Arrhenius Analysis of Anisotropic Surface Self-Diffusion on the Prismatic Facet of Ice

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Introduction

Light-scattering properties of cirrus clouds influence the Earth's radiative bugdet. The optical properties of cirrus clouds are related to the surface mesoscopic (micrometer-scale) structure of the ice crystals that comprise those clouds. The ice-crystal surface morphology is not static with time: an ice crystal can grow, and eventually fall and ablate in underlying warm air.

Scanning Electron Microscope (SEM) experiments show:

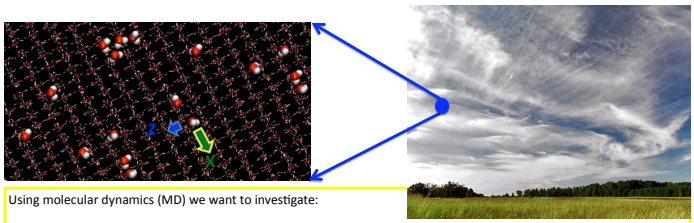
1) Growing and ablating of ice crystals appears to occur in a distinctively facet-specific way.

2) Prismatic facets exhibit anisotropy growing and ablating by trans-prismatic strands[1].

Theoretical/computational work show:

3) Surface diffusivity is a key factor that governs ice crystal surface morphology.

4) Surface diffusivity on primary prismatic ice facet is anisotropic[2].



Using molecular dynamics (MD) we want to investigate:

1) At temperature closer to melting one, a quasi liquid layer (QLL) would be expected to hide the underlying crystal structure; how does prismatic surface diffusion anisotropy evolve with temperature?

2) In the context of Arrhenius analysis, which is the activation energy barrier for the in-plane diffusion on the primary prismatic facet?

Computational Methods

MD simulations performed with GROMACS 4.5.4 using the six site (NE6) water model [3].

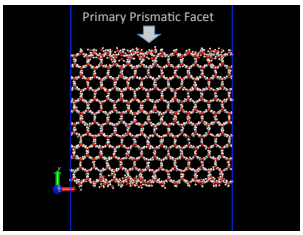
Ice crystal of 2880 water molecules (5.4nm X 4.7 nm X 3.7 nm in x, y, z directions) using proton disordering algorithm.

12 bi-layers perpendicular to the primary prismatic facet.

The initial ice crystals were annealed from 0K to the desire temperature (230, 240, 250, 260, 270, 278 K) in 1.5 ns using zero-pressure barostate.

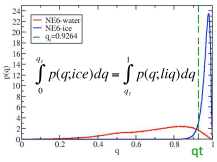
Two primary prismatic $(10\bar{1}1)$ facet/vacuum interfaces were created enlarging the y-dimension of the box to 12 nm.

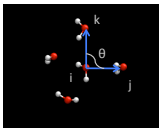
Production run of 100 ns, constant volume simulation (NVT) with dt=2 fs. First 4 ns of each trajectory were excluded to allow formation of ice-QLL.



Structure of the Primary Prismatic QLL

•For each water molecule we define an order parameter to determine if it belongs to the liquid or solid phase using the four nearest-neighbour oxygen.



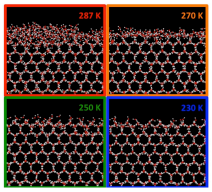


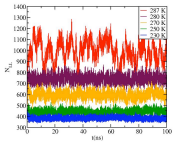
$$q_t = \left[1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos(\theta_{i,j,k}) + \frac{1}{3}\right)^2\right]$$

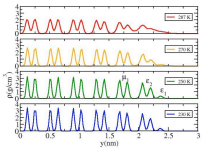
•Using the probability densities for bulk ice and bulk liquid water we can define q_t such that:
$q>q_t$ => Ice like water molecule;
$q<q_t$ => Liquid like water molecule.

•At the vacuum/ice interface, liquid like layer (called QLL) is present on the top of the ice crystal.

•The thickness of the QLL increases with the temperatur







•With increasing temperature, water molecules from the inner bi-layers start to contribute to the formation of the ice-QLL.

•Upon increasing the temperature, more interfacial water molecules become mobile and contribute to the diffusion in the QLL.

