Review

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Surface phase transitions in ice: from fundamental interactions to applications

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Interfaces divide all phases of matter and yet in most practical settings it is tempting to ignore their energies and the associated implications. There are many reasons for this, not the least of which is the introduction of a new pair of canonically conjugate variables—interfacial energy and its counterpart the surface area. A key set of questions surrounding the treatment of multiphase flows concerns how and when we must account for such effects. I begin this discussion with an abbreviated review of the basic theory of lower-dimensional phase transitions and describe a range of situations in which the bulk behaviour of a two-phase (and in some cases two-component) system is dominated by surface effects. Then I discuss a number of settings in which the bulk and surface behaviour can interact on equal footing. These can include the dynamic and thermodynamic behaviour of floating sea ice, the freezing and drying of colloidal suspensions (such as soil) and the mechanisms of protoplanetesimal formation by inter-particle collisions in accretion discs.

This article is part of the theme issue ‘The physics and chemistry of ice: scaffolding across scales, from the viability of life to the formation of planets’.

1. Interfacial phase transitions

(a) Equilibrium phenomena

Intermolecular forces across surfaces shift the equilibrium states of matter from bulk coexistence, holding a wide range of consequences spanning natural science and technology [1–4]. For example, thin films of liquid

are stabilized against their subsaturated vapours by attractive interactions with their substrates [5], colloidal materials such as clays possess cohesion due to attractive interactions between the particles [2,6], and such forces can stabilize the liquid phase in the solid region of the bulk phase diagram [1]. This latter effect is referred to as *interfacial premelting*.

There are a host of effects that can shift the equilibrium domain of one phase into the bulk region of the phase adjacent to it on a normal pressure–temperature phase diagram. Often, despite their common origin in intermolecular forces, these are distinguished in terms of whether the phase boundary is convex, concave or planar. However, regardless of phase boundary geometry, the key issue is the introduction of a new canonically conjugate pair of variables—the surface free energy and the surface area. Thus, because the melting of virtually every solid originates at its boundaries, a unified picture emerges. Most familiar is the observation that a solid convex (concave) into its melt has a lower (higher) melting temperature than the bulk value. Whereas, for a planar geometry, depending on the basic material properties of the contacting medium, the shift in equilibrium stabilizing the liquid phase is called *surface melting* (at the vapour interface), *interfacial melting* (against a foreign substrate) or *grain boundary melting* (between crystallites of the same substance). Collectively, they are referred to as *premelting*. The phenomenon occurs in all classes of materials including molecular solids such as ice, wherein there are a host of astrophysical, geophysical and technological consequences [1,4].

The change begins at a temperature below the bulk melting point, as a molecularly thin liquid like film. The film thickness and its temperature dependence are extremely sensitive to the state of the surface, so that surface melting might be turned into a useful gauge for characterizing surface quality. The sensitivity has a special importance in the case of ice, because of the significant roles that ice plays in many environmental processes. Surface and interfacial melting of ice are involved in ozone chemistry, thunderstorm electrification, scavenging of impurities by snow, the sequestering of ancient atmospheres in ice cores, the flow of glaciers and low-temperature habitability [1,3,4,7]. As a consequence of its environmental importance the premelting of ice has been examined in many laboratory studies. There are a variety of mechanisms, involving intermolecular or electrostatic forces, that underlie premelting. However, the most commonly understood effect in the rubric of the wide range of researchers who study porous media is associated with interfacial curvature, discussed in the following paragraph. Within a tortuous medium (such as a soil) containing water, scientists have long known that capillarity underlies the distribution of liquid [8], whereas the underlying physics of this catch-all phrase involves a complex confluence of interfacial curvature and long-range intermolecular forces [9]. An emphasis of relevance to this meeting is the fact that a ‘sub-freezing’ water-filled porous media is a multiphase system with a rich fluid mechanics tied uniquely to interfacial thermodynamics [4].

Clearly, in a confined medium a solid–liquid phase boundary may be curved, in which case, as originally explained by William Thomson, the material will melt at a lower temperature than the bulk substance, due to the combination of surface curvature and surface energy [1]. This shift, now referred to as the Gibbs–Thomson Effect, has been studied with a variety of substances dispersed on inert substrates or confined in porous media. The simplest expression for this Gibbs–Thomson shift of the actual temperature T relative to the bulk melting temperature T_m is described for a system with a single interfacial free energy between the liquid and solid, γ_{sl} , that is independent of crystallographic orientation. If the interfacial curvature is given by $\mathcal{K}$ then

$$T_m - T = \frac{\kappa_v \gamma_{sl} T_m}{\rho_s q_m} \mathcal{K}, \quad (1.1)$$

which for the case of a sphere of radius r and curvature $\mathcal{K} = 2/r$ shows that the freezing point is depressed for solids convex into their melts ($\mathcal{K} > 0$). The solid density is ρ_s , the quantity q_m is latent heat per unit mass and the term κ_v arises from the pressure dependence of T_m ; if the system is in equilibrium with the vapour, $\kappa_v = 1 - (dP/dT)_{sv}/(dP/dT)_{sl}$ where the Clapeyron slopes are the values at the solid–vapour and solid–liquid phase boundaries. For ice and water near the

triple point κ_v differs from unity by only a few ppm [1]. Similarly, there is a shift in equilibrium vapour pressure over a curved surface.

