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Special Topic Preface: Nucleation: Current Understanding Approaching 150 Years After Gibbs

by

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Nucleation is the fluctuation-driven formation of microscopic nuclei of a new phase, where this process eventually leads to the spontaneous formation of the new bulk phase within a metastable parent phase¹. It is a ubiquitous phenomenon that plays a key role in processes as diverse as the formation of ice in the atmosphere^{2,3}, gas hydrates⁴, and biomolecular condensates in living cells⁵; the crystallization of therapeutic drugs⁶, the setting of concrete⁷, and the boiling of liquids.⁸

Almost 150 years ago, as part of his magisterial paper “On the Equilibrium of Heterogeneous Substances”⁹, Gibbs formulated the thermodynamics of fluid interfaces and addressed the reversible work required to form a nucleus of a new phase within a bulk mother phase. Because of the high sensitivity of the rate of nucleation to the reversible work of nucleus formation, such thermodynamic considerations have formed the basis of theories of nucleation and the analysis of experimental data, including the most widely used framework, classical nucleation theory^{10,11}.

Despite its usefulness, simplicity and conceptual clarity, the classical theory relies on a number of simplifying assumptions. These include the assignment of bulk properties to microscopic nuclei and their interface with the mother phase. The theory further adopts a highly idealized view of the pathway by which nuclei can grow or shrink, and fails to take into account the progressively non-spherical shapes of clusters near stability limits or critical points. There is, therefore, a major drive to formulate new theories and computational methods that can accurately describe the mechanisms and rates of nucleation, taking into account complexities including finite-size, transient and non-equilibrium effects, non-classical pathways, critical fluctuations, stochastic effects, and confinement.

Nucleation occurs infrequently yet rapidly: it is a rare event. It also takes place on the molecular length scale. These temporal and spatial characteristics make nucleation challenging to study experimentally. A number of advances in microscopy, microfluidics, neutron scattering, expansion chamber fabrication, and time-of-flight spectrometry among others, are allowing increasingly sensitive and detailed views into microscopic details of nucleation in real systems.

This Special Topic collection of articles provides a panoramic overview of the state of the art in experiments, theory, and numerical simulation of nucleation phenomena. It also brings forth challenges, open questions, and emerging issues in this rich and important area and highlights its

impact on the physical, atmospheric, climate and biological sciences. There emerges a picture of continued intellectual vitality, open inquiry, and broadly consequential scholarship, approaching 150 years after one of Gibbs' major scientific contributions⁹.

The key topics addressed in this collection are highlighted below.

The nucleation of ice receives much attention due to its importance in a vast range of systems and phenomena, such as cryopreservation, cloud formation, frost heave, and experimental studies of deeply supercooled water. Ice (and ices) are addressed in both experimental and theoretical articles. Eickhoff et al.¹² study the impact of poly(vinyl alcohol) (PVA) molecular size on ice nucleation using a microfluidic setup. They show that shorter PVA chains, especially oligomers, exhibit reduced ice nucleation activity, supporting the role of PVA polymers acting as heterogeneous ice nucleators. Within the context of studies of low-temperature non-crystalline forms of water and the experimental challenges posed by ice formation, the review by Tonauer et al.¹³ surveys experimental and some computational studies of the formation of crystalline ice from amorphous ices, including amorphous solid water, hyperquenched glassy water, and low-, high-, and very-high-density amorphous water. Complexity is shown to arise from the different degrees by which crystalline nuclei are absent from samples, affecting crystallization kinetics and making direct comparison with results reported by different laboratories challenging.

Montero de Hijes et al.¹⁴ explore homogeneous ice nucleation in stretched water (-2600 to 500 bars), using the TIP4P/2005 model and the seeding technique. They find that the critical nucleus size, interfacial free energy, free energy barrier and nucleation rate exhibit very minor pressure dependence as a function of supercooling. The observed universality of homogeneous nucleation is ascribed to the pressure-dependent behavior of the interfacial free energy at coexistence, which exhibits a shallow minimum around -2000 bars that is linked to the excess entropy and the slope of the melting line. The latter displays reentrant behavior at the same negative pressure. Zhao and Li¹⁵ study heterogeneous ice nucleation on an FCC (211) surface using forward flux sampling (FFS) and the mW coarse-grained model of water. They find that the commonly adopted size-based order parameter is inadequate. By incorporating the geometric anisotropy of the ice nucleus, a new order parameter reveals two competing ice nucleation pathways—primary-prism-planed path and secondary-prism-planed path—which calls for a two-path model to address statistical uncertainties in FFS rate constant calculations in the presence of multiple pathways.

