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An analytical solution for the coupled heat and mass transfer during the freezing of high-water content materials

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Abstract

The coupled problem of heat and mass transfer during the solidification of high-water content materials like soils, foods, tissues and phase-change materials is developed. Assuming quasi-steady heat conduction in the frozen region, the system leads to a set of coupled ordinary differential equations. The model takes into account the influence of material characteristics and process variables on the advance of the freezing and sublimation fronts, temperature and water vapour profiles and weight loss. It was validated against the analytical solution of the freezing (without surface ice sublimation) of a semi-infinite medium and was extensively used to perform a parametric study.

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1. Introduction

Ice sublimation takes place from the surface of high-water content systems like moist soils, aqueous solutions, vegetable or animal tissues and foods that freeze uncovered or without an impervious and tight packaging material. The rate of both phenomena (solidification and sublimation) is determined both by material characteristics (mainly composition, structure, shape and size) and cooling conditions (temperature, humidity and rate of the media that surrounds the phase change material). The sublimation process, in spite of its magnitude being much less than that of freezing process, determines fundamental features of the final quality for foods and influences on the structure and utility of frozen tissues.

Modelling of these simultaneous processes is very difficult owed to the coupling of the heat and mass transfer balances, the existence of two moving phase-change fronts that advance with very different rates and to the involved physical properties which are, in most cases, variable with temperature and water content.

The process with only-solidification (with no sublimation) has been extensively studied [1–3]. A large bibliography on free and moving boundary problems for the heat diffusion equation is given by Tarzia [4]. The system has been modelled both by analytical procedures [2,5], and with numeric methods [1,2,6]. Due to the non-linearity of the problem, solutions usually involve mathematical difficulties and analytical methods can only be developed for idealized systems or for those with plain structure and constant properties. Numerical methods, instead, allow to consider the structural and compositional implicancies through detailed models [1,7], and to produce a data set of predicted data from which to develop approximate solutions which only enable to predict process times [1,8,9]. The

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Nomenclature

C	mass concentration of water, kg/m^3
C_p	specific heat, J/(kg K)
D_{ef}	effective diffusion coefficient of water, m^2/s
h	heat transfer coefficient, W/(m^2 K)
k	thermal conductivity, W/(m K)
K_{m}	mass transfer coefficient, m/s
L_{s}	sublimation heat of water, J/kg
L_{f}	solidification heat of water, J/kg
m	geometrical index (=0 for slabs, =1 for infinite cylinders, =2 for spheres)
m_{f}	frozen mass by unit volume, kg/m^3
m_{s}	sublimated mass by unit volume, kg/m^3
M	molecular weight, kg/mol
R_{g}	universal gas constant, (=8.31 J/(mol K))
s	position of the moving front, m
t	time, s
T	temperature, K
x	spatial coordinate, m

Greek symbols

ε	porosity
ρ	density, kg/m^3

Subscripts

a	water vapor in the air
d	dehydrated phase
f	frozen phase
i	initial (unfrozen material)
if	initial freezing
o	sublimation front temperature
s	surrounding medium
va	water vapour in air within the material

process with only sublimation of the already-frozen system has been extensively studied for freeze-drying of food and pharmaceutical materials [10,11].

In the case of freezing with simultaneous ice sublimation, published developments are scarce and no analytical solution to the coupled problem has been developed. Ice sublimation has been surveyed by several authors in different systems: in freeze-drying [10,12], in geomorphology [13] and in the case of frozen food products several experimental studies have been published: weight losses of lamb [14], tylose and beef [15], potatoes [16] and meat products [17,18]. Additionally there are no experimental data on temperature and concentration profiles during freezing with simultaneous ice sublimation and on the rate of freezing and dehydration fronts.

On the other hand, theoretical models were proposed to describe the heat and mass transfer in these processes but, in most of the published works, only semi-empiric or numerical methods are used. Aguirre Puente and Sukhwal [19] presented a description of the heat and mass balances to be solved; meanwhile Pham and Willix [14] suggested the use of simple equations based on drying theory and on the use of the psychometric chart to calculate weight loss. Campañone [20] and Campañone et al. [21] developed a detailed numerical model that allows to predict temperature and composition profiles, as well as freezing time and weight loss. Besides, approximate equations were developed to predict freezing time and weight loss in food freezing with simultaneous surface dehydration [22,23].

Based on the abovementioned situation, the objectives of this work were:

- To develop a physical model and to implement the related quasi-analytical solution that enables us to account for the influence of material characteristics and process variables on the advance of the freezing and sublimation fronts, temperature and water vapour profiles and weight loss during the freezing of high-water content materials.
- To use the quasi-analytical solution to predict the influence of material characteristics and freezing conditions on the dependent variables (freezing and sublimation fronts position, weight loss and temperature and composition profiles).

1.1. The physical problem

When high-water content materials like foods, tissues, gels, soils or water solutions of inorganic or organic substances, held in open, permeable or untightly-sealed containers are refrigerated to below their initial solidification temperature, two simultaneous physical phenomena take place:

- liquid water solidifies (freeze), and
- surface ice sublimates.

The rate and extent of these transfers is determined by different factors:

(a) Material characteristics as shape, size, composition and structure. These last two determine the value of those physical properties relevant to heat and mass transfer: heat capacity, density, thermal conductivity and mass diffusivity. In a first instance, all of these properties depend on temperature and composition, and the last three of them also on material structure.
(b) Environmental characteristics: Temperature, humidity and rate of the refrigerating medium.
(c) Characteristics of the material–environment interphase: Mainly type, shape and material of container and if this is permeable or not to water vapor, as well

as its tightness to material surface (these characteristics influence on the resulting heat and mass transfer coefficients and on the "microclimate" that surrounds material surface).

From a physical point of view, it is usual to consider these materials as a combination of a solid matrix, an aqueous phase and a gaseous phase (air and water vapour).

For the description of the freezing process, the material can be divided into three zones: unfrozen, frozen and dehydrated as can be seen in Fig. 1.

Freezing begins from the refrigerated surface/s, at a temperature (T_{if}) lower than that of pure water, due to the presence of dissolved materials, and continues along an equilibrium line, whose exact analytical shape is not known for most materials. Besides, in most cases, not all of the liquid water is accessible to the freezing process, because part of it is linked to solutes and structural materials (bound water). Simultaneously, ice sublimation begins at the frozen surface and a dehydration front penetrates the material, whose rate of advance is again determined by all the abovementioned characteristics of the material and environmental conditions. Normally this rate is much lower than that of the freezing front [20].

1.2. The mathematical problem

A complete mathematical model has to solve both, the heat transfer (freezing) and the mass transfer (weight loss) simultaneously.

When applying the principles of process simulation and considering solid or semi-solid systems (with neither bulk flow nor deformation) at atmospheric pressure, with unidirectional heat and mass transfer and variable properties, the following microscopic balances are obtained:

$$\rho C_{\mathrm{p}} \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \frac{\partial k}{\partial x}\frac{\partial T}{\partial x} + \frac{mk}{x}\frac{\partial T}{\partial x} \tag{1}$$

$$\varepsilon \frac{\partial C_{\mathrm{va}}}{\partial t} = D_{\mathrm{ef}} \frac{\partial^2 C_{\mathrm{va}}}{\partial x^2} + \frac{\partial D_{\mathrm{ef}}}{\partial x}\frac{\partial C_{\mathrm{va}}}{\partial x} + \frac{mD_{\mathrm{ef}}}{x}\frac{\partial C_{\mathrm{va}}}{\partial x} \tag{2}$$

Normally uniform initial temperature and composition is supposed and convective boundary conditions at the surface for both heat and mass transfer are the usual modelling assumptions.

Phase-change is accounted for in the following way:

- Solidification (freezing) as a freezing front ($x = s_{\mathrm{f}}(t)$) located in the point where material temperature reaches the initial freezing temperature (T_{if}), determined by material composition. For temperatures lower than T_{if} (the zone nearer to the refrigerated surface) the amount of ice formed is determined by an equilibrium line (ice content vs temperature and water content) specific to the material.
- On the dehydration front ($x = s_{\mathrm{d}}(t)$) we impose Stefan-like conditions for temperature distribution and vapor concentration.

