"SuperStretch”
PICS collaboration
Lyon-Madrid
in progress

Ice nucleation:

What we have learned so far, and what still needs to be understood

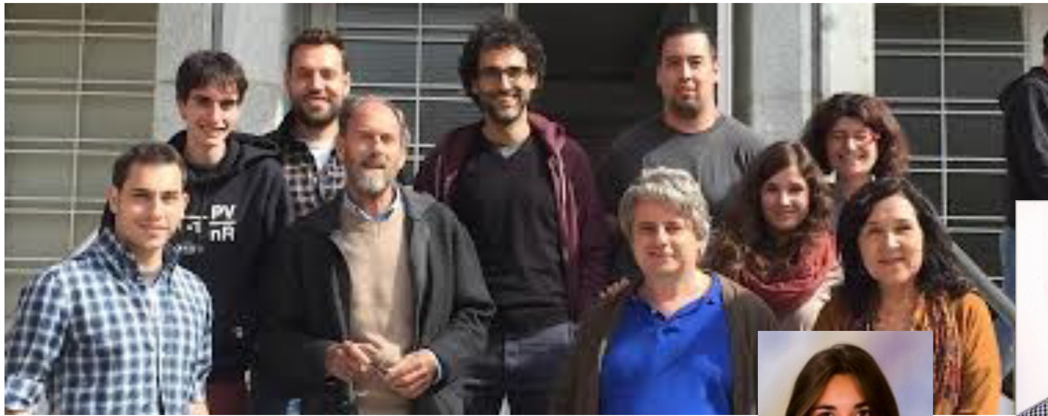
Chantal Valeriani

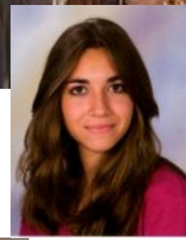
Universidad Complutense de Madrid

RES workshop, Santiago, September 2017

The ice nucleation team

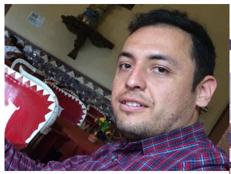
Universidad Complutense de Madrid





- Eduardo Sanz
- Jose Luis Abascal
- Carlos Vega

- Jorge Espinosa
- Pablo Rosales
- Alberto Zaragoza
- Pablo Montero
- Anibal Pandiani
- Victor Cruces
- Marta Garcia
- Raul Martinez



- Miguel Angel Gonzalez
- Francisco Alarcon

Universidad Politecnica de Madrid

- Jorge Ramirez

Universidad de Guanajuato (Mexico)

- Analaura Benavides

Ice nucleation

However, nucleation is still not fully understood in many systems

Why is the mechanism of water freezing still not known?

Experimentally: it is not possible to directly observe the formation of ice clusters being too small and too short lived

SIMULATIONS CAN PLAY A RELEVANT ROLE!

Outline

- How to simulate water in a computer
- How to study nucleation in a computer
- Ice nucleation
- Ice nucleation at high pressure
- Ice nucleation from salty water
- Future work

Scientific impact of our work on nucleation, thank to RES

Since 2013, when we started the nucleation project

We have published 18 papers (among those 2 PNAS, 1 PRL, 1 JACS and 1 J.Phys.Chem.Lett.)

Our papers on nucleation have already received 299 citations (WOS, September 2017)

We have been invited to internationally renown conferences to present our work (such as LIQUIDS, Stat Phys, CECAM, Thermodynamics)

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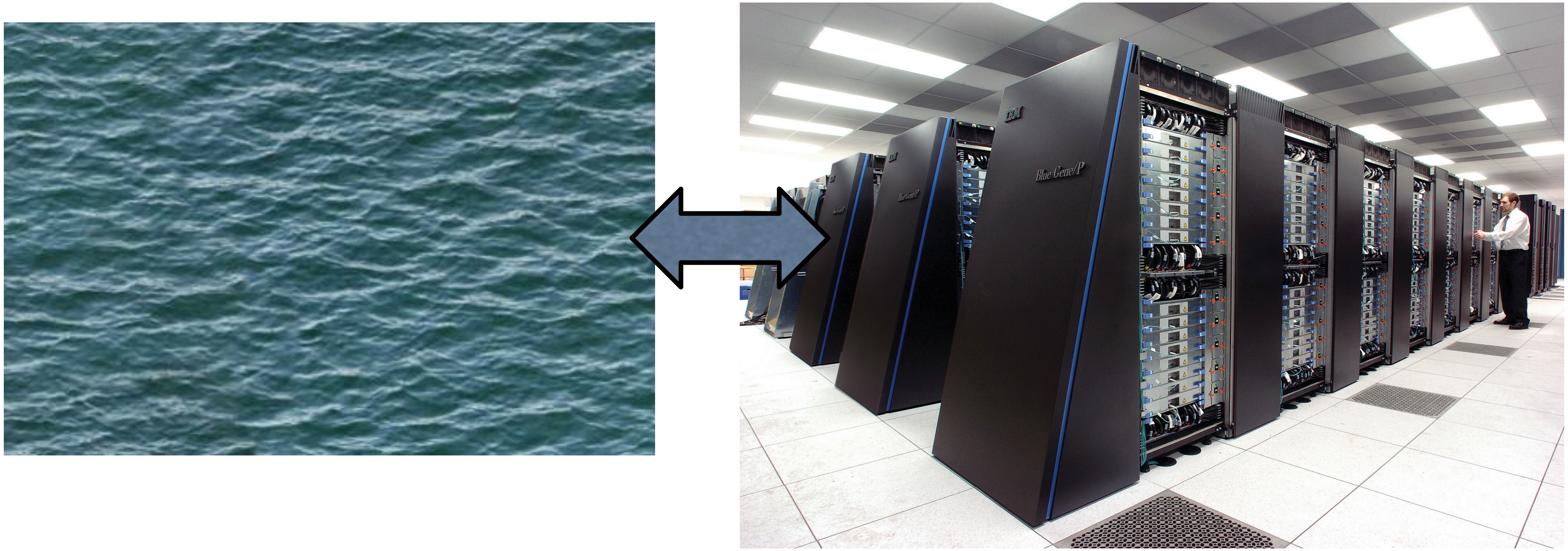
Simulations:
water in a computer



how do we simulate water at a microscopic level?

How can we study water in a computer?

Classical statistical mechanics

$$-\nabla_{Ri}\left(E_e(\vec{R}^N) + V_N\right) = m_i \frac{d^2\vec{R}_i}{dt^2}$$

$$E = \frac{\int (E_e(\vec{R}^N) + V_N) e^{-\beta(E_e(\vec{R}^N)+V_N)} d\vec{R}^N}{\int e^{-\beta(E_e(\vec{R}^N)+V_N)} d\vec{R}^N}$$

(1) Empirical expression for $E_e(\vec{R}^N) + V_N$

+

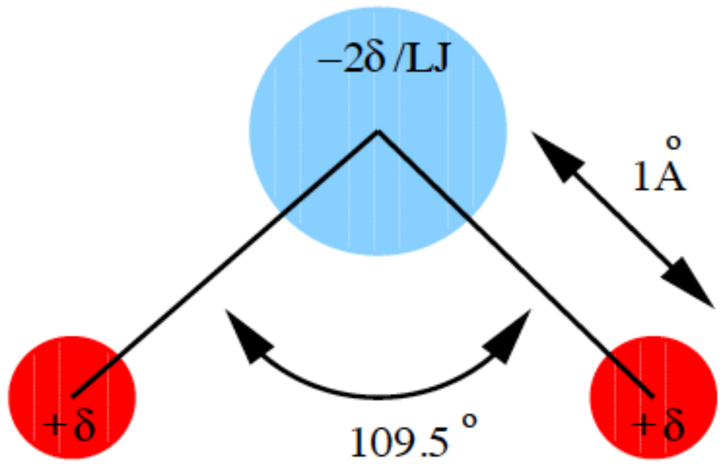
(2) Classical statistical mechanics

Which water models?

SPC/E, Berendsen et al. (1987)

TIP3P, Jorgensen et al. (1983)

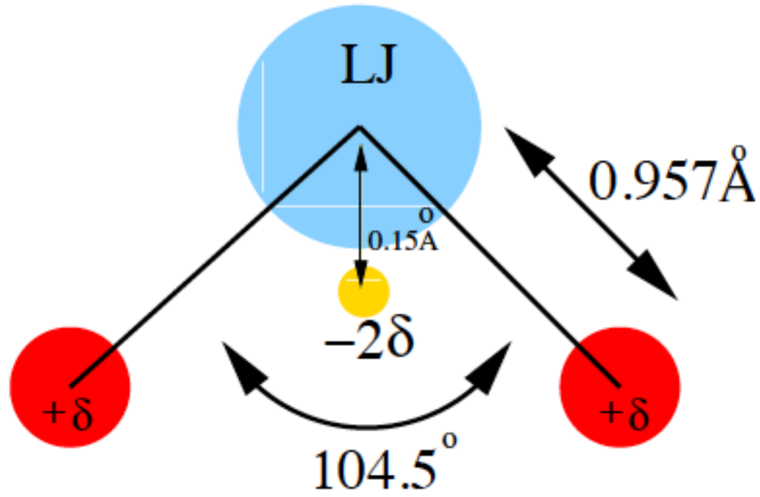
TIP4P, Jorgensen et al. 1983



1 center LJ

3 charges

SPC/E = 3000 citas

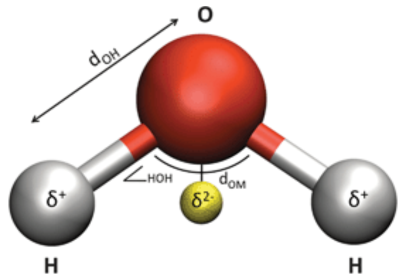


1 center LJ

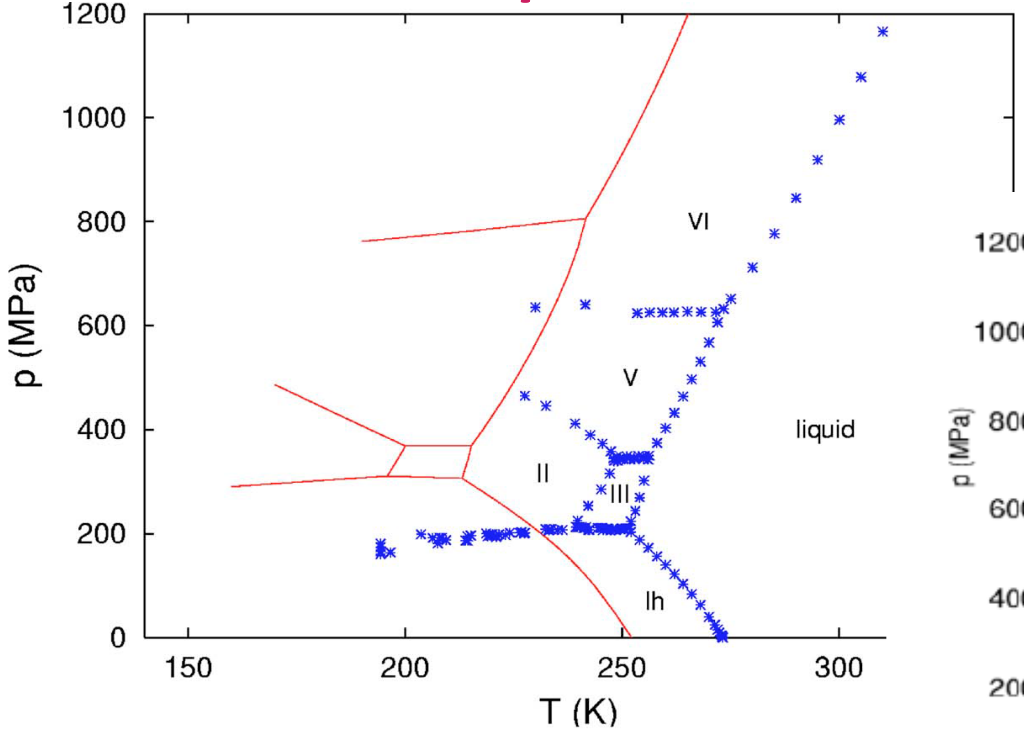
3 charges

TIP3P+TIP4P = 10000 citas

Which water models?



