

# A phase field approach to solidification and solute separation in water solutions

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**Abstract.** We propose a phase field model for the solid-liquid phase transition in a water-salt (sodium chloride) solution in absence of macroscopic motion, under possibly non-isothermal conditions. A thermodynamic approach based on a free energy functional is assumed. The model consists of three evolution equations: a time-dependent Ginzburg-Landau equation for the solid-liquid phase change, a diffusion equation of the Cahn-Hilliard kind for the solute dynamics and the heat equation for the temperature change. The proposed system is aimed to contribute to the modeling of the brine channels formation in the ice of the polar seas.

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**Keywords.** Phase field, Ginzburg-Landau-Cahn-Hilliard system, Saline water freezing, Brine channels.

## 1. Introduction

The phase field approach to multiphase systems, to be contrasted with the sharp interface approach, traces back to Van der Waals [1]. He argued that the interfaces between different coexisting phases of a substance (liquid-vapour, solid-liquid) have a finite thickness through which the physical quantities such as density, concentration etc. do not suffer jumps, but rather change smoothly between two equilibrium values. Accordingly, the expression *diffuse interface* approach is also used. In the first half of the 1900's, the development of the Landau theory of the second order phase transitions with the introduction of the concept of *order parameter* [2] enlarged the scope of the phase field approach. Later, also phase separation phenomena in binary mixtures received a phase field description through the works of Cahn and Hilliard [3, 4, 5]. Nowadays, the phase field description enjoys a renewed interest for its peculiar advantages as a computational tool for predictions of phenomena involved in phase changes, especially when the focus is on the morphological aspects [6, 7]. In fact, the phase field method overcomes the difficulties faced by the sharp interface models whenever interfaces are to be created or destroyed (or, in any case, undergo topological changes).

In this paper we consider a diffuse interface model for the ice formation in a water-salt solution at rest, a process which involves both the liquid-solid phase transition and the solute separation. These phenomena are described by two phase fields, representing the state of aggregation and the solute concentration; they follow a coupled first order kinetic, according to “model C” in the classification of dynamic critical phenomena by Hohenberg and Halperin [8]. We also account for the non isothermal effects accompanying the phase changes by adding an evolutionary equation for the temperature, in such a way that the compatibility of the system with the second law of thermodynamics is fulfilled [10, 11, 12]. On the other hand, we neglect mechanical effects, e.g. fluid flow and ice floating.

The problem of the solidification in salted water is of interest, among others, in environmental sciences, because of the modes and the consequences of sea ice formation in polar areas. The freezing of the salted water produces, for effect of the salt segregation out of the ice crystals, complex pattern of more concentrated solution (*brine channels*). These liquid channels are the habitat of micro-organisms in polar seas and their structure is important in establishing the energy and the nutrient transport along them. The phase field model we are proposing could find useful applications in the theoretical investigation of brine channel formation in sea ice from a phenomenological point view, such as the one in [13], which has inspired the present work. In fact, the authors also assume a phase field approach. One important difference is that they adopt a reaction-diffusion equation for the salinity parameter, whereas we consider a Cahn-Hilliard type equation to ensure the solute conservation. Moreover, here stress is put on the thermodynamic setting, including thermal effect; also, the phase field equations are obtained starting from a free energy functional which is able to reproduce the equilibrium conditions for the coexistence of (pure) ice and solute at critical concentration.

The paper is organised as follows. In Section 2 the phase diagram of a sodium chloride solution is recalled; the phase and concentration fields are introduced and a thermodynamically consistent evolutionary scheme is set which comprises non isothermal effects. In Section 3 the constitutive expression of the free energy is discussed in connection to the phase equilibrium conditions. Then, an analytic solution for the static phases profiles at an interface is provided for one-dimensional spatially varying fields (Section 4); some comments are added on the role of the non local part of the chemical potential. Finally, some conclusions are drawn in Section 5.

## 2. Phase field description and thermodynamic consistence

We consider a water-salt solution (brine) in a domain  $\Omega$ ; for definiteness we focus on pure sodium chloride ( $NaCl$ ) as solute. The local salt concentration, expressed as a *mass fraction*, is defined by

$$c := \frac{dm_s}{dm_s + dm_w} \in [0, 1], \quad (1)$$

being  $dm_s$  and  $dm_w$  the mass content respectively of salt and water in a given volume element  $dV$ . The essential features of the phase diagram of the water-salt solution are reproduced in Fig. 1 for easy reference (see for example [14]). Some details not relevant for our purposes are ignored (for example, the different occurrence of solid salt crystals as halite ( $NaCl$ ) or hydrohalite ( $NaCl \cdot H_2O$ ) respectively above and below  $0.1^\circ C$ ). We are mainly interested in the water-ice phase transition and its interplay with the solute diffusive dynamics, so we are concerned with the region of the temperature-concentration phase diagram around the *solidification line*; we indicate with  $c_*(\theta)$  the defining function of that line, with the inverse  $\theta_*(c)$ . We will not deal with the formation of salt precipitate beyond the *saturation line*  $c_s(\theta)$ , so we will assume hereafter  $c < c_s(\theta) \leq 0.263$ . We also point out for later use that, in the case of a sodium-chloride solution, the function  $c_*(\theta)$  is well approximated near the origin by the straight line

$$c_*(\theta) = -0.0143 \cdot (\theta - \theta_*), \quad (2)$$

where  $\theta_* = 273.15 K$  is the freezing temperature of pure water. Note that in Fig. 1 the Celsius temperature  $(\theta - \theta_*)$  is represented in the ordinate axis.

Any homogeneous solution (brine) at temperature  $\theta$  and constant concentration  $\bar{c} > c_*(\theta)$  (that is  $\theta > \theta_*(\bar{c})$ ), is stable. By lowering the temperature to a value  $\theta' < \theta_*(\bar{c})$  (thus crossing downward the solidification line), the solution becomes unstable and crystals of ice are formed (possible under-cooling phenomena can delay the ice formation in absence of crystallisation germs). As ice crystals are made of pure water, the surrounding solution becomes more and more enriched with solute. The process of ice formation (at fixed temperature  $\theta'$ ) stops as soon as the concentration of the surrounding brine reaches the value  $c' = c_*(\theta') > \bar{c}$ . This is the value of the salt concentration at which ice is in equilibrium with the brine at temperature  $\theta'$ ; further ice formation with increasing of the brine salinity would create a non-equilibrium state. If  $m$  is the mass of the initial brine (that is of the whole system), the solute mass is  $m_s = \bar{c}m$ ; then, the final ice mass  $m_{ice}$  is obtained according to  $c_*(\theta')(m - m_{ice}) = \bar{c}m$ .

