MESOSCOPIC MODELS OF LIQUID/SOLID PHASE TRANSITIONS*

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A generalization of mesoscopic Lattice-Boltzmann models aimed at describing flows with solid/liquid phase transitions is presented. It exhibits lower computational costs with respect to the numerical schemes resulting from differential models. Moreover it is suitable to describe chaotic motions in the mushy zone.

Keywords:

1. Introduction

Mathematical and numerical modeling of liquid/solid phase transition play an important role in many areas of applied science and technology. In the foundry, the study of the heat and mass transfer phenomena occurring during the solidification of molten metals allows us to determine the conditions for the production of strong and resistent structures. In artificial crystal growth from melts, the numerical simulation of the process describes successfully the occurrence of undesiderable temperature oscillations which cause inhomogeneities in the crystal. Such a result is very interesting for the electronic industry that needs semiconductor crystals to be as pure and homogeneous as possible. In general, numerical experimentation

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in the field of liquid/solid phase transition is highly recommended as the large temperatures of the phenomena makes physical experimentation quite difficult.

Conceptually, solidification and melting phenomena belong to the general framework of nonequilibrium statistical mechanics, a challenging discipline in which the powerful methods of equilibrium thermodynamics, as well as the comfortable distinction between the three basic states of matter, gas, liquid and solid, become some how questionable. This makes analytical progress slow and resorting to computer modeling becomes highly desirable.

To date, mathematical modeling of liquid/solid phase transition is mostly based on continuum models whose evolution is governed by (nonlinear) partial differential equations (PDEs).[1,2] The numerical solution of these equations is often very difficult due to the necessity of matching the solid to liquid regions, where different PDEs are applied, and tracking the corresponding liquid/solid interface.[3,4]

It is therefore desirable to look for alternative formulations no longer based on continuum assumptions, but able instead to capture the mesoscopic nature of the flow: the interface between the liquid phase and the solid phase is a kind of amorphous state which is neither liquid or solid, but rather a mix of the two, so called "mush". Mesoscopic methods such as the Lattice-Boltzmann equation (LBE) might have a word to say in this context.

In this paper we present an explorative study aimed at assessing whether suitable generalizations of the existing LBE models can provide a serious alternative/complement to current numerical methods for flows with phase transitions (Φ-flows).

The paper is organized as follows: in Sec. 2 we describe the main feature of the LBE model for Φ-flows. In Sec. 3 we present some preliminary results of numerical simulations, and finally, in Sec. 4 we comment on current limitations and future developments of the method.

2. The Model

The main idea in this paper is to simulate liquid/solid phase transitions by means of an LB model with chemical reactions.[5]

For the sake of simplicity we shall refer to a one-dimensional LBE scheme known as D1Q5, namely five discrete speeds in one dimension ($c_0 = 0$, $c_{\pm 1} = \pm 1$, $c_{\pm 2} = \pm 2$).

The plain D1Q5 model for single-phase flows evolves according to the following LBE equation:

$$f_i(x + c_i, t + 1) - f_i(x, t) = -\omega(f_i - f_i^e) \qquad i = 0, \pm 1, \pm 2 \,, \tag{1}$$

where $f_i(x, t)$ is the probability of finding a particle in x at time t propagating along c_i. The quantity f_i^e in the r.h.s. is a local equilibrium to which the discrete distribution f_i relaxes to in a time lapse $\tau = 1/\omega$, $0 < \omega < 2$.

This local equilibrium takes the form

$$f_i^e = \rho[A_i + B_i u_i + C_i u^2 + D_i u_i^2 + E_i u_i u^2 + F_i u_i^3 + G_i u_i^2 u^2 + H_i u^4]\,, \qquad (2)$$

where ρ is the fluid density, $u_i = uc_i$ and the parameters $A_i, B_i, \ldots$ are chosen in such a way to reproduce the Navier–Stokes equations with heat-transfer.[6]

The main macroscopic quantities to be reproduced are:

$$\rho = m \sum_i f_i \qquad \text{(mass density)}$$

$$\rho u = m \sum_i f_i c_i \qquad \text{(current density)}$$

$$\rho T = m \sum_i f_i (c_i - u)^2 \qquad \text{(temperature)}$$

$$q = m \sum_i f_i (c_i - u)^3 \qquad \text{(heat flux)} \qquad (3)$$

In order to describe solidification/melting phenomena, we must generalize (1) in several respects. First we need to account for two different species, f_{i1}, f_{i2}, representing the liquid/solid phases respectively. Second, we must allow for mass, momentum and energy exchanges between these species so as to describe the solidification/melting event. In equations:

$$f_{i\sigma}(x + c_{i\sigma}, t + 1) - f_{i\sigma}(x, t) = -\omega_\sigma(f_{i\sigma} - f_{i\sigma}^e) + R_{i\sigma}\,, \qquad (4)$$

where $\sigma = 1, 2$ labels liquid/solid respectively.

