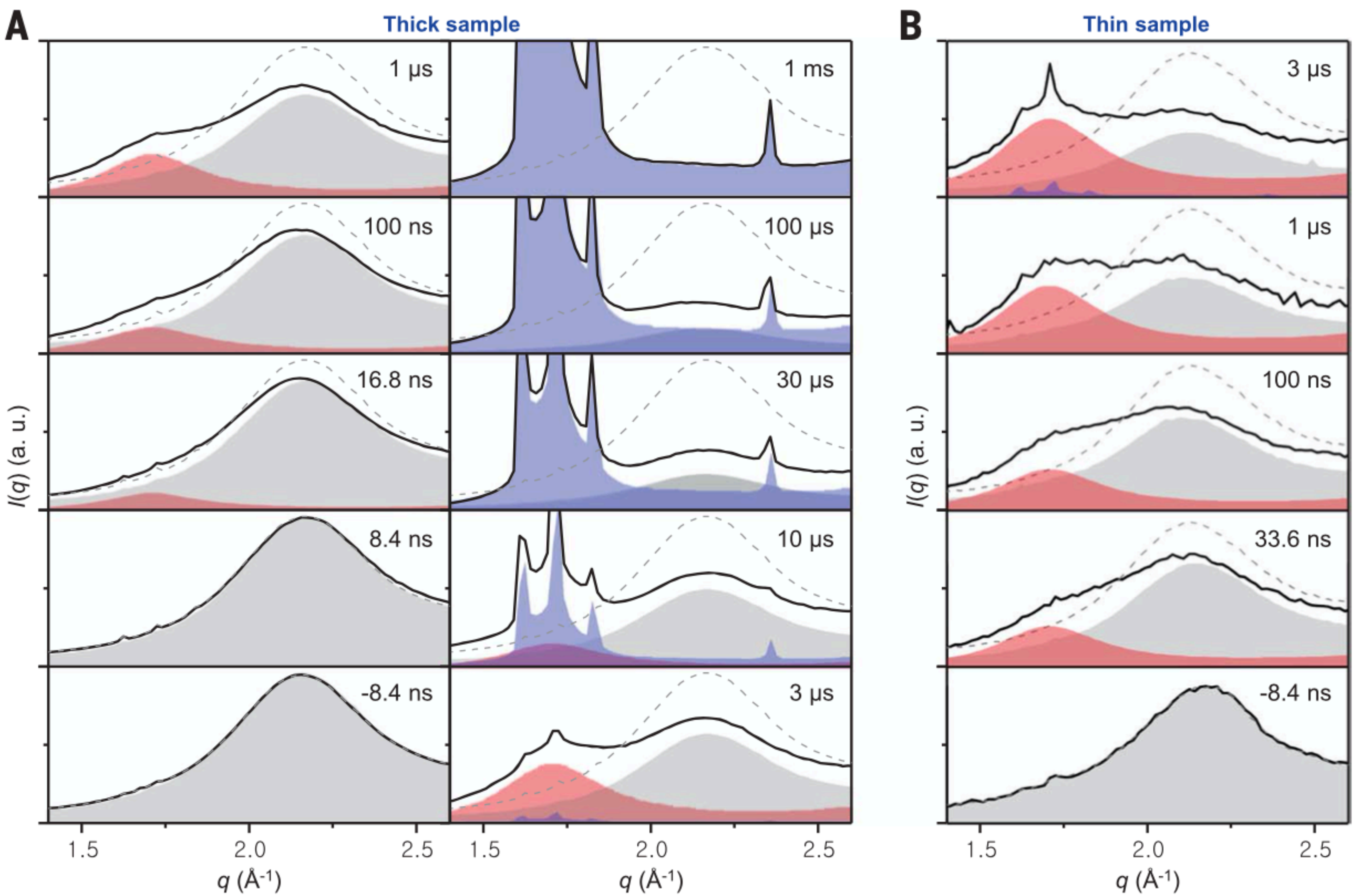
WATER PHASES

Experimental observation of the liquid-liquid transition in bulk supercooled water under pressure

Kyung Hwan Kim[1,2]*, Katrin Amann-Winkel[1]*, Nicolas Giovambattista[3,4], Alexander Späh[1], Fivos Perakis[1], Harshad Pathak[1], Marjorie Ladd Parada[1], Cheolhee Yang[2], Daniel Mariedahl[1], Tobias Eklund[1], Thomas. J. Lane[5,6], Seonju You[2], Sangmin Jeong[2], Matthew Weston[1], Jae Hyuk Lee[7], Intae Eom[7], Minseok Kim[7], Jaeku Park[7], Sae Hwan Chun[7], Peter H. Poole[8], Anders Nilsson[1]†



A beautiful recent experiment:



WATER PHASES

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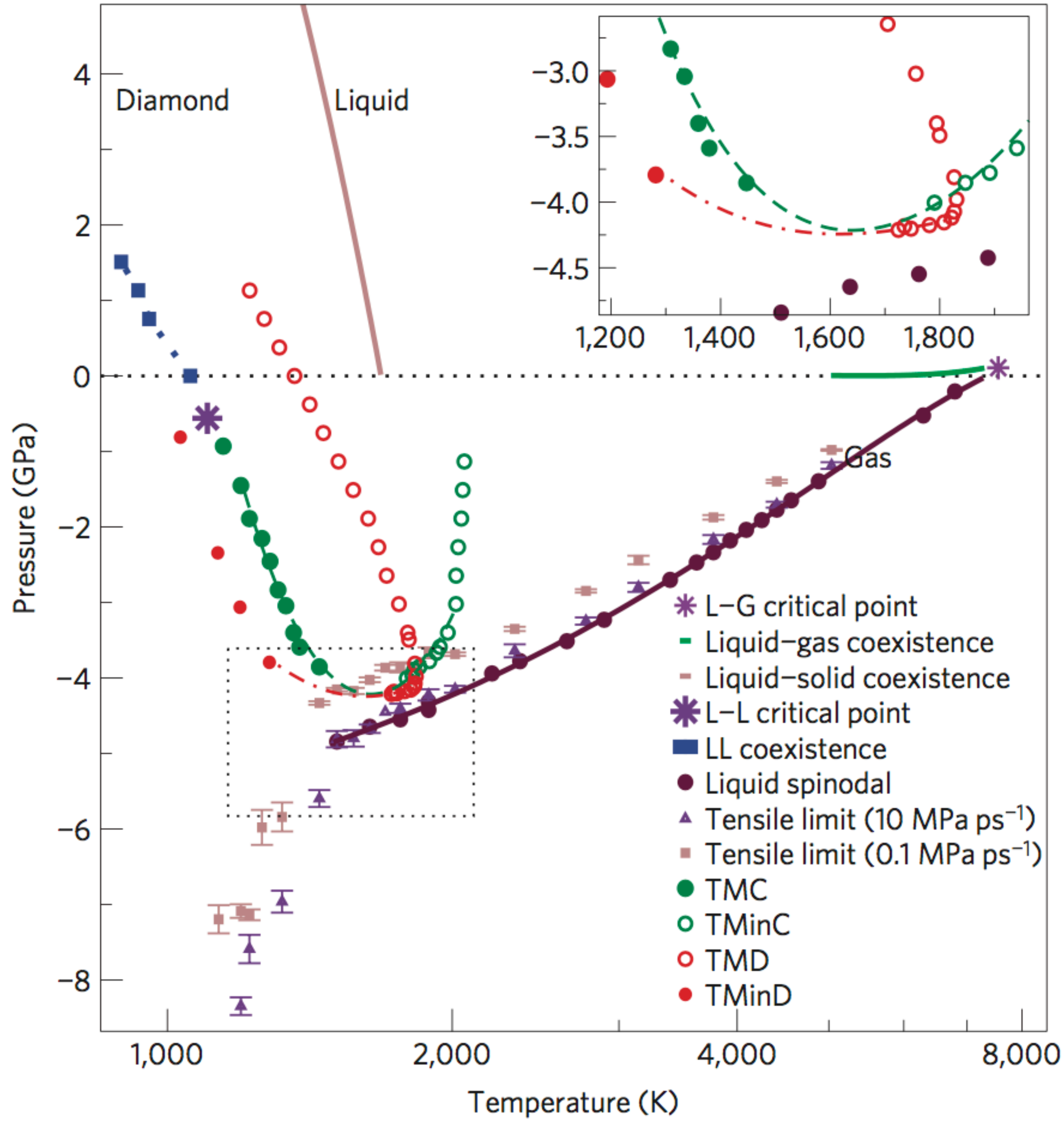
Kim *et al.*, *Science* **370**, 978–982 (2020)   20 November 2020

How general is this phenomenon in tetrahedral systems ?

Silicon

(Stillinger-Weber model)



Vasisht, V. V.; Saw, S.; Sastry, S. Liquid-Liquid Critical Point in Supercooled Silicon. Nat. Phys. 2011, 7, 549–553.

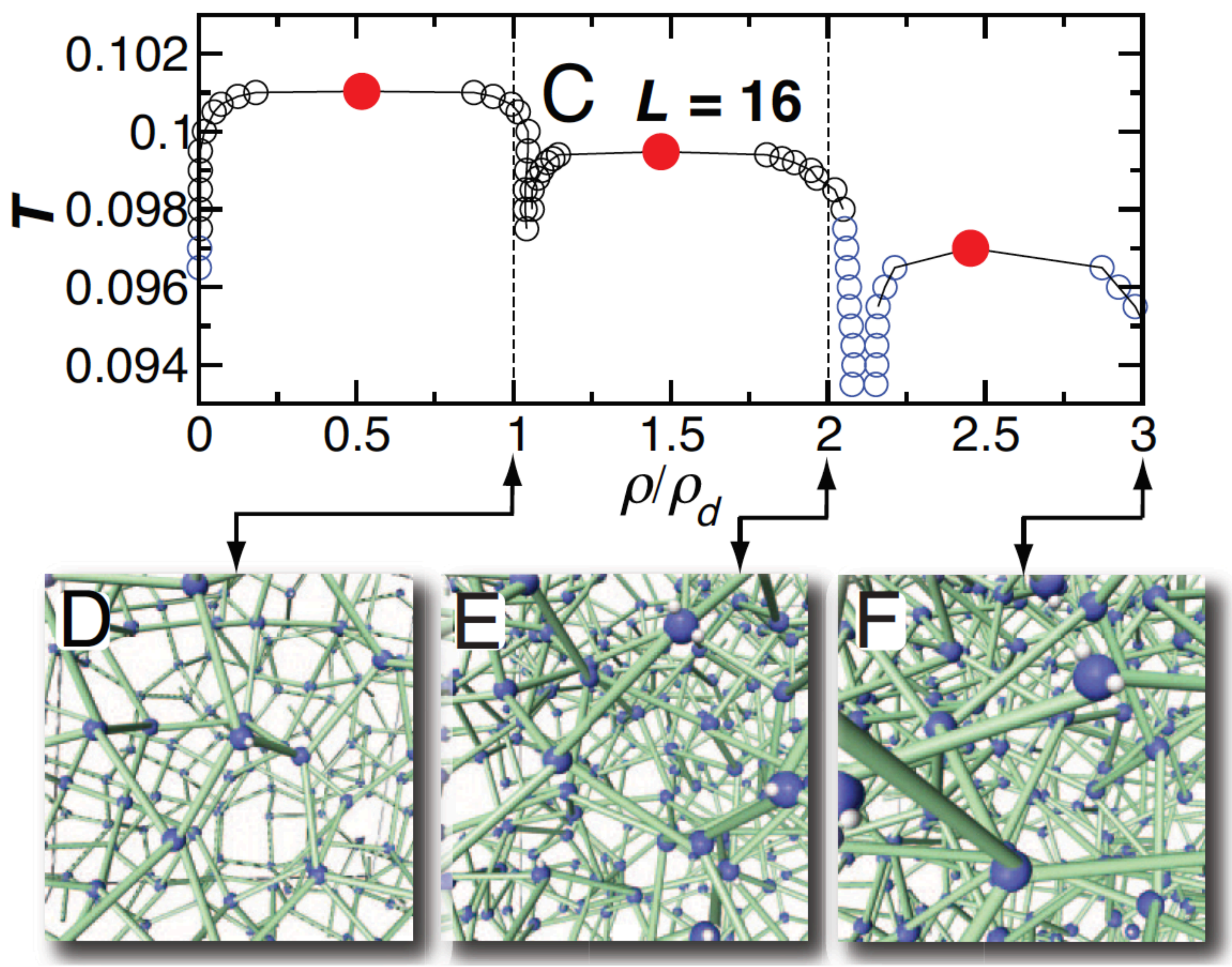
Others… tetrahedral particles

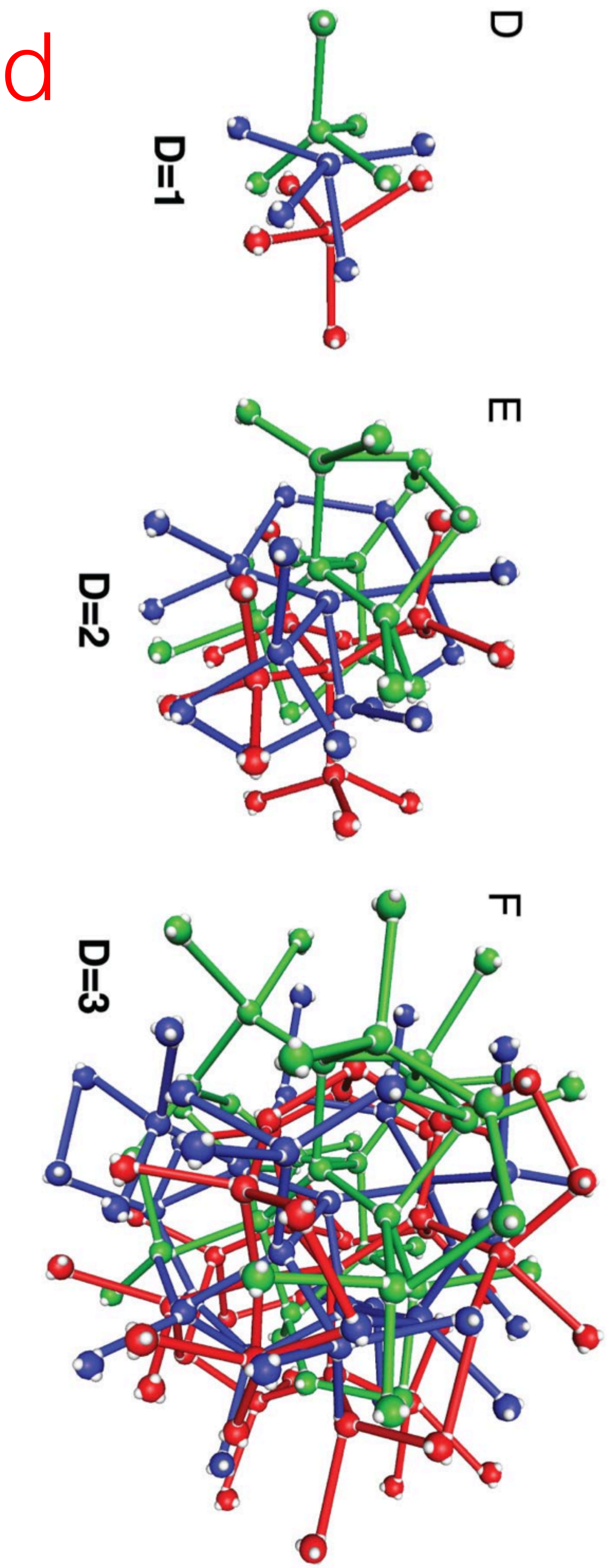
Sticky tetrapod

Hierarchies of networked phases induced by multiple liquid–liquid critical points

Chia Wei Hsu*, Julio Largo†‡, Francesco Sciortino†, and Francis W. Starr*§

*Department of Physics, Wesleyan University, Middletown, CT 06459; †Dipartimento di Fisica and Consiglio Nazionale delle Richerche-Instituto Nazionale per la Fisica della Materia-Soft: Complex Dynamics in Structured Systems, Università di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185 Rome, Italy; and ‡Departamento de Fisica Aplicada, Universidad de Cantabria, Avda. Los Castros s/n Santander, 39005, Spain





Interpenetrating flexible colloidal (tetrahedral) particles

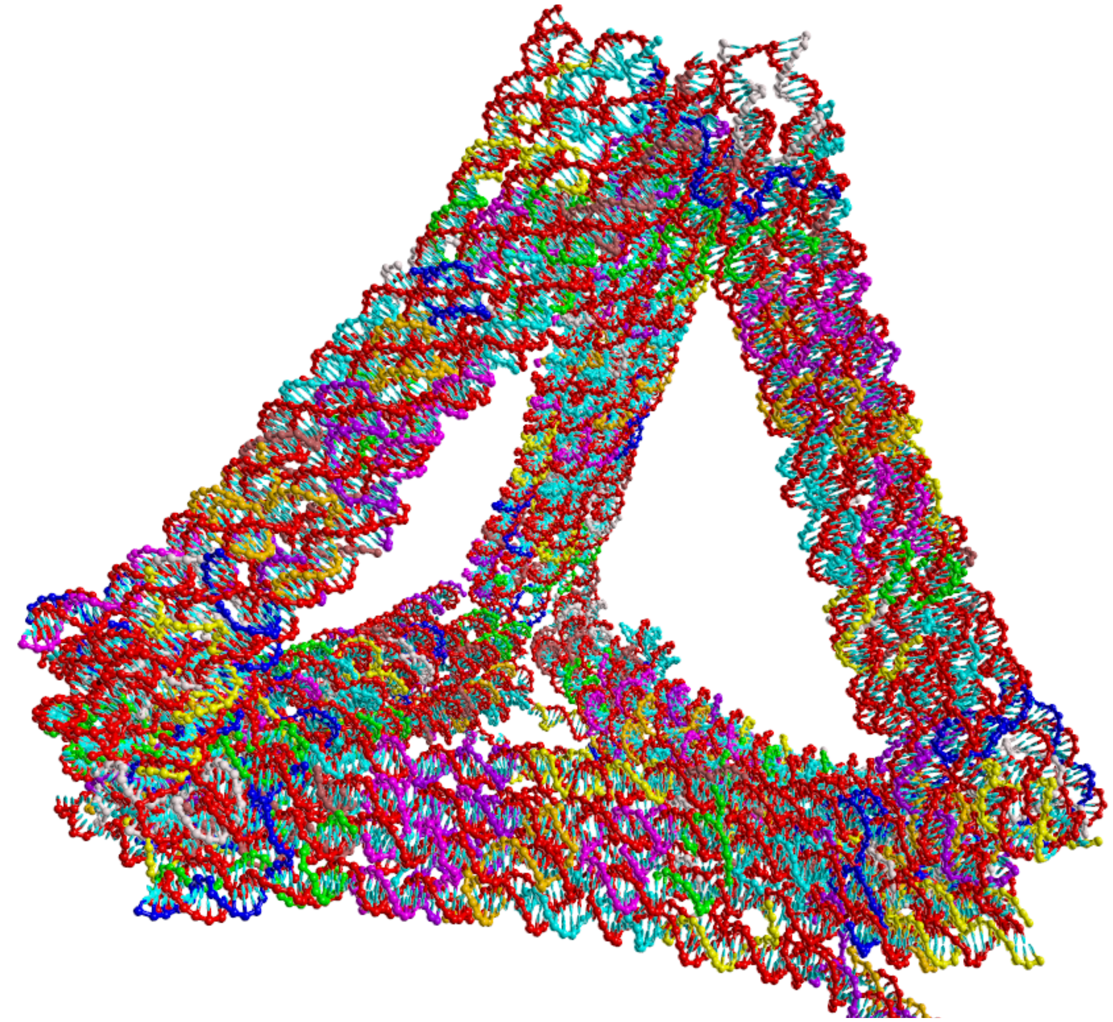
Eur. Phys. J. E (2016) **39**: 131
DOI 10.1140/epje/i2016-16131-5

