The crystal-fluid interfacial free energy and nucleation rate of water from simulations.

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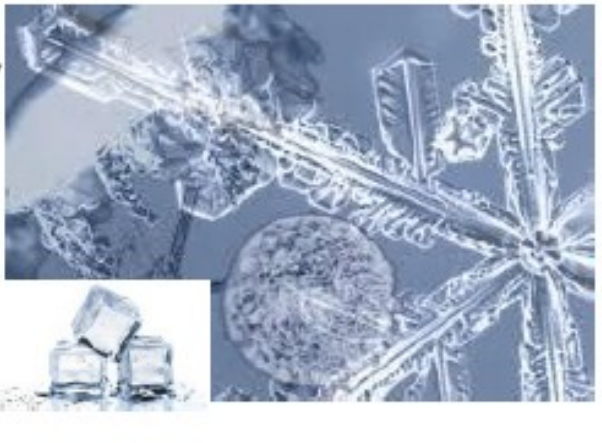
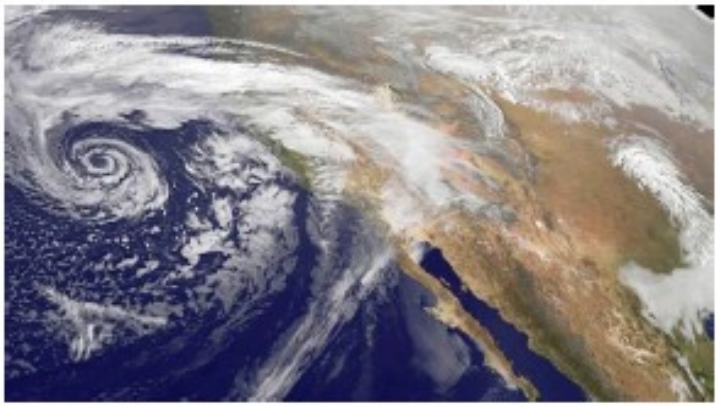
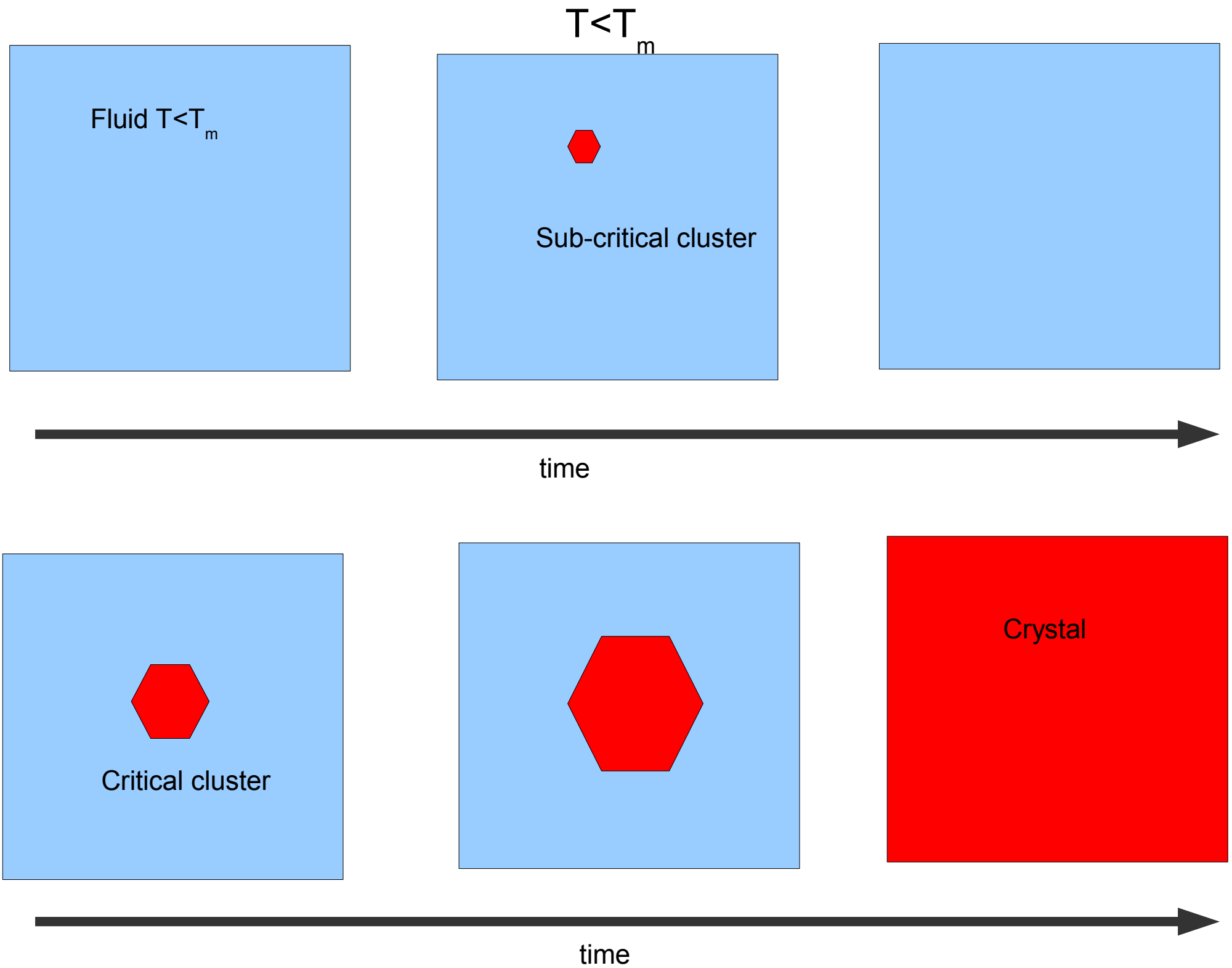
Why study ice nucleation?






