Recent Progress in Food Science and Engineering

Review

Advances In Food Freezing/Thawing/Freeze Concentration
Modelling and Techniques

Quang Tuan PHAM

School of Chemical Sciences and Engineering, University of New South Wales
Sydney 2052, Australia

This paper reviews recent developments on various aspects of food freezing. The various effects of freezing and frozen storage on food quality are described, including the role of glass transition. Methods for calculating freezing time and the evolution of temperature and phase change are reviewed and their underlying assumptions and limitations are critically examined. Finally, recent developments in freezing, thawing and freeze concentration techniques are reviewed: high pressure freezing and thawing, ultrasound assisted freezing, progressive freeze concentration, osmodehydrofreezing, immersion freezing in ice slurry, and the use of antifreeze proteins.

Key words: freezing, thawing, freeze concentration, frozen food, modelling.

1. Introduction

Among all food preservation methods, freezing is usually considered the best for long term preservation of high quality foods, and properly frozen products are considered by consumers to be closest to fresh foods. This situation is likely to continue in the foreseeable future. Nevertheless, various physical, chemical and biochemical processes take place during food freezing, frozen storage and thawing that are of concern to manufacturers and consumers. Food engineers are interested in designing efficient equipment and processes that will satisfy their requirements at minimal cost while optimizing product quality: for this they must rely on various calculation methods, which have evolved rapidly in recent years due to the advent of cheap, powerful computers. This paper reviews these important aspects of food freezing and some recent advances in freezing techniques.

2. How Freezing Affects the Quality of Foods

2.1 Effect of freezing

Freezing is commonly believed to be the best method for the long-term preservation of food qualities. However, there may still be significant changes during freezing and frozen storage, especially if the freezing is not done properly. In this paper, we will describe what happens to the food during freezing and how it can affect quality.

Virtually all foods have complex composition and microstructures. During freezing, heat is removed from the material, the water and perhaps other components such as some oils and fats crystallize out, and there is movement of water and other molecules on various scales.

For cellular food with water both inside and outside the cells, such as meat, in normal (slow to moderate) freezing, ice will not form inside the cell, due to supercooling. However, as water converts to ice outside the cells, the remaining extracellular liquid becomes more concentrated than the intracellular liquid, causing an osmotic pressure that forces water to migrate from the cells to the outside through the cell walls. This causes the cell to dehydrate and shrink (Fig. 1).

When freezing is very fast, water does not have time to diffuse through the cell walls, and the cells will have significant supercooling before its water is lost. In this case nucleation will occur inside the cells, causing intracellular ice. The faster the cooling, the more nuclei will form, leading to large number of small crystals. If the freezing rate is slightly reduces, only one or a few large intracellular crystals will form.

If you are trying to preserve living tissue, for example
for transplantation, intracellular ice formation is very bad: it invariably kills the cells. However, with foodstuff where cell viability is not a concern, intracellular ice is not necessarily bad. In fact the formation of a large number of small intracellular crystals will ensure that the cell is not distorted or dehydrated, and so quality may be improved. There are reports, however, that at some intermediate freezing rate where a single large crystal forms in the cell, the crystal may cause excessive distortion and rupture the cell, causing excessive drip on thawing [1].

At a faster rate still, crystallization does not have time to occur inside or outside the cell. Thus the tissue does not separate into ice and non-ice phases, but becomes a glass. This is the best situation for preserving viability or food quality; unfortunately this freezing rate can only be obtained in extreme cases (very small samples in liquid nitrogen) and is unlikely to be obtained in industrial food freezing. Furthermore, even if it can be done, much of the good could be undone during thawing, as crystals may form during that stage.

Having examined what happens during a typical freezing process, we can now list the factors that may affect food quality:

(a) Macro-scale water migration: during air freezing, water will evaporate from the surface of the food into the air, because the surface is warmer than the air and therefore its vapor pressure is high. During immersion freezing, water may diffuse into the food or out of it depending on the solute concentration, i.e. water activity, of the water.

(b) Freeze concentration effect: as the water freezes, the remaining solution becomes more and more concentrated in solutes. This freeze-concentration phenomenon is illustrated on the phase diagram of Fig. 2, which represents a simple solution such as salt and water. The increased concentration may have significant effects on some fresh foods, since high solute concentration may denature the cells of fresh foods. This denaturation is faster at higher temperatures (Arrhenius law), and therefore it is worsened by slow freezing since the food spends longer at high temperature and high solute concentration. Note that this effect will also occur during thawing.

(c) Physical effect of ice formation on the microstructure: ice formation may cause distortion, cell wall detachment, cell rupture.

(d) Large scale mechanical effect of ice: upon crystallization, water expands by around 9%, causing very high stresses and in some case cracking.

(e) Osmotic dehydration effect: loss of water from the cells, causing distortion of the cells, high drip rates on thawing due to insufficient resorption.

