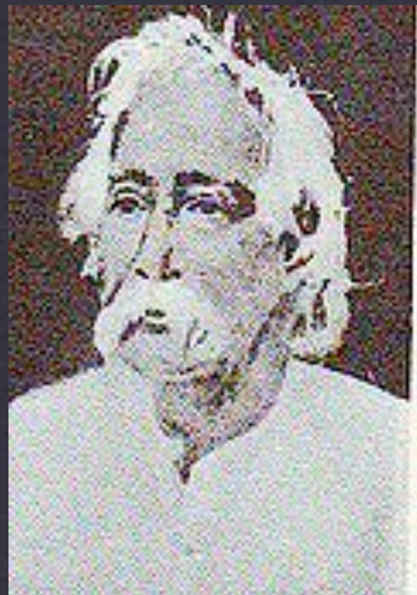
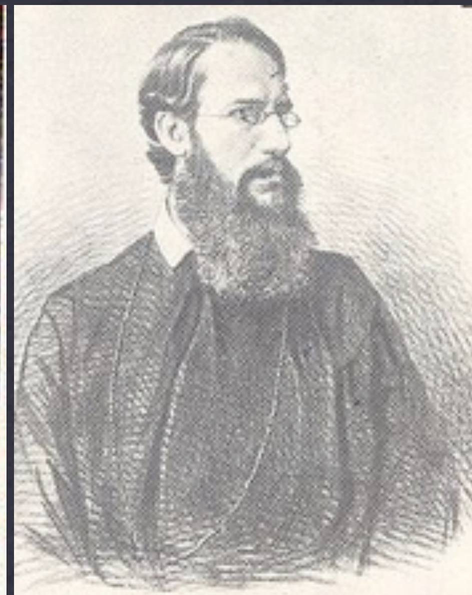
# Solid-solid NAG

**Surajit Sengupta**

*Indian Association for the Cultivation of Science, Kolkata*

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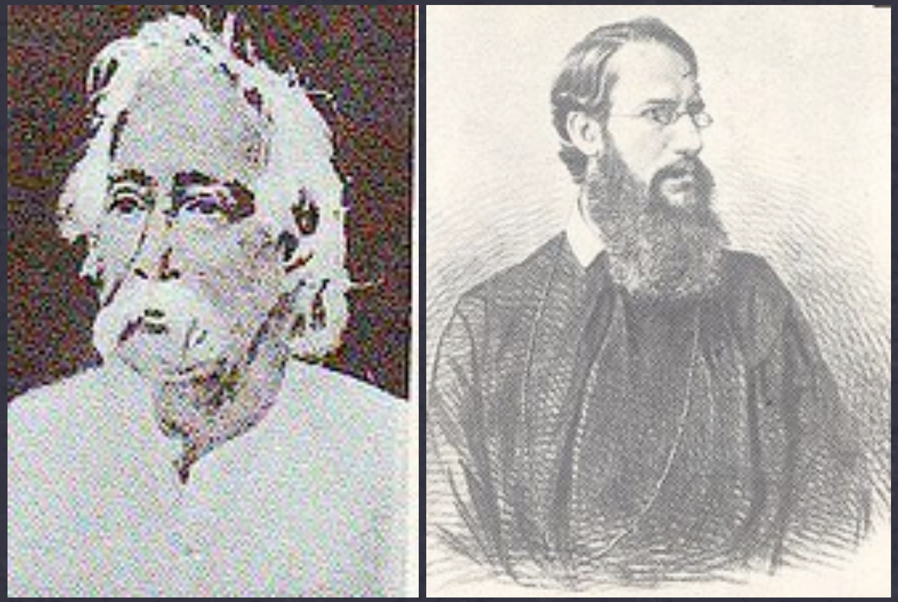

*... CARRY ON THE WORK WITH OUR OWN EFFORTS UNAIDED BY THE GOVERNMENT ...*

*I WANT IT TO BE SOLELY NATIVE AND PURELY NATIONAL ...* M.L. SIRCAR (1876)

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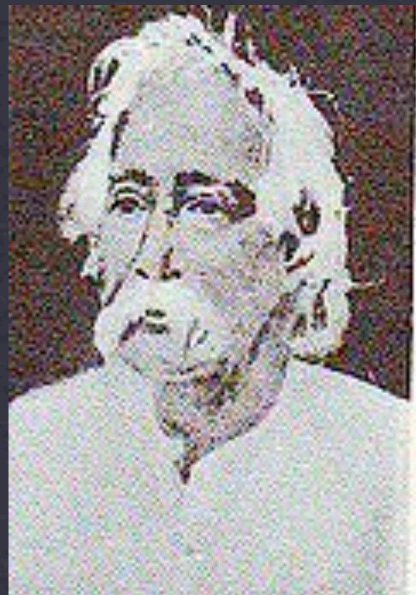
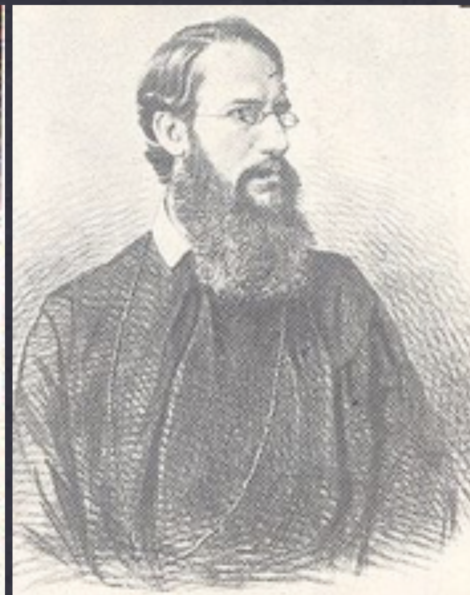


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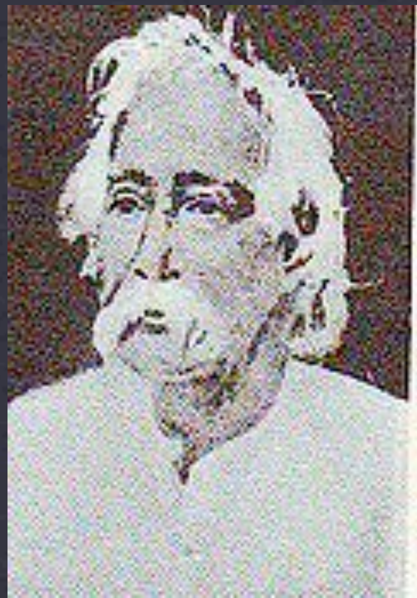

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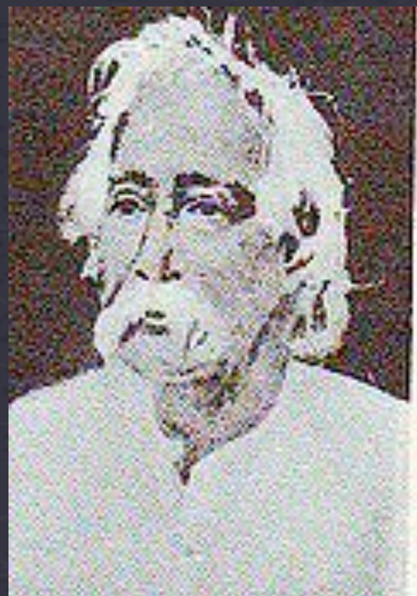 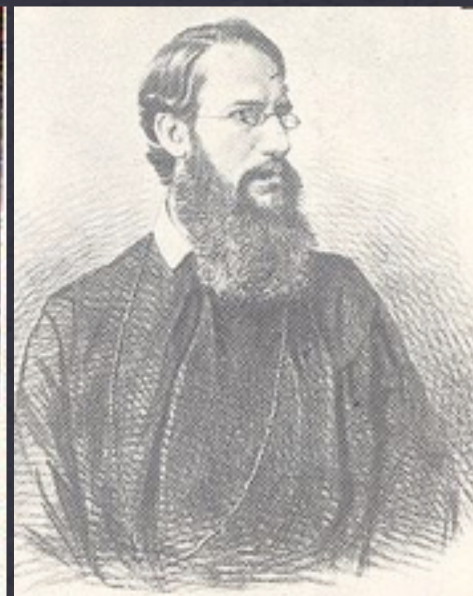   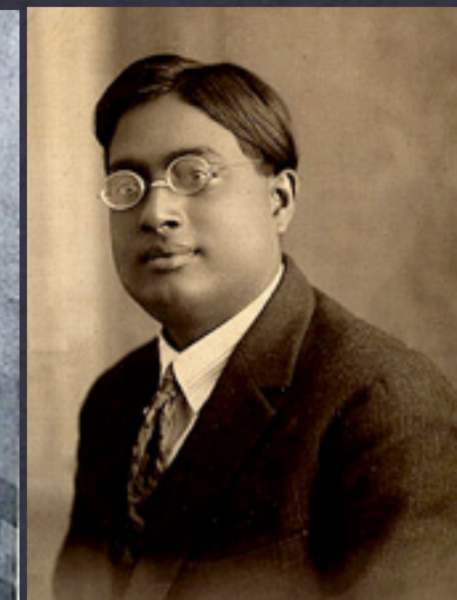

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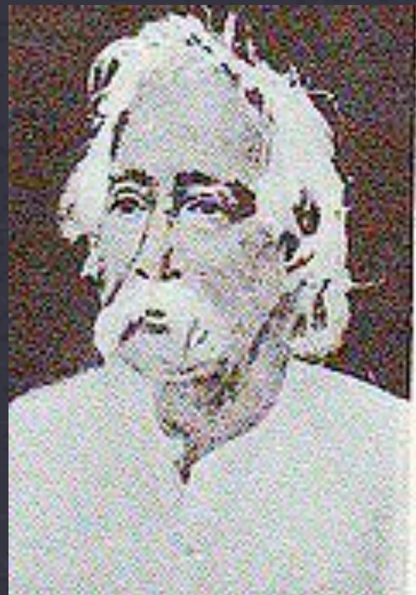 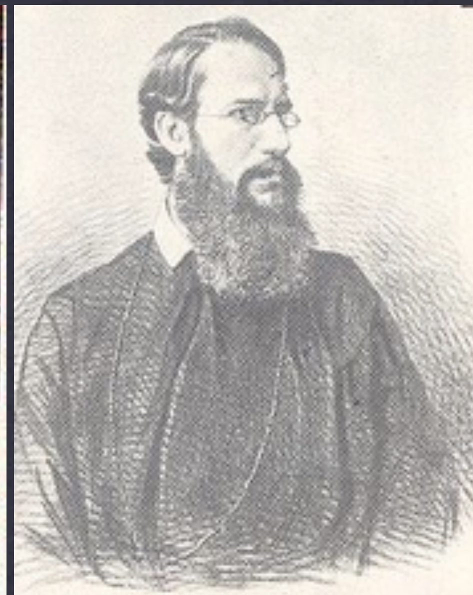   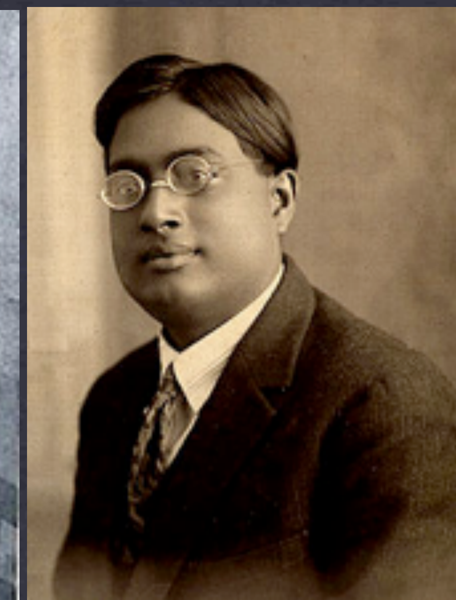

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# Solids in solids: a really difficult problem

- Solids are anisotropic.
- Solids are rigid, need to generalize Gibbs-Thompson relations to include stress.
- The chemical potential is non-uniform.
- Atomic rearrangements, defects, vacancies, dislocations, etc.
- Both *ballistic* and *diffusive* trajectories are possible.

***SOLIDS FAR FROM EQUILIBRIUM,*** C. GODRECHE, EDS. (CUP, 1992)

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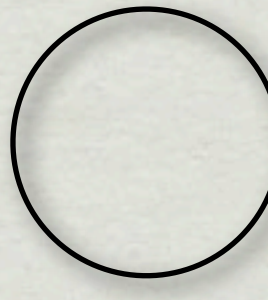
$$\Delta P = \gamma / R$$



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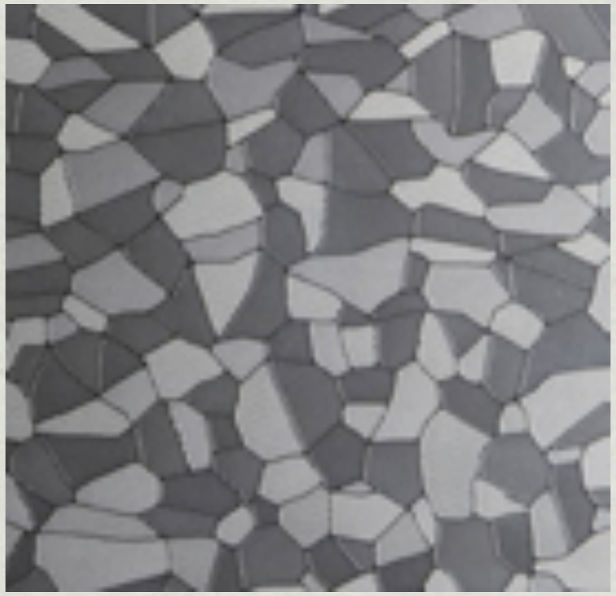
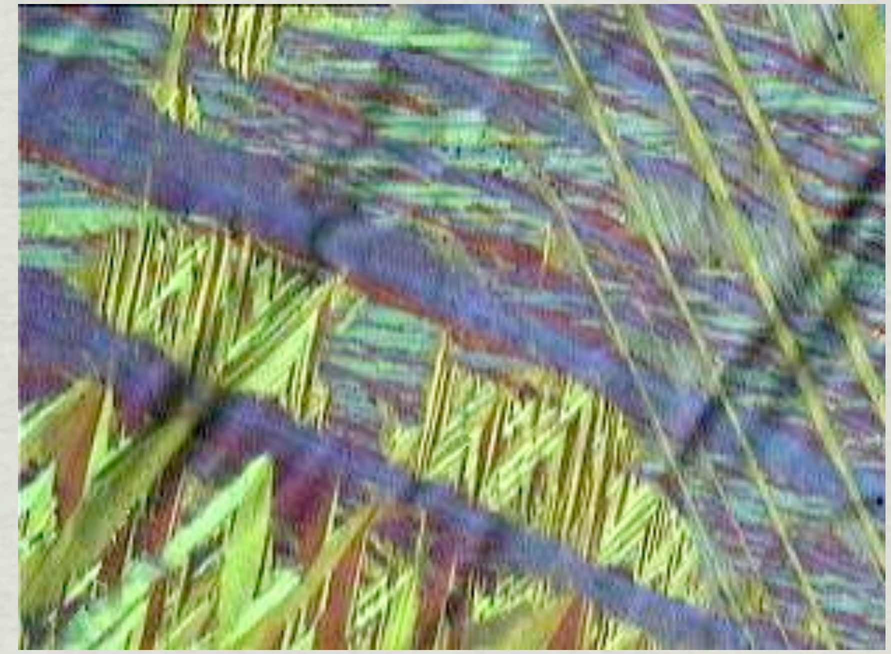
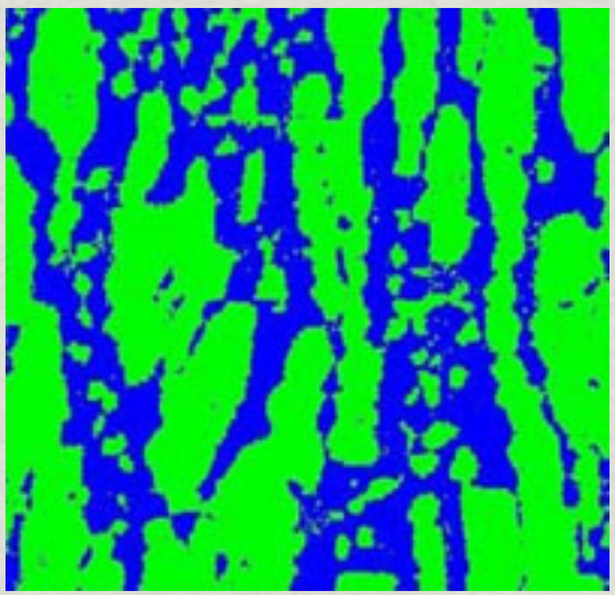
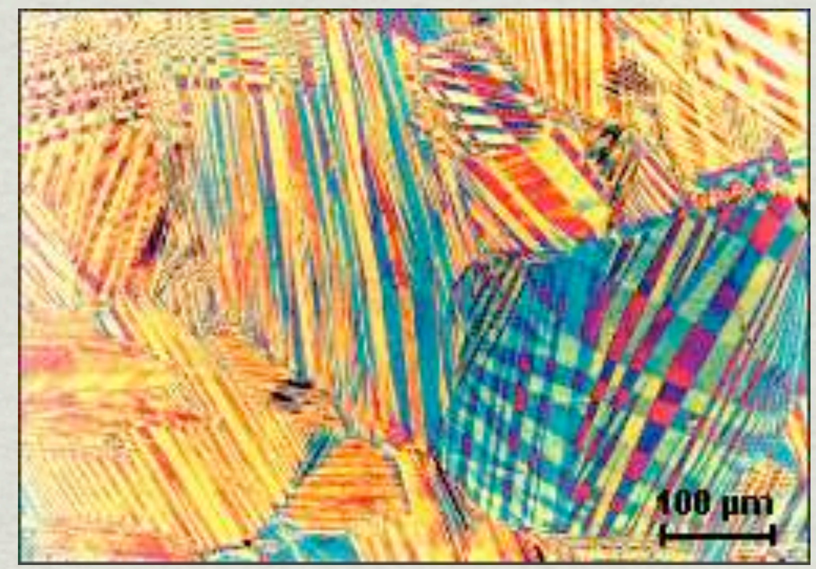
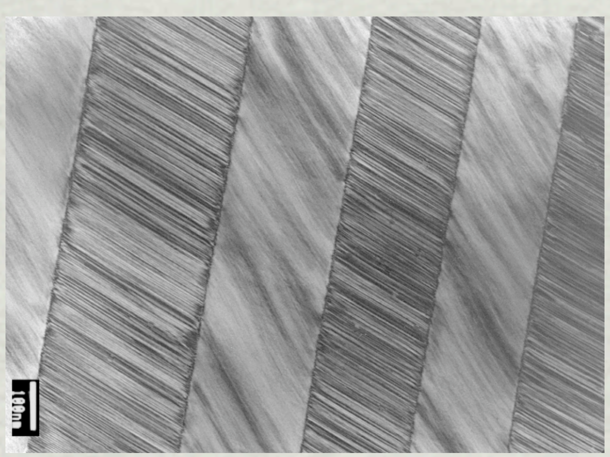
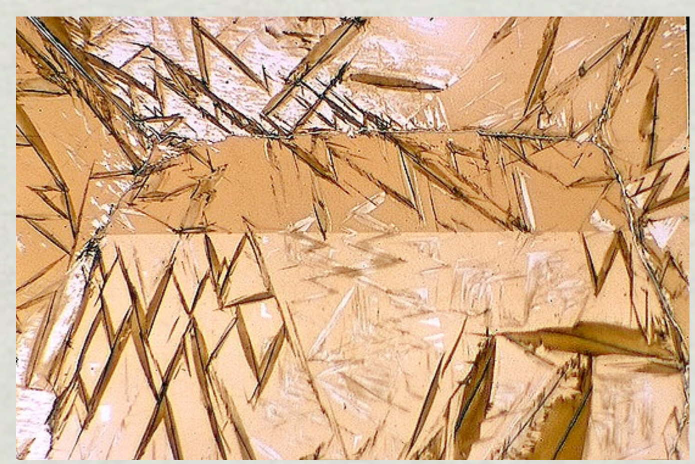







100 µm





- Equilibrium shapes of inclusions.
- Instabilities of solid fronts and dendrites.
- Importance of stress and compatibility: the Eshelby problem.
- Microstructure selection, TTT diagrams, martensite and ferrite.
- Early stage solid solid nucleation process.

