Structure and Pattern Formation in Material Systems

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Project Supervisor: Dr. Provatas

September 5, 2011

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Landau Free-Energy Expansion

L. D. Landau

$$f_0(\phi) = a_0 + \underbrace{\frac{1}{2}\, a_2\, \phi^2 + \frac{1}{4}\, a_4\, \phi^4}_{\text{symmetry}} + \underbrace{a_1 \phi}_{\text{non-ideal excess/external}}$$

- Free-energy can be written in polynomial expansion near phase transitions

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- Extremals of free-energy describes equilibrium state
- Describes symmetry breaking
- A mean field theory (uses an order parameter, ϕ), homogeneous/non-functional

Cahn-Hilliard Equation

J.W. Cahn, J.E. Hilliard (1958).

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- Functional derivative $\rightarrow$ boundary layer.
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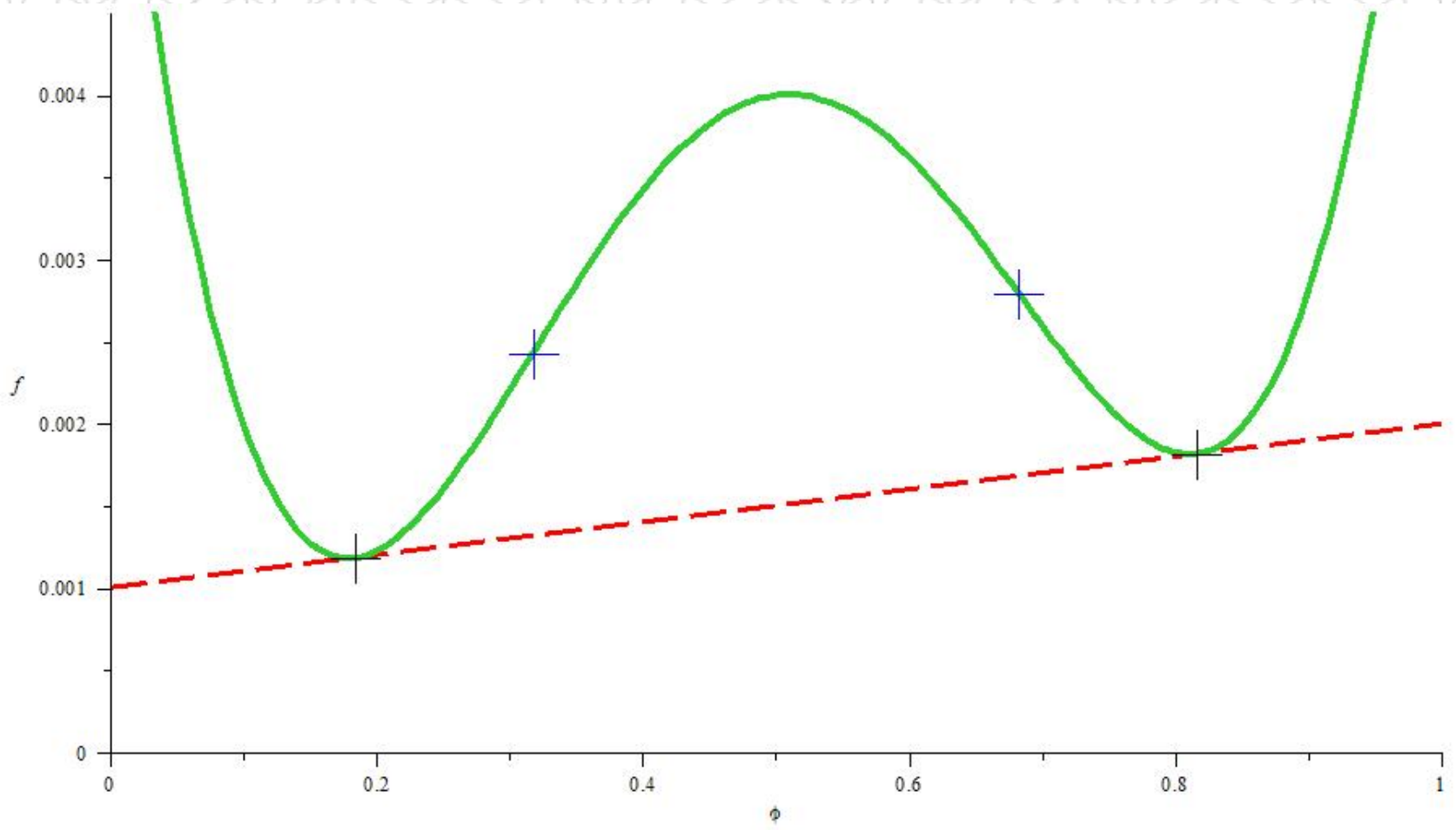
- Interface free-energy density is $2\sqrt{\gamma\,(f - f_{eq})}$
- Used to model phase segregation, or incorporate anisotropic surface tension (crystal-like)

