Anomalous diffusion of water molecules at grain boundaries in ice I_h

*Ingrid de A. Ribeiro[1], P. A. F. P. Moreira[2], R. G. de Aguiar Veiga[3], R. Freitas[4], J. Helfferich[5], Maurice de Koning[1]

[1]Instituto de Física "Gleb Wataghin", UNICAMP, Campinas, São Paulo, Brazil
[2]Departamento de Física, UFSCar, São Carlos, São Paulo, Brazil
[3]Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, UFABC, Santo André, São Paulo, Brazil
[4]Department of Materials Science and Engineering, University of California, Berkeley, United States
[5]Karlsruhe Institute of Technology, Institute of Nanotechnology, Eggenstein-Leopoldshafen, Germany

Abstract

Using *ab initio* and classical molecular dynamics simulations, we study pre-melting phenomena in pristine coincident-site-lattice grain boundaries (GBs) in proton-disordered hexagonal ice I_h at temperatures just below the melting point T_m. Regarding the molecular mobility, the simulations provide a key new insight: the translational motion of the water molecules is found to be subdiffusive for time scales from $\sim$10 ns up to at least 0.1 μs. Moreover, the fact that the anomalous diffusion occurs even at temperatures just below T_m where the bulk supercooled liquid still diffuses normally suggests that it is related to the confinement of the GB pre-melt layers by the surrounding crystalline environment. Furthermore, we show that this behavior can be characterized by continuous-time random walk models in which the waiting-time distributions decay according to power-laws that are very similar to those describing dynamics in glass-forming systems.

Computational approach

Due to the complexity of the ice I_h structure [1], building a sample containing GBs is non-trivial. In this way, a Σ35 symmetric tilt grain boundary (GB), which is characterized by a rotation of 34.05^o about the $\langle\bar{1}100\rangle$ direction and the $(11\bar{2}\bar{1})$ intersection plane was built with GBstudio [2]. For the AIMD simulations, we also create a smaller periodic cell, containing 156 molecules in an arrangement with a pair of Σ35 GBs.

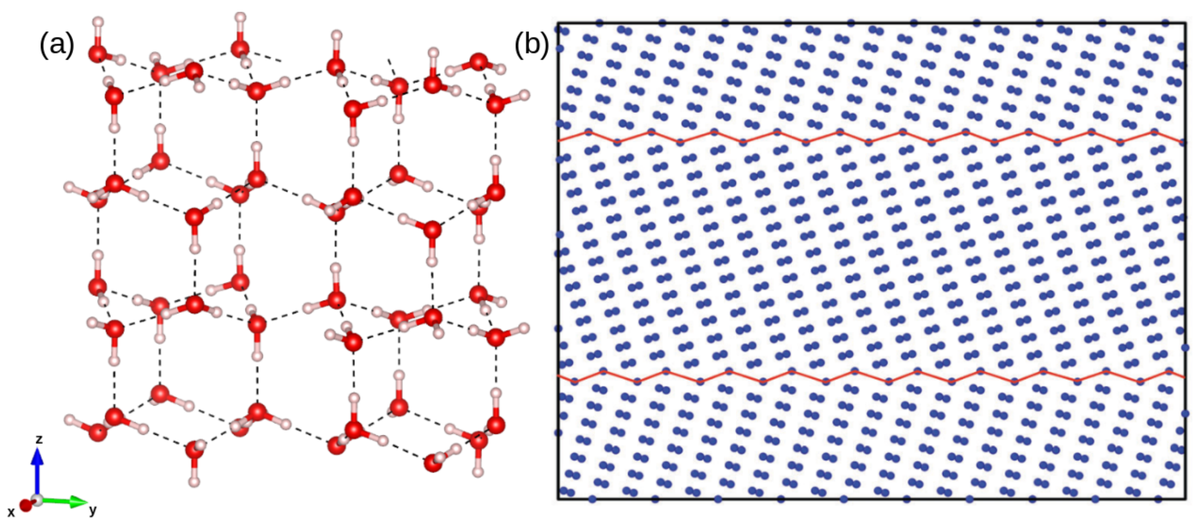

Figure 1. (a) ice I_h structure (b) Σ35 periodic cell with 10 800 oxygen atoms used for MD simulations.

