A theory of dendritic growth is reviewed, which accounts, in principle, for the growth rate and shape of dendrites in solidification, electrochemical deposition, and two-phase fluid flow. A variety of different growth forms is possible, depending upon both the degree of anisotropy and the deviation from equilibrium of the system. The possible morphologies have been explored in both fluid systems, which are an analogue for solidification, and electrochemical deposition. Speculation as to how dendritic growth in batteries can be controlled is briefly mentioned.
the content of the present article. In addition, the prospects for controlling the self-destructive tendencies of batteries in solution, where the growth of a deposit between the electrodes can cause the battery to fail, will be considered briefly.

Dendritic growth during solidification

Dendritic growth is usually considered to be the generic mode of solidification of crystalline materials. The solidification front propagates at a uniform velocity, \( v_0 \), into the supercooled solution of the solidifying material in the form of a smooth, almost paraboloid tip with tip radius \( \rho_0 \), followed by a train of sidebranches which are almost stationary in the laboratory frame of reference. The dendrite always propagates along the same crystallographically preferred direction, with the tip apparently preserving its shape. In the classic experiments of Glicksman et al. [3], isolated dendrites were studied; \( v_0 \) and \( \rho_0 \) were reproducible and approximately satisfied the relation

\[
v_0 \sim \frac{1}{\rho_0} \sim \Delta^{2.6}
\]

where \( \Delta \) is the undercooling measured in dimensionless units:

\[
\Delta = \frac{T_M - T_\infty}{L/C_p}
\]

Here, \( T_M \) and \( T_\infty \) are the melting temperature and the temperature at infinity, respectively, \( L \) is the latent heat released during the phase transition to the solid state and \( C_p \) is the specific heat at constant pressure of the liquid. \( \Delta \) is a parameter which plays the role of a driving force, maintaining the system out of equilibrium. Wherever possible, physical quantities are defined in a dimensionless way, in order that the equations describing different systems can easily be compared. The principal focus of theory was, for many years, to account for the observed shape of dendrites, the values of \( \rho_0 \) and \( v_0 \), and to explain eqn. (1).

The physics of dendritic growth is as follows: As the supercooled liquid solidifies, latent heat is generated. If the solidification front is to be able to advance, then the latent heat must be transported away from the front, otherwise the solid will simply melt back. In idealised situations, the only mechanism for transport is diffusion, although other mechanisms, such as convection are, in general, certainly important. In this case, the temperature \( T \) varies in space \( x \) and in time \( t \), and when normalised in the same way that \( T_M \) is normalised in eqn. (2), obeys the diffusion equation

\[
\frac{\partial u}{\partial t} = Du^2 u
\]
where \( D \) is the thermal diffusion coefficient and \( u \) is the normalised temperature. For simplicity, we can consider the diffusion to occur only in the liquid; no new points of principle emerge if a more realistic assumption is used. Equation (3) also applies in the case of the isothermal solidification of a binary alloy, in which case \( u \) describes the concentration of one of the species, and the assumption about no diffusion in the solid is quite realistic. The diffusion equation has to be solved subject to boundary conditions applied at infinity and at the solidification front, and subject to an initial condition for the temperature field and the solidification front. At infinity, the normalised temperature tends to zero. At each point \( s \) on the solidification front, conservation of energy requires that the latent heat generated during the motion of the solidification front create a flux into the liquid:

\[
v_n(s) = -D \nabla u(s) \cdot \hat{n}(s)
\]  

(4)

where \( v_n(s) \) is the velocity of the interface along the unit normal, \( \hat{n}(s) \), to the interface at position \( s \). Note that at this stage, we do not know the position of the solidification front, so we do not know where to apply this boundary condition! In fact, we wish to determine the position of the front, as well as the temperature field. To do this, we need an extra boundary condition, which states how the shape of the front affects its temperature, \( u_s \). This condition is the Gibbs–Thomson condition, modified to take into account the fact that the solidification front is moving, and so is not in equilibrium:

\[
u_s = \Delta - d_0 \kappa - \beta v_n
\]  

(5)

If the interface were planar and stationary, it would just be at the melting temperature, which is \( \Delta \) in our units. However, its motion and its curvature, \( \kappa \), reduce the temperature. Since \( u_s \) is dimensionless, \( d_0 \) has the dimensions of a length, and is known as the capillary length. It is proportional to the surface tension, and is typically of the order of 10 - 20 \( \text{Å} \). The coefficient \( \beta \) is known as the kinetic coefficient, and is frequently ignored for small \( \Delta \), although it must be non-zero. Equations (3) - (5) are traditionally considered to be sufficient to describe dendritic growth, and we shall refer to them as the standard model.