(f) Lethal effect of intracellular ice (if any) on living cells.

Of course, different foods respond in different ways to freezing. Thus with non-cellular foods such as bean curds (tofu) we are not worried about cellular rupture but only about freeze concentration and consistency.

2.2 Effect of storage - The role of glass transition

When food is cooled slowly below its freezing point, water separate out to form crystals of pure ice, leaving behind a more and more concentrated solution. Thus we
Food freezing and thawing

have two distinct phases that are in thermodynamic equilibrium. Theoretically, the non-ice phase will also eventually reach its own crystallization point and from that point onwards, the two phases crystallize together as a eutectic mixture (Fig. 2).

In practice, due to a combination of high solute concentration and low temperature, the non-ice phase will become extremely viscous well before it reaches its crystallization temperature. Due to the very high viscosity, the molecules of the non-aqueous components will not be able to re-arrange and crystallize. These components remain liquid, with their viscosity continuously increasing. Eventually a point is reached where the viscosity becomes so high that for all intent and purposes the non-ice phase has become a solid: this is called the glass transition point $T_g$ (Fig. 3).

A distinction must be made between glass transition and vitrification. Vitrification happens when cooling is so fast ($>3 \times 10^{-6}$ K/s) that no ice crystal is formed at all, and the water molecules remain intimately mixed with the other molecules. The whole mixture simply cools until it becomes a glass – a liquid with extremely high viscosity. On the above diagram vitrification is represented by a vertical line from A down to a very low temperature. In practice, vitrification can only happen when very small samples are frozen in liquid nitrogen, especially if cryoprotectants are added to hinder crystallization.

The glass transition temperature is an important property because food stored below this temperature will have reduced rate of quality loss, at least when the rate of damage is controlled by molecular diffusion. Thus, ice re-crystallization and water loss by sublimation can be expected to be reduced by storage below $T_g$.

3. Design and Optimization of Freezing Processes and Equipments

3.1 Simple equations for calculating the freezing time

3.1.1 Heat transfer controlled freezing

Let’s look at a material such as meat being frozen in an air blast freezer. Unlike water, which freezes at 0°C, meat has an initial freezing point of around 1°C, due to the presence of dissolved salts. However, ice crystals do not appear immediately as the temperature reaches this freezing point: due to supercooling, the temperature will continue falling at approximately the same rate for a few degrees, before jumping up towards -1°C, indicating that the first ice crystals have formed at the surface (Fig. 4).

The ice crystals will then grow towards the centre of the food. This takes some time, during most of which the unfrozen core of the food hovers around the freezing point – this is called the freezing plateau. During normal food freezing, the crystal will grow as dendrites, spreading inwards along channels in the space between the cells.

For many years the Plank equation [2, 3] has been used to predict the freezing time. For solid foods of simple shapes, this equation can be written as follows:

$$t_{\text{plank}} = \left[ \frac{Q_I}{k \Delta T} \right] \left[ 1 + \frac{1}{2} \frac{R}{k} \right]$$

where $Q_I$ the total latent heat of freezing contained in the food (J), $A$ the surface area of the food (m$^2$), $\Delta T$ the difference between freezing point and environment temperature (K), $R$ the distance from the centre of the food to the sur-

![Fig. 3 Actual freezing process on a phase diagram, showing glass transition.](image)

![Fig. 4 Temperature evolution during freezing, showing supercooling at the surface and freezing plateau at the center.](image)
face (i.e. half thickness or radius), and $h$ the heat transfer coefficient, or $htc$ ($W/m^2K$), which depends on the surface conditions and wrapping.

The Plank equation can be considered as the product of two factors:

1. \( \frac{Q_t}{kh\Delta T} \) is the freezing time according to Newton's law of cooling. It measures the freezing time if the food was a well mixed liquid, i.e. if temperature was uniform in the food, and if the food is initially at the freezing temperature and no warmer. Such a food is said to have no internal resistance, all the heat transfer resistance is at the surface.

2. \( \frac{1}{2} \left( \frac{kR}{h} \right) \) measures the effect of internal resistance to heat transfer. The latent heat that evolves on freezing has to travel from the inside of the food to the surface, then cross over to the cooling medium. For each of these steps, there is a given resistance. If $k$ is very large then the food material is a very good conductor of heat and therefore $\frac{kR}{h}$ will be negligible. The same happens if $h$ is small, because the surface resistance will be so large that internal resistance becomes negligible, or when $R$ is small, because released latent heat has a small distance to travel from the inside to the surface. The number $\frac{kR}{h}$ is so important that it has been given a name, the Biot number: $Bi = \frac{kR}{h}$. If $Bi \ll 1$ then external (surface) resistance to heat transfer predominates, if $Bi \gg 1$ then internal resistance to heat transfer predominates. This has important applications for the optimization of freezing equipment and processes.

