XFEL Virtual Satellite Meetings

Studying molecular water

Date: Friday, 21 January 2022

Time: 09:00 - 16:30

Organizer: Chris Milne

Computational studies of the liquid-liquid transition in supercooled water

(45 years in 45 minutes)

one molecule – two liquids

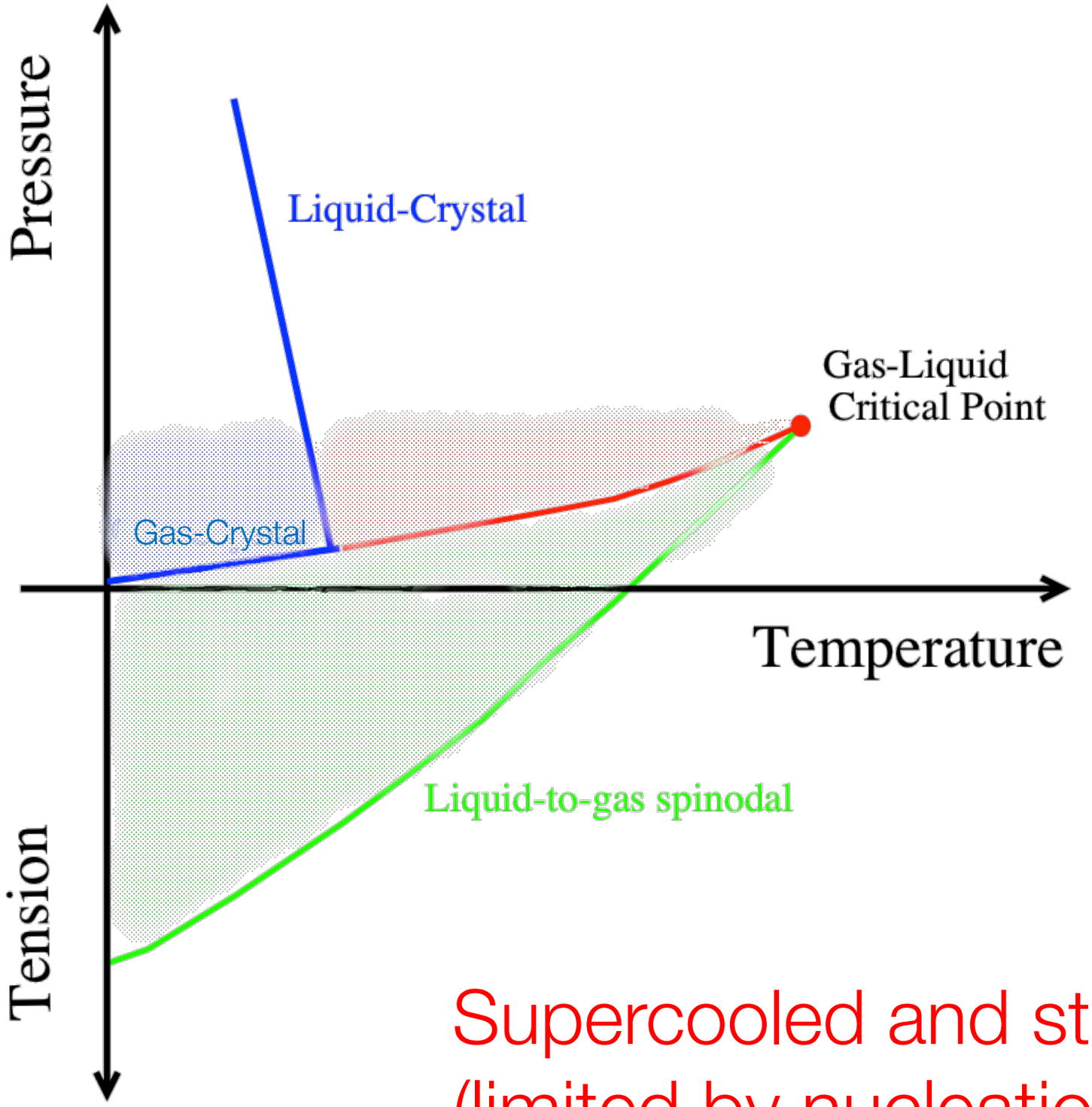
Francesco Sciortino

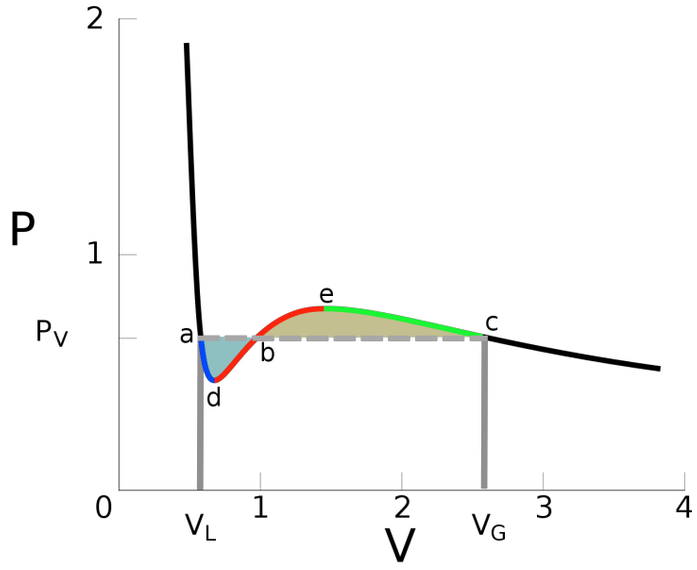
Sapienza University of Rome, Italy

francesco.sciortino@uniroma1.it

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

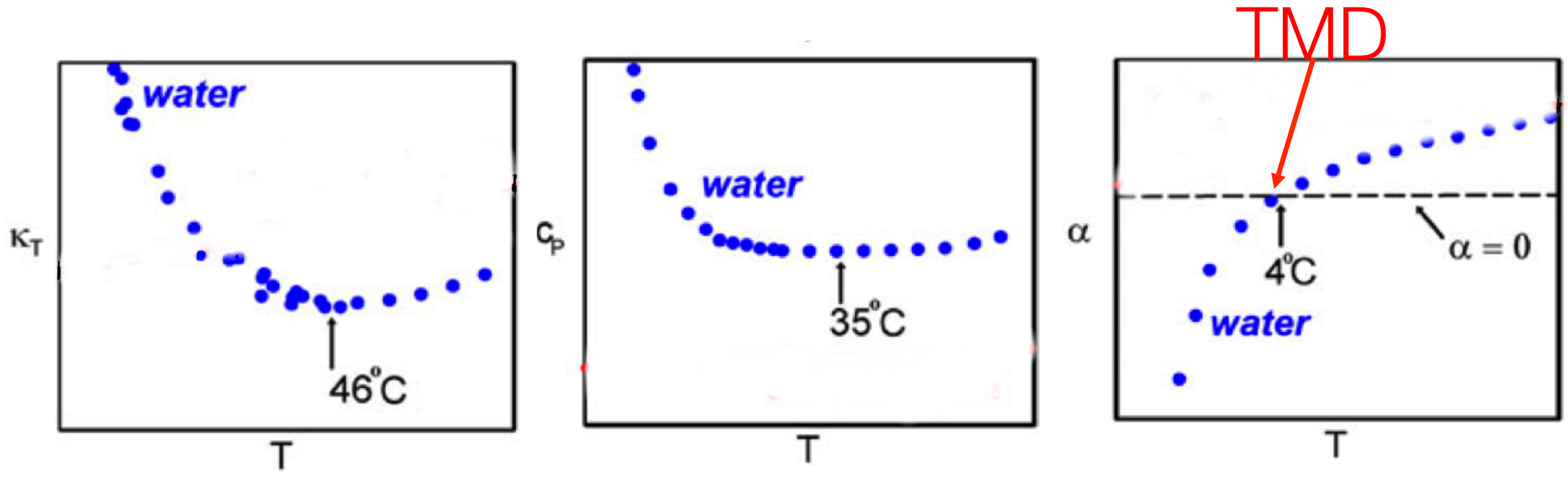
The “liquid” in the P-T plane





Supercooled and stretched liquid states !
(limited by nucleation or dynamic arrest)

Water is special: Thermodynamic Anomalies



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

$$< \Delta S^2 >$$

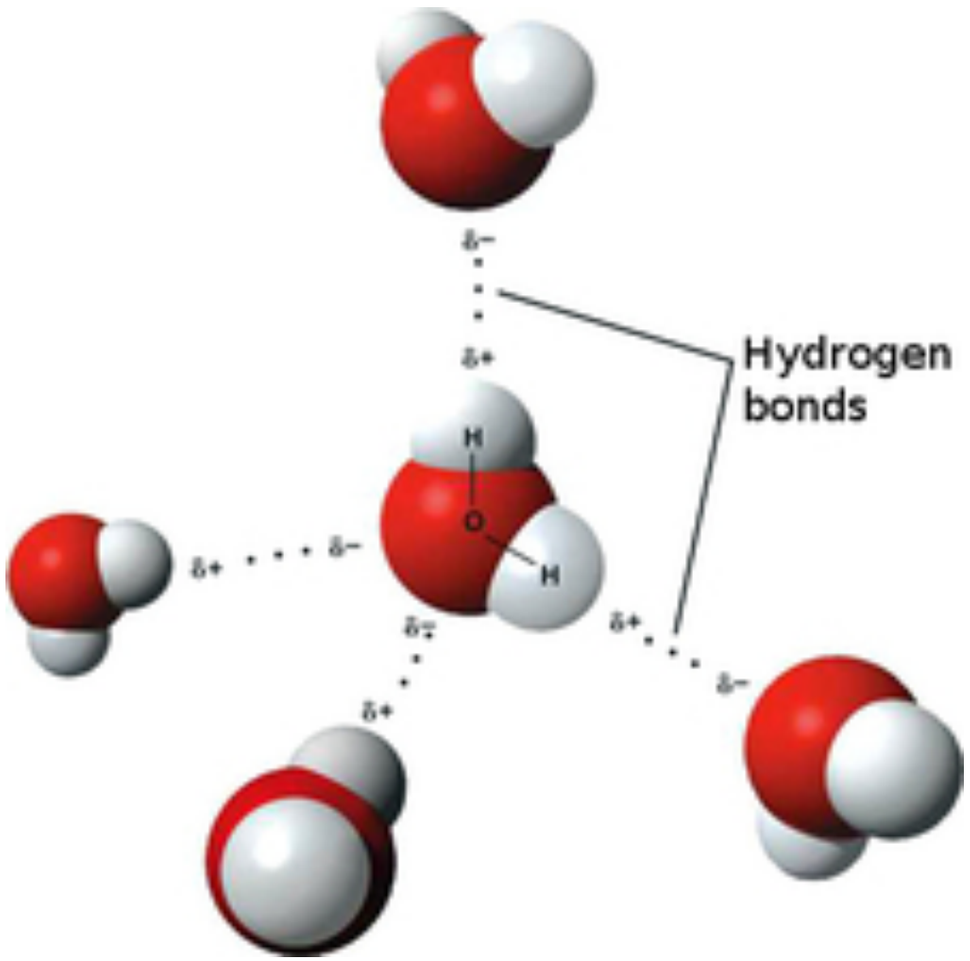
$$< \Delta H^2 >$$

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

Supercooling enhances fluctuations…..

There must be regions with…….

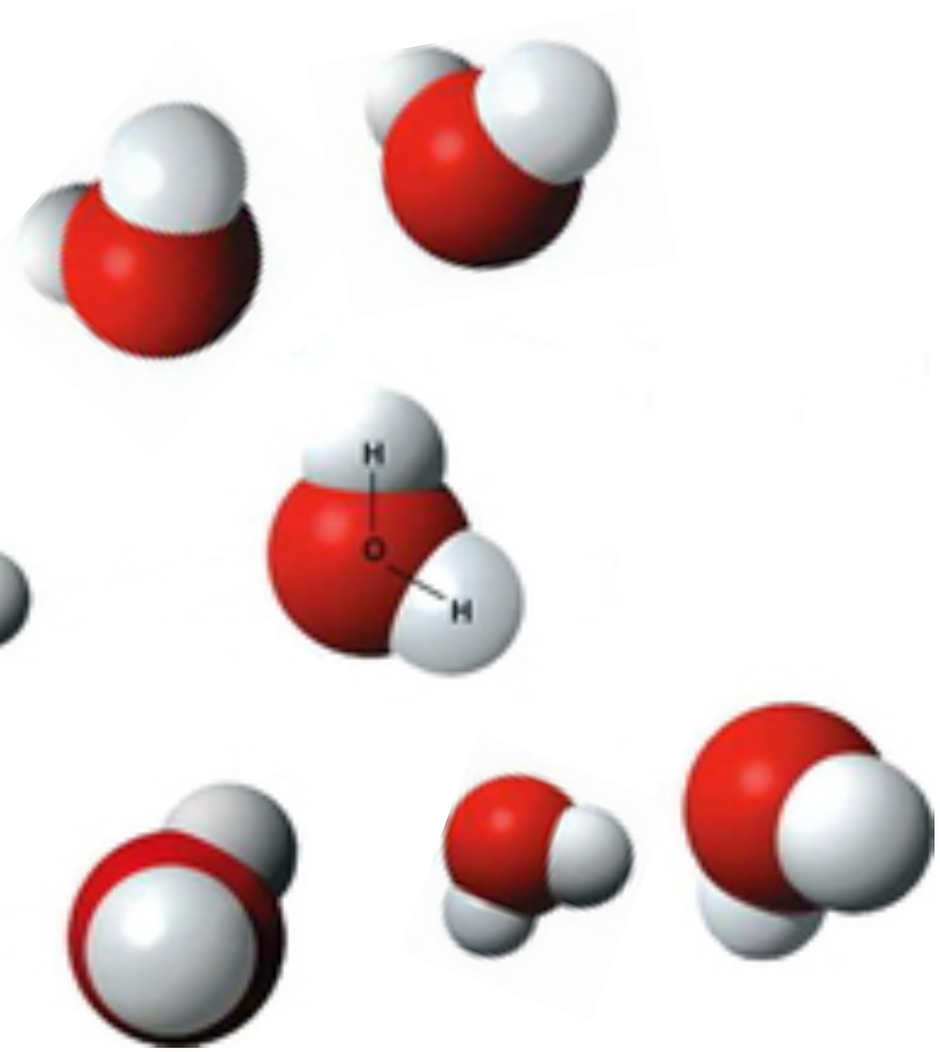
Low Entropy
Large Volume



Tetrahedral Linear
Hydrogen Bonds

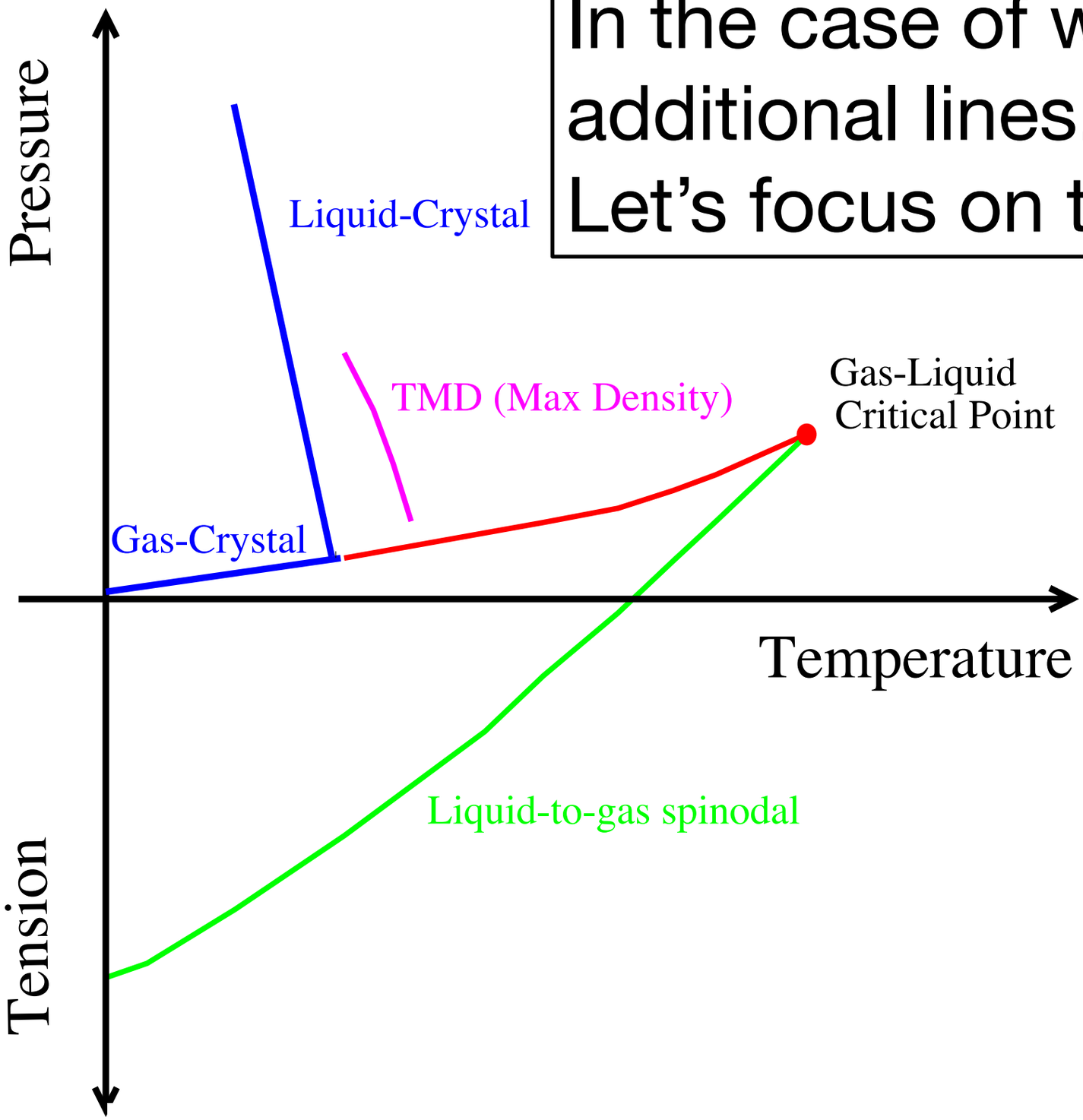
Directional interactions
Limited number of bonds

Large Entropy
Small Volume



"less tetrahedral"
Bent (bifurcated) HB
Interpenetrating

In the case of water... some additional lines.
Let's focus on the TMD(P) !!!



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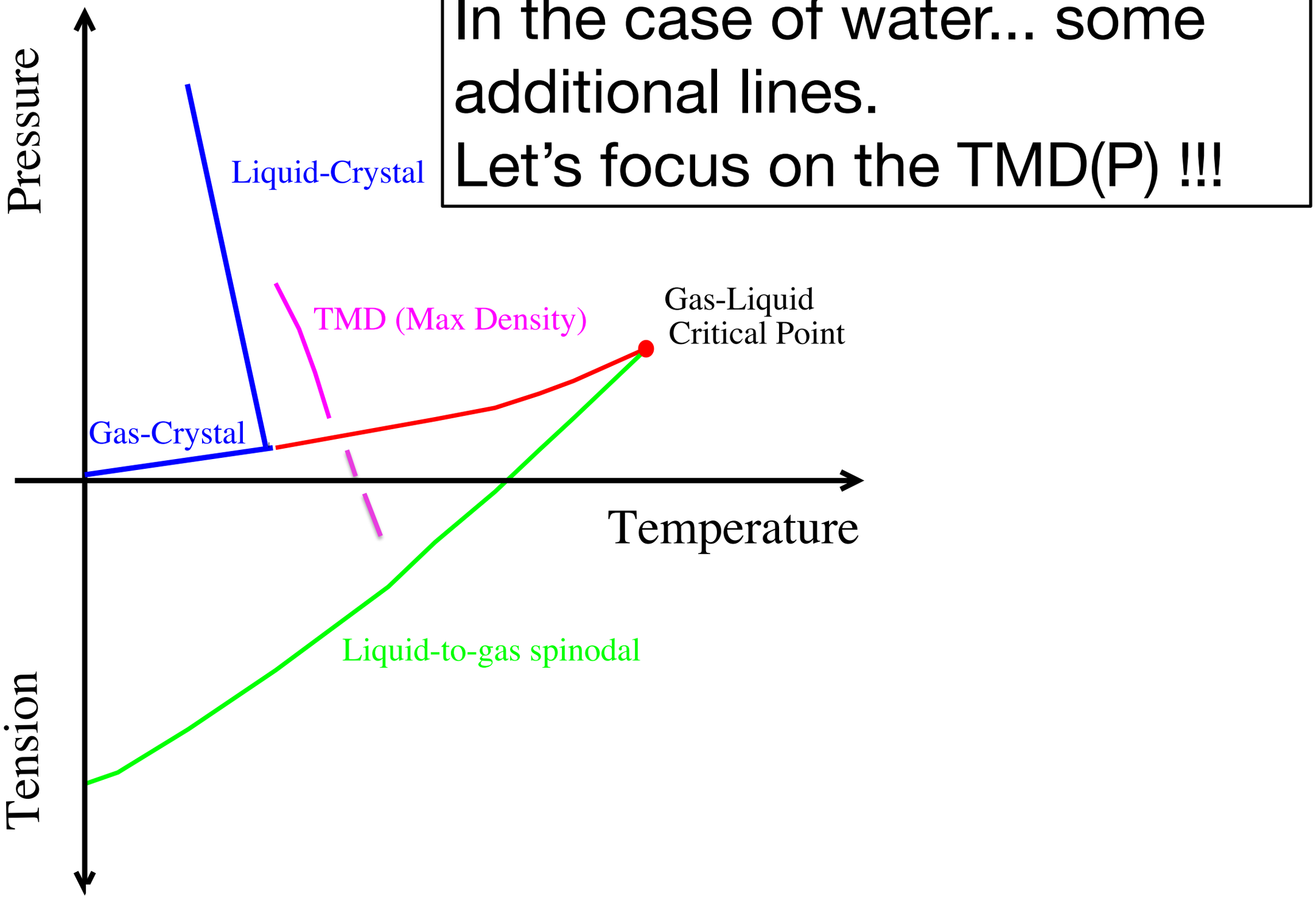
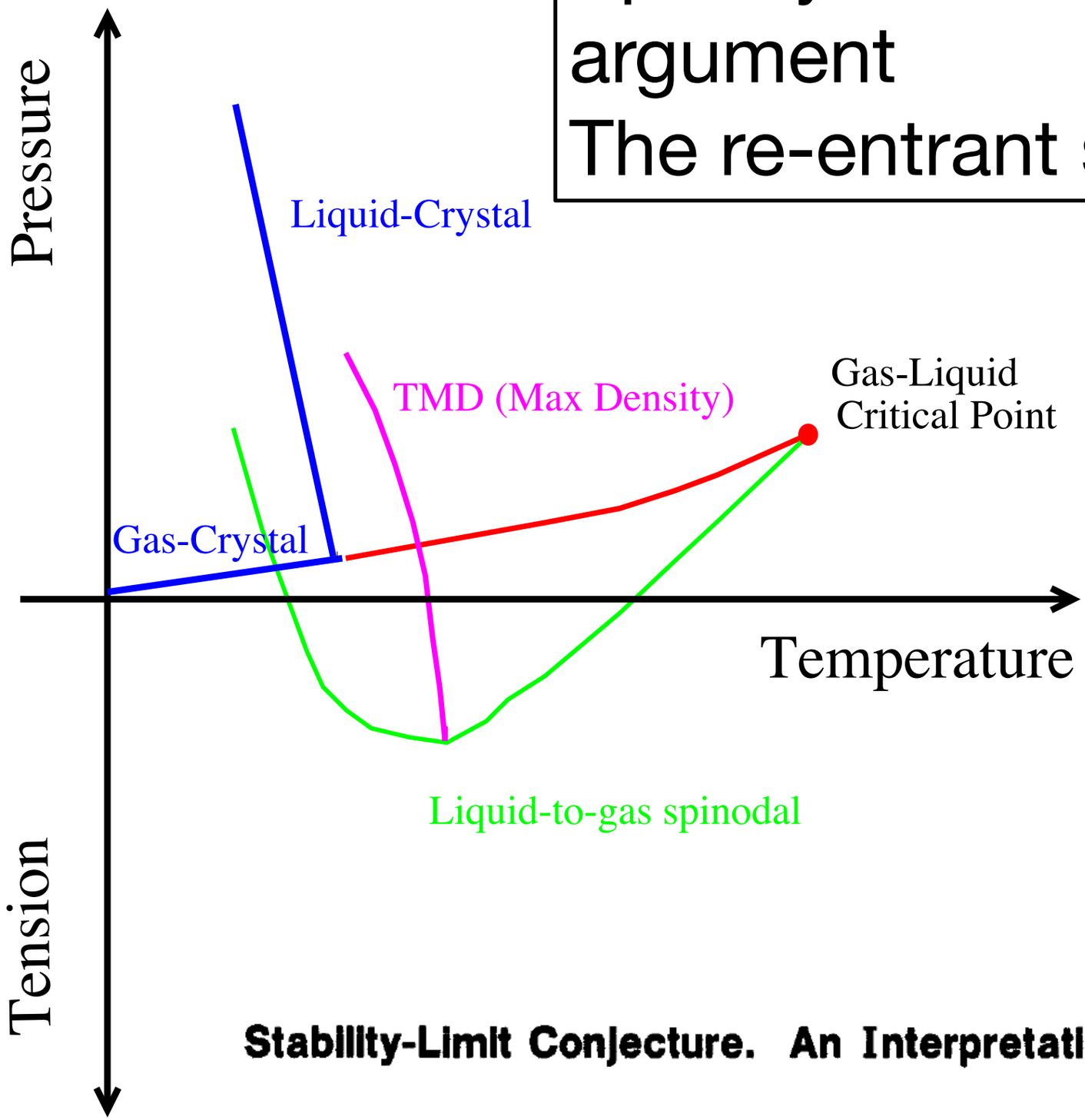


Speedy's thermodynamic argument
The re-entrant spinodal

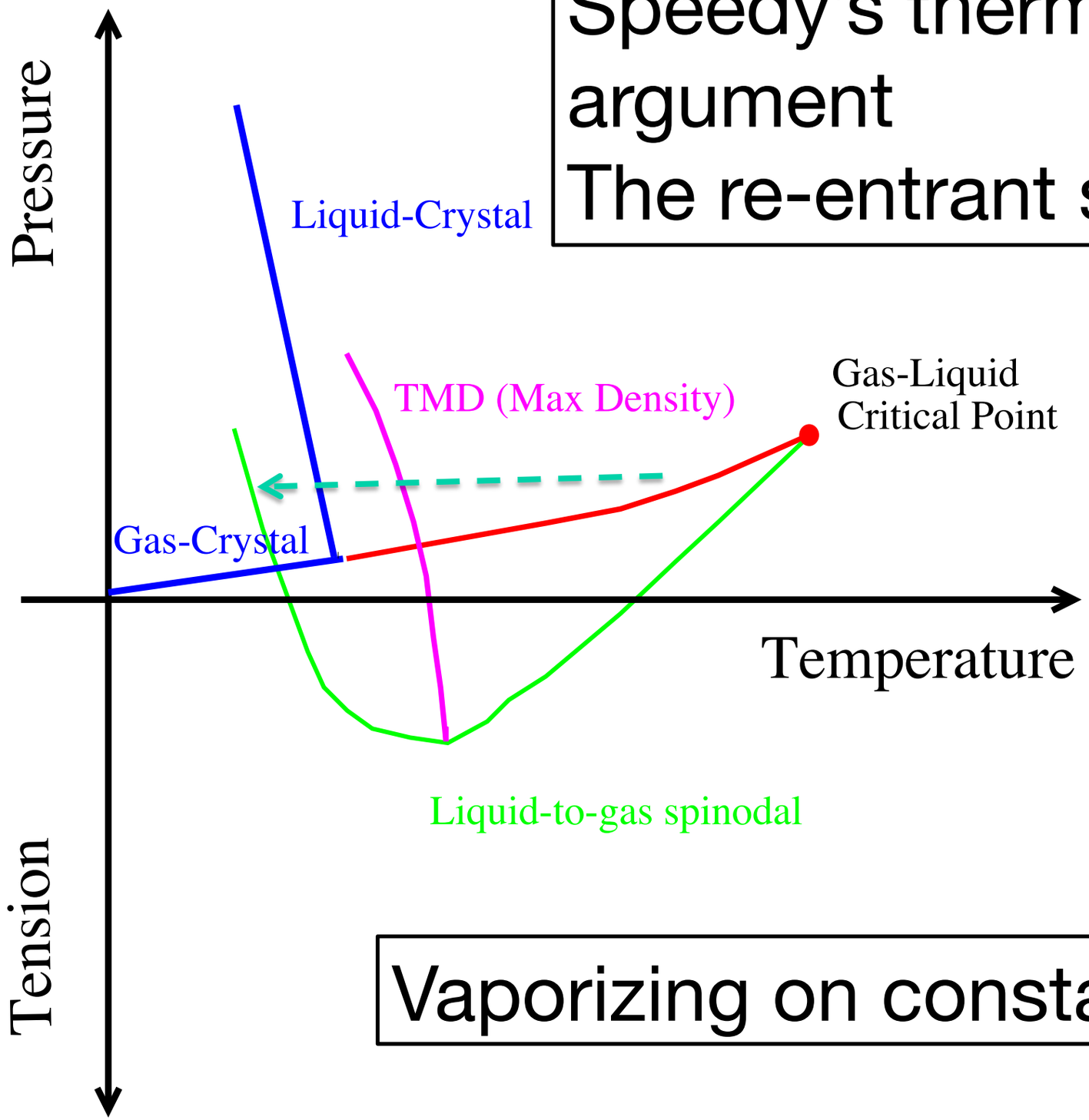


Stability-Limit Conjecture. An Interpretation of the Properties of Water

Robin J. Speedy

Chemistry Department, Victoria University of Wellington, Wellington, New Zealand *(Received: April 8, 1981; In Final Form: October 20, 1981)*