The physical origin of the instability of the interface giving rise to dendritic growth was identified by Mullins and Sekerka [4]. They considered a bump on an otherwise planar solidification front, and asked how fast it would grow relative to the rest of the interface. In the vicinity of the tip, the thermal gradients are steeper than elsewhere, essentially because of the point-effect or lightning rod effect in electrostatics. The steep thermal gradients cause the velocity of the bulge to be greater than elsewhere, i.e., the bulge grows. Surface tension cuts off the growth of bulges smaller than a certain size

\[
\lambda_s = 2\pi(d_0 l)^{1/2}
\]  

(6)

where
is the diffusion length, over which the temperature field falls by a factor of $e = 2.71828...$ from its value at the interface. So the interface evolves under two competing tendencies, one of which is due to diffusion and maximises the area of the interface; the other is due to surface tension and minimises the area of the interface. The actual coupling between these two tendencies is highly non-linear due to the curvature term in eqn. (5). A successful theory of dendritic growth must cope with this difficulty.

Progress in the field until about 1980 has been excellently reviewed by Langer [5], but much of this material has been superseded by the developments mentioned below (the article remains invaluable, however). The principal defect of all work prior to 1983 is the assumption that the standard model is a sufficient description of the physics. It is not. The missing ingredient is anisotropy in the surface tension and in the kinetic coefficient due to the presence of the crystal lattice in the solid phase. This anisotropy does more than simply control the asymmetry of the growing crystal. It influences the dynamics in a rather profound way. The surprisingly important role of anisotropy was first discovered [6] in a simplified model of solidification, to which we now turn.

Simplified models of interface dynamics

The complexity of the standard model prevented any reliable analytical or even numerical calculations to determine whether or not the solutions of the equations reproduced, even qualitatively, the experimentally observed features of dendritic growth. As a first step towards further simplification of the problem, phenomenological models for interface motion in two dimensions were considered. Brower et al. [7] stripped the problem down to its bare essentials, and considered the motion of an interface whose dynamics was simply given by the prescription that the velocity $v_n$ was a given function of the curvature and its second derivative with regard to the arc-length $s$ of the interface. The function was chosen to mimic certain features of the Mullins–Sekerka instability. In this model, the geometrical model (GM), much analytical and computational work could be performed. In the boundary-layer model [6] (BLM) of Ben-Jacob et al., the interface is coupled to a field obeying the diffusion equation, just as in the standard model, but the diffusion length $l$ is assumed to be small compared with the radius of curvature of the interface. In this case, the diffusion of heat mainly occurs in a thin boundary layer around the interface, and many simplifications result [8].

The principal conclusion which emerged unambiguously from computer simulations of the BLM, and later the GM, was that only when the anisotropy in $d_0$ or $\beta$ was taken into account were the qualitative features of dendritic growth reproduced. Without sufficient anisotropy the interface evolves
via a succession of tip-splitting instabilities into a branched structure.

It was also discovered how to predict the growth rate of the dendrites in the simple models [9, 10]. It turns out that there exist steady state solutions of the equations of motion, which describe a steadily propagating 'needle crystal' without sidebranches. The needle crystals are approximately parabolic solidification fronts. Their velocity is 'quantised'; only certain velocities are allowed, and there is a maximum velocity permissible. This maximum velocity is, indeed, that at which the dendrites grow in the computer simulations of these models. Furthermore, the smooth region near the tip of these dendrites precisely matches the tip of the needle crystals. Away from the tip, the dendrites develop sidebranches, whereas the needle crystals remain smooth [9]. Analytic theories for the growth rate were subsequently developed [11]. Physically, the velocity quantisation is a result of the fact that surface tension is a singular perturbation. In the absence of surface tension, needle crystals exist for any velocity [12].

Why are the needle crystals never seen in the computer simulations or, indeed, in the experiment? Why do dendrites have sidebranches? To answer these questions it is necessary to consider the stability of the needle crystals to small perturbations. Perturbations can grow in magnitude and spread laterally; in addition, they can be advected down the body of the needle crystal, so the definition of stability has to be made with some care. The most useful concept has been stability at a point on the interface at a fixed distance from the tip. Calculations of the stability spectrum have been made for both the GM [10] and the BLM [13]. In the GM, it was found that as the anisotropy strength increases from zero, there is a critical point at which the fastest needle crystal becomes linearly stable. This transition occurs through a Hopf bifurcation involving an oscillatory mode. By contrast, in the BLM the fastest needle crystal is linearly stable for all non-zero anisotropy strength. The slower moving needle crystals are, however, always linearly unstable, and so are not observed. The results in the BLM are consistent with the suggestion that sidebranches originate from the selective amplification of noise [14], although other dynamical mechanisms are also possible [15]. This explanation for the origin of sidebranches also explains why the fastest needle crystal precisely matches the tip of the dendrites observed in the time-dependent solutions of the equations of motion for the BLM. Experimental support for this scenario comes from measurements of the correlations between sidebranches [16].

