

Generalized Phase Field Models with Anisotropy and Non-Local Potentials

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Ruelle, Fisher, Dyson, Lieb, Lebowitz 1960s: In the thermodynamic limit

$$F(\Omega) = |\Omega| f_{\infty} + \dots$$

The next term should be a surface free energy term, f_{surface} .

C & Fisher papers 1977-1980 (Comm. Math. Phys.) for lattice systems

$$F(\Omega) = |\Omega| f_{\infty} + |\partial\Omega| f_{\text{surface}} + \dots$$

Liquid

$$\partial u / \partial t = D \Delta u$$

The Classical Stefan Problem

Find $\Gamma(t)$ and $u(x,t)$

Solid

$$\partial u / \partial t = D \Delta u$$

n

Interface $\Gamma(t)$

$$l_v / D = \{ \nabla u(\text{Solid}) - \nabla u(\text{Liquid}) \} \cdot n$$

$$u = 0$$

- Classical Stefan problem (Lame and Clapeyron 1831, Stefan 1889)

$$\begin{aligned}u_t &= D\Delta u \quad \text{in } \Omega \setminus \Gamma \\lv_n &= D[\nabla u \cdot n]_+^- \quad \text{on } \Gamma \\u &= 0 \quad ? \quad \text{on } \Gamma\end{aligned}$$

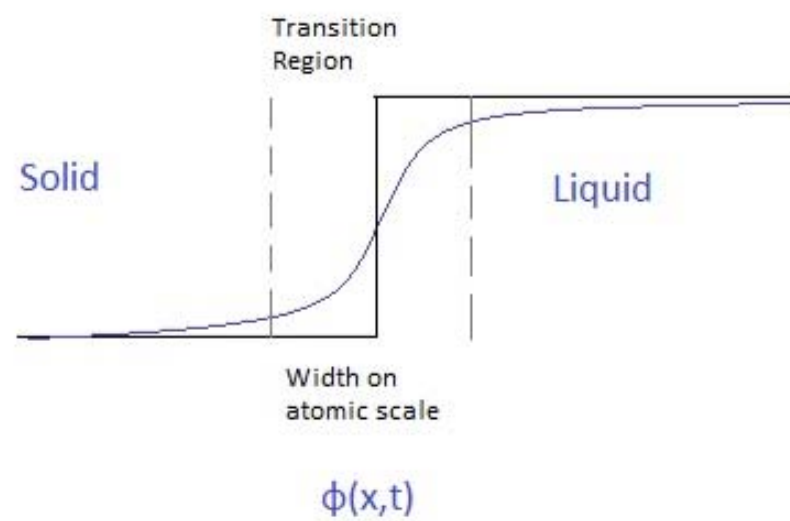
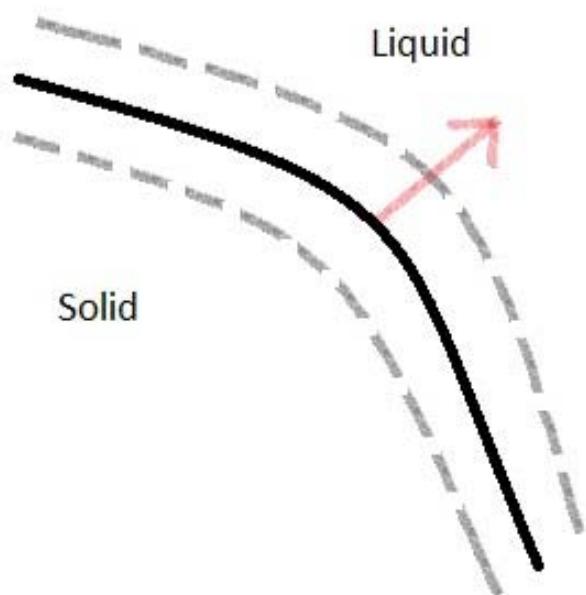
- In Classical Stefan model temperature plays dual role. Around 1900 it became clear to materials scientists that $u \neq 0$ at interface. But the Stefan problem dominated mathematics of interfaces separating phases.
- If temperature does not distinguish phases, we need a new variable, ϕ (order parameter).

- Oleinik formulation consolidates first two eqs:

$$u_t + \frac{l}{2}\phi_t = D\Delta u$$

where ϕ is just a step function.

- How do we obtain the second variable ϕ ?



