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Review

# Water crystallization and its importance to freezing of foods: A review

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In this review, different aspects of water crystallization including modelling approaches, process evaluation methods and the effect of novel freezing techniques is presented. There are different methods available to explain the nucleation and growth of crystals. The characteristics of ice crystals are studied by light and electron microscopy methods for many years, and recently a number of novel methods including magnetic resonance imaging, X-ray analysis, and infrared spectroscopy are employed. Several emerging techniques are developed to improve the crystallization of water during freezing, including ultrasound assisted freezing, high pressure freezing, ice nucleating proteins, and supersession of nucleation. Understanding the mechanisms of these new techniques and their relationship to the crystallization phenomenon can be helpful for improving freezing processes.

## Introduction

Freezing is among the most popular and efficient methods of food preservation and consists of three stages, i.e., cooling the product to its freezing point (pre-cooling or chilling stage), removing the latent heat of crystallization (phase transition stage) and finally cooling the product to the final storage temperature (tempering stage). The phase transition part of the freezing process involves the conversion of water to ice through the crystallization process and is the key step determining the efficiency of the process and the quality of the frozen product (Alizadeh, Chapleau, de-Lamballerie & Le-Bail, 2009; Alvarez, Fernández & Canet, 2010; de Paula, Colet, de Oliveira, Valduga & Treichel, 2011; Fennema, Powrie, & Marth, 1973; Jin *et al*., 2010; Le-Bail, Nicolitch & Vuillod, 2010; Maity, Raju & Bawa, 2009; Steffolani, Ribotta, Perez, Puppo & León, 2011; Zaritzky, 2006). In the freezing of tissue foods, formation of large ice crystals which are mostly extracellular, results in significant damages to the tissue (Ahmad, Yaghmaee & Durance, 2010; Delgado, Zheng & Sun, 2009; Ming, Rahim, Wan & Ariff, 2009; Streit, Corrieu & Béal, 2010; Yu, Ma, Zheng, Liu & Sun, 2011). On the other hand, formation of fine crystals that are evenly distributed both inside and outside the cells, leads to the quality of the product to be better preserved due to less damages to the tissue (Sun & Zheng, 2006). However, in some processes such as freeze drying and freeze concentration, large crystals are more desired (Saclier, Peczalski, & Andrieu, 2010). Therefore, the control, understanding and prediction of the crystallization process and related phenomena in regard to the crystal characteristics are very essential for the improvement of freezing processes.

Crystallization is a general term used to describe several different phenomena related to the formation of a crystalline lattice structure (Hartel, 2001). This process consists of two main successive stages; nucleation and crystal growth. The interaction between these two steps determines the crystal characteristics, i.e., size, distribution and morphology of the crystals. Although the process of formation and growth of the crystals is complicated and therefore difficult to understand, some theoretical modeling approaches have been proposed for the description of both nucleation and growth (Hartel, 2001; Mullin, 2001; Martins, Castro & Lopes, 2011; Myerson, 2002a, 2002b). The theories employ different thermodynamic, mass transfer and heat transfer principles to explain the crystallization process. In addition to the theoretical modeling approaches, several experimental studies have been carried out to link the crystal characteristics to different processing parameters including cooling rate and heat transfer (Bald, 1986; Bevilacqua, Zaritzky, & Calvelo, 1979; Bevilacqua & Zaritzky, 1980; Woinet, Andrieu, Laurent, & Min, 1998) as well as mass transfer phenomena (Bae, Miyawaki, & Yano, 1993; Miyawaki, 2001; Miyawaki, Abe, & Yano, 1992).

Experimental evaluation of crystallization of water and its impacts on the texture of frozen products have been

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**Nomenclature**

| | |
|---|---|
| $\Delta G$ | overall excess free energy, J |
| $\Delta G_c$ | critical free energy for nucleation, J |
| $\Delta G_{c,het}$ | nucleation energy of heterogeneous nucleation, J |
| $\Delta G_{max,s}$ | nucleation energy, J |
| $\Delta G_s$ | surface excess free energy, J |
| $\Delta G_v$ | volume excess free energy, J |
| $\Delta G_v$ | free energy change of the transformation per unit volume, J $m^{-3}$ |
| $\Delta T_s$ | supercooling, °C |
| a | constant |
| A | surface area, $m^2$ |
| $a_{for}$ | the volumetric surface of foreign particles, $m^2$ $m^{-3}$ |
| b | constant |
| B | rate of nucleation, nuclei per unit volume per unit time |
| $B_{het}$ | rate of heterogeneous nucleation, nuclei per unit volume per unit time |
| $B_{hom}$ | rate of homogeneous nucleation, nuclei per unit volume per unit time |
| $B_s$ | rate of surface nucleation, nuclei per unit area of crystal surface per unit time |
| C | actual concentration, mol $L^{-1}$ |
| $C_1$ | constant |
| $C_2$ | constant |
| $C_{ad}$ | concentration on the surface, mol $kg^{-1}$ |
| $C_C$ | the molar density of the solid, $m^3$ $mol^{-1}$ |
| D | diameter of ice crystals, m |
| $D_{AB}$ | diffusivity, $m^2$ $s^{-1}$ |
| $d_m$ | molecular diameter, m |
| $D_{surf}$ | the surface-diffusion coefficient of units moving on the foreign surface |
| $D_W$ | the diffusion coefficient of water, $m^2$ $s^{-1}$ |
| $\frac{dT}{dt}$ | cooling rate, °C $s^{-1}$ |
| $\frac{dX}{dt}$ | velocity of the moving freezing front, m $s^{-1}$ |
| $\frac{dm}{dt}$ | crystal growth rate, kg $s^{-1}$ |
| $\frac{dq}{dt}$ | rate of heat transfer, J $s^{-1}$ |
| $f$ | geometric correction factor for homogeneous nucleation |
| $f$ | natural frequency, $s^{-1}$ |
| g | constant |
| G | rate of crystal growth, kg $s^{-1}$ |
| h | film heat transfer coefficient, W $m^{-2}$ °$C^{-1}$ |
| $He_{ad}$ | adsorption constant |
| k | Boltzmann constant |
| $K_1$ | thermal conductivity, W $m^{-1}$ °$C^{-1}$ |
| $K_G$ | overall crystal growth coefficients |
| m | constant |
| n | constant |
| $n_0$ | concentration of monomers in the supersaturated solution |
| $N_A$ | Avogadro's number ($N_A = 6.023 \times 10^{23}$ $mol^{-1}$) |
| $n_c$ | number of stable nuclei |
| r | particle radius, m |
| $r_c$ | critical nucleus radius, m |
| s | initial freezing front position, m |
| S | supersaturation ratio |
| $S_{met,s}$ | relative supersaturation |
| T* | melting point, °C |
| T | temperature, °C |
| t | time, s |
| $t_c$ | characteristic freezing time, s |
| $T_f$ | initial freezing temperature, °C |
| $T_i$ | interfacial temperature, °C |
| U | velocity, m $s^{-1}$ |
| W | work, J |
| $W_s$ | work required to form a surface, J |
| $W_v$ | work required to form bulk of a particle, J |
| Z | imbalance factor |
| x | length, m |
| $\beta$ | constant |
| $\rho_1$ | density of frozen phase, kg $m^{-3}$ |
| $\sigma$ | surface energy of the particle per unit area, J $m^2$ |
| $\nu$ | the number of molecules or ions |
| $\theta$ | the wetting or contact angle, deg |
| $\gamma_{CL}$ | the surface tension |

carried out by using visualization and monitoring methods including light microscopy (Chow, Blindt, Chivers, & Povey, 2003; Chow, Blindt, Kamp, Grocutt, & Chivers, 2004; Olmo, Baena, & Risco, 2008), electron microscopy (Delgado & Rubiolo, 2005; Fernandez, Otero, Guignon, & Sanz, 2006; Sun & Li, 2003) as well as non-invasive detection techniques (Bischof, Mahr, Choi, Behling, & Mewes, 2007; Hills & Remigereau, 1997; Hindmarsh, Wilson, Johns, Russell, & Chen, 2005; Lee, Kwon, & Ramamoorthy, 2008; Mahdjoub, Chouvenc, Seurin, Andrieu, & Briguet, 2006; Mousavi, Miri, Cox, & Fryer, 2005, 2007; Zelent & Vanderkooi, 2009). These kinds of evaluation have been considered as an important part of studies of freezing process and have resulted in practical knowledge of the ice formation mechanism and also the microstructure of frozen foods.

Improvements of the freezing process through the control of crystallization of water have also been an important subject of research. Along with rapid freezing techniques (Sun & Zheng, 2006), some new methodologies have been employed recently to control the crystallization of water (Inada, Zhang, Yabe, & Kozawa, 2001; Saclier *et al.*, 2010; Sun & Li, 2003; Zhang, Inada, Yabe, Lu, & Kozawa, 2001) and enhance the

freezing process (Li & Sun, 2002a; Sun & Li, 2003) *via* reducing ice crystal size or restricting water crystallization. These new developments include ultrasound assisted freezing, high pressure freezing, ice nucleating proteins, antifreeze proteins, magnetic resonance freezing and microwave assisted freezing (Fikiin, 2003; Jackson, Ungan, Critser, & Gao, 1997; Li & Sun, 2002b). The novel methods have been used to control the crystallization process and therefore ice crystal characteristics.

The aim of this article is to provide an overview of the theoretical and experimental approaches towards the crystallization modeling in relation to the freezing process; and review the methods available for evaluating, visualizing and monitoring the crystallization phenomenon and ice crystal characteristics during or after freezing. Novel methods that are developed to control the crystallization during freezing, thus improving the freezing process are also reviewed.

