Ice Film Morphologies and the Structure Zone Model

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Abstract. Ice, the solid phase of water, is ubiquitous. A knowledge of ice helps us to comprehend water, a simple molecule, but one with much complex behaviour. Our aim is to understand the morphologies and physics of thin icy films. To treat this complex system we have developed new experimental capabilities with an environmental scanning electron microscope (ESEM) capable of working with ice films, at the same time as new simulation approaches to understanding the physics of ice morphology. A comprehension of the physics of thin-film morphologies has applicability beyond ice to thin films of metals, ceramics, and other materials.

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INTRODUCTION

Water exists all around us, as vapour, liquid, and solid. Despite its ubiquity and importance, there remains much to be discovered about this simple molecule. The anomalous nature of water is manifest to anyone who has pondered why, unlike the great majority of substances, the solid floats on the liquid. Although there are myriad forms of the solid phase of water — ice — found on Earth, from snowflakes to icebergs, with very different bulk properties, at the molecular scale they are all composed of the same polymorph, hexagonal ice — ice Ih — which is the stable version at the temperatures and pressures in our biosphere. However, in the laboratory, beyond the range of natural terrestrial temperatures and pressures, ice crystallizes as many other polymorphs [1]. It also appears to have more than one amorphous state. At least two apparently quite distinct amorphous ices have been described: low density amorphous (LDA) and high density amorphous (HDA). These amorphous forms are glasses, and have been investigated intensively, being phases that help us to understand the structure on the molecular scale of liquid water [2, 3, 4].

There is considerable debate surrounding amorphous ice obtained in the laboratory. LDA and HDA have different densities and other physical properties, and the transition between them is reminiscent of a first-order phase transition. This has led to the suggestion that there may be two associated liquid phases, low density liquid (LDL) and high density liquid (HDL), together with a second critical point in the phase diagram of water. LDA and HDA, as structurally arrested versions of these two liquid phases, would then constitute genuinely distinct amorphous solid phases, or polyamorphs. This viewpoint is challenged by others who note that amorphous ices produced using different methods have somewhat different physical properties such as density and thermal conductivity. Do these differences simply reflect differences in bulk morphologies, while the underlying phase is either LDA or HDA, just as both snowflakes and icebergs are composed of ice Ih, or are LDA and HDA not really distinct polymorphs, but just the two extremes of a continuum of amorphous states?

On the other hand, the study of the thin-film deposition of materials such as ceramics and metals is an extremely active field. For some time it has been known that, independently of the material being deposited, similar deposition conditions lead to similar characteristic morphologies. A structure zone model has been developed, which predicts the bulk morphology depending on the film surface temperature and the gas pressure [5, 6]. The main experimental aim of this work has been to determine whether the morphologies characteristic of thin-film deposition of other materials are seen in ice deposited by ballistic deposition. Alongside our experimental work, we have investigated with computer simulations the dynamical basis of the structure zone model of thin-film deposition. With this we wish to gain insights into the physical basis of the different morphologies observed in thin-film deposition experiments and eventually to answer the question: How does the structure zone model arise from the basic physics of the deposition process? The applicability of these results is much more general than to ice alone, as understanding the structure zone model applies to metallic, ceramic, and other solid films.

Water has a complex phase diagram, due to hydrogen bonding and proton disorder effects. It exhibits an ex-
tensive range of crystalline solid phases, or polymorphs, most of which are stable only under high pressure. The physical properties of the polymorph, such as density, conductivity, vapour pressure and sublimation rate, are dictated by its crystalline structure. The phases can be distinguished from each other by the arrangement of water molecules in the crystal lattice, and by the degree of proton disorder within the network. In all crystalline ices, the water molecules have four-fold coordination, donating two hydrogen bonds, and accepting two others, even if the bonds are distorted. Thirteen ices are polymorphs are known at present: ices I to XIII (the phases are numbered with Roman numerals in the order they were discovered). Most phases are thermodynamically stable under some range of pressure–temperature conditions, with some phases also exhibiting metastable zones, and a few having no regions of absolute stability at all (ices Ie, IV, IX, and XII are only ever metastable).

If we disregard now the high-pressure polymorphs, and consider only those phases stable at normal atmospheric pressure and below, we find that hexagonal ice, Ih, that encountered on Earth, is the thermodynamically stable phase down to around 72 K. Below this temperature, ice XI is the thermodynamically stable phase, but in pure ice Ih the molecular relaxation rate is too slow for the transformation process to be observed, and ice Ih continues to be metastable. The phase change can however be mediated by doping the ice with OH\(^+\) ions, which are relatively mobile in the ice, even at 72 K. Ice Ic should be mentioned at this point. It is always metastable to ice Ih; there is the same relationship between ices Ic and Ih as between cubic and hexagonal close packing structures in metals. In vapour deposition experiments, ice Ih is formed above ~150 K, while ice Ic appears between ~130–150 K. Below ~130 K, the deposit produced is of amorphous ice.

