Frontiers in Water Biophysics, Erice,
September 7-12, 2015

The Liquid-Liquid Critical Point in Water

Francesco Sciortino
Sapienza, Universita' di Roma

The Liquid-Liquid Critical Point in Water

Supercooled Water….

The anomalies

The early explanations

The liquid-liquid critical point hypothesis

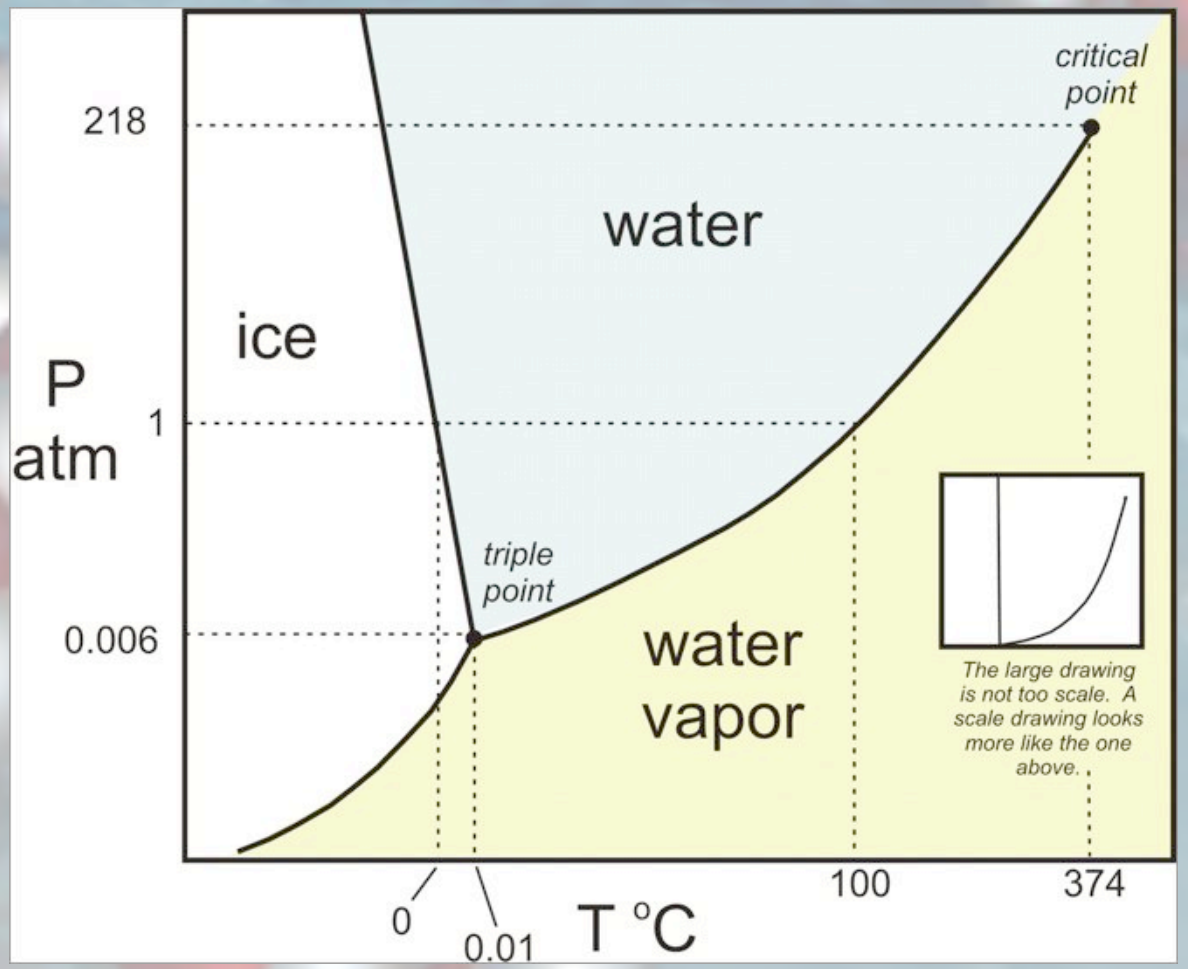
Some experimental results supporting the LLCP idea

The recent debate

Some recent results

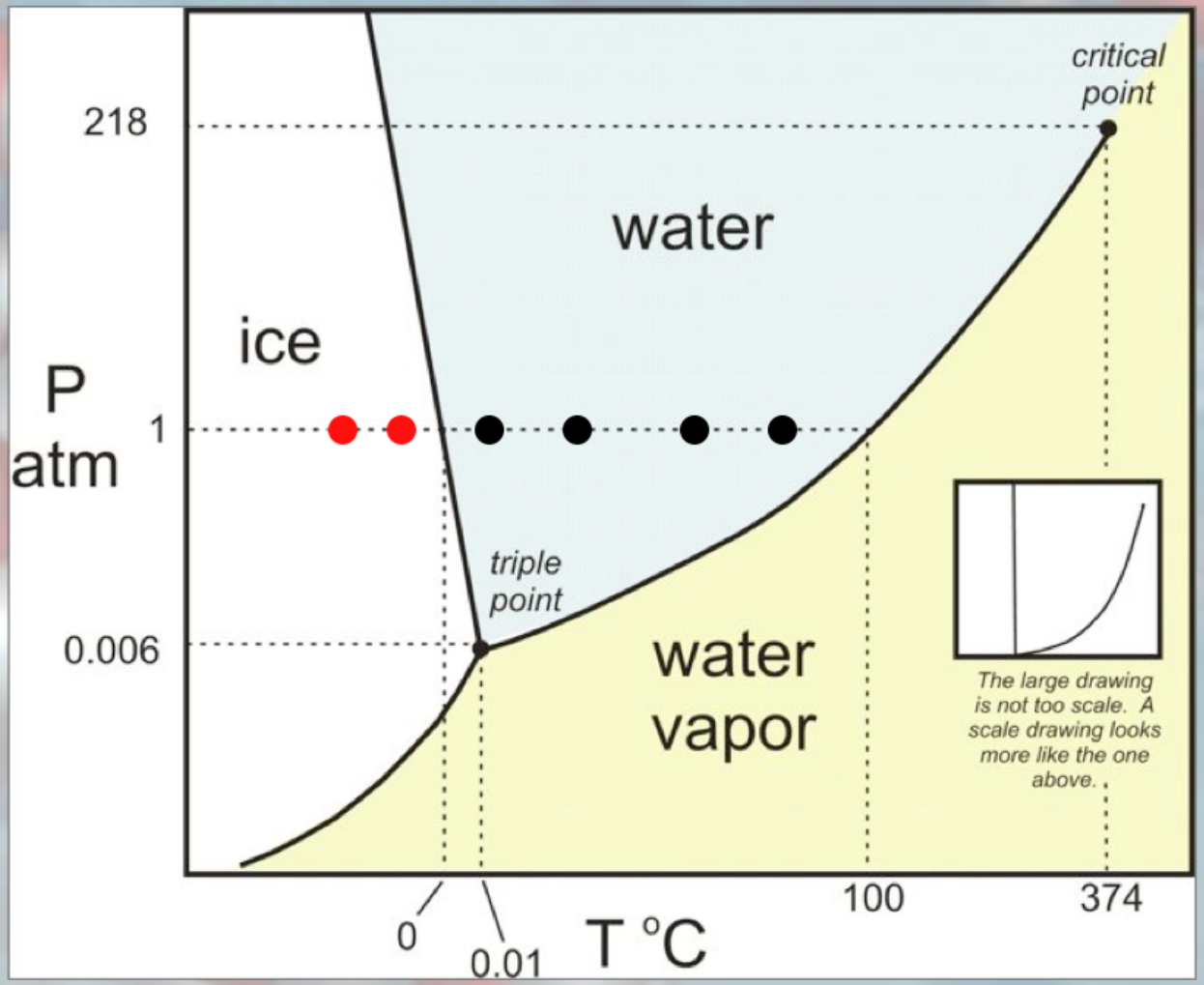
Supercooling……

- The equilibrium phase diagram



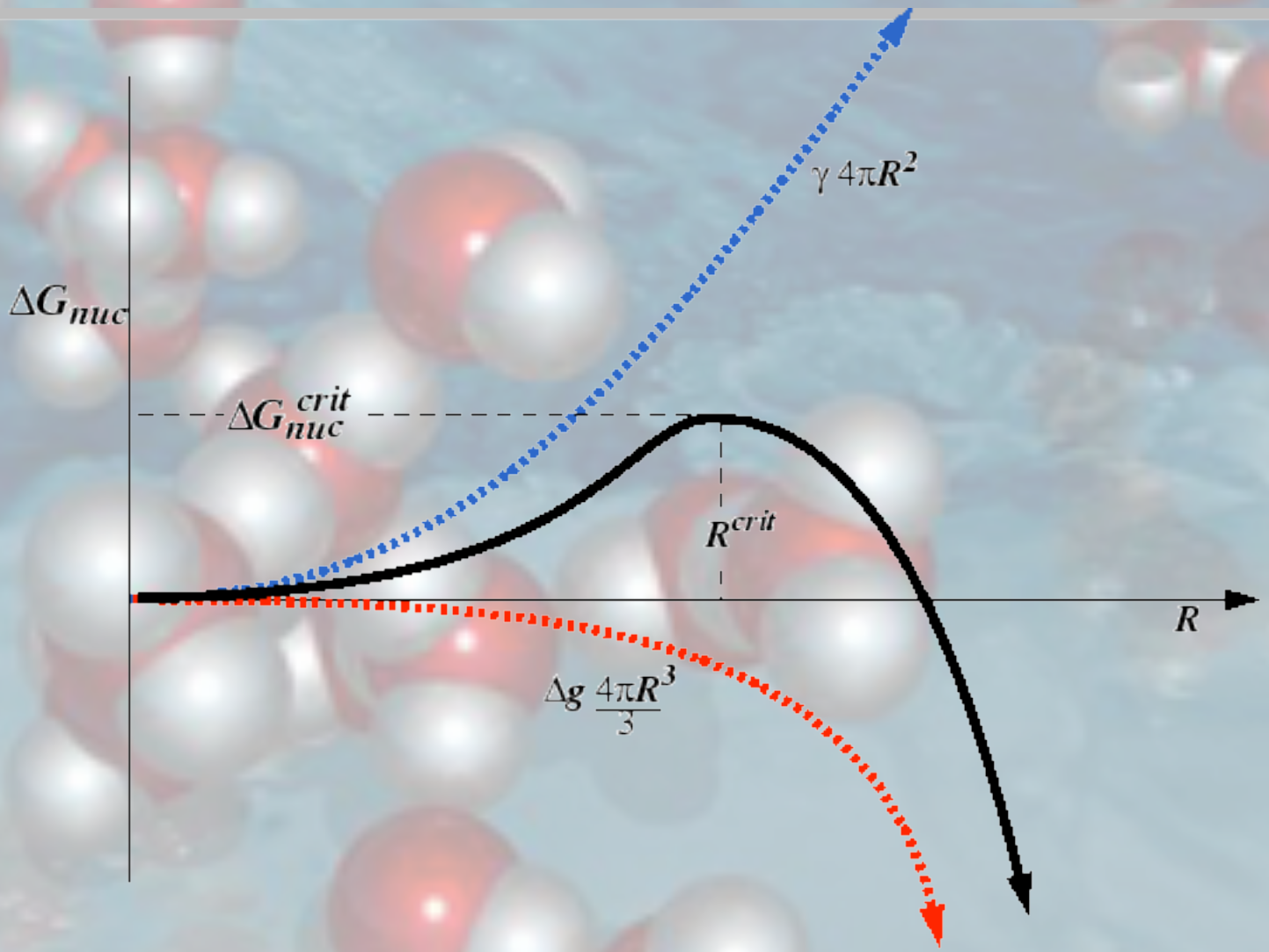
Supercooling……

- The red dots

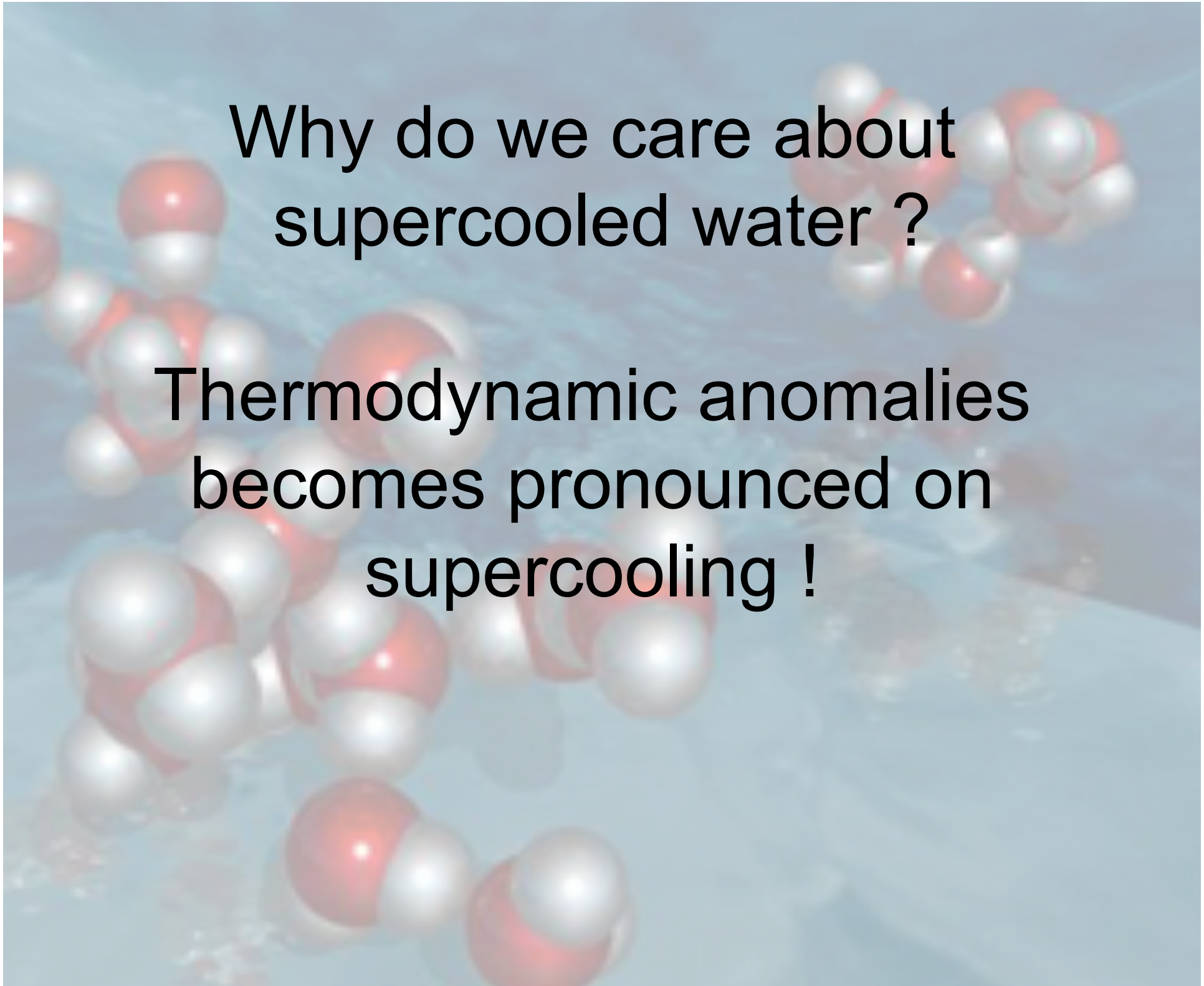


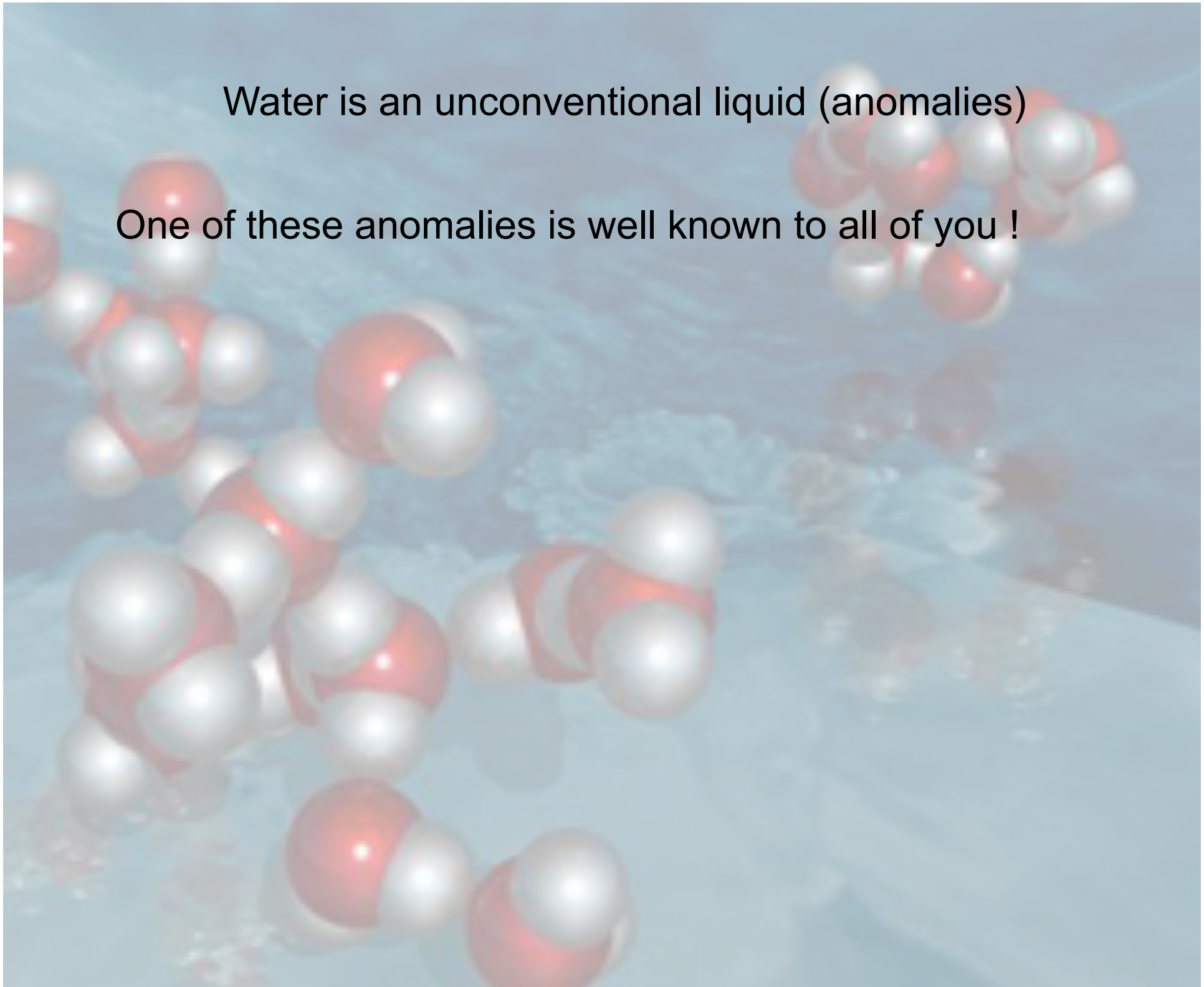
Why supercooling is possible ?

Classical Nucleation Theory




https://www.youtube.com/watch?v=wzHXiGdMvkU


Why do we care about supercooled water ?
Thermodynamic anomalies becomes pronounced on supercooling !



Water is an unconventional liquid (anomalies)

One of these anomalies is well known to all of you !

Ice is less dense than water….


http://www.lsbu.ac.uk/water/anmlies.html

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter 15 (2003) R1669–R1726 PII: S0953-8984(03)21725-2

TOPICAL REVIEW

Supercooled and glassy water

Pablo G Debenedetti

Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA

E-mail: pdebene@princeton.edu

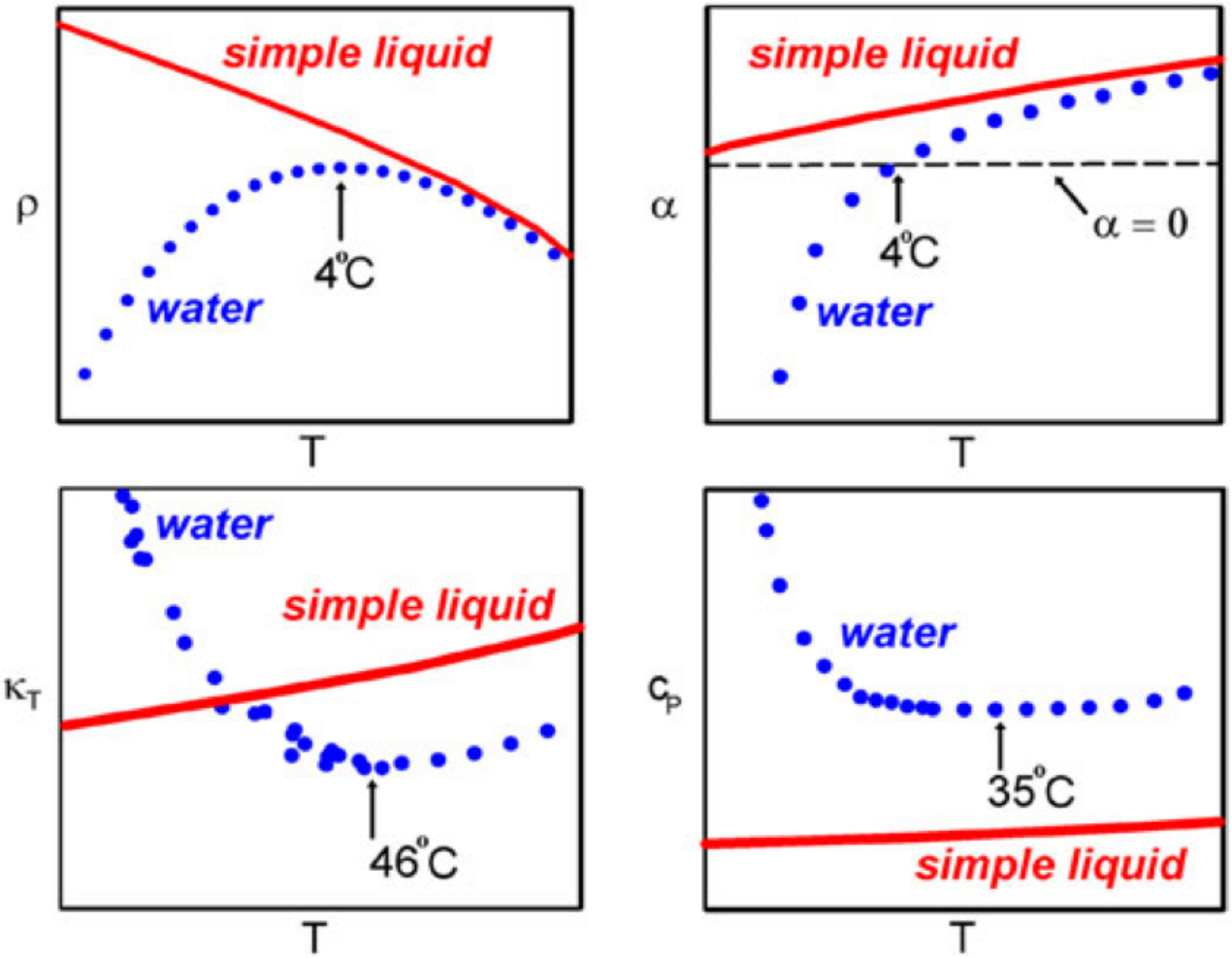
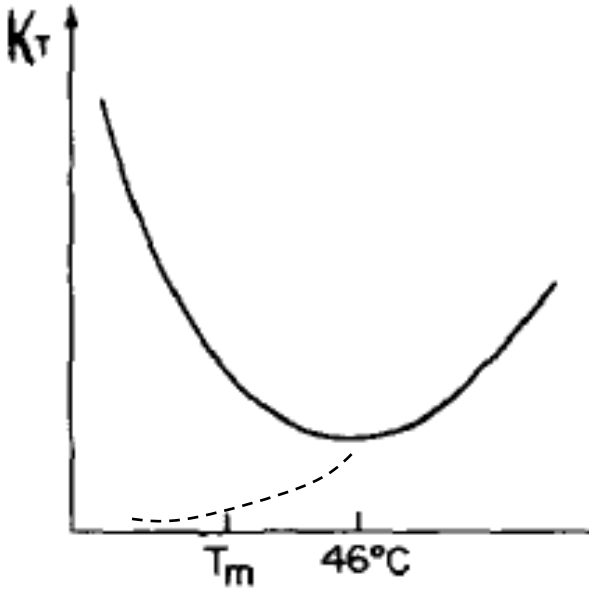
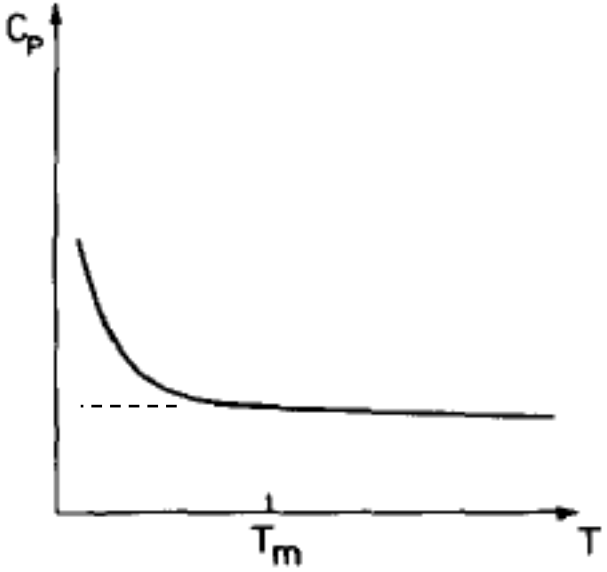
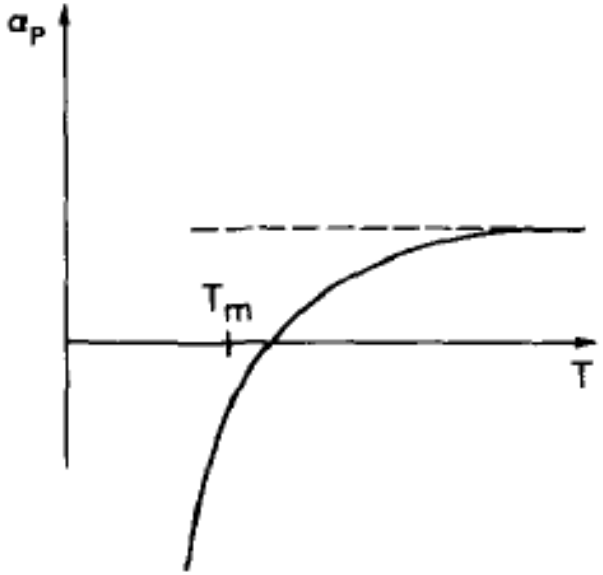


Figure 3. A schematic comparison of the isobaric temperature dependence of the density ρ, thermal expansion coefficient α, isothermal compressibility K_T and isobaric heat capacity c_p for water and a simple liquid.

