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Interfacial dynamics in rapid solidification processes

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Abstract

The broad interest in rapid solidification processes originates from the variety of non-equilibrium microstructures found in the solidified materials; most familiar examples are dendrites, lamellar eutectics, cellular and banded structures. In spite of the deep efforts devoted to this subject by the scientific community, the interfacial dynamics is far from being well understood. The aim of this article is to review some recent theoretical developments, which give a diffuse picture of the interfacial region. A new microscopic approach, based on the stochastic dynamics of a lattice of Potts spins, is also discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rapid solidification phenomena play a major role in many fields such as material engineering, crystal growth, chemistry and physics [1]. As the final properties of the solid material depend significantly on the details of the growth process, the understanding and prediction of the interfacial dynamics is of crucial importance. For pure substances, the growth rate is controlled by the diffusion of the latent heat released at the solid–liquid interface; for alloy solidification both heat and solute diffusion are the limiting factors. The classical approach to describe the interfacial dynamics is formulated in terms of a moving boundary problem. The diffusion equation of heat (and

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eventually of solute) is complemented with boundary conditions at the moving front, reflecting two different constraints: (i) conservation law for energy (and solute) at the interface, and (ii) constitutive law which relates the chemical potential jump across the interface to the growth rate. Point (ii) requires a separate modellization of the interface kinetics. It should be mentioned that the contradiction between the sharp boundary conditions and the diffuse nature of the interfacial region poses delicate problems when the model is applied to the description of fast transient growth [2]. A more recent method to investigate solidification processes is based on the phase-field model (PFM) [3,4]. In this model a non-conserved order parameter characterizes the phase of the system at each point. A suitable free-energy (or entropy) functional is then constructed, that depends on the order parameter as well as on the associated (conserved) fields and their gradients. The functional derivatives of this functional with respect to such order parameter and fields determine the evolution of the system towards equilibrium. Studies conducted on solidification of both pure substances and binary alloys [5,6] pointed out that the PFM incorporates in a natural fashion the effects of interface curvature and non-equilibrium phenomena as the trapping of solute into the solid phase and the kinetic undercooling of the solid–liquid interface. Moreover, describing the interface as a region of finite thickness, gives a more natural and consistent picture of the solidification front.

The existing approaches to the problem represent at different degrees a coarse-grained picture of the microscopic processes. In fact, thermal fluctuations are not included in either model. An alternative approach consists in starting from the level of description of the Hamiltonian together with a microscopic dynamics of stochastic character, and to recover the observed macroscopic behavior at a macroscopic and mesoscopic scale without coarse graining the model [7,8]. This task avoids some of the traditional difficulties such as the use of adhoc free-energy functional in the PFM and the need to postulate sharp boundary conditions, in contradiction with the diffuse nature of the interfacial region, in the free-boundary model. This microscopic statistical model (MSM) has been exploited in some recent studies on rapid solidification of both pure substances and binary alloys.

Some of the most relevant results obtained starting from the PFM and MSM are reviewed hereafter. Section 2 is devoted to solidification of pure substances, and Section 3 to alloy solidification. The concluding remarks follow in Section 4.