Idea of "order parameter" in statistical mechanics

Originally proposed by Landau in 1940's for critical phenomena. Review article by Hohenberg and Halpern 1977 on "Dynamics of critical phenomena" Model A, B... Cahn-Hilliard model etc.

Some speculation that perhaps order parameter could be used for ordinary phase transitions.

1. Landau "order parameter" based on idea that "correlation length" diverges to infinity near critical point.
2. It was shown to be wrong in that region.
3. For an ordinary phase transition, the correlation length is very small, not infinite.
4. For an ordinary phase transition, we "cannot hide behind 'universality.'" We need to obtain exact answers with exact physical parameters.
5. Even if all of this is OK how to compute with an interface thickness $\varepsilon = 10^{-8}$?

Is it possible that the idea could work well for the opposite region (atomic correlation length) when it does not work for the intended region (divergent correlation length)?

The entropic part of the free energy involves

$$\{\phi_k \ln \phi_k + (1 - \phi_k) \ln(1 - \phi_k)\}$$

is often approximated in applications by a smooth double well potential, denoted $W(\phi_k)$, which takes its minimum values on the bulk (i.e., single phase) material.

- Write a free energy $\mathcal{F}[\phi, u] := \int_{\Omega} \left\{ (\nabla \phi)^2 + w(\phi) + uh(\phi) \right\}$ with w double well and e.g., $h'(\phi) = (1 - \phi^2)^2$ or $h'(\phi) = 1$.
- Dynamics $\partial \phi / \partial t = -\delta \mathcal{F} / \delta \phi$ coupled with heat equation

Phase Field to Sharp Interface Model

$$\begin{aligned}\alpha \varepsilon^2 \phi_t &= \varepsilon^2 \Delta \phi + \frac{1}{2} (\phi - \phi^3) + \frac{5\varepsilon}{8d_0} h'(\phi) u \\ (u + \frac{1}{2}\phi)_t &= \Delta u\end{aligned}$$

$$u := \frac{T - T_E}{l/c}, \quad D := \frac{K}{\rho c}, \quad d_0 := \frac{\sigma}{[s]_E l/c}$$

As $\varepsilon \rightarrow 0$ does this system converge to the sharp interface problem below?

$$\begin{aligned}u_t &= D \Delta u && \text{in } \Omega(t) \setminus \Gamma(t) \\ v_n &= D \hat{n} \cdot \nabla u|_+, && \text{on } \Gamma(t) \\ u &= -d_0 (\kappa + \alpha v_n) && \text{on } \Gamma(t)\end{aligned}$$

Sketch of formal asymptotics

Let r be the signed distance from the interface, $\rho := r/\varepsilon$

$$\begin{aligned}\phi(x, t; \varepsilon) &= \phi^0(x, t) + \varepsilon \phi^1(x, t) + \dots \\ &\approx \Phi(\rho, t; \varepsilon) = \Phi^0(\rho, t) + \varepsilon \Phi^1(\rho, t) + \varepsilon^2 \Phi^2(\rho, t) + \dots\end{aligned}$$

$$-\frac{\partial \phi(x, t; \varepsilon)}{\partial t} = \varepsilon v \Phi_\rho^0(\rho, t), \quad \varepsilon^2 \Delta \phi = \Phi_{\rho\rho}^0 + \varepsilon \kappa \Phi_\rho^0 + \dots$$

So the phase equation is roughly

$$\begin{aligned}-\varepsilon v \Phi_\rho^0(\rho, t) &= \Phi_{\rho\rho}^0 + \varepsilon \Phi_{\rho\rho}^1 + \varepsilon \kappa \Phi_\rho^0 \\ &\quad + \frac{1}{2} \left\{ \Phi^0 + \varepsilon \Phi^1 - (\Phi^0 + \varepsilon \Phi^1)^3 \right\} + \frac{c}{d_0} \varepsilon u\end{aligned}$$

$O(1)$ balance

$$\Phi_{\rho\rho}^0 + \frac{1}{2} \left\{ \Phi^0 - (\Phi^0)^3 \right\} = 0 \quad \Rightarrow \quad \Phi^0(\rho) = \tanh(\rho/2) \quad (1)$$

$O(\varepsilon)$ balance

$$\mathcal{L}\Phi^1 := \Phi_{\rho\rho}^1 + \frac{1}{2} \left\{ 1 - 3(\Phi^0)^2 \right\} \Phi^1 = \nu\Phi_{\rho}^0 + \kappa\Phi_{\rho}^0 + \frac{c}{d_0}u =: F \quad (2)$$

