Review on the control of ice nucleation by ultrasound waves, electric and magnetic fields

Mohsen Dalvi-Isfahan a,*, Nasser Hamdami a, Epameinondas Xanthakis b, Alain Le-Bail c

a Department of Food Science and Technology, College of Agriculture, Isfahan University of Technology, Isfahan, 84156-83111, Iran
b SP-Technical Research Institute of Sweden, Food and Bioscience Unit, Gothenburg, Sweden
c UMR GEPEA (CNRS 6144), ENITIAA, Rue de la Géraudière BP 82225, 44322, Nantes Cedex 03, France

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Abstract
Freezing is the most popular and widely used food preservation method of the modern times. The freezing process of food matrices is related to their high water content and its metamorphoses into ice on cooling. The final quality of the frozen product is highly dependent on the ice crystal morphology because it can cause irreversible damage on the microstructure of the food matrix. Supercooling and ice nucleation temperature need to be controlled both in suppressing and inducing the solidification to improve technological processes such as freeze drying, freeze concentration, cryopreservation, ice formation and cold-energy storage both in food industry and domestic preservation. However, the mechanism of freezing is not yet well known and it is affected by several factors.

Several emerging technologies have been recently proposed for ice nucleation control during freezing. This review article is focused on the alternative freezing methods such as ultrasound waves, magnetic, electric, and electromagnetic field assisted freezing. In addition, the properties, mechanism of action and possible applications of electrofreezing are extensively discussed.

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1. Introduction

Water is the major but Janus-faced component of almost all the fresh food materials. The two faces of water lie in the facts that although water is an essential constituent for the freshness characteristics of foods, it is also actively involved in all the deteriorative mechanisms which influence their texture, appearance, quality, as well as in the acceleration of their microbial, chemical, and biochemical degradation. Water in food matrices exists in two states, namely as “non-bound” and “bound.” First, the term “non-bound” is related to the freely available solvent water, condensed within the capillary structure or in the cells of a food that behaves physically and chemically as pure water. Second, water fraction is “bound” to polar groups or ionic sites on molecules such as starches, pectins, and proteins, thus becoming less active (Belton, 1997; Choi and Kerr, 2003; Fellows, 2009; Fessas and Schiraldi, 2001, 2005). During freezing, water is converted into ice crystals and the water activity of the food system decreases due to the reduction of the available liquid water. The reduced water activity helps to preserve foods for longer periods of time, and freezing temperatures reduce the rate of chemical reactions as well as the activity of microorganisms and enzymes, thereby extending the storage life of frozen foods. Although freezing causes minimal deterioration of original color, flavor, texture or nutritional values in comparison with thermal processing, food materials are prone to be subjected to irreversible tissue damage due to the solute-concentration damage, dehydration damage and mechanical damage from ice crystals (Reid, 1993). The quality of frozen food is considered inversely related to the extent of freezing-induced cellular dehydration, the size of the ice crystals and their location inside the foods (Delgado and Sun, 2001; Li and Sun, 2002b). It is well-known that rapid freezing like cryogenic freezing results in the formation of smaller and more numerous ice crystals, which is preferable for minimizing the damage to the cellular structure. However, the major disadvantages of this freezing method are: the high total cooling costs, the environmental impacts and the susceptibility of some products to crack or even shattering when exposed directly to extreme low temperature (Kim and Hung, 1994; Smith, 2011). Therefore, the selection of methods that maximize the quality of frozen food while lowering the costs and the power consumption, are of major importance for the frozen food industry.

The last decades, several studies and many promising technologies have been introduced providing the potentials for better quality attributes of frozen food matrices while lowering the energy demands. The novel freezing methods can be categorized in three different classes with respect to their approach. i) Improvement of the heat transfer rate during freezing like hydro- fluidization or impingement freezing, ii) change the properties of food material like ice nucleation protein and antifreeze protein and iii) assisted freezing methods which can alter the nucleation, crystal growth and nucleation rate of food materials during freezing like high pressure freezing, microwave assisted freezing, radiofrequency assisted freezing, magnetic freezing and electrofreezing (James et al., 2015).

Among all the assisted freezing methods, we will focus on the effects of ultrasound, magnetic fields, electric fields and electromagnetic wave. The aim of this paper is to explore the effects of ultrasound waves, magnetic, electric and electromagnetic field assisted freezing and to discuss their potential applications in frozen food technology. The outputs of recent studies as well as the mechanism of action, the thermodynamics and the influence on crystallization of electrofreezing will be comprehensively discussed.

2. Freezing

In principle freezing process consists of three stages namely, pre-cooling or chilling stage, in which the material is cooled from its initial temperature to the freezing point temperature; phase change period which represents the crystallisation of most of the water; and sub cooling or tempering stage in which the product reaches the finally established temperature (Kiani and Sun, 2011; Xanthakis et al., 2014a). The crystallisation comprises nucleation and crystal growth. Nucleation refers to the process by which an adequate amount of molecules associate in three dimensions to form a thermodynamically stable aggregate, the so called critical nucleus, which provides surfaces suitable for crystal growth. The growth stage, which immediately follows the nucleation, is governed by the diffusion of particles to the surface of the critical nuclei and their ordered assembling onto the growing crystal (Russo Krauss et al., 2013). Two distinct processes are identified in the nucleation of crystals, namely, primary and secondary or contact nucleation. Primary nucleation involves the formation of crystal in a solution containing no existing crystals. Primary nucleation can take place in two categories; Homogenous and heterogeneous. Homogeneous nucleation occurs when the nuclei is formed spontaneously from the random density fluctuation within the supercooled liquid but heterogeneous nucleation takes place due to the presence of solid impurities that form stable surfaces for nuclei formation (Gülseren, 2008; Sahagian and Goff, 1996). The distinction between heterogeneous and homogenous nucleation can be made using DSC techniques by evaluating the differential heat flow signals (Gülseren, 2008; Ozligen and Reid, 1993).

