Review

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Characterizing key features in
the formation of ice and gas
hydrate systems

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Crystallization in liquids is critical to a range of important processes occurring in physics, chemistry and life sciences. In this article, we review our efforts towards understanding the crystallization mechanisms, where we focus on theoretical modelling and molecular simulations applied to ice and gas hydrate systems. We discuss the order parameters used to characterize molecular ordering processes and how different order parameters offer different perspectives of the underlying mechanisms of crystallization. With extensive simulations of water and gas hydrate systems, we have revealed unexpected defective structures and demonstrated their important roles in crystallization processes. Nucleation of gas hydrates can in most cases be characterized to take place in a two-step mechanism where the nucleation occurs *via* intermediate metastable precursors,

which gradually reorganizes to a stable crystalline phase. We have examined the potential energy landscapes explored by systems during nucleation, and have shown that these landscapes are rugged and funnel-shaped. These insights provide a new framework for understanding nucleation phenomena that has not been addressed in classical nucleation theory.

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. Introduction

Crystallization in molecular liquids is critical in many fields ranging from fundamental science to industrial engineering, where aqueous phase crystallization processes, specifically ice and gas hydrate formation, are of substantial interest in their own right [1]. Ice formation, or its suppression, plays an important role in the food industry [2], clinical applications [3], atmospheric chemistry and climate [4,5]. Gas hydrates are ice-like substances consisting of water and small gas molecules such as methane, ethane, carbon dioxide or hydrogen sulfide. The inhibition of gas hydrate formation in oil/gas pipelines costs hundreds of millions of US dollars annually [6], while exploration of natural gas hydrate resources (as a future energy source) is currently facing many technical challenges [7,8]. Consequently, much research has been done on aqueous phase crystallization to help drive diverse scientific and technological advancements. A principle barrier to realizing such advancements is incomplete understanding of the molecular-level details of crystallization processes.

There have been many studies, both computational and experimental, aimed at addressing this knowledge gap. In the past few decades, there have been significant improvements in experimental technologies for monitoring molecular processes, such as rotational-vibrational spectroscopy, X-ray and neutron diffraction [9]. However, the small length scales (nanometre) and short timescales (nanosecond) in which crystallization occurs present major challenges for most studies probing molecular behaviour experimentally. Molecular dynamics (MD) simulations have been playing an increasingly important role in our current understanding of the molecular mechanisms of crystallization processes. One of the authors pioneered MD simulations to investigate the molecular mechanism of nucleation in molecular liquid systems. For example, by exploiting an electrofreezing method [10,11], the homogeneous nucleation of water was achieved for the first time. This group was also the first to report nucleation of liquid CO₂ in MD simulations [12]. Since that time, we have extensively studied the crystal growth and nucleation processes for ice and gas hydrate systems under a range of different conditions, revealing a number of interesting characteristics and important structural features, many of which will be reviewed here.

The transformation of a liquid system into a crystal occurs in two main steps, nucleation and crystal growth. Nucleation is the initial process whereby a small ordered cluster forms from disordered, liquid-state molecules; crystal growth is then the subsequent propagation of the order in the system. Nucleation is a stochastic and rare event, characterized by a large activation-free energy barrier in a typical supercooled liquid system. Classical nucleation theory (CNT) [13] is widely used as the theoretical framework to describe nucleation, although some of its assumptions have been recently questioned [14,15]. Whereas CNT assumes that the structure of the initial nucleus resembles that of the final crystal, recent simulations and experimental investigations [14–21] of nucleation reveal more complex pathways in which metastable intermediate (or precursor) structures appear that subsequently reorganize into stable crystalline phases. Alternative perspectives on nucleation are possible that look to better capturing its underlying mechanisms and key kinetic factors. For example, one can consider the energy landscape explored by a system during nucleation as shown schematically in one dimension in *figure 1a*. However, ordering processes such as crystallization and protein-folding

Figure 1. (a) An ‘energy landscape’ representation for a crystallization process. The horizontal axis represents a parameter capturing the ordering of the system. (b) An ‘entropic search’ representation for a crystallization process. The brown surface represents the configurational space associated with the liquid state in which the system is evolving (green trajectory). (c) A ‘funnel-shaped’ energy landscape for a crystallization process. The vertical axis is the potential energy of the system, while the horizontal axes capture the entropy of the system. The surface then represents the states available to the system in that parameter space. (Online version in colour.)

can be characterized by extensive searches in large configurational spaces, as pictured in figure 1*b*, and hence this entropic aspect typically dominates earlier stages of the process since the associated decrease in enthalpy is insufficient to compensate the entropic losses. We have recently appropriated the funnel model of protein folding [22–24] as embodied by rugged, funnel-shaped potential energy landscapes (figure 1*c*) to describe and rationalize crystallization processes [25]. Within such theoretical frameworks, it is apparent that an initial reduction in entropy, not immediately balanced by a decrease in potential energy, gives rise to the free energy barrier for crystal nucleation. An analogous phenomenon can be used to describe the origin of the surface free energy of a crystal growing interface [26]. Figure 2 presents the corresponding enthalpy, entropy and the resultant free energy profiles determined for an ice–water interface. We can see the interplay between energy and entropy results in a peak in the free energy profile at the interface. Our work has largely focused on understanding the important kinetic aspects of how entropy reduction occurs during crystallization processes and how entropy reduction may relate to energetics.

In this paper, we summarize many of the findings from our extensive set of simulation studies concerning nucleation and crystal growth. We will briefly discuss different measures of order and how they can offer different perspectives on the underlying processes. Important mechanistic features and their relationships to structure will be presented; the crucial role of defects and ordering in stages will be reoccurring themes. Structural biases during ice and gas hydrate nucleation and growth will be considered, and we will explore how the rugged funnel model of crystallization can provide useful insights into the behaviour of these systems. Several more general reviews on crystallization of ice and gas hydrates can be found elsewhere [1,9,27,28].

