Nucleation and anomalous properties of pure and salty water

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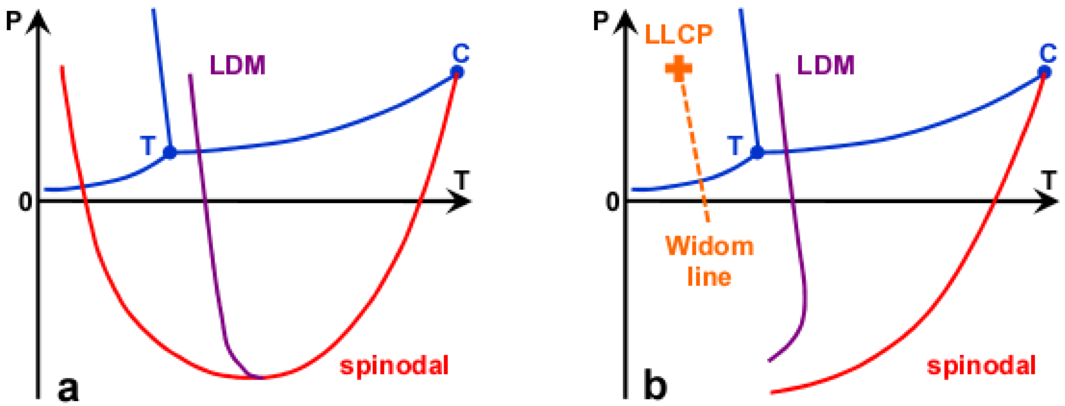
Motivation

In 1976 Speedy and Angell provided experimental evidence of a divergence in the isothermal compressibility of supercooled water

Possible Scenarios



Stability limit conjecture

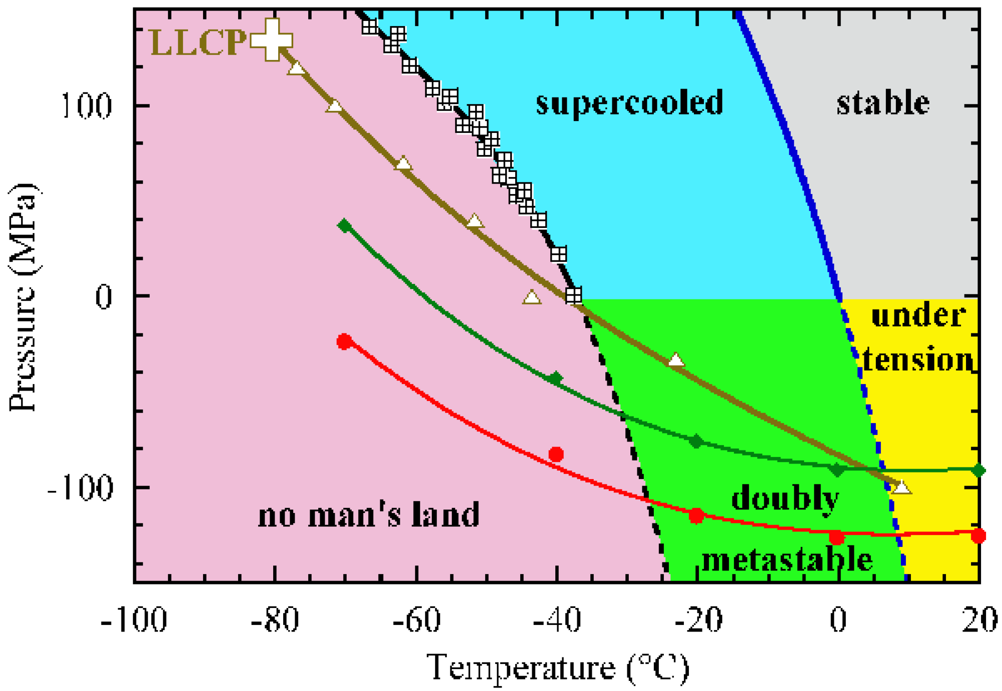
(retracing spinodal)

Liquid-liquid critical point

(retracing TMD)

The interesting region lies in the no man's land, not accessible to experiment because it is beyond the homogeneous nucleation line

The no man's land region

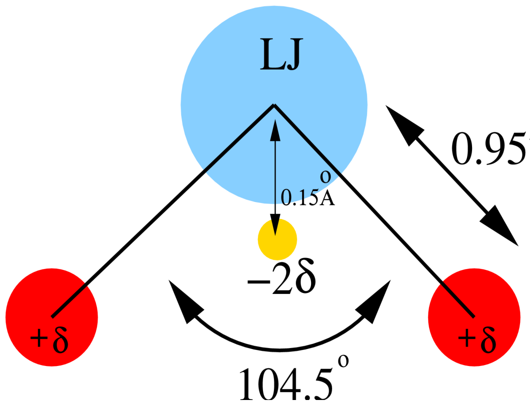


A difficult puzzle to solve

Because of the experimental difficulties (no man's land region), numerical simulation may provide important information

but …

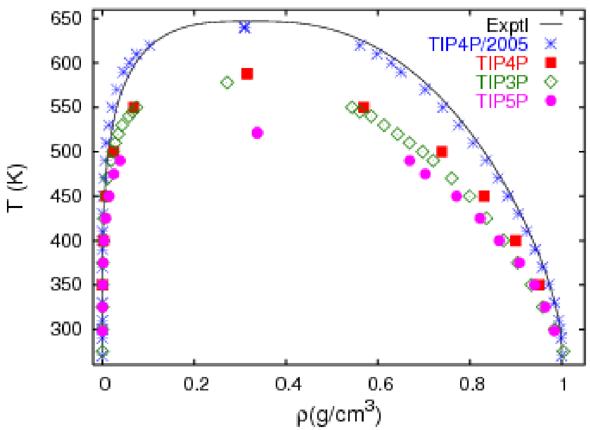
is the water force field accurate enough?



