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Review

An Overview on Magnetic Field and Electric Field Interactions with Ice Crystallisation; Application in the Case of Frozen Food

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Academic Editor: Geun Woo Lee
Received: 4 September 2017; Accepted: 29 September 2017; Published: 4 October 2017

Abstract: Ice nucleation is a stochastic process and it is very difficult to be controlled. Freezing technologies and more specifically crystallisation assisted by magnetic, electric and electromagnetic fields have the capability to interact with nucleation. Static magnetic field (SMF) may affect matter crystallisation; however, this is still under debate in the literature. Static electric field (SEF) has a significant effect on crystallisation; this has been evidenced experimentally and confirmed by the theory. Oscillating magnetic field induces an oscillating electric field and is also expected to interact with water crystallisation. Oscillating electromagnetic fields interact with water, perturb and even disrupt hydrogen bonds, which in turn are thought to increase the degree of supercooling and to generate numerous fine ice crystals. Based on the literature, it seems that the frequency has an influence on the above-mentioned phenomena. This review article summarizes the fundamentals of freezing under magnetic, electric and electromagnetic fields, as well as their applicability and potentials within the food industry.

Keywords: food preservation; freezing; electric field; magnetic field; supercooling

1. Introduction

Freezing is an efficient and widely used method of food preservation. It is a process which transforms free water available in the food products to ice, resulting in a reduction of water activity in the food matrix. The immobilisation of free water inhibits the microbial growth, and slows down enzymatic and chemical degradation reactions resulting in slower rates of deterioration of food products [1,2]. The size of ice crystal is pivotal to textural and physical properties of frozen and frozen-thawed foods and to processes such as lyophilisation, and freeze concentration [3]. In food commodities with cellular structure (e.g., fruits, vegetables and meat, etc.), small size ice crystals distributed both in intra and/or extracellular domains are preferred as they cause minimum damage to the cellular structure and preserve higher overall quality of the product upon thawing. Ice cream is another representative case where the smaller ice crystals are desired because large crystals results in an icy texture with sandy mouth feel which is not accepted by consumers [4]. Freeze drying process is also concerned by specific objectives in terms of ice crystal size. The drying rate is dependent on the ice crystals morphology; the larger the ice crystals size are, the shorter the primary freeze drying time would be [5]. However an optimal ice crystal size is to be adjusted to obtain specific properties for the final freeze-dried product. In freeze concentration, larger size ice crystals of uniform size are desired as it will facilitate the separation of ice crystals from the concentrated mother solutions.

Moreover, they are characterised by low surface area per unit of mass, and therefore, the loss of entrained juice concentrate can be minimized [3,6,7].

To date, the most common approach opted to control ice crystal size is by varying the cooling rate during the freezing of a food product. In general, lower cooling rates will result in the formation of ice crystals with larger size in the food product. On the contrary, higher cooling rates would yield smaller size of ice crystals. In the recent years, several new approaches have been proposed for controlling the ice nucleation; among them are the uses of high-pressure shift [8], ultrasound waves [9], electric fields [10–12], magnetic fields [13], electromagnetic waves [14], ice nucleation agents [3], antifreeze proteins [15], ice nucleating bacteria [15] and others. This review article summarizes the fundamentals of freezing under magnetic, electric and electromagnetic fields, and their applicability in the food industry.

2. Freezing Assisted by Magnetic Field (FA-MF)

Magnetic fields (MFs) can influence the properties of water [16,17]. In the absence of externally applied MF, water lacks the intrinsic magnetic dipole moment. Water is a diamagnetic substance, which means when it is placed in external MFs, a weak magnetic dipole moment is induced in the direction opposite of the applied field. MF is required to both induce a magnetic moment, and exert a force on the magnetic moment [18]. According to Beaugnon & Tournier [19], the magnetic force exerted on a diamagnetic or paramagnetic substance is proportional to the strength of the external MF, the gradient of external MF and the magnetic susceptibility. Since, magnetic susceptibility (χ) of water is low (e.g. $\chi = -9.07 \times 10^{-9}$ $m^3\ kg^{-1}$ at 20 °C [20]), weak MFs will have a slight effect on water, while strong MFs (>10 T) can exert substantial force to levitate water against the gravity [18–21].

Former studies revealed that specific properties of water such as surface tension force and viscosity, optical property (changes in optical feature of water including infrared, Raman, visible, ultraviolet lights and X-ray spectra), electromagnetic property (refractive index, dielectric constant and electrical conductivity), thermodynamic property (enthalpy of vaporization), dynamic property (self-diffusion coefficient) and molecular structure of water (hydrogen bond structure) change upon the application of MFs [16,17,22–30].

Cai et al. [22] detected a decrease in the surface tension and an increase in the viscosity of purified water circulated at a constant flow rate in a 0.5 T MF at 298 K The decrease in surface tension indicated that the inner structure of water turned to be more stable with less molecular energy under the influence of MFs. The stable water structure means more hydrogen bonds were formed under MF [22]. Moreover, Cai et al. [22] suggested that the mean size of water cluster would be larger under MF. Pang & Bo [17] observed that the static magnetic fields (SMFs) (0.44 T) significantly decreased the surface tension forces and the viscosity. Meanwhile, the refractive index, dielectric constant and electric conductivity of water are increased upon magnetization [17]. In contrary, Toledo et al. [23] observed an increase in the surface tension and viscosity of water subjected to an external MF of 45–65 mT for 3 hours.

Spectrum techniques such as infrared, Raman, visible, ultraviolet lights and X-ray have confirmed that optical properties of water change on MF treatment [16,17]. For instance, when water was exposed in the SMF of 0.44 T, the absorbance of UV spectrum increased in the region of 191–220 nm, the diffraction intensity increased, and the absorbance of infrared spectra was increased both in the mid and near infrared regions [24]. Moreover, the infrared absorbance value of magnetized water reached to saturation when water was exposed in the SMF for sufficient time. Based on the absorbance value, they concluded that the magnetized effect does not fade out immediately but remains for a time period upon removal of SMF. This property was metaphorically described as memory effect of water by some scientists [24].

Hosoda et al. [25] found *circa* 0.1% increase in the refractive index of pure water at an applied 10 T MF with respect to no field. This refractive index difference has been related to the more stable formation of hydrogen bonds under applied SMF [25]. Pang & Bo [17] reported that the refractive index value of magnetized water (exposed to MF of 0.44 T for 30 min) was ≈ 0.08% greater than the non-magnetized at 25 °C. Further, the dielectric constant and the electric conductivity increased upon magnetization. The electrical conductivity of magnetized water was higher due to the greater population of charged particles (for e.g., hydrogen ions (H^+), or H_3O^+ and OH^-) present in it. The use of strong electric field obligates the polarized water molecules in the cluster to separate as H^+ or H_3O^+ and OH^- [17].

