Slippery when wet?



The surface of ice, what are its properties, and why is it slippery?





Naaah!

the nature of surface chemical bonds. 10 Dec 2013

A thin layer of liquid water is what makes ice slippery and not directly the ice itself. Liquid water naturally forms on the surface of all ice, even at very low temperatures, because of

Ice is slippery





April 26, 1860. Sir BENJAMIN C. BRODIE, Bart., President, in the Chair. The following communications were read :— I. "Note on Regelation." By MICHAEL FARADAY, D.C.L., F.R.S. &c. Received March 13, 1860.

Two pieces of thawing ice, if put together, adhere and become one; at a place where liquefaction was proceeding, congelation suddenly occurs. The effect will take place in air, or in water, or in vacuo. It will occur at every point where the two pieces of ice touch; but not with ice below the freezing-point, i.e. with dry ice, or ice so cold as to be everywhere in the solid state.

Three different views are taken of the nature of this phenomenon.

- I explained it by supposing that a particle of water, which could retain the liquid state whilst touching ice only on one side, could not retain the liquid state if it were touched by ice on both sides;
- Professor J. Thomson, who discovered that pressure lowered the freezing-point of water, attributed the regelation to the fact that two pieces of ice could not be made to bear on each other without pressure; and that the pressure, however slight, would cause fusion at the place where the particles touched,
- Professor Forbes assents to neither of these views; but admitting Person's idea of the gradual liquefaction of ice, and assuming that ice is essentially colder than ice-cold water, i. e. the water in contact with it, he concludes that two wet pieces of ice will have the water between them frozen at the place where they come into contact.

Conclusion: in a solid molecules cannot move, so there must be a liquid present

Is ice slippery due to a lubricating water layer? No!

Pressure melting

Premelting



Frictional melting



Can't explain ice skating colder than $-22^{\circ}C$

Only close to melting point

Can't explain low velocity ice skating

Lubrication? Stribeck curve



Ice skating and water on HDPE

Ice skating and skating on HDPE with water: no lubricated regime



So we need to think about the surface of ice.....why is it different?



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Pressure melting

Premelting



Frictional melting



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1. Pressure melting: let's think about phase transitions



Temperature



There is one ordered phase, but this diagram source rect of the diagram of the diagram solids, liquids, and gases. The arrow to the right of the diagram

demonstrates that these three phases have different enthalpies: gas has the highest enthalpy, liquid has an intermediate enthalpy, and solid has the lowest enthalpy. Hence, each of the phase transitions shown in this figure involves a change in the enthalpy of the substance.

Why are there crystals? Piling up oranges can be done in 2 ways: random or regular



Random Close Packing: $\phi = 0.64$ Face Centered Cubic lattice $\phi = 0.74$

(see. though. the Jar of Life https://www.youtube.com/watch?v=SqGRnlXplx0)

Interactions:

- Van der Waals
- Electrostatic
- Covalent bonds
- Metallic bonds
- Hydrogen bonds
- Hydrophobic interactions

And entropy!

F=U-TS

Why are there liquids and gases? $(P + \frac{an^2}{V^2})(V - nb) \neq nRT$ der Waals EOS The Vander Waals constant (a) Signify the magnitude of intermolecular forces of attraction between the gas p

effective size of gas molecules.



- This is a cubic polynomial with three solutions for V as a function of p, of which two stable and one unstable.
- Physically that means that there will be two volumes for a given pressure, corresponding to the liquid and gas state.
- In general a<0, so the pressure is lower than without the correction: van der Waals forces give an attraction between the atoms/molecules

Important Note

Why are these liquids and gases? $\mathcal{O} \longleftrightarrow \mathcal{O}$ 1- 1/12 lennard - Jones (short - range repulsion (Poudi) long - range athachon (Vd Wals) molecule Inhoducing an athaction leads for certain poten-tials to de vol Waals EOS $\left(p + \frac{qN^2}{V^2}\right)\left(V - Nb\right) = Nk_BT$ L'effective attraction can also be obtained e.g. from a virual expansion Thigh TION for a given P. 3 solutions for V F coexistence $C = \frac{N}{V}$ Cliquid Cgas athaction between molecules leads to emergence of liquid an gas phases



Freezing is a strange phase transition: Pointy ice drops





5uL drop of dyed water, video speed x0.5

With Etienne Jambon-Puillet, Noushine Shahidzadeh (Nature Comms. 9, 4191 (2018)) (see also Snoeijer and collaborators)

Clausius Clapeyron gives the slope op the liquidus:







dP

(a)

(b)



2. Premelting. Let's think about surface tension and wetting **Premelting**

From Wikipedia, the free encyclopedia

Premelting (also **surface melting**) refers to a <u>quasi-liquid</u> film that can occur on the surface of a solid even below melting point (T_m) . The thickness of the film is temperature (T) dependent. This effect is common for all crystalline materials. Premelting shows its effects in <u>frost heave</u>, the growth of <u>snowflakes</u> and, taking grain boundary interfaces into account, maybe even in the movement of <u>glaciers</u>.