Note that Φ_{ρ}^0 solves the homogenous equation, $\mathcal{L}\Phi_{\rho}^0 = 0$, so Fredholm alternative theorem implies, $\mathcal{L}\Phi^1 = F$ has a solution only if $(F, \Phi_{\rho}^0)_{L^2} = 0$. This means

$$\int_{-\infty}^{\infty} \left(\nu\Phi_{\rho}^0 + \kappa\Phi_{\rho}^0 + \frac{c}{d_0}u \right) \Phi_{\rho}^0 d\rho = 0, \quad \text{so} \quad (3)$$
$$u \simeq c_1 d_0 \kappa + c_2 \nu.$$

Match "inner solution" Φ with "outer solution" ϕ .

Ultimately, we want a rigorous proof that in some norm $\|\cdot\|$ one has

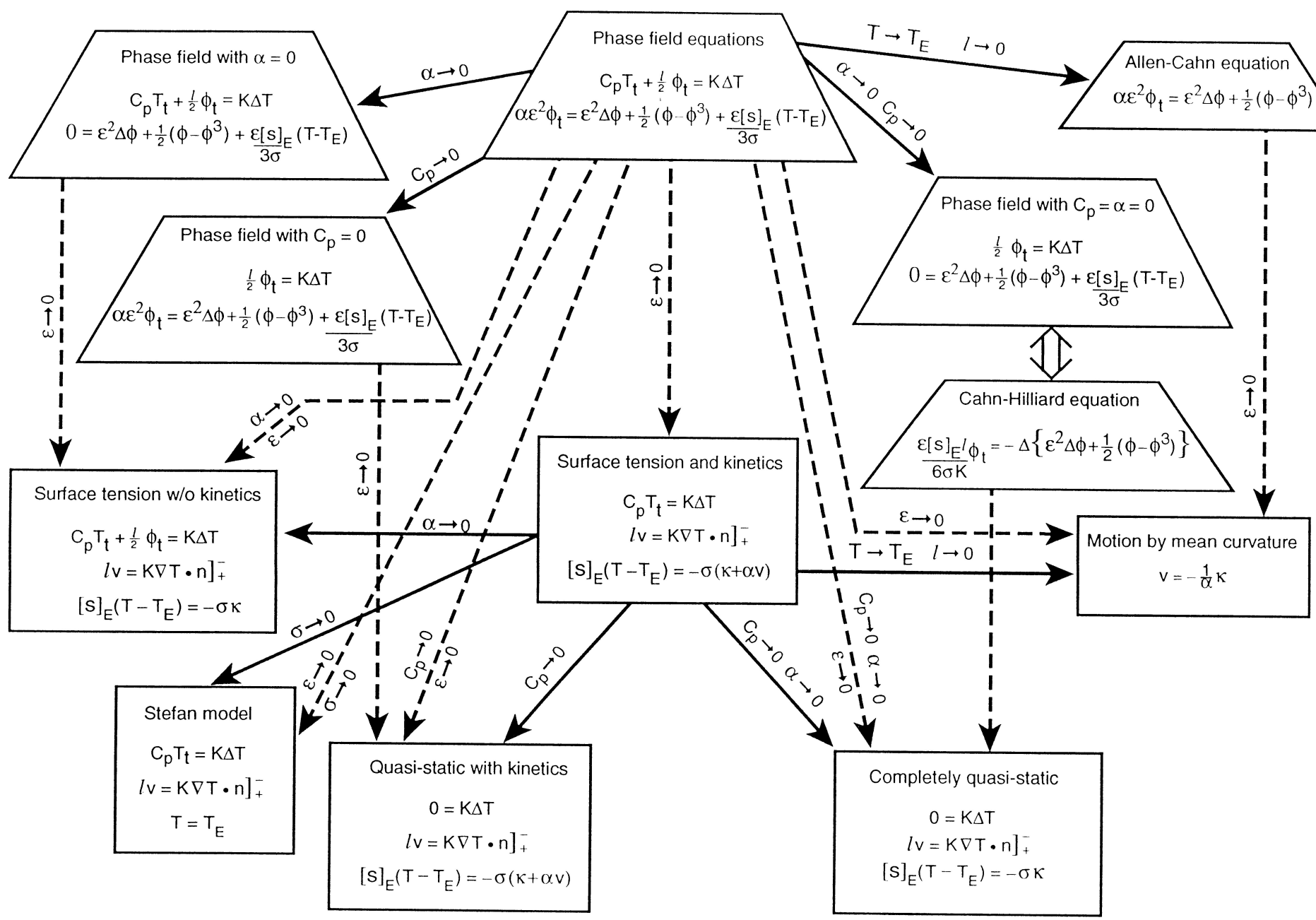
$$\left\| \text{True Solution } \phi_\varepsilon - (\phi^0 + \varepsilon\phi^1 + \dots + \varepsilon^k\phi^k) \right\| \leq C_{k+1}\varepsilon^{k+1}. \quad (4)$$

