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# Solidification of viscous melts: the interplay between nanoscale physics and macroscopic behaviour

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**Abstract:** As the undercooling of a liquid melt is increased, one observes several qualitatively different regimes of solidification, each dominated by a different set of physics. I discuss the different regimes, their phenomenology, their physics, and the transitions between them. The experimental focus is on soft-condensed-matter systems, whose widely variable time scales allow one to easily explore the different solidification







2.1 *Sharp-interface models*

From linear, non-equilibrium thermodynamics, one can derive a minimal model of diffusion-limited growth [10]:

$$D^2 T = -T,$$



WKB techniques [7, 8, 9]. In the end, a plausible case has been made that one can account for the fractal-like shapes of dendrites (including tip shape and sidebranch frequency) and for the observed solidification velocities. The strong influence of the surface-tension term explains how small anisotropies in the surface tension can nonetheless create large effects on the macroscopic shape. Thus, we now understand how the hexagonal symmetry of ice leads to the six branches of a typical snowflake – a scenario first posed by Kepler in 1611 [12].

Sharp-interface models may seem a natural way to model solidification, and they



where the minimum corresponding to the liquid is at  $\phi = 0$  and that of the solid at  $\phi = 1$ . The parameter  $W$  sets the height of the energy barrier separating the two phases (and is related to the surface tension), while  $L$  is the latent heat. As written,  $W$  and  $L$  are scaled by an energy chosen so that the time  $\tau$  in Eq. 4 corresponds to the order-parameter relaxation scale. The ‘interpolating function’  $\rho(\phi)$  increases monotonically from 0 to 1 as  $\phi$  goes from liquid to solid values. (The obvious choice  $\rho = \phi$  is inconvenient because it does not keep the liquid and solid phases at  $\phi = 0$  and 1 for all undercoolings.) In Eq. 5, the  $\tau^{-1}$  term describes the release of latent heat. In Eq. 6, the last term describes how the released latent heat affects the degree of order in Eq. 4 (e.g., modeling how released heat can melt the solid).

Now let us consider solving Eqs. 4–6. Compared to the sharp-interface equations, there are two fields (temperature and order-parameter), rather than one, and they are coupled. The advantage, though, is that the equations are solved on a single domain, of simple geometry (the liquid container). The sharp-interface equations, by contrast, must be solved on a domain bounded by a solid-liquid interface that can change not only its shape but also its topology (as domains coalesce, etc.). One can show that the phase-field model contains all of the physics of the sharp-interface model (e.g., the Gibbs-Thomson effect relating the curvature of the solid-liquid interface to a shift in coexistence temperature) [14]. Indeed, it also contains non-equilibrium, kinetic effects (which can be added to sharp-interface models but are not in the simplified one presented above).

One difficulty with phase field models is the wide disparity between the interface-thickness scale (nanometers) and the scale of the diffusion fields (microns to millimeters). There is a corresponding disparity between the microscopic relaxation time (picoseconds) to the times required to form structures (seconds to minutes). In principle, a numerical simulation should span the full range of length and time scales present, a seemingly impossible task. Recently, though, Karma and colleagues have shown that by cleverly scaling dimensional variables, one can relate the results of simulations done at relatively large microscopic length and time scales to parameters that match experimental situations [15, 16]. The microscopic parameters must still be small compared to the macroscopic variations, but the range of scales needed for the simulation is drastically reduced.

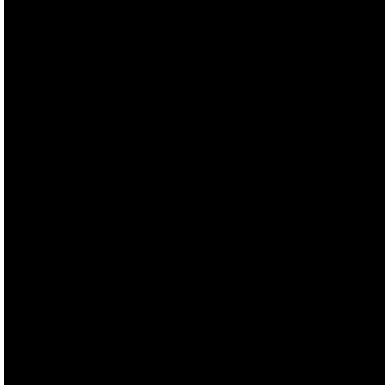
Besides being able to represent situations where the interface shape is extremely complex, phase-field models also allow one to include other types of physics by straightforward extension. Thus, one can include a large surface tension anisotropy to study the effects of faceting (both equilibrium and non-equilibrium) [17]. One can include the effects of multiple grains, each with its own crystal orientation. One can also include convective flow in the fluid [14]. Such flexibility will be important when considering growth farther from equilibrium, below.