Simulation details

We carried out density-functional-theory (DFT)-based AIMD simulations on the 156-molecule cell containing a pair of Σ35 symmetric tilt GBs. All DFT-based MD simulations rely on the PBE functional [3] and the PAW approach as implemented in the VASP code [4, 5]. Brillouin-zone integrations were performed only at the Γ point, and the plane wave cutoff set as 700eV. These simulations were done within the NVT ensemble using the Langevin equations of motion integrated using a time step of 0.5 fs. The temperature was set at 400 K, which was 17 K below the melting temperature of PBE ice I_h.

We also use classical MD simulations based on the TIP4P/Ice model [6] by using LAMMPS [7]. The simulations were carried out within a zero-pressure isobaric-isothermal ensemble in which all three sides of the orthogonal cell were allowed to vary independently. The temperature was set at T = 266 K, which was 5 K below the melting temperature T_m= 271 K of the TIP4P/Ice model. The equations of motion were integrated using a time step of 2 fs.

Results

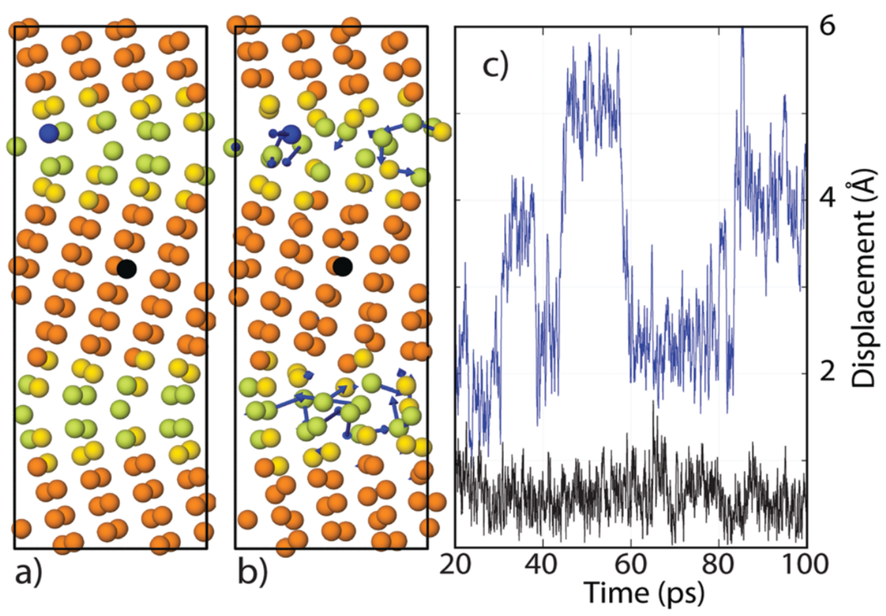

Figure 2. DFT-based MD simulations. (a) initial configuration (b) oxygen positions after 100 ps (c) displacement with respect to the initial configuration of oxygens.

Results

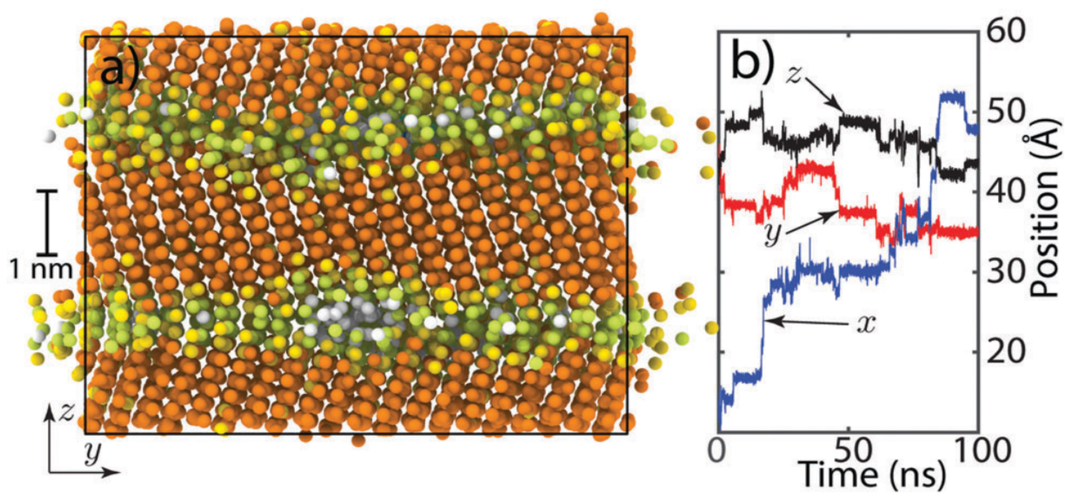

Figure 3. (a) Snapshots of the oxygen positions in the Σ35 cell obtained after an MD simulation using the TIP4P/Ice model over an interval of 0.1 μs (b) x, y and z coordinates of a particular oxygen atom in the upper GB region as a function of time.