Thermodynamic Anomalies







$< \Delta\rho^2 >$

$< \Delta S^2 >$

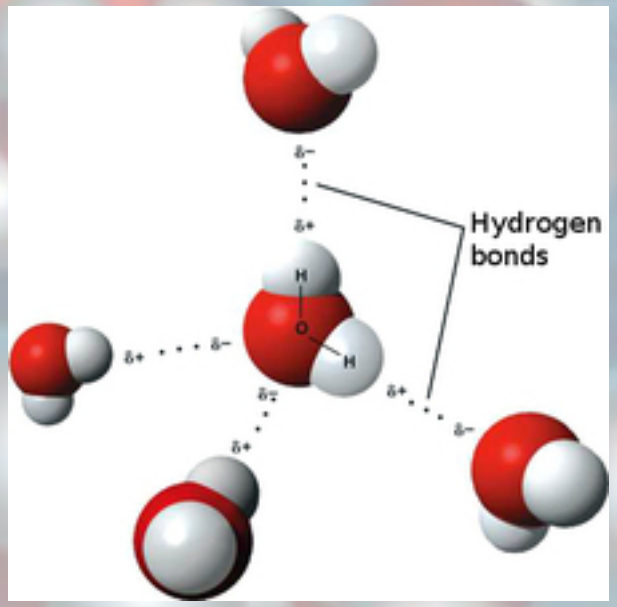
$< \Delta H^2 >$

$< \Delta S \Delta V >$

Supercooling enhances the fluctuations…..

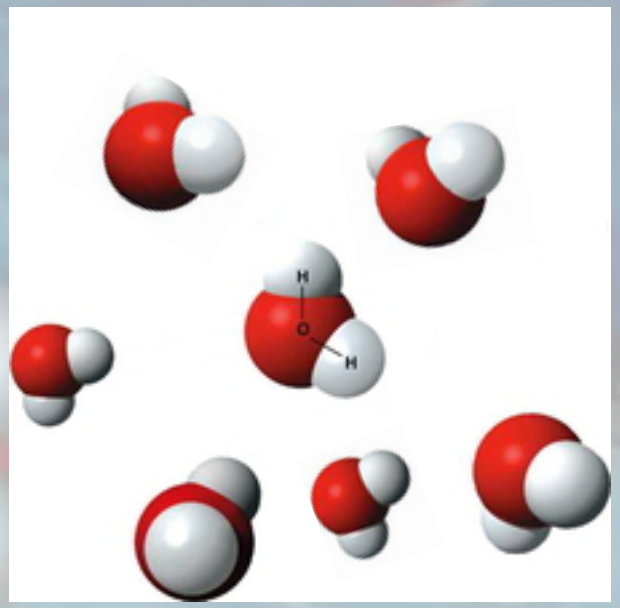
There must be (at least) two local structures

Low Entropy
Large Volume

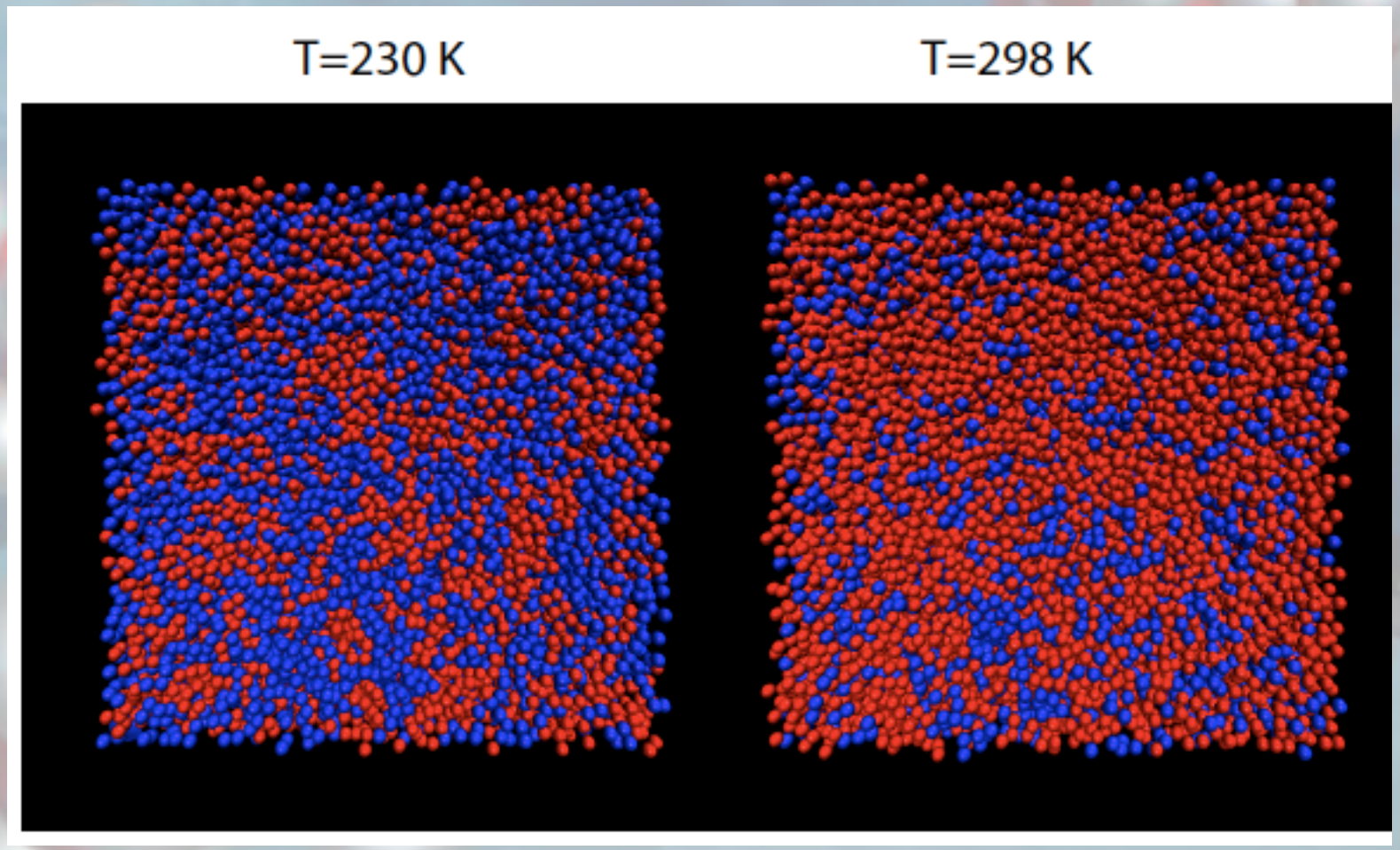


Tetrahedral
Linear Hydrogen Bonds

Large Entropy
Small Volume



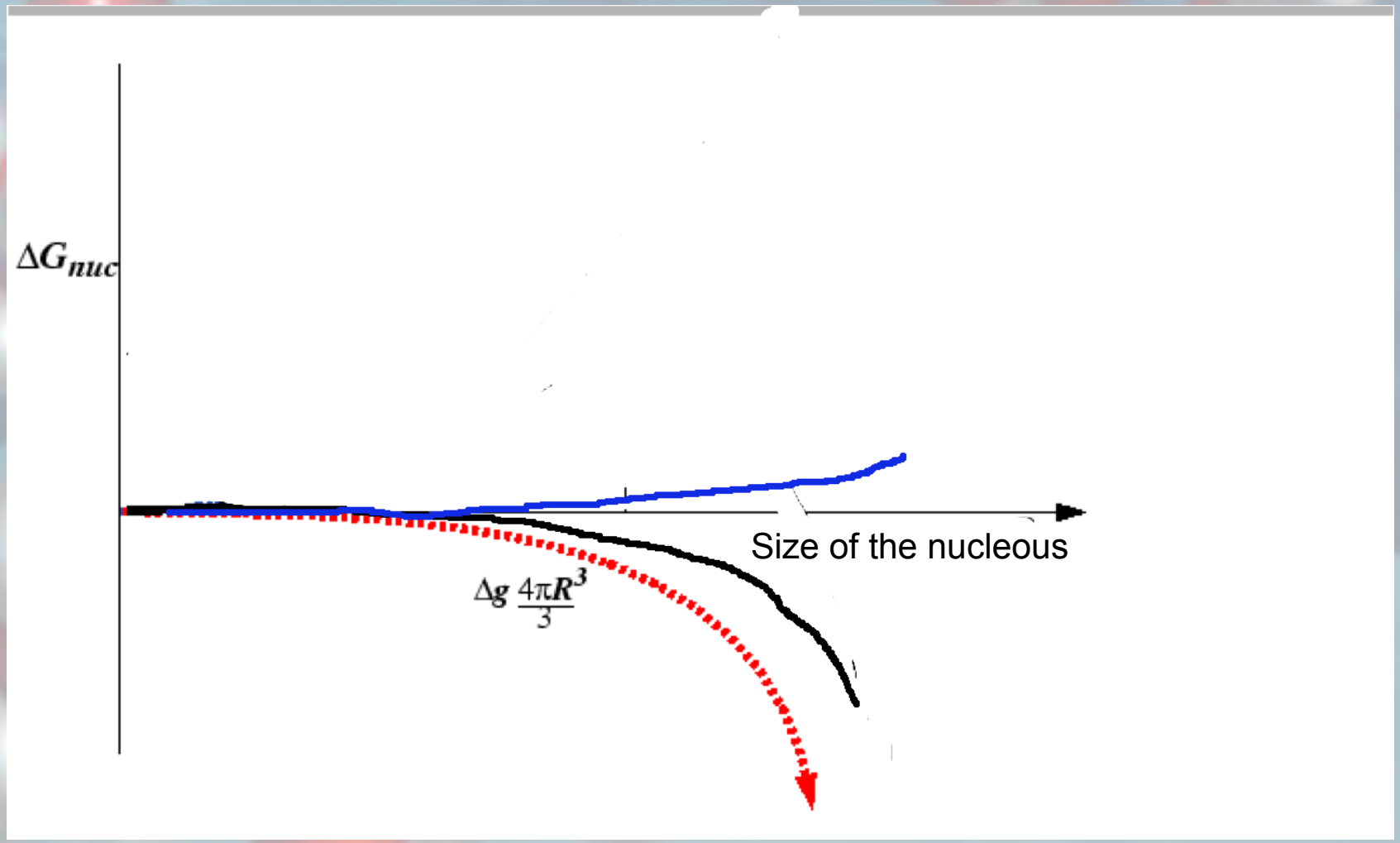
“less tetrahedral”
Bent, distorted, bifurcated
Interpenetrated



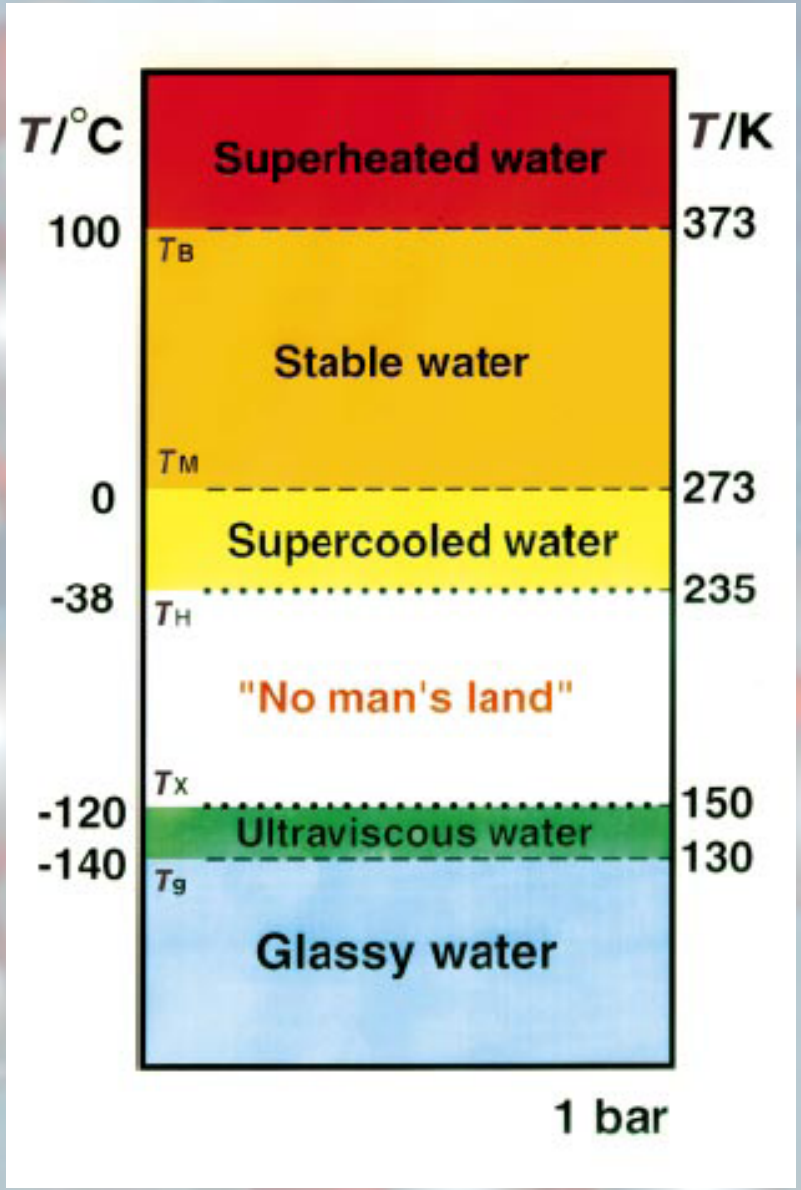
Red/Blue: Large/Small Local Density

K. T. Wikfeldt[1], A. Nilsson[1,2] and L. G. M. Pettersson[1]

Why don’t we keep supercooling ?
The black barrier disappears !



Supercooling enhances fluctuations…

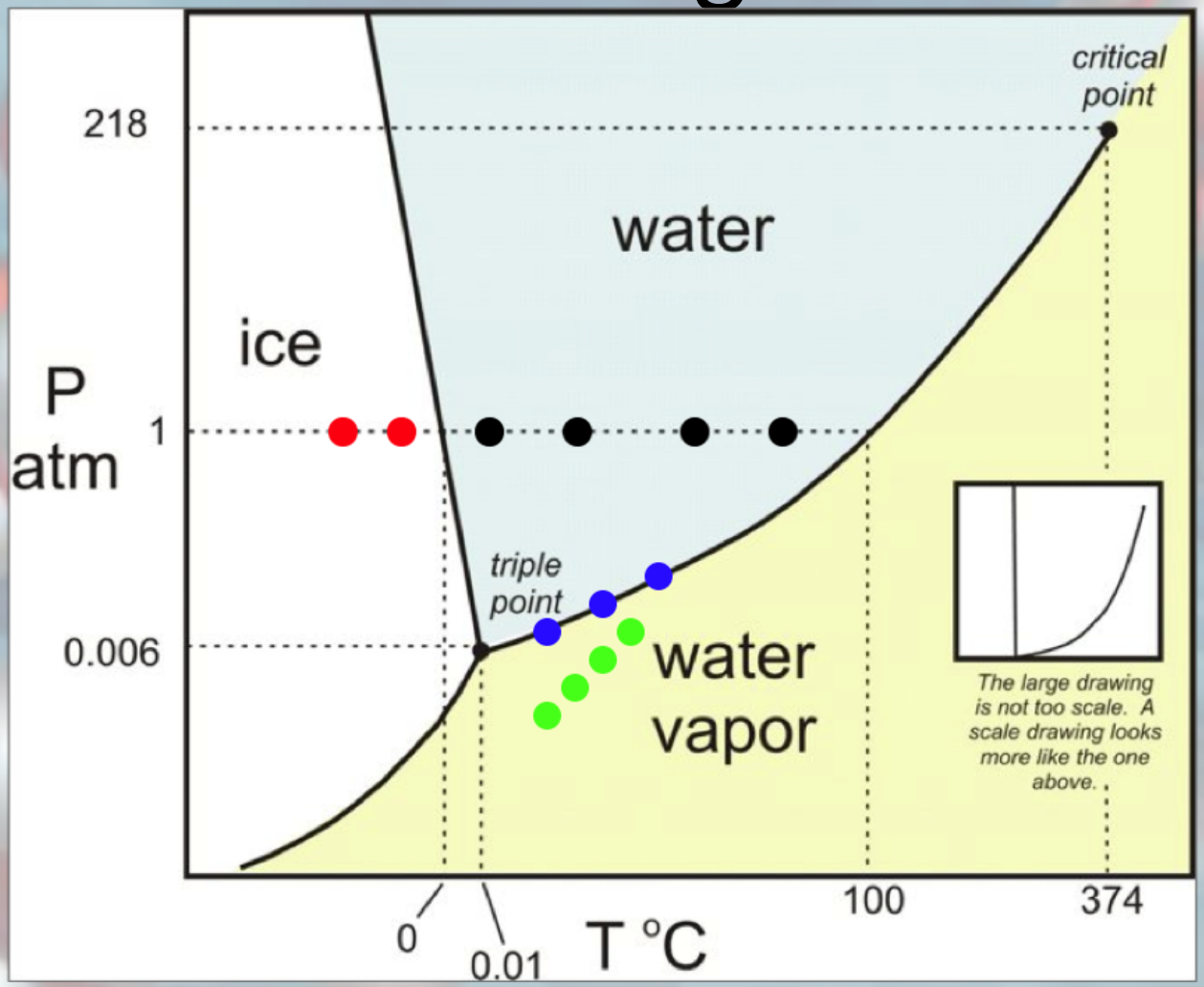


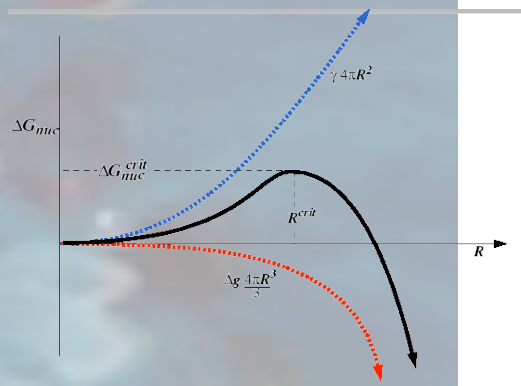
But crystallization prevails below -38 C

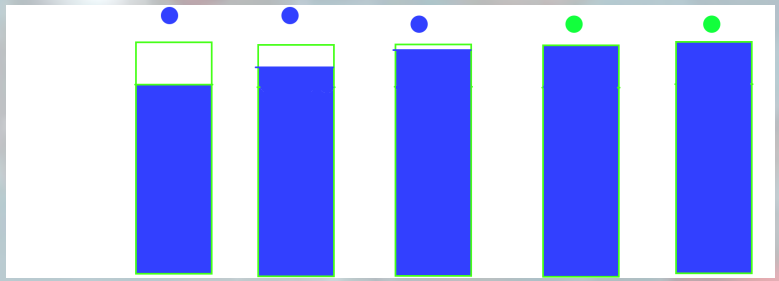
The early explanations……

- Re-entrant spinodal (Speedy)
- Percolation of fully bonded molecules (Stanley-Teixeira). Singularity Free Scenario

Stretching water…..







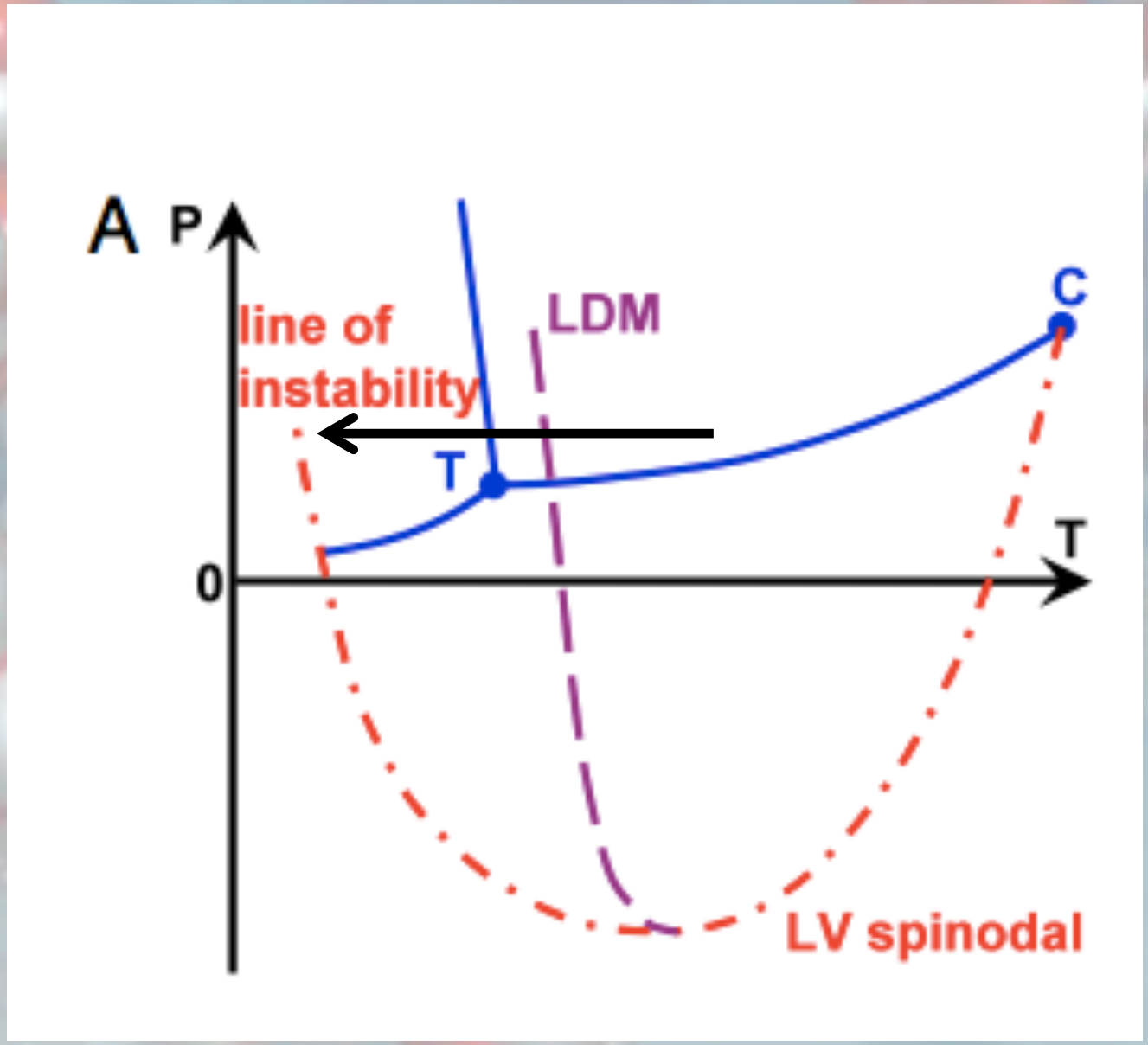
Anomalies in bulk supercooled water at negative pressure

Gaël Pallares[a], Mouna El Mekki Azouzi[a], Miguel A. González[b], Juan L. Aragones[b], José L. F. Abascal[b], Chantal Valeriani[b], and Frédéric Caupin[a,1]

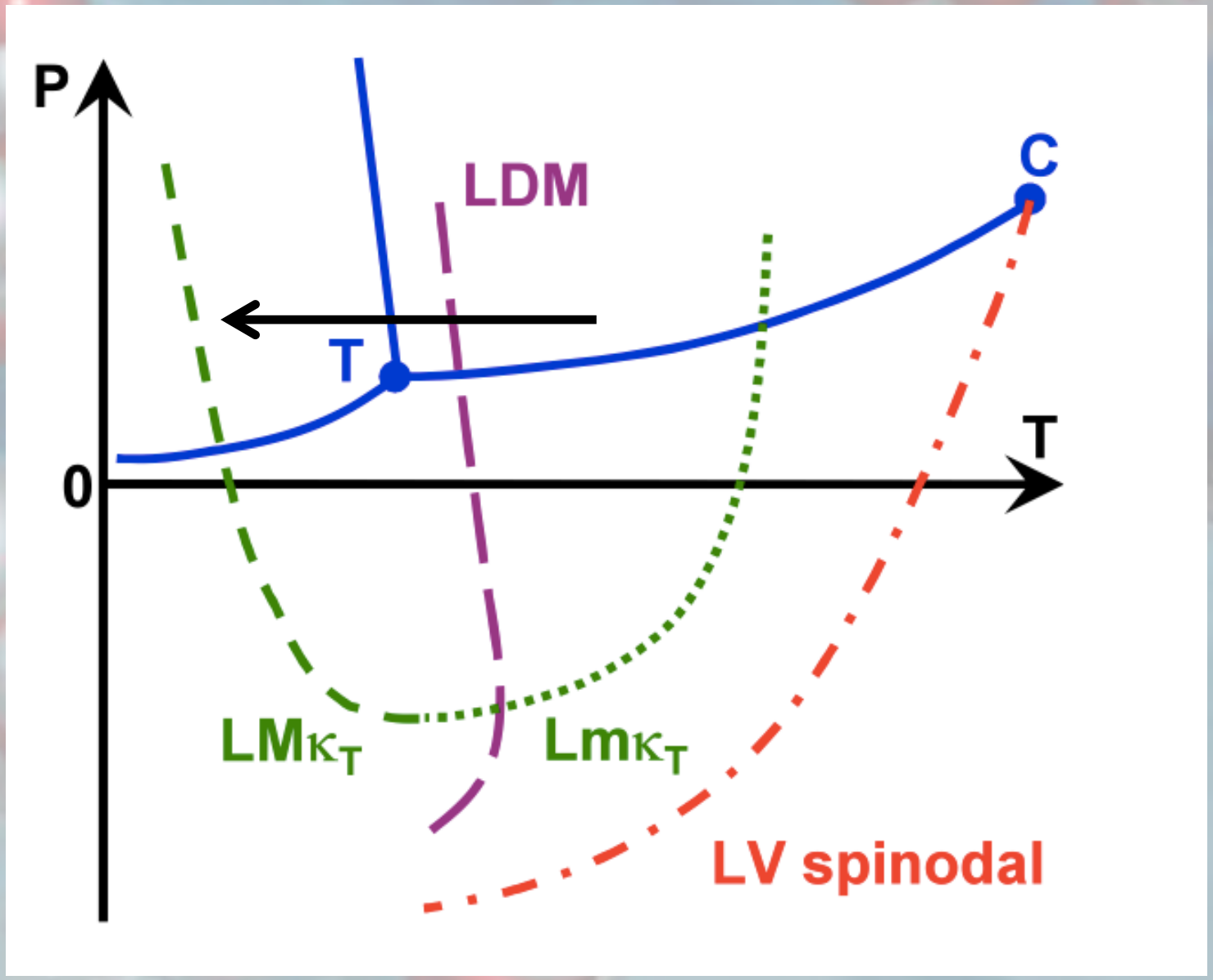
[a]Institut Lumière Matière, Unité Mixte de Recherche 5306 Université Lyon 1, Centre National de la Recherche Scientifique, Université de Lyon and Institut Universitaire de France, 69622 Villeurbanne Cedex, France; and [b]Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

Edited by Pablo G. Debenedetti, Princeton University, Princeton, NJ, and approved April 11, 2014 (received for review December 17, 2013)

Speedy Reentrant Spinodal



Singularity Free

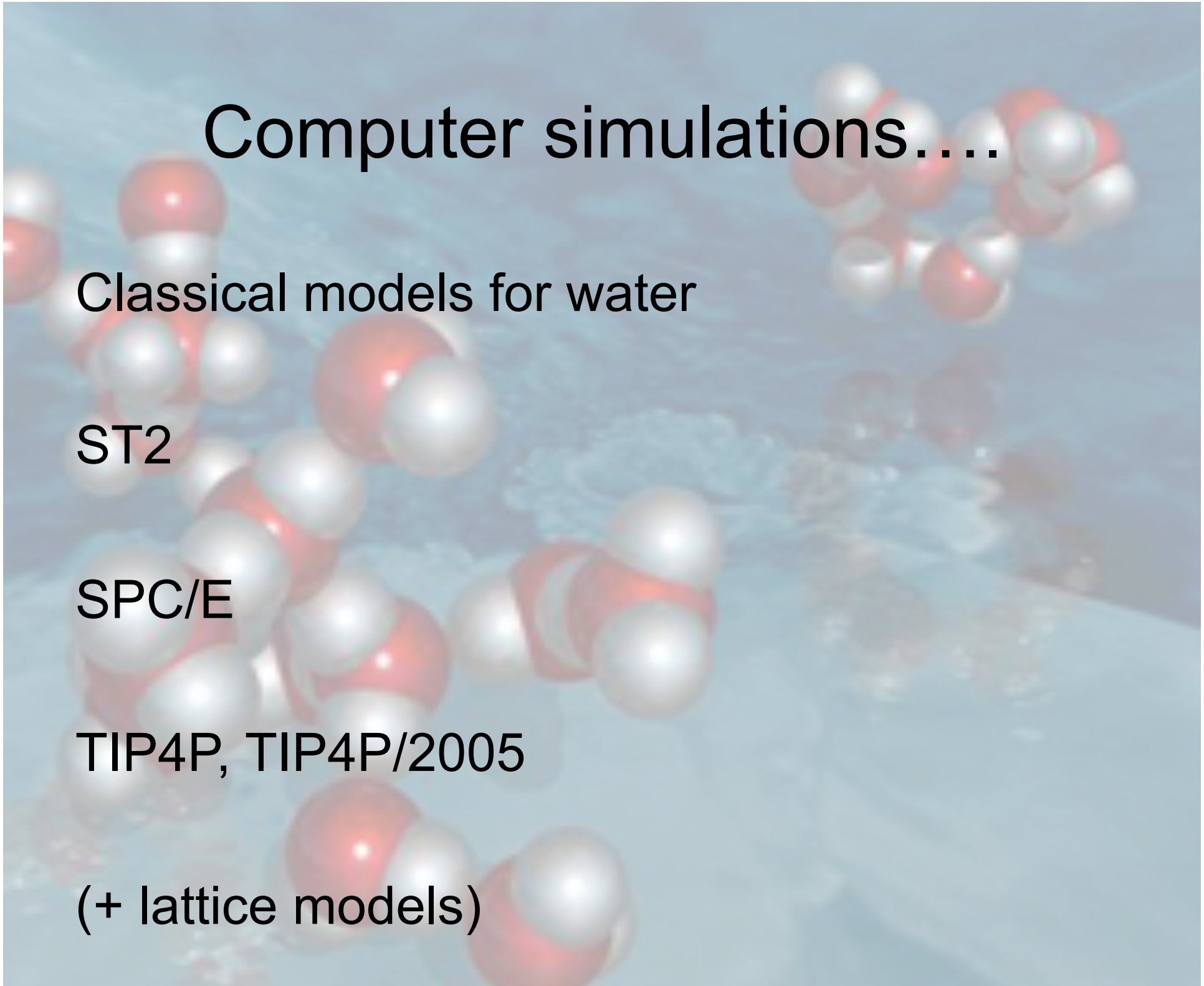


What happen in the no-man region?