### 3 Spherulitic growth

In the diffusion-limited regime, there is a clear distinction between the nucleation of a domain and its growth. No matter how complicated a snowflake or



one investigates the crystal structure of these objects, they are seen to be polycrystalline, not monocrystalline. As discussed above, spherulitic growth is seen in almost all classes of materials (including metals, minerals, polymers, organics, liquid crystals, and biological molecules) [18, 19]. The main requirement is the ability to crystallize at relatively large undercoolings; often the melt is relatively viscous, too. There are many variants of spherulitic growth, but all are polycrystalline, with at least approximate radial symmetry, as illustrated in Fig. 3. (The figures in this section are all examples of spherulitic growth that are also banded. We discuss the banding aspects in the next section.)



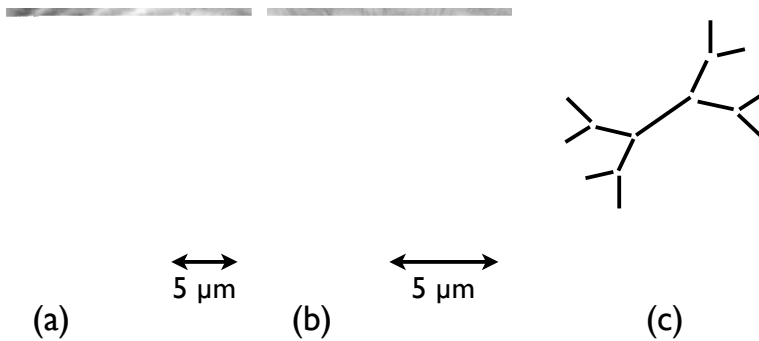
**Figure 3** Optical microscope image of ethylene-carbonate — 6.56 wt.% polyacrylonitrile spherulite growing into the melt at an undercooling  $T = 8.6$  °C. Reflected light illumination, with the azimuthal contrast coming from the angle between source and the radial fibres. Band spacing is  $750 \mu\text{m}$ . (Image by J. Kirkby.)

In the spherulitic regime, diffusive transport plays at most a minor role in the growth. Diffusion-limited growth is affected by boundary conditions once the front is within a few diffusion lengths ( $D/v$ ) of the container. A snowflake grown in a square box will have an overall square shape once its diffusion field begins to interact with the boundary. By contrast, spherulite growth in small droplets shows no effect on such length scales [20]. Further, in very thin samples, much of the latent heat is effectively conducted away into the sample substrate with little observable effect, other than a possible shift in the temperature at the front [21, 22]. In the simplest case, the sample is thin enough and growth slow enough that one may regard the solidification as isothermal. Finally, while the chemical-segregation effects that control the growth of alloys are present also in spherulites, they do not play a controlling role, as may be noted by varying alloy (or impurity) concentration. In particular, spherulitic growth is present even in very pure materials [23, 20].

its edges) has nucleated. By contrast, an atomically flat plane has no steps, which hinders attachment.

Another relevant factor concerns the transport of molecules to the interface. The solid phase is typically 10% denser than the liquid phase, meaning that liquid molecules must be brought in from ever longer distances to pack into the solid. In a viscous fluid, this transport time can limit the growth velocity [26].

Why do spherulites show an overall radial order with non-crystallographically oriented orientations? One of the most detailed analyses of spherulite structure has been done on spherulites in elemental selenium, a metal where molecules in the liquid spontaneously form chains of ‘living polymers’. Bisault et al. [23] give evidence for a regular structure whose dominant motif is the presence of repeated small-angle-branching events, which cause local crystallites to be rotated with respect to each other by a few degrees. They also conclude that the small-angle branching is not due either to twinning or to tip-splitting of the growing crystal face. To get a feel for how such processes might work, one can look at the core region of a spherulite, which often has a ‘sheaf-of-wheat’ texture [Fig. 4(a)]. The standard view of this is that the spherulite starts initially from a single needle, from which new needles branch [23]. The repeated small-angle branches eventually close in among themselves, creating a defect line and two cavities, and also lead to an approximately radial ordering of the outer branches. In our work on banded spherulites, we see similar ordering about the core (Fig. 4). Figure 4(c) illustrates how growth as highly anisotropic needles, coupled with small-angle branching, can start to produce a symmetric shape. Recently, the groups of Chan and Li have shown this process in real time by AFM by studying slowly freezing spherulites [27].



**Figure 4** Optical (a) and AFM (b) micrographs of 10OCB spherulite nuclei with sheaf structures. (c) Illustration of the growth of the initial lamellae. Adapted from [20].