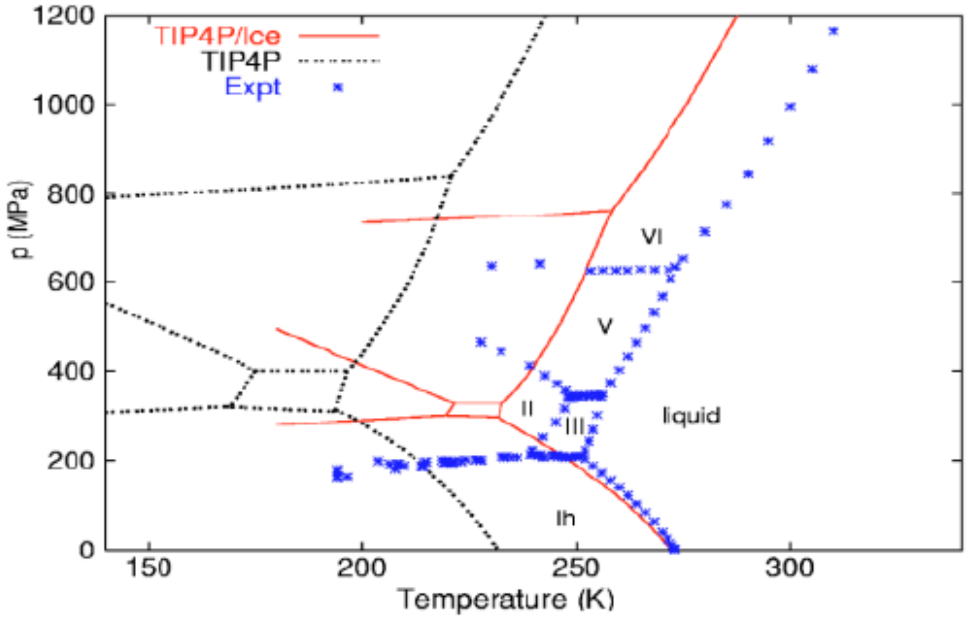
TIP4P/2005 water



Abascal and Vega, JCP 123 234505

Abascal, Sanz, Vega, PCCP 11 556 (2009)

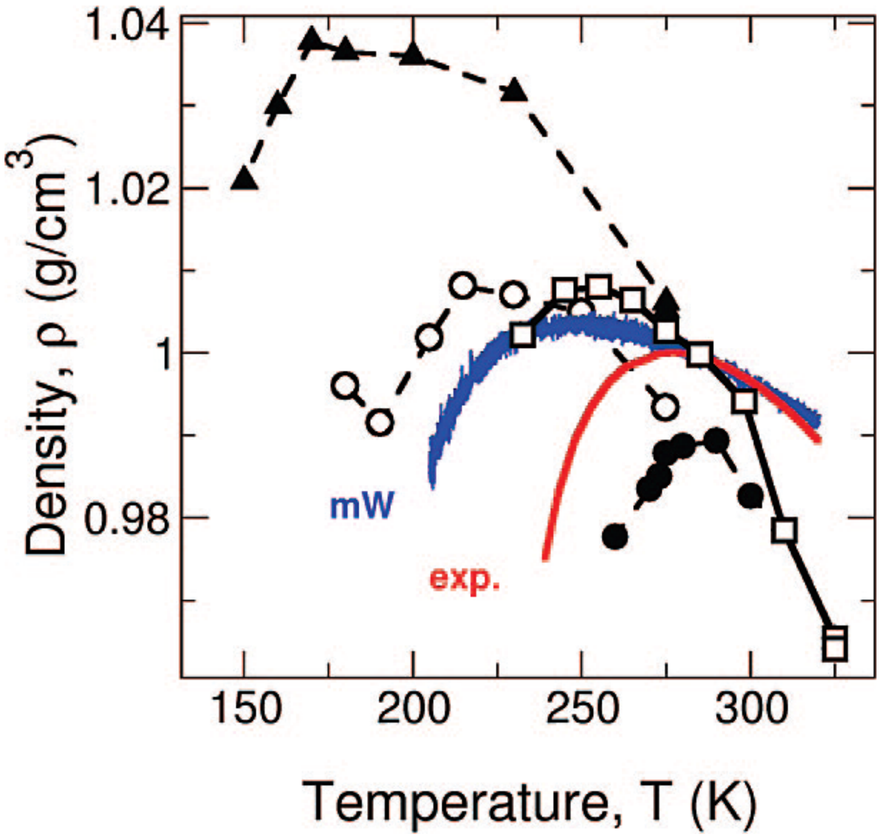
TIP4P/ICE water

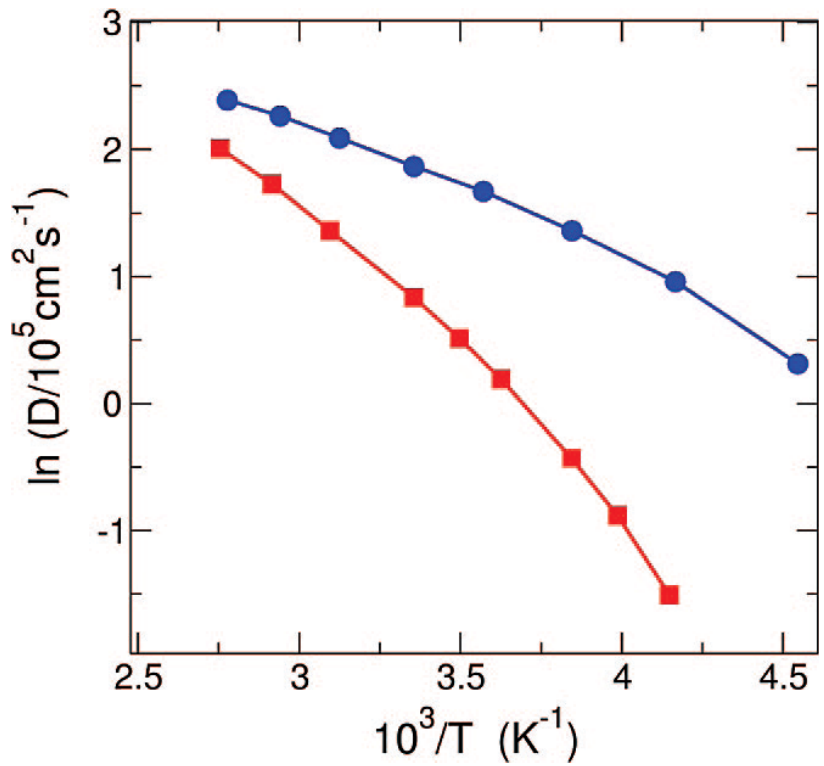


J.L.F. Abascal, E.Sanz, R.Garcia Fernandez and C.Vega,
J. Chem.Phys. 122 234511 (2005)

Which water models?

mW water





Molinero&Moore, J.Phys.Chem.B(2009)

✓coarse grained model
✓tetrahedral environment mimicked by a 3-body angular potential
✓it reproduces ice melting temperature

Outline

- How to simulate water in a computer
- How to study nucleation in a computer: the seeding method
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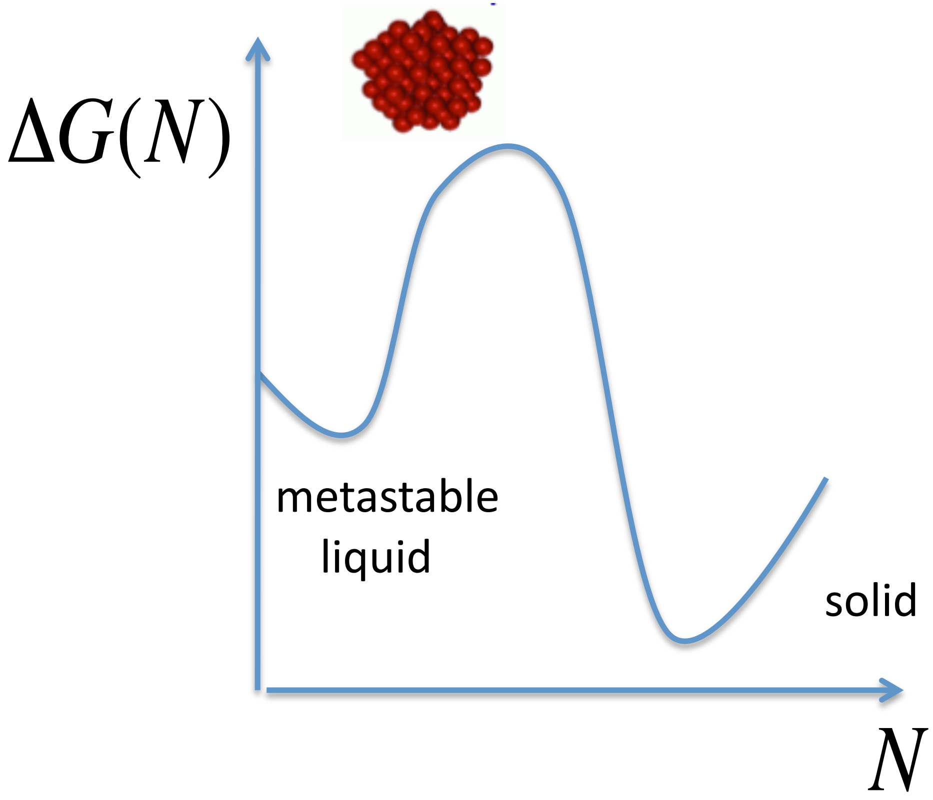
Classical Nucleation Theory (CNT)

activated process

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



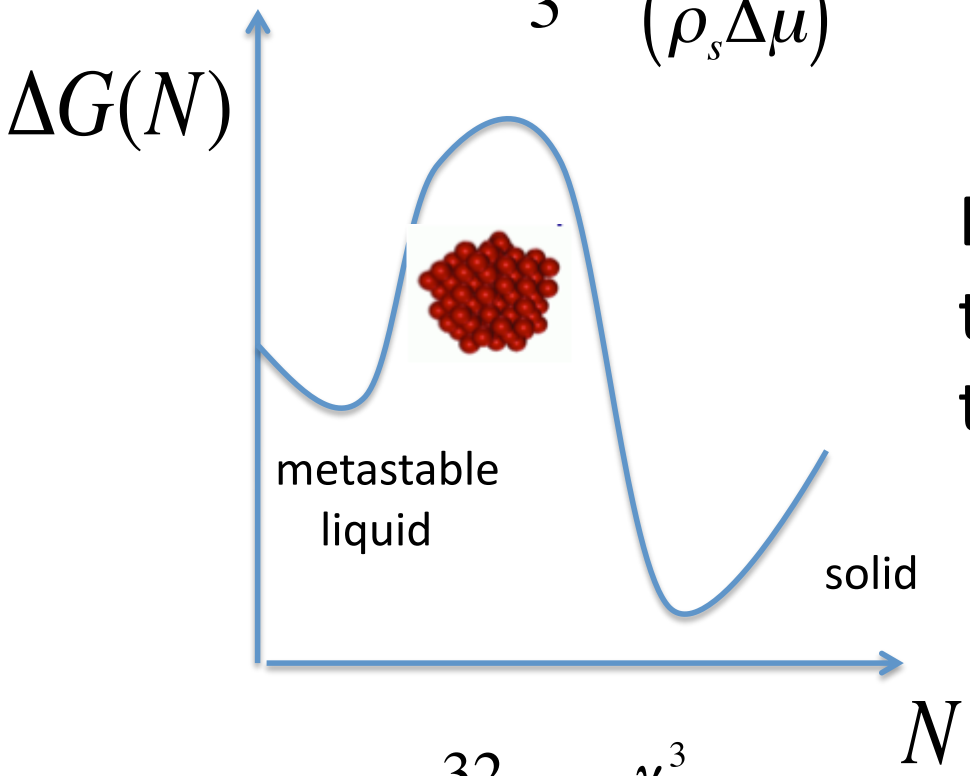
γ Liquid-solid interfacial free-energy at coexistence

Order parameter:
number of ice molecules
in the largest crystalline cluster

Classical Nucleation Theory (CNT)

activated process

$$\Delta G_c = \frac{16}{3}\pi\frac{\gamma^3}{(\rho_s \Delta\mu)^2}$$



$$N_c = \frac{32}{3}\pi\frac{\gamma^3}{\rho_s^{\,2}|\Delta\mu|^3}$$

Experimentally it is not possible to observe the critical cluster: too small and short lived

Steady-state nucleation rate

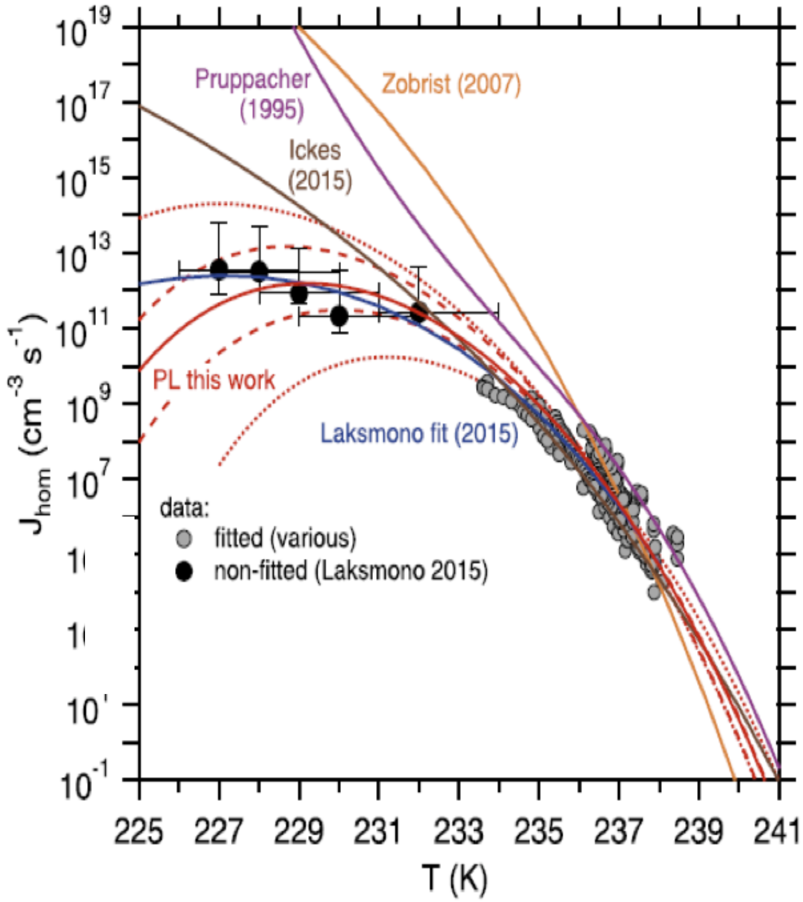
- J can be measured experimentally
- J can be computed numerically

