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Ice Formation on Organic Crystals: Molecular Simulations Tell their Stories

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The formation of ice is one of the most ubiquitous examples of crystal nucleation and growth, affecting our everyday life as well as technologies such as cryotherapy [1] or fossil fuel extraction [2]. However, pure water freezes only when cooled about 30 K below its melting point [3]. Thus, ice on earth forms mostly heterogeneously, facilitated by substrates which lower the free energy cost needed to nucleate a sufficiently large (or critical) ice nucleus. Experiments can assess whether a specific material is good or bad at promoting ice formation. For instance, both inorganic and biological particles have been found capable of boosting the ice nucleation rate at few degrees only below the freezing point of water [4], with great impact on the formation of clouds in the atmosphere. In particular, recent evidence suggests that some materials such as pyroelectric systems or polar crystals have the potential to induce local electric fields within the water network [5,6], with a spectacular enhancement of the kinetics of crystal nucleation and growth. However, the microscopic details of ice formation on this class of most promising ice nucleating agents remain largely unknown.

Here, we have investigated by means of atomistic simulations the formation of ice on two organic crystals: cholesterol (CHL) and metaldehyde (MDHE) - a polar crystal [7]. The low Miller index surfaces of these crystals are characterized by the presence of hydroxyl (-OH, MDHE) and etheric (R-O-R', MDHE) groups. The presence of these functional groups influences the structure and the dynamics of the water network in proximity of the water-crystal interface, consolidating the hydrogen bond network in different, albeit similarly effective, ways. This evidence directly translates into a huge boost of the ice nucleation rate, which we quantify by means of enhanced sampling (forward flux sampling [8]) simulations that also allow us to unravel the molecular-level details of the nucleation mechanism on both CHL and MDHE

These results offer a comprehensive, microscopic picture of ice formation enhanced by organic crystals, paving the way to long-awaited molecular simulations of ice formation in biological matter. While the vast majority of the literature has been focusing on hydroxylated surfaces, we demonstrate the importance of functional groups such as the etheric R-O-R'groups in the context of heterogeneous ice nucleation.

[1] R. Y. Tam, C. N. Rowley et al., J. Am. Chem. Soc. 131, 15745 (2009).[2] C. A. Koh, Chem. Soc. Rev. 31, 157 (2002).[3] J. A. Sellberg, C. Huang et al., Nature 510, 381 (2014).
[4] B. J. Murray, D. O'Sullivan et al., Chem. Soc. Rev. 41, 6519 (2012).
[5] D. Ehre, E. Lavert et al., Science 327, 672 (2010).
[6] A. Belitzky, E. Mishuk et al., J. Phys. Chem. Lett. 7, 43 (2016).
[7] N. Fukuta, Nature 199, 475 (1963).
[8] R. J. Allen, C. Valeriani et al., Journal of Physics: Condensed Matter 21, 463102 (2009).

Significance statement

We report the first (to our knowledge) atomistic simulations of ice formation on organic crystals. We provide microscopic insight into the mechanism and the kinetics of ice nucleation in the presence of organic compounds characterized by different functional groups - a first step toward the simulations of ice in biological matter.

Primary author: Dr SOSSO, Gabriele Cesare (University of Warwick)

Co-authors: Dr KISELEV, Alexei (Institute of Meteorology and Climate Research , Karlsruhe Institute of Technology); Prof. MICHAELIDES, Angelos (Thomas Young Centre, London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom); Prof. MURRAY, Benjamin (Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom); Dr HOLDEN, Mark (Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom); Dr PEDEVILLA, Philipp (Thomas Young Centre, London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom); Dr WHALE, Thomas (Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom)

Presenter: Dr SOSSO, Gabriele Cesare (University of Warwick)

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