THE EUROPEAN PHYSICAL JOURNAL E

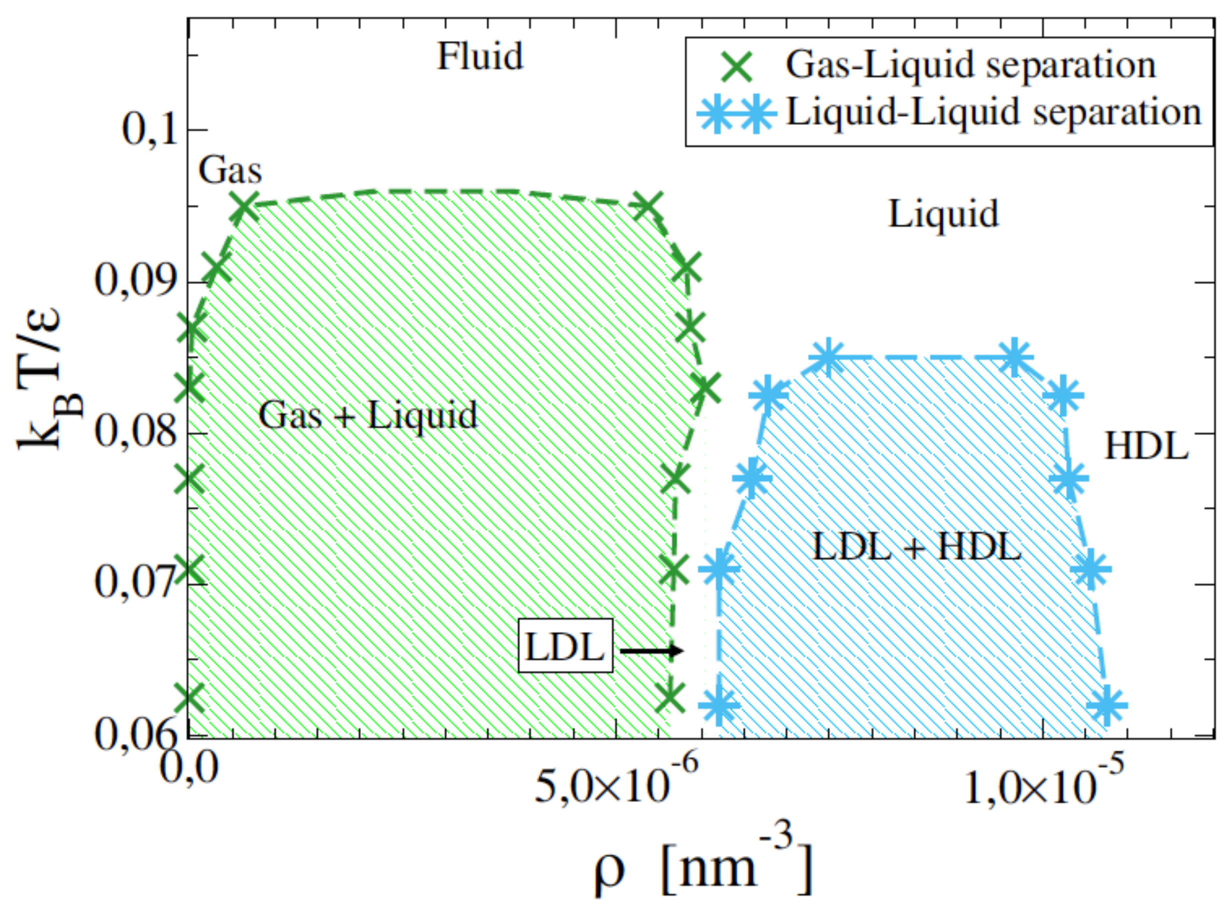
Regular Article

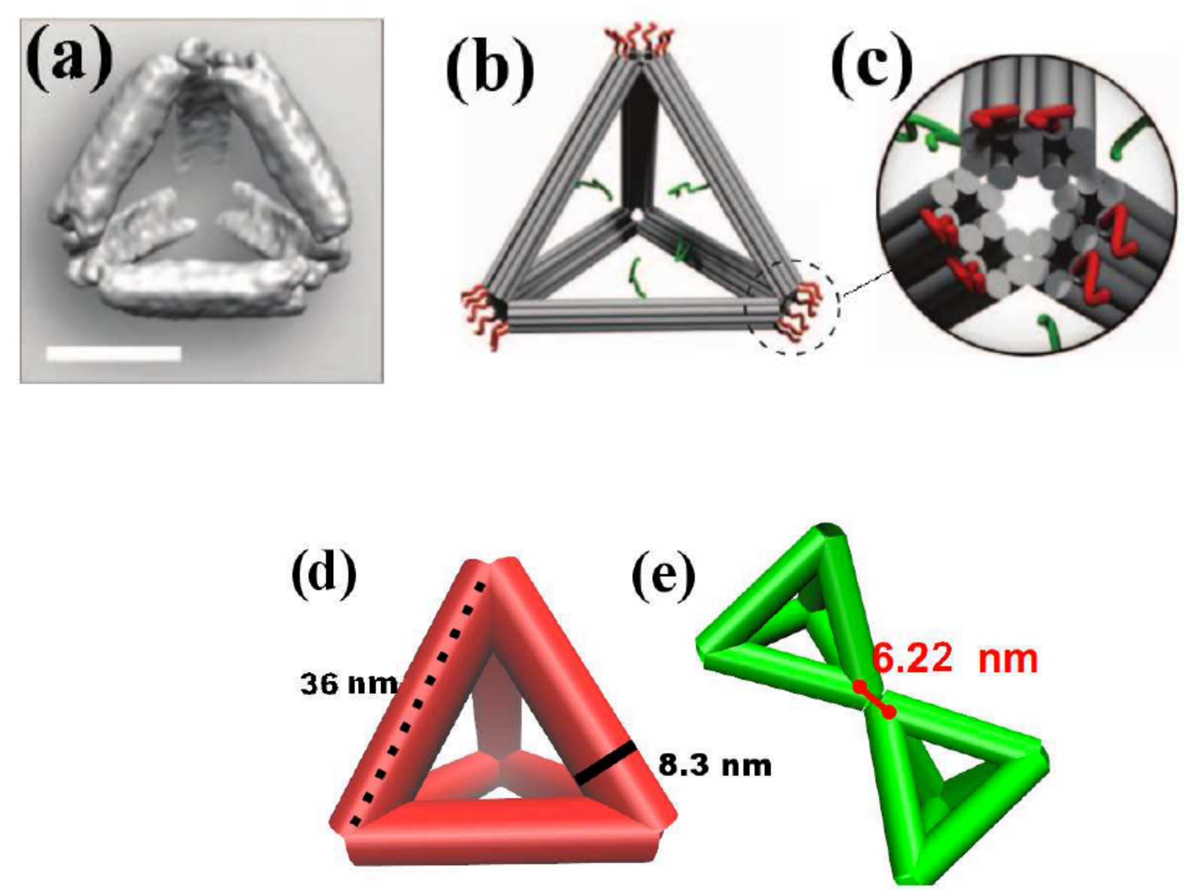
Toward the observation of a liquid-liquid phase transition in patchy origami tetrahedra: a numerical study

Simone Ciarella[1,a], Oleg Gang[2], and Francesco Sciortino[1]

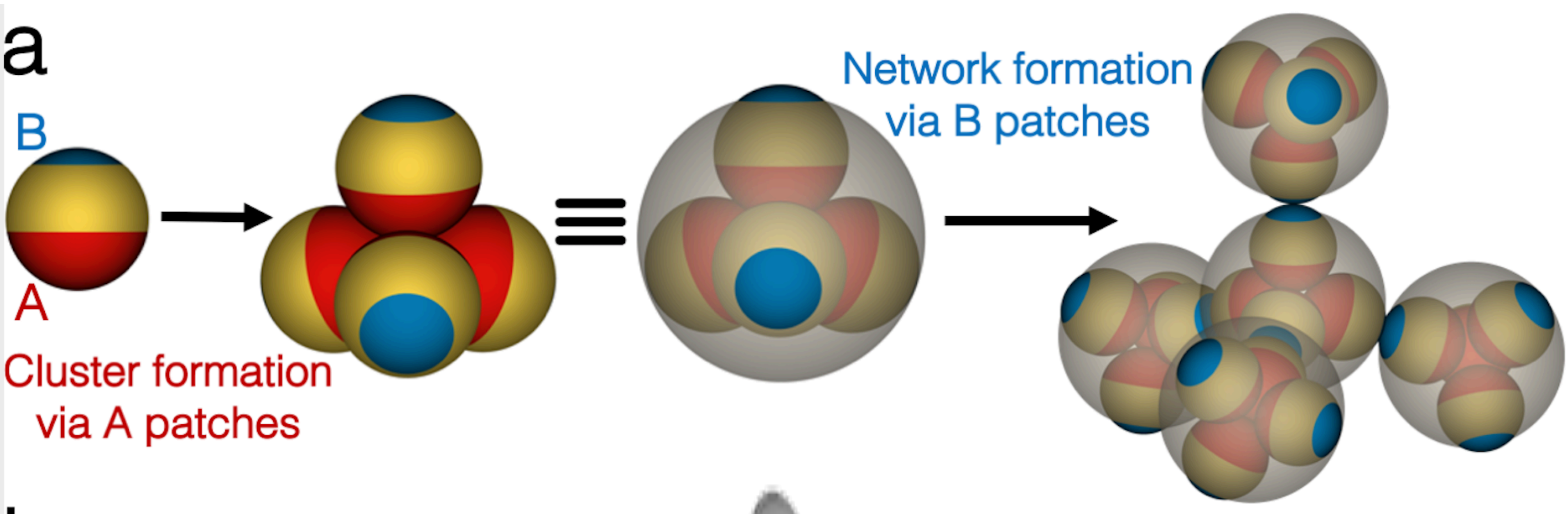


Eur. Phys. J. E (2016) **39**: 131



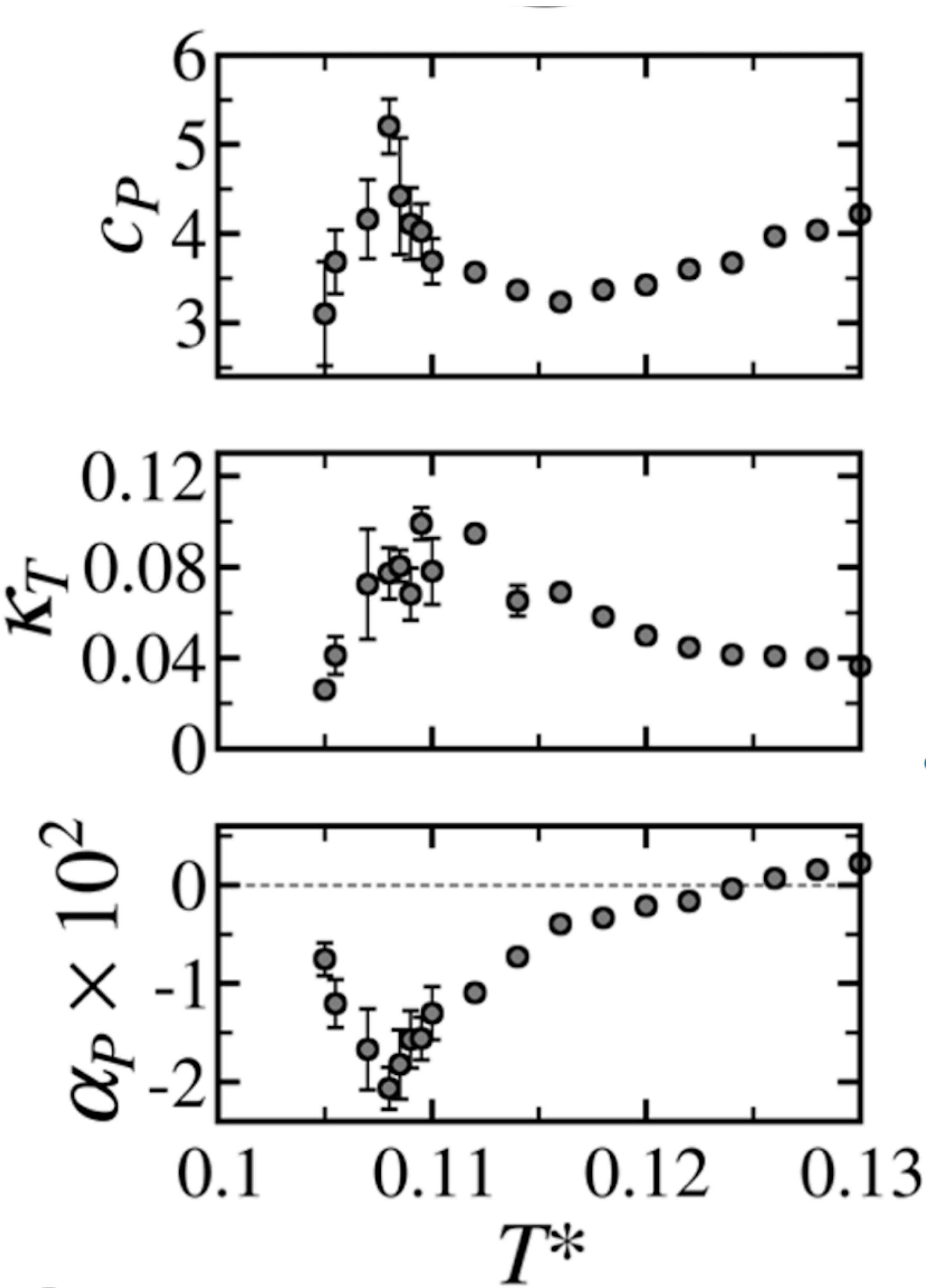


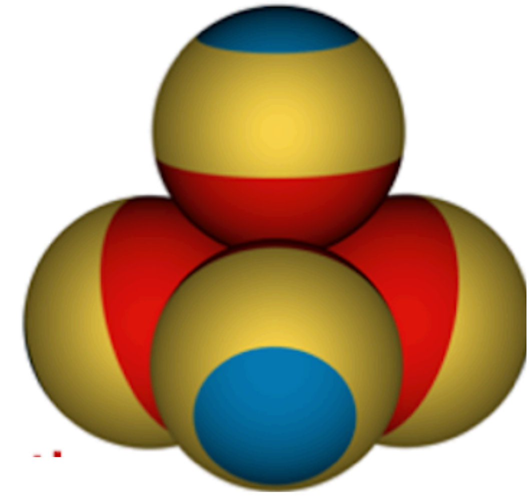
Triblock Janus Particles (Steve Granick's Lab)

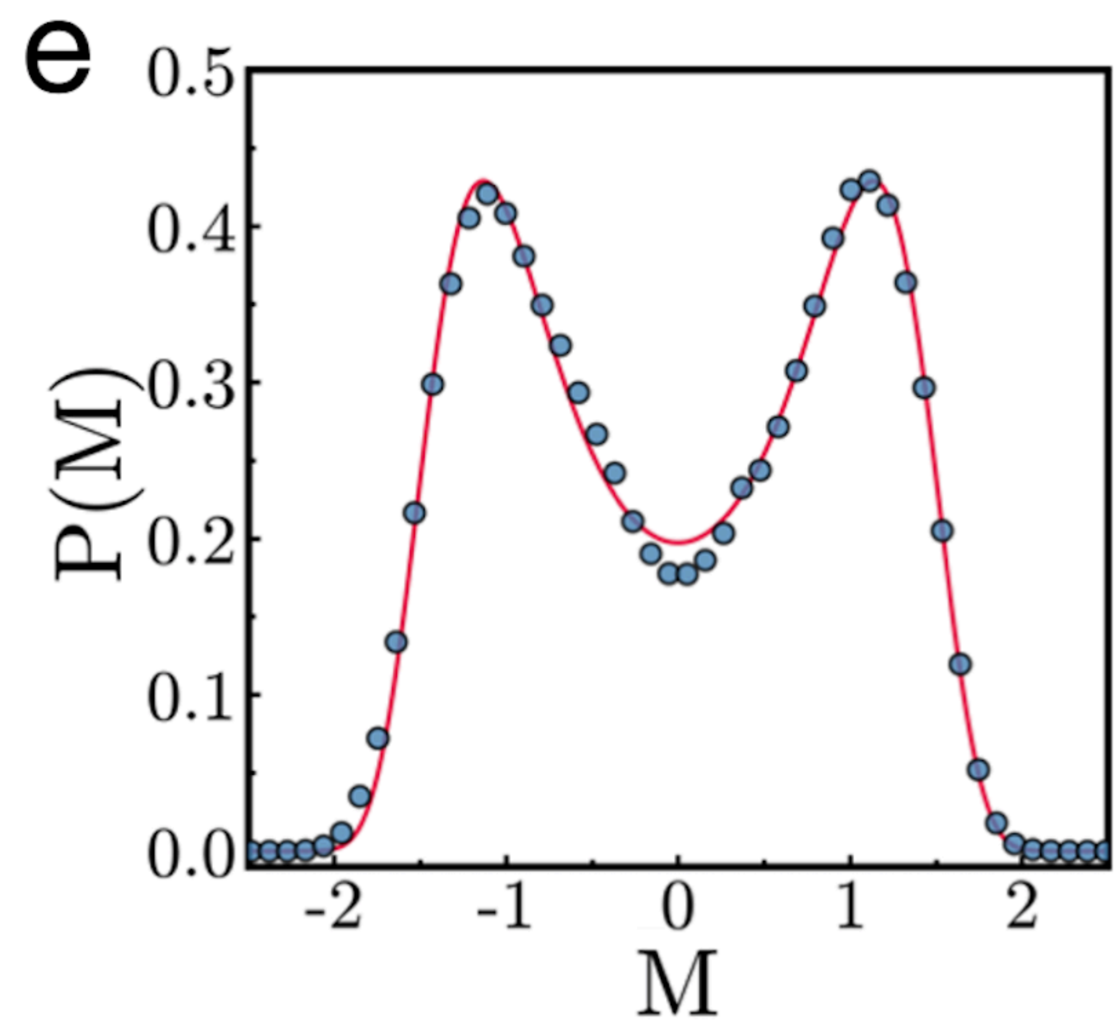


Two-step self-assembly model proposed by Dwaipayan Chakrabarti (Birmingham)