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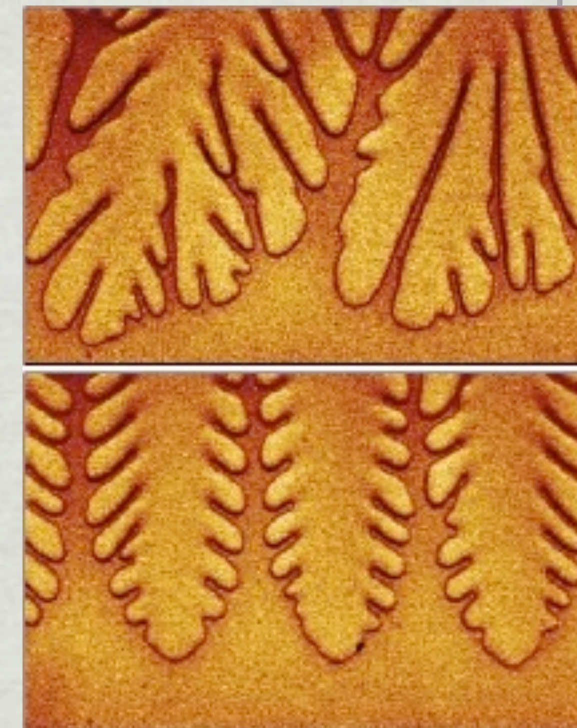

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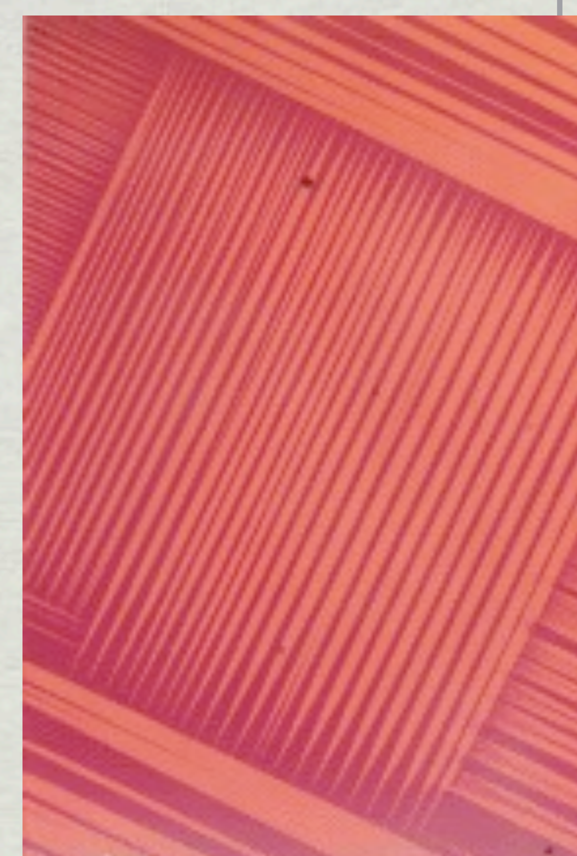


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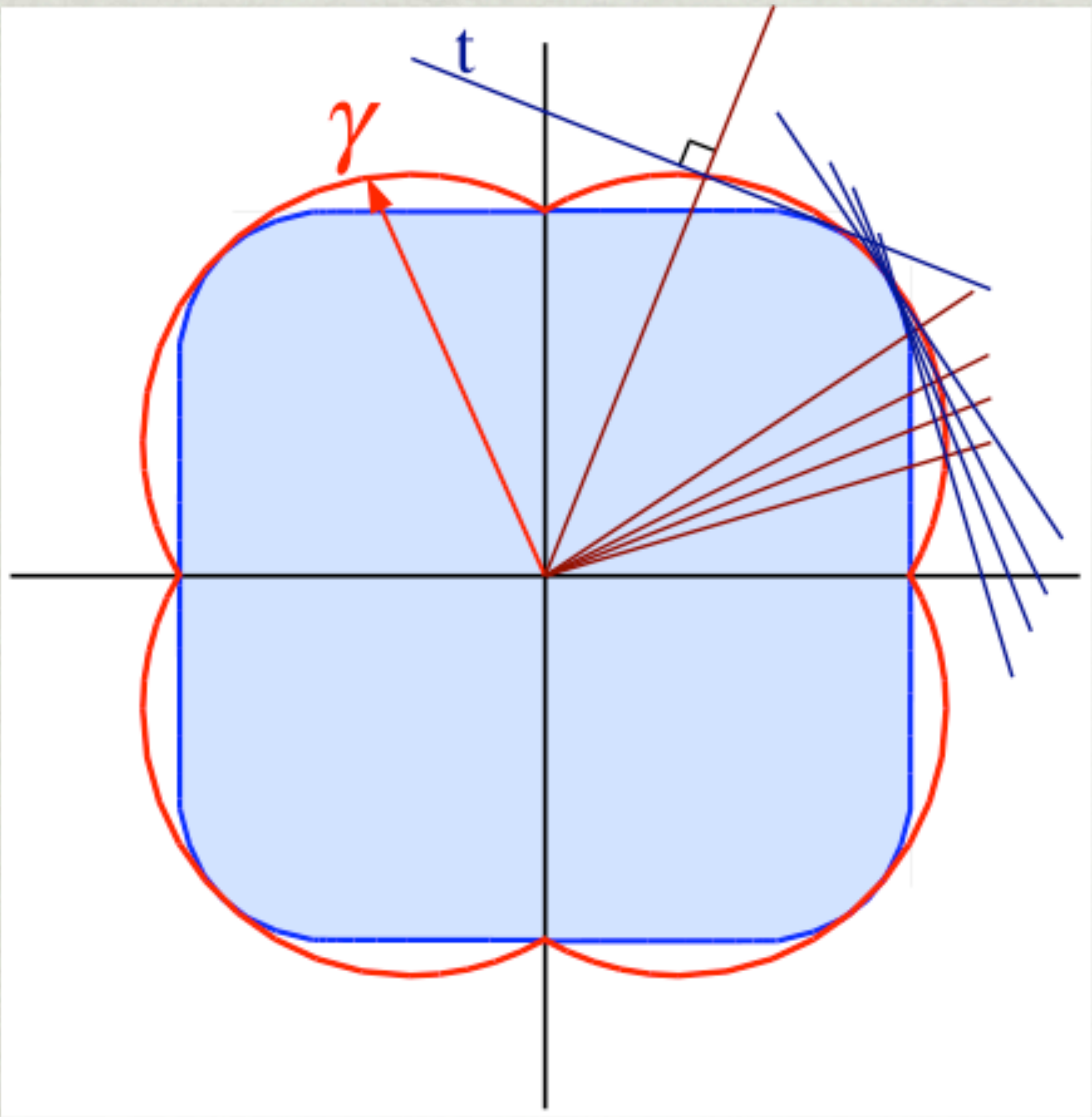
# The Wulff construction




$$\Delta G(N) = \sum_i \gamma_i O_i \quad \textbf{min}$$

$$\delta \Delta G(N) = \sum_i \gamma_i \delta O_i = 0$$

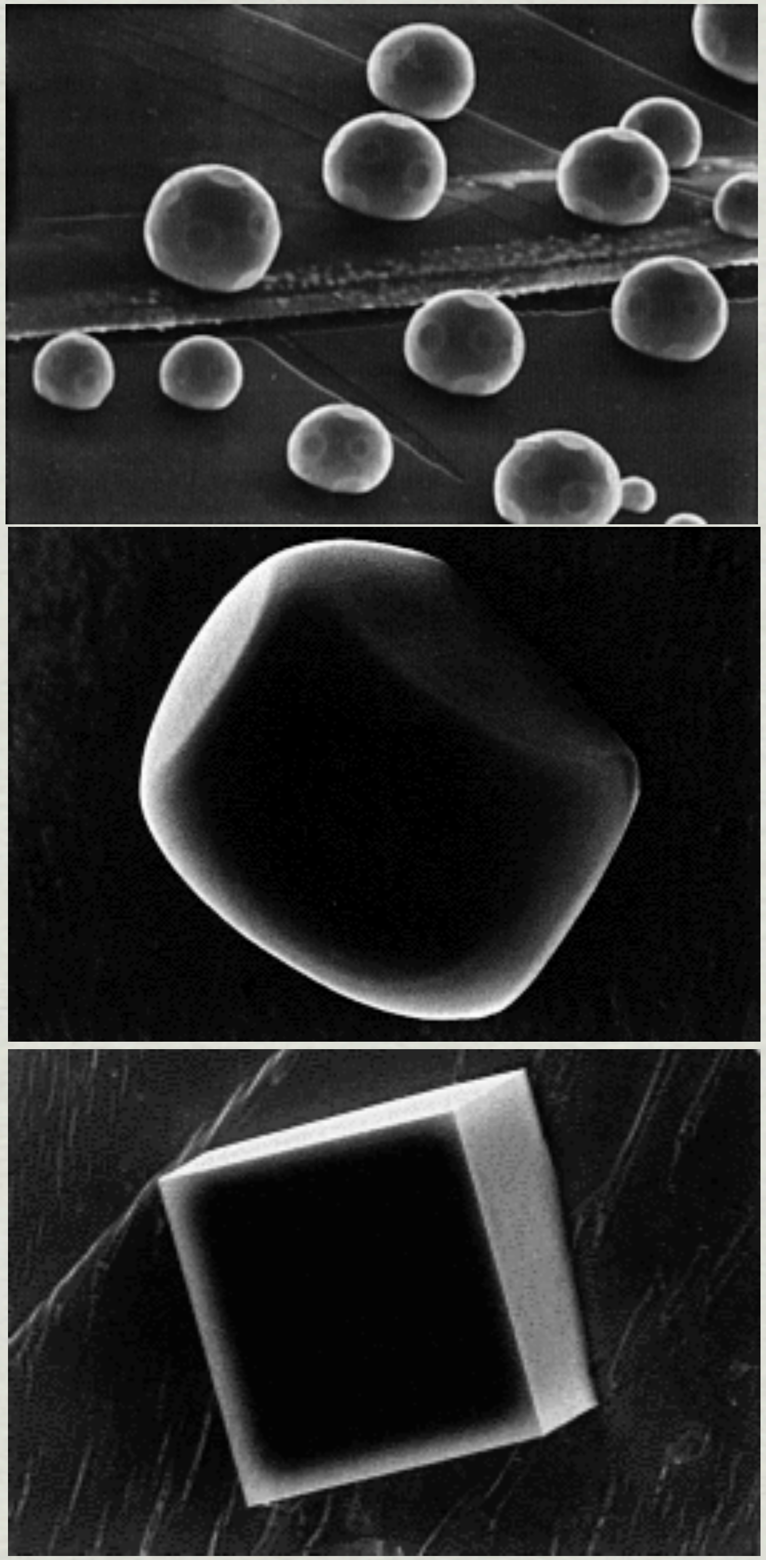
$$\delta V(N) = \delta \sum_i h_i O_i = 0$$

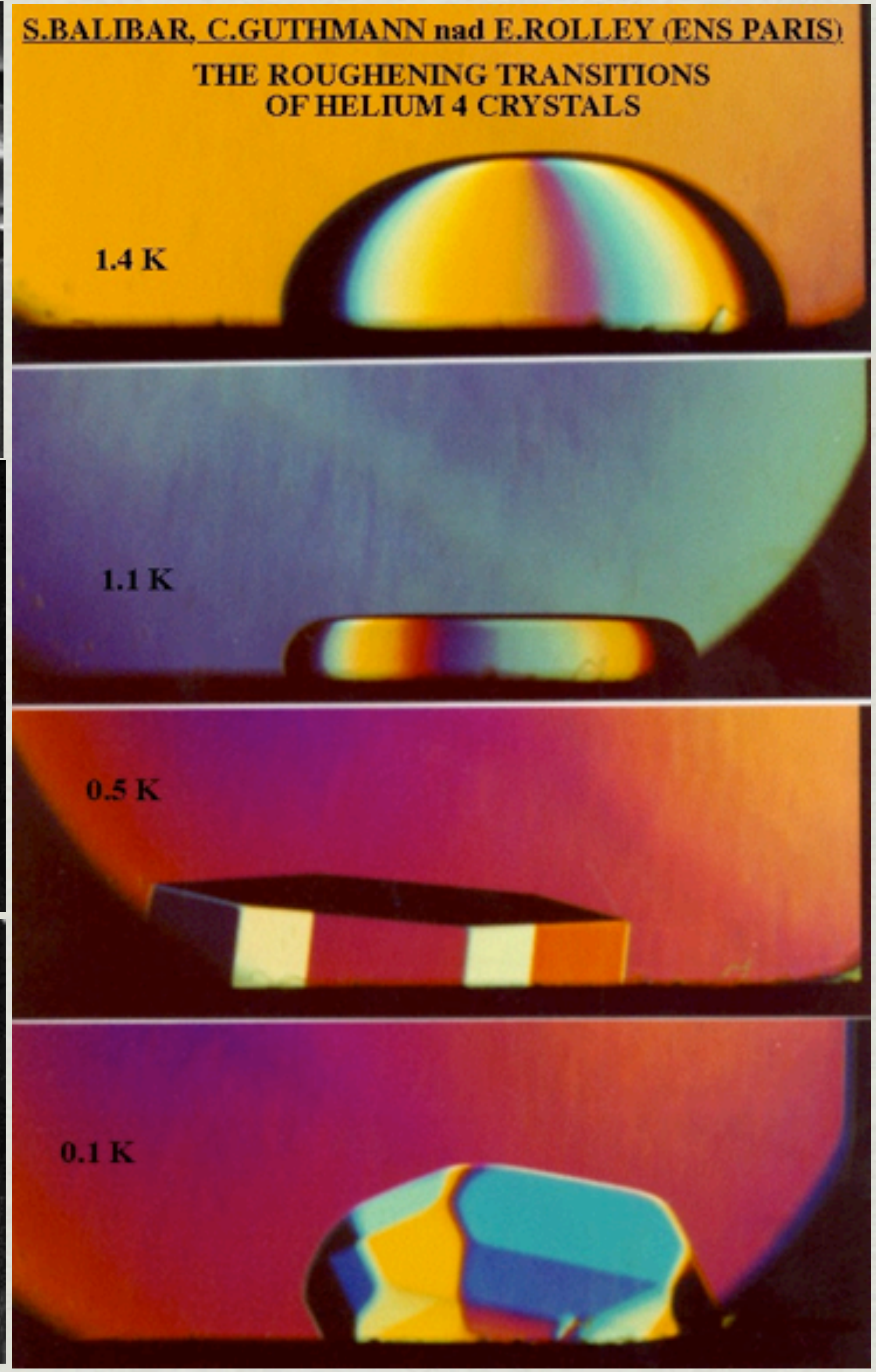
$$\begin{aligned} \delta \sum_i h_i O_i &= \sum_i O_i \delta h_i + \sum_i h_i \delta O_i \\ &= \sum_i h_i \delta O_i \end{aligned}$$

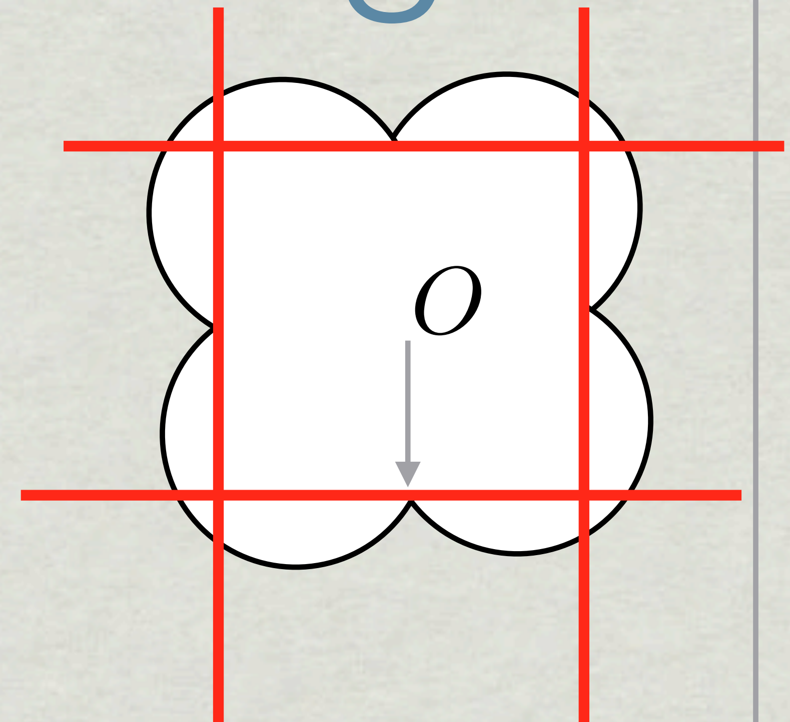
$$\sum_i (h_i - \lambda \gamma_i) \delta O_i = 0$$

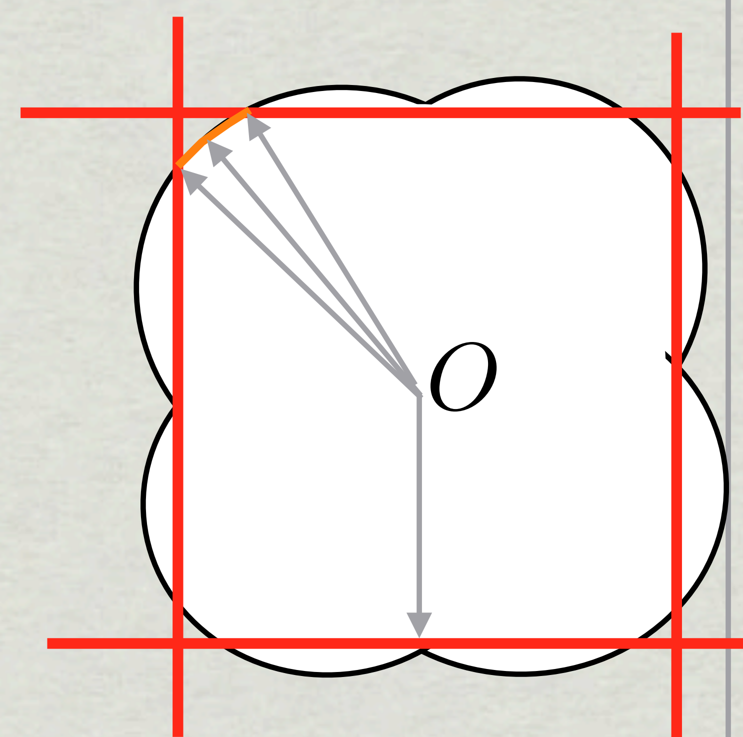
$$\therefore h_i = \lambda \gamma_i$$

# Facets and roughening



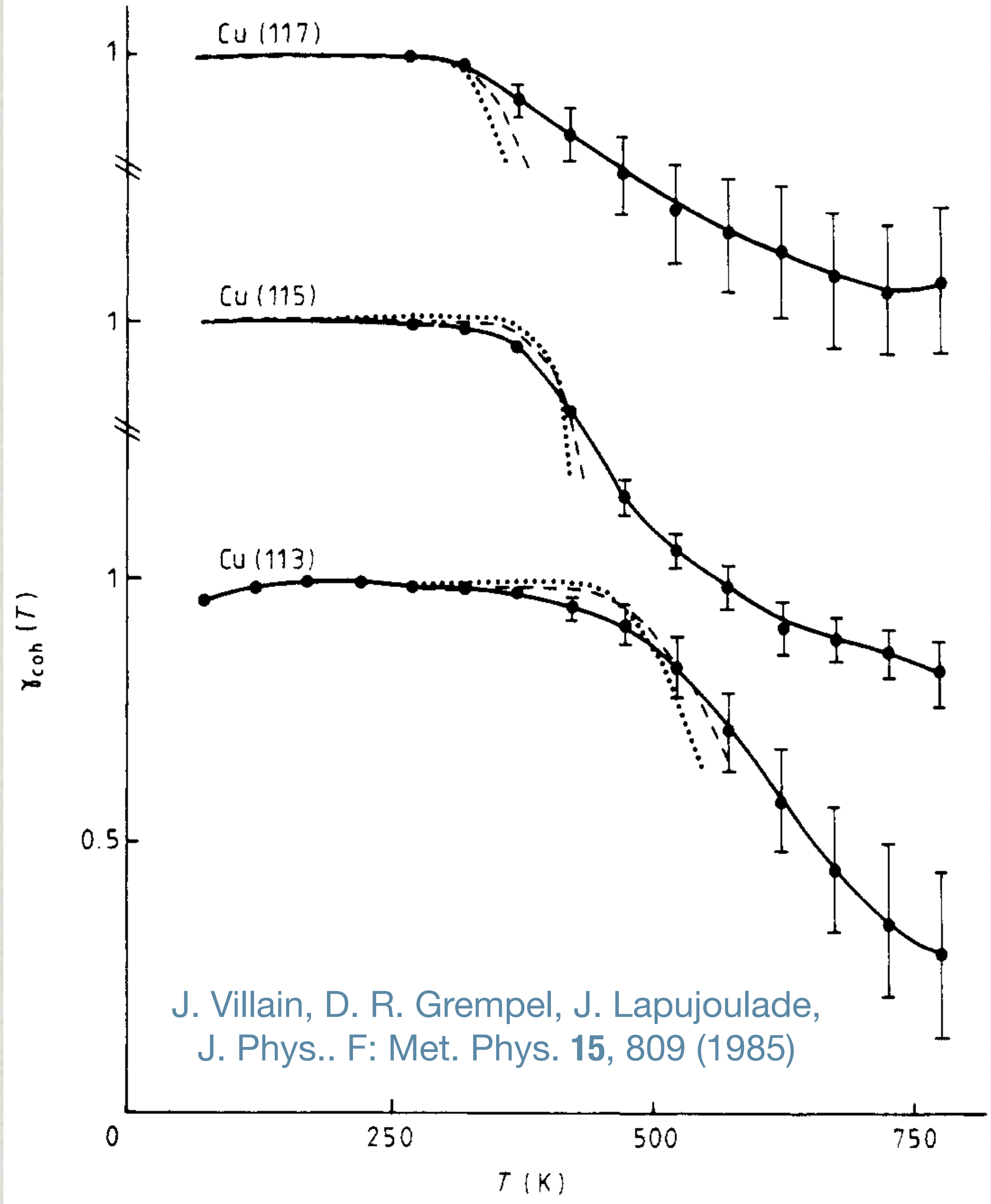


**Universal issues:** Roughening transition in 3D crystals mapped onto the KT transition in X-Y models.
Chui and Weeks, PRB, **14,** 4978 (1976)

