Slow dynamics and thermodynamics of water in aqueous solutions

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"WATER AND WATER SYSTEMS "

3nd course within the School of Neutron Science and Instrumentation

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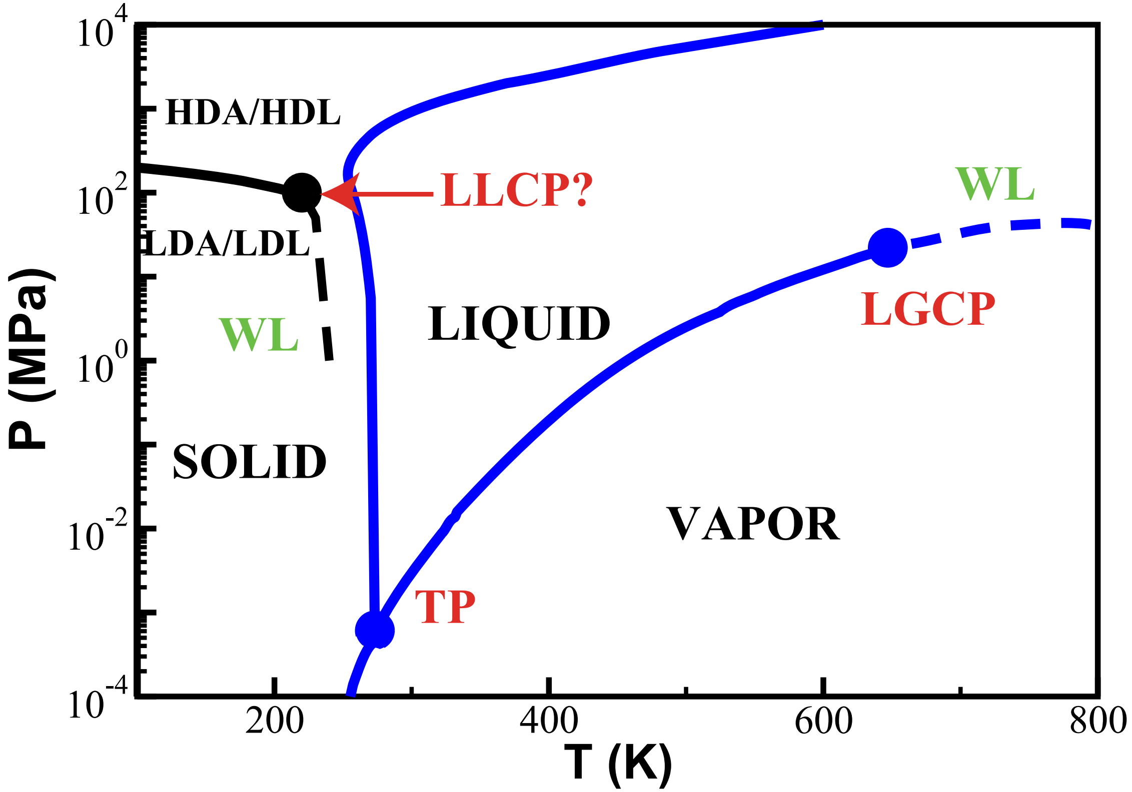
Outline of the talk

- Water phase diagram
- Widom line definition
- Widom line and its connection to dynamics in the supercritical state
- Aqueous solution as a route to reach no man's land
- Widom line and its connection to dynamics (Fragile to strong) in TIP4P and TIP4P/2005 in supercooled states
- Widom line and its connection to dynamics (FTS) in aqueous solitions of NaCl
- Widom line and its connection to dynamics (FTS) in Jagla water + Hard Spheres
- Conclusions

Polymorphic and polyamorphic water: phase diagram and critical points



Water: A Tale of Two Liquids

Paola Gallo, Katrin Amann-Winkel, Charles Austen Angell, Mikhail Alexeevich Anisimov, Frédéric Caupin, Charusita Chakravarty, Erik Lascaris, Thomas Loerting, Athanassios Zois Panagiotopoulos, John Russo, Jonas Alexander Sellberg, Harry Eugene Stanley, Hajime Tanaka, Carlos Vega, Limei Xu, and Lars Gunnar Moody Pettersson

Chemical Reviews 116, 7463-7500 (2016) DOI: 10.1021/acs.chemrev.5b00750

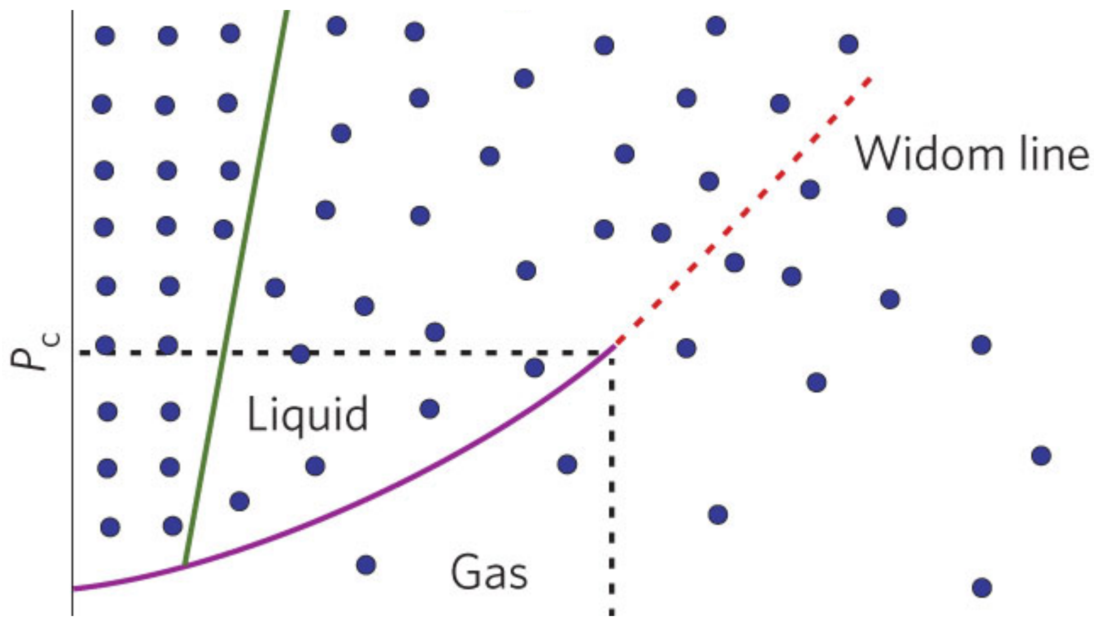
The Widom Line (WL)

- In a fluid, when moving from the critical point to the single phase region it is expected that the correlation length keeps a maximum reminiscent of the critical divergence.
- In fact in this region quantities like the specific heat and the isothermal compressibility show maxima that merge on a pseudo-critical single line terminating at the critical point.
- The maxima of those response functions collapse on the same line upon approaching the critical point since they become proportional to power laws of the correlation length.
- This line is the Widom Line.

The Widom Line (WL) in supercooled water

- The concept of WL in the last few years was extensively considered in supercooled water in connection with the possible existence of a liquid-liquid transition terminating in a second critical point. [L. Xu, P. Kumar, S. V. Buldyrev, S.-H. Chen, P. H. Poole, F. Sciortino and H. E. Stanley, Proc. Natl. Acad. Sci. USA **102**, 16558 (2005).]
- For potentials that show a LLCP: ST2, TIP4P, TIP4P/2005, JAGLA a crossover in dynamic quantities is found upon crossing the Widom line.
- The crossover is from a Fragile to a Strong liquid for all potentials and also found in ionic solutions with TIP4P water

Widom Line in supercritical fluids



Picture from "Liquid phases: Going supercritical" Paul F. McMillan & H. Eugene Stanley *Nature Physics* 6, 479-480 (2010)

- In the case of the liquid gas transition the WL can be also expected to separate liquid-like from gas-like regions of the supercrititical phase.
- Recently experimental work has detected a crossover in sound velocity of supercritical fluids of noble gases that can be connected to the Widom line

F. A. Gorelli, T. Bryk, M. Krisch, G. Ruocco, M. Santoro, and T. Scopigno, Sci. Rep., **3**, 1203 (2013); G. G. Simeoni, T. Bryk, F. A. Gorelli, M. Krisch, G. Ruocco, M. Santoro, and T. Scopigno, Nature Phys., **6**, 503 (2010).

How about supercritical water?

- SC water is important in chemical engineering, in carbon capture and storage, in pharmaceutics, in waste disposal and in several other areas of applications like *gasification of biomass*
- The studies of supercritical region have been so far limited by technical difficulties in experiments
- **We analyze the properties of Super Critical water in experiments and for TIP4P/2005 water and other popular water models in connection to the WL in the super critical state**

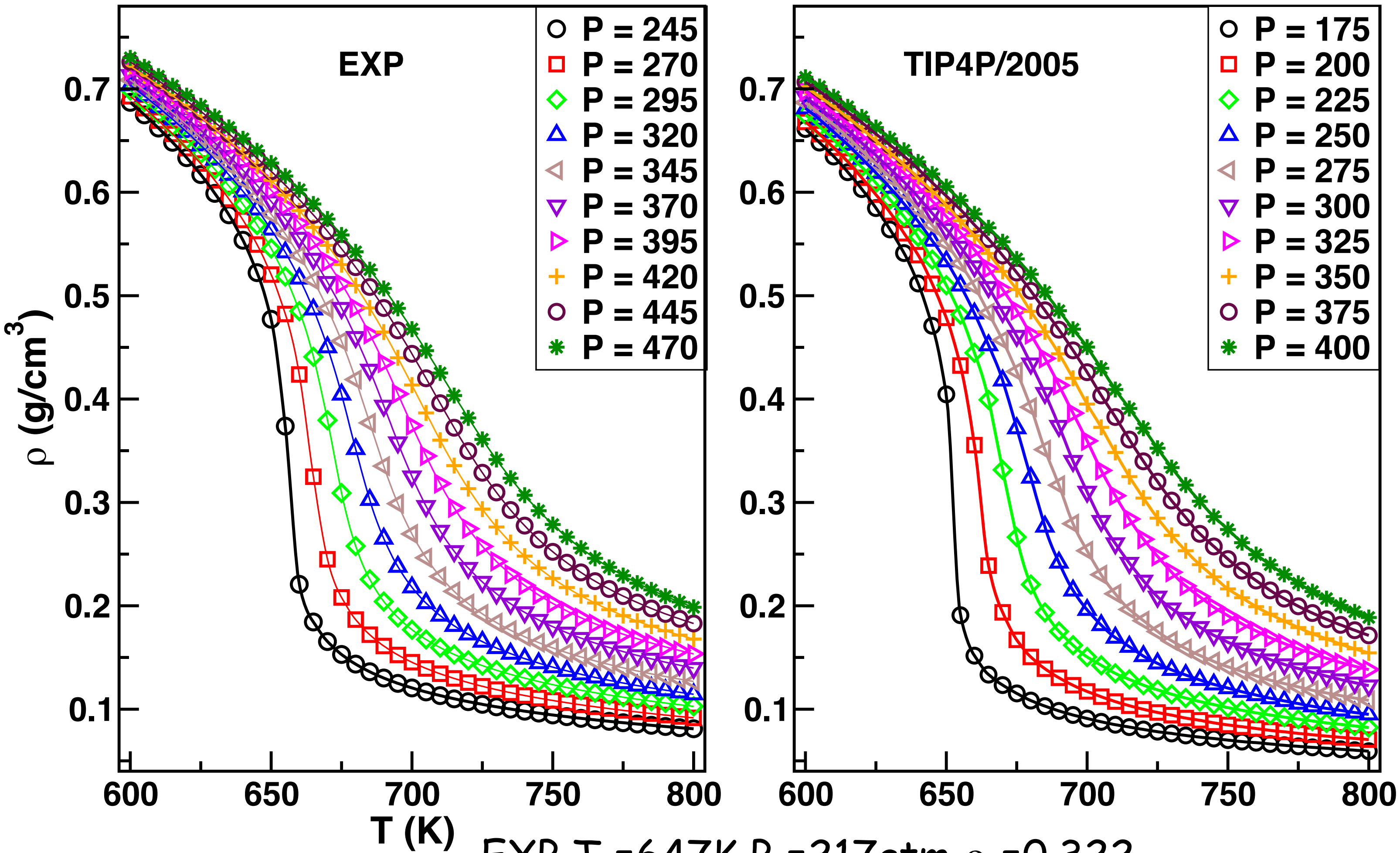
[P. Gallo, D. Corradini and M. Rovere, Widom line and dynamical crossovers as routes to understand supercritical water, Nature Comm. 5:5806 (2014).]

[D. Corradini, M. Rovere and P. Gallo, The Widom line and dynamical crossover in supercritical water: popular water models versus experiments J. Chem. Phys., 143 , 114502 (2015)]

Critical point for experimental water and popular potential model

System	T_c(K)	P_c(bar)	ρ_c(g/cm^3)
EXP	647.096	220.640	0.322
TIP4P/2005	640	146	0.31
TIP4P	588	149	0.315
SPC/E	638.6	139	0.273
TIP5P	521	86	0.337
TIP3P	578	126	0.272

Supercritical isobars for experimental water and TIP4P/2005

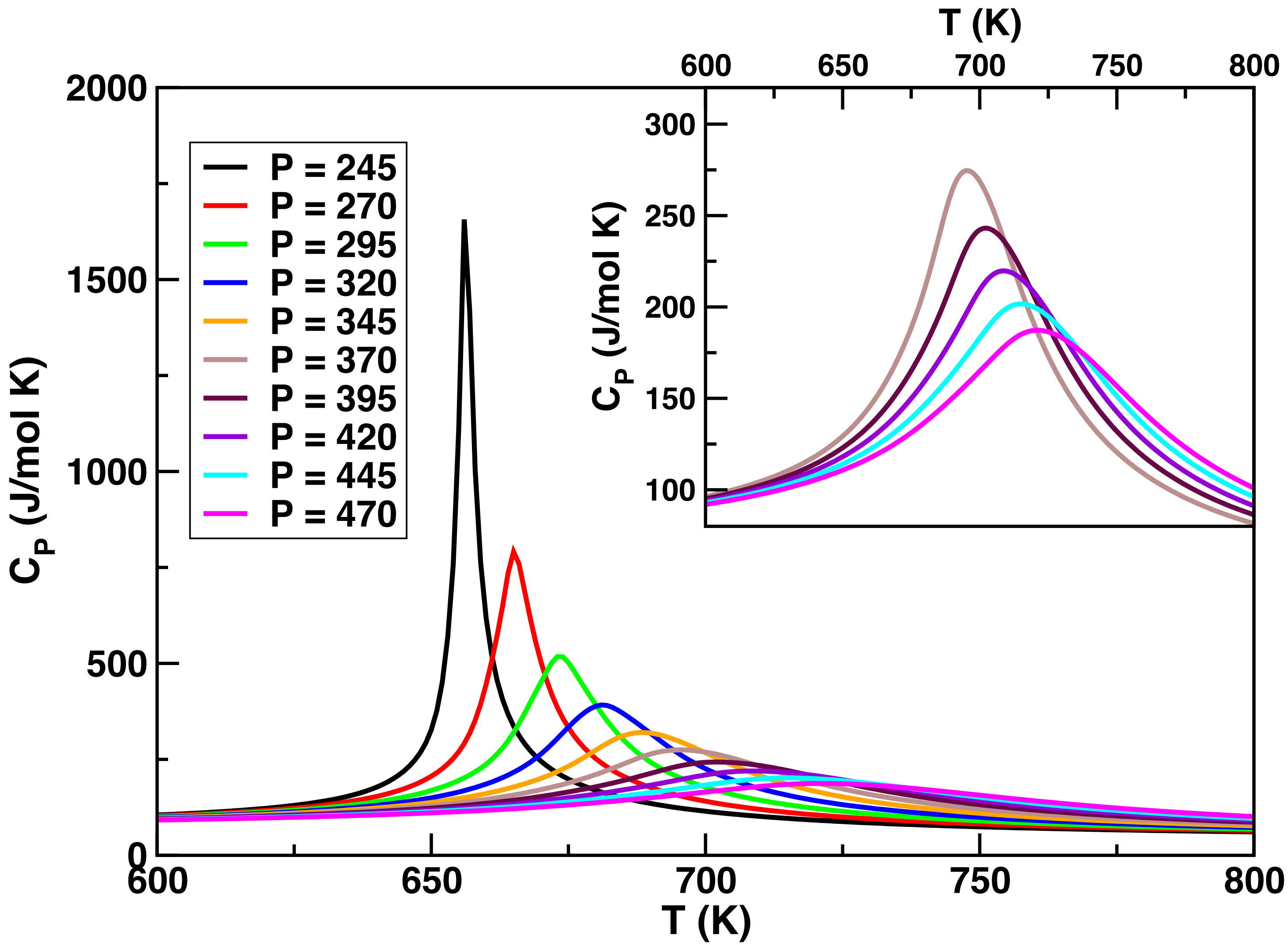


EXP T_c=647K P_c=217atm ρ_c=0.322

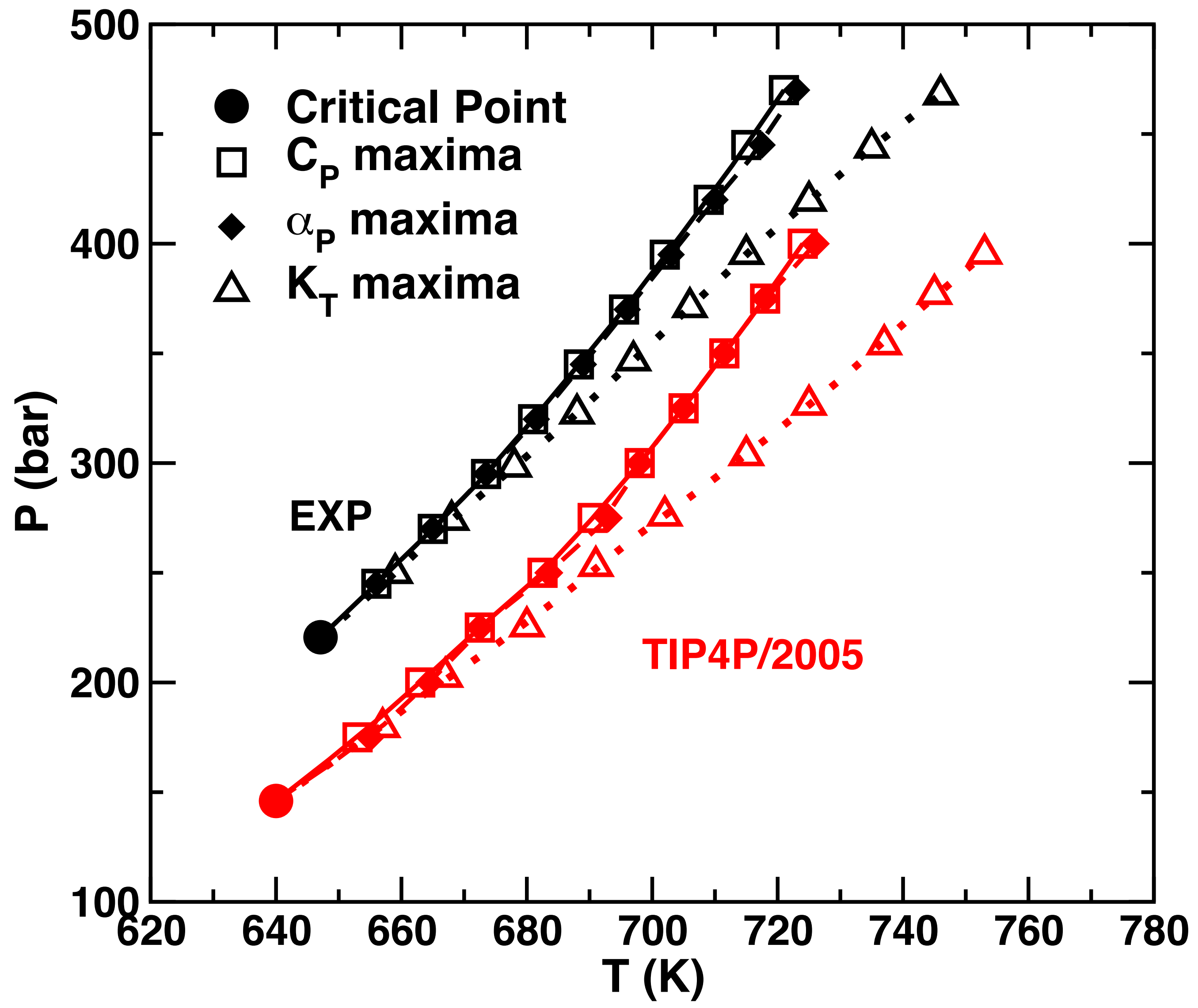
TIP4P/2005 T_c=640K P_c=146atm ρ_c=0.31

Curves are calcultated at the same distances from the respective critical values

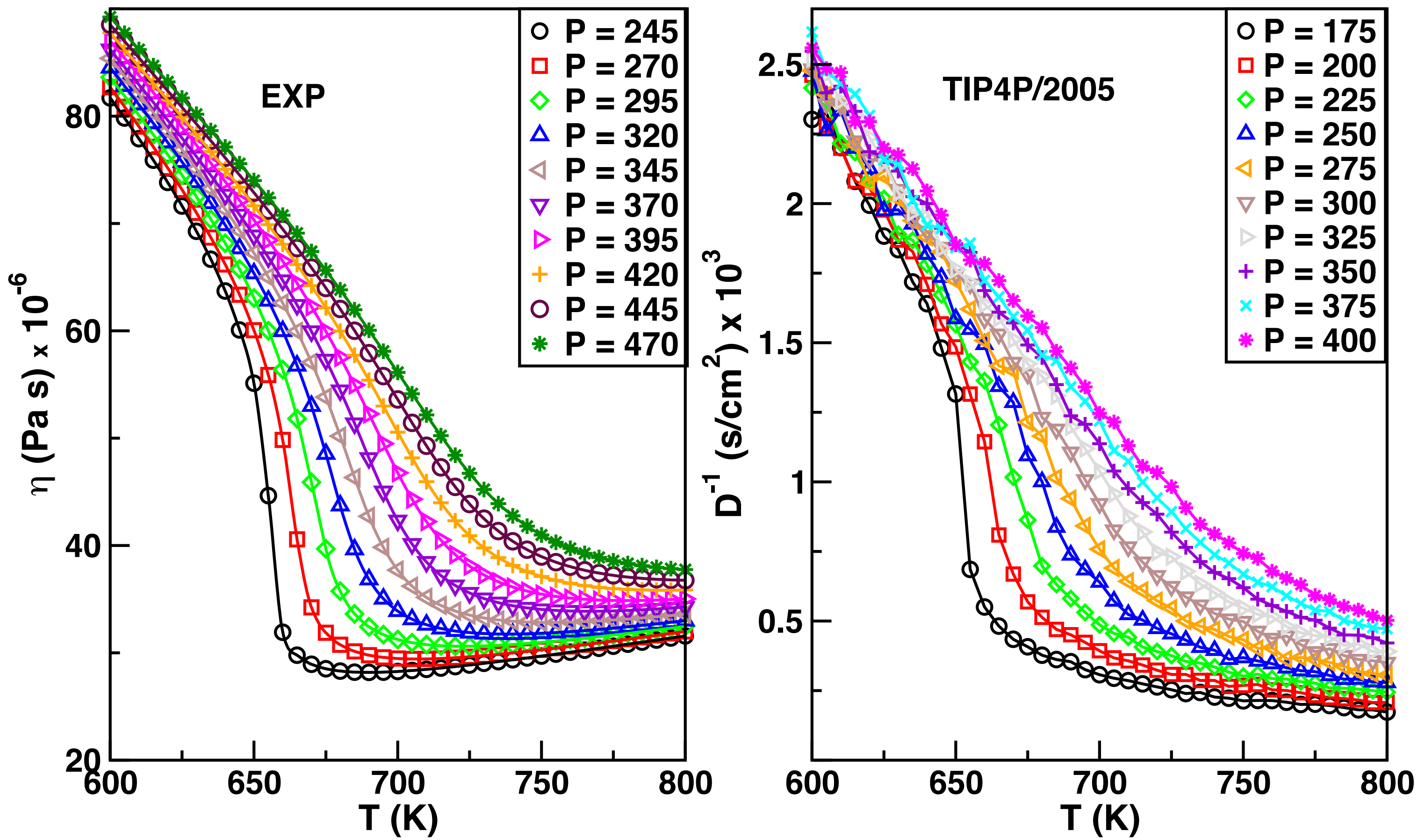
Specific heat maxima for experimental water



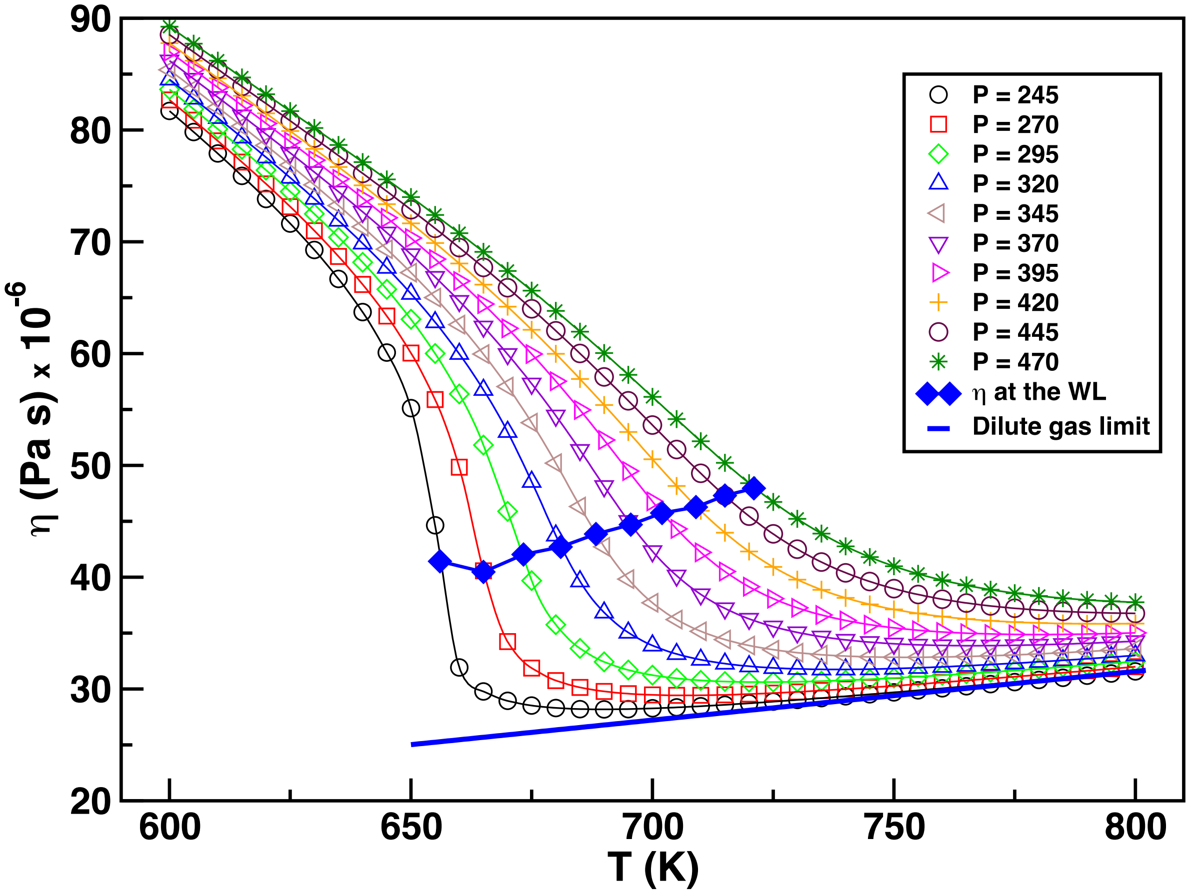
Maxima of the response functions and Critical point for experimental water and TIP4P/2005