Secondary nucleation involves the production of new crystals in a solution containing pre-existing crystals, and it can occur either by the crystals acting as templates for new crystals nuclei to be formed or by the crystals fragmenting to produce more nucleation sites (Adriana and Da-Wen, 2011). It is believed that the nucleation is the most important step during crystallization, since it can affect both crystal size and distribution of ice crystals (Sachler et al., 2010b). But the nucleation temperature (Tn), which is the temperature at which crystallization starts, is quite variable and is affected by several factors such as foreign particles, the surface area, process conditions, sample volume, composition of the matrix and contact area between sample and container. The aforementioned and other factors are responsible for the random and stochastic nature of ice nucleation (Anuj, 2012; Kiani et al., 2012a; Petersen et al., 2006). On the other hand, the ability to control supercooling (temperature difference between the freezing point of a matrix and the nucleation temperature) and ice nucleation is essential to produce a homogeneous and uniform frozen batch (Anuj, 2012; Passot et al., 2009), to increase food quality (Orlowska et al., 2009) and to the
survival of many biological organisms that experience subfreezing temperature (Diller, 1975; Schwartz and Diller, 1984). The crystal growth rate is the rate at which the radius of a nucleus grows after formation. The growth rate of the crystals is determined by the heat and mass transfer in the liquid phase and by the liquid-solid interphase. In most high moisture foods there are plenty of water and solute molecules, but it appears that mass transfer of these molecules towards and away from the crystals do not limit the rate of growth except at late stages of freezing. Therefore, during freezing, it is heat transfer rate that controls crystallization.

The rate of crystal growth ($G$) is also a function of the supercooling ($\Delta T_s$) reached by the specimen according to the phenomenological expression

$$G = \beta(\Delta T_s)^n$$

where $\beta$ and $n$ are experimental constants (Petzold and Aguilera, 2009). The interaction between the steps of ice nucleation and crystallization determines the crystal characteristics such as their size, distribution and morphology (Russo Krauss et al., 2013).

There are many studies published aiming to control induction or suppression of ice formation at desirable temperature. Induced ice nucleation may lead to a reduced range of ice nucleation temperatures during cryopreservation (Morris and Acton, 2013), and also to produce larger ice crystals which has some benefits for some technological processes such as freeze drying and freeze concentration (Geidobler and Winter 2013; Petzold and Aguilera, 2009; Searles et al., 2001). Moreover, electrical energy demands for refrigeration and freezing time can be reduced (Okawa et al., 2010). Suppression may lead to finer ice crystals formation, enhance the quality and can also be effective in reduction of freezing injury (Woo and Mujumdar, 2010). Different methods and approaches have been employed to promote or inhibit ice nucleation. We can divide them in three general categories: physical, chemical and biological methods. But only some of them provide a true control of nucleation, while others just enable statistically increasing or decreasing the mean nucleation temperature (Anuj, 2012; Geidobler and Winter 2013). Table 1 represents different methods to control ice nucleation.

Other existing methods to control ice nucleation are based on temperature dependency of nucleation and growth which allow to change them by manipulating the rate of heat transfer (cooling rate

| Table 1 | Comparison of Methods proposed for controlling ice nucleation. |
|---------|---------------------------------------------------------------|
| **Method** | **Induction** | **Suppression** | **Effect** | **Reference** |
| **Physical** | Seedin0067 (ice fog) | | Reduced range of ice nucleation temperatures, no true control, and increase of nucleation temperature. | (Patel et al., 2009). |
| **Mechanical method** | (Shaking, tapping and agitation) | | Induce spontaneous nucleation, reduced degree of supercooling | (Hozumi et al., 2002; Woo and Mujumdar, 2010). |
| **Static electric fields** | 1. Charge type | | Controls ice nucleation and decreases the degree of supercooling by increasing nucleation temperature, changes the shape of ice crystal. | (Hozumi et al., 2005; Hozumi et al., 2003). |
| | 2. Static Electric fields | | | (Dalvi-Isfahan et al., 2016; Orlowska et al., 2009; Wei et al., 2008). |
| **High Pressure freezing** | | | Enhances supercooling degree | (Le-Bail et al., 2002; Otero and Sanz, 2003) |
| **Ultrasonic irradiation** | | | Controls ice nucleation and decreases the degree of supercooling by increasing nucleation temperature, changes the size and shape of ice crystals. | (Kiani et al., 2011; Kiani et al., 2013; Sun and Li, 2003). |
| **Membrane** | | | Decreases the degree of supercooling. | (Okawa et al., 2010). |
| **Electromagnetic wave** | - Microwave irradiation | | Decreases the degree of supercooling; produces smaller ice crystals. | (Xanthakis et al., 2014b). |
| | - Radio frequency | | | (Anese et al., 2012). |
| **Magnetic** | 1. Static Magnetic fields | | Contradictory results has been reported but Freezing temperature may shift to higher value and increase the degree of supercooling Smaller ice crystals formation. | (Cai et al., 2009; Inaba et al., 2004). |
| | 2. Resonant or oscillating magnetic fields | | | (Fikin, 2008; Kaku et al., 2010; Kojima et al., 2013; Mohanty, 2001). |
| **Chemical** | chemical ice nucleating agents such as silver iodine, Aliphatic alcohols, Crystalline Cholesterol, Philoroglucinol | | Raises the nucleation temperature, reduces the degree of supercooling. | (Okawa et al., 2001). |
| | chemical suppressing agent such as polyvinyl alcohol hydrophilic surfactant Osmotically active materials | | Increases the degree of supercooling. | (Gavish et al., 1990). |
| **Biological** | Biological ice nucleating agent | | | (Massie et al., 2011). |
| | Anti-freeze protein | | Raises the nucleation temperature, reduces the degree of supercooling and catalyses ice formation. | (Gao et al., 1999). |
| | | | Decreases the freezing temperature, retards recrystallisation, suppresses the growth of ice nuclei, inhibits ice formation and alters the ice habit and growth rate. | (Kumano et al., 2009; Matsumoto et al., 2013; Blanshard and Franks, 1987; Li and Lee, 1998). |
| | | | | (Feeney and Yeh, 1998). |
| | | | | (Hassan-Roudsari and Goff, 2012). |
control) or based on the water-ice phase transition under the pressure (high pressure shift freezing), sudden pressure releasing may lead to high degree of supercooling, high nucleation rate and instantaneous, homogeneous nucleation throughout the sample leading to smaller ice crystals (Le-Bail et al., 2002).