Articles also address biomedical and biophysical contexts for ice formation and its control. Consiglio et al.¹⁶ develop a model for heterogeneous ice nucleation of relevance to cryopreservation of tissues and organs. Quantifying freezing probability as a function of temperature, duration of supercooling, and system volume while accounting for heterogeneous nucleation site variability, the approach provides a basis for rational design of cryopreservation protocols for biological materials. Farag and Peters¹⁷ focus on the theory underlying the role of anti-freeze proteins (AFPs), which protect organisms from damage under freezing conditions. They present a model for the "critical profile" and free energy barrier for the engulfment process that occurs when metastability is lost and ice swallows the AFP. The ice–water interface is

optimized, and the barrier is estimated as a function of supercooling, AFP footprint size, and distance to neighboring AFPs.

Zimoń and Martelli¹⁸ use computational methods to investigate heterogeneous nucleation in high-pressure glassy water on plastic ice VII as a substrate, under conditions relevant to exoplanets and icy moons. Using the TIP4P/Ice model, they uncover a martensitic transition of ice VII to a plastic FCC crystal under conditions of sluggish molecular rotation. When molecular rotations are active, they observe heterogeneous crystallization of the glass into plastic FCC in addition to the martensitic transition. These findings challenge the reported stability of plastic ice VII in favor of plastic FCC, highlight the influence of molecular rotations in heterogeneous nucleation, and present evidence of enduring icosahedral structures in water. This offers novel insights into the behavior of water under exoplanetary conditions.

Gas hydrates are naturally-occurring, ice-based clathrate structures in which small non-polar molecules such as methane and carbon dioxide are trapped within the crystalline cages. They are present in very large quantities in ocean sediments and permafrost regions, and have enormous implications for methane storage, sustainable energy production, and global warming. This vital topic is the subject of multiple articles in this issue. Grabowska et al.¹⁹ estimate the homogeneous nucleation rate of methane hydrate at 400 bars and a supercooling of 35 K. Utilizing the TIP4P/ICE model for water and a Lennard-Jones center for methane, nucleation rates are first inferred through direct molecular dynamics simulations at large supersaturations, guiding the selection of appropriate order parameters for seeding runs. Arjun and Bolhuis²⁰ employ transition path sampling (TPS) simulations to investigate the homogeneous nucleation of methane hydrates from a supersaturated aqueous solution of methane. They find that in the supercooled, supersaturated regime, nuclei form amorphous structures below 260 K, while they form crystalline structure I (sI) arrangements above 260K. They analyze the TPS results using a model based on classical nucleation theory and provide valuable microscopic insights into the hydrate formation process.

Lauricella et al.²¹ compare the nucleation and growth characteristics of methane clathrate using the mW coarse-grained water model and the all-atom TIP4P force field. Although energetics align (critical nucleus size, interfacial free energies), significant differences in dynamical properties (characteristic nucleation time, growth rate) impact the kinetics of crystallization, resulting in different characteristics of crystalline nuclei and methane concentration dependencies between the two models. Algaba et al.²² employ computer simulations to determine the solubility of carbon dioxide (CO₂) in water under conditions relevant to hydrate nucleation. Using the TIP4P/Ice and TraPPE models for water and CO₂, respectively, the simulations show that the solubility of CO₂ in water when in contact with liquid CO₂ decreases with temperature, while it increases with temperature in a hydrate–liquid water system. The two solubility curves intersect at 290 K, thus determining the dissociation temperature of the hydrate at 400 bar, in good agreement with previous direct coexistence calculations.

Many important functional materials such as glass-ceramics – materials that find applications for example as bone-implant materials and heat-resistant ceramics – are formed by the controlled

emergence of crystalline particles within a glass matrix. Nucleation from an amorphous glass is the subject of a number of experimental studies. Abyzov et al.²³ examine the often-employed assumption that crystal nucleation in glass-forming substances occurs in a completely relaxed supercooled liquid. By studying nucleation in a lithium silicate glass treated for long periods in deeply supercooled states, they show that structural relaxation strongly affects crystal nucleation in deeply supercooled states at temperatures well below the glass transition. They report very large discrepancies between the observed nucleation rate and theoretical predictions based on the assumption that the relaxed metastable state has been reached, and conclude that structural relaxation strongly affects crystal nucleation in supercooled states at temperatures well below T_g .

