



Three types of liquid water in icy surfaces of celestial bodies

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ABSTRACT

It is shown that, at temperatures far below the triple point and under appropriate conditions, liquid water can stably or temporarily exist in upper ice-covered surfaces of planetary bodies (like Mars) in three different types:

- (i) undercooled interfacial water (due to freezing point depression by van der Waals forces and “premelting”),
- (ii) water in brines (due to freezing point depression in solutions), and
- (iii) sub-surface melt water (due to a solid-state greenhouse effect driven heating).

The physics behind and the related conditions for these liquid waters to evolve and to exist, and possibly related consequences, are discussed. These calculations are mainly made in view of the possible presence of these sub-surface liquids in the upper surface of the present Mars.

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1. Introduction

Thermodynamic arguments and experimental results indicate the existence of nanometre-sized thin films of undercooled liquid interfacial (ULI) water on surfaces of mineral grains in icy environments far below the triple point temperature (cf. Anderson, 1968; Anderson et al., 1973; Cahn et al., 1992; Möhlmann, 2009). This thermodynamically stable liquid interfacial water is due to the freezing point depression in course of the interfacial pressure of attractive van der Waals forces between the grain surfaces and the water film. This ULI-water is one type of liquid water, which is expected to exist in ice-covered the surfaces like on Mars, comets and asteroids.

Another type of liquid water may evolve in course of the necessary presence of interfacial water around salt grains, which are embedded in ice: brines. These brines can have a freezing point depression with remarkably low eutectic temperatures (Brass, 1980; Clark and Van Hart, 1981; Fairén et al., 2009; Hecht et al., 2009; Chevrier et al., 2009).

Furthermore, the solid-state greenhouse effect can be effective in water ice and snow (“snow/ice”) if these are optically thin in the visible and opaque in the thermal infrared. The absorbed insolation will deposit energy in form of heat in the optically accessible upper depths of the sub-surface. The related heat will cause an increase in sub-surface temperature, possibly up to the melting temperature at these sub-surface depths. The internal

(i.e. sub-surface) energy transport is by heat conduction mainly. Cooling happens by IR re-radiation and sublimation at the upper surface only, which therefore will be forced to be cooler than the sub-surface. Thus, the surface can remain solid while underlying the layers are warmed up and possibly molten, at least temporarily. This phenomenon of sub-surface melting of ice and snow is known to happen on Earth, e.g. on Antarctica and Greenland (Koh and Jordan, 1995; Liston and Winther, 2005). Matson and Brown (1989) have studied the possible relevance of the solid-state greenhouse effect for icy satellites in the outer solar system. The outcome was that surface regions and interiors of these bodies are expected to be much warmer than previously thought. Sub-surface melting was not considered. Kaufmann et al. (2006) have started to perform detailed laboratory experiments to study the solid-state greenhouse effect in planetary ices. These experiments have verified that this process can act in ice. Davidsson and Skorov (2002) have shown that the solid-state greenhouse effect can cause a remarkable sub-surface heating in cometary surfaces.

The processes, which will cause the mentioned above types of liquid water in iced shallow planetary surfaces, will be described in the following.

2. Undercooled liquid interfacial water

“Undercooled” liquid interfacial water can stably exist on hydrophilic mineral surfaces at nanometre scales. Fig. 1 schematically describes this configuration of directly neighbouring

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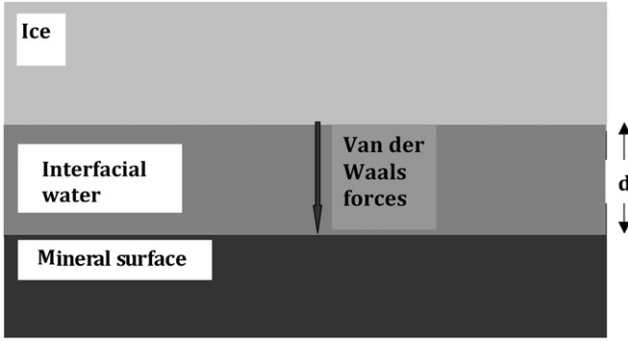


Fig. 1. Liquid interfacial water stabilizes the otherwise thermodynamically unstable contact-interface between water ice and mineral surfaces.

surfaces of water ice and mineral grains, which are stabilized by the interfacial layer of undercooled liquid water. The van der Waals pressure p_{vdw} is for neighbouring plane surfaces S of distance d given by $p_{vdw} = F_{vdw}/S = A/(6\pi d^3)$, as described, e.g. by Tadmor (2001). Note that this relation is to be modified for other geometrical arrangements that indicates a broad variety of conditions for ULI water to occur. The strength of the interfacial interaction in presence of ice, interfacial water, and a mineral surface is characterized by the effective Hamaker constant A , which is typically in the range between 10^{-19} and 10^{-18} J. Thermodynamically, this pressure causes a freezing point depression in the ice within the molecular layers nearest to the ice surface, which therefore melts.

This situation is analogously given at a surface of ice but without a neighbouring solid surface: The molecular layers nearest to the ice surface are subject of an effective inward directed intermolecular force from the bulk of the ice. This force is not compensated in the near vicinity of the ice surface. This acts like an additional pressure. The related phenomenon of near surface melting of ice is called “premelting of ice” (Dash et al., 2006). The formalism to describe premelting of ice can analogously be applied to describe interfacial ice–mineral interactions. Mineral and other surfaces adjacent to ice can support this melting, which is to be described then by an effective Hamaker constant.