Why fluctuations are increasing in supercooled states ?
(do fluctuations keep increasing on cooling ?)

Several scenarios are possible

Smooth cross-over from dense to less dense configurations at all P
Abrupt cross-over from dense to less dense configurations P> Pc



Computer simulations….

Classical models for water

ST2

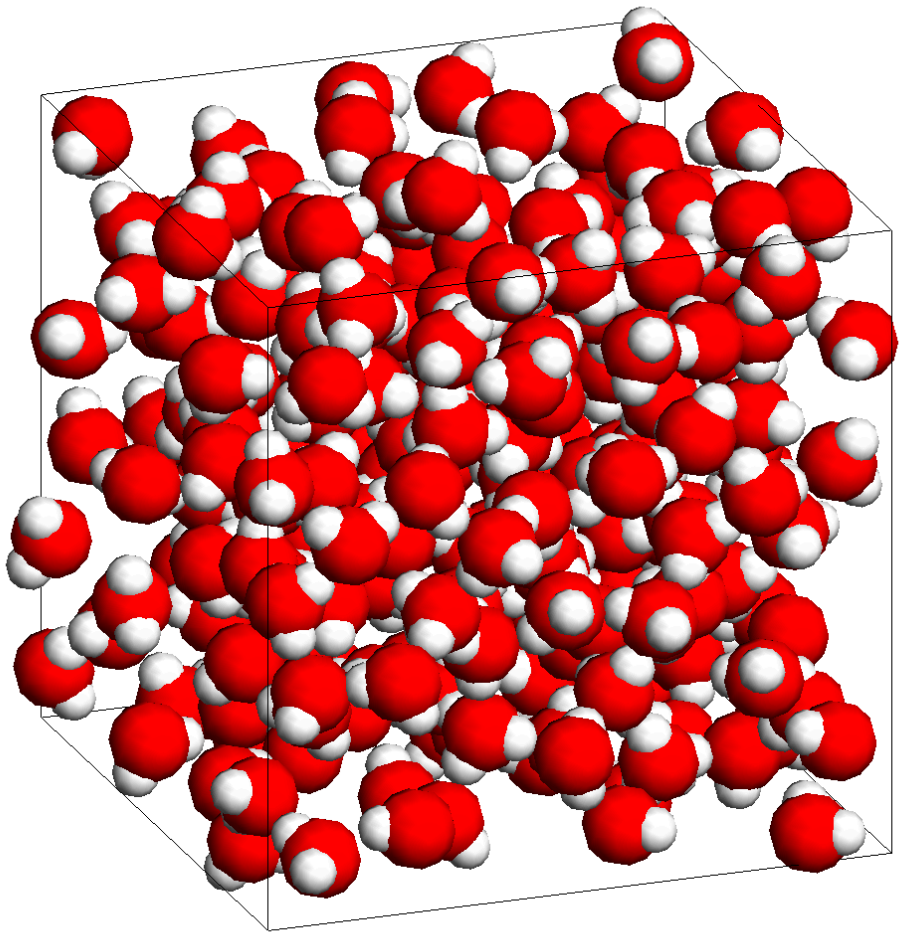
SPC/E

TIP4P, TIP4P/2005

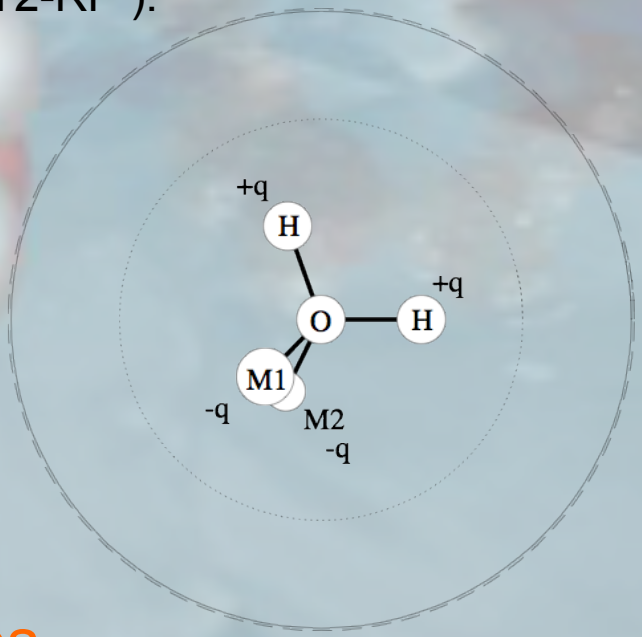
(+ lattice models)

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

ST2 model of water



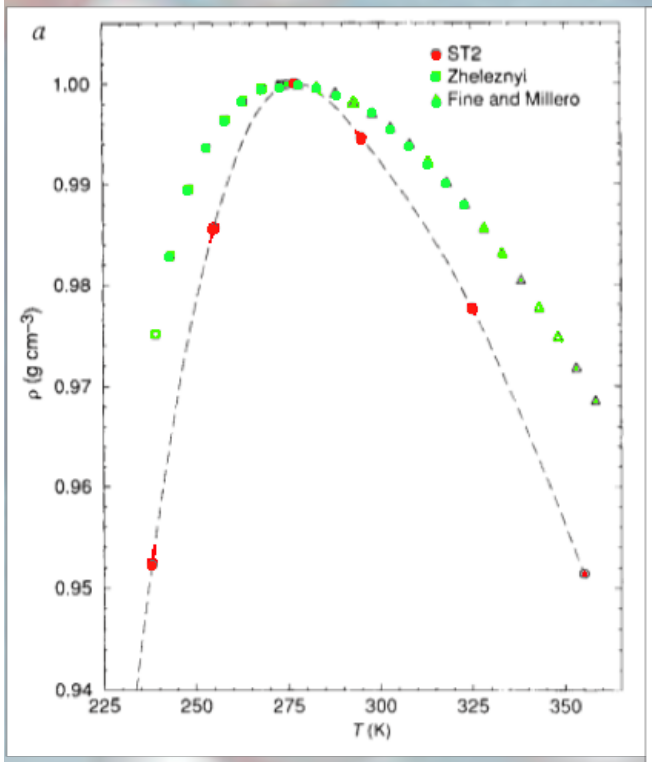
- ST2 water pair potential of Stillinger and Rahman (JCP, 1974).
- Five-site rigid molecule: one O atom, two H atoms, and two “lone pair” sites.
- Direct interactions smoothly tapered to zero. Long-range electrostatics approximated by reaction field method (“ST2-RF”).



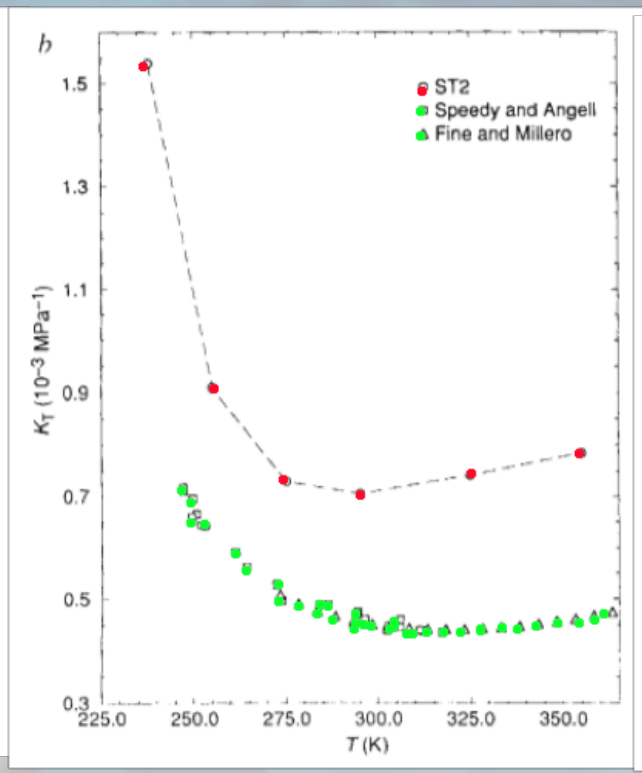
This model reproduces the anomailies….

The ST2-RF model reproduces the anomalies….

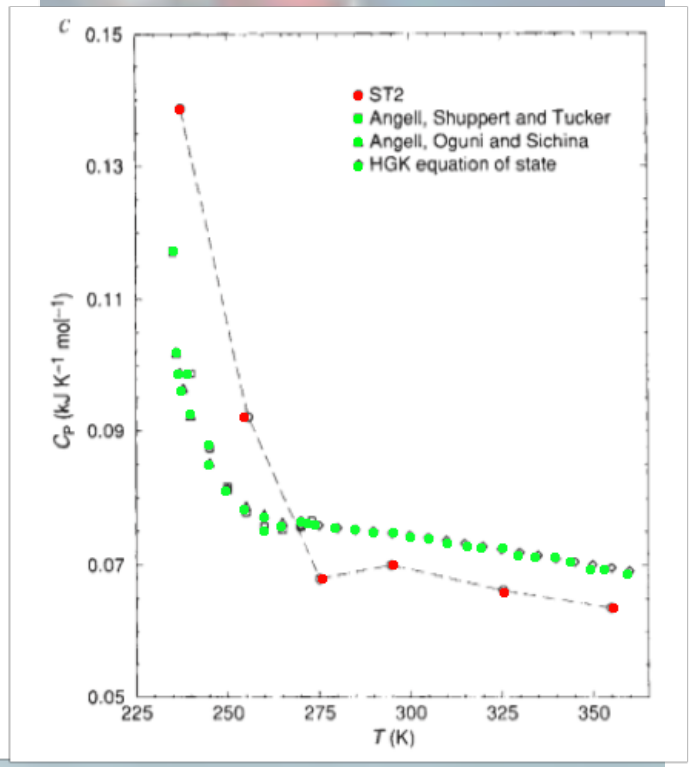
- ST2
- EXPERIMENTS



Density



Compressibility



Specific Heat

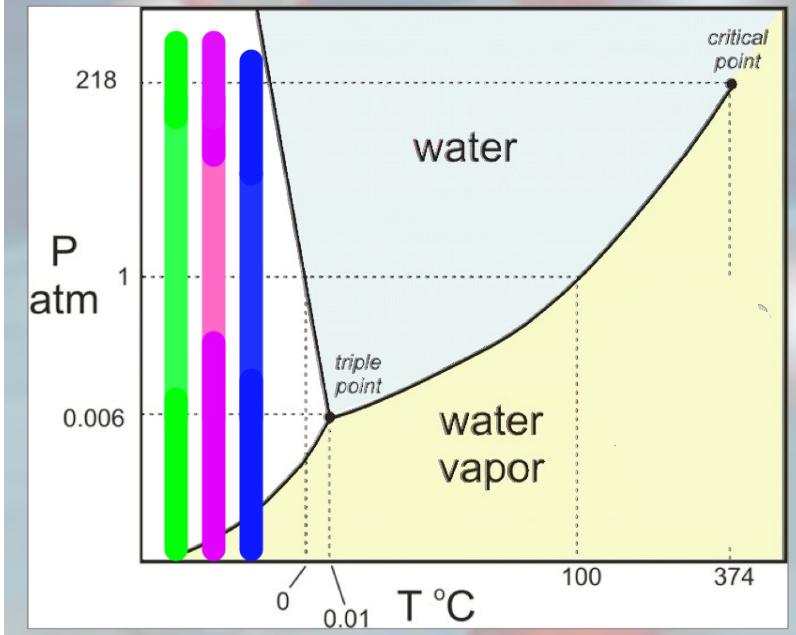
Why Simulations

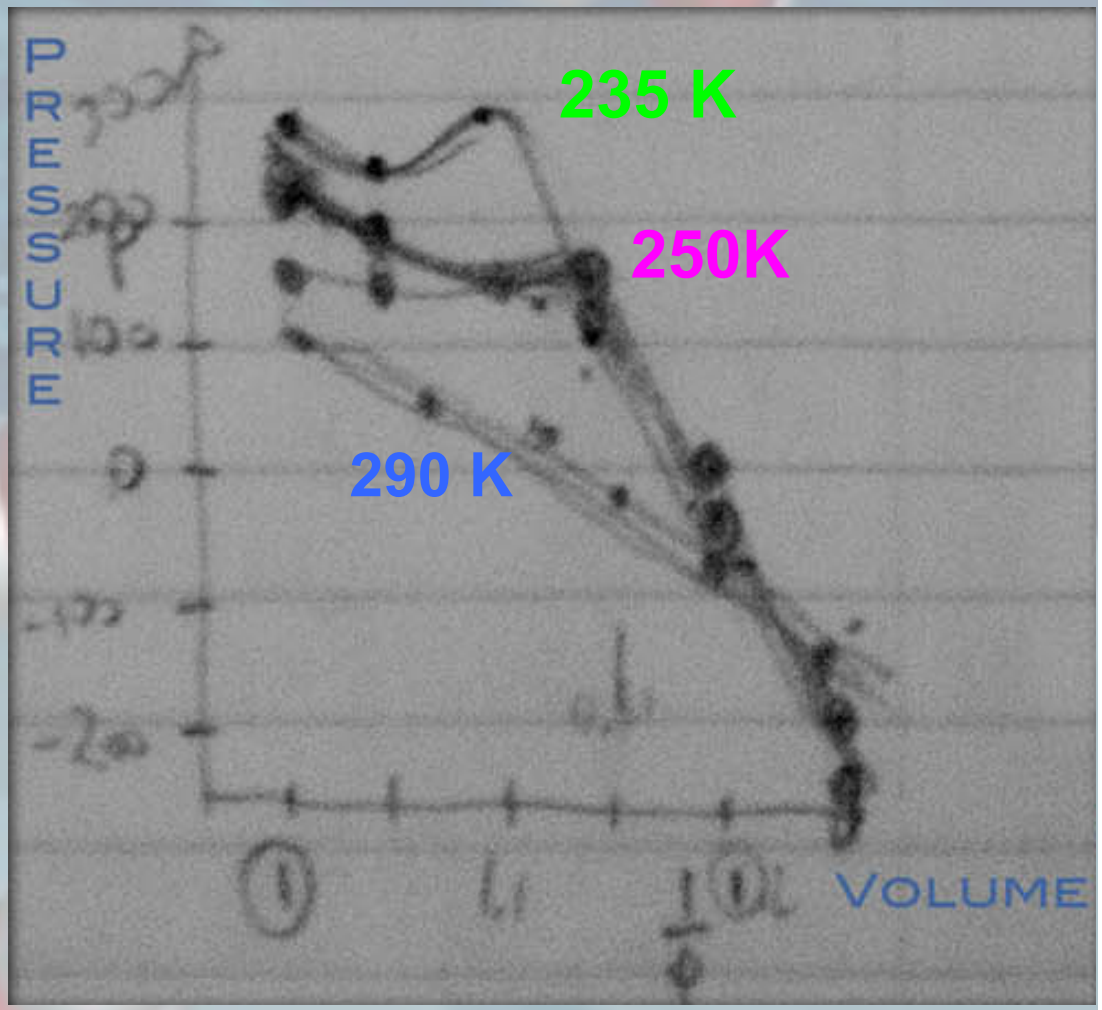
- Clean Samples (no impurities)
- Small samples (200-1000 water molecules)
- Relatively short times (ms)

- NO SPONTANEOUS CRYSTALLIZATION

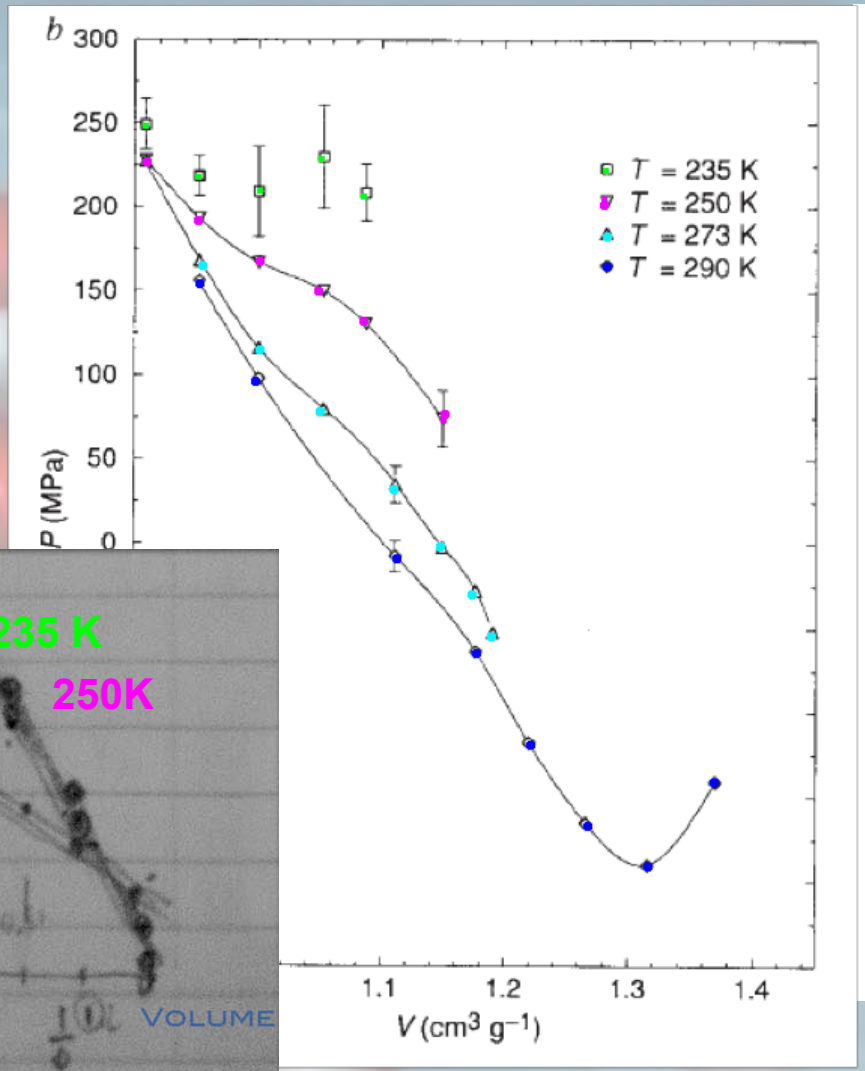
Calculating the equation of states at low T

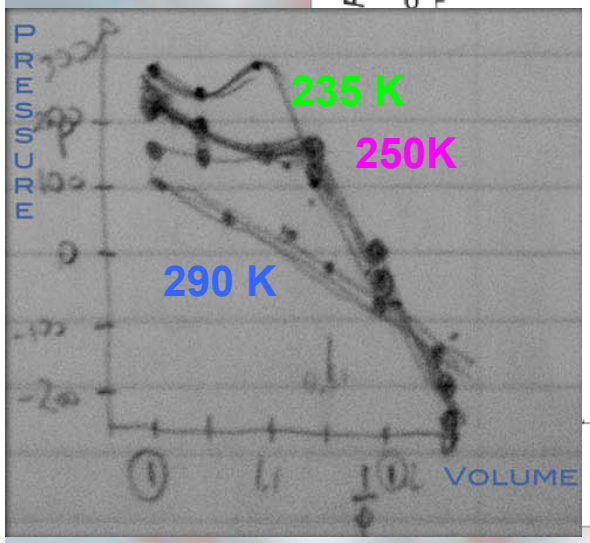
A van der Waals loop at low T !!!!!

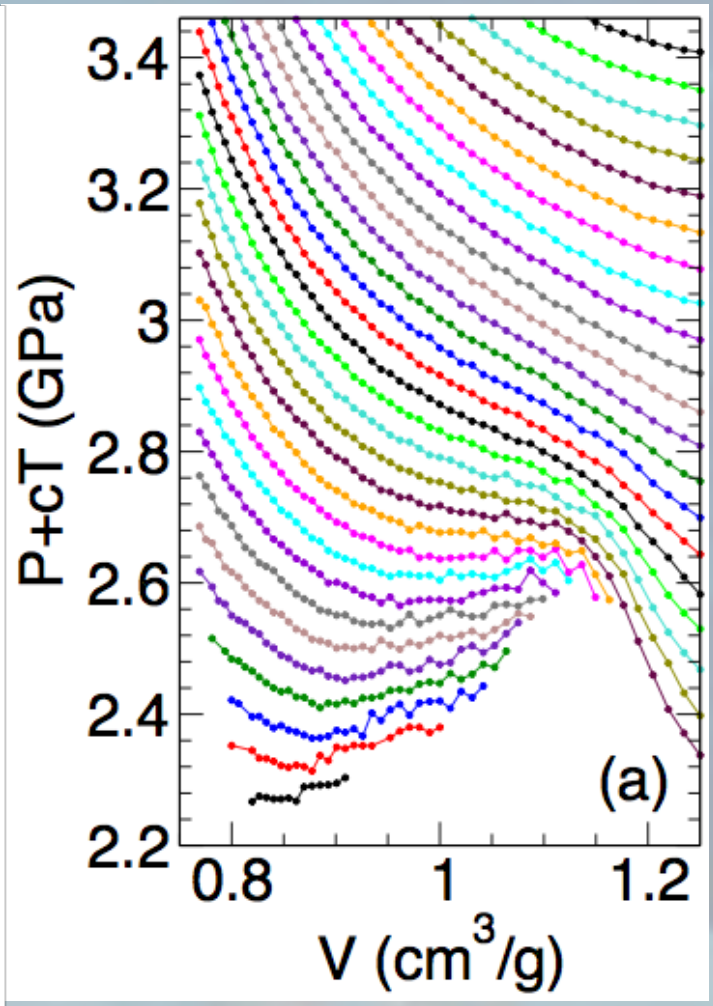




The very first data….. (1990)







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

A complex scenario of thermodynamic anomalies (Widom line)

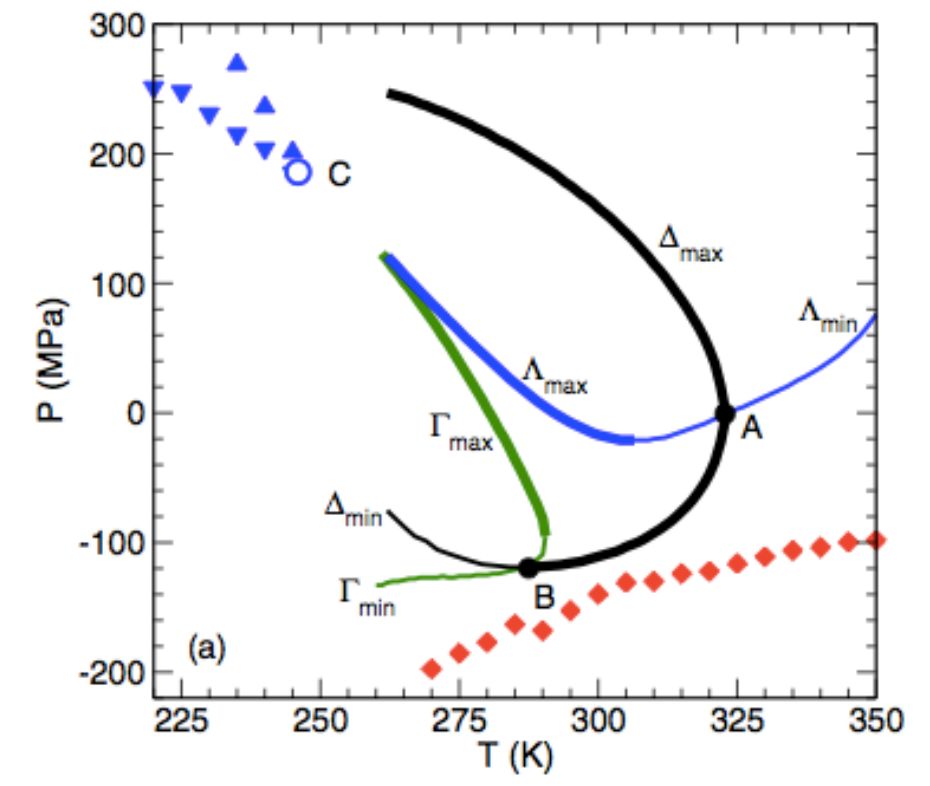
INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