Example: Spinodal Decomposition

Movie.
User: http://www.youtube.com/user/fabiogarofalophd
Source: http://www.youtube.com/watch?v=sysya3Lo78Y
Legend: Black is one phase, and white is the other.
The system was initialized as random.

Typical free-energy,



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$$\frac{\partial \phi}{\partial t} = -\vec{\nabla} \cdot \vec{J_\phi} = -\vec{\nabla} \cdot (-D\,\vec{\nabla}\mu) = D\,\nabla^2 \frac{\delta \mathcal{F}}{\delta \phi}$$

or in Fourier space,

$$\frac{\partial \hat{\phi}(k)}{\partial t} = -D\,k^2 \widehat{\frac{\delta \mathcal{F}}{\delta \phi}}(k),$$

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Scales

$\Delta t \propto \frac{D}{\gamma}$, $\Delta x \propto \sqrt{\gamma}$

γ is the interface width/energy.

The Idea

- We try to simulate *non-equilibrium* systems whose dynamics are driven by an ordering potential (or, as was in my case, material chemical potential).
- One such method is called ‘Phase-field’.

Digression

Digression

- Non-equilibrium: ergodic breaking/glassy states (PFC)
- Noise is not modeled
- Length and time scales are mesoscopic (diffusive), but fluctuation to energy ratio unknown.
- Diffusion is numerically unstable under time reversal

Content

The Swift-Hohenberg Equation

P.C. Hohenberg, J.B. Swift (1977)

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- Applets by Michael Cross.

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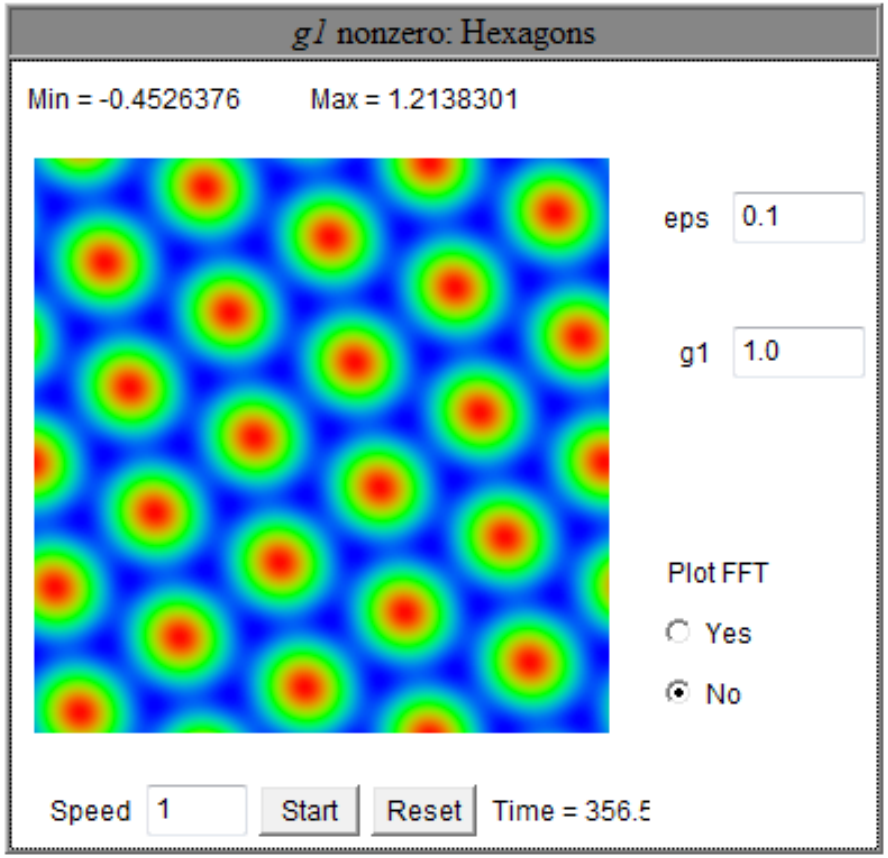

$$\dot{\psi} = \varepsilon\psi - \left(\nabla^2 + 1\right)^2 \psi + g_1\psi^2 - \psi^3$$