$$J = A \exp^{-\beta \Delta G_c}$$

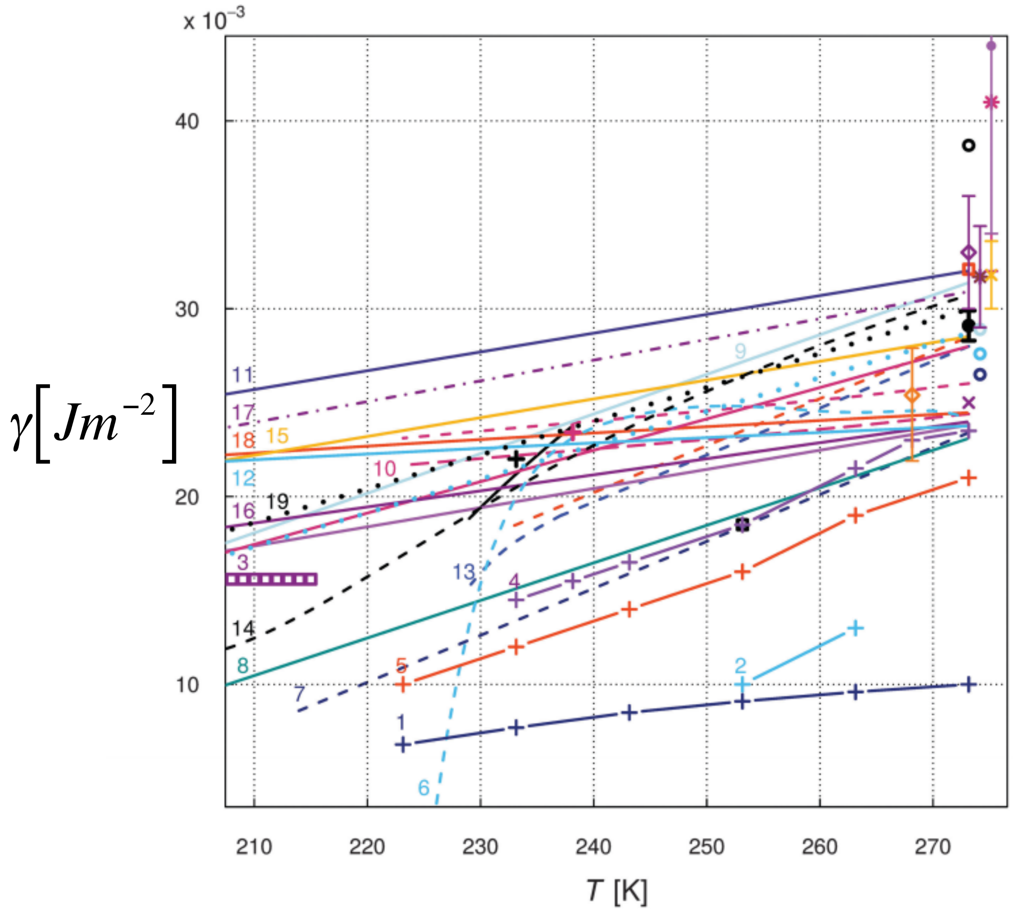
kinetic prefactor (flux across the barrier)

probability to form the critical cluster at the top of the free-energy barrier

Experimental results for γ and J



Murray, Koop, JCP 2016



Ickes et al PCCP, 2015

Given that an experimental consensus has not yet been reached, computer simulations could play a role

Seeding method to compute J

- CNT & Numerical simulations
- It is an approximated method, based on the apriori assumption of the cluster structure
- It allows to evaluate nucleation rates within broad thermodynamic conditions

Sanz, Vega, Espinosa, Caballero-Bernal, Abascal, Valeriani JACS (2013)

Espinosa, Vega, Valeriani, Sanz JCP (2016)

Applying the seeding method

Make use of the CNT expression of the nucleation rate and compute each term by means of computer simulations

$$J = A \exp^{-\beta \Delta G_c}$$

$$J = \sqrt{\frac{|\Delta\mu|}{6\pi\kappa_B T N_c}}\rho_f f^+ \exp\left(-\frac{N_c|\Delta\mu|}{2\kappa_B T}\right)$$

Applying the seeding method

Make use of the CNT expression of the nucleation rate and compute each term by means of computer simulations

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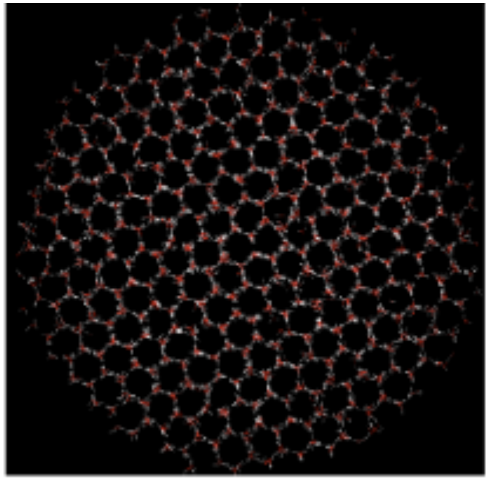
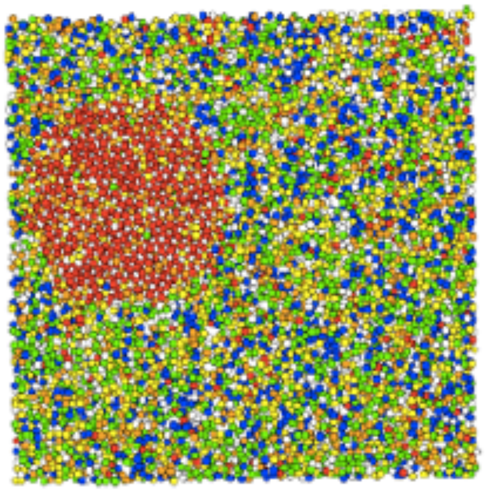
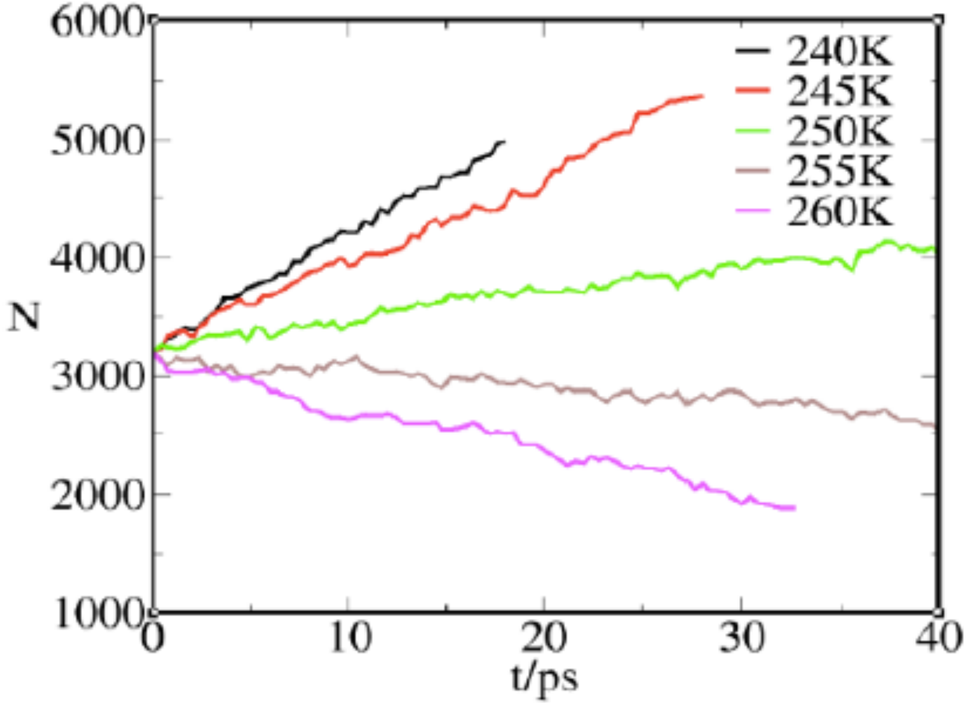
Computing Nc (critical cluster size)



1- Prepare a crystal seed

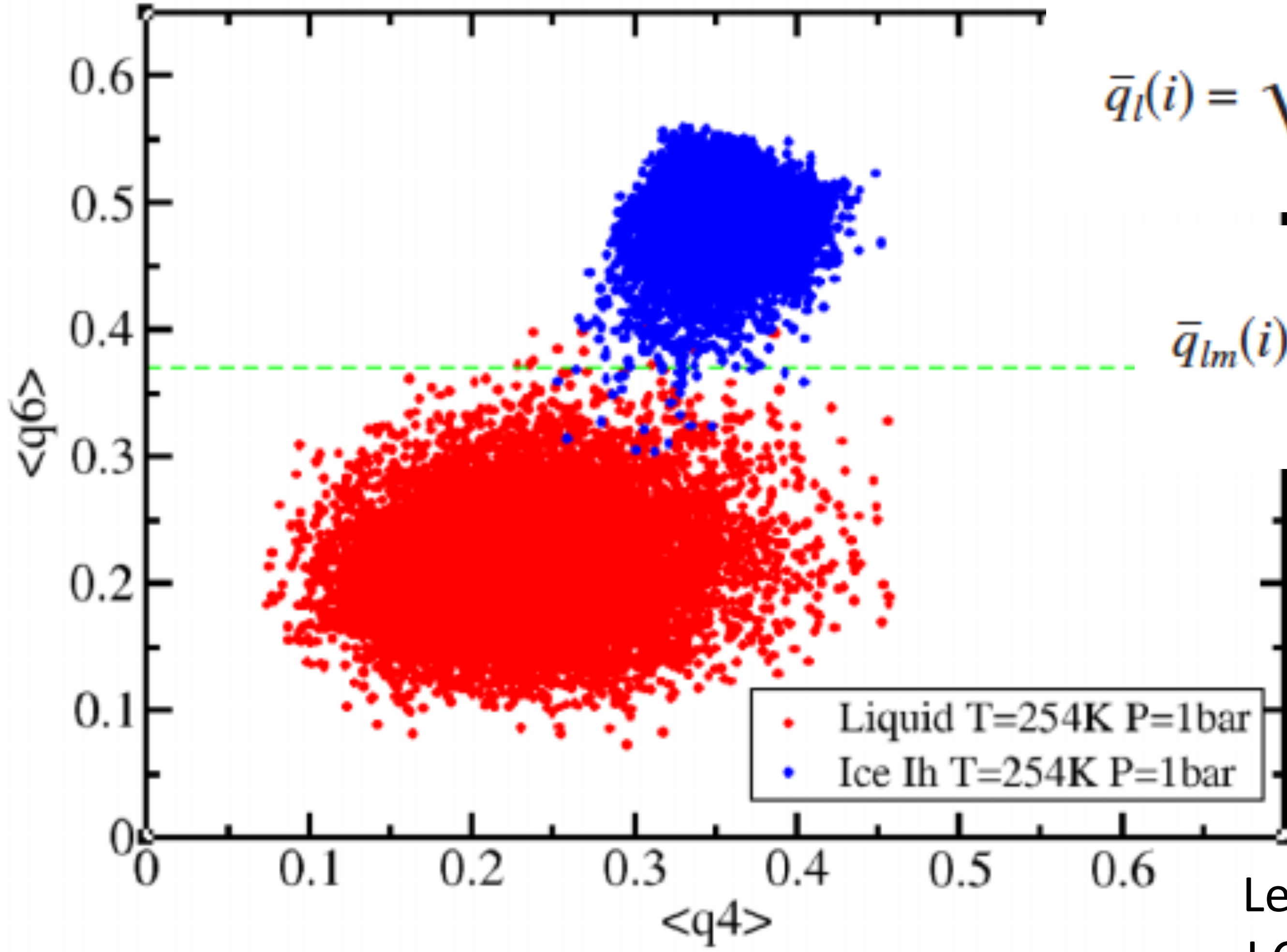


2-Embed the seed in the supercooled melt



3- Launch simulations at different temperatures to find the temperature at which the cluster is critical: T_2=252.5 K in this case.