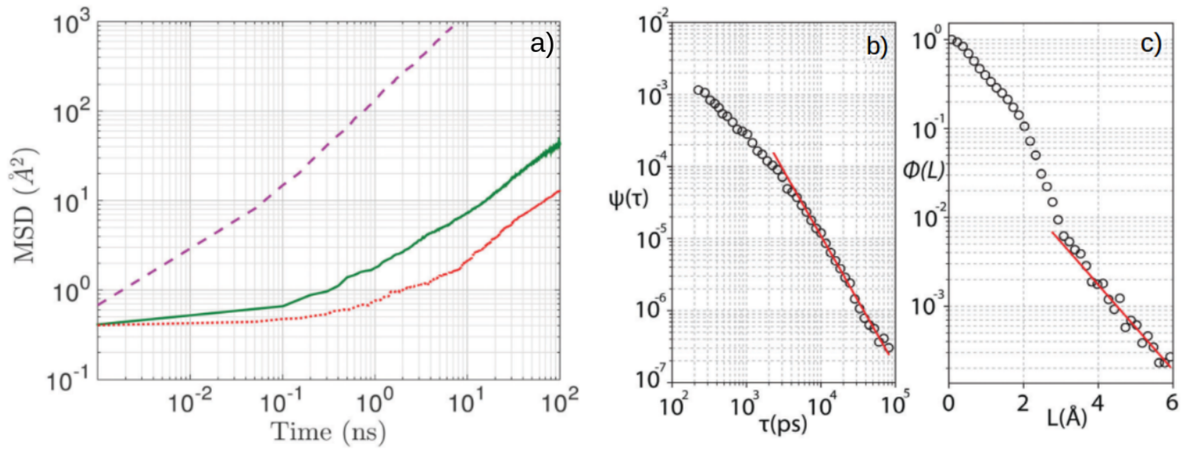

Figure 4.(a) Full (green) line describes the Σ35 MSD for the GB molecules. Dotted (red) line depicts the corresponding results for the Σ14. Dashed (purple) line describes the results for the bulk supercooled TIP4P/Ice liquid at the same temperature. (b) WTD as a function of the waiting time t, and (c) JLD as a function of the jump length L, for the GB molecules in the Σ35 boundary.

Conclusion

The DFT-based MD simulations presented qualitatively that there is an anomalous diffusion of water molecules at the GB regions for temperatures just below the melting point. Quantifying the GB vs. bulk contributions to the total diffusivity requires further analysis, which for the AIMD approach is unfeasible due to the computational cost required for such a system. From MD simulations, the translational motion of the water molecules is subdiffusive for time scales of $\sim$10 ns up to at least 0.1 μs. Moreover, given that the subdiffusive behavior occurs even at temperatures just below T_m where the bulk supercooled liquid still diffuses normally, its origin appears closely related to the confinement of the GB pre-melt layers within the crystalline environment. Coarse-graining the MD trajectories in terms of a CTRW model gives rise to waiting-time distributions with a power-law decay that is very similar to those seen in a variety of glass-forming systems, suggesting that the anomalous diffusion of water molecules in the pre-melt layers at the GBs in ice may bear noticeable similarities to glassy dynamics [8].

References

[1] V. F. Petrenko and R. W. Whitworth, *Physics of Ice*, Oxford University Press, (1999).

[2] Ogawa, H., Materials transactions, **47**, 2706–2710 (2006).

[3] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., **77**, 386 (1996).

[4] G. Kresse and J. Furthmüller, Comput. Mater. Sci., **6**, 15 (1996); Phys. Rev. B, **54**, 11169 (1996).

[5] G. Kresse and J. Hafner, Phys. Rev. B, **47**, 558 (1993); Phys. Rev. B, **49**, 14251 (1994).

[6] J. L. F. Abascal, E. Sanz, R. G. Fernandez and C. Vega, J. Chem. Phys., **122**, 234511, 2005.

[7] S. Plimpton, J. Comput. Phys., **117**, 1-19, 1995.

[8] P. A. F. P. Moreira, R. G. de Aguiar Veiga, I. de Almeida Ribeiro, R. Freitas, J. Helfferich, and M. de Koning. (2018). Phys. Chem. Chem. Phys., **20**, 13944 (2018).