The fluid-solid transition in simulation studies of water: thermodynamic and kinetic aspects

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Modelling water

A	B	C	D
(1) Electronic structure calculations (MP2,DFT) + (2) Path integral simulations "Feynman"	(1) Electronic structure calculations (MP2,DFT) + (2) Classical statistical mechanics	(1) Empirical expression for $E_e(\vec{R}^N) + V_N$ + (2) Path integral simulations "Feynman"	(1) Empirical expression for $E_e(\vec{R}^N) + V_N$ (TIP3P,SAFT) + (2) Classical statistical mechanics

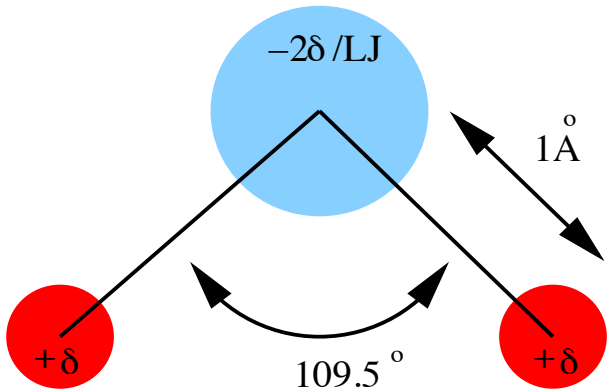
Classical Statistical Mechanics

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

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

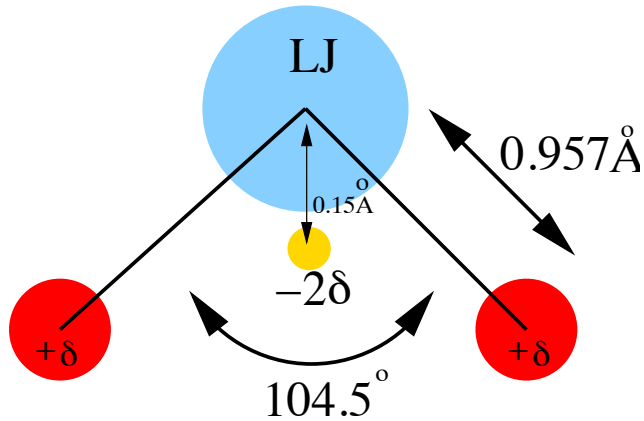
Team D. WATER MODELS

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



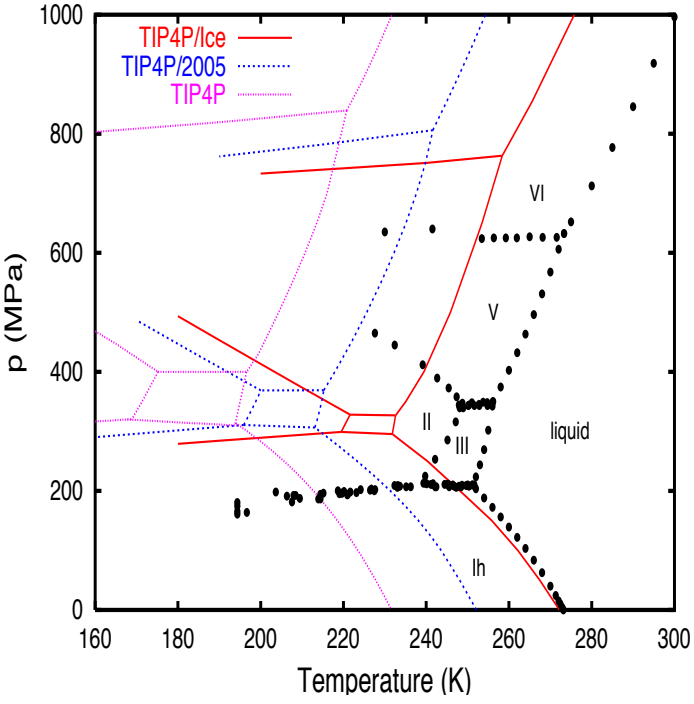
1 center LJ
3 charges
SPC/E

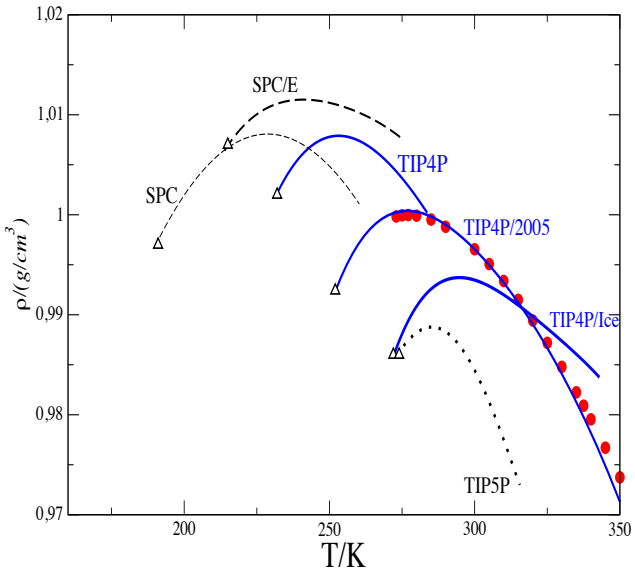
TIP4P, Jorgensen et al. 1983



1 center LJ
3 charges
TIP4P

TIP4P/Ice and TIP4P/2005



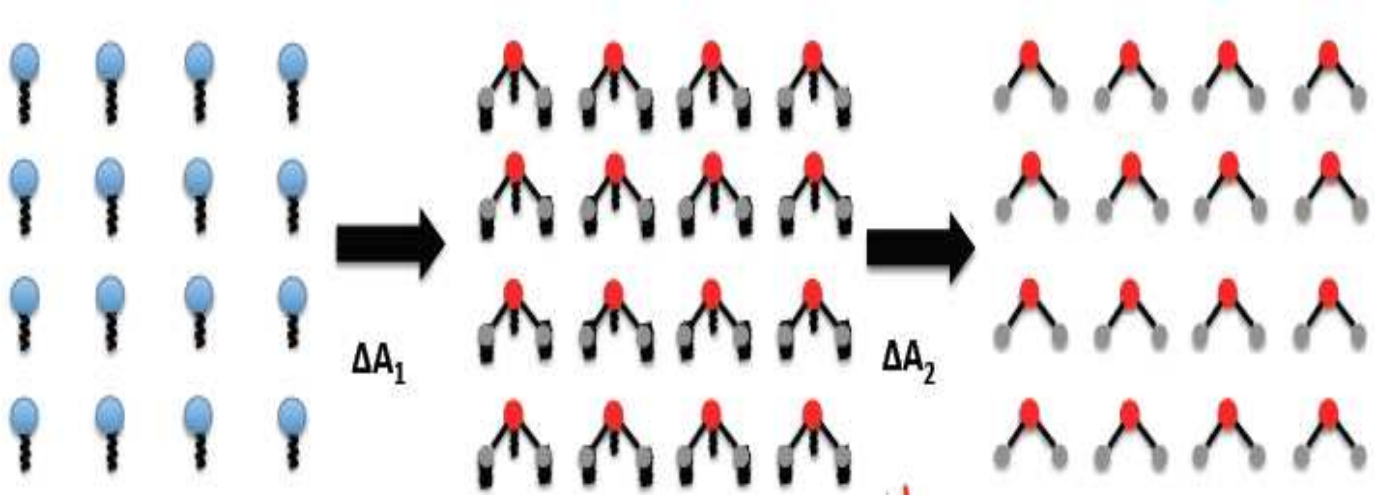


TIP4P/Ice: J.L.F.Abascal, E.Sanz, R.Garcia Fernandez and C.Vega, JCP 122, 234511 (2005)

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

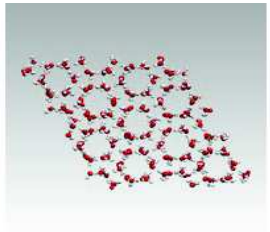
THE EINSTEIN CRYSTAL METHOD

Frenkel-Ladd, 1984, JCP Vega and Noya JCP, (2007),
Noya,Conde,Vega, JCP (2008)

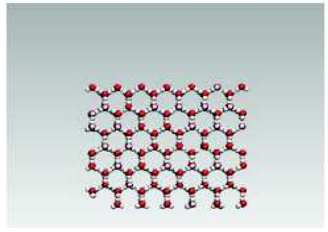


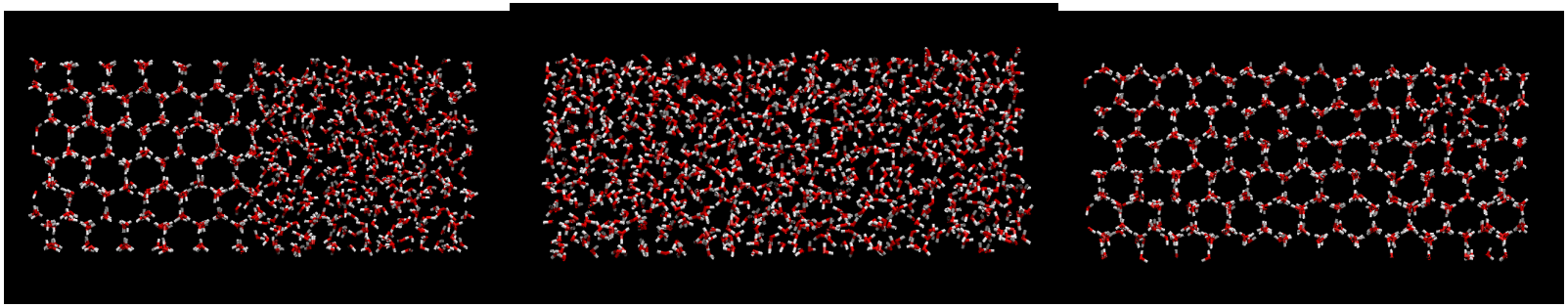
$$A_{sol}(T,V) = A_0(T,V) + \Delta A_1(T,V) + \Delta A_2(T,V)$$

