GRADIENT CONTINUUM NANOMECHANICS
[Applications to NCs and UFGs]

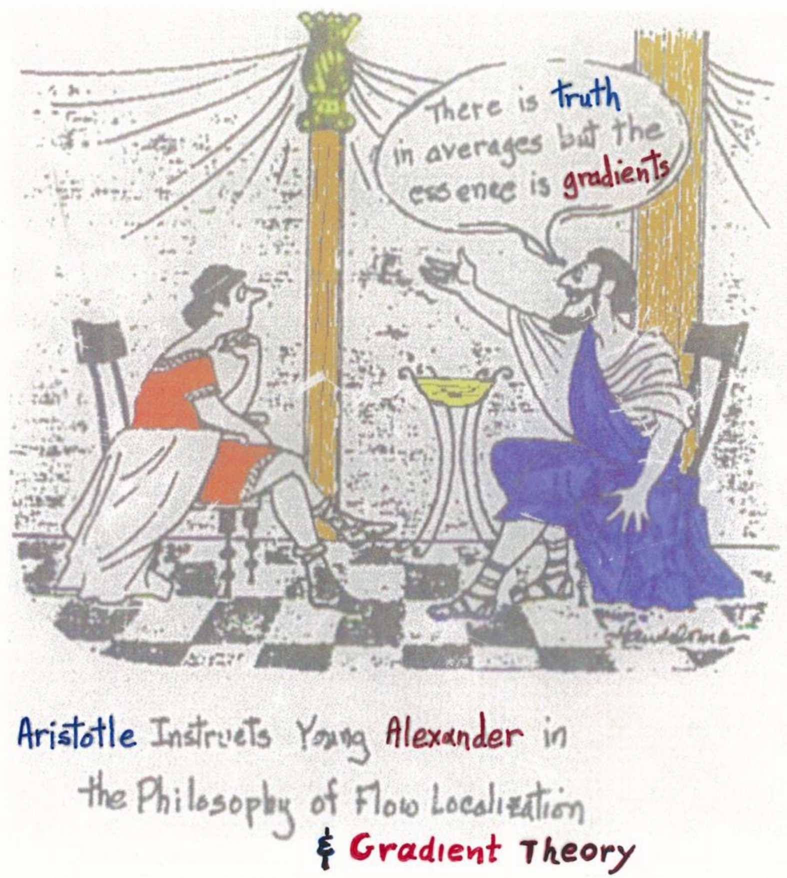
- ❑ Quotation from Richard E. Smalley [American Scientist 85, 324, 1997]

"The Laws of Continuum Mechanics are amazingly robust for treating even intrinsically discrete objects only a few atoms in diameter"

- ❑ Present Modification of Smalley's Quotation: Gradient Continuum Mechanics

- ❑ Slide from Owen Richmond – Lev Pitaevskii

[1990 Int. Conf. on Aristotle's 2300th Birthday – 50 USSR Participants at Philippion]



Distant Past

■ Homer's Automata

- ***Iliad***

  E 749: Hera opens the Gates automatically
  Σ 372: Hephaestus' 20 golden self-moving tripods } → *telecontrol?*

  Σ 468-473: Hephaestus' automated Lab → *modern casting unit?*

  Σ 410-420: Young Servant Girls (made out of gold with mind/voice/movement) assisting "crippled" Hephaestus to walk → *human robots?*

- ***Odyssey***

  Θ 555-563: Phaeacians' Ships possessing "mind of their own " traveling at extremely high speeds at night and in clouds without fear to sink → *modern auto-pilots?*

Recent Past

R. Feynmann (1918-88) Prophet of Nanotechnology
Caltech's Lecture: Dec 29th 1959

"There's Plenty of Room at the Bottom"

Recent Examples of New Fields

- Kamerlingh Onnes: Low-Temperature physics
- Percy Bridgman: High-Pressure physics

New Emerging Field

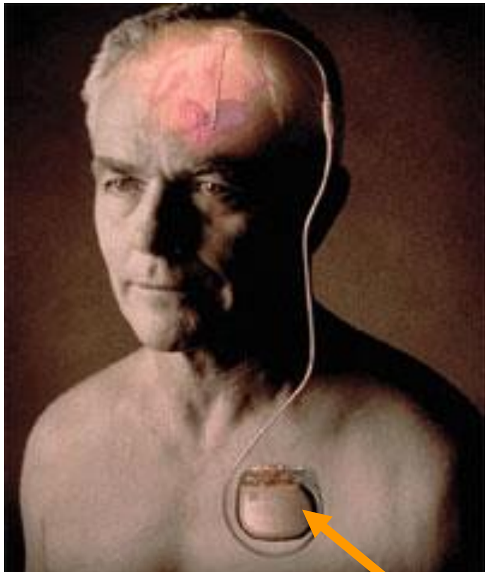
- **Fabricating/manipulating/controlling things on small scale**
  In 2000 we will wonder why it was not until 1960 that anybody began seriously moving in this direction

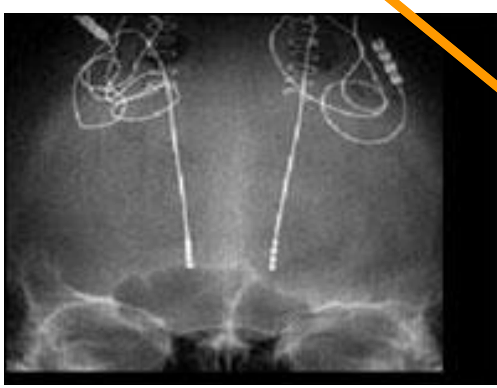
∴ Nanoscience / Nanotechnology

Present – Future

■ Nanostructured Li-batteries / Nanosurgeons

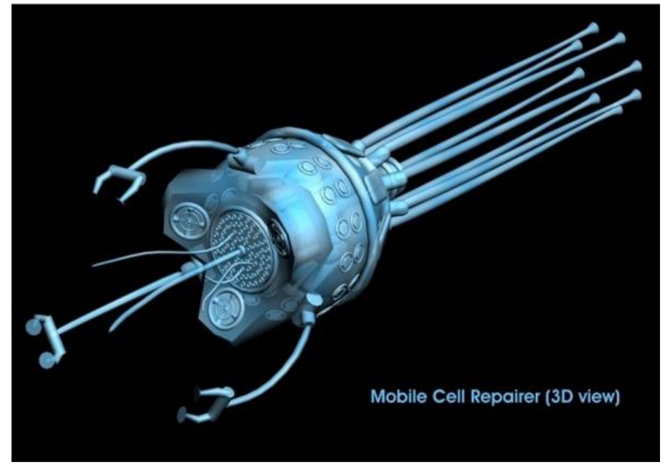
Cure of Alzheimer's/Parkinson Diseases and Brain Damage/Paralysis





Li-battery

Deep Brain Stimulation
Dr. H. Mayberg, Univ. Toronto



Mobile Cell Repairer
Y. Svidinenko, Nanotechnology News Network

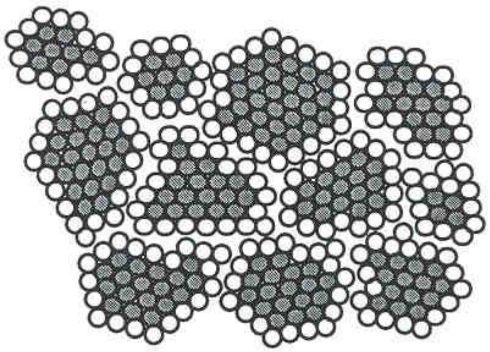
Mobile Artery Cleaner

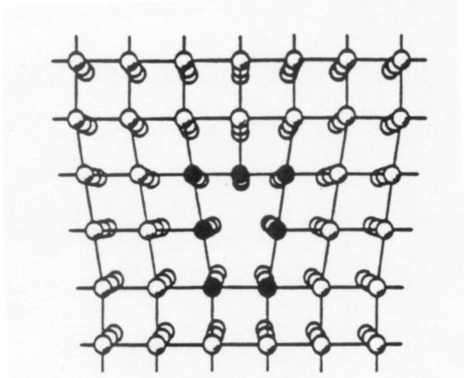
NCs/UFGs: Nanoelasticity/Nanoplasticity/Nanodiffusion
Motivation: Grain Configuration at the Nanoscale

Traditional Polycrystals ……10 – 100 μm Nanopolycrystals……………5 – 100 nm

Grain d

1-50 nm



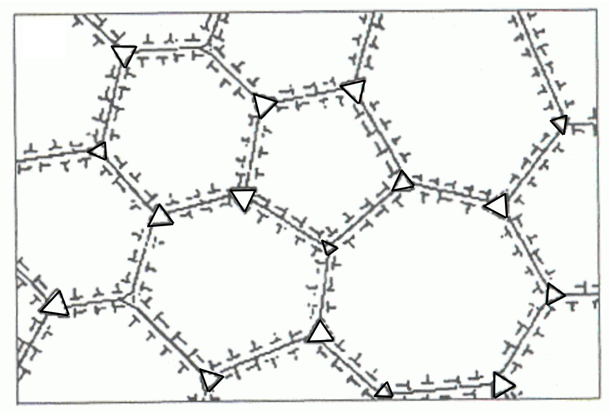


Core r_0

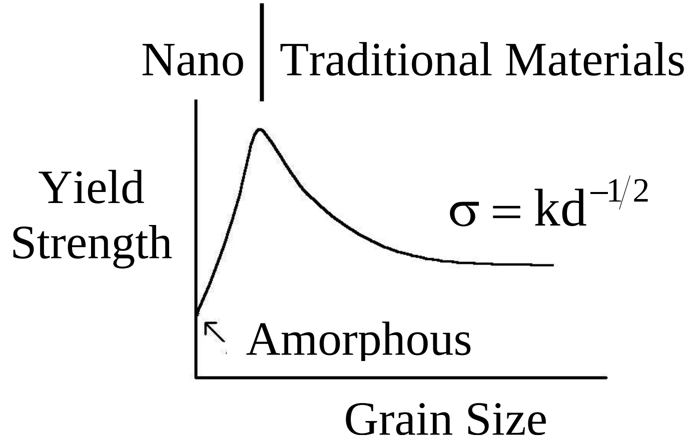
~1 nm

Grain size (d) of the same order as dislocation core (r_0)

10 nm grain size: 30% of atoms in the boundary



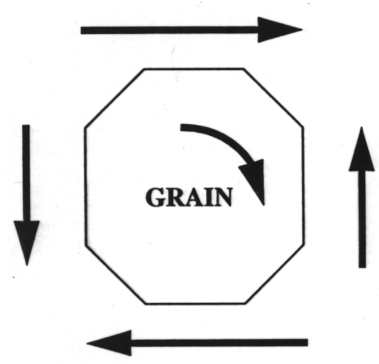
Plasticity Mechanisms ?

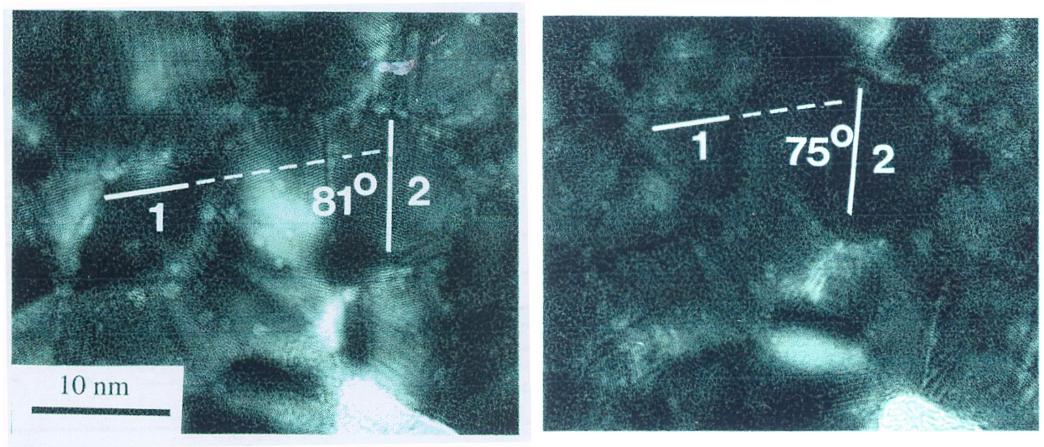


Inverse Hall-Petch Relation ?

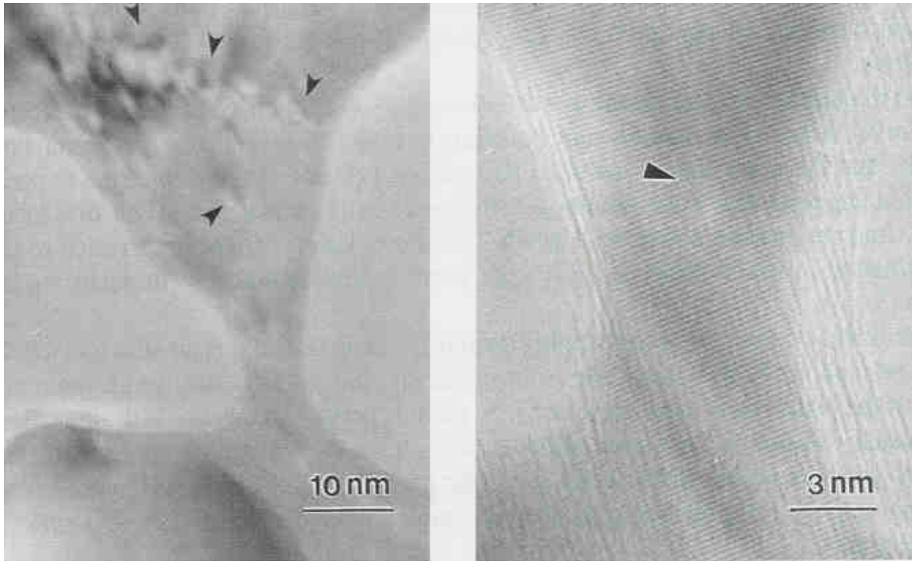
Early MTU Experimental Observations

- *Grain Boundary Sliding/ Grain Rotation*

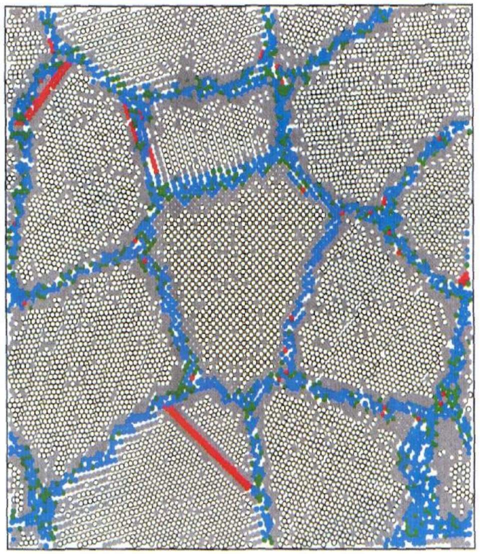




10 nm Au: 6-15 degrees relative grain rotation due to inhomogeneous GB sliding (unbalanced shear stress)



100 nm Ag film



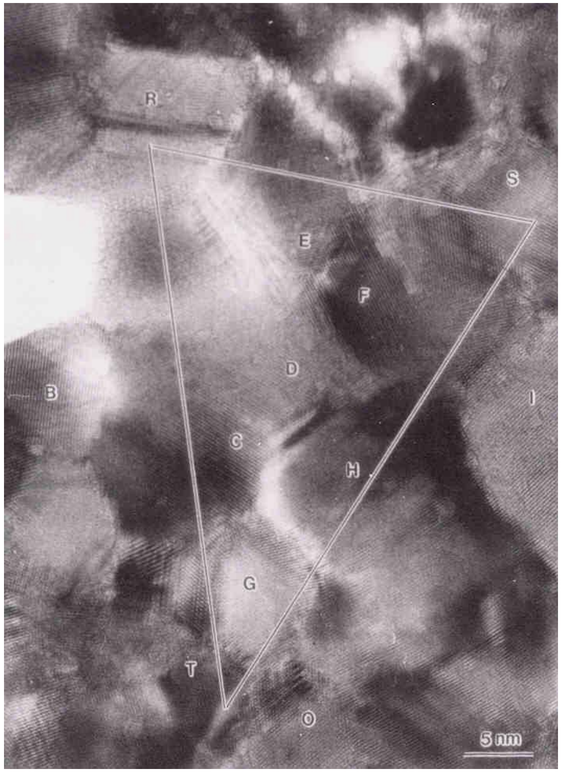
~12 nm Ni nanopolycrystals

- ***Grain Rotation / Dislocation Emergence***

Elementary Rosette Analysis

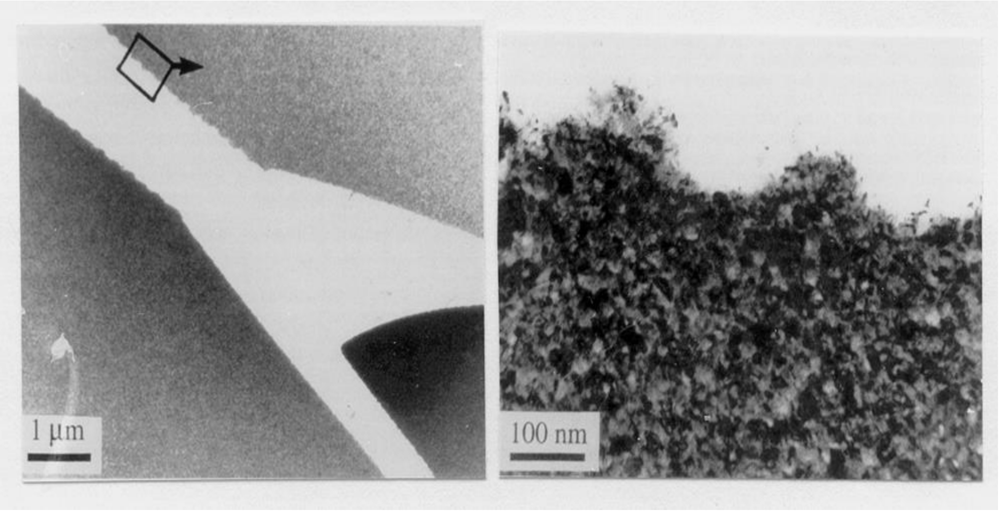
	Triangle angles (deg)			Triangle lengths (nm)		
Step	α	β	γ	a	b	c
Start	89	36	55	22.2	27.7	16.4
1	91	35	54	22.6	27.9	17.4
2	96	36	48	23.4	31.2	18.9
3	102	33	45	21.7	32.0	18.0