**Non-universal properties:** Still need microscopic theory for anisotropic surface energies at finite temperatures

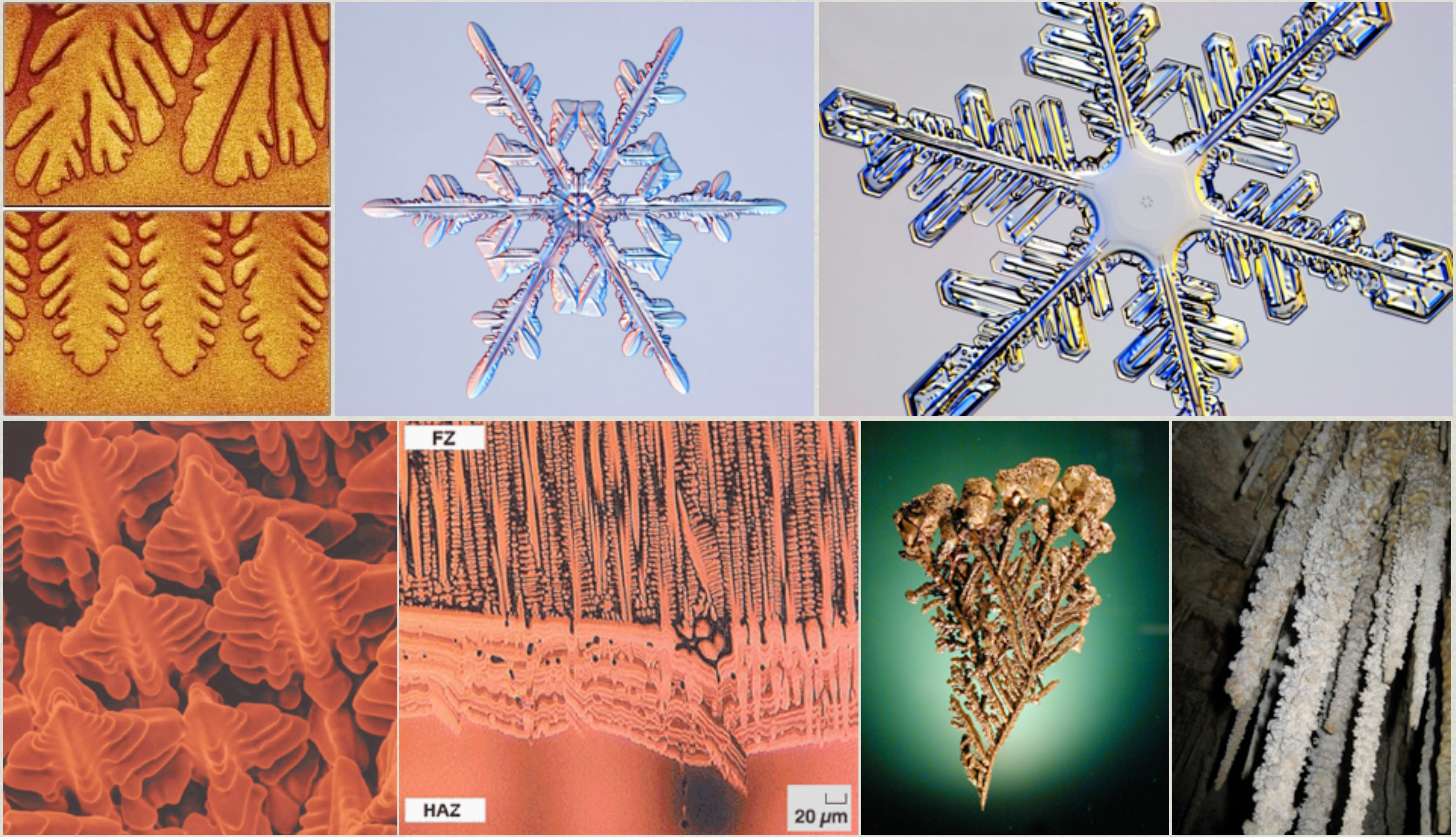



J. Villain, D. R. Grempel, J. Lapujoulade, J. Phys.. F: Met. Phys. **15**, 809 (1985)

**For He crystal surfaces see:**

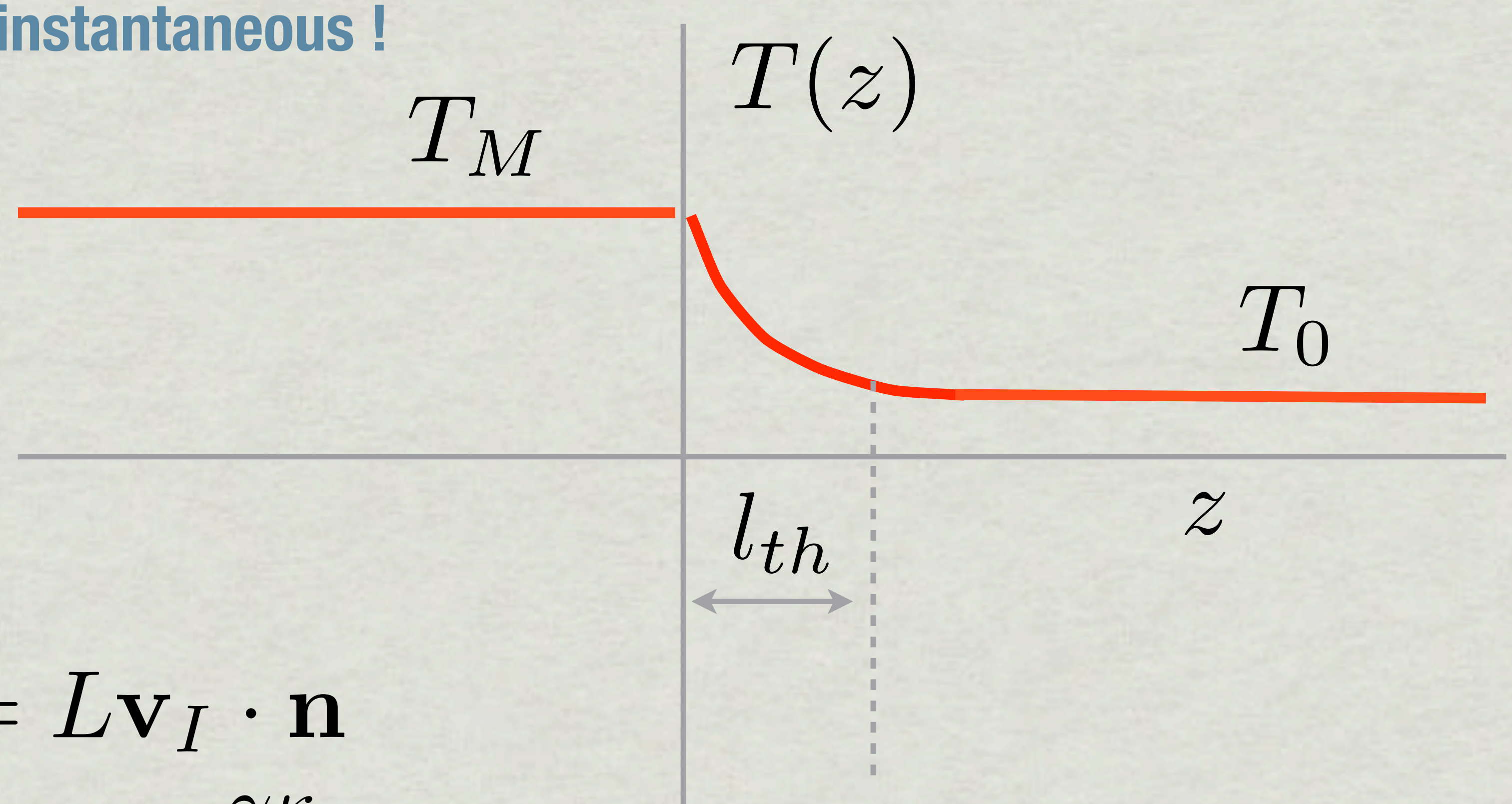
S. Balibar *et al*., Rev. Mod. Phys. **77**, 317–370 (2005)

# Dendritic growth



## THE PLANAR FRONT

The growing front releases latent head, solutes etc. which diffuse away from the front. This diffusion is *not* instantaneous !




*Bulk:*

$$\frac{\partial T_\alpha}{\partial t} = D_\alpha \nabla^2 T_\alpha$$

*Interface:*

$$\mathbf{n} \cdot (K_S \nabla T_S - K_L \nabla T_L) = L \mathbf{v}_I \cdot \mathbf{n}$$

*Boundary condns:*

$$T_S = T_L = T_M(1 - \frac{\gamma\kappa}{\rho L})$$

$$\lim_{z \to +\infty} T(z) = T_0$$

### THE SOLUTION

$$T_L^0(z) = T_0 + (T_M - T_0)\exp(-\frac{z}{l_{th}})$$

$$l_{th} = D_{th}/\mathbf{v}_I \cdot \mathbf{z}$$

needs to satisfy the heat balance condition i.e.

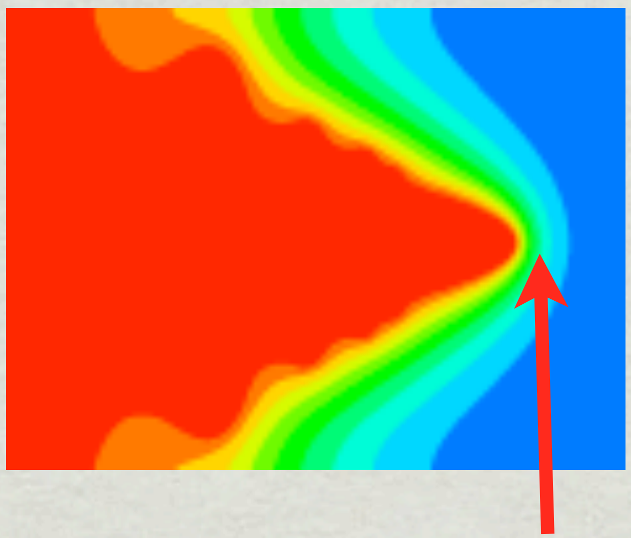
$$L\delta V = C_p(T_M - T_0)\delta V$$

# THE MULLIN-SEKKERKA INSTABILITY

Substitute:

$$\zeta(r_\perp, t) = \zeta_k \, e^{i\mathbf{k}\cdot\mathbf{r}_\perp + \Omega t}$$

$$\delta T(r_\perp, z, t) = \delta T_k \, e^{i\mathbf{k}\cdot\mathbf{r}_\perp + \Omega t}$$



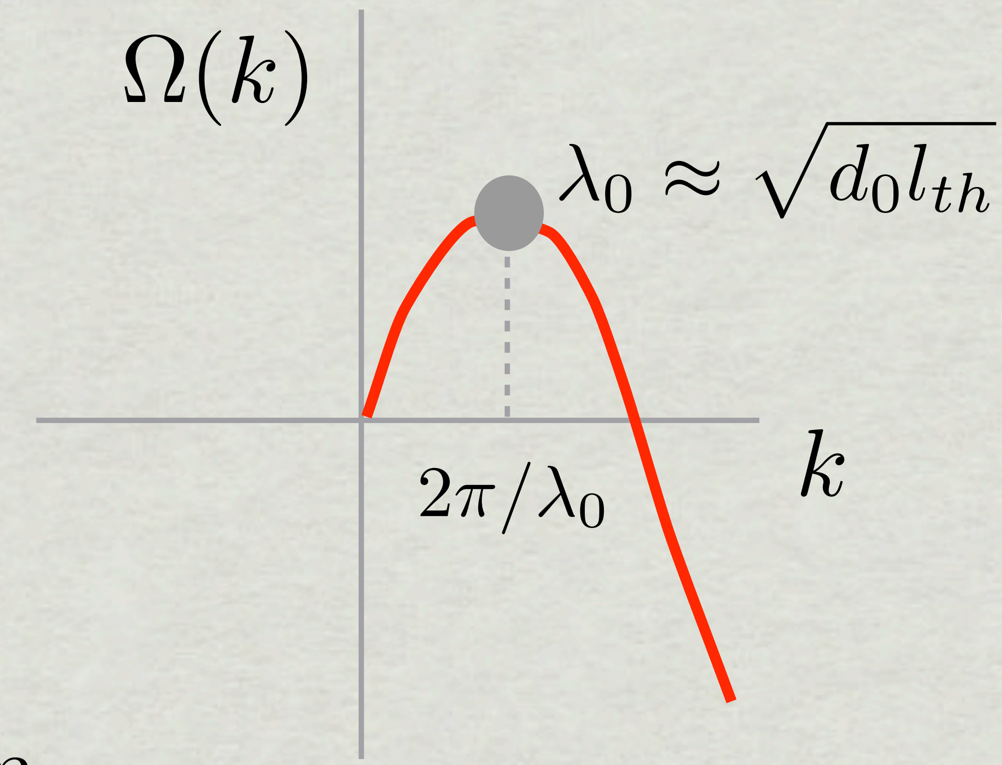

Boundary conditions:

$$\lim_{z\to 0} \delta T_k(z) = 0$$

$$\mathbf{v}_I = \mathbf{V} + \mathbf{z}\partial\zeta/\partial t$$

Obtain:

$$\Omega \approx k|\mathbf{V}|[1 - d_0 l_{th}^2 (1 + \frac{K_S}{K_L}) k^2]$$




$$d_0 = \frac{\gamma T_M C_p}{\rho L^2}$$ (capillary length)

instability wavelength $\lambda_0 \approx 1 - 10\mu\mathrm{m}$

FREE
DENDRITE
GROWTH

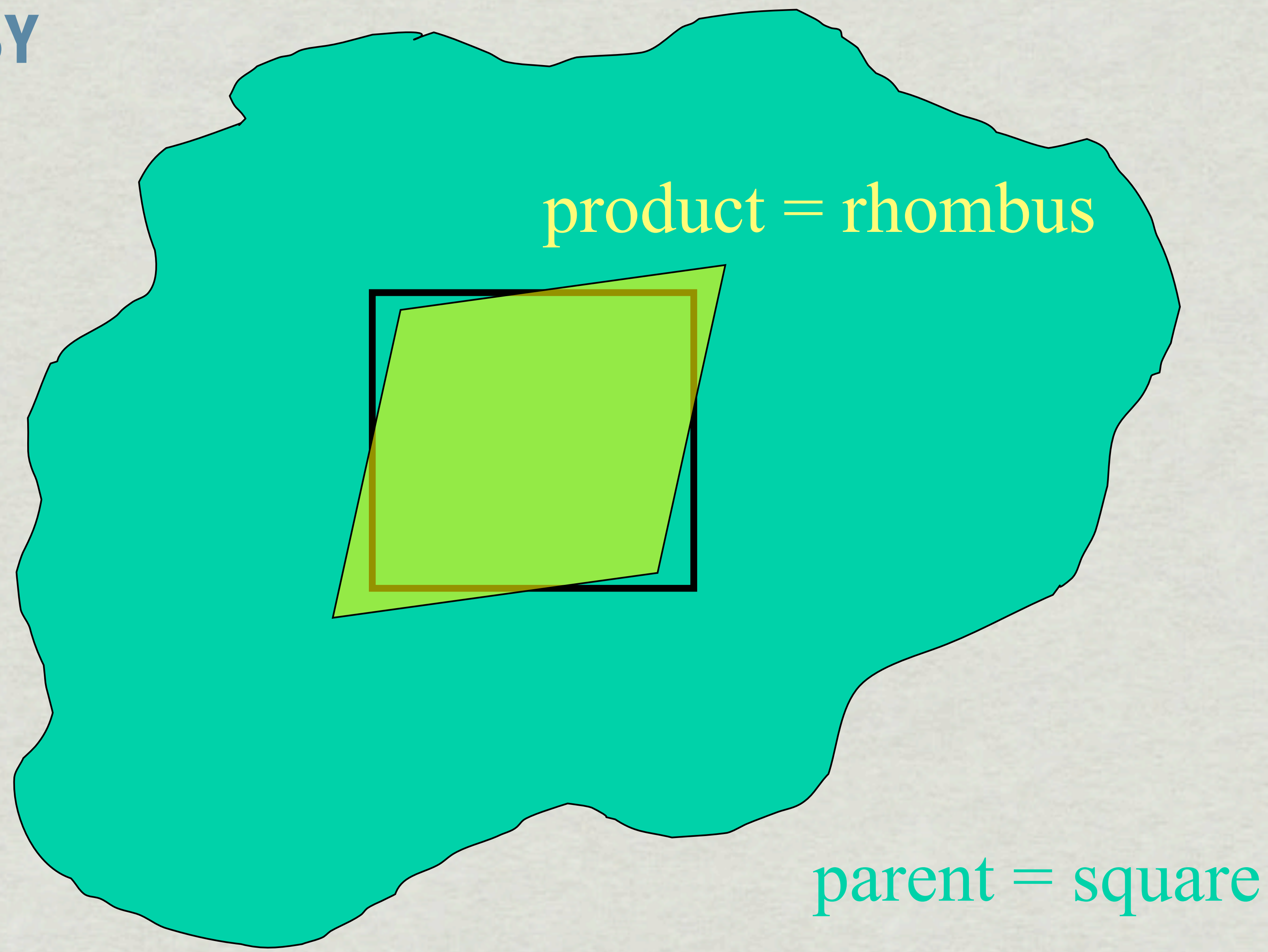
HTTP://LNSM.EU/

# Complications

- Effect of crystalline anisotropy in surface tension and mobilities?
- Effect of rigidity?
- How valid are these equations at atomic scales?

# Incompatible solids

**THE ESHELBY PROBLEM**




K. Bhattacharya, *Microstructure of Martensites* (OUP, 2003)

# ST. VENANT'S COMPATIBILITY CONDITIONS

E. Kröner, *Continuum Theory of Dislocations and Self-Stresses* (Springer-Verlag, Berlin, 1958).

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j}\right)$$

$$\nabla \times (\nabla \times \epsilon)^T = 0$$

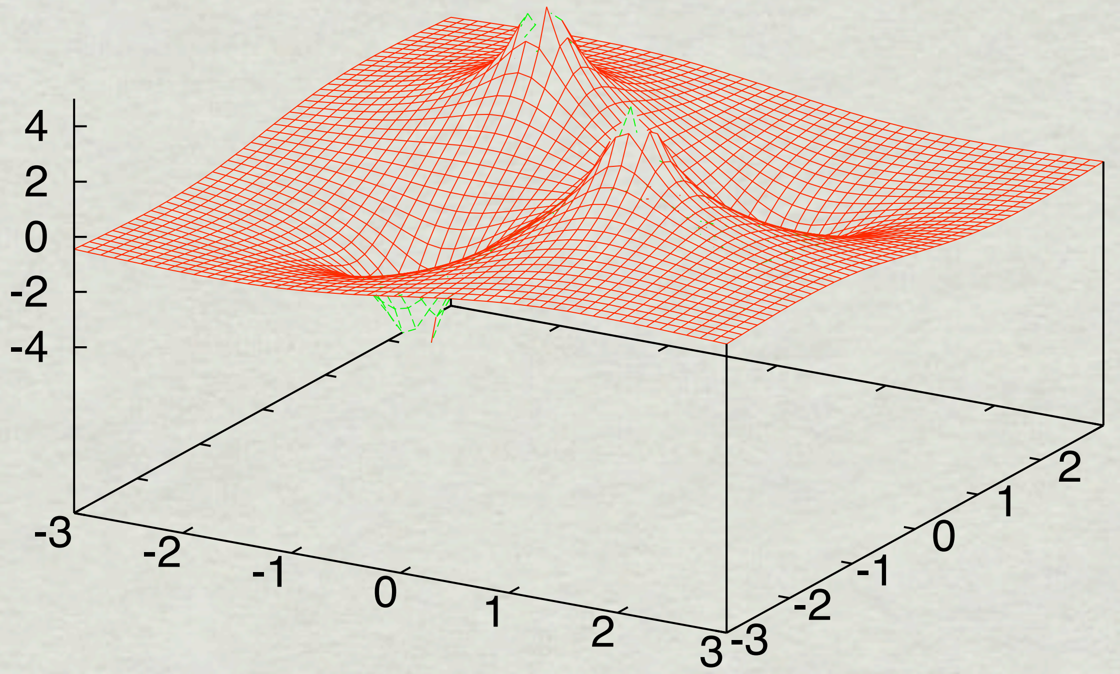
$$\begin{aligned} e_1 &= \epsilon_{xx} + \epsilon_{yy} \\ e_2 &= \epsilon_{xx} - \epsilon_{yy} \\ e_3 &= \epsilon_{xy} \end{aligned}$$

# MECHANICAL EQUILIBRIUM

$$\nabla \cdot \sigma = 0 \text{ with } \sigma_{ij} = C_{ijkl}\epsilon_{kl}$$

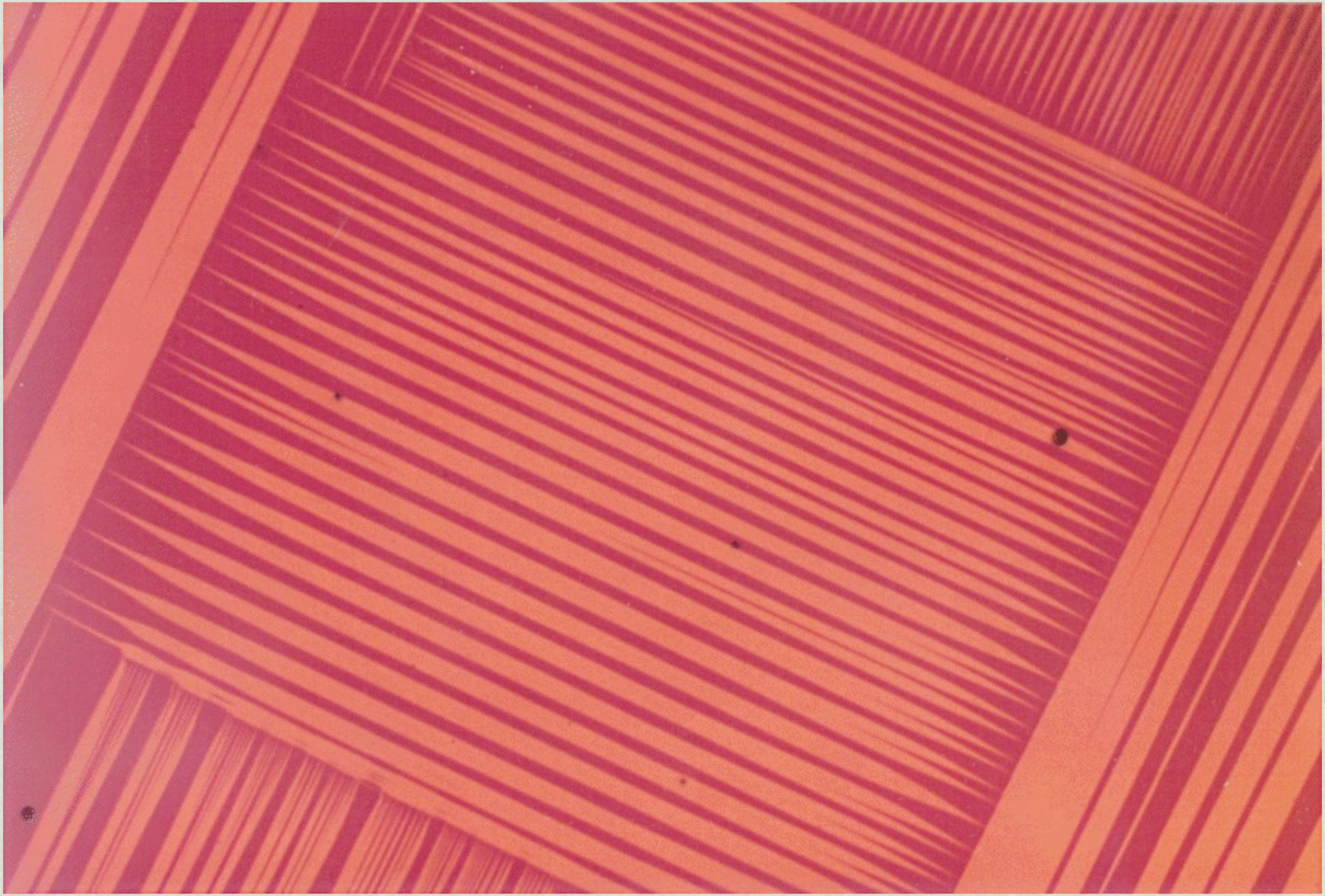
## Obtain:

$$\nabla^2 e_1 = Q_{13}\frac{\partial^2 e_3}{\partial x \partial y}$$




$$\begin{aligned} e_3 &= e_0\Theta(a+x)\Theta(a-x) \\ &\quad \Theta(a+y)\Theta(a-y) \end{aligned}$$

