Manuscript version: Author’s Accepted Manuscript
The version presented in WRAP is the author’s accepted manuscript and may differ from the published version or Version of Record.

Persistent WRAP URL:
http://wrap.warwick.ac.uk/163780

How to cite:
Please refer to published version for the most recent bibliographic citation information. If a published version is known of, the repository item page linked to above, will contain details on accessing it.

Copyright and reuse:
The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions.

Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Publisher’s statement:
Please refer to the repository item page, publisher’s statement section, for further information.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk.
How do interfaces alter the dynamics of supercooled water?

Piero Gasparotto
Scientific Computing Division
Paul Scherrer Institute
Villigen 5232, Switzerland
piero.gasparotto@gmail.com

Martin Fitzner
Thomas Young Centre
London Centre for Nanotechnology and
Department of Physics and Astronomy
University College London
London WC1E 6BT, United Kingdom

Stephen J. Cox
Yusuf Hamied Department of Chemistry
University of Cambridge
Cambridge CB2 1EW, United Kingdom

Gabriele C. Sosso
Department of Chemistry
University of Warwick
Coventry CV4 7AL, United Kingdom

Angelos Michaelides
Yusuf Hamied Department of Chemistry
University of Cambridge
Cambridge CB2 1EW, United Kingdom
am452@cam.ac.uk

March 1, 2022

Abstract

The structure of liquid water in the proximity of an interface can deviate significantly from that of bulk water, with surface-induced structural perturbations typically converging to bulk values at about \( \sim 1 \) nm from the interface. While these structural changes are well established it is, in contrast, less clear how an interface perturbs the dynamics of water molecules within the liquid. Here, through an extensive set of molecular dynamics simulations of supercooled bulk and interfacial water films and nano-droplets, we observe the formation of persistent, spatially extended dynamical domains in which the average mobility varies as a function of the distance from the interface. This is in stark contrast with the dynamical heterogeneity observed in bulk water, where these domains average out spatially over time. We also find that the dynamical response of water to an interface depends critically on the nature of the interface and on the choice of interface definition. Overall these results reveal a richness in the dynamics of interfacial water that opens up the prospect of tuning the dynamical response of water through specific modifications of the interface structure or confining material.

Keywords Supercooled water · Confined water · Molecular Dynamics · Dynamical heterogeneity · Water Dynamics · Water Structure · Interfaces

1 Introduction

In apparent contradiction with everyday experience, it is surprisingly difficult to crystallize water into ice. Liquid water can remain in a supercooled state at below 0 \(^\circ\)C for hours and even days. In the absence of impurities, the homogeneous
freezing point of water is $-41 \, ^\circ C$ and experimental evidence shows that nanodroplets, composed of a few thousand water molecules, can be cooled down to $-70 \, ^\circ C$ without a hint of crystallization.\textsuperscript{11} The study of supercooled liquid water dates back to at least the time of Fahrenheit and his seminal temperature-defining measurement.\textsuperscript{6} Supercooled liquid water droplets are ubiquitous in clouds, while plants and mammals adapted for survival in cold climates exploit supercooled water for survival.\textsuperscript{9} The study of supercooled water is also critical for rationalising the anomalous properties of water and as a means to understand ice formation.\textsuperscript{7}

Previous studies have shown that supercooled liquids (particularly glass forming liquids) exhibit very interesting dynamical properties. Specifically, upon supercooling, a phenomenon known as dynamical heterogeneity (DH) emerges.\textsuperscript{8–12} DH involves spatially separated domains of slow- and fast-moving molecules. These domains are mobile and dynamic and their correlation length-scale grows as the temperature decreases towards the glass transition temperature. Simulations have shown that in water and other liquids there exist specific structural hallmarks that characterize immobile and mobile domains.\textsuperscript{13–16} In addition, in recent simulation studies of bulk water we have shown that the relatively immobile domains are the birthplace of ice.\textsuperscript{17}

Studies of DH have generally focused on exploring bulk homogeneous systems.\textsuperscript{4,18–20} Notwithstanding exciting work on highly stable vapour deposited glasses,\textsuperscript{21–24} the effect of interfaces on DH is less well explored. Some pioneering studies investigated dynamical heterogeneity of water in the first adlayer at metal\textsuperscript{41–42} and protein\textsuperscript{43} surfaces using molecular dynamics (MD) simulations. Simulations have also shown that the diffusion of water molecules can increase in the liquid when confined in nano-porous material.\textsuperscript{44–46} Nonetheless, significant gaps in our understanding of DH at interfaces persist, despite the fact that interfaces are omnipresent and often of crucial importance to the physicochemical properties and processes of materials. For example, ice nucleation in nature happens at interfaces rather than in the bulk.\textsuperscript{47–48} In addition, the dynamics of interfacial water is of increasing importance and interest for water flow through nanometric pores and membranes,\textsuperscript{49–51} as well as at the surface of proteins and large biomolecules.\textsuperscript{52–54} Thus, understanding how the presence of interfaces perturbs DH is of broad interest and here we seek to address the following key questions. Is DH in liquid water altered at interfaces and, if so, how does it vary from one interface to another? In addition, how is DH coupled with the structural changes that are inevitably present at the surfaces of liquids?

To answer these questions we have performed an extensive set of molecular dynamics simulations, using a classical intermolecular potential for free-standing and confined water films as well as water nano-droplets. All the systems considered here are in equilibrium at 0 atm and 250 K, which corresponds to a point in the phase diagram at which the supercooling is such that DH is clearly noticeable.\textsuperscript{5} We find that interfaces impact the qualitative nature of DH, changing it from a phenomenon that spatially averages out in time to one where the differences in terms of mobility persist over time and correlate with the distance from the interface. In addition, we find that the extent of the observed dynamical influence of the surface depends on how the interface is defined as well as on the nature of the interface.

## 2 Materials and Methods

The MD simulations performed in this work were done using the large-scale atomic/molecular massively parallel simulator (LAMMPS) code\textsuperscript{56} and the TIP4P/Ice model of water,\textsuperscript{57} which is especially well-suited to explore DH in supercooled liquid water given its ability to accurately reproduce the dynamical properties of even deeply supercooled liquid water.\textsuperscript{60} The melting temperature of bulk TIP4P/ICE is reported as 272 K\textsuperscript{59,61–64}; as we truncate and shift Lennard-Jones interactions at 8.5 Å (see below), recent work estimates a slight increase to approximately 275 K.\textsuperscript{65} For the droplets, we expect the freezing point to be depressed (see e.g., Ref. 66). As expected, we did not observe ice nucleation in any of our simulations.