Strain Tensor $$\boldsymbol{\varepsilon} = \begin{bmatrix} 0.05 & -0.11 & 0 \\ -0.11 & 0.16 & 0 \\ 0 & 0 & -0.24 \end{bmatrix} \quad \varepsilon_{eff} = 20\ \%$$



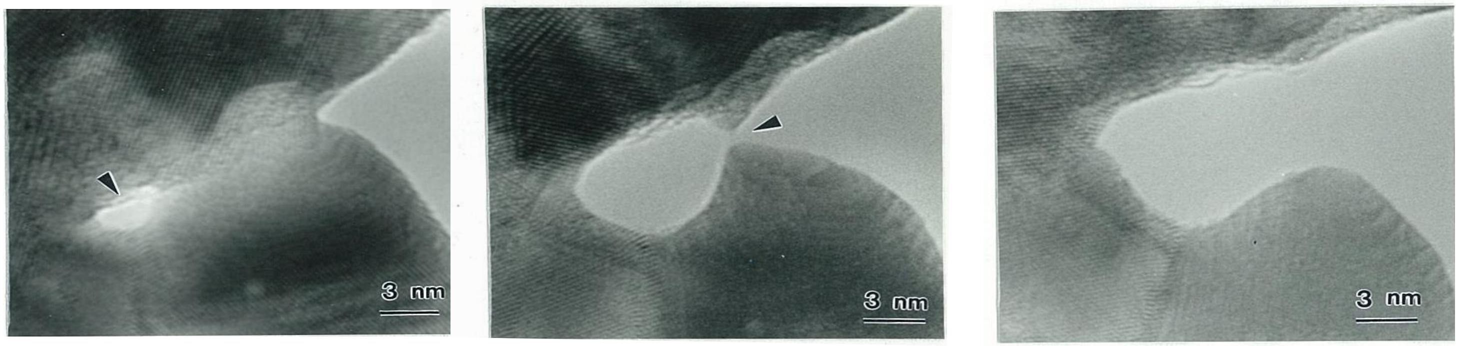
TEM Strain Rosette

- ***Oscillatory Crack Propagation***

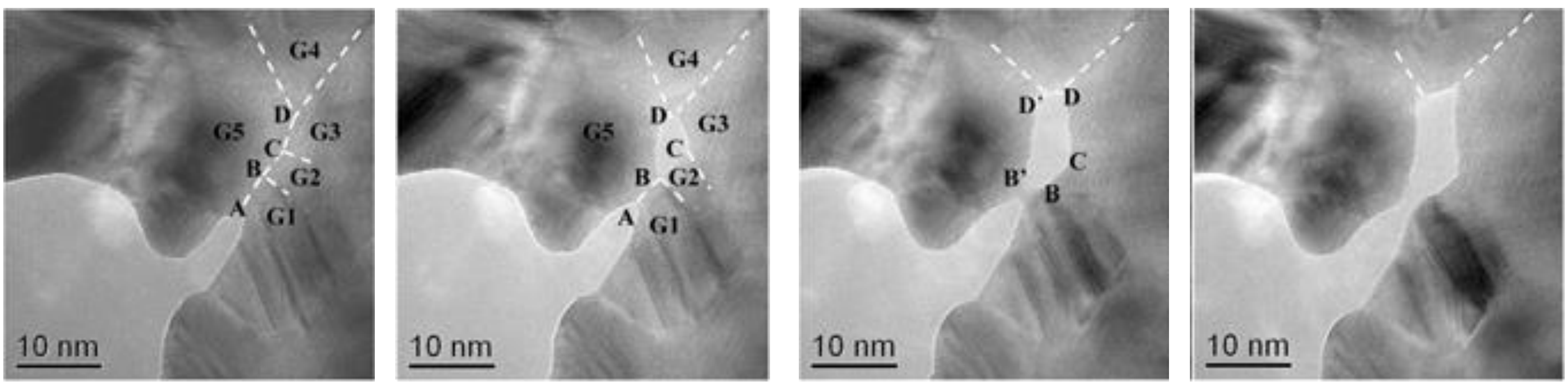


25 nm Au on C: Periodic Crack profiles and bifurcation

- ***Crack Propagation mechanism: Nanovoid Nucleation at the Tip***

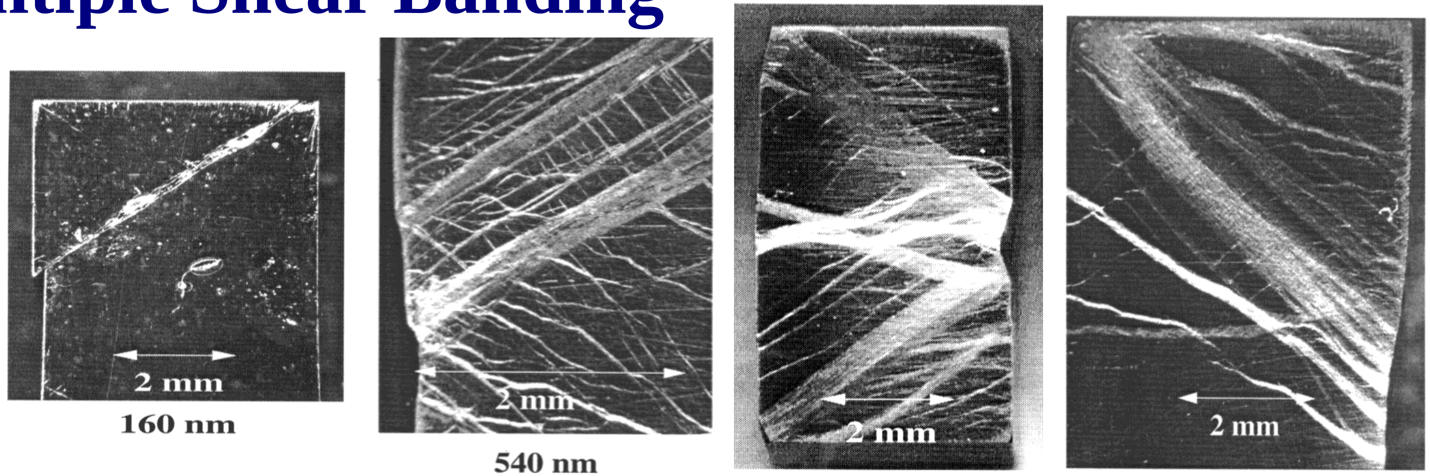


8 nm Au on C: Nanocrack growth via nanopore/nanovoid formation/nucleation at triple GB junction



[Wei et al, Science / Scripta Met., 2011/2014]

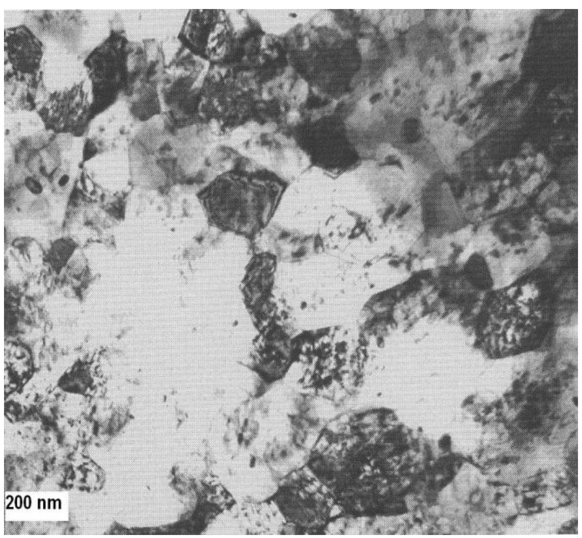
■ Multiple Shear Banding



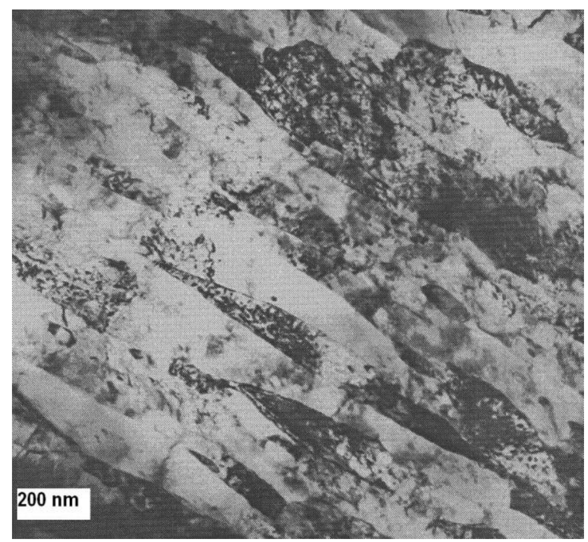
160 nm 540 nm 1370 nm 1680 nm

Optical micrographs showing deformation and fracture behavior under compression of nanostructured Fe-10% Cu alloy for different grain sizes.

(a)



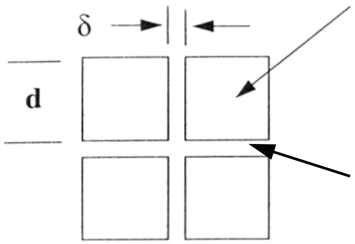
(b)



TEM micrographs of a compression-tested sample with a 100-nm grain size. **(a)** Undeformed area outside the shear band region; **(b)** heavily deformed area in the shear band region.

Early MTU Simple-Minded Models

- ***Continuum Two-Phase Model***



"Bulk" Phase, Hall – Petch relation

$$\sigma_G = \sigma_0 + k/\sqrt{d}$$

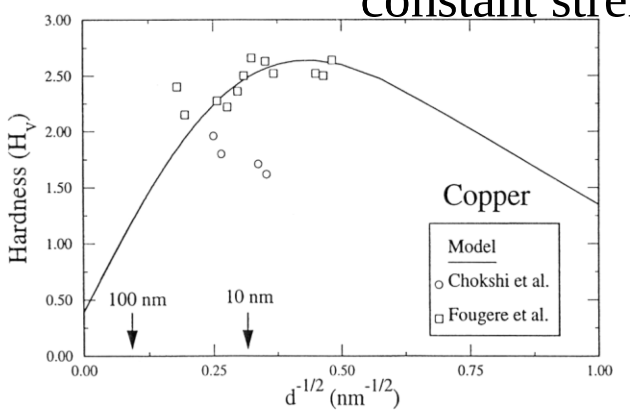
"Boundary" Phase/Amorphous constant strength (σ_{GB})

- Volume Fraction

$$f = d^3/(d+\delta)^3$$

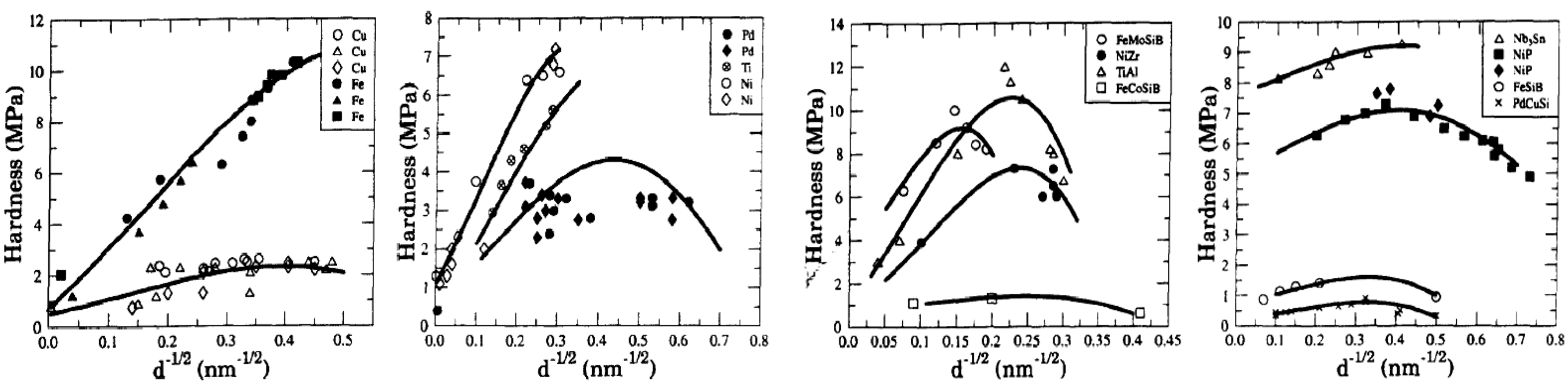
- Rule of Mixtures

$$\sigma = f\sigma_G + (1-f)\sigma_{GB}$$



•*Continuum Model predicts behavior of NanoCrystalline Materials*

•*Continuum Model can sort out conflicting Materials Science data*

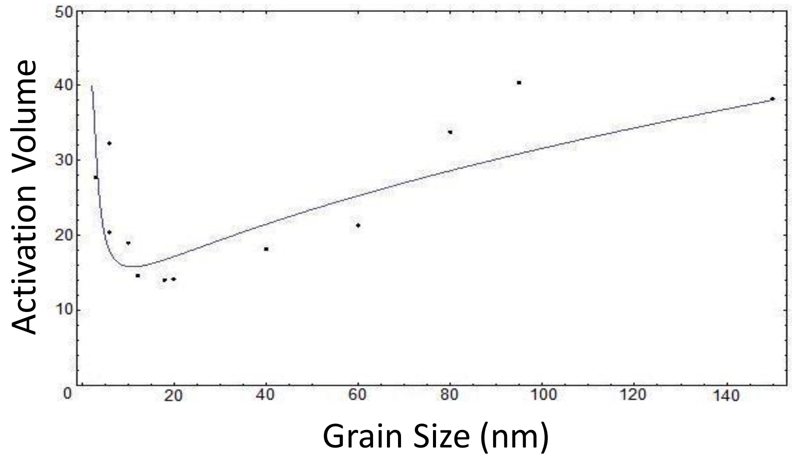


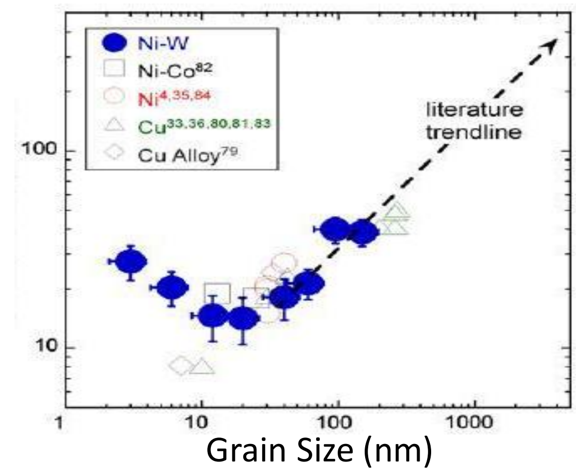
(a) (b) (c) (d)

(a) & (b): nanocrystalline metals; (c) & (d): intermetallics

■ Activation Volume (υ)

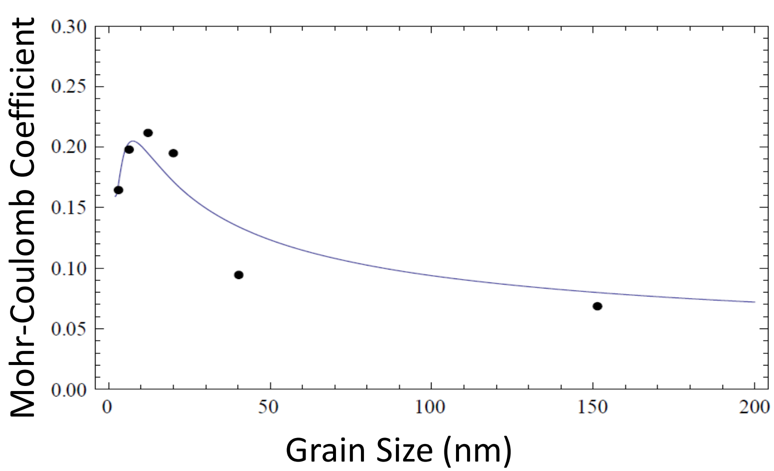
- $$\upsilon = \sqrt{3}\, kT \frac{\partial \ln \dot{\varepsilon}}{\partial \sigma} \quad ; \quad \frac{1}{\upsilon} = f \frac{1}{\upsilon_g} + (1 - f)\frac{1}{\upsilon_{gb}}$$

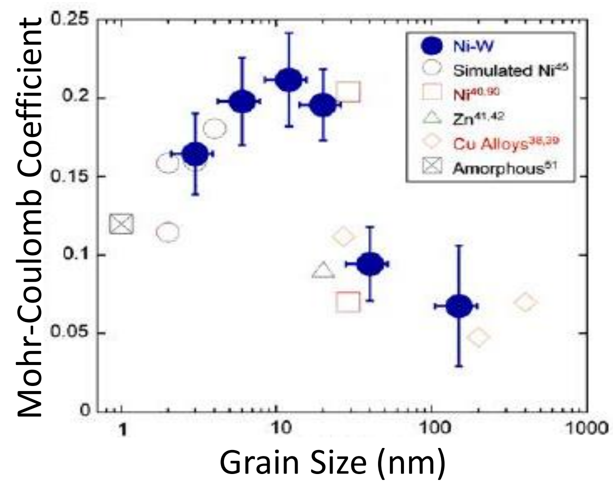




■ Pressure – Sensitivity Parameter (α)

- $$\sqrt{J} + \alpha p - \kappa = 0 \quad ; \quad \alpha = f \alpha_g + (1 - f)\alpha_{gb}$$



