Computational Studies of Ice Nucleation

Carlos Vega
Departamento de Química Física
Universidad Complutense
Madrid,SPAIN
J.L.F.Abascal, E.Sanz, C.Valeriani
J.R.Espinosa,P.Rosales,A.Zaragoza,C.Navarro

Modelling water

A

(1) Electronic structure calculations (MP2,DFT)
+
(2) Path integral simulations "Feynman"

B

(1) Electronic structure calculations (MP2,DFT)
+
(2) Classical statistical mechanics

C

(1) Empirical expression for $E_e(\vec{R}^N) + V_N$
+
(2) Path integral simulations "Feynman"

D

(1) Empirical expression for $E_e(\vec{R}^N) + V_N$ (TIP3P,SAFT)
+
(2) Classical statistical mechanics

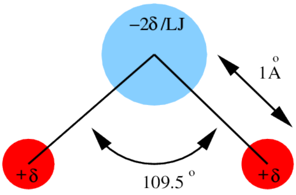
Classical Statistical Mechanics

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

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

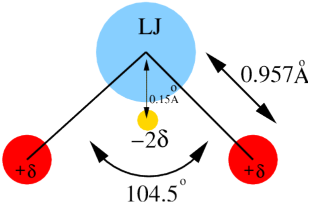
Team D. WATER MODELS

SPC/E, Berendsen et al. (1987)
TIP3P, Jorgensen et al. (1983)



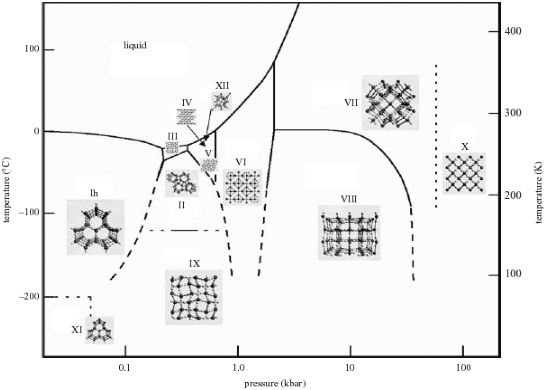
1 center LJ
3 charges
SPC/E = 5000 citations

TIP4P, Jorgensen et al. 1983



1 center LJ
3 charges
TIP3P+TIP4P = 14000 citations

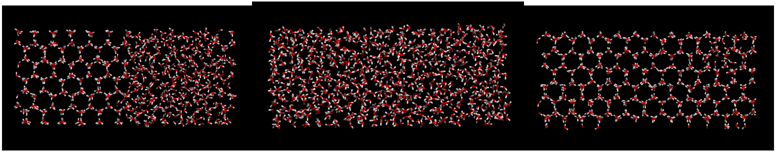
The phase diagram of water



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

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

DIRECT DETERMINATION OF THE FLUID-SOLID EQUILIBRIA



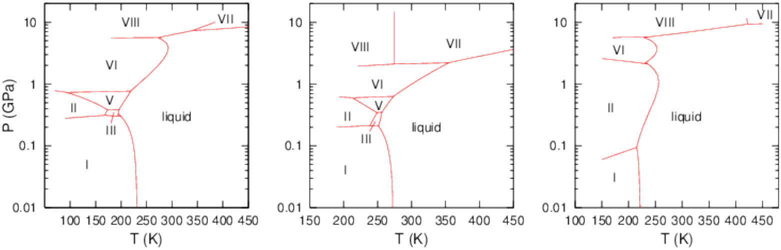
Melting temperatures obtained by direct coexistence are in agreement with those obtained from free energy calculations

R.G.Fernandez, J.L.F.Abascal and C.Vega, *JCP* **124** 144506 (2006)

A. J. C. Ladd and L. V. Woodcock, *CPL* **51** 155 (1977)

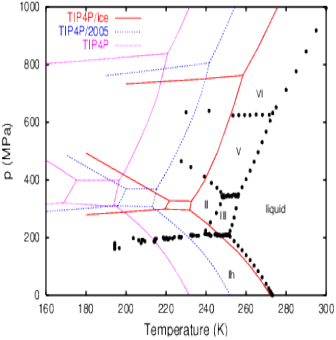
The phase diagram of the TIP4P and SPC/E models

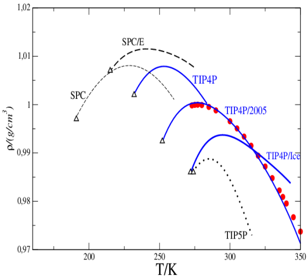
E. Sanz, et al., *PRL* **92** 255701 (2004)



