





Minimalistic Models of Water



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What is the purpose of developing water models?

Understand the interplay between microscopic interactions and water properties.

Predict water properties and processes under conditions or at a resolution difficult to access through experiment.

Reveal unexpected phenomena that may occur in water.

Solvate, dissolve, etc…: be a good supporting actor in the study of other systems that contain water.

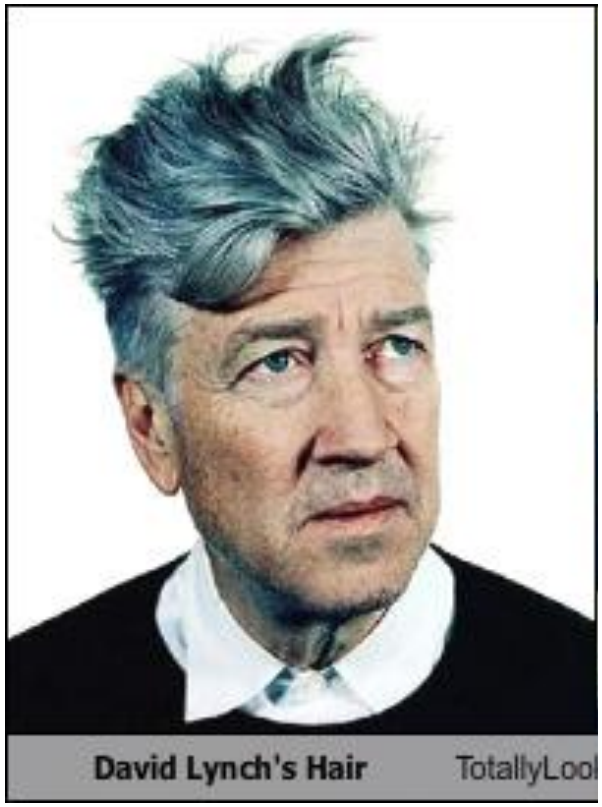
"Minimalistic" models:

Speed up calculations.

Provide physical insights.




after
葛飾北斎 神奈川沖浪裏
art © 2011 tony burns


David Lynch's Hair
TotallyLoo



Outline

Paradigms in classical modeling of water

What is essential in modeling water?

A monatomic model of water with "hydrogen-bonds"

reproduces the structure, anomalies and phase behavior of water

--- intermezzo

Ice crystallization with coarse-grained water

What determines the freezing temperature of water?

There are several ways to simplify water modeling:

Dismiss **quantum nature** of particles

Dismiss **flexibility** of the molecule

Dismiss effect of electronic **polarizability**

Dismiss **multi-body** nonbond interactions

Classical rigid nonpolarizable water models

Dismiss **long-range** contributions to the potential

Dismiss **atomistic detail** of water molecule

Lump several waters into a single effective particle

Coarse-grained models



A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions

J. D. Bernal and R. H. Fowler, *University of Cambridge, England*

(Received April 29, 1933)

Short Summary

On the basis of the model of the water molecule derived from spectral and x-ray data and a proposed internal structure for water, the following properties of water and ionic solutions have been deduced quantitatively in good agreement with experiment.

(1) The crystal structure of ice.
(2) The x-ray diffraction curve for water.
(3) The total energy of water and ice.
(4) The degree of hydration of positive and negative ions in water.
(5) The heats of solutions of ions.
(6) The mobility of hydrogen and hydroxyl ions in water.

And the following inferred in a qualitative way.

(7) The density and density changes of water.
(8) The explanation of the unique position of water among molecular liquids.
(9) The dielectric properties of water and ice.
(10) The viscosities of dilute ionic solutions.
(11) The viscosities of concentrated acids.

!

Full Summary. Part I

1

A consideration of the spectroscopic molecular model of H_2O, , of the crystal structure of ice, and of the density of water, leads to the proposing of an irregular four-coordinated structure for water. This structure is tested and found to account for the positions of the maxima of x-ray diffraction by water, and for the change in these positions with temperature, which are quite different from those of a simple liquid such as mercury. Three different intermolecular arrangements are postulated for water at different temperatures.

(1) Ice-tridymite-like (four-coordinated) at low temperatures below 4°C.

(2) Quartz-like (four-coordinated) between 4–200°C, roughly.

(3) Ammonia-like, close-packed, 200–340°C.

These forms are not distinct and pass continuously into each other. This hypothesis accounts for the abnormal changes of density of water. It is further tested by the behaviour of water under pressure, and by the Raman spectra of water at different temperatures.

Proposes structure for liquid water

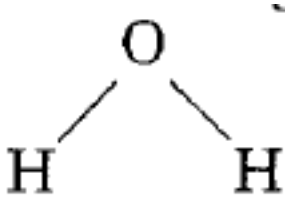
Liquid water as mixture of distinct orders

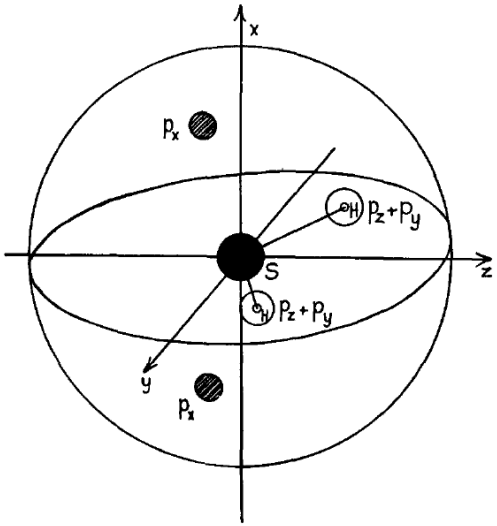
Geometry of water molecule elucidated the year before

r_{OH} 0.96 A HOH angle 103-106

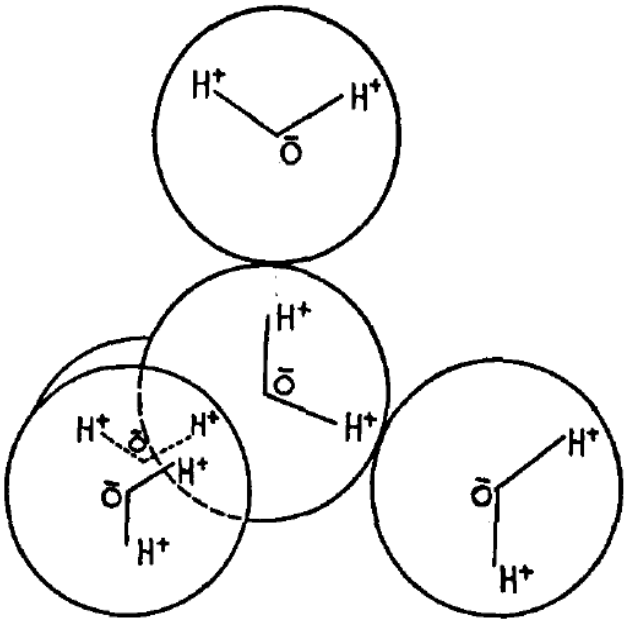
J Chem Phys 1, 515–548 (1933).

Water forms tetrahedrally coordinated structures





Tetrahedral distribution of the electronic density

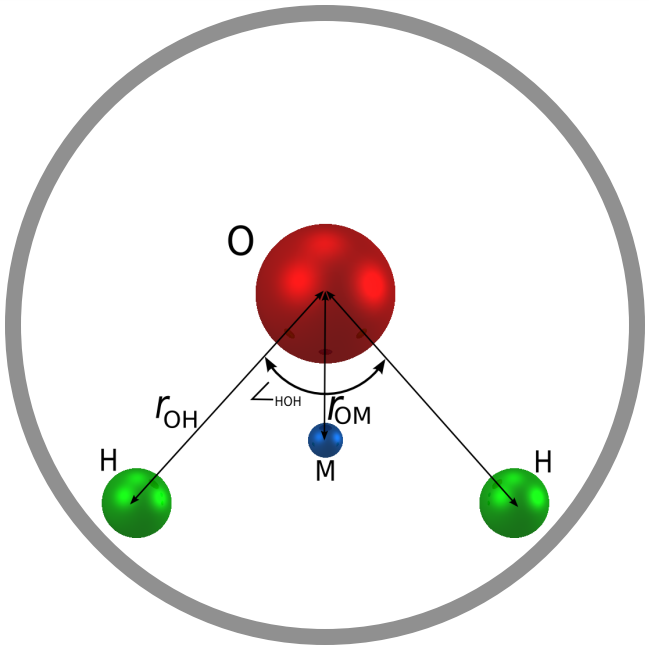


Tetrahedral order

Bernal and Fowler set the paradigm in water modeling:
Use of long-ranged forces (electrostatics)
to produce directional short-ranged order (hydrogen bonds)

Bernal &Fowler J Chem Phys (1933).

Bernal & Fowler proposed first model of water: 4-sites



$$E_{ab} = \sum_{i}^{\text{on } a} \sum_{j}^{\text{on } b} \frac{k_C q_i q_j}{r_{ij}} + \frac{A}{r_{OO}^{12}} - \frac{B}{r_{OO}^{6}}$$

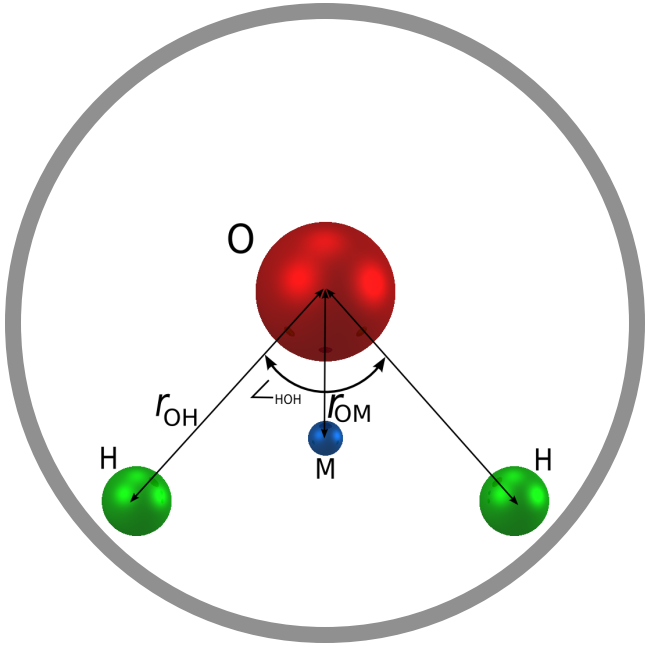
$\Delta E_{sublimation}$ predicted: **11.5** kcal/mol
experimental: **10.7** kcal/mol

Charges and their positions selected to reproduce the dipole of H_2O in vapor. **15.3 – 1.1**

Attractive "B" van der Waals attraction determined from polarizability of H_2O **4.6**

Repulsive "A" parameter selected to reproduce O – O distances in ice. **-6.8**

Bernal & Fowler proposed first model of water: 4-sites

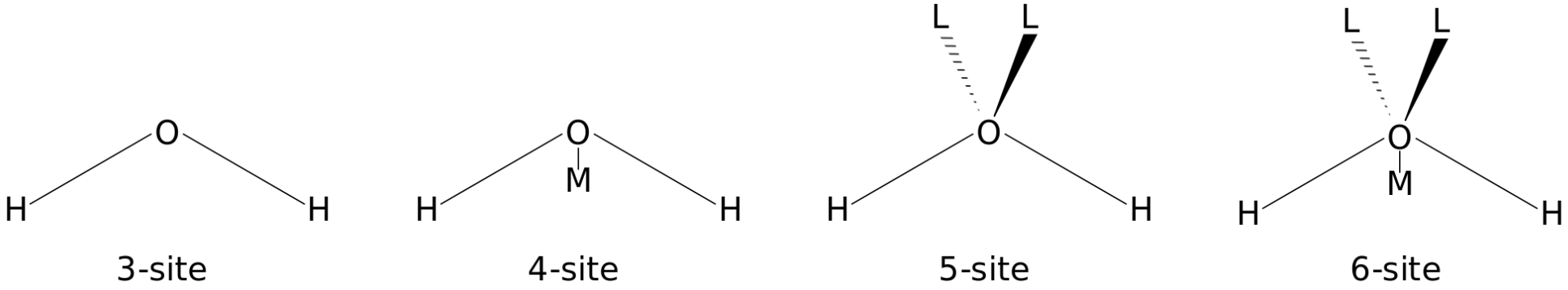


$$E_{ab} = \sum_{i}^{\text{on } a} \sum_{j}^{\text{on } b} \frac{k_C q_i q_j}{r_{ij}} + \frac{A}{r_{OO}^{12}} - \frac{B}{r_{OO}^{6}}$$

BF model is the parent of the TIP4P family

	BF[12]	TIPS2[13]	TIP4P[6]	TIP4P-Ew[14]	TIP4P/Ice[15]	TIP4P/2005[16]
r(OH), Å	0.96	0.9572	0.9572	0.9572	0.9572	0.9572
HOH, deg	105.7	104.52	104.52	104.52	104.52	104.52
r(OM), Å	0.15	0.15	0.15	0.125	0.1577	0.1546
A × 10^{-3}, kcal $Å^{12}$/mol	560.4	695.0	600.0	656.1	857.9	731.3
B, kcal $Å^6$/mol	837.0	600.0	610.0	653.5	850.5	736.0
q(M)	–0.98	–1.07	–1.04	–1.04844	–1.1794	–1.1128
q(H)	+0.49	+0.535	+0.52	+0.52422	+0.5897	+0.5564

Atomistic classical nonpolarizable rigid water models follow the paradigm set up by Bernal: fixed partial charges +Lennard-Jones



BF 1933

BNS1972
ST2 1974

SPC1981
TIP3P 1983
SPC/E1987

TIP4P 1983

TIP5P 2000

Nada 2003

TIP4P/ice 2005
TIP4P/2005

Does accuracy increase with number of sites?

More sites do not make a better model

Order of Accuracy :	5	2	3	1	5
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
Orthobaric densities and TMD	1.8	5.5	4.0	8.5	4.0
Isothermal compressibility	2.5	7.5	2.5	9.0	4.0
Gas properties	2.7	0.7	1.3	0.0	1.0
Heat capacity at constant pressure	4.5	3.5	4.0	3.5	0.0
Static dielectric constant	2.0	2.3	2.3	2.7	2.3
T_m–TMD–T_c ratios	3.7	6.7	8.7	8.3	6.7
Densities of ice polymorphs	3.5	5.0	6.0	8.8	2.3
EOS high pressure	7.5	8.0	7.5	10	5.5
Self-diffusion coefficient	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	6.0	6.0	7.5	7.5
Phase diagram	2.0	2.0	8.0	8.0	2.0
Final score	2.7	5.1	4.7	7.2	3.7

For same level of detail, not all parameterization strategies have same payoff.

Representability issues

- Gas/liquid and ice equilibrium cannot be simultaneously predicted
- Tm and TMD cannot be both matched with accuracy.
- Heat capacity and dielectric constant cannot be reproduced accurately.

Vega & Abascal, Phys Chem Chem Phys 13, 19663–19688 (2011).

+Dismiss **quantum nature** of particles

+Dismiss **flexibility** of the molecule

+Dismiss effect of electronic **polarizability**

+Dismiss **multi-body** nonbond interactions

Classical rigid nonpolarizable water models

+Dismiss **long-range** contributions to the potential

Dismiss **atomistic detail** of water molecule

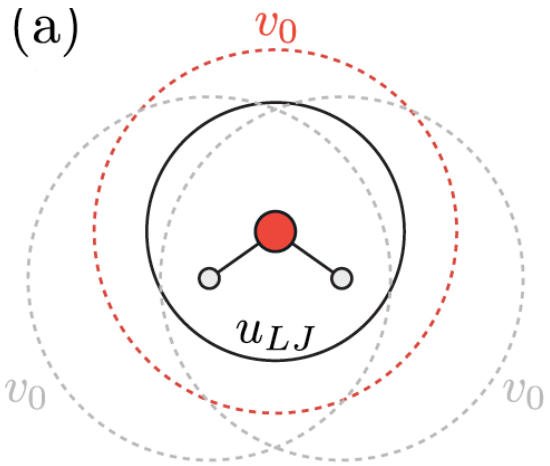
Lump several waters into a single effective particle

Coarse-grained models

Computational cost

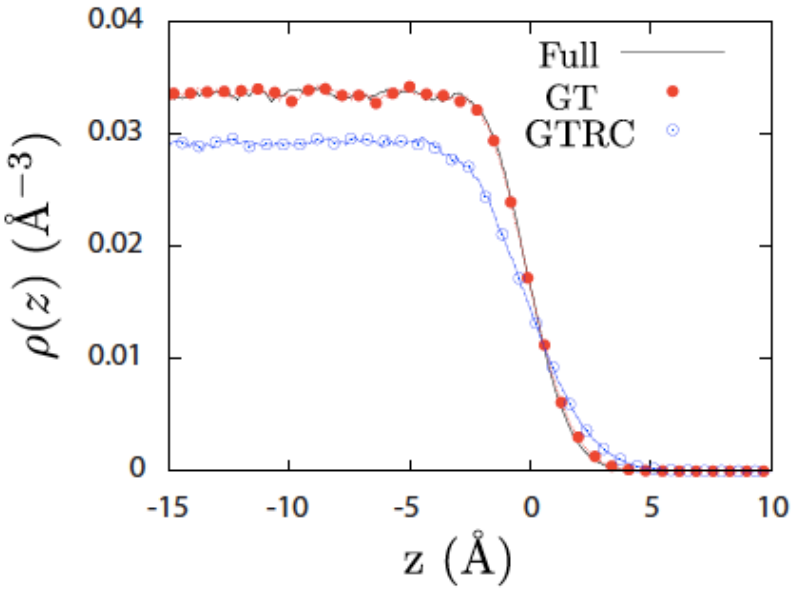
Fully atomistic models with short range interactions

How relevant are long-range interactions?



Short SPC/E Water (John Weeks and coworkers)

$$v(r) = \frac{1}{r} = \frac{\mathrm{erfc}(r/\sigma)}{r} + \frac{\mathrm{erf}(r/\sigma)}{r} = v_0(r) + v_1(r)$$



Neglect of long range coulomb does not affect density and structure **or the interfacial width**

Neglect of long range coulomb and attractive part of LJ results in very low density, wrong structure **and too wide interface**

Remsing, Rodgers, & Weeks, J Stat Phys 145, 313–334 (2011).

Competition between short ranged attractive/repulsive forces determine the structural properties of water

+Dismiss **quantum nature** of particles

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+Dismiss effect of electronic **polarizability**

+/-Dismiss **multi-body** nonbond interactions

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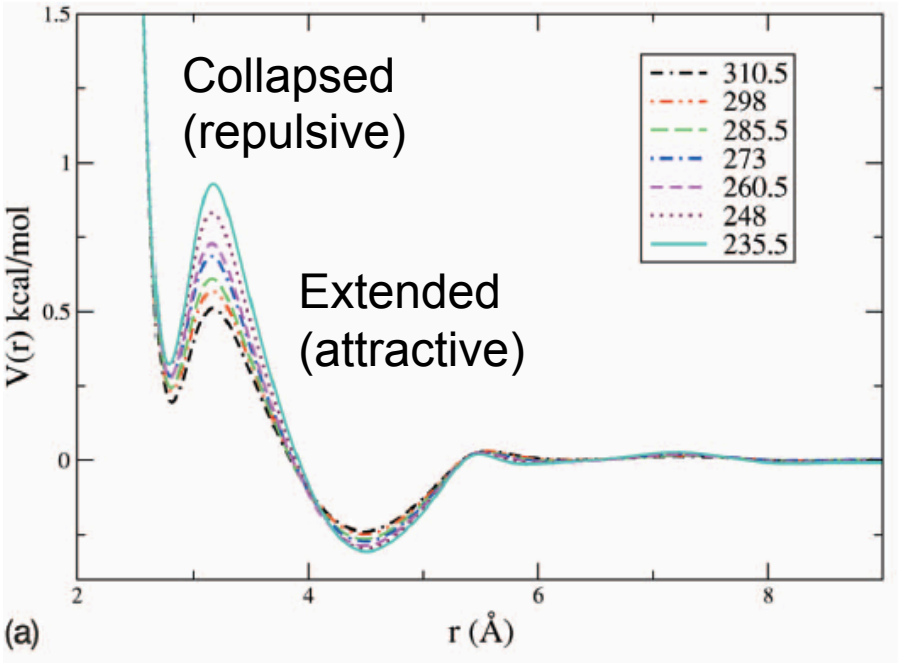
Computational cost

Two families of water models:

+ isotropic models with two length scales

- anisotropic models with three-body interactions

Water modeled as a single isotropic particle with two length scales presents severe representability issues



For each radial distribution function, there is a unique isotropic pair potential that reproduces it.

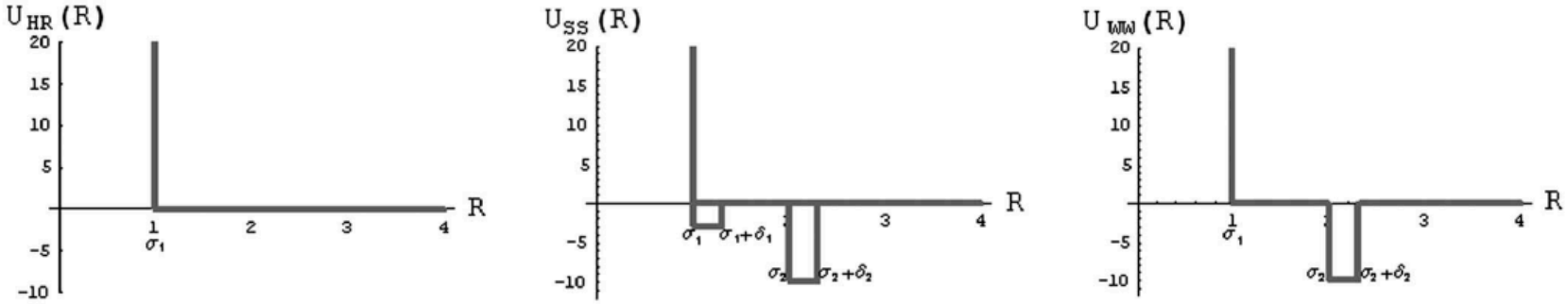
* 3-body order is not reproduced.

* Potentials that reproduce g(r) cannot reproduce the thermodynamics even if the potentials are state dependent.