The following assumptions are needed for an adequate simulation of the system:

- Variable properties (D_{ef}, C_{p}, k, ρ) as a function of composition, temperature and structure, with three distinct zones: unfrozen, frozen and dehydrated. The possible difference between densities of the liquid and frozen phases induces negligible volume change.
- Vapor diffusion in the dehydrated zone must be considered through an adequate effective diffusion coefficient D_{ef}. This is an important parameter very difficult to measure or calculate, as well as the sorption isotherm of water on the material at subzero temperatures (there is an only one set of values in literature, belonging to beef).
- Uniform initial temperature T_{i} higher than T_{if}.

The physical description of the freezing-sublimation process presented previously, which led to the balances and initial and boundary conditions presented in this section has no analytical solution and – up to now – the only way to solve these balances was through fully numerical models developed in finite differences or finite elements, as previously stated.

2. Developed model

Consider a semi-infinite material with characteristics similar to a very dilute gel (whose properties can be supposed equal to those of pure water). The system has initial

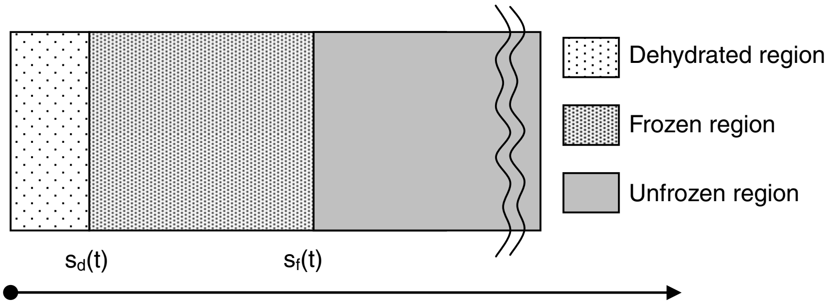

Fig. 1. Simple scheme of the system.

uniform temperature equal to T_{if} and uncovered flat surface which at time $t = 0$ is exposed to the surrounding medium (with constant temperature T_{s} (lower than T_{if}) and heat and mass transfer coefficients h and K_{m}). We assume that $T_{\mathrm{s}} < T_0(t) < T_{\mathrm{if}}$, $t > 0$ where $T_0(t)$ is the unknown sublimation temperature.

The system behaviour is ruled by balances (1) and (2). To calculate the evolution of temperature and water content in time, we will consider the following free boundary problem:

Find the temperatures $T_{\mathrm{d}} = T_{\mathrm{d}}(x,t)$ and $T_{\mathrm{f}} = T_{\mathrm{f}}(x,t)$, the concentrations $C_{\mathrm{va}} = C_{\mathrm{va}}(x,t)$, the free boundaries $s_{\mathrm{d}} = s_{\mathrm{d}}(t)$ and $s_{\mathrm{f}} = s_{\mathrm{f}}(t)$ and the temperature $T_0 = T_0(t)$ at the sublimation front $x = s_{\mathrm{d}}(t)$ which must satisfy the following:

- Differential equations at the dehydrated region:

$$\rho_{\mathrm{d}} C_{p_{\mathrm{d}}} \frac{\partial T_{\mathrm{d}}}{\partial t} = k_{\mathrm{d}} \frac{\partial^2 T_{\mathrm{d}}}{\partial x^2}, 0 < x < s_{\mathrm{d}}(t), \quad t > 0 \tag{3}$$

$$\varepsilon \frac{\partial C_{\mathrm{va}}}{\partial t} = D_{\mathrm{ef}} \frac{\partial^2 C_{\mathrm{va}}}{\partial x^2}, 0 < x < s_{\mathrm{d}}(t), \quad t > 0 \tag{4}$$

- Differential equations at the frozen region:

$$\rho_{\mathrm{f}} C_{p_{\mathrm{f}}} \frac{\partial T_{\mathrm{f}}}{\partial t} = k_{\mathrm{f}} \frac{\partial^2 T_{\mathrm{f}}}{\partial x^2}, \quad s_{\mathrm{d}}(t) < x < s_{\mathrm{f}}(t), \quad t > 0 \tag{5}$$

Free boundary conditions at the sublimation front $x = s_{\mathrm{d}}(t)$:

$$T_{\mathrm{d}}(s_{\mathrm{d}}(t),t) = T_{\mathrm{f}}(s_{\mathrm{d}}(t),t) = T_0(t), \quad t > 0 \tag{6}$$

$$k_{\mathrm{f}} \frac{\partial T_{\mathrm{f}}(s_{\mathrm{d}}(t),t)}{\partial x} - k_{\mathrm{d}} \frac{\partial T_{\mathrm{d}}(s_{\mathrm{d}}(t),t)}{\partial x} = L_{\mathrm{s}} m_{\mathrm{s}} \dot{s}_{\mathrm{d}}(t), \quad t > 0 \tag{7}$$

$$D_{\mathrm{ef}} \frac{\partial C_{\mathrm{va}}(s_{\mathrm{d}}(t),t)}{\partial x} = m_{\mathrm{s}} \dot{s}_{\mathrm{d}}(t) \tag{8}$$

$$C_{\mathrm{va}}(s_{\mathrm{d}}(t),t) = \frac{M P_{\mathrm{sat}}(T)}{R_{\mathrm{g}} T_0(t)} = Ma \frac{\exp\left(b - \frac{c}{T_0(t)}\right)}{R_{\mathrm{g}} T_0(t)} \tag{9}$$

where $C_{\mathrm{va}}(s_{\mathrm{d}}(t),t)$ is the equilibrium vapor concentration at $T_0(t)$ and the saturation pressure $P_{\mathrm{sat}}(T)$ is evaluated according to [24].

- Free boundary conditions at the freezing front $x = s_{\mathrm{f}}(t)$:

$$T_{\mathrm{f}}(s_{\mathrm{f}}(t),t) = T_{\mathrm{if}}, \quad t > 0 \tag{10}$$

$$k_{\mathrm{f}} \frac{\partial T_{\mathrm{f}}(s_{\mathrm{f}}(t),t)}{\partial x} = m_{\mathrm{f}} L_{\mathrm{f}} \dot{s}_{\mathrm{f}}(t), \quad t > 0 \tag{11}$$

- The convective boundary conditions at the fixed interphase $x = 0$:

$$k_{\mathrm{d}} \frac{\partial T_{\mathrm{d}}(0,t)}{\partial x} = h(T_{\mathrm{d}}(0,t) - T_{\mathrm{s}}), \quad t > 0 \tag{12}$$

$$D_{\mathrm{ef}} \frac{\partial C_{\mathrm{va}}(0,t)}{\partial x} = K_{\mathrm{m}}(C_{\mathrm{va}}(0,t) - C_{\mathrm{a}}), \quad t > 0 \tag{13}$$

- The initial conditions at $t = 0$:

$$s_{\mathrm{f}}(0) = s_{\mathrm{d}}(0) = 0 \tag{14}$$

$$T = T_{\mathrm{if}} \quad \text{for } x \geqslant 0 \tag{15}$$

We will solve the system (3)–(15) by using the quasi-steady method [2]. In general, it is a good approximation when the Stefan number tends to zero, i.e. when the latent heat of the material is high with respect to the heat capacity of the solid material. This approximation has often been used when modelling the freezing of high-water content materials [2,25]. Therefore, the temperatures T_{f}, T_{d} and the concentration C_{va} are given by the following expressions:

$$T_{\mathrm{d}}(x,t) = A(t) + B(t)x, 0 < x < s_{\mathrm{d}}(t), \quad t > 0 \tag{16}$$

$$C_{\mathrm{va}}(x,t) = D(t) + E(t)x, 0 < x < s_{\mathrm{d}}(t), \quad t > 0 \tag{17}$$

$$T_{\mathrm{f}}(x,t) = F(t) + G(t)x, s_{\mathrm{d}}(t) < x < s_{\mathrm{f}}(t), \quad t > 0 \tag{18}$$

where $A(t)$, $B(t)$, $D(t)$, $E(t)$, $F(t)$ and $G(t)$ are unknown functions to be determined, as well as the free boundaries s_{d} (t) and $s_f(t)$ and the temperature $T_0(t)$. We have nine unknown functions and we must impose nine conditions (Eqs. (6)–(15)). By considering them we obtain the following system of differential algebraic equations:

$$k_{\mathrm{d}} B(t) = h(A(t) - T_{\mathrm{s}}) \tag{19}$$

$$D_{\mathrm{ef}} E(t) = K_{\mathrm{m}}(D(t) - C_{\mathrm{a}}) \tag{20}$$

$$A(t) + B(t) s_{\mathrm{d}}(t) = T_0(t) \tag{21}$$

$$F(t) + G(t) s_{\mathrm{d}}(t) = T_0(t) \tag{22}$$

$$D(t) + E(t) s_{\mathrm{d}}(t) = Ma \frac{\exp\left(b - \frac{c}{T_0(t)}\right)}{R_{\mathrm{g}} T_0(t)} \tag{23}$$

$$F(t) + G(t) s_{\mathrm{f}}(t) = T_{\mathrm{if}} \tag{24}$$

$$k_{\mathrm{f}} G(t) - k_{\mathrm{d}} B(t) = L_{\mathrm{s}} m_{\mathrm{s}} \dot{s}_{\mathrm{d}}(t) \tag{25}$$

$$D_{\mathrm{ef}} E(t) = m_{\mathrm{s}} \dot{s}_{\mathrm{d}}(t) \tag{26}$$

$$k_{\mathrm{f}} G(t) = m_{\mathrm{f}} L_{\mathrm{f}} \dot{s}_{\mathrm{f}}(t) \tag{27}$$

