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Control of Ice Nucleation for Subzero Food Preservation

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Abstract
Freezing processes have long been employed for the preservation of foods, providing minimum nutrition loss with a long shelf life period. Freezing plays an essential role in ensuring the safety of food products in all regions of the world. Nonetheless, slow freezing rates and frequently freezing/thawing lead to permanent physicochemical changes, damage of structure, degradation of nutrition values, and color changes through the formation of large ice crystals in food matrix during the cold storage. The size of ice crystals is highly related to the duration of phase transition and degree of supercooling. This paper reviews that the degree of supercooling and nucleation temperature can be controlled by positive or negative pressure and vibration of the dipole and dipole rotation water molecule techniques. Controlling nucleation temperature and suppression of ice crystals in the food matrix could not be achieved by current freezing methods such as air blast, contact, and immersion freezing in the food industry. These present freezing methods are especially focused on increasing the heat transfer rate in foods. Rapid freezing technology may depend on the size and shape of food. However, the size of ice crystals and the suppression of nucleation could be achieved by alternative freezing technologies to overcome the drawbacks of current freezing technologies in the food industry. Conventional freezing technologies can be replaced by emerging freezing techniques, ultrasound irradiation, high pressure, electric field, magnetic field, and microwave-assisted freezing to control the properties of the nucleation and degree of supercooling in the food industry.

Keywords Freezing process · Ultrasound · High pressure · Electric and magnetic fields · Microwave · Supercooling preservation

Abbreviations

Symbol	**Description**
CAS	Cell alive system
CNT	Classical nucleation theory
HNT	Homogenous nucleation temperature
HFT	Heterogeneous freezing temperature
ATLA	Automatic lag time apparatus
FUP	Freezing under high pressure
PSF	Pressure shift assisted freezing
MF	Magnet field
EF	Electric field
PEF	Pulsed electric field
SEF	Static electric filed
SMF	Static magnetic field
CA	Cryoprotectant agents
SEM	Scanning electron microscope
OMF	Oscillating magnetic field
RF	Radio frequencies

Introduction

Perishable foods need proper temperature-controlled environments during storage, transportation, and sales processes to assure food quality and minimize nutrient loss so that the food available for consumption meets consumer's quality expectation. With the rising accessibility of food markets and broader integration of food supply chains throughout the world, the assurance of food quality has become a major concern. Numerous circumstances can occur where fresh produce is exposed to inappropriate storage conditions, resulting in undesired changes in color, odor, and texture, leading to an overall decrease in food quality. A continuation of food quality loss in one or more of the quality parameters eventually renders the product unacceptable. Moreover, improper food storage has a direct and negative impact on the economic value of food products, causing a waste of resources used in production such as land, water, energy, and other inputs. Thus, the maintenance of food quality during the food supply chain would

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help to improve the efficiency of the food distribution system and increase access to consumers [1].

Freezing preservation retains the quality of food products over long storage periods. Freezing is generally regarded as a superior method of long-term preservation for fruits and vegetables compared to canning and curing with respect to sensory attributes and nutritive properties [2]. Nonetheless, the consequences of freezing and thawing remain a significant problem in the quality of food products. During the freezing process, water crystallization can result in irreversible damages to tissue structures [3, 4]. Freezing also manipulates the sensory properties of foods that are consumed after deliveries and storages. Improvements in low-temperature preservation have made international trades of perishable foods possible. Food industries are continually making efforts for innovation of freezing technologies to serve products to the consumer that are not only safe, fresh, and delicious but also minimally processed, nutritious, and stable [5]. Bringing all these attributes into a food product and keeping the product as inexpensive as possible for the consumers are significant challenges for today's food technology industries.

Due to the demand for fresh fruits and vegetables, a variety of freezing systems have been developed for adequate storage of produces at a constant low temperature for a short period of time [6]. Commercial freezers have been designed based on the properties of fresh produce. Although current freezing systems offer many advantages, there still exist losses of food qualities during frozen storage. The physical aspects in consideration include low surface heat transfer (air blast freezer), dilution of the solution with the product, and limitation on regular-shaped materials (contact freezer) and high operating cost (cryogenic freezer) [7]. Damage caused to fruit and vegetable tissues are irreversible and depend on storage time-temperature conditions and product types.

Within general freezing storage, the undesirable chemical changes and nutritional quality deterioration include insolubility protein, lipid oxidation and hydrolysis, natural pigment degradation, vitamin deterioration, and brown pigment formation [8–13]. Particularly in fruits and vegetables, textural changes throughout frozen storage can give rise to structural alteration of protein membranes and disruption of cellulosic cell walls due to ice crystal growth [14]. To overcome these technical issues, some emerging methods have been developed to control ice crystallization during freezing.

Thus, it is critical to control the size and location of ice crystals within food products under proper storage conditions with a constant subfreezing temperature. Research efforts have been made to shorten the phase transition time, increase the degree of supercooling, and maintain temperature stability during freezing storage. Alternative techniques have also been developed, such as ultrasound-assisted food freezing [15–18], high-pressure food freezing [19, 20], ice-nucleating protein [21], anti-freeze proteins [22], superchilling technology [23], and Cell Alive System (CAS) technology ("Cell Alive System (CAS) technology for the idealistic food") [24]. Both an electric field (EF) and magnetic field (MF) have been introduced for the extension of supercooling or application of quick freezing to the food sample in 2011 [25]. The combination of an external EF and MF has a great potential to influence ice formation through non-thermal mechanisms and could also be the preferred method to achieve rapid and uniform ice formation. However, at present, very little research has been carried out on the combination of external static EF and MF.

Freezing Theory

A phase transition in a sample occurs due to the development of a supersaturated state caused by changes in chemistry, pressure, temperature, and other physical conditions such as electromagnetic fields or acoustic waves [26–28]. Freezing is an example of a phase transition from liquid to solid due to changes in temperature. In general, ice nucleation in supercooled liquid can be occurred by homogeneous and heterogeneous. Homogeneous nucleation occurs in homogenous particle-free supercooled liquids when thermal fluctuations in the molecular arrangement can lead to spontaneous formation of a stable structure that serves as the critical nucleus without the involvement of foreign substances. Homogeneous nucleation does not occur in most systems because it requires very large supercooling degrees; however, it is basically taken into consideration in theoretical approaches due to the complexities of nucleation. [29, 30]. Advances in the field have led to the widely used classical nucleation theory (CNT) developed by Becker and Döring, Band and Frenkel [31–33]. The theory attempts to describe the freezing process in terms of a freezing rate (°C/h) via thermodynamic and kinematic components of a sample (e.g., water). The freezing rate given by CNT can be better understood as the rate of cluster formation in a known volume of sample leading to complete phase change. The use of CNT has been limited to simple systems with well-defined thermodynamic and kinematic components. Uncertainties associated with these parameters can lead to large uncertainties in freezing rates estimated by CNT. For example, Ickes et al. (2015) have shown a minor difference of 0.5% within thermodynamic parameter led to a 94% uncertainty in the freezing rate given by CNT [34]. In addition, CNT fails to account for other factors which influence freezing such as interaction potentials, solvent/impurities, influences, and mechanisms of nucleation. Thus, to better understand the freezing process, alternative nucleation theories such as dynamical nucleation theory, diffuse interface theory, and density functional theory have been developed; however, CNT remains the most popular model used in nucleation related research despite its limitations.

Most fundamental research associated with freezing has focused upon homogenous nucleation; however, in practice, achieving homogenous nucleation is very difficult. This type of cluster formation often requires a highly supersaturated state within the test sample. For example, liquid water's homogenous nucleation temperature (the temperature required to induce homogenous nucleation, HNT) for freezing is roughly − 39 °C [29], with a tendency to be slightly volume dependent. Under laboratory conditions, homogenous nucleation can be observed with ultrapure samples of water within the microliter to pico-liter range. Hence, it is widely believed most if not all types of nucleation encountered in the laboratory or elsewhere is non-homogenous.

Heterogeneous freezing or practical freezing has been hypothesized to occur in four separate ways: contact freezing [35], deposition freezing [36], condensation freezing [37], and immersion freezing [38]. Any four of these nucleation mechanisms in tandem with several environmental factors can promote or suppress cluster formation within a sample. This can be demonstrated by studying heterogeneous freezing temperature (HFT) which has been shown to be highly dependent upon the mechanism of freezing. Pruppacher and Klett have determined that the HFT associated with contact freezing is higher than that of immersion freezing [39]. Furthermore, HFT has also been shown to be dependent upon volume size, sample purity, and vessel type [40–42]. Barlow and Haymet explored HFT further with an automatic lag time apparatus (ATLA) with which repeated measurements of a single sample where taken to gauge changes in HFT [43]. From 200 individual freezing cycles, they found a variance of 0.7 °C in HFT. In addition, CNT prediction in comparison with ATLA samples spiked with freezing catalysts showed orders of magnitude difference in results. Nucleation remains an enigmatic phenomenon due to the stochastic nature of cluster formation; predicting such events is perhaps impossible; however, there is evidence some influence can be exerted on the freezing process. In food industry field, the quality of the end food product will be dependent upon the efficiency of the freezing process and physical factors of the food being frozen (i.e., thermal conductivity, dimension/shape of food, surface heat transfer coefficient). Thus, selection of the proper freezing technology for foods becomes critical in minimizing ice damage and maintaining quality. Also, it is noted that the heat transfer coefficient can play a major role in the freezing quality [3].