This paper is organized as follows. In §2, we discuss the molecular models we have used and present key features of the ice and gas hydrate structures. We then introduce the methodologies we have developed and employed in our crystal growth and nucleation simulations. In §3, we review various methods we have used for the visualization and characterization of crystallization processes. We highlight our investigations of crystal growth in §4 and 5, where the fluctuating nature of solid–liquid interfaces and the presence of defective structures are important aspects. In

Figure 2. Profiles for the enthalpy, entropy and free energies, $\Delta H(z)$, $T\Delta S(z)$ and $\Delta G(z)$, respectively, as obtained across a model growing ice interface. Here, the entropy change was estimated using the profile of a tetrahedral order parameter; details can be found in [26]. The area under this curve essentially gives the interfacial free energy between solid and liquid. A representative configuration of the system, appropriately positioned, is included as a background with the profiles. Reprinted with permission from [26] (Copyright © 2012 American Chemical Society). (Online version in colour.)

§6, we focus on our results from simulations of the nucleation of ice and gas hydrates through the lens of ordering in stages. Finally, we offer our perspectives for future studies in §7.

2. Models and methods

(a) Models

Both ice and gas hydrates are water-rich systems, making it important to choose appropriate water models when performing nucleation and crystal growth studies of these systems. More specifically, the selected molecular models should be able to provide reliable descriptions of the structure, dynamics, and phase equilibria of water during nucleation and crystal growth. Many rigid fixed-charge water models exist (e.g. the TIP4P family) [29], and previous work has demonstrated that the TIP4P/2005 and TIP4P/Ice models can reproduce well a wide variety of structural, thermodynamic and kinetic properties of condensed water phases [30,31]. Consequently, we have used the TIP4P/2005 and TIP4P/Ice models throughout most of our nucleation and crystal growth simulations of ice and gas hydrate systems. Although polarizable models or *ab initio* simulation methods might provide a better description of the underlying physics, they are generally too expensive for simulations of nucleation of ice and gas hydrate systems. Both ice and gas hydrate nucleation have also been successfully modelled using the coarse-grain mW model [17,21,32–36], which captures well water’s thermodynamic properties and is expected to provide insights into the thermodynamics of nucleation processes, for example, nucleation free energy barriers. However, the mW model, treating a water molecule as a single site and lacking explicit hydrogen atoms, has been reported to exhibit ‘non-physically’ fast dynamics for nucleation [37], so we have not used it in our work. For guest molecules in gas hydrate simulations, we have chosen models optimized for condensed phase simulations, for example, the OPLS model for methane [38], and a four-site model for H_2S [39].

Ice and gas hydrates represent different crystalline structures within which water molecules form hydrogen-bonded structures where each water molecule has four neighbouring molecules in a tetrahedral arrangement. In gas hydrates, water molecules form hydrogen-bonded polyhedral (cage) structures that can host small gas molecules such as methane, ethane, carbon dioxide, hydrogen sulfide, etc. The most common gas hydrate structures are the cubic structure I (sI), cubic structure II (sII) and the hexagonal structure (sH), each comprised different cage structures [40]. All three hydrate structures are composed of face-sharing polyhedra (cages) of hydrogen-bonded water molecules, where the notation X^nY^m is conventionally used to describe a cage consisting of n X-sided and m Y-sided polygons (i.e. water rings). Figure 3a shows an example of sI gas

Figure 3. Ice and gas hydrate crystal structures. (a) A view of the 001 face of a sl hydrate crystal. (b) The building blocks of sl hydrate, a 5^{12} cage, containing 20 water molecules, and a $5^{12}6^2$ cage containing 24 water molecules. (c) A view of the basal face of hexagonal ice, I_h . (d) The building blocks of hexagonal ice, a 6^5 cage containing 12 water molecules, and the building block of cubic ice, a 6^4 cage containing 10 water molecules. (Online version in colour.)

hydrate structures, where the sI crystal comprises 5^{12} and $5^{12}6^2$ cages, as shown in figure 3*b*. Hexagonal ice (I_h) is the most stable form of ice at ambient pressures [41]. Figure 3*c* presents the crystalline structure of ice I_h , where the hexagonal ring structure of the basal face is shown. Like gas hydrates, the structures of ice I_h and cubic ice (ice I_c) can also be envisaged to consist of cages, specifically 6^5 and 6^4 cages, as shown in figure 3*d*. One key difference between the ice and gas hydrate structures is that the water rings in gas hydrates are essentially planar while in ice the rings are in chair or boat conformations.

(b) Steady-state crystal growth simulation

We have developed a novel steady-state simulation methodology allowing us to study continuous crystal growth. Figure 4 shows two typical crystal growth simulation set-ups. We can see that the system has two solid–liquid interfaces, one crystal growing and one crystal melting. In figure 4*b*, a temperature pulse is introduced at the crystal melting interface while the rest of the system is maintained undercooled to induce crystal growth at the propagating interface. One clear advantage of these set-ups is that the growing crystal interface can be kept at a reasonably long and constant distance from the other interface in the system to avoid artificial interactions between the interfaces. For systems like a gas hydrate with two or more molecular species, the solution composition can be an important driving force in crystal growth and it is desirable for it to remain constant over time. In the steady-state approach, the melting of the hydrate can serve as a source of gas molecules into the solution to compensate the decrease in the gas concentration due to gas hydrate formation. Since gas molecules have a low solubility in water, while they are relatively rich in the hydrate phase, crystal growth simulations of gas hydrates have proven to be somewhat difficult [44]. To help overcome the low solubility and slow diffusion of gas molecules in aqueous solutions, which introduces a mass-transfer problem, an active transport approach was developed to help drive gas molecules out of the melting region and towards the crystal

