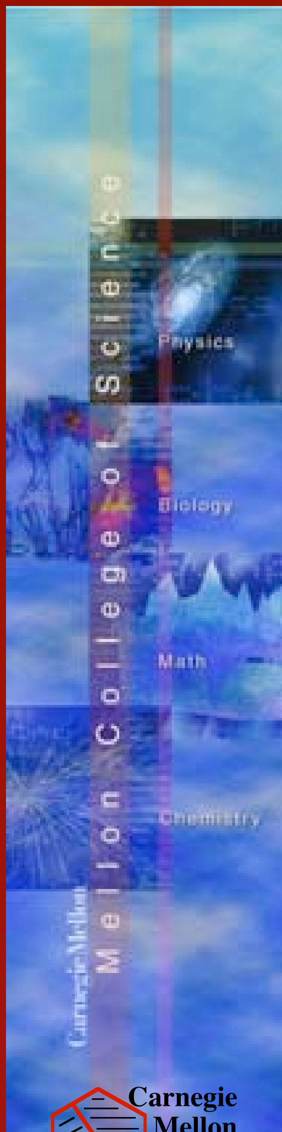
the mesoscale view of interfaces



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Carnegie Mellon MRSEC

CNA Center for Nonlinear Analysis

C N A Summer School
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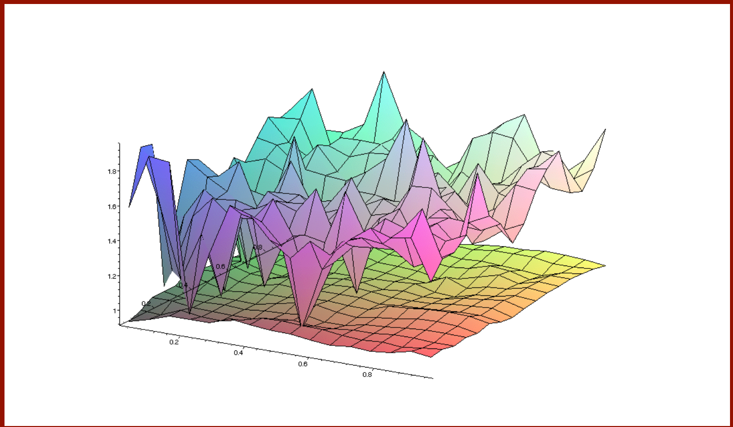
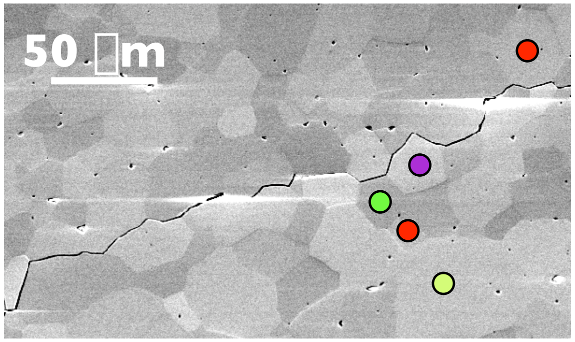


Motivating Physical Phenomena

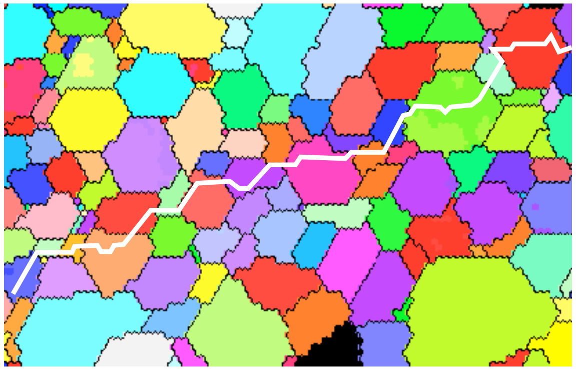
The performance of a polycrystalline material is influenced by the types of grain boundaries in the material and the way that they are connected.

Examples:

- Superconducting Critical Current Density
- Electromigration Damage Resistance
- Stress Corrosion Cracking
- Electrical activity
- Creep Behavior

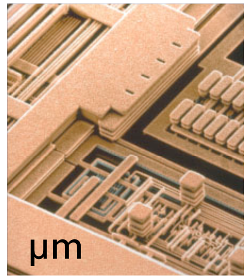


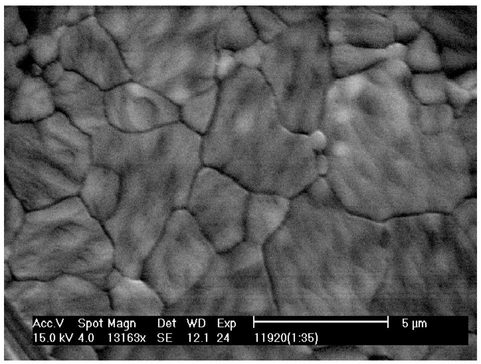
fracture follows grain boundaries



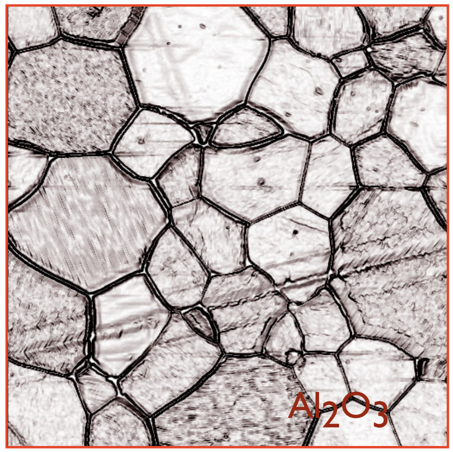
Viewpoint: Multiscale

- use and occurence





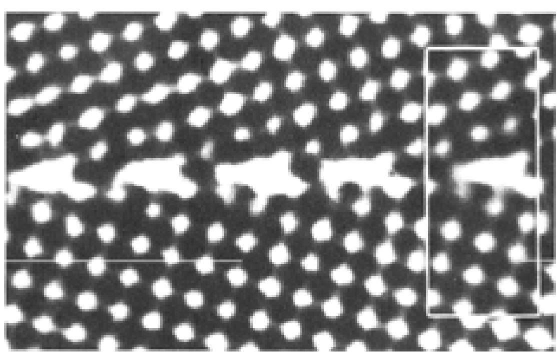
Al



100 µm

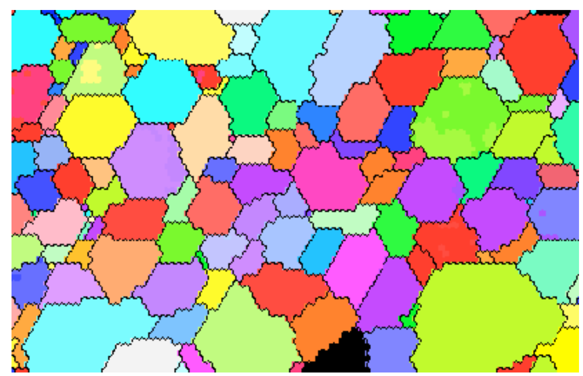
cm

- interrogation



TEM

or orientation imaging microscopy (shown on previous slide)



- theory and simulation

  atomic level

  embedded atom methods

  first principle computations

  mesoscale

  thermodynamics of surfaces (Mullins, Herring, et seq.)

  simulations via random methods (Monte Carlo or Potts, Anderson, Srolovitz, Grest & Sahni, et seq.)

  simulations via resolution of the time dependent equations of motion

  ensembles of grains

  theories of the statistics of grain growth (very large literature)

- rising role of automated data acquisition in materials science

  information arrives at a scale at which it can be acquired:

  typically a mesoscale

  here the scale of geometric and crystallographic information

  involves ingredients in relations rather than the desired quantities

- an integral and essential role for simulation and modeling — today's focus

Poster child for grain boundary engineering: Pb for batteries from Ontario Hydro

Changing the Grain Boundary Network Improves Performance

Both electrodes polarized at 200 mV for 12 days (70°C) in H_2SO_4.