Freezing in Food Industry

Freezing is one of the most widely used food preservation techniques in the commercial and domestic markets due to its simplicity and ability to preserve a wide variety of foods. The freezing process involves lowering of food temperatures to or below − 18 °C (0 °F) [2], during which foods will experience a change in their physical state when ice nucleation occurs. Within these cold conditions, biological and chemical reactions attributed to food spoilage are reduced, allowing for an upwards of a 12-month preservation period depending on food item [3]. However, unavoidable degradation in food quality will occur during the freezing process. This degradation is attributed to ice formation within foods as liquid water undergoes a phase change to solid ice [44, 45]. The degree of damage associated with the phase change process is often attributed to the rate of freezing; it has been demonstrated that fast freezing rates produce smaller and more evenly distributed ice crystals [46]. The growth of ice crystals is highly related to the freezing time and rate [47].

The global frozen food market in the year 2015 has exceeded US$250 billion; within the USA, the market is estimated to be US$51.97 billion, with the bulk of its value concentrated in the ready-to-eat frozen foods sector, followed by frozen meats and frozen fruits and vegetables [48]. Growth within the American market is estimated to reach US$72.98 billion by 2024. Various social and economic factors have been attributed to this future trend, and the advancement in freezing technology has focused on improvements to freezing rate and cost reduction to meet the changing global landscape [3]. In today's world, freezing is the only large-scale food preservation technique capable of dampening variations in seasonal foods, consumer demand, and supply and provide a means of safe mass transport of bulk foods across long distances [44, 49, 50].

The freezing process associated with foods follows five basic steps (Fig. 1). First, an initial cooling period occurs, followed by a supercooled stage, which can potentially be sustained under certain circumstances. During this metastable period prior to ice nucleation, free water within the food matrix exists in a supersaturated state. However, inadvertently ice nucleation occurs, resulting in a release of latent heat which raises the internal food temperature to its freezing temperature [49]. Ice crystal growth and its associated size will mainly be determined in this stage, as the rate of latent heat removal becomes the critical factor in achieving small and uniform ice crystal sizes [51]. Pure water undergoing the freezing process in Fig. 1 would reveal a freezing point of 0 °C. However, foods can exist as a solid or liquid with mixtures of various solutes which can result in slightly different freezing temperatures amongst the same food types. Furthermore, within foods, slight temperature gradients have been observed due to the differences in solute concentration and free water throughout their matrix [50]. However, all food products follow a similar freezing process of Fig. 1.

In the past few decades, the most commonly used freezing technology in the food industry today are air blast, contact plate, immersion, and cryogenic methods [49]. Air Blast is by far the oldest and most widely used technology, which is simple and cost-effective; however, the time to freeze and freezing rate are slow in comparison with other conventional technologies. It is suitable for irregularly shaped foods such as fruits and vegetables, but it has major limitations associated with temperature disequilibrium of foods [52]. Several variants of air blast technology exist such as belt

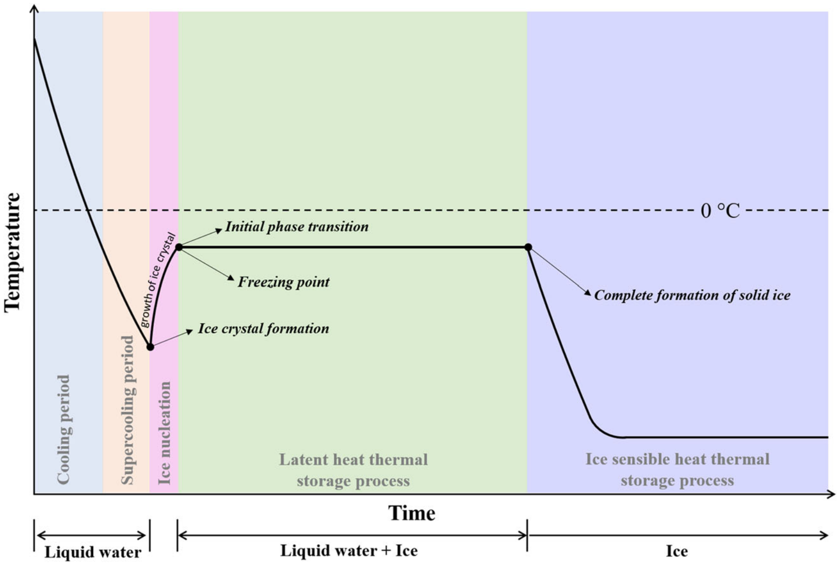


Fig. 1 A typical temperature time curve of food placed within a freezer

freezers and fluidized bed freezers which are more specialized for certain food type or continuous inline production. Contact plate technologies use cold metallic contact plates containing refrigerant to increase freezing rates of foods. During the freezing process, pressure is occurred to the food by the contact plates from opposing ends. The high thermal conductivity of the metal plates allow for a faster freezing rate and shorter freezing times, but the technology is only suitable for foods which exhibit regular shapes such as hamburger patties or fish fillets [53]. Immersion freezing technology uses a liquid medium, usually glycerol, glycol, sodium chloride, calcium chloride, or some derivative of a salt or sugar mixture in which the foods to be frozen are immersed. The higher heat conducting properties of liquids vs. air makes this an effective method in decreasing freezing time, but the major drawback to immersion is the possibility of transferring solutes of the immersion fluid to the food. Often flexible membranes are used to shield the food products from direct contact with the fluid medium and if full immersion is not appropriate the fluid can be applied in aerosolized form [49]. Cryogenic freezing technology applies cooling refrigerant directly onto the food and is divided into three major ways: (i) vaporization of the refrigerant to be blown over foods, (ii) foods are immersed into the refrigerant, or (iii) the refrigerant is sprayed directly onto the food. Method (iii) is the most commonly used technique; the refrigerants used within food applications are liquid nitrogen or carbon dioxide. Due to the high heat transfer rates and very low freezing temperature associated with refrigerants, the process is very efficient, but the high costs of refrigerants have limited the application of this technology to premium products [49].

Innovative Food Freezing Processes at Subzero Temperature

Control of Ice Nucleation in Food Matrix

A recent example of improvements made upon an existing technology is impingement freezing. This new technique has shown freezing time reductions of up to 79% over traditional blast freezers [54]. As a result, impingement has seen quick adoption by industry. However, an interesting development in freezing technology research has been a shift from optimizing the freezing process to attempting direct control over ice nucleation because of high-quality freezing. Several methods are currently under investigation which all aim to either inhibit, induce, or control ice formation within foods. Emerging food freezing technologies can be broken down into two major categories: (i) attempting direct control over ice crystal formation and (ii) suppression of the ice crystal formation.