Figure 4. (a) A schematic of an MD set-up used for the simulation of crystal growth. Reprinted with permission from [42] (Copyright © 2006 American Chemical Society). (b) Schematic of the simulation cell together with the profile of the temperature through the system. The temperature in the system is constant except for a small region around the melting interface where a Gaussian-shaped temperature pulse is applied. Reprinted with permission from [43] (Copyright © 2007 American Chemical Society). It should be noted that in (a) and (b) periodic boundary conditions are applied in all three Cartesian directions and the use of two interfaces allows for steady-state crystal growth to be attained. (Online version in colour.)

growing interface [43,45]. It also allows a control of the gas composition of the liquid region at reasonably constant levels during simulations, and has been used extensively in studies of the kinetics of crystal growth of gas hydrate systems [42,43,45–50].

Figure 5. A potential energy profile (blue line) and interface discriminating criterion (red line) based on the potential energy profile (see text). The abscissa axis is the standardized z position along the box. The corresponding molecular configuration is shown below, where the solid-like and liquid-like molecules (see text) are labelled as green and red, respectively. Reprinted with permission from [45] (Copyright © Elsevier). (Online version in colour.)

Since crystal growth is intrinsically a competition between stochastic ordering and disordering processes, a crystal will typically not grow at a uniformly constant rate. Thus it is advantageous for the propagation of the temperature pulse at the melting interface to be able to respond to the fluctuations of the system. In the steady-state simulations, a constant predefined distance (typically half the length of the simulation box) between the crystal growing interface and the temperature pulse is maintained during the simulations. This requires monitoring of the evolution of the position of the crystal growing interface, and adjusting of the position of the temperature pulse. This is not a trivial task because of the thermal motion of the individual molecules and the finite thickness and roughness of the interfaces [47]. For this purpose, we have developed robust tools for determining the position of solid–liquid interfaces using different profile functions, such as the density, energy and structural parameters [26,43,45,51]. Figure 5 shows an example where the potential energy profile is used to determine the solid–liquid interface positions, the discrimination criterion curve is smooth, and the extracted positions for the solid–liquid interfaces coincide with the system structure. The reliability and relative simplicity of this approach have proven to be very useful in steady-state simulations of crystal growth processes [42,43,45–50].

(c) Nucleation simulations

Nucleation is typically a stochastic process with a very long quiescent (i.e. induction) period, thereby requiring extensive computer resources to study. Many sampling methods such as umbrella sampling [52,53], metadynamics [54,55] and forward flux sampling [56,57] have been used to aid investigations of ice and gas hydrate nucleation. These methods, while being computationally efficient for rare event processes, usually require *a priori* knowledge of the process' free energy landscape or selection of suitable structural parameters for identifying the nuclei being formed. We have primarily used direct, unbiased MD simulations to observe nucleation. For gas hydrates, we have typically used systems with elevated gas concentration

[18], or imposed relatively high pressure and low temperatures compared to typical experimental studies [58]. Such unbiased simulations typically require long simulation times, but have also afforded observation of previously unknown or uncharacterized nucleation behaviour, such as amorphous phases intermediating the solution and gas hydrate crystalline phases, as will be discussed below. Nucleation of ice using atomistic water models has proven very difficult [59]. Therefore, rather than trying to nucleate ice directly from liquid water, we have applied iso-configurational ensemble approaches [60,61] in conjunction with nucleus-containing system configurations from previous works [59] to probe key mechanistic details of ice nucleation and their relationship to potential energy landscapes.

3. Characterization and visualization of the ordering processes

In molecular simulations of crystal nucleation and growth, it is crucial to identify order parameters that can be used to characterize molecules in liquid, solid, and possibly intermediate states, and to pinpoint the solid–liquid interface(s). For ordered and symmetric crystalline structures, a function based on their specific local structures can be defined and evaluated to distinguish molecules in their crystalline phases and those in other phases. In ice and gas hydrate crystals, the four nearest neighbours of each water molecule have essentially a perfect tetrahedral structure, while in liquid water such tetrahedral arrangements are distorted. A number of geometric order parameters for water systems have been developed [57,62,63], among which the Steinhardt order parameters [64], such as q_3 , q_4 and q_6 , and the parameters S_g [65] and F_4 [66] are widely used, where each of them will have different average values for water molecules in solid (i.e. ice or hydrate) and liquid phases. A threshold value can be defined to distinguish between ‘liquid-like’ and ‘solid-like’ molecules. Identifying liquid-like and solid-like molecules is a challenging task due to the fluctuations in local structure in liquid and solid systems. Relatively broad distributions of order parameters are typically observed, and these distributions for liquid-like and solid-like molecules can strongly overlap. Hence, the order parameters calculated using the arrangement of the immediate neighbours of a molecule are typically not sufficient to differentiate solid-like and liquid-like molecules with high confidence.

A commonly used approach [64,67–70] to improve the selectivity of such order parameters is to consider the coherence between the order parameter of a central particle i and its neighbour j by evaluating $q_l(i) \cdot q_l(j)$, where q_l is a $(2l + 1)$ -dimensional complex vector [69,70]. In the case of the bond order parameter [69,70], if the value of $q_l(i) \cdot q_l(j)$ is larger than a threshold then the neighbour j is considered to be connected to i ; if i has at least N_{con} connected neighbours, it is labelled as solid-like. As schematically shown in figure 6, such an order parameter not only takes into account the arrangement of the particles in the first coordination shell of i (orange particles), but also the arrangement of the first coordination shell of all its first neighbours j . Consequently, the arrangement of all the coloured particles in figure 6 will contribute to determining the order parameter value of particle i . While this usually improves the differentiation of liquid-like and solid-like particles, we can also see from figure 6 that the spatial resolution of the measure becomes limited and the sets of particles used to determine order parameters for particles i and j strongly overlap. This limited resolution can make it difficult to fully characterize structural changes (such as for the interface pictured in figure 5) occurring on the length scale used by the measure, strongly limiting one’s ability to resolve the topology at solid–liquid interfaces, for example.