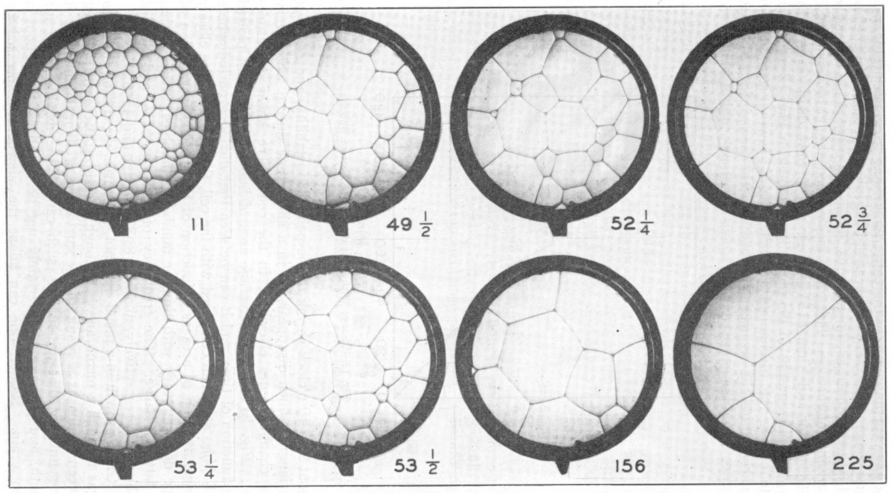
The as cast electrode disintegrated during the test.

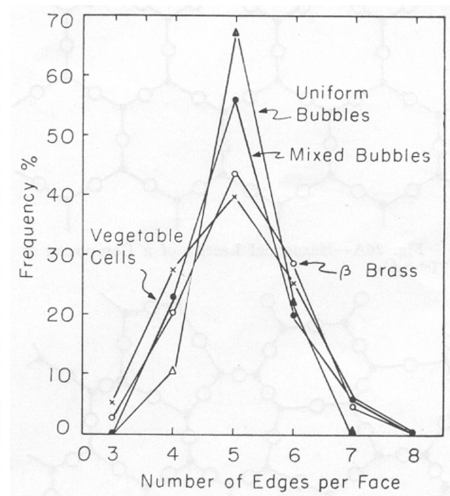
The GBE™ electrode maintained its integrity.

As cast = 10% special boundaries
GBE™ = 71% special boundaries

Lehockey, Palumbo, Lin, and Brennenstuhl, Met. Trans. 29A (1998) 387.

Are microstructures like soap froth?

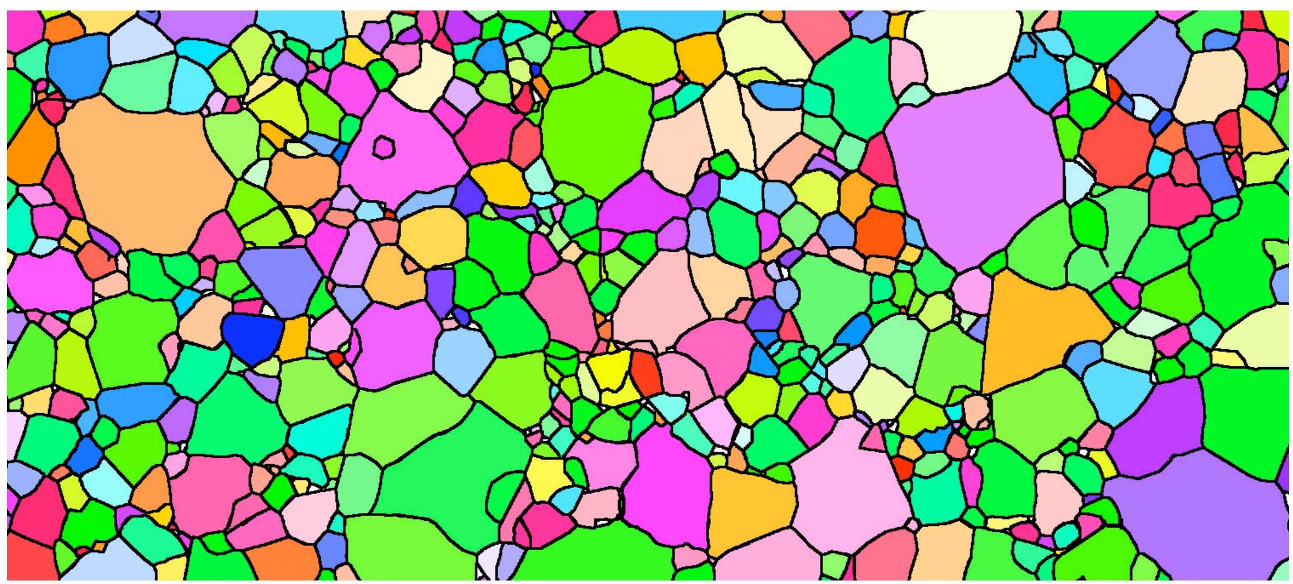




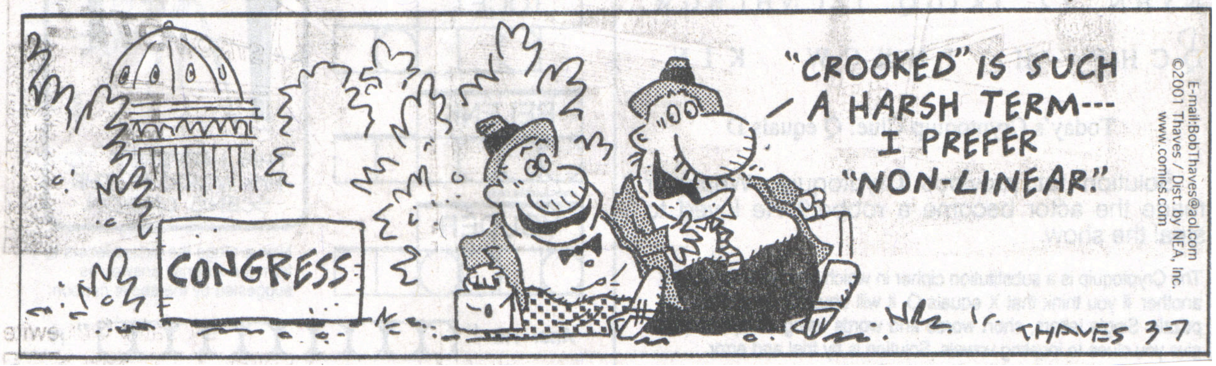
C.S. Smith, 1951
more alike than unlike

late stage MgO

very unlike
yet appearances can deceive

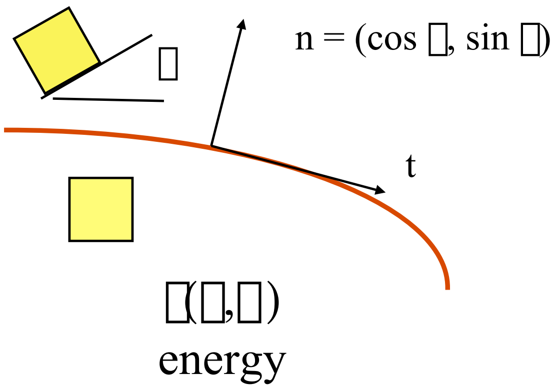


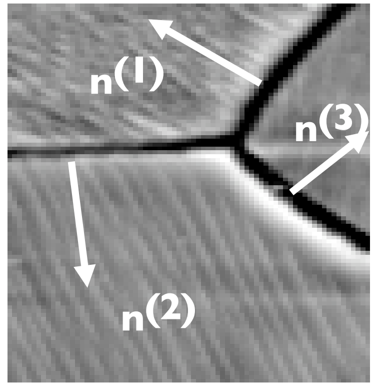
Frank and Ernest By Bob Thaves

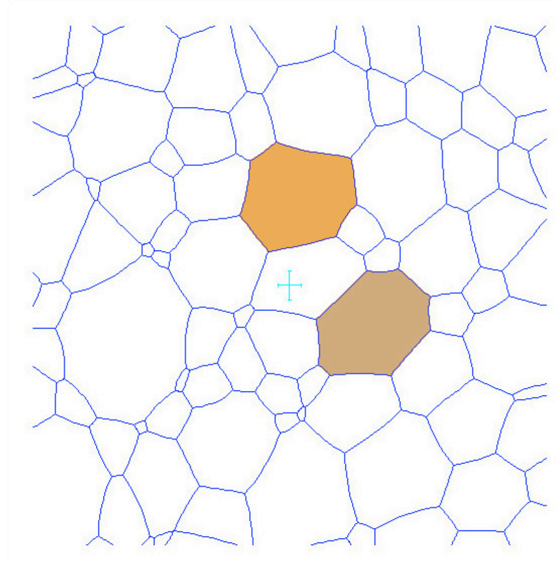


Grain Growth in 2D everything in 2D today

equilibrium theory







E total energy
□ gb energy
n normal
t tangent
□ angle of normal
□ misorientation
□ curvature of □

network of curves $\{ \square^{(i)} \}$ $\qquad E = \Sigma \int_{\square^{(i)}} \square \,|\, t \,|\, ds$

local equilibrium of network $\qquad \square E = 0$

□

$$\left(\frac{d^2\square}{d\square^2} + \square\right)\square = 0 \quad \text{on } \square^{(i)}$$

