Pathways to self-assembly: Crystallization by nucleation and growth

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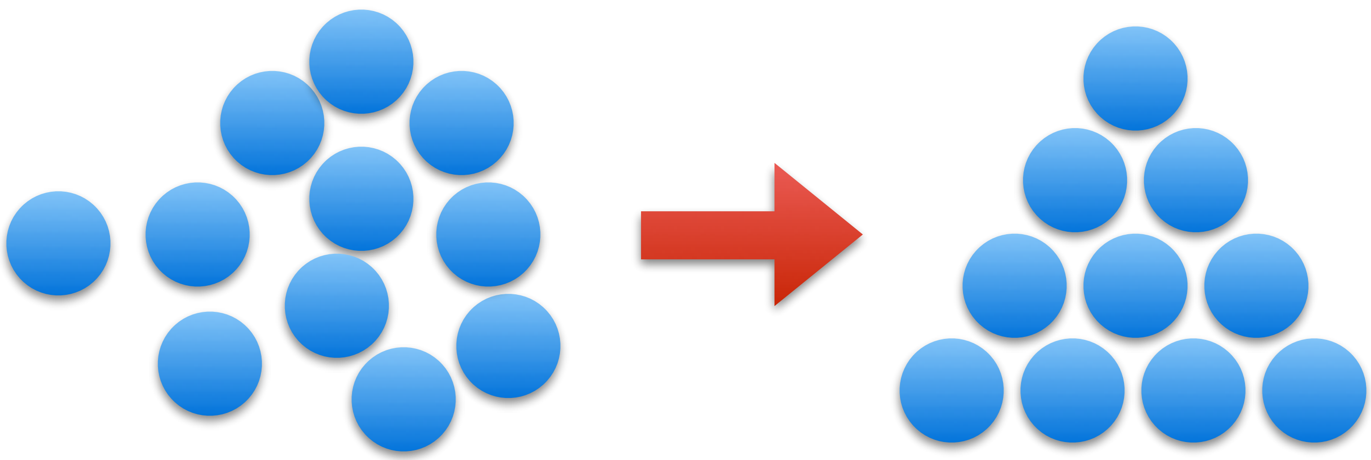
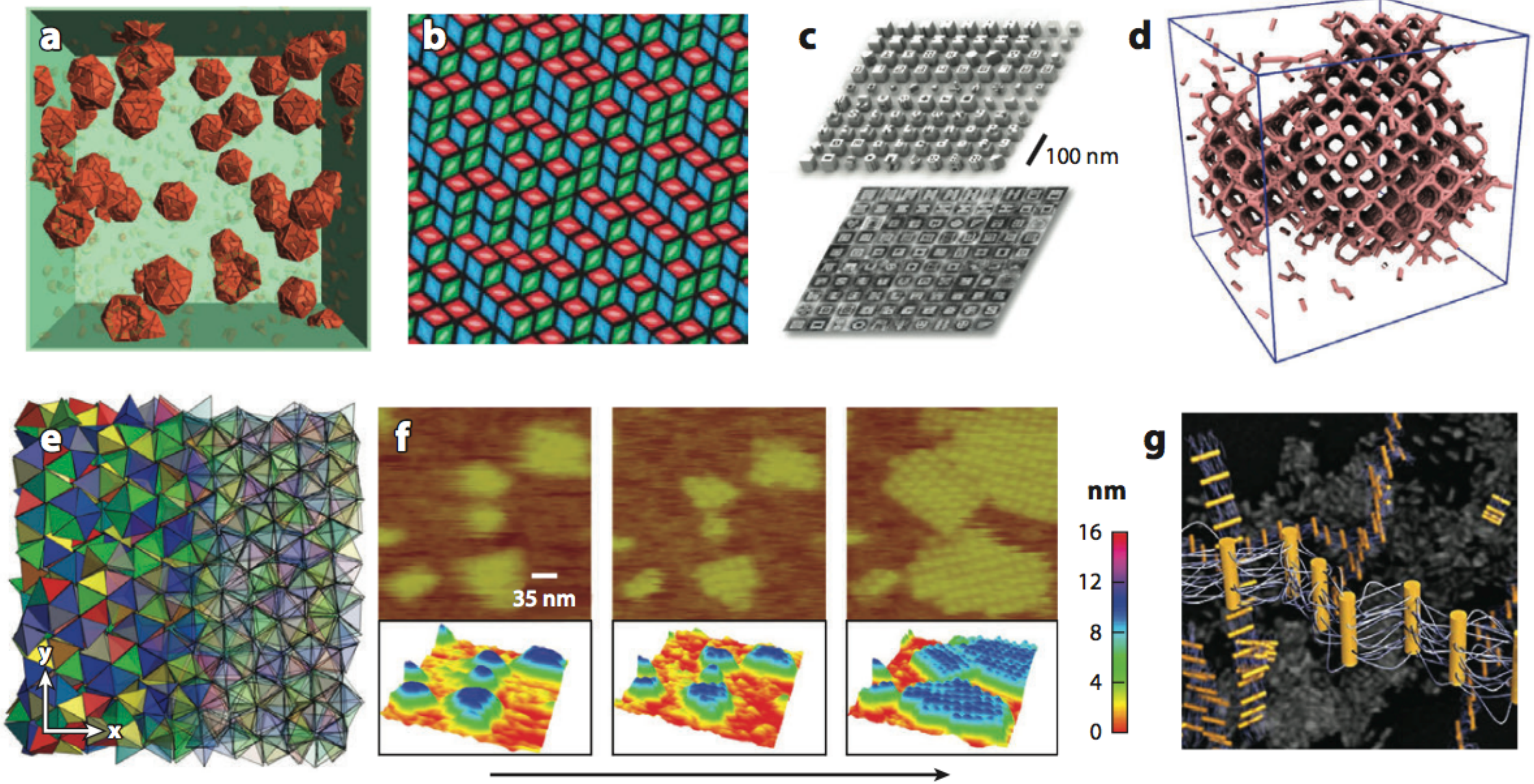


Self assembly

Dynamical process ⇒ spontaneous organization into ordered structures

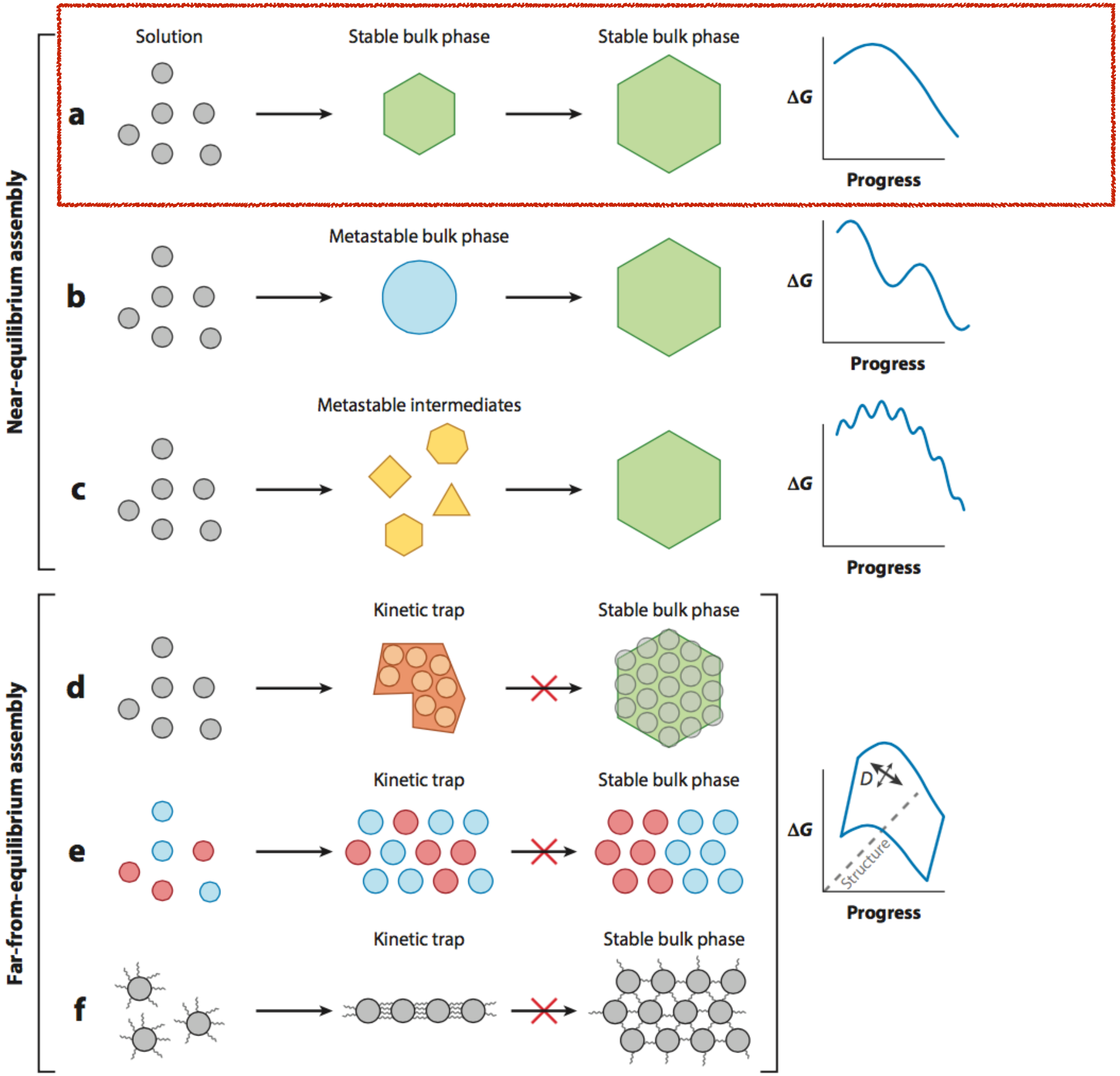
viral capsids | surface adsorbed molecules | DNA bricks | patchy particles