An alternative approach for improving the differentiation of solid-like and liquid-like molecules is to average molecular coordinates over a specific time window, and use these temporally averaged coordinates to determine values of the order parameters [71]. The average position of a molecule over a time window τ , or N timesteps, can be determined by,

$$\langle x \rangle_\tau = \frac{1}{N} \sum_{t=1}^N x_t, \quad (3.1)$$

Figure 6. Schematic of a local structural order parameter. The orange particles are the nearest neighbours of particle i , the magenta particles correspond to particles that are second neighbours of particle i , and the particles outlined with blue dashed lines are the nearest neighbours of the particle j . As discussed in the text, the set of all coloured particles (red, orange, magenta) is used to determine that value of the bond order parameter for particle i . (Online version in colour.)

Figure 7. Schematic of trajectory segments of (a) solid-like and (b) liquid-like particles. In (a,b), the red lines are the trajectories and the yellow stars represent the corresponding average positions for the time segments τ . (c,d) Schematic of the underlying energy landscapes on which the solid-like and liquid-like particles, respectively, have evolved. In (c,d), the blue curves represent the energies while the brown dashed lines correspond to the inherent structures, i.e. positions of the energy minima. (Online version in colour.)

where x_t is the particle's (instantaneous) position at time t . An expression for average orientational coordinates can be obtained similarly [72]. Figure 7a,b shows a schematic of trajectory segments and the corresponding average positions for solid-like and liquid-like particles. The choice of the time τ usually requires careful consideration. It should be small enough to capture the molecular behaviour of interest, but long enough to effectively remove extraneous motion, e.g. the thermal fluctuations of molecules, to achieve good differentiation between solid-like and liquid-like molecules. As also schematically shown in figure 7, the average positions of solid-like particles tend to coincide with their inherent structure coordinates [73], i.e. positions of the (local) energy minima, while this will generally not be true for liquid-like particles. Figure 8 presents the

Figure 8. Instantaneous (a) and averaged (b) configurations of a prism face system of ice I_h . The averaged configuration uses coordinates averaged over 20 ps. Adapted from [71], with permission from Springer. (Online version in colour.)

Figure 9. Probability distributions for values of $q_6(i) \cdot q_6(j)$ for LJ liquid (triangles) and crystal (dots) systems at a reduced temperature of 0.65. Inst, 100 and 400 indicate instantaneous, 100- and 400-timestep average coordinates, respectively. Adapted from [71], with permission from Springer. (Online version in colour.)

instantaneous and averaged configurations of a prism face system of ice I_h , where the structural resolution of the solid part is clearly improved through averaging the molecular positions over only 20 ps [71].

Figure 10. Probability distribution functions of translational MSD values for the liquid (red lines) and solid (blue lines) molecules (see text). The segment times are (a) 0.5 ps, (b) 4.0 ps and (c) 16.0 ps, respectively. Reprinted from [45], with permission from Elsevier. (Online version in colour.)

The temporal coarse-graining represented by average positions can be effectively used to improve significantly the selectivity of order parameter measures [71]. For example, figure 9 shows the probability distribution functions for values of $q_6(i) \cdot q_6(j)$ from simulations of liquid and solid LJ systems. When instantaneous coordinates are used, the values of this order parameter have rather broad distributions for both liquid and solid particles with moderate overlap of the distributions. When average positions are used, we can see a rather dramatic improvement in the resolution of the distributions from solid and liquid systems. While the distribution for liquid particles remains relatively unchanged, for solid particles it becomes significantly sharper for relatively modest averaging time windows (of 100–400 timesteps or roughly 0.5–2 ps).

Figure 11. (a–c) Molecular configurations at different stages in a crystal growth simulation of methane hydrates, where the positions of the molecules are their averaged positions over 20 ps, and the water molecules are labelled as solid-like (green spheres) and liquid-like (red spheres) by the measurement of their translational mobility (see text for details). Reprinted with permission from [50]. (Online version in colour.)

In addition to the averaging of particle positions, measurement of the second moments of particle position distributions can also be very useful. For translational motion, these second moments, or the mean square displacement (MSD), over a time window τ (or N timesteps) can be defined as,

$$\langle \Delta x^2 \rangle_\tau = \frac{1}{N} \sum_{t=1}^N (x_t - \langle x \rangle_\tau)^2, \quad (3.2)$$

where x_t is the instantaneous position at time t , and τ is the average position given by equation (3.1). This measure can be related to the Debye–Waller factor [71], which captures a molecule’s local mobility. In the liquid phase, a molecule’s (translational) MSD is expected to grow linearly with time at longer times, while for molecules in solid phases their MSD will quickly saturate to a finite value (as the motion becomes vibrational). MSD values can be used to differentiate solid-like from liquid-like behaviour and hence provide a structurally independent (i.e. making no assumptions of specific molecular arrangements) means of labelling molecules in nucleation or crystal growth simulations. An appropriate threshold value can be determined by comparing distributions of MSD values for molecules in liquid and solid phases (an example of such is presented in figure 10).