Consider the planar surface ($\mathcal{K} = 0$) between a solid s (such as ice) and a chemically inert wall w (such as the surface of a porous medium or colloidal particle) at a given temperature T and pressure P . The shift of bulk phase coexistence is $\Delta\mu = \mu_s(T, P) - \mu_l(T, P) = \mu_{\mathcal{I}}(d)$, where $\mu_{\mathcal{I}}(d) < 0$ is the field energy/molecule in the film, leads to a reduction in the free energy of the solid/liquid/wall ($s/l/w$) system relative to the dry solid/wall (s/w) system. Thus the liquid phase intervenes to form a stable interfacial film of thickness d . The origin of the shift, $\mu_{\mathcal{I}}(d) < 0$, is the intermolecular attractions (polarization forces) between the layers in the system; the ice attracts the water with a greater force than it attracts the wall. In consequence the chemical potential μ_f of a thin liquid film in equilibrium with the solid is lower than that of the bulk liquid μ_l ; $\mu_f(T, P, d) = \mu_l(T, P) - |\mu_{\mathcal{I}}(d)| = \mu_s(T, P)$. Moreover, a variety of forms of disorder lower μ_f ; surface roughness, polycrystallinity, excess strain produced intrinsic or surface induced, dislocations, Frank–Read sources, impurities or kinetic effects, all further reduce the free energy of the liquid phase by an amount μ_D [10]. Depending on its history and exposure to impurities, all such forms of disorder can be present on a surface. Importantly, regardless of the history, we know that the sign of the effect of disorder is the same for all, and we can embody them as $\mu_D < 0$, and hence, separate from the role of impurities, the combined influence of intermolecular forces, preexisting and damage induced disorder is to reduce the chemical potential of the interfacial liquid as $\mu_f(T, P, d, \mathcal{D}) = \mu_l(T, P) - |\mu_{\mathcal{I}}(d)| - |\mu_D|$.

Expanding $\Delta\mu$ about a point at coexistence, T_m, P_m , in the absence of a damage effect, leads to an expression for the premelted film thickness in the form

$$d = \left[\frac{|\mathcal{A}_H|}{\rho_\ell(q_m/T_m)(T_m - T) + [(\rho_\ell - \rho_s)/\rho_s](P_m - P) - k_b T \mathcal{N}} \right]^{1/3}, \quad (1.2)$$

where ρ_ℓ is the density of the liquid, $\mathcal{N}$ is the concentration of molecular impurities and $\mathcal{A}_H$ is the Hamaker constant divided by 6π and is negative when the film is present. One can think of $\mathcal{A}_H$ as the lower-dimensional version of the strength of the pair potential in a volume–volume interaction, such as the van der Waals interaction, and thus it is the microscopic origin of cohesion as it can be calculated from the basic electrodynamics governing attractions/repulsions in materials [1,2]. One sees that as $T \rightarrow T_m^-$ the disorder and impurity effects intervene to further shift the onset of interfacial liquidity to values away from bulk coexistence, creating an arbitrarily thick film at a planar interface.

(i) Premelting in complex media

The equilibrium distribution of premelted liquid in complex media combines many of the effects just described. For example, as the temperature of a densely packed colloidal suspension or a saturated porous medium is lowered, the unfrozen phase depends on the impurity content, the particle packing and dielectric properties and the number of grain boundaries in the pores [11]. Both the geometry of the medium and the detailed nucleation processes may lead to a finely polycrystalline solid phase immediately after freezing, but it gradually develops into one or a small number of distinct crystals, driven by the tendency to reduce the grain boundary energy. Eventually, each pore will be filled with one or a small number of crystals separated from the pore wall by a dense film of the same substance, which acts as a thermodynamically distinct phase. The core itself is composed of a number of crystals and, at the junctions between adjacent pores, premelting occurs in the crystal grain boundaries as well as at the wall interface. As the temperature rises melting spreads to other orientations, and the remaining solid tends toward a free growth shape, ‘floating’ within,¹ and convex toward, its pure or impure melt phase. In this limit, the solid melts abruptly at a temperature T below the bulk transition T_m . The system specificity to such basic phenomena includes the dielectric properties of the host matrix, its

¹The term is put in quotes to emphasize it is not Archimedean buoyancy to which we refer. Rather, an analogous process of *thermodynamic buoyancy* is at play here [12].

geometry and the impurity loading. Hence, the overall liquidity and thermomolecular forces will influence the effective cohesion and large-scale properties of the system. Considerations along these lines may ultimately be used to create phase diagrams capable of classifying the complex phase behaviour in systems involving colloids or porous medium and ice [13].