PARENTHESIS:
distinguishing liquid from ice



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

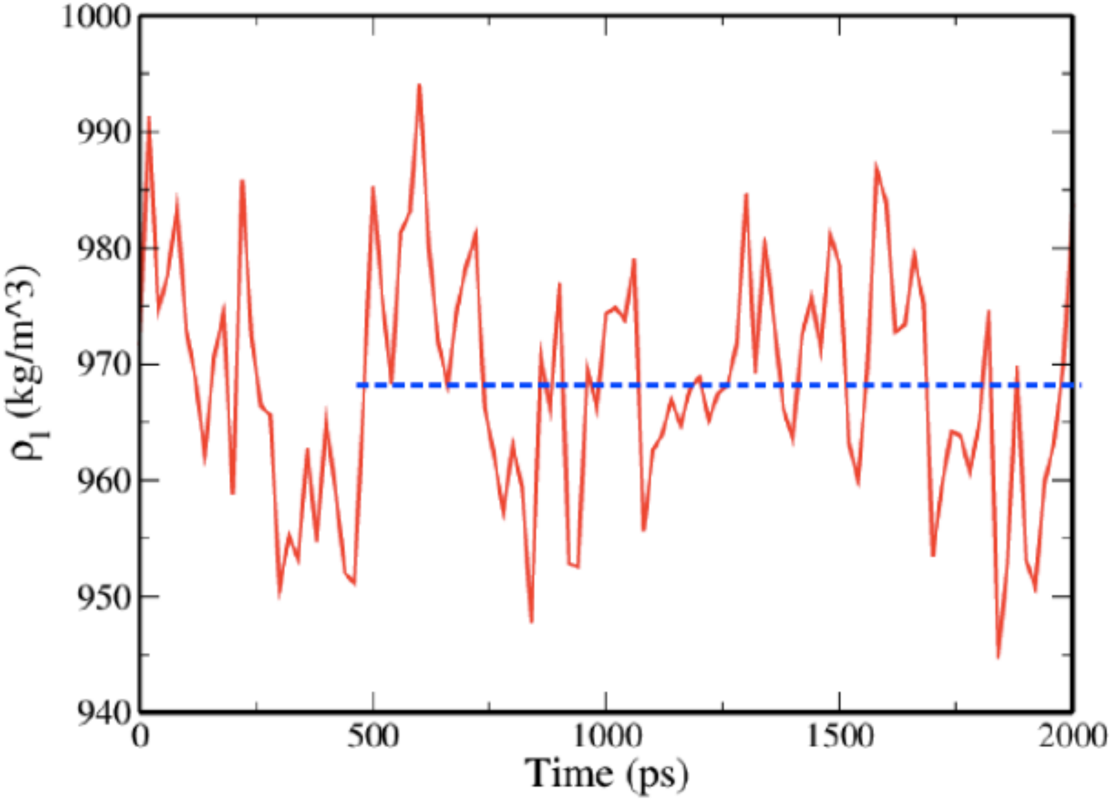
$$\bar{q}_{lm}(i) = \frac{1}{\tilde{N}_b(i)} \sum_{k=0}^{\tilde{N}_b(i)} q_{lm}(k)$$

Lechner&Dellago
J.Chem.Phys. (2008)

Computing ρ_f $\Delta\mu$ f^+

$$J = \sqrt{\frac{|\Delta\mu|}{6\pi\kappa_B T N_c}}\rho_f f^+ \exp\left(-\frac{N_c|\Delta\mu|}{2\kappa_B T}\right)$$

- ρ_f via a NPT simulations:



Computing $\rho_f \ \Delta\mu \ \ f^+$

$$J = \sqrt{\frac{|\Delta\mu|}{6\pi\kappa_B T N_c}}\rho_f f^+ \exp\left(-\frac{N_c|\Delta\mu|}{2\kappa_B T}\right)$$

- ρ_f via a NPT simulations:

- $\Delta\mu$ via thermodynamic integrations:

Thermodynamic integration

$$J = \sqrt{\frac{|\Delta\mu|}{6\pi\kappa_B T N_c}} \rho_f f^+ \exp\left(-\frac{N_c|\Delta\mu|}{2\kappa_B T}\right)$$

By means of thermodynamic integration

$$\Delta\mu \left\{ - \begin{array}{l} \dfrac{\mu_{ice}(T_2, p)}{k_B T_2} = \dfrac{\mu_{ice}(T_1, p)}{k_B T_1} - \displaystyle\int_{T_1}^{T_2} \dfrac{H_{ice}(T)}{N k_B T^2} dT \\ \dfrac{\mu_{water}(T_2, p)}{k_B T_2} = \dfrac{\mu_{water}(T_1, p)}{k_B T_1} - \displaystyle\int_{T_1}^{T_2} \dfrac{H_{water}(T)}{N k_B T^2} dT \end{array} \right.$$

Computing $\rho_f \; \Delta\mu \; f^+$

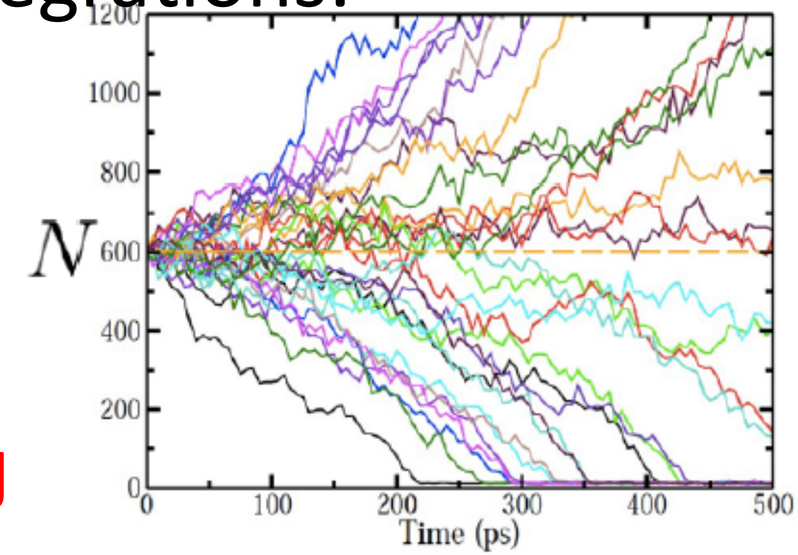
$$J = \sqrt{\frac{|\Delta\mu|}{6\pi\kappa_B T N_c}}\rho_f f^+ \exp\left(-\frac{N_c|\Delta\mu|}{2\kappa_B T}\right)$$

- ρ_f via a NPT simulations:

- $\Delta\mu$ via thermodynamic integrations:

- $f^+ \equiv \left\langle \frac{(N - N_c)^2}{2t} \right\rangle$

Auer&Frenkel Nature (2001)



Now we compute the rate J

Why do we need a supercomputer?

To compute the nucleation rate J for three crystalline clusters (i.e. at three super-coolings), we have used 300000 CPU hours.

Running only on 1 processor, would take about 30 years!

Supercomputers are needed to speed up our work

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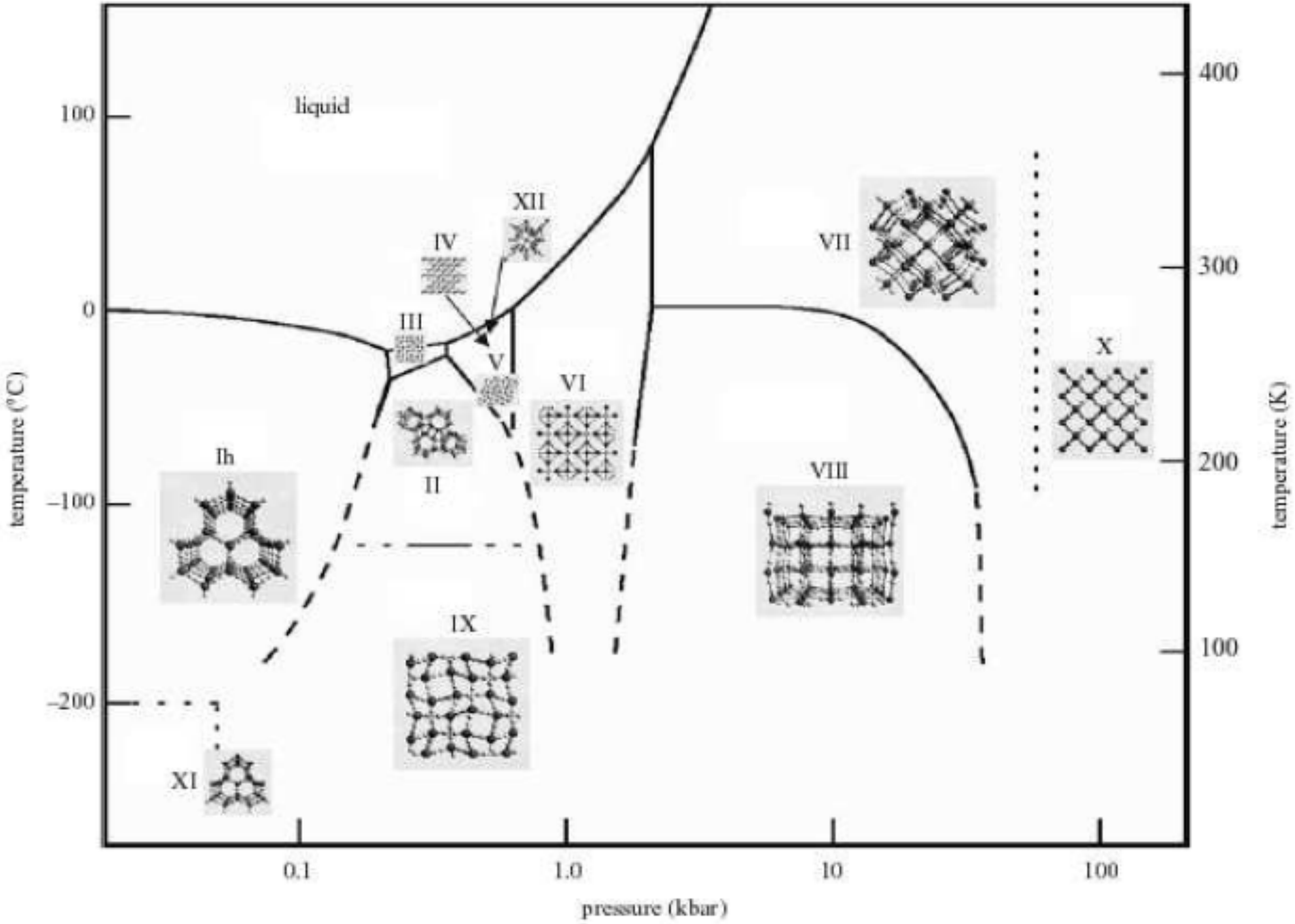
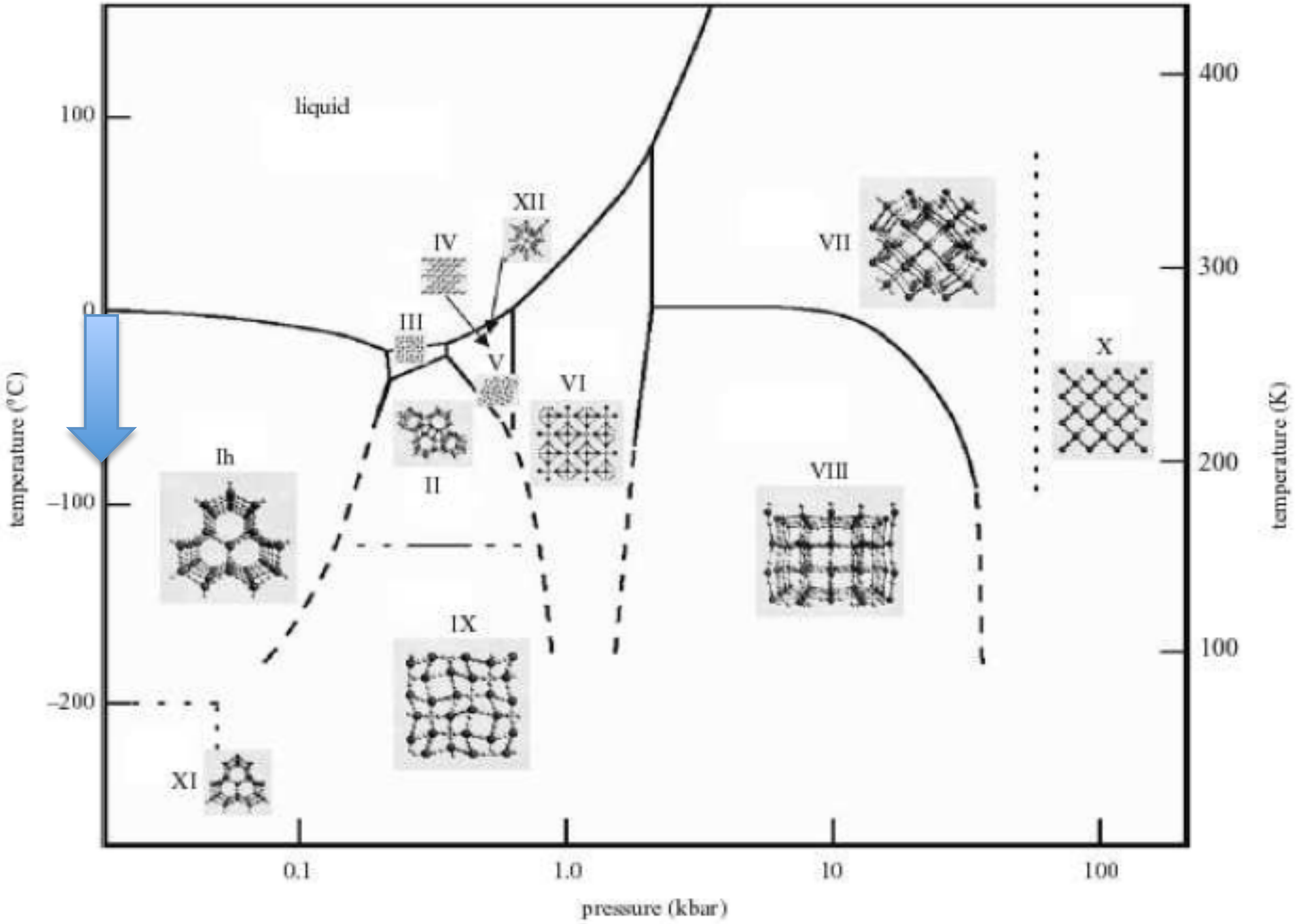
Water’s phase diagram



J.Finney, Phyl.Trans.R.Soc.Lond.B,(2004)

