Modelling crystal nucleation and growth

David Quigley

Overview

- Why study nucleation?
- Strategies for atomistic nucleation
- How quantitative can we be and under what circumstances?
- Polytypes and stacking disorder in ice nuclei
- Nucleation via metastable phases - ice 0

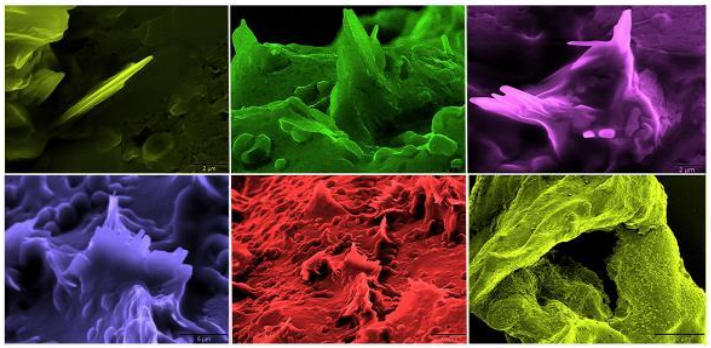
Motivation

https://www.youtube.com/watch?v=0JtBZGXd5zo

Science News

Cholesterol Crystals Linked To Cardiovascular Attacks

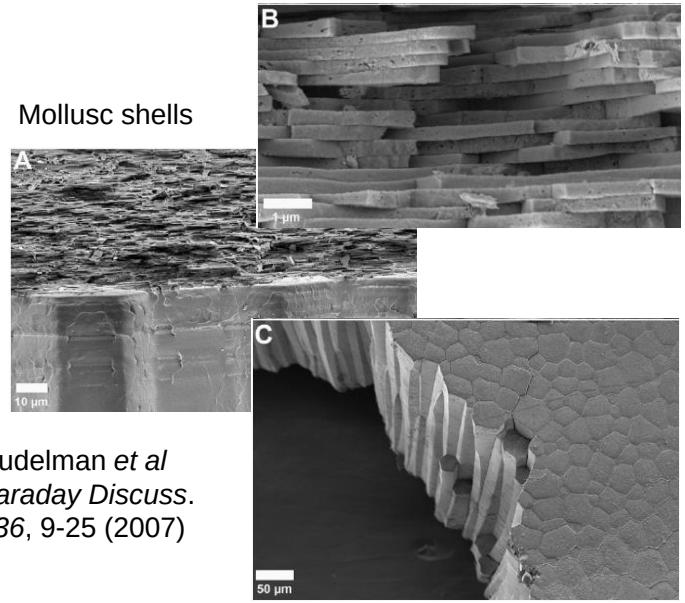
ScienceDaily (Apr. 2, 2009) — For the first time ever, a Michigan State University researcher has shown cholesterol crystals can disrupt plaque in a patient's cardiovascular system, causing a heart attack or stroke.



[Vedre *et al* Atherosclerosis, March **2009**, Abela *et al* American Journal of Cardiology, April **2009**]

Sheets of aragonite tablets

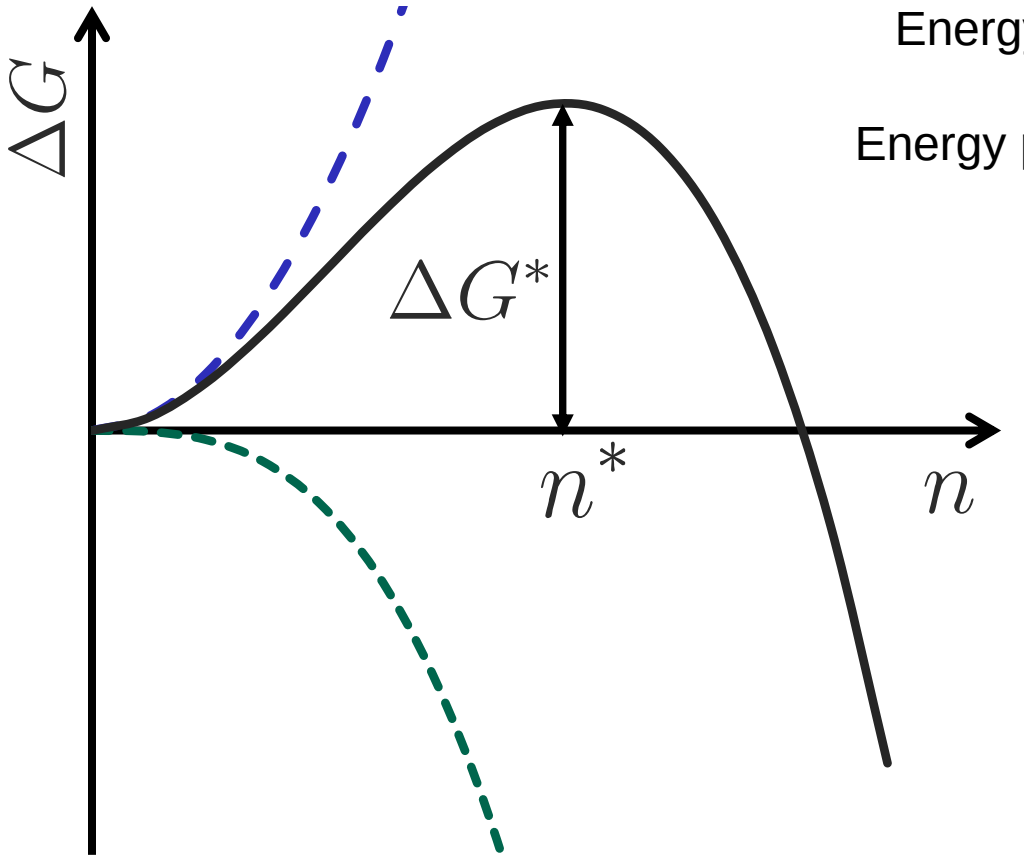
Mollusc shells



Nudelman *et al* *Faraday Discuss*. *136*, 9-25 (2007)

Columns of calcite

Classical nucleation theory (CNT)



Energy benefit (bulk) :

Energy penalty (surface) :

$$\Delta G = n^{2/3}\phi\gamma - n\Delta\mu$$

$$n^* = \left(\frac{2\phi\gamma}{3\Delta\mu}\right)^3$$

Classical nucleation theory (CNT)

