

Crystal Growth Theory

NG July 2001 ①

General References:

J. Gollub + Langer Rev. Mod. Phys. 71, 5396-5403 (Mar 1999)

D. Kessler et al. Adv. Phys. 37, 255 (1988).

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Outline

I. Free dendritic growth, directional solidification

- basic phenomena
- steady states and solubility theory
- sidebranching

II. Simulation methods

- phase fields
- level sets
- Monte Carlo

III. What's next? Open questions.

State of the art references.

Solidification in flow fields, in 3D. J.H. Jeong, NG, J. Dabrig.
cond-mat/0105568 accepted in Phys. Rev. E.

Methods to relate phase field models and sharp interface models.
A. Karma + N. Rappel, Phys Rev E 53, 3017 (1995).

<http://guava.physics.uiuc.edu/~nigel>

① Q. Why is crystal growth theoretically interesting?

A: (i) Dendritic growth is generic mode of solidification for all metals, alloys and even polymers in certain situations.

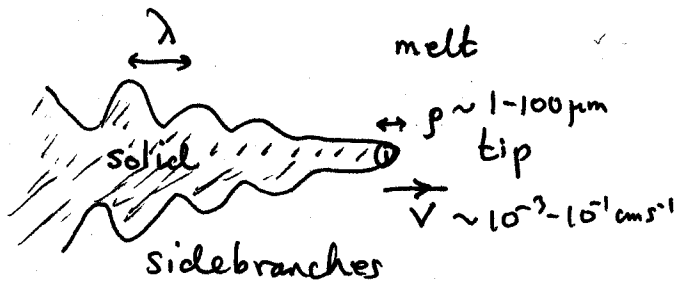
(ii) Would like to understand size of dendrites, speed of growth, morphology phase diagram - Predict and control properties of materials: e.g. mechanical and electrical properties determined by microstructure, a bunch of interlocking dendrites. [This justification works well on grant proposals, but is also genuine! E.g. I collaborate with an engineer in my own work.]

(iii) Excellent example of multiscale physics. The most challenging physics problems are those where phenomena on many scales cooperate and interfere. In solidification we discovered that microscopic physics on the scale of Angstroms controls morphology on scales of microns - millimetres or more! Usually in physics we do not expect scale interference. For example, the mass of the top quark should not influence too much the critical temperature of YBCO. Scale separation is what enables us to actually do physics. It makes sense to have separate groups of physicists, who call themselves high energy physicists, nuclear physicists, atomic physicists, condensed matter physicists, The job of each member of this hierarchy is to calculate the phenomenological parameters and constants for the physicists downstream.

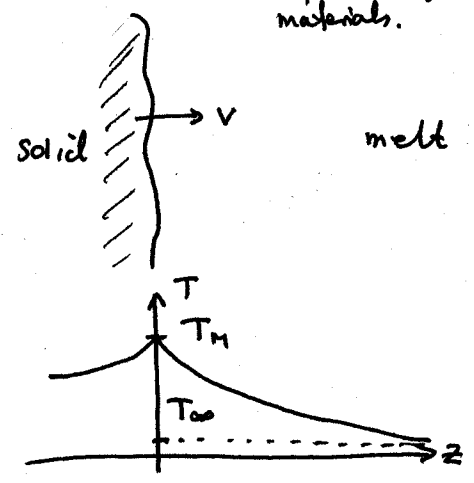
In solidification we need analytic and numerical methods than can cope simultaneously with a wide variety of length scales.

(iv) Excellent example of a spatially-extended dynamical system. Dendritic growth is a highly unstable dynamical process, and therefore poses serious modelling challenges. How do you accurately compute the behaviour, when any numerical error can easily be amplified by the genuine physical instabilities present? How does one describe the sequence of bifurcations which lead to the space-time patterns observed in experiment?

② Basic phenomenology.



Temperature or concentration can both diffuse: pure or alloy materials.

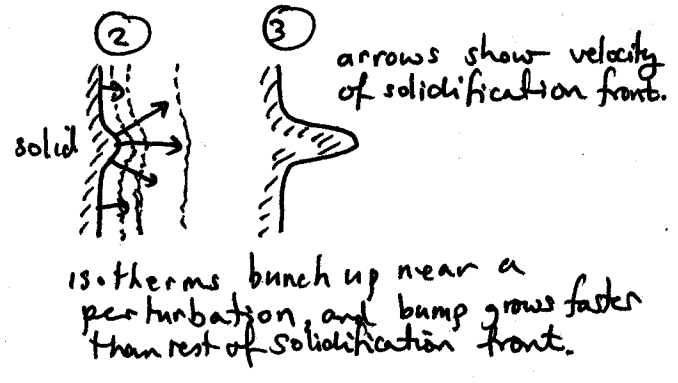
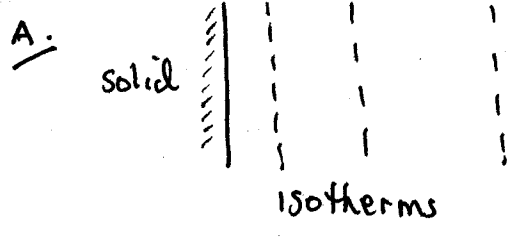


ρ, v, λ all determined by undercooling
 $\Delta \propto T_M - T_{\infty}$

As $\Delta \uparrow$, $\rho \downarrow$, $v \uparrow$, $\lambda \downarrow$.

Q. How do ρ, v, λ depend on Δ and other material parameters?

Q. What is the basic reason for the characteristic dendritic or "snowflake" morphology?



This answer presupposes that the underlying physics is diffusion - controlled growth. The rate-determining step that governs how rapidly the solidification front advances is how quickly heat can be transported away from the front. This requires that it is very easy to attach atoms to the growing crystal, so that attachment is not the rate-determining step. In other words, the solidification front must be molecularly rough, not smooth

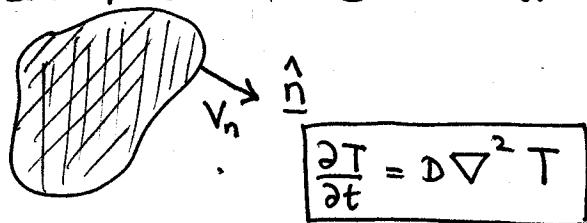


rough interface, so many niche's for new atoms to bind with low energy.



flat interface, so there is a nucleation barrier to overcome to put a new atom on the surface.

Let's derive the governing equations. neglect heat flow in the solid.



Suppose for simplicity we

In a time interval δt , the interface advances $v_n \delta t$ locally, and so latent heat is released, which must be dissipated as a heat current.

$$L v_n \delta t = C_l^{\text{liquid}} J \cdot \delta t$$

$$J = -D \nabla T \cdot \hat{n}$$

$$\Rightarrow \boxed{L v_n = -C_l D \nabla T \cdot \hat{n}}$$

This equation tells the interface how fast to move along its outward normal at each point along the interface.

The heat equation together with appropriate boundary conditions determines the temperature field away from the solidification front.