1900 Tammann , 1912 Bridgman, 1968 Whalley , 2009 Finney et al.

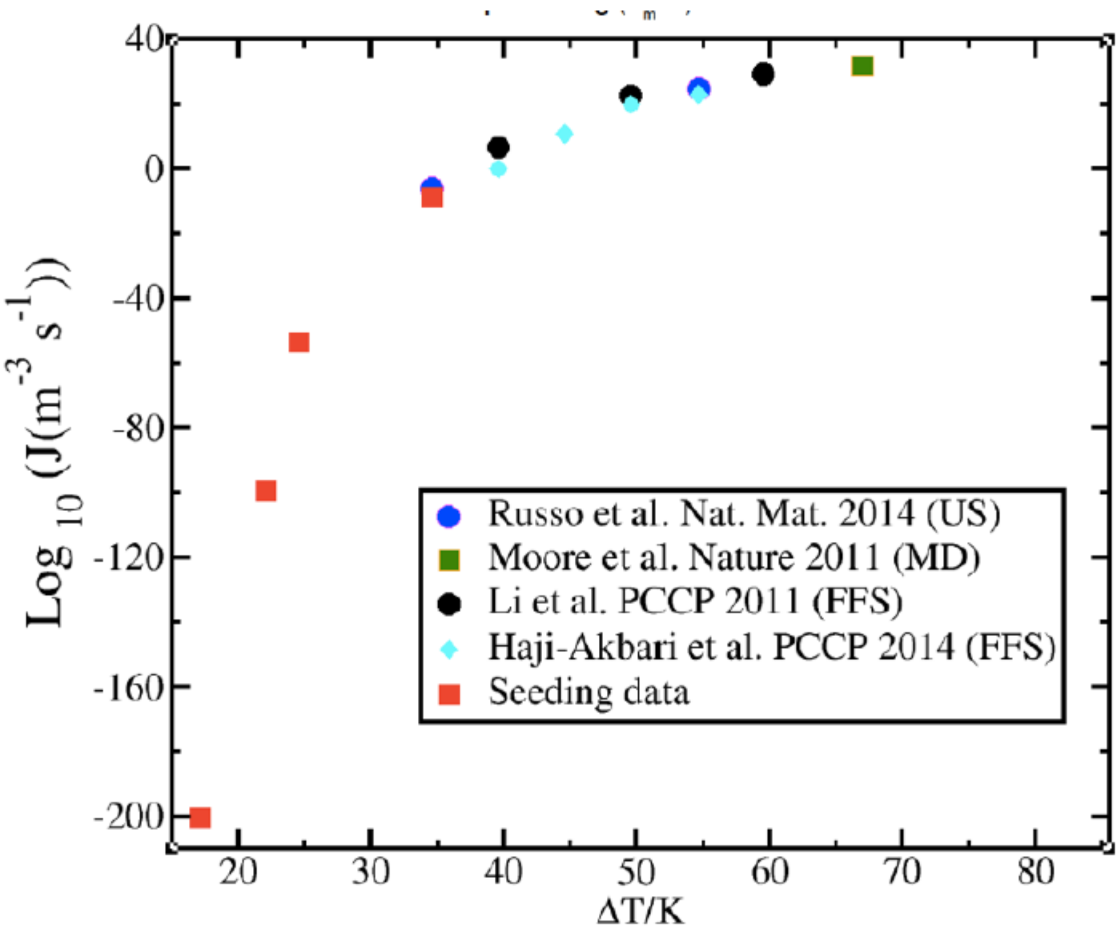
Water’s phase diagram



J.Finney, Phyl.Trans.R.Soc.Lond.B,(2004)

1900 Tammann , 1912 Bridgman, 1968 Whalley , 2009 Finney et al.

Ice nucleation rate at 1 bar

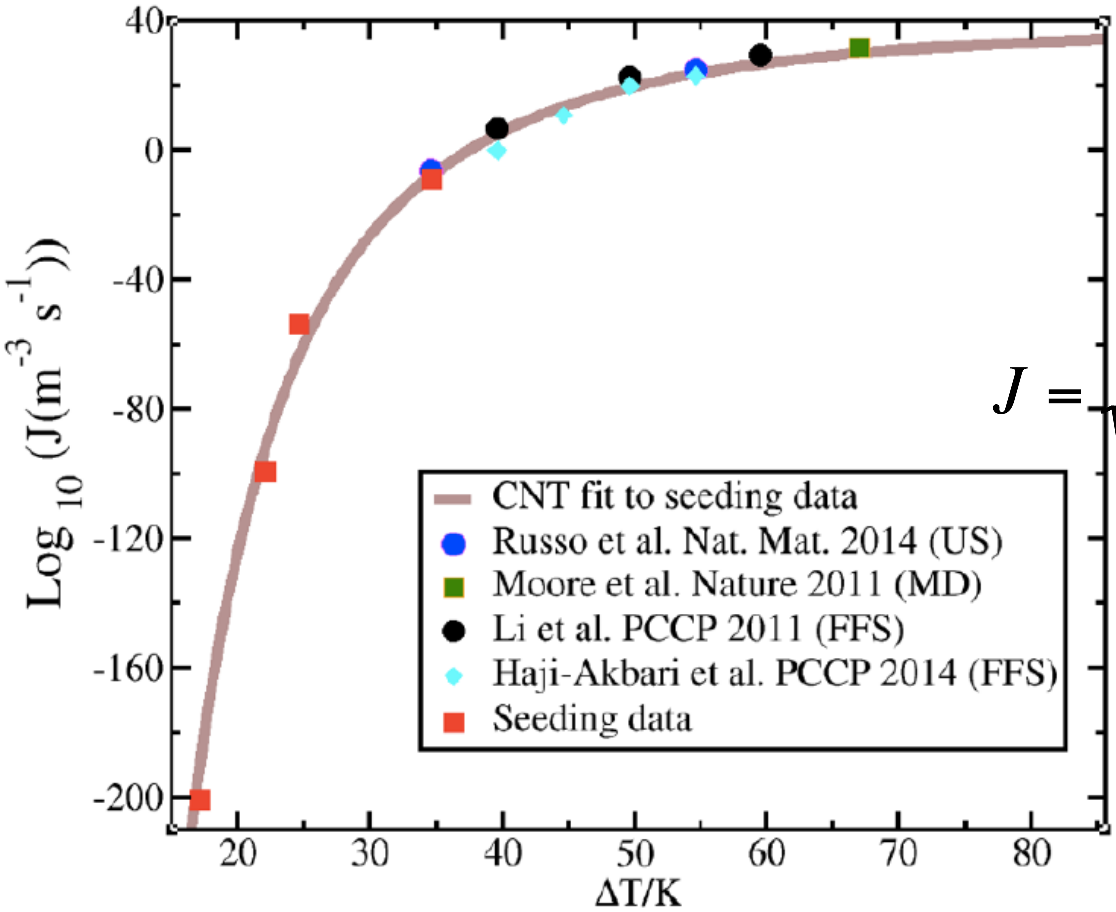


mW water

Molinero&Moore, J.Phys.Chem.B(2009)

J.Espinosa, E.Sanz,C.Valeriani and C.Vega JCP (2014)

Ice nucleation rate at 1 bar



Interpolating all quantities within a broad T range

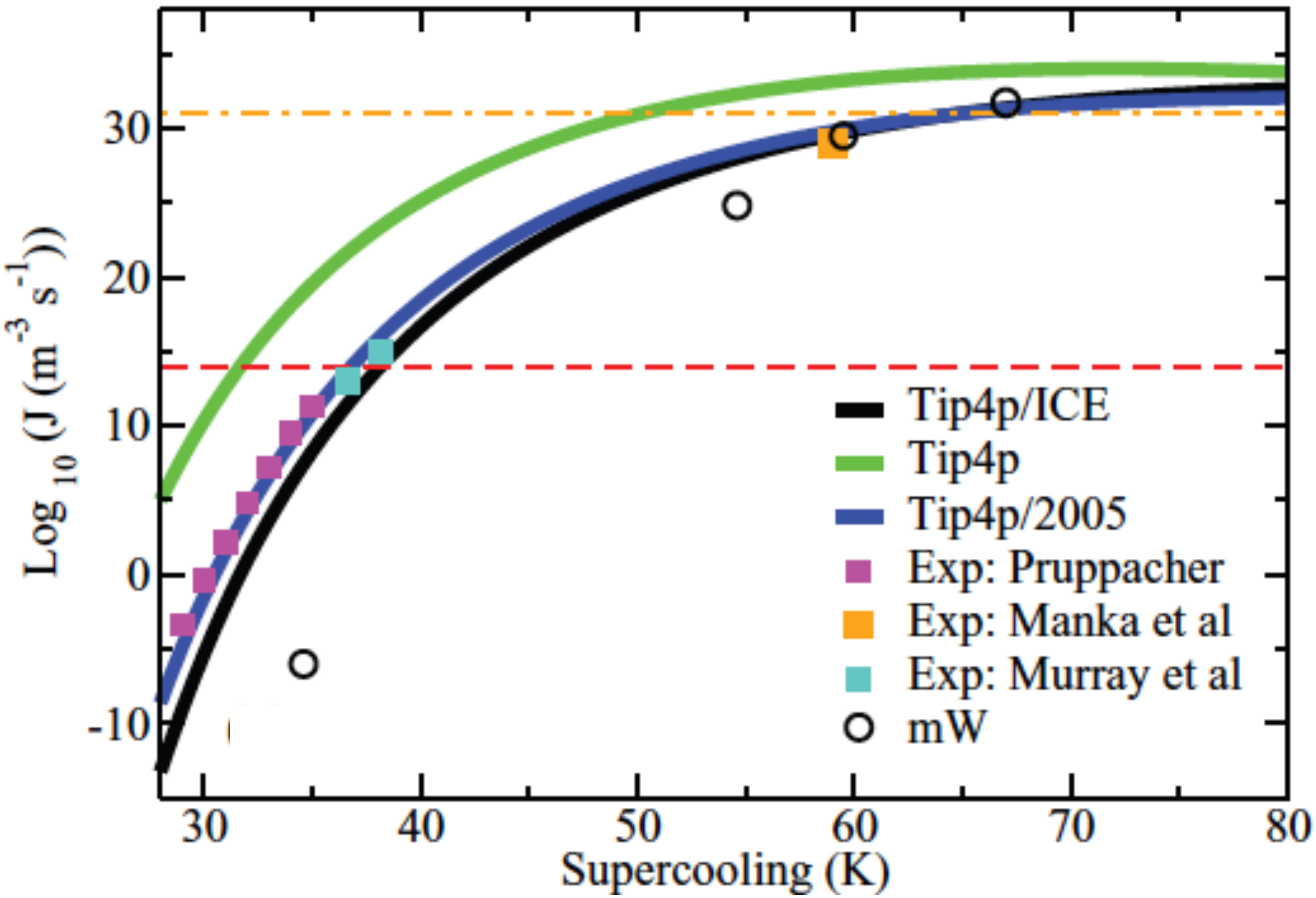
$$J = \sqrt{\frac{|\Delta\mu|}{6\pi\kappa_B T N_c}}\,\rho_l\, f^{+} \exp\left(-\frac{N_c|\Delta\mu|}{2\kappa_B T}\right)$$

according to CNT

$$f^{+} \equiv \frac{24 D N_c^{2/3}}{\lambda^2}$$

J.Espinosa, E.Sanz,C.Valeriani and C.Vega JCP (2014)

Comparing several water models to experiments

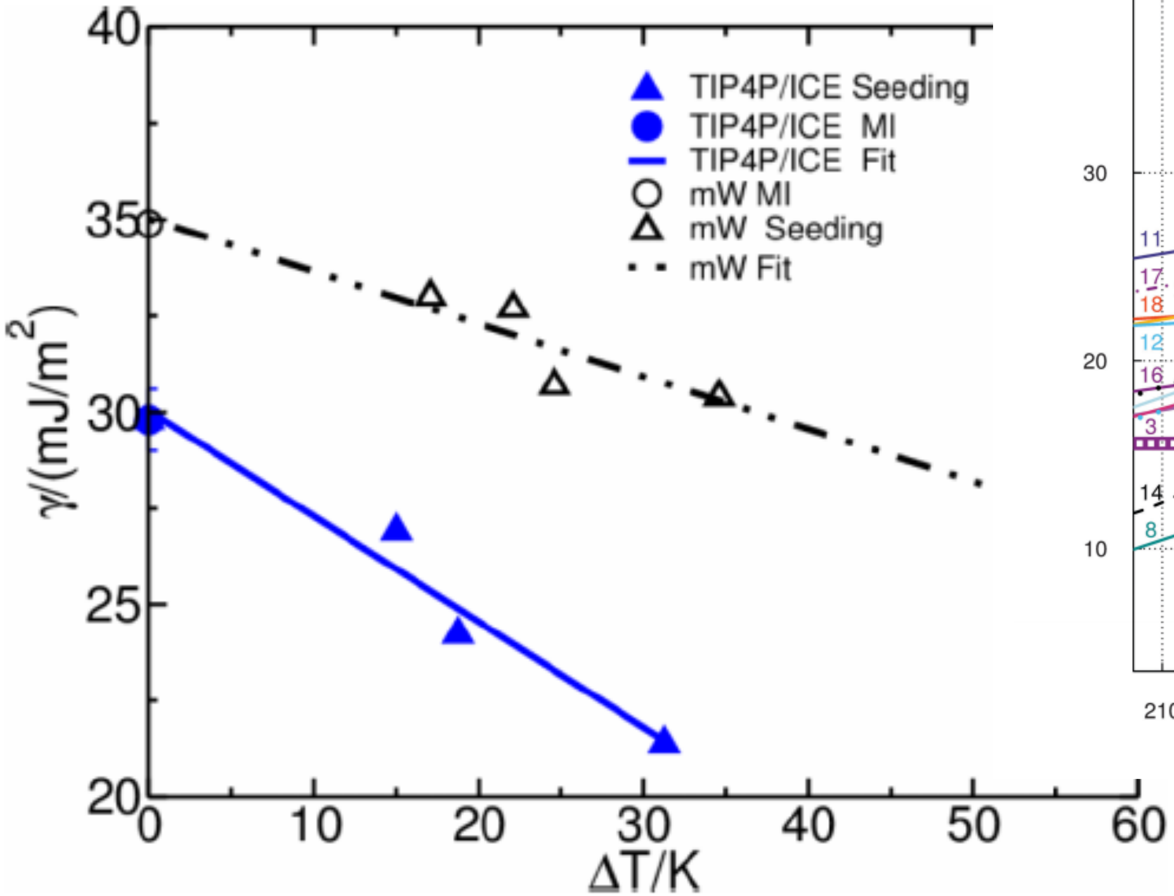


E.Sanz, C.Vega, J.Espinosa, R.Bernal, J.Abascal and C.Valeriani JACS (2013)