Melting point of ice Ih and phase diagram

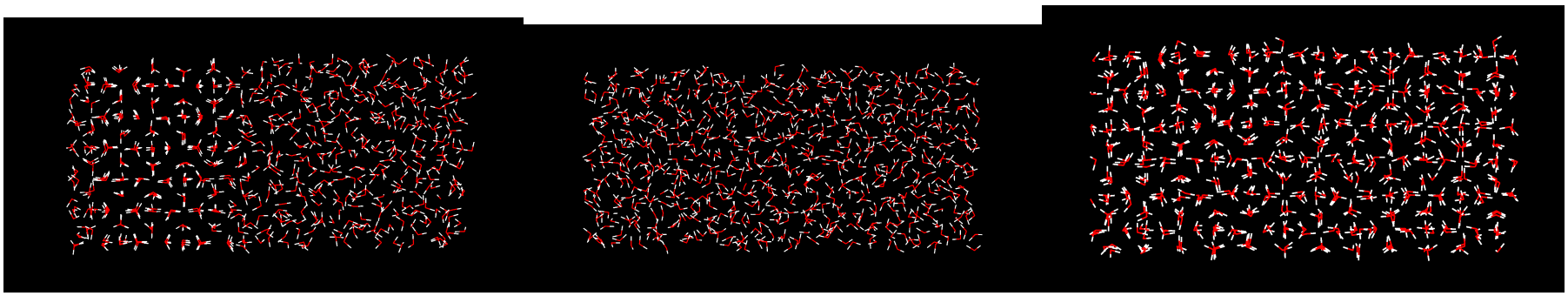


		ρ(N/V)	A_0	ΔA_1	ΔA_2	$A_{sym.}$	$S^{Pauling}$	A_{sol}
G	II	0.03929	27.594	-37.08(1)	-15.359(3)	-0.69	-	-25.54(4)
Ref. 23	II	0.03929	-	-	-	-	-	**-25.563**
MC*	Ih	0.03103	27.59	-37.70(1)	-15.75(1)	-	-0.405	-26.27(2)
MC	Ih	0.03103	27.59	-37.70(1)	-15.05(1)	-0.69	-0.405	-26.26(2)
G	Ih	0.03103	27.59	-37.70(1)	-15.05(3)	-0.69	-0.405	-26.26(4)
Ref. 23	Ih	0.03103	-	-	-	-	-	**-26.252**



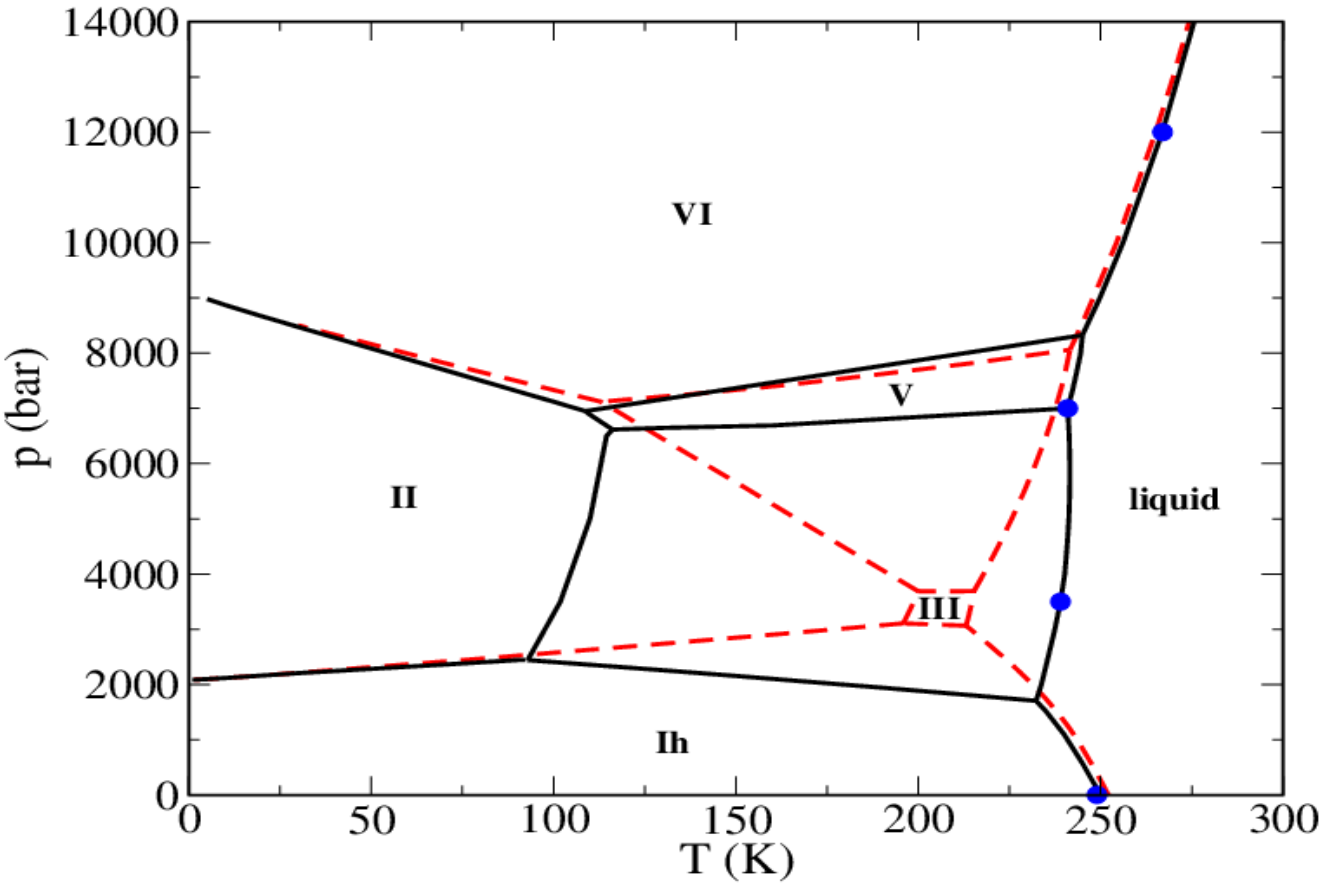


DIRECT COEXISTENCE SIMULATIONS. Ice VI.



M.M.Conde,M.A.Gonzalez,J.L.F.Abascal,C.Vega,J.Chem.Phys.,139,154505,(2013)

PHASE DIAGRAM OF TIP4P/2005

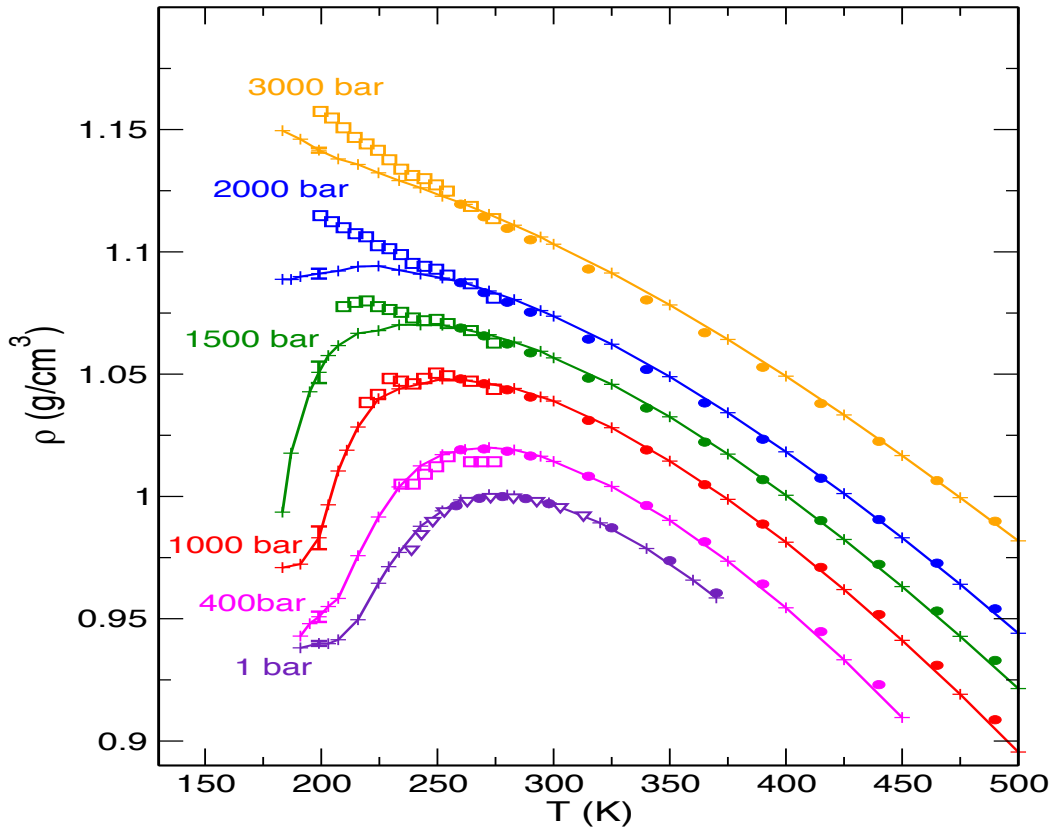


M.M.Conde,M.A.Gonzalez,J.L.F.Abascal,C.Vega,J.Chem.Phys.,139,154505,(2013)

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**

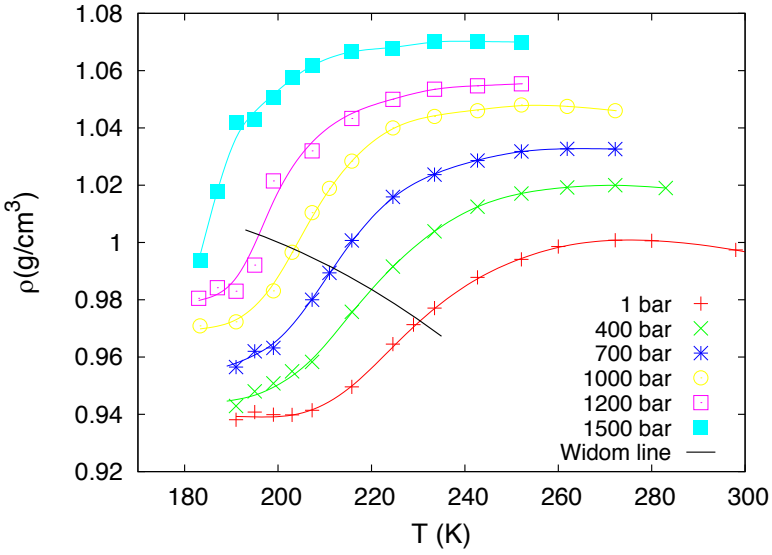
WATER BELOW THE MELTING POINT

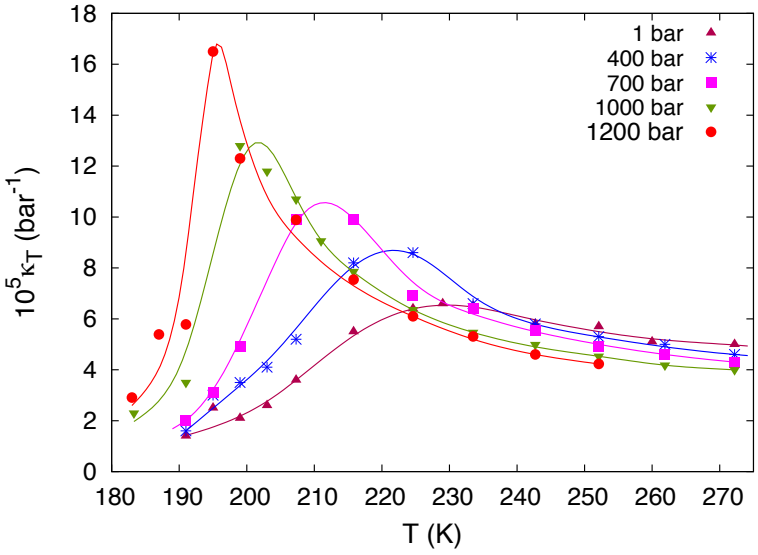
I. LIQUID PROPERTIES



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)

J.C.Palmer, F.Martelli, Y.Liu, R.Car, A.Z.Panagiotopoulos, and P. G. Debenedetti, Nature, 510, 385, (2014).