In practice the Plank equation is not accurate because it neglects several phenomena:
1. The food may not be at the freezing point initially.
2. Its shape may not be one of the simple shapes but may be more complicated or asymmetrical.
3. Real foods freeze gradually over a range of several degrees.

Many corrections to Plank’s equation have been proposed to make it more accurate. The following [4] is one of the simplest and most accurate. For foods of simple shape (slabs, infinite cylinders or spheres):

$$ t_1 = \frac{1}{hA} \left( \frac{Q_{cool}}{\Delta T_{cool}} + \frac{Q_{freeze}}{\Delta T_{freeze}} \right) \left( 1 + \frac{Bi}{2} \right) \quad (2) $$

In this equation, the effect of the food not being at the freezing point initially is taken into account by replacing the ratio $\frac{Q_t}{\Delta T}$ by $\frac{Q_{cool}}{\Delta T_{cool}} + \frac{Q_{freeze}}{\Delta T_{freeze}}$, where $Q_{cool}$ is the heat for cooling the food from the initial temperature to the freezing point and $Q_{freeze}$ is the heat for freezing it. $\Delta T_{cool}$ is the mean temperature difference during cooling and $\Delta T_{freeze}$ is the mean temperature difference during freezing (Fig. 5). These temperature are precisely calculated from

$$ Q_{cool} = V \rho \phi \rho (T_i - T_{m}) \quad (3) $$

$$ \Delta T_{cool} = \frac{(T_i + T_{m})}{2} - T_a \quad (4) $$

$$ Q_{freeze} = V \rho \phi \rho \left( L_d + c(T_{m} - T_f) \right) \quad (5) $$

$$ \Delta T_{freeze} = T_{m} - T_a \quad (6) $$

$T_m$ is the “mean freezing temperature” given by:

$$ T_m = 1.8 + 0.263 T_c + 0.105 T_a \quad (7) $$

When the shape of the food is not simple, the easiest approach is to calculate the freezing time $t_{slab}$ for an infinite slab (plate) with the same thickness as the smallest dimension of the food, then apply a shape factor $E$:

$$ t_1(\text{any shape}) = \frac{t_1(\text{slab})}{E} \quad (8) $$

For example, if the food is an infinite cylinder then $E=2$ and if the food is a sphere then $E=3$. Shape factors have been found for many regular shapes (rectangular rods, bricks, finite cylinders, ellipses and ellipsoids). Irregular shapes can also be approximated by the closest regular shapes for which there is a shape factor available.

### 3.1.2 Application of the freezing time equation in process design

The freezing equation, when written in the form

$$ t_i = \frac{\rho V}{hA} \left( \frac{\Delta H_{cool}}{\Delta T_{cool}} + \frac{\Delta H_{freeze}}{\Delta T_{freeze}} \right) \left( 1 + \frac{1}{2} \frac{kR}{h} \right) \quad (9) $$

is a very simple and convenient tool to optimize a freezing process. For example:

1. The freezing time is dependent on the surface heat transfer coefficient $h$, which represents the effect of the effect of thermal contact between the product and the cooling medium. This depends on
   a. the freezing medium – immersion and plate freezing are better than air freezing
   b. the velocity of the fluid – fast flowing is better than...
Food freezing and thawing

slow flowing, impingement is better still
c. the wrapping - wraps cause an insulation layer, especially if it is loose and air is trapped between wrap and product.

2. $1/k$ is called the surface resistance and is the sum of all the resistances at the surface: resistance of the fluid near surface+resistance of the wrap+resistance of the air trapped under the wrap. We must know which is the biggest resistance in order to try to reduce it.

3. Increasing the heat transfer coefficient will decrease the freezing time, but the effect is significant only if the Biot number $Bi = hR/k$ is large, i.e. if external resistance is controlling (Fig. 6). Therefore, before you worry about modifying the process, for example by increasing the air velocity, you should look at the Biot number first. If $Bi \ll 1$ there is no point trying, unless you can reduce $Bi$ (by reducing $R$ i.e. make the product smaller or thinner).

4. On the other hand a reduction in freezing medium temperature always have a similar effect on all products large or small, conducting or not.

5. Reducing the size, especially the thickness of the product, is doubly rewarding: it increase the area-to-volume ratio (first factor) and it reduces the internal resistance (third factor).

3.1.3 Nucleation-controlled freezing

The simplified freezing equations, as well as most numerical software, are accurate only if the phase change is controlled by heat transfer. In some materials such as butter, water is dispersed in tiny bubbles so nucleation has to proceed individually in each bubble. The rate of nucleation then becomes the controlling factor and the effect of supercooling is very significant. Nahid et al. [5] found that phase change in butter takes place a considerable time after the freezing point is passed, as shown by a late latent heat peak (Fig. 7).

3.2 Numerical methods for modelling the heat transfer process

Simple formulas such as the above will give the freezing time but often we need to know much more about what happens during processing – temperature, moisture, water activity--- to predict the quality of the product. For this we have to use numerical methods, which have become popular in the food industry in the last two or three decades with the wide availability of computers.