Speedy's thermodynamic argument
The re-entrant spinodal



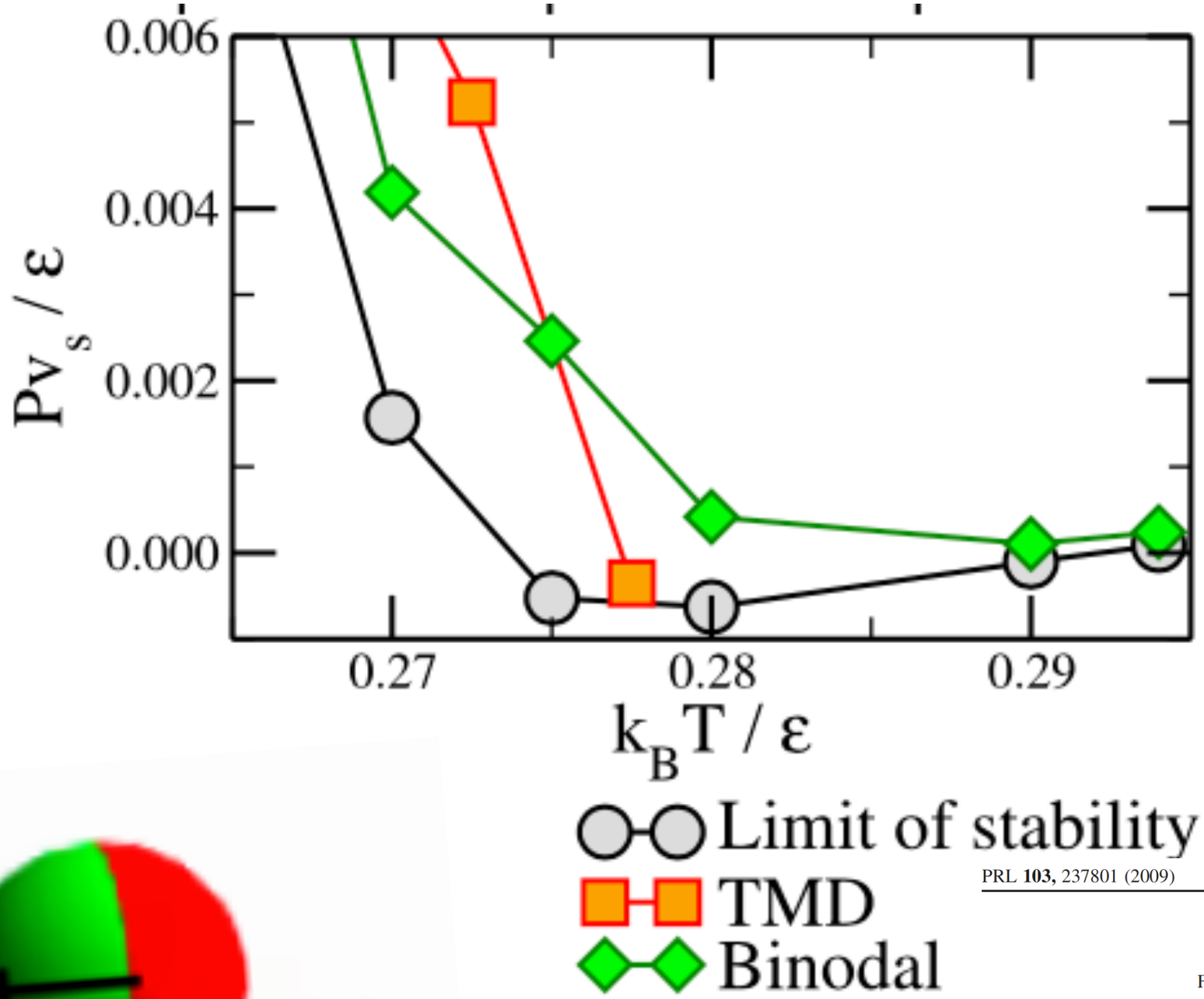
Vaporizing on constant P cooling !!!!

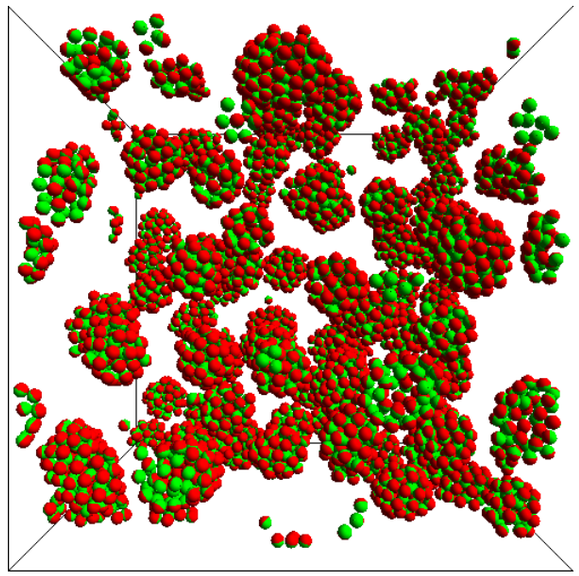
Stability-Limit Conjecture. An Interpretation of the Properties of Water

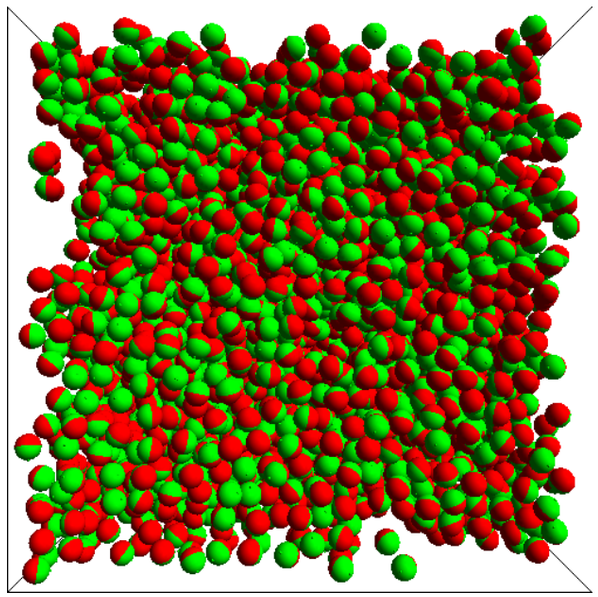
Robin J. Speedy

Chemistry Department, Victoria University of Wellington, Wellington, New Zealand (Received: April 8, 1981; In Final Form: October 20, 1981)

Interlude: The re-entrant Spinodal in a colloidal system: Janus particles







PRL **103,** 237801 (2009) PHYSICAL REVIEW LETTERS week ending 4 DECEMBER 2009

Phase Diagram of Janus Particles

Francesco Sciortino,[1] Achille Giacometti,[2] and Giorgio Pastore[3]

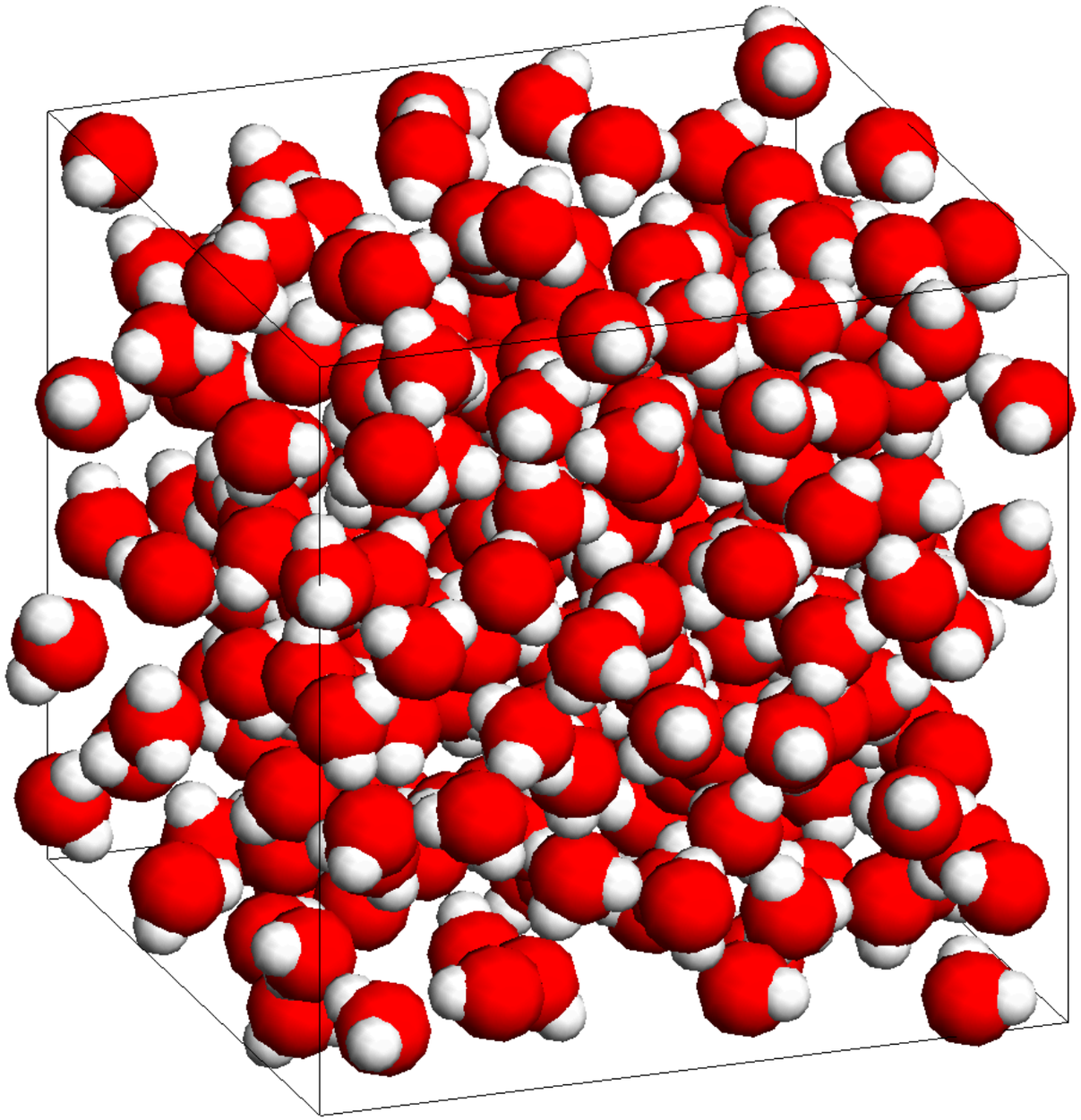
Communication: Re-entrant limits of stability of the liquid phase and the Speedy scenario in colloidal model systems

Lorenzo Rovigatti, Valentino Bianco, José Maria Tavares, and Francesco Sciortino

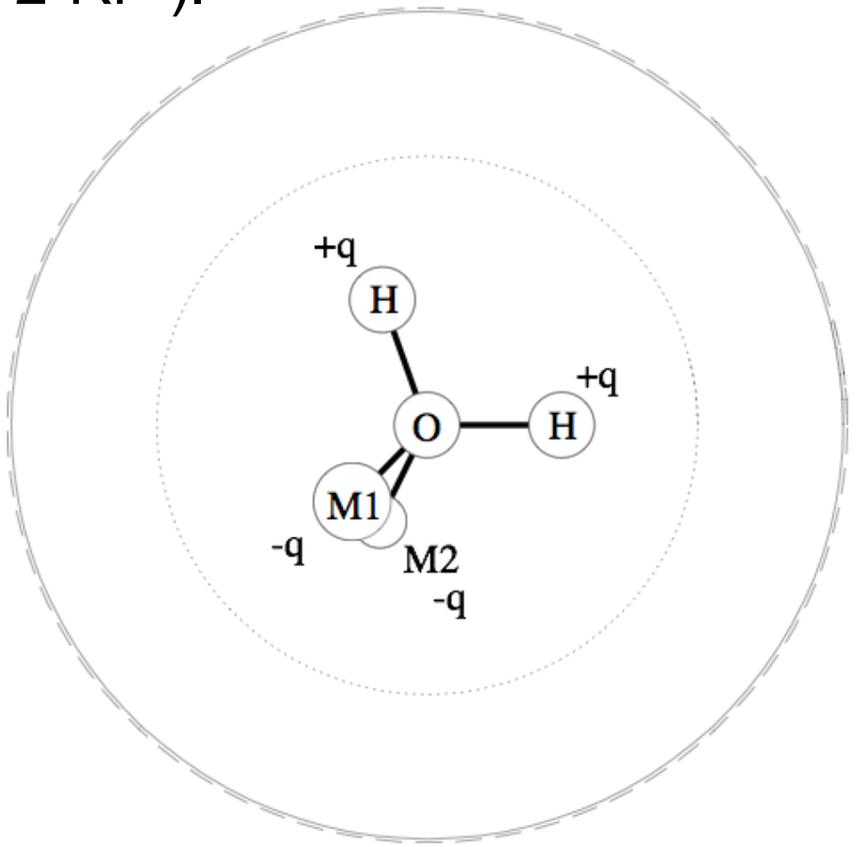
Citation: The Journal of Chemical Physics **146**, 041103 (2017); doi: 10.1063/1.4974830

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

ST2 model of water

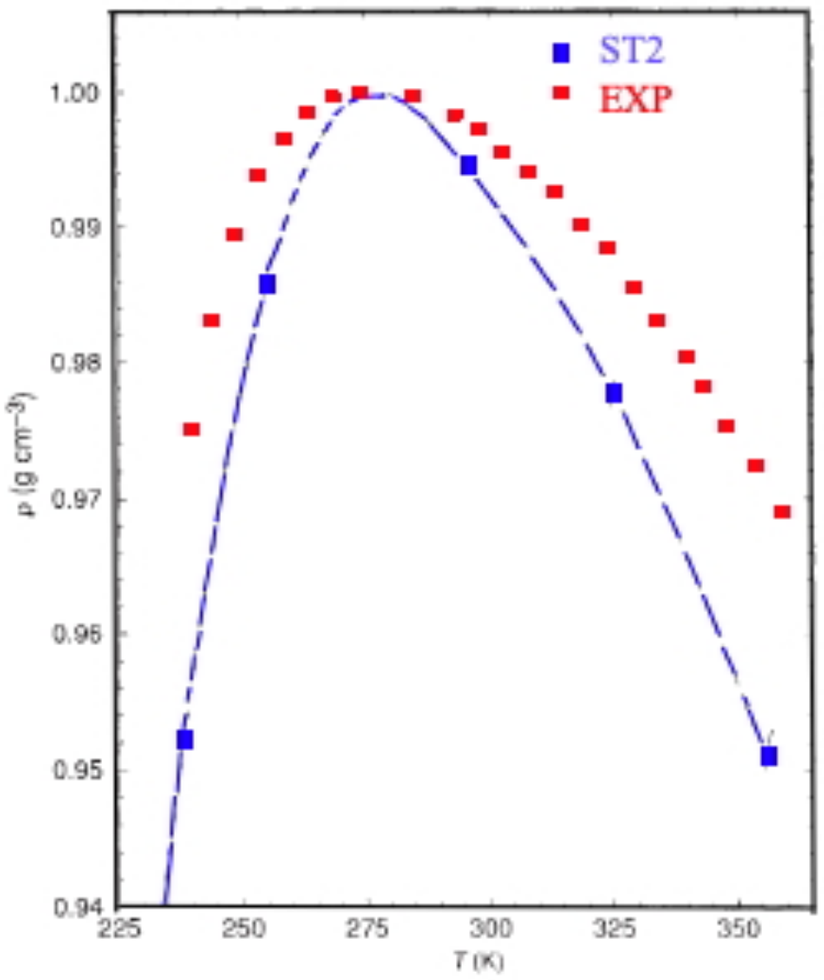


- ST2 water pair potential of Stillinger and Rahman (JCP, 1974).
- Five-site rigid molecule: one O atom, two H atoms, and two “lone pair” sites.
- Direct interactions smoothly tapered to zero. Long-range electrostatics approximated by reaction field method (“ST2-RF”).

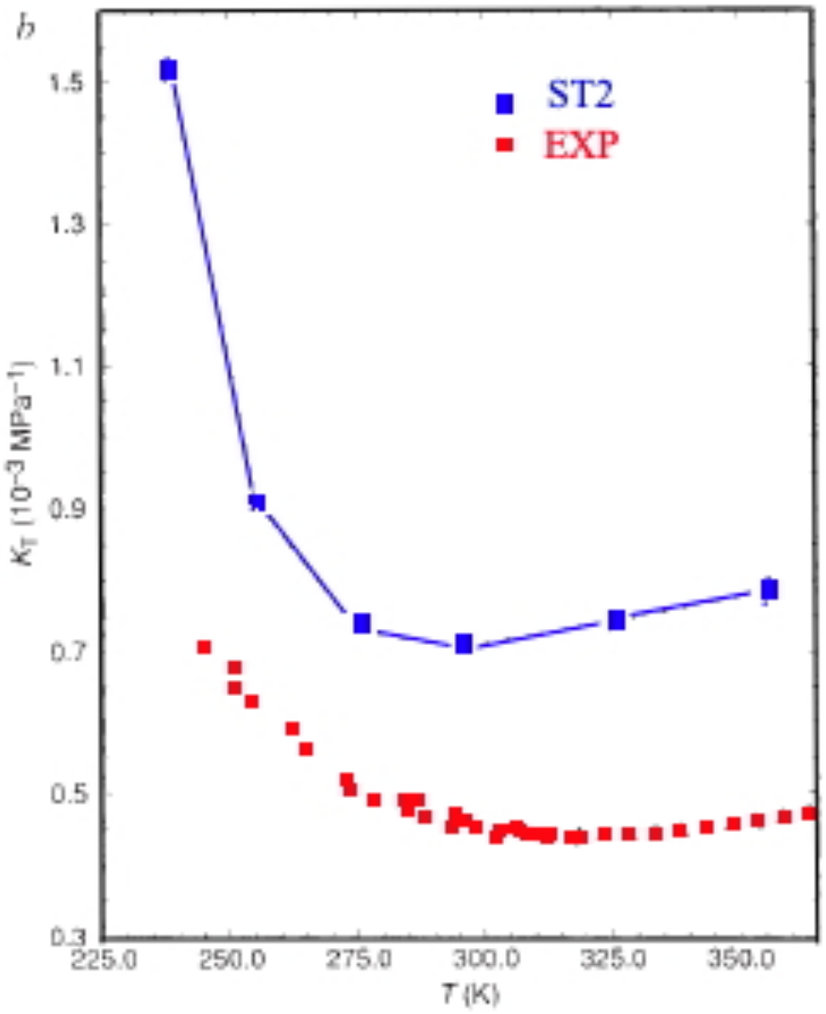


This model reproduces the anomailies….

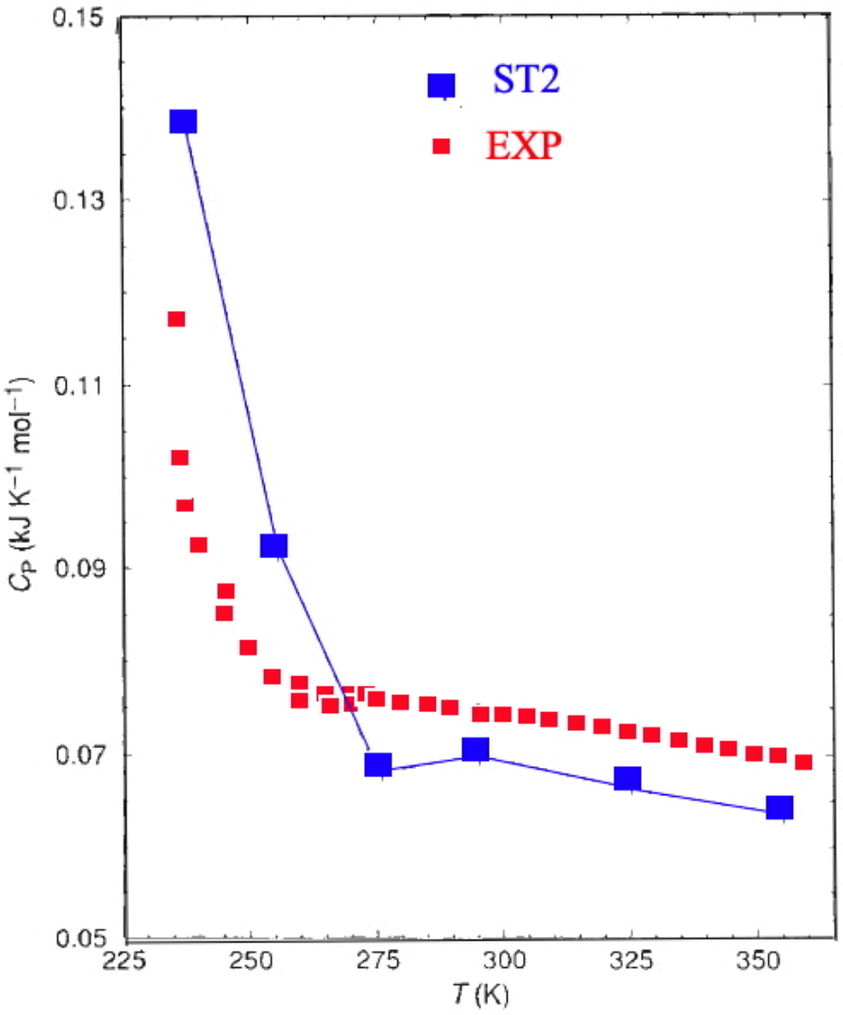
Search for the origin of the anomalies via computer simulations (1990)
ST2 model of water



Density



Compressibility

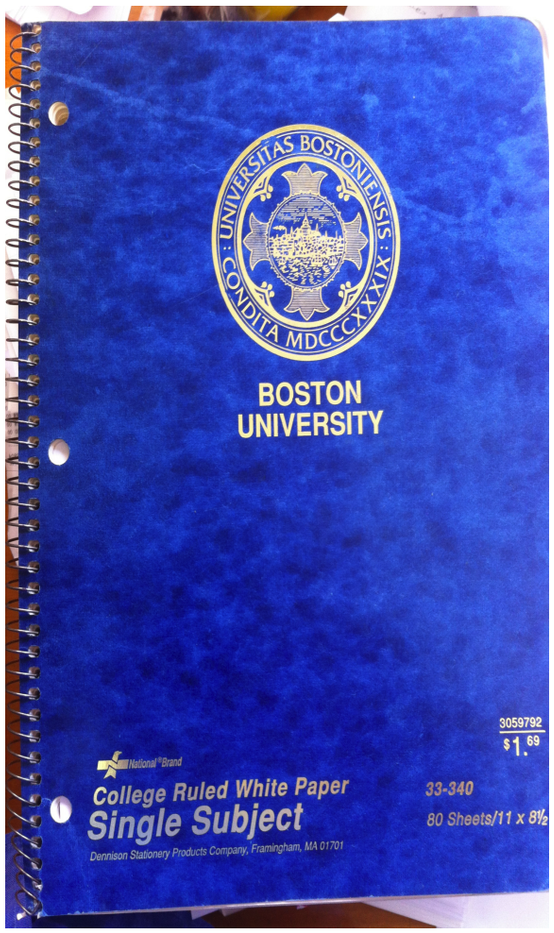


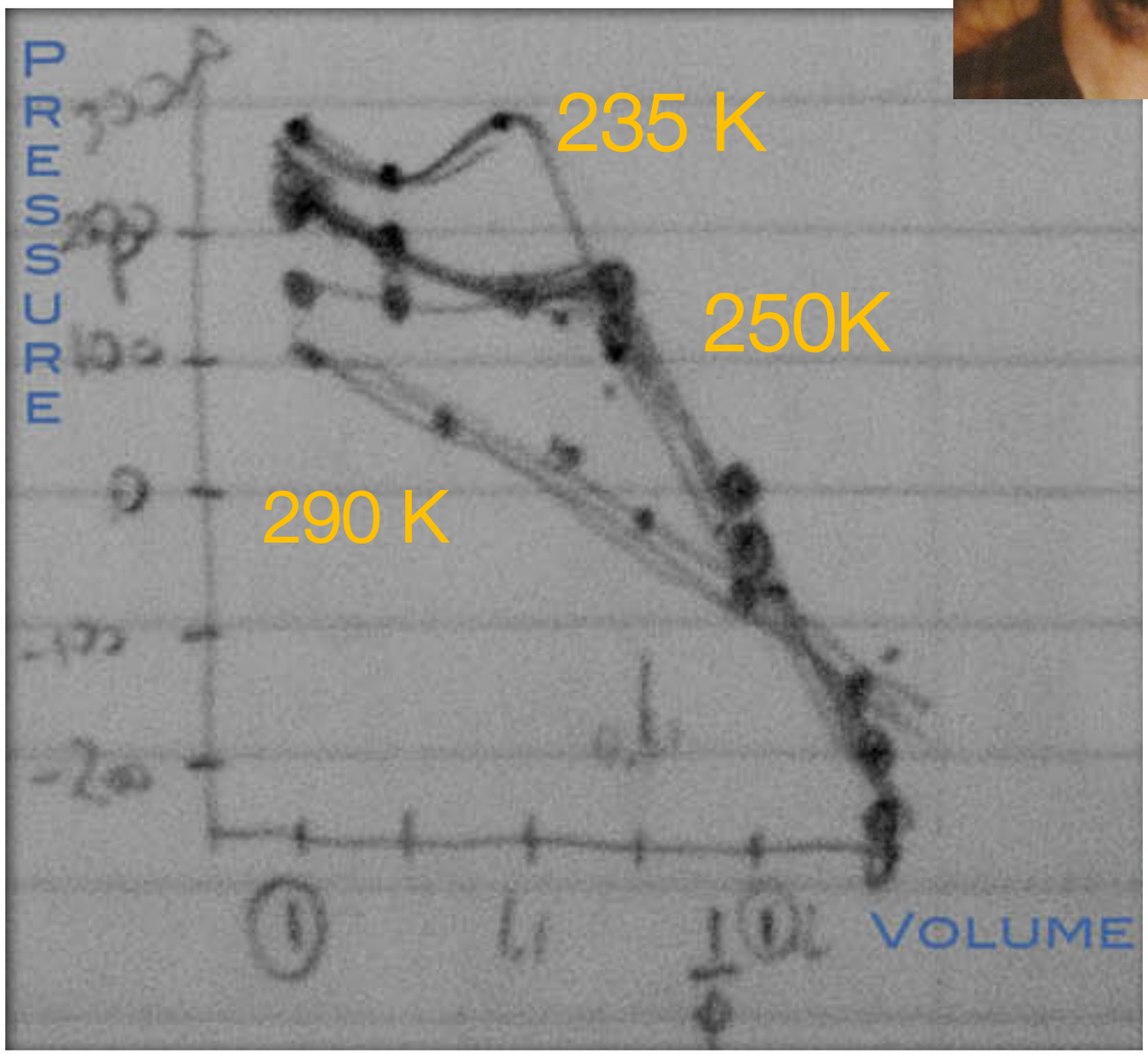
Specific Heat

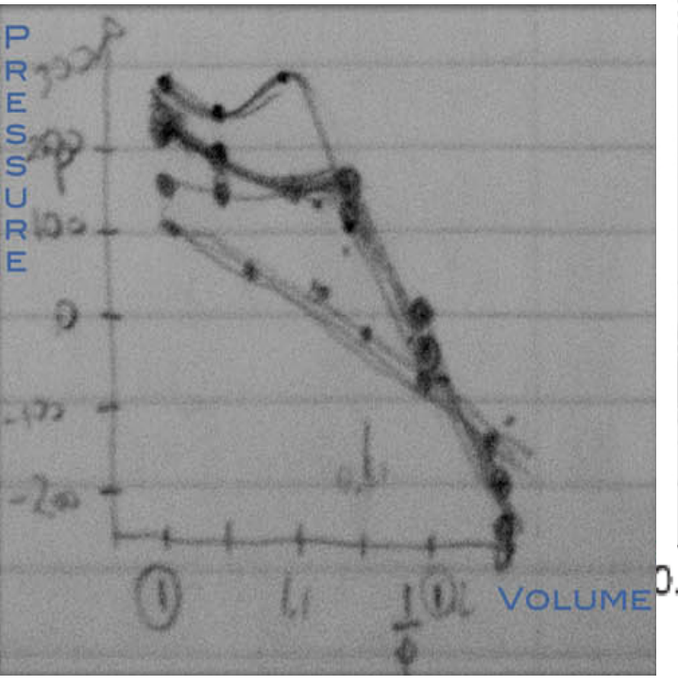
A different scenario for ST2 water...