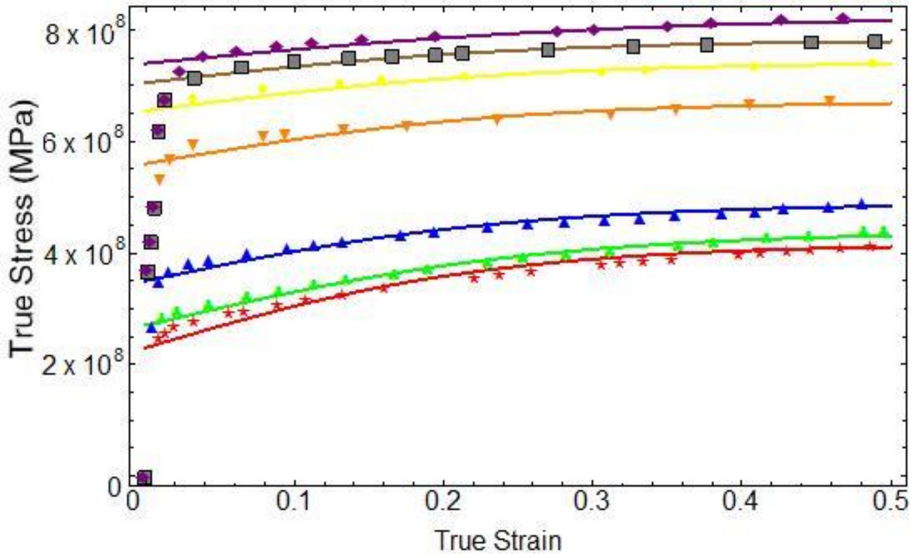


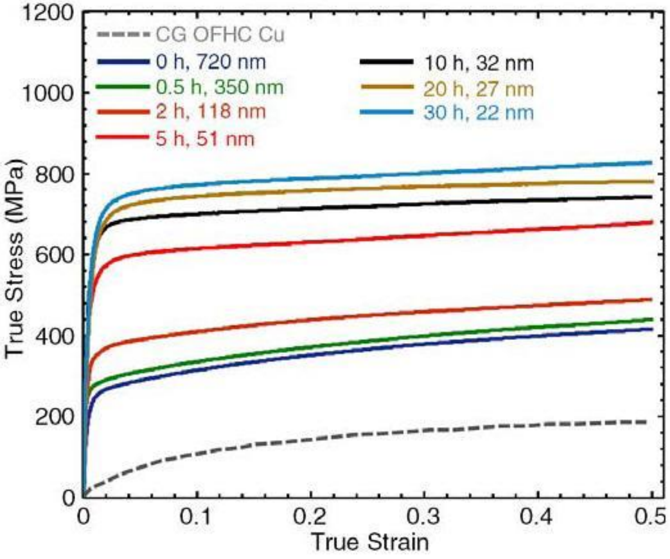
■ Extension to stress – strain curves

- ***H-P Type Behavior***

$$\sigma = \sigma_f + \left(\sigma_s - \sigma_f\right) \tanh\left[\frac{h\varepsilon^p}{\sigma_s - \sigma_f}\right]$$

$$\sigma_{s,f} = \sigma^0_{s,f} + k_{s,f} d^{-1/2}, \qquad h = h_0 - k_h d^{-1/2}$$



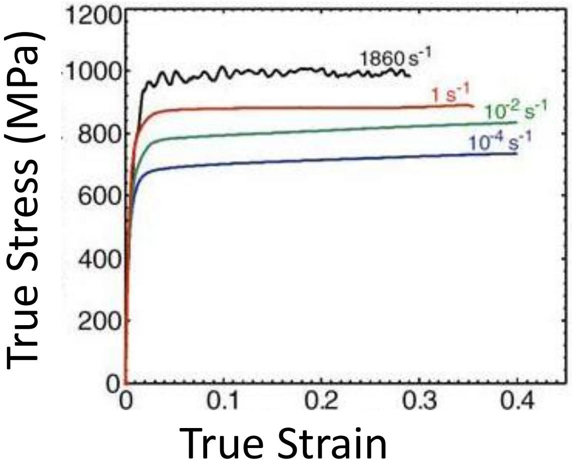


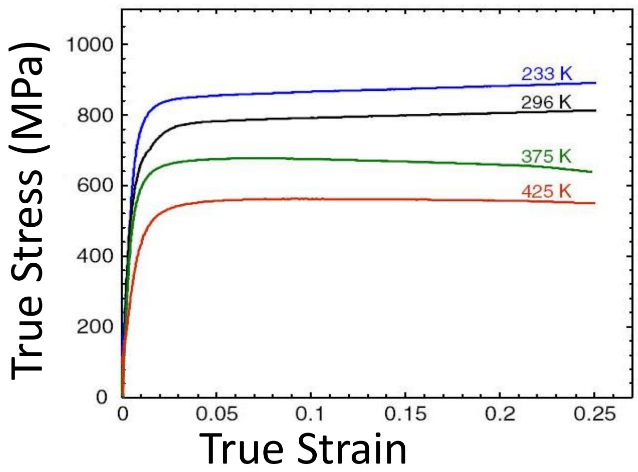
$$\sigma^0_s = 230\,\text{MPa}, \quad k_s = 92.5\,\text{kPa}\sqrt{\text{m}}, \quad \sigma^0_f = 70\,\text{MPa},$$

$$k_f = 104\,\text{kPa}\sqrt{\text{m}}, \quad h_0 = 827\,\text{MPa}, \quad k_h = 86\,\text{kPa}\sqrt{\text{m}}$$

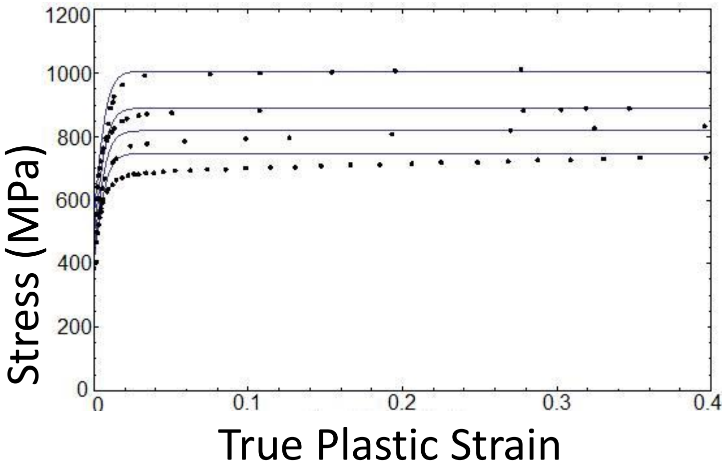
- ***Strain Rate & Temperature Effects***

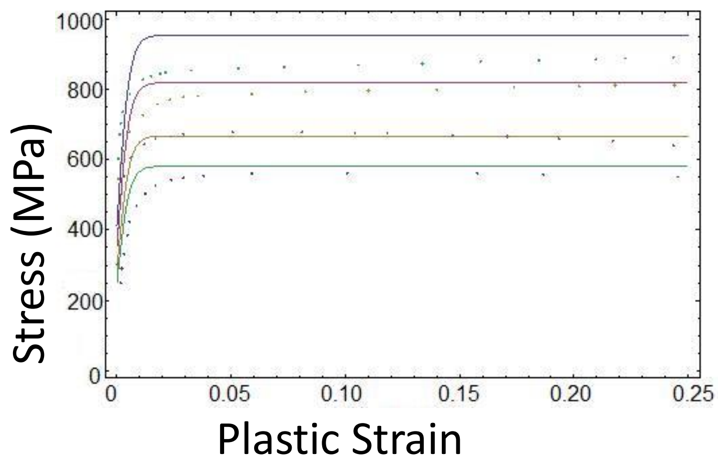
$$\sigma_s \rightarrow \propto \left(1 + c\ln\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right) \qquad \sigma \rightarrow \left\{1 - \left[\left(T - T_{ref}\right)/\left(T_{melt} - T_{ref}\right)\right]^m\right\}$$



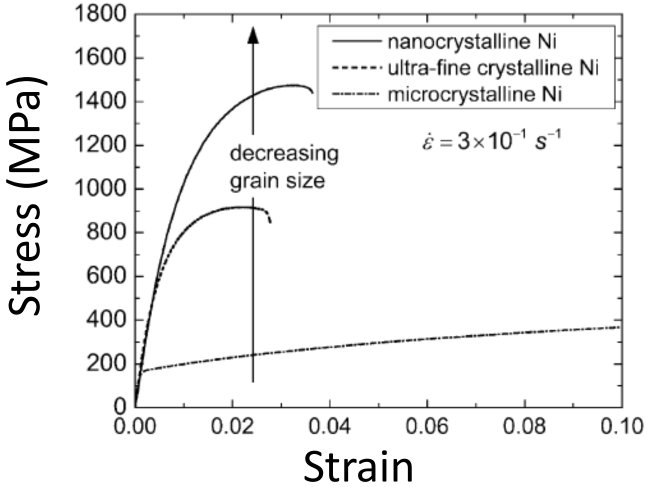


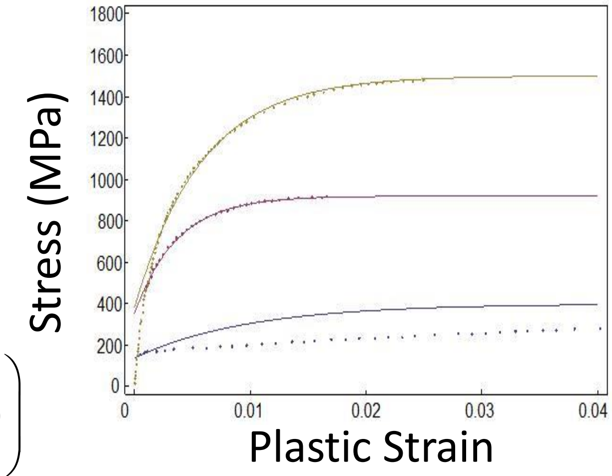
$$\sigma_s = 890 + 15\ln\dot{\varepsilon}$$
$$(\text{MPa})$$
$$\sigma_f = 383\,(\text{MPa})$$
$$h = 95\,\text{GPa}$$
$$T_{ref} = 296\text{K}$$
$$T_{melt} = 1356\text{K}$$
$$m = 2.6$$





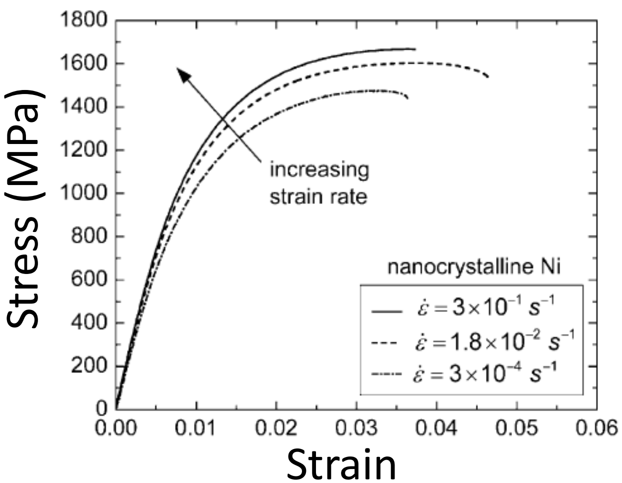
• Simultaneous Grain Size & Strain Rate Dependence

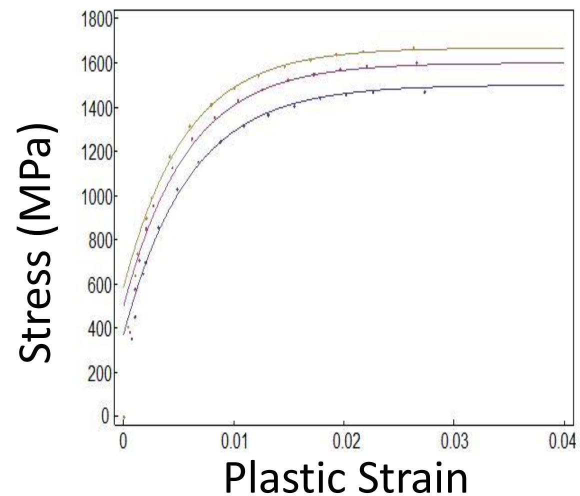




$$\sigma_f = \left(\sigma_f^0 + \frac{k_1}{\sqrt{d}} - \frac{k_2}{d}\right)\left(1 + m_f \ln\left(\frac{\dot{\varepsilon}_p}{\dot{\varepsilon}_p^0}\right)\right)$$

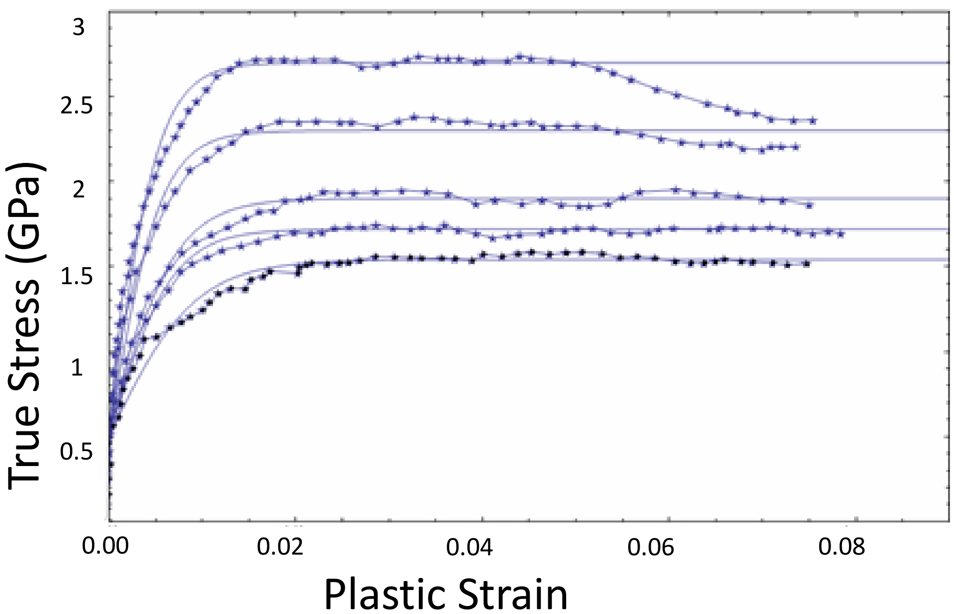
$$\sigma_s = \left(\sigma_s^0 + \frac{k_3}{\sqrt{d}} - \frac{k_4}{d}\right)\left(1 + m_s \ln\left(\frac{\dot{\varepsilon}_p}{\dot{\varepsilon}_p^0}\right)\right)$$

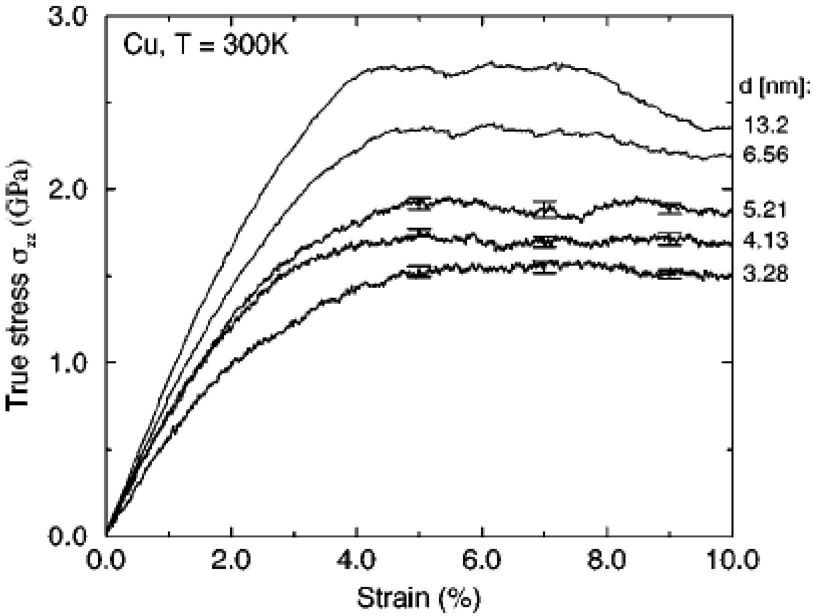




$\sigma_f^0 = 70$ MPa			$\sigma_s^0 = 265$ MPa			$h_0 = 3$ GPa	
k_1 kPa$\sqrt{m}$	k_2 kPa$\sqrt{m}$	m_f	k_3 kPa$\sqrt{m}$	k_4 kPa$\sqrt{m}$	m_s	k_5 kPa$\sqrt{m}$	k_6 kPa$\sqrt{m}$
386	1634	0.045	437	1207	0.016	60851	216646

- ***Inverse H-P Type Behavior***



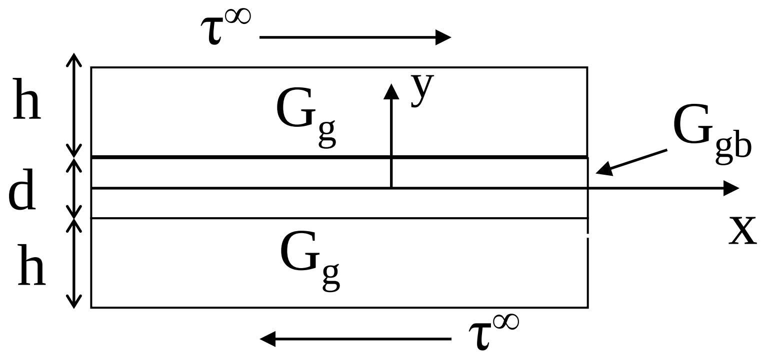


$$\sigma_f = 0.5\text{GPa}, \quad \sigma_s^0 = 4\text{GPa}, \quad k_s = -140\text{kPa}\sqrt{\text{m}}$$

∴ Continuum Model Compares Well with MD Simulations (Shiotz et al, Phys. Rev., 1999/Science, 2003)