In terms of premelting, the freezing point depression can generally be described by the relation (cf. Dash et al., 2006)

$$\rho_S q \frac{T_m - T}{T_m} = \frac{A}{6\pi d^3} + \kappa \sigma + (p_L - p_m) \left(1 - \frac{\rho_S}{\rho_L} \right) \quad (1)$$

$\Delta T = T_m - T$ is the freezing point depression, T_m is the melting point temperature, ρ_L is the mass density of ULI-water, $\rho_S = 916.8 \text{ kg m}^{-3}$ is the mass density of ice, d is the thickness of the layer of ULI-water, and A (J) is the Hamaker constant (cf. also Möhlmann, 2008), p_L and p_m are the (different!) pressures in ULI-water and ice, respectively, where p_m is the reference pressure that corresponds to the coexistence pressure for the melting temperature T_m . The latent heat per mass is given by q (J kg^{-1}), κ is the curvature of the ice–liquid surface.

The first r.h.s.-term in Eq. (1) describes premelting due to attractive van der Waals interactions, the second one gives the curvature and surface tension caused melting (enhanced pressure in the fluid due to surface tension), and the third part describes the so called pressure melting (what, by the way, is often but incorrectly believed to permit skiing and ice skating, which are possible due to the van der Waals force driven premelting). The last r.h.s.-term is under normal conditions small, if compared to the other terms of microscopic origin.

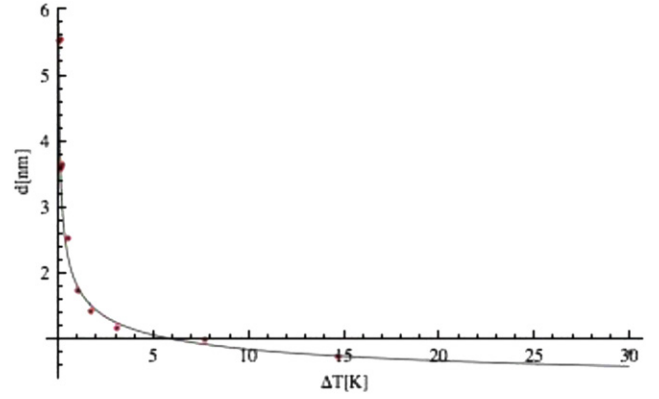


Fig. 2. Experimentally determined thickness of a film of undercooled interfacial water on a SiO_2 -surface (dots), according to Engemann (2004) and Engemann et al. (2004). The curve is fitted according to Eq. (3) for $A = 1.84 \times 10^{-19}$ J.

The minimum temperature of ULI-water to remain liquid is given in case of interfacial van der Waals forces only by

$$T = T_m \left(1 - \frac{A}{6\pi q \rho_S d^3} \right) \quad (2)$$

The thickness d of the layer of ULI-water is then given by

$$d = \left(\frac{A T_m}{6\pi q \rho_S (T_m - T)} \right)^{1/3} \quad (3)$$

Fig. 2 gives an example of an experimentally determined thickness d of ULI-water in dependence on the freezing point depression ΔT of ULI on a SiO_2 surface (Engemann, 2004; Engemann et al., 2004). Note that the thickness of one molecular layer is about 0.35 nm. Obviously, about two molecular layers can exist on this surface at -30°C and lower.

Terrestrial examples of ULI-water can be found in permafrost soil. Nersesova (1950), Anderson (1968), Anderson et al. (1973), Low et al. (1968), and Cahn et al. (1992) have published measurements of the content of “unfrozen”, i.e. of stable ULI-water in soils of terrestrial permafrost. A remarkable conclusion of these investigations is that unfrozen water will exist at -30°C and lower (Anderson, 1968). The content of ULI-water in porous soil can be estimated according to the above given relations via

$$a_m(T) = \frac{M_{\text{H}_2\text{O}}(d(T))}{m_{\text{dry}}} = \rho_{\text{H}_2\text{O}} S_M d = S_M \rho_{\text{H}_2\text{O}} \left(\frac{A T_m}{6\pi q \rho_S \Delta T} \right)^{1/3} \quad (4)$$

here, $M_{\text{H}_2\text{O}}$ is the mass of ULI-water in otherwise dry soil of mass m_{dry} , and S_M ($\text{m}^2 \text{ kg}^{-1}$) is the specific surface per soil mass. This formula describes with good accuracy the experimentally determined and above mentioned measurements of the water content in permafrost (cf. Möhlmann, 2010), and it can analogously be applied to determine the water content in extraterrestrial ice–mineral mixtures, which necessarily must evolve interfacial films of undercooled liquid water in between the surfaces of mineral grains and ice. This content of ULI-water can well reach the orders of 10% and more.

3. Brines

ULI-water, i.e. liquid interfacial water films between water ice and minerals can evolve in porous media of “sub-zero temperature” by freezing of atmospheric water vapour at the internal surfaces.

If the porous mineral consists also of soluble salts, the formation of ULI-water will only be a pre-conditional intermediate

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