# Liquid-solid phase transitions in a deformable container

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**Abstract** We propose a model for water freezing in an elastic container, taking into account differences in the specific volume, specific heat and speed of sound in the solid and liquid phases. In particular, we discuss the influence of gravity on the equilibria of the system.

## Introduction

Water is a substance with extremely peculiar physical properties. A nice survey of the challenges in modeling water behavior can be found on the web page [22]. Being aware of the obstacles, we try to develop some mathematical models related to freezing of water in a container. In [11] and [12], we have proposed an approach to model the occurrence of high stresses due to the difference between the specific volumes of the solid and of the liquid phase, assuming first that the speed of sound and the specific heat are the same in solid and in liquid. We have proved there the existence and uniqueness of global solutions, as well as the convergence of the solutions to equilibria. In reality, the specific heat in water is about the double, while the speed of sound in water is less than one half of the one in ice. The main goal of this contribution is to include this dependence into the model. We discuss here the modeling issues and investigate in detail the equilibria. For containers of reason-

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able shape and reasonable height (a few kilometers at most), filled with water in a uniform gravity field, we obtain a unique equilibrium, which is either pure solid, or pure liquid, or a solid layer above a liquid layer separated by a horizontal surface, in dependence on the surrounding temperature. New mathematical and modeling challenges arise and it is not our aim here to solve the problem completely. In particular, the proof of well-posedness of the resulting nonlinear evolution system will be the subject of a subsequent paper.

There is an abundant classical literature on phase transition processes, see e.g. the monographs [2], [4], [20] and the references therein. It seems, however, that only few publications take into account different mass densities/specific volumes of the phases. In [5], the authors proposed to interpret a phase transition process in terms of a balance equation for macroscopic motions, and to include the possibility of voids. Well-posedness of an initial-boundary value problem associated with the resulting PDE system is proved there and the case of two different densities $\rho_1$ and $\rho_2$ for the two substances undergoing phase transitions has been pursued in [6].

Let us also mention the papers [16] and [17] dealing with macroscopic stresses in phase transitions models, where the different properties of the viscous (liquid) and elastic (solid) phases are taken into account and the coexisting viscous and elastic properties of the system are given a distinguished role, [13] and [14], which pertains to nonlinear thermoviscoplasticity, and [3] where another coupled system for temperature, displacement, and phase parameter has been derived in order to model the full thermomechanical behavior of shape memory alloys. First mathematical results were published in [3], while a long list of references for further developments can be found in the monographs [4] and [20].

The main advantage of our approach is that we deal exclusively with physically measurable quantities. All parameters have a clear physical meaning. The derivation is carried out under the assumption that the displacements are small. This enables us to state the system in Lagrangian coordinates. The main difference with respect to the Eulerian framework e.g. in [6] is that in Lagrangian coordinates, the mass conservation law means that the mass density is constant and does not depend on the phase, while the specific volumes of the liquid and solid phases are possibly different. For simplicity, we still assume that viscosity and thermal expansion coefficient do not depend on the phase, the evolution is slow, and the shear viscosity, shear stresses, and inertia effects are negligible.

In Section 1, we describe the model, and the balance equations (energy balance, quasistatic momentum balance, and a phase dynamics equation) are derived in Section 2. Questions of thermodynamic consistency are discussed in Section 3, and in Section 4 we state and prove Theorem 1 on existence and uniqueness of equilibrium configurations in the limit case of rigid boundary. The elastic case can be treated in a similar way, just the computations are slightly more involved.

## 1 The model

As reference state, we consider a liquid substance contained in a bounded connected container $\Omega \subset \mathbb{R}^3$ with boundary of class $C^{1,1}$. The state variables are the absolute temperature $\theta > 0$, the displacement $\mathbf{u} \in \mathbb{R}^3$, and the phase variable $\chi \in [0,1]$. The value $\chi = 0$ means solid, $\chi = 1$ means liquid, $\chi \in (0,1)$ is a mixture of the two.

We make the following modeling hypotheses.

**(A1)** The displacements are small. Therefore, we state the problem in *Lagrangian coordinates*, in which mass conservation is equivalent to the condition of a constant mass density $\rho_0 > 0$.
**(A2)** The substance is isotropic and compressible; the speed of sound and the specific heat may depend on the phase $\chi$.
**(A3)** The evolution is slow, and we neglect shear viscosity and inertia effects.
**(A4)** We neglect shear stresses.

In agreement with **(A1)**, we define the strain $\varepsilon$ as an element of the space $\mathbb{T}^{3\times 3}_{\mathrm{sym}}$ of symmetric tensors by the formula

$$\varepsilon = \nabla_s \mathbf{u} := \frac{1}{2}(\nabla \mathbf{u} + (\nabla \mathbf{u})^T). \tag{1}$$

Let $\delta \in \mathbb{T}^{3\times 3}_{\mathrm{sym}}$ denote the Kronecker tensor. By **(A4)**, the elasticity matrix $\mathbf{A}$ has the form

$$\mathbf{A}\varepsilon = \lambda(\chi)(\varepsilon : \delta)\,\delta\,, \tag{2}$$

where "$:$" is the canonical scalar product in $\mathbb{T}^{3\times 3}_{\mathrm{sym}}$, and $\lambda(\chi) > 0$ is the Lamé constant (or *bulk elasticity modulus*), which may depend of $\chi$ by virtue of **(A2)**.

We model the situation where the specific volume $V_i$ of the solid phase is larger than the specific volume $V_w$ of the liquid phase. In a homogeneous substance, the speed of sound $v_0$ is related to the bulk elasticity modulus $\lambda$ through the formula $v_0 = \sqrt{\lambda/\rho_0}$. Here, in agreement with the Lagrange description, the speeds of sound $v_w$ in water and $v_i$ in ice are related to the corresponding elasticity moduli $\lambda_w, \lambda_i$ through the formulas $\lambda_w = v_w^2/V_w$, $\lambda_i = v_i^2/V_i$. For the moment, we do not specify any particular interpolation $\lambda(\chi)$ between $\lambda_i$ and $\lambda_w$ for $\chi \in (0,1)$. This will only be done in Section 4 together with a motivation for the corresponding choice.