Herring Condition

$$\Sigma_{TJ}\left(\frac{\partial\square}{\partial\square} n + \square t\right) = 0 \quad \text{at TJ's}$$

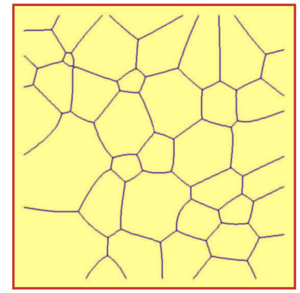
dynamics of grain growth Mullins

curvature driven growth dynamical problem:
must impose boundary conditions
use Herring Relation, the natural boundary condition for equilibrium

$$v_n = \mu\left(\frac{\partial^2\gamma}{\partial\theta^2} + \gamma\right)\kappa \quad on\ \Gamma^{(i)}$$

$$\sum_{TJ}\left(\frac{\partial\gamma}{\partial\theta}n + \gamma t\right) = 0 \quad at\ TJ's$$

$\mu > 0$ mobility
different from tension



$$E = \sum \int_{\Gamma^{(i)}} \gamma|t|ds$$

$$\frac{d}{dt}E = -\sum \int_{\Gamma^{(i)}} \frac{1}{\mu}(v_n)^2|t|ds + \sum v \cdot \sum_{TJ}\left(\frac{\partial\gamma}{\partial\theta}n + \gamma t\right)$$

$$= -\sum \int_{\Gamma^{(i)}} \frac{1}{\mu}(v_n)^2|t|ds < 0$$

vanishes when
Herring holds

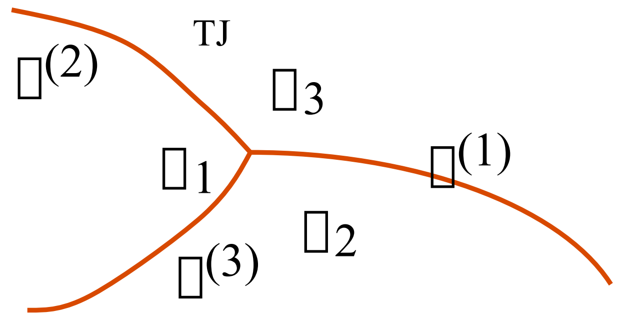
dynamical system is
dissipative

curvature driven growth
Herring Relation at TJ's → dissipative system → trend to equilibrium
tends to equilibrium but still 'metastable'

- When □ = constant, Herring condition means segments meet at 2□/3.

When □ = □(□), Herring condition is 'Young's Law'

$$\frac{\gamma(\alpha_1)}{sin(\psi_1)} = \frac{\gamma(\alpha_2)}{sin(\psi_2)} = \frac{\gamma(\alpha_3)}{sin(\psi_3)}$$

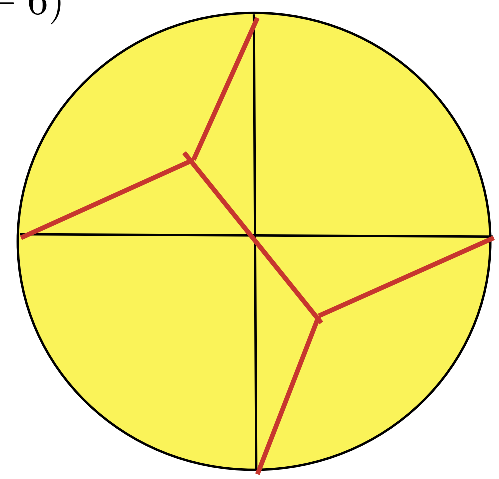


- Mullins – Von Neumann n – 6 rule

□ = constant, Herring condition

$$\frac{dA}{dt} = \alpha(n-6)$$

large grains grow and small grains shrink

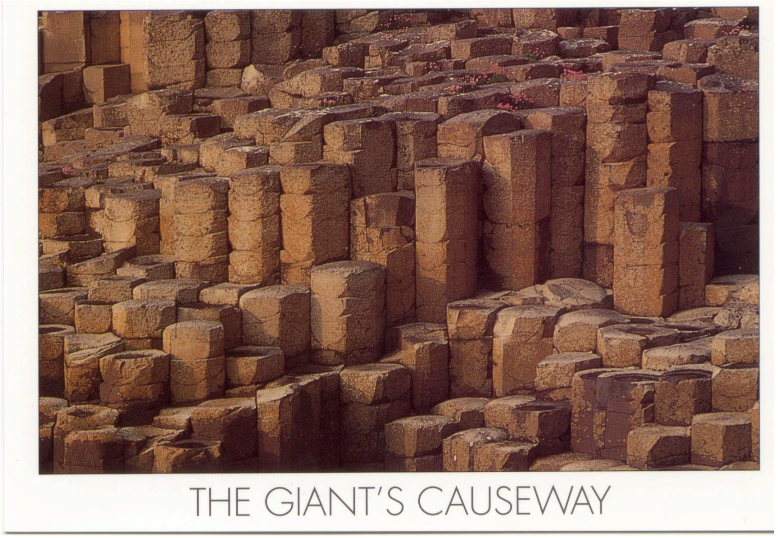


- Typically triple junctions are stable

- Much analysis related to curve shortening, approximations of multiphase boundaries (Cahn Hilliard, Allen Cahn, ...), and Wulff-type problems (Taylor, Fonseca, ...)

- Direct precursors:
  - Bronsard & Reitich short time local existence: system satisfies complementing conditions, very important!
  - K & Liu long time existence close starting near a stationary solution

excursion



Giant's Causeway (Ireland) probably cleavage/fracture

suggests interesting example
based on Mullins-Von Neumann n–6 rule:
deform curves conserving area and HC
$< A > \; = \text{constant}$
although system in motion

E = min –> no interfaces

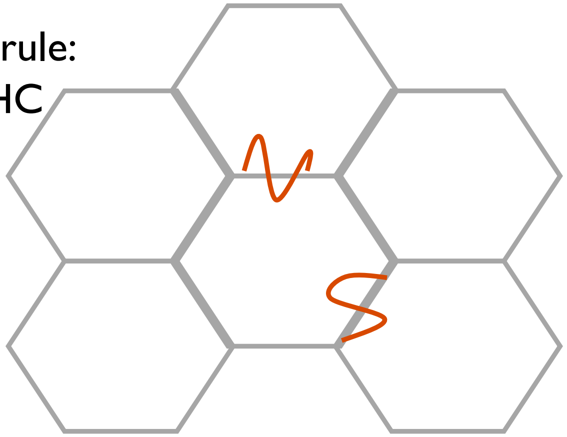


illustration of metastability
of grain growth system

Simulation and interpretation: strategy

- must fulfill two requirements
  accurate: fidelity to Mullins-Herring
  statistical significance: very large scale

- interpret solution through statistics - only possibility

- derive coarse grained descriptions of the simulation useful for prediction
  equation satisfied by distribution function (histograms of relative area)
  system of equations satisfied by partial distributions functions (by number of grain facets), which we term a master equation model

- however other issues also intervene (will return to this): we will have some dynamic statistics but we need to ascertain their 'information' content

- identify the material - reconstruct the energy - from the simulation?
  tantalizing new features