Although the existence of small-angle branching is well-documented, its origins are less clear. Possibilities that have been suggested are that surface-tension imbalances on the different faces of crystallites can bend or rotate them [28, 29] and that the fluid flow induced by the density difference between solid and liquid phases leads to what is essentially channel flow between growing crystallites [26]. The higher pressure present between the tips can be sufficient to splay the fibers, if they are long (and hence floppy) enough. (For polymers, Bassett[30] has suggested that the splaying of nearby crystallites may be due to the steric interaction of nearby dangling chains. Such an explanation, of course, would not be relevant for small-molecule spherulites, such as those formed in liquid crystals [20].)



### 3.1 Theoretical approaches to spherulitic growth

For many years, work on spherulitic growth has been primarily experimental, and much of that work (e.g., [18]) has been qualitative, with little reference to detailed theory. Most of the sustained theoretical effort has been to develop theories of polymer crystallization that focus on the homogenous nucleation and subsequent growth of individual lamellae. These works have historically concentrated on understanding what distinguishes polymer crystallization from that of small molecules. For example, a celebrated observation by Keller in the 1950s was that polymers crystallized in narrow lamellae with folded chains whose longitudinal axis is normal to the growth direction [31], and many theories have focused on this aspect (e.g., on what sets the thickness of the lamellae) [32, 33]. Much more detailed simulations of 'ideal' polymers can now be done on computer, and recent studies are injecting a number of new ideas into the field (e.g., the sharing of polymer strands among several nuclei [34] and the role of metastable phases [33, 35]).

The work on polymer crystallization cited above also consider spherulitic growth. But because such theories put in so many details specific to polymers (chain entanglement, reptation, etc.), it becomes difficult to understand the general features of spherulitic growth common to polymeric and non-polymeric materials. Another approach is to search for a minimal model that can generate the range of observed phenomena. From this point of view, the recent paper by Gránásy et al., which generalizes the phase-field model of Sec. 2.2 to describe spherulitic growth, is a major advance [36].

Gránásy et al. focus on isothermal growth of a two-component alloy, which in effect amounts to replacing the undercooling field  $u$  by a concentration field  $c$ . (The free energy is slightly more complicated, including the contributions from the solution energy and the entropy of mixing.) The important new feature is an field that is strongly coupled to the order field  $\phi$ . In the solid phase, the value of  $\phi$  gives the orientation of the local crystal. An anisotropy is included that has local minima at  $\phi = 0$  (which favors extended domains of a single orientation) and  $\phi = \phi_0$  (which favours domain boundaries at a preferred angle  $\phi_0$ ). In the liquid phase, the orientation field fluctuates randomly in space with a correlation length of microscopic dimension, reflecting the *local* orientation order in liquids. A second important feature is the addition of noise terms for all three fields, which allows for nucleation of new domains.

The 'minimal' model of Gránásy et al., while complicated (and requiring the equivalent of 40 CPU years of 2-GHz processor power for their study!) is the first model that can generate essentially the entire range of observed types of spherulitic growth merely by changing the simulation parameters of a single model. The crucial parameters turn out to be the ratio of rotational to translational diffusion constants and the above-mentioned attachment anisotropy. Both slow rotational diffusion and the formation of grain boundaries with finite misorientation can lead to non-crystallographic branching. The former is more relevant for highly viscous melts, the latter for pure materials at relatively low undercoolings. In both cases, secondary nucleation takes place continually at the growing front and leads to a growth envelope that has a spherical envelope. This confirms the picture of small-angle branching and non-crystallographic branching discussed above but does not entirely explain the origin of the branching. (The anisotropy term, while plausible,

is essentially put in by hand.) Nonetheless, the correspondence between simula-





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8000 Å

0

5 μm

**Figure 6** AFM micrograph of spherulite nucleus with a spiral structure. From [20].

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Padden [29]). While surface force imbalances no doubt exist, it is less obvious to know whether they are in fact the dominant driving force. Owen has given a simple argument that the twisting produced by surface-stress imbalances should vary as  $T^{-3/2}$ . We have carefully measured the divergence in the ethylene-carbonate-polyacrylonitrile system and found, instead, that the transition is analogous to a second-order transition, with a banding wavelength diverging as  $(T - T_c)^{-1}$ , with  $\nu = 1$  and  $T_c$



also be local stresses generated, for example, by the density difference between solid and liquid. This last suggestion recalls an idea of Tiller and Geering, who used hydrodynamic flows generated by the solid-liquid density difference to account for the splay of spherulites [50, 26]. In unpublished work, we have investigated this 'hydrodynamic scenario' in the context of a fiber growing in the mean field of other



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