Considering the liquid phase as the reference state, we introduce the dimensionless phase expansion coefficient $\alpha = (V_i - V_w)/V_w > 0$, and we define the phase expansion strain $\tilde{\varepsilon}$ by

$$\tilde{\varepsilon}(\chi) = \frac{\alpha}{3}(1-\chi)\delta\,. \tag{3}$$

The stress tensor $\sigma$ is decomposed into the sum $\sigma^v + \sigma^e$ of the viscous component $\sigma^v$ and elastic component $\sigma^e$, which are assumed in the form

$$\sigma^v = \nu(\varepsilon_t : \delta)\delta \tag{4}$$

$$\sigma^e = (\lambda(\chi)(\varepsilon : \delta - \alpha(1-\chi)) - \beta(\theta - \theta_c))\,\delta\,, \tag{5}$$

where $\nu > 0$ is the volume viscosity coefficient and $\beta$ is the thermal expansion coefficient, which are both assumed constant.

Our main concern is to define the free energy properly. We proceed formally, assuming that the absolute temperature remains positive. This will have to be proved in a subsequent analysis. The process is governed by the following three physical principles:

$$-\operatorname{div}\sigma = \mathbf{f}_{vol} \qquad \text{(mechanical equilibrium)} \tag{6}$$

$$\rho_0 e_t + \operatorname{div}\mathbf{q} = \sigma : \varepsilon_t \qquad \text{(energy balance)} \tag{7}$$

$$\rho_0 s_t + \operatorname{div}\frac{\mathbf{q}}{\theta} \geq 0 \qquad \text{(entropy inequality)} \tag{8}$$

where $\mathbf{f}_{vol}$ is a given volume force density (the gravity force)

$$\mathbf{f}_{vol} = -\rho_0 g\,\delta_3\,, \tag{9}$$

with standard gravity $g$ and vector $\delta_3 = (0,0,1)$, $e$ is the specific internal energy, $s$ is the specific entropy, and $\mathbf{q}$ is the heat flux vector that we assume for simplicity in the form

$$\mathbf{q} = -\kappa(\chi)\nabla\theta \tag{10}$$

with a heat conductivity $\kappa(\chi) > 0$ depending possibly on $\chi$.

We assume the specific heat $c_V(\chi,\theta)$ in the form

$$c_V(\chi,\theta) \;=\; c_0(\chi)c_1(\theta)\,. \tag{11}$$

This is still a rough simplification, and further generalizations are desirable. According to [9, Chapter VI] or [15, Section 5], the purely caloric parts $e_{cal}$ and $s_{cal}$ of the specific internal energy and specific entropy are given by the formulas $e_{cal}(\chi,\theta) = c_0(\chi)e_1(\theta)$, $s_{cal}(\chi,\theta) = c_0(\chi)s_1(\theta)$, with

$$e_1(\theta) = \int_0^\theta c_1(\tau)\,\mathrm{d}\tau\,, \quad s_1(\theta) = \int_0^\theta \frac{c_1(\tau)}{\tau}\,\mathrm{d}\tau\,. \tag{12}$$

By virtue of (7)–(8), the specific free energy $f = e - \theta s$ satisfies the conditions $\sigma^e = \rho_0\partial_\varepsilon f$, $s = -\partial_\theta f$. With a prescribed constant latent heat $L_0$ and freezing point at standard atmospheric pressure $\theta_c > 0$, the specific free energy $f$ necessarily has the form

$$\begin{aligned} f = {} & c_0(\chi)f_1(\theta) + \frac{\lambda(\chi)}{2\rho_0}((\varepsilon - \tilde{\varepsilon}(\chi)) : \delta)^2 \\ & - \frac{\beta}{\rho_0}(\theta - \theta_c)\varepsilon : \delta + L_0\chi\left(1 - \frac{\theta}{\theta_c}\right) + \tilde{f}(\chi)\,, \end{aligned} \tag{13}$$

where

$$f_1(\theta) \;=\; e_1(\theta) - \theta s_1(\theta) \;=\; \int_0^\theta c_1(\tau)\left(1 - \frac{\theta}{\tau}\right) \mathrm{d}\tau\,,$$

and $\tilde{f}$ is a arbitrary function of $\chi$ (integration “constant” with respect to $\theta$ and $\varepsilon$). We choose $\tilde{f}$ so as to ensure that the values of $\chi$ remain in the interval $[0,1]$, and that the phase transition under standard pressure takes place at temperature $\theta_c$. More specifically, we set

$$\tilde{f}(\chi) \;=\; L_0 I(\chi) - c_0(\chi)\, f_1(\theta_c)\,.$$

where $I$ is the indicator function of the interval $[0,1]$. Below in (38)–(40), we come back to the principles of thermodynamics.

For specific entropy $s$ and specific internal energy $e$ we obtain

$$s = -\partial_\theta f = c_0(\chi)s_1(\theta) + \frac{\beta}{\rho_0}\varepsilon : \delta + \frac{L_0}{\theta_c}\chi\,, \tag{14}$$

$$e = c_0(\chi)(e_1(\theta) - f_1(\theta_c)) + \frac{\lambda(\chi)}{2\rho_0}(\varepsilon : \delta - \alpha(1-\chi))^2$$
$$+ \frac{\beta}{\rho_0}\theta_c \varepsilon : \delta + L_0(\chi + I(\chi)). \tag{15}$$