By considering the first six equations of the previous system we can obtain, by direct replacement and rearrangement, $A(t)$, $B(t)$, $D(t)$ and $E(t)$ as a function of $T_0(t)$ and $s_{\mathrm{d}}(t)$, as well as $F(t)$ and $G(t)$ as a function of $T_0(t)$, $s_{\mathrm{d}}(t)$ and $s_{\mathrm{f}}(t)$, given by the following expressions:

$$A(t) = \frac{T_0(t) + T_{\mathrm{s}} \frac{h}{k_{\mathrm{d}}} s_{\mathrm{d}}(t)}{1 + \frac{h}{k_{\mathrm{d}}} s_{\mathrm{d}}(t)} \tag{28}$$

$$B(t) = \frac{h}{k_{\mathrm{d}}} \frac{T_0(t) - T_{\mathrm{s}}}{1 + \frac{h}{k_{\mathrm{d}}} s_{\mathrm{d}}(t)} \tag{29}$$

$$D(t) = \frac{\frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}} C_{\mathrm{a}} s_{\mathrm{d}}(t) + Ma \frac{\exp(b - \frac{c}{T_0(t)})}{R_{\mathrm{g}} T_0(t)}}{1 + \frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}} s_{\mathrm{d}}(t)} \tag{30}$$

$$E(t) = \frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}} \frac{Ma \frac{\exp\left(b - \frac{c}{T_0(t)}\right)}{R_{\mathrm{g}} T_0(t)} - C_{\mathrm{a}}}{1 + \frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}} s_{\mathrm{d}}(t)} \tag{31}$$

$$F(t) = \frac{T_0(t) s_{\mathrm{f}}(t) - T_{\mathrm{if}} s_{\mathrm{d}}(t)}{s_{\mathrm{f}}(t) - s_{\mathrm{d}}(t)} \tag{32}$$

$$G(t) = \frac{T_{\mathrm{if}} - T_0(t)}{s_{\mathrm{f}}(t) - s_{\mathrm{d}}(t)} \tag{33}$$

By considering now the last three conditions of the system (28)–(33) and performing mathematical manipulations we obtain the following system of two ordinary differential equations and one algebraic equation for $s_{\mathrm{d}}(t)$, $s_{\mathrm{f}}(t)$ and $T_0(t)$ given by:

$$1+\frac{h}{k_{\mathrm{f}}}\frac{T_{\mathrm{s}}}{T_{\mathrm{if}}}s_{\mathrm{f}}(t)+hs_{\mathrm{d}}(t)\left(\frac{1}{k_{\mathrm{d}}}-\frac{T_{\mathrm{s}}}{T_{\mathrm{if}}k_{\mathrm{f}}}\right)-\frac{T_0(t)}{T_{\mathrm{if}}}\left[1+\frac{h}{k_{\mathrm{f}}}s_{\mathrm{f}}(t)+hs_{\mathrm{d}}(t)\left(\frac{1}{k_{\mathrm{d}}}-\frac{1}{k_{\mathrm{f}}}\right)\right]$$

$$=\frac{L_{\mathrm{s}}K_{\mathrm{m}}}{T_{\mathrm{if}}k_{\mathrm{f}}}\frac{\left(1+\frac{h}{k_{\mathrm{f}}}s_{\mathrm{f}}(t)\right)(s_{\mathrm{f}}(t)-s_{\mathrm{d}}(t))}{1+\frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}}s_{\mathrm{d}}(t)}\left[Ma\frac{\exp\left(b-\frac{c}{T_0(t)}\right)}{R_{\mathrm{g}}T_0(t)}-C_{\mathrm{a}}\right] \tag{34}$$

$$\dot{s}_{\mathrm{d}}(t)=\frac{k_{\mathrm{f}}T_{\mathrm{if}}}{m_{\mathrm{s}}L_{\mathrm{s}}}\frac{1+\frac{h}{k_{\mathrm{f}}}\frac{T_{\mathrm{s}}}{T_{\mathrm{if}}}s_{\mathrm{f}}(t)+hs_{\mathrm{d}}(t)\left(\frac{1}{k_{\mathrm{d}}}-\frac{T_{\mathrm{s}}}{k_{\mathrm{f}}T_{\mathrm{if}}}\right)-\frac{T_0(t)}{T_{\mathrm{if}}}\left[1+\frac{h}{k_{\mathrm{f}}}s_{\mathrm{f}}(t)+hs_{\mathrm{d}}(t)\left(\frac{1}{k_{\mathrm{d}}}-\frac{1}{k_{\mathrm{f}}}\right)\right]}{\left(1+\frac{h}{k_{\mathrm{d}}}s_{\mathrm{f}}(t)\right)(s_{\mathrm{f}}(t)-s_{\mathrm{d}}(t))} \tag{35}$$

$$\dot{s}_{\mathrm{f}}(t)=\frac{k_{\mathrm{f}}T_{\mathrm{if}}}{m_{\mathrm{f}}L_{\mathrm{f}}}\frac{1-\frac{T_o(t)}{T_{\mathrm{if}}}}{s_{\mathrm{f}}(t)-s_{\mathrm{d}}(t)} \tag{36}$$

$$s_{\mathrm{f}}(0)=s_{\mathrm{d}}(0)=0 \tag{37}$$

The system (34)–(37) can be written in an equivalent form given by Eqs. (38)–(41) by defining the following parameters:

$$\delta_1=\frac{m_{\mathrm{f}}L_{\mathrm{f}}}{k_{\mathrm{f}}T_{\mathrm{if}}},\quad \delta_2=\frac{m_{\mathrm{s}}}{C_{\mathrm{a}}K_{\mathrm{m}}},\quad \delta_3=\frac{L_{\mathrm{s}}m_{\mathrm{s}}}{hT_{\mathrm{if}}},$$

$$\delta_4=\frac{Ma}{C_{\mathrm{a}}R_{\mathrm{g}}T_{\mathrm{if}}},\quad \delta_5=\frac{m_{\mathrm{f}}L_{\mathrm{f}}}{hT_{\mathrm{if}}},\quad \delta_6=\frac{T_{\mathrm{s}}}{T_{\mathrm{if}}}$$

$$T_0(t)=T_{\mathrm{if}}[1-\delta_1(s_{\mathrm{f}}(t)-s_{\mathrm{d}}(t))\dot{s}_{\mathrm{f}}(t)] \tag{38}$$

$$\delta_2\left(1+\frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}}s_{\mathrm{d}}(t)\right)\dot{s}_{\mathrm{d}}(t)=T_{\mathrm{if}}\delta_4\frac{\exp\left(b-\frac{c}{T_0(t)}\right)}{T_0(t)}-1 \tag{39}$$

$$\delta_5\left[1+\frac{h}{k_{\mathrm{d}}}s_{\mathrm{d}}(t)+\frac{h}{k_{\mathrm{f}}}(s_{\mathrm{f}}(t)-s_{\mathrm{d}}(t))\right]\dot{s}_{\mathrm{f}}(t)$$