3. Ultrasound irradiation and freezing

Power ultrasound, a kind of ultrasound waves with low frequency (20–100 kHz) and high intensity (generally higher than 1 W cm$^{-2}$), has proven to be useful in controlling the crystallization process during freezing (Sun and Li, 2003). It plays effective roles in the initiation of nuclei and subsequent crystal growth (Li and Sun, 2002a). The mechanism of ultrasound induced nucleation has not yet been totally elucidated and different theories have been proposed. The first theory was suggested by Hickling (1965) who claimed that the collapse of cavitating bubble generated high pressure which increased the equilibrium freezing temperature of water and thus increased the supercooling which is the driving force of ice nucleation (Saclier et al., 2010a). However, Zhang et al. (2003) and Dodds et al. (2007) have found that the flow streams of stable cavitation bubbles and molecular segregation due to the pressure gradient of cavitation bubbles could also cause nucleation.

The major consequences of power ultrasound irradiation within a liquid are cavitation and agitation, which are useful in improving heat transfer and freezing rate (Kiani et al., 2012b; Li and Sun, 2002a; Lima and Sastry, 1990). In addition, the collapse of cavitation bubbles could trigger nucleation (Kiani et al., 2013) which may induce intracellular nucleation or may also increase the nucleation rate in the extracellular region, which is favorable for an overall smaller crystal size distribution (Petzold and Aguillera, 2009). Due to heat generation when ultrasound passes through the medium, applications of ultrasound for freezing require optimization of the levels of two key parameters in the process: ultrasonic power and duration (Li and Sun, 2002a). Li and Sun (2002a) also claimed that ultrasound with a power level of 15.85 W applied for 2 min improved the freezing rate and gave a better cellular structure of potato.

The ultrasound technology has also been successfully implemented as a means of controlling the nucleation temperature within vials in the same batch (Passot et al., 2009). In a more recent study the effect of irradiation temperature, duration and intensity on agar gel were investigated by (Kiani et al., 2013). Their results showed that ultrasound irradiation was able to initiate nucleation at different supercooled temperatures under appropriate conditions. Moreover, when the nucleation temperature was decreased smaller ice crystals were formed. On the other hand, application of ultrasound at higher degrees of supercooling will cause the formation of many nuclei, which can only grow to a limited size, originating many small crystals (Kiani et al., 2013). This is in agreement and consistent with the results reported by Nakagawa et al. (2006) for mannitol and bovine serum albumin (BSA) who reported that small and numerous ice crystals were obtained at lower nucleation temperature (higher supercooling degree), while large and directional ice crystals (dendrite type) were obtained at higher nucleation temperature (lower supercooling degree) (Fig. 1). In order to optimize the industrial freeze drying of pharmaceutical proteins, Nakagawa et al. (2006) applied ultrasound waves to control the freezing step of the process. The nucleation temperature was controlled at selected values below the equilibrium freezing temperature. According the authors, the morphological modifications driven by the nucleation temperature differences clearly influenced the water vapour permeability and subsequently the sublimation rate during of the freeze drying process. The aforementioned studies indicate that ultrasound assisted freezing follows the same principles with conventional freezing regarding the supercooling and ice crystal size.

Saclier et al. (2010b) also reported that the number of nuclei depends not only on the supercooling degree, but also on other parameters such as the level, the amplitude and frequency of the applied acoustic signal. In addition, the initial size distributions of gas bubbles are crucial factors. Their model showed that the nucleation could be initiated with moderated acoustic pressure amplitude (around 1 bar) even at low supercooling levels (around few degrees of Celsius).

Fig. 1. Ice crystal morphologies on vertical cross sections (10% mannitol): (A) upper position, nucleated at –2.04 °C; (B) lower position, nucleated at –2.04 °C; (C) upper position, nucleated at –8.17 °C; (D) lower position, nucleated at –8.17 °C (Nakagawa et al., 2006).
It has been reported in many studies that ultrasound-assisted freezing was applied to freeze many different kinds of food materials including potato (Li and Sun, 2002a; Sun and Li, 2003), red radish (Xu et al., 2015a, 2015b), mushroom (Islam et al., 2014) and strawberry (Cheng et al., 2014). A typical trend from these reports is that the ultrasound-assisted freezing significantly improves the quality attributes and microstructure of frozen product. However, almost all these studies used the technique of immersion freezing while ultrasound was applied; recently, Islam et al. (2015) investigated the influence of ultrasound irradiation on the ice crystal size and distribution in mushroom during contact freezing. Their results indicated that ultrasound triggered the nucleation of ice crystals and further controlled the nucleation and thus reduced the ice crystal size.

4. Electrofreezing

Although the phenomenon of electrofreezing has been known since 1861 (Dufour, 1861), the first effort to induce ice nucleation in supercooled water droplet by high voltage electric fields was reported by Rau in 1951 (Rau, 1951). This technology has also already been used to induce organic molecules nucleation in crystallization processes (Hammadi and Veesler, 2009). Different approaches and methods have been proposed within the electrofreezing area. We could divide them in two general categories: charged surface and externally or static applied electric fields in which electrodes do not come into contact with the sample (Braslavsky and Lipson, 1998). Experiments have demonstrated the effect of both the charge flow and static electric fields methods to induce ice nucleation and decrease the degree of supercooling by increasing nucleation temperature (Shichiri and Araki, 1986; Wei et al., 2008). The application of charge flow or static electric fields for controlling the nucleation phenomena through a repeatable and predictable process (due to stochastic behavior of this event) was also proposed by (Orlowska et al., 2009; Petersen et al., 2006) respectively. Fig. 2.

4.1. Charged surface or charge flow-type nucleation

Electrostatically charged surfaces method is generally carried out by applying continuous or pulsed high electric fields between narrowly spaced electrodes immersed in the solution; this method has been used to induce and control ice nucleation in supercooled solutions (Anuj, 2012). A typical application of this method could be freeze drying of pharmaceutical products where higher nucleation temperatures which are induced by electric fields are desired because they generate larger ice crystals, which result in larger pores upon sublimation. These larger pores can dramatically increase the mass transfer and reduce resistance to vapour flow. As a result, a shorter drying time can be obtained (Anuj, 2012; Awotwe-Otoo et al., 2013; Geidobler and Winter 2013; Nakagawa et al., 2006; Passot et al., 2009).