T<T m
Fluid T<T m
Sub-critical cluster
time
Critical cluster
Crystal
time

Critical cluster:

Size?

Shape?

Structure?

Experiments can not answer these questions (cluster too small (nm) and short-lived (ns) to be observed experimentally).

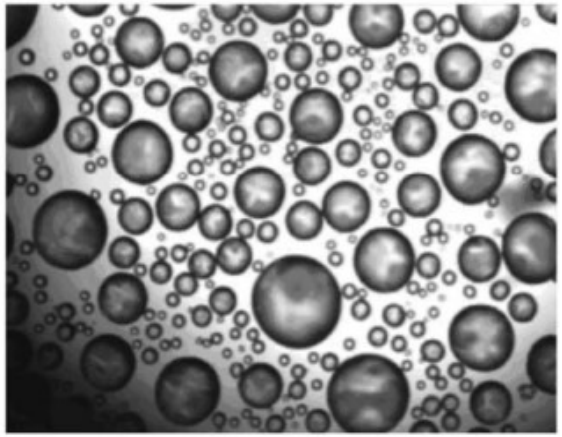
Computer simulations can. (Molecular Dynamics simulations with classical potentials for the interaction between water molecules (TIP4P-like, mW)).

Can we compare our results to experiments?:

Yes, via the nucleation rate $J = \frac{critical\ clusters}{tV}$

- High J: Small crystallites
- Low J: Large crystallites

Experiments:



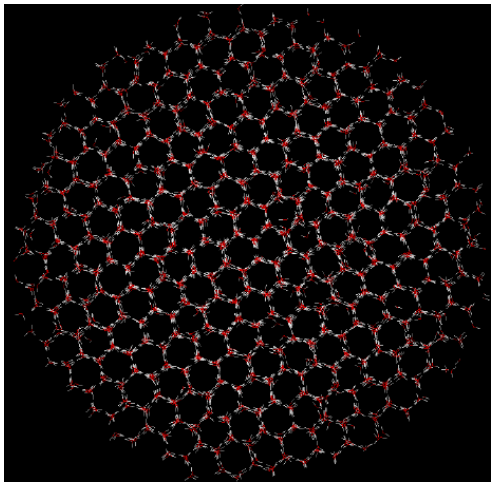
Count how many droplets freeze along time

Simulations:
Use Classical Nucleation Theory:

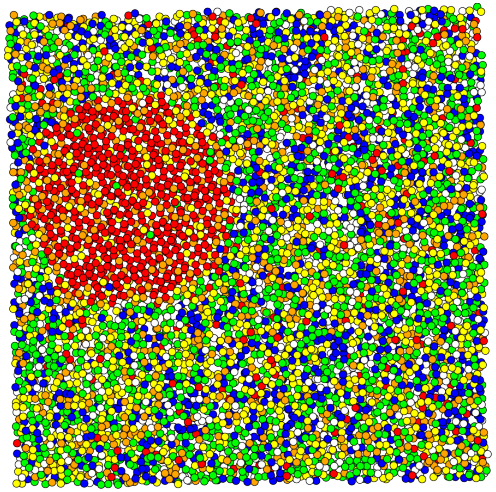
$$J = \sqrt{\frac{|\Delta\mu|}{6\pi_B T N_c}}\rho_f f^+ \exp\left(-\frac{N_c|\Delta\mu|}{2k_B T}\right)$$

- $|\Delta\mu|$ |Chemical potential fluid – chemical potential crystal|
- N_c Number of particles in the critical cluster
- ρ_f Density of fluid phase
- f^+ Attachment rate of particles to the critical cluster

