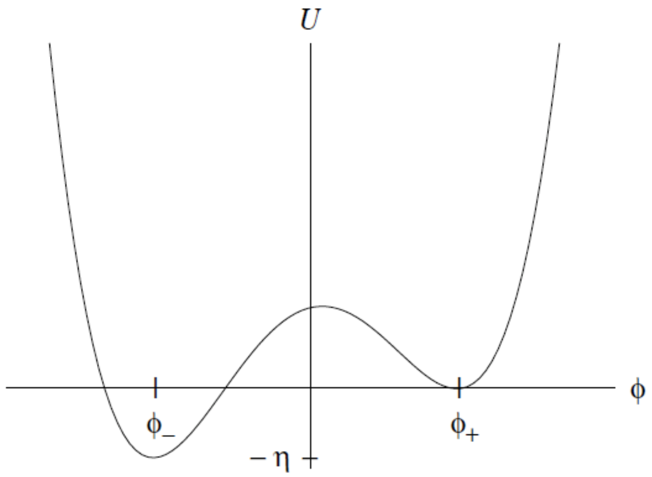
Microstructure selection in solids: a space time transition of particle trajectories?

Surajit Sengupta (IACS, & SNBNCBS, Kolkata)

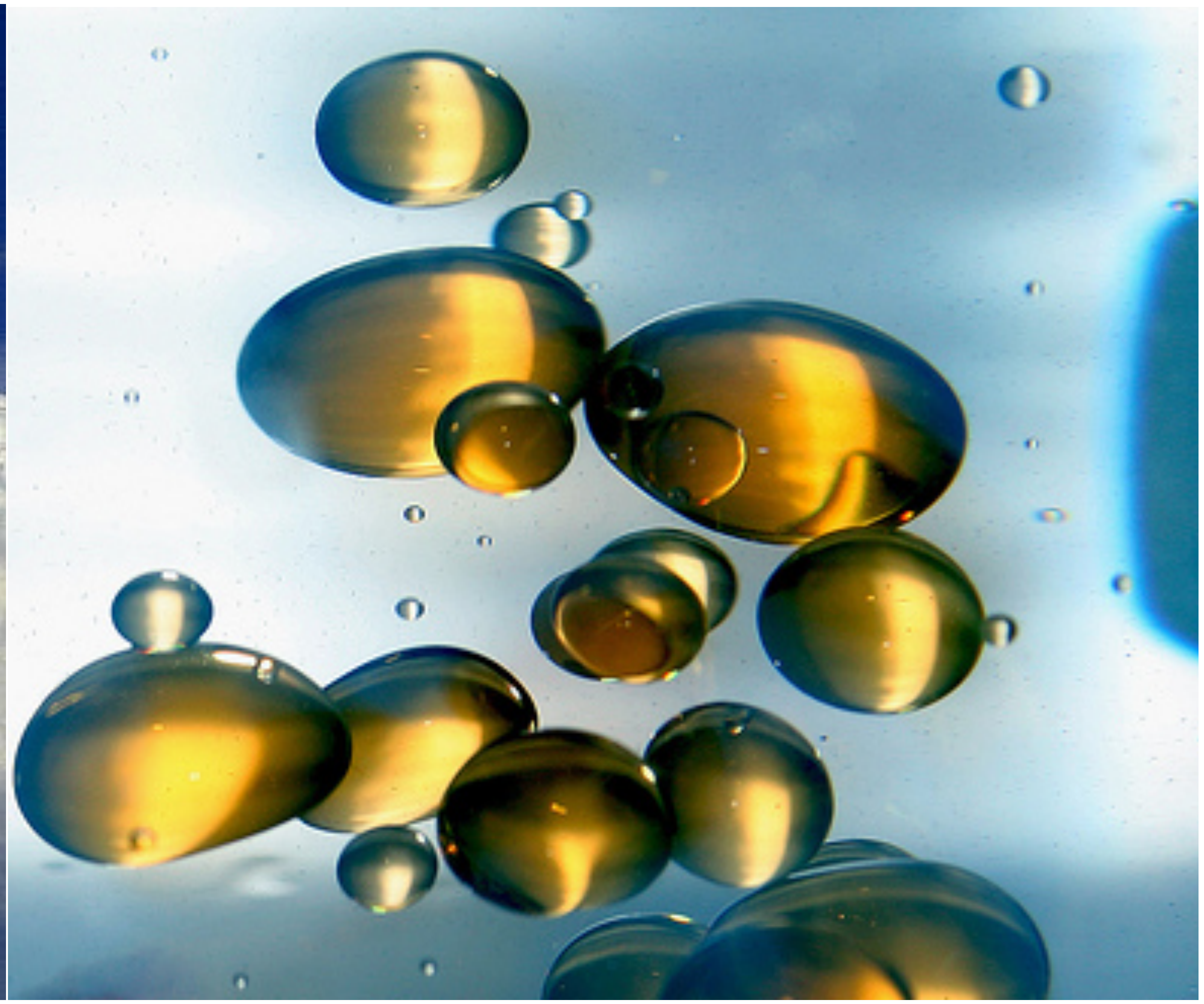
Nucleation:

Decay of a metastable phase following a first order phase transition



Liquid in gas

Liquid in liquid



Gas in liquid

Nucleation:

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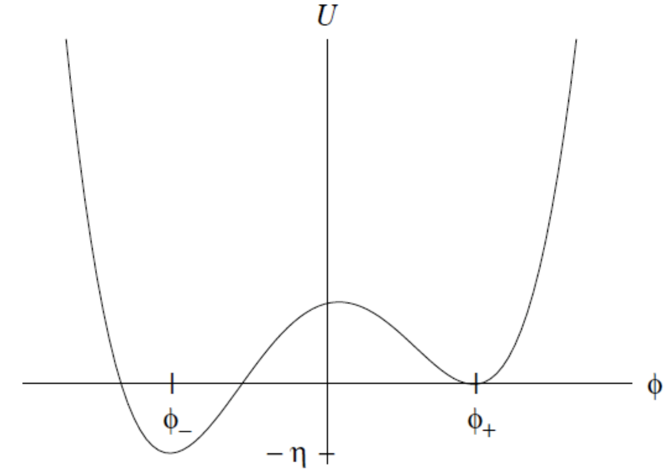


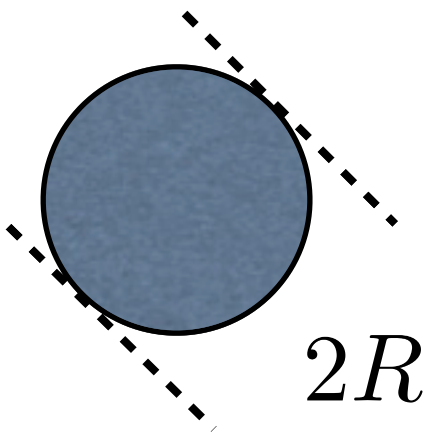
Liquid in gas

Liquid in liquid

Gas in liquid

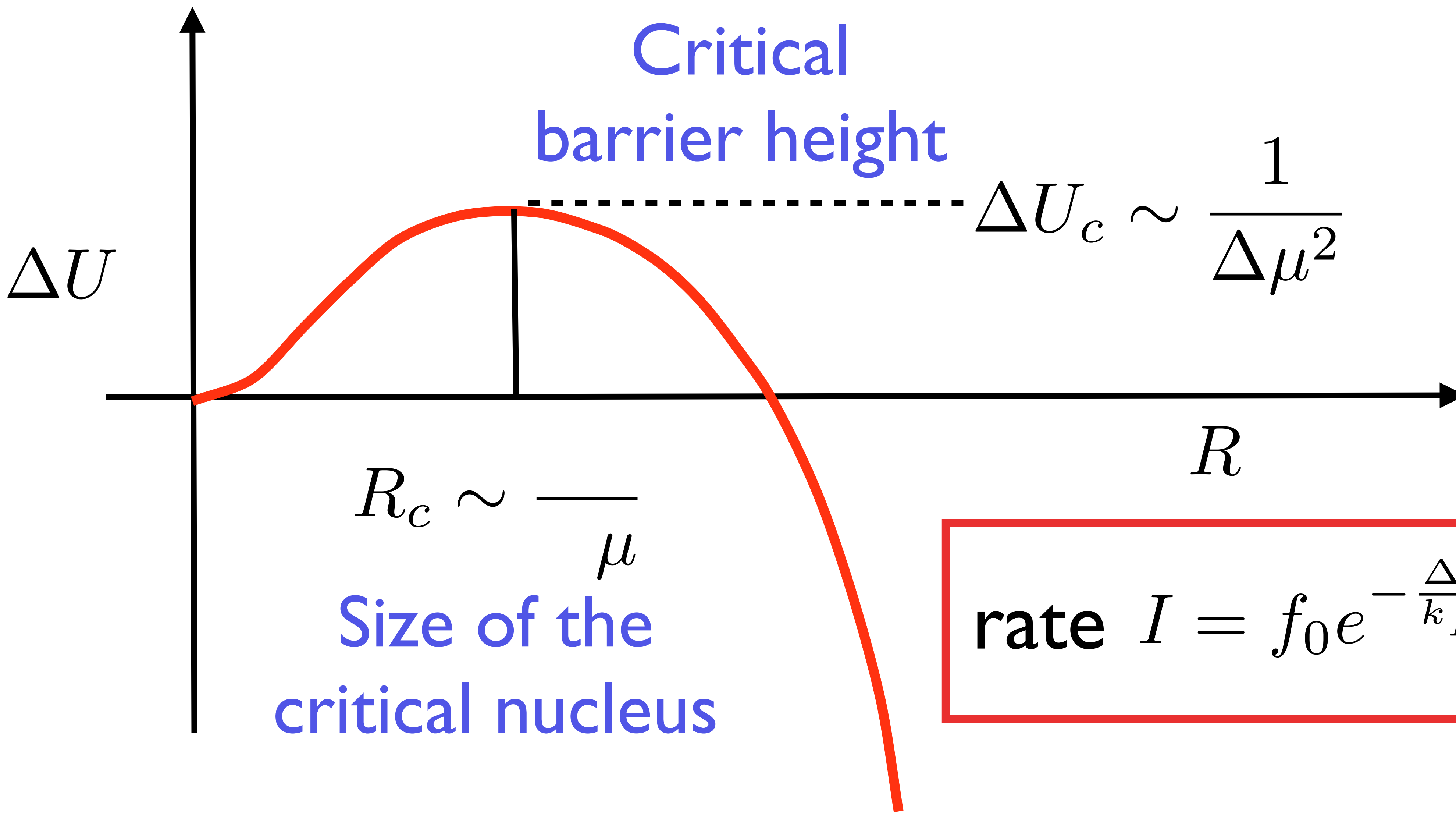
Classical Nucleation Theory

Homogeneous nucleation:

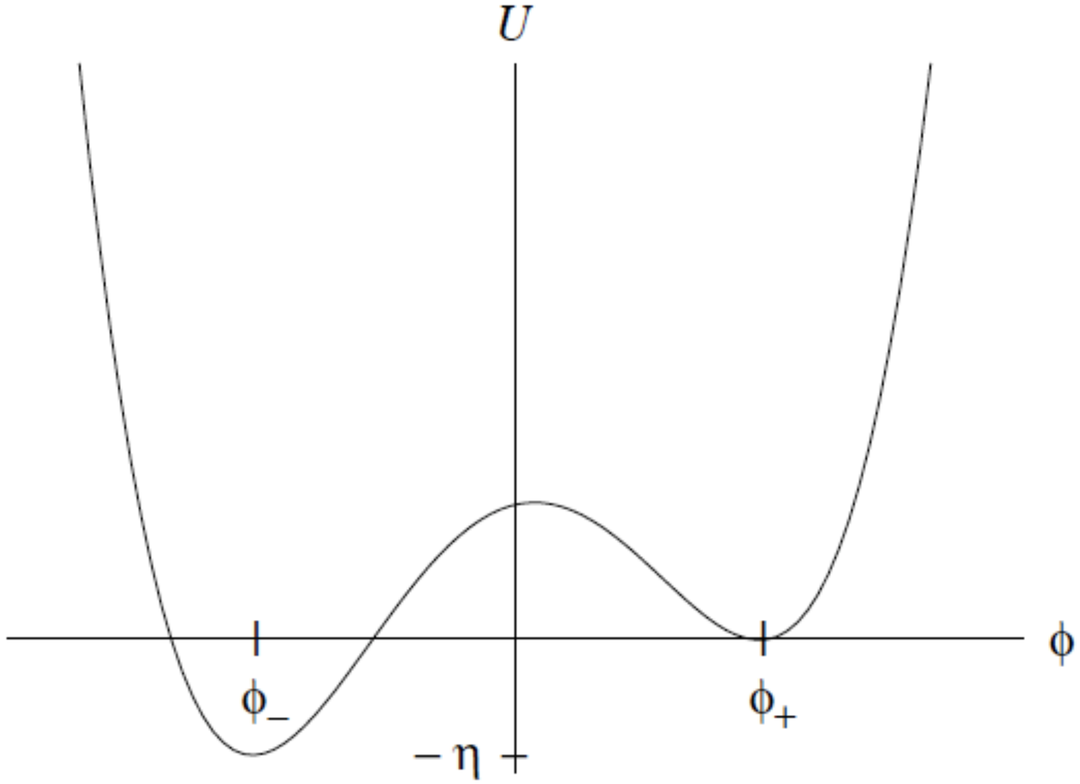


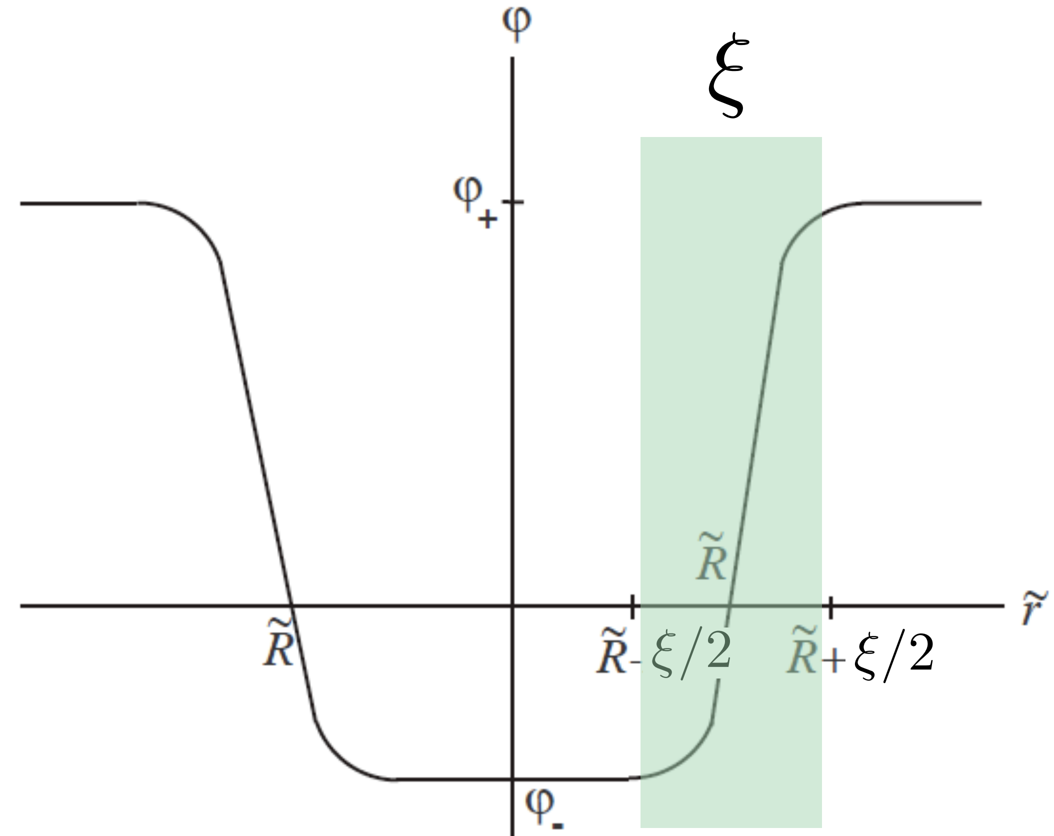
Free energy gain: $\frac{4\pi}{3}\rho R^3 \Delta\mu$

Free energy loss: $4\pi R^2 \gamma$

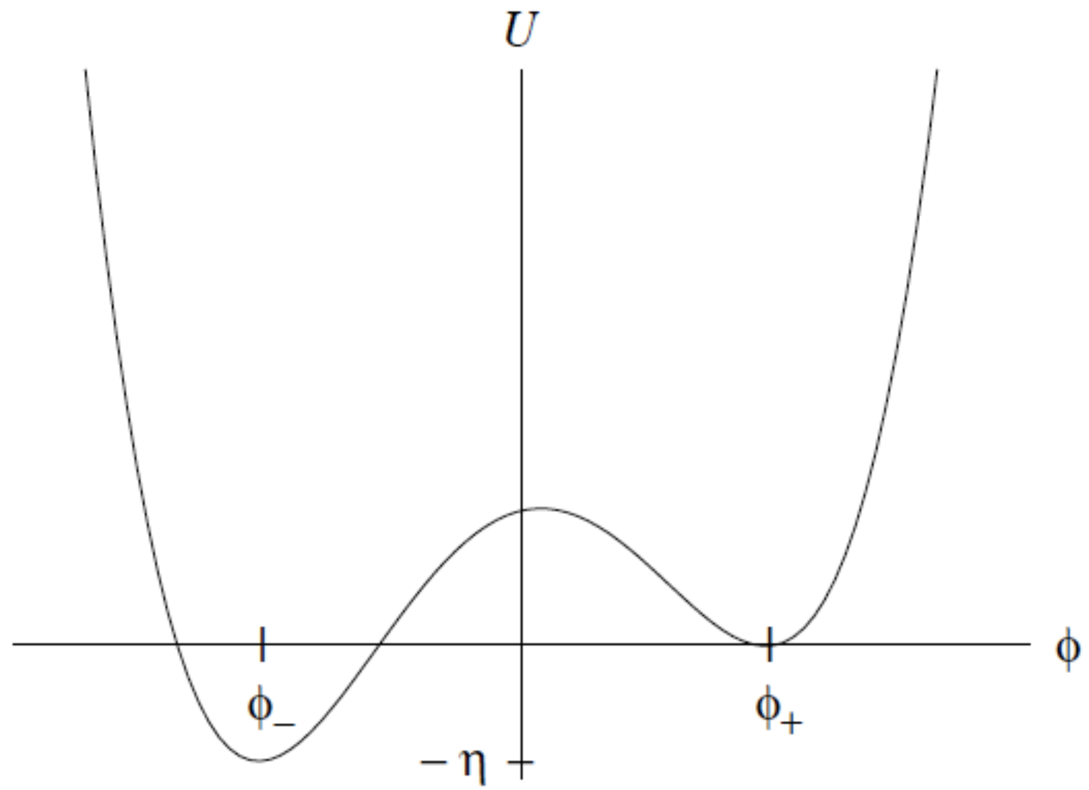


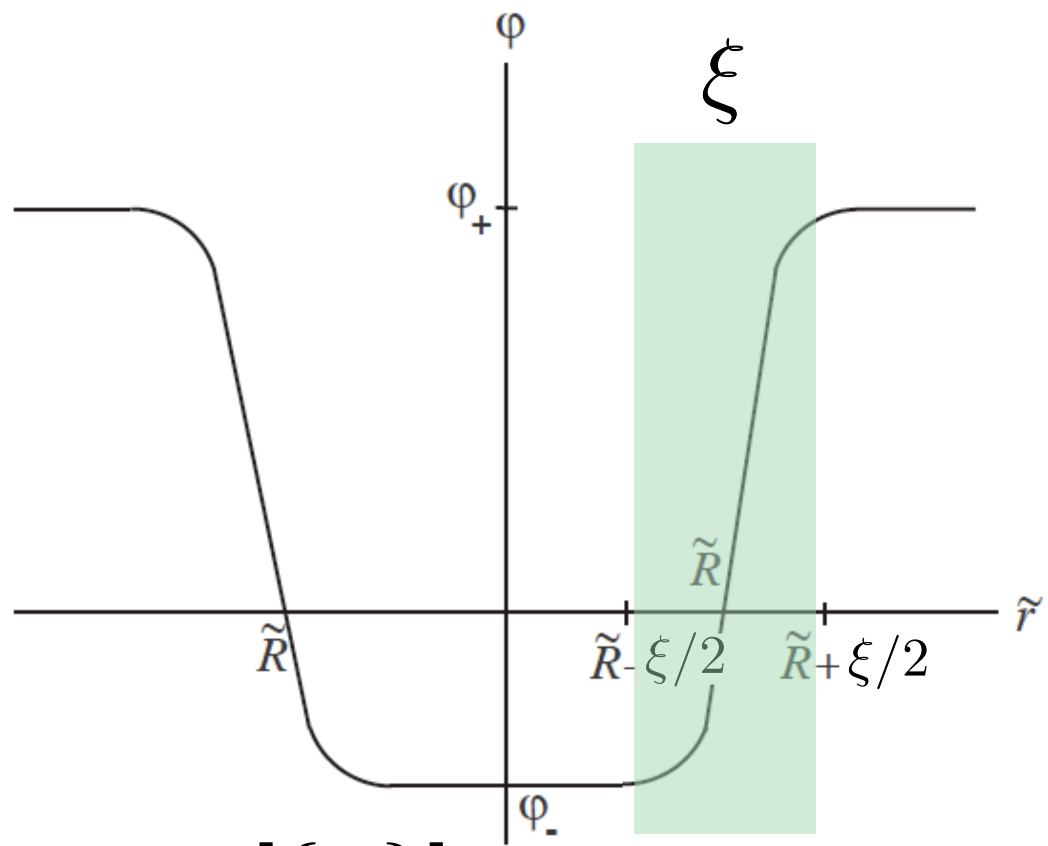
rate $I = f_0 e^{-\frac{\Delta U_c}{k_B T}}$





$$\beta U = \int d\mathbf{r} f(\phi) + (\nabla\phi)^2 + \eta\phi \qquad \frac{\delta U[\{\phi\}]}{\delta\phi} = 0$$



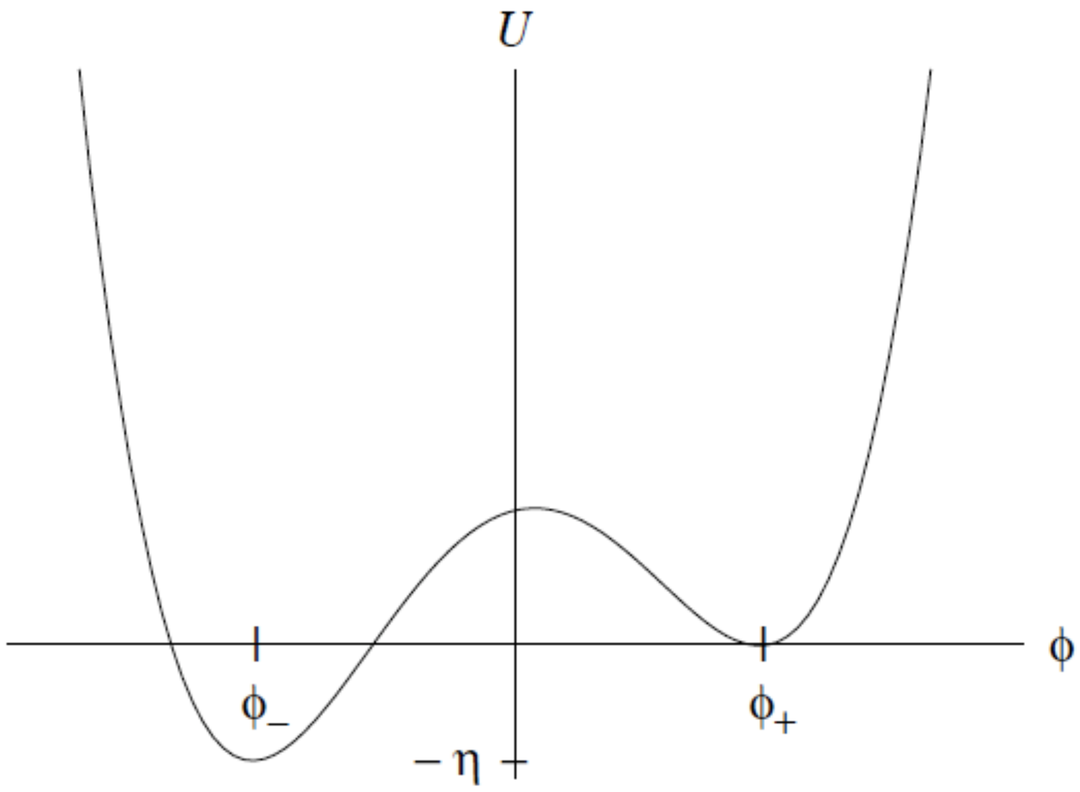


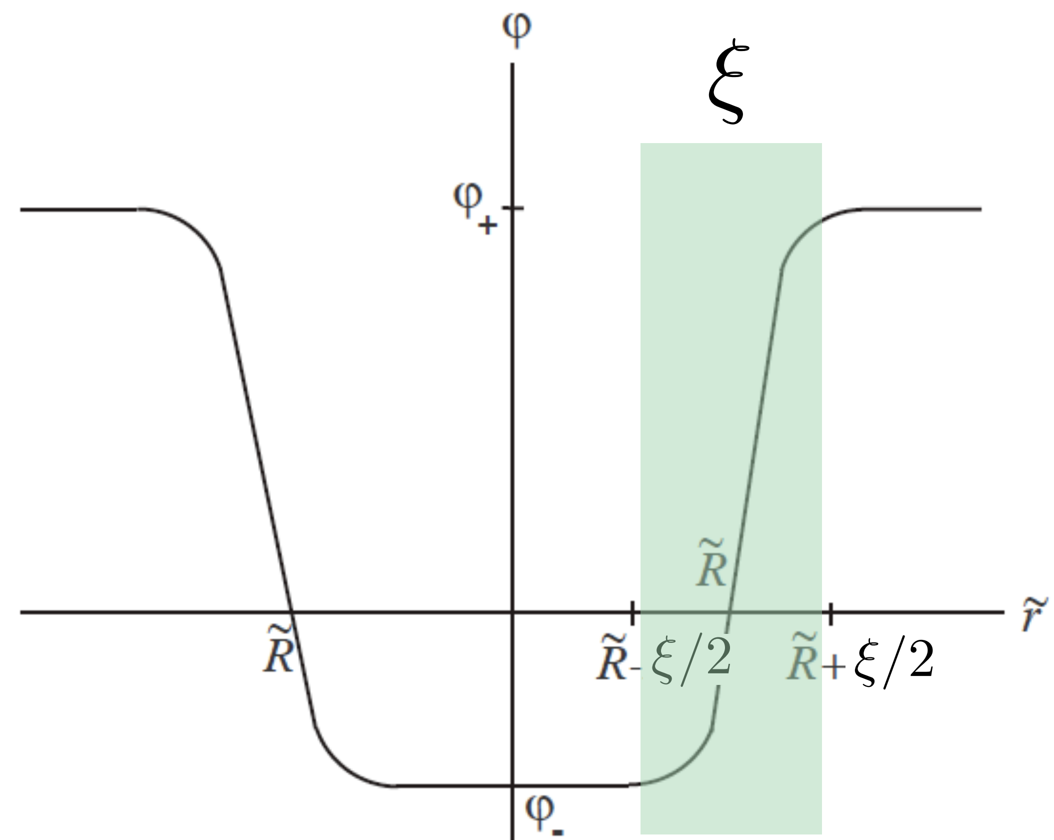
$$\beta U = \int d\mathbf{r} f(\phi) + (\nabla\phi)^2 + \eta\phi \quad \frac{\delta U[\{\phi\}]}{\delta\phi} = 0$$

Crucial assumptions:

1. $\xi << R_c$ or $\Delta\mu \sim 0$

2. Interfacial widths are “fast” variable





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Solid in liquid?