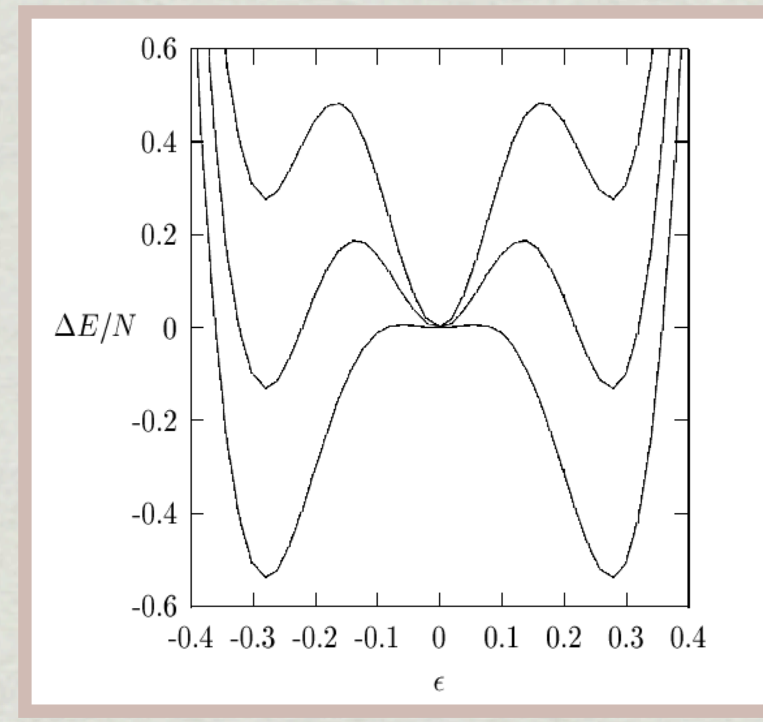
$$e_1 = \frac{e_0}{2}\left[\log\left(\frac{(x-a)^2+(y-a)^2}{(x+a)^2+(y-a)^2} \times \frac{(x+a)^2+(y+a)^2}{(x-a)^2+(y+a)^2}\right)\right]$$



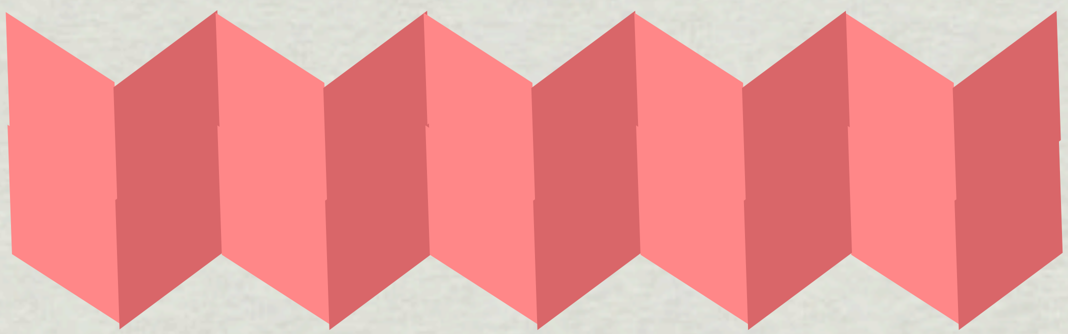
# Landau theory

Lookman T *et al* 2003 *Phys. Rev.* B **67** 024114

$$\mathcal{F} = \int \sum_i [a_i e_i^2 + c_i(\nabla e_i)^2] + b_3 e_3^4 + d_3 e_3^6$$




$L$



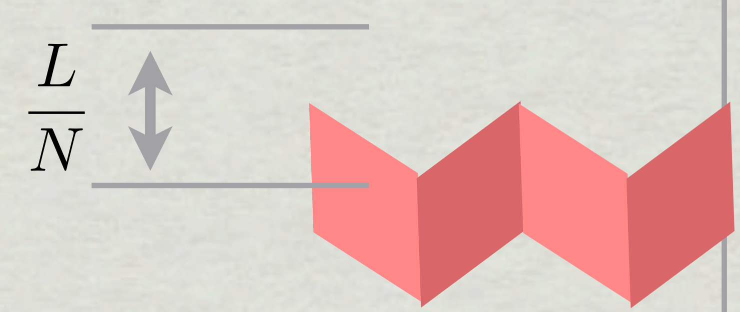
$W$

$N = 10$

$$\mathcal{F} = \Delta\mu LW + 2\gamma_1(L+W) + N\gamma_2 W + \gamma_3 \frac{L^2}{N}$$

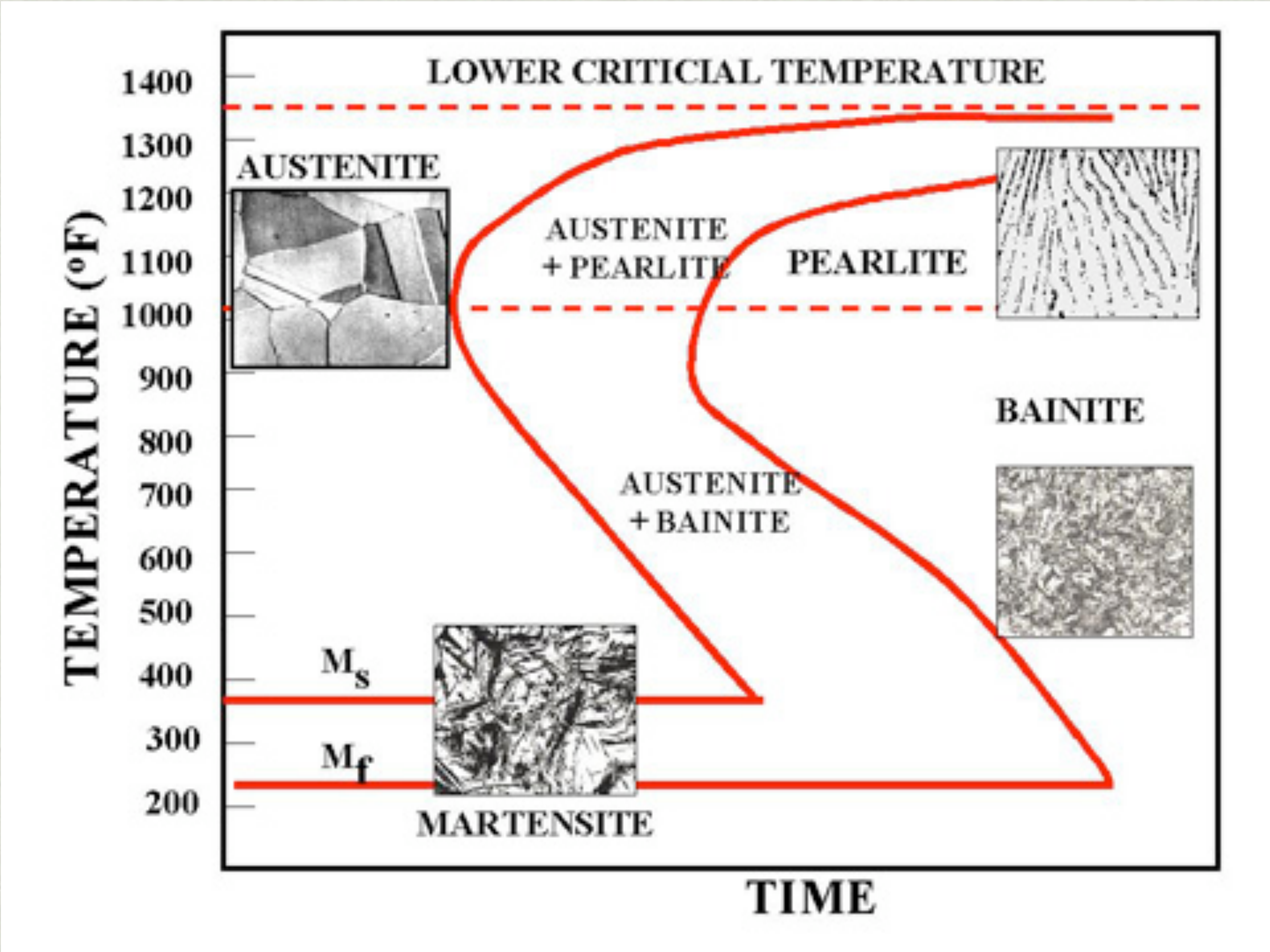
**BULK** **SURFACE** **ELASTIC**

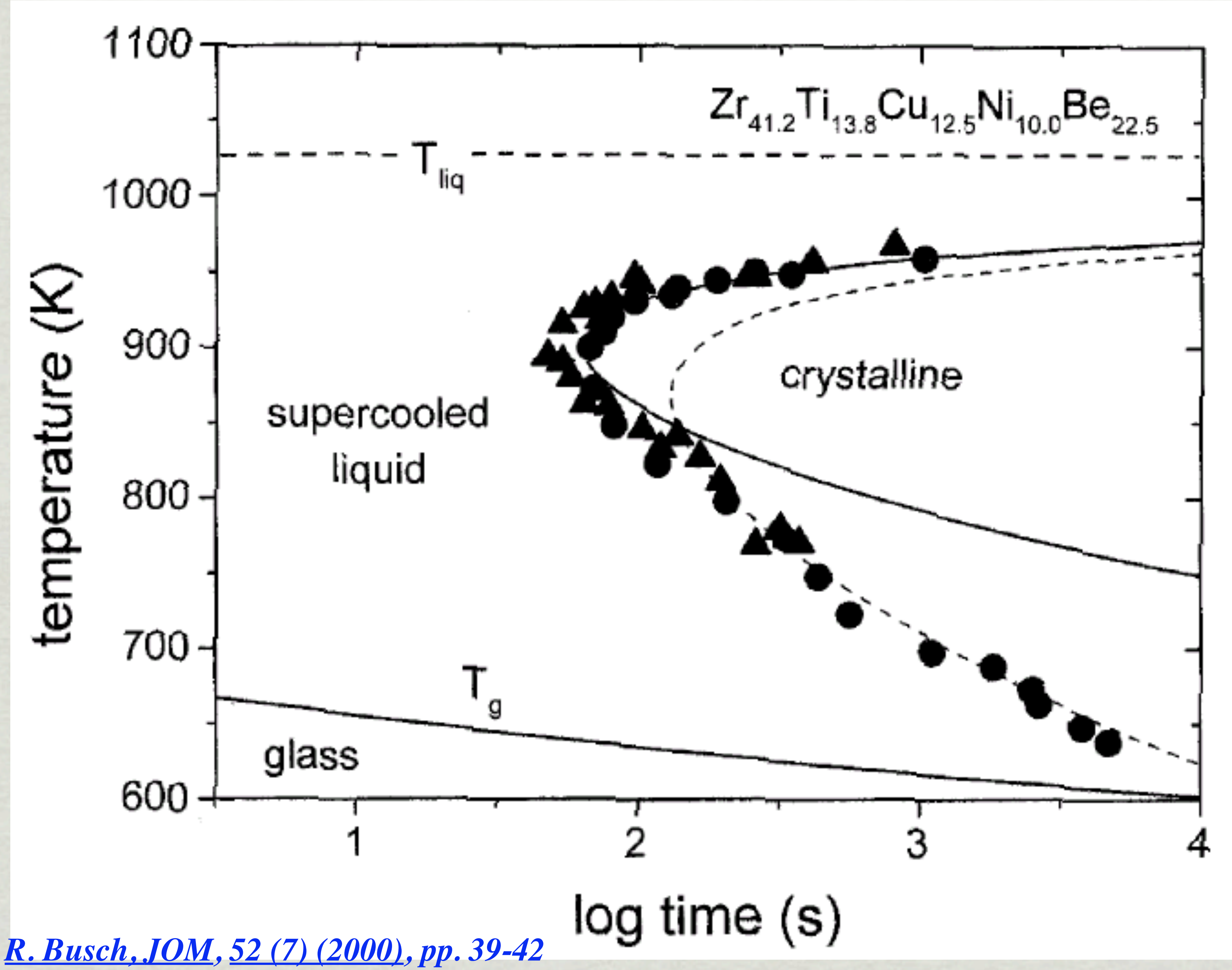
Optimum number of twins? $\frac{L}{N} \sim W^{\frac{1}{2}}$



# Microstructure selection

## NON RIGID INTERFACES: WHEN SOLIDS CAN FLOW






[R. Busch, JOM, 52 (7) (2000), pp. 39-42](#)

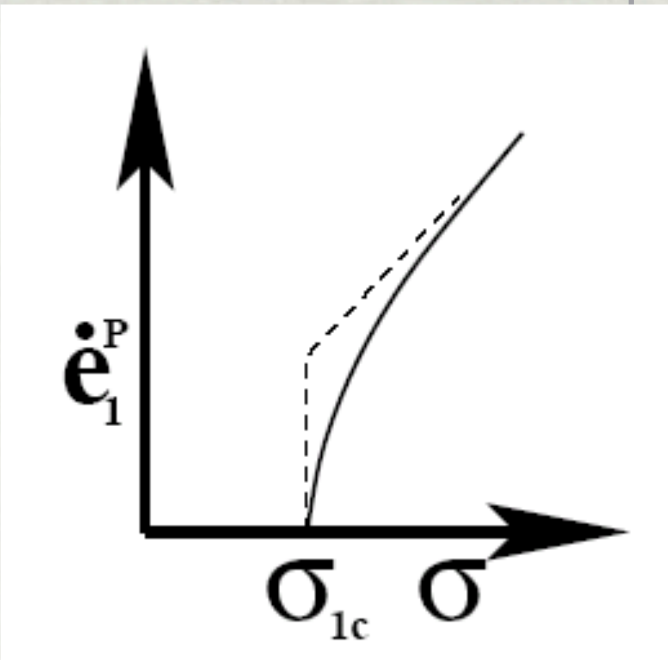
# Incompatibility $\nabla \times (\nabla \times \epsilon)^T \neq 0$

## NON-AFFINE STRAINS

$$\nabla \times (\nabla \times \epsilon)^T \neq 0 = \nabla^2 e_1^P$$

$$e_1 = e_1^A + e_1^P$$

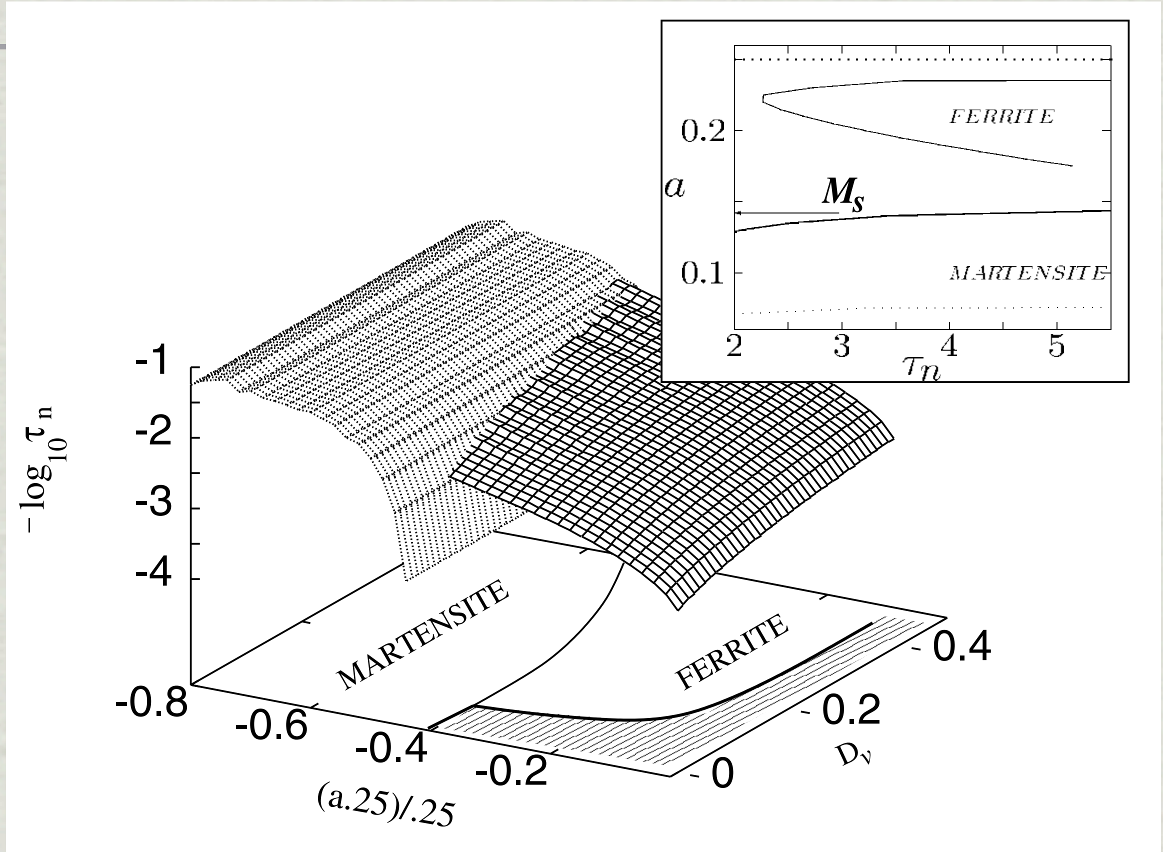
$$\begin{aligned} \dot{e}_1^P &= -\frac{1}{\nu}\int_{-\infty}^{t} \sigma_1(t') e^{-\frac{(t-t')}{\tau}} dt' + c_p \nabla^2 e_1^P & \text{if } |\sigma_1| > \sigma_{1c} \\ &= c_p \nabla^2 e_1^P & \text{otherwise} \end{aligned}$$




A. Paul *et al. J. Phys. Condens. Matt.* **20**, 365211 (2008)

- $e_1^P$ *screens* elastic interactions by reducing stresses
- for small $e_1^P$ L/N is still ~ $W^{1/2}$ but with reduced pre-factor
- large $e_1^P$ destroys twin structure completely
- How does non-affineness influence nucleation?
- Growth dynamics

M. Rao and SS, *PRL.* **91**, 045502, (2003)

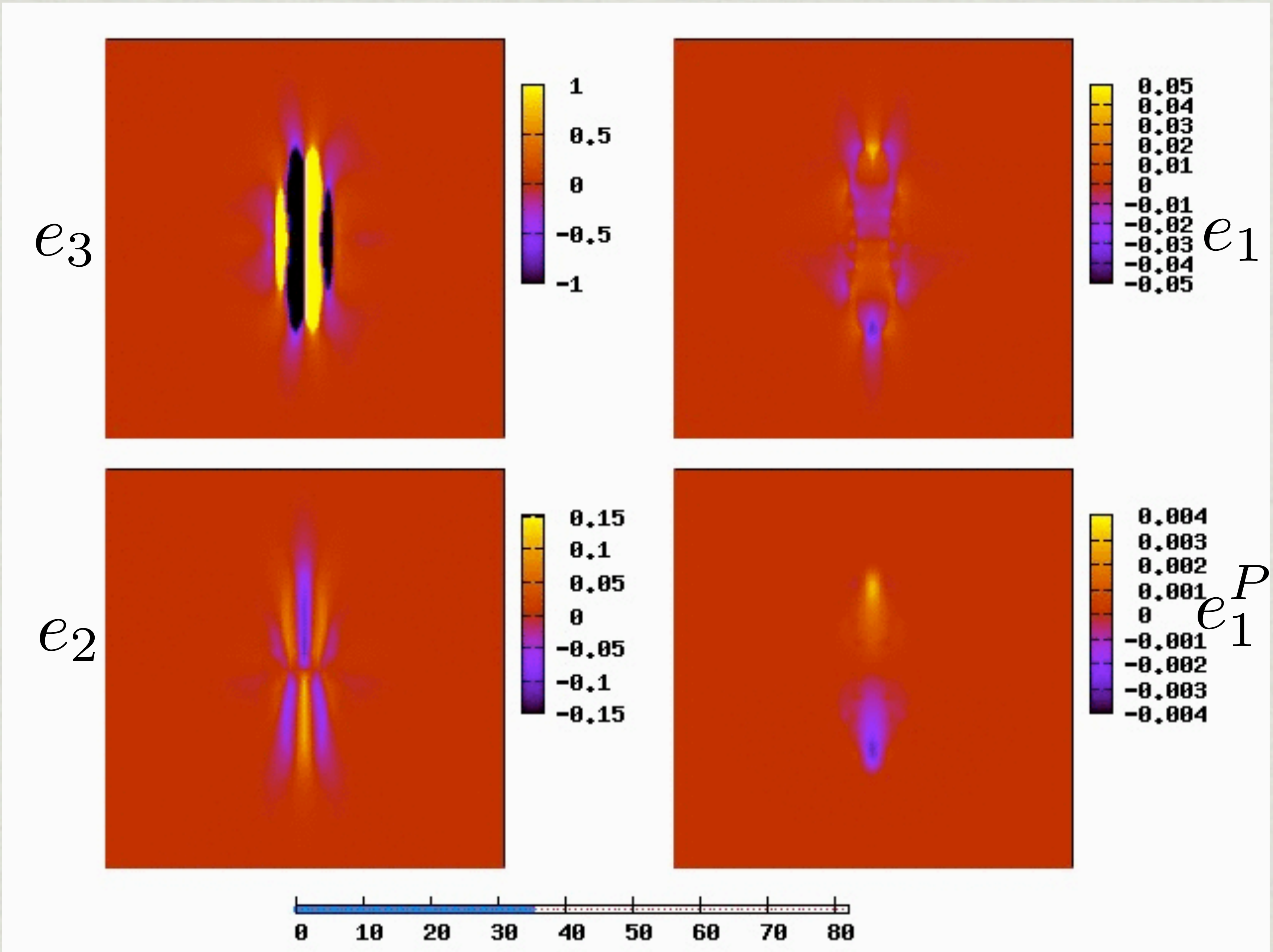



- Consider only N=1 and N=2
- Find barrier height in L-W plane
- Barrier depends on time through $e_1^P(t)$
- Mean first passage time obtained by solving Kramers equation $\tau = \Gamma^{-1} \exp(-\beta \Delta E(\tau))$
- Obtain TTT curve between ferrite (N=1) and martensite (N=2) nuclei.
- Final phase depends on time scale of barrier relaxation vs. MFPT