## 2 Balance equations

As another formal consequence of the entropy balance (8), we have the inequality $\chi_t \partial_\chi f \leq 0$ for every process. This will certainly be satisfied if we assume that $-\chi_t$ is proportional to $\partial_\chi f$ with proportionality constant (relaxation time) $\gamma_0 > 0$. It determines how fast the system reaches an equilibrium. We thus consider the evolution system

$$-\mathrm{div}\, \sigma \;=\; \mathbf{f}_{vol}\,, \tag{16}$$

$$\rho_0 e_t + \mathrm{div}\, \mathbf{q} \;=\; \sigma : \varepsilon_t\,, \tag{17}$$

$$-\gamma_0 \chi_t \;\in\; \partial_\chi f\,, \tag{18}$$

where $\partial_\chi$ is the partial Clarke subdifferential with respect to $\chi$. The scalar quantity

$$p := -\nu \varepsilon_t : \delta - \lambda(\chi)(\varepsilon : \delta - \alpha(1-\chi)) + \beta(\theta - \theta_c) \tag{19}$$

is the *pressure* and the stress has the form $\sigma = -p\,\delta$. The equilibrium equation (16) can be rewritten in the form $\nabla p = \mathbf{f}_{vol}$, hence

$$p(x,t) = P(t) - \rho_0 g x_3\,, \tag{20}$$

where $P$ is a function of time only, which is to be determined. Recall that in the reference state $\varepsilon : \delta = \varepsilon_t : \delta = 0$, $\chi = 1$, and at standard pressure $P_{stand}$, the freezing temperature is $\theta_c$. We thus see from (19) that $P(t)$ is in fact the deviation from the standard pressure. We assume also the external pressure in the form $P_{ext} = P_{stand} + p_0$ with a constant deviation $p_0$. The normal force acting on the boundary is $(P(t) - \rho_0 g x_3 - p_0)\mathbf{n}$, where $\mathbf{n}$ denotes the unit outward normal vector. We assume an elastic response of the boundary, and a heat transfer proportional to the inner and outer temperature difference. On $\partial\Omega$, we thus prescribe boundary conditions for $\mathbf{u}$ and $\theta$ in the form

$$(P(t) - \rho_0 g x_3 - p_0)\mathbf{n} = \mathbf{k}(x)\mathbf{u}\,, \tag{21}$$

$$\mathbf{q}\cdot\mathbf{n} = h(x)(\theta - \theta_\Gamma) \tag{22}$$

with a given symmetric positive definite matrix $\mathbf{k}$ (elasticity of the boundary), a positive function $h$ (heat transfer coefficient), and a constant $\theta_\Gamma > 0$ (external temperature). This enables us to find an explicit relation between $\operatorname{div}\mathbf{u}$ and $P$. Indeed, on $\partial\Omega$ we have by (21) that $\mathbf{u}\cdot\mathbf{n} = (P(t) - \rho_0 g x_3 - p_0)\mathbf{k}^{-1}(x)\mathbf{n}(x)\cdot\mathbf{n}(x)$. Assuming that $\mathbf{k}^{-1}\mathbf{n}\cdot\mathbf{n}$ belongs to $L^1(\partial\Omega)$, we set

$$\frac{1}{K_\Gamma} = \int_{\partial\Omega} \mathbf{k}^{-1}(x)\mathbf{n}(x)\cdot\mathbf{n}(x)\,\mathrm{d}\sigma(x)\,, \quad m_\Gamma = K_\Gamma \int_{\partial\Omega} \mathbf{k}^{-1}(x)\mathbf{n}(x)\cdot\mathbf{n}(x)\,x_3\,\mathrm{d}\sigma(x)\,, \tag{23}$$

and obtain by Gauss' Theorem that

$$U_\Omega(t) := \int_\Omega \operatorname{div}\mathbf{u}(x,t)\,\mathrm{d}x = \frac{1}{K_\Gamma}(P(t) - \rho_0 g\, m_\Gamma - p_0)\,. \tag{24}$$

Under the small strain hypothesis, the function $\operatorname{div}\mathbf{u}$ describes the local relative volume increment. Hence, Eq. (24) establishes a linear relation between the total relative volume increment $U_\Omega(t)$ and the relative pressure $P(t) - p_0$. We have $\varepsilon : \delta = \operatorname{div}\mathbf{u}$, and thus the mechanical equilibrium equation (20), due to (19) and (24), reads

$$\nu \operatorname{div}\mathbf{u}_t + \lambda(\chi)(\operatorname{div}\mathbf{u} - \alpha(1-\chi)) - \beta(\theta - \theta_c) + \rho_0 g(m_\Gamma - x_3) = -p_0 - K_\Gamma U_\Omega(t)\,. \tag{25}$$

As a consequence of (10), (13), and (15), the energy balance and the phase relaxation equation in (17)–(18) have the form

$$\begin{aligned} &\rho_0 c_0(\chi) e_1(\theta)_t - \operatorname{div}(\kappa(\chi)\nabla\theta) + \rho_0 c_0'(\chi)\chi_t(e_1(\theta) - f_1(\theta)) \\ &\quad = \nu(\operatorname{div}\mathbf{u}_t)^2 - \beta\theta \operatorname{div}\mathbf{u}_t + \rho_0\gamma_0\chi_t^2 - \rho_0 L_0 \frac{\theta}{\theta_c}\chi_t\,, \end{aligned} \tag{26}$$

$$\begin{aligned} &-\rho_0\gamma_0\chi_t - \frac{\lambda'(\chi)}{2}(\operatorname{div}\mathbf{u} - \alpha(1-\chi))^2 - \alpha\lambda(\chi)(\operatorname{div}\mathbf{u} - \alpha(1-\chi)) \\ &\quad \in \rho_0 c_1'(\chi)\,(f_1(\theta) - f_1(\theta_c)) + \rho_0 L_0\left(1 - \frac{\theta}{\theta_c}\right) + \partial I(\chi)\,. \end{aligned} \tag{27}$$

Note that mathematically, the subdifferential $\partial I(\chi)$ is the same as $\rho_0 L_0 \partial I(\chi)$. For simplicity, we now set

$$c(\chi) := \rho_0 c_0(\chi)\,, \quad \gamma := \rho_0 \gamma_0\,, \quad L := \rho_0 L_0\,. \tag{28}$$

The system now reduces to the following three scalar equations – one PDE and two "ODEs", for three unknown functions $\theta, \chi$, and $U = \operatorname{div} \mathbf{u}$.