■ Effective Moduli of Nanopolycrystals

- ***Idealized Unit Cell***

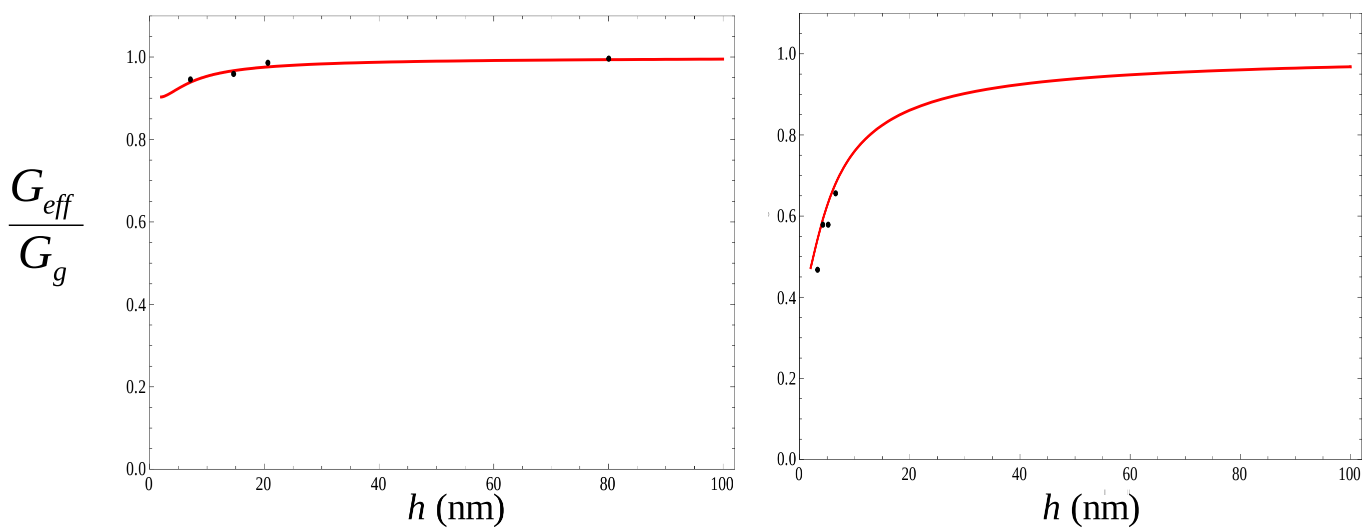


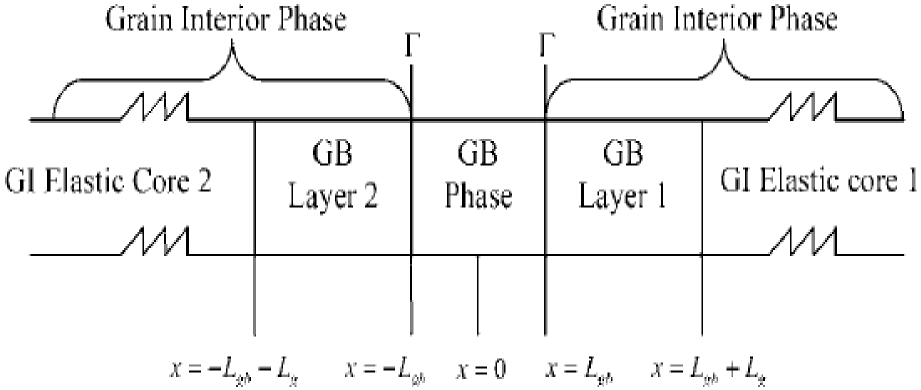
$$\tau = \kappa_i(\gamma) - c_i \nabla^2 \gamma = \tau^\infty$$

$$\text{Bc's} \begin{cases} \partial_y \gamma_{gb} = 0 & , \quad y=0 \\ \left.\begin{array}{l} \gamma_g = \gamma_{gb} \\ \partial_y \gamma_g = \partial_y \gamma_{gb} \end{array}\right\} & , \quad |y| = d/2 \\ \gamma_g = \tau^\infty / G & , \quad |y| = h + d/2 \end{cases}$$

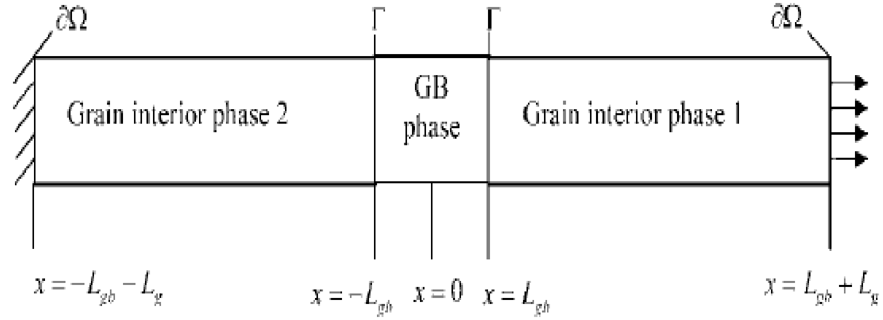
- ***Average Strain/Effective Modulus***

$$\bar{\gamma} = \frac{1}{(h + d/2)} \left(\int_0^{d/2} \gamma_{gb} dy + \int_0^{h+d/2} \gamma_g dy \right), \quad G_{eff} = \tau^\infty / \bar{\gamma}$$



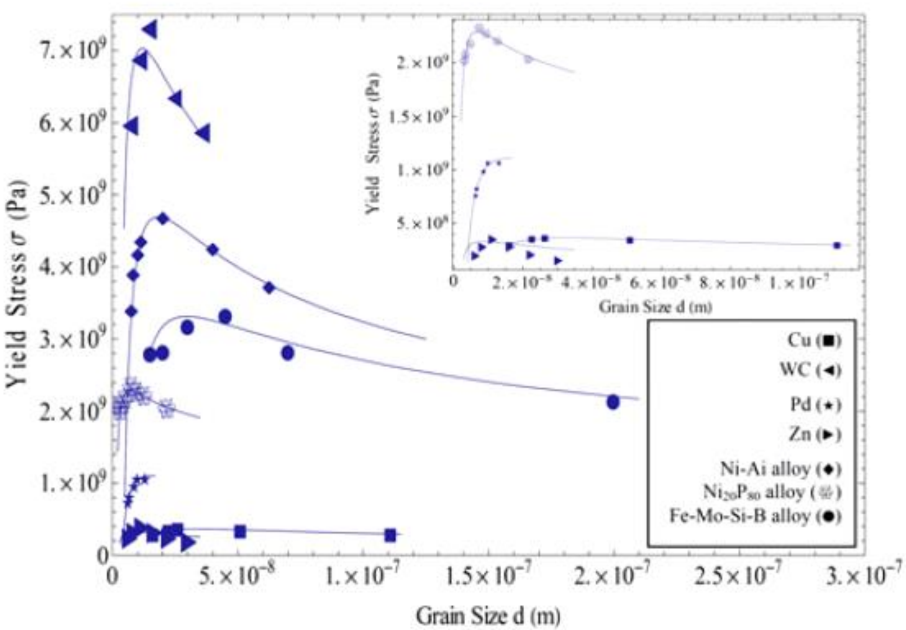


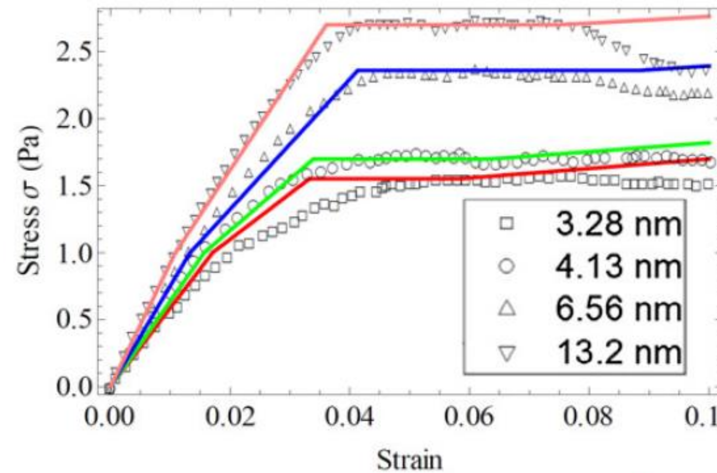
Unit cell model with GB phase, GI phase comprised of GI-GB layers, and elastic GI cores



Unit cell consisting of a GB and a GI phase, for size-dependent stress-strain prediction

$$\bar{\sigma}=\sigma_0+\frac{k}{\sqrt{d}}+\frac{\gamma_{gb}}{2ad};\quad d_c=\left(\gamma_{gb}/ak\right)^2$$

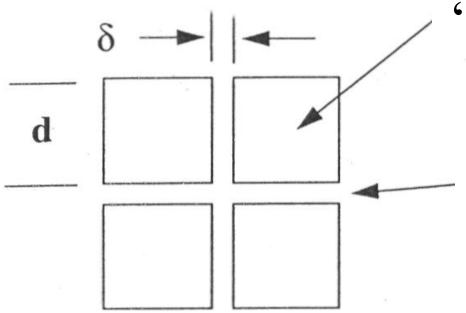




	L_g = 3.28 nm	L_g = 4.13 nm	L_g = 6.56 nm	L_g = 13.2 nm	
σ^0_{gb} (GPa)	1	1	1	1	
σ^0_g (GPa)	1.55	1.70	2.36	2.70	
E_g (GPa)	E_{gb} (GPa)	L_{gb} (nm)	ℓ_{gb} (nm)	β_{gb} (GPa)	β_g (GPa)
127	27	1.5	1	10	2

I. NANOELASTICITY
[Gradient Elasticity at the Nanoscale]

■ Nanopolycrystal Elasticity



- ***"Bulk" phase and "boundary" phase*** *occupy the same material point and interact via an internal body force*

•*Equilibrium*

$$\mathit{div}\boldsymbol{\sigma}_1 = \mathbf{f}, \quad \mathit{div}\boldsymbol{\sigma}_2 = -\mathbf{f} \; \text{.......}\textit{for each phase}$$
$$\mathit{div}\boldsymbol{\sigma} = 0, \quad \boldsymbol{\sigma} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 \; \text{.......}\textit{total}$$

•*Elasticity for each phase:* *Assume that each phase obeys Hooke's Law and that the interaction force is proportional to the difference of the individual displacements*

$$\boldsymbol{\sigma}_\mathbf{k} = \mathbf{L}_\mathbf{k}\mathbf{u}_\mathbf{k}, \quad k = 1,2; \quad \mathbf{L}_\mathbf{k} = \lambda_k \mathbf{G} + \mu_k \hat{\nabla}; \quad \mathbf{G} = \mathbf{I}\,\mathit{div}\;; \quad \hat{\nabla} = \nabla + \nabla^T$$

$$\mathbf{f} = \alpha(\mathbf{u}_1 - \mathbf{u}_2)$$

•*Uncoupling* $\Rightarrow$

$$\mu\nabla^2\mathbf{u} + (\lambda+\mu)\mathit{grad}\,\mathit{div}\mathbf{u} - c\nabla^2\left[\mu\nabla^2\mathbf{u} + (\lambda+\mu)\mathit{grad}\,\mathit{div}\mathbf{u}\right] = \mathbf{0}$$

- ***Gradient Elasticity (Gradela)***

The above implies the following gradient-elasticity relation

$$\boldsymbol{\sigma} = \lambda(tr\boldsymbol{\varepsilon})\mathbf{I} + 2\mu\boldsymbol{\varepsilon} - c\nabla^2\left[\lambda(tr\boldsymbol{\varepsilon})\mathbf{I} + 2\mu\boldsymbol{\varepsilon}\right]$$

i.e.

elasticity of nanopolycrystals depends on higher – order gradients in strain or the Laplacian of Hookean stress

- ***Ru-Aifantis Theorem***

$$\boldsymbol{u} - c\nabla^2\boldsymbol{u} = \boldsymbol{u}_0$$

$\boldsymbol{u}$...*Gradela solution* ; $\boldsymbol{u}_0$ ...*classical elasticity solution*

- ***Nanocomposites***

Another possible configuration to be treated with Gradela

■ Gradela Dislocation Nanomechanics

- ***Gradela:*** $$(1-\textcolor{red}{c}\nabla^2)\begin{bmatrix}\sigma_{ij}\\ \varepsilon_{ij}\end{bmatrix}=\begin{bmatrix}\sigma^0_{ij}\\ \varepsilon^0_{ij}\end{bmatrix}$$

- ***Screw Dislocation :***

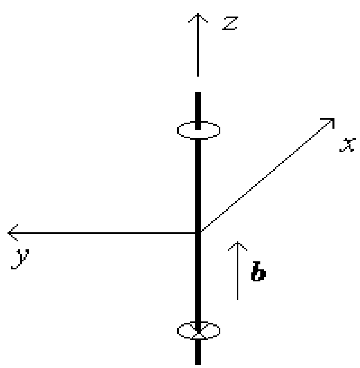
  - Stress / Strain :

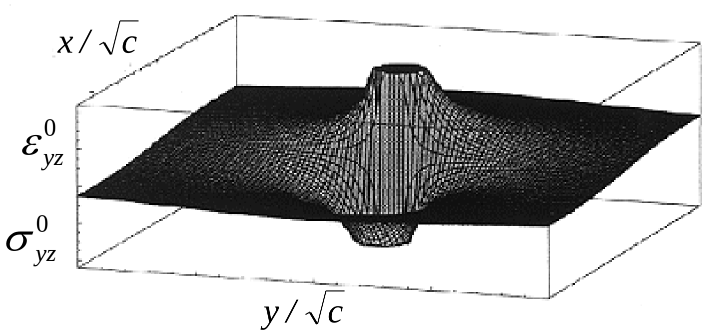
$$\begin{cases}\sigma_{xz}=\dfrac{\mu b_z}{4\pi}\left[-\dfrac{y}{r^2}+\dfrac{y}{r\sqrt{\textcolor{red}{c}}}K_1\left(r/\sqrt{\textcolor{red}{c}}\right)\right]; & \sigma_{yz}=\ldots\\[2ex] \varepsilon_{xz}=\dfrac{b_z}{4\pi}\left[-\dfrac{y}{r^2}+\dfrac{y}{r\sqrt{\textcolor{red}{c}}}K_1\left(r/\sqrt{\textcolor{red}{c}}\right)\right]; & \varepsilon_{yz}=\ldots\end{cases}$$

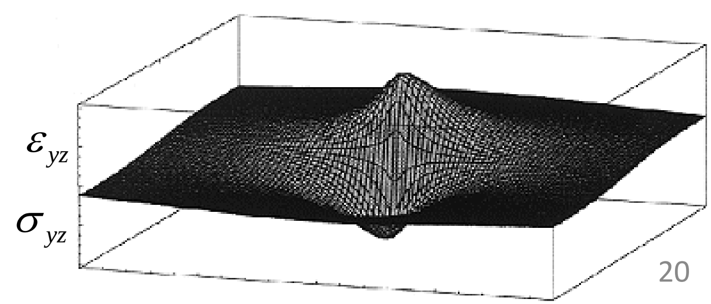
$$\therefore\quad \mathbf{r}\to\mathbf{0}\quad\Rightarrow\quad \mathbf{K}_1\left(\mathbf{r}/\sqrt{\textcolor{red}{\mathbf{c}}}\right)\to\frac{\sqrt{\textcolor{red}{\mathbf{c}}}}{\mathbf{r}}\quad\Rightarrow\quad\left(\boldsymbol{\sigma}_{\mathbf{xz}},\boldsymbol{\varepsilon}_{\mathbf{yz}}\right)\to\mathbf{0}$$

  - Self – energy : $$W_s=\frac{\mu b_z^2}{4\pi}\left\{\gamma^E+\ln\frac{R}{2\sqrt{c}}\right\}\quad\ldots\quad \gamma^E=0.577;\ \text{Euler constant}$$

$$\therefore\quad \mathbf{r}\to\mathbf{0}\quad\Rightarrow\quad \textbf{no need for ad hoc dislocation core } \mathbf{r_0}$$



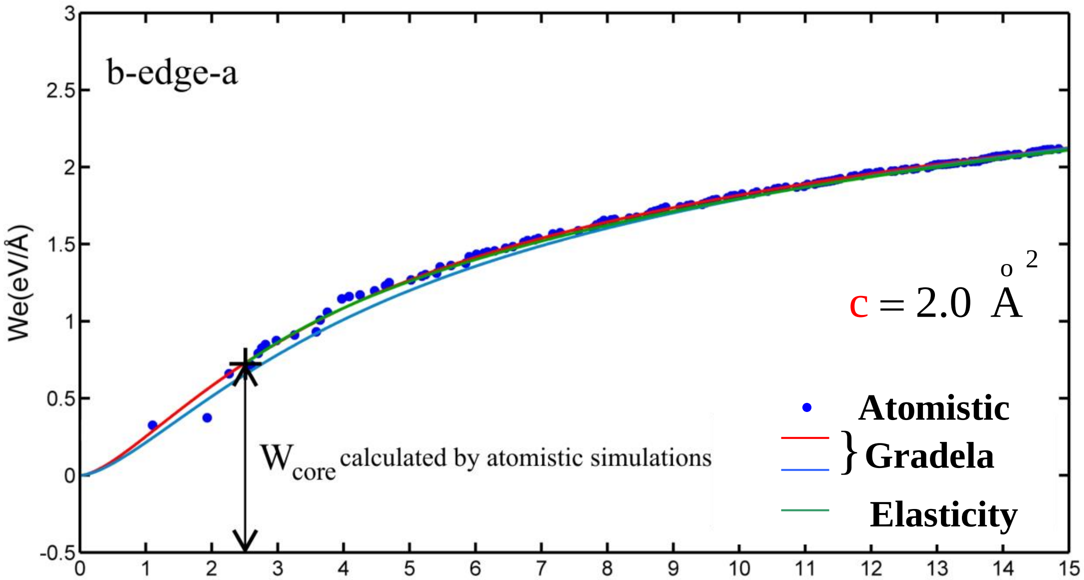


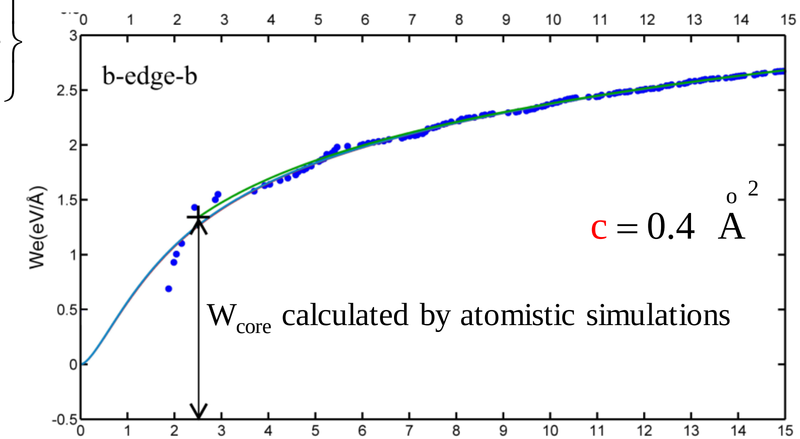


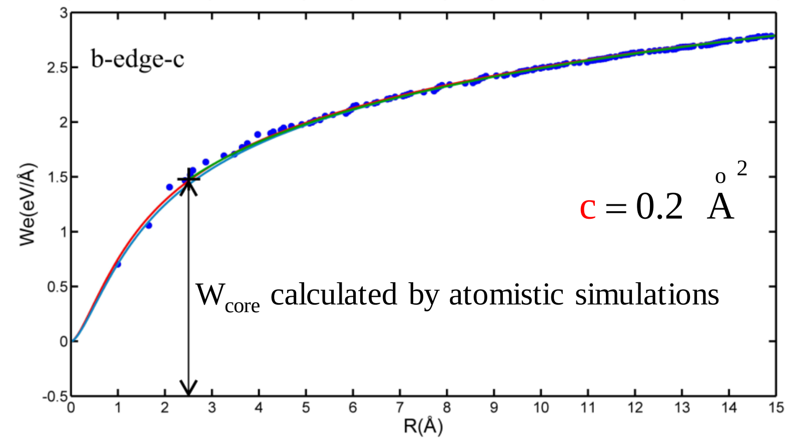
- ***Comparison with MD Simulations (Stilliger – Weber Potential)***

$$W = \frac{b^2}{4\pi(1-\nu)}\left\{\ln\frac{R}{2\sqrt{c}} + \gamma + 2K_0\left(\frac{R}{\sqrt{c}}\right) + 2\frac{\sqrt{c}}{R}K_1\left(\frac{R}{\sqrt{c}}\right) - \frac{2c}{R^2}\right\}$$

$$R \to \infty \Rightarrow W = \frac{b^2}{4\pi(1-\nu)}\left\{\ln\frac{R}{2\sqrt{c}} + \gamma + \frac{1}{2}\right\}$$







$$\sqrt{c} = 0.2 - 2.2\ \ \text{Å}$$

Invariant Relations: $\frac{W_{core}\sqrt{c}}{r_0} = 0.33 \pm 0.008\,\frac{eV}{\text{Å}}$; $\frac{W^g(b)\sqrt{c}}{b} = 0.3 \pm 0.008\,\frac{eV}{\text{Å}}$

