



REVIEW

Morphologies of Freezing Water Droplets: Mechanisms, Effects of Scenarios and Composition

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ABSTRACT: The freezing of water droplets represents a fundamental phase-change phenomenon with far-reaching implications across anti-icing technologies, additive manufacturing, cryopreservation, and atmospheric science. The solidification process is governed by a complex interplay of heat transfer, phase-change kinetics, interfacial phenomena, and solute redistribution in multicomponent systems. The final frozen morphology emerges from competition among multiple physical mechanisms: the degree of supercooling, recalescence and dendritic growth, freezing front propagation, freezing-induced volume expansion, vapor release and frost halo formation, and freezing segregation coupled with interfacial flow. This review provides a comprehensive synthesis of droplet freezing morphology, organized around three interconnected themes. First, we examine the fundamental physical mechanisms governing droplet solidification and their roles in driving morphological change. Second, we survey morphological outcomes across distinct scenarios, sessile droplets on supercooled substrates, sessile droplets in supercooled chambers, impinging droplets onto supercooled substrates, and acoustically levitated droplets, highlighting how thermophysical conditions determine the subsequent freezing pathway. Third, we explore how droplet composition (dissolved gases, ions, organic solvents, and nanoparticles) and special cases (bubbles and liquid marbles) influence morphological evolution. Finally, we discuss the modulating effects of substrate properties, external fields, and ambient conditions on freezing morphology. By integrating experimental observations with theoretical models, this review establishes a unified framework for understanding droplet freezing morphology and outlines key directions for future research.

KEYWORDS: Droplet freezing; recalescence; volume expansion; substrate wettability; ice morphology

1 Introduction

The freezing of water droplets is a fundamental phase-change phenomenon of remarkable scientific richness and practical importance, with implications spanning atmospheric science [1,2], aviation safety [3,4], energy infrastructure [5,6], and emerging technologies in additive manufacturing [7,8] and cryopreservation [9–11]. When a droplet undergoes solidification, whether suspended in air, deposited on a substrate, or acoustically levitated, its transformation from liquid to solid is governed by the coupled dynamics of heat transfer, phase-change kinetics, interfacial phenomena, and associated volumetric expansion. The outcome is not a simple, geometrically predictable solid but rather a complex morphological landscape, most famously, a sharp conical tip at the droplet apex that has fascinated researchers for decades. This “tip singularity” arises not merely from volume expansion during freezing but from a self-similar

freezing front governed by the perpendicularity condition between the ice-air interface and the advancing freezing front [12,13]. The scientific challenge lies in understanding how this fundamental mechanism is modulated by droplet freezing scenarios, composition, and external conditions to produce the rich diversity of observed frozen morphologies as shown in Fig. 1 [14–21]. Over the past two decades, advancements in experimental techniques, including high-speed cameras, infrared thermography, acoustic levitation, and synchrotron X-ray microscopy, have transformed droplet freezing from a phenomenological curiosity into a quantitatively tractable problem, enabling unprecedented observation of freezing dynamics across multiple temporal and spatial scales [22–25]. These technological advances have provided the foundation for the mechanistic understanding synthesized in this review.

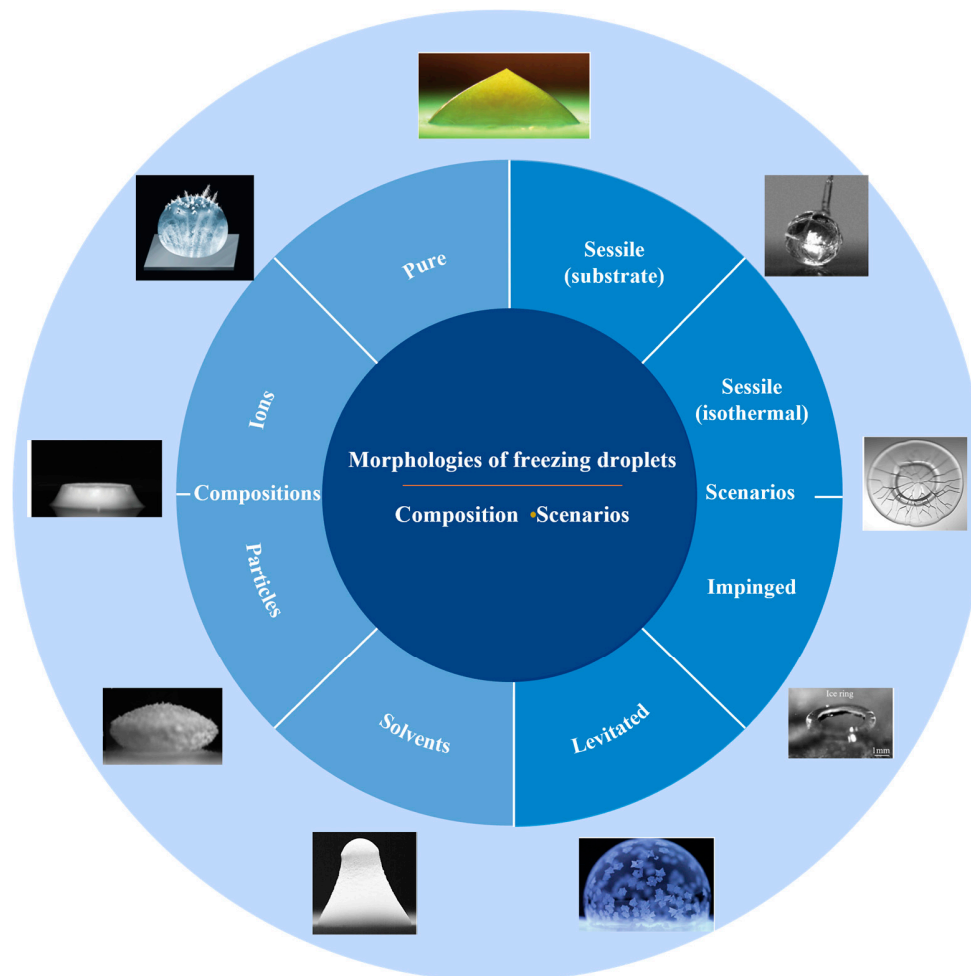


Figure 1: Morphologies of freezing droplets with varying compositions at different scenarios. Each morphology reflects the dominant physical mechanism governing solidification: conical tip from heat-transfer-limited freezing front propagation and volume expansion [14]; self-lifting from solutal Marangoni flow in organic-water mixtures [15]; flat plateau from capillary-driven flow induced by nanoparticle segregation [16]; ice ring from shape-dependent heat transfer in acoustically levitated droplets [17]; ice sprouting from ion exclusion and brine film dynamics in salty droplets [18]; self-peeling from competition between impact hydrodynamics and rapid solidification [19]; flying-saucer morphology from Marangoni-driven flow in liquid marbles [20]; and snow-globe effect from Marangoni flow in freezing soap bubbles [21].

The classical understanding of droplet freezing was fundamentally shaped by the discovery of a universal tip angle of approximately 131° to 139° , which arises from heat-transfer-limited solidification and geometric constraints at the three-phase contact line [26]. Marín et al. [14] established that the tip singularity is self-similar, remaining independent of substrate temperature and initial wetting angle, underscoring the robustness of the underlying heat conduction mechanism. However, this canonical picture has been substantially refined by more recent investigations that reveal how various factors modulate the universal behavior. Using *in situ* synchrotron X-ray imaging, researchers have demonstrated that the tip angle varies with substrate temperature due to bubble formation during freezing, bubble-free frozen droplets produced in vacuum conditions recover the universal tip angle regardless of substrate temperature, confirming that trapped gases are responsible for deviations from universal behavior [27]. Furthermore, the morphological landscape extends far beyond the tip singularity to encompass dendritic networks, frost halos, flat plateaus, and burr-like structures that emerge from the interplay of multiple physical mechanisms [28]. In nanosuspension drops, the competition between dendritic ice formed during recalescence and planar ice formed during isothermal growth determines whether the frozen droplet exhibits a singular tip or a flat plateau [29,30]. Studies on micropillar-encapsulated droplets have revealed three distinct tip morphologies emerging from competing heat transfer pathways [31]. This morphological diversity highlights that the classical tip singularity represents only one facet of a rich landscape shaped by the interplay of fundamental mechanisms with composition and boundary conditions. The central challenge, therefore, is to understand how the fundamental mechanisms, nucleation, recalescence, dendritic growth, freezing front propagation, freezing segregation, and interfacial flow, interact with droplet configuration, composition, and external factors to produce the observed morphological outcomes.

This review addresses this challenge through a systematic, hierarchical organization that builds understanding from fundamental mechanisms to increasingly complex systems. Section 2 establishes the foundational physical mechanisms governing droplet solidification, progressing from nucleation and supercooling through recalescence and dendritic growth to freezing front propagation, volume expansion, vapor release, frost halo formation, and freezing segregation with interfacial flow. Section 3 examines how these mechanisms manifest across different droplet configurations, sessile droplets on substrates, sessile droplets in isothermal chambers, acoustically levitated droplets, and impacting droplets, highlighting how thermal and contact boundary conditions determine freezing pathways and morphological outcomes. Section 4 explores the influence of droplet composition, proceeding systematically from pure water through dissolved gases, salts, the 2nd miscible or immiscible Liquids, and nanoparticles to establish a hierarchy of complexity and identify how each additive introduces new physical effects that modulate morphology. Two special cases, i.e., bubbles and liquid marbles, that lie outside conventional droplet paradigms but offer unique insights into interfacial freezing phenomena, are also included. Section 5 concludes with a synthesis of key findings and outlines critical directions for future research. By integrating experimental observations with theoretical models across this structured framework, this review establishes a unified understanding of droplet freezing morphology and identifies the key gaps and opportunities that will shape the next decade of research in this rapidly evolving field.

2 Fundamental Physical Mechanisms of Droplet Freezing

2.1 Nucleation and the Degree of Supercooling

The degree of supercooling, defined as the temperature difference between the equilibrium freezing temperature and the actual nucleation temperature ($\Delta T = T_{f,eq} - T_n$), serves as the primary thermodynamic parameter governing droplet freezing dynamics. This parameter fundamentally determines the driving

force for nucleation, the rate of recalescence, and the subsequent morphological evolution of the freezing droplet. The classical nucleation theory (CNT) proposed by Fletcher provides the most widely accepted framework for understanding ice nucleation, describing how the formation of an ice nucleus involves a trade-off between the decrease in volume free energy of the system and the increase in interfacial free energy at the ice-liquid boundary [32]. This intricate balance determines the energy barrier that must be overcome for nucleation to occur. However, for nearly a century, the existence of the critical ice nucleus, i.e., the minimum size required for a stable ice embryo to form, remained experimentally unproven due to its transient and nanoscale nature.