Crucial assumptions:

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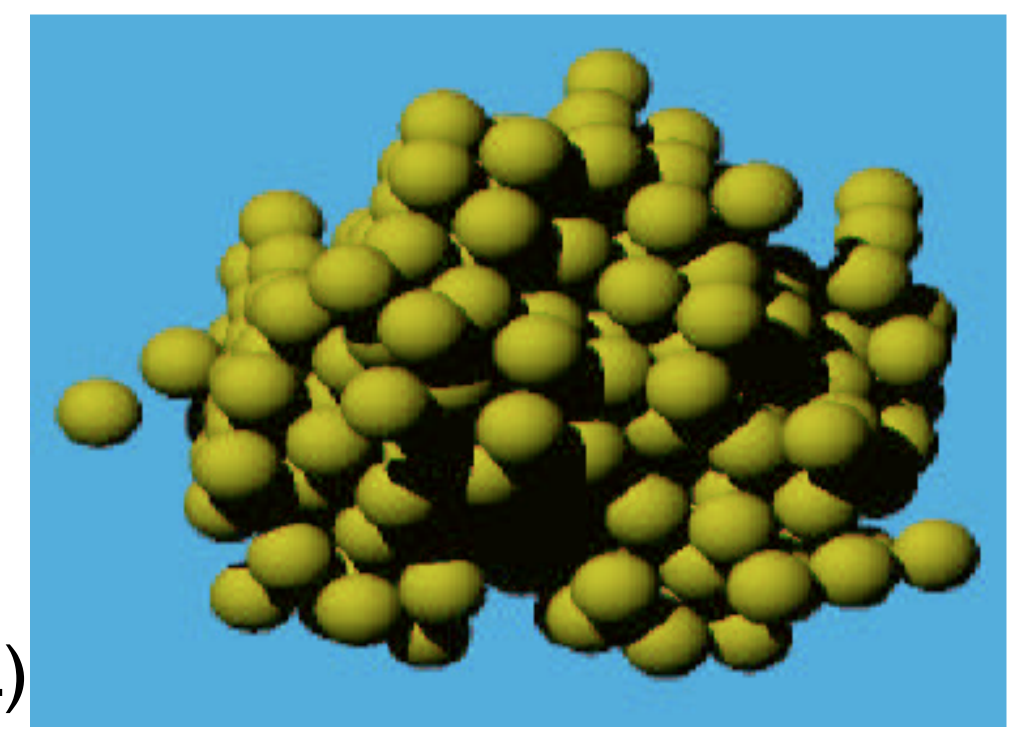
Ten-Wolde, Auer, Frenkel (2002)



Solid-Solid transitions (structural transition, precipitation reaction etc.)

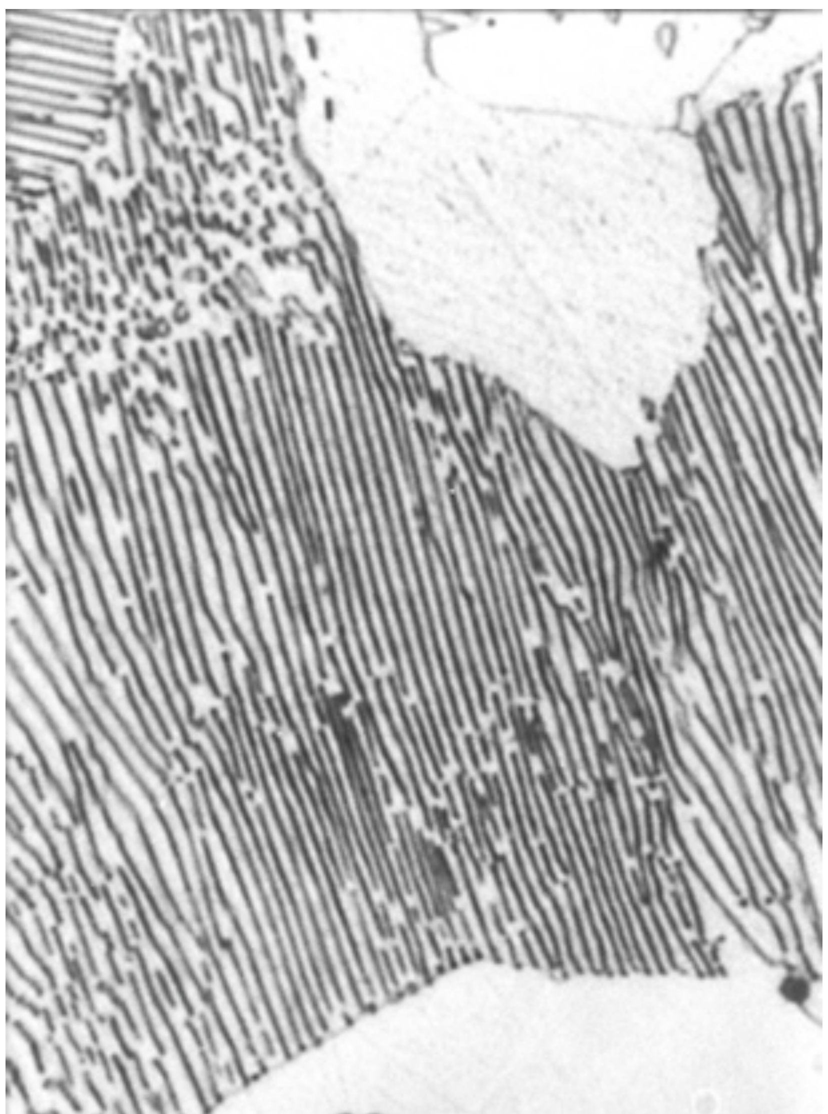
- Critical nucleus is non-spherical: anisotropy
- Homogeneous nucleation rate too small so usually defect assisted
- $\xi \sim R$ at early times
- Complex jamming-unjamming dynamics
- Elastic stresses present - long range effects
- Long lived arrested states - Microstructures

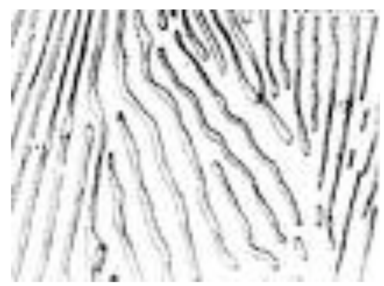
Eutectic mixtures

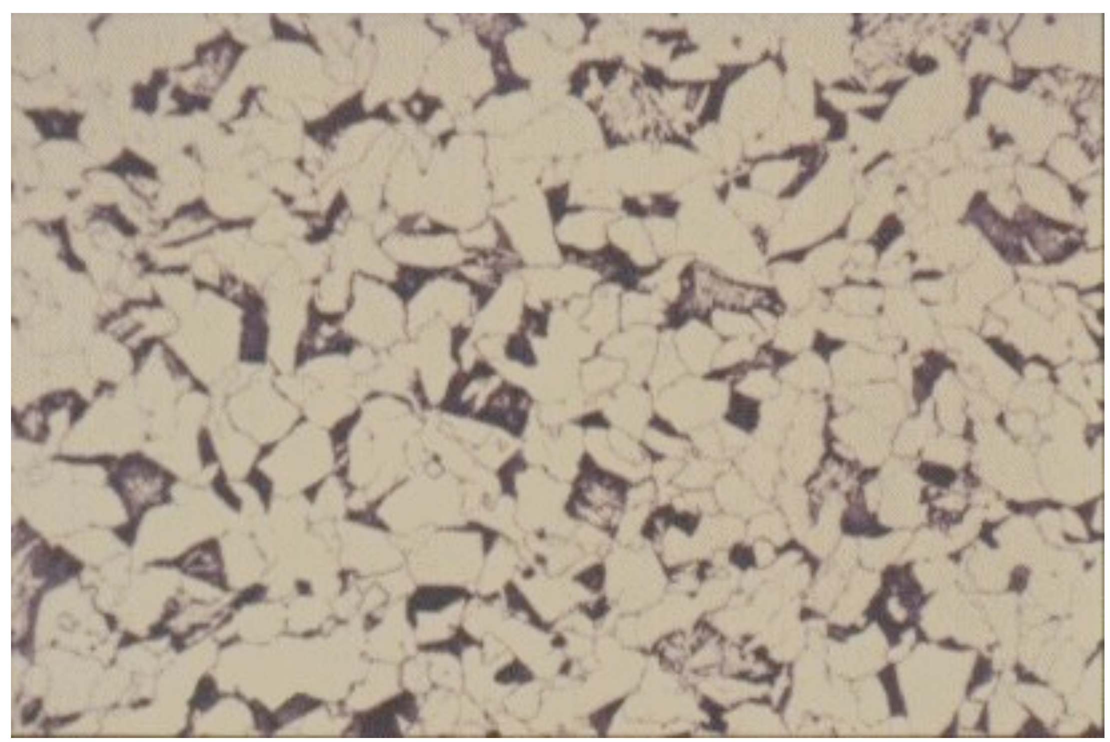
Requires *diffusive* motion of atoms over large lengths.

LuMnO + LaSrMnO

ferrite (b.c.c. Fe) + Fe_3C

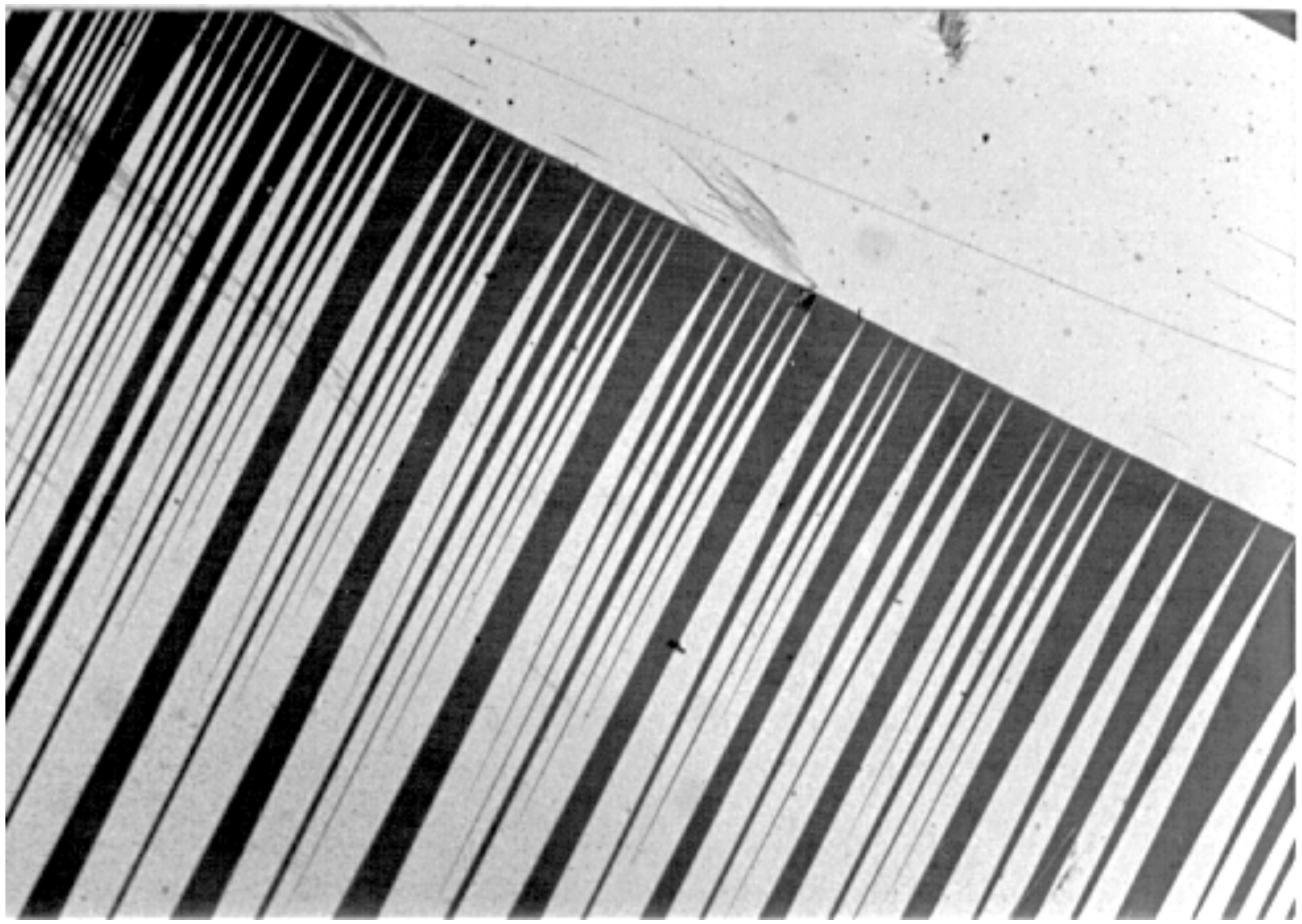


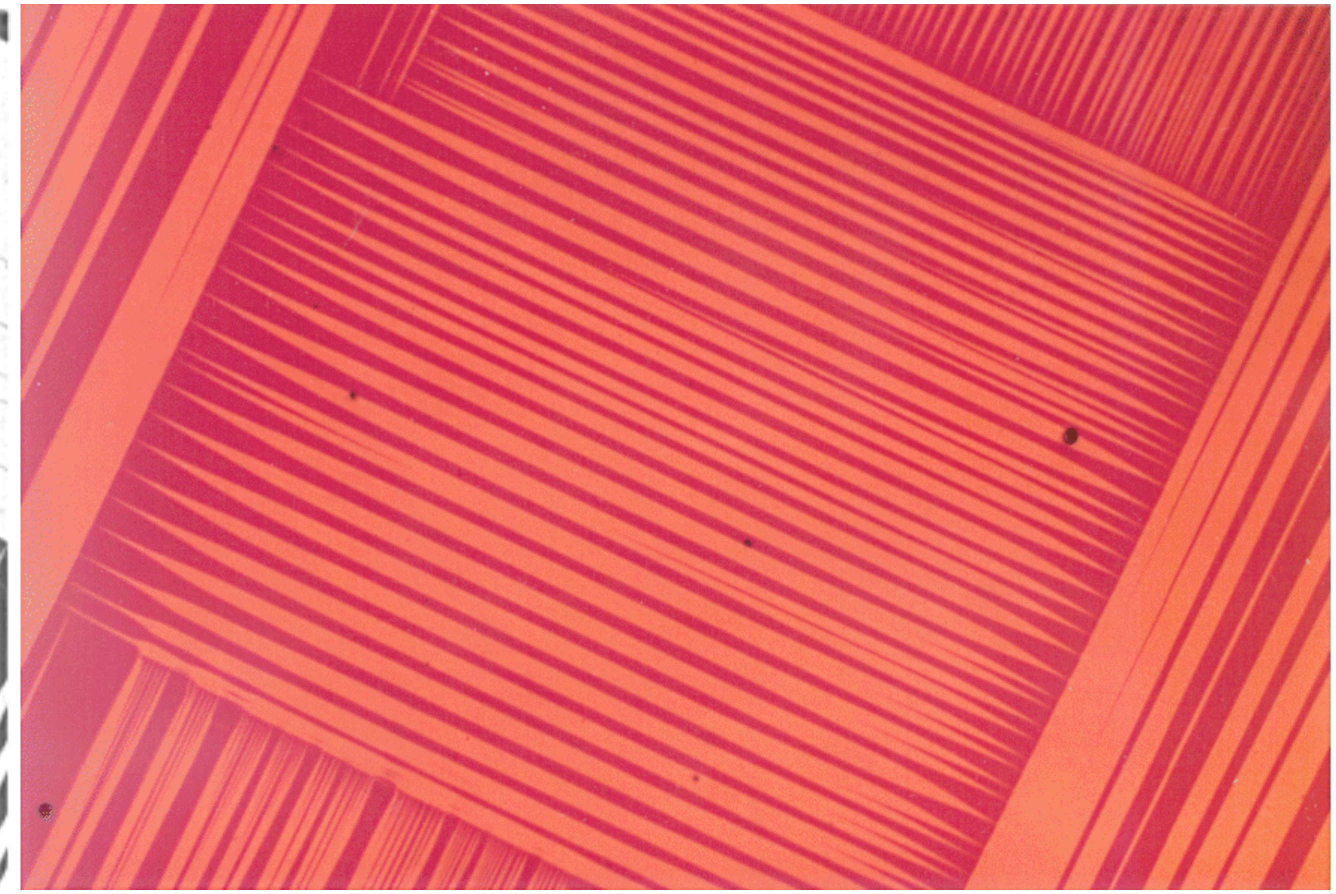


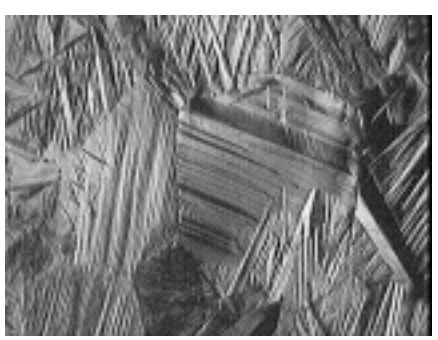


$$\lambda^2 \propto D d_0 / v$$

Martensites



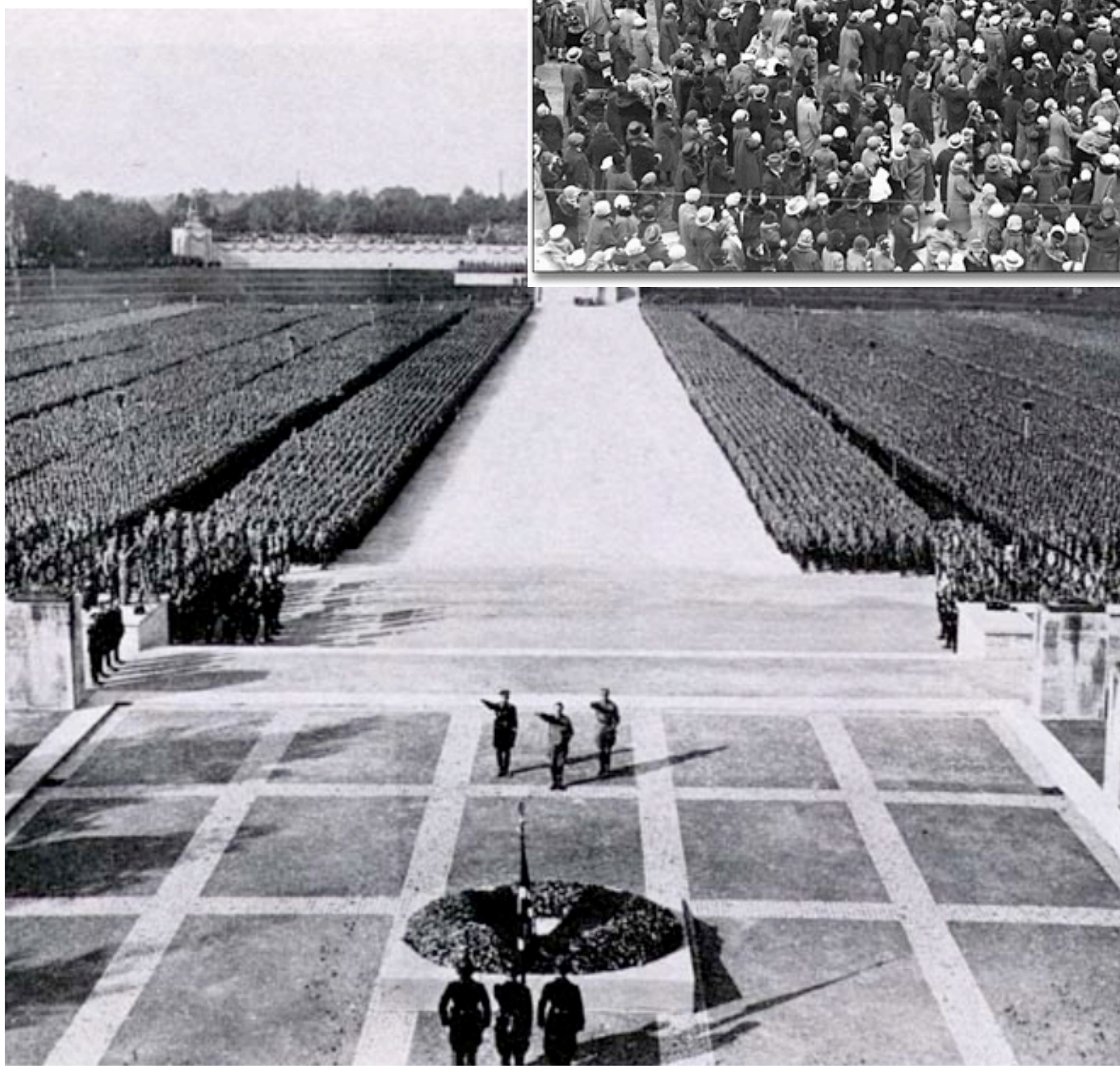




Formed by *ballistic* motion of atoms

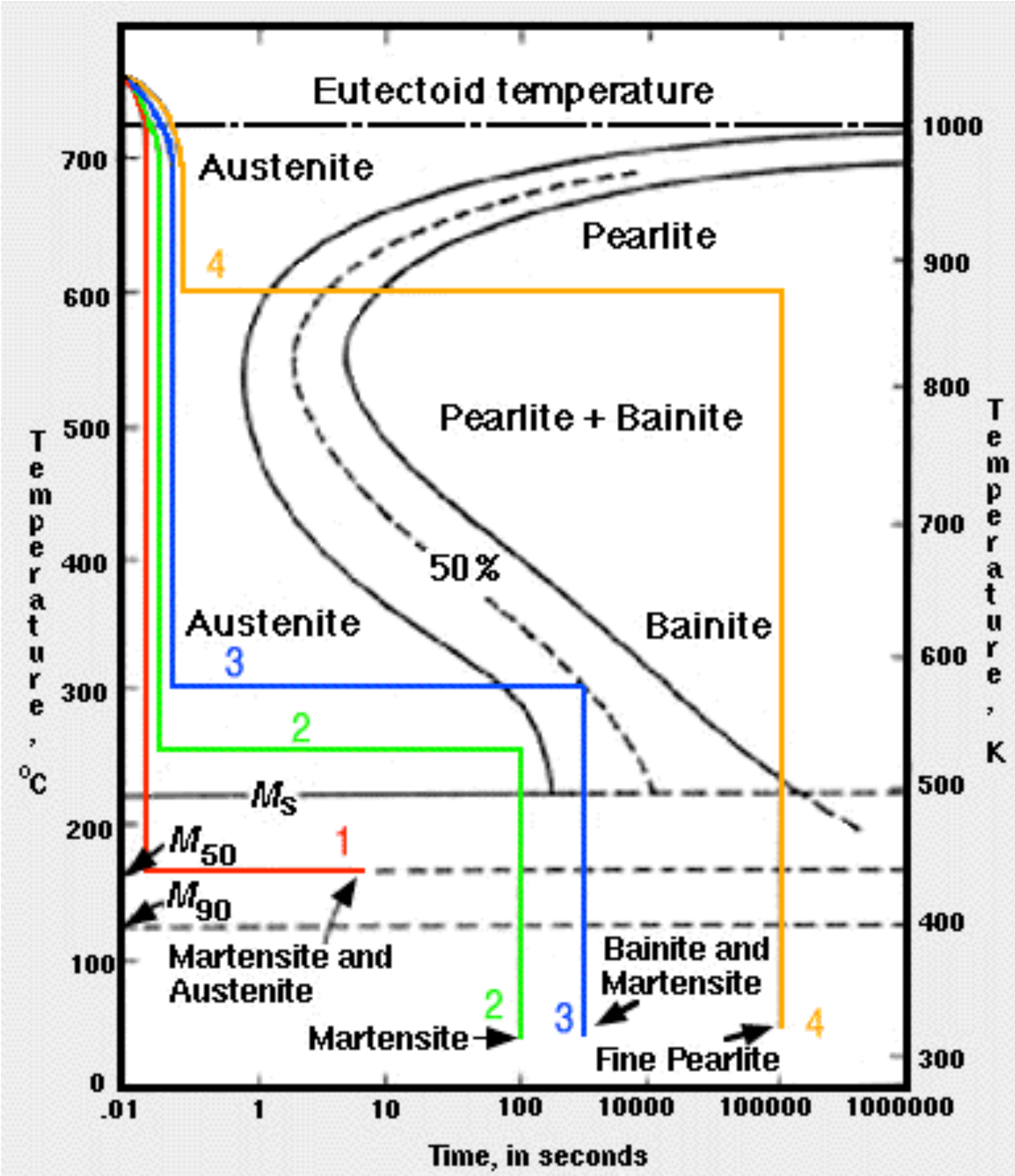
J. P. Sethna : http://www.lassp.cornell.edu/sethna/Tweed/What_Are_Martensites.html

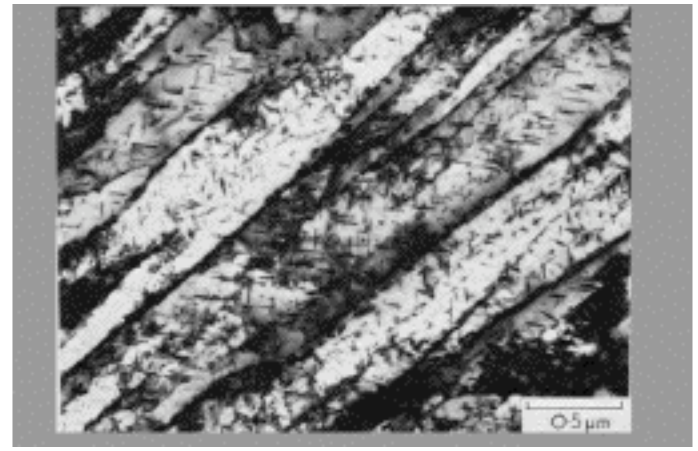
“Civilian”

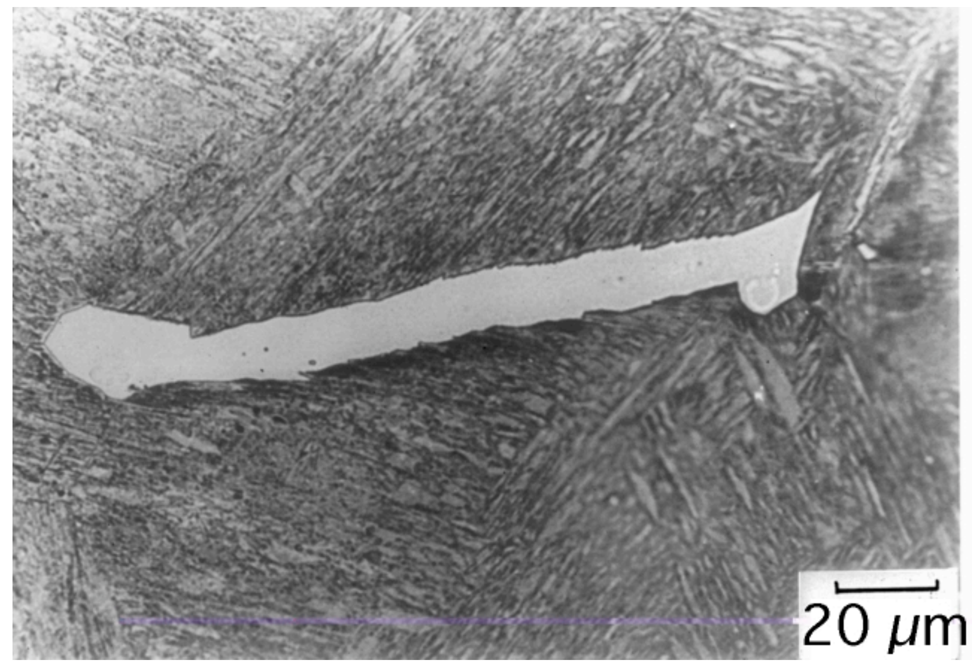


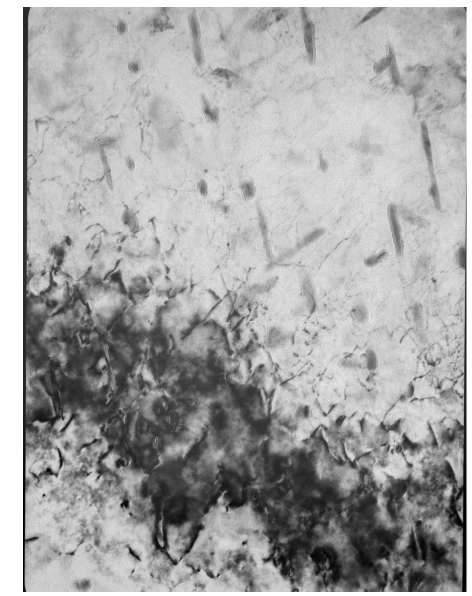
“Military”