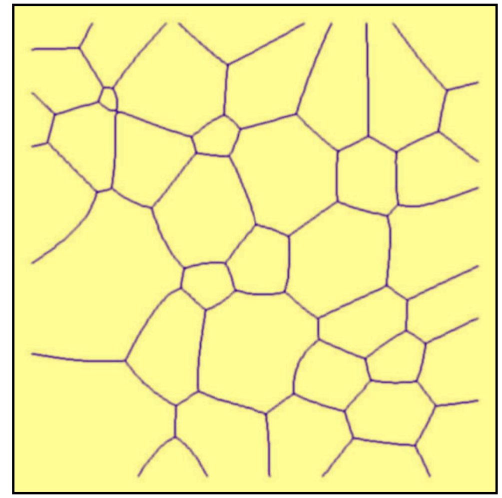
simulation

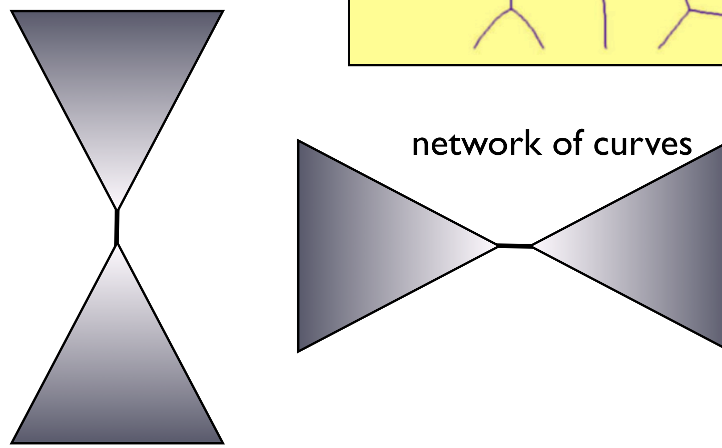
calibration $\gamma = 1$ = 1

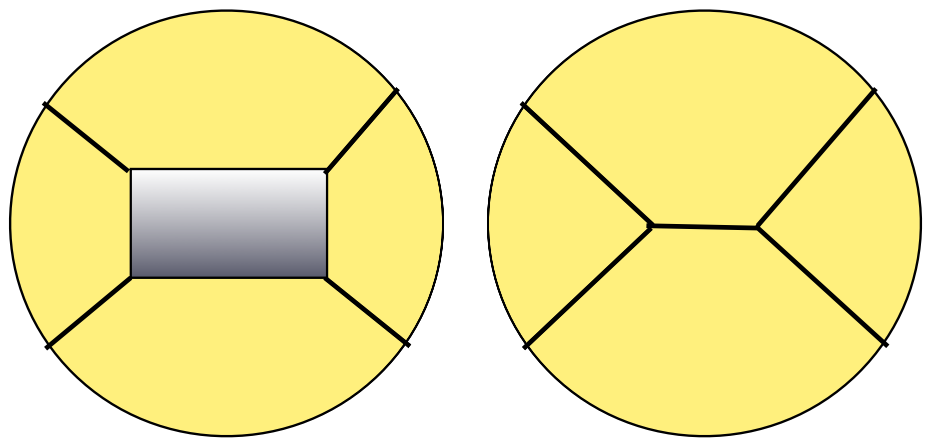
evolve as network of curves:
data structure of inferior dimension
present data structure up to 50,000 grains
evolve to 1/4 starting number (typically)
and 1600 time steps (typically)

- strategy:
  - discretize energy with evolution
  - designed to maximize dissipation
  - maintain Herring BC
  - agrees with PDE to 2nd order in space

- critical events:
  - loss of facet (facet flipping)
  - loss of small grain
  - rules based on results of Monte Carlo
  - MD simulations and geometry

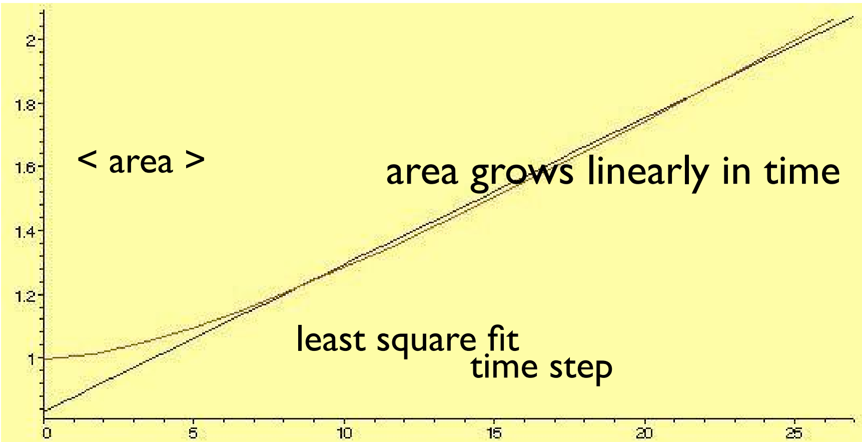






First look at results

general features and diagnostics

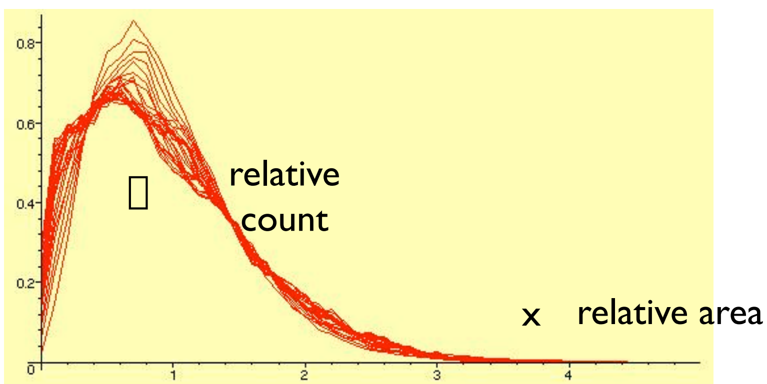


diagnostics

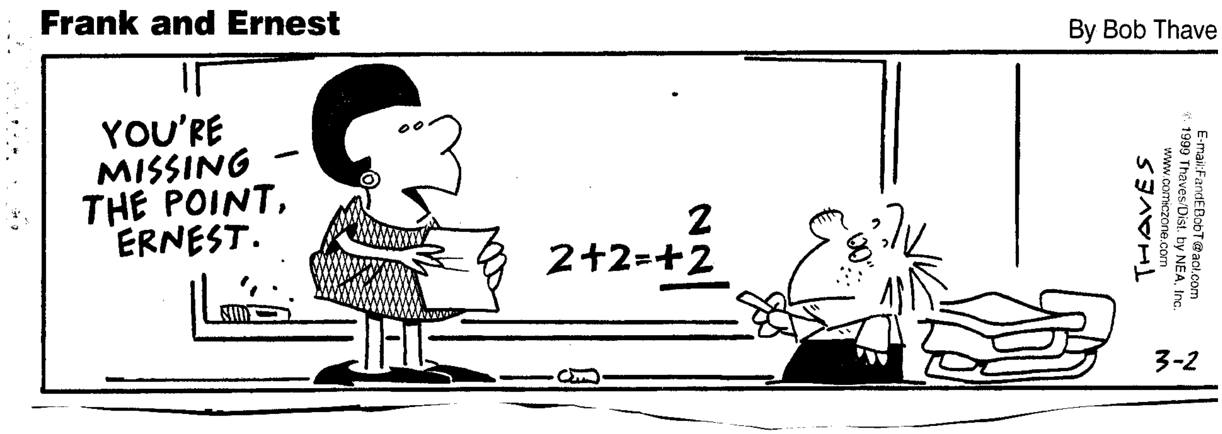
area: grows linearly in time
n-6 rule: satisfied for individual grains
not subject to critical events
curvature: second order accurate with
respect to spatial discretization

(boundary condition is very important)

25,000 grains
histograms at time steps
1 - 16 x 1000



surprisingly high
degree of self-similarity
robust across sample size
and system size