$$=1-\delta_6+\delta_3\left(1+\frac{h}{k_{\mathrm{d}}}s_{\mathrm{d}}(t)\right)\frac{T_{\mathrm{if}}\delta_4\frac{\exp\left(b-\frac{c}{T_0(t)}\right)}{T_0(t)}-1}{\delta_2\left(1+\frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}}s_{\mathrm{d}}(t)\right)} \tag{40}$$

$$s_{\mathrm{d}}(0)=s_{\mathrm{f}}(0)=0 \tag{41}$$

Moreover, functions $F(t)$ and $G(t)$ can be now rewritten as follows:

$$F(t)=\frac{T_0(t)s_{\mathrm{f}}(t)-T_{\mathrm{if}}s_{\mathrm{d}}(t)}{s_{\mathrm{f}}(t)-s_{\mathrm{d}}(t)}=T_{\mathrm{if}}[1-\delta_1 s_{\mathrm{f}}(t)\dot{s}_{\mathrm{f}}(t)] \tag{42}$$

$$G(t)=\frac{T_{\mathrm{if}}-T_0(t)}{s_{\mathrm{f}}(t)-s_{\mathrm{d}}(t)}=T_{\mathrm{if}}\delta_1\dot{s}_{\mathrm{f}}(t) \tag{43}$$

and, therefore, the temperatures $T_{\mathrm{d}}(x,t)$ and $T_{\mathrm{f}}(x,t)$ are given by the following expressions:

$$T_{\mathrm{d}}(x,t)=\frac{T_0(t)\left(1+\frac{h}{k_{\mathrm{d}}}x\right)+T_{\mathrm{s}}\frac{h}{k_{\mathrm{d}}}(s_{\mathrm{d}}(t)-x)}{1+\frac{h}{k_{\mathrm{d}}}s_{\mathrm{d}}(t)},$$

$$0<x<s_{\mathrm{d}}(t),\quad t>0 \tag{44}$$

$$T_{\mathrm{f}}(x,t)=T_{\mathrm{if}}[1-\delta_1\dot{s}_{\mathrm{f}}(t)(s_{\mathrm{f}}(t)-x)],$$

$$s_{\mathrm{d}}(t)<x<s_{\mathrm{f}}(t),\quad t>0 \tag{45}$$

and the concentration $C_{\mathrm{va}}(x,t)$ is given by:

$$C_{\mathrm{va}}(x,t)=\frac{\frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}}C_{\mathrm{a}}(s_{\mathrm{d}}(t)-x)+Ma\frac{\exp\left(b-\frac{c}{T_0(t)}\right)}{T_0(t)}\left(1+\frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}}x\right)}{1+\frac{K_{\mathrm{m}}}{D_{\mathrm{ef}}}s_{\mathrm{d}}(t)},$$

$$0<x<s_{\mathrm{d}}(t),\quad t>0 \tag{46}$$

Moreover, the temperature T_{d} and the concentration C_{va} at the fixed surface $x=0$ are given by the following expressions:

$$T_{\mathrm{d}}(0,t)=A(t)=\frac{T_0(t)+T_{\mathrm{s}}\frac{h}{k_{\mathrm{d}}}s_{\mathrm{d}}(t)}{1+\frac{h}{k_{\mathrm{d}}}s_{\mathrm{d}}(t)} \tag{47}$$

$$C_{\mathrm{va}}(0,t)=C_{\mathrm{a}}(1+\delta_2\dot{s}_{\mathrm{d}}(t)) \tag{48}$$

As previously expressed, the whole system (3)–(15) with the assumptions (16)–(18) (quasi-steady model) has been solved with a semi-analytical method. As a result, Eqs. (38)–(40) give expressions that relate $s_d(t)$, $s_f(t)$ and $T_0(t)$ with the first derivates of $s_d(t)$ and $s_f(t)$. The differential equations (39) and (40) with initial conditions (41) cannot be solved analytically, then it must be solved approximately by using an explicit scheme of finite differences that is coupled with conditions (38) which predicts the freezing temperature $T_0(t)$. These computed values for $s_{\mathrm{d}}(t)$, $s_{\mathrm{f}}(t)$ and $T_0(t)$ were then used for predicting the temperatures $T_d(x,t)$, $T_f(x,t)$ and the concentration $C_{\mathrm{va}}(x,t)$ through the expressions (44)–(48). The resulting algorithm was coded in Scilab version 4.1.

3. Results and discussion

3.1. Validation of the model

At a first instance, it is important to validate any approximate model against the analytical solution for the related physical system. Normally this situation is impossible, that is why approximate models are developed, and the only option is to compare against the exact solution of a simplified problem.

In this case the system that has analytical solution is that of a semi-infinite medium with constant initial temperature that freezes (without surface ice sublimation) and constant surface temperature (very high heat transfer coefficient). This is called the Lamé–Clapeyron–Stefan problem and its solution can be found elsewhere [2,26].

To this aim the prediction program was run with a very high heat transfer coefficient $h = 3000\ \mathrm{W/(m^2\ K)}$, with a very low mass transfer coefficient $K_m = 0.000001$ m/s and $T_s = 263$ K, so as to secure getting almost instantaneously a constant surface temperature and to make negligible the contribution of the dehydrated zone. If the assumptions done during the development of this method are correct, results provided by the model should tend to those of the analytical problem with equal surface temperature.

Fig. 2 shows the comparison of the variation of $s_f(t)$ with time for both cases. As can be seen, results coincide.

In the same sense, Fig. 3 presents the predicted temperature profiles in the frozen zone $T_f(x,t)$ for different times. Again results are almost perfectly coincident.

We consider that these results are adequate to validate the developed model.

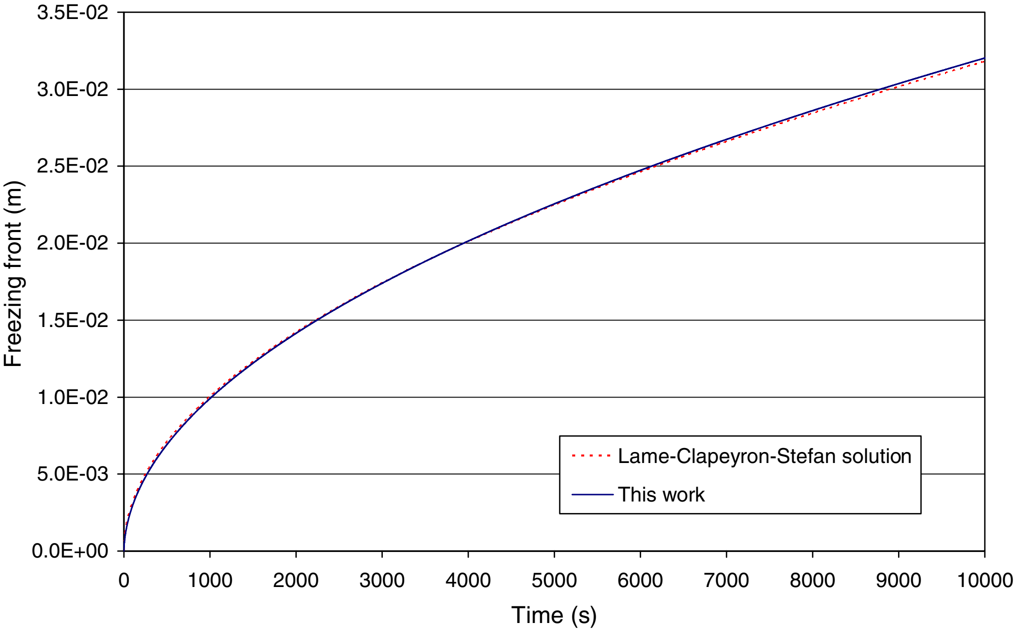

Fig. 2. Comparison of the freezing front position provided by the Lamé–Clapeyron–Stefan solution and this work