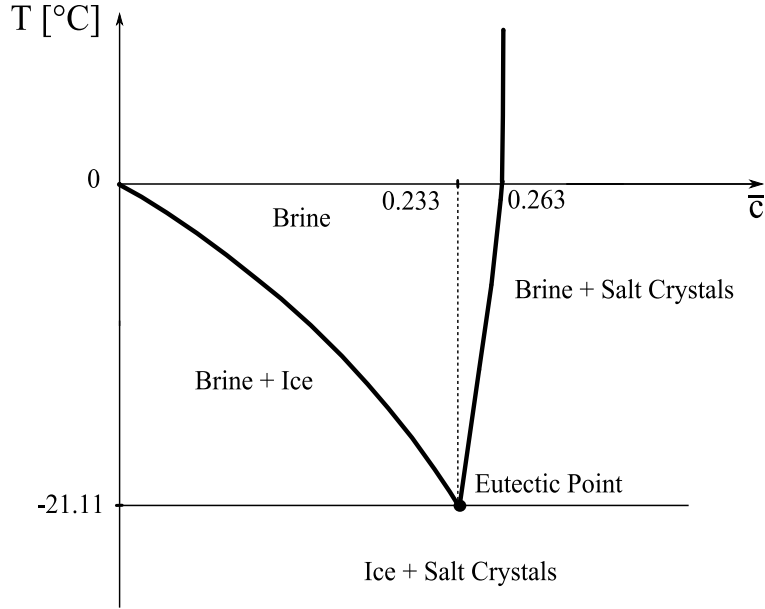


FIGURE 1. Phase diagram of a water-salt ( $NaCl$ ) solution. The *solidification line*, connecting the origin with the eutectic point, and the nearly vertical *saturation line*, departing from the eutectic point, are shown.

We emphasise that, at any temperature  $\theta < 273 K$ , only the values  $c = 0$  and  $c \geq c_*(\theta)$  can represent a punctual equilibrium value, that is the concentration of a *stable homogeneous* portion of matter. The values  $0 < \bar{c} < c_*(\theta)$  in the phase diagram are the resulting mean concentration (hence the use of the bar overlying the  $c$  symbol in Fig. 1) of a non-homogeneous mixture, referred to as ‘Brine+Ice’; alternatively,  $0 < c < c_*(\theta)$  could be the punctual concentration in a (thin) transition layer between brine and ice, according to the diffuse interface setting.

We also adopt the phase field approach to describe the solid-liquid phase transition. An order parameter  $\varphi$  is introduced to distinguish the liquid phase ( $\varphi = 0$ ) from the solid one ( $\varphi = 1$ ).

The model has to describe the evolution of the concentration field  $c$ , the phase field  $\varphi$  and the temperature field  $\theta$ . We disregard any macroscopic motion, assuming that all parts of the system remain at rest, even if the ice formation in presence of the gravity generally causes a motion in the system.

The evolution of the phase field is ruled by a time-dependent Ginzburg-Landau equation, while the concentration field is governed by a Cahn-Hilliard equation which encompasses both the solute diffusion and the solute separation phenomena. These equations can be compactly written in terms of a free energy functional

$$\Psi[\theta, \varphi, c] = \int_{\Omega} \psi(\theta, \varphi, c, \nabla\varphi, \nabla c) dx, \quad (3)$$

where  $\psi$  will be identified with the free-energy density (see the thermodynamic discussion below). In fact, denoting with  $\delta/\delta\varphi$ ,  $\delta/\delta c$  the (partial) functional derivatives with respect to the fields  $\varphi$ ,  $c$ , the evolution equations are expressed by

$$\tau \dot{\varphi} = -\frac{\delta\Psi}{\delta\varphi} = \nabla \cdot \psi_{\nabla\varphi} - \psi_{\varphi}, \quad (4)$$

$$\dot{c} = \nabla \cdot (M \nabla \mu), \quad (5)$$

where

$$\mu := \frac{\delta\Psi}{\delta c} = -\nabla \cdot \psi_{\nabla c} + \psi_c \quad (6)$$

is named the *chemical potential*. The above system falls into the class of relaxational dynamic models labelled as *model C* in the review of Hohenberg and Halperin [8].

The time coefficient  $\tau = \hat{\tau}(\sigma) > 0$ , where  $\sigma := (\theta, \varphi, c, \nabla\varphi, \nabla c)$  is the list of state variables, determines the time scale of the freezing process. The coefficient  $M = \hat{M}(\sigma) \geq 0$  is named the *mobility* and the vector

$$\mathbf{J} = -M\nabla\mu \quad (7)$$

is identified with the diffusion flux of solute particles. So the equation for  $c$  is the continuity equation  $\dot{c} = -\nabla \cdot \mathbf{J}$ , ensuring the conservation of the concentration field, that is of the global solute mass:

$$\frac{d}{dt} \left( \int_{\Omega} c(x) dx \right) = 0, \quad (8)$$

provided that the normal component  $\mathbf{J} \cdot \boldsymbol{\nu}$  of the current at the boundary would vanish (see [9] for a review).

We examine the thermodynamic consistence of systems expressed in the general form of eqs. (4) and (5), accompanied with a suitable equation for temperature.