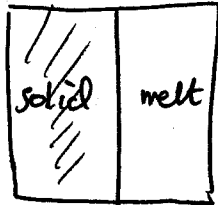
c.f. "Matter tells space how to curve; space tells matter how to move". J.A. Wheeler's one line epigram for general relativity.

What are the appropriate boundary conditions? (5)

If the solidification front were perfectly flat, then

$$T_s = T_m.$$

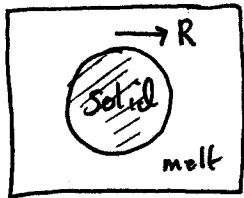
This is just the statement of thermodynamic equilibrium at a first order phase transition, where solid and melt coexist.



$$T_s = T_m$$

$T_s = T_m$ is the unique temperature at which this system is in equilibrium and the solidification front is stationary.

Now what happens if the solidification front is curved?



What temperature do we need to keep the system at for the solidification front to be stationary? The front has more broken bonds than in the straight case, so as we imagine raising the temperature from below, atoms find it easier to escape than they did in the flat case. In other words, we

expect $T_s < T_m$. In fact

$$T_s = T_m - A/R$$

where A is a constant, which measures the surface energy of the solid-melt interface. This equation is known as the

Gibbs-Thomson boundary condition.

Summary: $u = \frac{T - T_{\infty}}{L/c_p}$

$$\Delta = \frac{T_m - T_{\infty}}{L/c_p} \quad d_0 = \frac{A}{L/c_p}$$

$$\begin{aligned} \partial_t u &= D \nabla^2 u \\ v_n &= -D \nabla u \cdot \hat{n} \\ u_s &= \Delta - d_0 K \\ u &\rightarrow 0 \quad @ \quad |x| \rightarrow \infty \end{aligned}$$

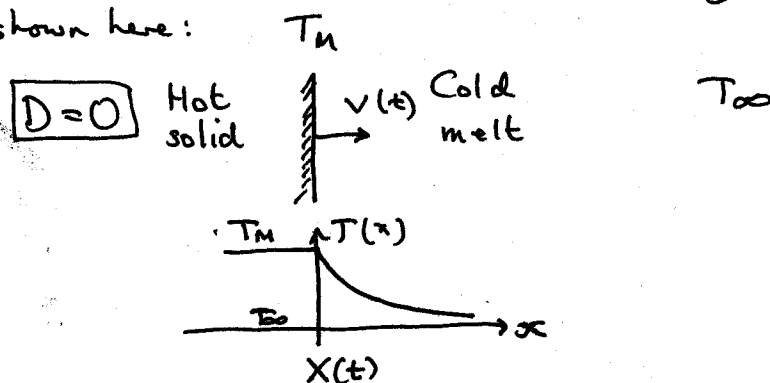
A complete description of diffusion-controlled solidification?

Successorible: $T_m = 58.2^\circ\text{C}$ $D = 1.14 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$
 $L = 4.5 \times 10^8 \text{ erg cm}^{-3}$ $T_m - T_{\infty} \sim 0.1 - 1.0^\circ\text{C}$
 $L/c_p = 23.1^\circ\text{C}$ $v \sim 10^{-3} - 10^{-1} \text{ cm s}^{-1}$
 $A = 8.95 \text{ dyne cm}^{-1}$ $d_0 \sim 192 \text{ \AA}$

Q: Why are these equations so hard to solve?

A: There are moving boundary problems. Unlike boundary value problems in electrostatics or fluid mechanics that you may have run across, here the position — indeed, the shape — of the boundary is not known. It is determined by the solution of the heat equation away from the boundary. So it is a self-consistent 'circular logic' that advances the system in time. This creates difficulties for both analytical and numerical treatments.

As an example, let's try to solve the problem in one dimension. We consider a planar interface advancing into a supercooled liquid, as shown here:



The equations are

$$\partial_t u = D \partial_x^2 u \quad x > X(t)$$

$$u(X(t)) = \Delta$$

$$V \equiv \dot{X} = -D \frac{\partial u}{\partial x}(X(t))$$

$$u(x) \rightarrow 0 \quad \text{as } x \rightarrow +\infty.$$

Our intuition should tell us that for a planar interface, the latent heat generated as solid grows into melt will build up in front of the interface, and so the front will generally slow down.

Let's first try to look for solutions that move with a constant speed v .

Thus we look for solutions of the form

$$u(x,t) = u(x-vt)$$

$$z \equiv x-vt.$$

The interface is then at $z=0$, and we will seek steady states in the moving frame of the interface:

$$u(z,t) = u(z).$$

Then $\partial_t u = -v \partial_x u$

so that

$$u'' + \frac{v}{D} u' = 0$$

$$u(z=0) = \Delta$$

$$v = -D \partial_z u(z=0)$$

If we try $u = e^{mz}$ as a trial solution we get

$$m^2 + \frac{1}{l} m = 0$$

where we have defined a length scale

$$l \equiv D/v$$

which is known as the diffusion length. Solving

$$u = A + B e^{-z/l}$$

showing that as anticipated the diffusion field decays exponentially away from the solidification front, which a characteristic scale of l . Applying the boundary

condition:

$$z \rightarrow \infty \quad u \rightarrow 0 \quad \Rightarrow \quad \underline{A=0.}$$

$$u(0) = \Delta \quad \Rightarrow \quad B = \Delta \quad \Rightarrow \quad u(z) = \Delta e^{-z/l}$$

$$v = -D \partial_z u(z=0) \quad \Rightarrow \quad v = -D \left(-\frac{1}{l}\right) \cdot \Delta \cdot e^0$$

$$\Rightarrow \quad \underline{\underline{v = v \cdot \Delta}} \quad ??$$

We conclude two things:

- (i) Only for $\Delta = 1$ do there exist uniformly translating solutions of the problem.
- (ii) For this special value of Δ , the driving force ($T_M - T_0$) is sufficient that just at that Δ the heat generated is diffused away to infinity. However, there is nothing to tell us what is the velocity!

This is our first encounter with selection of a sort. Solving the steady state problem has not led to a unique prediction for the characteristics of the steady state.

We will see later that one can find systems with a family of stable steady states, not just a unique steady state.

Which of these corresponds to what one would see in experiment or numerical computation? This problem is called the pattern selection problem, and proposed or real solutions to it are often referred to as selection mechanisms.

So what happens for $\Delta \neq 1$? We'll seek a similarity solution of the form

$$u(x,t) \xrightarrow[t \rightarrow \infty]{} u_0\left(\frac{x}{X(t)}\right)$$

for some $X(t)$ to be determined. This is clearly not invariant under a shift of the origin by any finite amount a . Hence we must understand that this solution is only an asymptotic

solution when $x \gg a$, $X \gg a$, $a = X(0)$.