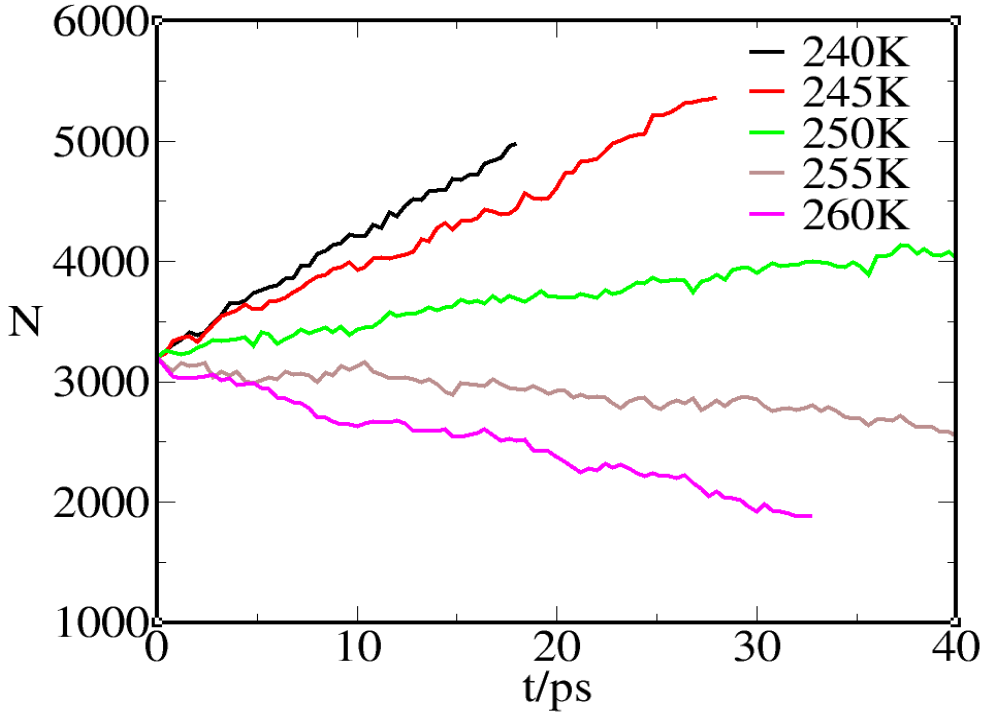
Size, N_c: "Seeding" technique



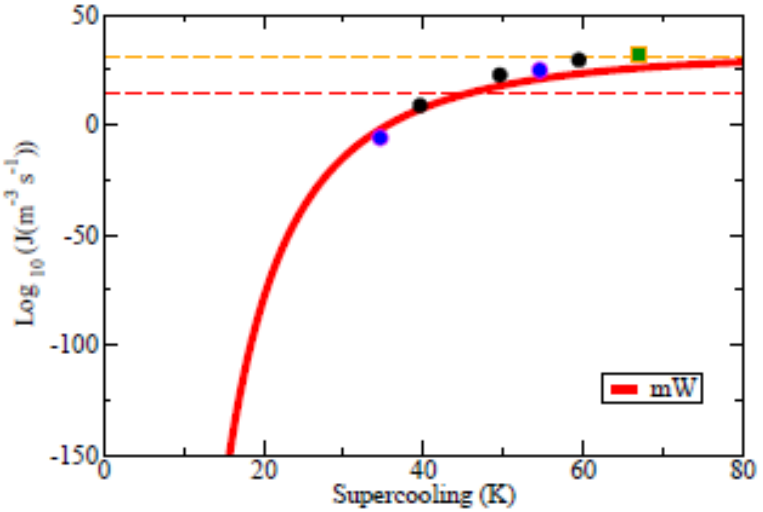
1- Prepare a crystal seed

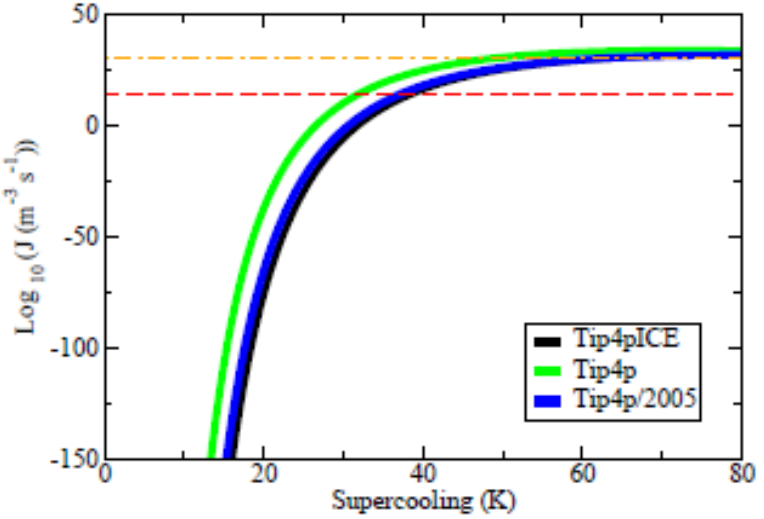


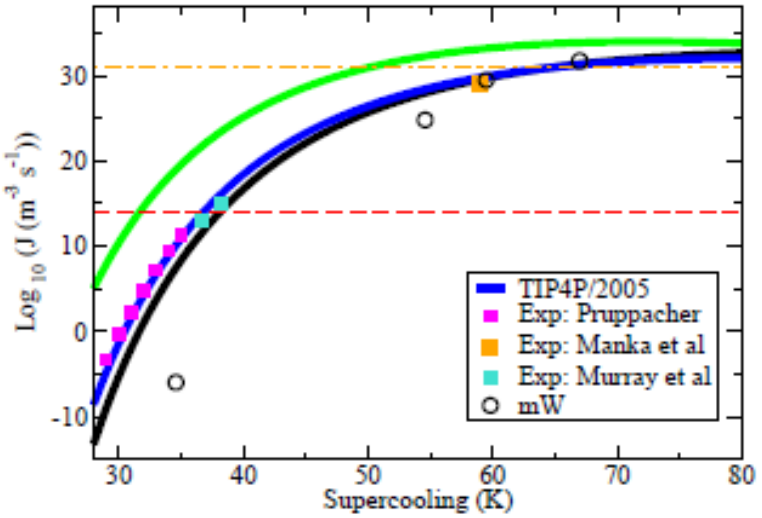
2-Embed the seed in the supercooled melt