Recent groundbreaking work by Bai et al. [33] provided the first direct experimental evidence for the critical nucleus size in ice formation using graphene oxide (GO) nanosheets as a probing platform. By preparing GO nanosheets with precisely controlled lateral sizes ranging from 3 nm to 50 nm, the researchers demonstrated that GO nanosheets only exhibit significant ice nucleation activity above a certain size threshold that varies with the degree of supercooling. Specifically, Fig. 2a shows water droplets containing 8 nm GO nanosheets which froze at approximately -27.6°C , whereas droplets containing 11 nm GO nanosheets froze at approximately -17.6°C under identical conditions, a remarkable 10°C difference arising from a mere 3 nm increase in GO size. Through systematic measurements of nucleation temperatures and delay times across different GO sizes, concentrations, and cooling rates, the researchers inferred that the critical size of the GO nanosheet reflects the size of the critical ice nucleus itself. When GO nanosheets are smaller than the critical ice nucleus, pinning at the periphery of the nanosheet deforms the ice nucleus as it grows, giving rise to a much higher free-energy barrier that suppresses the promoting effect of the GO. By contrast, when the nanosheets are sufficiently large, the critical ice nucleus forms atop their surface, yielding ice formation behavior consistent with classical nucleation theory.

Complementing these findings, Li et al. [34] conducted a comprehensive molecular dynamics investigation of nucleation kinetics in heterogeneous ice crystallization, examining the roles of cooling rate, surface energy, surface nanostructure, and wetting state through over 300 simulated cases using the monatomic water (mW) model. Their results revealed that increasing cooling rates and higher surface energies promote ice nucleation but may simultaneously induce the formation of metastable interfacial ice structures and 4-coordinated molecule types. Critically, they identified that the size match effect between the accessible surface width and the ice lattice constant depends on the wetting state: in the Cassie-Baxter state, matching the surface feature size to the ice lattice constant promotes nucleation, whereas in the Wenzel state, this effect is less pronounced, and increasing the nanogroove width suppresses nucleation by reducing the contact area. This work provides valuable guidance for designing surfaces that either promote or inhibit ice formation through rational control of nanostructure and wetting characteristics.

Further experimental evidence for size-dependent nucleation has emerged from studies on other nanomaterials. Whale et al. [35] investigated the ice nucleation properties of oxidized carbon nanomaterials, including graphene oxide and carbon nanotubes, and demonstrated that the ice nucleating ability depends strongly on the particle size and oxidation state. Additionally, Häusler et al. [36] examined the ice nucleation activity of graphene and graphene oxides with different oxidation degrees, finding that moderately oxidized graphene oxide exhibits the highest ice nucleation activity, while fully reduced or highly oxidized samples show reduced efficiency. These results highlight the complex interplay between surface chemistry, nanoscale morphology, and nucleation efficiency, reinforcing the importance of understanding the critical nucleus size in designing materials for ice nucleation applications.

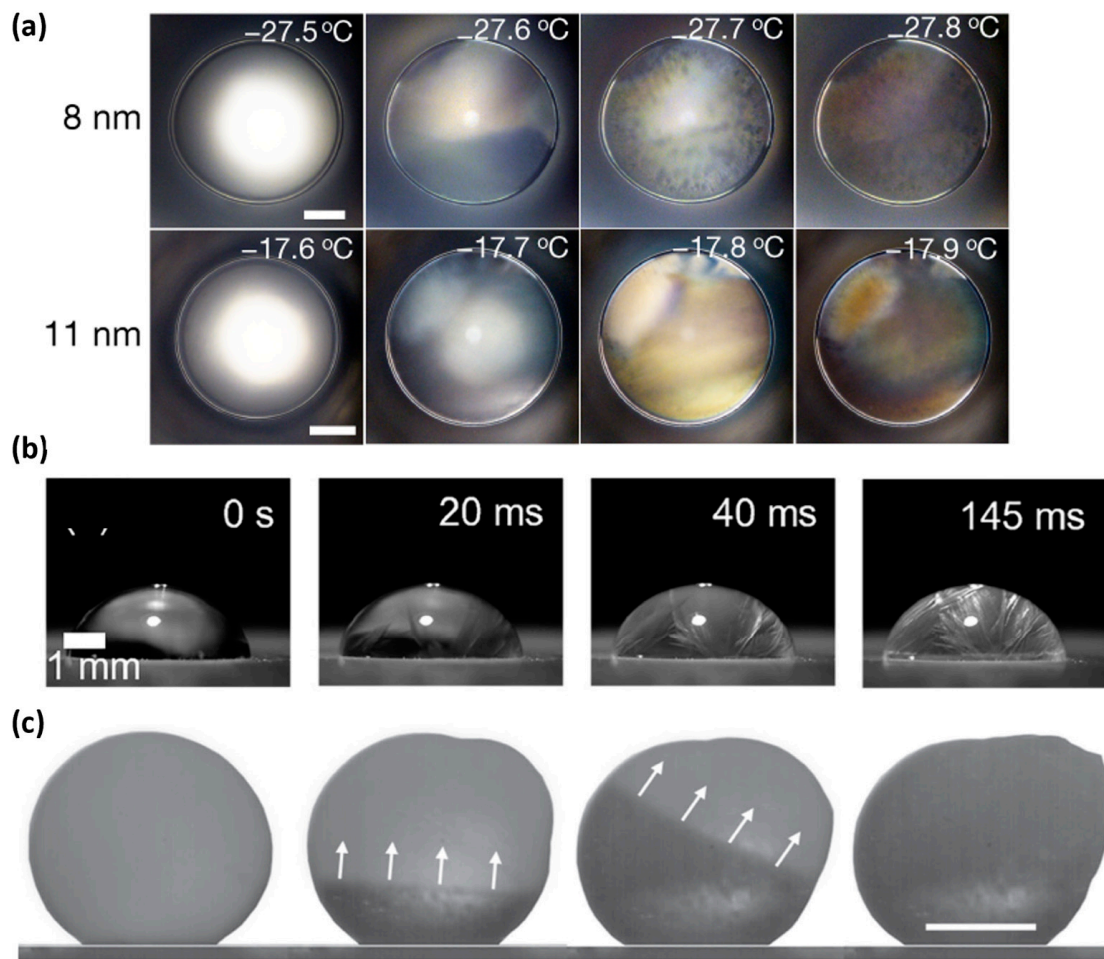


Figure 2: Droplet freezing morphologies across different stages and conditions. (a) Typical freezing sequences of water droplets containing 8 nm and 11 nm graphene oxide nanosheets, as observed by optical microscopy [33]; (b) Dendrites growth in the recalescence stage at a moderate supercooling [28]; (c) Growth of the planar freezing front in the isothermal stage (snapshots at 0, 5, 9, 13 s) [37].

2.2 Recalescence and Dendritic Growth

Recalescence is the rapid initial stage of freezing in a supercooled liquid, characterized by a sudden release of latent heat and a sharp temperature rise. When nucleation occurs in a supercooled droplet, a rapid kinetic phase change ensues. Latent heat is abruptly liberated, causing the liquid temperature to jump from the nucleation temperature back up to the equilibrium freezing point (i.e., 0°C in 1 atm). Zong et al. [28] conducted a systematic experimental investigation revealing that surface temperature profoundly influences dendritic morphology: at higher surface temperatures (e.g., -6.5°C), discrete and sparse dendrites grow independently from the substrate, forming a porous scaffold with high transparency; at intermediate temperatures (e.g., -8.4°C) as shown in Fig. 2b, clustered dendrites with secondary branches emerge, with side-arms developing multiple branch generations; and at lower temperatures (e.g., -12.6°C), dense needle-like dendritic networks form rapidly, with highly compacted structures and significantly reduced transparency.

The initial microstructure of these dendrites subsequently influences the propagation of the freezing front and the final frozen morphology. Jung et al. [37] established that the freezing process comprises two partially overlapping stages following nucleation: the recalescence stage, and the subsequent isothermal freezing stage where the temperature remains constant. During the recalescence stage, which takes place over approximately 18 ms for a droplet in forced convection, dendritic ice grows rapidly and occupies approximately 20% of the droplet volume. During the subsequent isothermal stage, which takes place over tens of seconds and is several orders of magnitude slower, the remaining liquid freezes isothermally and gradually fills the interspace of the ice scaffold, with the released latent heat dissipating by conduction through the substrate. The freezing front of the slower isothermal stage moves faster at the upstream side of the droplet than at the downstream side under flow conditions due to convective cooling asymmetry, leading to an inclination of the freezing front and a markedly shorter freezing time compared to the absence of external flow as shown in Fig. 2c.

Recent advances in modeling have incorporated interface kinetics effects and the Gibbs-Thomson curvature effect into dendritic growth predictions, extending applicability to high supercooling regimes. Snoeijer and Brunet [13] established that the formation of dendritic structures during recalescence is a consequence of the morphological instability of the freezing front, where the ice-water interface becomes unstable when the supercooling exceeds a critical threshold, with perturbations growing preferentially in directions determined by the crystal anisotropy. Wildeman et al. [38] provided additional insights by investigating droplet freezing from the outside in using high-speed photography, revealing that when nucleation occurs at the free surface, the recalescence stage is characterized by rapid dendritic growth inward from the outer surface, with the formation of an ice shell creating a confined volume that leads to pressure buildup and eventual explosion for droplets larger than a critical size. This work demonstrated that the location of nucleation, whether at the free surface or at the substrate, significantly influences the subsequent recalescence dynamics and the final morphology. These quantitative relationships between thermal conditions and dendritic structural parameters provide crucial experimental evidence for understanding the microscopic mechanisms of supercooled droplet freezing and for controlling dendritic microstructures in applications ranging from anti-icing to freeze-casting.

2.3 Freezing Front Propagation and Volume Expansion

The propagation of the freezing front and the accompanying volume expansion constitute the second major stage of droplet freezing, following the rapid recalescence phase. During this stage, which proceeds at a rate nearly three orders of magnitude slower than recalescence, the remaining liquid solidifies isothermally as the freezing front advances through the droplet. The dynamics of this process are governed by heat-transfer-limited considerations: latent heat released at the freezing front must be conducted through the solid ice phase to the cold substrate, while the surrounding air, with its much lower thermal conductivity, provides an inefficient pathway for heat dissipation. Consequently, the freezing front evolves to optimize heat conduction, adopting a geometry that remains locally perpendicular to the gas-liquid free interface. This perpendicularity condition has been confirmed through Hele-Shaw cell experiments, which revealed that the angle between the ice-water interface and the air-water interface averages $87^\circ \pm 8^\circ$ during the final stages of solidification [14].

Recent theoretical and experimental investigations have significantly advanced our understanding of freezing front dynamics. Seguy et al. [39] developed a comprehensive thermal and geometrical analytical model for the freezing front dynamics of water drops on a copper substrate for temperatures ranging from -9°C to -79°C . Their model assumes propagation of the front at the center described by the three-phase

(liquid, ice, substrate) Stefan model in one dimension, with growth characterized by an effective diffusion coefficient that increases as the substrate temperature decreases. They also considered a spherical front that meets the edges of the drop perpendicularly, which captures experimental data well between -9°C and -40°C . Importantly, they found that beyond these temperatures, the adhesion of the drops to the copper decreases, and the substrate temperature must be considered equal to -41°C to rationalize the experimental findings, highlighting the role of droplet-substrate adhesion in freezing dynamics. Tembely and Dolatabadi [40] further proposed general governing equations for water droplet freezing by accounting for the physical properties of each phase present, including the Gibbs–Thomson effect, natural convection, and substrate thermal properties, enabling modeling of a more realistic frozen droplet shape without a prior assumption for the freezing growth angle. This approach successfully predicts the experimentally observed features such as volume expansion, concave freezing front, and the cusp singularity, with the proposed equation for the tip angle explaining its observed variability.