$e_3$ $e_1$

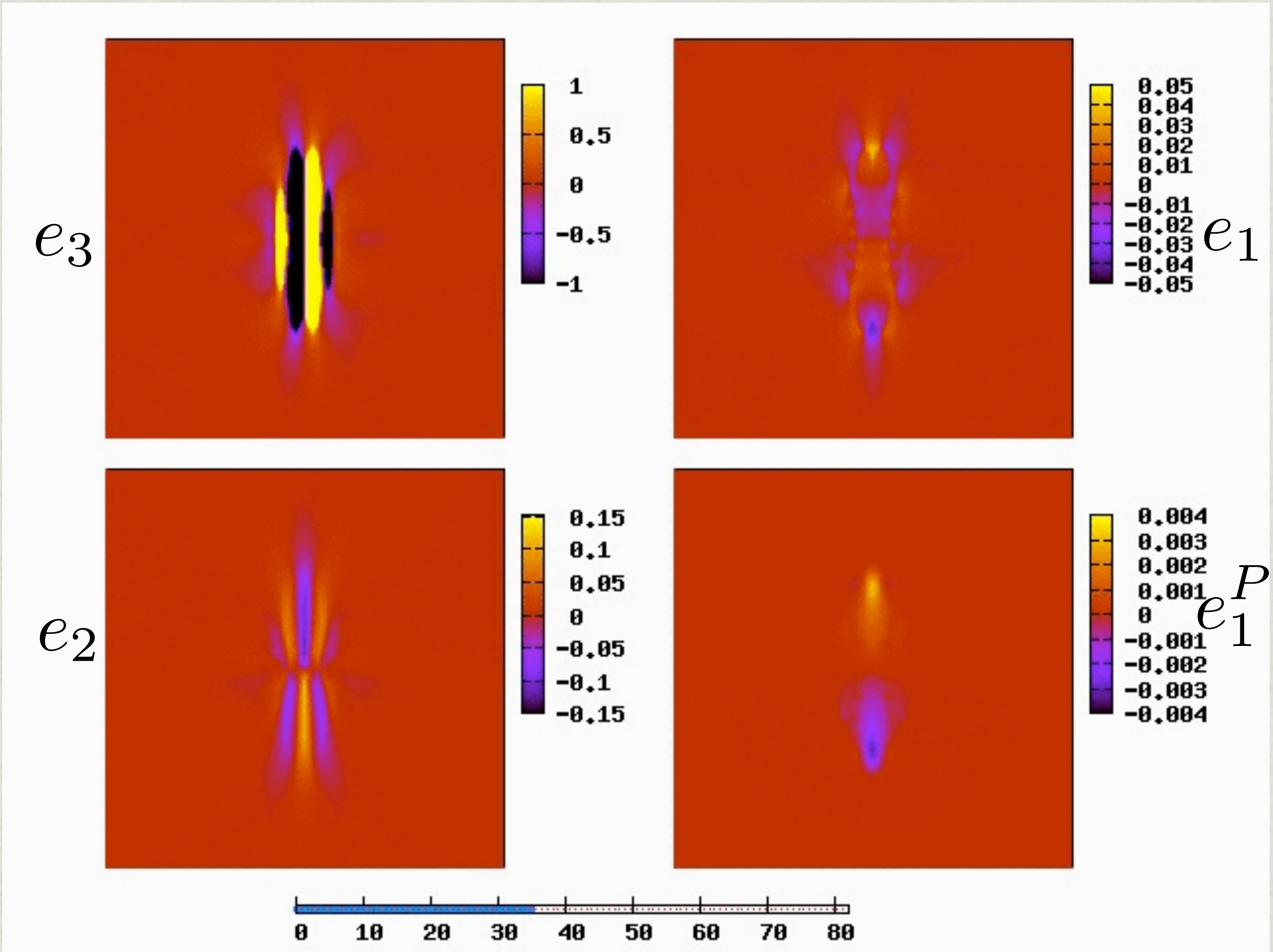
$e_2$ $e_1^P$

A. Paul *et al.* *J. Phys. Condens. Matt.* **20**, 365211 (2008)




A. Paul *et al. J. Phys. Condens. Matt.* **20**, 365211 (2008)

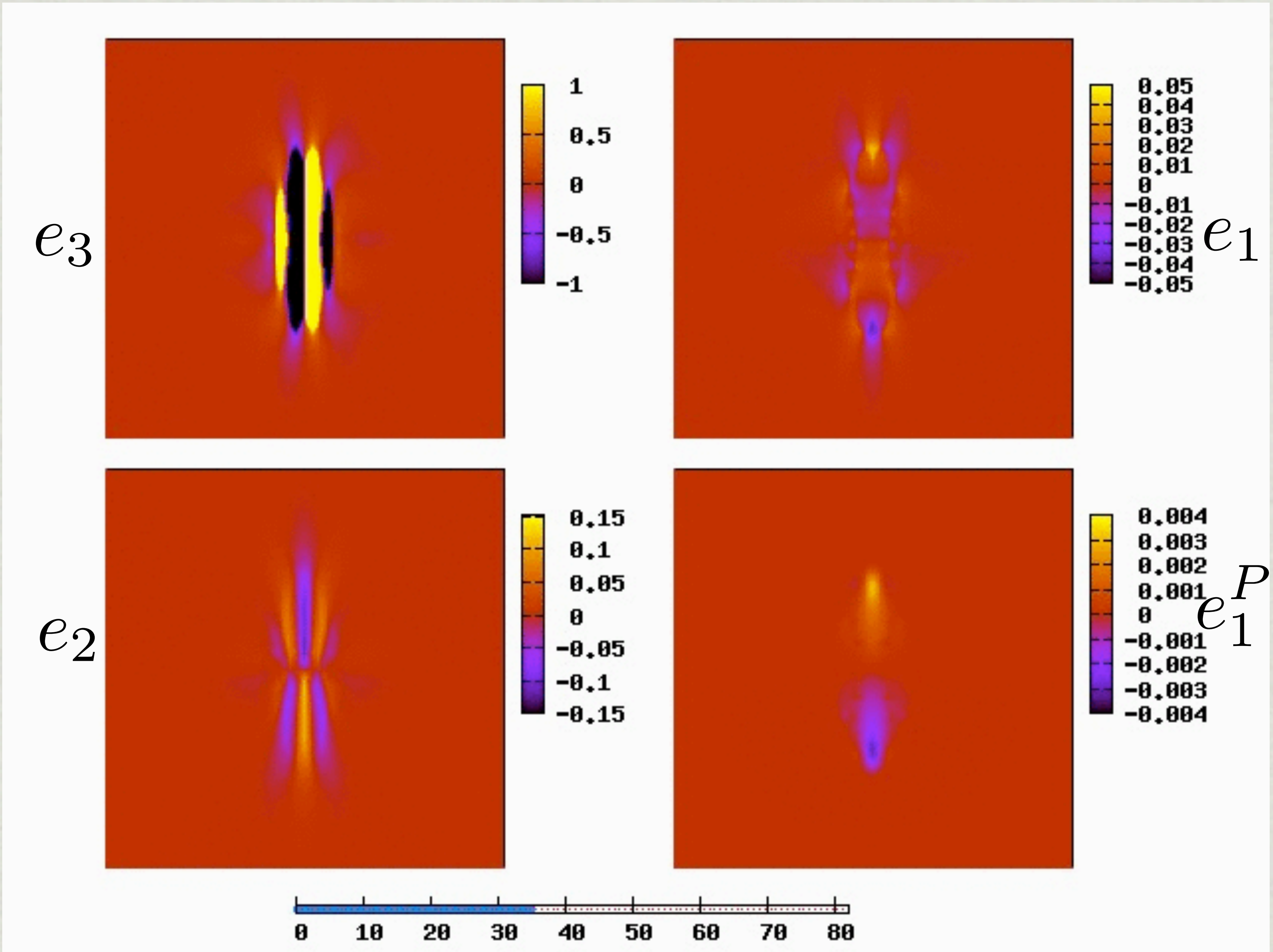
$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{u}}}\right) = \frac{\partial L}{\partial \mathbf{u}} - \frac{\partial R}{\partial \dot{\mathbf{u}}},$$




A. Paul *et al. J. Phys. Condens. Matt.* **20**, 365211 (2008)

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{u}}}\right) = \frac{\partial L}{\partial \mathbf{u}} - \frac{\partial R}{\partial \dot{\mathbf{u}}},$$

$$L[e_i, e_i^p, \dot{u}_x, \dot{u}_y] = \sum_{\mathbf{r}} \left[\frac{m}{2}(\dot{u}_x^2 + \dot{u}_y^2) - F[e_i(\mathbf{r}), e_i^P(\mathbf{r})]\right]$$



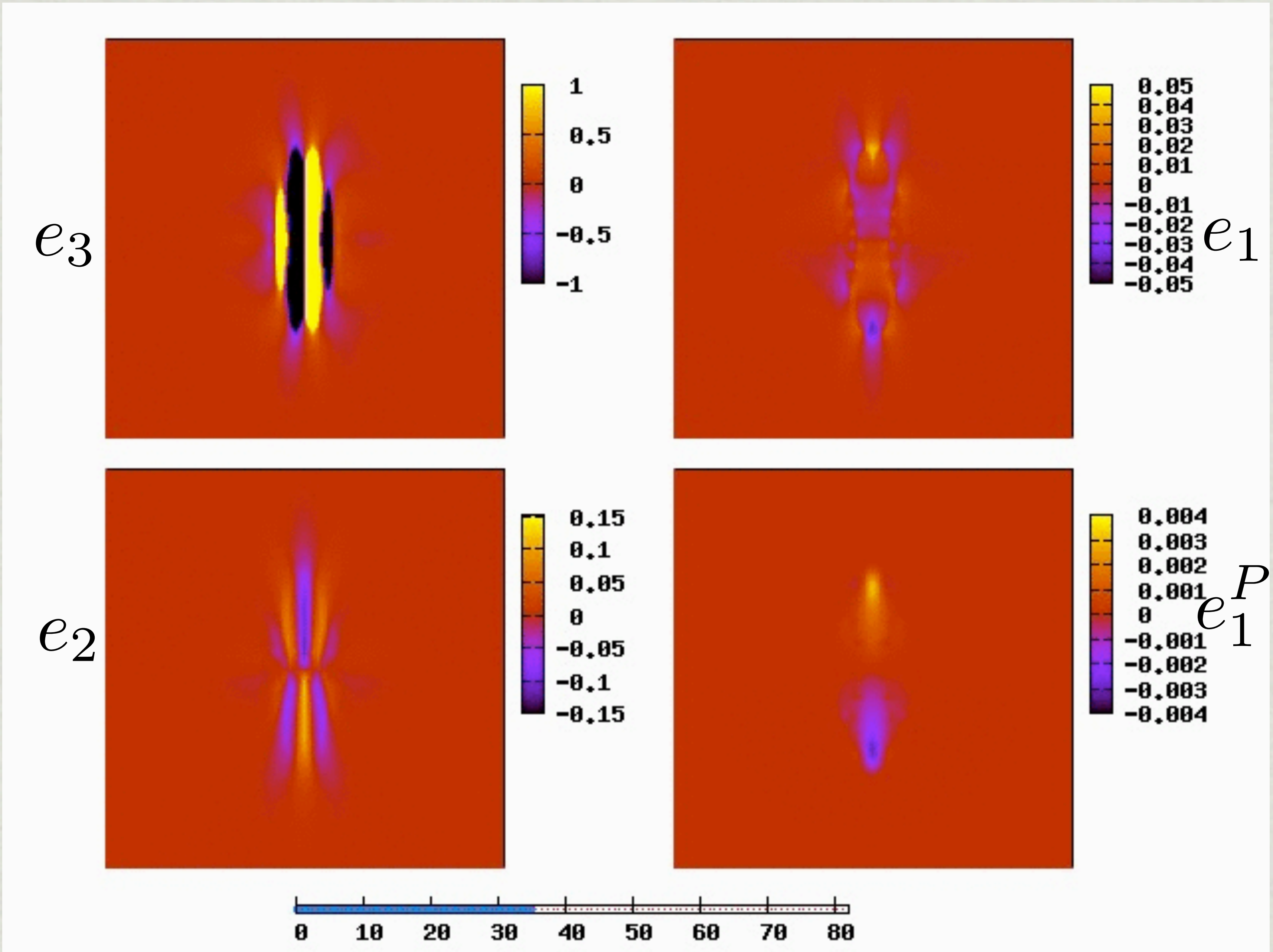

$e_3$ $e_1$ $e_2$ $e_1^P$

A. Paul *et al.* *J. Phys. Condens. Matt.* **20**, 365211 (2008)

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{u}}}\right) = \frac{\partial L}{\partial \mathbf{u}} - \frac{\partial R}{\partial \dot{\mathbf{u}}},$$

$$L[e_i, e_i^p, \dot{u}_x, \dot{u}_y] = \sum_{\mathbf{r}} \left[\frac{m}{2}(\dot{u}_x^2 + \dot{u}_y^2) - F[e_i(\mathbf{r}), e_i^P(\mathbf{r})]\right]$$

$$R[e_i] = \frac{1}{2}\sum_{\mathbf{r}} \left[\gamma_1 \dot{e}_1^2(\mathbf{r}) + \gamma_2 \dot{e}_2^2(\mathbf{r}) + \gamma_3 \dot{e}_3^2(\mathbf{r})\right]$$




A. Paul *et al.* *J. Phys. Condens. Matt.* **20**, 365211 (2008)

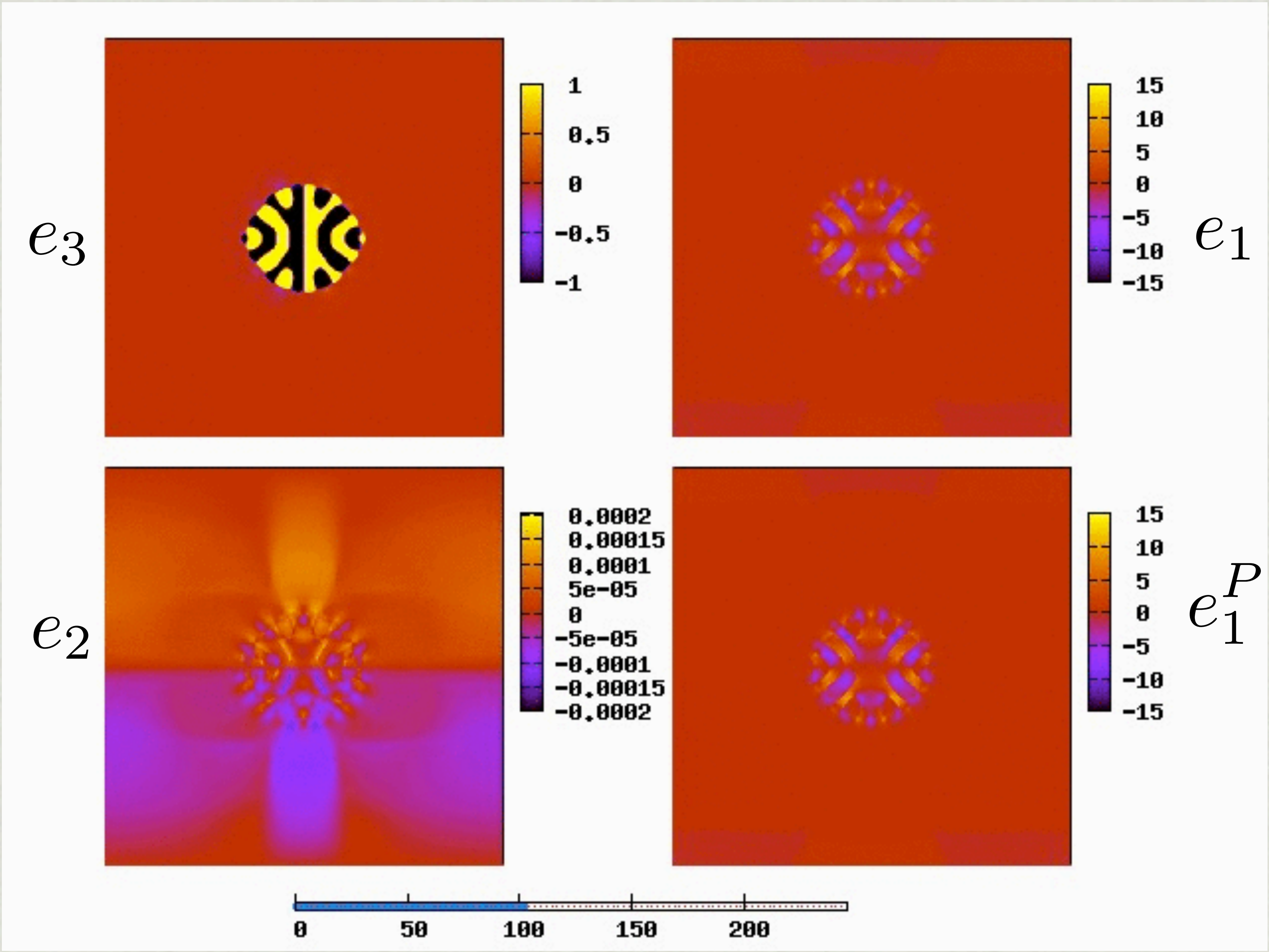
$e_3$

$e_1$

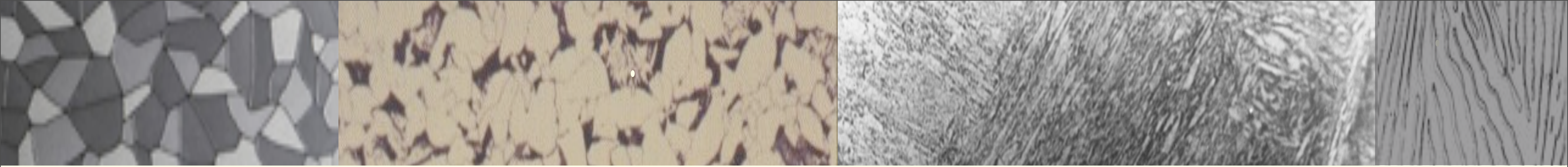
$e_2$

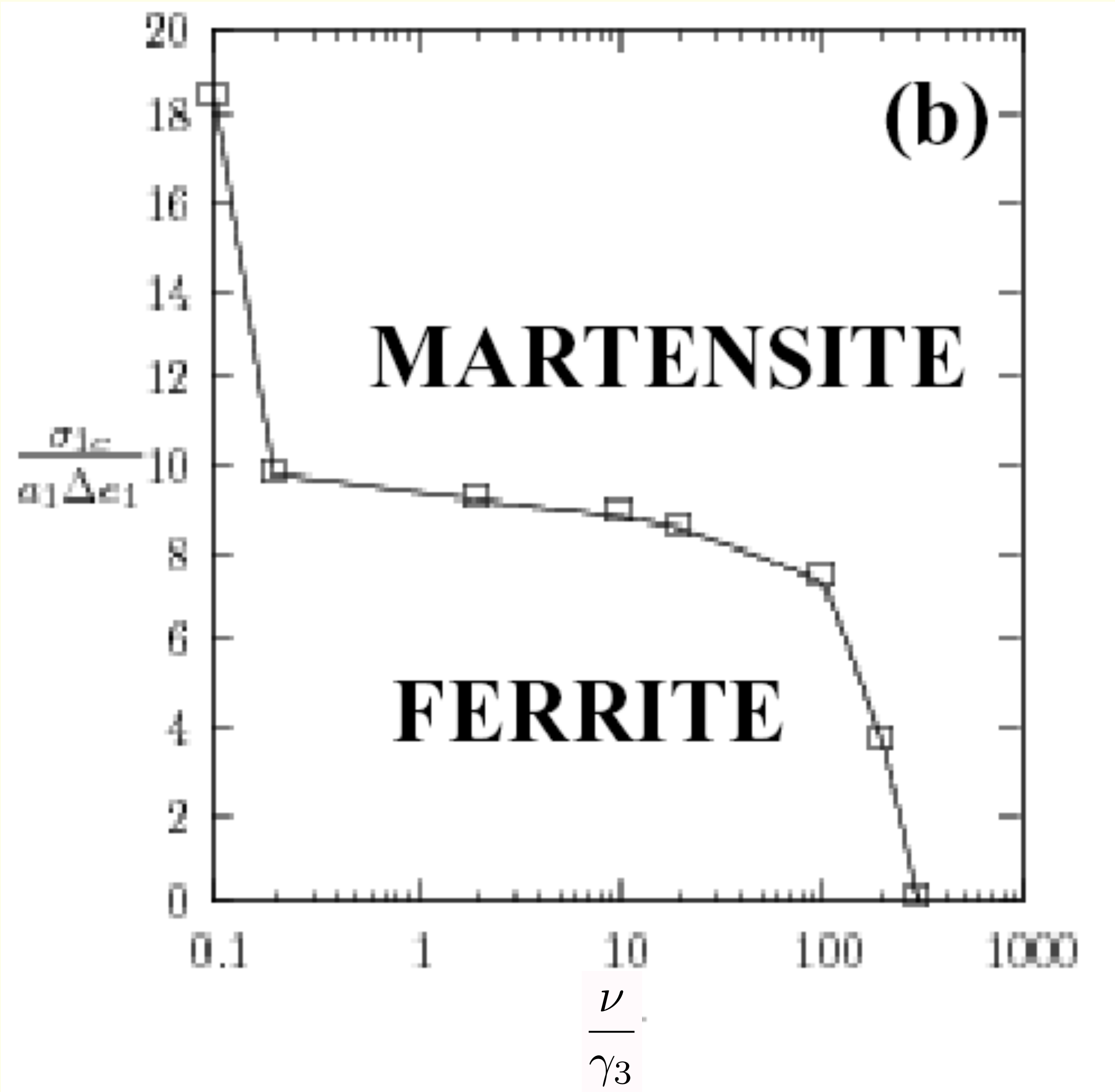
$e_1^P$

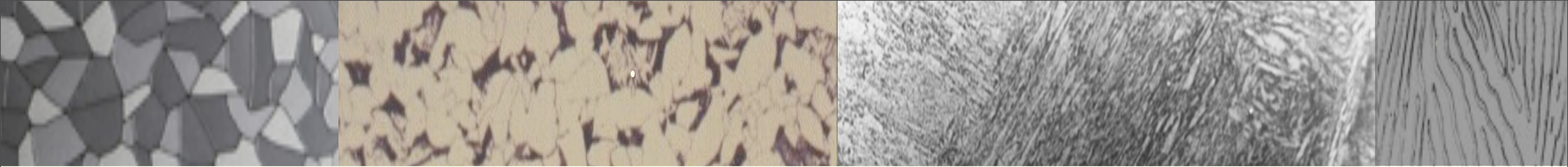
A. Paul *et al. J. Phys. Condens. Matt.* **20**, 365211 (2008)