$$\begin{aligned} c(\chi) e_1(\theta)_t - \operatorname{div}(\kappa(\chi)\nabla\theta) &= c'(\chi)\chi_t (f_1(\theta) - e_1(\theta)) \\ &\quad + \nu U_t^2 - \beta\theta U_t + \gamma\chi_t^2 - L\frac{\theta}{\theta_c}\chi_t\,, \end{aligned} \tag{29}$$

$$\nu U_t + \lambda(\chi)(U - \alpha(1-\chi)) - \beta(\theta - \theta_c) = \rho_0 g(x_3 - m_\Gamma) - p_0 - K_\Gamma U_\Omega(t)\,, \tag{30}$$

$$\begin{aligned} &-\gamma\chi_t - \frac{\lambda'(\chi)}{2}(U - \alpha(1-\chi))^2 - \alpha\lambda(\chi)(U - \alpha(1-\chi)) \\ &\qquad \in c'(\chi)\,(f_1(\theta) - f_1(\theta_c)) + L\left(1 - \frac{\theta}{\theta_c}\right) + \partial I(\chi) \end{aligned} \tag{31}$$

with $U_\Omega(t) = \int_\Omega U(x,t)\,\mathrm{d}x$, and with boundary condition (22), (10). To find the vector function $\mathbf{u}$, we first define $\Phi$ as a solution to the Poisson equation $\Delta\Phi = U$ with the Neumann boundary condition $\nabla\Phi \cdot \mathbf{n} = (K_\Gamma U_\Omega(t) + \rho_0 g(m_\Gamma - x_3))\mathbf{k}^{-1}(x)\mathbf{n}(x) \cdot \mathbf{n}(x)$. With this $\Phi$, we find $\tilde{\mathbf{u}}$ as a solution to the problem

$$\operatorname{div}\tilde{\mathbf{u}} = 0 \qquad \text{in } \Omega \times \infty\,, \tag{32}$$

$$\left.\begin{aligned} \tilde{\mathbf{u}} \cdot \mathbf{n} &= 0 \\ (\tilde{\mathbf{u}} + \nabla\Phi - (K_\Gamma U_\Omega + \rho_0 g(m_\Gamma - x_3))\mathbf{k}^{-1}\mathbf{n}) \times \mathbf{n} &= 0 \end{aligned}\right\} \quad \text{on } \partial\Omega \times (0,\infty)\,, \tag{33}$$

and set $\mathbf{u} = \tilde{\mathbf{u}} + \nabla\Phi$. Then $\mathbf{u}$ satisfies a.e. in $\Omega$ the equation $\operatorname{div}\mathbf{u} = U$, together with the boundary condition (21), that is, $\mathbf{u} = (K_\Gamma U_\Omega + \rho_0 g(m_\Gamma - x_3))\mathbf{k}^{-1}\mathbf{n}$ on $\partial\Omega$.

For the solution to (32)–(33), we refer to [8, Lemma 2.2] which states that for each $\mathbf{g} \in H^{1/2}(\partial\Omega)^3$ satisfying $\int_{\partial\Omega} \mathbf{g} \cdot \mathbf{n}\,\mathrm{d}\sigma(x) = 0$ there exists a function $\tilde{\mathbf{u}} \in H^1(\Omega)^3$, unique up to an additive function $\mathbf{v}$ from the set $V$ of divergence-free $H^1(\Omega)$ functions vanishing on $\partial\Omega$, such that $\operatorname{div}\tilde{\mathbf{u}} = 0$ in $\Omega$, $\tilde{\mathbf{u}} = \mathbf{g}$ on $\partial\Omega$. In terms of the system (32)–(33), it suffices to set $\mathbf{g} = ((\nabla\Phi - (K_\Gamma U_\Omega + \rho_0 g(m_\Gamma - x_3))\mathbf{k}^{-1}\mathbf{n}) \times \mathbf{n}) \times \mathbf{n}$ and use the identity $(\mathbf{b} \times \mathbf{n}) \times \mathbf{n} = (\mathbf{b} \cdot \mathbf{n})\,\mathbf{n} - \mathbf{b}$ for every vector $\mathbf{b}$. Moreover, the estimate

$$\inf_{\mathbf{v} \in V} \|\tilde{\mathbf{u}} + \mathbf{v}\|_{H^1(\Omega)} \le C\,\|\mathbf{g}\|_{H^{1/2}(\partial\Omega)} \le \tilde{C}\|\Phi\|_{H^2(\Omega)} \tag{34}$$

holds with some constants $C, \tilde{C}$. The required regularity is available here by virtue of the assumption that $\Omega$ is of class $C^{1,1}$, provided $\mathbf{k}^{-1}$ belongs to $H^{1/2}(\partial\Omega)$. Note that a weaker formulation of problem (32)–(33) can be found in [1, Section 4].

Due to our hypotheses **(A3)**, **(A4)**, we thus lose any control on possible volume preserving turbulences $\mathbf{v} \in V$. This, however, has no influence on the system (29)–

(31), which is the subject of our interest here. Inequality (34) shows that if $U$ is small in agreement with hypothesis **(A1)**, then also $\mathbf{v}$ can be chosen in such a way that hypothesis **(A1)**, interpreted in terms of $H^1$, is not violated.

## 3 Energy and entropy

In terms of the new variables $\theta, U, \chi$, the energy $e$ and entropy $s$ can be written as

$$
\begin{aligned}
e = c_0(\chi)(e_1(\theta) - f_1(\theta_c)) + \frac{\lambda(\chi)}{2\rho_0}(U - \alpha(1-\chi))^2 \\
+ \frac{\beta}{\rho_0}\theta_c U + L_0(\chi + I(\chi)) \,, \qquad (35)
\end{aligned}
$$

$$
s = c_0(\chi)s_1(\theta) + \frac{L_0}{\theta_c}\chi + \frac{\beta}{\rho_0}U \,. \qquad (36)
$$

The energy functional has to be supplemented with the boundary energy term

$$
E_\Gamma(t) \;=\; \frac{K_\Gamma}{2}\left(U_\Omega(t) + \frac{p_0 + \rho_0 g m_\Gamma}{K_\Gamma}\right)^2 , \qquad (37)
$$

as well as with the gravity potential $-\rho_0 g x_3 U$. The energy and entropy balance equations now read

$$
\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_\Omega \rho_0(e(x,t) - g x_3 U)\,\mathrm{d}x + E_\Gamma(t)\right) = \int_{\partial\Omega} h(x)(\theta_\Gamma - \theta)\,\mathrm{d}\sigma(x)\,, \qquad (38)
$$

$$
\rho_0 s_t + \operatorname{div}\frac{\mathbf{q}}{\theta} \;=\; \frac{\kappa(\chi)|\nabla\theta|^2}{\theta^2} + \frac{\gamma}{\theta}\chi_t^2 + \frac{\nu}{\theta}U_t^2 \;\geq\; 0\,, \qquad (39)
$$

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \rho_0 s(x,t)\,\mathrm{d}x = \int_{\partial\Omega}\frac{h(x)}{\theta}(\theta_\Gamma - \theta)\,\mathrm{d}\sigma(x) \qquad (40) \\
+ \int_\Omega\left(\frac{\kappa(\chi)|\nabla\theta|^2}{\theta^2} + \frac{\gamma}{\theta}\chi_t^2 + \frac{\nu}{\theta}U_t^2\right)\mathrm{d}x\,.
\end{aligned}
$$

The entropy balance (39) says that the entropy production on the right hand side is nonnegative in agreement with the second principle of thermodynamics. The system is not closed, and the energy supply or the energy loss through the boundary is given by the right hand side of (38).