The bulk simulation cells were first equilibrated in the NPT ensemble at 0 atm for 10 ns. We discarded the first 6 ns for equilibration and used the last 4 ns to compute the average volume and define the length of the cubic box used in all the subsequent NVT simulations. NVT trajectories run for a further 35 ns, with the first 5 ns discarded to properly equilibrate both structural and dynamical properties.

The rigidity constraint of molecules in the TIP4P/Ice model is imposed with the Rattle algorithm\textsuperscript{67} and long-range electrostatic interactions are computed by using the Particle-Particle-Particle-Mesh (PPPM) algorithm\textsuperscript{68} with non-electrostatic interactions are truncated and shifted at 8.5 Å; this setup ensures that the density in bulk simulations without interfaces (e.g., Fig. 1) is equivalent to the density found in the center of the planar slabs (e.g., Fig. 2b).\textsuperscript{4}

For a cubic box containing 3,072 molecules we find an equilibrium box length of 45.960 Å at 250 K and 0 atm. In order to check for possible finite size effects due to the box size, we tested different lateral lengths and aspect ratios, finding that the cubic box used is large enough to converge the bulk LD distribution (see Section S6 of the SI).\textsuperscript{5}

---

\textsuperscript{3}This statement neglects effects of Laplace pressure which are present in the droplets. For simplicity, we use a bulk reference of 0 atm throughout.
The equations of motion were integrated using a 2 fs time step and a 10-fold Nosé-Hoover chain with a relaxation time of 2 ps to control temperature (see Section S7 of the SI for an in depth analysis of the effect of the thermostat on DH). For all film calculations, initial configurations are prepared from the equilibrated bulk, by increasing the \( c \) lattice vector to add a vacuum region five time larger than the confinement length. In the slab geometry, the Yeh-Berkowitz slab correction was applied, as implemented in LAMMPS. Each slab has been further equilibrated for 35 ns. More information about the equilibration of the slabs can be found in the SI. For the free-standing slab, several thicknesses have been explored in this study: 4,020 (2 nm-thick), 5,994 (3 nm-thick) and 9,216 (5 nm-thick) molecules. The same procedure has been used to equilibrate a 10 nm-thick slab (18,432 atoms) interacting on one side with an hard LJ substrate. Indeed, the cell is long enough in the z-dimension so that the water condenses and forms both a water-substrate and a water-vacuum interface. Although the overall simulation cell is held at constant volume, the presence of the free water-vacuum interface acts as a natural barostat to the liquid. We choose to use a 9-3 LJ potential to mimic a smooth planar solid/water interface, inspired by the recent work of Brandenburg et al., where they showed how water at graphitic interfaces can be modelled effectively by combining classical water force fields with LJ parameters tuned to reproduce the desired oxygen-surface interaction. Using different LJ potential walls with varying adsorption strengths, they were able to demonstrate how modest changes in the adsorption energy lead to drastic changes in the wetting properties of the surface. Here, the standard 9-3 wall implemented in LAMMPS was used with \( \sigma = 3.37265 \) Å and \( \epsilon =0.1 \) and 0.7 eV, thus changing the hydrophilicity of the surface over a broad range. The LJ structured slab was built using the \texttt{diamond100} function of the ASE library by setting \texttt{size=(12,12,10)} and scaling the final coordinates to match the box size used for all the other planar systems at 250 K (i.e. lateral size of 45.96 Å). The atomic positions in the substrate are kept constant during the MD trajectory. Droplets were created from the bulk at equilibrium density (at 0 atm) adding a vacuum region five times larger than the droplet diameter and equilibrated for 1 ns. Three droplet sizes have been explored: 1,344 (3 nm), 6,213 (5 nm) and 49,608 (10 nm) atoms.

Finally, to aid the comparison, the dynamical profiles are normalized by the diameter of a water molecule (which we indicatively take to be 2.8 Å).

### 2.1 Characterisation of the local liquid dynamics

![Image of dynamical heterogeneity in bulk TIP4P/ICE water](image)

**Figure 1:** Dynamical heterogeneity in bulk TIP4P/ICE water. a) Snapshots of liquid water from an equilibrated NVT MD simulation at 250 K. Only oxygens are shown and colored according to the MM (red) and MI (blue) definition shown in panel b). Gray arrows represent the directions where Periodic Boundary Conditions (PBC) are applied. b) The bulk LD probability distribution at 250 K. Red and blue represent the top and bottom 5 percentiles, which define respectively MM and MI molecules.

To compute DH directly from atomistic simulations we used the so-called iso-configurational analysis (ISOCA). ISOCA is a computationally demanding technique that, given a snapshot drawn from an equilibrated trajectory, allows LD to be determined for each water molecule. LD represents the tendency of the molecule to move and is defined as \( LD_i = \frac{\langle |r_i(t_0) - r_i(0)| \rangle_{iso}}{t_0} \), where \( r_i(t) \) is the position vector of molecule \( i \) at time \( t \). The time of maximum heterogeneity, \( t_0 \), is a function of the temperature \( T \) (increases with decreasing \( T \)) and represents the time needed, starting from a specific time frame \( t = 0 \), to observe the most heterogeneous distribution of nearest-neighbor displacements. The workflow to characterize the liquid dynamics together with the values of \( t_0 \) for different supercoolings is reported in detail in Ref. Note that the value of 5% as the threshold for MM and MI molecules does not affect the results presented in this work, as shown in SI. In this work the ISOCA for the different systems is

---

10.1039/D2NR00387B
How do interfaces alter the dynamics of supercooled water? 10.1039/D2NR00387B

done using the $t_0$ estimated for the liquid bulk at the corresponding $T$; this ensures consistency in the treatment of the interfacial and bulk systems.

Figure 2: Dynamical heterogeneity at liquid/vapor interfaces for slab (left) and droplet (right) geometries at 250 K. a) Top panels: The average LD profile (median value) normalised by the diameter of a water molecule (2.8 Å) as a function of the distance from the centre for the different slabs (left) and droplets (right). Only for the 3 and 4 nm thick slabs does the dynamics away from the interface converge to the bulk value. Bottom panels: convergence of the average density profile as a function of the distance from the slab’s (left) and the droplet’s (right) centre. The structure converges to bulk values within 1 nm from the interface for all the systems but the 3 nm droplet. b) Snapshots of liquid water from an equilibrated NVT MD simulation at 250 K. On the left is a free-standing 5 nm-thick slab, while on the right is a 10 nm-droplet in vacuum. Only oxygens are shown and colored according to the MM and MI definition shown Fig. 1b. Gray arrows represent the directions where PBC are applied. One can notice that DH is heavily influenced by the presence of the interfaces.