## Crystallization phenomenon

Crystallization is an important thermo-physical phenomenon through which a substance precipitates due to supercooling or supersaturation. As mentioned before, this phenomenon consists of two stages, i.e., nucleation and crystal growth. The nucleation step is defined as the formation of a new crystal and happens either in a crystal-free solution, which is then called primary nucleation, or at the presence of formerly created crystals, which is defined as secondary nucleation. Primary nucleation can be either homogeneous, if the solution contains neither solid foreign particles nor crystals, or heterogeneous, if foreign particles are present.

The main driving force for the deposition of a solid crystalline phase from liquid and gaseous solutions, pure liquids and pure gases is the supersaturation or supercooling achieved in the system (Mullin, 2001). In the case of primary nucleation, and especially for the homogeneous type, usually large supercooling driving force is required. Secondary nucleation is brought about by breakage of parent crystals, fracture due to collisions between crystals and removal of semi-ordered surface layers through fluid shear (Myerson, 2002b; Price, 1997).

After the formation of the nuclei, the next step of crystallization process is crystal growth. The initial few crystals appeared at the beginning of crystallization provide a structural template upon which all the material is deposited in the form of the crystals (Mersmann, 2001b; Price, 1997). However, nucleation and crystal growth can occur simultaneously as well. In addition, the initially formed nuclei may also be numerous causing the growth of each crystal to be limited. Therefore, the interaction between the growth and nucleation steps defines the crystal size distribution (Mersmann, 2001b; Price, 1997). Furthermore, many other factors affect the formation and growth of the crystals including concentration, temperature, impurities, mass and heat transfer in the system and the particular characteristics of the material to be crystallized, which need to be considered when dealing with crystallization process (Price, 1997).

Water, a main substance present in food and biological materials, crystallizes during freezing. Similar to other crystallization processes, very large supercooling degrees are required for homogeneous nucleation in pure water. However, heterogeneous nucleation is the dominant nucleation mechanism in food materials (Zaritzky, 2006).

Ice nucleation appears to be a key parameter for the optimization of industrial processes related to freezing. However, ice nucleation occurs spontaneously and stochastically and is affected by several factors such as impurities, asperities, surface properties, etc. that in general cannot be easily monitored and manipulated (Nakagawa, Hottot, Vessot, & Andrieu, 2006).

## Crystallization modeling

In order to better understand the crystallization process, various mathematical models have been developed to describe the nucleation and crystal growth. The models are mostly based on different thermodynamic properties of the system including the Gibbs free energy, molecular activity, surface properties, heat and mass transfer phenomena, etc.

### Nucleation

As previously discussed, there are two types of nucleation: primary nucleation or secondary nucleation. Primary nucleation can occur in a homogeneous or heterogeneous environment. Although different types of nucleation have similarities in their mechanism, the thermodynamic properties of the system undergoing nucleation for each type and therefore the rate of nucleation are different.

#### *Primary nucleation*

The classical theory of primary nucleation defines the total work W, required to create a nucleus as the sum of the work required to form a surface, $W_s$, and the work required to form the bulk of the particle, $W_v$ (Mullin, 2001; Myerson, 2002b):

$$W = W_s + W_v \tag{1}$$

$W_s$ is a positive quantity since the molecules should be arranged in a new way to create the new phase surface but $W_v$ is a negative quantity because the state of the new bulk phase is more stable and some amount of energy is released upon attachment of the molecule to the crystal. In the other word, nucleation exhibits a volume term and a surface term. The relationship between these two terms indicates the nature of the nucleation. Volume term is an exothermic process leading to a reduction in Gibbs free energy (Grant, 1999) through the system that is in favor of nucleation. In contrast, surface term acts against nucleation, permitting molecular aggregates to dissolve or to utilize some amount of energy for nucleation (Banga, Chawla & Bansal, 2004). Therefore, Eq. (1) can be rewritten based on Gibbs energy as the following (Mullin, 2001):

$$\Delta G = \Delta G_s + \Delta G_V \tag{2}$$

and for a spherical particle:

$$\Delta G = 4\pi r^2\sigma + \frac{4}{3}\pi r^3 \Delta G_v \tag{3}$$

where ΔG is the overall excess free energy between a small solid particle of solute and the solute in solution, $\Delta G_s$ is the surface excess free energy, $\Delta G_v$ is the volume excess free energy, σ is the surface energy of the particle per unit area, r is the particle radius and $\Delta G_\upsilon$ is the free energy change of the transformation per unit volume and is a negative quantity. This relationship consists of two terms with opposite signs and in the form shown is Eq. (3), has a maximum amount in a critical nucleus radius, $r_c$, representing the maximum amount of ΔG which is called critical free energy for nucleation, $\Delta G_c$. If the radius of the created cluster is lower than $r_c$, an attaching molecule requires energy to reach $\Delta G_c$. On the other hand, ΔG for a molecule to be absorbed on a crystal with a radius higher than $r_c$ will be lower than $\Delta G_c$. As a result, this crystal will be stable and will grow.

Since only the nuclei with radii larger than the critical nucleus radius can develop spontaneously to macroscopic sizes, the nucleation rate, B, defined as the number of stable nuclei formed in the system per unit time and per unit volume or area is an important kinetic parameter of the nucleation process (Kashchiev & van Rosmalen, 2003). The rate of nucleation is generally related to different thermodynamic properties including temperature, the number of stable nuclei formed per unit time per unit volume, the diffusion coefficient $D_{AB}$, the supersaturation S, the molar density of the solid $C_C$, the surface tension, $\gamma_{CL}$, etc.

The number of stable nuclei formed follows a probability distribution and can be described by an Arrhenius type distribution relationship. Formation of a primary nucleus or in fact passing through the critical radius barrier does not occur suddenly, since a nucleus may contain many monomers, but instead clusters of molecules are first created by the attachments of the molecules due to the colliding through the random movements. The clusters aggregate as a result of population increase leading to form an embryo. The size of the embryos, however, do not meet the criteria of crystal formation but further collisions between the embryos results in the formation of stable nuclei (Banga *et al.*, 2004). The most often used formula of nucleation theory in terms of nucleation rate, B, which is historically the first expression, is an Arrhenius type relationship with exponential and pre-exponential terms proposed by Volmer and Weber (Volmer & Weber, 1926) which then was developed based on thermodynamic considerations and Gibbs free energy (Gibbs, 1948; Kashchiev & van Rosmalen, 2003; Mersmann, 2001a; Mullin, 2001; Turnbull, 1956; Turnbull & Fisher, 1949; Volmer, 1939; Zeldovich, 1992):

$$B = A \exp\left(\frac{-\Delta G_c}{kT}\right) \tag{4}$$

where the pre-exponential term, A is described as:

$$A = z f^* C_0 \tag{5}$$

where k is the Boltzman constant, T is the temperature, $f^*$ is the frequency of monomer attachment to nucleus (that is related to the surface area of the particle, the diffusion coefficient of the molecules, temperature and concentration), $C_0$ is the concentration of nucleation sites and z is the Zeldovich or imbalance factor (which relate the number of critical nuclei in the equilibrium distribution to the number in the steady-state distribution and is a function of surface tension, temperature, concentration, Avogadro number and surface area).

Eq. (4) implies that nucleation is a statistical phenomenon and that the greater the supercooling or supersaturation degree, the higher the rate of nucleation is. The probability of the nucleation also depends on other different parameters. As it can be observed in Eq. (5), the pre-exponential term, A, is the product of z, $f^*$ and $C_0$ and is therefore a kinetic quantity accounting for the kinetic ($f^*$) and spatial ($C_0$) peculiarities in each particular case of nucleation.

Eq. (4) can be used for all kinds of nucleation with some modifications (Kashchiev, 2000; Kashchiev & van Rosmalen, 2003; Mersmann, 2001a; Mullin, 2001; Turnbull, 1956; Turnbull & Fisher, 1949). With taking different thermodynamic considerations of the system into account and estimating the main terms of the equation, the relationship among $\Delta G_c$, $f^*$ and z, can be re-written for homogeneous nucleation, $B_{hom}$, as (Mersmann, 2001a):

$$B_{hom} = \frac{3}{2} D_{AB} (C N_A)^{\frac{7}{3}} \sqrt{\frac{\gamma_{CL}}{kT}} \frac{1}{C_C N_A} \exp\left[ -\frac{16}{3} \pi \left(\frac{\gamma_{CL}}{kT}\right)^3 \left(\frac{1}{C_C N_A}\right)^2 \frac{1}{(\nu \ln S)^2} \right] \tag{6}$$

and for heterogeneous nucleation, $B_{het}$, as (Mersmann, 2001a):

$$B_{het} = \frac{1}{2\pi} a_{for} d_m He_{ad} (C N_A)^{\frac{7}{3}} \sqrt{\frac{f \gamma_{CL}}{kT}} V_m \left( \frac{(\sin\theta) D_{surf}}{r_c} He_{ad} d_m^{-\frac{3}{2}} (C N_A)^{\frac{1}{6}} + 3\pi D_{AB} (1 - \cos\theta) \right) \exp\left[ -f \left(\frac{16}{3}\right) \pi \frac{\gamma_{CL}}{kT} r_c^2 \frac{1}{(\nu \ln S)^2} \right] \tag{7}$$

where C is the actual concentration, $N_A$ is the Avogadro's number, $C_C$ is the molar density of the solid, $\gamma_{CL}$ is the surface tension, ν is the number of molecules or ions, S is the supersaturation ratio, $f$ is the geometric correction factor for homogeneous nucleation, $a_{for}$ is the volumetric surface of foreign particles, $d_m$ is the molecular diameter, $He_{ad}$ is the adsorption constant, θ is the wetting or contact angle, $D_{surf}$ is the surface-diffusion coefficient of units moving on the foreign surface.