Now let's transform the diffusion equation to new variables

$$\begin{aligned} t &\equiv t \\ \eta &\equiv x/X(t). \end{aligned}$$

Then

$$\partial_x u = \frac{1}{X} \partial_\eta u_0$$

$$\partial_x^2 u = \frac{1}{X^2} \partial_\eta^2 u_0$$

$$\partial_t u = -\frac{x}{X^2} (\partial_\eta u_0) \cdot \frac{dX(t)}{dt}$$

and the diffusion equation becomes

$$-\frac{x}{X^2} \dot{X} \frac{du_0}{d\eta} = D \frac{1}{X^2} \frac{d^2 u_0}{d\eta^2}$$

$$\Rightarrow \frac{d^2 u_0}{d\eta^2} + \frac{x \dot{X}}{D} \frac{du_0}{d\eta} = 0$$

$$\Rightarrow \frac{d^2 u_0}{d\eta^2} + \frac{X(t) \dot{X}(t)}{D} \eta \frac{du_0}{d\eta} = 0.$$

We can make this an ordinary differential equation in η if

$$X \dot{X}(t) = \text{constant}, \text{ which we'll call } \gamma D.$$

$$\Rightarrow u_0'' + \gamma \eta u_0' = 0.$$

The solution of this equation is simply

$$u_0(\eta) = u_0(0) + a' \int_0^\eta e^{-\frac{1}{2}\gamma \eta'^2} d\eta'$$

Since $u_0 \rightarrow 0$ as $\eta \rightarrow \infty$, it is convenient to write this as

$$u_0(\eta) = a \int_\eta^\infty e^{-\frac{1}{2}\gamma \eta'^2} d\eta'$$

Now we must apply boundary conditions.

There are:-

First: $u_0(1) = \Delta$. This is the reason why we SE should have looked for these similarity solutions in the first place. The idea is to make sure that whatever is the motion that ultimately transpires, we choose a coordinate system so that the solidification front is always at the same place $\eta = 1$.

Second: $\dot{X}(t) = -\frac{D}{X} \frac{du_0}{d\eta}(1)$.

This implies that

$$X\dot{X} \equiv \gamma D = Da e^{-\frac{1}{2}\gamma}$$
$$\Rightarrow \gamma = a e^{-\frac{1}{2}\gamma} \Rightarrow \underline{\underline{a = \gamma e^{\gamma/2}}}$$

The first b.c. \Rightarrow

$$\Delta = a \int_1^{\infty} e^{-\frac{1}{2}\gamma \eta'^2} d\eta'$$

Let $s^2 \equiv \frac{\gamma}{2} \eta'^2 \Rightarrow$
$$\Delta = \sqrt{2\gamma} e^{\gamma/2} \int_{\gamma/2}^{\infty} e^{-s^2} ds$$

We'll introduce a dimensionless number called the Peclet Number:

$$Pe \equiv \frac{V_0(t) X(t)}{2D} = \frac{\gamma}{2}$$

Then, in terms of the complementary error function

$$\operatorname{erfc}(s) \equiv \frac{2}{\sqrt{\pi}} \int_s^{\infty} e^{-t^2} dt$$

we have

$$\Delta = \sqrt{\pi Pe} e^{Pe} \operatorname{erfc}(\sqrt{Pe})$$

This equation can be inverted to yield

$$P_c = P_c(\Delta).$$

Now we solve for the interface dynamics by

$$\frac{d}{dt} \left(\frac{1}{2} X^2 \right) = X \dot{X} \equiv \gamma D = 2 P_c D$$

$$\Rightarrow \frac{X^2}{2} \sim 2 P_c D t \quad t \rightarrow \infty.$$

In other words, the interface position moves as

$$X(t) \sim 2 \sqrt{P_c D t}$$

and so it slows down: $V(t) \sim \dot{X} \sim t^{-1/2}$ as $t \rightarrow \infty$.

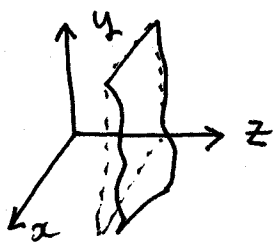
STABILITY

We appear to have found the asymptotic steady state of this problem, for $\Delta \leq 1$. But what we'd really liked to have solved would be the initial value problem. i.e. the time dependence, starting from arbitrary initial conditions. We can't solve this in general. So let's ask a simpler question: will all initial conditions attain the steady state we have found?

This is not so easy either, so let's ask an even simpler question: if we start infinitesimally close to the steady state, will the system relax back to the steady state, or will it diverge away. This sort of question is asked all the time in studying spatially-extended dynamical systems. And it is usually easy to answer if the steady state solution is simple too.

The only genuine steady state we found was for $\Delta=1$.

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Interface position is $z(x,y) = \xi(x,y)$.

Steady state interface is $z(x,y) = z_0 = 0$

$\xi(x,y)$ represents the deviation of the interface from $z=0$.

We'll sometimes write $\underline{x}_\perp \equiv (x,y)$. The perturbation $z(\underline{x}_\perp, t)$ can be decomposed into Fourier components, and allowing for the time dependence too, we write

$$\xi(\underline{x}_\perp, t) = \sum_{\underline{k}} e^{i \underline{k} \cdot \underline{x}_\perp + \omega t}$$

What are we hoping to find? We'd like to examine ω for every \underline{k} -mode and see if it is +ve, or -ve. If $\text{Re}(\omega) > 0$, then the perturbation grows away from $z=0$, i.e. an indication of instability. If $\text{Re}(\omega) < 0$, then the perturbation will eventually decay exponentially to zero, so we conclude that the flat interface is linearly stable. We will restrict our analysis to first order in the perturbation ξ , and so this is known as linear stability analysis.

If we had a dynamical equation for the interface $z(x,y,t)$ then we could get started easily. But we don't. We only know $z(\underline{x}_\perp, t)$ implicitly through the diffusion equation and its boundary conditions. Let's write out in three dimensions:

$$\nabla^2 u + \frac{1}{l} \frac{\partial u}{\partial z} = \frac{1}{D} \frac{\partial u}{\partial t} \quad D = d/V$$

$$u_0(z) = e^{-z/l}$$

is the one dimensional steady state solution.

How is the diffusion field perturbed by perturbations of the solidification front? We'll write

$$u(z, x_{\perp}, t) = u_0(z) + u_k e^{i k \cdot x_{\perp} + \omega t} e^{-qz}$$

this term accounts for perturbations parallel to the interface

putting in this will speed up the algebra. It expresses the fact that the perturbation should decay exponentially away from the interface in a way which we'll determine

Our strategy will be to follow Mullins and Sekerka (1960) and linearise in u_k and ξ_k .

