Towards Understanding of the Homogeneous Nucleation of Ice

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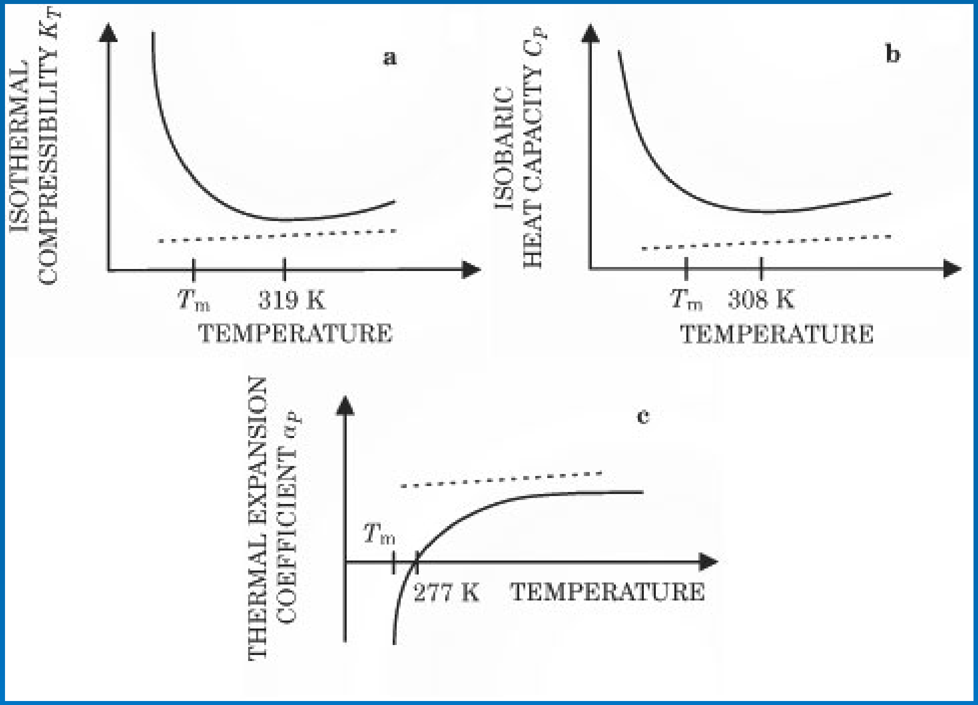
Anomalies in response functions of water



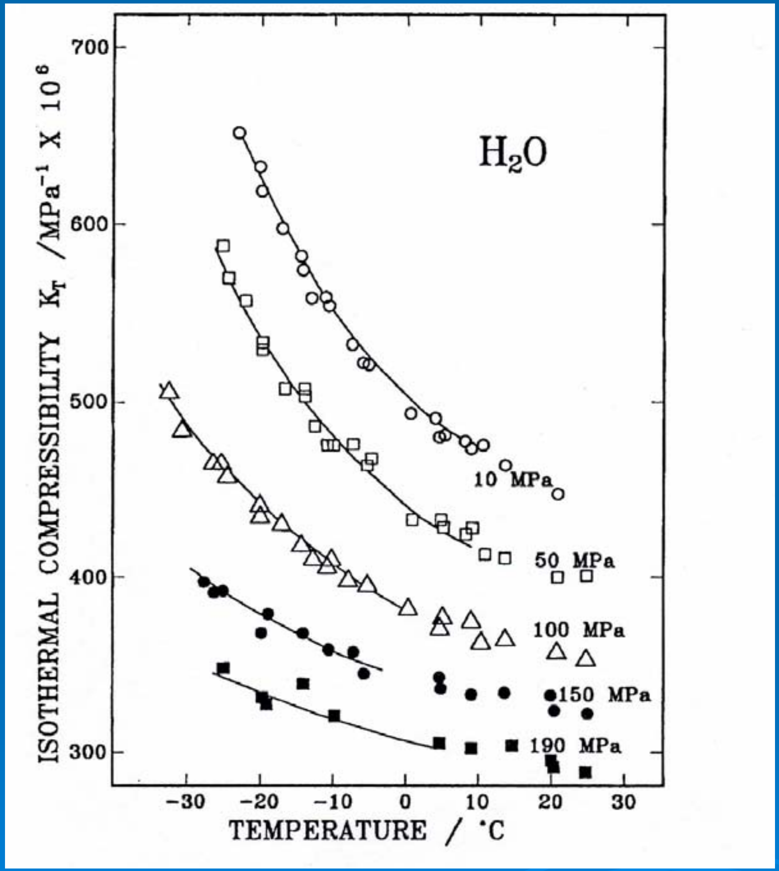
$$\kappa_T \equiv -\left(\partial \ln v / \partial P\right)_T$$