Water-like thermodynamic anomalies of colloidal water







Topological Nature of the Liquid-Liquid Phase Transition in Tetrahedral Liquids

Andreas Neophytou[1], Dwaipayan Chakrabarti[1], and Francesco Sciortino[2]

[1]School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom
[2]Dipartimento di Fisica, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185 Roma, Italy

Why am I here:

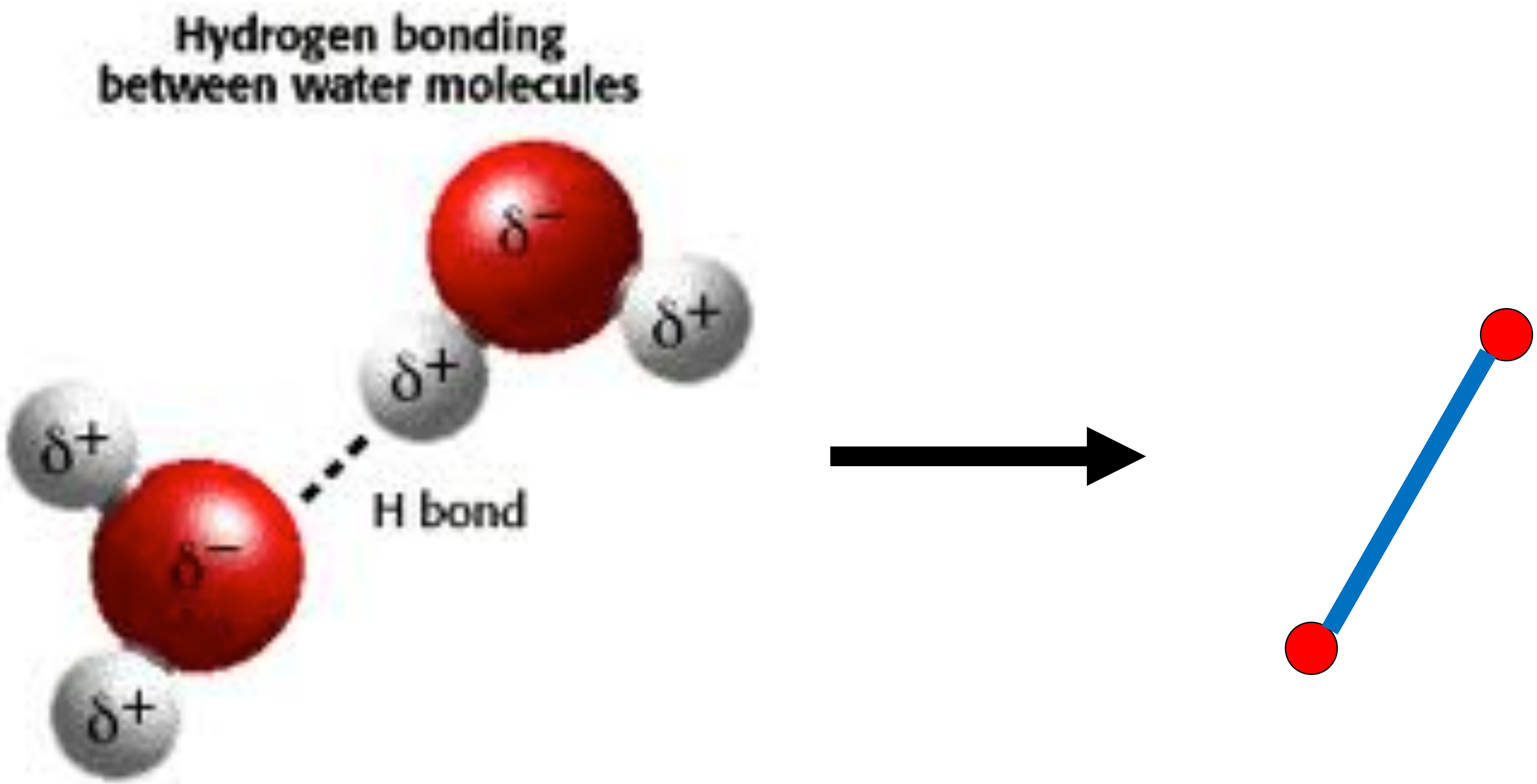
A fresh look at the LL transition

Focus on the bond network

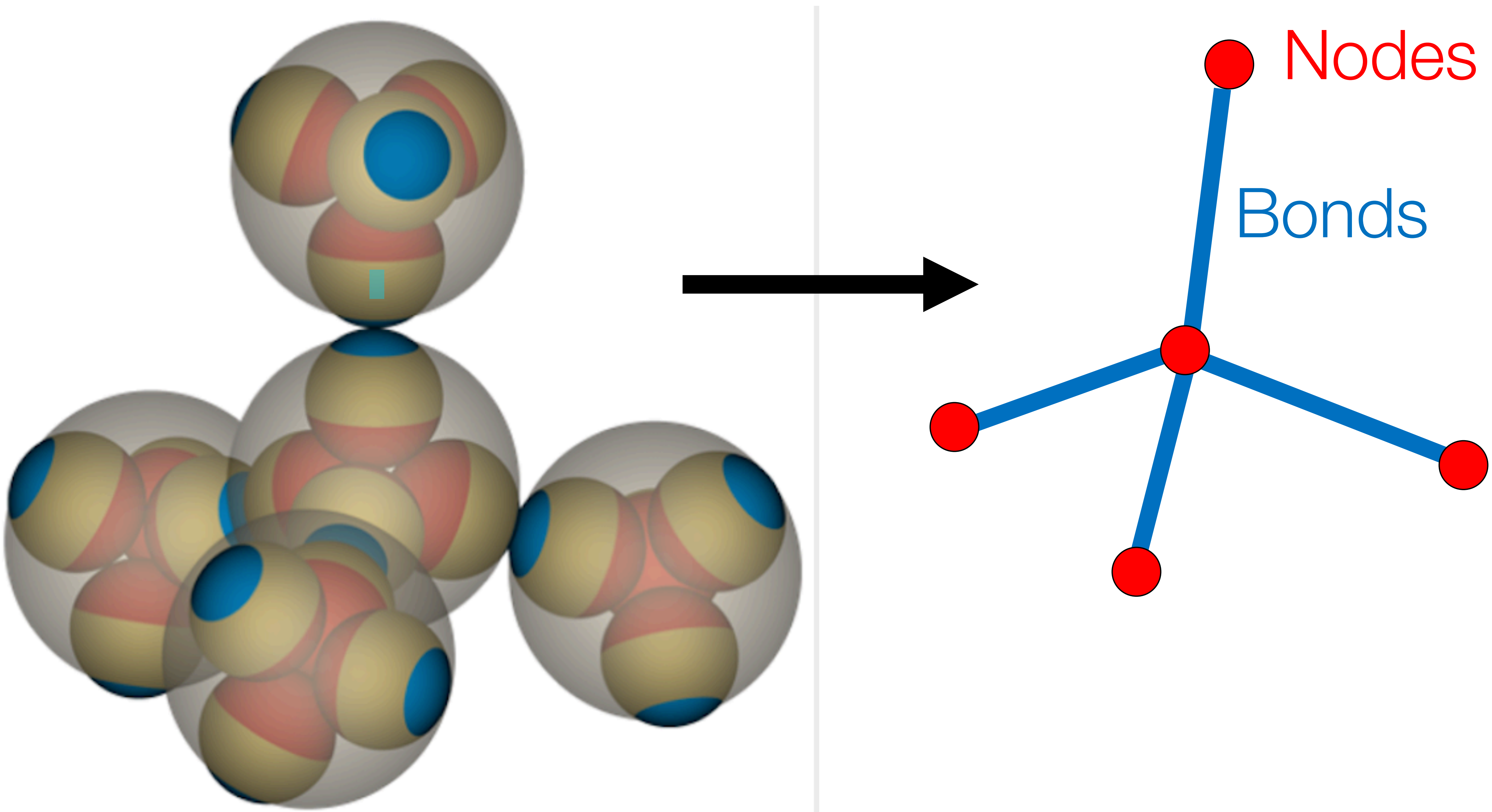
Identify the rings in the network

Look how rings are linked

From a physical network to an abstract network



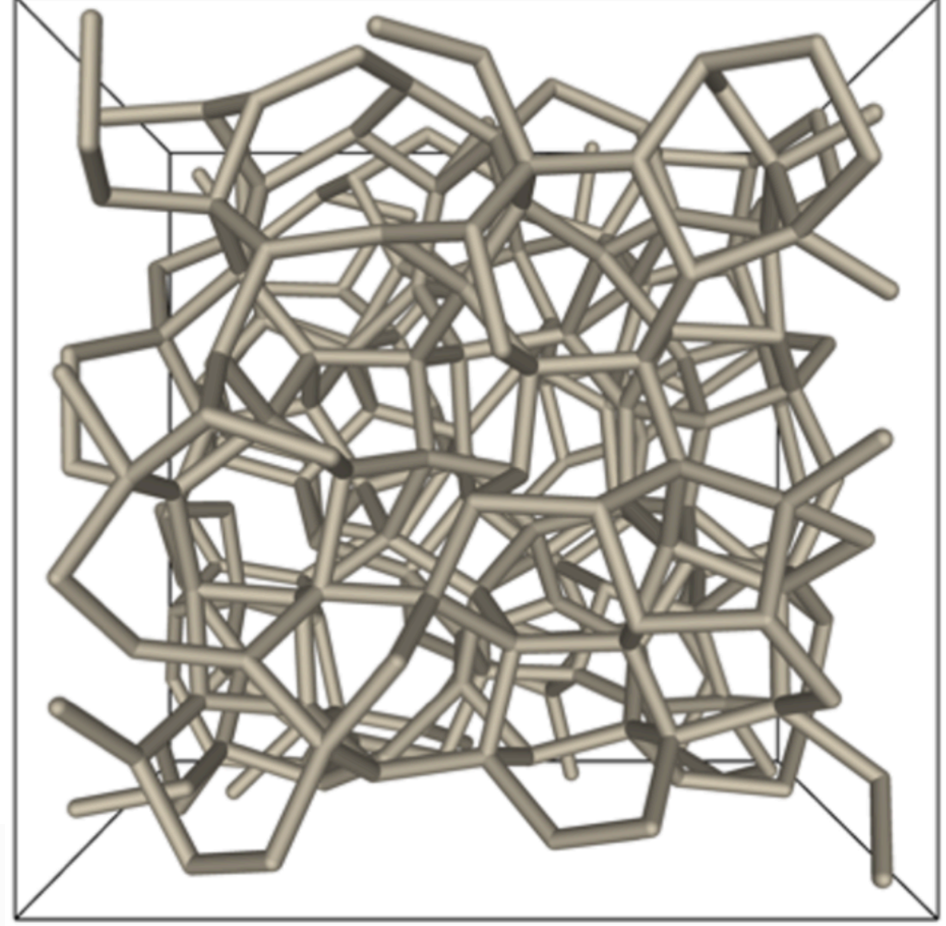
From a physical network to an abstract network



The colloidal water bond network

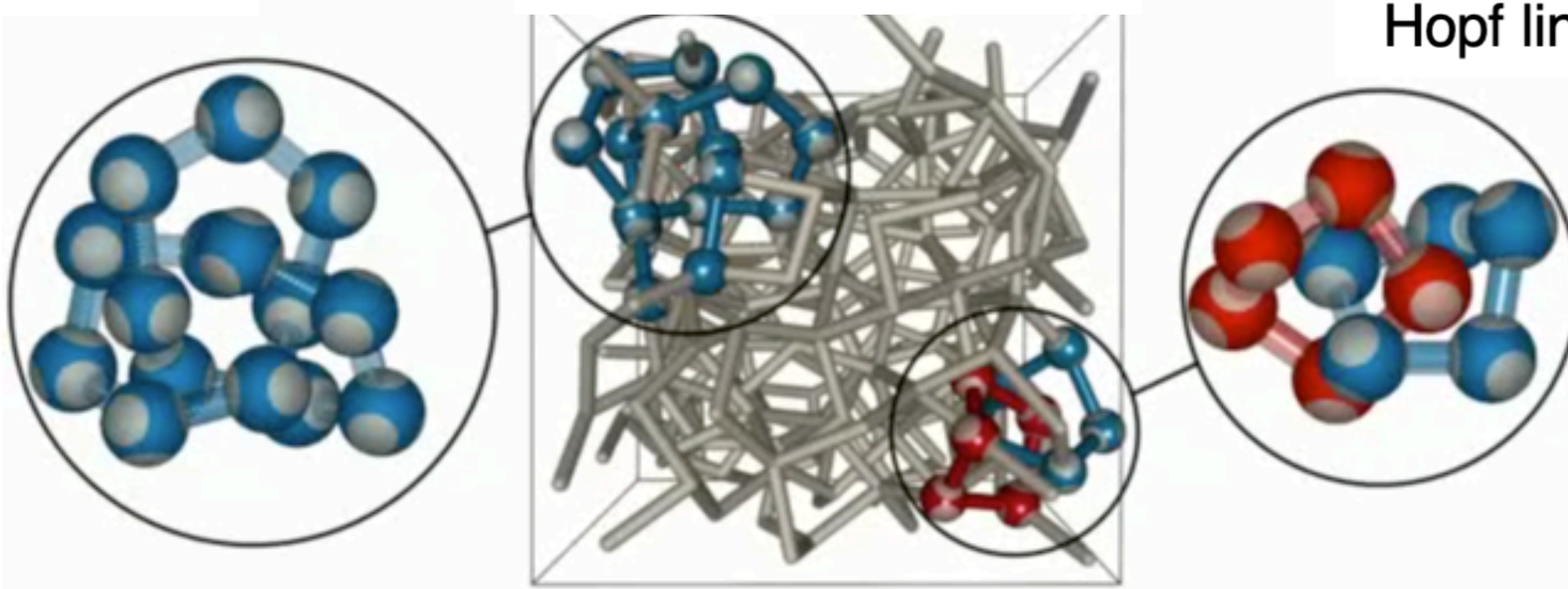
Idea:
Focus on the rings and look how they are “linked” and/or entangled

trefoil knot

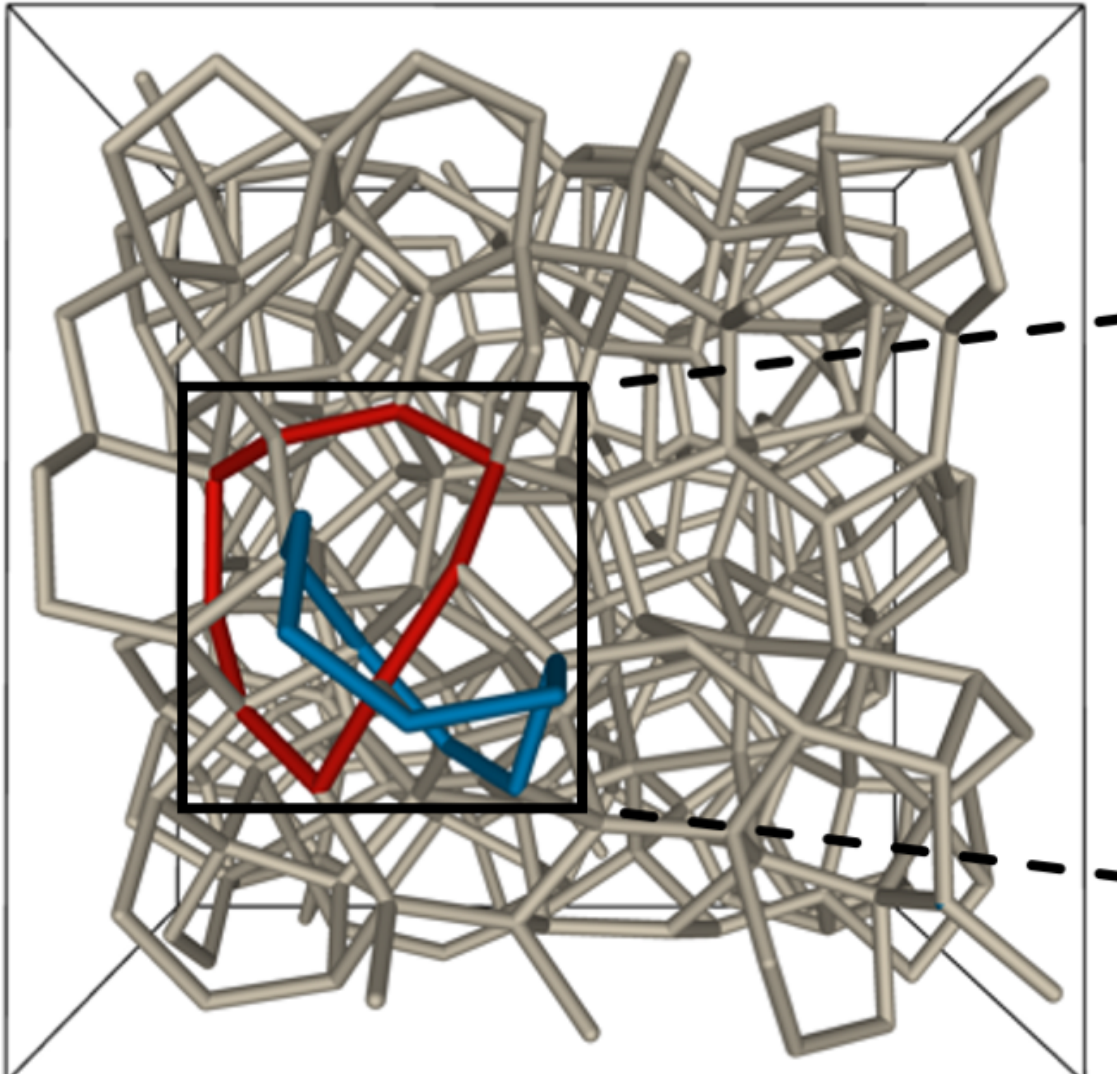


LDL (network)

Hopf link



HDL (network)



Two important quantites:

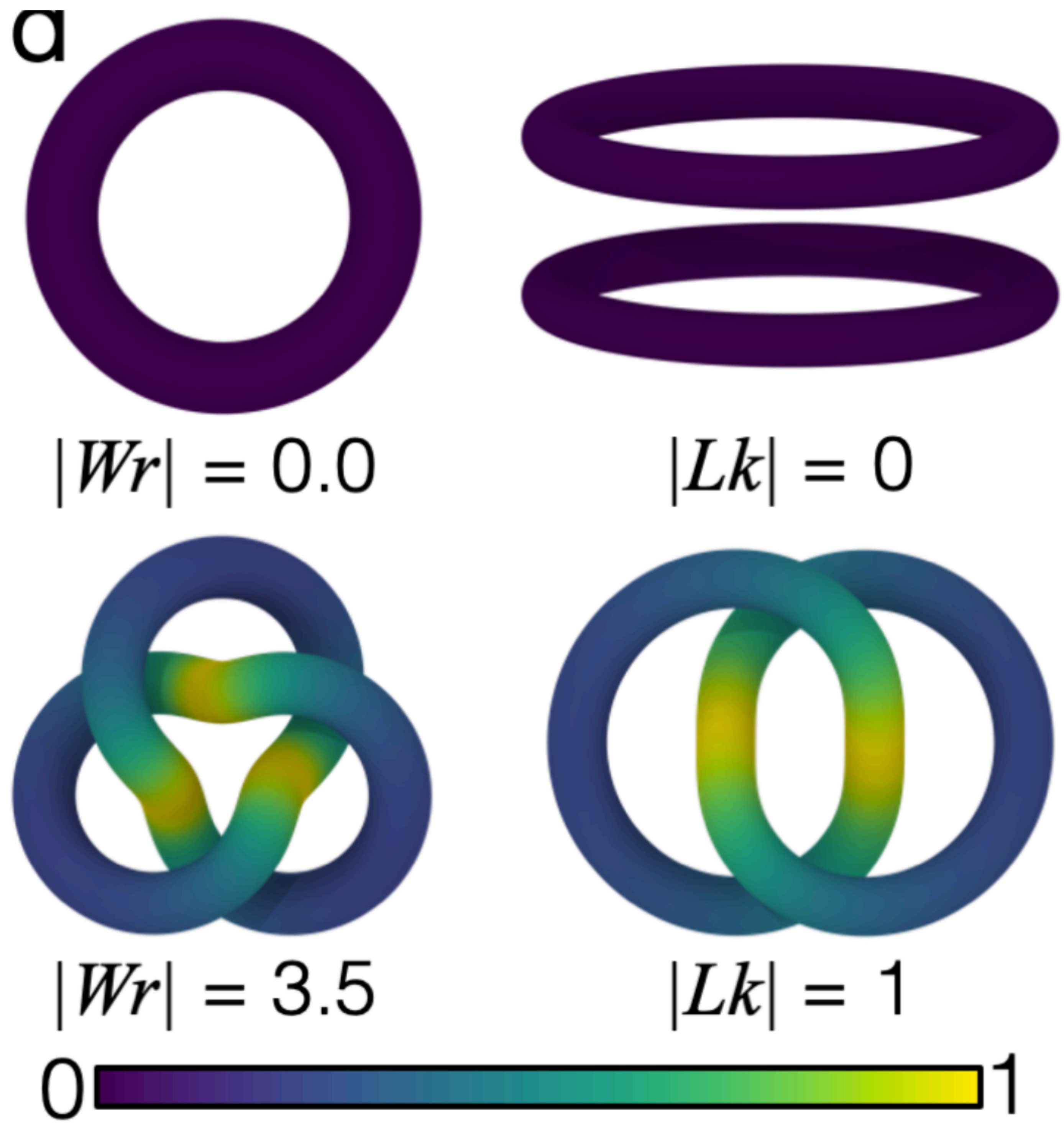
The linking number (are rings I and J linked ?)

$$Lk_{ij} = \frac{1}{4\pi} \oint_{R^i} \oint_{R^j} \frac{\boldsymbol{r}_j - \boldsymbol{r}_i}{|\boldsymbol{r}_j - \boldsymbol{r}_i|^3} \cdot (\mathrm{d}\boldsymbol{r}_j \times \mathrm{d}\boldsymbol{r}_i)$$

The Writhe number (is ring I coiled and knotted ?)

$$Wr_i = \frac{1}{4\pi} \oint_{C^i} \oint_{C^i} \frac{\boldsymbol{r}'_i - \boldsymbol{r}_i}{|\boldsymbol{r}'_i - \boldsymbol{r}_i|^3} \cdot (\mathrm{d}\boldsymbol{r}'_i \times \mathrm{d}\boldsymbol{r}_i)$$

Two important quantites:

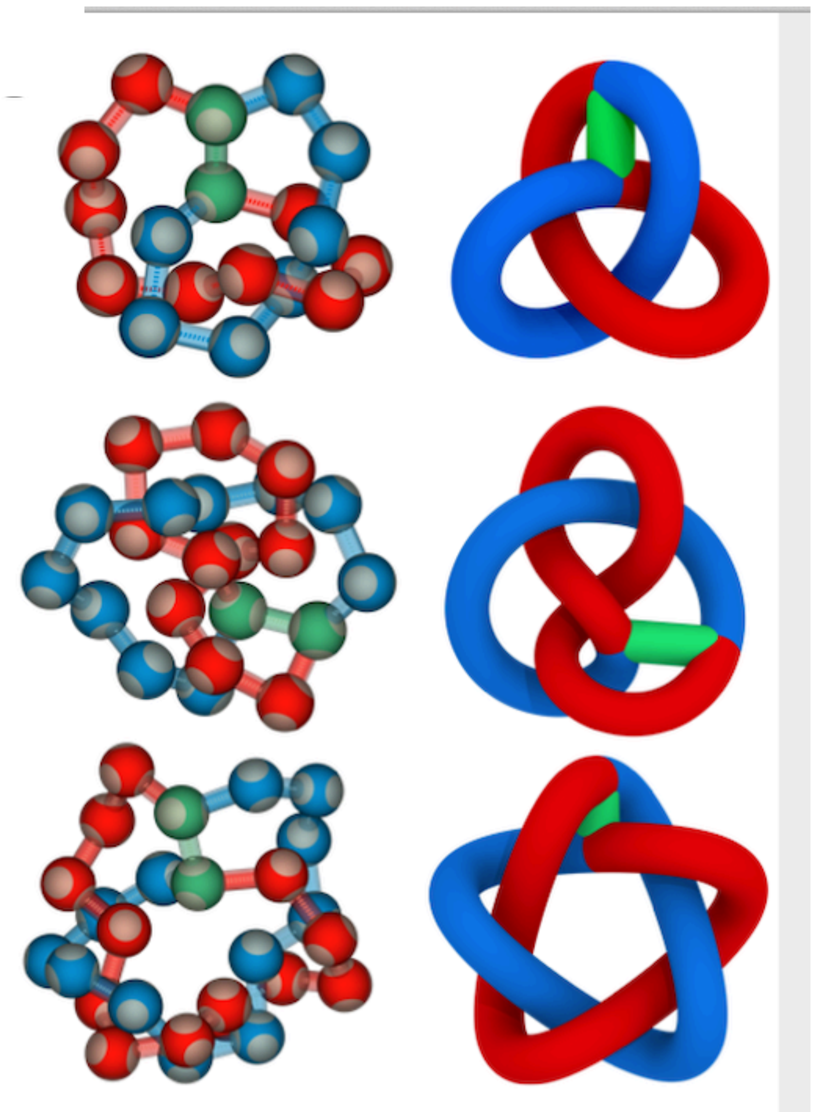


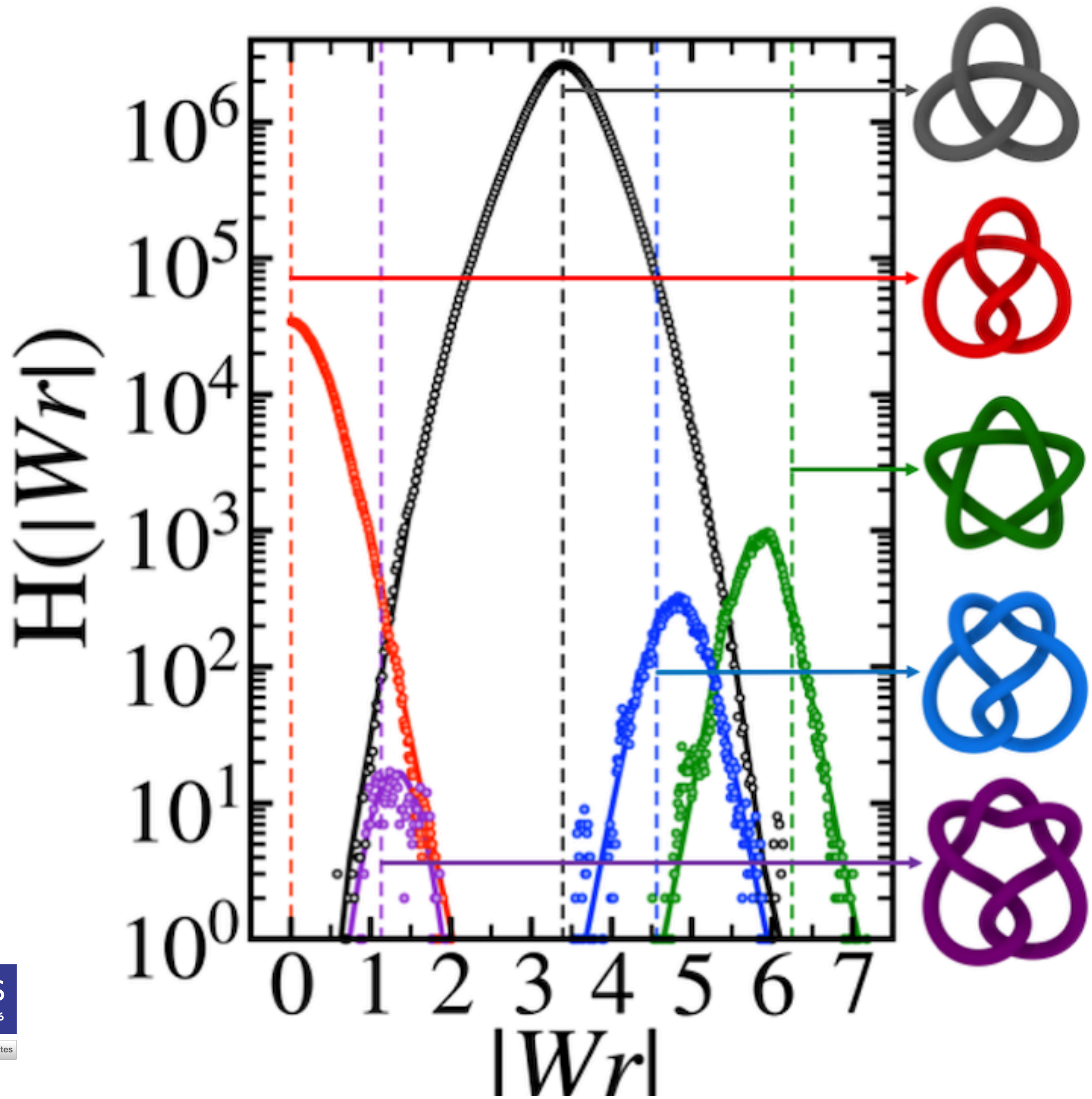
Linking and Writhe of one configuration

$$\mathcal{L}_n = \sum_{i>j}^{\mathcal{N}_{\mathrm{R}}} |Lk_{ij}|$$

$$\mathcal{W}_n = \sum_{i=1}^{\mathcal{N}_{\mathrm{R}}} |Wr_i|$$

Variety of knotted structures in HDL (colloidal model)





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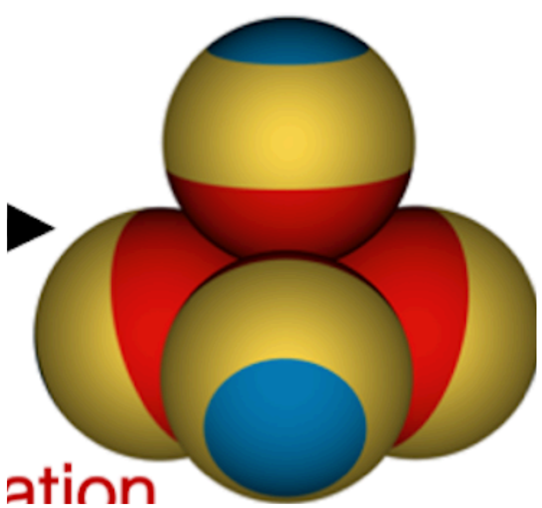
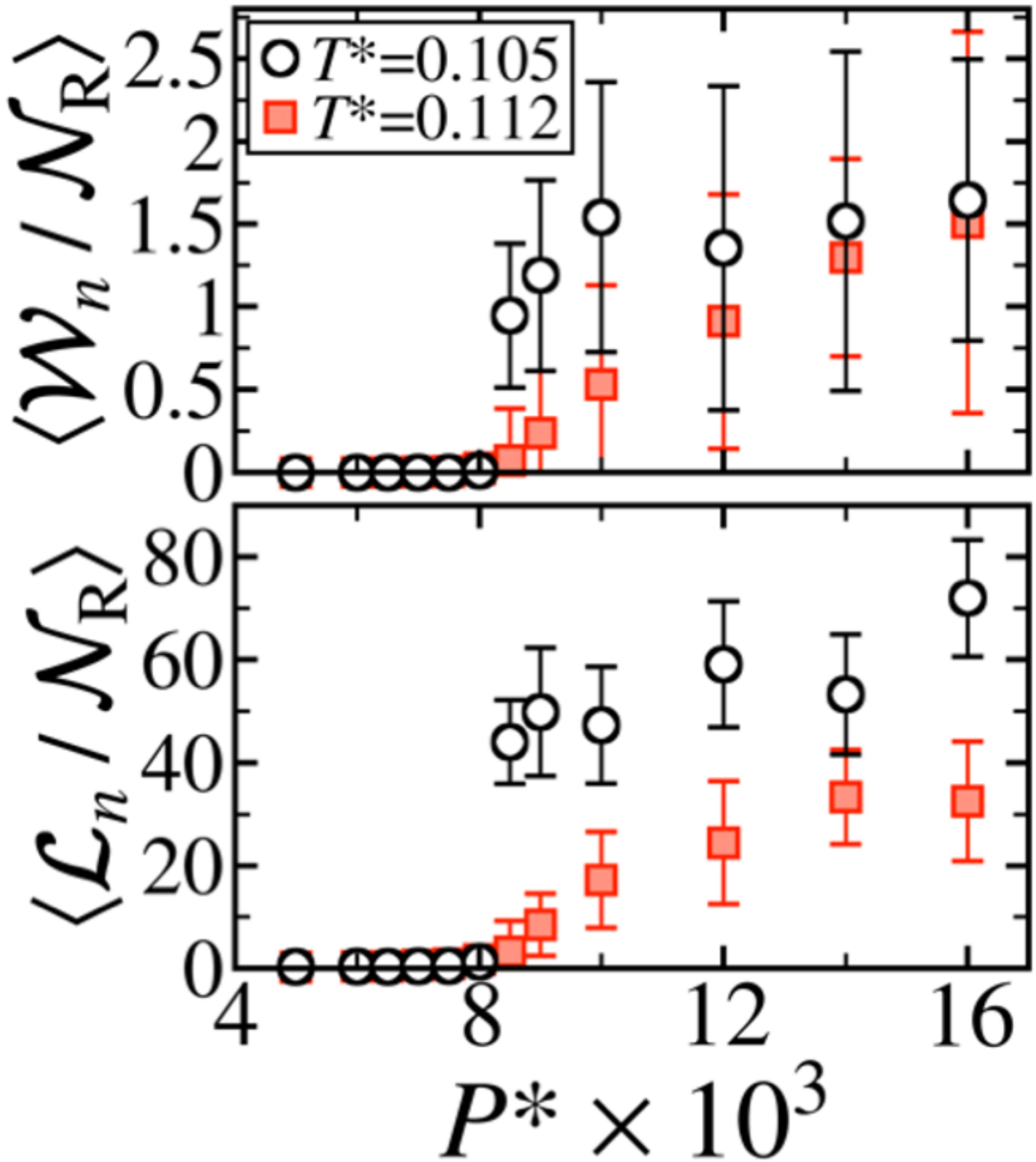
Topological nature of the liquid–liquid phase transition in tetrahedral liquids

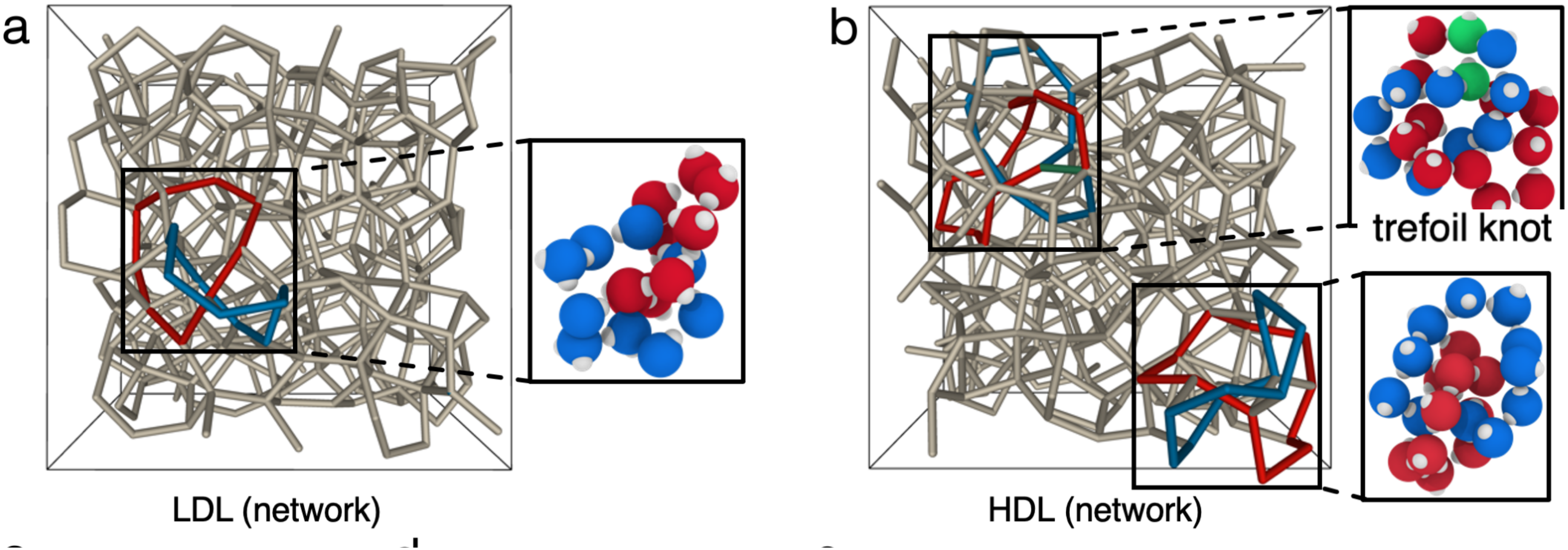
Andreas Neophytou[1], Dwaipayan Chakrabarti[1] and Francesco Sciortino[2]

The writhe and the linking as order parameters





Does it holds also for molecular water ?