Ice is one of the materials that has been hypothesized to possess more than one amorphous phase, a phenomenon termed amorphous polymorphism, or polymorphism [7]. LDA and HDA are seen as glassy versions of two proposed liquid phases, low density liquid (LDA) and high density liquid (HDL), which, in turn, are associated with a putative liquid–liquid phase transition in water [8]. A similar amorphous–amorphous transition has been reported in silicon [9], and associated with a liquid–liquid phase transition in that system [10]. While the coexistence of two liquid phases is well known for liquid crystals and multicomponent systems (e.g., protein solutions), it has only recently been described for pure isotropic substances. Apart from water, other liquids show signs of such a phase transition [11]; there is strong experimental evidence for the phenomenon in liquid phosphorus [12].

The high density amorphous ice HDA was first observed on compressing ice Ih at low temperature and high pressure (77 K, 1 GPa) [13]. Upon heating this material to around 120 K at atmospheric pressure (0.1 MPa), it transforms to a low density amorphous ice termed LDA [14]. At 135 K and 0.6 GPa, the transition can be reversed [15]. Large quantities of liquid water cannot be cooled into the glassy solid state of an amorphous ice, as crystallization always occurs first. Supercooled liquid droplets, however, can form amorphous solid particles when cooled rapidly (~10\(^5\) K s\(^{-1}\)) in a cold air or cryogenic liquid flow: this phase is referred to as hyperquenched glassy water (HGW) [16, 17]. This, after annealing at around 130 K, relaxes to a form that some consider to be LDA [2], while others see as essentially different [18]. On the other hand, rapid cooling of emulsified liquid water under pressure (~10\(^3\)–10\(^5\) K s\(^{-1}\); 0.5 GPa) produces HDA [19].

As well as production from the liquid or solid phases, amorphous ice is also obtained from condensation from the gas phase. In fact, amorphous ice was first found in vapour deposition experiments. In 1935 Burton & Oliver [20] announced that below about 163 K, the condensate in their experiments was no longer crystalline, but rather amorphous ice (their proposed transition temperature is rather high, and most investigators take 130 K as more typical). This ice was later termed amorphous solid water (ASW). Much later, it was shown that ASW differs when deposited at lower and higher temperatures. At low temperatures (below ~30 K), a higher density amorphous ice is formed, while at higher temperatures (~30–130 K) a low density amorphous ice is deposited [21, 22]. These ices are similar to the HDA and LDA produced in solid and liquid state transformations. As before, while some see essential differences, others propose that any variations arise from differing annealing times and microporosities [22].

Amorphous ice is also of interest to astronomers and astrochemists [23], as at the low temperatures of interstellar space, water adsorbing onto dust grains solidifies in an amorphous state [22]. This ice is built up by ballistic deposition; molecules stick directly where they land, without surface diffusion, owing to the very low temperature (3–90 K) of the interstellar medium. It has been estimated that most of the ice in the universe is to be found on these interstellar dust grains, which implies that the majority of the ice in existence is in this amorphous form.

For many years thin films of many different materials, both crystalline and amorphous, have been deposited from the vapour phase onto substrates. The field is driven by a huge number of technological applications, but also has much scientific interest. There are many deposition techniques: sputtering, chemical vapour deposition, molecular beam epitaxy, etc, based on three fundamental processes for vapour generation and subsequent deposition — temperature, bombardment, and chemistry.
One of the key differences between thin films and bulk materials is in their morphologies. The study of thin-film morphology has a long history. From the 1960s efforts have been made to construct a classification of the morphology of a film depending on its deposition conditions. This has culminated in a structure-zone model showing the morphology obtained for different film surface temperatures and gas pressures. This model has been progressively revised and updated, and there are now recognized to be at least five distinct zones with different morphologies: see Figure 1. From lower to higher substrate temperatures and ion energies: Zone 1 has a porous morphology consisting of tapered columns separated by voids, and from above looks like the surface of a cauliflower; Zone M has a matchstick morphology consisting of parallel columns with domed tops; Zone T is a transition morphology with no long-range structure beyond the nanometre level; Zone 2 has a columnar crystalline grain structure; and finally Zone 3 has a recrystallized crystalline grain structure. There is also recent mention of a spongelifke morphology between zones T and 2.