$$\alpha_p \equiv \left(\partial \ln v / \partial T\right)_p$$

$$c_p \equiv T\left(\partial S / \partial T\right)_p$$

Debenedetti and Stanley, 2003

Isothermal compressibility



$$\kappa_T = \frac{1}{kVT}\langle(\delta V)^2\rangle$$

$$\alpha_P = \frac{1}{kVT}\langle\delta S\delta V\rangle$$

$$c_P = \frac{1}{kN}\langle(\delta S)^2\rangle$$

Kanno and Angell, 1979

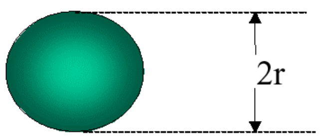
Classical nucleation theory

Homogeneous nucleation

(e.g. Liquid ⇒Solid)

Crystallization requires supercooling

($\mu_{solid} < \mu_{liquid}$)



Crystal nucleus

r^3

Free - energy gain

$$\Delta G_{Bulk} = \frac{4\pi}{3}\rho r^3 \Delta\mu_{s,l} < 0$$

Free - energy loss :

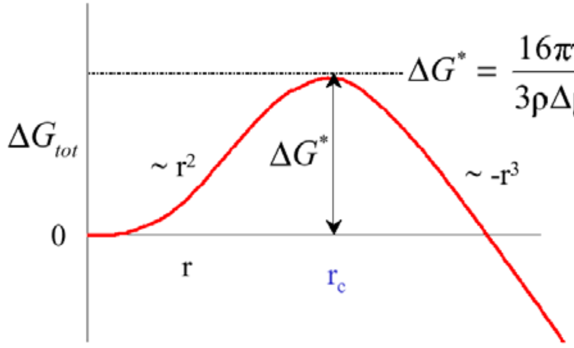
$$\Delta G_{Surface} = 4\pi r^2 \gamma_{s,l} > 0$$

r^2

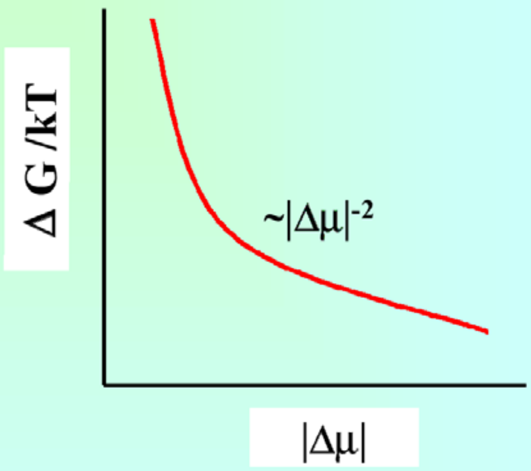
$$\Delta G = -\Delta f \cdot V + \gamma A$$

$$\Delta f = f_l - f_s = \rho_s \Delta\mu$$

Nucleation barrier



$$r_c = \frac{2\gamma}{\rho_s \Delta\mu}$$



According to CNT:

Barrier decreases monotonically with |Δμ|

Nucleation rates

Probability to find a critical configuration is a very strong function of temperature

$$P_c \propto \exp\left(-\frac{\Delta G_c}{k_B T}\right)$$

Nucleation rate is a product of the probability and the rate of growth of critical nucleus