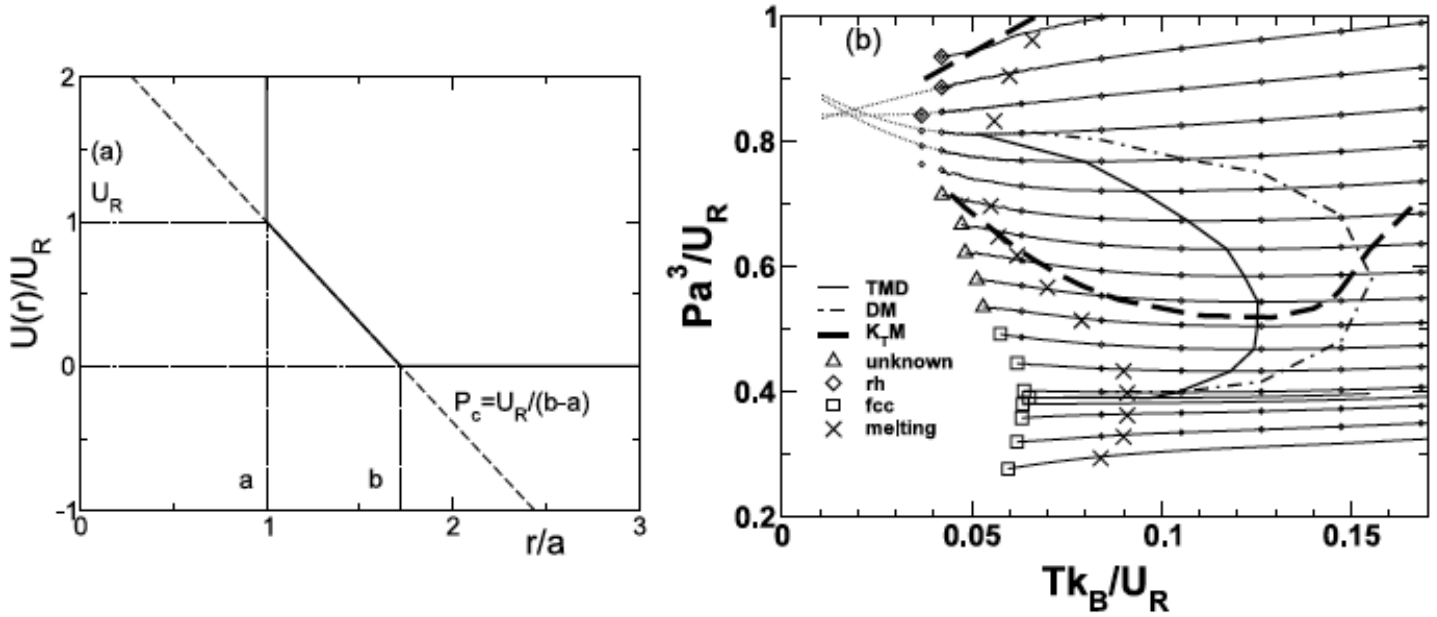
*Density and diffusivity anomaly are only obtained if the potential varies with state.

Head Gordon & Stillinger,. J Chem Phys (1993).
Johnson, Head-Gordon & Louis J Chem Phys (2007).
Chaimovich & Shell Phys Chem Chem Phys (2009).

Other isotropic potentials with two length scales present the anomalies, but not the structure or energetics, of water



Ben-Naim's "the principle" for models to present water-like anomalies: correlation between strong binding energy and low local density



Ben-Naim Plenum (1992), J. Chem. Phys. (2008); Buldyrev et al. J. Phys. Cond. Matt. (2009)

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Classical rigid nonpolarizable water models

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Outline

Paradigms in classical modeling of water

What is essential in modeling water?

A monatomic model of water with "hydrogen-bonds"

reproduces the structure, anomalies and phase behavior of water

--- intermezzo

Ice crystallization with coarse-grained water

Low-density liquid water is the structure of ice

Water forms tetrahedrally coordinated structures

Bernal & Fowler, JPC 1933

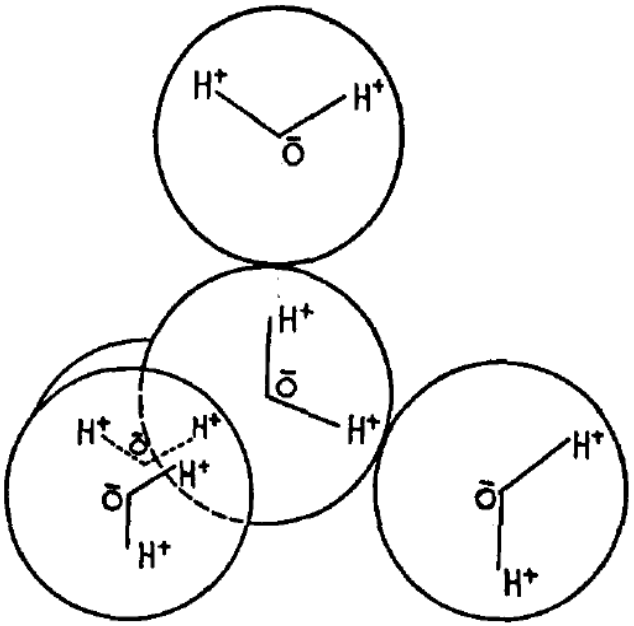


FIG. 4. Tetrahedral coordination of water molecules.

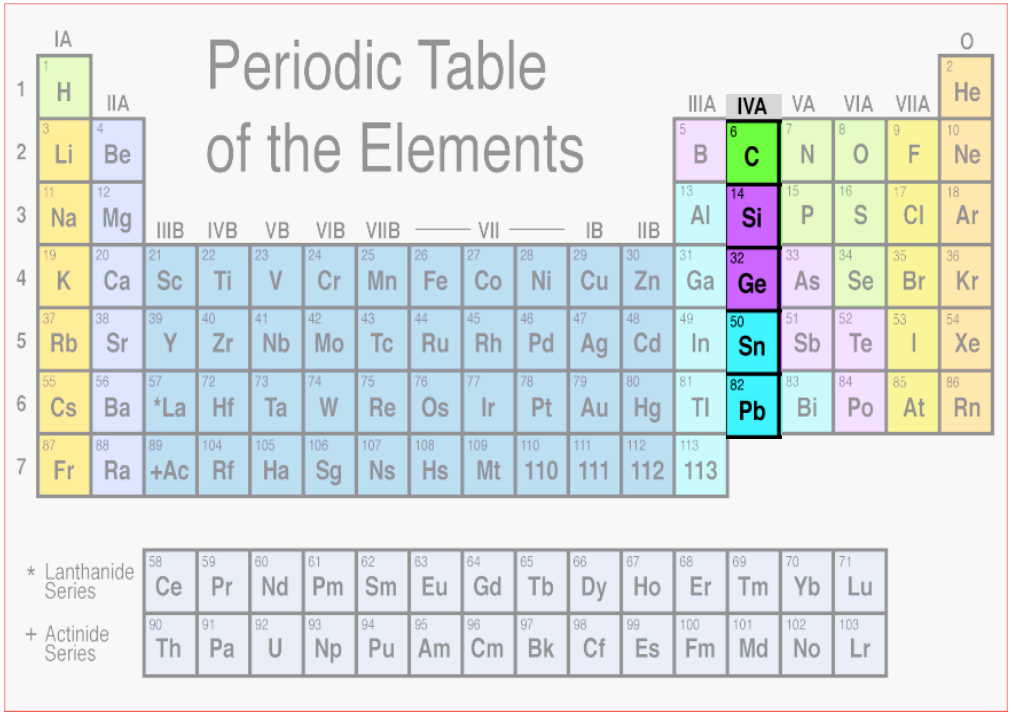
Paradigm in water modeling:

Use of long-ranged forces (coulomb)

to produce short-ranged structure (hydrogen bonds)

Water made simple

mimic the effect of hydrogen bonds with a **monatomic** model and only **short ranged** interactions.

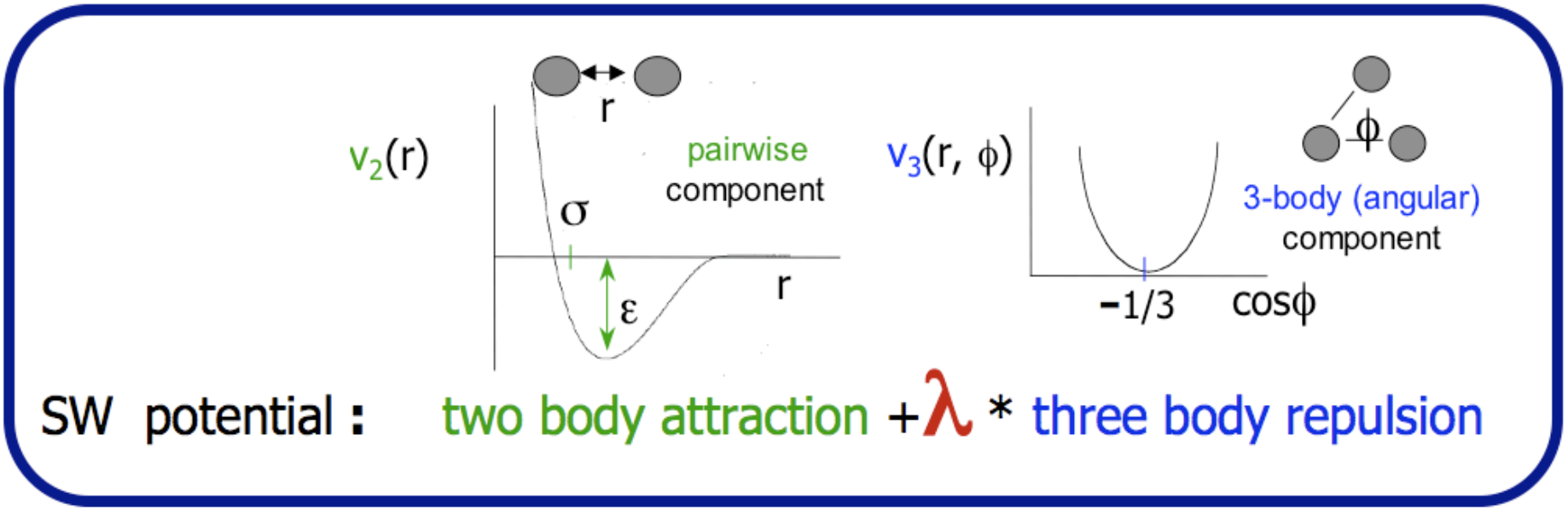


Carbon, silicon and germanium are monatomic tetrahedral substances with short range interactions.

Making water out of silicon

Reparameterize the Stillinger-Weber silicon potential[1] to produce a

coarse-grained model of water



SW potential has 9 parameters for silicon,
only the **tetrahedrality λ**, the energy scale ε and the molecular size σ are tuned to reproduce the melting temperature, the enthalpy of vaporization and liquid density of water at 298K.

[1] *Stillinger and Weber, Phys. Rev. B (1985)*

Water modeled as an intermediate element between C and Si

	λ	ε kcal/mol	σ Å
6 C	26.2	83	1.37
	23.15	6.19	2.39
14 Si	21	50	2.09
32 Ge	20	45	2.18
50 Sn	~18.5		

No hydrogen & no electrostatics. Force cutoff at 4.3 Å

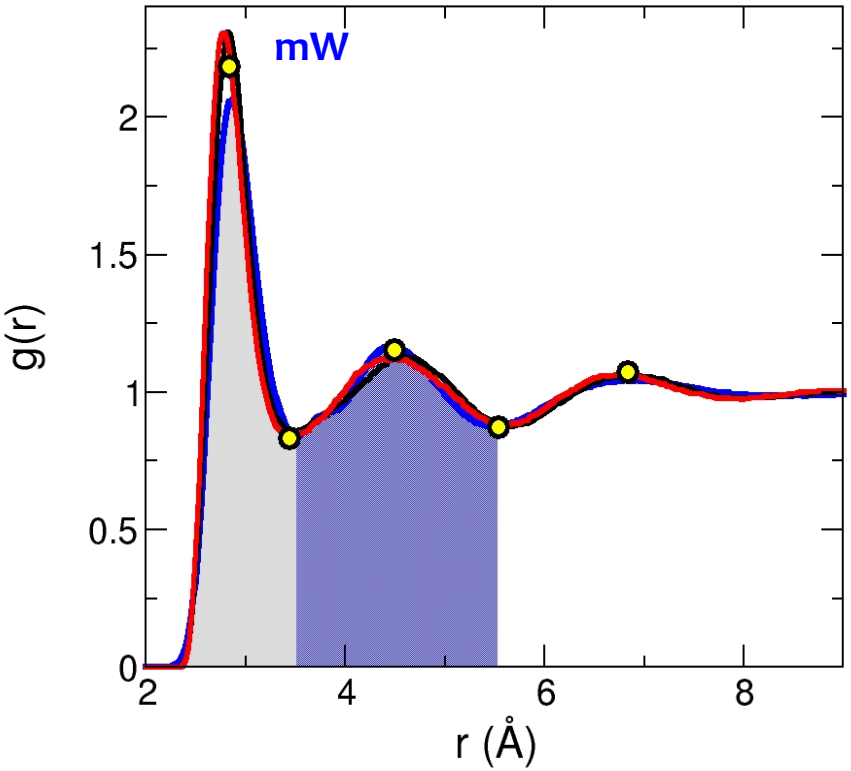
~180 times faster than atomistic models with Ewald

Molinero and Moore J Phys Chem B (2009)

Long range forces are not needed to model the structure of water

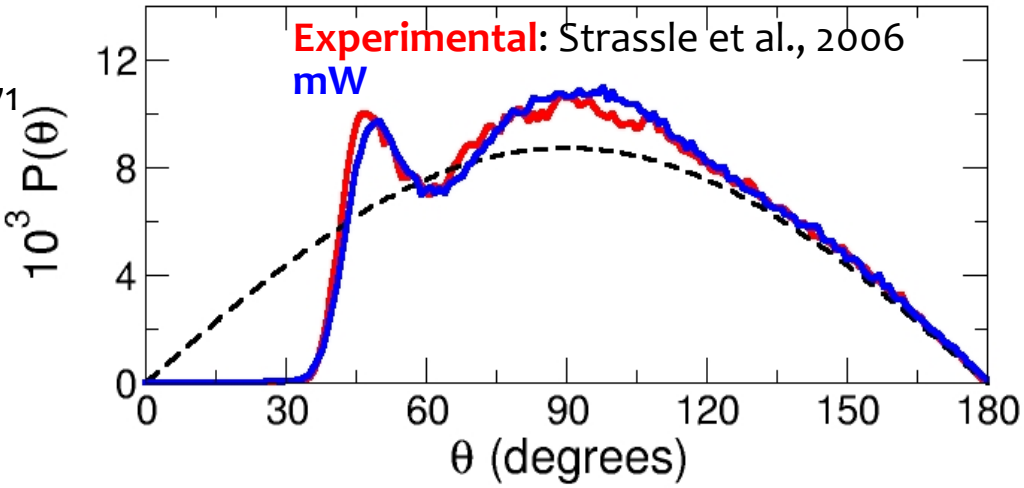
OO radial distribution

Experimental: Soper, 2007, Narten and Levy, 1971

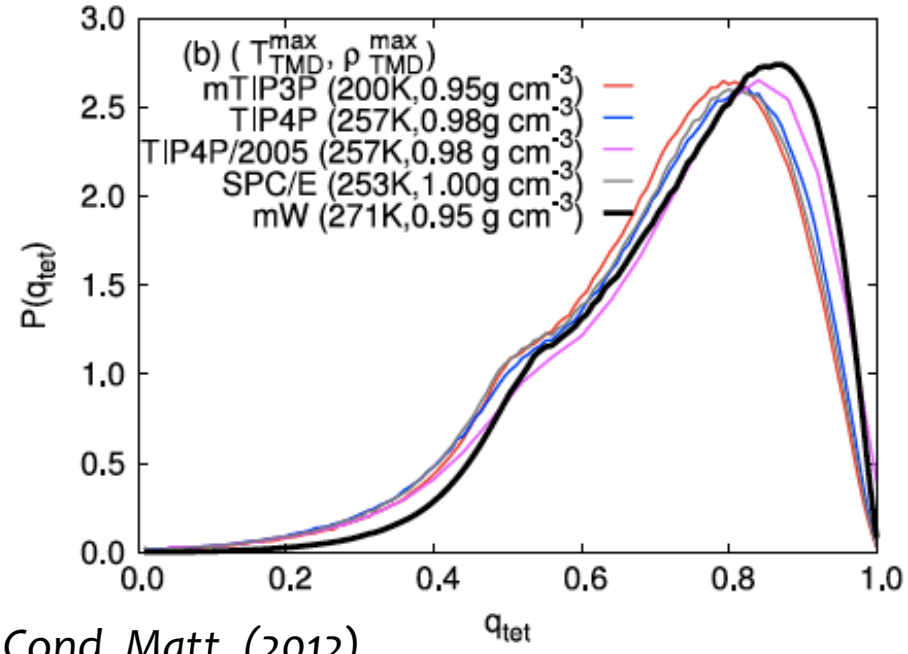


OOO angular distribution

of 8 closest neighbors.



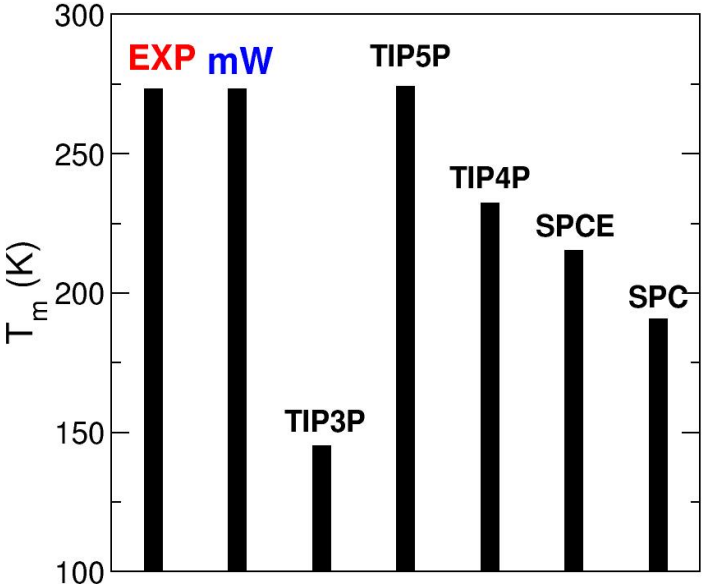
Tetrahedrality parameter



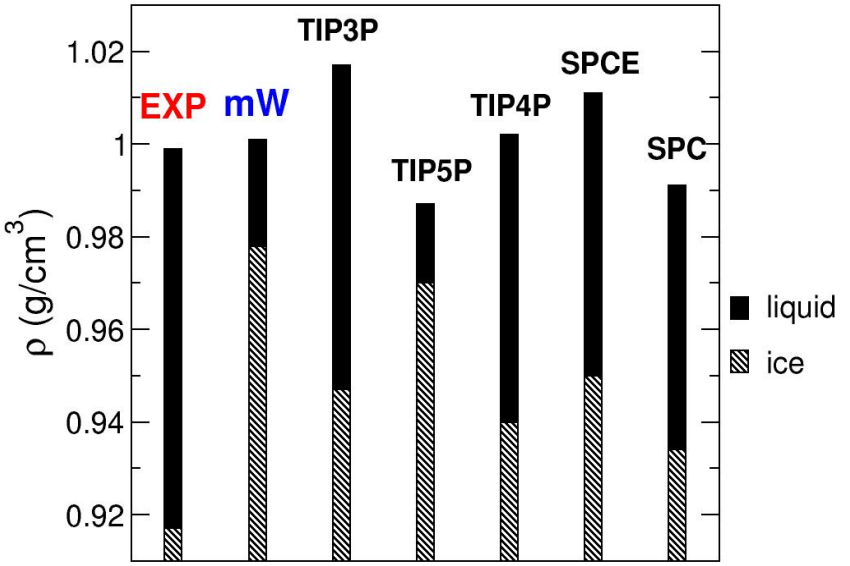
Molinero and Moore, J. Phys. Chem. B. (2009)
Jabes, Nayar, Dabhal, Molinero, Chakravarty, J. Phys. Cond. Matt. (2012)

