Measurement of self-diffusion on ice surface

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The self-diffusion coefficient on ice surface has been measured by studying the formation of grain boundary (GB) grooves on the surface of polycrystalline ice samples annealed at temperatures between $-2$ and $-15$ $^\circ$C. Samples were encapsulated with silicone oil, enabling the assumption that the formation of the groove takes place only by surface diffusion. Photographs of polycrystalline ice samples viewed between crossed-polaroid filters were used to determine the time taken by the groove to grow to a width of approximately 10 $\mu$m. It was shown that ice surface has a self-diffusion coefficient very close to those measured in supercooled water.

It is well known that at temperatures near the melting point, ice surface has a disordered structure with characteristics similar to those of a liquid; this surface is referred to as quasi-liquid layer (QLL). The QLL has been clearly observed measuring different ice properties at temperatures above $-20$ $^\circ$C and is in general associated with rapid H$_2$O surface diffusion. Dash et al. [1] have presented a very complete review of experiments performed on ice surface properties prior to 1995. Since then, many new experiments have been carried out, using a variety of methods, including atomic force microscope [2], infrared spectroscopy [3] and other experimental techniques (reviewed by Huthwelker et al. [4]). However, few experimental data are available for the self-diffusion coefficient on ice surface. In fact, as far as we know, experimental values of the self-diffusion coefficient on ice surface have only been reported by Mizuno and Hanafusa [5] and by Nasello and Di Prinzio [6]. Mizuno and Hanafusa determined the self-diffusion coefficient on ice surface by performing pulsed nuclear magnetic resonance on samples prepared using small ice particles with large surface to volume ratios. They found that the self-diffusion coefficient in the QLL is three orders of magnitude smaller than the corresponding value in supercooled water [5]. On the other hand, Nasello and Di Prinzio reported values of ice surface diffusion coefficients at $-6$ $^\circ$C close to those in supercooled water. The self-diffusion coefficient values were obtained by performing grain boundary (GB) migration studies in pure ice bicrystalline samples [6].

The main propose of this work was to obtain, experimentally, the self-diffusion coefficient on ice surface at temperatures near the melting point. According to the theoretical work of Mullins and co-workers [7-9], the surface self-diffusion coefficient can be determined by studying the time evolution of grooves produced on a free surface. In the present study, the time taken for a groove to grow to a determined width is estimated from photographs of polycrystalline ice samples, taken at regular intervals. The values of the surface self-diffusion coefficient were determined on samples annealed at constant temperatures between $-2$ and $-15$ $^\circ$C.

According to Mullins [7], the relationship between the separation $d$ between the two peaks of the GB groove and the evolution time $t$ (diffusion process only) is given by

$$d = 4.6(Bt)^{1/4},$$

where $B = \frac{D \gamma s \Omega^2 v}{kT}$,

where $\Omega$ is the atomic volume, $\gamma s$ is the surface energy, $v$ is the number of atoms per unit area ($v \approx \Omega^{3/2}$), $D_s$ is the surface diffusion coefficient, $k$ is the Boltzmann constant and $T$ is the temperature.

In order to determine the surface self-diffusion coefficient, photographs of polycrystalline ice samples viewed between crossed polaroid filters were taken at 1 h...
intervals, using a digital camera attached to a microscope. In the digital images, the grains were identified by the differences in gray tones caused by the polarized light and the GB grooves were viewed as a fine line located on the GB. Initially, no grooves were observed on the GBs (Fig. 1a). As time went on, a line over the GB began to appear, indicating that the grooves had formed (Fig. 1b). We considered the time lapse \( t \) until the groove reached a minimal width \( d \approx 10 \mu \text{m} \), i.e. three times the minimum appreciation of our digital system.

The polycrystalline samples were prepared by freezing a drop of water obtained from a MilliQ filter on a sanded glass located in a cold room at \(-10^\circ \text{C}\). The frozen drop was polished, in the same cold room, using a microtome to a thickness of 0.3 mm. Each thin sample of ice was left over the sanded glass and put immediately in a hermetic and transparent cylindrical box filled with silicone oil where it was annealed for about 400 h at \(-2, -5, -10 \) or \(-15^\circ \text{C}\). The ice samples were immersed in silicone oil in order to avoid the evaporation and condensation effects that impeded the measurement of the surface diffusion coefficient by Itagaki and Tobin [10], who used a similar method (Mullins [9]).