Nucleation *rates* connect directly to experiment

$$k = \rho_l Z D_n \exp\left[-\Delta G^* / k_B T\right]$$

D_n Diffusivity of n

ρ_l Density of liquid

Z Zeldovich factor, related to curvature at barrier top

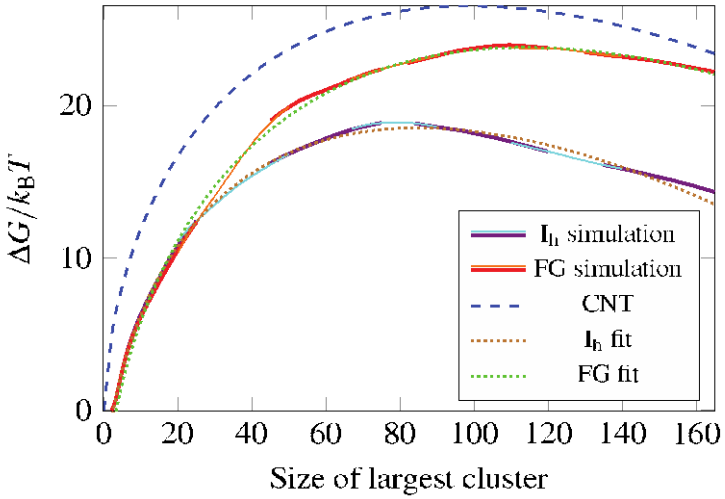
For spherical nuclei

$$Z = \sqrt{|\Delta\mu| \,/\, (6\pi k_B T n^*)}$$

Strategies for computer simulation

Use classical nucleation theory (CNT)

1. Use biased sampling (MD/MC) method to measure $\Delta G\,(n)$
2. Fit $\phi\gamma$ and $\Delta\mu$ to resulting curve to calculate n^* and Z
3. Simulate at n^* and compute D_n from MSD of n



Requires specialist codes, but structure of critical nucleus extracted from the MD/MC

Useful when barrier is high and dynamics are slow and diffusive

Reinhardt, A. & Doye, J. P. K. *J. Chem. Phys.*, **2012**, *136*, 054501

Strategies for computer simulation

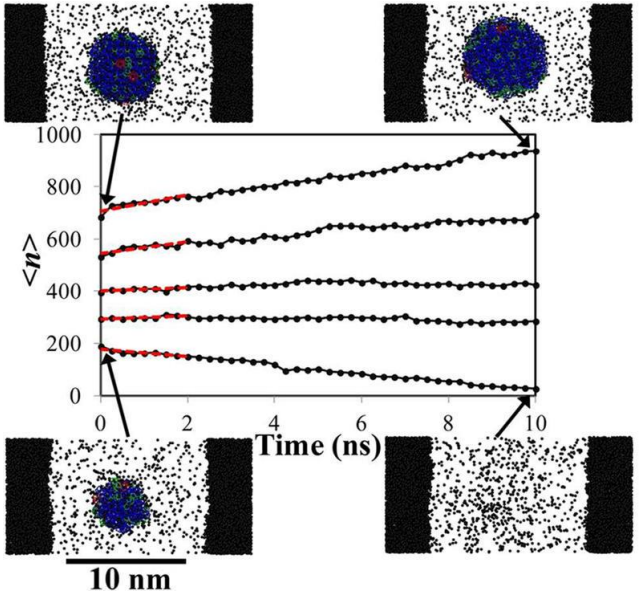
Use classical nucleation theory (CNT)

1. Run swarms of standard MD trajectories with seed nuclei of size n
2. Compute mean drift velocity $\mathrm{d}\langle n \rangle / \mathrm{d}t$ at each n
3. Identify n^* as n with zero mean drift
4. Compute D_n from gradient of $\langle (\delta n)^2 \rangle$ at n^*
5. Fit $\phi\gamma$ and $\Delta\mu$ to CNT $\Delta G(n)$ using

$$\frac{\mathrm{d}\langle n \rangle}{\mathrm{d}t} = -\frac{D_n}{k_B T}\frac{\mathrm{d}G(n)}{\mathrm{d}n}$$

Requires assumption of particular nucleus structure, but only off-the-shelf MD codes

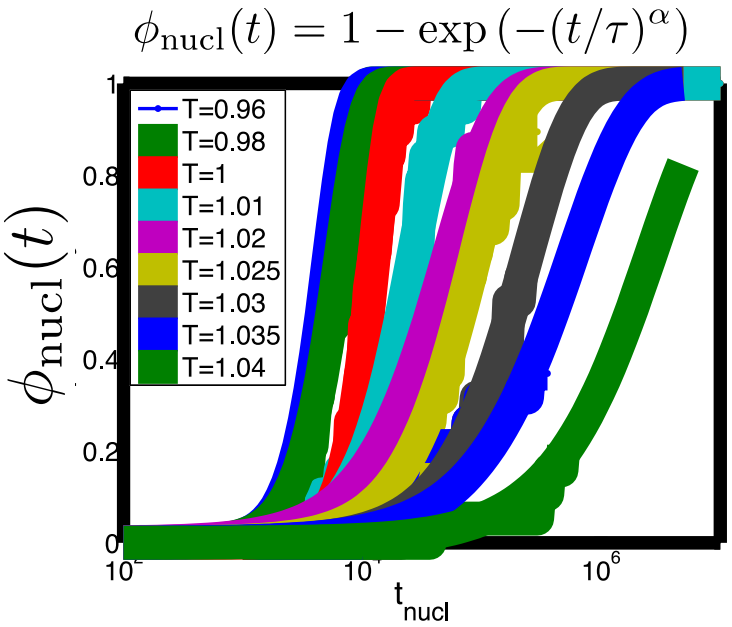
Useful when barrier is high, and dynamics are slow and diffusive