The notation $\langle \ldots \rangle$$_{iso}$ indicates an ensemble average, i.e. we run many trajectories starting from the same initial configurations, but with different initial velocities and we eventually average the local displacements at time $t_0$ over the ensemble. Normalising the displacement of each molecule by the oxygen’s mean-square displacement (MSD) one would get a similar quantity, referred to as dynamical propensity (DP). We chose not to normalise by the MSD in order to get an estimate of LD comparable between systems types. Given the size of the boxes used in this work we carefully checked the minimum number of replicas needed in the ISOCA to converge the LD distribution in bulk. We found that at least 30 ISOCA runs are needed to obtain a converged LD (see Section S2 of the SI), with at least 10 independent starting frames necessary to converge the total LD distribution. All the results shown here were computed from 45 ISOCA. To obtain a smooth estimate of the LD($z$) profile improved statistics is needed, and at least about 30 independent frames are necessary. More information on the convergence of the LD statistics can be found in the SI. The value of $t_0$ varies as a function of the temperature and pressure. Following the procedure described in Ref. 28 we find that $t_0 = 53$ ps for TIP4P/Ice at 250 K and 0 atm.

2.2 Definition of the intrinsic frame of reference

To generate the intrinsic frame of reference we utilize the construction introduced in Ref. 72 and implemented in a Python-based tool to calculate instantaneous interfaces and concentration/orientation profiles from molecular simulation trajectories in slab geometry. The tool uses the Lewiner marching cubes algorithm and is partly an adaptation of the Willard-Chandler module of the Pytim code. The Willard-Chandler procedure consists of associating a continuous Gaussian density function with the discrete position of each water molecule in the system, thus obtaining a density
as the sum over all the Gaussian functions. For each system’s snapshot we define the instantaneous interface as the set of points on the density field whose value is equal to half the average equilibrium density of the bulk liquid at the corresponding pressure and temperature. To measure the liquid’s molecular properties as a function of the distance from the intrinsic interface we project the mean property of interest along the axis perpendicular to the instantaneous intrinsic surface.

3 Results

Figure 3: Effect of the interface definition on both structure and dynamics for TIP4P/Ice water supercooled at 250 K. a) Snapshot of a 5 nm-thick free-standing slab with the instantaneous intrinsic interface rendered as a green mesh and the standard interface depicted as a red dashed line. The slab is periodically replicated in the x and y directions. b) LD profile (median value, normalized by the diameter of a water molecule) as a function of the distance from the instantaneous WC interface plotted on top of the density profile. Dashed line represent the converged values at the slab’s centre. The green arrows qualitatively represent the distance at which both structure and the dynamics converge to bulk values. c) Difference between the structural and dynamical decays in proximity of the standard interface. Clearly, the dynamics appears to converge to bulk values differently from structure when using the intrinsic surface as reference.

We begin by reviewing briefly DH in bulk water. Fig. 1a shows a visual representation of DH in bulk TIP4P/Ice water at T=250 K and P=0 atm, taken from a molecular dynamics simulation in a 5 nm³ box. The TIP4P/ICE model is well-suited for this study as it reproduces the melting point of hexagonal ice (Ih)\textsuperscript{64}, as well as both the densities of water and ice and the coexistence curves\textsuperscript{59}. Following previous studies\textsuperscript{28,76,77}, we label each molecule as Most Immobile (MI) or Most Mobile (MM) when its local diffusivity (LD) respectively falls into the lower or higher 5% tail of the total LD probability distribution function of the bulk (Fig. 1b). As noted in the Methods section, LD is an explicit measure of the extent to which the dynamics of the liquid, over the time scale of structural relaxation\textsuperscript{78–80}, is determined by the initial configuration. Fig. 1a provides a vivid picture of DH in bulk water, which appears as distinct domains of relatively immobile (blue) and relatively mobile (red) water molecules. Dynamical domains, in bulk, average out in space over time, continuously growing, shrinking, and fluctuating in size and shape. The stronger the supercooling, the larger the size of the domains\textsuperscript{28}, and at the level of supercooling shown in Fig. 1a a single dynamical domain typically does not
exceed a few nanometers, which we take to be indicative of the dynamical correlation length in our system. This length scale should not be confused with the correlation lengths typically reported to quantify the cooperative motion of water molecules within DH clusters \cite{72,94,85,92,93}. Through a careful series of studies on systems in different sized simulation boxes, we established that in the temperature range 230–270 K, a cubic box with lateral size of 5 nm is sufficient to converge the average dynamical properties in the bulk \cite{72, S1, S3, S6}. Length scales corresponding to the size of the dynamical domains observed in bulk are, however, comparable to confinement lengths often observed in biological and technological systems ($\gtrsim$1–2 nm) \cite{92, 93, 94}.

In order to understand dynamical heterogeneity in supercooled interfacial water we performed a range of simulations on different types of interfaces. Specifically we considered free-standing slabs of thickness between 2 to 5 nm and spherical droplets of diameter between 3 to 10 nm. Confined water films were also considered and these are discussed further below. A summary of the key results obtained for water films and water nanodroplets is presented in Fig. 2. We find that, irrespective of whether we have a nanodroplet or a free-standing film, a clear dependence of DH on the very different in the interfacial systems (Fig. 2b) compared to the bulk (Fig. 1a). Fig. 2a also illustrates how the mean structured surface the mobility of the first layer drops toward zero, while at the structureless wall dynamical fluctuations going further, in an attempt to gain some initial understanding of the difference between a structureless wall and a interfacial water molecules can either be reduced or enhanced compared to the bulk (see e.g. Refs. 89, 95–98). Interestingly, we find that the dynamical response of water to the substrates is quite different to the structural response: variations in LD are much less pronounced whilst \cite{72, 92, 93}. However, what we learn from the current analysis is: (i) how the recovery of bulk dynamical properties depends precisely on the size of the water film or droplet; and (ii) that the spatial arrangement of the MM and MI domains is very different in the interfacial systems (Fig. 2b) compared to the bulk (Fig. 1a). Fig. 2a also illustrates how the mean density of the films and droplets varies as a function of $z$. By comparing the median dynamical (top panel) and mean structural (bottom panel) profiles it appears that structural and dynamical properties converge to bulk values (gray line) on different length scales \cite{72, S1}. However, this result depends on how the interface is defined.