The volume expansion accompanying the liquid-to-solid phase change plays a pivotal role in shaping the final frozen morphology. Water exhibits a unique 9% volumetric expansion upon freezing, a property that, when combined with the geometric constraint of the perpendicular freezing front, drives the formation of the characteristic conical tip at the droplet apex. Zhang et al. [41] further developed a model that considers both supercooling and gravity effects and assumes the freezing front to be a spherical surface. Their model successfully simulates the whole droplet freezing shape variation, including the triple-phase line movements, the formation of the pointy tip, and the variations of droplet volume and expansion rate, with calculated freezing times agreeing with measured ones within 2%.

Recent numerical advances have enabled more sophisticated modeling of freezing front propagation. A hybrid VOF-IBM method has been developed for simulating freezing liquid films and drops, considering the volume expansion due to the density difference between ice and liquid [42]. This approach successfully reproduces the tip formation controlled by both volume dilatation and surface tension effects, providing temperature, pressure, and velocity profiles for code benchmarking, with the final drop shape showing very good agreement with experiments. The effect of gravity and surface tension on freezing processes has been systematically investigated, and the CSF-VOF spurious currents were shown to induce no effect on the icing process due to the small value of both the corresponding Weber and Capillary numbers. Hu et al. [43] reported frozen patterns for water droplets impacting on a cold substrate, identifying four types of patterns including single and double-concentric toroidal shapes, and attributed these patterns to the correlation between impacting dynamics and freezing process. Their scaling analysis revealed that toroidal shapes arise from the balance between the impacting hydrodynamics and solidification, with the inner hole formation explained by an ice front-advection model. These advanced numerical approaches demonstrate that the tip angle is determined by the balance between geometric constraints and volume conservation, with the perpendicularity condition emerging naturally from heat-transfer-limited solidification. The role of droplet adhesion and geometry in determining the freezing front dynamics highlights the importance of understanding the interplay between substrate properties and phase change behavior for predicting and controlling droplet freezing morphologies.

2.4 Vapor Release and Frost Halo Formation

During droplet freezing, the release of water vapor from the droplet surface plays a critical role in shaping the surrounding thermal and humidity fields. As the droplet freezes, latent heat is released during the rapid recalescence stage, driving explosive evaporation from the droplet surface. This vapor release can form distinctive ring-like structures, or frost halos which around freezing droplets on substrates. Jung et al. [44]

first demonstrated that evaporation from a freezing supercooled sessile droplet generates a condensation halo that crystallizes and drastically affects surface behavior. The process involves simultaneous multiple phase transitions and may spread icing by initiating sequential freezing of neighboring droplets in a domino effect. Experiments using substrates with thermal conductivities spanning three orders of magnitude established that a delicate balance between heat diffusion and vapor transport determines the final expanse of the frozen condensate halo. The halo forms when the droplet temperature rises from its supercooled state to 0°C during recalescence, creating local supersaturation in the droplet's vicinity as shown in Fig. 3a.

The physical mechanism underlying frost halo formation involves competition between vapor diffusion and condensation kinetics. During recalescence, the rapid release of latent heat raises the droplet temperature to approximately 0°C , creating a temperature difference with the surrounding cold substrate. This thermal gradient drives water vapor from the droplet surface, which diffuses outward and condenses on the colder substrate, forming a ring of condensed droplets. The vapor pressure at the ice interface during recalescence equals the saturation vapor pressure over ice at 0°C ; vapor can deposit as condensate if the supersaturation required for nucleation on the substrate is less than this value [45]. The extent and survival of the halo depend on how long this condition remains true, essentially the entire duration of the isothermal freezing stage plus part of the time for the fully frozen droplet to cool back toward the substrate temperature.

Recent theoretical investigations have provided quantitative models for frost halo formation. Kavuri et al. [46] developed a comprehensive numerical model using lubrication approximation within a finite element framework, encompassing solid-liquid phase change, heat balance across the liquid-gas interface, and mass conservation. They observed a negative evaporation flux enveloping the droplet in the initial stages, indicating that vapor produced during freezing condenses on the substrate near the contact line. Condensate accumulation triggers re-evaporation, causing a temporal shift of the halo region away from the contact line until it disappears due to the diffusive nature of water vapor. Increasing relative humidity extends the halo lifetime by reducing evaporation and prolonging net condensate presence. Increasing liquid volatility increases evaporation flux, with condensation occurring closer to the droplet. Decreasing substrate thermal conductivity increases total freezing time and the amount of vaporized liquid, resulting in condensation reaching supersaturation. Zhen et al. [47] identified three distinct stages of halo evolution, formation, growth, and fading, occurring on timescales from milliseconds to seconds under standard laboratory conditions on hydrophobic surfaces with low thermal conductivities. The halo extends to its full size during recalescence, continues growing during the slower isothermal freezing stage, and fades after the droplet completely freezes to ice. This interconnected behavior highlights the complex coupling between heat transfer, mass transfer, and phase change during droplet solidification. The frost halo phenomenon is best observed on a low-energy, thermally insulating substrate where the heat transfer timescale exceeds the vapor diffusion timescale.



Figure 3: *Cont.*

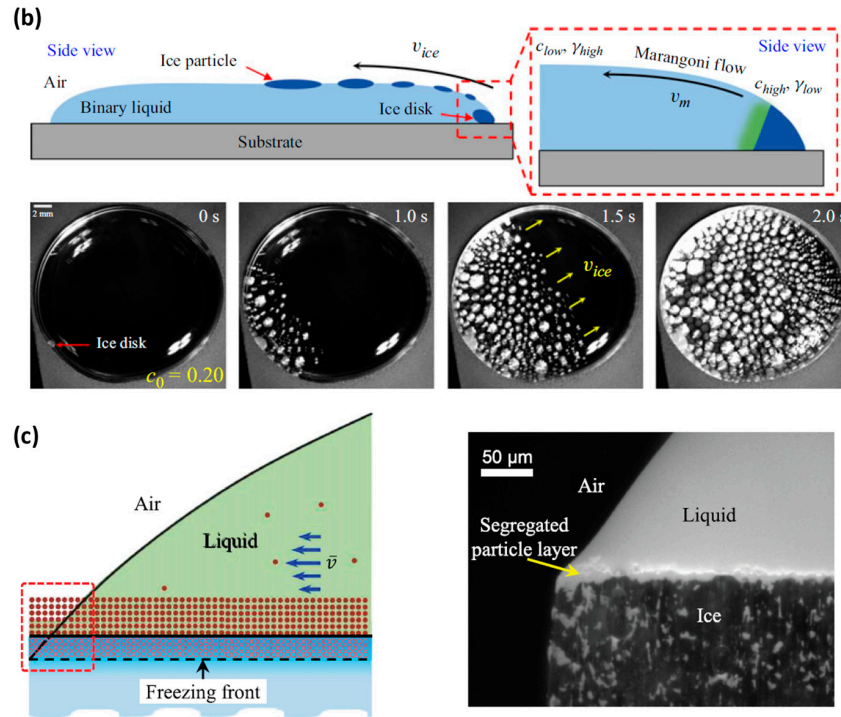


Figure 3: (a) Frost halo formed due to the vapor release upon droplet freezing [44]; (b) Schematics and experimental observations showing the solute-driven Marangoni flow [48]; (c) Particle segregation and the capillary-driven compensating flow [16].

2.5 Freezing Segregation and Interfacial Flow

The freezing of multicomponent droplets involves complex interplays among water, ice, and solutes, where the solidification process fundamentally alters the spatial distribution of chemical species and drives interfacial flows that dramatically modify the freezing dynamics and final morphology. When a solution freezes, the solvent crystallizes preferentially, and solutes are rejected from the advancing freezing front, a phenomenon known as “freezing segregation”. This process creates concentration gradients in the residual liquid that profoundly affect the local freezing conditions, interface stability, and morphological development [49,50]. As the freezing front advances, dissolved ions, organic molecules, and solid particles are expelled, and when local solute concentration exceeds solubility limits, precipitation or bubble nucleation may occur [51], establishing a competitive dynamic between the advancing front driving solute enrichment and precipitation consuming the excess solute.

In saltwater droplets, ion exclusion from the advancing freezing front modifies local freezing point depression, creating conditions that promote irregular front morphologies. Recent studies [52] have revealed that the freezing interface in saltwater droplets exhibits distinct burr-like structures, irregular, short, and sharp protrusions that differ markedly from dendritic patterns observed in pure water. Under enhanced supercooling, these burr-like structures evolve into more typical dendritic patterns, indicating a continuous morphological transition dependent on thermal conditions. The resulting morphology directly influences the mechanical properties of saltwater ice, with increased salinity governing freezing depth and reducing ice hardness. The disappearance of the freezing singularity with increasing salinity has been successfully reproduced by Lattice Boltzmann Method simulations incorporating ion exclusion effects, validating the model’s ability to capture the coupled effects of heat transfer, fluid flow, and solute transport.

The solute rejection process drives interfacial flow through concentration-gradient-driven Marangoni convection, which can dominate the freezing dynamics in binary mixtures. Wang et al. [48] reported a counterintuitive self-lifting behavior in frozen ethanol-water droplets, resulting in a nearly doubling in height that defies gravitational effects. This phenomenon is attributed to an internal solutal Marangoni flow driven by enriched ethanol concentration near the freezing front as shown in Fig. 3b. Since surface tension decreases with ethanol concentration, the local surface tension at the bottom is reduced, generating a solutal Marangoni flow with velocities up to 1 mm/s along the droplet interface. Particle image velocimetry confirmed a pronounced downward flow at the droplet center for binary droplets, contrasting with the upward flow in pure water droplets driven by thermal Marangoni effects. A theoretical model incorporating the propagation of freezing front and the dynamic growth angle quantitatively predicts the spatiotemporal evolution of droplet shape, demonstrating excellent agreement with experiments. Furthermore, in super-cooled ethanol-water droplets, ice particles detach from the freezing front and migrate unidirectional across the droplet interface, with migration velocity determined by the solutal Marangoni flow and growth rate governed by a balance between latent heat release and enhanced thermal dissipation.

The segregation of nanoparticles during freezing introduces additional morphological complexity through the formation of particle-depleted or particle-enriched regions as shown in Fig. 3c. Zhao et al. [16,53] reported that the presence of nanoparticles breaks down the universal pointy tip formation in freezing water droplets, instead producing a flat plateau shape at the droplet apex that becomes more pronounced at higher particle concentrations. This phenomenon is attributed to a capillary-driven compensating flow due to segregated particles moving along the freezing interface, where nanoparticles are rejected by the advancing freezing front and accumulate into a porous matrix layer at the tri-junction region. The advancing particle layer drives an outward compensating flow from the droplet interior to its vertexes, a mechanism analogous to the classic “coffee ring” effect. This phenomenon is universal, independent of contact angle, droplet volume, particle size, and particle material. The fundamental understanding of freezing segregation and interfacial flow in multicomponent systems provides crucial insights for controlling microstructure in applications ranging from sea ice properties to cryopreservation, where the redistribution of solutes during solidification critically determines the final material properties and functionality.