Density Functional Theory/"Functional Taylor Expansion"

Density functional theory says that we can generally write the free-energy $\frac{\mathcal{F}[\rho,\partial^n\rho]}{k_B T}$ as,

$$\mathcal{F}_{ideal}[\rho] + \sum_{n=2}^{\infty} \frac{1}{n!} \int_{\mathcal{V}} \prod_{i=1}^{n} d\vec{r}_i \, \rho(\vec{r}_i) \, C_n\left(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n\right) .$$

the functions C_n are the n-point correlation functions defined by,

$$C_n(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) \equiv \frac{\delta^n \Phi[\rho]}{\prod_{i=1}^{i=n} \delta\rho(\vec{r}_i)}.$$

$\Phi[\rho]$ is the interaction potential energy.

Phase-field Crystal (PFC) Model

K.R. Elder and M. Grant (2004)

$$\mathcal{F} = \mathcal{F}_{ideal} + \frac{1}{2}\iint d\vec{r}\, d\vec{r'}\, \rho(\vec{r}) C_2(|\vec{r} - \vec{r'}|)\rho(\vec{r'})$$

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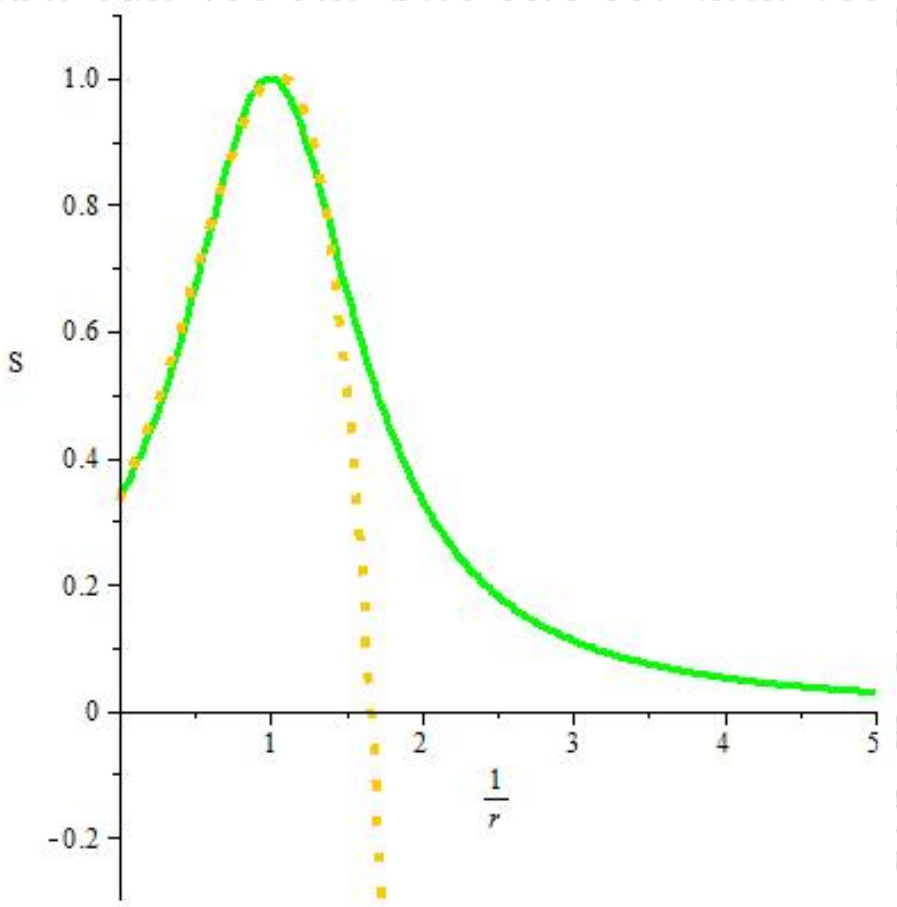
- Atomic diffusion time-scale, long compared to phonons
- Computationally feasible for simulating mesoscopic crystalline structures

More Details



This is a qualitative structure factor for a triangular lattice.