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

WATER BELOW THE MELTING POINT: NUCLEATION

TIP4P

- Brute force crystallization of ice , 512 molecules, Matsumoto and Ohmine, Nature, (2002). (230K, 0.96 g/cm^3, -5 C , -1000bar)
- Amir Haji-Akbari,P. G. Debenedetti, PNAS 2015, FFS values of J for TIP4P/ICE

Free energy barrier ΔG^* at -50 C , 1bar

- Radhakrisnan and Trout , JACS, (2003), **63** kT
- Quigley and Rodger, JCP, (2008) , **79** kT
- Brunko,Anwar,Davidchak and Handel, JPCM, (2008), **130** kT
- Buhariwalla,Bowles,Saika-Voivod,Sciortino, Eur. Phys. J. , (2015), **38**

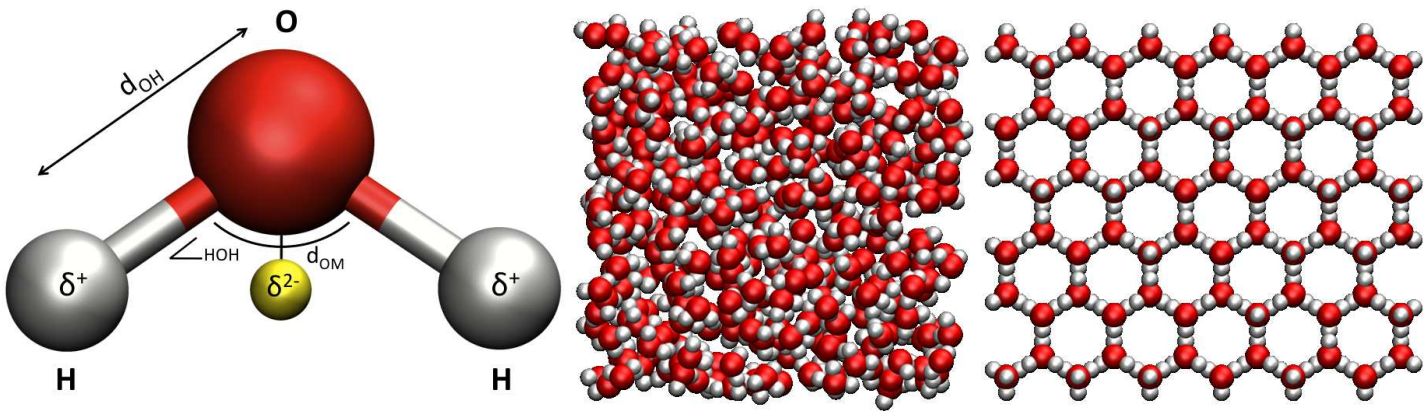
mW model of water

- Spontaneous crystallization below 205K, Moore and Molinero, Nature, (2011)
- Values of J from Forward Flux Sampling (220K-240K) , Li, Donadio, Russo and Galli, PCCP, (2011)
- Value of J from umbrella sampling at 220K, Reinhardt and Doye, , JCP, (2012)
- Brute force and umbrella sampling, Russo, Romano and Tanaka, Nature Materials, (2014)

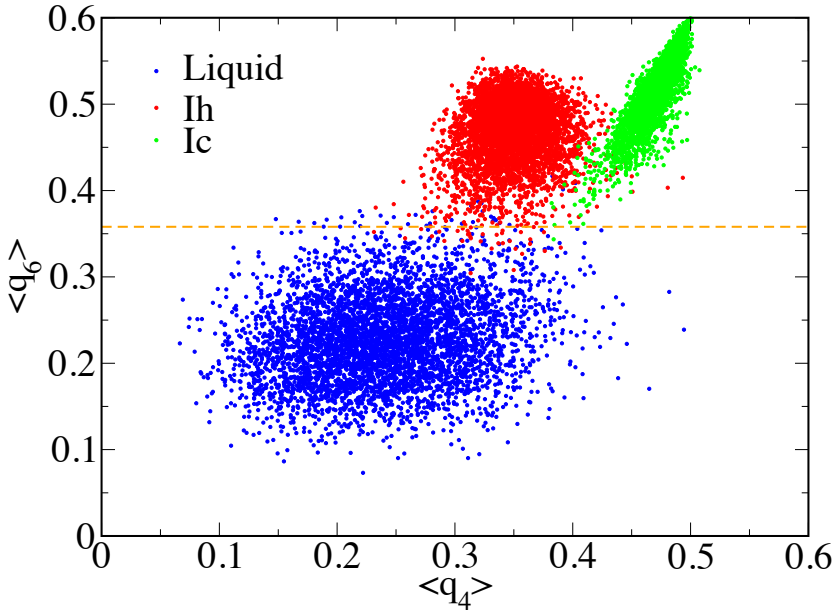
SIMULATION STUDY OF THE NUCLEATION OF ICE

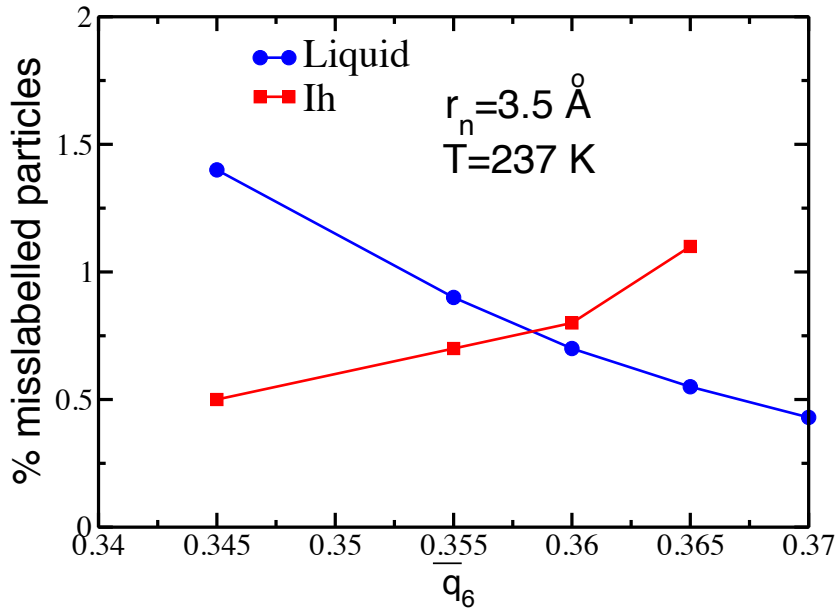
What do we need ?

- We need a reasonable potential model for water
- We need an order parameter to identify the formation of ice



SEARCHING FOR AN ORDER PARAMETER TO DISTINGUISH WATER AND ICE





If $\bar{q}_6 > 0.358$ is ice (otherwise is water)

Order parameter : Size of the largest cluster of solid particles

Properties at melting for the models considered in this work

model	T_m/K	ρ_s	ρ_f	$\Delta H_m \frac{kcal}{mol}$	γ/(mN/m)	$\frac{dp}{dT} \frac{bar}{K}$
TIP4P	230	0.94	1.002	1.05	25.6	-160
TIP4P/ICE	272	0.906	0.985	1.29	30.8	-120
TIP4P/2005	252	0.921	0.993	1.16	29.0	-135
Experiment	273.15	0.917	0.999	1.44	29	-137

Simulation methods to determine J

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

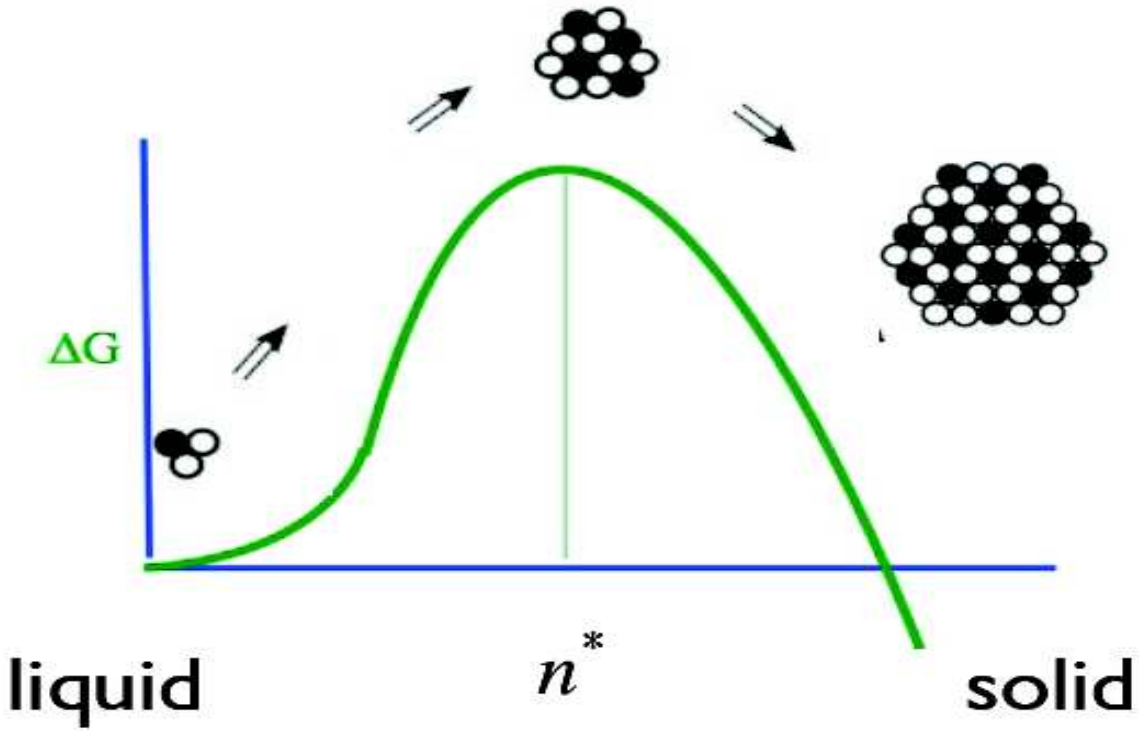
Rigorous methods

- Brute force simulations
- Transition path sampling
- Forward flux sampling
- Umbrella sampling(*)