The vaporization enthalpy of magnetized water was found to be higher than the non-magnetized water. For instance, vaporization enthalpy of non-magnetized water was 50.86 ± 0.46 kJ mol^{-1} and its value increased to 68.86 ± 0.49 kJ mol^{-1} on exposure to MF with strength 45–65 mT for 3 hours [23]. Simulation techniques, such as Monte Carlo (MC) and Molecular Dynamics (MD) simulation techniques have been used to examine the changes induced at a molecular level in liquid water by the application of MFs [23,26,27]. The observations by these groups were dissimilar. For instance, Zhou et al. [27] performed a MC simulation at 300 K to study the effects of MF (B = 0, 0.05, 0.10 and 0.20 T) on water (the number of water molecules used for simulation, N = 64 and 125). They found that the MF of 0.05 T had no significant effect on hydrogen bond structure of water, whereas MF of 0.1–0.2 T increased the mean distance between the water molecules. Thus, MF application can weaken the hydrogen bonds and consequently decrease the average hydrogen bonding number between the water molecules. The average number of hydrogen bond is a good indicator to show the changes in water structure induced by a MF [28]. On the contrary, Chang & Weng [26] through a series of MD simulations showed that the number of hydrogen bonds increased slightly (≈ by 0.34%) when the MF strength was increased from 1 to 10 T. The increase in the number of hydrogen bonds implies that the size of water cluster would be bigger under a MF, and hence the structure of the water molecules would be more compact. Moreover, they reported that the self-diffusion coefficient of water decreased as the strength of MF was increased. This reduction indicated that MF constrains the movement of water molecules.

Similarly, the structural changes of water molecules due to MF application have also been studied experimentally. Wang et al. [29] based on their frictional experiment results reported that the application of SMF weakens the hydrogen bonding in water. The investigators assumed that the thermal motion of the partially charged atoms of H_2O under the MF gives rise to the Lorentz force which will be exerted on the charge center of the polar molecule. The direction of the Lorentz force on the positive charge center are opposite with the negative center, and this results in the rotation of the charge center. Thus, the positive and negative charge center will be relocated, and the distance between them will become larger. Since, the energy of the hydrogen bond is very sensitive to the distance between the molecules, it can be concluded that, the MF exposure can weaken or partially break hydrogen bonding in a water system. Based on the theoretical and experimental interpretations, Toledo et al. [23] reported that MF would weaken or disrupt the intra-cluster hydrogen bonds, breaking large water clusters and forming smaller clusters with stronger inter-cluster hydrogen bonds. However, considering the life time of a hydrogen bond which is in the range of 0.1 ps [30], it is difficult to understand how and why a pretreatment under MF would modify specific physical properties during a subsequent freezing process.

Aleksandrov et al. [31] reported that the critical supercooling during solidification of water drops (0.5 g) under SMF decreased with the increase of magnetic field strength in the range of 0–0.5 T. MFs stronger than 0.5 T made the supercooling negligible and provoked equilibrium solidification of water. They believed that MFs assisted the orientation ordering of nuclei, presumably by virtue of the diamagnetic effect, and ensured their coagulation at a lower supercooling. On the contrary, Zhou et al. [32] during freezing of tap water under a series of several SMF (up to 5.95 mT) observed increase in the degree of supercooling with the increase in MF strength. More specifically, the degree of supercooling increased by 1.2 °C at 5.95 mT compared to no field conditions. Inaba et al. [33] studied the MF effect on the freezing point of H_2O and D_2O by using a high resolution and supersensitive DSC working in a magnetic bore. The authors of this study observed that the exposure to SMFs increased the freezing temperature of both H_2O and D_2O. For example, at MF strength of 6 T, the freezing temperature increased by 5.6×10^{-3} °C and 21.9×10^{-3} °C for H_2O and D_2O respectively. Moreover, they found that the temperature shift due to MF application was proportional to the square of the magnetic field strength. Similarly, Zhang et al. [34] reported that the freezing temperature of water confined between the parallel plates shifted to a higher value upon application of external SMF of 10 T along the direction perpendicular to the plates. Furthermore, they found that the freezing temperature of water was proportional to the denary logarithm of the external SMF. They concluded that the effect of MF on the freezing of confined water was similar with the effect of pressure increase on the freezing of confined water [34]. The phase transition time can also be altered by the application of MF. Mok et al. [35] proposed that the SMF can affect the phase transition time of 0.9% NaCl solution both positively (reduce the phase transition time) and negatively (increase the phase transition time) depending on the types of SMF (either attractive or repulsive). In their study, the samples placed between two permanent disc magnets and were frozen under different types of SMF. They acquired attractive and repulsive SMF by changing the positions of magnet poles: attractive SMF was obtained when unlike poles of two magnets were placed facing each other, whereas like poles of two magnets facing each other generated repulsive SMF. The magnetic flux densities in the case of attractive and repulsive SMF were 480 and 50 mT, respectively. When repulsive SMF was used, the phase transition time reduced by 32.1% and 42.0% compared to the control (2215 ± 16 s) and attractive SMF (2593 ± 15 s) respectively. It has to be noted that the attractive SMF prolonged the phase transition time compared to other two conditions. This might be due to the distortion of hydrogen bonds, because unidirectional attractive MF tends to form weaker polygonal rings such as hexagonal rings and rhombic rings. Moreover, they also result in a shift of the second shell to the nearest neighbours in bilayer of ice, resulting in a longer freezing time [34,35].

Besides SMF, the use of oscillating magnetic field (OMF) has also proven to affect the freezing behaviour of water and other aqueous solutions. The water (bi-distilled water) subjected to a weak OMF (B = 0.025 μT to 0.88 mT and frequencies between 10^{-2} and 200 Hz) for 5 h had a larger degree of supercooling compared to the untreated sample [36]. It was also found that the degree of supercooling was dependent on the strength and frequency of applied OMF. Moreover, when a particular strength of OMF was used, the maximum degree of supercooling was obtained at a specific MF frequency. Similar results were obtained by Mihara et al. [37] and Niino et al. [38]. They studied the relationship between the frequency of OMF (50 Hz to 200 kHz) and the degree of supercooling in physiological saline solutions at a fixed strength of OMFs (0.12 ± 0.02 mT). Among all the frequencies been studied, the highest degree of supercooling (≈ 18 °C) was observed for the sample which was treated by OMF of 2 kHz frequency. James et al. [39] noticed that the oscillating magnetic field (OMF) application during the freezing of garlic bulbs using CAS technology (Cell Alive System marketed by ABI Co., Ltd. of Chiba, Japan) (MF of 0.1–0.4 mT at frequencies ≤ 50 Hz) had minor additional effect on the degree of supercooling when compared to similar freezing conditions in the absence of OMF. Naito et al. [40] reported that the 0.5 mT MF at 30 Hz did not affect the degree of supercooling of both distilled water and saline water. Thus, it can be concluded that a perfect combination of frequency and strength of OMF is needed to cause any noticeable change to the degree of supercooling of water and other aqueous systems.