The shape of the electrode is of great importance to induce crystallization (Hozumi et al., 2005). Based on their research the probability of the freezing in the case of flat end anode (0.5 mm diameter) was larger than sharp end anode (0.1 mm in min. and 0.5 mm in max. diameter) due to more micro convex in the case of flat end anode which led to high electrical density in these protruding parts (Hozumi et al., 2003). In fact, an electrode having a perfectly smooth surface does not exist. There is a large number of small protruding parts on the electrode surface and hence the electrical charges concentrate on them. The smaller the protruding part the larger the electrical charge density is. Since these charges attract water molecules, the layer of water in contact with the electrode will be oriented due to polarity of the water molecule. This orientation of molecules of water near the electrode enhances the possibility of ice nucleation (Sivanesan and Gobinathan, 1991). Furthermore, the effect of electrode material has an importance on the nucleation process. If the electrode material has a high tendency to ionization (like aluminum) the probability of formation between electrode and water molecules will increase, which could induce ice nucleation (Hozumi et al., 2003). The probability of freezing occurring with respect to the electrode material was ordered as follows: Al > Cu > Au > Ag > Pt. The results of Shichiri and Nagata (1981) also showed a similar trend and they concluded that when the tendency of material to ionization is high the nucleation is favorable to occur on the anode, and when it is small, the nucleation occurs on the cathode (Shichiri and Nagata, 1981).

4.2. External electric fields (static electric fields)

Electrostatic field means that no currents or varying voltages may be defined or analyzed during the freezing experiment. Electrostatic freezing system involves the application of high voltage DC power supply to foods placed between two electrodes during freezing. It must be designed so that it can operate at high electric fields strength while dielectric breakdown inside the system must be prevented (Dalvi-Isfahan et al., in press). The experimental set up design for freezing under external electric fields is still in the research gate and most of them have been designed on a trial and error basis. But the main parts of static electric fields are similar to the setup used by Orlowska et al. (2009) and Wei et al. (2008) for controlled and induced ice nucleation under high voltage electrostatic fields condition. Their system consists of a DC voltage generator, one pair of plate electrodes placed in parallel, cooling system, temperature measurement and recording system, dielectric spacers to isolate electrically two electrodes from each other and decrease the probability of current flow through the sample. Le-Bail et al. (2011a) put the upper electrode 2 mm above the sample surface to avoid direct contact and electrical connection between sample and electrode and finally, treatment region where the sample was placed (measurement cell).

In order to create a uniform electric field and reduce the probability of corona discharge, parallel plate electrodes are usually used instead of needle—plate electrodes. Corona discharge was able to promote higher rates of heat transfer and increase cooling efficiency. The resulted ion form corona wind could have an effect on nucleation but under these conditions of nucleation, electric fields is not the sole cause for inducing nucleation of ice (Stan et al., 2010).

The shape and size of the electrode depend on the sample and sample volume, but it is recommended that 1) electrodes surface should be polished to avoid possible occurrence of sparks when high voltage is applied (Wei et al., 2008). 2) Since electric fields magnitude is relatively higher near the edge of the electrode due
to fields enhancement, it is recommended to gradually decrease the radius of curvature (Harrison, 1967). 3) the distance between the electrodes depends on the food material being used and the level of its processing but as a general rule, the distance between the electrodes should be smaller than the diameter of the electrodes and 4) the size of lower electrode should be larger than upper electrode in order to collect surface charge. In the treatment region between the two parallel plate electrodes, the potential drop is nearly uniform and strong electric fields is generated. On the other hand, in the non-treatment zone most of the potential drop is found inside the dielectric spacer, thus the electric fields is quite weak in the outside of the treatment region (Barbosa-Canovas et al., 1997; Muthukumar et al., 2009).

Determination of actual or effective electric fields which develops in the sample could be calculated by modeling the experimental system using Maxwell equations (Havet et al., 2009). There is not much published data about the static electric fields and in all these experiments, small volume of water (1–4 ml) or alcoholic solutions were used and pulsed or continuous DC electric fields while the samples were continuously cooled was utilized (Le-Bail et al., 2011; Wei et al., 2008). Static electric fields (SEF) tend to induce ice nucleation at a lower degree of supercooling, and subsequently shorter nucleation time and longer solidification time has been reported however, the total freezing time is close to control sample in all the experiments. The modification of the solidification time may be caused by the amount of refrigeration energy stored during the supercooling. Since SEF decreases nucleation time, a larger amount of heat had to be removed during phase transition, which resulted in longer solidification time (Orłowska et al., 2014).

The strength of electric fields and electrode gap (the distance between electric fields from the surface) are the most important factors which influence the probability of freezing under electric fields. Yan and Patey (2012) based on molecular dynamic simulation showed that the minimum electric fields strength required to nucleate ice depends a little on how far the fields extends from the surface. Recently Carpenter and Bahadur (2015) showed that both electric fields and the electric current influence electrofreezing; they applied electric fields and charge flow in the solid-liquid interface of droplets instead of inside of the liquid. It has been clearly seen that freezing temperatures can be increased by controlling the electric fields. However the effect of electric field on freezing temperature has not been reported by the other researcher.

4.3. Mode of action

The precise mechanisms of electric fields are not well understood but the effect of electric fields will be discussed from two aspects namely, molecular dynamic simulation and thermodynamic point of view.