In a similar way, the nucleation of ice crystals can also be expressed in relation to the degree of supercooling present in the specimen. According to this approach, one of the

general equations for nucleation rate is given by (Calvelo, 1981; Zaritzky, 2006):

$$B = C_1 T \exp\left(\frac{-C_2 T_f^2}{T^2 \Delta T_s}\right) \quad (8)$$

where $C_1$ and $C_2$ are coefficients depending on the type of product in which nucleation occurs, T is the system temperature, $\Delta T_s$ is the supercooling, and $T_f$ is the initial freezing temperature of the system. This equation is a general equation and is similar to Eq. (4).

From the equations presented above, it can be concluded that the rate of both homogeneous and heterogeneous nucleation depends on the supersaturation or supercooling, the actual concentration and the equilibrium concentration, temperature, surface tension, diffusivity, and molar density. Therefore, it can be initially suggested that the driving force of the nucleation is the supersaturation or supercooling achieved in the system which can be a function of temperature or concentration. On the other hand the nucleation phenomenon is limited by mass transfer and surface properties of the material. The rate of heterogeneous nucleation, which is much higher than that of homogeneous nucleation, is also affected by additional parameters including the volumetric surface $a_{for}$ of foreign particles present in the solution, the adsorption constant $He_{ad}$, the contact angle θ or the factor *f* (which is a function of the contact angle) and the surface-diffusion coefficient $D_{surf}$. It is also essential to state that it is not the number of foreign particles but their volumetric surface $a_{for}$ that is the critical factor for heterogeneous nucleation (Mersmann, 2001a). However, estimation of these parameters is difficult, bringing complexity to the precise modeling approaches toward nucleation.

### *Secondary nucleation*

Formerly created crystals are able to catalyze the nucleation phenomena, and therefore, the rate of secondary nucleation is higher than spontaneous nucleation which occurs in a lower supersaturation degree. Several theories and investigation can be found in the literature but the mechanisms and kinetics are not fully understood (Myerson, 2002a). Different parameters including supersaturation, cooling, agitation and impurities affect the secondary nucleation.

As mentioned earlier, secondary nucleation may occur as a result of different driving forces. In general, however, it is believed that the surface of a parent crystal can catalyze the nucleation as surface nucleation. This kind of nucleation occurs at the surface of seeded or formerly created crystals when the relative supersaturation is exceeded. The rate of surface nucleation, $B_s$, in nuclei per square meter crystal surface and per second depends on the diffusivity, $D_{AB}$, and the nucleation energy, $\Delta G_{max,s}$, and can be expressed in a similar way to the primary nucleation as the following (Dirksen & Ring, 1991; Mersmann, 2001a; Nielsen, 1981):

$$B_s = \frac{D_{AB}}{d_m^4} \exp\left(\pi \frac{-\gamma_{CL}^2 d_m^4}{(KT)^2 \nu \ln S_{met,s}}\right) \quad (9)$$

where $S_{met,s}$ is the relative supersaturation.

Although various modeling approaches have been proposed to evaluate the secondary nucleation phenomenon including the above-mentioned equation, secondary nucleation is difficult to be precisely modelled and controlled. This might be arising from the fact that a range of mechanisms acts as the driving forces of secondary nucleation.

### Crystal growth

The main theories used to explain the crystal growth phenomenon include surface energy, adsorption layer and diffusion-reaction theories (Chernov, 1989; Mullin, 2001). The surface energy theory is based on the fact that the most stable state of a droplet and similarly a crystal in equilibrium with its surrounding at constant temperature and pressure is achieved when its surface energy, and thus its area, is minimum. The growth of a crystal in a supersaturated medium is assumed to follow this statement and therefore the growth rates of crystal faces are proportional to their surface energies (Wulff, 1901). According to the adsorption layer theory a stepwise build up of a layer through the crystal is followed that can then be described by an Arrhenius type equation based on Gibbs-Volmer theory, similar to the approaches provided for nucleation modeling (Volmer, 1939). The diffusion-reaction theory assumes that the rate of crystal growth is considered to be a function of difference between concentration at the solid surface and in the bulk of the solution (Noyes & Whitney, 1987).

The above mentioned theories mainly describe the deposition of a solute from a mixture i.e., a solution.

For those crystallization phenomena in which the main driving force is temperature reduction or, the so-called crystallization from melts (for example freezing of water), the main controlling factor of crystallization is the heat transfer rate from the crystal face to the bulk of the liquid (Mullin, 2001). The temperature at the surface of the crystal is higher than the supercooled melt due to the liberation of the latent heat of crystallization and therefore a gradient of temperatures is created. Since, in this case, the heat transfer is the driving mechanism of crystallization, the Newton law of cooling can be applied to describe the heat transfer phenomena from the face of the crystal to the surrounding medium through the boundary film layer. The rate of heat transfer, $dq/dt$ can be described as below (Mullin, 2001):

$$\frac{dq}{dt} = hA(T_i - T) \quad (10)$$

The heat flux due to conduction in the $x$-direction, $q_x$, through the material being frozen is also given by the Fourier's first law of conduction:

$$q_x = -K_1 A \frac{dT}{dx} \tag{11}$$

and the crystal growth rate, $dm/dt$ (mass per unit time):

$$\frac{dm}{dt} = K_G A (T^* - T)^g \tag{12}$$

where A is the area of the growing solid surface or the crystal surface area, h is a film coefficient of heat transfer, m is mass of solid deposited in time t, $T_i$ is interfacial temperature, T is the temperature of bulk of supercooled material, T* is melting point, $K_G$ is overall crystal growth coefficients, $K_1$ is thermal conductivity, T is temperature, and $x$ is length (m). The exponent g is usually referred to as the order of the overall crystal growth process and generally has a value in the range 1.5–2.5. The rate of crystallization of a supercooled melt achieves a maximum value at a lower degree of supercooling, i.e. at a temperature higher than that required for maximum nucleation (Mullin, 2001).

Crystal growth during freezing of foodstuff obeys a similar pattern. The main attempts have been made for calculation of freezing time based on heat transfer models which were reviewed by Delgado and Sun (Delgado & Sun, 2001). The simplest and the well-known model used for the prediction of freezing time according to the heat transfer equation is an analytical solution to the heat transfer equation for freezing (Plank, 1913). It should, however, be noted that there are several limitations to the Planck's equation for estimation of freezing times for foods (Heldman, 2007). One of the problems is selection of the amount of latent heat and a suitable value for the thermal conductivity which is assumed to be constant. In addition, the basic equation does not account for the time required for removal of sensible heat from unfrozen product above the initial freezing temperature or for removal of frozen product sensible heat.

Many other analytical modeling approaches have been proposed, most of which are modifications to the Plank equation. Some other numerical solutions have also been suggested (Cleland, Cleland, Earle, & Byrne, 1987; Delgado & Sun, 2001; Pham, 1985). The mentioned models mostly consider the temperature change in the whole product and do not take the growth regime of the crystals in the product into account. However, experimental relationships can also be used to explain the growth rate of the ice crystals. For example, the following relationship which is similar to Eq. (12) has been introduced between water crystal growth, G, and supercooling (Zaritzky, 2006):

$$G = \beta(\Delta T_s)^n \tag{13}$$

where β and n are experimental constants and $\Delta T_s$ is supercooling.

A summary of different modeling approaches for crystallization is provided in Table 1.

## Crystal size

The size and distribution of ice crystals are an important property of frozen products having been studied widely. Modeling the size of ice crystals and linking it to different processing parameters has been one of the main research areas. The modeling approaches towards ice crystal size can be divided into two categories. The first category includes equations relating the cooling rate or heat transfer rate to the size of ice crystals and the second category consists of the application of mass transfer principles for the prediction of ice crystal size.

The rate of heat removal from a product during the phase change stage of freezing processes or in other words the time to pass this step is known to affect the ice crystal size significantly (Bald, 1986, 1991; Bevilacqua *et al.*, 1979; Bevilacqua & Zaritzky, 1980). In fact, the critical zone of water crystallization in food, from about −1 °C to −8 °C which occurs in the phase change period is the

**Table 1. Crystallization steps and their description and modeling approaches.**

| Crystallization steps | | | Description | Equations[a] | Modeling approach |
|---|---|---|---|---|---|
| Nucleation | Primary | Homogeneous | The solution contains neither solid foreign particles nor crystals | $B = A \exp\left(\frac{-\Delta G_c}{kT}\right)$ <br> $A = z f^* C_0$ | The attachment of molecules is stepwise, therefore an Arrhenius type distribution relationship considering different thermodynamic properties can be used. |
| | | Heterogeneous | Foreign particles are present in the solution | | |
| | Secondary | | At the presence of formerly created crystals | $B_s = \frac{D_{AB}}{d_m^4} \exp\left(\pi \frac{-\gamma_{CL}^2 d_m^4}{(KT)^2 \nu \ln S_{met,s}}\right)$ | The surface of a parent crystal can catalyze the nucleation as surface nucleation. A relationship similar to that of primary nucleation can be applied. |
| Crystal growth | | | The material is deposited on the structural template provided by nucleation | $\frac{dq}{dt} = hA(T_i - T)$ <br> $q_x = -K_1 A \frac{dT}{dx}$ <br> $\frac{dm}{dt} = K_G A (T^* - T)^g$ | Different theories including surface energy, adsorption layer and diffusion theories; In the case of crystallization from melts: Newton's law of cooling and Fourier's first law of conduction. |

[a] References: (Heldman, 2007; Kashchiev, 2000; Kashchiev & van Rosmalen, 2003; Mersmann, 2001a; Mullin, 2001; Myerson, 2002a).

zone of maximum formation of the crystals. This zone determines the crystal characteristics of the frozen foods. The size, morphology and location of the ice crystals, freezing rate and therefore the freezing efficiency is directly linked to the time required to pass this zone which is known as the characteristic freezing time (Li & Sun, 2002a). The following experimental equation is suggested for the relationship between the diameter of ice crystals, D, and the characteristic freezing time, $t_c$, (Bevilacqua & Zaritzky, 1980):

$$D = a + b \ln t_c \tag{14}$$

where a and b are regression constants.