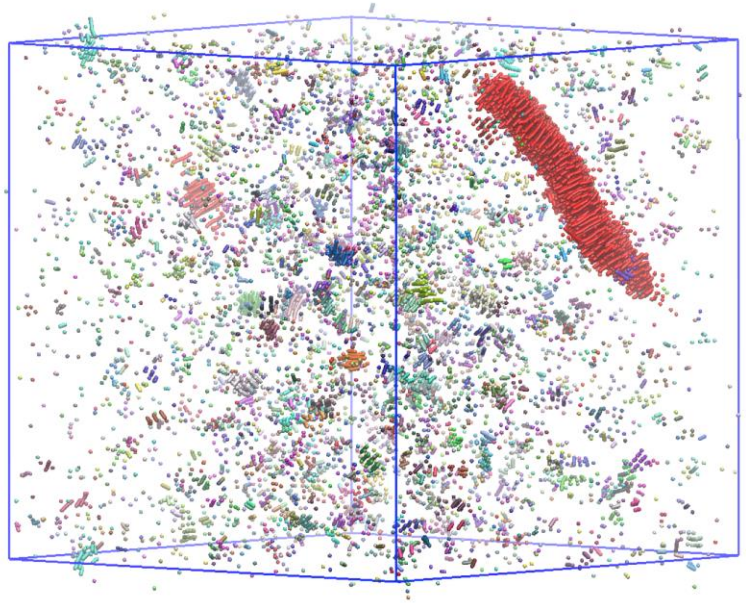


Knott *et al. J. A. C. S.*, **2012**, *134*, 19544

Strategies for computer simulation

Brute force molecular dynamics simulation





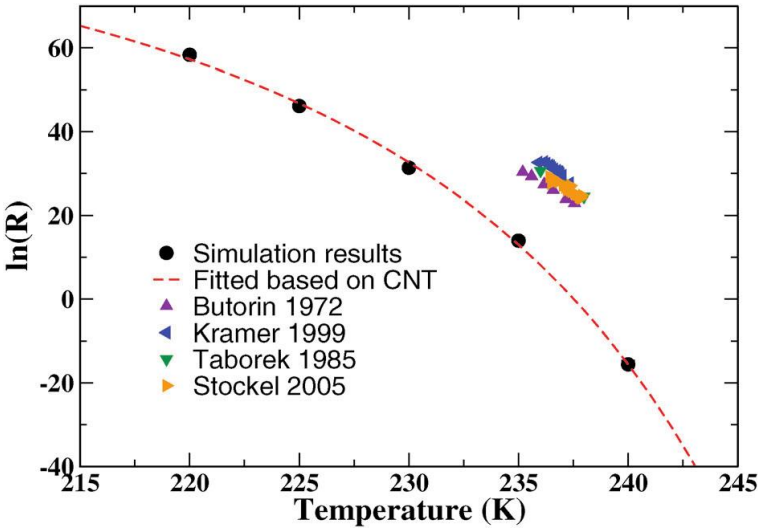
Useful when barrier is low and dynamics are fast

B. Vorselaars and DQ, in preparation 2015

Strategies for computer simulation

Use a transition path sampling method

1. Count the rate at which some small n is reached
2. Use specialist methods (FFS/TIS) to sample pathways crossing n
3. Determine fraction of these pathways which reach solid phase



Various attempts to implement as wrapper to standard MD packages, however how best to compute n is an issue

Useful when barrier is high and dynamics are fast enough to sample a large number of trajectories

Li *et al* PCCP., **2011**, 13, 19807

Modelling water

4008 J. Phys. Chem. B 2009, 113, 4008–4016

Water Modeled As an Intermediate Element between Carbon and Silicon†

Valeria Molinero* and Emily B. Moore

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112

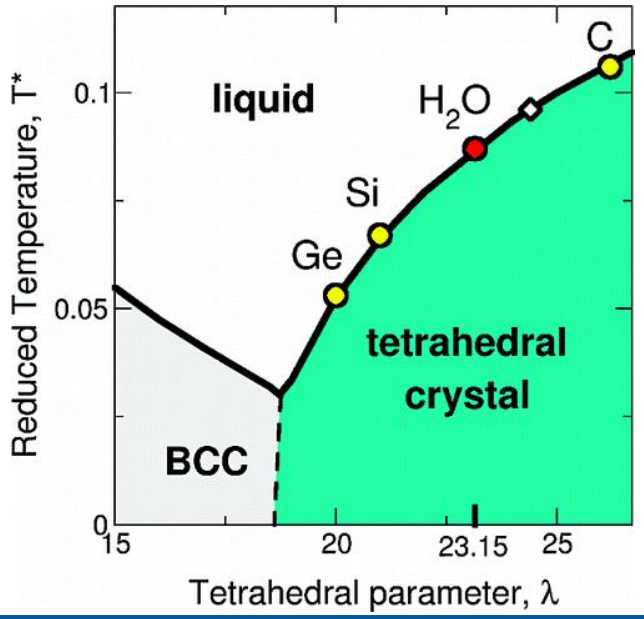
Received: June 13, 2008; Revised Manuscript Received: September 4, 2008

Short-ranged two and three-body potential

$$E = \sum_i \sum_{j>i} \varphi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \varphi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\varphi_2(r) = A\varepsilon\left[B\left(\frac{\sigma}{r}\right)^p - \left(\frac{\sigma}{r}\right)^q\right]\exp\left(\frac{\sigma}{r - a\sigma}\right)$$

$$\varphi_3(r, s, \theta) = \lambda\varepsilon[\cos\theta - \cos\theta_o]^2\exp\left(\frac{\gamma\sigma}{r - a\sigma}\right)\exp\left(\frac{\gamma\sigma}{s - a\sigma}\right)$$



Nucleation simulations with mW

Homogeneous ice nucleation from supercooled water

Tianshu Li,*[a] Davide Donadio,[b] Giovanna Russo[c] and Giulia Galli[cd]

Received 1st July 2011, Accepted 27th September 2011
DOI: 10.1039/c1cp22167a

Homogeneous ice nucleation from supercooled water was studied in the temperature range of 220–240 K through combining the forward flux sampling method (Allen *et al.*, *J. Chem. Phys.*, 2006, **124**, 024102) with molecular dynamics simulations (FFS/MD), based on a recently developed coarse-grained water model (mW) (Molinero *et al.*, *J. Phys. Chem. B*, 2009, **113**, 4008).