The diffusion equation yields

$$q^2 - k^2 + \frac{1}{l} \cdot -q = \omega / D$$
$$\Rightarrow \boxed{\frac{\omega}{D} = -\frac{q}{l} - k^2 + q^2} \quad (1)$$

Now that we are (for the first time) encountering a curved interface we'll need to use the Gibbs-Thomson boundary condition. The curvature, is to the order we're working

$$K \cong -\nabla_{x_{\perp}}^2 \xi(x_{\perp})$$

We will also Taylor expand the diffusion field around the steady state:

$$u_0(\xi) = u_0(0) + u_0'(0) \xi + O(\xi^2)$$

$$\Rightarrow \underbrace{1}_{\Delta=1} - d_0 k^2 \xi_k e^{i k \cdot x_{\perp}} = \underbrace{1}_{u_0(0)} + u_k e^{i k \cdot x_{\perp}} + u_0'(0) \xi_k e^{i k \cdot x_{\perp}}$$

$$\Rightarrow \boxed{-d_0 k^2 \xi_k = u_k - \frac{1}{l} \xi_k} \quad (2)$$

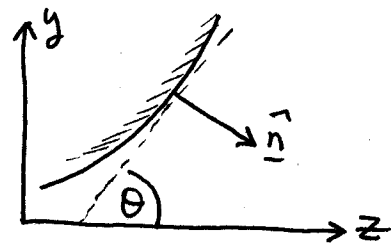
Now let's use the equation of continuity:

(51)

$$v_n = v_z \hat{n} \cdot \hat{z} \approx v + \frac{\partial \xi}{\partial t}(0, t)$$

What is \hat{n} ?

$$\hat{n} = \hat{z} - i k_x \xi_k e^{i k_x x} \hat{x} - i k_y \xi_k e^{i k_x x} \hat{y}$$



$$\tan \theta = \frac{dy}{dz}$$

$$\Rightarrow \frac{dz}{dy} = \cot \theta = \xi'$$

$$\nabla u \cdot \hat{n} \Big|_{z=2} \text{ is } \frac{du}{dz}$$

which is just

$$\begin{aligned} \frac{du}{dz} &= u_0'(z) - q u_k e^{i \underline{k} \cdot \underline{x}_\perp - qz} \\ &= -\frac{1}{l} e^{-z/l} - q u_k e^{i \underline{k} \cdot \underline{x}_\perp - qz} \end{aligned}$$

Now evaluate at $z = \xi_k e^{i \underline{k} \cdot \underline{x}_\perp}$

$$= -\frac{1}{l} + \frac{1}{l^2} \xi_k e^{i \underline{k} \cdot \underline{x}_\perp} + q u_k e^{i \underline{k} \cdot \underline{x}_\perp}$$

$$\cancel{v} + \omega \xi_k e^{i \underline{k} \cdot \underline{x}_\perp} = \cancel{\frac{D}{l}} - \frac{D}{l^2} \xi_k e^{i \underline{k} \cdot \underline{x}_\perp} + \frac{q}{D} u_k e^{i \underline{k} \cdot \underline{x}_\perp}$$

$$\Rightarrow \boxed{\frac{\omega}{D} \xi_k = -\frac{1}{l^2} \xi_k + q u_k} \quad (3)$$

From equations (1), (2), (3) we hope to determine ω , ξ_k , u_k .

Our most important question is: what is the sign of ω , meaning $\omega = \omega(\underline{k})$?

We'll make some useful simplifications to proceed here:

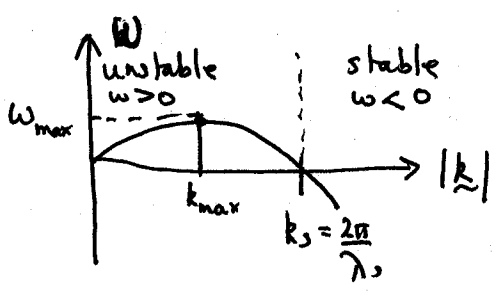
First simplification is $k \ll l^{-1}$, so that the diffusion length is much greater than the scale of the perturbation. Second is the quasi-static approximation: $\omega \ll Dk^2$. In other words, the time for heat to diffuse a distance $\frac{2\pi}{k}$ is much less than the time required for the perturbation to grow. Then

$$q^2 - \frac{1}{l}q - k^2 \approx 0 \Rightarrow q = \frac{1}{2} \pm \frac{\sqrt{\frac{1}{4} + 4k^2}}{2} \approx |k|$$

because $k \gg l^{-1}$. Then

$$\frac{\omega}{D} \sim \frac{1}{l}|k|(1 - d_0 l |k|^2)$$

i.e. $\omega \sim v|k|(1 - d_0 l k^2)$



The crossover scale $\frac{\lambda_s}{2\pi} = \sqrt{d_0 l}$

This scale basically sets the scale of emergent patterns, because the fastest growing

wavelength ω_{max} occurs at $k_{max} = \frac{k_s}{\sqrt{3}}$.

Let's also check that this calculation is self-consistent:

$$k_s l = (l/d_0)^{1/2} \gg 1$$

and

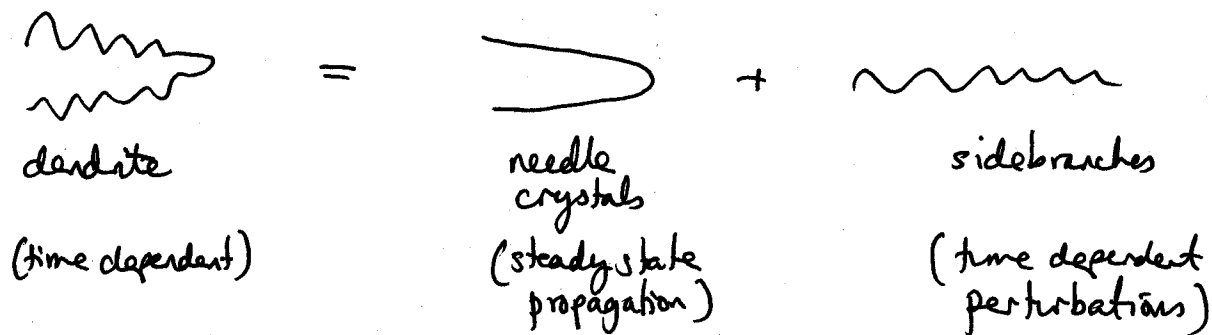
$$\frac{Dk_s^2}{\omega} \approx D \frac{1}{(d_0 l)^{1/2}} \frac{l}{D} \sim \left(\frac{l}{d_0}\right)^{1/2} \gg 1$$

as required.

This rough estimate of the pattern scale is often used even for $\Delta \ll 1$ because the motion of the interface $x \sim \sqrt{t}$ is much slower than the exponential growth $\exp(\omega t)$ of perturbations.

③ Needle crystals.

How should we go about making a theory for patterns as complex as solidification patterns? The approach most workers have adopted is to write



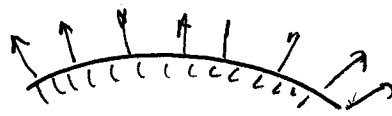
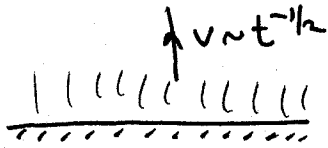
The prayer is that we can learn something about the tip radius, speed, shape from the steady state solution, and understand sidebranching dynamics from perturbation theory.

(a) Steady states when $d_0 = 0$.