TIP4P **Experimental** **SPC/E**

TIP4P/Ice and TIP4P/2005



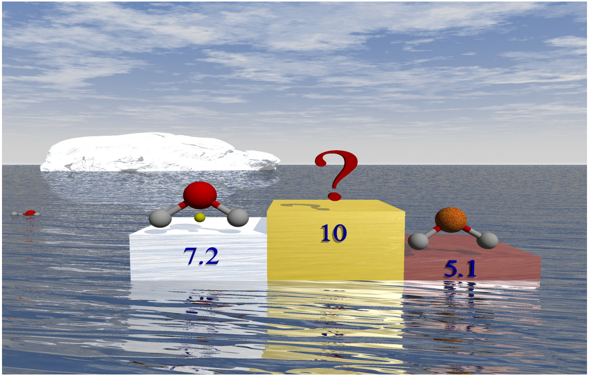


TIP4P/Ice: J.L.F.Abascal, E.Sanz, R.Garcia Fernandez and C.Vega, JCP 122, 234511 (2005)

TIP4P/2005: J.L.F.Abascal, and C.Vega, JCP 123, 234505 (2005)

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
C_p	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/T_c, TMD-T_m	4.3	6.7	8.3	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
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	**2.9**	**5.0**	**5.0**	**7.2**	**3.8**

Graphical summary



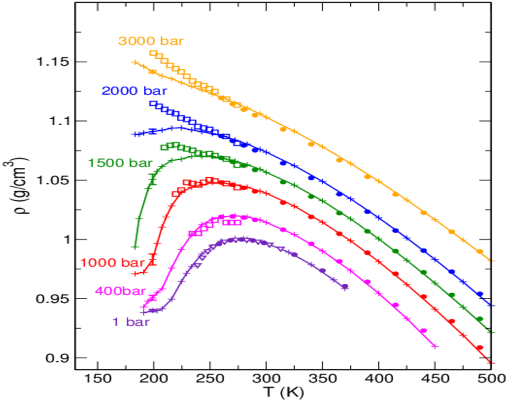
C.Vega and J.L.F.Abascal, Simulating water with rigid non-polarizable models: a general perspective , Phys.Chem.Chem.Phys. 13 19663 (2011)

PCCP special issue: The Physics and Chemistry of Water and ice , volume 13, issue 44, (2011)

Editors: C. Vega, J.L.F.Abascal and P.G. Debenedetti

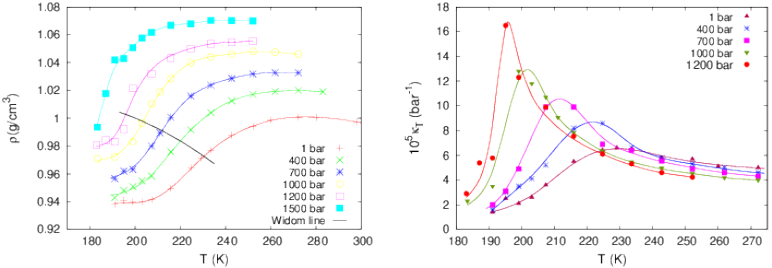
TIP4P/2005 , 850 citations (150 citations/year in the last two years)

Supercooled water: Water below the melting point (metastable with respect to freezing)



Simulation: J.L.F.Abascal and C. Vega , *JCP* **134** 186101 (2011)
Experiment(open symbols) O.Mishima , *JCP* **133** 144503 (2010)

Widom line (maximum in κ_T) for TIP4P/2005



Maxima in κ_T close to minimum in α (inflection point in EOS)

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

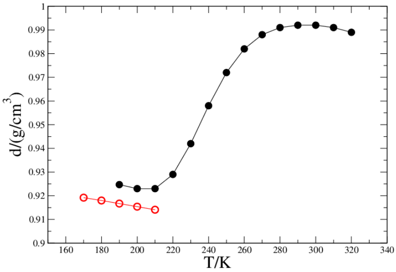
A strong debate is going on the possible existence of a second critical point for water !

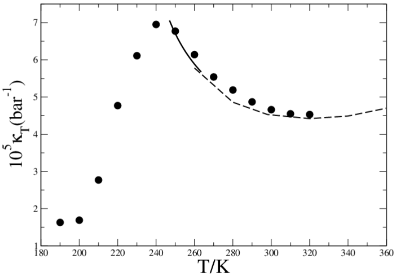
P.H.Poole,F.Sciortino,U.Essmann,H.E.Stanley,Nature,360,324,(1992)

Y.Liu,J.C.Palmer,A.Z.Panagiotopoulos,P.G.Debenedetti,JCP,137,214505,(2012)

D.T.Limmer,D.Chandler,JCP,135,134503 (2011).