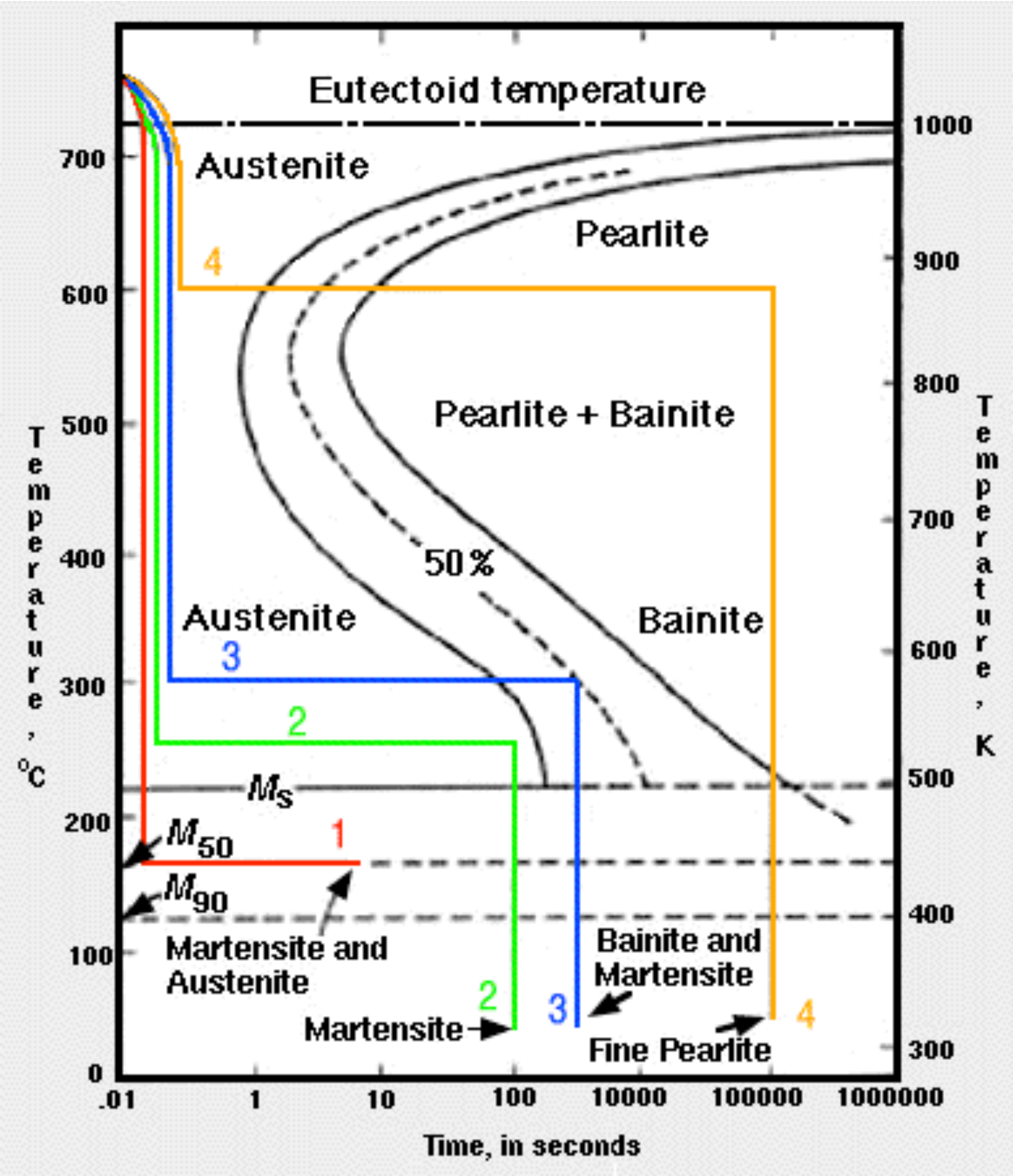
Who gives the orders?

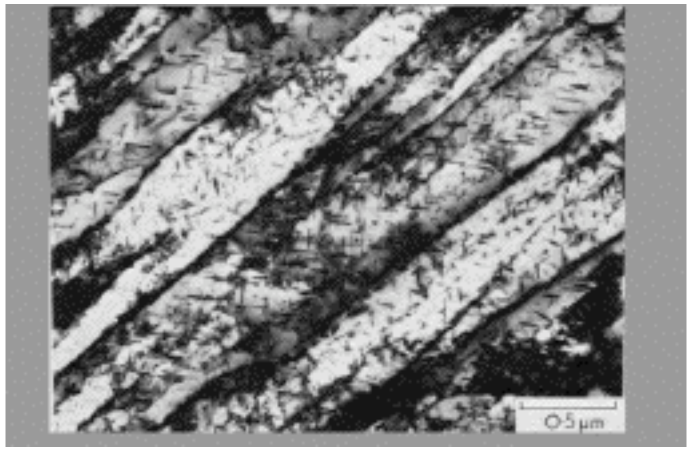

Eutectoid temperature
Austenite
Pearlite
Pearlite + Bainite
50%
Austenite
Bainite
M_S
M_{50}
M_{90}
Martensite and Austenite
Martensite
Bainite and Martensite
Fine Pearlite
1
2
3
4
Temperature, °C
Temperature, K
Time, in seconds
0
100
200
300
400
500
600
700
300
400
500
600
700
800
900
1000
.01
1
10
100
10000
100000
1000000

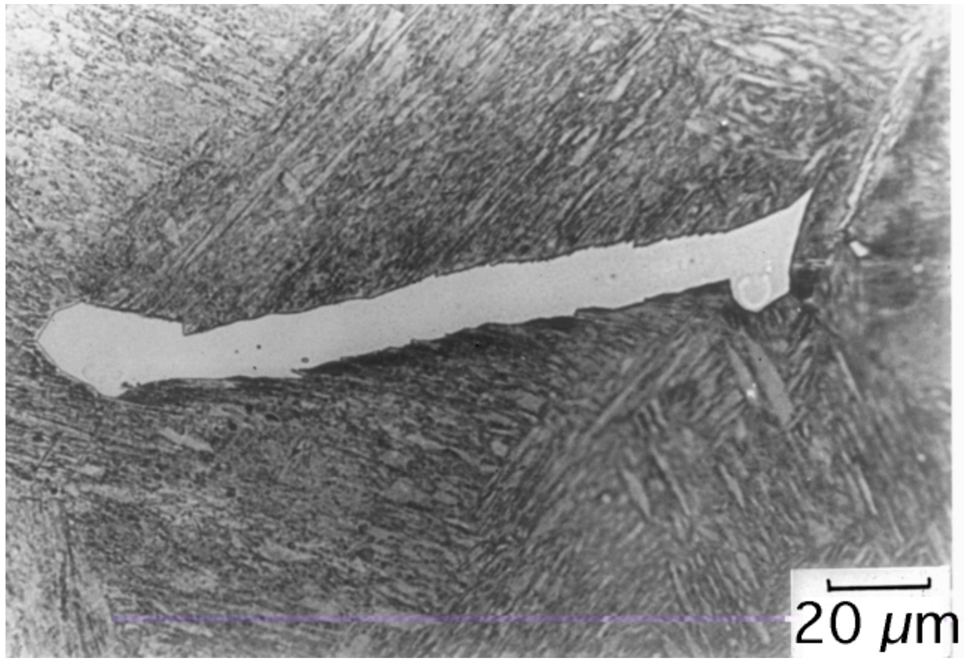


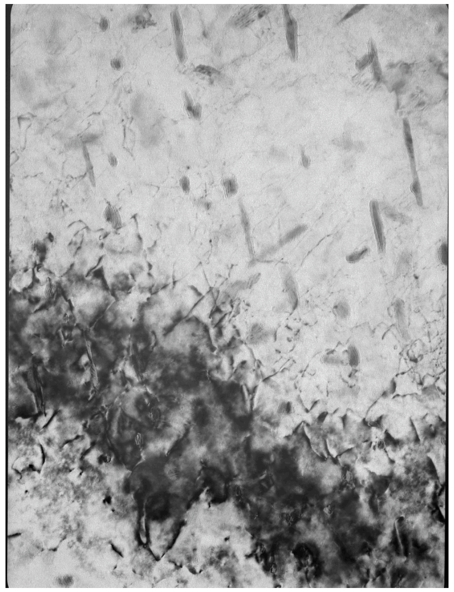

20 µm





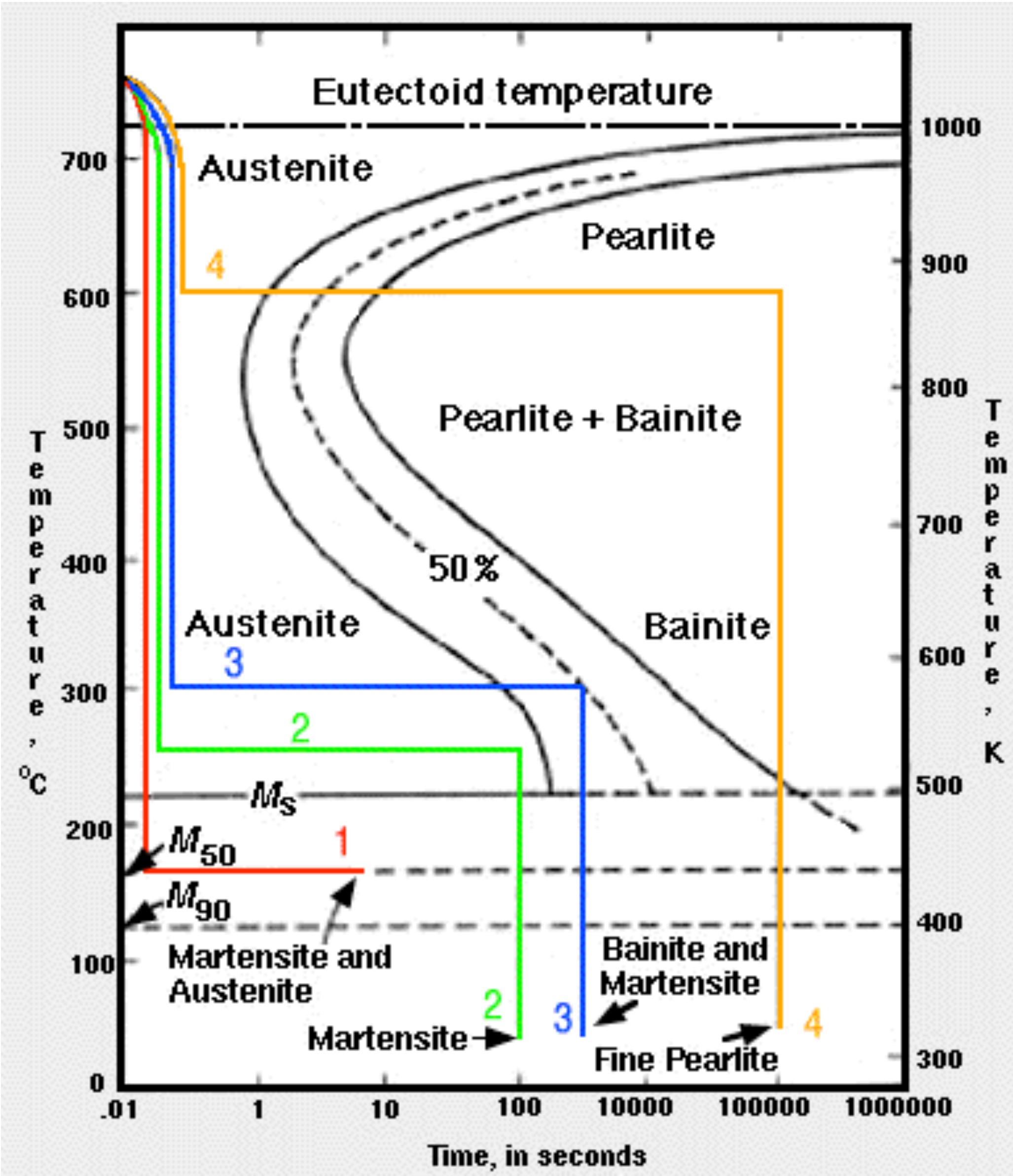


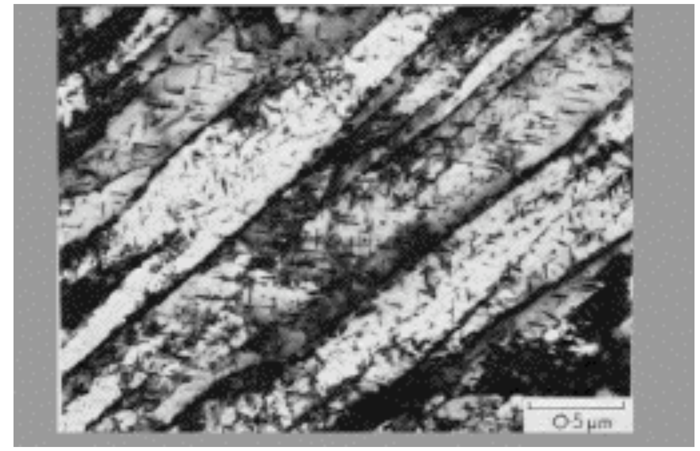


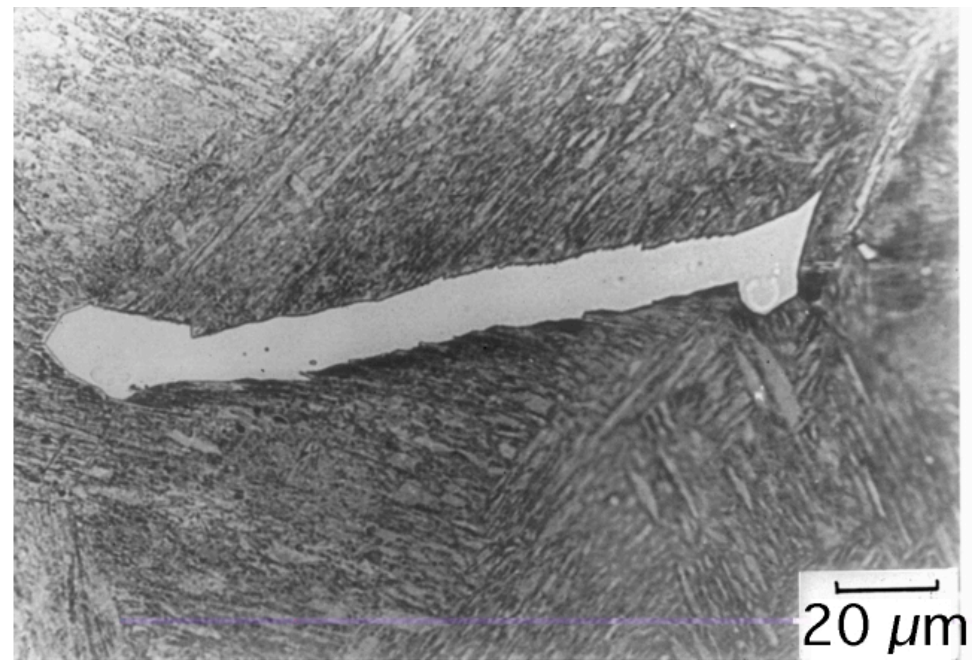


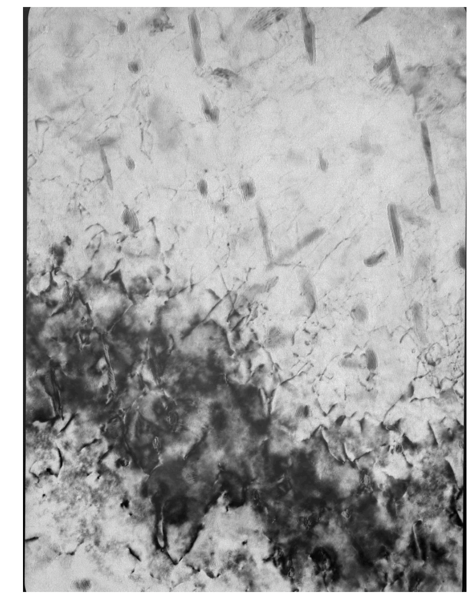
Solid-Solid Phase Transformations in Inorganic Materials 2005

May 29-June 3, 2005 • Pointe Hilton Resort at Squaw Peak • Phoenix, Arizona









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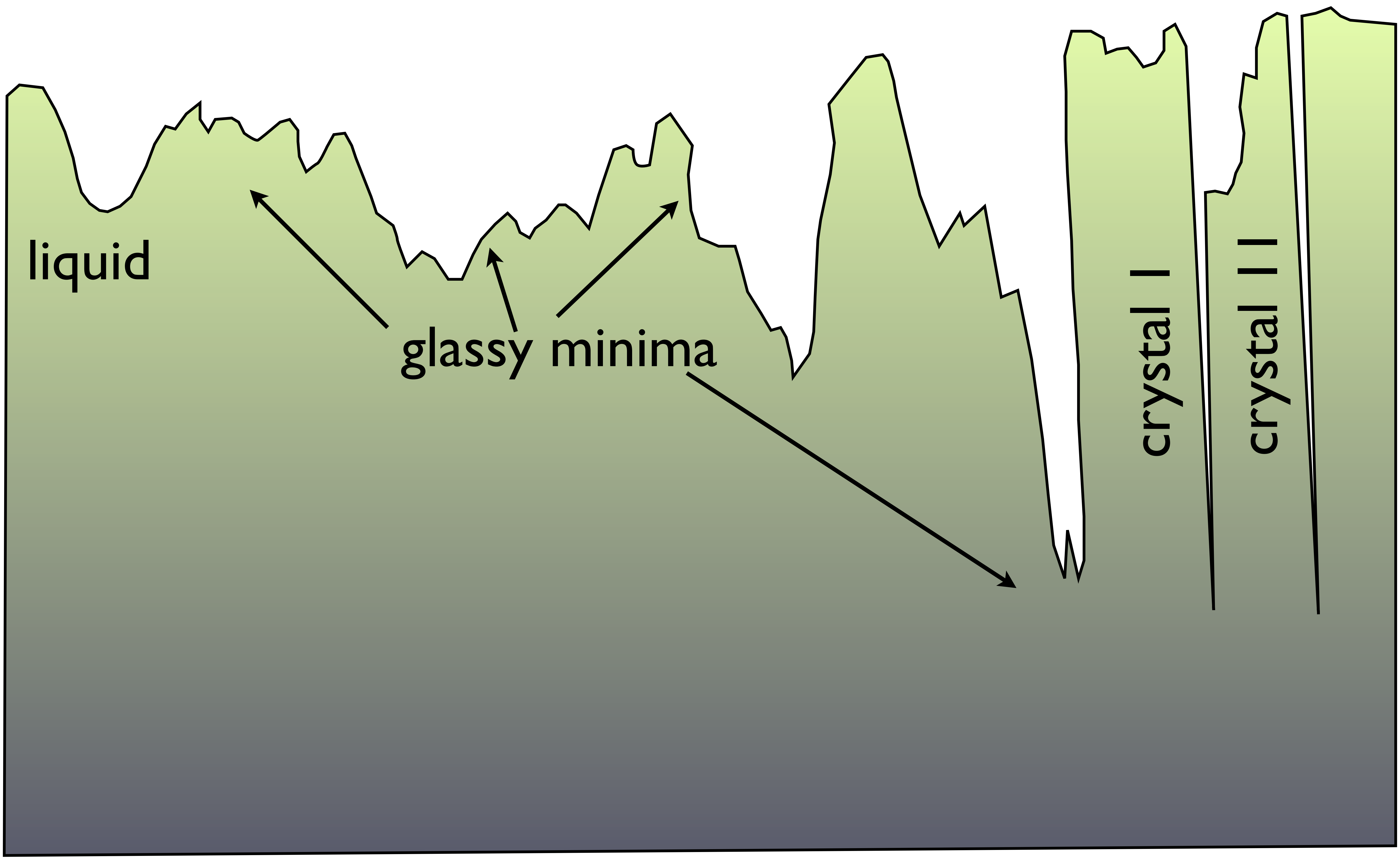
Gree energy landscape

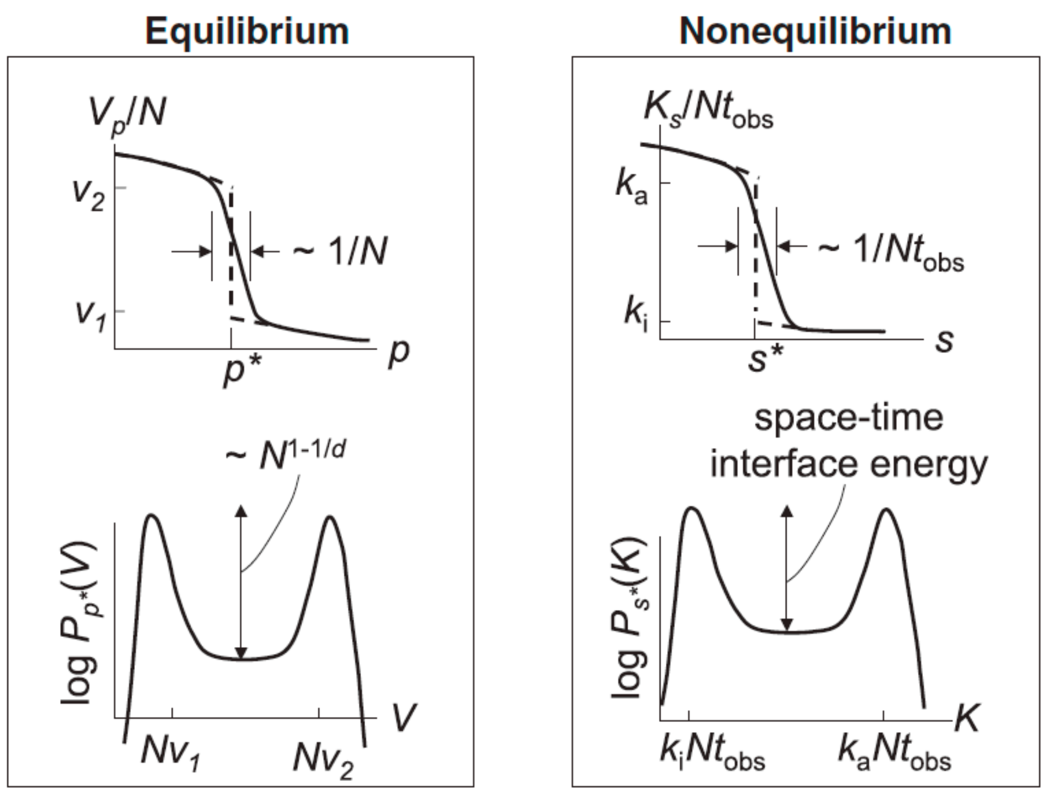


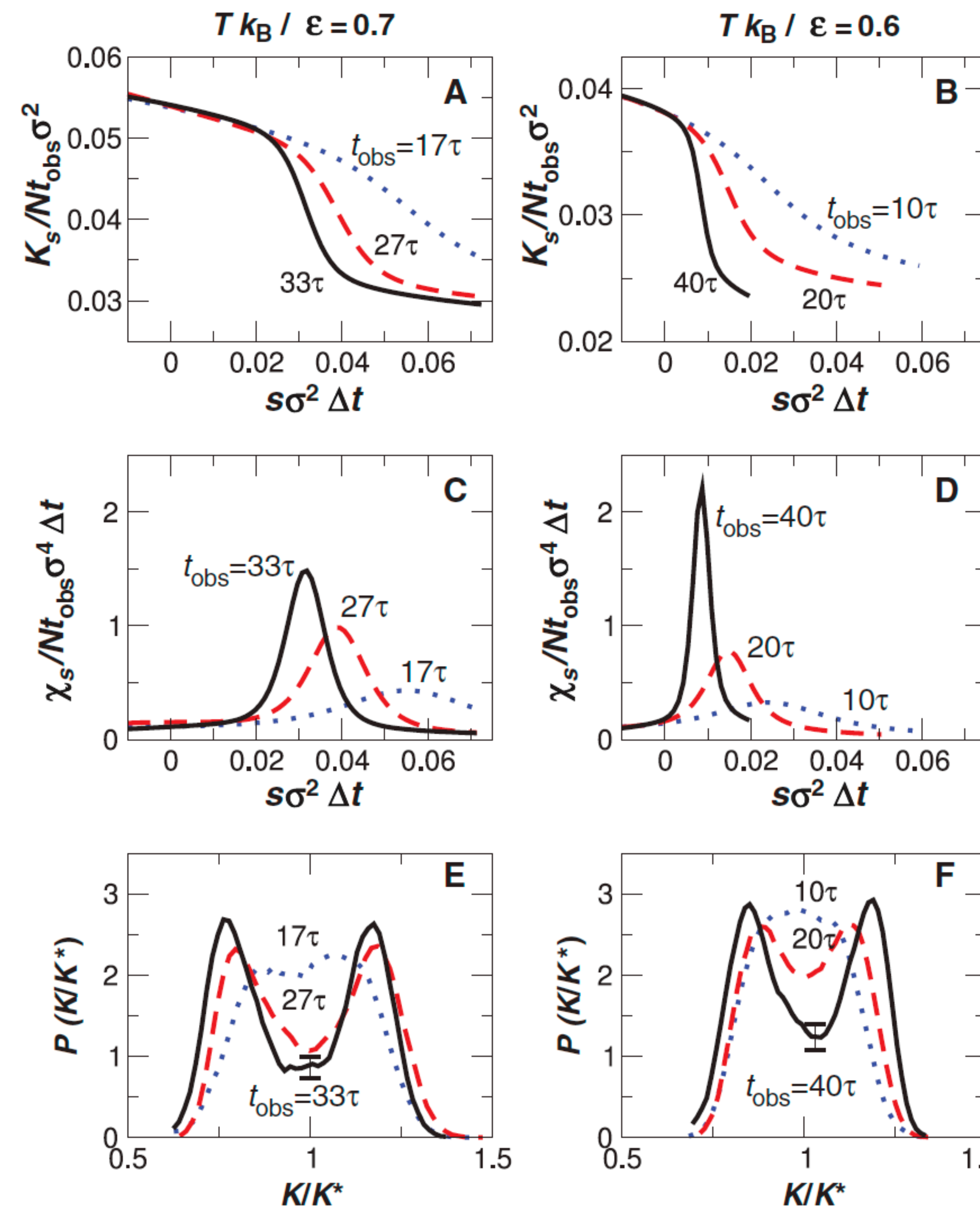
IITK-GJ 2010

Space-time transitions

Hedges, Jack, Garrahan, Chandler, *Science* **323**, 1309 (2009)

Fig. 1. Finite size effects of equilibrium and nonequilibrium phase transitions. The mean volume V_p manifests an equilibrium first-order phase transition at pressure $p = p^*$, whereas the mean dynamical activity K_s manifests a dynamical first-order phase transition at the dynamical field $s = s^*$. At conditions of phase coexistence, the volume distribution function, $P_p(V)$, and the dynamical activity distribution, $P_s(K)$, are bimodal. Configurations or trajectories with intermediate behaviors lie at much higher free energies (or lower probabilities) than those of the basins. For finite systems, discontinuous phase transitions become crossovers with widths that vanish as system size, N, and observation time, t_{obs}, grow to infinity.





$$K[x(t)] = \Delta t \sum_{t=0}^{t_{obs}} \sum_{j=1}^{N} |\mathbf{r}_j(t+\Delta t) - \mathbf{r}_j(t)|^2$$

$$P_s[x(t)] \propto P_0[x(t)] \exp\{-sK[x(t)]\}$$

- Early time nucleation dynamics determines microstructure in solid-solid transitions
- Diffusive to ballistic transition is a space-time transition with an appropriate order parameter.
- Emergence of hydrodynamic description for late time microstructure.