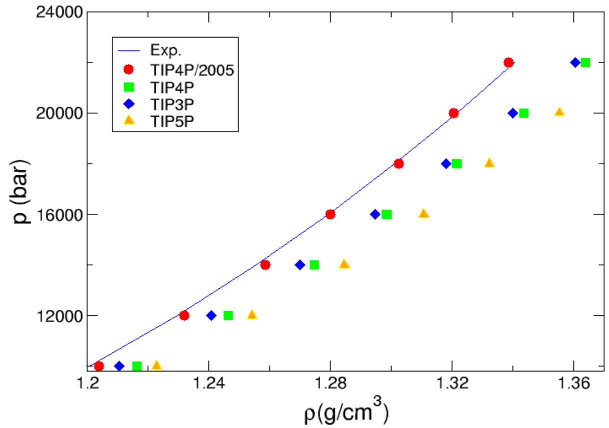
TIP4P/2005

Performance of TIP4P/2005

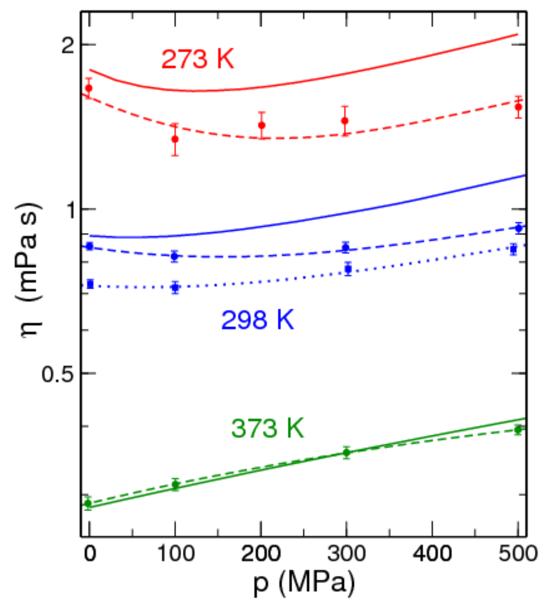
VLE



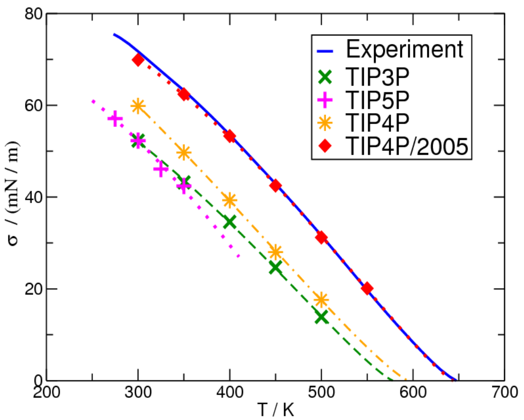
EOS high pressure



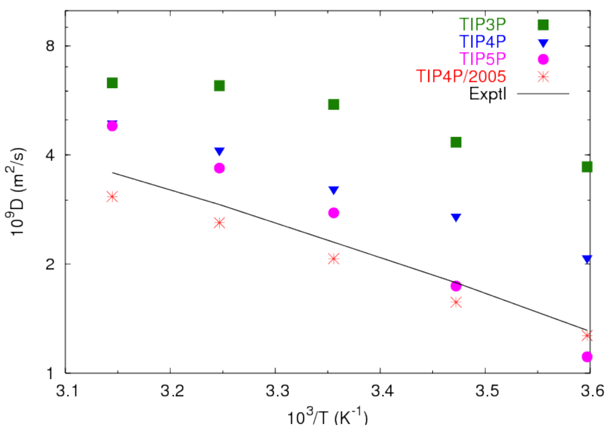
Shear Viscosity



Surface Tension



Self Diffusion Coefficient

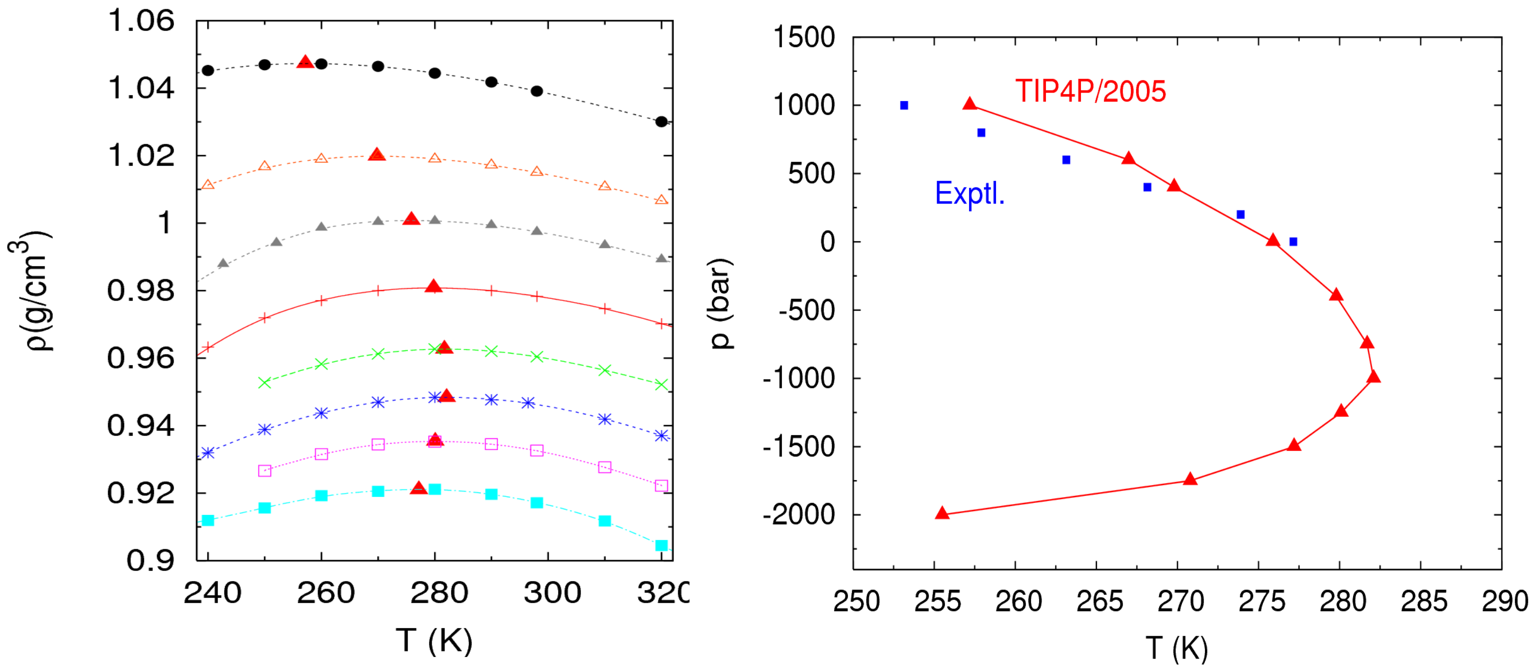


Property	TIP3P	SPC/E	TIP4P	TIP4P/2005	TIP5P
Enthalpy of phase change	4.0	2.5	7.5	5.0	8.0
Critical point properties	3.7	5.3	6.3	7.3	3.3
Surface tension	0.0	4.5	1.5	9.0	0.0
Melting properties	2.0	5.0	6.3	8.8	4.5
Liquid densities and TMD	1.8	5.5	4.0	8.5	4.0
Isothermal compressibil.	2.5	7.5	2.5	9.0	4.0
Gas properties	2.7	0.7	1.3	0.0	1.0
C_p	4.5	3.5	4.0	3.5	0.0
Dielectric constant	2.0	2.3	2.3	2.7	2.3
T_m/T_c, TMD-T_m	4.3	6.7	8.3	8.3	6.7
Densities of ices	3.5	5.0	6.0	8.8	2.3
EOS high pressure	7.5	8.0	7.5	10	5.5
Self diffusion coeff.	0.3	8.0	4.3	8.0	4.5
Shear viscosity	1.0	7.5	2.5	9.5	4.0
Orientational relaxation time	0.0	6.0	2.0	9.0	4.0
Structure	4.0	6.5	7.0	8.5	8.0
Phase diagram	2.0	2.0	8.0	8.0	2.0
Final score	**2.7**	**5.1**	**4.7**	**7.2**	**3.7**

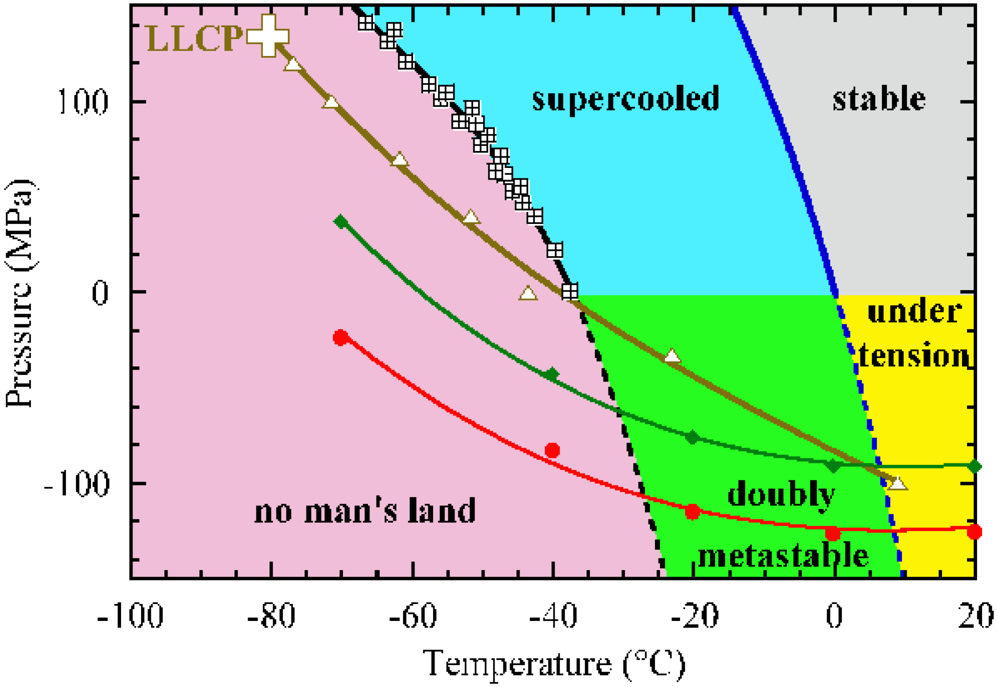
C. Vega and J.L.F. Abascal, PCCP 13, 19663 (2011)

Temperature of maximum density

(TIP4P/2005 vs experiment)