- Forward Flux Sampling from 220K to 240K
- Critical nuclei contain ~ 50% cubic

Is it cubic? Ice crystallization from deeply supercooled water

Emily B. Moore and Valeria Molinero*

Received 20th June 2011, Accepted 29th September 2011
DOI: 10.1039/c1cp22022e

Ice crystallized below 200 K has the diffraction pattern of a faulty cubic ice, and not of the most stable hexagonal ice polymorph. The origin and structure of this faulty cubic ice, presumed to form in the atmosphere, has long been a puzzle. Here we use large-scale molecular dynamics

- Brute force molecular dynamics at 180K
- Critical nuclei ~ 66% cubic

Free energy landscapes for homogeneous nucleation of ice for a monatomic water model

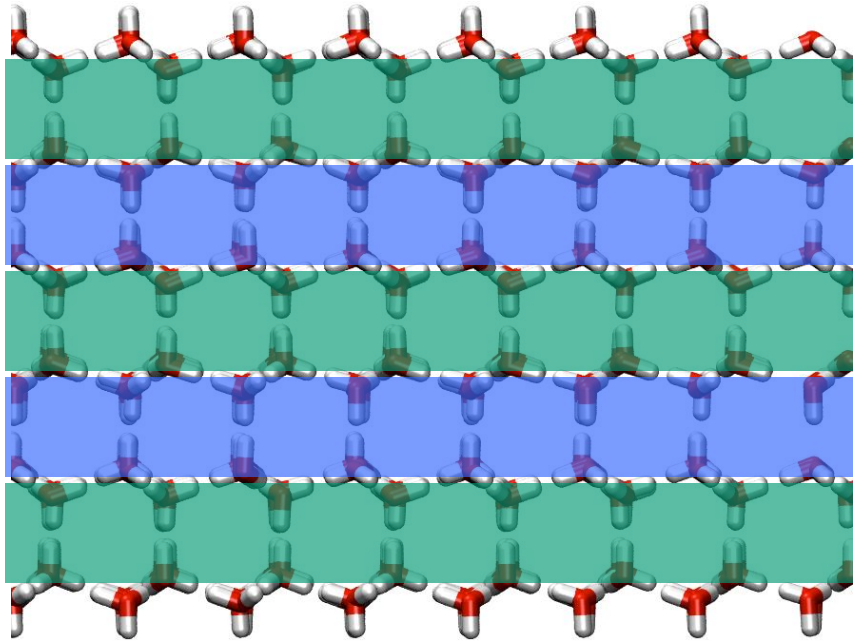
Aleks Reinhardt and Jonathan P. K. Doye[a)]
Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3QZ, United Kingdom

(Received 30 September 2011; accepted 26 December 2011; published online 1 February 2012)

We simulate the homogeneous nucleation of ice from supercooled liquid water at 220 K in the isobaric-isothermal ensemble using the MW monatomic water potential. Monte Carlo simulations using umbrella sampling are performed in order to determine the nucleation free energy barrier.

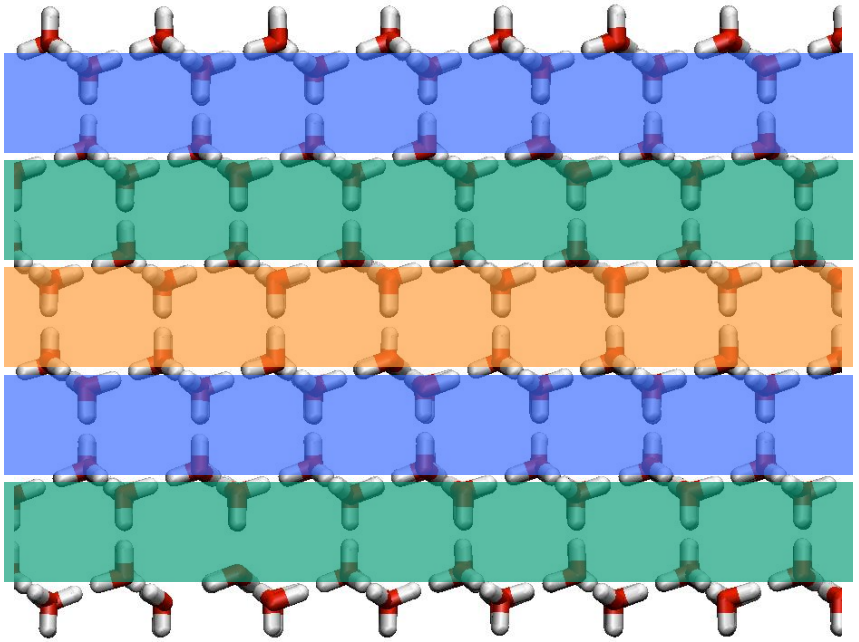
- Umbrella sampling Monte Carlo at 220K
- Critical nuclei “predominantly cubic”

Ice 1 has two polytypes



Hexagonal ice 1h

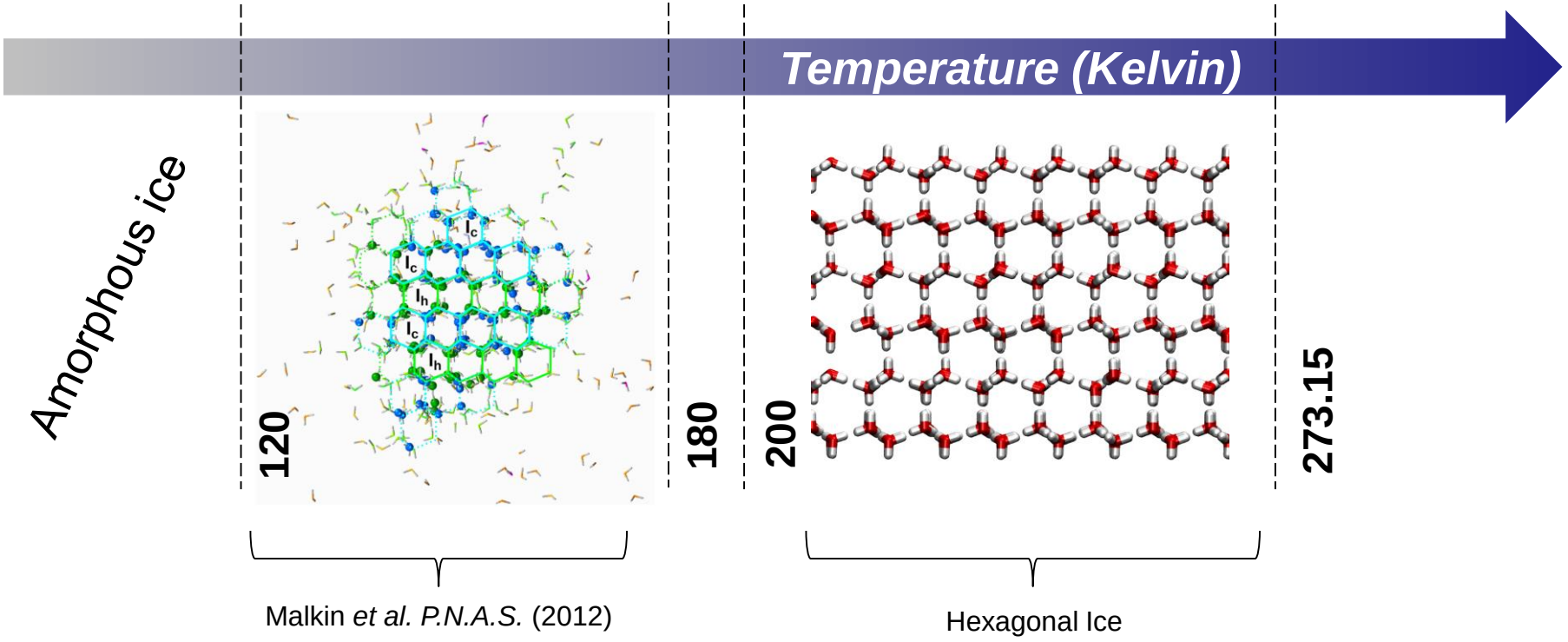
Layers stack as ABABABA…..