hard tetrahedra | surface-layer proteins | DNA-linked nano rods

S. Whitelam and R. Jack, Annu. Rev. Phys. Chem. 2015.

Pathways to self assembly



Nucleation & growth

S. Whitelam and R. Jack, Annu. Rev. Phys. Chem. (2015)

Outline of the Lectures

Lecture 1: Nucleation and the rare event problem

Lecture 2: Classical nucleation theory

Lecture 3: Path sampling methods

Lecture 4: Path analysis: finding the mechanism

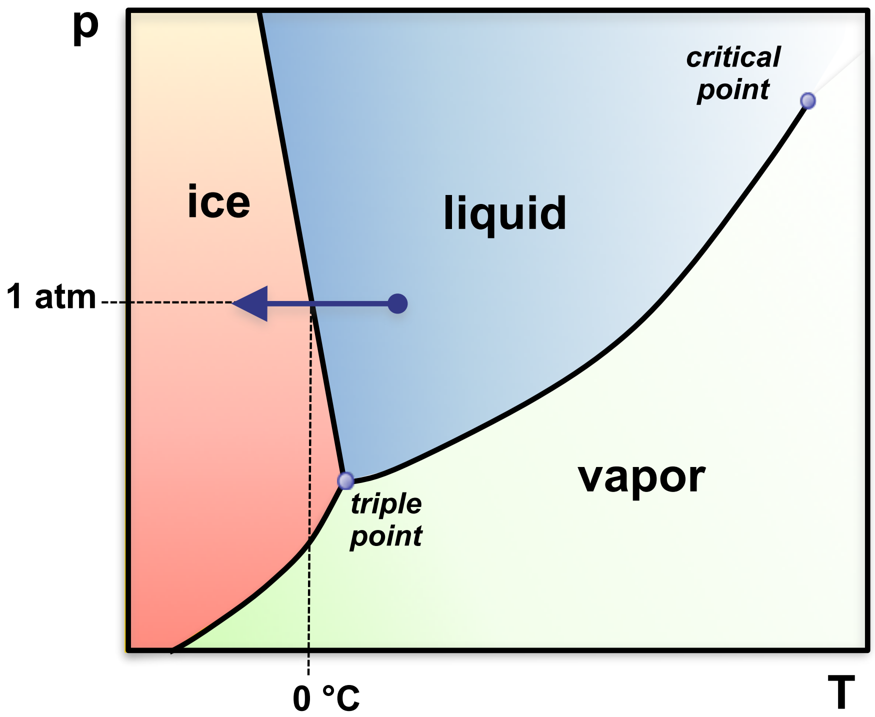
Lecture I

Nucleation and the rare event problem in molecular simulations

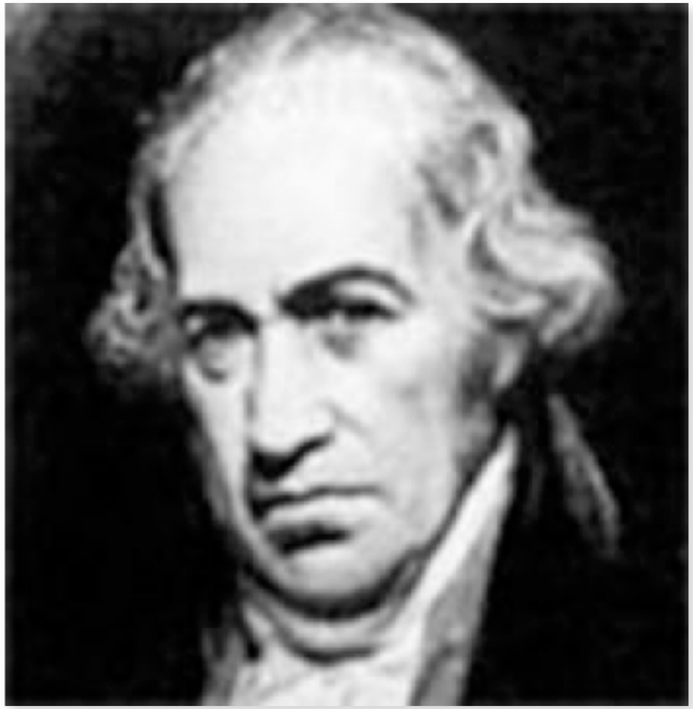
Outline

1. First order phase transitions
2. Nucleation and growth
3. Time scale problem in molecular simulation

A little experiment



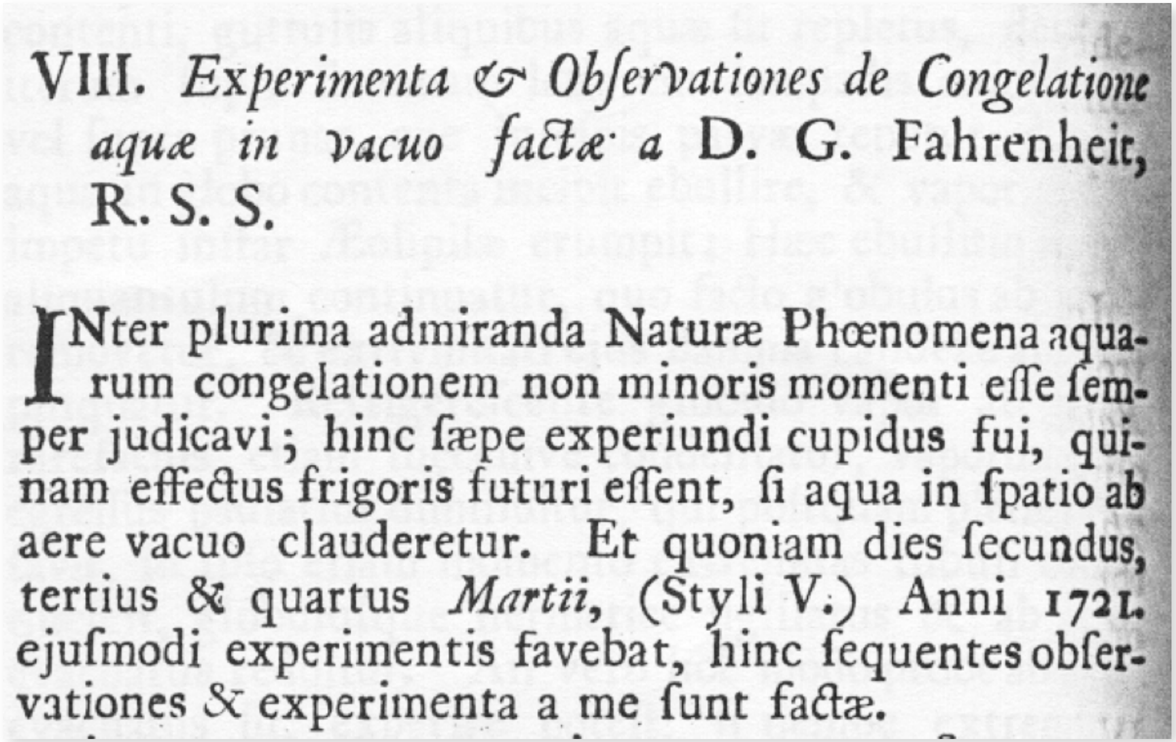
Fahrenheit's discovery



Daniel Gabriel Fahrenheit

* 1686 Danzig

† 1736 Den Haag

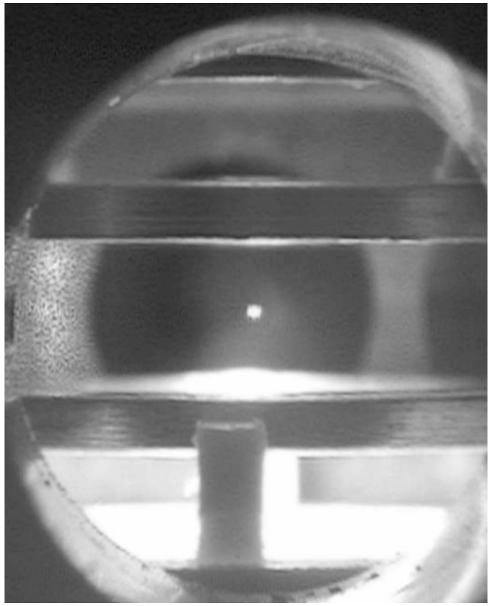


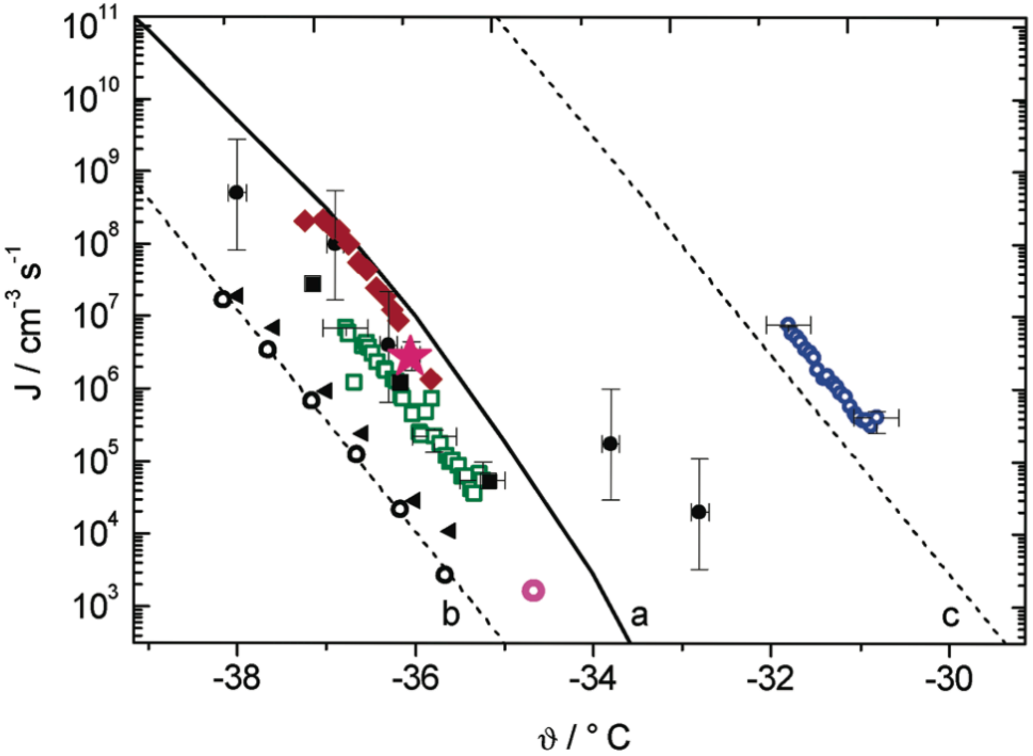
VIII. *Experimenta & Obſervationes de Congelatione aquæ in vacuo factæ a* D. G. Fahrenheit, R. S. S.

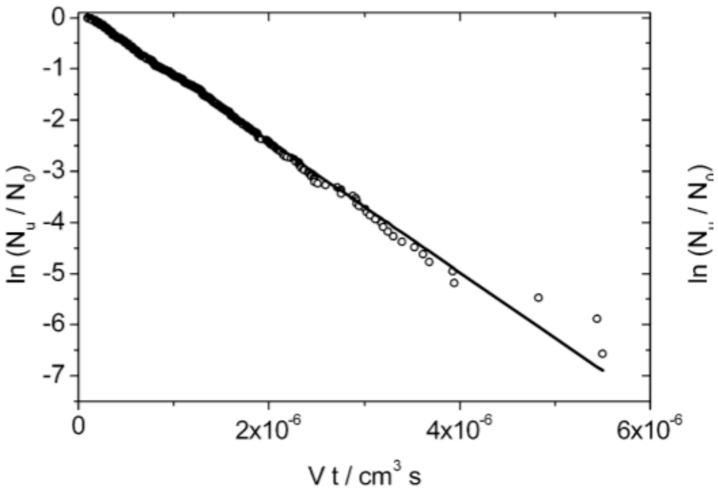
INter plurima admiranda Naturæ Phœnomena aquarum congelationem non minoris momenti eſſe ſemper judicavi; hinc ſæpe experiundi cupidus fui, quinam effectus frigoris futuri eſſent, ſi aqua in ſpatio ab aere vacuo clauderetur. Et quoniam dies ſecundus, tertius & quartus *Martii*, (Styli V.) Anni 1721. ejuſmodi experimentis favebat, hinc ſequentes obſervationes & experimenta a me ſunt factæ.