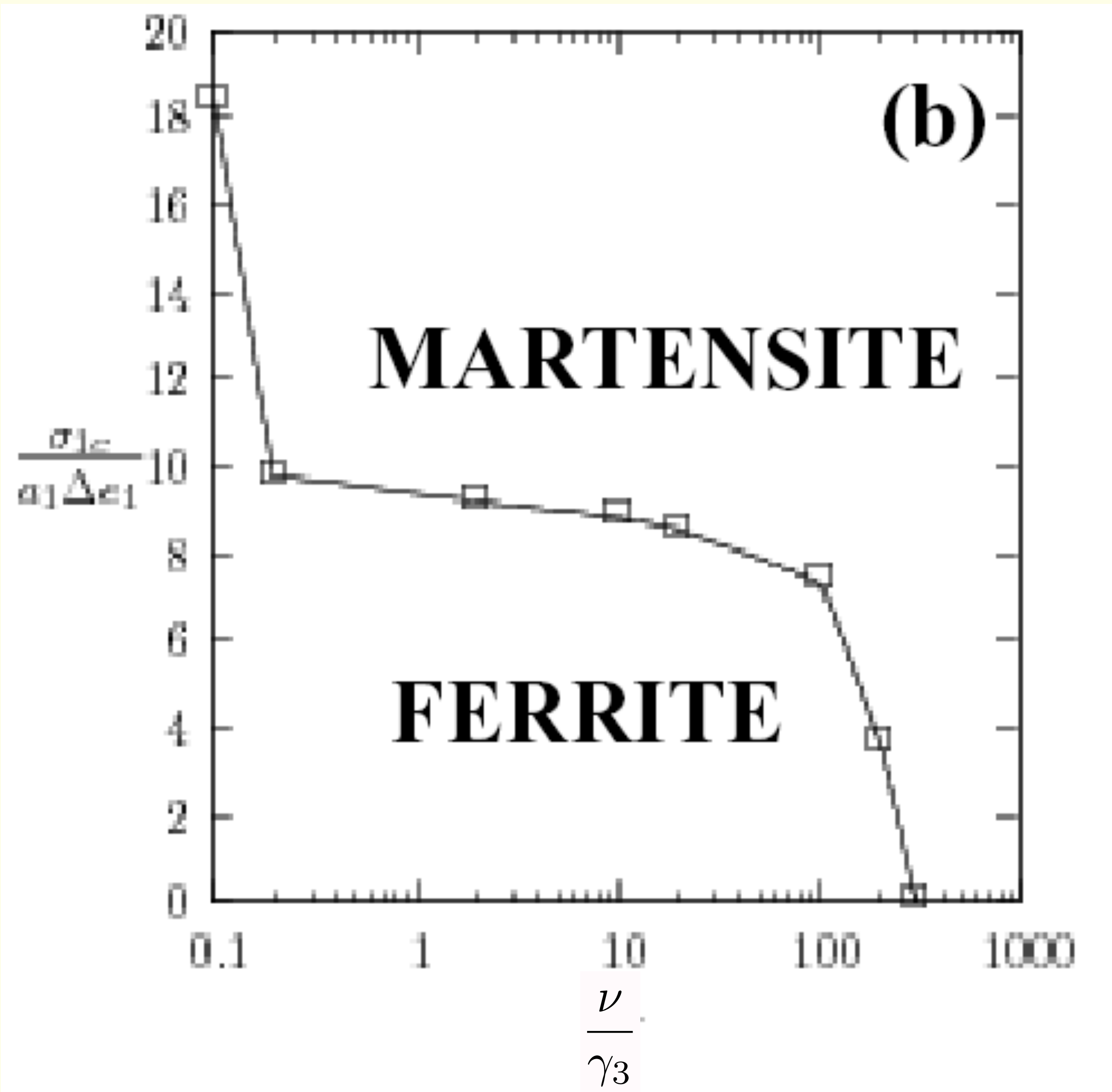



A. Paul *et al. J. Phys. Condens. Matt.* **20**, 365211 (2008)



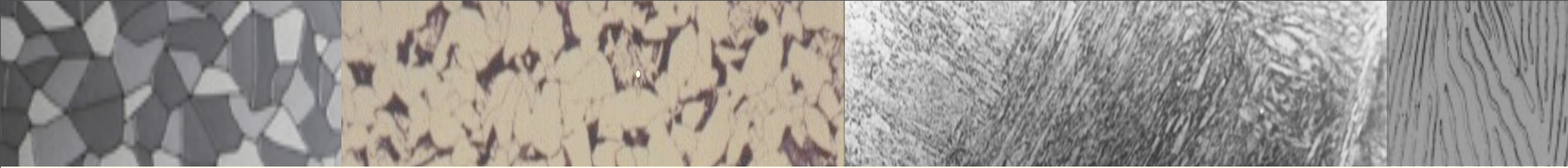

(b)
MARTENSITE
FERRITE
$\frac{\sigma_{1c}}{a_1 \Delta e_1}$
0
2
4
6
8
10
12
14
16
18
20
0.1
1
10
100
1000
$\frac{\nu}{\gamma_3}$

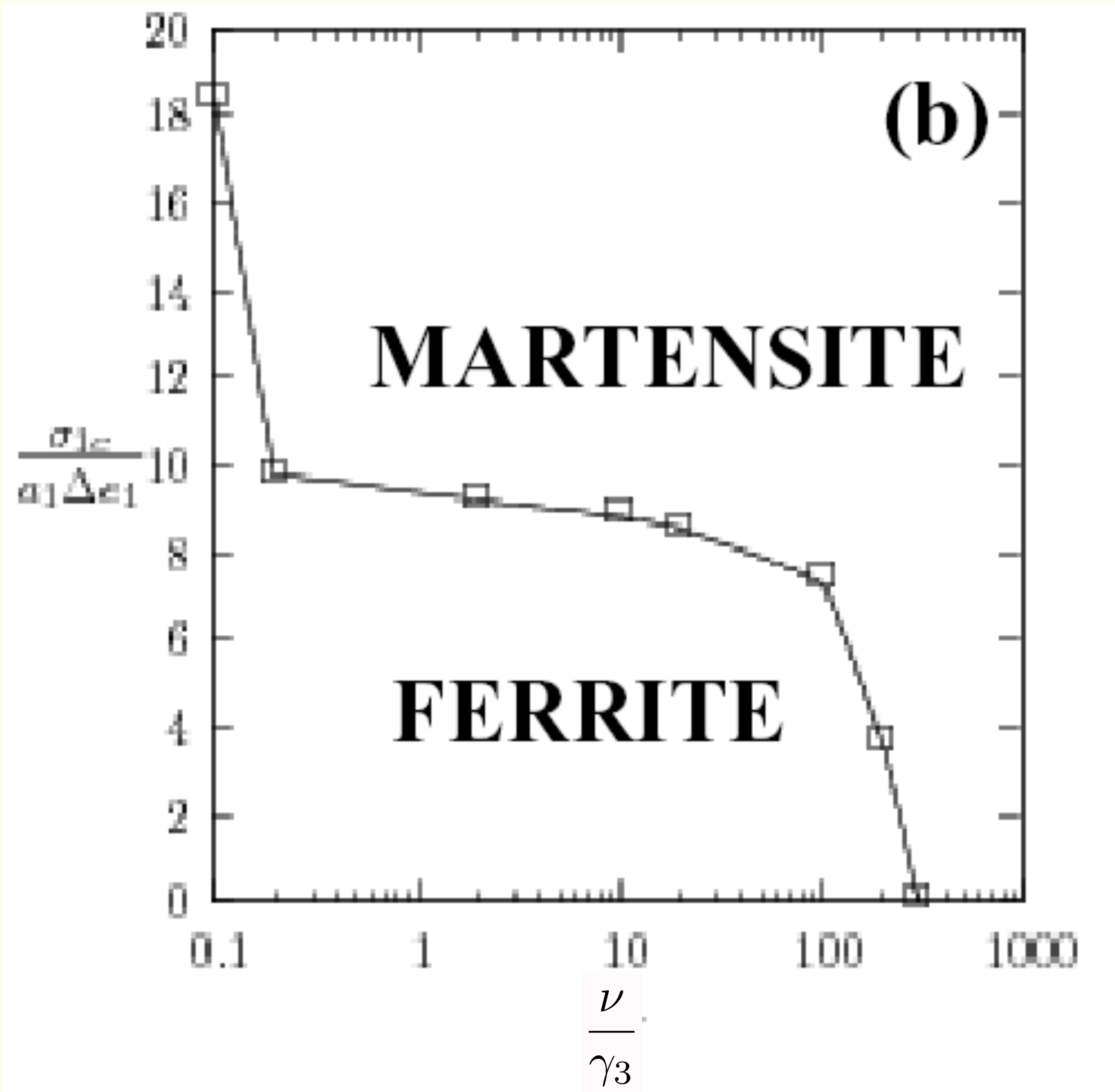





$\sigma_{1c}$

given by local elastic modulus times atomic strain threshold



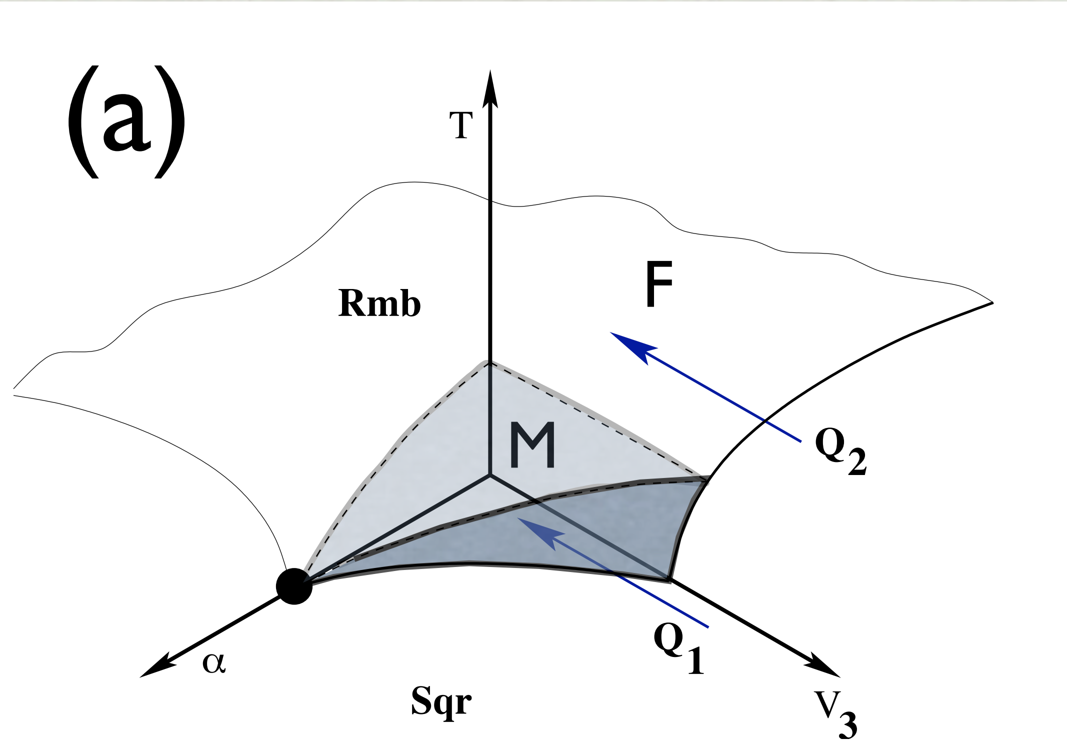



$\sigma_{1c}$

given by local elastic modulus times atomic strain threshold

$\frac{\nu}{\gamma_3}$ is a *Deborah* number $= \dfrac{\text{Growth velocity}}{\text{plasticity production rate}}$

# Early time events during nucleation in solids




J. Bhattacharya *et al.,* J. Phys. Condens. Matt. (2008);

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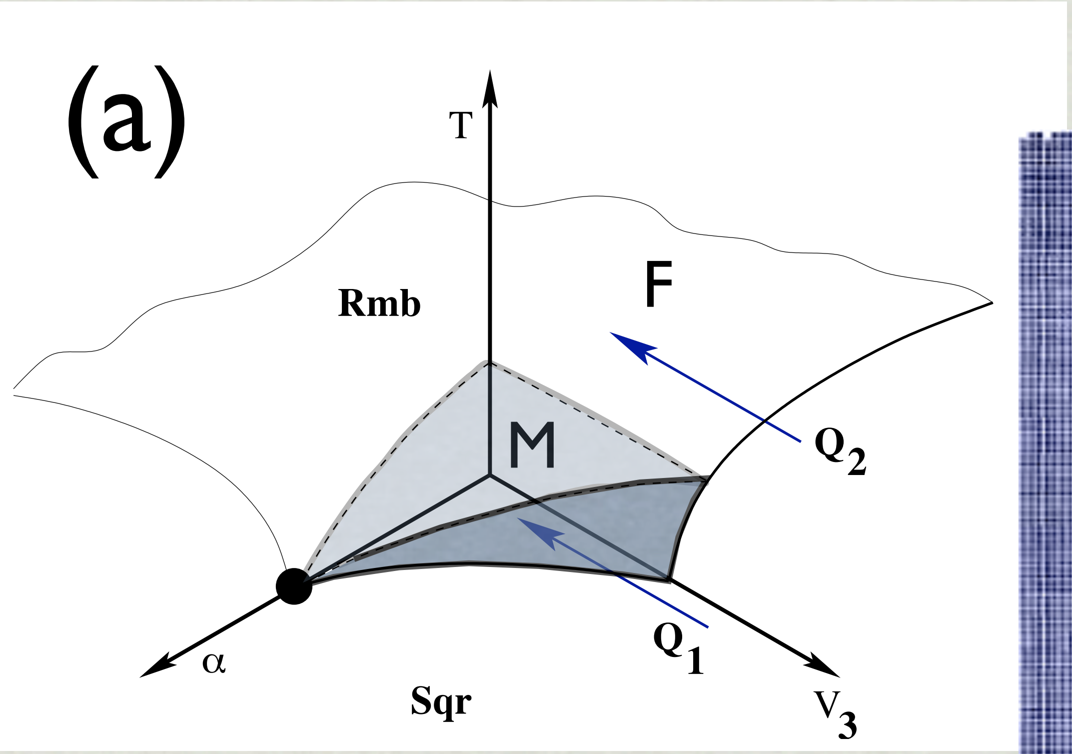


