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Experimental and Theoretical Study of Model Food Freezing. Part I. Heat Transfer Modelling

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ABSTRACT

Textural or organoleptic quality of frozen foods is strongly related to freezing operating conditions which govern the ice crystal size. During this work, gelatin gel was used as a model food and was frozen in a freezing device which ensured a unidirectional heat transfer. The temperature profiles recorded inside the material determined the position of the initial freezing front versus time and the initial freezing temperature. Temperature profiles were obtained for several gelatin gel compositions, cooling temperatures and initial temperature values. The heat transfer could be approximately fitted by the Neumann model. Relationships between gel composition and initial freezing temperature value were also discussed. © 1998 Elsevier Science Limited. All rights reserved.

NOMENCLATURE

a_j	Thermal diffusivity of the j zone (m^2/s)
$c_{p,j}$	Heat capacity of j component (J/Kg °C)
k	Constant of the freezing front rate (m^2/s)
m	Slope of the water–solute liquidus curve (°C m^3/kg) or (°C)
s	Initial freezing front position (m)
t	Time (s)
T	Temperature (°C)
T_j	Temperature of the j zone (°C)
T_1	Cooling temperature (°C)

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T_{11}	Initial temperature (°C)
Tc_j	Thermocouple j
T_m	Initial freezing temperature (°C)
x_j	Mass fraction of j component
z	Abscissa in the heat flux direction (m)

Greek symbols

$\alpha = a_2/a_1$	Unfrozen and frozen zones heat diffusivity ratio
δ	Neumann adimensional characteristic number
ΔH_s	Latent heat of solidification (J/Kg)
ε_j	Volumic fraction of j component
$\gamma = \rho_2/\rho_1$	Unfrozen and frozen zones density ratio
λ_j	Thermal conductivity of j component (W/m °C)
ρ_j	Density of j component (Kg/m^3)

Subscripts

0	Initial
1	Frozen zone
2	Unfrozen zone
a	Solute (sodium chloride)
E	Eutectic
w	Water
i	Ice
s	Solid matter (gelatin)
sw	Salt water solution
T_j	j temperature

Mathematical expressions

$$F[x] = \sqrt{\pi}\cdot x\cdot exp(x^2)\cdot \mathrm{erfc}(x)$$

$$H[x] = \sqrt{\pi}\cdot x\cdot exp(x^2)\cdot \mathrm{erf}(x)$$

INTRODUCTION

Freezing is a food preservation technology which ensures a high food quality with a long storage duration (Reid, 1990). Many researches have optimized the quality at each step in the 'cold chain' of the foodstuff, from the preparation prior to freezing until the delivery to the consumer. The objective is to reach an eating quality as similar as possible to the original one.

Freezing is one of these steps during which the water changes into ice crystals. These ice crystals contribute to deterioration of the food texture depending on their size. So, there is a close relationship between the crystal size and the textural quality. It is empirically known that a quick freezing gives small crystals whereas a slow one gives more large crystals. Several authors (Bevilacqua *et al.*, 1979; Bomben & King, 1982; Miyawaki *et al.*, 1992) proposed simple relationships between the crystal size and the operating conditions, but no complete theoretical analysis had been yet developed. The main objective of this study was to determine quantitatively the factors which, among the characteristics of the material and the operating conditions, are responsible for the crystal size obtained in the frozen foodstuffs. From this study an analytical model has been proposed, in order to quantify and to explain some empirical rules applied daily in the industry.

Our work was composed of two parts. This first part introduced the material chosen for the freezing experiments: the gelatin gel, with or without sodium chloride as solute. The knowledge of its microscopic structure was fundamental to understand the freezing phenomenon. Its thermophysical properties were modelled for the theoretical study. A freezing apparatus was designed. The temperature profiles inside the frozen sample were interpreted by the Neumann model. The thermograms analysis allowed us to determine the freezing front rate and the initial freezing temperature. These data were used in the second part of this work (Woinet *et al.*, 1998) to correlate the ice crystal size with the process operating conditions.

MATERIALS AND METHODS

Model food: structure and thermophysical properties

The model food for this study was gelatin gel, with subsequent addition of sodium chloride as solute. This material was chosen for its good homogeneity and for the good reproducibility of its texture, which could not be ensured with commercial foodstuffs. The other main advantage of the gelatin gel was its good transparency in the unfrozen state which allowed us to observe the crystallization phenomenon during the freezing stage. However, this material had a non-cellular structure, unlike that of the main commercial foodstuffs.