In Fig. 2 the water/vapor interface was defined simply by the mean density profile within a Cartesian frame of reference. We refer to an interface such as this as the “standard” interface. An alternative and often more informative definition of the interface is the so-called “instantaneous” interface first introduced by Willard and Chandler \cite{92, 93}. The instantaneous surface can be used to set a dynamic frame of reference, performing a spatial transformation that defines the $z$-position of each water molecule relative to the local instantaneous surface rather than a fixed Cartesian plane. Fig. 3a shows a rendering of the 5 nm-thick slab and the corresponding standard (red) and intrinsic (green) interface. Panel b and c reveal how crucial the definition of the interface is: considering the standard interface as reference, the dynamics converges to bulk on a length scale that is twice that of structure. If instead, the intrinsic interface is used as reference, dynamical and structural fluctuations converge to bulk values on a much more similar length scale, with the liquid/vapor structural profile resembling that of the liquid/hydrophobic-substrate interface. This sensitivity of the density profile to the definition of the interface is similar to that reported in Ref. 94 and shows that the instantaneous surface of the liquid/vapor interface is a soft collective variable that fluctuates spatially. These fluctuations induce a macroscopic structure that is essentially indistinguishable from that of the liquid water interface adjacent to an extended non-polar hydrophobic substrate \cite{91}.

So far, we have looked at the dynamics of water in the proximity of flat or curved water-vacuum interfaces. We now discuss water films confined between solid surfaces and explore how the dynamics depends on the interaction strength of water with the interface as well as the structure of the solid substrate. To this end, we performed simulations of a 5 nm-thick film of water confined between either smooth structureless walls or confined between a structured wall. The key results of these simulations are reported in Fig. 4. Focusing on the structureless wall first, we find that: (i) there are strong density oscillations up to about 1.5 nm from the interface; and (ii) the strength of these oscillations grows with the interaction strength. Density oscillations such as these are well-known and have been observed many times before \cite{57, 58, 72, 75, 85, 88}. Interestingly, we find that the dynamical response of water to the substrates is quite different to the structural response: variations in LD are much less pronounced whilst at the same time extending to slightly larger distances from the surface. In particular, the layering clearly seen in the density is much less apparent in the DH. In addition, depending on the strength of the interaction, the mobility of the interfacial water molecules can either be reduced or enhanced compared to the bulk (cf. the 0.1 versus 0.7 eV data). Going further, in an attempt to gain some initial understanding of the difference between a structureless wall and a structured surface, we performed a simulation of water in contact with an ideal (100) surface of atoms. Interestingly, we find that (for the same 0.1 eV interaction strength) very different dynamical behaviour is observed: in the presence of a structured surface the mobility of the first layer drops toward zero, while at the structureless wall dynamical fluctuations are still larger on average than in bulk.
How do interfaces alter the dynamics of supercooled water?

To summarize our findings, we have seen that the presence of an interface has a profound effect on the liquid’s mobility. Our simulations of water confined between different types of interfaces suggest that there is a non-trivial link between average structural and dynamical inhomogeneities as a function of the distance from the interface. This is governed by the strength of the interaction between water molecules, as well as by the geometry and the nature of the confining substrate.

4 Conclusions

In this work, we have examined how dynamical properties of supercooled interfacial water differ from that of bulk water. We now proceed to discuss some of the implications of these findings with a particular emphasis on ice formation and vitrification of supercooled liquid water.

Recently, Fitzner et al. reported that in supercooled bulk water there is a strong preference for nucleation to occur in relatively immobile regions. The question as to where nucleation happens in interfacial water naturally arises. Indeed, Haji-Akbari and Debenedetti investigated this specific problem using the same TIP4P/Ice water model and a 5 nm free-standing film (in this study we have investigated the same system, see Fig. 2’s panels b and c). Through a highly computationally demanding set of enhanced sampling simulations, they found that nucleation starts in the interior of the water film, which is in line with our observation that MI domains are found almost exclusively in the interior of the film.

Let us now move beyond nucleation in pure water to heterogeneous systems, where a substrate or impurity in the liquid enhances the nucleation rate. Traditionally, enhancements in nucleation rates by substrates have been attributed to the structural (often templating) influence of the substrate on the liquid. Our findings provide an intriguing perspective, wherein the substrate alters the dynamics of the liquid in a manner that predisposes it to nucleation. We suggest that a bottom-up design of the interface could allow engineering the local dynamical properties in the liquid already at moderate supercooling. To be clear, we do not suggest that structural and thermodynamic properties are unimportant for heterogeneous nucleation. Rather, “dynamical heterogeneous nucleation” may provide a complementary framework by which to investigate heterogeneous nucleation. In a similar vain, it would be interesting to investigate the potential role that solutes have on nucleation via their influence in dynamical heterogeneity. Even though the mobility of the water phase enters the nucleation rate in the form of a kinetic prefactor, which is usually overshadowed by the exponential term, the role of mobility is bound to be more and more important as we approach stronger supercoolings, where the kinetic prefactor can sometimes even outweigh the exponential.
Dynamical effects of supercooled water at interfaces are not only of paramount importance to ice nucleation, but they are also critical to the vitrification of supercooled liquid water into amorphous ice. Vitrification represents one of the main approaches currently used to achieve the cryopreservation of biological material: cooling the aqueous phase down as quickly as possible helps to avoid the nucleation of potentially lethal ice crystals. A substantial body of work (see e.g. Ref. [107] for a review) has been devoted to investigating the structure and the dynamics of supercooled liquid water at the interface with some of these systems (perhaps most prominently trehalose [108,109]). However, knowledge of how cryoprotectants influence the dynamical heterogeneity of the surrounding liquid phase is lacking.

On the computational side, our results also show that when investigating dynamical properties at interfaces, defining the interface in the first place can be crucial, as different definitions of the dividing surface can lead to a misinterpretation of the subtle correlations emerging between structure and dynamics; this will be most important for soft interfaces, such as the liquid/vapor interface, or biological membranes in contact with aqueous solution.

Finally, we note that ISOCA is an extremely computationally demanding analysis technique, which limits severely the system sizes and time windows tractable, even when harnessing modern HPC facilities such as those listed in the Acknowledgements section. A great benefit for the field would come from a methodological speed up of DH analysis, e.g. by approximating the LD computation using machine learning to capture the local structure/local dynamics relationship. This would allow extracting LD for a water molecule directly from the position of surrounding molecules, thus reducing the computational cost by several orders of magnitude.