Thermodynamics of water is well reproduced by mW

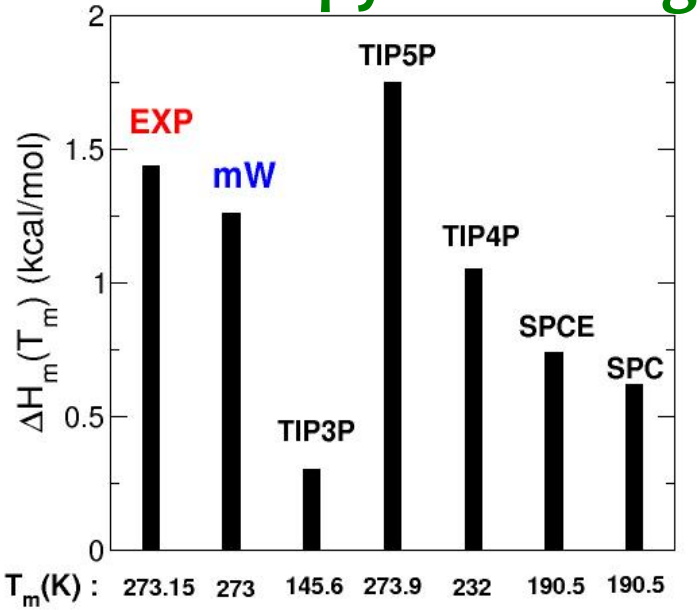
Melting temperature of ice I



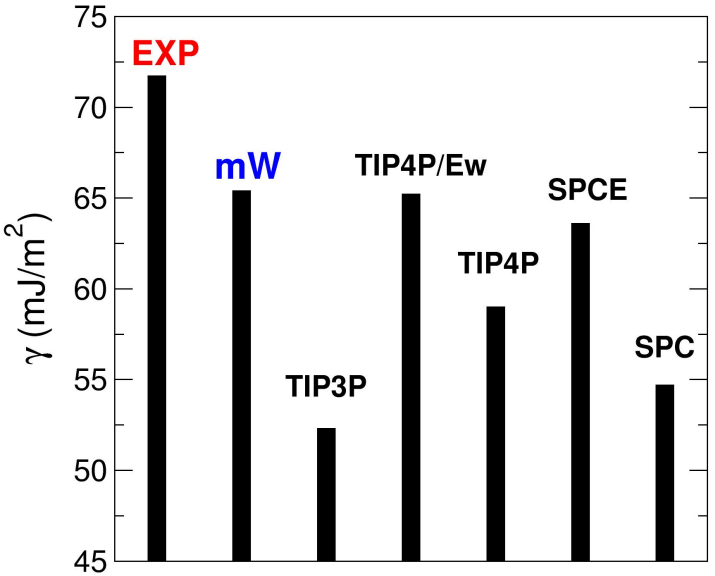
Density at melting



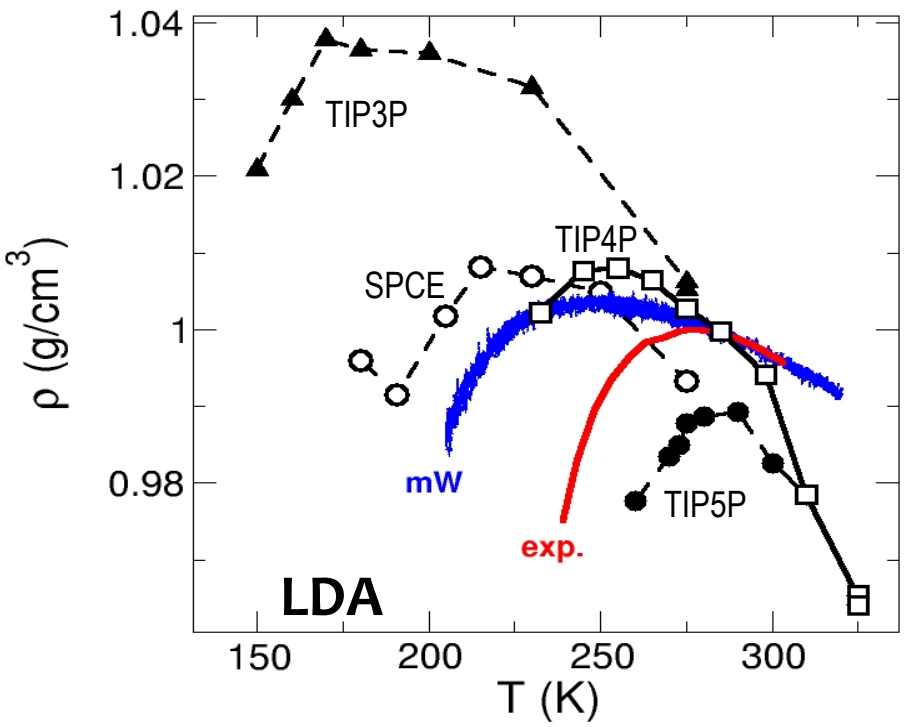
Enthalpy of melting



Liquid-vapor surface tension



The monatomic water model mW displays the anomalies of water



Thermodyamic anomalies

←**Density maximum**

-Heat Capacity increase on cooling

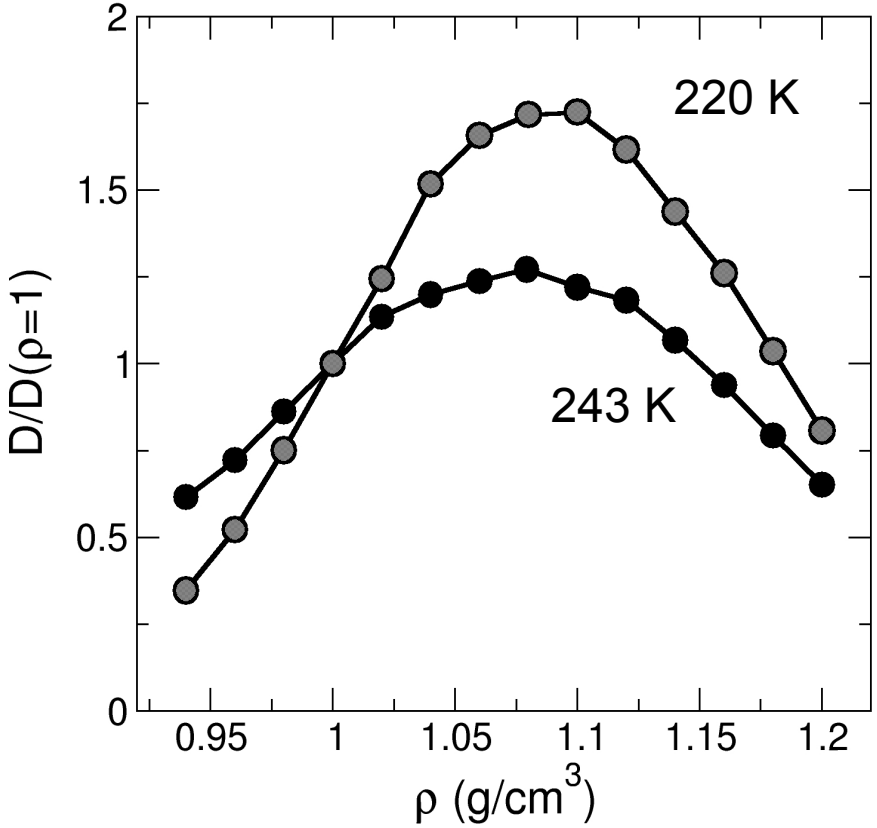
-Compressibility increase on cooling

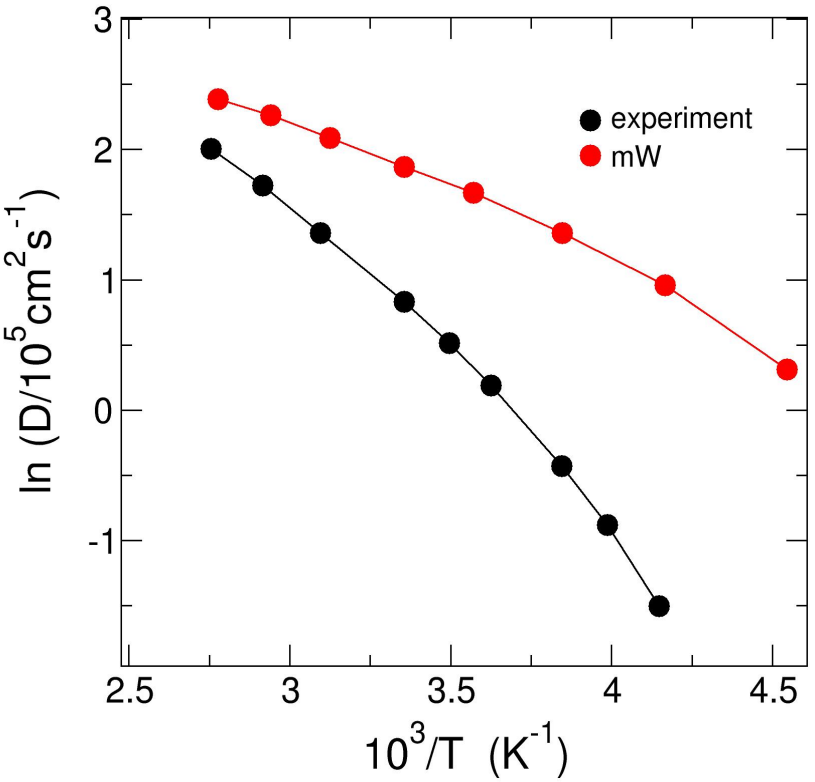
Structural anomalies

-Order maps as in atomistic water

Molinero and Moore, J. Phys. Chem. B. (2009)
Moore and Molinero, Nature (2011)
Limmer and Chandler, J. Chem. Phys. (2011)
Jabes et al, J. Phys. Cond. Matt. (2012)

The monatomic model presents the diffusivity anomaly of water



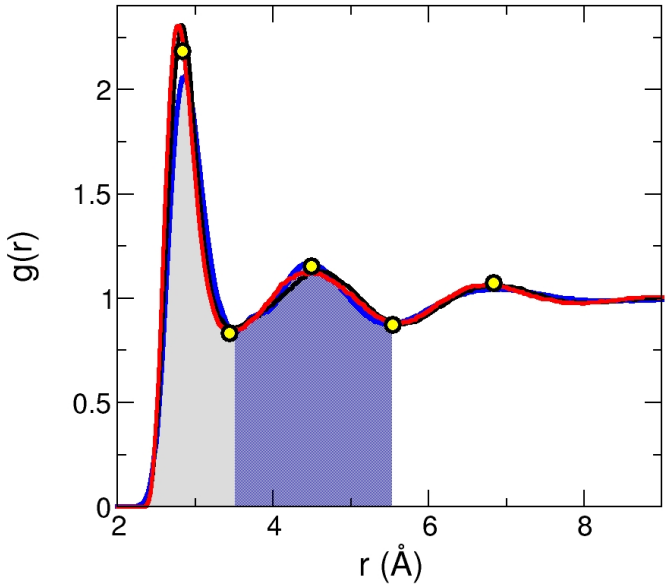


*mW is **more fluid** than real water (2.5 times more diffusive at 300 K)*

*Dynamics of mW **is less sensitive to temperature.***

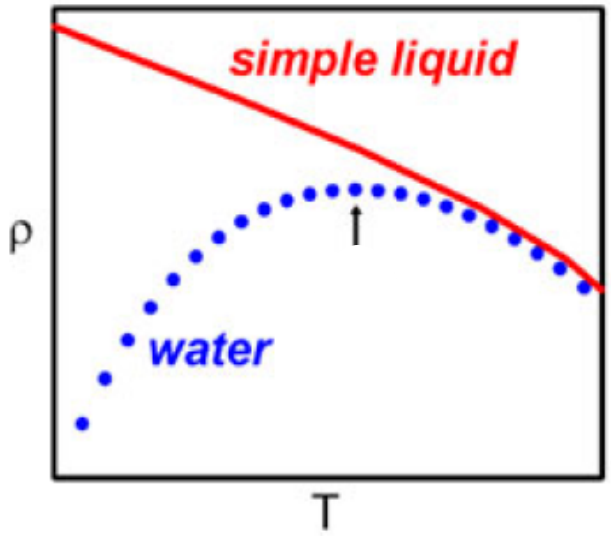
*Molinero and Moore, J. Phys. Chem. B., **113**, 4008 (2009)*

Liquid structure



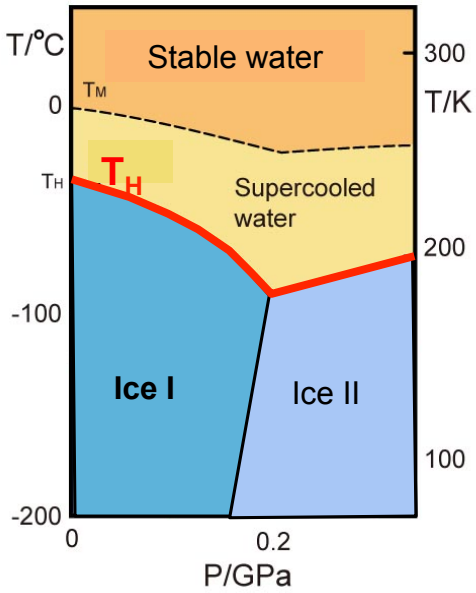
Moore and Molinero, J. Chem. Phys. (2009)

Thermodynamic anomalies



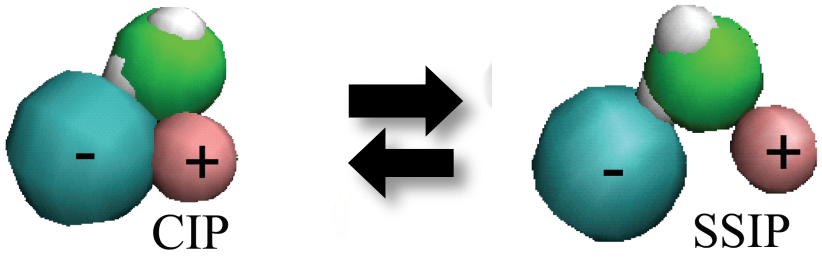
Molinero and Moore, J. Phys. Chem B (2009)

Phase behavior



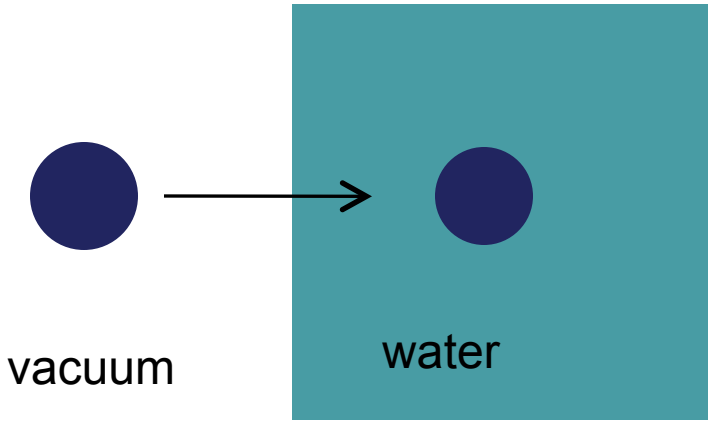
Moore and Molinero, Nature (2011)

Solvation structure and association of ions in water



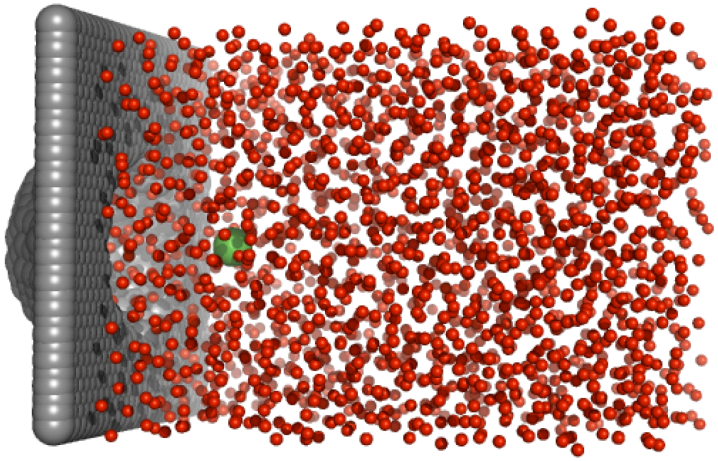
Demille and Molinero, J. Chem. Phys. (2009)

Hydration thermodynamics



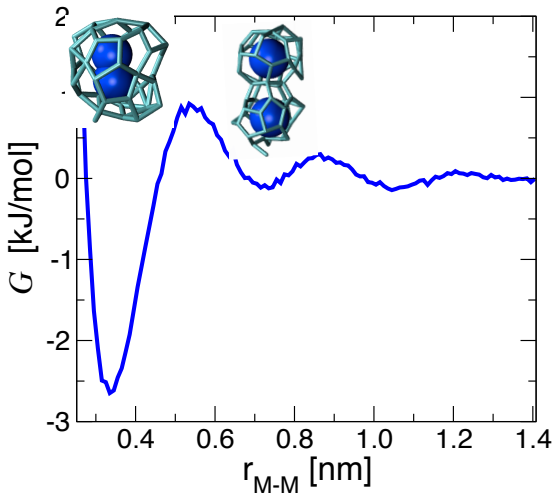
Spencer, Baron and Molinero, in preparation

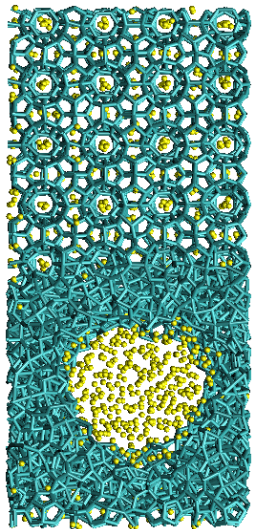
Water-mediated cavity-ligand attraction



Baron and Molinero, J. Chem. Theo. Comp. (2012)

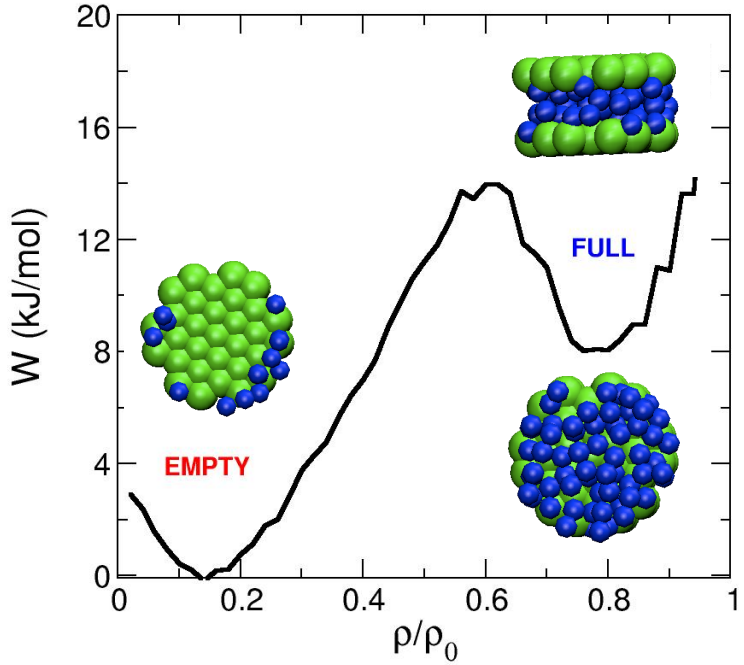
Small hydrophobes in water (bubble vs clathrate)





Jacobson, Hujo and Molinero, JACS (2010)
Song and Molinero, J Chem. Phys. (2013)

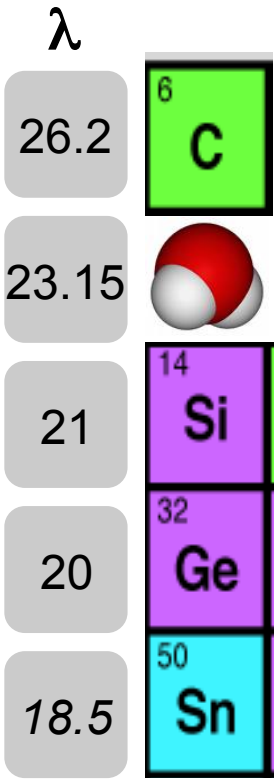
Wetting-Drying transitions



Xu and Molinero, J. Phys. Chem. B (2010)

Water modeled as an intermediate element between C and Si

The monatomic water model mW reproduces the structure, anomalies and phase behavior of water at less than 1% of the cost of atomistic models



- Topology matters more than nature of interactions

Coarse-grained models relate water to a wider class of chemically unrelated substances

Water model: *Molinero and Moore, J. Phys. Chem. B. (2009)*

Comparison of tetrahedral liquids: *Hujo et al. J. Stat. Phys. (2011); Jabes et al. J. Phys. Cond. Matt. (2012)*

Main messages

Models of water are not water: they are simplified Hamiltonians that attempt to emulate some results of a more complex (intractable) Hamiltonian H^{real}.

H^{real} is not H^{model} plus a perturbation: adding more detail to the model does not result in systematic improvement.

H^{model} cannot represent all the properties of H^{real}. We are still learning the relationship between properties and potential in water models.

There is no free lunch, but not all lunches cost the same price. Good payoff:

-long range interactions are not as important as we tend to believe

-many body correlations are significant

-tetrahedral interactions seem to be key for increasing representability

We need better assessments of the precision of coarse-grained models and the sensitivity of their properties to the interaction parameters.

Outline

Paradigms in classical modeling of water

What is essential in modeling water?

A monatomic model of water with "hydrogen-bonds"

reproduces the structure, anomalies and phase behavior of water

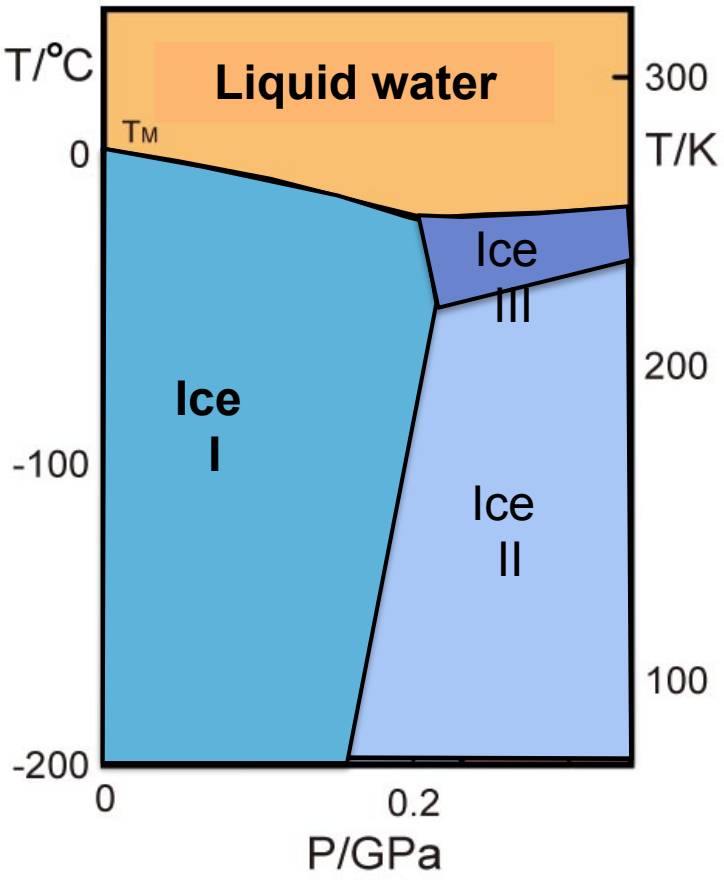
--- intermezzo

Ice crystallization with coarse-grained water:

Homogeneous crystallization of water and solutions
is controlled by a structural transformation within the liquid.

Heterogeneous freezing of water on carbon surfaces
is promoted by ordering of interfacial water.

Is it possible to predict the crystallization rate of water?



Water crystallization requires the spontaneous formation of ice nuclei within the liquid: significant supercooling.

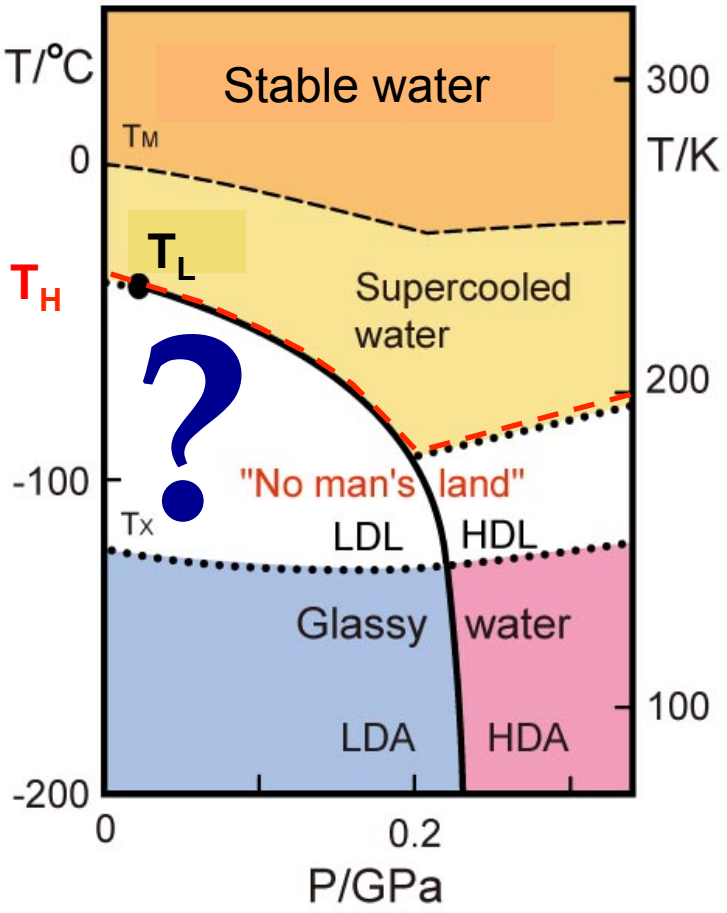
Homogeneous ice nucleation is unimportant until ~ -32 C;
by -40 equilibration of the liquid is not possible in experiments.