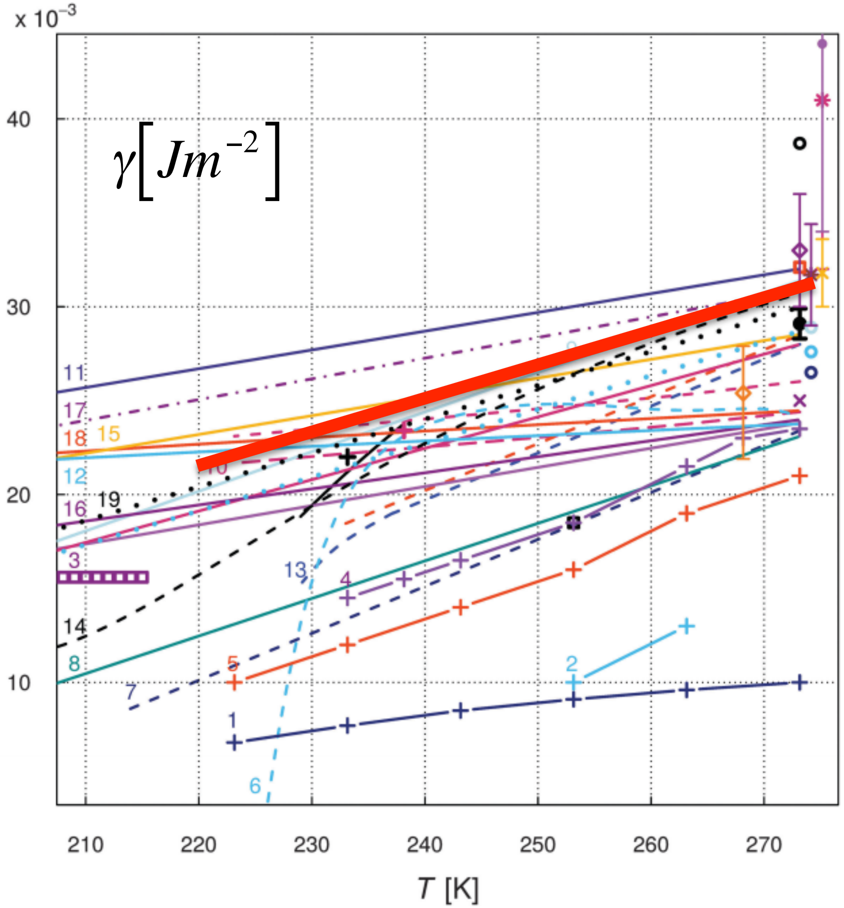
J.Espinosa, E.Sanz, C.Valeriani and C.Vega JCP (2014)

Consequence 1:
liquid-ice interfacial free-energy

$$N_c = \frac{32}{3}\pi \frac{\gamma^3}{\rho_s^2 |\Delta\mu|^3}$$



Espinosa, Navarro, Sanz, Valeriani, Vega JCP (2016)



Ickes et al PCCP, 2015

Consequence 2:

Ice Ih versus ice Ic

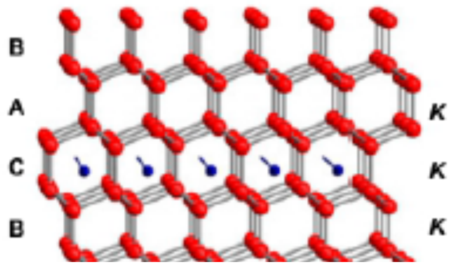
PNAS

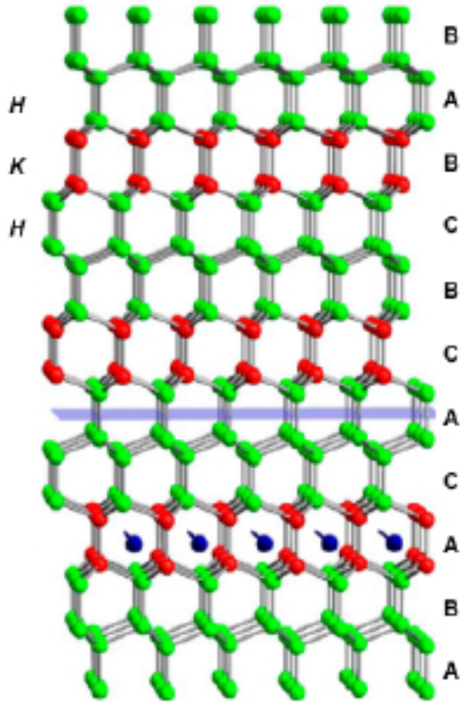
Extent and relevance of stacking disorder in "ice I_c"

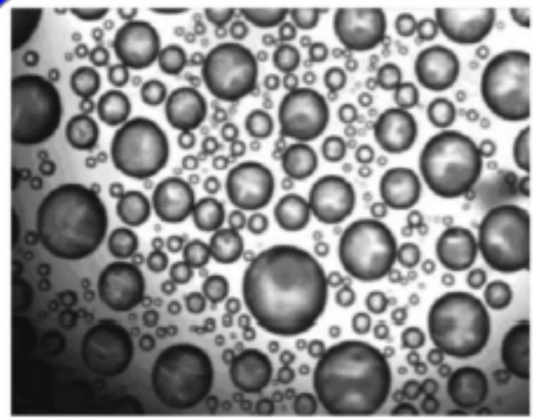
Werner F. Kuhs[a,1], Christian Sippel[a,b], Andrzej Falenty[a], and Thomas C. Hansen[b] (2012)

Structure of ice crystallized from supercooled water

Tamsin L. Malkin[a], Benjamin J. Murray[a,1], Andrey V. Brukhno[b], Jamshed Anwar[c], and Christoph G. Salzmann[d,2] (2012)





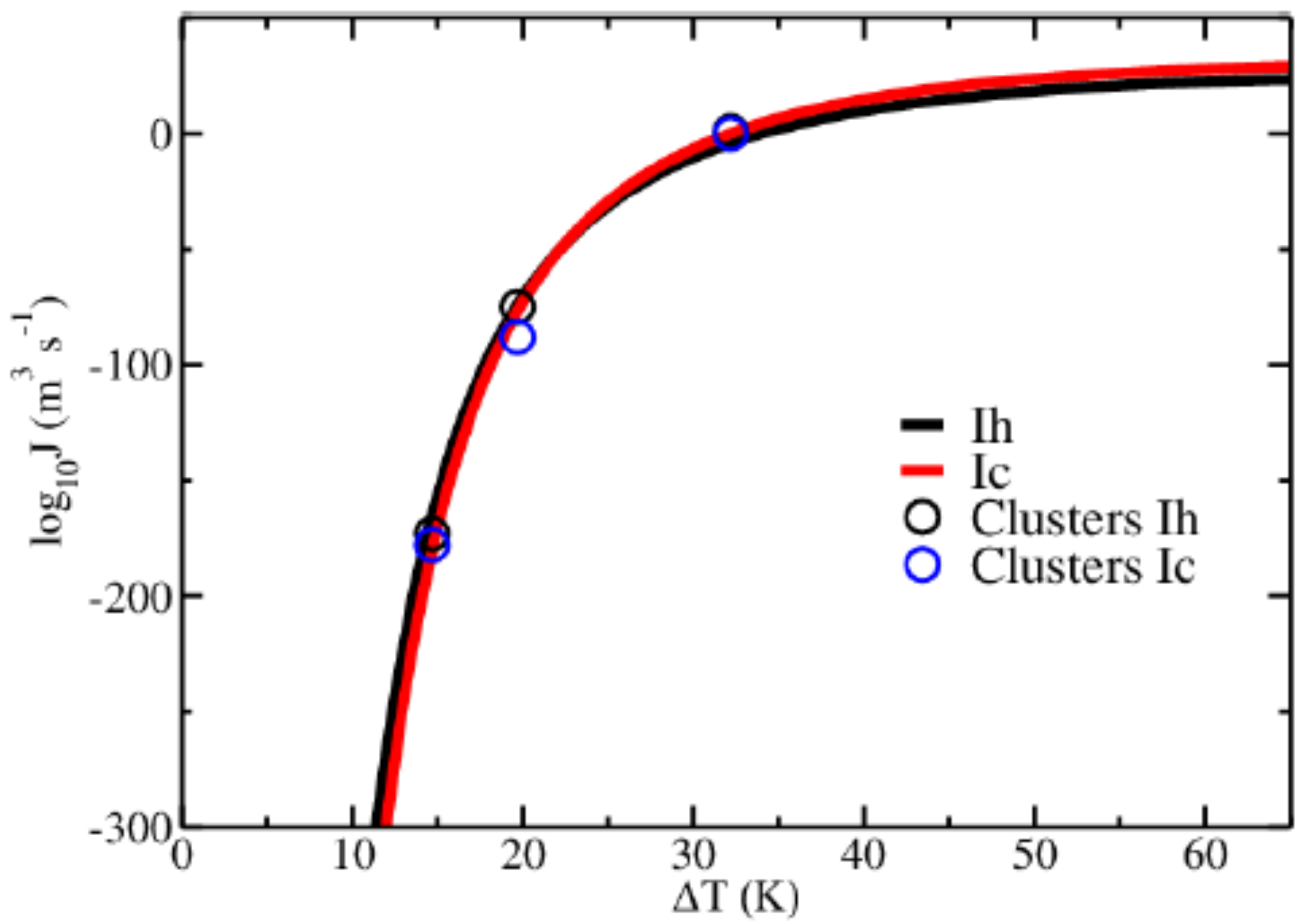


As observed in computer simulations with mW water

Hudait, Qiu, Lupi and Molinero PCCP(2016)

B.J.Murray et al. *"Kinetics of the homogeneous freezing of water"* Physical Chemistry Chemical Physics. (2010)

Ice nucleation rate at 1 bar



TIP4P/ICE water

Ice Ih/Ic stacking faults during ice nucleation

Zaragoza, Conde, Espinosa, Valeriani, Vega, Sanz JCP (2015)