Dynamics in experiments and in simulations of TIP4P/2005

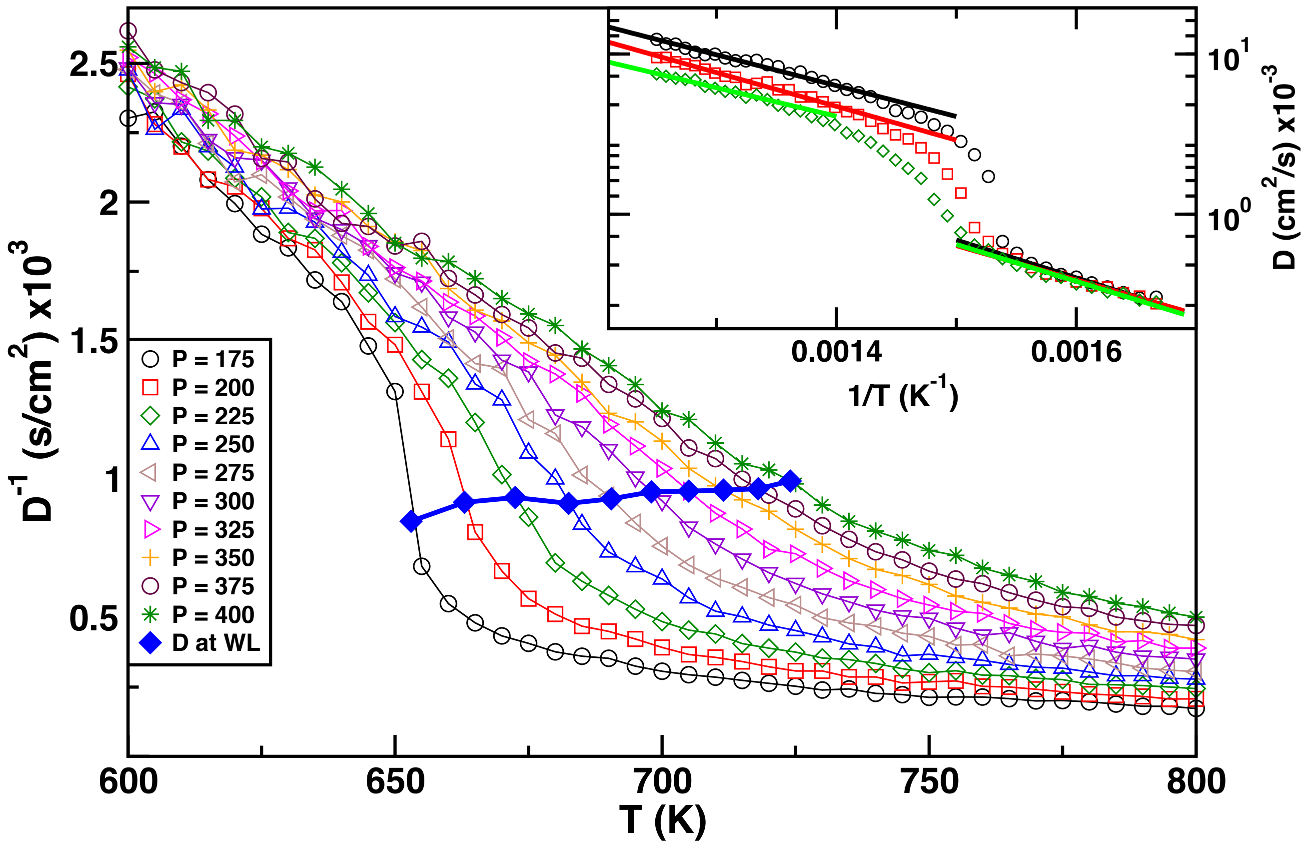


Dynamics in experiments



The experimental viscosity is shown together with the maxima of the isobaric specific heat that define the WL close to the Critical point. The bold line is the viscosity in the diluite gas limit

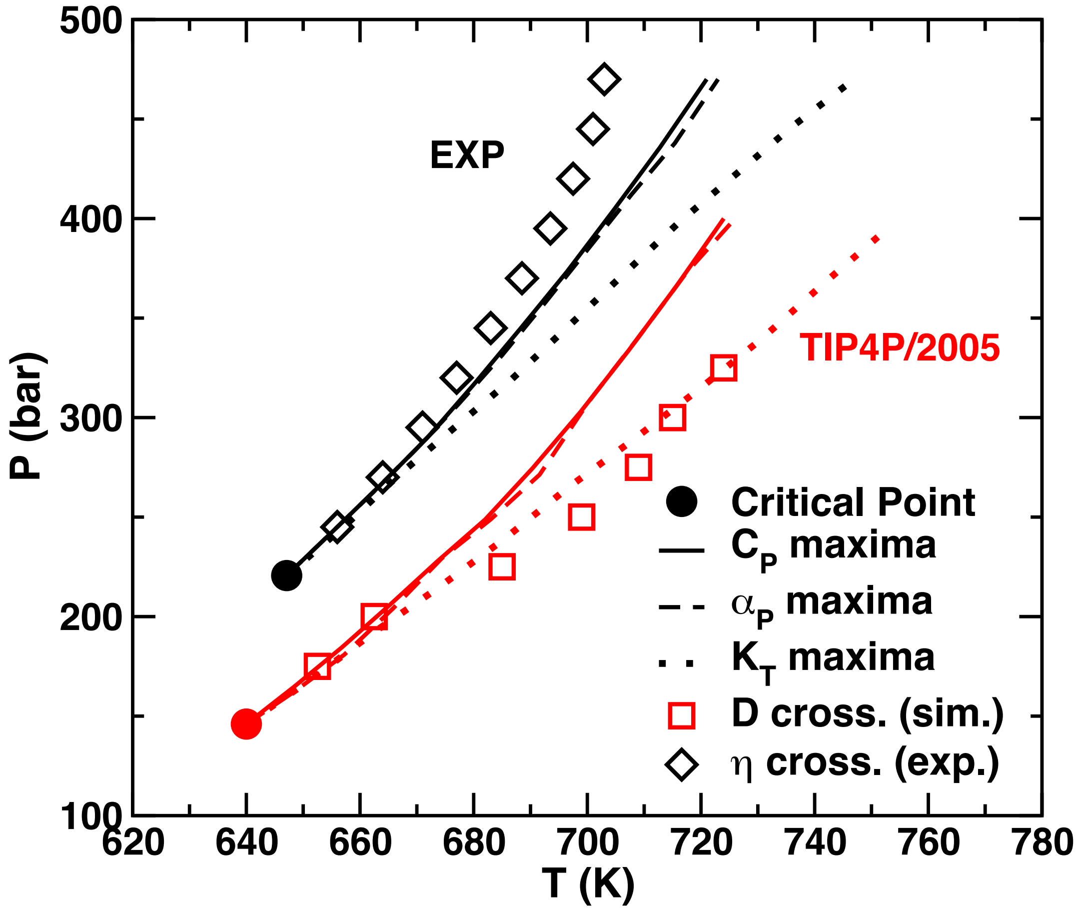
Dynamics in simulations of TIP4P/2005



For high T E_A = 25.7 kJ/mol for P = 175 bar, E_A = 28.2 kJ/mol for P = 200 bar, E_A = 23.8 kJ/mol for P= 225 bar

For low T E_A = 31.5 kJ/mol for P = 175 bar, E_A = 28.7 kJ/mol for P = 200 bar, E_A = 30.8 kJ/mol for P = 225 bar.

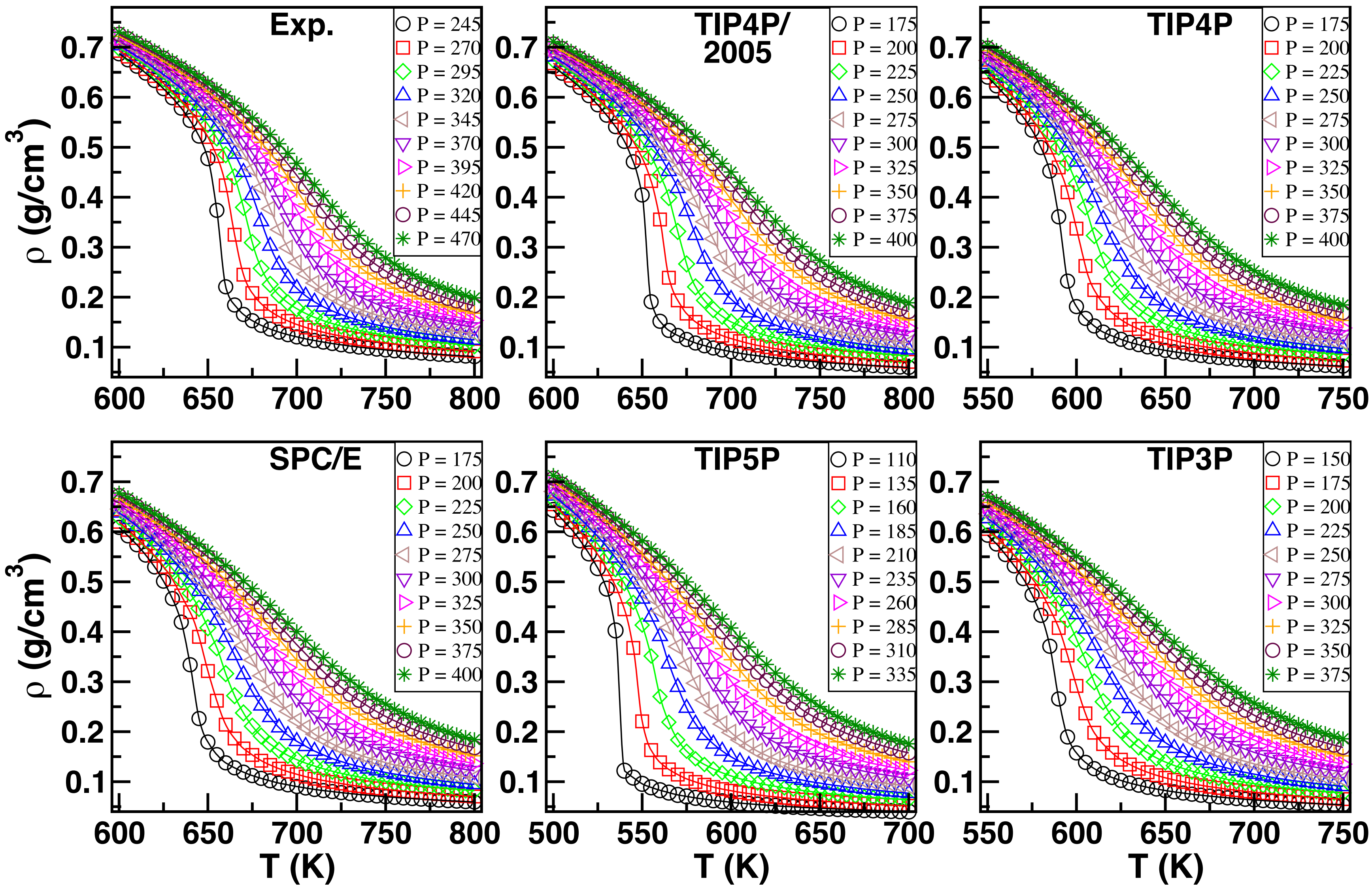
Thermodynamic and dynamic lines all converge on the WL for a range of circa 30 K and 90 bar



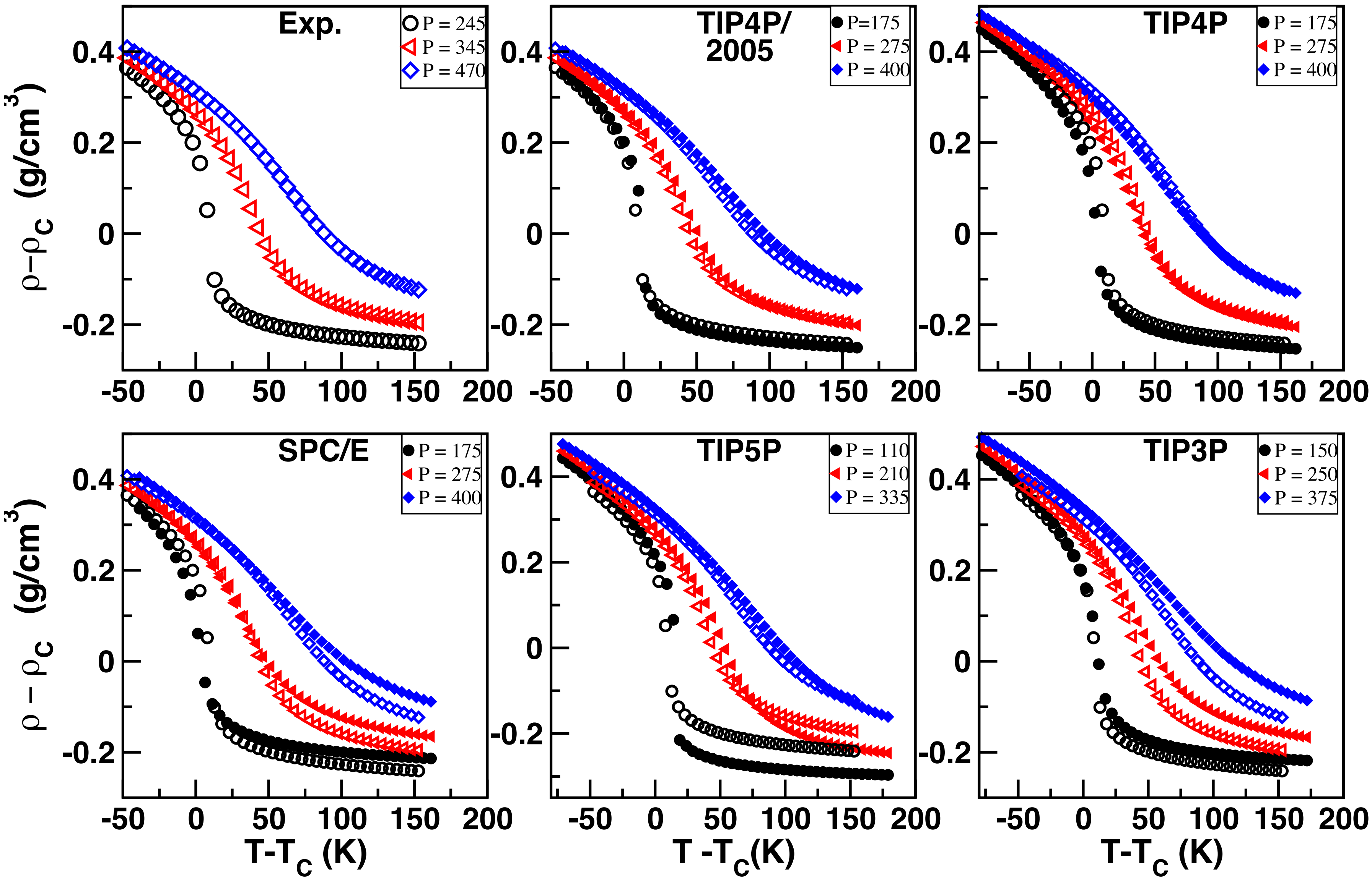
The crossovers are changes of slope of the transport coefficients D and viscosity

P. Gallo, D. Corradini and M. Rovere, Widom line and dynamical crossovers as routes to understand supercritical water Nature Comm. **5:5806** (2014).

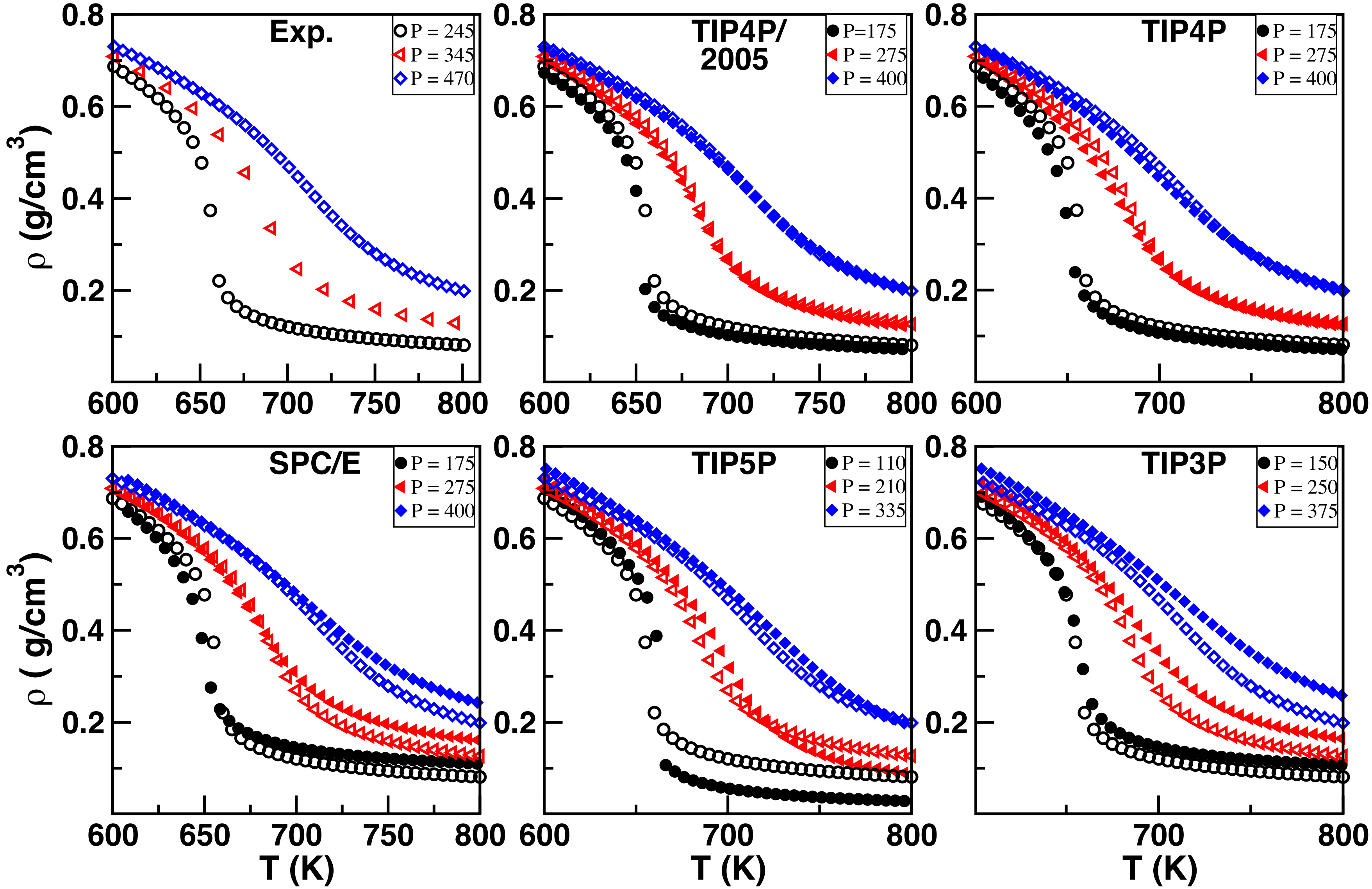
Supercritical isobars for experimental water and popular water models



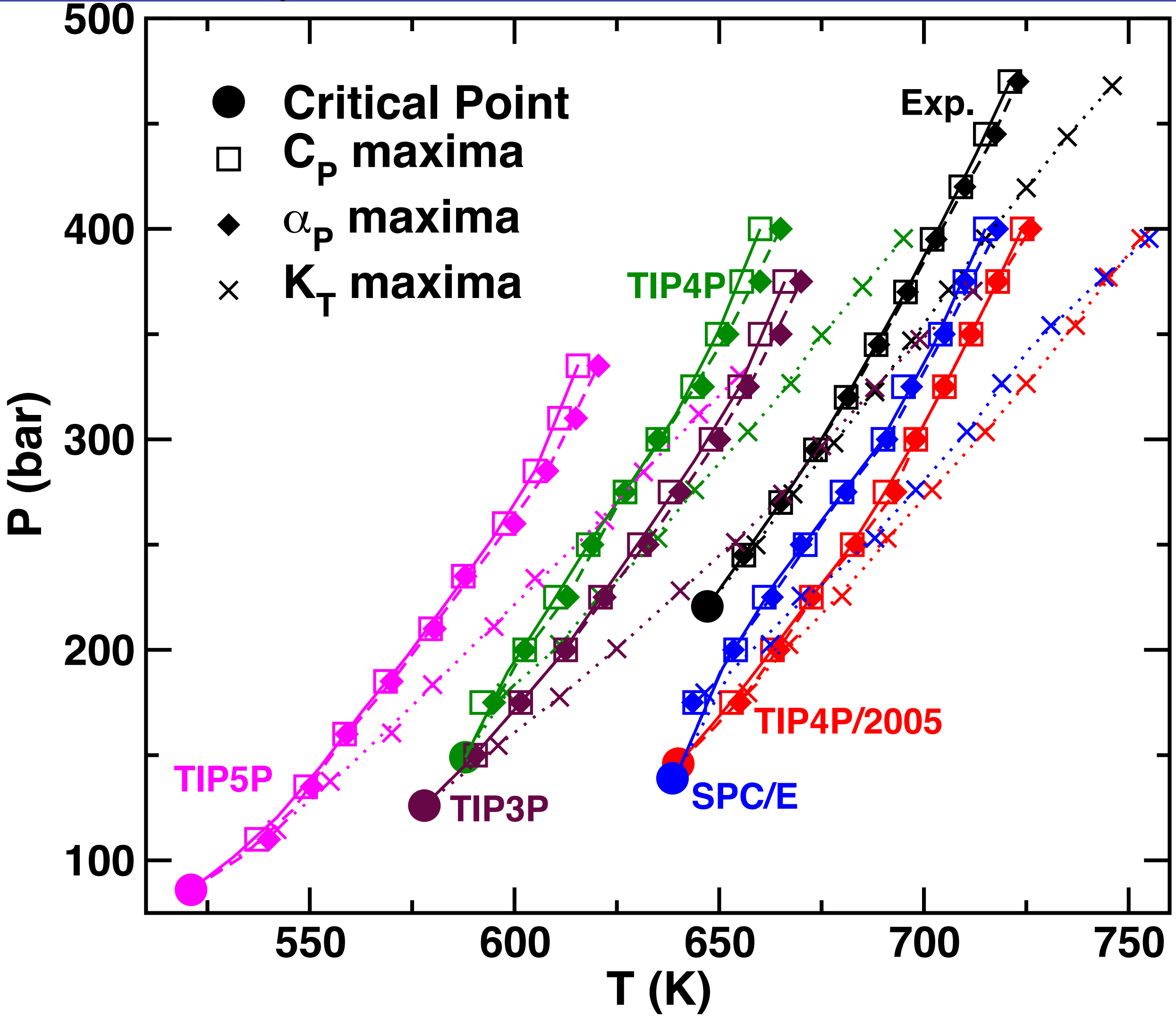
Supercritical isobars of popular water models. Agreement with experiments: $\rho - \rho_C$ vs $T - T_C$



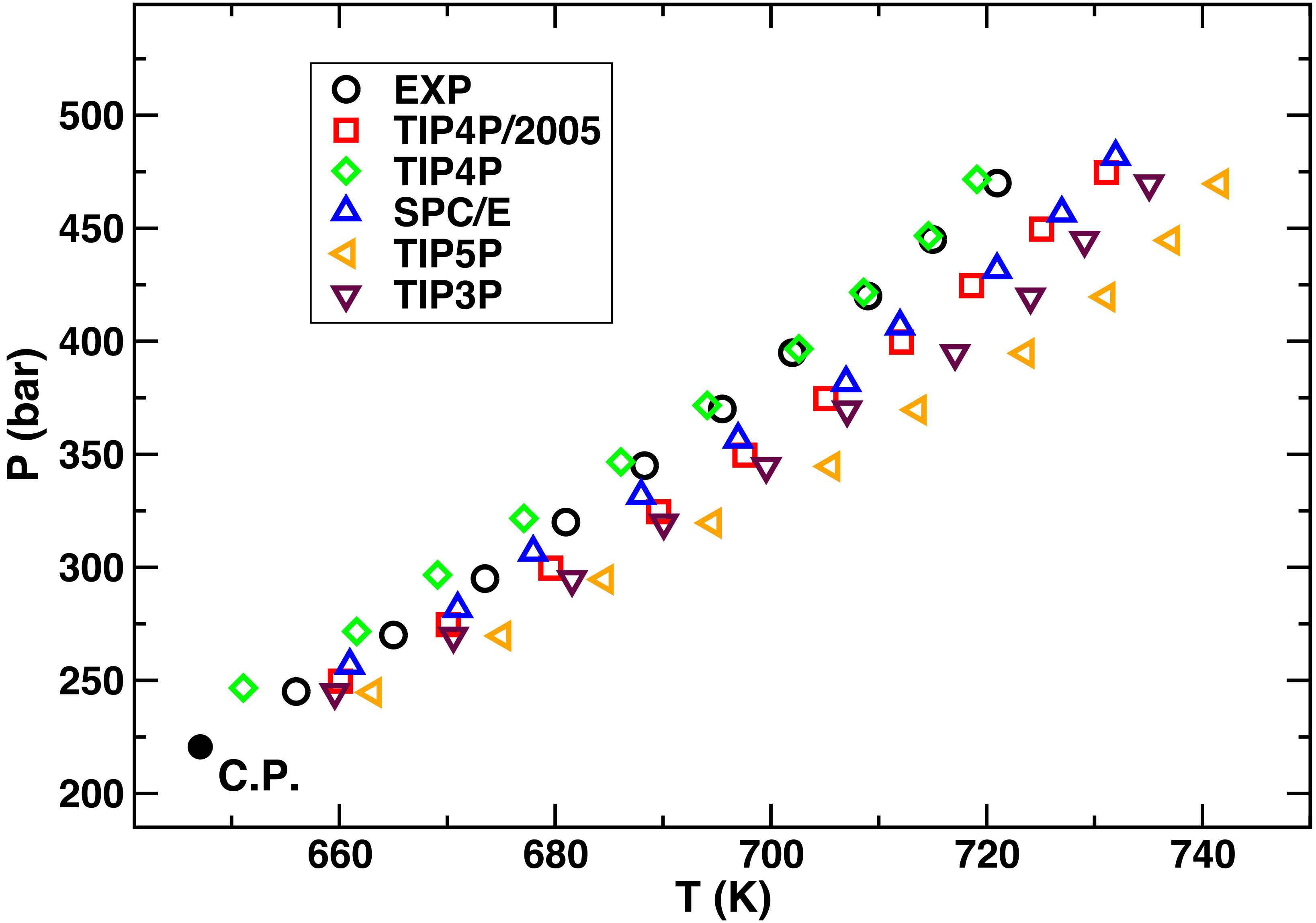
Supercritical isobars of popular water models shifted so that their ρ_c coincides with the ρ_c of the experiment