In another study, Bald (1991) employed the following empirical model of dendritic growth of crystals, which has been previously proposed for rapid cooling of metals, for the developments of a relationship between the cooling rate and crystals size:

$$D = m\left(\frac{dT}{dt}\right)^{-n} \tag{15}$$

where D is mean crystal size, $dT/dt$ is cooling rate at the freezing front and m and n are constants. This author (Bald, 1986) developed a general relationship between ice crystal size and critical cooling rate at the freezing front in an idealized freezing system. The general relationship proposed was an analytically derived equation based on the theoretical assumption that dendritic crystals propagate radically outwards from the critical nucleus at some velocity U. This type of crystal growth was assumed to continue until the heat flux produced along any radial arm by the phase transformation balances the heat flux in the ice crystal region due to the cooling process. This author also assumed that the dendritic growth occurs in a uniform temperature field and uniform heat flux associated with the freezing front. The analytically derived relationship was as follows (Bald, 1986):

$$\frac{dT}{dt} = \left[\frac{\pi U \rho_1 L}{\left(128 K_1\left(\frac{D}{2} r_c - 1\right)\right)^2}\right] \frac{dX}{dt}\left[1 + \sqrt{1} + 32\left(\frac{D}{2} r_c - 1\right)\right]^2 \tag{16}$$

where $dX/dt$ is the velocity of the moving freezing front as it propagates into the food product, $r_c$ is critical radius of ice nucleus, $\rho_1$ is the density of frozen phase and $K_1$ is the thermal conductivity of frozen phase.

By re-writing Eq. (15) in the form shown by Eq. (16), m and n are given as the followings (Bald, 1991):

$$n = 0.5 \tag{17}$$

$$m = \left(\frac{\pi U r_c}{2}\right)\sqrt{\frac{\rho_1}{K_1}} \tag{18}$$

Bald (1991) also compared the predicted crystal sizes by the developed equation with the average ice crystal diameters in frozen beef measured by Bevilacqua *et al.* (1979) and detected some deviations in different assumed values for U. It was concluded that U may be a function of the cooling rate and is not constant.

Mass transfer phenomenon of water during freezing has also been considered as another controlling factor of ice crystal size leading to the second category of ice crystal size modeling. Miyawaki (2001) and Miyawaki *et al.* (1992) tried to analyze the ice crystal growth phenomenon quantitatively as a diffusion-limited process of water molecules in a limited time, which is determined by the freezing rate. According to this explanation, in the crystallization process, a necessary time, t, for an ice crystal to grow to a size D is represented by:

$$t = \frac{D^2}{D_w} \tag{19}$$

where $D_w$ is the diffusion coefficient of water. Ice crystals are allowed to grow only in a limited time, which is determined by an advance rate of ice front, U, and a representative scale, D. This time scale for ice crystals allowed to grow is expressed by:

$$t = \frac{D}{U} \tag{20}$$

As these two time scales in Eqs. (19) and (20) must be equal, the following equation is obtained (Miyawaki, 2001; Miyawaki *et al.*, 1992):

$$\frac{UD}{D_w} \sim 1 \tag{21}$$

Eq. (21) was compared with the experimental results of ice crystal size obtained in frozen soy protein gels (Miyawaki *et al.*, 1992). According to the explanations and observations by Miyawaki (2001) and Miyawaki *et al.* (1992), ice crystal size, D, was inversely proportional to the advance rate of ice front. The ice crystal size formed in agar gel measured by using mercury porosimetry method was also shown to follow Eq. (21) (Bae *et al.*, 1993; Miyawaki, 2001). These results showed that the advance rate of ice front is a very important parameter, corresponding to thermal properties and various operating conditions, to determine ice crystal structure in frozen food (Miyawaki, 2001).

Miyawaki (2001) and Miyawaki *et al.* (1992) compared the results achieved for the structure and size of ice crystals in frozen apple samples studied by Bomben and King (1982) with the modeling approaches and concluded that they appeared to be different from both Eqs. (13) and (21) but were theoretically similar to Eq. (21).

In another study, Woinet *et al.* (1998) proposed a theoretical model taking the effect of mass transfer properties of water to account. They neglected the effect of temperature gradient and assumed that the heat diffusion speed is much

higher than the mass diffusion rate. Their model was based on the supercooling resulting from the maximum concentration difference in the interdendritic zone and suggested that the molecular diffusion of water is the dominant mechanism for the ice crystal to grow in frozen food (Bae *et al*., 1993; Miyawaki, 2001; Miyawaki *et al*., 1992). Based on this expression, the size of ice crystals, D, is a function of the freezing front position, s, maximum supercooling, $\Delta T$, solute mass diffusion coefficient, $D_w$, thermal gradient, and thermal diffusivity, k.

$$D \approx S \cdot \sqrt{\frac{16 \Delta T D_w}{k(T_m - T_1)}} \quad (22)$$

where, $T_m$ is the initial freezing temperature and $T_1$ is cooling temperature. Since during the freezing of a sample, the supercooling, diffusion coefficient, and thermal gradient can be considered to be constant, the second term of the right hand side of Eq. (22) is a constant. As a result, the size of the crystals can be represented as a function of freezing front position.

### Ice morphology

Ice morphology is also an important factor affecting both the freezing efficiency and the quality of frozen foods and is determined by the freezing conditions (Petzold & Aguilera, 2009). At low supercooling degrees crystals with disk morphologies are created so that the water molecules will arrange in the hexagonal units (Petzold & Aguilera, 2009; Wathen, Kuiper, Walker, & Jia, 2004). On the other hand, higher cooling rates and greater supercooling degrees affect the morphology of ice crystals and cause the disk morphology to change into other forms like perturbed disk, dendrite, needle, and platelet (Petzold & Aguilera, 2009; Tressler, Van Arsdel, & Copley, 1968). However, the only ice crystal form of importance at atmospheric pressure in most foods is the hexagonal crystallization unit or "regular dendrite" (Damodaran, Parkin, & Fennema, 2007; Petzold & Aguilera, 2009). Dendrite morphology is defined by sinusoidal perturbations at the solid–liquid interface. The wavelength of these perturbations is dependent on the rate of crystal growth, the temperature gradient in frozen region, and the degree of supercooling. There is a threshold wavelength which leads to the formation of stable dendrites; below this critical wavelength, the perturbations disappear. This limit is known as the limit of morphological stability and is used to define the crystal size in relation to freezing kinetics (Pardo, Suess, & Niranjan, 2002; Petzold & Aguilera, 2009).

## Methods for examining crystallization during freezing

Crystallization modeling is important for prediction and analysis of freezing processes; however any models developed should be validated by experimental data. In order to measure the rate of ice formation and ice crystal characteristics, and monitor the freezing process directly while it is happening, various methods are developed. The structural examination of frozen foods have also been carried out for a number of reasons that include evaluation of the extent of microstructural damage to the cells and tissues resulting from the freezing process, observation of re-distribution of solutes, establishment of the degree of the heterogeneity of the foodstuff and draw important correlations between microstructure and mouth texture (Wilson, 1991). To follow these different aims, a range of methods and equipments have been employed by researchers (Table 2). Light microscopy and electron microscopy have been among the mostly used methods and some novel techniques have also been developed including CLSM (Confocal Laser Scanning Microscopy) (Kirk, Skepper, & Donald, 2009), MRI (Magnetic Resonance Imaging) (Hindmarsh *et al*., 2004; Mahdjoub *et al*., 2006), NMR (Nuclear Magnetic Resonance) (Hills & Remigereau, 1997; Hindmarsh *et al*., 2005), X-ray (Mousavi *et al*., 2005, 2007) and infrared (IR) (Fuller & Wisniewski, 1998; Stier, Filiault, Wisniewski, & Palta, 2003; Zelent & Vanderkooi, 2009) analysis.

The crystal size, distribution and structure have been studied by visualization with the above-mentioned methods both qualitatively and quantitatively. Although descriptive and qualitative images provide useful information on the structure of frozen foods, a number of methods including image processing, fractal analysis, digital reconstruction of serial images of sections to build a 3D image, and micro-slicer image processing system have been used for a better explanation of ice crystal structure (Do, Sagara, Tabata, Kudoh, & Higuchi, 2004; Hagiwara, Wang, Suzuki, & Takai, 2002; Kourosh, Crawford, & Diller, 1990; Kourosh, Diller & Crawford, 1990; Neils & Diller, 2004; Ueno, Do, Sagara, Kudoh, & Higuchi, 2004).