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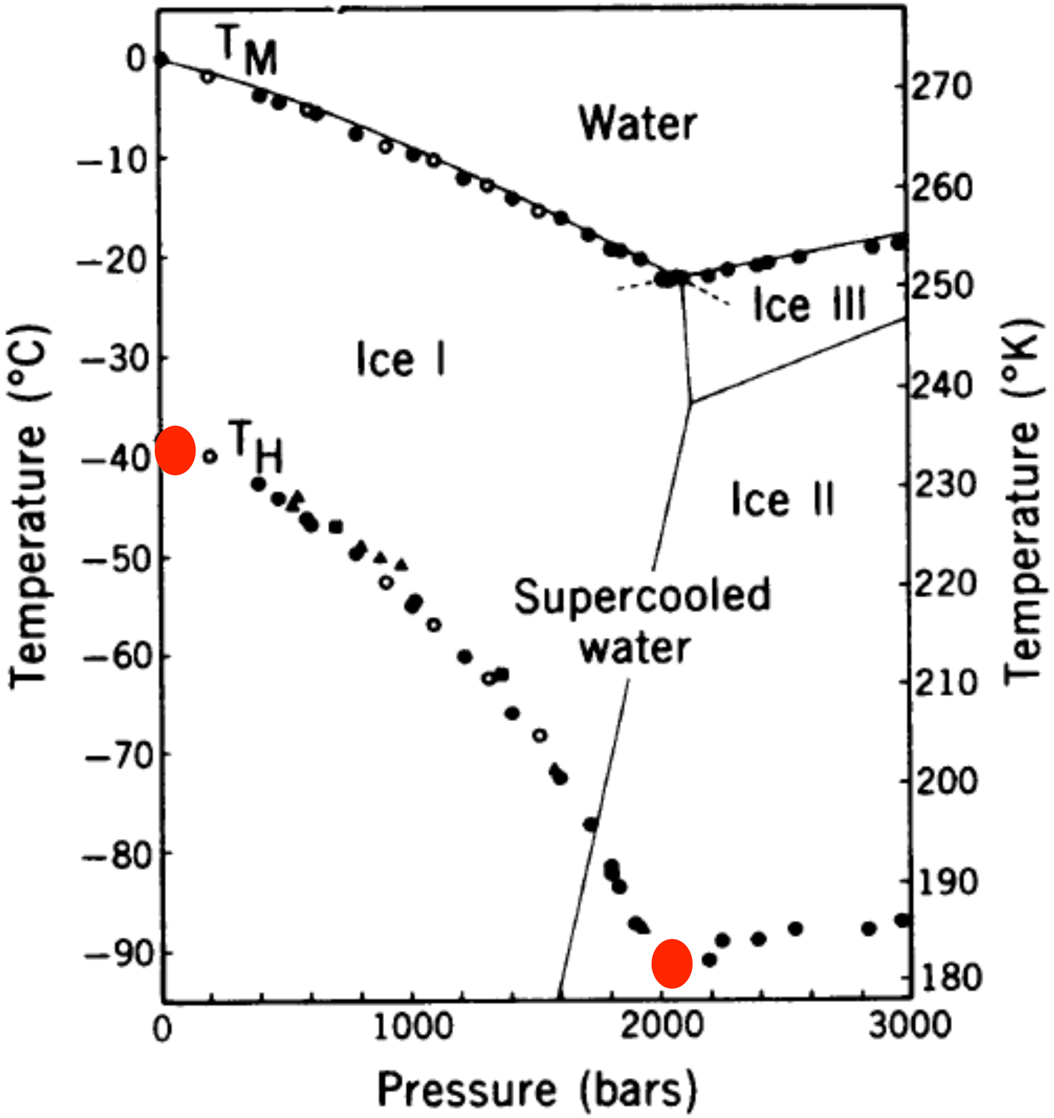
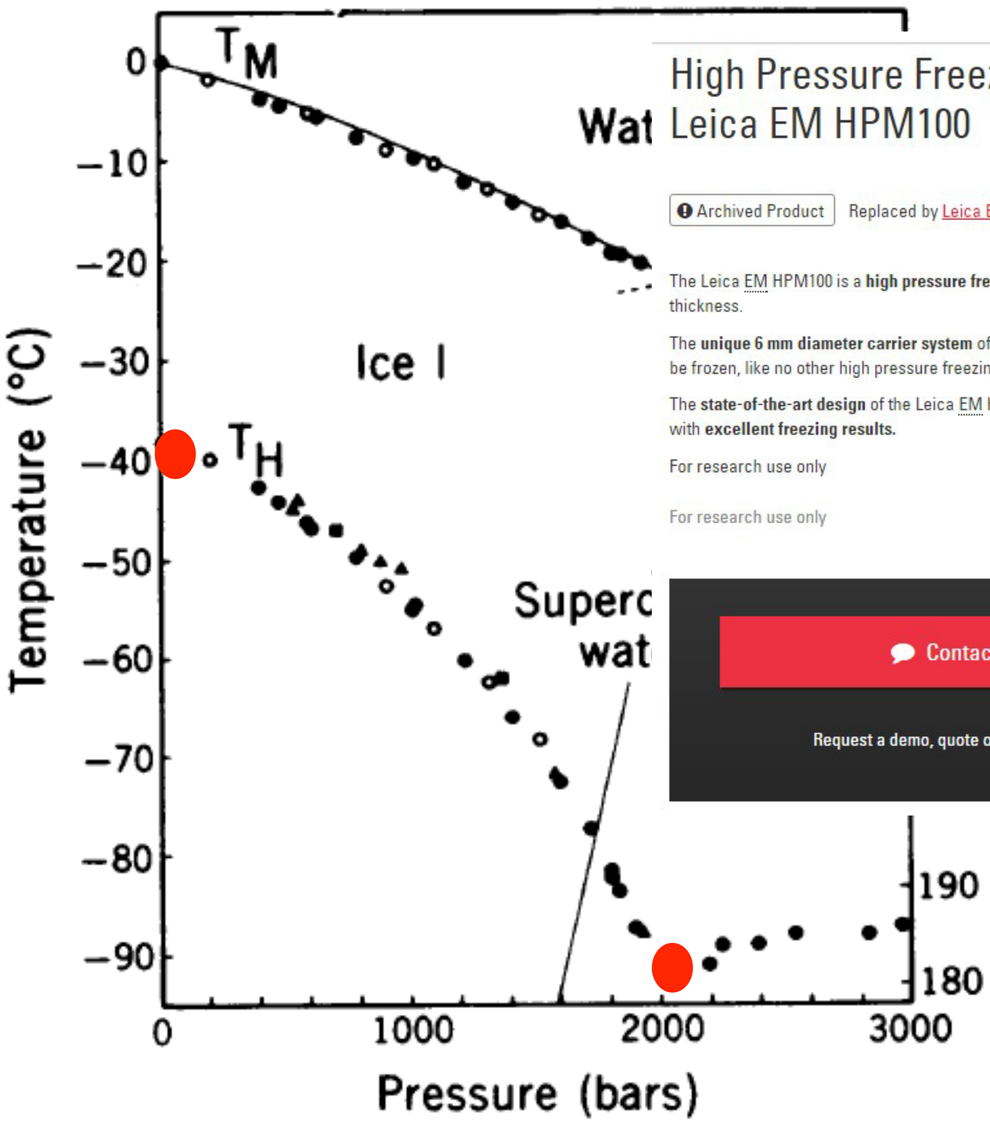
Effect of pressure on ice nucleation



Kano, Speedy, Angell Science (1975)

Effect of pressure on ice nucleation



High Pressure Freezer for Cryofixation of Biological And Industrial Samples Leica EM HPM100

Archived Product Replaced by Leica EM ICE

The Leica EM HPM100 is a **high pressure freezing** system for vitrifying samples up to 200µm in thickness.

The **unique 6 mm diameter carrier system** of the Leica EM HPM100 allows even more sample area to be frozen, like no other high pressure freezing instrument.

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For research use only

For research use only

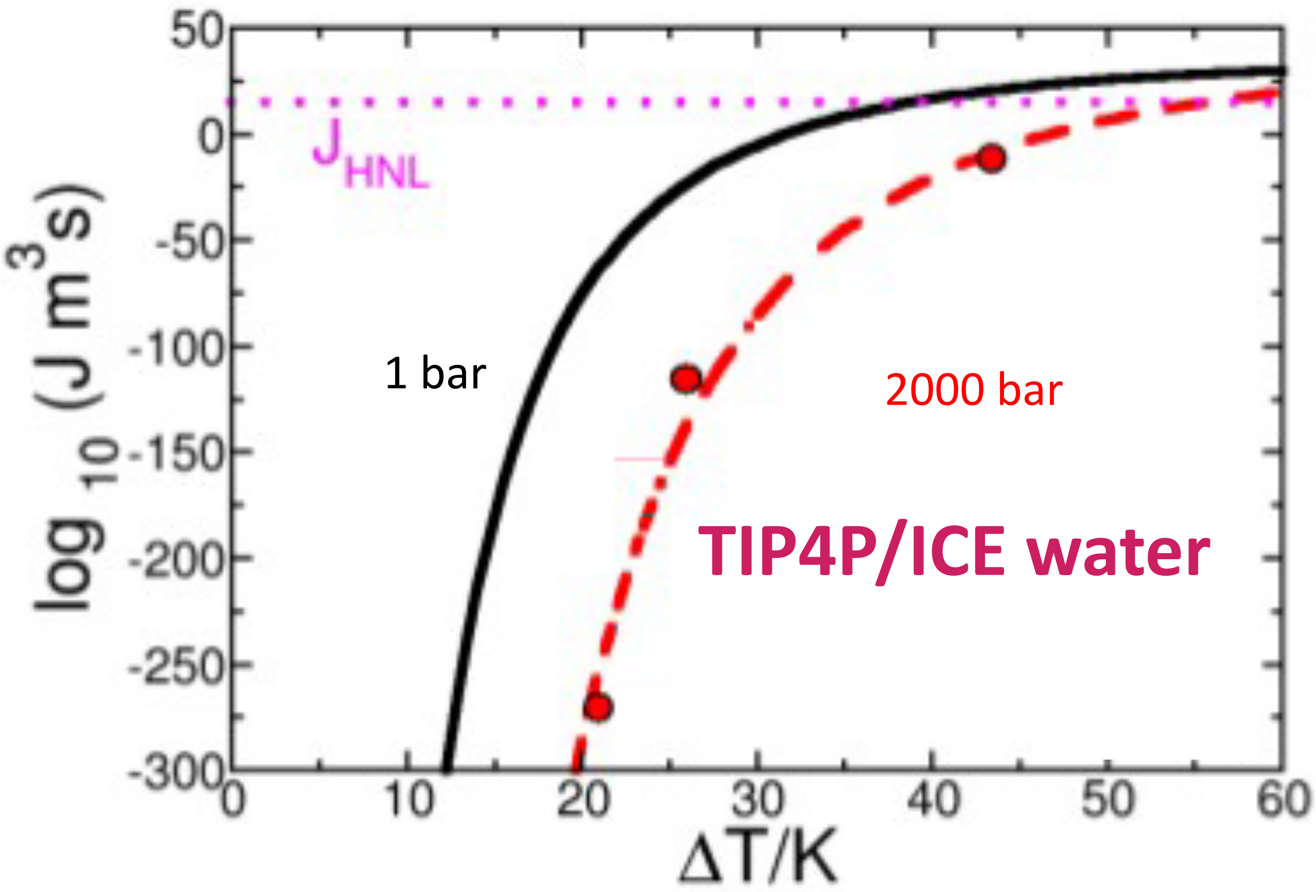
Contact Us

Request a demo, quote or ask a question

Why does it work?

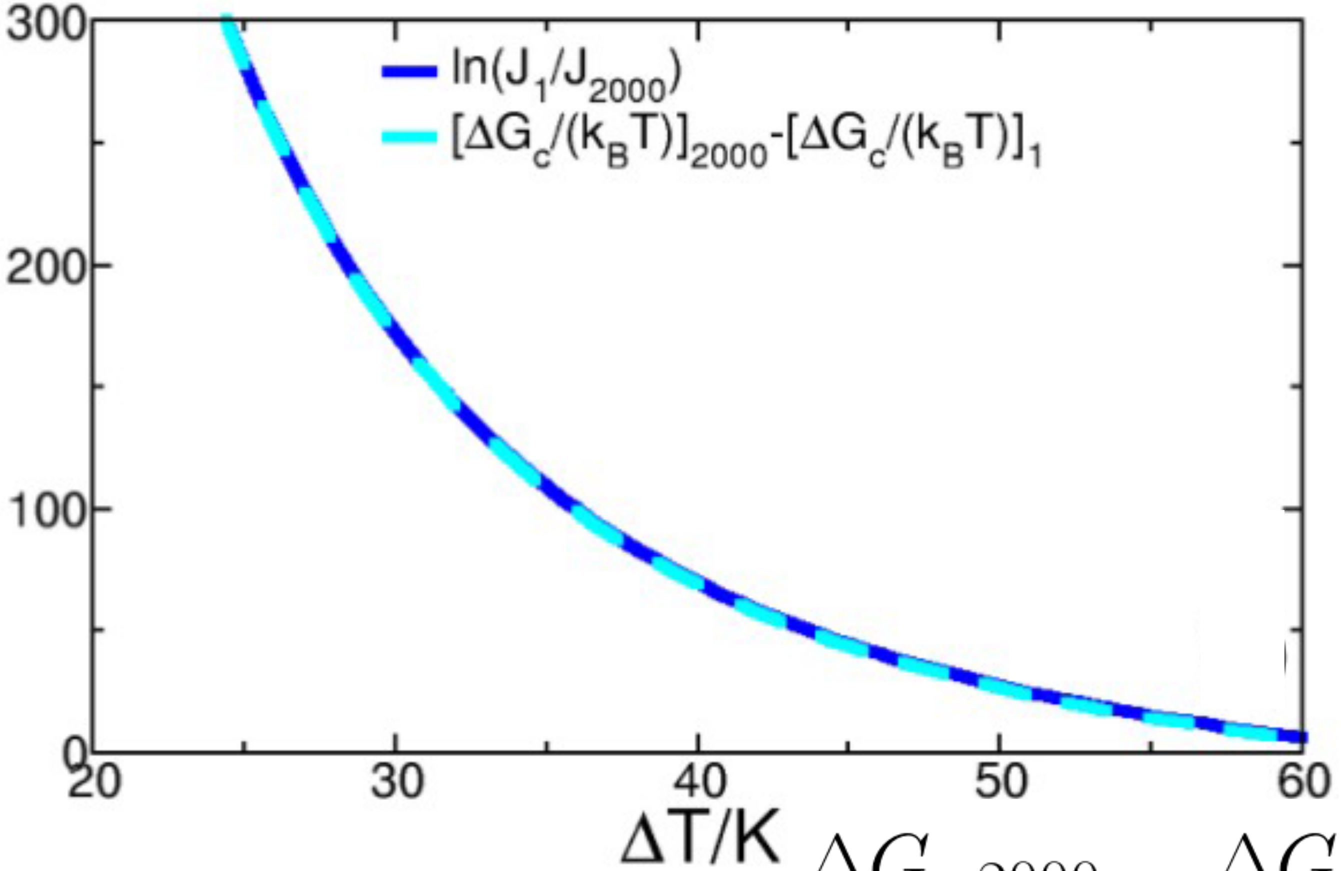
Kano, Speedy, Angell Science (1975)

Homogeneous nucleation rate of ice Ih from supercooled water



What does it depend on?