Note that the discrete speeds $c_{i\sigma}$ also get species index σ since liquid and solid particles should be allowed in principle to move at different speeds.

The chemical term R_{i_σ} is designed to implement the fictitious chemical reaction

$$nL = S\,, \qquad (5)$$

whereby n "molecules" of liquid transform into one "molecule" of solid, if temperature T is below a given threshold T_c, the solidification temperature, and vice versa if $T > T_c$.

The effective coefficient n, not necessarily an integer, allows for several liquid "molecules" to transform into a single solid "molecule" in order to fulfill the requirement of mass conservation during the reaction.

This analogy:

$$\text{phase transition } \sim \text{ chemical reaction} \qquad (6)$$

deserves some further comment.

At a microscopic level, (6) is obviously ill-posed: liquid and solid are exactly the same molecules, the difference being that solid molecules are bound by potential energy whereas liquid ones are allowed to move around due to their higher kinetic energy.

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At a mesoscopic level, however, the analogy (6) is much more tenable. A mesoscopic "molecule" is de-facto a collection of many elementary physical molecules so that the distinction between an aggregate of molecules in a solid crystal and one in a liquid state becomes perfectly meaningful.

To make the terminology clear, we shall hereafter refer to particles as computational aggregates of (many) physical molecules in either liquid or solid state. This is perfectly in line with the usual definition of computational particles in statistical physics.

3. The "Chemical" Term R_{i_σ}

As is well known, solidification of a liquid substance implies (latent) heat release, whereas melting of a solid requires heat supply from the exterior.

Thus, the analogy (6) can be further qualified as

$$\text{melting} \sim \text{exothermic chemical reaction}$$
$$\text{solidification} \sim \text{endothermic chemical reaction.} \tag{7}$$

At a microscopic level, this corresponds to the following energy-conservation

$$\frac{1}{2}m_l c_l^2 + V_l = \frac{1}{2}m_s c_s^2 + V_s \,, \tag{8}$$

where $V_{l,s}$ are the potential energies of the L/S phases respectively.

The difference

$$\lambda = |V_s - V_l| \tag{9}$$

is the energy supply needed to break the bond between two solid particles and bring them into the liquid state

Manifestly, λ is associated with the latent heat of the reaction. With this microscopic picture in mind, the conservation constraints on R_{i_σ} read as follows:

$$\dot{\rho}_l + \dot{\rho}_s = m_l \sum R_{i_l} + m_s \sum R_{i_s} = 0 \ \text{(mass)}$$
$$\dot{J}_l + \dot{J}_s = m_l \sum R_{i_l} c_{i_l} + m_s \sum R_{i_s} c_{i_s} = 0 \ \text{(momentum)} \tag{10}$$
$$\dot{E}_l + \dot{E}_s = \sum R_{i_l} \left(\frac{m_l c_{i_l}^2}{2} + V_l \right) + \sum R_{i_s} \left(\frac{m_s c_{i_s}^2}{2} + V_s \right) = 0 \ \text{(energy)} \,.$$

These are only three equations for ten unknowns $R_{i_\sigma}, i = 0, \ldots, 4; \sigma = 1, 2$ and leave plenty of freedom. A possible way to close the system is to impose two further constraints on the 3th and 4th order momenta

$$\dot{q}_l + \dot{q}_s = \sum R_{i_l} m_l (c_{i_l} - u)^3 + \sum R_{i_s} m_s (c_{i_s} - u)^3 = 0$$

$$\dot{Q}_l + \dot{Q}_s = \sum R_{i_l} m_l (c_{i_l} - u)^4 + \sum R_{i_s} m_s (c_{i_s} - u)^4 = 0 \,. \tag{11}$$