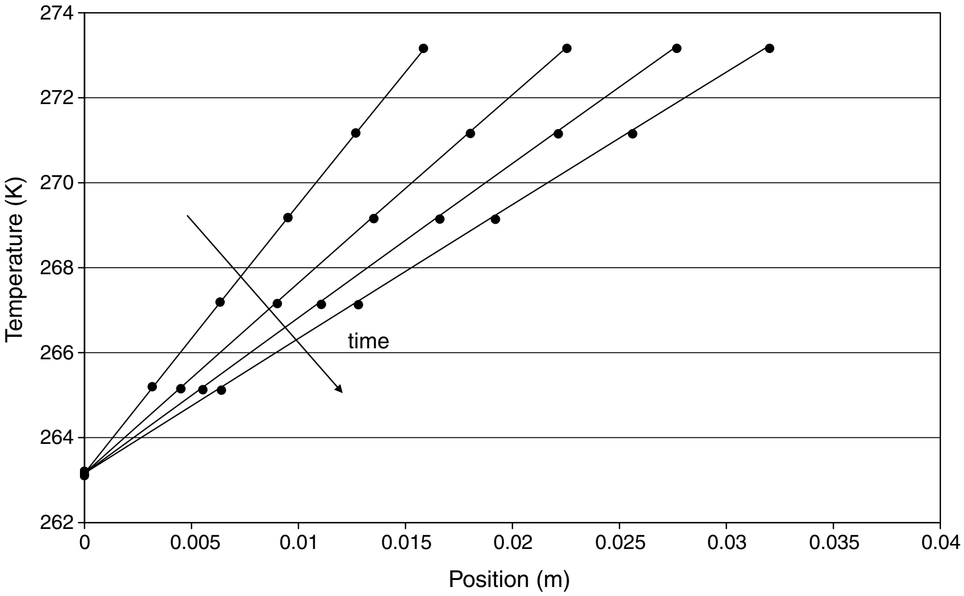

Fig. 3. Temperature profile in the frozen zone. (—-) Lamé–Clapeyron–Stefan solution, (•) this work.

3.2. Use of the model

The developed model was extensively used to study the influence of system parameters and freezing conditions on the characteristic dependent variables of the system: $T_f(x,t)$, $T_d(x,t)$, $s_d(t)$, $s_f(t)$ and $T_o(t)$.

Calculations were performed simulating the freezing of a high-water content solid material with physical and thermal properties of a very dilute agar–agar gel. So, for most properties, values of pure water or ice could be used. For other properties, like those of the dehydrated phase, values for freeze-dried materials were taken as a valid approach [20]. Table 1 presents a list of the values of the main properties used.

A wide range of possible values of external parameters was covered, so as to have a clear knowledge of their specific influence under different combinations of freezing conditions. Heat transfer coefficients in the range of 10–150 W/(m^{2}K) were considered. This range is feasible to find in practical freezing conditions. In the same sense, external temperatures from 233 to 263 K were used (−40 to −10 °C). In all cases a total pressure of 1 atm was used. A maximum calculation time of 10,000 s was considered sufficient to determine the desired system characteristics.

Table 1
Physical properties and other parameters

Physical properties	Frozen zone	Dehydrated zone
ρ (kg/m^3)	1000	20
C_p (J/(kg K))	1900	1000
D_{ef} (m^2/s)	–	9.66×10^{-6}
k (W/(m K))	1.7	0.07
Other parameters		
ε	0.98	
C_a (kg/m^3)	8.29×10^{-5}	
h (W/(m^2 K))	10–150	
K_m (m/s)	0.0072–0.1082	
L_f (J/kg)	3.30×10^5	
L_s (J/kg)	2.83×10^6	
m_f (kg/m^3)	980	
m_s (kg/m^3)	980	
M (kg/mol)	0.018	
Parameters of Eq. (9) and subsequents	$a = 133.33$, $b = 23.986$, $c = 6139.9094$	
T_{if} (K)	273.16	
T_s (K)	233–268	

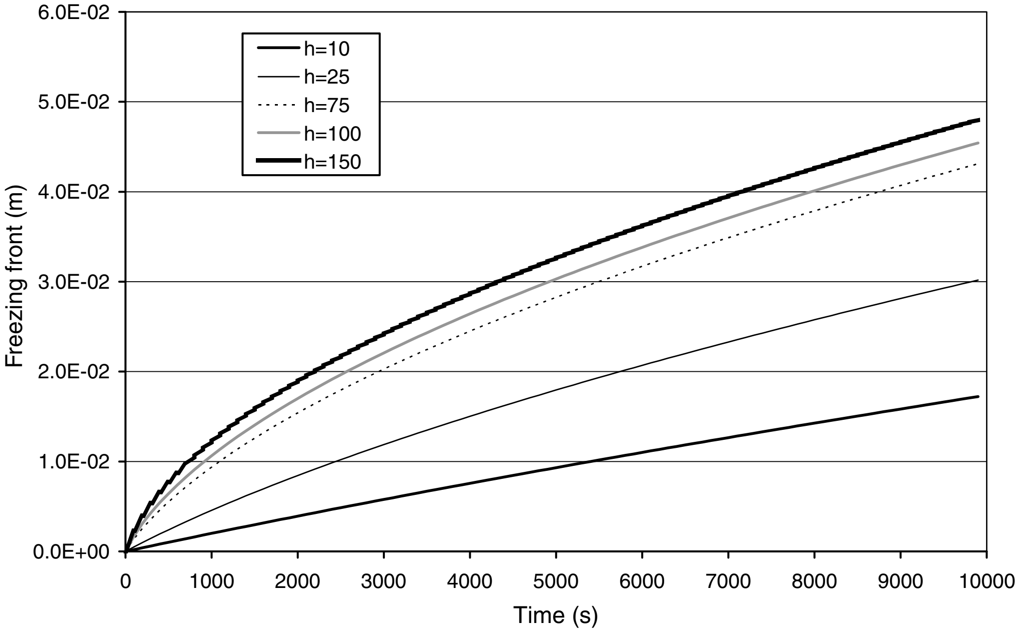

Fig. 4. Influence of the heat transfer coefficient in the freezing front evolution, $T_s = 243$ K. The other parameters are given in Table 1.

In Figs. 4 and 5 the evolution of both moving boundaries is shown, studying the influence of the transfer coefficients h and K_m (K_m is directly proportional to h). We can see that both $s_f(t)$ and $s_d(t)$ increase linearly for very short times, but as the dehydrated layer grows, both processes (freezing and sublimation) continue at steadily lower rates. This is due, as shown in Fig. 1, to the development of the dehydrated surface layer that has lower k and D_{ef} than the frozen zone, so lowering heat and mass transfer rates.

Another fact observed from Fig. 4 is that $s_f(t)$ is monotonely increasing with respect to the parameter h meanwhile the same is not valid for $s_d(t)$ (Fig. 5). In the second case there is a double and opposed influence of the increase of h: it means higher sublimation rate by an increase of K_m but, at the same time, a lower driving force due to the rapid cooling of the surface that decreases water vapor pressure. At short times the first effect prevails, but with time the second factor has heavier weight and at sufficiently long times higher h implies lower water loss.

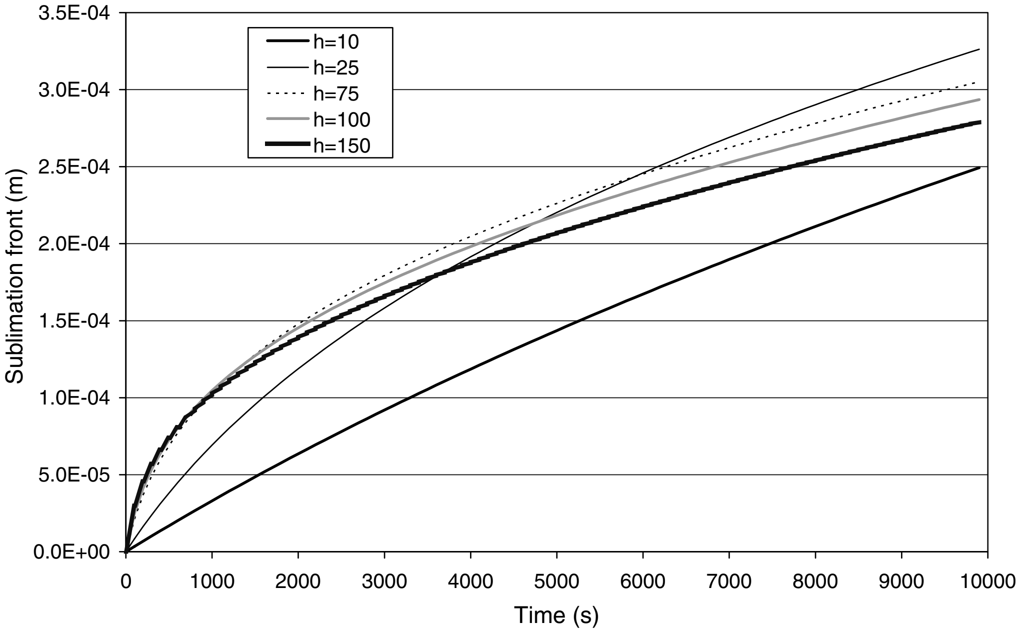

Fig. 5. Influence of the heat transfer coefficient in the sublimation front evolution, $T_s = 243$ K. The other parameters are given in Table 1.