Equations (4) and (5) are considered as field equations associated with their own power balance [10, 11, 12, 15, 16]. The internal powers  $\mathcal{P}_{\varphi}^i$ ,  $\mathcal{P}_c^i$ , associated respectively with the Ginzburg-Landau and Cahn-Hilliard equations, are essential in writing the energy balance equation, which determines the temperature evolution (see below). The power balance of the Ginzburg-Landau equation is obtained by multiplying both members of (4) by  $\dot{\varphi}$ ; after a little manipulation of the gradient term, it turns out [11, 12]

$$\tau\dot{\varphi}^2 + \psi_{\nabla\varphi}\nabla\dot{\varphi} + \psi_{\varphi}\dot{\varphi} = \nabla \cdot (\dot{\varphi}\psi_{\nabla\varphi}). \quad (9)$$

The first member defines the internal power of the phase field

$$\mathcal{P}_{\varphi}^i := \tau\dot{\varphi}^2 + \psi_{\nabla\varphi}\nabla\dot{\varphi} + \psi_{\varphi}\dot{\varphi}, \quad (10)$$

while the second member is the external power

$$\mathcal{P}_{\varphi}^e := \nabla \cdot (\dot{\varphi}\psi_{\nabla\varphi}). \quad (11)$$

We define the power balance of the solute transport equation by multiplying eq. (5) by  $\mu$  [12]:

$$\mu\dot{c} = \mu\nabla \cdot (M\nabla\mu) = \nabla \cdot (\mu M\nabla\mu) - M|\nabla\mu|^2.$$

Rewriting the first member as  $\mu\dot{c} = \psi_c\dot{c} + \psi_{\nabla c}\nabla\dot{c} - \nabla \cdot (\dot{c}\psi_{\nabla c})$ , we recast the power balance in the form

$$\psi_c\dot{c} + \psi_{\nabla c}\nabla\dot{c} + M|\nabla\mu|^2 = \nabla \cdot (M\mu\nabla\mu + \dot{c}\psi_{\nabla c}); \quad (12)$$

the first (or second) member defines the internal (or external) power for the solute transport:

$$\mathcal{P}_c^i := \psi_c\dot{c} + \psi_{\nabla c}\nabla\dot{c} + M|\nabla\mu|^2, \quad \mathcal{P}_c^e := \nabla \cdot (M\mu\nabla\mu + \dot{c}\psi_{\nabla c}). \quad (13)$$

The temperature equation is obtained from the balance of energy, which we express in terms of the internal energy  $e$  and the internal power expenditures:

$$\dot{e} = \mathcal{P}_{\varphi}^i + \mathcal{P}_c^i + h, \quad (14)$$

where  $h$  is the internal thermal power absorption obeying the classical balance

$$h = -\nabla \cdot \mathbf{q} + r, \quad (15)$$

with  $r$  the external heat supply and  $\mathbf{q}$  the heat flux.

Next we assume the following constitutive laws for the entropy  $\eta$  and the internal energy density:

$$\eta = -\psi_{\theta}, \quad e = \psi + \theta\eta, \quad (16)$$

which identify  $\psi$  as the Helmholtz free energy density. We make more explicit the energy balance equation (14) in terms of the free energy  $\psi$ . First, summing up the eqs. (10) and (13), we note that

$$\mathcal{P}_{\varphi}^i + \mathcal{P}_c^i = \dot{\psi} - \psi_{\theta}\dot{\theta} + \tau\dot{\varphi}^2 + M|\nabla\mu|^2.$$

Now,  $\dot{e} = \dot{\psi} - \dot{\theta}\psi_\theta - \theta(\dot{\psi}_\theta)$ , so the following temperature equation is readily obtained

$$-\theta(\dot{\psi}_\theta) = \tau\dot{\varphi}^2 + M|\nabla\mu|^2 - \nabla \cdot \mathbf{q} + r. \quad (17)$$

As a consequence, the classical Clausius-Duhem inequality

$$\dot{\eta} \geq -\nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right) + \frac{r}{\theta}, \quad (18)$$

easily follows, provided that  $\mathbf{q} \cdot \nabla\theta \leq 0$  and  $\theta > 0$ . In fact,  $\eta = -\psi_\theta$  and (17) implies

$$\dot{\eta} \geq \frac{-\nabla \cdot \mathbf{q}}{\theta} + \frac{r}{\theta} = -\nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right) + \frac{r}{\theta} - \frac{\mathbf{q} \cdot \nabla\theta}{\theta^2}$$

and the statement follows.

For the heat conduction in water, the classical Fourier law

$$\mathbf{q} = -k\nabla\theta, \quad k > 0, \quad (19)$$

satisfying  $\mathbf{q} \cdot \nabla\theta \leq 0$ , is appropriate.

The field variables are physically defined only in the domains  $\varphi \in [0, 1]$  and  $c \in [0, 1]$ . Actually, in the present model,  $c$  makes sense only if it is less than the saturation concentration  $c_s$ . As it regards the Ginzburg-Landau equation, if the free energy is always increasing with respect to the variable  $\varphi$  for  $\varphi \geq 1$ , while it is decreasing for  $\varphi \leq 0$ , then it is generally possible to prove a maximum theorem which guarantees that the order parameter will remain in the interval  $[0, 1]$  [11]. In any case, it is always possible to add a suitable constraint to the Ginzburg-Landau equation, which can be expressed formally by introducing the *sub-differential* of the indicator function of the admissible domain [16]; then the equation is modified as

$$\tau\dot{\varphi} - \nabla \cdot \psi_{\nabla\varphi} + \psi_\varphi + \partial I_{[0,1]}(\varphi) \ni 0, \quad (20)$$

where

$$I_{[a,b]}(x) = \begin{cases} 0 & \text{if } x \in [a, b] \\ +\infty & \text{otherwise} \end{cases} \quad (21)$$

is the indicator function of the interval  $[a, b]$ . From a physical point of view, this amounts to add an infinite energy barrier to the free energy in correspondence to the boundary of the allowed domain.

As for the Cahn-Hilliard equation, existence results, along with a maximum principle, have been proved for a quite general class of potentials and for degenerate mobility (that is  $M(c)$  vanishing at the end points 0 and 1); see for example [17, 18]. Also for free energies with the singular contribution  $I_{[0,1]}(c)$  (causing a sub-differential in the chemical potential) weak solutions, automatically bounded in  $[0, 1]$ , have been proven to exist in the case, for example, of a polynomial potential [17, 19, 20]. The presence of the indicator function is generally connected with the need to allow the existence of *pure phases* in the system, such as  $c = 0$ ; this is just the case of our model, in which we idealize the ice as a pure (salt-free) phase.