This leaves five free unknowns. To close the system we postulate phenomenological expressions for the rates $\dot{\rho}_l, \dot{J}_l, \dot{E}_l, \dot{q}_l, \dot{Q}_l$ in terms of the thermodynamics variables

$\rho_l, J_l, E_l, q_l, Q_l$. A possible choice is:

$$m_l \sum R_{i_l} = \dot{\rho}_l = -K_{ls}\rho_l^n - K_{sl}\rho_s$$

$$m_l \sum R_{i_l} c_{i_l} = \dot{J}_l = \dot{\rho}_l \left| u_l - u_s \right| \alpha_J$$

$$\sum R_{i_l} \left(\frac{m_l c_{i_l}^2}{2} + V_l \right) = \dot{E}_l = \dot{\rho}_l \left| E_l - E_s \right| \alpha_E \tag{12}$$

$$\sum R_{i_l} m_l (c_{i_l} - u)^3 = \dot{q}_l = \dot{\rho}_l \left| q_l - q_s \right| \alpha_q$$

$$\sum R_{i_l} m_l (c_{i_l} - u)^4 = \dot{Q}_l = \dot{\rho}_l \left| Q_l - Q_s \right| \alpha_Q \,.$$

This generates a 5×5 system for the unknowns R_{i_l}.

The phenomenological expressions (13) are to a large extent empirical in nature: they simply state that the change $\dot{X}_l$ of a given hydrodynamical quantity X_l under chemical reactions is rate of the mass rate $\dot{\rho}_l$ times the unbalance of X between the liquid and solid state.

The prefactor $\dot{\rho}_l$ is physically sound, since it reflects the stoichiometry of the reaction (5). It also guarantees that when the chemistry is over, no thermodynamic change can take place.

The deviatoric part $(X_l - X_s)$ is arbitrary, simply reflecting the idea that the chemistry should turn off if $X_l = X_s$. The coefficients $\alpha_J, \alpha_E, \alpha_q, \alpha_Q$ are tunable parameters, in fact, physical parameters related to the material and to the conditions at which the phase transition occurs.

The mass change rate $\dot{\rho}_l$ is the "driver" of our model and deserves some further comment. First, we observe that the liquid $\to$ solid frequency factor K_{ls} is chosen in the form of a sigmoid function taking the value zero sufficiently below T_c and $K_{ls} = A$ sufficiently above. The amplitude A (frequency factor) controls the time-scale of the chemical reaction. The range of temperature values for phase transition controls the size of the liquid/solid interface.

The complementary coefficient K_{sl} is chosen in the form

$$K_{sl} = E(1 - K_{ls}) \,, \tag{13}$$

where the amplitude E controls the liquid-to-solid fraction within the interface according to the relation:

$$\frac{\rho_l^\nu}{\rho_s} = E \,. \tag{14}$$

This means that high values of E promote liquid-rich interface whereas low E's favor solid-rich ones.

As it stands the present model treats liquid and solid particles on the same formal footing, i.e., via the kinetic Eq. (1). The distinction between liquid/solid is therefore entirely dependent on the actual numerical values of the parameters $m_\sigma, V_\sigma, \omega_\sigma, c_{i_\sigma}$. The generic idea is to treat the solid phase as a dense, highly viscous, non-ideal fluid. The same applies to the liquid particles, although to a different

quantitative extent. Density is controlled via the elementary mass m_s which can be chosen higher than m_l. Viscosity is controlled by the relaxation parameter ω_σ via the (ideal-gas) relaxation

$$\nu_\sigma = \frac{T}{6}\left(\frac{1}{\omega_\sigma} - \frac{1}{2}\right),\tag{15}$$

where $0 < \omega_\sigma < 2$ for numerical stability. By making ν_s sufficiently high one can achieve very small macroscopic solid speeds, of the order of $\mu_s \tilde{} p_s L/\nu_s$, where L is a typical macroscopic length scale. Here $p_s = \rho_s T_s$ like for an ideal gas, an awkward feature for a solid.

This can be cured by augmenting the solid kinetic equation with an extra force term F_{i_s} such that it contributes exactly $\boldsymbol{\nabla} p_s$ to the solid momentum and nothing to all other momenta.