The structure of the gelatin gel is made of macromolecular strands which are soluble in water above approximately 40°C. Below this temperature they progressively create local junctions between themselves, which gradually forms a three-dimensional network characteristic of the gel structure. The higher the gelatin concentration, the stronger the rigidity of the gel strands due to a greater junction density. A part of the constitutive water is 'bound' to the macromolecular strands with an approximate ratio of 0.45 $g/g_{gelatin}$ (Djabourov *et al.*, 1988). If sodium chloride is added it can be assumed that 3.35 g of water per gram of salt is bounded, which corresponds to the NaCl–water eutectic ratio (Weast *et al.*, 1986). The other part of water is considered to be freezable water.

Previous work was carried out by Renaud (1990) and Cornillon (1993) in our laboratory in order to measure and to model the thermophysical properties of the gelatin gel without salt. They determined the intrinsic properties of the gel components; those of water and of ice were taken in the literature (Weast *et al.*, 1986; Choi & Okos, 1984). The intrinsic properties of gelatin are gathered in Table 1.

The gel density, denoted ρ, was calculated with a weighted additive model according to the following relationships:

$$\text{for } T_2 > T_m \text{ unfrozen gel: } \rho_2 = \left(\frac{x_s}{\rho_{s,T_2}} + \frac{(1-x_s)}{\rho_{w,T_2}} \right)^{-1} \qquad (1)$$

TABLE 1
Intrinsic Thermophysical Properties of Gelatin

Properties	*Heat dependant expression (T in °C)*	*Reference*
ρ (kg/m^3)	$1355.4-0.51840\cdot T$	Renaud (1990)
c_p (J/kg°C)	$1616.2+6.964\ T$	Cornillon (1993)
λ (W/m°C)	$0.303+1.20\times10^{-3}\cdot T-2.72\times10^{-6}\cdot T^2$	Renaud (1990)

$$\text{for } T_1<T_m \text{ frozen gel: } \rho_1=\left(\frac{x_s}{\rho_{s,T_1}}+\frac{0.45\cdot x_s}{\rho_{w,T_1}}+\frac{(1-1.45\cdot x_s)}{\rho_{i,T_1}}\right)^{-1} \tag{2}$$

The gel heat capacity, noted c_p, was calculated also with a weighted additive model, according to the following relationships:

$$\text{for } T_2>T_m \qquad c_{p,2}=x_s\cdot c_{p,s,T_2}+(1-x_s)\cdot c_{p,w,T_2} \tag{3}$$

$$\text{for } T_1<T_m \qquad c_{p,1}=x_s\cdot c_{p,s,T_1}+0.45\cdot x_s\cdot c_{p,w,T_1}+(1-1.45\cdot x_s)\cdot c_{p,i,T_1} \tag{4}$$

Concerning the heat conductivity, denoted λ, we chose the parallel model because the frozen structure of our gelatin gels looked like the structure assumed by this model:

$$\text{for } T_2>T_m \qquad \lambda_2=\varepsilon_{s,T_2}\cdot\lambda_{s,T_2}+(1-\varepsilon_{s,T_2})\cdot\lambda_{w,T_2} \tag{5}$$

$$\text{for } T_1<T_m \qquad \lambda_1=\varepsilon_{s,T_1}\cdot\lambda_{s,T_1}+0.45\cdot\varepsilon_{s,T_1}\cdot\lambda_{w,T_1}+(1-1.45\cdot\varepsilon_{s,T_1})\cdot\lambda_{i,T_1} \tag{6}$$

Volume fractions of both zones were obtained from the mass fractions:

$$T_2>T_m \qquad \varepsilon_{s,T_2}=x_s\frac{\rho_2}{\rho_{s,T_2}}\ ;\ T_1<T_m \qquad \varepsilon_{s,T_1}=x_s\frac{\rho_1}{\rho_{s,T_1}} \tag{7}$$

In the gel without salt we assumed that all the water crystallized at one temperature, namely T_m, the initial freezing temperature. For the gels with salt the water was assumed to crystallize in a temperature interval, namely between its initial freezing temperature T_m and a temperature of complete crystallization chosen as the eutectic point of the water–sodium chloride phase diagram, namely $T_E=-21$°C. The component 'water' was replaced by the component 'salt water', the thermophysical properties of which (Mihori & Watanabe, 1994) are gathered on Table 2. For a given composition, in the unfrozen and frozen zones the thermophysical properties of salt water vary only as a function of temperature. But in the crystallization zone they vary also as a function of salt amount, due to the progressive salt concentration. Thus, for purpose of simplification, we assumed a straight liquidus line of the salt–water system in this interval.