Rohatgi et al. [41] found that both SMF and OMF can affect the ice crystal morphology, such as the shape and the spacing of the formed ice dendrites. The effects of both MF types depended on the used freezing system. For example, when freezing system imparted negligible thermal gradients in the sample (small drops of NaCl solution in a column of cold organic liquid at −20 °C), both MF forms (SMF = 200 mT to 4 T and OMF = 400 mT, 60 Hz) promoted side branching of the dendrites and increased their spacing in the droplet system. On the contrary, SMF and OMF of same strength as mentioned above did not affect the dendrite structures in unidirectional solidified samples (In the unidirectional freezing system the sample was poured into a tygon tube mounted on a cold copper plate at –70 °C, from which the freezing initiated). At this point, we need to remark that in droplets the nucleation and crystal growth are free in the whole volume of the sample, and thus, there is a high probability that the entire liquid is in supercooled condition before the freezing begins, whereas in the unidirectional system, except in the immediate vicinity of the chill, constrained growth takes place in a liquid essentially near its liquidus temperature. They also observed that the concentration of NaCl in the solution directly influences the branching of the dendrites at a fixed MF intensity. For instance, at SMF of 400 mT and NaCl concentration of 10.47% (wt %), the dendrites had an extensive side branching. While at the same salt concentration and in the absence of MF, the dendrites had a limited side branching. Mok et al. [35] observed that the ice crystals formed under the influence of SMF were more irregular shaped than those obtained without MF. The pattern of ice crystals formed depended on the type of the applied external SMF (attractive or repulsive). For instance, 'parting' pattern of ice crystals was obtained under attractive SMF, while repulsive SMF yielded a unique pattern of ice crystals. Iwasaka et al. [42] reported that the freezing of aqueous solution under pulsed magnetic field (PMF) up to 325 T/s at 6.5 mT produced ice crystals which were much larger and more uniform than the ice crystals obtained without PMF. According to the study, PMFs up to 325 T/s induced an electric field in the aqueous solution. The induced electric field stirred the small ice crystals and promoted their amalgamation, forming a grain. As an aftermath, the PMF treated sample had broad areas with a uniform ice crystal, while the untreated sample showed only a grid pattern.

Freezing of Food Matrices under MFs

Over the last years a few patents have been filed in the area of MF assisted freezing of food matrices claiming the beneficial impact of MF on the final quality of the frozen products. Owada [43] claimed in his patent that the exposure of OMF (0.5–0.7 mT, 50 Hz) combined with or without SMF (1 mT) lessened the time required to cool the central temperature of product (chicken and tuna samples) from 0 °C to −20 °C by 20% to 50%. They also claimed that the thawed sample hardly showed any evidence of cell damage, while the colour, flavour, and taste were found similar to raw food. Another patent related to MF application during freezing of food products was granted to Sato & Fujita in the year 2008 [44]. The inventors claimed that the developed freezer can restrain the quality of food from deterioration and ensure long term preservation of food product. The freezer comprised of a freezer main body, a cluster fragmenting device (MF-generator) for fragmenting the water clusters contained in the matrix, a loading part, a heat exchanger, and a cold gas supply device attached with a dehumidifier. Different food matrices were frozen under various test conditions and they were stored in the freezer for a certain period of time prior to quality evaluation (storage period of Chinese noodles was three months, while spinach, packed pasta, lumps of pork, and tofu blocks were stored up to 150 days). According to the inventors, it was observed that food frozen in their freezer under the OMF (MF of 200–300 mT at frequencies 60–100 Hz) and a cold atmosphere with low water vapour content satisfactorily maintained the quality attributes (e.g., good flavour, appearance, fragrance, no or little change to texture and less drip loss, etc.) of the product upon thawing. In contrast, they observed higher degree of quality loss when the same products were frozen in the same freezer at a similar freezing condition but with no MF and dehumidifying devices. According to their results, it is not clear whether the observed effects were related to the MF, the dehumidifying device, or to a synergistic impact. The inventors proposed that the fluctuating MF breaks the hydrogen bonds between the water molecules and thereby fragments the water cluster efficiently. As a result, small size ice crystals are formed in the frozen objects and thus prevent the quality of food from degradation. Owada & Kurita [45] in another patent froze tuna, sardine, pork, juices, wines, oranges, and cakes under the combined influence of SMF (10 mT), OMF (0.5 mT, 50 Hz), SEF (static electric field) (6×10^5 V/m) and sound waves (20–2000 Hz). They claimed that freezing under the above conditions reduced the time required to achieve the target temperature of −50 °C compared to the conventional freezing method. According to the inventors, the conventionally frozen products showed greater quality loss on thawing after 4 months of storage at −50 °C, such as: (i) tuna, sardine and pork sample showed higher drip loss, discoloration and off flavour development; (ii) juice and wines sample had a phase separation; (iii) deterioration of colour and smell in orange samples; and (iv) change in taste and taste of cake sample. In contrast, the samples frozen in their invention showed no such drawbacks and maintained freshness of the product at a high standard even after 4 months of storage at −50 °C. Furthermore, freezing under MFs combined with electric field and sound waves reduced the number bacteria in the frozen product compared to the conventional method.

The mechanisms for MF assisted freezing adduced in patents according to the inventors rely on various phenomena. The inventors stated that when unidirectional MF is applied, the magnetic moment of the electron spin is aligned in one direction, and thus, the influence of the electron spin on the thermal vibration cannot be mutually cancelled. As a result, the thermal vibration caused by electron spin is strengthened and increased. Therefore, when the temperature is dropped to an extent at which freezing is generally initiated, the vibration of the free water molecules are still too large to turn into ice, and the free water is brought into a supercooled state for longer time instead. During the extended period of supercooling, a heat quantity, equivalent to the latent heat required for solidification, is taken away. At this point, by a sudden lowering of the vibration level either by reducing the temperature to a certain extent, or, by relieving the magnetic field instantaneously, permits the molecules to get rearranged according to the hydrogen bond, and rapid freezing can be achieved [45,46]. In short, MF application will delay the formation of ice crystals, and as a consequence, most of the ice crystals form at the same time resulting in formation of numerous ice crystals. Moreover, according to the inventors, MF application divides water cluster (aggregations of free water molecules) into smaller groups. These fragmented water clusters form hydrogen bonds with the polar groups of a tertiary structure of proteins that face outwards from the outer surface, and thus, the free water is turned into bound water. The decrease in amount of free water indirectly restrains free water crystals from growing too large [45,46]. Moreover, the bound water may act as an envelope to the tertiary structures of proteins and prevent it from getting oxidised [45].

Also when the MF fluctuates, the magnetic flux changes and an electromagnetic induction occur within the object-to-be-frozen. Thus, the induced electromotive force caused by the electromagnetic induction generates free electrons within the object. These free electron can interact with water molecules present in food matrix and produce hydroxyl-radicals capable of destroying the cell membranes of microbes [45]. According to the inventors such technology could be used to reduce the population of live bacteria.

