SOLIDIFICATION AND SEPARATION IN SALINE WATER

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Abstract. Motivated by the formation of brine channels, this paper is devoted to a continuum model for salt separation and phase transition in saline water. The mass density and the concentrations of salt and ice are the pertinent variables describing saline water. Hence the balance of mass is considered for the single constituents (salt, water, ice). To keep the model as simple as possible, the balance of momentum and energy are considered for the mixture as a whole. However, due to the internal structure of the mixture, an extra-energy flux is allowed to occur in addition to the heat flux. Also, the mixture is allowed to be viscous. The constitutive equations involve the dependence on the temperature, the mass density of the mixture, the salt concentration and the ice concentration, in addition to the stretching tensor, and the gradient of temperature and concentrations. The balance of mass for the single constituents eventually result in the evolution equations for the concentrations. A whole set of constitutive equations compatible with thermodynamics are established. A free energy function is given which allows for capturing the main feature which occurs during the freezing of the salted water. That is, the salt entrapment in small regions (brine channels) where the cryoscopic effect forbids complete ice formation.

1. **Introduction.** Saline water exhibits interesting phenomena which call for an appropriate modelling within continuum mechanics. The presence of salt (solute) in water (solvent) results in the freezing point depression or *cryoscopic effect*: by adding a solute to a solvent (as salt in water) produces a decrease in the freezing point of the solvent. In addition, the extent of freezing point depression depends only on the solute concentration and can be estimated by a simple linear relationship. Approximately, in a uniform water-salt (NaCl) solution the freezing temperature θ_T linearly decreases with salt concentration,

$$\theta_T(c) = \theta_\tau - \alpha_0 c, \qquad \alpha_0 > 0, \tag{1.1}$$

where θ_τ is the *solidification temperature of pure water* ($\approx 273°$K) and α_0 is a positive constant that will be specified later.

In saline water at room temperature the spatial variability of salinity is not so important because of the solubility. However, as water reaches the temperature where it begins to crystallize and form ice (phase transition), salt ions are rejected from the lattices within the ice: they are either forced out into the surrounding water, or trapped among the ice crystals in pockets called *brine cells*, where the high concentration of salt and the cryoscopic effect prevent complete ice formation.

1.1. **Brine rejection process.** During the freezing of saline water, the dissolved salts are not incorporated into the ice crystals, but increases the salinity of the liquid phase. When the salinity c is over $\xi_b = 0.05$, the solution is named *brine*, and the process creating saltier, denser brine within the sea ice is a separation process referred to as *brine rejection* [14]. At the end of the freezing process, the salt concentration of the remaining liquid solution never reaches the unit value. Indeed, it has an upper limit which depends on temperature and is referred to as *solubility limit of salt relative to the water*. At room temperature ($\theta_r \approx 291°$K), its value is $\xi_s \approx 0.27$. When c overcome this limit, then salt begins to crystallize and precipitates. In the phase diagram of a salt-water mixture there exists a characteristic point, named *eutectic point*, at which ice, salt and the water solution are in equilibrium. The specific concentration and temperature at which this equilibrium is found are called *eutectic concentration*, ξ_ℓ (≈ 0.23), and *eutectic temperature*, θ_σ ($\approx 252°$K), respectively (see Fig. 1).
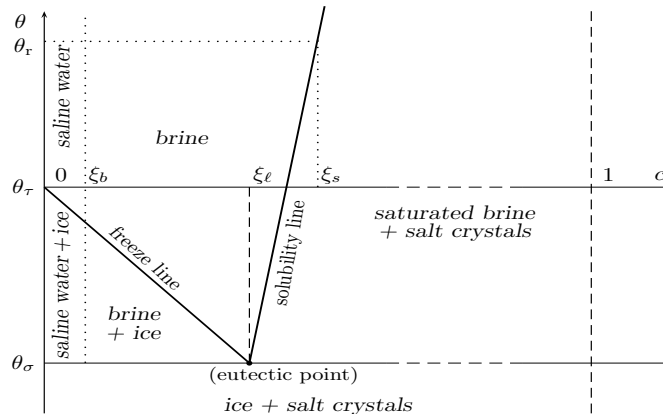

FIGURE 1. Phase diagram of a water-salt (NaCl) solution.

Since the eutectic temperature equals the freezing temperature at the eutectic concentration, $\theta_\sigma = \theta_T(\xi_\ell)$, from the *freeze-line* equation (1.1) it follows

$$\alpha_0 = (\theta_\tau - \theta_\sigma)/\xi_\ell \approx 91,3°\text{K}.$$

At temperatures below the eutectic point, the solution becomes a mixture involving ice and salt crystals separately (see, for instance, [12]). This phenomenon is referred to as *eutectic freeze crystallization* (EFC).

1.2. **Brine channels formation.** The formation of *brine channels* in sea ice is a typical outcome of the spatial variability of salinity and the brine separation process. This phenomenon occurs in frozen sea water that forms in the Arctic Ocean, and in the Southern Ocean surrounding Antarctica. During the brine rejection process, salt ions are trapped among the ice crystals in pockets called *brine cells*. The faster that this freezing process occurs, the more brine cells are left in the sea ice. They create a porous (mushy) layer in which concentrated liquid surrounds nearly pure solid ice crystals. Once this layer reaches a critical thickness (≈ 15 cm), the concentration of salt ions in the liquid around the ice begins to increase, as leftover liquid begins to leave the brine cells. This increase is associated with the appearance of strong convective plumes, which flow from channels within the ice and carry a significant salt flux. The brine that drains from the mushy layer is replaced by a weak flow of relatively fresh water, from the liquid region below it. The new water partially freezes within the pores of the mushy layer, increasing the solidity of the ice, and partially remains between the crystals to form brine channels with average diameters of 100 μm that may increase to millimeter sized tubes.

1.3. **A new theoretical approach.** Useful references to the subject are given in a paper by Kutschan et al [13] where experimental observations are commented upon and a theoretical approach is set up. In [13] the pertinent variables are taken to be the water salinity and an order parameter (tetrahedricity) which accounts for the ice microstructure. The temperature is regarded as a parameter governing the phase transition. The model equations are two reaction-diffusion equations which trace back to the Ginzburg-Landau theory.

Though the experimental observations show an involved set of physical effects, here we set aside some features about the microscopic properties (ice microstructure, presence of air bubbles, pH value) and develop a consistent scheme where balance and constitutive equations are framed within continuum thermodynamics. We take the mass density and the concentrations of salt and ice to be the pertinent variables describing saline water. Hence we write the balance equations for them as with a mixture of three constituents (salt, water, ice).

To keep the model as simple as possible we account for the balance of momentum and energy as for a single constituent. However, due to the internal structure of the mixture we allow for an extra-energy flux, in addition to the heat flux. Also we account for motion and diffusion effects by letting the stress in the mixture have additive viscous terms. As a result we obtain a whole set of evolution equations for the mass density, the concentrations, the velocity, and the temperature through the balance of mass, linear momentum, and energy.

The main aspects to emerge from this paper are summarized as follows. The constitutive equations allow for the dependence on the temperature θ, the mass density ρ, the salt concentration c and the ice concentration ϕ in addition to the stretching tensor, and the gradient of θ, c, and ϕ. The balance of mass is established for the single constituents and the corresponding equations provide eventually the evolution equations for c and ϕ. A whole set of constitutive equations compatible with thermodynamics are established. A free energy function is given by borrowing from the separate modelling of phase separation and phase transition. This choice allows us to capture the main feature which occurs during the freezing of the salted water, namely, the salt entrapment in small regions where the cryoscopic effect forbid complete ice formation. The generalization with respect to previous approaches is pointed out.

