Microstructures, Coarsening, Entropy and the Grain Boundary Character Distribution

Yekaterina Epshteyn, The University of Utah

Mesoscale and Continuum Scale Modeling of
Materials Defects
IPAM, November 13-16 2012

Collaborators

- **Katayun Barmak (Material Science), Columbia University**
- **Eva Eggeling, Fraunhofer, Graz**
- **Maria Emelianenko, George Mason University**
- **David Kinderlehrer, Carnegie Mellon University**
- **Richard Sharp, Carnegie Mellon University**
- **Shlomo Ta'asan, Carnegie Mellon University**

Introduction: Challenges in understanding polycrystalline microstructure

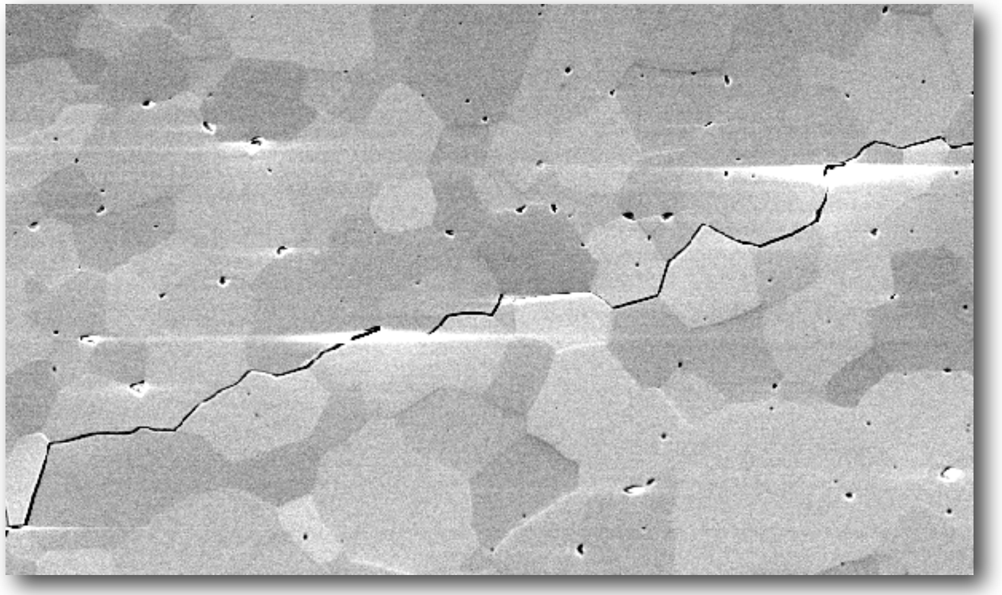
Examples of Polycrystalline Materials: Metals, Ceramics

A central problem in materials science is *the understanding and control of microstructure: ensemble of grains that comprise polycrystalline materials.*

Performance is influenced by the types of grain boundaries in the material and the way that they are connected.

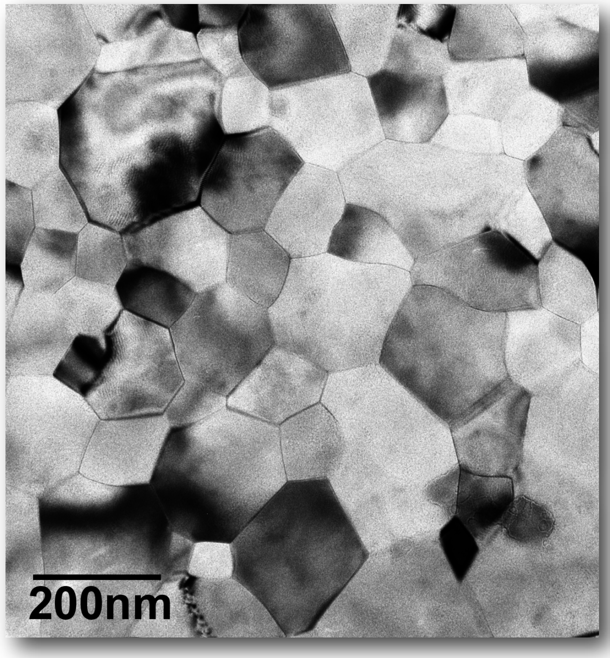
Structure sensitive properties:

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



fracture follows boundaries

Coarsening Networks, Processes: Bubbles in the Beer, Coalescence of Stars into Galaxies
- smaller ones disappear and the average size of the object increases over time



Al thin film
Barmak

Prologue

despite large phenomenological literature and variety of experimental and computational techniques and antiquity of the subject
➥ little is known about the coarsening of networks

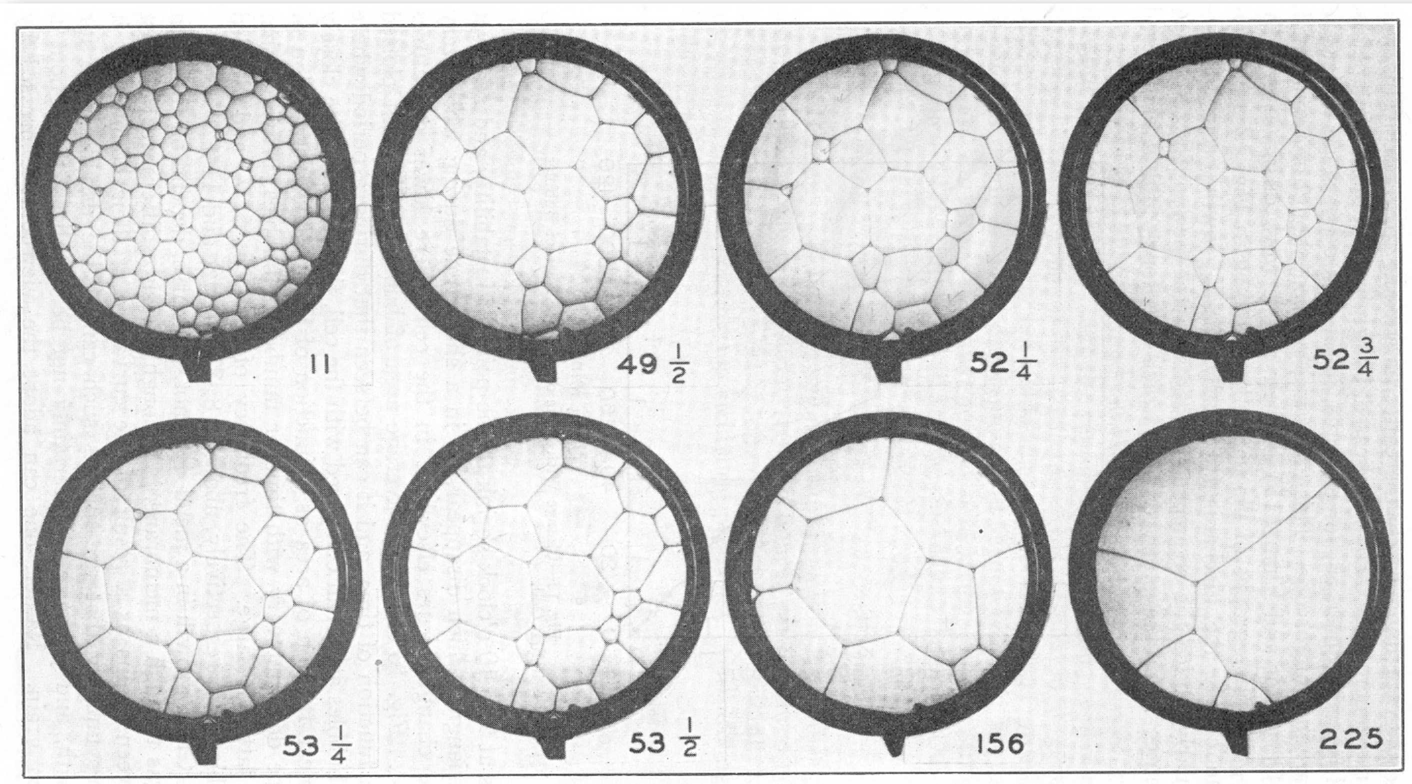
focus is simulation and modeling a large metastable system:

- **competition of growth and space filling**
- **role of interfacial energy**

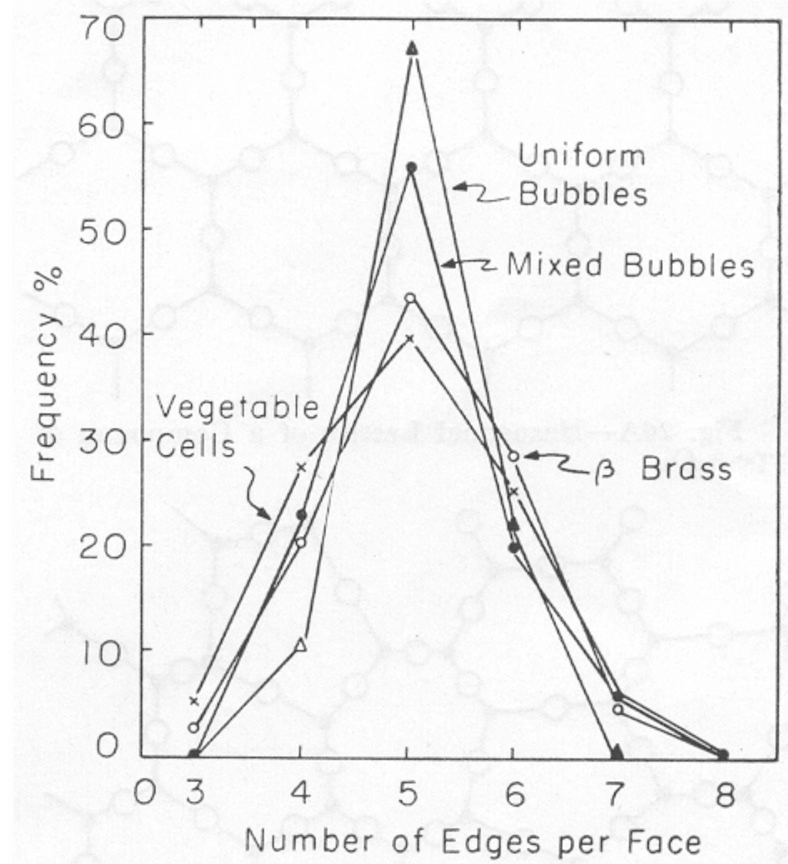
- **what is a stable property?**
- **can it be identified, i.e., as a recognizable stochastic process?**

simulation offers important opportunities

- Early questions: Are microstructures like soap froth? Are all natural cellular networks alike?
- Study geometrical features of networks

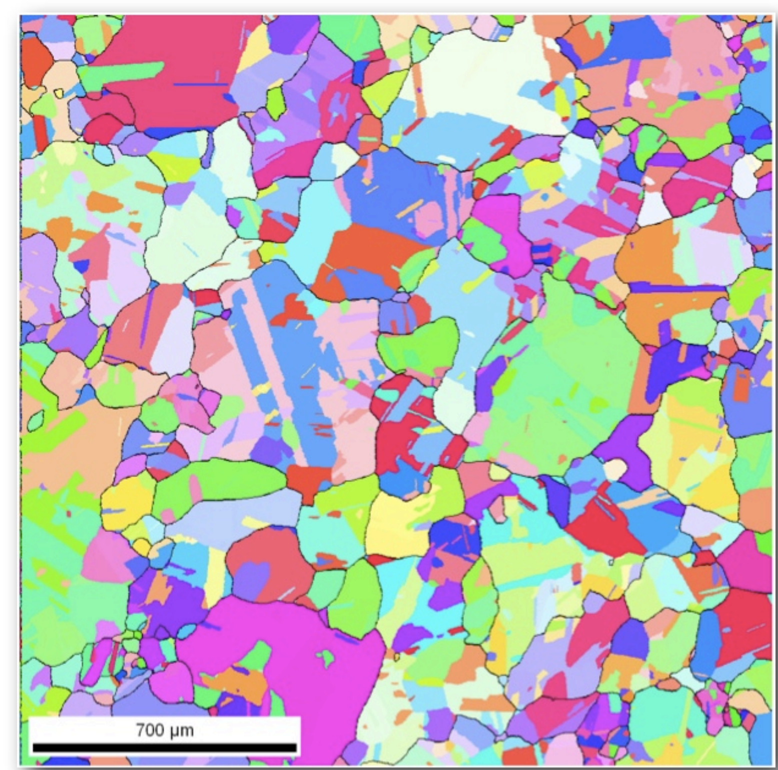


Soap froth



C.S. Smith, 1951 more alike than unlike (Le Caer's Law)

Ni
unlike soap froth
yet appearances
can deceive
but maybe they don't

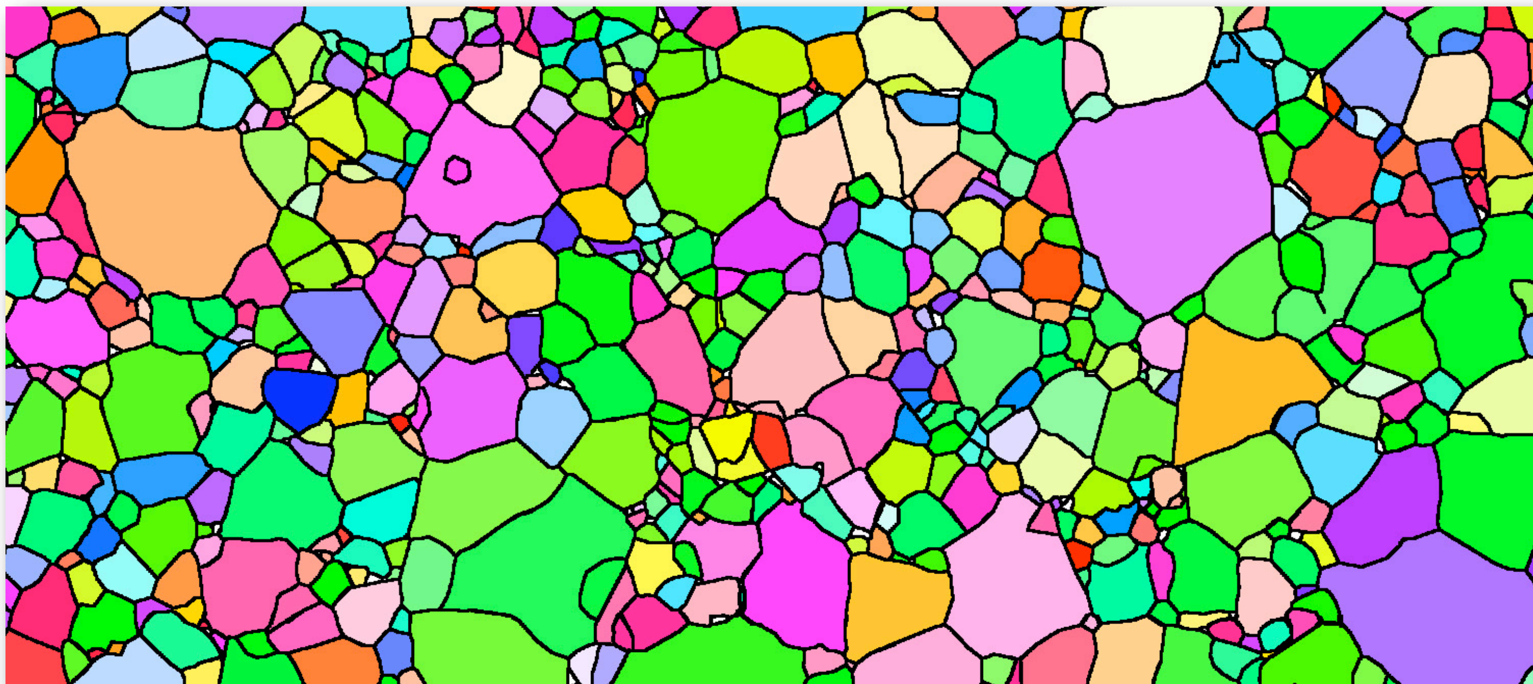


Motivation: Orientation Imaging Microscopy (OIM)

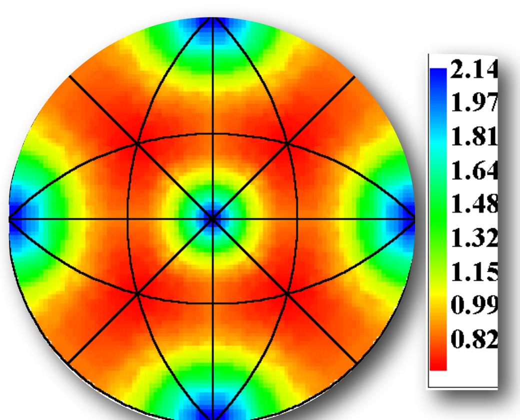
Why now:

OIM: orientation imaging microscopy

automated data acquisition (for texture) now available!