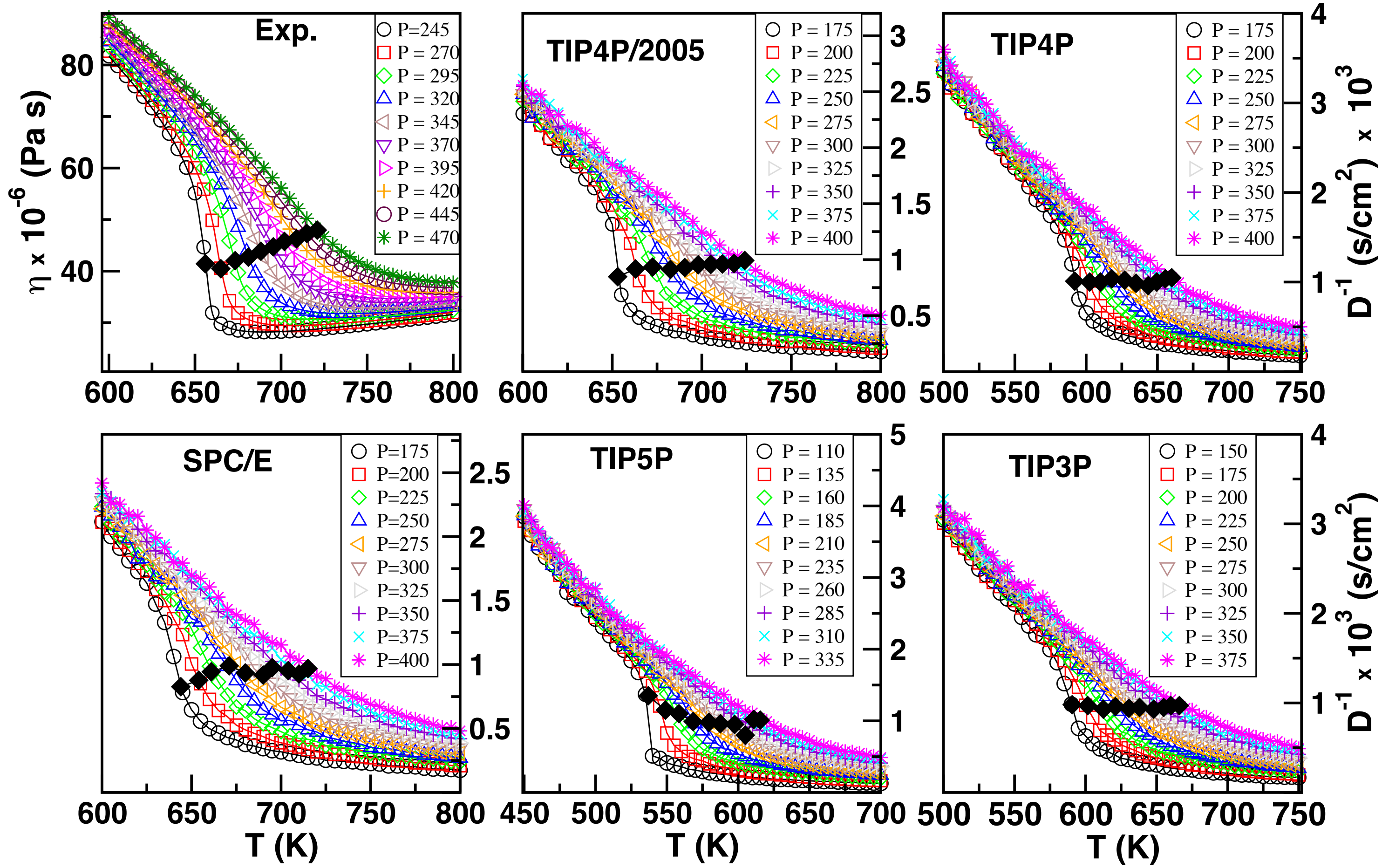
Maxima of the response functions and Critical point for experimental water and water potentials



Widom line in experimental water and in water models

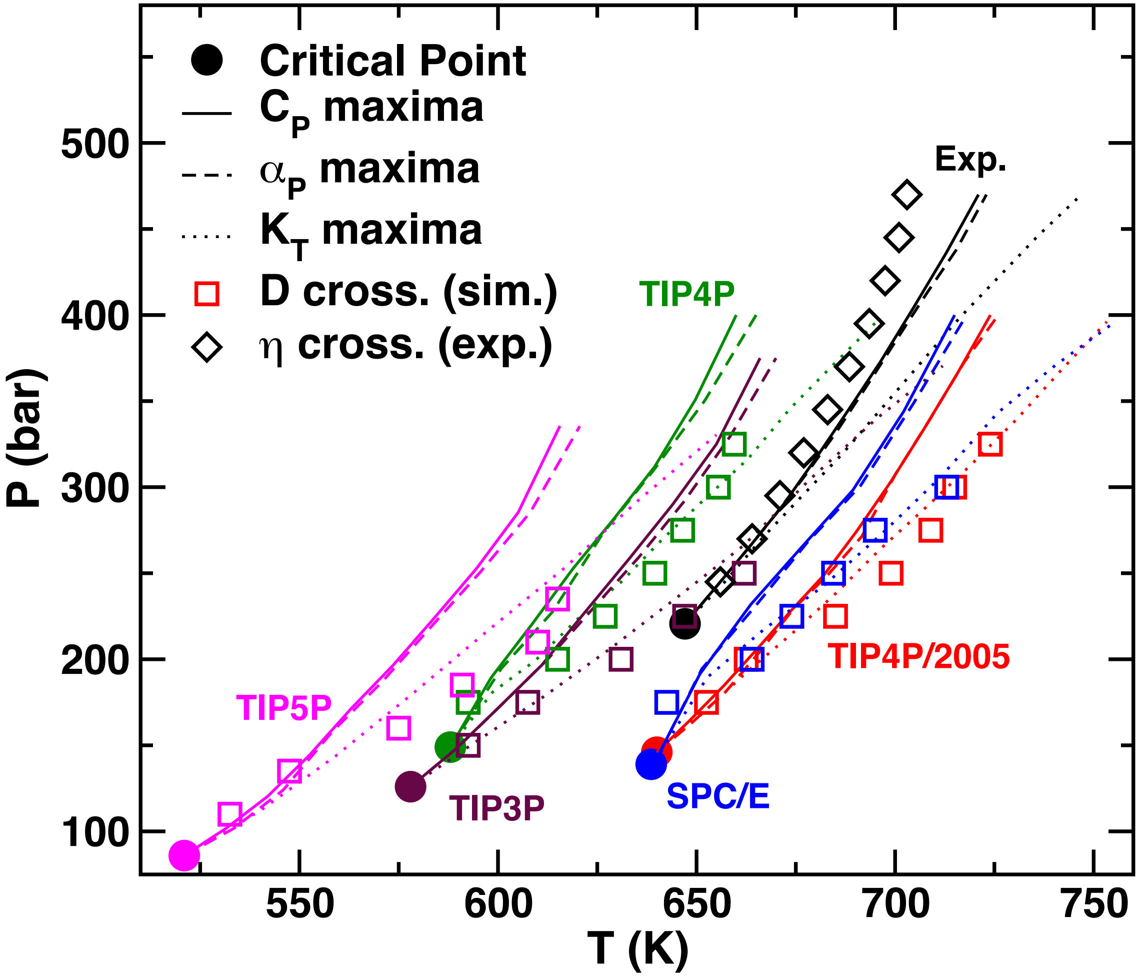


Dynamics in experiments and simulations



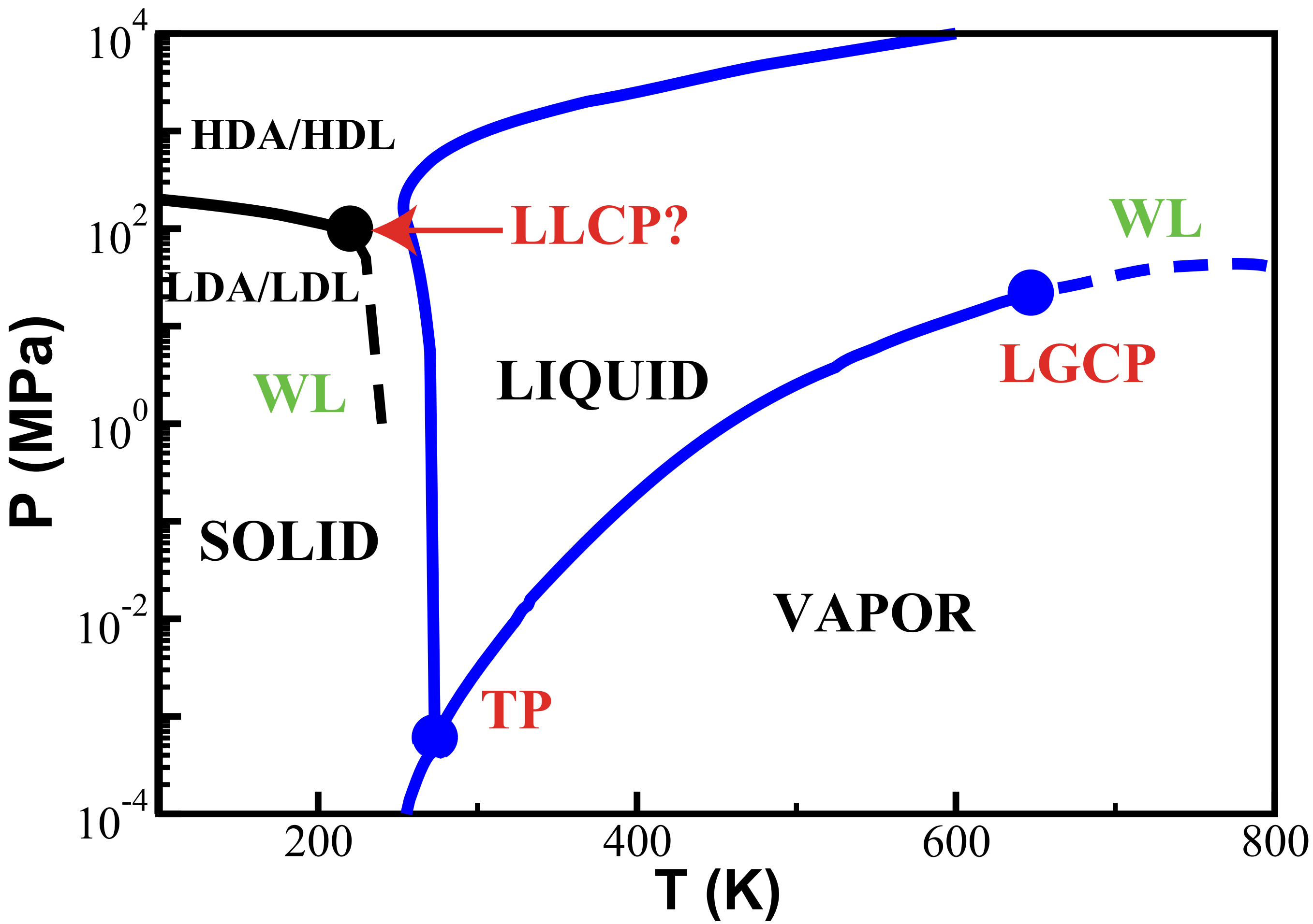
Black diamonds mark the location of the Widom line

Thermodynamics and dynamics all converge on the WL for popular water model

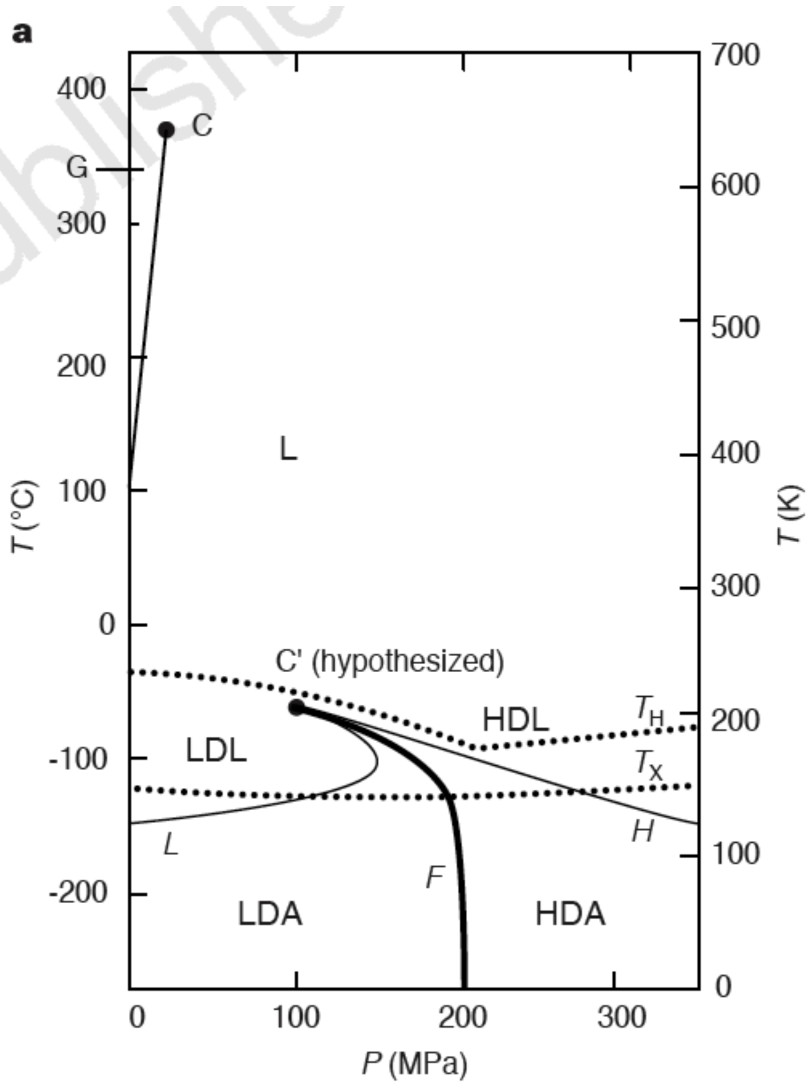


D. Corradini, M. Rovere and P. Gallo, The Widom line and dynamical crossover in supercritical water: popular water models versus experiments J. Chem. Phys., **143** , 114502 (2015)

Now we move to the supercooled state

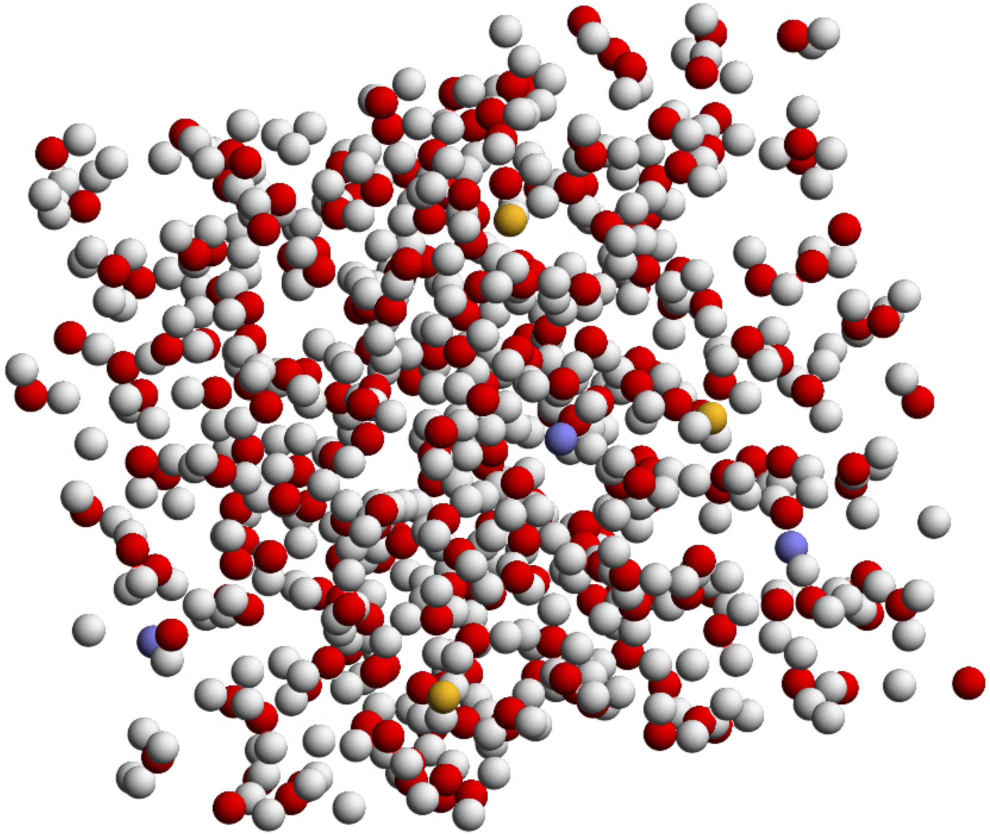


No man's land: Difficoult to reach, confinement (see my previous talk) and aqueous solutions can help



Complete Phase diagram of the supercooled region for TIP4P bulk and NaCl solution

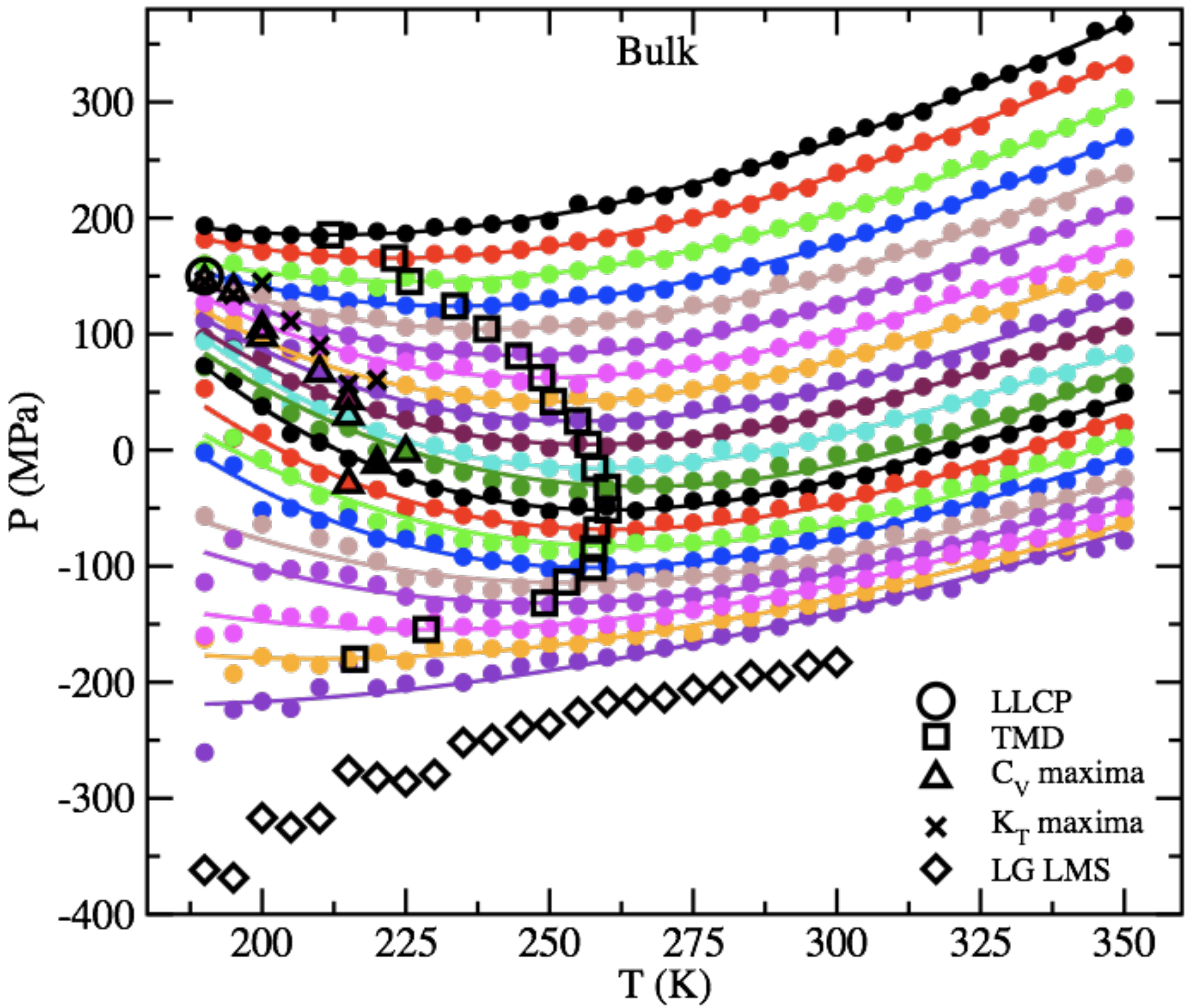
We performed extensive MD simulations on bulk TIP4P water and c = 0.67, 1.36 and 2.10 mol/kg NaCl(aq)



We employed Jensen and Jorgensen [1] ion-ion and ion-water LJ parameters for the interaction potential.

[1].K. P. Jensen, W. L. Jorgensen, J. Chem. Theory Comput. 2, 1499 (2006).

Isochore planes for pure water TIP4P



ρ = 1.10 g/cm^3

- ○ LLCP
- □ TMD
- △ C_V maxima
- x K_T maxima
- ◇ LG LMS

ρ = 0.90 g/cm^3

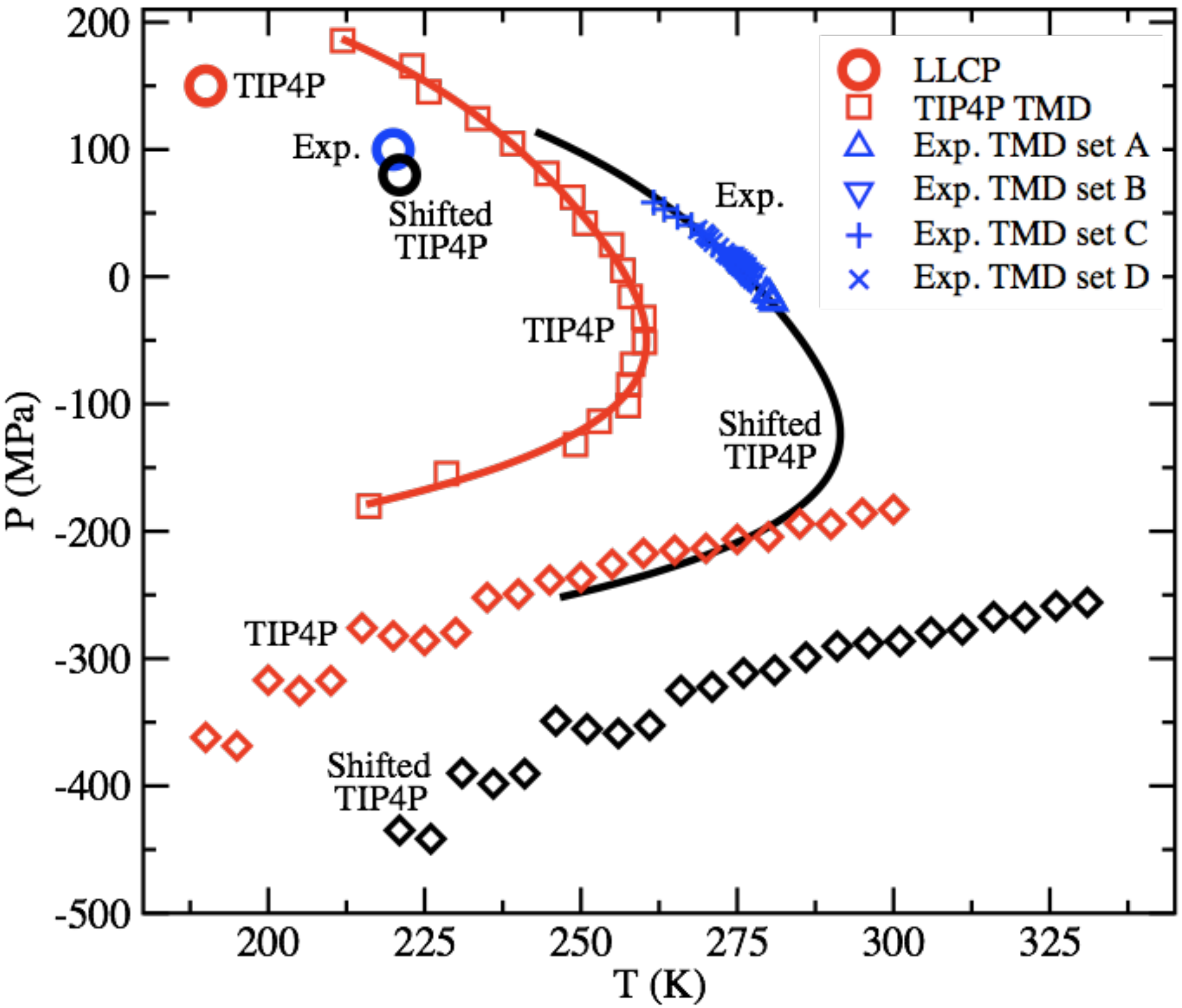
T_c = 190 K

P_c = 150 MPa

ρ_c = 1.06 g/cm^3

D. Corradini, M. Rovere, P. Gallo, JCP (2010)

TIP4P model and experiments



Shift

ΔT = + 31 K
ΔP= - 73 MPa

Experimental values:

Mishima and Stanley (1998) ○

Henderson and Speedy (1987) △

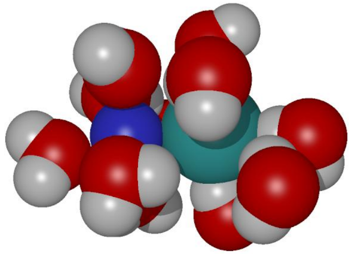
NIST Chemistry WebBook (2008) ▽

Harrington et al. (1997) +

Hill (1990) x

Widom line of supercooled bulk water and solutions of NaCl

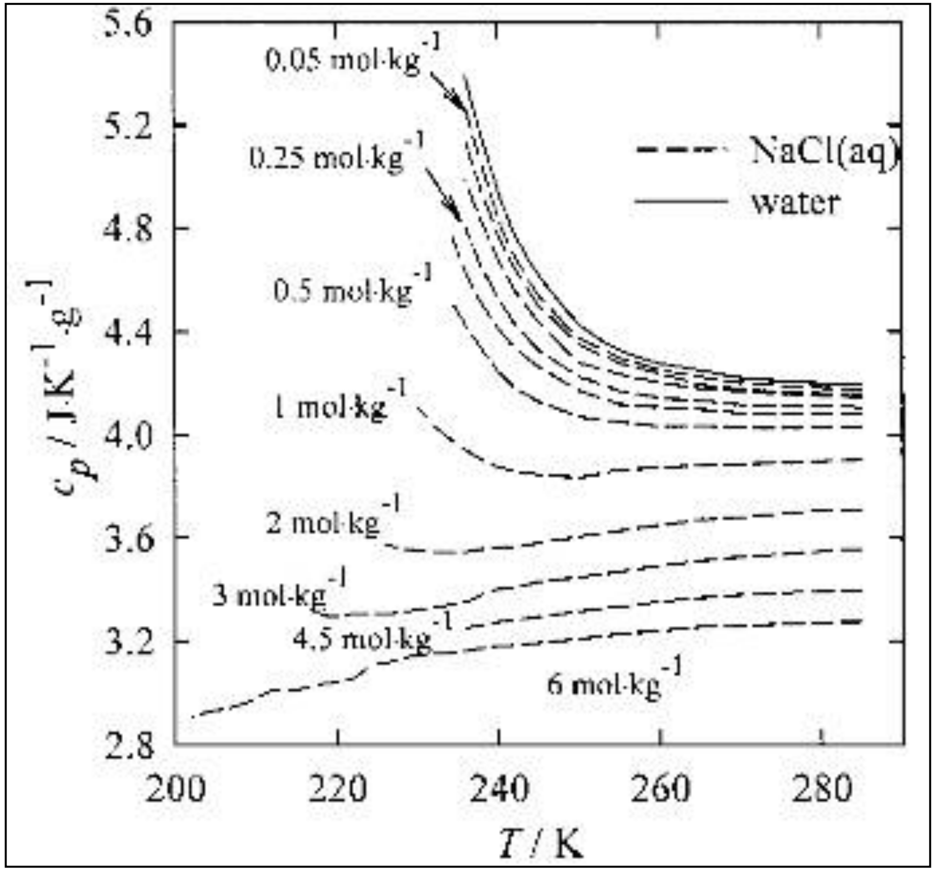
- Thermodynamics and structural properties of aqueous solutions of electrolytes are important in electrochemical and biological processes

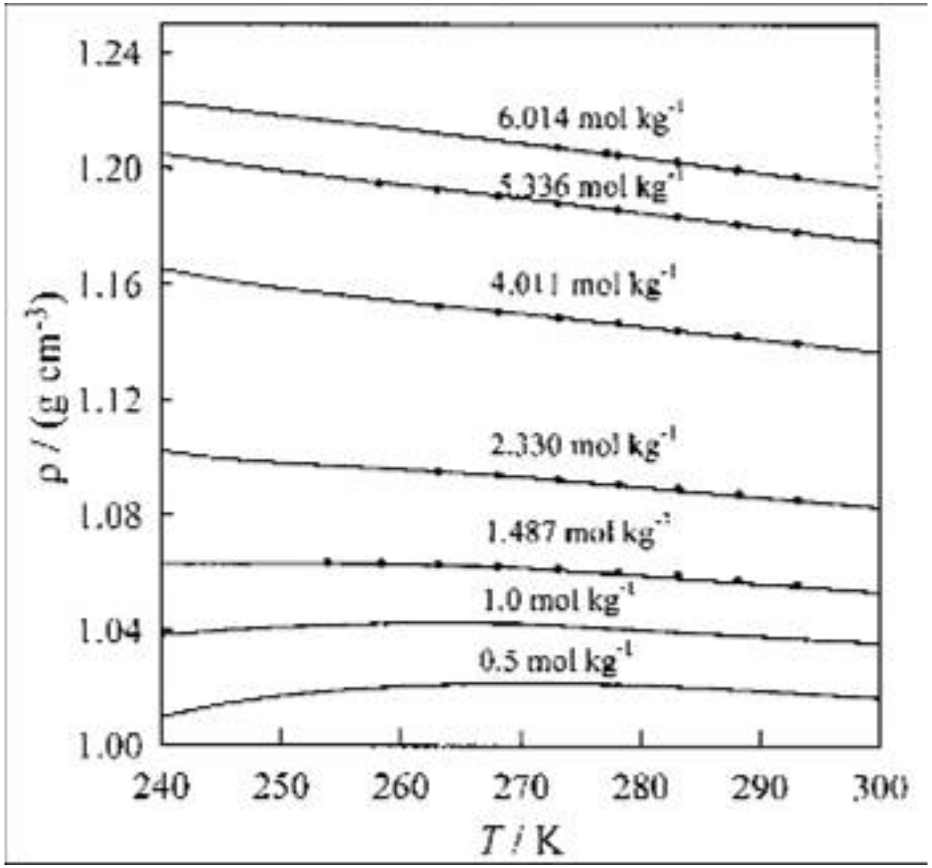


- Properties like melting point, boiling point and viscosity are influenced by the presence of the solutes

- But can aqueous solutions also help to shed light on the anomalous behaviour of water upon supercooling?