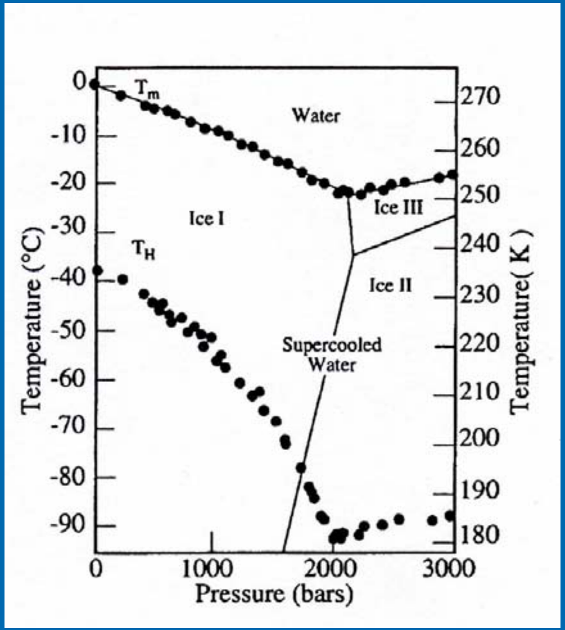
$$I = \Gamma \exp\left(-\frac{16\pi}{3k_B T}\frac{\gamma^3}{(\rho_s \Delta\mu)^2}\right)$$

Nucleation is a kinetic process and becomes observable when $I \sim 1$ $cm^{-3}s^{-1}$

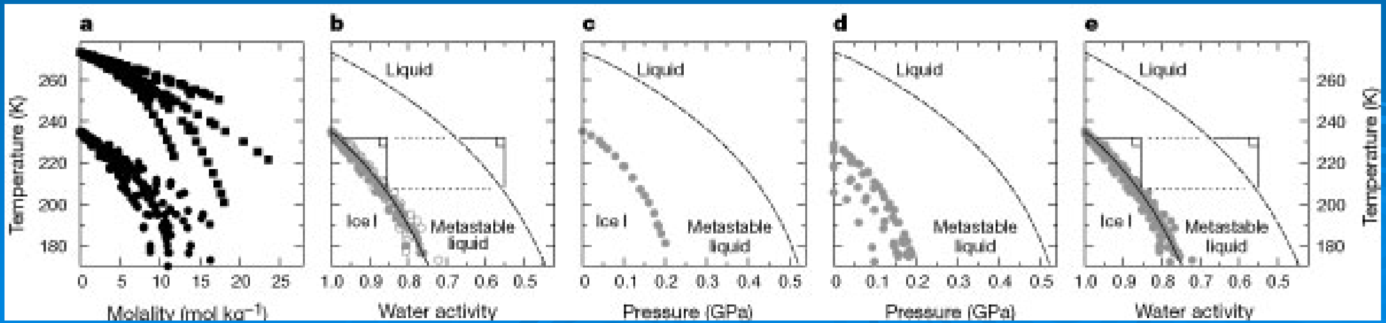
Problems with classical nucleation theory

- Results of atmospheric measurements produce large number of mutually inconsistent models
- Constant γ? What is surface tension away from coexistence?
- Macroscopic thermodynamic description of a microscopic object - critical ice embryo at 235 K contains only 100 molecules
- Complicated pathways – Ostwald's step rule: phase that nucleates is the one with the lowest nucleation barrier