D.G. Fahrenheit, Proc. Roy. Soc. London 33, 78 (1724)

Fahrenheit's experiment revisited





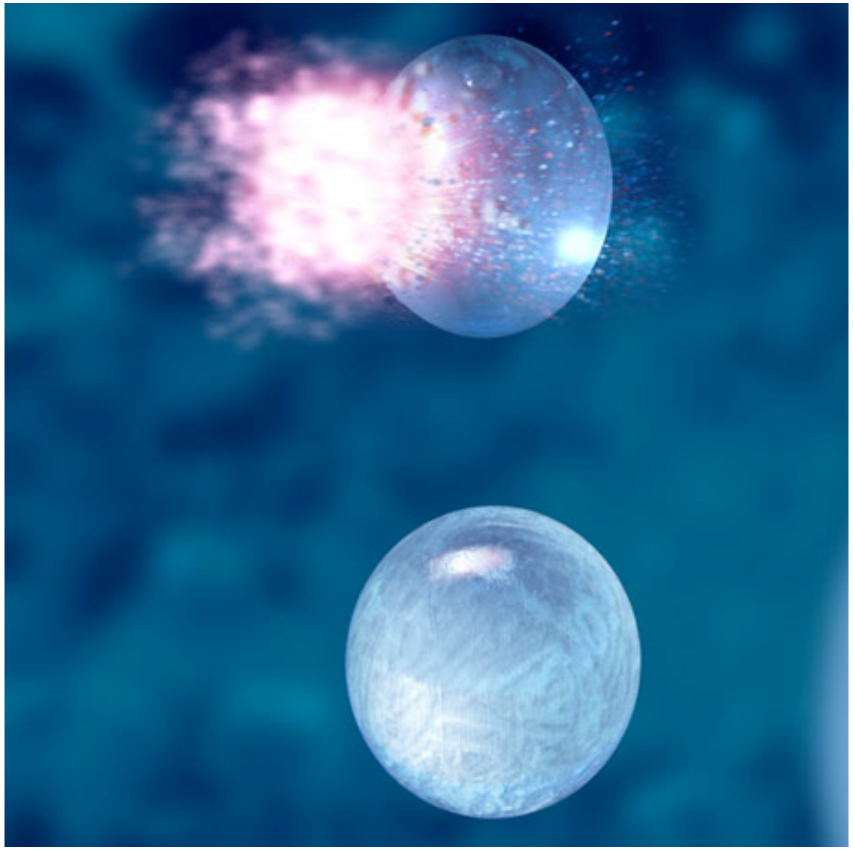


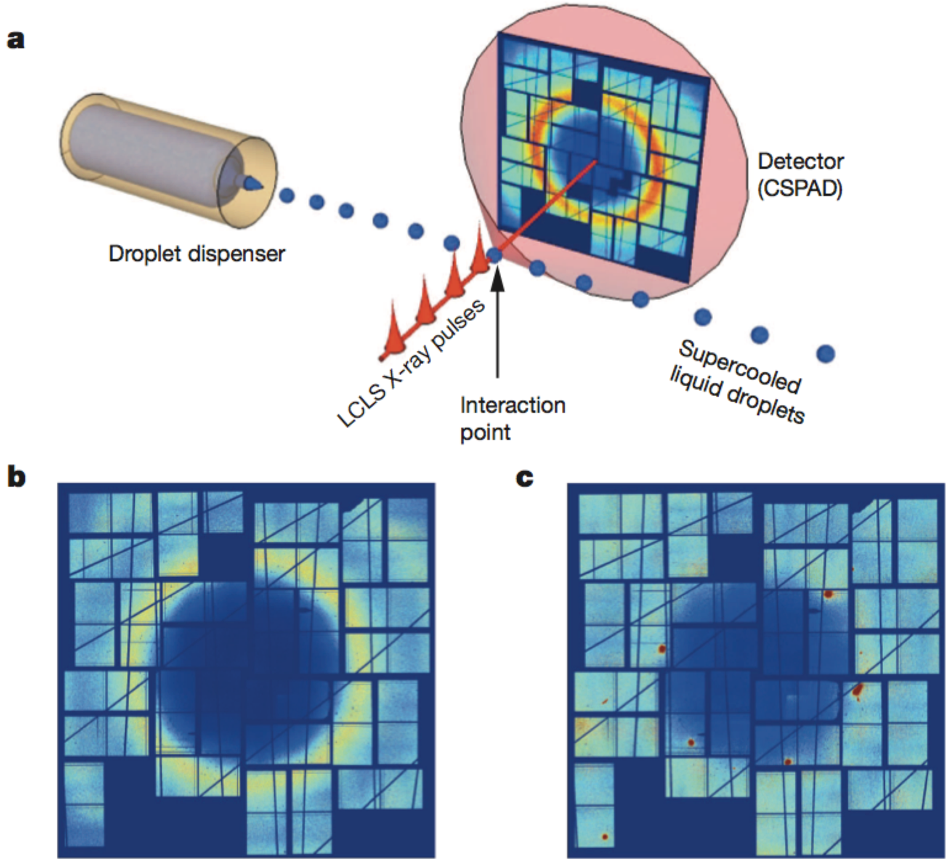
$$\ln \frac{N_u}{N_0} = -J(T)Vt$$

J = nucleation rate

Stöckel, Weidinger, Baumgärtel, Leisner, J. Phys. Chem. A 109, 2540 (2005)

Record low temperature for water



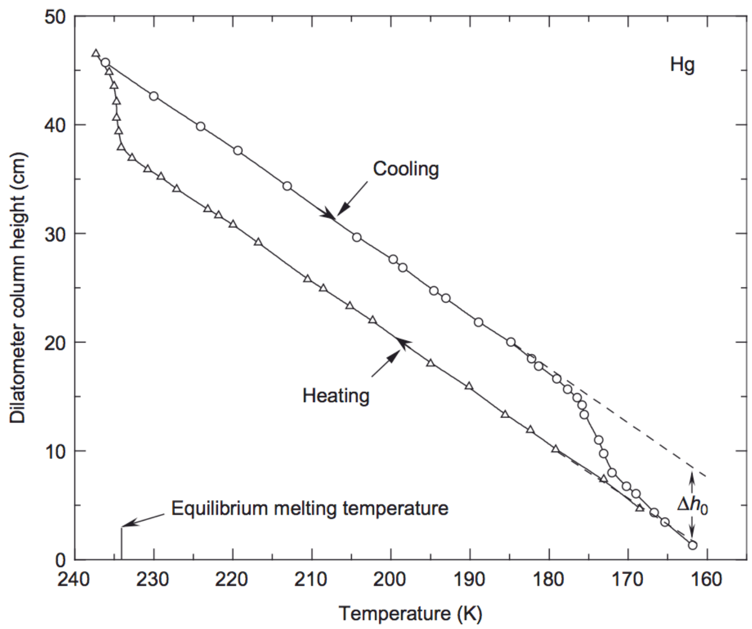


liquid droplet at -46° Celsius

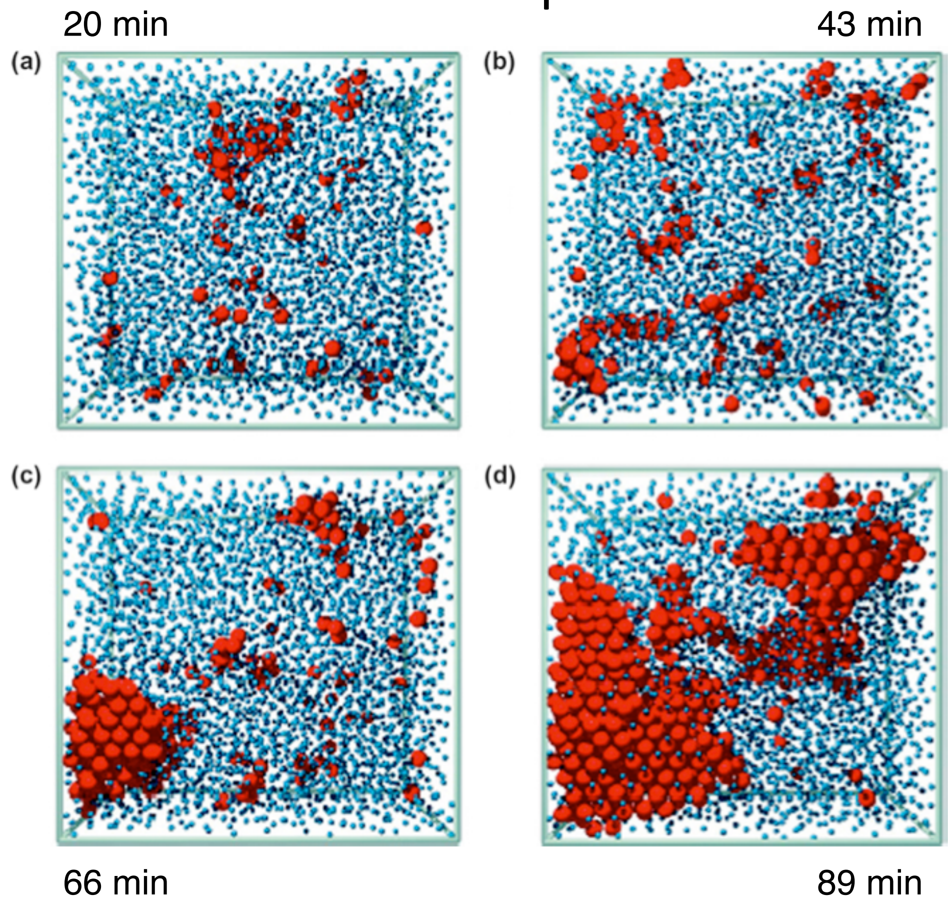
J.A. Sellberg et al., Nature 510, 381 (2014)

Supercooling occurs in many substances

Mercury

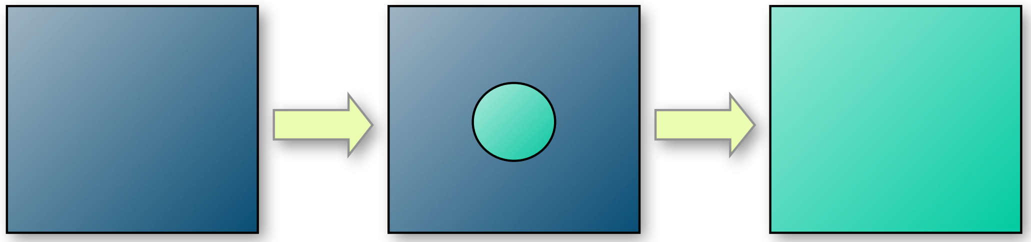


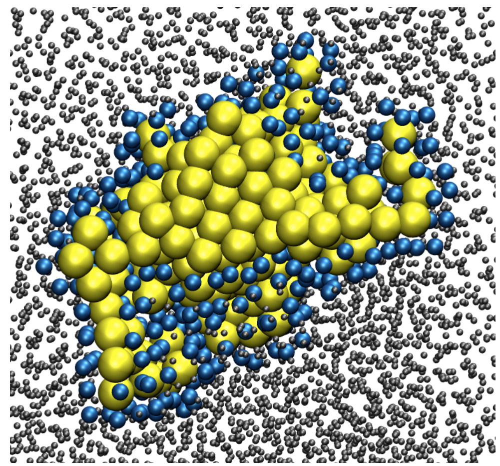
Colloidal suspension



D. Turnbull, J. Chem. Phys. 20, 411 (1952)
U. Gasser, E.R. Weeks, A. Schofield, P.N. Pusey, D.A. Weitz, Science 292, 258 (2003)