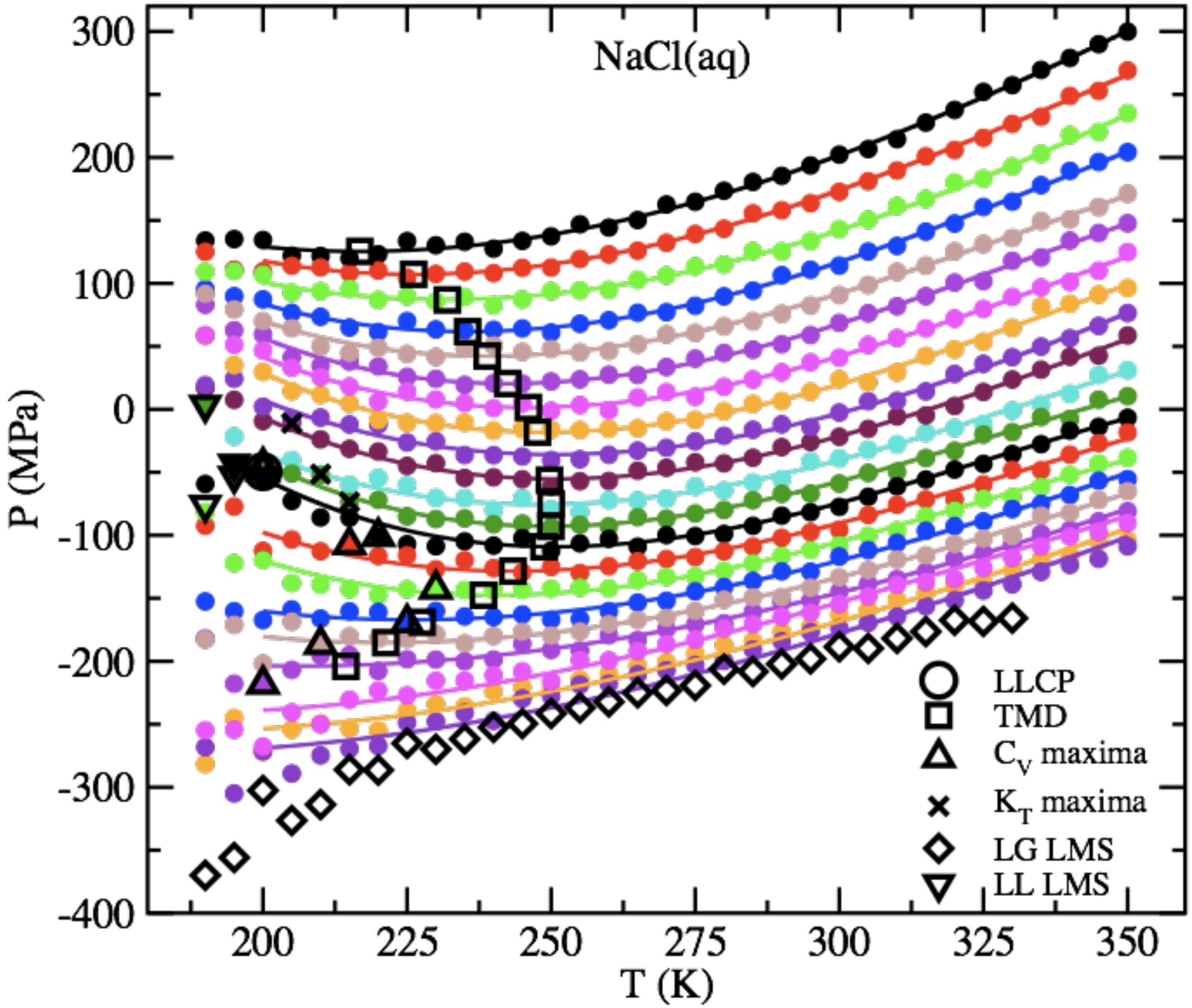
Aqueous solutions NaCl(aq): experimental results





D. G. Archer and R.W. Carter J. Phys. Chem. B (2000)

Isochores planes for c = 0.67 mol/kg NaCl(aq)



ρ = 1.10 g/cm^3

- ○ LLCP
- □ TMD
- △ Cv maxima
- x KT maxima
- ◇ LG LMS
- ▽ LL LMS

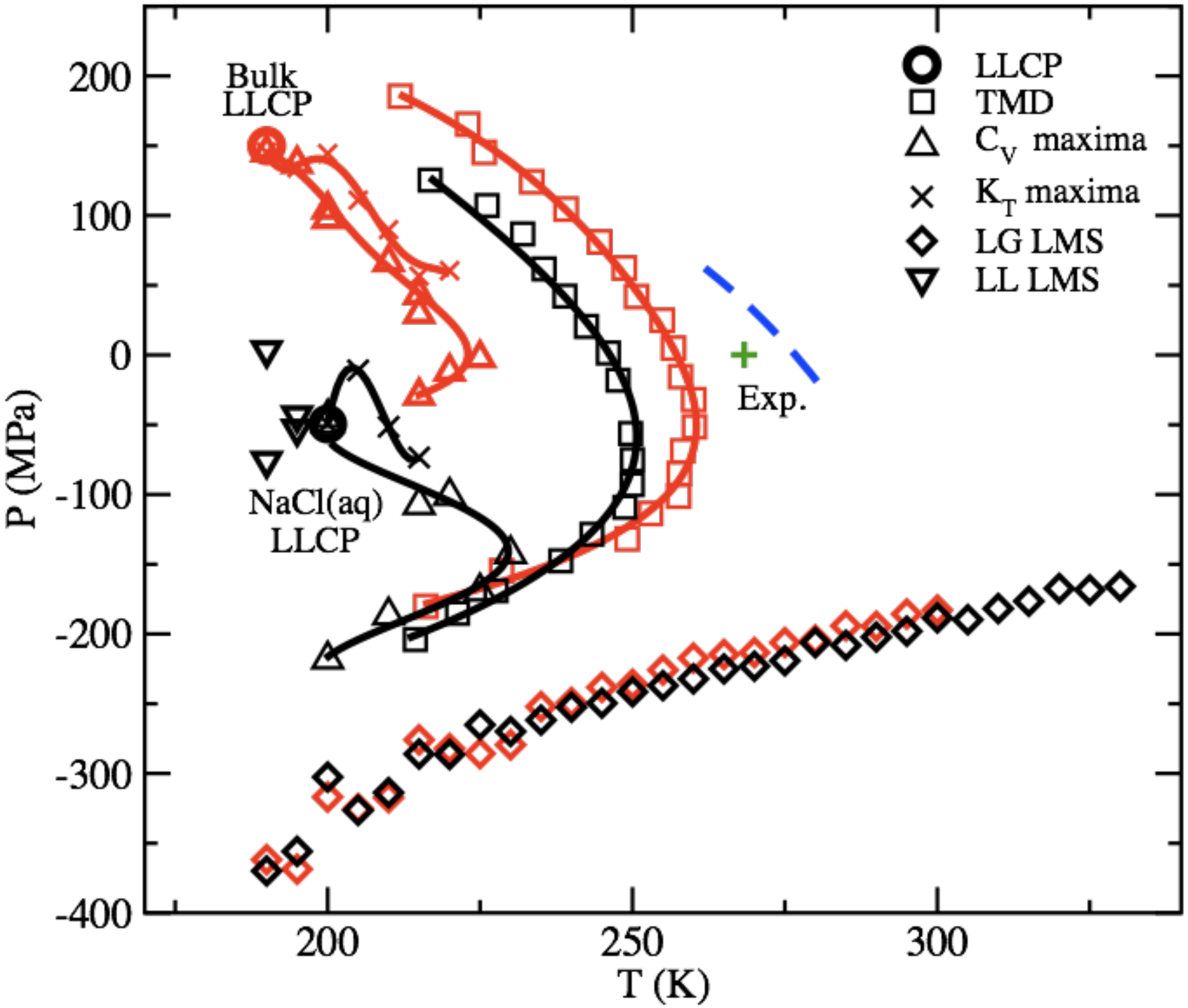
ρ = 0.90 g/cm^3

T_c = 200 K

P_c = - 50 MPa

ρ_c = 0.99 g/cm^3

Comparison between pure water and c = 0.67 mol/kg NaCl(aq)



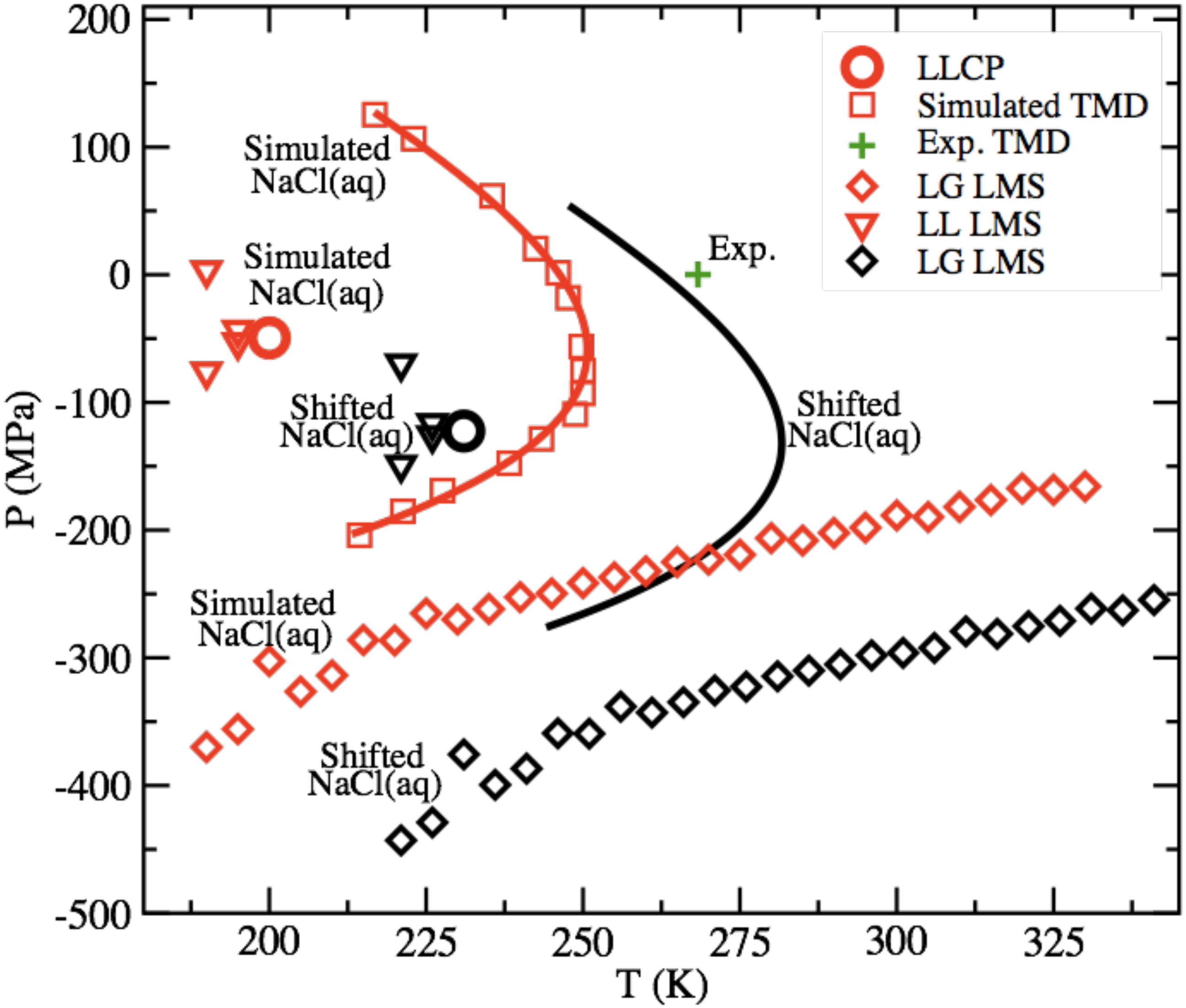
Shift of the critical point
ΔT = + 10 K
ΔP= - 200 MPa

- ○ **LLCP**
- □ **TMD**
- △ **Cv maxima**
- x **K_T maxima**
- ◇ **LG LMS**
- ▽ **LL LMS**

Experimental values:

Archer and Carter (2000) +

Simulations phase diagram NaCl(aq) and its shifted clone



Experimental value:
Archer and Carter (2000)

Translation

ΔT = + 31 K
ΔP= - 73 MPa

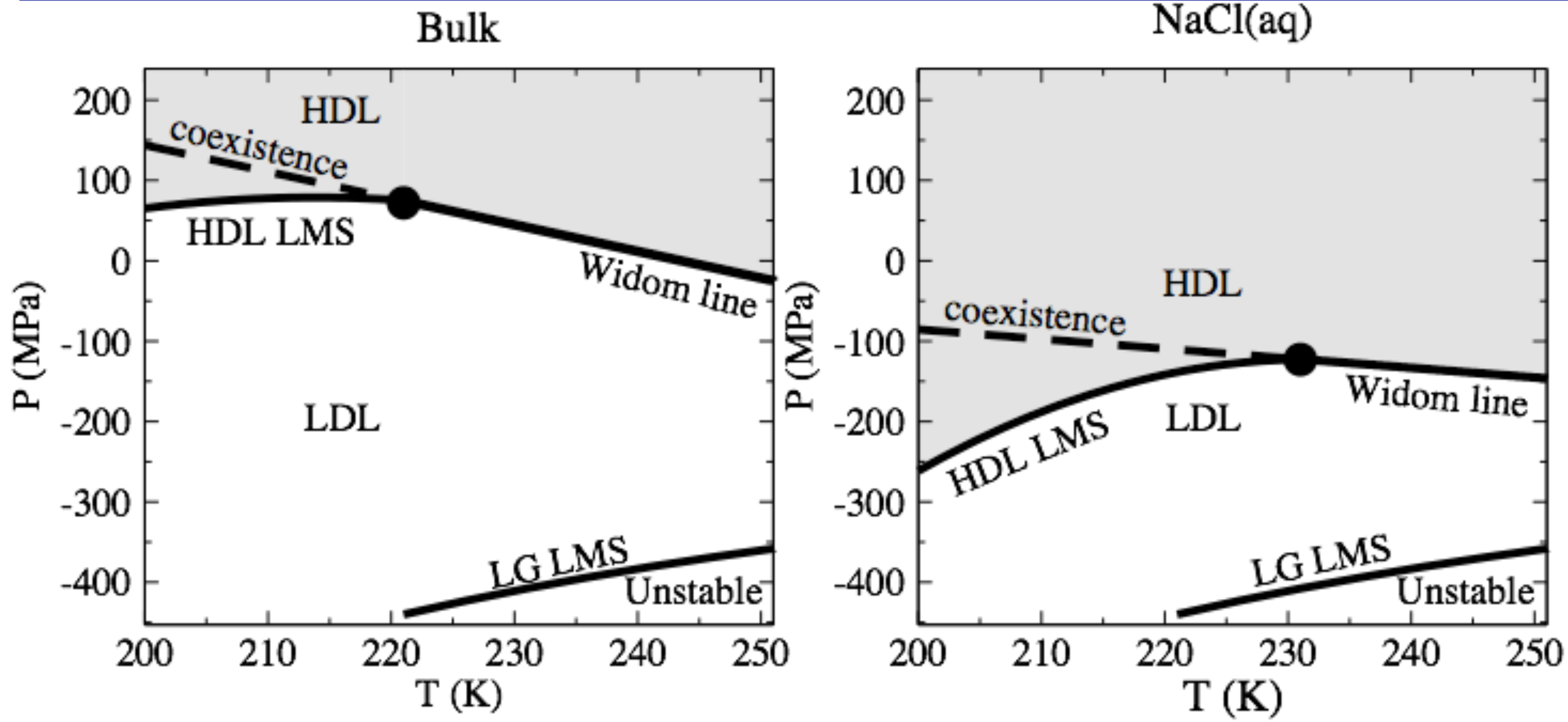
NaCl(aq) 0.67

$T_c \approx 230$ K

$P_c \approx -120$ MPa

Corradini, Rovere, Gallo JCP (2010)

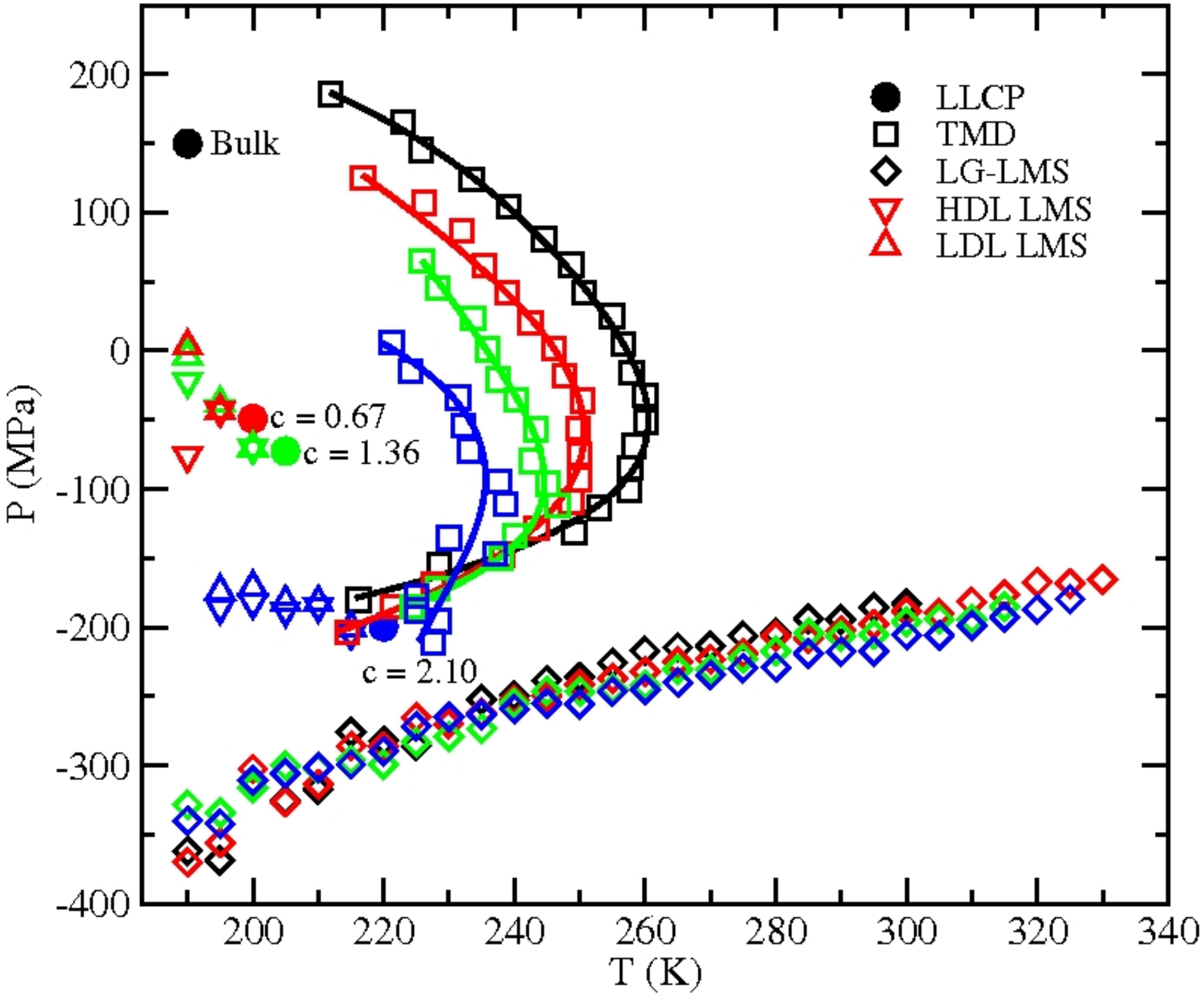
Schematic phase diagram obtained from simulation and shifted to match to experimental known values



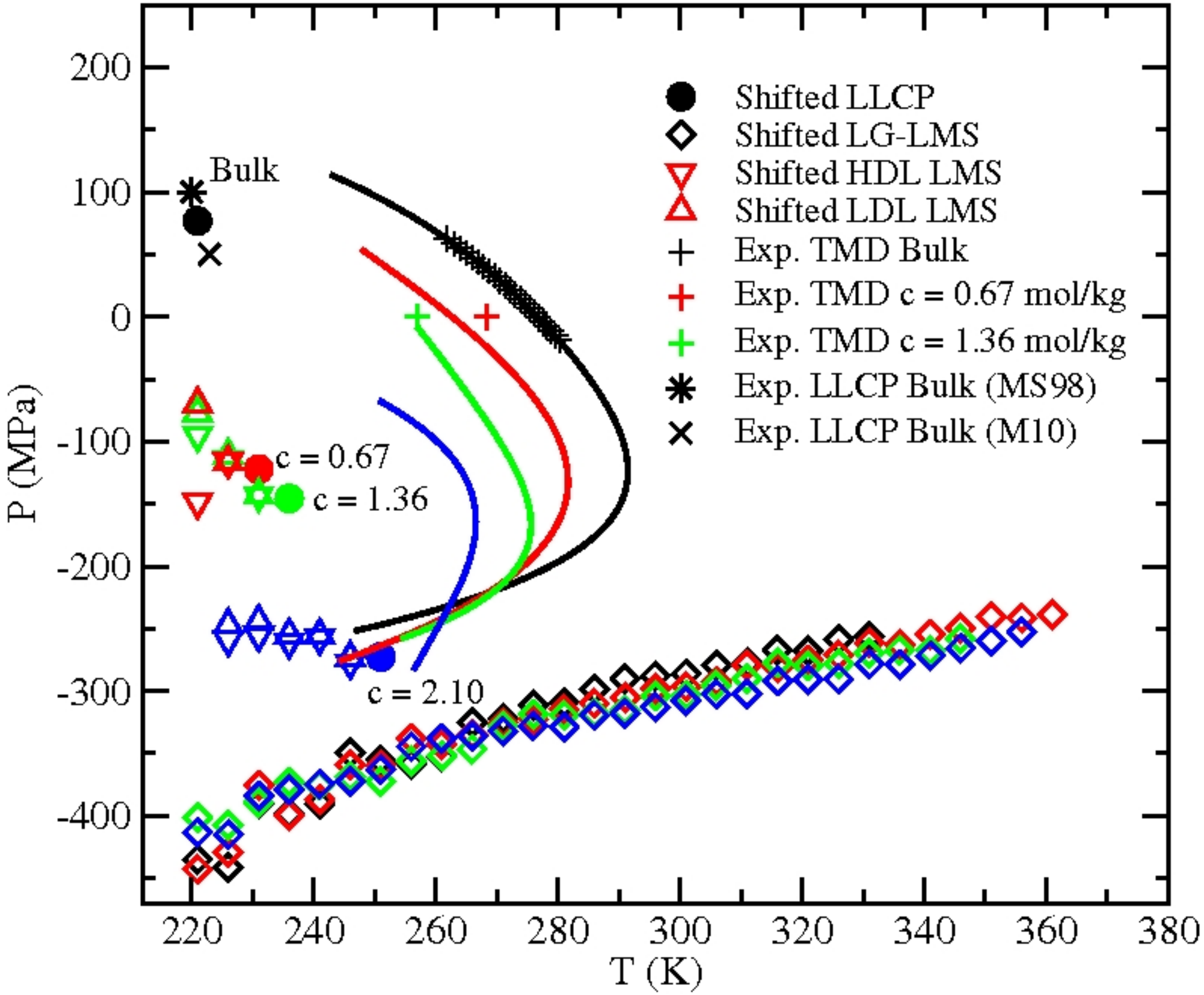
Exp: NaCl(aq) with concentration *c=1mol/kg rupture occurs at P = −140MPa (Green et al. Science 1990)*

From (Myiata et al Chem. Phys. Lett. 2002 and Kanno at al science 1975) we estimate that with this concentration LLCP falls above the temperature of homogeneous nucleation.