In conclusion, we have shown that the dynamics of supercooled interfacial water differs from that of the bulk and depends on the nature of the interface. Overall, rich and subtle variations have been observed, which offers great potential for tuning the dynamical response of water through variation of the interface structure or confining material.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

P.G., M.F., and A.M. were supported by the European Research Council (ERC) under the European Union’s Seventh Framework Program (FP/2007-2013)/ERC Grant Agreement 616121 (HeteroIce project). S.J.C is a Royal Society University Research Fellow (URF/R1/211144) at the University of Cambridge. Computational support for our work has come from the UKCP consortium (EP/F036884/1) and the UK Materials and Molecular Modelling Hub (EP/P020194/1 and EP/T022213/1).

References

[1] CA Jeffery and PH Austin. Homogeneous nucleation of supercooled water: Results from a new equation of state. Journal of Geophysical Research: Atmospheres, 102(D21):25269–25279, 1997.
[2] Jonas Sellberg, C Huang, T McQueen, N. Loh, Hartawan Laksmono, Daniel Schlesinger, R Sierra, Dennis Nordlund, C Hampton, Dmitri Starodub, D DePonte, Martin Beye, C Chen, Andrew Martin, A Barty, Kjartan Wikfeldt, T Weiss, C Caronna, Jan Feldkamp, and A Nilsson. Ultrafast x-ray probing of water structure below the homogeneous ice nucleation temperature. Nature, 510:381–384, 06 2014. doi:10.1038/nature13266.
[3] Hartawan Laksmono, Trevor A. McQueen, Jonas A. Sellberg, N. Duane Loh, Congcong Huang, Daniel Schlesinger, Raymond G. Sierra, Christina Y. Hampton, Dennis Nordlund, Martin Beye, Andrew V. Martin, Anton Barty, M. Marvin Seibert, Marc Messerschmidt, Garth J. Williams, Sébastien Boutet, Katrin Amann-Winkel, Thomas Loetting, Lars G. M. Petersson, Michael J. Bogan, and Anders Nilsson. Anomalous behavior of the homogeneous ice nucleation rate in “no-man’s land”. The Journal of Physical Chemistry Letters, 6(14): 2826–2832, 2015. doi:10.1021/acs.jpclett.5b01164.
[4] Kyung Hwan Kim, Alexander Späh, Harshad Pathak, Fivos Perakis, Daniel Mariedahl, Katrin Amann-Winkel, Jonas A. Sellberg, Jae Hyuk Lee, Sangsoo Kim, Jaehyun Park, Ki Hyun Nam, Tetsuo Katayama, and Anders Nilsson. Maxima in the thermodynamic response and correlation functions of deeply supercooled water. Science, 358(6370):1589–1593, 2017. doi:10.1126/science.aap8269.
[5] Daniel Gabriel Fahrenheit. Vi. experimenta & observationes de congelatione aquæ in vacuo factæ a dg fahrenheit, rs s. Philosophical Transactions of the Royal Society of London, 33(382):78–84, 1724.
[6] Paul F Valerio, Ming H Kao, and Garth L Fletcher. Fish skin: an effective barrier to ice crystal propagation. Journal of Experimental Biology, 164(1):135–151, 1992.
How do interfaces alter the dynamics of supercooled water?

10.1039/D2NR00387B

[7] Emily B Moore and Valeria Molinero. Structural transformation in supercooled water controls the crystallization rate of ice. *Nature*, 479(7374):506, 2011.

[8] Takeshi Kawasaki, Takeaki Araki, and Hajime Tanaka. Correlation between dynamic heterogeneity and medium-range order in two-dimensional glass-forming liquids. *Physical review letters*, 99(21):215701, 2007.

[9] Emilia La Nave and Francesco Sciortino. On static and dynamic heterogeneities in water. *The Journal of Physical Chemistry B*, 108(51):19663–19669, 2004.

[10] Philip H Handle and Francesco Sciortino. The adam–gibbs relation and the tip4p/2005 model of water. *Molecular physics*, 116(21-22):3366–3371, 2018.

[11] Mark D Ediger. Spatially heterogeneous dynamics in supercooled liquids. *Annual review of physical chemistry*, 51(1):99–128, 2000.

[12] Ludovic Berthier. Dynamic heterogeneity in amorphous materials. *arXiv preprint arXiv:1106.1739*, 2011.

[13] Hans Sillescu. Heterogeneity at the glass transition: a review. *Journal of Non-Crystalline Solids*, 243(2-3):81–108, 1999.

[14] Tadashi Muranaka and Yasuaki Hiwatari. β relaxation in a highly supercooled state via molecular dynamics simulation. *Physical Review E*, 51(4):R2735, 1995.

[15] Ryoichi Yamamoto and Akira Onuki. Dynamics of highly supercooled liquids: Heterogeneity, rheology, and diffusion. *Physical Review E*, 58(3):3515, 1998.

[16] Eric R Weeks, John C Crocker, Andrew C Levitt, Andrew Schofield, and David A Weitz. Three-dimensional direct imaging of structural relaxation near the colloidal glass transition. *Science*, 287(5453):627–631, 2000.

[17] Victor Teboul. Pressure dependence of dynamical heterogeneity in water. *Journal of Physics: Condensed Matter*, 20(24):244116, 2008.

[18] Victor Teboul, S Maabou, LC Fai, and André Monteil. A molecular dynamics investigation of dynamical heterogeneity in supercooled water. *The European Physical Journal B-Condensed Matter and Complex Systems*, 43(3):355–362, 2005.

[19] Sean Garrett-Roe, Fivos Perakis, Francesco Rao, and Peter Hamm. Three-dimensional infrared spectroscopy of isotope-substituted liquid water reveals heterogeneous dynamics. *The Journal of Physical Chemistry B*, 115(21):6976–6984, 2011.

[20] GG Malenkov, DL Tytik, and EA Zheligovskaya. Structural and dynamic heterogeneity of computer simulated water: ordinary, supercooled, stretched and compressed. *Journal of molecular liquids*, 106(2-3):179–198, 2003.

[21] GG Malenkov. Structural and dynamical heterogeneity of stable and metastable water. *Physica A: Statistical Mechanics and its Applications*, 314(1-4):477–484, 2002.