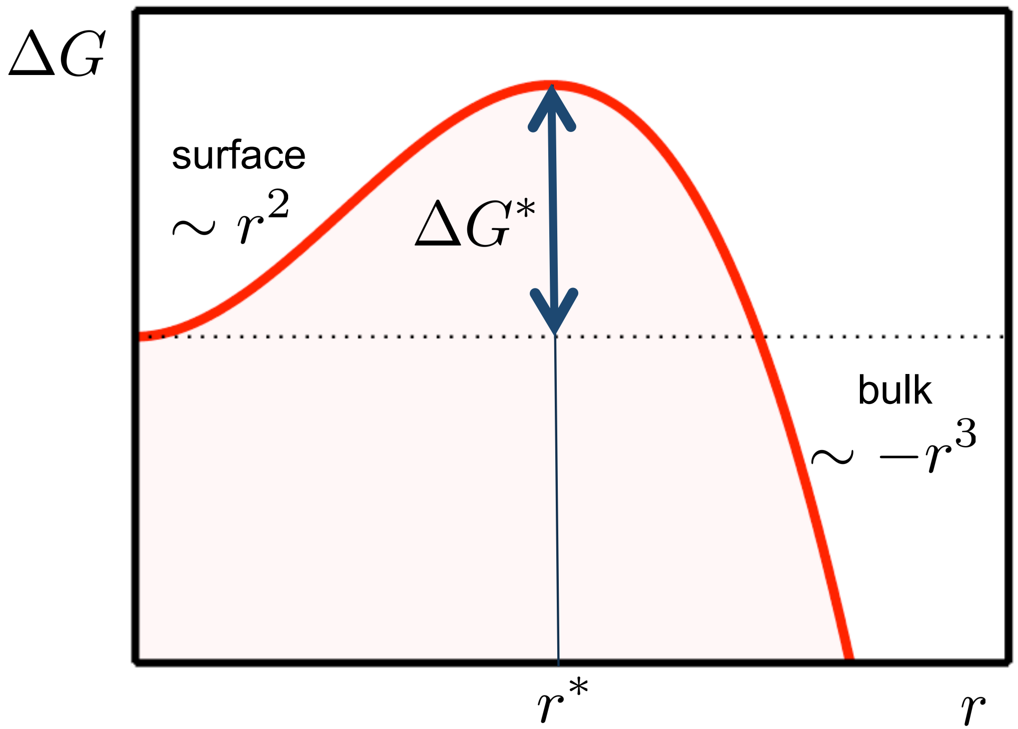
Classical nucleation theory



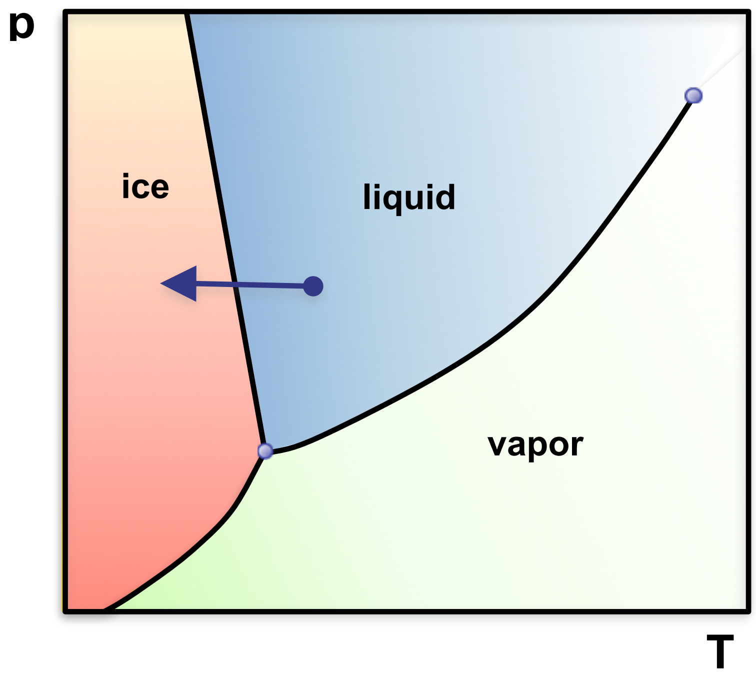


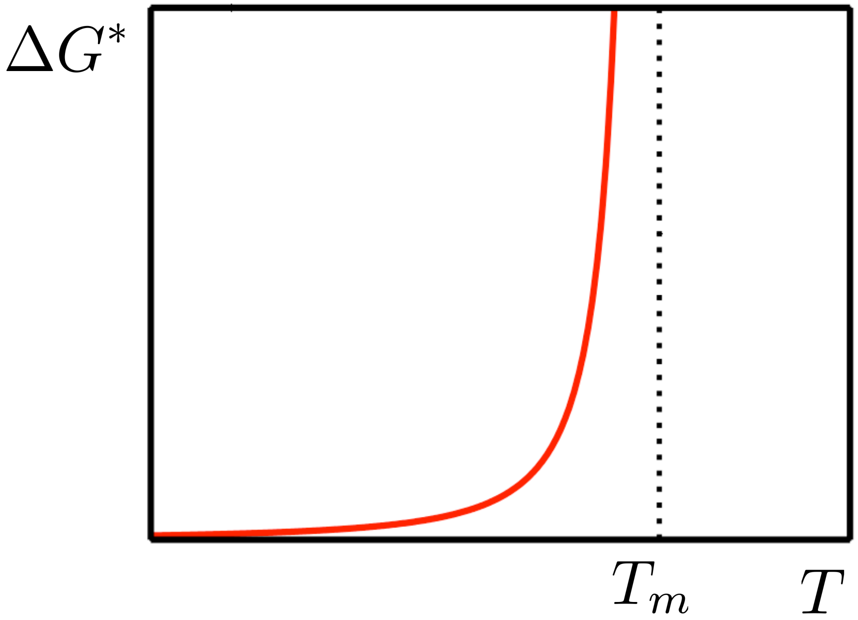
$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \rho_s \Delta\mu$$