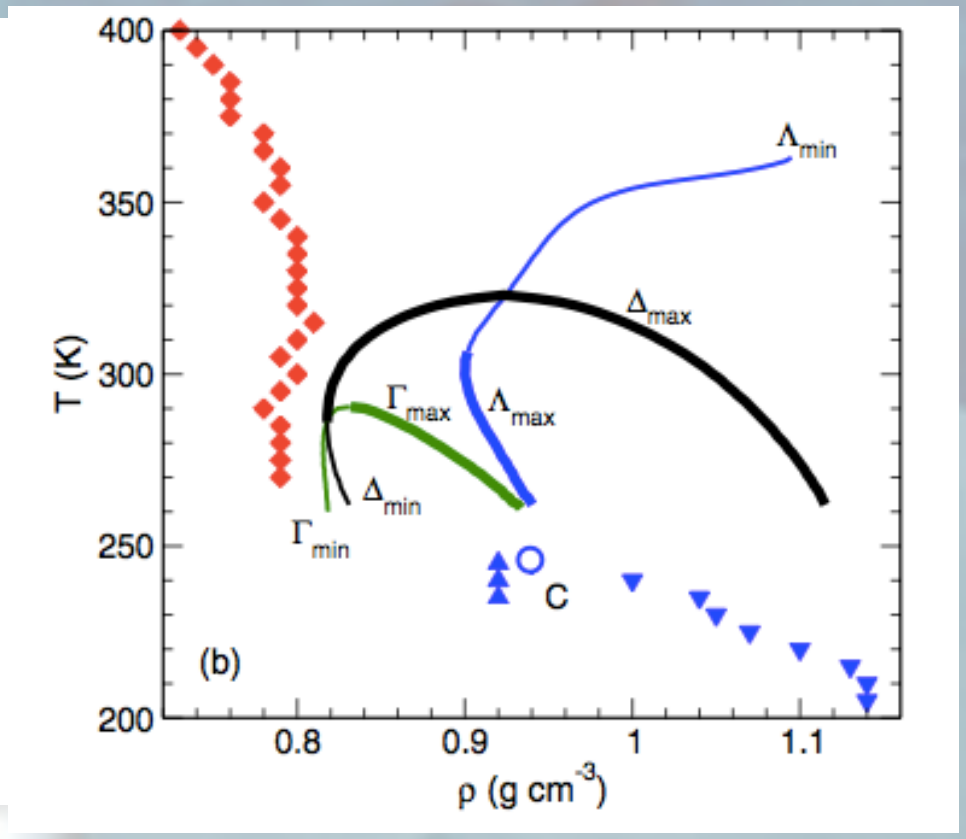
J. Phys.: Condens. Matter **17** (2005) L431–L437 doi:10.1088/0953-8984/17/43/L01

LETTER TO THE EDITOR

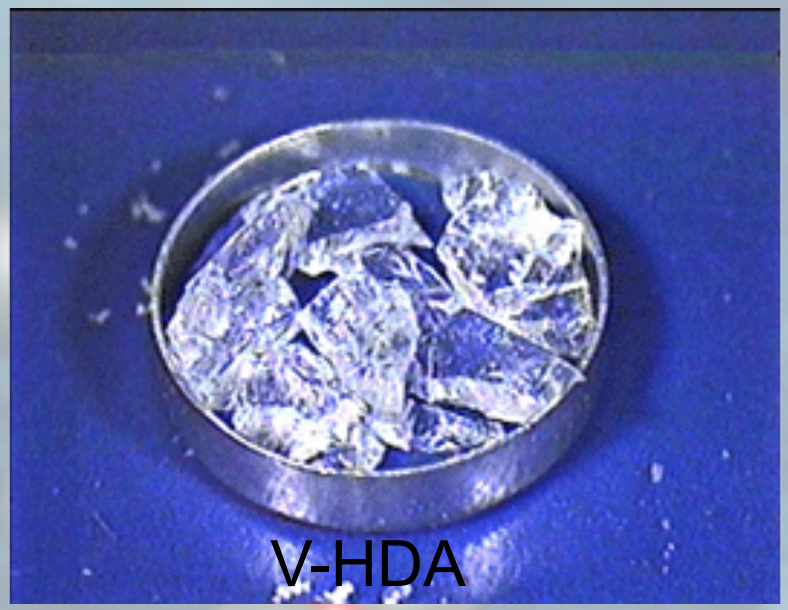
Density minimum and liquid–liquid phase transition

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





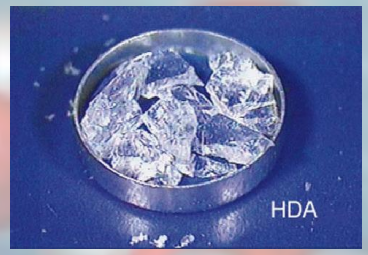
Two (or more) disordered solid forms (glasses)



http://www.nims.go.jp/water/

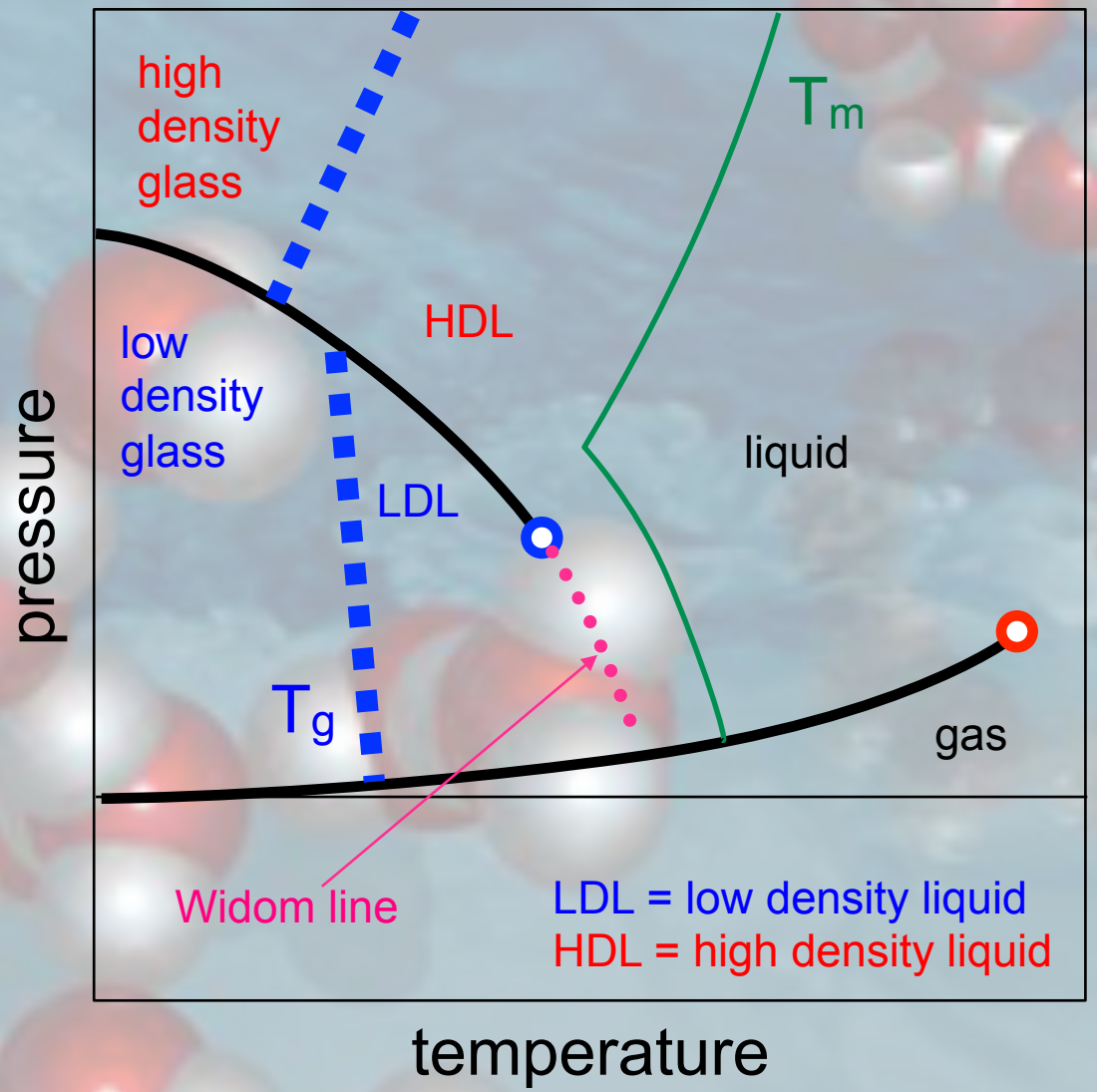
Osamu Mishima

Liquid-liquid phase transition in supercooled water



O. Mishima,
http://www.nims.go.jp/water/

Two forms of amorphous ice



• Poole, Sciortino, Essmann, Stanley, Nature (1992)

Why is this hypothesis worth investigating ?

- New phenomenon, perhaps not only limited to water (what are the ingredients to generate a LL critical point?)

  (Franzese, Jagla, Buldyrev, Gallo, Sastry, Angell, …..)

- Explains the anomalies in water as originating from the LDL-HDL critical point. A link between the LL-CP and ambient T properties.

- Rationalize the amorphous polymorphism phenomenon

Experiments – two forms

Structures of High-Density and Low-Density Water

Alan K. Soper*
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom

Maria Antonietta Ricci
Dipartimento di Fisica "E. Amaldi," Universita' di Roma Tre, Istituto Nazionale per laFisica della Materia, Unita' di Roma Tre, via della Vasca Navale 84, 00146-Roma, Italy
(Received 12 November 1999)

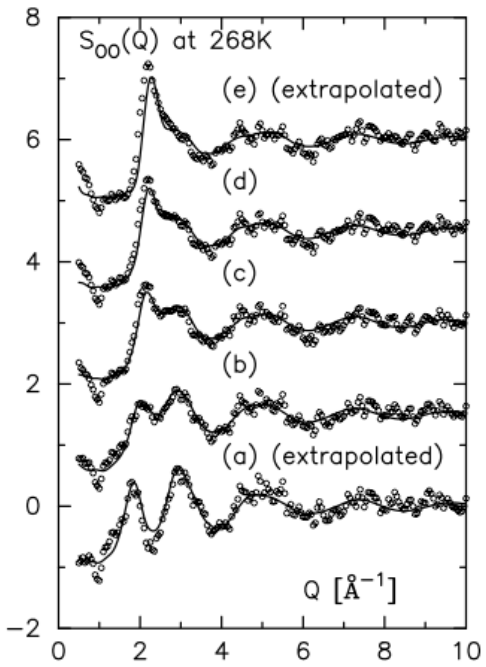


FIG. 1. Values of the measured OO partial structure factors of water at 268 K and pressures of 26 MPa ($\alpha = 0.4$) (*b*), 209 MPA ($\alpha = 0.63$) (*c*), and 400 MPa ($\alpha = 0.8$) (*d*) for several Q values. The remaining curves (*a*) and (*e*) correspond to the linear extrapolation of these data to $\alpha = 0.0$ and $\alpha = 1.0$, respectively, corresponding to number densities 0.0295 and 0.0402 molecules/Å^3, respectively. The circles show the measured or extrapolated data as appropriate, while the lines show EPSR fits to these data.

in each phase (Fig. 3). Here we discover that the first coordination shell is tetrahedral in shape for *both* high- and low-density forms of water. The coordination number of this shell is about four water molecules in each case. The second shell retains its overall orientational symmetry between the two forms, but for LDW it sits at approximately the tetrahedral distance ($\sim\sqrt{8/3}$ times the near neighbor distance), while for HDW it has substantially collapsed, to a point where it is almost coincident with the first shell. This also implies that the distribution of the O-O-O angle between three neighboring molecules is almost flat in HDW, while it is peaked at ~70° in LDW (data not shown). The evidence here supports therefore the notion that water can exist in two distinct structural forms, depending on the density. The primary distinction between these forms is the distance of the second shell away from the first, and the breaking of the hydrogen bonds between the two shells which occurs in HDW.

Experiments: two forms

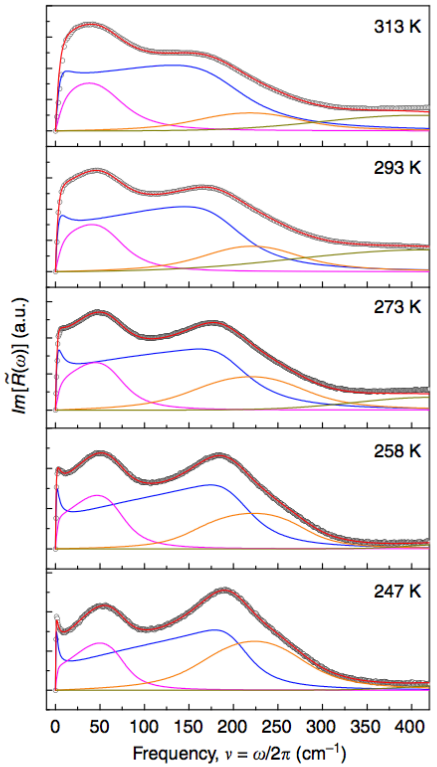


Figure 4 | Water spectrum and vibrational components. The Fourier transform of the time-dependent OKE response, $\tilde{R}(\omega)$, is directly related to the frequency-dependent spectrum measured in the dynamic light-scattering experiments. The imaginary part of the Fourier transform of the HD-OKE data (open circle), after which the contribution of the instrumental function has been removed by de-convolution, and of SMC fits (red line) at 247, 258, 273, 293 and 313 K are reported. The SMC model enables to disentangle the dynamical features that generate the simulated response function. The contributions of the three slave correlators are reported in the figure as magenta-blue-orange lines. Moreover, a simple damped harmonic oscillator (dark yellow) has been added to the SMC response to reproduce the very high-frequency vibrational contributions ($\nu > 400$ cm^{-1}); this does not affect the response function in the lower frequency range, where the dynamics relevant to our investigation takes place. The simulation of HD-OKE data by SMC model requires two vibrational modes to fit the intermolecular stretching band of water (blue and orange lines). The characteristics of these two modes are clearly different in terms of spectrum shape and temperature dependence.

NATURE COMMUNICATIONS | ARTICLE

Evidence of two distinct local structures of water from ambient to supercooled conditions

A. Taschin, P. Bartolini, R. Eramo, R. Righini & R. Torre

Affiliations | **Contributions** | **Corresponding author**

Nature Communications **4**, Article number: 2401 | doi:10.1038/ncomms3401

Received 08 April 2013 | Accepted 05 August 2013 | Published 13 September 2013

and strongly coupled to structural rearrangements. The surprising similarities of the spectra of LDA and HDA glass forms with those of the two high-frequency distinct modes, reported in this work, suggest attributing them to the LD and HD water structures, respectively. The LD water forms are expected to consist of aggregates of a small number of molecules; being mostly localized in space (at least in the temperature range investigated), their dynamics show negligible coupling with the structural relaxation. The two local configurations of liquid water

Experiments: confinement

PRL 95, 117802 (2005) PHYSICAL REVIEW LETTERS week ending 9 SEPTEMBER 2005

Pressure Dependence of Fragile-to-Strong Transition and a Possible Second Critical Point in Supercooled Confined Water

Li Liu,[1] Sow-Hsin Chen,[1,*] Antonio Faraone,[1,2] Chun-Wan Yen,[3] and Chung-Yuan Mou[3]

[1]*Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[2]*Department of Material Science and Engineering, University of Maryland, College Park, MD 20742, USA and NIST Center for Neutron Research, Gaithersburg MD, 20899-8562, USA*
[3]*Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, Republic of China*

(Received 12 June 2005; published 9 September 2005)

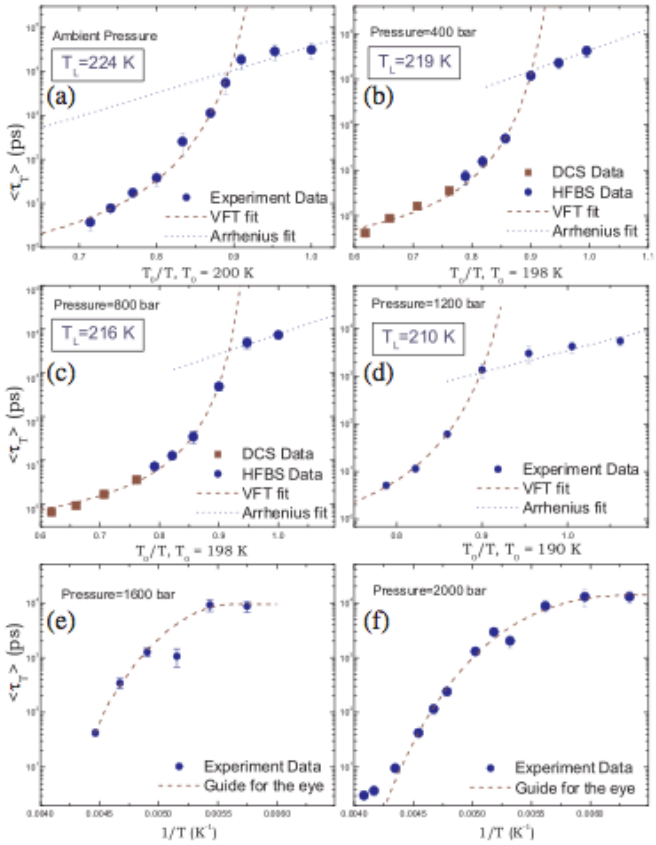


FIG. 2 (color online). Temperature dependence of $\langle \tau_T \rangle$ plotted in $\log(\langle \tau_T \rangle)$ vs T_0/T or $1/T$. Data from ambient pressure, 400, 800, 1200, 1600, and 2000 bars are shown in panels (a), (b), (c), (d), (e), and (f), respectively.

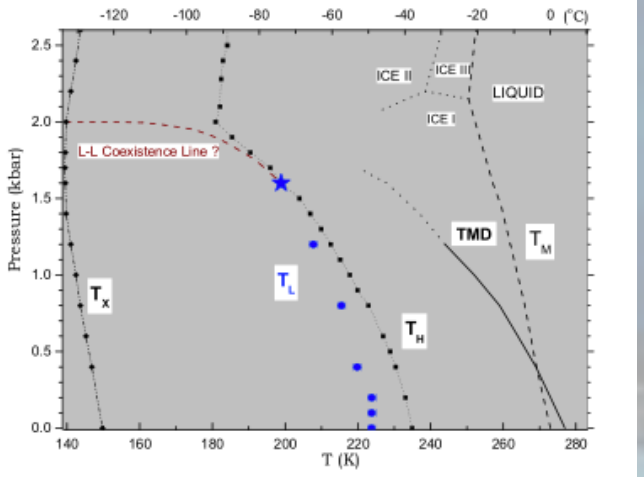


FIG. 3 (color online). The pressure dependence of the FS dynamic transition temperature, T_L, plotted in the P-T plane (solid circles). Also shown are the homogeneous nucleation temperature line, denoted as T_H [25], crystallization temperatures of amorphous solid water [26], denoted as T_X, and the temperature of maximum density line, denoted as TMD [27].

This experimental result further supports that the FS transition we observed at 225 K at ambient pressure is caused by the crossing of the Widom line in the one-phase region above the critical point [23].

Experiments: confinement

PRL 113, 215701 (2014) PHYSICAL REVIEW LETTERS week ending 21 NOVEMBER 2014

Experimental Evidence for a Liquid-Liquid Crossover in Deeply Cooled Confined Water

Antonio Cupane,* Margarita Fomina, and Irina Piazza
University of Palermo, Department of Physics and Chemistry, via Archirafi 36, 90123 Palermo, Italy

Judith Peters
Institut Laue Langevin, 71 avenue des Martyrs, F-38000 Grenoble, France,
Université Joseph Fourier, F-38041 Grenoble Cedex 9, France,
CNRS, CEA–Institut de Biologie Structurale, 71 avenue des Martyrs, 38000 Grenoble, France

Giorgio Schirò
CNRS–Institut de Biologie Structurale, 71 avenue des Martyrs, 38000 Grenoble, France
(Received 16 June 2014; published 21 November 2014)

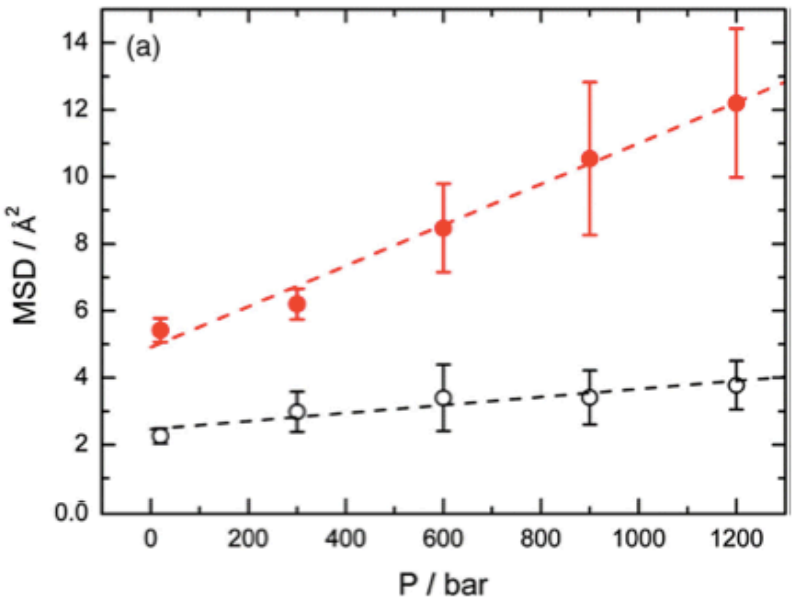
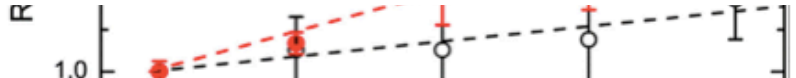


FIG. 2 (color online). (a) MSD and (b) $R(P) = \mathrm{MSD}(P)/\mathrm{MSD}(P = 20\ \mathrm{bar})$ as a function of pressure. Black open circles, $T = 210$ K; red circles, $T = 250$ K. Dashed lines are linear fits.



In conclusion, the pressure-dependent ENS data presented in this work shed light on the physical state of deeply cooled water confined in the 3D disordered SiO_2 matrix and, together with calorimetric data, provide new experimental evidence of the presence of a crossover in the behavior of confined water occurring at about 230 K. In fact, at 210 K water is in a liquid state, as shown by the fact that it exhibits an anomalous pressure effect (increasing MSD as pressure is increased) and confirmed by the thermodynamic transitions probed by DSC; however, the comparatively small pressure effect indicates the presence of an almost fully developed, locally icelike, hydrogen bond network less deformable by pressure and suggests that water is essentially in the LDL state. By increasing the temperature, a first-order-like liquid-liquid calorimetric transition is observed at ~230 K so that at 250 K water is essentially in the HDL state in which the local, tetrahedrally coordinated, hydrogen bond network is not fully developed and is therefore more deformable by a

Experiments: from the amorphous glass side

Water's second glass transition

Katrin Amann-Winkel[a,1], Catalin Gainaru[b,1], Philip H. Handle[a], Markus Seidl[a], Helge Nelson[b], Roland Böhmer[b], and Thomas Loerting[a]

[a]Institute of Physical Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria; and [b]Fakultät Physik, Technische Universität Dortmund, D-44221

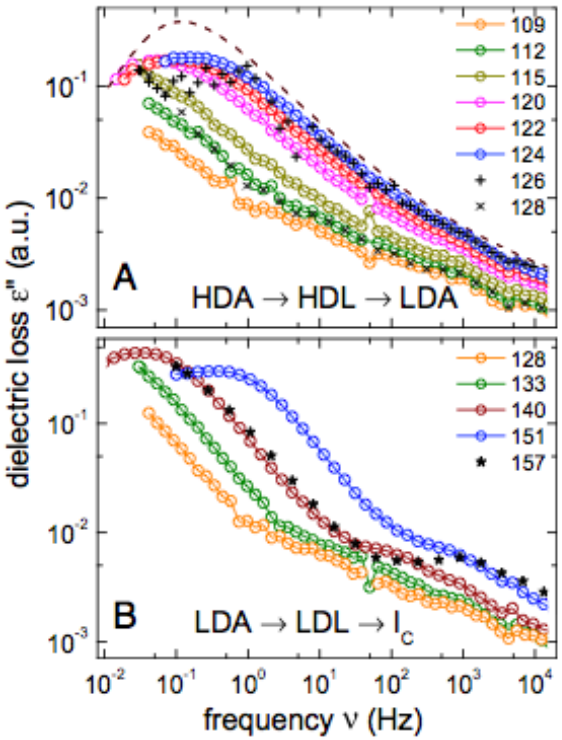


Fig. 3. Dielectric loss spectra of (*A*) HDL and (*B*) LDL are plotted as connected open symbols for several temperatures. (*A*) At 126 K the plusses reflect measurements acquired while HDL transforms to LDL. The crosses demonstrate that the relaxation in LDL is slower than in HDL. For comparison, the dielectric loss spectrum of ultraviscous glycerol (at $T = 196$ K, loss divided by 60) (44) is added (dashed line). (*B*) The transformation of LDL to cubic ice (stars) takes place above 151 K and is recognized from a shift of the spectra to lower frequencies.

The main experimental finding of the present work is the observation of two distinct glass transitions at ambient pressure, an observation ruling out a connection of water's "old" ambient-pressure glass transition at $T_{g,1} \sim 136$ K with the recently reported high-pressure glass transitions of water (12–15). That is, the single T_g scenario in Fig. 1*A* does not describe water. Instead, we suggest that the here-reported $T_{g,2}$ at ambient pressure connects with the high-pressure glass transition, whereas the liquid emanating from LDA is thermodynamically not continuously connected with high-pressure water, in accord with the double T_g scenario depicted in Fig. 1*B* and with simulations of the ST2 water model, but not of the SPC/E model (17). Just like in our experiments, ST2 water shows the low-pressure glass transition

Relevance to protein (glass transition) ?