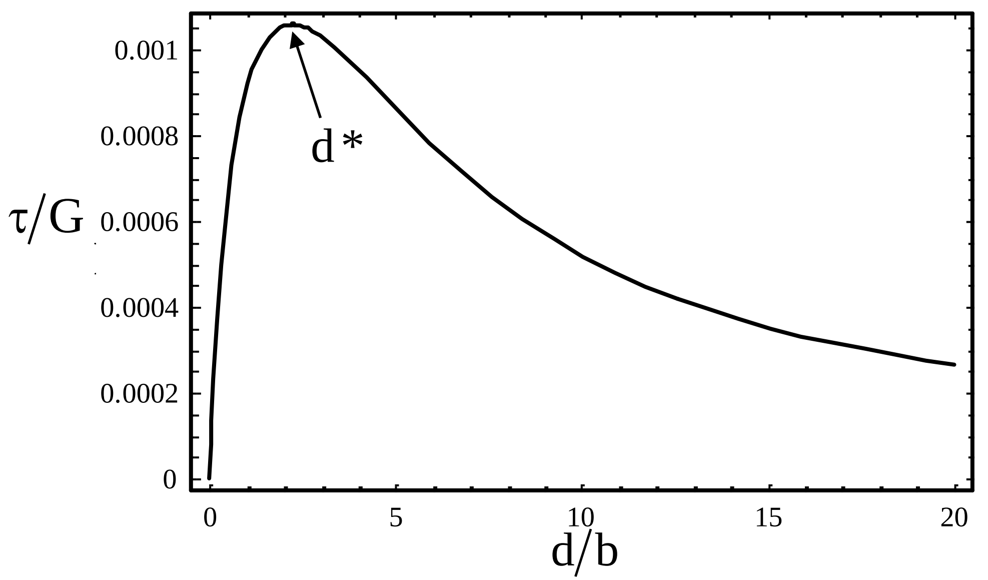
- ***Image Force – Inverse Hall Petch Behavior***

  - *Self -energy:* $$W = \frac{Gb^2}{2\pi}\left[\ln\frac{R}{2\sqrt{c}} + \gamma^E + K_0\left(\frac{R}{\sqrt{c}}\right)\right]$$

  - *Image Stress:* $$\tau = \frac{Gb}{2\pi}\left[\frac{1}{d} - \frac{1}{2\sqrt{c}}K_1\left(\frac{d}{2\sqrt{c}}\right)\right]$$

derived by differentiation and evaluation at $R = d/2$ (d … grain diameter)

- stress to move a dislocation situated at the center of a grain of diameter d



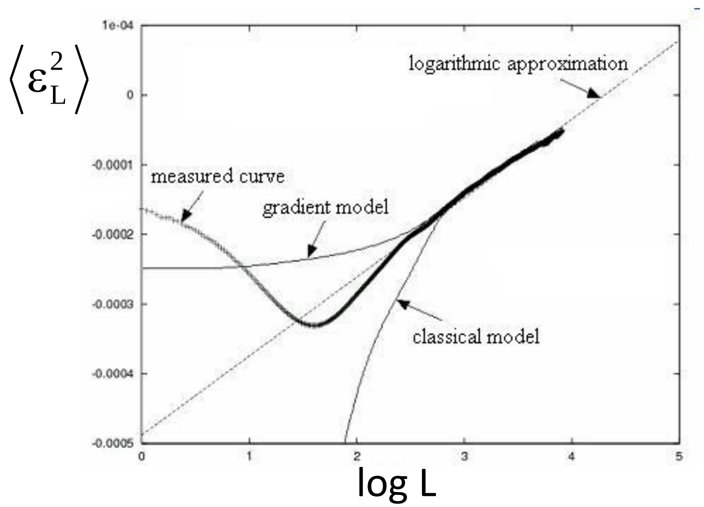
$d^* \approx 9$ nm

i.e. d^* critical grain size for inverse Hall-Petch behavior

• *X-ray Line Profile Analysis*

- *Gradela Soltn for ε_{xx} of edge $\perp$* $(\mathbf{b} = b\,\mathbf{e_x})$

$$\varepsilon_{xx} = -\frac{b}{4\pi(1-\nu)}\frac{(1-2\nu)r^2 + 2x^2}{r^4} + \frac{b}{2\pi(1-\nu)}y\left[(y^2 - \nu r^2)\Phi_1 + (3x^2 - y^2)\Phi_2\right]$$

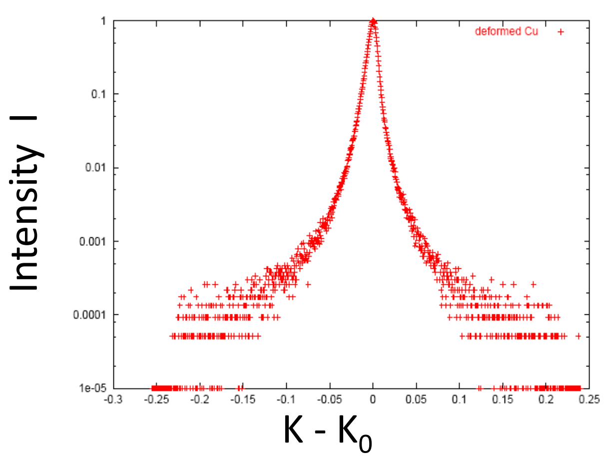


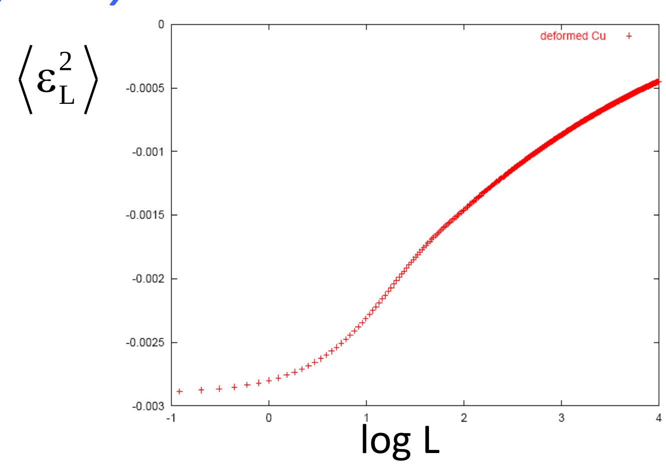
$$\Phi_1 = \frac{1}{r^3\sqrt{c}}K_1\left(r/\sqrt{c}\right),$$

$$\Phi_2 = \frac{1}{r^4}\left[\frac{2c}{r^2} - K_2\left(r/\sqrt{c}\right)\right],$$

$$r^2 = x^2 + y^2$$

- *X-ray line profile for deformed Cu single crystal*





■ Gradela Crack Nanomechanics (Mode III)

• *Gradela: Mode III Cracking*

- ***Gradela:*** $(1-c\Delta)\boldsymbol{\sigma}_{ij} = \boldsymbol{\sigma}_{ij}{}^{\mathbf{0}}$ & $(1-c\Delta)\boldsymbol{\varepsilon}_{ij} = \boldsymbol{\varepsilon}_{ij}{}^{\mathbf{0}}$; $\boldsymbol{\sigma}^{\mathbf{0}} = \lambda\, \mathrm{tr}\boldsymbol{\varepsilon}^{\mathbf{0}}\, \mathbf{1} + 2\mu\boldsymbol{\varepsilon}^{\mathbf{0}}$

Target: Non-Singular Stresses/Strain Estimation at the crack tip

- ***Boundary Conditions***

Far field coincidence of stresses: $\lim\limits_{\mathbf{r}\to\infty} \boldsymbol{\sigma}_{ij} = \boldsymbol{\sigma}_{ij}{}^{\mathbf{0}}$

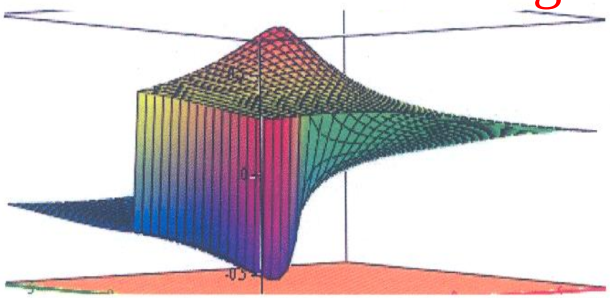
Vanishing of stresses at the origin: $\lim\limits_{\mathbf{r}\to 0} \boldsymbol{\sigma}_{ij} = 0$

Zero tractions on crack surfaces: $\sigma_{zy}(x, 0^{\pm}) = 0 \;\; ; \;\; |x| \le a$

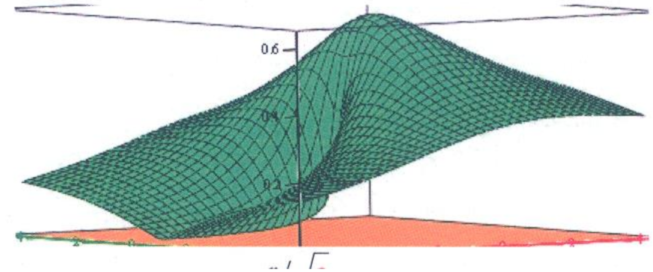
• *Nonsingular stress distribution in Mode III*

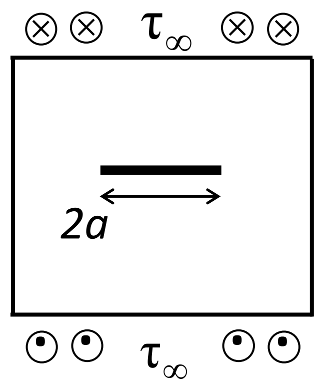
$$\sigma_{xz} = -\frac{K_{III}}{\sqrt{2\pi r}}\left[\sin\frac{\theta}{2}\left(1-\exp\left[-r/\sqrt{c}\right]\right)\right] \qquad \sigma_{yz} = \frac{K_{III}}{\sqrt{2\pi r}}\left[\cos\frac{\theta}{2}\left(1-\exp\left[-r/\sqrt{c}\right]\right)\right]$$

Gradient Stress non-singular

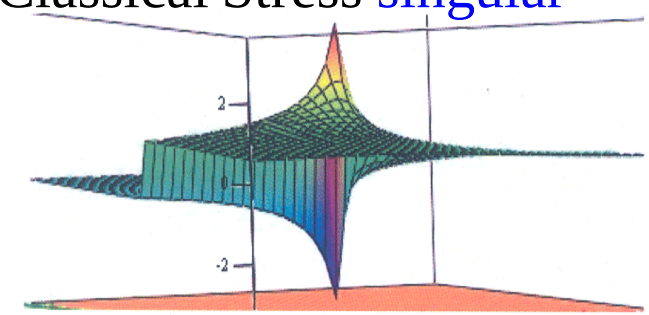


Gradient Stress non-singular

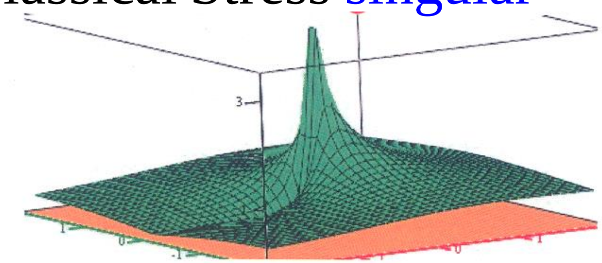




Classical Stress singular



Classical Stress singular



Note: $\left(1-e^{-r/\sqrt{c}}\right)\Big/\sqrt{r}$ max at $r \cong 1.25\sqrt{c}$

$$\therefore\ \sigma_{yz}^{max} = \sigma_{xz}^{max} \cong 0.254\frac{K_{III}}{\sqrt[4]{c}} \cong \frac{K_{III}}{4\sqrt[4]{c}}$$ **(Stress Fracture Criterion)** $K_{III} = \tau_\infty\sqrt{\pi a}$

II. NANOPLASTICITY

[Gradient Plasticity at the Nanoscale]

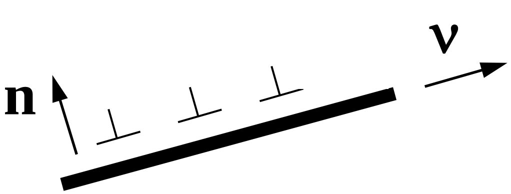
■ Motivation from Dislocation Slip

- ***Momentum Balance for Dislocated State***

$$\mathrm{div}\mathbf{T}^{\mathbf{D}} = \hat{\mathbf{f}}\ ; \quad \mathbf{T}^{\mathbf{D}} = \mathbf{S} - \mathbf{T}^{\mathrm{L}}\ ; \quad \mathrm{div}\mathbf{S} = 0$$

$\mathbf{T}^{\mathbf{D}}$...dislocation stress; $\hat{\mathbf{f}}$...dislocation-lattice interaction force

- ***Yield Condition:*** $\mathrm{f} = \hat{\mathbf{f}} \cdot \boldsymbol{\nu} = 0; \quad \hat{\mathbf{f}} = \left(\hat{\alpha} + \hat{\beta}\mathrm{j} - \hat{\gamma}\tau^{\mathrm{L}}\right)\boldsymbol{\nu}, \quad \tau^{\mathrm{L}} = \mathbf{T}^{\mathrm{L}} \cdot \mathbf{M}$



$$\mathbf{M} = \left(\boldsymbol{\nu} \otimes \mathbf{n}\right)_{\mathrm{s}}, \quad \mathbf{D}^{\mathrm{p}} = \dot{\gamma}^{\mathrm{p}}\mathbf{M}; \quad \mathbf{T}^{\mathrm{D}} = \mathrm{t}_{\mathrm{m}}\mathbf{M} + \mathrm{t}_{\mathrm{n}}\mathbf{N}$$

$$\max\left\{\mathrm{tr}\mathbf{T}^{\mathrm{L}}\mathbf{D}^{\mathbf{p}}\right\};\ \mathrm{tr}\mathbf{M} = 0,\ \mathrm{tr}\mathbf{M}^{2} = 1/2 \quad \Rightarrow \quad \mathbf{D}^{\mathbf{p}} = \frac{\dot{\gamma}^{\mathrm{p}}}{2\sqrt{\mathrm{J}}}\mathbf{T}^{\mathrm{L}'}; \quad \mathrm{J} = \frac{1}{2}\mathrm{tr}\left(\mathbf{T}^{\mathrm{L}'}\mathbf{T}^{\mathrm{L}'}\right)$$

$$\therefore \quad \tau = \sqrt{\mathrm{J}} = \kappa\left(\gamma^{\mathrm{p}}\right)$$

- ***Structure of Macroscopic Anisotropic Hardening Plasticity***

$$\mathbf{D}^{p} = \frac{\dot{\gamma}^{p}}{2\sqrt{J}}\left(\boldsymbol{\sigma}' - \boldsymbol{\alpha}'\right)$$

$$\overset{o}{\boldsymbol{\alpha}} = \left(\frac{\dot{t}_{m}}{\dot{\gamma}^{p}} - \frac{\dot{t}_{n} t_{m}}{t_{n}\dot{\gamma}^{p}}\right)\mathbf{D}^{\mathbf{p}} + \frac{\dot{t}_{n}}{t_{n}}\boldsymbol{\alpha}, \qquad \overset{o}{\boldsymbol{\alpha}} = \dot{\boldsymbol{\alpha}} - \boldsymbol{\omega}\boldsymbol{\alpha} + \boldsymbol{\alpha}\boldsymbol{\omega}$$

$$\boldsymbol{\omega} = \mathbf{W} - \mathbf{W}^{\mathbf{p}}, \qquad \mathbf{W}^{\mathbf{p}} = -\frac{1}{t_{n}}\left(\boldsymbol{\alpha}\mathbf{D}^{\mathbf{p}} - \mathbf{D}^{\mathbf{p}}\boldsymbol{\alpha}\right)$$

$$\dot{\gamma}^{p} = \frac{\boldsymbol{\sigma}' \cdot \left(\boldsymbol{\sigma}' - \boldsymbol{\alpha}'\right)}{\kappa\left(t'_{m} + 2\kappa'\right)}; \qquad \begin{cases} \dot{f} = 0 \\ f = \frac{1}{2}\left(\boldsymbol{\sigma}' - \boldsymbol{\alpha}'\right)\cdot\left(\boldsymbol{\sigma}' - \boldsymbol{\alpha}'\right) - \kappa^{2} = 0 \end{cases}$$