I hope that I shall not miss the point

relative area histograms and their interpretation

interpret simulation: find an equation histograms satisfy
simulated histogram is self similar over a long range but ultimately is dynamic quantity

f(Area,t) = g(Area/t) self similar form

try to find by inverse methods
many theories about equations for , generally have form:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x}(\psi' \rho)$$

possibly nonlinear transport

Hillert
Mullins
Ryum & Hunderi

$$\frac{\partial \rho}{\partial t} = \sigma \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial}{\partial x}(\psi' \rho)$$

diffusion or Fokker-Planck

Louat

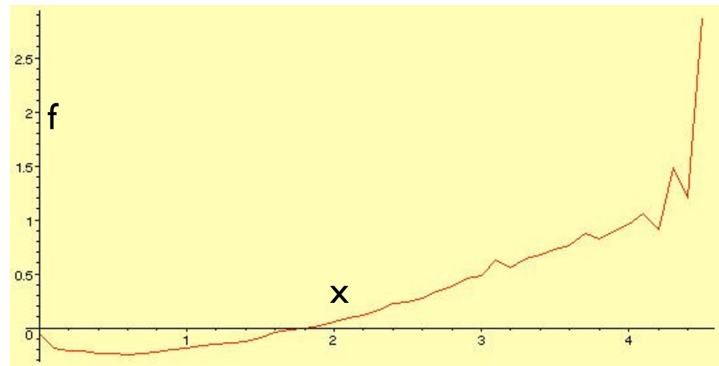
Atkinson no known physical reason for
Mullins cannot have origins at molecular time scales

but information loss/disorder can give rise to entropy
entropy in an equation is manifested by diffusion
…know from many directions

will look for F-P equation

inverse method to discover Fokker-Planck

a. identify an equilibrium solution



equilibrium solution □

shape of potential f

$$\sigma \frac{\partial^2}{\partial x^2}\phi + \frac{\partial}{\partial x}(b\phi) = 0 \quad x > 0$$

$$\Rightarrow$$

$$\phi(x) = \frac{1}{Z} exp(-\psi(x)/\sigma) \quad with\ b = \psi'$$

can determine a pattern or shape

$$f(x) = -log\ \phi(x) \quad and \quad \psi(x) = \sigma f(x)$$

b. find diffusion coefficient
recall how □(x,t) determined

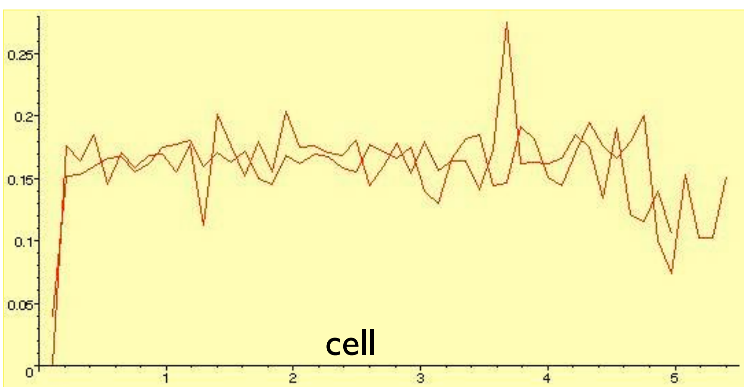
can regard the information that gives the relative histograms as data for determining the equation

Δt

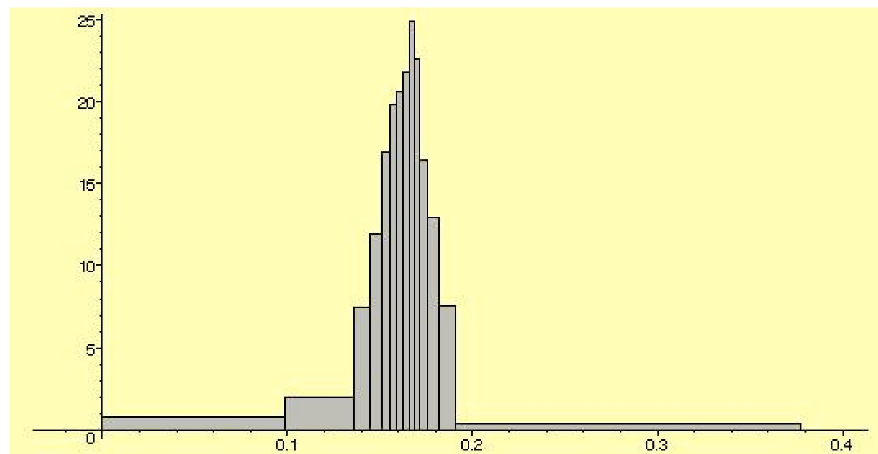
diffusion coefficient = $\sigma = \frac{1}{2}\,\frac{v}{\Delta t} = 0.17$

and $\Delta t = h^2$ by scaling

v



variances in cells at several times

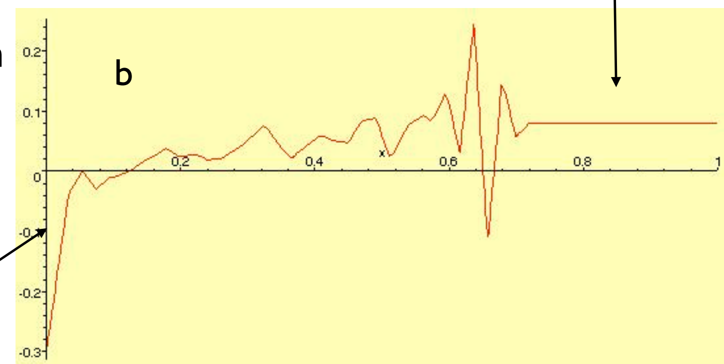


histogram of empirical variances (diff coeffs) over simulation: **nearly constant** final step:

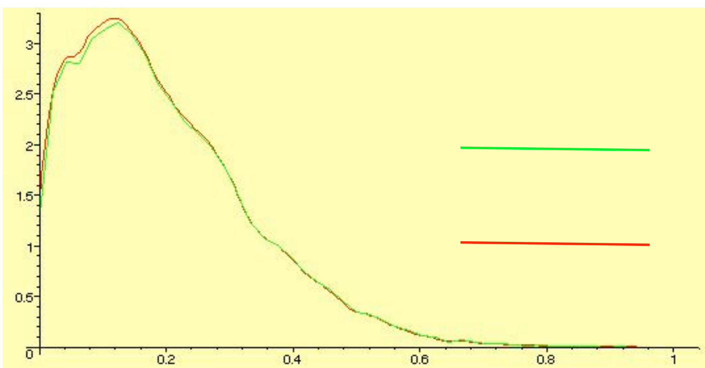
for derived □ and □ solve the F-P equation
for time = transient time

(unable to significantly vary initial configurations

but …)