We prescribe the initial conditions

$$
\theta(x,0) \,=\, \theta^0(x) \qquad (41)
$$

$$
U(x,0) \,=\, U^0(x) \qquad (42)
$$

$$\chi(x,0) = \chi^0(x) \tag{43}$$

for $x \in \Omega$, and compute from (35)–(36) the corresponding initial values $e^0$, $E_\Gamma^0$, and $s^0$ for specific energy, boundary energy, and entropy, respectively. Let $E^0 = \int_\Omega \rho_0 e^0\,\mathrm{d}x$, $S^0 = \int_\Omega \rho_0 s^0\,\mathrm{d}x$ denote the total initial energy and entropy, respectively. From the energy end entropy balance equations (38), (40), we derive the following crucial (formal for the moment) balance equation for the "extended" energy $\rho_0(e - \theta_\Gamma s)$:

$$\begin{aligned}
&\int_\Omega \left( c(\chi)(e_1(\theta) - f_1(\theta_c)) + \frac{\lambda(\chi)}{2}(U - \alpha(1-\chi))^2 \right)(x,t)\,\mathrm{d}x \\
&\quad + \int_\Omega (\beta\theta_c U + L\chi - \rho_0 g x_3 U)(x,t)\,\mathrm{d}x \\
&\quad + \frac{K_\Gamma}{2}\left( U_\Omega(t) + \frac{p_0 + \rho_0 g\, m_\Gamma}{K_\Gamma} \right)^2 \\
&\quad + \theta_\Gamma \int_0^t \int_\Omega \left( \frac{\kappa(\chi)|\nabla\theta|^2}{\theta^2} + \frac{\gamma}{\theta}\chi_t^2 + \frac{\nu}{\theta}U_t^2 \right)(x,\tau)\,\mathrm{d}x\,\mathrm{d}\tau \\
&\quad + \int_0^t \int_{\partial\Omega} \frac{h(x)}{\theta}(\theta_\Gamma - \theta)^2(x,\tau)\,\mathrm{d}\sigma(x)\,\mathrm{d}\tau \\
&= E^0 + E_\Gamma^0 - \theta_\Gamma S^0 + \theta_\Gamma \int_\Omega \left( c(\chi)s_1(\theta) + \frac{L}{\theta_c}\chi + \beta U \right)(x,t)\,\mathrm{d}x\,.
\end{aligned} \tag{44}$$

We assume that both $c(\chi)$ and $\lambda(\chi)$ are bounded from above and from below by positive constants. The growth of $s_1(\theta)$ is dominated by $e_1(\theta)$ as a consequence of the inequality

$$\frac{s_1(\theta) - s_1(\theta^*)}{e_1(\theta) - e_1(\theta^*)} \le \frac{1}{\theta^*} \qquad \forall \theta > \theta^* > 0\,.$$

Hence, there exists a constant $C > 0$ independent of $t$ such that for all $t > 0$ we have

$$\begin{aligned}
&\int_\Omega \left(e_1(\theta) + U^2\right)(x,t)\,\mathrm{d}x + \int_0^t \int_\Omega \left( \frac{|\nabla\theta|^2}{\theta^2} + \frac{\chi_t^2}{\theta} + \frac{U_t^2}{\theta} \right)(x,\tau)\,\mathrm{d}x\,\mathrm{d}\tau \\
&\qquad + \int_0^t \int_{\partial\Omega} \frac{h(x)}{\theta}(\theta_\Gamma - \theta)^2(x,\tau)\,\mathrm{d}\sigma(x)\,\mathrm{d}\tau \;\le\; C\,.
\end{aligned} \tag{45}$$

## 4 Equilibria

It follows from (22) and (29) that the only possible equilibrium temperature is $\theta = \theta_\Gamma$, and the equilibrium configurations $U_\infty, \chi_\infty$ for $U, \chi$ satisfy for a.e. $x \in \Omega$ the equations

$$\lambda(\chi_\infty(x))(U_\infty(x) - \alpha(1 - \chi_\infty(x))) \;=\; \beta(\theta_\Gamma - \theta_c)$$

$$+\rho_0 g(x_3 - m_\Gamma) - p_0 - K_\Gamma \int_\Omega U_\infty(x')\,\mathrm{d}x', \tag{46}$$

$$\begin{aligned} L\left(\frac{\theta_\Gamma}{\theta_c} - 1\right) &+ c'(\chi_\infty(x))\,(f_1(\theta_c) - f_1(\theta_\Gamma)) \\ &-\frac{1}{2}\lambda'(\chi_\infty(x))(U_\infty(x) - \alpha(1-\chi_\infty(x)))^2 \\ &-\alpha\lambda(\chi_\infty(x))(U_\infty(x) - \alpha(1-\chi_\infty(x))) \in \partial I(\chi_\infty(x)), \end{aligned} \tag{47}$$

as a consequence of (30), (31). We now eliminate $U_\infty$ from the above equations. To simplify the formulas, we introduce the notation

$$\left.\begin{array}{ll} S := \int_\Omega (1-\chi_\infty(x'))\,\mathrm{d}x', & U_\Omega := \int_\Omega U_\infty(x')\,\mathrm{d}x', \\ \Lambda := \int_\Omega \frac{\mathrm{d}x'}{\lambda(\chi_\infty(x'))}, & m_\lambda := \frac{1}{\Lambda}\int_\Omega \frac{x_3'}{\lambda(\chi_\infty(x'))}\,\mathrm{d}x'. \end{array}\right\} \tag{48}$$