Considering a solid-vapour interface, complete and incomplete premelting can be distinguished. During a temperature rise from below to above T_m in the case of complete premelting, the solid melts homogeneously from the outside to the inside; in the case of incomplete premelting, the liquid film stays very thin during the beginning of the melting process, but droplets start to form on the interface. In either case, the solid always melts from the outside inwards, never from the inside.

History

The first to mention premelting might have been <u>Michael Faraday</u> in 1842 for ice surfaces.^[1] He compared the effect which holds a snowball together to that which makes buildings from moistured sand stable. Another interesting thing he mentioned is that two blocks of ice can freeze together. Later Tammann and Stranski suggested that all surfaces might, due to the reduction of surface energy, start melting at their surfaces. Frenkel strengthened this by noting that, in contrast to liquids, no overheating can be found for solids. After extensive studies on many materials, it can be concluded that it is a common attribute of the solid state that the melting process begins at the surface.^[2]

Digression: what is a surface tension?

Molecular Dynamics Liquid-vapor interface

$$u(r) = 4\epsilon \left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^6 \right]$$





Surface tension

In a liquid, molecules are in a condensed state.

<u>A molecule in the bulk:</u> cohesive interaction with neighbouring moelcules

<u>A molecule at the surface</u> Interaction with its neighbors below and to either side, No attraction operating in the 180° solid angle above the surface.



As a consequence, a molecule at the surface will tend to be drawn into the bulk of the liquid.



Intermolecular attractive forces act to minimize the surface area of a liquid ('cohesion).

Liquids tend to reduce their surface.

Sphere
$$\frac{4\pi r^2}{4_{/2}\pi r^3} = \frac{3}{r}$$

smallest ratio of surface to volume

(e.g. cube: surface to volume ratio=6/r)



surface tension: a force (/length)



Many movies: DVD "Interfaces mobiles", (coming with the De Gennes/Brochard/Quere book...)

How to measure the Surface tension?

The Wilhelmy plate technique

A plate with a good wetting properties is put in contact with the horizontal surface of the liquid. The force (F) vertically acting on the plate is measured using a microbalance.



Perimeter
$$P = 2(L+t)$$

Du NoÜy ring method

Measurement of the force (F) needed to remove a ring from the liquid using a microbalance



f is correction factor which depends: -Ring (R,r) -wettability (θ) -fluid density (ρ)

Perimeter
$$P = 4\pi R$$



Encyclopedia of Surface and Colloid Science Copyright © 2002 by Marcel Dekker, Inc. All rights reserved.

Thermody namices of the surface d= = gdA - SdT - pdV - ndu 36 8= $\left(\frac{d \Omega}{d A}\right)_{T,V,P}$ to interface is an open system and can exchange with the ball

define excess quaakties : leading to dy= -EOIT - Tdr $\begin{pmatrix} d_{Y} \\ \delta T \end{pmatrix} = - \Sigma$ surface enhopy $\left(\frac{d\Gamma}{d\mu}\right)_{T} = -\Gamma \text{ excess particle number}$ $\left(= adsorption\right)$

Surface tension

Direct measurement of surface free energy and entropy: not possible for 3d systems



attractions (' cohesion').

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How to calculate the surface tension - a = F- JUN F $C = \frac{N}{V}$ phanid Egas lass Cliquid P 1 Ruquid / As culeiface $\chi = \int dz \ \frac{\Omega(p(z))}{N}$ (92) but if you by to muumize this, you will get a step function 7 vol Waals (again !): too skep gradients also cast energy. Taylor expansion around the step profile then gives: $\begin{cases} = \int dz \left[\frac{\Omega\left(\rho(z)\right)}{V} + \frac{k}{2} \left(\frac{d\rho(z)}{\partial z} \right)^2 \right] \end{cases}$ leads to a tank. profile and allows to predict the surface tension from the equation of state



Wettability: cohesion vs. adhesion







Wettability and contact angles

Three interfaces meet at the contact line:

The balance of forces projected in the plane of the solid surface:





Young Thomas lawrence 1773

 $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta$

Perfect wetting (spreading): Θ=0° <u>Partial wetting</u>: 0° < Θ < 90° <u>Non wetting</u>: 90° < Θ <180° Perfectly non wetted Θ=180°







Long range forces: van der Waals (dipole/induced dipole)



 $V_{vdW}(l) = -C/l^{6}$

 $V_{vdW}(l) = -W/l^3$

 $V_{vdW(l)} - W/12\pi l^2$

W positive -> energy decreases with decreasing separation -> attraction between the two surfaces -> no wetting

 $\Pi_{vdW}(l) = -dV_{vdW}/dl = -W/6\pi l^3$: Disjoining pressure

) nuagetal calculating desita a feuse Thus: calculate $2\chi = \int TT(\ell) d\ell$ $= \frac{4}{24 \pi D_0^2}$ munij where have Ð and the 2-1

Works well for the liquid-vapor surface tension!

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INTERMOLECULAR AND SURFACE FORCES

TABLE 11.4 Comparison of experimental surface energies with those calculated on the basis of the Lifshitz theory

Material (ɛ) in ordering of increasing ɛ Liquid helium (1.057) n-Pentane (1.8) n-Octane (1.9) Cyclohexane (2.0) n-Dodecane (2.0) n-Hexadecane (2.1)	Theoretical <i>A</i> (10 ⁻²⁰ J)	Surface energy, γ (mJ m ⁻²)	
		$A/24\pi D_0^2 (D_0 = 0.165 \text{ nm})$	Experimental ^a (20°C)
Liquid helium (1.057)	0.057	0.28	0.12-0.35(4-1.6 K)
n-Pentane (1.8)	3.75	18.3	16.1
n-Octane (1.9)	4.5	21.9	21.6
Cyclohexane (2.0)	5.2	25.3	25.5
n-Dodecane (2.0)	5.0	24.4	25.4
n-Hexadecane (2.1)	5.2	25.3	27.5
PTFE (2.1)	3.8	18.5	18.3
CCl ₄ (2.2)	5.5	26.8	29.7
Benzene (2.3)	5.0	24.4	28.8
Polystyrene (2.6)	6.6	32.1	33
Polyvinyl chloride (3.2)	7.8	38.0	39
Acetone (21)	4.1	20.0	23.7
Ethanol (26)	4.2	20.5	22.8
Methanol (33)	3.6	18	23
Glycol (37)	5.6	28	48
Glycerol (43)	6.7	33	63
Water (80)	3.7	18	73
H_2O_2 (84)	5.4	26	76
Formamide (109)	6.1	30	58

$$\Pi_{vdW}(l) = -dV_{vdW}/dl = -W/6\pi l^3$$
 : Disjoining pressure

Israelachvili, J., Intermolecular and Surface Forces, Academic Press (London, 1985), p.145

$$W = W_{v=0} + W_{v>0}$$

$$W_{v=0} = \frac{3}{4} kT \left(\frac{\varepsilon_1(0) - \varepsilon_3(0)}{\varepsilon_1(0) + \varepsilon_3(0)}\right) \left(\frac{\varepsilon_2(0) - \varepsilon_3(0)}{\varepsilon_2(0) + \varepsilon_3(0)}\right)$$
and
$$W_{v>0} = \frac{3hv_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2) (n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2} (n_2^2 + n_3^2)^{1/2} \{(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2} \}$$



W positive -> pressure tends to approach the two surfaces -> no wetting



 $n_3 > n_2$: WATER DOES NOT WET ICE



Small differences, large absolute value: probably irrelevant contribution

Israelachvili, J., Intermolecular and Surface Forces, Academic Press (London, 1985), p.145 $W = W_{v=0} + W_{v>0}$ $W_{v=0} = \frac{3}{4} \text{ kT } \left(\frac{\varepsilon_1(0) - \varepsilon_3(0)}{\varepsilon_1(0) + \varepsilon_3(0)}\right) \left(\frac{\varepsilon_2(0) - \varepsilon_3(0)}{\varepsilon_2(0) + \varepsilon_3(0)}\right)$ and $W_{v>0} = \frac{3hv_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2} (n_2^2 + n_3^2)^{1/2} \{(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2} \}}$

n	1 =N vapor	
n	3 =N water	

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Young Thomas lawrence 1773

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Usual Zisman Plot



Zisman Plot for a Low Density Polyethylene Film

Liquid Surface Tension [mN/m]

Modified Zisman Plot (Silanized Glass)





Contact angle of water on ice



Premelting film?