Observation of fragile-to-strong dynamic crossover in protein hydration water

S.-H. Chen*†, L. Liu*, E. Fratini‡, P. Baglioni‡, A. Faraone§¶, and E. Mamontov§¶

partment of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; ‡Department of Chemistry and Consorzio runiversitario per lo Sviluppo dei Sistemi a Grande Interfase (CSGI), University of Florence, via della Lastruccia 3, 50019 Florence, Italy; §NIST Center for tron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-8562; and ¶Department of Materials Science and Engineering, ersity of Maryland, College Park, MD 20742-2115

municated by H. Eugene Stanley, Boston University, Boston, MA, March 28, 2006 (received for review March 11, 2006)

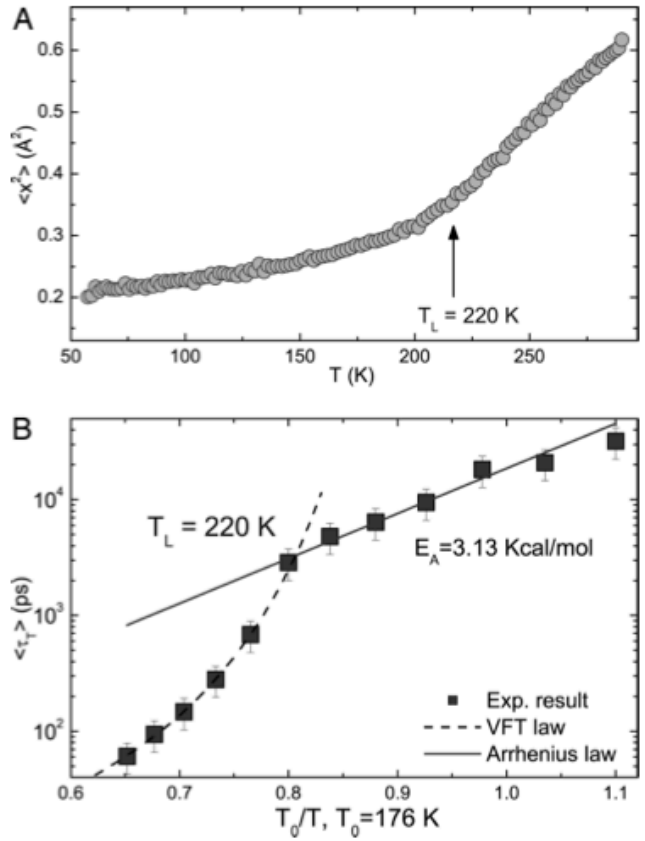


Fig. 3. Evidence for the dynamic transition. (*A*) The temperature dependence of the mean-squared atomic displacement of the hydrogen atom at 2-ns time scale measured by an elastic scan with resolution of 0.8 μeV. (*B*) Temperature dependence of the average translational relaxation times plotted in $\log(\langle \tau_T \rangle)$ vs. T_0/T, where T_0 is the ideal glass transition temperature. Here, there is a clear and abrupt transition from a Vogel–Fulcher–Tammann law at high temperatures to an Arrhenius law at low temperatures, with the fitted crossover temperature T_L = 220 K and the activation energy E_A = 3.13 kcal/mol extracted from the Arrhenius part indicated in the figure.

water at ambient pressure (15). The Widom line is originated from the existence of the second critical point of water and is the extension of the liquid–liquid coexistence line into the one-phase region. Therefore, our observation of the FSC at ambient pressure implies that there may be a liquid–liquid phase transition line in the protein hydration water at elevated pressures. This dynamic crossover, when crossing the Widom line, causes the layer of the water surrounding a protein to change from the "more fluid" high-density liquid form (which induces the protein to adopt more flexible conformational substates) to the "less

Relevance to protein (glass transition) ?

Glass Transition in Biomolecules and the Liquid-Liquid Critical Point of Water

Pradeep Kumar,[1] Z. Yan,[1] L. Xu,[1] M. G. Mazza,[1] S. V. Buldyrev,[2,1] S.-H. Chen,[3] S. Sastry,[4] and H. E. Stanley[1]

[1]*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215, USA*
[2]*Department of Physics, Yeshiva University, 500 West 185th Street, New York, New York 10033, USA*
[3]*Nuclear Science and Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[4]*Javaharlal Nehru Center for Advanced Scientific Research, Jakur Campus, Bangalore, 560061, India*
(Received 29 May 2006; published 27 October 2006)

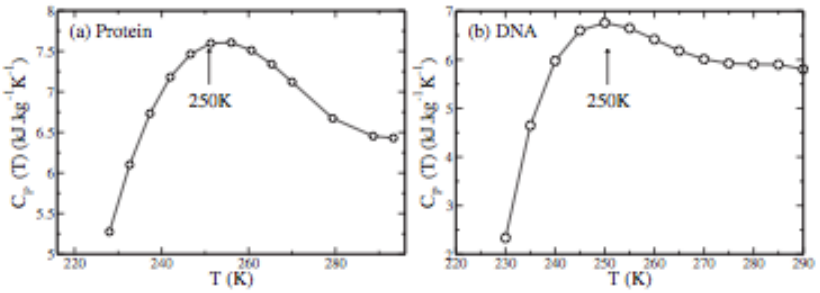


FIG. 2. The specific heat of the combined system (a) lysozyme and water and (b) DNA and water display maxima at 250 ± 10 and 250 ± 12 K, respectively, which are coincident within the error bars with the temperature T_p where the crossover in the behavior of $\langle x^2 \rangle$ is observed.

hydration water thermodynamics [Fig. 2(a)]. Thus, our results are consistent with the possibility that the protein glass transition is related to the Widom line (and hence to the hypothesized liquid-liquid critical point). Crossing the Widom line corresponds to a continuous but rapid transition of the properties of water from those resembling the properties of a local HDL structure for $T > T_W(P)$ to those resembling the properties of a local LDL structure for $T < T_W(P)$ [15,20]. A consequence is the expectation that the

Recent two-state models with LL CP

NATURE COMMUNICATIONS | ARTICLE

Understanding water's anomalies with locally favoured structures

John Russo & Hajime Tanaka

Affiliations | Contributions | Corresponding author

Nature Communications **5**, Article number: 3556 | doi:10.1038/ncomms4556
Received 03 September 2013 | Accepted 05 March 2014 | Published 02 April 2014

Spatially inhomogeneous bimodal inherent structure of simulated liquid water

K. T. Wikfeldt,[a] A. Nilsson[ab] and L. G. M. Pettersson*[a]

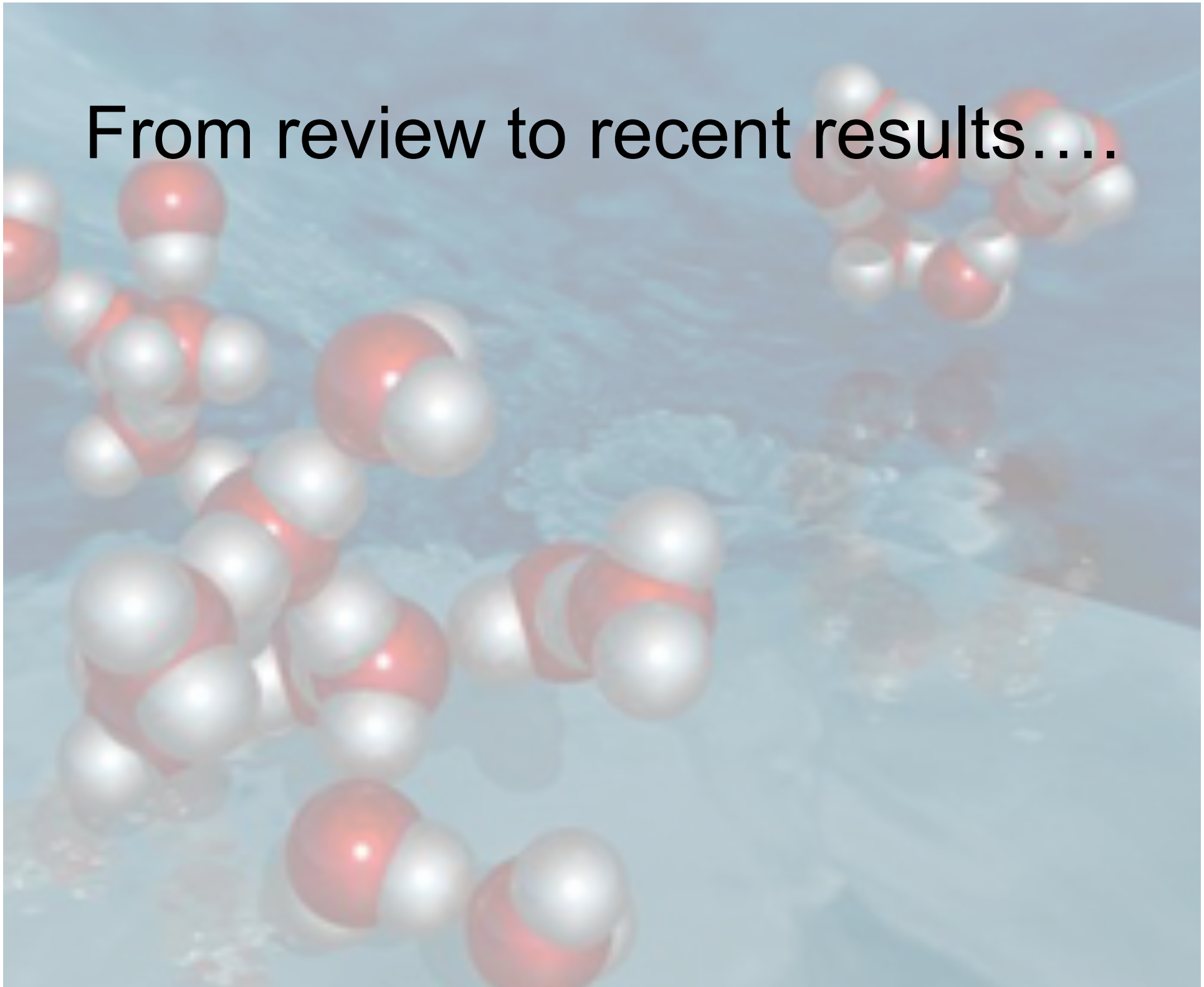
Received 24th June 2011, Accepted 26th August 2011
DOI: 10.1039/c1cp22076d

Mixturelike Behavior Near a Liquid-Liquid Phase Transition in Simulations of Supercooled Water

Megan J. Cuthbertson and Peter H. Poole
Department of Physics, St. Francis Xavier University, Antigonish, NS, B2G 2W5, Canada
(Received 18 December 2010; revised manuscript received 7 February 2011; published 17 March 2011)

Two-state thermodynamics of the ST2 model for supercooled water

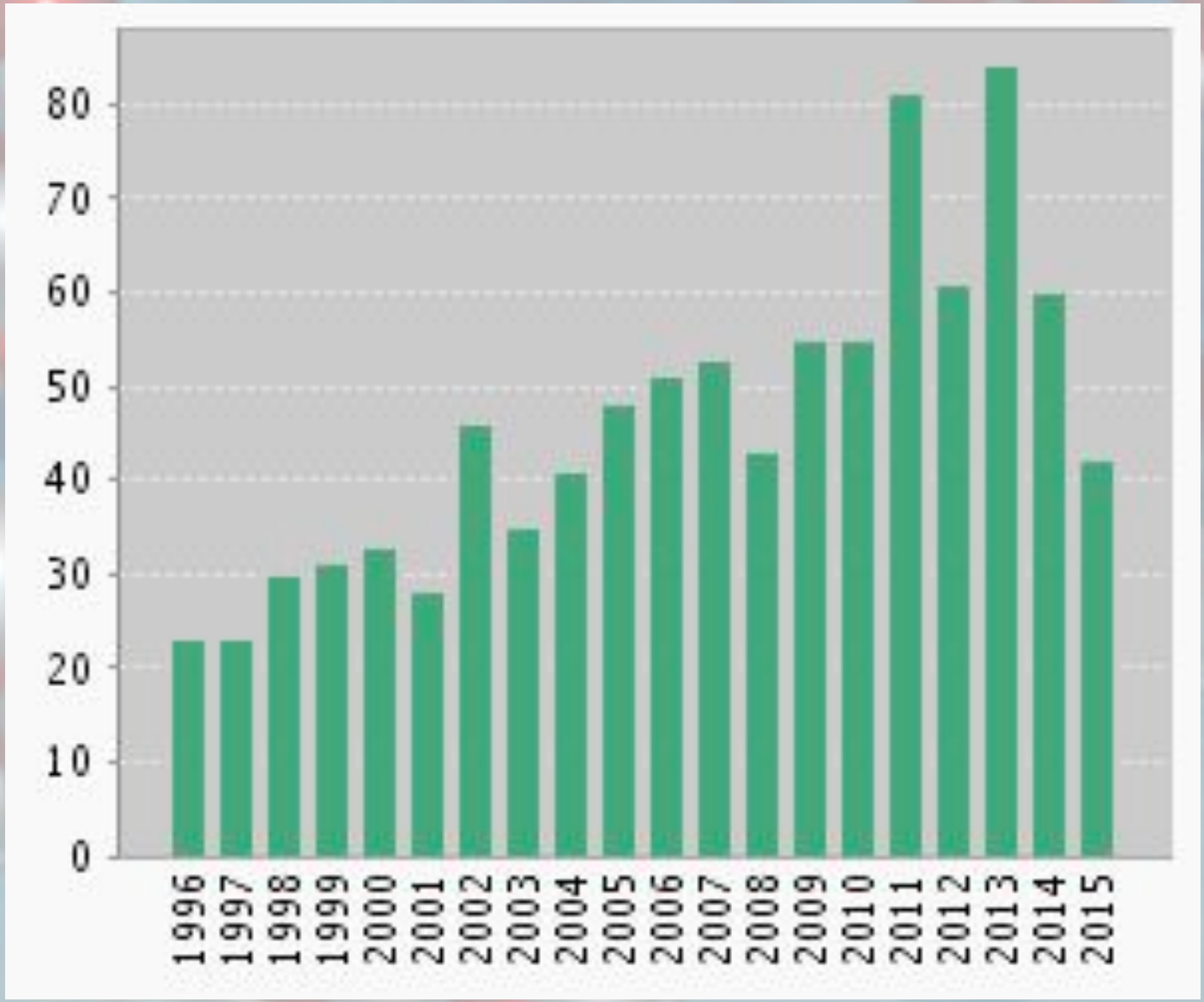
Vincent Holten,[1] Jeremy C. Palmer,[2] Peter H. Poole,[3] Pablo G. Debenedetti,[2] and Mikhail A. Anisimov[1,a)]
[1]*Institute for Physical Science and Technology and Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, USA*
[2]*Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, USA*
[3]*Department of Physics, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada*


From review to recent results….

PHASE-BEHAVIOR OF METASTABLE WATER

By: POOLE, PH; SCIORTINO, F; ESSMANN, U; et al.

NATURE Volume: 360 Issue: 6402 Pages: 324-328 Published: NOV 26 1992



AIP | The Journal of Chemical Physics

The putative liquid-liquid transition is a liquid-solid transition in atomistic models of water

David T. Limmer[1] and David Chandler[1,a)]

+ VIEW AFFILIATIONS

a) Electronic mail: chandler@berkeley.edu.

J. Chem. Phys. **135**, 134503 (2011); http://dx.doi.org/10.1063/1.3643333

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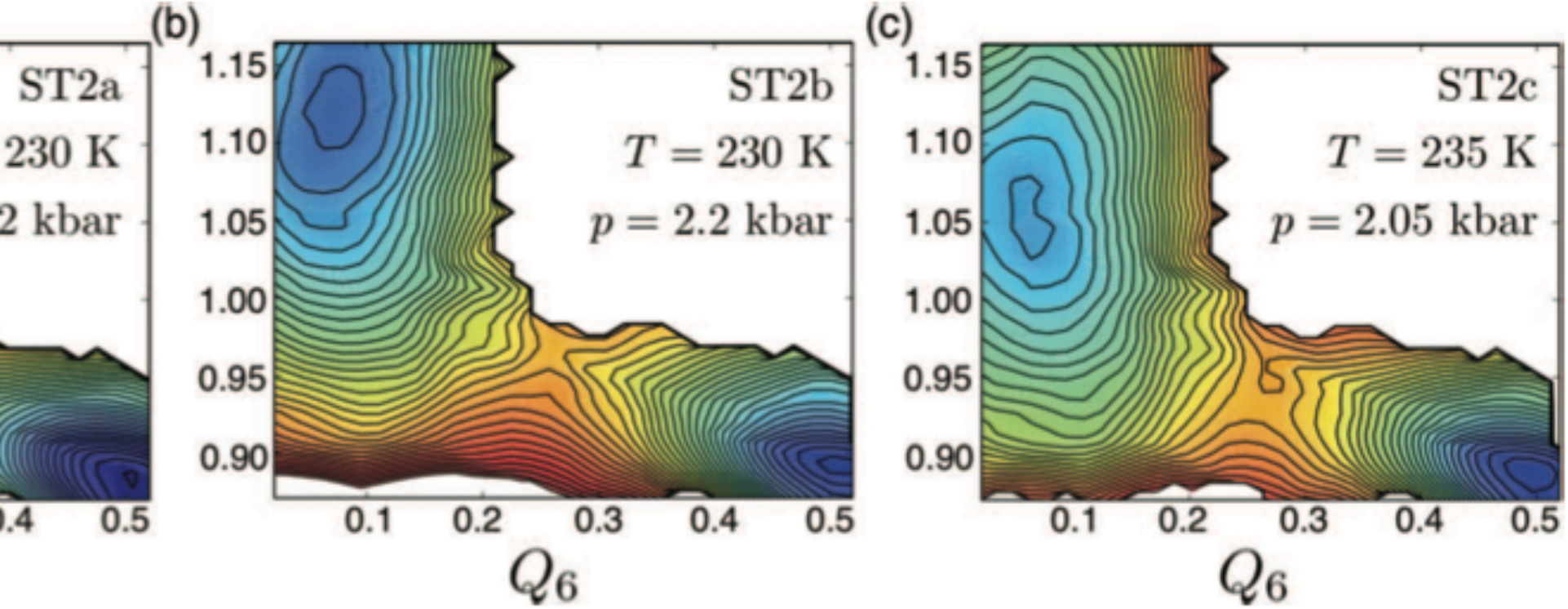
..... This result excludes the possibility of the proposed liquid-liquid critical point for the models we have studied. Further, we argue that behaviors others have attributed to a liquid-liquid transition in water and related systems are in fact reflections of transitions between liquid and crystal.



three variants of the ST2 model at temperatures where others report evidence of liquid-liquid coexistence for ence require changes in convexity, as re-weighting through Eq. (2) in that case can produce two basins of equal he value $p + \Delta p$ at which there is equal statistical weight. For the three variants considered, the only changes een a liquid (low Q_6) and a crystal (high Q_6). (a) Free energy for the ST2a variant at $T = 230$ K and $p = 2.2$ variant at $T = 230$ K and $p = 2.2$ kbar with $N = 216$. (c) Free energy for the ST2c variant at $T = 235$ K and p of the different variants. Contour lines are separated by $1.5 k_B T$ and statistical errors over the surfaces average ge with system size. For example, as N grows, the mean value of Q_6 in the liquid basin will vanish as $1/N^{1/2}$,

Response:

Prove that Chander's calculations
are wrong (Poole, Debenedetti and coworkers)

Better understand the connection between
crystal formation and liquid-liquid transition

Metastable liquid–liquid transition in a molecular model of water

Jeremy C. Palmer, Fausto Martelli, Yang Liu, Roberto Car, Athanassios Z. Panagiotopoulos & Pablo G. Debenedetti

Affiliations | Contributions | Corresponding author

Nature **510**, 385–388 (19 June 2014) | doi:10.1038/nature13405

Prove that Chander's calculations are wrong (Poole, Debenedetti and coworkers)

Free energy surface of ST2 water near the liquid-liquid phase transition

Peter H. Poole, Richard K. Bowles, Ivan Saika-Voivod, and Francesco Sciortino

Citation: The Journal of Chemical Physics **138**, 034505 (2013); doi: 10.1063/1.4775738

Liquid-liquid transition in ST2 water

Yang Liu, Jeremy C. Palmer, Athanassios Z. Panagiotopoulos, and Pablo G. Debenedetti

Citation: The Journal of Chemical Physics **137**, 214505 (2012); doi: 10.1063/1.4769126

Nanoscale Dynamics of Phase Flipping in Water near its Hypothesized Liquid-Liquid Critical Point

T. A. Kesselring[1], G. Franzese[2], S. V. Buldyrev[3], H. J. Herrmann[1,4] & H. E. Stanley[5]

Study of the ST2 model of water close to the liquid–liquid critical point

Francesco Sciortino,[a] Ivan Saika-Voivod[b] and Peter H. Poole[c]

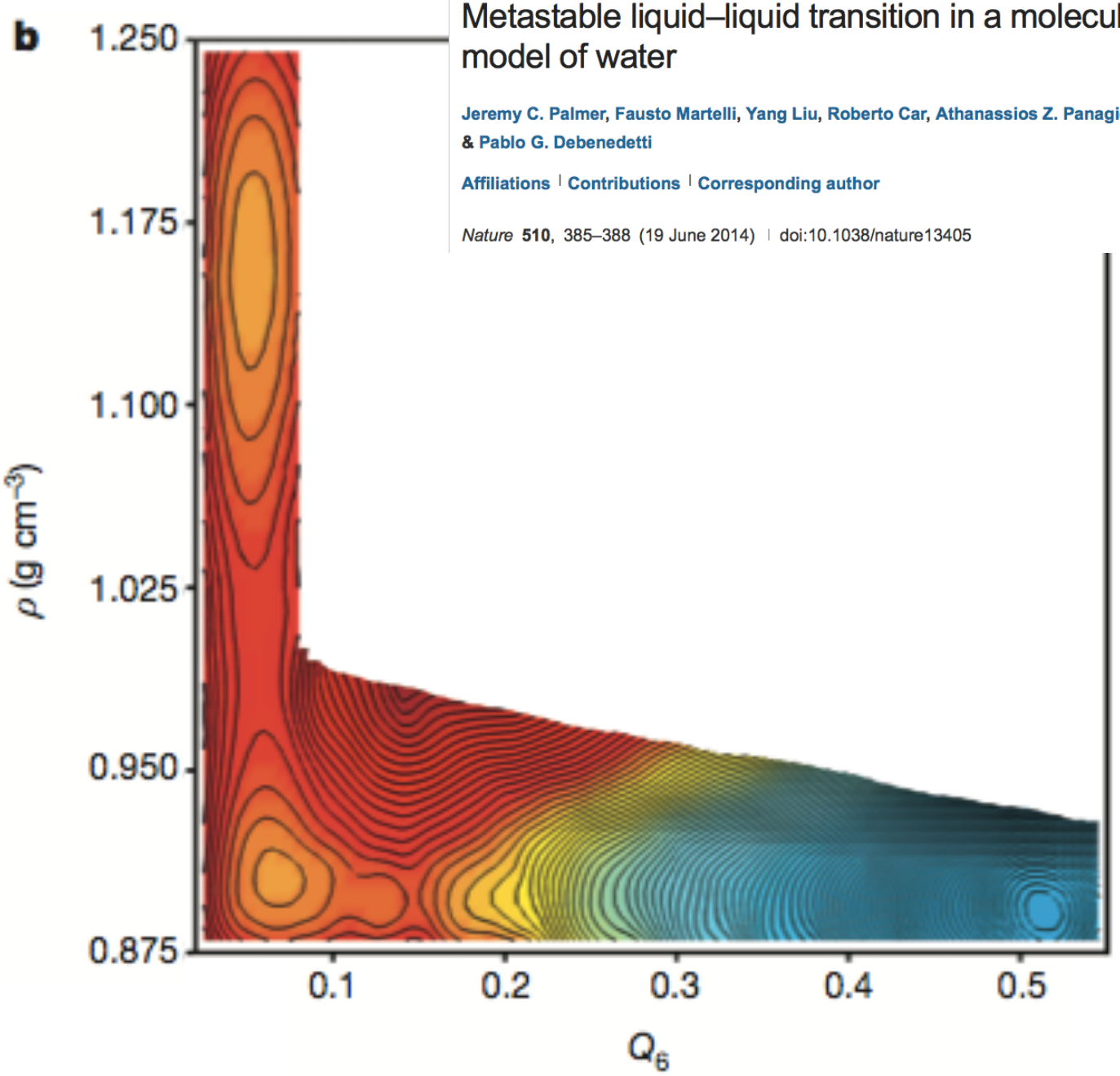
Received 15th July 2011, Accepted 5th September 2011
DOI: 10.1039/c1cp22316j

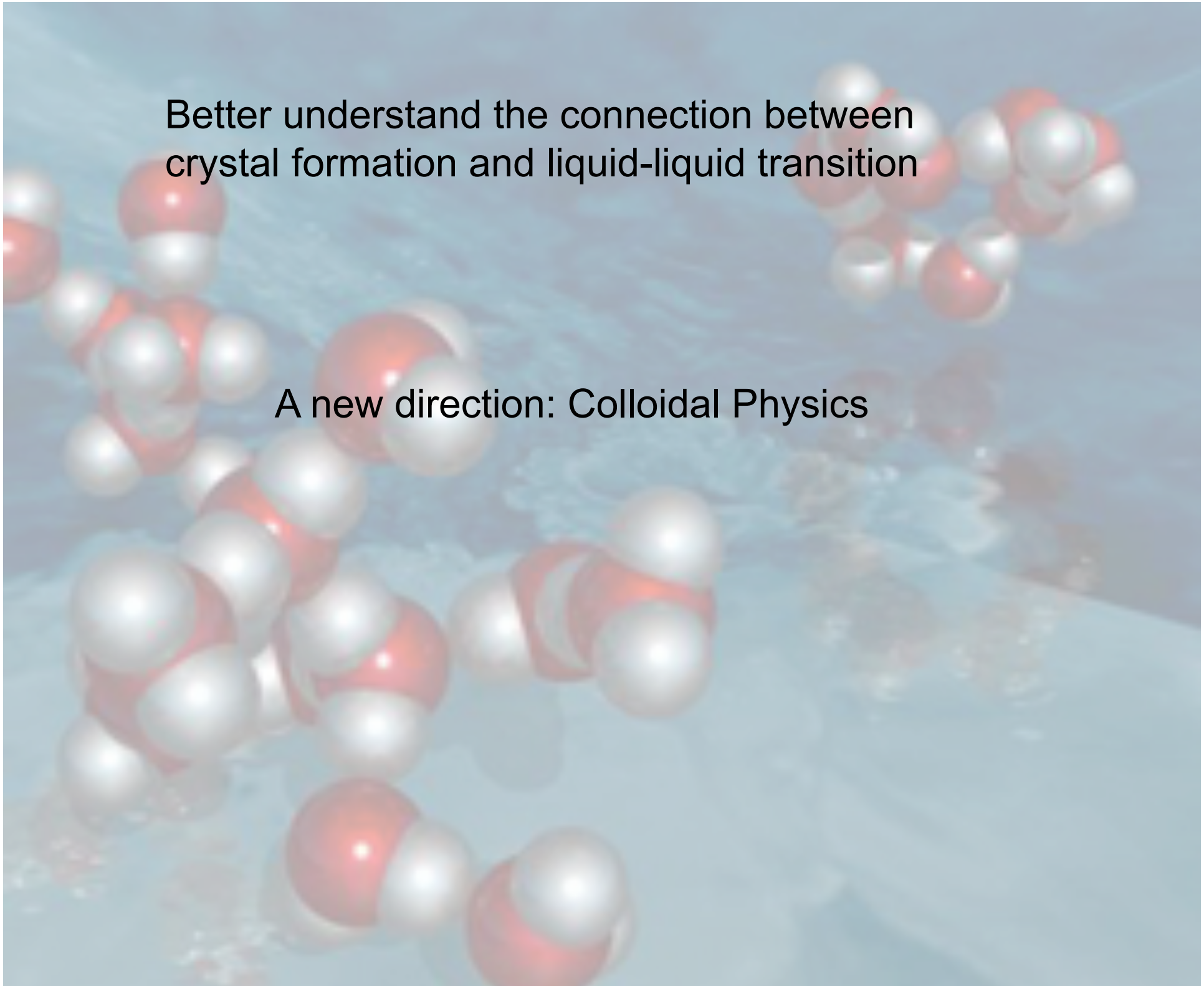
Metastable liquid–liquid transition in a molecular model of water