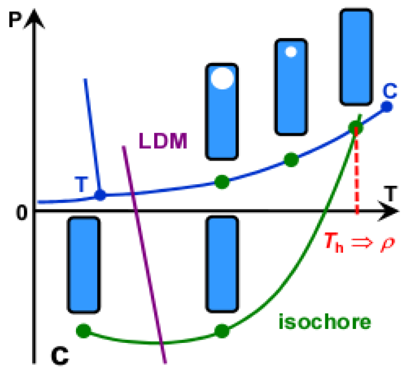
The doubly metastable region

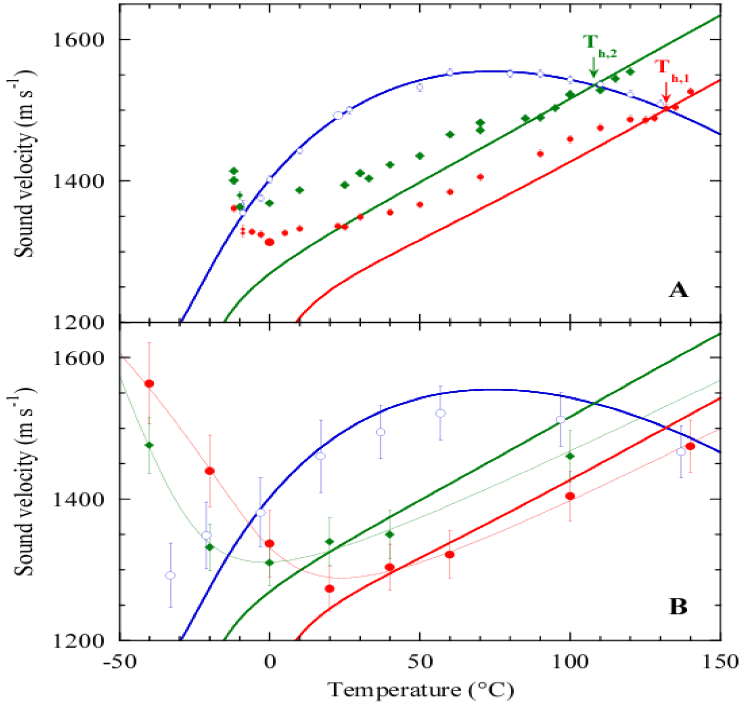


It is possible to cross the (κ_T) Widom line before the system nucleates!

Speed of sound

$$c = \sqrt{\frac{1}{\rho \kappa_S}} = \sqrt{\frac{C_P}{C_V}\frac{1}{\rho \kappa_T}}$$





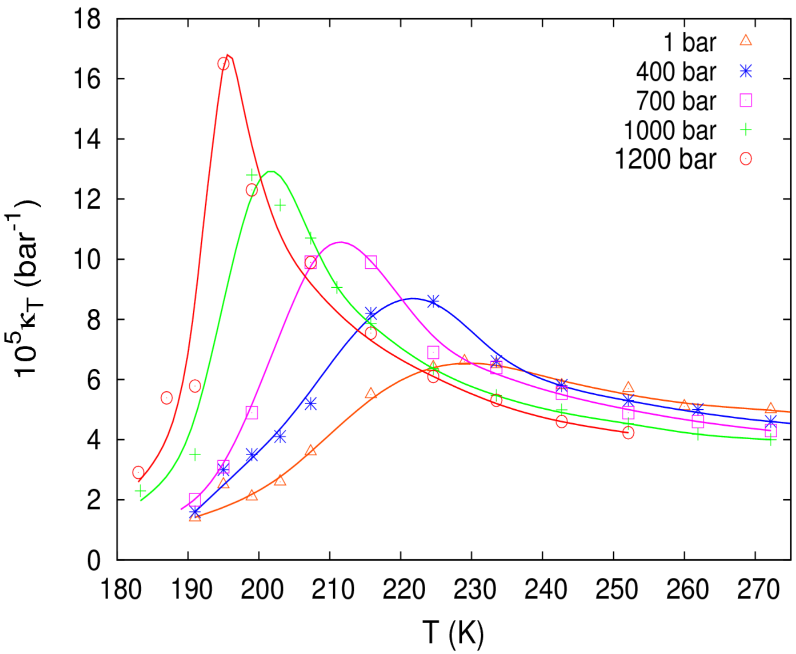
Experiment

Simulation

This is the first **experimental** report of extrema for a response function in supercooled **bulk** water!

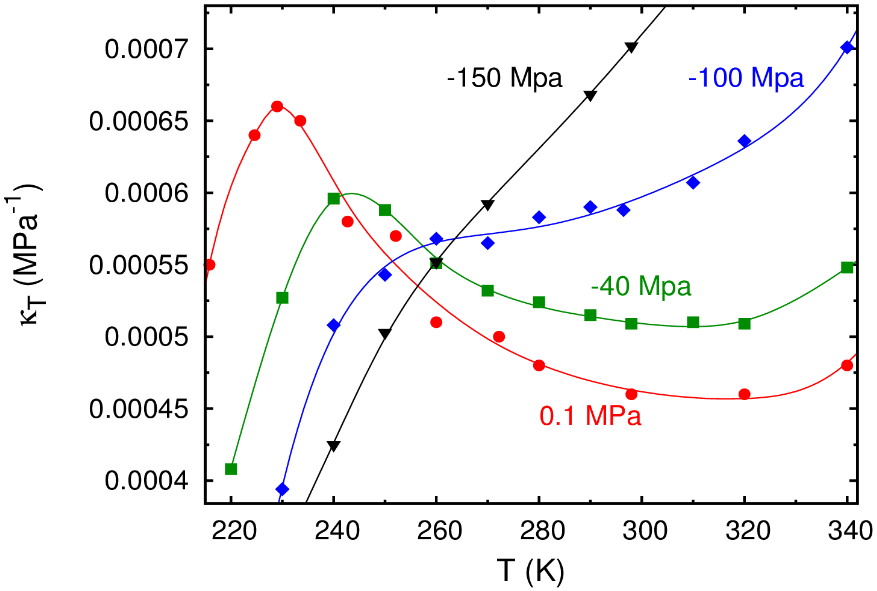
Pallares et al., PNAS 111, 7936 (2014)

Isothermal compressibility



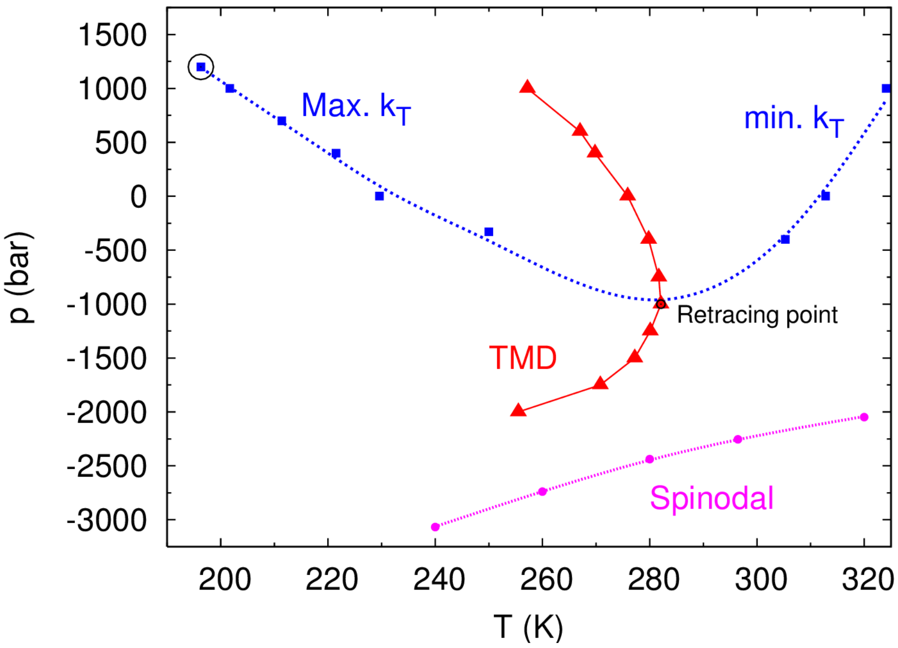
Positive pressures

Negative pressures

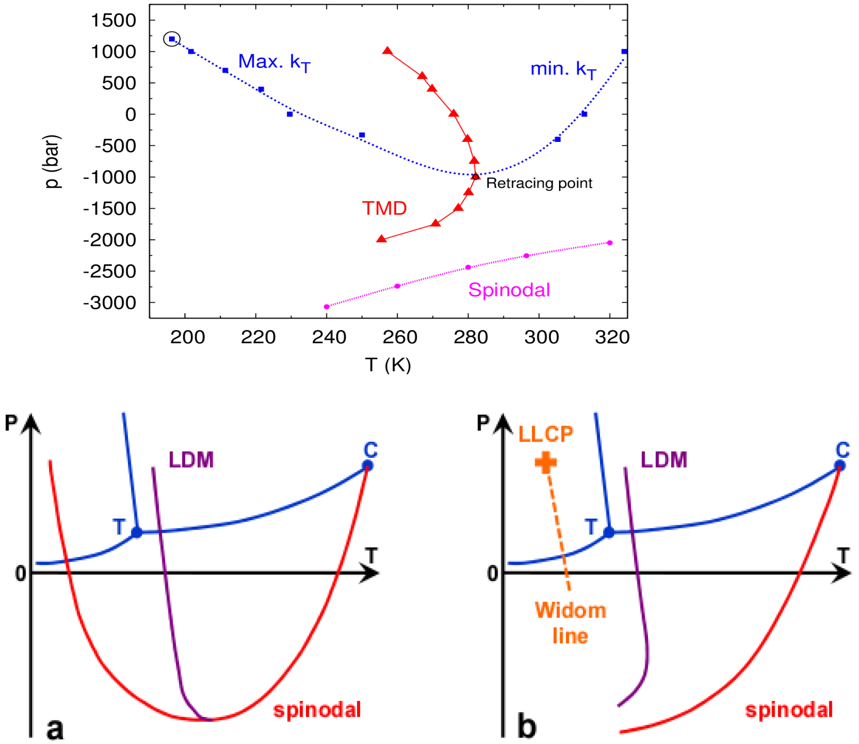


Maxima and minima collapse below -100 MPa

Scenario of water anomalies for TIP4P/2005 (I)