This brief piece is intended to act as a written accompaniment to a lecture and as such in part summarizes my approach, and that of my colleagues, as has appeared in the literature; particularly relevant are reviews that cover various aspects of the matters discussed here [1–4]. It is, however, not intended to act as a systematic and complete review of the field, for which it will be found lacking by those seeking such and thus demanding a more thorough citation set of the literature.

2. Premelting dynamics and frost heave

(a) Premelting dynamics

A natural question is to understand how a local quantification of the existence of a layer of premelted liquid separating a foreign particle from ice (or some other material of interest) influences the collective dynamical behaviour of a porous media [4]. Consider then a single, impurity free, premelted interface between ice and a foreign wall, which may represent a foreign particle. In such a case $\mathcal{A}_H < 0$, so that the liquid film is attracted to the solid with a greater force than is the wall. From another perspective, we say that there is a repulsive disjoining force between the media—the ice and the wall—bounding the liquid film. The external pressure applied to the wall P_W is equal to that applied to the solid P_s , which balances the *thermomolecular pressure* $P_T = -\mathcal{A}_H d^3$, written here for non-retarded van der Waals forces, and the hydrodynamic pressure P_ℓ , giving

$$P_W = P_s = P_T + P_\ell. \quad (2.1)$$

The essentials of premelting dynamics are demonstrated through this force balance. Having fixed the pressure in the solid P_s , we envisage imposing a temperature gradient parallel to the ice–wall interface. At higher temperatures, the film thickness *increases* and hence the thermomolecular pressure P_T *decreases*. Therefore, the hydrodynamic pressure P_ℓ *increases with temperature* thereby driving interfacially premelted liquid from high to low temperatures. Any liquid in excess of the equilibrium value freezes.

We can further simplify the arguments as follows. The Gibbs–Duhem relationship can be applied on each side of a solid–melt interface to show in general that when the system is in equilibrium at temperature T then

$$P_s - P_\ell = \frac{\rho_s q_m (T_m - T)}{T_m}. \quad (2.2)$$

Finally, if we ignore the pressure effects of melting (see discussion following eqn (3.4) of Wettlaufer & Worster [4]), which are included in equation (1.2), this is equivalent to letting $\rho_s = \rho_\ell \equiv \rho$. Hence, combining equations (2.1) and (2.2) and using the form of the disjoining pressure above provides a simplified form of the equilibrium thickness of the liquid film as

$$d = \lambda \left(\frac{T_m - T}{T_m} \right)^{-1/3}, \quad (2.3)$$

where $\lambda^3 = -\mathcal{A}_H / \rho q_m$. Equation (2.3) shows that for $\mathcal{A}_H < 0$ a premelted liquid film exists at temperatures below the bulk melting point and its thickness grows with temperature. This description of interfacial premelting is that which has received detailed experimental confirmation for many different materials [1]. Now we explore some of the multiphase fluid mechanical phenomena associated with premelting dynamics.

(i) Confinement effects

Generally, liquids confined between solids of other materials behave differently than their bulk counterparts. For example, as a confined liquid approaches a thickness of some number of molecular layers, the bulk melting and freezing transitions vanish and molecular mobilities take values intermediately between those found in bulk solid or bulk liquid [14–16]. Molecular hydrodynamics show a layering normal to walls that depends on the nature of the wall–fluid interactions, but the rheology is complex, ranging from shear thinning to shear thickening, so that new dynamical behaviour emerges when a liquid is confined in a narrow gap [17].

The consequences for premelting dynamics thus depend on temperature, and have only recently been examined quantitatively [18]. It is found that as the temperature is reduced the concept of a bulk liquid will break down at thicknesses greater than a molecular scale, with the nature of the breakdown depending on the material under consideration. Indeed, as the film thins, the ordering imposed on the liquid by the solid may eventually span the interfacially melted gap, imprinting properties that are intermediate between a liquid and a solid. For example, at the bulk ice–water interface, the density and diffusivity transition from the bulk solid to the bulk liquid over tens of angstroms, depending on crystallographic orientation and the degree of disequilibrium (e.g. [19–21] and references therein). Hence, by treating the increase in viscosity associated with the thinning of films it was possible to study a range of interactions that are known to underlie interfacial premelting and examine the difference between the cases with and without the confinement effect. The increase in the viscosity as the film thickness decreases has serious implications for experiment and the intuition for how flows at even very low temperatures can persist. In particular, this should be relevant during premelted flow within rocks and their breakdown (e.g. [22,23]).

(b) Ice segregation and frost heave

Over the last 40 years, there has been much experimental research aiming to elucidate the mechanisms at work in the ice segregation process. The most well-known configuration leads to the beautifully regular ice lens formations that were seen in the early experiments of Taber shown in figure 1a [24,26]. For a given geometry of the medium, the equilibrium effects are, suitably non-dimensionalized, the same for rare gas solids and other materials as they are for ice. This ensures that the study of freezing colloids has a generality that has not been appreciated until relatively recently [1,28] and it speaks to the relevance of taking a basic approach to the problem.