 $\Pi(l) = -W/6\pi l^3 + \Delta\mu = 0 \text{ Mechanical equilibrium}$ Leads to $l \sim \Delta\mu^{-1/3} \sim \Delta T^{-1/3}$, temperature distance from melting

Surface melting of ice? 4 out of 5 techniques say no...



Angelos Michaelides, Ben Slater PNAS 2017





Wetting of water on ice, or: On the shape of icicles

With Menno Demmenie- Paul Kolpakov – Lars Reus – Sander Woutersen – Noushine Shahidzadeh



Motivation

A MODEL OF ICICLE GROWTH

By LASSE MAKKONEN

(Laboratory of Structural Engineering, Technical Research Centre of Finland, 02150 Espoo, Finland)

ABSTRACT. A theory of icicle growth is presented. It is shown that icicles elongate as hollow tubes of ice with liquid water trapped inside the tip. A time-dependent computer model based on the theory shows that the growth of an icicle is a complicated process, which is very that the diameter of the pendant drop, and the diameter of the tip of the icicle, is 4.8-5.0 mm regardless of growth conditions (Maeno and Takahashi, 1984[a]).

When an icicle grows, the latent heat of fusion released in the freezing of ice beneath the water film must be amound from the ice/water interface. The rate of heat loss

Icicles are nice to look at, and they are useful in that

In cold areas of the world icicles are commonly seen. Wherever cold water flows from an overhang at freezing temperatures, icicles will form. They hang from the roofs of buildings, ledges, and tree branches after periods of snow melt or freezing rain, and as a result of water seepages.

Icicles are nice to look at, and they are useful in that they can be used as a guide to the quality and movement of ground water (Reesman, 1973), and that their formation on buildings reveals thermal leaks. It is not always recognized that icicles are also a problem. They may fall on people and cause serious injuries. When hanging from the roof of a railway tunnel they may penetrate the small and heat conduction to the interior of the icicle is negligible. The water film on the surface is supercooled only by less than 0.02° C everywhere on the icicle walls (Hillig and Turnbull, 1956), so that changes in the film temperature do not significantly contribute to the heat balance. The pendant drop, on the other hand, may cool more significantly and may therefore release heat to the tip of the icicle.

Icicles are long spikes of ice. In order to form, their growth in length must be typically 10-30 times faster than their growth in width. When considering a cross-section of an icicle, there are two surfaces growing horizontally and one growing vertically. Therefore, the elongation rate of the tie of an icids is tronically 20-60 times the radial growth

always buildings reveals leaks. not thermal on recognized that icicles problem. They are also a from hanging cause ser10 people and

been made (Hatakeyama and Nemoto, 1958; Laudise and Barns, 1979), but the only quantitative study of icicle growth is that by Maeno and Takahashi (1958[a]), in which empirical relationships between icicle growth and environmental conditions were obtained by laboratory tests. In the present paper, a quantitative theory of icicle growth is developed. The theory can be used in simulating the evolution of the shape and mass of icicles. vertical and horizontal heat-transfer rates trom a cylindrical body are of the same order of magnitude. Yet, we know that icicles do grow much faster in length than in width.

There is only one plausible explanation of the abovementioned paradox. As the observed vertical growth rate of an icicle is much higher than one based on heat loss, it must only be the vertical dimension of the tip of the icicle that is growing fast, not the mass of ice. In other words, the tim of the icide must grow vertically as a thin cover of





Controversy



* Phys. Fluids Shorts, Goldstein., 2006, 18, 083101

† Phys. Fluids Ueno et al., 2007, 19, 093602

* New J. Phys. Morris et al., 2013, 15, 103012







Experiment



0.26 g/L NaCl







Similar to the work of Stephen Morris (A.K.A. 'the Iceman') and collaborators





Cone shape?



50

(Roughly) self-similar



51

Instability?

Ripple theory

Assumption: complete wetting Outcome: wavelength ~capillary length

Phys. Fluids Ueno et al., 2007, 19, 093602

Ripple analysis

First order Landau: $A_{norm} = a(C - C_t)^{0.5}$

MilliQ

Salty

Small salt concentrations create a thin wetting film

MilliQ water flows along the icicle as distinguishable droplets in stick-slip motion

See, again, Stephen Morrris' similar video's https://www.youtube.com/watch?v=L5UzN52AWkI

Effect of salt on the contact angle

57

ŝ

All 0.1 wt%

Conclusions

- The ice surface is not 'wet' for the practical purposes of ice skating and icicle growing
- Beautiful icicles need a pinch of salt, to prevent the drop edge from freezing (stay tuned.....)