The two axes of the structure-zone model are the ratio of the substrate temperature to the melting point of the deposited material, and the specific energy of the arriving growth units (molecules, ions, atoms, etc). This latter variable is inversely related to the gas pressure used in sputtering deposition. The structure-zone model describes well the trends seen in experiments with many different materials. So far, however, there has not been a comprehensive explanation of the patterns seen in the model in terms of simple dynamical effects.

**EXPERIMENTS**

In our experiments we used a FEI Quanta 200 environmental scanning electron microscope (ESEM) equipped with a liquid helium cold stage to grow ice films in situ at low pressures and at temperatures of 6–220 K. We began by evacuating the chamber in the high-vacuum mode of the microscope and lowering the substrate to the working temperature. The microscope was set up so that the helium cold finger, together with a thermostat, was directly beneath the substrate on which we grew the ice film. We used several substrates; we did not detect differences in film morphology between them once the film coverage was complete over the surface. To grow an ice film we switched the microscope to low-vacuum mode, in which we could inject water vapor into the chamber for a given length of time and at a determined target pressure. We either used demineralized water alone, or else bubbled helium through the water prior to injection to provide an inert auxiliary gas in the chamber and to reduce the partial pressure of water vapour. The ice film was then deposited on top of the substrate, which was the coldest point within the microscope. We switched again to high-vacuum mode to image the results.

The region of lowest substrate temperature in the structure zone model is occupied by zone 1. Zone 1, or cauliflower morphology, consists of competing void-separated tapered columns whose diameters expand with the film depth according to a power-law. The surface resembles a cauliflower, showing self-similarity over a range of scales. We produced this morphology in the example in Fig. 2 using water vapor accompanied by helium as an auxiliary gas in the chamber. By depositing...
the ice film at the same substrate temperature as in Fig. 2, but this time at a higher water vapor pressure for a shorter time without an auxiliary gas, we obtained zone T, or transition morphology, in which there is no long-range structure above the nanoscale. In qualitative terms, the morphology of zone 1 is clearly driven by a competitive process of growth of clusters at all scales, leading to a fractal geometry, while greater gas-induced mobility of admolecules in zone T than in zone 1 smoothes out the surface. As they occur at the lowest temperatures, both zone 1 and zone T morphologies can be presumed to be composed of high-density amorphous ice. We noted when heating our samples that at close to 30 K the water vapor pressure in the chamber increased sharply, which we attribute to sublimation during the transition from high- to low-density amorphous ice. We did not however see any mesoscale structural change associated with this transformation at the molecular scale.

At substrate temperatures above those of the transition morphology of zone T, a spongelike morphology has been described for metallic films [25]. We were able to reproduce this morphology with an ice film, by injecting for a longer time than for zone T. This morphology is characterized by a three-dimensional open network of material like a sponge. On the other hand at substrate temperatures above those corresponding to cauliflower morphology (zone 1), and for relatively high gas-induced admolecule mobility there appears the final zone in the low-temperature region of the structure zone model: zone M, or matchstick morphology. In the example of this morphology we reproduce in Fig. 3 we see very large columns tens of micrometers in diameter resulting from ice deposition over several minutes using helium as an auxiliary gas. The columns display the domed tips characteristic of matchstick morphology, and also show interesting substructures both on the tip and along their length, presumably from their growth process; their shape is biomimetic, like an icy worm. The transition from zone 1 to zone M we can view qualita-

FIGURE 2. Zone 1, cauliflower morphology, film produced with water bubbled through with helium injected with a target pressure of 10 Pa for 6 s deposited on a titanium substrate at 6 K.

FIGURE 3. Zone M, matchstick morphology, film produced with water bubbled through with helium injected with a target pressure of 133 Pa for 6 minutes deposited on a platinum substrate at 6 K.

FIGURE 4. Film with a dendritic morphology resembling a palm tree produced with water injected with a target pressure of 10 Pa for 15 minutes deposited on a carbon substrate at 6 K.

tively in terms of competitive growth leading to a fractal morphology giving way to noncompetitive growth producing a columnar morphology. These large matchsticks may have been the morphology seen by Laufer et al. [26], who described an ice film grown at somewhere between 20–100 K as looking like “a shaggy woolen carpet”. With regard to the temperatures involved for zone M, it should typically be composed of low-density amorphous ice.
The propensity of hexagonal crystalline ice to form complex dendritic structures is familiar from examples such as snowflakes. This knowledge should forewarn us that the structures we should encounter in zones 2 and 3 of the structure zone model, at high substrate temperatures corresponding to the deposition of crystalline ice, would reflect this complexity. Nevertheless we were taken aback by the beauty of the structures we grew in these conditions, seen in Fig. 4. The hexagonal crystalline nature of this ice is reflected in the angles of growth of the branches, shown in Fig. 4(c). This fascinating morphology of branched whiskers is intermediate between whiskers and dendritic growth. One interesting open question regarding these higher temperature zones is how the amorphous to crystalline transition at the molecular scale relates to the transition from zones 1 and T to zones 2 and 3 on the mesoscale.