Our calculations of planar interfaces have shown us that for $\Delta < 1$, the interface slows down as it advances: $v = \dot{x} \sim t^{-1/2}$ because latent heat piles up in front of the interface. We also learned that a planar interface experiences a long wavelength instability, but what is the state that it tries to attain? Now we'll answer that question.

Planar interfaces slow down because the heat has nowhere to go. If we could bend the interface a little, the heat would have more than just a half-space in which to diffuse

away.



v constant

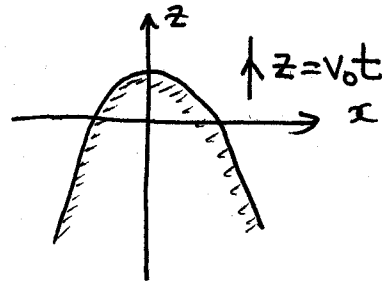
Let's guess what shape of interface we need so that the hat just gets out of the way at the right rate to allow steadily translating growth at $\Delta < 1$.

Locally, on a scale \ll local curvature, the interface must move along its outward normal $\hat{n}(x)$ with speed $t^{-1/2}$. Let the shape be

$z = f(x)$. But we want

$z = v_0 t$, and locally, $x \sim t^{1/2}$.

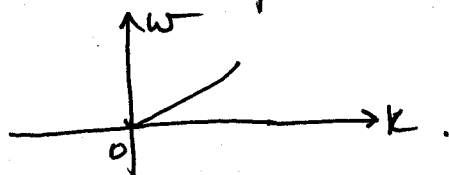
$\Rightarrow \underline{z \sim x^2}$.



i.e. the steady state needle should be a parabola. If there is no surface tension, then the boundary conditions on the interface will be

$u_s = \Delta$

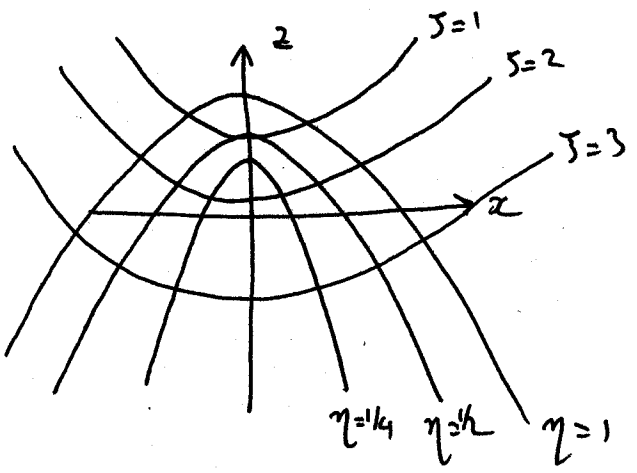
on the surface of the parabola. We also expect that this parabola will be dynamically unstable for all k , because $d_0 = 0$, so the spectrum will look like



i.e. $w(k) > 0 \quad \forall k$.

Let's solve this problem more systematically now, following the work of Ivanov (1947). We use parabolic coordinates

$$\xi = \frac{r-z}{\rho} \quad \eta = \frac{r+z}{\rho}$$



$$r = \sqrt{x^2 + z^2}$$

We use these orthogonal curvilinear coordinates because we already used physical reasoning to guess the answer. Mathematically we use them because they are one of the 13 coordinate

systems in which ∇^2 can be separated. Write

$$\left(\nabla^2 + \frac{2}{l} \frac{\partial}{\partial z} \right) u = 0$$

$$l = 2D/V$$
$$Pe \equiv \rho l = \frac{\rho V}{2D}$$

Then

$$2\eta \frac{\partial^2 u}{\partial \eta^2} + (1 + 2Pe\eta) \frac{\partial u}{\partial \eta} + 2\xi \frac{\partial^2 u}{\partial \xi^2} + (1 - 2Pe\xi) \frac{\partial u}{\partial \xi} = 0$$

We seek a general solution

$$u = \sum_{n=0}^{\infty} A_n V_n(Pe\eta) Q_n(Pe\xi)$$

For $do = 0$, the interface is an isotherm, so we take

$$u(\eta, \xi) = u(\eta)$$

so that the $n=0$ term in the expansion is the only term, and

$$Q_0(Pe\xi) = 1, \dots$$

$$u = A_0 V_0(\eta Pe)$$

and

$$2w V_0'' + (1 + 2w) V_0' = 0 \quad w \equiv Pe\eta.$$

$$\Rightarrow V_0(w) = \int_{w^{1/2}}^{\infty} e^{-y^2} dy$$

(9)

$$\text{and } \frac{dV_0}{dw} = -\frac{1}{2} w^{-1/2} e^{-w}$$

Now we need to satisfy the boundary conditions $V_n = -D \nabla u \cdot \hat{n}$ and $u_s = \Delta$ to determine A and p_c in terms of Δ .

We put the interface at $\eta = 1$. Then position along the interface is given by the ξ coordinate.

$$V_n = -D \nabla u \cdot \hat{n} \Rightarrow \frac{V}{(1+\xi^2)^{1/2}} = -\frac{2D}{\rho(1+\xi^2)^{1/2}} \frac{d}{d\xi} A V_0(p\xi) \Big|_{\eta=1}$$

$$\Rightarrow V = \frac{2D}{\rho} A \frac{\sqrt{p_c}}{2} e^{-p_c} \Rightarrow A = 2\sqrt{p_c} e^{p_c}$$

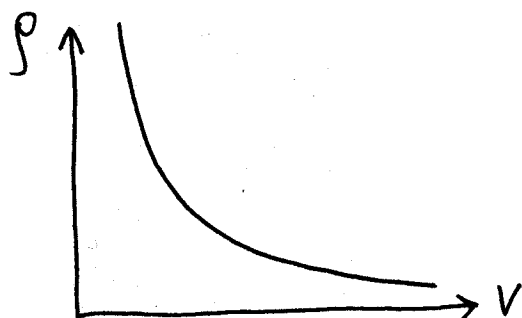
$$u(\eta) \Big|_{\eta=1} = \Delta \Rightarrow 2\sqrt{p_c} e^{p_c} \int_{\sqrt{p_c}}^{\infty} e^{-y^2} dy = \Delta$$

$$\text{i.e. } \boxed{\Delta = \sqrt{p_c \pi} e^{p_c} \text{erfc}(p_c)}$$

(Just as was found for the planar interface with $p_c \equiv \frac{x(t)V(t)}{2D}$)

Notice that we were only able to determine the product

$$\rho V = 2D p_c(\Delta)$$

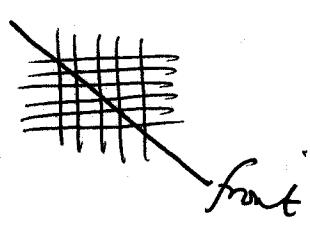


i.e. we found a family of unstable steady states.