Non-rigorous methods

- Seeding

CLASSICAL NUCLEATION THEORY



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

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

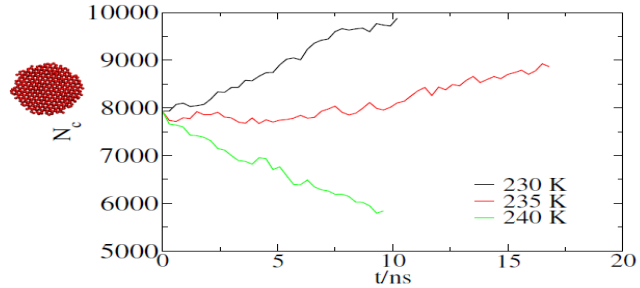
An approximate technique : seeding

- X.M. Bai and M. Li, J. Chem. Phys., 124, 124707, (2006)
- B. C. Knott , V. Molinero, M. Doherty and B. Peters, J. Am. Chem. Soc., 134, 19544, (2012)
- E. Sanz , C. Vega , J. R. Espinosa , R. Caballero-Bernal , J.L.F. Abascal and C.Valeriani J. Am. Chem. Soc. 135 15008 (2013)

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

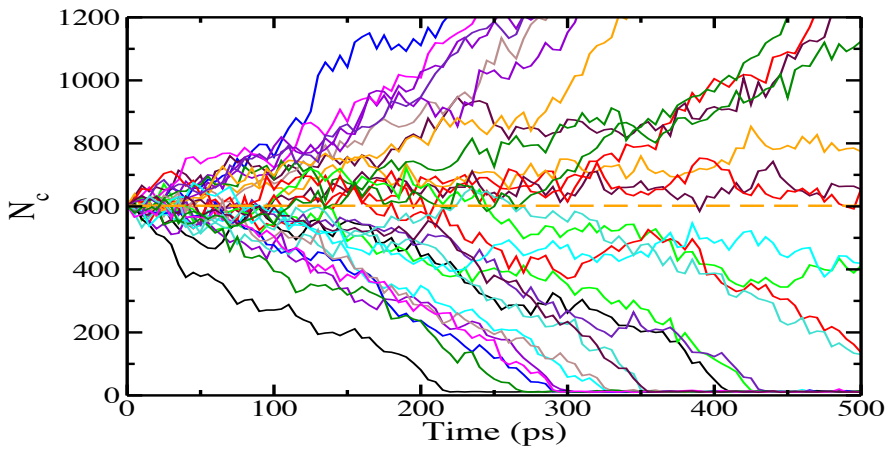
- Determine from simulations the temperature at which a solid cluster is critical T_c
- From simulations determine ρ_s , ρ_f and $\Delta\mu$ at T_c
- Determine the attachment rate f_+ from computer simulations at T_c
- Use CNT expression for N_c to estimate γ
- Use CNT expression for ΔG^* and Z

AT WHICH T IS THE CLUSTER CRITICAL ?



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

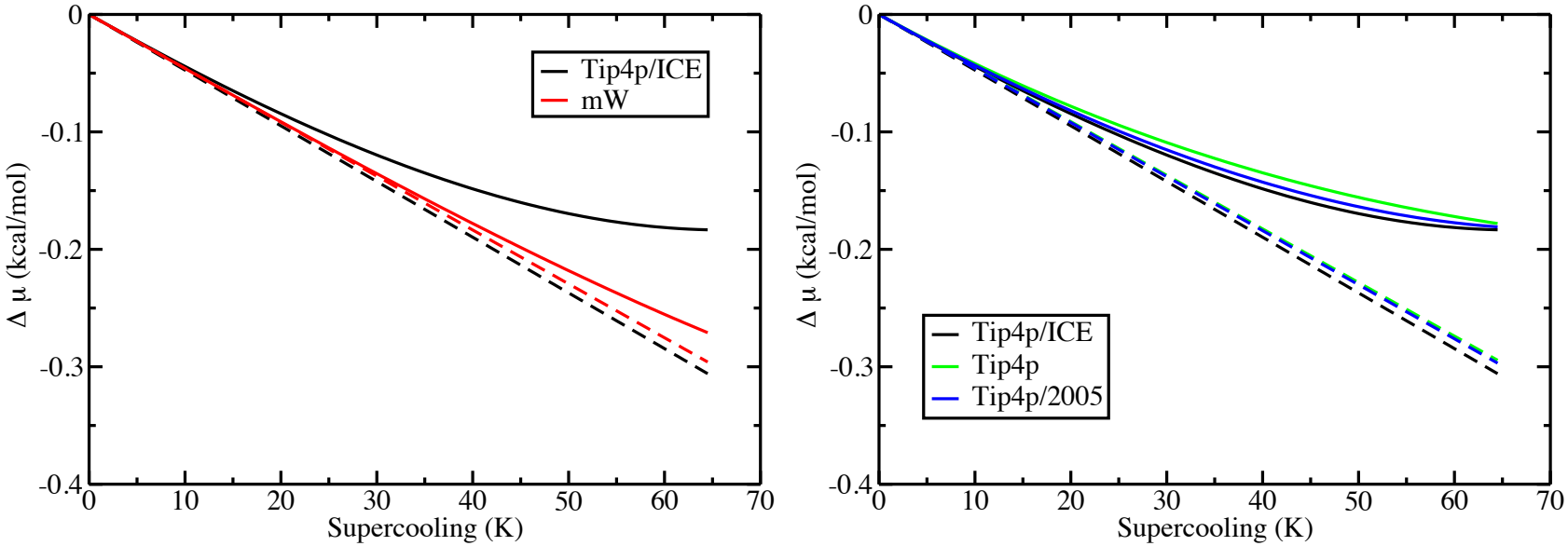
Nc=7900 ⟶ Tc=237.5K



Results for the mW at T=240K and p=1bar

N_t	N_c
22712	600
76781	3170
182585	7931

Variation of $\Delta\mu$ with supercooling



$$\Delta\mu = \Delta H_m \left(1 - \frac{T}{T_m}\right) \tag{1}$$

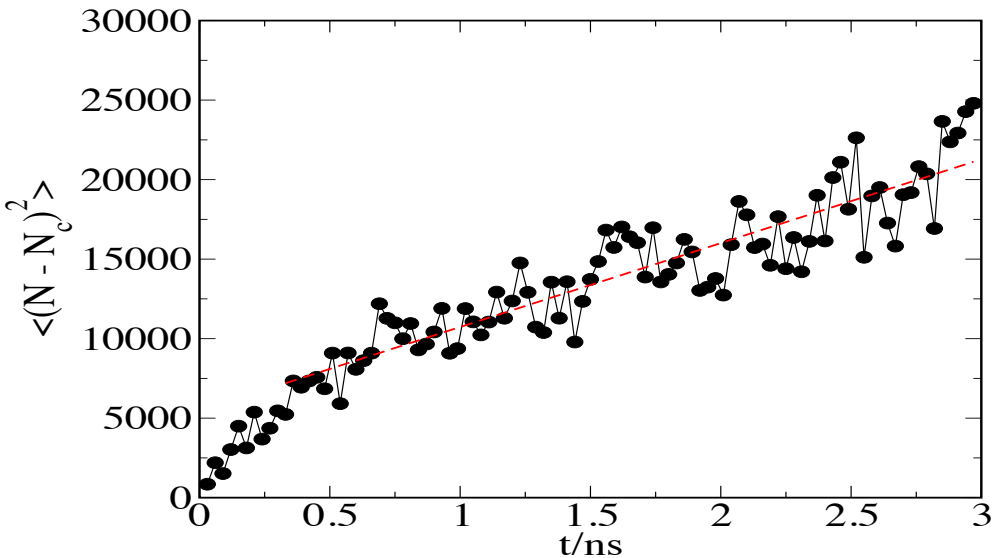
Solid lines: Thermodynamic integration (rigorous)
Dashed lines: Linear approximation (approximate)