OIM scan
late stage MgO
Rohrer



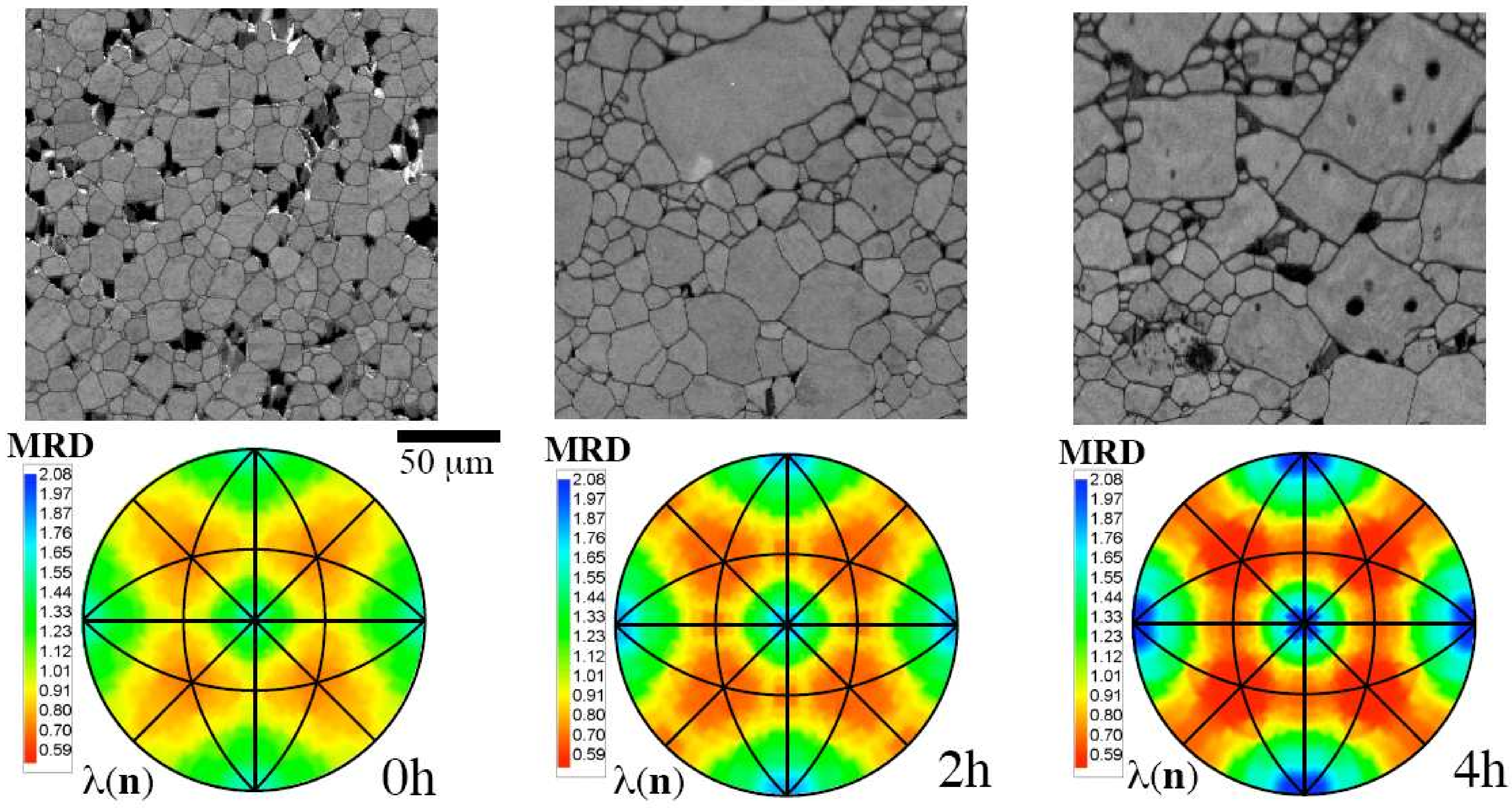
grain orientations or grain boundary orientations: color coded by frequency on a 'pole figure' depicts a particular sample

But: difficult to form a predictive quantitative theory

Opportunity for the simulation and analysis?

Motivation: Grain Boundary Orientations

Experiment: evolution of Grain boundary character distribution (GBCD)
GBCD = relative areas of grain boundaries sorted by misorientation angles and normal



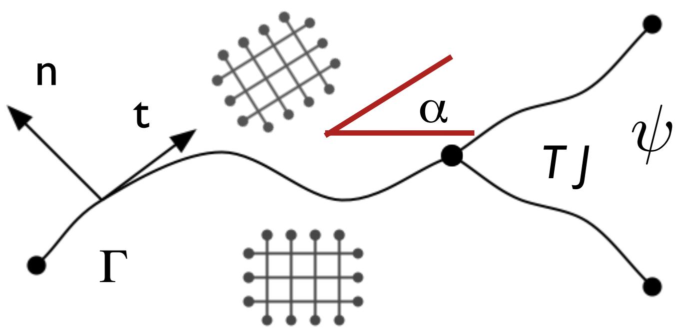
Gorzkowski et al. Zeitschrift fur Metallkunde, 96 (2005) 207.

$Pb(Mg_{1/3}Nb_{2/3})O_3$ – *35* $PbTiO_3$

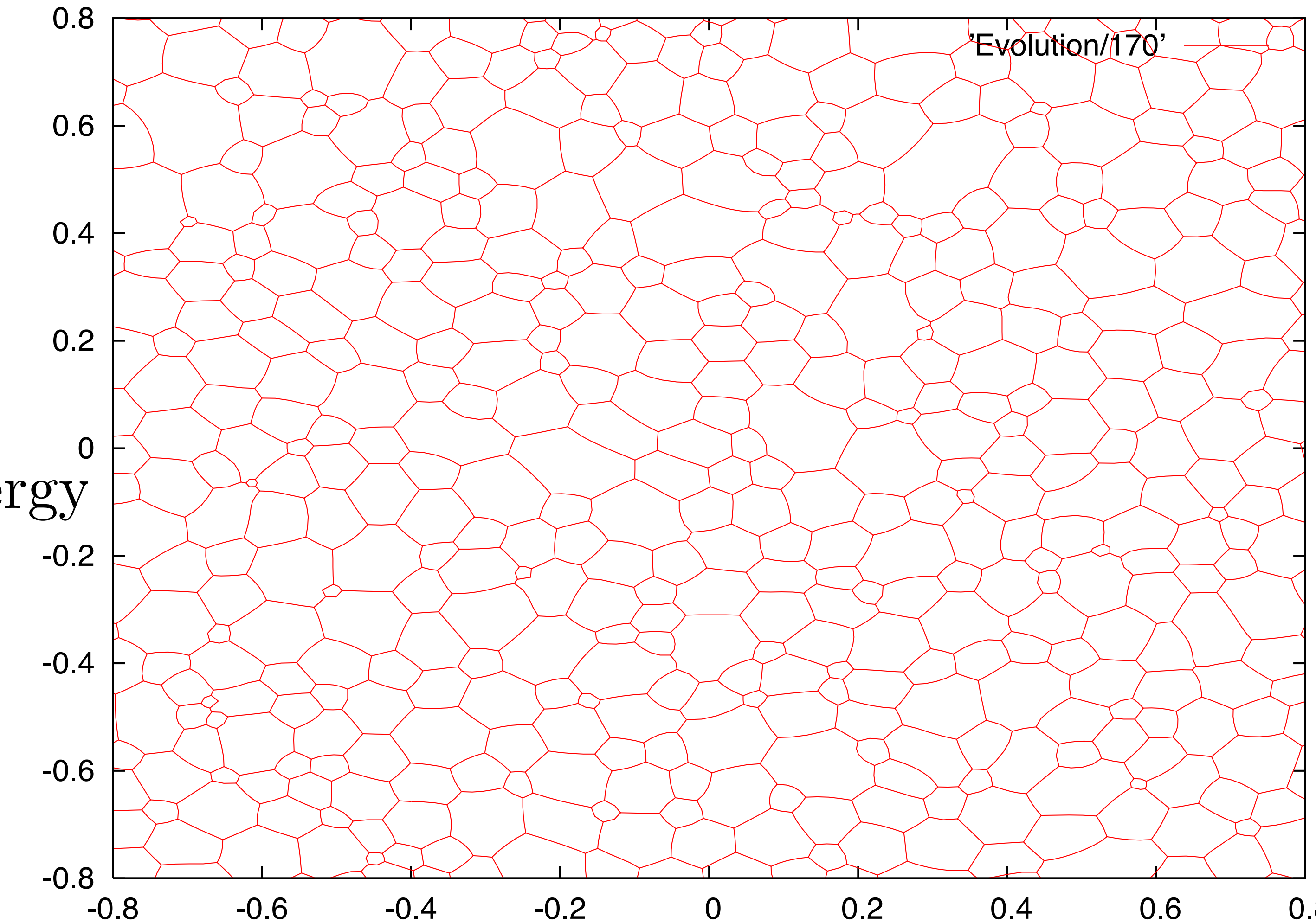
- **local thermodynamics**

  curvature driven growth

$$n = (\cos\theta, \sin\theta)$$



$$\psi(\theta,\alpha) = \text{GB energy}$$



$$v_n = \text{normal velocity}$$

$$\kappa = \text{curvature of } \Gamma$$

$$v_n = (\psi_{\theta\theta} + \psi)\kappa \text{ on } \Gamma$$ **Mullins Equation**

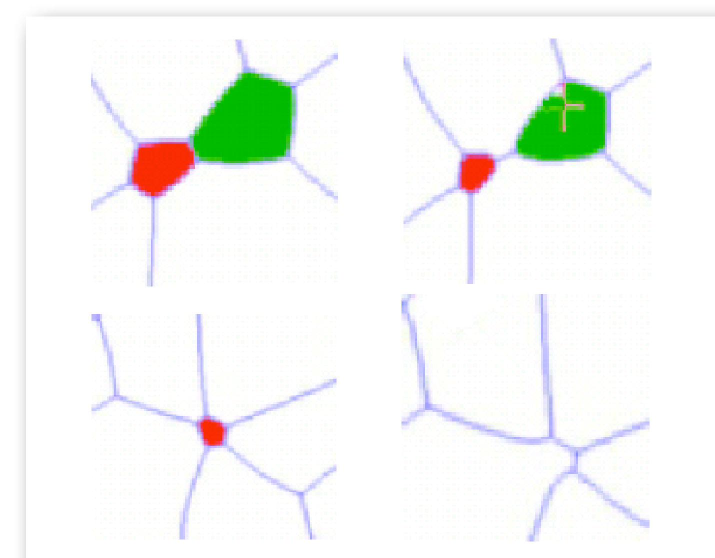
$$\sum_{TJ} (\psi_\theta n + \psi t) = 0 \text{ at TJ's}$$ **Herring Condition**

- **space filling** **constraint**

  critical events

  facet interchange

  grain deletion



Coarsening Cellular Networks - Dissipative System

Total Energy

$$E = \sum_{\Gamma} \int_{\Gamma} \psi(\theta, \alpha)|t|ds$$

Dissipation

$$\begin{aligned} \frac{dE}{dt} &= -\sum_{\Gamma} \int_{\Gamma} v_n^2 ds + \sum_{\{TJ\}} v \cdot \sum_{TJ} (\psi_\theta n + \psi t) \\ &\leqq 0 \end{aligned}$$

Local dissipation equation (no critical events)

$$\sum_{\Gamma} \int_0^{\tau} \int_{\Gamma} v_n^2 ds dt + E(\tau) = E(0)$$

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Coarsening Cellular Networks: 2D Simulation and Experiment

Anisotropic Evolution of Large Metastable Network:

- ***Energy cost tends to reduce the amount of interface in the configuration***
- ***Available space must be filled***
- ***Energy decreases, cells increase in size and small cells and interfaces tend to be eliminated to maintain space filling constraints***

2D Simulations

CoPt thin film (Barmak)