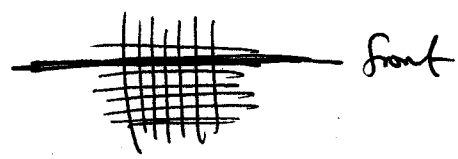
(b) Steady states when $d_0 \neq 0$.

There are none!

This astounding fact was discovered in 1984-1985 from studying simplified models of solidification. There must be some physics missing, because we expect that it is inconceivable that there are no stable extensions of Ivantsov's solution. The missing ingredient is anisotropy. Dendrites are single crystals and the surface energy in the Gibbs-Thomson condition depends on orientation of the solidification front with respect to the crystallographic axes.



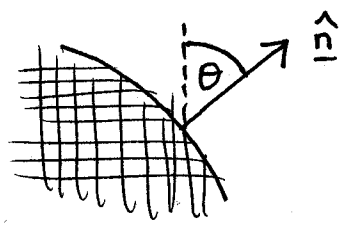
fewer bonds broken per unit length of solidification front



more bonds broken per unit length of solidification front

Thus we should write

$$u_s = \Delta - d_0(\theta) K$$



In most model calculations a form (suitable for 2D only) (11)

$$d_0(\theta) = d_0(1 - \epsilon \cos 4\theta)$$

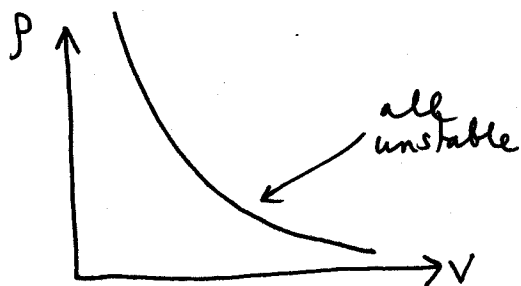
is used. The governing equations are most conveniently solved by Green's functions and yield

$$\Delta - \frac{d_0(\theta)k}{l} = \frac{1}{\pi} \int_{-\infty}^{\infty} dx' e^{(y(x') - y(x))} K_0 \left\{ \left((x-x')^2 + (y(x') - y(x))^2 \right)^{1/2} \right\}$$

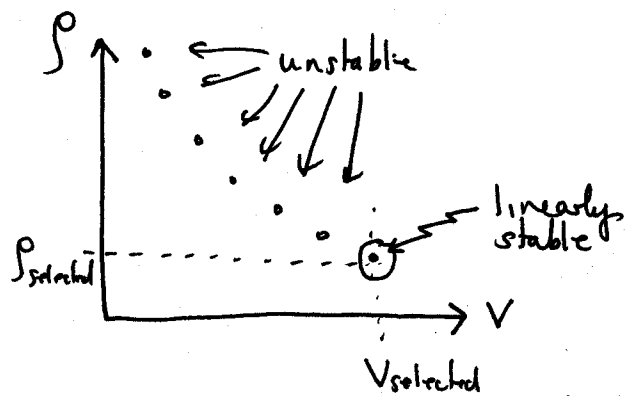
for the shape $y(x)$ of the needle crystal, and v determined implicitly by adjusting l so that a solution exists.

The mathematical theory of this integral equation is beyond the scope of this lecture, but only for certain values of l do solutions of the equation exist. This is an example of a non-linear eigenvalue problem. The solution with the fastest velocity is the one which corresponds to what is seen experimentally (numerically).

To summarise the solution to this selection problem:



l arbitrary $d_0 = 0$



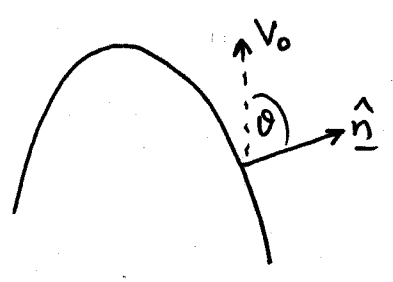
$d_0 \neq 0$ Microscopic solvability

This has become known as microscopic solvability.

4 Sidebranching.

We can readily understand heuristically why sidebranching occurs using our result for the linear stability spectrum of a planar interface

$$\omega = v k (1 - d_0 k^2)$$



If we apply this locally to a segment of a dendrite at normal orientation θ using

$$l(\theta) = D / v_0 \cos \theta$$

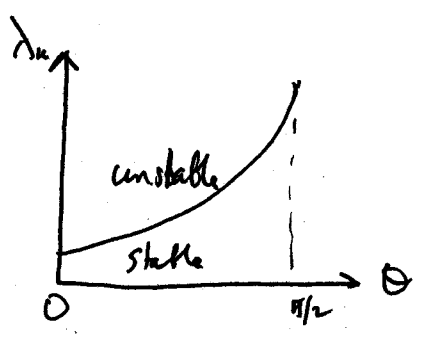
so that

$$\omega = v_0 k (\cos \theta - d_0 k^2)$$

then for fixed k , there is a θ_k such that for $\theta < \theta_k$ the planar interface is unstable.

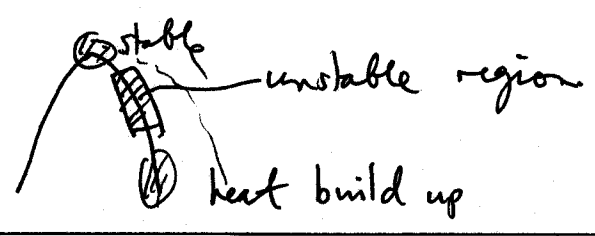
$$\cos \theta_k = d_0 k^2 \implies \theta_k = \cos^{-1}(d_0 k^2)$$

$$\lambda < \lambda_c = 2\pi/k \implies \text{stable.}$$



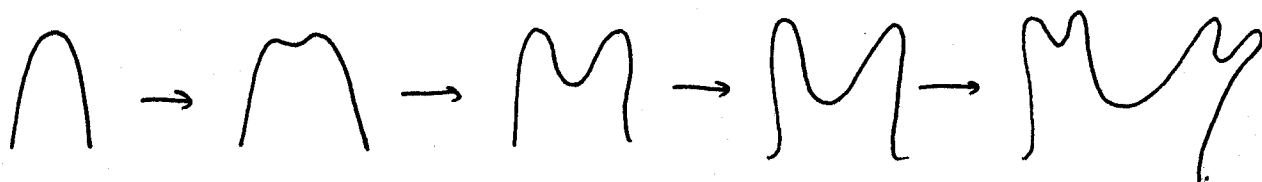
At the tip, a dendrite is stable \because surface tension. Deep in the tail, there is a huge heat build up and lateral growth is very slow.

In the intermediate region, small, thermal fluctuations can be amplified and grow out of the regime of linear stability analysis, to be advected down the body of the dendrite as sidebranches.