Comparing segregation behaviors across ions [18,52], organic solvents [15,48], and nanoparticles [16, 53] reveals a common physical principle: rejection of solutes from the advancing freezing front creates concentration gradients in the residual liquid. However, the fate of rejected species differs fundamentally: dissolved ions generate osmotic pressure and freezing point depression, leading to brine films and ice sprouting [18]; organic solvents reduce surface tension, driving Marangoni flows that produce self-lifting and particle migration [15,48]; and nanoparticles accumulate into a porous matrix at the tri-junction, driving capillary compensating flow analogous to the “coffee ring” effect [16,53]. The resulting morphologies, rounded tips for salts, elevated droplets for ethanol-water mixtures, and flat plateaus for nanofluids, reflect these different physical mechanisms operating on the common foundation of freezing segregation. A universal feedback loop emerges: as the freezing front rejects solutes, concentration gradients drive flow (Marangoni, capillary, or osmotic), which modifies the concentration field ahead of the front, creating a self-reinforcing cycle that determines the final morphology.

2.6 Theoretical and Computational Modeling of Droplet Freezing

Complementing experimental investigations, theoretical and computational modeling has emerged as an indispensable tool for elucidating the coupled multiphysics processes governing droplet freezing. These

approaches range from analytical heat-transfer models to sophisticated numerical frameworks that resolve the interplay among fluid dynamics, phase change, solute transport, and interfacial phenomena.

2.6.1 Governing Equations and Dimensionless Parameters

The fundamental physics of droplet freezing is rooted in the classical Stefan problem, which describes heat transfer during solidification with a moving phase-change interface. For a droplet cooled through substrate conduction, the thermal field is governed by the heat conduction equation in each phase, coupled through the Stefan condition at the freezing front [26]:

$$\rho_s L_f \frac{dR_f}{dt} = k_s \frac{\partial T_s}{\partial r} - k_l \frac{\partial T_l}{\partial r}$$

where ρ_s is ice density, L_f is latent heat of fusion, R_f is the freezing front position, and k_s and k_l are the thermal conductivities of ice and liquid water, respectively. This formulation assumes conduction-dominated heat transfer, a reasonable approximation for sessile droplets where the substrate provides the primary heat extraction pathway [39].

To systematically characterize droplet freezing dynamics, several dimensionless groups have been established. The Stefan number ($Ste = c_p \Delta T / L_f$) represents the ratio of sensible heat to latent heat, with c_p and ΔT being the specific heat capacity of water and degree of supercooling, respectively. The Biot number ($Bi = h_c H / k_l$) quantifies the relative thermal resistance between convective heat transfer at the droplet surface and conduction within the droplet, with h_c and H being the convective heat transfer coefficient and characteristic length scale (typical the droplet height or radius), respectively. The Fourier number ($Fo = \alpha t / H^2$) characterizes the dimensionless time for heat diffusion, with α being the thermal diffusivity of water. These dimensionless parameters provide a systematic framework for interpreting experimental observations and validating numerical models across diverse operating conditions [39,40].

2.6.2 Macro-Scale Numerical Approaches

At the continuum scale, the Volume of Fluid (VOF) method, often coupled with an enthalpy-porosity formulation for phase change, is one of the most widely adopted approaches for simulating droplet impact and freezing [42]. In this framework, a scalar fraction field tracks the liquid-gas interface, while the enthalpy method handles solidification through a mushy-zone treatment where the liquid fraction varies between 0 and 1. Recent parametric studies have shown that the mushy-zone constant A_{mush} requires careful calibration, though the VOF-enthalpy-porosity framework has successfully captured the transition from central-pointy to central-concave freezing morphologies and reproduced self-peeling behaviors observed in impact-freezing experiments [19,42].

Front-tracking and level-set methods explicitly represent the freezing front as a moving interface, offering high accuracy for interface evolution [13]. Level-set methods describe the interface as the zero contour of a signed distance function, naturally accommodating topological changes but requiring reinitialization procedures to maintain numerical stability. Both approaches have been applied to droplet freezing simulations, though they face challenges in capturing the intricate dendritic structures that emerge during recalescence.

2.6.3 Mesoscopic and Phase-Field Methods

The Lattice Boltzmann Method (LBM) has emerged as a powerful alternative for simulating droplet impact and solidification, particularly for supercooled droplets where the metastable state imposes stringent

numerical requirements [30,42]. Unlike macroscopic CFD methods, the LBM solves the enthalpy equation directly to determine the motion of the freezing front, avoiding the calibration of semi-empirical parameters. Recent developments have incorporated enhanced multiphase cascaded LBM schemes for fluid dynamics coupled with multi-relaxation-time schemes for heat transfer, enabling simulations of supercooled droplet impingement and solidification under realistic conditions. These models have successfully reproduced distinct impact outcomes, i.e., full rebound, partial rebound, and full adhesion of supercooled droplets [42].

The phase-field method circumvents the need for explicit interface tracking by introducing continuous order parameters that distinguish phases across diffuse interfaces [30]. For droplet icing simulations, three-phase Allen-Cahn–Cahn–Hilliard–Navier–Stokes phase-field models have been established, where the Allen-Cahn equation captures phase change from water to ice (accounting for latent heat release), while the Cahn–Hilliard equation tracks the water–air interface. This approach has successfully reproduced the formation of the pointy tip, demonstrating that this morphological feature arises primarily from vertical expansion during the freezing process [26,30].

Hybrid approaches have also emerged, such as the hybrid VOF-IBM (Immersed Boundary Method) approach for simulating freezing liquid films and drops, accounting for volume expansion due to density differences between ice and liquid [42]. This approach successfully reproduces tip formation governed by both volume dilatation and surface tension effects, with final droplet shapes showing excellent agreement with experiments.

2.6.4 Challenges and Future Directions

Despite significant progress, several challenges remain. First, the incorporation of nucleation dynamics within macro-scale solidification formulations remains a critical gap: most models assume a spatially uniform or prescribed nucleation event rather than predicting nucleation stochastically based on local supercooling. Second, the coupling between freezing segregation and interfacial flow in multicomponent systems demands more sophisticated treatment of solute transport and its feedback on phase-change kinetics. Third, the simulation of dendritic growth during recalescence requires resolving morphological instabilities at scales ranging from micrometers to millimeters, necessitating adaptive mesh refinement or multiscale approaches. Finally, the role of dissolved gases in bubble formation and its influence on tip angle deviations remains largely unaddressed in computational models [27]. Future developments in holistic mathematical frameworks that rigorously couple heat transfer, mass transport, and phase-change kinetics across multiple scales will be essential for advancing both fundamental understanding and predictive capabilities in droplet freezing applications.

3 Droplet Configurations and Freezing Scenarios

3.1 Sessile Droplets on Supercooled Substrates

The sessile droplet deposited on a substrate maintained below the freezing point represents the most extensively studied scenario in droplet freezing research. Under such scenario, the droplet cools gradually in a quasi-steady manner, and the freezing front propagates from the substrate upward due to conduction-dominated heat transfer, yielding the classical tip singularity as shown in Fig. 4a. This configuration has been the subject of most fundamental studies due to its relevance to natural and industrial icing phenomena, including aircraft icing, frost formation on refrigeration systems, and atmospheric ice accretion.

The substrate temperature profoundly influences the freezing dynamics and final morphology of sessile droplets. Zhang et al. [54] systematically investigated the shape variation and unique tip formation of sessile water droplets during freezing, revealing that the substrate temperature determines the final

frozen morphology through its effect on the solidification rate and heat extraction pathway. At lower substrate temperatures, the freezing process accelerates, producing sharper tips and smaller trapped bubbles due to the rapid solidification that leaves insufficient time for bubble growth. Conversely, at higher supercooling temperatures, slower freezing allows more bubble formation and results in blunter tip angles. Recent synchrotron X-ray imaging studies by Im et al. [27] have directly quantified the relationship between substrate temperature and tip angle, demonstrating that the deviation from the universal tip angle originates from temperature-dependent bubble formation during freezing. Through three-dimensional tomography, they showed that bubble-free frozen droplets produced in vacuum conditions recover the universal tip angle regardless of substrate temperature, confirming that trapped gases are responsible for the observed deviations.

Substrate properties, such as thermal conductivity and wettability, profoundly influence droplet freezing dynamics and final morphology. Zheng et al. [55] demonstrated that while thermal conductivity has only a minor effect on recalescence time, it significantly affects the total freezing time, which is inversely proportional to substrate thermal conductivity. Specially, on high-conductivity substrates ($k_s \geq 10 \text{ W/(m·K)}$), freezing time exhibits an exponential dependence on substrate wettability. Contact angle and roughness strongly influence freezing delay on both conductive and insulating materials, with conductive, smooth, and hydrophobic surfaces identified as most efficient for delaying freezing in unsaturated environments. Hydrophilic surfaces promote droplet spreading into flat profiles with wide bases, while hydrophobic surfaces yield taller, more spherical droplets with pronounced tips. However, the tip angle remains close to the universal value regardless of contact angle, suggesting the local singularity mechanism is robust. Only on topologically-structured surfaces, Yue et al. [56] reported the formation a tip angle of $122 \pm 2^\circ$, significantly smaller than the $136 \pm 3^\circ$ observed on smooth surfaces. Studies on sessile droplets on inclined surfaces have shown that tip asymmetry increases with surface inclination angle, changing from 0° to 15° as the surface angle increases from 0° to 75° [57]. These findings collectively demonstrate that both thermal conductivity and wettability govern the freezing kinetics and morphology, with their relative importance depending on the specific freezing stage and environmental conditions.

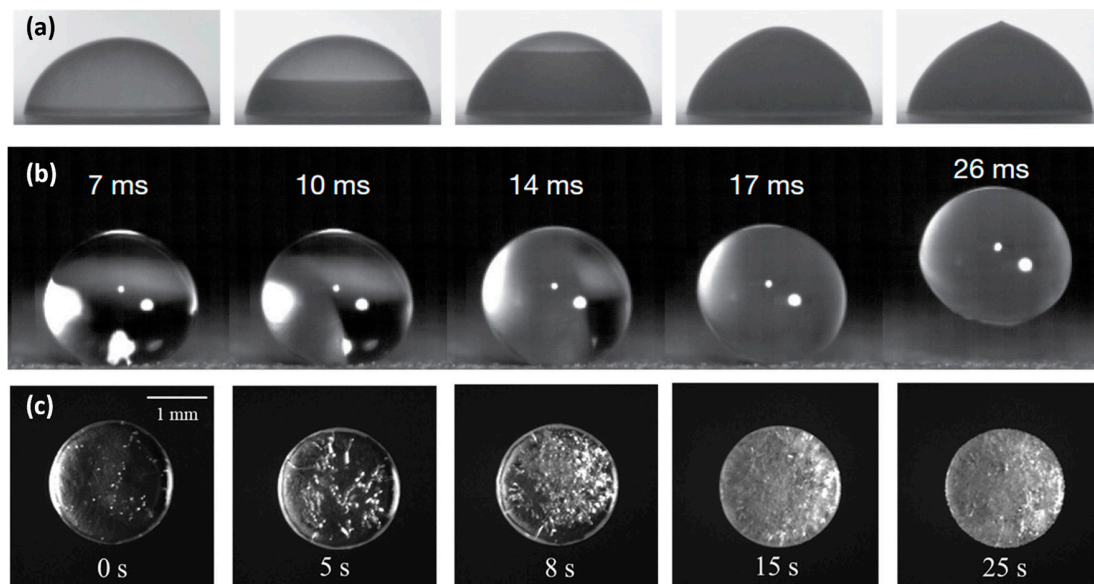


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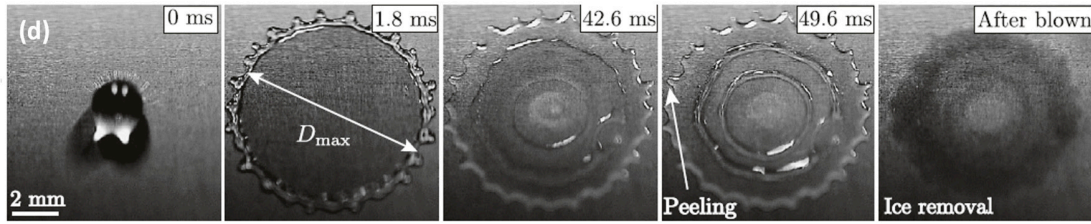


Figure 4: Diverse freezing morphologies and dynamic behaviors of droplets under different scenarios. (a) Freezing dynamics of a sessile droplet on a supercooled substrate [54]; (b) Freezing-induced droplet departure in a supercooled vacuum chamber [23]; (c) Evaporation-induced freezing dynamics of a levitated droplet [58]; (d) Self-cracking of a frozen droplet upon impacting onto a supercooled substrate [19].