2. Solidification of pure substances

Investigations on the solidification of pure substances conducted through the phase-field model were at first directed to demonstrate that the model equations reduced asymptotically to the free-boundary formulation when the interface width tends to zero. The control parameter for the interface velocity v is the non-dimensional undercooling Δ, defined as $\Delta = c_p(T_m - T_\infty)/L$, where c_p is the specific heat, T_∞ the far-field temperature and T_m the equilibrium melting temperature; L is the heat of fusion. One-dimensional numerical simulations [9] showed that the model properly described the diffusional regime for $\Delta < 1$ (with v decaying as $\propto t^{-1/2}$) and the steady regime for $\Delta \geqslant 1$. Numerical studies of the growth of a single dendrite were conducted in two dimensions and attention was focussed on the selection mechanism of the dendrite tip operating state, which intrigued the scientific community for a long time. It was confirmed that in free growth conditions in order to have a stable and steady tip propagation, anisotropy of the surface energy is required [10]: the dendrite tip radius ρ and the velocity v_{tip} are related to the anisotropy strength α through the dependence $\rho^2 v_{\text{tip}} \propto \alpha^{-7/4}$. When the growth occurs in a narrow channel, the intrinsic anisotropy induced by the channel boundaries allows steady tip propagation even for isotropic surface tension [11]. The phase-separation dynamics of an initially undercooled melt was also studied numerically within the framework of the phase-field model. In the later stage of the growth process, the evolution is dominated by the diffusion of the residual heat in the system and leads to a scaling regime characteristic of a conserved dynamics, with characteristic power-law growth of the average domain size proportional to $t^{1/3}$ [12]. These numerical results were corroborated by the solution of a spherical version of the PFM which lead to the prediction of crossover from a $t^{1/2}$ behavior to an asymptotic $t^{1/3}$ growth law [13–15].

The microscopic statistical model (MSM) is based on a lattice dynamics in which a Potts spin variable describing the local phase is associated to each lattice point; the heat conduction mechanism is implemented adding to each site additional degrees of freedom, the Creutz demons, which follow a conserved dynamics. The model has proved able to properly describe the diffusive ($\Delta < 1$) and the kinetic ($\Delta > 1$) regimes for the one-dimensional growth [7]. In two dimensions a morphological instability results in a front pattern which characteristic length is in good agreement with the predictions of the Mullins Sekerka analysis.

3. Alloy solidification

The analysis of the microstructures formed in rapid solidification of binary alloys, evidenced that the partition coefficient k (i.e., the ratio c_s/c_l of the solute concentration in the growing solid to that in the liquid at the interface) increases from the equilibrium value k_e towards unity at large growth rate. This phenomenon was termed “solute trapping”. Aziz [16], starting from a diffusional analysis across a steadily moving interface, was able to determine a dynamic phase diagram; the dependence of the partition coefficient on the growth velocity is given in the form

$$k(v) = \frac{k_e + v/v_d}{1 + v/v_d} \tag{1}$$

being k_e the equilibrium value for a stationary interface, and v_d a characteristic velocity describing the diffusional solute redistribution across the moving front; v_d is generally expressed as $v_d = D/a$, where D is the interface solute diffusivity and a is the width of the interfacial layer.

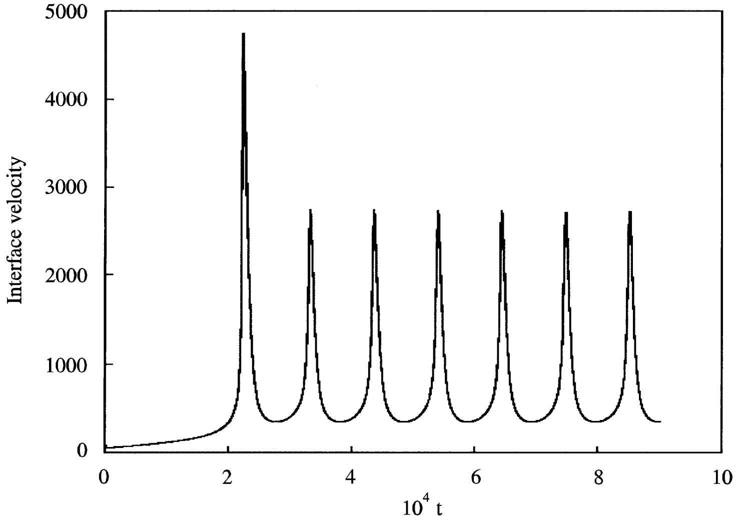

Fig. 1. The oscillatory dynamics of the solidification front.