Widom line (maximum in κ_T) for TIP4P/ICE





Maxima in κ_T

J.R.Espinosa et al. , J.Chem.Phys., submitted, (2016)

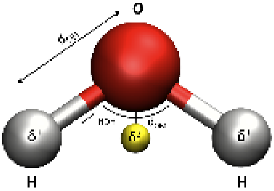
Does the isothermal compressibility diverge (Angell) ?

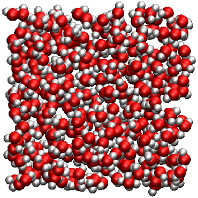
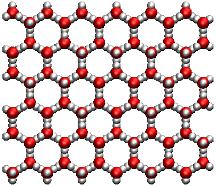
Is the maximum in the isothermal compressibility due to the transient formation of ice (Chandler) ?

SIMULATION STUDY OF THE NUCLEATION OF ICE

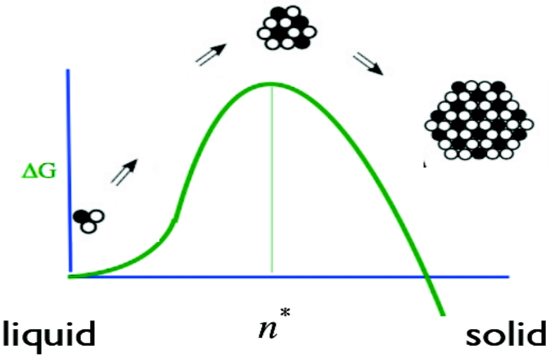
What do we need ?

- We need a reasonable potential model for water
- We need a procedure to estimate the nucleation rate J (number of critical clusters of ice per unit of time and volume)



CLASSICAL NUCLEATION THEORY



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

$$\Delta G^* = \frac{16\pi\gamma^3}{3\rho_s^2|\Delta\mu|^2}$$

Simulation methods to determine J

$$J = \frac{Number \quad of \quad critical \quad clusters}{tV}$$

Rigorous methods

- Brute force simulations
- Transition path sampling
- Forward flux sampling
- Umbrella sampling

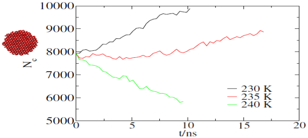
An approximate technique : seeding

J. R. Espinosa, C. Vega, C. Valeriani and E. Sanz, J. Chem. Phys. , 144 , 034501, (2016)

$$J_{US,seeding} = \rho_{liq} f_+ Z exp(-\beta \Delta G^*)$$

- Insert a solid cluster and determine the temperature at which is critical T_c
- Determine ρ_s and $\Delta\mu$ at T_c from NpT runs + TI
- Determine the attachment rate f_+ from computer simulations at T_c
- Use CNT expression for N_c to estimate γ
- Use CNT expression for ΔG^* and Z

AT WHICH T IS THE CLUSTER CRITICAL ?



we find the temperature range within which
the cluster can be considered critical

Nc=7900 ⟶ Tc=237.5K

MD simulations of water (TIP4P/2005 and/or TIP4P/ICE) using GROMACS (RES)

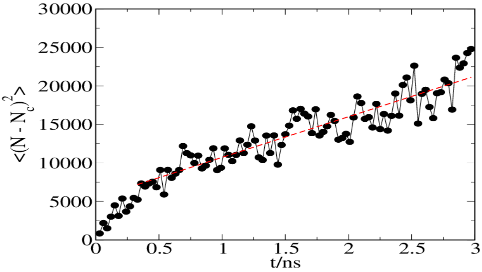
Number of liquid molecules	Number of ice molecules (cluster)
22712	600
76781	3170
182585	7931

EVALUATING THE KINETIC PREFACTOR κ

$$\kappa = \rho_{liq} f_+ Z$$

$$Z = \sqrt{\frac{-G''}{2\pi kT}} = \sqrt{\frac{\Delta\mu}{6\pi k_B T N_c}}$$

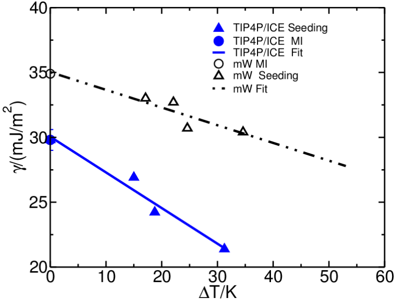
f_+ is one half of the slope of this plot

