A microscopic model for solidification

M. Conti, U. Marini Bettolo Marconi and A. Crisanti

1 Dipartimento di Matematica e Fisica, Università di Camerino and Istituto Nazionale di Fisica della Materia, Unità di Camerino, Via Madonna delle Carceri, I-62032, Camerino, Italy, 2 Dip. di Fisica, La Sapienza, Roma, Italy

(accepted)

PACS. 64.60.-i – General studies of phase transitions.
PACS. 64.60.Cn – Order disorder transformations.

Abstract. – We present a novel picture of a non isothermal solidification process starting from a molecular level, where the microscopic origin of the basic mechanisms and of the instabilities characterizing the approach to equilibrium is rendered more apparent than in existing approaches based on coarse grained free energy functionals à la Landau.

The system is composed by a lattice of Potts spins, which change their state according to the stochastic dynamics proposed some time ago by Creutz. Such a method is extended to include the presence of latent heat and thermal conduction.

Not only the model agrees with previous continuum treatments, but it allows to introduce in a consistent fashion the microscopic stochastic fluctuations. These play an important role in nucleating the growing solid phase in the melt. The approach is also very satisfactory from the quantitative point of view since the relevant growth regimes are fully characterized in terms of scaling exponents.

A remarkable feature, observed in solidification processes, is the occurrence of different morphologies of the solid-liquid boundary, namely flat, cellular or dendritic, according to the initial undercooling, which acts as control parameter for the growth process.

The theoretical models employed so far to study this kind of non equilibrium phase transformations represent at different degrees a coarse grained, mesoscopic picture of the underlying microscopic processes. They miss consequently an important point, i.e. the stochastic character of the thermal fluctuations and disregard the nucleation of the growing phase in the melt. It has also been argued that small a thermal noise can account for the enhanced sidebranch activity during dendritic growth.

The state of affairs is as follows: in the free boundary model the solidification process is formulated in terms of a sharp moving boundary, acting as a source for the diffusion field, while the thermodynamic information enters the model only via the boundary conditions; in the phase field model, instead, employing a local order parameter formulation, whose evolution

Typeset using EURO-L\TeX
depends on some coarse grained Ginzburg-Landau functional, one regards the transition region between the two phases as smooth and characterized by arbitrary topology. In spite of its merits the latter approach is frankly mesoscopic and the temperature acts only as a parameter which controls the relative stability of the two phases, but does not play a role in the nucleation processes.

In the present paper we shall adopt a molecular point of view, instead of a continuum formulation. In spite of the fact that in many cases of interest, neither of the methods can provide information which is not also accessible to the other, the microscopic approach is required for the study of phenomena involving large spatial gradients and is able to account for noise effects. In the following we shall discuss how to incorporate in a consistent fashion the stochastic character of fluctuations into a microscopic model of solidification.

The formulation of a minimal model to explain the occurrence of the instabilities and the variety of patterns during the crystal growth from the melt needs to include four basic effects:

i) the tendency of the molecules towards an ordered state which minimizes their configurational energy.

ii) the opposite tendency of the system towards a disordered state which maximizes its entropy.

iii) the release of latent heat during the liquid/solid transformation

iv) the diffusion of such a heat away from the two phase boundaries.