[22] Biman Jana and Biman Bagchi. Intermittent dynamics, stochastic resonance and dynamical heterogeneity in supercooled liquid water. *The Journal of Physical Chemistry B*, 113(8):2221–2224, 2009.

[23] Ch Alba-Simionesco, G Dosseh, E Dumont, B Frick, B Geil, D Morineau, Victor Teboul, and Y Xia. Confinement of molecular liquids: Consequences on thermodynamic, static and dynamical properties of benzene and toluene. *The European Physical Journal E*, 12(1):19–28, 2003.

[24] Victor Bapst, Thomas Keck, A Grabksa-Barwińska, Craig Donner, Ekin Dogus Cubuk, Samuel S Schoenholz, Annette Obika, Alexander WR Nelson, Trevor Back, Demis Hassabis, et al. Unveiling the predictive power of static structure in glassy systems. *Nature Physics*, 16(4):448–454, 2020.

[25] Rui Shi, John Russo, and Hajime Tanaka. Origin of the emergent fragile-to-strong transition in supercooled water. *Proceedings of the National Academy of Sciences*, 115(38):9444–9449, 2018.

[26] J Ariel Rodriguez Fris, Eric R Weeks, Francesco Sciortino, and Gustavo A Appignanesi. Spatiotemporal intermittency and localized dynamic fluctuations upon approaching the glass transition. *Physical Review E*, 97(6):060601, 2018.

[27] Abhinav Srivatsava, Smarajit Karmakar, and Ananya Debnath. Quantification of spatio-temporal scales of dynamical heterogeneity of water near lipid membranes above supercooling. *Soft Matter*, 2019.

[28] Martin Fitzner, Gabriele C Soso, Stephen J Cox, and Angelos Michaelides. Ice is born in low-mobility regions of supercooled liquid water. *Proceedings of the National Academy of Sciences*, 116(6):2009–2014, 2019.

[29] Nicolas Giovambattista, Marco G Mazza, Sergey V Buldyrev, Francis W Starr, and Eugene Stanley. Dynamic heterogeneities in supercooled water. *The Journal of Physical Chemistry B*, 108(21):6655–6662, 2004.
How do interfaces alter the dynamics of supercooled water?

10.1039/D2NR00387B

[30] Nicolas Giovambattista, Sergey V Buldyrev, H Eugene Stanley, and Francis W Starr. Clusters of mobile molecules in supercooled water. Physical Review E, 72(1):011202, 2005.

[31] Mark D Ediger. Perspective: Highly stable vapor-deposited glasses. The Journal of Chemical Physics, 147(21):210901, 2017.

[32] Ricardo Gutiérrez and Juan P Garrahan. Front propagation versus bulk relaxation in the annealing dynamics of a kinetically constrained model of ultrastable glasses. Journal of Statistical Mechanics: Theory and Experiment, 2016(7):074005, 2016.

[33] Sébastien Léonard and Peter Harrowell. Macroscopic facilitation of glassy relaxation kinetics: Ultrastable glass films with frontlike thermal response. The Journal of Chemical Physics, 133(24):244502, 2010.

[34] Sadanand Singh, Mark D Ediger, and Juan J De Pablo. Ultrastable glasses from in silico vapor deposition. Nature Materials, 12(2):139–144, 2013.

[35] Kenneth L Kearns, MD Ediger, Heiko Huth, and Christoph Schick. One micrometer length scale controls kinetic stability of low-energy glasses. The Journal of Physical Chemistry Letters, 1(1):388–392, 2010.

[36] Yue Zhang, Ethan C Glor, Mu Li, Tianyi Liu, Kareem Wahid, William Zhang, Robert A Riggelman, and Zahra Fakhraai. Long-range correlated dynamics in ultra-thin molecular glass films. The Journal of Chemical Physics, 145(11):114502, 2016.

[37] Simone Peter, Hendrik Meyer, and Jörg Baschnagel. Thickness-dependent reduction of the glass-transition temperature in thin polymer films with a free surface. Journal of Polymer Science Part B: Polymer Physics, 44(20):2951–2967, 2006.

[38] David T Limmer, Céline Merlet, Mathieu Salanne, David Chandler, Paul A Madden, René Van Roij, and Benjamin Rotenberg. Charge fluctuations in nanoscale capacitors. Physical Review Letters, 111(10):106102, 2013.

[39] David T Limmer, Adam P Willard, Paul Madden, and David Chandler. Hydration of metal surfaces can be dynamically heterogeneous and hydrophobic. Proceedings of the National Academy of Sciences, 110(11):4200–4205, 2013.

[40] Adam P Willard, David T Limmer, Paul A Madden, and David Chandler. Characterizing heterogeneous dynamics at hydrated electrode surfaces. The Journal of Chemical Physics, 138(18):184702, 2013.

[41] David T Limmer and Adam P Willard. Nanoscale heterogeneity at the aqueous electrolyte–electrode interface. Chemical Physics Letters, 620:144–150, 2015.

[42] Aoife C Fogarty and Damien Laage. Water dynamics in protein hydration shells: The molecular origins of the dynamical perturbation. The Journal of Physical Chemistry B, 118(28):7715–7729, 2014.

[43] Victor Teboul and Ariadni P Kerasidou. Specific properties of supercooled water in light of water anomalies. Molecular Simulation, 45(4-5):304–309, 2019.

[44] Gabriele C Sosso, Ji Chen, Stephen J Cox, Martin Fitzner, Philipp Pedevilla, Andrea Zen, and Angelos Michaelides. Crystal nucleation in liquids: Open questions and future challenges in molecular dynamics simulations. Chemical reviews, 116(12):7078–7116, 2016.

[45] James D Atkinson, Benjamin J Murray, Matthew T Woodhouse, Thomas F Whale, Kelly J Baustian, Kenneth S Carslaw, Steven Dobbie, Daniel O'Sullivan, and Tamsin L Malkin. The importance of feldspar for ice nucleation by mineral dust in mixed-phase clouds. Nature, 498(7454):355, 2013.

[46] L Canale, J Comtet, A Niguès, C Cohen, C Clanet, A Siria, and L Bocquet. Nanorheology of interfacial water during ice gliding. Physical Review X, 9(4):041025, 2019.

[47] E Charlaix and L Bocquet. Hydrodynamic slippage of water at surfaces. Soft Interfaces: Lecture Notes of the Les Houches Summer School: Volume 98, July 2012, 98:133, 2017.