Ultrasound Irradiation

The application of power ultrasound to liquid freezing has potential and has had promising results over the last few years. Ultrasound is widely utilized in the food industry because it plays a prominent role in food manufacturing and preservation [55]. Ultrasound in food industry can be divided into two categories: low-intensity (less than 1 W/cm^2) and high-intensity (higher than 1 W/cm^2) [56, 57]. Power ultrasound could be applied to food industry for two reasons. Ultrasound can be utilized as an alternative to conventional food processing or in tandem with traditional food processing methods to increase their efficiency [58]. Power ultrasound demonstrated the ability to control the size of ice crystals during freezing. Ultrasound plays an important role in the initial stages of ice nuclei and the increase in crystal growth in the food matrix [59]. Sun and Li (2003) found that a high powered ultrasound treatment can accelerate the heat transfer. This means that small ice crystals were formed by power ultrasound (15.85 W, 25 kHz) (Fig. 2). However, the mechanism of ultrasound that causes reduced ice crystal size has not been completely explained, although two hypotheses have been proposed. The first theory is that ultrasound energy generates physical effects in the receiving medium such as cavitation, causing the formation of gas bubbles. The gas bubbles can serve as nuclei for ice nucleation [15] or affect the crystallization by their collapse and motion. Furthermore, the ultrasound (less than 250 W) influences the initiation of crystal nucleation, controls the rate of crystal growth, ensures the formation of small and even-sized crystals, and prevents fouling of surfaces by the newly formed crystals [60, 61]. Another theory claims that the gradient of cavitation bubbles could affect ice nuclei in food matrix through the formation of a stable cavitation bubble with 4.4 kW/m^2 (39 kHz) [62, 63]. The important role of power ultrasound plays in freezing is cavitation, which enhances heat and mass transfer rate and the freezing rate through liquid medium. So, the nucleation process could be controlled by power ultrasound because power ultrasonic can be applied during initial nucleation in the food matrix as well as in a liquid medium (Fig. 3) [17, 64–66]. Power ultrasound was applied in the food industry for inducing the initiation of nucleation, controlling ice crystal size (with 0.7 W/mL, 20 kHz) [67] and changing the freezing rate (with 288 and 360 W (25 kHz, 0.5 duty cycle)) [68], recently. Inada and colleagues utilized ultrasound to change the phase transition from supercooled water to ice. When ultrasound is applied, the possibility of nucleation in supercooled water is greatly increased. However, it can be seen that the results can vary greatly depending on the intensity of the ultrasound [42]. Zhang and colleagues compared and analyzed the possibilities of acoustic cavitation and nucleation. The researchers found that the probability of phase transition is highly correlated with the number of bubble nuclei caused by ultrasound vibration [69]. Comandini et al. (2013) and Cheng et al. (2014) confirmed that ultrasound can be induced high degree of supercooling; thus, fast phase transition occurs by fast instantaneous ice nucleation in frozen potato and strawberry with 300 W (35 kHz) and 0.51 W/cm^2 (30 kHz), respectively. Therefore, the total freezing time can be controlled by power ultrasound. The authors concluded that collapse of cavitation bubbles play a critical role of initiation of ice nucleation in the food matrix. Studies by Ashokkumar and Grieser (1999) show that positive pressure could be created through the collapse of a cavitation bubble in a very short time [70]. This violent collapse induces instantaneous ice nucleation in food matrix [71]. Therefore, the collapse of cavitation bubbles, which can act as the driving force in nucleation, could be induced through the high localized pressure of power ultrasound [17, 64].

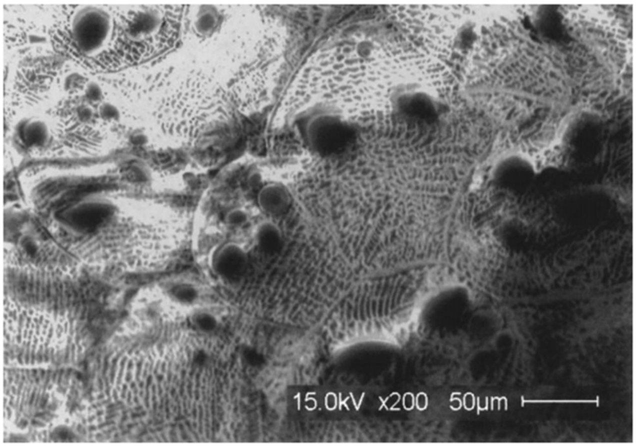


Fig. 2 Cryo-SEM (scanning electron microscope) micrograph for potato tissue by ultrasonically assisted immersion freezing under power of 15.85 W. Source: [59]

In freezing storage, small size and evenly distributed ice crystals have a positive effect on ingredient, texture, flavor, and lipid oxidation in frozen food due to the damage caused in the food structure by larger ice crystals [72–75]. Therefore, the size and distribution of ice crystals in the food matrix is one of main important factors in frozen food industry. Several researchers have tackled this issue with ultrasound. Sun and colleagues found that the microstructure of frozen potato tissue was not affected when they applied ultrasound during the freezing process, causing smaller ice crystal formation. [22]. They claimed that ultrasound can not only increase the freezing rate but also maintain cellular structure of potato under 15.85 W for 2 min. Their results were supported by findings in Xin's research group, which found that the microstructure and texture properties of broccoli frozen with ultrasound can be maintained due to the small size and evenly distributed ice crystals with 150 (30 kHz) and 175 W (20 kHz) [76]. The results show that the intercellular structure and texture properties of broccoli in commercial freezers were affected by the large size of ice crystals in their tissue. Therefore, ultrasound can avoid cellular structure damage, reduce drip loss, and maintain firmness during the freezing process [76]. Kiani's and Islam's research group reported that ultrasound can control the nucleation within different supercooling temperatures with 0.25 W/cm^2 (25 kHz) and 300 W (20 kHz), respectively [64, 77]. When the nucleation temperature was decreased with ultrasound, the ice crystals that formed were smaller than using the conventional freezing process. However, several problems stand in the way for future development of this technology. One problem is that if such processes are not well controlled, nucleation and subsequent crystallization can occur randomly, resulting in a poor-quality product. More fundamental research is needed in order to identify the most important factors that affect the ability of power ultrasound to achieve small and uniform ice crystal formation. Considerable research effort will also be required for the design, the scale-up, and the development of adequate industrial equipment.

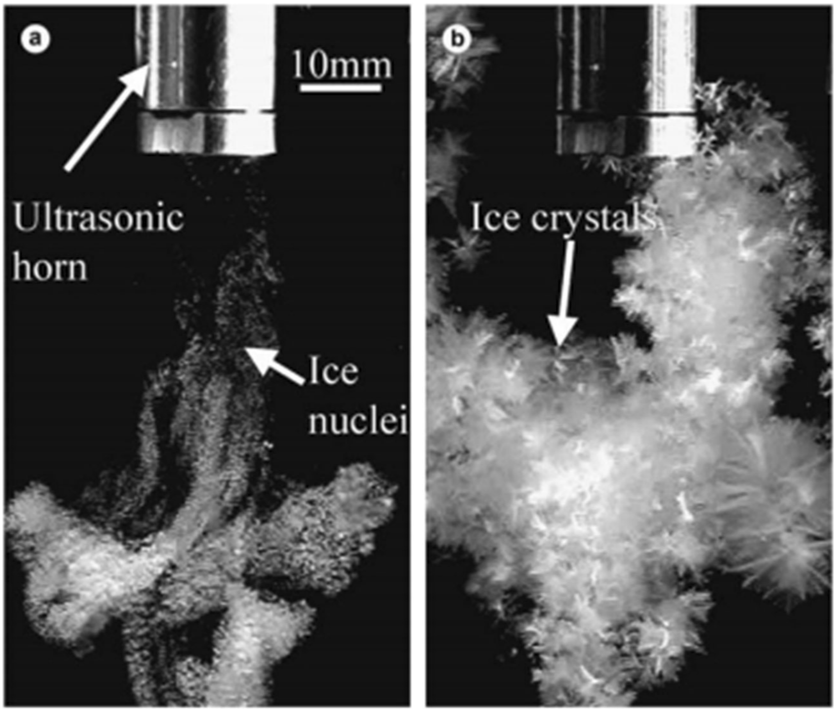


Fig. 3 Photographs of ice crystals nucleated in a 15 wt% sucrose solution at − 3.4 °C by a commercial ultrasonic device (output 4, 10% duty cycle). **a** Ice crystals following an ultrasonic pulse. **b** Crystals 5 s later. Source: [17]

High Pressure

An interesting development in freezing technology research has been a shift from optimizing the freezing process to attempting direct control over ice nucleation. Several methods are currently under investigation, all of which aim to either inhibit, induce, or control ice formation within foods. Perhaps the most widely researched technology in this new field is pressure assisted freezing, which can be broken down into two categories, freezing under high pressure (FUP) and pressure shift assisted freezing (PSF). High hydrostatic pressure has been known as a new protocol to enhance the freezing process and has been a subject of research in recent decades [19, 78–80]. FUP has been used frozen foods such as tofu, carrot, and cabbage [81–83]. Fuchigami and Teramoto (1997) found that microstructure and texture of frozen tofu (from − 20 to − 80 °C) have been maintained in freezer under 200, 340, and 400 MPa. The phase diagram for solid phases has been confirmed (Fig. 4). When food in the freezing process is exposed to static high pressure, different kinds of high pressure ices (ice I to VIII), which have different properties, were form under 2400 MPa pressure. The use of high pressure allows for high degrees of supercooling resulting in rapid ice nucleation and growth all over the sample under pressure release. Therefore, in contrast with conventional methods in which an ice front moving through the sample is produced, fine ice crystals are formed. This means that the working principle behind FUP is to increase density of ice by the application of high pressures (up to 400 MPa) during the entirety of a freezing process [79, 81, 86]. By doing so, different forms of ice with densities higher than that of liquid water can be created. In such states, ice exists in a non-crystalline structure which has been theorized to reduce