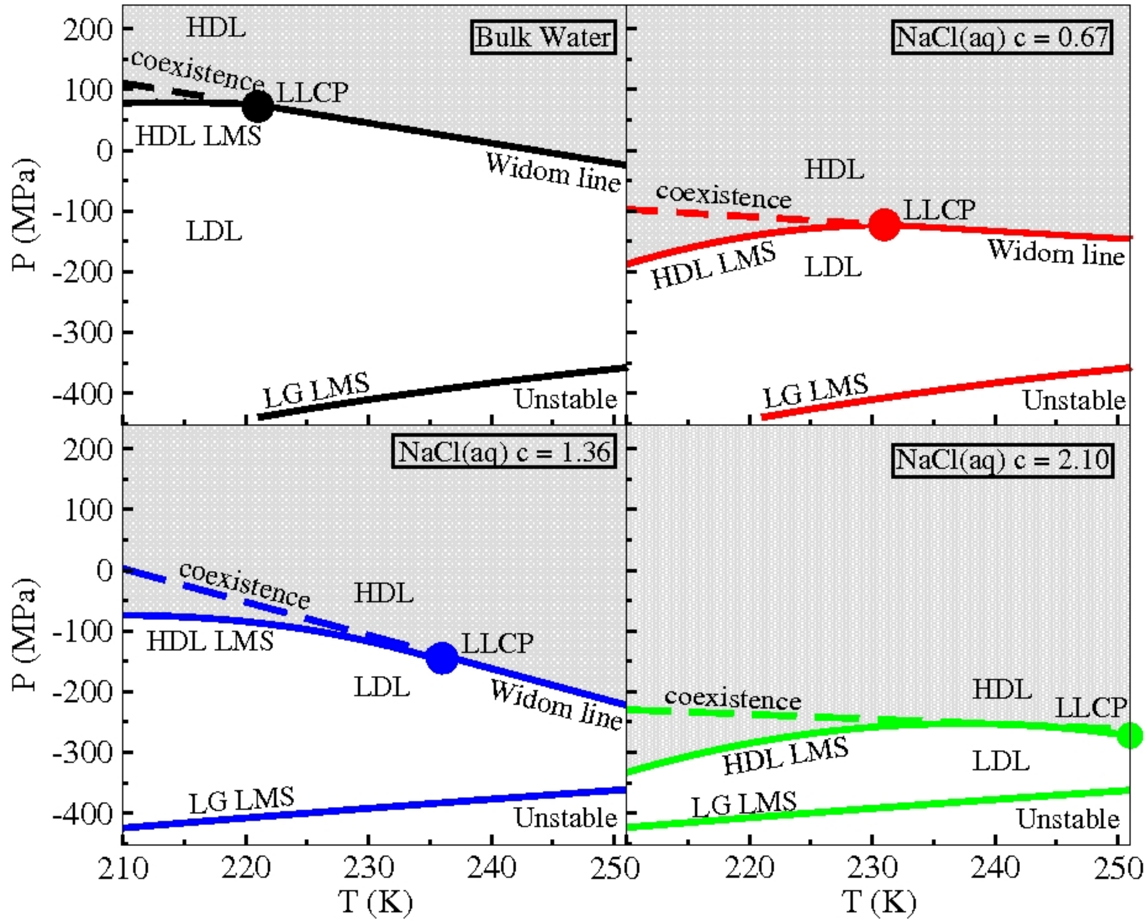
Phase diagram for several concentrations of NaCl(aq)



Same diagrams shifted to match experiments

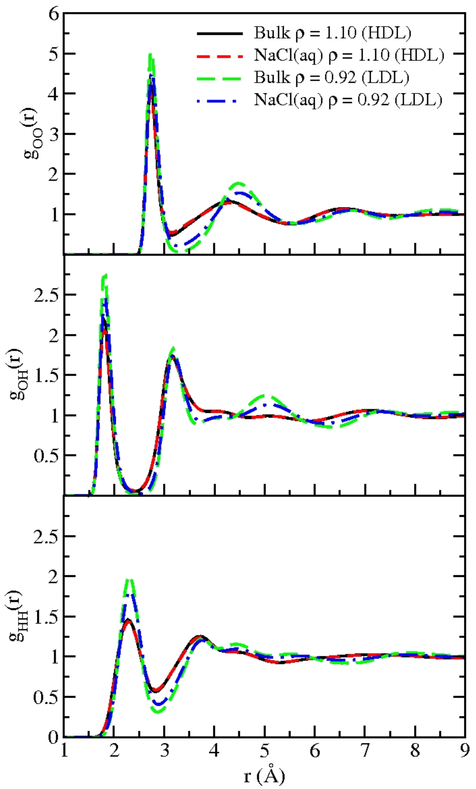


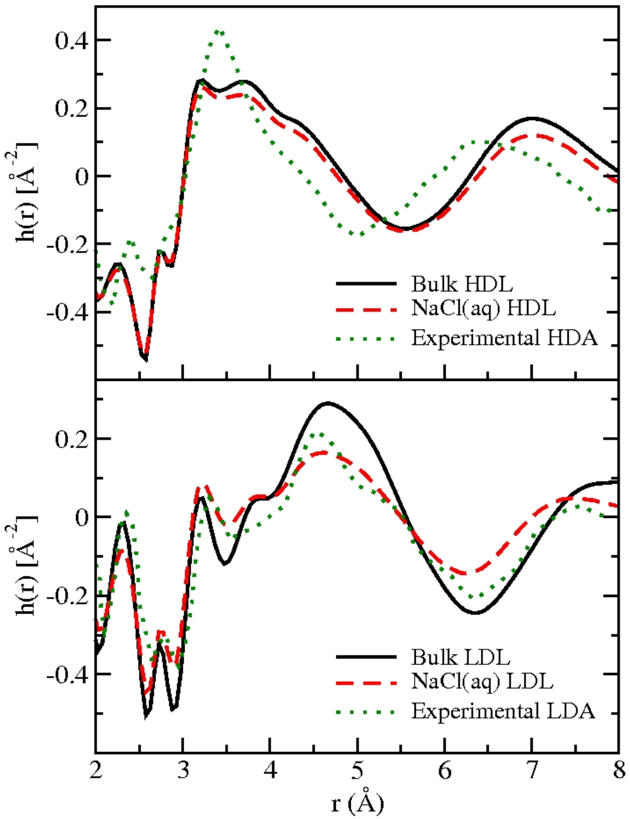
Schematic representation of the MD phase diagram as measureable in experiments



D. Corradini and P. Gallo JPCB (2011)

HDL and LDL liquids in solution: structure at T=190K for pure water and T=200K for 0.67 NaCl solution

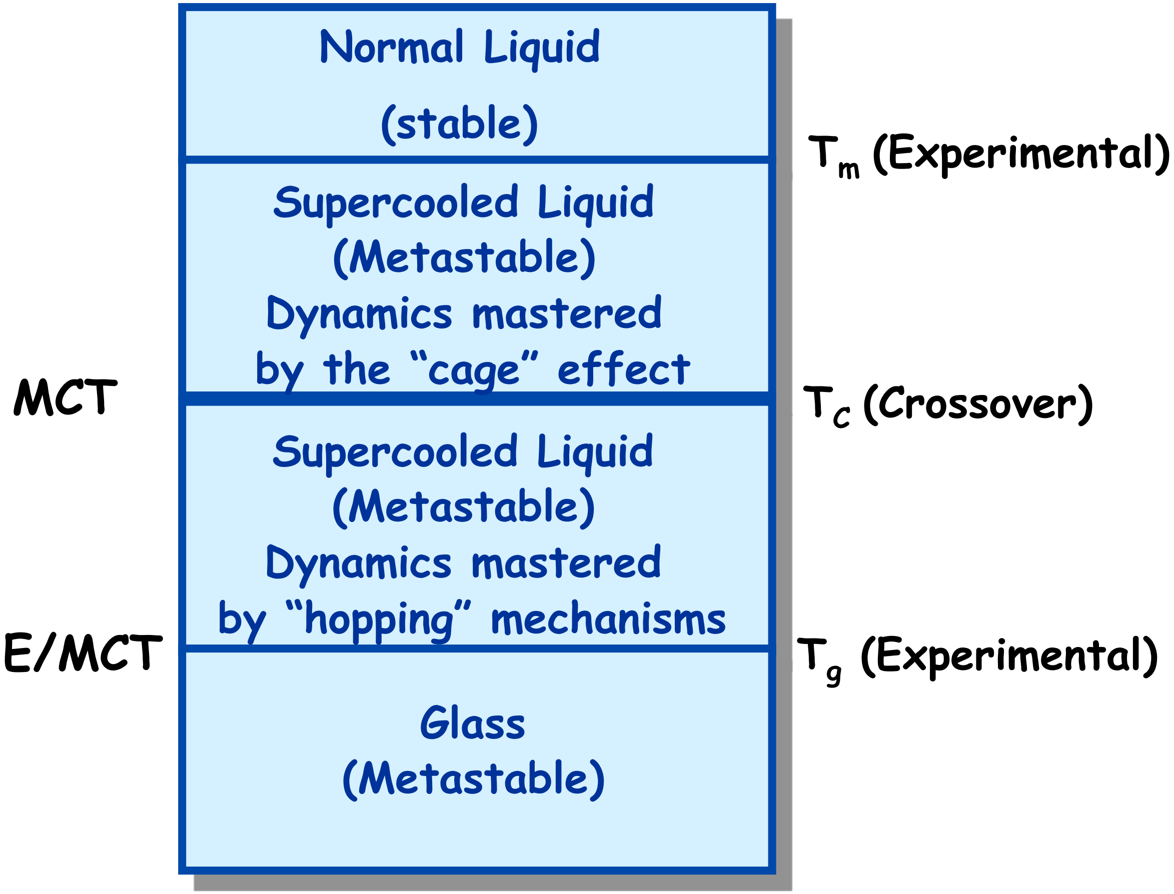




$$h(r) = 4\pi\rho r[0.092 g_{OO}(r) + 0.422 g_{OH}(r) + 0.486 g_{HH}(r) - 1]$$

Ions modify the bulk LDL structure, rendering water- water structure more similar to the bulk HDL case. The modification of the bulk LDL structure in the solution is identified in the substitution of the oxygen by the chloride ion in oxygen coordination shells. **(D.Corradini, M. Rovere and P. Gallo JCPB (2011)**

Glass Transition in supercooled water



[Complex dynamics of glass forming liquids: a mode coupling theory, W. Götze, Oxford (2009)]

In bulk water MCT works and T_c=T_s (=WL!)

[P. Gallo, F. Sciortino, P. Tartaglia, S.-H. Chen PRL 1996; F. Sciortino, P. Gallo, P. Tartaglia, S.-H. Chen, PRE 1996, EXP: Sokolov et al. PRB (1994),Torre et al Nature 2004]

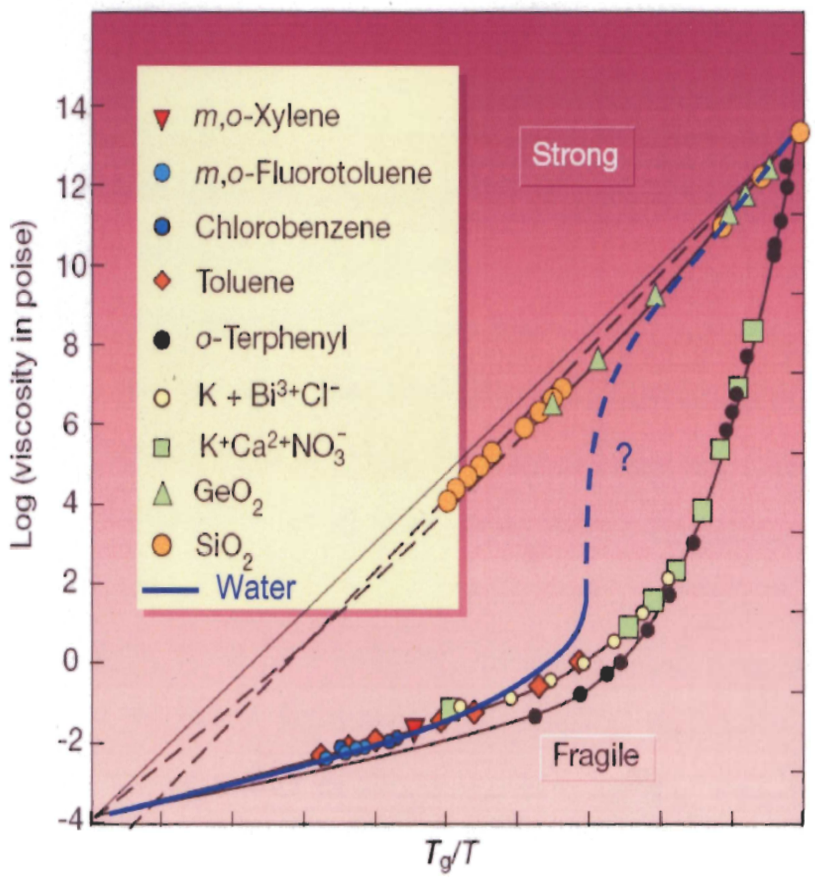
In confinement (Vycor glass pores) T_c is still present

[P. Gallo, M. Rovere and E. Spohr, PRL 2000; ibid JCP 2000]

In MCM-41 MCT still works and we have the FTS transition pointing to the LLCP

[Faraone et al. JCP 2004. L. Liu, SH Chen A. Faraone CW Yen CY Mou PRL 2005. P. Gallo, M. Rovere and S.-H. Chen, JPCL (2010)]

Fragile to Strong transition in water and the LLCP



P.G. Debenedetti, F.H. Stillinger, *Nature* **410**, 259 (2001)

$$\eta = G_\infty \tau$$ (Maxwell's Relation)

Fragile VFT $$\tau = \tau_0 \exp\left[\frac{BT_0}{T - T_0}\right]$$

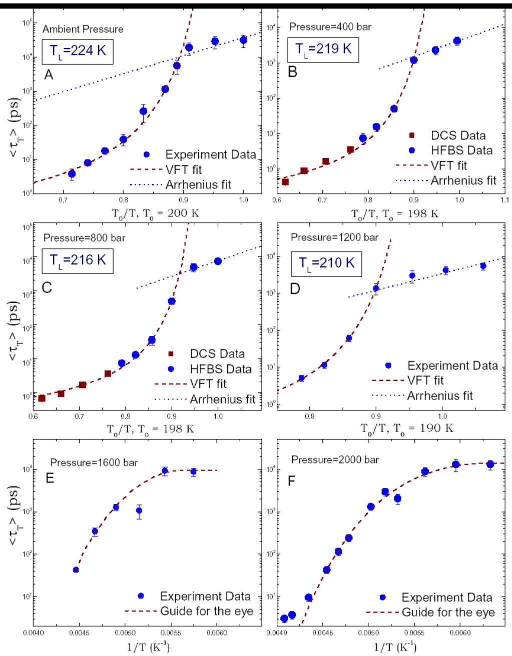
Fragile MCT $$\tau \propto (T - T_C)^{-\gamma}$$

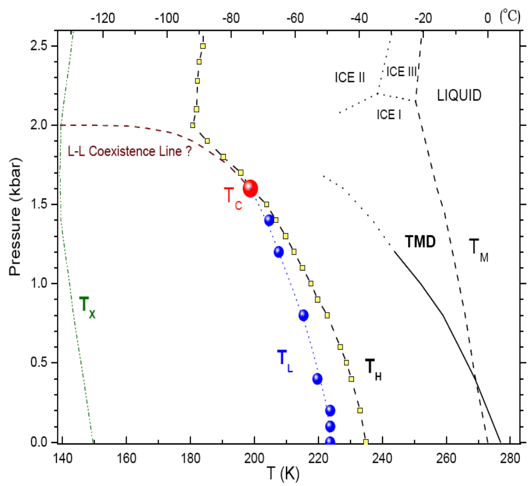
Strong $$\tau = \tau_0 \exp\left[\frac{E_A / k_B}{T}\right]$$

The occurrence of a fragile-strong transition in water [1] pointing to the LLCP [2] has been connected to WL emanating from the LLCP [3].

[1]F.W. Starr, F. Sciortino, H.E. Stanley Phys. Rev. E 60, 6757(1999)
[2] L. Liu, S.-H. Chen, A. Faraone, C.-W. Yen and C.-Y. Mou, Phys. Rev. Lett. **95**, 117802 (2005)
[3] L. Xu, P. Kumar, S. V. Buldyrev, S.-H. Chen, P. H. Poole, F. Sciortino and H. E. Stanley, Proc. Natl. Acad. Sci. USA **102**, 16558 (2005).

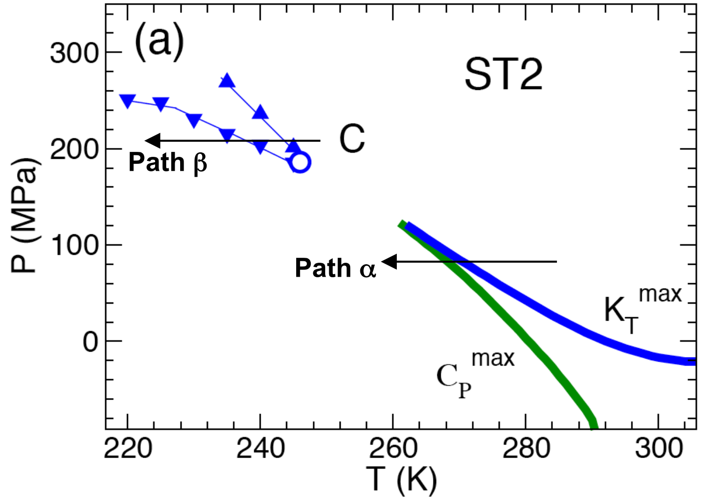
Experiments water in MCM-41 Fragile-to-Strong Dynamic Transition under Pressure

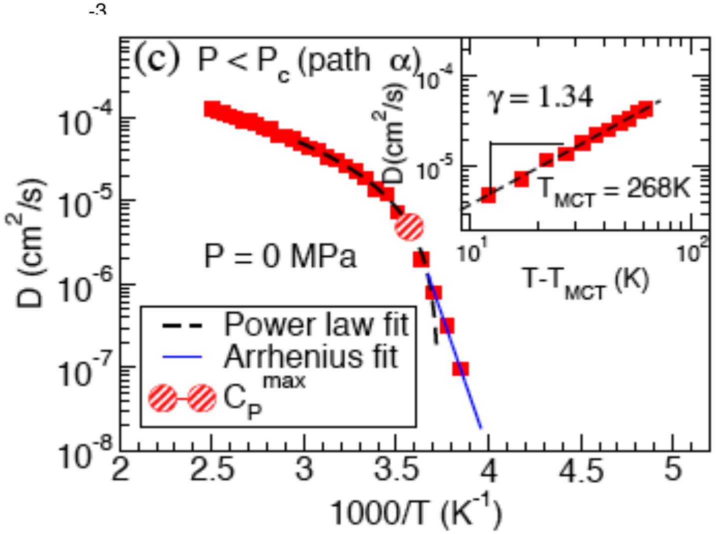




[L. Liu, S.H. Chen, *A. Faraone, C.W. Yan and C.Y. Mou, Phys. Rev. Lett. 95, 117802* (2005). Mallamace et al JCP 2006] .

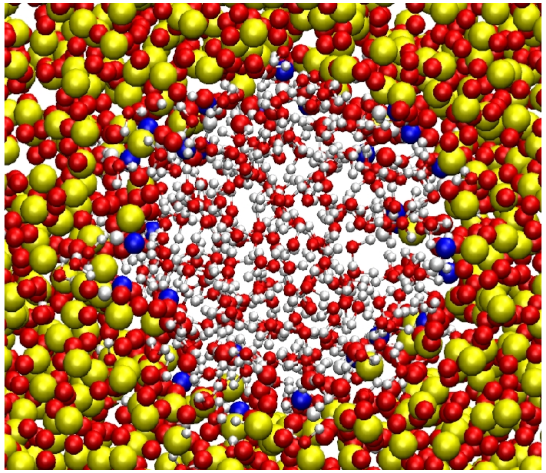
Comparison between our QENS results and MD simulation of bulk ST2 model water

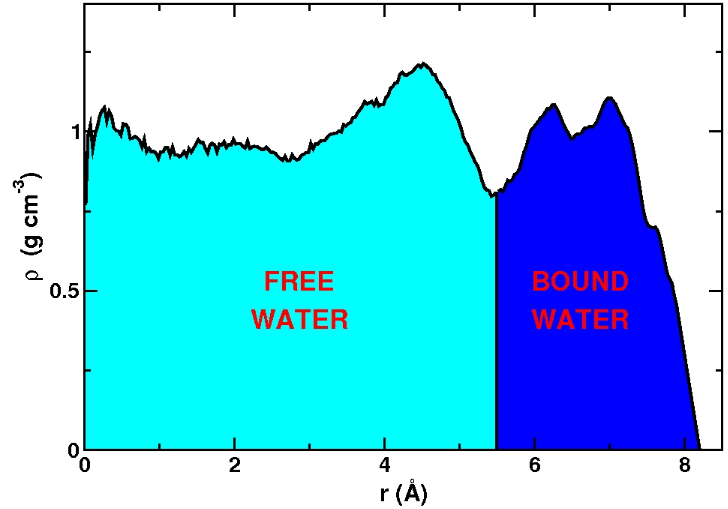


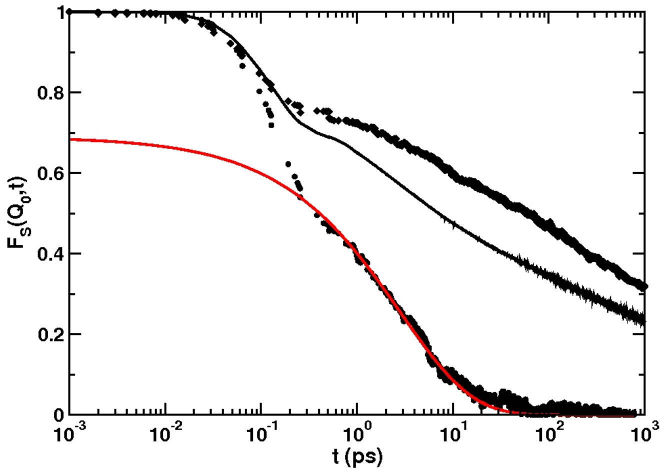


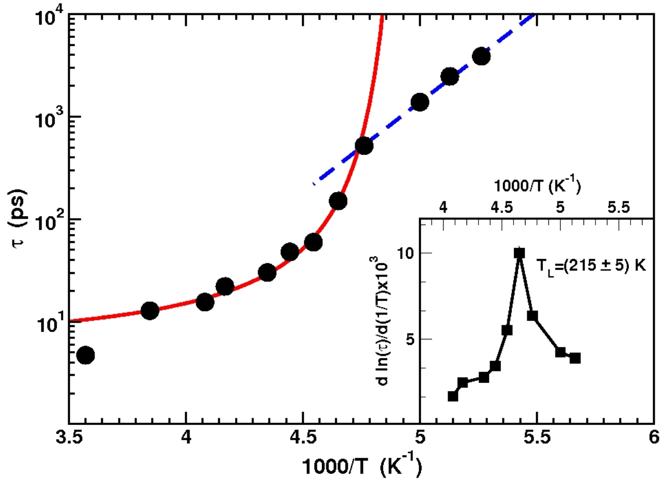
According to ST2 model of water, the locus of F-S transition coincides with the locus of Cpmax. Also TIP5P supports the connection between the Widom line and F-S xu et al. PNAS 2005.

MD simulations of water inside the MCM-41 pore in a nutshell









P. Gallo, M. Rovere, S.-H. Chen, J. Phys. Chem. Lett. 2010

β ranges from 0.58 to 0.46 similar to what found in QENS experiments by Faraone et al JCP 121, 10843 (2004)

Parameters of the transition

Fragile behaviour from fit to VFT

T_0=200 K EXP: 190÷200 K [1] BULK SPCE: 210 K [2]

Crossover temperature: T_{cross}= 215 K EXP: 210÷224 K [1]

Strong behaviour from fit to Arrhenius law

Activation energy E_A= 34 kJ/mol BULK: 65 kJ/mol [2]

Peak in the specific heat at the crossover

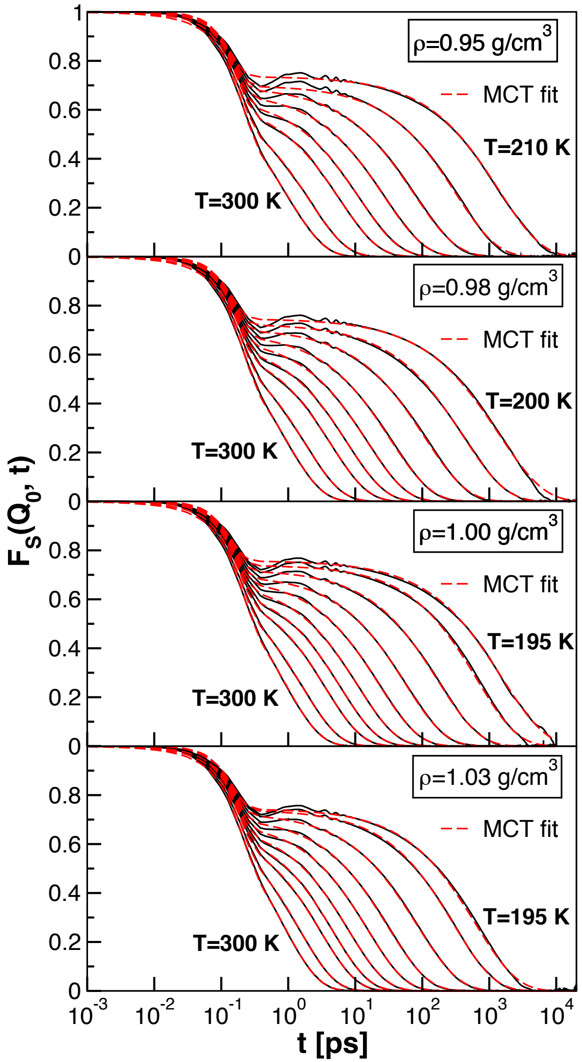
[1] L. Liu, S.-H. Chen, A. Faraone, C.-W. Yen and C.-Y. Mou, Phys. Rev. Lett. **95**, 117802 (2005); A. Faraone, L. Liu, C.-W. Yen C.-Y. Mou and S.-H. Chen, J. Chem. Phys. **121**, 10843 (2004).

[2] F. Starr, F. Sciortino and H. E. Stanley Phys. Rev. E **60**, 6757 (1999).