The dynamic phase diagram is generally employed to provide the non-equilibrium boundary conditions needed to solve the free-boundary diffusional problem. However, this method hides a basic contradiction. The moving front is treated, under all respects, as infinitely thin layer, whereas Eq. (1) originates from a diffuse interface picture of the solidification process (for a sharp interface $a = 0$, $v_d = \infty$ and no solute trapping should occur). This ambiguity emerges in the description of time dependent processes: solute relaxation across the interface is not instantaneous but takes time of the order $\tau \sim a^2/D = a/v_d$, and the free-boundary equations give an unrealistic picture of the process when the transient characteristic time is of the order of τ. On the contrary, the phase-field model intrinsically accounts for finite time effects in the interfacial dynamics. As an example [2], we refer to the oscillatory dynamics observed in some rapid directional solidification experiments (i.e., solidification driven by a thermal field which moves at constant velocity V_0 with a thermal gradient G). Fig. 1 shows the results of a phase-field simulation for a Ni–Cu alloy: the interface velocity is represented versus time, for $V_0 = 700$ and $G = 40$ K (except for temperatures, dimensionless units are used, scaling lengths to the interface width a and times to a^2/D. The process never reaches a steady regime, and the interface velocity continuously oscillates around the average value V_0. Here τ is of the order of 10^{-5}, and the fast transients shown in Fig. 1 exhibit Fourier components comparable with $1/\tau$; then we should observe a breakdown of the free-boundary picture. This suggestion is confirmed by Fig. 2, where the cycle described by the partition coefficient, as given by the phase-field simulation (solid dots), is compared with the predictions of Eq. (1) (solid line). We note that the partition coefficient is not a uniquely defined function of the interface velocity, but shows an hysteretic behaviour and deviates from the free-boundary predictions during

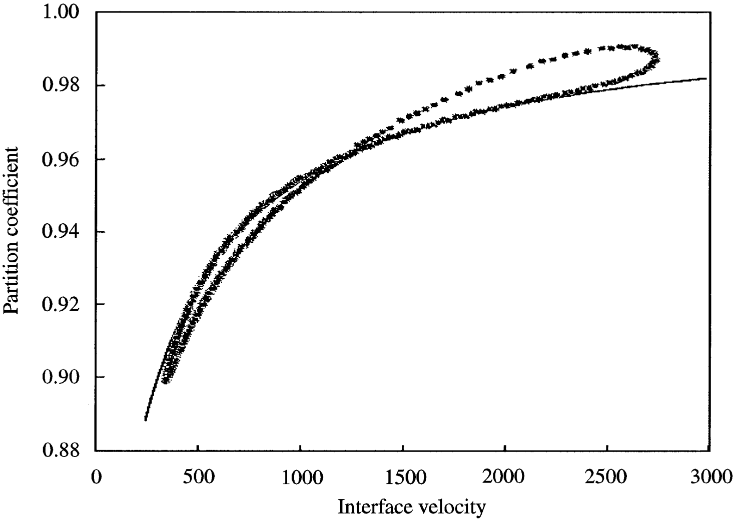

Fig. 2. The partition coefficient versus the interface velocity along the cycle described by the solidification process.

a significant portion of the cycle. In the MSM [8] for alloy solidification the local phase is described through a discrete Potts state variable which follows a stochastic non-conserved dynamics; the chemical species is associated with a spin variable changing according to Monte Carlo spin-exchange dynamics in order to conserve the number of particles of each species. These two variables allow to define an Hamiltonian which models a binary mixture undergoing a solid–liquid phase separation, driven by the competition between the larger entropy of the liquid and the lower energy of the solid. The mean field approximation of the model results in a lens-shaped equilibrium phase diagram, characteristic of ideal solutions. The off equilibrium dynamics is characterized by the different frequencies with which one attempts to change the two variables, reflecting the two different time scales of the solidification process and of the solute diffusion. The model has been solved in directional solidification conditions. It was observed that the width of the interfacial layer is of the order of several lattice sites. Figs. 3 and 4 show the solute profile for two different values of the rate of attempts f_d for the species variable. It can be observed that the concentration gap at the interface increases with increasing f_d. This is a manifestation of the trapping of solute into the solid phase. At high diffusion rates the solute redistribution across the advancing front is very effective and the partition coefficient approaches the equilibrium value k_e. At low values of f_d the diffusional mechanism is too slow with respect to the growth rate and the solute has no time to be effectively rejected across the interface; as a consequence the concentration gap decreases and the partition coefficient approaches unity.