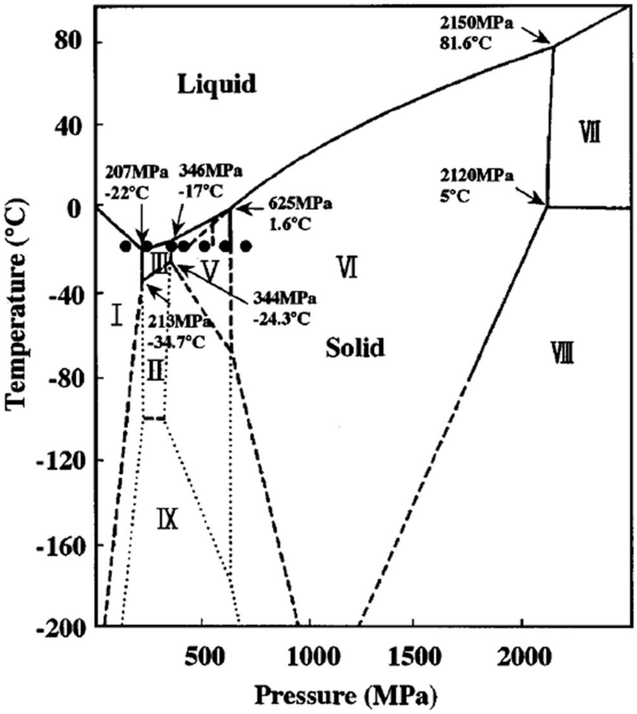


Fig. 4 Phase diagram of the solid phases of water. Filled circle, pressurizing points; leftwards arrow, triple point [84]; straight line, measured stable lines; dashed line, extrapolated or estimated lines; dotted line, extrapolated or estimated metastable lines. Source: [85]

tissue damage in food. PSF, on the other hand, is a more economical alternative to FUP as high-pressure conditions are only require partially during the freezing process. PSF has been utilized to many frozen foods such as potato, broccoli, carrot, strawberry, and sea bass [87–92]. Buggenhout et al. (2005) reported that frozen carrots by PSF at 200 MPa have been kept their original structure. Therefore, the frozen carrot's hardness was harder than regular frozen carrots. When samples have reached a desired subzero temperature, a sudden release in pressure induces homogenous-like ice nucleation throughout the food resulting in evenly distributed small ice crystal [4]. PSF in particular has been demonstrated to inactivate carious microorganisms at 207 MPa in smoked salmon mince [93], but even with the added benefits, pressure-assisted freezing remains within the realm of research due to the high capital costs associated with high pressure treatment [79]. PSF can change the degree of supercooling during freezing process. Su's research group found that proper pressure and freezing temperature can control the degree of supercooling (Fig. 5). Small evenly distributed ice crystals were obtained in shrimp and porcine liver during the freezing process. However, the shape of ice crystal could not be controlled by pressure [94]. With the advantage of pressure during freezing process, PSF can improve the microstructure of ice crystals. However, this process is limited by poor effectiveness in the cooling process under the pressure, protein denaturation induced by high pressure, and different types of food exhibiting different resistances to higher pressure.

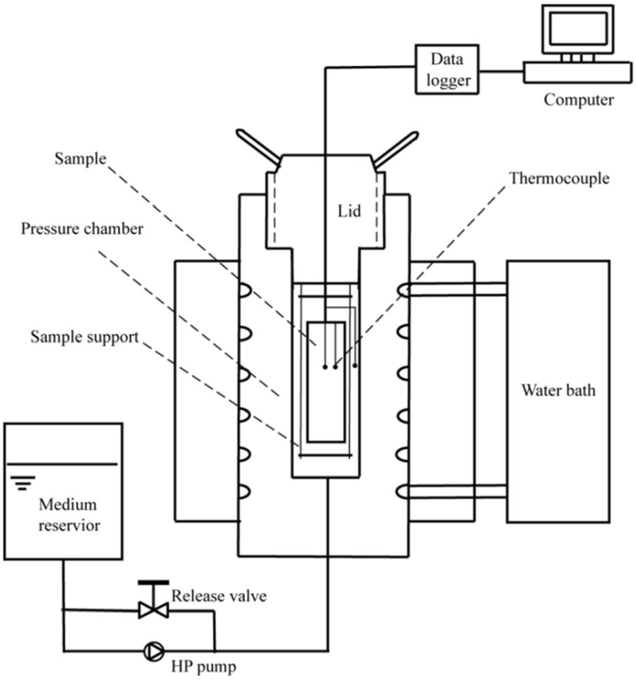


Fig. 5 Schematic of the experimental apparatus for pressure shift freezing. Source: [94]

Electric and Magnetic Fields

Magnetic field (MF) and electric field (EF) applications during the food freezing process have seen growing interest in recent years. EF treatment studies have shown more measurable effects on food during freezing when in comparison to MF studies. Static electric filed (SEF) treatment on pork samples during the freezing process has shown smaller ice crystal formations [95], indicating a desirable positive effect for SEF treatment during freezing. Pulsed electric field (PEF) treatments have been theorized to increase membrane permeability within foods, leading to increased accessibility to intracellular materials and cutting down on freezing times [96, 97]. This reduction in freezing was observed during PEF treatment of potatoes; however, a significant degradation in structural texture was also observed (Fig. 6). PEF treatments prior to and during the freezing process have also been used to enhance the uptake of cryoprotectant agents (CA) as a combination technology [98–100]. Moreover, other positive effects of electric field on ice formation have been reported [101–105]. The nucleation temperature shifted towards higher values with an increase in applied electrostatic field strengths [105]. Mok et al. (2015) show that with a high-frequency PEF, solutions had a tendency to form small and uniform ice crystal under freezing conditions at − 20 °C (Fig. 7). With an alternative EF, the ice crystallization properties, such as the degree of supercooling, freeze time, and ice crystal size, are dependent on the applied frequency [107]. A transient PEF was also reported as an alternative to achieve the same effect as an alternative EF. The suggested beneficial effects are derived from the vibration of the dipole water molecules [108]. In particular, high-frequency pulsed square waves are generated by charging and discharging in fractions of a second and causing no build-up of electrons on the electrical double layers. Thus, the PEF can influence physical and chemical characteristic of treated products depending on its pulse wave shape, frequency, and processing temperature [109]. However, the basic mechanism of SEF in ice crystallization is still contentious and most of previous studies of a PEF were focused on pre-treatment steps before freezing [97, 110–112].

Theoretical and experimental results have shown that static magnetic field (SMF) could induce ice crystallization [108]. The hydrogen bonds between water molecules are stronger and form a more ordered and stable configuration under SMF. This results in the formation of homogeneous ice crystals and enables control of the sample cooling rate and rate of crystal growth after nucleation [113]. Thus, the application of SMF has a high potential to control the freezing time and freezing characteristics by changing its direction and strength on the substrate. Moreover, the period of phase transition time reduced dramatically and the formation of uniformly round ice crystal was achieved under the combination of PEF and repulsive SMF which are shown in Fig. 8 [106]. However, there is

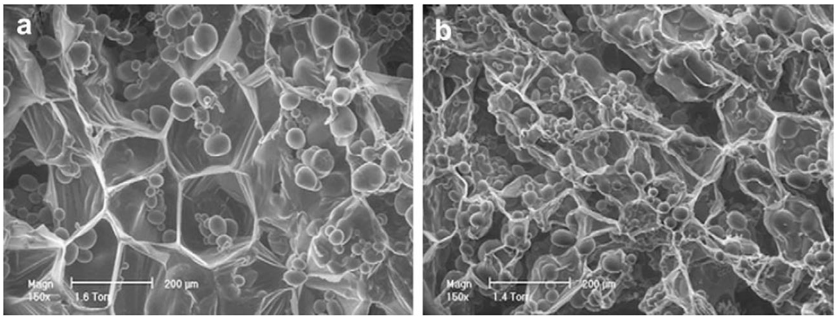
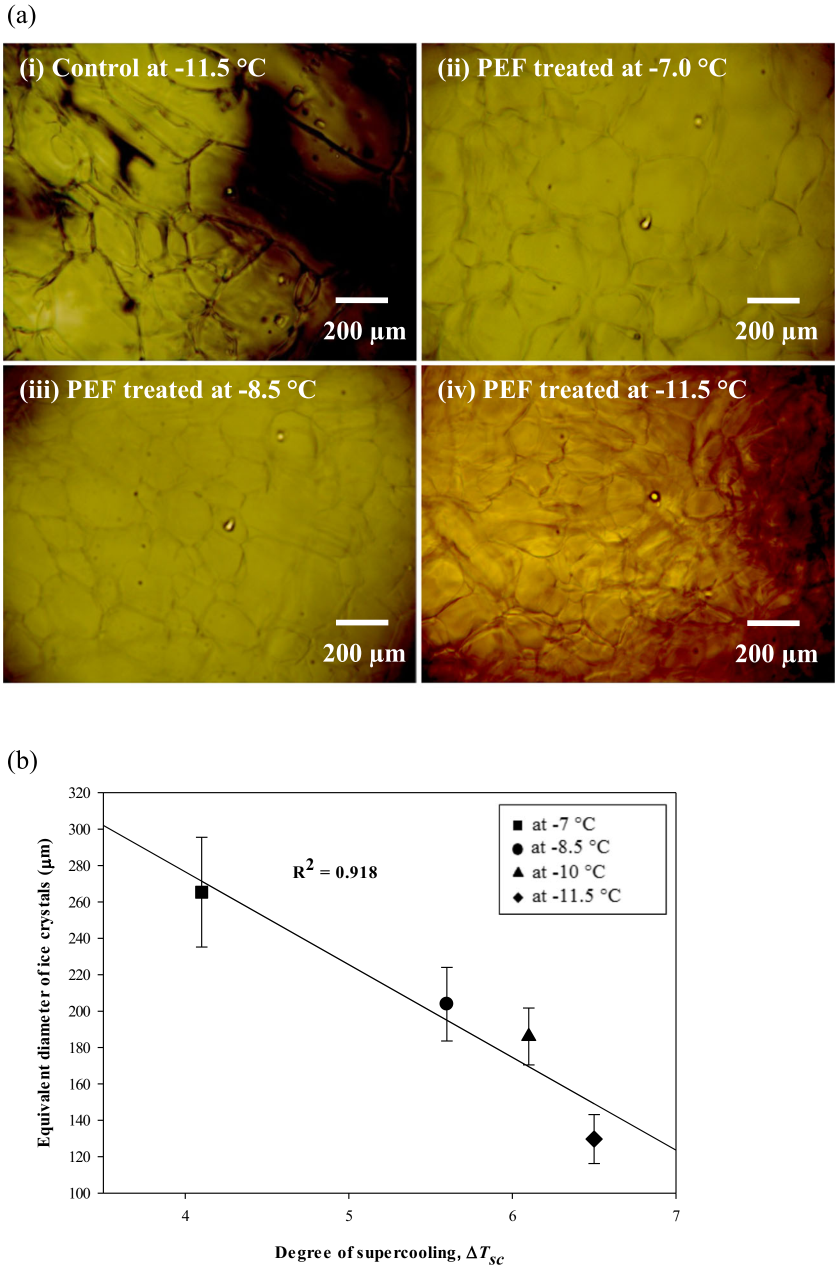


