Fluctuation spectroscopy of surface melting of ice without, and with impurities

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Water, in its three phases, is ubiquitous, and the surface properties of ice is important to clarifying the process of melting, as well as to various other fields, including geophysics1–3. As such, the subject has been studied both theoretically and experimentally, for over a hundred years, while being an active field of research today. It has been established that surface melting, or premelting, exists below the melting point, and a “liquid-like layer” (LLL) exists on the surface of ice. Here, we use the surface thermal fluctuation spectra to study the properties of LLL, including its thickness, for pure ice, and for ice with impurities. We find that the properties of LLL are consistent with those of bulk liquid water, and for layers thicker than 10 nm, their properties are experimentally indistinguishable from those of liquid water. Measured thicknesses are found to be much smaller than the previous experimental measurements close to the bulk melting temperature2,3. We find that the additions of impurities at ppm levels cause LLL to be thicker, as well to be quite inhomogeneous, with properties depending on the dopant. This is revealed by scanning the surface at μm level resolution, and can contribute to the slipperiness of ice in natural settings.

The importance of understanding the surface properties of ice in air can not be understated, which is crucial for the clarification of the melting, freezing process itself2,3. These properties have important consequences in various branches of science, including physics, chemistry, geophysics, atmospheric sciences, biology, and food science, as well as winter sports, such as skating or curling2,3. Theoretically, the existence of LLL (sometimes also called “quasi-liquid layer”) has been discussed since 19th century, and its properties, including its existence, has been studied from various points of view — thermodynamic arguments4–7, and more recently, state of the art molecular dynamics simulations have been employed8–10. Due to its importance, and its experimental difficulty, surface melting of ice has been analyzed experimentally using a multitude of methods, such as ellipsometry11–13, X-ray diffraction14, proton backscattering15, photoelectron spectroscopy16, and atomic force microscopy17–19. For a number of reasons, including the thinness of LLL, which can be nm order or smaller, the similarity of the optical and chemical properties of ice and water, the sensitivity of LLL to external stimuli, the study of LLL remains to be an experimentally challenging problem. This difficulty is evidenced by the thickness measurements of LLL of ice, which varies by orders of magnitude3,13,20.

In this work, we optically measure the thermal fluctuations of LLL surface on ice in air. By measuring the thermal motions of the molecules directly, in addition to clearly differentiating the liquid and solid phases, the properties of the material become apparent. Such a method, while previously not applied to surface melting, has proven to be effective in understanding the properties of various liquids, complex fluids, and viscoelastic materials21–26. This experimental method for measuring the properties of LLL, distinct from previous methods, enables us to obtain a different perspective on LLL. The surface thermal fluctuations, which are spontaneous, reveal the properties of the material underneath, providing information whether LLL has the properties of water in the bulk, in addition to the behavior of its thickness26–31. Compared to the traditional optical methods, such as ellipsometry, we are in addition utilizing the time domain information to observe molecular thermal motion, and gain further insight into the behavior of LLL. Additionally, unlike ellipsometry, we observe surface fluctuations and do not need a transparent layer for measurement, so that the method can also be used for non-transparent materials, such as metals or ceramics, and we believe it can contribute to elucidating the dynamics of solids at high temperatures. Also, unlike photoelectron spectroscopy, proton scattering, or X-ray diffraction, the method itself is not affected by the chemical composition of the material, so that it can be applied to various materials, and to matter with a large amount of impurities, in the same fashion.

The experimental setup is shown in Fig. 1: Light is shone on the surface of ice, with LLL expected to be on it. The reflected light is detected by the dual-element photodiode (DEPD). The surface acts as a partial mirror, and the two elements in DEPD produce the same photocurrent, if the surface is not fluctuating. The surface fluctuates thermally, and produces fluctuations in the photocurrent difference, whose power spectrum is the inclination fluctuation spectrum of the surface, up to a constant. The measurement is performed using two light sources with different wavelengths, in order to use correlation analysis to statistically reduce the extraneous noise23 to orders of magnitude below the shot-
FIG. 1: Experimental setup. Linearly polarized light from laser light sources with two wavelengths 491, 532 nm are shone on the sample ice surface. The reflected light is directed to two dual-element photodiodes (DEPD1,2), corresponding to each light source. DEPDs effectively measure the average inclination of the sample surface within the beam spot. The difference in the light beam powers in the two elements in DEPDs are digitized using analog-to-digital converters (ADC). The digital data is Fourier transformed (FFT), the averaged correlation is computed (averager) on a computer. Isolators are used to stabilize the light source. Faraday rotator (FR) is used to rotate the polarization of the light by $\pi/4$, each way, so that the polarized beam splitter (PBS) reflects the light from the sample. Dichroic mirrors (DM1,2) are used to merge, and separate the light with different wavelengths. The sample is temperature controlled through thermoelectric cooling (Peltier), and an x-y scanner is used for positioning the sample for scanning its surface.