2. **A mixture model for saline water and ice.** We model saline water and ice as a mixture of three constituents occupying a time-dependent region $\Omega \subset \mathbb{R}^3$. Denote by the subscripts s, w, i the quantities pertaining to salt, water and ice. Accordingly, ρ_s, ρ_w, ρ_i are the mass densities of salt, water and ice and

$$\rho = \rho_s + \rho_w + \rho_i$$

is the mass density of the mixture. We let at least one of the components be compressible and this makes the use of concentrations more convenient than that of volume fractions. Let c, ϕ be the concentrations of salt and ice,

$$c = \frac{\rho_s}{\rho}, \qquad \phi = \frac{\rho_i}{\rho}.$$

Also let

$$\xi = \frac{\rho_s}{\rho_s + \rho_w}$$

be the concentration of salt relative to water. It follows that

$$\frac{1}{c} = \frac{\rho_i}{\rho_s} + \frac{\rho_s + \rho_w}{\rho_s} = \frac{\phi}{c} + \frac{1}{\xi}$$

and hence

$$c = \xi(1 - \phi). \tag{2.1}$$

Since $\phi, c, \xi \in [0, 1]$, each of them can be regarded as a phase field. As a consequence, we may regard as independent variables the triplet ρ, ϕ, c or ρ, ϕ, ξ, the two triplets being in 1-1 correspondence except when $\phi = 1$ or $\rho_w = 0$. In terms of the two triplets we have

$$\rho_s = \rho c = \rho(1 - \phi)\xi, \qquad \rho_i = \rho\phi, \qquad \rho_w = \rho(1 - c - \phi) = \rho(1 - \xi)(1 - \phi).$$

Let M_s, M_w, and M_i be the whole masses of salt, water, and ice of the mixture. We define

$$c_* := \frac{M_s}{M_s + M_w + M_i}, \qquad \xi_* := \frac{M_s}{M_s + M_w}.$$

So c_* (ξ_*) is the mean value of c (ξ) when the salt is distributed uniformly in the mixture (in the water). On the other hand, ξ_* cannot exceed ξ_s, the solubility of salt relative to water. According to their definitions, we infer that $c_* \leq \xi_* \leq \xi_s$. Typically, seawater in the world's oceans has a uniform salinity $c_* \approx 0.035$.

For further convenience, we shall identify ξ_ℓ and ξ_s, since they differ for less than 4%. Accordingly, the phase diagram in the concentration-temperature plane may be represented in a simplified form (see Fig. 2). Since the aim of this study is brine rejection, we are not interested in the precipitation phenomena which occurs for concentration values beyond ξ_ℓ. Then, hereafter, we restrict our attention to $c \in [0, \xi_\ell]$.

We now state the local form of the balance equations. Let $\mathbf{v}_s, \mathbf{v}_w, \mathbf{v}_i$ be the velocity fields. The barycenter velocity $\mathbf{v}$ is given by

$$\mathbf{v} = c\mathbf{v}_s + \phi\mathbf{v}_i + (1 - c - \phi)\mathbf{v}_w.$$

Let $\mathbf{u}_s, \mathbf{u}_i$ be the diffusion velocities and $\mathbf{j}_s, \mathbf{j}_i$ the mass fluxes,

$$\mathbf{u}_s = \mathbf{v}_s - \mathbf{v}, \quad \mathbf{u}_i = \mathbf{v}_i - \mathbf{v}, \qquad \mathbf{j}_s = \rho c \mathbf{u}_s, \quad \mathbf{j}_i = \rho\phi\mathbf{u}_i.$$

The mass of salt is conserved and hence ρ_s satisfies the continuity equation

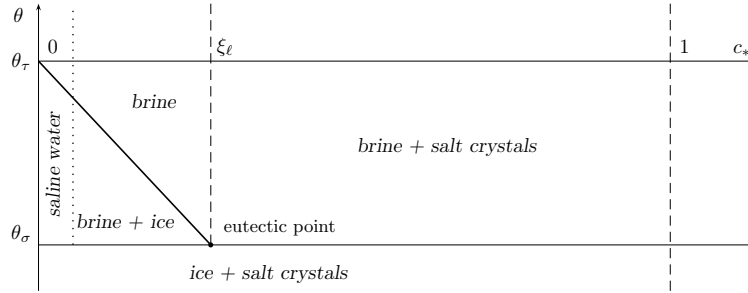$$\partial_t \rho_s + \nabla \cdot (\rho c \mathbf{v}_s) = 0, \tag{2.2}$$

FIGURE 2. Simplified phase diagram of a water-salt (NaCl) solution.

where ∂_t denotes the partial derivative with respect to time t. Given any function $\psi(t, \mathbf{x})$, $t \in \mathbb{R}, \mathbf{x} \in \Omega$, we denote by a superposed dot the barycentric time derivative so that

$$\dot{\psi} = \partial_t \psi + \mathbf{v} \cdot \nabla \psi.$$

Hence by (2.2) it follows that

$$\rho \dot{c} = -\nabla \cdot \mathbf{j}_s. \tag{2.3}$$

The global conservation of mass for salt implies that

$$\int_\Omega \rho c \, dv = \text{constant}.$$

Hence it follows that

$$0 = \frac{d}{dt} \int_\Omega \rho c \, dv = \int_\Omega \rho \dot{c} \, dv.$$

By (2.3) and the divergence theorem we have

$$\int_{\partial \Omega} \mathbf{j}_s \cdot \mathbf{n} \, da = 0, \tag{2.4}$$

where $\mathbf{n}$ is the unit outward normal to the boundary $\partial \Omega$ of Ω. For definiteness we account for (2.4) by letting

$$\mathbf{j}_s \cdot \mathbf{n} = 0 \qquad \text{at} \quad \partial \Omega.$$

Because of the phase transition, ice and water are regarded as chemically reacting continua so that ρ_i satisfies the continuity equation

$$\partial_t \rho_i + \nabla \cdot (\rho \phi \mathbf{v}_i) = \tau, \tag{2.5}$$

where τ is the mass of ice produced per unit time and unit volume because of the phase transition. Hence it follows that

$$\rho \dot{\phi} = -\nabla \cdot \mathbf{j}_i + \tau. \tag{2.6}$$

Accordingly, the continuity equation for ρ_w becomes

$$\partial_t \rho_w + \nabla \cdot (\rho_w \mathbf{v}_w) = -\tau. \tag{2.7}$$

Summation of (2.2), (2.5), (2.7) provides the continuity equation for the mixture,

$$\dot{\rho} = -\rho \nabla \cdot \mathbf{v}. \tag{2.8}$$

We might go on and consider the evolution equation for $\mathbf{j}_s$ and $\mathbf{j}_i$. For simplicity, though, following a standard view in the modelling of mixtures, we regard $\mathbf{j}_s$ and $\mathbf{j}_i$ as unknown functions subject to thermodynamic restrictions.

When focusing on the triplet of independent variables (ρ, ϕ, ξ), by virtue of (2.1) we have

$$\dot{c} = (1 - \phi)\dot{\xi} - \xi\dot{\phi},$$

and then it is convenient to replace (2.3) with

$$\rho(1 - \phi)\dot{\xi} = \xi\tau - \nabla \cdot \mathbf{j}_s - \xi\nabla \cdot \mathbf{j}_i. \tag{2.9}$$

The balance of linear momentum for the mixture is given in the standard form

$$\rho\dot{\mathbf{v}} = \nabla \cdot \mathbf{T} + \rho\mathbf{f}, \tag{2.10}$$

where $\mathbf{T}$ is the stress tensor and $\mathbf{f}$ is the body force density. The stress $\mathbf{T}$ is taken to be symmetric, as it follows from the balance of angular momentum.