Also, we would like to know that the solution to the phase field and the sharp interface problems satisfy

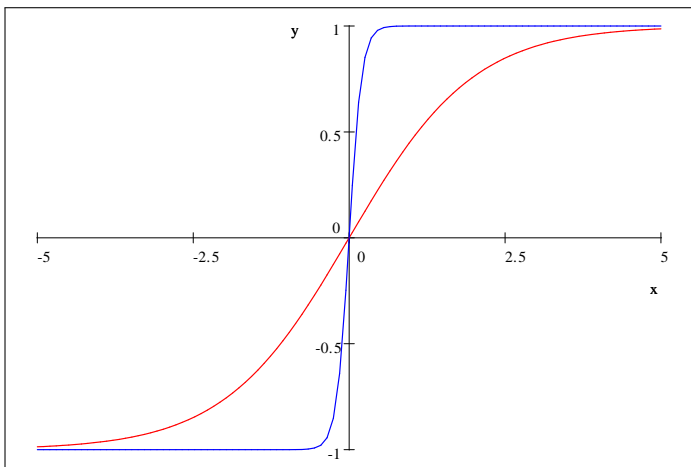
$$\|\phi_\varepsilon - \phi_0\| \leq C\varepsilon. \quad (5)$$

- Do solutions exist? Is ϕ even bounded?
- Does the interface remain at the same "thickness" etc.
- Can we establish (4) and (5) in some suitable norm?

Main analytical thrust of research in the 1980s.



- Real physical thickness of interface is 10^{-8} cm; capillarity length 10^{-6} or 10^{-7} cm; sample 1 cm; radius of curvature 10^{-4} cm.
- Computations would be impossible with these parameters.
- Ansatz: If we extract the surface tension from the interface thickness, then we can increase the interface thickness by a factor of 1000 without influencing motion of the interface (C & Socolovsky 1989, 1991).



$\phi(x, t; \varepsilon)$ actual ε , and stretched.

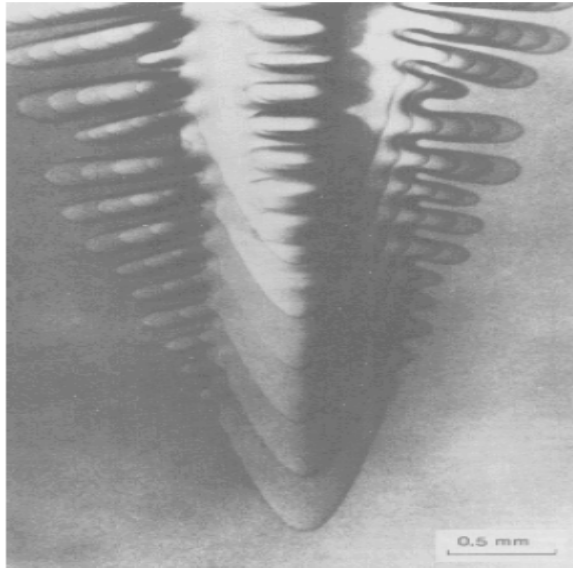
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- N. Dirr, A Stefan Problem with surface tension as the sharp interface limit of a nonlocal system of phase field type, J. Stat. Phys. (2004).

Discuss three projects (see www.pitt.edu/~caginalp)

- (with Christof Eck and Xinfu Chen) Second order asymptotics (in ε) on the PF eqs;
- (with Emre Esenturk) Anisotropy and higher order PF eqs;
- (with Xinfu Chen and Emre Esenturk) New perspective in PF: use potential with non-local interactions and anisotropy to obtain elegant expressions for interface from microscopic considerations

- Interest in the materials community in refined computations as computing advances.
- Better understanding of detailed anisotropy needed
- Understand relationships between molecular anisotropy, surface tension, equil shapes and dynamics

- Rubinstein & M. Glicksman (1991); and other experiments
- Need for fine resolution within computing capacity



- Isotropic: Gibbs-Thomson relation

$$u[s]_E = -\sigma\kappa$$

σ is the surface tension,

$[s]_E$ is entropy difference between the phase per unit volume,

κ is the sum of principal curvatures, c is heat capacity and l is latent heat,

$u := (T - T_m)c/l$ is the reduced temperature,

T_m is the equilibrium melting temperature). When there is anisotropy, surface tension can be written as a function of surface normal, i.e. $\sigma(\hat{n})$.