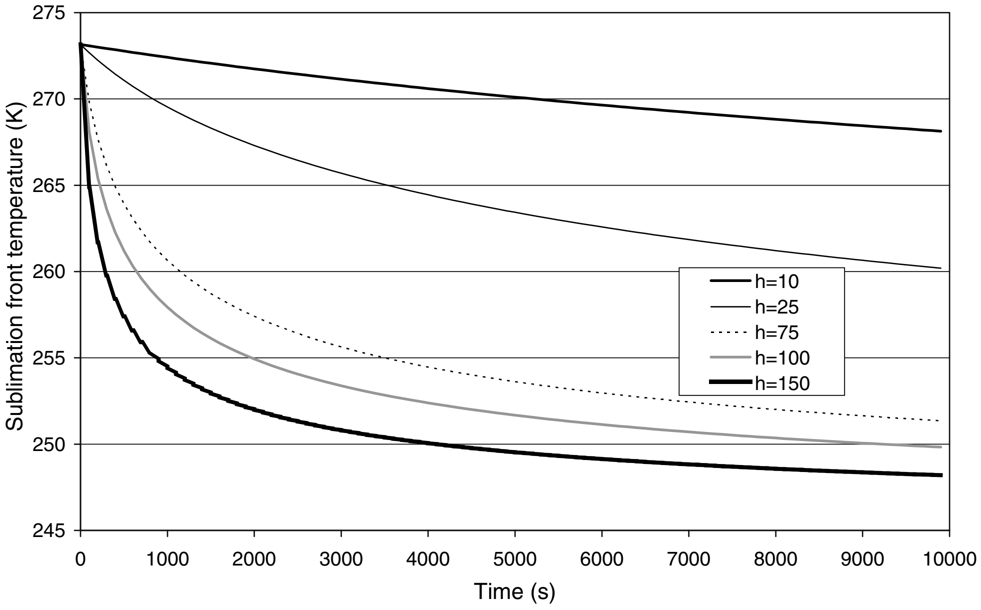

Fig. 6. Influence of the heat transfer coefficient in the sublimation front temperature, $T_s = 243$ K. The other parameters are given in Table 1.

Another characteristic of the influence of h is that a higher h means lower sublimation front temperature T_o. The effect of the increase in h is more remarkable at low values of this parameter, and tends to an asymptote for high-h values (Fig. 6).

When we consider T_s as parameter, we obtain that $s_f(t)$ is a monotonely decreasing and $s_d(t)$ is a monotonely increasing function of T_s (Figs. 7 and 8, respectively). In the case of $s_d(t)$, initially T_s has no traceable influence, but at higher times there is a clear influence of external temperature on its value.

Besides, data given in Figs. 4–8 clearly show that for equal system characteristics and freezing conditions the value of $s_f(t)$ is – at least – two orders of magnitude higher than that of $s_d(t)$ and that for any real system and normal freezing times ice sublimation is constrained to a very thin surface layer. For the examples given in this work the highest values of $s_d(t)$attained after 10,000 s were less than 0.3 mm.

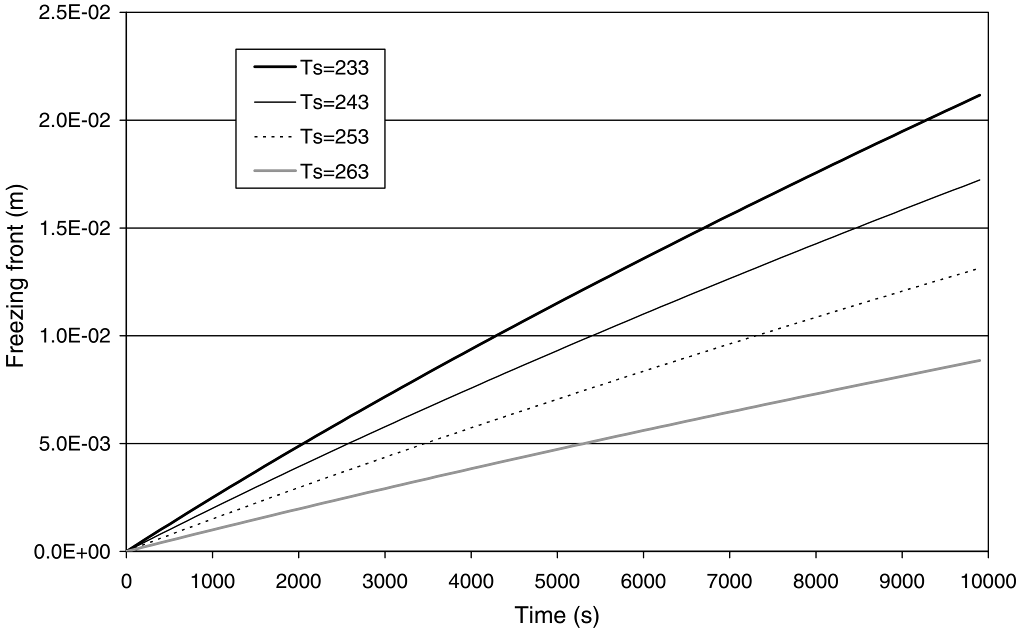

Fig. 7. Influence of the surrounding temperature in the evolution of the freezing front, $h = 10$ W/(m^{2}K). The other parameters are given in Table 1.

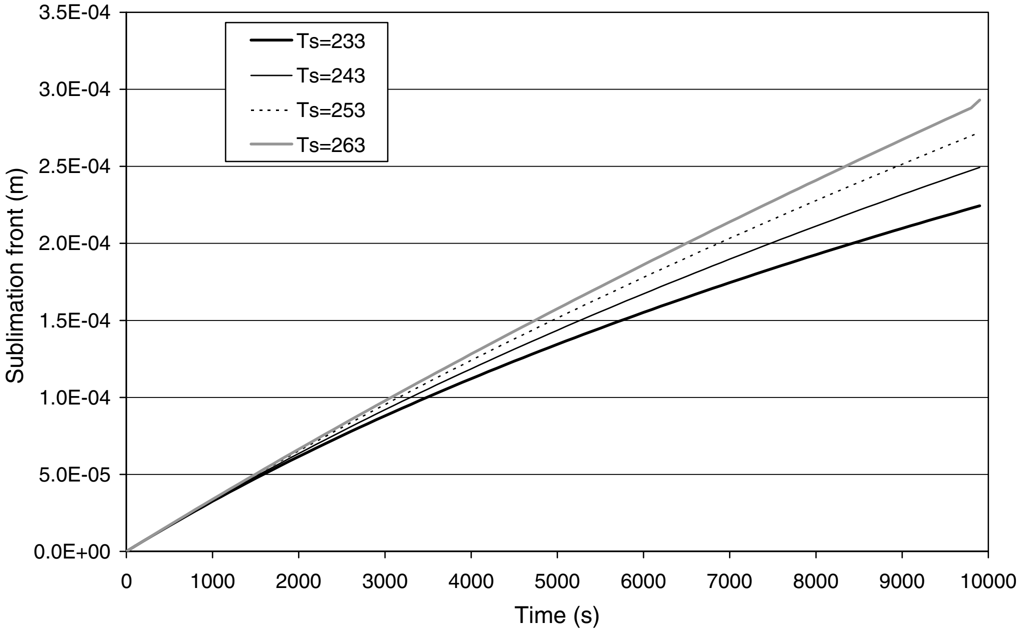

Fig. 8. Influence of the surrounding temperature in the evolution of the sublimation front, $h = 10$ W/(m^{2}K). The other parameters are given in Table 1.

Fig. 9 presents the influence of T_s on T_o. It shows that a lower external temperature always means lower sublimation temperature and that its influence increases with time (higher separation between sublimation temperatures for different external temperatures).