Cubic ice 1c

Layers stack as ABCABCABC…

Growing ice from supercooled water



Ice homogeneously nucleated at low temperatures is ***stacking disordered****.*
NOT cubic OR hexagonal but a mixture.

Stacking fault statistics in nuclei

- Stacking model

$$\mathcal{H} = \sum_{i=2}^{L-1} \Delta g N_l (1 - \delta_{L,R})$$

Δg = free energy difference per molecule between cubic and hexagonal ice.

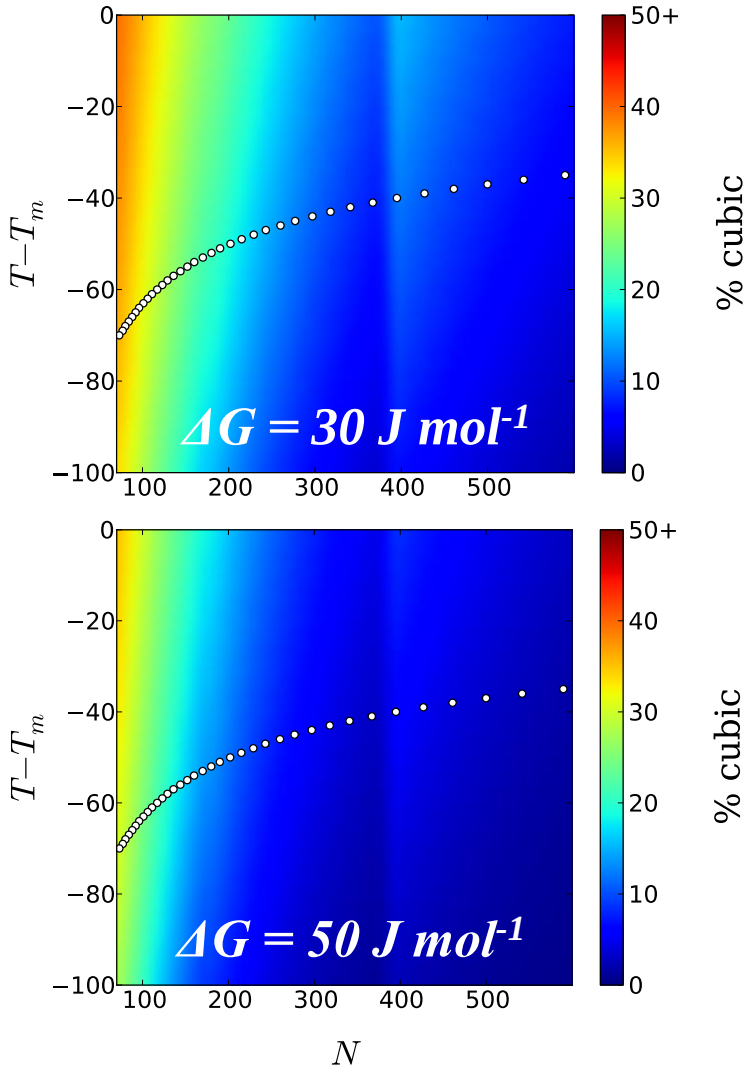
N_l = molecules per layer.

- E.g. $L = 5$

Sequence	Energy	Entropy
ABABA	0	0
ABCBC ABACA	$N_l \Delta g$	$kln(2)$
ABCAC ABCBA	$2N_l \Delta g$	$kln(2)$
ABCAB	$3N_l \Delta g$	0

(Removing sequences identical under cyclic permutations of labels or reversal)

ΔG and classical nucleation theory



- Expectation of % cubic molecules
- Points show CNT estimate of critical nucleus size using:

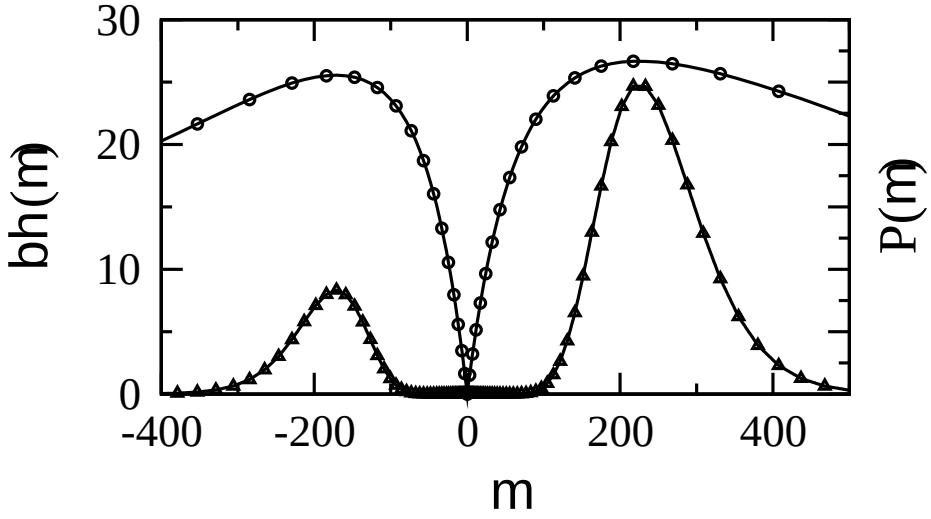
$$\gamma_{sl} = 33\,\mathrm{mJ\,m^{-2}}$$