Water, being a diamagnetic substance will not produce any effect above thermal noise (thermal noises are the electrical fluctuations arising from the random thermal motion of electrons) when exposed to the weak OMFs (<10 Gauss or 1 mT) used in the CAS freezers (Cell Alive Systems commercial freezers manufactured by ABI Corporation, Japan) [18,47]. Therefore, the hypothesis proposed by Owada & Kurita [45] related to enhancement of thermal vibrations and subsequent increase in degree of supercooling upon submission of water to weak external oscillating MF (<10 Gauss or 1 mT) comes under scrutiny. Kobayashi & Kirschvink [47] reported that the mechanism of action postulated by ABI Company (Japan) do not agree basic biophysics. Their group [47,48] also proposed a credible theory for the disruption of ice-crystal nucleation in supercooled water by a weak, extremely low-frequency OMFs. The theory is based on action of MF on the magnetite nanoparticles (ferromagnetic substances) present in the biological tissue. It states that the weak OMFs with extremely low-frequency can oscillate the magnetite nanoparticles present in many plant and animal tissues, and prevent the ice crystals nucleation on the surface of magnetite nanoparticles. As an outcome, local supercooling could be enhanced.

All those promising claims of the recently arisen patents, regarding the applications of MF in food freezing and their positive impact on the final food quality, need validations and in depth understanding of the underlying phenomena by research studies. More and more researchers are carrying out studies in order to investigate and explain the role of MF in freezing of food matrices over the last years and some of them are discussed below.

Suzuki et al. [49] investigated the effect of weak MF (about 0.5 mT) on freezing process of several kinds of foods by using a specially designed freezer coupled with a magnetic field generator. They found that the weak MF had no significant difference on the time-temperature history during freezing and on the quality (drip loss, color and texture, microstructure, and sensory evaluation) of frozen foods compared with no MF experimental conditions.

In contrast, James et al. [39] studied the effect of freezing under CAS conditions, using an ABI freezer (ABI Co Japan), had on the degree of supercooling of garlic bulbs when compared to freezing under the same conditions without CAS (4 CAS conditions: off, 0%, 50% and 100% at frequencies ≤ 50 Hz were studied). They reported that freezing under the OMF conditions had minor increase of the degree of supercooling of garlic bulbs in comparison to freezing under the same conditions without OMF. For instance, when the samples were frozen from an ambient state (21 ± 1 °C), the degree of supercooling at 50% CAS condition was 4.0 °C compared to 2.7 °C and 3.1 °C in the case of 0% CAS condition and conventional freezer, respectively. Moreover, the time before nucleation (i.e. the time period till which the product remained under the supercooled state) was longest when the freezing was performed under 50% CAS condition. Yamamoto et al. [50] froze chicken breasts in an ABI freezer (B = 1.5 to 2 mT at 20, 30 and 40 Hz) maintained at −45 °C and they compared the quality with the product frozen in conventional rapid freezer (CRF; −45 °C) and a slow freezer (SF; −20 °C). The samples frozen by ABI freezer and CFR were stored at −30 °C while the sample frozen in slow freezer was stored at −20 °C for a certain period of time before the quality evaluation (quality evaluation was performed after 1 week and 6 months storage, respectively). They reported that there was no difference in drip loss and fracture properties among the samples that were frozen by the three freezing methods and stored for one week. The rupture stress of meat frozen under MF did not change in refrigerated storage from one week to six months, and was lower than those with SF and CRF, while samples frozen with SF and CRF and stored for six months showed significantly higher rupture stress values than those stored for one week. Hence, the MF application during freezing prevented an increase in the firmness of the samples during storage period. Moreover, the microscopic observations revealed that the meat frozen with CRF had large space in the muscle fibers after six months of storage, while these spaces were small and scattered throughout the muscle fibers for samples frozen under MF and stored for six months. According to the researchers, the observed change in CFR-frozen sample might have been caused by protein denaturation during freezing and storage. Choi et al. [51] investigated the changes in microstructure and quality attributes during storage period (at −20 °C for 8 months) of beef sample frozen by ABI freezer (ABI Co. Japan) using CAS technology (Cell Alive System) and air blast freezer to −55 °C and −45 °C, respectively. They reported that beef sample frozen under MF had small size ice crystals and their rate of size increase during the storage period was lower compared to those of an air blast frozen sample. The drip loss and protein denaturation (in terms of water holding capacity) was significantly lower for sample frozen under MF than compared to the air blast frozen sample on 8 month storage. Moreover, their sensory evaluation results showed that the beef samples stored after MF assisted freezing did not show the difference until 4 months, and it showed higher acceptability in comparison with the beef sample stored after the air blast freezing. At this point, it has to be mentioned that the freezing temperature for MF assisted freezing was 10 °C lower than the air blast freezing; therefore it is difficult to say whether observed effects were because of the MF or due to the reduced temperature.

3. Freezing under Electric Field

Electric field assisted freezing can be divided into two main categories such as under the application of fluctuating electric field (FEF) and static electric field (SEF). One of the difficulties that appear when compiling literature is that the authors used different ways to determine the value of the electric field. Most of the time they divided the voltage by the distance between electrodes, which is a first approach. More precise determinations have been proposed by some authors based on modelling of electric field lines while taking into account the dielectric properties of the different material installed between the electrodes [52].

3.1. Freezing using Fluctuation Electric Field

Fluctuating electric field (FEF) can interfere with both the steps of crystallization: the nucleation of ice crystal in the supercooled water and the subsequent ice crystal growth from the existing nuclei. The effect of FEF on crystallization process depends on the frequency and intensity of FEF applied to the system [53–55]. For instance, Sun et al. [53] studied the effect of FEF frequencies (frequency ranging from 50 Hz–5 MHz) on the degree of supercooling during freezing of a 0.9% NaCl aqueous solution at a relatively slow cooling rate (0.26 K/min). They found that the application of FEF up to 500 kHz led to a decrease in the degree of supercooling, while with further rise in frequency to 5 MHz caused an increase in the degree of supercooling. Salt [56] reported that the use of 60 Hz FEF (strength of 15 kV) favoured the freezing of water at a higher temperature than the no-field freezing temperature (reduced supercooling). For instance, in the presence of electric field, 20 mm^3 water drops froze only at temperatures below −6 °C, whereas all drops encased in rubber cement froze at temperatures above −5 °C. In contrast, when no electric field was applied, both of sample sets supercooled at least by 10 °C. Sun et al. [54] studied the relationship between the ice formation in 0.9% K_2MnO_4 water and the frequency of applied FEF in the range of 1–200 kHz: the ice morphology and freezing time were observed by a simple microscope system. They reported that the frequency of applied electric field strongly affected the ice crystal size and the freezing time. More specifically, with the increase of the electric field frequency, both the ice crystal size and the freezing time decreased and reached the minimum value at a frequency of 50 kHz. Further increase in the frequency beyond 50 kHz led to longer freezing times which followed by ice crystal size increase. The polarization induced by FEF resulted in a rapid reorientation of H_2O molecules, which was assumed as one of candidate factors to enhance the aggregation of H_2O and the forming of the nucleus. The increase in frequency of electric field results in the rise of vibration frequency of the H_2O dipole until the frequency reaches close to 48 kHz, at which the orientation of H_2O dipole become difficult to keep pace with the alternation of electric field. At this point the relaxation loss becomes largest, and the effect of electric field on the forming of nucleus reaches to the utmost. If the frequency increases more than relaxation peak, the polarization of H_2O dipole orientation will disappear gradually and weakens the influence of electric field [54]. Mok et al. [35] investigated the phase transition of 0.9% sodium chloride (NaCl) solution at −20 °C under various pulsed electric field (PEF) (PEF strength of 1.78×10^2 V/m, duty ratio: 0.5, and frequency ranging between 0–20 kHz). Their result indicated that the phase transition time (time duration from the onset of nucleation to the end of the crystallization process) decreased with the increase of the described frequencies showing a high correlation ($R^2 = 0.968$). The shortest phase transition time recorded was 1443 ± 2 s at 20 kHz. They also observed that the ice crystal morphology was dependent on the freezer temperature and the applied frequency of PEF. The pattern of ice crystal under PEF were more evenly round (roundness: 0.88–0.90) compared to those acquired under zero field conditions. Bartlett et al. [57] reported that the use of 50 Hz FEF having strength of 2.5×10^5 V/m had no impact on the growth rate of ice crystals from water vapour. The strength of FEF can also affect the homogeneous nucleation of ice in supercooled water [55]. It was found that the FEF at frequency of 100 kHz and strength up to $(1.6 \pm 0.4) \times 10^5$ V/m neither enhanced nor suppressed the homogeneous nucleation of ice. Furthermore, based on thermodynamic models, it was estimated that fields with the frequency of 100 kHz and strength ranging from 10^7–10^8 V/m might cause an evident increase in the rate of nucleation [55].