EVALUATING THE KINETIC PREFACTOR κ

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

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

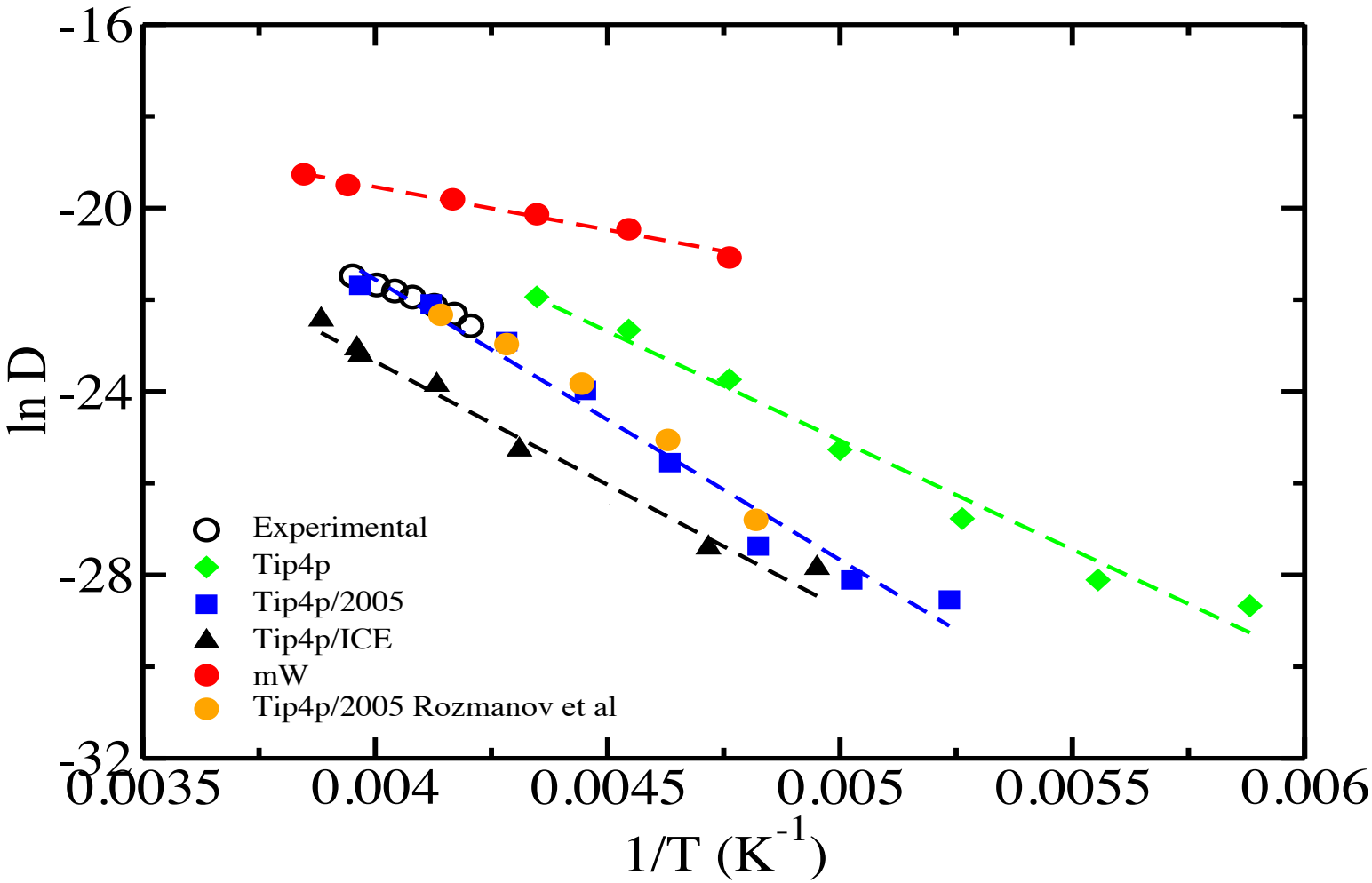
f_+ is one half of the slope of this plot



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

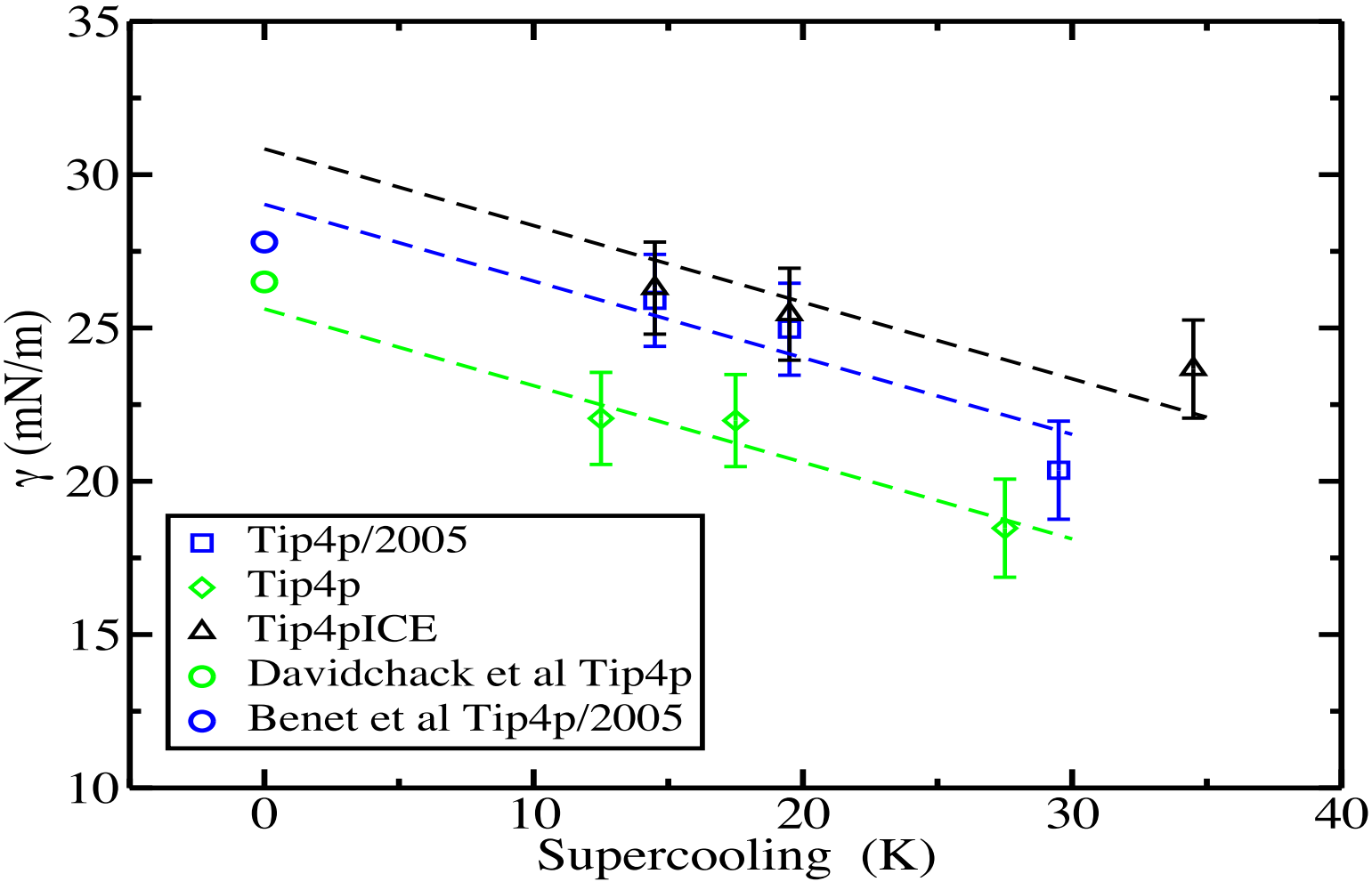
λ is the attachment length($\lambda \simeq \sigma$ provides good estimates of f^+)

Diffusion coefficient of supercooled water

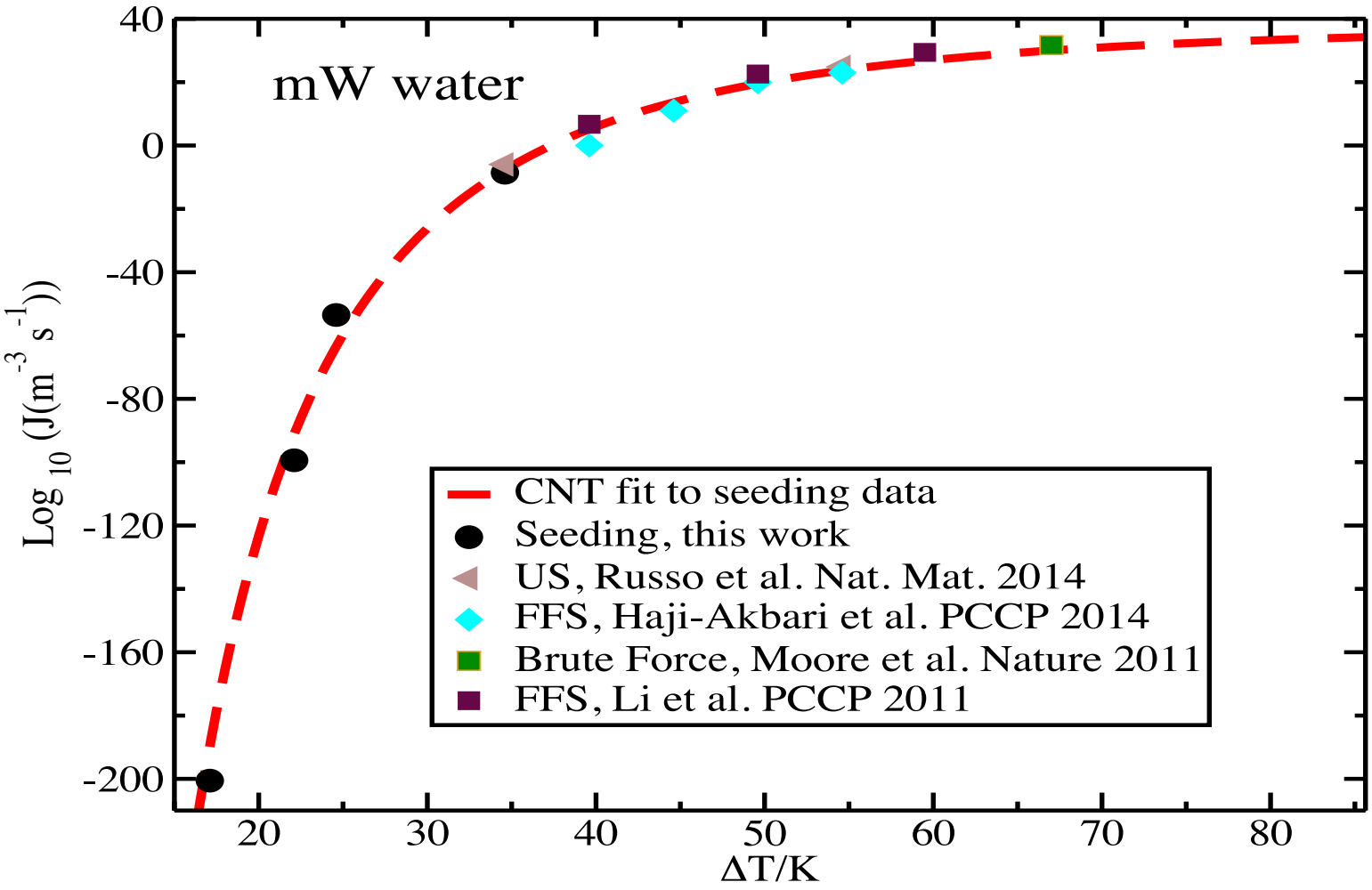


ESTIMATING γ USING CNT

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



Nucleation rate J for the mW model



Homogeneous nucleation temperature T_H

- T_H is the temperature below which water does not exist in its liquid phase (because it freezes).
- T_H is defined through kinetics not through thermodynamics
- To define T_H, it is necessary to specify both the sample size and the duration of the experiment.