### Light microscopy

Observation and visualization of the structure of frozen foods with light microscopy can be performed at low temperatures when the sample is frozen or may be done at ambient temperatures after thawing or dehydration of the sample. The first method needs to be carried out in a cold room or by using a cryo-microscope. The advantage of using this method is that the ice crystals and the structure of frozen food can be observed directly when it is frozen. In addition, it is possible to evaluate the structure during the freezing and thawing processes when the ice is being formed or melted. Cryo-microscopy is referred to the microscopical observation of chemical and biological systems during cooling (McLellan, Morris, Grout, & Hughes, 1991). A cryo-microscope consists of a temperature controlling system or a heat transfer stage installed on a light microscope. The microscope can be equipped with a camera and the freezing process can be monitored. The potential applications for a cryo-microscope in freezing of foods is to determine the nucleation temperature of ice, size, shape and location of ice crystals, mechanical effect of ice crystal

**Table 2. Methods for evaluation of freezing process and ice crystal characteristics.**

| Method | Advantages | Drawback | References |
|---|---|---|---|
| Light microscopy | | | |
| Low temperature observation | Direct observation | Low temperature equipment is needed | |
| Cryo-microscopy | Evaluation of the structure during process | Difficult to combine with freezing equipment | (Chow *et al.*, 2003, 2005; McLellan *et al.*, 1991; Olmo *et al.*, 2008) |
| Ambient temperature observation | Chemical fixation, Freeze substitution, Freeze drying | Shrinkage, preparation errors | (Alizadeh *et al.*, 2007; Bevilacqua *et al.*, 1979; Bevilacqua & Zaritzky, 1980; Chevalier *et al.*, 2000a, b; Steffolani *et al.*, 2011) |
| Other light microscopy methods | | | |
| Fluorescence microscopy | | | (Neils & Diller, 2004) |
| Stereomicroscopy | No need to cut the sample into very thin specimen | | (Hottot *et al.*, 2004; Woinet *et al.*, 1998) |
| Episcopic coaxial lighting | No need to cut the sample into very thin specimen | | (Arnaud *et al.*, 1998; Caillet *et al.*, 2003; Faydi *et al.*, 2001; Neils & Diller, 2004) |
| Electron microscopy | | | |
| TEM | | Sample preparation, cost bearing | |
| SEM | Studying both surface and internal features, a wide range of magnification, sample preparation easier than that for TEM | Total dehydration is required, cost bearing | (Bomben & King, 1982; Delgado & Sun, 2003) |
| Cryo-SEM | Avoids the risk of shrinkage | High cost | (Fernandez *et al.*, 2006; Sun & Li, 2003) |
| ESEM | No preparation step, useful to evaluate the structural damages after thawing | High cost | (Kirk *et al.*, 2009) |
| Novel evaluation methods | | | |
| NMR and MRI | Non-invasive, can be quantitative | Not enough sensitive, the spatial resolution is limited | (Hills & Remigereau, 1997; Hindmarsh *et al.*, 2004; Hindmarsh *et al.*, 2005; Lee *et al.*, 2008; Mahdjoub *et al.*, 2006) |
| X-ray | Visualization of three dimensional object without sample preparation, rapid, non-invasive, 3-D information, cheaper than NMR | | (Bischof *et al.*, 2007; Mousavi *et al.*, 2005, 2007) |
| IR spectroscopy | Very useful because the IR absorption spectra of ice and water are very different | | (Fuller & Wisniewski, 1998; Stier *et al.*, 2003; Vadivambal & Jayas, 2011; Zelent & Vanderkooi, 2009) |
| Other methods | | | |
| Zender optical interferometry | | | (Butler, 2001) |
| Confocal laser scanning microscopy | | | (Baier-Schenk *et al.*, 2005; Evans *et al.*, 1996; Ishiguro & Koike, 1998) |
| Mercury porosimeter and size analyzer | | | (Bae *et al.*, 1993) |

on cells/tissues, the volumetric and morphologic changes of the cells and to study the effect of different parameters on the mentioned events (McLellan *et al.*, 1991).

Novel freezing methods employ particular equipments such as high pressure vessels or ultrasonic transducers for the enhancement of freezing process. However, application a cryo-microscope during these processes is difficult but some researchers have developed some particular instruments. For example, (Chow *et al.*, 2003; Chow, Blindt, Chivers, & Povey, 2005) used an especially developed cryo-stage equipment to monitor the nucleation of ice crystals induced by ultrasound. Olmo *et al.* (2008) also used direct microscopy to observe the ultrasound induced nucleation in water droplets.

Evaluation of the frozen foods with a light microscope at ambient temperature is carried out after thawing the sample; or the water is removed from the sample by freeze drying or freeze substitution before observation. A fixation method is also used to fix the lipids and proteins. Freeze substitution technique (Martino & Zaritzky, 1986) has been employed to evaluate the spaces left by the ice crystals in different products including Atlantic salmon frozen by different freezing methods (Alizadeh, Chapleau, de Lamballerie, & Le-Bail, 2007), pork muscle (Zhu, Le Bail, Ramaswamy, & Chapleau, 2004) and gelatin gel (Zhu, Ramaswamy, & Le Bail, 2005) frozen by pressure shift freezing and classical freezing methods, sea bass muscle (Tironi, de Lamballerie & Le-Bail, in press), beef

(Bevilacqua *et al*., 1979; Bevilacqua & Zaritzky, 1980) and oil in water emulsions (Thiebaud, Dumay, & Cheftel, 2002). Freeze-substitution is based on solution substitution of ice at temperatures well below 0 °C. Different polar solutions capable of substituting ice, such as methanol or acetone can be employed (Feder & Sidman, 1958; Wilson, 1991). Freeze drying is another common method used to study the voids and spaces left by the ice crystals through sublimation of ice (Chevalier, Le Bail, & Ghoul, 2000a, b; Kochs, Korber, Heschel, & Nunner, 1993; Sagara & Ichiba, 1994; Woinet *et al*., 1998; Zhu *et al*., 2005). However, difficulties in adjustment of pressure and temperature (Wilson, 1991) and shrinkage are the drawbacks of this method. Histological evaluation of the frozen food tissue after thawing have also been among the methods employed for the evaluation of ice crystal characteristics and the damages to the tissue (Bevilacqua *et al*., 1979). Even though this method may bring some errors due to the changes after thawing, it can provide useful information.

In addition to the conventional light microscopy, other microscopic methods such as fluorescence microscopy (Neils & Diller, 2004), stereomicroscopy (Hottot, Vessot, & Andrieu, 2004; Woinet *et al*., 1998) and optical microscopy with episcopic coaxial lighting (Arnaud, Gay, Barnola, & Duval, 1998; Caillet, Cogne, Andrieu, Laurent, & Rivoire, 2003; Faydi, Andrieu, & Laurent, 2001; Neils & Diller, 2004) have also been employed to observe the structure of ice crystals. In stereomicroscopy and episcopic coaxial lighting microscopy the surface of the frozen sample can be observed after freezing. The advantage of this method is that the sample does not need to be cut into very thin specimen and observation of the ice morphology can be performed with minimum preparation of the sample at low temperature (Hottot *et al*., 2004). Freeze dried or thawed samples can also be studied with this method (Woinet *et al*., 1998).

## Electron microscopy

Electron microscopy has been widely employed for the evaluation of the microstructure of food and biological products. In this method, electron beams are used to observe the specimen rather than light and therefore preparation is needed for biological materials. This preparation is much complicated than that required for light microscopy. In the case of analyzing frozen samples, the sample needs to be thawed and dehydrated or freeze dried before observation. Different electron microscopy techniques including transmission electron microscopy (TEM), scanning electron microscopy (SEM), cryo-SEM, and environmental scanning electron microscopy (ESEM) have been employed for the evaluations related to freezing. Delgado and Rubiolo (2005) employed SEM to observe the microstructure of frozen strawberries. Freeze drying method was used to prepare the samples for analysis and good results on cell wall and membranes were achieved. Holes where ice and cell contents existed before were detectable but not distinguishable from each other. Bomben and King (1982) also used SEM for observation of ice crystals. Compared to light microscopy, SEM has been very attractive for food scientists because both surface and internal features can be studied, a wide range of magnification is possible, and the SEM can achieve a depth of field roughly 500 times that of the light microscopy. Sample preparation is easier than that for TEM, so it combines the features of light microscopy and TEM (Aguilera & Stanley, 1999). However, total dehydration is required for biological materials and the electron beam may damage the specimen. Moreover, it is very costly and cannot be used widely. Another method used for evaluation of frozen foods is cryo-SEM microscopy. Sun and Li (2003) employed a cryo-SEM microscope to observe the microstructure of potatoes. Fernandez *et al*. (2006) also employed this method to observe the ice crystals formed during high-pressure shift freezing and high-pressure assisted freezing. The cryo-SEM method provides rapid physical fixation and avoids the risk of introducing artefacts entailed in chemical fixation, structural collapse or shrinkage as sometimes occurs in typical preparation methods. However, similar to SEM method, its main drawback is its high cost.

Environmental scanning electron microscopy (ESEM) can also be used with the advantage of not requiring any preparation step (Kirk *et al*., 2009). Fig. 1 displays an example of fresh and frozen then thawed carrot observed by ESEM. Cells are affected by freezing, some broken apart cell walls are observed in the frozen-thawed sample. Samples need to be thawed but preparation is not necessary. This method can be very useful to evaluate the structural damages after thawing.

Also electron microscopy remains an important tool for the evaluation of freezing process, its drawbacks, including the high cost and sample preparation procedures, has resulted in the development of some alternative methods.

## Non-invasive methods

Non-invasive methods including NMR, MRI, X-ray micro-computed tomography and Infrared analysis (IR) have been used for studying the freezing process and for monitoring the state of water during freezing. Since these methods are non-invasive, they introduce no processing artefacts and permits repeated observation on the same sample as it undergoes controlled changes during processing (Hills & Remigereau, 1997).

NMR microscopy and MRI (a more complicated instrumentation of NMR using Fourier transformation which provides digital images) have proved to be good methods for monitoring the freezing process. They benefit the advantage of being non-invasive. Moreover, the total proton NMR signal from any region of the sample is directly proportional to the proton density, so they can be quantitative (Hills & Remigereau, 1997). However, NMR is not sensitive enough and the spatial resolution of this technique is limited, and specialized developments for different practical applications are needed.