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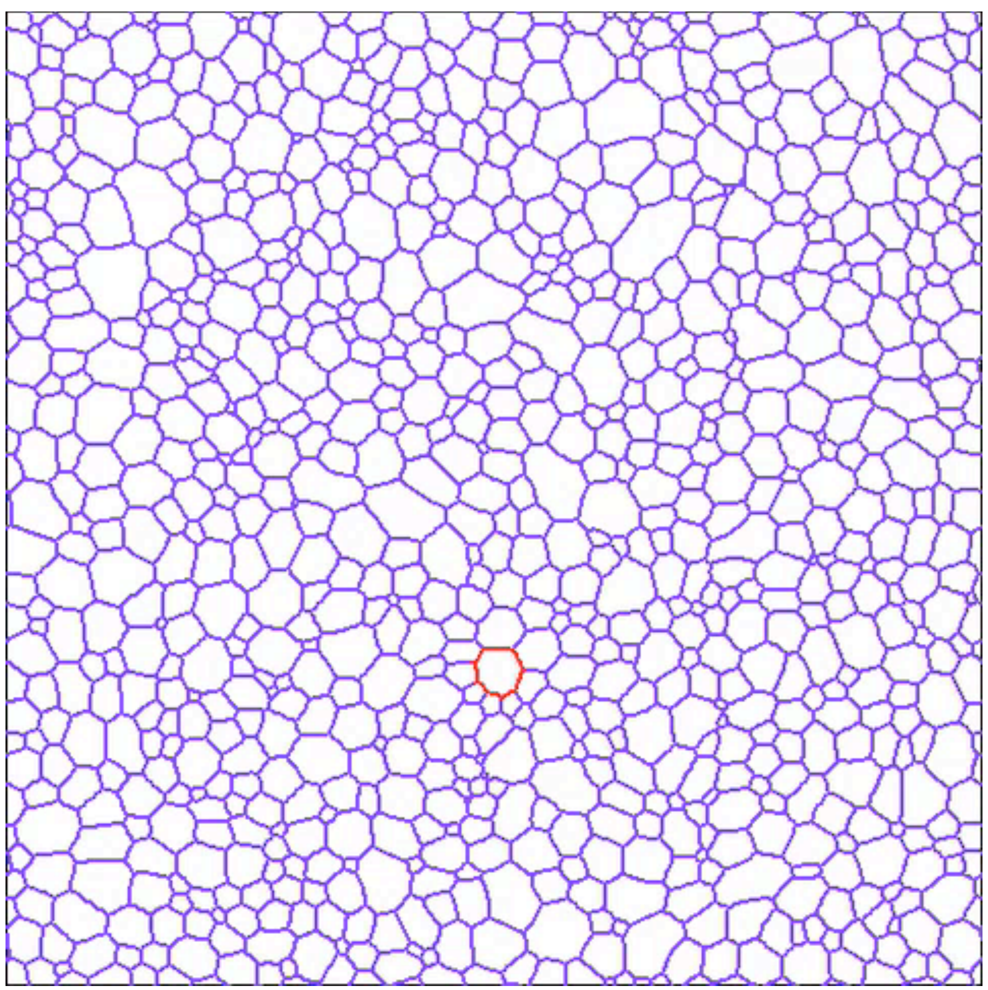
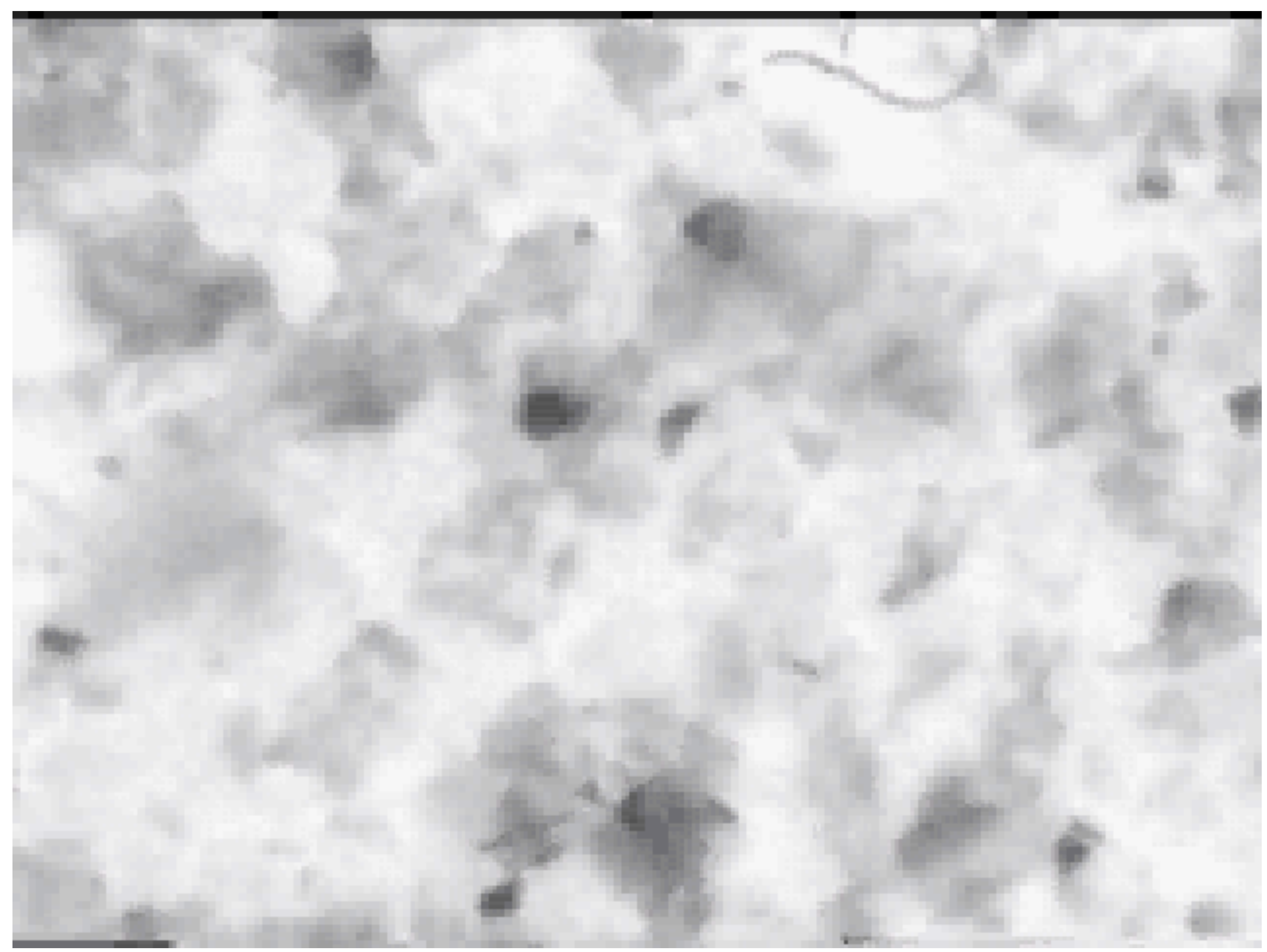


2D Simulations



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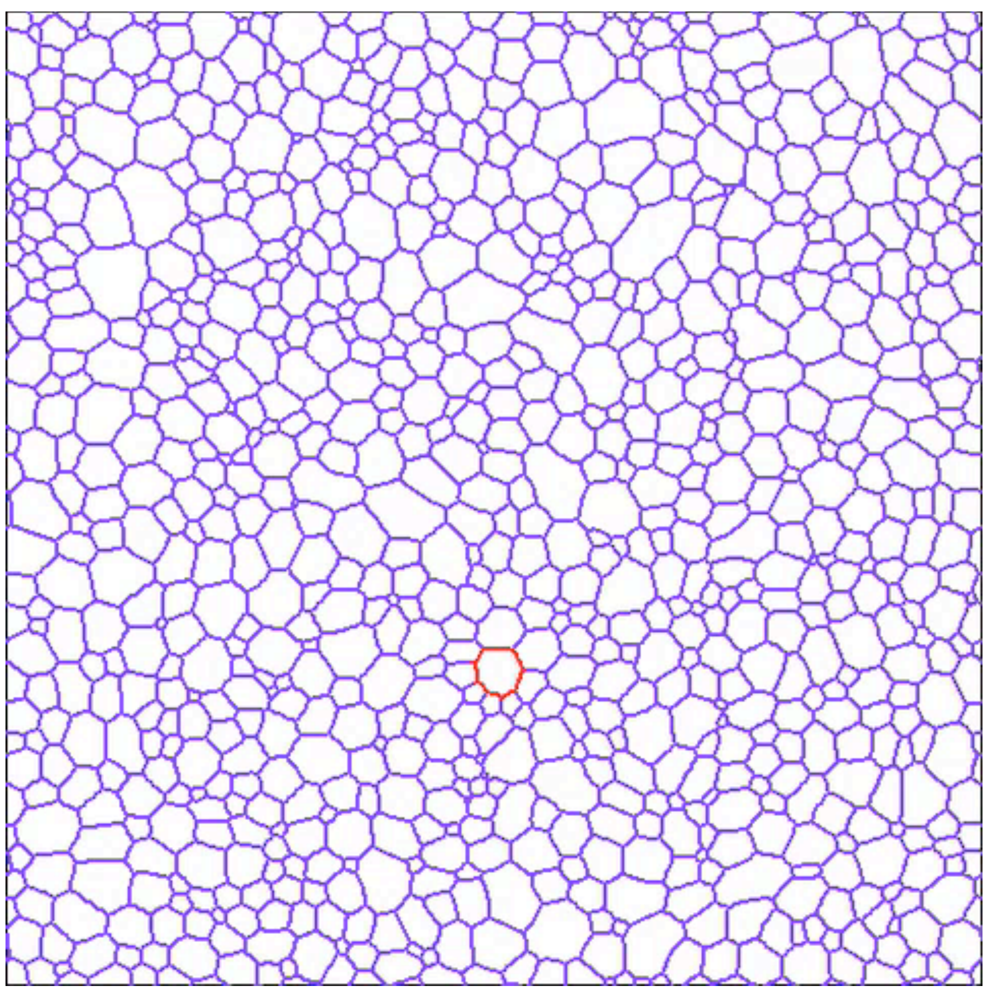

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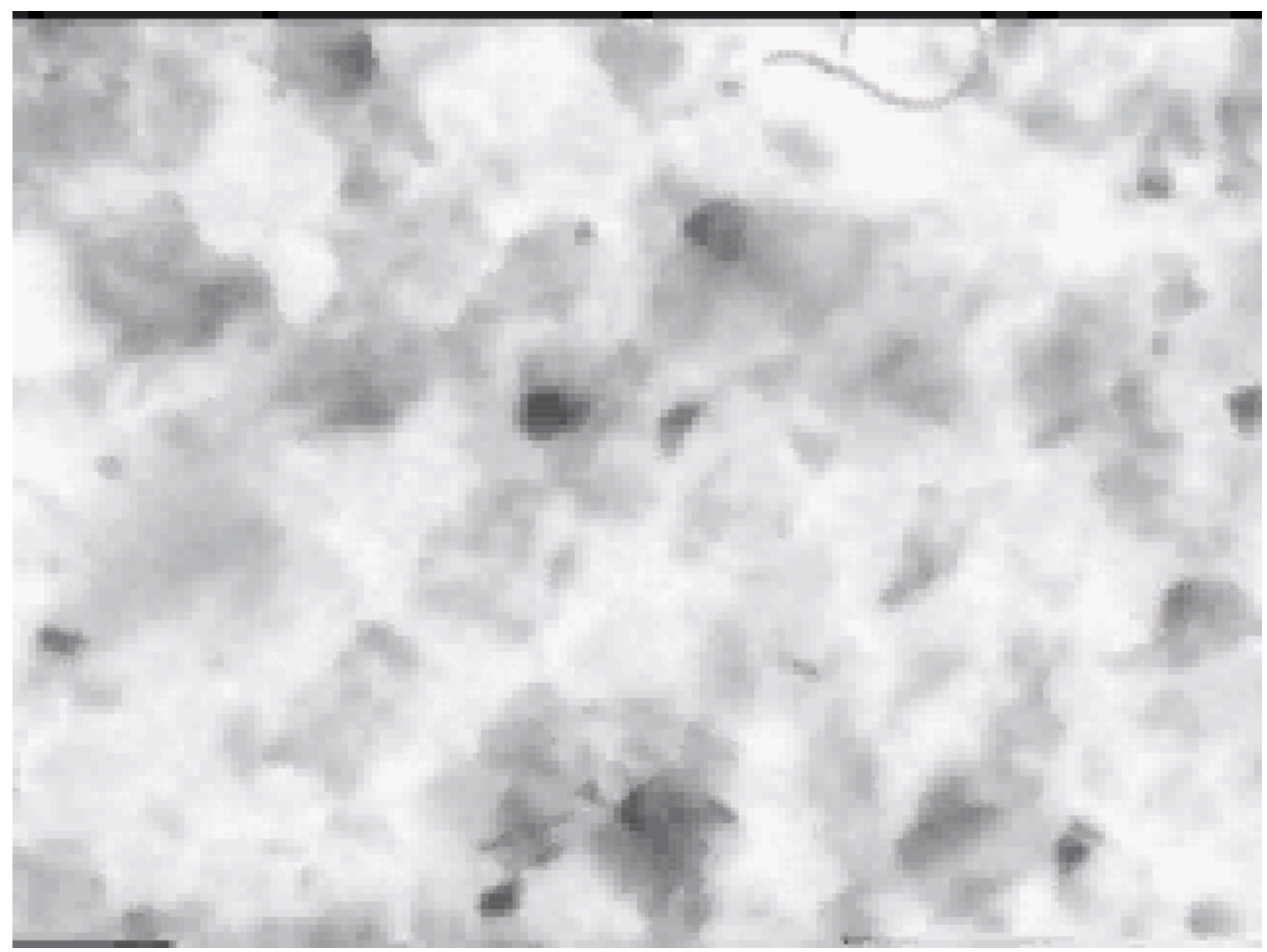


CoPt thin film (Barmak)

What Do We Know About Grains - How Do We Measure Coarsening ?

Geometric Coarsening:

Rate of change of area A of isotropic n sided grain

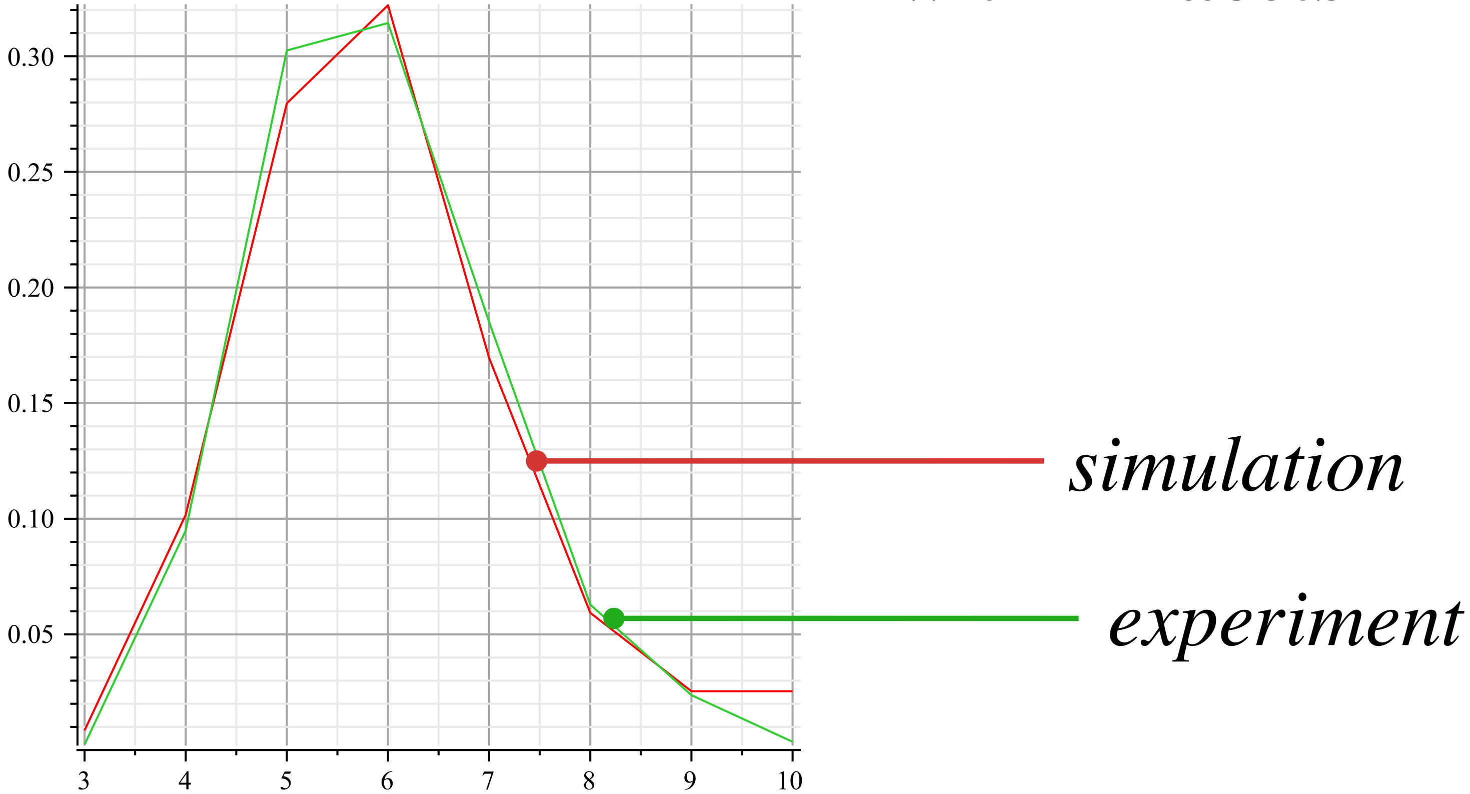
von Neumann Mullins n – 6 rule

Mac Pherson Srolovitz high dimensional generalization

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

Networks

Relative proportion of grains/cells with n facets



Grain Boundary Character Distribution (GBCD)- 2D

What about the relationship between the grain boundary (GB) population and the energy during coarsening ?