A final feature to be carefully examined is the solid diffusivity inside the liquid and vice versa, which results from the fact that solid particles are allowed to hop in the lattice as well as liquid ones. This "anomalous" mobility is effectively taken care of by the "chemical reactions" which prevent the solid particles from penetrating into the liquid phase on distances longer than the thickness of the thermal interface. Eventually reduced solid speeds $c_{is} = \varepsilon c_{i_l}$, with $\varepsilon \ll 1$ can also be employed, even though this solution has not been implemented in the present work.

Thermal conductivity is also controlled by the same parameter ω_σ so that a unit Prandtl number results

$$\mathrm{Pr}_\sigma \equiv \nu_\sigma/k_\sigma = 1.\tag{16}$$

This is unrealistic for both solid and liquid phases and calls for amendments to the model, as will be discussed later.

Finally the non-ideal nature of the fluids is taken into account via a nonzero potential energy V_σ. In the present model, the main purpose of this parameter is to allow the definition of a latent heat

$$\lambda = |V_s - V_l|\tag{17}$$

into the system.

As mentioned previously, solids should have $\nu \to \infty$ and for liquids Pr should be significantly less than 1.

One possible way to meet this requirement is to implement a multi-relaxation operator of the form

$$-\omega_{\sigma 1}(f_{i_1\sigma} - f^e_{i_1\sigma}) - \omega_{\sigma 2}(f_{i_2\sigma} - f^e_{i_2\sigma}),\tag{18}$$

where i_1 and i_2 are two parity-conjugate directions ($\boldsymbol{c}_{i_1} + \boldsymbol{c}_{i_2} = 0$). This decouples heat from momentum transfer and allows $\mathrm{Pr} \neq 1$.[7]

4. Numerical Results

To demonstrate the model described in the previous section, we present the results of a simple 1D simulation.

We start with a liquid at rest at $t = 0$, with a linear temperature profile $T(x) = T_0 + (2\Delta T/L)x - (L/2)$, where L is the extension of the one-dimensional domain. For the sake of simplicity, periodic boundary conditions are imposed, which is why $T(x)$ is chosen to be symmetric about $x_0 = L/2$.

By choosing $T_0 < T_c$, and $T_1 \equiv T_0 + \Delta T > T_c$, the following dynamics is expected: as the solid phase grows where the liquid is at a temperature below T_c, the latent heat released during the process induces the temperature to rise; this happens also in the solidifying material due to thermal conduction. As a result the temperature is expected to grow up to the point where eventually the entire profile lies above T_c, so that solid formation stops, the liquid starts to form again and the system reaches an equilibrium solution with a flat temperature profile.

The numerical simulation is set up with the following parameters:

$$T_0 = 0.48, \ T_c = 0.5, \ \Delta T = 0.05$$

$$\omega_{l_1} = 0.5, \ \omega_{l_2} = 0.05, \ \omega_{s_1} = 1.0, \ \omega_{s_2} = 0.01$$

$$m_l = 1, \ m_s = 1.1, \ \lambda = |V_s - V_l| = 0.25$$

$$A = 10^{-5}, \ E = 1. \tag{19}$$

This corresponds to a Stefan number

$$\text{Ste} = \frac{c_p \Delta T}{\lambda} = \frac{3 \times 0.05}{0.25} = 0.6. \tag{20}$$

(Please note that $c_p = 3$ in a one-dimensional LBE gas) and $P_{r_l} = 8.8x10^{-2}$, $P_{r_s} = 7.5x10^{-3}$. In Fig. 1 we show the evolution of temperature profile up to $t = 1000$ time units, every 200 time-steps. The trend towards a uniform equilibrium profile is clearly visible.

The solidification process is also clearly visible, as reported in Fig. 2 for the same time sequence as Fig. 1. As expected, the growth of the solid germ takes place in the region where $T < T_c$ since the solid density responds almost adiabatically to the chemical source term. It is interesting to monitor the position of the solid front x_{sf} as time unfolds. According to the chemical solution of the 1D Stefan problem,[8] one expects a behavior of the form

$$x_{sf}(t) - x_{sf}(0) = \alpha\sqrt{t}. \tag{21}$$

This is indeed the type of behavior displayed by Fig. 3.