Duan et al.²⁴ investigate the high nucleation rate of aluminum nanocrystals during primary crystallization in Al-based metallic glasses, emphasizing the role of Al-like medium-range order (MRO) regions as important spatial heterogeneities. Their proposed MRO-seeded nucleation model, supported by structural analysis and kinetic data, offers a comprehensive picture of nanocrystal evolution, aligning with experimental results, and can be applied more generally to materials characterized by the presence of heterogeneities. Lucas et al.²⁵ review experimental evidence showing that several phase change materials (PCMs) and likely other hyperquenched molecular and metallic systems can crystallize from a glassy state upon reheating, where PCMs annealed below the glass transition temperature exhibit slower crystallization kinetics. Employing flash calorimetry, they uncover a glass transition endotherm hidden by crystallization, a distinct change in kinetics during the switch from the glassy to the supercooled liquid state, and a non-exponential decay in crystallization temperature during annealing that is characteristic of structural relaxation in the glass.

A number of articles also focus on the role of nucleation in the formation of structural and functional inorganic materials, such as concrete and metal nanoparticles. Sowoidnich et al.²⁶ investigate the nucleation and growth of calcium–silicate–hydrate (C–S–H), which is critical to concrete durability, by applying inductively coupled plasma–optical emission spectroscopy and analytical centrifugation to the aqueous phase of hydrated tricalcium silicate. The authors find that C–S–H formation follows a non-classical pathway characterized by the presence of two types of pre-nucleation clusters. Using a combination of potentiometry, microscopy and spectroscopic tools, Lauer et al.²⁷ investigate SrSO₄ nucleation under varying solution conditions. They find that below a threshold supersaturation, nucleation is driven by bound species, leading to the direct formation of the stable phase celestine, SrSO₄. At higher supersaturations, free ion consumption dominates, with the process involving a hemihydrate metastable phase that eventually transforms into celestine. The findings highlight the significance of ion association during the prenucleation stage in determining whether the nucleation pathway involves an intermediate phase or not.

Shima et al.²⁸ use experiment and theory to study the kinetics of heterogeneous nucleation during chemical vapor deposition (CVD). They investigate the effect of concentration and the sticking probability of film-forming species on the incubation period, observing a remarkably prolonged incubation period for SiC-CVD from CH₃SiCl₃/H₂ onto boron nitride underlayers. This is

attributed to the notably lower sticking probability on heterogeneous surfaces than on homogeneous ones, coupled with a higher activation energy for the former. Cui et al.²⁹ utilize the theory of absorbing Markov chains to predict a range of shapes (decahedra, nanorods, nanowires) in the growth of penta-twinned decahedral seeds produced via atom deposition and surface diffusion. In practice, crystals with penta-twinned structures are produced from a range of FCC metals. The authors find that the resulting product type depends sensitively on seed morphology. Model predictions show consistency with experimental nanowire observations.

Systems comprising colloidal particles are often employed to gain insight into nucleation mechanisms because they offer a unique chance to watch the behavior of individual particles in real time using confocal microscopy techniques. Complementary insights, including interpretation of experimental data, can be obtained from simulations. In this issue, Lorenz et al.³⁰ experimentally explore the crystallization of a binary mixture of charged colloidal spheres suspended in low-salt aqueous solutions. They compare the solidification process occurring in a homogeneous shear-melt to that taking place during mechanically undisturbed deionization in a slit cell, where global and local gradients in salt concentration, number density, and composition are present. Imaging and optical microscopy provide a detailed characterization of the crystallization process. The study reveals that substitutional alloys formed in bulk experiments through homogeneous nucleation and subsequent growth are mechanically stable in the absence of solid–fluid interfaces, but thermodynamically metastable.

Several articles use simulations and theory to explore nucleation in colloidal systems. de Jager and Fillion³¹ use Monte Carlo simulations and free energy calculations to investigate nucleation and phase behavior of nearly hard charged colloidal particles. The phase diagrams are mapped via the freezing density onto the corresponding hard sphere systems. The study shows that even minimal charge repulsion significantly influences phase behavior, with phase boundaries and nucleation barriers predominantly dependent on the Debye screening length. The authors demonstrate that even mildly charged colloids do not behave as effective hard spheres. Beneduce et al.³² explore two-step nucleation in a binary mixture of patchy particles designed to nucleate into a diamond lattice. Through Gibbs-ensemble and direct nucleation simulations, they clarify the role of the underlying metastable liquid-gas phase transition on the crystal nucleation process and show that the most significant enhancement of crystallization occurs at an azeotropic point with the same stoichiometric composition as the crystal.