TIP4P/Ice
(a water model)

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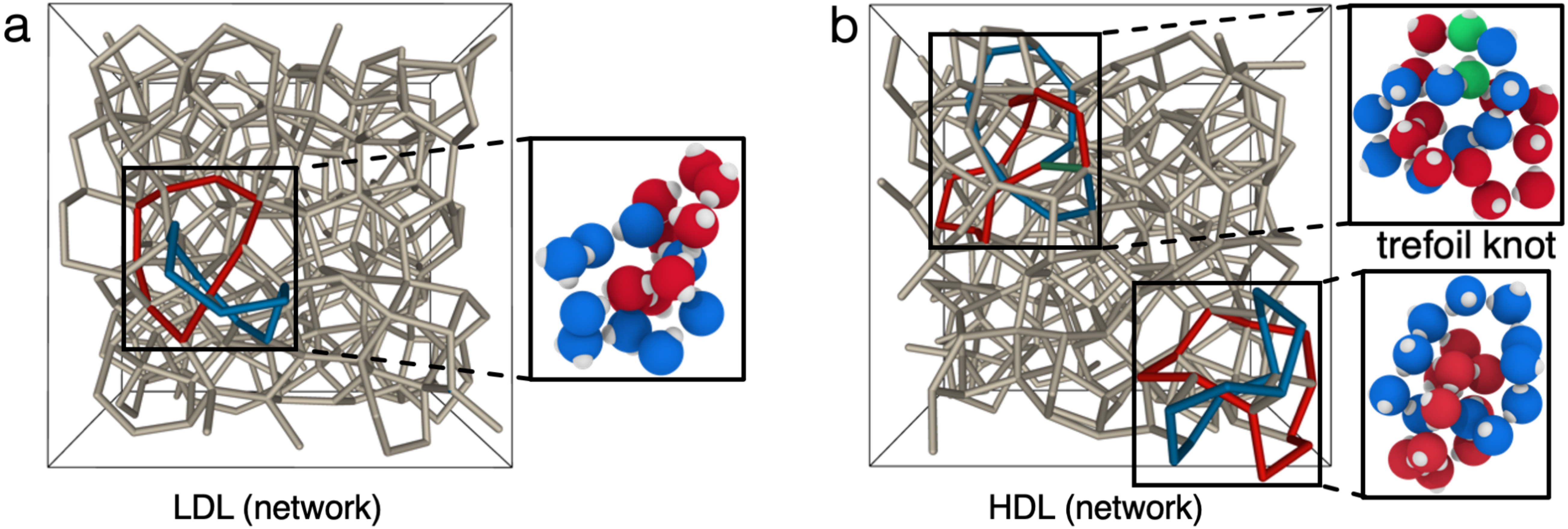

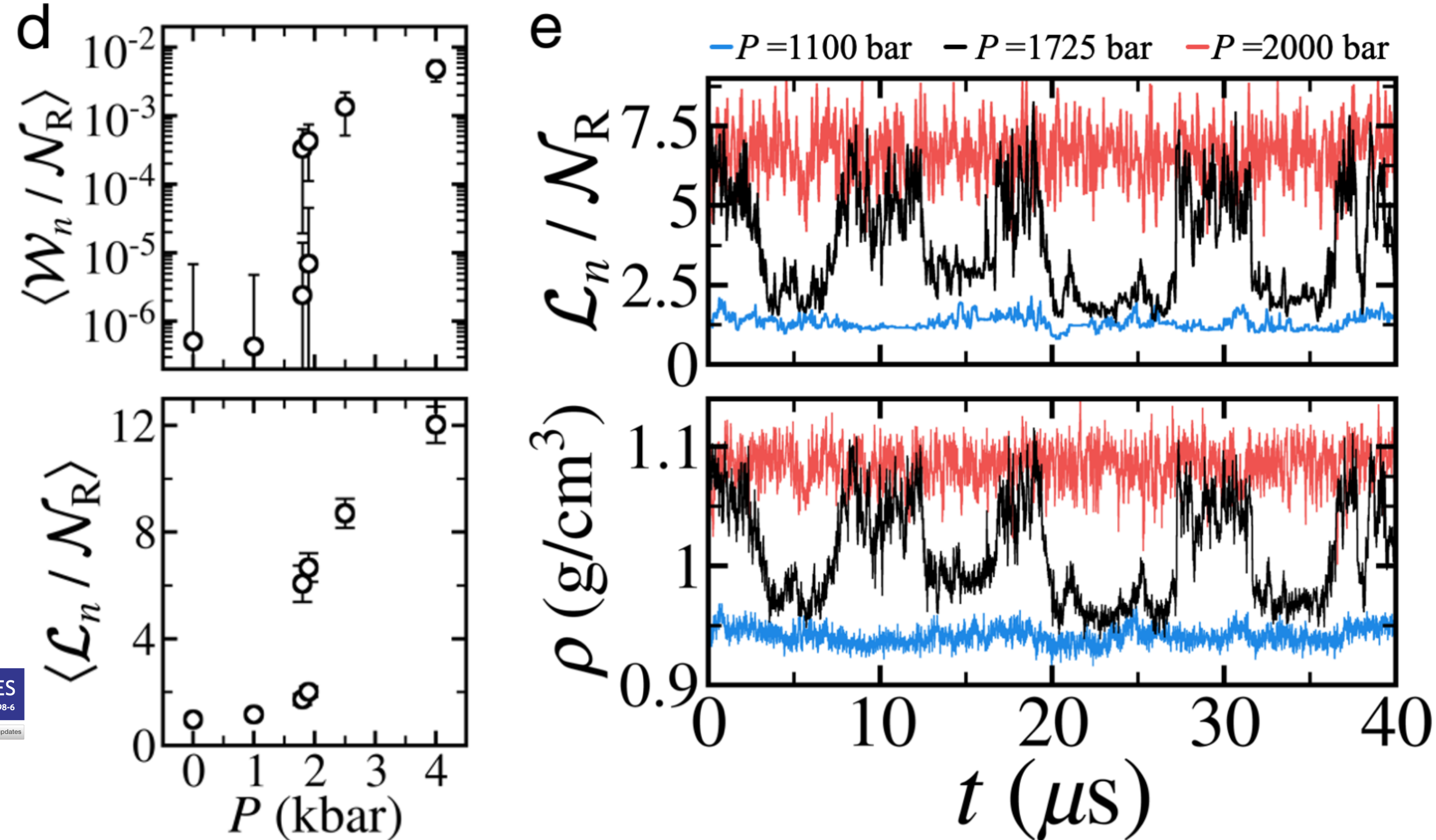

TIP4P/Ice

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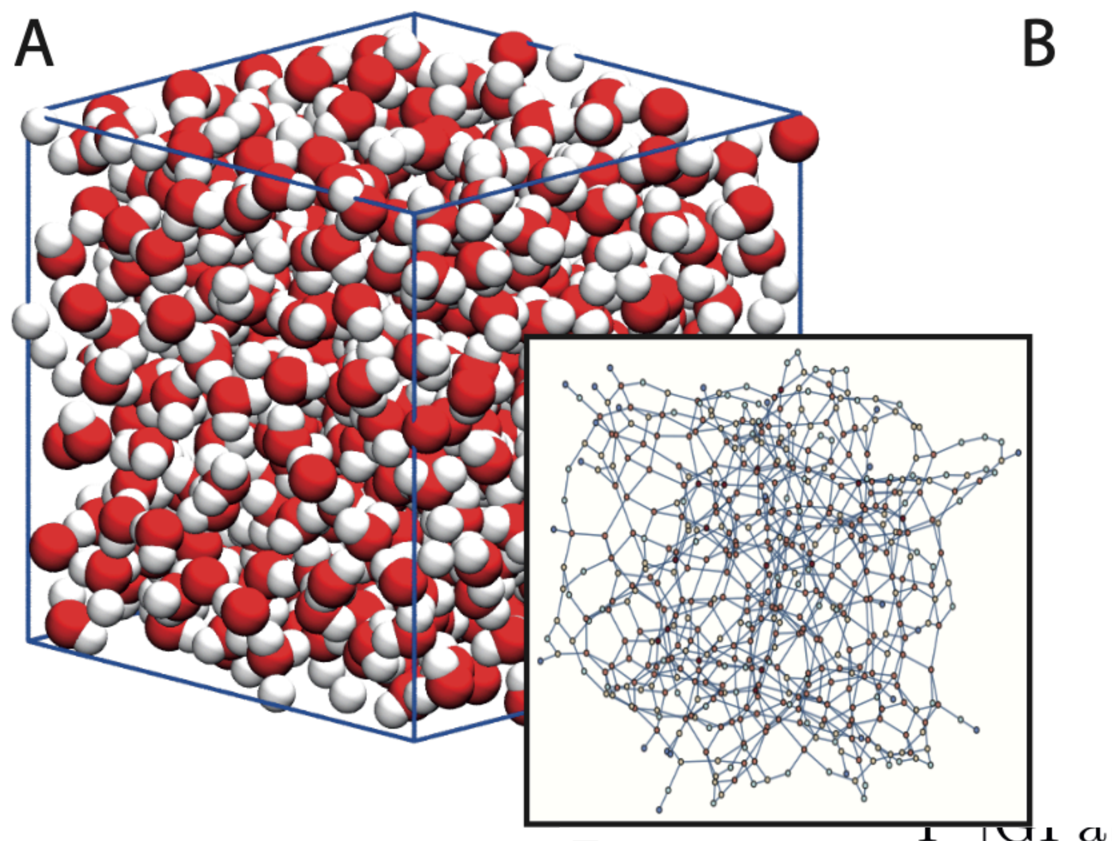
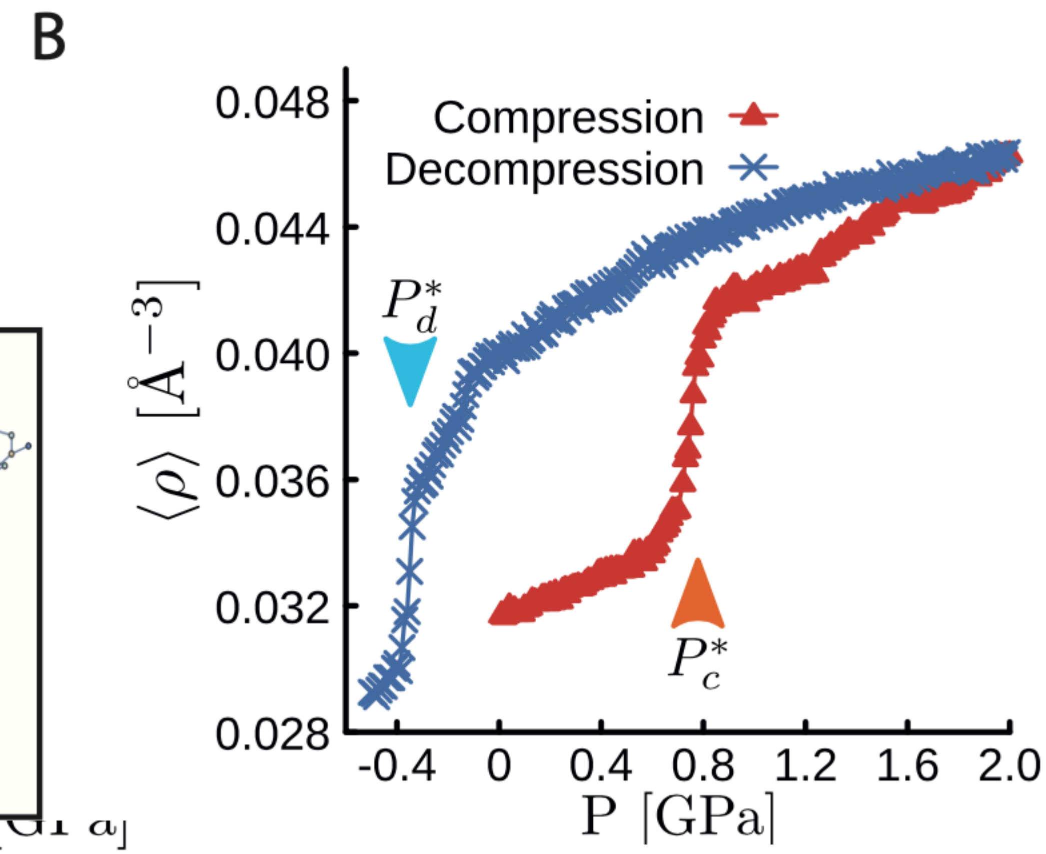
Topological nature of the liquid–liquid phase transition in tetrahedral liquids

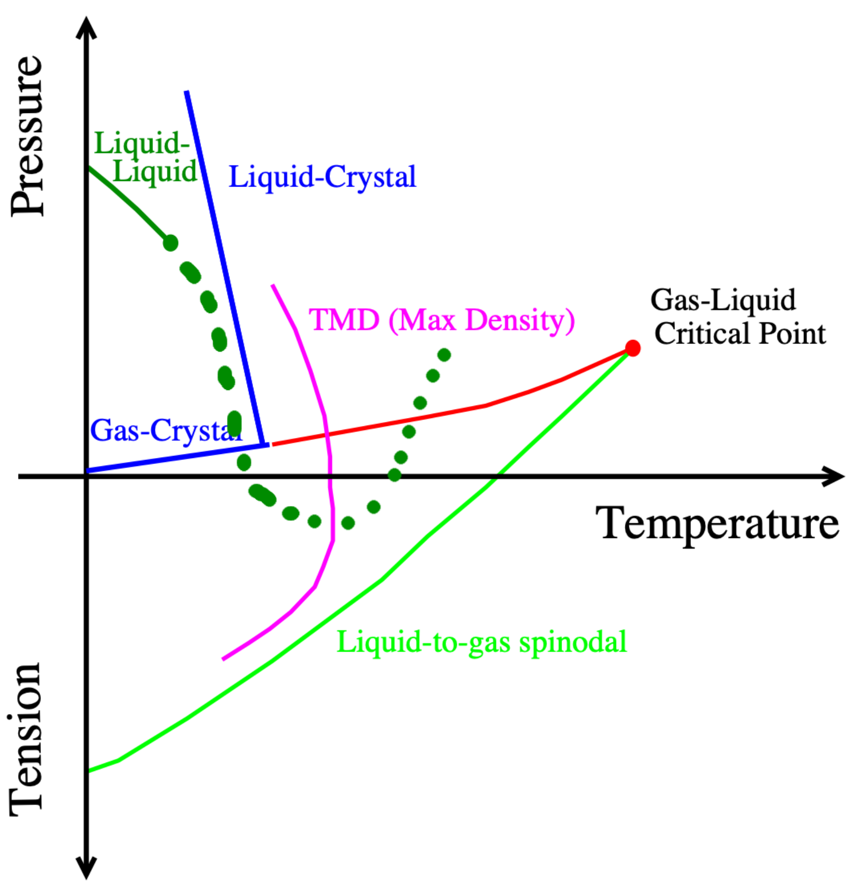
Andreas Neophytou[1], Dwaipayan Chakrabarti[1] and Francesco Sciortino[2]

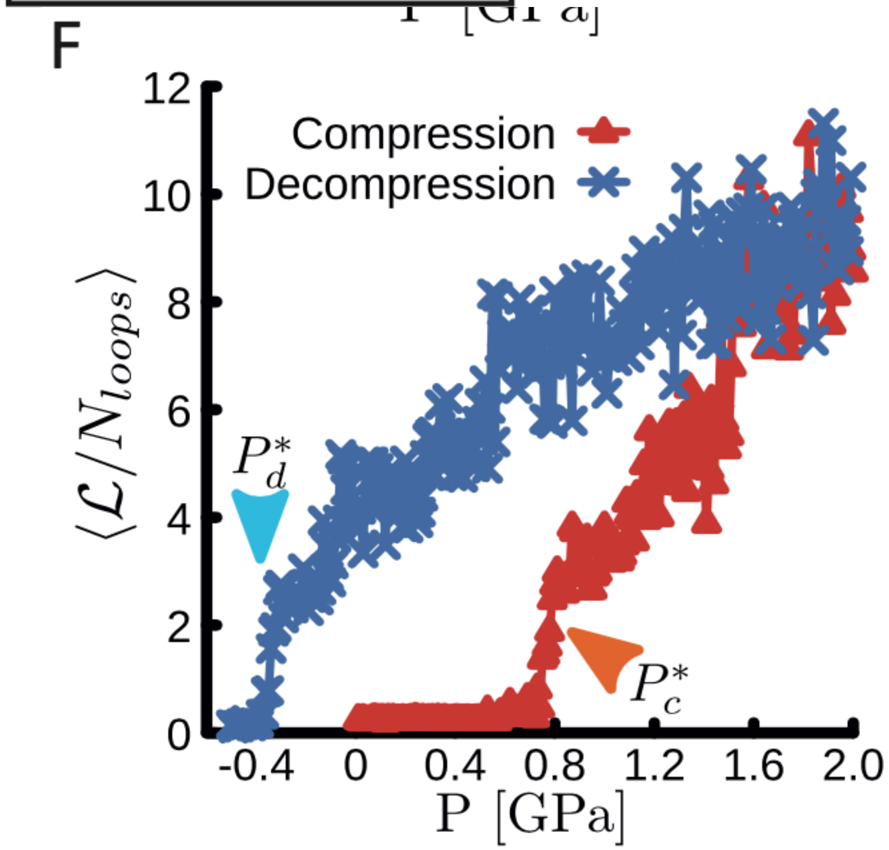
Link to Densify: Topological Transition During the Compression of Amorphous Ices

Yair Augusto Gutiérrez Fosado,[1] Davide Michieletto,[1,2] and Fausto Martelli[3,4]