3.2 Droplets in Isothermal Supercooled Chambers

When droplets together with carrying substrates rest inside an isothermal supercooled chamber, whether at the standard atmosphere pressure or near vacuum, the freezing dynamics diverge markedly from sessile droplets on supercooled substrates due to the absence of preferential heat extraction through a solid interface. In such scenario, evaporative cooling becomes the dominant mechanism driving the droplet into a supercooled state, fundamentally altering the ice nucleation site and the pathway of freezing front propagation. Jung et al. [37] demonstrated that the freezing process is initiated by either spontaneous homogeneous nucleation near the gas-liquid interface or heterogeneous nucleation at the droplet-substrate contact interface, depending on environmental conditions. For droplets in unsaturated gas environments, rapid evaporation reduces the liquid temperature locally at the free surface, creating a temperature differential of approximately 0.34 K under forced convection conditions. This evaporative cooling can render homogeneous nucleation at the gas-liquid interface thermodynamically preferred over the expected heterogeneous nucleation at the substrate, fundamentally switching the crystallization mechanism. Handa et al. [59] recently investigated 40 μm water droplets introduced into a vacuum, employing high-speed imaging to capture oscillatory distortion reflecting surface tension and viscosity of supercooled droplets, and observed fragmentation upon freezing. Their thermodynamic simulations based on the Knudsen theory allowed determination of homogeneous ice nucleation rates between 232 and 235 K, filling a critical gap in the understanding of ice nucleation in the supercooled regime.

In low-pressure environments, the high vaporization rates experienced by supercooled droplets can induce dramatic self-removal phenomena. Schutzius et al. [23] demonstrated that water droplets resting on superhydrophobic textured surfaces in a near-vacuum chamber can spontaneously levitate and exhibit trampoline-like bouncing behavior, with restitution coefficients greater than unity. They found that this counterintuitive behavior results from an overpressure beneath the droplet produced by fast vaporization, while substrate adhesion and surface texture restrict vapor flow. They further observed that the high vaporization rates and associated cooling can induce freezing from a supercooled state, which triggers a sudden increase in vaporization, since the rapid recalcitrant partial solidification of supercooled droplets is accompanied by a sudden temperature rise to 0°C , and the severely undersaturated environment leads to an explosive increase in vaporization from the droplet surface. This effect can spontaneously remove surface icing by lifting away icy drops the moment they freeze, with fragment velocities of the order of 1 m/s as shown in Fig. 4b. The phenomenon has been observed across diverse superhydrophobic surfaces, including silicon micropillar arrays, etched aluminum, and fluoropolymer-carbon nanofiber composites, demonstrating the generality of the mechanism. Yan et al. [60] recently elucidated the role of vaporization momentum in the self-jumping dynamics of freezing supercooled droplets at reduced pressures, revealing

that the vaporization momentum arises from vaporization at the droplet's free surface, progressed and intensified by recalescence, subsequently inducing droplet compression and finally self-jumping. By incorporating liquid-gas-solid phase changes involving vaporization, freezing recalescence, and liquid-solid interactions, they resolved the vaporization momentum and droplet dynamics, establishing a size-scaled jumping velocity and a nucleation-governed jumping direction.

The self-confinement of a droplet by a rigid ice shell during radially symmetric freezing presents an intriguing mechanical conundrum: the expansion of water upon freezing is incompatible with the confining shell, leading to intermittent fracturing and eventual explosion. Wildeman et al. [38] used high-speed imaging to reveal that this conflict is resolved through an intermittent fracturing of the brittle ice shell and cavitation in the enclosed liquid, culminating in an explosion of the partially frozen droplet. They found that the process unfolds through a sequence of events: after the droplet is completely encapsulated by a solid ice shell, an ice spicule is pushed out from a weak spot in the shell as a first sign of increasing internal pressure due to the expansion of the thickening ice shell. They further proposed a model revealing that for millimetric droplets, fragment velocities are independent of droplet size and depend only on material properties such as the tensile stress of ice and the bulk modulus of water, with a maximum in explosion energy occurring when the ratio of inner to outer radius is approximately 0.57. Their model further predicts that for sub-millimetric droplets, surface tension becomes dominant, and droplets with radii below 50 μm are unlikely to explode at all. These findings are particularly relevant for understanding ice formation in clouds, where fragmentation of freezing droplets can play a role in rapid glaciation and precipitation development, and for designing passive anti-icing surfaces that exploit these self-removal mechanisms.

3.3 Acoustically Levitated Droplets

Acoustic levitation provides a unique environment for studying droplet freezing in the complete absence of substrate contact and contact line pinning, offering invaluable insights into fundamental phase transition dynamics that are otherwise masked by wall effects. In this scenario, the droplet is suspended at a pressure node of a standing acoustic wave, isolated from solid surfaces, with its shape determined by the competition between gravity, surface tension, and acoustic radiation force. Zhang et al. [17] demonstrated that by varying the emitter-reflector distance, the acoustic radiation force exerted on the droplet surface can be tuned, allowing precise control over the droplet's initial shape, from an ellipsoid (aspect ratio $a/b \sim 1.5$) to a flattened liquid disk (a/b up to 8.2). They found that the final frozen morphology depends critically on this initial shape: ellipsoidal droplets freeze into ice saucers, moderately flattened droplets form ice cakes, and highly flattened liquid disks ultimately transform into ice rings. The formation of the ice ring is particularly striking, arising from the atomization rupture of the central liquid film during freezing. They found a Marangoni flow from the droplet center to its periphery progressively thins the central liquid film until capillary waves are excited by parametric resonance with the sound field, ultimately leading to atomization rupture and the formation of a levitated ice ring. This work highlights the coupling between thermodynamically driven phase transitions and mechanically driven droplet dynamics in acoustic levitation, demonstrating that containerless freezing can produce morphologies, such as levitated ice rings that are unattainable on solid substrates.

The containerless environment of acoustic levitation also enables unique evaporation-induced freezing dynamics that are fundamentally different from substrate-mediated freezing. Mitsuno et al. [58] investigated the evaporation-induced freezing of pure cyclohexane droplets levitated in an acoustic field, revealing that rapid evaporative cooling drives the droplet into a supercooled state, followed by a phase transition at a critical point as shown in Fig. 4c. They found that the high vapor pressure of cyclohexane (13.0 kPa at

25°C) leads to rapid evaporation, with the droplet surface temperature dropping below the freezing point (6.5°C) within seconds of levitation. Through simultaneous high-speed imaging and infrared thermography, they observed that the droplet remains in a supercooled liquid state despite being below the freezing point until the temperature reaches a critical threshold, at which point the surface temperature increases due to heat recovery, indicating complete solidification. The transition from supercooling to freezing is affected by acoustic pressure fluctuations, external flow dynamics, and interfacial motion, with the containerless environment facilitating the supercooled state by eliminating heterogeneous nucleation sites on container walls.

Building upon these findings, recent studies have extended acoustic levitation freezing research to more complex systems. He et al. [61] investigated NaCl crystallization in acoustically levitated droplets, revealing that the acoustic field introduces forced convection within the droplet that significantly influences evaporation rate, supersaturation degree, and crystal product morphology. Their comparison between levitated and sessile droplets demonstrated that the decoupling of the crystallization system from surface physical and chemical properties enables *in situ* investigation of early-stage nucleation and crystal growth mechanisms, while highlighting the importance of accounting for acoustic field-induced internal flow that is often neglected in crystallization studies. Furthermore, simultaneous crystallization effects in multiple levitated nanofluid droplets have also been explored [62], revealing that the addition of nanoparticles enhances crystal growth rates through improved mass transfer at the growing freezing front, producing higher instantaneous nucleation pressures and more cracking in the primary ice shell, while nucleation times remain unaffected as freezing is initiated by secondary ice nucleation particles. These findings demonstrate that acoustic levitation freezing research is expanding from pure solvents to complex fluid systems, offering unprecedented opportunities for containerless material synthesis and fabrication. The ability to control droplet shape through acoustic fields, combined with the absence of wall effects, positions acoustic levitation as a powerful platform for investigating fundamental phase transition physics and for developing non-contact fabrication methods for ring-shaped and other advanced materials.

3.4 Impacting and Spreading Droplets

When droplets impact a cold surface, the freezing process couples with fluid dynamics, spreading, and splashing, producing a rich variety of frozen morphologies that depend critically on impact velocity, substrate temperature, and surface wettability. The impact-freezing process is governed by the competition between droplet spreading hydrodynamics and solidification kinetics, where the characteristic spreading time (typically milliseconds) must be compared with the freezing time to determine the final morphology. Zhu et al. [63] systematically investigated the freezing behaviors of deposited water droplets on hydrophilic and hydrophobic aluminum surfaces at low impact velocities (Weber number $We \sim 0.642$), revealing that deposited droplets start to freeze from the liquid–solid interface immediately after the spreading contact line is arrested by the cold surface, without the recalescence stage observed in sessile droplets. They found that the apparent contact angle of deposited droplets follows a scaling law $\theta \propto \Delta T^{1/3}$, independent of surface wettability. Furthermore, the frozen shapes of deposited droplets depend only on surface temperature, while sessile droplets exhibit shapes that change with wettability but are insensitive to temperature.

At higher impact velocities, the coupling between droplet spreading and solidification becomes more pronounced, leading to diverse frozen morphologies. Zhu et al. [64] investigated water droplets impacting on an inclined (45°) superhydrophilic surface under substrate temperatures ranging from -45°C to -25°C and impact velocities from 1.33 to 3.96 m/s. They discovered four distinct frozen morphologies: elliptical cap, half ring + cap I, half ring + cap II, and half ring + single ring, depending upon the competition between

the timescale for the shrinking film to merge and the solidification timescales of the lamella and elliptical pancake. Shang et al. [65] further reported a central-pointy to central-concave icing transition by increasing surface supercooling on hydrophilic surfaces. At higher substrate supercooling, an additional interior circular freezing front emerges from the droplet center, expanding outward and upward, while the exterior front recedes from the edge; the two fronts eventually merge, producing a volcano-like central-concave ice profile. This transition occurs when the heat conduction rate through the droplet exceeds a critical threshold, characterized by a dimensionless factor that reflects the heat conduction rate, and the transition line in the regime map descends with increasing Weber number.