To fulfill the above requirements and maintain a microscopic point of view we shall consider a novel lattice model by assigning to each site \( i \) a Potts spin variable which takes on the integer values \( 1 \leq n_i \leq q \). When \( n_i = 1 \), the spin energy is negative and given by \( -\lambda < 0 \), otherwise it is zero. An interface between a spin in a state 1 and a spin at a nearest neighbor site \( j \) whose state is \( n_j > 1 \) has a surface cost \( J > 0 \). At equilibrium and in the thermodynamic limit such a model displays two macroscopic phases, characterized by an order parameter \( m = (q - \delta_{1,n} > -1)/(q - 1) \). The ordered phase \( m \approx 1 \), and the disordered phase constituted by a mixture of the \( (q - 1) \) microscopic states with \( n_i > 1 \) coexist at \( T_m \approx \lambda/\ln(q - 1) \). Beneath \( T_m \), the melting temperature, the ordered phase is absolutely stable, whereas above \( T_m \) the entropic phase \( m \approx 0 \) has a lower free energy. The competition between the large Boltzmann weight of the state with \( n = 1 \) and the larger number of microscopic configurations of the disordered state determines the dominance of one phase over the other. The analysis of the free energy gives a complete description of the equilibrium properties of the system. Our interest, however is to study the evolution towards equilibrium, when the system is prepared in a metastable initial state.

To achieve that we introduce a dynamics by adding \( p \) auxiliary degrees of freedom at each site, the Creutz demons, characterized by energies \( \epsilon_i^\alpha \) (with \( 1 \leq \alpha \leq p \)) which act as energy reservoirs and control the evolution of the spin subsystem. When a variable changes from a value \( n_i \) to \( n'_i \), the demon energy varies from \( \epsilon_i^n \) to \( \epsilon_i^{n'} - \Delta \epsilon \), having chosen \( \alpha \) randomly among the \( p \) possible values and where \( \Delta \epsilon \) represents the spin energy change. Attempted moves which render negative \( \epsilon_i^\alpha \) are rejected. To complete the model we must include a heat conduction mechanism by assuming that at every time step an elastic collision event takes place with probability \( \kappa \) between the nearest neighbors demons \( i \) and \( j \) according the rule that the postcollisional energies are \( \epsilon_i^\alpha = (\epsilon_i^\alpha + \epsilon_j^\beta) r \) and \( \epsilon_j^\beta = (\epsilon_i^\alpha + \epsilon_j^\beta)(1 - r) \) where \( r \) is a random number chosen from a uniform distribution in the unit interval. Physically one can think of the demons as kinetic degrees of freedom, irrelevant, as far as equilibrium configurational properties are involved, but necessary to mediate the energy exchanges during the approach to equilibrium. Since the temperature may have spatio-temporal fluctuations, one needs to consider a local temperature given by the average energy of a demon over a small time interval. It can be shown redistributing the energy, i.e. in conducting the heat, even in the absence...
of spin dynamics [7]. It is interesting to stress that such a mechanism allows to obtain the correct Maxwell-Boltzmann distribution and that with different rules of energy redistribution such a behaviour is not recovered.

Thus sweeping randomly the lattice and updating sequentially the spins and the demons the system behaves ergodically and one can compute meaningful statistical averages. With the set of rules stated above we are able to simulate a system which evolves in adiabatic conditions, i.e. at constant energy, but at varying temperature. This approach can be employed in many cases where the more traditional isothermal Kawasaki and Monte Carlo methods [8] do not represent faithful descriptions of the transients encountered in experimental situations. As we shall see below we are able to capture many features relevant in solidification processes. Of course, after an appropriate thermalization run the demon energy distribution becomes statistically uniform, i.e. the temperature attains a uniform value, and the algorithm becomes equivalent to the Metropolis Monte Carlo method.

As a first check we verified that a two dimensional system of demons, with fixed temperatures at the top and bottom boundaries, reaches a steady state in which the temperature profile is linear from the cold to the hot wall and the thermal conductivity is independent of the temperature. To tune the thermal conductivity we allowed only a randomly chosen fraction $\kappa$ of the demons to undergo the collisional dynamics.

Instead, in order to recover the standard picture of the solidification we consider a demon with low energy next to a site in state 1; it can be seen that such a demon favors the transformation of liquid into solid; as a consequence the interface advances and the demon energy increases. But since the energy produced by the phase change must be diffused away before new solid can be formed, the process is slowed down: the ordered phase may also form protrusions into the colder phase in order to diffuse away more efficiently the latent heat, maximizing its surface. An appropriate choice of ratio bulk-gain versus surface-cost $\lambda/J$ renders the system stable with respect to the formation of solid islands within the liquid phase, and the growth proceeds only at the interphase boundaries. Conversely, if the demon energy is high all the states become equally accessible, and there is no tendency to crystallize.