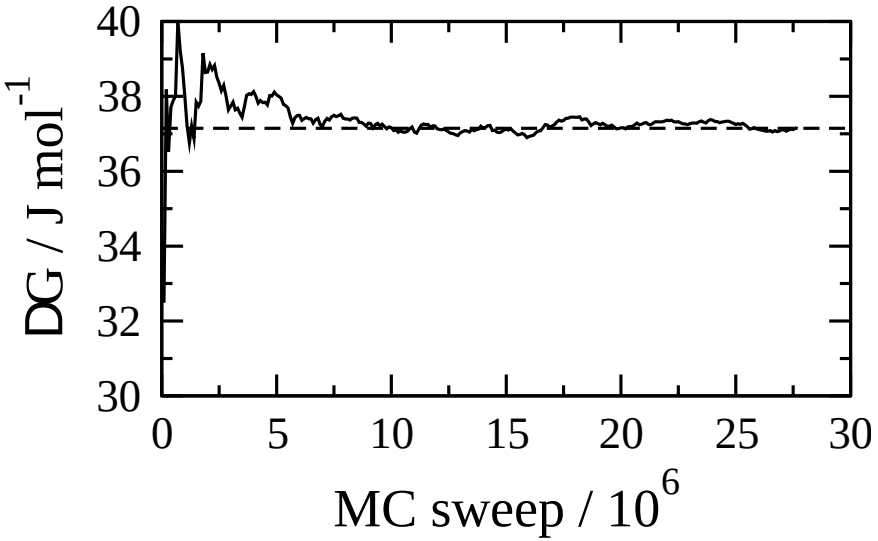
$$\Delta H_{fus} = 6.01\,\mathrm{kJ\,mol^{-1}}$$

Units:

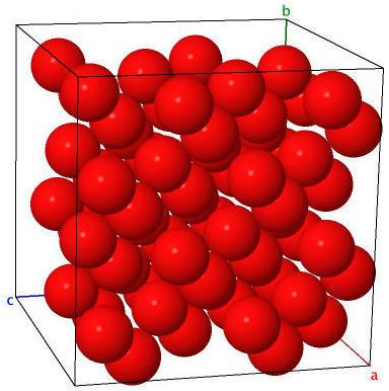
10 *J mol*$^{-1}$ ≈ 0.0001 *eV* per H_2O
≈ 0.006 k_BT per H_2O (200K)

Lattice switching Monte Carlo

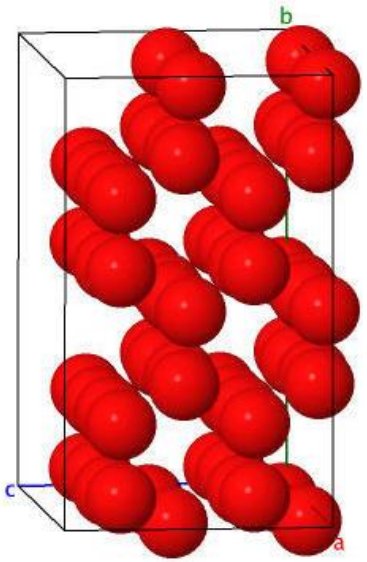




- 200K, 64 molecule unit cells
- 200-400 times faster than TIP4P



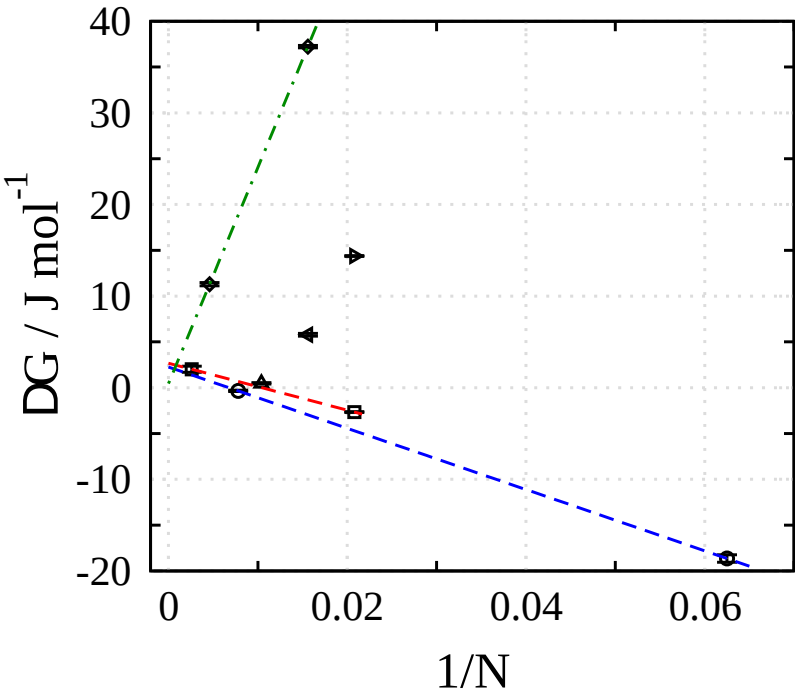
cubic
(diamond)



hexagonal
(lonsdalite)