Recent studies have revealed remarkable self-peeling and self-deicing behaviors during droplet impact freezing at high substrate supercooling. Jin et al. [66] reported ultra-low ice-substrate adhesion (0–50 kPa) and spontaneous self-deicing during droplet impact freezing on copper surfaces at supercooling from 30°C to 80°C. They found that the circumferential edge of the frozen droplet detaches from the substrate, leaving an air gap with a maximum peeling height of approximately 60 μm , with peeling initiating immediately after bulk freezing completion. The self-peeling is governed by mechano-thermo-hydraulic coupling: rapid cooling induces thermal contraction that bends the ice lamella rather than generating cracks, facilitated by the instantaneous freezing at the droplet–substrate interface that entraps air and creates gaps. The apparent shear adhesion strength decreases sharply with increasing Weber number and substrate supercooling, reaching ultralow values (<50 kPa) at $We > 90$. A regime map delineates four distinct regimes: peeling with low adhesion, peeling with high adhesion, sticking with low adhesion, and sticking with high adhesion. Fang et al. [19] confirmed self-peeling of frozen water droplets upon impacting cold hydrophobic surfaces, demonstrating that complete self-peeling occurs on hydrophobic surfaces with contact angles $\geq 104^\circ$ as shown in Fig. 4d, while cracking dominates on hydrophilic surfaces. They developed a thermal-mechanical model showing that the peeling time scales as $\tau_p \propto \Delta T^{-2}$. These findings demonstrate that the interplay between impact hydrodynamics and rapid solidification can be harnessed for passive ice removal, offering a promising strategy for anti-icing applications.

The impact of partially frozen binary droplets introduces additional complexity through the interplay between phase transition and hydrodynamic instabilities. Kant et al. [67] investigated the impact of hexadecane-diethyl ether binary droplets that partially freeze from the outside due to evaporative cooling prior to impact on a cold substrate. Using total-internal-reflection imaging, they observed unexpected fingered growth of the solid phase along the substrate, reminiscent of viscous fingering patterns. The instability originates from the accumulation of pre-solidified material at the advancing contact line, locally enhancing flow resistance and creating a mobility contrast that drives particle-induced viscous fingering. The onset of fingering coincides with the lamella ejection time, governed by viscous effects within the expanding lamella, and the emergent patterns exhibit continuous tip splitting and merging of azimuthal undulations. At higher impact velocities ($Re > 550$), the lamella initially lifts off from the substrate, leading to disconnected fingered growth patterns, with the width of the unfrozen annular gap widening monotonically with increasing Re . This work demonstrates that the presence of solidified material at the droplet interface fundamentally alters the impact-freezing dynamics, offering new perspectives for understanding ice accretion from partially frozen rain droplets in atmospheric and aviation applications.

Comparing sessile, isothermal chamber, acoustically levitated, and impacting droplets reveals that while the fundamental mechanisms (nucleation, recalescence, front propagation) remain the same, their relative importance depends on thermal boundary conditions. In sessile droplets, conduction through the substrate dominates, producing the classical tip singularity [14,26]. In isothermal chambers, evaporative cooling dominates, switching nucleation modes and inducing self-removal [23,37]. In acoustic levitation,

the absence of substrate contact enables container-less studies and produces ice rings unattainable on solid surfaces [17]. In impacting droplets, competition between spreading time and freezing time governs morphology [63,64]. The tip singularity ($\sim 136^\circ$) represents a reference state achieved when conduction is the sole rate-limiting process. Deviations from this universal behavior, whether tip rounding, self-lifting, or ice rings, provide a quantitative measure of the importance of additional mechanisms (solute segregation, Marangoni flow, or altered heat transfer pathways).

4 Composition Effects on Droplet Freezing Morphology

4.1 With Dissolved Gas

Air, together other types of gases, is widely present in water as a dissolved phase. Upon freezing, dissolved gases are rejected from the ice lattice and accumulate at the advancing freezing front to form bubbles, a phenomenon that fundamentally alters the freezing dynamics and final frozen morphology. Chu et al. [68] systematically characterized the bubble formation process across a large spectrum of drop sizes, from micrometre-sized condensed drops to millimetre-sized sessile drops. They demonstrated that while dendritic ice formation in the recalescence stage hardly rejects any gas, most bubbles are formed during the isothermal stage where the planar freezing interface interacts with gas molecules, leaving isolated bubbles either engulfed or rejected. They also proposed a theoretical model correlating the bubble formation rate with influencing factors including the degree of supercooling, drop contact angle, and gas solubility. Li et al. [69] further investigated the effect of dissolved gas on the nucleation and growth of ice crystals in freezing droplets at various gas concentrations as shown in Fig. 5a. They found that dissolved gas acts as a heterogeneous medium, promoting the nucleation of liquid droplets at a significantly lower degree of supercooling compared with pure water droplets. During the freezing process, the existence of bubbles alters the solid-liquid density ratio and changes the shape of the droplets. A quantitative analysis of the tip angles revealed that the tip angle of the frozen ice droplet decreases with increasing gas concentration, and the presence of bubbles promotes the growth of the initial frost crystal.

The growth and morphology of gas bubbles trapped in ice have been extensively elucidated by recent theoretical and experimental studies. Meijer et al. [51] elucidated the initial growth dynamics of gas bubbles near an advancing freezing front through a combined experimental and numerical approach. They demonstrated that bubble growth is governed by diffusion and is enhanced by the presence of a background gas concentration gradient combined with the motion of the approaching freezing front. By recasting the problem into mass transfer to a moving spherical object in a homogeneous concentration field, they found good agreement between experimental data and existing scaling relations, highlighting the delicate interplay between mass transfer rate and freezing rate in dictating final bubble shapes and sizes.

The presence of dissolved gases and the resulting bubble formation have profound implications for the thermal and mechanical behavior of freezing droplets. Bubbles trapped within the ice matrix act as effective thermal insulators due to the low thermal conductivity of air, locally altering heat transfer pathways and influencing the propagation of the freezing front [51,68]. This localized thermal resistance can create temperature gradients that further modify the dendritic growth patterns and the final frozen morphology. Moreover, the volumetric expansion associated with bubble formation contributes to internal pressure buildup within the droplet, which can lead to cracking or fragmentation of the ice shell, particularly during rapid freezing events. The interaction between bubble growth and the advancing freezing front represents a complex feedback loop: as bubbles nucleate and grow, they alter the local concentration field and thermal environment, which in turn affects the kinetics of ice growth and the rejection of additional dissolved gases. Understanding these coupled phenomena is essential for predicting the freezing behavior of gas-

containing droplets in natural and industrial contexts, from atmospheric ice formation to cryopreservation and freeze-drying processes.

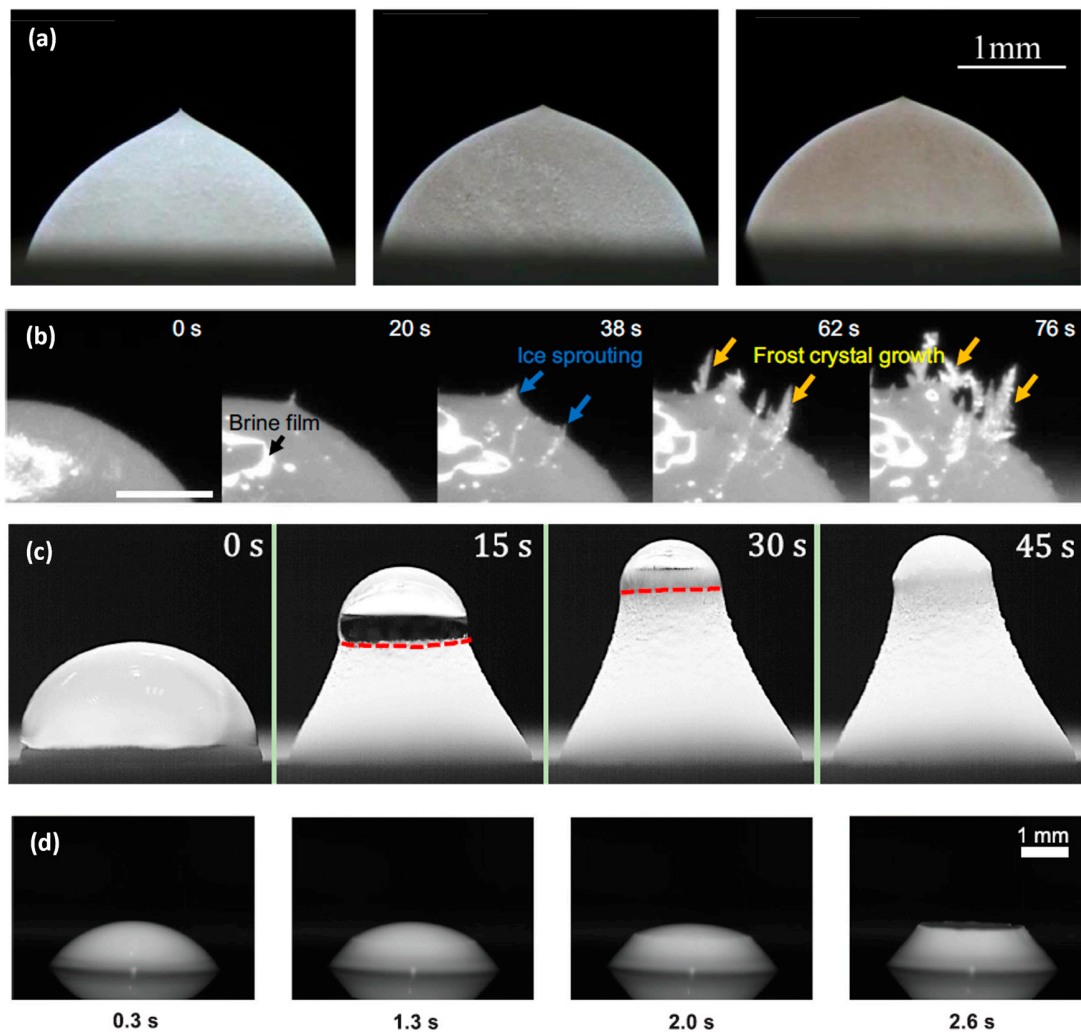


Figure 5: Composition-driven morphological transitions in freezing droplets. (a) Opacity of frozen water droplets with different gas concentration [69]; (b) Ice sprouting dynamics of a freezing brine droplet [18]; (c) Lifting of a freezing binary droplet on a supercooled substrate [15]; (d) Formation of a plateau for the freezing a nanofluid droplet [16].

4.2 With Ionic Components (Salts)

The presence of ionic components fundamentally alters the freezing behavior of water droplets, affecting not only the thermodynamic properties such as freezing point depression, but also the morphological evolution during solidification. Boulogne and Salonen [70] investigated the effect of NaCl on the conical angle of frozen sessile droplets at extremely dilute concentrations ranging from 10^{-3} to 10^{-8} M. They observed a sharp increase in the conical angle with increasing salt concentration, attributing this trend to the enhanced electrical conductivity resulting from the dissociation of sodium and chloride ions. At considerably higher salinity levels, Singha et al. [71] reported that the characteristic two-stage freezing process observed in pure water droplets disappears entirely in saltwater droplets. Although freezing point

depression introduces a substantial delay in ice nucleation, the most significant morphological change is the progressive loss of the tip singularity; the sharp apex becomes increasingly rounded and eventually vanishes when the salinity exceeds 0.4 M. This suppression of the freezing singularity has been attributed to ion exclusion at the advancing freezing front, which modifies local freezing point depression and promotes irregular front morphologies.