About the balance of energy and entropy, the (total) energy flux $\mathbf{h}$ and the entropy flux $\boldsymbol{\Phi}$ need not be merely related by

$$\boldsymbol{\Phi} = \frac{1}{\theta}\mathbf{h}.$$

Also, different definitions of $\mathbf{h}$ and $\boldsymbol{\Phi}$ lead to significantly different consequences about thermodynamic restrictions. To fix ideas we let

$$\mathbf{h} = \mathbf{q} + \mathbf{w}$$

and regard $\mathbf{q}$ as the heat flux and $\mathbf{w}$ as an extra-energy flux as is done e.g. in [15] where the extra-energy flux is considered as $\mathbf{t}\dot{c}$, $\mathbf{t}$ being an appropriate generalized force. The balance of energy is then taken in the form

$$\rho(e + \frac{1}{2}\mathbf{v}^2)\dot{} = \nabla \cdot (\mathbf{T}\mathbf{v} - \mathbf{q}) - \nabla \cdot \mathbf{w} + \rho\mathbf{f} \cdot \mathbf{v} + \rho r,$$

where e is the energy density, $\mathbf{L}$ the velocity gradient and r the heat supply (per unit volume). In view of (2.10) it follows that

$$\rho\dot{e} = \mathbf{T} \cdot \mathbf{L} - \nabla \cdot \mathbf{q} - \nabla \cdot \mathbf{w} + \rho r. \tag{2.11}$$

Beacuse of its internal character, and hence differently from $\mathbf{q}$, $\mathbf{w}$ is required to satisfy the boundary condition

$$\mathbf{w} \cdot \mathbf{n} = 0 \quad \text{at } \partial\Omega.$$

The second law is taken as the statement that the entropy density η satisfies the inequality

$$\rho\dot{\eta} \geq \frac{\rho r}{\theta} - \nabla \cdot \frac{\mathbf{q}}{\theta}$$

for every process compatible with the balance equations (2.3), (2.6), (2.8), (2.10), (2.11). Hence substitution of $\rho r - \nabla \cdot \mathbf{q}$ from (2.11) and use of the free energy $\psi = e - \theta\eta$ provide the Clausius-Duhem (or second law) inequality in the form

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \mathbf{T} \cdot \mathbf{L} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \nabla \cdot \mathbf{w} \geq 0. \tag{2.12}$$

3. **Thermodynamic restrictions.** Let $\mathbf{D} = \mathrm{sym}\mathbf{L}$ be the stretching tensor. A superposed ring $\circ$ denotes the deviatoric part. Since $\mathrm{tr}\,\mathbf{L} = \mathrm{tr}\,\mathbf{D} = \nabla \cdot \mathbf{v}$ then

$$\overset{\circ}{\mathbf{L}} = \mathbf{L} - \frac{1}{3}(\nabla \cdot \mathbf{v})\mathbf{1}, \qquad \overset{\circ}{\mathbf{D}} = \mathbf{D} - \frac{1}{3}(\nabla \cdot \mathbf{v})\mathbf{1}.$$

We assume that $\mathbf{j}_s$, $\mathbf{j}_i$, $\mathbf{T}$, $\mathbf{w}$ are determined by the set of variables

$$\Gamma = (\theta, \rho, c, \phi, \nabla\theta, \nabla c, \nabla\phi, \mathbf{D}, ...),$$

through appropriate constitutive functions, the dots indicating possible higher-order gradients of $\theta, c, \phi, \mathbf{D}$. Also we let ψ be given by a C^2-function of

$$\Gamma_0 = (\theta, \rho, c, \phi, \nabla\theta, \nabla c, \nabla\phi).$$

For a direct interpretation of the results, we eventually regard ξ and ϕ as independent variables instead of c and ϕ. Technically, though, because of (2.3) and (2.6) it is convenient to start with c and ϕ as independent variables and next to regard the dependence on c and ϕ through that on ξ and ϕ.

Time differentiation of $\psi(\Gamma_0)$ and substitution in (2.12) gives

$$-\rho[(\partial_\theta\psi + \eta)\dot{\theta} + \partial_\rho\psi\dot{\rho} + \partial_c\psi\dot{c} + \partial_\phi\psi\dot{\phi} + \partial_{\nabla c}\psi \cdot \overline{\dot{\nabla c}} + \partial_{\nabla c}\psi \cdot \overline{\dot{\nabla c}}$$

$$+\partial_{\nabla\phi}\psi \cdot \overline{\dot{\nabla\phi}} + \partial_{\nabla\phi}\psi \cdot \overline{\dot{\nabla\phi}}] + \mathbf{T} \cdot \mathbf{L} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \nabla \cdot \mathbf{w} \geq 0,$$

We first infer that this inequality holds for any value of $\dot{\theta}$ only if

$$\eta = -\psi_\theta.$$

For any function g on $\Omega \times \mathbb{R}$, the identity

$$\overline{\dot{\nabla g}} = \nabla\dot{g} - \mathbf{L}^T \nabla g$$

holds. Substitution for c and ϕ and use of the balance equation (2.8) allow us to write

$$[\mathbf{T} + \rho^2\partial_\rho\psi\mathbf{1} + \rho\nabla c \otimes \partial_{\nabla c}\psi + \rho\nabla\phi \otimes \partial_{\nabla\phi}\psi] \cdot \mathbf{L} - \rho\partial_c\psi\dot{c} - \rho\partial_\phi\psi\dot{\phi}$$

$$-\rho\partial_{\nabla c}\psi \cdot \nabla\dot{c} - \rho\partial_{\nabla\phi}\psi \cdot \nabla\dot{\phi} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \nabla \cdot \mathbf{w} \geq 0. \qquad (3.1)$$

Letting

$$\delta_c\psi := \rho\,\partial_c\psi - \nabla \cdot (\rho\,\partial_{\nabla c}\psi),$$

and the like for ϕ, we can write (3.1) in the form

$$[\mathbf{T} + \rho^2\partial_\rho\psi\mathbf{1} + \rho\nabla c \otimes \partial_{\nabla c}\psi + \rho\nabla\phi \otimes \partial_{\nabla\phi}\psi] \cdot \mathbf{L} - \delta_c\psi\,\dot{c} - \delta_\phi\psi\,\dot{\phi}$$

$$-\frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \nabla \cdot (\rho\,\partial_{\nabla c}\psi\dot{c} + \rho\,\partial_{\nabla\phi}\psi\dot{\phi} + \mathbf{w}) \geq 0.$$

In view of (2.3) and (2.6) we can replace $\dot{c}$ and $\dot{\phi}$ to obtain

$$[\mathbf{T} + \rho^2\psi_\rho\mathbf{1} + \rho\nabla c \otimes \partial_{\nabla c}\psi + \rho\nabla c \otimes \partial_{\nabla c}\psi] \cdot \mathbf{L} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta$$

$$+\frac{1}{\rho}\delta_c\psi\nabla \cdot \mathbf{j}_s + \frac{1}{\rho}\delta_\phi\psi\nabla \cdot \mathbf{j}_i - \frac{\tau}{\rho}\delta_\phi\psi + \nabla \cdot (-\mathbf{w} - \rho\,\partial_{\nabla\phi}\psi\dot{\phi} - \rho\,\partial_{\nabla c}\psi\dot{c}) \geq 0. \qquad (3.2)$$