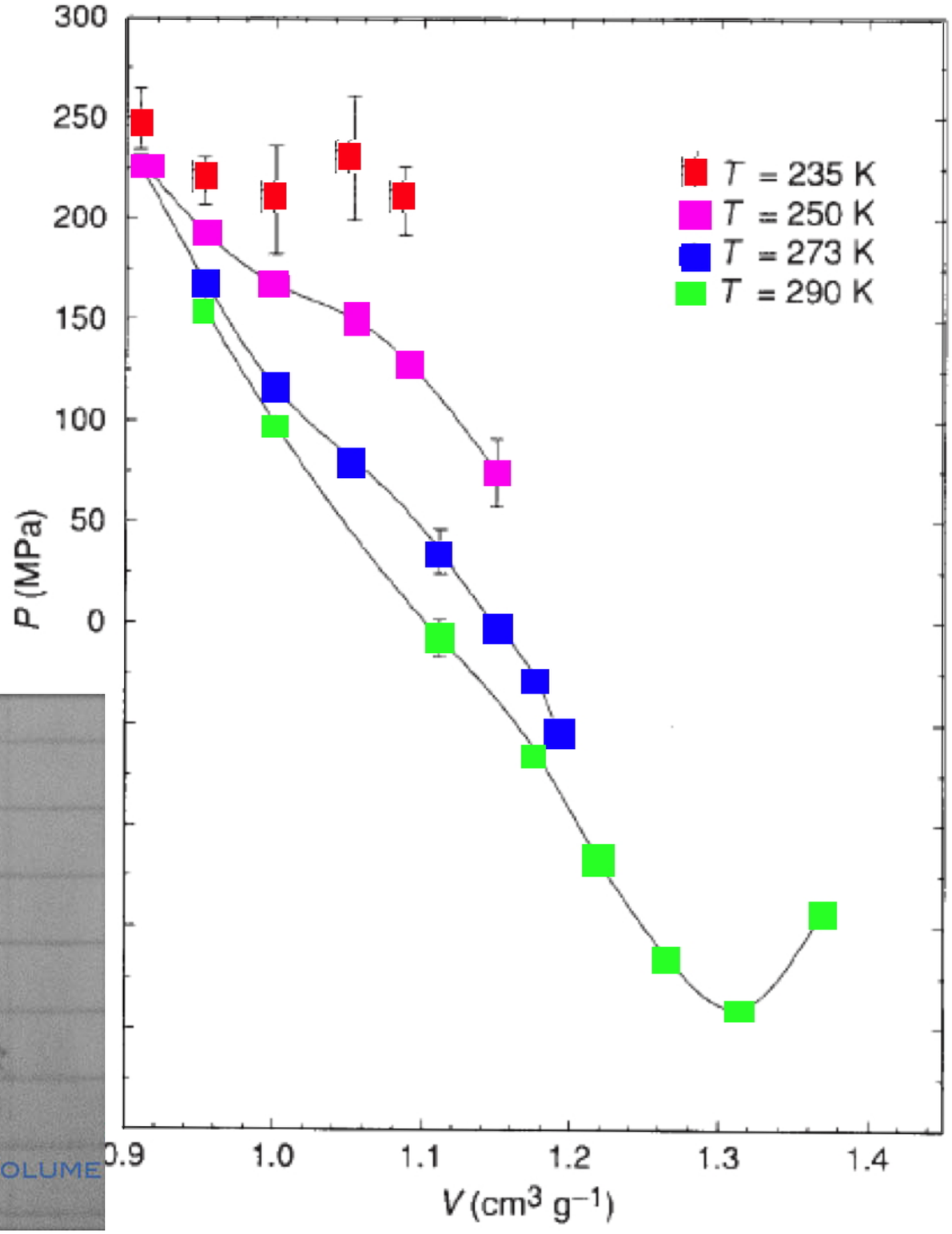
A van der Waals loop at low T !

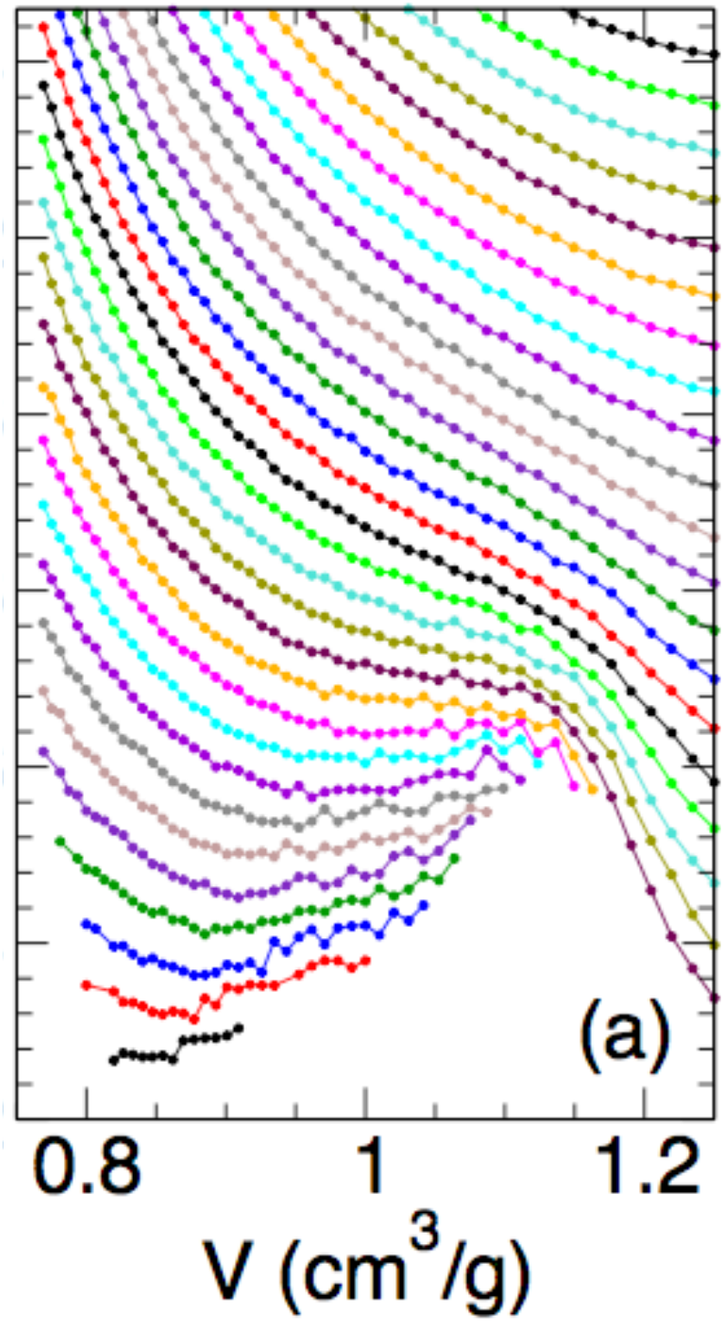
The very first data..... (1990)







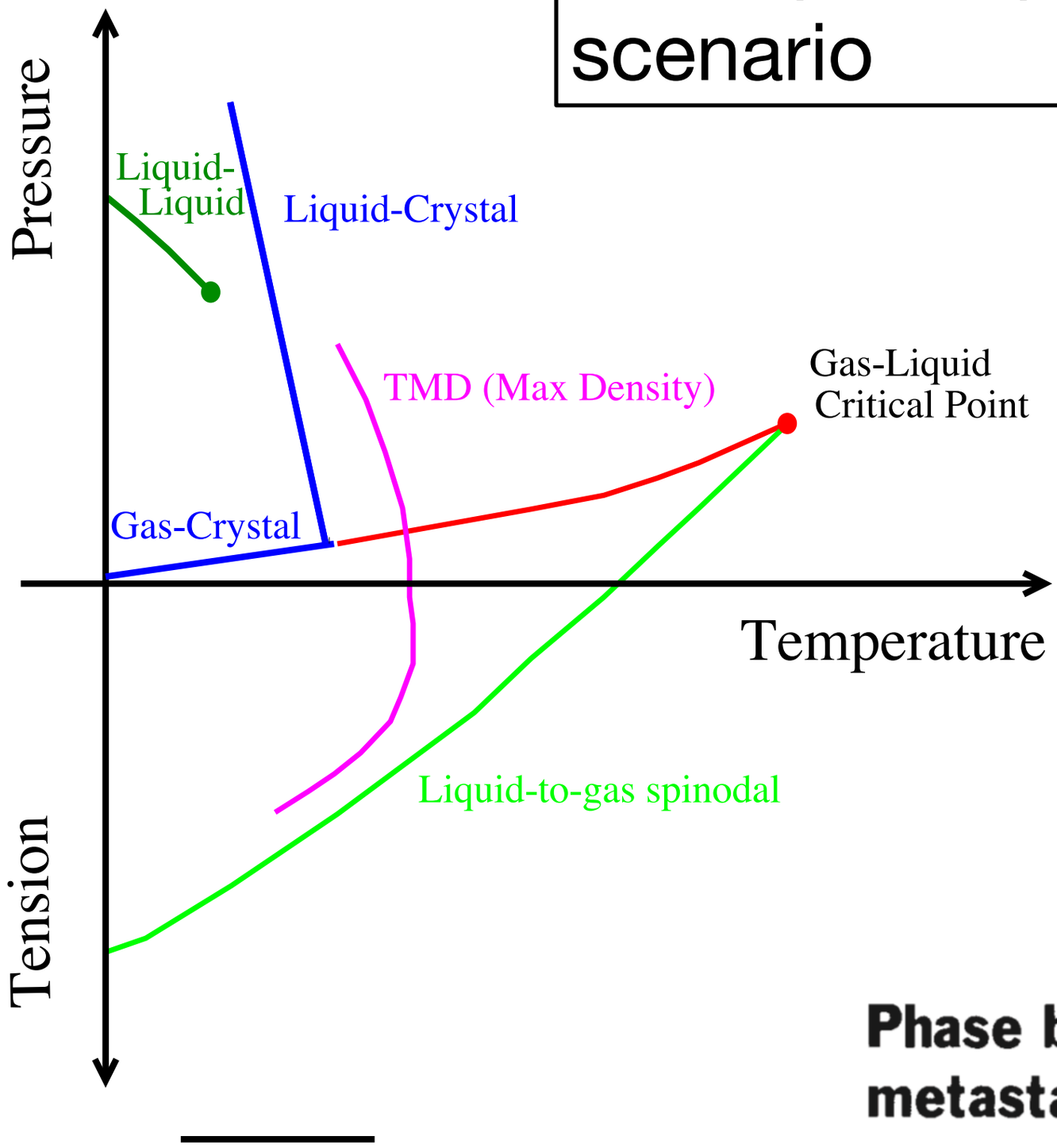




P. H. Poole, F. Sciortino, U. Essmann, H. E. Stanley
Phase behavior of metastable water
Nature 360, 324-328, 1992

P.H. Poole, I. Saika-Voivod, F. Sciortino
Density minima and the liquid Liquid phase transition
J. Phys. Cond. Matt.17, L431-L437, 2005

The liquid-liquid critical point scenario



Phase behaviour of metastable water

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

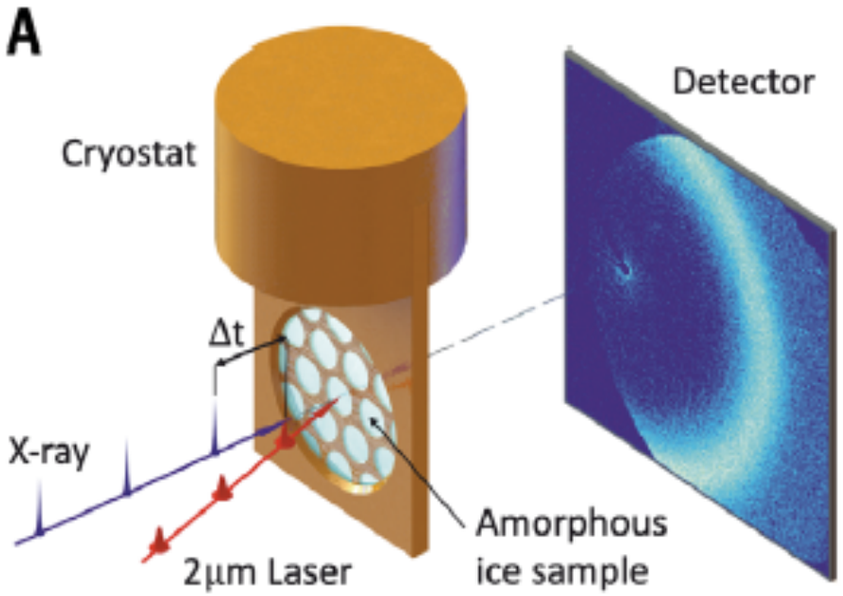
NATURE · VOL 360 · 26 NOVEMBER 1992

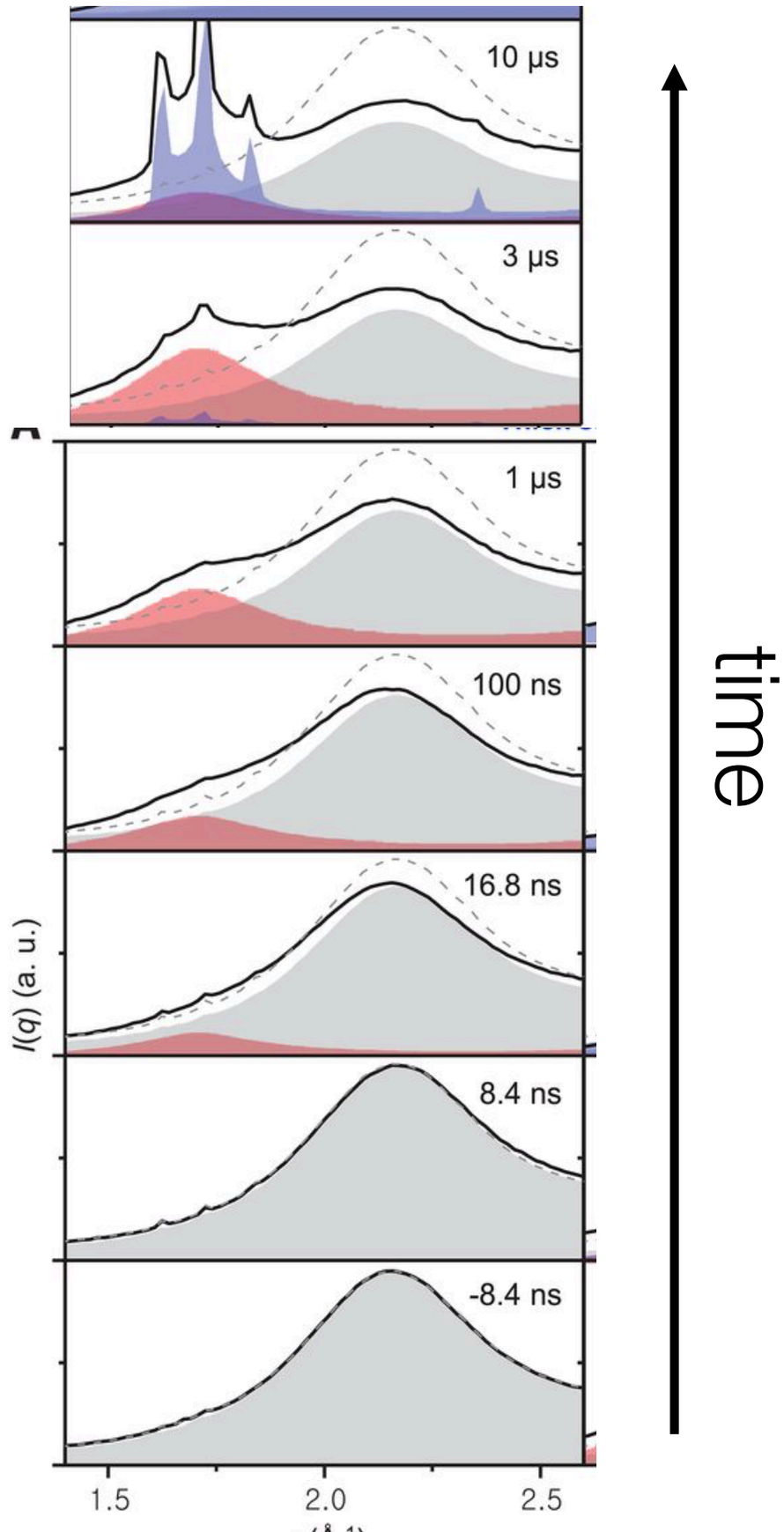
WATER PHASES

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]†

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

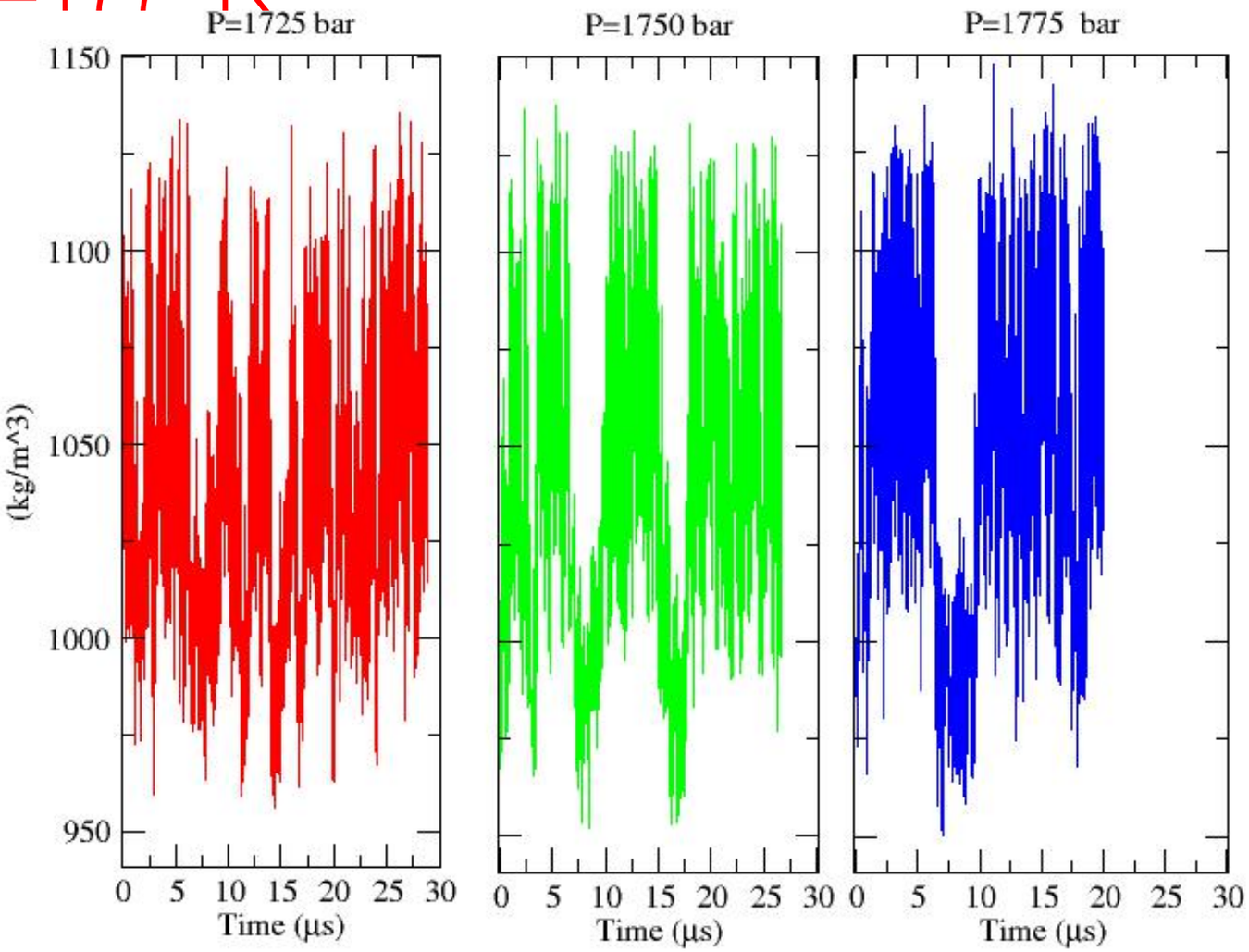


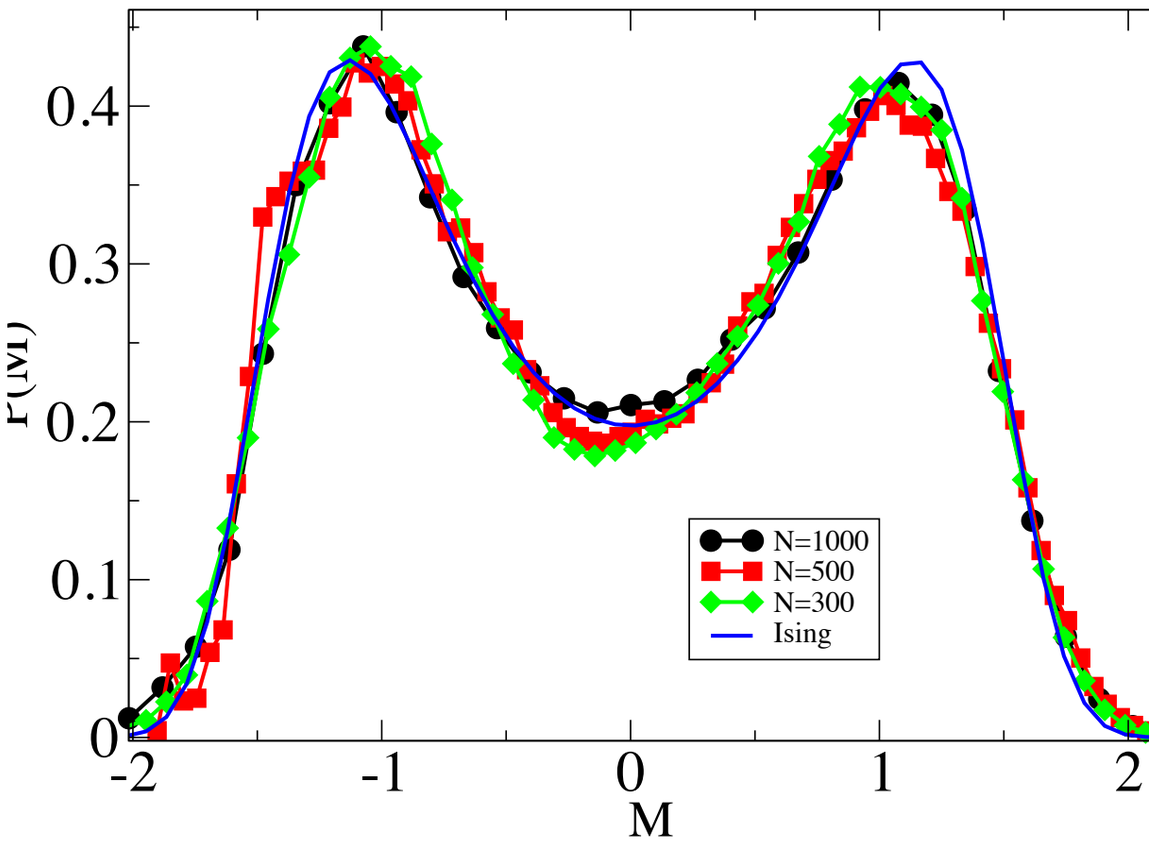


Other molecular models: TIP4P-2005

A general purpose model for the condensed phases of water: **TIP4P/2005**
JLF Abascal, C Vega - The Journal of chemical physics, 2005 - aip.scitation.org
A potential model intended to be a general purpose model for the condensed phases of water is presented. **TIP4P/2005** is a rigid four site model which consists of three fixed point charges and one Lennard-Jones center. The parametrization has been based on a fit of the …
☆ Citato da 2185 Articoli correlati Tutte e 20 le versioni

T=177 K





P_c=1861 bar
T_c=172 K

Real (computer) time:
several hundred of cores and GPUs
running 1.5 years

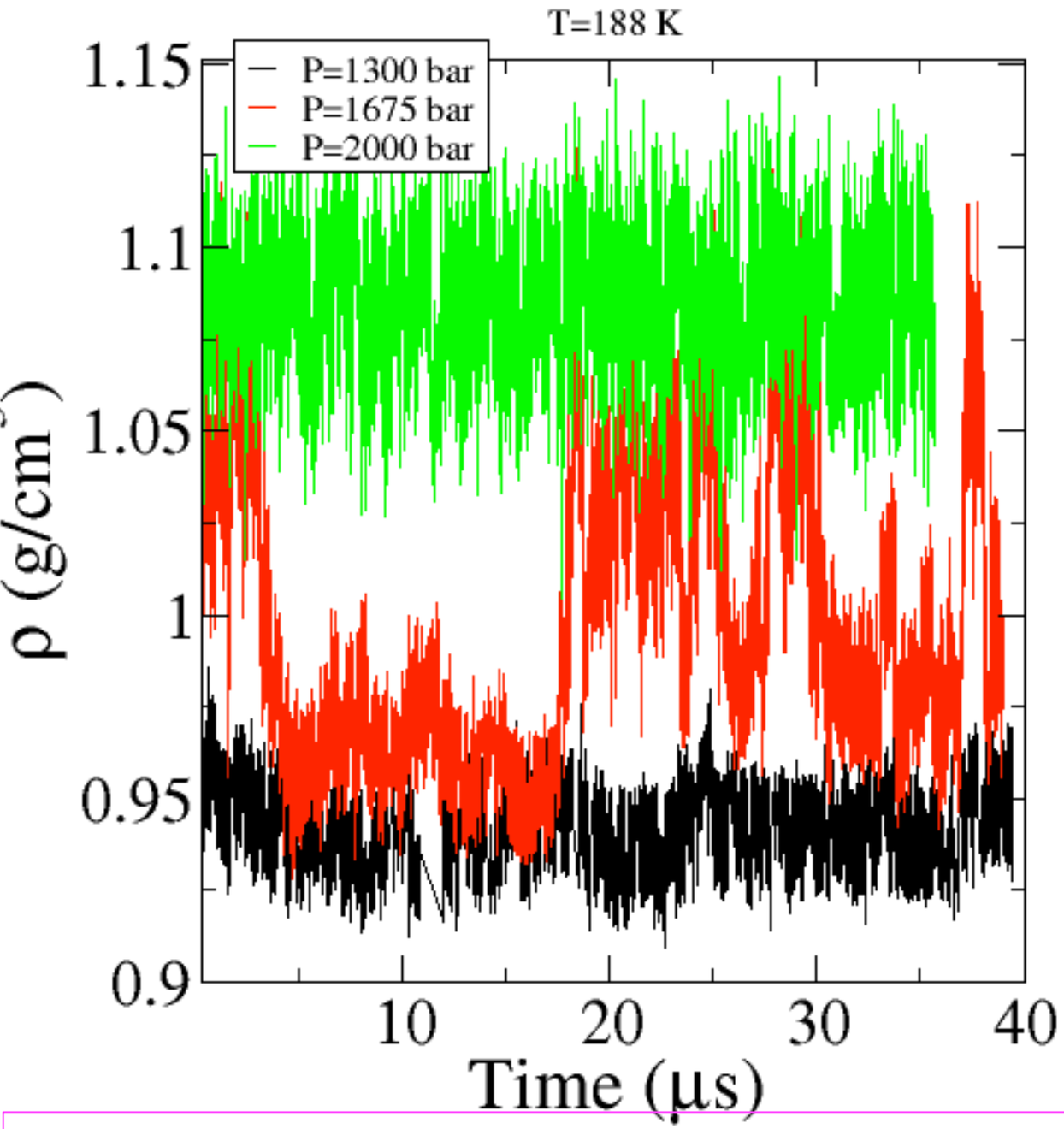
Second critical point in two realistic models of water