Outline

- A model solid with square to rhombus transformation.
- Early time behavior (atomistic scale)
- Late time behavior (coarse grained scale)
- Shape transformations (macroscopic scale)

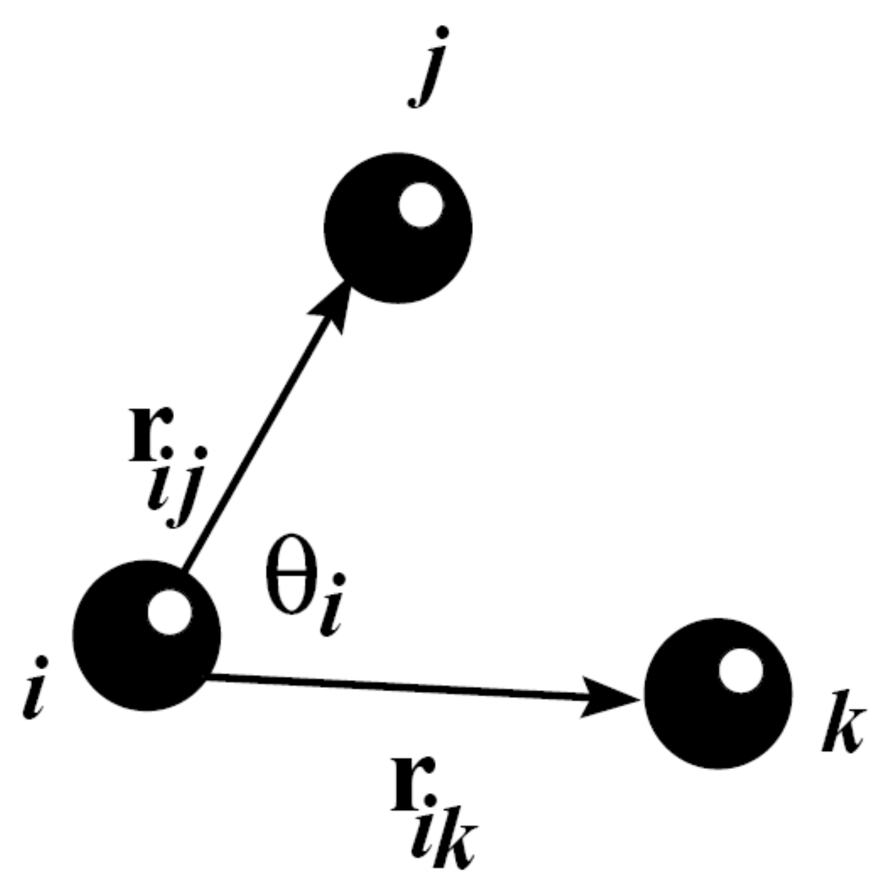
The model solid

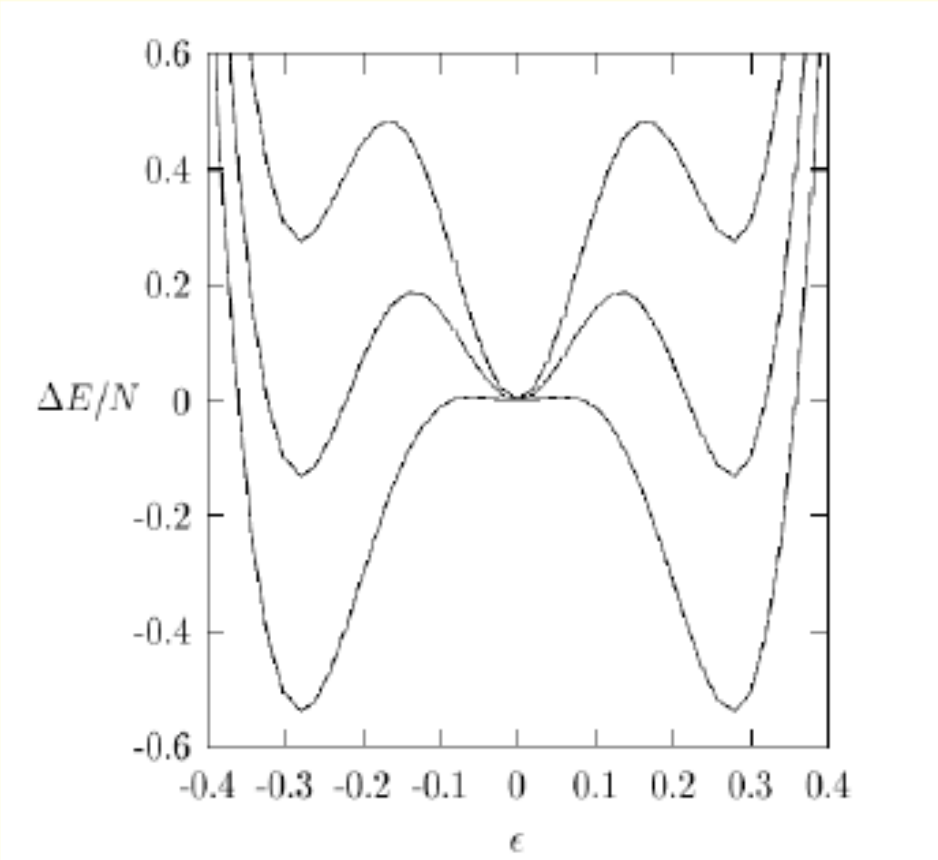
$$E = \frac{1}{2}\Sigma_{i\neq j}\Psi_2(\mathbf{r}_{ij}) + \frac{1}{6}\Sigma_{i\neq j\neq k}\Psi(\mathbf{r}_{ij},\mathbf{r}_{jk},\mathbf{r}_{ki})$$

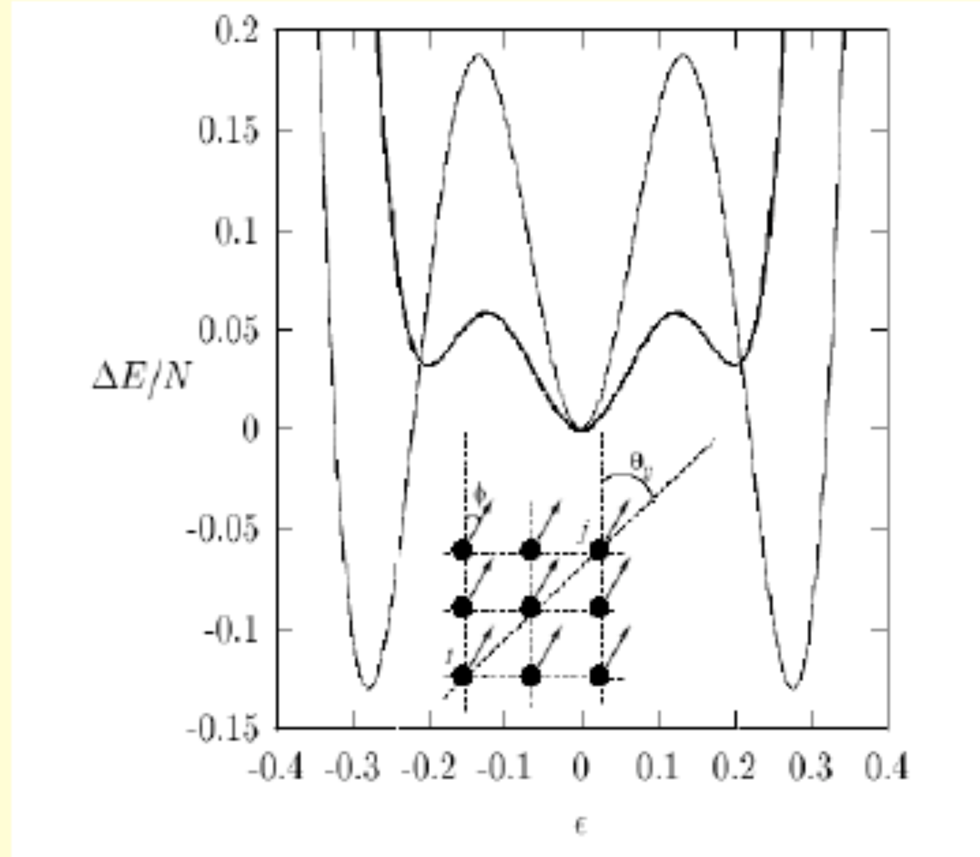
$$\Psi_2 = V_2(\frac{\sigma}{r_{ij}})^{12} \times (1+\alpha\sin^2 4(\theta_{ij}-\phi))$$

$$\Psi = V_3[f_{ij}\sin^2(4\Theta_{ijk})f_{ik} + \cdots]$$

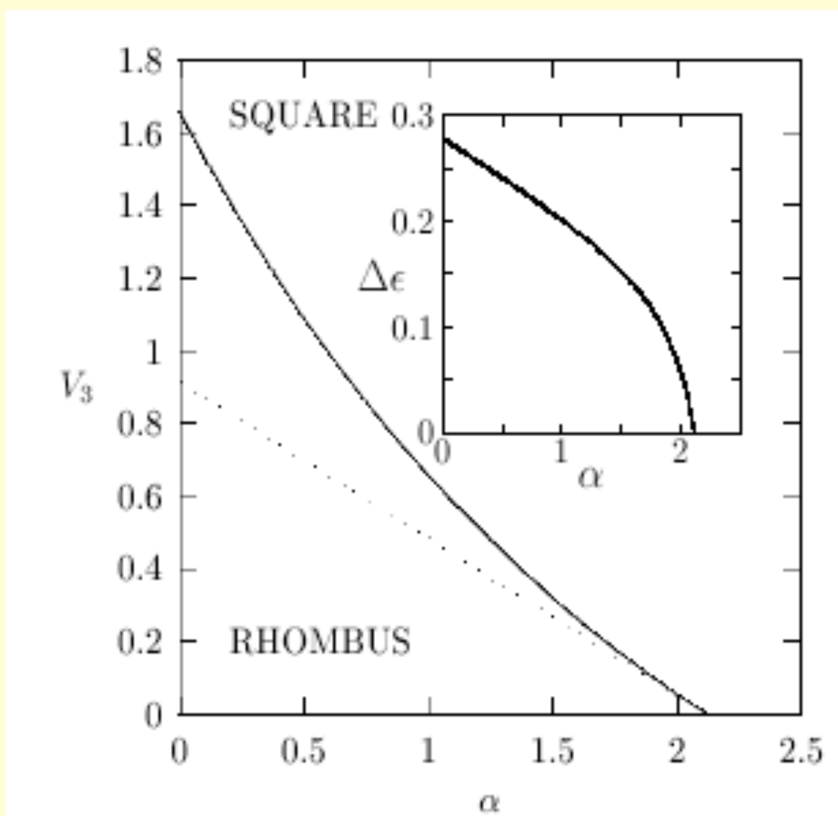
$$\begin{aligned} f_{ij} &= (r_{ij}-r_0)^2 \quad r_{ij} < r_0 \\ &= 0 \qquad \text{otherwise} \end{aligned}$$







$\alpha = 0$

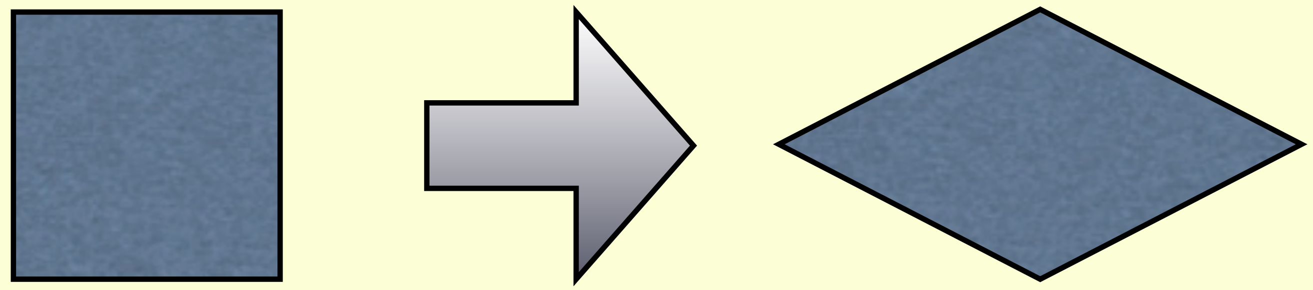


$\alpha \neq 0$

$$\varepsilon = \frac{1}{2}\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right)$$

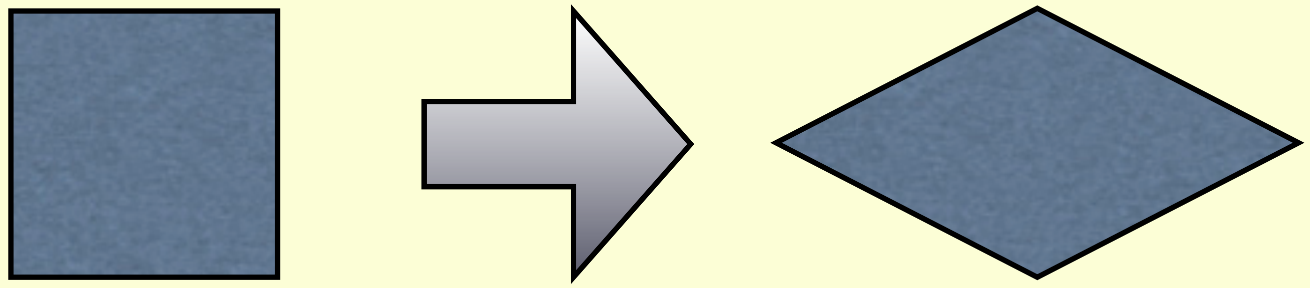
OP strain

From Square to Rhombic lattice in 2d



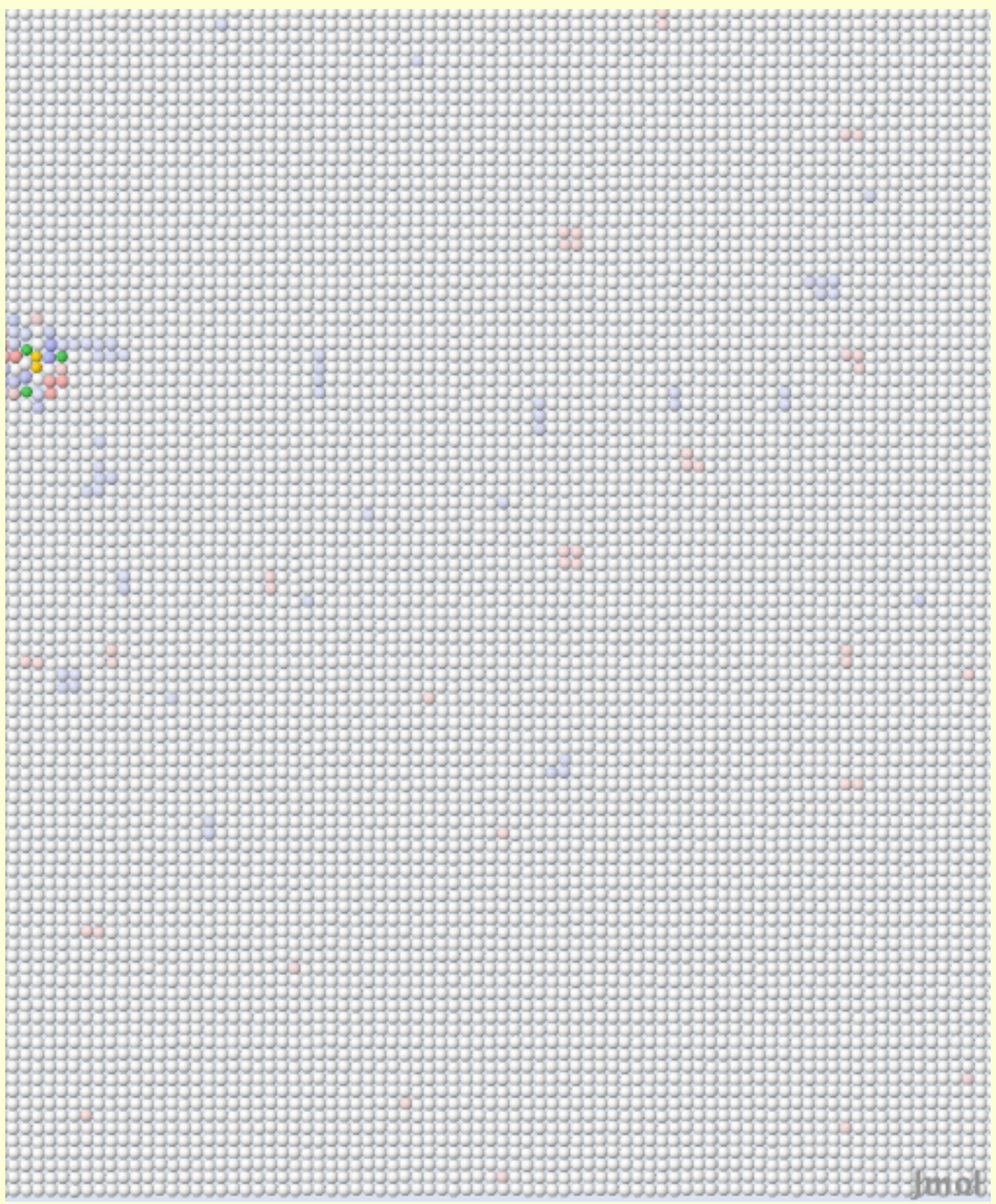
low temperatures high temperatures

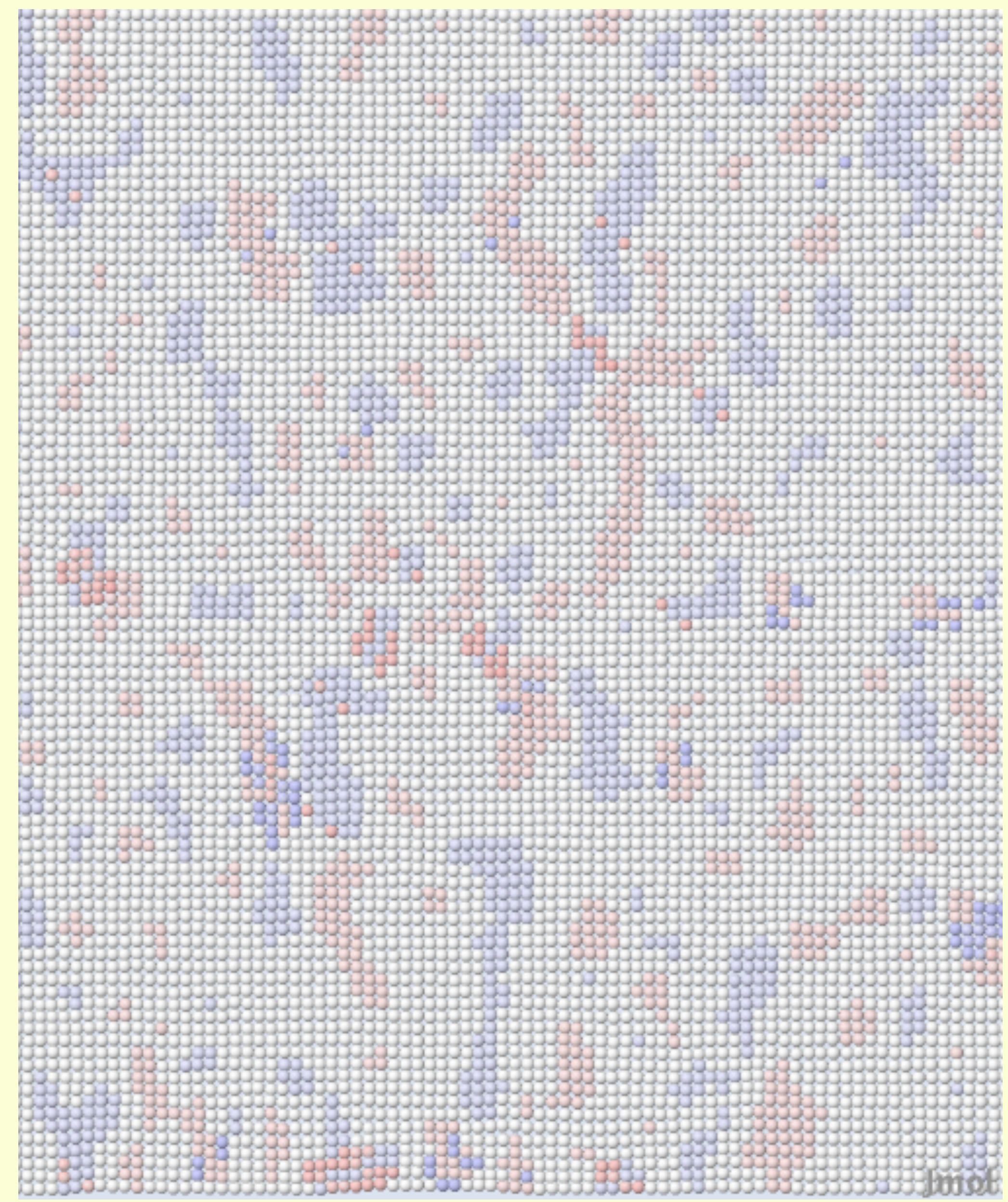
From Square to Rhombic lattice in 2d



low temperatures

high temperatures





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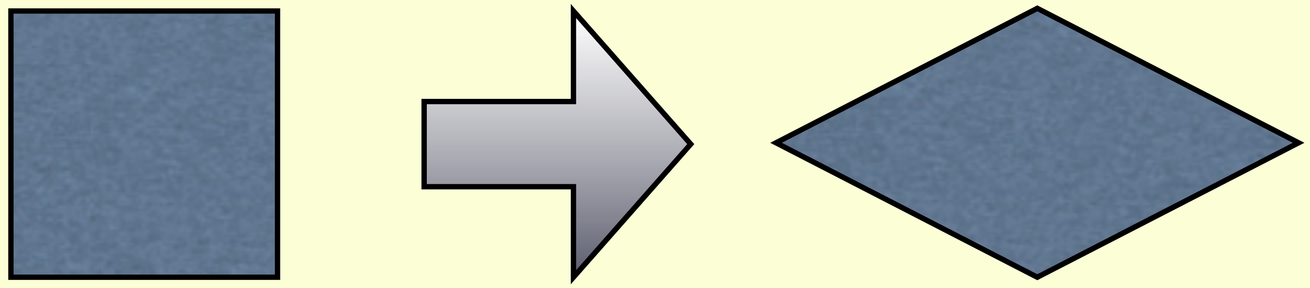
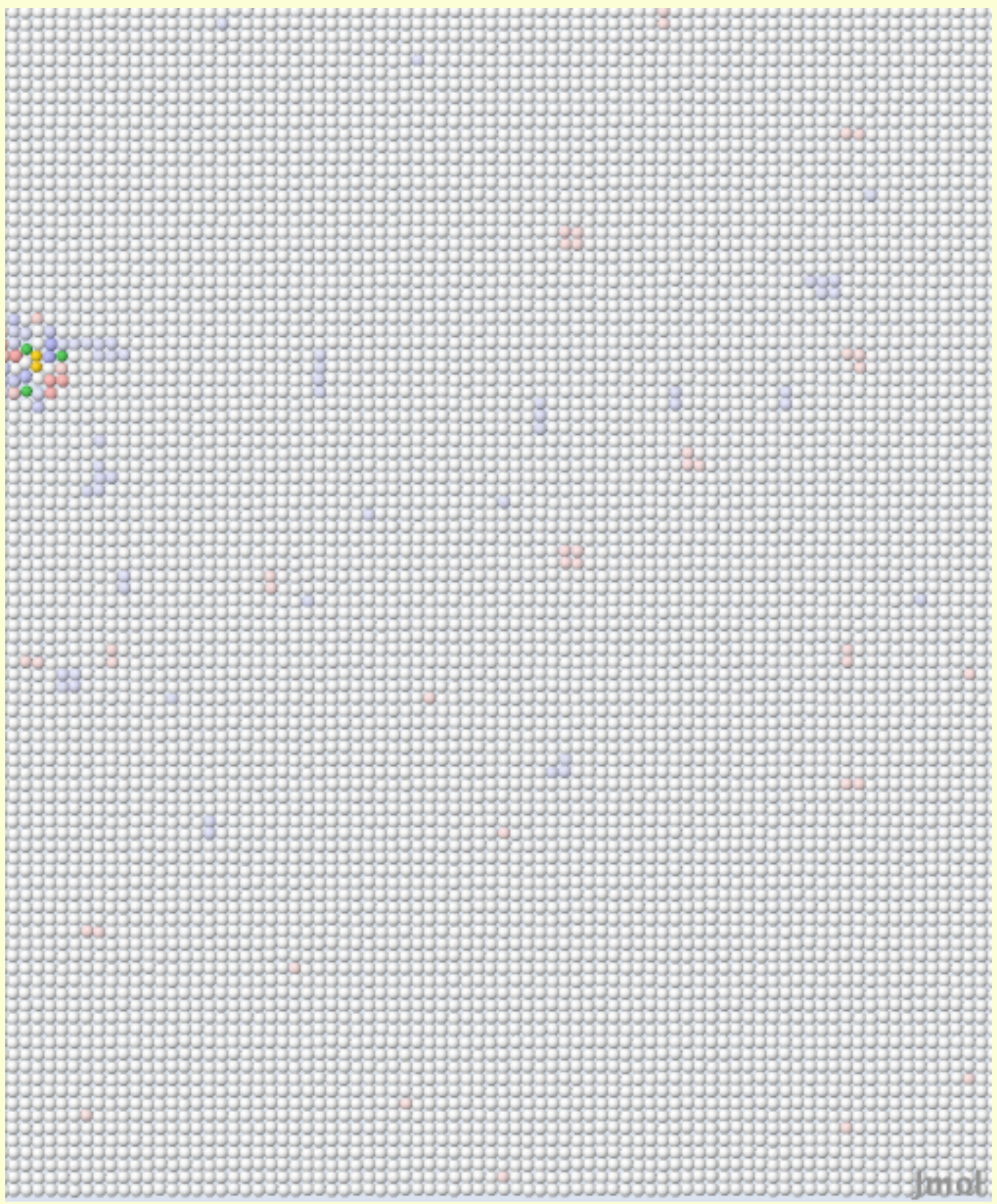
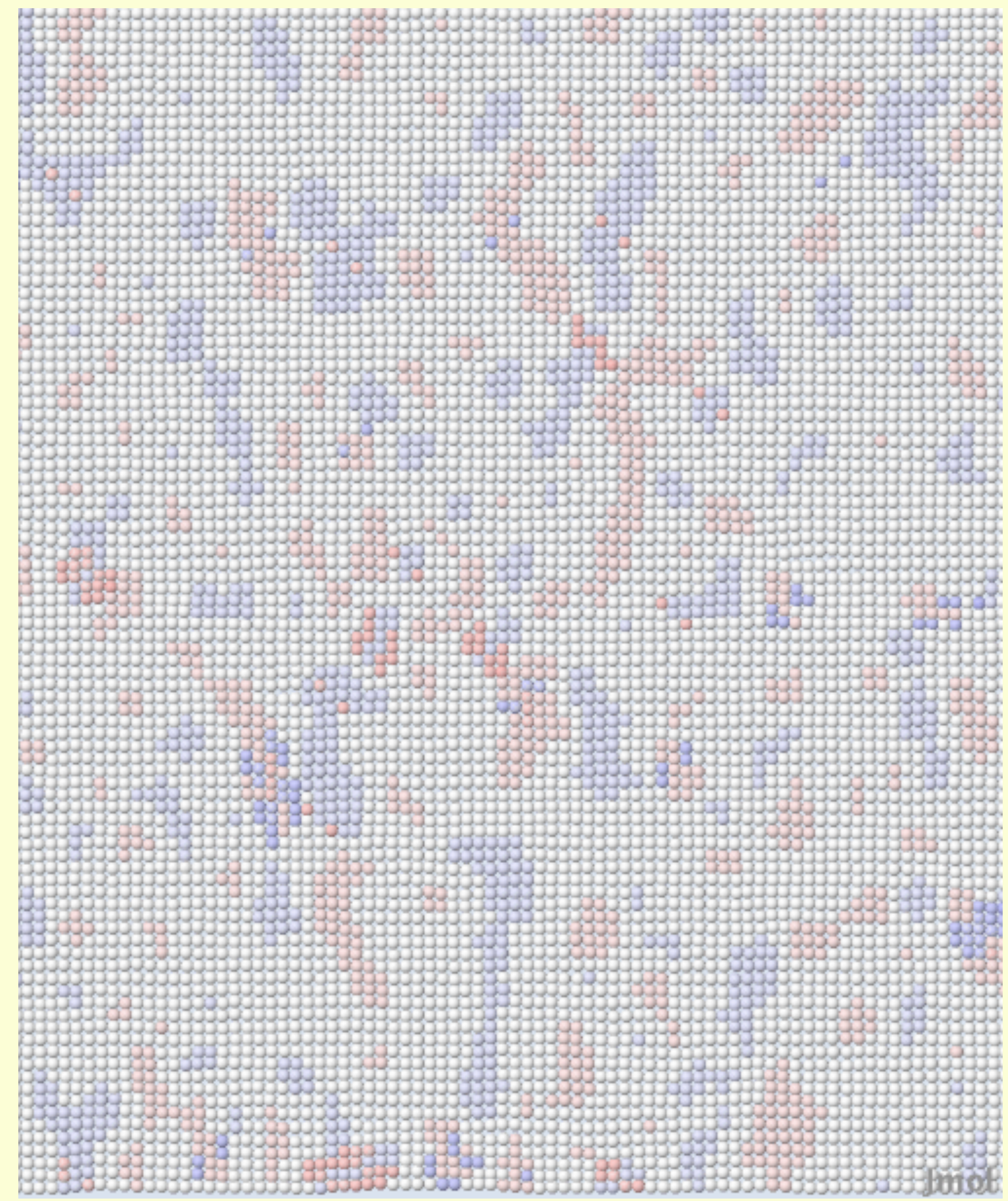
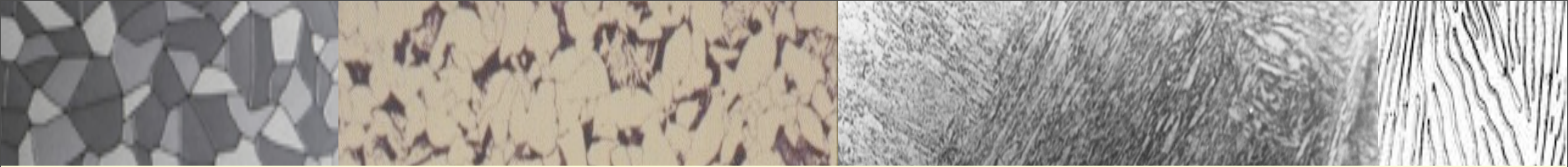