approximate b
to solve F-P
arrows point to deviations
from the differenced □

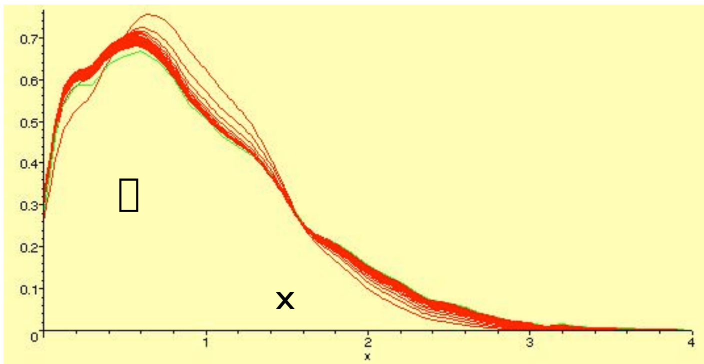


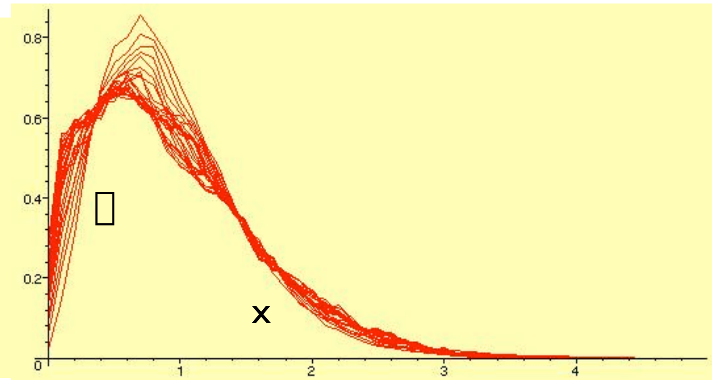
□
from simulation

□
from solving F-P

distribution

this checks that we obtain
the correct equilibrium state

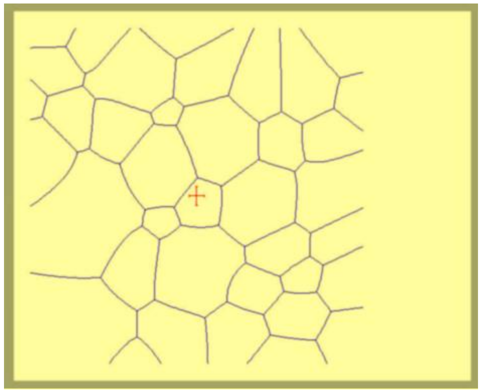




solution of Fokker-Planck simulation

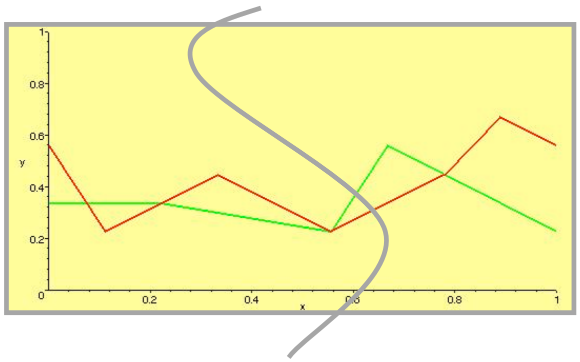
grain boundary simulation histograms

have managed to approximately capture the transient in fact, there are other considerations



large scale simulation

computation at 'microscale'
need to interpret

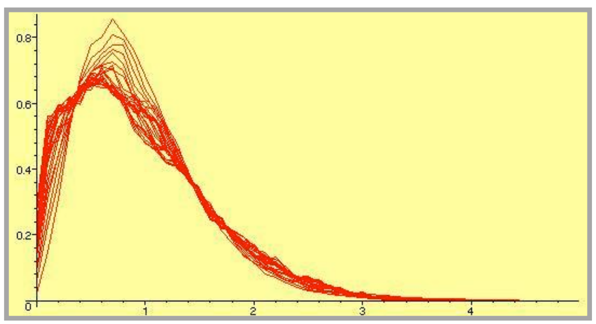


master equation description

'mesoscale'
grain trajectories: Mullins von Neumann n – 6 rule

$$\frac{dA}{dt} = \alpha(n-6)$$

interrupted by random edge loss/gain or grain disappearance



relative area histograms

one point statistics
suggests Fokker-Planck

Interpretation of system:
at intermediate scale by master equation model

$F_n(x,t)$ = *density of n-facet grains with area x at time t*

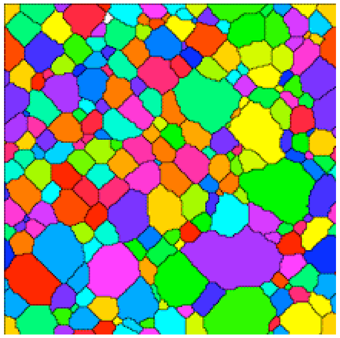
$$\frac{\partial}{\partial t}F_n(x,t) + c(n-6)\frac{\partial}{\partial x}F_n(x,t) = I_n(x,t)$$
$$F_n(N_a,t) = 0, \quad n = 3,4,5 \quad and \quad F_n(0,t) = 0 \quad n = 6,...$$
$$I_n = -p_nF_n + p_{n+1}F_{n+1} - (q_n + r_n)F_n + q_{n+1}F_{n+1} - r_{n-1}F_{n-1}$$

$p_n(x,t)$ = *facet loss from grain disappearance (depends on* $F_n(0,t)$*)*
$q_n(x)$ = *facet loss from grain boundary flipping*
$r_n(x)$ = *facet gain from grain boundary flipping*

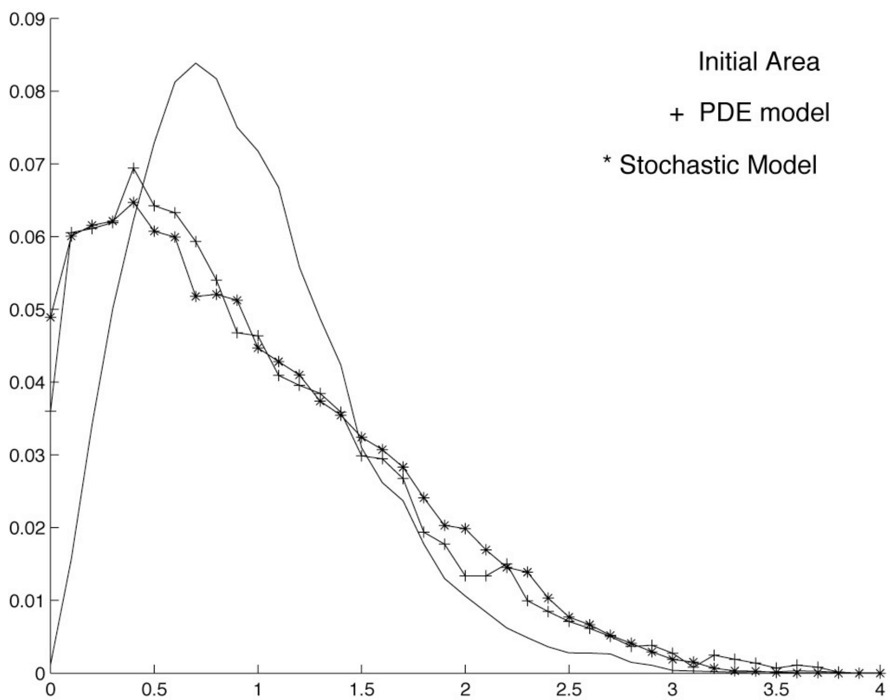
determine from the the first few time steps of the simulation tend to vary with 1/< area >

earlier work by
Fradkov
Flyvberg

other descriptions:
Monte Carlo/Potts models
vertex models (also Henseler, Niethammer, Otto)



preliminary results

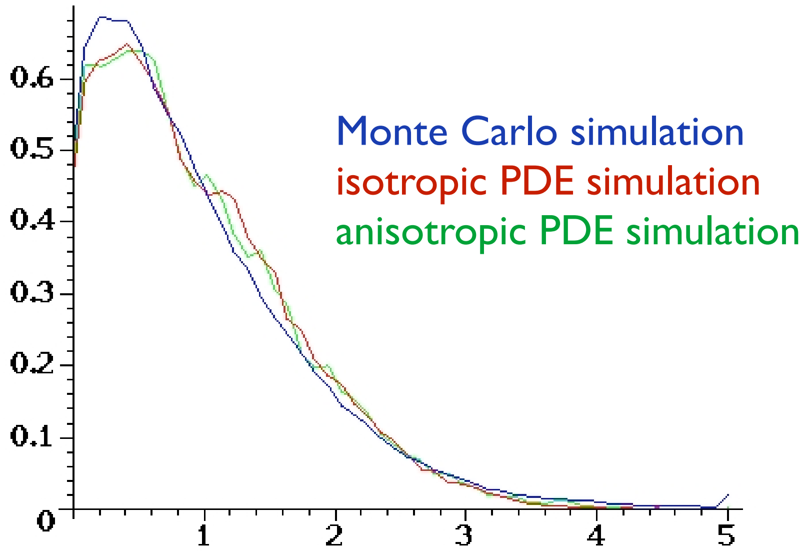


area distributions

master equations give good description of stationary distribution

a few statistics from the initial time period of the evolution, determines stationary distribution:
so in some fashion
can predict the stationary distribution but do not understand how to unravel this

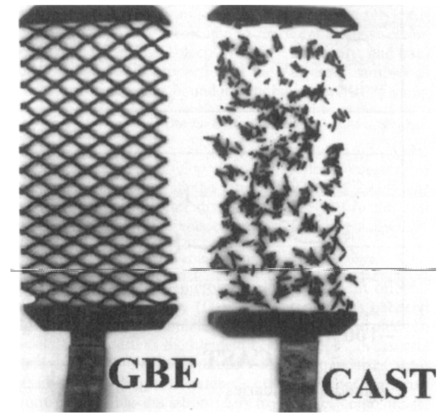
only one difficulty

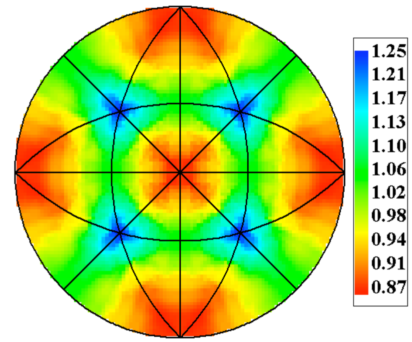


- stationary relative area histogram is extremely robust
- relative area histograms do not distinguish the energy (or mobility)

Crucial role of anisotropy

is anisotropy important?





occurence

Interrupted grain growth experiment on Al specimen to monitor change in l(Δg,n) (relative normal averaged over misorientations) during growth.

fracture toughness optimized by specific arrangements of grains

corrosion resistance depends on high fraction of low energy boundaries

what is the ideal distribution of boundaries in a well annealed sample?

all boundaries minimum energy?