Fig. 6 The SEM micrographs for the untreated (**a**) and PEF pre-treated (**b**) potato tissues, which were air-blast frozen and then thawed. The freezing-thawing results in noticeable deformation and damage of polyhedral shaped cells (**a**). The PEF pre-treatment increase the structural disorder and formation of intercellular voids is observed (**b**). Source: [97]

Fig. 7 Effects of ΔT_{sc} on ice crystal sizes in the presence of PEF. **a** Ice crystal sizes with and without PEF at freezer temperatures between − 7 and − 11.5 °C. R roundness. **b** ΔT_{sc} vs. ice crystal size in the presence of PEF. $R^2 = 0.918$. Source: [106]



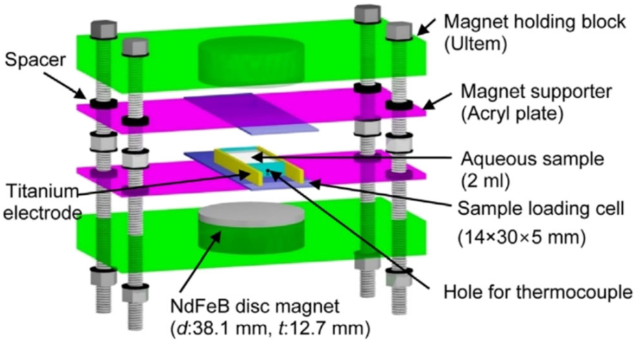


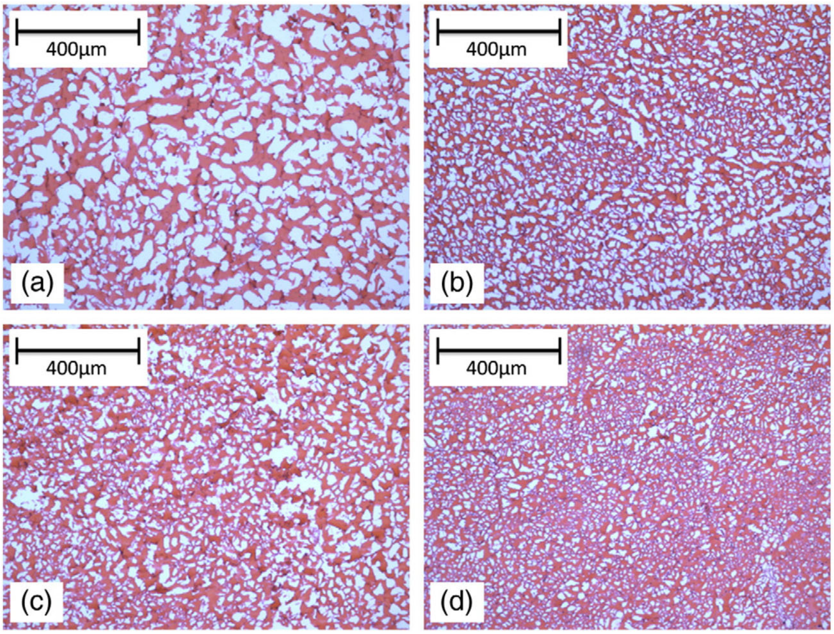
Fig. 8 A schematic diagram of the fabricated freezing device. Two milliliters of sample was placed in the cell. Two disc magnets were placed in magnet holding blocks and fixed by acryl plates. The voltage was applied between the titanium electrodes for PEF. Source: [106]

neither sufficient data nor a detailed description for the underlying mechanisms in a MF to control the freezing process. Time-varying applications have been studied with various food types, giving mixed results. For example, the application of an oscillating magnet field (OMF) at intensities of 0.5 to 0.7 mT at 50 Hz during the freezing process of various foods has reportedly shown advantageous results over traditional freezing [114]. A separate study showcasing OMF application of 200 to 300 mT at 60 to 100 Hz in combination with a dehumidifying device maintained fresh-like qualities in test food samples [115]. However, these studies were funded with commercial interests and are in sharp contrast with results presented in peer-reviewed research papers. When comparing food quality factors between OMF treated foods with non-OMF treated foods, Suzuki [116] and Watanabe [117] found no difference in result between treatment with and without the application of 0.55 mT OMF at 50 Hz. James et al. (2015a, 2015b) have also shown no measurable differences between treated and un-treated OMF samples using commercial freezing systems with built-in OMF technology.

Microwave

Microwave frequencies are a small portion of the radio frequency spectrum, and any application of such radiation outside of the strictly defined microwave frequency range can be considered radio frequencies application (RF). Radio frequencies work in the same theorized manner as microwave frequencies in that interaction with water molecules at the atomic level can influence ice nucleation. In particular, the interaction between water and electromagnetic forces has been the primary focus in such investigations. Microwaves operating at frequencies of 2.45 GHz are used within the food industry and domestically to heat foods; it is well known that interactions between microwaves and water molecules induce a dipole rotation at the atomic level, which in turn generates heat by collisions with other water molecules. This same concept has been applied during the freezing process to investigate its effects upon ice cluster formation at subzero temperatures. Therefore, the thermal conductivity of foods is critical and fast freezing rate could be achieved by low value as 0.5–1.0 W/m K [59]. Early studies have shown a 92% reduction in the degree of supercooling with a 62% reduction in ice crystal size. A rather counter intuitive outcome considering that a reduced degree of supercooling is often associated with larger ice crystals at − 20 °C with 700 W, 2.45 GHz, and 60% duty cycle (Fig. 9) [118, 119]. The freezing of pork loin with RF treatment has shown reduced ice crystal size [119], and the authors of the study postulate the heating effects of RF application are responsible for prolonging the rapid surface

Fig. 9 Micrograph images of frozen pork tenderloin transversal cuts under different levels of microwave power radiation. **a** 0% (conventional freezing). **b** 40%. **c** 50%. **d** 60%. Source: [118]



freezing of their foods during cryogenic treatment, which prevents large fracturing in their samples using a nitrogen spray. The power and duty ration were set as 3.5 kW, 27.12 MHz, and two different duty cycles (5 pulses of 10 s each delivered after 20 s of cryogenic flow with 20 s interval and 1 pulse of 50 s delivered after 50 s of cryogenic flow), respectively. Both microwave- and radio frequency–assisted freezing are new fields of research and little published data is available for examination.