- $\widehat{C(r)}$ is the crystallographic structure factor $S(k)$
- 4th order spline is used to approximate structure factor
- Maxima correspond to crystal planes

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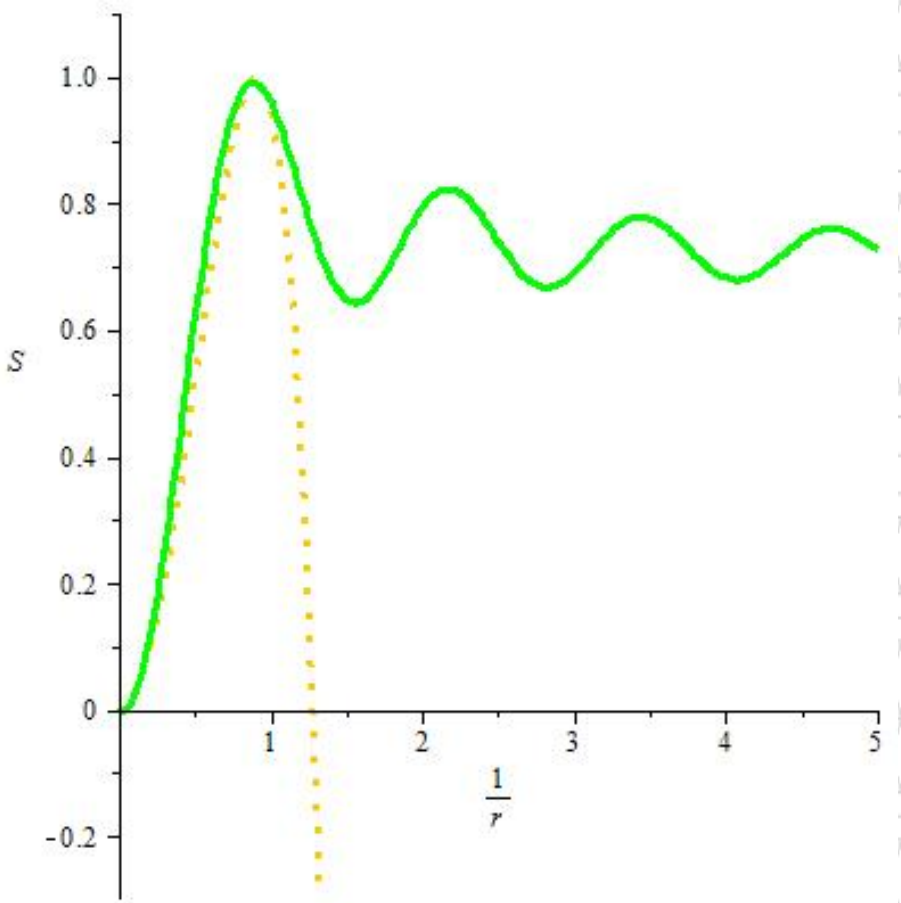

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K.R. Elder et al. (2007)
We theoretically model the binary correlation function as,

$$C_{eff} = \psi^2 \, C_{\alpha\alpha} + (1-\psi)^2 \, C_{\beta\beta} + \psi(1-\psi) \, C_{\alpha\beta}$$

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- Phase diagram indicates that system can be an eutectic forming alloy.

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Binary Eutectic Solidification