To the best of our knowledge, to date, no peer-reviewed research articles are available in literature concerning the freezing of real food matrix under FEF, but there are a few recent patents which claim that freezing under FEF results in better food preservations. Owada [43] patented an invention describing it as a highly-efficient freezing apparatus capable of producing a good quality frozen product with minimal damage to their cells. They claimed that the freezing of chicken and tuna under the influence of OEF at 1.5×10^4 V/m and the frequency in the range from 50 Hz to 5 MHz reduced the time for lowering the core temperature of the samples from 0 °C to −20 °C and −40 °C by 20% to 50% respectively. Moreover, they claimed that upon thawing the cells were hardly destroyed and thus, the colour, flavour, and taste were maintained and found to be similar to those of the original raw food. According to the inventors, the oscillating electric field with variable frequency can eliminate the growth of ice crystal nuclei, and thus, a high degree of supercooling can be achieved. In addition, they support that the suppression of the ice crystallization prevents the surface of the objects from freezing and therefore, increases the heat transfer from inside of the object to the surrounding cooling medium. Thus, the cooling rate of the objects can be remarkably increased. They also proposed hybrid methods in which FEF and MF (either SMF or OMF or both) was applied simultaneously during the freezing of food products. They claimed that the hybrid method, such as: (a) freezing under the influence of FEF ($E = 1.5 \times 10^4$ V/m at frequency in the range from 50 Hz to 5 MHz), SMF (1 mT), and OMF (0.5–0.7 mT, 50 Hz), and (b) freezing under FEF ($E = 1.5 \times 10^4$ V/m, 50 Hz to 5 MHz) and OMF (0.5–0.7 mT, 50 Hz) reduced the time for cooling the central temperature of products from 0 °C to −20 °C or −40 °C by 50% or more. Moreover, it was claimed that the cells in the thawed product were not destructed and the quality of the product like colour, flavour, and taste were maintained in the same levels like those of the original raw food. The inventors also proposed that when FEF was applied simultaneously with the OMF, the free water in the food matrix interacted with proteins and carbohydrates and turned into bound water forming molecules of hydrated higher order structures. According to them, this reduction in the amount of free water decreased the probability of ice crystallization and consequently led to a higher cooling rate. Kim et al. [58] patented a non-freezing refrigerator. In this patent it is claimed that it can maintain the contents in a non-frozen state by applying an FEF generated by a radio frequency voltage when it is supercooled at temperatures in the range of 0 to −5.8 °C. The inventors proposed that the torques exerted by FEF would continuously rotate and vibrate the water molecules. As a result, the ice crystal formation can be inhibited and the water in the product remains in the supercooled state. According to the inventors, their invention can keep the food products (meat, fish, fruits and vegetables) in highly fresh state for a longer period of time as the product would be kept below the freezing temperature and with minimum chances for the microstructure to be damaged due to ice crystal formation. The claims made in the aforementioned patents are promising, but they lack validations by research studies.

Mechanism of Action of FEF

The actual mechanism of action of FEF is still obscure, but few hypotheses have been depicted clearly by various researchers. The FEF exerts a torque which can displace water molecules from the equilibrium state in a cluster and, thereby, may inhibit or retard spontaneous ice nucleation [54,59,60]. Similarly, it can also interfere with the kinetic processes of crystal growth. The crystal growth happens when molecules cross the liquid/solid interface and integrate into the crystal lattice. In order to achieve its occurrence, each molecule must have an appropriate spatial orientation, position, and energy. Water is the highly associated substance which favours the crystal growth by joining the crystal lattice collectively. The rate of crystal growth would be higher if the molecular cluster and the ice lattice shares edges and faces without the induction of mutual strains. Torques exerted by the FEF at given temperature, may increase the number of isomeric configurations, thereby reducing the chance of configuration of cluster of molecules which is well suited to integrate into a crystal lattice. As a consequence, the crystal growth rate will decrease extensively [59,61]. Another hypothesis states that the vibration and collision induced by the FEF could produce thinner solid-liquid boundaries and decrease heat transfer resistance, similar to acoustic stress [35,62].

3.2. Freezing Assisted by Static Electric Field (FA-SEF)

Freezing of supercooled water assisted by static electric field was firstly studied by Dufour in 1861 [63]. FA-SEF has been investigated, so far, at a laboratory scale in both model and real food systems. The application of SEF can affect the freezing process and the quality parameters (drip loss, colour, texture, water holding capacity, and microstructure) [12,64–68]. For instance, exposure of SEF during freezing process is thought to promote ice nucleation at a higher temperature than the spontaneous nucleation temperature resulting in lower degree of supercooling, to reduce the induction time (nucleation time), to trigger the nucleation, to elongate the phase transition time and, to interfere with the growth mechanics of ice crystals [12,64–66,68]. Moreover, SEF application can induce ice nucleation at a desired degree of supercooling [12]. The probability of ice nucleation in above case depends on the strength of SEF and the nucleation temperature. Especially, the probability of nucleation increases as the nucleation temperature approaches to the spontaneous nucleation temperature and at a greater strength of SEF [12]. With respect to the quality, freezing under SEF produces numerous small sized ice crystals in frozen matrices, and thus, minimizes the cell disruption, reduce the drip loss, lessen the protein denaturation, and preserve the texture of the fresh food to a greater extent after thawing [64,66,67]. Key published studies on the use of SEF assisted freezing for model and real food systems are summarized in Table 1. So far, FA-SEF for model and real food systems has been performed at a laboratory scale on small sample size. This technique needs tailored optimization of parameters and conditions, and scale up in order to compete with the existing freezing techniques at an industrial level.