Compartments and movement of water can be monitored by using purpose-built NMR instruments and MRI. For

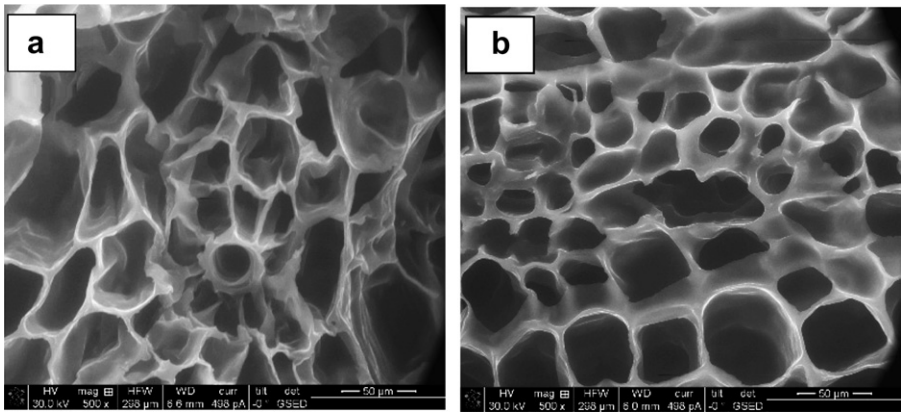


**Fig. 1**. Environmental scanning electron micrographs of fresh (a) and frozen-thawed carrots (b). The scale bars are 50 microns (Kiani & Delgado 2010, internal notes).

example, Hills and Remigereau (1997) used NMR water proton relaxation to monitor the changes in sub-cellular water compartmentation in the parenchyma tissue of apple during drying, freezing and rehydration. By this method they found that the vascular compartment is the first to freeze at 270 K, but because of their higher biopolymer content, the cytoplasm and cell wall compartments require temperatures below 263 K before they freeze. They also detected similar results for potatoes but, in contrast with apples, the freeze thawing process revealed a hysteresis for potatoes. Lee *et al*. (2008) also applied NMR spectroscopy to evaluate the freezing temperature and the mobility of water in model fabricated phospholipid membranes representing the cellular membranes and found that water molecules exhibit motional behavior even at temperatures as low as −20 °C when trapped in the membranes and freeze at a much lower temperature than pure water.

NMR spectroscopy has also been used to obtain liquid fraction data during freezing of droplets of water and sucrose solution (Hindmarsh *et al*., 2005). By using NMR spectrometry it was possible to calculate the liquid fraction from the magnetic resonance $^{1}H$ signal intensity. This is related to the mass of liquid solution present in a sample volume because a frozen solution gives a negligibly small NMR signal (Hindmarsh *et al*., 2005). Studies in sucrose solutions revealed that the rapid crystallization of ice crystals forms regions of concentrated sucrose inclusions within the matrix of the ice; in these regions the concentration reaches levels at temperatures where the sucrose is mobile enough to undergo nucleation and subsequent crystallization (Hindmarsh *et al*., 2005). In another study, Hindmarsh *et al*.. (2004) applied MRI method to visualize the freezing process of sucrose solution. With the feature of fast imaging techniques, it was possible to image both nucleation and subsequent crystal growth during both recalescence and the subsequent heat-transfer governed freezing stage. From the images, it was possible to calculate the unfrozen liquid mass fraction ratio of the droplet as a function of time following nucleation, which was subsequently used to estimate the crystal growth rate during both recalescence and the subsequent freezing stage. They concluded that magnetic resonance techniques have been shown to be very valuable tools for the analysis of small droplet freezing behaviur, both in terms of structural and compositional transitions. In a similar study, Mahdjoub *et al*. (2006) employed MRI technique for monitoring the freezing process of sucrose solution to evaluate the glass transition temperature and the duration of crystallization phenomena quantitatively by monitoring, *in situ* and noninvasively, the freezing of the solution. Their results introduced MRI as a suitable method for imaging the phase behavior of sucrose solutions during cooling where the solution becomes opaque due to ice formation.

Another new method employed for the evaluation of frozen products is the application of X-ray. The X-ray micro-computed tomography (CT) system, for example, allows visualization and measurement of complete three dimensional object structures without sample preparation or chemical fixation. It uses a combination of X-ray microscopy and tomographical algorithms, based on the contrast in X-ray images generated by differences in X-ray attenuation (absorption and scattering) arising from differences in density of material within the specimen (Mousavi *et al*., 2005). The advantage of the X-ray method is that the measurements can be made rapidly and non-invasively, producing 3-D information that can be manipulated numerically (Mousavi, Miri, Cox, & Fryer, 2007). In comparison with NMR, CT is cheaper (in investment and operating costs) and simpler (in accessibility and material restrictions like ferromagnetic metals) (Bischof *et al*., 2007). Mousavi *et al*. (2005) demonstrated the potential of X-ray micro-CT system as a non-destructive technique for the study of the internal microstructure of foods, using mycoprotein as a model material. They employed the X-ray method for observing the spaces left by ice crystals after freeze drying of frozen products. They also concluded that measurements of the voids by X-ray and conventional microscopy give the same results. Mousavi *et al*. (2007) investigated ice crystals

in different frozen food materials qualitatively and quantitatively using conventional microscopy and X-ray micro-CT after freeze drying to create voids in the material. The X-ray technique could clearly show the difference in the material microstructure with decreasing freezing rate away from the freezing surface. Electron microscopy gave more information on the microstructure of the materials; although the X-ray method does not show structural detail, it is possible to use it to determine ice crystal size and morphology. Moreover, the data acquisition and handling are significantly faster than using conventional electron microscopy techniques (Mousavi *et al.*, 2007). In another study, Bischof *et al.* (2007) investigated the formation of amorphous vs. crystalline phases and some other parameters following freezing in solutions and tissues loaded with glycerol using X-ray CT. They concluded that CT was a powerful tool to measure concentration during chemical loading, and crystalline vs. amorphous phase after freezing, and provided sufficient information about specimen pretreatment (i.e. thermal and chemical processing steps). In addition, CT can be used to measure both the ice ball edge and temperature within the ice phase.

In addition to the above-mentioned methods, some other emerging and potential techniques have been developed for the analysis of freezing process. IR spectroscopy has shown to be a trustable and good method to detect the ice nucleation and to study the crystal growth because the IR absorption spectra of ice and liquid water are very different (Fuller & Wisniewski, 1998; Stier *et al.*, 2003; Zelent & Vanderkooi, 2009). Zender optical interferometry (Butler, 2001), confocal laser scanning microscopy (Baier-Schenk *et al.*, 2005; Evans, Adler, Mitchell, Blanshard, & Rodger, 1996; Ishiguro & Koike, 1998) and Mercury porosimeter and size analyzer (Bae *et al.*, 1993) have also been among the methods employed to observe the ice crystals in frozen materials.

## Novel freezing methods in relation to crystallization control

As ice crystals play an important role in the freezing of food and biological materials and their characteristics are a critical factor of this process, novel freezing methods are developed to alter the ice formation phenomenon. These novel methods employ various physical and biological trends to control the crystallization process i.e. ultrasonic cavitation, high pressure, biological control of ice formation, etc. This section will review the methods having been emerged recently dealing with the process of ice formation concerning their mechanism and their effect on the crystallization phenomenon.

### Ultrasound assisted crystallization of water

Power ultrasound has known as a promising tool to improve the freezing and crystallization processes (Acton & Morris, 1992). The major consequence of power ultrasound transmission within a liquid is cavitation (Ashokkumar & Grieser, 1999; Gong & Hart, 1998; Prosperetti, 1984a, b; Zheng & Sun 2005). Cavitation results in the formation of gas bubbles, which can serve as nuclei for ice nucleation (Mason, Paniwnyk, & Lorimer, 1996) or affect the crystallization by their collapse and motion (Sun & Zheng, 2006). With the application of power ultrasound during the freezing process the freezing efficiency can be improved and the microstructural properties of frozen foods are better preserved. Increase in heat and mass transfer rates, and initiation of ice nucleation are among other advantages (Li & Sun, 2002a; Sun & Li, 2003; Zheng & Sun 2005). Experiments with concentrated sucrose solution have shown that the nucleus number is increased with the application of power ultrasound (Suslick, 1988). Ice crystals also fracture under the alternating acoustic stress, which was demonstrated by the study carried out by Acton and Morris (1992).

Ultrasound waves may provide different mechanisms to improve or alter the freezing process. However, nucleation, as an important stage of freezing process, can be affected significantly by the ultrasound waves, and as a result, the process can be strongly influenced by this phenomenon. Nucleation is spontaneous and stochastic and the temperature at which nucleation occurs cannot be predicted or estimated with certainty. A tool to control the nucleation phenomena and turn its stochastic behavior towards a repeatable and predictable manner can be highly valuable. Ultrasound has known as a controlling tool simply applied to manipulate nucleation and improve the repeatability of the process. Ultrasound waves have been shown to initiate nucleation in different supercooled solutions (Chalmers, 1964) including aqueous solutions (Fig. 2) (Chow *et al.*, 2003, 2004, 2005; Inada *et al.*, 2001). This method has also been employed for the trigger of nucleation in industrial crystallization processes of organic molecules (Ruecroft, Hipkiss, Ly, Maxted, & Cains, 2005; Saclier *et al.*, 2010).

Acton and Morris (1992) proposed that ultrasound waves with the frequency of 16–100 kHz and preferably 20–40 kHz, can be employed to control the crystallization of water. In the process of freeze drying little and large ice crystals are desired. Up to 5 s and most preferably up to 1 s ultrasound irradiation at the temperatures close to the freezing point results in formation of large ice crystals. On the other hand, small ice crystals can be produced by irradiating the sample at greater levels of supercooling, i.e. up to 5 °C below its melting point. Ultrasound waves can also fracture the ice crystals and create fine crystals giving rise to the number of nuclei which causes the reduction of crystal size (Acton & Morris, 1992).