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

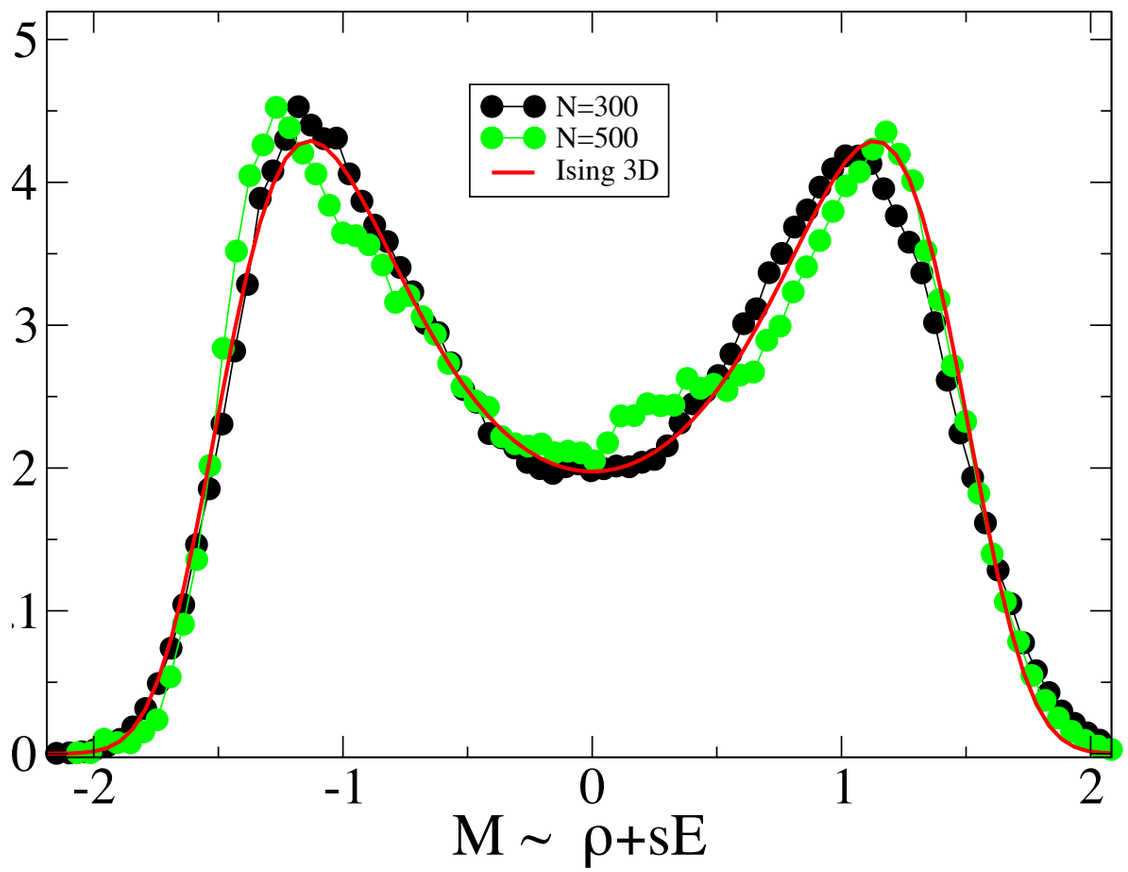
Science **369**, 289–292 (2020) 17 July 2020

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 …
☆ Citato da 671 Articoli correlati Tutte e 15 le versioni

TIP4P/Ice



P_c=1725 bar
T_c=188.6 K



Real time (computer time) - 1 year

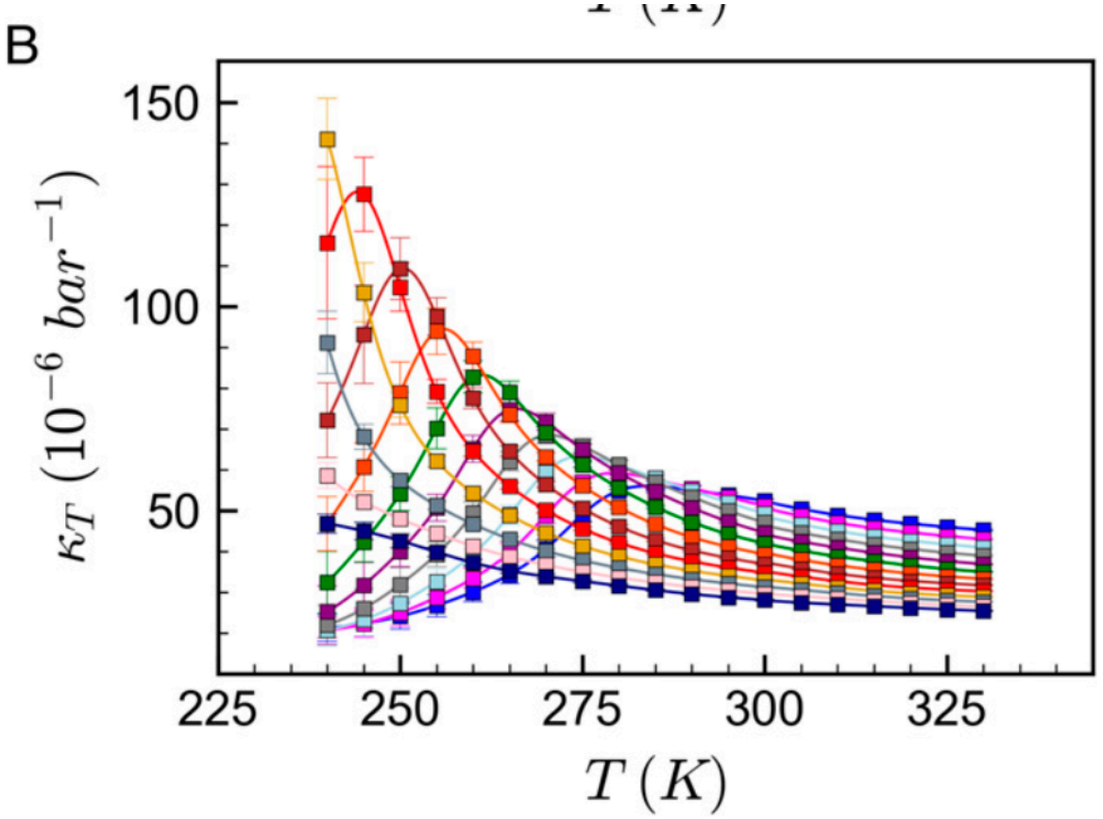
Second critical point in two realistic models of water

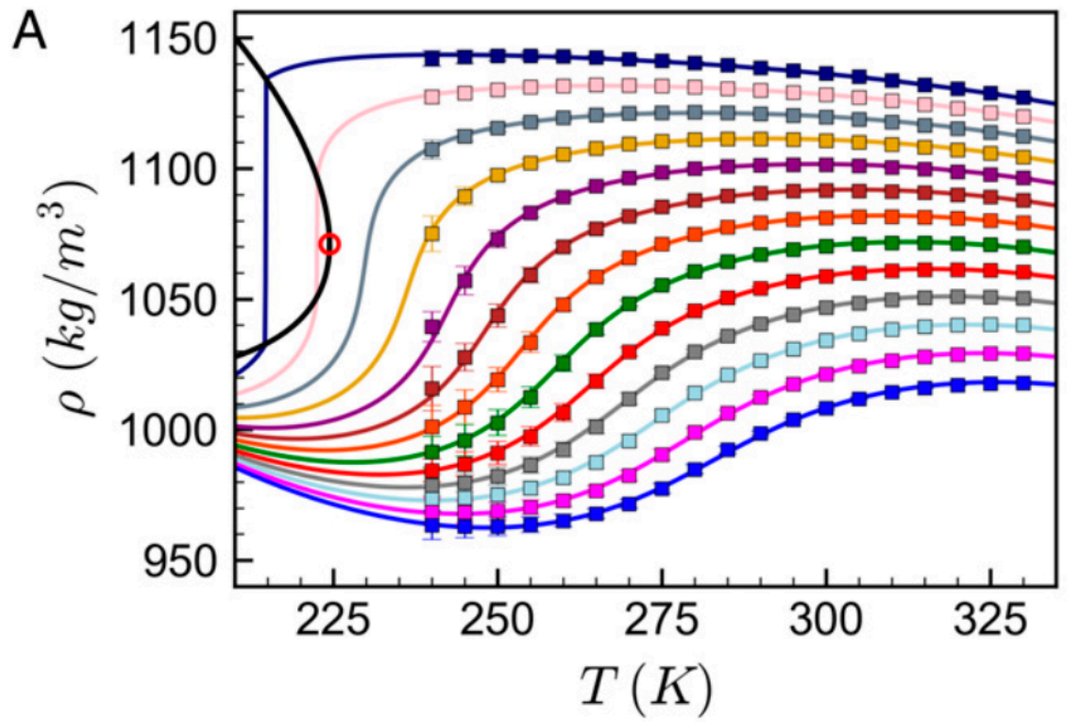
Pablo G. Debenedetti[1]*†, Francesco Sciortino[2]†, Gül H. Zerze[1]†

Science **369**, 289–292 (2020) 17 July 2020

Signatures of a liquid–liquid transition in an ab initio deep neural network model for water

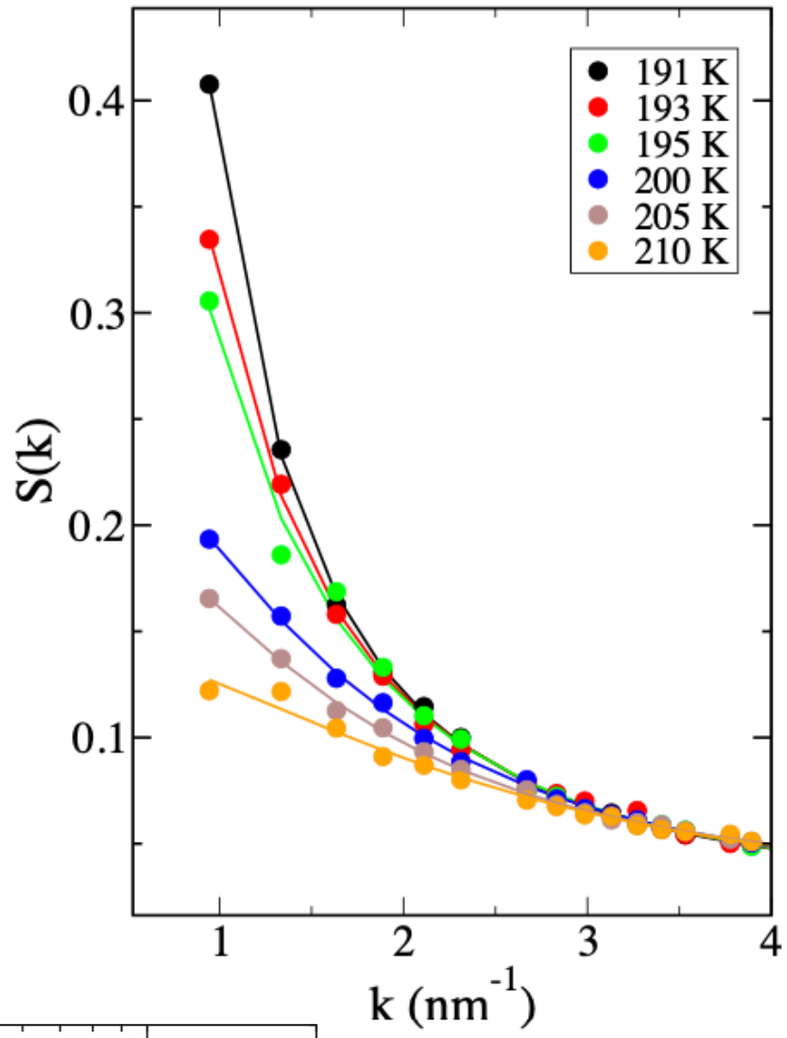
Thomas E. Gartner III[a], Linfeng Zhang[b], Pablo M. Piaggi[a], Roberto Car[a,b,c,d], Athanassios Z. Panagiotopoulos[d,e,1], and Pablo G. Debenedetti[e,1]

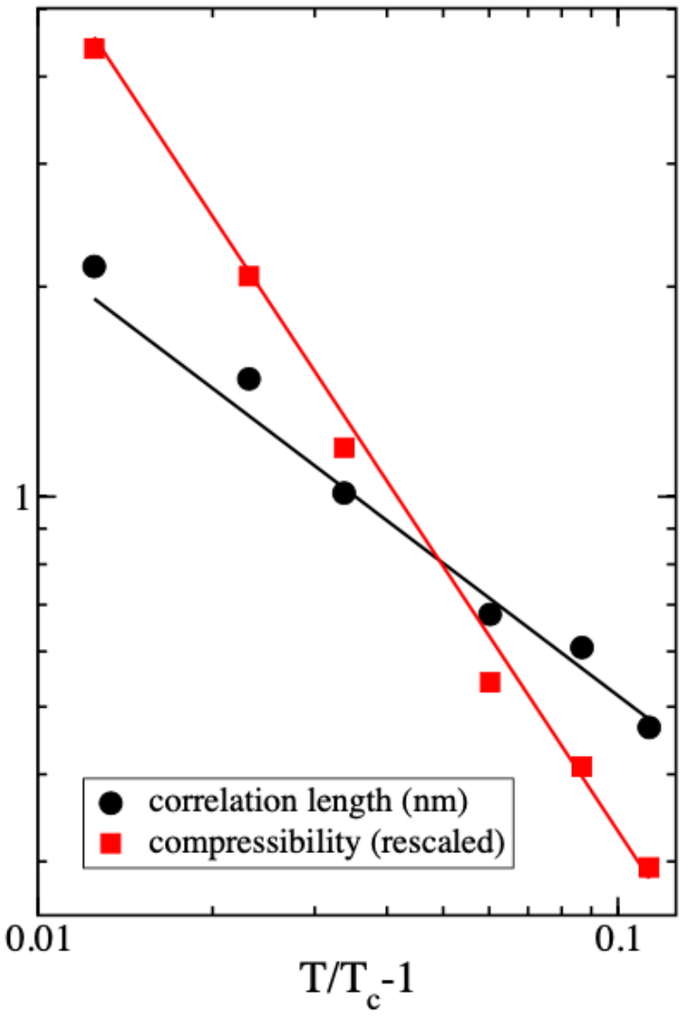


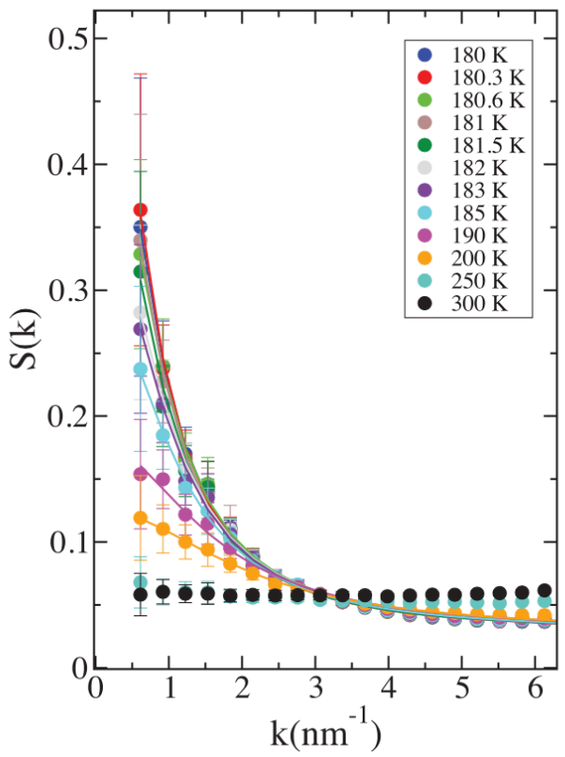


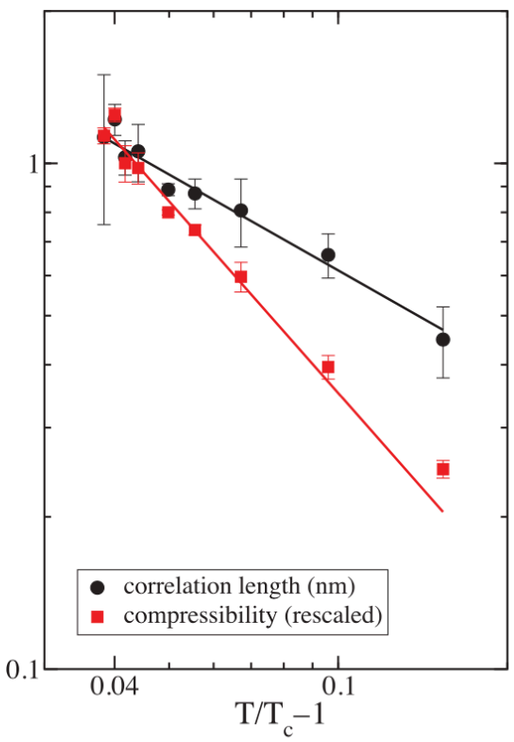
Structure factor and compressibility

Consistence with Ising critical exponents

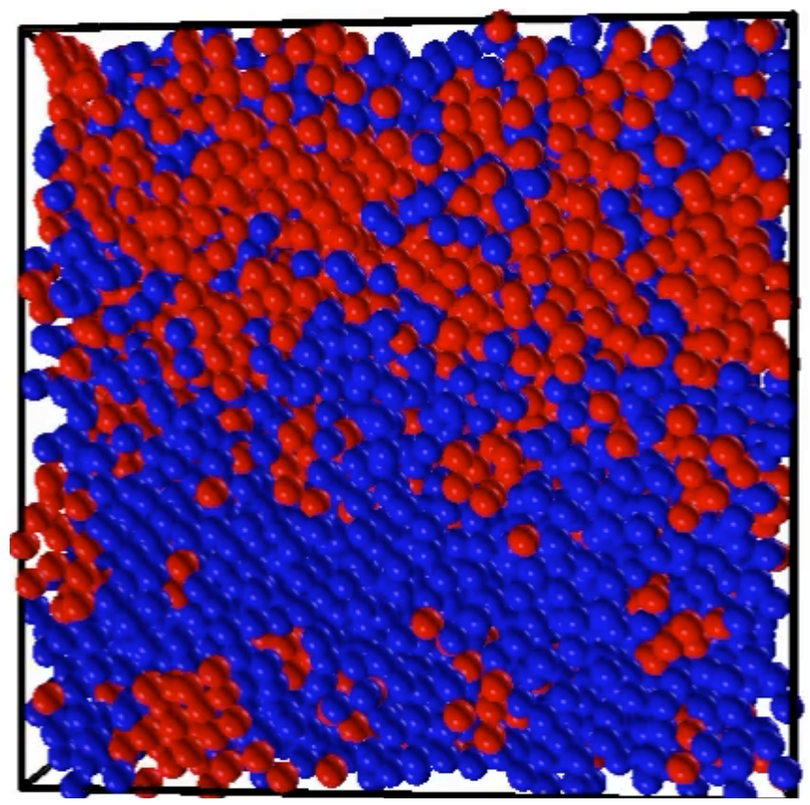






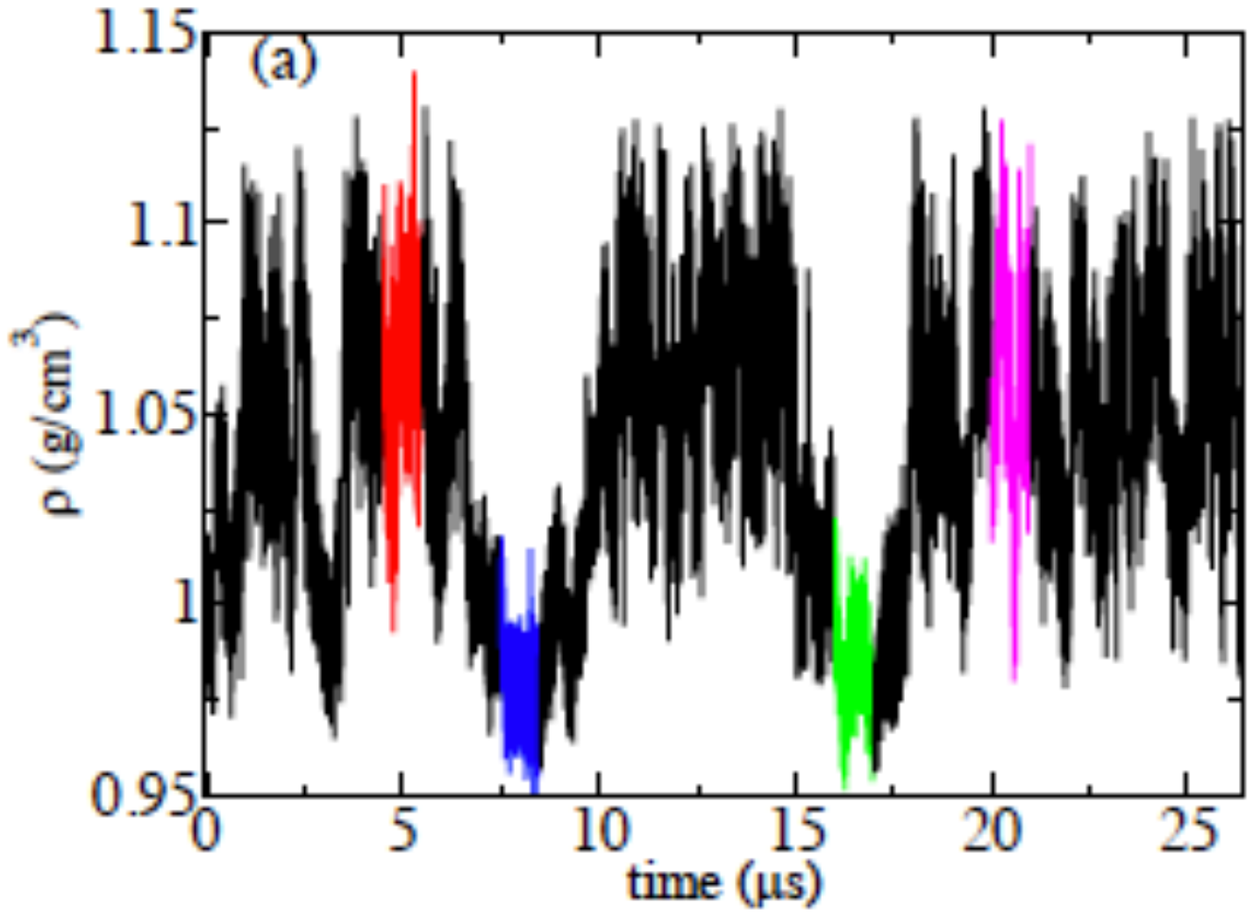


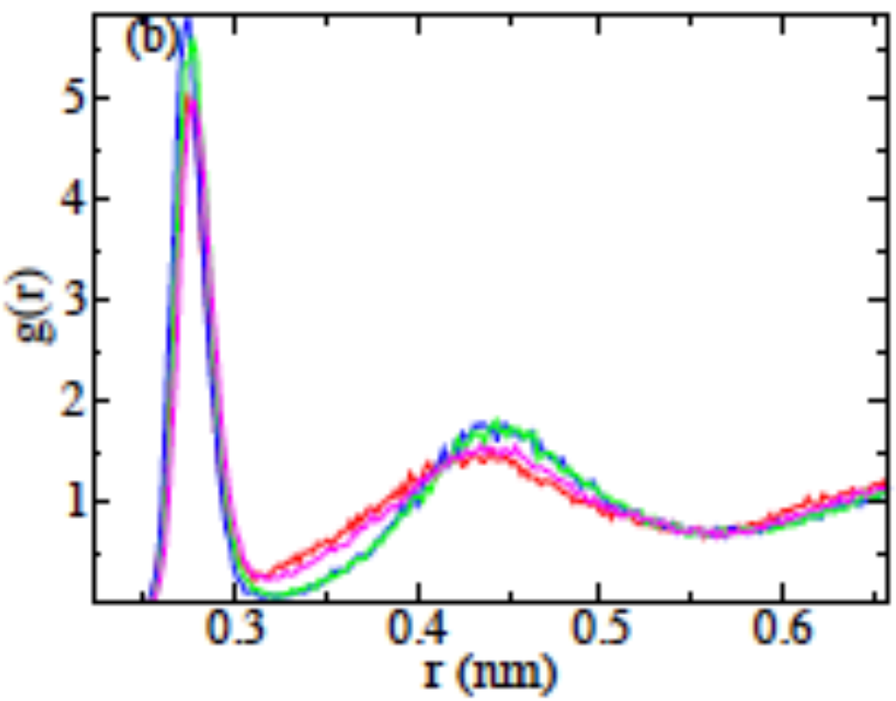
Science **369**, 289–292 (2020)

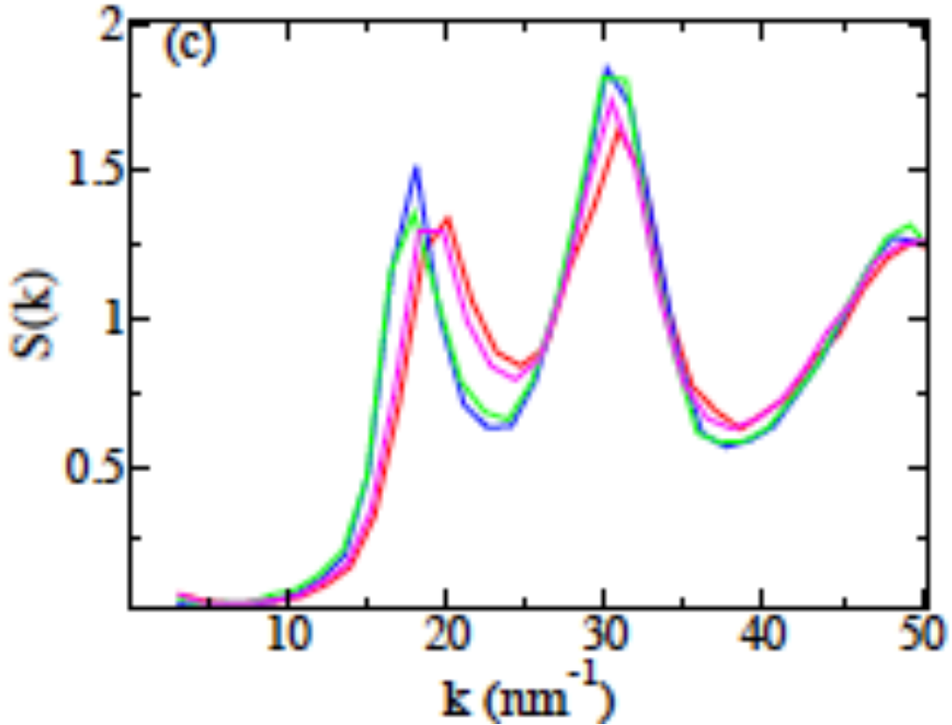


30000 molecules

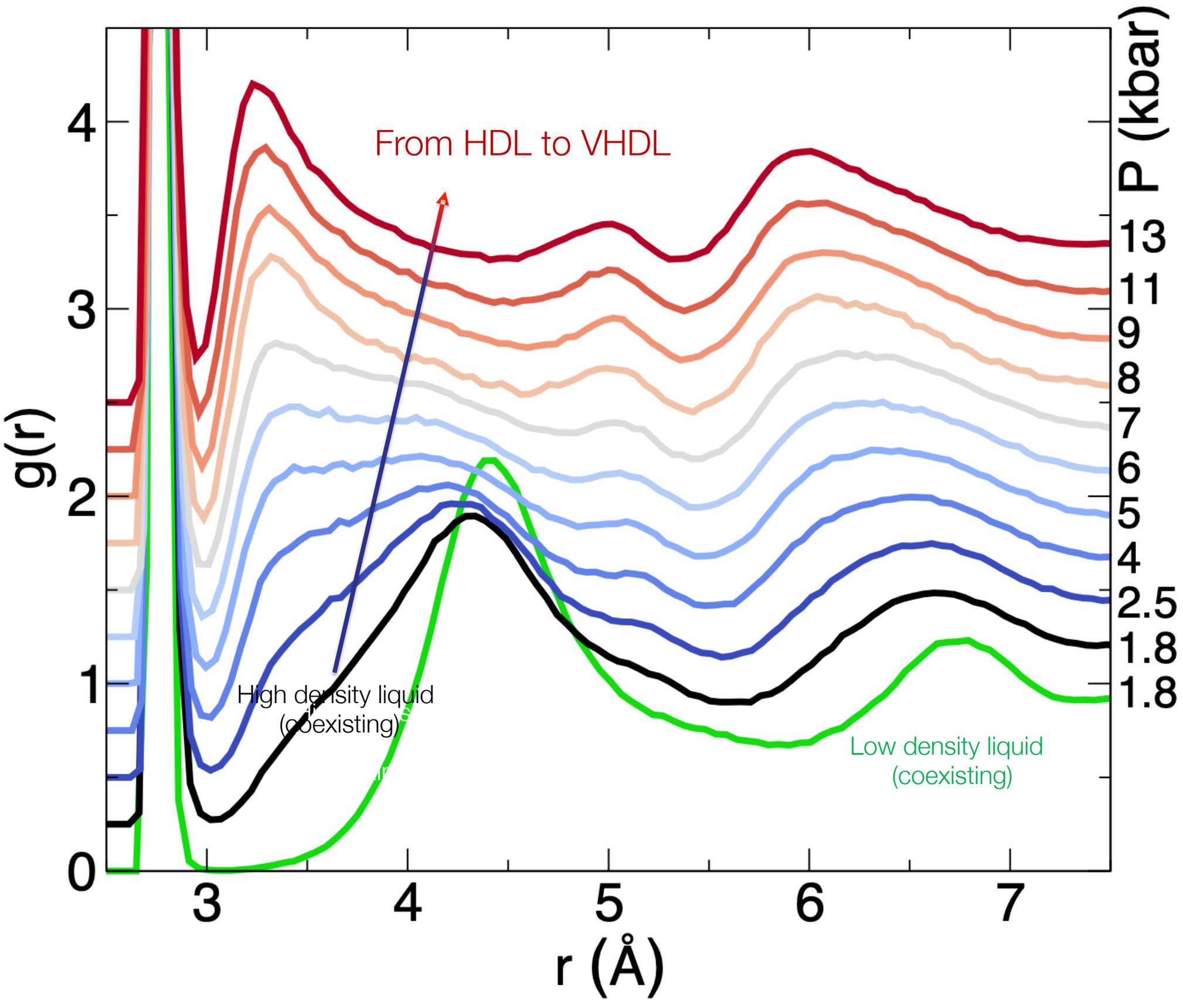
Structural changes close to the critical point