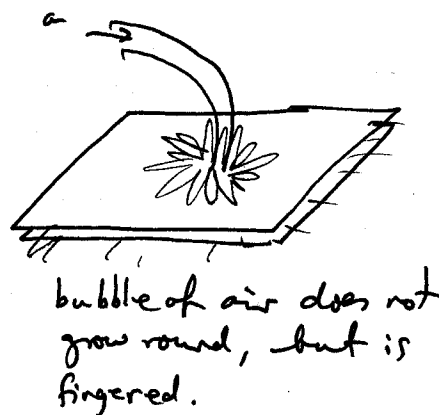
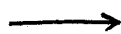
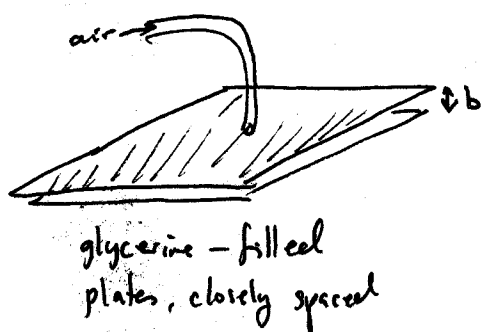
⑤ Morphology.

We saw that if there was no anisotropy, steady state solutions of the equations of motion do not exist. There are no needle crystals. What happens instead? The answer is that there is a never ending sequence of tip-splitting instabilities



resulting in a complex branching pattern that has been seen in crystal growth, bacteria colonies, viscous fingering, ... any system where diffusion occurs.

Visualisation of this is possible using a fluid analogue of dendritic growth:



bubble of air does not grow round, but is fingered.

Equation: ① viscous fluid only moves due to pressure gradient, as

$$\underline{v} = -\frac{b^3}{k\mu} \underline{\nabla} P, \quad \mu = \nu/\beta$$

$$\textcircled{2} \quad \underline{\nabla} \cdot \underline{v} = 0 \Rightarrow \nabla^2 p = 0$$

$$\text{Small compressibility} \Rightarrow \nabla^2 p = \frac{\partial p}{\partial t} \approx 0.$$

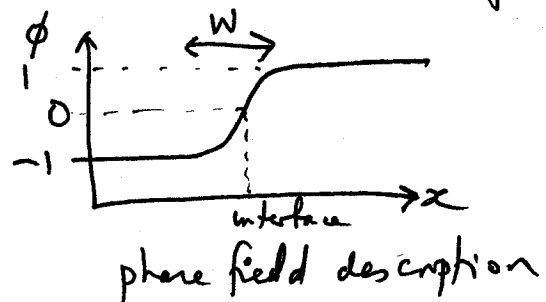
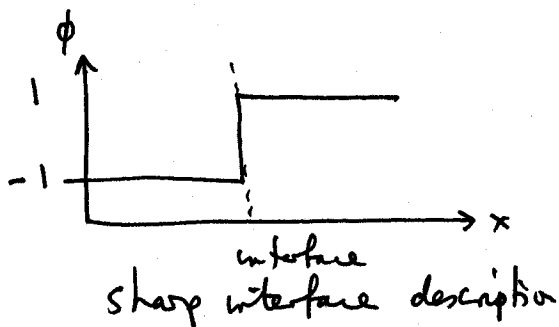
③ Laplace's eqn: $\Delta P = -\gamma K$ (pressure drop over a curved surface). (14)

These equations are the same as those describing dendritic growth! Putting in anisotropy, (e.g.) by engraving a grid on one of the plates, which modulates b , gives bubbles of air that grow in snowflake patterns!

⑥ Simulation methods.

Because the solidification equations are inherently unstable, it is very unpleasant to try and solve them. One must track where an interface is and if one has discretised, it is easy to make mistakes in the position that become amplified. In addition to this, it is necessary to impose boundary conditions on the interface and this is also tricky. The best way to proceed in such a situation is to avoid the interface all together.

The idea, due originally to Langer, is to define an order parameter ϕ which smoothly interpolates between solid and liquid. e.g. $\phi = \begin{cases} 1 & \text{solid} \\ -1 & \text{liquid} \end{cases}$ $\phi = 0$ defines solidification front.



We then regularize the interface by giving it a 15 width w , which will ultimately be taken to $w \rightarrow 0$. Then we will try to develop a Partial Differential Equation for $\phi(x, t)$ and $u(x, t)$ so that in the limit $w \rightarrow 0$, the original sharp interface equations are recovered.

There is no unique way to do this, but an example that is frequently used is

$$\partial_t u = D \nabla^2 u + \frac{1}{2} \partial_t \phi$$

$$A^2(\underline{n}) \partial_t \phi = \nabla \cdot [A^2(\underline{n}) \nabla \phi] + [\phi - \lambda u (1 - \phi^2)] (1 - \phi^2) + \partial_x \left(|\nabla \phi|^2 A(\underline{n}) \frac{\partial A}{\partial \phi_x} \right) + \partial_y \left(|\nabla \phi|^2 A(\underline{n}) \frac{\partial A}{\partial \phi_y} \right)$$

$$A(\underline{n}) = (1 - 3\epsilon) \left[1 + \frac{4\epsilon}{1 - 3\epsilon} \frac{(\phi_x)^4 + (\phi_y)^4}{|\nabla \phi|^4} \right]$$

$$\hat{n} = (\phi_x \underline{x} + \phi_y \hat{y}) / (\phi_x^2 + \phi_y^2)^{1/2}$$