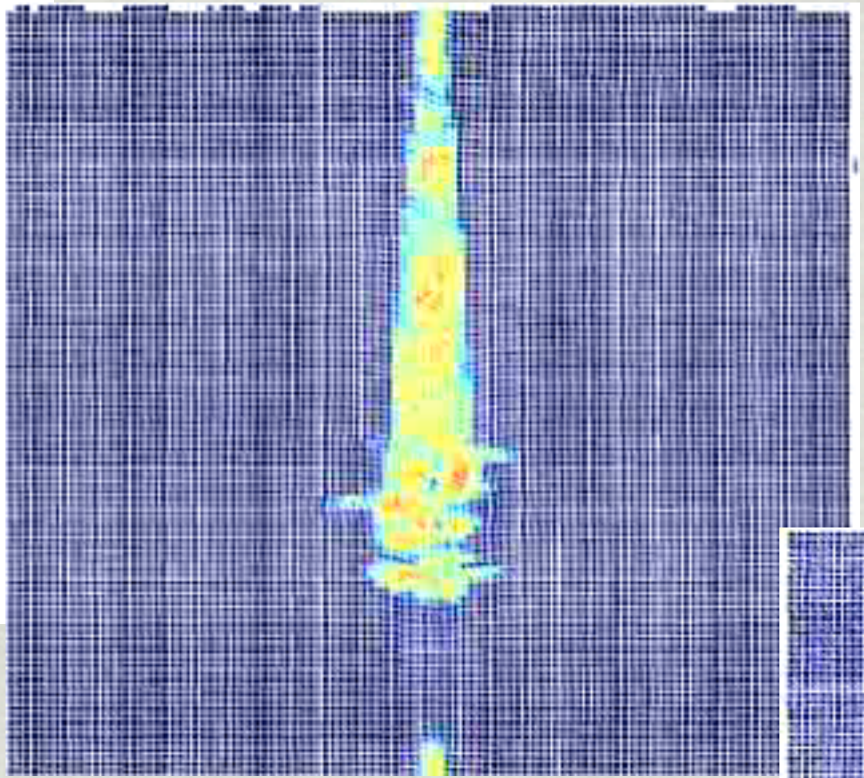

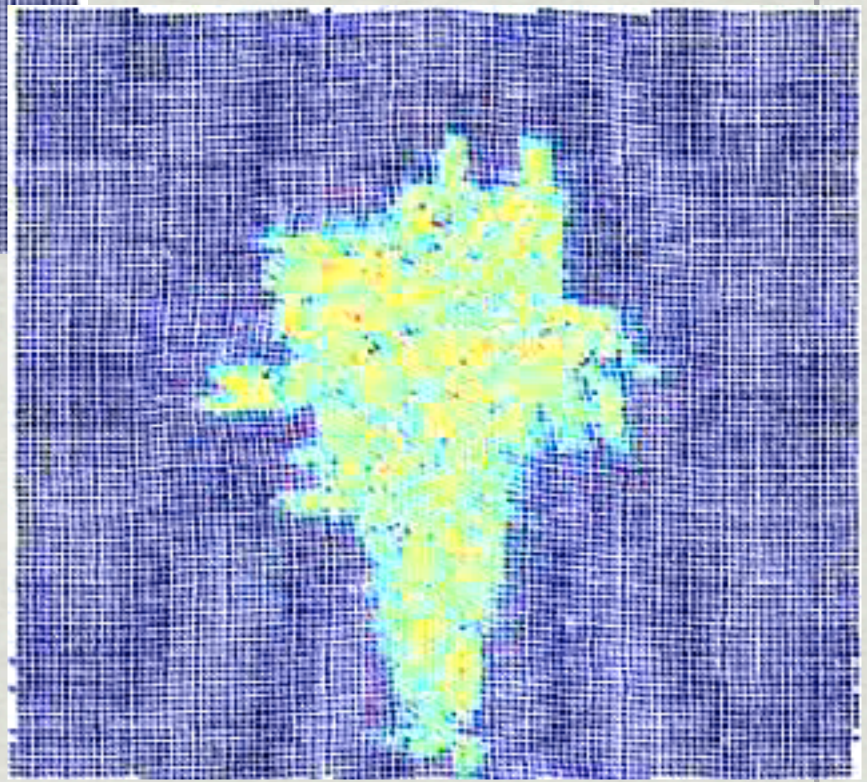

J. Bhattacharya *et al.*, J. Phys. Condens. Matt. (2008);

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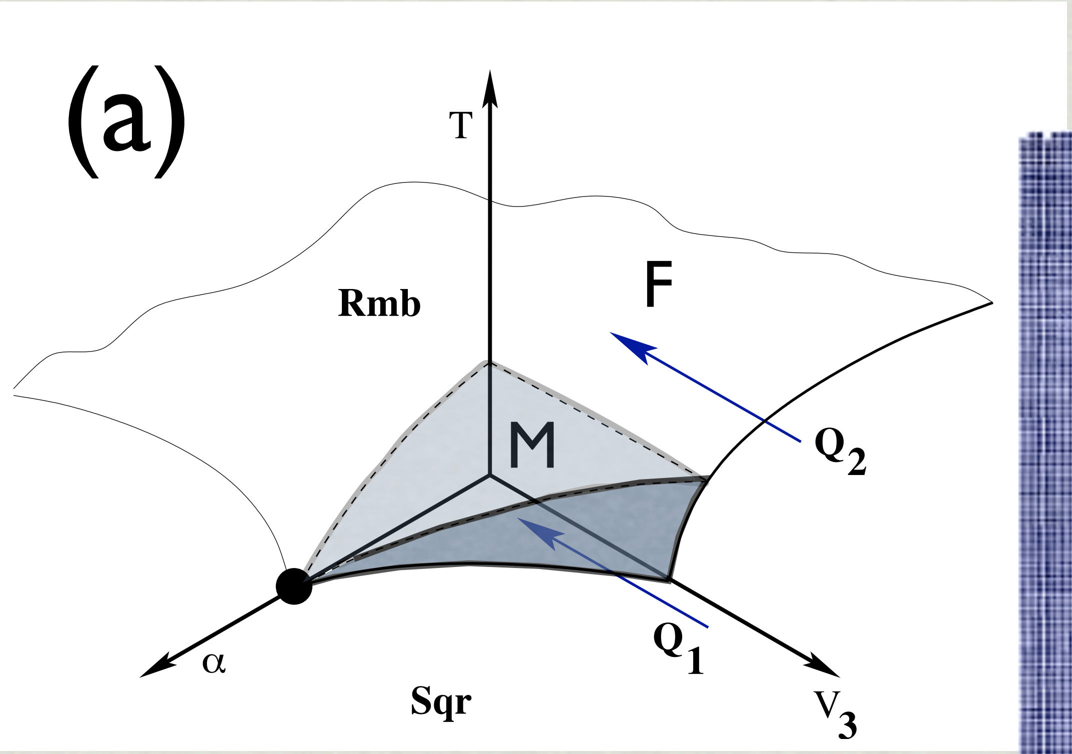
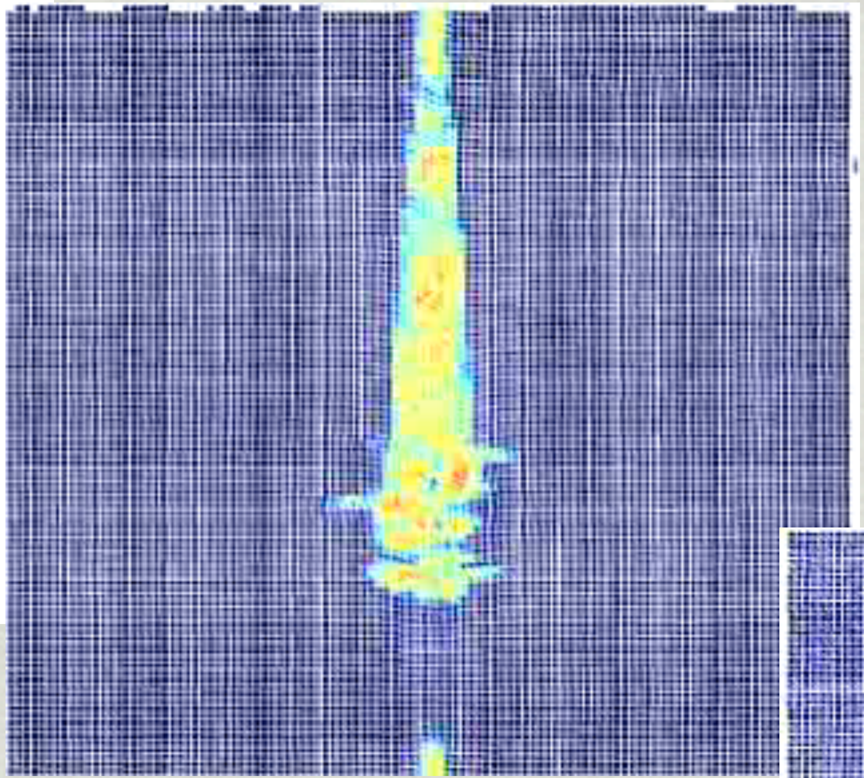
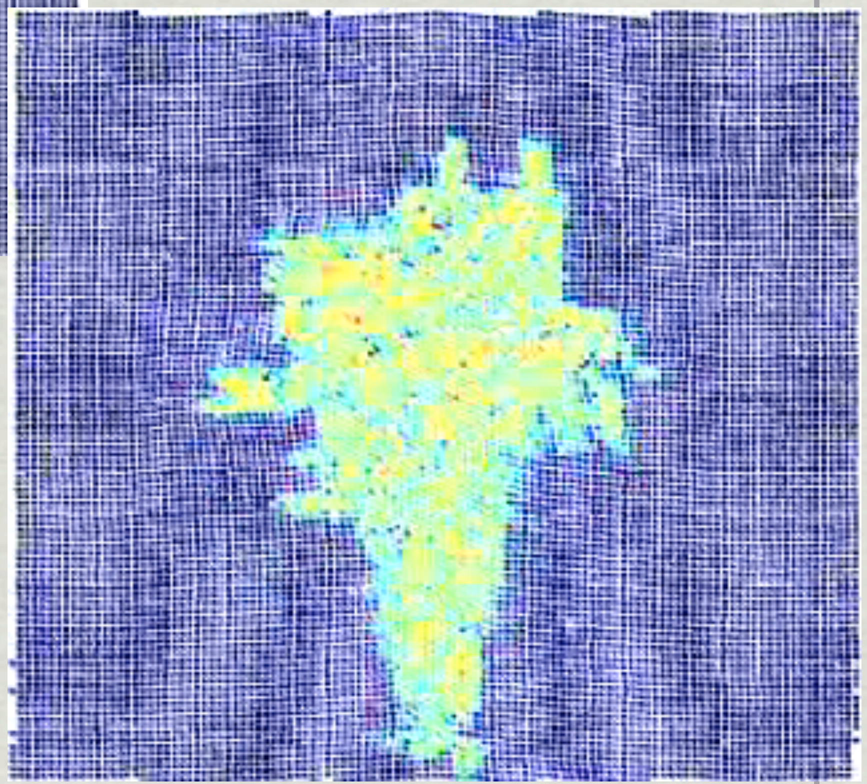
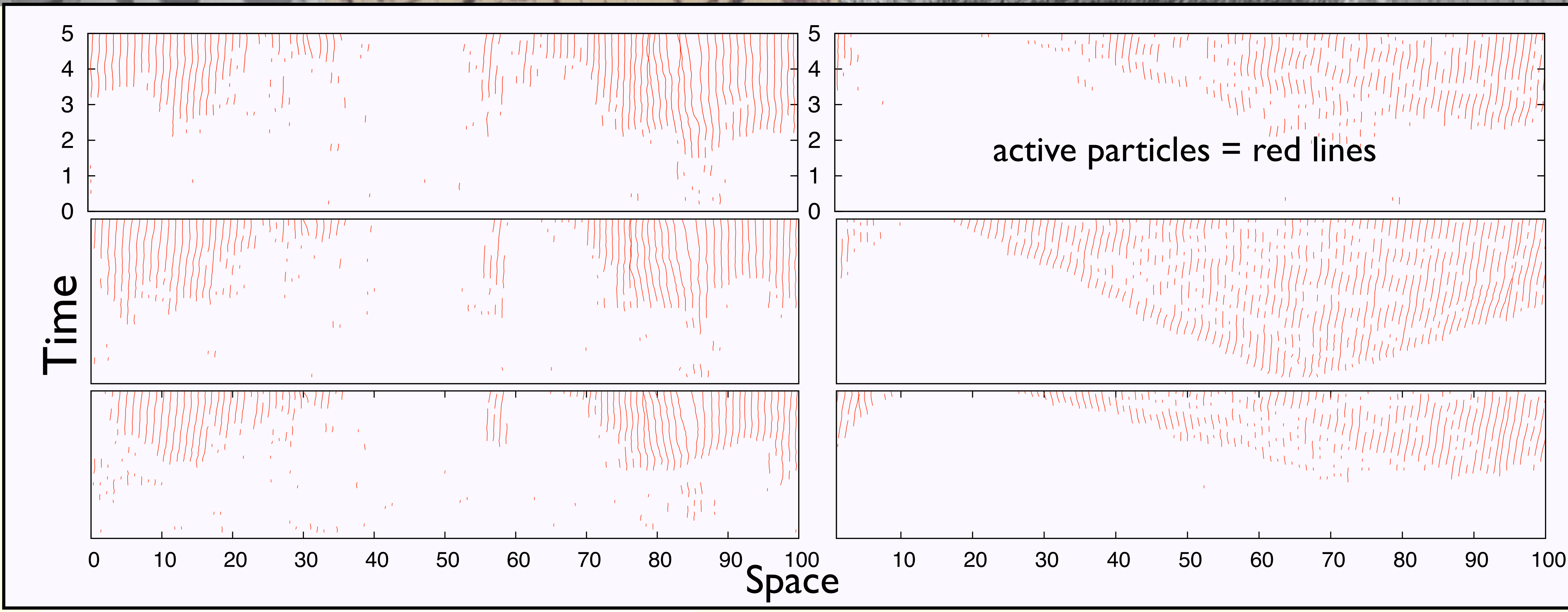


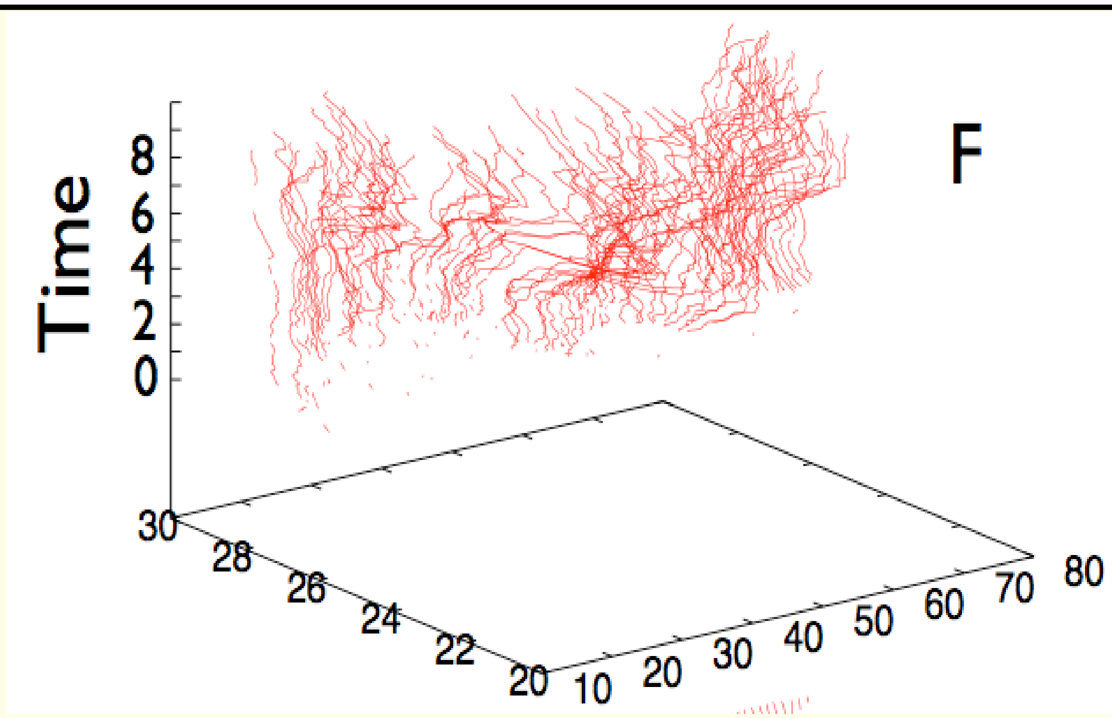



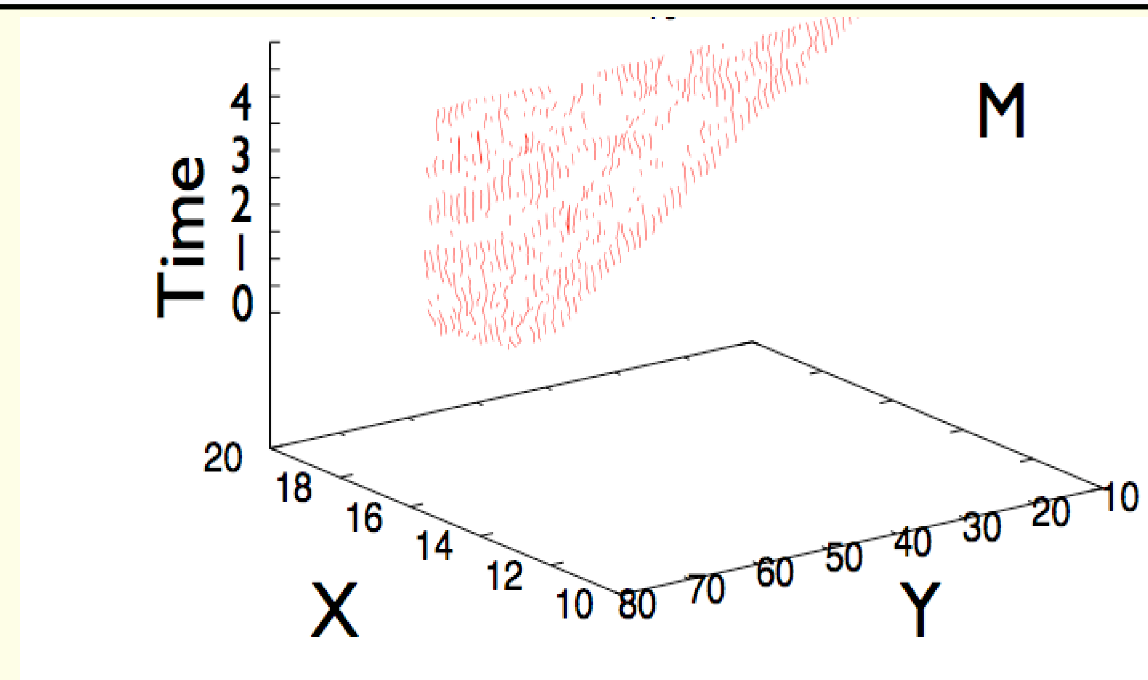


J. Bhattacharya *et al.*, J. Phys. Condens. Matt. (2008);

# Single particle trajectories - “kymographs”




SS, J. Bhattacharya, M. Rao, arXiv: (2010)

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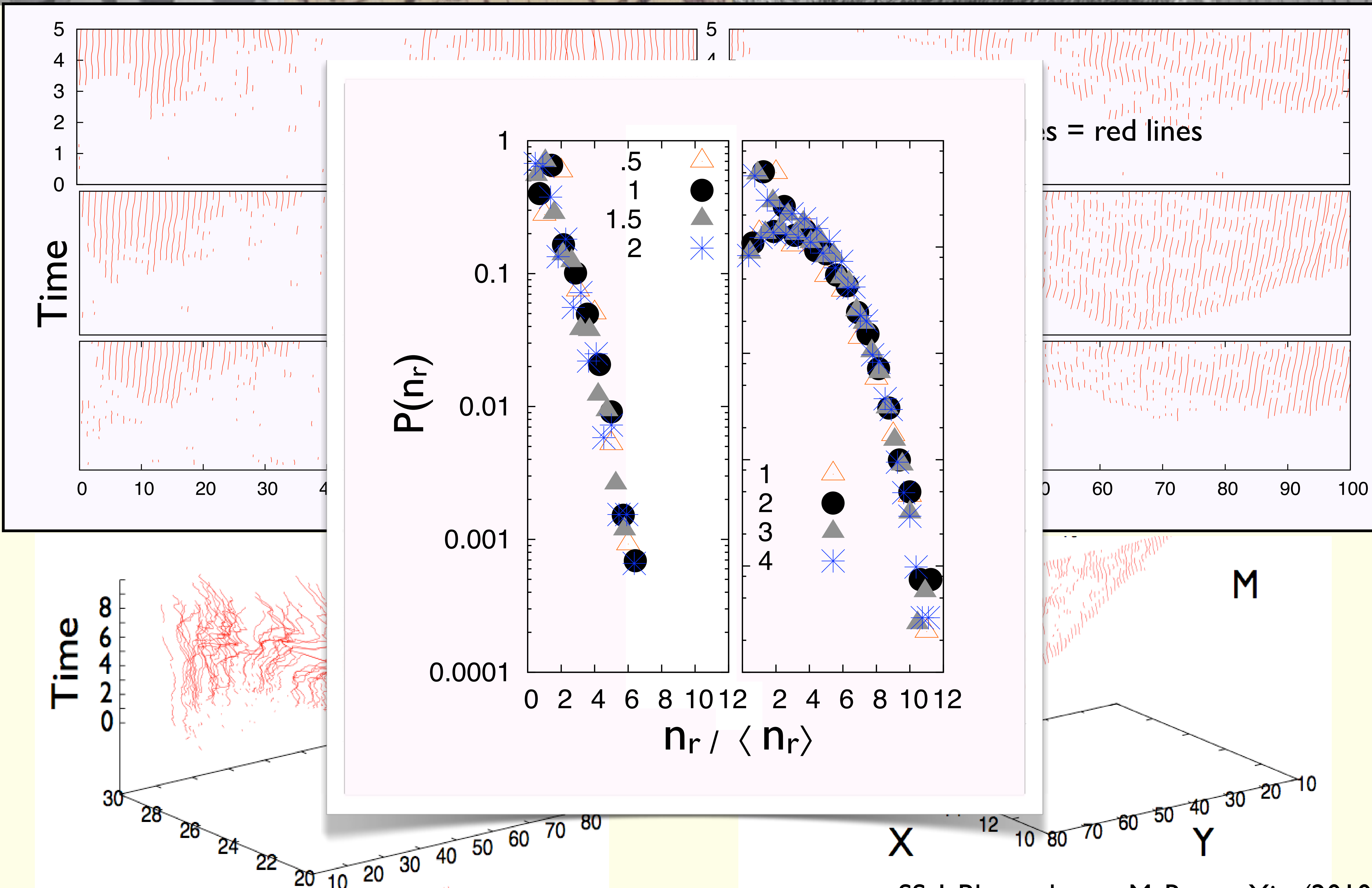


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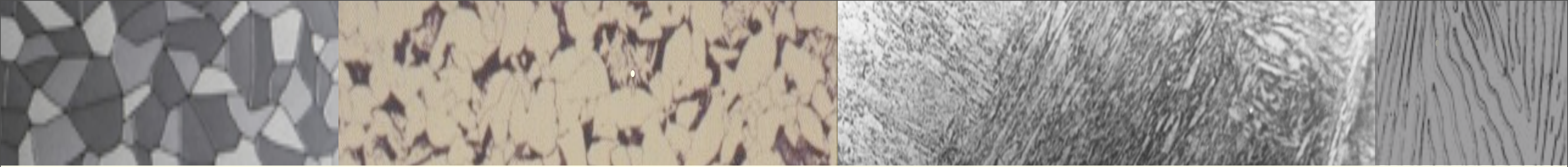
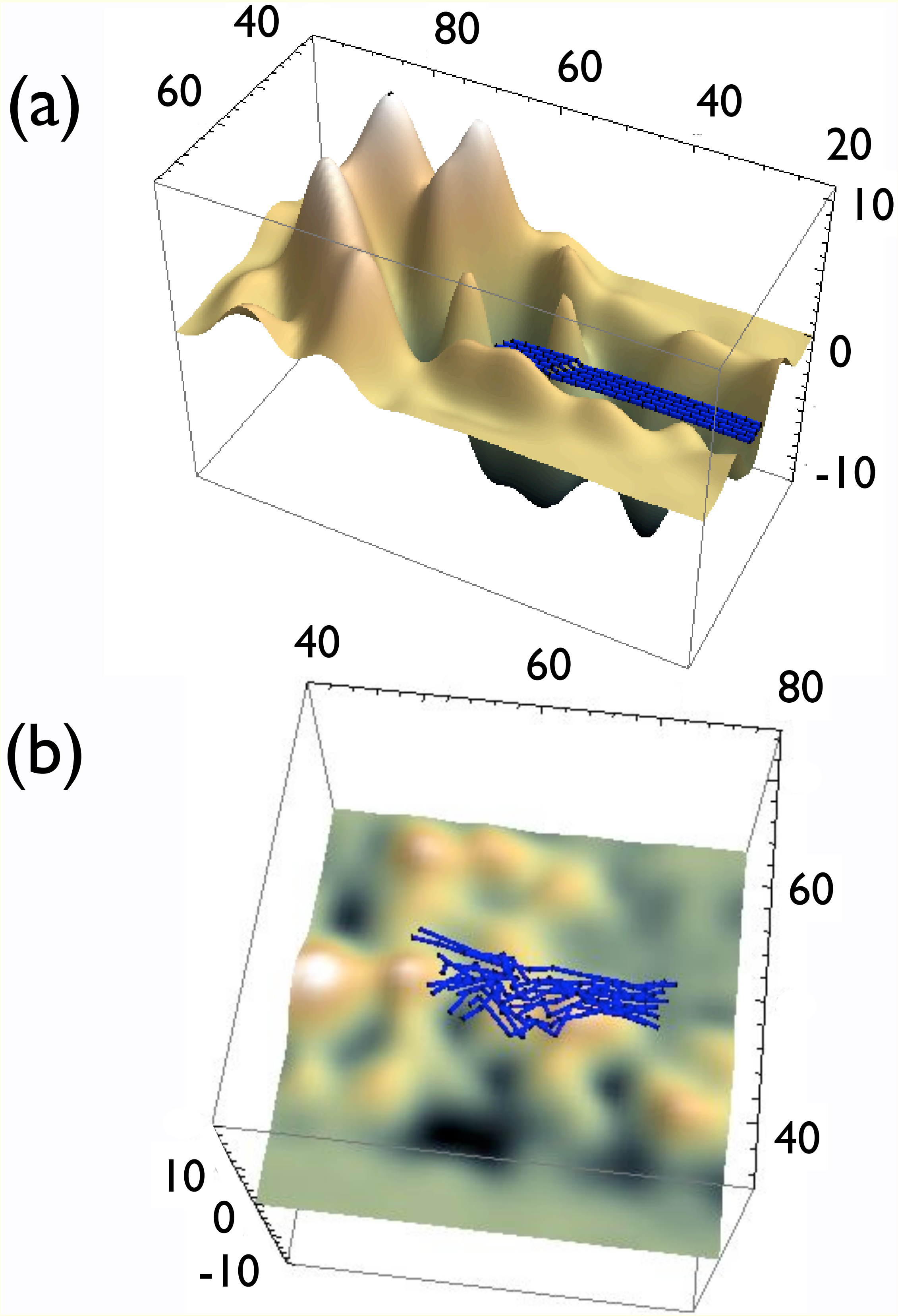
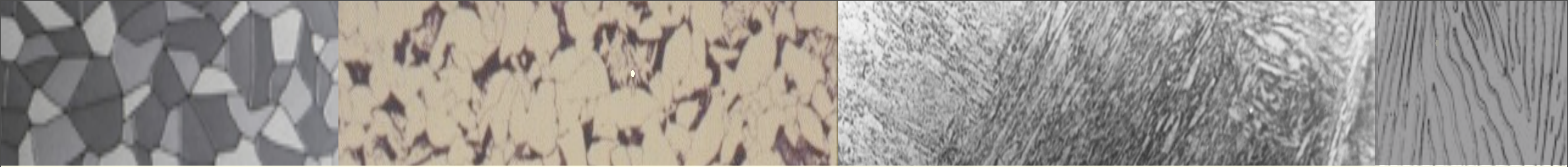
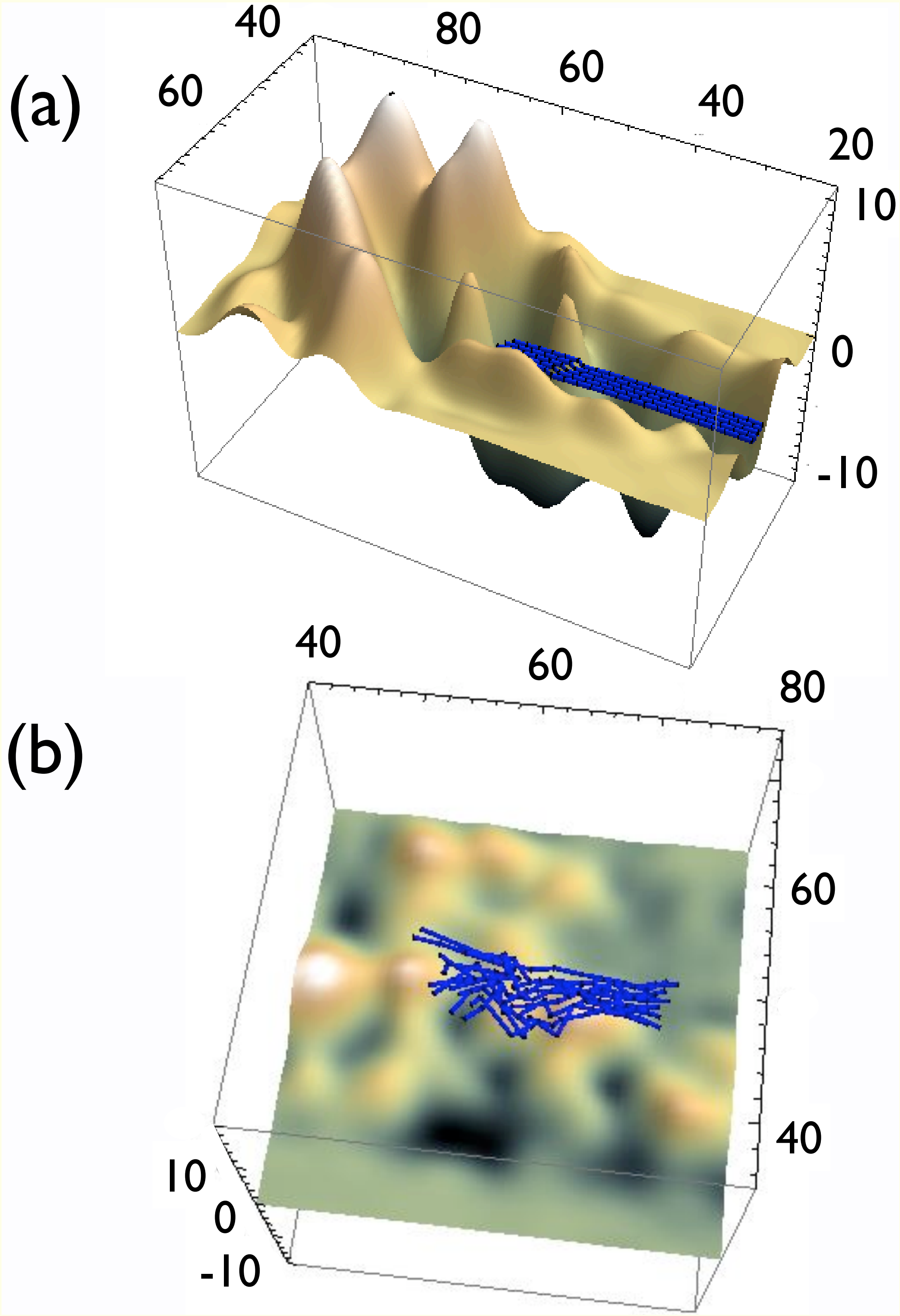