Jeremy C. Palmer, Fausto Martelli, Yang Liu, Roberto Car, Athanassios Z. Panagiotopoulos & Pablo G. Debenedetti

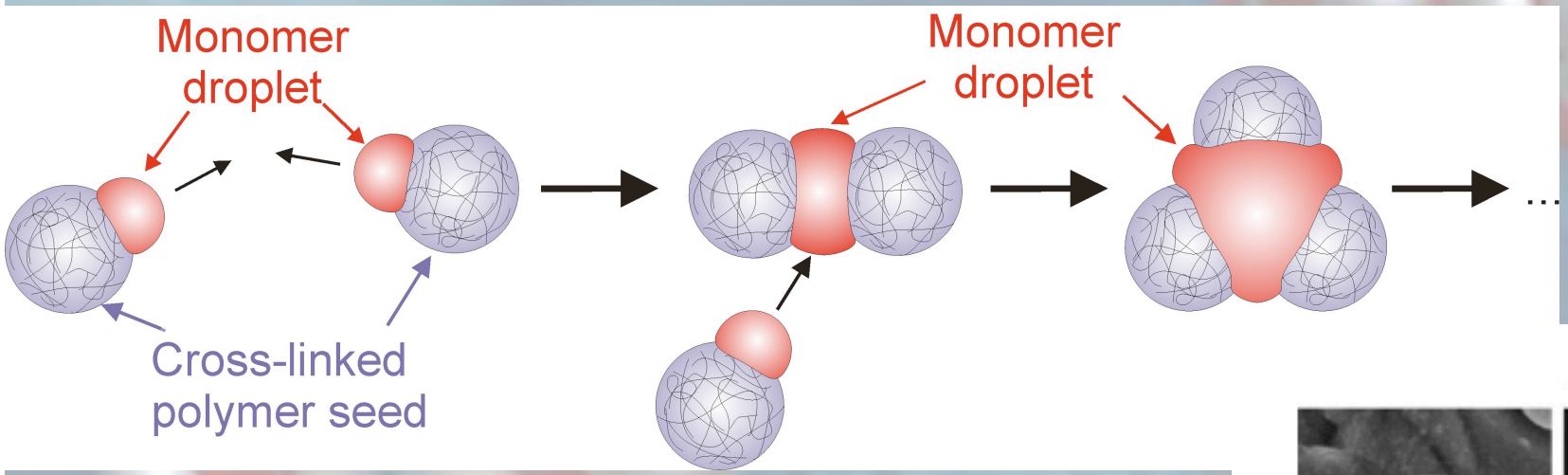
Affiliations | Contributions | Corresponding author

Nature **510**, 385–388 (19 June 2014) | doi:10.1038/nature13405




Better understand the connection between
crystal formation and liquid-liquid transition
A new direction: Colloidal Physics

Colloidal Molecules

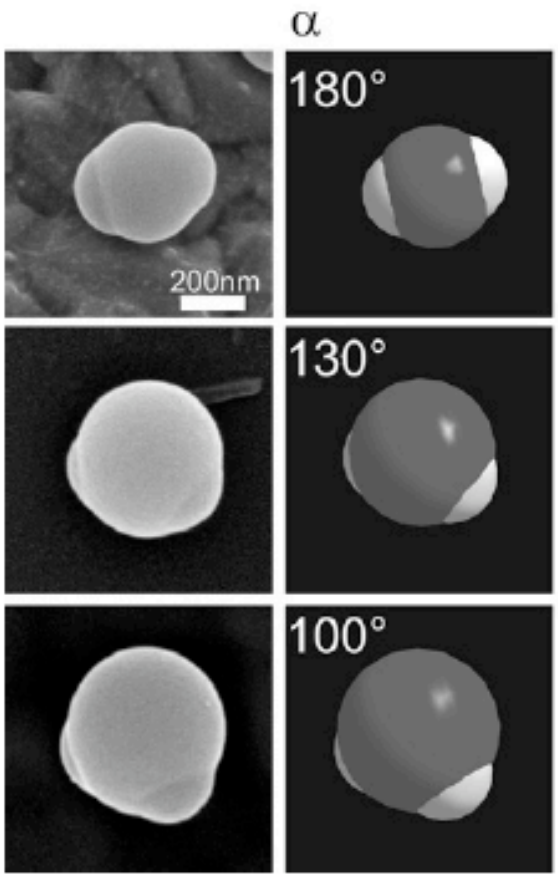


Monomer swollen cross-linked polymer particles

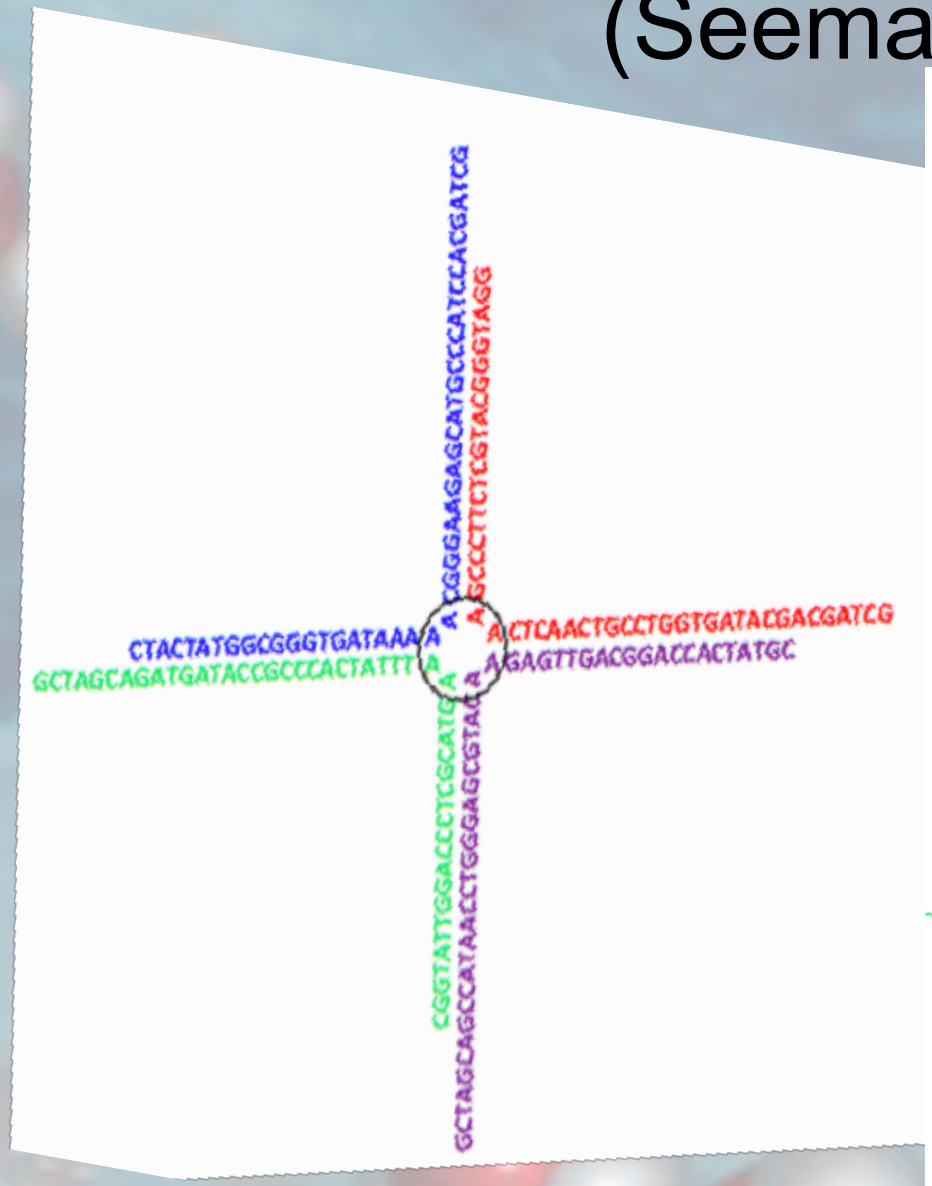
Colloidal molecules with well-controlled bond angles†

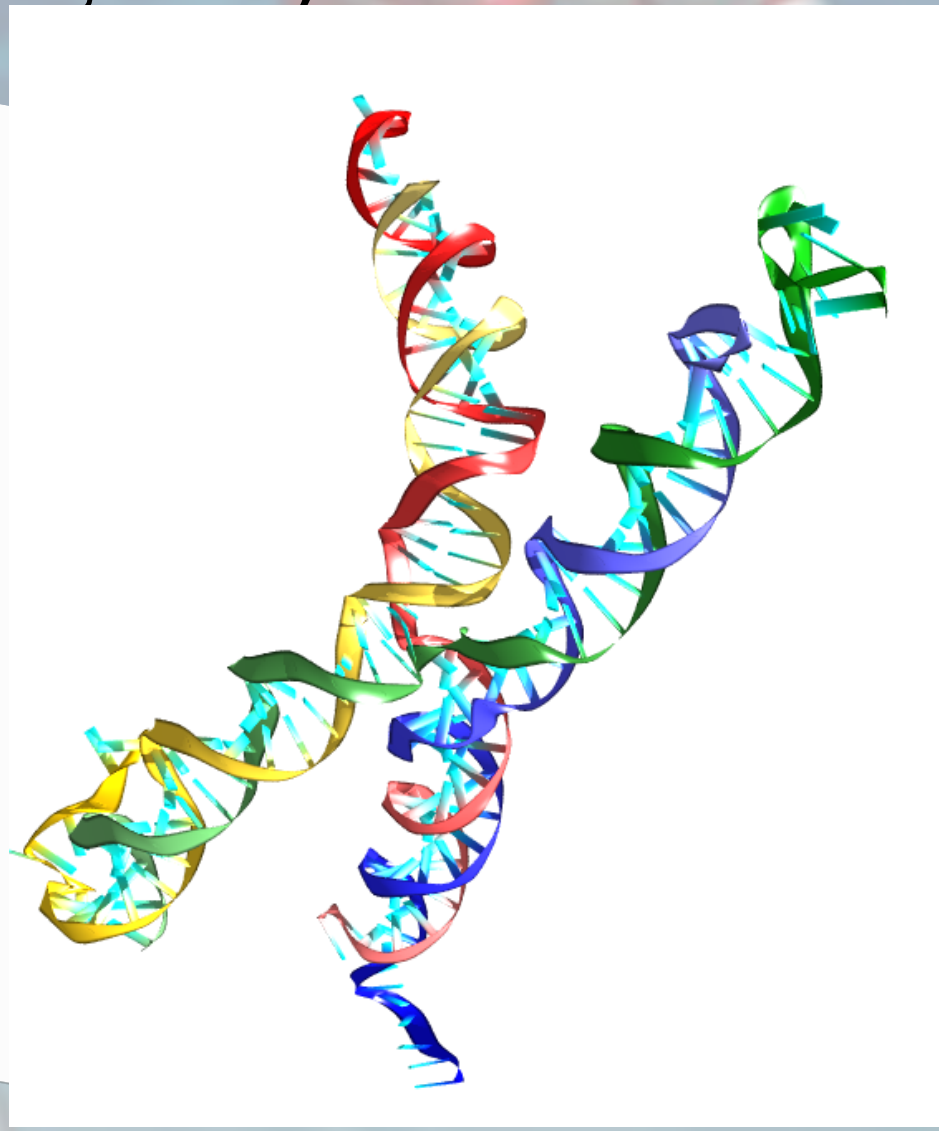
Daniela J. Kraft,* Jan Groenewold and Willem K. Kegel*

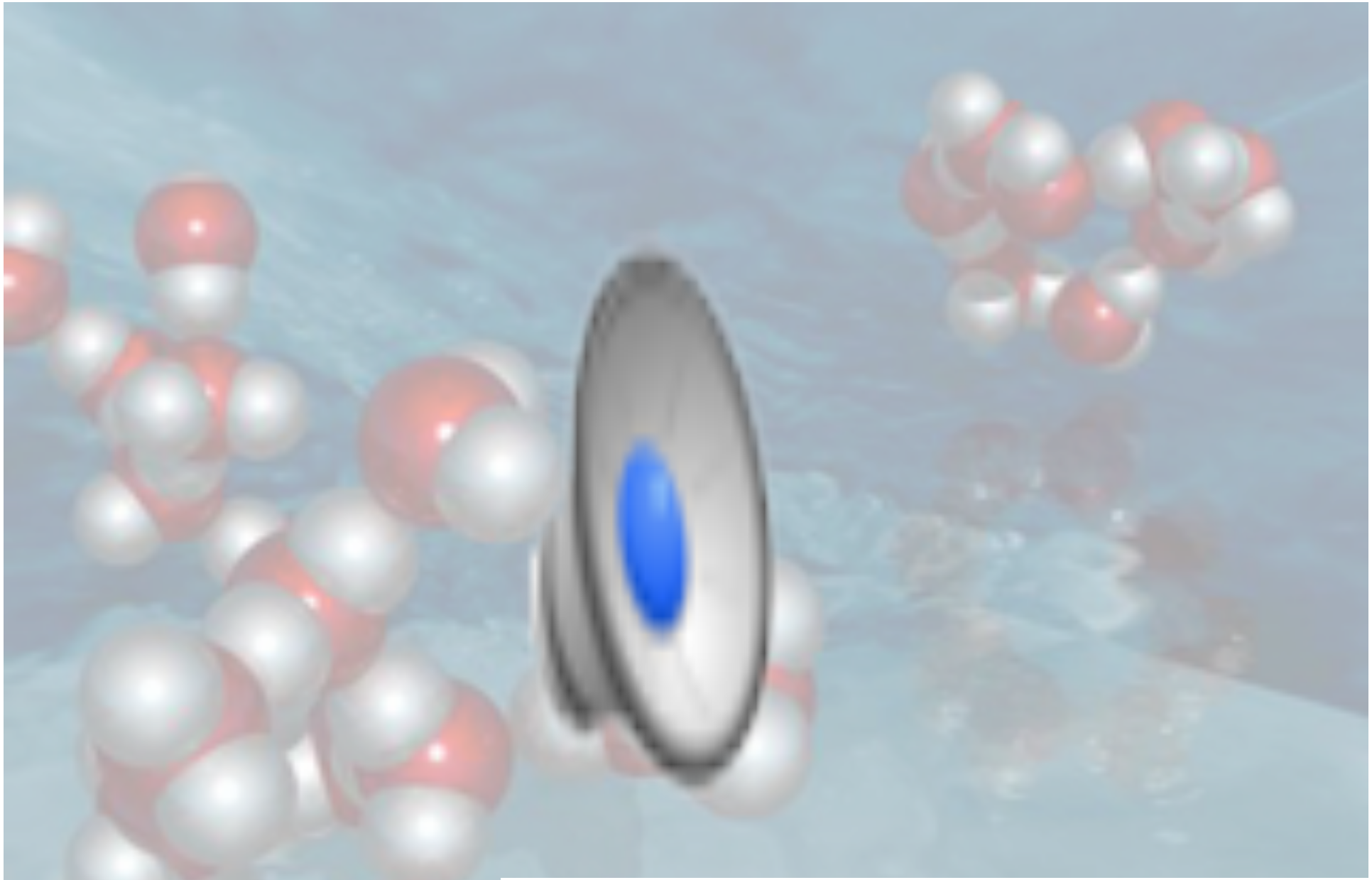
Soft Matter, 2009, **5**, 3823–3826 | 3823



How to make a “flexible” tetrahedral fluid (Seeman, Luo)



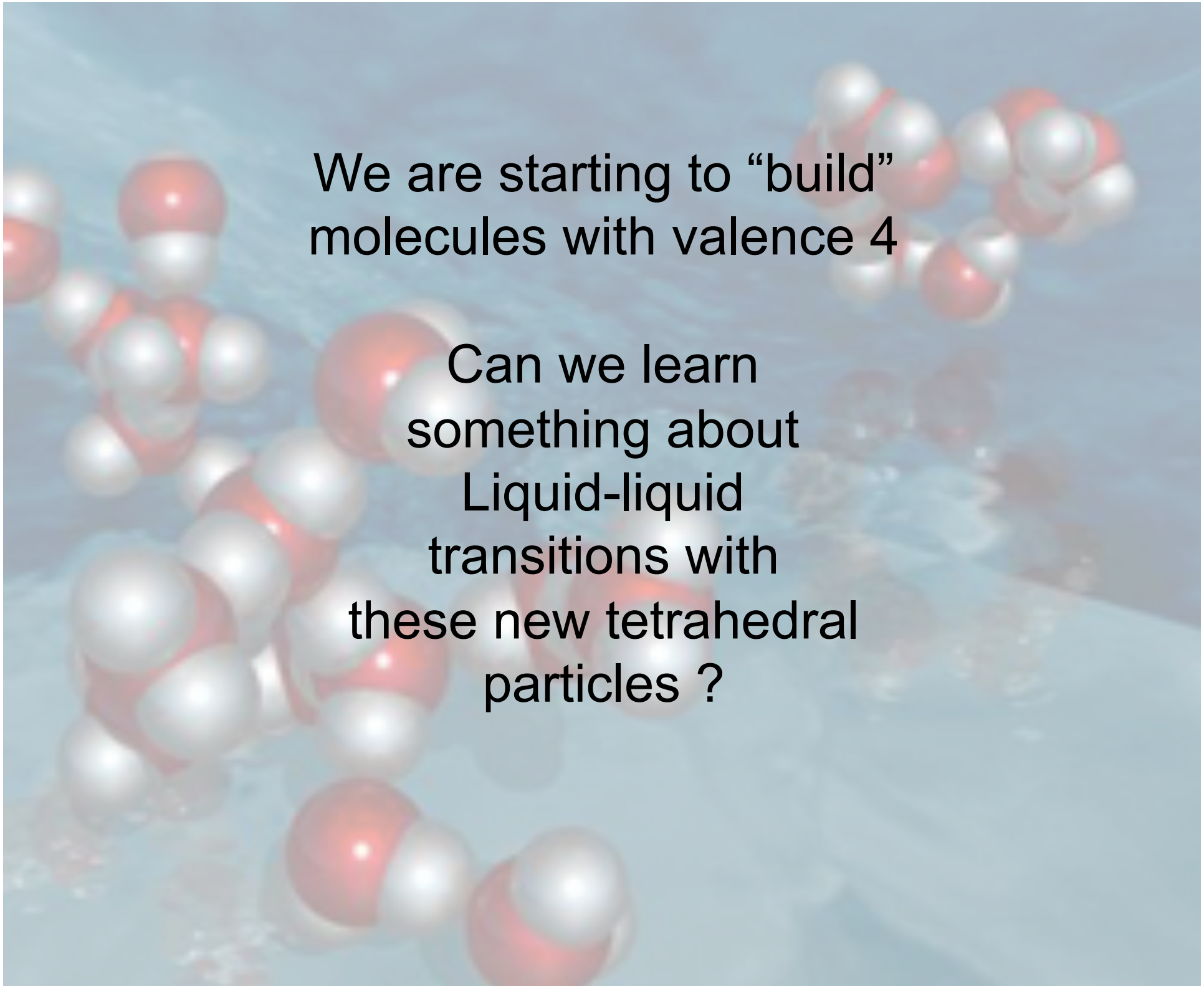




Phase behavior and critical activated dynamics of limited-valence DNA nanostars

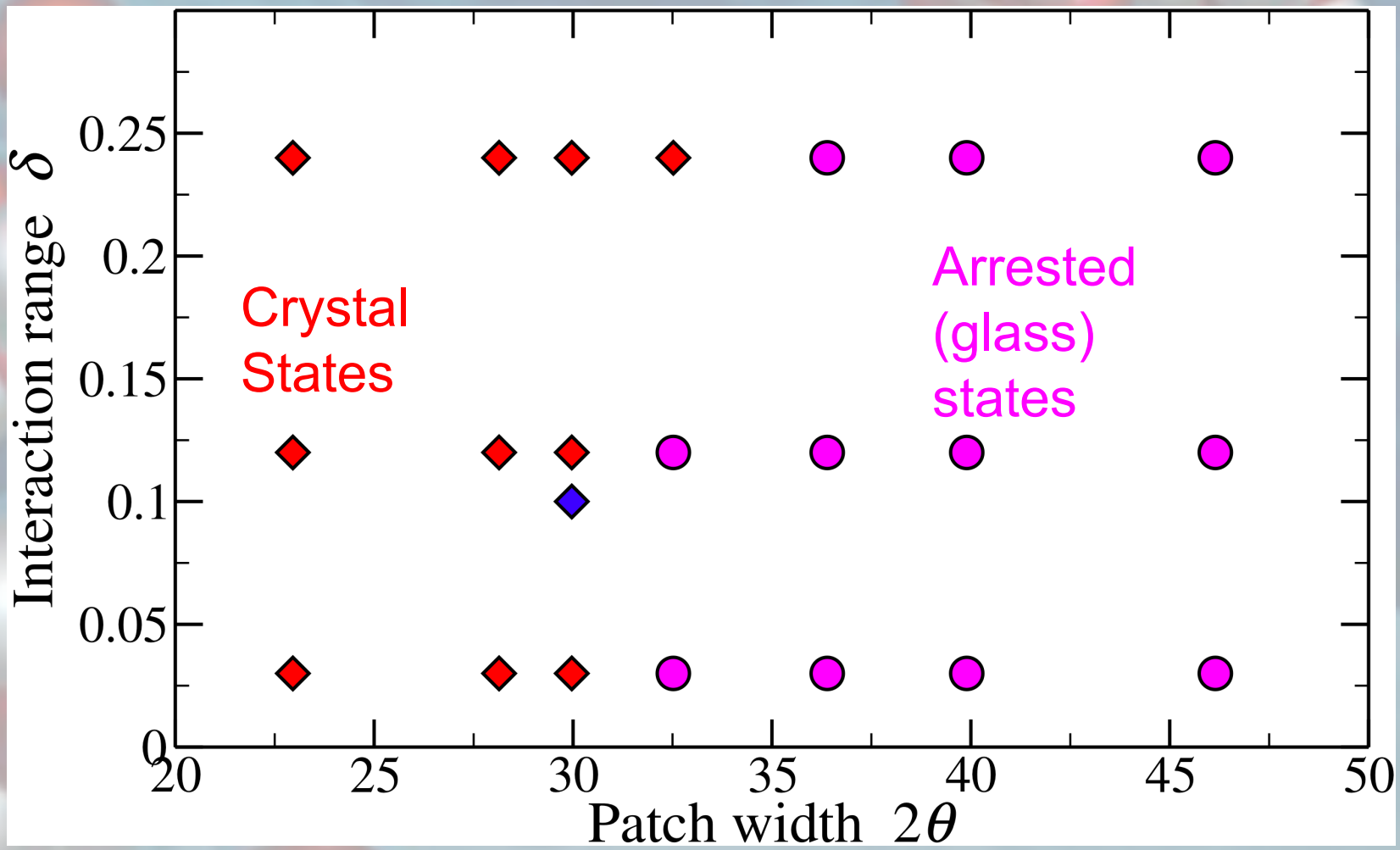
Silvia Biffi[a], Roberto Cerbino[a], Francesca Bomboi[b,c], Elvezia Maria Paraboschi[a], Rosanna Asselta[a], Francesco Sciortino[b,1], and Tommaso Bellini[a,1]

[a]Department of Medical Biotechnology and Translational Medicine, Universitá degli Studi di Milano, I-20133 Milan, Italy; [b]Department of Physics, Sapienza, Universitá di Roma, I-00185 Rome, Italy; and [c]Department of Physics, Università degli Studi Roma Tre-Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia, I-00146 Rome, Italy


We are starting to “build”
molecules with valence 4
Can we learn
something about
Liquid-liquid
transitions with
these new tetrahedral
particles ?

What is controlling crystallization in an open diamond structure

Which model parameters ?



Small angle widths favor crystallization !

Why ?

Flavio Romano, Eduardo Sanz and FS

Crystallization of tetrahedral patchy particles insilico

J. Chem. Phys. 134, 174502 (2011)

ΔS….

$\Delta S = S_{xt} - S_{fluid}$

S_{xt} --- Vibrational Entropy

S_{fluid} --- Vibrational Entropy + “Configurational Entropy”

The crystal is stable when it has a vibrational entropy sufficiently large to compensate for the configurational entropy of the fully bonded disordered fluid network !

The more directional the bonding is, the larger is $S_{xt} - S_{fluid}$

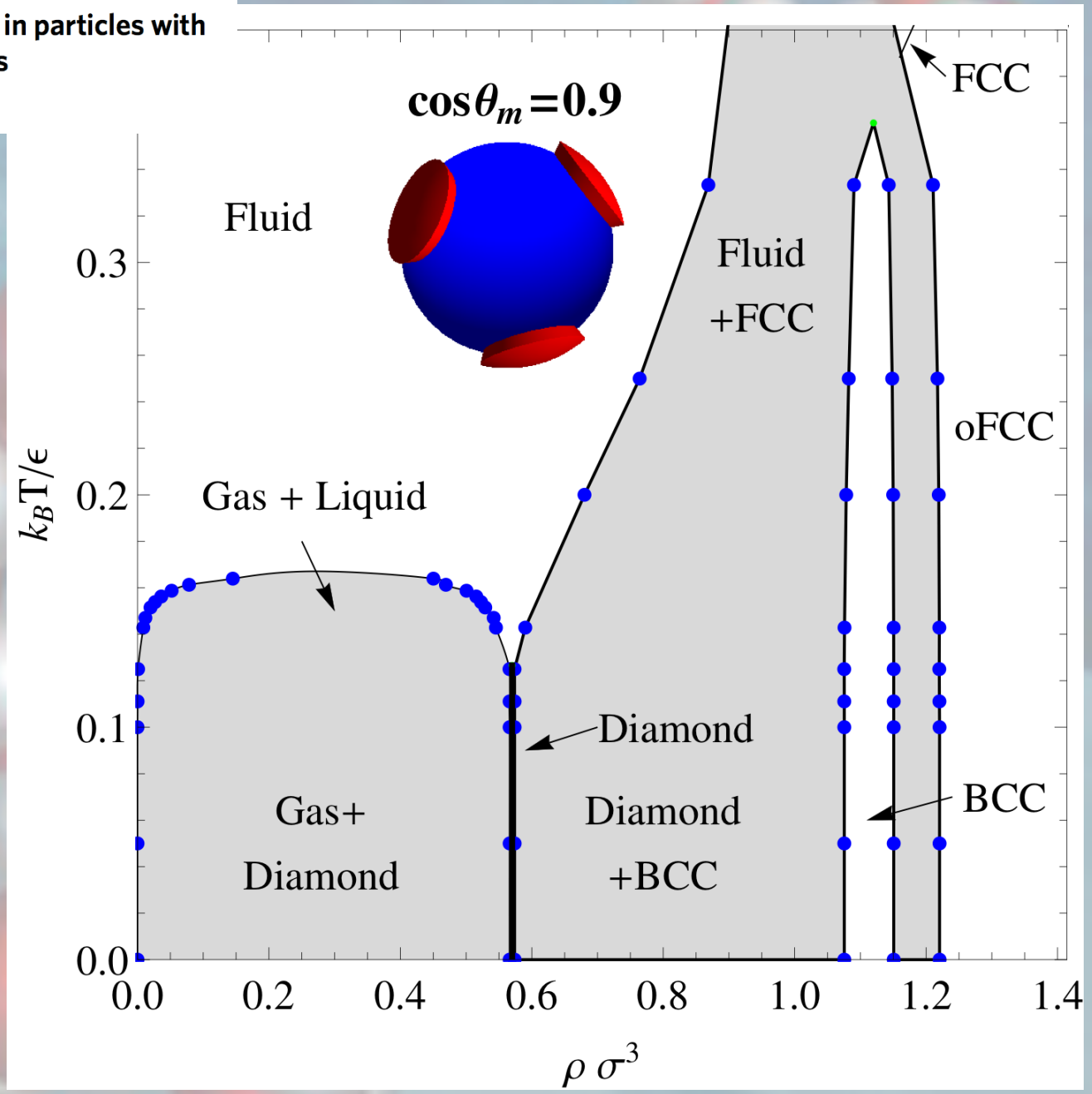
This suggests that, going in the opposite direction, adding flexibility can EVEN change sign to $S_{xt} - S_{fluid}$ and provide stability to the liquid phase !!!!