$$T_H^{exp}$$

Size : 2 μm ; Time : 1 minute

$$J = \frac{1}{\frac{4}{3}\pi(2\ \ 10^{-6})^3 60} = 10^{14}/(m^3 s). \tag{3}$$

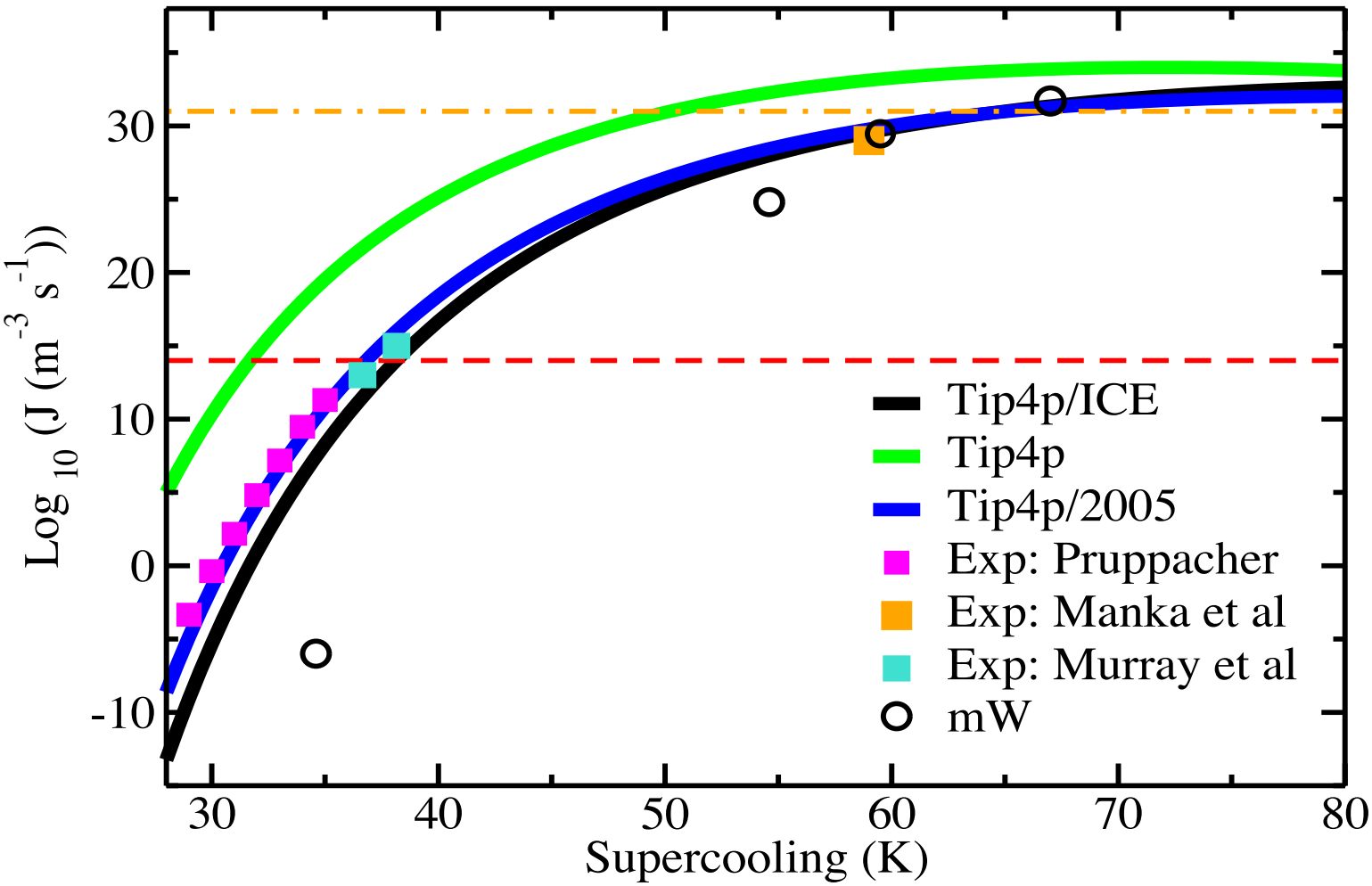
$$T_H^{sim}$$

Size : 40 $\AA$ (2000 molecules) Time : 1 μs

$$J = \frac{1}{(40\ 10^{-10})^3 10^{-6}} = 10^{31}/(m^3 s) \tag{4}$$

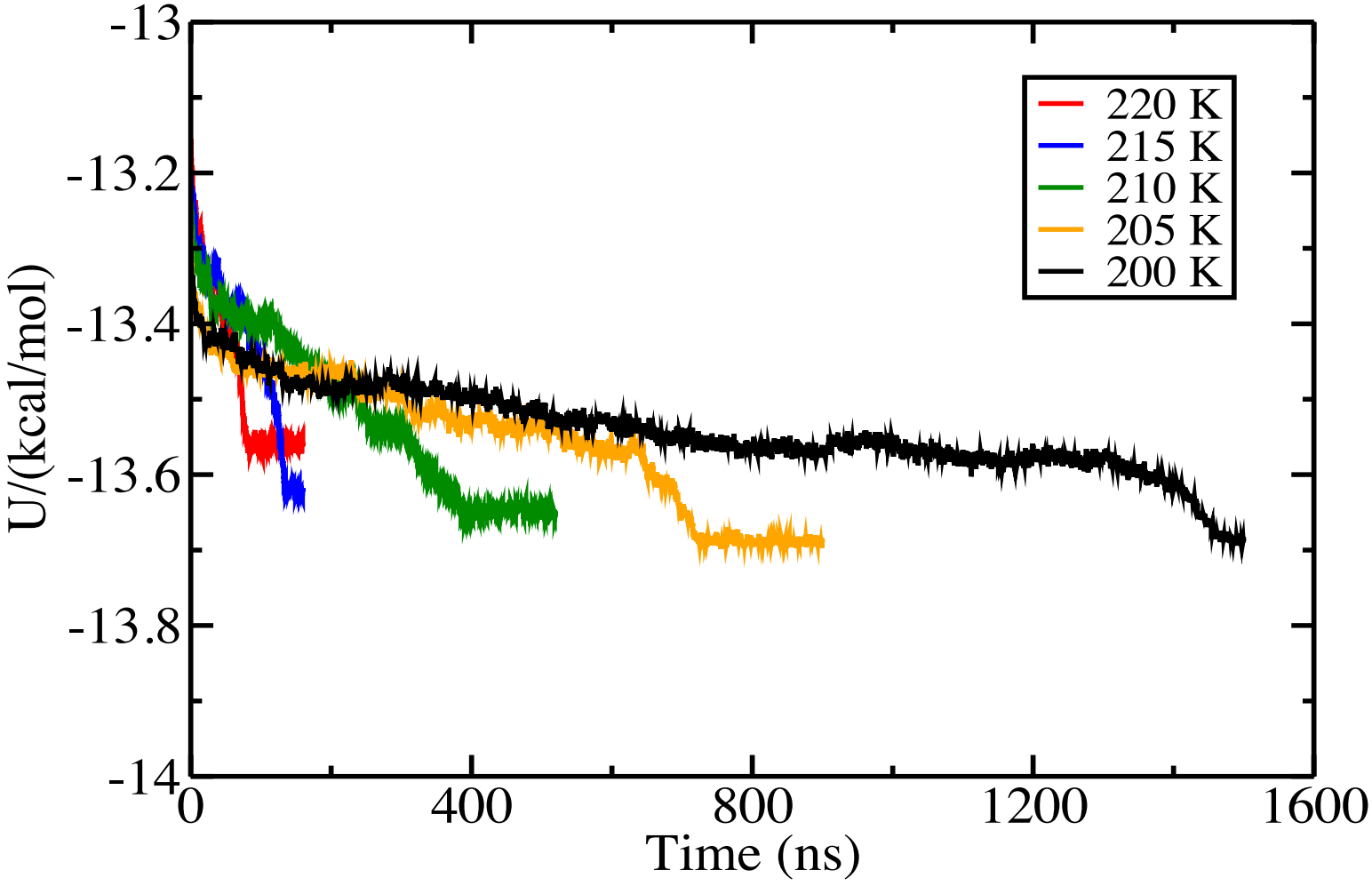
T_H^{exp} occurs when $log_{10}(J/(m^3 s)) = 14$
T_H^{sim} occurs when $log_{10}(J/(m^3 s)) = 31$