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







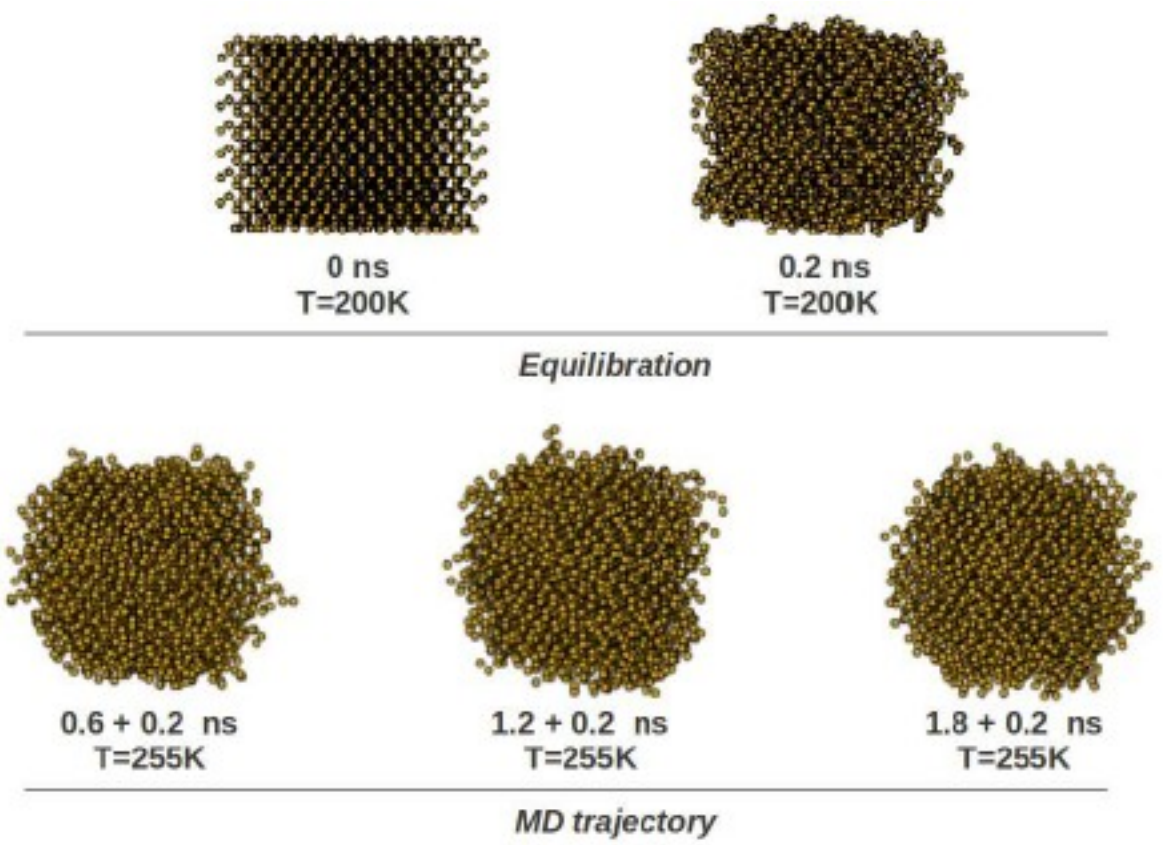
Compare the performance of several water models

E. Sanz, C. Vega, J. R. Espinosa, R. Caballero-Bernal, J. L. F. Abascal, and C. Valeriani, Journal of the American Chemical Society 135, 15008 (2013).

J.R.Espinosa, E.Sanz., C.Valeriani, and C.Vega, J. Chem. Phys. 141, 18C529 (2014).

Size: ~2 nm radius at experimental supercooling (35-40 K)

Shape:



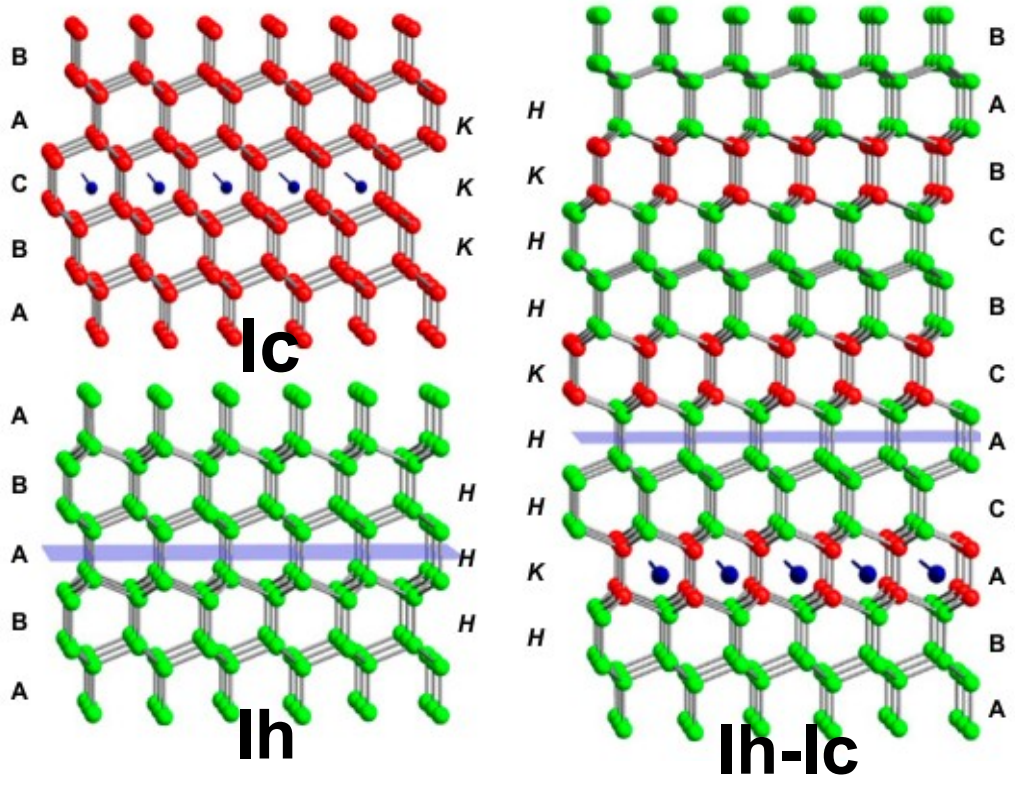
Structure: competition between ices I-cubic (Ic) and I-hexagonal (Ih)