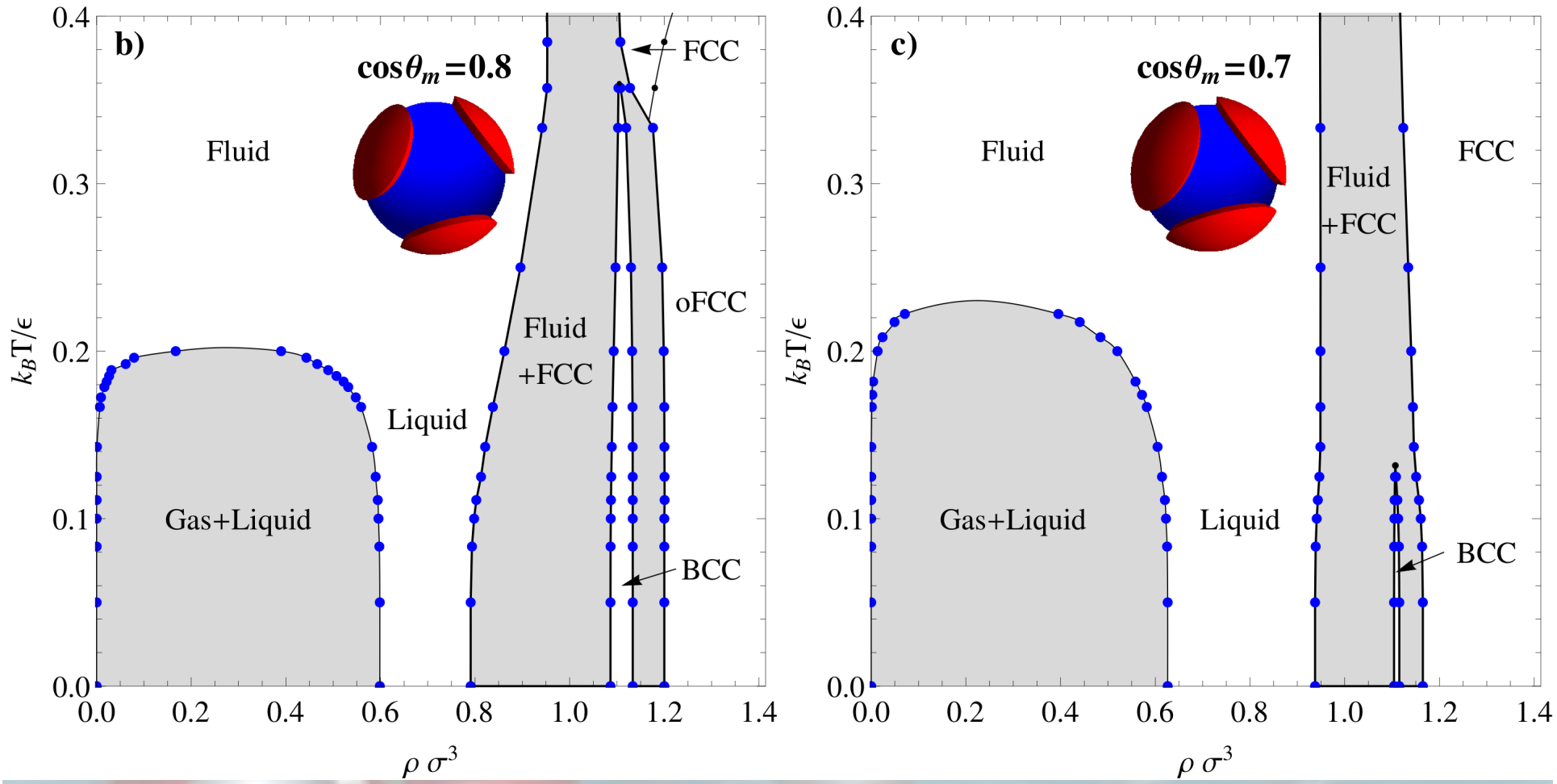
nature physics
LETTERS
PUBLISHED ONLINE: XX MONTH XXXX | DOI: 10.1038/NPHYS2693

Liquids more stable than crystals in particles with limited valence and flexible bonds

Frank Smallenburg* and Francesco Sciortino

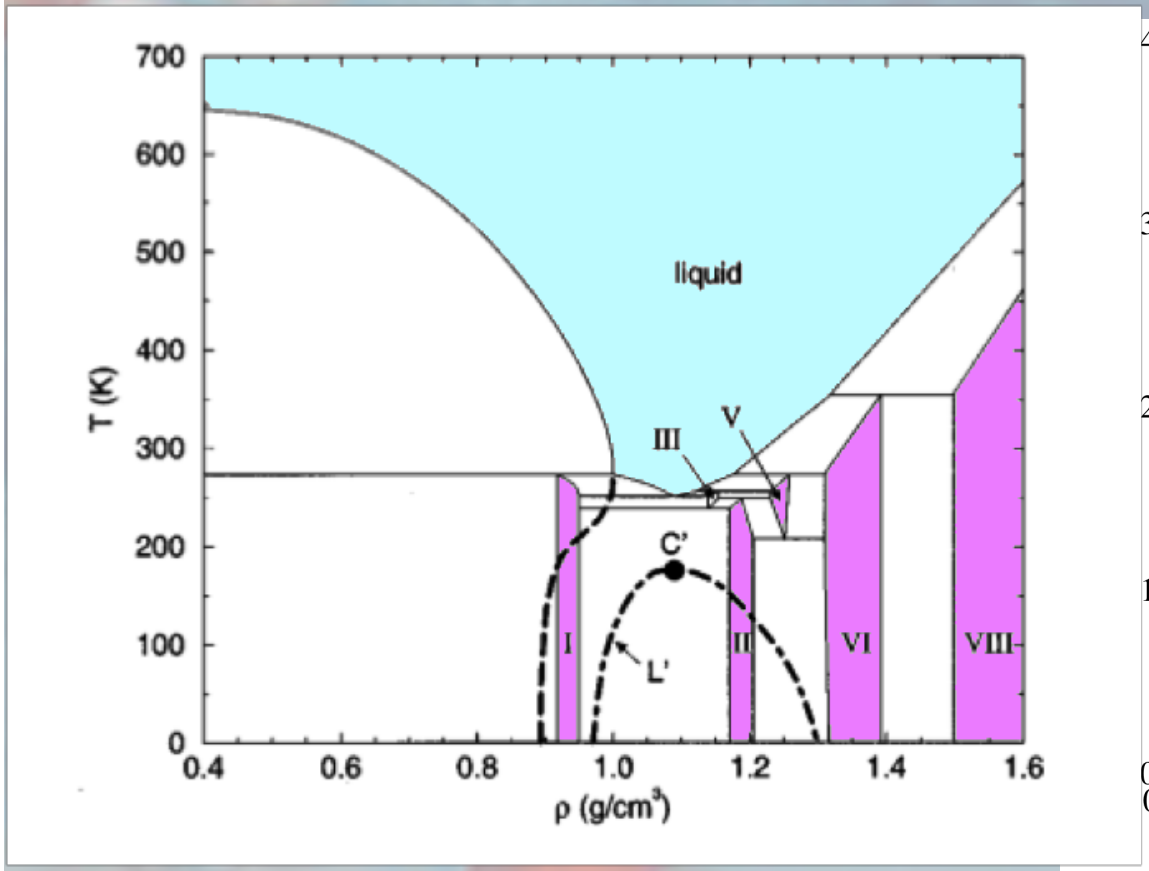
No liquid phase at low T

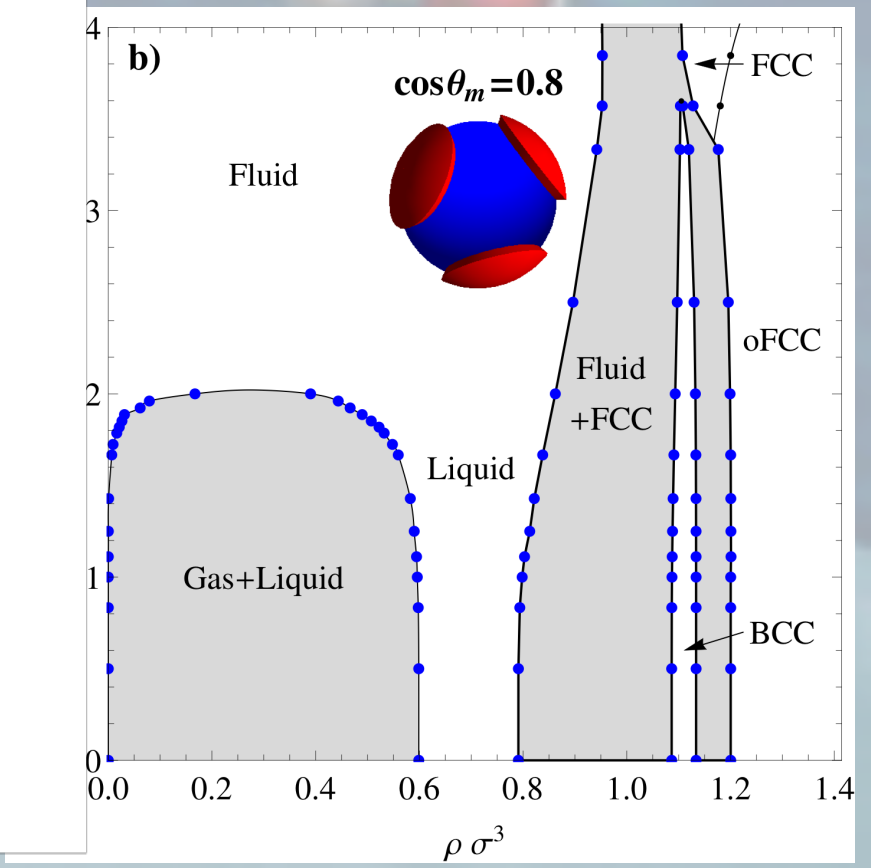




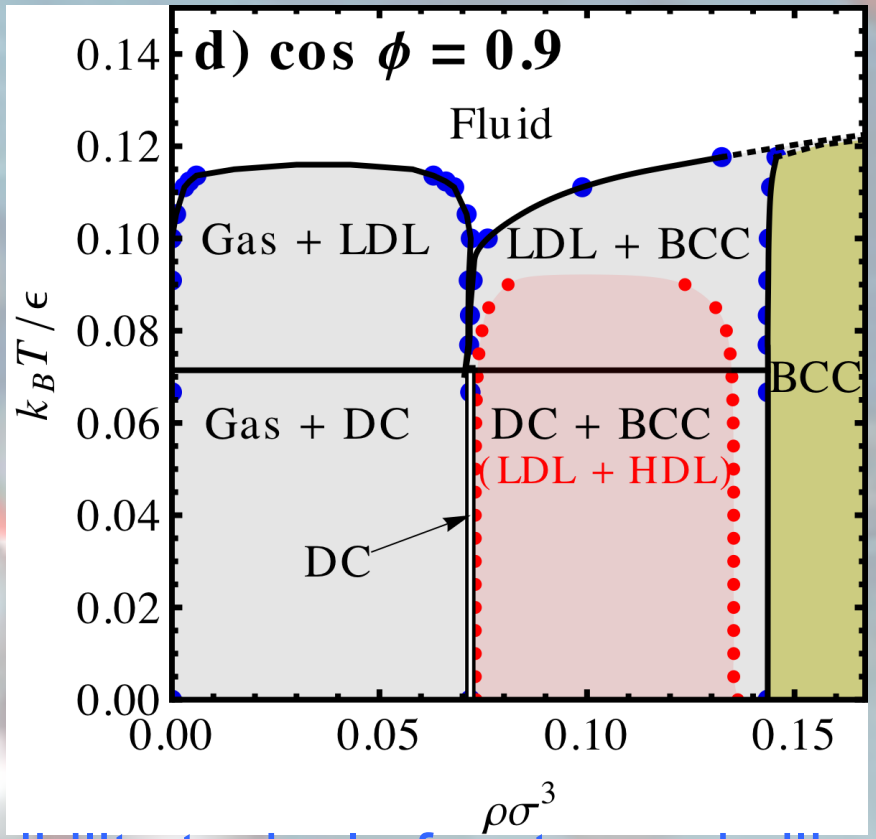
Liquid phase stable down to low T !!!!!!

Can we continuously go from a metastable LL critical point to a stable LL critical point by destabilizing the crystal ?





Role of the bond flexibility on the phase behavior (at a fixed intermediate softness)



"directional bonds"

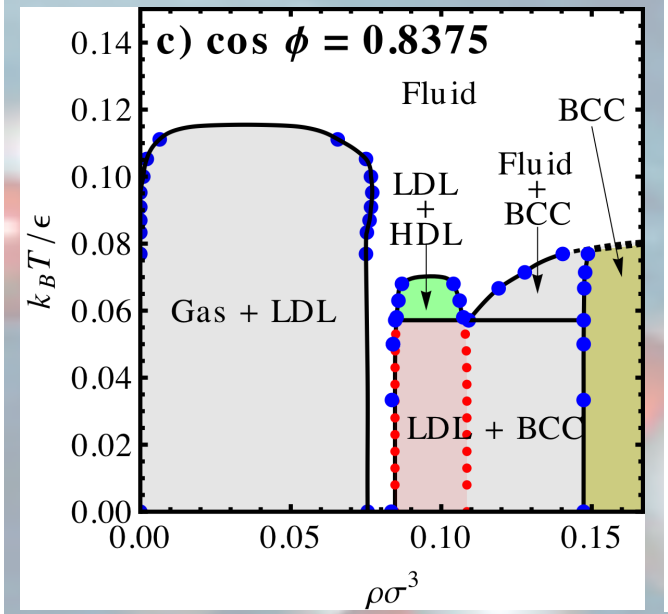
(flexibility typical of water and silicon)

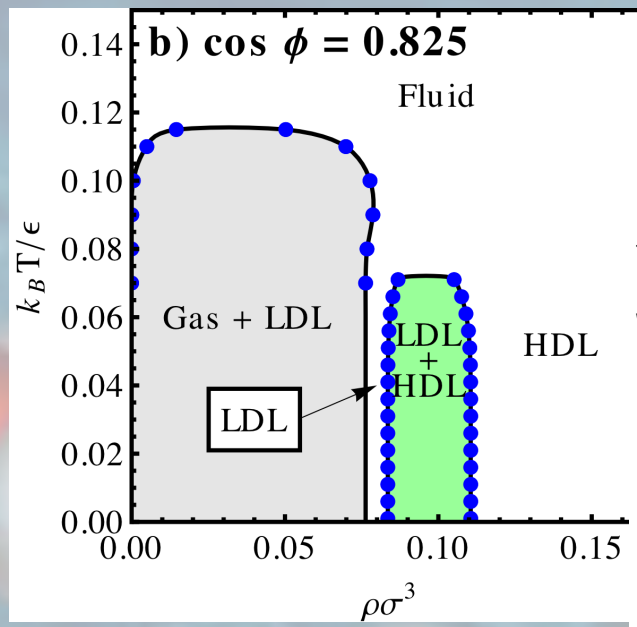
nature physics
LETTERS
PUBLISHED ONLINE: XX MONTH XXXX | DOI: 10.1038/NPHYS3030

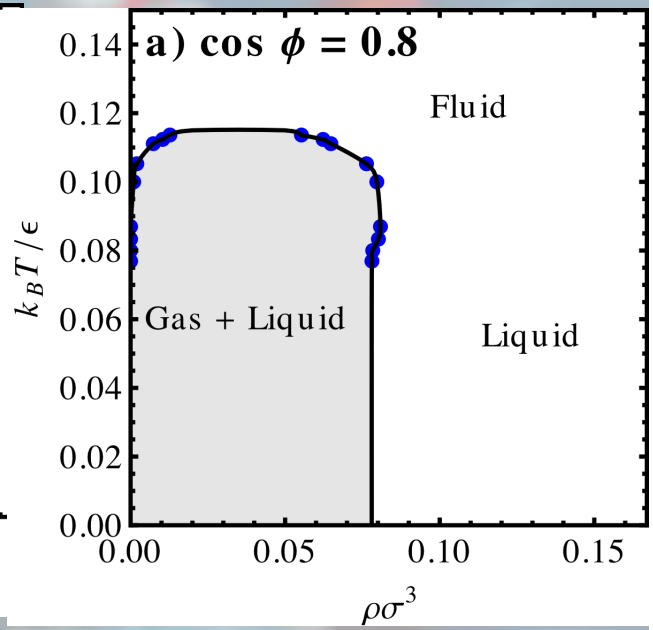
Erasing no-man's land by thermodynamically stabilizing the liquid–liquid transition in tetrahedral particles

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

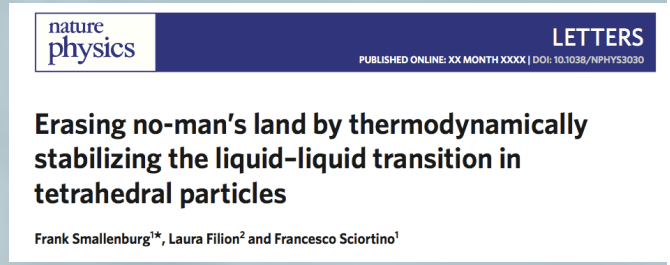
Intermediate bonding angles….







Search for intermediate flexibility valence four colloidal particles


nature physics LETTERS

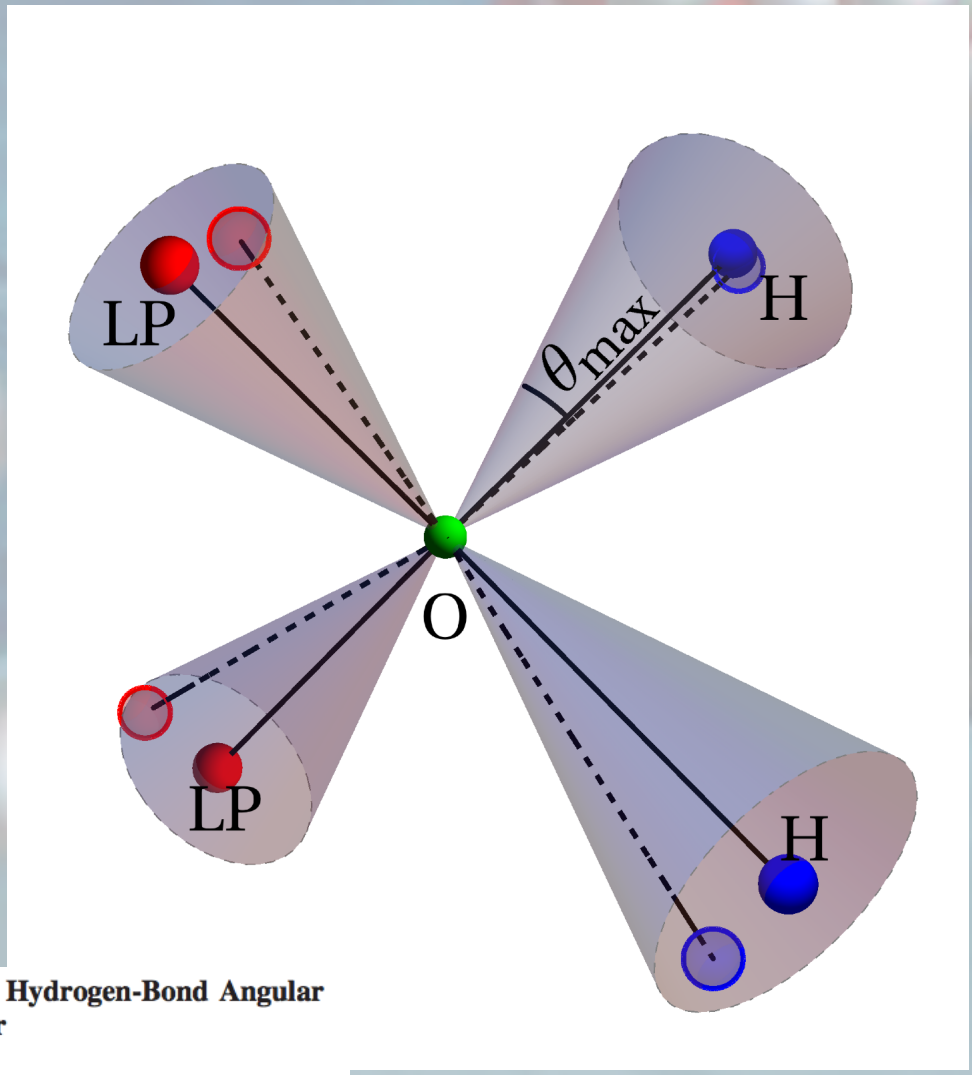
PUBLISHED ONLINE: XX MONTH XXXX | DOI: 10.1038/NPHYS3030

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]

Does it also apply to (ST2) water ?

A continuous
modification
of the ST2 model

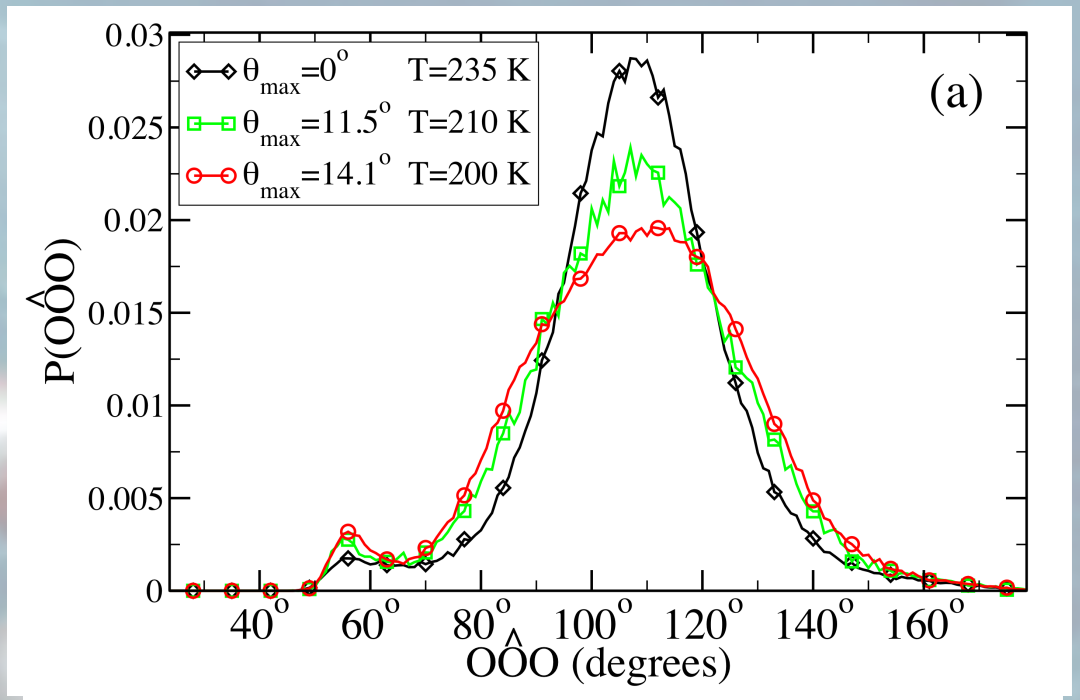


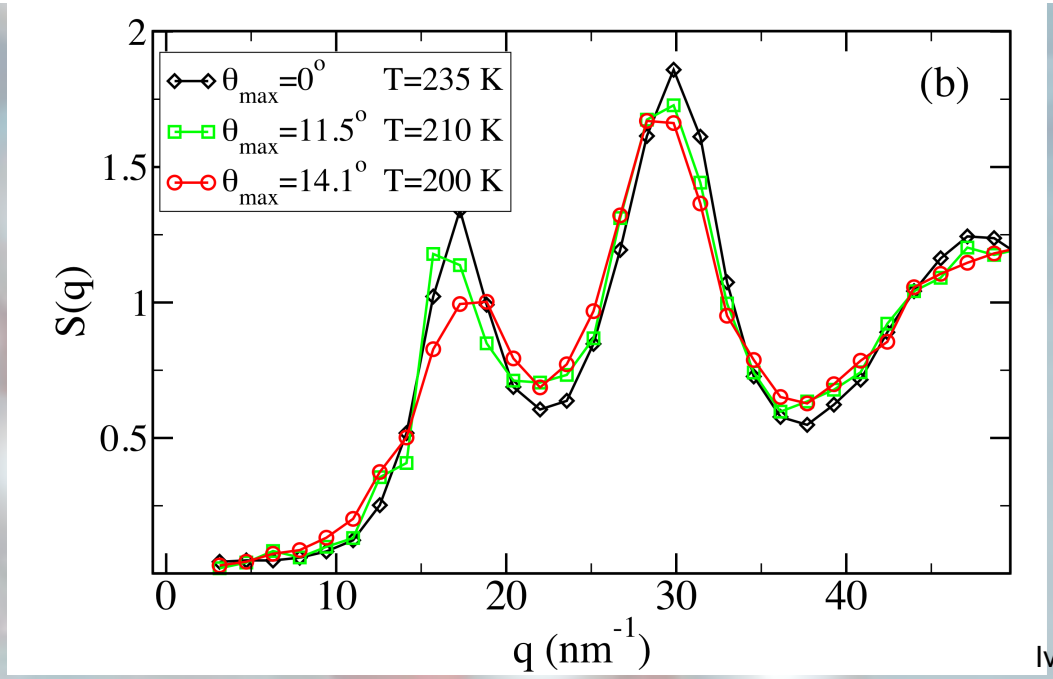
Tuning the Liquid-Liquid Transition by Modulating the Hydrogen-Bond Angular Flexibility in a Model for Water

Frank Smallenburg
Institut für Theoretische Physik II: Weiche Materie, Heinrich-Heine Universität Düsseldorf, Universitätstrasse 1, 40225 Düsseldorf, Germany