Finney and Salvalaglio³³ apply the variational approach to Markov processes to study crystallization from supersaturated colloidal suspensions. They show that collective variables, specifically those correlating with the number of particles in the condensed phase, system potential energy, and approximate configurational entropy, function as effective order parameters. This highlights the value of the variational approach in exploring control mechanisms for crystal nucleation. Weatherspoon and Peters³⁴ introduce a broken bond model for the nucleation of spheres with a face-centered-cubic packing, which form tetrahedral magic clusters, i.e., metastable faceted nanoparticles that are thought to be important in the nucleation of certain faceted crystallites. The model yields the driving force, interfacial free energies, and magic cluster size-dependent free energies. The approach provides insights for constructing free energy

models and rate theories for nucleation via magic clusters, based on atomic-scale interactions and geometric considerations.

In practice, the vast majority of crystallization processes take place at interfaces. The important topic of heterogeneous nucleation occupies center stage in two articles. Yao et al.³⁵ measure crystal nucleation rates at the liquid/vapor interface and in the bulk liquid phase of Posaconazole, a rod-like molecule. They find pronounced rate enhancement in the former case, as well as different polymorph selection. The results shed light on the effect of the liquid/vapor interface on crystal nucleation and polymorph selection. Men and Fan³⁶ investigate, via molecular dynamics, prenucleation and heterogeneous nucleation in the liquid Pb/solid Al system, which has a large lattice misfit. They find that prenucleation occurs at an undercooling of 15K, forming a 2-dimensional ordered structure at the interface that transforms the substrate into a potent nucleant. This study offers new insights into the atomistic mechanism of heterogeneous nucleation for systems with large lattice misfits.

The last 10-15 years have seen major progress in our understanding of nucleation processes, driven by advances in experimental techniques and modeling capabilities. This is reflected in four articles that employ novel experimental methods to study nucleation. Povey et al.³⁷ outline techniques for controlling and measuring the nucleation of crystalline materials using low-power, non-cavitating ultrasound, demonstrating the approach for the case of n-eicosane nucleation and crystallization in a heptane/toluene solvent. They propose combining experimental measurements with a mathematical-physical approach and computational modeling to predict the impact of low-power oscillating pressure fields on nucleating systems, potentially offering new industrially significant methods of process control in crystallization.

Andrianov et al.³⁸ present an experimental method using fast scanning calorimetry to determine important microscopic crystal nucleation characteristics, including features of the cluster size distribution. Their approach also enables estimates of radial growth rates. In poly(L-lactic acid), nanometer-sized clusters show lower radial growth rates compared to micrometer-sized spherulites, likely due to stochastic effects and the size dependence of growth processes on the nanoscale. Feusi et al.³⁹ investigate water–nonane binary and unary nucleation (50–110 K) using pulsed supersonic expansion in nozzle flow, coupled with time-of-flight mass spectrometry. Cluster compositions and nucleation rates reveal independent nucleation processes for water and nonane, with interspecies interaction affecting water cluster growth only at the lowest temperature investigated (51 K).

Cedeno et al.⁴⁰ present a stochastic treatment of NaCl-water nucleation kinetics, utilizing a microfluidic system and an evaporation model. The results demonstrate excellent agreement between measured interfacial energies and theoretical predictions. Analysis of nucleation parameters in microdroplets reveals an interplay between confinement effects and shifting nucleation mechanisms in microdroplets of different sizes. These findings highlight the importance of a stochastic treatment for a fuller understanding of nucleation processes.

A number of theoretical and computational papers address general questions that largely transcend the specific system considered in each case. Goswami and Sastry⁴¹ explore the kinetic reconstruction of free energy surfaces defined by multiple order parameters. In their proposed approach such free energy surfaces are estimated from a steady-state ensemble of trajectories. They demonstrate the method's effectiveness by reconstructing the free energy surface of supercooled liquid silicon with density and degree of crystallinity as order parameters, which yields results consistent with umbrella sampling. Blow et al.⁴² investigate two numerical aspects of forward flux sampling (FFS) simulations performed simulations of crystal nucleation from the melt. Using the Lennard-Jones liquid they explore the impact of the positioning of the liquid basin and first interface in the order parameter space, highlighting their significance for ensuring consistent FFS results. The study also addresses scenarios with multiple crystalline nuclei of size comparable to the largest one, demonstrating that they can be safely ignored for converging a full FFS calculation.