Nucleation in pure water and in solutions

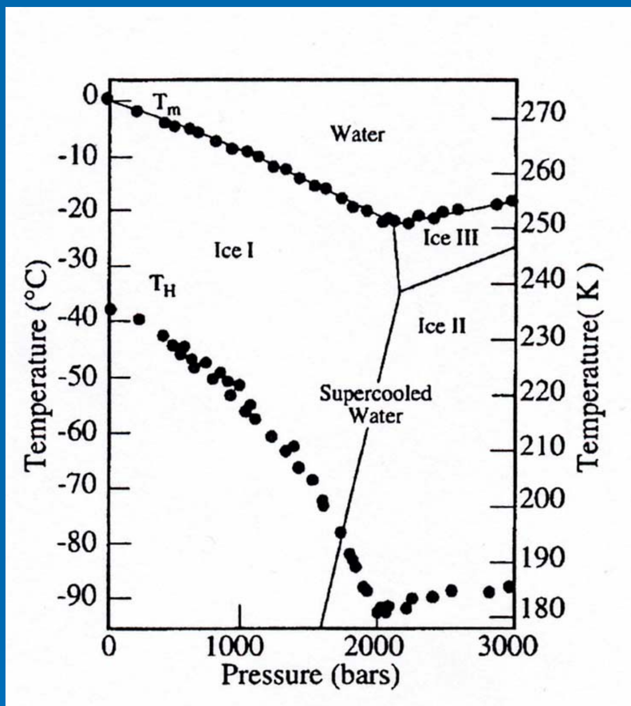


Kanno and Angell, 1975

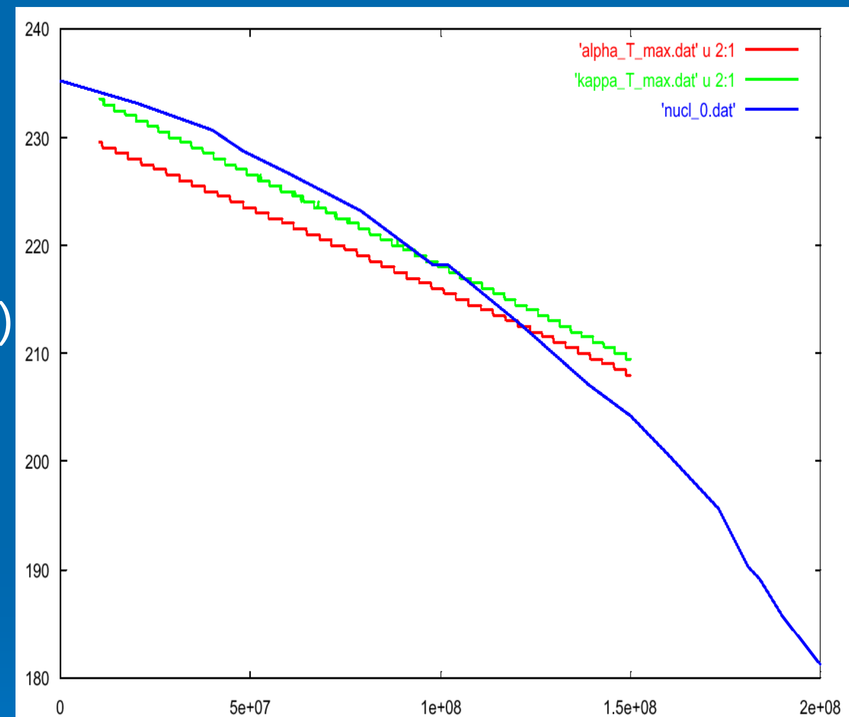


Koop et al., 2000

Nucleation in Water



T (K)