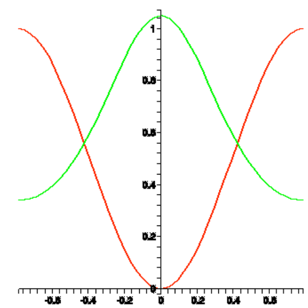
cannot satisfy Herring condition

independent trials with respect to energy?

for $\gamma = \gamma(\alpha), \ \alpha \ = misorientation$

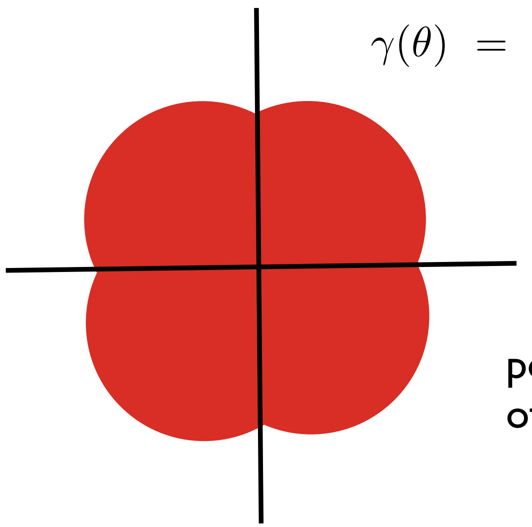
$$\rho(\alpha) = e^{k\gamma(\alpha)}/Z$$

can verify this and confirm work of Holm et al., Upmanyu et al.

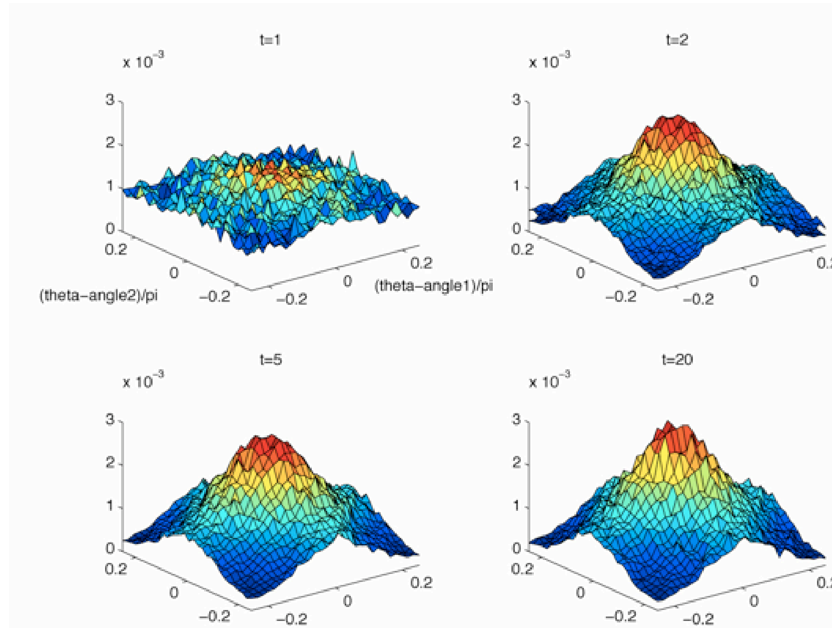


energy depends also on normal
our's is the first (perhaps the only) with ability
to execute large scale simulations with $\gamma = \gamma(\theta, \alpha)$

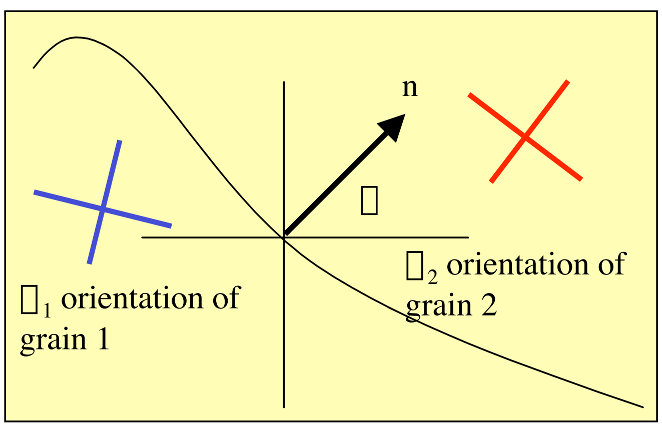
$$\gamma(\theta) = 1 + \epsilon sin^2(2\theta)$$



polar plot
of energy



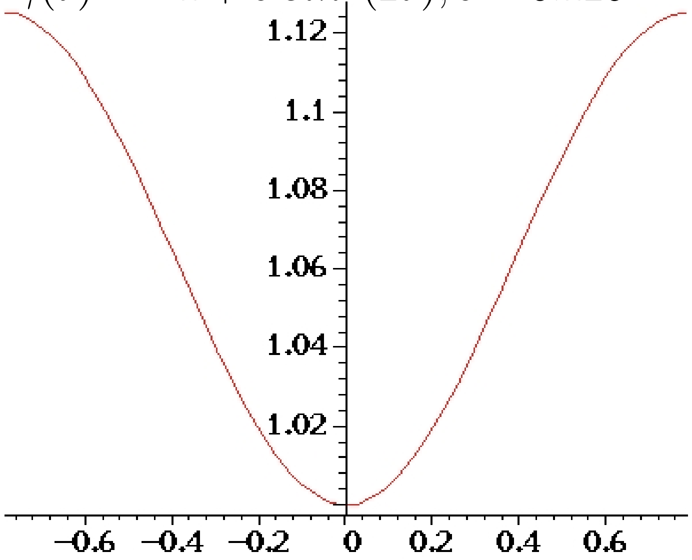
simulation shows development of a structure
where low energy boundaries predominate



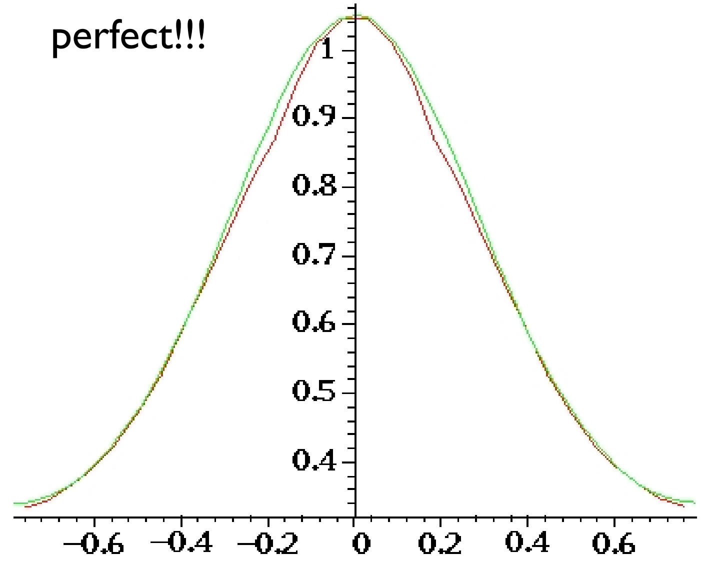
approximate grain boundary energy as average
of two surface energies as seen in experiments
on MgO:

$$\gamma(\theta; \omega_1, \omega_2) = 1 + \epsilon(sin^2(2(\theta - \omega_1) + sin^2(2(\theta - \omega_2))$$