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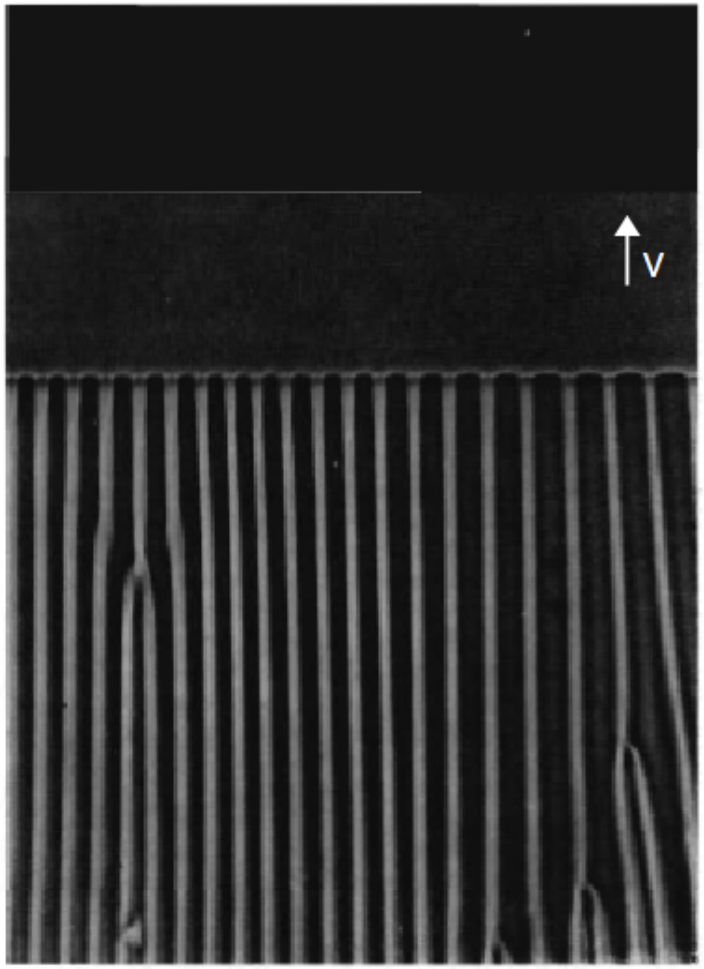
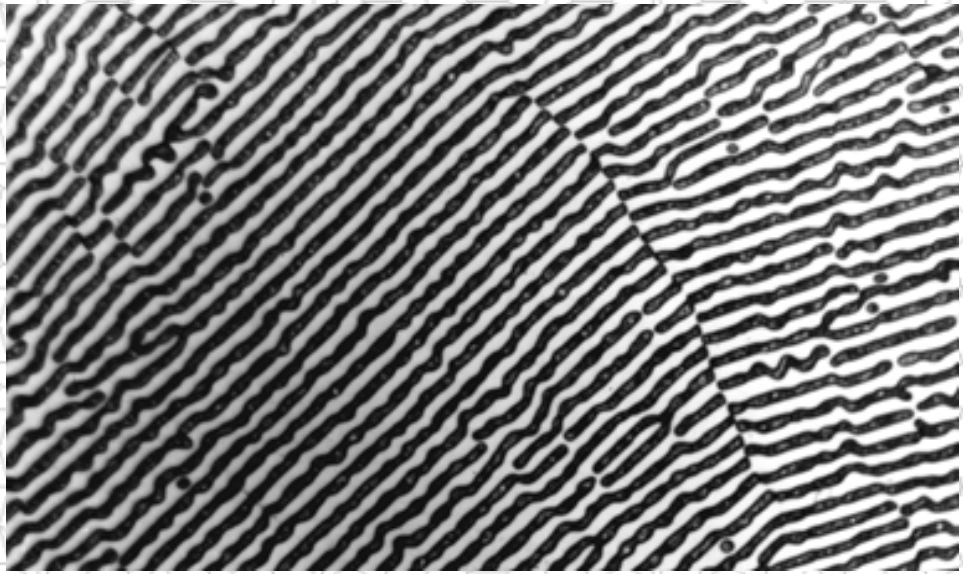
  $\rightarrow$ Interface instabilities (Mullins-Sekerka type) and surface energy.

Eutectic Solidification



Carbon tetrabromide-hexachlorethane eutectic.
Image from (*arrow added*): K.A. Jackson, J.D. Hunt (1966).

Eutectic Solidification



Pb-Sn eutectic.
Image from:
http://www.mete.metu.edu.tr/pages/sdml/Research/leadfree.html.