From this figure, we see that the asymptotic behavior $\sqrt{t}$ is well captured by our model, and also the prefactor $\alpha \sim 0.5$ is in a reasonable agreement with the analytical solution.
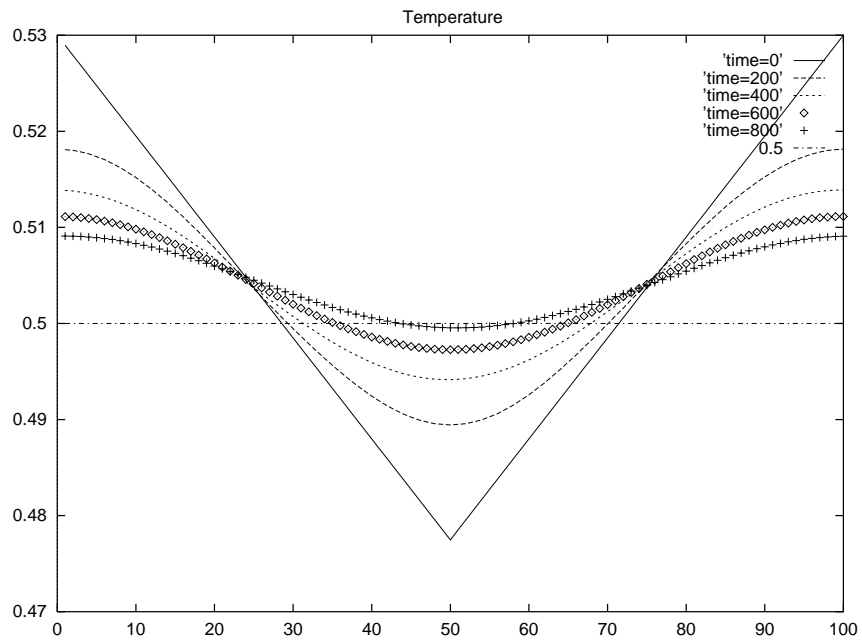
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Fig. 1.   Time evolution of the temperature profile at $t = 0, 200, 400, 600, 800$ as a function of the space coordinate.
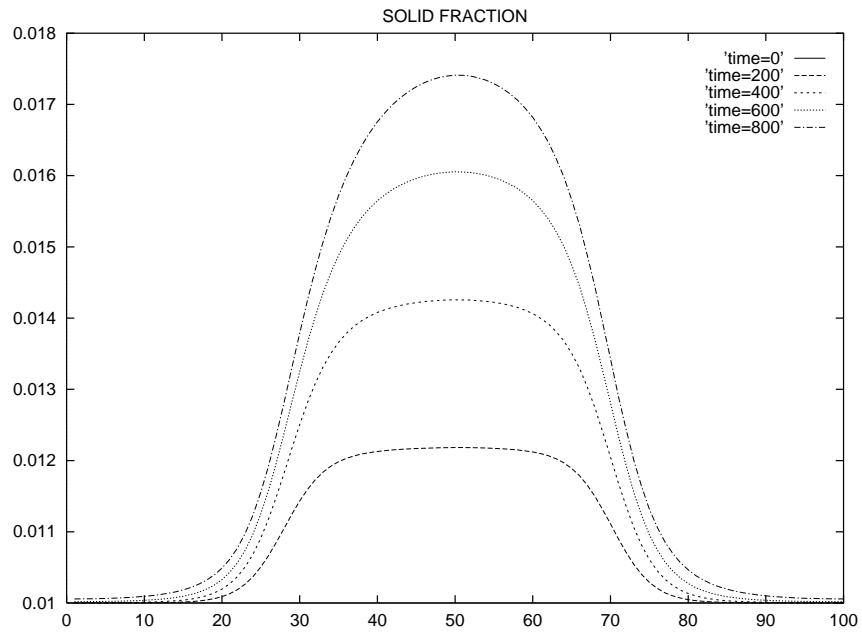