Experimental evidence[1] that water activity determines the temperature of homogeneous nucleation of ice

[1]Koop et al. Nature, ***406***, 611-614 (2000)

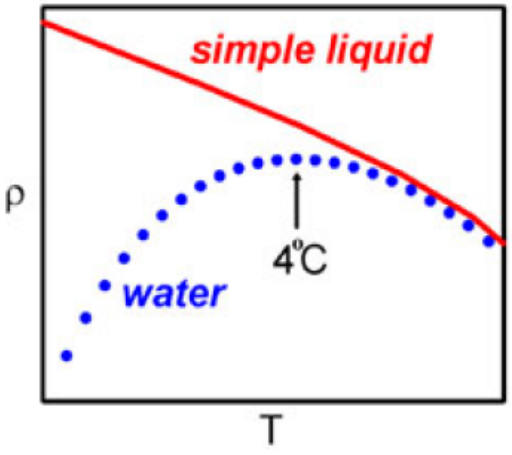
Water is an anomalous liquid

Mishima, 2007

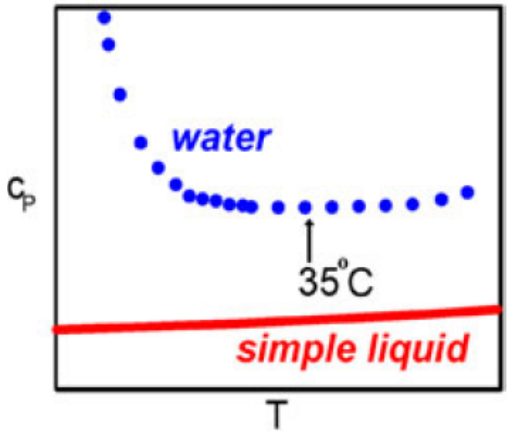


Debenedetti, JPCM 2003

Density is non monotonous



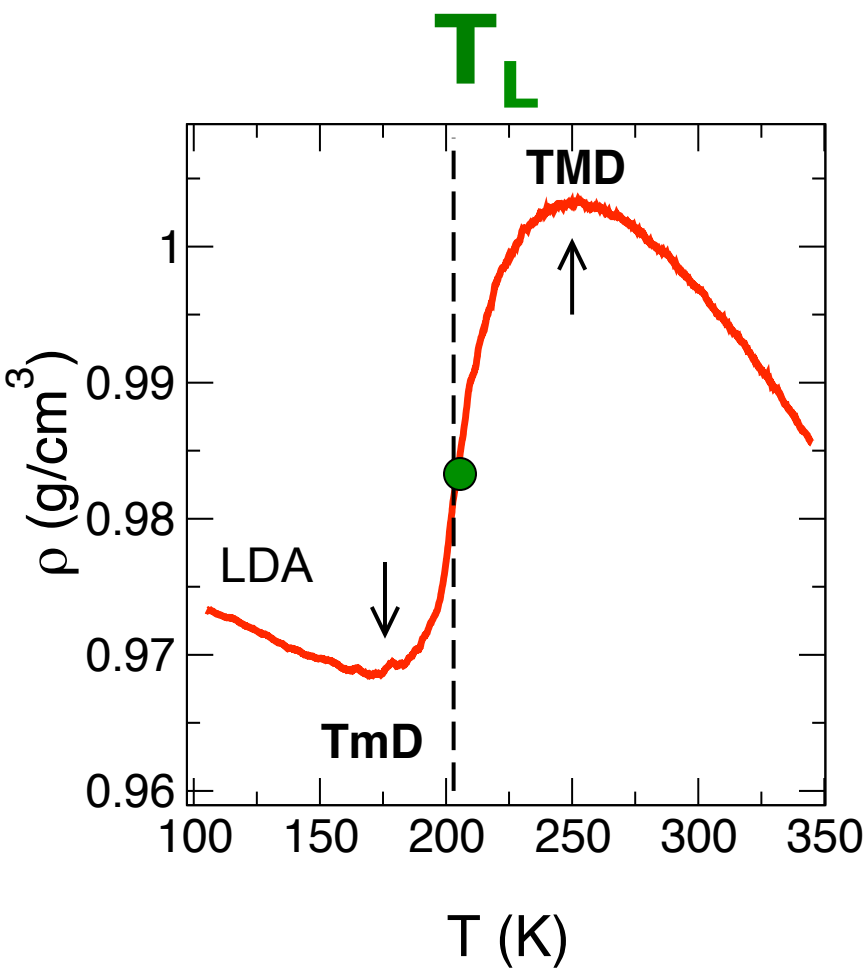
Heat capacity increases on cooling



Is there a relationship between the anomalies and the crystallization?

What's going on in water's "no-man's land"?

Fast cooling of liquid water results in a continuous transformation towards the tetrahedrally coordinated LDA glass



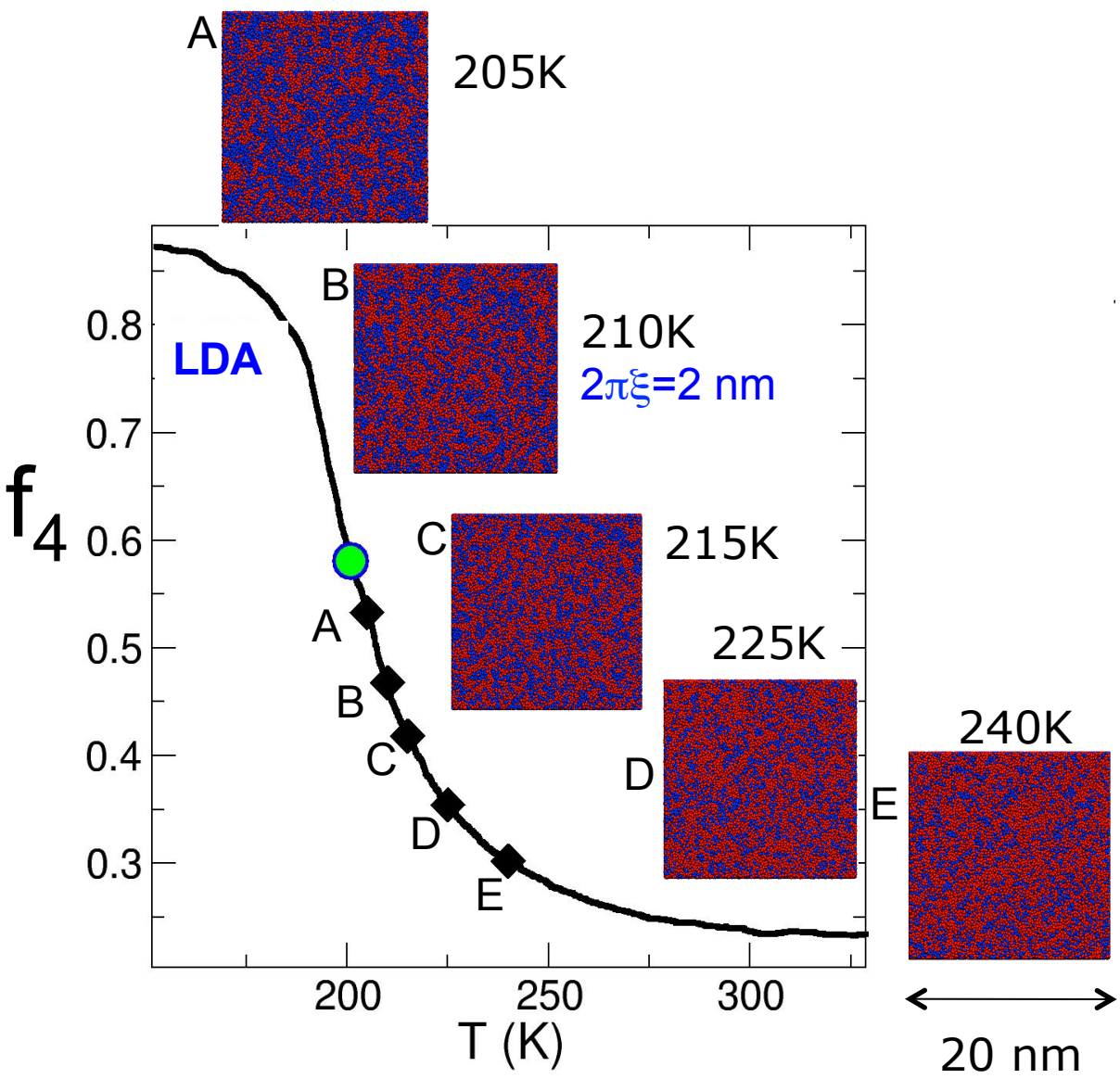
Density change is sharpest at the **liquid transformation temperature T_L** = 202 K

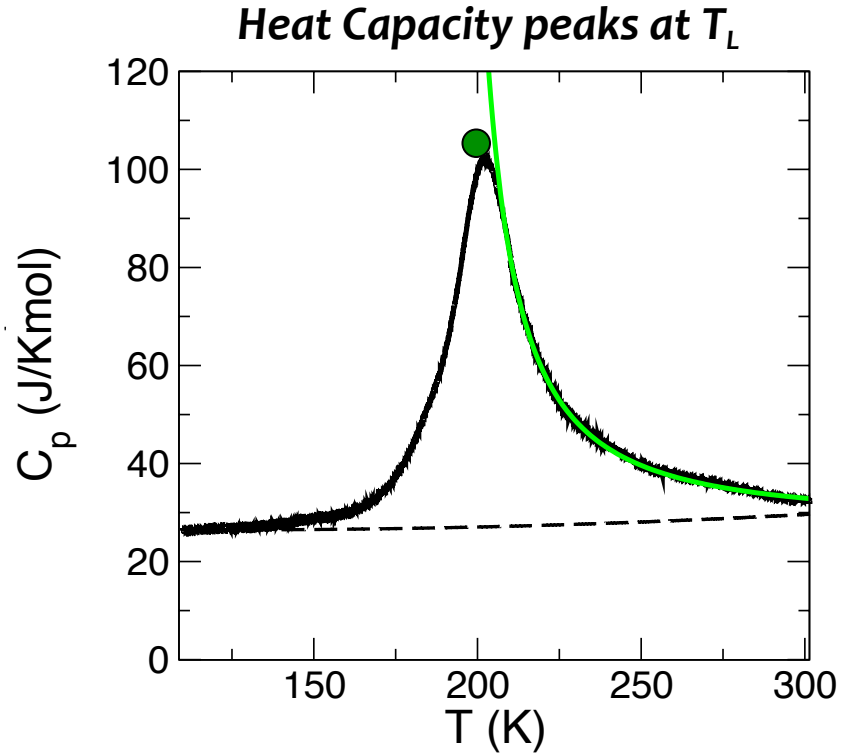
Anomalies displaced ~27 K down with respect to experiments. **TL in experiments would be at T_L ~223 K, close to TH**

How does the structure of liquid water change when is cooled towards T_L?

Moore and Molinero J. Chem. Phys., ***130***, 244505 (2009)

Fluctuating patches of 4-coordinated water molecules start growing well above the liquid transformation temperature



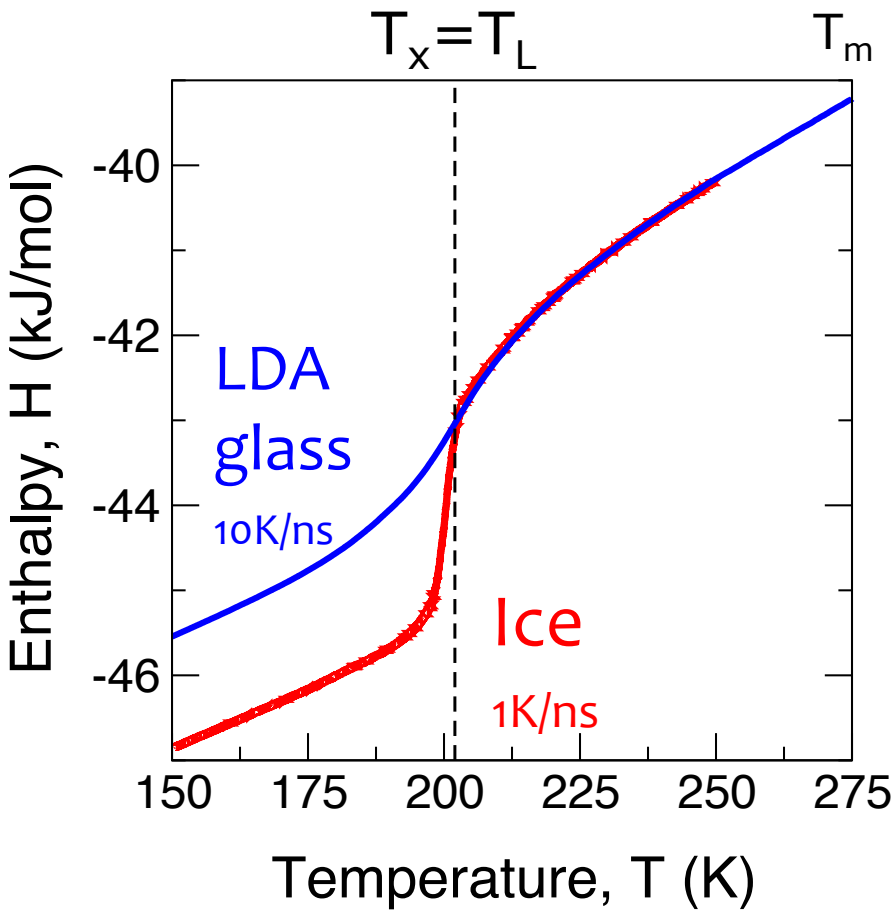


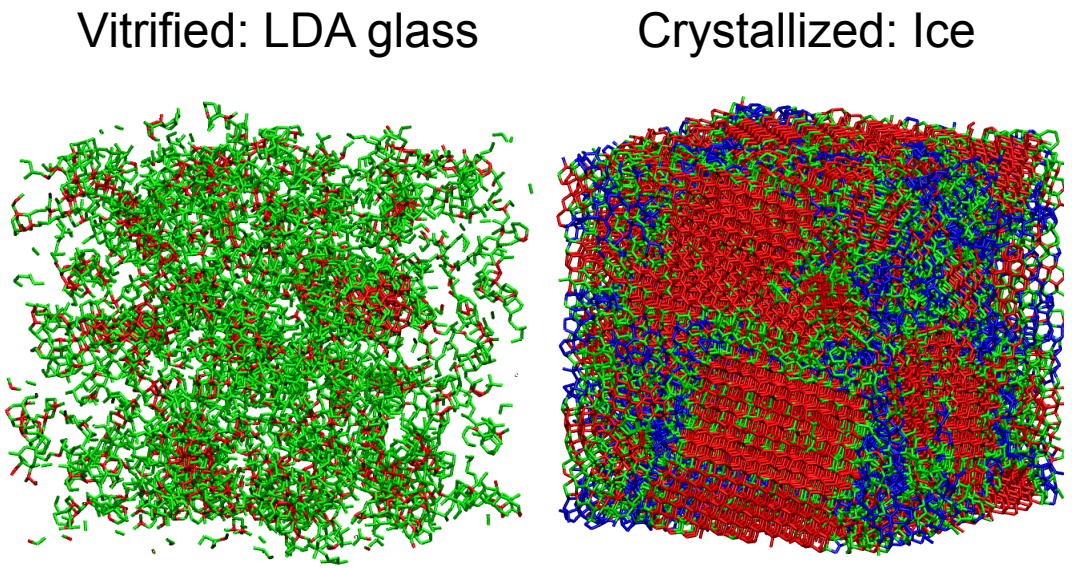
f_4=fraction of 4-coordinated molecules

Moore and Molinero, Nature, ***479,*** *505 (2011)*

Moore and Molinero J. Chem. Phys., ***130,*** *244505 (2009)*

The liquid transformation competes with crystallization



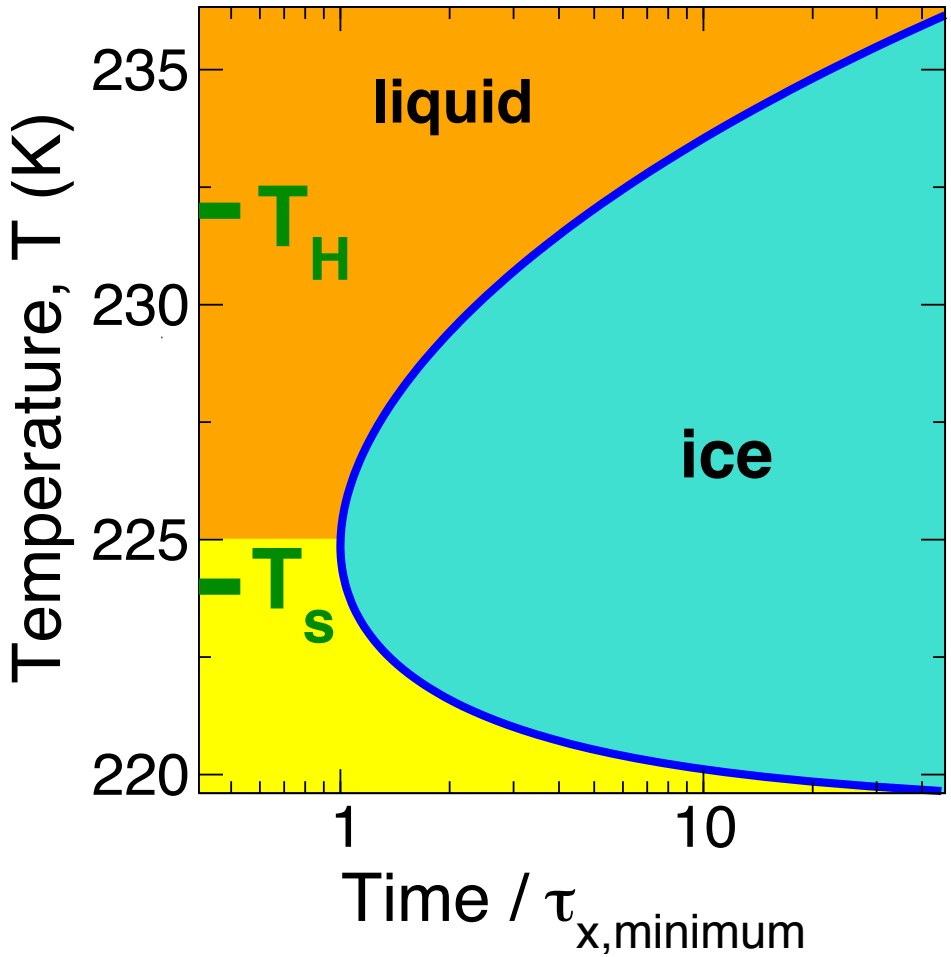


Ice, amorphous
Interfacial or intermediate-ice

The LDA glass is crisscrossed by threads of ice-like order and ice crystallites.

Moore and Molinero, Nature, ***479****, 505 (2011)*

Ice crystallization is the fastest around T_L



We predict that water presents a **maximum crystallization rate below but close to T_H**

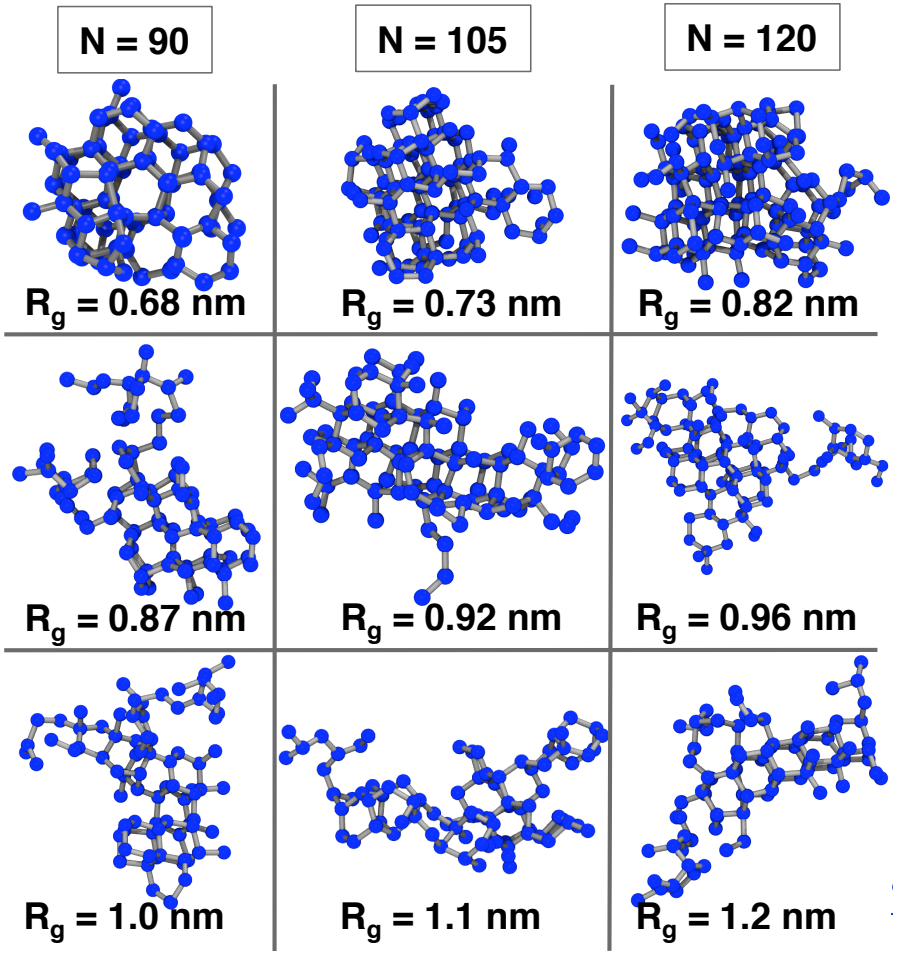
New prediction: ***Tx = 216 K***

Limmer and Chandler, Faraday Discussions (2013)

Crystallization rates determined with **classical nucleation theory** and the **experimental** excess free energy and diffusion of water

Moore and Molinero, Nature, ***479****, 505 (2011)*

Critical ice embryos at the freezing temperature T_H contain ~100 water molecules and are preferentially solvated by four coordinated liquid water



Size of Critical Nuclei at TH

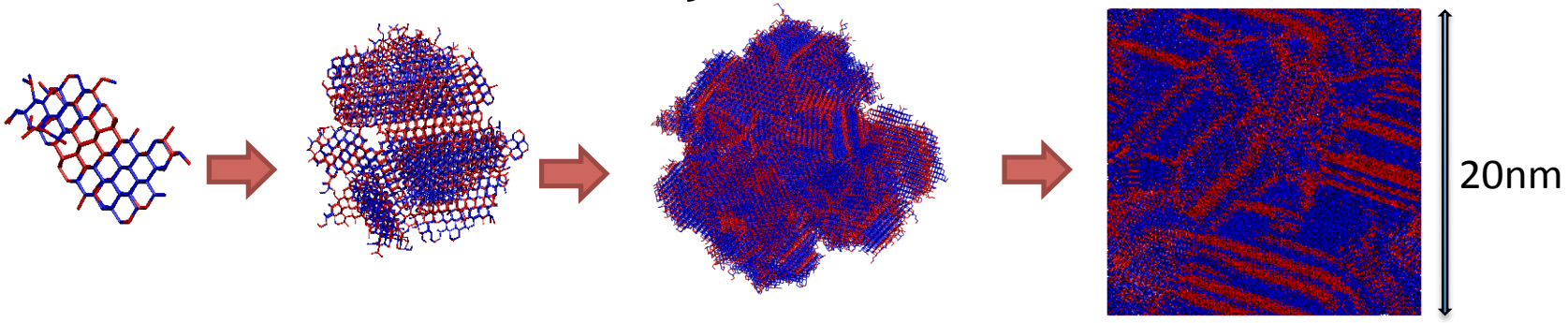
	n*	Rg*
simulations[1]	90-130	0.7-1.2 nm
Exp. (Micelles) [2]	70-210	0.7-1.2 nm
EOS/CNT[3]	90-380	0.9-1.4 nm

Critical ice embryos can be quite non spherical consistent with small ice-liquid surface tension

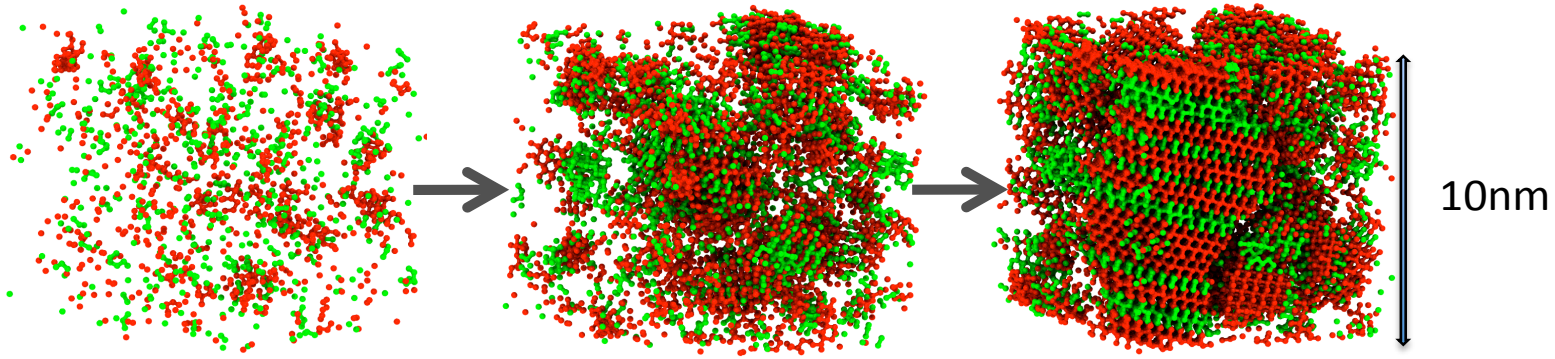
Simulations: *Moore and Molinero, Nature,* ***479****, 507 (2011)*
Experimental, in micelles: *Liu et al., Langmuir,* ***23****, 7286 (2007);*
Classical Nucleation Theory/ equation of state: *Kiselev, Int. J. of Thermophys.,* ***22****, 1421 (2001)*