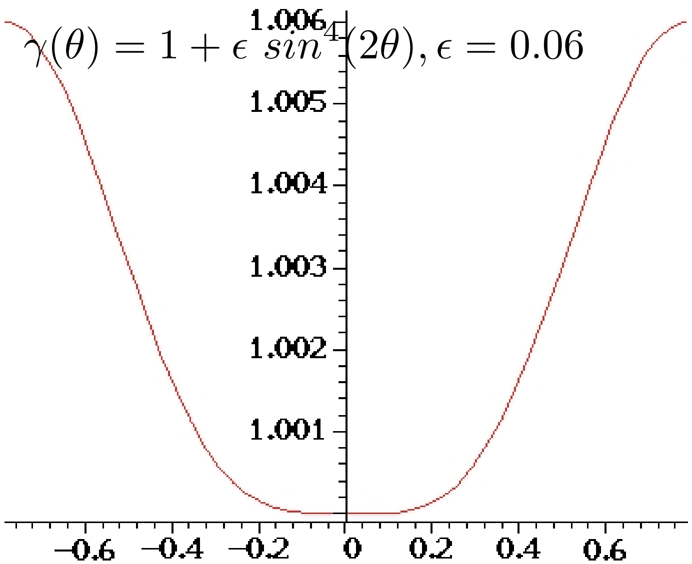
$\gamma(\theta) \; = \; 1 + \epsilon \; sin^2(2\theta), \epsilon = 0.125$



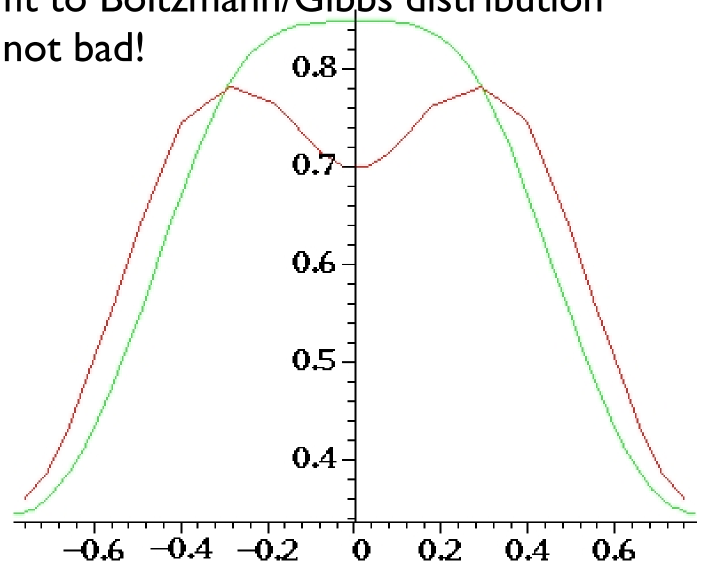
fit to Boltzmann/Gibbs distribution
perfect!!!

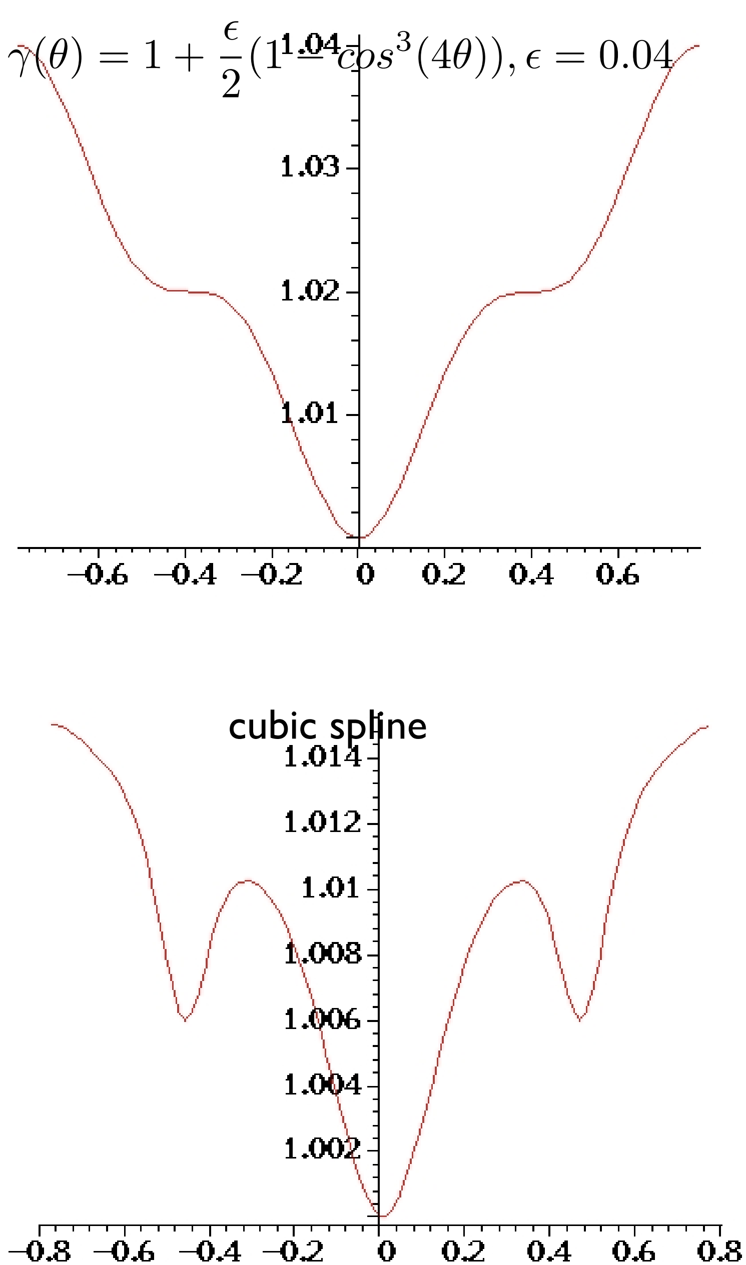


$\gamma(\theta) = 1 + \epsilon \; sin^4(2\theta), \epsilon = 0.06$

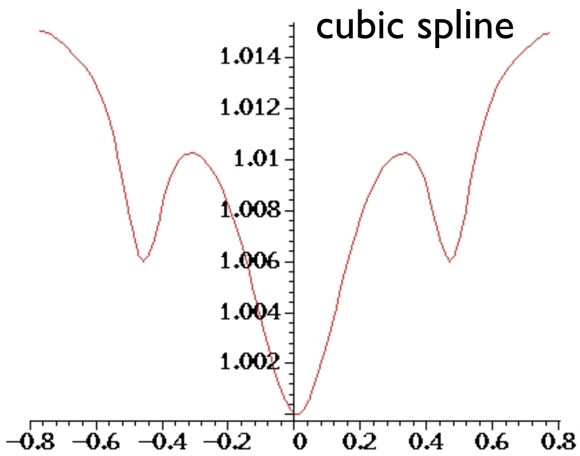


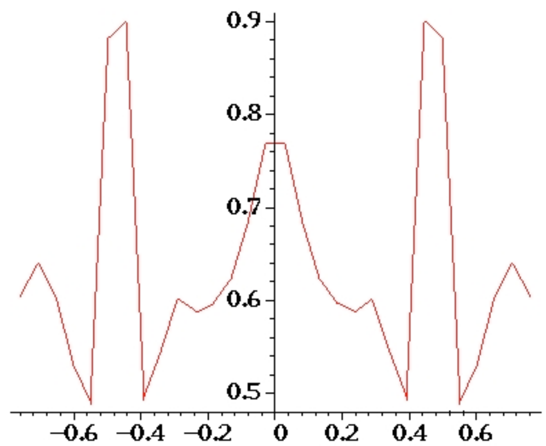
fit to Boltzmann/Gibbs distribution
not bad!





$\gamma(\theta) = 1 + \frac{\epsilon}{2}(1 - cos^3(4\theta)), \epsilon = 0.04$
fit to Boltzmann/Gibbs distribution
cannot fit
cubic spline
fit to Boltzmann/Gibbs distribution
impossible





- grain boundary character distribution depends on anisotropy
- simple cases may be interpreted as independent trials with respect to the Boltzmann/Gibbs distribution of the energy
- but all of our data for all of our materials show that distribution is not the Boltzmann/Gibbs
- complex energy landscape enables solution to remain in a region of phase space from which equilibrium is inaccessible
- understanding this issue will be a major goal of the project!