$$\Delta\mu = \mu_s - \mu_l < 0$$



Nucleation rate





$$J = c \exp\{-\beta \Delta G^*\}$$

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

$$\Delta\mu = -\frac{\Delta h}{T_m}(T_m - T)$$

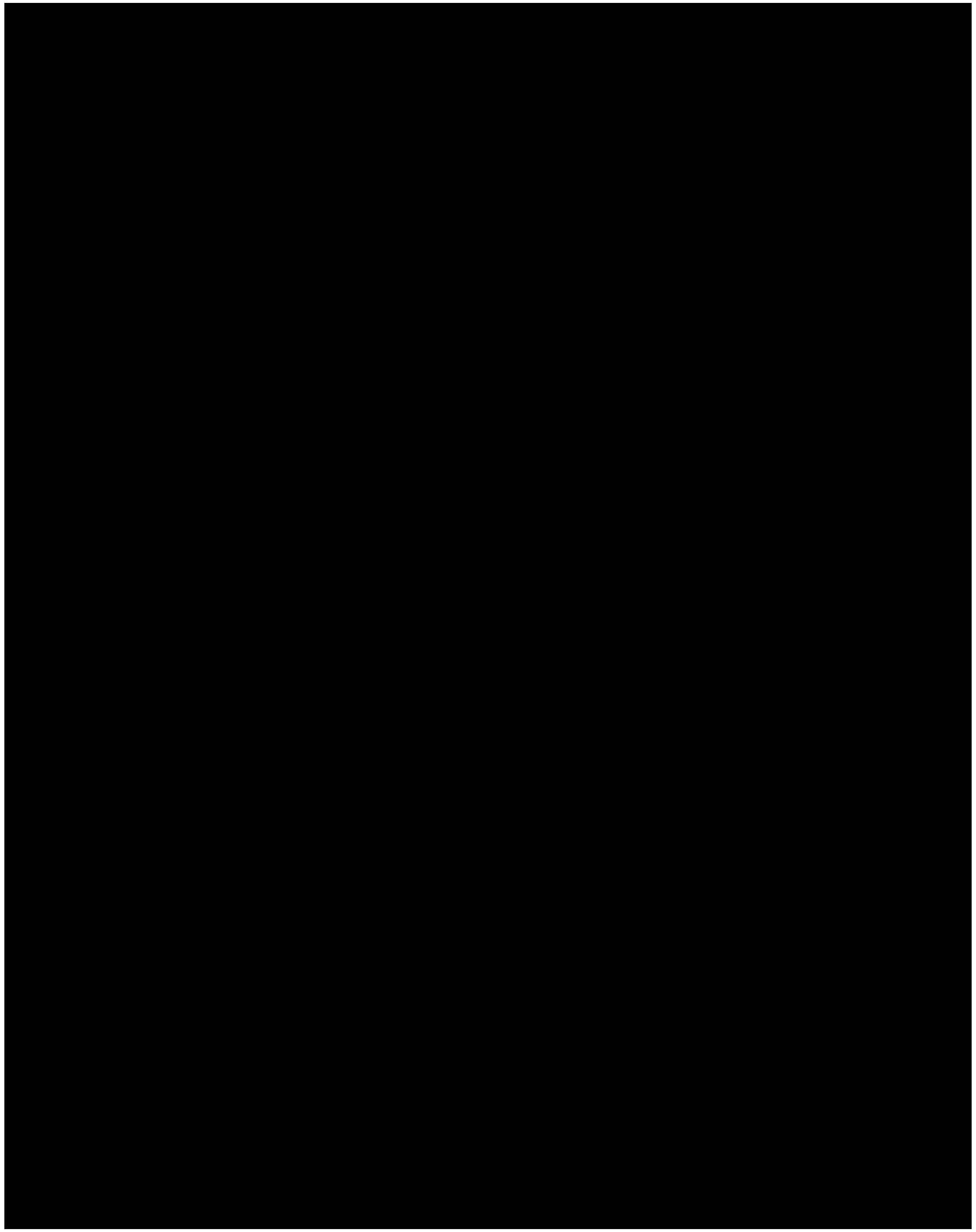
T_m = melting temperature

Δh = heat of fusion

Molecular dynamics simulation

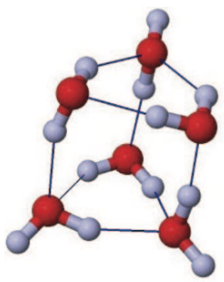
$$\dot{q}_i = p_i / m_i$$

$$\dot{p}_i = F_i(q)$$



Modelling water

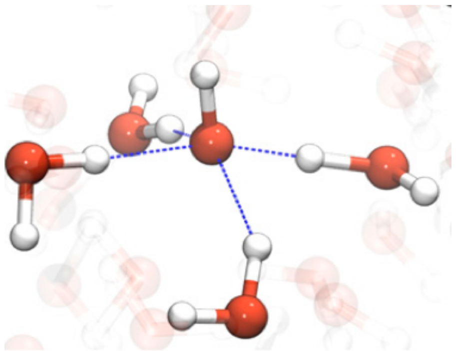
QMC



N=6
energy minimum

Alfe, Bartok, Csanyi, Gillan
JCP 2013

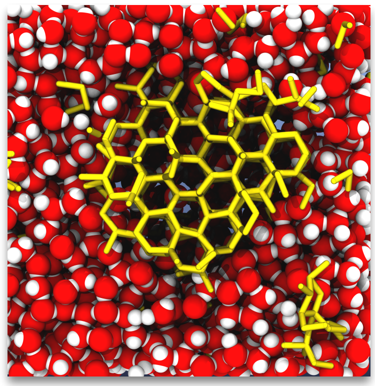
DFT



N=128
t=100 ps

Hassanali, Giberti, Cuny, Kühne, Parrinello
PNAS 2013

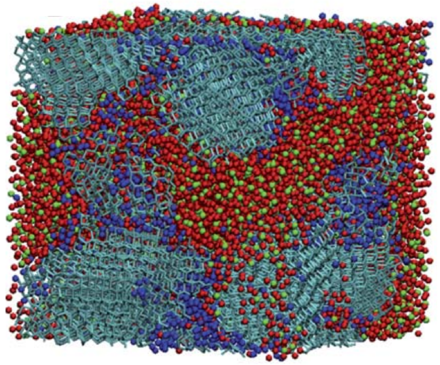
atomistic
(SPC, TIP3P, TIP4P,..)