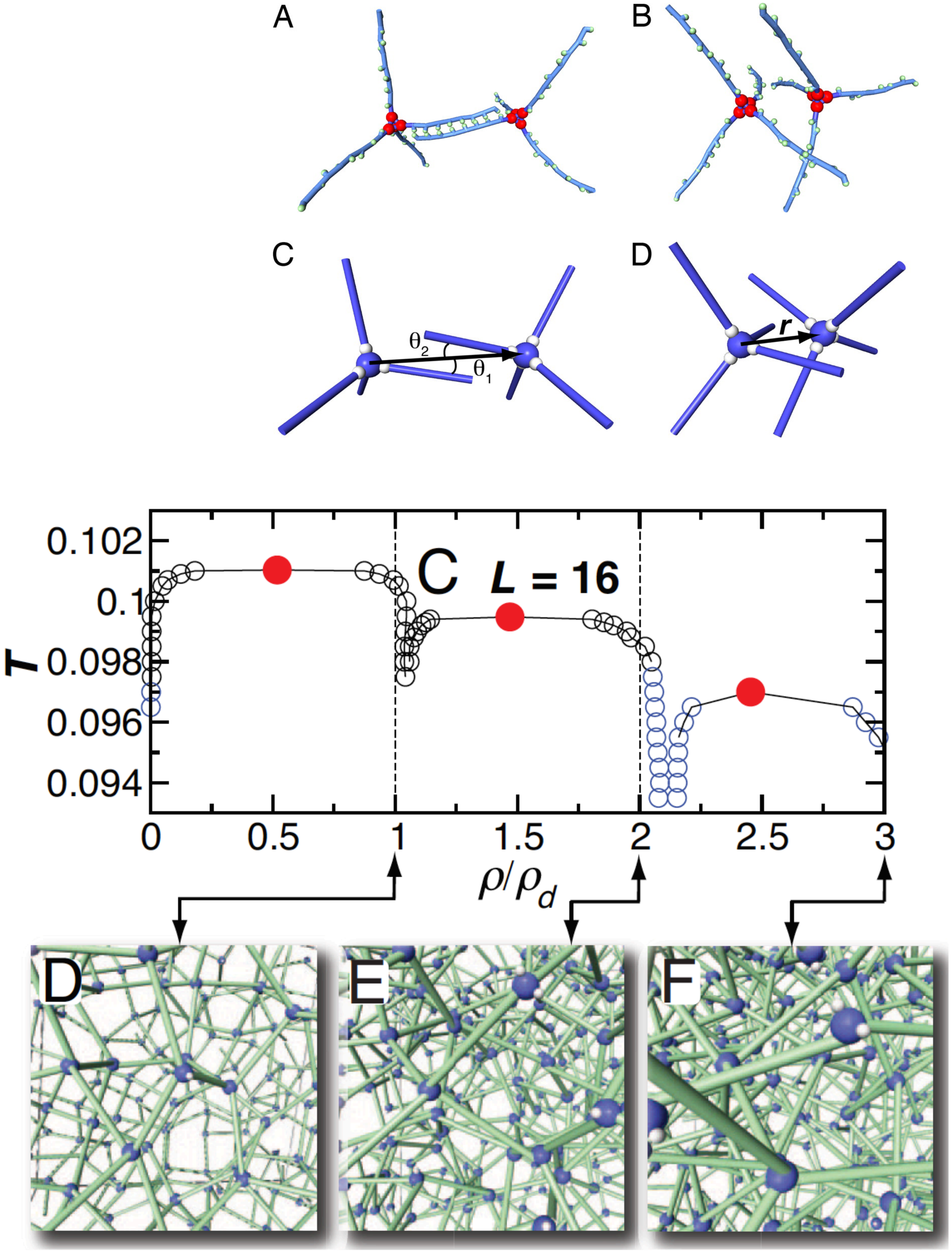


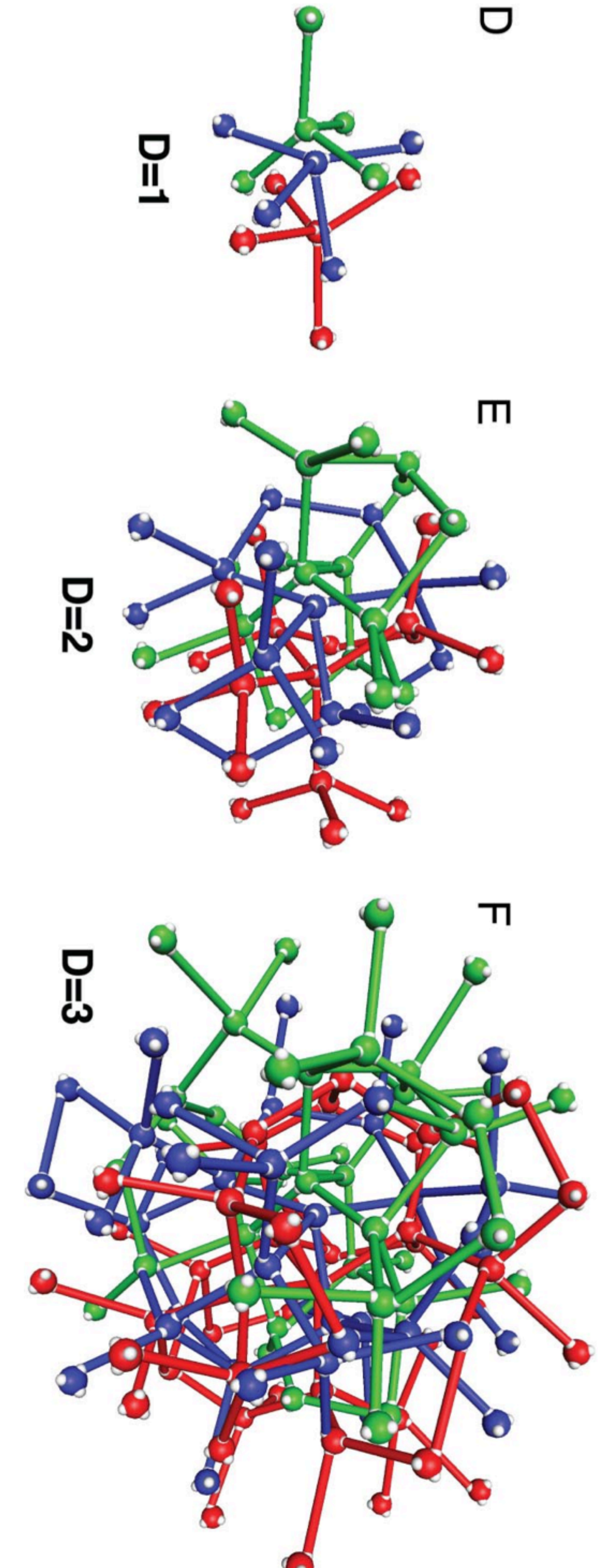
Strong coupling between density and linking (entanglement)

This coupling arises from the physical nature of the network (directionality of the bonds, valence, excluded volume)

The spatial distribution of the network nodes and edges assumes critical importance.

How general is the coupling ? Can we learn more ?

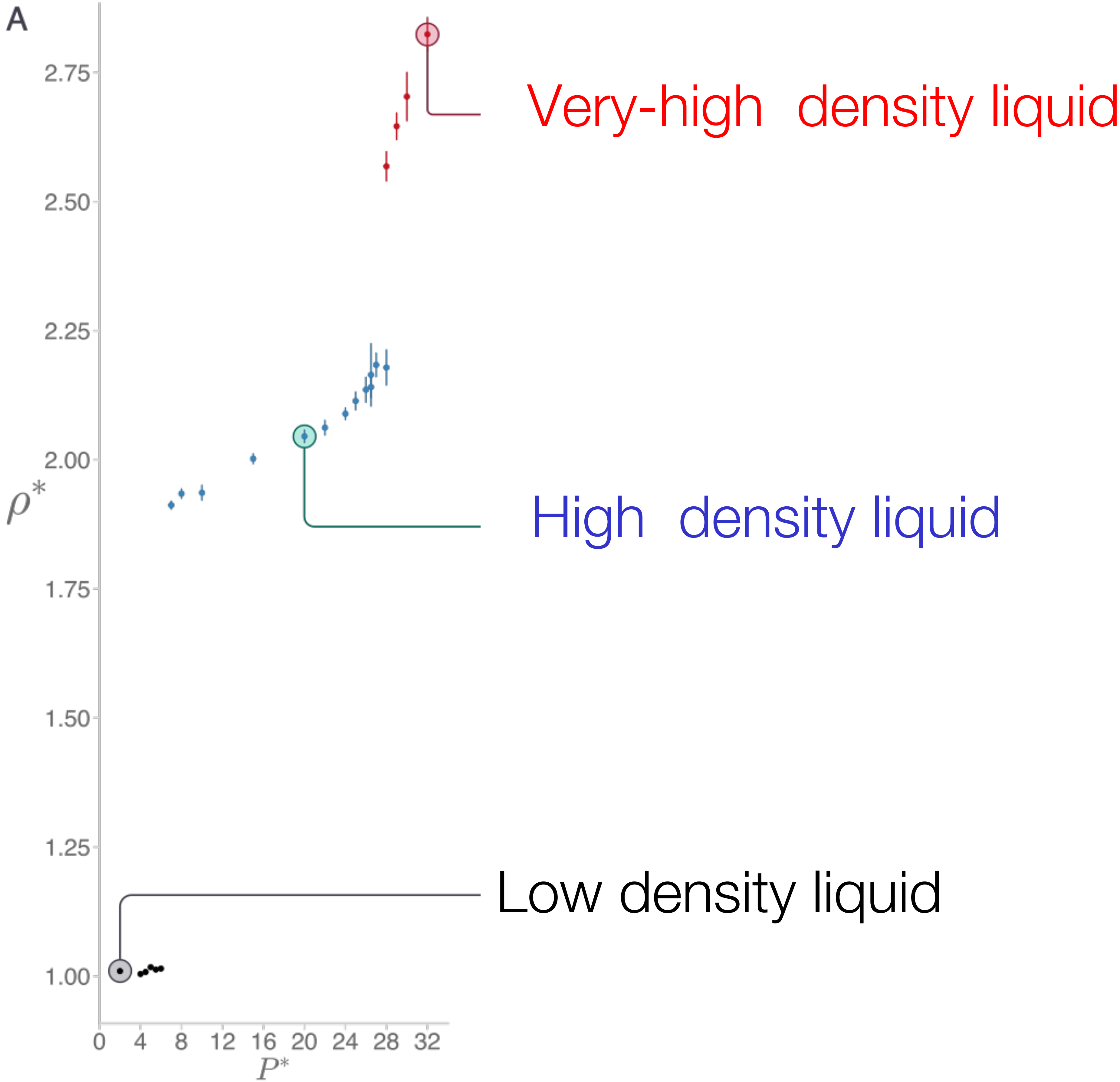




Hierarchies of networked phases induced by multiple liquid–liquid critical points

Chia Wei Hsu*, Julio Largo†‡, Francesco Sciortino†, and Francis W. Starr*§

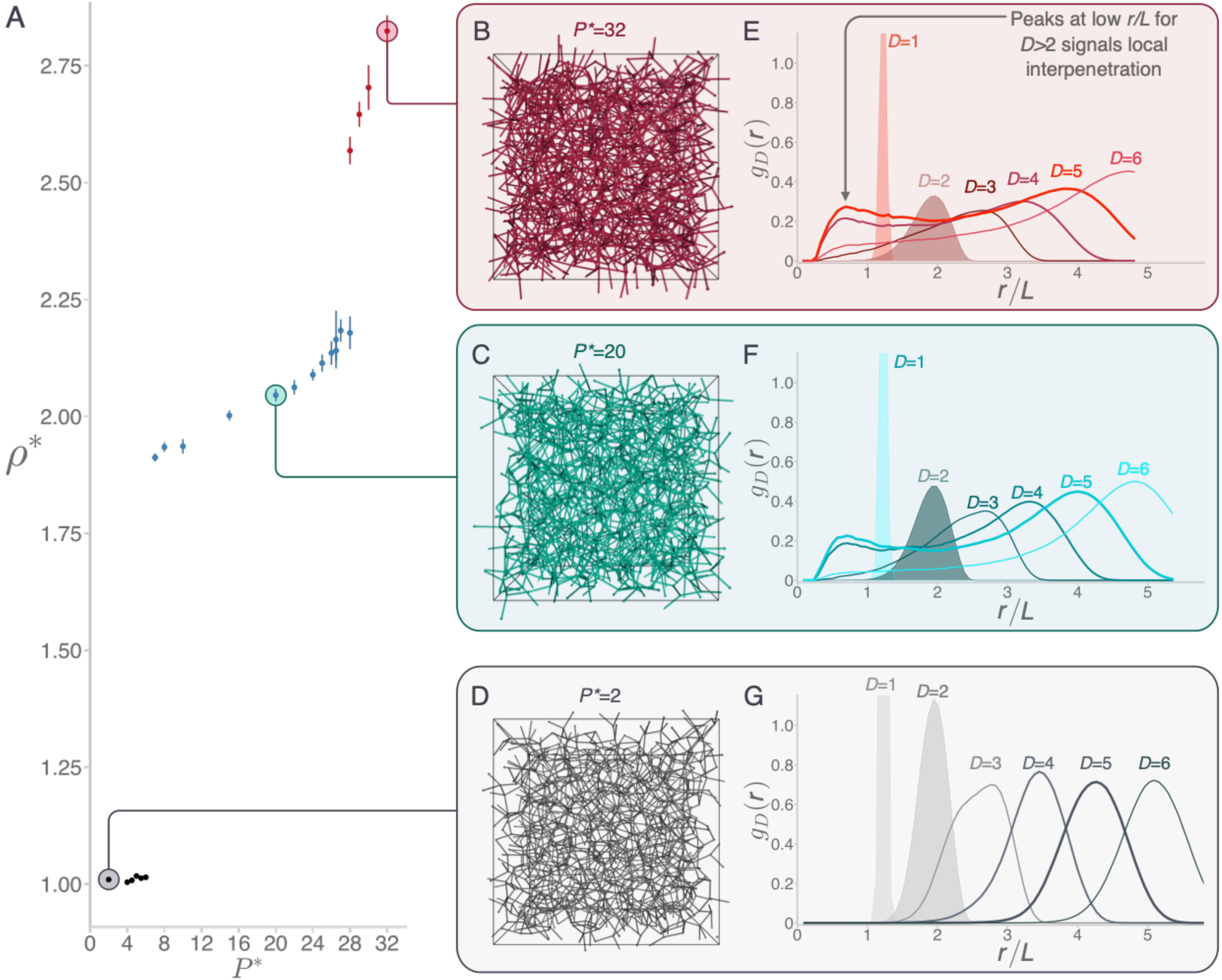
*Department of Physics, Wesleyan University, Middletown, CT 06459; †Dipartimento di Fisica and Consiglio Nazionale delle Richerche-Instituto Nazionale per la Fisica della Materia-Soft: Complex Dynamics in Structured Systems, Università di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185 Rome, Italy; and ‡Departamento de Fisica Aplicada, Universidad de Cantabria, Avda. Los Castros s/n Santander, 39005, Spain



Hierarchy of Topological Transitions in a Network Liquid

Andreas Neophytou[a,b,1], Francis W. Starr[c], Dwaipayan Chakrabarti[b,d], and Francesco Sciortino[a]

PNAS, in press



Hierarchy of Topological Transitions in a Network Liquid

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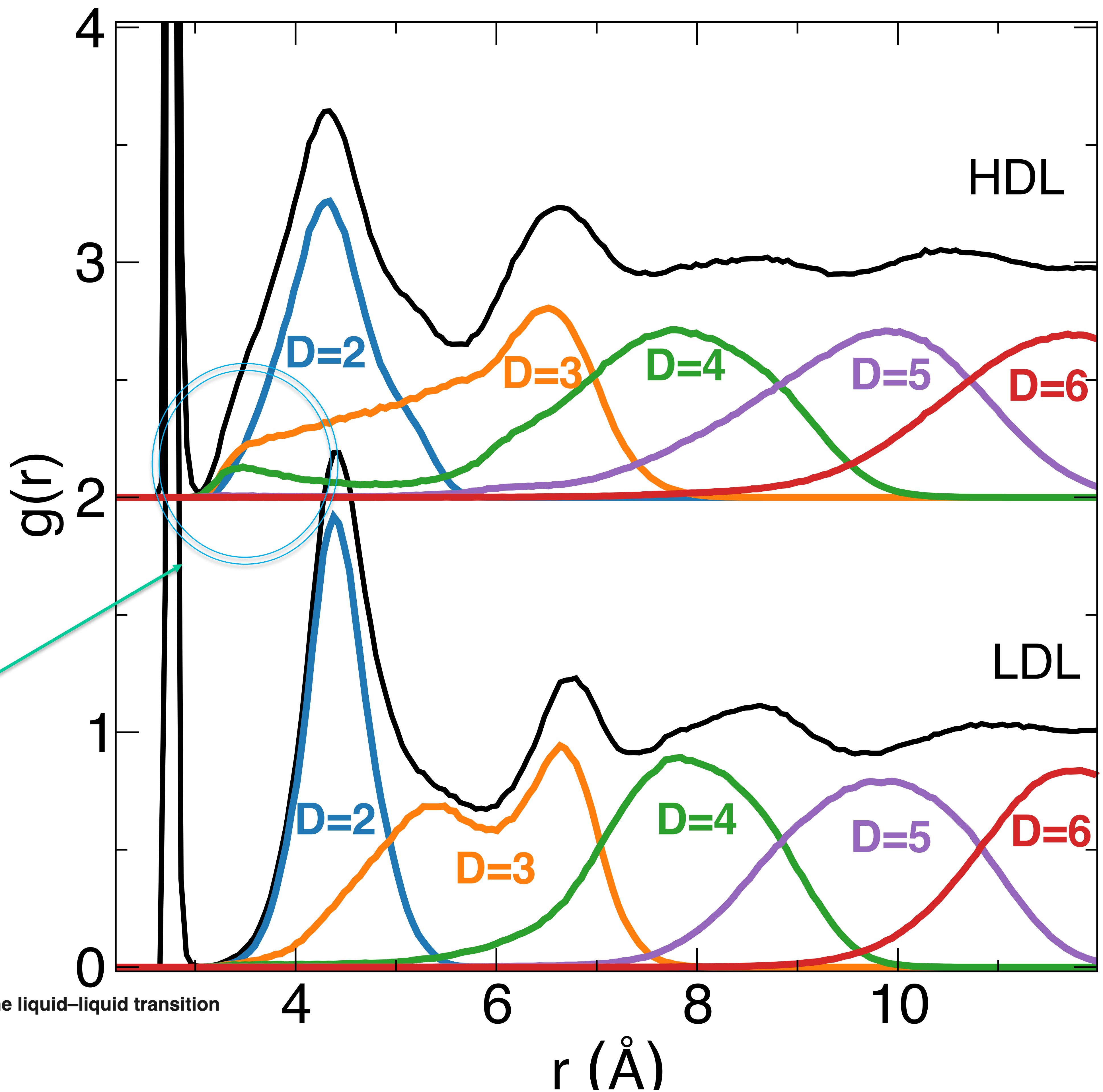
PNAS, in press

Comparing LDL and HDL g(r) for water



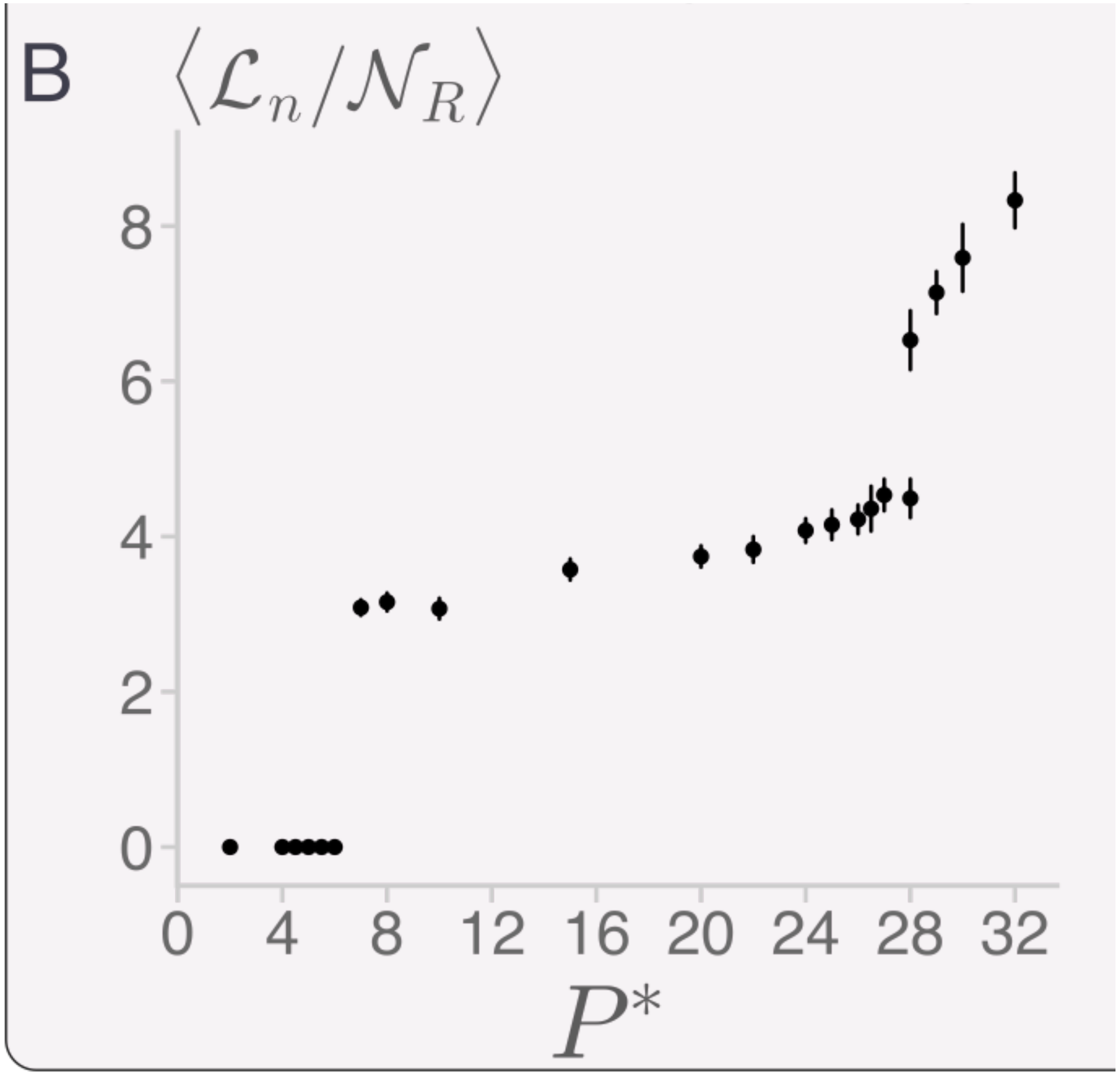
Molecules far in # of bonds but close in space !