Thermophysical properties of gelatin gels with salt were described by the same models as in the case of gels without salt. The temperature dependent ice fraction was calculated by the following relation (Woinet, 1997):

TABLE 2
Thermophysical Properties of Salt Water (x_a in Mass Ratio, T in °C)

Thermophysical property	*General equation*	*Temperature interval*	*x_a expression*
Density	$999.5 - 0.0003806 \cdot T + 0.7841 \cdot x_a$	$T > T_m$ $T_E < T < T_m$ $T < T_E$	$x_{a,0}$ $-T/m$ $-T_E/m$
Heat capacity	$4184 + 0.001342 \cdot T - (5.734 - 0.0871 \cdot x_a) \cdot x_a$	$T > T_m$ $T_E < T < T_m$ $T < T_E$	$x_{a,0}$ $-T/m$ $-T_E/m$
Heat conductivity	$0.5693 + 0.0154 \cdot T - 0.579 \cdot x_a$	$T > T_m$ $T_E < T < T_m$ $T < T_E$	$x_{a,0}$ $-T/m$ $-T_E/m$

$$x_{i(T)} = (1 - 1.45 \cdot x_s - 4.35 \cdot x_a) \cdot \frac{T_m - T}{T_m - T_E} \tag{8}$$

where the expression into brackets represents the mass fraction of freezable water, and the ratio corresponds to the linear relationship between temperature and ice fraction in the crystallization zone. So, the temperature dependent salt water fraction was obtained from this mass balance:

$$x_{sw(T)} = 1 - 1.45 \cdot x_s - x_{i(T)} \tag{9}$$

The main difference between thermophysical properties of the gelatin gel with or without salt was as follows:

- — in the case of gels without salt there was a strong change of the values around T_m, between the frozen zone and the unfrozen zone,
- — in the case of gels with salt there was a regular evolution of these values all through the crystallization zone between the values of both the frozen zone and the unfrozen zone.

Freezing apparatus

The freezing apparatus (Woinet, 1997) was set up in order to ensure one-dimensional heat transfer (Fig. 1). The freezing cell was made with a 74 mm diameter Plexiglas cylinder thermally insulated at the top and at the external surface. The bottom was made with a flat copper plate whose temperature was controlled by two cooling devices; the first one ensured the initial temperature T_{II} before the freezing starting and the second one ensured the constant cooling temperature T_I. In some cases, liquid nitrogen replaced the cooling fluid for freezing at very low temperatures. This device allowed a temperature step change from T_{II} to T_I, and the heat flux inside the sample was principally a one-dimensional type heat transfer. Six chromel–alumel thermocouples (0.25 mm diameter) were regularly located at

