

05.03.2016

Scattering length density for D_2O :

$$6,38 \cdot 10^{-6} \text{ \AA}^{-2}$$

from: www.nist.gov/programs/sans/pdf/part_i_introduction_to_neutron_scattering.pdf
(page 13)

06.03.2016

Paper: Stacking disorder in ice I

(Halkin et al., PCCP, 2015 (17) 60)

Data suggests that whenever ice grows from supercooled water in nature or technological applications, it initially grows as ice I_{sd} with randomly arranged 50% hexagonal and 50% cubic stacking sequences.

higher freezing temperatures (or lower cooling rates) lead to higher I_h/I_c ratios in the frozen I_{sd}.

Paper: Spectroscopic Signature of Stacking Disorder in Ice I_h

(Carr^{et al}, Phys. Chem. Lett. 2014 (5) 2469)

Data indicate that Ice I_{sd} to ice I_h phase transition does not occur at a precisely defined temperature, but that it is more a gradual process that depends upon the annealing conditions (time and temperature).

Paper: Extend and relevance of stacking disorder in "Ice I_c" (what stacking order called Ice I)

(Kuhls et al, PNAS, 2012 (109) 52)

Decrease in cubicity with time and temperature was accompanied by an increase of the mean crystallite size. [...] must be ascribed to larger crystallites that had grown at the expense of smaller ones. The likely processes are a differential sublimation and recondensation at the crystallite surface as well as a local water molecule migration across grain boundaries.

Some stacking disorder (few percent cubicity) remains at temperatures above 200 K and easily persists up to ~ 240 K.

Published data of ice formed below 240 K often shows deviations from good hexagonal ice - most noticeable in the hexagonal (002) powder peak, which has a higher intensity than expected for ice I_h .

Some molecular scale computer simulations of the freezing of supercooled water support the experimental finding of a coexistence of "ice I_c " ($= I_{\alpha}$) and amorphous ice.

(Their exp. show no significant amorphous amounts.)

07.03.16

Paper: Structure of ice crystallized from supercooled water (Malikm et al. PNAS, 2012 (103) 4)
X-ray diffraction studies of frozen water droplet

[...] characteristic hexagonal peaks at $2\theta = 26^\circ, 34^\circ, 61^\circ$ (101, 102, 203) of I_h are absent, remaining intensities inconsistent with I_h .

The experimental pattern has a strong peak at $\approx 23^\circ$ (100, I_h) and the region between 23° and 26° is elevated above the baseline; both of these features are incompatible with cubic symmetry.

[...] high angle peaks ($58^\circ, 64^\circ = 400, 331$) of I_c are absent.

Pattern cannot be reproduced by simple phase mixture of crystallites of I_c and I_h

\rightarrow ice from supercooled water is neither I_c nor

I_h nor mixture of distinct phases

\rightarrow stacking disorder

Presence of stacking disorder in layered materials can, however, result in the appearance of "streaks" in reciprocal space, which means that diffraction intensity is found along continuous values of the [2am] index l [hkl] if the layers are

oriented perpendicular to the crystallographic c axis, consequently, asymmetric peak broadening can be observed in powder diffraction. Only Bragg peaks where $\frac{(h-k)}{3}$ is not integral are affected by the stacking disorder (e.g. 100, 101, 102 are all broadened / absent). Peaks with greater values of l are more susceptible to stacking disorder \rightarrow need special simulation software (DIFFaX) to reproduce diffraction patterns observed.

Liquid-like layers in the literature

(LIS on Jay Particle)

1995 Dash et al.: The premelting of ice and its environmental consequences (review)

premelting = existence of liquid at temperatures and pressures below the normal phase boundary

regelation = sintering

ice segregation = water is drawn to the freezing site from elsewhere by the freezing process itself

first deductions of surface melting: Tammann (1910), Strauski (1942), Frankel (1946) - absence of superheating for ice (as possible for liquid) \Rightarrow activation energy for formation of thin liquid layer must be zero.

experimental proof exists for formation of liquid-like layer on surfaces of metals, semiconductors, solid rare gases, molecular solids.

typically surface melting begins with one or two monolayers thickness at $T < 0.9$ of bulk melting temperature T_0 , thickness increases with T

thickness^(d) determined by minimum of surface's free energy:

$$d = \left(-2 \sigma^2 \frac{\Delta \gamma}{\rho_L q_m} \right)^{1/3} t^{-1/3}, \quad t = \frac{T_0 - T}{T_0}, \quad \rho_L = \text{liquid density}$$

$$\Delta \gamma = \gamma_{\text{liquid-vapor}} + \gamma_{\text{liquid-solid}} - \gamma_{\text{solid-vapor}} \quad (\text{chemical potential } \gamma)$$

q_m = latent heat of melting per molecule

σ = constant (order of 1 molecular diameter)

in case of short-range forces ($f(d) = \frac{d^2}{d^2 + \sigma^2}$), $d \gg \sigma$: $d \propto |\ln t|$

pressure effects very small (3 ppm for water)

prediction: thickness is larger for particles of smaller radius

disorder will tend to induce premelting (roughness, polycrystallinity, dislocations, impurities: everything that increases contact area at grain-wall boundary will support melting), also crystal orientation jumps at boundaries can be "smoothed" by liquid

stability: super-cooled liquid bulk: metastable, premelt: stable below T_0

experimental evidence for liquid-like surface films:

- Golecki & Jaccard 1978: proton backscattering, disordered surface layer on ice in pure vapour 223 - 271 K, thickness increasing with T up to 800 Å
- Beaglehole & Nason: ellipsometry, liquid-like layer on prism face in air 253 - 271.5 K, increasing thickness with T up to 130 Å
- Furukawa et al. 1987: ellipsometry, liquid-like layer on prism/basal interface above 263/271 K, thickening with T
- Kouchi et al.: (X-ray) diffuse scattering, equally strong from polycrystalline/prism/basal facets at $T \geq 271$ K
- Lied et al. (1994): quasiliquid on polycrystalline (prism/basal facets) at $T \ll 271$ K (not specified)

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experimental evidence for ^(complete)no surface wetting:

- Ketcham & Hobbs 1969 / Knight 1971: crystal growth studies (standing water droplets just below triple point (6 mbar, 273.16 K)), wetting only incomplete (very small but finite contact angles)
 \Rightarrow conclusion \leadsto no surface melting

experimental evidence for surface wetting:

- Elbaum et al. 1993: thicknesses of ≥ 12 Å (detection limit) observed in air or pure vapour for $T \geq 271$ K (depending on crystal plane), thickness increased with T, then (just below 273.16 K) droplets suddenly formed on surface

theoretical prediction of film thickness:

- Elbaum & Schick 1991a: ≈ 3 Å @ 272 K, increasing with T

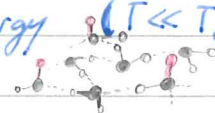
diffusion coefficient: of quasi-liquid layer \approx that of supercooled water (quasi-elastic neutron scattering - QENS), Maruyama et al. 1992, Gay et al. 1992, Fu 1993

2007 Li & Somorjai: Surface premelting of Ice (review)

experimental evidence for intrinsic premelting: Kouchi et al. 1987 (X-ray diffraction)

reason for premelting: lowering of the surface free energy ($T < T_0$)

experiments on ice surface: dangling O-H-bonds



(sliding out of

surface) have higher vibrational amplitude (0.25-0.33 Å) than bulk (0.1 Å)

(Braun 1998, Gebauer 2000), low-energy electron diffraction (LEED)

Continue with: Liquid-like layers in the literature

disorder of dangling OH bonds becomes detectable at 200 K and increases with increasing T (Wei et al. 2001, Wei 2002). vibrational spectroscopy / sum-frequency generation, SFG)

⇒ consistent with X-ray scattering and proton channeling results (Golecki & Jaccard 1978, Dosch et al. 1995)

inconsistent with simple model, which assumes premelting as uniform water layer

theoretical: molecular dynamics study (Ideka-Fukazawa & Kawamura 2004) fully supports these exp. observations

summary of previous experiments: It is commonly believed that the onset pre-melting temperature is around 243 K. Thickness of layer increases with T (exp. disagree on exactly how). Layer does not exactly behave like super-cooled liquid water ⇒ "quasi-liquid" layer

techniques detecting molecular structural changes at the surface are generally more sensitive and usually suggest lower onset temperatures for premelting.

surface premelting is not unique to ice; it occurs on all types of solid molecules in the surface layer of ice are very dynamic. even at temperatures of 30 K, the large amplitude of vibrational motion of the first surface layer can make it invisible to LEED

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1995 Dosch et al.: Glancing-angle X-ray scattering studies of the premelting of ice surfaces (skim read)

Experimental: single crystal ice samples (prepared at 258 K, less than 10^{-9} impurities (e.g. CO_2), surfaces with adjusted crystallographic orientation created by pressing gently heated (slightly above 273 K) glass plate to surface and refreezing, pressure: $\frac{\Delta p}{p} \approx 2.5 \cdot 10^{-4}$, Δp = saturation vapour pressure ($\approx 25 \text{ mbar}$ @ 263 K) ⇒ $p \approx 6 \cdot 10^{-3} \text{ mbar}$ ⇒ sublimation rate @ 263 K $\approx 10 \text{ Å/s}$

Results: small sublimation rate does not lead to noticeable disturbances in thermodynamic surface phenomena.