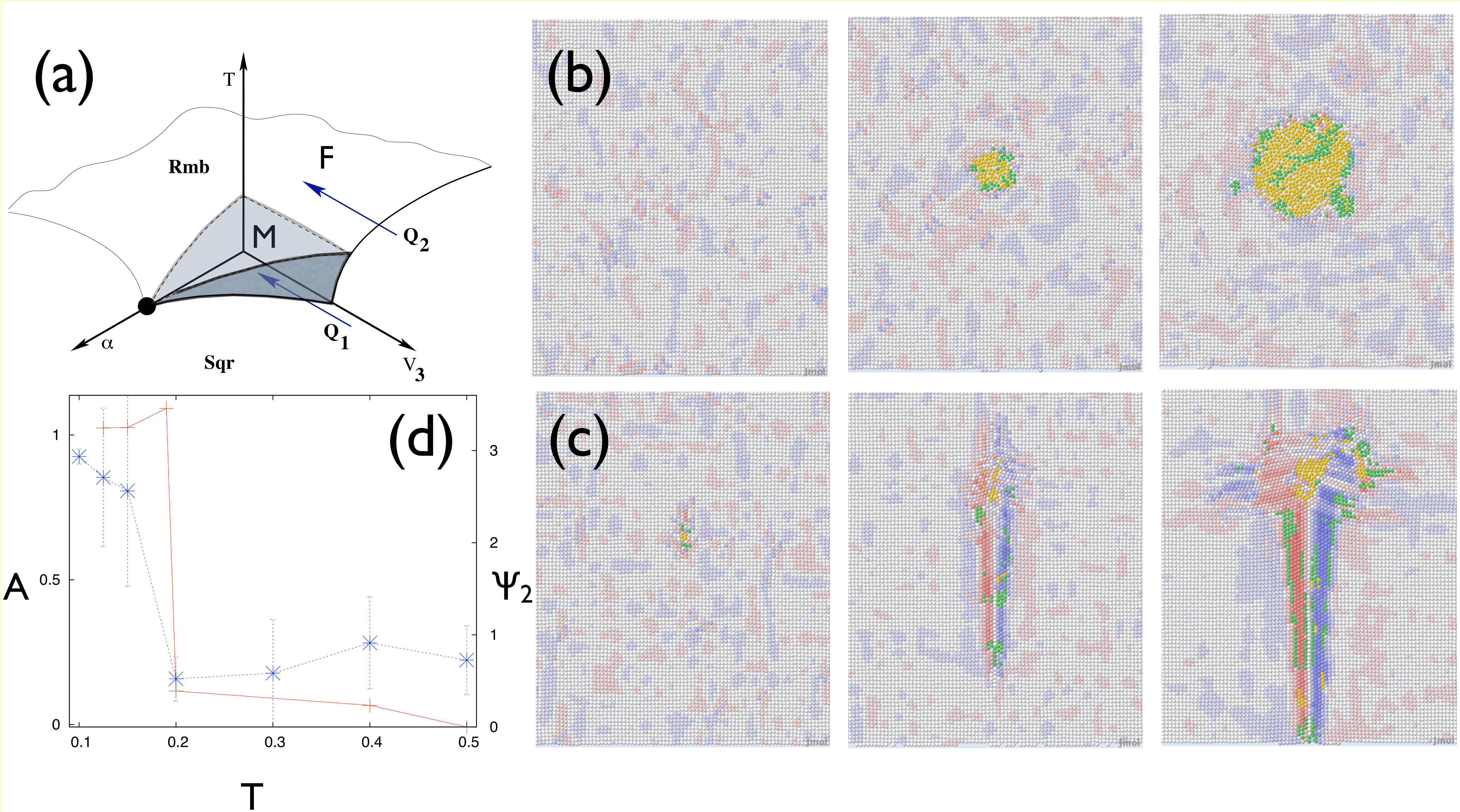
low temperatures

high temperatures

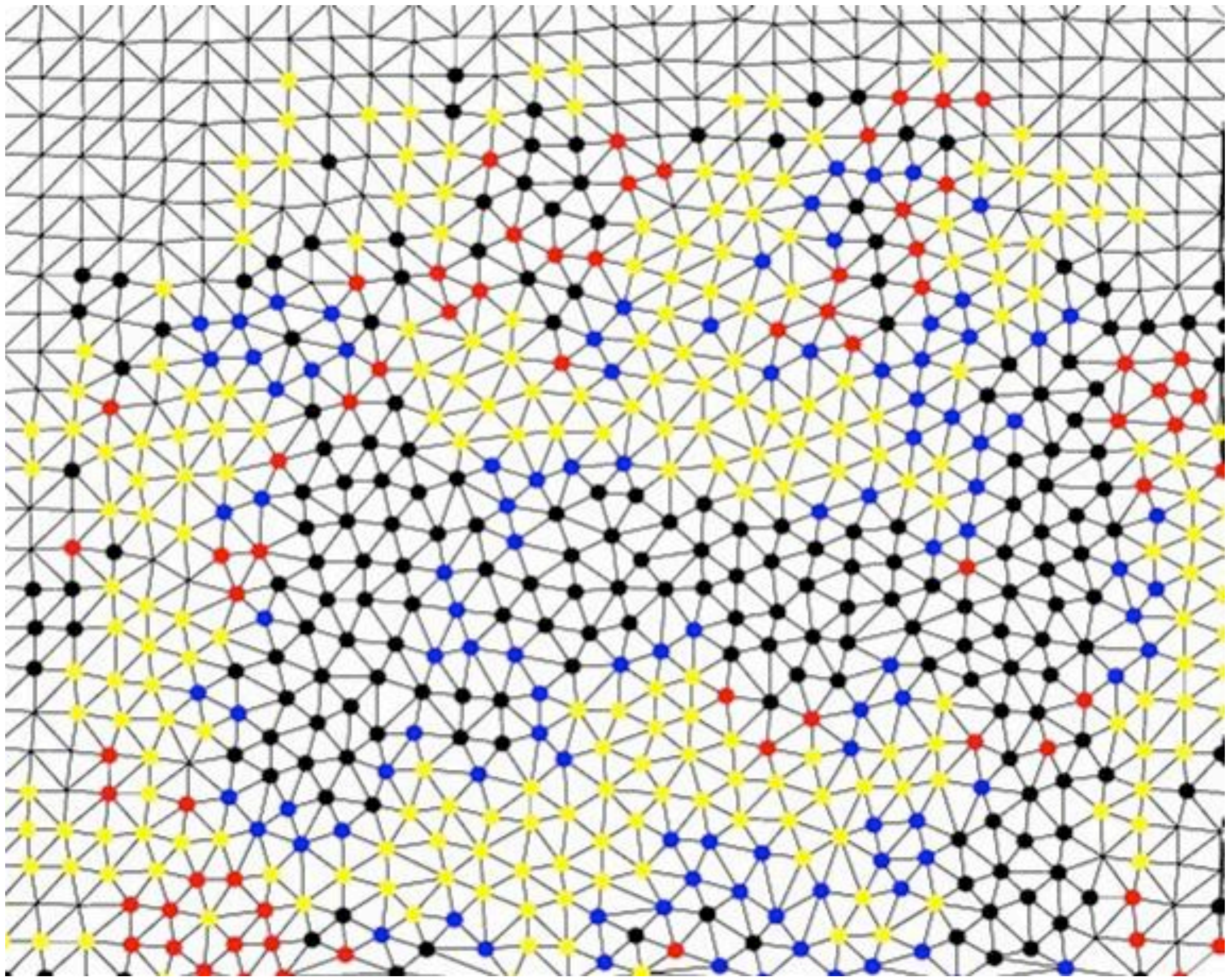


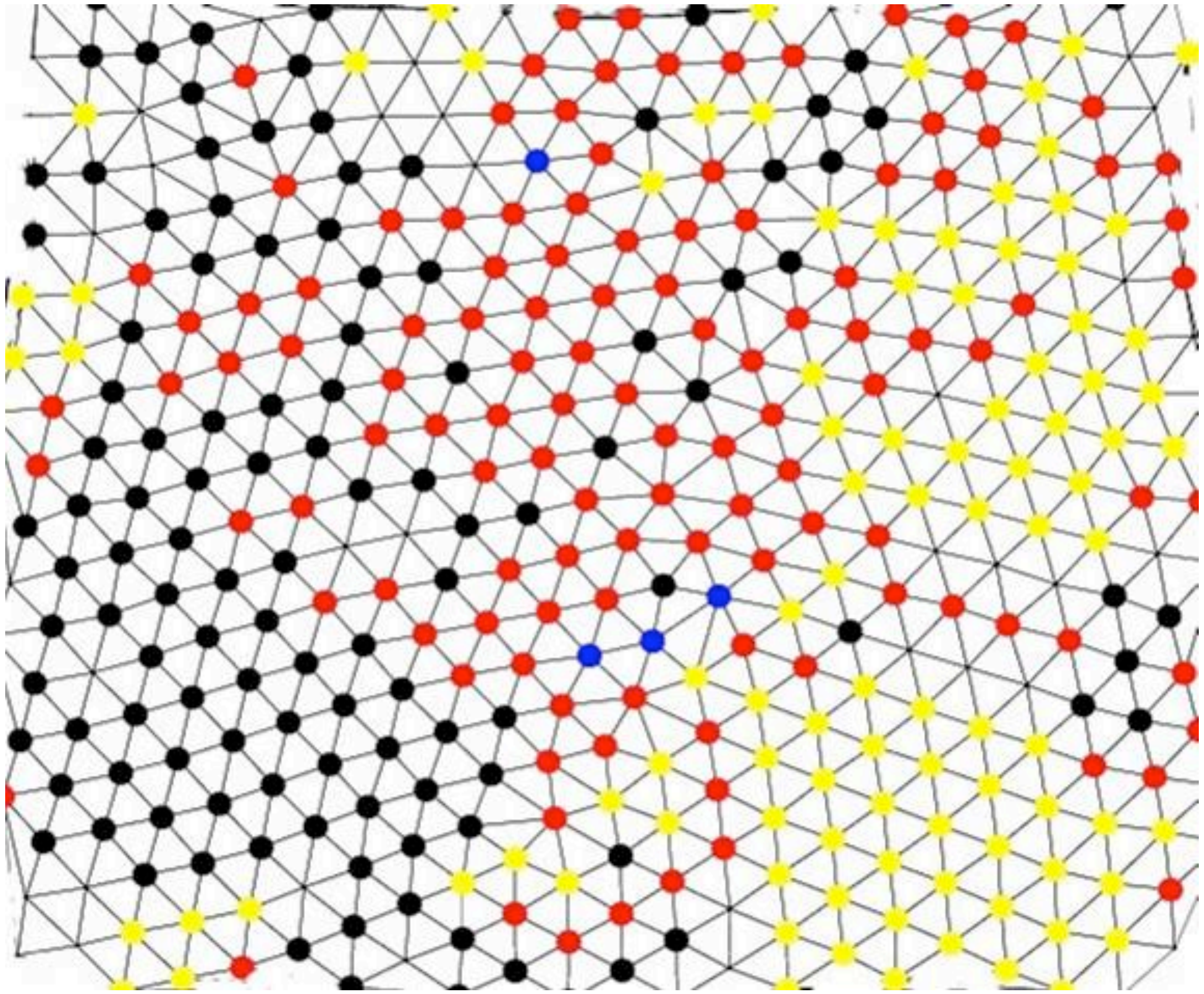




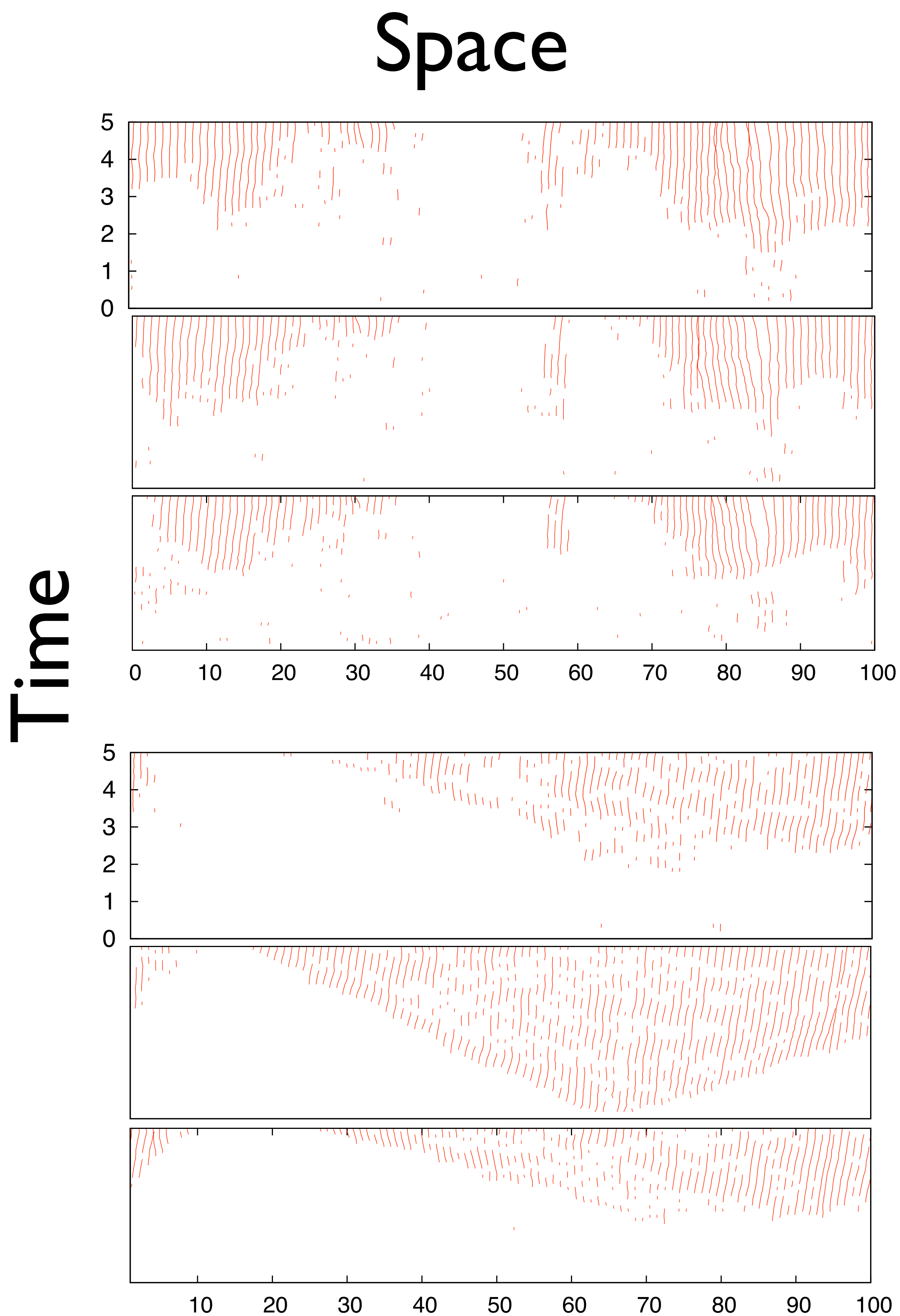


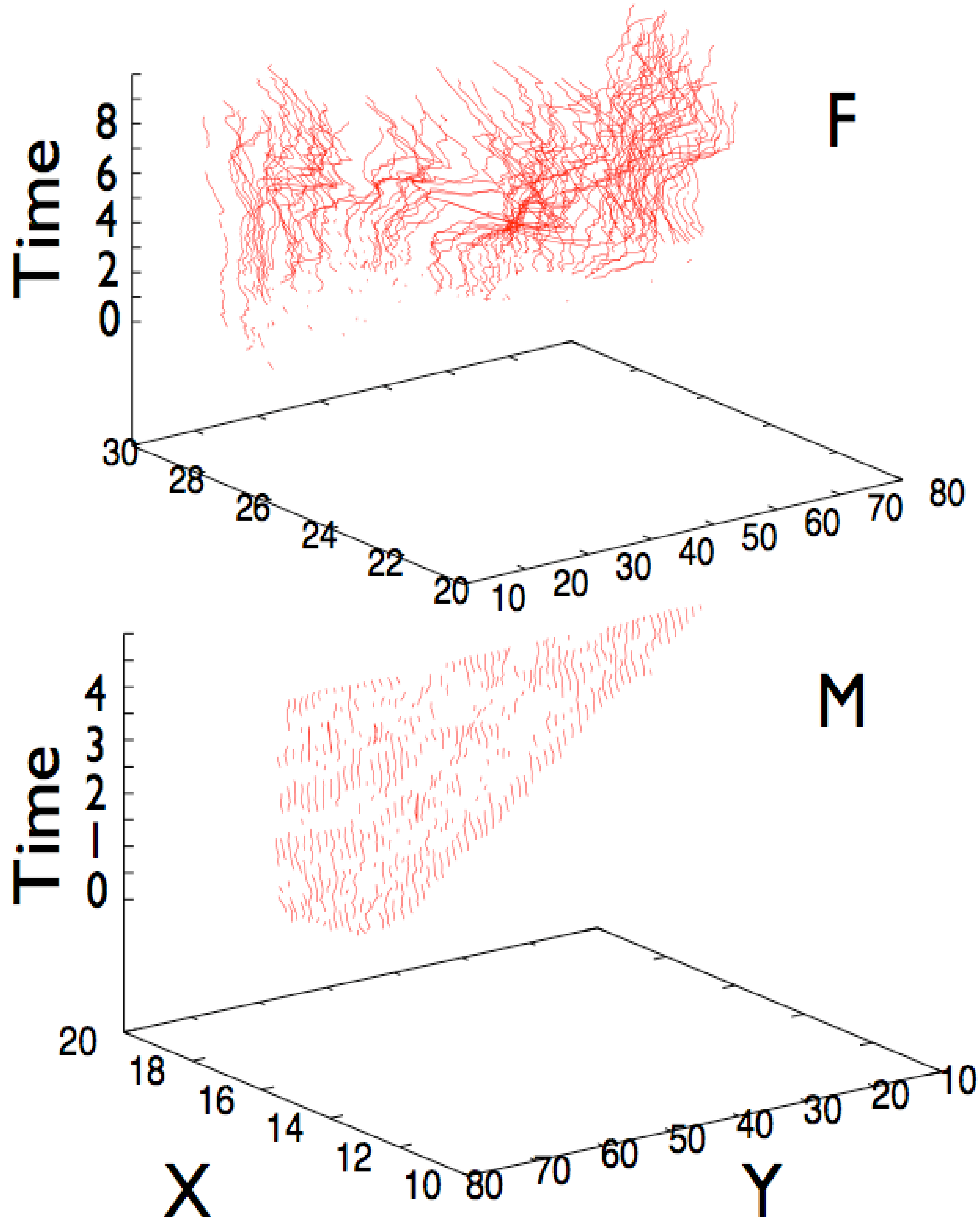
Color codes: red-blue = ε ; gold = jammed : green = un-jammed

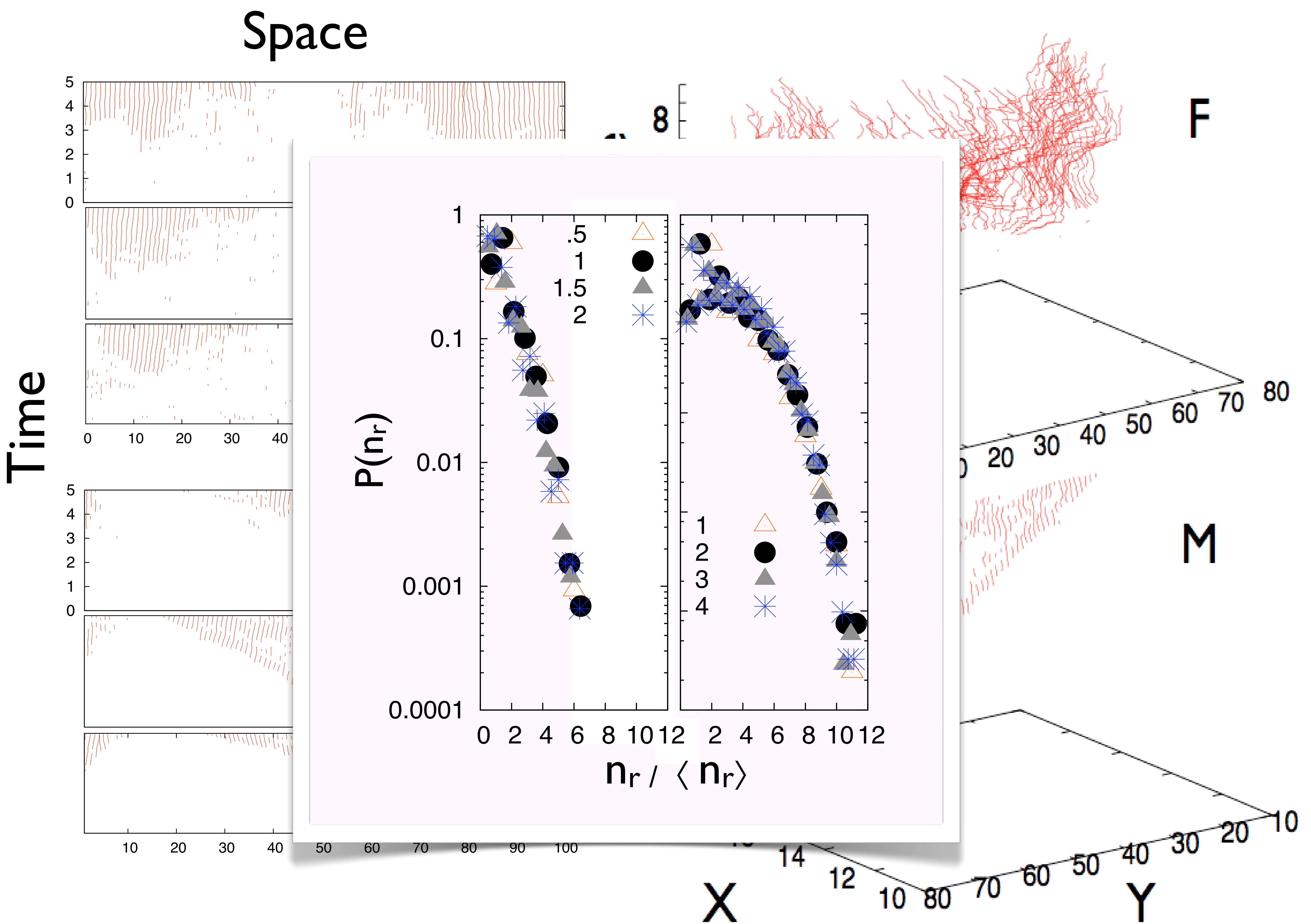


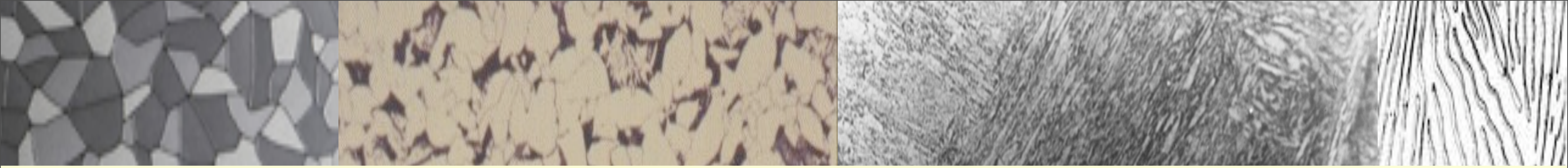


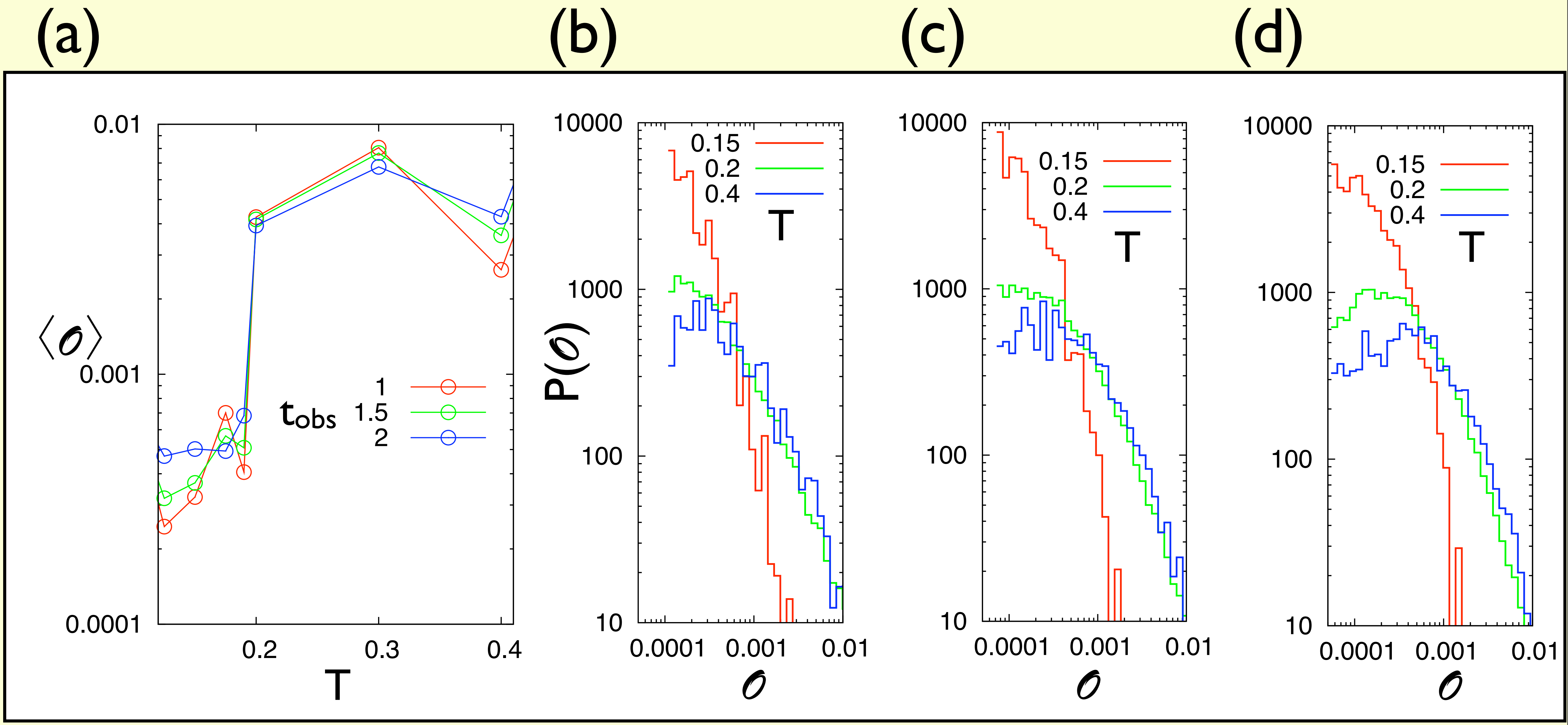
Active regions have high local density of defects