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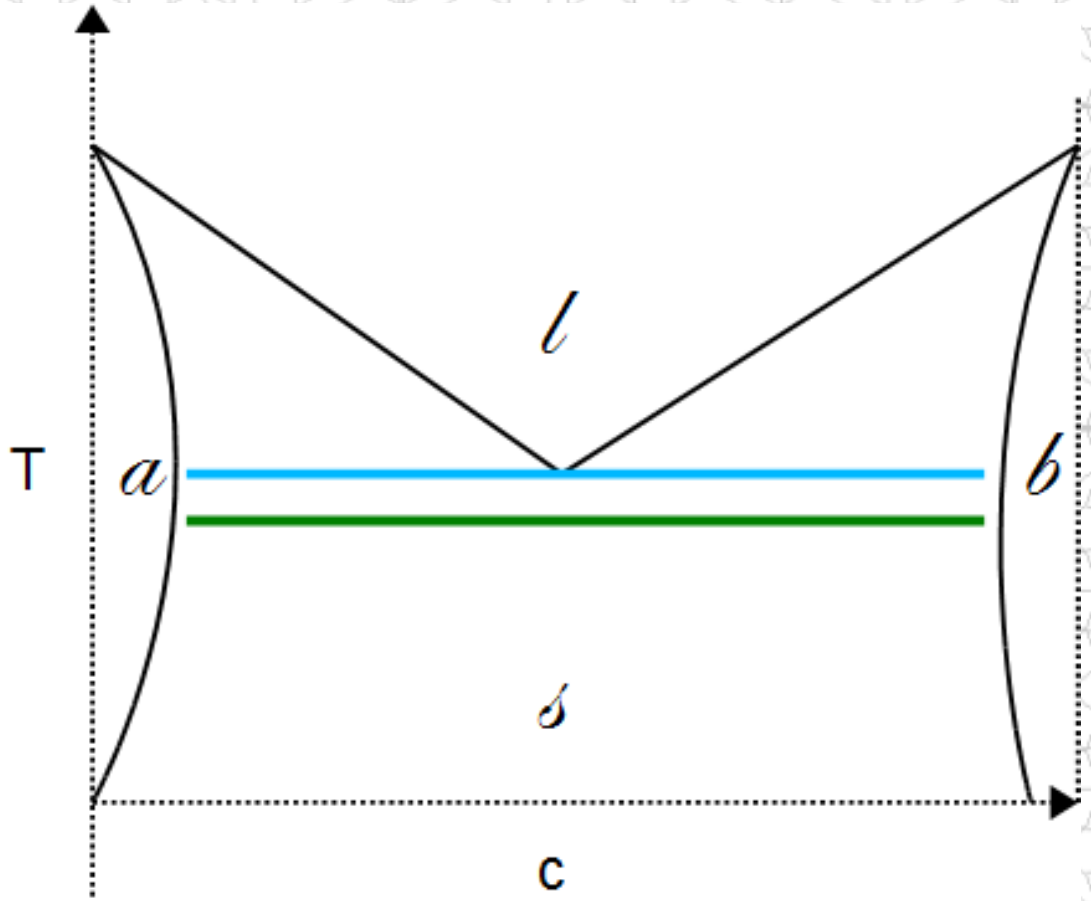

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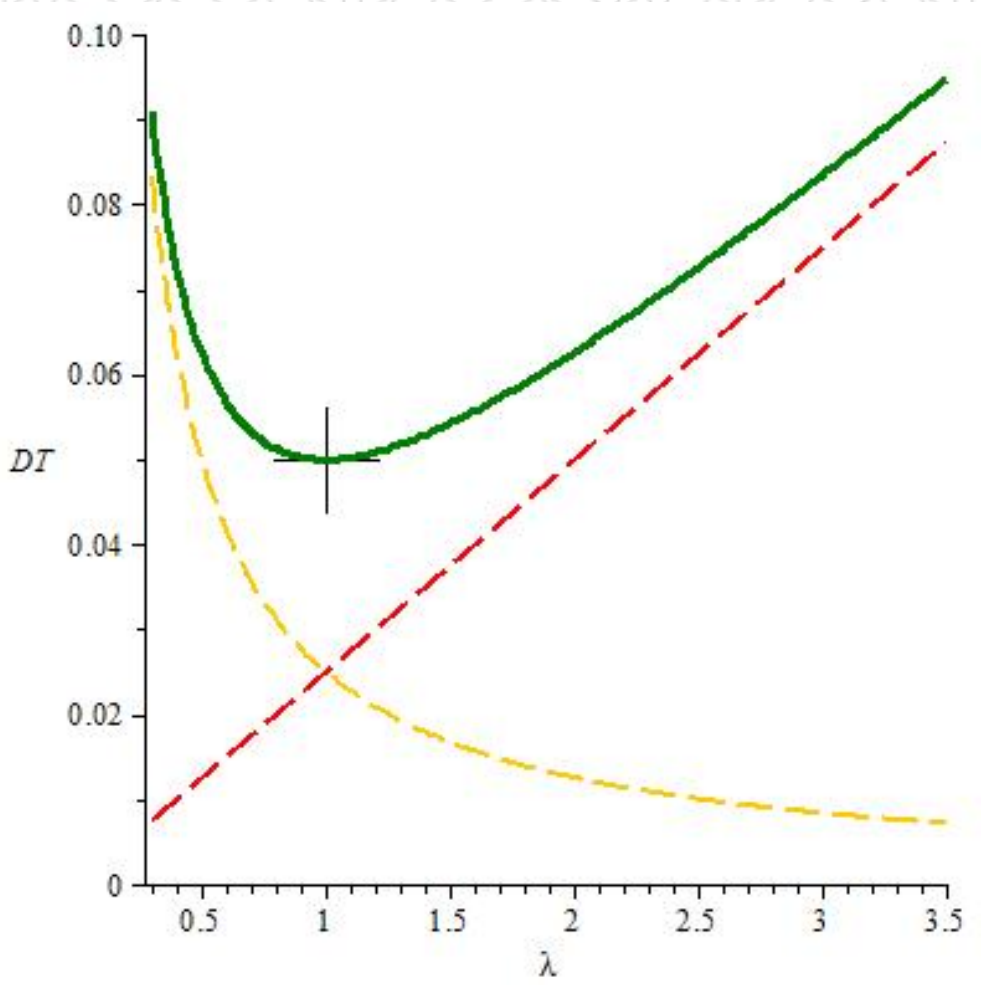