4.3.1. Molecular dynamic simulation

The exact mechanism of electrofreezing remains uncertain and probably various reasons contribute including, acoustic shock, bubble generation by electrolysis, and coordination formation between electrode and water molecules (Braslavsky and Lipson, 1998; Hozumi et al., 2003). But it seems the most important reason of electrofreezing in static electric fields type may be attributed to local dipole – field interaction and dipole polarization of the water molecules by the electrostatic field. Several molecular dynamic (MD) simulations have been performed in order to investigate the influence of an electric field on water phase transition. The first study of employing MD simulations was performed by Svishchev and Kusalik (1994). They reported that the presence of electric field near the surfaces or within the confined geometries can play an important role in the crystallization of liquid water to form ferroelectric cubic ice. These results are further verified by Vrbka and Jungwirth (2006) who observed that ice preferred to nucleate in the subsurface layers, rather than in bulk region of the sample and furthermore, Yan and Patey (2012) concluded that an electric field acts very near a surface and induces heterogeneous ice nucleation. This is in agreement with the results reported by Wei et al. (2008) and He and Liu (2009). They employed the Boltzmann distribution to describe the distribution of water molecules under the influence of electric field and reported that the variation of Boltzmann function is small in bulk phase and the effects of electrostatic field may become largely strong at the interface and affect the dynamical state of the interface.

Molecular dynamics simulation studies showed that bulk and clusters of water (under the influence of sufficiently high electric fields of 1.0–1.5 × 107 V/cm, respectively) will undergo an abrupt structural change including all molecular dipoles pointing to the directions less than 90° with respect to the electric field vector, enhancement of the molecular reorientation rates and hydrogen bonds becoming stronger along the field than along orthogonal directions (Vegiri, 2004a, b).

Electric field not only causes restructuring transitions of water but also influences some physical properties. Srivastava et al. (2012) showed that the application of electric field decreases the phase density in the saturated liquid and increases the saturated vapour phase density of the confined water on the vapour-liquid phase transition (Srivastava et al., 2012). Yeh and Berkowitz (1999) reported that the dielectric constant of water is reduced to half of its value under a relatively modest electric strength (50 mV/A) and this reduction is due to the resultant partial destruction of the hydrogen-bonded network (Yeh and Berkowitz, 1999).

Although MD simulation is a powerful tool for understanding the response of water molecules to an applied electric field and allows a better understanding of the electrical properties for a wide range of electric field, their results might not be experimentally confirmed. For example, Svishchev and Kusalik (1994) reported that the application of electric field of the order of 2.0 × 106 V/m can induce crystallization in bulk water; however, such strong fields are scarcely attainable in the laboratory and this electric field magnitude is much larger than the dielectric breakdown strength of pure water (Kolodziej et al., 1975). Weaker electrostatic field strength in the range of E = 105–106 V/m, is sufficient to induce the nucleation temperature and increase supercooling degree of water in the experiment (Woo and Mujumdar, 2010).

4.3.2. Thermodynamic point of view

When water is exposed to an external electric field, the dipoles have the tendency to turn into the field. This behavior results in a weakening or destruction of some hydrogen bonds which in turn reduces the entropy of the system (Yan and Patey, 2012). Electric field also changes the free energy barrier for phase transition (ΔGm). The free energy of a spherical crystallite in a solution is equal to the sum of two competing forces; The first is the surface or interface free energy which is associated with the formation of a new interfacial area between the solid and the liquid and destabilizes the nuclei under a certain critical size (ΔG_{Surface}). The second, is the volumetric free energy, (ΔG_{Volume}) which is associated with the bulk energy of phase change and stabilizes the nuclei.
implies that when the supercooling becomes small (the typical nucleation, respectively (Kiani and Sun, 2011). The above equation term, Boltzman constant, temperature and critical free energy for polarizability multiplied by the electric field.

Similar results have been obtained for phase transition of transition, allowing water to nucleate with lower degree of supercooling. Other words, electric field also shifted to lower values (Fig. 3) (Le-Bail et al., 2011a, 2011b). In other terms, electric field reduces the energy barrier for the phase transition, allowing water to nucleate with lower degree of supercooling. Similar results have been obtained for phase transition of water confined between hydrophobic plates. Vaitheswaran et al. (2005) also reported that the free energy barrier for capillary evaporation of water confined between the plates was lowered when electric field was applied. This condition may lead to a change in the nucleation rate (the number of stable nuclei formed in the system per unit of time and per unit of volume) in both increasing and decreasing directions. The general equation for the rate of nucleation which was developed based on thermodynamic expression is an Arrhenius type relationship with pre-exponential and exponential terms.

\[ B = A \exp \left( -\frac{\Delta G_n}{kT} \right) \]  

where B, A, k, T and \( \Delta G_n \) are rate of nucleation, pre-exponential term, Boltzman constant, temperature and critical free energy for nucleation, respectively (Kiani and Sun, 2011). The above equation implies that when the supercooling becomes small (the typical trend from DC electric field), the nucleation rate becomes really small. On the other hand, the electrostatic field can modify and helps lower the free energy necessary (\( \Delta G_{n} \)), to overcome the phase change then, nucleation rate increase and allows the phase transition to occur faster (Dalvi-Isfahan et al., 2016). Marand et al. (1988) studied the influence of external electric field on crystallization of polyvinylidene fluoride (PVF). They observed (theoretically and experimentally) that a static electric field increases the nucleation rate of polar phase. Stan et al. (2010) also estimated that the increase of the nucleation rate might be observable for field intensities on the order of \( 10^7 \) V/m and larger intensities on the order of \( 10^8 \) V/m might enhance the nucleation of ice through ferroelectric ice XI.

The thermodynamic analyses for boiling nucleation under an external electric field are analyzed by Quan et al. (2013). Their results showed that both the critical radius and nucleation availability increase with the enhancement of electric field strength, indicating that nucleation becomes more difficult to occur under an externally imposed electric field. Cheng (1984) also using the thermodynamic theory of phase transitions showed that an electric field increases the critical size and work for bubble nucleation in a superheated liquid and impedes the process; it decreases the critical size and work for liquid droplet formation in a supercooled vapour and enhances the process (Cheng, 1984).  

4.4. Crystal growth

The polar water molecules (or clusters) maybe torqued, rearranged, and forced to join the ice lattice via a special orientation and position under the action of the electrostatic field. Thus the rate of attachment (or detachment) of water molecules on the ice interface is affected by external electrostatic field. He and Liu (2009) investigated ice crystal formation under electrostatic field via phase field method. They reported that the application of electric field can induce the change of surface tension and result in asymmetric ice crystal growth of dendritic ice.