N = 2.000
t = 10 ns

Geiger, Dellago
JCP 2013

coarse grained
mW



N = 30.000
t = 50 ns

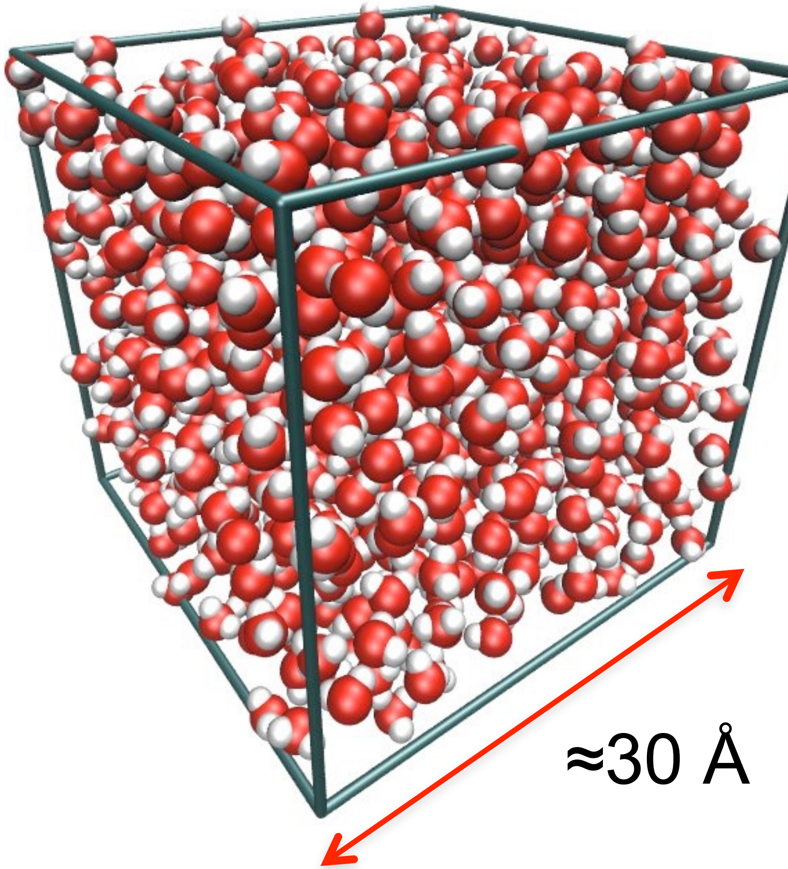
Bullock, Molinero
Farad. Disc. 2013

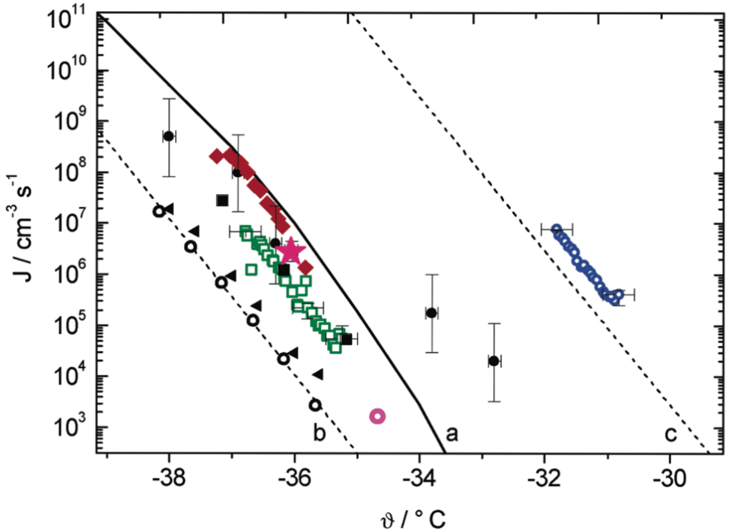
speed →

← **accuracy?**

Long time scales

Experimental nucleation rates J = 10^4-10^9 cm^{-3} s^{-1}





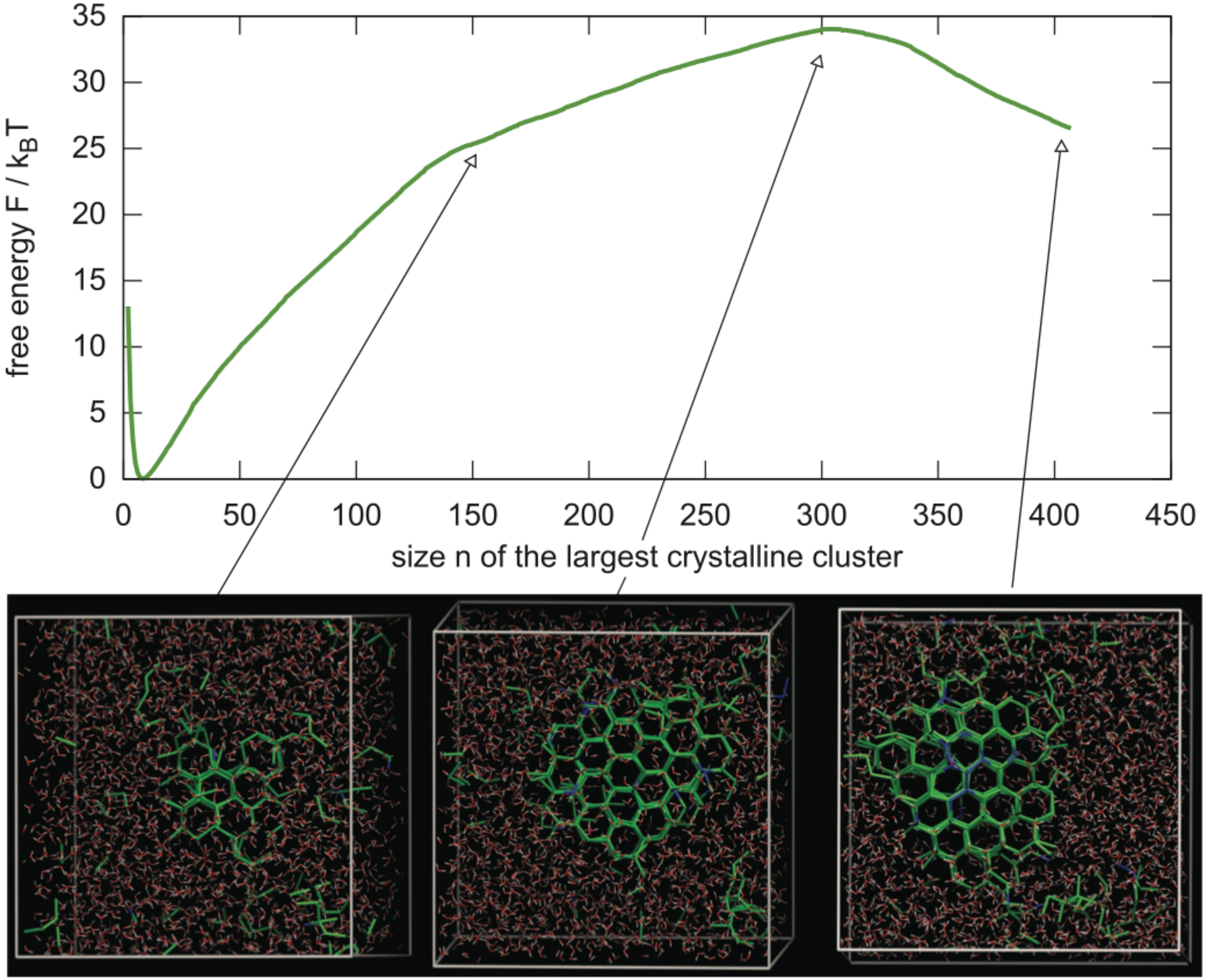
N = 1000

V = 3 x 10^{-20} cm^3

1 event per 10^{10}-10^{15} sec

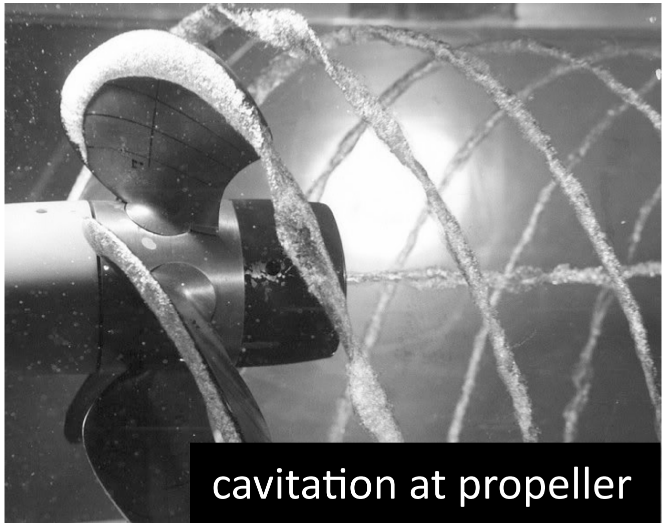
10^{25}-10^{30} MD steps

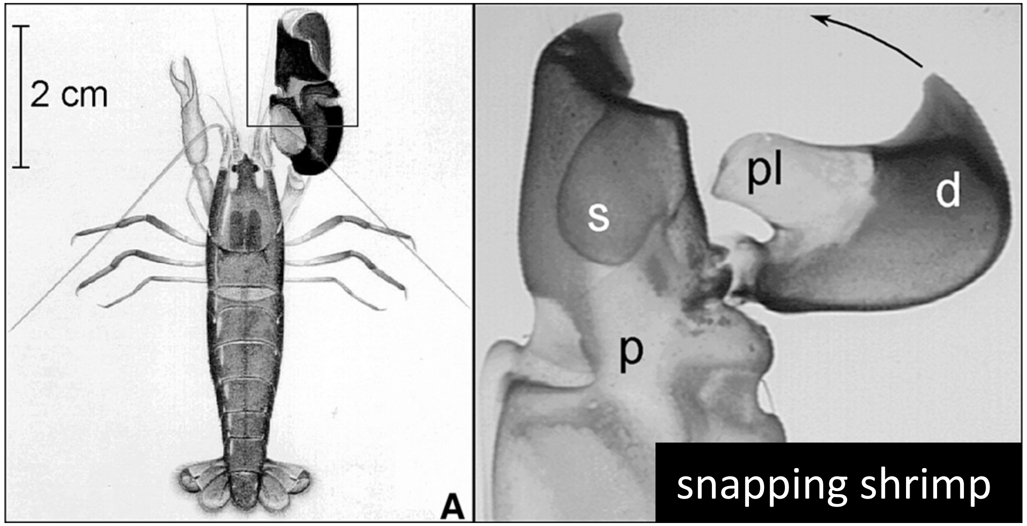
Crystallization of supercooled water

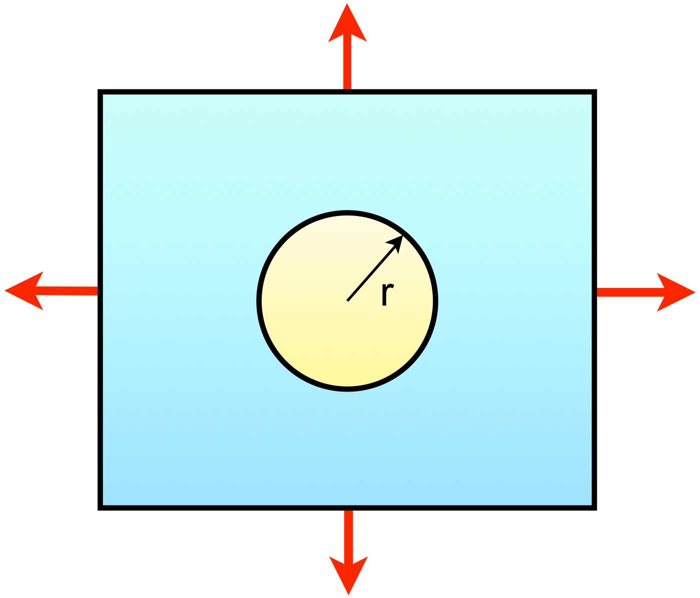


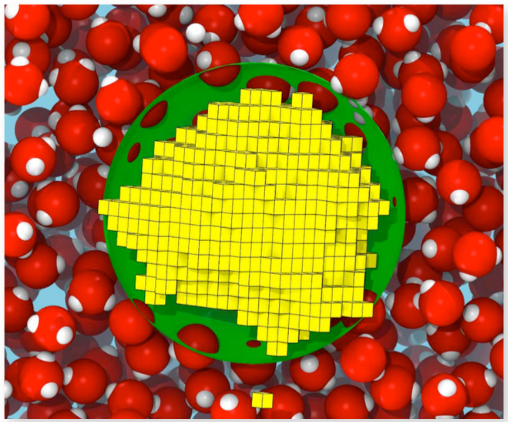
P. Geiger and C. Dellago, JCP (2013)

Cavitation - water at negative pressure



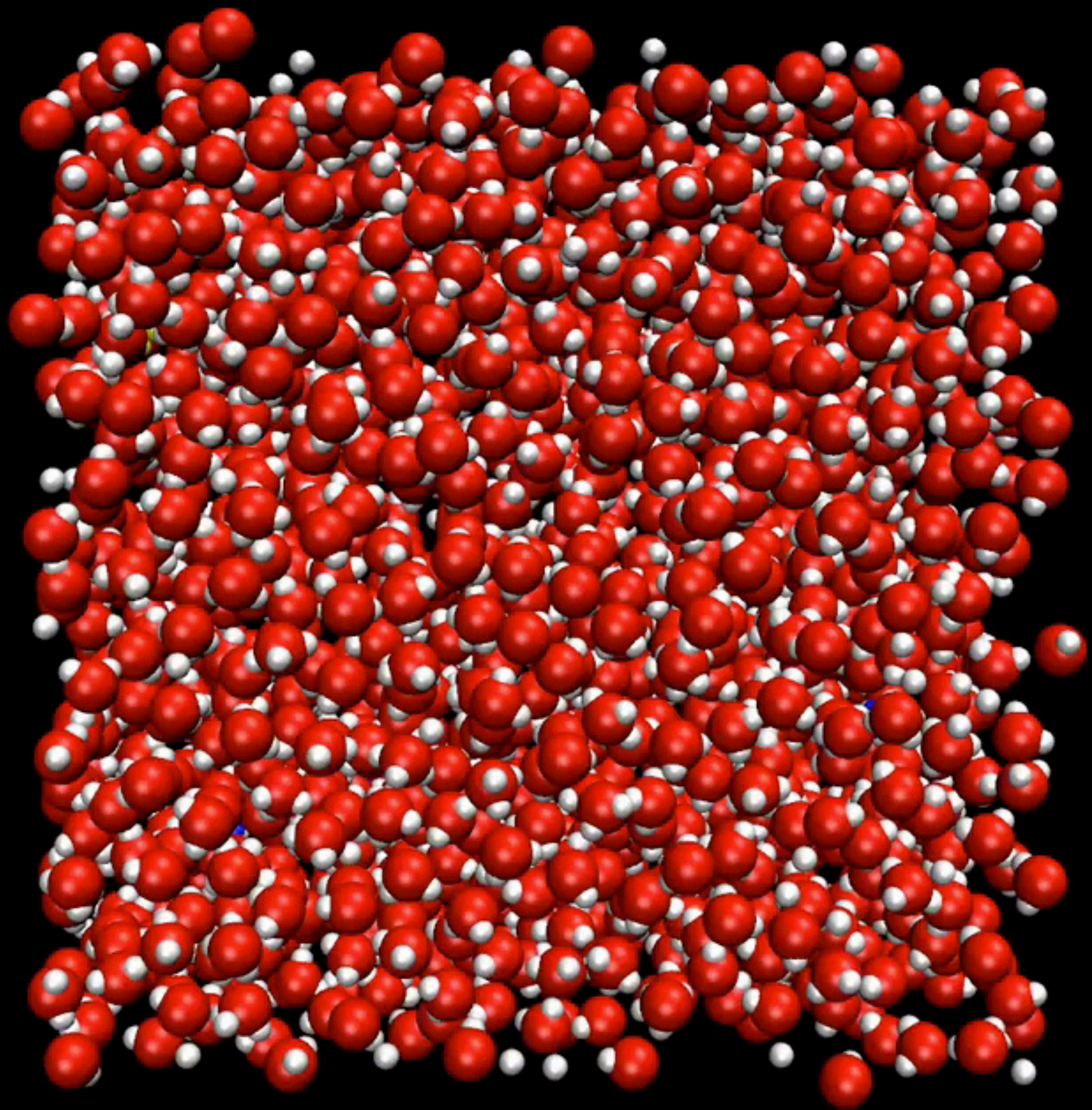




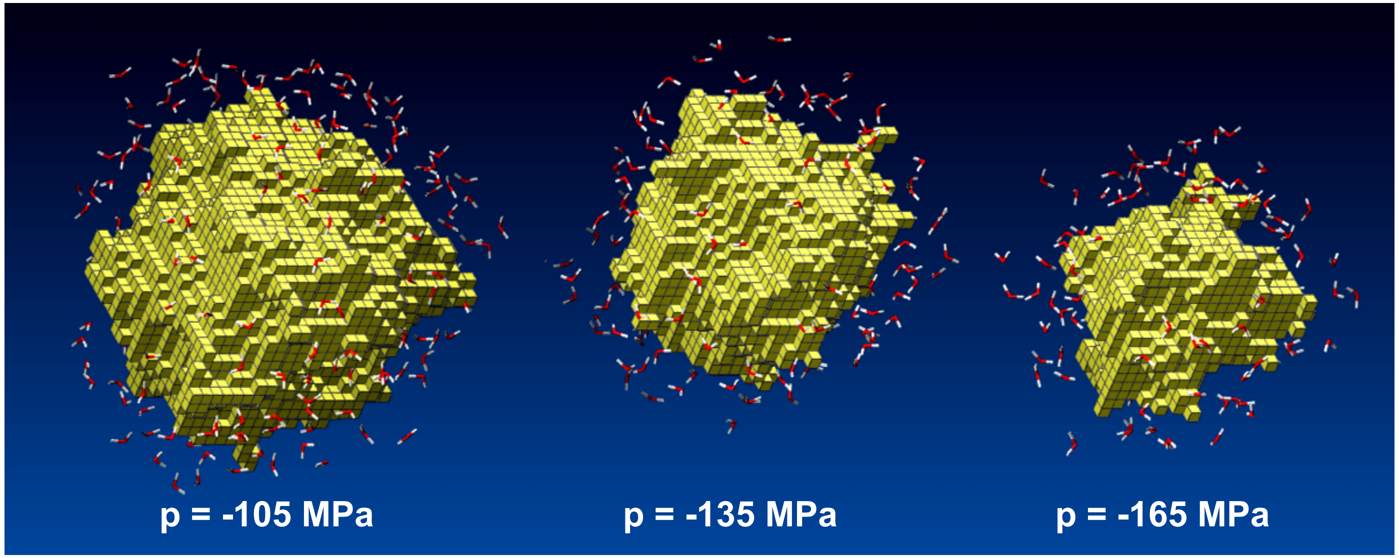


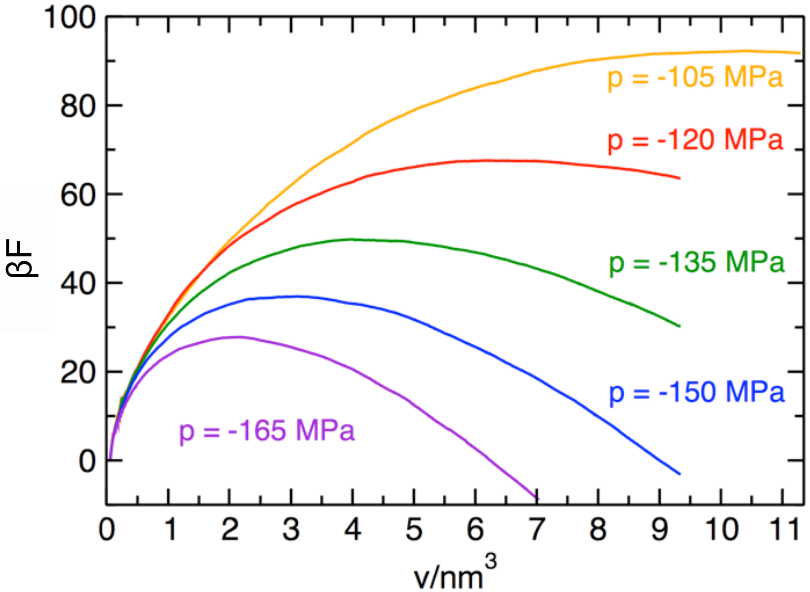
$$\Delta G(r) = 4\pi r^2 \sigma + \frac{4\pi}{3} r^3 (p - p_{\mathrm{sat}})$$