Table 1. Key published studies on the use of SEF assisted freezing for model and real food systems.

Sample	Conditions	Observations	Reference
Water drops of a few millimeters in diameters	2–6 × 10^6 V/m, Electric field was applied once the water got supercooled to a temperature between −4° to −7 °C	-Freezing of water drops initiated in the presence of electric field than compared to without field conditions	Rau [69]
Distilled Water and water with organic nuclei	6 × 10^5 V/m	-The SEF up to 6 × 10^5 V/m had no intrinsic effect on the heterogeneous freezing process	Doolittle & Vali [70]
Interfacial water	10^6 V/m, at a room temperature	-The researchers were able to freeze interfacial water at room temperature by using a weak electric field (10^6 V/m)	Choi et al. [71]
Distilled water (1 mL)	Sample was cooled from 5 °C to −30 °C in the presence of electric field varying from 1.0 × 10^3–1.0 × 10^5 V/m	-Application of electric field induced nucleation at higher temperature compared to no field (SEF application led to a lower supercooling degree) -SEF greater than 1.0 × 10^4 V/m was required to have a significant effect on water freezing process	Wei et al. [65]
Distilled water (1.6 mL)	The SEF equivalent of 0–6.0 × 10^6 V/m was applied when distilled water sample was cooled from 1 to −16 °C	-SEF influenced water freezing process: the degree of supercooling decreased and the phase transition time increased with increasing strength of the SEF (For e.g., SEF strength of 6.0 × 10^6 V/m decreased the supercooling degree approximately by 52% than compared to zero field condition. While at same SEF strength crystallization time increased by 22%) -Controlled ice nucleation at a small degree of supercooling (ΔT = 4 °C) with a probability of 100% was possible by using higher SEF strength of 6.0 × 10^6 V/m	Orlowska et al. [12]

Table 1. *Cont.*

Sample	Conditions	Observations	Reference
Pork tenderloin (1 g)	0–12 kV, sample was cooled from 1 to −20 °C with a cooling rate of 1 °C/min	-Lower supercooling under DC voltage was observed -Ice crystal size reduced under DC voltage conditions (For instance, the average ice crystal size obtained at 12 kV was around 44% lower than that obtained at zero field condition)	Xanthakis et al. [64]
Water (5 μL)	Up to 8×10^7 V/m	-Freezing temperature significantly increased by 15 °C with the increase in strength of the SEF with a saturation at 2.0×10^7 V/m -Also current passing through the water droplets elevated the freezing temperature	Carpenter & Bahadur [68]
Deionized water droplets	$4.28 \pm 0.13 \times 10^5$ V/m, cooling rate of 1.0 ± 0.2 K/min	-Ice nucleation was promoted under a 10^5 V/m electric field and was independent of the field direction -The ice nucleation rates were found to be higher under an electric field	Zhang et al. [72]
Lamb meat (2.3–2.5 g), (Ø = 10 mm, *H*=10 mm)	0–5.8×10^4 V/m, sample was cooled to −20 °C	-Ice crystal size reduced with increasing magnitude of SEF -Freezing under SEF reduced the drip loss, meanwhile, it kept hardness and microstructure of lamb meat on thawing	Dalvi-Isfahan et al. [67]
Deionized water and Pork tenderloin: fresh meat was cut into cuboids (50 × 50 × 10 mm^3)	DC voltage of magnitude 0–10 kV was applied at the same time upon initiation of cooling the samples to less than −15 °C	-Freezing of deionized water under DC voltage resulted in lower supercooling -Freezing in combination with exposure to a 10 kV led to smaller ice crystals in the meat samples than ordinary freezing treatments. Moreover, the meat quality indicators, such as color, pH, and water holding capacity of sample frozen under 10 kV treatment were closer to those of fresh pork tenderloin, while freezing without DC voltage gave inferior quality product	Jia et al. [66]
Agar gel (Ø = 20 mm, *H* = 10 mm)	Agar gels were frozen under SEF 0–5.8×10^4 V/m at −20 °C	-SEF aided in production of smaller size ice crystals, but did not cause any obvious change in syneresis and texture of the samples	Dalvi-isfahan et al. [73]

Ø = diameter, *H*= height.

Mechanisms of Action of FA-SEF

From thermodynamic point of view it can be understood that the SEF can modify the free energy barrier for phase transition (ΔG_n) and consequently influence the nucleation process. More precisely, SEF tends to reduce the critical radius which in turn decreases the Gibbs free energy of the system and consequently increases the nucleation rate [12,35,55,74–78]. Furthermore, application of SEF shortens the induction time [74]. The theoretical approach to FA-SEF is discussed below in brief.

The free energy of formation of a spherical crystallite in the mother phase in the absence of electric field, ΔG_n is equal to the sum of the surface free energy, $\Delta G_{(S)}$, and the volume free energy, $\Delta G_{(V)}$.

$$\Delta G_{\mathrm{n}} = \Delta G_{(s)} + \Delta G_{(\mathrm{V})} \; or \; \Delta G_{\mathrm{n}} = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta G_{\mathrm{v}} \tag{1}$$

Where r is the nucleated particle radius, σ is the surface tension, and ΔG_v is the free energy change of the transformation per unit volume. Under a SEF a new term is added to the volumetric energy (PE, polarizability (P) multiplied by the electric field (E)). Hence, the final equation for Gibbs free energy of formation of a spherical nucleus under the presence of SEF, can be presented as follows [12,74,78]

$$\Delta G_{\mathrm{n}} = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 (\Delta G_{\mathrm{v}} + PE) \tag{2}$$

Upon maximizing the above equation, setting $\frac{d\Delta G_n}{dr} = 0$, one can get the equation for the critical radius (r^*) and critical free energy (ΔG_{n}^*) under the influence of SEF as:

$$r^* = \frac{2\sigma}{(\Delta \mathrm{G_v} + PE)} \text{ and } \Delta G_{\mathrm{n}}^* = \frac{16\pi\sigma^3}{3(\Delta \mathrm{G_v} + PE)^2} \tag{3}$$

The corresponding equations for r^* and ΔG_n^* obtained in the absence of SEF do not contain the second term (PE) of the denominator.