3.2.1 Finite difference method (FDM)

FDM is the easiest and fastest numerical method. The product is represented by a (usually) regular orthogonal grid of nodes connected by heat conductors, similar to an electrical grids of resistors and capacitors. The equations of heat conduction become discretized and become similar to those describing an electrical network of capacitors and resistors. Each capacitor represents the heat capacity of a subvolume of product, while each resistor represents the heat conduction path between the centres of these subvolumes. This gives a system of equations which can be written in matrix form

$$C \frac{dT}{dt} + KT = f$$

where $T$ is a vector of nodal temperatures, $C$ is the global capacitance matrix containing the specific heat $c$, $K$ the global conductance matrix containing the thermal conductivity $k$, and $f$ the global forcing matrix containing known

---

**Fig. 6** Effects of varying fluid velocity for a typical product at different $Bi$.

**Fig. 7** Temperature during freezing of butter [5] (with permission).
terms arising from boundary conditions. This equation is solved for each small time step until the process is finished.

FDM is the earliest form of numerical method to be used. Its advantages are:
- It is easy to understand and to program
- It is very fast, especially in one and two dimensions

Its main disadvantage is that it can be used only for regular geometries (slabs, cylinders, spheres, brick shapes etc.)

For example, FDM can be easily applied to the modelling of cartoned products. Other products can also be modelled by a similar regular shape. For example, a steak slice of any shape can be modelled by an (infinite) plate, since one dimension is much smaller than the other so heat transfer is practically in 1-D. A leg of lamb or beef can be modelled by a cylinder or perhaps a sphere. A whole beef side has been modelled as a combination of plates and cylinders [6]. If the approximate shape is reasonable then the results can be quite accurate.

3.2.2 Finite element method (FEM)

FEM is probably the most popular method for modelling heat transfer and various other physical phenomena. It consists of dividing the product into subvolumes or elements, each of which contain some nodes which represent points in the solid. As in FDM, equations are set up to describe the heat flow between the nodes.

FEM equations are more time consuming to set up than FDM equations and take a longer time to solve. However, FEM can easily handle complex shapes and composite products (for example, meat with bone, fat and lean meat, or a carton with cardboard, air gaps and food). The discretization of the product into elements can be automated, so all the user has to do is to enter the product’s shape (using some graphical interface) then tell the computer program to mesh.

Some researchers write their own FEM programs to get maximum flexibility and speed of execution. For example, Pham and Davey [7] use FEM to model a beef side with a series of “slices”. Most people will use one of the several commercial FEM packages available, such as COMSOL (formerly FEMLAB), ANSYS, ABAQUS and NASTRAN.

3.2.3 The finite volume method (FVM)

In FVM grid, the product is again divided into volume elements (as in FEM), and the thermal capacity of each volume element is assumed to be concentrated at its centre, or node. Each node is connected to surrounding nodes by heat conduction links, just as in FDM, except that the grid does not have to be regular. FVM is therefore just as flexible as FEM with respect to product shape.

3.2.4 Computational fluid dynamics (CFD) models

CFD models calculate the fluid flow and temperature around the products as well as inside it. They may discretize space using FDM, FEM or FVM, although the latter two are most often used. In non-solid regions, the equations of fluid flow must be solved to calculate fluid velocities. The great advantage of CFD is that they allow the heat transfer coefficients to be calculated rather than guessed or measured experimentally. So, in principle, the rate of cooling and freezing for any product in any situation can be predicted without doing any experiment, provided the product’s properties are known.

The biggest problem with CFD programs is that the flow is usually turbulent, i.e. subject to random and very fast fluctuations. These random fluctuations cannot be solved from first principles. They are very complicated and depend highly on the geometry of the flow. They must be solved approximately by a so-called turbulence model. For example, in the $k-\varepsilon$ model, transport equations for the turbulent kinetic energy $k$ and the turbulent dissipation rate $\varepsilon$ are set up and solved. To a large extent these models are not rigorous, and they require empirical parameters obtained from experiments. Therefore the results can not be guaranteed to be accurate. This is particularly so when the flow is highly swirling, or when there is a large amount of recirculation.

The second problem with CFD is that it is very time consuming to run. Due to the nature of the fluid flow equations, a very fine grid has to be used, usually millions of nodes or elements. The number of equations to be solved at each time steps is even greater, and they have to be solved by an iterative method. For example, to solve for the chilling of a beef side above (20 hours in real time) takes about a week on a supercomputer.

Due to these problems, a full CFD solution is usually not the best method to use at the moment. Instead CFD can be used to calculate the surface heat transfer coefficient, which is then used as input parameter for a FDM or FEM program that calculate heat conduction inside the product only.