We see that $S$ is the total solid content, and $U_\Omega$ is the total volume increment. We now divide (46) by $\lambda(\chi_\infty(x))$ and integrate over $\Omega$. This yields

$$(1+K_\Gamma\Lambda)U_\Omega = \alpha S + \Lambda(\beta(\theta_\Gamma - \theta_c) - p_0 + \rho_0 g(m_\lambda - m_\Gamma)).$$

This enables us to replace $U_\Omega$ on the right hand side of (46) and to obtain

$$\begin{aligned} &\lambda(\chi_\infty(x))(U_\infty(x) - \alpha(1-\chi_\infty(x))) \\ &\qquad = \frac{\beta(\theta_\Gamma - \theta_c) - p_0 - \alpha K_\Gamma S}{1+K_\Gamma\Lambda} + \rho_0 g(x_3 - m^*), \end{aligned} \tag{49}$$

where $m^*$ is a convex combination of $m_\Gamma$ and $m_\lambda$, given by

$$m^* = \frac{1}{1+K_\Gamma\Lambda} m_\Gamma + \frac{K_\Gamma\Lambda}{1+K_\Gamma\Lambda} m_\lambda. \tag{50}$$

Eq. (47) can thus be rewritten as

$$\begin{aligned} L\left(\frac{\theta_\Gamma}{\theta_c} - 1\right) &+ c'(\chi_\infty(x))\,(f_1(\theta_c) - f_1(\theta_\Gamma)) \\ &-\frac{\lambda'(\chi_\infty(x))}{2\lambda^2(\chi_\infty(x))}\left(\frac{\beta(\theta_\Gamma - \theta_c) - p_0 - \alpha K_\Gamma S}{1+K_\Gamma\Lambda} + \rho_0 g(x_3 - m^*)\right)^2 \\ &-\alpha\left(\frac{\beta(\theta_\Gamma - \theta_c) - p_0 - \alpha K_\Gamma S}{1+K_\Gamma\Lambda} + \rho_0 g(x_3 - m^*)\right) \in \partial I(\chi_\infty(x)). \end{aligned} \tag{51}$$

Approximate values of the physical constants are listed in Table 1, see [7, 18, 19, 22].

| | | | |
|---|---|---|---|
| Specific volume of water | $V_w = 1/\rho_0$ | $10^{-3}$ | $m^3/kg$ |
| Specific volume of ice | $V_i$ | $1.09 \cdot 10^{-3}$ | $m^3/kg$ |
| Speed of sound in water | $v_w$ | $1.5 \cdot 10^3$ | $m/s$ |
| Speed of sound in ice | $v_i$ | $3.12 \cdot 10^3$ | $m/s$ |
| Elasticity modulus of water | $\lambda_w = v_w^2/V_w$ | $2.25 \cdot 10^9$ | $Pa = J/m^3 = kg/ms^2$ |
| Elasticity modulus of ice | $\lambda_i = v_i^2/V_i$ | $9 \cdot 10^9$ | $Pa = J/m^3 = kg/ms^2$ |
| Specific heat of water | $c_w$ | $4.2 \cdot 10^3$ | $J/kgK = m^2/s^2K$ |
| Specific heat of ice | $c_i$ | $2.1 \cdot 10^3$ | $J/kgK = m^2/s^2K$ |
| Latent heat | $L_0$ | $3.34 \cdot 10^5$ | $J/kg = m^2/s^2$ |
| Thermal expansion coefficient | $\beta$ | $4.5 \cdot 10^5$ | $J/m^3K = kg/ms^2K$ |
| Melting temperature at standard pressure | $\theta_c$ | 273 | $K$ |
| Standard atmospheric pressure | $p_0$ | $10^5$ | $Pa = J/m^3 = kg/ms^2$ |
| Phase expansion coefficient | $\alpha = (V_i - V_w)/V_w$ | 0.09 | |
| Gravity constant | $g$ | 9.8 | $m/s^2$ |

**Table 1** Physical constants for water

In order to draw some conclusions about the solutions to (51), we eliminate the $\chi$-dependence and non-monotonicities in $\theta_\Gamma$ on the left hand side of (51) by choosing the following nonlinearities:

$$\lambda(\chi) = \left(\frac{1}{\lambda_i} + \left(\frac{1}{\lambda_w} - \frac{1}{\lambda_i}\right)\chi\right)^{-1}, \tag{52}$$

$$c(\chi) = \frac{c_i}{V_i} + \left(\frac{c_w}{V_w} - \frac{c_i}{V_i}\right)\chi\,, \tag{53}$$

$$c_1(\theta) = \left(\frac{\theta}{\theta_c}\right)^{\xi}, \tag{54}$$

with a constant $\xi > 0$. The function $f_1$ is, consequently,

$$f_1(\theta) = -\frac{1}{\xi(1+\xi)}\frac{\theta^{1+\xi}}{\theta_c^{\xi}}. \tag{55}$$

This is again a very rough approximation. In reality, for temperatures near zero Kelvin, the exponent $\xi$ should be 3 according to the Einstein-Debye law, while for large temperatures, it should vanish. Our choice is motivated by the effort to keep the number of parameters as low as possible.