Anisotropy and Diffusion Activation Energy in the Primary Prismatic QLL

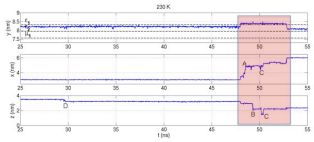
•Diffusivity calculated from the slope of the one-dimensional mean square displacement as a function of time.

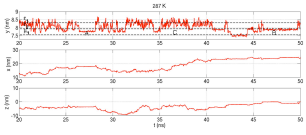
$$D_i = \frac{1}{2}\frac{dMSD_i(t)}{dt}$$

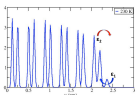
•The immobile water molecule in the ice crystal do not contribute to the diffusion coefficient: we scaled the diffusivity by the effective number of mobile water molecules.

$$D^*_i = D_i / Q$$
$$Q = (N_{QLL} - N_{EV})/(N_{SLAB} - N_{EV})$$
$$i = x, z$$

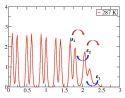
T (K)	T-T_m (K)	D^*_x (10^{-9} m^2s^{-1})	D^*_z (10^{-9} m^2s^{-1})	D^*_{xz} (10^{-9} m^2s^{-1})	D^*_x/D^*_z
287	-2	1.31±0.08	1.41±0.09	1.4±0.06	0.93±0.08
280	-9	0.83±0.03	0.76±0.06	0.79±0.03	1.09±0.09
270	-19	0.35±0.03	0.33±0.03	0.34±0.02	1.09±0.09
260	-29	0.162±0.003	0.1552±0.0008	0.158±0.002	1.04±0.02
250	-39	0.076±0.004	0.0741±0.0009	0.075±0.002	1.03±0.05
240	-49	0.0445±0.0008	0.0328±0.0008	0.039±0.0006	1.36±0.04
230	-59	0.0198±0.0008	0.0152±0.0008	0.018±0.0006	1.30±0.09



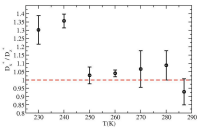




•Trajectory of one particular water molecule at 230 K in x, y, z directions. Lateral diffusion in x-z plane associated with vertical y-transition from ε_2 to ε_1 (and vice versa) sub-layers.

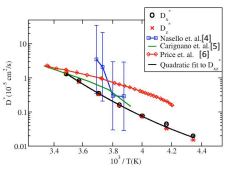


•Trajectory of one particular water molecule at 287 K in x, y, z directions: ε_2 and ε_1 are merged in one layer. Molecules from μ_1 also contribute to the in-plane diffusion.



•At lower temperature, horizontal diffusivity is associated with vertical exchange of molecules between ε_1 and ε_2 bi-layers. This contribution is generally different in the x or z directions because water molecules move on the underling primary prismatic crystalline structure ***(facet-proximate mechanism)***
=> Anisotropy of diffusivity (D*x/D*z≠1).

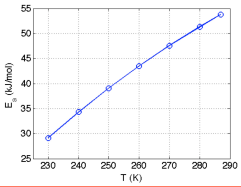
•At higher temperature the outer part of the QLL is farther from the underlying crystalline structure ***(facet-distant mechanism)*** => quasi 3-D diffusion, isotropic diffusivity (Dx* /D*z ~1).



•The bulk liquid water diffusivity in supercooled regime has a negative slope of the Arrhenius plot suggesting an activation energy that decreases with the temperature.

•The water diffusivity in the QLL agrees with available experimental data within the quoted precision.

•Positive curvature of the Arrhenius plot of surface diffusivity on ice suggests an activation energy that increases with the temperature.



•***In the QLL, the facet-proximate diffusion*** may be expected to have an higher activation energy than the ***facet-distant diffusion*** because the vertical motion takes a molecule from a more hydrated environment closer to the surface where fewer hydrogen bonding partners are available.

Conclusions

•The self-diffusion on ice surface occurs by significantly different mechanism compared to bulk self-diffusion in supercooled water.

•At low temperature, the water molecules are exposed to the anisotropic underlying crystalline terrain leading to anisotropic in-plane diffusion.

•At high temperature, thick QLL leads to quasi 3-D liquid-like diffusivity.

•The Arrhenius analysis show an activation energy for in-plane diffusion in the QLL increasing with the temperature as a result of a thicker QLL where molecules move vertical from more to less hydrogen bonding environment.

References

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Acknowledgements

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