Space
Time
5
4
3
2
1
0
0 10 20 30 40 50 60 70 80 90 100
10 20 30 40 50 60 70 80 90 100


Time
F
8
6
4
2
0
30 28 26 24 22 20
10 20 30 40 50 60 70 80
Time
M
4
3
2
1
0
20 18 16 14 12 10
80 70 60 50 40 30 20 10
X
Y


Space
Time
F
M
X
Y
P(n_r)
n_r / ⟨n_r⟩
.5
1
1.5
2
1
2
3
4



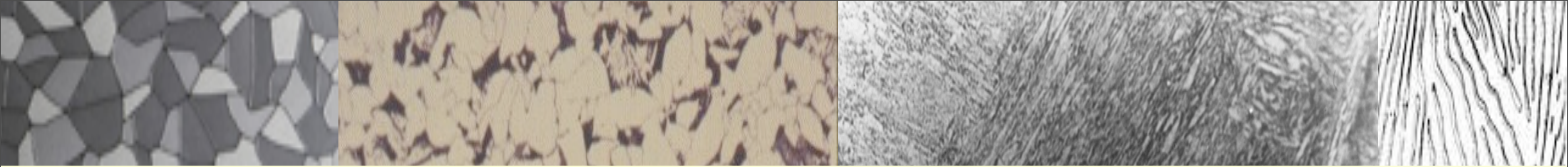


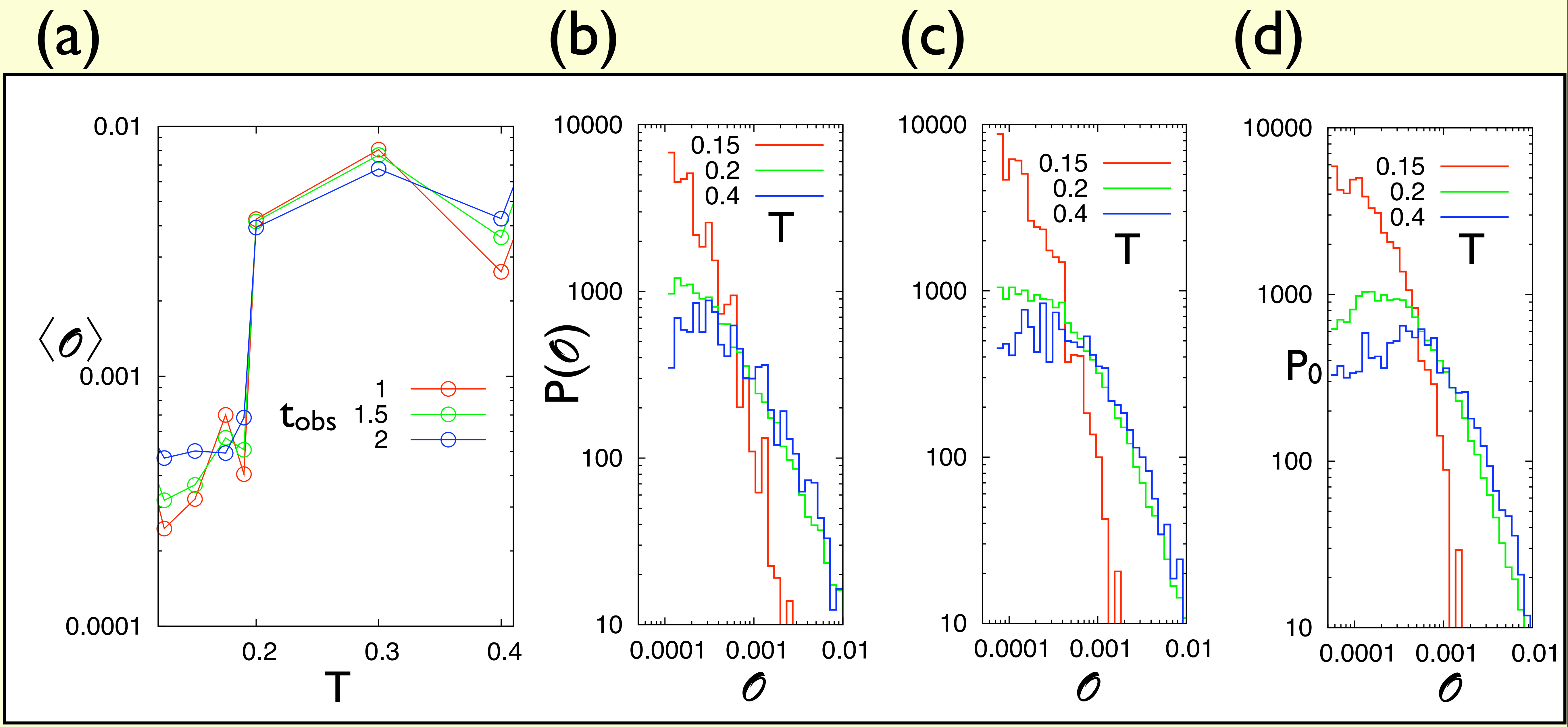
"off-diagonal" order parameter:

$$\mathcal{O}/N \equiv \frac{1}{t_{obs} N} \int_0^{t_{obs}} dt \sum_i |\Delta^i_{\alpha\beta}(t)|^2$$

with

$$\Delta^i_{\alpha\beta}(t) = u_{i\alpha}(t) u_{i\beta}(t) \ (\alpha \neq \beta) \quad i \in \text{active}$$





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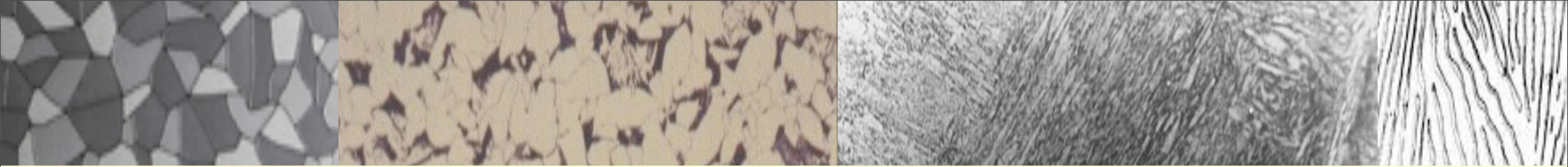

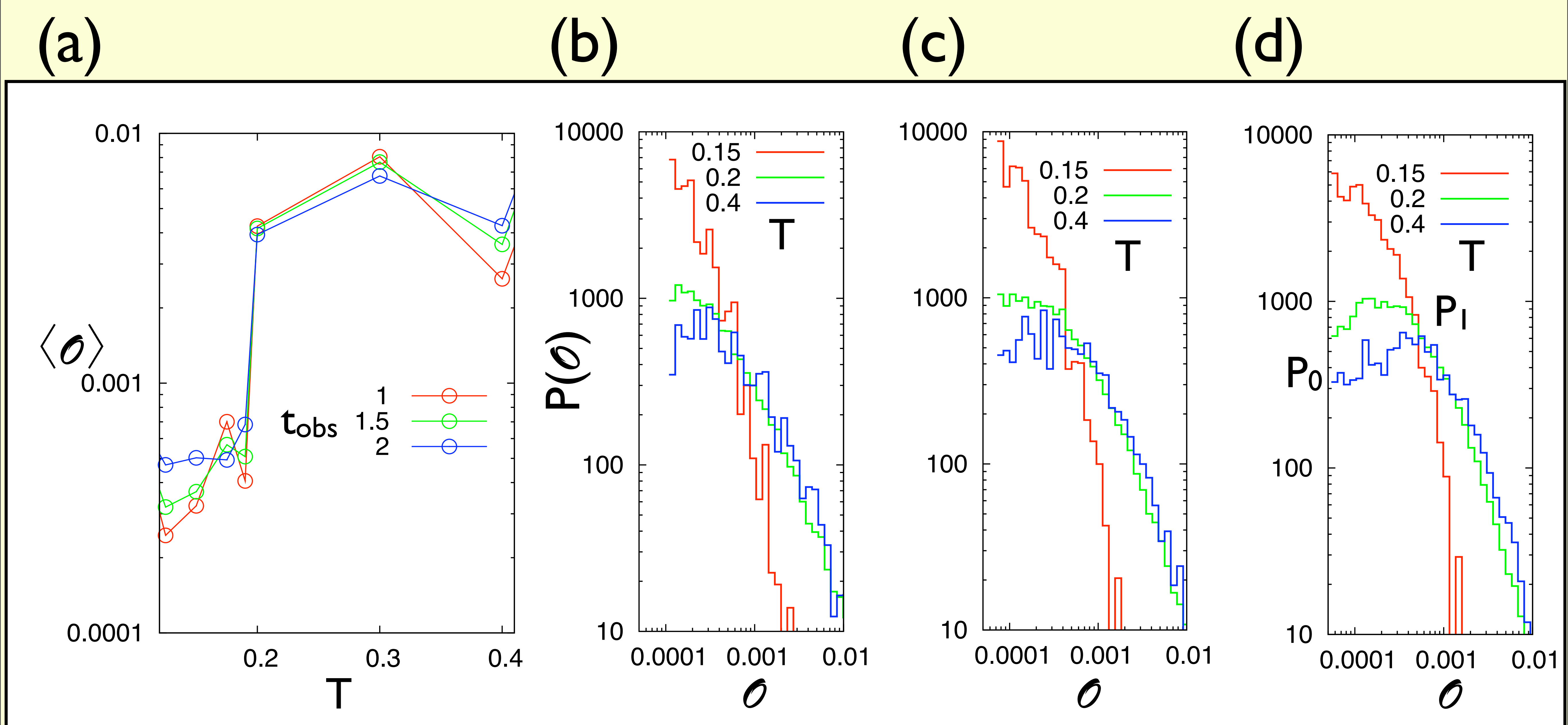

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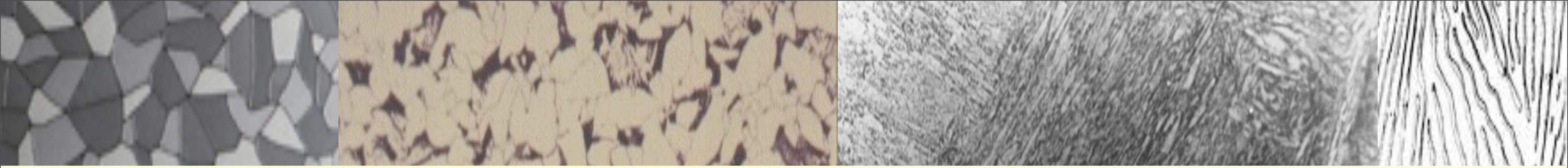
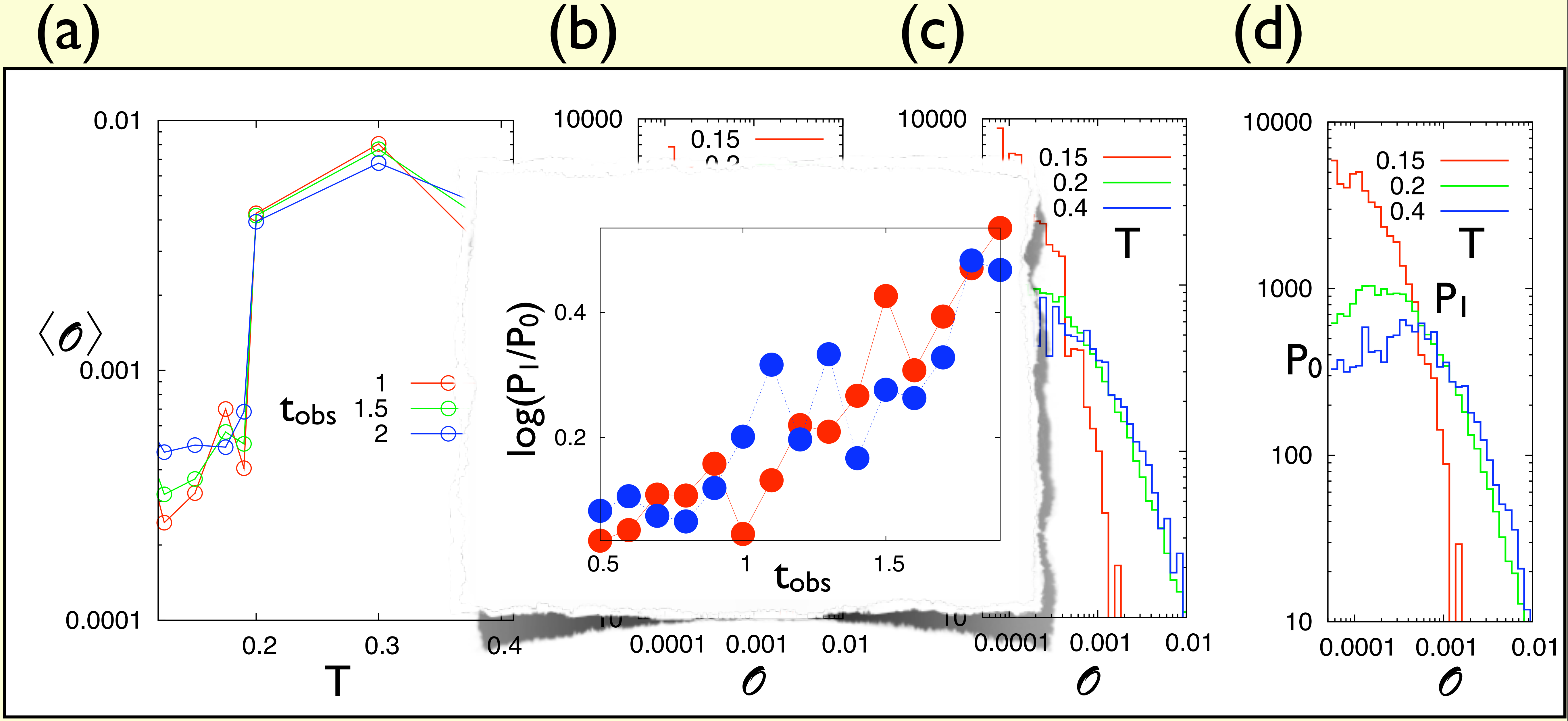
$$\mathcal{O}/N \equiv \frac{1}{t_{obs} N} \int_0^{t_{obs}} dt \sum_i |\Delta^i_{\alpha\beta}(t)|^2$$

with

$$\Delta^i_{\alpha\beta}(t) = u_{i\alpha}(t) u_{i\beta}(t) \ (\alpha \neq \beta) \quad i \in \text{active}$$



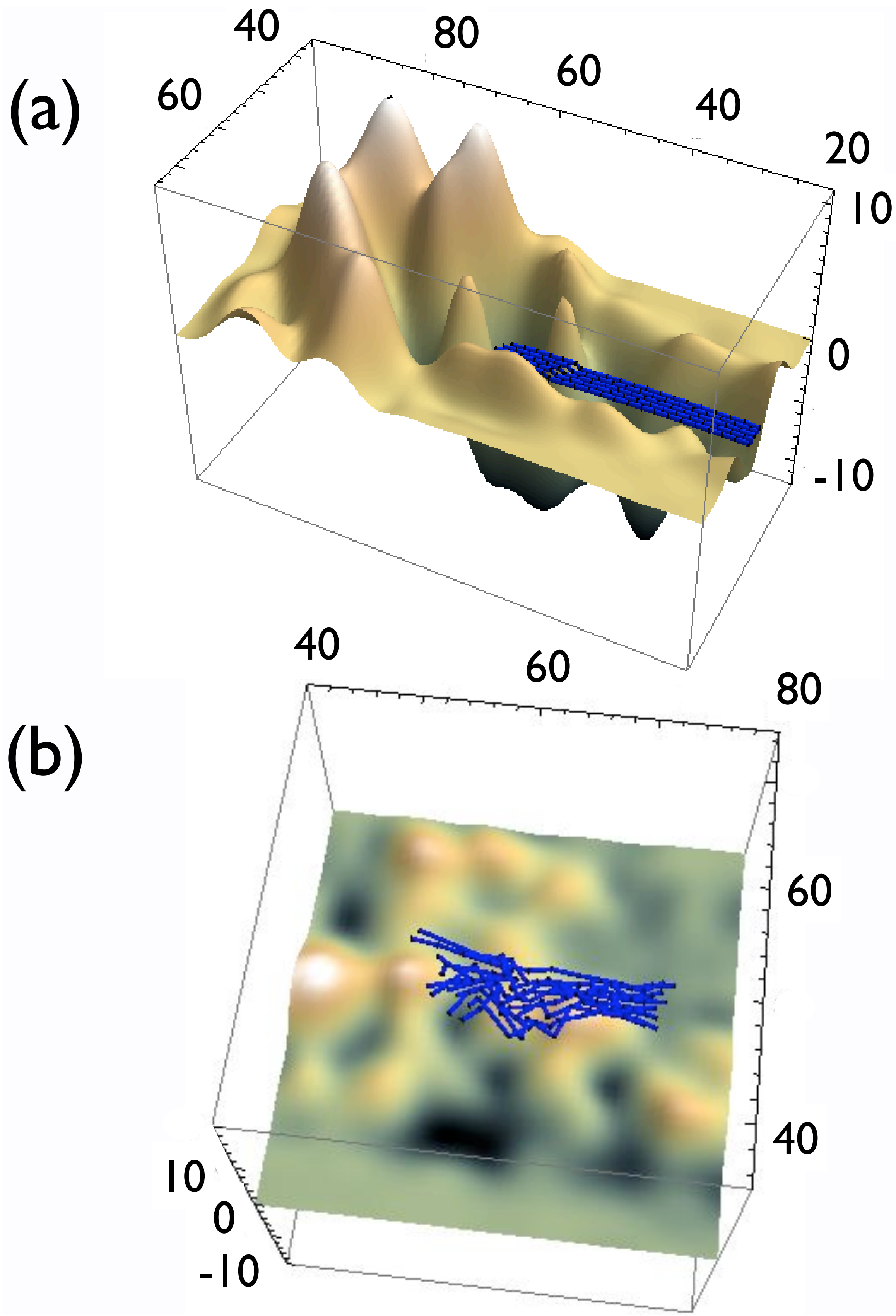


"off-diagonal" order parameter:

$$\mathcal{O}/N \equiv \frac{1}{t_{obs} N} \int_0^{t_{obs}} dt \sum_i |\Delta^i_{\alpha\beta}(t)|^2$$

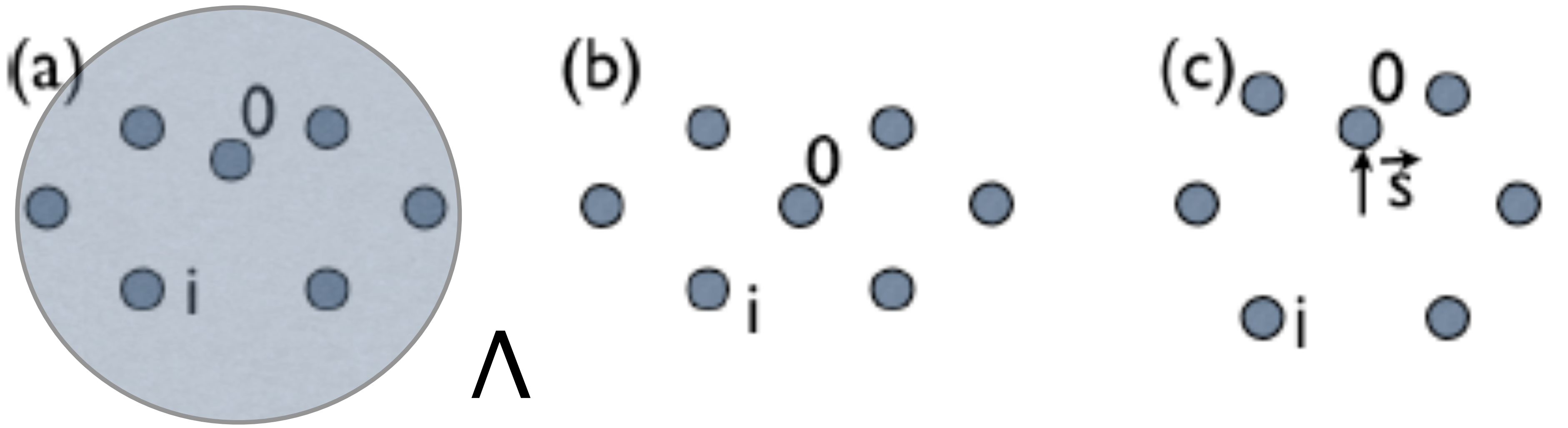
with

$$\Delta^i_{\alpha\beta}(t) = u_{i\alpha}(t) u_{i\beta}(t) \ (\alpha \neq \beta) \quad i \in \text{active}$$



- dynamical heterogeneities at transformation front
- active particles undergo rapid jamming-unjamming transitions
- stresses generated by the transformation.
- jammed particles ⇒ large stresses creating channels
- active particles flow within these channels
- Low temps - few channels - confining potential - ballistic trajectory ⇒ M
- High temps - many intersecting channels - no confining potential - disordered trajectories ⇒ F
- particles become inactive when transformation is complete

Non Affineness

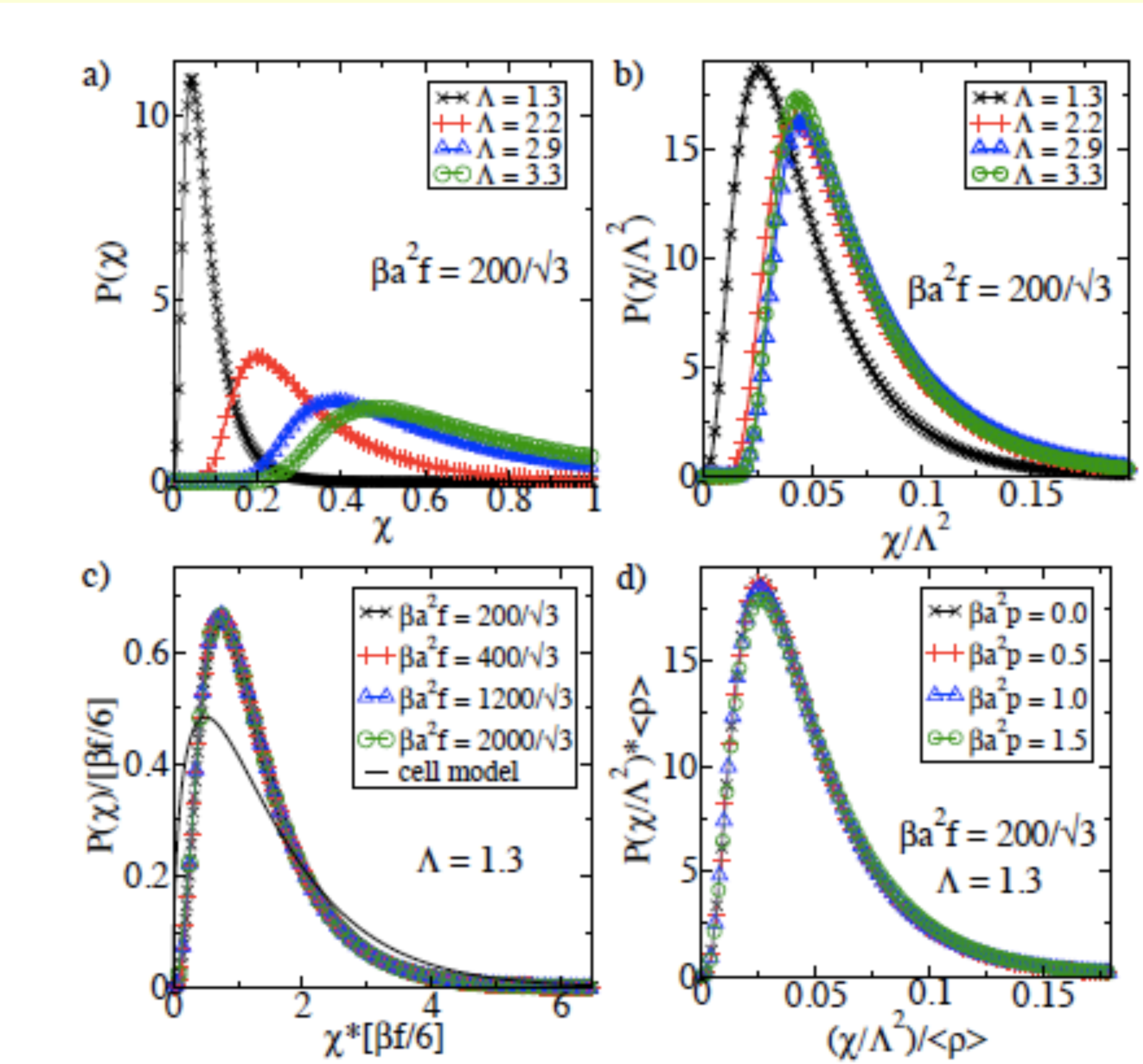


Coarse-graining volume

$$\chi(\vec{r}_0) = \sum_{m=1}^{N_B} \sum_{i=1}^{2} \left(r_m^i - r_0^i - \sum_{j=1}^{2} (\delta_{ij} + \epsilon_{ij}) [R_m^j - R_0^j] \right)^2$$

“Non- affineness”

The Harmonic Solid



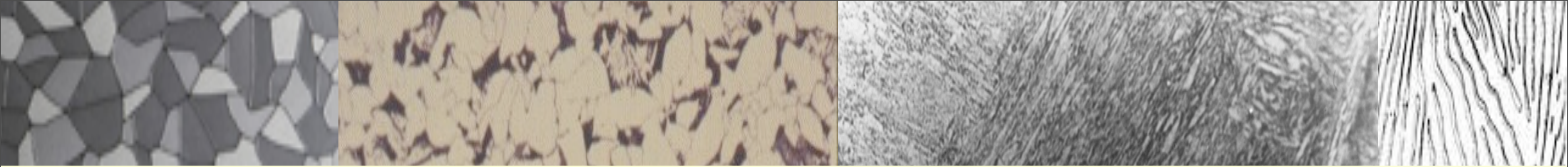
$$P(\mathcal{X}) = \left((1+0.27\cdot z)^{(-1/0.27)-1}\, e^{-(1+0.27\cdot z)^{-1/0.27}}\right)/2.012$$