- ***Inhomogeneous Back Stress:*** $\boldsymbol{T}^{D} = \boldsymbol{\alpha} + \boldsymbol{T}^{inh}$
  - $\boldsymbol{\alpha}$ = *homogeneous back stress … as before*

$$\mathbf{T}^{\mathbf{inh}} = \hat{\mathbf{g}}\left(\mathbf{n}, \boldsymbol{\nu}, \nabla\gamma^{p}\right)$$

$$\approx \left[\mathbf{n} \otimes \nabla\gamma^{p} + \left(\nabla\gamma^{p}\right) \otimes \mathbf{n}\right] + \left[\boldsymbol{\nu} \otimes \nabla\gamma^{p} + \left(\nabla\gamma^{p}\right) \otimes \boldsymbol{\nu}\right]$$

$$\mathrm{div}\mathbf{T}^{\mathbf{inh}} \approx \left(\mathbf{n} + \boldsymbol{\nu}\right)\nabla^{2}\gamma^{p} + \left(\mathbf{grad}^{2}\gamma^{p}\right)\left(\mathbf{n} + \boldsymbol{\nu}\right)$$

$$\left(\mathrm{div}\mathbf{T}^{\mathbf{inh}}\right) \cdot \boldsymbol{\nu} \approx \nabla^{2}\gamma^{p} + \gamma^{p}_{,ij}\left(\nu_{i}\nu_{j} + \nu_{i}n_{j}\right)$$

  - *Integrate over all possible orientations of* $(\boldsymbol{n}, \boldsymbol{\nu})$

$$\left(\mathrm{div}\mathbf{T}^{\mathbf{inh}}\right) \cdot \boldsymbol{\nu} \rightarrow \nabla^{2}\gamma^{p}$$

$$\therefore \quad \tau = \kappa\left(\gamma^{p}\right) - c\nabla^{2}\gamma^{p}$$

- ***Same Procedure for Nanopolycrystals***
  - *Representative slip plane → Representative planar GB*

■ More on Motivation … Laplacians

- ***Adiabatic Approximation for Defect/Dislocation Density***

  - $\tau = \kappa(\gamma, \alpha) \quad ; \quad \dot{\alpha} = D\nabla^2\alpha + g(\gamma, \alpha) \quad \rightarrow \quad \tau = \kappa^*(\gamma) - c\nabla^2\gamma$

  - Example: $\tau = \hat{\kappa}(\gamma) - \lambda\alpha\,, \quad \dot{\alpha} = D\alpha_{xx} + \Lambda\gamma - M\alpha \quad ; \quad \{\lambda, \Lambda, M\} = \text{constants}$

$$\dot{\alpha}_q = -Dq^2\alpha_q + \Lambda\gamma_q - M\alpha_q \;;\; \dot{\alpha}_q \approx 0\,, \;\; \frac{Dq^2}{M} << 1 \;\Rightarrow\; \alpha \approx \frac{\Lambda}{M}\gamma - \frac{\Lambda D}{M^2}\gamma_{xx}$$

$$\Rightarrow \quad \tau = \kappa(\gamma) - c\gamma_{xx} \quad ; \quad \kappa(\gamma) \equiv \hat{\kappa}(\gamma) - (\lambda\Lambda/M)\gamma\,, \quad c \equiv \lambda\Lambda D/M^2$$

- ***Non-local Approximation for Strain***

  - $\bar{\gamma} = (1/V)\int_V \gamma(\boldsymbol{x}+\boldsymbol{r})dV, \quad V = (4/3)\pi R^3 \Longrightarrow \quad \bar{\gamma} \approx \gamma + \frac{R^2}{10}\nabla^2\gamma\,, \quad R = d/2$

$$\left[\gamma(\boldsymbol{x}+\boldsymbol{r}) = \gamma(\boldsymbol{x}) + \nabla\gamma\cdot\boldsymbol{r} + \frac{1}{2!}\nabla^{(2)}\gamma\cdot\boldsymbol{r}\otimes\boldsymbol{r} + \ldots;\; \int_V \nabla^{2n+1}\gamma\cdot\boldsymbol{r}^{2n+1}dV = 0\right]$$

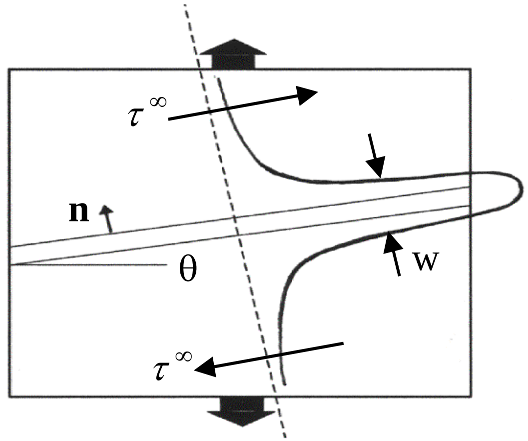
  - $\bar{\tau} = \kappa(\bar{\gamma})\,, \quad \tau = \bar{\tau} - \beta\Delta\gamma \quad ; \quad \Delta\gamma = \gamma - \bar{\gamma}$

$$\therefore \quad \tau = \kappa(\gamma) - c\nabla^2\gamma\,; \quad c = Cd^2,\; C = R^2(\beta + h)/10,\; \beta = \alpha\mu(7-5\nu)/15(1-\nu)$$

- *Note:* Maxwell's 1871 Interpretation of the Laplacian

■ Implications to Localization of Plastic Flow

- ***Constitutive Equation***



$$\mathbf{S}' = -p\mathbf{1} + 2\mu\mathbf{D} \quad ;$$

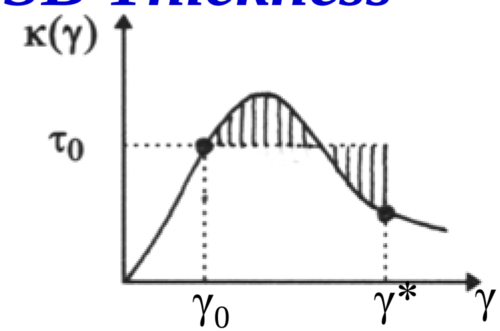
$$\mu = \frac{\tau}{\dot{\gamma}} \quad , \quad \begin{cases} \tau \equiv \sqrt{\tfrac{1}{2}\mathbf{S}'\cdot\mathbf{S}'} \\ \dot{\gamma} \equiv \sqrt{2\mathbf{D}\cdot\mathbf{D}} \end{cases} ; \quad \tau = \kappa(\gamma) - c\nabla^2\gamma$$

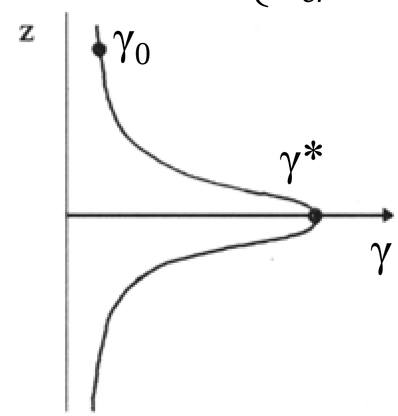
- ***Linear Stability / SB Orientation***

$$\mathrm{v} = \mathrm{L}_{\infty}\mathrm{x} + \tilde{\mathrm{v}}\mathrm{e}^{\mathrm{iqz}+\omega\mathrm{t}} ; \qquad \omega > 0 \quad (\&\omega_{\max}) \;\rightarrow\; \theta_{cr} = \frac{\pi}{4} \quad \& \quad \begin{cases} h_{cr} = 0 \\ q_{cr} = 0 \end{cases}$$

- ***Nonlinear Solution / SB Thickness***

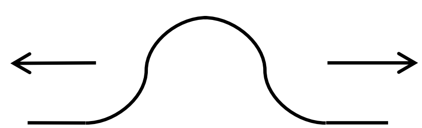
$$c\gamma_{zz} = \kappa(\gamma) - \tau_0$$





- ***Front Propagation***

Similar Procedure



■ Thermodynamics

- ***Thermodynamics applied to gradient theories: The theories of Aifantis and Fleck & Hutchinson and their generalization / JMPS 57, 405-421 (2009)***

[M.E. Gurtin/Carnegie-Mellon & L. Anand/MIT]

- **Abstract :** We discuss the physical nature of flow rules for rate-independent (gradient) plasticity laid down by Aifantis and Fleck and Hutchinson. As central results we show that:
  - The flow rule of Fleck and Hutchinson is incompatible with thermodynamics unless its nonlocal (gradient) term is dropped.
  - If the theory is augmented by a defect energy dependent on γ^p and $\nabla\gamma^p$, then compatibility with thermodynamics requires that its flow rule reduces to that of Aifantis.

- **References :** E.C. Aifantis, On the microstructural origin of certain inelastic models, *Trans. ASME, J. Engng. Mat. Tech.* **106**, 326-330 (1984); E.C. Aifantis, The physics of plastic deformation, *Int. J. Plasticity* **3**, 211-247 (1987).

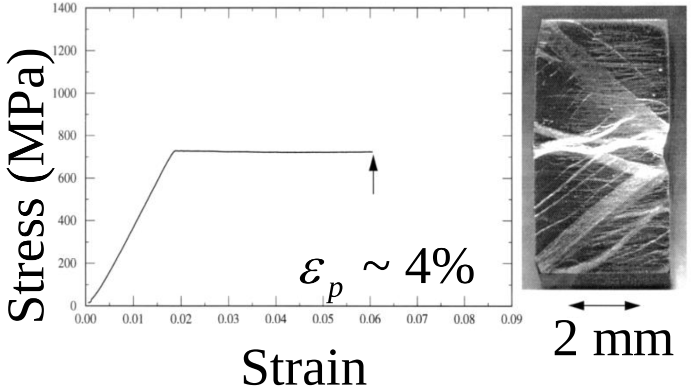
N.A. Fleck and J.W. Hutchinson, A reformulation of strain gradient plasticity, *J. Mech. Phys. Solids* **49**, 2245-2271 (2001).

M.E. Gurtin, E. Fried, L. Anand, The Mechanics and Thermodynamics of Continua, Chapter 89 [Gradient Theory of Aifantis], Cambridge University Press (2010).

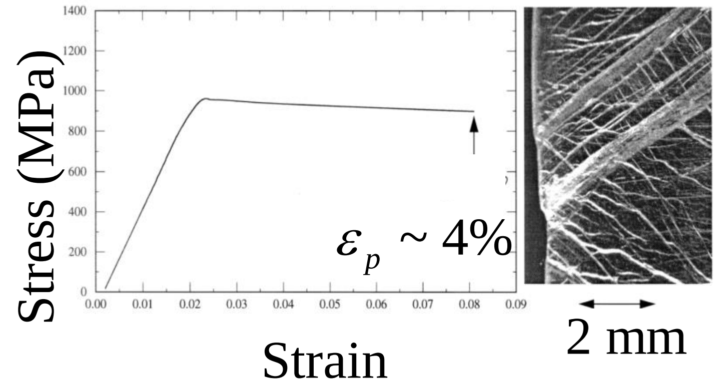
■ Multiple Shear Banding

- Compression of Bulk Nanostructured Fe – 10% Cu Polycrystals (UFGs)

d ~1370 nm, σ_y ~750 MPa, angle ~ 49^0



d ~540 nm, σ_y ~960 MPa, angle ~ 49^0



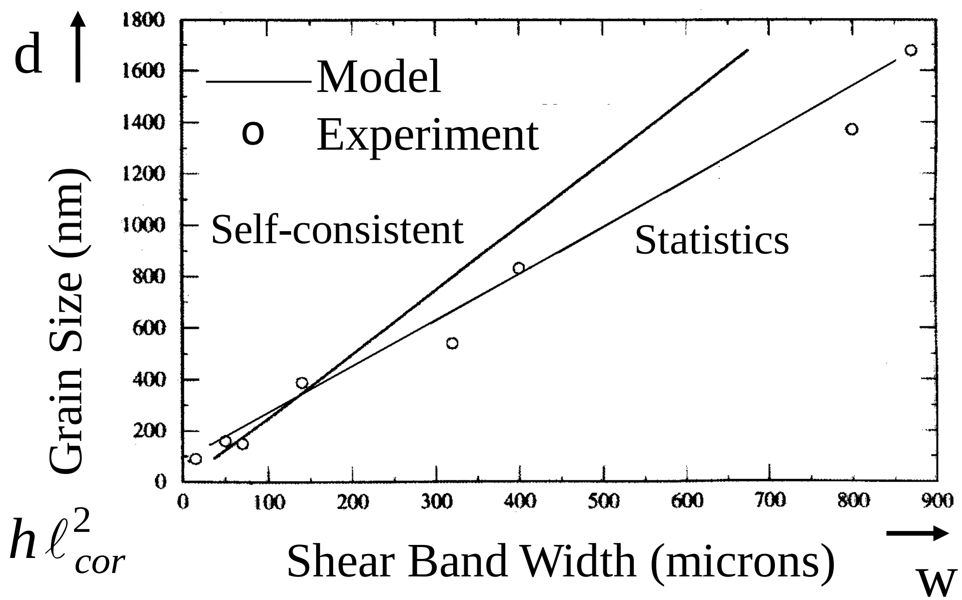
- Shear band width analysis

$$\tau = \kappa(\gamma) - c\nabla^2\gamma$$

$$w \sim \sqrt{c}\,; \qquad c \sim d^2\,(\beta + h)$$

$$\beta = \alpha G \frac{7-5\nu}{15(1-\nu)}$$

$$c = -h\left(\left.\frac{\partial^2 \Lambda(r)}{\partial r^2}\right|_{r=0}\right)^{-1}, \quad w \sim \sqrt{c},\; c \sim h\,\ell_{cor}^2$$

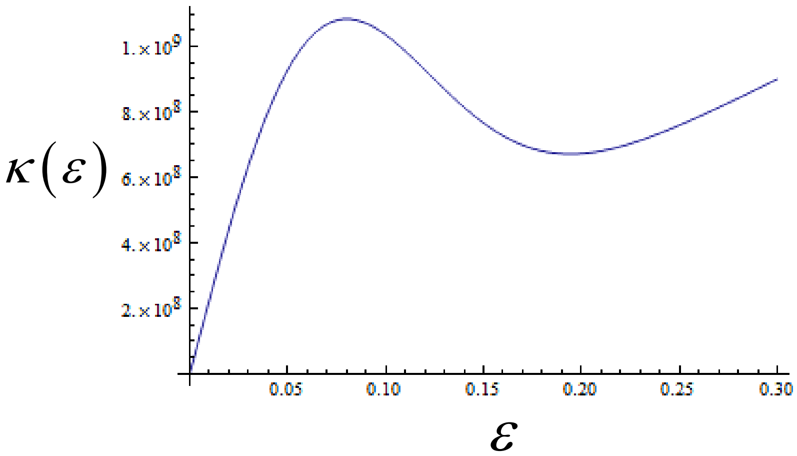


■ Combined Gradient – Stochastic Model

- ***2D Gradient Deterministic Model***

$$\sigma_0 = \kappa(\varepsilon) - \left[c_1 \frac{\partial^2 \varepsilon}{\partial x^2} + c_2 \frac{\partial^2 \varepsilon}{\partial y^2} \right] \; ;$$

$$\kappa(\varepsilon) = h\varepsilon + E\,\varepsilon\, exp\left[-\varepsilon^2 / \alpha \right]$$



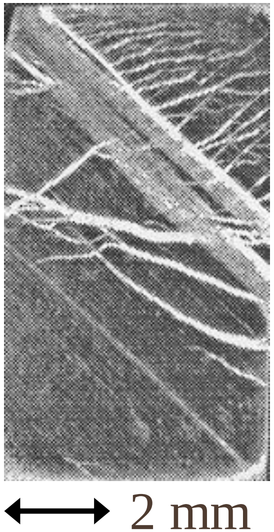
- ***Stochasticity in Yield Stress***

$$\kappa(\varepsilon) = h\varepsilon + \delta \left[E\,\varepsilon\, exp\left(-\frac{\varepsilon^2}{\alpha} \right) \right]; \quad \delta: \text{ Weibull random variable}$$