Inada *et al.* (2001) evaluated the effect of ultrasound waves on the nucleation of supercooled water and showed that ultrasound strongly promotes phase change. They showed that ultrasound waves are able to increase the probability of nucleation in supercooled water strongly. However, the selection of cavitation intensity is important for

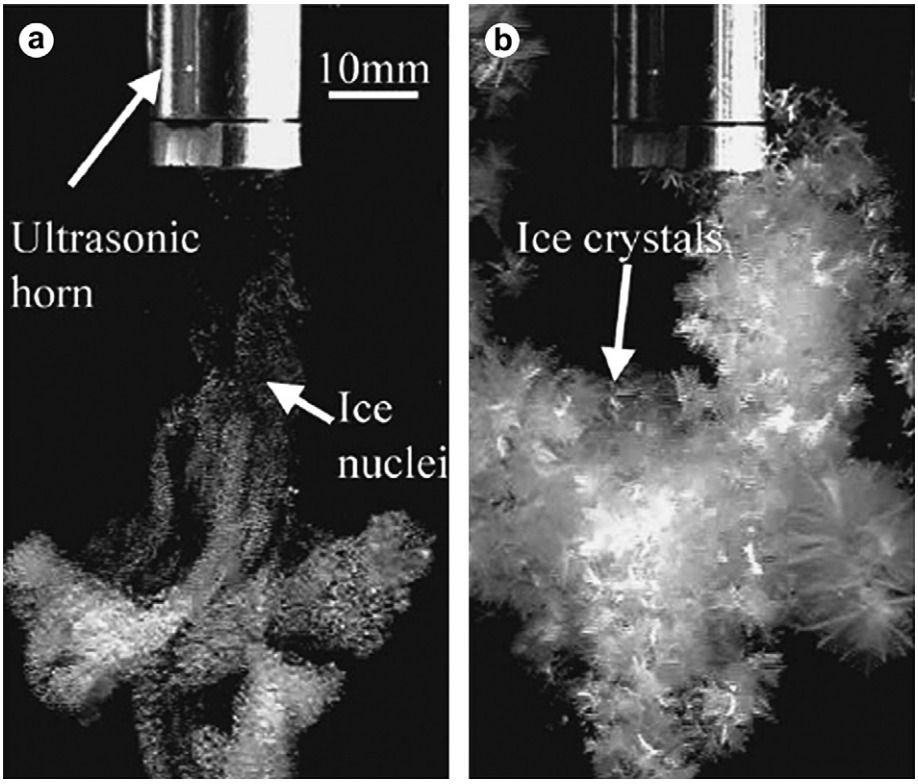


**Fig. 2**. Photographs of ice crystals nucleated in a 15 wt% sucrose solution at −3.4 °C by a commercial ultrasonic device (output 4, 10% duty cycle): (a) ice crystals following an ultrasonic pulse, (b) crystals 5 s later (from Chow *et al.*, 2005).

reproducible results. In a similar study by Zhang *et al.* (2001), the relationship between cavitation intensity and nucleation probability was analyzed. They indicated that upon application of ultrasound to a supercooled water (−6 °C) for 1 s, a large number of ice crystals were created and grew as dendrites. Their results indicated that the growth pattern was similar to the growth of normal structures initiated with a seed crystal and therefore ultrasound induced nucleation does not affect the growth and structure of the crystals (Zhang *et al.*, 2001). Nevertheless, it has recently shown that ultrasound can incorporate in secondary crystallization by breaking the dendrites and therefore changes the overall growth pattern of the crystals (Fig. 3) (Chow *et al.*, 2003, 2004, 2005).

Chow *et al.* (2003) evaluated the effect of ultrasound on the primary and secondary nucleation of water in sucrose solutions. They measured the primary nucleation according to the temperature changes during freezing and studied the secondary nucleation by using an ultrasonic microscope stage (simultaneous freezing and microscopic observation). Their results indicated that the primary nucleation of ice in sucrose solutions can be achieved at higher nucleation temperatures at the presence of ultrasound. The nucleation temperatures can be reproduced with a greater precision than under the control conditions (without ultrasound). They also concluded that cavitation bubbles appear to be important in the fragmentation of the dendrites, although ultrasonic streaming and flow patterns are certainly present, as Zhang *et al.* (2001) observed, and may also be significant causing the secondary nucleation to occur. It was also shown that the nucleation temperatures of ice increase with the increasing ultrasonic power (Chow *et al.*, 2003, 2005).

## Crystallization of water during high-pressure freezing

The application of high hydrostatic pressure to control and enhance the freezing process has been an interesting subject of research in recent decades (Norton & Sun, 2008; Schlüter, Foerster, Geyer, Knorr & Herppich, 2009). The use of high pressure makes high degrees of supercooling possible resulting in even and fast ice nucleation and growth all over the sample on pressure release. Therefore, in contrast with the conventional methods in which an ice front moving through the sample is produced, fine ice crystals are formed (Fig. 4).

The phase change temperature of water decreases with pressure from 0 °C at 0.1 MPa to −21 °C at 210 MPa and the opposite effect is observed above this pressure level and therefore, different processes can be performed using high pressure (Kalichevsky, Knorr, & Lillford, 1995; LeBail, Chevalier, Mussa, & Ghoul, 2002; Li & Sun, 2002b). Pressure shift freezing is one of the possible processes involving cooling the sample under pressure up to −21 °C without freezing before the pressure release. Upon pressure release, the rate of nucleation is boosted

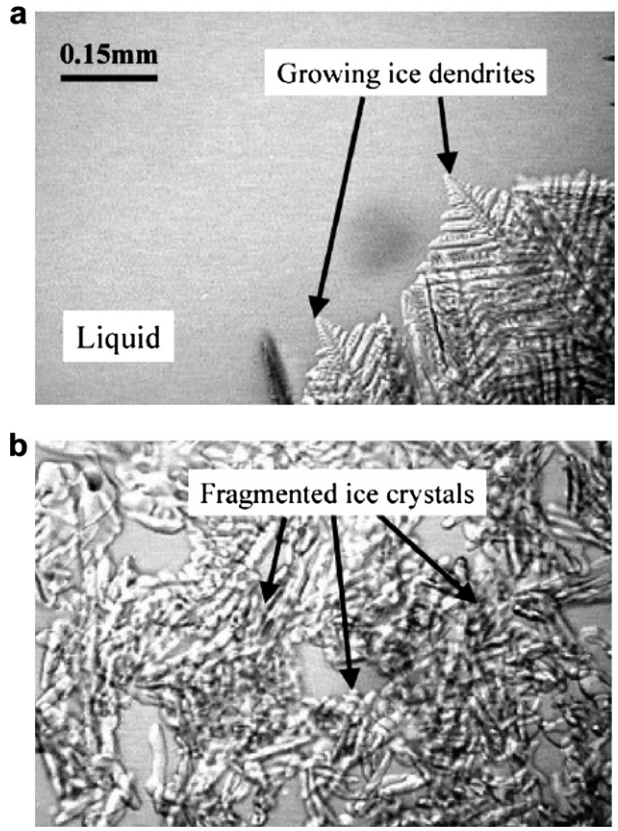


**Fig. 3**. Secondary nucleation of ice in a 15 wt% sucrose solution with ultrasound (a) ice dendrite (no ultrasound) and (b) fragments of crystals remaining after sonication (4 s of ultrasound). Image width = 0.92 mm (from Chow *et al.*, 2005).

significantly due to the high supercooling achieved (Kalichevsky *et al.*, 1995; Li & Sun, 2002b).

The fin ice crystal created during the high pressure freezing can help the quality of the product to be better preserved (Chevalier, Sentissi, Havet, & Le Bail, 2000c; Martino, Otero, Sanz, & Zaritzky, 1998). Experiments on different frozen foods including meat (Martino *et al.*, 1998), Norway lobster (Chevalier *et al.*, 2000c), carrots

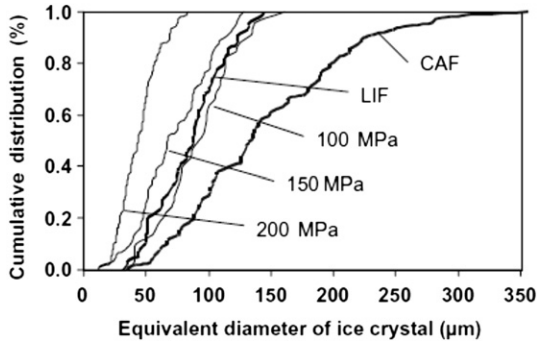


**Fig. 4**. Relative cumulative distributions of the equivalent diameter of the ice crystals in gelatin gel (2%, w/w) frozen by conventional air freezer (CAF), liquid immersion freezing (LIF), and pressure shift freezing at 100, 150 and 200 MPa (from Zhu *et al.*, 2005).

(Fuchigami, Kato, & Teramoto, 1997), Chinese cabbage and tofu (Fuchigami, Kato, & Teramoto, 1998; Fuchigami & Teramoto, 1997), peach and mango (Otero, Martino, Zaritzky, Solas, & Sanz, 2000) has shown that high-pressure freezing can improve the quality of these products.

One of the main issues of the application of high pressure in freezing process is the amount of ice form instantaneously after pressure release. In fact, the amount of ice instantaneously formed after expansion determines the advantages of high pressure freezing (Otero, Sanz, Guignon, & Aparicio, 2009). Different approaches have been used to evaluate this phenomenon. Some researchers have used the heat balance to predict the amount of ice crystals formed (Barry, Dumay, Cheftel, & , 1998; Otero & Sanz, 2000, 2006). In this modeling approach it is assumed that the latent heat released by nucleation is equal to the sensible heat absorbed by the sample to pass from metastable conditions to its equilibrium freezing/melting curve. The models propose that increasing the pressure or decreasing the temperature prior to the expansion result in larger amounts of ice formed, and therefore, the phase transition time is decreased (Otero *et al.*, 2009).