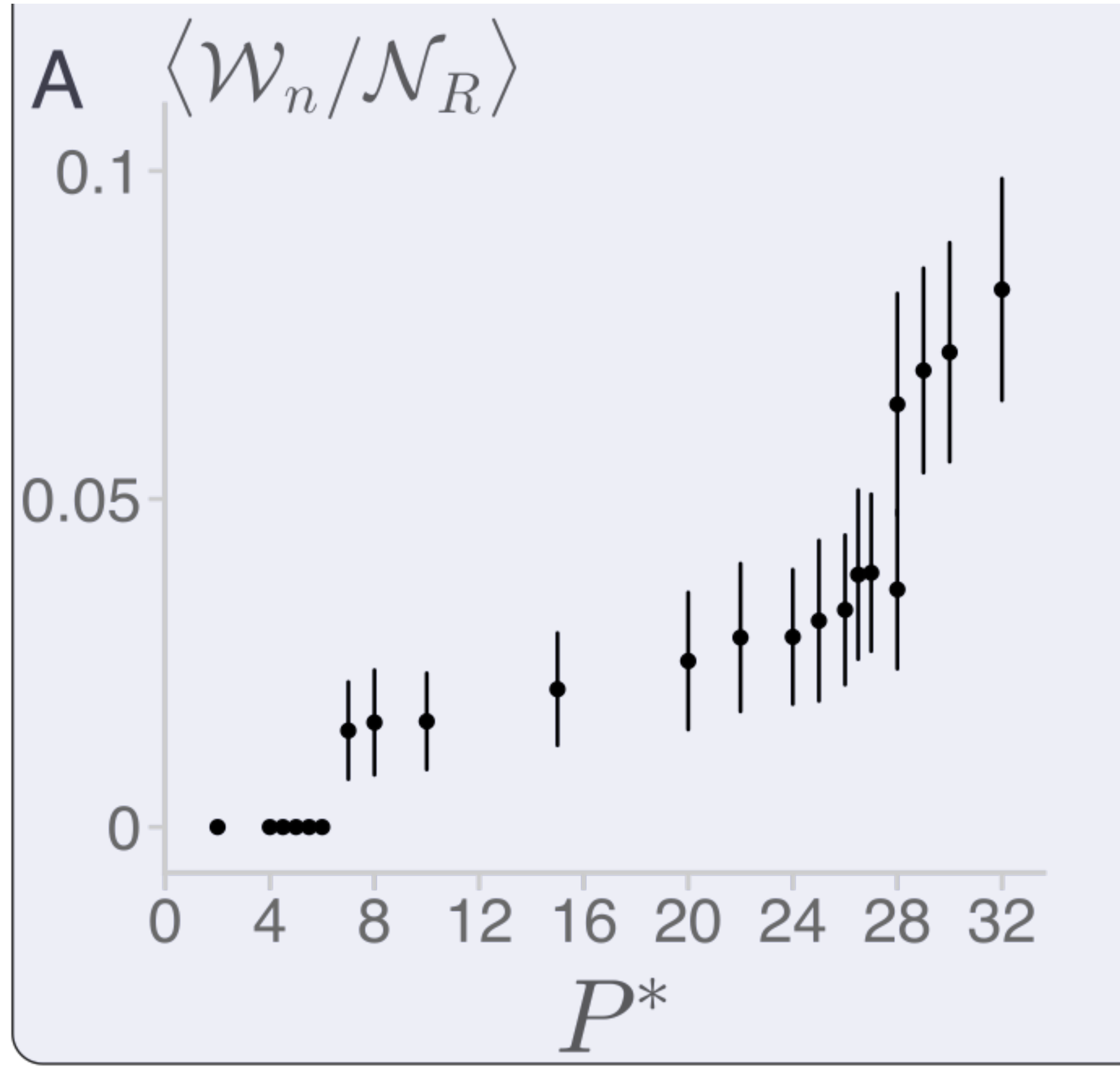
Structural and topological changes across the liquid–liquid transition in water

Special Collection: JCP Editors' Choice 2021

Riccardo Foffi ; John Russo ; Francesco Sciortino

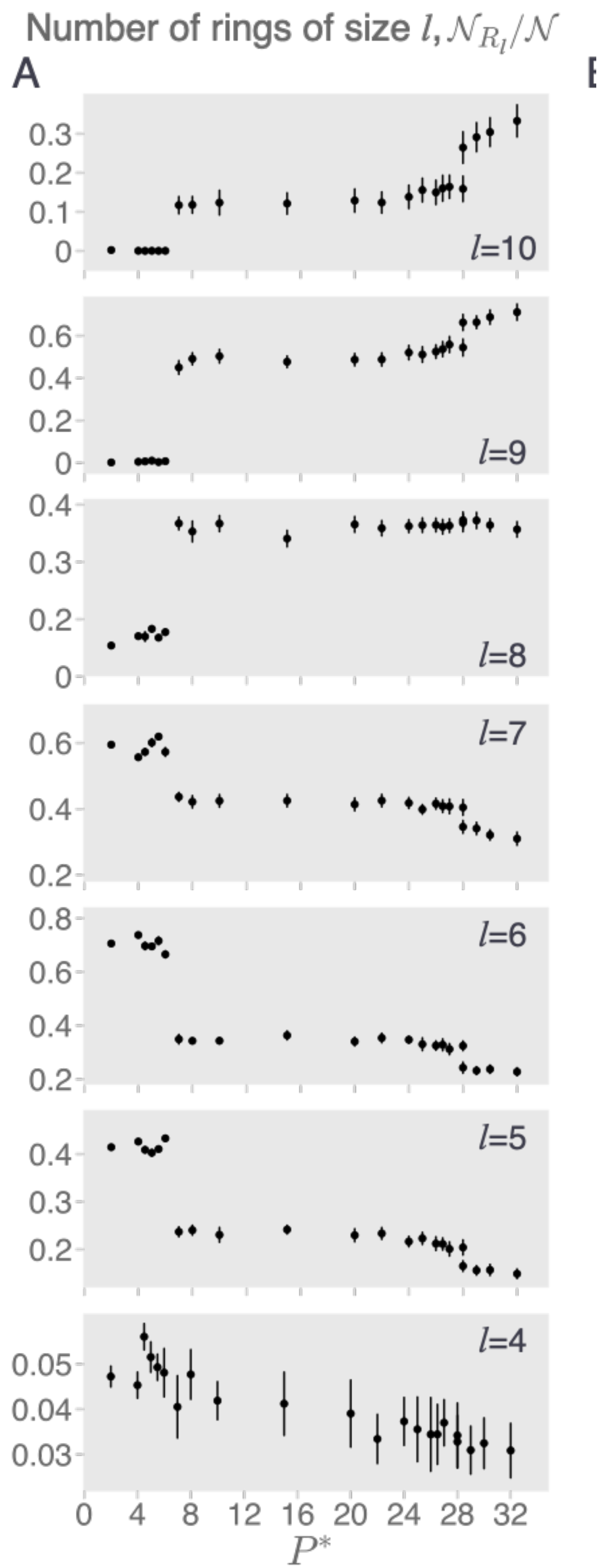
The transition(s) as seen by the topological order parameters