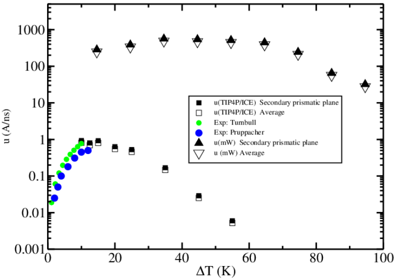


$$f^+ = \frac{24D(N_c)^{2/3}}{\lambda^2} \tag{1}$$

λ is the attachment length

Interfacial free energy and growth rate

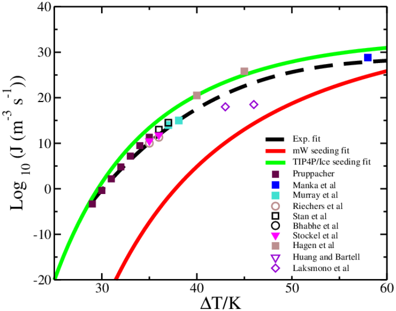


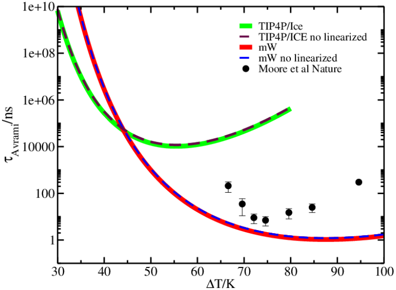


$$\gamma^3 = N_c \frac{3\rho_s^2|\Delta\mu|^3}{32\pi}$$

J.R.Espinosa et al. , J.Chem.Phys., submitted, (2016)

Nucleation rate J from simulations

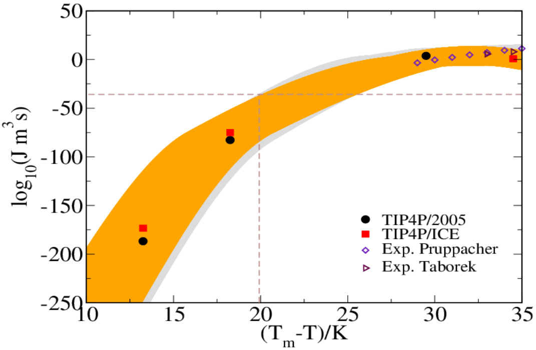




J.R.Espinosa et al. , J.Chem.Phys., submitted, (2016)

- TIP4P/ICE Good agreement with experiment
- T_H^{exp} well predicted
- Cooling rate $10^7 K/s$ required to avoid the formation of ice and to form a glass

NUCLEATION RATES J FOR TIP4P/2005 AND TIP4P/ICE



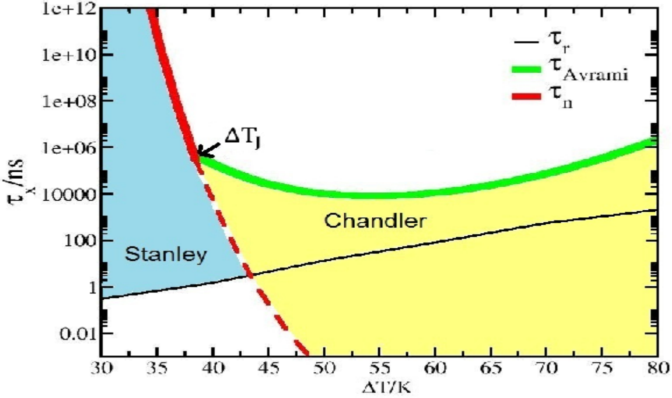
E. Sanz,C.Vega ,J. R. Espinosa ,J.L.F. Abascal and C.Valeriani , JACS, 135, 15008, (2013)

- For temperatures higher than -20 $^\circ$C, it would take more than the age of the universe to find a nucleation even with all the water of the hydrosphere !

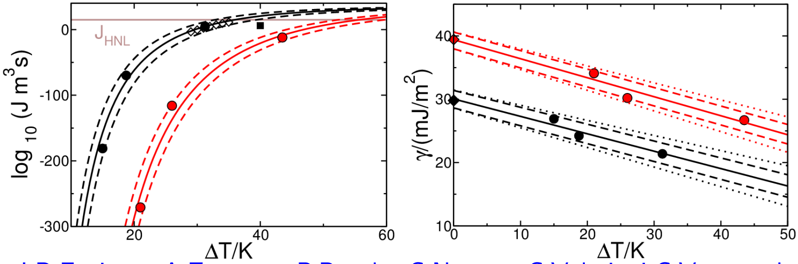
Global scenario in the Crystallization of water