In this case, the equation above needs to be modified.

Generalization of Phase Field for second order convergence

$$u := \frac{T - T_E}{l/c}, \quad D := \frac{K}{\rho c}, \quad d_0 := \frac{\sigma}{[s]_E l/c}.$$

the sharp interface problem has the form

$$\begin{aligned} u_t &= D \Delta u && \text{in } \Omega(t) \setminus \Gamma(t) \\ v_n &= D \hat{n} \cdot \nabla u]_{+}^{-}, && \text{on } \Gamma(t) \\ u &= -d_0 (\kappa + \alpha v_n) && \text{on } \Gamma(t) \end{aligned}$$

Let

$$\begin{aligned} W(\pm 1) &= 0 < W(s) \quad \text{for all } s \neq \pm 1, \quad W''(\pm 1) > 0, \\ G'(\pm 1) &= 0, \quad G(1) - G(-1) = \int_{-1}^1 \sqrt{2W(s)} ds. \end{aligned}$$

The phase field equations corresponding are

$$\begin{aligned} \varepsilon^2 (\alpha_\varepsilon \phi_t - \Delta \phi) + W'(\phi) &= \varepsilon \frac{1}{d_0} G'(\phi) u \\ (u + \frac{1}{2} \phi)_t &= \Delta u \end{aligned}$$

where $\alpha_\varepsilon := \alpha + \varepsilon \alpha_1$ and α_1 is defined by

$$\alpha_1 := \frac{\frac{1}{d_0} \int_{\mathbb{R}} \{G(1) - G(\Phi(s))\} (1 + \Phi(s)) ds}{2 \int_{\mathbb{R}} \dot{\Phi}^2(s) ds}$$

where Φ is the (unique) solution to

$$\ddot{\Phi} - W'(\Phi) = 0 \quad \text{on } \mathbb{R}, \quad \Phi(\pm \infty) = \pm 1, \quad \int_{\mathbb{R}} s \dot{\Phi}(s) ds = 0.$$

- Previous works used distance from the level set

$$\Gamma_\varepsilon(t) := \{x : \phi_\varepsilon(x, t) = 0\}$$

We used reference frame the level set corresponding to $\varepsilon = 0$,
i.e., $\Gamma_0(t)$.

- THEOREM. With the conditions above, there exists $\varepsilon_0 > 0$ and $C > 0$ such that solutions $(u_\varepsilon, \phi_\varepsilon)$ to the Phase Field equations satisfy

$$\text{distance} \{\Gamma_\varepsilon, \Gamma_0\} \leq C\varepsilon^2 \quad \text{for all } 0 < \varepsilon < \varepsilon_0.$$

$$\begin{aligned}
\partial_t &= -v\partial_r + \partial_t^\Gamma, \quad \partial_t^\Gamma := \partial_t + \sum_{i=1}^{n-1} S_t^i \partial_{s^i}, \\
\nabla &= N\partial_r + \nabla^\Gamma, \quad \nabla^\Gamma := \sum_{i=1}^{n-1} \nabla S^i \partial_{s^i} \\
\Delta &= \partial_{rr} + \Delta R \partial_r + \Delta^\Gamma, \quad \Delta^\Gamma := \sum_{i=1}^{n-1} \Delta S^i \partial_{s^i} + \sum_{i,j=1}^{n-1} \nabla S^i \cdot \nabla S^j \partial_{s^i s^j}
\end{aligned}$$

where $\nabla S^i(x, t)$, $S_t^i(x, t)$, $\Delta R(x, t)$, $R_t(x, t)$ are evaluated at $x = X_0(s, t) + rN(s, t)$, and are regarded as functions of (r, s, t) .