Structural changes on increasing P (TIP4P/Ice T=188 K IS)



A new way to look at structural changes

(in network forming liquids)

Central Molecule

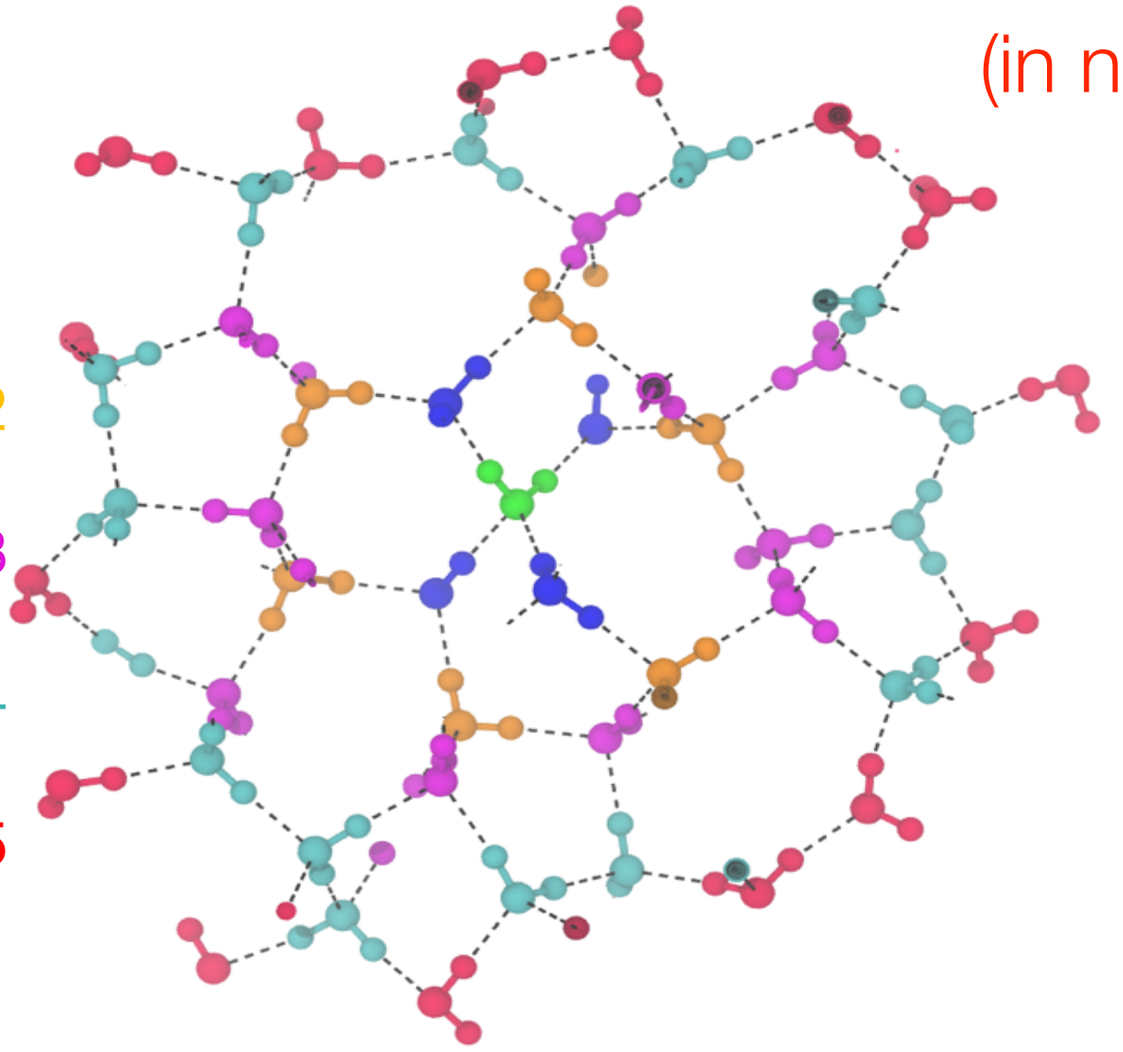
Chemical Distance D=1

Chemical Distance D=2

Chemical Distance D=3

Chemical Distance D=4

Chemical Distance D=5



$$g(r) = \sum_D g_D(r)$$

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

Cite as: J. Chem. Phys. **154**, 184506 (2021); https://doi.org/10.1063/5.0049299
Submitted: 03 March 2021 . Accepted: 20 April 2021 . Published Online: 12 May 2021

Riccardo Foffi, John Russo, and Francesco Sciortino

PHYSICAL REVIEW LETTERS **127,** 175502 (2021)

Structure of High-Pressure Supercooled and Glassy Water

Riccardo Foffi and Francesco Sciortino*
Department of Physics, Sapienza Università di Roma, Piazzale Aldo Moro, 2, 00185 Rome, Italy

Looking for structural information

Central Molecule

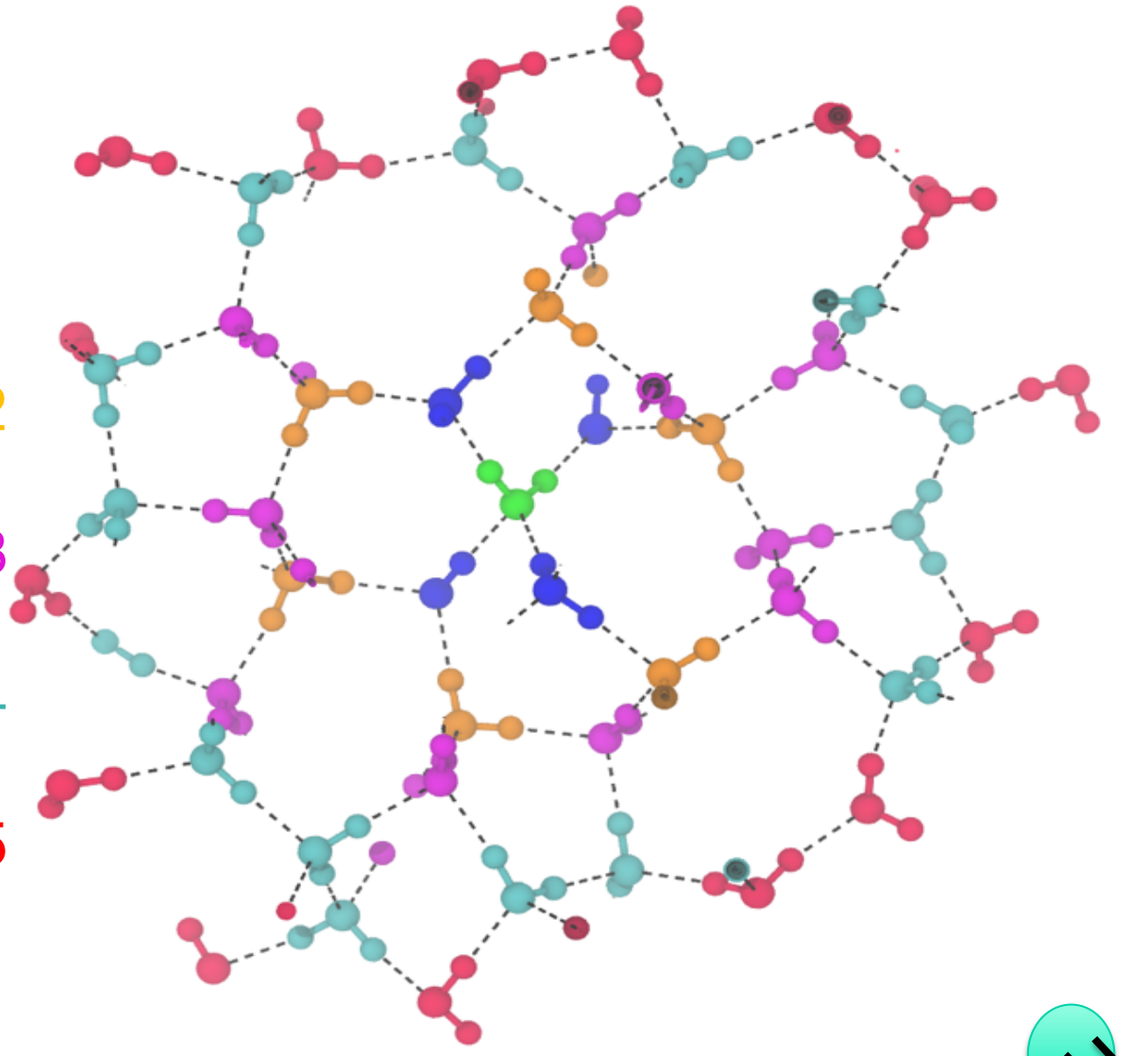
Chemical Distance D=1

Chemical Distance D=2

Chemical Distance D=3

Chemical Distance D=4

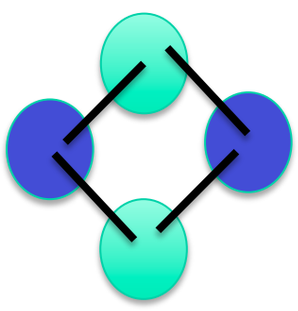
Chemical Distance D=5



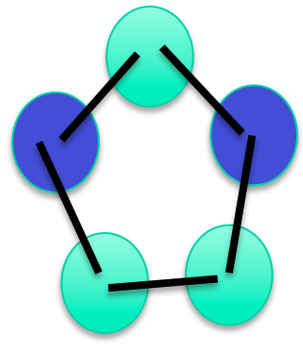
$$g(r) = \sum_D g_D(r)$$

Associating chemical distance D to ring length L

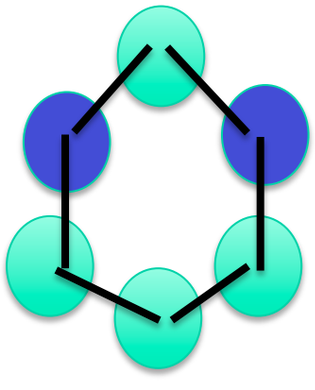
$$g_D(r) = \sum_L g_D^L(r)$$



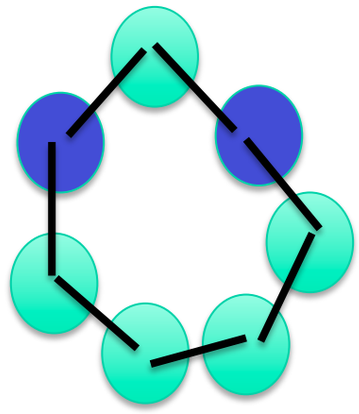
D =2
L =4



D =2
L =5



D =2
L =6



D =2
L =7

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

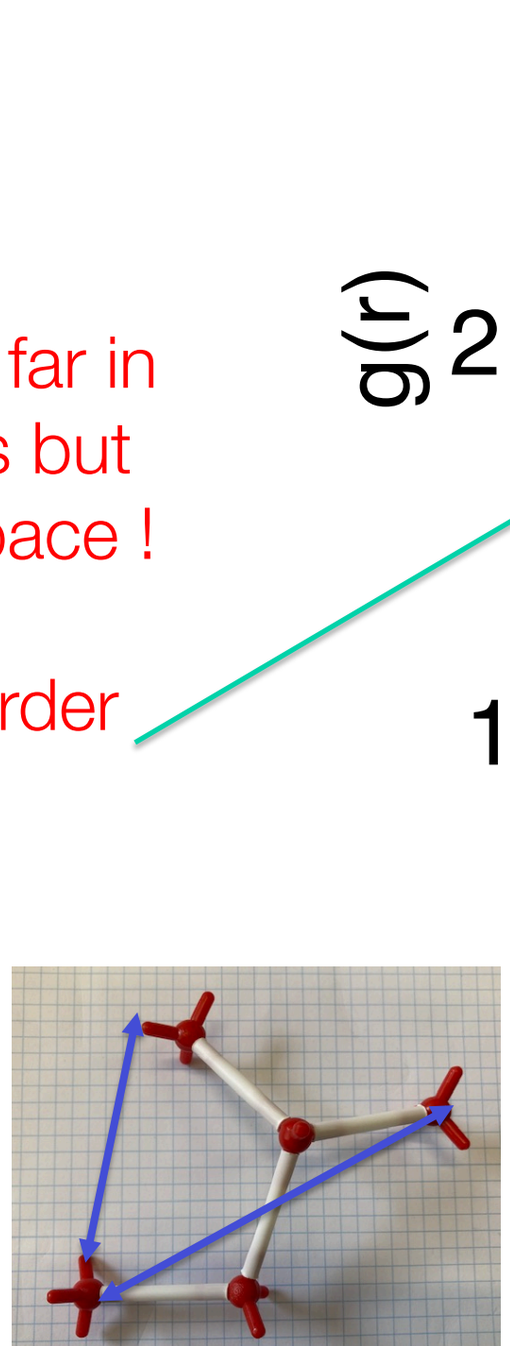
Cite as: J. Chem. Phys. **154**, 184506 (2021); https://doi.org/10.1063/5.0049299
Submitted: 03 March 2021 . Accepted: 20 April 2021 . Published Online: 12 May 2021

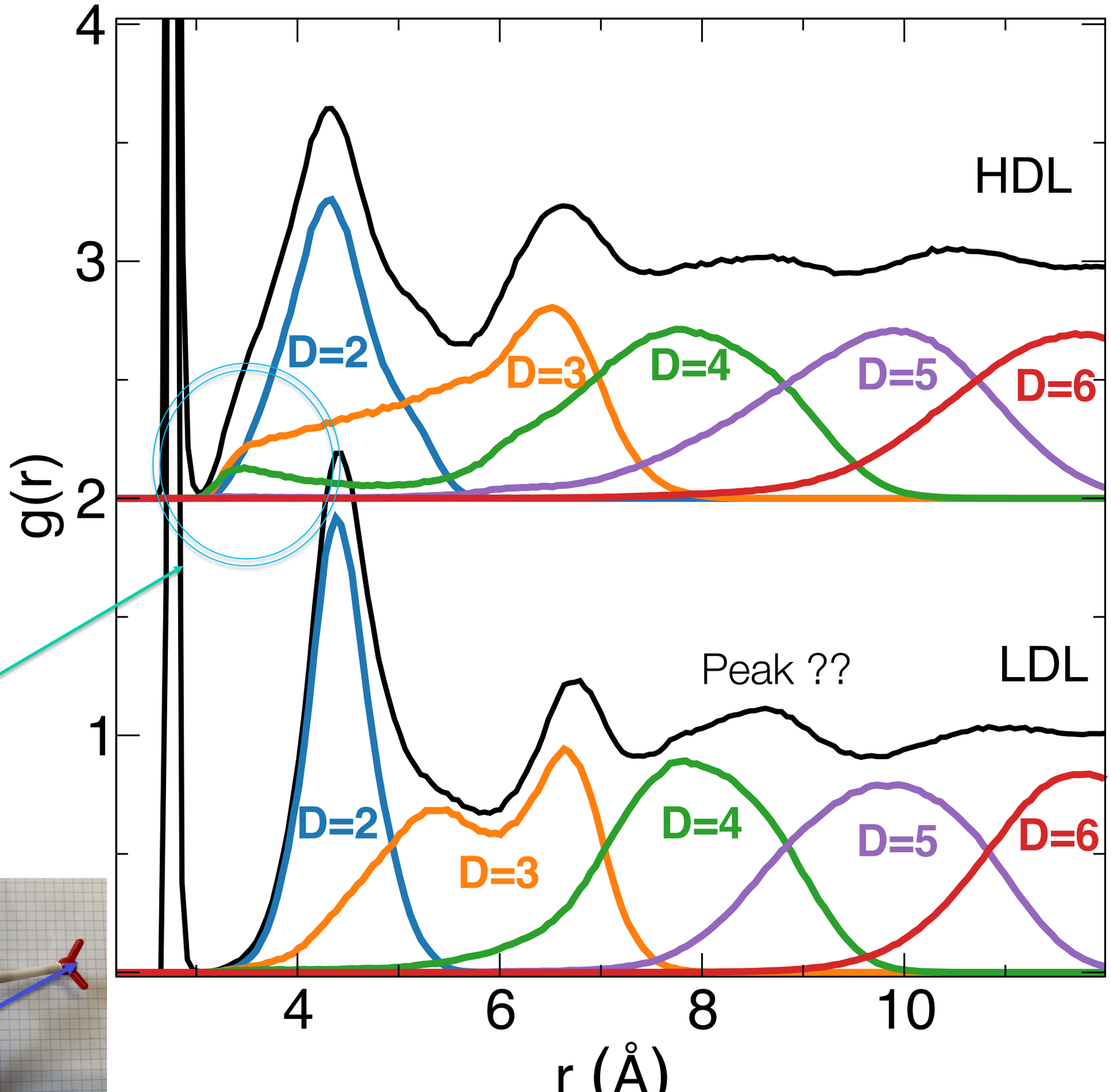
Riccardo Foffi, John Russo, and Francesco Sciortino

From LDL to HDL (coexisting liquids)

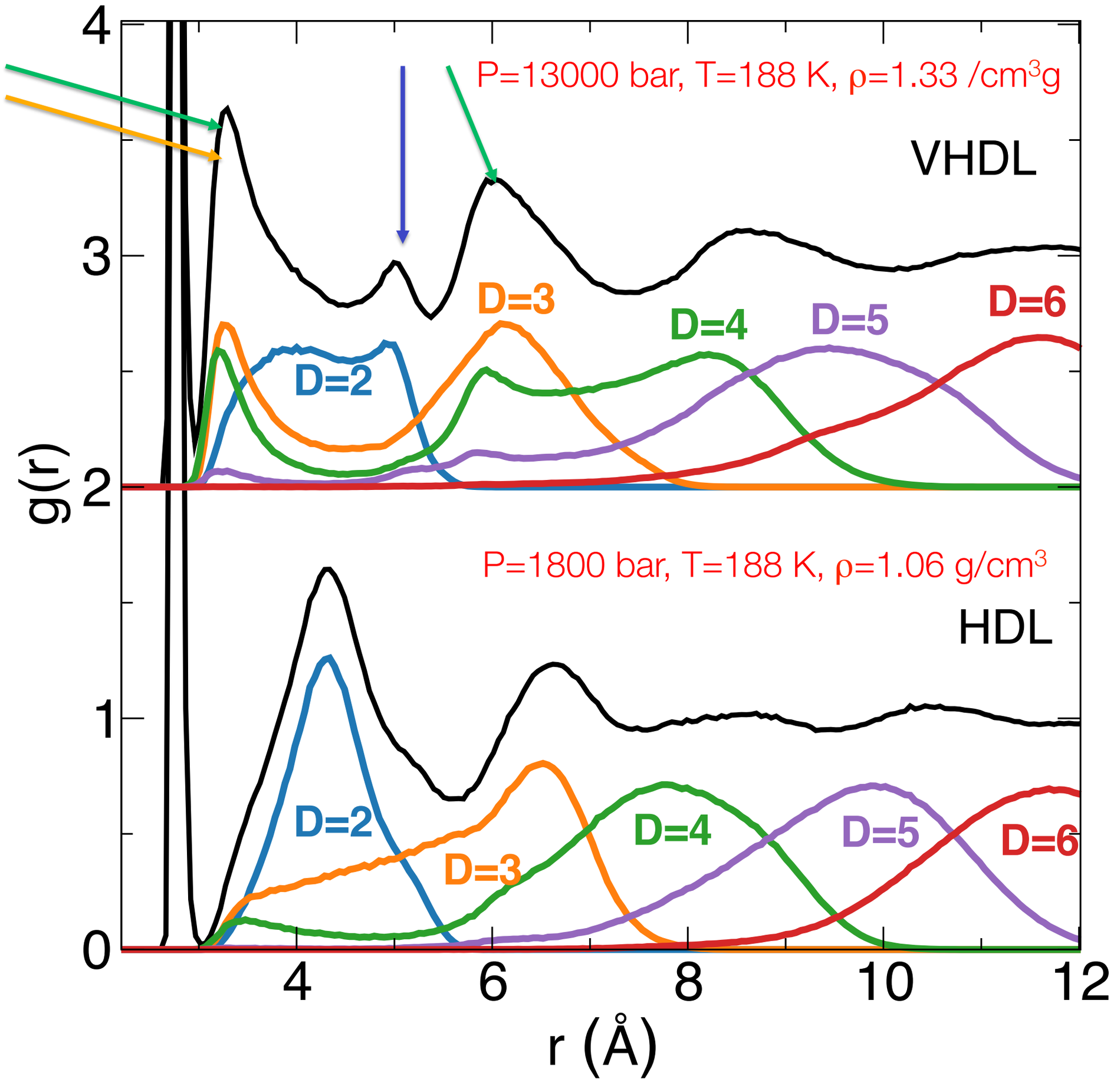
Molecules far in # of bonds but close in space !

Possible order parameter





From HDL to VHDL

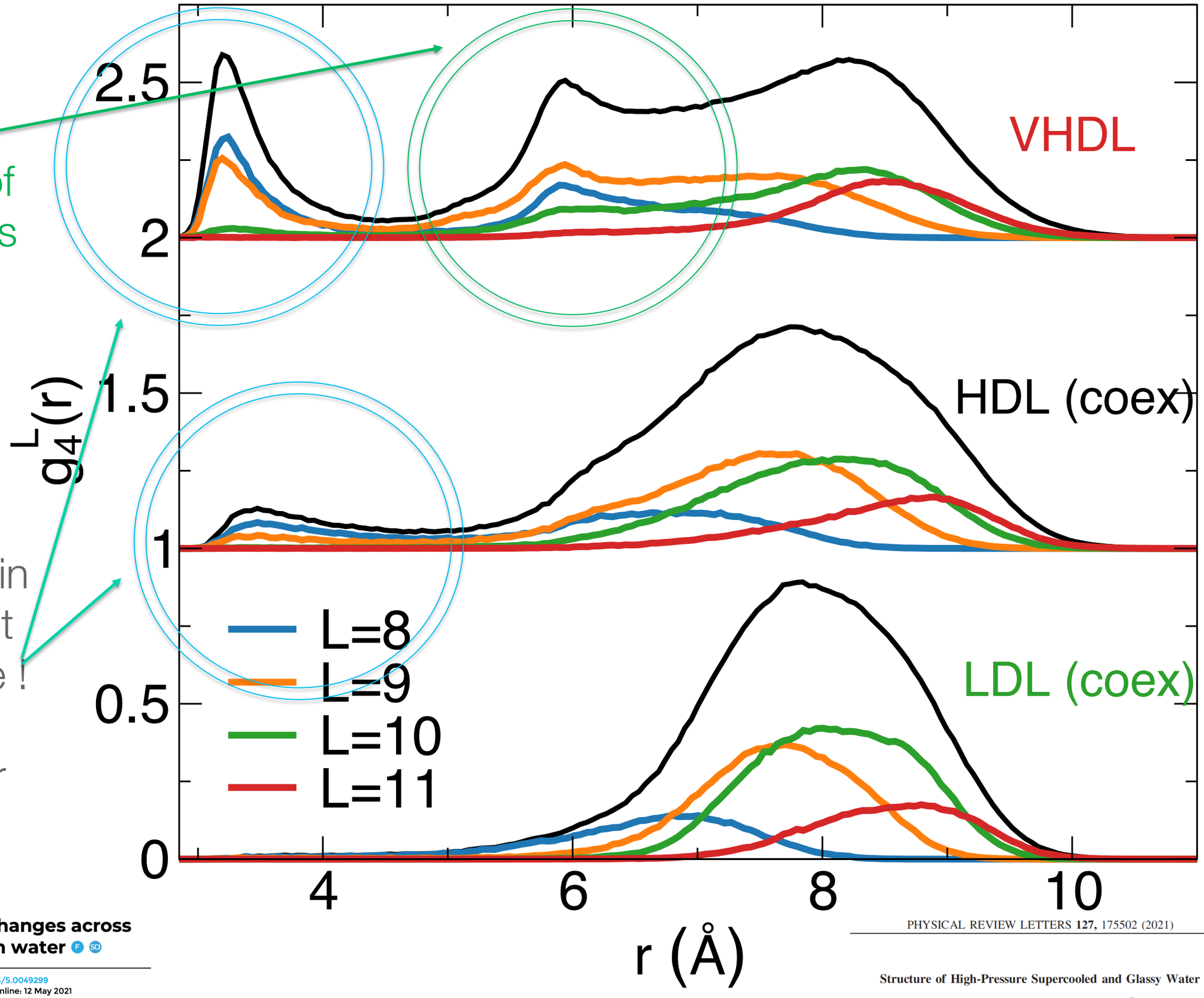


Chemical distance D=4

R=6 A
Specific
geometry of
dense states

Molecules far in
# of bonds but
close in space !

Possible order
parameter



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

Cite as: J. Chem. Phys. **154**, 184506 (2021); https://doi.org/10.1063/5.0049299
Submitted: 03 March 2021 . Accepted: 20 April 2021 . Published Online: 12 May 2021

Riccardo Foffi, John Russo, and Francesco Sciortino

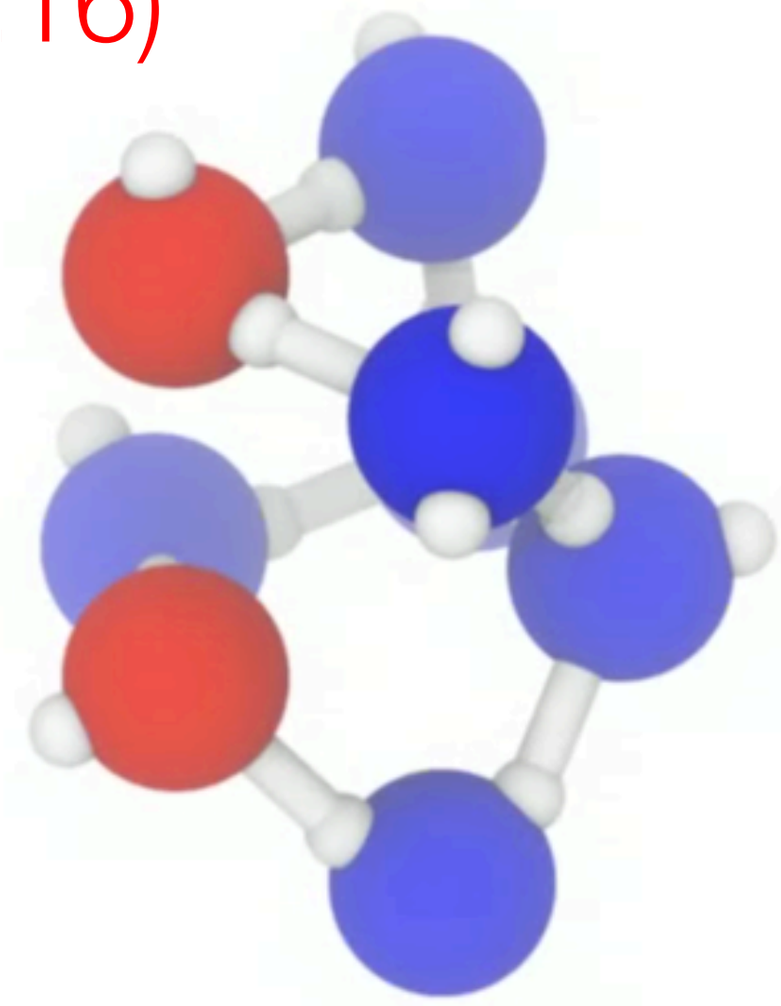
PHYSICAL REVIEW LETTERS **127,** 175502 (2021)

Structure of High-Pressure Supercooled and Glassy Water

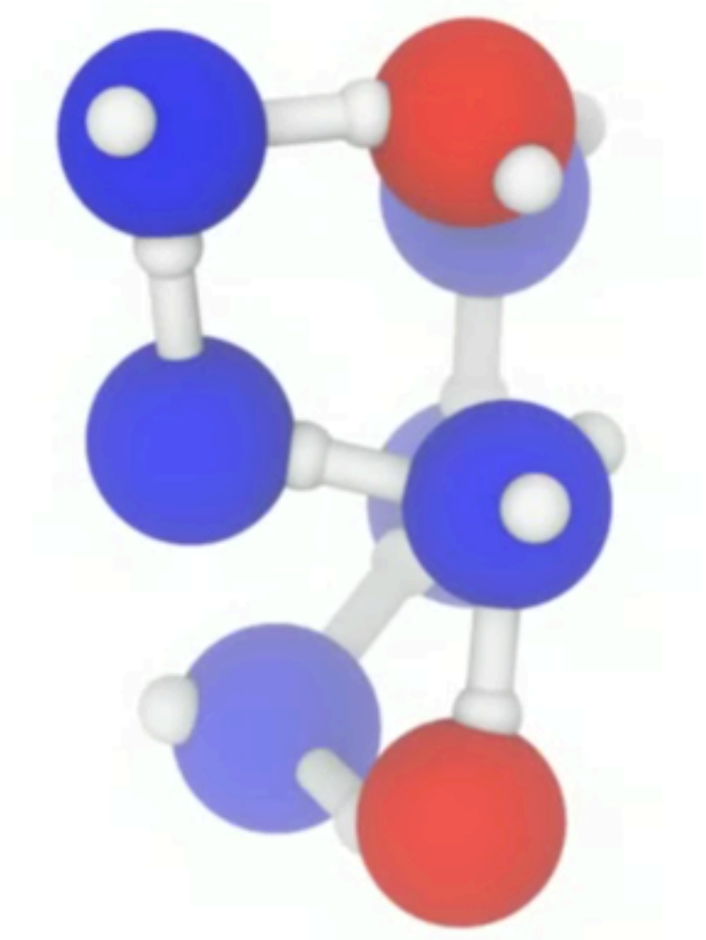
Riccardo Foffi and Francesco Sciortino*
Department of Physics, Sapienza Università di Roma, Piazzale Aldo Moro, 2, 00185 Rome, Italy

Characteristic geometries….