noise level, which is often referred to as the “Standard Quantum Limit”\textsuperscript{32}. The beam radius (waist) at the sample, $w$, is 1.2 $\mu$m, and the sample can be moved horizontally in two dimensions by 15 $\mu$m in each direction, allowing us to scan the surface.

FIG. 2: Surface thermal fluctuation spectra of water layer of various thicknesses. Fluctuation spectra for supercooled water ($\Delta T = 17.89$ K, red), and LLL for ($\Delta T[K], h [m]$) = (0.003, 3.0 $\times$ 10$^{-6}$) (green), (0.004, 6.0 $\times$ 10$^{-7}$) (blue), (0.006, 2.5 $\times$ 10$^{-7}$) (magenta), (0.014, 1.0 $\times$ 10$^{-8}$) (grey), (0.024, 3.6 $\times$ 10$^{-9}$) (orange), (1.39, 1.4 $\times$ 10$^{-9}$) (cyan), (24.89, 1.0 $\times$ 10$^{-9}$) (yellow). The spectra depend strongly on the thickness of LLL. Corresponding theoretical spectra for water with finite depth are also shown (black), and agree well with the measured spectra.

The spectral function of the thermal fluctuations of the fluid surface has been derived previously, and depends on the properties of the fluid, as well as the thickness of the fluid layer\textsuperscript{30}. Our experimental setup measures the thermal fluctuation spectra of the averaged inclination within the beam spot on the sample. Some examples of spectra for LLL, and water at various $h$, $\Delta T = T_m - T$ are shown in Fig. 2. $h$ is the thickness of LLL, $T$ is the temperature of the sample surface, and $T_m$ is the bulk melting temperature of ice. It can be seen that the spectral shape depends strongly on $h$, and the experimental spectra agree quite well with the theoretical spectra of surface thermal fluctuations of water with finite thickness. The known bulk properties of supercooled water\textsuperscript{33–36} were used to compute the theoretical spectra. We note that surface thermal fluctuations of solid ice without LLL should not only be much smaller, but behave as $1/f^{2,23}$, which is incompatible with the measurements. For LLL with $h \gtrsim 10$ nm, the spectral shape and the magnitude are sensitive to the fluid properties of LLL, density, surface tension, and viscosity, as well as its thickness, in our experimental setting. In particular, in all the spectra analyzed, the viscosity inferred from the spectrum is consistent with the known physical properties of supercooled water. For $h \lesssim 10$ nm, while the spectral magnitude is
quite sensitive to the thickness, varying as $h^3$, the spectral shape is rather insensitive to the properties of LLL. $1/f^2$ behavior observed for thinner LLL agrees with the theory of thermal fluctuations of the water surface.

FIG. 3: The temperature dependence of the thickness of LLL of pure ice. The three types of points (○, △, □) correspond to three data sets taken with three different samples, on three different days, which are seen to be consistent within error.

The dependence of $h$ for LLL of pure ice on the temperature is shown in Fig. 3, where $h$ was estimated from the surface thermal fluctuation spectra (Fig. 2). The dependence has been studied previously by a number of authors, using various other methods, and $h$ differs by orders of magnitude, depending on the method used$^{3,13,20}$. Our results extend over a much wider range of temperatures than that previously covered with any one method. Our results for $h$ are smaller than most of those previously measured for $\Delta T < 1$, close to the bulk melting temperature. Previous results are almost non-existent for $\Delta T > 10$ K, except for photoelectron emission spectroscopy study of LLL of ice in pure water vapor$^{16}$. Compared with this, our results for $h$ are of the of the same order but slightly larger in this temperature range. On the theoretical side, some thermodynamic considerations predict much thicker$^{5,6}$, and also thinner$^7$ LLL. Recent molecular dynamics simulation results exist for $\Delta T \gtrsim 1$ K$^{9,10}$, with thicknesses smaller than ours by a factor of few. It should be noted that the previous literature with thinner LLL$^{7,9,10,16}$ all deal with ice in pure water vapor, without air, unlike our results. Whether this is the cause of the difference would be interesting to investigate. For thin layers, viscosity might be larger than its value in bulk, though whether it is, and by how much if so, is an unsettled question$^{2,37–39}$. Since the surface thermal fluctuation spectrum behaves as $\sim h^3/(\eta f^2)$ for thin LLL, larger viscosities lead to larger $h$ values in our results (Fig. 3), so that a dramatic rise in the viscosity for smaller $h$ seems unlikely.

