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The Structural Origins of Dynamical Heterogeneity in Water Pinpoint the Source of Ice-Nucleation

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The dynamical properties of liquid water play a role of great importance in the context of hydrophobic interactions, where the mobility of water molecules affects e.g. both the thermodynamics and the kinetics of ionic and proton transfer, as well as the mass diffusion of molecular species in aqueous environment. Not least, the ubiquitous phenomena of the glass transition and, as we argue in this work, of ice nucleation are intimately connected to the dynamics of supercooled water. For most atomic and molecular liquids it has been shown that their dynamics are heterogeneous in nature: different regions of the system are characterized by different degrees of mobility, yielding macroscopic effects such as e.g. the breakdown of the Stokes-Einstein relation. This dynamical heterogeneity is at the heart of phenomena of practical relevance such as the formation of ice in clouds, ruling the water cycle on Earth, and low-temperature science including cryobiology.

However, obtaining experimental insight into the microscopic details of water dynamics within its supercooled regime is a most challenging task. For instance, how exactly the dynamics of water molecules at low temperatures influences solvation processes is still largely unknown. Most importantly, it is presently unclear whether there exists a specific correlation between the heterogeneous dynamics of supercooled water and the molecular-level details of its structure.

In this work [1], we assessed the structural origins of dynamical heterogeneity in supercooled water by means of molecular dynamics simulations, using coarse-grained and fully atomistic water models. We described the emergence of heterogeneous dynamics in terms of domains of slow and fast moving water molecules identified by iso-configurational analysis. We found that slow moving regions are on average less defective in terms of the hydrogen bond network, which translates into more “tetrahedrality” in agreement with the existing literature. Most importantly we could pinpoint a specific hallmark of these slow-moving regions, namely the abundance of five, seven, and most prominently six-membered rings. Interestingly, most of the water molecules belonging to these rings cannot yet be labelled as ice-like per common topological criteria.

We argue that the substantial presence of six-membered rings within slow-moving domains has the potential to facilitate ice nucleation. This is because the building blocks of ice (six-membered hydrogen bonded rings of water molecules) are already present in the slow-moving domains, hence a spatial re-arrangement of this topological feature can very well result in the onset of crystallization. This in turn means that a change of dynamical order parameters could precede the structural ordering –a fresh point of view on ordering phenomena such as ice nucleation. Our results provide a new link between two of the most fundamental aspects of water and other tetrahedral liquids.

[1] M Fitzner, GC Sosso, SJ Cox and A Michaelides, in preparation

Significance statement

Dynamical heterogeneity affects many interactions of supercooled water like mass diffusion and solvation whilst ice nucleation is ubiquitous (e.g. cloud formation or cryobiology). Our results uncover the structural origins of dynamical heterogeneity in water and suggest a fundamental connection with ice nucleation, opening new avenues to understand the latter.

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