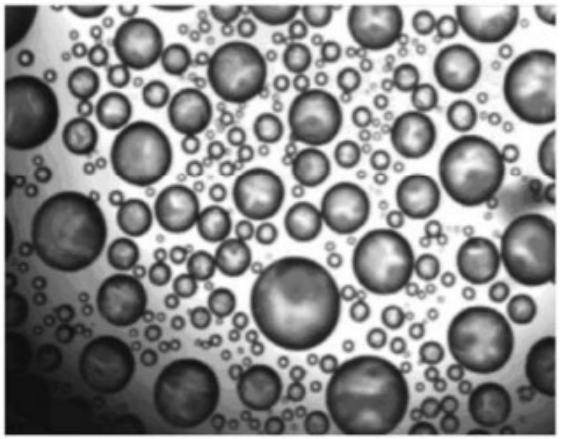
Extent and relevance of stacking disorder in "ice I_c"

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

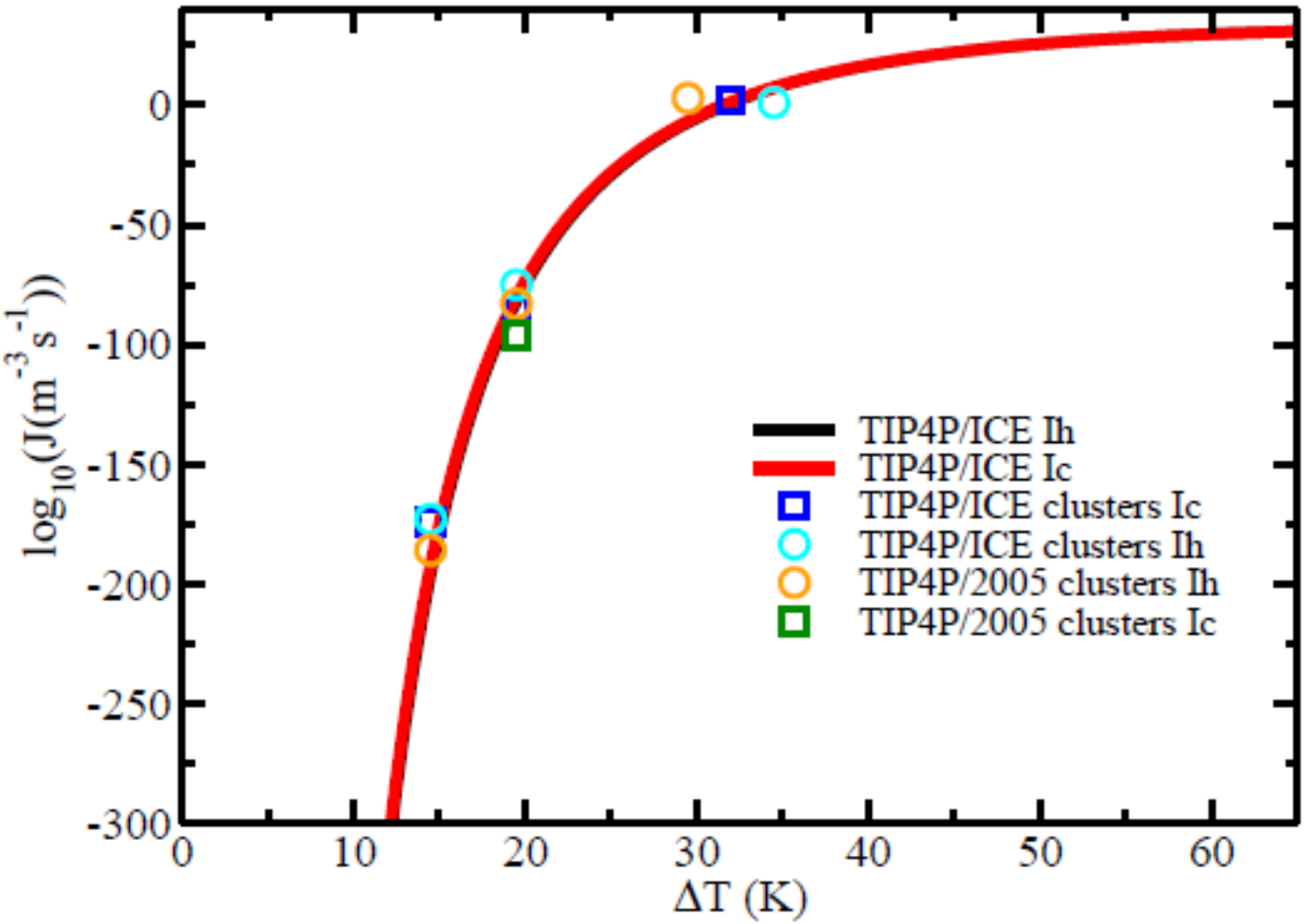
Structure of ice crystallized from supercooled water

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





B.J.Murray et al. *"Kinetics of the homogeneous freezing of water"* Physical Chemistry Chemical Physics. (2010) *[3]*