To obtain restrictions placed by (3.2) we need to specify the dependence of $\mathbf{T}$ on $\mathbf{L}$. We let

$$\mathbf{T} = \mathbf{T}_0 + 2\nu\,\overset{\circ}{\mathbf{D}} + \sigma(\nabla \cdot \mathbf{v})\mathbf{1}, \qquad \nu, \sigma \geq 0$$

where $\mathbf{T}_0$ is independent of $\mathbf{D}$. Also, let $-p$ be the isotropic part of $\mathbf{T}_0$ so that

$$\mathbf{T}_0 = -p\mathbf{1} + \overset{\circ}{\mathbf{T}}_0.$$

In view of (2.8), substitution in (3.2) and some rearrangements yield

$$(\overset{\circ}{\mathbf{T}}_0 + \rho\, \overline{\overset{\circ}{\nabla c \otimes \partial_{\nabla c}\psi}} + \rho\, \overline{\overset{\circ}{\nabla\phi \otimes \partial_{\nabla\phi}\psi}}) \cdot \overset{\circ}{\mathbf{L}} + 2\nu\, \overset{\circ}{\mathbf{D}} \cdot \overset{\circ}{\mathbf{D}} + \sigma(\nabla \cdot \mathbf{v})^2$$

$$+ (-p + \rho^2 \partial_\rho \psi + \frac{1}{3}\rho\nabla c \cdot \partial_{\nabla c}\psi + \frac{1}{3}\rho\nabla\phi \cdot \partial_{\nabla\phi}\psi)\nabla \cdot \mathbf{v} - \frac{\tau}{\rho}\delta_\phi\psi - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta$$

$$+ \mu_s\nabla \cdot \mathbf{j}_s + \mu_i\nabla \cdot \mathbf{j}_i + \nabla \cdot (-\mathbf{w} - \rho\partial_{\nabla\phi}\psi\dot\phi + \partial_{\nabla c}\psi\nabla \cdot \mathbf{j}_s) \geq 0, \quad (3.3)$$

where μ_s and μ_i are defined by

$$\rho\mu_s := \delta_c\psi, \qquad \rho\mu_i := \delta_\phi\psi. \tag{3.4}$$

Hence we can write (3.3) in the form

$$(\overset{\circ}{\mathbf{T}}_0 + \rho\, \overline{\overset{\circ}{\nabla c \otimes \partial_{\nabla c}\psi}} + \rho\, \overline{\overset{\circ}{\nabla\phi \otimes \partial_{\nabla\phi}\psi}}) \cdot \overset{\circ}{\mathbf{L}} + 2\nu\, \overset{\circ}{\mathbf{D}} \cdot \overset{\circ}{\mathbf{D}} + \sigma(\nabla \cdot \mathbf{v})^2$$

$$+ (-p + \rho^2 \partial_\rho \psi + \frac{1}{3}\rho\nabla c \cdot \partial_{\nabla c}\psi + \frac{1}{3}\rho\nabla\phi \cdot \partial_{\nabla\phi}\psi)\nabla \cdot \mathbf{v} - \frac{\tau}{\rho}\delta_\phi\psi - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta$$

$$- \mathbf{j}_s \cdot \nabla\mu_s - \mathbf{j}_i \cdot \nabla\mu_i + \nabla \cdot (-\mathbf{w} - \rho\partial_{\nabla\phi}\psi\dot\phi - \rho\partial_{\nabla c}\psi\dot c + \mu_s\mathbf{j}_s + \mu_i\mathbf{j}_i) \geq 0.$$

It then follows that the Clausius-Duhem inequality (2.12) holds if

$$\mathbf{T}_0 = -\rho^2\partial_\rho\psi\mathbf{1} - \rho\nabla c \otimes \partial_{\nabla c}\psi - \rho\nabla\phi \otimes \partial_{\nabla\phi}\psi, \tag{3.5}$$

$$\mathbf{w} = \mu_s\mathbf{j}_s + \mu_i\mathbf{j}_i - \rho\partial_{\nabla c}\psi\dot c - \rho\partial_{\nabla\phi}\psi\dot\phi, \tag{3.6}$$

$$\frac{\tau}{\rho}\delta_\phi\psi + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta + \mathbf{j}_s \cdot \nabla\mu_s + \mathbf{j}_i \cdot \nabla\mu_i \leq 0. \tag{3.7}$$

In addition, since $\mathbf{T}$ (and hence $\mathbf{T}_0$) is symmetric then ψ is required to satisfy

$$\nabla c \otimes \partial_{\nabla c}\psi = \partial_{\nabla c}\psi \otimes \nabla c, \qquad \nabla\phi \otimes \partial_{\nabla\phi}\psi = \partial_{\nabla\phi}\psi \otimes \nabla\phi.$$

As a consequence, there exist two scalar functions, χ and ζ, such that

$$\partial_{\nabla c}\psi = \chi(\theta,\rho,c,\phi)\nabla c, \qquad \partial_{\nabla\phi}\psi = \zeta(\theta,\rho,c,\phi)\nabla\phi.$$

Hence it follows that

$$\psi = \Psi(\theta,\rho,c,\phi) + \frac{1}{2}\chi(\theta,\rho,c,\phi)|\nabla c|^2 + \frac{1}{2}\zeta(\theta,\rho,c,\phi)|\nabla\phi|^2. \tag{3.8}$$

Though the inequality in (3.7) involves both $\mathbf{q}$ and $\mathbf{j}_s, \mathbf{j}_i$, for the sake of simplicity we require each term to be non-positive, which in turn implies that

$$\tau = -\gamma\delta_\phi\psi, \qquad \mathbf{j}_s = -\kappa\nabla\mu_s, \qquad \mathbf{j}_i = -\lambda\nabla\mu_i, \qquad \mathbf{q} = -k\nabla\theta, \tag{3.9}$$

γ, κ, λ and k being positive-valued functions of Γ_0.

Some remarks are in order about the constitutive equation for the stress tensor $\mathbf{T}$ and the chemical potential μ. It is natural to regard $\rho^2\partial_\rho\psi$ as the (dynamic) pressure P which is then a function of $\theta,\rho,c,\nabla c,\nabla\phi$. Also, by (3.5) and (3.8),

$$p = -\frac{1}{3}\mathrm{tr}\,\mathbf{T}_0 = P + \frac{1}{3}\rho\,\chi|\nabla c|^2 + \frac{1}{3}\rho\,\zeta|\nabla\phi|^2.$$

This means that the spherical part p of $\mathbf{T}$ consists of a pressure term P and additional contributions, $\rho\,\chi|\nabla c|^2/3$ and $\rho\,\zeta|\nabla\phi|^2/3$, due to the inhomogeneity of the concentration c and of the phase variable ϕ.

4. **Evolution equations.** The evolution of the mixture is governed by eqs (2.3), (2.6), (2.7), (2.10), (2.11) in the unknowns $c, \phi, \rho, \mathbf{v}, \theta$. Based on the thermodynamic restrictions (3.4) and (3.9), in view of the general form (3.8) of the free energy we have

$$\mu_s = \partial_c \psi - \frac{1}{\rho} \nabla \cdot (\rho \chi \nabla c), \quad \mu_i = \partial_\phi \psi - \frac{1}{\rho} \nabla \cdot (\rho \zeta \nabla \phi), \quad \tau = -\gamma[\rho \partial_\phi \psi - \nabla \cdot (\rho \zeta \nabla \phi)].$$