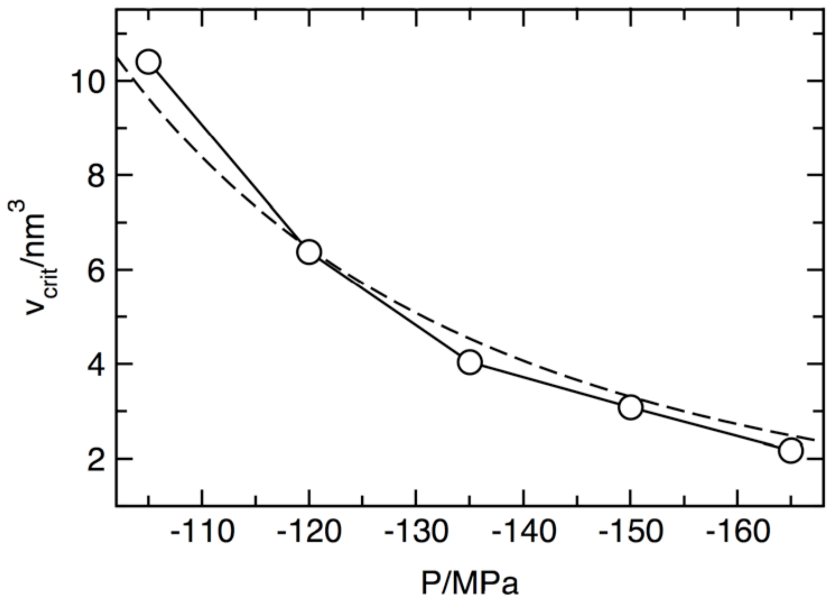
P=-120 MPa
P=296 K
N=2000



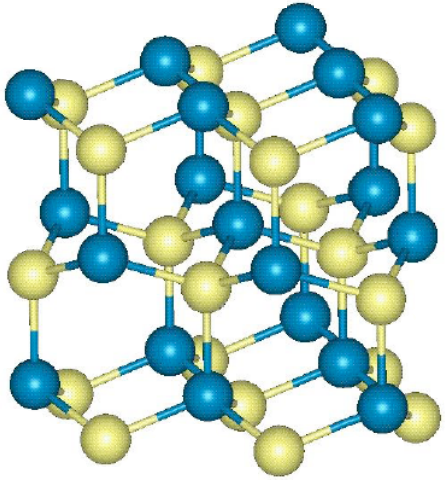
Free energy of bubble nucleation





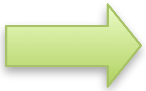


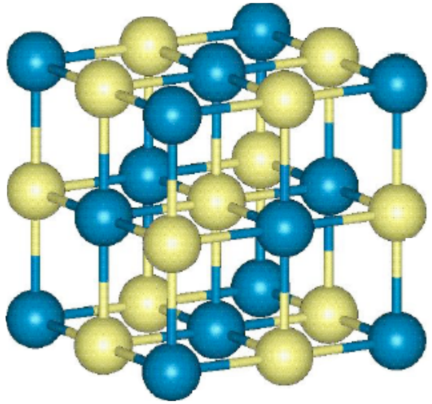
Structural transformation in CdSe



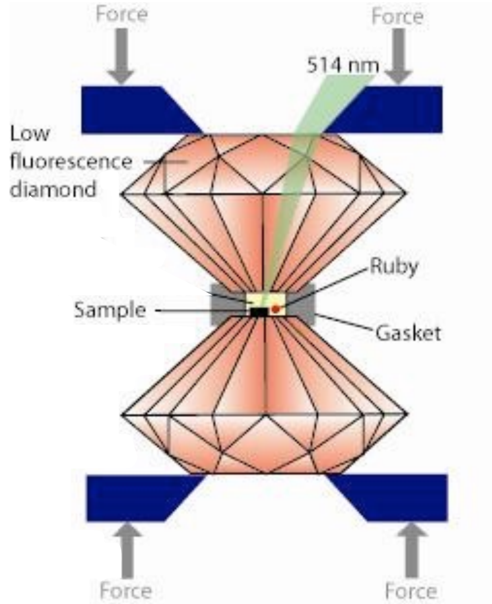
Wurtzite

2.5 GPa

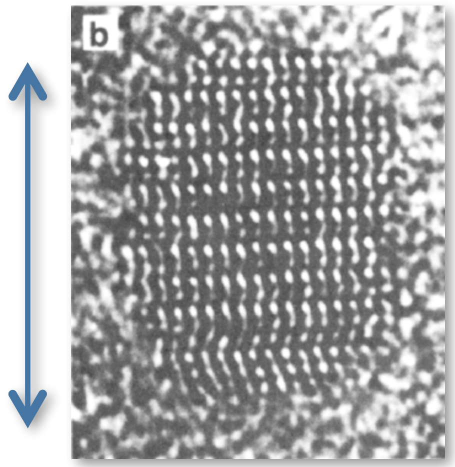


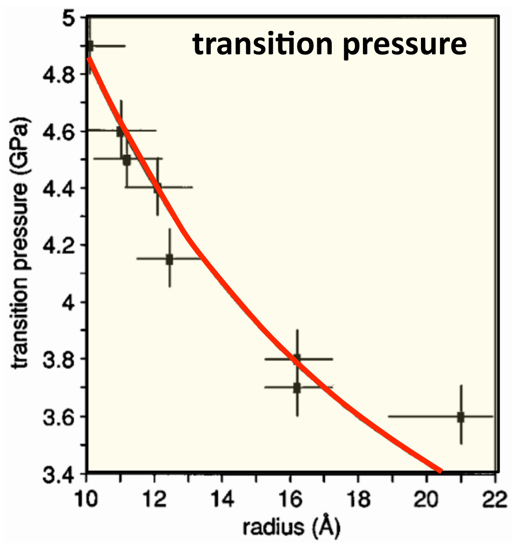


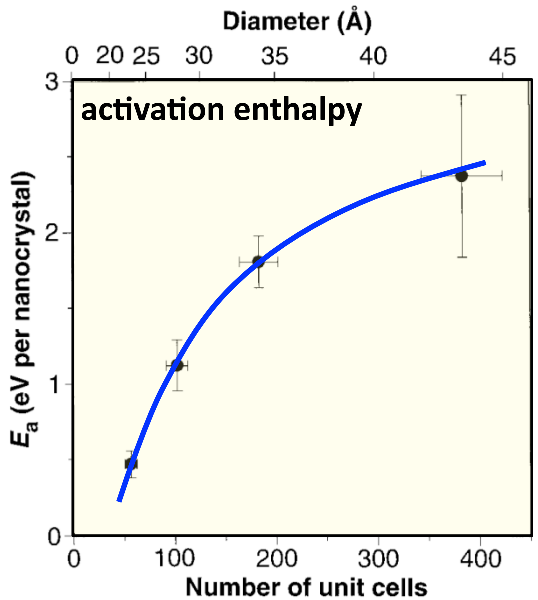
Rocksalt



10-30 Å

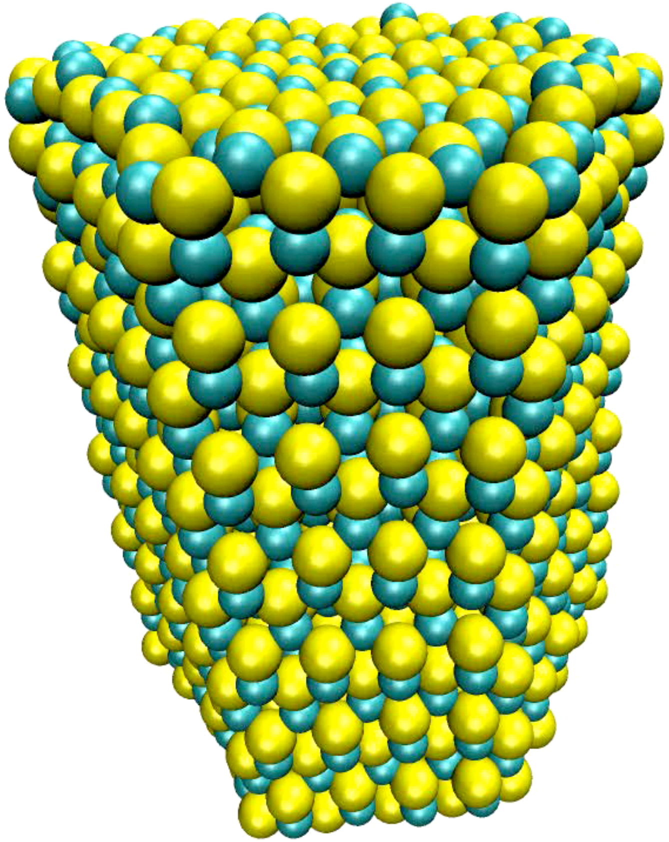


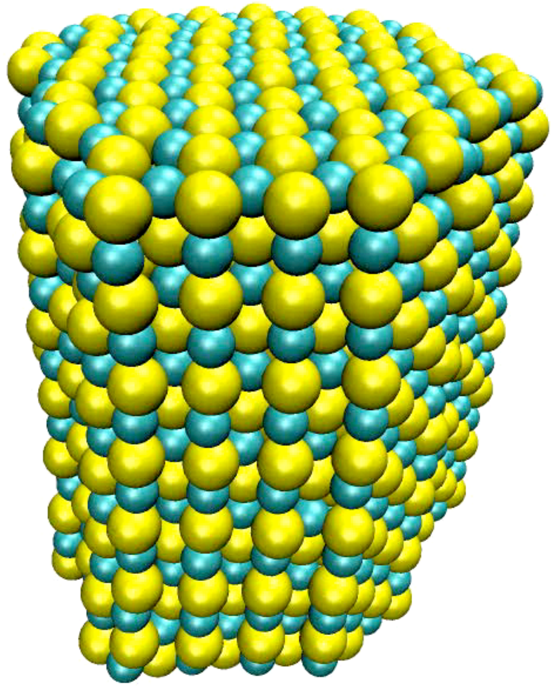




S. H. Tolbert and A. P. Alivisatos, JCP 102, 4642 (1995); Science 265, 373 (1994)

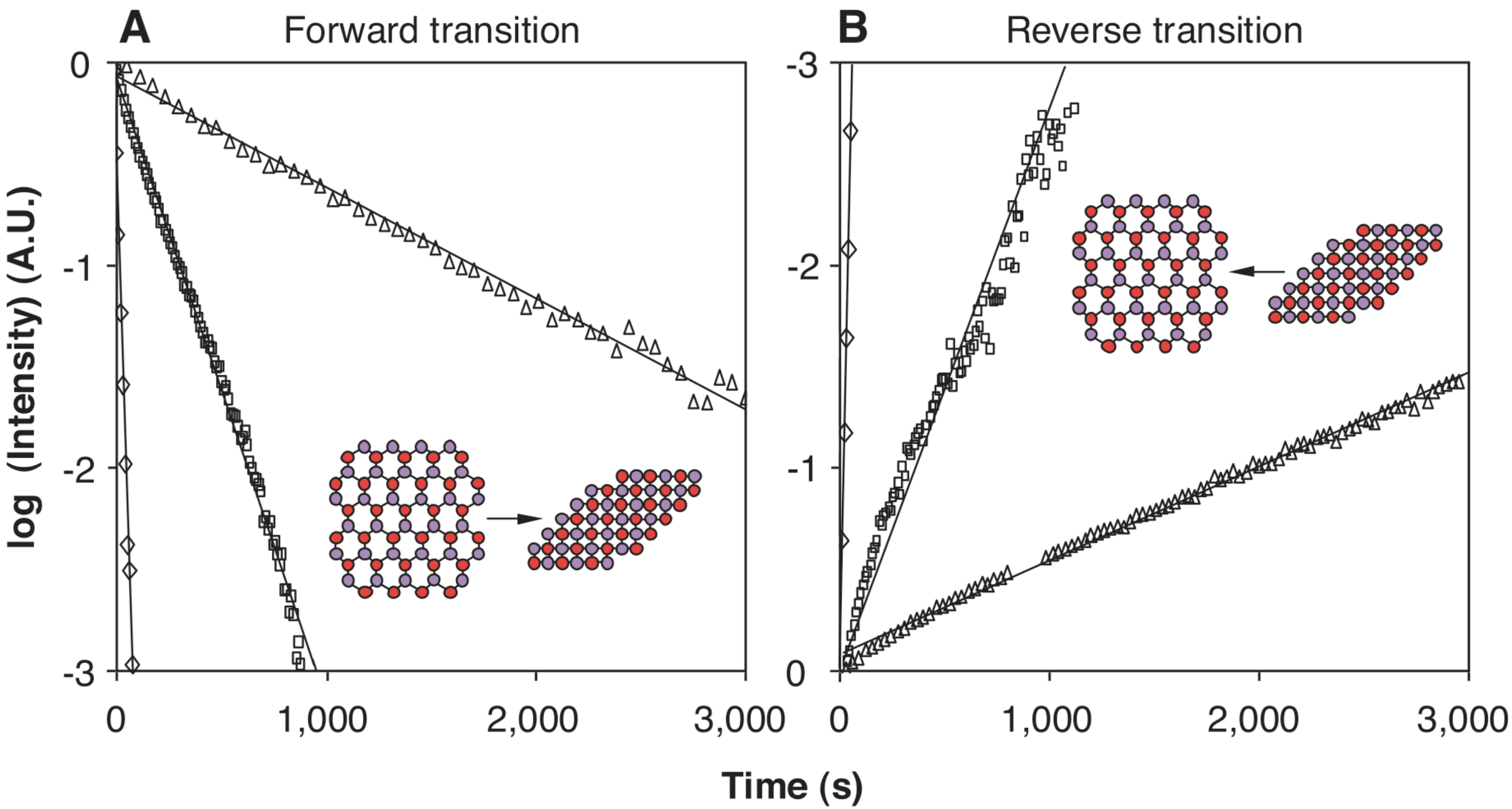
Forward and backward transition