As for average positions, the length of the time window in the calculation of MSD values can also be of importance. Figure 10 shows the distribution of the MSD values for liquid (i.e. aqueous solution) and solid (i.e. hydrate crystal) water molecules [45]. We can see that a time window of at least 4.0 ps is needed to provide a reasonable separation of the two distribution curves. A further increase to 16.0 ps (figure 10c) results in virtually no overlap between the distributions for solid and liquid molecules, indicating that MSD can be an effective criterion for distinguishing between solid-like and liquid-like water molecules. We remark that the length of the time window can also

Figure 12. Average configurations from the simulations of the crystal growth of the prism face of ice I_h . The time for each configuration is noted. Molecules have been coloured according to their mobility characteristics. Water molecules with red and magenta oxygens are translationally solid-like and liquid-like, respectively, while molecules with white and yellow hydrogens are rotationally solid-like and liquid-like, respectively. The green arrow indicates the average position of the interface, and the green bar its average width. Reprinted with permission from [74]. (Online version in colour.)

be seen as a time filter, which will select only those structures (of solid-like molecules) that persist essentially unchanged over the time τ .

In nucleation and crystal growth simulations for aqueous systems, time windows of between 10–100 ps have been found to yield very good solid-/liquid-like discrimination while still providing a reasonable vantage point from which to observe the complex processes characterizing the molecular behaviour at liquid–solid interfaces. Figures 4, 11–13 display examples where

Figure 13. (a,b) Non-planar topology of the basal face of ice I_h at 3 K undercooling. Only hexagonal (red) and cubic (blue) cages are shown using 10 ps average configurations. The molecular configurations were adopted and replotted from MD trajectories reported in [75]. (c) During crystal growth of the secondary prism face of ice I_h one can observe microfacets corresponding to the (primary) prism face (yellow lines). The configuration was adopted and replotted from MD trajectories reported in [76]. (Online version in colour.)

average molecular coordinates and their MSDs have been employed in the visualization of these configurations [50]. This approach can be very powerful for tracking the evolution of a system during nucleation and crystal growth simulations, characterizing the topology of the liquid–solid interfaces, and detecting unexpected structures and behaviours, as we discuss below.

4. Crystal growth characterizations

Through our extensive simulation studies of crystal growth of ice and gas hydrate systems, we have observed many interesting aspects in the behaviour. In this section, we discuss several key features that are common to the growth of both systems, including the fluctuations at the solid–liquid interface, the temperature dependence of the growth rate, and microfacets at the interfaces.

Crystal growth processes can be seen as a competition between ordering and disordering of molecules at the solid–liquid interfaces. Fluctuations of the interface position and topology can be observed in MD simulations [74]. Figure 12 presents system configurations from a crystal growth simulation of the prism face of ice Ih [74]. While the system was under temperature and pressure conditions where ice Ih is the stable phase, we observed occasional ice melting events (compare the system configurations at 4.6 ns and 6.2 ns in figure 12) during the crystal growth [74]. The growth of the basal face of hexagonal ice at temperatures below the melting point has been analysed in detail to investigate the underlying growth rate statistics (figure 14) [77]. The positions of interfacial planes were monitored during steady-state growth simulations (figure 14a), and probability distributions for growth rate values, as measures over various time windows, were determined (figure 14b). Considerable fluctuations in growth rate were observed, and even when 6 K undercooled and over a 5 ns observation window, net melting could be observed. Moreover, it was further determined that at shorter times (i.e. less than 1 ns) there is correlation in the growth rates (figure 14c), which disappears at longer times (i.e. the rate statistics exhibit the expected stochastic behaviour). Figure 15a shows such fluctuations during a crystal growth simulation of methane hydrates [42], where a layer of well-formed crystal melted and subsequently reformed in a timescale of 1 ns. In a crystal growth simulation of H_2S hydrate [48], the crystal growth rates were measured with a short time interval of 10 ps; the distribution of these growth rates exhibit a well-defined Gaussian shape, as shown in figure 15b. These observations point to the stochastic nature of molecular ordering processes at the solid–liquid interfaces and suggest that at least a period of approximately 10 ns is required to meaningfully sample crystal growth behaviour, or at least approximately 10 Å of crystal should be formed before assuming that net crystal growth has occurred.

Figure 14. Growth rate analysis. (a) Time dependence of the position of the growing interface for three basal face systems observed over 80 ns at 6 K undercooling. (b) Probability distributions, as red, green and blue bars, for growth rate values determined over 0.5, 1.0 and 5.0 ns time windows, respectively, for the runs shown in (a). The global average growth rate determined for this dataset is $0.43\text{ \AA ns}^{-1}$. (c) The dependence on the time window width of the standard deviations of growth rate distributions for the runs shown in (a). Two linear fits (red) to the log-scale data are provided, where the slope of the line for longer times is -0.5 (i.e. consistent with stochastic behaviour of uncorrelated rates). Reprinted with permission from [77]. (Online version in colour.)

Figure 15. (a–c) Molecular configurations of water molecules at a crystal growing interface of a methane hydrate system. Reprinted with permission from [42] (Copyright © 2006 American Chemical Society). (d) The crystal growth rate for an H_2S hydrate determined over 10 ps time windows. Reprinted with permission from [48] (Copyright © 2006 American Chemical Society). (Online version in colour.)