Times of nucleation and growth are comparable at T_L

8 K **above Tx:** limited by nucleation



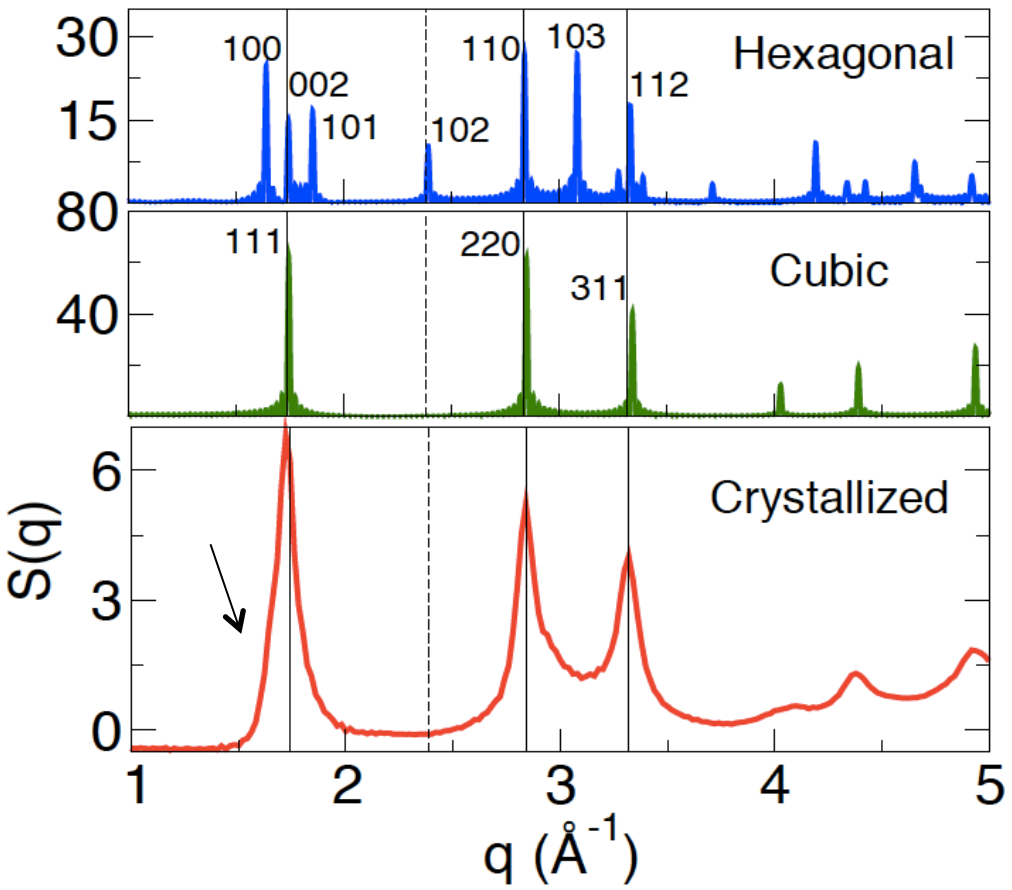
20 K **below Tx:** limited by growth



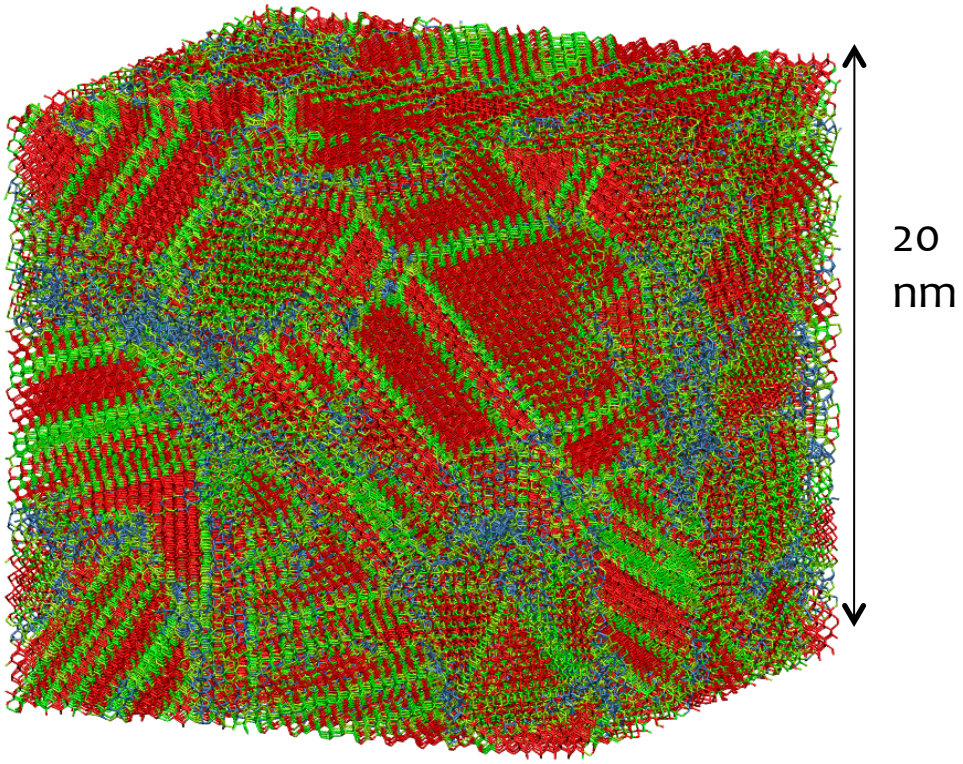
Liquid mW water cannot be equilibrated in no-man's land

Ice formed from deeply supercooled water is a hybrid with comparable fraction of cubic and hexagonal layers

Diffraction patterns from molecular simulations with mW water



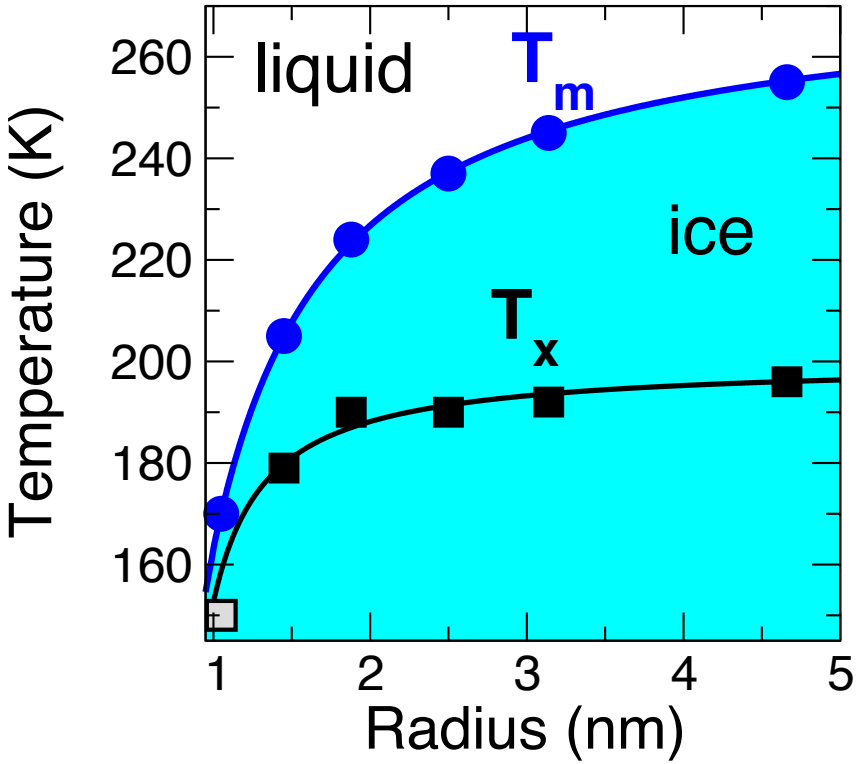
cubic / hexagonal layers in ratio ~2:1



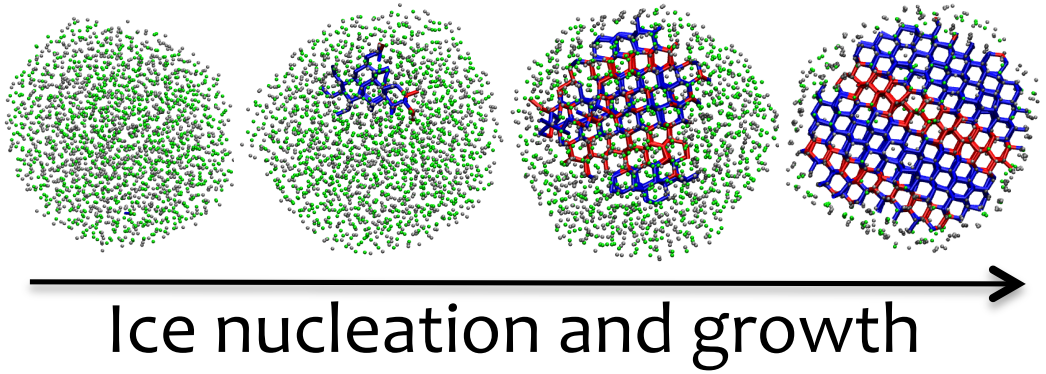
Formation of hybrid ice is kinetically controlled.

Bulk ice: simulations: *Moore and Molinero, PCCP,* ***13****, 20008 (2011); Qiu and Molinero, to be submitted*
experiments: *Kuhs, Bliss, Finney, J. Phys. Colloques* ***48****, C1–631 (1987); Elarby-Aouizerat et al. J Non-Cryst Solids,* ***104****, 203 (1988);, Hansen et al, J Phys-Condens Mat,* ***20****, 285104 (2008), Malkin et al. PNAS* ***109****, 1041 (2012), Kuhs et al. PNAS* ***109*** *221259 (2012)*

Hybrid ice I confined in nanopores or nanoparticles does not transform to hexagonal ice before melting



The melting temperatures of hexagonal, cubic and hybrid ice nanoparticle are indistinguishable.

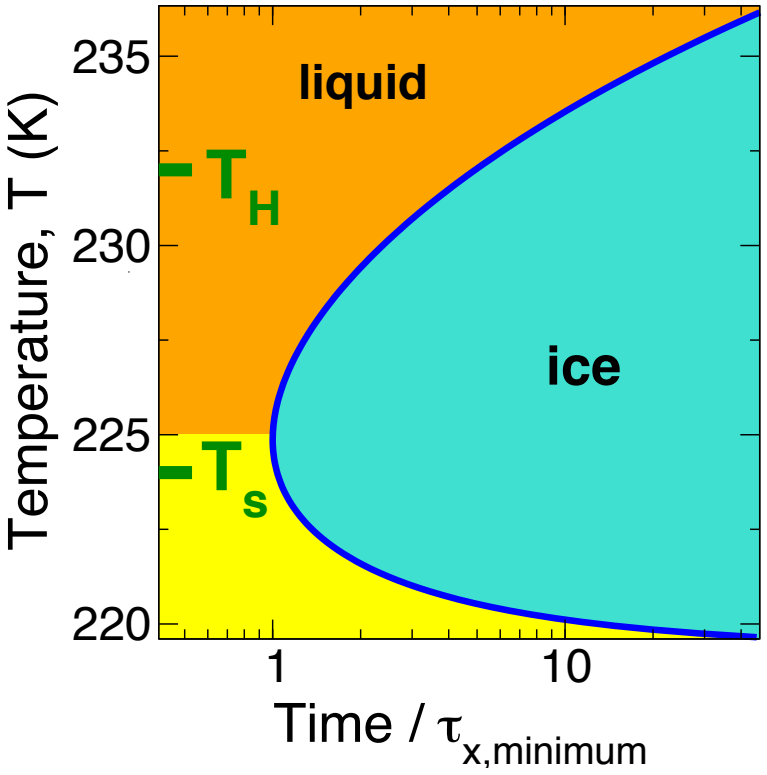


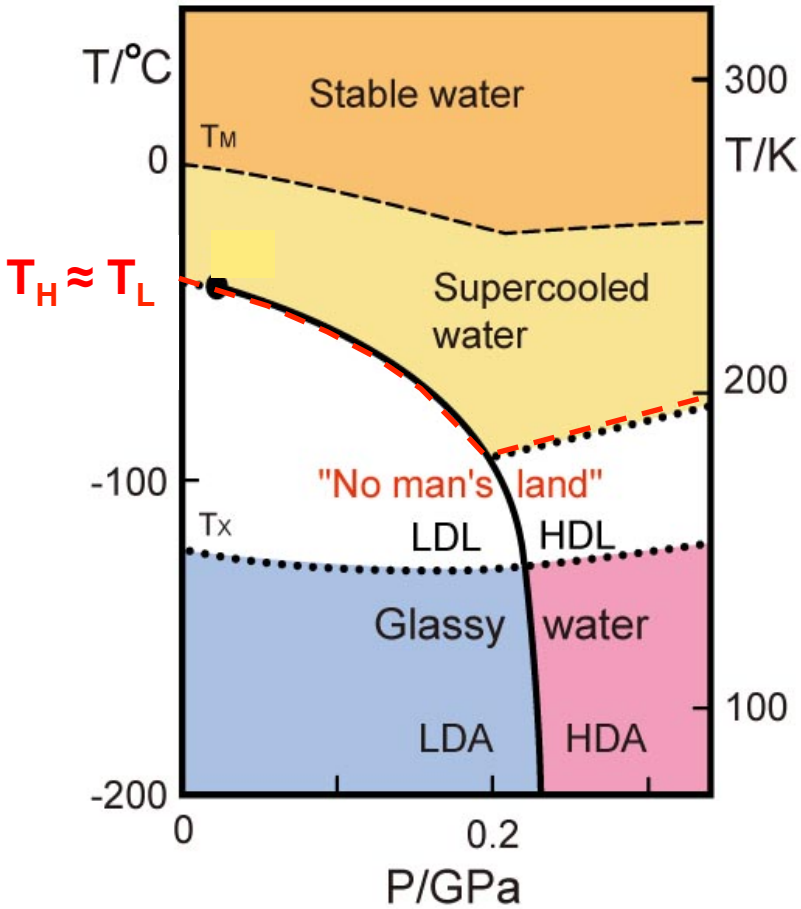
Ice nanoparticles: *simulations Johnston and Molinero, JACS, **134**, 6650 (2012)*
*experiments: Bartell and Huang J. Phys. Chem. **98**, 7455-7451 (1994)*

Nanopores: *simulations: Moore et al. PCCP, **12**, 4124 (2010); Gonzalez et al. J. Phys. Chem. B., **115**, 14196 (2011); experiments: Morishige et al, J Chem Phys, **122**, 044711 (2005), Liu et al. JPCM, **18**, 10009(2006).*

The temperature of homogeneous nucleation of ice T_H can be predicted from the location of the thermodynamic liquid transformation temperature T_L

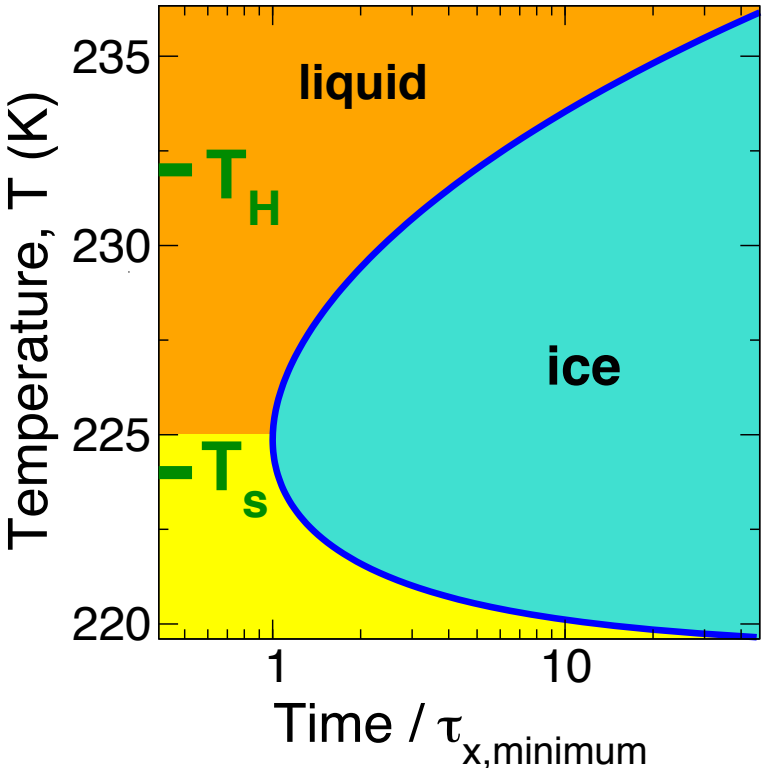
A structural transformation within the liquid sets a lower limit of metastability for supercooled water.

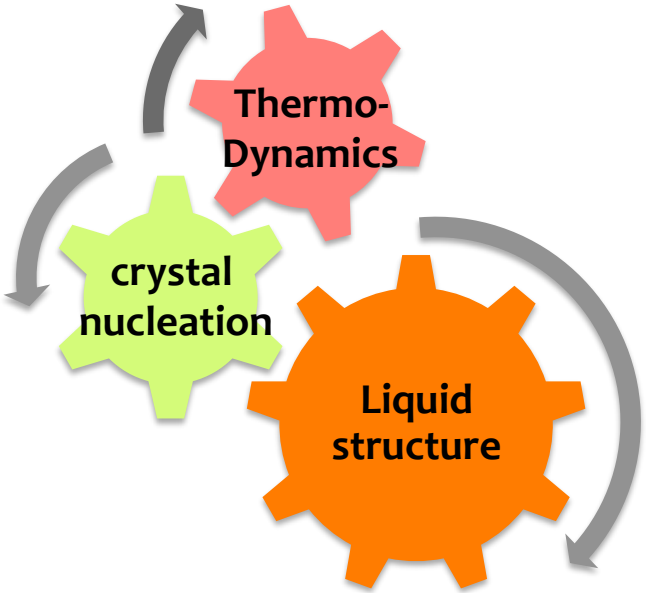




The temperature of homogeneous nucleation of ice T_H can be predicted from the location of the thermodynamic liquid transformation temperature T_L

A structural transformation within the liquid sets a lower limit of metastability for supercooled water.

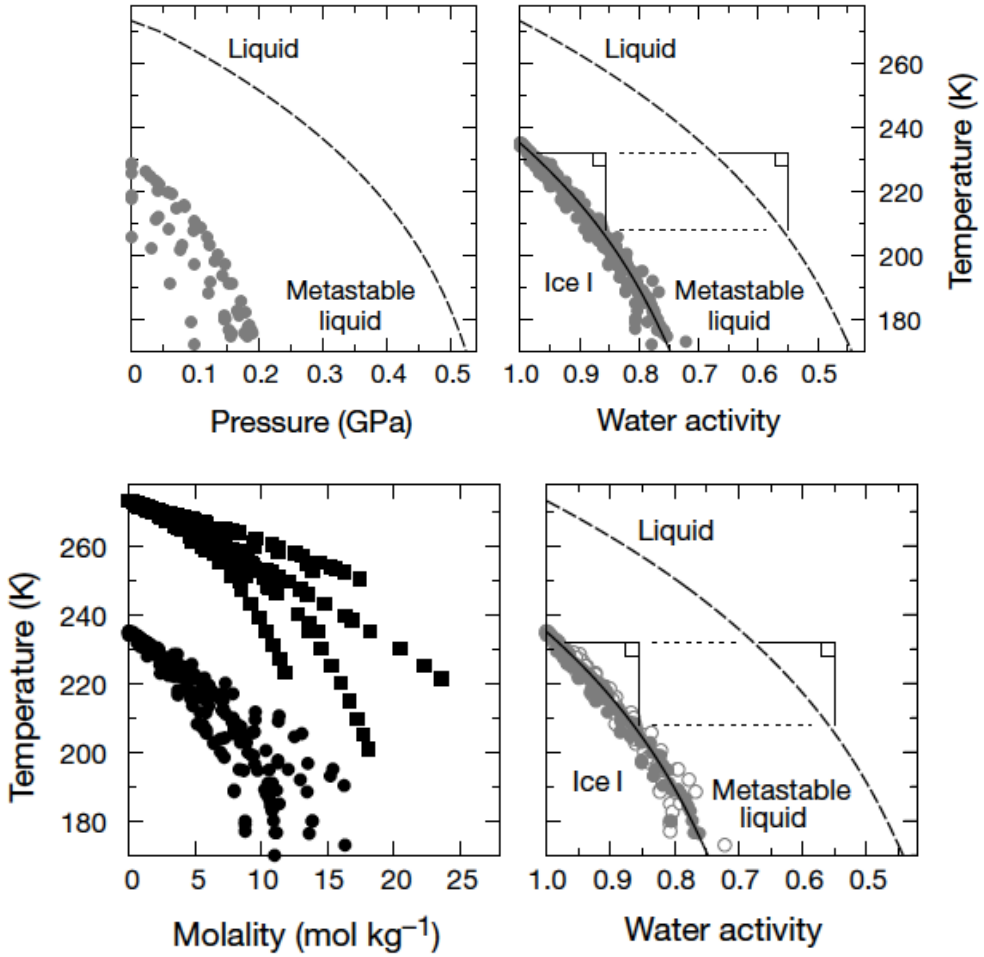


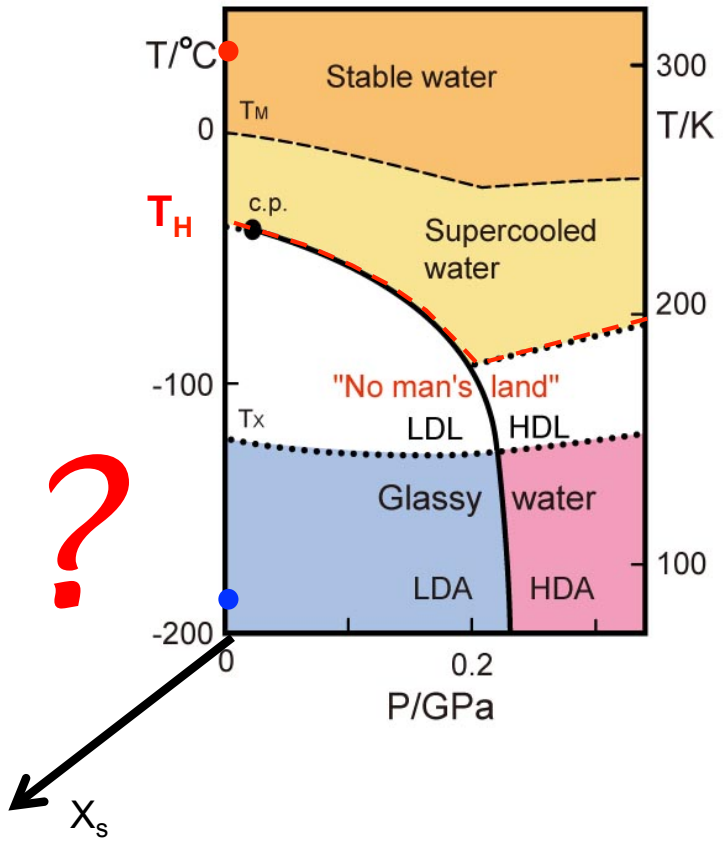


Bulk: *Moore and Molinero, Nature,* ***479****, 507 (2011)*
Moore and Molinero, J. Chem. Phys. ***132****, 244504 (2010)*
Droplets*: Johnston and Molinero, JACS,* ***134****, 6650 (2012)*
Nanopores*: Moore et al. PCCP,* ***12****, 4124 (2010)*
Gonzalez et al. J. Phys. Chem. B., ***115****, 14196 (2011)*

Ice crystallization in aqueous solutions

Thermodynamics (activity) of water determines the temperature of homogeneous nucleation of ice Koop et al. Nature, ***406***, 611-614 (2000)

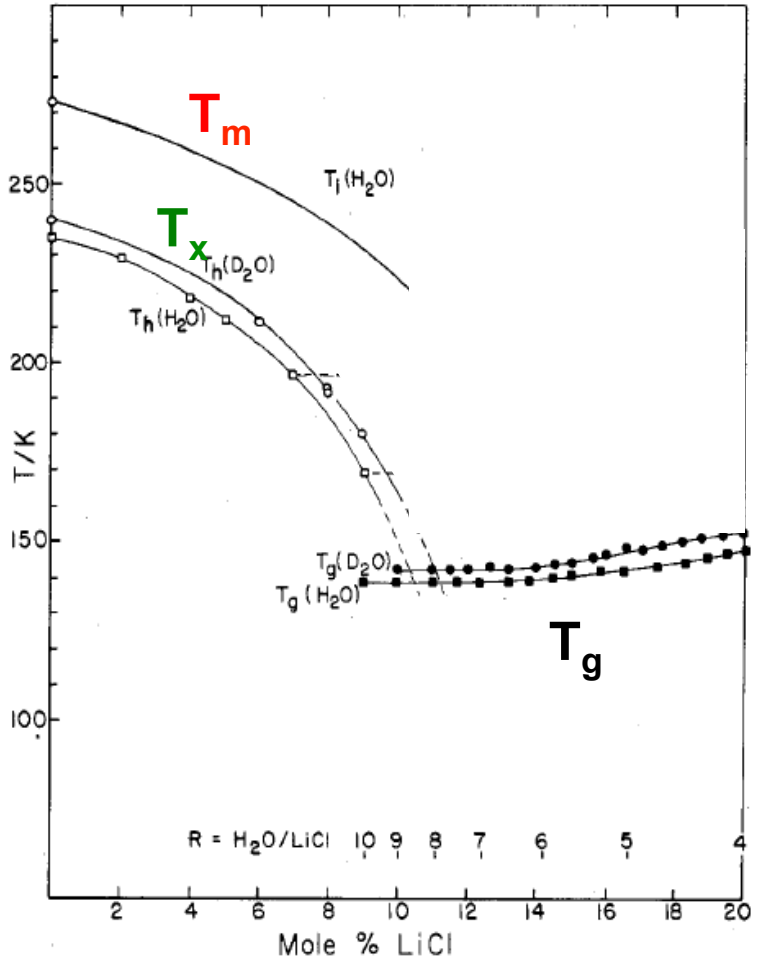




What is the microscopic origin for this relation?