FIG. 4: Spatial distribution of LLL thickness of pure ice. $h$, at four temperatures, $\Delta T = 0.033, 0.010, 0.008, 0.007, 0.006$ K. $h$ is larger at lower temperatures (larger $\Delta T$). $h$ distributions are seen to be relatively uniform, with slight variations.

An important questions is whether LLL is homogeneous: Our measurement system allows for scanning at $\mu$m level, since the light beam is focused, with $w = 1.2 \mu$m. In Fig. 4, the dependence of the $h$ on the surface location is shown, for the surface of pure ice, at different temperatures. $h$ values are seen to be reasonably uniform in the scanned region, for LLL of pure ice. For small $\Delta T$, $h$ is strongly dependent on the temperature (Fig. 3), so some variation is visible.
FIG. 5: Spatial distribution of the LLL thicknesses of ice with impurities, at various temperatures. Spatial distribution of $h$ for ice with NaCl (a,b,c,d,e), and Volvic (f,g,h,i,j), as the temperature is lowered, for the same area. LLL with $h \gtrsim 0.1\,\mu m$ persists for $\Delta T > 1\,K$, unlike LLL of pure ice. Inhomogeneities arise in LLL thickness, and channel like structures are observed for Volvic. Regions with relatively thick LLL gradually decrease at lower temperatures.
Theoretically, impurities can greatly affect the overall thickness of LLL\textsuperscript{40,41}, and are perhaps the cause of their large observed disparities\textsuperscript{2}. To study the effect of impurities, in Fig. 5, the spatial dependences of $h$ are shown for frozen NaCl solution (10 ppm by weight before freezing), and Volvic (water with minerals roughly 60 ppm by weight)\textsuperscript{42} at various temperatures, as they are being cooled. We chose Volvic, which contains various minerals, as a model of water in a natural setting. The concentrations of the impurities are low enough that the effects to the bulk properties of water are expected to be negligible within the experimental precision. There are clear qualitative differences from the properties of LLL of pure ice, and also between LLL with different impurities. First, we see that in both cases, LLL with $h > 0.1 \mu m$ exists for $\Delta T > 1 K$, in contrast to that of pure ice, seen in Fig. 3. Furthermore, unlike pure ice LLL, $h$ distributions are quite inhomogeneous. There is also a distinct difference between the effect of two impurities: A reasonably thick LLL exists for frozen NaCl solution down to temperatures much lower than that for Volvic, which is not as inhomogeneous as the latter. For Volvic, channels of LLL form, which have the bulk properties of water, that grow narrower and shallower as the temperature lowers. Vein like structures have been observed in glaciers\textsuperscript{2,43}, and it is interesting to study possible relations of our results to them further. The cause for the distinct difference between ice with NaCl and Volvic can perhaps be attributed to the difference in the solubility of the impurities. Minerals within Volvic are not as soluble in water as NaCl, in general. We have scanned the surface of ice with glucose, and have found that the behavior is similar to that of NaCl solution. We have further scanned surfaces of ice with NaCl at various concentrations, and frozen Evian water\textsuperscript{44}, and have found the results to be consistent with these considerations. The concentration per unit area of the NaCl solution in Fig. 5 can be estimated to be $90 \mu mol/m^2$. The observed thicknesses of LLL seem roughly consistent with those of the theory\textsuperscript{40}, though at lower temperatures, the inhomogeneity of LLL should be taken into account.

An interesting classic problem is the ability to skate on ice, or the slipperiness of ice. One explanation is the existence of a relatively thick LLL. We found that pure ice only supports LLL with thicknesses under 1 nm for $\Delta T > 1 K$. However, in a natural setting, water inevitably contains a certain amount of impurities. Our results show that impurities thicken LLL, and create inhomogeneities, which can contribute to the slipperiness of ice. One observation from our results is that frozen mineral water supports surface melting in the form of veins, which essentially disappear for temperatures below $-10^\circ C$. This is intriguing considering that optimal skating conditions are considered to be between $-5$ to $-9^\circ C$. Frictional heating\textsuperscript{2}, and other mechanisms have also been recently suggested\textsuperscript{46,47}, and further investigation remains to be done.

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