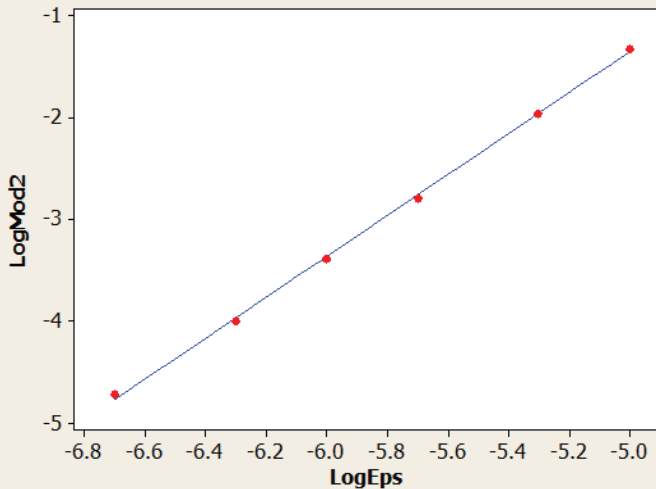
$$\begin{aligned}
w_t &= \{-v_0 \varepsilon^{-1} - \partial_t^\Gamma h_\varepsilon\} w_\rho + \partial_t^\Gamma w \\
\nabla w &= \{N \varepsilon^{-1} - \nabla^\Gamma h_\varepsilon\} w_\rho + \nabla^\Gamma w, \\
\Delta w &= \{\varepsilon^{-2} + |\nabla^\Gamma h_\varepsilon|^2\} w_{\rho\rho} + \{\Delta R \varepsilon^{-1} - \Delta^\Gamma h_\varepsilon\} w_\rho \\
&\quad - 2 \nabla^\Gamma h_\varepsilon \cdot \nabla^\Gamma w_\rho + \Delta^\Gamma w
\end{aligned}$$

where $\nabla^\Gamma, \partial_t^\Gamma, \Delta^\Gamma$ are again differentiations with ρ fixed.

- Are C and ε_0 too big or small to be useful?
- Take specific W , G and α_1 that satisfy conditions.
- Relative difference between true soln and computed.
- Computations show difference goes as ε^2 .
- Several sets of parameters, including dendritic.

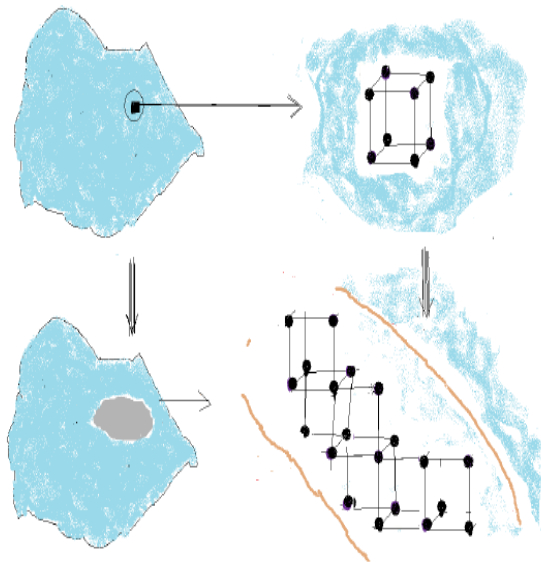
Fitted Line Plot

$$\text{LogMod2} = 8.676 + 2.007 \text{ LogEps}$$



S	0.0379180
R-Sq	99.9%
R-Sq(adj)	99.9%

Microscopic interactions to macro behavior



Two basic approaches we have used.

1. The usual phase field equations arise from truncating Fourier expansion after q^2 (so we have second order). (C in Annals 1986) The molecular anisotropy is largely "averaged out" when we do this. By retaining higher order Fourier modes, and using higher order differential equations, we can obtain the classical Gibbs-Thomson-Herring relation (in $2d$) at the interface (Gibbs-Thomson-Herring Condition):

$$u[s]_E = -(\sigma + \sigma'')\kappa$$

and its dynamical generalization.

In $3d$ things are more complicated.

A new approach to anisotropy (with or w/o non-local interactions) in arbitrary spatial dimension

Idea of working directly on the integral form (avoiding higher order DEs).
Include non-local interactions.

How is the information (e.g., anisotropy) in interactions, J_{kl} ,
communicated to the macro interface.