Depending on the nature and packing of the particles, ice can segregate in a range of morphologies [25,27,29,30] as shown in the experimental images of figure 2. The observation of the formation of lenses perpendicular to the temperature gradient as shown in figure 1 has inspired several theories that aim to explain how this pattern formation occurs (e.g. [31–34]). While we understand much of the physics of lens growth, a fundamental conundrum is the mechanism of lens formation. Experiments using Raman Spectroscopy in porous media of Vycor glass particles with a mean diameter of $9.7\text{ }\mu\text{m}$ probed the high-temperature region (but still at $T < T_m$) ahead of the warmest ice lens and found no evidence of pore ice that would characterize a ‘frozen fringe’ [35], which is a region of partially frozen porous media on the warm side of the warmest lens. These experiments showed the formation of discrete ice lenses without partial freezing of the material ahead of the warmest ice lens and thus suggest that, while the premelting dynamics described above is essential for lens growth, an alternative mechanism must be at work in forming ice lenses in these cases. In addition, it remains an outstanding question to determine precisely what controls the variety of patterns shown in figure 2 [13].

Another approach, motivated by the experiments finding lens formation in the absence of a frozen fringe [35], treats the growth of an ice-filled crack in a freezing porous medium [36]. The idea here is that as the temperature decreases, the ice in the crack exerts large pressures on the crack walls that eventually drive the opening of the crack and subsequent propagation across the sample to form a new lens. In this theory, there are two controlling factors: the cohesion of the

Figure 1. (a) Ice lens formation in a freezing clay (kaolinite) [24], (b) the formation of argon lenses (shown as the clear regions denoted with the vertical, white, two-headed arrow ≈ 0.5 mm) in colloidal silica, (c) a close up of the interface between a lens and the particles [25]. The time sequence (in minutes) is labelled in the argon experiment. The temperature gradient is vertical and perpendicular to the lenses in both experiments. Thus, frost heave is not associated with the expansion of the solid upon solidification but rather the transport of interfacially premelted liquid as described below. (Online version in colour.)

Figure 2. Segregated ice (dark regions) formed during the unidirectional solidification of a bentonite colloid. Depending on the particle concentration and freezing rate, the ice completely rejects the particles (a), forms aligned dendrites (b) or more exotic patterns such as polygons (c) [27]. (Online version in colour.)

medium and the so-called *geometrical supercooling* of the water in the medium. The new concept of *geometrical supercooling* was introduced to measure the energy available to form a new ice lens, but awaits quantitative experimental tests. The idea is that when the critical supercooling exceeds a value proportional to the cohesive strength of the medium, a new ice lens forms. This theory predicts periodic ice lens formation with or without the presence of a frozen fringe.

(c) Some open questions on lens dynamics

(1) A number of frost heave models reproduce the discrete lensing characteristics observed in experiments, but there are several issues that impede progress and generalization. These come in two classes. First, some models parameterize phenomena using assumptions that are either

unjustifiable from fundamental physical principles or cannot be examined to unambiguously test constitutive arguments. Second, all models must make assumptions regarding the existence of the frozen fringe, whereby the system is assumed to be partially frozen in front of the warmest ice lens. The nature of the frozen fringe is basic to the mechanisms of lens formation. Although two different types of models that we have developed predict multiple lens formation [34,36], they do so in rather different manners. We understand that, while the premelting dynamics described above is essential for lens growth, we do not understand which mechanism must be at work in forming ice lenses in cases where no frozen fringe exists. Hence, because existing theories, whatever their particular set of assumptions [31–34], predict new ice lenses will grow within the frozen fringe, experimental tests require fine probes under well-controlled growth conditions. A promising direction is to combine macroscopic measurements that can be used with models to infer interfacial premelting [37] with direct microscopic probes such as X-ray scattering [38,39].

(2) Models of frost heaving commonly neglect cohesion between the soil/colloidal particles [40]. Although the underlying forces have an origin that is model-dependent, clearly, a new ice lens will form when the interparticle force becomes negative. However, the corpus of forces in a partially frozen suspension that lead to such a condition can involve both long ranged electrostatic and dispersion forces between the constituents of the colloid/water/ice system, the relative strengths of which are sensitive to impurity concentration [11]. Thus, while we have an equilibrium theoretical framework to understand the microscopic basis of the effective (homogenized over a control volume of the constituents of the system) cohesion to use in a continuum description, it remains a challenge to translate these to a disequilibrium setting. Because the cohesion manifests itself in the existence of a non-zero yield stress, quantifying this should play an important role in determining the inter-lens spacing.

(3) Most models of ice lens formation are one-dimensional in nature. This means that ice lenses are assumed to appear across a layer of freezing colloidal suspension, and the problem of how ice lenses nucleate and propagate across the layer is left untreated. Although experiments appear to indicate that ice-lens formation may be ‘crack-like’ in nature, the process is rapid. Thus, the propagation of a new ice lens across a section of a freezing cell resembles both a propagating fracture and a one-dimensional nucleation process. We cannot yet distinguish between the two.