Fig. 2.   Time evolution of the solid fraction at $t = 0, 200, 400, 600, 800$ as a function of the space coordinate.
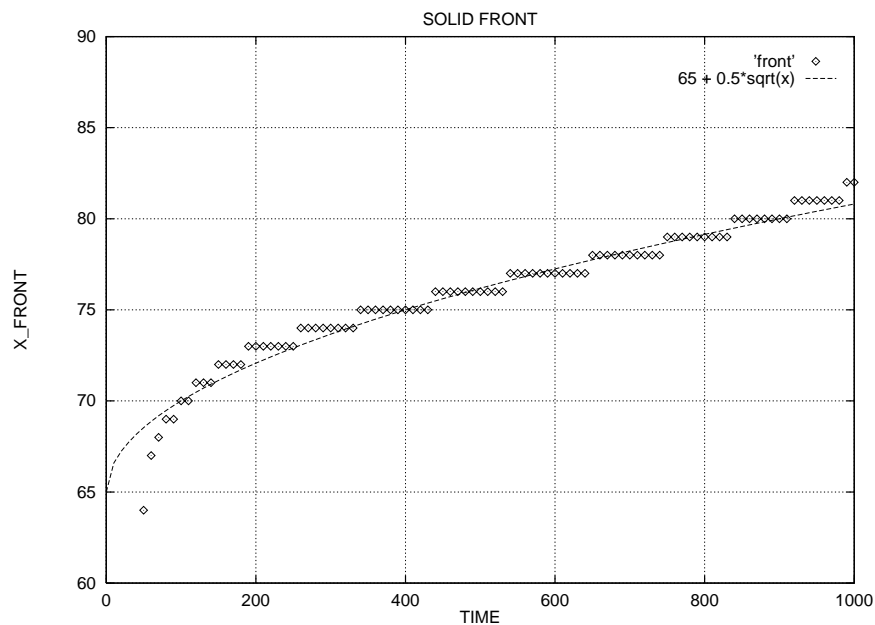
Fig. 3.   Time evolution of the solid front position.

5. Conclusions

Research in liquid/solid phase transition has produced several mathematical differential models which are acceptable in many respects. Dynamics of the liquid phase is described successfully like a newtonian fluid; where it is considered, the moving phase front, it is treated either as an explicit unknown variable of the model — Stefan formulations[8] — or it can be detected by comparing the temperature field versus the critical values of the material — enthalpic models,[2] and other global formulations.[1] The inclusion of the dynamics of the solid phase is obtained, at a high computational cost, within the global models, where the whole effects of the different phases over the contiguous ones are taken into account. The correct description of the phase change duration, the pressure and the temperature fields, the identification and control of the shape of the forming solid are possible results of the aforementioned models.

The model proposed here should describe in principle the whole phase change process as the classical ones do. In fact not only should the LB mesoscopic viewpoint facilitate the detection of the microstructures of the mushy region but it is also quite suitable for the study of the turbulent flow that develops there through its fine texture; turbulence in this context and its effects on the phase change process have never been investigated to date. Moreover the peculiar approach of the presented model should allow for quite detailed descriptions at a lower computational cost than in the case of the differential models. For example in order to obtain results

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by the global model,[1] the most sophisticated one, it is necessary to solve a huge set of nonlinear algebraic equations. The success of this procedure depends on the use of sophisticated and costly preconditioners. On the contrary, these nonlinearities are automatically accounted for by the **local mesoscopic** LB representation. Even though quantitative statements can only be made case-by-case, from our experience it is clear that the present **explicit local** LB formulation is an order of magnitude (or more) faster than the aforementioned one-dimensional global models.

We have shown the results of a simple 1D simulation: the evolution towards an equilibrium configuration of a melt material, that, starting from a temperature distribution partially below the solidification point, solidifies and, due to heat transport, melts again. The profile of the phase front position versus time results $\sqrt{t}$-like according to the expectations and also the evolution of the temperature distribution is qualitatively responding to the physics of the process.

Our model is based on a daring analogy — phase transition $\sim$ chemical reaction. We think that this analogy is promising and deserves to be investigated more deeply.

The simulation of two-phase flows via LB modeling is successful and the idea to represent the solid material as a highly viscous fluid has been already used with good results in the context of differential modeling. The main limitation of the model proposed here is the dependence on the "physical" parameters α_J, α_E, α_q, α_Q and K_{ls} in the equations (12) for the "chemical" terms R_{i_σ}, $i = 0, \ldots, 4, \sigma = 1, 2$; those are to be calibrated on each different material. However this drawback is common to any new mathematical model simulating a material, as analogous scalings have to be done through experiments.

In future work we shall approach a 2D numerical test in order to look at the formation of the mushy zone and the turbulent regime of the liquid.

Acknowledgments

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