Moreover, in Fig. 10, we see the change in the temperature profiles in the dehydrated and frozen zones with time for a given value of parameters h and T_s. From the figure a sharp profile is seen in the dehydrated zone and a more gradual – but always linear – variation in the frozen zone. Both profiles are each time less steep as moving boundaries advance towards the interior of the system.

To get a better scope of temperature evolution, Fig. 11 presents the influence of h and T_s on the predicted temperature profiles at a given time (1000 s) for the dehydrated zone. Plots have the expected trends with lower temperatures for higher h and lower T_s, and can be matched to get a complete temperature profile of the system. Plot shows the width and range of the dehydrated zone at the time of calculation (1000 s) and is equivalent to those of

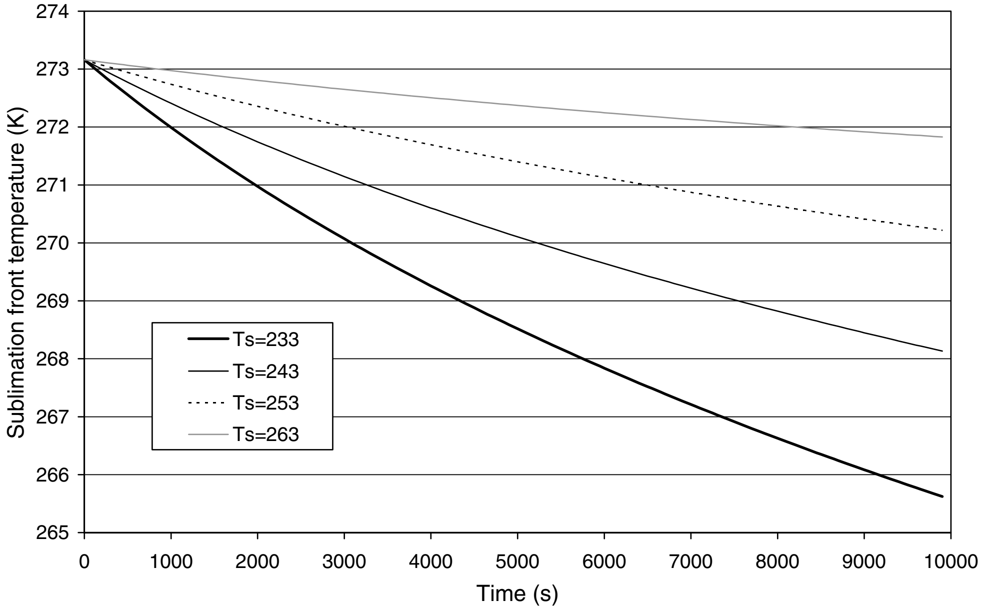

Fig. 9. Influence of the surrounding temperature in the sublimation front temperature. The other parameters are given in Table 1.

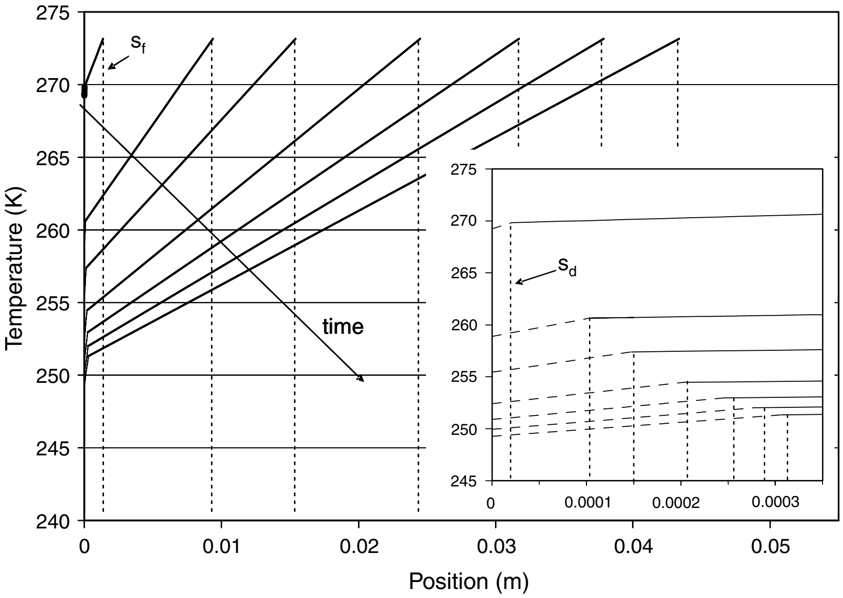

Fig. 10. Temperature profiles, in dehydrated and frozen zones, and position of freezing and sublimation fronts at different times (from 100 to 10,000 s), $h = 75$ W/(m^{2}K), $T_s = 243$ K. The other parameters are given in Table 1.

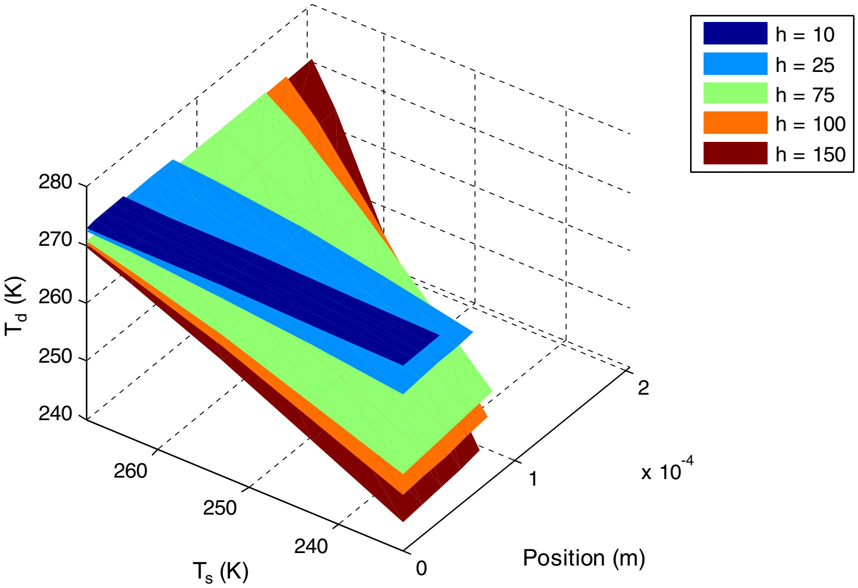

Fig. 11. Temperature profiles in the dehydrated zone at time = 1000 s, as a function of h and T_s. The other parameters are given in Table 1.

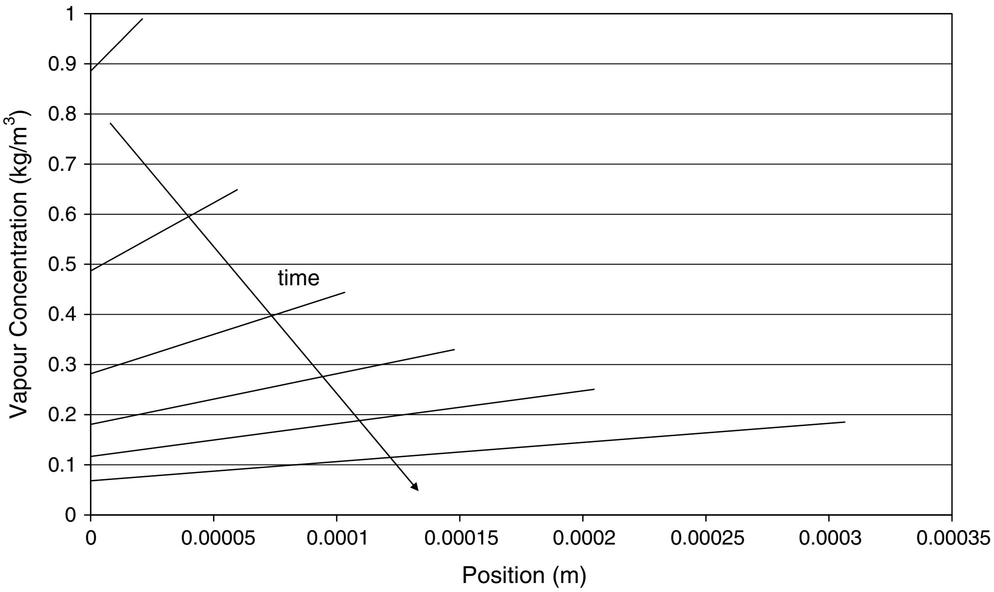

Fig. 12. Vapour concentration profiles at different times (from 100 to 10,000 s), in dehydrated zone, $h = 75$ W/(m^{2}K), $T_s = 243$ K. The other parameters are given in Table 1.

previous figures. A similar plot for the frozen zone can be developed using the present model.