The size of the ice crystals formed is crucial for the final quality of the frozen food as they can cause irreversible damage to the cellular structure, which in turn degrades the texture, color, taste, and nutritional value. A study by Xanthakis et al. (2013) demonstrated that the average equivalent circular diameter of ice crystal size in pork meat showed a decreasing trend with an increasing strength of the static electric filed under a static electric field (Fig. 4). The most recent study of Dalvi-Isfahan et al. (2016) showed the impact of electrostatic field on the food quality of frozen lamb meat. Their results showed that although static electric field had no significant effect on the color, hardness and freezing rate of meat during freezing, the drip loss and ice crystal size significantly

![Fig. 4. Micrograph images of frozen pork tenderloin transversal cuts under different magnitude static electric fields.](https://example.com/fig4.png)
Further studies in the application of static electric field during freezing would be interesting to be carried out with different configurations as well as on more sensitive food matrices such as fruit and vegetables.

5. Alternating currents and freezing

Alternating current electric field (AC) with a frequency of at least in the radio frequency band or oscillating electric field allows water molecules to vibrate and may inhibit nucleation, since the alternating or oscillating electric field exerts a torque which can displace water molecules from their equilibrium relationship in a cluster without inducing thermal effect. Recently, experiments have demonstrated that the AC electric field might actually increase the allowable degree of supercooling (enhance supercooling), suppress or retard spontaneous ice nucleation, and represent a kinetic constraining to ice formation by interfering with both ice nucleation and kinetics of crystal growth (Hanyu et al., 1992; Woo and Mujumdar, 2010; Wowk, 2012). The potential of alternating electric field to assist freezing has been studied by a few researchers (Stan et al., 2010; Sun et al., 2007).

Wei et al. (2006) applied electric field of sine-wave with different frequencies ranging from 50 Hz-5MHz during freezing of 0.9% NaCl solution, using relatively low cooling rate (0.26 K/min). It was found that an increase in frequency of alternate electric field up to 500 KHz decreases the supercooling degree while with further rise in frequency to 5 MHz, supercooling degree seems to

### Table 2

| No | Specimen                  | Condition                          | Result                                                                 | Reference                  |
|----|----------------------------|------------------------------------|------------------------------------------------------------------------|----------------------------|
| 1  | Water (100 ml)            | 0–1.0 × 106 V/m                   | Application of electric current (>0.1 mA) increases the nucleation temperature. Ice nucleation occurred at cathode. Electrodes, when electrode with small ionization tendency was used and when the ionization tendency of the electrode is large, nucleation was apt to occur at the anode. Nucleation process is related to occurrence of electrochemical process at the electrode. | (Shichiri and Nagata, 1981). |
| 2  | Water (n.d.)              | 0–1.0 × 106 V/m                   | Increase ice nucleation temperature. Bubble generation by electrolysis has an effect on the nucleation and orientation of water molecules near the electrode enhances the possibility of ice nucleation. | (Shichiri and Araki, 1986). |
| 3  | Water (50 ml) + 50 mg nucleants (AgI-CuBr) system | 104 V/m                            | The effect of electric field on ice nucleation in the presence of nucleants (AgI-CuBr) system showed that production and collapse of bubbles could be enhanced ice nucleation temperature. | (Sivanesan and Gobinathan, 1991). |
| 4  | Water (4 ml)              | Electric charge (50–120 V) and electrode gap 300 μm (~1.7 × 10⁻²–4.0 × 10³ V/m) | The probability of the freezing was larger in the case of flat end anode and material with high tendency to ionization. | (Hozumi et al., 2005). |
| 5  | Ionic and non-ionic solution | Pulse electric V = 4.5 kV applied for 3 s ~Cooling rate 1 K/min | Induce nucleation and control ice nucleation temperature. | (Petersen et al., 2006). |
| 6  | Water (1 ml)              | 1 × 10⁻⁵                          | Increasing supercooling degree and phase transition time. | (Wei et al., 2008). |
| 7  | Water (200 μl)            | 5 × 10⁻⁴                          | No significant change in the nucleation temperature. | (Wilson et al., 2009). |
| 8  | Water (1.6 ml)            | Internal electric field 4.5 × 10⁴ V/m – 1.1 × 10⁵ V/m | Increasing supercooling degree and phase transition time. | (Havet et al., 2009; Orlowska et al., 2009). |
| 9  | 1.6 ml Ethanol and Propanediol aqueous solution (10% v/v) | Internal electric field 4.5 × 10⁴ V/m – 1.1 × 10⁵ V/m | Increasing supercooling degree. | (Le-Bail et al., 2011a). |
| 10 | 0.5 ml NaCl solution (0.9%) | 1-10⁻³ cooling rate of 5 °C/min | Increasing supercooling degree and relative dielectric constant. | (Ma et al., 2010). |
| 11 | Pork meat (Average weight 1.06 g) | 0–12 kV cooling rate of 1°C/min | Ice crystal size reduced and quality of frozen pork meat improved. | (Xanthakis et al., 2013). |
| 12 | NaCl Solution (0.9%)      | 0–5 MHz Cooling Rate of 0.26 K/Min | Increasing the alternated electric field up to 500 kHz decreases the supercooling degree significantly. | (Wei et al., 2006). |
| 13 | Water droplet             | 1.6 × 10⁻⁵ frequencies from 3 to 100 kHz | Uniform electric fields in water neither enhanced nor suppressed the homogeneous nucleation of ice. | (Stan et al., 2010). |

* (n.d) = Not defined.
increase and is close to control sample. Water molecule polarization theory and ion moving were used for their analyses, while ion moving was indicated as a major factor. Sun et al. (2007) studied freezing in the presence of oscillating electric fields at frequencies between 1 and 200 kHz, and they found ice crystal domain size to be minimized at a frequency of 50 kHz. The aforementioned different approaches of electrofreezing are summarized in Table 2.

6. Microwave and radio frequency waves and freezing

Jackson et al. (1997) showed that 2.45 GHz microwave radiation could reduce the amount of ice formed during attempted vitrification of ethylene glycol solutions. The application of microwaves during freezing of food material has also been investigated by Xanthakis et al. (2014b). Their results showed that the average ice crystal size decreased significantly and application of microwave radiation may reduce the damage of meat tissue during freezing process. From their study also arose that the degree of supercooling decreased as well as the freezing rates by increasing the levels of microwave power due to the MW-generated heat.