Assuming (52)–(54), we write (51) in explicit form

$$L\left(\frac{\theta_\Gamma}{\theta_c} - 1\right) + \frac{\theta_c}{\xi(1+\xi)}\left(\frac{c_w}{V_w} - \frac{c_i}{V_i}\right)\left(\left(\frac{\theta_\Gamma}{\theta_c}\right)^{1+\xi} - 1\right)$$
$$+\frac{1}{2}\left(\frac{1}{\lambda_w} - \frac{1}{\lambda_i}\right)\left(\frac{\beta(\theta_\Gamma - \theta_c) - p_0 - \alpha K_\Gamma S}{1 + K_\Gamma \Lambda} + \rho_0 g(x_3 - m^*)\right)^2$$

$$-\alpha\left(\frac{\beta(\theta_\Gamma-\theta_c)-p_0-\alpha K_\Gamma S}{1+K_\Gamma\Lambda}+\rho_0 g(x_3-m^*)\right) \in \partial I(\chi_\infty(x)), \quad (56)$$

with

$$\Lambda=\frac{1}{\lambda_w}|\Omega|-\left(\frac{1}{\lambda_w}-\frac{1}{\lambda_i}\right)S. \quad (57)$$

To estimate an appropriate value of $\xi$, let us neglect the gravity forces (which are indeed very small as we shall see) and assume the rigid limit $K_\Gamma\to\infty$. We have

$$R:=\frac{S}{\lambda_i\Lambda} = \frac{\frac{1}{\lambda_i}\frac{S}{|\Omega|}}{\frac{1}{\lambda_w}-\left(\frac{1}{\lambda_w}-\frac{1}{\lambda_i}\right)\frac{S}{|\Omega|}} \in [0,1]. \quad (58)$$

Eq. (56) then reads in dimensionless form

$$\frac{L}{\alpha^2\lambda_i}\left(\frac{\theta_\Gamma}{\theta_c}-1\right)+\frac{1}{\xi(1+\xi)}\frac{\theta_c}{\alpha^2\lambda_i}\left(\frac{c_w}{V_w}-\frac{c_i}{V_i}\right)\left(\left(\frac{\theta_\Gamma}{\theta_c}\right)^{1+\xi}-1\right)$$
$$+\frac{1}{2}\left(\frac{\lambda_i}{\lambda_w}-1\right)R^2+R \in \partial I(\chi_\infty(x)). \quad (59)$$

For $\theta_\Gamma\geq\theta_c$, the left hand side of (59) is nonnegative, hence necessarily $\chi_\infty(x)=1$ for (almost) all $x\in\Omega$ and $S=R=0$. Because of the pressure increase due to solidification, the liquid phase persists also for temperatures below $\theta_c$. We only obtain pure ice $\chi_\infty=0$ if the left hand side of (59) with $R=1$ is nonpositive, that is, if $\theta_\Gamma\leq y\theta_c$, where $y\in(0,1)$ is the solution (if it exists) to the equation

$$C_1(y-1)+\frac{C_2}{\xi(1+\xi)}(y^{1+\xi}-1)+C_3 = 0, \quad (60)$$

with dimensionless constants

$$C_1=\frac{L}{\alpha^2\lambda_i}, \quad C_2=\frac{\theta_c}{\alpha^2\lambda_i}\left(\frac{c_w}{V_w}-\frac{c_i}{V_i}\right), \quad C_3=\frac{1}{2}\left(\frac{\lambda_i}{\lambda_w}-1\right)+1.$$

For the values of the constants in Table 1, we obtain

$$C_1\approx 4.58, \quad C_2\approx 8.5, \quad C_3\approx 2.5, \quad (61)$$

hence the solution $y=y(\xi)$ to (60) exists for all $\xi>0$, and we easily compute the limits $\lim_{\xi\to 0+}y(\xi)=1$, $\lim_{\xi\to+\infty}y(\xi)=1-C_3/C_1$. Assume that we know the full solidification temperature $\theta_s$, and that

$$(1-C_3/C_1)\theta_c<\theta_s<\theta_c. \quad (62)$$

Then we identify the value of $\xi$ from the equation $y(\xi)=\theta_s/\theta_c$, that is,

$$\varphi(\xi) := C_2\left(\frac{\theta_s}{\theta_c}\right)^{1+\xi} + \left(C_3 + C_1\left(\frac{\theta_s}{\theta_c} - 1\right)\right)\xi(1+\xi) \;=\; 1\,. \tag{63}$$

The function $\varphi$ is convex in $(0,\infty)$, $\varphi(0) < 1$, $\varphi(+\infty) = +\infty$. Eq. (63) thus determines the desired value of $\xi$ uniquely.

Still in the rigid limit $K_\Gamma \to \infty$, consider now the gravity effects in Eq. (56). Then, by (48) and (50), we have $m^* = m_\lambda \in (a,b)$, and the counterpart of Eq. (59) reads

$$(C_3-1)(R-\eta(x_3-m_\lambda))^2 + (R-\eta(x_3-m_\lambda)) - C_4(\theta_\Gamma) \;\in\; \partial I(\chi_\infty(x))\,, \tag{64}$$

where

$$C_4(\theta_\Gamma) := C_1\left(1-\frac{\theta_\Gamma}{\theta_c}\right) + \frac{C_2}{\xi(1+\xi)}\left(1-\left(\frac{\theta_\Gamma}{\theta_c}\right)^{1+\xi}\right),$$

$C_1, C_2, C_3$ are as above, and

$$\eta \;=\; \frac{\rho_0 g}{\alpha\lambda_i} \;\approx\; 1.2\cdot 10^{-5}\;[m^{-1}]\,. \tag{65}$$

The left hand side of (64) is a function of $x_3$ only. Let the interval $(a,b)$ be the projection of $\Omega$ onto the $x_3$-axis, that is,

$$x_3 \in (a,b) \;\Leftrightarrow\; \exists (x_1,x_2) \in \mathbb{R}^2 : (x_1,x_2,x_3) \in \Omega\,.$$

We prove the following result.

**Theorem 1.** *Let the height $b-a$ of the container satisfy the inequality*

$$2\eta(b-a)(C_3-1) < 1\,. \tag{66}$$

*Then Eq. (64) admits a solution $\chi_\infty \in L^\infty(\Omega)$. Moreover, there exist temperatures $\theta_w > \theta_c > \theta_i > 0$ such that $\chi_\infty \equiv 1$ if $\theta_\Gamma \ge \theta_w$, $\chi_\infty \equiv 0$ if $\theta_\Gamma \le \theta_i$, and for $\theta_\Gamma \in (\theta_i,\theta_w)$ there exists $z \in (a,b)$ such that $\chi_\infty(x) = 1$ for $x_3 < z$, $\chi_\infty(x) = 0$ for $x_3 > z$.*

Condition (66) is not too restrictive. With the values in (61) and (65), the maximal admissible height is almost 30 km. The solution may not be unique if the shape of $\Omega$ is very irregular. If $\Omega$ is a straight vertical cylinder $\Omega = \Omega_{2D} \times (a,b)$, for example, where $\Omega_{2D} \subset \mathbb{R}^2$ is fixed, the proof below shows that the solution is unique.