The liquid transformation temperature of the solution sets the temperature of homogeneous nucleation of ice

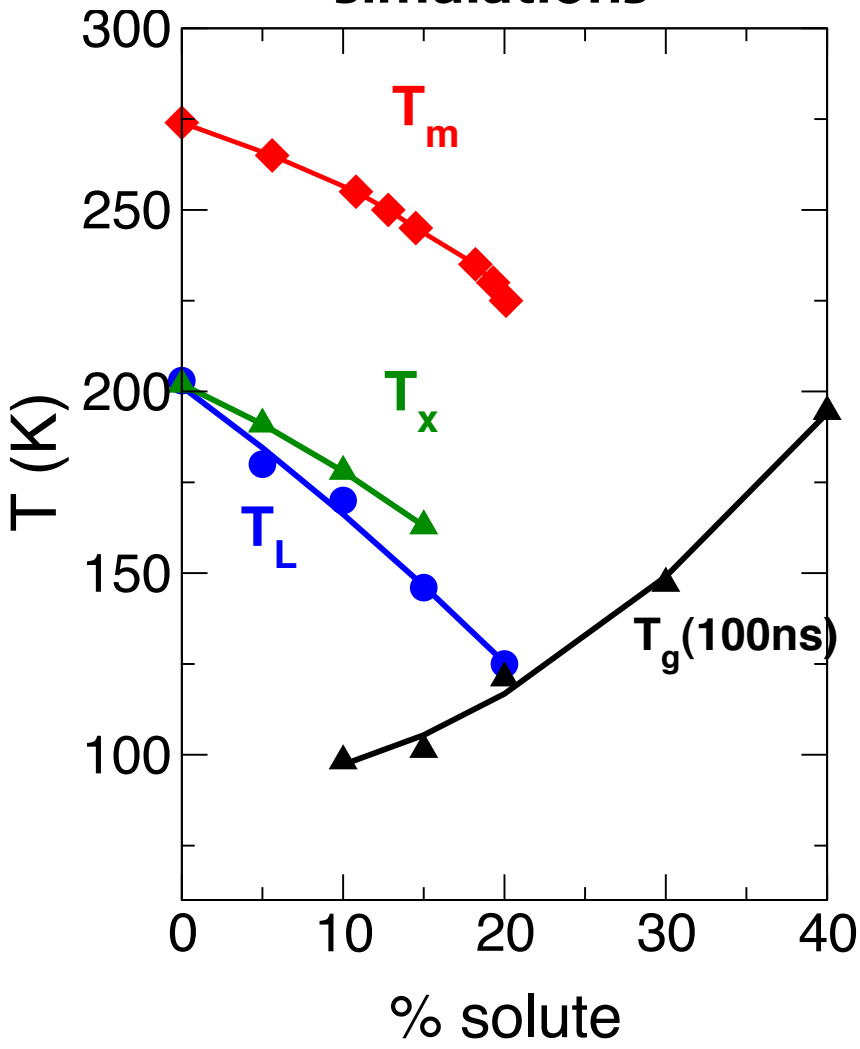
experimental



%LiCl = ½ % solute

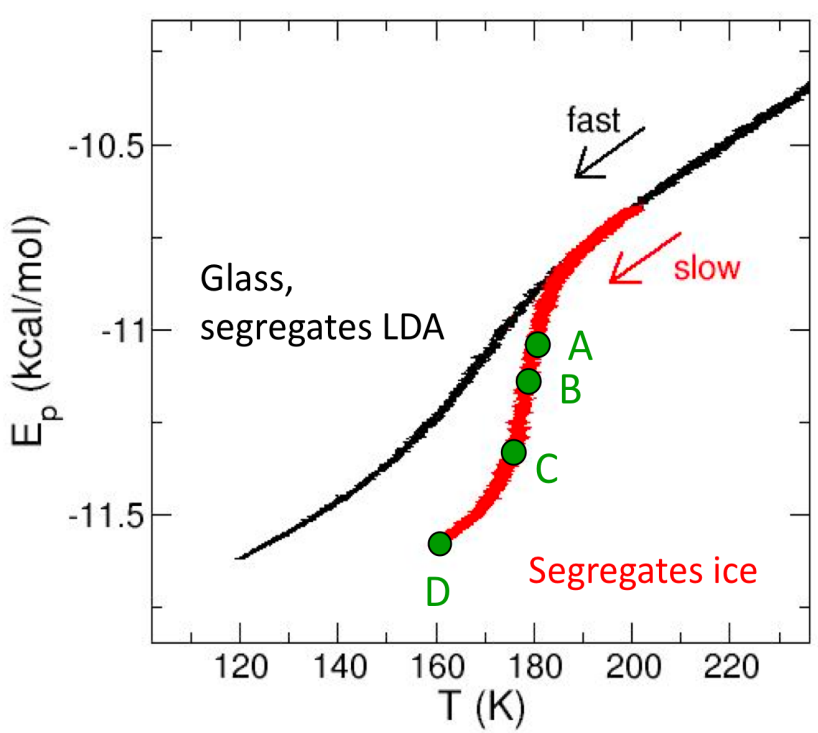
Angell et al, J. Phys. Chem, ***85****, 1461 (1981)*

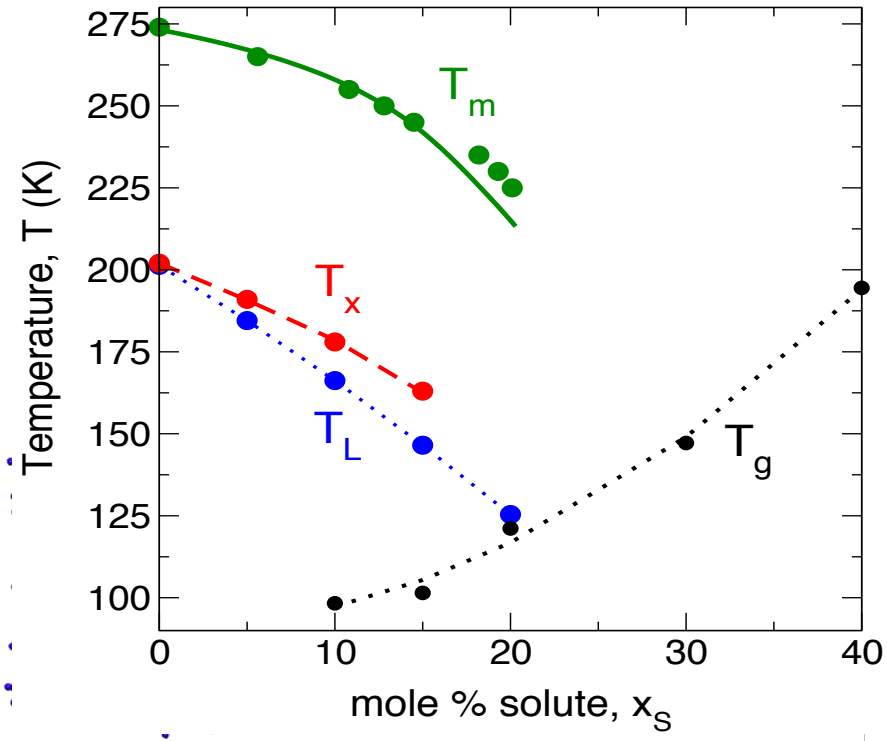
simulations

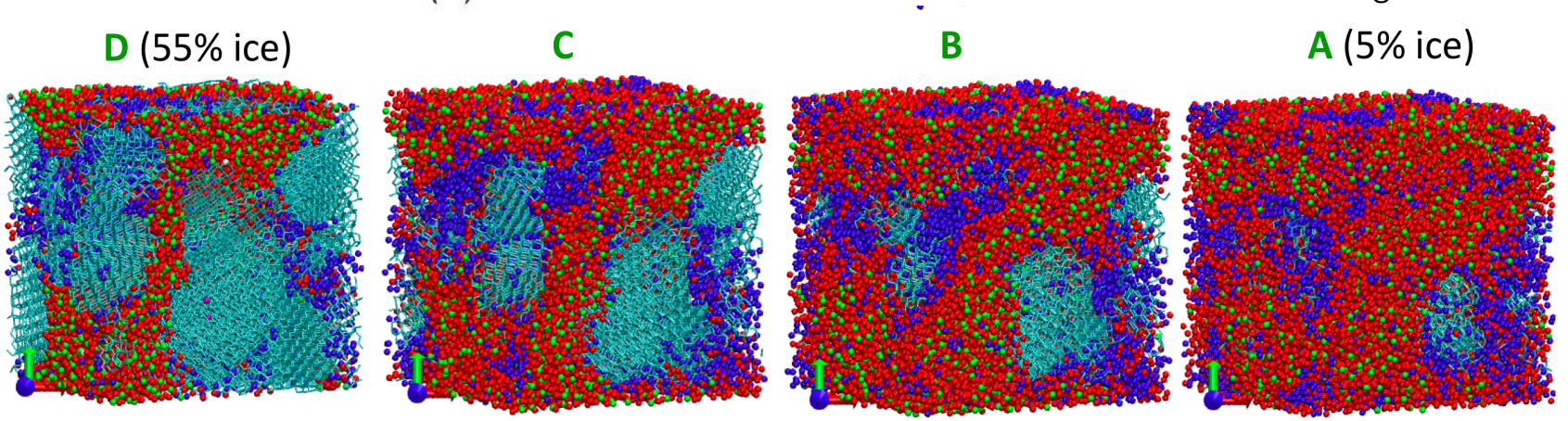


Le and Molinero, J Phys Chem A, ***115****, 5900 (2011)*
Bullock and Molinero, Faraday Discussions (2013)

Crystallization of ice in solutions is also preceded by the formation of nanodomains of four-coordinated liquid water







Bullock and Molinero, "Low-density liquid water is the mother of ice:…" Faraday Discussions (2013)

The depression of the crystallization temperature reflects the depression of the LDA/mixture "equilibrium"

Melting line (ice/solution equilibrium)

$$\mu_W^{ice}(T) = \mu_W^{mixture}(T, a_W) \longrightarrow T_m(a_W) = \left(\frac{1}{T_m^*} - \frac{R(\ln a_W)}{\Delta H_m^*} \right)^{-1}$$

Crystallization line (LDA/solution "equilibrium")

$$\mu_W^{LDA}(T) = \mu_W^{mixture}(T, a_W) \longrightarrow T_X(a_W) = \left(\frac{1}{T_X^*} - \frac{R(\ln a_W)}{\Delta H_L^*} \right)^{-1}$$

(kJ/mol)	ΔH_m^*	ΔH_L^*
experiments	6.0	2.2±0.2
simulations	5.3	2.0±0.1

ΔH_L^* is 37% of ΔH_m^*

Bullock and Molinero, Faraday Discussions (2013)

Outline & main messages

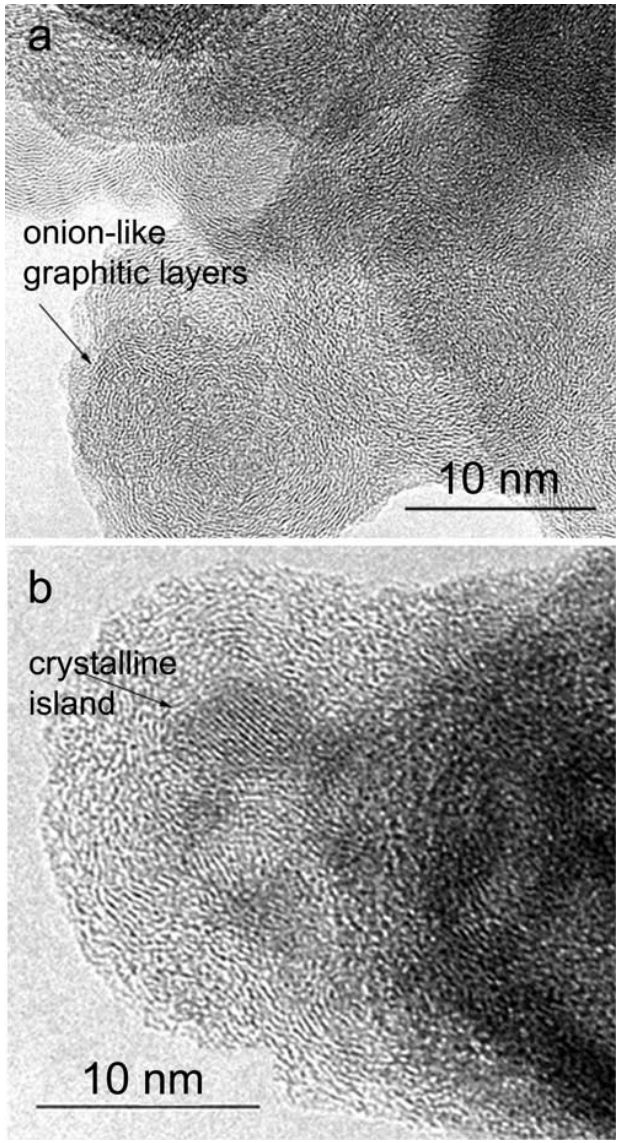
Homogeneous freezing of water and solutions
is controlled by a structural transformation within the liquid.
***Low-density liquid water is the mother of ice.**

***Ice crystallization rate reaches a maximum not far below T_H.**

***The freezing temperature of solutions is a colligative property with steeper composition dependence than Tm.**

Heterogeneous freezing of water on carbon surfaces
is promoted by ordering of interfacial water.

~20 million tons of carbonaceous particles emitted yearly



Soot is composed mostly of graphitic layers

Radius of curvature range from 2 to 50 nm.
(Vander Wal et al. Combustion and Flame 2004)

Lamella dimensions from 0.5 to 6 nm
(Vander Wal et al. Aerosol Science 2010)

Highly porous ~1/3 of area from pores < 2 nm
(Rockne et al. Chemosphere 2000)

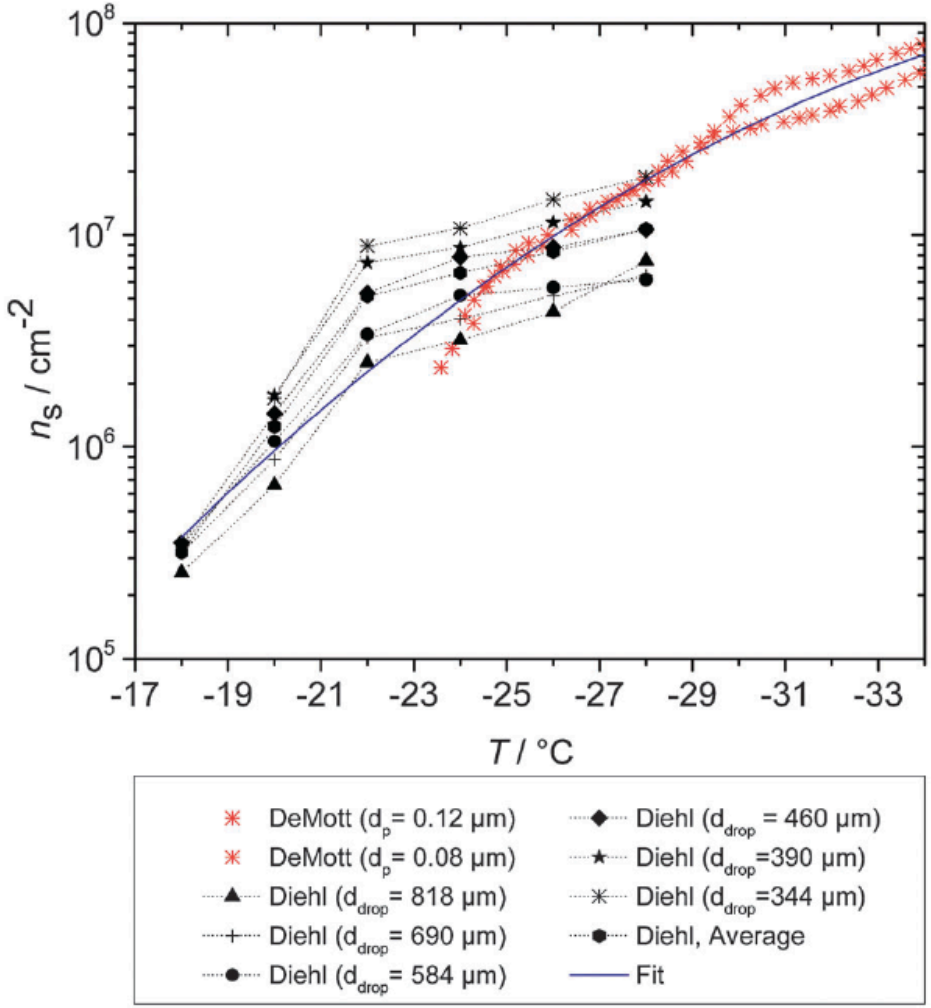
Carbon particles **oxidize** as they age in the atmosphere (incorporate -OH, -COOH, -CO)

Oxidation increases soot **hydrophilicity** and **hygroscopicity**

Pósfai et al., J. Geophys. Res. D (2003).

Soot particles can serve as nuclei for heterogeneous freezing of ice

Ice nucleation efficiency is quite variable



Murray et al., Chem. Soc. Rev. (2012)

Homogeneous ice nucleation at ~ -35 °C

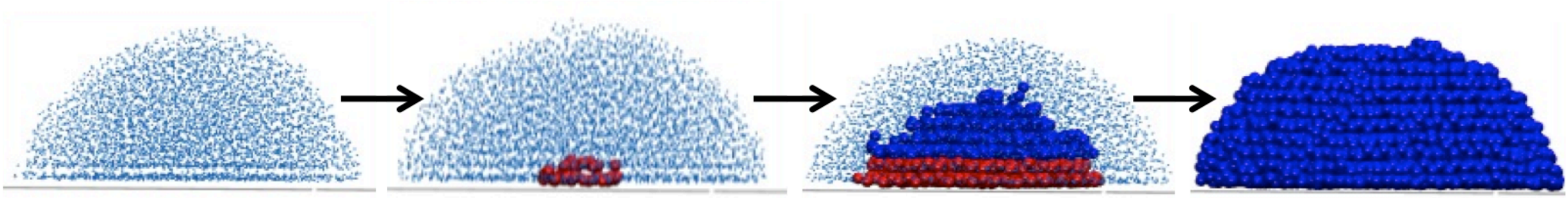
Soot particles increase crystallization temperature by up to 16°C

Some experiments indicate that surface oxidation increases freezing temperature
(Friedman et al. J. Geophys. Res. D (2011))

It has been suggested that increase in freezing efficiency is due to an increase In hydrophilicity of the particles

Graphene promotes heterogeneous nucleation of ice

Isothermal freezing T_f + 4 °C , water droplet (5500 molecues) on graphene



Critical ice nuclei form only at the carbon surface.

Subcritical nuclei, everywhere.

No sign of crystallization at the water/vapor interface.

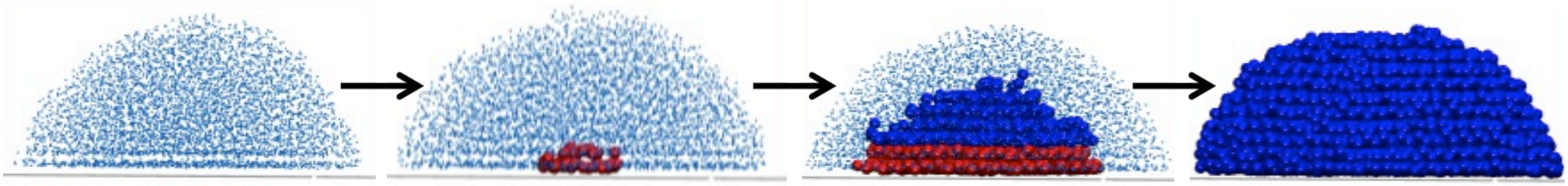
Freezing temperature on graphene is 14 °C higher than homogeneous.

Consistent with upper range of experimental data (16 °C)

Freezing temperature for droplet and bulk water on top of graphene are the same.