The dynamics of recalescent freezing are also strongly influenced by dissolved salts. Bauerecker et al. [72] employed acoustic levitation to monitor the freezing of saline droplets at various concentrations. While a pure water droplet nucleates at -24°C with a planar freezing front propagating at 0.12 m/s, a 1M NaCl solution nucleates at -30°C and exhibits an explosive, barrel-shaped ice cloud with a propagation velocity only one-quarter of that of pure water. Further increasing the salt concentration to 3M results in a similarly drastic reduction in propagation velocity. The supercooling capacity of salt solutions is not only concentration-dependent but also ion-specific. Lü and Wei [73] compared NaCl and KCl solutions and found that while both exhibit linearly enhanced supercooling with increasing concentration, NaCl solutions achieve 2–3 times greater supercooling than KCl at equivalent concentrations. Emelyanenko et al. [74] extended this investigation to other alkali metal chlorides, further confirming the ion-specific nature of supercooling behavior, which arises from differences in cation hydration structures and their effects on water ordering at the ice-liquid interface.

Beyond the changes in freezing dynamics and supercooling capacity, the presence of salts also gives rise to unique interfacial phenomena that fundamentally distinguish salty droplet freezing from that of pure water. Chu et al. [18] provided comprehensive insights into salty droplet icing through combined experiments, theory, and molecular dynamics simulations, revealing that salty droplet freezing is governed by salt rejection accompanied by ice crystal growth, resulting in freezing dynamics distinct from pure water. They demonstrated that ice crystals grow throughout the entire process while brine is repelled and concentrated gradually, making the boundary between nucleation/recalescence and the isothermal freezing stages no longer obvious. Unlike pure water droplets that form a pointy tip, salty droplets exhibit a liquid brine film on top after the isothermal freezing stage, inside which ice crystals sprout, grow, and eventually puncture the film, a phenomenon termed “ice sprouting” as shown in Fig. 5b. The ice sprouting mechanism was revealed to be governed by condensation at the brine film free interface: water vapor in humid air condenses on the brine film, diluting it and triggering ice precipitation to re-saturate the brine film.

Instead of simple salt solutions, ionic components in complex mixtures also affect freezing morphology. Dang et al. [75] studied the freezing characteristics of urine droplets, complex mixtures of various inorganic and organic salts, and found that during supercooling, the droplet gradually turns white due to the precipitation of inorganic salts, with the nucleation site becoming difficult to identify during recalescence. Upon complete solidification, the frozen urine droplet exhibits a more rounded tip compared to the sharp apex of a frozen pure water droplet. Sun et al. [76] demonstrated that salt-saturated water and propylene glycol microdrops deposited on supercooled substrates can absorb ambient moisture that would otherwise condense and freeze, thereby maintaining ice-free regions for extended periods. These findings collectively demonstrate that ionic components not only suppress the tip singularity and alter freezing kinetics but also introduce ion-specific effects that can be exploited for morphological control and anti-icing applications.

4.3 With Miscible or Immiscible Liquids

Liquid mixtures are ubiquitous in both natural and industrial settings, and understanding their freezing characteristics is of fundamental and practical importance. Miscible fluids can be readily mixed with water across a wide spectrum of volume concentrations, giving rise to complex freezing behaviors driven by

solute redistribution and interfacial flows. Wang et al. [15] investigated the freezing characteristics of water-ethanol binary drops using high-speed imaging, revealing a counterintuitive self-lifting behavior that results in a noticeable increase in droplet height during freezing as shown in Fig. 5c. They attributed this anti-gravitational flow to an internal solutal Marangoni flow triggered by the enrichment of ethanol near the advancing freezing interface, which elevates the droplet as solidification progresses. Zeng et al. [77] extended this work to more complex acoustically levitated ternary mixtures containing hexadecane, ethanol, and diethyl ether. During the evaporative cooling-induced freezing process, they observed three distinct successive stages, referred to as the “Ouzo state”, “Janus state”, and “Encapsulating state”, which are characterized by unique phase separation and morphological transitions.

The freezing of polymer solutions introduces additional complexity through the interaction between polymer chains and the advancing freezing front. Kharal and Louf [78] investigated the unidirectional freezing dynamics of polyvinyl alcohol (PVA) solution droplets, demonstrating that polymer addition enables manipulation and even suppression of the pointy tip formation observed in pure water. The tip sharpness decreases with increasing polymer concentration until completely disappearing above the overlap concentration (~1.5 wt%), while the total freezing time increases concomitantly under the same supercooling conditions. By combining geometrical arguments with heat flux measurements, they developed a theoretical model that captures the spatial and temporal evolution of polymer droplets, revealing that adding PVA modifies thermal properties without altering the fundamental physics controlling freezing time. This behavior stems from the freeze-induced swellability of the solution being controlled by the PVA hydration number, which transitions at the overlap concentration. The adsorption of polymer molecules on the ice surface creates a physical barrier restricting ice crystal growth, thereby reducing the volume expansion upon freezing.

The freezing of suspension drops in immiscible fluids mixed with water, often with the assistance of surfactants or homogenizers, has also attracted significant research attention. Hauptmann et al. [79] experimentally studied the freezing and thawing characteristics of water-in-oil emulsions, observing that at ambient temperature, the water/oil mixture appears featureless even at the microscale. Under deep supercooling, a dark branch made of solidified water drops becomes visible. As reheating proceeds, some sharp structures disappear due to edge-melting, and upon further heating to room temperature, all solid phases melt and merge into discrete drops. These findings collectively demonstrate that the presence of miscible or immiscible liquids introduces complex physicochemical interactions, ranging from solutal Marangoni flows to polymer-induced tip suppression that fundamentally alter the freezing dynamics and final morphology of droplets.

4.4 With Nanoparticles

The presence of suspended nanoparticles fundamentally alters droplet freezing dynamics through mechanisms that are directly observable via optical microscopy, distinguishing this system from the freezing segregation of dissolved species. Ivall et al. [80] examined the freezing and melting behavior of sessile drops containing multiwall carbon nanotubes (MWCNTs), observing slower freezing rates and the emergence of a concentration gradient perpendicular to the freezing interface upon complete solidification. Notably, even after thawing, substantial MWCNT clusters persisted atop the droplet surface. Extending their investigation to more concentrated suspensions, they [81] later found that the freezing outcome depends critically on the degree of supercooling: at low supercooling, MWCNTs are largely expelled from the ice phase and remain suspended in the residual liquid; at high supercooling, the nanotubes become trapped within the

solid matrix. The advancing freezing front destabilizes the dispersed nanotubes, promoting the formation of large particle agglomerates due to compromised dispersion stability.

Beyond particle segregation and accumulation, recent investigations have uncovered remarkable morphological transitions in freezing nanofluid droplets. Zhao et al. [16] investigated TiO_2 nanofluid droplets and discovered that even at a dilute particle concentration of 0.05 vol%, the characteristic pointy tip is supplanted by a flat plateau as shown in Fig. 5d, with the plateau dimension expanding monotonically with particle loading. Through systematic variation of particle material, size, droplet volume, and surface wettability, they established the universal nature of this plateau formation. To elucidate the underlying mechanism, Zhang et al. [30] developed a lattice Boltzmann model that captures the expulsion of particles from the advancing freezing front, their accumulation at the tri-junction, and the resultant capillary-driven flow that redistributes liquid toward the droplet periphery, with simulations confirming that the plateau size is independent of the initial contact angle. Miao et al. [53] compared the freezing of sessile versus deposited nanofluid drops under identical supercooling and freezing front velocity, demonstrating that the frozen morphology, whether singular tip or flat plateau, can be selectively produced by simply tuning the thermal condition at nucleation onset. Hele-Shaw cell experiments revealed that this morphological bifurcation arises from the interplay between nanoparticles and dendritic ice structures: microcells formed by dendritic ice disrupt global freezing segregation, thereby promoting plateau formation.

Building upon these fundamental insights, Jiang et al. [29] introduced an innovative three-dimensional shaping strategy by combining nanoparticle-induced plateau formation with wettability-patterned substrates. By anchoring the contact line of a nanofluid drop using predefined two-dimensional polygonal patterns, they achieved versatile out-of-plane shape control, with the top plateau of a frozen “triangle” nanofluid drop transitioning sequentially from an initial triangle through a hexagon and a counter triangle to a final hexagon as the drop height increased. For a given drop height and corresponding plateau shape, the plateau size could be further modulated by adjusting particle concentration. Their theoretical analysis, grounded in the assumption that the liquid confined within polygonal contact lines behaves as an assembly of multiple slices with varying contact radii and a shared axis, successfully explained the observed shape evolution for both triangular and square base patterns. Their work demonstrates that the combination of nanoparticle addition and wettability patterning enables precise control over both in-plane and out-of-plane droplet shapes, offering a promising low-cost fabrication method for three-dimensional microstructures.

The manipulation of nanoparticles via external fields introduces additional avenues for controlling freezing morphology. Zhang et al. [82] demonstrated that magnetic fields can actively reshape ferrofluid droplets during solidification, with the field orientation dictating whether the droplet elongates or flattens, thereby modulating both freezing time and final droplet height. Fang et al. [19] further developed numerical and scaling analyses to quantify the relationship between magnetic field characteristics and droplet morphology evolution. They established that the magnetic force arising from field gradients dominates over magnetization effects, driving either droplet flattening or elongation under magnetic squeeze or lift conditions. In the low magnetic strength regime, the droplet height exhibits a nearly linear dependence on field strength, transitioning to a nonlinear scaling behavior under high magnetic squeeze conditions. Collectively, these investigations demonstrate that nanoparticle incorporation not only eliminates the tip singularity and generates flat plateaus but also enables active morphological control through external fields and wettability patterning, offering versatile strategies for droplet-based additive manufacturing and microstructure engineering.

4.5 Special Cases: Bubbles and Liquid Marbles

Recent investigations have uncovered intriguing freezing phenomena in specialized droplet configurations where additional interfaces or confining structures fundamentally alter the solidification dynamics, yielding behaviors distinct from conventional sessile, levitated, or impinging droplets. Ahmadi et al. [21] explored the freezing behavior of soap bubbles deposited on supercooled surfaces, revealing a captivating “snow globe effect” characterized by swirling ice crystals that detach from the advancing freezing front and circulate along the free interface. This phenomenon arises from a strong Marangoni flow driven by temperature gradients along the bubble surface, which dislodges and entrains growing ice crystals from the base of the bubble. The resulting dynamic crystallization process produces a visually striking pattern of mobile ice particles that persist until complete solidification as shown in Fig. 6a, demonstrating how the thin-film geometry of a bubble introduces unique flow-crystallization coupling not observed in bulk droplets.