We can then write the evolution equations in the form

$$\rho \dot{c} = \nabla \cdot (\kappa \nabla \mu_s), \tag{4.1}$$

$$\rho \dot{\phi} = \nabla \cdot (\lambda \nabla \mu_i) + \tau, \tag{4.2}$$

$$\dot{\rho} = -\rho \nabla \cdot \mathbf{v}, \tag{4.3}$$

$$\rho \dot{\mathbf{v}} = \nabla \cdot \{-\rho^2 \partial_\rho \psi \mathbf{1} - \rho \chi \nabla c \otimes \nabla c - \rho \zeta \nabla \phi \otimes \nabla \phi + 2\nu \overset{\circ}{\mathbf{D}} + \sigma (\nabla \cdot \mathbf{v}) \mathbf{1}\} + \rho \mathbf{f}, \tag{4.4}$$

$$\rho \dot{e} = -\rho^2 \partial_\rho \psi \nabla \cdot \mathbf{v} - \rho \chi \nabla c \cdot \mathbf{D} \nabla c - \rho \zeta \nabla \phi \cdot \mathbf{D} \nabla \phi + 2\nu \overset{\circ}{\mathbf{D}} \cdot \overset{\circ}{\mathbf{D}}$$
$$+ \sigma (\nabla \cdot \mathbf{v})^2 + \nabla \cdot (k \nabla \theta) - \nabla \cdot \mathbf{w} + \rho r. \tag{4.5}$$

By virtue of (3.6) and (3.9), the energy flux $\mathbf{w}$ takes the form

$$\mathbf{w} = -\frac{1}{2} \kappa \nabla \mu_s^2 - \frac{1}{2} \lambda \nabla \mu_i^2 - \rho \chi \nabla c \, \dot{c} - \rho \zeta \nabla \phi \, \dot{\phi}, \tag{4.6}$$

where $\dot{c}$ and $\dot{\phi}$ stand for $1/\rho$ times the right-hand side of (4.1) and (4.2).

Equations (4.1)-(4.5) generalize corresponding evolution equations appeared in the literature. The relation to such equations is provided in §6. In particular, a Ginzburg-Landau equation can be obtained from (4.2) by letting $\lambda = 0$. This supports the view that the diffusion effect, which is proportional to λ, turns out to be negligible when a solid-liquid phase transition occurs. Then this phenomenon is usually ruled by an evolution equation of the second-order, rather than the fourth-order, in space (see, for instance, [7] and references therein).

Now, to be operative, we need a specific function for the free energy ψ of (3.8). This function is set up by borrowing from the separate modelling of phase separation and phase transition.

5. **Free energy.** Our goal is to capture the main feature occurring during the freezing of the salted water, namely, the salt entrapment in small regions where the cryoscopic effect forbid complete ice formation. This can be achieved by modeling the ice-water transition jointly with the salt separation and concentration into water. To get a model which accounts for both phase separation and phase transition we first set up separately the free energies for the two phenomena.

Hereafter, we introduce some simplifying assumptions in order to bring into focus the main features of the phenomenon we deal with. First, we restrict our attention to stationary conditions, so that stable states correspond to minima of the free energy function ψ. Then, we limit our analysis to local processes, so that we are allowed to assume $\nabla c = \nabla \phi = 0$ in a neighborhood of a point $\mathbf{x} \in \mathbf{\Omega}$. If this is the case, by virtue of (3.8) the function ψ reduces to Ψ.

Finally, for simplicity and a more immediate relation to classical model equations, we regard ρ as a parameter and omit the dependence of Ψ on ρ.

5.1. Phase separation in saline water. To fix ideas we let $\phi = 0$ so that the continuum consists of saline water. Hence, $c = \xi$ is the concentration of salt in water and we assume $c \in [0, \xi_\ell]$. In order to model the *eutectic freeze crystallization* as a phase separation phenomenon, we introduce a change of variables. Let $u = \hat{u}(c)$ be a monotone increasing function on $[0, \xi_\ell]$ such that

$$\hat{u}(0) = 0, \quad \hat{u}(c_*) = 1/2, \quad \hat{u}(\xi_\ell) = 1,$$

namely, u vanishes when the salt is absent, takes the mean value $1/2$ when the salt is distributed uniformly in the mixture, reaches its maximum value when $c = \xi_\ell \equiv \xi_s$, that is when the brine takes the maximum salinity value. For definiteness we let

$$\hat{u}(c) = \delta\, c^\gamma, \qquad \gamma = \frac{\ln 1/2}{\ln c_* - \ln \xi_\ell} \approx 0.339, \ \delta = \frac{1}{\xi_\ell^\gamma} \approx 1.555.$$

Let $\hat{K}$ and $\hat{H}$ be the functions

$$\hat{K}(u) = \begin{cases} A \sin^4 \pi u & u \in [0,1], \\ 4Au^2(1-u)^2 & \text{otherwise,} \end{cases}$$

$$\hat{H}(u) = \begin{cases} -2A \sin^2 \pi u & u \in [0,1], \\ 0 & \text{otherwise,} \end{cases}$$

where A is a positive scaling constant. Both $\hat{K}(u)$ and $|\hat{H}(u)|$ have a maximum at $u = 1/2$, and $\hat{K}(0) = \hat{K}(1) = \hat{H}(0) = \hat{H}(1) = 0$. The graphs in Fig. 3 are drawn by assuming $A = 1$, $c_* = 0.035$ and $\xi_\ell = 0.27$.
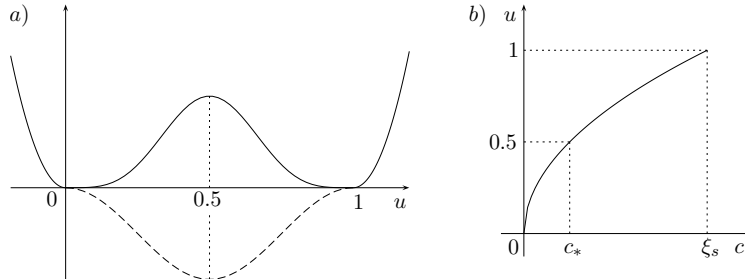

FIGURE 3. *a*) Plots of $\hat{K}$ (solid) and $\hat{H}$ (dashed); *b*) plot of $\hat{u}$.

Hereafter we let

$$K(\theta, c) = \hat{K}(\theta, \hat{u}(c)), \qquad H(\theta, c) = \hat{H}(\theta, \hat{u}(c)).$$

Unlike usual applications of the phase separation theory, we use here rescaled potentials which depend on c_* in order to adapt its techniques to the problem at hand. The phase-separation free energy Ψ is then defined to be

$$\Psi(\theta, c) = \hat{\Psi}(\theta, \hat{u}(c)) = \theta_S \hat{K}(\hat{u}(c)) + \theta \hat{H}(\hat{u}(c)), \qquad (5.1)$$

where θ_S is a reference temperature. Indeed, since the partial derivative $\partial_c \Psi$ is given by

$$\partial_c \Psi(\theta, c) = \partial_u \hat{\Psi}(\theta, \hat{u}(c))\hat{u}'(c) = 2A\pi \sin(2\pi\, \hat{u}(c))\, \hat{u}'(c)(\theta_S \sin^2 \pi\, \hat{u}(c) - \theta)$$

and $\hat{u}'(c) > 0$, $c \in [0, \xi_\ell]$, it follows that Ψ has an extremum when $\hat{u}(c) = 1/2$, namely at $c = c_*$, for any value of θ. Also, if $\theta < \theta_S$ then $\partial_c \Psi$ vanishes also when

$\hat{u}(c) = \frac{1}{2} \pm \frac{1}{\pi} \arccos \sqrt{\theta/\theta_S}$. Hence if $\theta \geq \theta_S$ then $\hat{\Psi}$ has a single minimum at $u = 1/2$. Instead, if $\theta < \theta_S$ then $\hat{\Psi}$ is double-well shaped with a maximum, at $u = 1/2$, and two minima, at $u = \frac{1}{2} \pm \frac{1}{\pi} \arccos \sqrt{\theta/\theta_S}$. This ascribes to θ_S the meaning of critical temperature for separation (see Fig. 4).
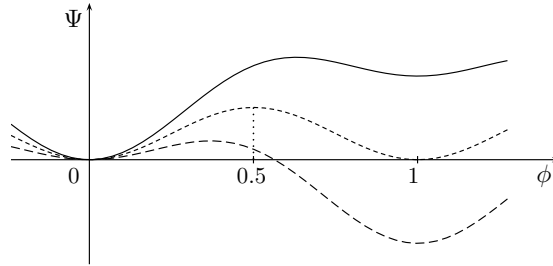

FIGURE 4. Plots of $\hat{\Psi}(\theta, \cdot)$ at $\theta/\theta_S = 2/3$ (solid), $\theta/\theta_S = 1$ (short dashes) and $\theta/\theta_S = 4/3$ (long dashes) when $A = 1$.