1. These ideas lead to a free energy:

$$F[\phi] = \sum_{k,l} \frac{1}{4} J_{kl} (\phi_k - \phi_l)^2 + \sum_k W(\phi_k) + \sum_k u G(\phi_k).$$

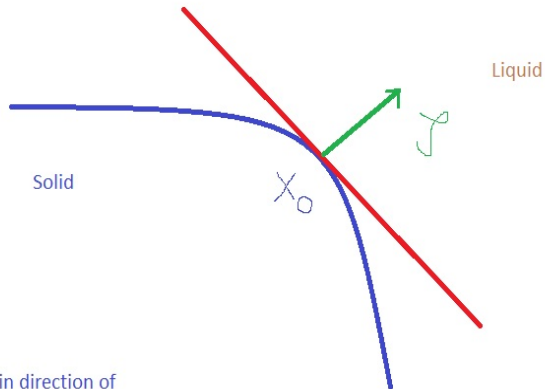
The free energy in the continuum limit:

$$\begin{aligned} \mathcal{F}[\phi] = & \frac{1}{4} \int J_\varepsilon(x-y) (\phi(x) - \phi(y))^2 dx dy \\ & + \int W(\phi(x)) dx + \int u G(\phi(x)) dx \end{aligned}$$

where $J_\varepsilon(z) = \varepsilon^{-N} J(\varepsilon^{-1}z)$, ε is an atomic length scale; $G(\phi)$ represent the entropy difference per unit volume. For simplicity we assume $\Omega = \mathbb{R}^d$ with $d \geq 2$.

2. The phase field equation can be obtained by the assumption that the variational derivative of the free energy should be proportional to the time derivative of the phase field, i.e.,

$$\alpha \varepsilon^2 \phi_t = J_\varepsilon * \phi - \phi - W'(\phi) + \varepsilon u G'(\phi)$$



Traveling wave in direction of
zeta at point x_0 .

The surface tension is the difference per unit area between the free energy with the interface and without, i.e.,

$$\sigma = \frac{\mathcal{F}[\phi] - (\mathcal{F}[-1] + \mathcal{F}[1])/2}{Area} ..$$

$$\begin{aligned}\sigma(\zeta) &:= \int_{\mathbb{R}} \left\{ W(Q(\zeta, z)) + \frac{1}{2} Q(\zeta, z) (Q(\zeta, z) - (j * Q)(\zeta, z)) \right\} dz \\ &= \int_{\mathbb{R}} (W(Q(\zeta, z)) - \frac{1}{2} Q(\zeta, z) W'(Q(\zeta, z))) dz,\end{aligned}$$

where the second line is obtained by making use of equation

$$\begin{aligned}0 &= [(j * Q)(\zeta, z) - Q(\zeta, z)] - W'(Q(\zeta, z)) \\ \pm 1 &= \lim_{z \rightarrow \pm\infty} Q(\zeta, z), \quad Q(\zeta, 0) = 0\end{aligned}$$

When $\zeta = \hat{n}$, i.e., the points located on the interface, $\sigma(\zeta) = \sigma(\hat{n})$ corresponds to the surface tension of the interface.

Let $h(x, t)$ be the signed distance (positive in the liquid) from the point x to Γ_t , the limit interface between liquid and solid at time t . Then, in the local coordinate system $(s', h) := (s^1, \dots, s^{N-1}, h) \in \mathbb{R}^N$, one has

$$x = x_0(s') + h\hat{n}(s'),$$

where \hat{n} is the unit normal. Thus, with these definitions, D^2h and $\vec{\nabla} \hat{n}$ are $N \times N$ matrices with components $(D^2h)_{ij} = \partial h_i / \partial x_j$ and $(\vec{\nabla} \hat{n})_{ij} = \partial \hat{n}_i / \partial x_j$ and are related to each other in the following way

$$\vec{\nabla} h = \hat{n}^T \quad \text{and} \quad D^2h = \vec{\nabla} \hat{n}.$$

Also, the velocity of the interface at an arbitrary point $x_0 \in \Gamma_t$ be expressed as

$$v(x_0, t) = \frac{\partial h(x_0, t)}{\partial t}.$$

Main Theorem

The solution ϕ of

$$\begin{aligned}\alpha \varepsilon^2 \phi_t &= J_\varepsilon * \phi - \phi - W'(\phi) + \varepsilon u G'(\phi) \\ (u + \frac{1}{2}\phi)_t &= \Delta u\end{aligned}$$

admits a formal asymptotic expansion only if the Gibbs-Thomson-Herring condition (with linear kinetics) is satisfied, i.e.,

$$u + \alpha(\hat{n})v + \text{Trace} \left\{ \overrightarrow{\nabla} \hat{n} D^2 \sigma(\hat{n}) \right\} = 0.$$

Using tensor notation this can also be expressed as

$$u + \alpha(\hat{n})v + \overrightarrow{\nabla} \hat{n} : D^2 \sigma(\mathbf{n}) = 0.$$

Constructing the Wulff shape

The Wulff shape is the shape of a solid under the undercooling temperature $u := -1$.