3. Climate proxies

The Earth’s past climate is recorded at the finest temporal resolution in the deep ice cores of both polar regions and *interfacial* and *grain boundary* premelting [41–43] plays an important role in the state of the climate signal [44–46]. This is due to the fact that meteoric ice (snow fall that accumulates to form the ice sheets) is by definition polycrystalline. Hence, at the boundaries between individual crystals (where two grains abut or at the veins and nodes where three and four grains come together, respectively) soluble impurities segregate providing high-resolution, long-term archives of climate proxies (e.g. an atmospheric trace-constituent). Major efforts by international teams (e.g. [47]) remove kilometre scale ice cores to analyse for their record of the state of past climates. However, the ice is an effective medium, which has two phases and multiple components, and it cannot be read directly unless a climate proxy stays ‘fixed’ to the ice with which it was deposited. For example, impurities that are detected in the vein network are dissolved in the liquid if the *in situ* temperature is above the eutectic temperature of their aqueous solution; the eutectic temperature of NaCl in water is roughly 252 K and that of H₂SO₄ solutions is 200 K [46]. Moreover, these proxies are transported from the surface of the ice sheet with the flowing (under the weight of subsequent annual layers) and deforming polycrystalline ice, which further warms at depth due to the geothermal heat flux. Hence, the vertical variations in the measured chemical and particle profiles reflect the temporal variations in their deposition that were caused by (a) changing climate conditions and (b) post-depositional processes that may lead to the separation of a climate proxy from the ice it was deposited with. Therefore, to accurately interpret these valuable and difficult to obtain records of past climate, care must be

Figure 3. The evolution of periodic bulk concentration (averaged over the liquid and solid phases)-profiles reproduced from [46]. These soluble species were deposited asynchronously on the surface of an ice sheet; the initial profiles are the dot-dashed lines marked '0'. The c_{B1} -profiles, shown in black online, have much lower concentrations than the c_{B2} -profile, shown in red online (note the different vertical scales). When the vertical axes are measured in units of micromoles per litre, the amplitudes of the c_{B1} and c_{B2} fluctuations are comparable to those of the methane sulfonate and sodium fluctuations observed in the Doleman Island ice core [50]. The horizontal axis represents the distance along the core, measured in terms of the period of the anomaly cycle, which can be thought of as the annual layer thickness (typically tens of centimetres). The dashed lines show the profiles at the subsequent times, labelled on the c_{B1} -profiles in terms of the diffusion timescale, as described in the text. The solid lines show that the low-amplitude c_{B1} -profile is in phase with the c_{B2} -profile after a dimensionless time of 0.1, which corresponds to just 1 year after diffusive transport began. Clearly, the c_{B2} -profile is not significantly altered. (Online version in colour.)

taken to account for processes that may have altered their spatial distribution during their long (approx. 10^5 – 10^6 years) residence times in the ice sheets.

Post-depositional processes begin in the uppermost 50–150 m of the ice sheet, before the snow densifies to become polycrystalline ice, taking the form of transport through the vapour phase network between the ice grains. This network provides the conduits for rapid gas diffusion, which leads to an age offset between the ice and the past atmospheric trace gases extracted from bubbles and clathrate crystals in the retrieved ice core. As the ice compacts and deforms this network becomes a premelted fluid as described above, enriched in soluble species. This premelted liquid is a key fluid reservoir that can facilitate interactions between trace constituents and 'short' the substantially slower solid-state diffusion through the ice crystals themselves. Moreover, because a liquidus controlling species will control the volume fraction of liquid, this species may determine the evolution of a secondary species [46]. This is because gradients in concentration of the liquidus controlling species drive gradients in the porosity and hence effective diffusivity of a polycrystal. A quantitative example is shown in figure 3 wherein the fate of a minor species is controlled by that which dominates the volume fraction of unfrozen liquid. Finally, a central 'paleothermometer' is the ratio of the heavy to light isotopes of oxygen and hydrogen, which are fractionated during precipitation [48]. Although the process is somewhat more complex than in the case of soluble species, premelted liquid also drives post depositional redistribution of this crucial climate proxy [49].

(a) Some open questions on the redistribution of proxies

(1) We have a basic understanding and experimental proof [43] of the confluence of processes that control premelting at the interfaces between ice crystals. However, there are a wide range of processes in the natural environment that need to be modelled in laboratory models in order to understand observations. The complex history dependence of diffusive processes insures

that observations of ice cores alone will not provide demonstrable evidence for which physico-chemical process controls the signal at a given place in the ice core. However, there are leading-order processes that provide a clear picture of proxy redistribution (e.g. [47]). Nonetheless, as scientists and society focus attention on rapid variations and short-term phenomena, the demand for evidence in the ice core record will increase, and this will require renewed efforts in quantifying the mechanisms discussed here, which often take place on length (and hence time) scales that are short relative to the typical core section analysed.