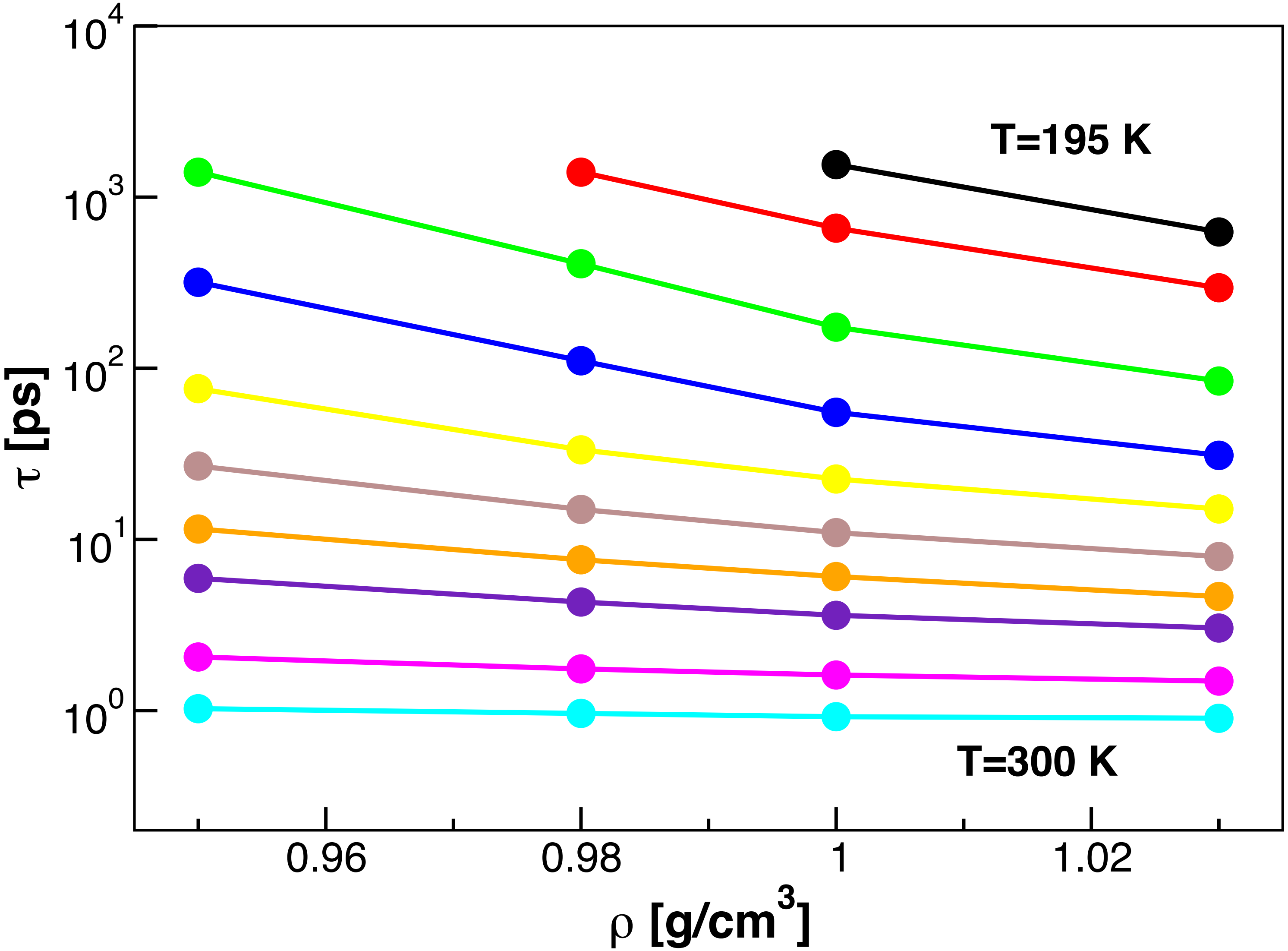
MCT, FTS and the role of hopping: recent results for MD on TIP4P/2005

- **We performed extensive MD simulations on bulk TIP4P/2005 water for ρ = 0.95, 0.98, 1.00 and 1.03 gr/cm^3 and T spanning from 300 to 195 K**

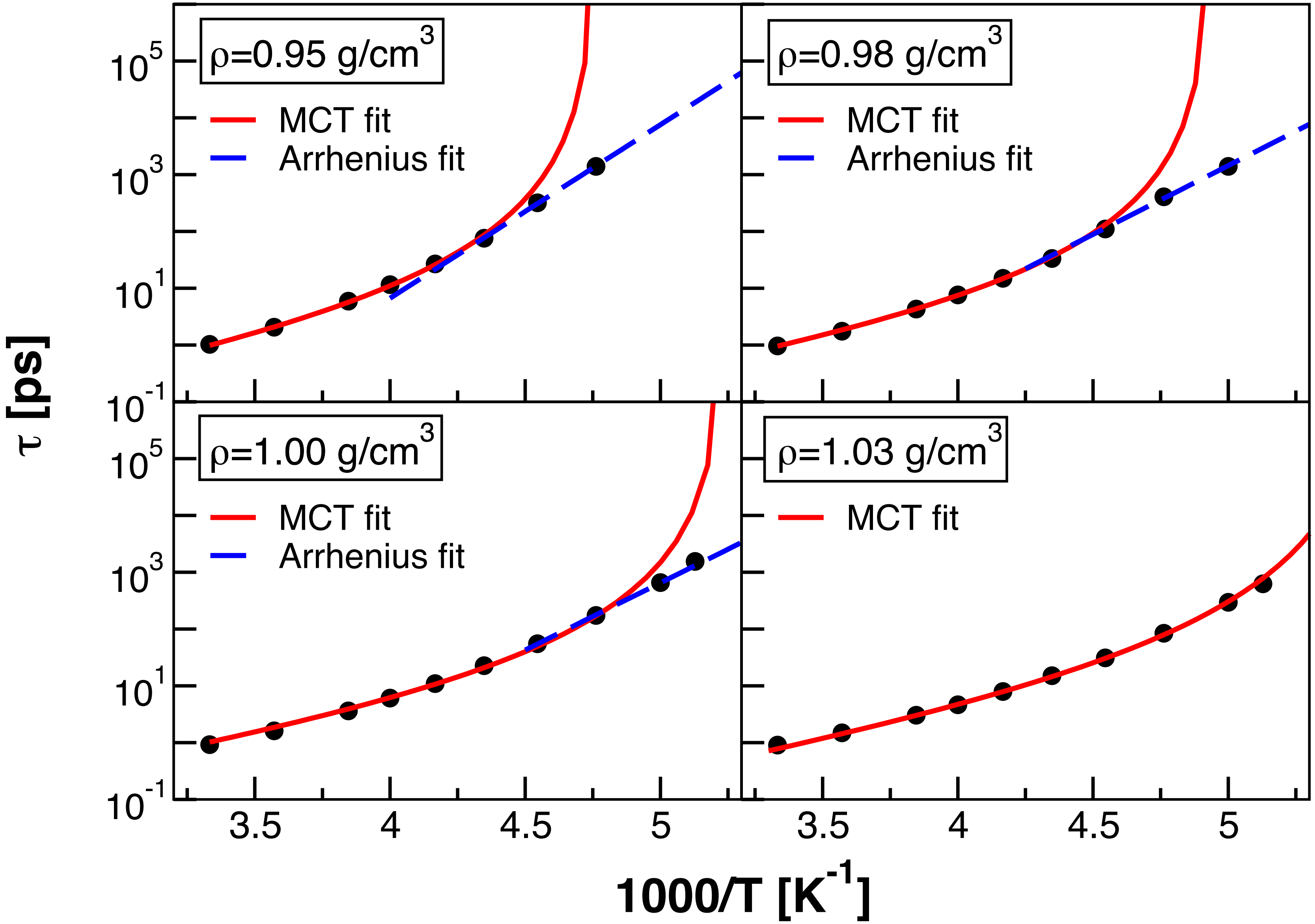
TIP4P/2005: Oxygen intermediate scattering functions and fit



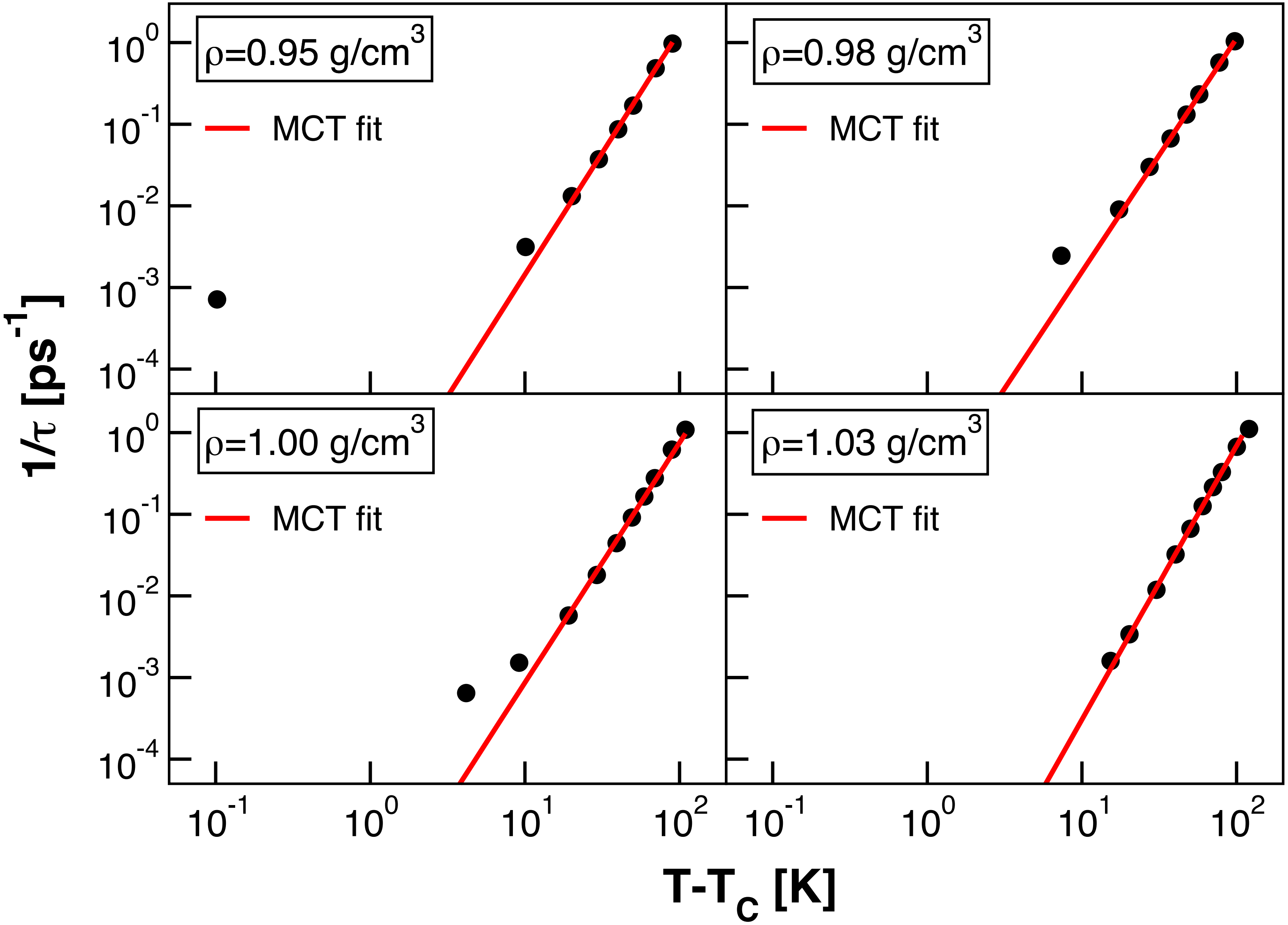
TIP4P/2005: τ values



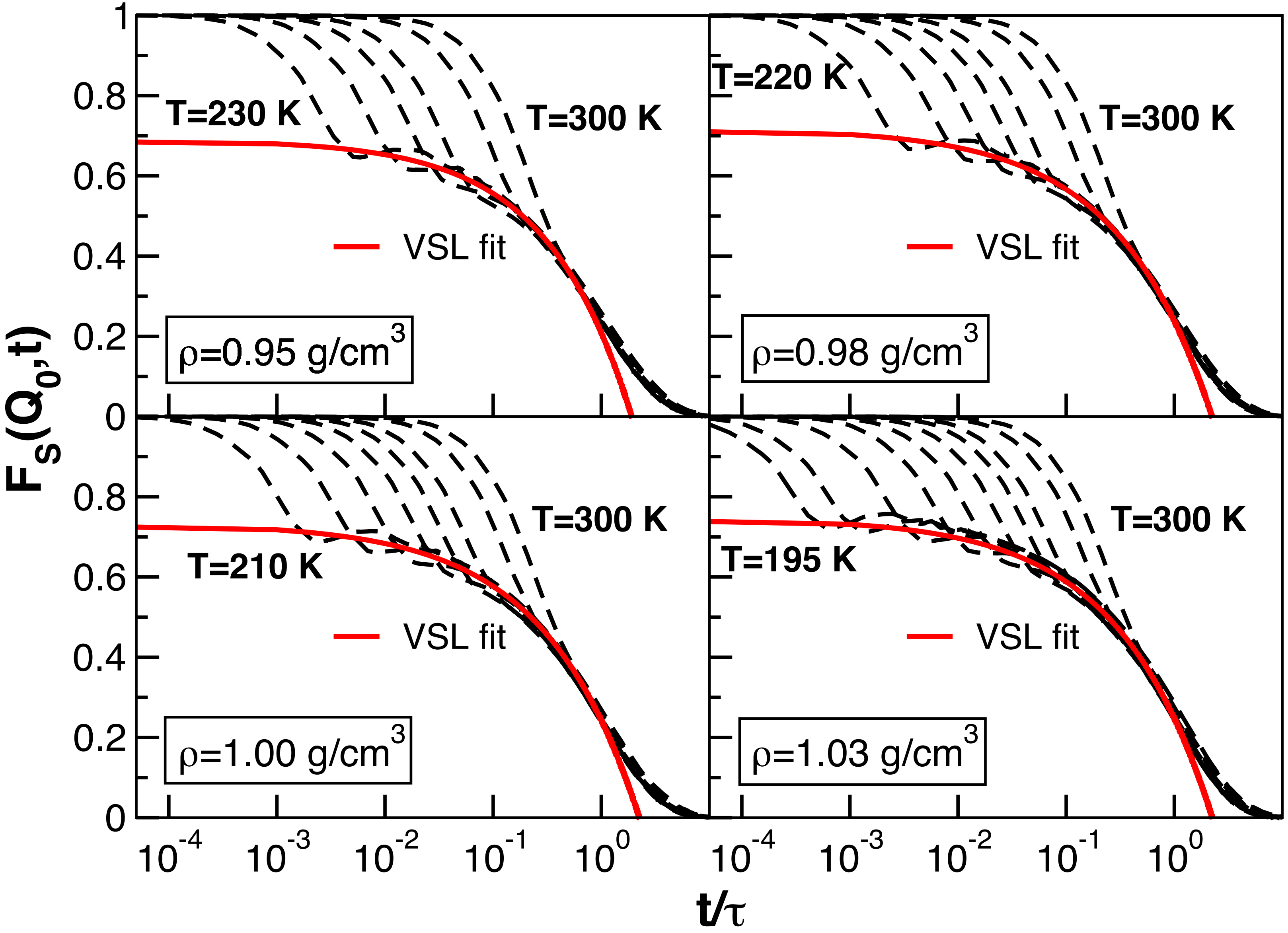
TIP4P/2005: FTS crossover



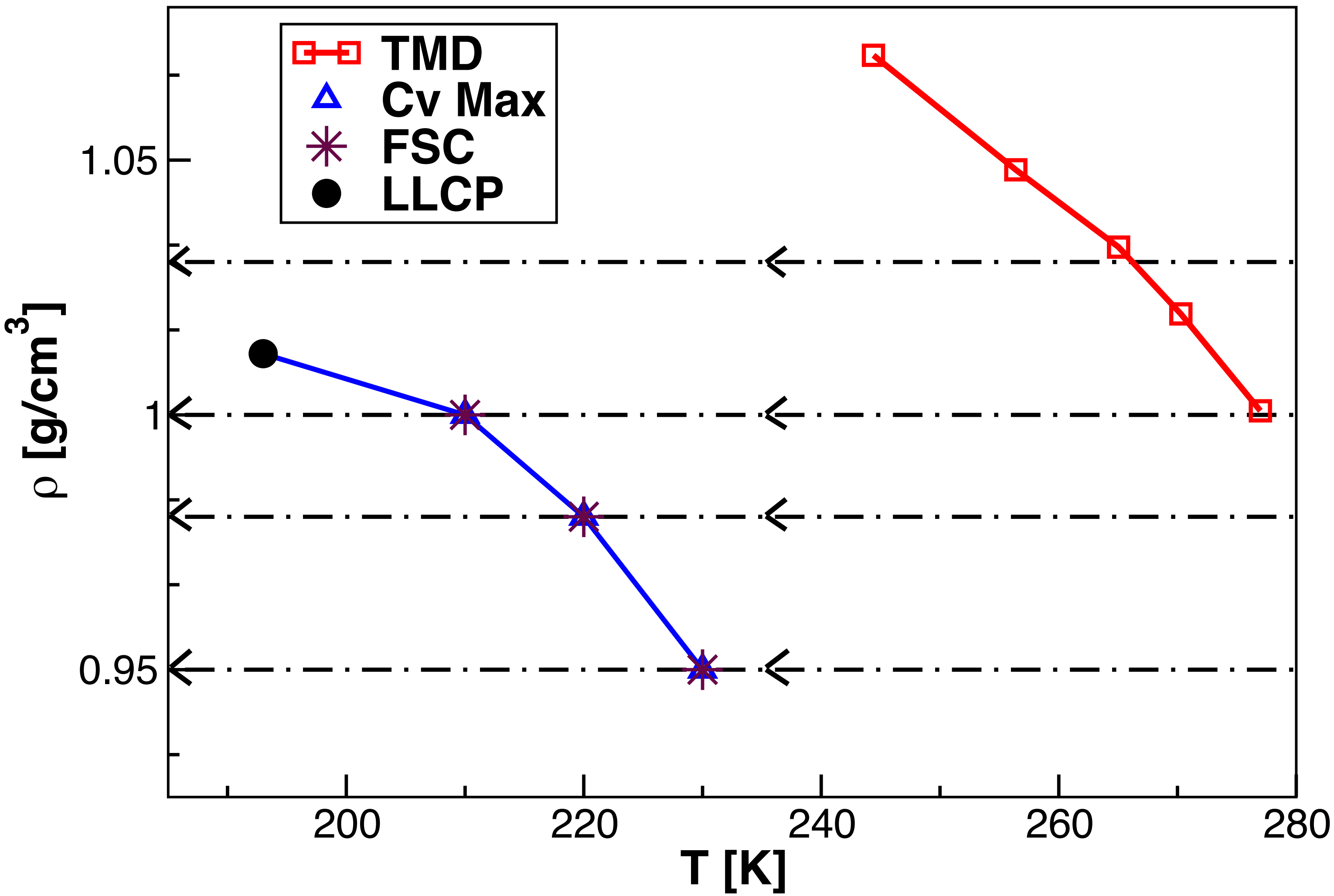
TIP4P/2005: FTS crossover



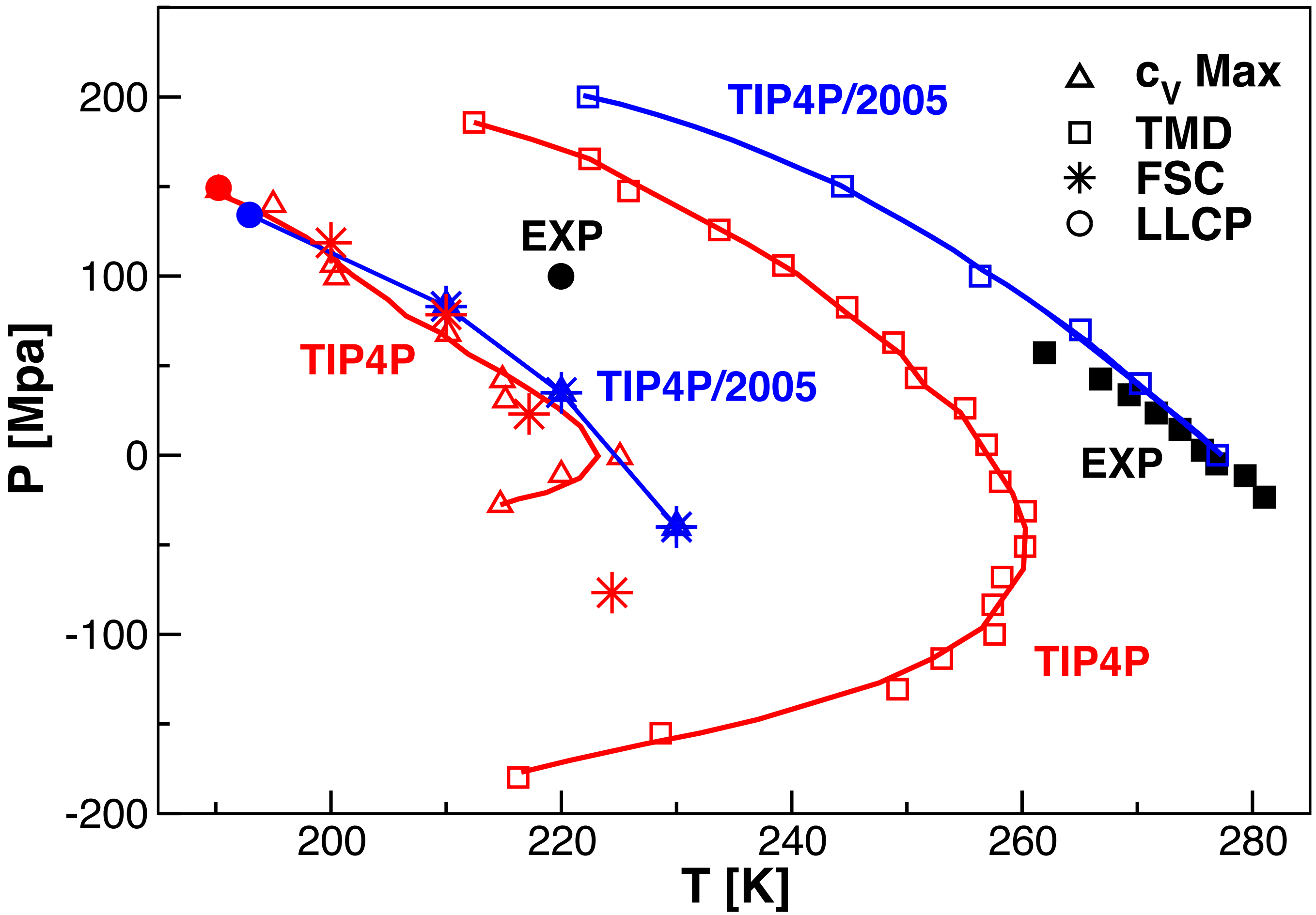
TIP4P/2005: MCT test von Schweidler law



TIP4P/2005: FTS crossover and Widom line in ρ,T plane

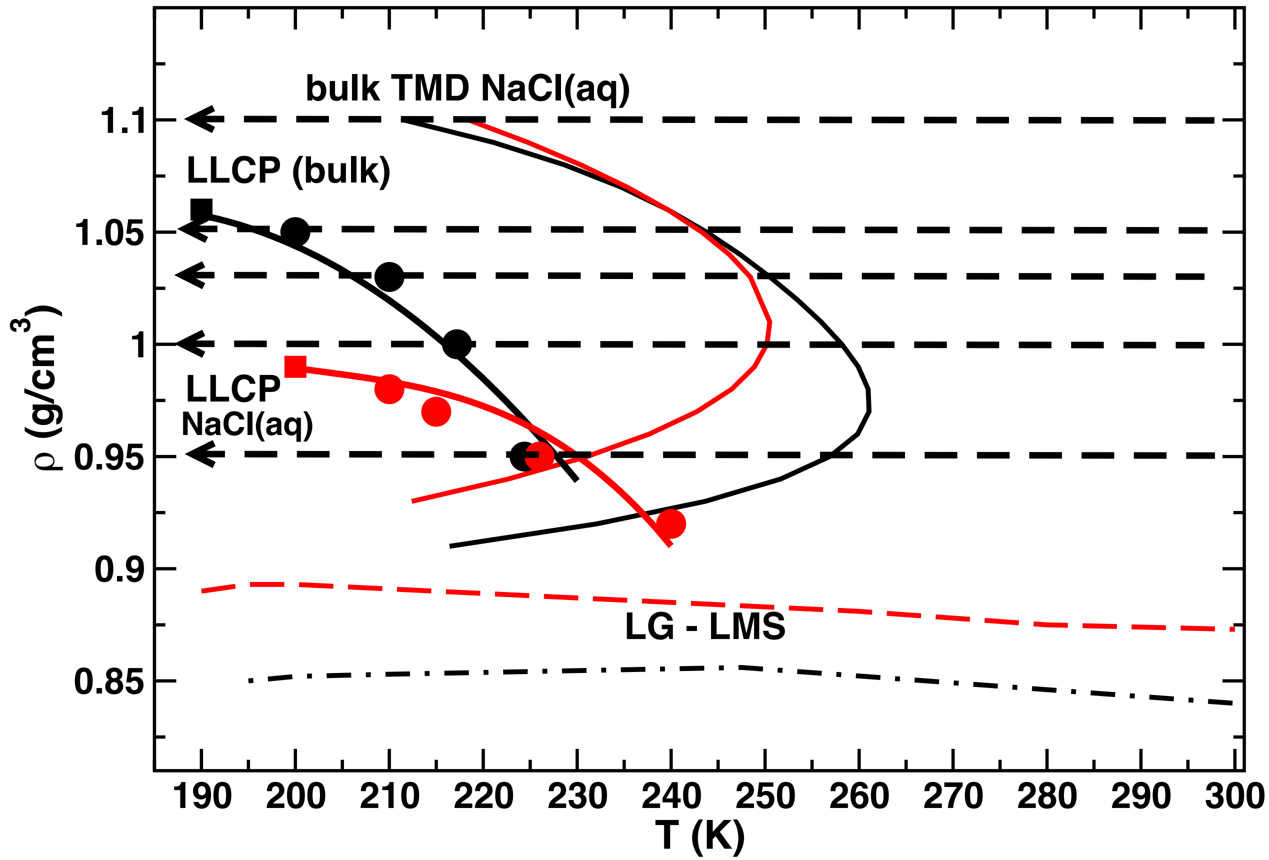


TIP4P/2005 and TIP4P FTS crossovers and Widom line in P,T plane



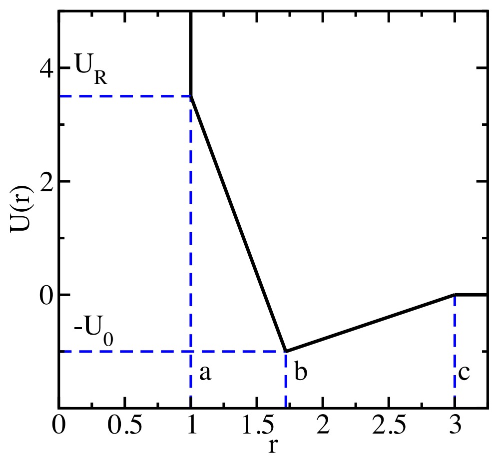
M. De Marzio, G. Camisasca, M. Rovere and P. Gallo, JCP (2016).