GBCD: Grain boundary character distribution - stable characteristic of a material
Assume that the GB energy density is $\psi = \psi(\alpha)$
Define $\varrho(\alpha,t)$ = (*relative) length (in 2D) of arc of grain boundaries sorted by misorientation angles* α *- "probability for the grain boundary element to have a given misorientation* α*"*

A typical property of coarsening - the network forgets the initial state and develops the statistical steady state at later time

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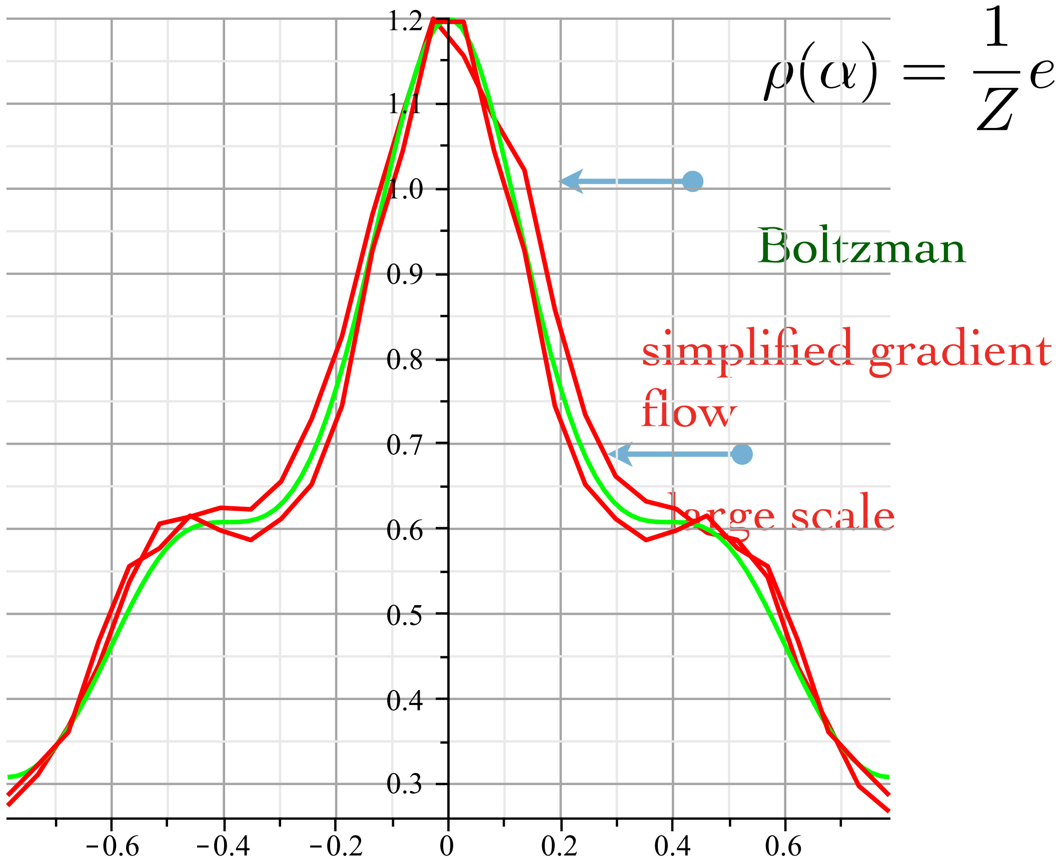
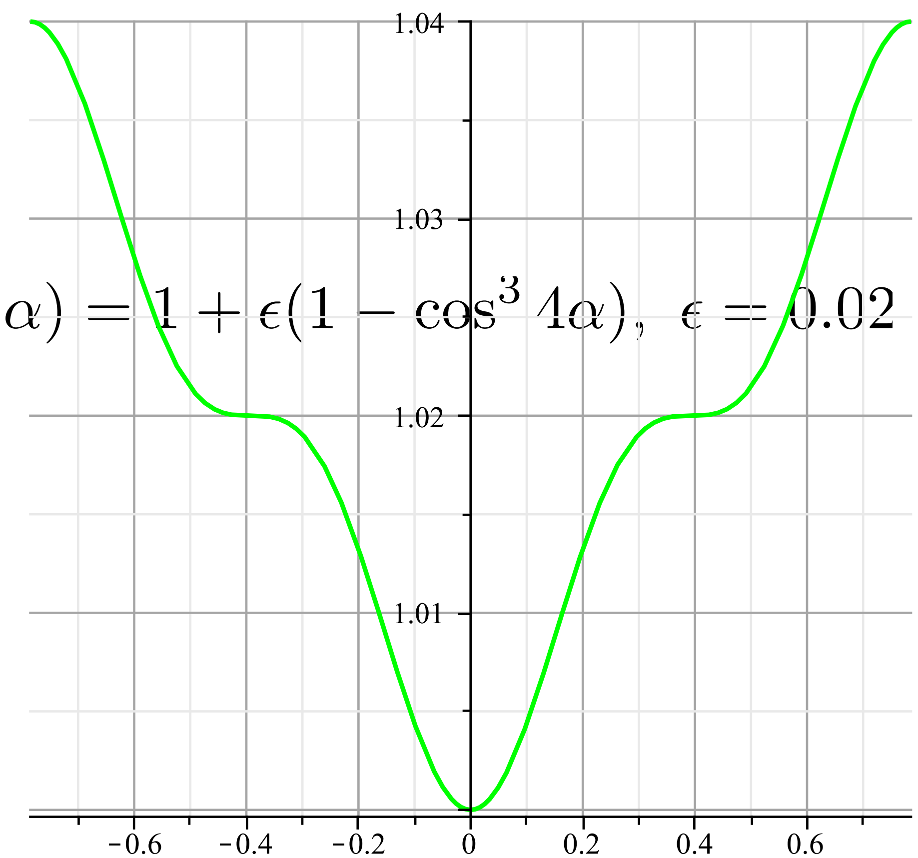
GBCD:
distribution of misorientation



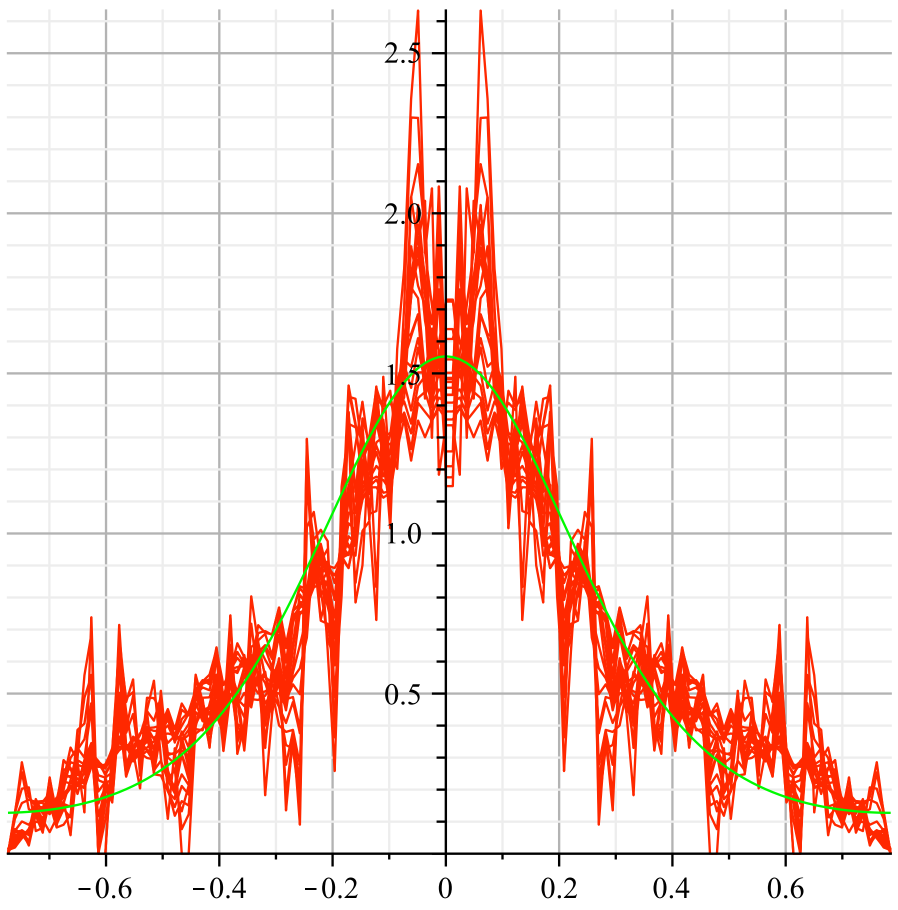
$$\rho(\alpha) = \frac{1}{Z} e^{-\frac{\psi(\alpha)}{\sigma}}$$

energy



$$\psi(\alpha) = 1 + \epsilon(1 - \cos^3 4\alpha), \;\; \epsilon = 0.02$$

A typical property of coarsening - the network forgets the initial state and develops the statistical steady state at later time



Simulation note:

GBCD histograms from a simulation which satisfies all 'generic' diagnostics:

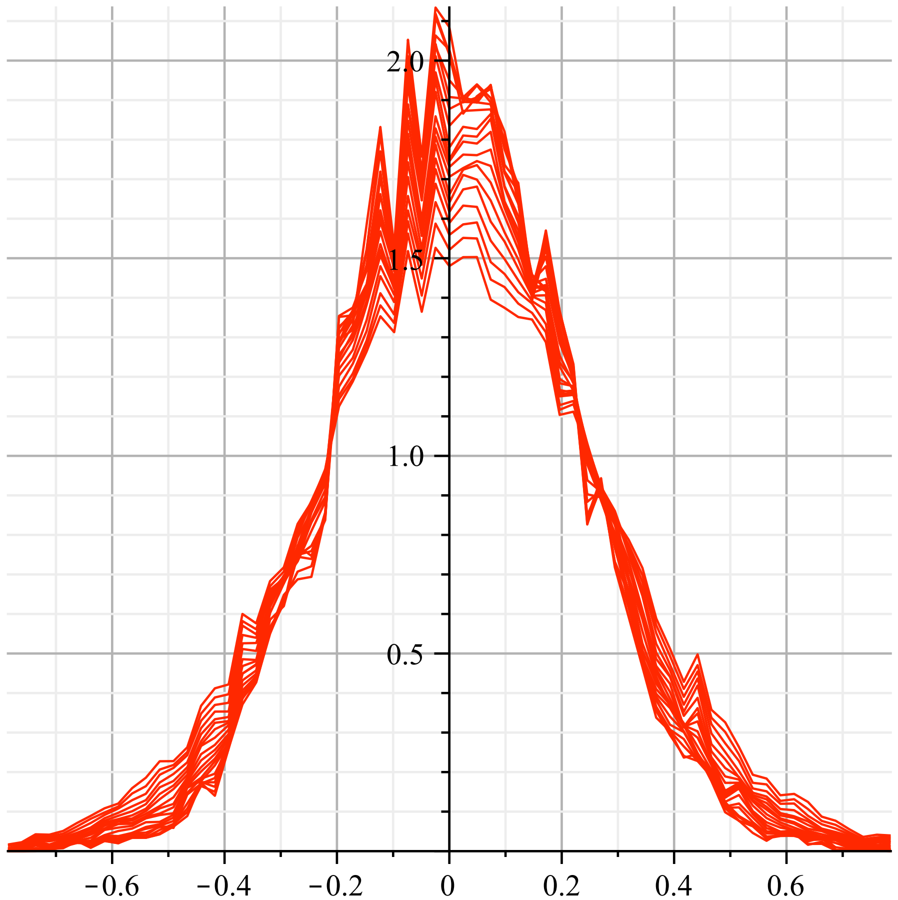
linear growth of average area

correct proportion of cells with n-sides

valid n - 6 rule

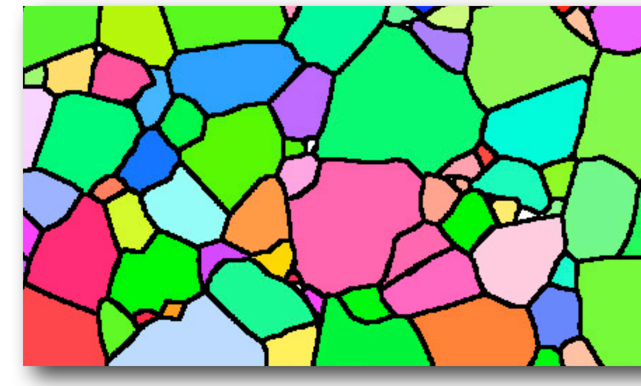
but

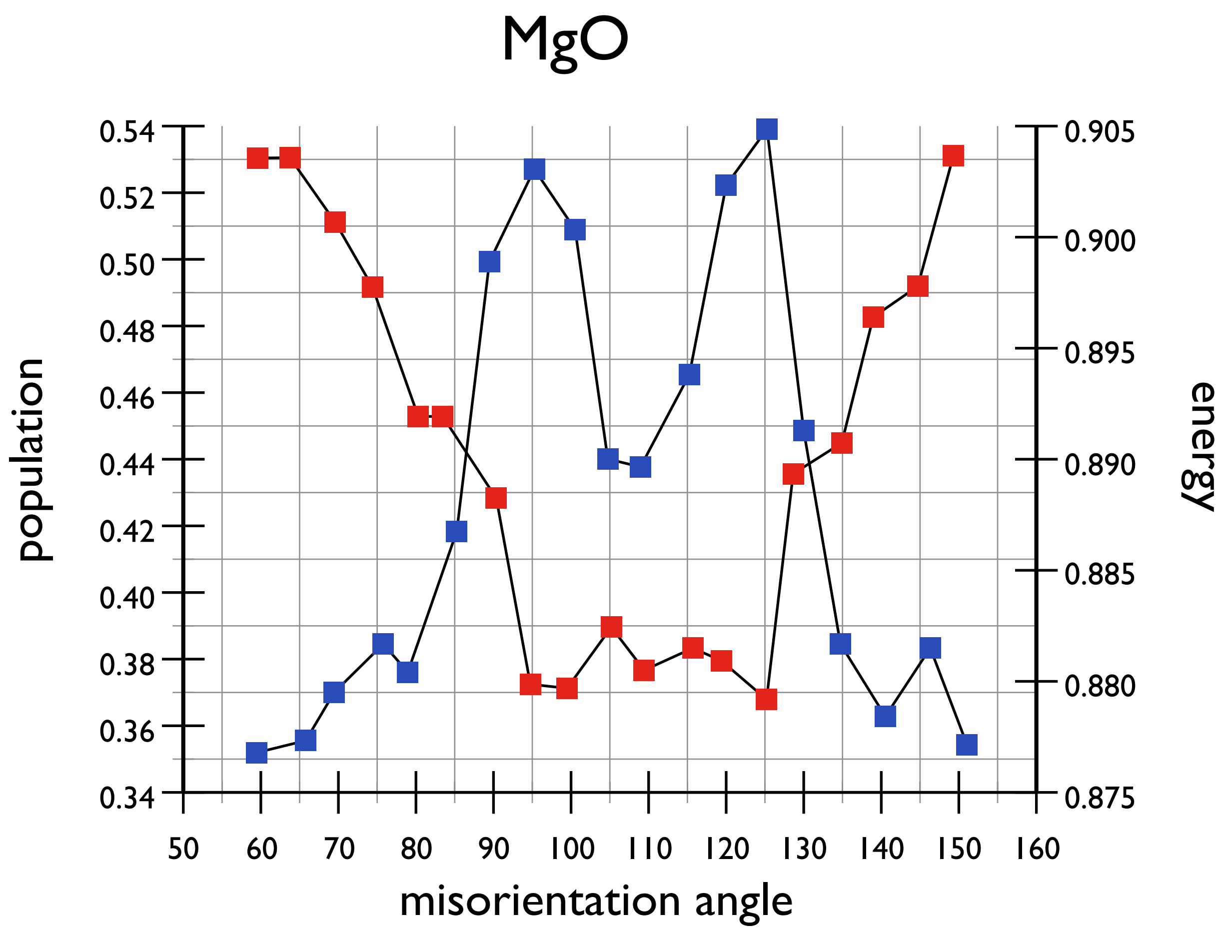
Herring condition not satisfied with accuracy