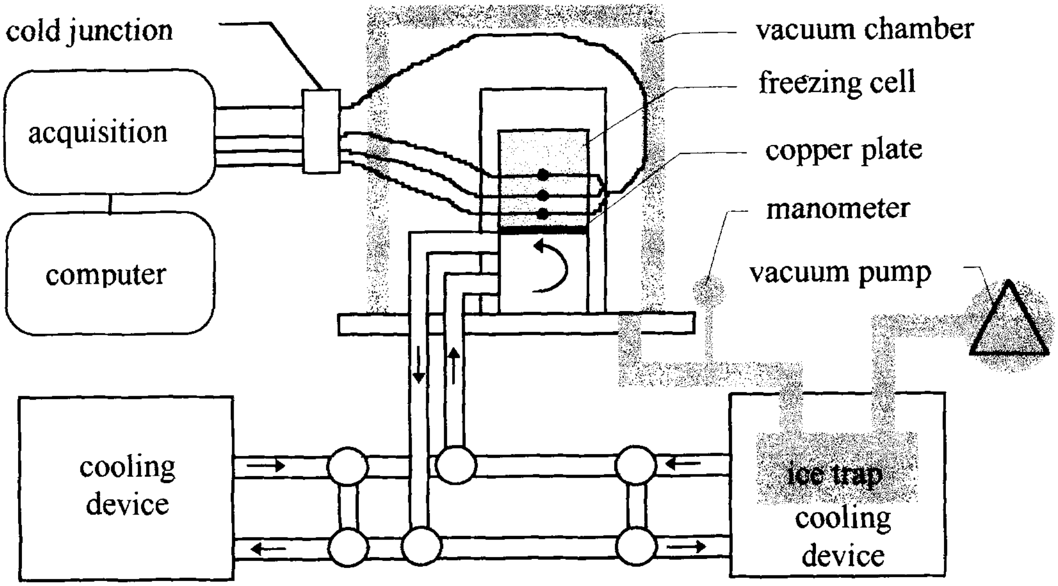

Fig. 1. Schematic diagram of the freezing apparatus.

several levels on the symmetry axis of the freezing cell, parallel to the isotherm surfaces. Their values were recorded with a data acquisition system driven by a computer. Thus, the controlled freezing operating conditions were the temperatures T_{II} and T_{I}.

RESULTS AND DISCUSSION

Thermogram analysis

During each freezing experiment, a thermogram was recorded. As shown on Fig. 2 the profile just above the freezing plate was not exactly a temperature step change, due to the thermal inertia of the freezing cell. The thermogram analysis allowed us to determine the exact operating conditions, the position of the initial freezing front versus time and the initial freezing temperature.

Before the freezing starting a low thermal gradient existed inside the sample. Thus, the initial temperature T_{II} was considered to be the sample mean temperature.

The cooling temperature T_{I} was considered to be the copper plate temperature at the end of the freezing experiment.

The position of the freezing front was determined from the slope discontinuity of the thermograms, due to the fact that the thermocouple entered in a higher heat conductivity zone, leading thus to a greater cooling rate. Sometimes, this slope

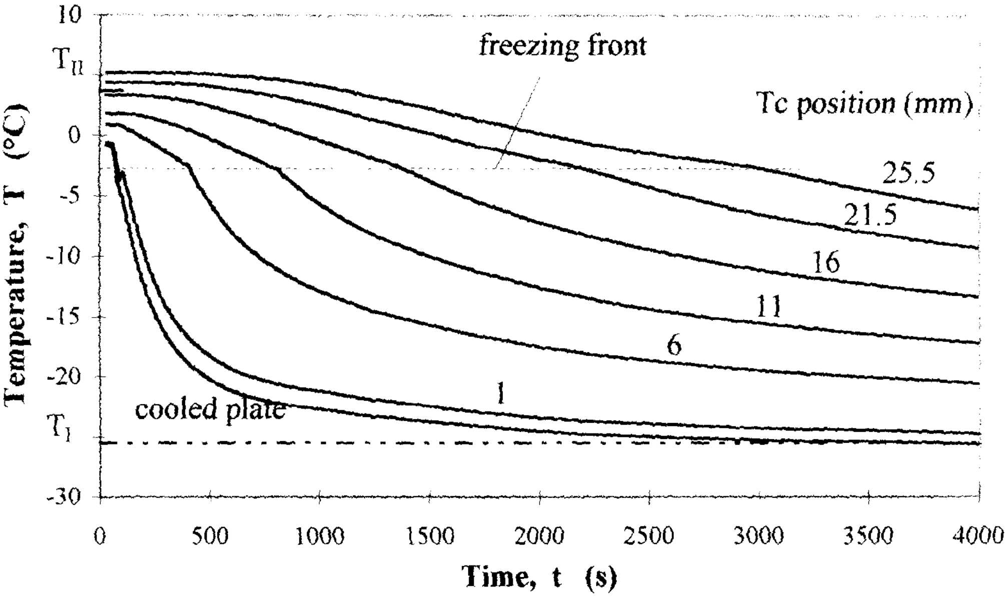

Fig. 2. Temperature profiles during a freezing experiment.

discontinuity was difficult to identify. The solution adopted consisted in calculating the difference between each two consecutive thermocouple profiles. This technique allowed to amplify the slope change at the freezing front. Furthermore, it had been previously verified by visual observation that the position of this slope discontinuity corresponded effectively to the initial freezing front. Indeed, it was possible, with a video-camera and a monitor, to follow the front progression inside the gel through the transparent freezing device.