The interval $(\theta_c,\theta_w)$ of "overheated ice temperatures" is very narrow, of the size of $\eta(b-a)$, and corresponds to the low pressure ice layer on the top of the container.

*Proof.* The left hand side of (64) is always nonnegative if $4C_4(\theta_\Gamma)(C_3-1)+1 \le 0$, that is, if $\theta_\Gamma$ is above a certain temperature slightly bigger than $\theta_c$. In this case, $\chi_\infty(x) = 1$ for all $x \in \Omega$ independently of the height $b-a$. Assume now

$$4C_4(\theta_\Gamma)(C_3-1)+1 > 0\,.$$

Then the left hand side of (64) is positive if and only if

$$\eta(x_3 - m_\lambda) < R + \frac{1}{2(C_3-1)}\left(1 - \sqrt{4C_4(\theta_\Gamma)(C_3-1)+1}\right) \tag{67}$$

or

$$\eta(x_3 - m_\lambda) > R + \frac{1}{2(C_3-1)}\left(1 + \sqrt{4C_4(\theta_\Gamma)(C_3-1)+1}\right). \tag{68}$$

Condition (68) is in contradiction with the assumption (66), hence the exists at most one

$$z = m_\lambda + \frac{1}{\eta}\left(R + \frac{1}{2(C_3-1)}\left(1 - \sqrt{4C_4(\theta_\Gamma)(C_3-1)+1}\right)\right) \in (a,b)$$

such that the left hand side of (64) is positive for $x_3 < z$ and negative for $x_3 > z$. By definition of the subdifferential of the indicator function on the right hand side of (64), we then have $\chi_\infty(x) = 1$ for $x_3 < z$, $\chi_\infty(x) = 0$ for $x_3 > z$, as expected. It remains to determine $z$. Assume first that such a $z$ exists. Then both $R = R(z)$ and $m_\lambda = m_\lambda(z)$ are functions of $z$. We denote

$$\Omega(z) \;=\; \{x = (x_1,x_2) \in \mathbb{R}^2 : (x_1,x_2,z) \in \Omega\}.$$

The set $\Omega(z)$ is empty for $z \geq b$ and for $z \leq a$. Let $\omega(z)$ be the 2D Lebesgue measure of $\Omega(z)$. Then, by (58), we have

$$R(z) \;=\; \frac{\frac{1}{\lambda_i}\int_z^b \omega(s)\,\mathrm{d}s}{\frac{1}{\lambda_w}\int_a^z \omega(s)\,\mathrm{d}s + \frac{1}{\lambda_i}\int_z^b \omega(s)\,\mathrm{d}s},$$

and by (48),

$$m_\lambda(z) \;=\; \frac{\frac{1}{\lambda_w}\int_a^z s\,\omega(s)\,\mathrm{d}s + \frac{1}{\lambda_i}\int_z^b s\,\omega(s)\,\mathrm{d}s}{\frac{1}{\lambda_w}\int_a^z \omega(s)\,\mathrm{d}s + \frac{1}{\lambda_i}\int_z^b \omega(s)\,\mathrm{d}s}.$$

The dependence of $z$ on $\theta_\Gamma$ is given by the equation

$$z - m_\lambda(z) - \frac{1}{\eta}R(z) = \frac{1}{\eta}\left(\frac{1}{2(C_3-1)}(1 - \sqrt{4C_4(\theta_\Gamma)(C_3-1)+1})\right). \tag{69}$$

The left hand side of (69) is a continuous function of $z$, which is negative for $z = a$ and positive for $z = b$, and the statement of Theorem 1 easily follows. For a straight cylinder $\Omega = \Omega_{2D} \times (a,b)$, where $\Omega_{2D} \subset \mathbb{R}^2$ is fixed, the left hand side of (69) is an increasing function of $z$, hence the solution is unique. □

*Remark 1.* We can interpret Eqs. (46)–(47) in another way. On the interface $x_3$ between water and ice, the left hand side of (47) vanishes, and (46) has the form

$$\lambda(\chi_\infty(x))(U_\infty(x) - \alpha(1-\chi_\infty(x))) \;=\; \beta(\theta_\Gamma - \theta_c) - P_\infty, \tag{70}$$

where $P_\infty = p_0 + K_\Gamma U_\Omega + \rho_0 g(m_\Gamma - x_3)$ is the equilibrium pressure in agreement with (19). Hence, (47) can be reformulated in terms of $P_\infty$ as

$$L\left(\frac{\theta_\Gamma}{\theta_c}-1\right)+\left(\frac{c_w}{V_w}-\frac{c_i}{V_i}\right)(f_1(\theta_c)-f_1(\theta_\Gamma))$$
$$+\frac{1}{2}\left(\frac{1}{\lambda_w}-\frac{1}{\lambda_i}\right)(\beta(\theta_\Gamma-\theta_c)-P_\infty)^2-\alpha(\beta(\theta_\Gamma-\theta_c)-P_\infty) \;=\; 0. \qquad (71)$$

This would be the Clausius-Clapeyron relation in the sense of [21, Equation (288)] if $c_w/V_w = c_i/V_i$ and $\lambda_i = \lambda_w$, namely

$$\frac{P_\infty}{\theta_\Gamma-\theta_c}=\frac{L_\beta}{\theta_c(V_w-V_i)},$$

where $L_\beta = L_0-(\alpha\beta\theta_c)/\rho_0$ is the modified latent heat. In our case, the modified latent heat contains additional terms related to the differences in elasticity moduli and in specific heat capacities.

*Remark 2.* Note that in the fully solidified rigid limit case, the equilibrium pressure is very high, namely (up to negligible contributions due to gravity and thermal expansion) $P_\infty \approx \alpha\lambda_i \approx 0.81\,GPa$.

**Conclusion**. A model is proposed for describing the dynamics of freezing/melting of water in an elastic container, taking into account the differences in specific volume, specific heat, and speed of sound in water and in ice. The process is described by one parabolic PDE, one integrodifferential ODE, and one differential inclusion for three unknown functions – the absolute temperature, relative volume increment, and liquid fraction. A study of the equilibria in the rigid limit is carried out in detail.

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