Besides the right limit of the plot in Fig. 11 give the value of the sublimation temperature at that time, h and T_s.

Related water vapor concentration, we can see in Fig. 12 the linear profiles of vapour concentration in the dehydrated zone, for different times (from 100 to 10,000 s), at specified h and T_s values. As expected, concentration values are lower at higher times due to the related diminution of $T_0(t)$ that, in turn, lowers $C_{va}(s_d(t), t)$.

These results are complemented by those of Fig. 13 which shows the influence of h and T_s on the predicted concentration profiles at a given time (1000 s). The depth and range of the dehydrated zone at the time of calculation are obviously equal to those of Fig. 11.

4. Conclusions

The developed quasi-analytical model, with few simplifying assumptions, enables to easily predict the influence of material characteristics and freezing conditions on the

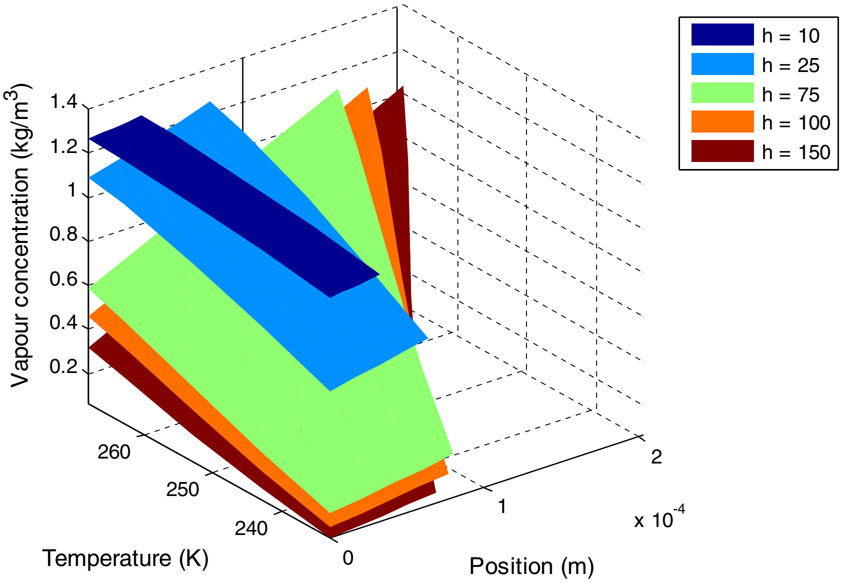

Fig. 13. Vapour concentration profiles in the dehydrated zone at time = 1000 s, as a function of h and T_s. The other parameters are given in Table 1.

evolution of both freezing and sublimation fronts, temperature in the frozen and dehydrated zones, temperature at the sublimation front and vapour concentration in the dehydrated layer.

It can be used to optimize the freezing conditions of certain types of materials as well as a base for the development of more detailed models that include a freezing range or initial temperatures different from that of material freezing.

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References

[1] A.C. Cleland (Ed.), Food Refrigeration Processes, Analysis, Design and Simulation, Elsevier, London, 1990, pp. 95–136.
[2] V.J. Lunardini (Ed.), Heat Transfer with Freezing and Thawing, Elsevier, London, 1991, pp. 1–167.
[3] A.V. Luikov, Systems of differential equations of heat and mass transfer in capillary porous bodies (review), Int. J. Heat Mass Transfer 18 (1975) 1–14.
[4] D.A. Tarzia, A bibliography on moving-free boundary problems for the heat diffusion equation. The Stefan and related problems, MAT – Serie A, # 2, Rosario, 2000, 297 pages. See <www.austral.edu.ar/MAT-SerieA/2>.
[5] E.A. Santillan Marcus, D.A. Tarzia, Explicit solution for freezing of humid porous half-space with heat flux condition, Int. J. Eng. Sci. 38 (2000) 1651–1665.
[6] R.H. Mascheroni, A. Calvelo, Relationship between heat transfer parameters and the characteristic damage variables for the freezing of beef, Meat Sci. 4 (1980) 267–285.
[7] A.E. Delgado, D.-W. Sun, Heat and mass transfer models for predicting freezing processes review, J. Food Eng. 47 (2001) 157–174.
[8] R. Plank, Beitrage zur Berechnung und Bewertung der Gefriergeschwindigkeit von Lebensmitteln, Beiheft zur Zeitschrit fur die gesamte Kalte-Industrie 3 (1941) 1–17.
[9] V.O. Salvadori, R.H. Mascheroni, Prediction of freezing and thawing times by means of a simplified analytical method, J. Food Eng. 13 (1991) 67–78.
[10] J.D. Mellor (Ed.), Fundamentals of Freeze Drying, Academic Press, London, 1978, pp. 16–125.
[11] M. Farid, The moving boundary problems from melting and freezing to drying and frying of food, Chem. Eng. Process. 41 (2002) 1–10.
[12] M. Kochs, Ch. Körber, B. Nunner, I. Heschel, The influence of the freezing process on vapour transport during sublimation in vacuum-freeze-drying, Int. J. Heat Mass Transfer 34 (1991) 2395–2408.
[13] J. Aguirre Puente, M. Frémond, G. Comini, Freezing of soils – physical study and mathematical models, Int. J. Refrig. 1 (1978) 99–106.
[14] Q.T. Pham, J. Willix, A model for food desiccation in frozen storage, J. Food Sci. 49 (1984) 1275–1281.
[15] R.N. Sukhwal, J. Aguirre Puente, Sublimation des milieux dispersés. Considerations theoriques et experimentation, Rev. Gen. Therm. 262 (1983) 663–673.
[16] G.P. Lambrinos, J. Aguirre Puente, Deshydratation des milieux dispersés congelés. Influence des conditions d'entreposage sur les pertes de masse, in: Proceedings of the XVI International Congress of Refrigeration, Paris, France, August 31–September 7, vol. 2, 1983, pp. 567–573.
[17] L.A. Campañone, L.A. Roche, V.O. Salvadori, R.H. Mascheroni, Monitoring of weight losses in meat products during freezing and frozen storage, Food Sci. Technol. Int. 8 (2002) 229–238.
[18] L.A. Campañone, L.A. Roche, V.O. Salvadori, R.H. Mascheroni, Structural studies on unpackaged foods during their freezing and storage, J. Food Sci. 71 (2006) E218–E226.
[19] J. Aguirre Puente, R.N. Sukhwal, Sublimation of ice in frozen dispersed media, in: Proceedings of the Third International Offshore Mechanics and Arctic Engineering Symposium, New Orleans, USA, February 12–16, 1983, pp. 38–44.
[20] L.A. Campañone, Transferencia de calor en congelación y almacenamiento de alimentos. Sublimación de hielo, calidad, optimización de condiciones de proceso, Doctor in Engineering Thesis, Universidad Nacional de La Plata, Argentina, 2001.
[21] L.A. Campañone, V.O. Salvadori, R.H. Mascheroni, Weight loss during freezing and storage of unpackaged foods, J. Food Eng. 47 (2001) 69–79.
[22] L.A. Campañone, V.O. Salvadori, R.H. Mascheroni, Food freezing with simultaneous surface dehydration. Approximate prediction of freezing time, Int. J. Heat Mass Transfer 48 (6) (2005) 1205–1213.

[23] L.A. Campañone, V.O. Salvadori, R.H. Mascheroni, Food freezing with simultaneous surface dehydration. Approximate prediction of weight loss during freezing and storage, Int. J. Heat Mass Transfer 48 (6) (2005) 1195–1204.

[24] O. Fennema, L.A. Berny, Equilibrium vapour pressure and water activity of food at subfreezing temperature, in: Proceedings of IV International Congress of Food Science and Technology, vol. 2, 1974, pp. 27–35.

[25] A.L. London, R.A. Seban, Rate of ice formation, Trans. ASME 65 (1943) 711–779.

[26] G. Lamé, B.P. Clapeyron, Memoire sur la solidification par refroidissement d'un globe liquide, Annal. Chim. Phys. 47 (1831) 250–256.