(2) Soluble species in relatively low concentrations can diffuse within the premelted liquid network as independent species. However, chemical reactions within the liquid pose a range of additional challenges that are geophysically and chemically interesting. As the liquid is a potential reservoir for nutrients, there are a host of biological questions of relevance to questions of both ancient life on Earth and that elsewhere [3]. Climatologically relevant events, such as volcanic eruptions, lead to particle transport and deposition on ice sheets. Hence, this suggests a range of interesting questions regarding quantitative predictions of how premelting dynamics displaces particles in temperature gradients [4,12].

(3) The form of anomalous diffusion that involves spatial variations in porosity is a fundamental consequence of the phase behaviour of any material. Hence, because ice is transparent, birefringent and relatively simple to hold near its melting point [51], it can act as a model system for the same class of problems as they occur in other, optically opaque or high/low melting temperature, materials. Because annealing of bulk polycrystalline samples is a key mechanism in materials processing, polycrystalline ice offers a unique opportunity as an analogue material.

4. Cosmogony and collisional fusion

Studies of the mechanisms of the origin of the solar system and the formation of planets generally centre around considerations based on the scenario in which there is an initial collapse of interstellar gas that nucleates the central protostar, after which the planets form. Within the framework of this ‘standard model’, the planets are argued to form by one of two general processes over time scales of several million years. The first focuses on building planetesimals from grain–grain accretion and the second proposes gravitational collapse of the disc—treated as either a one- or two-component (solid and gas) fluid—on length scales much larger than grain scale processes [52]. There is a competing model that argues for a concurrent collapse of both the star and the planets [53]. In all models, understanding the mechanism of particle–particle agglomeration is important and recently such a mechanism, which involves extensions of the theory of premelting, has been developed [10] and is outlined presently.

The aggregation of snow or dust on a floor is facilitated by weak interparticle collisional speeds and attractive forces such as van der Waals interactions. The crucial difference between snow and dust is the role of phase change. Snow crystals will fuse together (sinter) and then densify through annealing or coarsening driven by the tendency to reduce surface energy [54]. These processes are driven by either surface or volume diffusion or the transport of mobile surface films [1]. Indeed, they underlie the fact snow drifts soon form a crust on their surfaces or that one can form a solid metal object beginning with a metal powder [55]. Therefore, the agglomeration and densification of matter is facilitated by time and very low collisional speeds where weak attractive interactions dominate. When we gently toss a snowball against the wall it will bounce, falling to the floor and shattering. However, at higher speeds a non-trivial fraction of the snow will stick to the wall. The theory of collisional fusion considers the situation in which the wall is made of ice, and an ice ball is thrown at it some tens of ms^{-1} . Upon contact, the interfacial pressure rises dramatically and some fraction of the collisional energy acts to momentarily liquify a thin region shared by the two surfaces. In a solar nebula, the ambient temperatures are sufficiently low that any liquid will rapidly freeze thereby fusing the particles so long as their stored elasticity is not so large that rebound occurs first. The scenario is as follows: (a) At low collisional speeds there is fusion by surface forces and annealing of molecules and small particles. (b) At higher speeds stored

Figure 4. Drifting particle growth rates are calculated using the theory of collisional fusion outlined above and described in more detail in [10]. In (a), a 1 m sized drifting planetesimal seed begins its inspiral towards the central star at $R_o = 3.5$ AU, where $T = 150$ K, and grows by collisional fusion sufficiently fast that it settles into a stationary Keplerian orbit as shown in (b). The range of growth rates is determined by the range of collisional fusion rates with midplane particles of centimetre size with a concentration controlled by turbulence. Results for two different turbulent diffusivities are shown; $\alpha = 10^{-6}$ (light) and 10^{-4} (dark). In (b), the associated decrease in orbital distance $\Delta R(t)$ due to collisional fusion and growth is shown for the drifters in (a). The essential point is that drifters grow rapidly enough that they are not lost to the central star and thus remain to grow by gravitational attraction or other means. (Online version in colour.)

elasticity overcomes weak surface forces and particles bounce. (c) At even higher speeds, the interfacial liquid created by the collision refreezes before rebound and there is fusion. (d) Further increases in collisional speed rebound too quickly for freezing. This basic process is not specific to ice, but ice is particularly relevant astrophysically and terrestrially. The process of high-speed collisional fusion depends on the phase diagram of the material and the thermodynamic and mechanical conditions of a collision.

For ice the process is shown quantitatively in figure 4 and the results do not change significantly regardless of whether the particles that the drifter collides with in the midplane are 1 mm or 10 cm in size (shown here) or whether the drifter is 1 m (shown here) or 100 m when it begins its journey. It appears that this mechanism provides a firm basis for the previously assumed aspects of efficient sticking.