3.3 Conclusions on the state of freezing calculation

There are now many methods for calculating freezing
Food freezing and thawing

4. Novel Freezing Techniques

4.1 High pressure freezing and thawing

The effect of pressure $p$ on the freezing temperature $T_f$ of ice is related to the volume change $\Delta V$ and enthalpy change $\Delta H$ according to the Clausius-Clapeyron equation:

$$\frac{\partial T_f}{\partial p} = \frac{T_f \Delta V}{\Delta H}$$  \hspace{1cm} (11)

Because water, rather unusually, expands on freezing, $\Delta V$ is positive while $\Delta H$ is negative (heat is lost from the water) so that the right hand side is negative, and the freezing point decreases as pressure increases.

Pressure shift freezing (PSF) and other pressure assisted processing have been receiving increasing attention in the last 15 years. Because water expands on freezing, by Le Chatelier’s principle an increase in pressure will cause a decrease in the freezing point. The phase diagram in Fig. 8 shows that ice can exist in several phases. The normal form, which exists at low pressure, is called Ice I.

The various freezing processes are shown in Fig. 8:

- In normal freezing without pressure changes we go from A vertically down to D, G or I. Crystallization happens when temperature falls below 0°C (due to supercooling) causing the temperature to jump back towards 0°C momentarily.

- In pressure shift freezing we increase pressure to E, then cool the food to a point F still above the new freezing point. When enough time has been given for the food to equilibrate throughout to a low temperature, pressure is rapidly released to G. The great advantage of PSF is that because pressure can be release very quickly, we get from F to G in a very short time, before nucleation has time to occur. A large degree of supercooling can therefore be obtained, leading to simultaneous and uniform nucleation, and the formation of a large number of small crystals. This, as we have seen, can give a much higher product quality. Note that due to crystallization, the temperature will not stay at G but will rise causing some melting and refreezing, or at least limiting the amount of crystallization. Therefore we should aim for a temperature as low as possible before pressure release – in practice about -22°C at a pressure of 210 MPa which gives the minimum liquid temperature. The amount of ice that can form is limited by the temperature rise due to latent heat release. From a heat balance, it can be calculated that about 36% of the water in the food will turn to ice upon the adiabatic release of pressure (the precise figure depends on composition). Further freezing will take place due to crystal growth under atmospheric pressure. Therefore a full PSF cycle may be represented as in Fig. 9. The nucleation point varies and seems to depend on the pressure release rate - the faster the release, the lower the nucleation pressure. Also there is some cooling associated with pressure release, before nucleation occurs [9]. Note that longer freezing time is required for PSF compared to conventional freezing, due to the smaller temperature driving force (Fig. 10). Although the lowest liquid temperature is -210°C at $p=209$ MPa according to the phase diagram, liquid temperatures several degrees lower may be obtained with some foods by taking advantage of the metastable zones [10].

- Pressure freezing to ice III: Ice III is denser than ice I. By pressurizing (AE), cooling then freezing to ice III at constant pressure (EH), then releasing pressure (HI), Ice III is converted to ice I (HI), which involves a sudden expansion in crystal size. It has been found that this is effective in killing micro-organisms and thus it may be useful means to reduce micro-organisms in foods [11]. Pressure freezing to ice III has also been found to be detrimental to texture, possibly because of the slow freezing.

Fig. 8 High pressure freezing and thawing processes on the phase diagram. ABCD: pressure-assisted freezing, DCBA: pressure-assisted thawing, ABEGF: pressure shift freezing, GFEB: pressure-induced thawing, ABFHI: freezing to ice III, IHFEBA: thawing to ice III [8].
Fig. 9 Detailed path of pressure-assisted freezing. Left graph shows an idealized path: AE: pressurization, EF: cooling, FG: pressure release, GI: nucleation and initial phase change, IJ: continued cooling and freezing. Right graph shows an actual path, with cooling due to pressure release then nucleation followed by crystal growth.

Fig. 10 Temperature history in conventional freezing (full lines) and HP shift freezing (dotted lines). Thick curves: center, thin curves: surface.

- Pressure assisted thawing (PAT): Frozen food is pressurized (DC) until it reaches thawing point at C. Heat is then applied under pressure to melt the ice. When the food has completely thawed, pressure is released. The advantage of thawing under pressure is that the freezing point is depressed, therefore the temperature driving force (different between air temperature and product temperature) can be increased several times, while keeping the temperature low to avoid microbial growth. Normally thawing takes place at an air temperature of around 5°C. Therefore, by decreasing the freezing point to ~5°C, say, using pressure, the temperature driving force and hence the thawing rate is doubled. The minimum equilibrium freezing point is about ~22°C at 210 MPa, however by making use of the metastable region it can be as low as ~30°C [12]. High pressure has adverse effect on animal tissues due to protein denaturation. However plant tissue seems little affected.

Table 1 shows some experimental results on the applications of pressure shift freezing and Table 2 shows some results for pressure assisted thawing.