Furthermore, the initial freezing temperature was equal to the temperature of the thermocouple at the level of the slope break. Five to six quite close values were thus obtained for each experiment giving a mean initial freezing temperature, T_m.

It is important to note that the thermocouples were subjected to a shifting phenomenon due to ice formation because they were trapped inside the macromolecular network. So, the temperature profile analysis took into account this displacement phenomenon.

Evolution of the initial freezing front

The position of the initial freezing front, s, is plotted versus the *root square* of time in Fig. 3 and in Fig. 4. We can observe approximately a linear relationship between s and $t^{0.5}$ which can be written as follows:

$$s = \sqrt{k}\sqrt{t} \tag{10}$$

where k represents the constant of the freezing front rate.

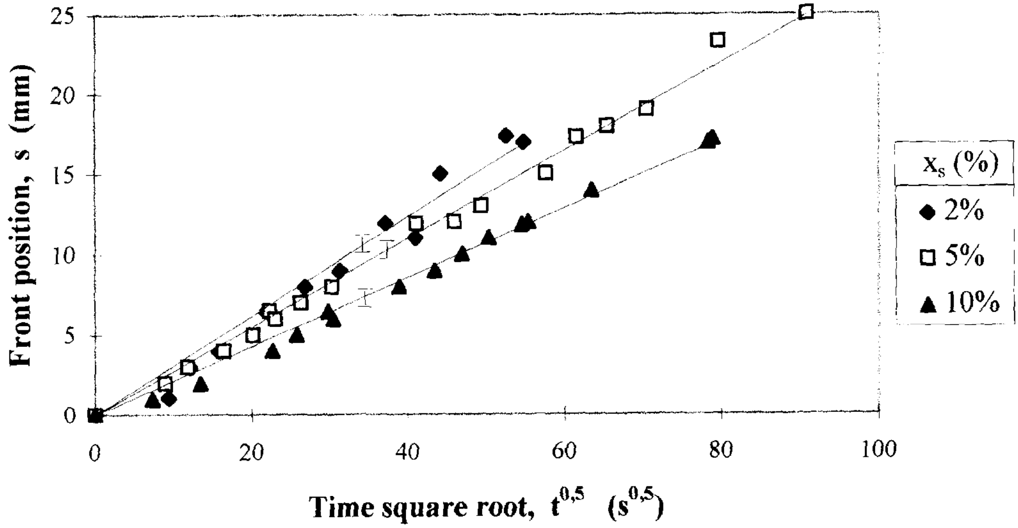

Fig. 3. Gel composition influence on the freezing front rate. Constant operating conditions: $T_I \cong -9.3$°C; $T_{II} \cong 3$°C.

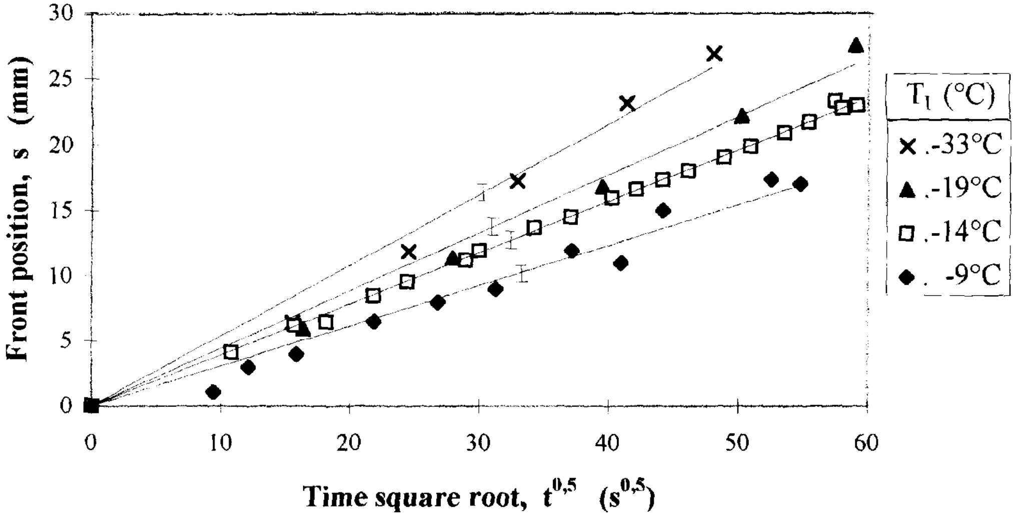

Fig. 4. Cooling temperature influence on the freezing front rate. Constant conditions: 2% gelatin; $T_{II} \cong 3$°C.