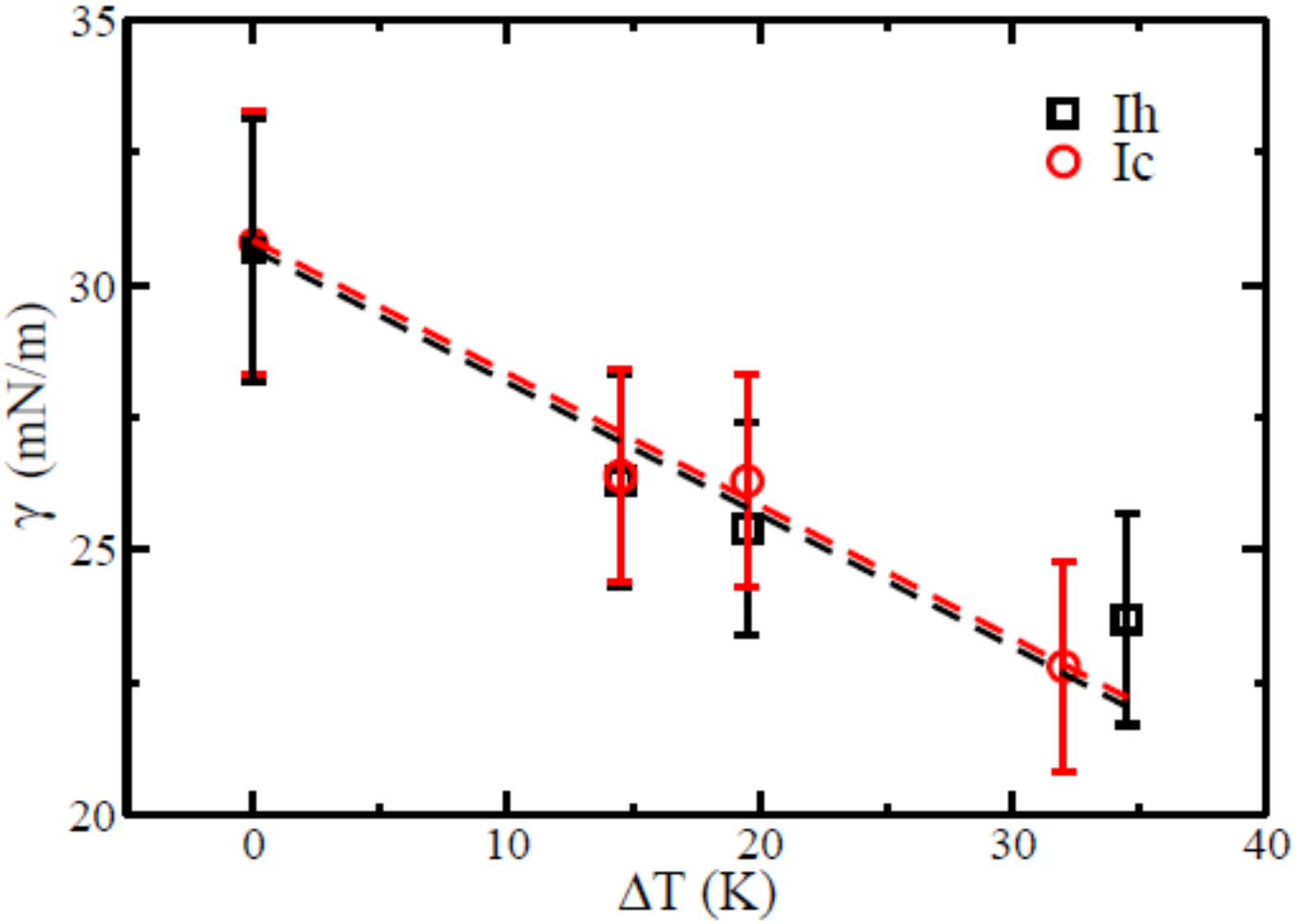


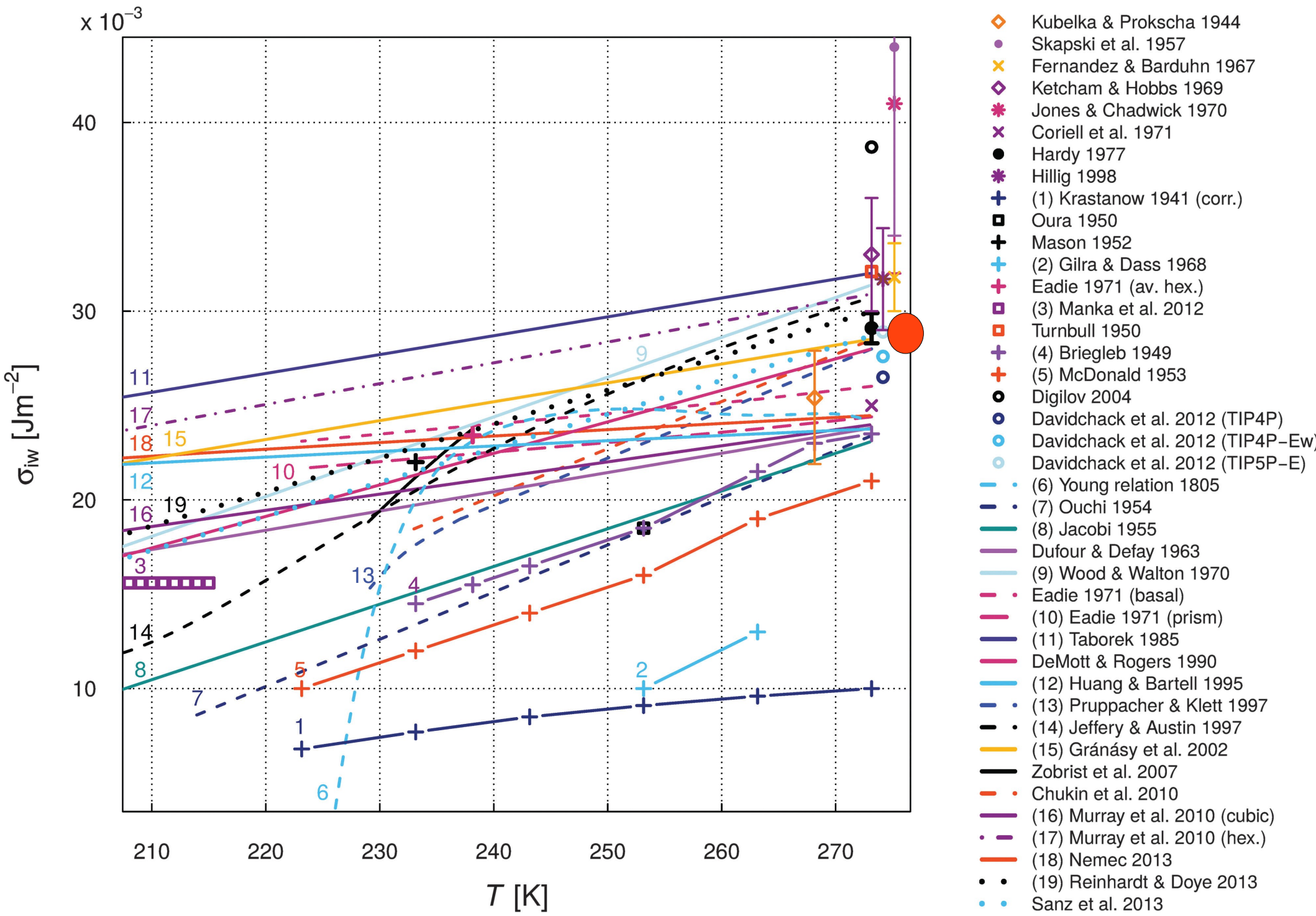
A. Zaragoza, M. M. Conde, J. R. Espinosa, C. Valeriani, C. Vega, E. Sanz, JCP, accepted, (2015)