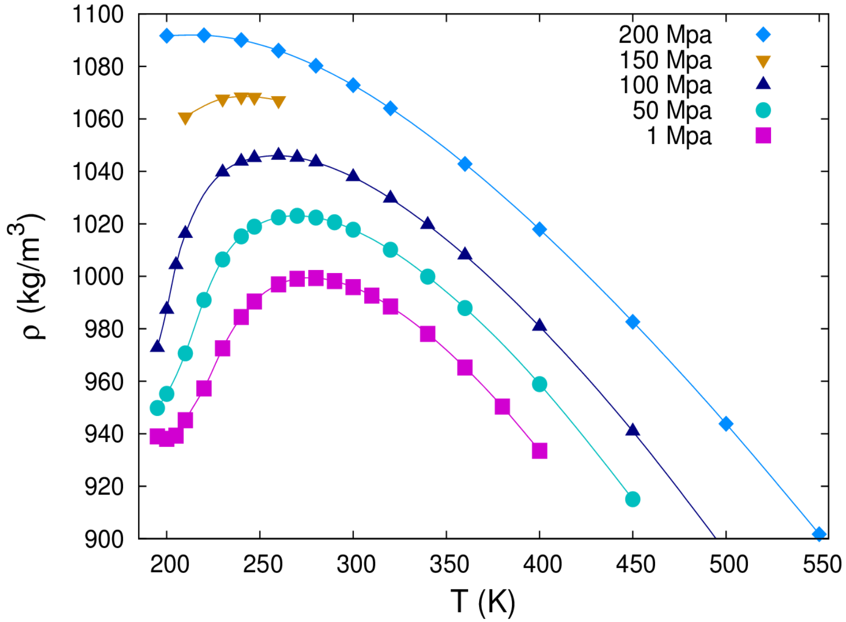
Scenario of water anomalies for TIP4P/2005 (I)



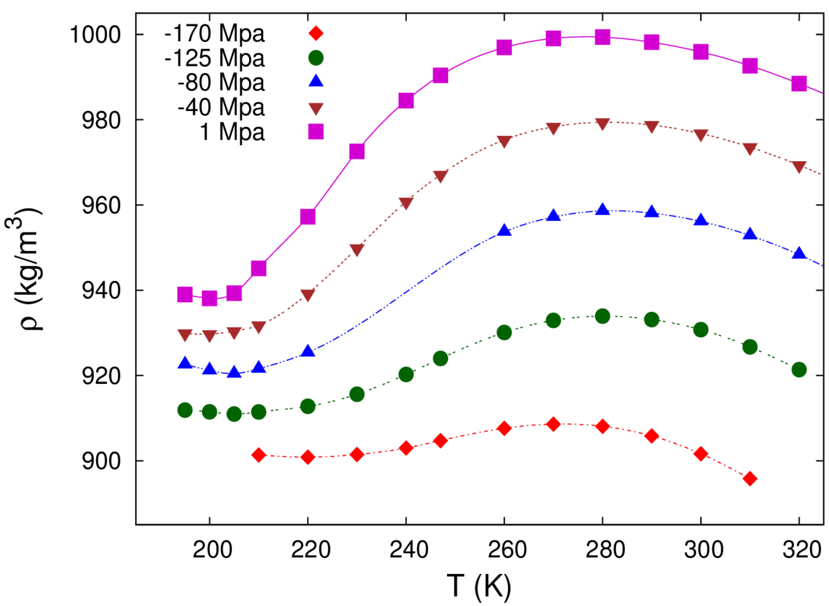
Singularity free scenario must be ruled out

TIP4P/2005 results compatible with the liquid-liquid critical point hypothesis

Temperature of minimum density (TmD)



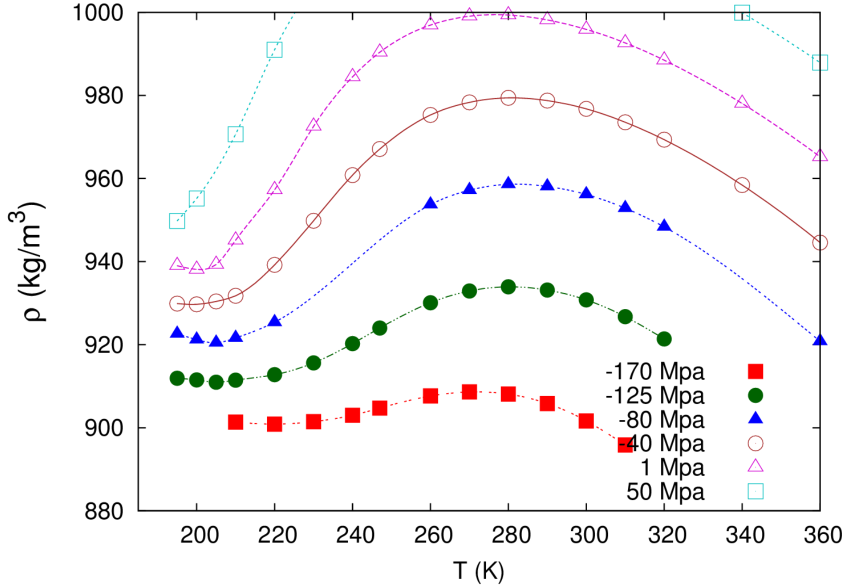
Positive pressures



Negative pressures

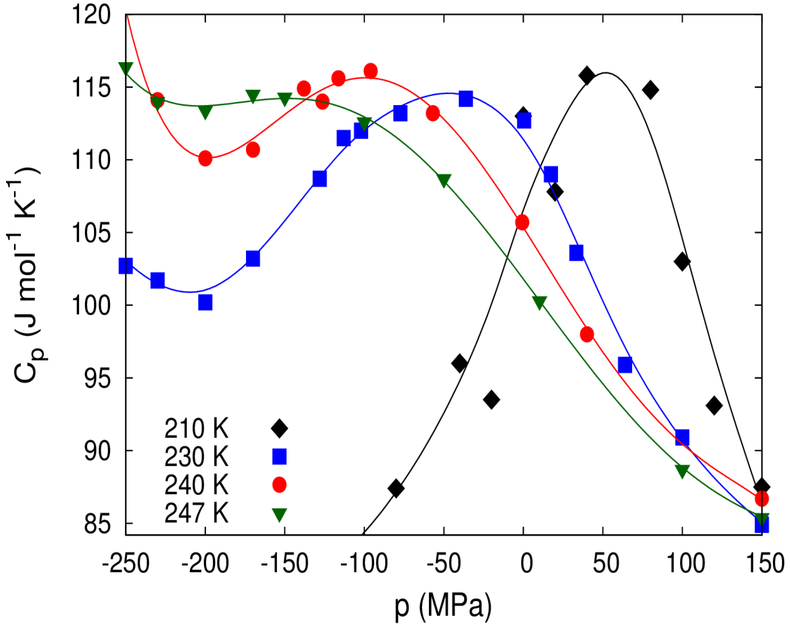
Density minima are featured in the stretched region

TmD and heat capacity extrema (C_p)

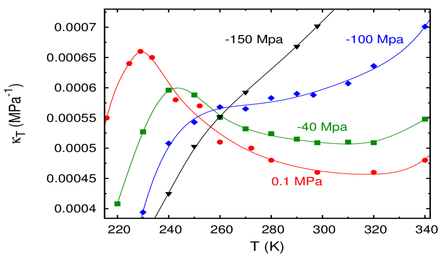


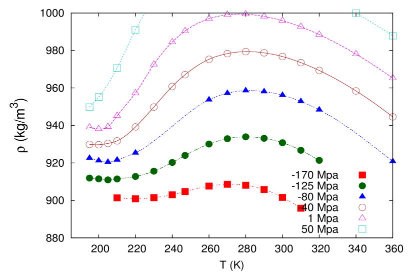
Density minima are featured in the stretched region

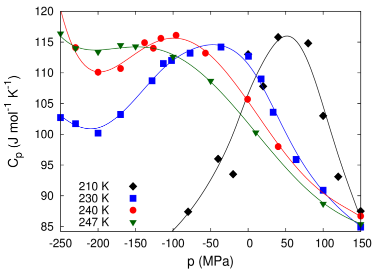
The maxima and minima of Cp appear only in the supercooled region (usually, in the doubly metastable region)