Let us turn to the quantitative predictions of the model and give numerical evidence on one and two dimensional lattices. The most relevant macroscopic control parameter in determining the dynamics of the process is the dimensionless undercooling $\Delta$, which in terms of the specific heat $C$ and of the latent heat of fusion $L$ can be written as $\Delta = C(T_m - T_0)/L$, where $T_m$ and $T_0$ represent the coexistence temperature of the two phases and the initial temperature of the melt, respectively. As we chose in all the simulations melting temperatures well below the temperature $T_i$, where the solid metastable branch shows a peak in the specific heat, for all practical purposes the only significant contribution to the specific heat is due to the $p$ degrees of freedom of the demons, so that $\Delta$ can be expressed in terms of our microscopic variables as: $\Delta = p(T_m - T_0)/\lambda$. Notice that such a formula represents an important link between the microscopic parameters $p$ and $\Delta$ and the macroscopic thermodynamic quantities $C$ and $L$.

Since $T_m$ is proportional to $\lambda$, it appears clear the physical motivation of having more than one demon per site, i.e. a large specific heat is needed in order to attain large undercoolings. In other words one can 'solidify' an arbitrary amount of material by being able to adsorb through the demons the latent heat released.

In one dimension a system with $L_x$ lattice sites aligned along the $x$ axis was prepared in a nonequilibrium initial state, with an interface boundary at $x = x_0$ separating a solid phase ($n_i = 1$) and a liquid phase in which $n_i$ was randomly distributed in the range $2 \leq n_i \leq q$. The average demon energy was set to $T_m$ in the solid and to $T_0 < T_m$ in the liquid. Then the evolution of the system was followed up to $N$ Monte Carlo steps per site (MCS), until a well identified growth regime was attained. For each simulation an ensemble average over
256 different runs was taken to get statistical significance. A value $L_x = 1400$ was sufficient to avoid finite size effects in all the simulations. To focus on the interface dynamics, and to prevent nucleation in the bulk liquid, we chose a high value of the interface energy cost ($J = 4$). Notice that in one dimension $J$ has a strong effect on the nucleation rate in the liquid but does not affect the interfacial growth rate, which depends solely on $\Delta$. Let us see how, in one dimension, the choice of $\Delta$ determines different growth regimes of the dynamical solutions of the model.

In fig. 1 the dashed lines show two different scaling laws: the upper one displays the interface position versus time for $\Delta = 1.2$, $\lambda = 1$, $p = 4$, $q = 20$ and the thermal conductivity parameter $\kappa = 0.08$. The long time behaviour of the interface motion clearly converges to a steady solution with constant velocity, in good agreement with the macroscopic free boundary model 8. The lower dashes instead, refer to the same set of parameters, but $\Delta = 0.8$; and the interface velocity decays as $v \sim t^{-1/2}$. We verified that, in general, when $\Delta > 1$ the front travels at constant velocity $v \propto (\Delta - 1)$, but shows a significant deviation from such a formula near the crossover point to the diffusive regime, $\Delta = 1$.