The exploitation of radiofrequency (RF) to assist food freezing was studied by Anese et al. (2012). They observed a better cellular structure of meat microstructure when low voltage (2 kV) RF pulses were applied and this could be attributed to RF ability to depress the freezing point thus producing more nucleation sites.

The underlying mechanisms behind the oscillating electric field freezing are unknown but they could be due to the ability of RF to decrease the freezing point and consequently promote the ice nucleation (Cheng et al., 2015) or interaction of water clusters to the electric field, which resulting in ice crystal disruption and fragmentation of preexisting ice crystals. Fragmentation of ice crystals under oscillating electric field will lead to the secondary nucleation and ice crystal size reduction.

7. Magnetic fields and freezing

Water is diamagnetic, which means that it develops a magnetic dipole moment in response to an applied magnetic field (Wowk, 2012). Magnetic fields have been shown to cause hydrogen strengthening which can change physical properties of confined liquid water such as heat capacity, light absorbance, electrical conductivity, self-diffusion coefficient, and surface tension (Zhang et al., 2010). Moreover, magnetic fields in the order of 14 T affect the infrared spectrum of water (showing its effect on water clusters and ice crystal size reduction).

The effectiveness of this method depends on several factors such as combination of food, freezing rate and magnetic field frequency, and the majority of those results suggested that the impact of this method on supercooling degree of a food material was considered as low. The effectiveness of this method depends on several factors such as combination of food, freezing rate and magnetic field frequency (James et al., 2014; Suzuki et al., 2009a; Watanabe et al., 2011).

7.3. Pulsed magnetic fields (PMF)

Iwasaka et al. (2011) observed ice crystal formation of aqueous solutions with an optical microscope that freezing under pulsed-electron field or oscillating magnetic fields (PMF) process consisted of two stages. In the first stage; food underwent continuous magnetic wave vibrations, which impeded the crystallization, the second stage occurred instantaneously by removing the magnetic field, which led to freezing (Fikiin, 2008; Mohanty, 2001). The change in ultrastructure and quality of beef muscle during the frozen storage by electro-magnetic resonance freezing and the air blast freezing were investigated by Choi et al. (2015). Their results showed lower increase and decrease ratio of the thawing loss and the water holding capacity of magnetic resonance in comparison with the air blast freezing according to the frozen storage because the shape and ice crystal size of magnetic resonance were small and uniformly formed in the early stage of frozen storage. There is very little scientific published data regarding the effect of magnetic resonance field on food materials and the majority of those results suggested that the impact of this method on supercooling degree of a food material was considered as low. The effectiveness of this method depends on several factors such as combination of food, freezing rate and magnetic field frequency (James et al., 2014; Suzuki et al., 2009a; Watanabe et al., 2011).

SMFs are naturally present everywhere as earth is surrounded by fields varying between 25 and 65 μT. Information on the effects of SMFs on the food materials is very limited. In a recent study, the potential of an innovative freezing technique by applying static magnetic field (0-480 mT, repulsive and attractive) on the freezing process of 0.9% NaCl solution was tested by Mok et al. (2015). The phase transition time in repulsive SMF reduced by 32.1% and 42% compared to control and attractive SMF respectively. Furthermore, the shape of ice crystals formed irregular shapes compared to control and they suggested that this reduction might be due to the possible distortion and breaking of hydrogen bonds. They have also reported that, under combination of pulse electric field and repulsive static magnetic field, phase transition time decreased remarkably while roundness and uniformity of ice crystal was observed. The cryoprotective effects of static magnetic fields (SMFs) with 0.4 T or 0.8 T on human dental pulp stem cells (DPSCs) during cryopreservation have been reported by Lin et al. (2015). Their results showed that, the survival rates of the thawed DPSCs increased 2- or 2.5-fold when the cells were exposed to 0.4T or 0.8T SMFs respectively. They also suggested that the SMF cryoprotective effect was due to an improved biophysical stability of the cell membrane during the slow cooling procedure.
conducted by the same group but their results are not in the public domain, the authors also declared that the eddy effect (also called Foucault currents) which arise during application of time-varying magnetic fields is one of the factors which affects the food freezing. Hence, when the effects of the OMF and PMF are studied, in addition to the direct effect of the magnetic field the effects of induced electric fields should also be considered.

7.4. Electro-magnetic freezer

Nowadays, at least two companies exist in the market dedicated to manufacture hybrid magnetic freezers: Cell alive system freezer manufactured by ABI Corporation Ltd. (Abi-ko, Japan) and Proton freezer manufactured by Ryoho Freeze Systems. The design of CAS freezer is based on the patent of (Owada and Kurita, 2001), CAS freezer applies static and low-frequency oscillating magnetic fields (OMF) during freezing while Ryoho freezer simultaneously applies static magnetic fields and electromagnetic waves to induce nuclear magnetic resonance in the hydrogen atoms of water. The producers claimed that these kind of freezers could preserve cells without intracellular ice formation and this is due to the applied electric and magnetic fields.

CAS manufacturer claimed that electric and magnetic fields cause vibration of water molecules by non-thermal mechanism, while these non thermal vibrations are amplified in sympathy with mechanical and thermal vibration (CAS vibration) and prohibit water molecule clusters during freezing process (Kojima et al., 2013). The potential applications of ABI’s CAS technology are not limited to food freezing and several studies have been completed or are ongoing on this device, including human transplant tissues like teeth (Lee et al., 2012), periodontal ligament (PDL) cells (Kaku et al., 2010), embryonic stem cells (Lin et al., 2013) and frozen small animals (drosophila) (Naito et al., 2012). A recent experimental study conducted by Kojima et al. (2013) showed that a CAS freezer can maintain high survival and proliferation rates of mesenchymal stem cells (MSCs) and maintain both their adiogenic and osteogenic differentiation abilities. In all of these experiments, it has been claimed that this method can improve the ability of much larger volumes of animal and vegetable matter to be frozen with minimal damage to cellular microstructure from ice crystal growth and it can be useful for long-term cell and tissue cryopreservation.