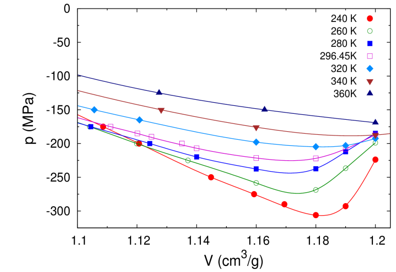


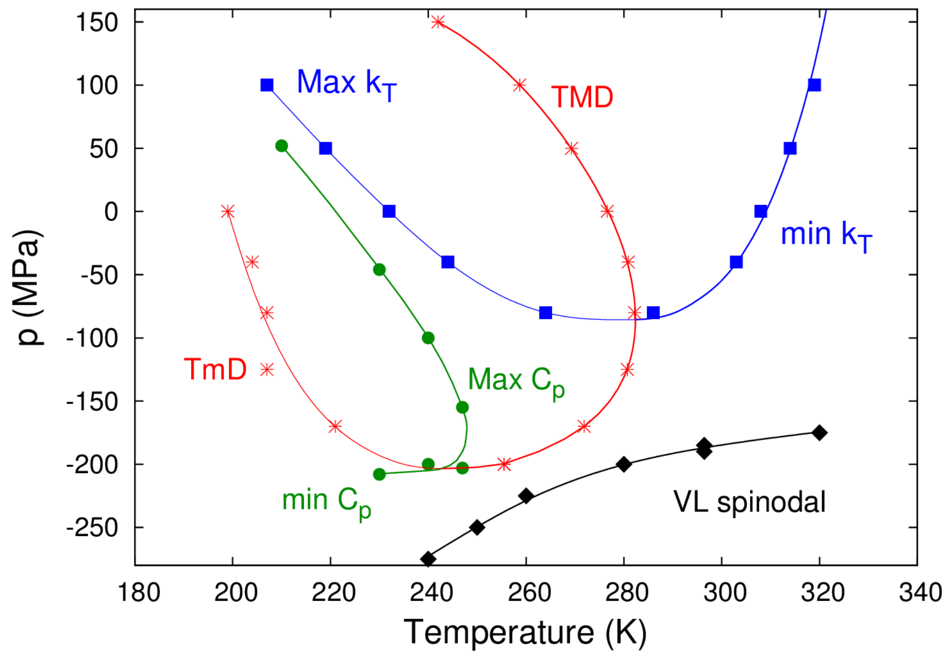
Full scenario of water anomalies (TIP4P/2005)





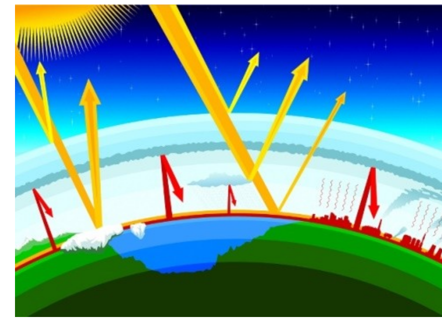


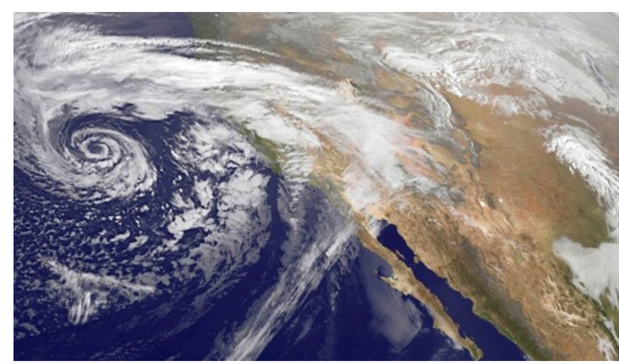




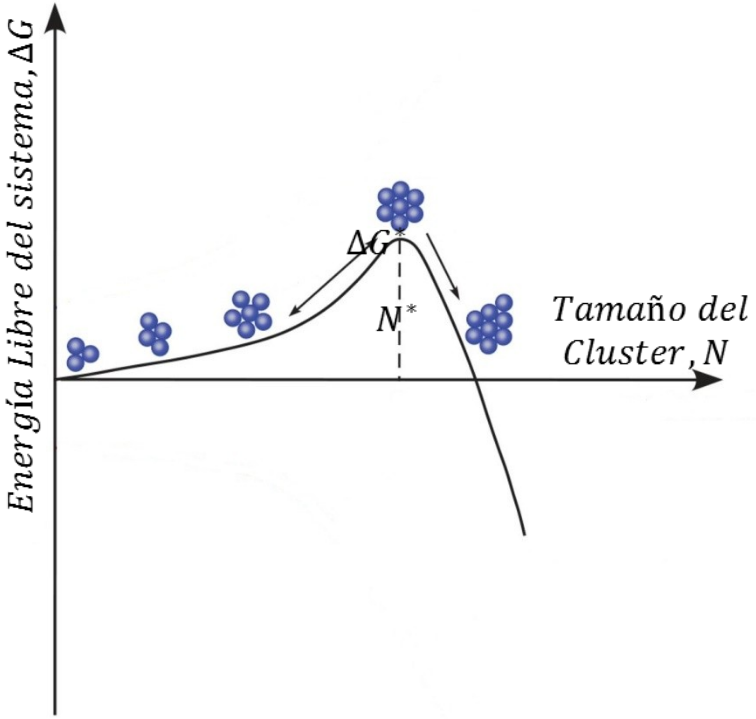
The liquid-liquid critical point scenario seems plausible but it could also be possible that T_c = 0 K

Relevance of ice nucleation





Homogeneous nucleation: free energy and nucleation rate



Classical nucleation theory (CNT):

$$\Delta G = -|\Delta\mu| \cdot N + A \cdot \gamma$$

$$\Delta G^* = \frac{|\Delta\mu| \cdot N^*}{2}$$

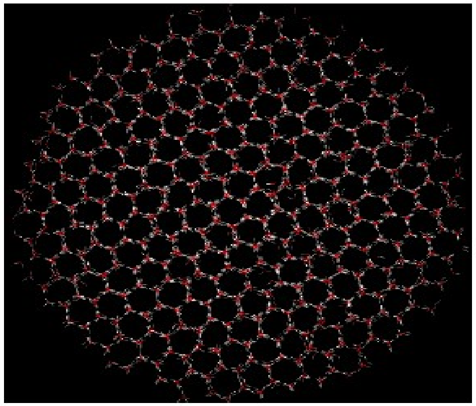
$$J = Z f^+ \rho_l \cdot e^{-\frac{\Delta G^*}{k_B T}}$$