(a) Some open questions on collisional fusion

(1) Clearly, as the collisional speeds approach the maximum shear strength of the material it will shatter. The state of a body (dislocation density, polycrystallinity, impurity concentration, etc.) will act as a major control on the maximum shear strength and in a setting such as the natural environment or in a solar nebula such information is unavailable. However, controlled

laboratory experiments can provide important clues from which statistical mechanical studies of net collisional fusion efficiency can be gleaned. For example, one can prepare samples with varying crystal sizes and perform collisions under otherwise identical conditions.

(2) The mechanism of energy loss during a collision is essential for understanding the fraction of the collisional energy stored elastically and hence available for rebound. For example, it was known empirically that the Hertz theory of elastic collisions makes predictions that are quantitatively accurate at up to 40% inelastic loss and yet the origin of this has only been recently understood [56]. Recently, we have combined our theory of viscous loss during collisions [56] with phase change processes to further refine the regimes of collisional fusion. However, there is a compelling and challenging free boundary problem involving the collisionally created squeeze-film and solidification with a moving contact line (e.g. as in [57]) that must be solved for a complete understanding of the process.

(3) The objects of interest in planet formation are ‘protoplanets’ and they move within the nebular gas. That gas hosts a distribution of particle sizes with which the incipient protoplanets collide. Because the mean-free-path of the gas depends on the distance from the central star, the degree to which a fraction of the particle size distribution couples to the gas is in the realm of theory or modelling. In the limit in which the small particles, which provide the growth material for the protoplanets, do not couple back to the gas, we have performed direct numerical simulations of the accretion of a two-dimensional protoplanet seed in a turbulent accretion disc [58]. Besides the obvious issue of dimensionality, a range of interesting questions remain such as how anisotropic accretion leads to protoplanet seed tumbling, how a particle size distribution couples to the gas and how these impact the fate of the protoplanet.

5. Other applications and implications

(a) Colloid and interface science

Colloidal particles (10^{-2} – $10\ \mu\text{m}$) are used extensively in physics as model systems to study molecular processes [59], and colloids are present in many natural and man-made systems such as rivers and soils, paints, milk and ink [60]. In aqueous colloidal systems cooled to subfreezing temperatures, the ice phase undergoes a morphological instability that organizes the particles into dynamic, nonlinear patterns [1,28]. The multiphase behaviour is rich and is central to a wide variety of technological and natural systems including fabrication of biomimetic composite materials [28], self-healing hazardous waste barriers [61], ice-enhanced water purification systems [62], sea ice [63], glaciers [64] and permafrost [1].

Recently, the underlying physical processes associated with freezing colloids have been partially elucidated, contributing to explosive growth in technological applications [28,60]. Fundamental questions remain, associated with microscopic surface physics to the effective medium properties of the matrix, be it a soil, biological tissue or ceramic nanosuspension [1,2,28]. For example, one of the simplest questions that one might consider asking—where do colloidal particles end up when the solvent freezes—require challenging bright X-ray scattering experiments [38,39]. Owing to the complexity of these systems, advances will come from a multidisciplinary approach using experimental and theoretical studies, continuum models of freezing colloidal suspensions and frost heave using testable local physics and mathematical models. Progress will provide knowledge of a fundamental nature for large-scale science and engineering applications such as described below.

(b) ‘Massive-ice’ and geomorphology

So-called massive-ice formations are an integral part of the periglacial landscape and their action is central to the geomorphology of polar land masses [65]. The migration of unfrozen water on particle lengthscales underlies the erosion of rocks in cold regions and is responsible for compelling patterned ground features [66]. Moreover, there is a grain size dependence of

soil organic carbon enrichment under the influence of frost heaving processes [67], thereby influencing inventories of soil organic carbon [68]. Thus, permafrost can act as a low temperature (but not necessarily frozen!) setting for microbial activity, providing a model setting for astrobiological [3] and bioremediation activity [69]. In glacier ice, unfrozen interfacial water on the surface of colloidal particles mediates the formation of Tyndall stars [70]. The snowflake-like figures, which occur also in laser welding operations, involve the compelling phenomenon of transient solid superheating [71].

(c) Nuclear power and safety

Nuclear power accounts for more than 10% of global energy production, and could in the future replace a significant portion of the fossil fuel-based energy production of the USA [72]. While nuclear energy production is much safer than in the past and does not directly contribute to an increase in CO₂, it is also responsible for the production of radioactive waste, which brings with it a combination of environmental and security risks. Hence, while we are in clear need of carbon neutral energy sources to meet energy demands, we must develop concomitant modalities of trapping and storing nuclear waste products. Moreover, the governments of nuclear states have responsibility for many waste sites at active and decommissioned facilities. Some presently contaminated areas and future design of sites could benefit from their location in cold regions, and/or from engineered ground freezing [73,74]. For example, a large ice barrier is currently under construction around the Fukushima reactor site [75]. Numerical models that are used to assist in the development of these technologies, and in particular the transport of hazardous ions through the ice, require the ability to incorporate the fundamental physical, chemical and transport processes [61,76].