Water layers at the graphene surface

Isothermal freezing T_f + 4 °C , 5500 water droplet on graphene. Ice identified with $q_6 > 0.55$

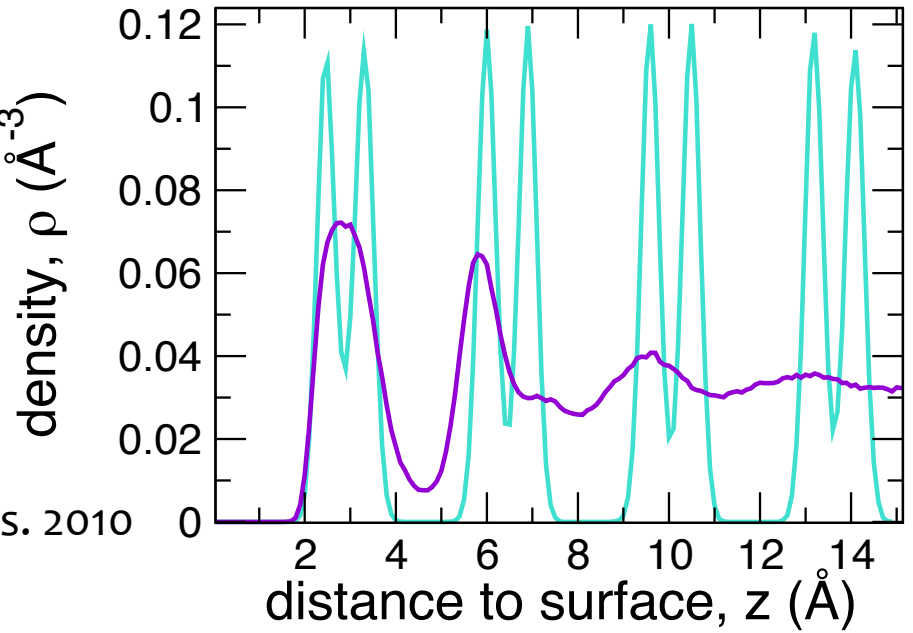


Ice wets the graphite surface

there is no premelted layer at the graphite/ice interface

(Kastelowitz, Johnston and Molinero, J. Chem. Phys. (2010))

Ice density peaks split
(normal ice I)



Liquid layers at the graphene surface

Layering significant already at 298 K

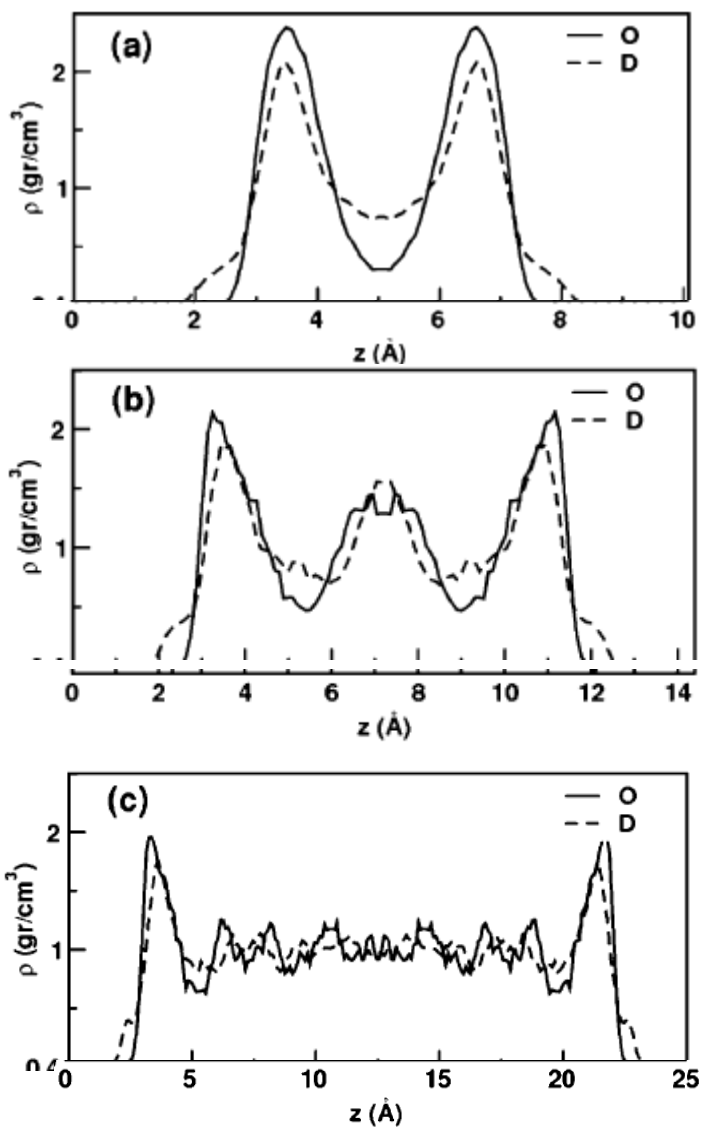
Cicero et al. JACS 2008, Kastelowitz et al J. Chem. Phys. 2010

Li and Zeng ACS Nano 2012

Layering of water noticeable at high temperarures

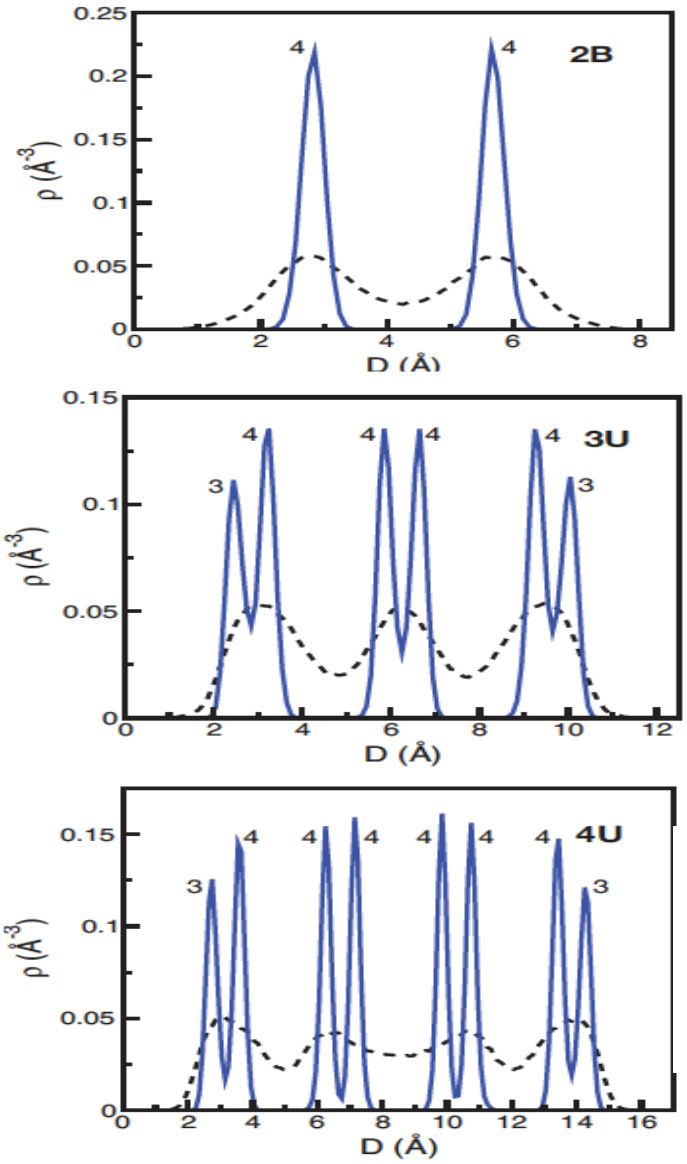
Ab-initio simulations of water between two graphene sheets at 400 K.

Cicero et al. JACS 2008

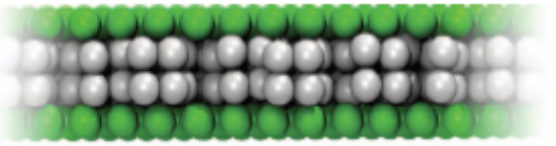


Coarse-grained simulations of mW water between flat sheets at melting temperature of confined ice

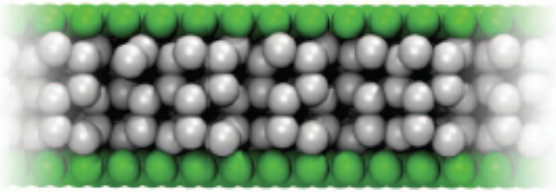
Kastelowitz et al. J. Chem. Phys. 2010



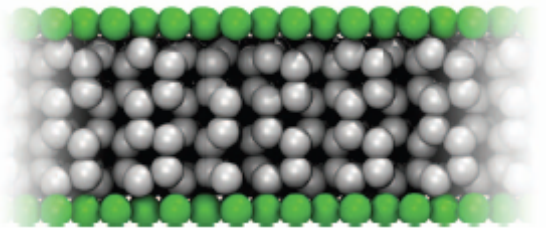
Bilayer ice: flat layers



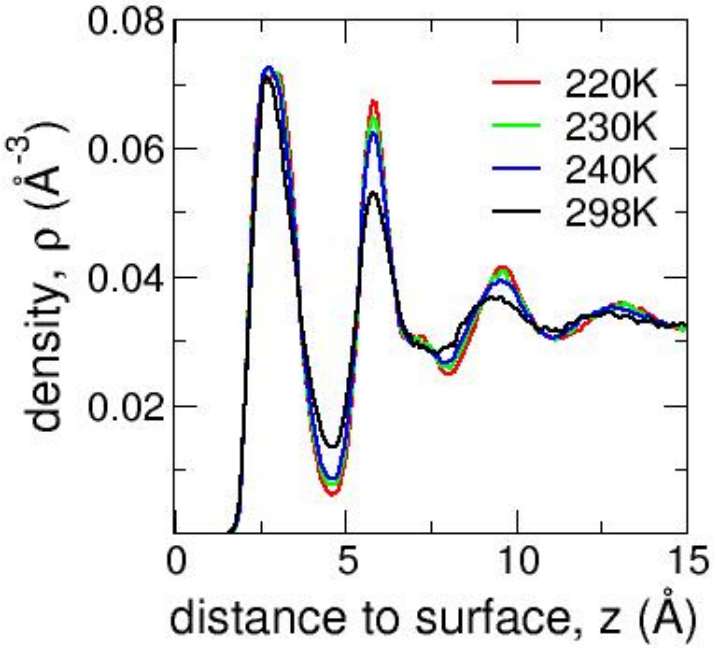
Trilayer ice: unbuckled



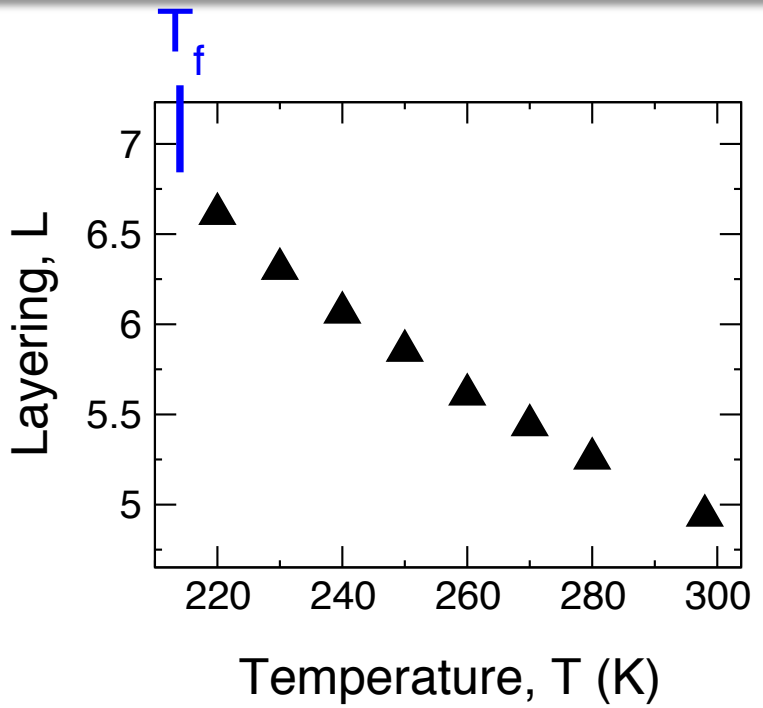
Four-layer ice: unbuckled



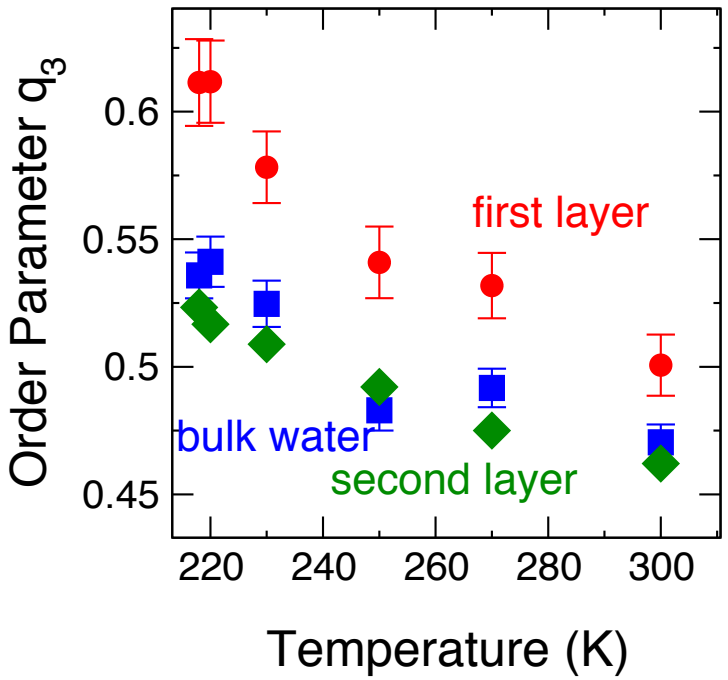
Ordering of interfacial water increases on cooling



$$L = \int \left| \frac{\rho(z)}{\rho_{bulk}} - 1 \right|^2 dz$$



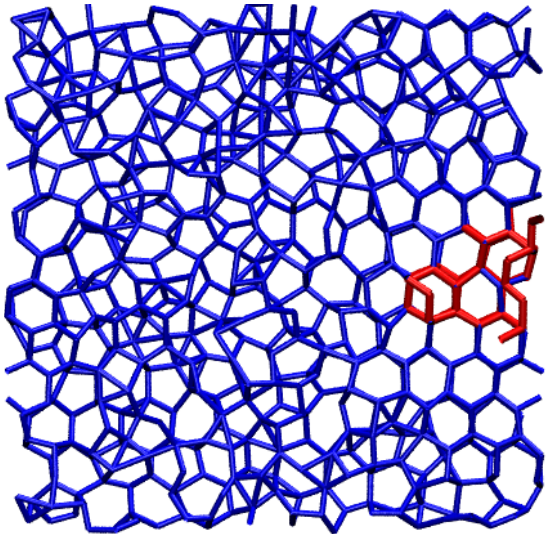
Graphite surface induces layering and ice-like ordering within the first layer of interfacial water



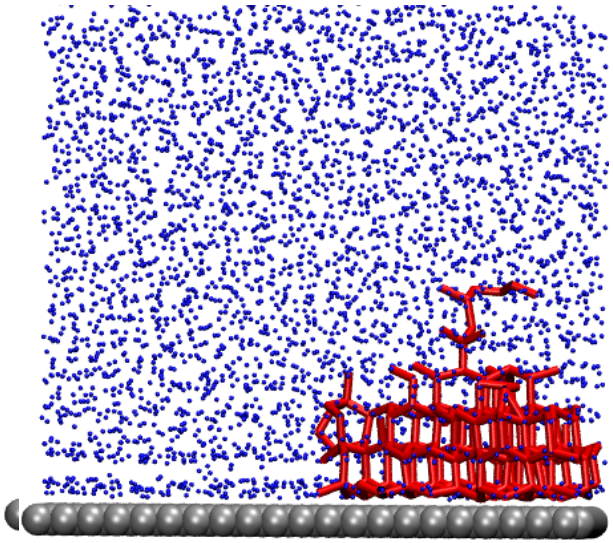
Lupi, Hudait and Molinero, to be submitted

Rugged surfaces do not present layering and do not nucleate ice

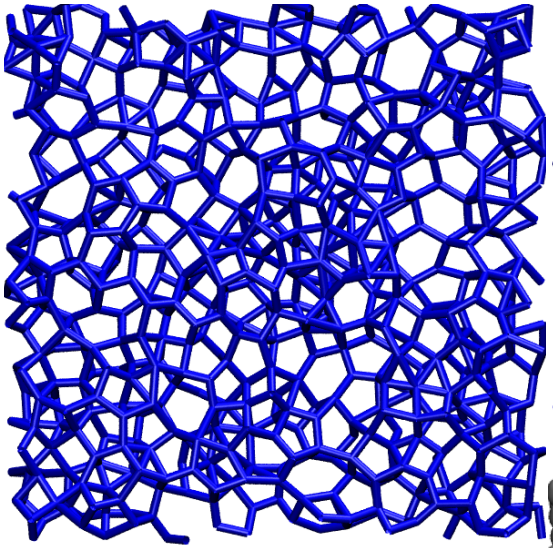
220 K

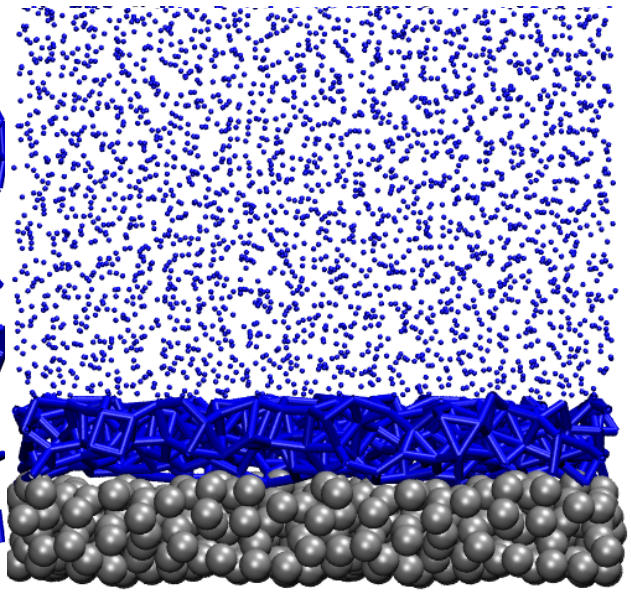


Flat (graphene)

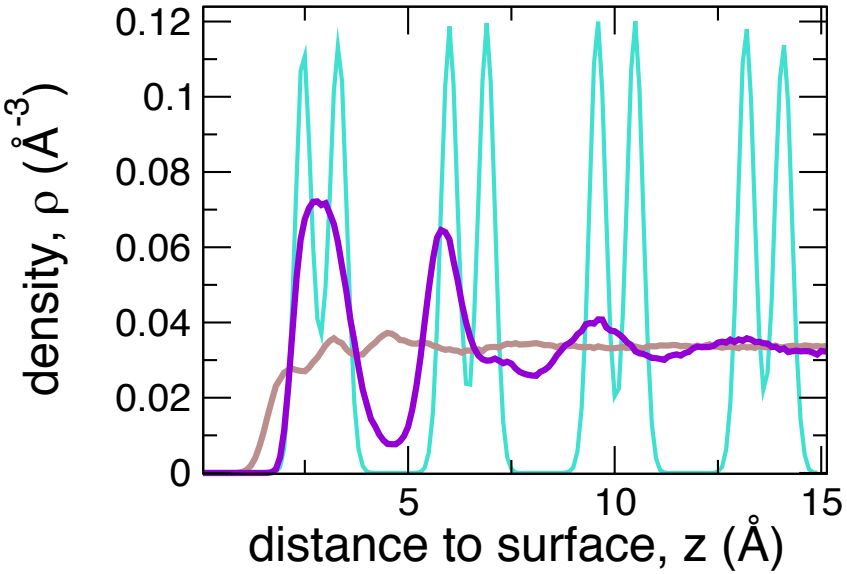


Rugged (water block)





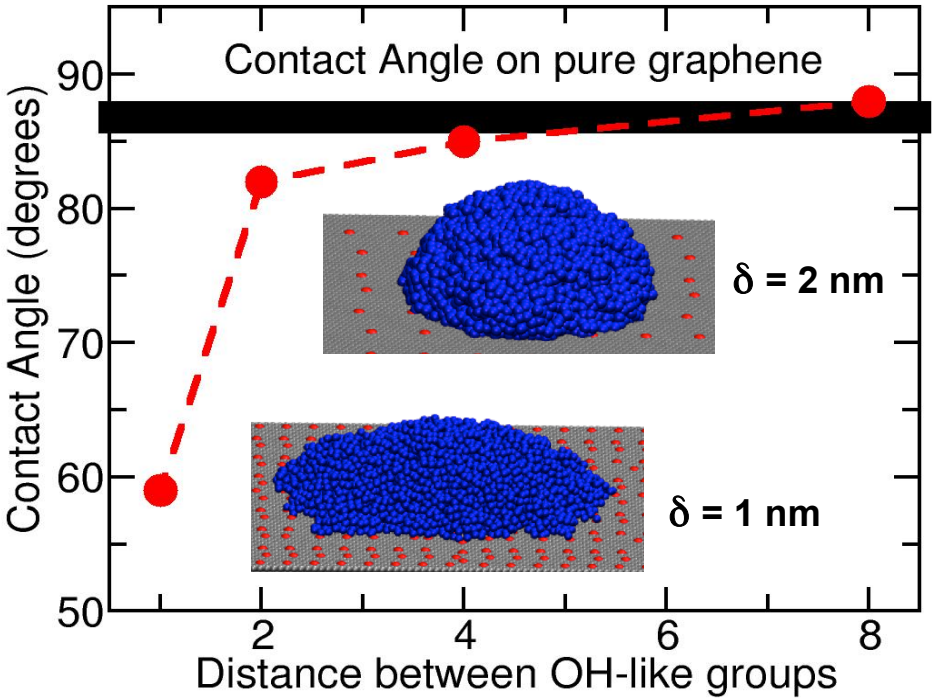
Heterogeneous freezing at 214 K



Homogeneous freezing at 200 K

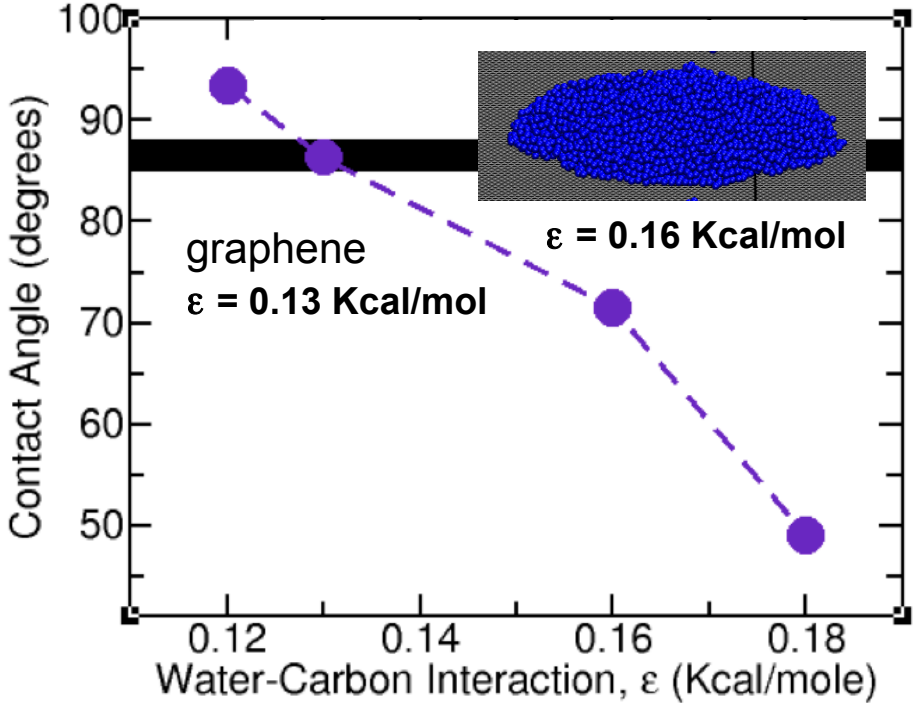
Rugged hydrophobic or hydrophilic : homogeneous nucleation for both