The influence of the gelatin concentration is shown on Fig. 3. The higher the gelatin concentration, the lower the k value, and so, the slower the freezing front rate. This variation can be easily explained by the influence of the gelatin concentration on the initial freezing temperature (Woinet, 1997).

The influence of the cooling temperature is shown on Fig. 4. For a gel of constant composition, the freezing front rate increases if the temperature is lower, due to the increase of the k value according to the Neumann model. So, it can be concluded that the bulk freezing phenomenon of model foods was mainly controlled by the heat transfer.

Neumann model validation

These experimental temperature profiles were compared with the Neumann model by taking into account the ice expansion phenomenon (Grigull & Sandner, 1984). The model equations are gathered on Table 3. The main model hypotheses are:

- — the heat transfer is by conduction,
- — the product has only one phase change temperature,
- — there are two zones — frozen and unfrozen — separated by the freezing front,
- — thermophysical properties are constant in both zones,
- — the heat transfer is one-directional.

This model can be solved analytically and leads to a proportional relationship between the freezing front position and the square root of time. This relation is written as:

$$s = 2\delta\sqrt{a_1 t} \tag{11}$$

where δ represents the Neumann dimensionless characteristic number. This number can be calculated with the following transcendental equation:

TABLE 3
Equation System of the Neumann Model

	Frozen zone	*Unfrozen zone*
Conservation equations	$\frac{\partial T_1}{\partial t} = a_1 \frac{\partial^2 T_2}{\partial z^2}$	$\frac{\partial T_2}{\partial t} = a_2 \frac{\partial^2 T_2}{\partial z^2}$
Initial condition		$T_2(z,0) = T_{\mathrm{ii}}$
Limit conditions	$T_1(0,t) = T_1$	$T_2(\infty,t) = T_{\mathrm{ii}}$
	$T_1(s,t) = T_{\mathrm{m}}$	$T_2(s,t) = T_{\mathrm{m}}$
Conditions at freezing front	$-\lambda \left.\frac{\partial T_1}{\partial z}\right\|_s + \lambda_2 \left.\frac{\partial T_2}{\partial z}\right\|_s + \rho_1 \Delta H_s \frac{\mathrm{d}s}{\mathrm{d}t} = 0$	

$$\Delta H_s = \frac{c_{p,1}\cdot(T_m - T_I)}{H[\delta]} - \frac{c_{p,2}\cdot(T_{II} - T_m)}{F[\delta/(\gamma\alpha^{0.5})]} \tag{12}$$

Finally two equations are obtained, which describe the temperature evolution in both zones as a function of axial position and time:

$$\text{frozen zone: } T_1(z,t) = T_I + \frac{(T_m - T_I)erf[z/(2\sqrt{a_1 t})]}{erf(\delta)} \tag{13}$$

$$\text{unfrozen zone: } T_2(z,t) = T_{II} + \frac{(T_m - T_{II})erfc\{\alpha^{-1/2}[z/(2\sqrt{a_1 t}) + (1-\gamma)\delta/\gamma]\}}{erfc(\delta/\gamma\alpha^{1/2})} \tag{14}$$

The experimental and theoretical temperature profiles for a given experiment are compared on Fig. 5. In the unfrozen zone, the profiles are slightly different because Neumann model assumes a constant initial temperature, whereas experimentally there is a small temperature gradient at time $t = 0$. In the frozen zone there is a pretty good agreement, except at the start of cooling because the actual temperature change was not exactly a step. When the sample is completely frozen, the temperature falls quickly, which is not observed on the theoretical profile because of the semi-infinite limit condition of the model.