D=4
L=8
R=3.2 A
(σ_{LJ}=3.16)

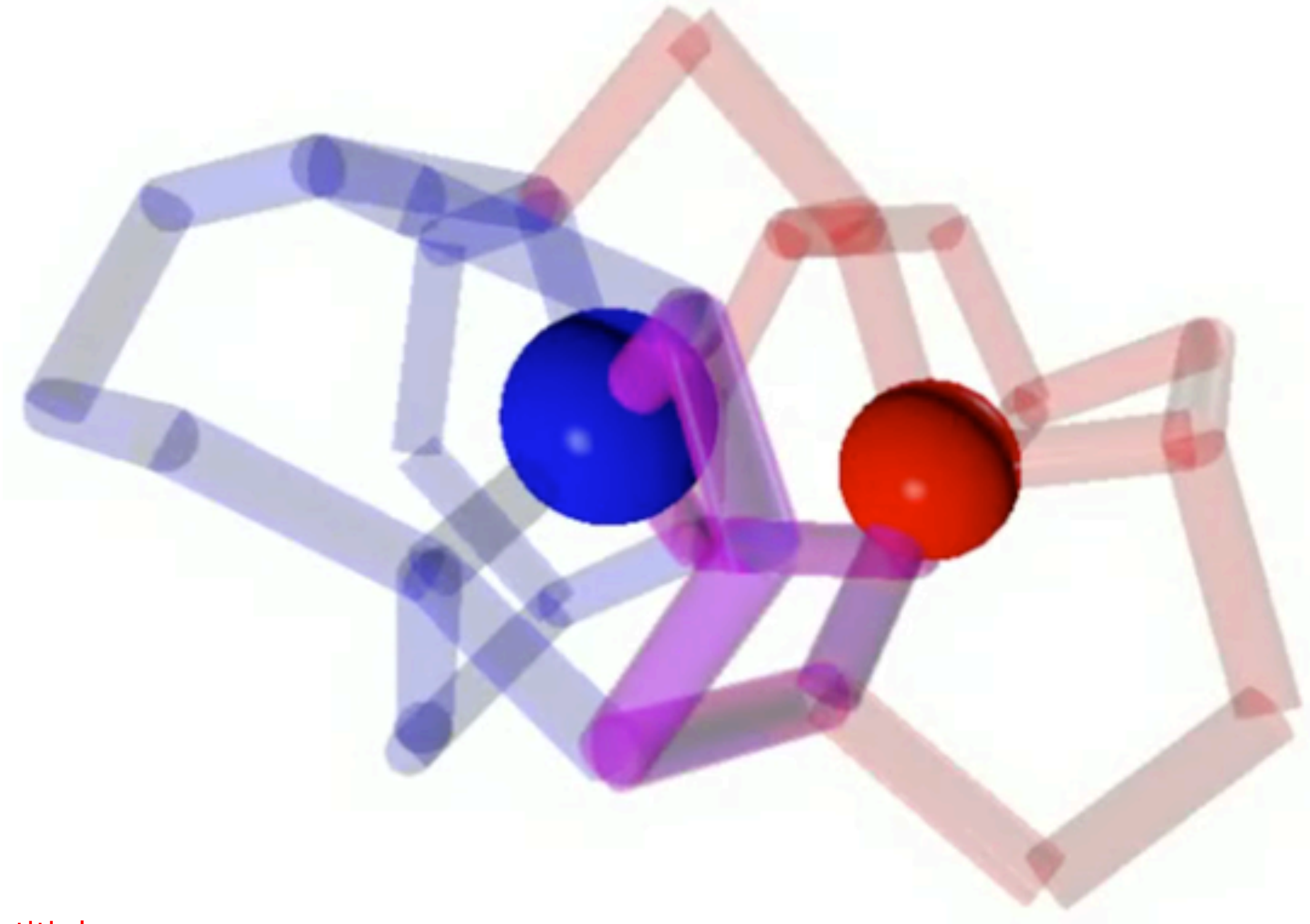


D=4
L=8
R=6 A



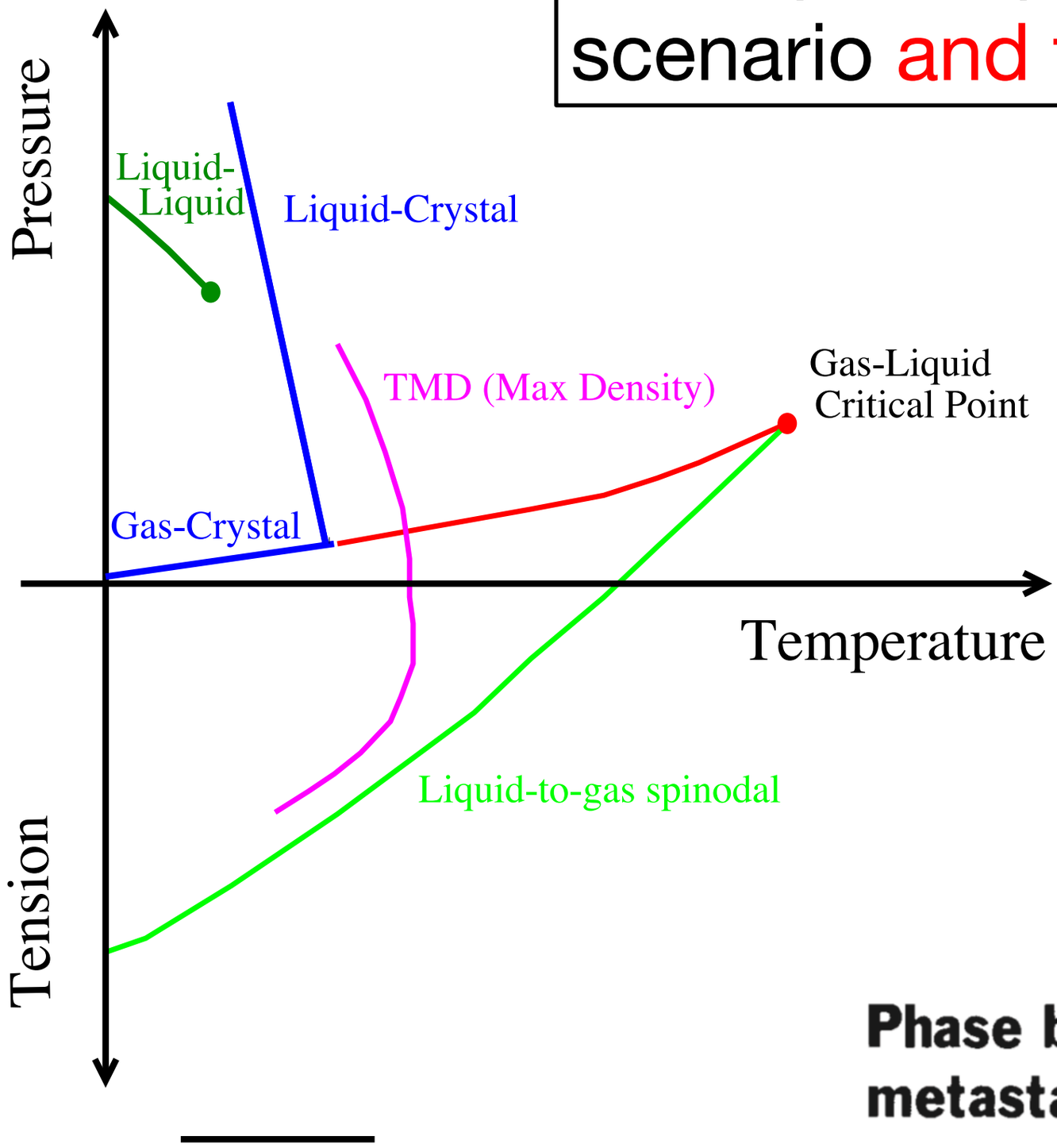
Interstitial molecules

A closer look at interstitial molecules



D=3
L=8
interstitial

The liquid-liquid critical point scenario and the anomalies



Phase behaviour of metastable water

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

NATURE · VOL 360 · 26 NOVEMBER 1992

A complex scenario of thermodynamic anomalies

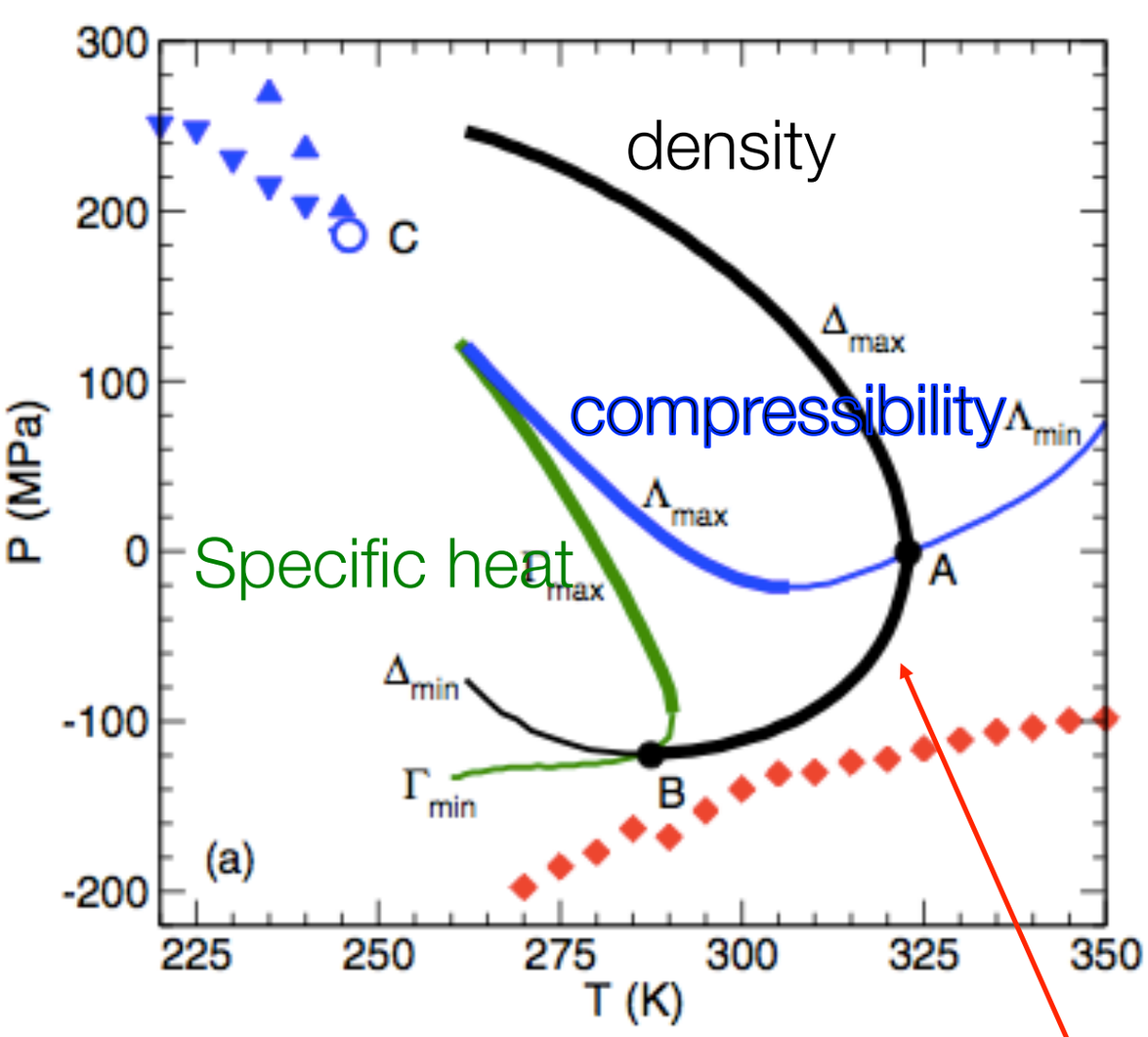
INSTITUTE OF PHYSICS PUBLISHING — JOURNAL OF PHYSICS: CONDENSED MATTER

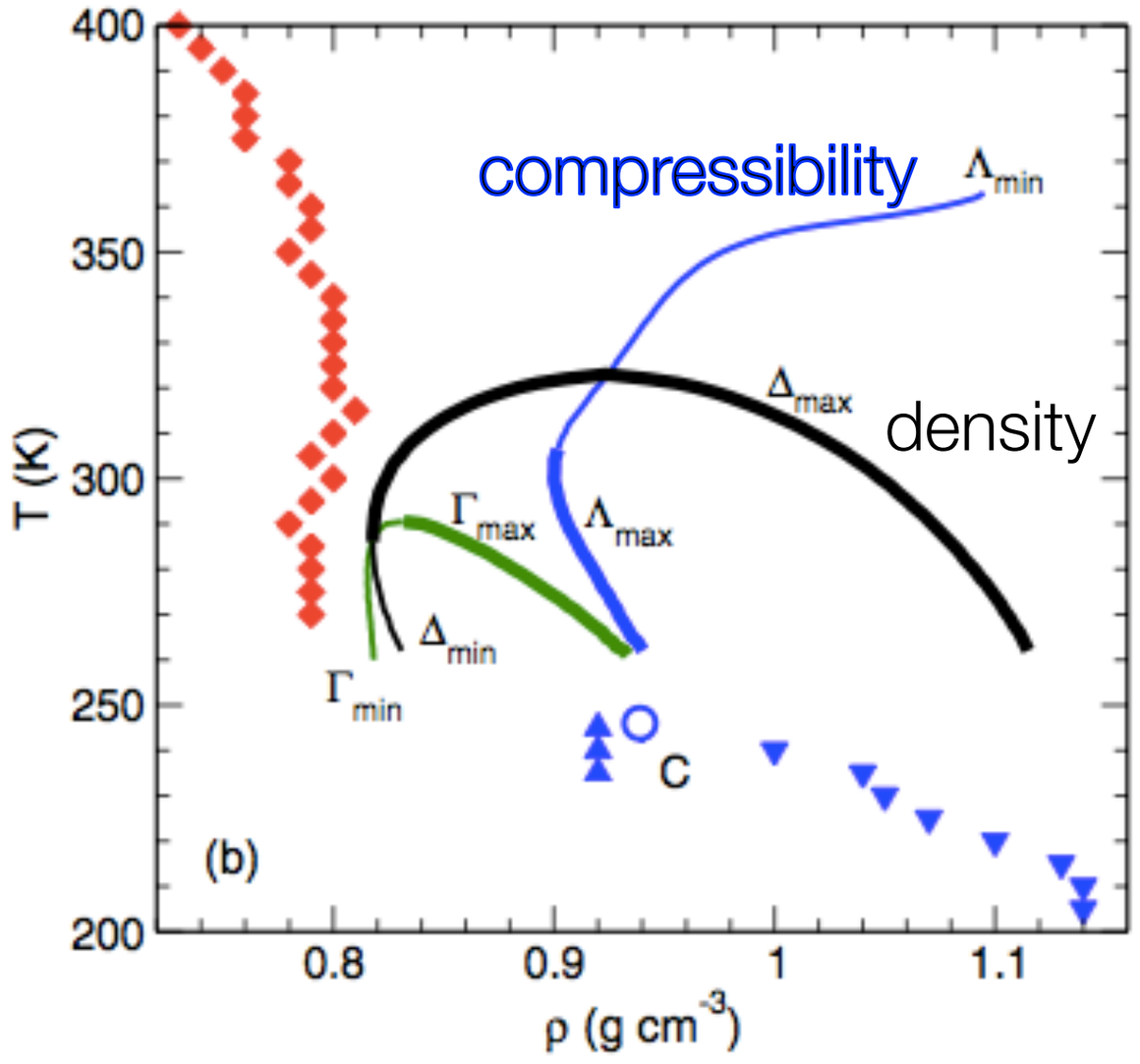
J. Phys.: Condens. Matter **17** (2005) L431–L437 — doi:10.1088/0953-8984/17/43/L01

LETTER TO THE EDITOR

Density minimum and liquid–liquid phase transition

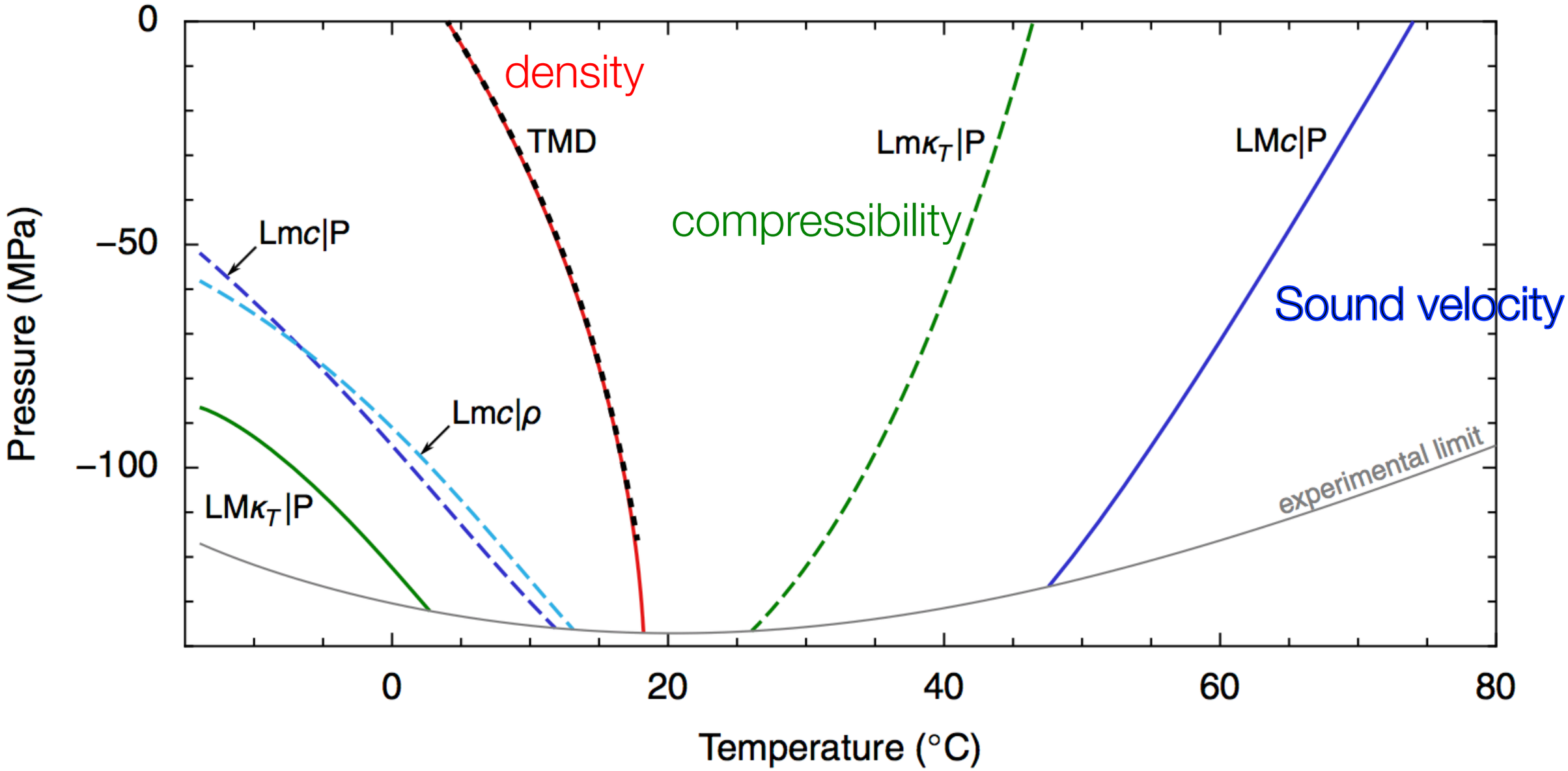
Peter H Poole[1], Ivan Saika-Voivod[2,3] and Francesco Sciortino[2]





TMD avoids collision with spinodal !

Experiments on stretched water. (Caupin)



Compressibility Anomalies in Stretched Water and Their Interplay with Density Anomalies

Vincent Holten†, Chen Qiu‡, Emmanuel Guillerm†, Max Wilke¶, Jaroslav Rička‡, Martin Frenz‡, and Frédéric Caupin*†

J. Phys. Chem. Lett., **2017**, *8* (22), pp 5519–5522

Measurements of K_T at ambient P

(also Cp .. see Ander's talk)

and older simulations

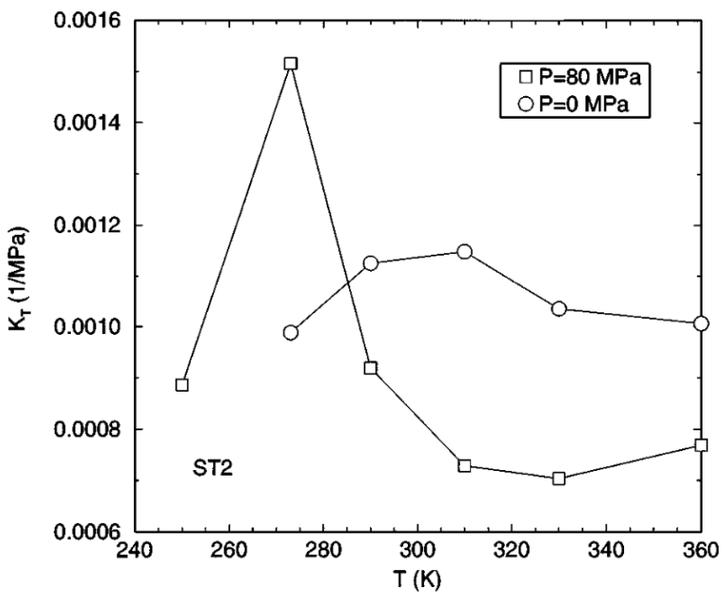


FIG. 5. Isobars of K_T as a function of T for $P=0$ MPa (○) and $P=80$ MPa (□). To construct these isobars, K_T was evaluated for each T at the given P from the splines shown in Fig. 3(a).

PHYSICAL REVIEW E VOLUME 55, NUMBER 1 JANUARY 1997

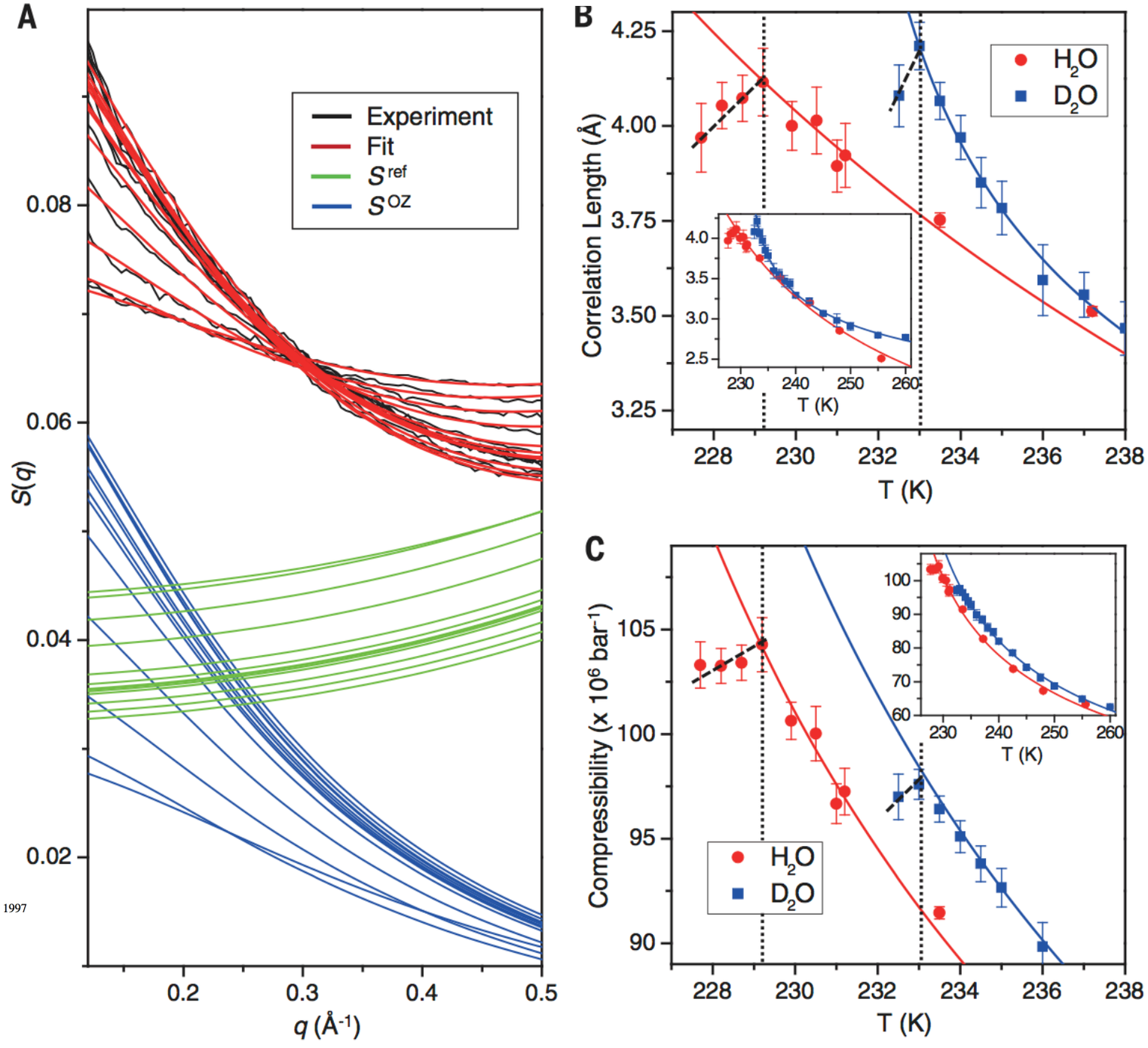
Line of compressibility maxima in the phase diagram of supercooled water