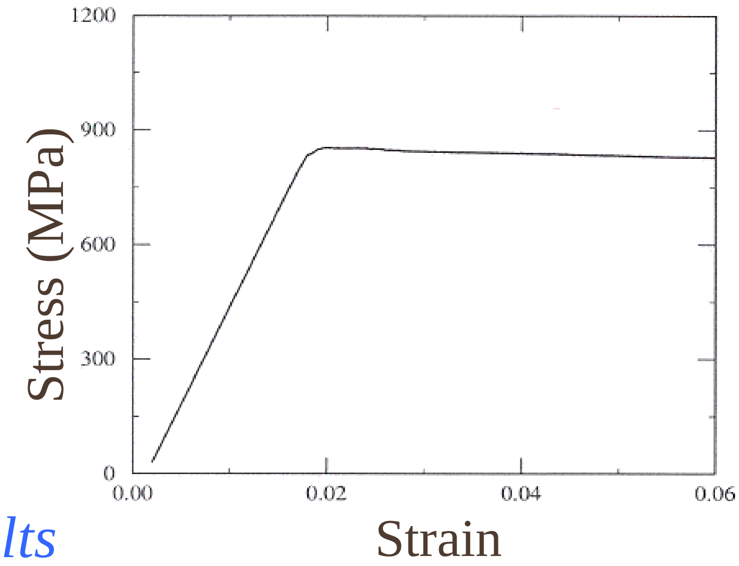
$$\text{PDF}(\delta) = \frac{k}{\lambda}\left(\frac{\delta}{\lambda}\right)^{\kappa-1} e^{-(\delta/\lambda)^k}; \qquad \bar{\delta} = \lambda\Gamma\left[1+(1/k)\right], \quad \left\langle \delta^2 \right\rangle = \lambda^2\Gamma\left[1+(2/k)\right] - \bar{\delta}^2$$

k / λ: shape/scale parameter of the Weibull distribution

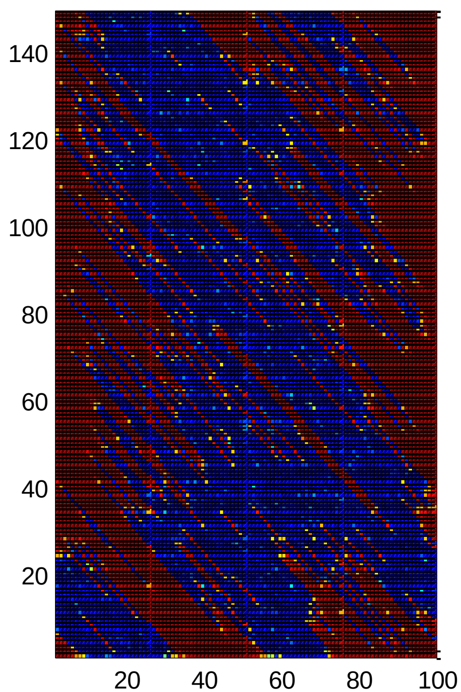
- *Compression Tests (Milligan, Hackney & Aifantis, 2001)*

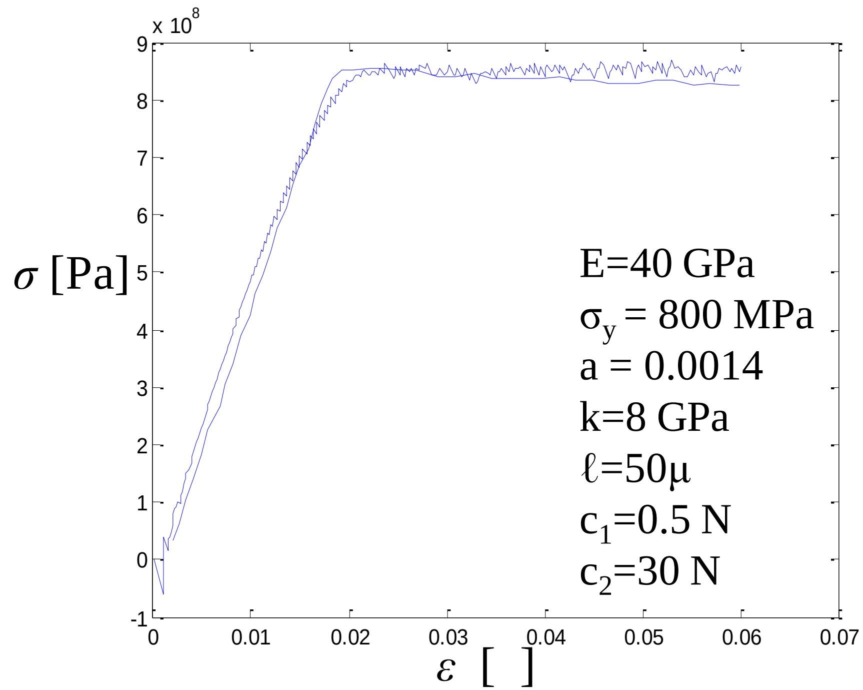


d ~0.5 μm
σ_y ~880 MPa

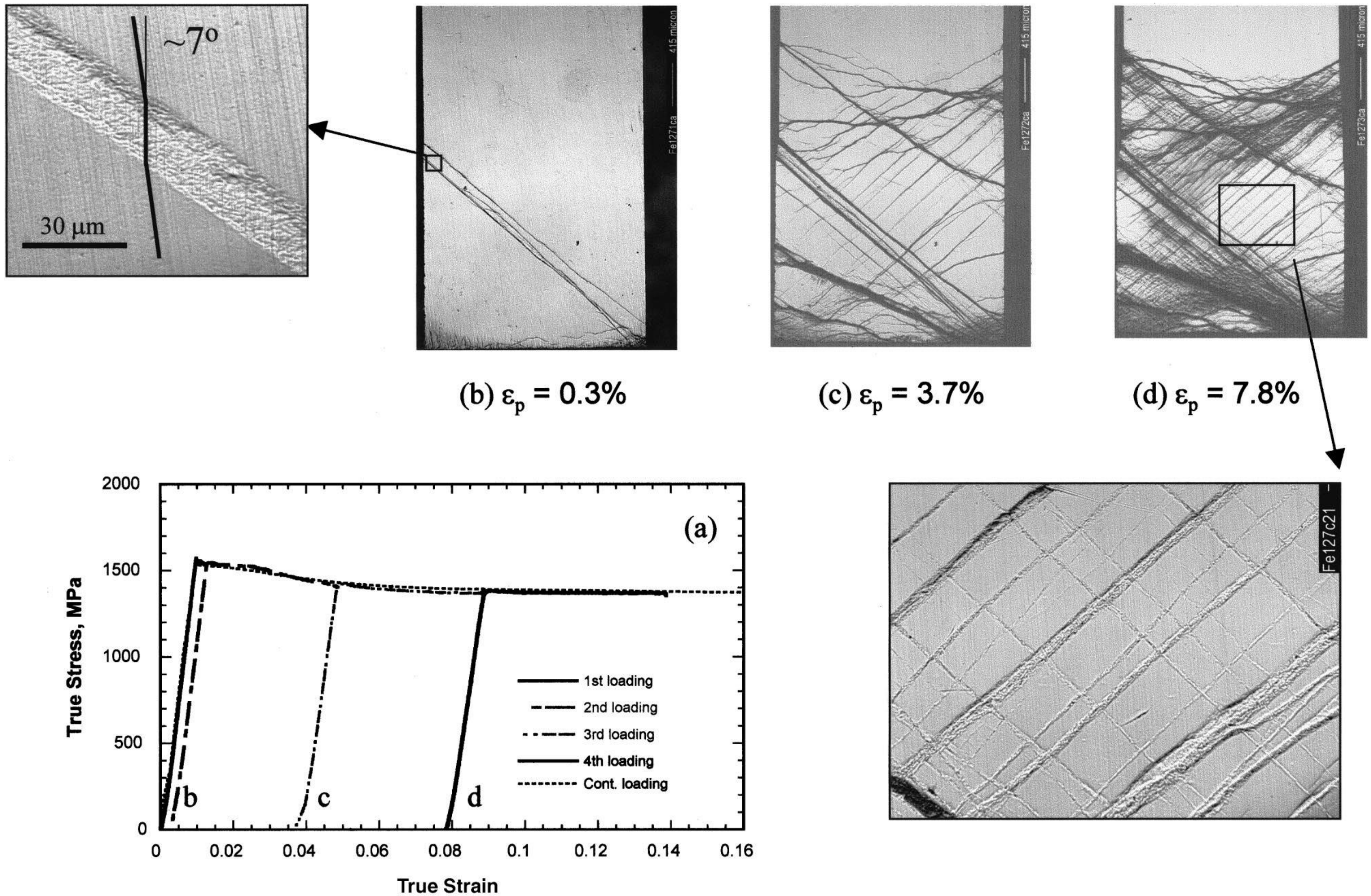


- *Cellular Automata Simulation Results*





- *More on Nano Shear Bands: n-Fe (Ma et al)*

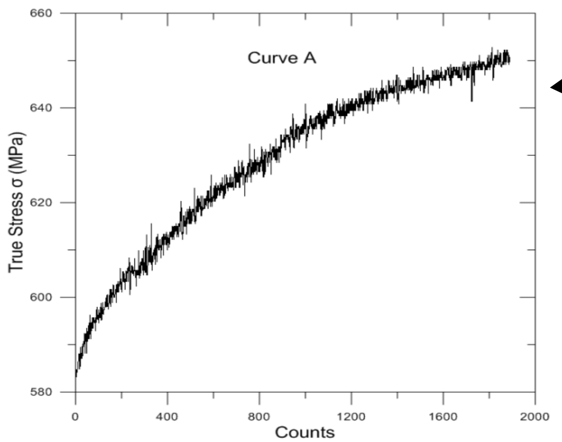


Stress-strain behavior and development of shear bands. Compression test of a Fe sample with an average grain size of 268 nm with loading, unloading, and reloading at various strain levels (~0.3%, 3.7%, and 7.8%).

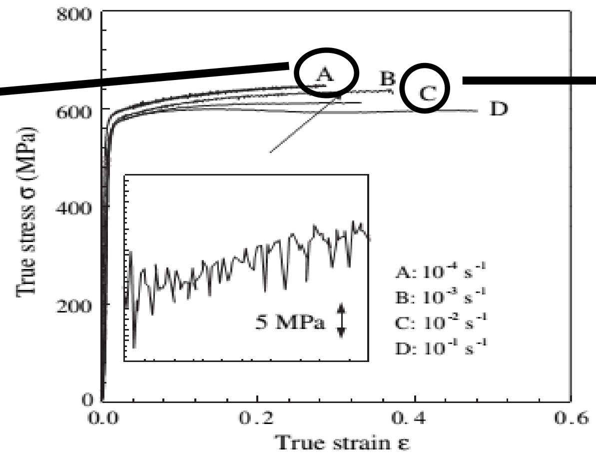
Statistical Aspects of UFGs

■ Serrated Plastic Flow & Multiple Shear Banding

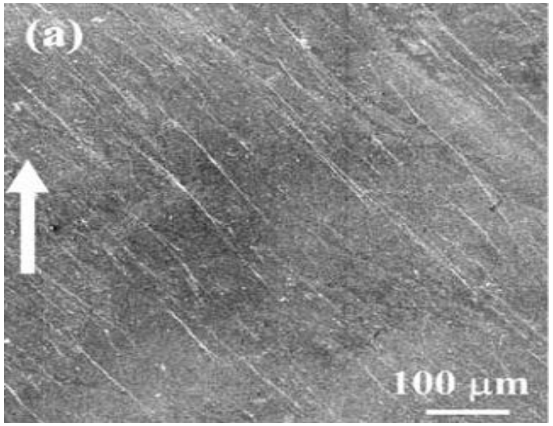
(Fan *et al*. Scripta/Acta Materialia 2005/2006)



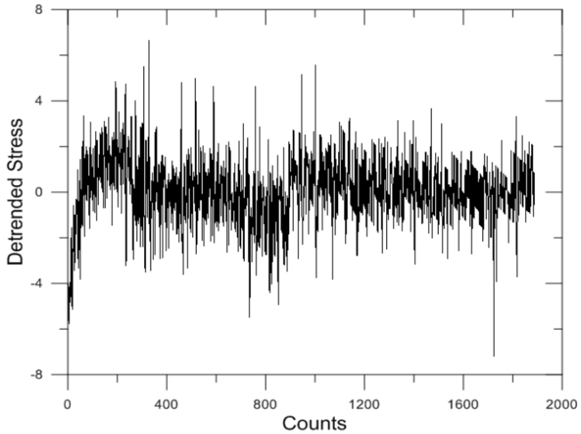
Low $\dot{\varepsilon}$ (10^{-4} s^{-1}) – Serrations



σ-*ε* curves (compression)



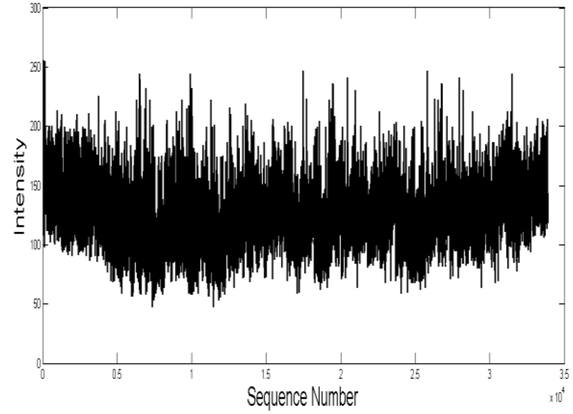
High $\dot{\varepsilon}$ (10^{-2} s^{-1})
Shear Bands (SEM)



Stress Drops time series

[Remove hardening effect (slope)]

Bimodal Grain Size Distribution
UFG matrix: 197 nm
Coarse grains : 3.1 μm (10 %)



Intensity series for Shear Band Distribution

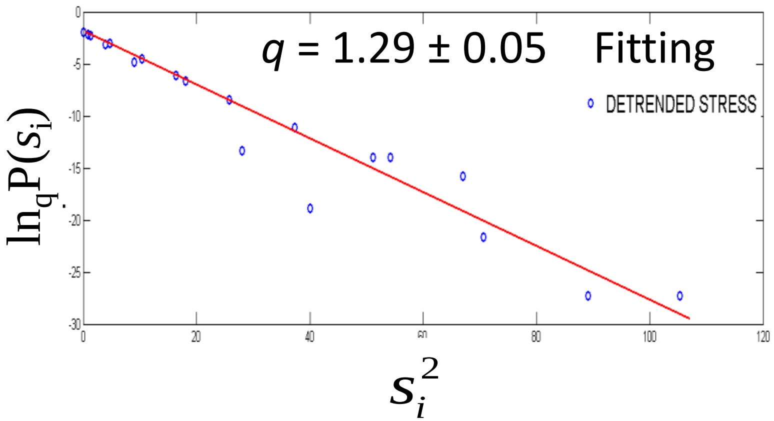
[2D → 1D: Space Filling Curve Method (Morton, 1966)]

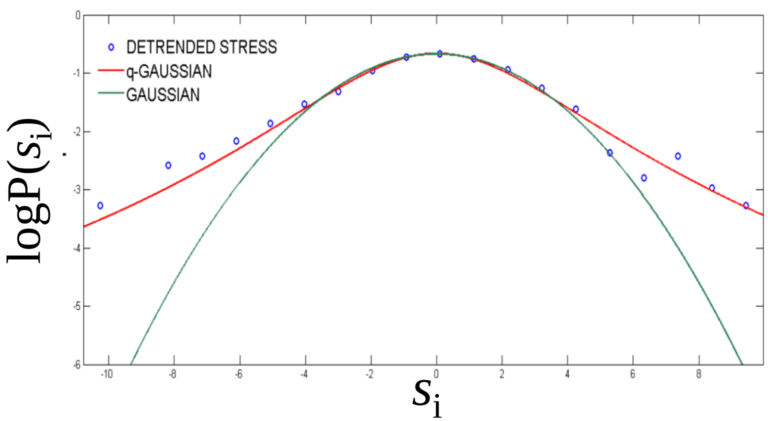
■ Serrations

• *Tsallis q- Gaussian:* $P(s) = p_0[1+(q-1)\beta_q(s)^2]^{1/(1-q)}$

• *Fitting:* $\ln_q(P(s_i))$ vs s_i^2

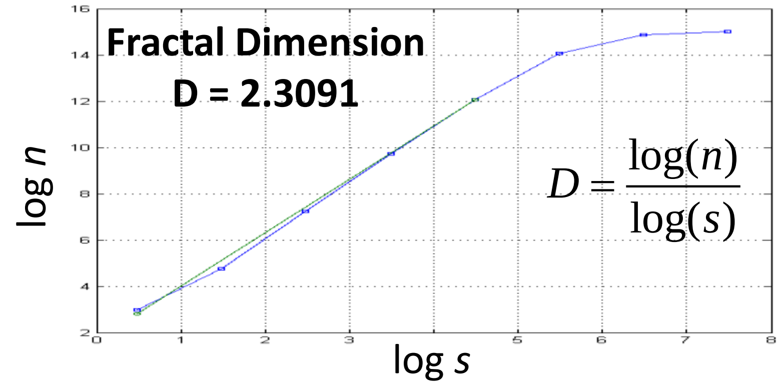
• *Power Law Tail (q>1):* $P(|s|) \sim |s|^{-2/(q-1)}$

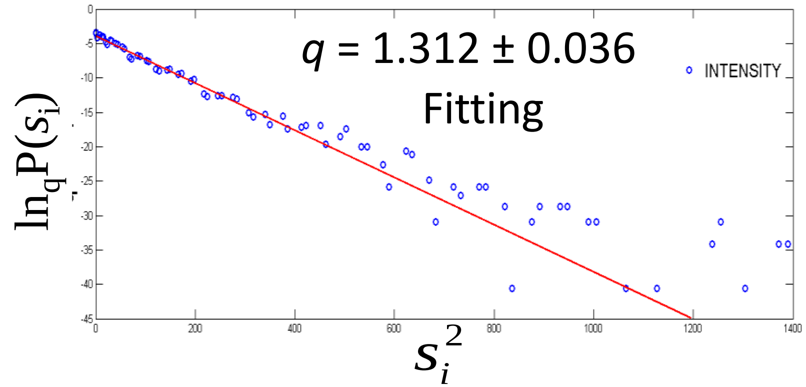


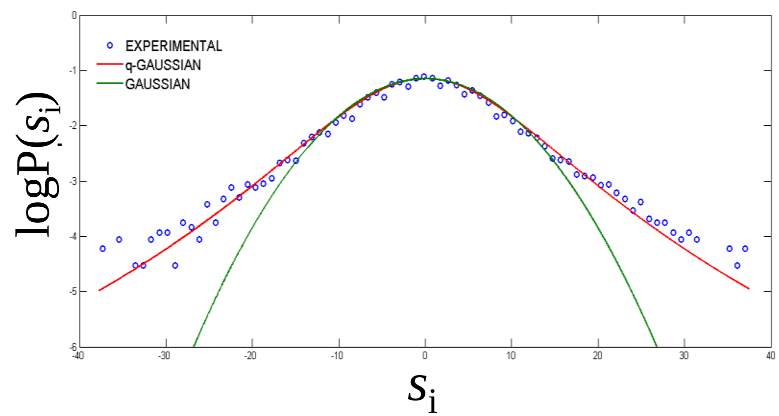


$q > 1 \longrightarrow$
- Non-Gaussian Statistics
- Tsallis Nonextensive Statistics,
- Temporal Long range correlations