In order to have a precise estimation of the model accuracy, both experimental and theoretical characteristic numbers were calculated from equations (10) and (11) and compared. The thermophysical properties of both unfrozen and frozen zones were calculated at the mean temperature of each zone. The difference between experimental and calculated data was in general under 10% for the case of gels without salt, but sometimes higher in the case of gels with salt, especially for cooling

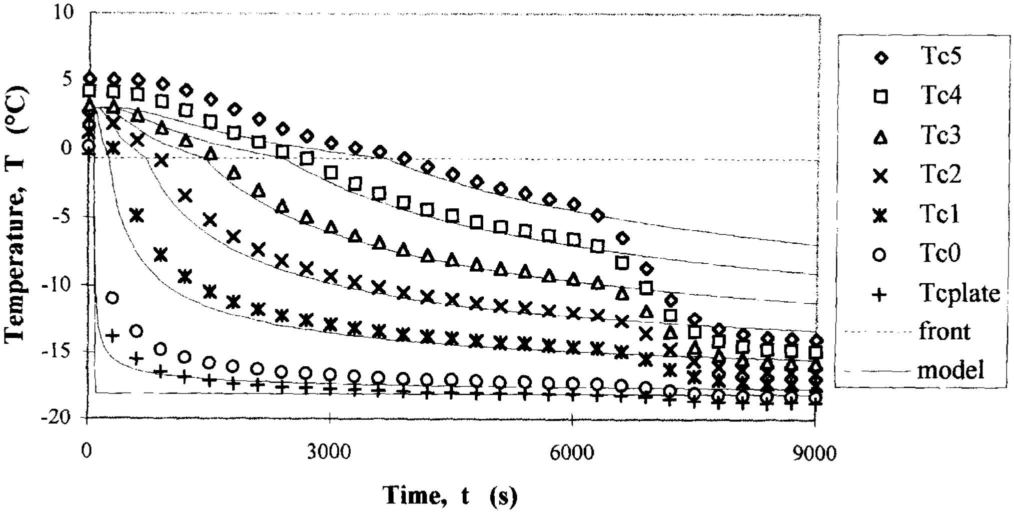

Fig. 5. Comparison between experimental and theoretical temperature profiles.

temperatures close to T_m because of the poor estimation of the thermophysical properties inside the crystallization zone (Woinet, 1997).

Initial freezing temperature values

In the case of gelatin gel without salt, the variation in the initial freezing temperature T_m with the gel concentration is shown on Fig. 6 (maximum standard error = 0.4°C). Firstly, no significant influence of the cooling temperature value on the T_m value was found for a given composition. Secondly, increasing the initial gel temperature T_{l1} had a decreasing effect on T_m values (see also Fig. 7). This was probably due to a quite different structure of the gel network: the ripening of the gelatin gel at low temperature was fast and created short junction areas; at higher temperatures the ripening was slower and allowed the creation of longer junction areas, giving a different mechanical resistance of the network (te Nijenhuis, 1981). Besides, the higher the gelatin concentration, the lower the T_m values; nevertheless, these values are very different from other literature values (Blond, 1988; Cornillon, 1993). But in fact these authors determined the melting temperature and not the freezing one. This high difference was produced by the modification of the gel structure, i.e. by the segregation phenomena during the freezing step, leading to pure ice domains and concentrated gelatin domains. Thus, during the thawing these ice domains melted at a temperature close to 0°C.

A typical example has been carried out to show the influence of the gel structure on T_m values. A 16.5% gelatin gel was submitted to several freezing-thawing cycles.

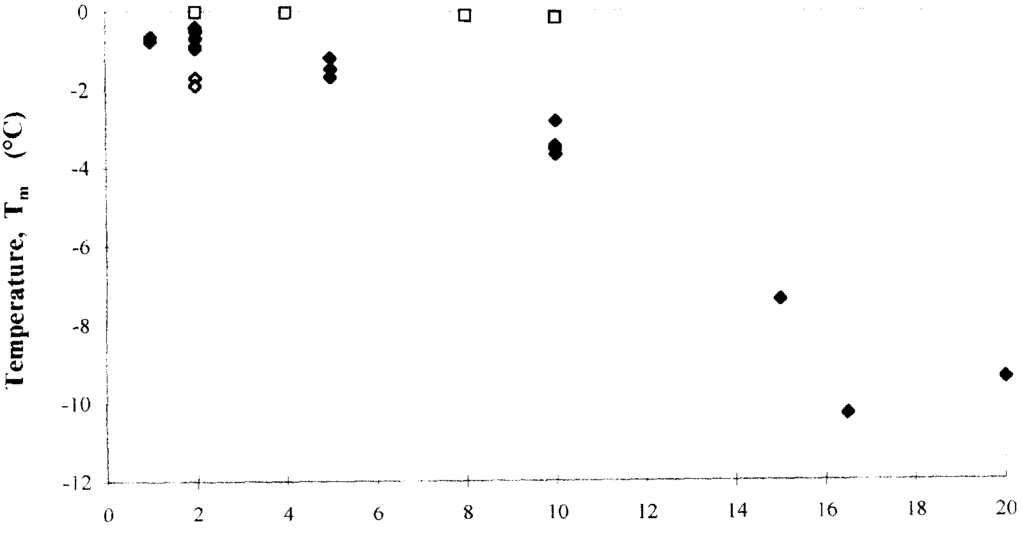

Fig. 6. Freezing temperature T_m of the water–gelatin system at different compositions. Ripening temperature between 0 and 7°C (◆) or 20°C (◇). (□): Blond (1988).