Finally, some words on the suitable boundary conditions for the differential problem. The phase field  $\varphi$  is given the b.c.:

$$\boldsymbol{\nu} \cdot \psi_{\nabla\varphi}|_{\partial\Omega} = 0. \quad (22)$$

where  $\boldsymbol{\nu}$  is the unit vector normal to the boundary. This is a natural boundary condition from a thermodynamic point of view, as it is a sufficient condition to have

$$\int_{\Omega} \mathcal{P}_\varphi^e dx = 0, \quad (23)$$

given the formula (11) for the external power. This, in turn, ensures that the global energy balance of the body is the classical one, that is the only global energy transfer process for a fluid at rest is the heat flux. In the following, we will assume, as it is customary in phase field theories, the constitutive law  $\psi_{\nabla\varphi} = \kappa\nabla\varphi$ , so (22) turns out to be a homogeneous Neumann b.c.

$$\boldsymbol{\nu} \cdot \nabla\varphi|_{\partial\Omega} = 0. \quad (24)$$

This condition means that the phase interfaces near the boundary tend to arrange normally to the boundary itself.

The conservation of mass requires that the normal solute current at the boundary is zero; so the following b.c. is assumed:

$$\boldsymbol{\nu} \cdot \nabla \mu|_{\partial\Omega} = 0, \quad (25)$$

The other b.c. for the (fourth order) Cahn-Hilliard equation is similarly obtained as a sufficient condition to ensure

$$\int_{\Omega} \mathcal{P}_c^e dx = 0. \quad (26)$$

Thanks to (13) and (25), it suffices to assume

$$\boldsymbol{\nu} \cdot \psi_{\nabla c}|_{\partial\Omega} = 0, \quad (27)$$

which reduces to  $\boldsymbol{\nu} \cdot \nabla c|_{\partial\Omega} = 0$  for the usual constitutive choices.

For the thermal field, different b.c.'s may be appropriate, according to the physical situation (fixed boundary temperature, adiabatic conditions, convective heat transfer conditions, etc.)

### 3. Free energy and phases stability

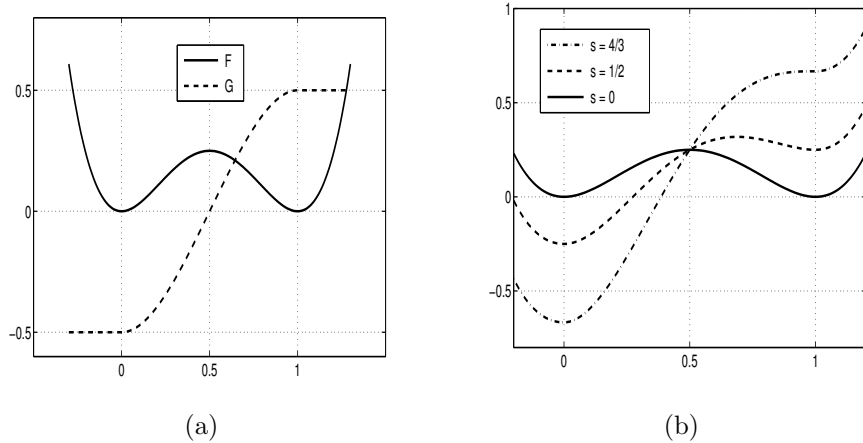


FIGURE 2. Functions  $F(x)$  and  $G(x)$  (left) and the potential  $F(x)+sG(x)$  for different values of  $s$  (right).

Following [15], we describe the first order phase transition between the liquid state, labelled by the phase value  $\varphi = 0$ , and the solid state, associated to the value  $\varphi = 1$ , through the phase equation

$$\tau \dot{\varphi} = \nabla \cdot (\kappa \nabla \varphi) - \epsilon [bF'(\varphi) + uG'(\varphi)] \quad (28)$$

corresponding to a free energy density

$$\psi = \frac{\kappa}{2} |\nabla \varphi|^2 + \epsilon [bF(\varphi) + uG(\varphi)]. \quad (29)$$

The non-dimensional parameter  $u$  depends on the physical fields which drive the transition (here, the temperature). The potentials  $F$  and  $G$  are given by

$$F(\varphi) = 4\varphi^2(1-\varphi)^2, \quad G(\varphi) = \begin{cases} 3\varphi^2 - 2\varphi^3 - 1/2 & \text{if } |\varphi| \leq 1 \\ -1/2 & \text{if } \varphi < 0 \\ 1/2 & \text{if } \varphi > 1 \end{cases} \quad (30)$$

and are plotted in Fig. 2-(a). For any value of  $u$  and  $b$ , the potential  $bF(\varphi) + uG(\varphi)$  has minima only at  $\varphi = 0, \varphi = 1$  (one or both), see Fig. 2-(b). Eq.(28) drives the phase parameter  $\varphi$  toward (local)

minima, excepted in transition regions with  $\nabla\varphi \neq 0$ . The value  $u = 0$  represents the coexistence temperature for liquid and solid phase: for pure water, for example,  $u$  is proportional to the temperature expressed in Celsius degrees. For  $u > 0$  the liquid phase is stable, while for  $u < 0$  the stable phase is the solid one. The value  $b/4$  represents the height of the barrier between the minima at  $\varphi = 0$  and  $\varphi = 1$  for  $u = 0$ . For  $3u > 4b$  ( $3u < -4b$ ) the barrier between the two minima disappears: a minimum at  $\varphi = 0$  ( $\varphi = 1$ ) and an inflection point at  $\varphi = 1$  ( $\varphi = 0$ ) are left. So, the value of  $b$  has no effect on the equilibrium properties; it influences the properties related to the intermediate values of the order parameter, for example the thickness of the interfaces. Also, the height of the potential barrier between the minima influences the activation dynamics of the phase transition: in order to start the transformation of a single-phase state at the equilibrium temperature, it is necessary a finite perturbation to overcome the potential barrier, such as the presence of a germ of the other phase or a finite local *over-heating* (or *under-cooling*).

The parameter  $\epsilon$  gives  $\psi$  the dimension of an energy density.