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

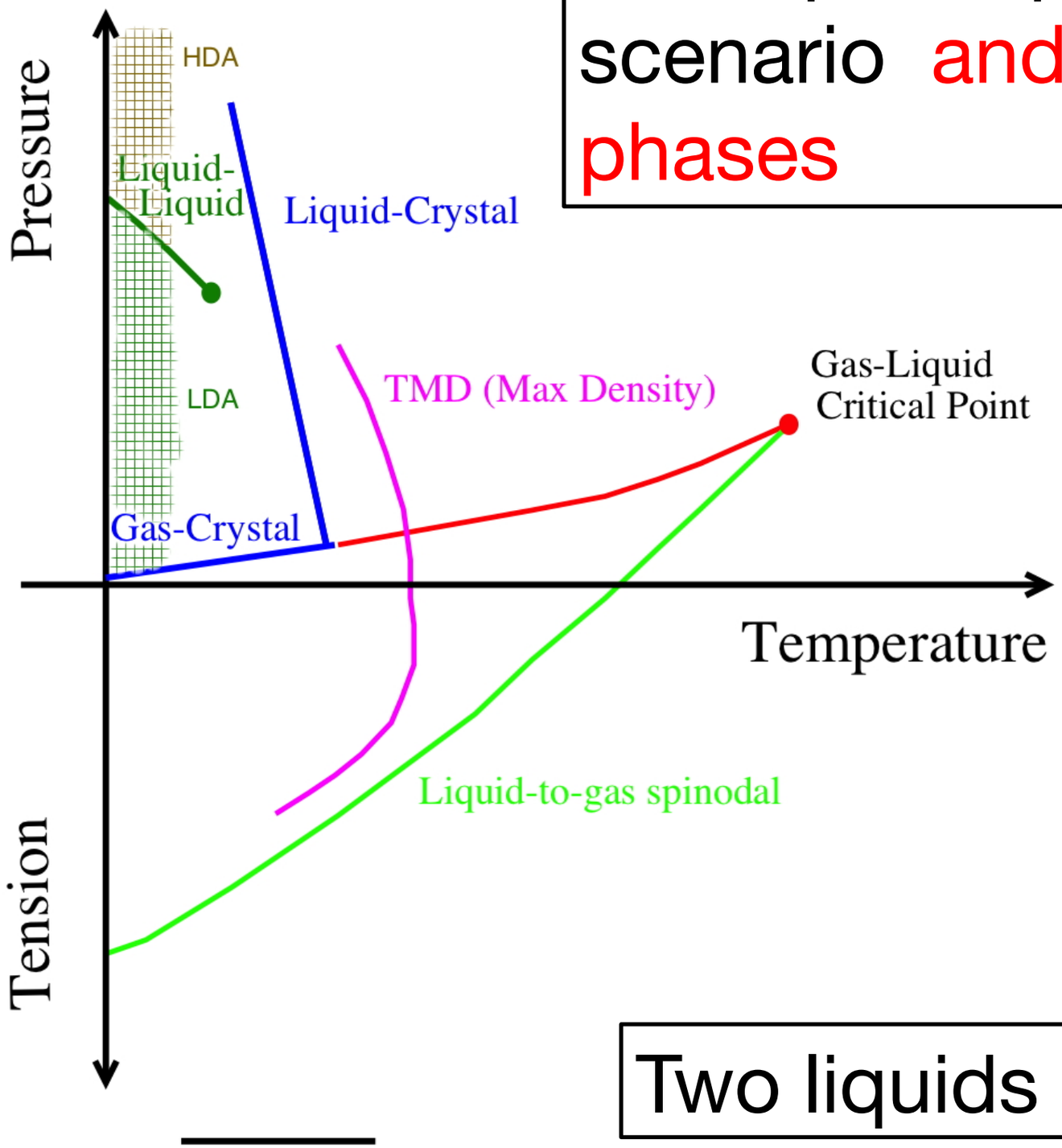
WATER THERMODYNAMICS

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]†

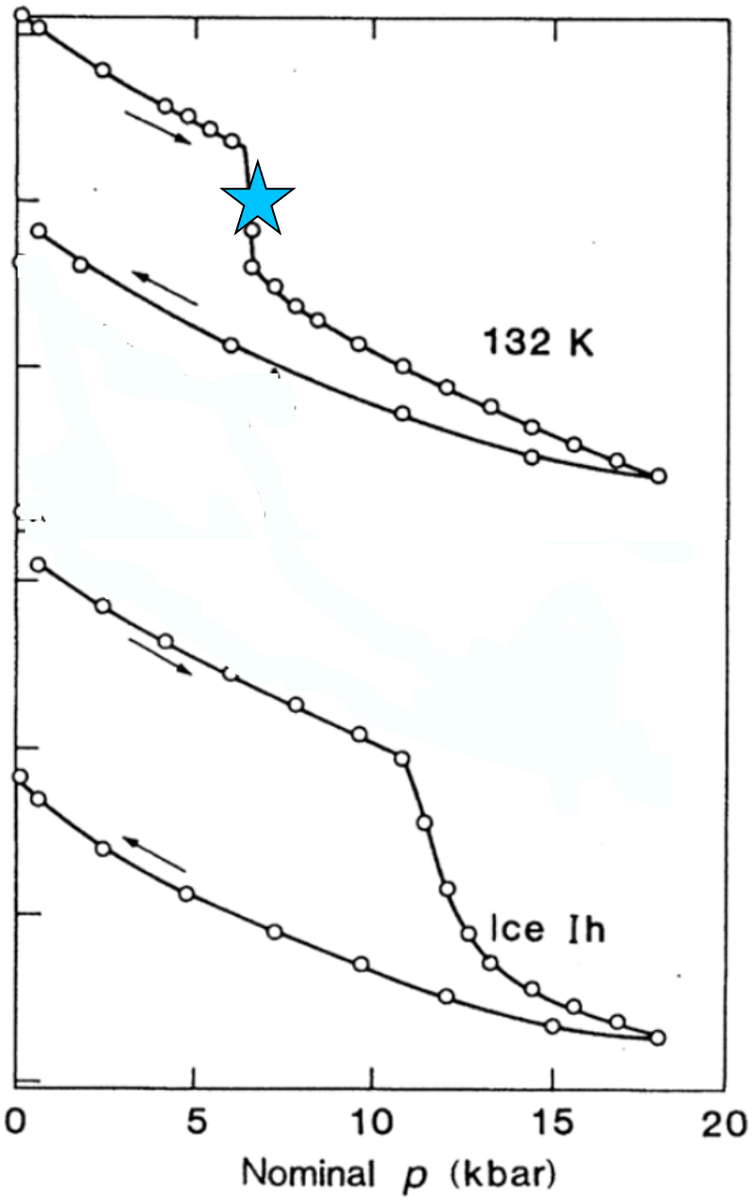


The liquid-liquid critical point scenario and the amorphous phases



Two liquids → Two glasses

Two amorphous states (LDA,HDA) in water



'Melting ice' I at 77 K and 10 kbar: a new method of making amorphous solids

O. Mishima, L. D. Calvert & E. Whalley

Nature **310**, 393–395 (1984) | Cite this article

THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

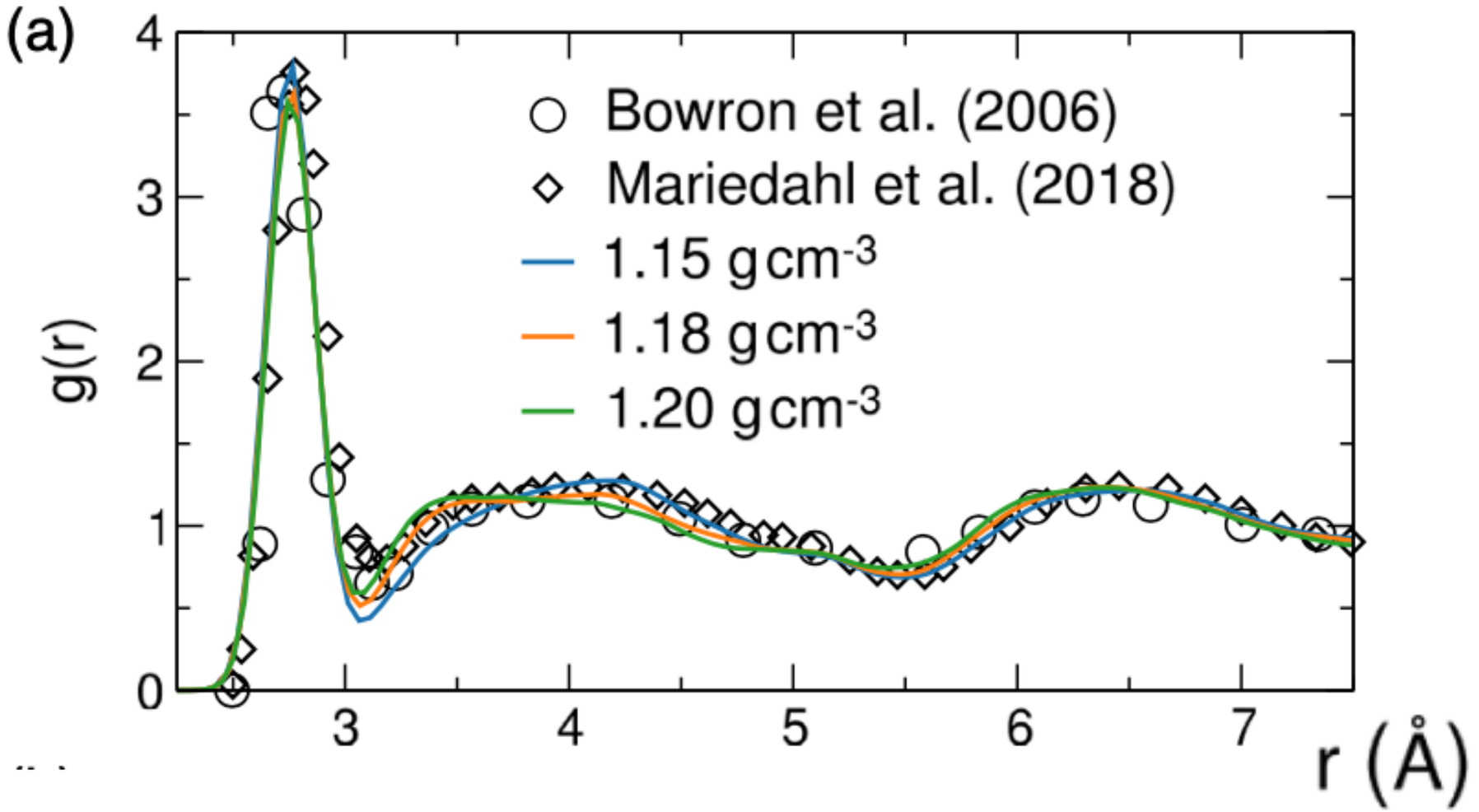
pubs.acs.org/JPCB

Equilibrated High-Density Amorphous Ice and Its First-Order Transition to the Low-Density Form

Katrin Winkel,[*,†,‡] Erwin Mayer,[†,§] and Thomas Loerting[‡]

[†]Institute of General, Inorganic and Theoretical Chemistry and [‡]Institute of Physical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

A comparison between a simulated "quenched" HDL and experimental HDA



PHYSICAL REVIEW LETTERS **127,** 175502 (2021)

Structure of High-Pressure Supercooled and Glassy Water

Riccardo Foffi and Francesco Sciortino*
Department of Physics, Sapienza Università di Roma, Piazzale Aldo Moro, 2, 00185 Rome, Italy

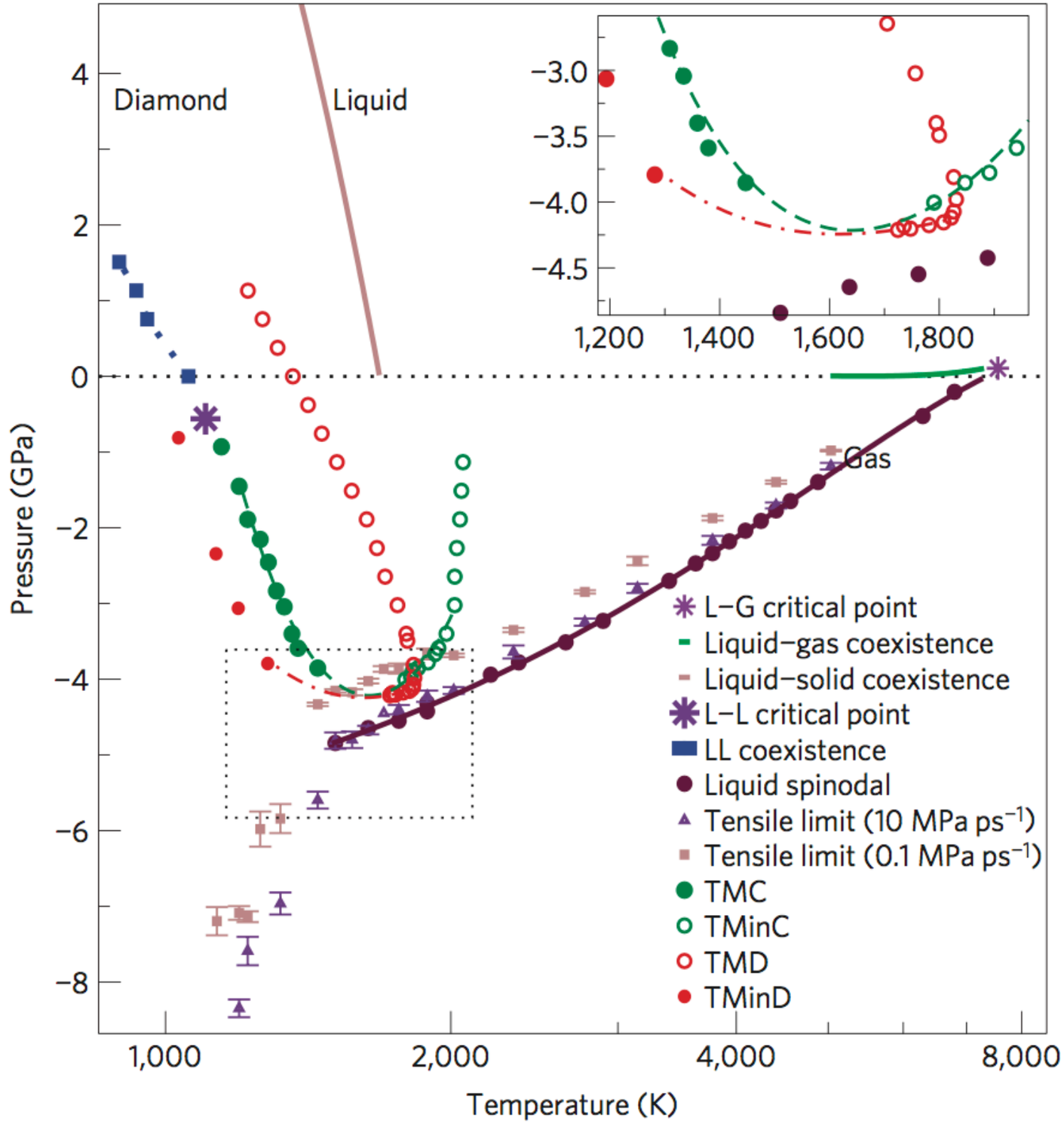
How general is the LL phenomenon ?

Simulations:

Water
Silicon
Carbon dioxide
Carbon
Hydrogen
Nitrogen

Experiments:

Water
Triphenill phosphite
Phosphorous
Sulfur
Tin
Tellurium



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

Liquid–liquid transition and critical point in sulfur

https://doi.org/10.1038/s41586-020-2593-1
Received: 24 April 2019

Laura Henry[1], Mohamed Mezouar[1✉], Gaston Garbarino[1], David Sifre[1], Gunnar Weck[2] & Frédéric Datchi[2]

S_8-polymer

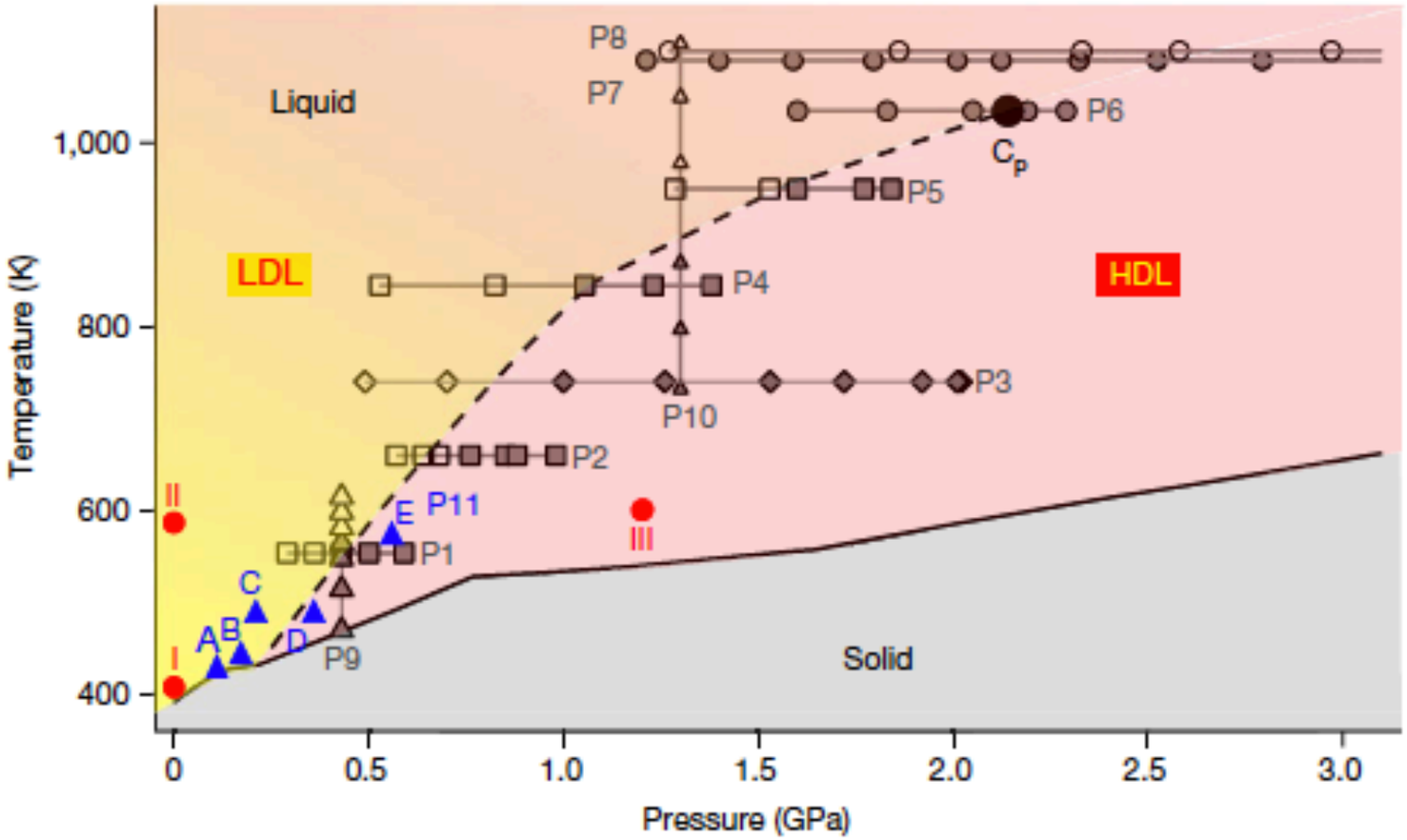
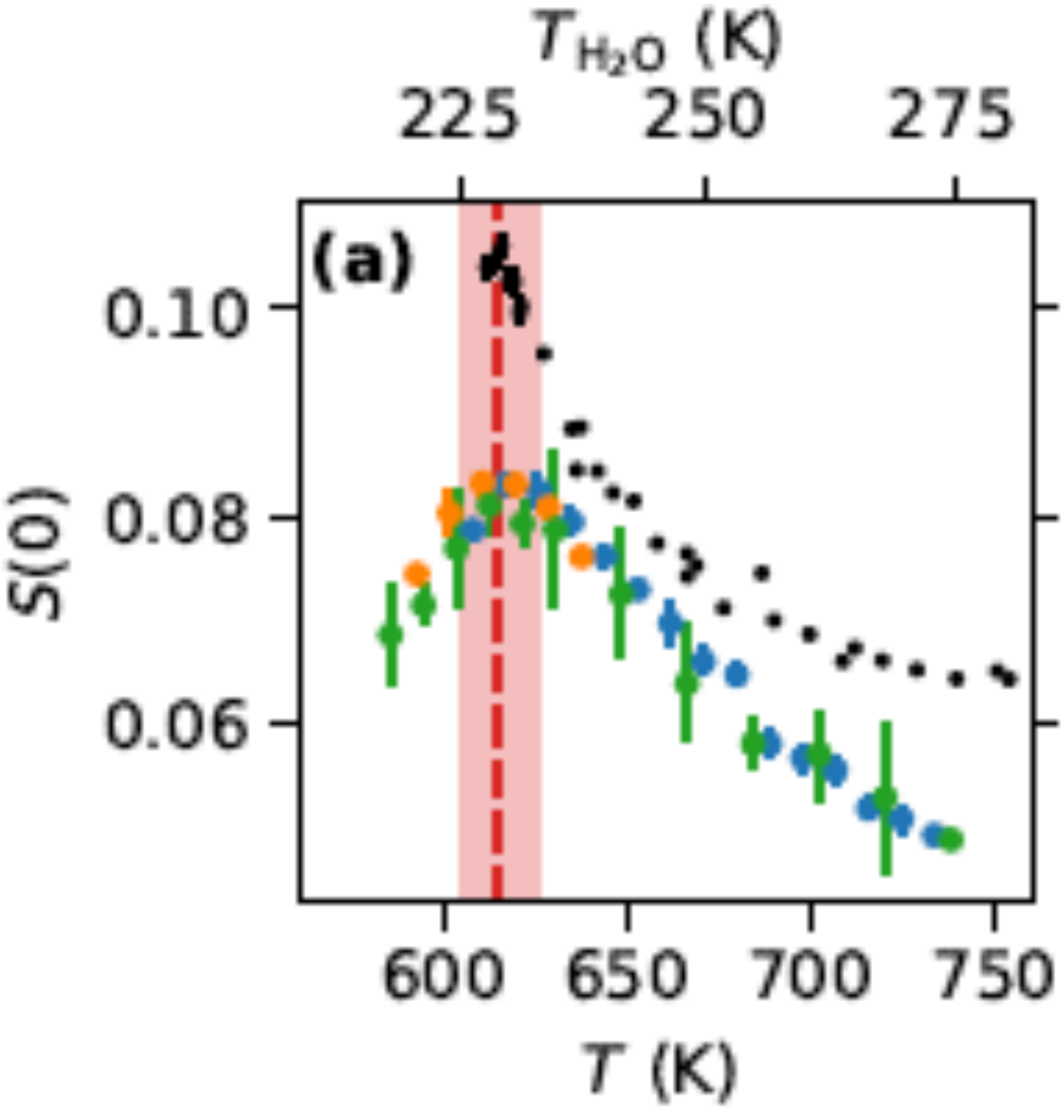
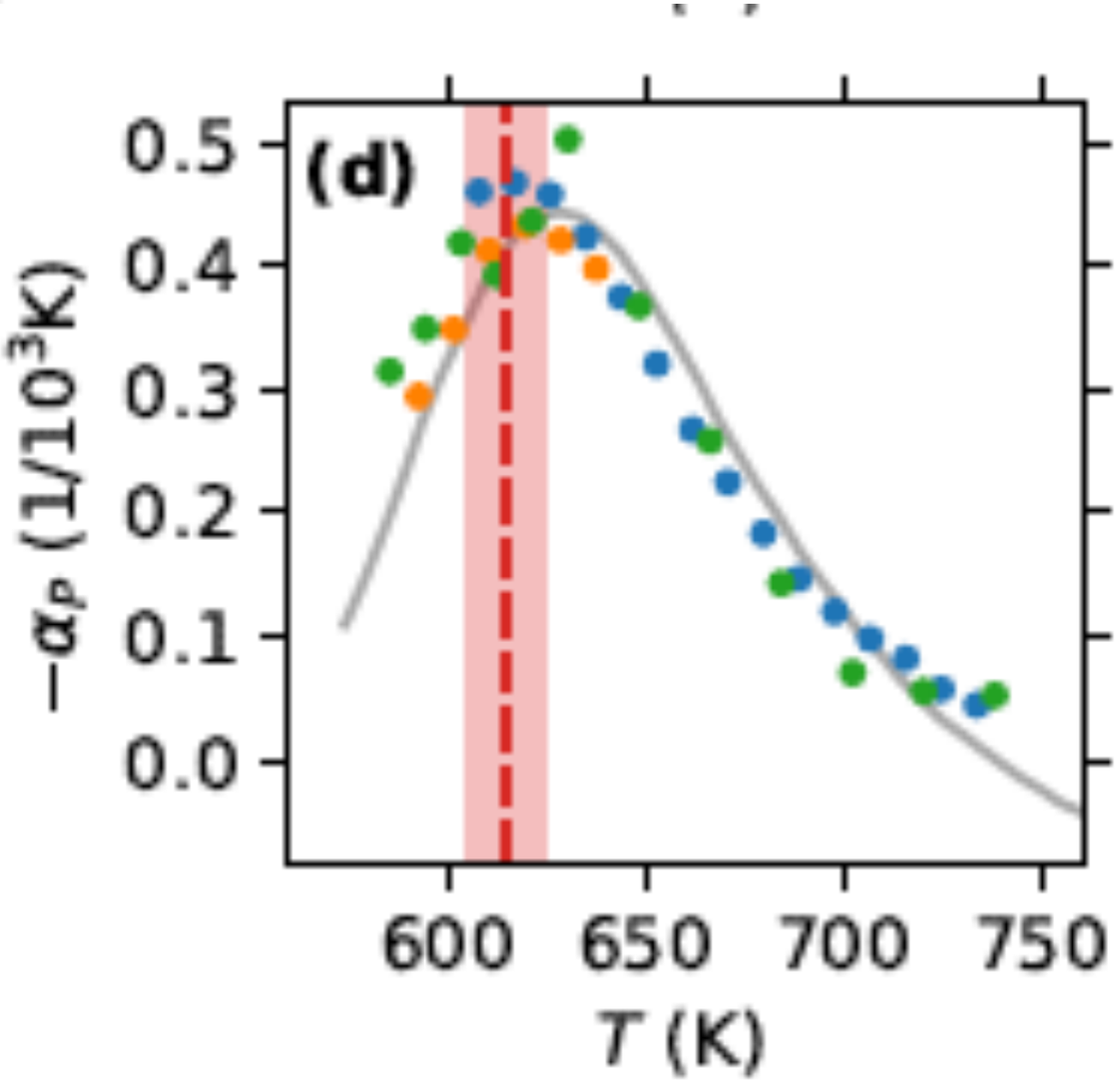


Fig. 1 | Phase diagram of sulfur around the LLT. P1–P8: isothermal pathways followed during the density measurements presented in Fig. 2. P1, P2, P4–P7 were made on compression, whereas P3 (diamonds) and P7 (open black circles) were made on decompression. For clarity, P7 and P8 are shown up to 3 GPa only. P9 and P10 are isobaric pathways followed during the density measurements presented in Supplementary Fig. 9 (Supplementary Information section S1). A, B, C, D and E (blue filled triangles) along path P11 indicate the *P*, *T* conditions of the selected X-ray diffraction data in Fig. 3. I, II and III are the (*P*, *T*) points of the Raman spectra presented in Fig. 3. The black dashed line is the transition line between the LDL domain (yellow) and the HDL domain (pink) that terminates at the critical point C_p (black solid circle).

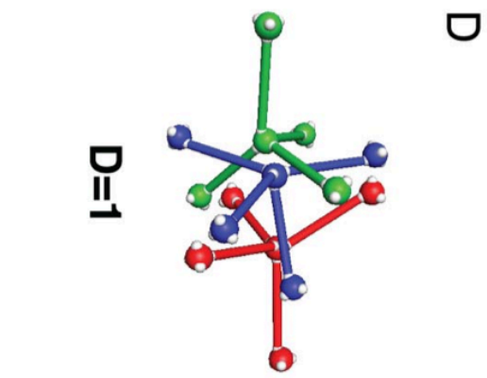
Structural changes across thermodynamic maxima in supercooled liquid tellurium: a water-like scenario?