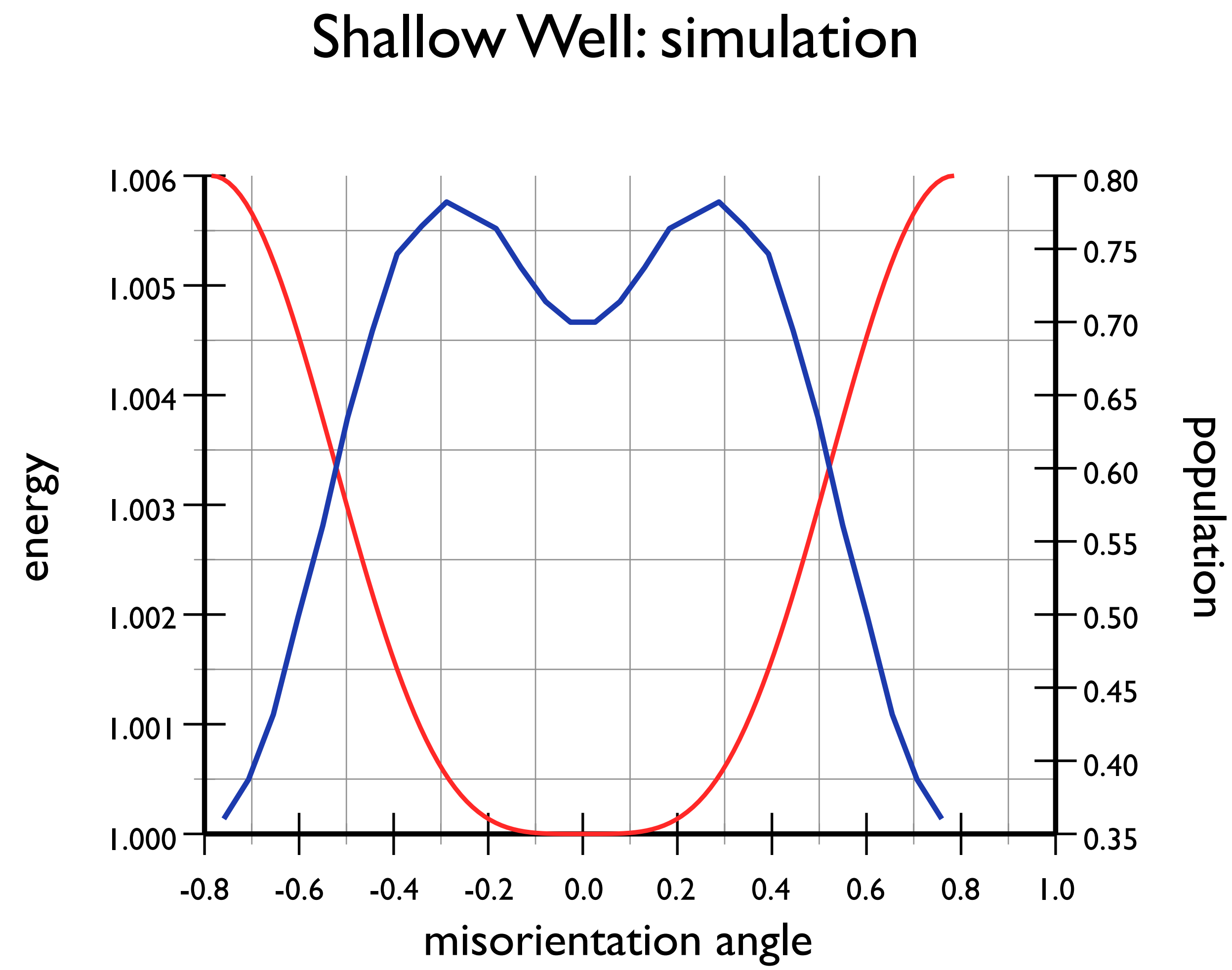


Herring condition resolved

Texture Evolution and Development Correlation: Experiment and Simulation





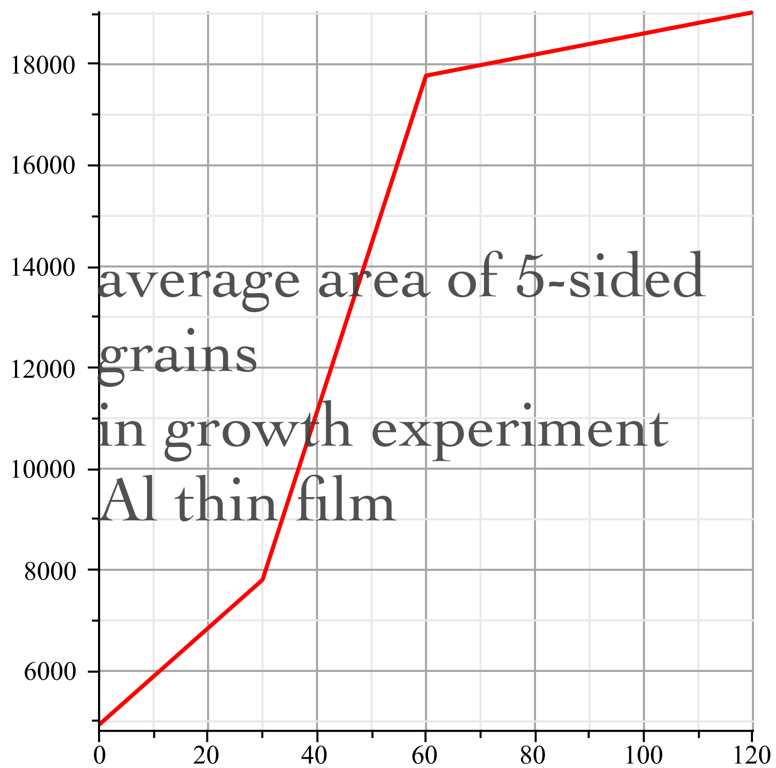


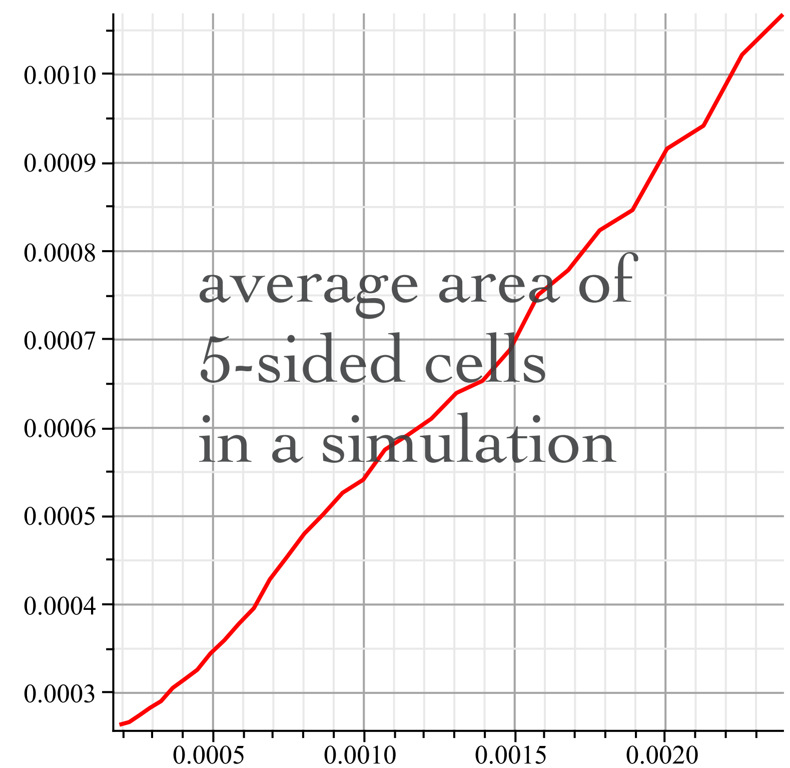
$$\psi = \psi(\theta, \alpha)$$

Each figure shows a shallow well structure (red) and a bimodal GBCD (blue)

Entropy method based on a critical event model: a simplified problem

Difficulty in developing a theory for the GBCD and understanding texture development, lies in the lack of understanding of the relationship between critical events and the system energy ➨ leads us to a reduced model

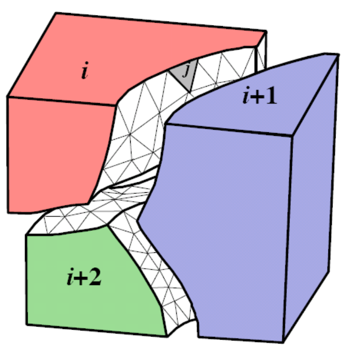




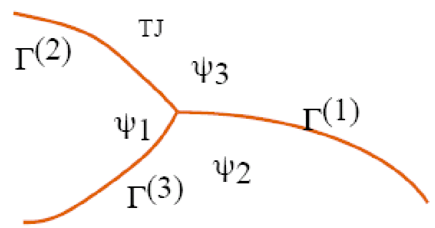
stochasticity in network coarsening: role of critical events

Critical Event Model: A Simplified Problem

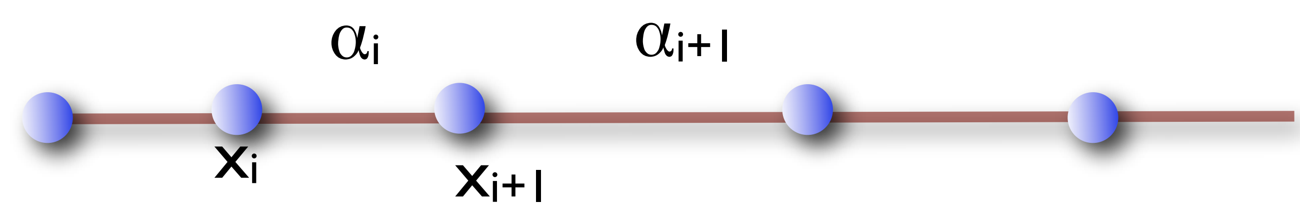
3D



2D



1D



segments: grain boundaries

points: triple junctions

gradient flow

dissipative

intervals $[x_i, x_{i+1}]$

misorientations α_i

assigned energy density $\psi(\alpha)$

$$\frac{dx_i}{dt} = \psi(\alpha_i) - \psi(\alpha_{i-1})$$

$$E = \sum \psi(\alpha_i)(x_{i+1}(t) - x_i(t))$$

$$\frac{dE}{dt} = -\sum \frac{dx_i}{dt}^2$$

when length of segment = 0, deleted from configuration

$$v_i = \frac{dx_{i+1}}{dt} - \frac{dx_i}{dt} = \psi(\alpha_{i-1}) - 2\psi(\alpha_i) + \psi(\alpha_{i+1})$$ **velocity of i^{th}-interval**

$v_i < 0 \Rightarrow$ interval i will eventually disappear: irreversible

$\Rightarrow$ system coarsens in time in a way which depends on $\{\psi(\alpha)\}$

1D Coarsening Model:

$$\frac{1}{4}\sum_{i=1..n}\int_0^\tau v_i^2 dt + E(\tau) \leq E(0)$$

Compare to 2D Grain Network:

$$\sum_{\Gamma_i}\int_0^\tau \int_{\Gamma_i} v_n^2 ds dt + E(\tau) = E(0)$$

Dissipation equation that echoes use of Herring (boundary) conditions

Analogous to grain growth system

Once a cell disappears do not know where the configuration originated (irreversible)

Upscale to character variable,

Add entropic contribution anyway, and hope that inequality conserved:

Unusual ensemble, non-equilibrium

$$\frac{1}{4}\sum_{i}\int_0^\tau v_i^2 dt + E(\tau) + \sigma Ent(\tau) \leqq E(0) + \sigma Ent(0)$$

$\sigma > 0$

Ent = ***configurational entropy***

perhaps better choices

express everything in terms of

$\rho(\alpha, t) = GBCD$

$$\frac{1}{4}\int_0^\tau \int_\Omega (\frac{\partial \rho}{\partial t})^2 d\alpha dt + \int_\Omega (\psi\rho + \sigma\rho\log\rho) d\alpha \leqq \int_\Omega (\psi\rho^* + \sigma\rho^*\log\rho^*) d\alpha$$

$\rho^*(\alpha) = \rho(\alpha, 0)$

Can we reorganize as an Monge-Kantorovich-Wasserstein (MKW) implicit scheme?

Interpret as the Wasserstein distance?

Recall the Monge-Kantorovich-Wasserstein Implicit Scheme for Fokker-Planck Equation

$d(\rho, \rho^*)^2 = \min_P \int_\Omega |x-y|^2 dp(x,y),\ P \text{ joint distributions for } \rho, \rho^*$ **Wasserstein(2-)metric**

$F(\rho) = \int_\Omega (\psi\rho + \sigma\rho\log\rho)d\alpha$ **Free energy**

Resolve iteratively: $\frac{1}{2\tau}d(\rho,\rho^*)^2 + F(\rho) = \min\{\frac{1}{2\tau}d(\eta,\rho^*)^2 + F(\eta)\}$

Set $\rho^{(\tau)} = \rho^{(k)}, k\tau \leqq t < (k+1)\tau,\ k = 1, 2, 3, \ldots$

Iterates of implicit scheme based on this variational principle known to give solution of Fokker-Planck Equation *(Jordan-Kinderlehrer-Otto)*

obtain

$$\rho(x,t) = \lim_{\tau\to 0}\rho^{(\tau)}(x,t)$$

$$\frac{\partial\rho}{\partial\alpha} = \frac{\partial}{\partial\alpha}(\sigma\frac{\partial\rho}{\partial\alpha} + \psi'\rho)$$ ***Fokker-Planck***

and

stationary distribution

$$\rho \to \frac{1}{Z}e^{-\frac{\psi}{\sigma}} \text{ as } t \to \infty \text{ exponentially fast}$$

$$\frac{1}{4}\int_0^{\tau}\int_{\Omega}(\frac{\partial\rho}{\partial t})^2 d\alpha dt + \int_{\Omega}(\psi\rho + \sigma\rho\log\rho)d\alpha \leqq \int_{\Omega}(\psi\rho^* + \sigma\rho^*\log\rho^*)d\alpha$$

$$\rho^*(\alpha) = \rho(\alpha, 0)$$

$$\frac{\mu}{2\tau}d(\rho,\rho^*)^2 \leqq \frac{1}{4}\int_0^{\tau}\int_{\Omega}(\frac{\partial\rho}{\partial t})^2 d\alpha dt$$

Wasserstein metric

$$\frac{\mu}{2\tau}d(\rho,\rho^*)^2 + F(\rho) \leqq F(\rho^*),\ \ F(\rho) = \int_{\Omega}(\psi\rho + \sigma\rho\log\rho)d\alpha$$

If we assume a minimum principle (most probable distribution):

$$\frac{\mu}{2\tau}d(\rho,\rho^*)^2 + F(\rho) = \inf_{P}\{\frac{\mu}{2\tau}d(\eta,\rho^*)^2 + F(\eta)\}$$

Success ⇒ ϱ(α,t) = GBCD, texture statistic

Resembles implicit scheme for a Fokker-Planck Equation and in particular

$$\rho \longrightarrow \rho_\sigma, \quad \rho_\sigma(\alpha) = \frac{1}{Z}e^{\frac{-\psi(\alpha)}{\sigma}}$$

What is σ ?