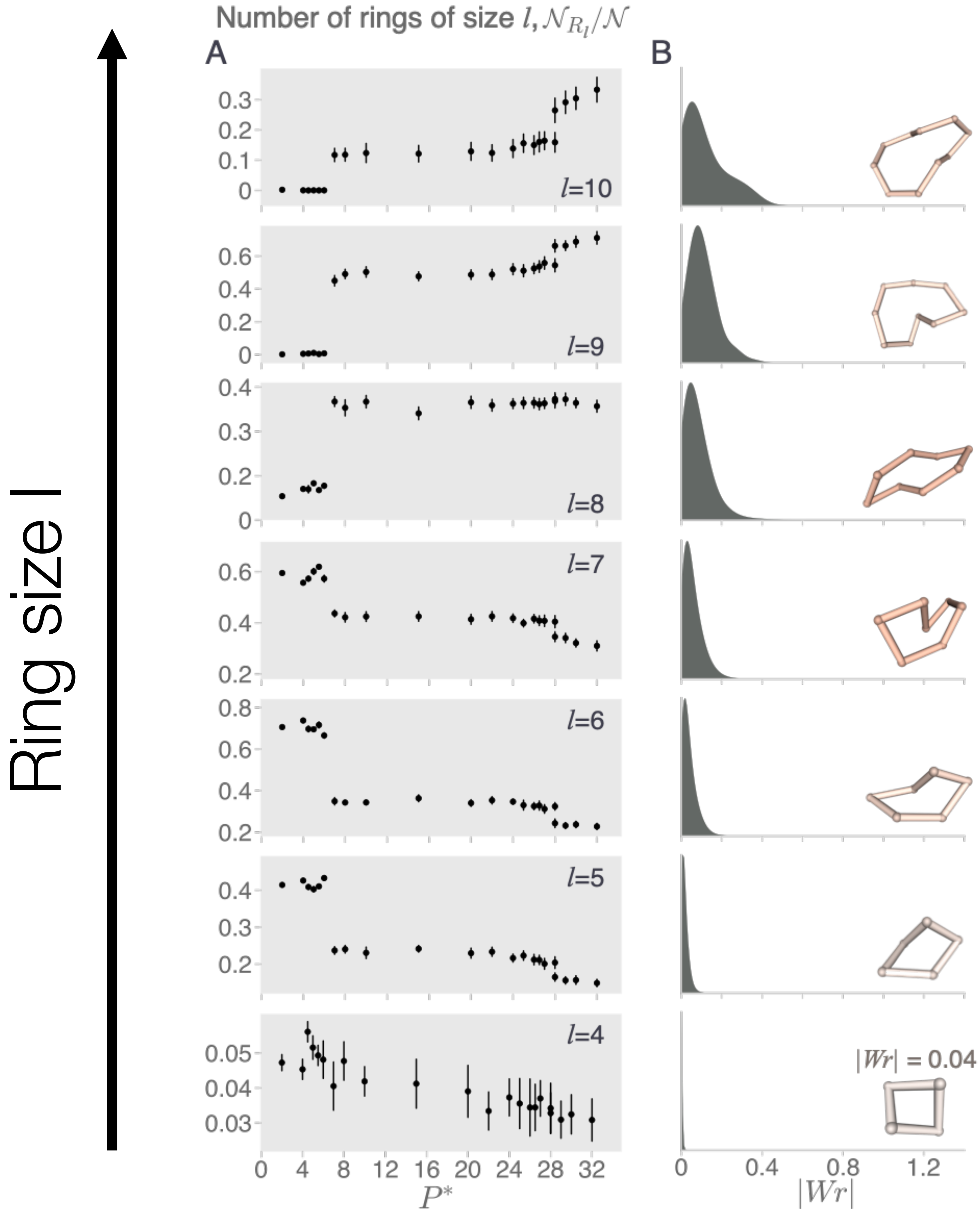


Rings properties as a function of their size l

Ring size l



Rings properties as a function of their size l

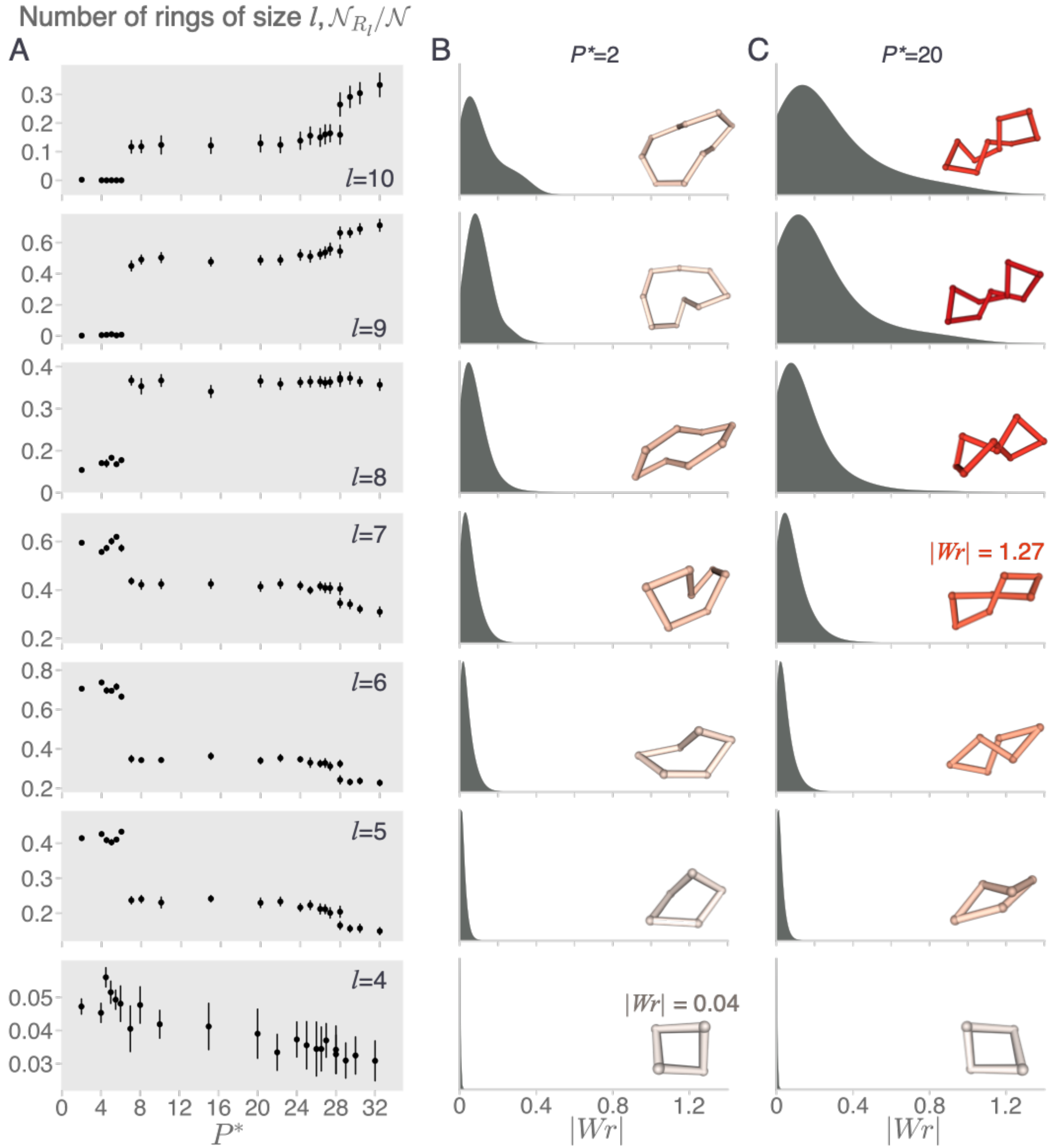


Low density liquid

Almost planar rings for all sizes

Rings properties as a function of their size l

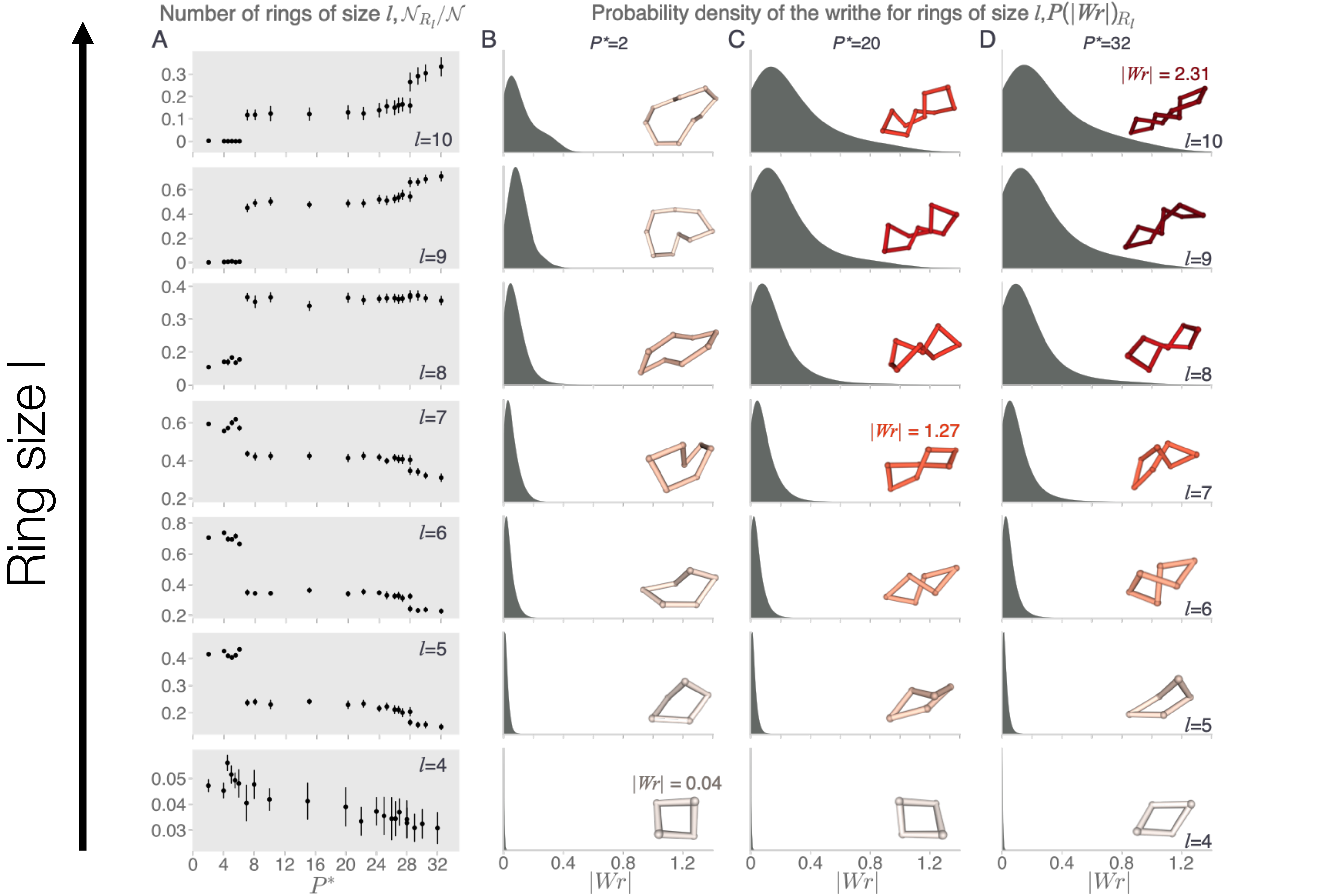
Ring size l

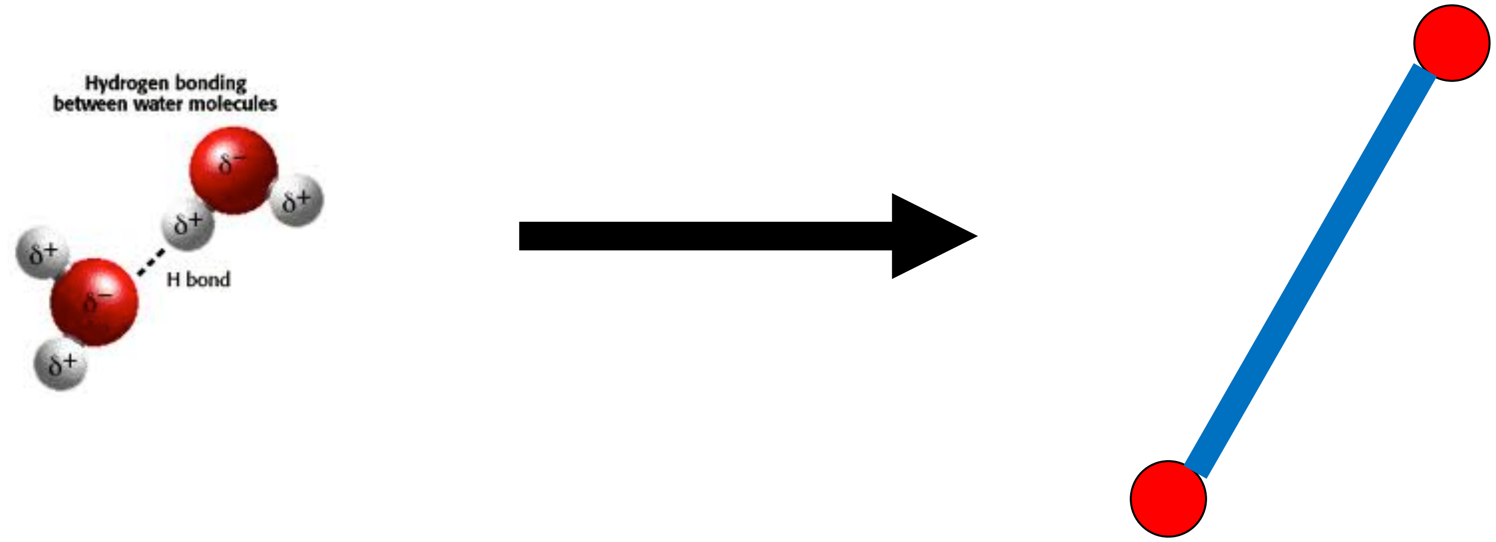


Intermediate density liquid

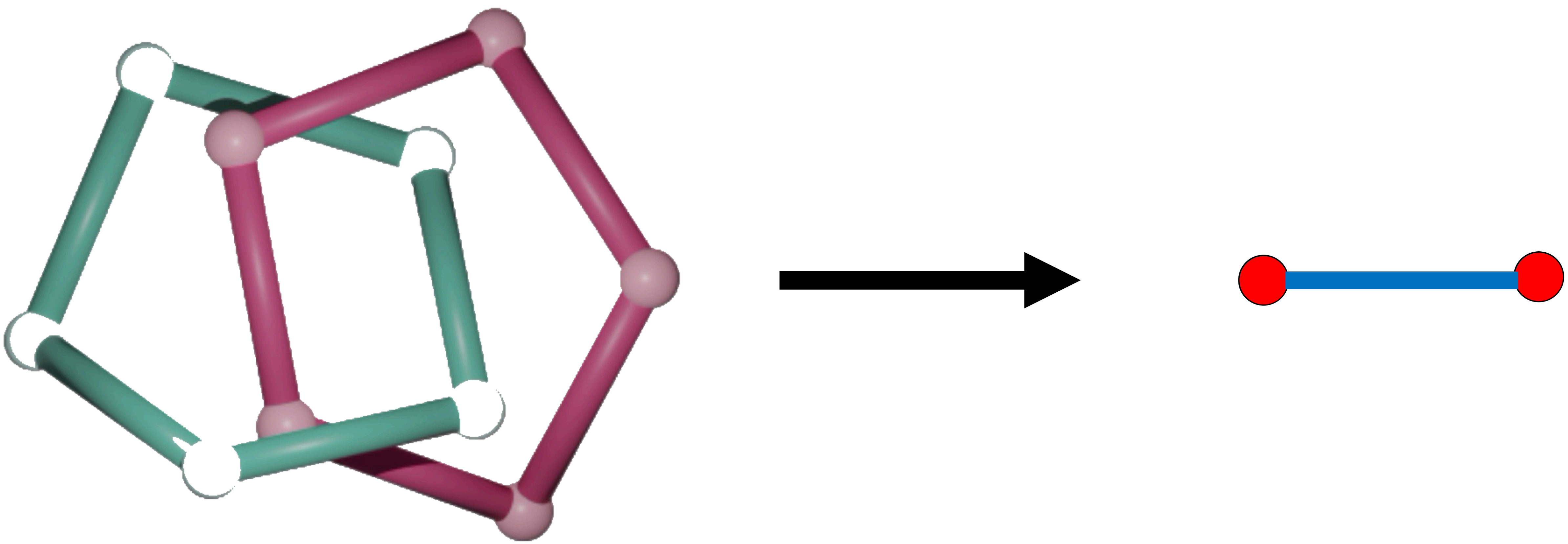
Twistings for large rings

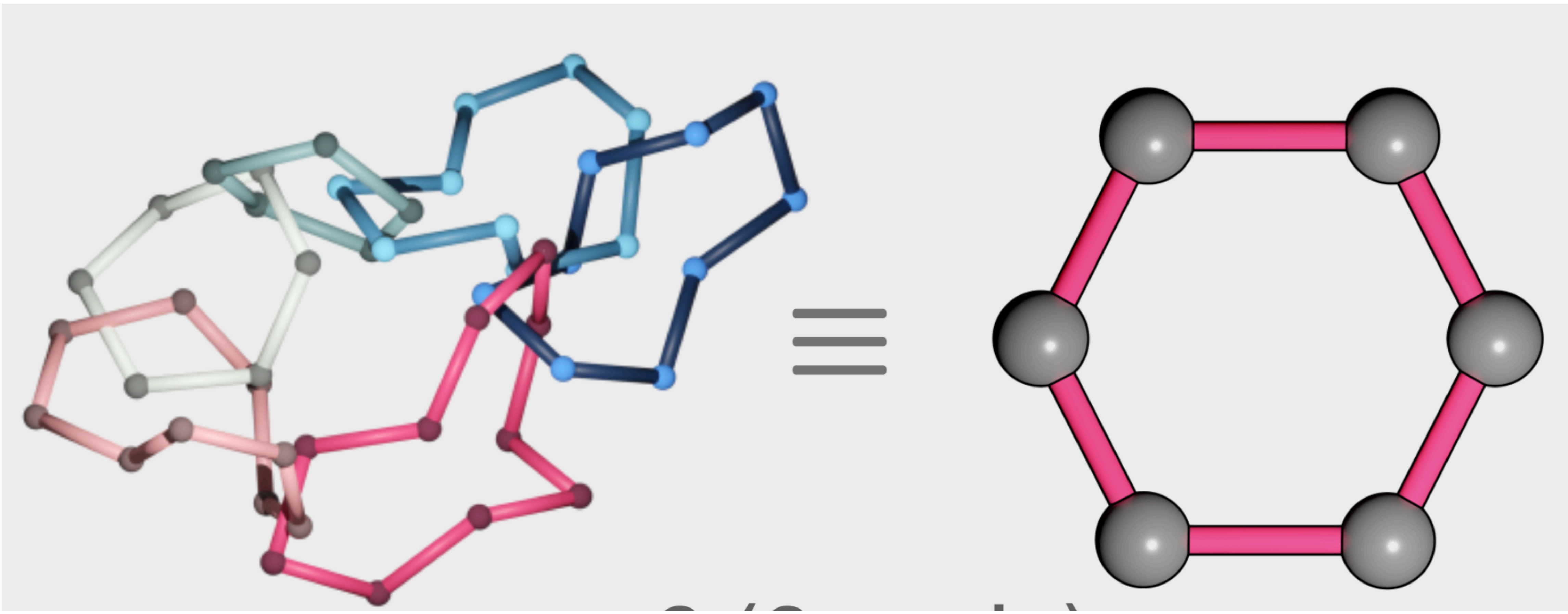
Rings properties as a function of their size l



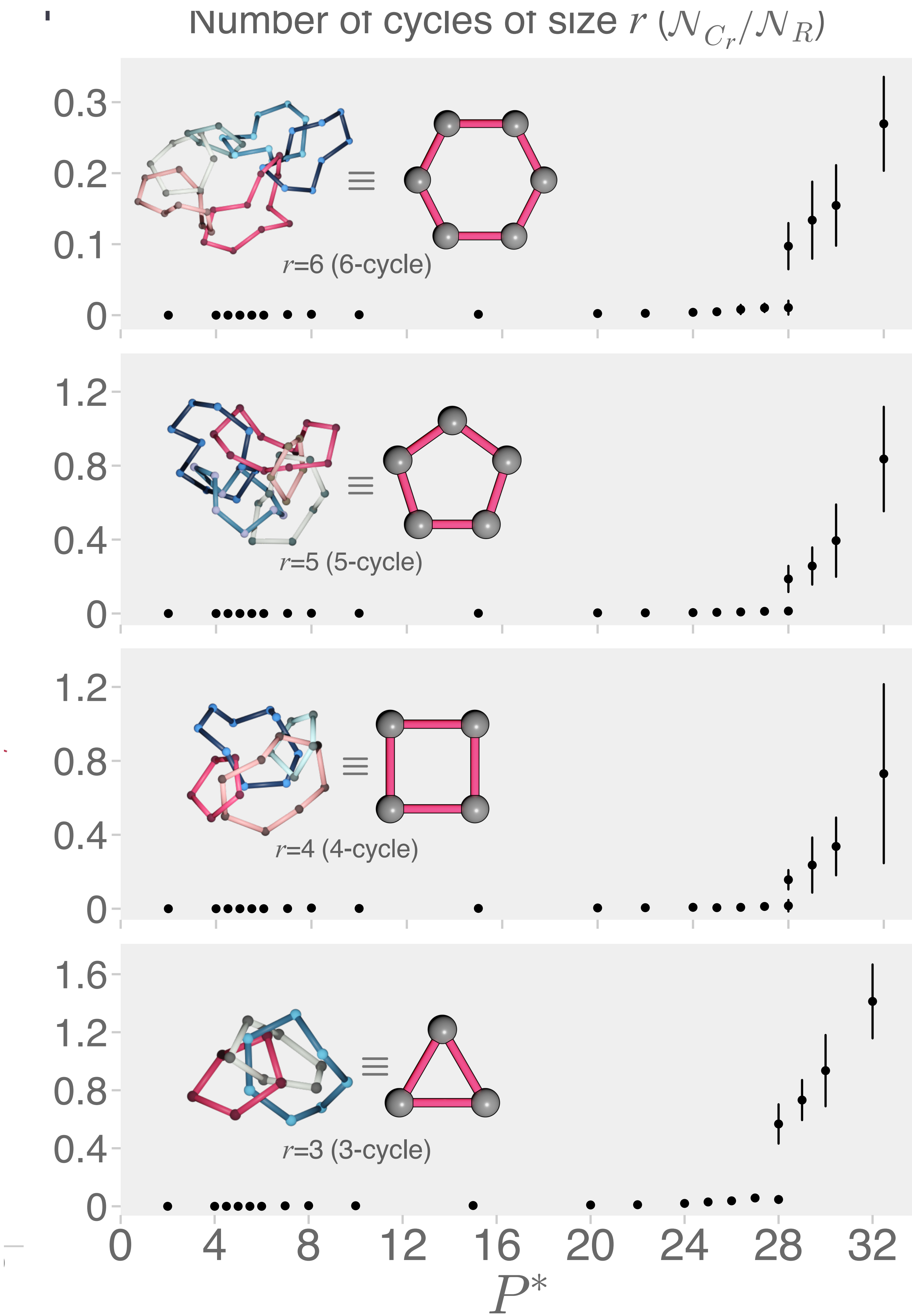


One higher-order network





A ring of rings (a cycle)…..



The very high-density network has cycles,

The intermediate density network has very few cycles

Conclusions:

A liquid-liquid transition (LLPT) provides an elegant scenario to interpret the origin of the thermodynamic anomalies in water (C_p, K_T, TMD). A LLPT has been definitively proved numerically for several water models. T_c, ρ_c and P_c model dependent. Experiments strongly support the LLPT idea

Conclusions:

Topology offers a key to describe the differences between LDL and HDL. The LLPT is a transition between an unentangled LDL and an entangled HDL, the latter containing an ensemble of topologically complex motifs.

Entanglement emerges as a general mechanism for densification. A physical network embedded in three-dimension space (where interactions between the nodes determine its layout) must increase its topological complexity to become more dense without changing its local connectivity.

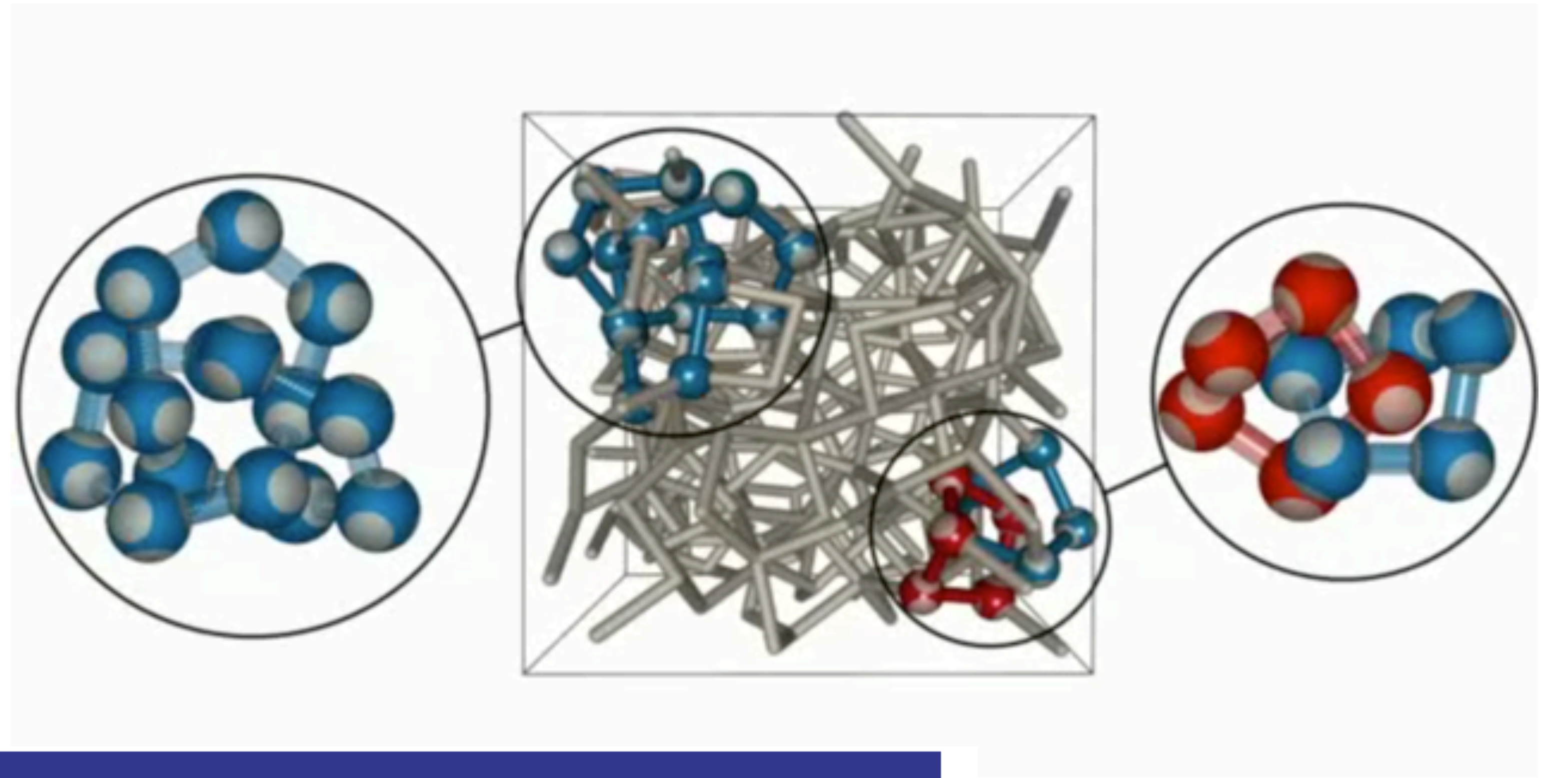
Where to go:

Is it possible to develop a thermodynamic description of the LLPT based on topological order parameters ?

How is dynamics affected by the topological organization of the network (transient bonds in physical networks) ?

Thanks to….. Among others…..

- **Andreas Neophytou, Dwaipayan Chakrabarti Francis Starr**



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