(d) Potable water

Besides the quest for safe, clean energy, another challenge facing humanity is ensuring an adequate global supply of fresh water [77]. Many areas are experiencing water shortages and efforts are being made to recycle and reuse. Of particular interest are industrial activities such as mines, oil sands and hydraulic fracturing operations, which produce large volumes of wastewater deposited in tailings ponds. Recently, a novel water purification technique that mimics the growth of sea ice has been introduced in which ice is used as a filtration membrane, known as unidirectional freeze purification, or UFP [62,78]. In UFP systems, ice is directionally grown into wastewater containing colloids, salts and dissolved contaminants. At low rates of freezing, the ice pushes all particles and impurities ahead, achieving nearly 100% filtration efficiency. At higher filtration rates, the ice interface tends to ramify, forming ice lenses and dendritic structures. Fundamental studies of ice–colloid interactions will impact numerical models developed to optimize the efficiency of UFP systems [79,80].

(e) Materials design

In the natural environment, one rarely finds a pure material and the same is true in the design of materials for applications. Indeed, controlling the properties of composite materials is a ubiquitous goal in fabrication. For example, it is now commonly understood that plasmonic nanostructures can be created by exploiting the ideally high optical transparency and dielectric properties of silica particles through the manipulation of metallic coatings [81]. From the design perspective, one can manipulate the nature of an interfacially premelted film by systematically changing the dielectric properties of a wall material [1]. Additionally, a rapidly expanding practice during the casting of composite materials is to suspend insoluble higher melting point colloidal particles (radius 0.1–100 µm) in the melt phase to be trapped during freezing and thereby influence the material properties of the final composite solid [28,82]. Importantly, after trapping, premelting dynamics can be used to redistribute particles in a controlled manner, further designing the properties of a sample [83]. The process is environmentally benign, and

the materials exhibit striking similarities to natural biomaterials such as nacre and bone tissue, including a complex hierarchical microstructure defined at multiple length scales, and exceptional strength and material toughness [84].

In these and many other natural environmental and materials engineering settings, the nature and distribution of inclusions influences ostensibly all of their physical properties. Therefore, from a materials science standpoint it is clearly desirable to solidify the bulk suspension and then manipulate the particle distribution for the desired local and global properties, whereas from the water purification and geophysics standpoint, we would like to know the underlying origins of the state of bulk materials at subzero temperatures. These apparently distinct settings come together when one considers the issue of nuclear energy, ranging from containing waste in either glass or ice [61] to extracting energy from the thorium sequestered as fluoride in molten salt [85]. The redistribution of colloidal particles in host matrices and the evolution of the interstitial material has an influence on the efficacy, evolution and stability of these technologies.

(f) Soft and porous matter

Tissue engineering [86], cryopreservation and cryosurgery [87] represent enormous fields in which the confluence of processes described here play out in soft systems. For example, the materials discussed in this contribution, such as ice, have a typical Young's modulus of order GPa. Hence, when we consider a situation such as thermodynamic buoyancy, wherein a particle migrates through a solid against which it premelts, the host solid (e.g. ice) can withstand the sort of shear stress created by the gradient in thermomolecular pressure. Thus, the particle moves by continuous solidification and melting of the interfacial film disjoining it from the host solid. However, recently we have been actively engaged in studies of very soft solids, with a typical Young's modulus of approximate kPa. Here, we find that classical laws (e.g. Young's Law and Eshelby's inclusion theory) in which surface energy plays a central role, can break down and a range of new phenomena emerges [88–92]. A key length scale in these phenomena is the *elastocapillary length*, which is the ratio of the surface tension to Young's modulus of the soft body under study. For example, we find an experimentally verified but counterintuitive result that a soft body filled with liquid inclusions will become stiffer than the inclusion free body when the radii of the liquid inclusions is less than the elastocapillary length [91].

These results suggest an amusing set of considerations in which a polycrystalline soft body undergoes some form of interfacial melting and is subjected to thermomolecular pressure gradients. The induced forces have the 'option' of transporting material or deforming the host matrix? This is analogous to what happens when a fluid saturated soft granular material is exposed to a fluid pressure gradient [93,94]. Whereas in a rigid matrix only the fluid can move in response to a pressure gradient, in a soft granular material both the fluid and the soft particles move.

6. Conclusion

All of the above processes and applications (and others yet to be envisaged) require a refined understanding of the fundamental nature of phase transitions and their influence on the mechanical response and far-from-equilibrium transport processes that accompany the freezing process in a wide range of media. The associated challenges will be advanced by controlled laboratory experimentation combined with rigorous mathematical and engineering- and physics-based modelling. Without such, interpretation of large-scale observations or desktop experiments will be mired by ambiguities as challenging as the problems that motivate them are compelling.

Data accessibility. This article has no additional data.

Competing interests. I declare I have no competing interests.

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was in press I was made aware of a very relevant paper [95], which unfortunately could not be incorporated with the attention it deserves.

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