We extend the free energy density to values  $c > 0$  assuming (see Fig. 3)

$$\psi(\sigma) = \frac{\kappa}{2}|\nabla\varphi|^2 + \frac{\lambda}{2}|\nabla c|^2 + \epsilon[bF(\varphi) + (u - H(c))G(\varphi)] + \psi_0(\theta), \quad (31)$$

with

$$H(c) = 2c \ln c. \quad (32)$$

We remark that, in the theory of mixtures, the expression

$$c \ln c + (1 - c) \ln(1 - c)$$

is proportional to the entropy of mixing [2]. In the regime  $c \ll 1$ , the second addendum is unimportant. However, in our phenomenological approach, the form of the free-energy is chosen in order to satisfy the relevant features of the phase equilibria, as it will be shown below.

It is convenient to choose the a-dimensional temperature parameter  $u$  as

$$u := \frac{\theta - \theta_*}{\theta_0}. \quad (33)$$

Recall that  $\theta_* = 273.15 \text{ K}$  is the pure water freezing point, so  $u$  is in fact proportional to the Celsius temperature and its critical value for pure water is  $u_* = 0$ . Furthermore, fixing  $\theta_0 \simeq 70 \text{ K}$ , the ice-brine coexistence line (2) is simply given by

$$c_*(u) = -u.$$

As for the meaning of  $\epsilon$  and  $\psi_0(\theta)$ , we refer to the discussion of the thermodynamic quantities at the end of this section.

It is clear that for  $c \equiv 0$  the free energy reduces to the form discussed above for pure water. On the other hand, in the liquid phase (brine), the free energy reduces to

$$\psi(\varphi = 0, u) = \frac{\lambda}{2}|\nabla c|^2 + \frac{\epsilon}{2}(H(c) - u) + \psi_0(\theta), \quad (34)$$

the free energy of a non-interacting solution for small  $c$ . So the expression (31) can be considered an extension of those particular cases. Motivations for such a choice will appear in the following discussion of the resulting equilibrium properties. However, the main point is that the contribution  $-G(\varphi)H(c)$  as a function of  $c$  is convex (which in Cahn-Hilliard models implies mixing) for  $\varphi < 1/2$ , i.e. for the water-prevalent phase, and concave (which implies separation) for  $\varphi > 1/2$ , i.e. ice-prevalent phase. In these conditions the salt will be forced to leave the ice during the freezing process.

The chemical potential is given by

$$\mu = \mu_{loc} - \nabla \cdot (\lambda \nabla c), \quad \mu_{loc} := -2\epsilon(1 + \ln c)G(\varphi). \quad (35)$$

Next, we assume the mobility coefficient

$$M = M_0 c. \quad (36)$$

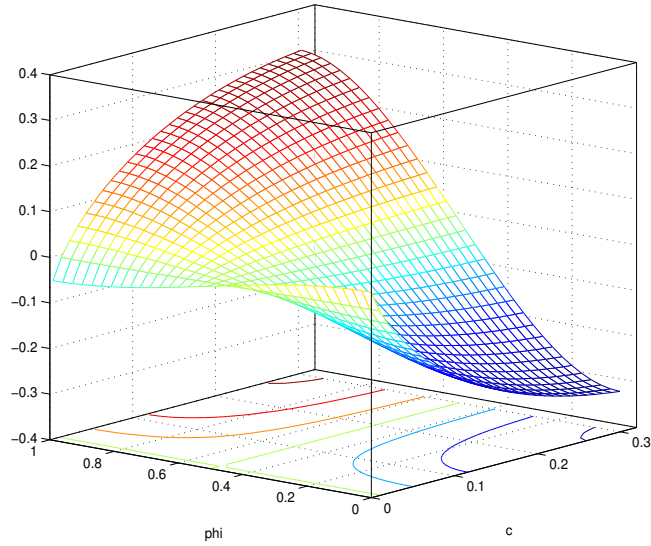


FIGURE 3. Local part of the free energy  $\psi(\varphi, c)$  for  $b = 0$  and  $u = -0.1$ .

This expression is the low  $c$  approximation for the commonly used mobility coefficient  $M = M_0 c(1 - c)$  [5, 9, 17, 18]. Then we obtain the flux

$$\mathbf{J} = -M\nabla\mu = \mathbf{J}_{nl} + \mathbf{J}_c + \mathbf{J}_\varphi \quad (37)$$

with

$$\mathbf{J}_{nl} = M\nabla[\nabla \cdot (\lambda\nabla c)], \quad (38)$$

$$\mathbf{J}_c = 2\epsilon M_0 G(\varphi)\nabla c, \quad (39)$$

$$\mathbf{J}_\varphi = 2\epsilon M_0 c(1 + \ln c)G'(\varphi)\nabla\varphi. \quad (40)$$

The first contribution, which we name *non local*, is the well known regularising term of the Cahn-Hilliard equation, which is needed if both the diffusive and anti-diffusive regimes are to be accounted for. Its function is to prevent the formation of sharp interfaces, that is discontinuities in the concentration field.

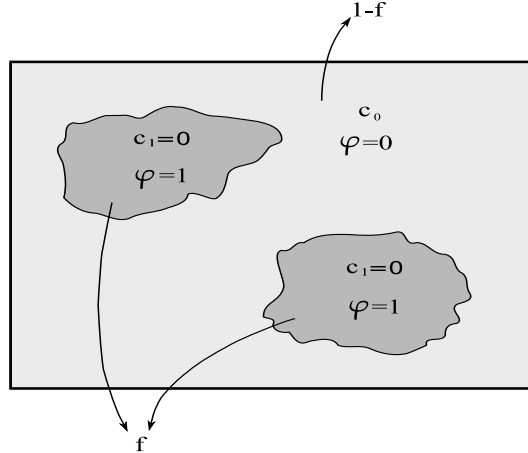
In the liquid phase  $\varphi = 0$ , we have  $\mathbf{J}_\varphi = 0$  and  $\mathbf{J}_c = -(\epsilon M_0)\nabla c$ , a diffusion flux.

For  $\varphi > 1/2$  (in the ice-prevalent region) we have  $\mathbf{J}_c = k_c(\varphi)\nabla c$ ,  $k_c > 0$  (anti-diffusive contribution). Moreover, for  $0 < c < 1/e$  (note that  $c_s < 1/e$ ),  $\mathbf{J}_\varphi = -k_\varphi(c, \varphi)\nabla\varphi$  with  $k_\varphi \geq 0$ : this current contribution in the solid-liquid transition layer is directed from the ice side to the water side.