Z: Zeldovich factor

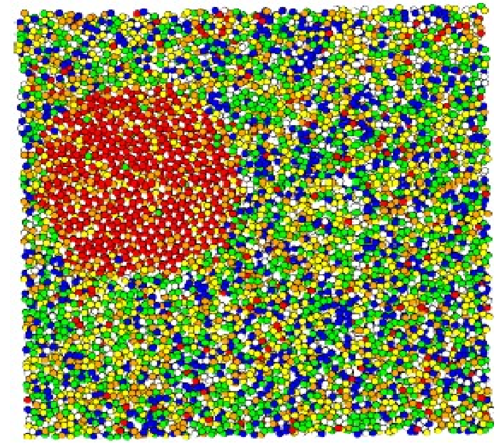
f^+: attachment rate

ρ_l: liquid density

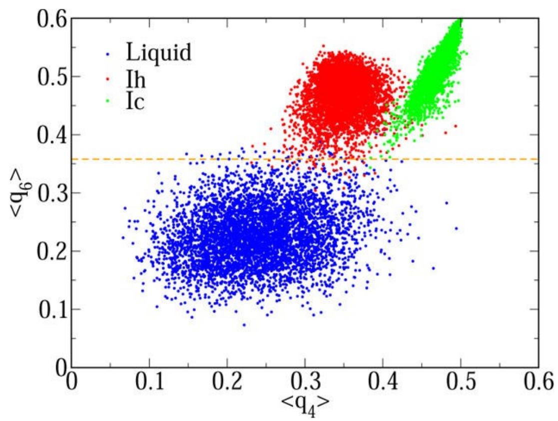
Seeding technique to evaluate N*



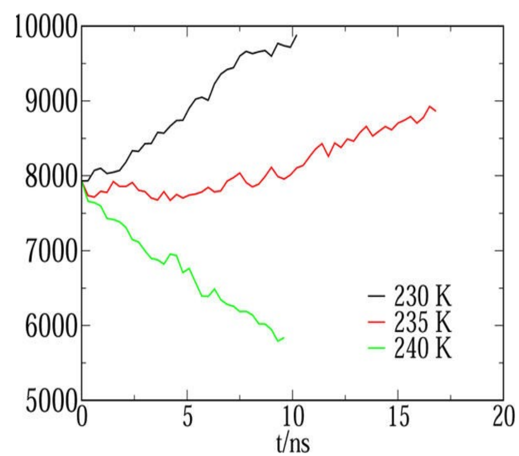
Generation of a spherical ice cluster



Insertion of the ice cluster in liquid water

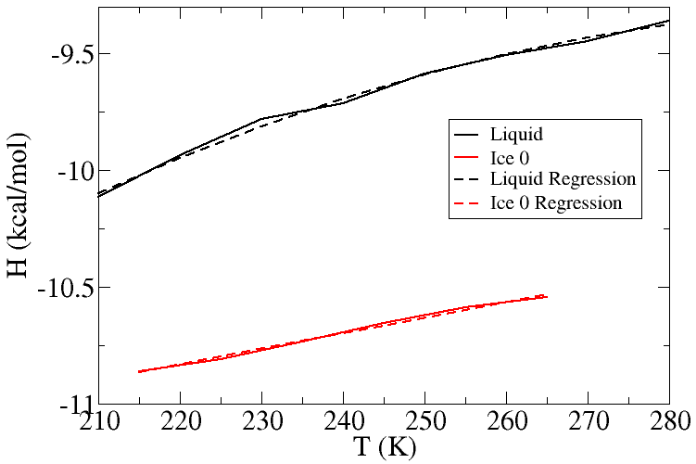


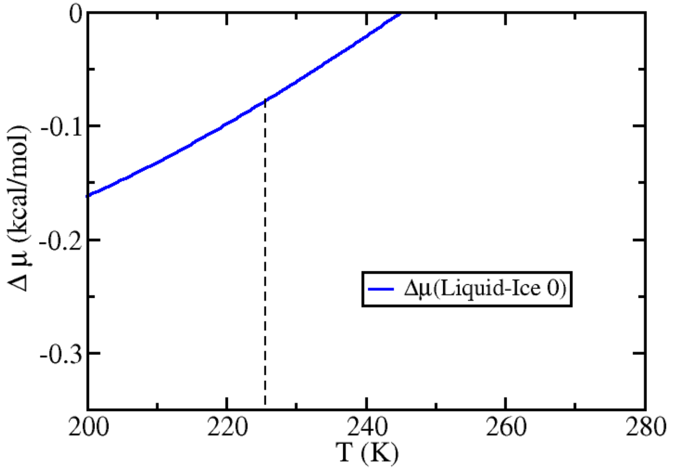
Order parameter to detect the ice molecules



Molecular Dynamics simulations at different temperatures lead to bound the temperature at which the cluster is critical

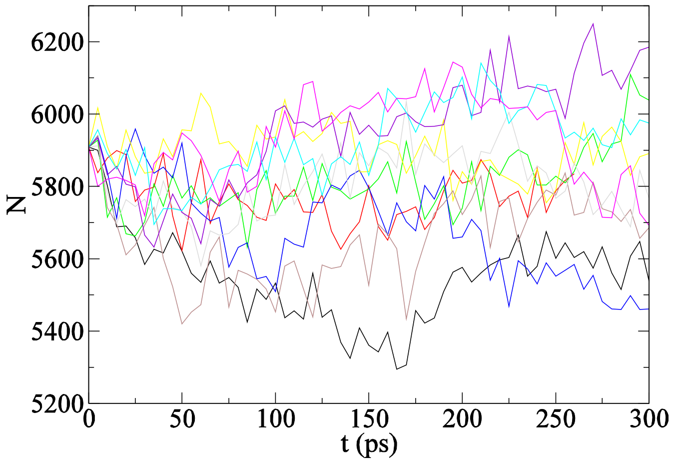
Calculation of Δμ: thermodynamic integration

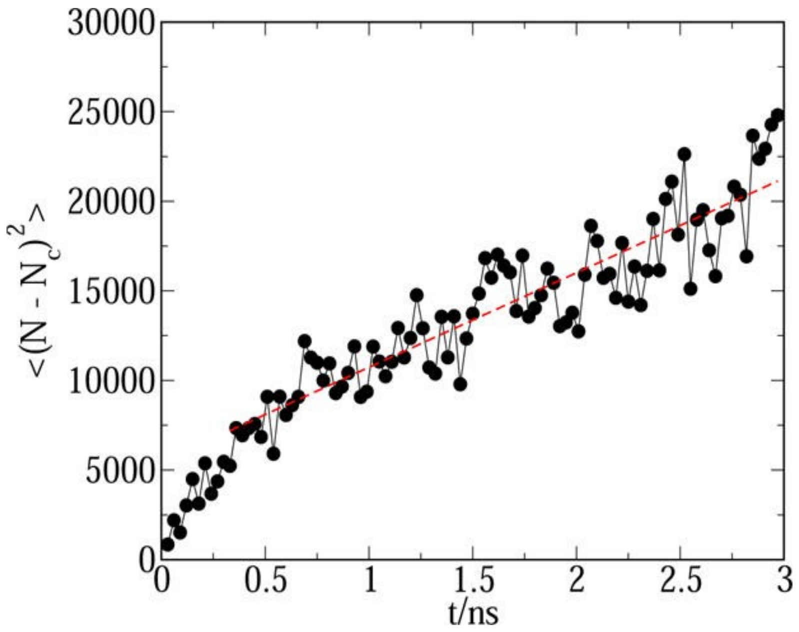




$$\frac{\mu(T_2,p)}{k_B T_2} - \frac{\mu(T_1,p)}{k_B T_1} = -\int_{T_1}^{T_2} \frac{H(T)}{N k_B T^2} dT$$

Calculation of the attachment rate f^+

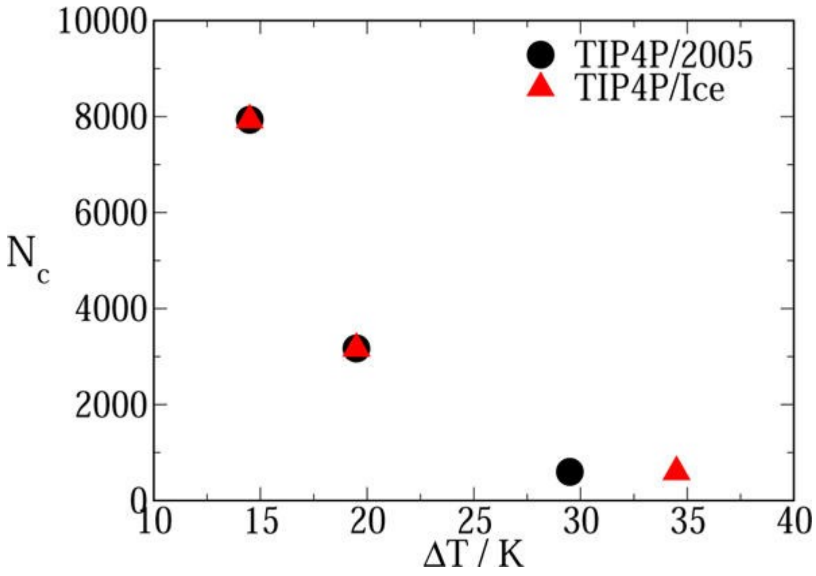


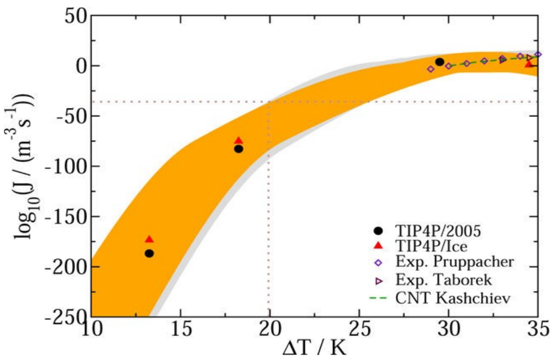


Perform a number of simulations of a cluster at the temperature at which the cluster is critical

f^+ = slope/2

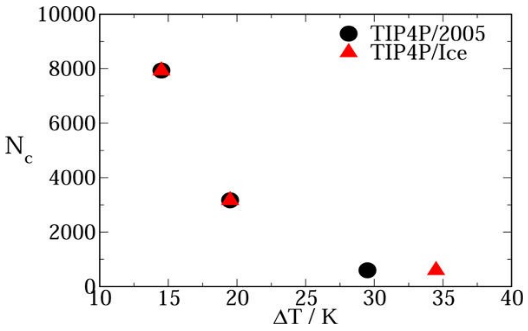
Relevant results: Size of the critical cluster and nucleation rates