Fragile to strong crossover (CIRCLES) and Widom lines: NaCl solution (TIP4P) and bulk (TIP4P) compared



Ramp potentials, bulk Jagla

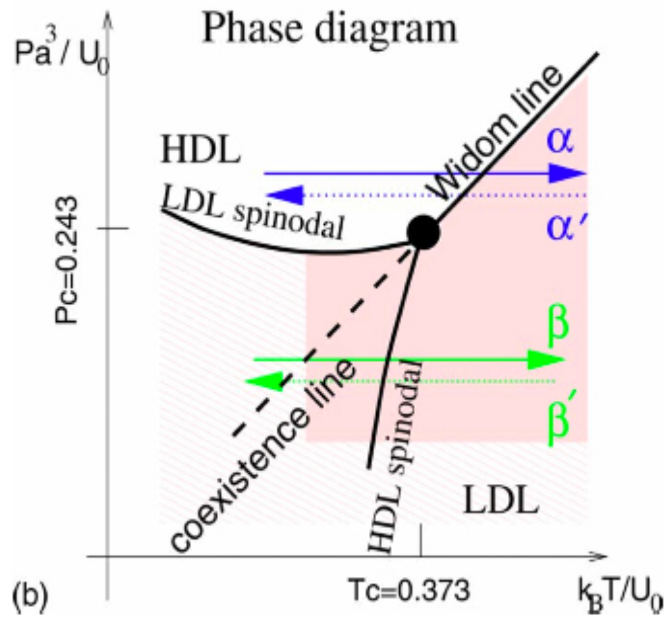
Jagla, spherically simmetric potential
Hard core → water 1st coord. shell
Soft core → water 2nd coord shell



$b/a = 1.72$

$c/a = 3$

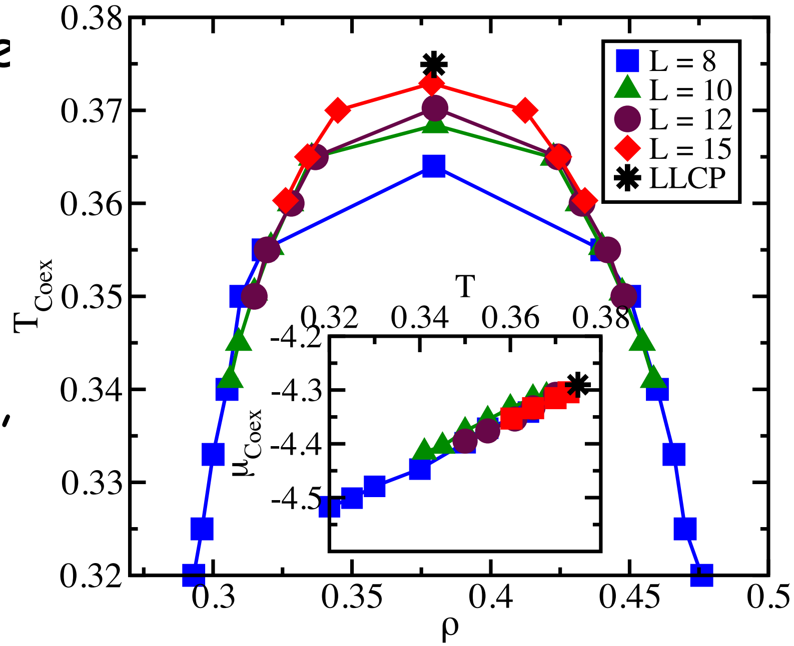
$U_R = 3.56\,U_0$



It has a LLCP and a FTS transition upon crossing the WL
Xu, Buldyrev, Angell and Stanley, Phys. Rev. E **74**, 031108 (2006) ;
Xu, Buldyrev, Giovambattista, Angell and Stanley, J. Chem. Phys. **130**, 054505 (2009)
The LLCP has been rigorously proven to be a second order critical point belonging ti the Ising Universality Class
Gallo, Sciortino, Phys. Rev. Lett. 109, 177801 (2012)

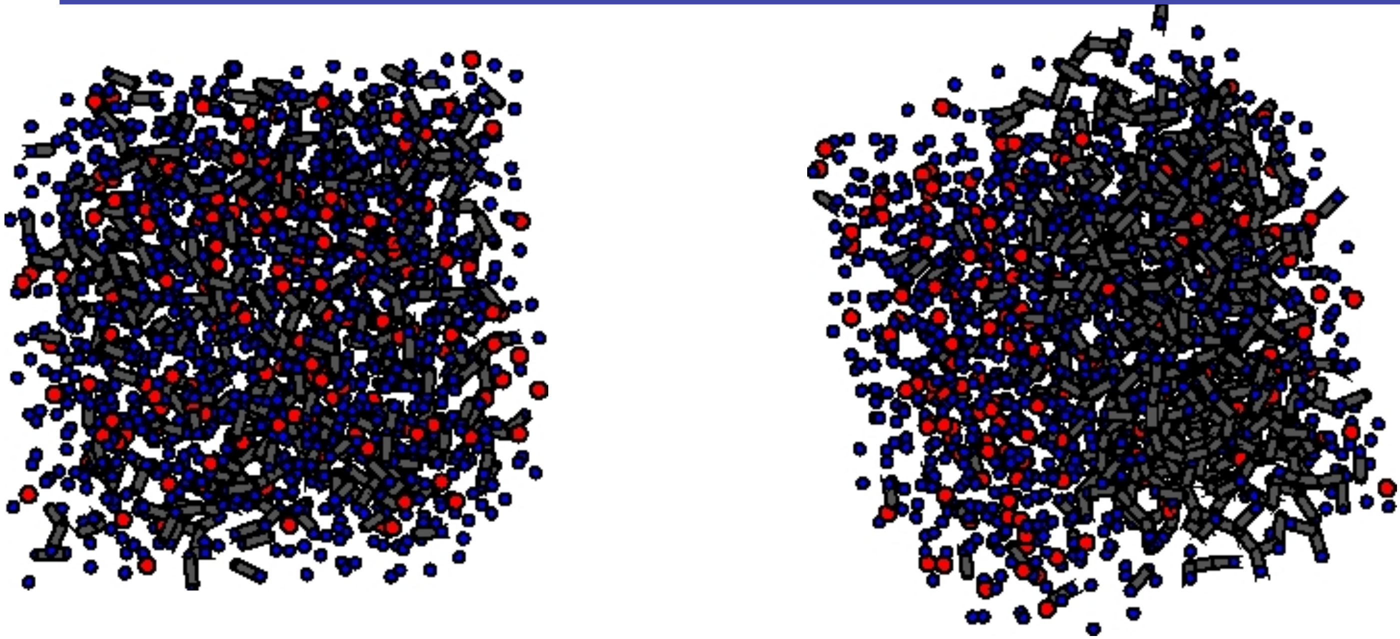
The LLCP in Jagla is a second order critical point that matches the Ising universality class

- A LL critical point, consistent with the three-dimensional Ising universality class, the same universality class of the gas liquid transition, does exist in the Jagla model (calculated by finite size scaling).
- T_C=0.3749, μ_C=-4.2902 ρ_C=0.3795 similar to the estimate of Xu, Buldyrev, Angell, Stanley PRE (2006) from DMD simulations.
- The study thus provides a rigorous proof of the second order nature of the LL critical point in the one-component Jagla model and do also prove that stable as in this case (or metastable) liquid-liquid critical points can indeed exist in models with competing structures.



Paola Gallo and Francesco Sciortino
Ising universality class for the liquid-liquid critical point of a one component fluid: A finite-size scaling test
Phys. Rev. Lett **109**, 177801 (2012).

Solution of hard spheres in Ramp Potential particles



DMD simulations of N_{tot} = 1728 particles (JRP+HS)

10 % (173 HS) $0.328 \leq \rho \leq 0.464$ $0.255 \leq T \leq 0.380$

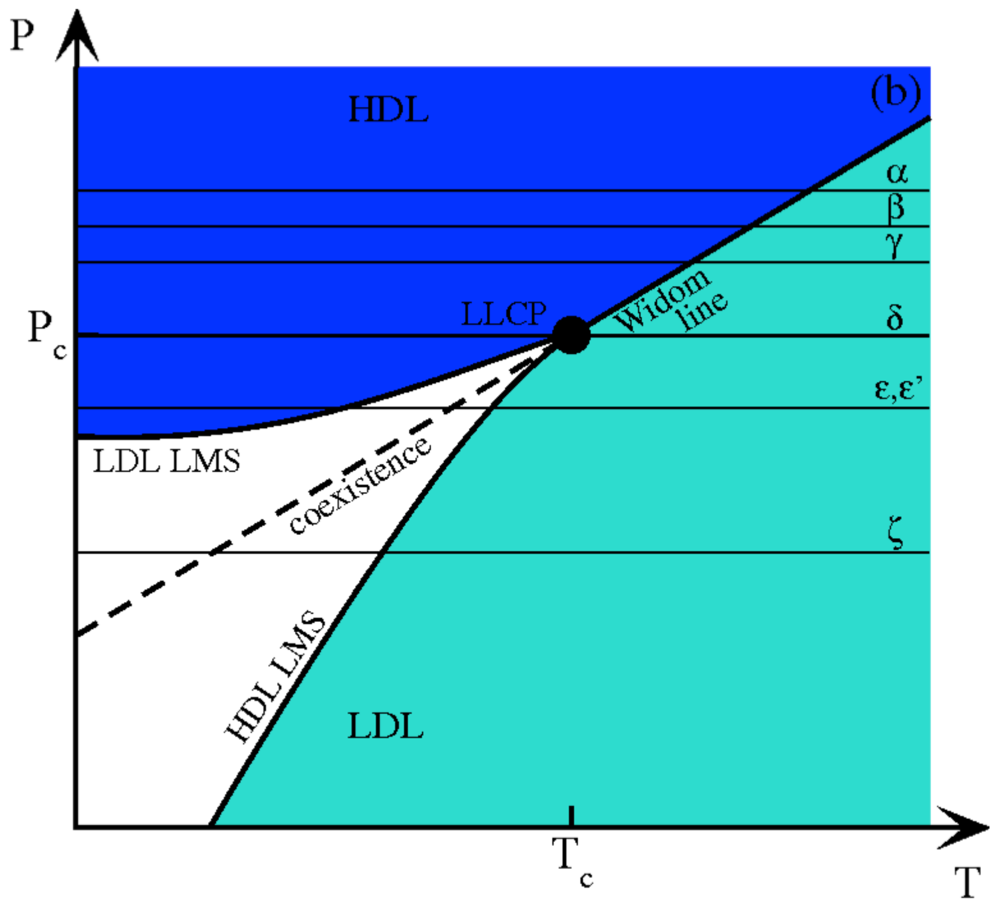
20 % (345 HS) $0.328 \leq \rho \leq 0.464$ $0.275 \leq T \leq 0.360$

15 % (260 HS) $0.328 \leq \rho \leq 0.464$ $0.275 \leq T \leq 0.360$

50 % (864 HS) $0.502 \leq \rho \leq 0.672$ $0.210 \leq T \leq 0.300$

Thermodynamics at constant *N*, *V* and *T*
Diffusion coefficients also at constant *N*, *P* and *T*

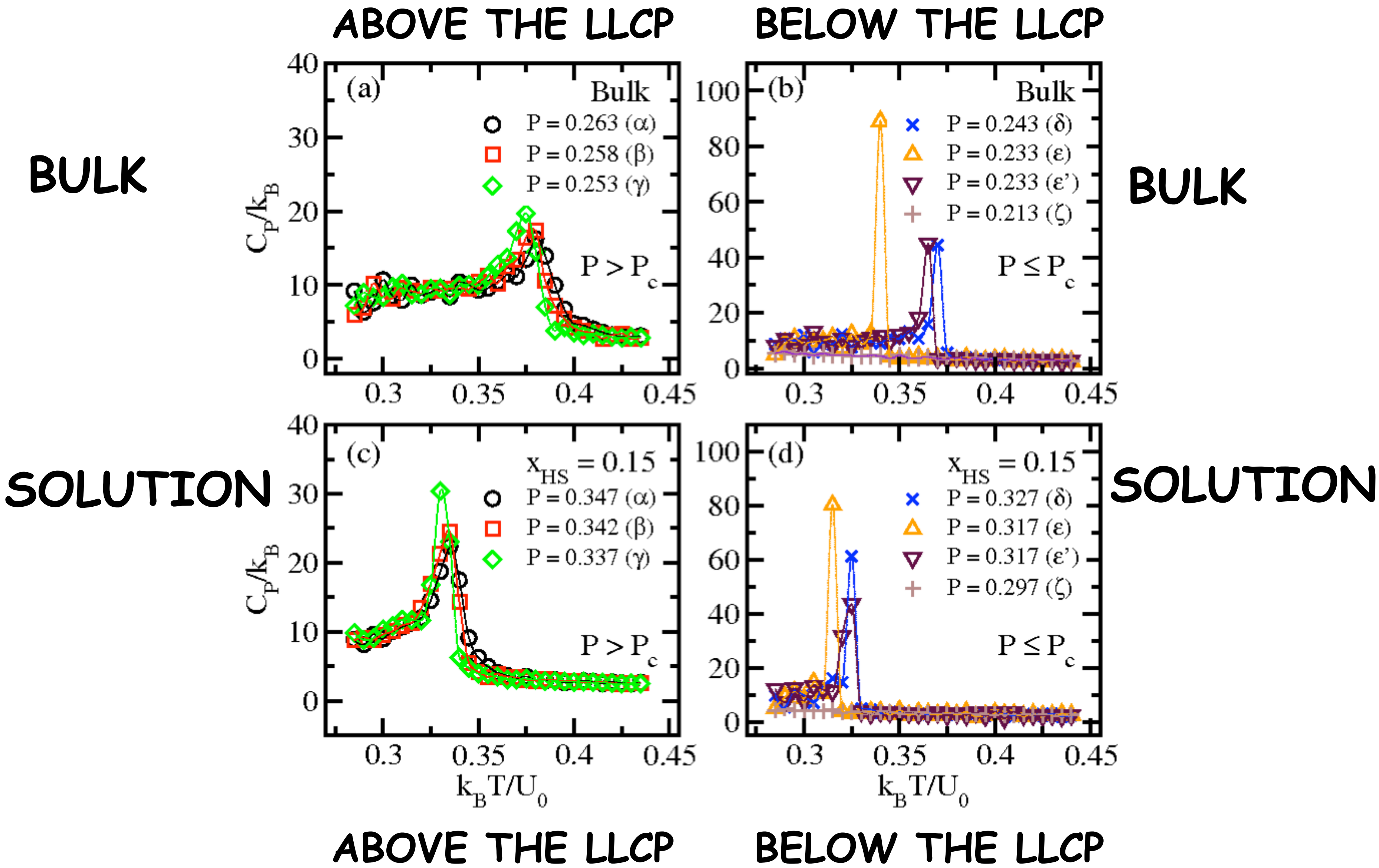
Dynamics: isobaric paths in a schematic diagram good for bulk and solutions



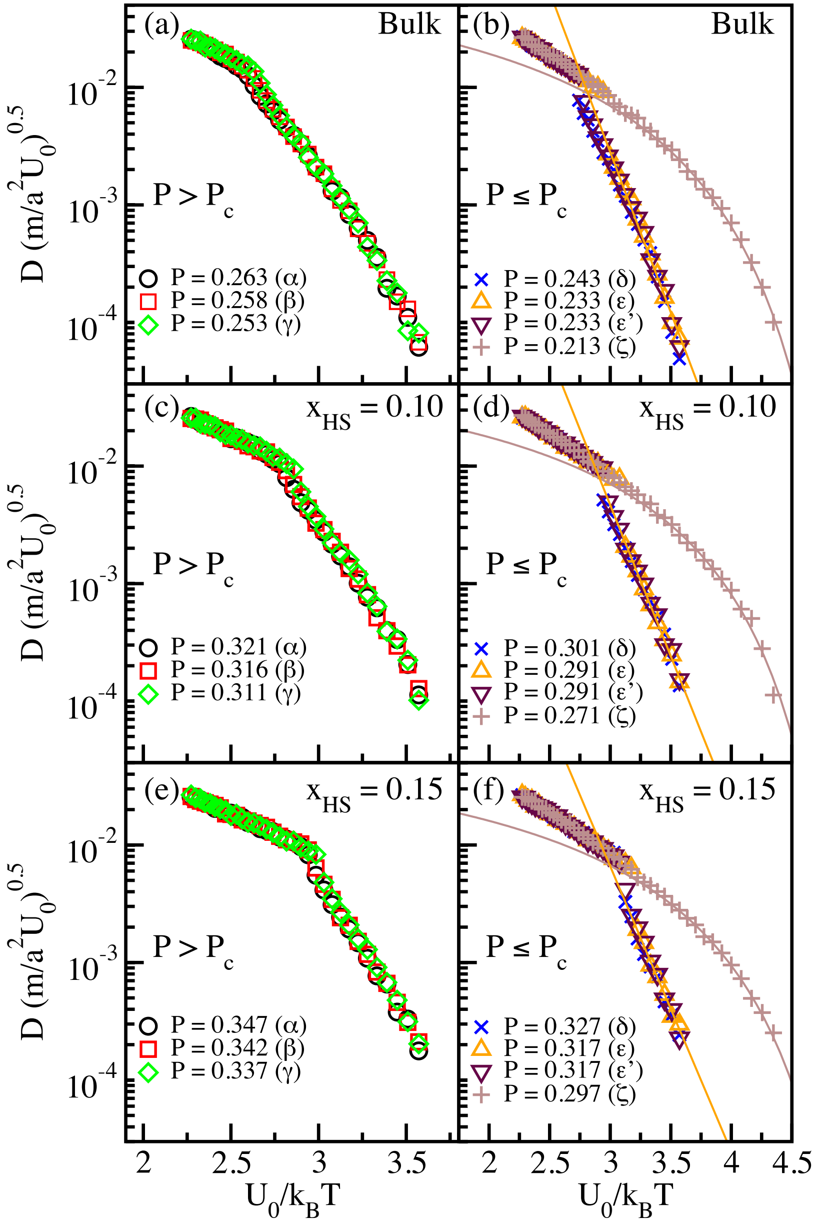
The path ζ does not crosses the limit of mechanical stability line nor the Widom line !

D. Corradini, P. Gallo, S.V. Buldyrev and H.E. Stanley
Fragile to strong crossover coupled to liquid-liquid transition in hydrophobic solutions
Phys. Rev. E **85**, 051503 (2012).

Specific heat peak on crossing the Widom line



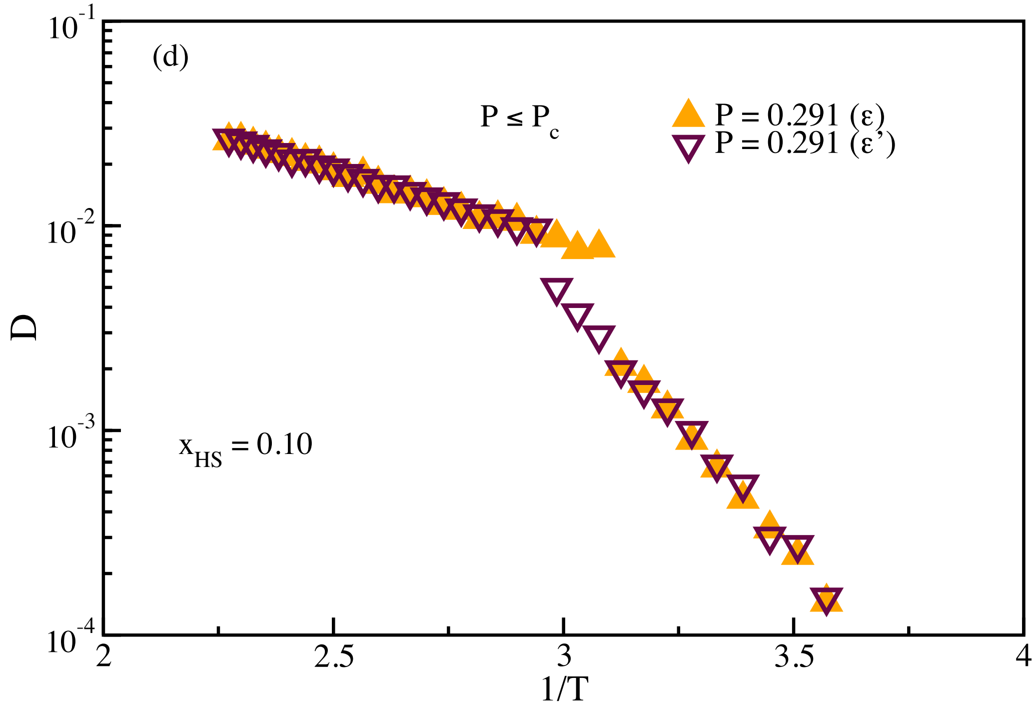
Diffusion coefficients at constant pressure paths done above and below the LLCP

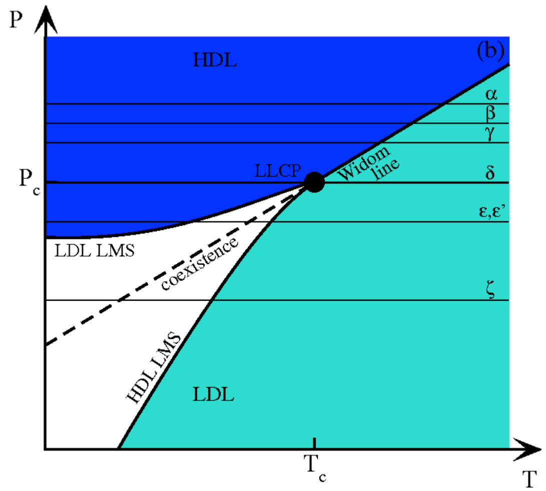


The critical pressure is Pc = 0.243 for bulk Jagla, Pc = 0.301 for x_{HS} = 0.10, Pc = 0.327 for x_{HS} = 0.15 and Pc=0.362 for x_{HS}=0.20.

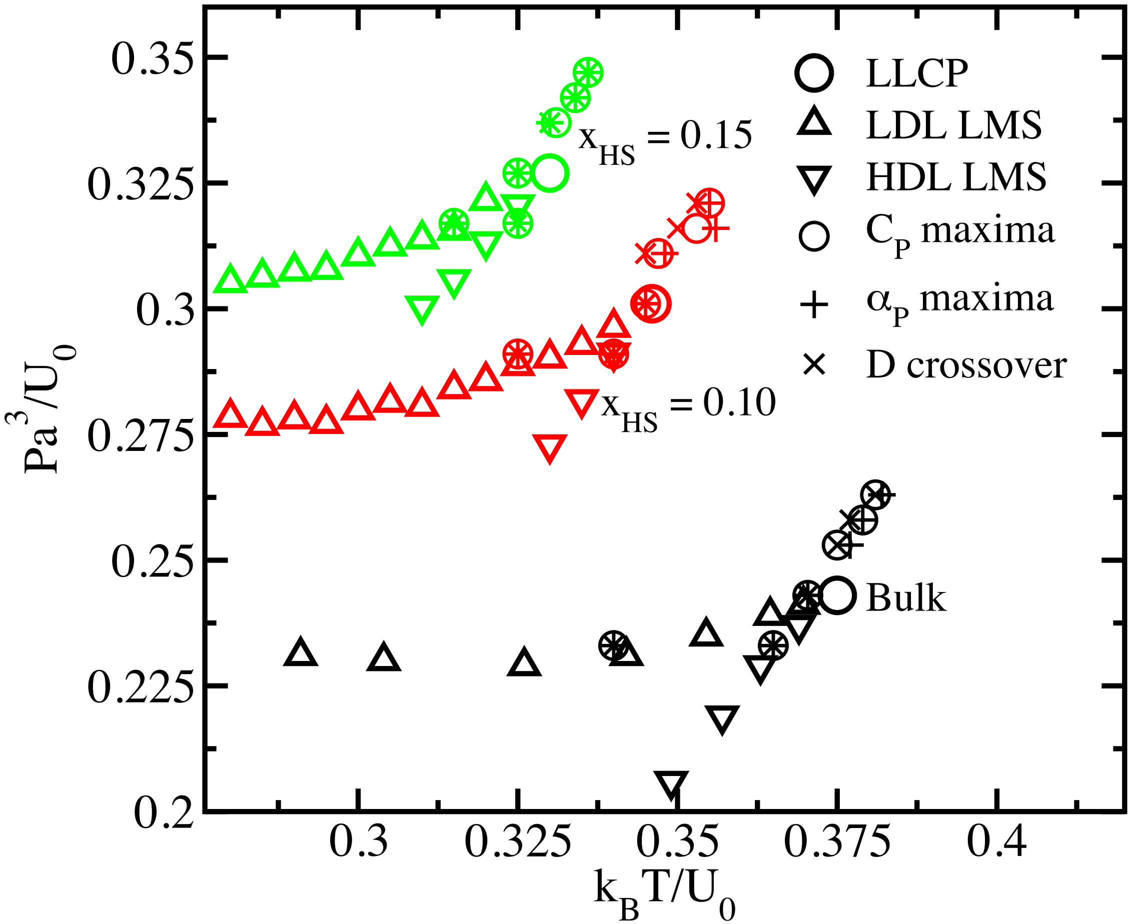
The solid curve is a VFT fit $D = D_0 \exp[-B/(T - T_0)]$ for paths ζ. The solid straight line is an example of Arrhenius fit $D = D_0 \exp(-E_A/k_BT)$ for paths ζ. The parameters of the fits are $B \simeq 0.25$, $T_0 \simeq 0.18$ for VFT and $E_A \simeq 6$ for Arrhenius, for all systems.

Diffusion coefficients at constant pressure same path done below the LLCP upon increasing and deceasing T to cross HDL-LMS and LDL-LMS





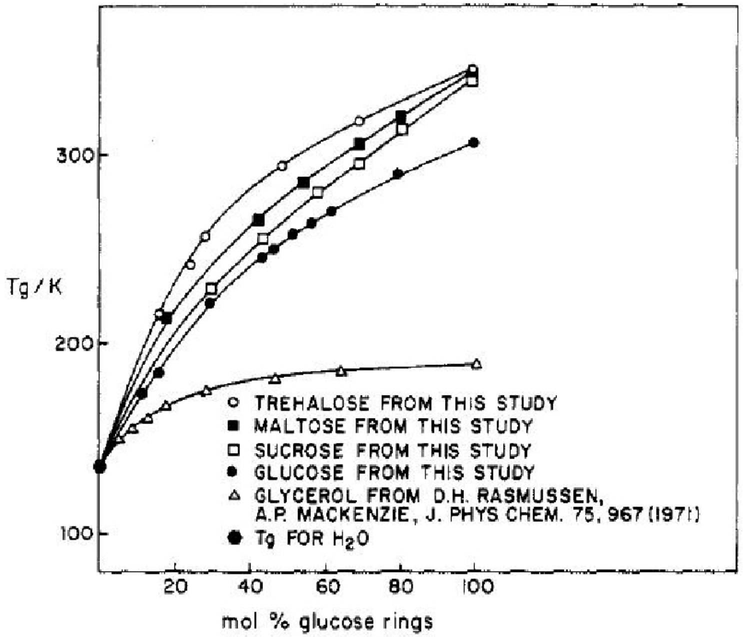
Specific heat and themal expansion coeff. peaks and fragile to strong crossover point from D



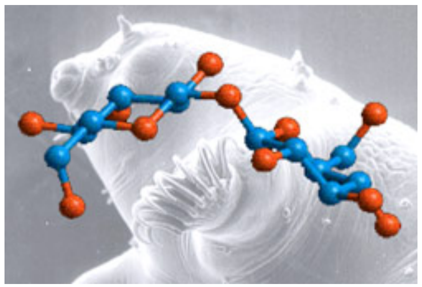
D. Corradini, P. Gallo, S.V. Buldyrev,H.E. Stanley, Phys. Rev. E 85, 051503 (2012)

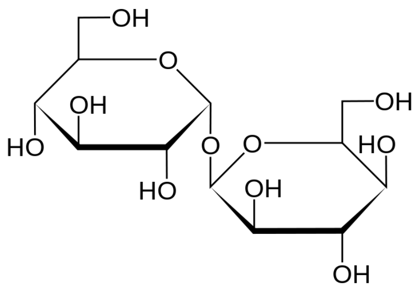
Aqueous solutions of water and trehalose

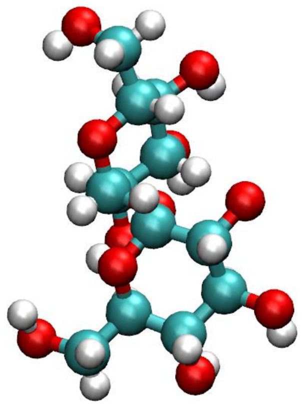
- Sugars are effective crioprotectants to prevent extracellular ice formation
- Trehalose is a crioprotector more efficient than other disaccarides and it is used for preservation of foods and organs.



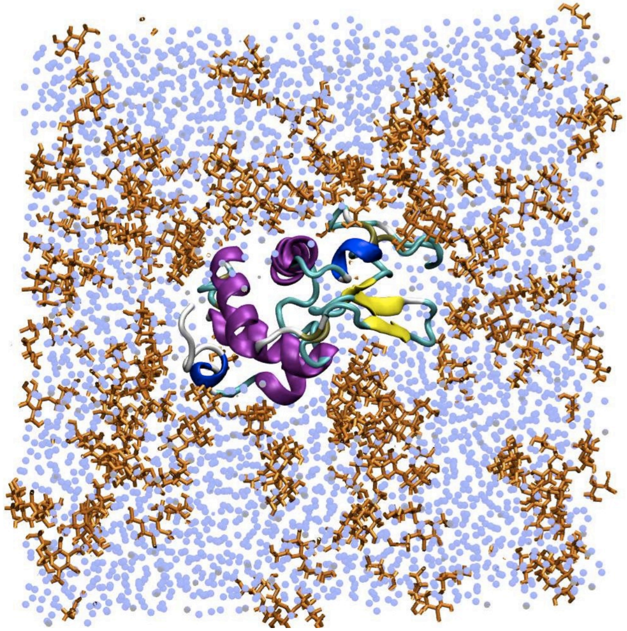
J. L. Green and C. A. Angell J. Phys. Chem. 93, 2880 (1989).