Now, through a global minimisation procedure, we show that this free energy reproduces the co-existence line  $c_*(u)$ .

Consider a solution with unit mass and *mean* concentration  $\bar{c}$  at  $u < 0$ ; we assume in general that it decomposes into a solid portion ( $\varphi = 1$ ) with mass  $f \in [0, 1]$  and a liquid one ( $\varphi = 0$ ) with mass  $1 - f$ ; in fact,  $\varphi = 0, 1$  are the only possible equilibrium values of the order parameter  $\varphi$ . Here, we are supposing that intermediate values of  $\varphi$  are involved only in thin transition layers and are not influential for the equilibrium bulk free energy. Now, if  $\varphi = 0$ , the current  $\mathbf{J}_c$  is diffusive, so a uniform value  $c_0$  of the concentration is energetically favourable in the liquid region. On the contrary, in the  $\varphi = 1$  region,  $\mathbf{J}_c$  is anti-diffusive for all the values  $0 \leq c \leq c_s$ . So, at constant  $\varphi = 1$ , the solute will separate in regions of maximum  $c = c_s$  and regions of  $c = 0$ . However, any region with  $(\varphi, c) = (1, c_s)$  will readily decay to the state  $(\varphi, c) = (0, c_s)$  as a result of the Ginzburg-Landau equation and of the



FIGURE 4. Non homogeneous mixture with solid fraction  $f$ .

form of the potential (see Fig. 3). The liquid portion of solution characterized by  $(\varphi = 0, c_s)$  will then evolve by a diffusion process toward the common equilibrium concentration  $c_0$  of the liquid fraction. So, only on the basis of the *local* structure of the free energy density, we can infer that in the solution two distinct homogeneous regions will form (possibly with a complicate spatial structure): one characterised by  $(\varphi, c) = (1, 0)$  and the other by  $(\varphi, c) = (0, c_0)$  (Fig. (4)). If  $\bar{c}$  is the (constant) mean concentration of the solution, then

$$(1 - f)c_0 = \bar{c}. \quad (41)$$

Now we examine the global free energy to determine  $c_0$  (and hence  $f$ ) as a function of  $\bar{c}$  and  $u$ . The bulk contribution to the free energy (that is neglecting the transition layers of non-uniform  $\varphi$  and  $c$ ) is the mass weighted sum of the free energies in the two homogeneous portions:

$$\begin{aligned} \Psi(c_0) &:= \int_{\Omega} \psi dx = f\psi(1, 0) + (1 - f)\psi(0, c_0) = \\ &= \epsilon \left[ fu + \bar{c} \ln c_0 - \frac{u}{2} \right] + \psi_0(u) = \epsilon \left[ -\frac{u}{2} + \bar{c} \ln c_0 + u \frac{c_0 - \bar{c}}{c_0} \right] + \psi_0(u). \end{aligned} \quad (42)$$

We are going to minimise with respect to  $c_0$ , so we compute

$$\frac{\partial \Psi}{\partial c_0} = \frac{\epsilon \bar{c}}{c_0^2} (c_0 + u).$$

We also remember that, by (41), the domain of  $c_0$  is  $c_0 \geq \bar{c}$ .

Now, for  $\bar{c} \leq |u|$  the derivative vanishes at the allowable value  $c_0 = -u = c_*(u)$ : the minimum<sup>1</sup> free energy state is a two-phase mixture made of pure ice ( $\varphi = 1, c = 0$ ) and critical liquid brine ( $\varphi = 0, c = |u|$ ). The corresponding frozen fraction is  $f = 1 - \bar{c}/|u|$ .

For  $\bar{c} > |u|$ , we have instead  $\partial \Psi / \partial c_0 > 0$  for every  $c_0 > \bar{c}$ , so the minimum is attained at the left boundary  $c_0 = \bar{c}$ , which implies  $f = 0$ : all the solution is in the liquid phase, as expected.

To sum up, starting from considerations on the local structure of the free energy (in particular: the location of the minima as for the non-conserved variable  $\varphi$  and the concavity-convexity properties as for the conserved concentration field  $c$ ) we can assume (42) as a trial minimal bulk free energy for the mixture, depending on the unknown  $c_0$ . Next, the minimization with respect to  $c_0$  has been

<sup>1</sup>Observe that

$$\frac{\partial^2 \Psi}{\partial c_0^2} \Big|_{c_0 = -u} = \frac{\epsilon \bar{c}}{u^2} > 0.$$

performed, obtaining the critical value  $c_0 = c_*(u)$  in conditions of possible ice-brine coexistence (otherwise the whole system would be in the liquid state at the initial mean concentration  $\bar{c}$ ). While the mere convexity of the free-energy with respect to  $c$  for  $\varphi < 1/2$  can be achieved by many choices of the function  $H(c)$ , the adopted logarithmic form effectively gives, through minimization of (42), the correct value of the critical brine concentration in equilibrium with ice. Had we assumed a polynomial expression for  $H(c)$ , as in most applications of Cahn-Hilliard models, the minimization of the corresponding expression (42) would have not given the correct  $c_*(u)$  (unless one allows a singular dependence of  $H(c)$  on  $u^{-1}$ , with the consequent drawbacks in the temperature equation). This is really not surprising from a physical point of view; in fact, polynomial Cahn-Hilliard models typically describes spinodal decomposition phenomena which involve intermediate concentrations far from the extreme ones  $c = 0$  and  $c = 1$ . On the other hand, in our case, the pure phase  $c = 0$  plays a leading role and the logarithmic potential (based on sound statistical mechanics arguments [2]) cannot be properly approximated with a polynomial near  $c = 0$ .

A further remark is appropriate at this stage. As for the  $c$ -concave form of the potential  $-G(\varphi)H(c)$  when  $\varphi > 1/2$ , the logarithmic expression of  $H(c)$  is not essential and any  $c$ -concave expression such as  $-G(\varphi)c(1-c)$  would be suitable: the equilibrium properties of the free energy would not be changed. In that case, the free energy would have a piecewise product structure. Indeed, from the mathematical point of view, the last option seems preferable for the well-posedness of the model. In fact, as observed in Section 2, there are existence results for Cahn-Hilliard models that include pure phases [19, 20], obtained by introducing the indicator function  $I_{[0,1]}(c)$  in the free energy beside a polynomial concave potential.