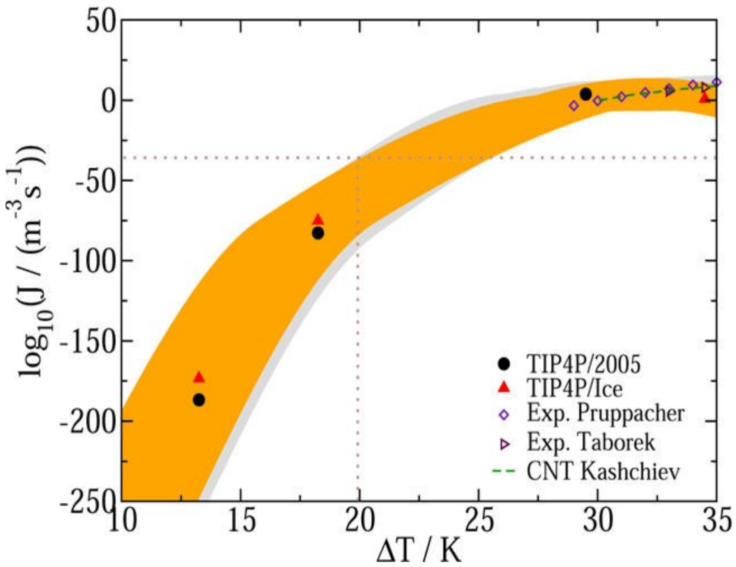


The size of the critical cluster is almost independent of the water model

Size of the critical cluster and nucleation rates

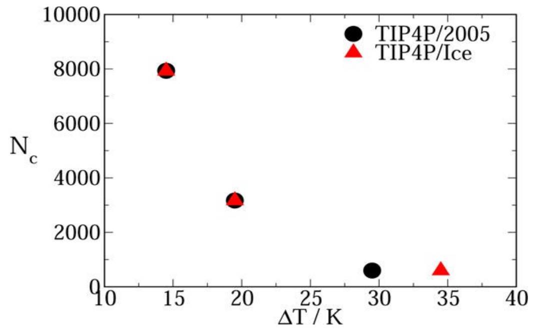


The size of the cluster cluster seems to be independent of the water model

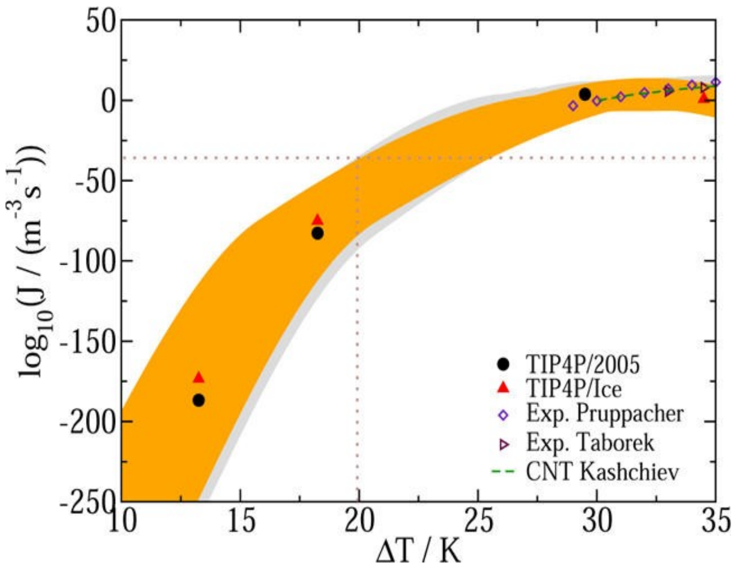


E. Sanz et al., JACS 135, 15008 (2013)

Size of the critical cluster and nucleation rates



The size of the cluster cluster seems to be independent of the water model

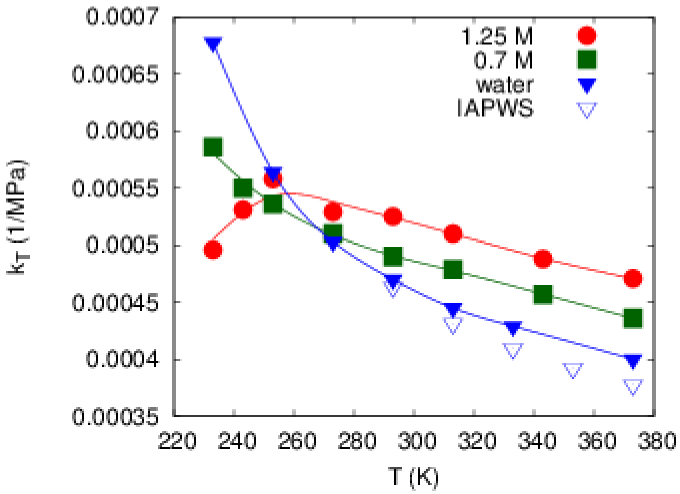


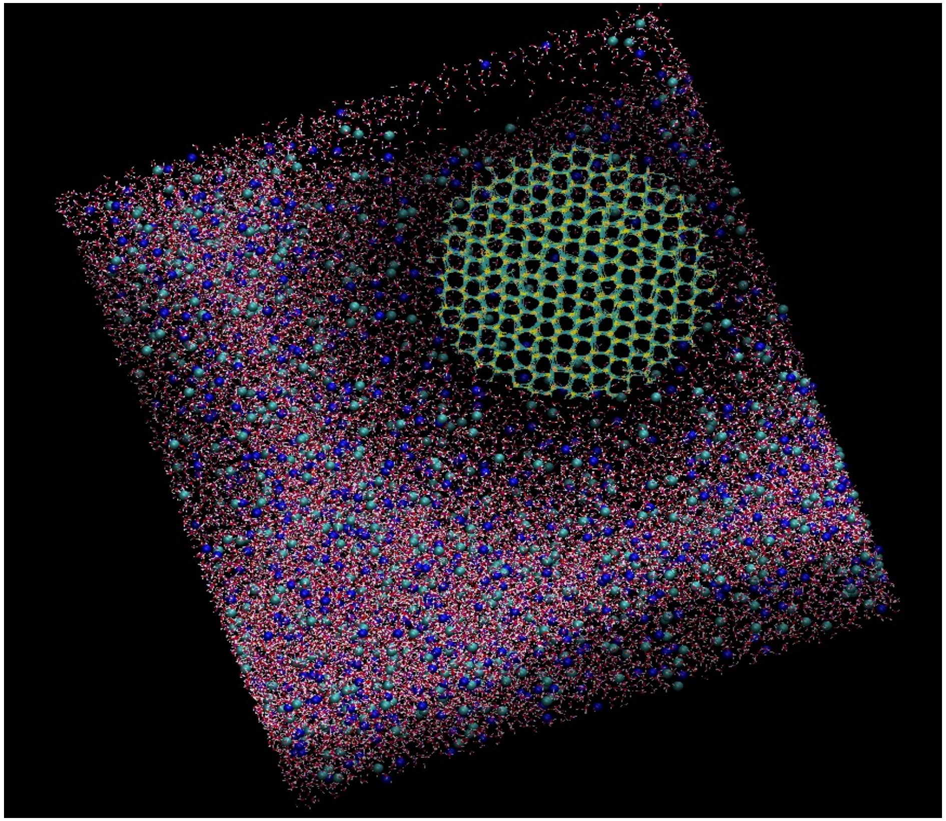
It is impossible that liquid water nucleates homogeneously in Earth for a supercooling ΔT < 20 K

E. Sanz et al., JACS 135, 15008 (2013)

Ongoing work on NaCl solutions

- Effect of salt on water anomalies (at extreme conditions)
- Effect of salt on nucleation rate
- Development of a force field for ionic solutions based on TIP4P/2005s