Solution of Fokker-Planck Equation

- **We now begin the validation step of our model**
- **Introduce the notation for the Boltzmann distribution with parameter λ**

$$\rho_\lambda(\alpha) = \frac{1}{Z_\lambda} e^{-\frac{1}{\lambda}\psi(\alpha)}, \alpha \in \Omega, \ \textbf{with } Z_\lambda = \int_\Omega e^{-\frac{1}{\lambda}\psi(\alpha)} d\alpha.$$

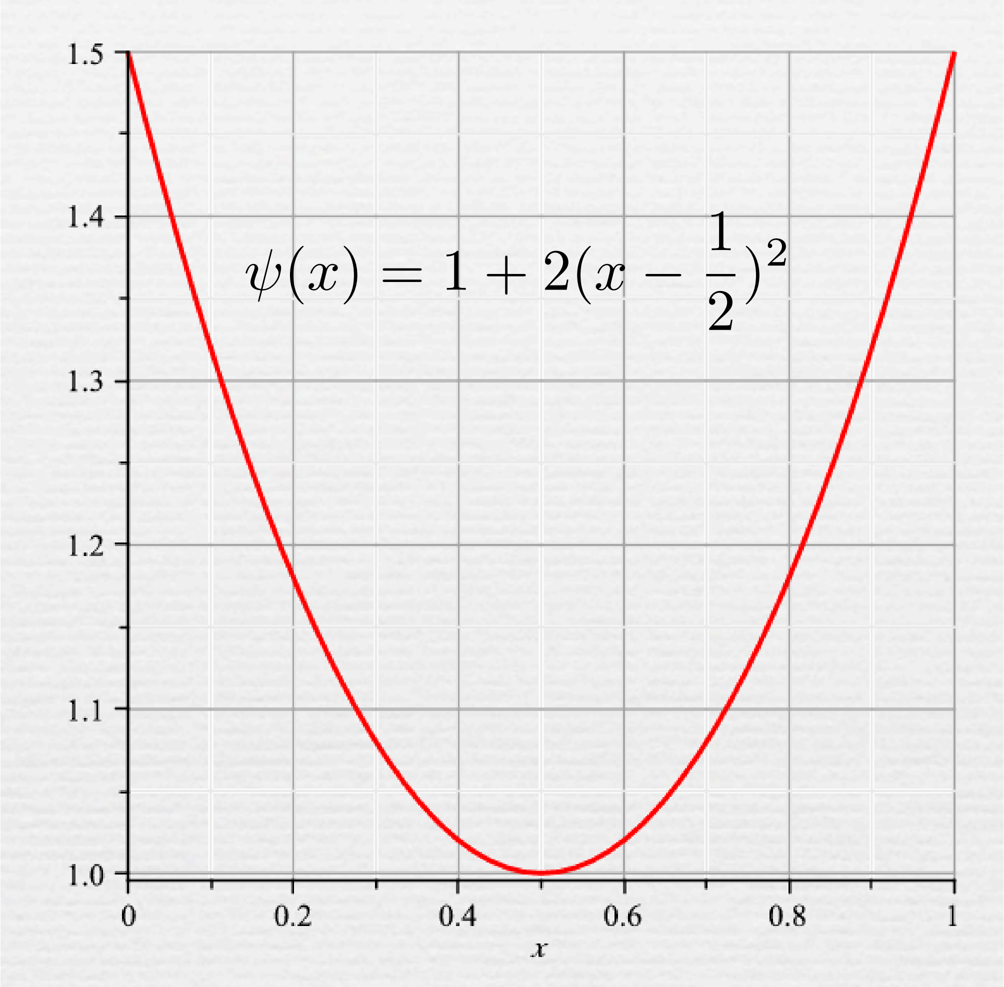
- **Introduce the Kullback-Leibler relative entropy for solution η to FP equation**

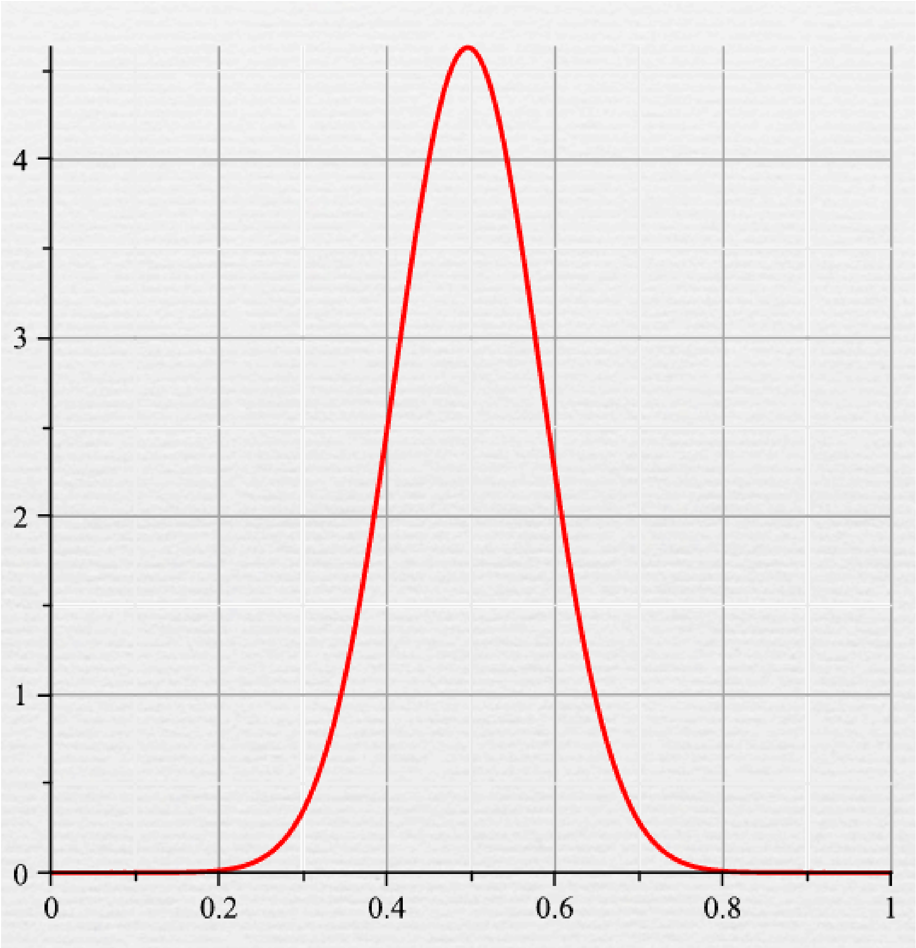
$$\Phi_\lambda(\eta) = \lambda \int_\Omega \eta \log \frac{\eta}{\rho_\lambda} d\alpha \ \textbf{where}$$

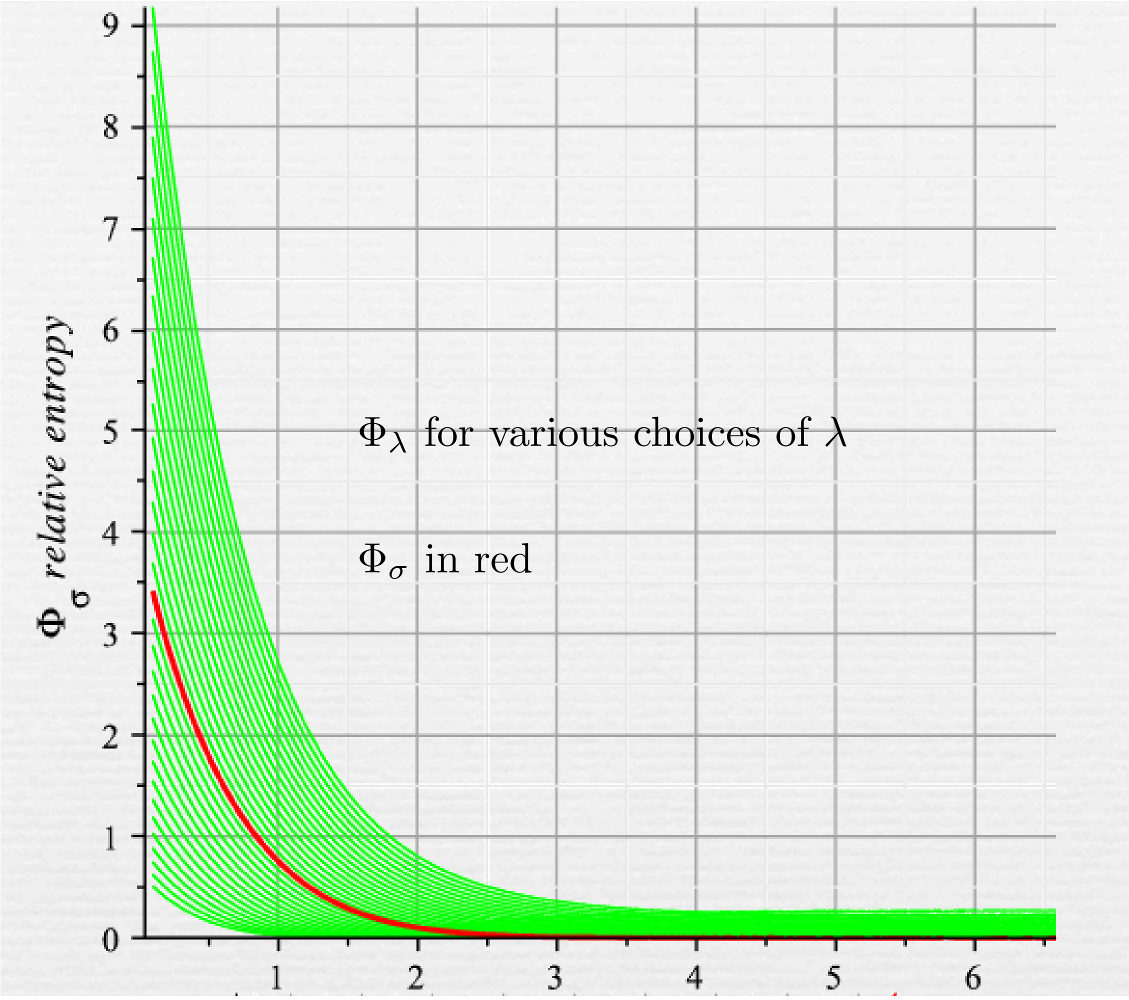
$$\eta \geqq 0 \ \textbf{in } \Omega, \ \int_\Omega \eta d\alpha = 1,$$

Solution of Fokker-Planck Equation

- **With this validation we would like** *to compare qualitative properties of the solutions to Fokker-Planck (FP) equation:* $\mu\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial\alpha}(\lambda\frac{\partial\rho}{\partial\alpha} + \psi'\rho)$ *and the GBCD* $\rho(\alpha, t)$
- **The solution to FP equation satisfies the following properties**
  - $\rho(\alpha, t) \to \rho_\lambda(\alpha)$ **as** $t \to \infty$**, and**
  - **this convergence is exponentially fast:**
  - **The Kullback-Leibler relative entropy for solution** $\rho(\alpha, t)$ **to FP equation tends to zero as** $t \to \infty$







$$\sigma = 0.296915$$

- choose σ with relative entropy tending to 0:

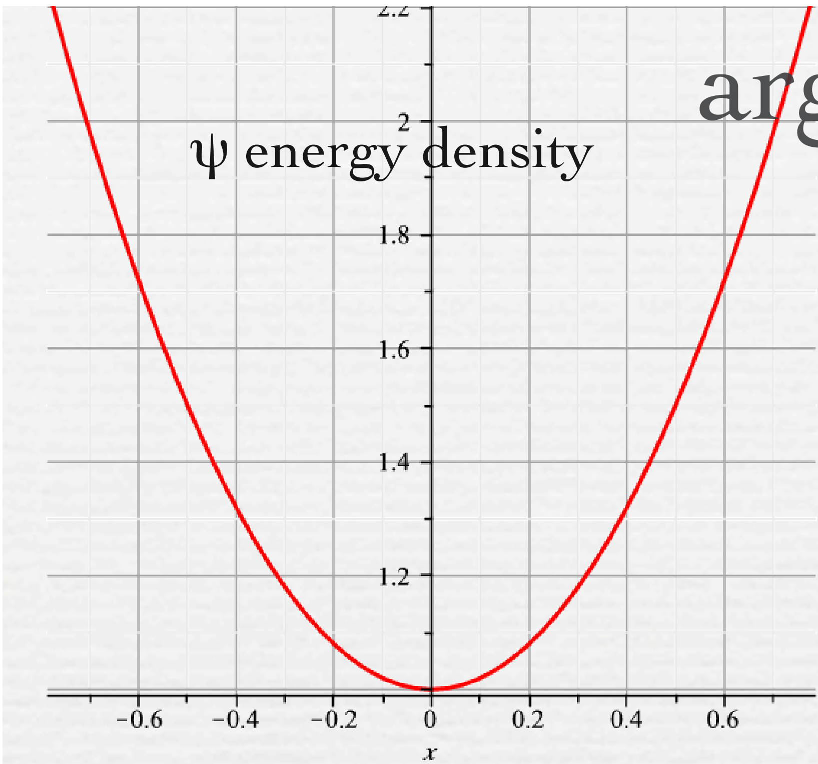
$$\Phi_\sigma \to 0, \ t \to \infty$$

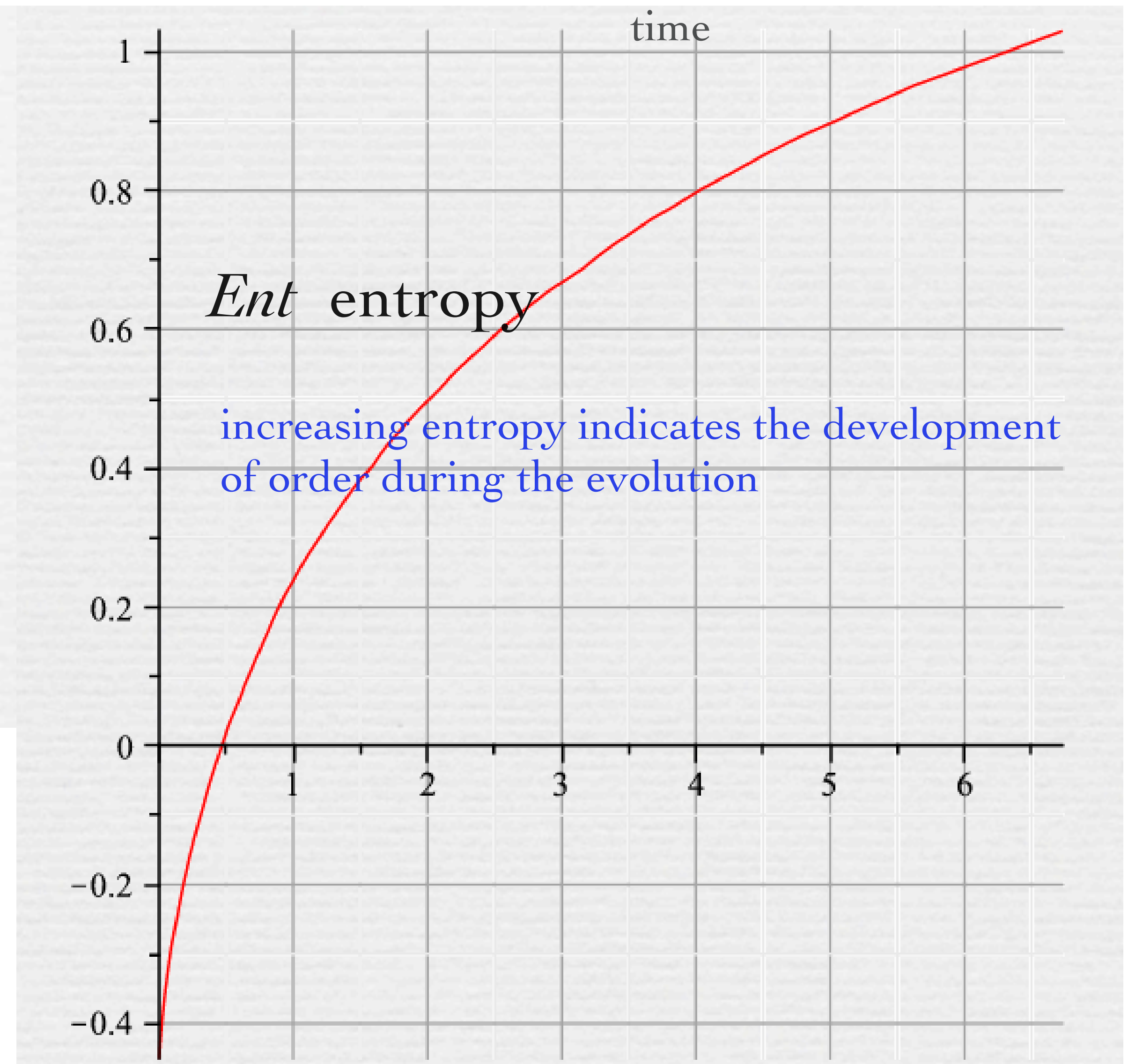
- now look at empirical distribution

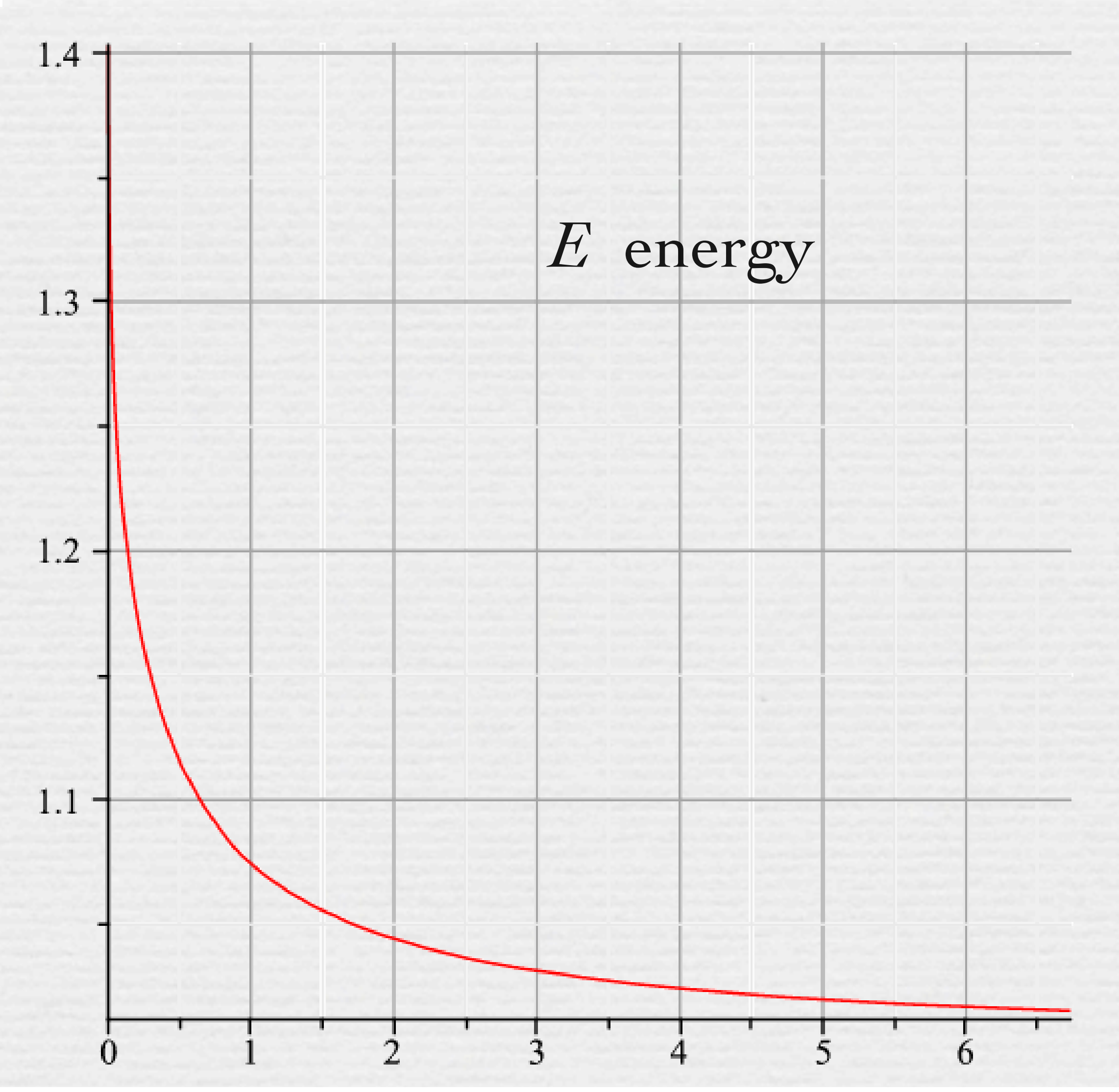
at final time: is it the Boltzmann for σ ?

Simplified Coarsening Model

argue by picture







plot relative entropy

$$\Phi_\lambda = \frac{1}{\lambda}E + Ent + \log Z_\lambda = \int_\Omega \rho \log \frac{\rho}{\rho_\lambda} d\alpha$$

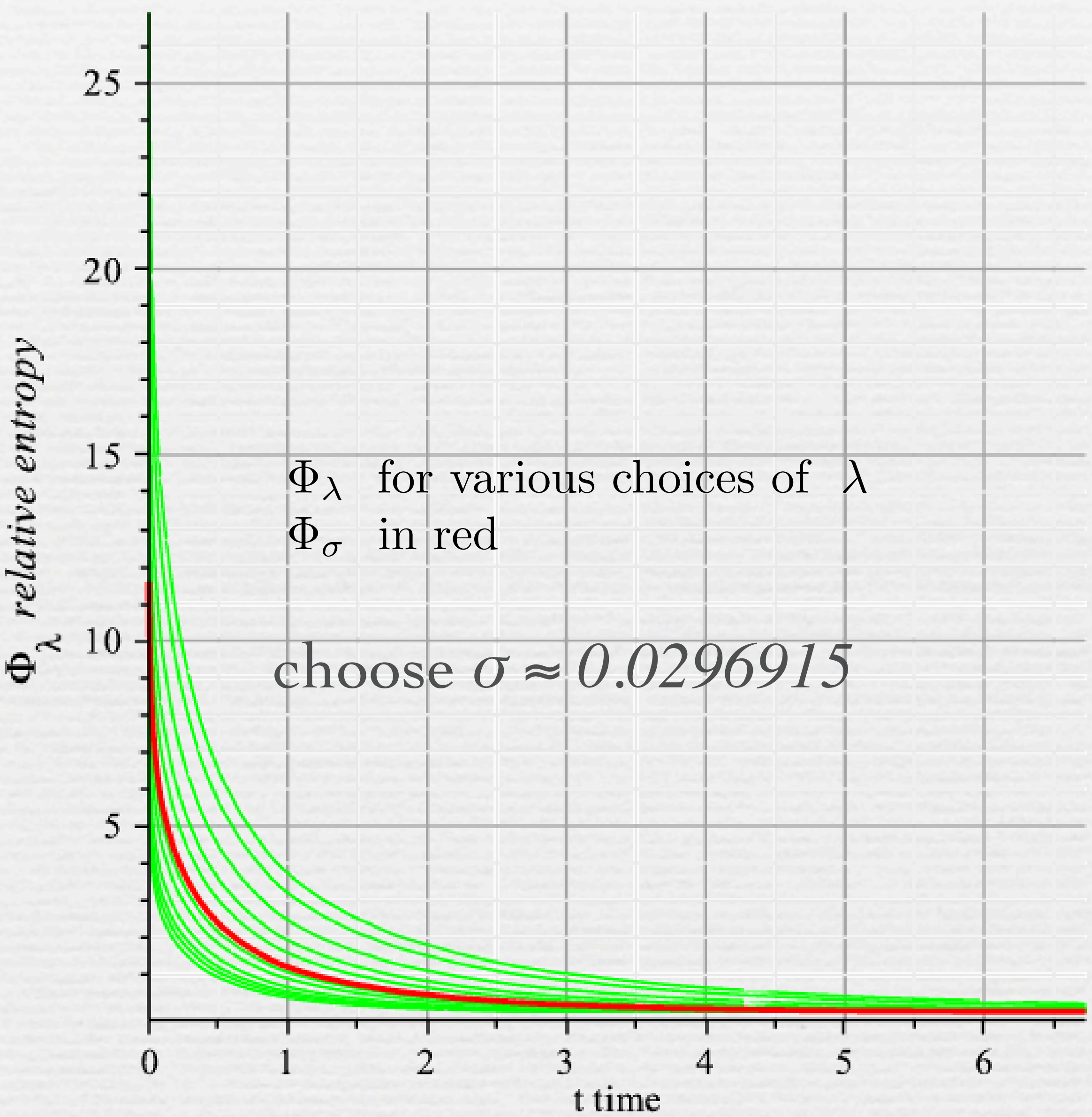
$$Z_\lambda = \int_\Omega e^{-\psi(\alpha)/\lambda} d\alpha$$

- choose σ with relative entropy

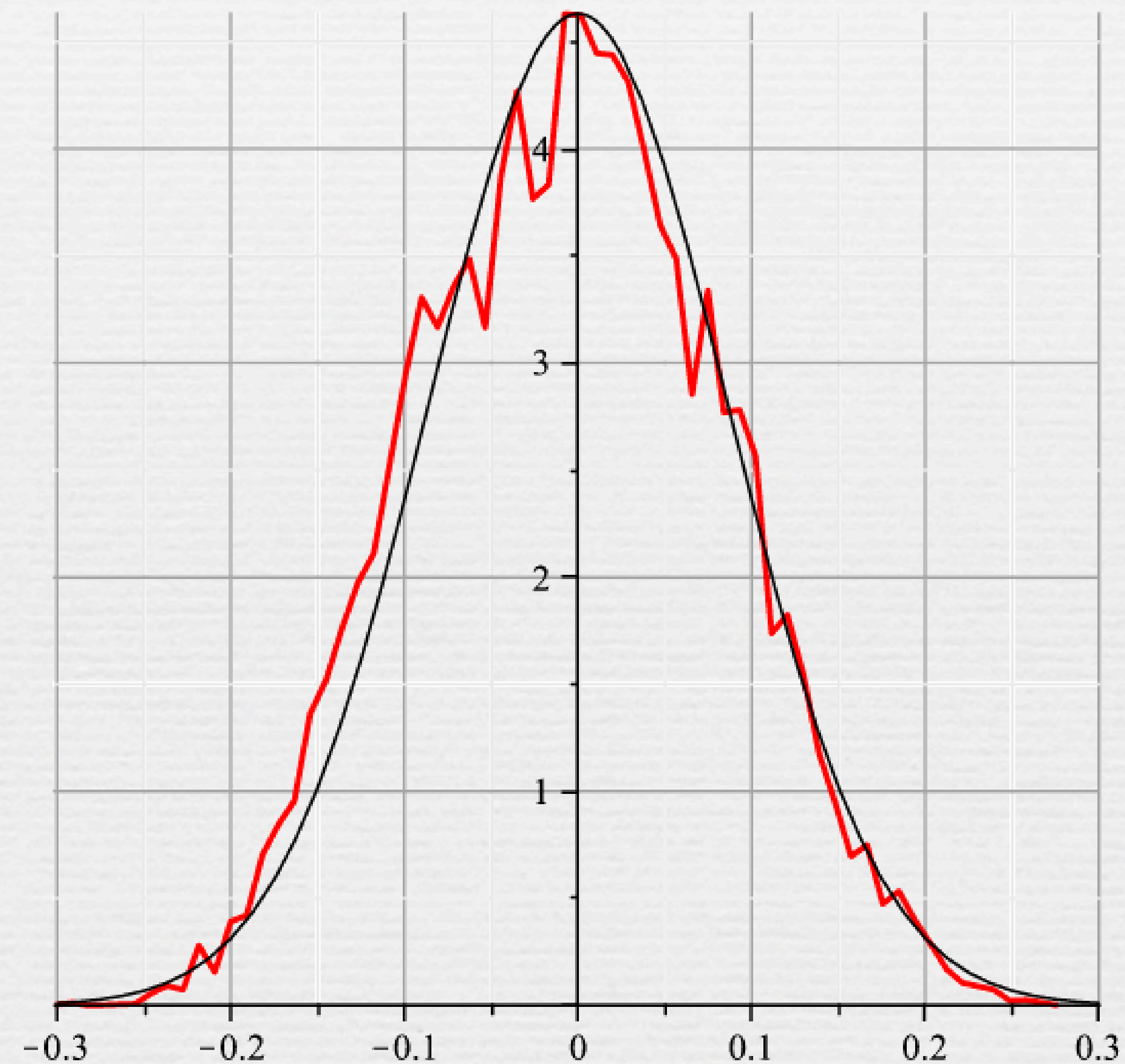
$$\Phi_\sigma \to 0, \; t \to \infty$$

- now look at empirical distribution

at final time: is it the Boltzmann for σ ?