Mixed cubic-hexagonal structure.

Classical nucleation theory:

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



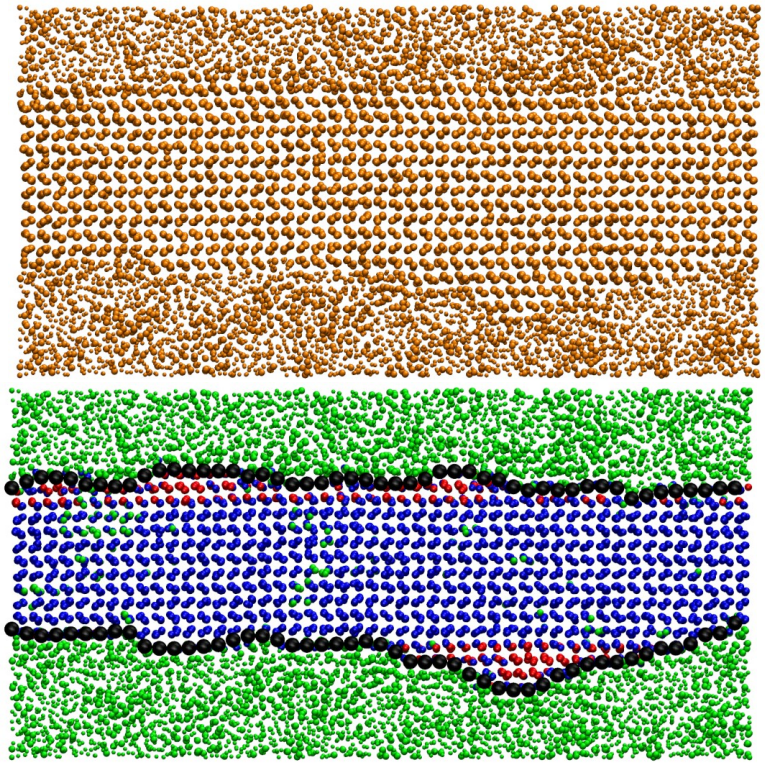


L. Ickes, A. Welti, C. Hoose, U. Lohmann, Phys. Chem. Chem. Phys. 2015, 17, 5515

The crystal-fluid interfacial free energy calculated directly at coexistence:

Capillary fluctuations method

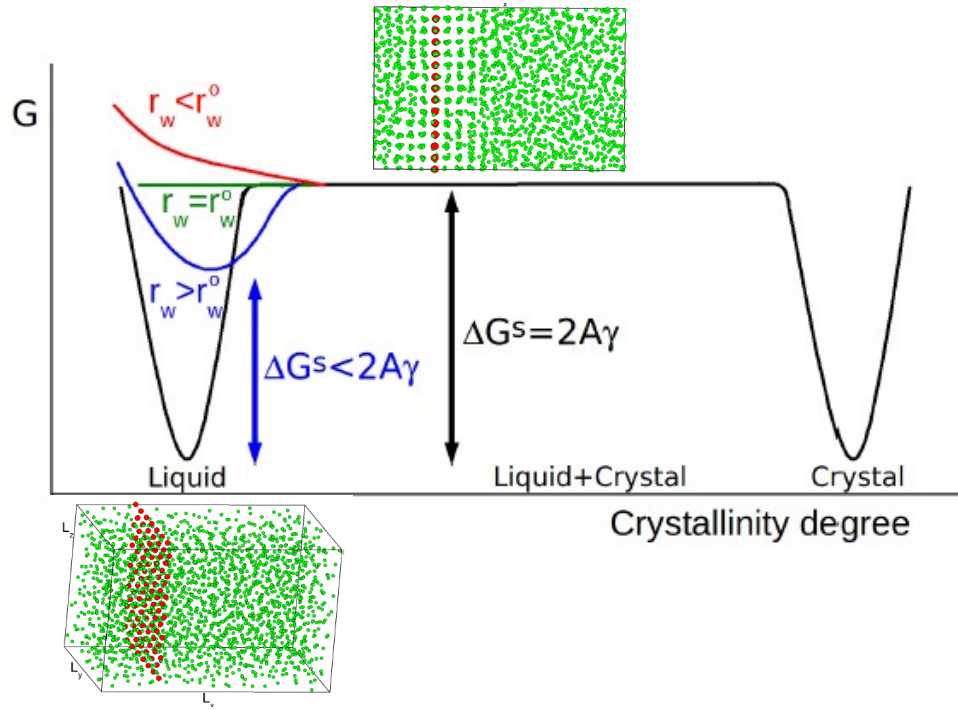
J. J. Hoyt, M. Asta, and A. Karma, Phys. Rev. Lett. 86, 5530 (2001).