Nucleation rate J for several water models



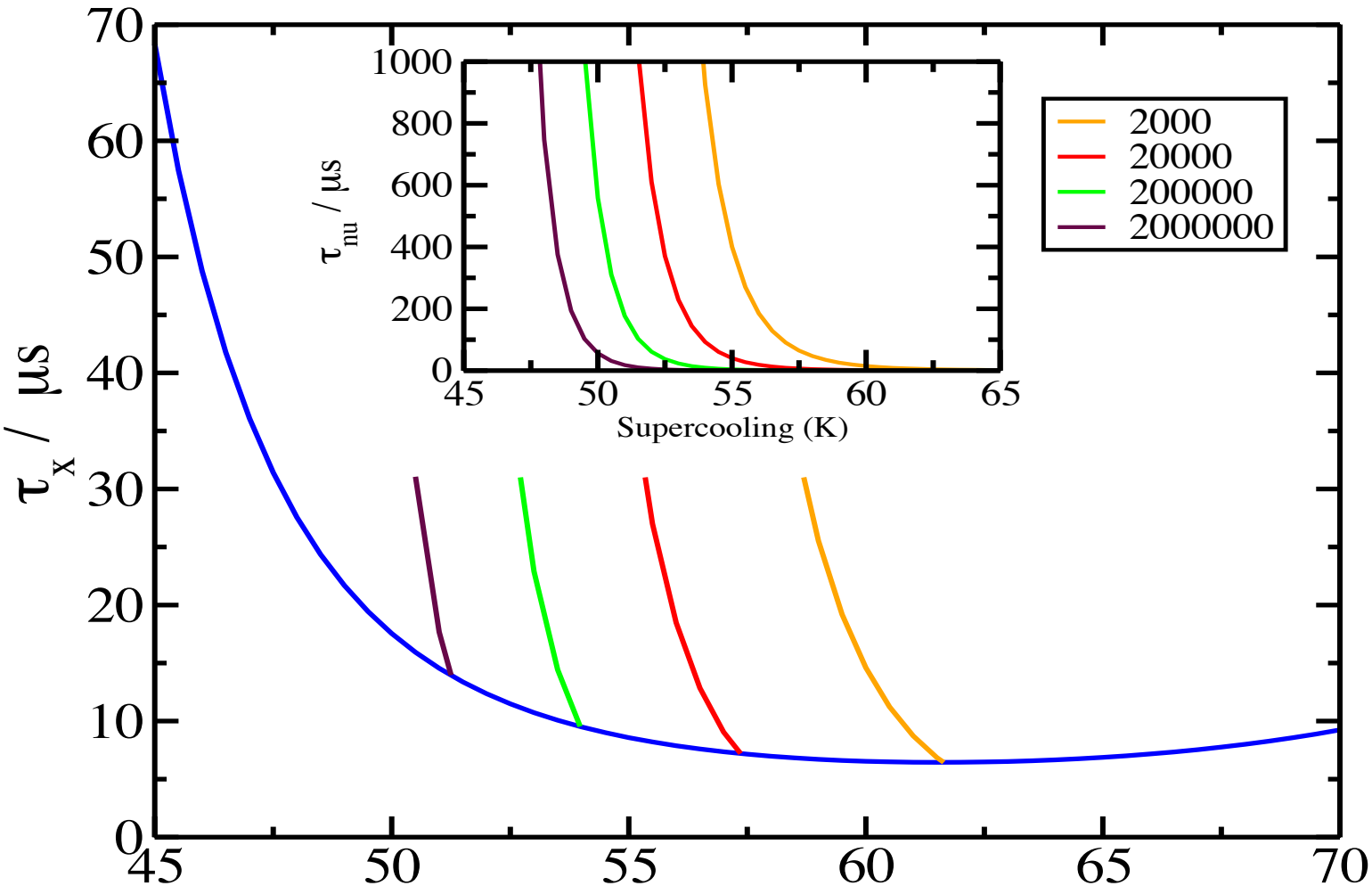
- TIP4P/2005 Good agreement with experiment
- T_H^{exp} well predicted
- T_H^{sim} at about ΔT 65K

Crystal growth of ice u for TIP4P/2005 at different ΔT



Planar interface. Growth of ice is not arrested at 200K ($\Delta T \simeq 50K$) ! Fit for u from Rozmanov and Kusalik (JCP,137,094702,2012) describes well the simulation results

Crystallization time τ_x from Avrami's equation for TIP4P/2005 $\phi = 0{,}7$

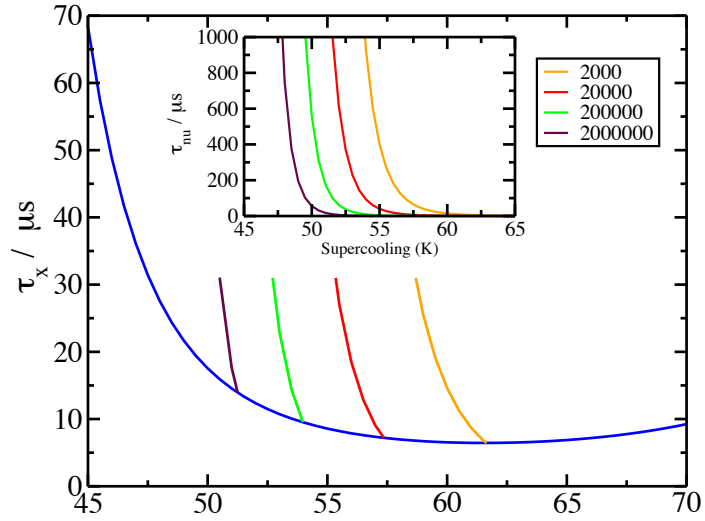


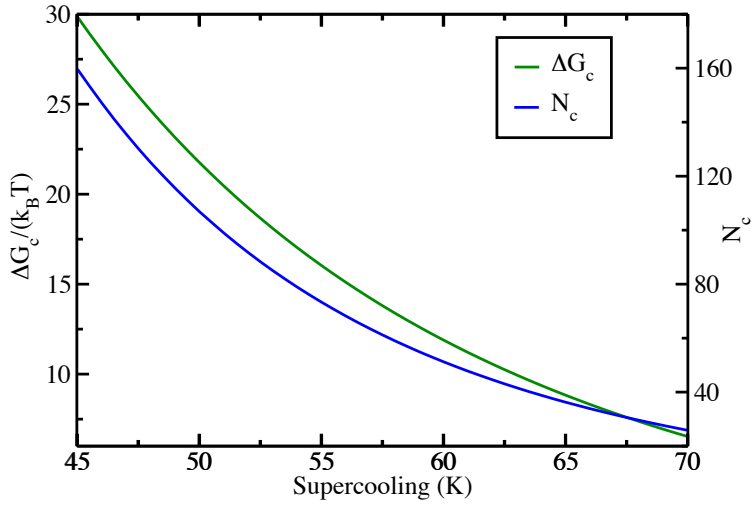
$$\tau_x^{Avrami} = ((3\phi)/(\pi J u^3))^{1/4} \quad (5)$$

$$\tau_{nu} = 1/(JV) \quad (6)$$

Finite Volume Avrami Theory , B. A. Berg et al. , PRL, 100, 165702, (2008)

Crystallization time τ_x

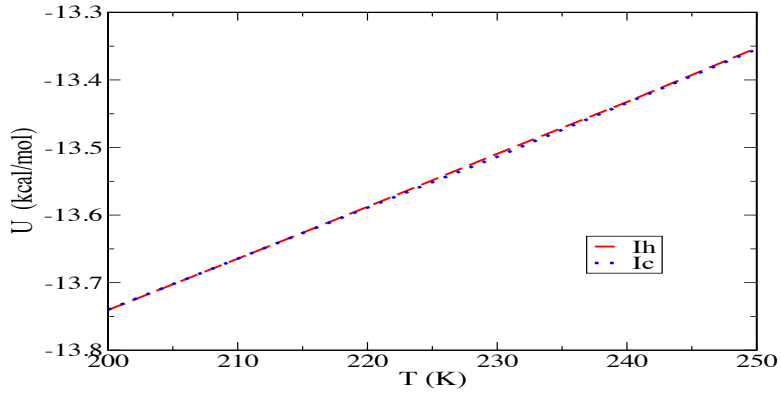


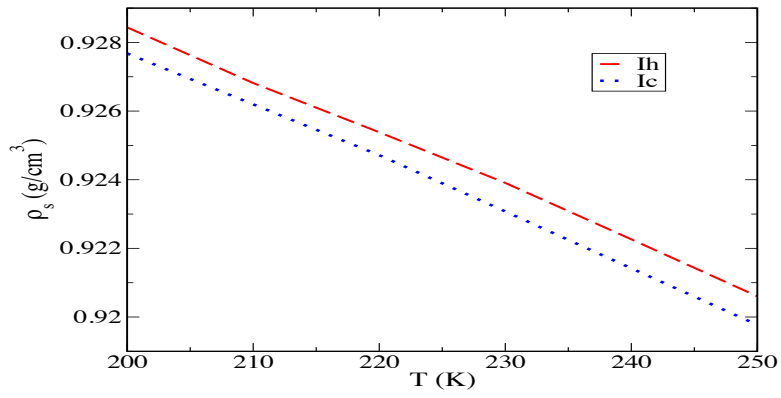


At the minimum in τ_x, $N_c = 50$, and $\Delta G_c = 13kT$

COMPETITION BETWEEN ICES Ih and Ic IN THE NUCLEATION OF ICE

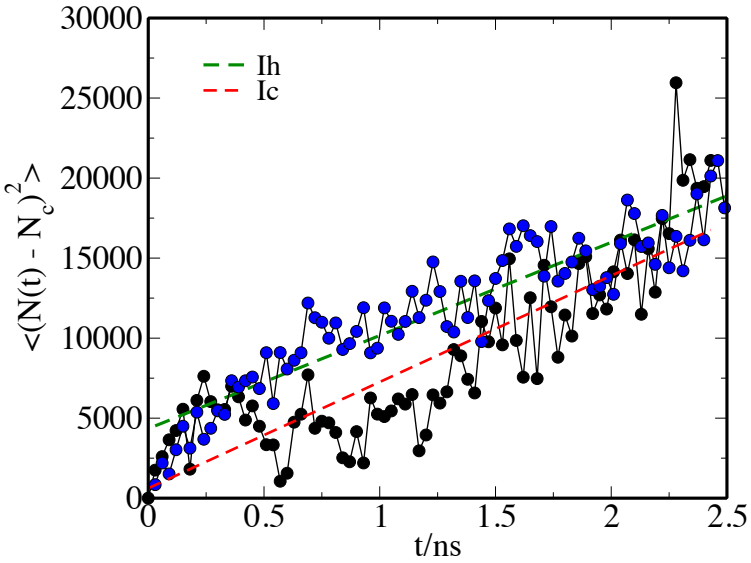
Internal energy and EOS for ices Ih and Ic (TIP4P/2005)

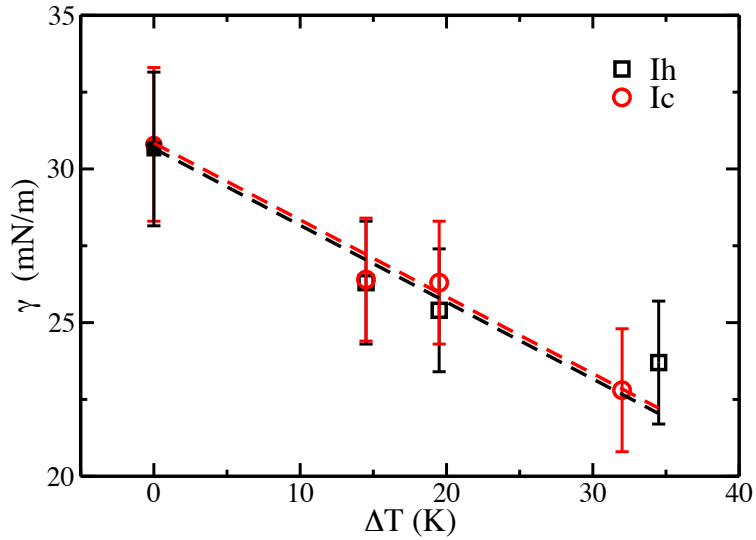




Ice	N	$\mu/(kT)$
Ih	432	-26.271(4)
Ih	512	-26.266(4)
Ic	512	-26.264(4)