4.2 Ultrasound assisted freezing

Ultrasound has several different effects, often contradictory [1]:
- Agitation, leading to enhanced heat and mass transfer and faster freezing near surfaces of food.
- Heating, leading to slower freezing
- Cavitation (formation of gas bubbles) near surfaces, leading slower freezing
- Triggering of nucleation, as long as the food is below nucleation temperature, leading to more and smaller crystals
- It has been surmised that ultrasound can even cause intracellular nucleation, which can normally happen only at very high freezing rates.
- Enhancing crystal growth when the food is above nucleation temperature but below freezing point, leading to bigger crystals
- Fragmentation of crystals, leading to smaller crystals

Thus, by tuning the power and timing of ultrasound, it can be used to
- accelerate freezing by increasing the rate of heat transfer at the surface
- reduce crystal size during food freezing, leading to better quality. The food is supercooled then nucleation is initiated by a short pulse of ultrasound. This has an effect somewhat similar to pressure-shift freezing.
- increase crystal size during freeze concentration by
repeated US pulses as soon as the food is below freezing point.

To reduce the heat effect, ultrasound should only be applied intermittently and at the right power level. It has been found [26] that a power level of 15.85 W applied for 2 minutes give the best reduction in freezing time.

Perhaps more important is the improvement in quality. Food frozen without ultrasound shows disruptions and separation of cells, while food frozen with ultrasound does not show these symptoms [26]. It is thought that ultrasound might have triggered intracellular nucleation, which stops cell loss of water and shrinkage.

### 4.3 Progressive freeze concentration (PFC)

Freeze concentration is the concentration of a solution by freezing out the ice and removing it. Compared to other forms of concentration such as evaporation, drying or membrane processes, it has the great advantage of low temperature and very gentle processing, and is thus excellent at preserving quality and avoiding thermal damage. It has been therefore use on very sensitive products such as coffee, dairy products and fruit juices.

PFC has previously been used for analytical purpose [27] but recently it has been applied by Miyawaki et al. [28] to food processing. Instead of forming crystals in a suspension in a stirred tank, the liquid is pumped past a cold surface (usually a cold tube) and ice forms on that surface (Fig. 11). The slow rate of growth leads to a better separation of water and solute. Coffee extract, tomato juice, and sucrose solution have been successfully concentrated to high concentrations with good yield. It has also been tested on water recovery from waste streams. In addition, it can be used as a low-temperature energy storage system, to exploit the cheap electric power during the night.

The partition (distribution) constant K (solute concentration in ice / solute concentration in liquid) increases with concentration and freezing rate and decreases with...
circulation flow rate, so these parameters have to be tuned to maximize yield.

### 4.4 Osmodehydrofreezing

In dehydrofreezing [29] the food is first dehydrated then frozen. The reduced amount of water decreases the number of ice crystals, their size (due to increased viscosity) and hence the freezing expansion, and so may reduce tissue damage during freezing, especially in fragile foods such as strawberries. At least 50% of the water must be removed to give improved texture after freezing and thawing. The increased solute concentration (due to both water loss and solute gain) decreases the freezing point and increase the glass transition temperature, leading to more supercooling and better stability, especially if cryoprotectants and cryostabilizers are used in the solution. Pigment, vitamin and aroma retention are all improved. The product will taste different and may be used as ingredient, for example, for yoghurt. The freezing time is less because there is less water to freeze. In addition the cost of packaging and transport is reduced due to reduced weight.

Typically about 70% of the water is removed. Dehydrofreezing has been applied to fruit and vegetable, because they contain a large amount of water: kiwifruit, strawberries, apples, melon, potatoes.

Dehydration can be air drying or osmotic dehydration (osmodehydrofreezing). The latter involves immersing the food in a concentrated solution of some solute. As water is sucked out of the fruit, some solute will diffuse into the food, therefore it will change the taste of the food. For fruit sucrose is the most popular although, glucose, fructose, lactose, maltodextrin, corn syrup can also be used. For vegetables sodium chloride can be used.

Recently oligofructose, trehalose and a high-DE maltodextrin were used [30]. They observed an improvement in texture and vitamin C retention. Sensory evaluation tests showed that color, texture, taste and overall acceptance of all osmodehydrofrozen food samples were significantly improved, when compared to the respective quality features of conventionally frozen samples.

### 4.5 Immersion freezing and freezing in ice slurry

Conventional immersion freezing used brines to lower the freezing point, or some refrigerant. The product is usually wrapped to prevent absorption of refrigerant. However, absorption may be an advantage for some processed foods such as desserts. Thus, ice slurries based on sugar–ethanol aqueous solutions have been used to freeze fruit for dessert. The advantages of this process are:

- short freezing time due to high heat transfer rate from ice slurry (Best results are obtained with low Biot numbers! e.g. small product such as peas.
- high quality due to small crystal size
- absorption of food additives (antioxidants, flavorings, aromas and micronutrients)
- improved quality and shelf life

Heat transfer coefficients can vary greatly depending on how well agitated the liquid is. In non agitated liquid the htc is about 100 Wm⁻²K⁻¹. In running liquid or sprinkling htc ≈ 400 Wm⁻²K⁻¹. Pumping cold liquid through orifices (Hydro Fluidisation Method or HFM) to create jets that agitate the liquid and fluidize the product: htc ≈ 900 Wm⁻²K⁻¹ or more. Using ice slurry as fluidization media give htc of 1000-2000 Wm⁻²K⁻¹ [31].