Aasen et al.⁴³ find good agreement between free energies of droplet formation in the Lennard-Jones fluid obtained from Monte Carlo simulations, gradient theory and density functional theory. The capillarity approximation significantly overestimates small droplet free energies, but incorporation of curvature corrections up to second order remedies the discrepancy for experimentally accessible situations. The authors propose a scaling function that reproduces the computed free energies of droplet formation across the full range of metastabilities (binodal to spinodal). Mandal and Quigley⁴⁴ present a lattice-gas model involving two types of interacting dimers, revealing complex pathways for nucleation of stable and metastable phases. The model, tuned for similar nucleation time scales of the stable and metastable phases, yields outcomes ranging from direct stable phase nucleation, dominance of long-lived metastable crystallites, or stable phase nucleation after multiple nuclei of the metastable phase appear. Sharma and Escobedo⁴⁵ employ Monte Carlo simulations of hard gyrobifastigia (GBF) to show that increasing particle aspect ratio reduces the kinetic barrier for the isotropic-crystal transition. The study also reveals that highly oblate and prolate shapes stabilize an intermediate nematic phase. The work supports two conjectures: a connection between low phase free energies and low transition barriers, and the facilitation of crystallization from the isotropic phase by a mesophase.

Bulutoglu et al.⁴⁶ investigate polymorph selection, using the competition between face-centered cubic (FCC) and hexagonal close-packed (HCP) in the Lennard-Jones fluid (LJ) as a case study. Through a combination of molecular dynamics and two-dimensional free energy surface, they find that polymorph selection occurs after the critical nucleus size is exceeded, challenging the classical nucleation picture. A comprehensive population balance modeling approach, integrating nucleation rates with post-nucleation kinetics, accurately predicts the polymorphic distribution in crystals generated from molecular dynamics simulations of the LJ system. Takano et al.⁴⁷ use supervised machine learning to search for local order parameters (LOPs) that can distinguish between crystalline and amorphous portions in polymer crystal lamellae. Such order parameters are useful in computational studies of order-disorder transitions between lamellae and melt upon heating, and more generally for understanding the mechanisms of microplastics degradation.

Several experimental, theoretical and computational studies address bubble and droplet nucleation and cavitation. Bal and Neyts⁴⁸ investigate bubble nucleation in the Lennard-Jones fluid via molecular dynamics, complemented with reweighted Jarzynski sampling and transition state theory. They find consistency with classical nucleation theory, direct molecular dynamics and seeding, but not with FFS calculations. Lamas et al.⁴⁹ demonstrate the applicability of the seeding technique in the (N,V,T) ensemble, combined with classical nucleation theory (CNT), to investigate cavitation rates in a symmetric and partially miscible binary Lennard-Jones mixture. They report good agreement with predictions based on CNT-independent methods, and find that the energetics of bubble formation is similar for the binary and pure liquid cases when computed at the same measure of metastability.

Tinti et al.⁵⁰ use extended classical nucleation theory (CNT), including line tension, to analyze vapor nucleation from a liquid confined between two solvophobic plates. They find that it aligns quantitatively with previous atomistic simulations at plate distances as small as 2 nm but becomes unsatisfactory in extreme confinement (<1.5 nm). The results suggest that CNT is a computationally inexpensive and accurate tool for modeling nanoconfined evaporation in diverse domains, including nanotechnology, surface science, and biology. Lamas et al.⁵¹ investigate cavitation in the TIP4P/2005 model of water through molecular simulations, combining spontaneous cavitation and the seeding technique to obtain a broad overview of the cavitation rate. The results, aligned with isobaric heating and isochoric cooling experiments, predict a decrease in the vapor–liquid interfacial free energy with increasing tension, and underscore the efficiency of molecular simulations in understanding water cavitation phenomena.

Sun et al.⁵² study the influence of subcritical methanol clusters on binary nucleation in dilute water-methanol mixtures during supersonic flow with nitrogen as carrier gas. They present the first data for this system in an expansion device. An extended equilibrium model, validated against previous measurements, highlights altered heat release dynamics with the addition of water, leading to droplet formation at higher temperatures. The authors discuss the challenges associated with comparing their results with predictions from binary nucleation theory. Using a modernized expansion chamber and the pulse method, Lukianov et al.⁵³ investigate the effects of different carrier gases, including argon, nitrogen, and nitrous oxide, on the homogeneous nucleation of water droplets. They demonstrate that, after accounting for deviations from ideal gas behavior, the influence of the carrier gas on the nucleation rate is only modest. The interaction of water with different species in the atmosphere is important in a number of processes that influence weather and climate.

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