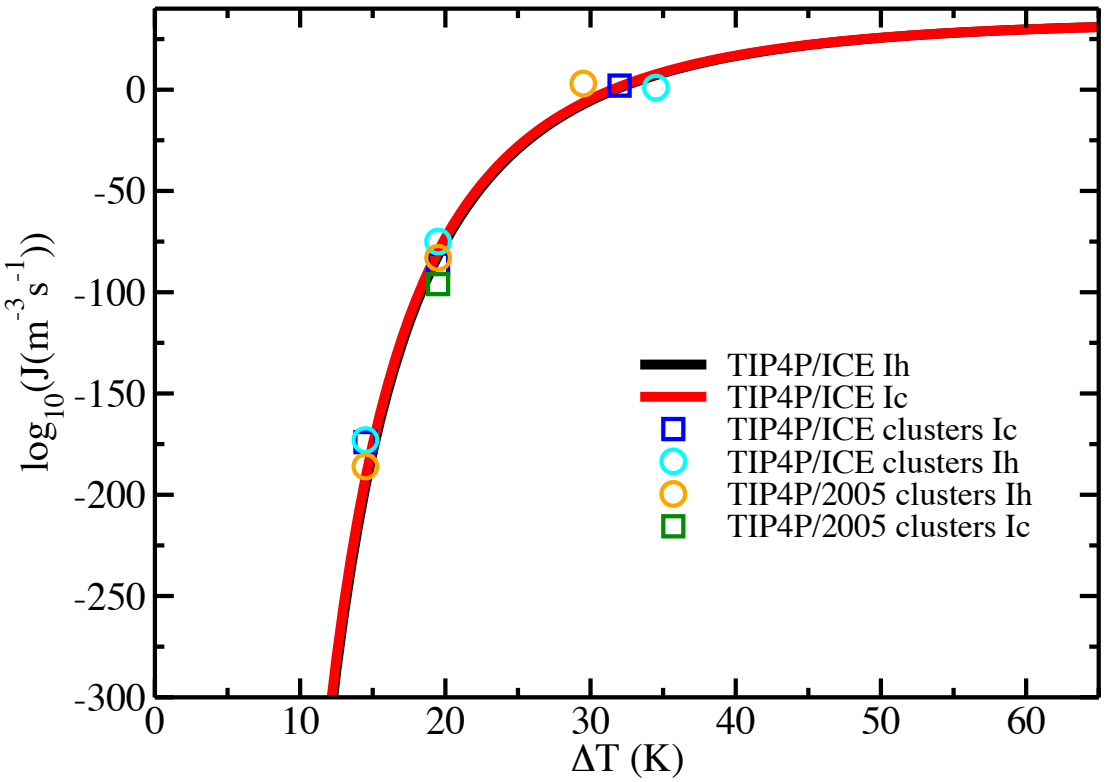
ATTACHEMENT RATES AND INTERFACIAL FREE ENERGIES FOR ICES Ih and Ic





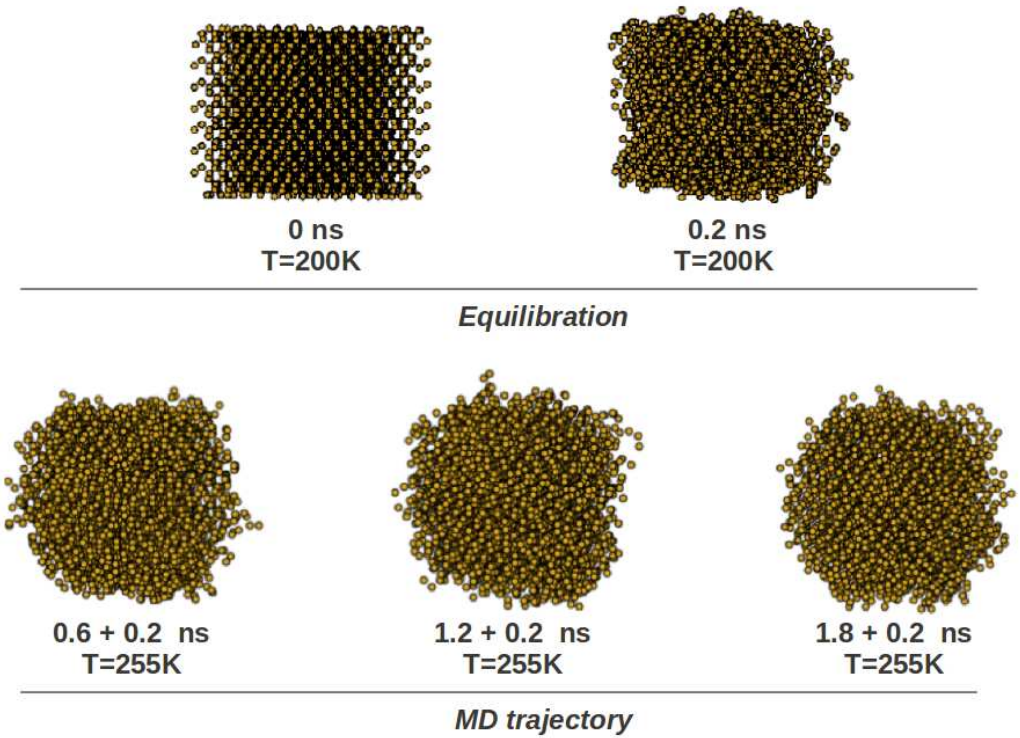
Attachement rate f^+ and interfacial free energy between ice and water for ices Ih and Ic. Results for the TIP4P/ICE model.

Nucleation rates J for ices Ih and Ic



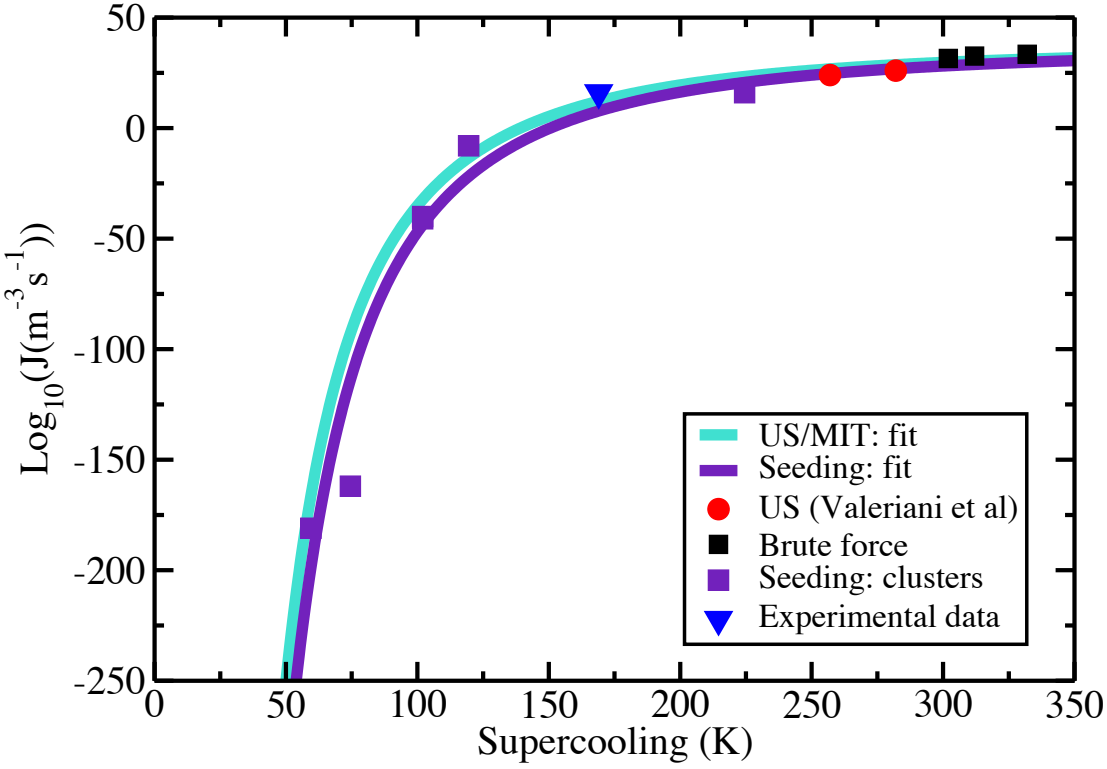
Zaragoza et al., *JCP* , in press, (2015)

Evolution with time of a cubic cluster of ice I_c



Does the seeding technique work for other substances ?

NaCl



J. R. Espinosa and C. Vega and C. Valeriani and E. Sanz, JCP, 142, 194709, (2015)

CONCLUSIONS

- The seeding technique although approximate describes reasonably well the values of J for the mW model obtained from more rigorous techniques
- γ was found to decrease with temperature with a slope (related to the excess interfacial entropy) of about -0.25 mN/(K.m).
- By extrapolating to the melting temperature an estimate of the interfacial free energy for the planar interface was obtained for several water models. The values of γ for the planar interface obtained for the different models of this work are consistent with the experimental values. Experimental values are in the range $25 - 35$ mN/m.
- The predictions of the TIP4P/2005 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.
- Homogeneous nucleation is not responsible for the freezing of water for temperatures above -20 $^{\circ}$C
- At T_H^{exp} the kinetic prefactor to be used in CNT should be of the order of $10^{37}(m^{-3}s^{-1})$ whereas the free energy barrier ΔG_c is of about 53 $k_B T$. At T_H^{sim}, ΔG_c is of about 14 $k_B T$.
- By using Avrami's equation we estimated that for large systems (i.e large enough to have at least one critical cluster in the simulation box) about 6 microseconds would be required to have a significant fraction of ice for a supercooling of about 60K.
- For TIP4P/2005 , J at 1bar and the temperature at which κ_T reach a maximum(Widom) is $J = 10^{-82}/(m^3 s)$. The maximum in κ_T for supercooled TIP4P/2005 can not be atributed to the trasient formation of ice !

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

Free energy calculations for molecular solids using GROMACS
J.L.Aragones , E.G.Noya, C.Valeriani and C.Vega , J.Chem.Phys. 139 034104 (2013)

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E. Sanz and C. Vega and J. R. Espinosa and R. Caballero-Bernal and J.L.F. Abascal and 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., 141 , 18C529 (2014)

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