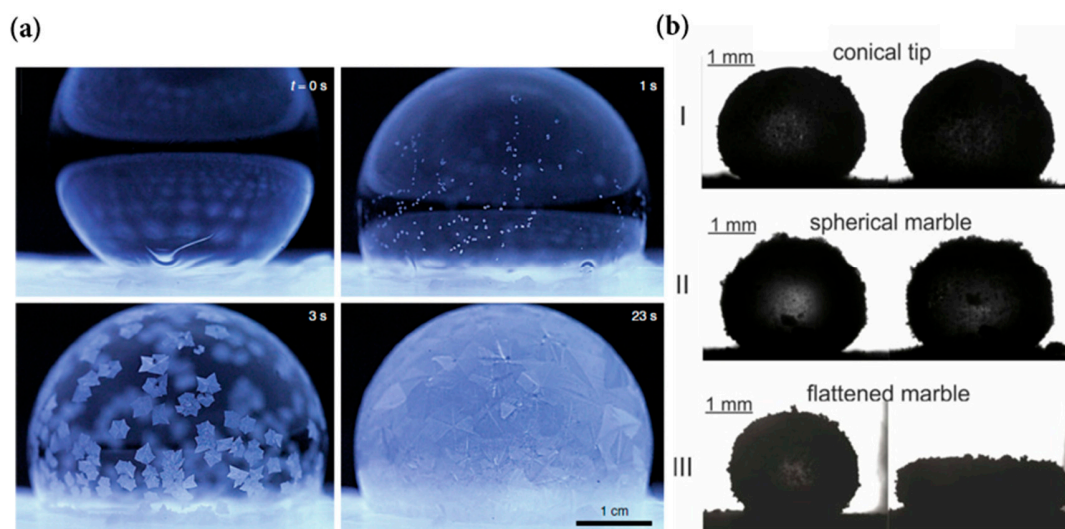


Figure 6: Freezing of special droplet configurations: liquid marbles and soap bubbles. (a) Freezing dynamics of a soap bubble deposited on an ice disk [21]; (b) Transition of liquid marbles to crystallized marbles of three distinguished shapes [83].

The freezing of liquid marbles, i.e., droplets are encapsulated by a shell of hydrophobic nanoparticles, presents another fascinating class of special cases where the confining particle layer profoundly influences morphological evolution. Hashmi et al. [20] documented a remarkable shape transformation during the freezing of liquid marbles, wherein the droplet transitions from a truncated sphere to a flying-saucer morphology. This deformation arises from Marangoni convection driven by solute or temperature gradients, which directs the remaining liquid to flow laterally around the frozen core, thereby reshaping the overall droplet geometry. Building upon this work, Starostin et al. [83] systematically characterized the freezing outcomes of liquid marbles, identifying three distinct final morphologies as shown in Fig. 6b: a conical tip reminiscent of pure water droplets, a spherical marble where the particle shell maintains the initial curvature, and a flattened marble where the frozen core is surrounded by a thin liquid layer that subsequently solidifies. The emergence of these distinct shapes underscores the critical role of the encapsulating particle shell in modulating heat transfer, confining volumetric expansion, and redirecting internal flows during solidification. Their recent studies have extended this understanding by revealing how asymmetric cooling conditions affect the orientation of the freezing tip in liquid marbles [84,85]. When cooled asymmetrically,

the freezing tip deviates from the vertical axis due to preferential freezing front propagation along the direction of enhanced heat extraction. The deflection angle depends on both the degree of cooling asymmetry and the surface wettability: on hydrophilic surfaces with large contact areas, symmetric heat extraction preserves tip alignment, while on hydrophobic surfaces with smaller contact areas, the tip becomes more susceptible to deflection. These findings demonstrate that the interplay between thermal boundary conditions and surface wettability governs not only the final morphology but also the spatial orientation of the freezing tip, offering new strategies for directional control of solidification in droplet-based applications.

Collectively, these special cases highlight how the presence of additional interfaces, whether a thin soap film or a particle-laden shell, introduces new physical mechanisms that fundamentally alter the freezing pathway and produce morphologies not attainable in conventional droplet systems. The liquid marble studies further reveal that beyond the shell confinement itself, the thermal boundary conditions and substrate properties can be exploited to achieve directional morphological control, an insight with potential implications for freeze-casting, additive manufacturing, and droplet-based microfluidics where precise spatial control over solidification is essential.

5 Conclusions and Future Directions

5.1 Conclusion

This review has systematically examined the morphological evolution of freezing water droplets across fundamental physical mechanisms, diverse droplet configurations, and varying compositions, revealing the rich interplay of heat transfer, phase-change kinetics, solute redistribution, and interfacial phenomena.

Fundamental Mechanisms: The freezing process is governed by a hierarchy of mechanisms spanning from nucleation to complete solidification. The degree of supercooling serves as the primary thermodynamic parameter, determining nucleation driving force, recalescence rate, and subsequent morphological evolution. Classical nucleation theory provides the framework for understanding ice formation, validated by recent experimental evidence on critical nucleus size. Following nucleation, recalescence and dendritic growth dominate the early stages, establishing the initial microstructure that serves as a scaffold for subsequent growth. The isothermal freezing stage proceeds three orders of magnitude slower, governed by heat-transfer-limited considerations where the freezing front adopts a geometry perpendicular to the gas-liquid interface. This heat-transfer-limited front propagation, coupled with the unique 9% volumetric expansion upon freezing, drives the classical conical tip formation through the perpendicularity condition between the ice-water and air-water interfaces. Vapor transport during recalescence produces frost halos when the heat transfer timescale exceeds the vapor diffusion timescale on low-conductivity substrates. In multicomponent systems, solute or particle segregation at the advancing front drives interfacial flows, whether Marangoni, capillary, or osmotic, that fundamentally alter the final morphology through concentration-gradient-driven redistribution of the residual liquid. This causal hierarchy reveals how each mechanism contributes to the observed morphological diversity: nucleation and recalescence determine the initial microstructure; heat-transfer-limited propagation with volume expansion produces the conical tip; vapor transport generates frost halos; and segregation-driven flows produce rounded tips, flat plateaus, self-lifting, and ice sprouting depending on the nature of the solute.

Droplet Configurations: The freezing pathway depends critically on droplet configuration and thermal boundary conditions. Sessile droplets on substrates exhibit conduction-dominated freezing with classical tip formation. Droplets in isothermal chambers experience evaporative cooling as the dominant mechanism, switching nucleation modes and inducing self-removal phenomena. Acoustically levitated droplets eliminate wall effects, enabling controlled shape manipulation and unique morphologies such as

ice rings. Impacting droplets exhibit diverse frozen morphologies governed by competition between impact hydrodynamics and rapid solidification, producing elliptical caps, half rings, central-concave profiles, and self-peeling behaviors at high supercooling.

Composition Effects: Solute addition fundamentally alters freezing morphology through segregation and interfacial flow. Dissolved gases form bubbles that act as nucleation sites and reduce tip angles. Ionic components suppress the tip singularity through ion exclusion and generate ice sprouting from brine films. Miscible liquids drive solutal Marangoni flow, producing self-lifting and particle migration. Polymer solutions enable manipulation of tip formation through freeze-induced swellability. Nanoparticles produce flat plateau formation through capillary-driven compensating flow, while wettability patterning enables three-dimensional shape control. Special cases such as soap bubbles and liquid marbles exhibit unique behaviors driven by Marangoni flow and particle shell confinement.

Synthesizing findings across configurations and compositions as shown in Table 1 reveals three unifying principles. First, the freezing pathway follows a universal sequence, nucleation, recalescence, isothermal freezing, and cooling, but the relative importance of each stage depends on boundary conditions. In sessile droplets on conductive substrates, the isothermal stage dominates, producing the classical tip. In evaporatively cooled droplets, recalescence becomes more prominent. In impacting droplets, cooling overlaps with spreading, freezing hydrodynamic instabilities. Second, the tip singularity is a robust reference morphology arising from the perpendicularity condition under conduction-dominated heat transfer. Deviations, rounded tips for salts, flat plateaus for nanoparticles, self-lifting for ethanol-water mixtures, and ice rings for levitated droplets, occur when additional mechanisms (solute segregation, capillary flow, solutal Marangoni, or altered heat transfer) compete with conduction-limited front propagation. The nature of the deviation reveals the dominant mechanism. Third, freezing segregation is a common thread across all multicomponent systems, manifesting through thermodynamic (freezing point depression), hydrodynamic (Marangoni flow), or capillary (particle accumulation) effects. This unified framework provides a foundation for predicting and controlling freezing morphology across diverse applications.

Table 1: Synthesis of dominant mechanisms and morphological outcomes.

System (Configuration and Composition)	Dominant Mechanisms	Morphological Signature	Reference No.
Pure water, sessile	Conduction-limited front propagation	Sharp conical tip ($\sim 136^\circ$)	[21,27,54]
Pure water, sessile (with dissolved gas)	Gas rejection + bubble formation	Reduced tip angle, opaque ice	[28,68,69]
Pure water, impacting	Competition: spreading vs. freezing	Self-peeling, rings, concave profiles	[19,64–66]
Pure water, levitated	Evaporative cooling	Ice rings, saucers, cakes	[16,58]
Saltwater, sessile	Ion exclusion	Rounded tip, ice sprouting	[17,52,71]
Nanofluid, sessile	Particle segregation	Flat plateau	[12,31,53]
Organic-water mixture	Solutal Marangoni flow	Self-lifting, migration	[18,48]
Liquid marble	Particle shell confinement	Deflected tip, flying-saucer morphology	[14,83–85]

5.2 Future Research Directions

Despite significant advances, several key challenges remain. Future research should focus on five interconnected areas:

Holistic Mathematical Models: Comprehensive frameworks coupling heat transfer, mass transport, and phase-change kinetics across multiple scales are needed. These models must incorporate stochastic nucleation, anisotropic ice growth, and feedback between solute redistribution and interface morphology. Machine learning approaches offer promising avenues for accelerating simulation and predicting freezing morphology.

Advanced Experimental Characterization: Advanced *in situ* techniques are essential for probing freezing dynamics with high spatial and temporal resolution. Synchrotron X-ray microscopy and ultrafast imaging should be extended to multicomponent systems with real-time chemical mapping. Acoustic levitation and containerless methods should be extended to more complex compositions. The role of dissolved gases in modifying tip angle and internal structure warrants further investigation.

Multicomponent System Dynamics: The coupling between freezing segregation and interfacial flow represents a frontier of current research. Solute rejection and Marangoni convection in organic solvent-water systems require systematic investigation. Ion-specific effects on nucleation and freezing dynamics demand further elucidation. Nanoparticle segregation dynamics must be characterized across particle sizes, concentrations, and material types to enable rational design of freeze-cast materials.

Extreme Conditions: Droplet freezing under extreme conditions, such as highly supercooled substrates, high pressure, microgravity, and rapid cooling rates, remains largely unexplored. Research should investigate supercooling limits, homogeneous nucleation transitions, and novel freezing morphologies. Microgravity experiments offer unique opportunities for fundamental studies of capillary-driven freezing dynamics.

Bridging Fundamentals to Applications: Insights must be translated into design guidelines for anti-icing surfaces, freeze desalination, cryopreservation, and additive manufacturing. Scalable strategies for controlling freezing morphology through surface engineering, compositional design, and external field manipulation are needed. Sustainable applications require systematic investigation under realistic conditions. By bridging fundamental understanding with practical applications, the next decade of research will advance both scientific knowledge and technological innovation.

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