Extremal condition *ansatz*:
Spacing should minimize undercooling.

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- Simulation very small, eutectics ≈ 1000 lattice spacings
- Annealing, zigzag bifurcation and (maybe) topology change.

Content

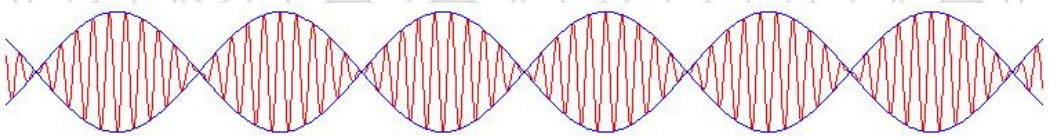
1D-QDRG,
1 dimensional quick and dirty renormalization group

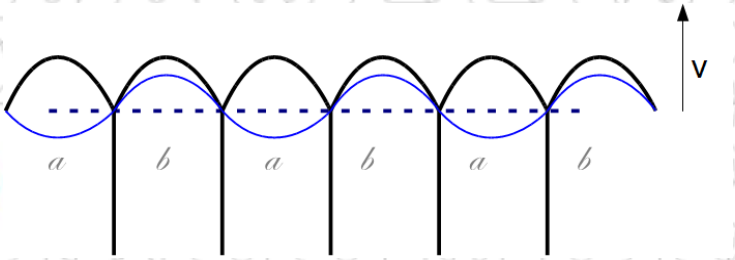
Amplitude Expansion: K. R. Elder, Z-F. Huang, N. Provatas (2010)

- Renormalize to scales of mesoscopic structures along the interface.

Scheme

$n = n_0 + \eta \exp(ix) + \eta^* \exp(-ix)$, $n_0 = 0$, and,
$\psi = \psi_0 + \psi_{-1} \exp(-ix) + \psi_1 \exp(ix) + \ldots$
Take, $\frac{\partial \eta}{\partial t}$, and $\frac{\partial \psi_0}{\partial t}$ modes only.
$*$ note that complex exponentials are linearly independent.





- Keeping symmetries (1-D, translation by lattice only)

Differential Operators

Field/Laplacian	∇^2	$\nabla^2 + \lvert k_m \rvert$
$\eta \exp(ix)$	$\frac{\partial^2}{\partial x^2} - 1$	$\frac{\partial^2}{\partial x^2}$
$\psi = \psi_0$	$\frac{\partial^2}{\partial x^2}$	$\frac{\partial^2}{\partial x^2} + 1$

- Solve for equilibrium amplitudes A, B.
- Perturb

$$\eta + \delta\eta = A\cos(G_{eut}x) + a\cos((G_{eut} + Q)x)$$
$$\psi + \delta\psi = B\cos(G_{eut}x) + b\cos((G_{eut} + Q)x)$$

- Linearize *w.r.t.* A and B and solve for eigenvalues in Q.

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- CALCULATION INCOMPLETE!

Thank you for your attention.
Presentation Done.
Any Questions?

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