While ordering processes become more dominant when the temperature is undercooled, the rate of molecular ordering, or crystal growth, depends on the mobility of the molecules, which becomes suppressed at sufficiently low temperatures. Therefore, the crystal growth rate is expected initially to increase upon decreasing the temperature, but to reach a maximum value at a certain temperature. Our systematic studies of crystal growth of ice Ih indicate that the growth rates exhibit maxima at 10–12 K below the melting temperature, and lowering the temperature further results in a decrease in the crystal growth rate [75]. Similar behaviour has recently been confirmed by both experimental and simulations studies [78–81]. Also in our crystal growth simulations of gas hydrate systems, maximum growth rates were obtained at 10–20 K below their melting temperature [42,47,48]. For gas hydrate systems, the crystal growth rate is more often limited by mass transfer processes due to the low solubility and slow diffusion of gas molecules in aqueous solutions. We found that by applying an active transport approach to speed up the mass transfer (see §2), the growth rate of gas hydrates can become much higher than that of ice under comparable conditions [42,47,48]. This observation suggests that in the presence of hydrophobic gas molecules, water molecules are able to order more readily.

A notable characteristic of the crystal growing interface is that clear microfacets are sometimes formed during crystallization. Two examples of such microfacets observed during MD simulations of basal [75] and prism [76] faces of ice growth are shown in figure 13. The crystallographic orientation of these microfacets is not related to the underlying crystallographic planes, and the detailed topology of the crystal growing interfaces vary over time. The appearance of microfacets is also apparent in figures 5 and 11 for configurations from crystal growth simulations of gas hydrates [45,50]. The observations of microfacets are consistent with the crystal growth behaviour found in monoatomic systems [82], ice [76], and gas hydrate systems [45,50]. Although a planar solid–liquid interface can be observed during crystal growth simulations with relatively small systems, microfacets are important features of the fluctuating environment of solid–liquid interfaces. For example, we have demonstrated that microfacets tend to exhibit a preferred crystalline plane for different crystal faces [82]. It is important to note these microfacets are not static, but are constantly changing as part of the inherent fluctuations at the interface that occur, for example, with a relaxation time of roughly a nanosecond for ice [77]. These microfacets are apparently related to the surface roughening of ice [83] and may contribute to the variations and spatial distributions observed for the thickness of the quasi-liquid layer at the surface of ice, as reported in recent thermal fluctuation spectroscopy experiments [84].

5. Importance of structural defects

We have discovered and identified several interesting defective structures in ice and gas hydrate systems. In this section, we highlight some examples of defect structures that are common to both systems and that apparently play key roles in the kinetics of their nucleation and crystal growth. We specifically focus on orientational and translational water defects, unexpected ring and cage structures, and cross-nucleation between different crystalline phases, as observed in MD simulations of ice and gas hydrates.

We have observed the formation of interstitial water molecules during the crystal growth processes of both ice and gas hydrate systems. There has been controversy about whether the transport of the gas or water molecules determines the growth rate of hydrates [85–91]. Our MD simulations reveal that interstitial water molecules can form during the crystal growth of gas hydrates, and these interstitial defects can further be transported through the solid gas hydrate through a mechanism facilitated by empty cages [49]. However, water vacancies were rarely found in gas hydrate lattices [92], although the transient formation of vacancy defects in gas hydrates have been observed at elevated temperatures [93]. The relative richness and high mobility of the interstitial defects observed in these studies suggest that the diffusion of interstitial defects could be an important mechanism for the mass transfer of water molecules in gas hydrates [94].

Hexagonal ice is composed of 6-membered water rings (figure 5c). Through a detailed analysis of the ring structures during ice growth, we have identified several other key ring motifs, such as 4-, 5-, 7- and 8-member rings and various coupled ring structures, during the ordering of water molecules into an ice crystal [95]. Interestingly, we found that the population of defective (e.g. 5- and 7-member) rings reaches a maximum in the interfacial region (figure 16). Similar ring structures have been characterized in experimental studies of water [41,96–99]. However, these defective rings subsequently transform into the expected 6-member ring structures as they organize to form a final ice crystal. Some unusual ring structures, such as coupled 5–8 rings, were observed to survive the fluctuations at the interface and to induce stacking faults in an ice crystal [100], as we discuss further below. For gas hydrate systems, we have also identified several unusual cages [18,45,58]. These unusual structures include cages not belonging to any known stable gas hydrate phases, such as $4^15^{10}6^2$ and $4^25^76^4$ cages, and cages belonging to meta-stable gas hydrate phases, such as $5^{12}6^3$ and $5^{12}6^4$ cages for a methane hydrate system under moderate temperature and pressure conditions. These unusual cages have also been reported and quantified using a cage recognition algorithm [101,102]. Similar structural defects have also been

Figure 16. (a) Water ring structure at the vicinity of an ice–water interface. Water rings are presented from average configurations (over 50 ps) during growth of the prism face of hexagonal ice. Only the hydrogen bonds of the ring structures are shown, where 4-, 5-, 6- and 7-member rings are coloured as purple, green, red and cyan, respectively. (b) Average populations of 4-, 5-, 6- and 7-member rings across the ice–water interface from averaged configurations, where z is the direction of heterogeneity (and L is the box length). The black, blue, red and green lines represent the populations of 4-, 5-, 6- and 7-member rings, respectively. The population of 6-member rings is presented on the right axis, while the other populations are on the left scale. In both (a,b), the relatively significant populations of 5- and 7-member rings near the ice–water interface are notable. Reprinted with permission from [95]. (Online version in colour.)

observed during the melting processes of gas hydrates [103], indicating a fundamental reciprocity of the crystal formation and melting processes.