Suppression of Ice Nucleation Below Freezing Point

Supercooling in relation to the study of foods is defined as lowering of a food product temperature below its usual freezing point with no phase change event occurring (i.e., ice nucleation). Within food science, the term supercooling has been interchangeably referred to as undercooled, subcooled, and freezing point depression [120]. A few examples of food products which have undergone supercooling studies include vegetables [120–123], fish [124–126], fruits [122], and meat [127, 128]. These studies have shown that the degree of supercooling is highly food specific, for example, when varying the concentration of orange juice across 46° and 66°Brix; the degree of supercooling shifted 90% [128]. Foods which have achieved and maintained supercooled conditions have exhibited longer shelf life due to lower storage temperatures compared with traditional chilled storage temperature ranges [129]. However, some studies have shown negative impacts on food samples during supercooled storage; Ando et al. (2007) experienced decreased firmness of yellow tail mackerel when stored at a supercooled temperature of − 1.5 °C. Supercooling technology in its current state has not shown reliable operation; however as a mature technology, supercooling has the potential to improve the shelf life of various highly perishable foods. Stonehouse and Evans (2015) recommend a more thorough review of supercooling for food applications [130].

The direct prevention of ice nucleation within food items is a new field of research, and as such, topics on the matter detailing the technologies and methods involved are scarce. According to Pham’s (1989) study, combination of freezing time and heat transfer coefficient can substantially affect property of supercooling during freezing. Water in two separate phases, intra- and intercellular, may affect its supercooling behavior due to lower nucleation point in cellular material. Most studies have focused on observing the natural supercooling phenomenon present within foods and determining which factors impact the degree and stability of supercooling the most. As a result, the most common approach to inducing and maintaining a supercooled state within foods has been strict temperature control, often achieved with commercial freezing equipment. James et al. (2009) used an unspecified commercial freezer with whole garlic bulbs placed within an insulated polystyrene vessel to prolong freezing rate and observe its impact upon supercooling (Fig. 10). Later he varied the static air temperature using an experimental wind tunnel with whole garlic bulbs placed within a polystyrene vessel. Fukuma et al. (2012) achieved static temperature control with a lab incubator (NH-60S, Ninomiya Sangyo, Chiba, Japan), of which the temperature setting was gradually reduced over a course of several days to prevent ice nucleation from thermally induced shock. These studies focused on temperature control with a special emphasis on cooling rate as being the most important factors in supercooling of foods, indicating no special technology is required in achieving and maintaining a supercooled state with the prior mentioned food items.

Studies focusing on a more fundamental approach to the supercooling enigma have attempted to address how static and time-varying uniform/non-uniform EF and MF interact with water. The basic conclusions indicate that EF in the excess of 10^9 V/m is required to re-orient crystalline water to achieve inhibition of ice [26], while weaker EF of 10^5 V/m inducing ice nucleation [131]. The former study used computer methods to derive its conclusion and the latter used an unspecified high DC voltage generator with two parallel plate noncontact electrodes for EF experimentation. The proposed mechanism upon which EF influences water within these studies is to either weaken or strengthen hydrogen bonds depending on orientation, strength, and frequency of the applied EF [123–125]. Especially, Sutmann (1998) studies the value of the polarization under an external electric field [132]. They

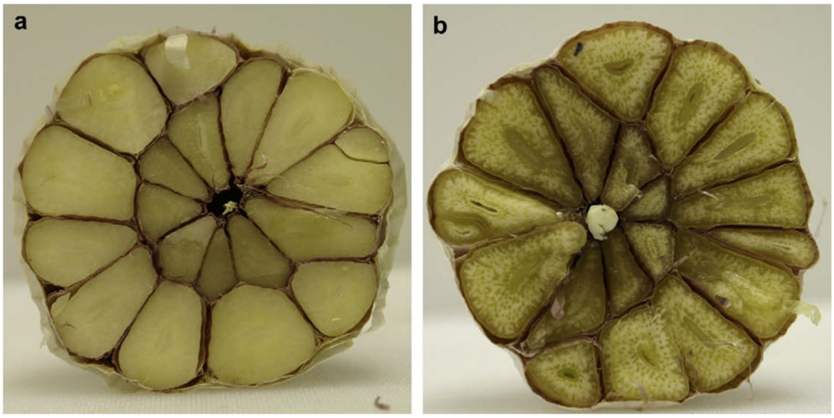


Fig. 10 Comparison of unpeeled garlic bulbs after storage for 1 week at supercooled (− 6 ± 0.5 °C) (**a**) and frozen (− 30 ± 0.5 °C) (**b**) temperatures, respectively. Source: [123]

found that transition (from linear to non-linear) behavior of hydrogen bond could be affected by low and high external EF. Other studies involving water in direct contact with EF electrodes often resulted in electrolysis, where O_2 is produced at the anode and H_2 at the cathode [133]. However, interestingly, when using direct contact metallic electrodes, the positioning of water molecules and ions can be greatly affected with a much smaller voltage level compared to non-contact EF. For example, a $-0.23\ V_{DC}$ applied to electrode resulted in a reorientation of water molecules away from electrode with a structured interfacial water layer extending out 15 A [134]. Ions found within water during contact EF application are attracted or repelled depending on electrode polarity and furthermore localized water orientation and structuring seen at the electrode surfaces have been reported to occur on surfaces of polar minerals. Within these studies, electrode material was often specified and chosen to achieve the desired effect of rapid nucleation or prevention; electrode type ordered from highest probability of nucleation to least is Al = Cu > Ag > Au > Pt > C [135]. MF application for food freezing processes has been met with larger criticism vs. EF application due to contradicting data and low repeatability of the studies. Again, the predominant mechanism postulated by various authors for MF effects on water is the strengthening or weakening of hydrogen bonds. Wang et al. (2013) and Zhou et al. (2000) theorize MF acts to weaken hydrogen bonds, which ultimately affect water properties governing the freezing mechanism to prevent nucleation [136, 137]. Chang and Weng (2006) believe the opposite to be the case, theorizing that MF fields act to strengthen hydrogen bonds within water to promote supercooling [138]. Inaba et al. (2004) demonstrated exposure of water to 6 T MF increased the freezing point of water by 0.0056 °C, providing evidence to the theory that MF strengthens hydrogen bonding [139]. Zhou et al. (2012) reported supercooling within water increased with the exposure to 5.95 mT MF [140]. Moreover, Kang et al. (2019) found that fresh-cut pineapple could be maintained supercooling under the OMF at − 7 °C. The pineapple of the supercooling state was maintained for 2 weeks under 10 mT of OMF and could be extended its shelf life without damage. They suggested that the OMF applied technology can suppress ice nucleation during freezing process and supercooled food can keep their visual appearance and quality (Fig. 11). In contrast, Aleksandrov et al. (2000), Zhao et al. (2017), and Otero et al. (2018, 2017) reported negative or no effects of MF on water supercooling with various MF strengths between 0 and 505 mT [142–145]. The studies which focused on static MF application mainly based on permanent neodymium magnets in various configurations and sizes to achieve a desired field strength and shape. In non-static MF studies, MF generation was most likely achieved with electromagnets; unfortunately, information regarding coil characteristics are unspecified (i.e., coil turns, coil geometry, wire diameter, wire composition, voltage/current applied, core material). However, Mok et al. (2017) suggested that the combination of EF and MF could be utilized to supercooling storage below freezing temperature. Using the combined EF and MF, it was possible to maintain a stable supercooled sample during the freezing process. External EF and MF may affect the onset of ice crystal formation during freezing and supercooling processes because water consists of dipole molecules and is also diamagnetic. Therefore, the water molecules naturally present in food tend to realign and re-orientate under EF and MF, meaning they are potentially able to prevent the ice crystallization process and may lead to a substantial change of the supercooling behavior of food products [146]. The optical microscopic images show

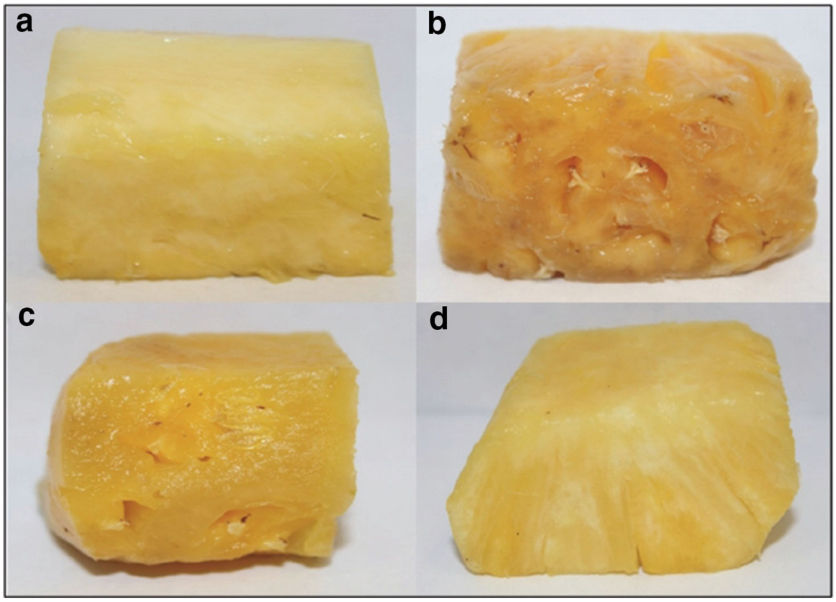


Fig. 11 Color differences between pineapple samples after 14-day treatment under different conditions. **a** Fresh. **b** Refrigeration. **c** Freezing and thawing. **d** Supercooling. Source: [141]