Finite size effects at 200K

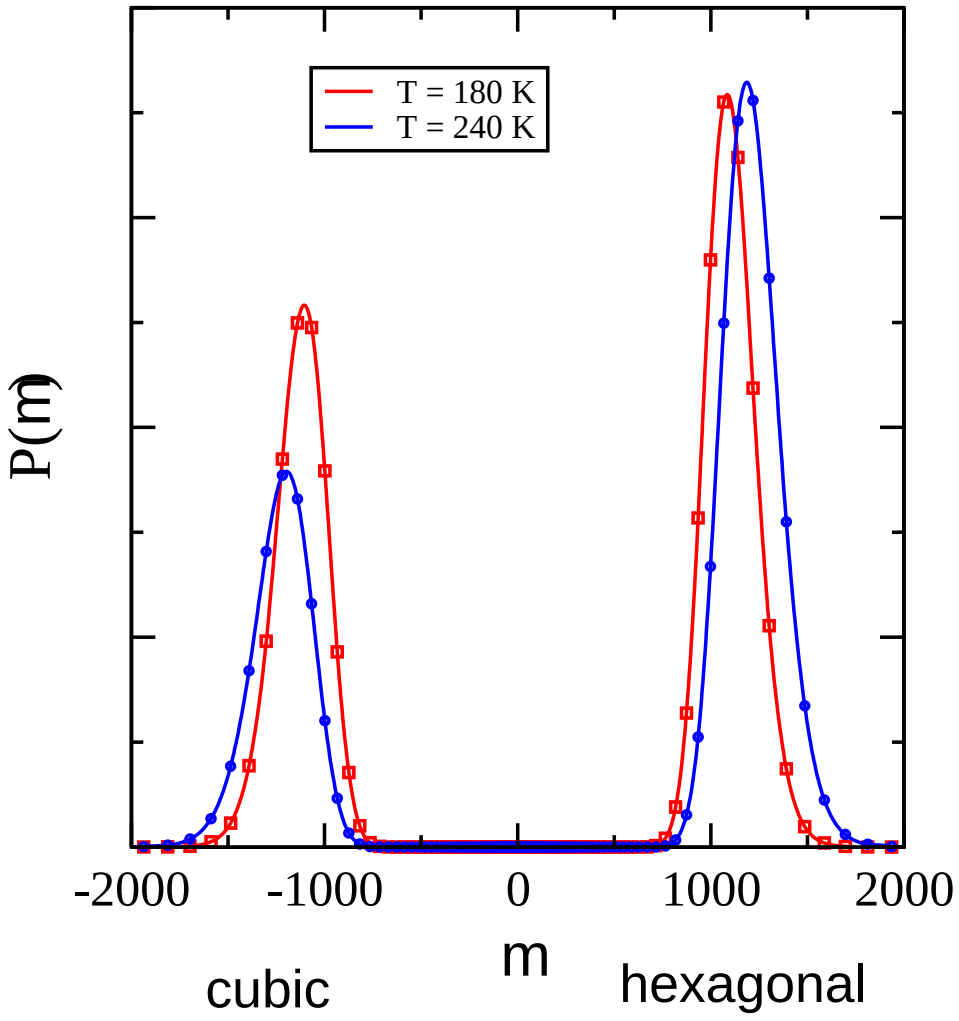
N	a, b, c / Å (cubic)			a, b, c / Å (hexagonal)			ΔG/ J mol^{-1}
48	13.2,	8.77,	12.4	7.16,	15.2,	13.2	14.37(5)
64	8.77,	17.5,	12.4	14.3,	15.2,	8.77	5.8(2)
96	17.5,	13.2,	12.4	14.3,	15.2,	13.2	-0.46(2)
16	8.77,	8.77,	6.20	7.16,	7.60,	8.77	-18.6(4)
128	17.5,	17.5,	12.4	14.3,	15.2,	17.5	-0.35(7)
64	12.4,	12.4,	12.4	14.3,	15.2,	8.77	37.2(1)
216	18.6,	18.6,	18.6,	21.5,	22.8,	13.2	11.2(2)
48	13.2,	8.77,	12.4	14.3,	7.60,	13.2	-2.7(5)
384	26.4,	17.5,	24.8	28.7,	15.2,	26.3	2.0(3)



$\Delta G = 0.4$ *to* 2.6 *J mol*$^{-1}$ in thermodynamic limit

c.f. published estimate 0 ± 30 *J mol*$^{-1}$
(Moore and Molinero PCCP 2011)

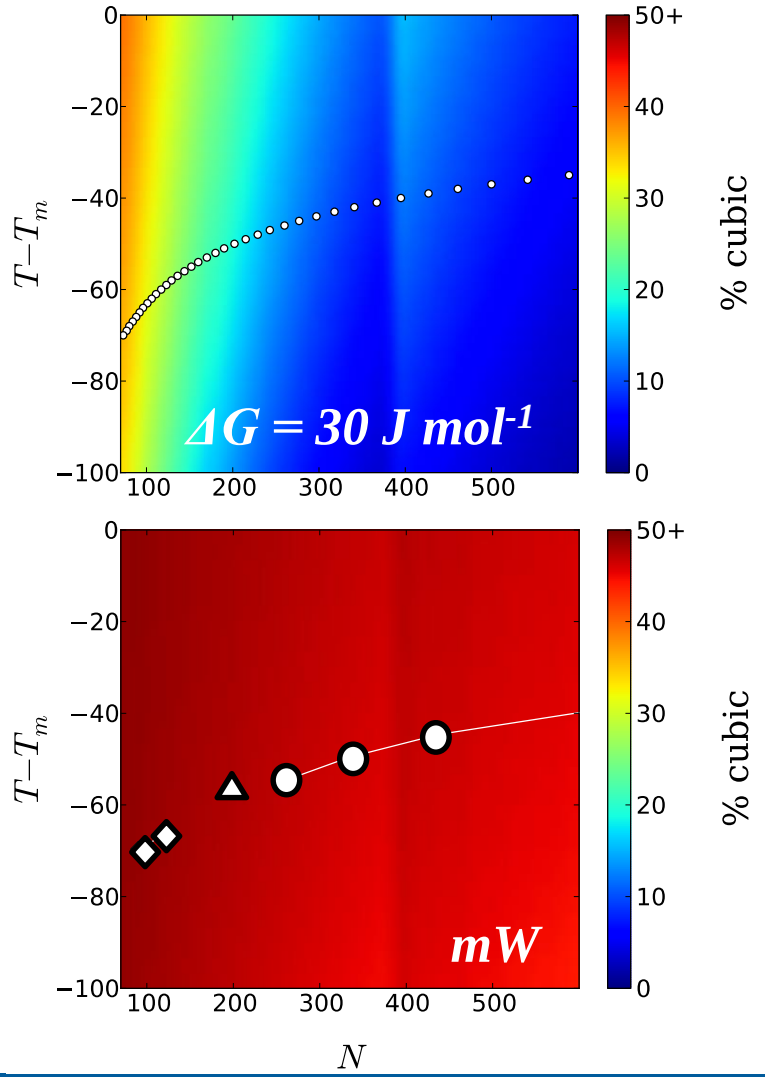
Temperature dependence



- N = 384

T (K)	ΔG / J mol^{-1}
180	2.47(3)
200	4.15(2)
220	3.55(3)
240	5.77(4)

Comparison of stacking energetics



- mW has almost exactly zero penalty for formation of cubic stacking faults
- Will nucleate stacking disordered ice at all temperatures