- $2d$ example with anisotropy, $J(x, y) =: \bar{J}(r, \theta)$.
- We will compute the Wulff shape by (i) utilizing the planar solutions, (ii) calculating the corresponding surface free energy $\bar{\sigma}(\theta) =: \sigma(\hat{n})$, and (iii) solving the differential equation

$$\bar{\sigma}(\theta) + \bar{\sigma}''(\theta) = -u[s]_E / \kappa(\theta)$$

Let $\bar{J}(r, \theta)$ be given by

$$\bar{J}(r, \theta) = f_0(r) + \delta \cos(n\theta) f_1(r), \quad r = \sqrt{x^2 + y^2}, \quad \tan \theta = \frac{y}{x},$$

As an illustration, we choose the following:

$$n = 6, \quad f_0(r) = \frac{e^{-r^2}}{\pi}, \quad f_1(r) = -\frac{r^6 e^{3-2r^2}}{27\pi}.$$

For $\hat{n} = (\cos \theta, \sin \theta)$ we have

We integrate \bar{J} in the direction orthogonal to the normal to obtain \bar{j}

$$\begin{aligned}\bar{j}(\theta, z) &: = \int_{-\infty}^{\infty} \bar{J} \left(\sqrt{z^2 + l^2}, \theta + \arctan \frac{l}{z} \right) dl \\ &= \hat{j}(\delta \cos n\theta, z)\end{aligned}$$

where

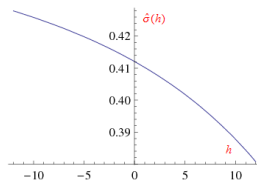
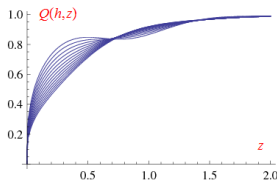
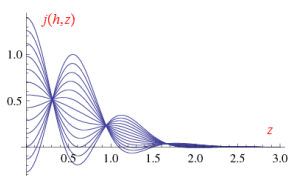
$$\begin{aligned}\hat{j}(h, z) &= j_0(z) + h j_n(z) \\ j_0(z) &: = 2 \int_0^{\infty} f_0(\sqrt{z^2 + l^2}) dl \\ j_n(z) &: = 2 \int_0^{\infty} f_1(\sqrt{z^2 + l^2}) \cos(n \arctan \frac{l}{z}) dl\end{aligned}$$

In our example, we have (recall $\delta \cos(n\theta)$ is form of anisotropy with $n = 6$)

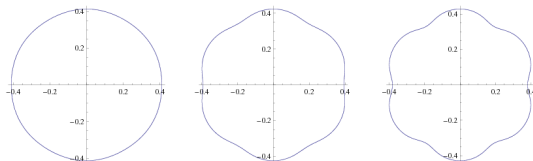
$$j_0(z) = \frac{e^{-z^2}}{\sqrt{\pi}}, \quad j_6(z) = \frac{e^{3-2z^2}(15 - 180z^2 + 240z^4 - 64z^6)}{1728\sqrt{2}\pi}.$$

Increasing δ (amplitude of anisotropy) means equil shape is more like a hexagon. At critical value of δ , one obtains sharp vertices of a hexagon.

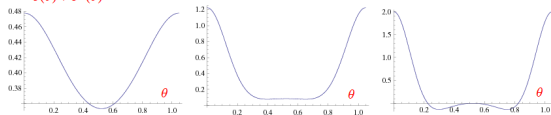
Plots of $\hat{j}(h, z)$, $Q(h, z)$ and $\hat{\sigma}(h)$. Horizontal axis is z in first two graphs.



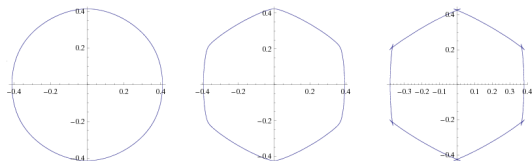
Polar Plot of $\bar{\sigma}(\theta)$



$\bar{\sigma}(\theta) + \bar{\sigma}''(\theta)$



Wulff Shape



Thank you!