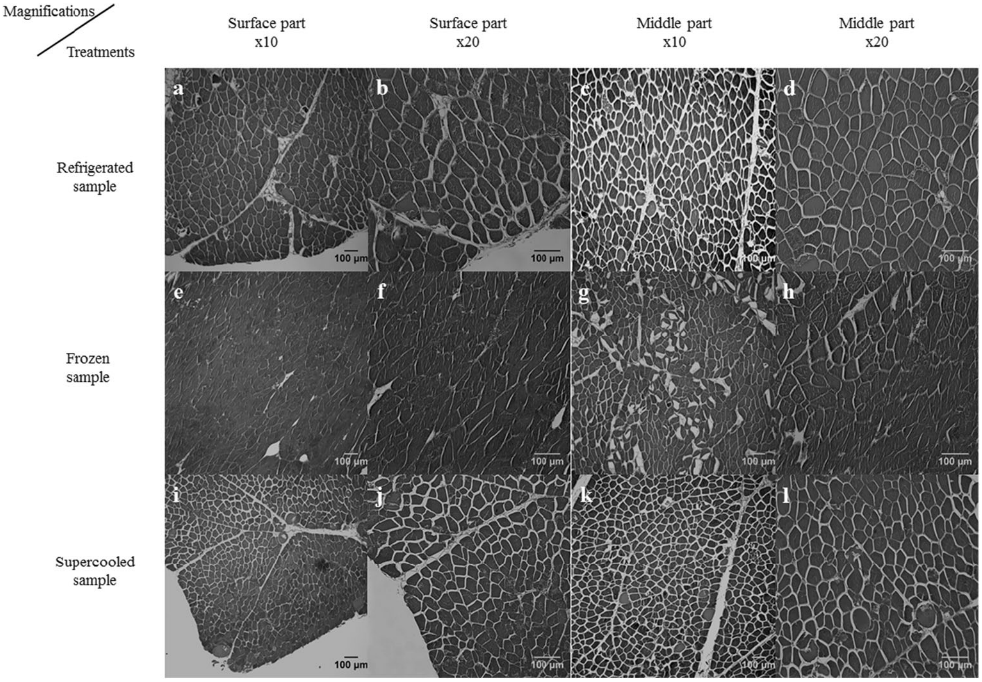


Fig. 12 Micrographs of chicken breast samples under different conditions. **a**–**d** Refrigerated at 4 °C, **e**–**h** partially frozen at − 7 °C, and **i**–**l** supercooled by PEF + OMF at − 7 °C. Source: [146]

that muscle fibers and endomysium were uniform, and no space was present between those in supercooled chicken breast. However, microstructure damages were observed in frozen chicken breast (Fig. 12).

Table 1 Patents on the application of supercooling technologies in food industries

Applications		Patent number	Title	Year of publication	Ref.
Temperature control	Accepted	US8677770B2	Supercooling method and supercooling apparatus	2014	[147]
		US7524521B2	Method of preserving food in a supercooled state	2015	[148]
		CA2465863C	Method of preserving food and method of producing unfrozen water	2009	[149]
		AU2006338350B2	Apparatus for supercooling and method of making slush through supercooling	2011	[150]
		US20100319368A1	Supercooling recognition method and supercooling apparatus	2010	[151]
	Abandoned	US20100242524A1	Supercooling apparatus	2010	[152]
		US20100242524A1	Storage apparatus and storage method	2011	[153]
		US20100083687A1	Refrigerator and frozen food preservation method	2010	[154]
Pressure	Abandoned	US20070042337A1	Isochoric method and device for reducing the probability of ice nucleation during preservation of biological matter at subzero centigrade temperatures	2007	[155]
Additive	Accepted	CA2393317C	Prevention of ice nucleation by polyglycerol	2001	[156]
	Publication	WO2017222473A1	Anti-freeze agents	2017	[157]
		WO2000016619A1	Polyvinyl alcohol compounds for inhibition of ice growth	2000	[158]
	Abandoned	US20130004936A1	Supercooling promoting agent	2013	[159]
Electromagnetic field	Accepted	US7237400B2	Highly efficient freezing apparatus and highly efficient freezing method	2007	[114]
		US20160302457A1	Method of supercooling perishable materials	2016	[160]
	Expired	JP2009153411A	Food preservation method, and food preservation device	2009	[161]
	Pending	JP2001086967A	Method for freezing and freezer using variance of magnetic field or electric field Abstract	2001	[162]
	Abandoned	US20090064689A1	Supercooling apparatus and its method	2009	[163]

Table 2 Summary of alternative techniques for food freezing process

Applications		Specimen	Conditions	Results	References
Ultrasound	Accelerate phase change	Dough	Immersion freezing at − 20 °C, thawed under 23 °C, 288 and 360 W power, 25 kHz frequency	Heat transfer can be improved at phase transition and solid state. The fine ice crystals were formed in matrix.	[68]
		Pure water (0.8 to 2.0 MΩ cm), tap water (2.6 to 2.9 KΩ cm)	Freezing at − 30 °C, 0 to 100 W power, 28 kHz frequency	The phase change from supercooled water to ice can be enhanced through the cavitation phenomena.	[42]
	Control the degree of supercooling	Potato	Immersion, glycerol and water (50%:50%, *w*/w), freezing at − 6 °C, 300 W power, 35 kHz frequency	Collapse of cavitation bubble promoted freezing equilibrium and reduction of freezing rate was achieved.	[165]
		Strawberry	Immersion, 30% (w/v) $CaCl_2$ solution, freezing at − 25 °C, 0.09 to 0.51 W power, 30 kHz frequency	Shortening the time required to reach supercooling stage can be induced by higher powered ultrasound.	[65]
		Mushroom	direct freezing at − 20 °C, 300 W power, and 20 kHz frequency	The nucleation temperature of an ultrasound treated sample is higher than that of a control sample.	[77]
	Initiate nucleation temperature	Radish	Immersion, 30% (w/v) $CaCl_2$ solution, freezing at − 20 °C, 0.09 to 0.37 W power, and 20 kHz frequency	Ice nucleation could be induced by the ultrasound irradiation duration and ultrasound intensity can affect the nucleation temperature.	[71]
		Agar gel	Immersion, ethylene glycol and water (50%:50% in volume) solution, freezing at − 20 °C, 0.07 to 0.42 W power, and 25 kHz frequency	Initiation of nucleation can be controlled through different ultrasound irradiation durations resulting in different supercooling temperatures.	[64]
	Control of size of ice crystal in food matrix	Broccoli	Immersion, 40% $CaCl_2$ solution, freezing at − 25 °C, 125 to 190 W power, 20 and 30 kHz frequency	Proper condition of ultrasound (150 W (30 kHz) or 175 W (20 kHz) power level can induce fast freezing and fine ice crystals in broccoli.	[76]
		Mushroom			[166]

Table 2 (continued)

Applications		Specimen	Conditions	Results	References
			Immersion, ethylene glycol ($C_2H_6O_2$) and water (50%:50%, *v*/v) solution, freezing at − 25 °C, 300 W power, 20 and 30 kHz frequency	Optimum power and frequency of ultrasound can make fine ice crystals due to the shortening of the phase transition stage.	
		Apple, Radish, and potato	Immersion freezing at − 18 °C, 0.62 W/cm^2 power, 28 kHz frequency	Increased ice nucleation temperature can control the phase transition time and make small ice nuclei.	[74]
Pressure	FUP	Dried cured ham slice	220 MPa, freezing at − 18 °C	High pressure pre-treated samples have damage in the microstructure due to the mobility of water and ions.	[167]
		Tofu	100 MPa (ice I), 200 MPa (liquid phase), 340 MPa (ice III), 400, 500, 600 MPa (ice V), or 700 MPa (ice VI), freezing at − 30 °C	200, 340, and 400 MPa of pressure can make fine ice crystals and maintain their original texture in the freezing process.	[81]
		Carrot	100 MPa (ice I), 200 MPa (liquid), 340 MPa (ice III), 400 (ice V), freezing at − 20 °C	Maintaining both texture and histological structures of frozen carrots can be achieved through high pressure (200, 340, and 400 MPa) at − 20 °C.	[86]
		Kinu-Tofu	200, 340, and 400 MPa, freezing at − 20, − 30, and − 40 °C	High pressure treated Kinu-Tofu sample have been maintained their original structure after freezing.	[81]
		Chinese cabbage	200, 340, and 700 MPa freezing at − 30 °C	High pressure was effective in keeping structure. Therefore, high pressure treated cabbage can maintain their texture after freezing.	[83]
	PSF	Shrimp and porcine liver	100, 150, and 200 MPa, freezing at − 8.4, − 14, and − 20 °C, respectively.	The supercooling stage is much shorter than conventional freezing and small, regular and	[94]