It was observed that freezing a gel which has just been thawed gave a higher T_m value, because the mechanical characteristics had changed (Woinet, 1997).

How can we explain the influence of the gelatin concentration on the T_m value? A higher concentration induced a higher mechanical resistance in the gelatin fibers; so the ice crystal, to push and to grow inside the network, had to exert a pressure against to this mechanical resistance. In agreement with the water pressure–temperature diagram, the higher the pressure, the lower the phase-change temperature. For example, for a 16.5% gelatin gel, the pressure value corresponding to $T_m = -10°C$ was around 100 MPa. This pressure is perhaps a little higher than is reasonable, but we think that it can partly explain the change in T_m values with gelatin concentration increase.

In the case of gelatin gel with salt, results are presented on Fig. 7 for 2% gelatin gel versus the salt concentration (standard error = 0.6°C). The higher the salt concentration, the lower the initial freezing temperature. Furthermore, we observe that this evolution is parallel to and close to the evolution of the water–salt binary liquidus, which could indicate that the freezing phenomenon takes place in conditions close to the thermodynamic equilibrium.

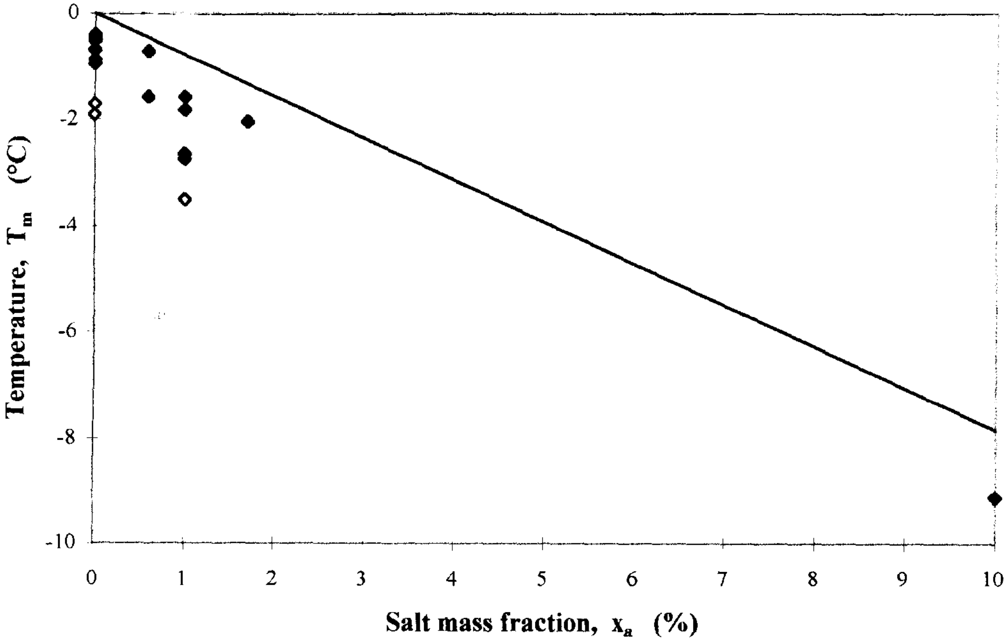

Fig. 7. Influence of the salt on the initial freezing temperature of the 2% gelatin gel. Ripening temperature: between 0 and 7°C (◆) or 20°C (◇). (———) literature values for NaCl + water system.

CONCLUSION

The Neumann analytical model was able to predict the temperature fields and the front position all along the freezing process. It could be improved with a numerical approach taking into account the evolution with temperature of gel thermophysical properties and composition. Nevertheless, this simple approach proves to be suited to analytically express the freezing parameters used in Part II of this paper to model the crystal size.

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