[48] Hiroaki Yoshida, Vojtěch Kaiser, Benjamin Rotenberg, and Lydéric Bocquet. Driplons as localized and superfast ripples of water confined between graphene sheets. Nature communications, 9(1):1496, 2018.

[49] Laura Fumagalli, Ali Esfandiar, Rene Fabregas, Sheng Hu, Pablo Ares, Amritha Janardanan, Q Yang, Boya Radha, Takashi Taniguchi, K Watanabe, Gabriel Gomila, kostya Novoselov, and Andre Geim. Anomalously low dielectric constant of confined water. Science, 360(6395):1339–1342, 2018.

[50] Mehdi Neek-Amal, Francois M Peeters, Irina V Grigorieva, and Andre K Geim. Commensurability effects in viscosity of nanoconfined water. ACS nano, 10(3):3685–3692, 2016.
How do interfaces alter the dynamics of supercooled water?

[51] Kalon Gopinadhan, S Hu, A Esfandiar, M Lozada-Hidalgo, FC Wang, Q Yang, AV Tyurmina, A Keerthi, B Radha, and AK Geim. Complete steric exclusion of ions and proton transport through confined monolayer water. *Science*, 363(6423):145–148, 2019.

[52] K-G Zhou, KS Vasu, CT Cherian, M Neek-Amal, Jason Chentian Zhang, H Ghorbanfekr-Kalashami, K Huang, OP Marshall, VG Kravets, J Abraham, et al. Electrically controlled water permeation through graphene oxide membranes. *Nature*, 559(7713):236, 2018.

[53] JY Chong, B Wang, and K Li. Water transport through graphene oxide membranes: the roles of driving forces. *Chemical communications*, 54(20):2554–2557, 2018.

[54] Cecilia Herrero, Gabriele Tocci, Samy Merabia, and Laurent Joly. Fast increase of nanofluidic slip in supercooled water: the key role of dynamics. *Nanoscale*, 12:20396–20403, 2020. doi:10.1039/D0NR06399A. URL http://dx.doi.org/10.1039/D0NR06399A.

[55] Baofu Qiao, Felipe Jiménez-Angeles, Trung Dac Nguyen, and Monica Olvera de la Cruz. Water follows polar and nonpolar protein surface domains. *Proceedings of the National Academy of Sciences*, 116(39):19274–19281, 2019.

[56] HE Stanley, P Kumar, S Han, Marco G Mazza, K Stokely, SV Buldyrev, G Franzese, F Mallamace, and L Xu. Heterogeneities in confined water and protein hydration water. *Journal of Physics: Condensed Matter*, 21(50):504105, 2009.

[57] Puja Banerjee and Biman Bagchi. Dynamical control by water at a molecular level in protein dimer association and dissociation. *Proceedings of the National Academy of Sciences*, 117(5):2302–2308, 2020.

[58] Steve Plimpton, A Thompson, P Crozier, and A Kohlmeyer. Lammmps molecular dynamics simulator, 2011.

[59] JLF Abascal, E Sanz, R García Fernández, and C Vega. A potential model for the study of ices and amorphous water: Tip4p/ice. *The Journal of chemical physics*, 122(23):234511, 2005.

[60] C Vega and JLF Abascal. Relation between the melting temperature and the temperature of maximum density for the most common models of water. *The Journal of chemical physics*, 123(14):144504, 2005.

[61] C Vega, E Sanz, and JLF Abascal. The melting temperature of the most common models of water. *Journal of chemical physics*, 122(11):114507, 2005.

[62] José LF Abascal, Ramón García Fernández, Carlos Vega, and Marcelo A Carignano. The melting temperature of the six site potential model of water. *The Journal of chemical physics*, 125(16):166101, 2006.

[63] C Vega, JLF Abascal, and I Nezbeda. Vapor-liquid equilibria from the triple point up to the critical point for the new generation of tip4p-like models: Tip4p/ew, tip4p/2005, and tip4p/ice. *The Journal of chemical physics*, 125(3):034503, 2006.

[64] MM Conde, M Rovere, and P Gallo. High precision determination of the melting points of water tip4p2005 and water tip4p/ice models by the direct coexistence technique. *The Journal of chemical physics*, 147(24):244506, 2017.

[65] Dominic Atherton, Angelos Michaelides, and Stephen J Cox. Can molecular simulations reliably compare homogeneous and heterogeneous ice nucleation? *arXiv preprint arXiv:2201.06338*, 2022.

[66] Ding Pan, Li-Min Liu, Ben Slater, Angelos Michaelides, and Enge Wang. Melting the ice: on the relation between melting temperature and size for nanoscale ice crystals. *ACS nano*, 5(6):4562–4569, 2011.

[67] Hans C Andersen. Rattle: A “velocity” version of the shake algorithm for molecular dynamics calculations. *Journal of Computational Physics*, 52(1):24–34, 1983.

[68] Roger W Hockney and James W Eastwood. *Computer simulation using particles*. crc Press, 1988.

[69] In-Chul Yeh and Max L Berkowitz. Ewald summation for systems with slab geometry. *The Journal of chemical physics*, 111(7):3155–3162, 1999.

[70] Jan Gerit Brandenburg, Andrea Zen, Martin Fitzner, Benjamin Ramberger, Georg Kresse, Theodoros Tsatsoulis, Andreas Gruneis, Angelos Michaelides, and Dario Alfé. Physisorption of water on graphene: Subchemical accuracy from many-body electronic structure methods. *The journal of physical chemistry letters*, 10(3):358–368, 2019.

[71] Ask Hjorth Larsen, Jens Jørgen Mortensen, Jakob Blomqvist, Ivano E Castelli, Rune Christensen, Marcin Dulak, Jesper Friis, Michael N Groves, Bjørk Hammer, Cory Hargus, et al. The atomic simulation environment—a python library for working with atoms. *Journal of Physical Chemistry B*, 114(5):1954–1958, 2010.
How do interfaces alter the dynamics of supercooled water?

10.1039/D2NR00387B

[73] Willard-chandler instantaneous interface calculator. https://github.com/gitesei/willard-chandler

[74] Thomas Lewiner, Hélio Lopes, Antônio Wilson Vieira, and Geovan Tavares. Efficient implementation of marching cubes’ cases with topological guarantees. Journal of graphics tools, 8(2):1–15, 2003.

[75] Marcello Sega, György Hantal, Balázs Fábián, and Pál Jedlovszky. Pytim: A python package for the interfacial analysis of molecular simulations, 2018.