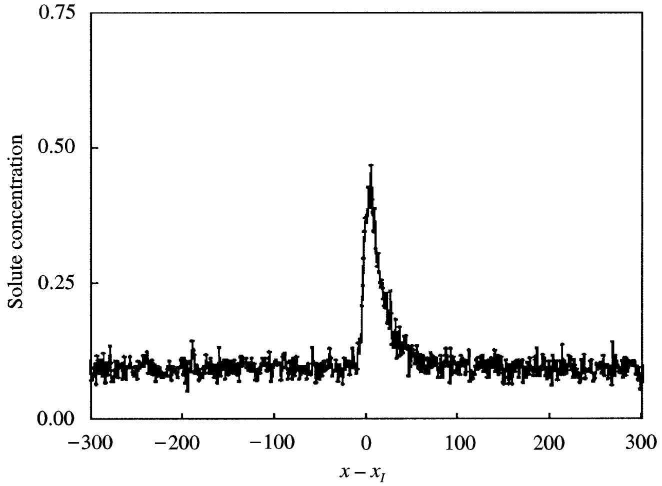

Fig. 3. The solute profile for directional solidification. The rate of attempts for the species variable is $f_d = 16$ per each Monte Carlo step; x_I locates the interface position.

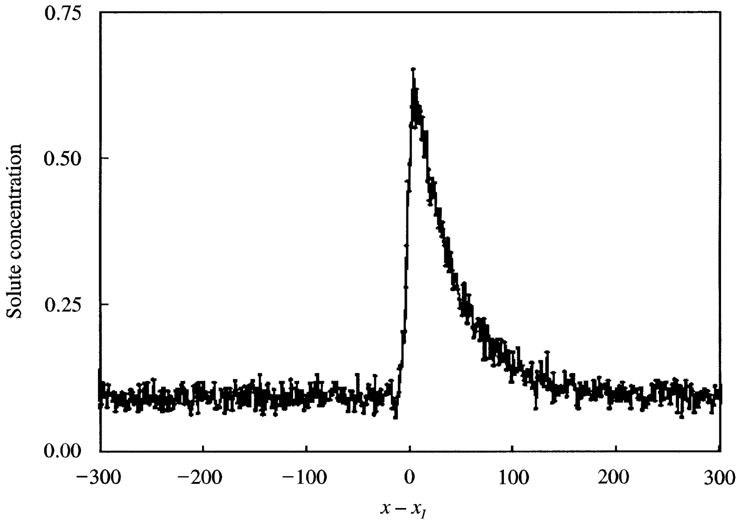

Fig. 4. The solute profile for directional solidification. The rate of attempts for the species variable is $f_d = 40$ per each Monte Carlo step; x_I locates the interface position.

4. Conclusion

Diffuse interface models give a realistic picture of rapid solidification processes, accounting for non-equilibrium phenomena and finite-time effects. Phase-field simulations allowed to gain more insight into the interfacial dynamics underlying the formation of dendritic patterns and the late stage coarsening of solid islands. With respect to the free-boundary approach alloy solidification is more accurately described for fast transient growth. The stochastic behavior intrinsic to the microscopic statistical model properly accounts for the fluctuations; the model has proved able to predict the morphological instability of the solidification front and non-equilibrium effects as solute trapping.

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