We now calculate some thermodynamic quantities. The entropy function is:

$$\eta = -\psi_\theta = -\psi'_0(\theta) - \frac{\epsilon}{\theta_0}G(\varphi). \quad (43)$$

So, the latent heat of fusion at temperature  $\theta = \theta_*(c)$  is given by

$$L(\theta) = \theta(\eta|_{\varphi=0} - \eta|_{\varphi=1}) = \epsilon \frac{\theta}{\theta_0}. \quad (44)$$

In particular, at temperature  $\theta = 273.15 K$ , we have  $L = 3.34 \cdot 10^5 J/Kg$ , so  $\epsilon = L\theta_0/\theta \simeq 0.8 \cdot 10^5 J/Kg$ . We can then further specify the heat equation as follows

$$C(\theta)\dot{\theta} - L(\theta)G'(\varphi)\dot{\varphi} = \tau\dot{\varphi}^2 + M|\nabla\mu|^2 + \nabla \cdot (k\nabla\theta) + r. \quad (45)$$

with  $C(\theta) = -\theta\psi''_0(\theta)$  the specific heat of water.

We summarize the equations of the model in the following differential system

$$\begin{cases} \tau\dot{\varphi} = \kappa\Delta\varphi - \epsilon[bF'(\varphi) + (u - 2c \ln c)G'(\varphi)], \\ \dot{c} = M_0\nabla \cdot [c\nabla(-\lambda\Delta c - 2\epsilon G(\varphi)(1 + \ln c))], \\ C(\theta)\dot{\theta} - \epsilon \frac{\theta}{\theta_0}G'(\varphi)\dot{\varphi} = \tau\dot{\varphi}^2 + M_0c|\nabla\mu|^2 + \nabla \cdot (k\nabla\theta) + r. \end{cases} \quad (46)$$

with  $\mu$  given by (35). They follow from the free energy (3) and the linear mobility function  $M = M_0c$  according the general scheme of Section 2.

#### 4. One-dimensional phases coexistence

Finally, we examine the equilibrium equations of our model in the one-dimensional case, with the further simplifying assumption of a vanishing non local current, that is  $\lambda = 0$ . Some remarks justifying

this choice will be made *a posteriori*. The equilibrium conditions  $\delta\Psi/\delta\varphi = 0$  and  $J = 0$ <sup>2</sup> then read

$$\begin{cases} \kappa\varphi_{xx} - bF'(\varphi) - (u - 2c \ln c)G'(\varphi) = 0, \\ G(\varphi)c_x + c(1 + \ln c)G'(\varphi)\varphi_x = 0. \end{cases} \quad (47)$$

To model a non homogeneous state, we consider the asymptotic boundary conditions

$$\begin{cases} \lim_{x \rightarrow -\infty} \varphi(x) = 0, & \begin{cases} \lim_{x \rightarrow +\infty} \varphi(x) = 1, \\ \lim_{x \rightarrow +\infty} c(x) = 0 \end{cases} \\ \lim_{x \rightarrow -\infty} c(x) = c_0 \end{cases} \quad (48)$$

which represent a brine phase in the left half line coexisting with a ice phase in the right half line. In order to avoid an over-determined problem, we treat  $c_0$  as a free parameter.

The differential equation for  $c$  is a separable variable ODE whose general non vanishing integral is

$$c(x) = \exp \left\{ \frac{h}{|G(\varphi(x))|} - 1 \right\} \quad (49)$$

for  $\varphi(x) \neq 1/2$  ( $h$  is an integration constant). The identically null function  $c(x) \equiv 0$  also solves the equation. We note that these solutions can match smoothly at  $\varphi = 1/2$  if  $h < 0$ .

The equation (47)<sub>1</sub> for  $\varphi$  can also be reduced to quadrature: by multiplying the equation by  $\varphi_x$  and substituting

$$(c \ln c) G'(\varphi)\varphi_x = -[cG(\varphi)]_x$$

from (47)<sub>2</sub>, the first member becomes a total derivative. Integrating, we obtain

$$\frac{\kappa}{2}\varphi_x^2 - [bF(\varphi) + (u + 2c)G(\varphi)] = k, \quad (50)$$

with  $k$  an integration constant. Using boundary conditions (48) in (50) and remembering  $F(0) = F(1) = 0$ ,  $G(0) = 1/2$ ,  $G(1) = 1/2$ , one obtains the conditions

$$\frac{1}{2}(u + 2c_0) = k, \quad k = -\frac{u}{2}, \quad (51)$$

which determine the integration constant  $k$  and the free parameter  $c_0$ . For the last, we obtain in fact  $c_0 = |u|$ , that is the concentration in the brine side in equilibrium with ice is just the critical concentration  $c_*(u) = -u$ , as desired. The corresponding value of  $h$  is (according to (49))

$$h = \frac{1}{2}(1 + \ln |u|).$$

As we consider  $|u| = c_0 \leq c_s \simeq 0.26$ , it follows  $h < 0$ .

Assuming  $\varphi$  monotonically increasing from 0 (at  $-\infty$ ) to 1 (at  $+\infty$ ), a solution for  $c(x)$  satisfying the boundary conditions is

$$c(x) = E(\varphi(x)), \quad (52)$$

where the function  $E$  on  $[0, 1]$  is defined by

$$E(\tau) := \begin{cases} \exp \left\{ \frac{1 + \ln |u|}{2|G(\tau)|} - 1 \right\}, & \text{for } \tau \in [0, 1/2), \\ 0 & \text{for } \tau \in [1/2, 1]. \end{cases} \quad (53)$$

As  $G$  vanishes at  $\varphi = 1/2$  and  $1 + \ln |u| < 0$ , the function  $E$  has the same regularity class of  $G$ , that is  $C^\infty(0, 1)$ .