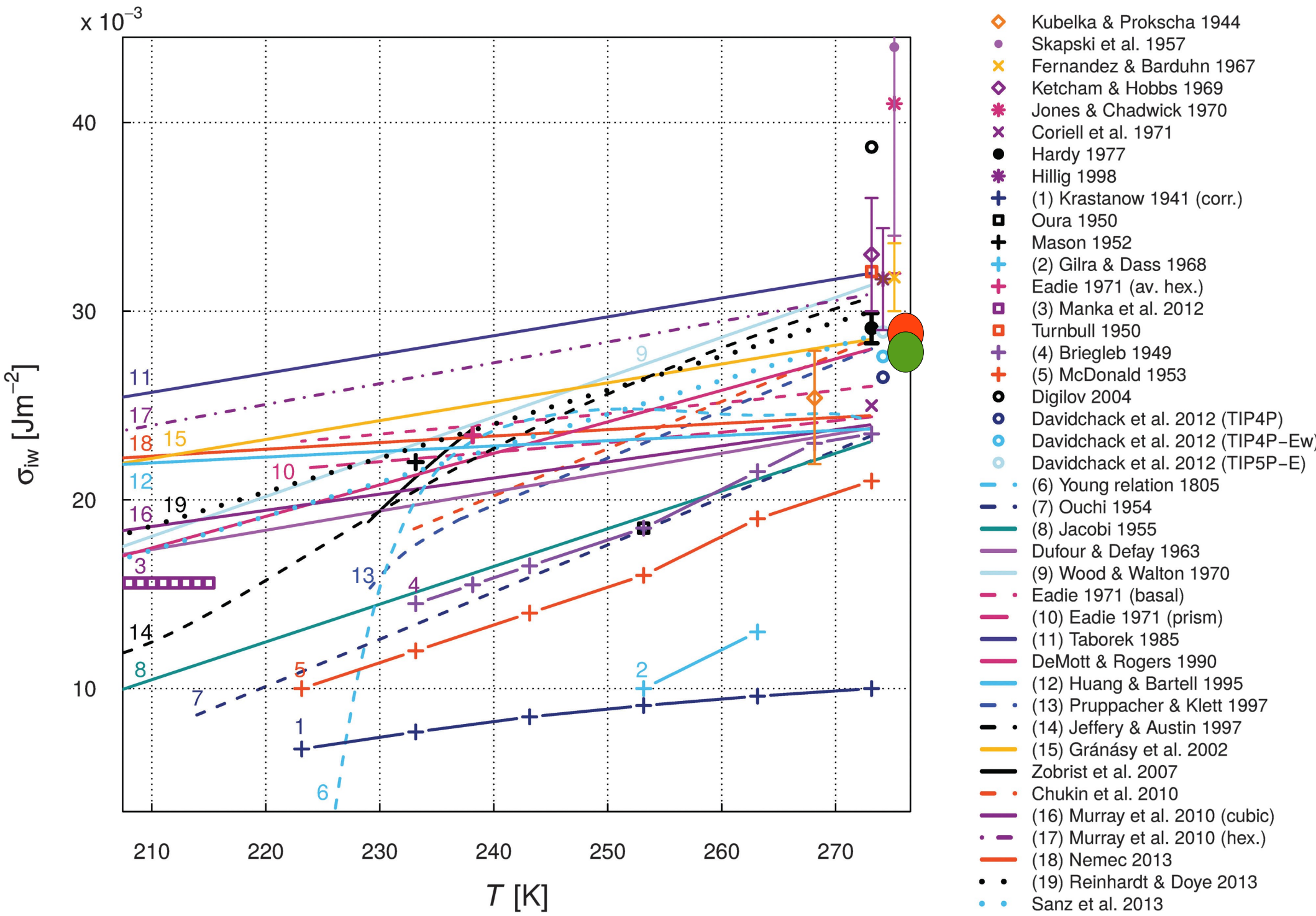


J. Benet, L. G. MacDowell, and E. Sanz, Phys. Chem. Chem. Phys. **16**, 22159 (2014).

Mold Integration method

J. R. Espinosa, C. Vega, and E. Sanz, The Journal of Chemical Physics 141, 134709 (2014).





L. Ickes, A. Welti, C. Hoose, U. Lohmann, Phys. Chem. Chem. Phys. 2015, 17, 5515

Conclusions:

There are classical models of water (TIP4P/2005, TIP4P/Ice)
that provide reasonable predictions of the nucleation rate.

With these models we can:

1) Get insightful information about the critical cluster (size, shape, structure)

2) Estimate the nucleation rate where experimental measures are not possible

3) Predict the true value for the crystal-fluid interfacial free energy.