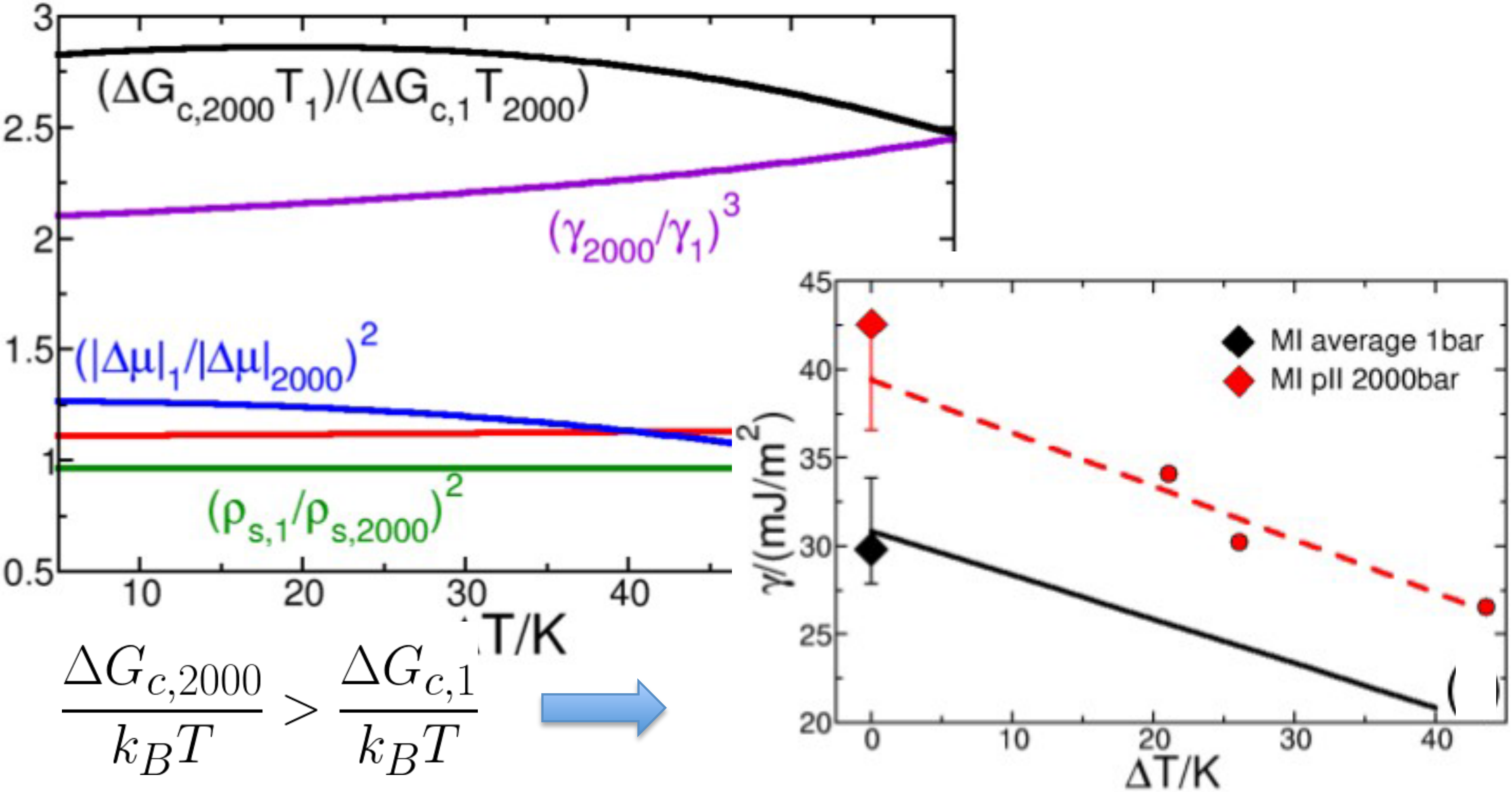
$$J = Ae^{-\Delta G_c / K_B T}$$



$$A_{2000} \approx A_1 \quad \Rightarrow \quad \frac{\Delta G_{c,2000}}{k_B T} > \frac{\Delta G_{c,1}}{k_B T}$$

What does it depend on?

$$\frac{\Delta G_c}{k_B T} = \frac{16\pi\gamma^3}{3\rho_s^2|\Delta\mu|^2 k_B T}$$



$$\frac{\Delta G_{c,2000}}{k_B T} > \frac{\Delta G_{c,1}}{k_B T}$$

Conclusions

High pressure could be a way to supercool water avoiding ice nucleaition

Given that the liquid-solid interfacial free-energy increases with pressure

Espinosa, Zaragoza, Rosales, Navarro, Valeriani, Vega and Sanz, PRL (2016)

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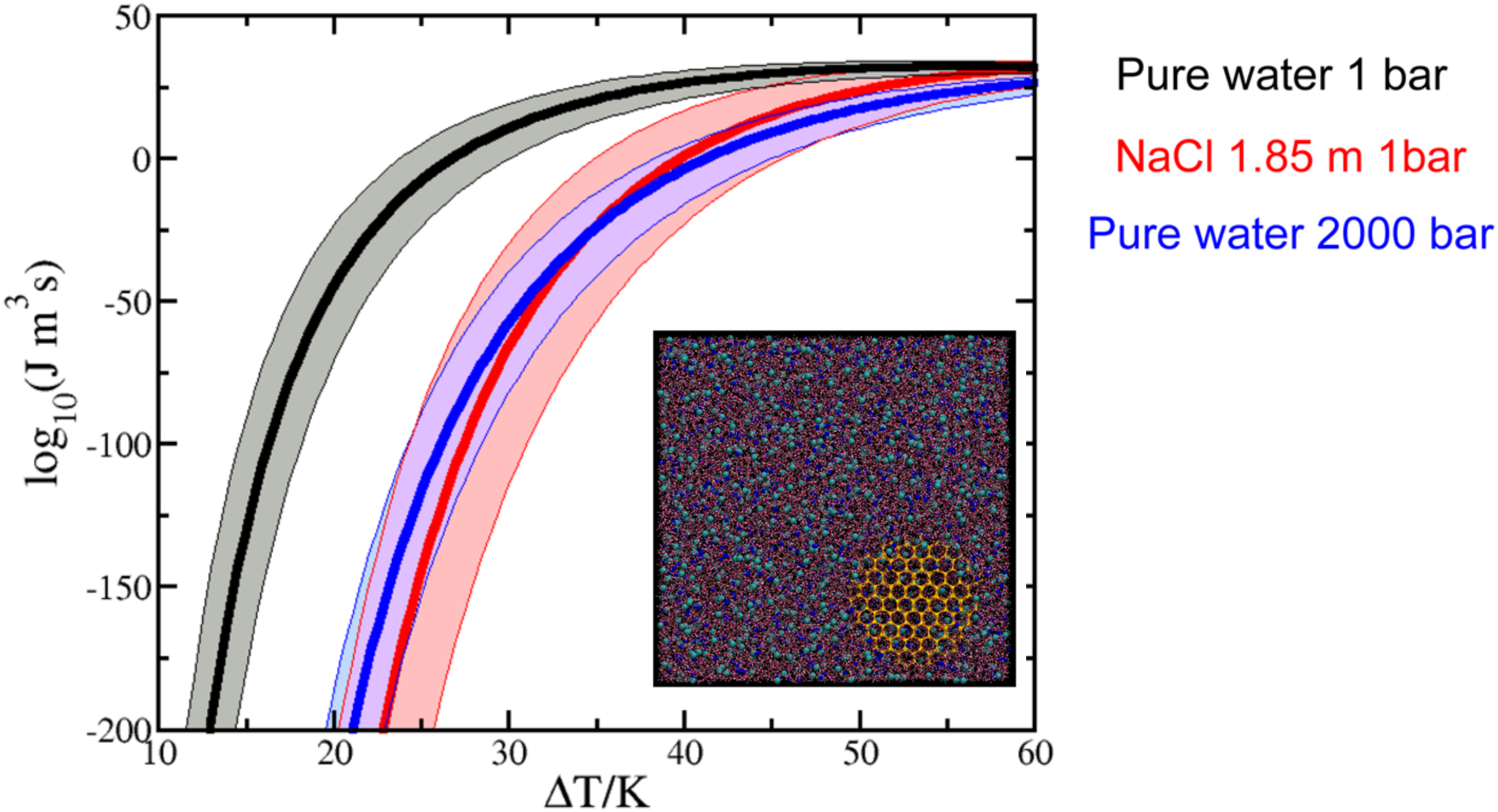
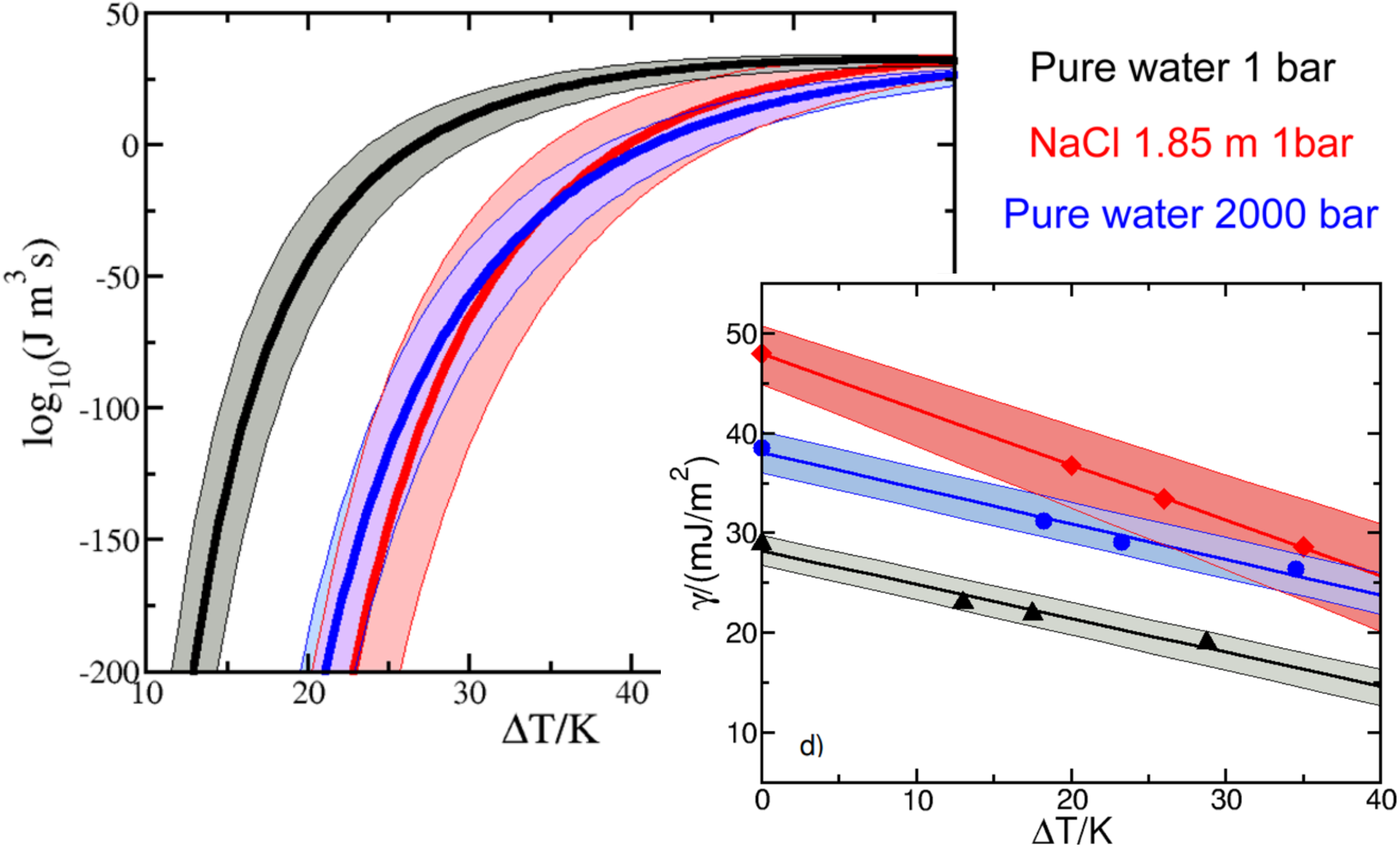
Ice nucleation from salty water



Espinosa, Soria, Ramirez, Valeriani, Vega and Sanz, J.Phys.Chem.Lett.(2017)

Ice nucleation from salty water



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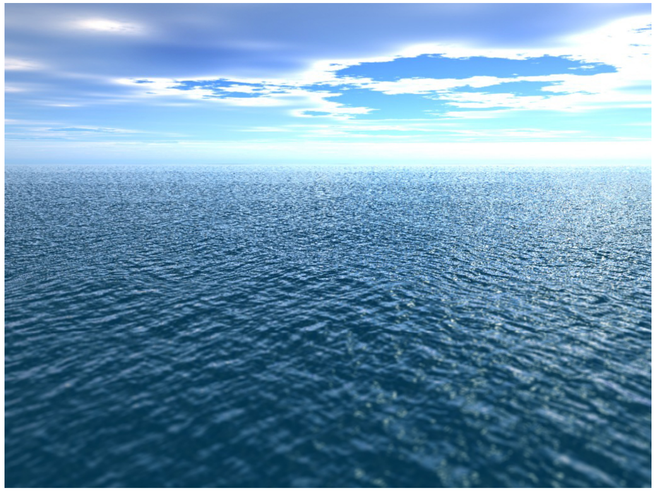
Future work:

At -20K

considering all water
in the hydrosphere



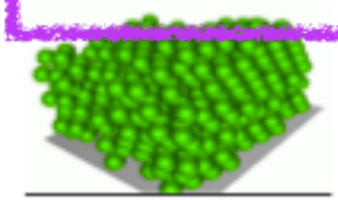
the average time to form homogeneously
a nucleus would be 10^{66} years!

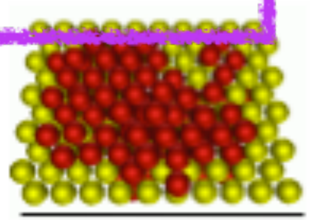
Maybe bulk ice nucleation in Nature is not homogeneous...

E.Sanz, C.Vega, J.Espinosa, R.Bernal, J.Abascal and C.Valeriani **JACS** (2013)

Homogeneous versus heterogeneous nucleation

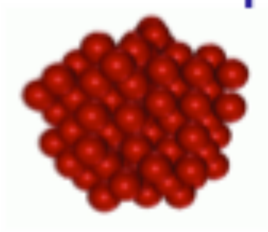
heterogeneous nucleation





crystal seeded by a smooth hard wall   crystal seeded by a regular template

homogeneous nucleation



spontaneous AND localized density fluctuation in the bulk system that overcomes a threshold (Nc)

"SuperStretch"
PICS collaboration
Lyon-Madrid
in progress

Muchas gracias!