### 4.6 The use of antifreeze proteins (AFP)

Animals that can survive subfreezing body temperatures do it in two ways that are quite different: by carefully controlling the freezing process in their body (freeze tolerance), or by maintaining their body fluids in a supercooled state (freeze avoidance). The first approach is taken by some amphibians and reptiles: they generate ice nucleating proteins that initiate ice nucleation as soon as body temperature reaches ~2 to ~3°C, but also produce cryoprotectants (glucose or glycerol) that lower the freezing point of the most sensitive organs, delaying or minimize freezing there. Freezing therefore takes place in a highly
controlled manner. The second approach is taken by some fish and insects, which produces antifreeze proteins to prevent their blood from freezing at -1.9°C (the freezing point of sea water), even though the freezing point of their blood is about -0.8°C (and there are ice crystals floating around that might cause nucleation). They do this by producing antifreeze proteins that bind to the surface of ice crystals and prevent their growth.

A potential food application is the use of antifreeze proteins to incorporate them in foods such as ice cream to prevent crystal growth during storage, especially when temperature fluctuates [32]. Antifreeze protein can be used to soak the meat or injected intravenously before slaughter (0.01 μg/kg AFGP injected 24 h before slaughter), resulting in frozen meat with smaller ice crystals and less drip. At the moment the main obstacle is cost. However, the use of genetically engineered AFP or synthetic AFP [33] may help overcome this.

5. Conclusions

Freezing continues to be the most popular and effective method for the long-term preservation of high quality food, and is likely to remain so in the future. While past research has concentrated on the prediction of temperatures and freezing rates, recent and future research are concentrating on the prediction and optimization of quality factors: weight loss, crystal size, flavor and color losses or enhancement. Novel processing methods combine freezing with osmotic dehydration, solute absorption, ultrasound, freeze concentration, high pressure regimes. The use of antifreeze proteins may also increase in the future as their cost comes down. Another vast area of research is in the area of pre-treatment (electrical stimulation of meat, blanching and additive impregnation of vegetables and fruit) which has not been reviewed in this paper, as they are very product-specific.

References

[1] M. C. Anon, A. Calvelo; Freezing rate effect on the drip loss of frozen beef. Meat Sci. 4, 1–14 (1980).
[2] R. Plank; Beitrage zur Berechnung und Bewertung der Gefriergeschwindigkeit von Lebensmitteln, Zeitschrift fur die gesamte Kalte Industrie, Reihe 3 Heft 10, 1–16 (1913).
[3] R. Plank; Die Gefrierdauer von Eisblocken, Zeitschrift fur die gesamte Kalte Industrie, 20, 109–114 (1913).
[4] Q. T. Pham; Simplified equation for predicting the freezing time of foodstuffs. J. Food Technol. 21, 209–221 (1986).
[5] A. Nahid, J. E. Bronlund, D. J. Cleland, B. Philpott; Modelling the freezing of butter. Int. J. refriger., In Press (2007).
[6] L. M. Davey, Q. T. Pham; Predicting the dynamic product heat load and weight loss during beef chilling using a multi-region finite difference approach. Int. J. Refrigeration 20, 470–482 (1997).
[7] L. M. Davey, Q. T. Pham; A multi-layered two-dimensional finite element model to calculate dynamic product heat load and weight loss during beef chilling. Int. J. Refrigeration, 23(6), 444–456 (2000).
[8] A. Le Bail, D. Chevalier, D. M. Mussa, M. Ghoul; High pressure freezing and thawing of foods: a review. Int. J. Refrig. 25, 504–513 (2002).
[9] L. Otero, P. D. Sanz; High-pressure-shift freezing: Main factors implied in the phase transition time. J. Food Eng 72, 354–363 (2006).
[10] O. Schluter, G. Urrutia Benet, V. Heinz, D. Knorr; Metastable States of Water and Ice during Pressure-Supported Freezing of Potato Tissue. Biotechnol. Prog. 20, 799–810 (2004).
[11] H. Moor, M. Hoechli; The influence of high pressure freezing on living cells. In: Societe Francaise de microscopie electronique. Proceedings of the 7th International Congress of Electron Microscopy, pp. 445–6 (1970).
[12] O. Schlüter, D. Knorr; Impact of the metastable state of water on the design of high pressure supported freezing and thawing processes. Paper number 026197, 2002 ASAE Annual Meeting (2002).
[13] Y. Kanda Y, M. Aoki, T. Kosugi; Freezing of tofu (soybean curd) by pressure-shift: freezing and its structure. J. Japan Soc Food Sci. Technol. 39, 608–14 (1992).
[14] M. Fuchigami, N. Kato, A. Teramoto; High pressure freezing effects on textural quality of carrots. J. Food Sci. 62, 804–8 (1997).
[15] M. Fuchigami, N. Kato, A. Teramoto; High pressure freezing effects on textural quality of Chinese cabbage. J. Food Sci. 63, 122–5 (1998).
[16] H. Koch, I. Seyderhelm, P. Wille, M.T. Kalishevsky, D. Knorr; Pressure-shift freezing and its influence on texture, colour, microstructure and rehydration behaviour of potato cubes. Nahrung 40, 125–31 (1996).
[17] L. Otero, M. T. Solas, P. D. Sanz, C. de Elvira, J. A. Carasco; Contrasting effects of high-pressure-assisted freezing and conventional air-freezing on eggplant microstructure. Z Lebens Unters Forsch 206, 338–42 (1998).
[18] H. Barry, E. M. Dumay, J. C. Cheftel; Influence of pressure-assisted freezing on the structure, hydration and mechanical properties of a protein gel. In: Isaacs N.S., editor. High
pressure food science, bioscience and chemistry. London: Royal Society of Chemistry, pp. 343–53 (1998).