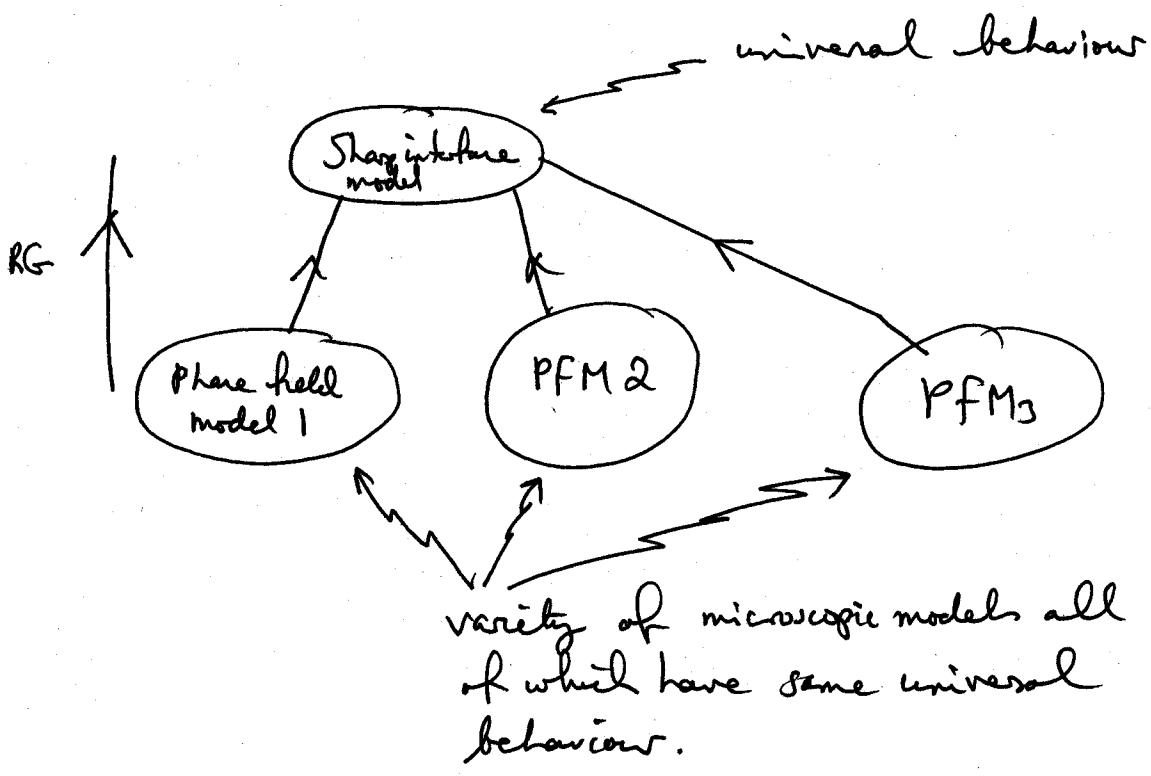
$$\phi_x \equiv \partial_x \phi$$

This is a complex nonlinear PDE! Still if we can solve it, we've solved the moving boundary problem without ever having to look for interfaces!

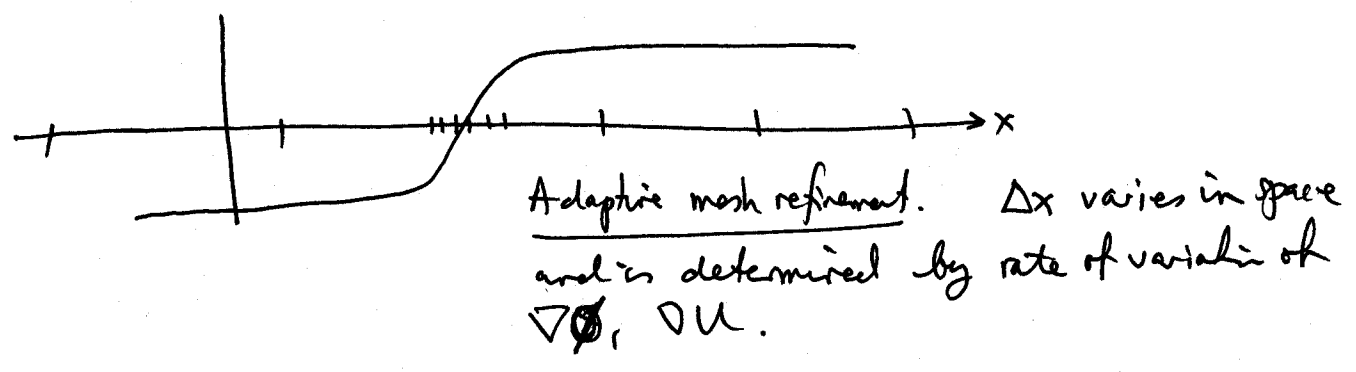
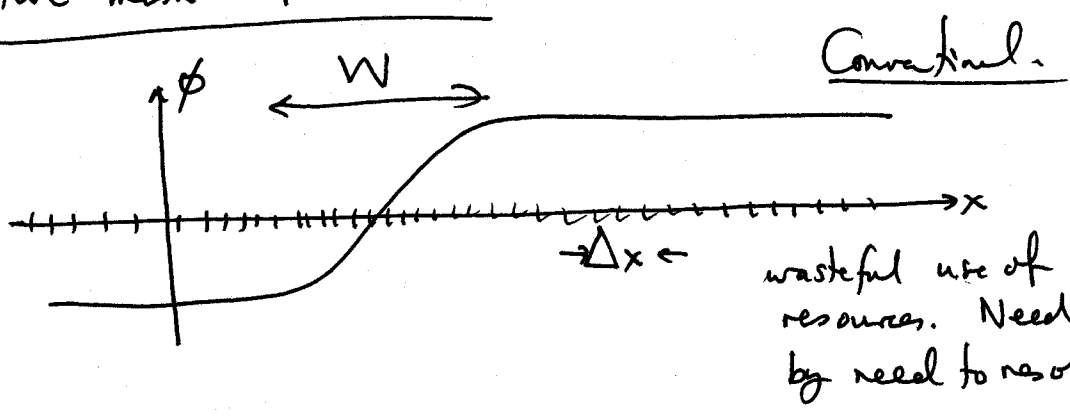
Q: How are the parameters in the phase field model related to those of the sharp interface model?

A: $d_0(\underline{n}) = d_0 [A(\underline{n}) + \partial_0^2 A(\underline{n})] \quad d_0 = 0.8839 / \lambda$
 $\lambda = 1.5957 D$

These sorts of relationships are usually derived by an asymptotic analysis, which is related to renormalisation group.



Adaptive mesh refinement.



Other simulation methods include level set dynamics and even Monte Carlo simulation. The basic idea of level sets is to introduce an auxiliary field, just as in the phase field approach. However, the field $\phi(x,t)$ is defined purely so that the locus of $\phi(x=0,t)$ is the interface, but there is no interface width defined. Then by kinematics:

$$\partial_t \phi + v \cdot \nabla \phi = 0$$

an exact equation. This equation serves to transport the solidification front, if the velocity at each point on the interface has been defined. If we use this in conjunction with the sharp interface model defined earlier, we have in principle an exact formulation of the dynamics, without requiring any $W \rightarrow 0$ limit and RG/asymptotic type relation between parameters of the sharp interface model and phase field model. Secondly, the resulting equation of motion for ϕ is hyperbolic and there exist, in principle, fast methods to solve. Remember that the phase field model equation is of the form

$$\partial_t \phi = \epsilon^2 \nabla^2 \phi + f(\phi, u) \quad \epsilon \rightarrow 0$$

$$f(\phi, u) = \text{non-linear function}$$

This equation is numerically stiff, which is why we used adaptive mesh refinement to solve the problem.

The disadvantage of level set methods is that one is still required to track the interface and impose boundary conditions. Nevertheless, until recently it was the only technique available to solve solidification problems with $D_{solid} \neq D_{melt}$.

The idea behind Monte Carlo simulation is

- (a) Write the dynamics as a Green function formulation
- (b) Evaluate the resultant multidimensional integrals by Monte Carlo simulation.

There is recent work by A. Karma on this, and unpublished work by me and Raul Benitez.

7) What's next?

I see the following areas and questions as emerging to the forefront over the next few years.

- ① Calculation of parameters in sharp interface model by microscopic atomic calculations. Bridging the micro-macro gap.
- ② Calculation and prediction and control of properties of materials with a specified microstructure. Will become

the key question once the ability to do realistic simulations in near real-time becomes routine, as computer power and numerical techniques become more powerful.

- ③ Improved computational techniques to fully exploit universality. Don't waste computer time calculating irrelevant quantities.
- ④ Elastic effects, fluid effects, mixed impurity and thermal diffusion.
- ⑤ Something that some young people like you will do!