During crystal growth simulations of hexagonal and cubic ice, we have found that coupled ring motifs, such as 5–8 coupled rings, can extend across an ice layer, resulting in a lattice shift within the ice structure and thereby forming a stacking fault [100]. These defective regions show a clear triangular character and their dimensions appear comparable to those captured by the scanning tunnelling microscopy experiments [104]. This observation provides a molecular basis for understanding the reported structural dislocations of ice [105–108]. Moreover, similar structural defects can be important in heterogeneous nucleation at the ice interface; in particular, interfacial defective intermediates were found to enable the heterogeneous nucleation of gas hydrates at an ice interface, as discussed in [109]. The structural interconversion and packing polymorphism between the three principal gas hydrate structures, sI, sII and sH, have also been observed in our simulations [110]. The interconversion between sI and sII hydrates is through intermediate $5^{12}6^3$ cages, and the interconversion between sI and sH hydrates is through intermediate $4^15^{10}6^2$ cages, as illustrated in figure 17. The transition structure between sI and sII involving the $5^{12}6^3$ cages was predicted to be a possible novel hydrate structure, HS-I, which was

Figure 17. Possible mechanisms of the structural interconversion between principal gas hydrate structures sI, sII and sH. The sI (top) and sII (bottom left) crystals can interconvert to each other through $5^{12}6^3$ cages, the sI and sH (bottom right) hydrates can be connected through intermediate $4^1 5^{10} 6^2$ cages. The sII and sH hydrates can be connected directly since the two crystals share compatible structural arrangements. Reprinted with permission from [110]. (Online version in colour.)

later confirmed experimentally [46,111,112]. These observations have emphasized that a great diversity of polymorph structures of ice and gas hydrates can occur, and have highlighted the importance of the transition layers, which represent defective structures that facilitate seamless transition between different crystalline phases without disrupting the hydrogen-bonded network of the water molecules.

6. Ordering in stage and funnel-shaped energy landscape

A common theme emerging from our work is that both crystal nucleation and growth involve ordering in stages. More specifically, spatial transitions between liquid and crystal as across interfaces, and temporal transitions as during nucleation involve progressive series of changes in collective molecular behaviour between those associated with the liquid and those of the crystal. In this paradigm, clear-cut binary crystal-liquid distinctions (e.g. as embodied in classical nucleation theory or Gibbs interfaces) give way to continuous spectra of behaviours bookended by those of the macroscopic crystal and liquid states. Envisioning the crystal-liquid transition as a non-binary process at the molecular level (i.e. one with possible immediate stages) is supported both by our work as detailed below, and by work from other groups on a variety of systems (e.g. see ref. [113] and references therein).

Our work on ice highlights ordering in stages during crystal growth. For example, we have shown that the S_g order parameter, which was designed to distinguish crystalline ordering in tetrahedral networks, smoothly transitions across water-ice interfaces and can provide empirical entropy estimates [26]. Moreover, potential energy, density and order parameter profiles do not perfectly align across ice-water interfaces, but instead exhibit detectable differences (e.g. slight staggering or differing amounts of asymmetry) [26,74], indicating not all characteristics of ice arise simultaneously as crystal growth proceeds. Even at the molecular level, it is possible to observe ordering in stages during ice growth. For example, molecular-level translational and rotational ordering do not occur simultaneously [74]. Moreover, even when interfacial water molecules are seemingly rotationally and translationally solid, they can still undergo some exchange [74], suggesting that ice-water interfaces are dynamic regions of intermediate character. Consistent

with the dynamic nature of ice–water interfaces, defective structures, such as 5–8 rings, can easily interconvert to ideal crystal structures during ice growth [100]. Staged ordering is also manifested in the prevalence and variation of larger scale motifs across ice–water interfaces (e.g. see the discussion of fused-ring structure populations and distributions at ice–water interfaces in [95]). Ordering in stages is thus critical to understanding water–ice phase transitions from the molecular level to higher order structures.

Ordering in stages is also a well-documented feature of gas hydrate nucleation. For example, we have previously observed an amorphous phase that intermediates the solution and gas hydrate crystalline phases in our gas hydrate nucleation simulations [18,58,114], consistent with the observations in other MD simulations using different molecular models [17,18,33,35,55,115–119]. The formation of an amorphous phase has also been reported in an experimental study of gas hydrates [120]. A common insight from the aforementioned studies is the sequential appearance of order during the transition from liquid-like to solid-like behaviour. The solution phase does not immediately adopt cage structures and arrangements characteristic to the thermodynamically preferred gas hydrate crystal phase. While historically there was an emphasis on considering particular subsets of cages encompassing both those of the preferred crystal phase and perhaps a few others (e.g. the $5^{12}6^n-4^{15}10^m$ cages where $n = 0, 2, 3, 4$ and $m = 2, 3, 4$), it is becoming increasingly clear that there is a plethora of transient cages from which more common and more stable cages arise as hydrate nucleation proceeds, again strongly indicating ordering in stages. For example, early on in the nucleation process, irregular and defective cages are prominent structural features, and appear in interfacial regions between the solution phase and the hydrate nucleus [119]. An ordering-in-stages perspective on gas hydrate nucleation is also supported by the fact that nascent ordering according to water-based molecular-level order parameters apparently precedes the appearance of cages, suggesting that lower level ordering (e.g. at the molecular level) is needed before larger and more elaborate ordered structures can appear [25]. Moreover, distributions of local order parameters (e.g. S_g and MSD) change and narrow continuously throughout the nucleation process. Order-in-stages phenomenology can thus be observed at a variety of length scales, and appears to be a progressive process in gas hydrate nucleation.