5.2. **Solid-liquid transition in pure water.** We now let $c = 0$ so that the continuum is a mixture of ice and water and $\phi \in [0, 1]$ is the ice concentration. Let G, L be the functions defined by

$$G(\phi) = \begin{cases} B(\sin^2 \pi\phi - \cos \pi\phi + 1) & \phi \in [0, 1], \\ B\phi^2 & \phi < 0, \\ B[(1 - \phi)^2 + 2] & \phi > 1. \end{cases}$$

$$L(\phi) = \begin{cases} B \cos \pi\phi & \phi \in [0, 1], \\ B & \phi < 0, \\ -B & \phi > 1. \end{cases}$$

where B is a positive scaling constant. Their sum, $F = L + G$, yields a double-well shaped function (see Fig. 5).
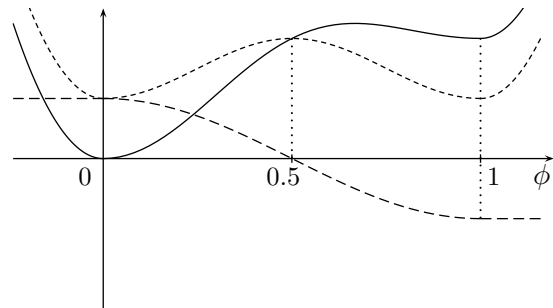

FIGURE 5. Plots of $G(\phi)$ (solid), $L(\phi)$ (long dashes) and $F(\phi)$ (short dashes) relative to $B = 1$.

The corresponding phase-transition potential is giving by

$$\Psi(\theta, \phi) = \theta_T L(\phi) + \theta G(\phi). \tag{5.2}$$

It is double-well shaped with minima at $\phi = 0$ and $\phi = 1$ for all values of θ. In order to compare this expression of the free energy to other ones which appeared in previous papers on phase-transition models (for instance, [6, 7]), we define the double-well shaped function $F = L + G$ so that Ψ takes the form (see Fig. 6)

$$\Psi(\theta, \phi) = \theta_T \left[F(\phi) + \frac{\theta - \theta_T}{\theta_T} G(\phi) \right].$$
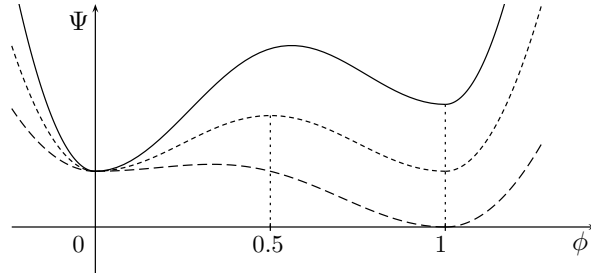

FIGURE 6. Plots of $\Psi(\theta, \cdot)$ at $\theta/\theta_T = 3/2$ (solid), $\theta/\theta_T = 1$ (short dashes) and $\theta/\theta_T = 1/2$ (long dashes).

In particular, when $\theta = \theta_T$ both minima have the same free energy value,

$$\Psi(\theta_T, \phi) = \theta_T[L(\phi) + G(\phi)] = B \, \theta_T \sin^2 \pi\phi, \qquad \phi \in [0, 1].$$

This allows θ_T to be viewed as the *transition temperature*.

5.3. **Solidification and separation.** It seems natural to think that both phase-transition and separation are described by combining the two free energies. This suggest that we may generalize the previous models by adding (5.2) to (5.1) and properly choosing the scaling constants A and B. For the sake of definiteness, hereafter we assume $A = B = 1$.

A realistic modelling have to account for two effects. First, the transition temperature θ_T may depend on the concentration c of the solute (salt). Such dependence may be roughly approximated by (1.1). Secondly, the ice-salt separation temperature θ_S is likely unaffected by the content of fluid relative to that of solid and hence by ϕ. These assumptions are in agreement with the simplified phase diagram depicted in Fig. 2 and may be written as follows

$$\theta_T = \theta_\tau - \alpha_0 c, \qquad \theta_S = \theta_\sigma.$$

As a consequence, we take the free energy for the mixture salt-water-ice in the form

$$\Psi(\theta, c, \phi) = \theta_\sigma K(c) + \theta[H(c) + G(\phi)] + [\theta_\tau - \alpha_0 c]L(\phi). \qquad (5.3)$$

For the ease in displaying, we express this potential as a function of $u \in [0, 1]$ rather than $c \in [0, \xi_\ell]$, as well as in subsection 5.1, namely

$$\Psi(\theta, c, \phi) = \hat{\Psi}(\theta, u(c), \phi) = \theta_\sigma \hat{K}(u(c)) + \theta[\hat{H}(u(c)) + G(\phi)] + [\theta_\tau - \alpha_0 c]L(\phi).$$

5.4. **Brine formation and salt separation.** According to (4.1), salt separation is governed by

$$\rho \dot{c} = \nabla \cdot \left[\kappa \left(\nabla \partial_c \Psi - \frac{1}{\rho} \nabla \cdot (\rho \chi \nabla c) \right) \right].$$

In order to discuss punctual equilibrium, it is convenient to write the free energy (5.3) in the equivalent form

$$\Psi(\theta, c, \phi) = \theta_\sigma K(c) + \theta H(c) + \theta_T \left[F(\phi) + \frac{\theta - \theta_T}{\theta_T} G(\phi) \right], \qquad (5.4)$$

and replacing c with u it follows

$$\hat{\Psi}(\theta, u, \phi) = \theta_\sigma \hat{K}(u) + \theta \big(\hat{H}(u) + G(\phi) \big) + \big(\theta_\tau - \alpha_0 \hat{u}^{-1}(u) \big) L(\phi),$$

where $\hat{u}^{-1}$ denotes the inverse function of $\hat{u}$. Setting aside the diffusion effects, we look for equilibria by restricting our attention to the minima of the free energy (5.4) with respect to c. Since

$$\partial_c \Psi(\theta, c, \phi) = \theta_\sigma K'(c) + \theta H'(c) - \alpha_0 L(\phi),$$

it is worth distinguishing between small values of ϕ, $\phi < 1/2$, when the mixture is mostly liquid, and large values of ϕ, $\phi > 1/2$, when the mixture is mostly icy.

The case $\phi = 0$ is quite close to that already discussed in section 5.1. First, let $0 < \phi < 1/2$, so that $L(\phi) > 0$. Fig. 7 shows the plot of $\hat{\Psi}$ as a function of u, corresponding to $\phi = 1/4$ and different values of θ.
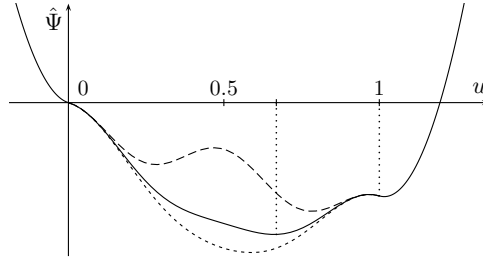

FIGURE 7. Plots of $\hat{\Psi}(\theta, \cdot, \phi)$ at $\phi = 1/4$, when $\theta/\theta_\sigma > 1$ (solid), $\theta = \theta_\sigma$ (dotted) and $\theta/\theta_\sigma < 1$ (dashed).