Sanz, Otero, de Elvira, and Carrasco (1997) predicted the amount of ice formed instantaneously in high-pressure freezing by mathematical modeling with regard to the thermodynamic properties of water under high pressure. The model considered the relationship between pressure, temperature and specific volume in the liquid water and ice I regions, and also in the boundary between both regions. The mathematical model developed by Sanz *et al.* (1997) predicted an instantaneous formation up to 36% of ice in water. Otero and Sanz (2000) also estimated an ice percentage of 29.1% in high-pressure shift frozen agar gel samples (99% water) in a similar way.

As another tool to study the high pressure freezing method, the latent heat released after expansion is measured using experimental evaluations such as calorimetric techniques which can then be related to the fraction of ice generated (Otero *et al.*, 2009). Zhu *et al.* (2004) and Zhu *et al.* (2005) examined the amount of ice formed in different samples including pure water, tylose, potato, salmon and pork frozen by high-pressure shift method. Their results led to a general relationship for predicting the amount of ice applicable to all the evaluated products. The proposed relationship suggested that the maximum achievable ice fraction after expansion from 210 MPa and −22 °C is 33.6%. Otero *et al.* (2009) determined the amount of ice formed, just after expansion, during high-pressure shift freezing at different pressure and temperature conditions by using a simple apparatus. Their experimental results agreed with the theoretical predictions by the heat balance model. Similar to the theoretical modeling approaches, their results proved that increasing the pressure or decreasing the temperature prior to the expansion resulted in a larger amount of ice formed. They also showed that the amount of ice also depended on the initial water content

of the sample, however the percentage of ice formed, was identical for all products (Otero *et al*., 2009).

### Ice nucleating proteins

There are some proteins detected in the nature which are in favor of the formation of ice crystals. Some species of bacteria, insects, intertidal invertebrates, plants, and lichen has known to be able to act as ice nucleation activators (INA) (Sun & Zheng, 2006; Zachariassen & Kristiansen, 2000).

Certain bacteria of the genera *Pseudomonas, Erwinia, and Xanthomonas* have very potent ice nucleators on their external membrane which nucleate water at a temperature just below 0 °C. These bacteria benefit the nutrients made available due to the injuries caused by ice crystal formation on the surface of different fruits and plants (Zachariassen & Kristiansen, 2000; Zhang, Wang, & Chen, 2010). Ice nucleators can also be useful to a number of plants. Ice nucleation at subzero temperatures release heat of fusion and some afroalpine plants utilize the heat generated by the freezing of water trapped in their inflorescence to survive at temperatures well below zero. It has been found that the trapped water contains INAs associated with bacteria (Zachariassen & Kristiansen, 2000). In addition to the bacterial INAs, evidences show that insects are also among the creatures with the ability of nucleating water inside their body. This phenomenon is recognized as a protective method against the very low temperature of the environment (Zachariassen & Kristiansen, 2000). For the bacterial INAs concentration does not affect the ice nucleation activity. However, it has shown that the activity of INA with insect origin is dependent upon the concentration (Zachariassen & Husby, 1982). The differences between the INAs arise from their size and their structure (Zachariassen & Kristiansen, 2000). The nucleation temperature of INAs is dependent on different parameters including the size, quality and quantity of the INAs as well as the properties of the solution in which they occur (Zachariassen & Kristiansen, 2000).

It has also found that INAs are not only able to induce ice nucleation at temperatures significantly higher than the initial freezing point, but also they influence the ice formation patterns. INAs can create large and long ice crystals in ordered directions (Arai & Watanabe, 1986).

The addition of INAs in food materials can be of great advantage. They elevate the temperature of ice nucleation, shorten freezing time, increase freezing rate, and change the texture of frozen foods, thus decreasing refrigeration cost and improving the quality (Li & Lee, 1995; Sun & Zheng, 2006; Zhang *et al*., 2010). These promising results have encouraged researchers to incorporate INA bacteria to foods and model foods. Watanabe and Arai (1994) evaluated the effect of INA bacteria of the freeze concentration of some liquid foods and their results indicated that the flavor, color and texture can be improved by using INA bacteria. Li and Lee (1998) studied the effect of INA bacteria of a liquid model food and found that the freezing efficiency can be increased as a result of higher nucleation temperature causing the freezing time to reduce. They also reported a fiber-like texture arising from the ability of the bacteria to crate long crystals. Zhang *et al*. (2010) studied the effect of INA bacteria on the freezing process of a solid model food, i.e., Tylose. Their results indicated that the addition of INA bacteria led to an increase in the nucleation temperature but had no obvious effect on glass transition temperature, and heat of fusion of the samples. They, however, did not detect a significant change in the freezing time of the samples but the ice crystal size was greatly reduced in the presence of INA bacteria as a potential result for improving the quality of solid frozen foods (Zhang *et al*., 2010).

### Suppression of ice formation

As a part of their protective system when living in subzero temperatures, or as a method to help for providing nutrients, some plants, insects or bacteria produce protein systems for controlling the ice formation phenomenon. Some of these proteins act against the crystallization of water. Suppression of ice crystal formation would be interesting for some reasons. Higher degrees of supercooling during the freezing process can produce finer ice crystals, enhancing the quality of frozen foods or biological materials. The inhibition of ice crystal formation can also be effective in reduction of freezing injury. Different methods can be used to suppress the formation of ice including antifreeze protein. Application of antifreeze proteins has been proved to be promising for preservation of foods and biological materials. In addition, magnetic resonance freezing and microwave assisted freezing have also already been introduced as promising methods for suppression of ice crystal formation.

Antifreeze proteins and glycoproteins having been known as the protective agents for different species such as fish (the most studied antifreeze protein), plants, insects, and bacteria living in subzero temperatures are capable of binding to ice crystals and affect their growth pattern (Griffith & Ewart, 1995). The mechanism of antifreeze proteins action does not follow the Rauolt's law, in which supercooling is a result of concentration, and the proteins interact in an active way with the ice structure. The proteins have a dipole nature and contain a hydrophilic and hydrophobic section (Li & Sun, 2002b; Yang, Sax, Chakrabartty, & Hew, 1988). When a growing ice front is encountered by the proteins, the hydrophilic portion will bind to specific planes in the crystal structure. This forces the ice to grow between the molecules and changes the planar ice front into a series of curved ice fronts. If the diameter of any curvature is less than the critical radius of ice nucleation, growth of this ice front is halted (Kennedy, 2000). Therefore, antifreeze proteins decrease the freezing temperature and suppress the growth of ice nuclei, hence inhibiting ice formation and changing the growth rate (Li & Sun, 2002b).

The application of microwave irradiation has also been introduced as another means of ice nucleation suppression (Jackson *et al*., 1997). Hanyu, Ichikawa, and Matsumoto (1992) found that microwave irradiation during freezing

results in the formation of an ice-free (vitrified) region adjacent to the cooling block. Jackson *et al.* (1997) studied the combined effect of microwave irradiation and cryoprotectant and revealed that ice formation was greatly influenced by microwave irradiation. For example, ice formation could be reduced by roughly 56% in 3.5 M ethylene glycol solutions and nn average reduction of 66% was observed in 4.5 M solutions. Their results showed that the main effects of microwave and ethylene glycol concentration as well as the interaction between these two factors significantly influenced the amount of ice formed. The underlying mechanism was assumed to be the electric field component of electromagnetic radiation interacting with dipolar $H_2O$ molecules and thereby disrupting ice nucleation phenomena (Jackson *et al.*, 1997).

Magnetic resonance freezing (MRF) has been claimed to be a novel method for suppression of ice formation (Fikiin, 2003). The temperature of food or biological materials can be decreased below their initial freezing point under continuous magnetic wave vibrations without freezing. The magnetic field is then suddenly removed and a flash freezing of the entire food volume occurs. By using this method, the critical zone of water crystallization can be passed quickly, fine ice crystals are formed, water migration and undesirable mass transfer phenomena is diminished, cellular dehydration is prevented, cracks and related damages are avoided and the integrity of food tissue is preserved (Fikiin, 2003; Mohanty, 2001). At present, MRF data are still kept as a confidential know-how of a number of companies, while MRF equipment still needs to prove its claimed advantages and capabilities through extensive tests within a sufficiently representative industrial environment (Fikiin, 2003).

All of the above mentioned methods of suppressing the ice formation can be potential techniques for improving the quality of frozen materials by controlling ice formation. However, more research is needed to develop and industrialize these methods.

## Conclusions

An overview of the theoretical and experimental approaches towards crystallization modeling in relation to the freezing process was provided, and the methods to evaluate, visualize and monitor the crystallization phenomenon and ice crystal characteristics during or after freezing were also presented. The novel methods dealing with the control of crystallization and the way in which they affect the process were reviewed as well.

Freezing of foods is a complex process involving the phenomenon of water crystallization. Analyzing the water crystallization in food materials theoretically and experimentally, and relating the processing parameters to the crystal size distribution, crystal location and crystal morphology is helpful for improving the freezing process. This will be useful for achieving the desired results during freezing in terms of process efficiency and the quality of the final product. In particular, novel methods such as ultrasound assisted freezing, high pressure freezing, ice nucleating proteins, antifreeze proteins, magnetic resonance freezing and microwave assisted freezing have shown to positively affect the nucleation or crystal growth steps of water crystallization and can then be useful in controlling the crystallization phenomenon. The final goal of any alteration or control of the process can be either creating fine and numerous crystals, which guarantees the better quality of frozen foods and biomaterials, producing large and little crystals that is useful in some processes such as freeze drying and freeze texturizing, or inhibiting ice crystal formation.

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