The groove formation times \( t \) obtained at different annealing temperatures are shown in Table 1. Using these values, the physical parameters of ice given by Hobbs [11] and taking \( d = 10 \mu \text{m} \), the surface self-diffusion coefficients \( D_s \) were obtained from Eqs. (1) and (2). The results are presented in the third column of Table 1.

Figure 2 shows, for each annealing temperature, the obtained surface self-diffusion coefficient with the corresponding experimental uncertainties. In this figure, the corresponding diffusion coefficient obtained by Nasello et al. [12] for GB, by Preilmeier et al. [13] for supercooled water, by Petrenko and Whitworth [14] for the bulk and by Mizuno and Hanafusa [5] for the surface are also presented. For each case, the analytical expressions used to calculate the corresponding values are given in the Appendix.

Figure 2 shows that surface self-diffusion values obtained in this work are very close to those corresponding to the supercooled water diffusion coefficient measured by Preilmeier et al. [13]. These results are in agreement with those previously obtained at \(-6^\circ \text{C}\) by studying the GB migration in bicrystalline samples [6]. In this figure, it is also seen that the values of \( D_s \) measured by Mizuno and Hanafusa [5] are close to the GB diffusion coefficient values obtained by Nasello et al. [12]. This behavior can be explained as suggested by Petrenko and Whitworth [15], who argue that a sintering occurred during the course of Mizuno and Hanafusa’s experiment, so the obtained diffusion coefficient values do not correspond to the ice surface. The region between two fused ice crystals may be considered very close to a GB as indicated by the results shown in Figure 2.

It was shown that the theoretical analysis performed by Mullins [7] can be satisfactorily used to determine self-diffusion coefficients on ice surface, following a very simple method to photographically study the time evolution of the GB groove. The evaporation and condensation processes were avoided by immersion in silicone oil. From the obtained results it can be concluded that the ice surface has a self-diffusion coefficient similar to that of the supercooled water in the temperature range from \(-2^\circ \text{C} \) to \(-15^\circ \text{C}\).

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Table 1. Time of groove formation \( t \) at different annealing temperatures \( T \)

<table>
<thead>
<tr>
<th>Temperature ( ^\circ \text{C} )</th>
<th>( t ) (h)</th>
<th>( D_s ) ( \times 10^{-10} \text{ m}^2 \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-2)</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>(-5)</td>
<td>13</td>
<td>21</td>
</tr>
<tr>
<td>(-10)</td>
<td>81</td>
<td>3.0</td>
</tr>
<tr>
<td>(-15)</td>
<td>91</td>
<td>2.9</td>
</tr>
</tbody>
</table>

\( t \) is associated with the time it takes a groove to grow to a width of \( d \approx 10 \mu \text{m} \). \( D_s \) is the ice surface self-diffusion coefficient obtained using Eqs. (1) and (2).

(1) Supercooled water diffusion coefficient obtained by Preilmeier et al. [13]:

\[
D_s = D_0 \left[ \frac{T}{T_s} - 1 \right]^{0.5},
\]

where \( D_0 = 8.66 \times 10^{-10} \text{ m}^2 \text{ J}^{-1} \text{ s}^{-1} \), \( \gamma = 1.809 \) and \( T_s = 220^\circ \text{K} \).
GB diffusion coefficient $D_b$ obtained by Nasello et al. [12]:

$$D_b = \frac{2KT}{\Omega^{2/3}}M,$$

where $\Omega = 3.6 \times 10^{-29} \text{m}^3$ [11]. $M = M_o \exp(-\frac{Q}{RT})$ with $M_o = 2.3 \text{m}^4 \text{J}^{-1} \text{s}^{-1}$ and $Q = 0.53 \text{eV}$.

(3) Surface self-diffusion coefficient obtained by adjusting Mizuno and Hanafusa’s data [5]:

$$D_b = D_0 e^{Q/RT},$$

where $D_0 = 1.4 \times 10^{-8} \text{m}^2 \text{s}^{-1}$ and $Q = 0.24 \text{eV}$.

(4) Bulk diffusion coefficient from Petrenko and Whitworth [14]:

$$D_b = D_0 e^{Q/2KT_0},$$

where $D_0 = 1.49 \times 10^{-15} \text{m}^2 \text{s}^{-1}$, $Q = 0.62 \text{eV}$ and $T_0 = 263 \text{K}$.