Thickness of quasi-liquid layer: $T < 263 \text{ K} \Rightarrow \approx 0 \text{ Å}$, then increasing with T ($\approx 20 \text{ Å}$ @ 263 K to $\approx 530 \text{ Å}$ @ 273 K)
roughness increasing from $\approx 10 \text{ Å}$ @ 259 K to $\approx 23 \text{ Å}$ @ 273 K

2001 Wei et al.: Surface Vibrational Spectroscopic Study of Surface Melting of Ice (skim-read)

observed dangling O-H-bonds' vibrational transition at 3695 cm^{-1}
 \Rightarrow calculate tilt angle θ and orientational order parameter S from line profiles

results: $T < 200 \text{ K}$: $S \approx 1, \theta = 0$ (solid-like ice surface)

$T > 200 \text{ K}$: S decreases, θ increases (quasi-liquid ice surface)
at $T \approx 240 \text{ K}$ S and θ reach the values of liquid water surfaces @ 273 K , but keep de-/increasing.

2008 Conde et al.: The thickness of a liquid layer on the free surface of ice as obtained from computer simulation (skim-read)

onset of liquid layer formation: 173 K (basal plane), 193 K (primary prismatic plane), 203 K (secondary prismatic plane)

thickness increasing with T to $\approx 5-7 \text{ \AA}$ @ 273 K

simulations performed at zero pressure (not sure, if sublimation taken into account)

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2000 Maruyama et al.: X-Ray Analysis of the Structure of Premelted Layers at Ice Interfaces (skim-read)

X-ray diffraction, premelted ice layer & liquid water surface

results: short range order in molecular distribution for both

average nearest neighbour distances 1-2% smaller in quasiliquid than in liquid water

experimental: powder sample (frost), grain sample (grown at 243 K , size $\approx 50 \mu\text{m}$)
several crystal seeds \leftarrow frost on liquid Nitrogen cooled rod, water at -0.1°C

\Rightarrow pressure not stated, but likely 10^{-3} mbar ; cold nitrogen gas flow to maintain temperature of sample

temperature: -0.2°C to 16°C

1997 Makkonen: Surface Melting of Ice (not sure how much I believe him)

Experiments: place liquid drop on solid surface (carefully to avoid flattening by inertia)

drop: T between 0 and 100°C (distilled water)

ice: -25°C , 20 mm thick, smooth

air: -25°C , 40% relative humidity (probably atmospheric pressure)

video recording of drop placement and deformation

\Rightarrow contact angle measurements

Results: eventual drop freezing does not alter contact angle

nowhere in observed T -range contact angle θ was close to 0°

\Rightarrow surface melting cannot be caused by free surface energy minimisation

static equilibrium (of θ) at $T_{\text{water}} = 95^\circ\text{C}$, $T_v < 95^\circ\text{C} \Rightarrow$ droplet freezing,

$T_v > 95^\circ\text{C} \Rightarrow$ ice melting at contact area

θ at $95^\circ\text{C} = 37^\circ$ ($= \theta_{\text{min}}$) \Rightarrow free surface energy of ice-vapour

interface: $\gamma_{iv} = 77 \frac{\text{mJ}}{\text{m}^2}$ at -25°C ($\Rightarrow 73 \frac{\text{mJ}}{\text{m}^2}$ @ 0°C)

Argument against previous experiments and free surface energy minimisation:

Young-Dupré equation (static equilibrium for drop on solid):

$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$ ($s = \text{solid}$, $l = \text{liquid}$, $v = \text{vapour}$, $\theta = \text{contact angle}$)

if $\gamma_{sv} > \gamma_{sl} + \gamma_{lv}$, free surface energy can be minimised by liquid layer

$\Rightarrow \theta = 0^\circ$

Problem: when a liquid film is present in the investigated system

a) water will spread on it, keeping $\theta = 0^\circ$

b) the solid vapour interface cannot be investigated, because it's not present in the system

In general, materials show higher surface energies for the higher density phase (for water that is the liquid, for everything else the solid).

New mechanism for surface melting proposed (unique to water ice):

Surface pressure P , caused by net molecular force (difference between inward pull of bulk and at interface), determined by Lennard-Jones potential

$P(z) = \frac{25 \rho^2 A}{6z^3} \left[1 - \left(\frac{z_0}{z} \right)^6 \right]$, z_0 : equilibrium distance between molecules in the bulk, ρ : number of molecules per unit volume, A : attractive constant, z : distance

$\Rightarrow P_0 = 1.067 \frac{\gamma}{z_0}$ (total pressure @ surface)

With their results for γ that leads to surface melting temperature of -13°C and freezing temperature of bulk water of $+8^\circ\text{C}$ (similar to supercooling, but required nucleus size above 0°C infinite \Rightarrow no freezing in reality)