[19] M. N. Martino, L. Otero, P. D. Sanz, N. E. Zaritzky; Size and location of ice crystals in pork frozen by high-pressure assisted freezing as compared to classical methods. Meat Science 50, 303–13 (1998).

[20] D. Chevalier, M. Sentissi, M. Havet, M. Ghoul, A. Le Bail; Comparison between air blast freezing and pressure shift freezing of lobsters. J. Food Sci. 65, 329–333 (2000).

[21] D. Chevalier; Contribution à l'étude de la congélation par détente haute pression. These de doctorat, Université de Nantes, France (2000).

[22] F. Fernandez-Martín, L. Otero, M. T. Solas, P. Sanz; Protein denaturation and structural damage during high pressure-shift freezing of porcine and bovine muscle. J. Food Sci. 65, 1002–1008 (2000).

[23] J. M. Chourot. Contribution à l'étude de la décongélation par haute pression. These de doctorat, Université de Nantes, France (1997).

[24] Y. Zhao, R. A. Flores, D. G. Olson; High hydrostatic pressure effects on rapid thawing of frozen beef. J. Food Sci. 63, 272–5 (1998).

[25] D. Chevalier, A. Le Bail, J. M. Chourot, P. Chantreau; High pressure thawing of fish (whiting) : influence of the process parameters on drip losses. Leben Wissen Technol. 32, 25–31 (1999).

[26] B. Li, D.-W. Sun; Effect of power ultrasound on freezing rate during immersion freezing. J. Food Eng. 55, 277–282 (2002).

[27] J. S. Mattheis, N. D. Coggeshall, Concentration of impurities from organic compounds by progressive freezing, Analytical Chemistry 31, 1124–1125 (1959).

[28] O. Miyawaki, L. Liu, Y. Shirai, S. Sakashita, K. Kagitani; Tubular ice system for scale–up of progressive freeze–concentration. J. Food Eng. 69, 107–113 (2005).

[29] D. Torreigiani, G. Bertolo; Osmotic pre–treatments in fruit processing: chemical, physical and structural effects, J. Food Eng. 49, 247–253 (2001).

[30] E. Dermesolouoglou, P. Taoukis, Osmodehydrofreezing of sensitive fruit and vegetables: Effect on quality characteristics and shelf life. IUFoST 2006, Nantes.

[31] K. Fikiin, O. Tsvetkov, Yu. Laptev, A. Fikiin, V. Kolodyaznaya, Thermophysical and Engineering Issues of the Immersion Freezing of Fruits in Ice Slurries Based on Sugar–Ethanol Aqueous Solution. Ecolibrium, Aug. 2003, 10–15 (2003).

[32] C. J. Warren, C.M. Mueller, R. L. Mckown; Ice crystal growth suppression polypeptides and methods of preparation. US Patent 5, 118,792 (1992).

[33] S. Liu, W. Wang, E. von Moos, J. Jackman, G. Mealing, R. Monette, R.N. Ben, In Vitro Studies of Antifreeze Glycoprotein (AFGP) and a C–Linked AFGP Analogue. Biomacromolecules, 8, 1456–1462 (2007).

URLs cited

[i] L. Zheng, D.-W Sun; Enhancement of Food Freezing Process by Power Ultrasound (2004) http://www.imeche.org.uk/process/pdf/Da%20Wen%20Sun%20Full%20paper%202004.pdf (accessed Jan 31, 2007)