In the case of gas hydrate nucleation, the ordering in stages of the solution phase (reduction in system entropy) coincides with decreasing system potential energies. Recently, we have shown that this characteristic feature along with broader phenomenology of gas hydrate nucleation indicates that gas hydrate nucleation involves rugged, funnel-shaped potential energy landscapes (e.g. figure 1c) akin to those associated with protein folding [25]. An important distinction between the two is that a crystallization funnel arises from the molecules composing the crystallizing subsystem, whereas protein-folding funnels are generally discussed as landscapes associated with a unimolecular subsystem. In this paradigm, a system's potential energy dictates how far it is 'down' the funnel, and the funnel's width at a particular point represents the entropy of the system. Thus, the solution state is the broad, upper, rugged portion of the funnel while the crystalline state is the narrow tip of the funnel. The nucleation barrier corresponds to where the funnel rapidly narrows without a sufficiently compensating decrease in potential energy (from the perspective of free energy). Such an entropy-based barrier to crystal nucleation is consistent with ice–water interfaces where water molecules experience a reduction in entropy prior to realizing the full lower energy environment of the ice phase, as captured by the interfacial profiles in figure 2. The funnel-shaped potential energy landscape associated with hydrate nucleation is rugged in the sense that there are many local topological features (e.g. minima, maxima, saddle points). The amorphous hydrate structures commonly observed during simulations of gas hydrate nucleation correspond to systems trapped in local minima, and thus unable to proceed easily to the thermodynamically favoured crystalline phase. We have also argued that rugged, funnel-shaped potential energy landscapes are likely a more general feature of nucleation processes beyond gas hydrates (e.g. ice nucleation) [25].

Rugged funnel-shaped potential energy landscapes provide a basis for explaining additional crystallization phenomenology. For example, in the context of ice growth, our previous work has demonstrated that local environment affects the stability and lifetime of defective structures,

and thus modulates crystallization processes [95]. Moreover, local interfacial structure can substantially impact growth rates at ice–water interfaces on timescales of 1–2 ns [60], and local crystal growth rates at ice–water interfaces show correlated behaviour on sub-nanosecond timescales [77]. Given that crystallization involves rugged, funnel-shaped potential energy landscapes, we conclude that the aforementioned behaviours arise from local funnel topologies in connection with collective behaviours (e.g. molecular rearrangements).

We have explored these ideas further in connection to both ice and hydrate nucleation [61]. Given that crystal nucleation (e.g. hydrate nucleation) involves a rugged funnel-shaped potential energy landscape, one can envision that local characteristics of the landscape (e.g. local minima, maxima, saddle points) impact nucleus evolution at shorter times while the overall funnel shape is relevant at longer times. Conceptually, one can see this as being analogous to a hiker traversing a mountain pass, where the local path taken may deviate from the general saddle point structure of the pass. In turn, the local topology of the potential energy landscape arising from the system's structure can predispose a nucleus to evolve in specific ways at short times (e.g. 'melting' of specific cages) that might be distinct from its long-time behaviour (e.g. growth in the case of a 'post-critical' nucleus). We identify this phenomenon as structurally biased dynamics, and have demonstrated that during ice and hydrate nucleation local structure can bias behaviour on nanosecond timescales [61]. The hypothesis that structurally biased dynamics are at play during nucleation processes is supported by both experimental and computational studies (see [61] for a detailed discussion). As a further example, Fitzner *et al.* [121] very recently reported that: (i) nucleation occurs in the most immobile regions of supercooled water potentially via collective processes, and (ii) the most immobile regions of supercooled water are structurally distinct. Clearly, both these observations (in metastable water) can be seen to arise from similar features of the potential energy landscape. We also point out that our previous work [58] indicated that mobility could be reliably used as a parameter for identifying early stage ordered structures.

An important direction for future work will be quantifying and visualizing key characteristics of funnel-shaped potential energy landscapes. We envision that such work may exploit rare-event sampling strategies, while also drawing on ideas from other fields. For example, Leopold *et al.* leveraged a lattice model of protein folding in conjunction with kinetic modelling to extract folding landscapes for model proteins [122]. It would be interesting to explore similar ideas in the context of crystallization. Investigations into crystallization funnels may also benefit from insights provided by previous work on potential energy landscapes of clusters [123,124] and the use of disconnectivity graphs [123,125].

7. Concluding remarks

In this review, we have summarized several key insights into crystal formation in ice and gas hydrate systems. We have advanced molecular simulation and analysis methodologies, thereby enabling observation of several interesting phenomena, including the micro-faceted character of growing crystal interfaces, various structural defects, and novel crystalline and polycrystalline structures. We have identified several key factors impacting the kinetics of crystal formation, and have demonstrated that crystallization involves a continuous structural evolution accompanied by progressive entropy reduction. A rugged funnel model has been provided as a lens for understanding and explaining the observed crystallization phenomenology.

Similar behaviour in crystal formation may also be observed within other materials, such as SiO₂, Si and Ge, that can form tetrahedrally bonded structures resembling that of ice and gas hydrates [126–128]. In a broader context, understanding the key factors impacting the formation of crystalline, polycrystalline and defective structures is crucial for the design and characterization of a variety of novel materials, such as nanocrystals [129,130]. It should be stressed that while the insights provided here have already advanced fundamental understanding of crystallization, they are all from unbiased MD simulations where time-scale and finite-size limitations are evident. Future studies should aim to continue improving simulation methodologies to overcome these limitations (e.g. by adapting a driven energy conversion

approach to accelerate the nucleation rates independent of a structural bias) [131,132]. The continued improvement of molecular force fields and inclusion of nuclear quantum effects [133,134], along with advancements to data analysis and visualization methods, will also further enhance attempts to realize complete, realistic molecular-level pictures of crystallization, and improve our understanding of their roles in various physical, chemical and biological processes [135–138]. Through the confluence of technical and scientific advancements, we expect that it will soon be possible to characterize the key molecular events of crystallization processes, their probabilities, and lifetimes. Such characterization remains the principle barrier to constructing rich, molecularly realistic models of crystallization that are both operable and actionable while superseding existing frameworks. Much work remains to be done on a variety of important crystallization processes both including and beyond ice and gas hydrate formation.

Data accessibility. This article has no additional data.

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