<sup>2</sup>In a one-dimensional problem, the condition  $\nabla \cdot \mathbf{J} = 0$ , with vanishing boundary normal current, imply  $\mathbf{J} = 0$ ; this remains true in the three-dimensional case if  $\mathbf{J}$  is irrotational, for example when  $\mathbf{J} = -M_0 \nabla \mu$  with  $M_0$  constant. However, considering the full thermodynamic problem,  $|\mathbf{J}|^2$  appears as a dissipative term in the temperature equation, so at equilibrium one has  $\mathbf{J} = 0$  as well.

Then we integrate (50) with the initial condition  $\varphi(0) = 1/2$  (interface at  $x = 0$ ) to obtain the monotonically increasing function  $\varphi(x)$  defined by

$$\frac{x}{\sqrt{\kappa}} = \int_{1/2}^{\varphi(x)} [|u| + 2bF(\tau) + 2G(\tau)(u + 2E(\tau))]^{-1/2} d\tau. \quad (54)$$

As  $F(0) = F(1) = 0$  and  $G(0) = -1/2$ ,  $G(1) = 1/2$  with  $F'(0) = F'(1) = G'(0) = G'(1) = 0$ , the denominator has non integrable singularities at  $\tau = 0$  and at  $\tau = 1$  which effectively ensure the required asymptotic boundary conditions. More precisely, the integrand has singularities of the kind  $1/\tau$  and  $1/(1 - \tau)$  respectively in the neighbourhood of 0 and 1; then  $x \sim \ln \varphi$  for  $\varphi \rightarrow 0^+$  and  $x \sim -\ln(1 - \varphi)$  for  $\varphi \rightarrow 1^-$ . By inverting the function, it follows that  $\varphi$  tends to its asymptotic values exponentially (Fig.5).

To obtain an explicit solution, we have neglected the non local term in the chemical potential.

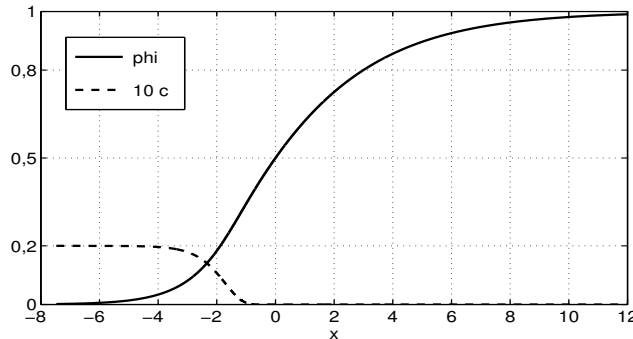


FIGURE 5. Profiles of  $c(x)$  and  $\varphi(x)$  for  $\kappa = 1$ ,  $b = 0$  and  $u = -2 \cdot 10^{-2}$ .

Generally speaking, the non local current  $\mathbf{J}_{nl}$  has an indispensable regularising role for the solutions of the Cahn-Hilliard equation in the anti-diffusive regime. This can easily be seen in the one-dimensional case, where the flux in the classical Cahn-Hilliard model is

$$J = \lambda c'''(x) + [(c(x) - 1/2)^2 + u]c'(x).$$

If  $J_{nl} = 0$ , that is  $\lambda = 0$ , the equilibrium configurations are characterised by

$$[(c(x) - 1/2)^2 + u]c'(x) = 0.$$

There is always the smooth homogeneous solution  $c'(x) = 0$ . However that solution is not the stable one at  $u < 0$ ; but any non homogeneous solution to that equation cannot be smooth.

In our case however, even in absence of the non local term  $\mathbf{J}_{nl}$ , a regular non homogeneous solution is obtained as a consequence of the coupling with the Ginzburg-Landau equation. This suggest that, at least in the one-dimensional case, the non local contribution  $\lambda|\nabla c|^2$  is not essential. Nevertheless, we do not mean that it would not be important at all, especially if one is interested in the structure of the interface. In fact, we observe that, as a result of our simplification, the concentration vanishes as soon as  $\varphi$  reaches the value  $\varphi = 1/2$ , rather than  $\varphi = 1$ , which seems slightly unnatural.

In the three-dimensional case, we are led toward the same conclusion by arguing as follows. For  $\varphi < 1/2$ , the current  $\mathbf{J}_\varphi$  is diffusive, so in the liquid-prevalent region, the concentration field has to be smooth. On the other hand, in the ice-prevalent region ( $\varphi > 1/2$ ), all the values  $0 < c < c_s$  have a spinodal instability, so they separate in regions with  $c = 0$  and  $c$  maximum. But, for high values of  $c$ , the value  $\varphi > 1/2$  becomes unstable and decays to  $\varphi = 0$ . So, the transition regions of  $c$  have to come along with those of  $\varphi$  and are determined by the condition  $\mathbf{J}_c + \mathbf{J}_\varphi = 0$ . The smoothness of  $\varphi$  then induces a smooth variation of  $c$ .

## 5. Conclusions

A phase field model for the solid-liquid phase transition in a saline solution, which accounts for the solute segregation out of the solid crystals, has been proposed. The model encompasses three evolutionary equations: a time-dependent Ginzburg-Landau equation ruling the evolution of the solid-liquid phase field, a Cahn-Hilliard-like equation describing the dynamics of the solute concentration and, finally, an energy balance equation which determines the evolution of the temperature field. A thermodynamically consistent system has been obtained, with both phase field equations deriving from the same free energy functional. The guideline for the choice of the free energy density has been the segregation property of the solid phase towards the solute and the equilibrium condition for ice-brine coexistence. The most simple one-dimensional and isothermal equilibrium situation has been considered to test analytically the capabilities of the model. Quite demanding numerical tests about the evolutionary behaviour on more interesting two- (or three-) dimensional domains are needed to ascertain the merits of the model, and they will be the subject of future investigations.

It should be mentioned that the model can be quite straightforwardly generalized to include mechanical effects, which here have been neglected in order to better focus on the structural transformations phenomena. This involves to add the Navier-Stokes equation to the differential system in a consistent way and to take into account the macroscopic motion in the phase fields equations through the use of the material time derivative. The setting is similar to the diffusive models of binary mixtures (apart from the solidification field  $\varphi$ ) which involve the Navier-Stokes-Cahn-Hilliard system (see for example [21]). From a physical point of view (slow) mechanical effects are important in presence of the gravity field, due to the density variation induced by freezing, which causes internal motions and the tendency of the brine to reach the bottom of the domain.

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