Francesco Sciortino
Department of Physics and CNR-ISC, Sapienza, Universitá di Roma, Piazzale Aldo Moro 2, I-00185 Roma, Italy
(Received 9 March 2015; published 1 July 2015)

Flexibility and structure

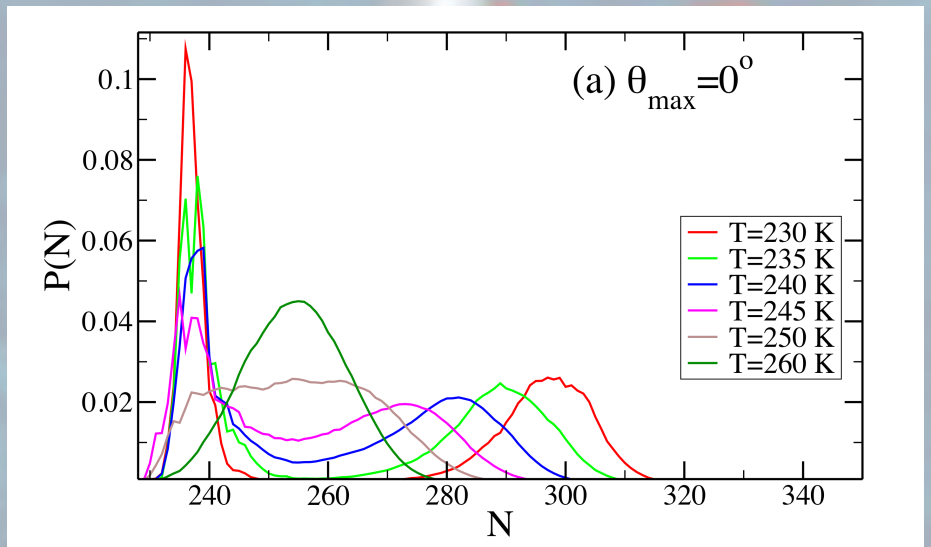


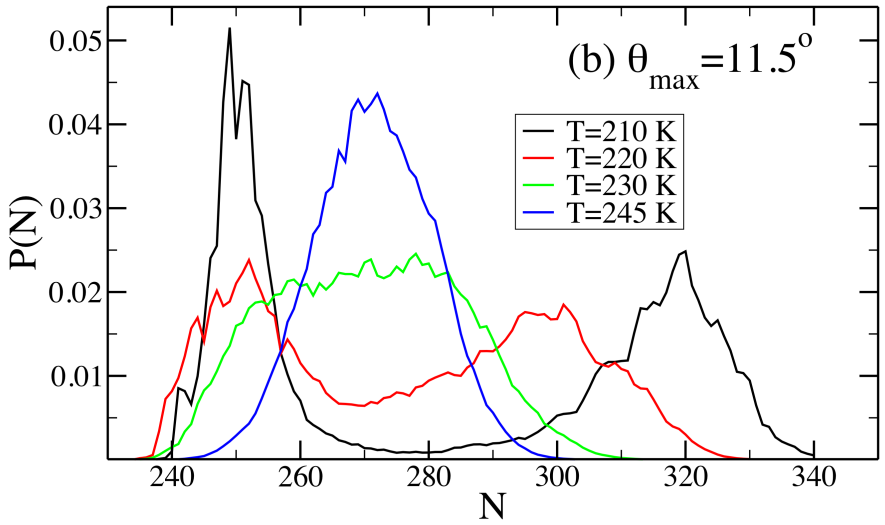


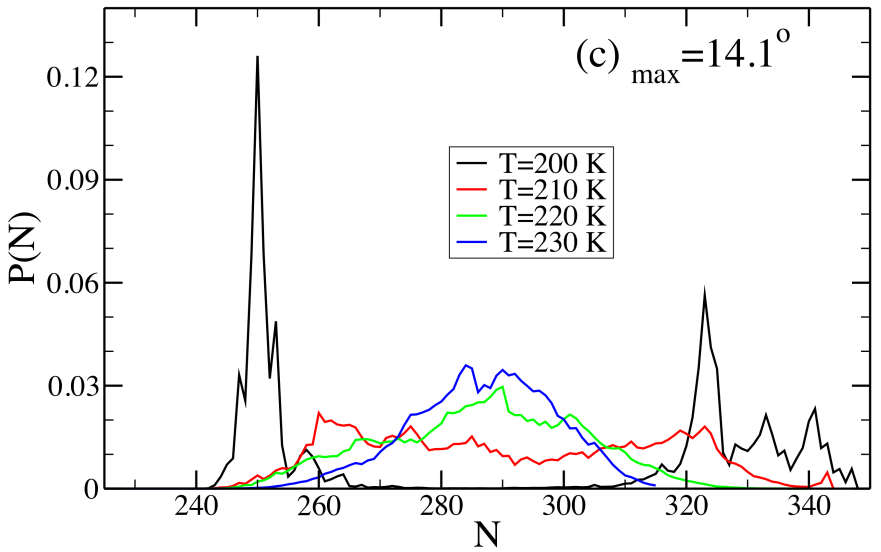
Ivan Saika-Voivod, Frank Smallenburg, and FS
Understanding tetrahedral liquids through patchy colloids
J. Chem. Phys. 139, 234901 (2013)

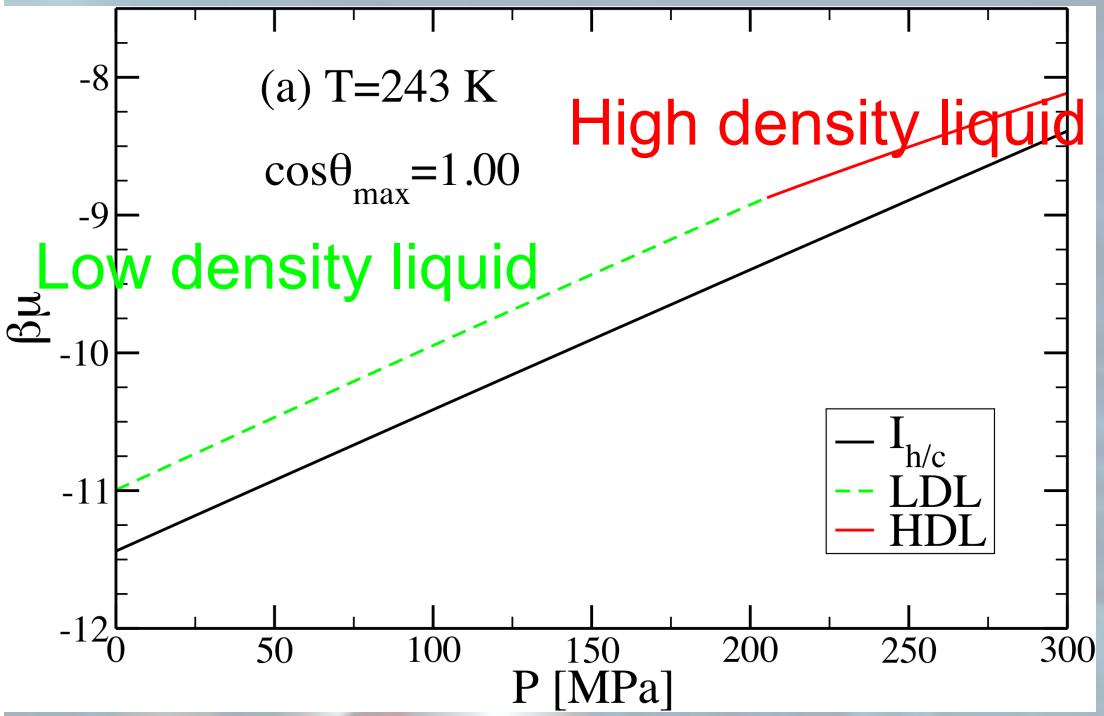
Evidence of the LL CP in ST2 and with added flexibility

P(N) SUS GCMC

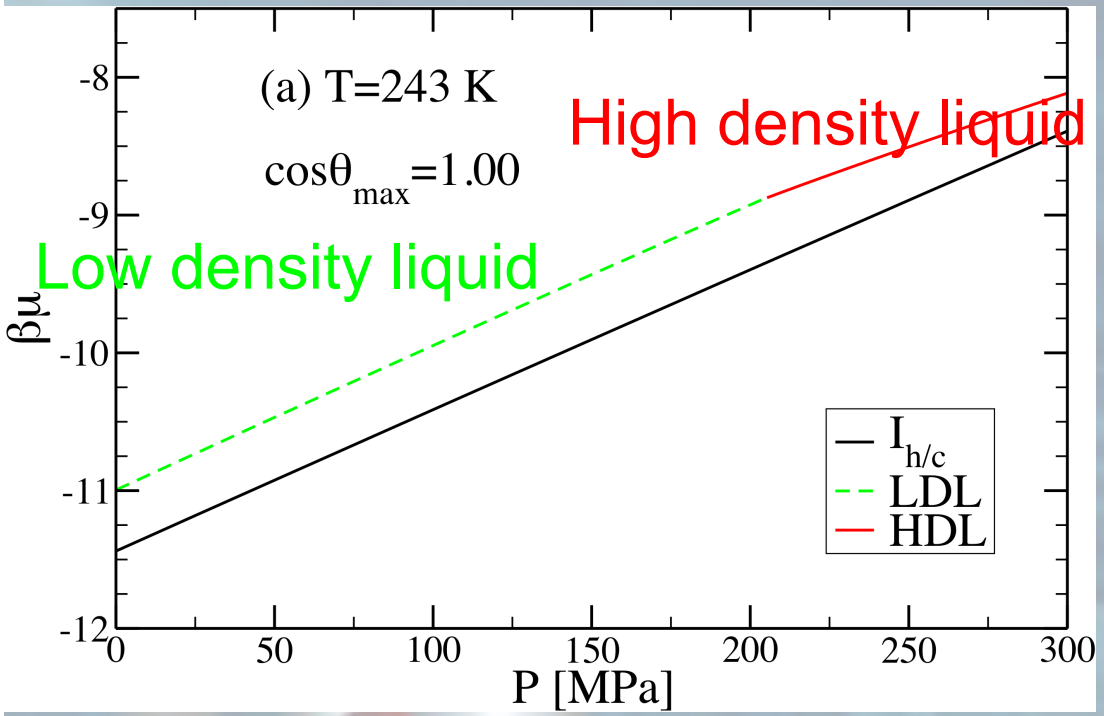








The original
ST2 case



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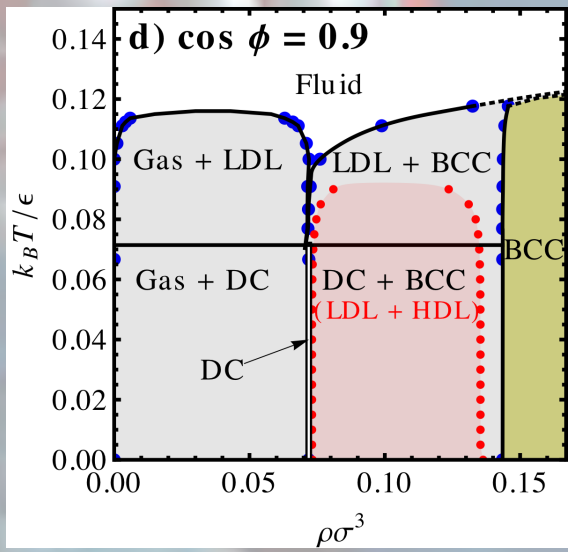

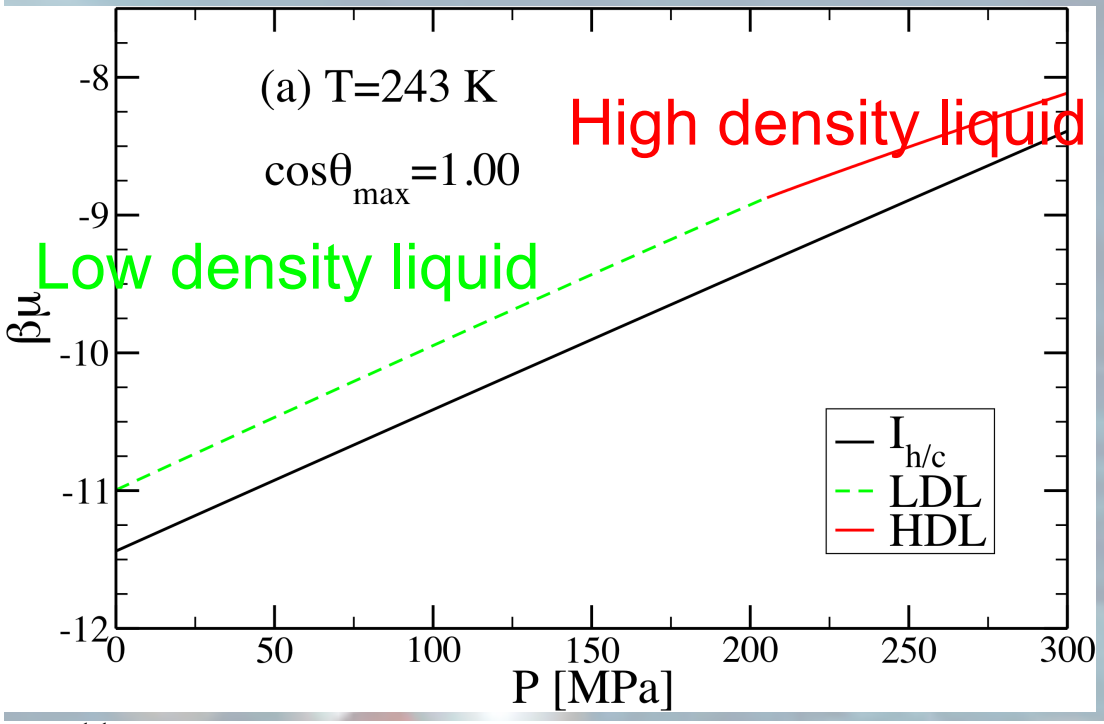

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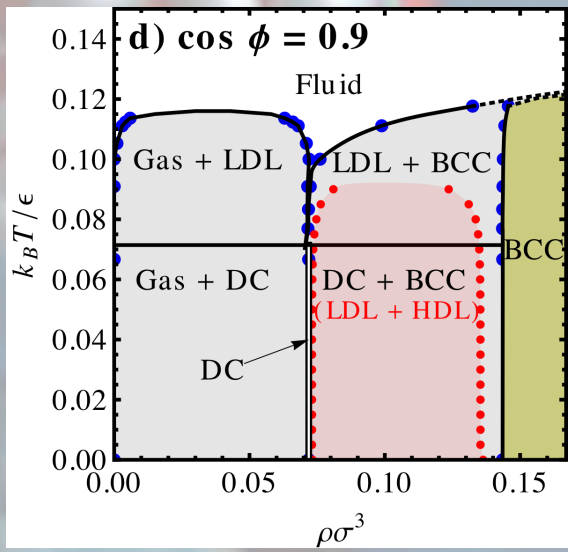
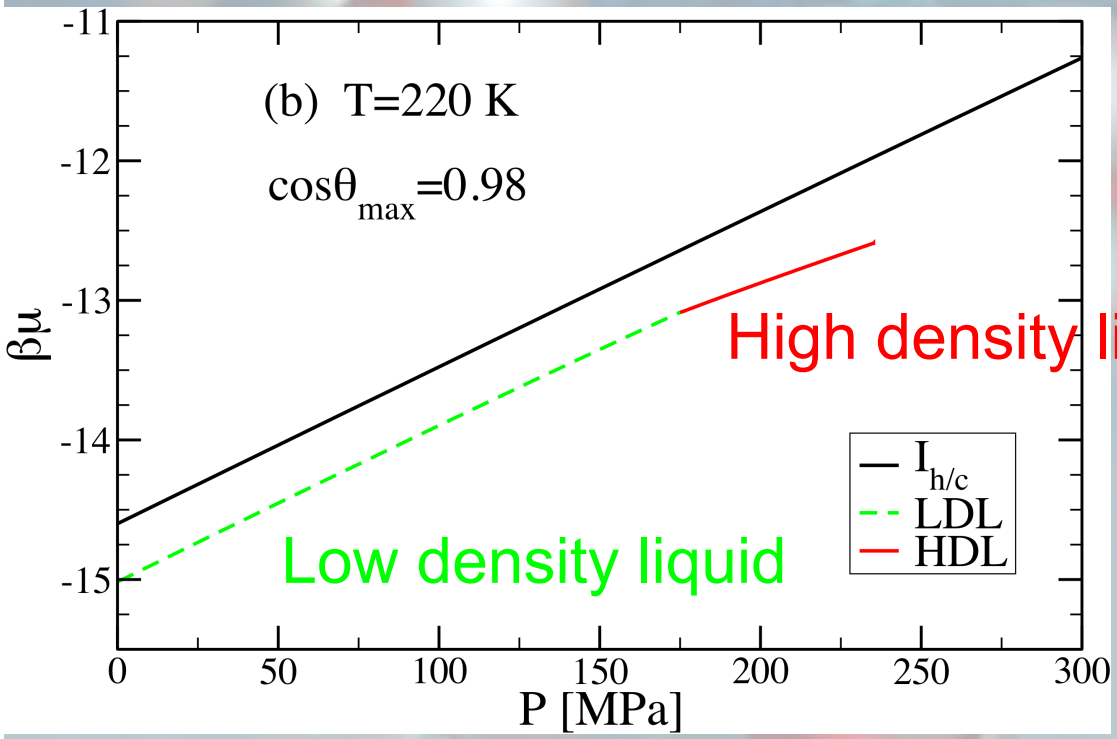
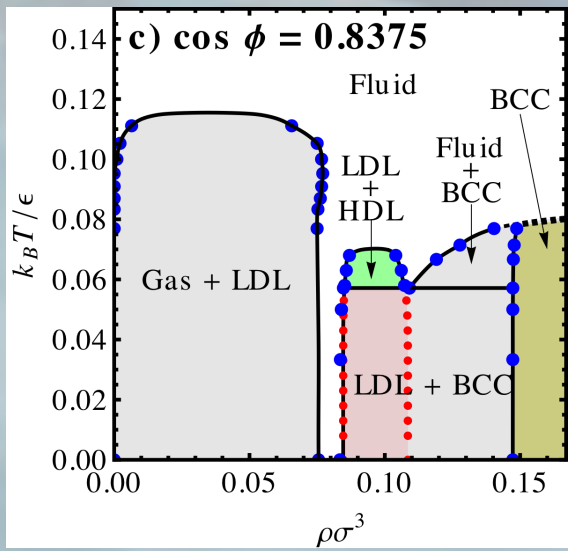
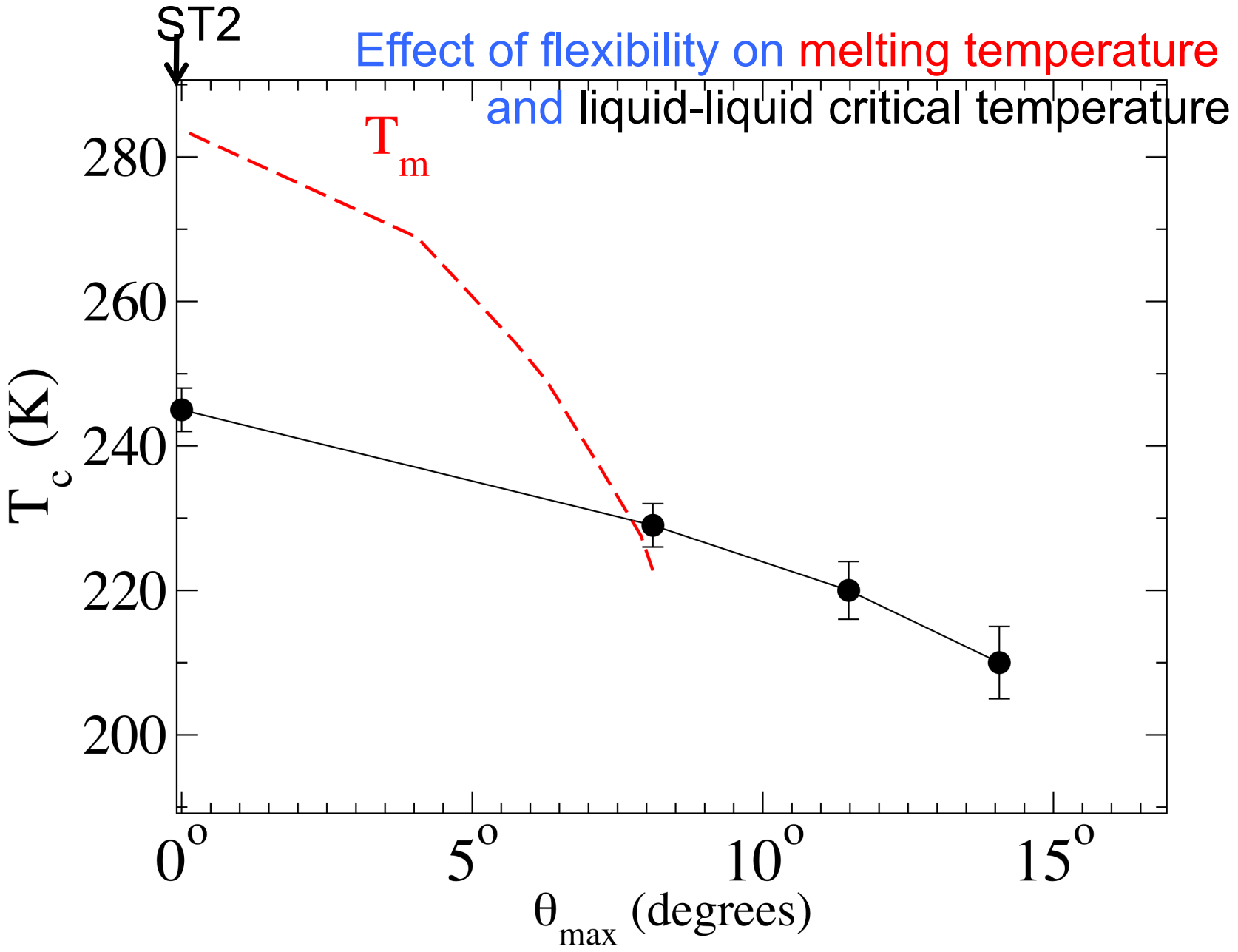
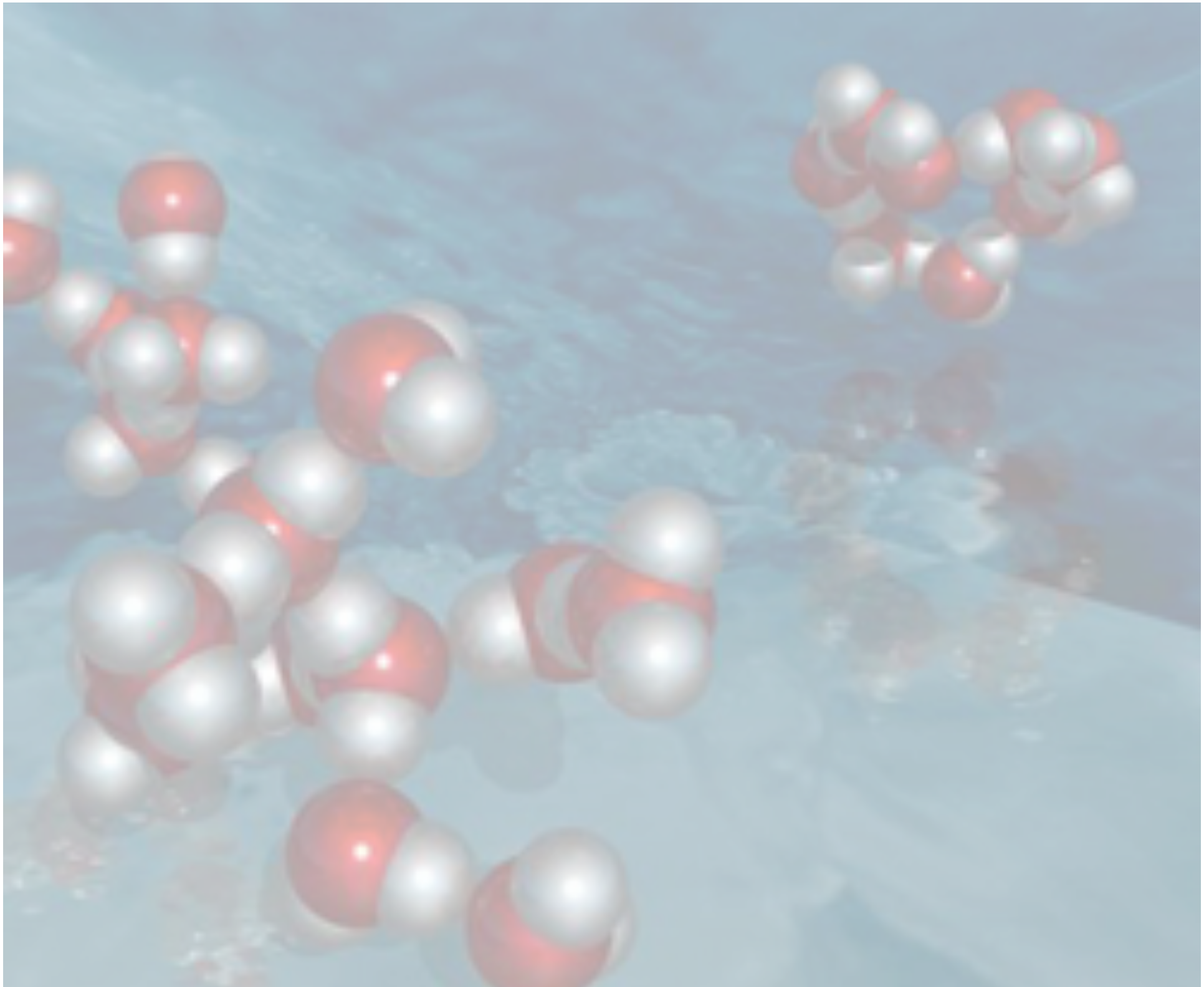




The flexible ST2 case




ST2
Effect of flexibility on melting temperature
and liquid-liquid critical temperature
T_m
280
260
240
220
200
T_c (K)
0°
5°
10°
15°
θ_{max} (degrees)



New work Conclusions

Bond flexibility is the key parameter controlling crystallization in diamond structures.

The liquid-liquid phase separation is a genuine feature of tetrahedral particles interacting if some interpenetration (softness) is allowed

For the ST2 model, a very mild addition of flexibility is sufficient to invert the relative stability of ice I and liquid(s). The LL in ST2 is NOT the reflection of a transition between liquid and crystal* but a genuine second order transition)

Conclusions…… after 20 years ….

We still do not know for sure if there is a
LL critical point in water… (but two distinct Tg)

We do know much better under which conditions
tetrahedral interacting particles do show a
stable or metastable LL transition

Can the LL transition have biological relevance ?
(if it is the source of the anomalies….).
How relevant is confinement in namoscopic pores ?

Collaborators: too many !

The most recent

Laura Filion, Frank Smallenburg (Rome, Utrecht)

Peter Poole, Ivan Saika-Voivod (Canada)

Francis Starr (US)

Thanks for your attention !