P.Gallo,.,C.Vega.,Water a Tale of Two Liquids,Chem.Rev.,116,7463,(2016)
J.R.Espinosa et al. , J.Chem.Phys., submitted, (2016)

$$\tau_{Avrami} = ((3\phi)/(\pi J u^3))^{1/4}$$
$$\tau_{nu} = 1/(JV)$$
$$\tau_x = max(\tau_{Avrami}, \tau_n)$$



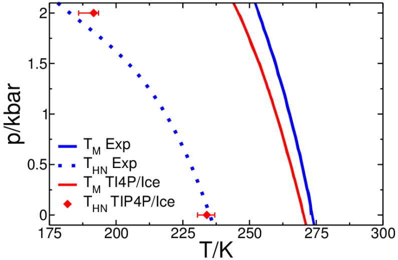
The effect of pressure on the nucleation of ice. I. Results from seeding

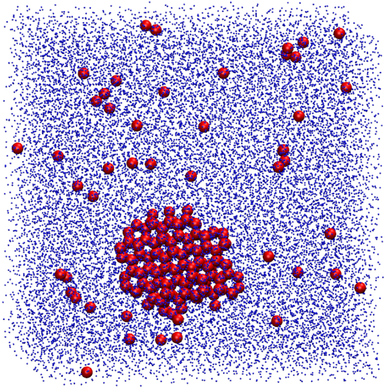


J.R.Espinosa,A.Zaragoza,P.Rosales,C.Navarro,C.Valeriani,C.Vega and E.Sanz , Phys.Rev.Lett.,in press,(2016)

- Pressure increase the value of γ thus reducing the nucleation rate J

The effect of pressure on the nucleation of ice. II. Comparison to experiment





J.R.Espinosa, C.Navarro, P.Rosales, C.Valeriani, C.Vega and E.Sanz ,

Phys. Rev. Lett. , in press, (2016)

- The homogeneous nucleation line is NOT paralell to the melting line due to the increase of γ with pressure

Conclusions

- The prediction of the phase diagram is a severe test for water models.
- The TIP4P/2005 is probably the best rigid non-polarizable models of water available now.
- The predictions of TIP4P/2005 (and TIP4P/ICE) for J are consistent (taking into account the uncertainties) with the experimental values. The model predicts a homogeneous nucleation temperature of about 37K , in agreement with experiments.
- The minimum time to freeze water is 10 microseconds and is obtained at 55K below the melting point. To obtain water in glassy state is necessary to cool at a rate higher than $10^7 K/s$.
- The maximum in κ_T found for TIP4P/ICE and TIP4P/2005 models is real and is not due to the formation of ice (the nucleation rate is very low at the temperature of the maximum). That reinforces the possibility of a liquid-liquid phase separation in supercooled water.
- Pressure makes the formation of ice more difficult (i.e it decreases the nucleation rate). The origin of this effect is the increase of the interfacial ice-water free energy with pressure. This effects has important practical applications as there are several areas where the formation of ice should be avoided: cryopreservation, food industry.

FURTHER DETAILS

Simulating water with rigid non-polarizable models: a general perspective
C.Vega,J.L.F.Abascal,Phys.Chem.Chem.Phys.,13,19663,(2011)

Homogeneous Ice Nucleation at Moderate Supercooling from Molecular Simulation
E.Sanz,C.Vega,J.R.Espinosa,R. Caballero-Bernal,J.L.F.Abascal,C.Valeriani
J.Am.Chem.Soc.,135,15008,(2013)

Homogeneous ice nucleation evaluated for several water models
J. R. Espinosa, E. Sanz, C. Valeriani and C. Vega
J.Chem.Phys., (2014), J.Chem.Phys. 141 18C529 (2014).

Competition between ices Ih and Ic in homogeneous water freezing
A.Zaragoza,J.R.Espinosa,C.Valeriani,C.Vega,E.Sanz,J.Chem.Phys.,143,134504,(2015)

Interfacial Free Energy as the Key to the Pressure-Induced Deceleration of Ice Nucleation
J.R.Espinosa,A.Zaragoza,P.Rosales,C.Navarro,C.Valeriani,C.Vega and E.Sanz , Phys.Rev.Lett.,in press,(2016)

On the time required to freeze water
J.R.Espinosa,C.Navarro,E.Sanz,C.Valeriani,C.Vega,J.Chem.Phys., submitted, (2016)

Water a Tale of Two Liquids
P.Gallo,..H.E.Stanley..C.Vega..,Chem.Rev.,116,7463,(2016)