The vanishing of $\partial_c \psi$ yields

$$\theta_\sigma K'(c) + \theta H'(c) = \alpha_0 L(\phi) > 0,$$

and when $c \in [0, \xi_\ell]$ it takes the form

$$2 A \pi \theta_\sigma \hat{u}'(c) \sin 2\pi \hat{u}(c) [\sin^2 \pi \hat{u}(c) - \theta/\theta_\sigma] = \alpha_0 L(\phi) > 0. \qquad (5.5)$$

If $\theta \geq \theta_\sigma$ then solutions to this equation occur only at $u \in (1/2, 1)$ or, possibly, at $u > 1$. The potential is convex in a large neighborhood of $u = 1/2$, which corresponds to the concentration mean value c_*. In particular, the local minimum occurring at $u > 1$ represents the salt precipitation, whereas the absolute minimum lying in $(1/2, 1)$ is a stable state which corresponds to a concentration of salt $c^\dagger$ greater than the mean value, namely $c_* < c^\dagger < \xi_\ell$. Moreover, the corresponding salinity of the water $\xi^\dagger$ is even greater, in that

$$c^\dagger < \xi^\dagger = c^\dagger/(1 - \phi) < 2c^\dagger.$$

If, instead, $\theta < \theta_\sigma$ then $\sin^2 \pi u(c) - \theta/\theta_\sigma$ may be positive or negative depending on u and then many solutions occur, both at $0 < u < 1/2$ and $1/2 < u < 1$, and also at $u > 1$. The potential is no longer convex around $u = 1/2$ and this is typical of separation phenomena. Nevertheless, the absolute minimum still belong to $(1/2, 1)$.

A symmetric behaviour occurs if $\phi > 1/2$, so that $L(\phi) < 0$. When $\theta > \theta_\sigma$ the absolute minimum is between 0 and $1/2$ and then corresponds to a salt concentration smaller than the mean value, $0 < c^\dagger < c_*$. By comparison with the previous result, we infer that the salt concentration is higher in the liquid phase than in the solid one (ice). If $\theta < \theta_\sigma$, the absolute minimum is near $c = 0$, so that the separation (precipitation) of salt is negligible. Fig. 8 shows the plot of $\hat\Psi$ as a function of u, corresponding to $\phi = 3/4$ and different values of θ.
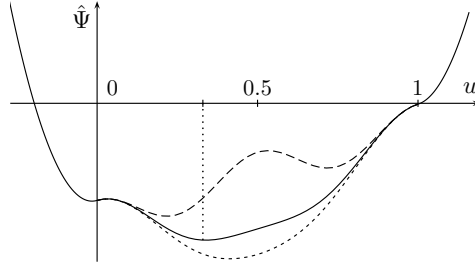

FIGURE 8. Plots of $\hat\Psi(\theta, \cdot, \phi)$ at $\phi = 3/4$, when $\theta/\theta_\sigma > 1$ (solid), $\theta = \theta_\sigma$ (dotted) and $\theta/\theta_\sigma < 1$ (dashed).

In words, if $0 < \phi < 1/2$ and hence the mixture is mostly liquid then u (and hence c) is higher. If, instead, $1/2 < \phi < 1$ and hence the mixture is mostly solid then the equilibrium concentration is smaller. At equilibrium, we can then say that the salt concentration becomes smaller and smaller as the ice concentration, ϕ, increases. We can conclude that during the freezing process the salt migrates from mostly icy to mostly liquid regions, so generating the so called *brine channels*.

Unfortunately, it is not possible to actually appreciate how close to 1 (the actual precipitated salt concentration) or to 0 are the absolute minima when $\theta > \theta_\sigma$ and either $0 < \phi < 1/2$ or $1/2 < \phi < 1$. However, this is not a real drawback for the aim of this study, which is the formation of brine channels by freezing sea water. In the previous discussion of the punctual equilibrium values, indeed, a crucial role is played by the fact that the initial salt concentration, c_0, is assumed to coincide with the mean value, $c_0 = c_*$, namely $u_0 = \hat u(c_*) = 1/2$. Hence, the non-convexity of the potential near the ends of the interval $[0, 1]$ play no role in the ice-salt separation phenomena.

5.5. **Freezing of salted water.** The ice formation in salted water is governed by (4.2) with $\lambda = 0$, namely

$$\rho \dot\phi = -\gamma \big[\rho \partial_\phi \Psi - \nabla \cdot (\rho \zeta \nabla \phi) \big],$$

where Ψ is given by (5.4). Setting aside the diffusion effects, we look for the minima of the free energy with respect to ϕ by evaluating

$$\partial_\phi \Psi(\theta, c, \phi) = (\theta_\tau - \alpha_0 c) L'(\phi) + \theta G'(\phi).$$

The vanishing of $\partial_\phi \Psi$ results in

$$(\theta - \theta_T) \sin \pi\phi + \theta_T \sin 2\pi\phi = 0,$$

where $\theta_T = \theta_\tau - \alpha_0 c$. In addition,

$$\partial_\phi^2 \Psi = B\pi^2[(\theta - \theta_T)\cos\pi\phi + 2\,\theta_T\cos 2\pi\phi].$$

If $\theta = \theta_T$ then $\partial_\phi\Psi$ vanishes at $\phi = 0, 1/2, 1$. At the solid and liquid phases, $\phi = 0, 1$, we have two minima with the same energy, whereas at the mixture of equal parts of liquid and solid phases, $\phi = 1/2$, there is a maximum. If $\theta > \theta_T$ then the maximum moves to the right and its abscissa exceeds $1/2$. Moreover, Ψ takes its absolute minimum at $\phi = 0$. On the contrary, if $\theta < \theta_T$ then the maximum moves to the left, its abscissa falls under $1/2$ and Ψ takes its absolute minimum at $\phi = 1$. Hence, if $\theta > \theta_T$ the liquid phase prevails and viceversa. This statement is confirmed by the plots of Fig. 6 and supports the view that θ_T is the transition temperature. In addition, since $\theta_T = \theta_\tau - \alpha_0 c$, $\alpha_0 > 0$, the cryoscopic effect follows.

6. **Relation to other approaches** . A phenomenological model for the formation of brine channels is given [13]. The model involves two fields, an order parameter u and the salinity v. Borrowing from the Ginzburg-Landau theory (see, e.g., [10, 6, 1]) of phase transitions, Kutschan et al. [13] establish the reaction diffusion system, in one space dimension (x), in the form

$$\partial_t u = f(u, v) + D_1\partial_x^2 u, \qquad (6.6)$$

$$\partial_t v = g(u, v) + D_2\partial_x^2 v, \qquad (6.7)$$

where $D_1, D_2, a_1, a_2, b_1, b_2, c, d$ are positive constants and the source terms, f and g, model the reaction kinetics and are taken to be

$$f(u, v) = a_1 u - cu^3 + du^5 + b_1 v,$$

$$g(u, v) = -a_2 v - b_2 u.$$

In particular, by letting (as suggested in [13])

$$\Psi(u) = \frac{1}{2}a_1 u^2 - \frac{1}{4}cu^4 + \frac{1}{6}du^6 - \frac{1}{2}D_1|\nabla u|^2$$

the first equation of the system takes the Ginzburg-Landau expression

$$\partial_t u = \partial_u \Psi - \nabla \cdot \partial_{\nabla u}\Psi + b_1 v.$$

At a first stage, the salinity v may be identified with the salt concentration. The order parameter u is taken to represent the tetrahedricity and may be viewed as the analogue of the ice concentration ϕ. It is worth noting that the salt exchange between ice and water is realized by the gain term $b_1 v$ and the loss term $-a_2 v$. Unfortunately, minima of Ψ with respect to u turn out to be unstable equilibria of this system when $v = 0$. If this is the case, neglecting the diffusion term it follows

$$\partial_t u = \partial_u \Psi,$$

so that if $u^\dagger$ is a local minimum of Ψ, then it is an equilibrium point, $\partial_t u = \partial_u\Psi(u^\dagger) = 0$, but $\partial_t u = \partial_u\Psi(u) > 0$ all around $u^\dagger$, which means that it is unstable. Hence, the resulting model cannot be compatible with thermodynamic principles.