Even more interestingly and more conclusively, we observe that the temperature at the interface, $T_i$, as measured through the demon energy distribution, is lower than the equilibrium melting temperature by a quantity which is proportional to the interfacial velocity $v$. This is the so called kinetic undercooling of the solid-liquid interface, which in the free boundary model must be introduced ad hoc through the constitutive law $T_i = T_m - \beta v$, to account for the necessity of a departure from local thermodynamic equilibrium (i.e. of a finite free energy difference between the two phases) to advance the solidification process. We evidenced the presence of kinetic undercooling at a microscopic level through a series of simulations performed with $\lambda = 1$, $p = 2$, $q = 4$ and $\kappa = 0.6$. The initial undercooling $\Delta$ ranged from $1.12 \leq \Delta \leq 1.82$. For each simulation, in the steady regime we evaluated the interface temperature $T_i$ through an ensemble average of the energy of the demons located at the solid-liquid boundary. The results are shown in fig. 2. One can see that the driving force for the solidification process, i.e. the shift $T_m - T_i$, is an increasing function of the growth rate; according to the predictions of both the free boundary and the phase field models the dependence $T_i(v)$ is found to be linear to a quite good extent. It is worth noting that the solid straight line, which represents the best fit of the data points, intersects the vertical axis at a temperature $T = 0.87$, very close to the equilibrium melting temperature $T_m \sim 0.91$.

As we consider the two dimensional case we see that the solid-liquid interface undergoes a morphological instability due to the competition between two effects. The necessity to diffuse the latent heat away from the interface favors the formation of protrusions of the growing solid into the supercooled melt; on the other hand the surface tension $\sigma$, via the Gibbs-Thomson effect, tends to restore the minimum surface configuration 11. The characteristic length scale for the resulting pattern has been identified by Mullins and Sekerka 11 as $\lambda_0 \sim 2\pi(3d_0\ell)^{1/2}$, where $d_0$ is the capillary length, defined as $d_0 = \sigma T_m C/L^2$ and $\ell$ is the thermal diffusion length. For steady growth we have $\ell = D/v$, where $D$ is the thermal diffusivity of the melt. We considered a rectangular domain $0 \leq x \leq L_x$, $0 \leq y \leq L_y$ with $L_x = 128$ and $L_y = 256$. The system was prepared with a solid phase ($x < 10$) and a liquid phase ($x > 10$) separated by an interface parallel to the $y$ axis; the demons energies were distributed to fix the initial temperature in the solid at $T_m$; the liquid was undercooled at $\Delta = 0.6$. The other parameters of the model were selected as $q = 20$, $p = 3$, $\lambda = 1$, $J = 0.24$, $\kappa = 0.02$. With this choice the growth process proceeded essentially through activated nucleations at the solid-liquid interface, while nucleation in the bulk liquid was almost suppressed. We checked also that the far field temperature was never affected by the finite size of the system. The upper portion of Fig. 3 shows the growing solid after $24 \cdot 10^3$ MCS. The dendritic structure of the pattern is clearly
visible. An analysis of the temperature field indicates a value of the thermal diffusion length $\ell \sim 35$ lattice sites. As the surface tension is of the order of $J$, the characteristic width of the fingers should be of the order of $\sim 30$ lattice sites, in good agreement with the numerical results.

Recent advances on pattern formation in diffusional fields indicate that no stable dendritic fingers can grow, unless a preferred direction is injected into the model through anisotropy of the surface tension or geometrical constraints such as the directional solidification in a channel \textsuperscript{[2]}. In order to render the surface tension anisotropic we differentiated the energy cost $J_n$ between the nearest neighbours and the next nearest neighbours $J_{nn}$. The lower part of Fig. 3 shows the dendritic pattern obtained with the same choice of parameters as above, and with $J_n = 0.36, J_{nn} = 0.12$. The directional growth of the fingers along the channel axis is now better established; the tip splitting dynamics and the competition between the different fingers is clearly recognizable.

Before concluding we notice that in the present approach the heat released to produce a solid particle from the melt increases the demon energy and the local temperature. The latter in turn, according to the Arrhenius relation \textsuperscript{[3]} increases the rate of nucleation $\tau^{-1} \simeq \exp(-\Delta F/k_BT)$, where $\Delta F$ represents the typical activation barrier to be overcome in order to crystallize. We observe that the liquid phase can be appreciably undercooled below $T_m$, but the solid cannot be overheated at the same extent; in other words we are able to eliminate the spurious symmetry between the two processes, which is present in the Phase Field treatment \textsuperscript{[3] - [14]}, where the temperature merely determines the relative stability of the two phases and the driving force towards equilibrium, but has no influence on the nucleation. Such a non-linear feedback mechanism is absent in all previous approaches to the problem and is one of the successes of the present model.