Acknowledgements

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UCM team

- Carlos Vega
- Eduardo Sanz
- Chantal Valeriani
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- Guiomar Delgado
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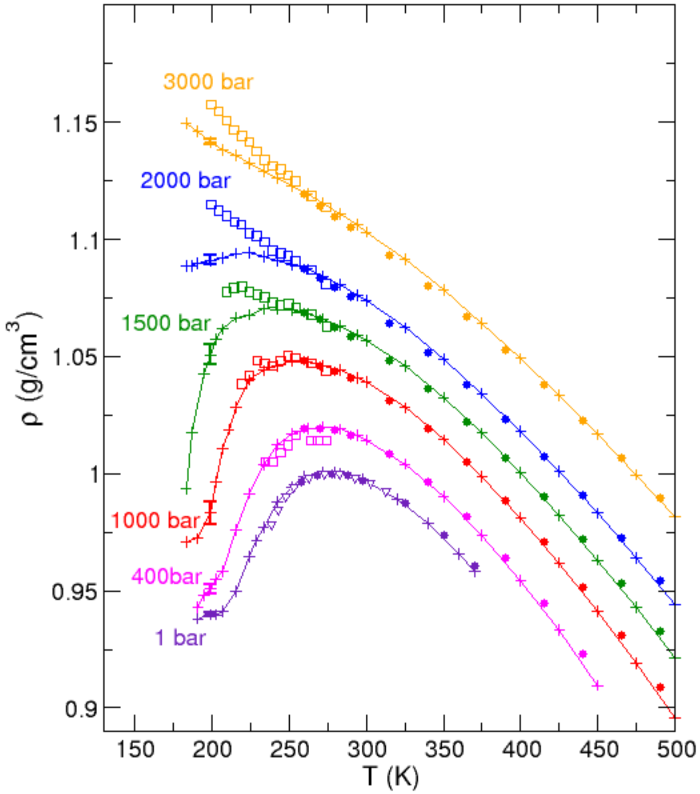
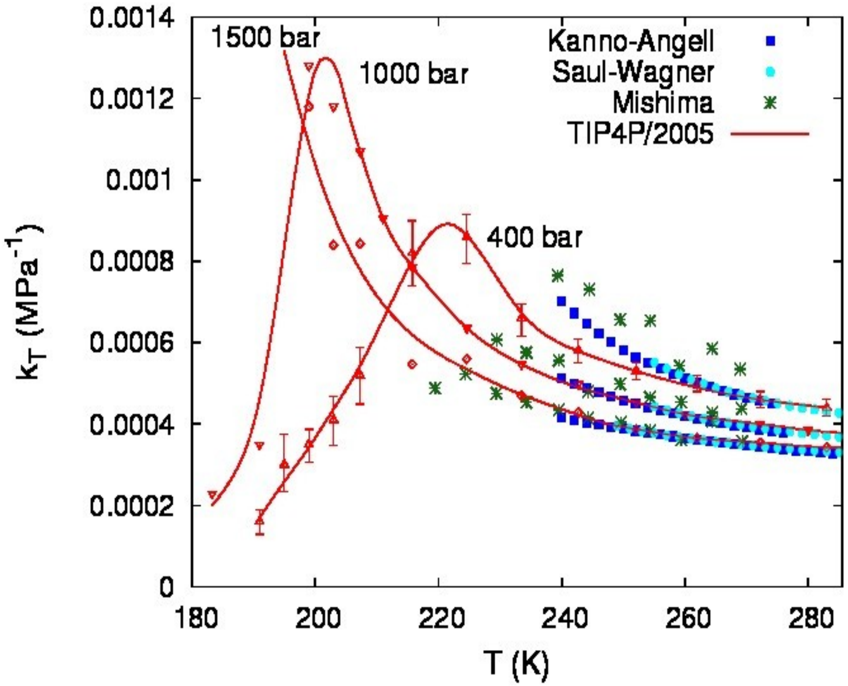
Université de Lyon

- Gaël Pallares
- Mouna El Mekki Azouzi
- Frédéric Caupin

Universidad Complutense Madrid

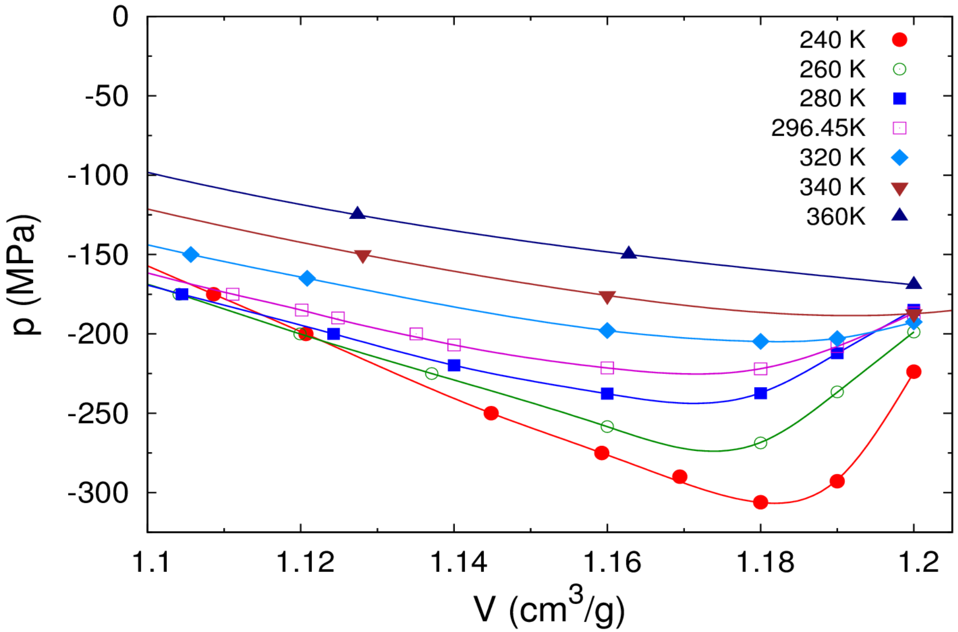
Supercooled TIP4P/2005 water: simulation *vs.* experiment



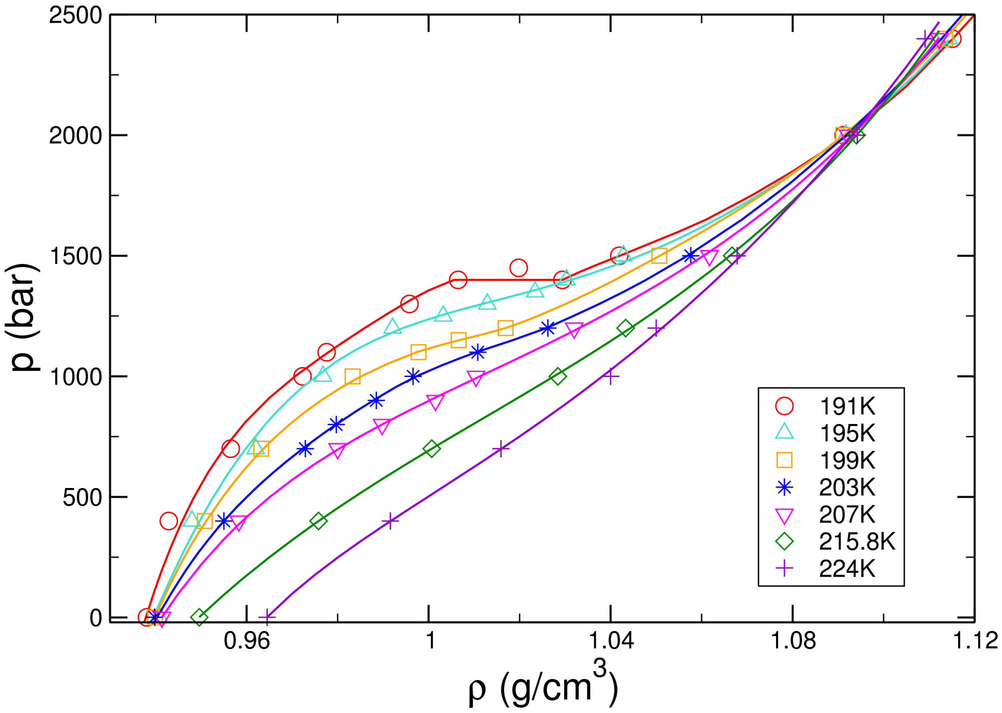


J.L.F.Abascal and C. Vega, JCP 134 186101 (2011)

liquid-vapour spinodal



A liquid-liquid critical point?



J.L.F.Abascal and C. Vega , JCP 133, 234502 (2010)

Cálculo de $\Delta\mu$: Integración Termodinámica

$$\frac{\mu(T_2,p)}{k_B T_2} - \frac{\mu(T_1,p)}{k_B T_1} = -\int_{T_1}^{T_2} \frac{H(T)}{N k_B T^2} dT$$

Hacemos $T_1 = T_{coex}$
$y\ T_2 = T^*$

$\Delta\mu$ —

$$\frac{\mu(T_2,p)}{k_B T_2} - \frac{\mu(T_1,p)}{k_B T_1} = -\int_{T_1}^{T_2} \frac{H(T)}{N k_B T^2} dT$$

$$\frac{\mu(T_2,p)}{k_B T_2} - \frac{\mu(T_1,p)}{k_B T_1} = -\int_{T_1}^{T_2} \frac{H(T)}{N k_B T^2} dT$$

$$\Delta\mu = [\mu_{fase1}(T_2) - \mu_{fase1}(T_{coex})] - [\mu_{fase2}(T_2) - \mu_{fase2}(T_{coex})] = \mu_{fase1}(T_2) - \mu_{fase2}(T_2)$$

Parámetros de Orden

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\overrightarrow{r_{ij}})$$

$$\bar{q}_{lm}(i) = \frac{1}{N_b{}'(i)} \sum_{j=0}^{N_b{}'(i)} q_{lm}(j)$$

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2}$$

$$\bar{q}_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{q}_{lm}(i)|^2}$$

$$N_b'^{(i)} \equiv Vecinosde\ la\ partícula\ i + partícula\ i$$