Despite its obvious importance and interest, research does not suggest any consistent evidence nor does it provide sufficient scientific support about the exact mechanism of CAS freezer. For example, treatment with weak oscillating magnetic field (0.0005 T) alone has no significant effect on temperature history during freezing and on the qualities of frozen vegetables (Suzuki et al., 2009b). Kobayashi and Kirschvink (2014) suggested that the mechanisms might be related to the two possible mechanisms. Firstly, corona discharge which causes higher rates of heat transfer and increases cooling efficiency and secondly, the biologically-precipitated ferromagnetic materials which are ubiquitously present in the biological tissues can strongly interact with weak, low frequency magnetic fields of freezer.

8. Summary

A summarized description and a comparison of the effects of the different food freezing processes are illustrated in Table 3.

9. Conclusions

The present article explored the effects of ultrasound waves, magnetic, electric and electromagnetic field during freezing and the following points emerged from the discussion that could be useful for their application in food freezing.

The industrial application of assisted freezing technologies will be certainly considered more in the future as they have the potentials to be utilized for controlling ice nucleation. When applied remotely and uniformly over the entire samples, they may create a homogeneous, cost effective, easy to operate, and quite easily integrated test system with commercially available freezing equipment. In addition, since they do not require a direct contact with food materials, they are safe, non-toxic, and they can comply with safety regulations. However, within electric field technology some safety issues may arise, such as high voltages (several kV) when operated in a humid environment. The task of applying high voltage electric fields safely during freezing should also be investigated in depth in order for this promising technology to fulfill the requirements for commercial exploitation. The effect of electric and magnetic fields can be related to the theory that ice nucleation occurs when a sufficient number of relatively long-lived hydrogen bonds develop spontaneously at the same location to form a fairly compact nucleus. Since electric (DC and AC) and magnetic fields

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**Table 3**

Comparison between different methods on the freezing process.

| Method                        | Nucleation temp. | Freezing temp. | Freezing time | Effects                                                                 | Mechanism                                                                 |
|-------------------------------|------------------|----------------|--------------|------------------------------------------------------------------------|--------------------------------------------------------------------------|
| Ultrasound assisted freezing  | ↑                 | ↑              | ↑            | • Triggering ice nucleation                                            | • Cavitation                                                              |
| (UAF)                         |                   |                |              | • Increase heat and mass transfer                                      | • Microstreaming                                                           |
| Electrostatic freezing         | ↑                 |                | ↑            | • Triggering ice nucleation                                            | • Fragmentation of large ice crystals                                     |
| (ESF)                         |                   |                |              | • Reduce ice crystal size                                              | • Triggering Secondary ice nucleation                                     |
| Alternating electric fields   | ↑                 |                | ↑            | • Increase phase transition time                                       | • Increase ice nucleation rate                                            |
| (AEFs)                        |                   |                |              | • Decrease or increase supercooling based on the frequency             | • Decrease the free energy barrier for phase transition                  |
| Electromagnetic fields         | ↑                 | ↑              | ↑            | • Inhibiting ice nucleation                                            | • Prevention from clustering of water molecules                            |
| (RF/MW)                       |                   |                |              | • Reduce ice crystal size                                              |                                                                                                                                       |
| Magnetic fields               |                  |                | ↑            | • Improve quality attributes                                           | • Fragmentation and ice crystal disruption                                 |
| (MFs)                         |                   |                |              | • Triggering ice nucleation                                            | • Triggering Secondary ice nucleation                                     |
|                               |                   |                |              | • Triggering ice nucleation                                            | • Prevention from clustering of water molecules                            |
|                               |                   |                |              | • Supercooling could be decrease or increase based on the MFs intensity | • Prevention from clustering of water molecules                            |
|                               |                   |                |              | • Reduced phase transition time                                        |                                                                                                                                       |

*Contradictory results have been reported and it strongly depends on the type of magnetic fields and operating conditions.*
could destruct or enhance hydrogen bonds, they are potentially able to modify the water crystallization process. In addition, it can be expected that quite small changes in the strength of hydrogen bond of water will lead to a substantial change on the physical properties of water. However, it is worth noting that based on the majority of experimental results, it seems the electric fields could not have a significant impact on the physical properties of water such as melting point, boiling point. Although that in conventional freezing processes the ice crystal size decreases by increasing the degree of supercooling and vice versa, studies regarding MW and SEF applications as well as other studies in ultrasound assisted freezing methods showed an opposed direction. This fact indicates that the exact mechanism of electric and magnetic fields is not yet well known and need to be clarified. Therefore, it can be assumed that probably a variety of mechanisms can contribute to the solidification processes which make the principles of conventional freezing unable to apply when external disturbances are present.

These technologies have not been fully optimized yet; but they are promising techniques for temperature-controlled nucleation, and the production of high quality food materials. A challenge that has arisen from the aforementioned studies is the scaling up of these novel processes and their becoming accessible and handy for the food industry. For their industrialization, identification and determination of effective independent variables that affect the processes as well as the development of an accurate theoretical model to describe ice crystals characteristics as a function of operating conditions are necessary.

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Nomenclature

| Symbol | Description |
|--------|-------------|
| A      | Pre-exponential term |
| B      | Rate of homogeneous nucleation, nuclei per unit volume per unit time |
| E      | Electric field, V/m |
| G      | Rate of crystal growth kg s$^{-1}$ |
| k      | Boltzmann constant |
| n      | Constant |
| P      | Polarizability (C/m$^2$) |
| r      | Nucleated particle radius, m |
| r$^*$  | Critical nucleus radius, m |
| T      | Temperature, °C |
| T$_N$  | Nucleation temperature, °C |
| β      | Constant |
| γ      | Interfacial energy, J/m$^2$ |
| $\Delta G_n$ | Critical free energy for nucleation, J |
| $\Delta G_{\text{Surface}}$ | Surface free energy, J |
| $\Delta G_{\text{Volume}}$ | Volume free energy, J |
| $\Delta G_v$ | Free energy change per unit volume, J/m$^3$ |
| $\Delta T_s$ | supercooling, °C |

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