○ Li, Donadio & Galli 2011

△ Reinhardt & Doye 2011

◇ Moore & Molinero 2011

DQ *J. Chem. Phys*. **2014**, 141, 121101

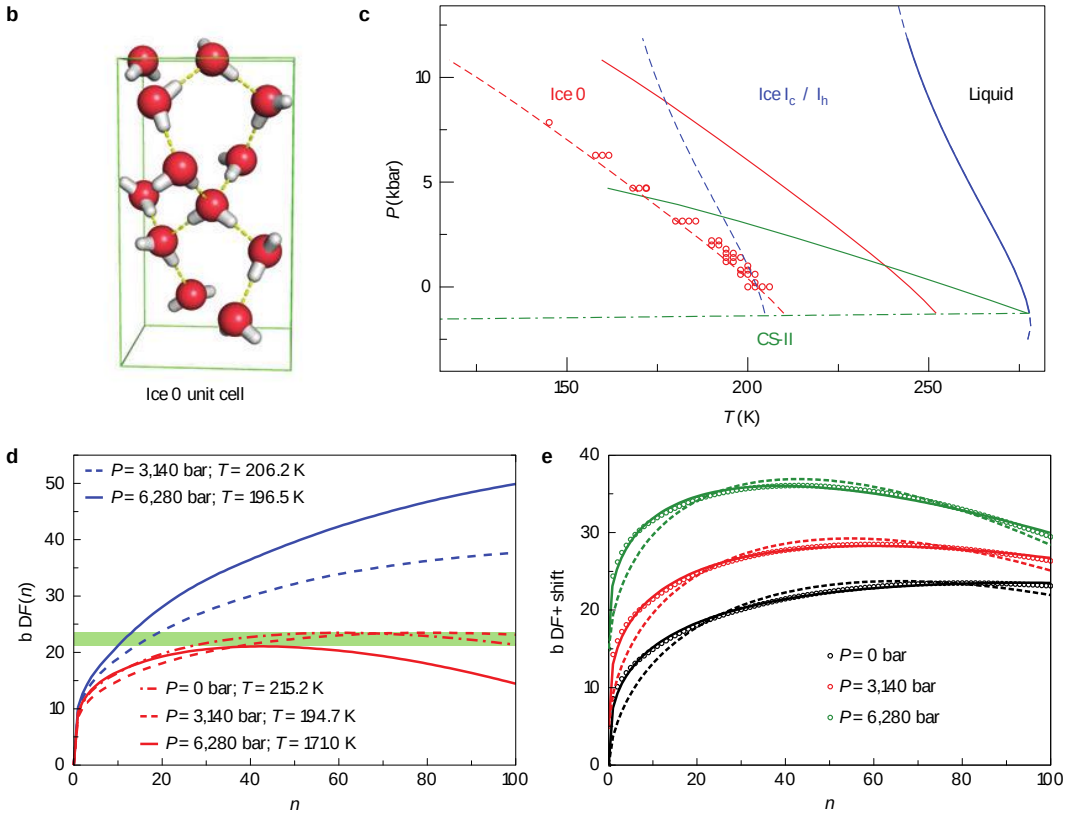
nature materials

ARTICLES

PUBLISHED ONLINE: 18 MAY 2014 | DOI: 10.1038/NMAT3977

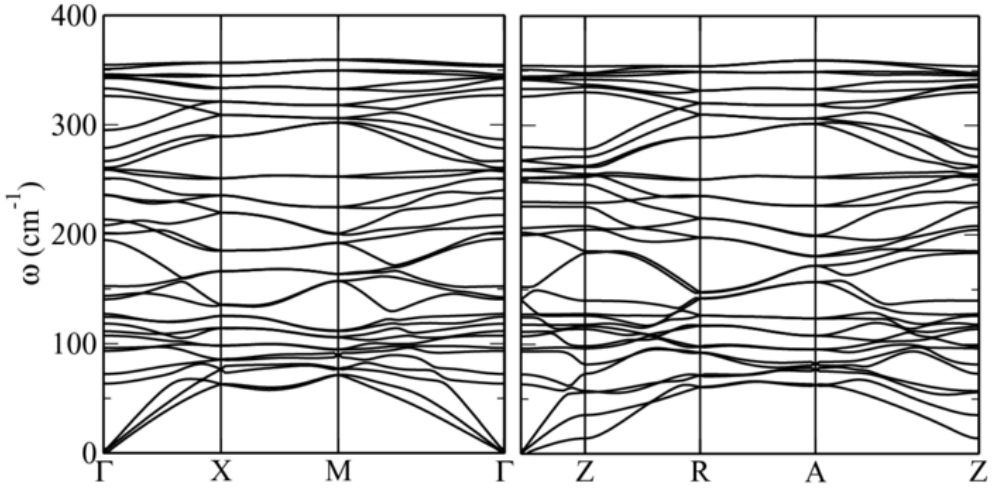
New metastable form of ice and its role in the homogeneous crystallization of water

John Russo[1†], Flavio Romano[1,2†] and Hajime Tanaka[1*]



Is ice 0 real?

	a (Å)	*b* (Å)	*c* (Å)	Δ*E* (meV)
TIP4P	6.04	6.04	10.94	7.21
mW	5.93	5.93	10.74	7.58
PBE	6.00	6.00	10.85	12.8
PBESOL+D3	5.70	5.71	10.30	15.3
PBE0+D3	6.03	5.94	10.67	12.5
PBE0	6.00	5.83	10.55	10.1
DMC	...	...	...	17 ± 5



Slater, B. & DQ
Crystal nucleation: Zeroing in on ice
Nat. Mater., **2014**, *13*, 670-671

DQ; Alfè, D. & Slater, B.
J. Chem. Phys., **2014**, *141*, 161102

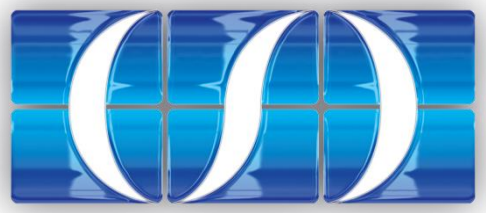
Summary

- Quantitative (if inaccurate) calculation of nucleation rates from molecular simulation is becoming possible for ‘real’ systems..
- .. provided (very) cheap models are available.
- Unlikely to be be predictive for some time, but trends should be accessible.
- Quantifying sources of error likely to be very challenging.
- Existing simulations do open up new questions!

Acknowledgements

Ice 0 stability

Ben Slater (UCL)
Dario Alfé (UCL)



Engineering and Physical Sciences Research Council

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