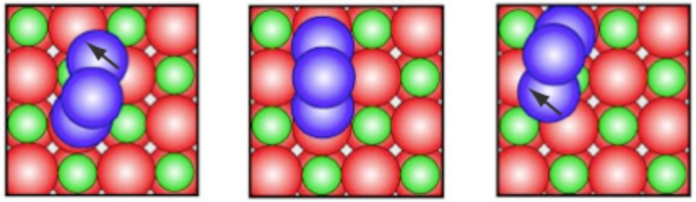
M. Grünwald and C. Dellago, Nano Lett. (2009)

Transformation kinetics - long time scales

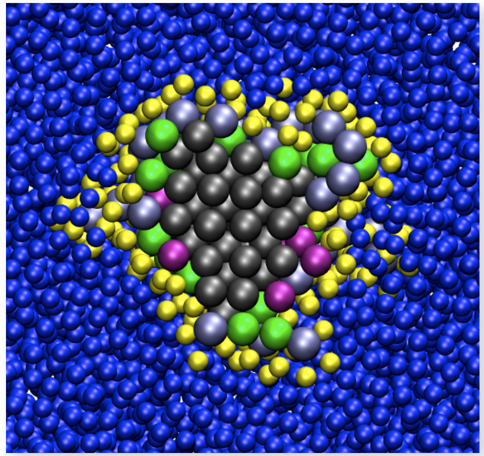


K. Jacobs, D. Zaziski, E. C. Scher, A. B. Herhold, and A. P. Alivisatos, Science 293, 1803 (2001)

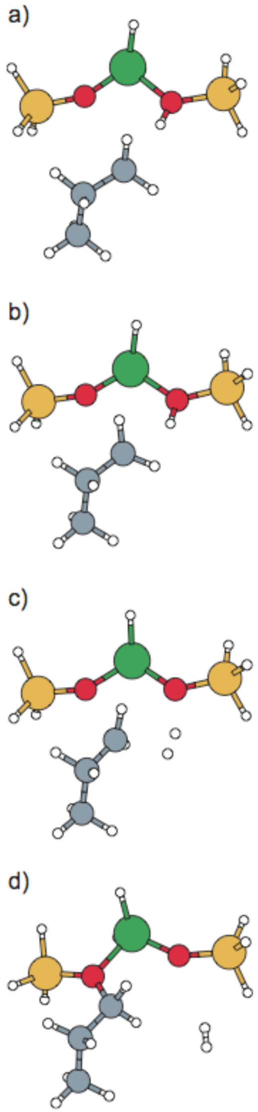
Processes dominated by rare events



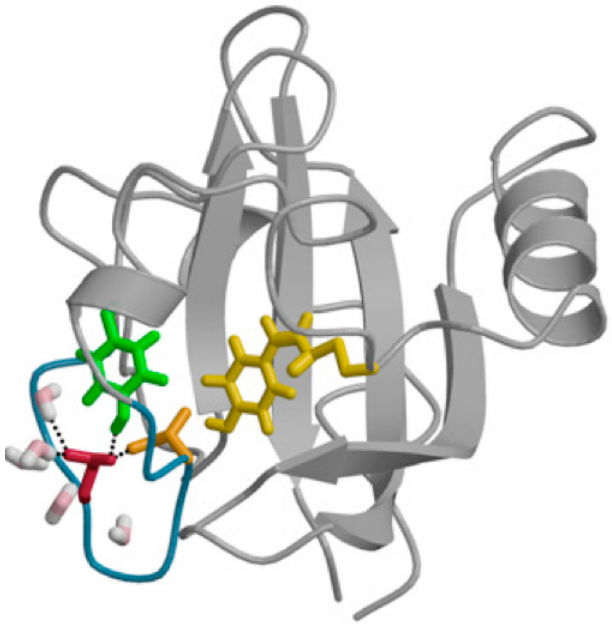
surface processes



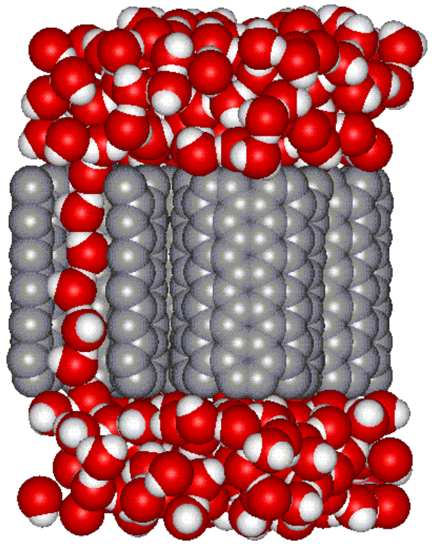
phase transitions



chemical reactions

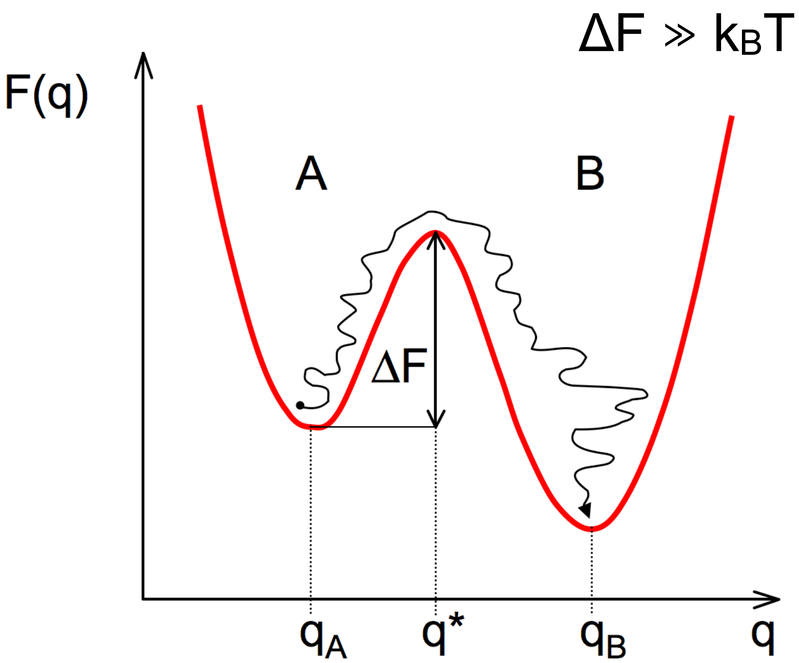


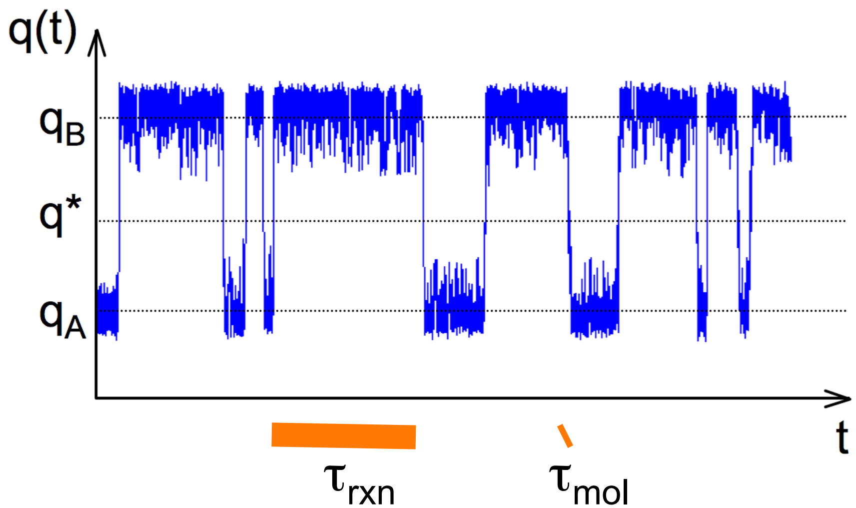
protein folding



transport/ion channels

Rare but important events





Time scale gap: $\tau_{rxn} \gg \tau_{mol}$