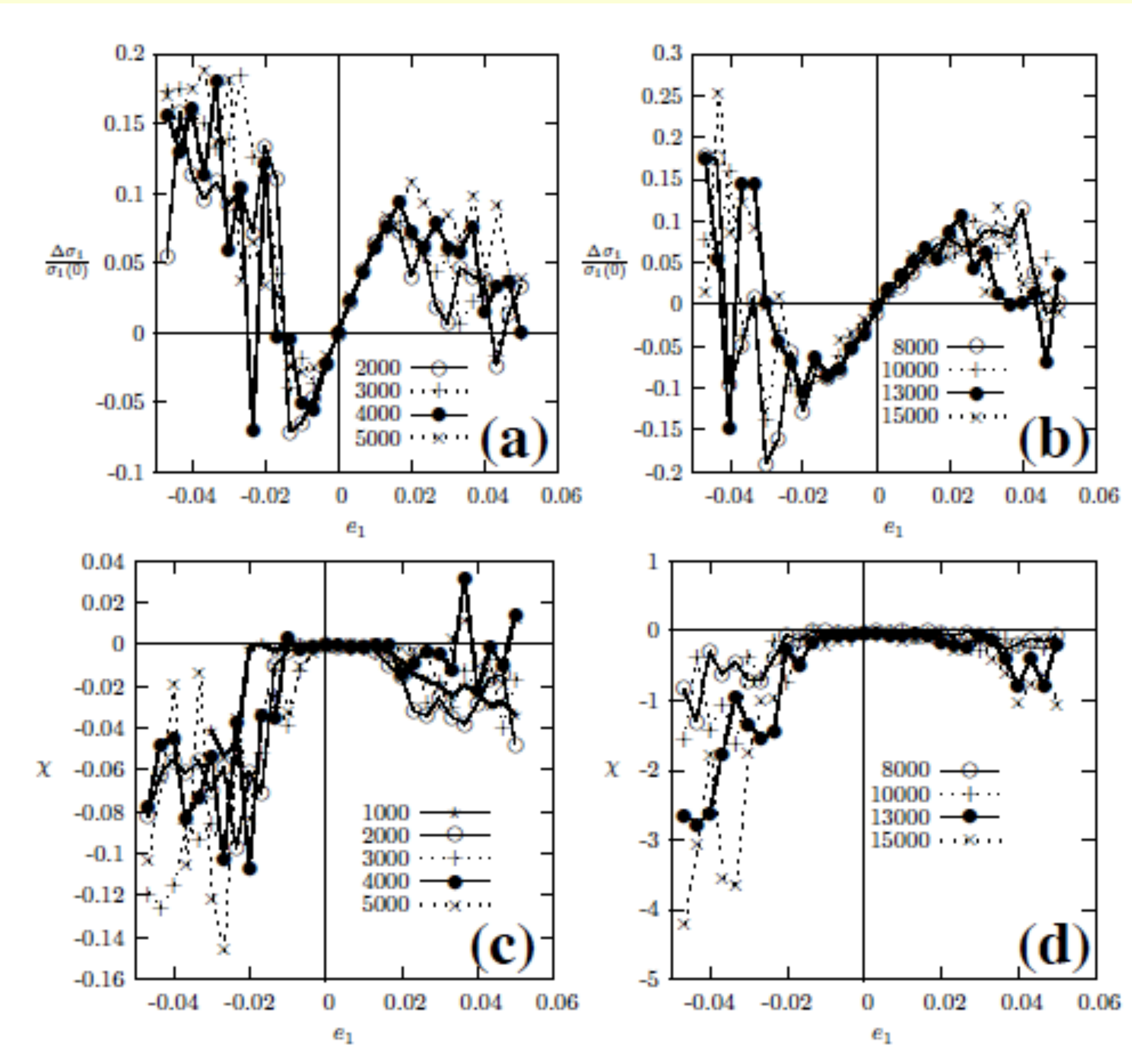
$$z = (\mathcal{X} - 3.127)/2.012 \quad \mathcal{X} = \chi\beta f/\rho\Lambda^2$$

Generalized Extreme Value Distribution

Cell model $\Rightarrow \chi \propto s^2 \propto$ Lindemann ratio

Structural criterion for an-harmonicity !!

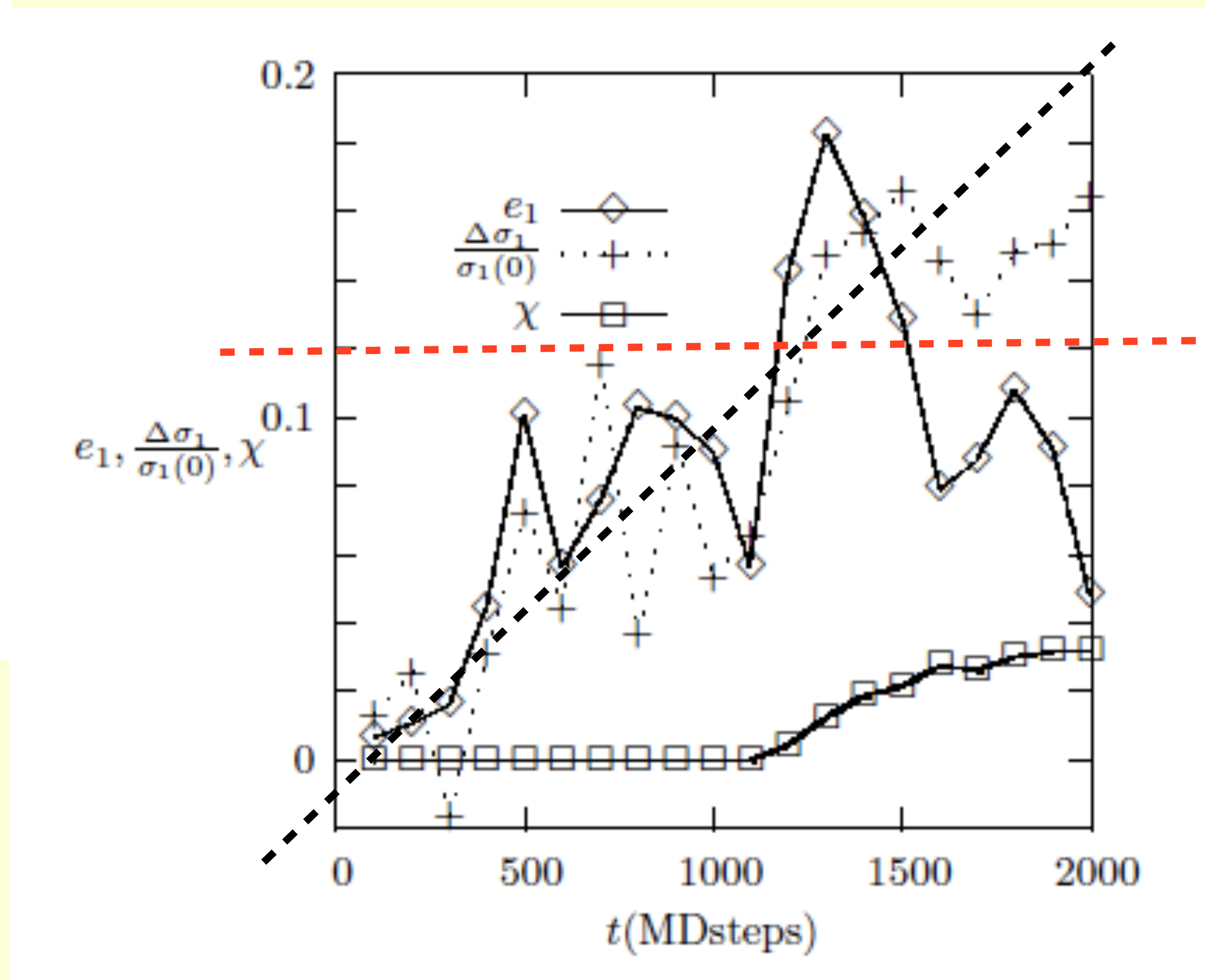




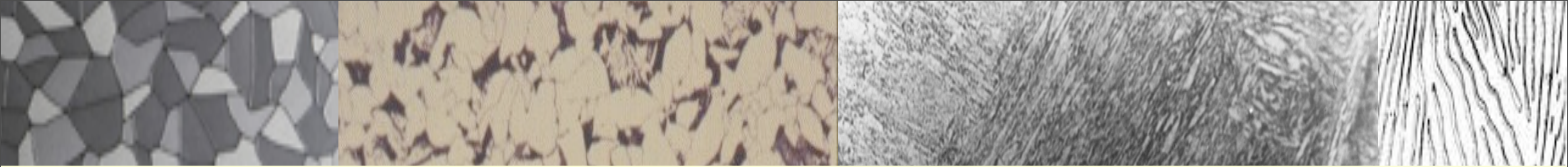
$$e_1 = \frac{1}{2}\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right)$$

$$e_2 = \frac{1}{2}\left(\frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y}\right)$$

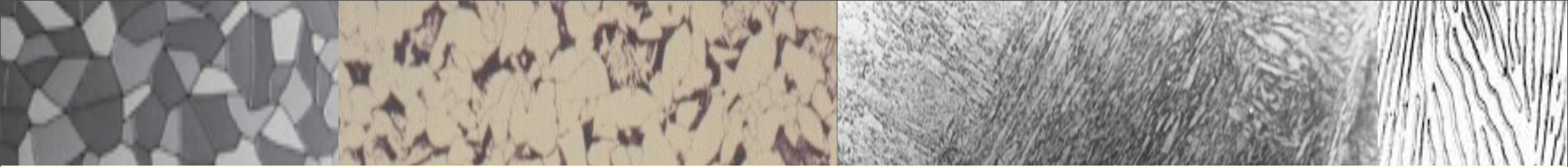
NOP strains



- NOP strains are automatically produced along with the OP strain.
- Non-affineness in the NOP strain is produced when stress crosses a threshold



Coarse grained theory



$$\mathcal{F} = \frac{1}{2}\int \mathrm{dxdy}\ \Big[a_1(e_1^A)^2 + a_2 e_2^2 + a_3 e_3^2 - b_3 e_3^4 + d_3 e_3^6$$

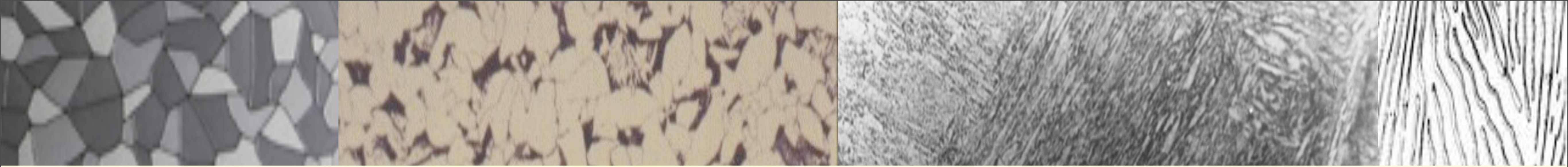
$$+ \quad c_1(\nabla e_1^A)^2 + c_2(\nabla e_2)^2 + c_3(\nabla e_3)^2\Big].$$

$$\mathcal{L} = \int \frac{\rho}{2}\left[(\dot{u}_x^2 + \dot{u}_y^2)\right] dxdy - \mathcal{F}.$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{u}_i} - \frac{\partial L}{\partial u_i} = -\frac{\partial R}{\partial \dot{u}_i}.$$

Rayleigh dissipation

$$\mathcal{R} = \frac{1}{2}\int \left[\xi(\dot{e}_1^A)^2 + \kappa \dot{e}_2^2 + \gamma \dot{e}_3^2\right] dxdy$$



$$\rho \ddot{e}_1^A = \nabla^2 \left(\frac{\delta \mathcal{F}}{\delta e_1^A} + \frac{\delta \mathcal{R}}{\delta \dot{e}_1^A} \right) + \frac{\partial^2}{\partial x \partial y} \left(\frac{\delta \mathcal{F}}{\delta e_3} + \frac{\delta \mathcal{R}}{\delta \dot{e}_3} \right) + \mathcal{W}^2 \left(\frac{\delta \mathcal{F}}{\delta e_2} + \frac{\delta \mathcal{R}}{\delta \dot{e}_2} \right),$$

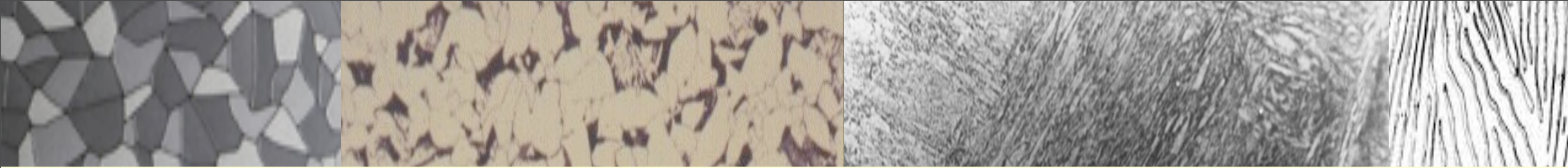
$$\rho \ddot{e}_2 = \nabla^2 \left(\frac{\delta \mathcal{F}}{\delta e_2} + \frac{\delta \mathcal{R}}{\delta \dot{e}_2} \right) + \mathcal{W}^2 \left(\frac{\delta \mathcal{F}}{\delta e_1^A} + \frac{\delta \mathcal{R}}{\delta \dot{e}_1^A} \right), \quad < e_2 >= 0$$

rhombus !!

$$\rho \ddot{e}_3 = \frac{1}{4} \nabla^2 \left(\frac{\delta \mathcal{F}}{\delta e_3} + \frac{\delta \mathcal{R}}{\delta \dot{e}_3} \right) + \frac{\partial^2}{\partial x \partial y} \left(\frac{\delta \mathcal{F}}{\delta e_1^A} + \frac{\delta \mathcal{R}}{\delta \dot{e}_1^A} \right).$$

The operator $\mathcal{W}^2 = \partial^2/\partial x^2 - \partial^2/\partial y^2$

Since the OP strain is a broken symmetry variable (slow), the dynamics of the NOP strain is *slaved* to that of the OP strain



Final set of equations to be solved:

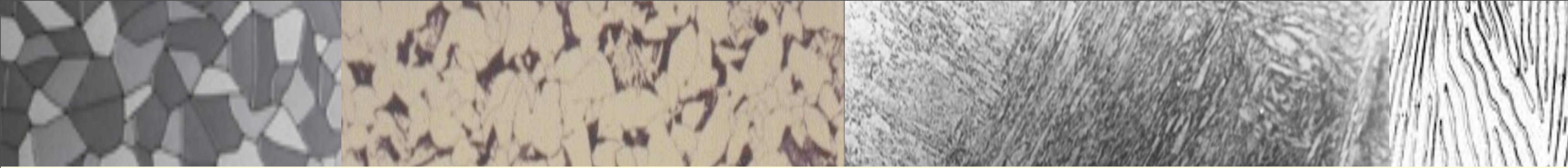
$$\nabla^2 e_1^A = \left(\frac{4a_2 - a_3}{a_1 + a_2}\right)\frac{\partial^2 e_3}{\partial x \partial y} - \left(\frac{a_2}{a_1 + a_2}\right)\nabla^2 e_1^P .$$

$$\begin{aligned} \rho \ddot{e}_3 &= \frac{1}{4}\nabla^2 \left(a_3 e_3 - b_3 e_3^3 + d_3 e_3^5 - c_3 \nabla^2 e_3 \right. \\ &- \left. 4c_1 \frac{\partial^2 e_1^A}{\partial x \partial y} + \gamma \dot{e}_3 \right) + \frac{\partial^2}{\partial x \partial y}\left(a_1 e_1^A + \xi \dot{e}_1^A\right) \end{aligned}$$

Equations automatically ensure:

$\nabla \cdot \sigma = 0$ *mechanical equilibrium*

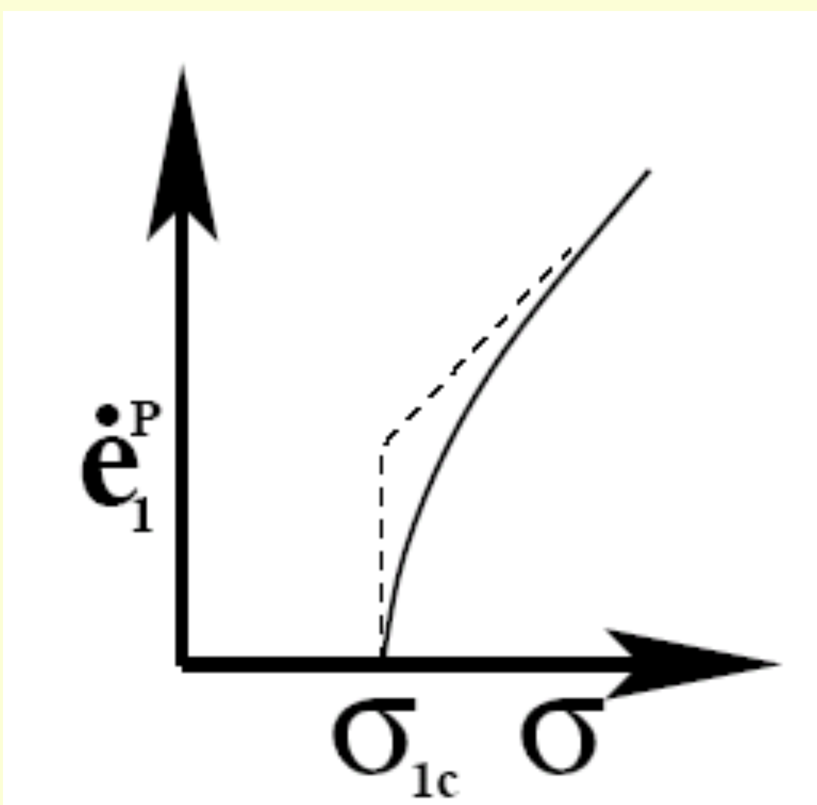
$\nabla \times (\nabla \times \epsilon_{\mathbf{ij}})^{\mathbf{T}} = 0$ *S^t. Venant's compatibility condition*



Plasticity to be introduced phenomenologically

$$e_1 = e_1^A + e_1^P$$ stress is given by: $$\sigma_1 = a_1 e_1^A$$

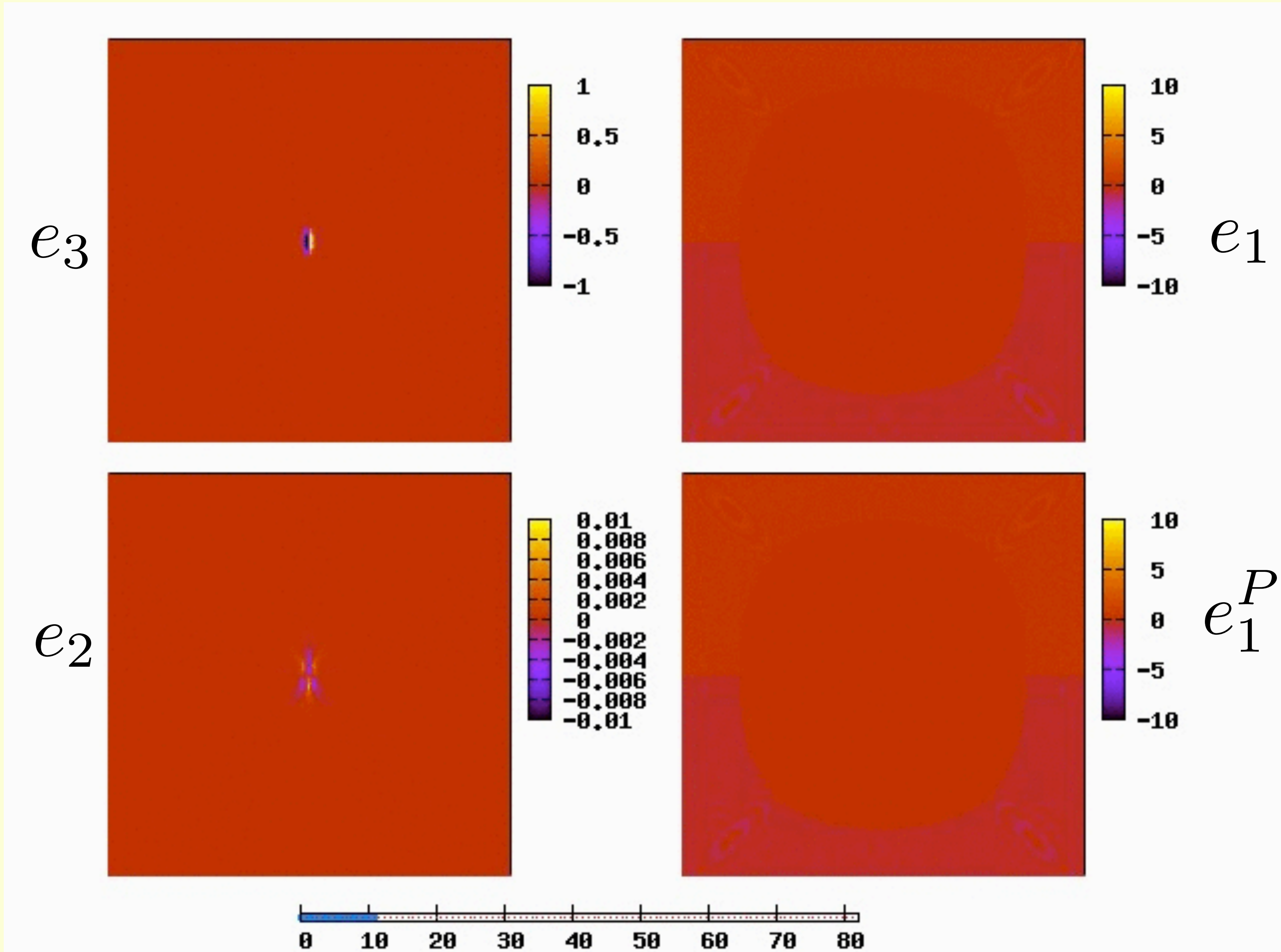
$$\begin{aligned} \dot{e}_1^P &= \frac{1}{h_1}\,\sigma_1 - c_p \nabla^2 e_1^P && \text{if } |\sigma_1| > \sigma_{1c} \\ &= -c_p \nabla^2 e_1^P && \text{otherwise} \end{aligned}$$



St. Venant compatibility is satisfied by e_1

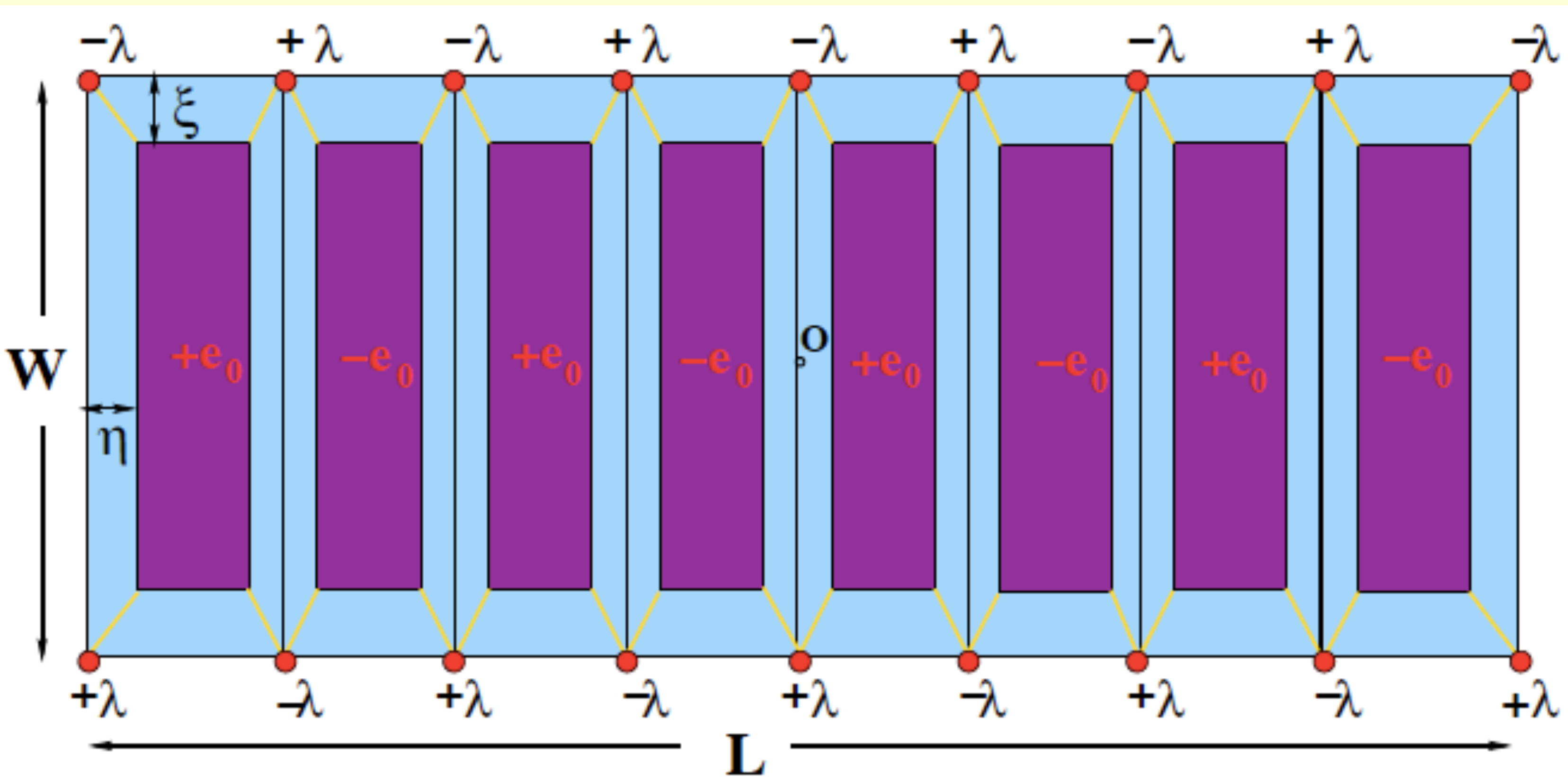
Defect concentration

$$\propto \nabla^2 e_1^P$$


e_3
1
0.5
0
-0.5
-1
e_1
10
5
0
-5
-10
e_2
0.01
0.008
0.006
0.004
0.002
0
-0.002
-0.004
-0.006
-0.008
-0.01
e_1^P
10
5
0
-5
-10
0 10 20 30 40 50 60 70 80

Why twins?