By (2.6), we have

$$\dot{\phi} = \frac{\tau}{\rho} - \frac{1}{\rho}\nabla \cdot \mathbf{j}_i. \qquad (6.8)$$

As a consequence, the source $f(u, v)$ in (6.6) is the analogue of τ/ρ. The evolution equation (4.1) for c has no source term because salt is not produced in the mixture. However salt is produced in water because of the salt exchange between ice and water. Hence the occurrence of g in (6.7) indicates that v has to be regarded as the

salt concentration *relative to water* only, that is ξ in the present notation. Indeed, by (2.9) we have

$$\dot{\xi} = \frac{\xi}{\rho(1-\phi)}\tau - \frac{1}{\rho(1-\phi)}\nabla \cdot \mathbf{j}_s - \frac{\xi}{\rho(1-\phi)}\nabla \cdot \mathbf{j}_i. \qquad (6.9)$$

Hence we find the direct correspondence between $g(u,v)$ and $\xi\tau/\rho(1-\phi)$. Finally, the linear approximation, as in (6.6) and (6.7), provides $\dot{\phi} \simeq \partial_t\phi$ and $\dot{\xi} \simeq \partial_t\xi$.

Continuing the comparison between (6.6)-(6.7) and (6.8)-(6.9), we observe that $D_2\partial_x^2v$ is the linear analogue of $\nabla \cdot \mathbf{j}_s/\rho$. This amounts to saying that $\mathbf{j}_i$ has to be proportional to $\nabla\phi$ or that, by (3.9), the chemical potential μ_i is a function of ϕ but is independent of $\nabla\phi$. This in turn means that the evolution equation (6.6) corresponds to letting the free energy be independent of $\nabla\phi$, or ∇u, that is $\chi = \zeta = 0$. This remark applies also to (6.7). Accordingly,

$$\tau = \gamma\rho\,\partial_\phi\psi, \qquad \mathbf{j}_i = -\lambda\nabla\partial_\phi\psi, \qquad \mathbf{j}_s = -\kappa\nabla\partial_c\psi = -\kappa\nabla\frac{\partial_\xi\psi}{1-\phi},$$

since $\partial_\xi c = 1 - \phi$ by (2.1). Furthermore, (6.8) involves both $\mathbf{j}_s$ and $\mathbf{j}_i$ and hence also a term ∂_x^2u seems to be in order, in addition to ∂_x^2v. Summarizing, from our original system (6.8)-(6.9) we derive the approximation

$$\rho\,\partial_t\phi = \gamma\rho\,\partial_\phi\psi + \lambda\Delta\partial_\phi\psi$$

$$\rho(1-\phi)\,\partial_t\xi = \gamma\rho\,\xi\partial_\phi\psi + \lambda\xi\Delta\partial_\phi\psi + \kappa\,\Delta\frac{\partial_\xi\psi}{1-\phi}$$

which is the analogue of (6.6)-(6.7).

A dependence of the free energy on ∇c and $\nabla\phi$, or $\nabla\xi$ and $\nabla\phi$, is in order also in standard approaches. The classical Cahn-Hilliard equation

$$\partial_t c + \alpha\Delta^2 c - \Delta h(c) = 0$$

follows by letting the chemical potential μ depend on the Laplacian Δc (see [3, 4, 10]), which in turn follows by letting the free energy be a function of ∇c.

7. **Conclusions.** In essence, the present approach improves classical models of the Cahn-Hilliard types by accounting for a parameter, c, related to the salinity of the fluid. Unlike [13], our model is compatible with thermodynamics, in particular with the second law in the form of the Clausius-Duhem inequality. This compatibility is guaranteed by introducing an extra-energy flux, $\mathbf{w}$, whose explicit expression (4.6) has been derived *a posteriori*. Also, it improves the model of [13] by accounting for a dependence of the free energy potential on ∇c and $\nabla\phi$. Such dependence is customary in the general setting of phase field models [2, 7]. The main feature which occurs during the freezing of the salted water, namely, the salt entrapment in the liquid part of the mixture, is modelled by a suitable choice of the free energy function and assuming that all the involved processes start from states whose salinity is closed to the mean value c_*. Finally, we stress that the temperature which rules the phase transition is regarded here as an independent variable and not as a parameter.

<div align="center">REFERENCES</div>

[1] V. Berti, M. Fabrizio and C. Giorgi, Well-posedness for solid-liquid phase transitions with a fourth-order nonlinearity, *Physica D*, **236** (2007), 13–21.

[2] M. Brokate and J. Sprekels, *Hysteresis and Phase Transitions*, Springer, Berlin, 1996.

[3] J. W. Cahn, On spinodal decomposition, *Acta Metall.*, **9** (1961), 795–801.

[4] J. W. Cahn and J. E. Hilliard, Free energy of a non-uniform system. I. Interfacial free energy, *J. Chem. Phys.*, **28** (1958), 258–267.

[5] J. E. Dunn and J. Serrin, On the thermomechanics of interstitial working, *Arch. Rational Mech. Anal.*, **88** (1985), 95–133.

[6] M. Fabrizio, Ice-water and liquid-vapor phase transitions by a Ginzburg-Landau model, *J. Math. Phys.*, **49** (2008), 102902, 13 pp.

[7] M. Fabrizio, C. Giorgi and A. Morro, A thermodynamic approach to non-isothermal phase–field evolution in continuum physics, *Physica D*, **214** (2006), 144–156.

[8] M. Fabrizio, C. Giorgi and A. Morro, Phase separation in quasi-incompressible Cahn-Hilliard fluids, *Eur. J. Mech.,* **30** (2011), 281–287.

[9] E. Fried and M. E. Gurtin, Continuum theory of thermally induced phase transitions based on an order parameter, *Physica D*, **68** (1993), 326–343.

[10] M. E. Gurtin, Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a micro-force balance, *Physica D*, **92** (1996), 178–192.

[11] M. E. Gurtin, D. Polignone and J. Viñals, Two-phase binary fluids and immiscible fluids described by an order parameter, *Math. Mod. Meth. Appl. Sci.*, **6** (1996), 815–831.

[12] C. Himawan, R. J. C. Vaessen, H. J. M. Kramer, M. M. Seckler and G. J. Witkamp, Dynamic modeling and simulation of eutectic freeze crystallization, *Journal of Crystal Growth,* **237-239** (2002), 2257–2263.

[13] B. Kutschan, K. Morawetz and S. Gemming, Modeling the morphogenesis of brine channels in sea ice, *Phys. Rev. E*, **81** (2010), 036106.

[14] R. A. Lake and E. L. Lewis, Salt rejection by sea ice during growth, *J. Geophys. Research,* **75** (1970), 583–597.

[15] J. Lowengrub and L. Truskinovsky, Quasi-incompressible Cahn-Hilliard fluids and topological transitions, *Proc. R. Soc. Lond. A*, **454** (1998), 2617–2654.

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