Aqueous solutions of lysozyme and trehalose: recap

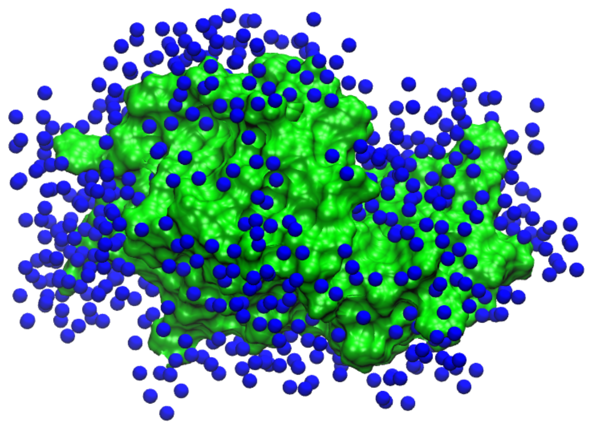


Lysozyme is part of the innate immune sistem can be found in tears, saliva, human milk etc.

- **Increase in protein thermal stability with trehalose (see for expample Exp.** ***G. Bellavia, S. Giuffrida, G. Cottone, A. Cupane and L. Cordone J. Phys. Chem. B 115, 6340 (2011).***
- ***Trehalose interacts preferentially with water and stiffens the protein (see for example Exp/Sim. A. Lerbret, F. Affouard, A. Hédoux, S. Krenzlin, J. Siepmann, M. C. Bellissent-Funel and M. Descamps J. Phys. Chem. B 116, 1103 (2012).)***
- ***See review paper*** **L. Cordone, G. Cottone, A. Cupane, A. Emanuele, S.Giuffrida, and M.Levantino, Curr. Org. Chem. 19, 1684 (2015).**

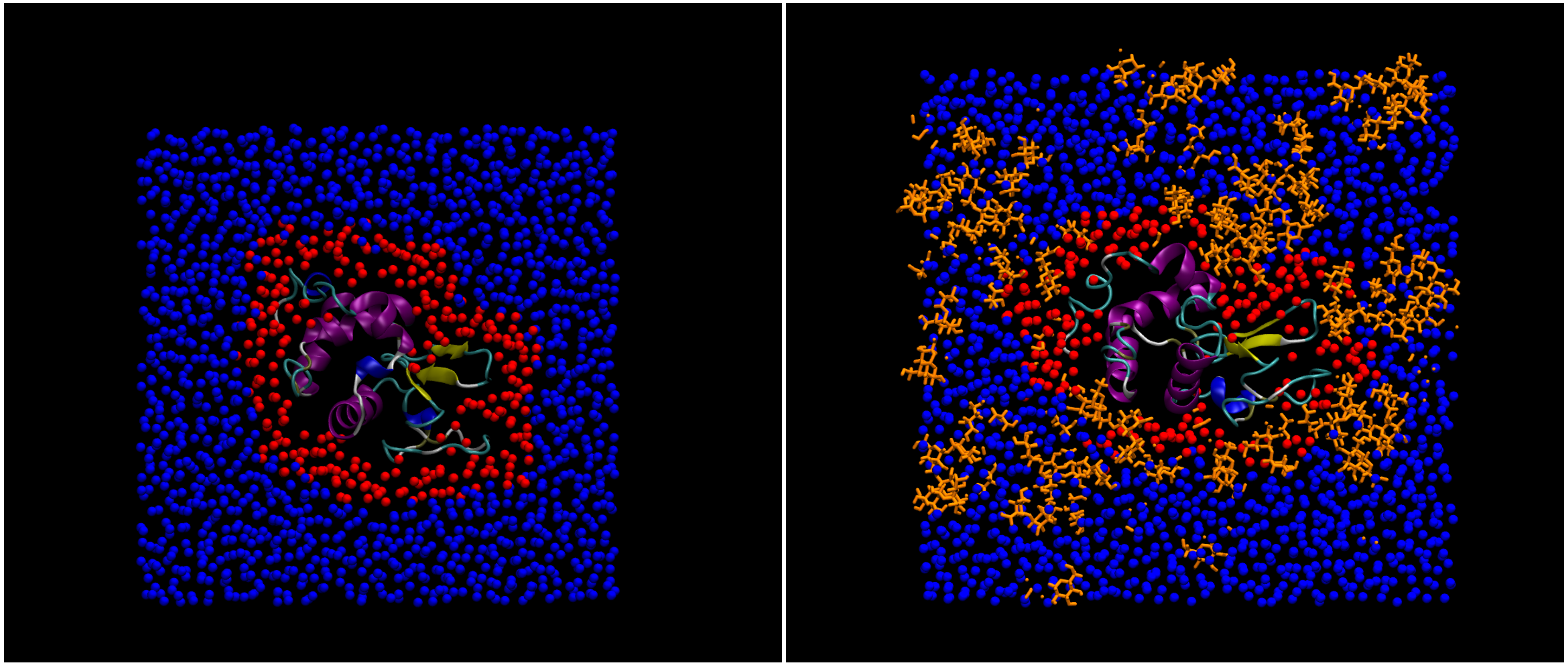
How about hydration water?

Two well distinct slow relaxations have been found in aqueous solutions of water and biomolecules and where possible experiments have shown that in particular hydration water has both. See for example references here below.



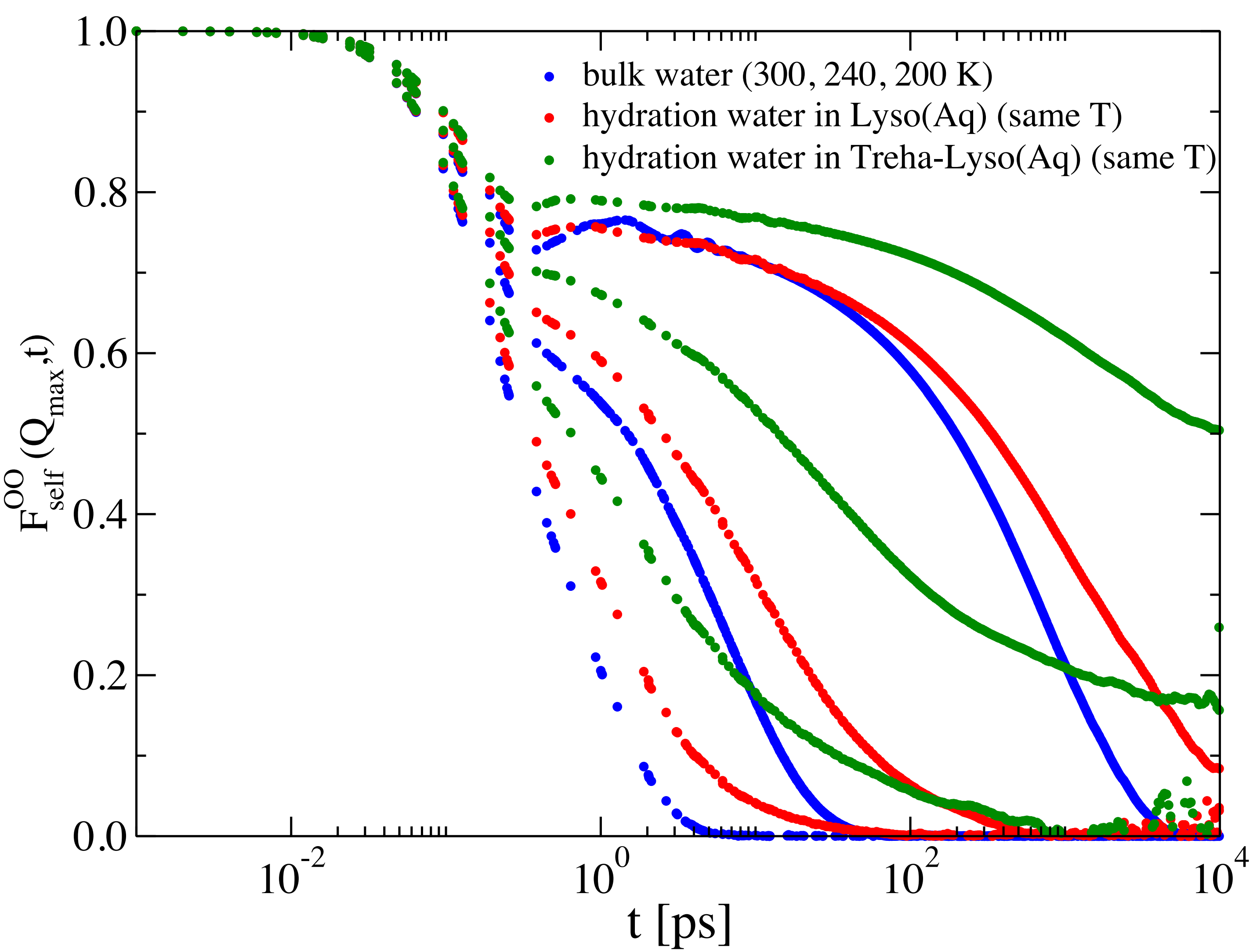
- S. Perticaroli, L. Comez, P. Sassi, M. Paolantoni,S. Corezzi, S. Caponi, A. Morresi, and D. Fioretto,5, J. Non. Cryst. Solids 407, 472 (2015).
- D. Corradini, E. G. Strekalova, H. E. Stanley, and P. Gallo, Sci. Rep. 3, 1218 (2013).
- L. Comez, L. Lupi, A. Morresi, M. Paolantoni, P. Sassi,and D. Fioretto, J. Phys. Chem. Lett. 4, 1188 (2013).
- A. Magno and P. Gallo,J. Phys. Chem. Lett. 2, 977 (2011).
- **L. Zhang, L. Wang, Y.-T. Kao, W. Qiu, Y. Yang, O. Okobiah, and D. Zhong, Proc. Natl. Acad. Sci. U. S. A. 104, 18461 (2007).**
- S. K. Pal, J. Peon, B. Bagchi, and A. H. Zewail, J. Phys. Chem. B 106, 12376 (2002).
- S. K. Pal, J. Peon, and A. H. Zewail, Proc. Natl. Acad. Sci. 99, 1763 (2002).

How about dynamics of our hydration water? Does it show these two relaxations and how does it change with the presence of trehaloses?



Comparison of behaviour of hydration water (water molecules within 6Å from the surface: it is the red hearth-shaped corona in the picture) for Lysozyme in water and the thernary system Lyso+Water+Treha

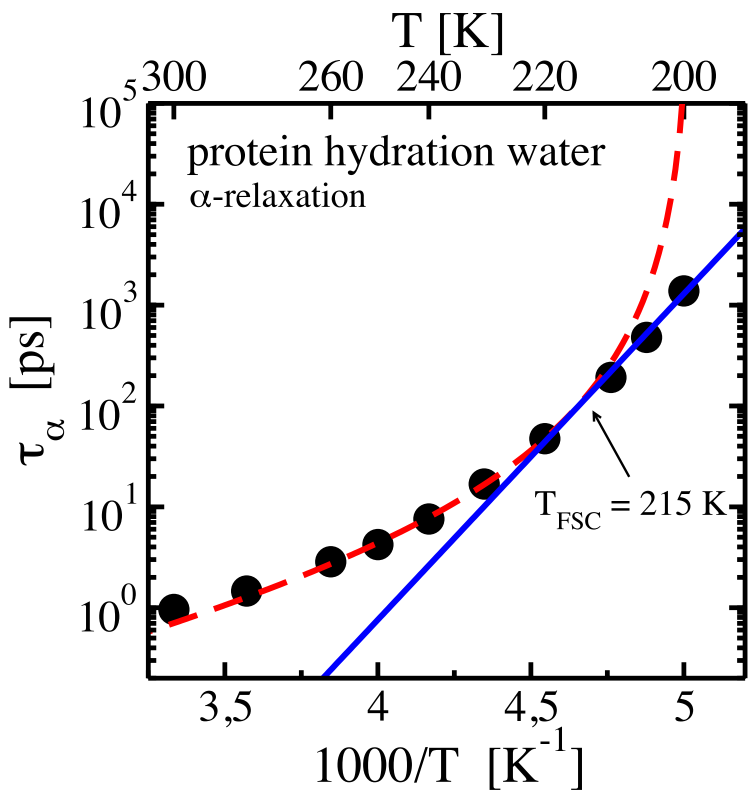
Slow dynamics gets slower with trehalose and long time tails present already in lyso(aq) get longer

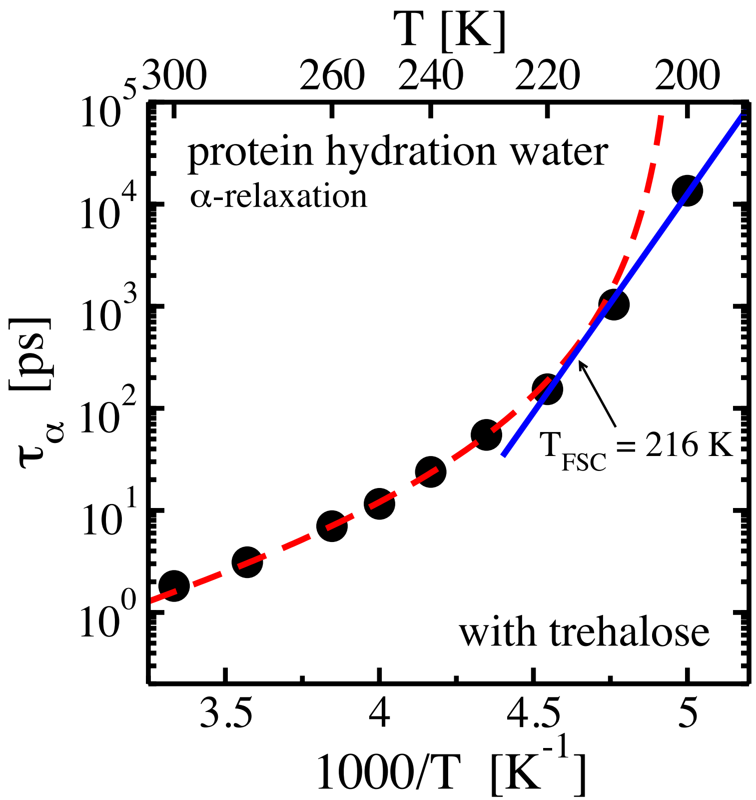


Fit for hydration water both relaxations are found! And both relaxation times have a crossover

$$F^{(S)}(Q,t) = (1-(f1-f2))\exp[-(t/\tau_{short})^2]+$$
$$f1\cdot\exp\left[-(t/\tau_{\alpha})^{\beta_{\alpha}}\right]+f2\cdot\exp\left[-(t/\tau_{long})^{\beta_{long}}\right]$$

α - relaxation times of hydration water

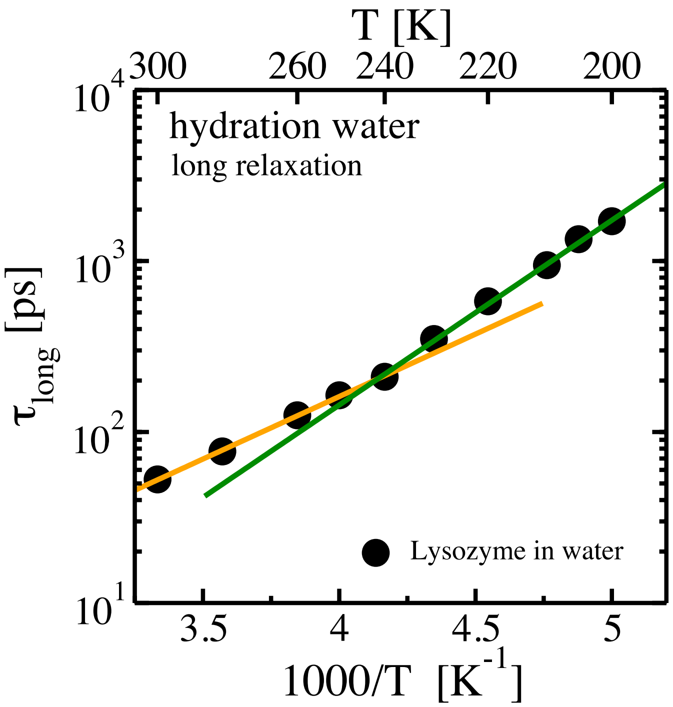


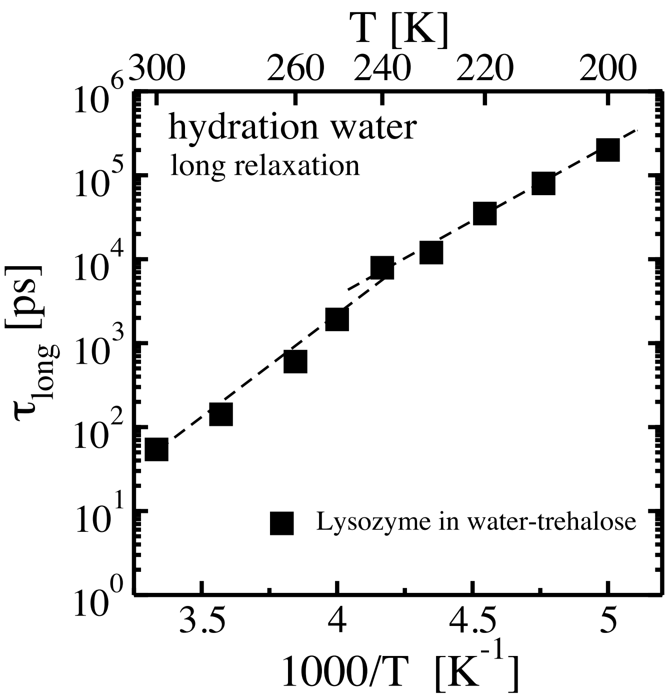


Results for protein alone similar to experiments on monolayer hydration: See S.-H. Chen, L. Liu, E. Fratini, P. Baglioni, A. Faraone, E. Mamontov, and M. Fomina, Proc. Natl. Acad. Sci. U. S. A. 103, 9012 (2006)

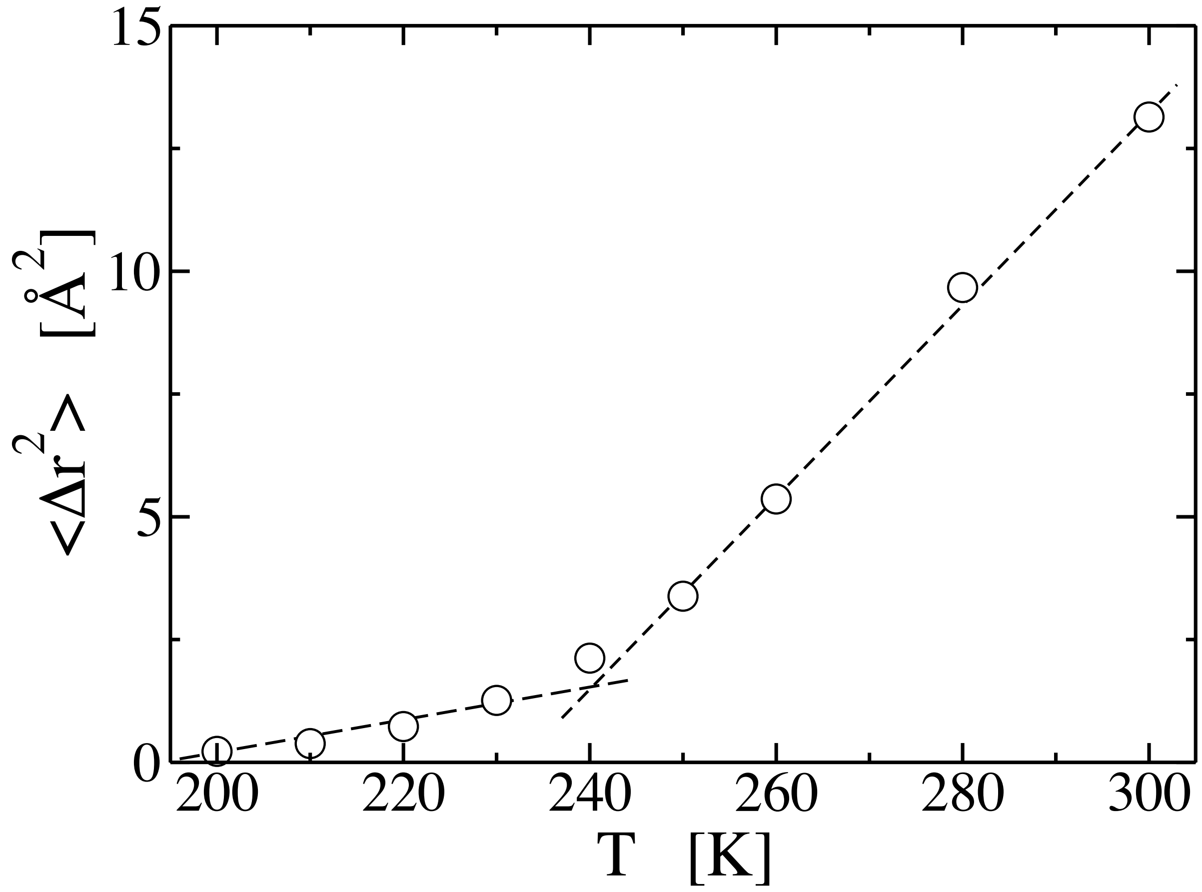
See also Schirò, Cupane, Mallamace and others.

Long relaxation times





Protein MSD: the wellknown Protein Dynamic Transition is at T=240 K



Conclusions

- The Widom line is an important line to characterize fluids behaviour above the critical points and it is connected to crossovers in dynamics in all investigated cases
- In supercritical water it can be well characterized and there is an agreement between experiments and simulations using TIP4P/2005 and other model potentials indicating that the supercritical state is far more complex than what thaught in textbook
- Also for supercooled TIP4P/2005 bulk, TIP4P bulk and TIP4P +NaCl solution thermodynamics and dynamics appear strongly related, the fragile to strong transition happens on crossing the Widom Line. (Also the twobody entropy s_2 shows the same crossover.)
- Jagla particles with hydrophobic solutes show the same phenomenology in the supercooled state and also the region below the LLCP (rigorous second order and Ising universality class)
- Experiments measuring the relaxation time in aqueous solutions anc confinement represent viable routes for solving the open questions in the field of supercooled water. In electrolites T_c is shifted to higher pressures and temperatures.
- Also hydration water crossovers can be analyzed in this framework.

Collaborators and main pubblications

Water in MCM-41

P. Gallo, M. Rovere and S.-H. Chen. Dynamic crossover in supercooled confined water: understanding bulk properties through confinement, J. Phys. Chem. Lett. 1 , 729 (2010). And also ibid, JPCM 2010 and JPCM 2012.

Bulk superheated TIP4P/2005 and experiments

P. Gallo, D. Corradini, M. Rovere,Widom line and dynamical crossovers as routes to understand supercritical water, nature comm. 5:5806 (2014)

D. Corradini, M. Rovere and P. Gallo JCP 143, 114502 (2015)

TIP4P/2005 bulk supercooled water

M. De Marzio, G. Camisasca, M. Rovere and P. Gallo, Mode Coupling Theory and Fragile to Strong Transition in Supercooled TIP4P/2005 Water JCP (2016).

TIP4P supercooled water in bulk and with NaCl(aq)

P. Gallo, D. Corradini and M. Rovere, Mode Coupling and fragile to strong transition in a supercooled aqueous solution of salt, J. Chem. Phys. (2013).

P. Gallo and M. Rovere, Mode Coupling and fragile to strong transition in supercooled TIP4P water. J. Chem. Phys., 137 , 164503 (2012).

P. Gallo and M. Rovere, Relation between the two body entropy and the relaxation time in supercooled water Phys. Rev. 91, 012107 (2015).

D. Corradini, M. Rovere and P. Gallo, A route to explain water anomalies from results on an aqueous solution of salt, J. Chem. Phys., 132, 134508 (2010).

Supercooled Jagla and Jagla with with Hard Spheres

D. Corradini, P. Gallo, S.V. Buldyrev and H.E. Stanley, Phys. Rev. E 85, 051503 (2012)

Paola Gallo and Francesco Sciortino, Phys. Rev. Lett. 109, 177801 (2012).

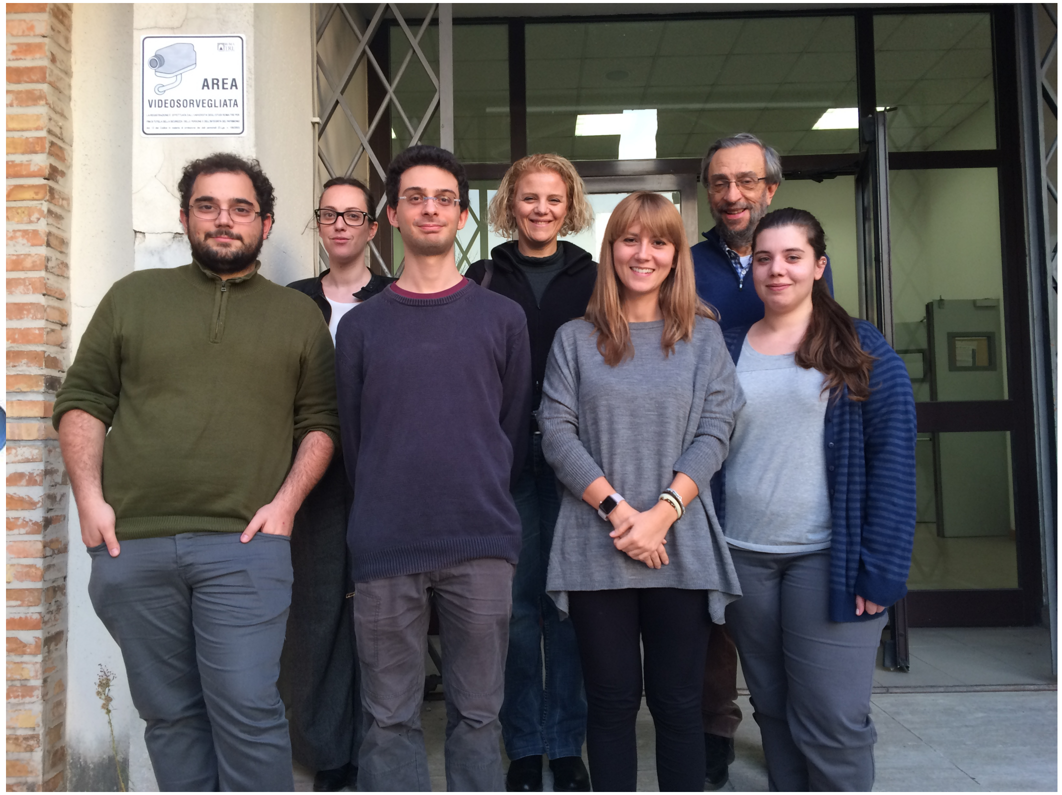
Dario Corradini, Sergey V. Buldyrev, Paola Gallo and H. Eugene Stanley,. Phys. Rev. E 81, 061504 (2010)

Hydration water

D. Corradini, E. Strekalova, H.E. Stanley and P. Gallo, Sci Rep. (2013)

G. Camisasca, M. De Marzio, D. Corradini and P. Gallo, TWO STRUCTURAL RELAXATIONS IN PROTEIN HYDRATION WATER AND THEIR DYNAMIC CROSSOVERS J. Chem. Phys. 145, 044503 (2016).

ROMA TRE GROUP OF: Simulations of Liquids and Soft Matter



MAIN RESEARCH TOPICS:

- Confined water: MCM41 and carbon nanotubes
- Supercooled and superheated water
- Aqueous solutions of electrolites
- Ices with ions, terrestrial and extraterrestrial
- Bio-aqueous solutions for cryopreservation

Prof. **PAOLA GALLO** (top center), **Prof.MAURO ROVERE** (top right), Dr. **MARIA MARTIN CONDE** Post Doc (top left), Dr. **GAIA CAMISTASCA** PhD (bottom right), Dr. **MARGHERITA DE MARZIO** PhD (Bottom center right), Dr. **ANTONIO IORIO** PhD (bottom center left), Dr. **PIETRO PUGLIESE** PhD **here in Erice works on water in carbon nanotubes** (bottom left)