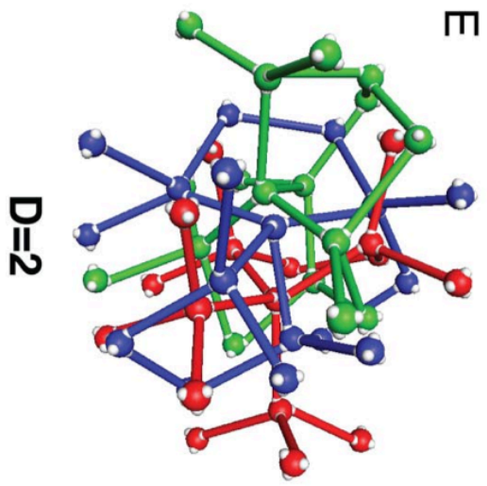
Peihao Sun,[1,2,*] Giulio Monaco,[2] Peter Zalden,[3] Klaus Sokolowski-Tinten,[4] Jerzy Antonowicz,[5] Ryszard Sobierajski,[6] Yukio Kajihara,[7] Alfred Q. R. Baron,[8] Paul Fuoss,[1] Andrew Chihpin Chuang,[9] Jun-Sang Park,[9] Jonathan Almer,[9] and J. B. Hastings[1,†]

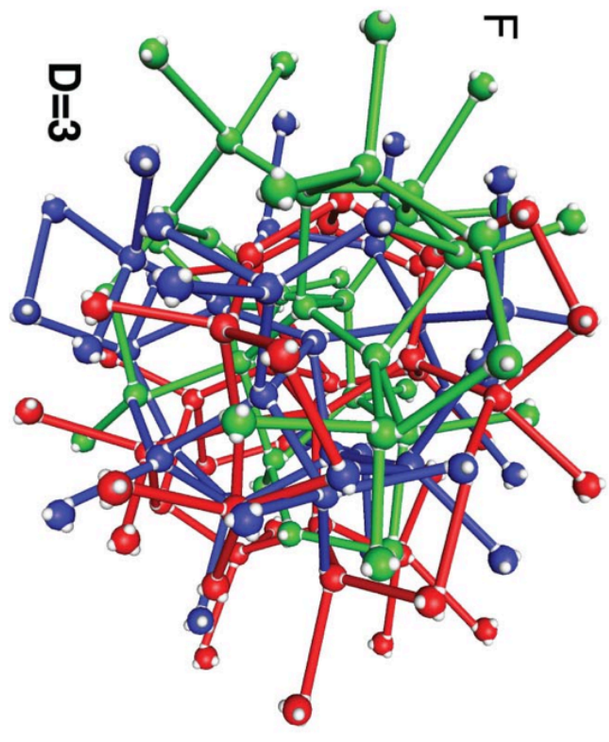




Others…. rigid tetrahedral particles (interpenetration at work)



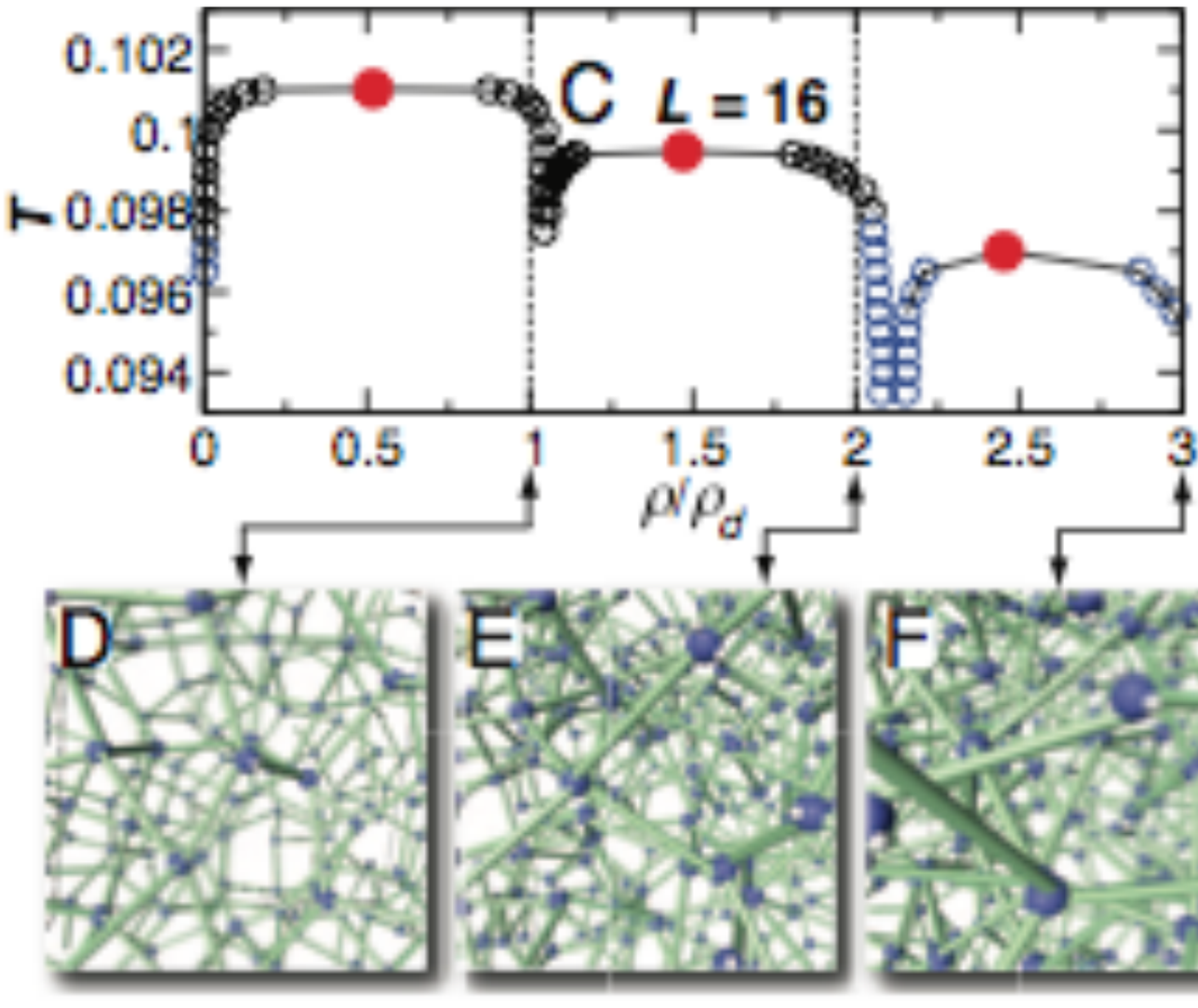




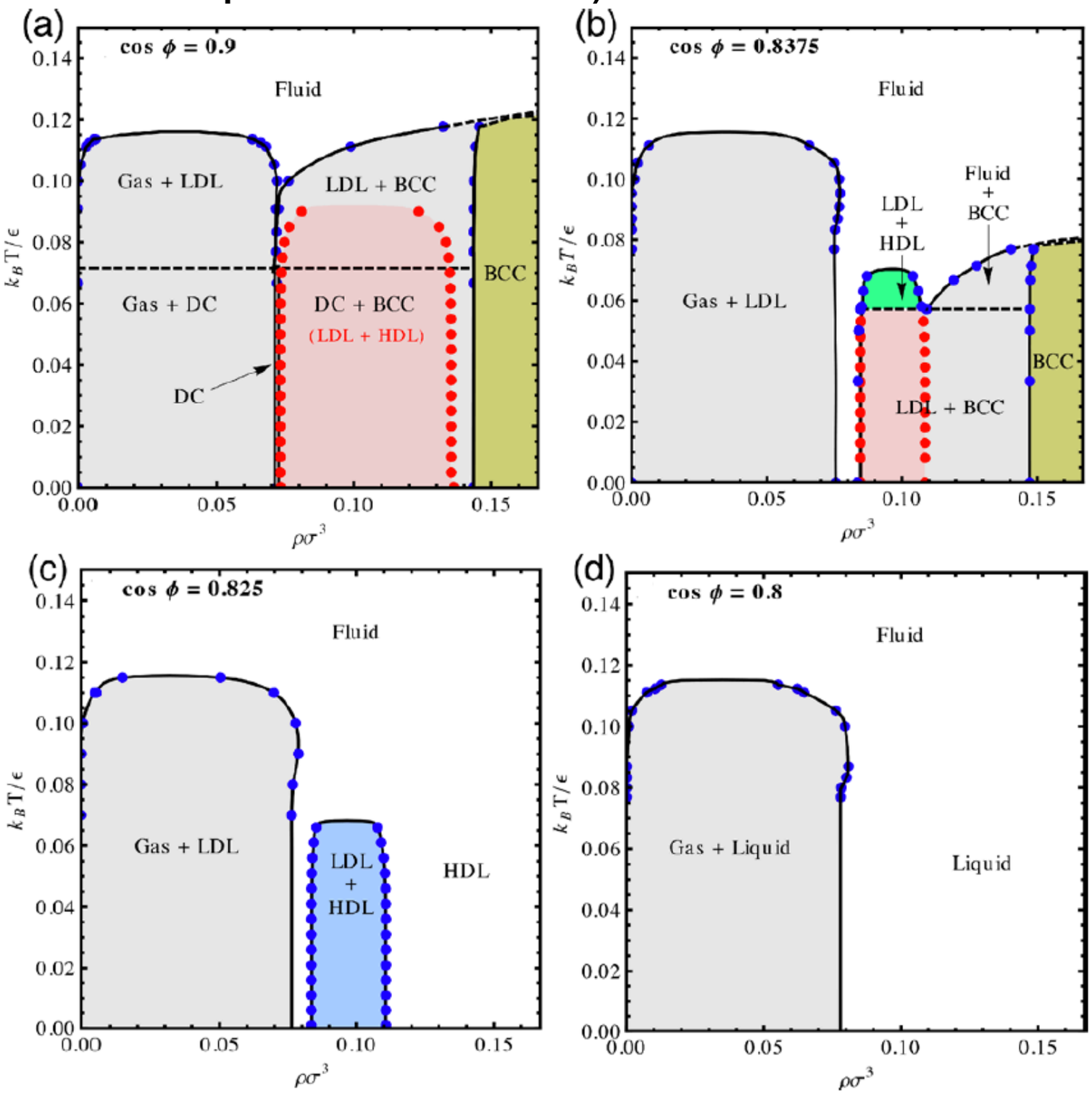
Hierarchies of networked phases induced by multiple liquid–liquid critical points

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



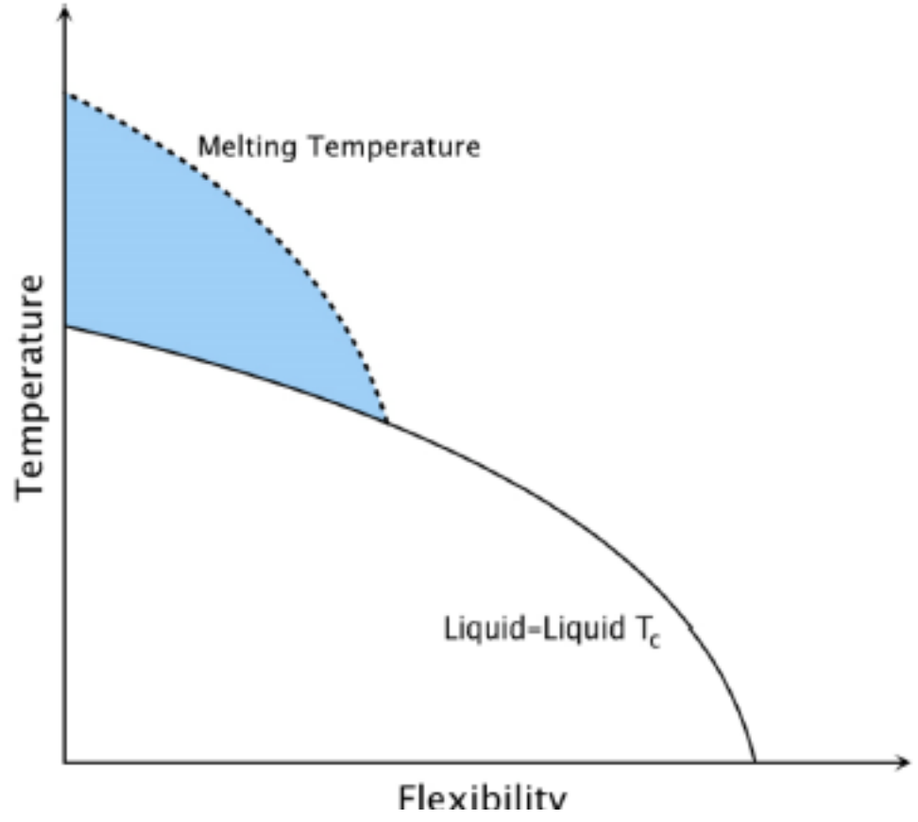
Can we create a colloidal water ? (directional interactions – softness-interpenetration)



nature physics
LETTERS
PUBLISHED ONLINE: 27 JULY 2014 | DOI: 10.1038/NPHYS3030

Erasing no-man's land by thermodynamically stabilizing the liquid–liquid transition in tetrahedral particles

Frank Smallenburg[1]*, Laura Filion[2] and Francesco Sciortino[1,3]



Getting closer to the real colloidal world

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

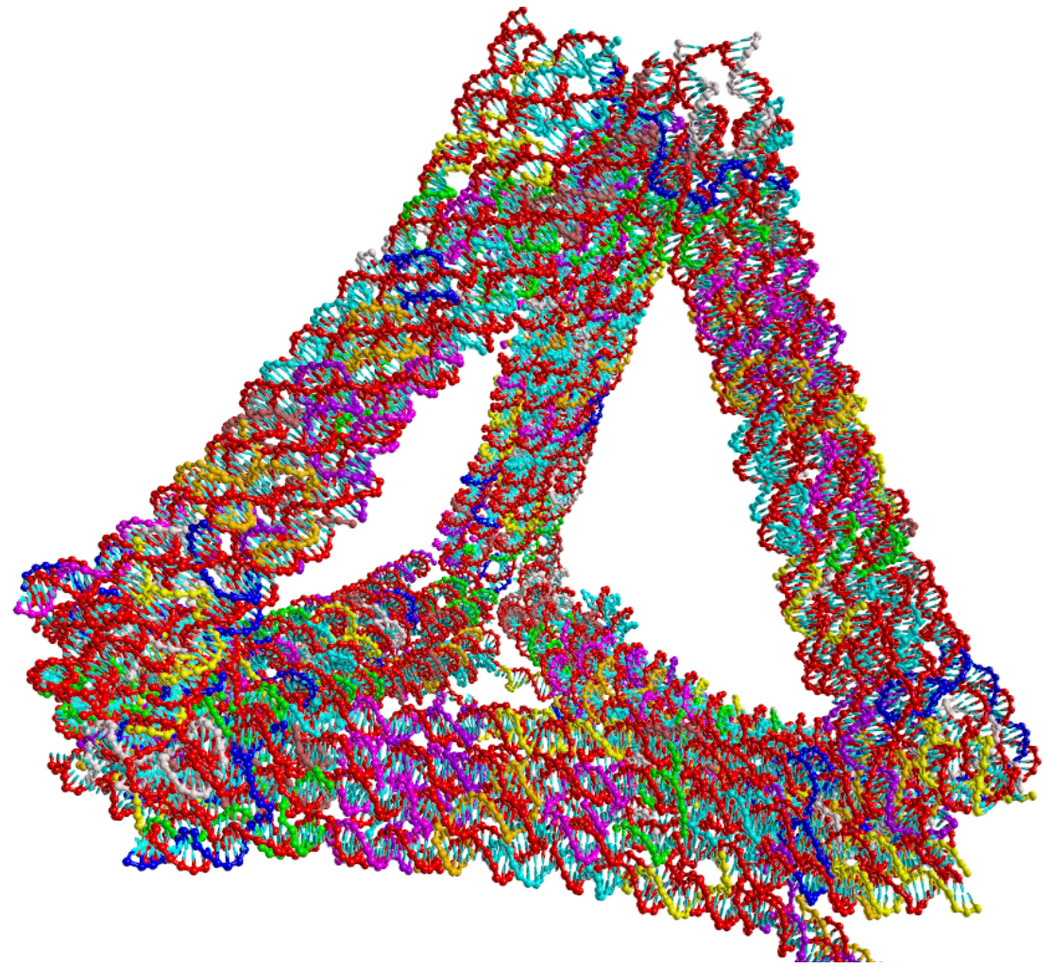
THE EUROPEAN PHYSICAL JOURNAL E

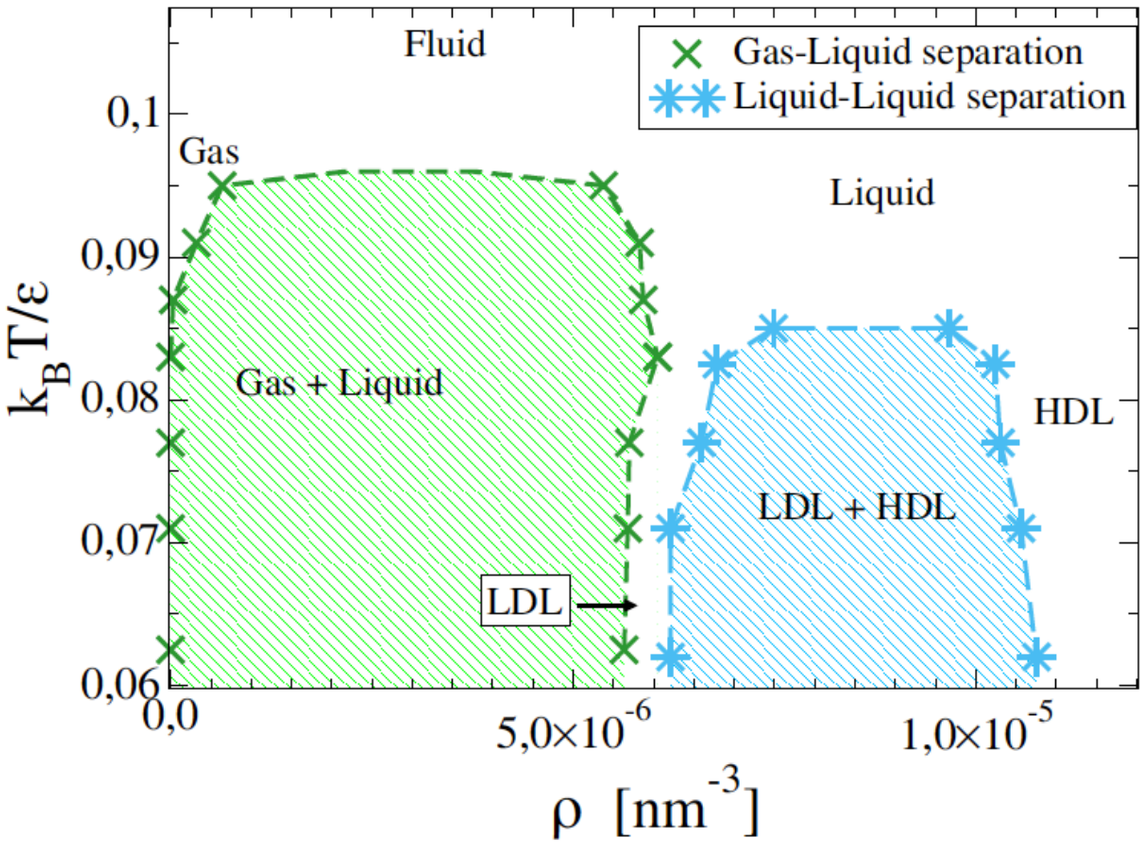
Regular Article

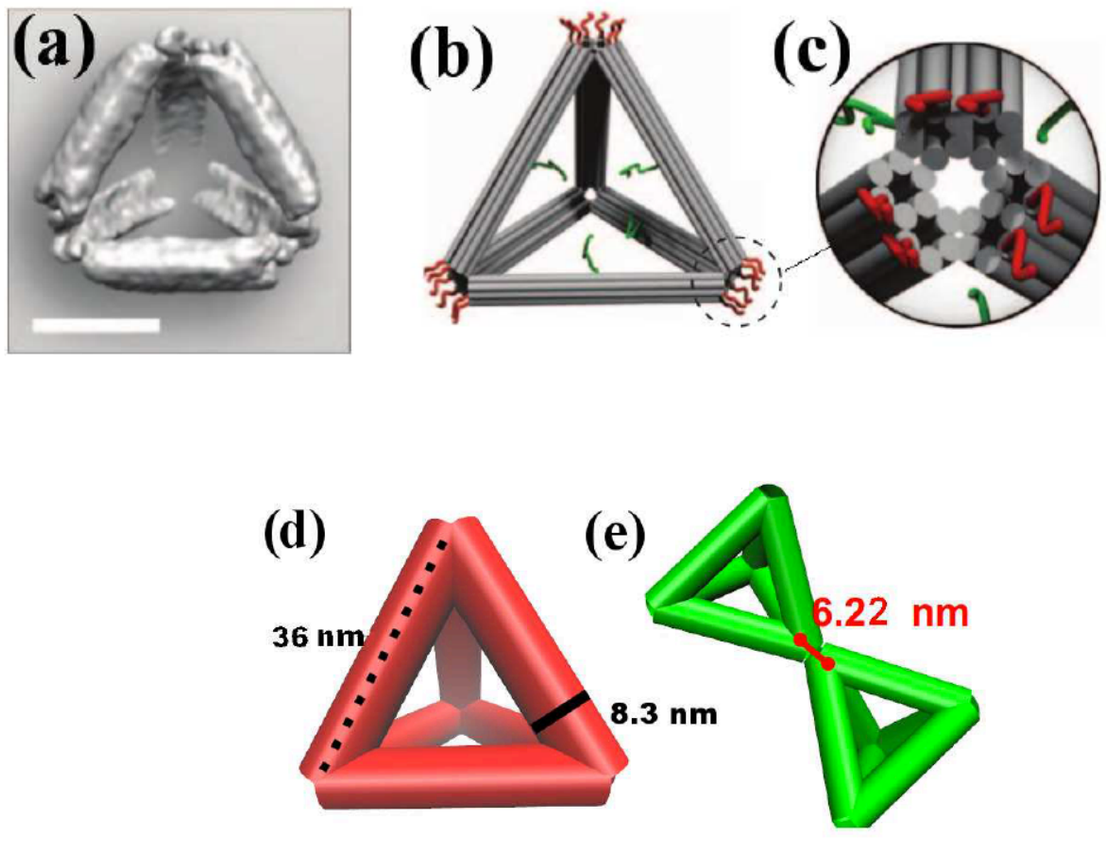
Toward the observation of a liquid-liquid phase transition in patchy origami tetrahedra: a numerical study

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

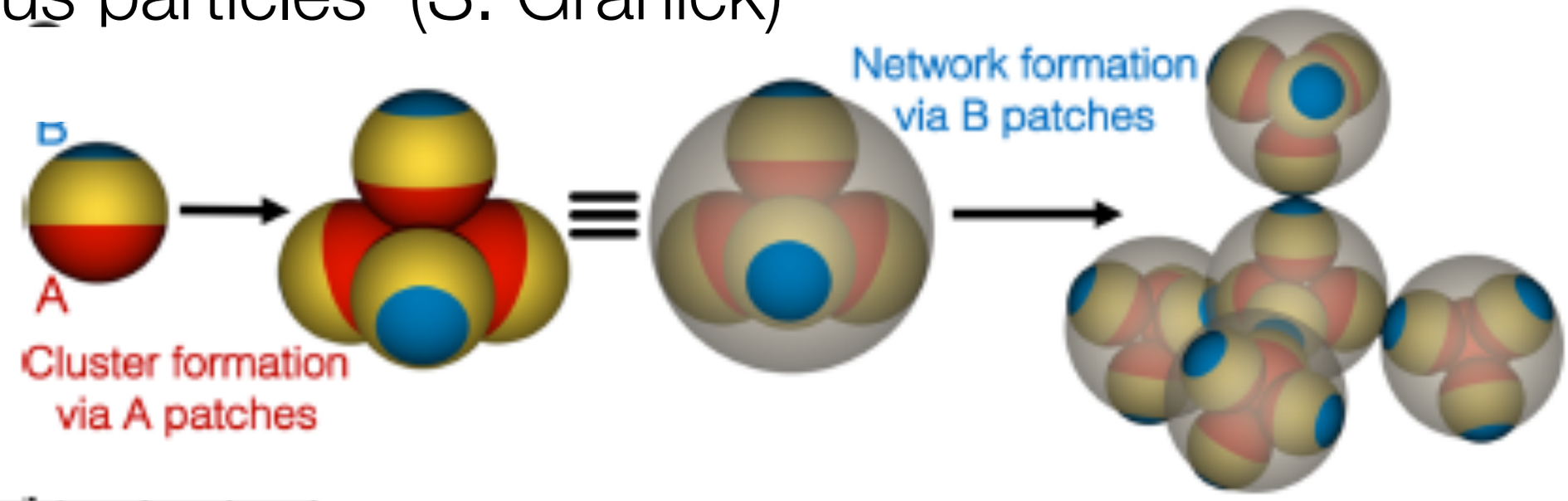
Eur. Phys. J. E (2016) **39**: 131

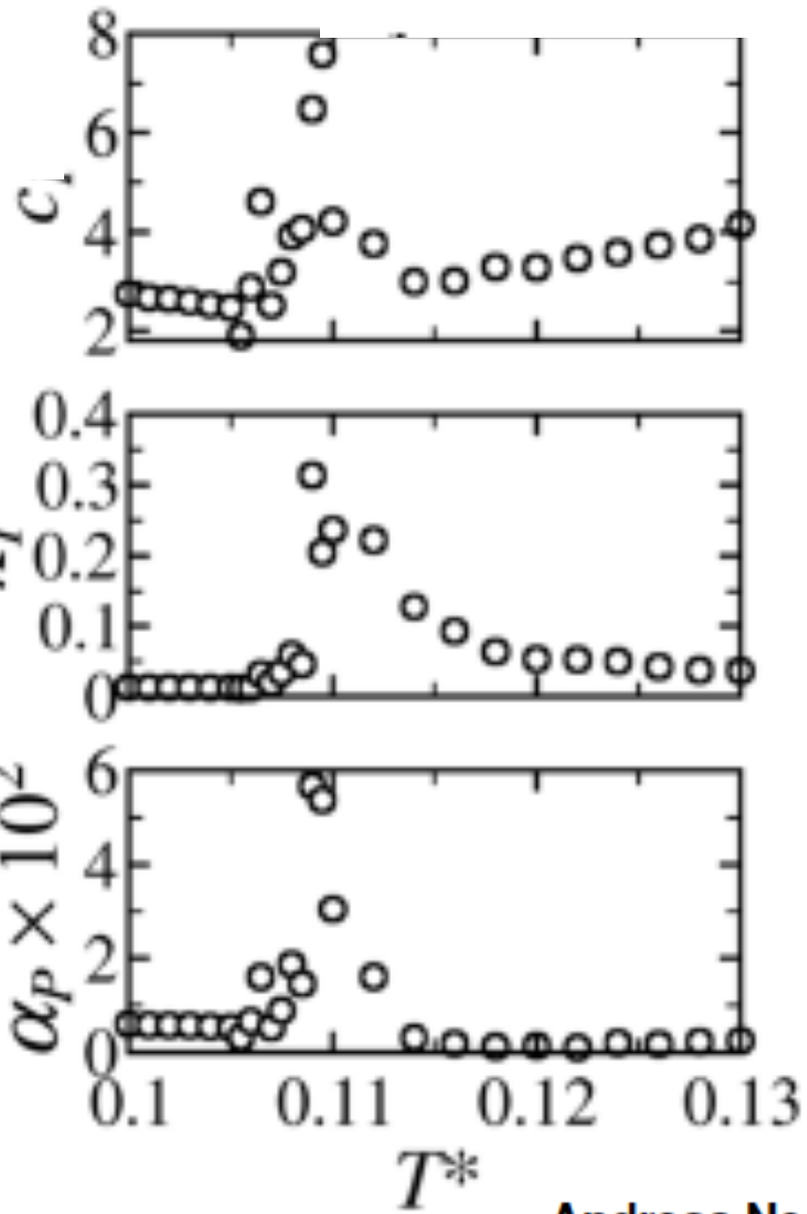


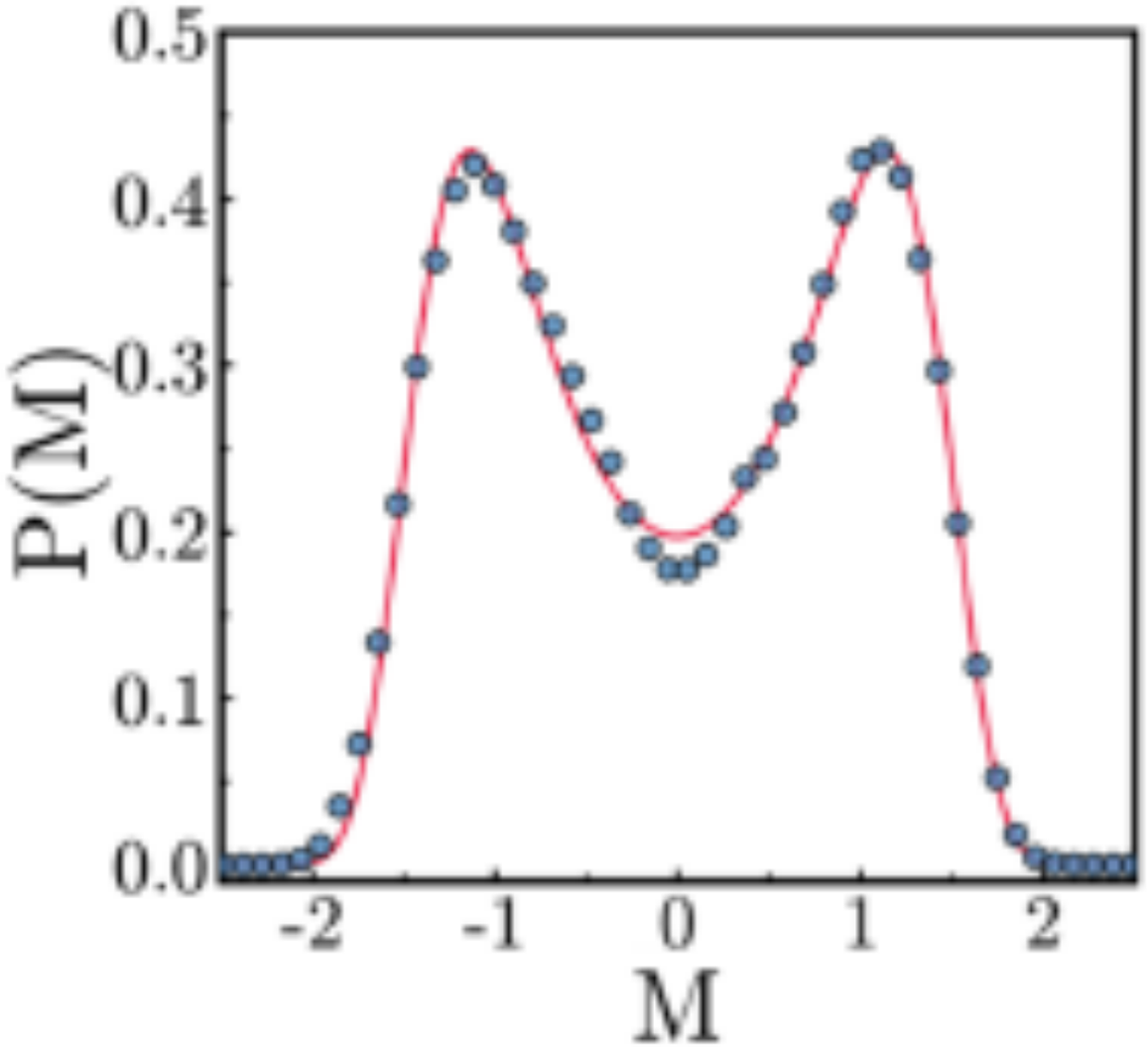




Triblock Janus particles (S. Granick)







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

Conclusions:

The LLPT hypothsis provides an elegant scenario to interpret the origin of the thermodynamic anomalies in water (C_p, K_T, TMD) as well as of the observed amorphous polyAmorphism.

A liquid-liquid transition has been definitively proved numerically for (several) molecular water models.

Sophisticated experiments (Nilsson's talk) are entering in the no-mans land, providing strong evidence consistent with the LLCP.

Colloidal systems, where crystallization can be tamed, will in the future offer a way to carefully study the LLCP physics.

Thanks for your attention

SPECIAL FEATURE: PERSPECTIVE

Supercooled and glassy water: Metastable liquid(s), amorphous solid(s), and a no-man's land

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CHEMICAL REVIEWS

Review

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Advances in Computational Studies of the Liquid–Liquid Transition in Water and Water-Like Models

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Reports on Progress in Physics

ACCEPTED MANUSCRIPT

The physics of Empty Liquids: from Patchy particles to Water

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