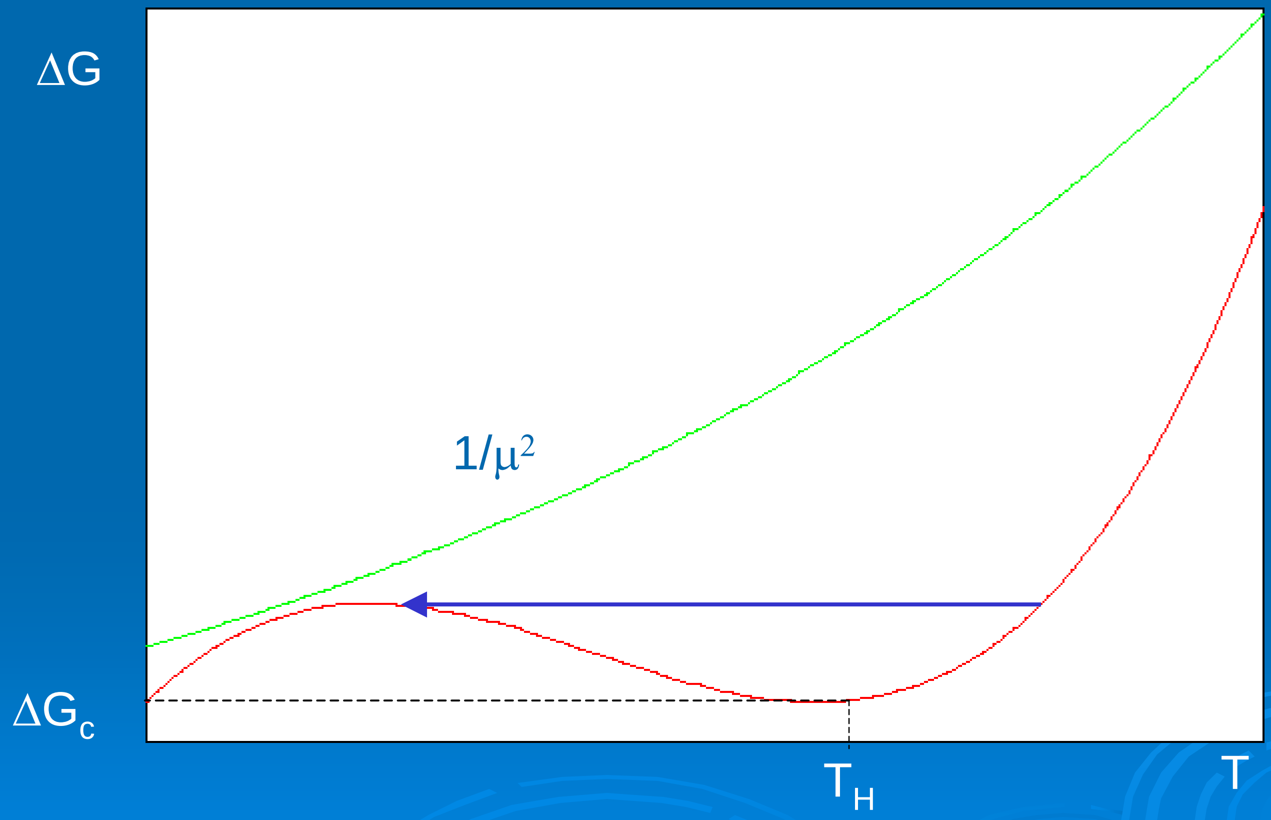
P (Pa)

Within a simple single-bond model (Truskett et al., 1999) the loci of extrema of response functions for supercooled water is very close to the homogeneous nucleation curve for a wide range of temperature and pressure. Other more sophisticated simulations show similar results at atmospheric pressure

Conjecture of the existence of the line of maximum fluctuations (LMF)

- A line (LMF) exists on the phase diagram of supercooled water along which all types of thermodynamic fluctuations are maxima.
- In particular, critical fluctuations leading to the formation of a critical ice embryo have maximum probability along this line.
- Homogeneous nucleation of ice takes place in the vicinity of this line.
- The LMF is very close to the locus of compressibility maxima.

Unusual behavior of the nucleation barrier



Implications of the conjecture for the homogeneous nucleation of ice

- The temperatures of homogeneous nucleation of ice both in pure water and in aqueous solutions are determined by the thermodynamic properties of bulk supercooled water
- Nucleation barrier may exhibit a minimum; then, it is possible to quench water below its homogeneous nucleation temperature and still leave it in a metastable liquid state – possible experimental test of the conjecture
- Only Monte Carlo calculations can and will show whether our conjecture is correct
- If correct, this conjecture will discriminate a single scenario for the behavior of supercooled water – a second-critical point scenario