SIMULATIONS

In our model atoms are described as hard disks of radius \( a \) located by the positions of their centers. Disks are deposited onto a one-dimensional substrate with periodic lateral boundary conditions via ballistic deposition at a given mean rate \( R \). Ballistic trajectories are taken normal to the substrate, which is formed of a monolayer of fixed adatoms in a close-packed arrangement. Bonds between adatoms are limited to nearest neighbors. On making a first contact, either with the adatoms on the film surface or directly with the substrate, incoming particles are accommodated instantaneously to the closest available site on the microstructure. For this purpose, we developed a generalization of the schema presented by Savaloni and Shahrai [28]. In their model, fixed lattice positions are replaced by a set of relative positions, active positions, defined around each film particle, representing the possible locations of bonded neighbors, so lattice sites are delocalized with respect to the substrate and instead are localized around adatoms for first nearest neighbor positions. Savaloni and Shahrai proposed this approach to deal with a complex microstructure formed by a superposition of two elementary bidimensional cells corresponding to the simple square and hexagonal lattices. However, it can be used for arbitrarily simple or complex microstructures. We present results for four different microstructures corresponding to the simple square (sq) and the simple hexagonal (hex) lattices; the hexagonal-square microstructure (hex-sq) comprising the superposition of the previous ones; and the square-square microstructure (sq-sq) obtained by the superposition at 45° of two simple square microstructures with horizontal and oblique orientations respectively. The available sites for accommodating the incoming particles from their first contact position with the film surface are the unoccupied and non-shadowed active positions associated with the surrounding surface adatoms. After a new surface adatom is accommodated, bonds with its nearest neighbors are established and the corresponding new unoccupied active positions are created around it. Simultaneously with the deposition of new particles, surface adatoms are allowed to diffuse thermally to any of the close active positions that are neither occupied nor shadowed. Adatoms are considered as belonging to the surface when they are not “buried” by the presence of neighbors in the top active positions. In our simulations, diffusive hops to active positions are restricted to a neighborhood of size \( 2a \) around the original adatom position, except for the square microstructure. In this case, the low number of available active positions makes difficult the compacting of mesoscopic structures without allowing diffusive hops to second-nearest neighbors. Hence we allow “over-a-step” hops for this microstructure. Simulations were performed with the deposition of 15000 particles onto a flat substrate 160 adatoms wide disposed in a close packed arrangement.

By varying the main deposition parameters: the substrate temperature and the deposition rate, one can observe the development of distinct characteristic mesoscopic film morphologies. In general, an essential equivalence has been observed between deposition rates and substrate temperatures as the parameter. In Fig. 5 we
show different film structures obtained at distinct substrate temperatures for a fixed deposition rate of one monolayer per second. In all cases we found a minimum substrate temperature below which are obtained low-density dendritic structures with a self-affine surface typical of ballistic deposition with negligible surface diffusion. As the substrate temperature increases, or equivalently at lower deposition rates, surface diffusion becomes significant and dendritic morphologies give way to more compact fibrous structures with a preferential growth axis parallel to the deposition trajectories. With greater surface diffusion, the fibrous structures compact to densely packed grains that grow vertically as competing columns whose thickness increases with the diffusion. Finally, when column thickness equals the system size, the resultant films are formed by a single compact structure without interstitial voids. This behavior, which is qualitatively independent of the underlying microstructure, corresponds to the typical morphologies of zones 1 and 2 of the structure zone model [24]. Since no significant parameters for grain boundary evolution other than the underlying microstructure and the competition between deposition rates and surface diffusion are present in our model, it is not suitable for characterizing other structure zones in which effects such as activated diffusion by ion bombardment of the surface, bulk diffusion, or the presence of impurities are determinant [24].

CONCLUSIONS

It is clear that structure zone morphologies do appear in ice films. Can this knowledge contribute to understanding the physics of the structure zone model? We are moving towards a physical understanding of the structure zone model as a consequence of the competition between the spatially disordered deposition of particles on the growing film surface and the ordering effect of activated particle mobility processes. An intriguing aspect of this work is the finding that ice on its own can form biomimetic structures under extreme conditions. Knowledge of this phenomenon is important for astrobiologists searching for life in similar extreme conditions in space, and is a reminder that biomimetic forms are not in themselves evidence of life.

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