To summarize in the present letter we have introduced a new lattice model to simulate the microscopic behavior of a system undergoing a first order transition with emission of latent heat. The dynamics we have proposed does not need fine tuning of parameters and differs from the existing stochastic approaches because the temperature varies in space and in time. We avoid the traditional difficulty with the Phase Field model of treating the temperature as an external field which controls the relative height of the two minima of the free energy, i.e. the difference in free energy between the liquid and the solid phase and not including noise terms. Doing so we can describe on equal footing the microscopic fluctuations which make possible the nucleation of new islands of solid and the field which drives the growth.

With respect to earlier work \textsuperscript{[7]} we observe that in a different model for solidification, based on a lattice approach, two important differences could be devised: i) the specific heat is only due to the spins and strongly temperature dependent, while in our case is proportional to the number, $p$, of demons and therefore mimics the Dulong-Petit law. ii) the thermal conductivity is associated only with the spin flip mechanism and vanishes in the infinite temperature limit while at low temperature becomes a thermally activated process, while in our work is nearly temperature independent.

Concerning future perspectives it remains to investigate to which macroscopic description our microscopic model corresponds; this can be achieved by a suitable coarse graining procedure. Besides one could apply the present approach to conserved order parameter dynamics, such as melting of binary alloys, or study systems quenched from a high temperature to a low temperature condition employing a finite cooling rate. Finally we mention the possibility of considering different energy redistribution laws among demons, i.e. different kind of noises.

REFERENCES

[1] A. Karma, Phys. Rev. Lett., 70, 3439, (1993)
The model was introduced by J.S. Langer in Directions in Condensed matter Physics, edited by G. Grinstein and G. Mazenko (World Scientific, Singapore, 1986) and is a descendant of Model C of critical dynamics in the classification of P.C. Hohenberg and B.I. Halperin, Rev. Mod. Phys. Vol. 49, p. 435 Year 1977.

Within the model solid droplets immersed in a sea of liquid display the Gibbs-Thomson effect, i.e. the lowering of the melting temperature due to the curvature. An analytical estimate of such shift is: 

\[ T(R) = T_m - J/[R \ln(q - 1)] \]

where \( R \) is the droplet radius.

W.W. Mullins and R.K. Sekerka, J. Appl. Phys., 35, 444 (1964).

J.S. Langer, in Solids Far From Equilibrium, edited by C. Godrèche, (Cambridge University Press, Cambridge, 1992).

F. Marinozzi, M. Conti and U. Marini Bettolo Marconi, Phys. Rev. E, 53, 5039 (1996).

M. Conti, F. Marinozzi and U. Marini Bettolo Marconi, Europhys. Lett., 36, 431 (1996).

U. Marini Bettolo Marconi, A. Crisanti and G. Iori, Phys. Rev. E, 56, 77 (1997). and U. Marini Bettolo Marconi e A. Crisanti, Phys. Rev. Lett., 75, 2168 (1995)
A microscopic model for solidification

Fig. 1. – Upper and lower dashes represent the average interface position in lattice units in the kinetic regime ($\Delta = 1.2$) and in the diffusive regime ($\Delta = 0.8$), respectively. The solid lines represent the power laws $\sim t$ (upper) and $\sim t^{1/2}$ (lower), respectively. Time units are in MCS.

Fig. 2. – The dots represent the interface temperature (in energy units) versus the interface velocity (lattice sites per MCS); the solid line is drawn as guide to the eye.

Fig. 3. – Typical growth patterns with anisotropy (bottom) and without (top). Notice the bulk nucleation away from the boundaries. The parameters are given in the text.