The standard model with anisotropy

The BLM is a physical, but not exact mathematical, limit of the standard model with anisotropy. All of the qualitative results mentioned above have been found to be valid in the standard model too, when supplemented by anisotropy. A list, by no means exhaustive, of the principle results is given
here. Computer simulations of the equations of motion have confirmed the role of anisotropy [17], and the existence of a discrete set of allowed needle crystals has been shown numerically [18] and analytically [19]. Very recently, the first direct comparisons of theory with experiment have been attempted [20]. The stability analysis follows that of the BLM (it was actually performed earlier for the standard model) [21], and the same scenario for sidebranches probably applies here too.

Hydrodynamic analogues of dendritic growth

When a viscous fluid is confined between two closely spaced parallel plates, and air is injected into the gap through a hole in one of the plates, the resulting bubble displays many similarities to a growing crystal [22]. Such an apparatus is known as a Hele-Shaw cell [23]. From the Navier–Stokes equations, it can be shown that [24] the pressure field in the quasi-two-dimensional viscous fluid obeys the diffusion equation (or the Laplace equation if the fluid is incompressible). The boundary conditions for the pressure at the edge of the bubble are Laplace's law, which is precisely the Gibbs–Thomson condition, eqn. (5), but with temperature replaced by pressure. It should come as no surprise to learn that the growing bubble does not grow in a stable, circular fashion, but becomes unstable and radiates 'fingers'. However, these fingers are not dendritic—they have no sidebranches and propagate in random directions, evolving by tip-splitting. This is a clear indication that diffusion and surface tension on their own—the standard model—are not sufficient to generate the characteristic features of dendritic growth, a result in agreement with theory.

A variety of experiments has been performed to demonstrate and study the analogy between two-phase fluid flow and dendritic growth. In ref. 22 air was injected at the centre of a Hele-Shaw cell, of which the lower plate had been engraved with a regular grid. The resulting bubble did not grow circularly, but instead generated a striking snowflake-like pattern. In the absence of anisotropy, a branching structure with radial symmetry was observed [25]. This, so-called, dense, branching morphology is ubiquitous as a pattern generated by diffusion-controlled interface motion. It is observed in (e.g.) electro-chemical deposition [26] and in the growth of polymeric and organic crystals [27]. In the dense branching morphology, the arms branch at non-crystallographic angles, in a manner quite distinct from dendritic growth.

An important concept to emerge from these experiments is that of the morphology diagram. For example, in the Hele-Shaw experiments, it is possible to vary the strength of the anisotropy by varying the plate spacing. As the anisotropy strength and the overpressure of the injected air are varied, different patterns are observed. For a fixed anisotropy strength, as the driving force (overpressure) $\Delta$ is increased, the patterns pass through the sequence: faceted crystals, dendrites (due to the anisotropy in the surface
tension), tip-splitting, dendrites (due to the anisotropy in $\beta$). Morphology diagrams have also been determined in electrochemical deposition [26, 28].

Precise experiments on the Hele-Shaw cell without an engraved lattice have also been performed [29]. A particularly interesting set of experiments has recently been reported in which the presence of a small bubble near the tip of one of the 'fingers' of air causes sidebranches to develop [30].

Control of dendritic growth in batteries

The breakdown of batteries often occurs when a deposit grows on the cathode, forming dendrites, or perhaps the dense, branching morphology. The arms grow through the porous material separating the electrodes, finally reaching the anode, and destroying the battery.

Can the progress in the field of dendritic growth assist in finding a solution to this problem? Although the level of understanding of dendritic growth is not yet sufficient to predict the morphology for a given set of experimental conditions, it can be helpful to, at least, know what are the possibilities for controlling the growth of electrode deposits. Experimentation is required to see if trends can be discerned. Although I am not sanguine about the prospects of improving battery performance by exploiting the research described above, I offer three vague speculations about possible directions to pursue, in the hope that they might trigger a successful attack on the problem.

The first possibility is to increase the size of the dendrites. They will then grow slower and prolong the lifetime of the battery. They may also be too big to penetrate the porous barrier. In practice, growth will always occur through the barrier, but the rate will depend upon the ratio of the pore size to the diffusion length (amongst other things).

Secondly, the more closed the structure that grows, the slower it will grow (all other things being equal). Whether or not there are impurities in the system can control whether or not the structure is dendritic or dense branching, and the openness of the resulting morphology.

Thirdly, it might be possible to find an impurity species which, when added to the battery, will become incorporated into the growing deposits in such a way that the resultant deposit is an insulator.

Even if the above suggestions turned out to be useful, it is by no means clear that the performance of the battery would not be seriously undermined.

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References

1 J. Kepler, *De Nive Sesangula*, Godfrey Tampach, Frankfurt am Main, 1611.
2 See (e.g.) F. Family and D. P. Landau (eds.), *Kinetics of Aggregation and Gelation*, North-Holland, Amsterdam, 1984.
12 In the context of the standard model, this result was discovered by G. P. Ivantsov, *Dokl. Akad. Nauk SSSR*, 58 (1947) 567.