Table 2 (continued)

Applications		Specimen	Conditions	Results	References
				homogeneously distributed ice crystal were obtained.	
		Sea bass	200 MPa, freezing at − 15 and − 20 °C	PSF has some negative effects exist such as rupture of protein and color change. However, frozen sea bass by PSF can achieve improvement on the cellular integrity	[92]
		Potato	400 MPa, freezing at − 18 °C	Pressure shift freezing improves crystallization rates, preserves the cell structure and improves quality retention with respect to texture.	[168]
		Salmon	207 MPa, freezing at − 21 °C	When salmon mince was exposed to PSF, 2 and 2.5 log cycles of *L. innocua* and *M. luteus* can be reduced, respectively. Color, texture, water retention and lipid oxidation values are higher than traditional freezing process.	[93]
		Carrot	200 MPa, freezing at − 18 °C	Texture of frozen carrot using HPSF have been maintained at − 18 °C	[89]
Electromagnetic field	EF	Pork	12 kV power of static electric field, freezing at − 20 °C	SEF can control the nucleation temperature, which plays an important role for ice crystal size. The final quality of the meat can be improved due to the reduction in ice crystal size.	[95]
		Potato	400 V/cm power, 0.5 kHz frequency of PEF with various durations from 10^{-4} to 0.3 s, freezing at − 35 °C	PEF can reduce freezing time of potatoes and the structural damage in freeze-thawed potato	[97]

Table 2 (continued)

Applications	Specimen	Conditions	Results	References
			samples is significant improved.	
	Carrot	The food sample is soaking in $CaCl_2$ solution, 1 kV/cm power, 4 Hz frequency of PEF with 25 µs duration, freezing at − 18 °C	Proper PEF conditions can maintain firmness and microstructure during the freezing process and the PEF-treated sample can keep their original color.	[100]
	Distilled water	0 to 6.0×10^6 V/m power of electrostatic filed, freezing at − 16 °C	An increase in electrostatic field strength increases the nucleation temperature. A high voltage electrostatic field is able to change the nucleation temperature of ice.	[105]
MF	Garlic	Less 1 mT magnet field, freezing at − 20 °C	Application of an OMF to garlic bulbs greatly resulted in a high degree of supercooling.	[121]
	0.9% NaCl solution	50 mT of SMF, freezing at − 20 °C	Phase transition time and ice crystal shape and size can be affected by SMF.	[106]
	Pineapple and agar gel	10 mT of OMF (1 Hz), freezing at − 7 °C	OMF can inhibit spontaneous nucleation during freezing storage. Supercooling storage can extend the shelf life of pineapple under OMF.	[141]
EF + MF	Chicken breast	10 V of PEF (20 kHz) and 25 V of OMF (− 150 to 150 mT) at − 7 °C	A combined PEF and OMF treatment can suppress sudden nucleation below the freezing point. Supercooled chicken breast can keep their original quality after storage.	[146]

HPF high pressure assisted freezing, *PSF* pressure shift assisted freezing, *EF* electric field freezing, *MF* magnetic field freezing, *SEF* static electric field, *PEF* pulsed electric field, *OMF* oscillating magnetic field, *SMF* static magnet field

Patents for Supercooling Preservation

Although many of the possible supercooling technology have not been applied in the scientific literature, numerous patents have reported that they have strong potential in creating a new food preservation method, i.e., supercooling preservation. Recent patents associated with the application of supercooling in food industries are summarized in Table 1. Patents search have been done using keywords, including food, supercooling, and preservation in the Google Patent from the year 2000 to 2019. The patents can be divided into four broad categories: cooling rate, pressure, EF or/and MF, and additive. Their common goal is to maintain a supercooling state of foodstuffs. According to recent patents, temperature control of a sample is one of the most investigated mechanisms to achieve a supercooled state [147, 148, 154]. Takahashi and Miyauchi (2015) preserved food in a supercooled state by the minimization of headspace in a storage container and applied cooling rate from − 0.5 to − 5.0 °C/h. Handa et al. (2010a) claimed that cold air flowing into the storage chamber lowered the sample temperature in a step-wise manner [164]. By implementing this method, the foods in the storage chamber were not frozen at a temperature equal to or less than a freezing point. Other groups utilized special freezing chamber to remove or melt ice formed on the object. Chung et al. (2010) claimed that their new invested cooling device can maintain liquid in a supercooled state below the freezing point. Their apparatus equipped with both heating and cooling devices provided hot and cold air and prevented freezing of water stored in the apparatus. Yuko's research group also controlled the formation of ice on an object during freezing storage. Storage device had a semiconductor element for generating a microwave which can be applied to the object. The strength of a microwave that they applied to the foods was below 100 W. Thus, employing high frequency could be a possible mechanism to melt the ice crystals in a very short time.

Since perishable food or biological material is susceptible to heat, methods to avoid are being proposed. Supercooling storage of foods has been achieved by isochoric method through the suppression of ice nucleation in foods. Krikelis and Szobota (2007) claimed that isochoric method can maintain supercooled state below freezing point. Low pressure (less than 200 MPa) can alter the ice nucleation probability through changing the thermodynamics of ice nucleation. This proposed apparatus also can be utilized to firm foodstuffs for extension shelf life. A substance which could prevent ice nucleation of water at temperature below the freezing is expected to be applicable in various fields such as environmental, horticultural, biomedical, and agricultural fields. In particular, incorporating edible agents which could prevent the formation of ice nucleation is promising in food industry. Some patents have proposed agents as supercooling promoting agent, 2,3,6-tri-*O*-galloyl-α,β-D-hamamelose, 1,2,6-tri-*O*-galloyl-β-D-glucose [159], and anti-freezing agents, such as poly(amido)amine (PAMAM) [157], polyglycerol (PGL) [156], and polyvinyl alcohol [158]. To overcome previous issues, such as heat, inedible, and complicated system, freezing techniques based on the manipulation of EF and MF have been developed. Machi et al. (2009) claimed that foodstuffs could be maintained in a supercooling state at subfreezing environment by the electrostatic atomization apparatus. The electrostatically atomizing water is provided from the electrostatic atomizer. The charged water particles applied to food could maintain supercooled status below the freezing point. Jun et al. (2016) utilized combination of EF and MF to foodstuffs. This proposed concept is to extend the supercooled state of foods by preventing ice nucleation from occurring by using PEF in tandem with OMF. The combination of PEF and OMF can vibrate water molecules in a foodstuff even below the freezing point. The supercooled foods can be preserved and stored over an extended period of time.

Conclusion

Freezing process is associated with different physical and chemical properties, involving heat thermal storage, ice crystal formation, latent heat thermal storage, and ice sensible heat thermal storage process. The most common freezing technologies in food industry have drawbacks, with different freezing rates depending on the size and shape of object, requirement of specific shape, slow freezing rate, and high costs of refrigerants, respectively. Alternative freezing processes, such as ultrasound irradiation, high pressure, electric field, magnetic field, and microwaves, have different strategies to improve freezing rate, which could maintain the quality of a frozen product. It is noted that faster freezing, lower migration of water, less breakage of cells, and subsequent less texture deterioration can be achieved using alternative food freezing processes. The theory about the cavitation effect of ultrasound is not fully established in freezing process; however, negative or positive pressure in cavitation bubbles can be have an effect on initiation of nucleation within a nanosecond. However, it is necessary to fully understand the role of the cavitation bubble in the initiation of nucleation by ultrasound in future work. High pressure can control the degree of supercooling by instantaneously changing the phase transition during the freezing process. However, the degradation of structure and high costs of operation are still challenges that need to be overcome before this technology can be widely adopted. EF treatments during the freezing process can reduce total freezing time due to the EF affected membrane permeability of cells. However, the effect of a EF and/or MF on the freezing process needs more research to fully understand the clear mechanisms of EF and MF on the various frozen food products. Microwaves can affect the internal water molecules in foods. This phenomenon can influence ice nucleation temperature, but during the freezing process, the degree of supercooling cannot be controlled by the strength of microwaves. The emerging techniques applied food freezing processes are summarized in Table 2.

However, even small ice crystals can induce the unavoidable damage to microstructure of food. The prevention of ice nucleation below freezing temperatures is a new field of research. Specifically, an EF and MF can suppress the ice nucleation below freezing temperature. Due to the external PEF applied, water molecules can be polarized and re-orientated by force momentum exerted on the dipole moment of the water molecule and tend to be aligned with the direction of EF. The application of a MF can weaken/strengthen the *van der Waals* bonding between water molecules and reduce/enhance hydrogen bonding strength. However, supercooling technology needs more studies because the mechanism is still not adequately understood. Supercooling is another alternative food preservation technique in the future.

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