Most recently, Jha et al. [74] proposed a theoretical approach to calculate the nucleation rate under the SEF with respect to the degree of supercooling as follows. The concentration of nuclei (N^*) formed in the mother phase within a given time period under the influence of SEF with respect to the degree of supercooling can be written as [74]

$$N^* = N_1 exp\left[\frac{-16\pi\sigma^3}{3kT\left(\frac{\Delta H_f \Delta T}{T^*} + PE\right)^2}\right] \tag{4}$$

Where N_1 is the concentration of monomers, k is the Boltzmann constant, ΔH_f is the enthalpy of fusion, T^* is the solid-liquid equilibrium temperature, $\Delta T = T^* - T$ is the degree of supercooling. Elimination of the second term (PE) in the above equation gives the concentration of nuclei in the absence of SEF (N_0^*) as

$$N_0^* = N_1 exp\left[\frac{-16\pi\sigma^3}{3kT\left(\frac{\Delta H_f \Delta T}{T^*}\right)^2}\right] \tag{5}$$

Consequently, the relative nucleation rate, i.e., the ratio of the nuclei concentration with field to that in the absence of field (N^*/N_0^*) and induction time (τ) can be expressed as

$$\log_{10}\left(\frac{N^*}{N_0^*}\right) = \left(\frac{2.32\,\pi\sigma^3}{kT}\right)\left[\left(\frac{1}{\frac{\Delta H_f \Delta T}{T^*}}\right)^2 - \left(\frac{1}{\frac{\Delta H_f \Delta T}{T^*} + PE}\right)^2\right] \text{ and}$$

$$\frac{1}{\tau} \propto \log_{10}\left(\frac{N^*}{N_0^*}\right) = \left(\frac{2.32\,\pi\sigma^3}{kT}\right)\left[\left(\frac{1}{\frac{\Delta H_f \Delta T}{T^*}}\right)^2 - \left(\frac{1}{\frac{\Delta H_f \Delta T}{T^*} + PE}\right)^2\right] \tag{6}$$

From the above thermodynamic study it can be understood that the strength of the electric field can affect the Gibbs free energy, nucleation rate and induction time. For instance with the increase of the electric field strength, the free energy and induction time will decrease, while nucleation rate would increase.

The mechanism of action of FA-SEF can also be tracked by performing simulation studies. The simulations studies have revealed that the SEF aligns the dipole of water molecules from random directions to the direction of the electric field vector. This reorientation phenomenon makes the hydrogen bond between the water molecules stronger in the direction of the electric field. As an outcome, the structure of water clusters can be reordered, which in turn may aid in the nucleation process [65,79–82]. For instance, Shevkunov & Vegiri [79], Vegiri [81], and Vegiri & Schevkunov [82] illustrated that the water cluster converged into an almost aligned state at the electric field strength of 1.5×10^9 V/m, owing to the dipoles in the direction less than 90° to the direction of the field. This reorientation of dipole moments in the electric field influences the spatial orientation of water molecule leading to change in the position of hydrogen atoms; the bonding hydrogen atoms progressively turns to the line joining the two oxygen atoms, thus forming a smaller oxygen-oxygen-hydrogen angle θ in average with the increasing strength of SEF [80]. As an outcome, the average number of hydrogen bonds per water molecule increases, and the water system with more ordered structure is formed. However, in the literature, there are two different opinions about the final changes of water structure in FA-SEF process. One is that the application of critical SEF of strength of 5×10^9 V/m for few hundred picoseconds transformed water completely into a polar crystal with the regular structure similar to that of cubic ice (I_c) [83]. On the other hand, Sun et al. [80] and Jung et al. [84] observed that the application of an external electric field to water system produced a more perfect structure similar to ice structure but still in liquid state. Although results from these groups are different in some aspects, all of them demonstrated that SEF favoured the ice nucleation process.

In the aforementioned simulation studies, the magnitude of the electric field used was quite larger than the dielectric strength of water (dielectric strength of distilled water = $6.5–7.0 \times 10^7$ V/m [85,86]. It is important to note that if the strength of the applied electric field exceeds the dielectric strength of water, then there is a possibility of dielectric breakdown of the water system. As a result, the current will flow through the water system and hence, ohmic heating will be taking place. Zhang et al. [72] found that the electric field of magnitude 10^5 V/m promoted ice nucleation and was independent of the field direction. Their result challenges the above mentioned mechanism of FA-SEF which is based on dipole polarization of water molecules in the direction of SEF.

4. Freezing under Electromagnetic Radiation (ER)

ER applied to freezing mainly comprises of microwaves and radiofrequency assisted freezing (MAF and RF-AF). Until now, only three approaches related to the application of ER during freezing have been investigated. One is the use of microwaves (MW) as a pre-treatment prior to freezing [87], the second one is the constant ER energy application throughout a cryo-freezing process [59], and the last one is the part time application of ER (in forms of pulses) during the freezing process [14,88].

Hanyu et al. [87] studied the final impact of MW application on biological matrices prior to freezing. They pre-treated the sample by applying MW (2.45 GHz and 500 W) for 50 ms prior to freezing. The researchers reported that MW irradiation followed by freezing produced smaller ice crystals in the frozen items with a good repeatability. Moreover, the zone of good freezing extended to a greater depth into the microwaves irradiated sample (squid retina, rat liver and heart muscle) than compared to the control sample. The zone of good freezing can be referred as the area where there is no sign of detectable ice-crystal damage. In other words, MW irradiated sample had a larger ice-free (vitrified) region compared to untreated sample. Jackson et al. [59] reported that the continuous application of MW (2.45 GHz and 1000 W) during attempted vitrification of ethylene glycol solution (cryo-protectant) caused a significant reduction in ice formation. Moreover, the effect of MW irradiation on ice formation depended on the molarity of the glycol solution. For example, at a fixed microwave power and frequency the reduction in ice formation was maximal at 3.5–4 M and minimal at 3.0 M (lowest concentration been used) and 5.5 M (highest concentration been investigated).

Recently, a different approach of MAF was applied for first time in a real food system by Xanthakis et al. [14]. Freezing of pork samples under different emitted microwave power levels (40%, 50% and 60% power settings) was performed. In this study, a prototype equipment was built to freeze a food sample inside a tailored modified domestic microwave oven. The power levels in common domestic microwave ovens are in general an average power level adjusted by electronic duty cycling. Hence, during duty cycling, the power ON and OFF can be referred as an application of pulsed MW energy. Their results revealed that at 60% microwave power level, the average ice crystal size and the degree of supercooling decreased by 62% and 92% when compared to the conventionally frozen sample. The degree of supercooling and the ice crystal size were found to be influenced by the level of the emitted power since at the low power level of 40% the degree of supercooling and the ice crystal size were greater than the ones observed at 60% of power level. Moreover, they found that freezing rate decreased with the increasing power level of microwaves due to the heat generated by MW. This study provided quantitative data regarding the ice crystal size and the impact of MW radiation during freezing of meat microstructure and highlighted the need to be further investigated and the potentials of this technology to be applied for the production of frozen food with improved quality.

A model to describe MAF has been proposed by Sadot et al. [89]. The simulations performed with COMSOL Multiphysics (COMSOL Inc.) showed a complex behaviour of electric field distribution and generated heat due to the phase change. In fact because dielectric and thermophysical properties are very different in frozen and fresh state, penetration depth and local heat generation evolved dramatically during unidirectional freezing. In their study microwaves reached the product at the same surface that the cooling fluid. It showed that due to the increase in penetration depth in frozen phase, a hot spot, so do a local maximum of electric field, was following the freezing front advance. Their method seems to be appropriate to study the impact of microwave irradiation on the phase change. Furthermore, the aforementioned study figured out that a complex behaviour of reflection at air/product interfaces and resonance within the product occurred during MAF process.