$$\psi(\alpha) = 1 + 2\alpha^2$$



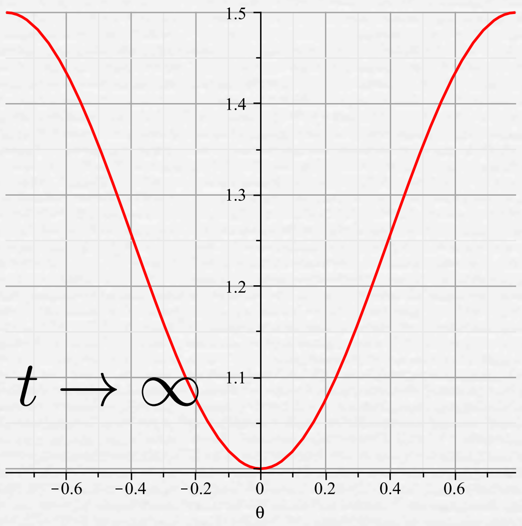
red: empirical distribution

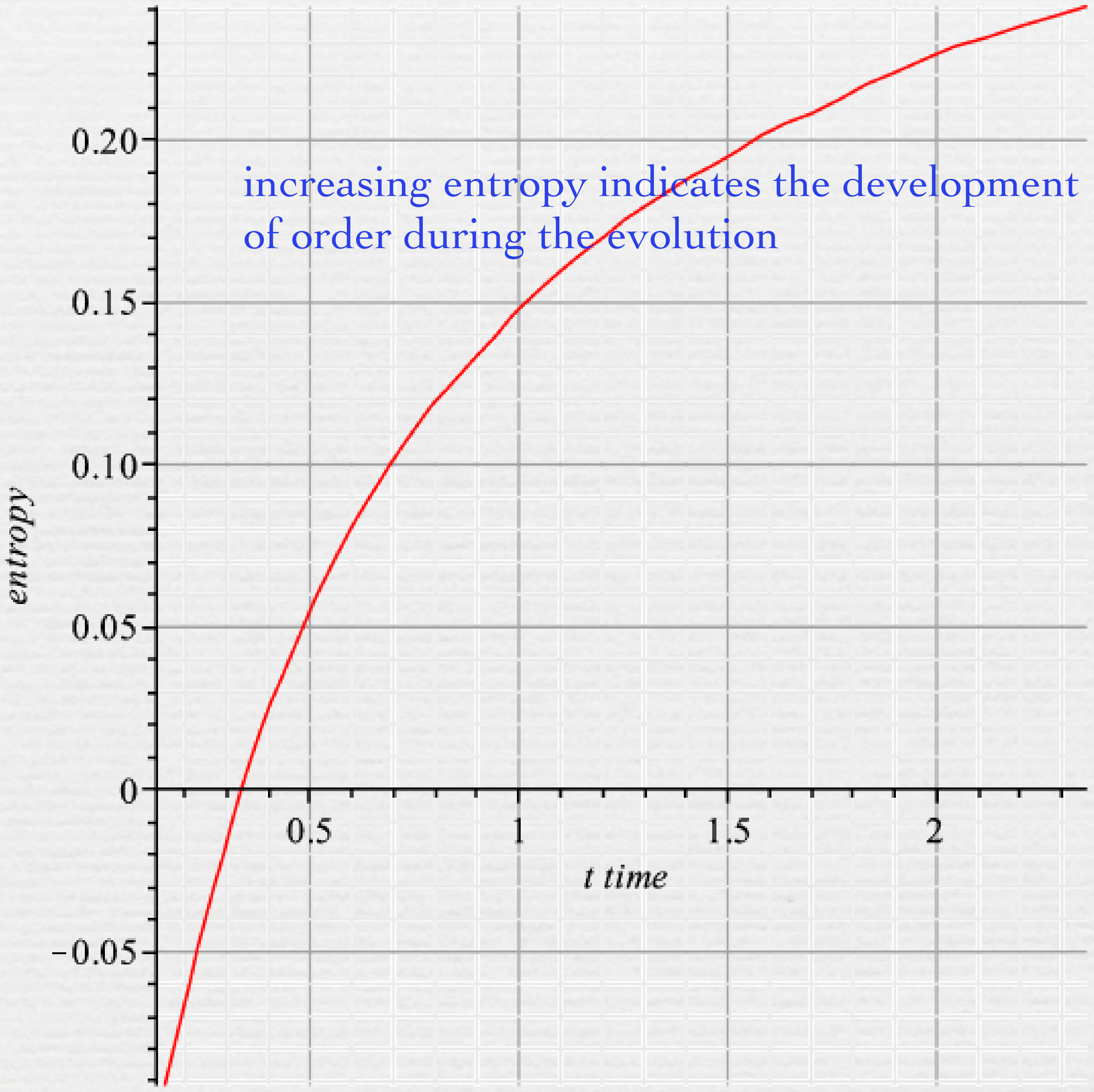
black: Boltzmann for σ determined by entropy condition

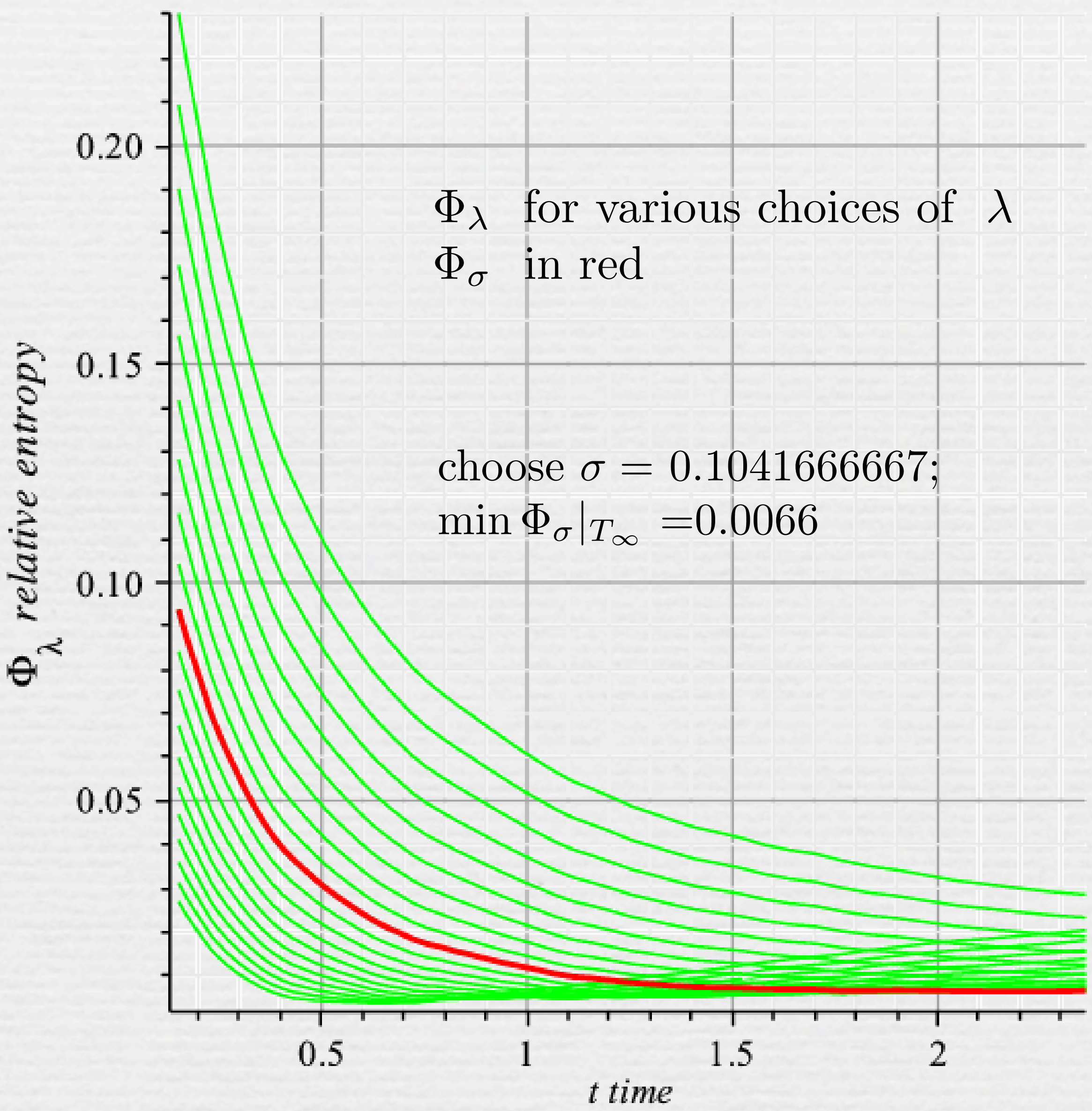
2D coarsening GBCD statistic averaged over 5 trials

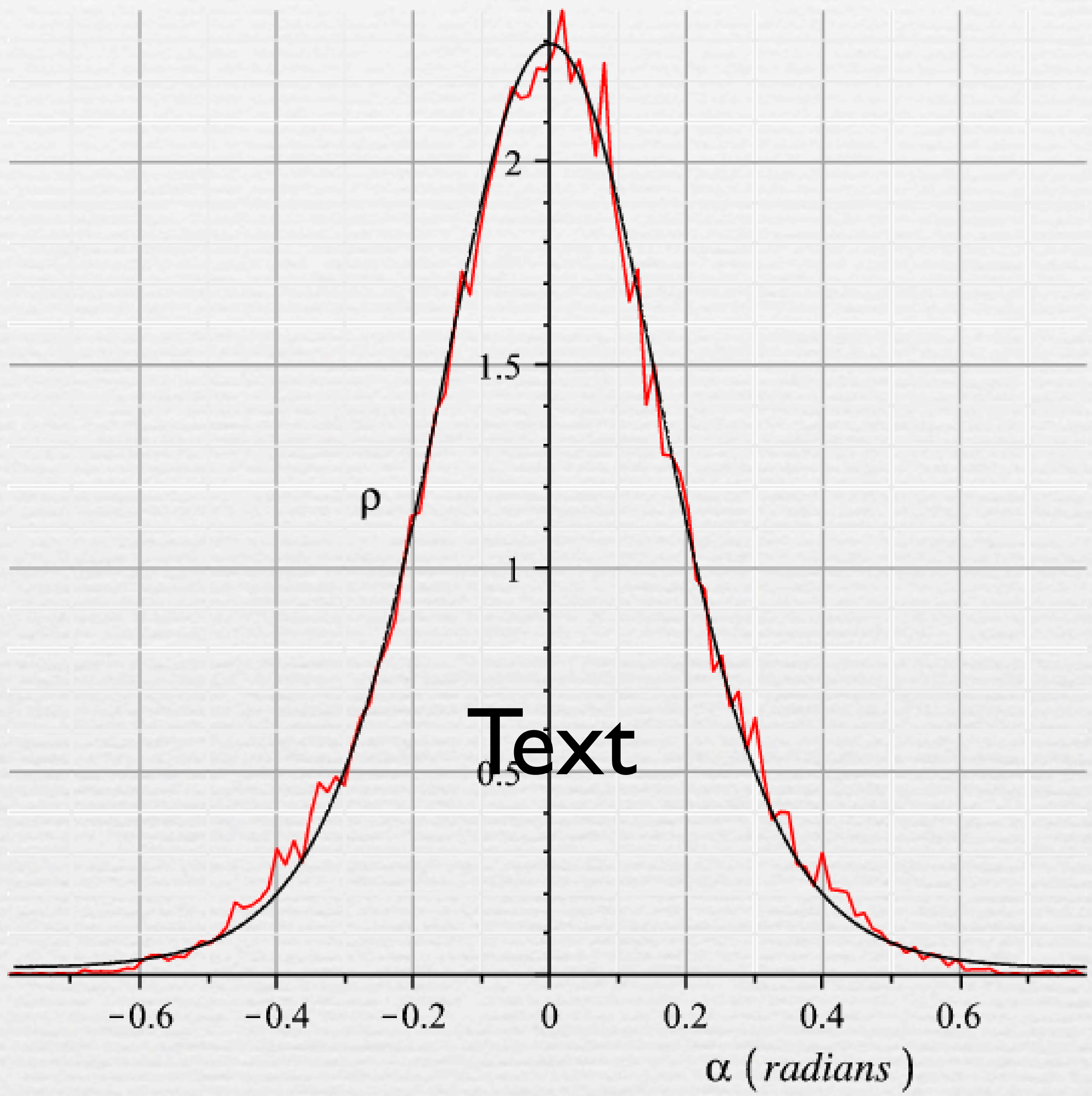
$$\psi(\alpha) = 1 + \epsilon \sin^2 2\alpha, \epsilon = \frac{1}{2} \qquad \rho_\lambda(\alpha) = \frac{1}{Z_\lambda} e^{-\frac{\psi(\alpha)}{\lambda}}$$

$$\Phi_\lambda = \int_\Omega \rho \log \frac{\rho}{\rho_\lambda} d\alpha \geqq 0; \quad \Phi_\sigma \to 0 \text{ as } t \to \infty$$





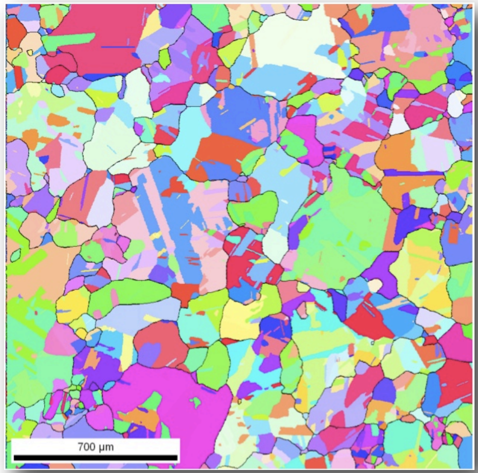


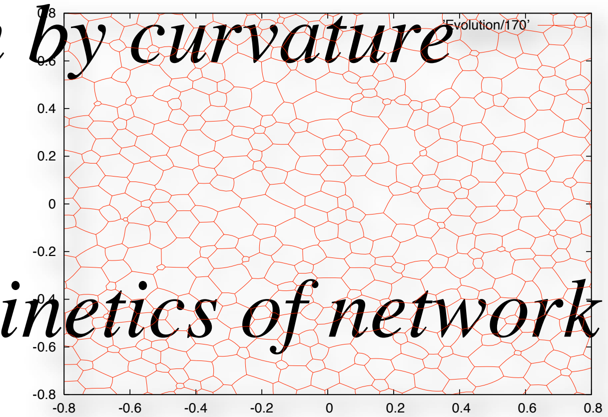


red: empirical distribution (5 trials)
black: Boltzmann for σ determined by relative entropy condition

$$\sigma = 0.104167$$

Summary

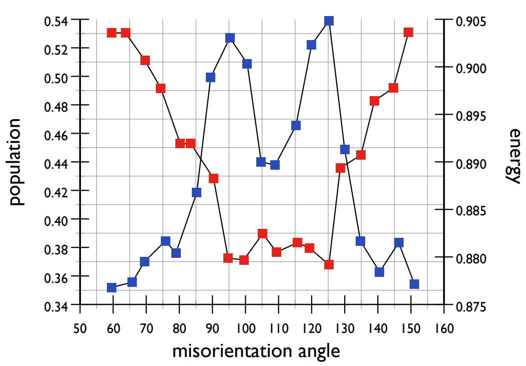




• *local thermodynamic equations of growth by curvature determine ideal network properties*

• *derived a theory which accounts for the kinetics of network evolution:*

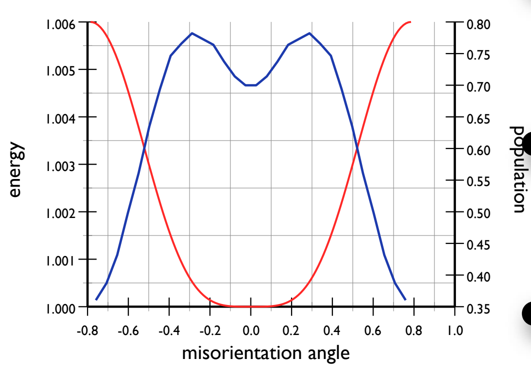
dissipation/entropy principle

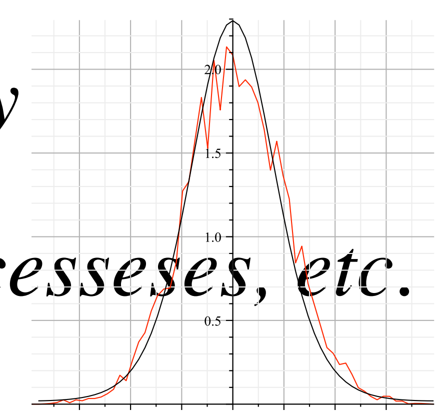


Shallow Well: simulation

• *simplified model: critical event model   many critical event models*

• *what is σ ?*





• *some hint of universality in the metastability*

• *many other questions: what stochastic processeses, etc.*

Thank You !