[76] Asaph Widmer-Cooper, Peter Harrowell, and H Fynnewever. How reproducible are dynamic heterogeneities in a supercooled liquid? Physical review letters, 93(13):135701, 2004.

[77] Asaph Widmer-Cooper and Peter Harrowell. On the relationship between structure and dynamics in a supercooled liquid. Journal of Physics: Condensed Matter, 17(49):S4025, 2005.

[78] Asaph Widmer-Cooper and Peter Harrowell. On the study of collective dynamics in supercooled liquids through the statistics of the isoconfigurational ensemble. The Journal of Chemical Physics, 126(15):154503, 2007.

[79] JA Rodríguez Fris, LM Alarcón, and GA Appignanesi. Do short-time fluctuations predict the long-time dynamic heterogeneity in a supercooled liquid? Physical Review E, 76(1):011502, 2007.

[80] Daekeon Kim, Daun Jeong, and YounJoon Jung. Dynamic propensity as an indicator of heterogeneity in room-temperature ionic liquids. Physical Chemistry Chemical Physics, 16(36):19712–19719, 2014.

[81] Lydéric Bocquet. Nanofluidics coming of age. Nature materials, 19(3):254–256, 2020.

[82] Antonio Scala, Francis W Starr, Emilia La Nave, Francesco Sciortino, and H Eugene Stanley. Configurational entropy and diffusivity of supercooled water. Nature, 406(6792):166–169, 2000.

[83] Francis W Starr, C Austen Angell, Emilia La Nave, Srikanth Sastry, Antonio Scala, Francesco Sciortino, and H Eugene Stanley. Recent results on the connection between thermodynamics and dynamics in supercooled water. Biophysical chemistry, 105(2-3):573–583, 2003.

[84] Nicolas Giovanbattista, Sergey V Buldyrev, Francis W Starr, and H Eugene Stanley. Connection between adam-gibbs theory and spatially heterogeneous dynamics. Physical review letters, 90(8):085506, 2003.

[85] Saumyak Mukherjee, Sayantan Mondal, and Biman Bagchi. Mechanism of solvent control of protein dynamics. Physical review letters, 122(5):058101, 2019.

[86] Philip Ball. Water as an active constituent in cell biology. Chemical Reviews, 108(1):74–108, 2008. doi:10.1021/cr068037a PMID: 18095715.

[87] Pu Liu, Edward Harder, and BJ Berne. Hydrogen-bond dynamics in the air- water interface. The Journal of chemical physics, 123(23):234505, 2005.

[88] Adam P Willard and David Chandler. The molecular structure of the interface between water and a hydrophobic substrate is liquid-vapor like. The Journal of chemical physics, 141(18):18C519, 2014.

[89] Olle Björneholm, Martin H. Hansen, Andrew Hodgson, Li-Min Liu, David T. Limmer, Angelos Michaelides, Philipp Pedevilla, Jan Rossmeisl, Huaze Shen, Gabriele Tocci, Eric Tyrode, Marie-Madeleine Walz, Josephina Werner, and Hendrik Bluhm. Water at interfaces. Chemical Reviews, 116(13):7698–7726, 2016. doi:10.1021/acs.chemrev.6b00045 PMID: 27232002.
How do interfaces alter the dynamics of supercooled water?

[96] Chyuan-Yih Lee, J Andrew McCammon, and PJ Rossky. The structure of liquid water at an extended hydrophobic surface. *The Journal of chemical physics*, 80(9):4448–4455, 1984.

[97] Adéle Poynor, Liang Hong, Ian K Robinson, Steve Granick, Zhan Zhang, and Paul A Fenter. How water meets a hydrophobic surface. *Physical review letters*, 97(26):266101, 2006.

[98] L Cheng, P Fenter, KL Nagy, ML Schlegel, and NC Sturchio. Molecular-scale density oscillations in water adjacent to a mica surface. *Physical review letters*, 87(15):156103, 2001.

[99] Amir Haji-Akbari and Pablo G Debenedetti. Computational investigation of surface freezing in a molecular model of water. *Proceedings of the National Academy of Sciences*, 114(13):3316–3321, 2017.

[100] Laura Lupi, Baron Peters, and Valeria Molinero. Pre-ordering of interfacial water in the pathway of heterogeneous ice nucleation does not lead to a two-step crystallization mechanism. *The Journal of chemical physics*, 145(21):211910, 2016.

[101] Laura Lupi and Valeria Molinero. Does hydrophilicity of carbon particles improve their ice nucleation ability? *The Journal of Physical Chemistry A*, 118(35):7330–7337, 2014.

[102] Martin Fitzner, Gabriele C Sosso, Stephen J Cox, and Angelos Michaelides. The many faces of heterogeneous ice nucleation: Interplay between surface morphology and hydrophobicity. *Journal of the American Chemical Society*, 137(42):13658–13669, 2015.

[103] Stephen J Cox, Shawn M Kathmann, Ben Slater, and Angelos Michaelides. Molecular simulations of heterogeneous ice nucleation. i. controlling ice nucleation through surface hydrophilicity. *The Journal of chemical physics*, 142(18):184704, 2015.

[104] Yuanfei Bi, Raffaela Cabriolu, and Tianshu Li. Heterogeneous ice nucleation controlled by the coupling of surface crystallinity and surface hydrophilicity. *The Journal of Physical Chemistry C*, 120(3):1507–1514, 2016.

[105] Michael Benedict Davies, Martin Fitzner, and Angelos Michaelides. Routes to cubic ice through heterogeneous nucleation. *Proceedings of the National Academy of Sciences*, 118(13), 2021.

[106] MD Ediger and Peter Harrowell. Perspective: Supercooled liquids and glasses. *The Journal of chemical physics*, 137(8):080901, 2012.

[107] Gloria D Elliott, Shangping Wang, and Barry J Fuller. Cryoprotectants: A review of the actions and applications of cryoprotective solutes that modulate cell recovery from ultra-low temperatures. *Cryobiology*, 76:74–91, 2017.

[108] A Magno and P Gallo. Understanding the mechanisms of bioprotection: a comparative study of aqueous solutions of trehalose and maltose upon supercooling. *The Journal of Physical Chemistry Letters*, 2(9):977–982, 2011.

[109] Eric Morssing Vilén and Corine Sandström. Nmr study on the interaction of trehalose with lactose and its effect on the hydrogen bond interaction in lactose. *Molecules*, 18(8):9735–9754, 2013.