Assume local mechanical equilibrium: calculate free energy cost of creating a Martensite droplet

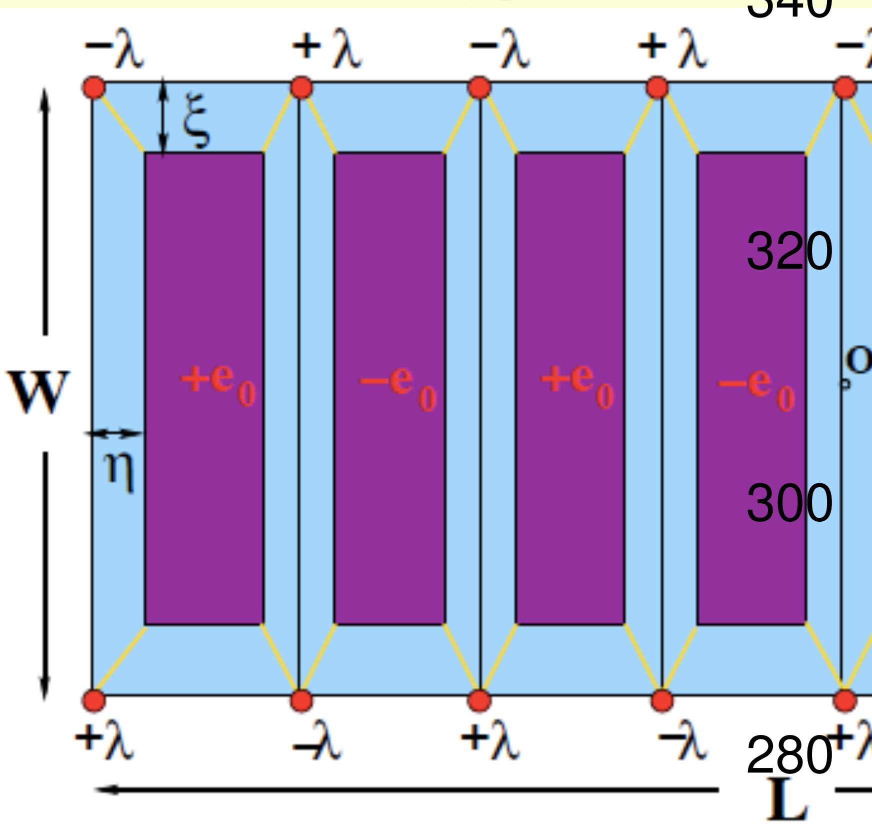


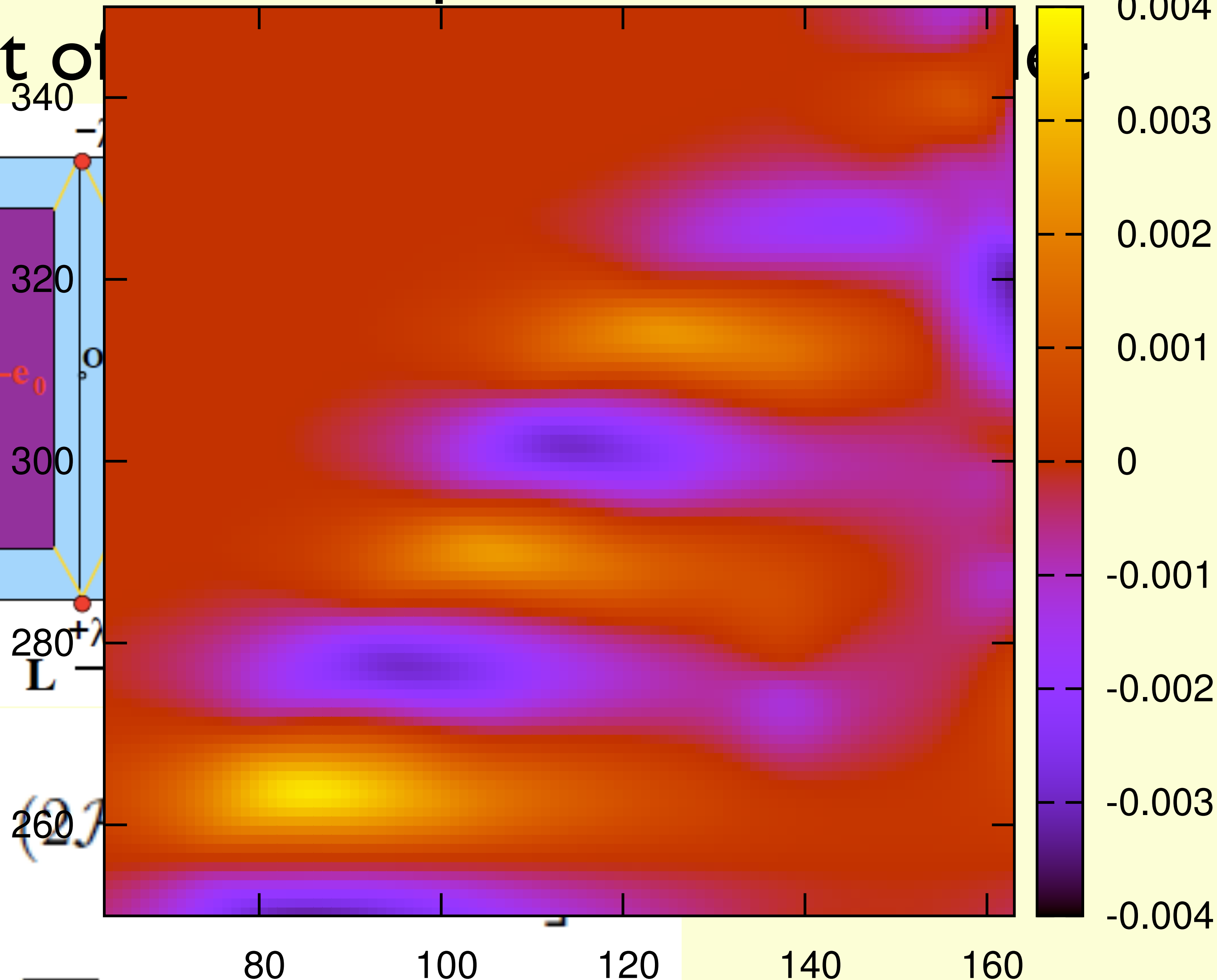
$$\frac{L^2}{N^2} = \left[\frac{2\pi\sqrt{2\pi}}{a_1\lambda^2}\left(2\mathcal{F}_s - \mathcal{F}_b\right) e_0\sqrt{\frac{c_3}{\mathcal{F}_s}}\right] W$$

$$\Rightarrow \quad \frac{L}{N} = \frac{\psi}{\lambda}\sqrt{W}$$

Why twins?

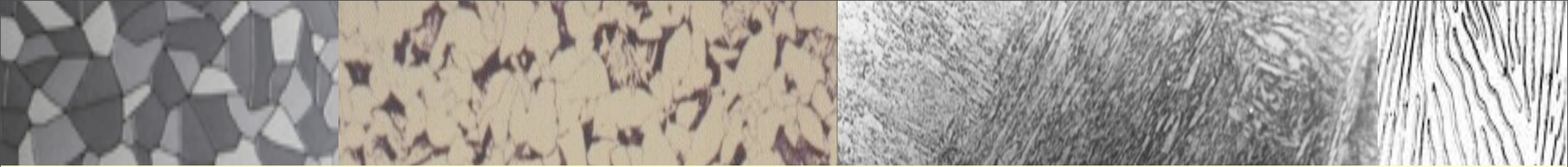
Assume local mechanical equilibrium: calculate free energy cost of ...

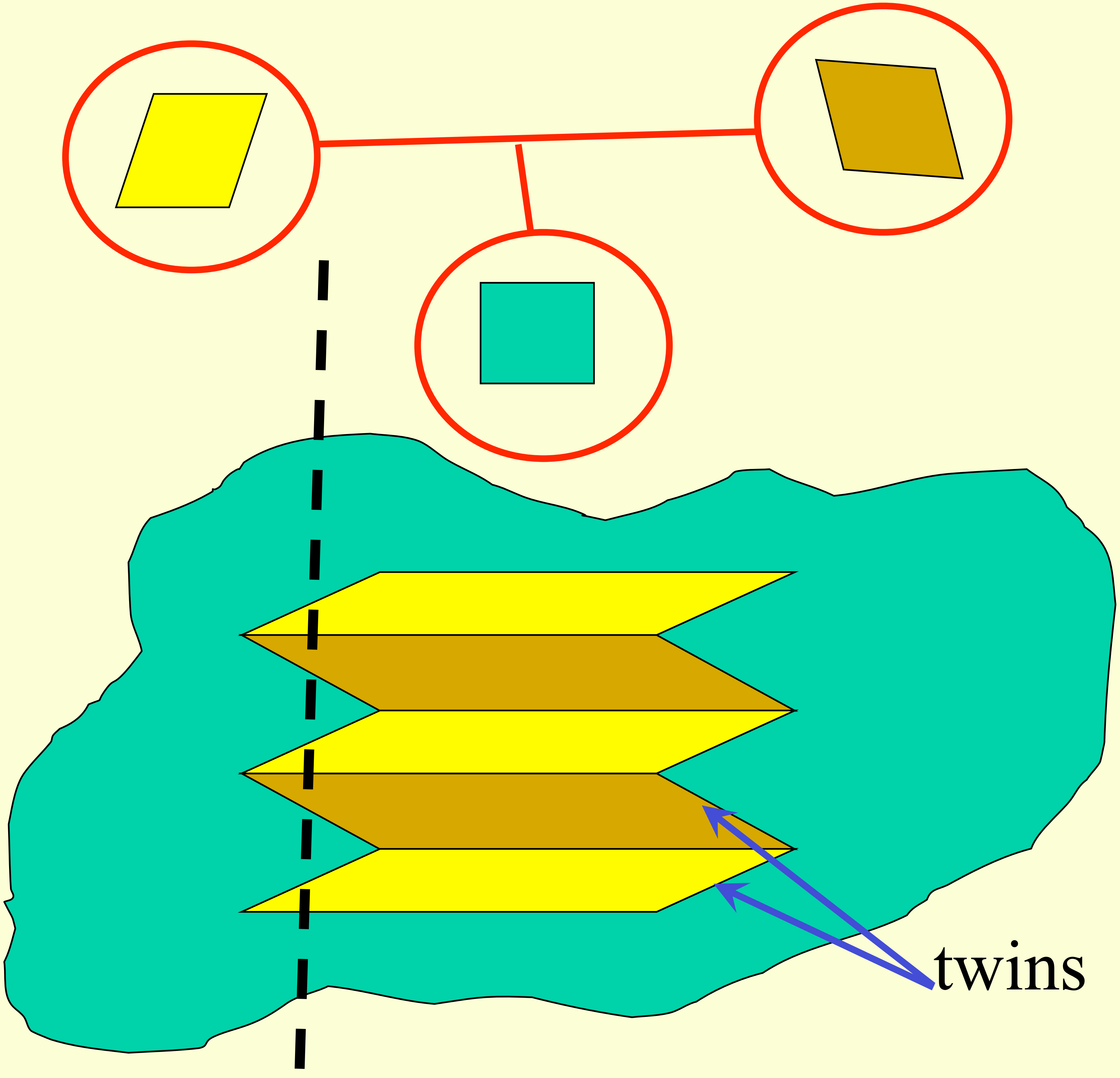


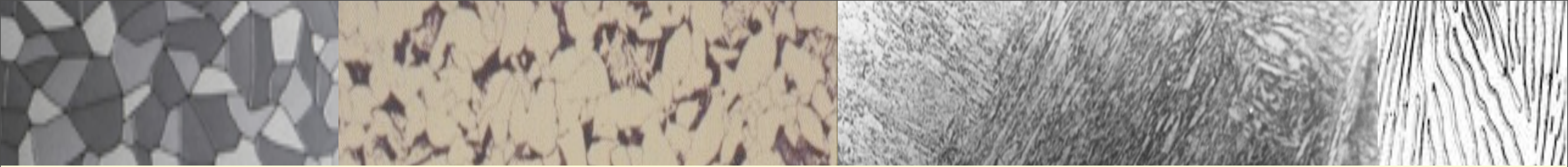


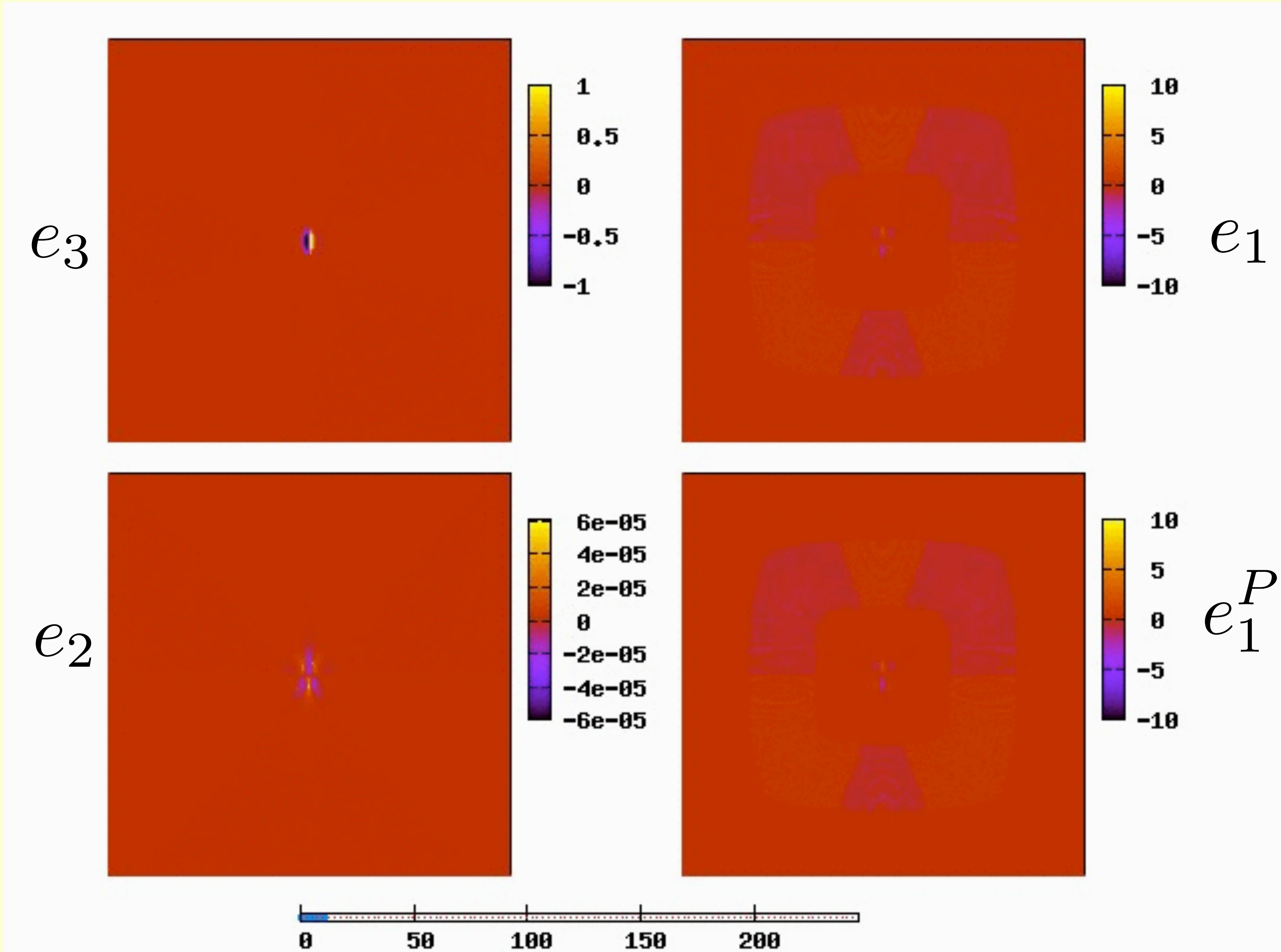
$$\frac{L^2}{N^2} = \left[\frac{2\pi\sqrt{2\pi}}{a_1\lambda^2} (2\lambda \ldots \right]$$

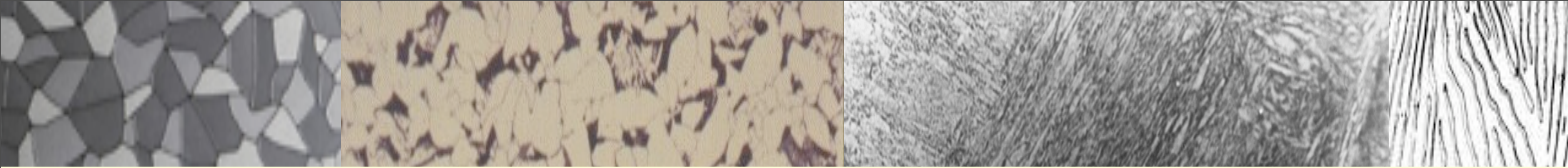
$$\Rightarrow \frac{L}{N} = \frac{\psi}{\lambda}\sqrt{W}$$

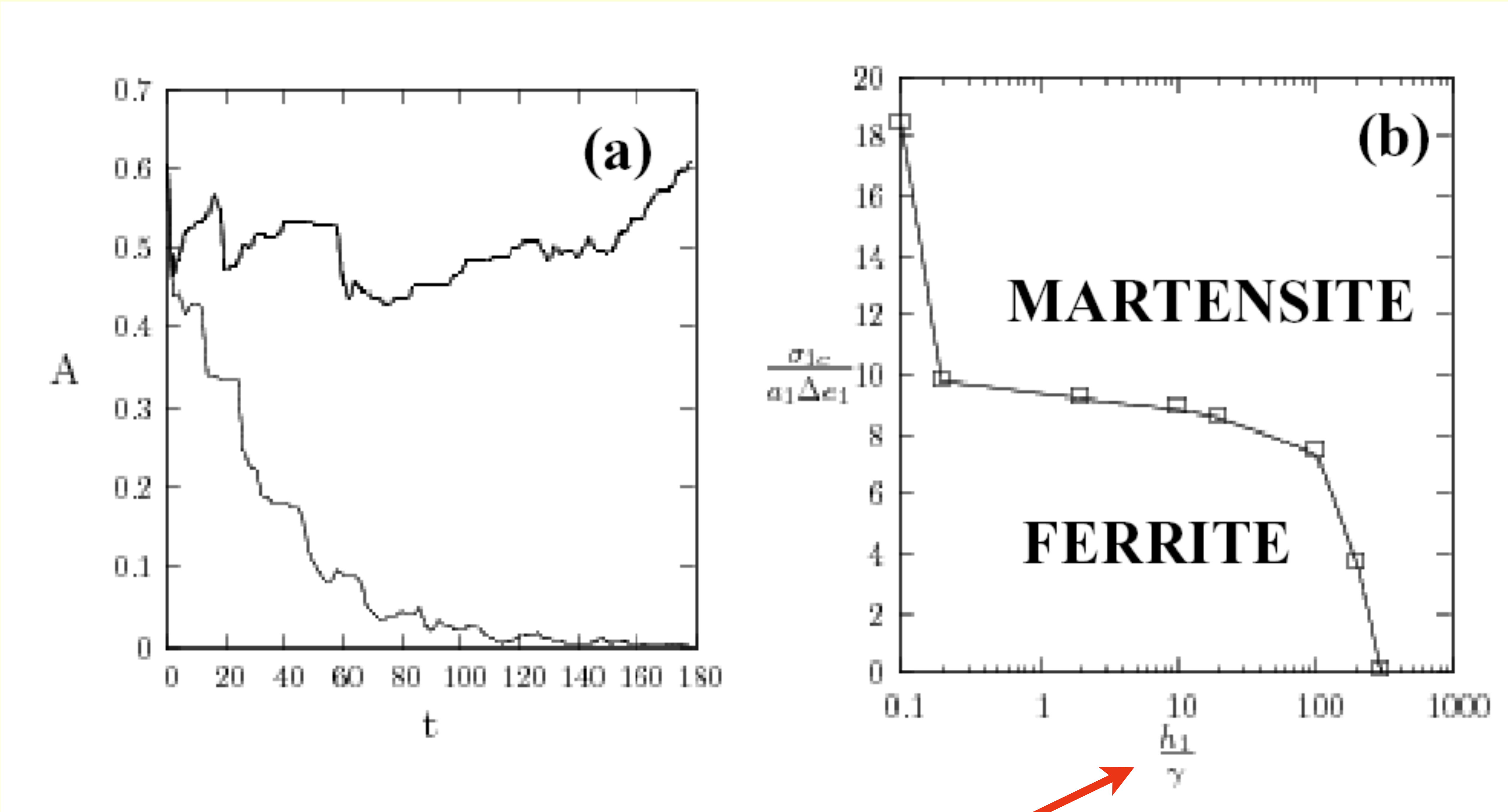



twins




e_3
1
0.5
0
-0.5
-1
10
5
0
-5
-10
e_1
e_2
6e-05
4e-05
2e-05
0
-2e-05
-4e-05
-6e-05
10
5
0
-5
-10
e_1^P
0
50
100
150
200



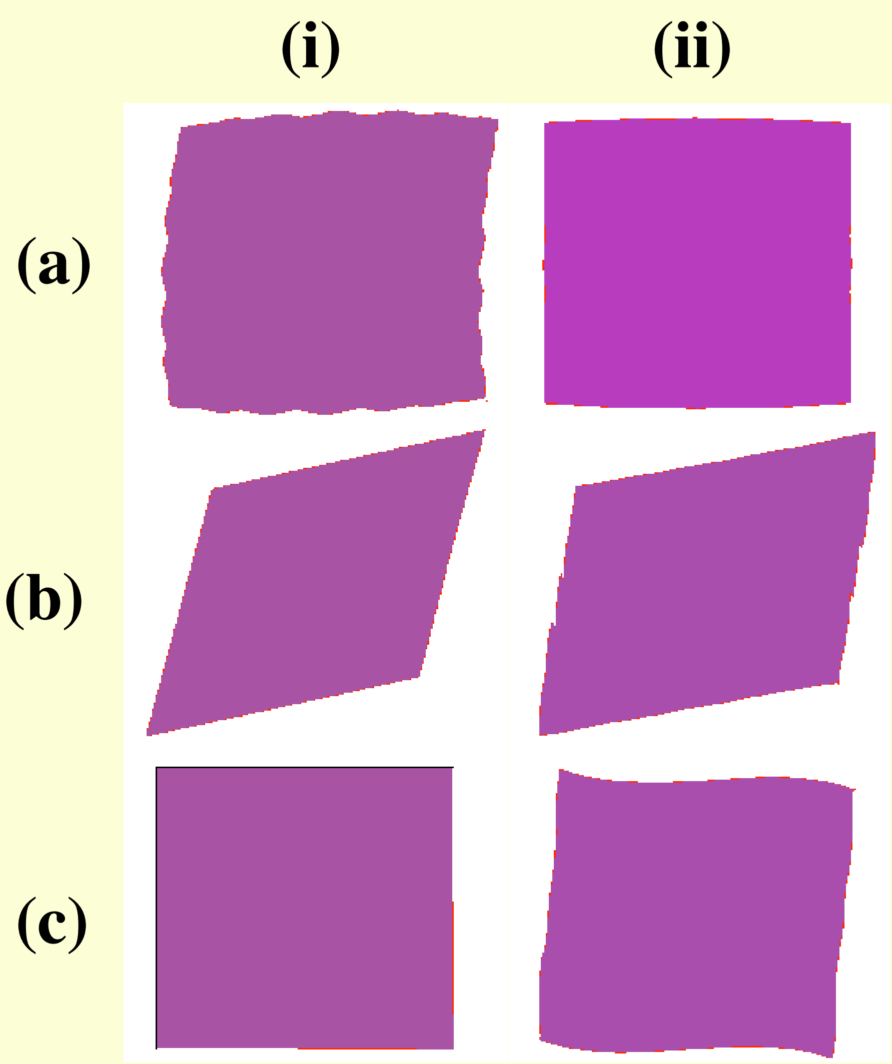


$\frac{h_1}{\gamma}$ is a Deborah number !!

Reversibility and shape

Shape from Kirchoff-Cesaro-Volterra equation

$$\mathbf{u}(\mathbf{r}) = \int_{C(\mathbf{r}_0,\mathbf{r})} [\mathbf{E}(\mathbf{l}) + (\mathbf{l} - \mathbf{r}) \times \nabla_{\mathbf{l}} \times \mathbf{E}(\mathbf{l})] \cdot d\mathbf{l}$$

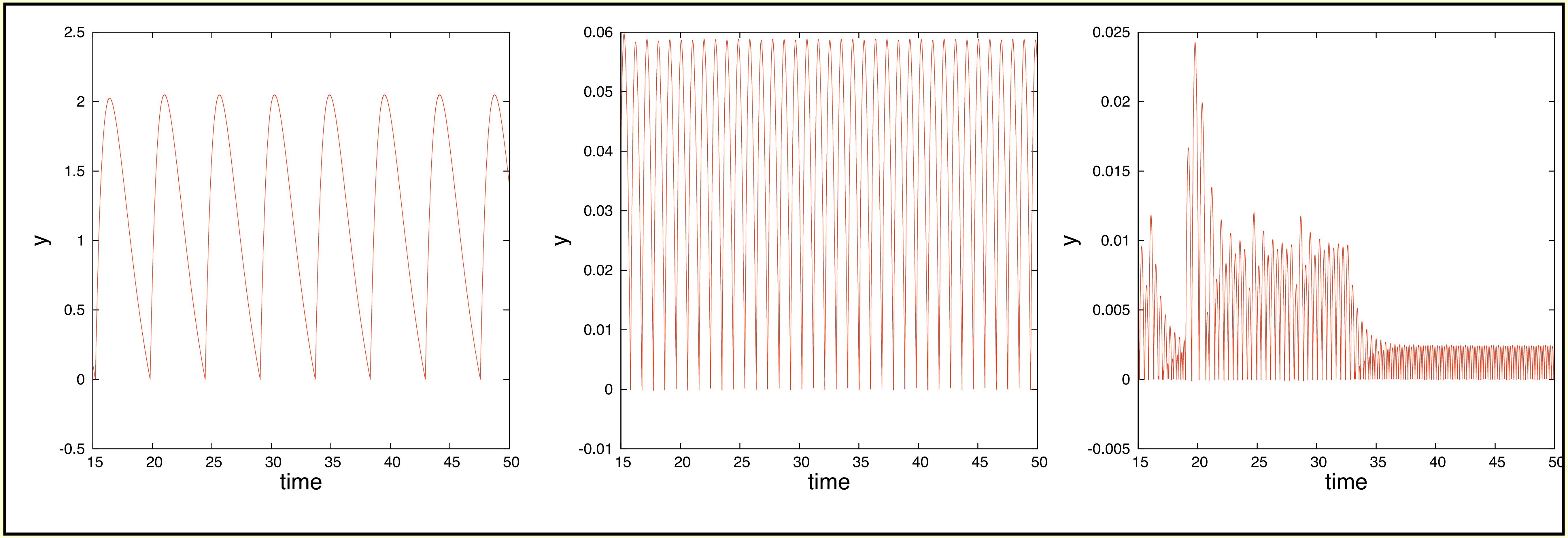


(i) plasticity only in the NOP sector

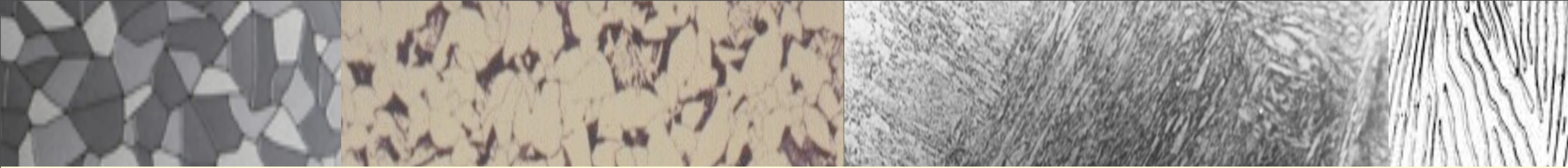
(ii) plasticity in the OP sector too

Stick slip motion

$$\dot{y}(t) = \int_{-\infty}^{t} dt' e^{-(t-t')}(A - Dy(t'))H[B - y(t')] - C\,y$$



- Reversibility possible only if plasticity in the NOP sector. Can explicitly demonstrate by calculating shape deformation under loading.
- Stick-slip motion of interface produced by nonlinear dynamics of plasticity.
- When elastic incompability becomes too large - possibility of a “microstructural glass”



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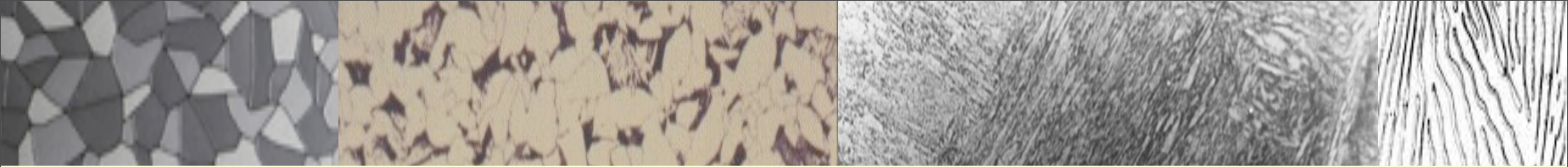

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