Anese et al. [88] explored the freezing assisted by RF. In their study, they compared RF assisted cryogenic freezing (RF-CF) with other freezing methods, such as: cryogenic freezing and air blast freezing. They found that the application of low voltage RF pulses during cryo-freezing of pork sample produced better microstructure compared to other two freezing methods. The product frozen in air blast freezer had ice crystals mostly in the intercellular domain. As an outcome, the cell damage increased and drip loss increased. While the product frozen by cryogenic freezing method and RF-CF method had ice crystal formation in both extracellular and intracellular domain. The ice crystals formed under RF-CF seemed to be greater number of smaller ice crystals in the intracellular domain than compared to cryogenic method but unfortunately this study was not supported by quantitative image analysis. Moreover, they found that the cryo-frozen meat cubes had large surface fractures in the direction of meat fibres contributing higher drip loss in the thawed sample. While RF-CF sample had lower drip loss compared to other conditions. According to them, application RF counterbalanced the cracking of sample and resulted in lower drip loss. Moreover, they found that the firmness of fresh meat (control) was not significantly different from that of the unfrozen sample. In contrary, air blast and cryogenic frozen meat sample showed significantly higher firmness value than compared to control and RF-CF sample. In the literature, there are two contradictory results available related to the change in texture of the meat product on freezing-thawing. The first hypothesis suggests that upon freezing-thawing the meat product, tenderness would increase. It happens due to the breakdown of muscle fibre by the enzymatic action during proteolysis, ageing, and loss of the structural integrity caused by the ice crystal formation [90,91]. While, Lagerstedt et al. [92] and Leygonie et al. [91] proposed that the loss of fluid during thawing resulted in less water needed to hydrate the muscle fibres; thus, a greater quantity of fibres per surface area seemed to increase the toughness of meat. In the study of Anese et al. [88], the increase in the firmness of air blast and cryo-frozen meat sample on thawing can be attributed to a higher drip loss in respective cases. It would have been interesting the results of this study to be correlated to freezing temperature histories in all the conditions tested, but temperature data were not provided in this study. Although the first promising results of RF radiation when was applied during cryogenic freezing, further research studies have not been carried out till now in order to investigate this technology in depth. Further analysis on freezing under electromagnetic radiation of food products are needed for two reasons: (i) to confirm the outcomes proposed in the literature from quality point of view, and (ii) to determine its economic viability.

The underlining mechanism behind freezing assisted by electromagnetic radiation is still unknown, but a few findings and assumptions have been put forward by some research groups. These are: (i) Anese et al. [88] claimed that the application of ER causes depression in the freezing point and thereby produces more nucleation sites (ii) the torque exerted by ER displaces the water molecules from their equilibrium relationships in the ice cluster resulting in break-down of existing ice crystals. The disintegrated ice crystals may act as a nucleation sites and promote the secondary nucleation, thus, causing ice crystal size reduction [14,59,61,87,88,93]; and, (iii) ER may decrease the ice crystal growth rate and consequently increase the number of ice crystals [59].

5. Conclusions

This review article has presented an overview of freezing under the magnetic, electric and electromagnetic fields. In general, ice nucleation is a stochastic process and it is very difficult to be controlled. Freezing technologies and more specifically crystallisation assisted by magnetic, electric and electromagnetic fields have the capability to interact with nucleation. Moreover, they give the potentials to have better control on the ice crystals size. The ability of these technologies to influence the ice nucleation widens its areas of application at an industrial level. Some of their industrial applicabilities can be in food freezing with improved quality as well as to applications related to cryofixation of biological tissues. The products frozen by these techniques are expected to have numerous small size ice crystals in the food matrix, and are expected to have less freeze damage upon thawing. Food commodities (like fruits, vegetables, meat and fish) when subjected to minimum damage of their microstructure during freezing, can retain their nutritional value and quality attributes. Similarly, ice cream frozen under these systems is expected to have a smooth texture with a good meltdown and cooling properties due to the formation of numerous small size ice crystals. These techniques can also be used for better cryofixation of biological tissues. As it was mentioned before, pre-treatments with MW prior to or the application of MW or RF electromagnetic radiations during cryo-freezing showed that they could minimize the damage to the cells due to reduced ice crystal formations, and subsequently to lead in better practices for freezing and cryofixation of biological tissues.

The use of SEF showed that improved freezing quality could be achieved with minor additional energy demands, and this fact may yield in energy saving due to the opportunity to switch the freezing process to less energy intensive freezing conditions such as higher set point temperature and/or lower air velocity. The above mentioned hypothesis, has taken ice crystal size into consideration, since from the experimental studies discussed in this review it was indicated that freezing at a particular set point temperature under SEF can result in smaller ice crystals compared to the conventional freezing without the presence of an electric field.

At last, all these studies have been conducted at a laboratory scale on small sample size. They need tailored optimization of parameters and conditions with respect to the quality of the final real size products, the energy demands and the safety prior to industrial large scale applications.

Acknowledgments: This work received financial support from the Swedish Research Council FORMAS and the French National Research Agency (ANR) under the FREEZEWAVE project (SUSFOOD-ERANET, SE: 2014-1925, FR: ANR-14-SUSF-0001).

Author Contributions: Piyush Kumar Jha compiled information from the literature, analyzed the data, and edited the manuscript. Epameinondas Xanthakis, Vanessa Jury and Alain Le-bail made comments and revised the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Symbol	Description
CAS	Cell Alive System
CFR	Conventional rapid freezer
ER	Electromagnetic radiation
FA-SEF	Freezing assisted by static electric field
FEF	Fluctuating electric field
MAF	Microwaves assisted freezing
MC	Monte Carlo
MD	Molecular Dynamics
MF	Magnetic field
MFs	Magnetic fields
MW	Microwaves
NaCl	Sodium chloride
OMF	Oscillating magnetic field
OMFs	Oscillating magnetic fields
PEF	Pulsed electric field
PMF	Pulsed magnetic field
RF	Radiofrequency
RF-AF	Radiofrequency assisted freezing
RF-CF	Radiofrequency assisted cryogenic freezing
SEF	Static electric field
SEFs	Static electric fields
SMF	Static magnetic field

Nomenclature

Symbol	Description	Units
B	Magnetic flux density	[T]
E	Electric field	[V/m]
f	Frequency	[Hz]
ΔG_n	Gibbs free energy	[J]
$\Delta G_{(S)}$	Surface free energy	[J]
$\Delta G_{(V)}$	Volume free energy	[J]
ΔG_v	Free energy change of the transformation per unit volume	[J/m^3]
H	Height	[m]
ΔH_f	Enthalpy of fusion	[J/g]
k	Boltzmann constant	[J/K]
M	Molarity	M or mol/L
p	Pressure	[Pa]
P	Permanent polarization	[C/m^2]
r	Radius of the nuclei	[m]
t	Time	[s]
t_{PEF}	Time of PEF treatment	[s]
T	Temperature	[K]
ΔT	Degree of supercooling	[K]
T*	Solid-liquid equilibrium melting temperature	[K]
V	Voltage	[V]
σ	Surface tension	[J/m^2]
τ	Induction period	[s]
ϱ	Mass density	[kg/m^3]
Ø	Diameter	[m]

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