- nucleation not a smooth process
- active - inactive transitions.
- active particles flow within channels in the free energy topography shaped by inactive particles.
- low temps - few channels - confining potential evolves very slowly - ballistic trajectory ⇒ M
- high temps - many intersecting channels - no confining potential or potential evolves fast - diffusive trajectories ⇒ F



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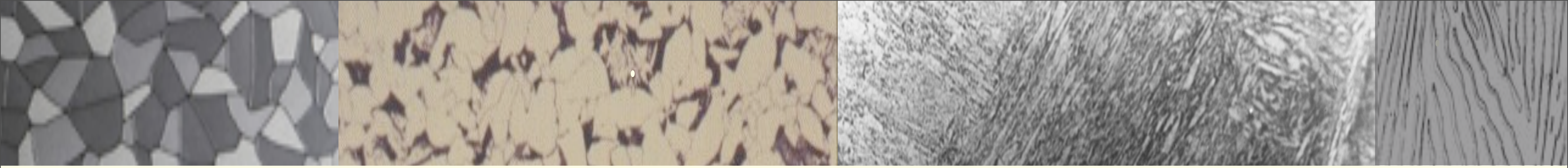
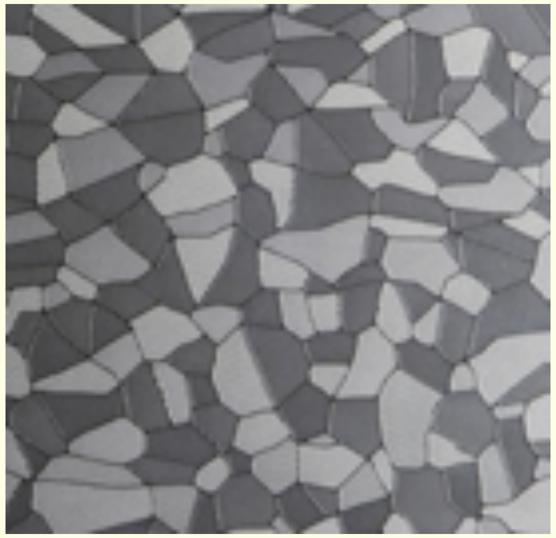
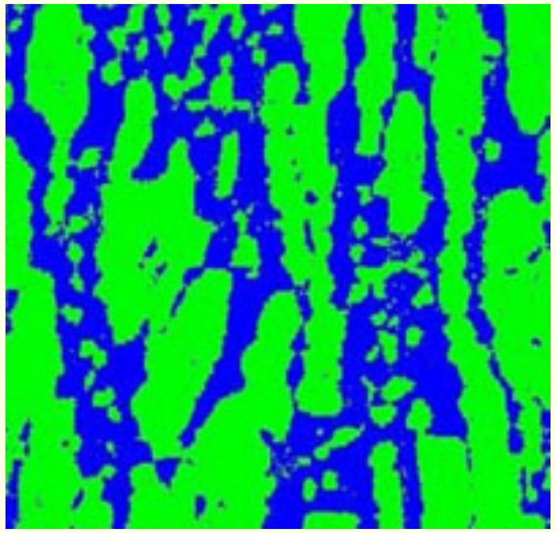
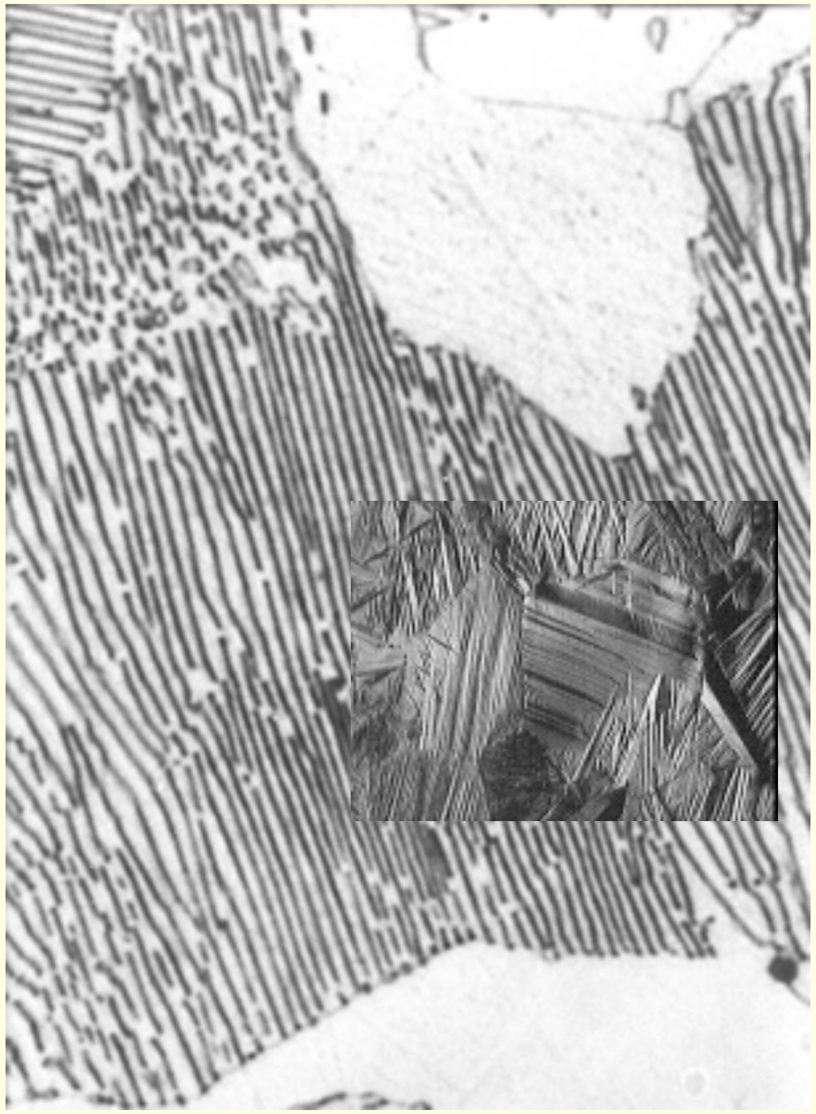
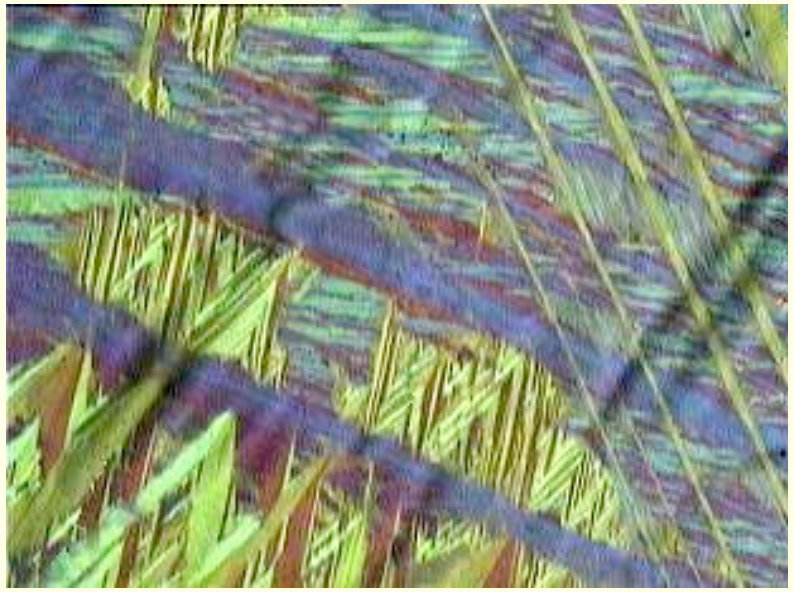
"The mountains flowed before the Lord" Deborah (Judges 5:5).

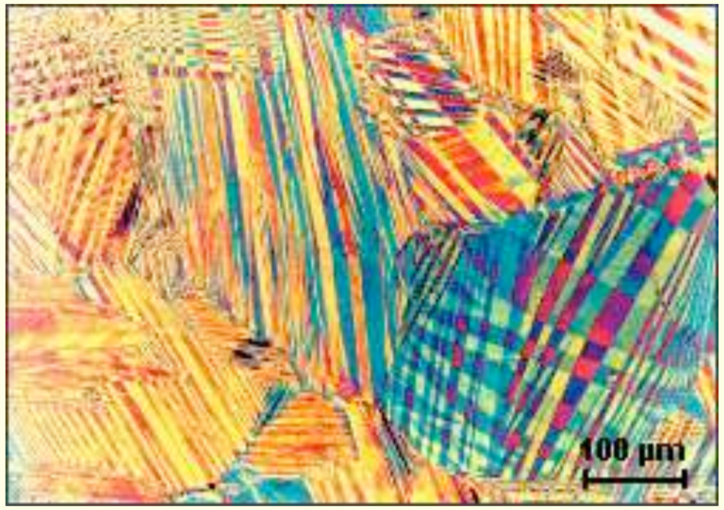


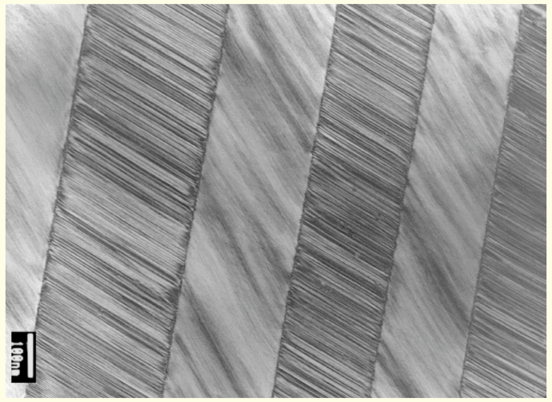


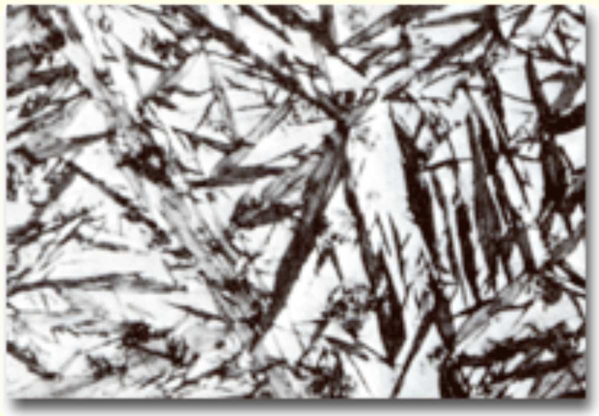


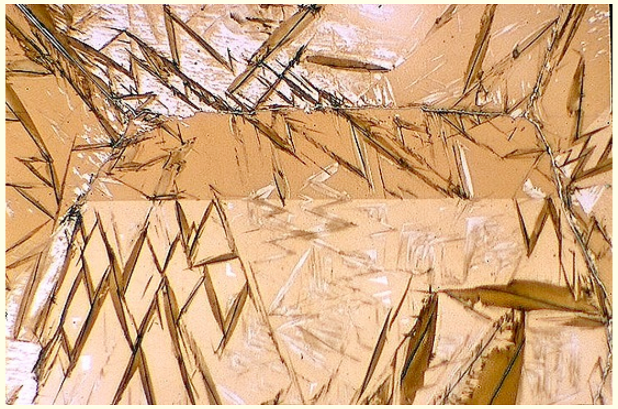


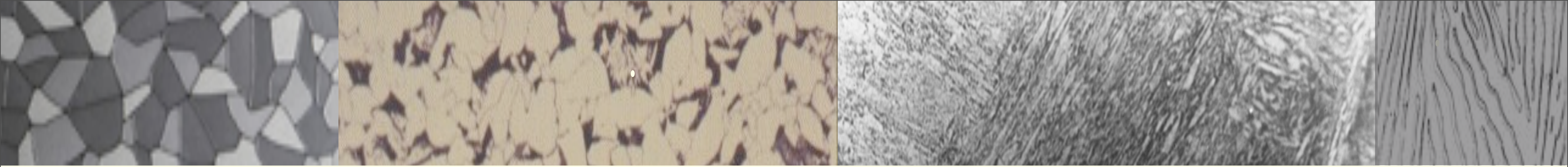


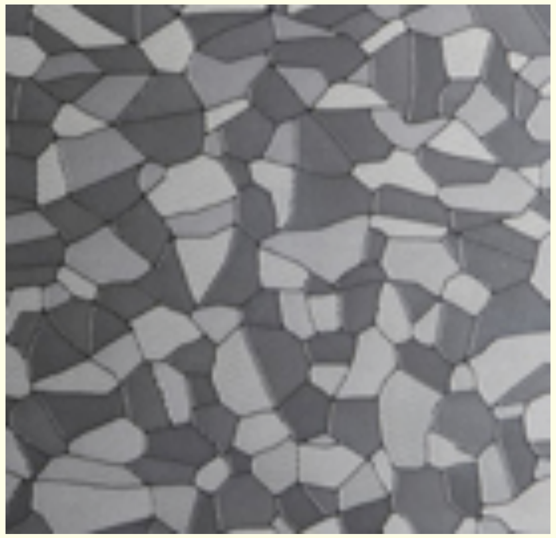

100 µm

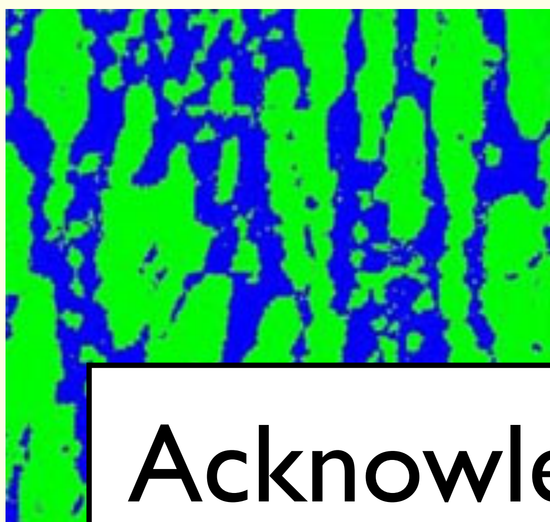


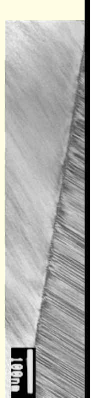


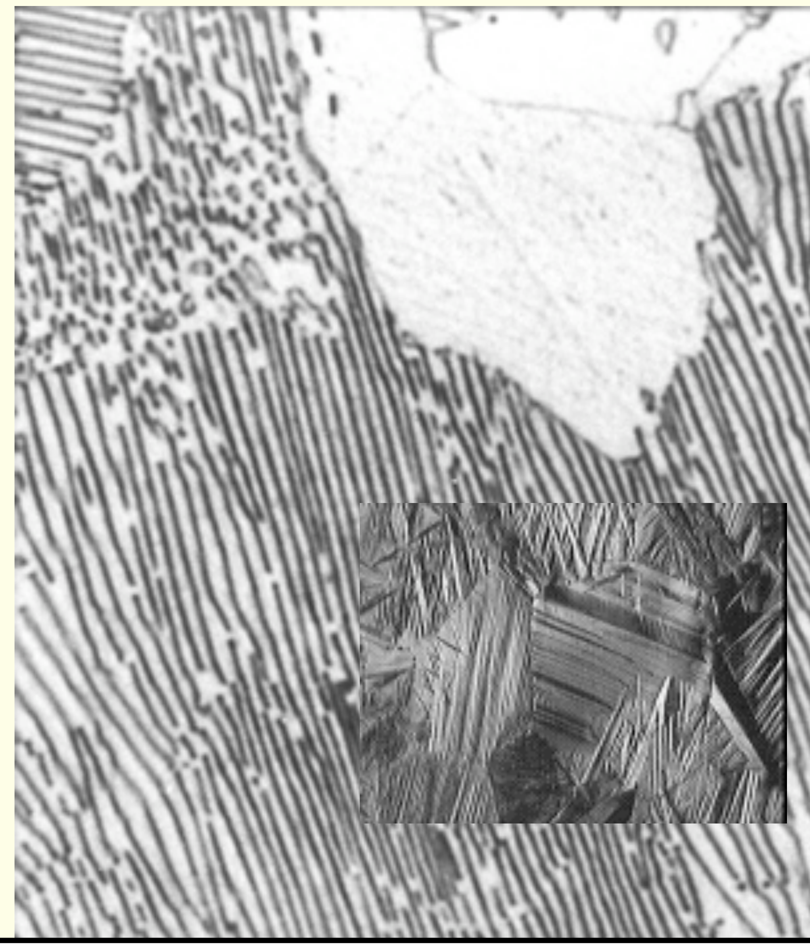


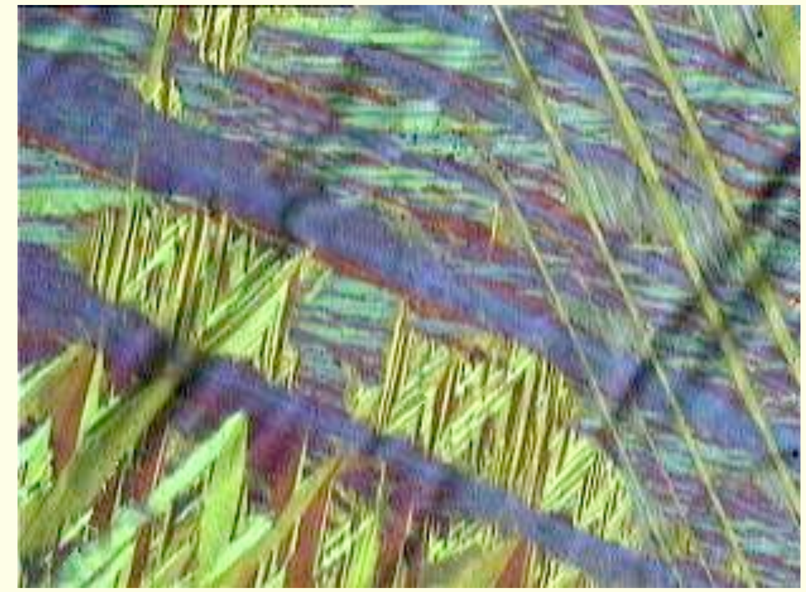










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Arya Paul (SNBNCBS)