Two ways of increasing the hydrophilicity of the surfaces



Heterogeneous:
Decorate graphene with -OH

OH modeled by replacing C→mW

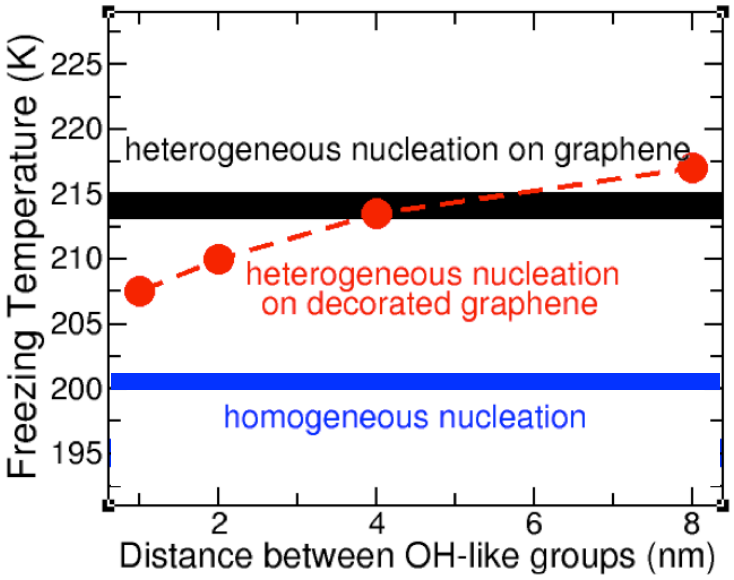


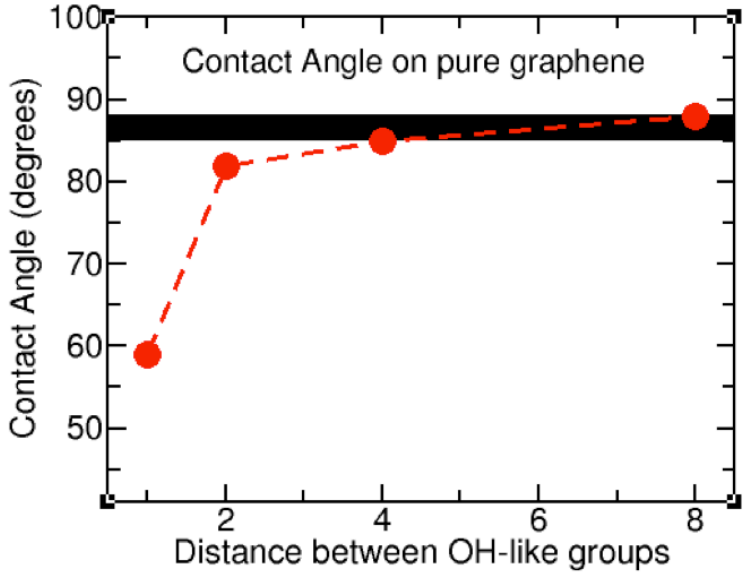
Homogeneous:
tune water-carbon attraction

Mimics graphene deposited on metal
(Rafiee et al Nature Mat. 2012)

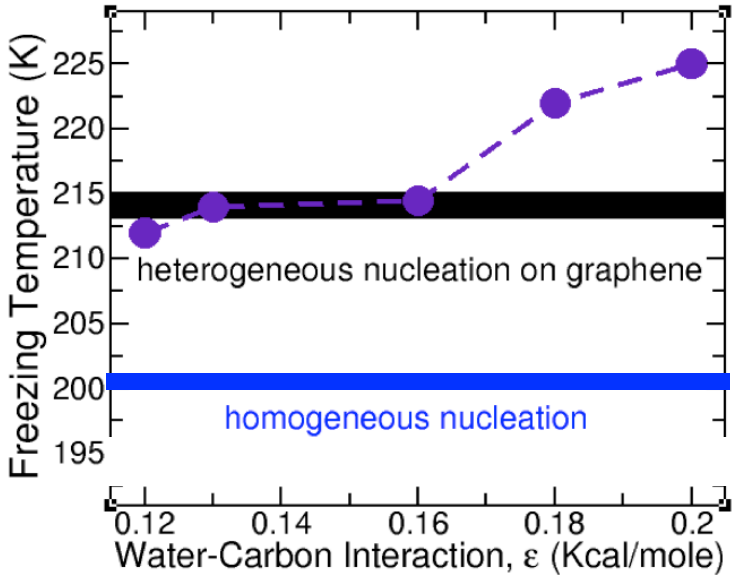
Surface hydrophilicity is not a relevant parameter for ice formation

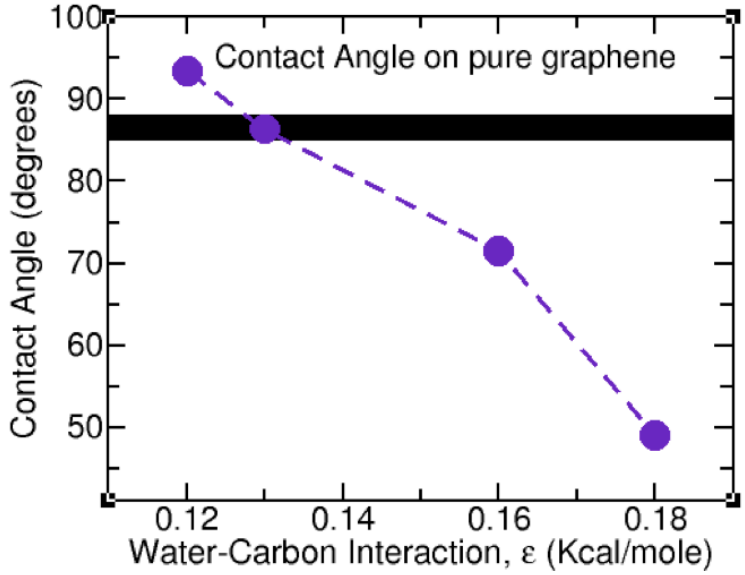
Decorated surfaces: T_f increases with θ



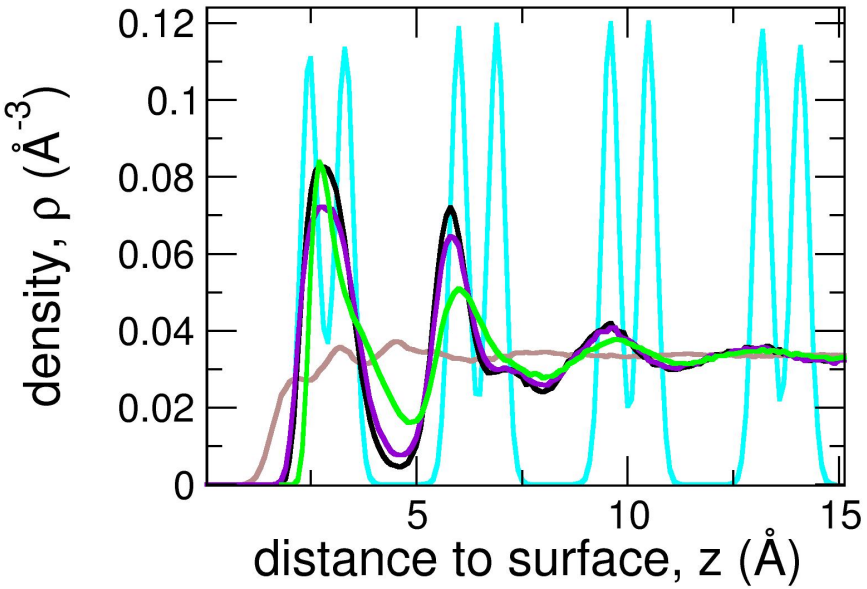


Homogeneous surfaces: T_f decreases with θ

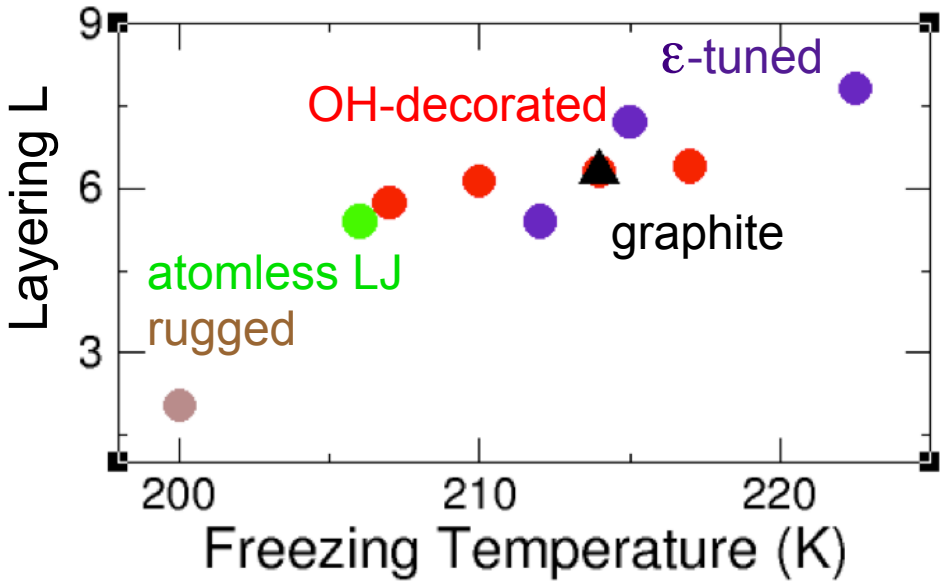




Ice freezing correlates with layering of liquid water at the surfaces



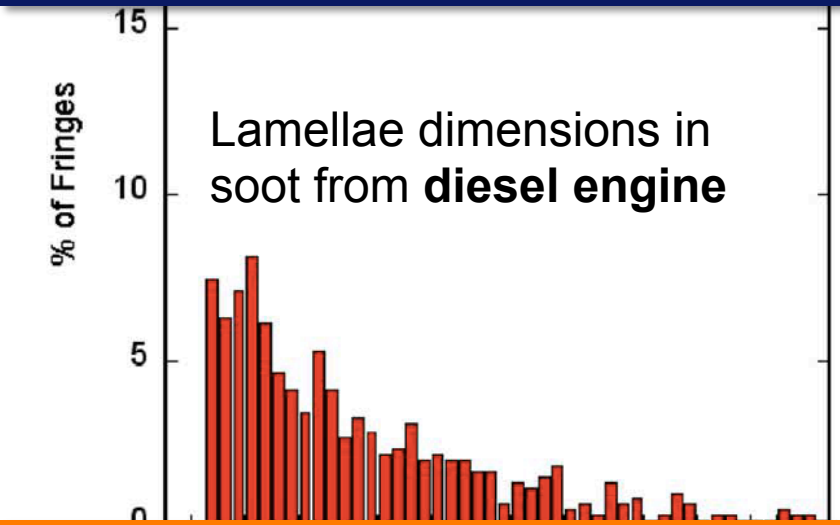
Quantify deviation from uniform distribution



Ice crystallization occurs at higher temperatures on surfaces that induce layering and ice-like ordering in the interfacial liquid.

Lupi, Hudait and Molinero, to be submitted

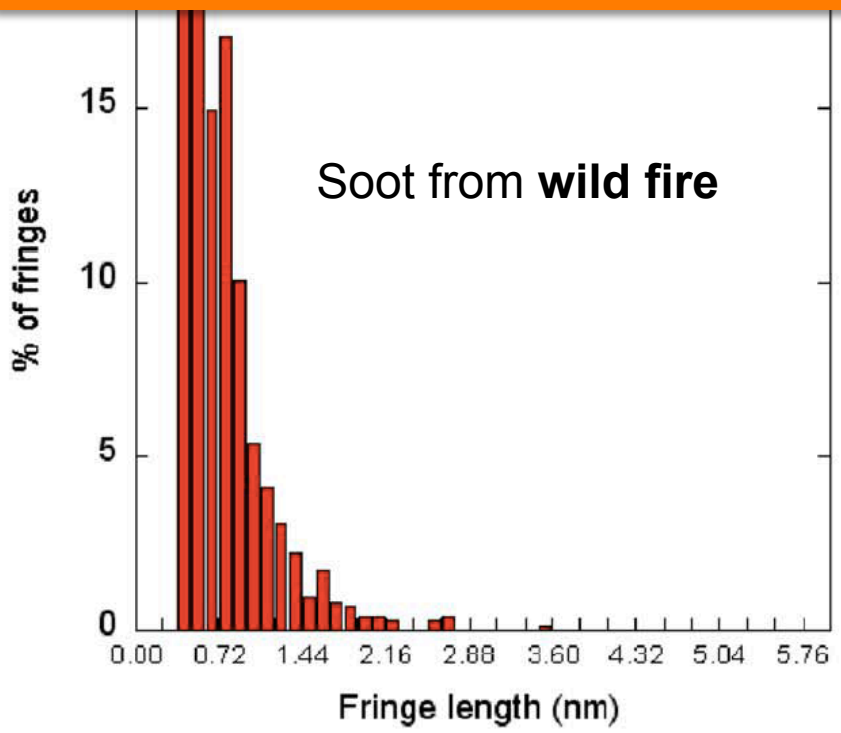
Soot displays distributions of lamella sizes and curvatures

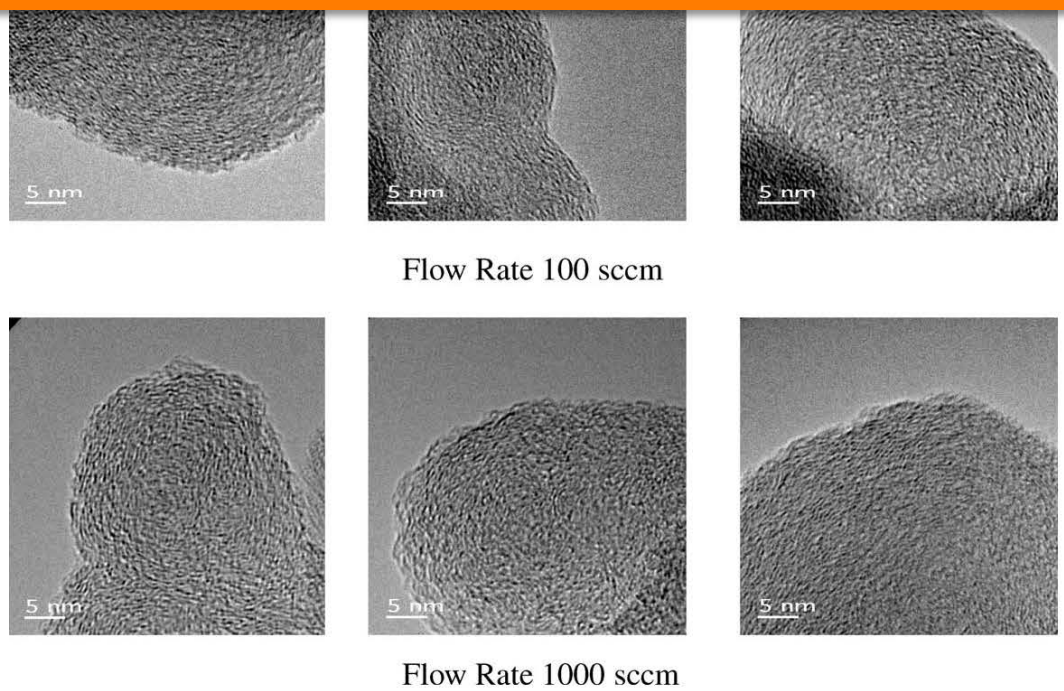


Lamellae dimensions from 0.5 to 6 nm
(Vander Wal et al. Aerosol Science 2010)

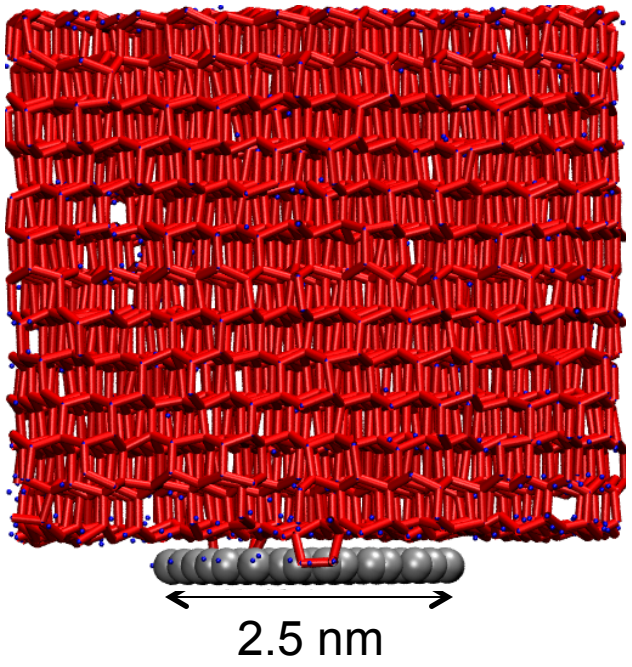
Radius of curvature range from 2 to 50 nm
(Vander Wal et al. Combustion and Flame 2004)

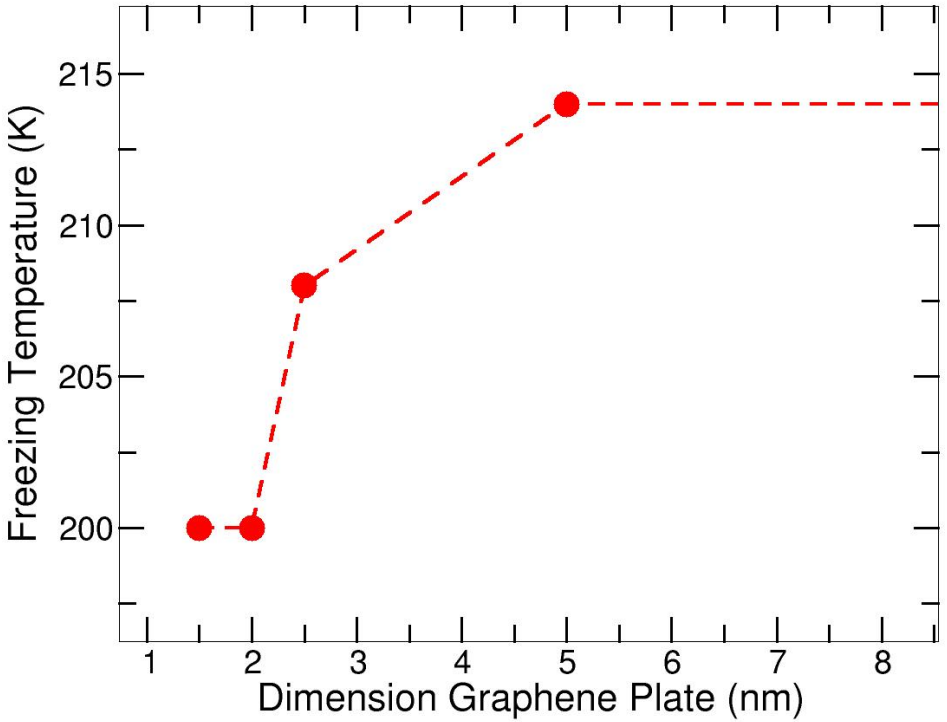
Can variability in nanostructure account for dispersion in ice freezing T?

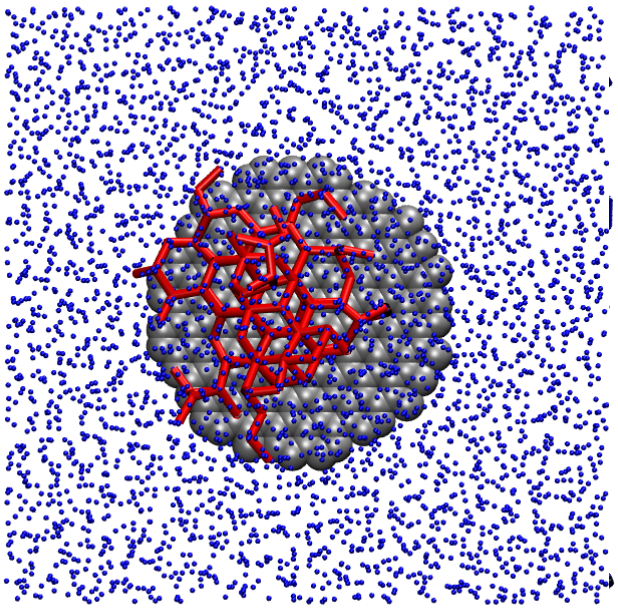




Decrease in size of the lamella reduces its effectiveness as IN







Hexagonal patches survive in D = 2.5 nm disk

IN effectiveness decreases as the size of the disk becomes comparable to the size of the critical ice nuclei for homogeneous freezing.

Lupi, Hudait and Molinero, to be submitted

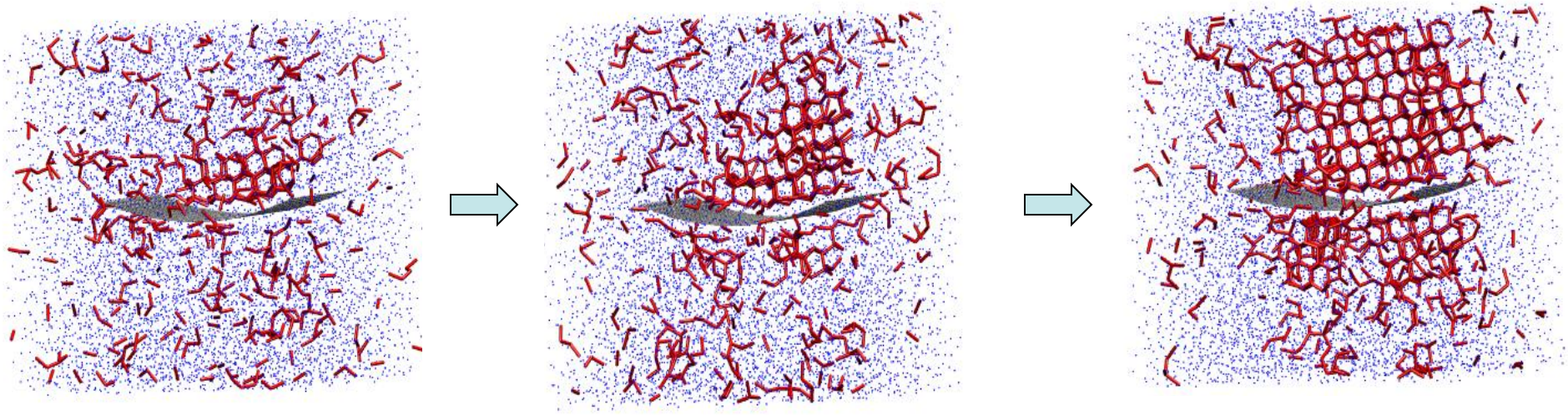
Curved graphitic surfaces are less effective IN than flat graphite

Radius of curvature (nm)	$T_f - T_f^{homo}$ (K)
Infinite (flat)	14
27.1	11
6.8	2
2.0	0 (homo)

Curved surfaces are 5 nm x 5 nm pieces of (100,100) and (400,400) carbon nanotubes

Freezing is faster at the concave surface

Rc = 6.8 nm, isothermal freezing at $T_f + 4$ K



Conclusions

Homogeneous freezing of water and solutions
is controlled by a structural transformation within the liquid.

***Low-density liquid water is the mother of ice.**

***Ice crystallization rate reaches a maximum not far below T_H.**

***The freezing temperature of solutions is a colligative property with higher composition dependence than Tm.**

Heterogeneous freezing of water on carbon surfaces
Is promoted by ordering of interfacial water.

***Layering of water at the surface correlated to freezing temperature.**

***Hydrophilicity of the surface is not a relevant variable for ice nucleation.**

***Variations in soot nanostructure could account for variability in freezing**

Coworkers & Funding

THE UNIVERSITY OF UTAH®

Emily Moore & Waldemar Hujo

Charusita Chakravarty (Delhi)

(water anomalies)

CHPC

Emily Moore & Jessica Johnston

(crystallization of water)

Arnold and Mabel BECKMAN FOUNDATION

Griffin Bullock & Ly Le

(crystallization and vitrification of solutions)

NSF

Laura Lupi & Arpa Hudait

(heterogeneous nucleation on carbon)

ARL