■ Shear Band Fractality





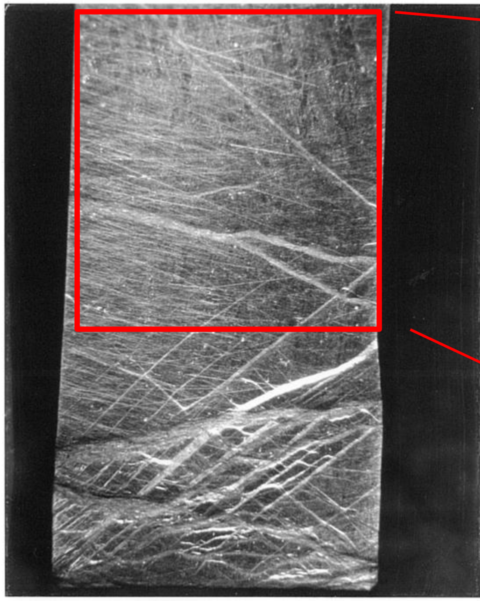


$D > 2 \longrightarrow$ Fractal Geometry of Shear Band network

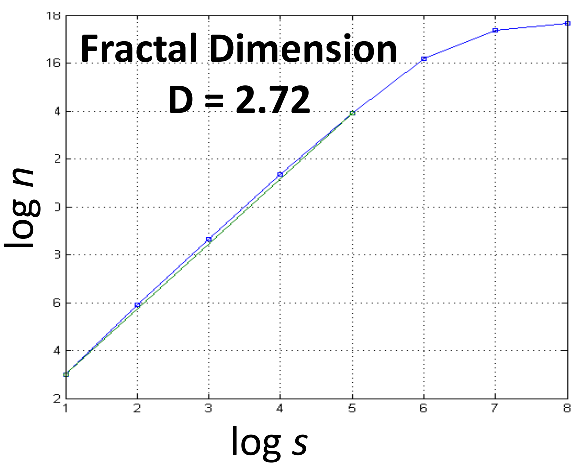
$q > 1 \longrightarrow$
- Non-Gaussian Pixels Distributions
- Spatial Long range correlations

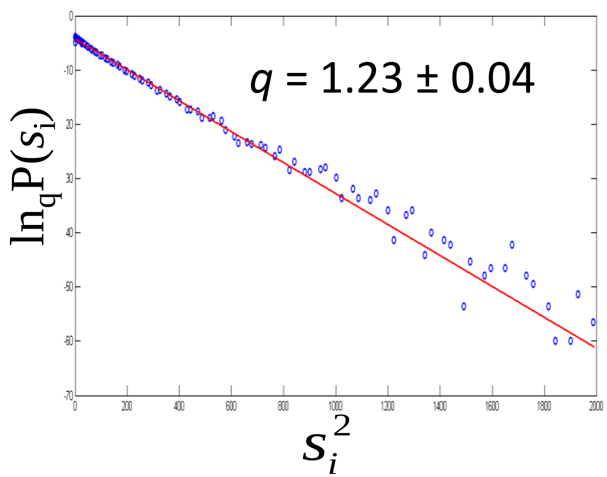
■ Shear Band Fractality in Fe – 10% Cu UFG Alloy

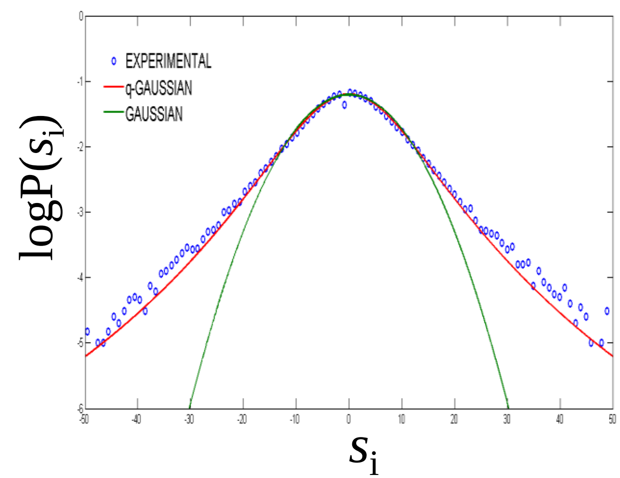
(Carsley *et al*. Metall. Mater. Trans 1998)



Shear Bands







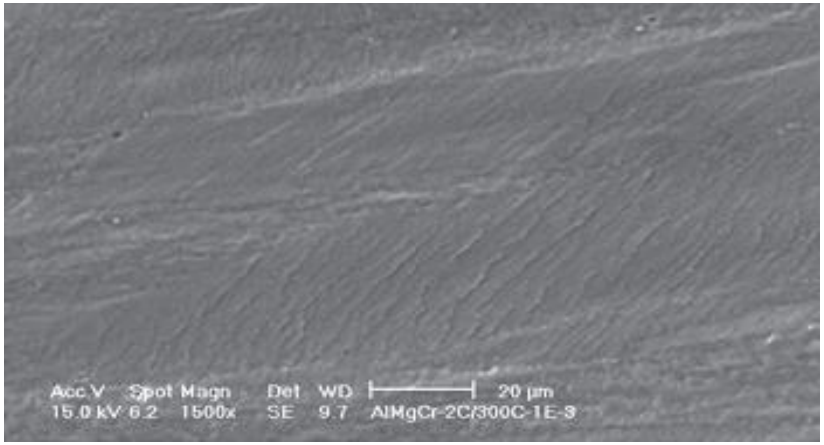
$D > 2 \longrightarrow$ Hierarchical Fractal Shear Band network

$q > 1 \longrightarrow$ { Non-Gaussian Pixels Distributions; Spatial Long range correlations }

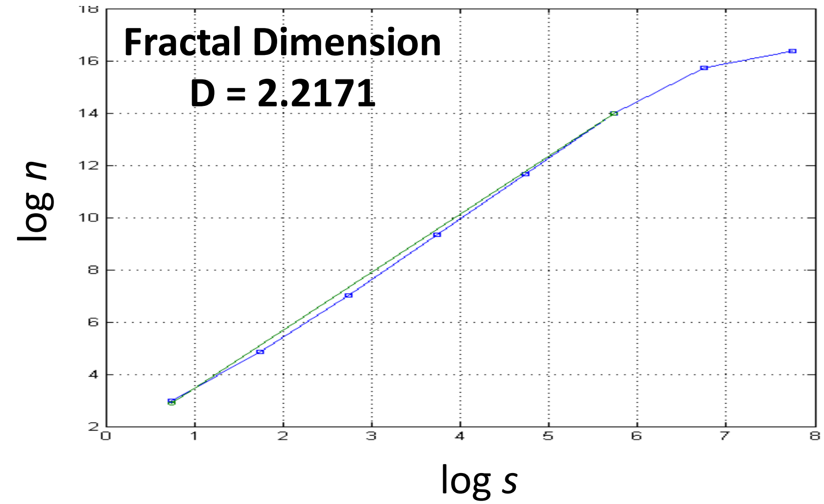
$D = 2 \longrightarrow$ No Fractality; $D = 3 \longrightarrow$ Extreme Fractality

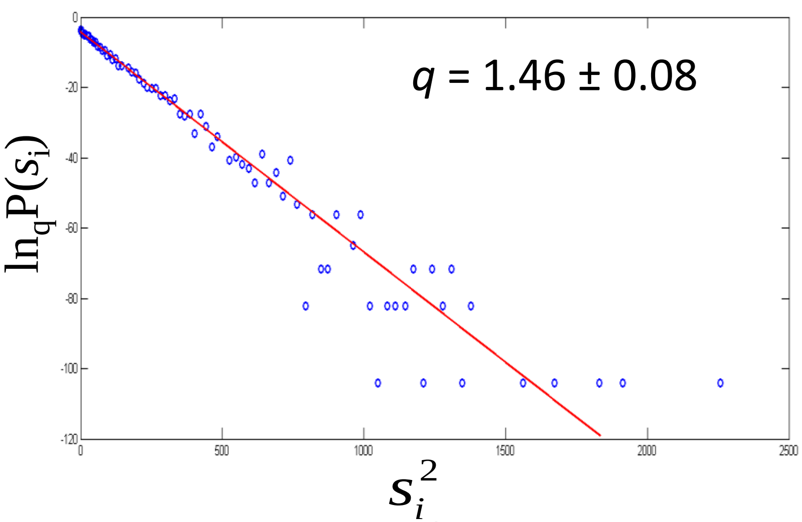
$q = 1 \longrightarrow$ { Gaussian Pixels Distributions; Spatial short range correlations }

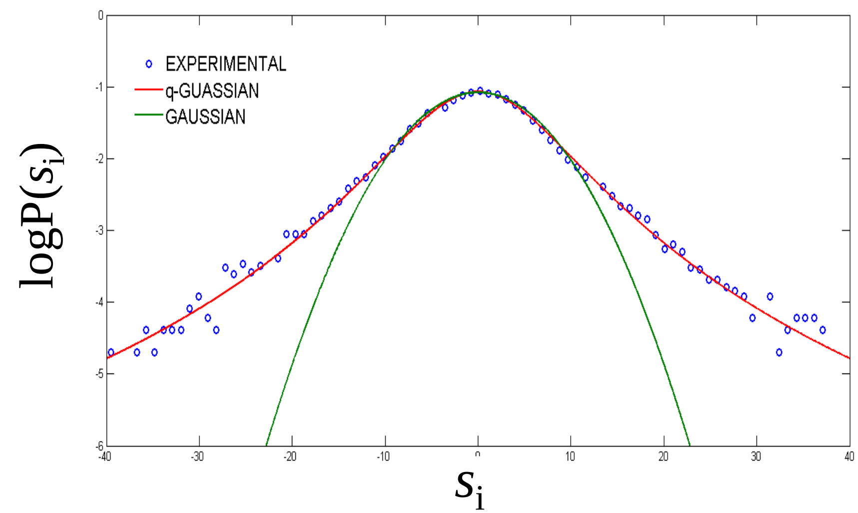
■ Shear Band Fractality in Al – 5%Mg - 1.2% Cr ECAP Alloy



Shear Bands
(Eddahbi *et al*. J. Matchar. 2012)



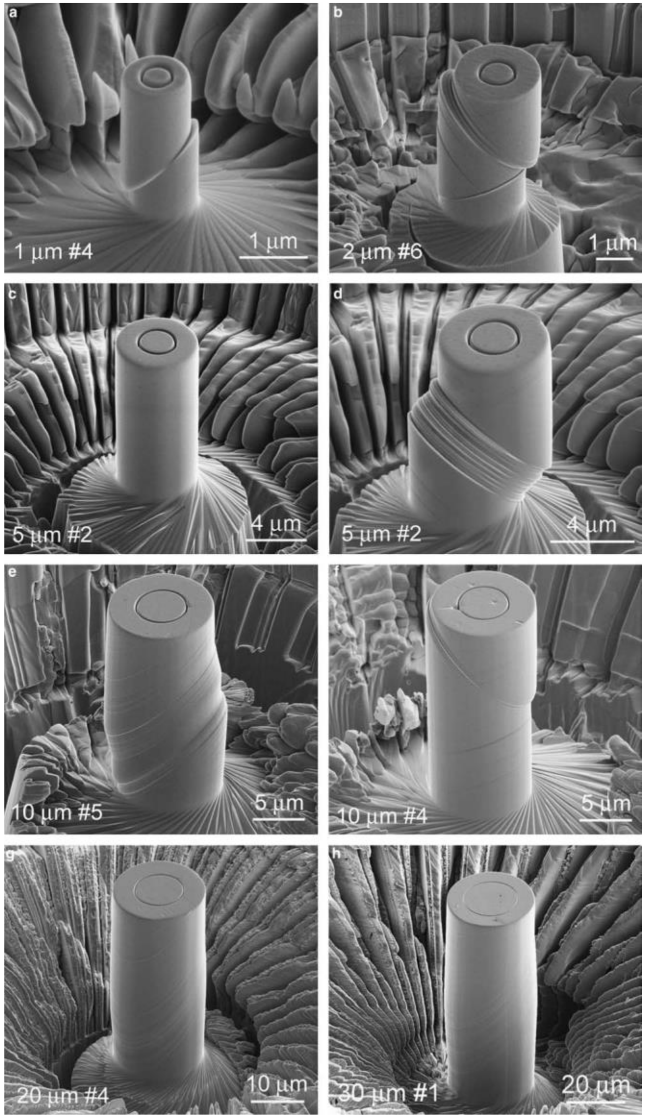


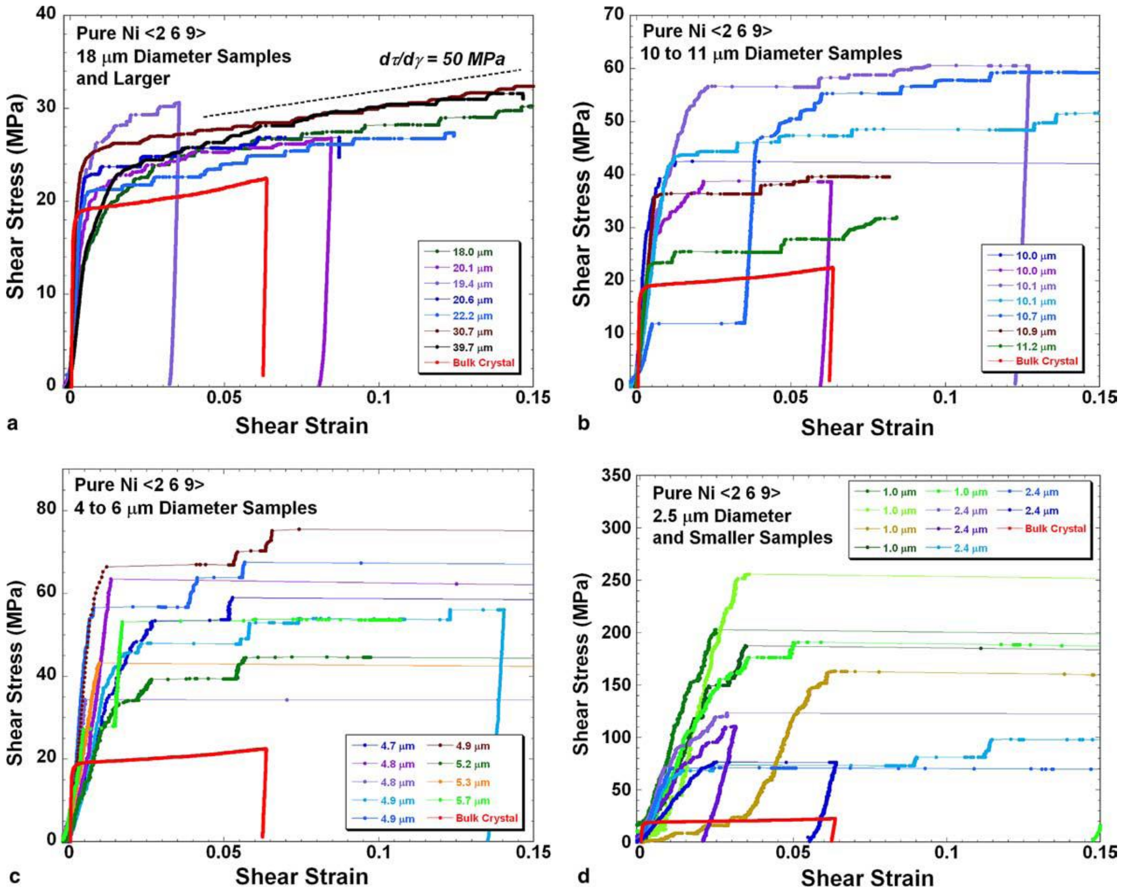


$D > 2$ ⟶ Hierarchical Fractal Shear Band network

$q > 1$ ⟶ { Non-Gaussian Pixels Distributions
Spatial Long range correlations

■ Stochasticity & Serrations in Compressed Micropillars





Dimiduk et al, 2005

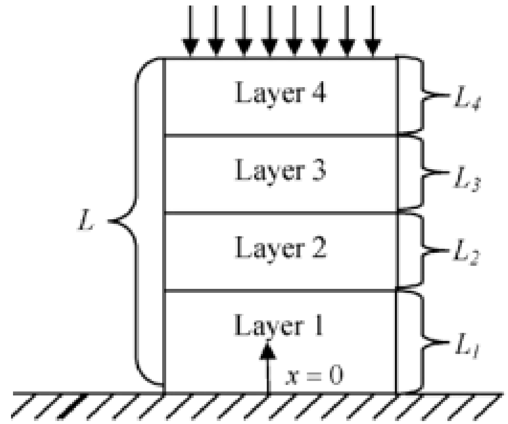
- ***Serrated Plastic Flow in Micropillars***

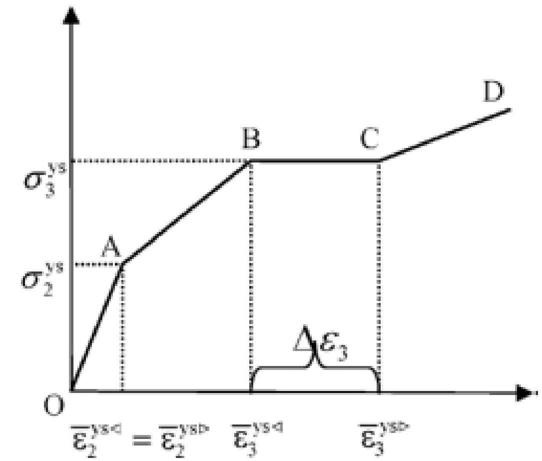
- *Governing Deterministic Equations*

$$\sigma_i = E_i(\varepsilon_i - \varepsilon_i^P),$$

$$\beta_i \varepsilon^p - \beta_i \ell_i^2 \frac{d^2\varepsilon_i^p}{dx^2} = \left(\sigma_0 - Y_i\right)$$

(Zhang and K.E. Aifantis, 2011)





- *Serrations*

Strain bursts ($\Delta\varepsilon$) are obtained due to the occurrence of discontinuity of the hyperstress $\tau = \beta\ell^2(d^2\varepsilon^p / dx^2)$ between "elastic/no-yielding" and "plastic/yielding" layers

- *Introducing Stochasticity*

$$Y_i = Y^0 + Y_i^{weib} = (1+\delta)\,Y^0$$

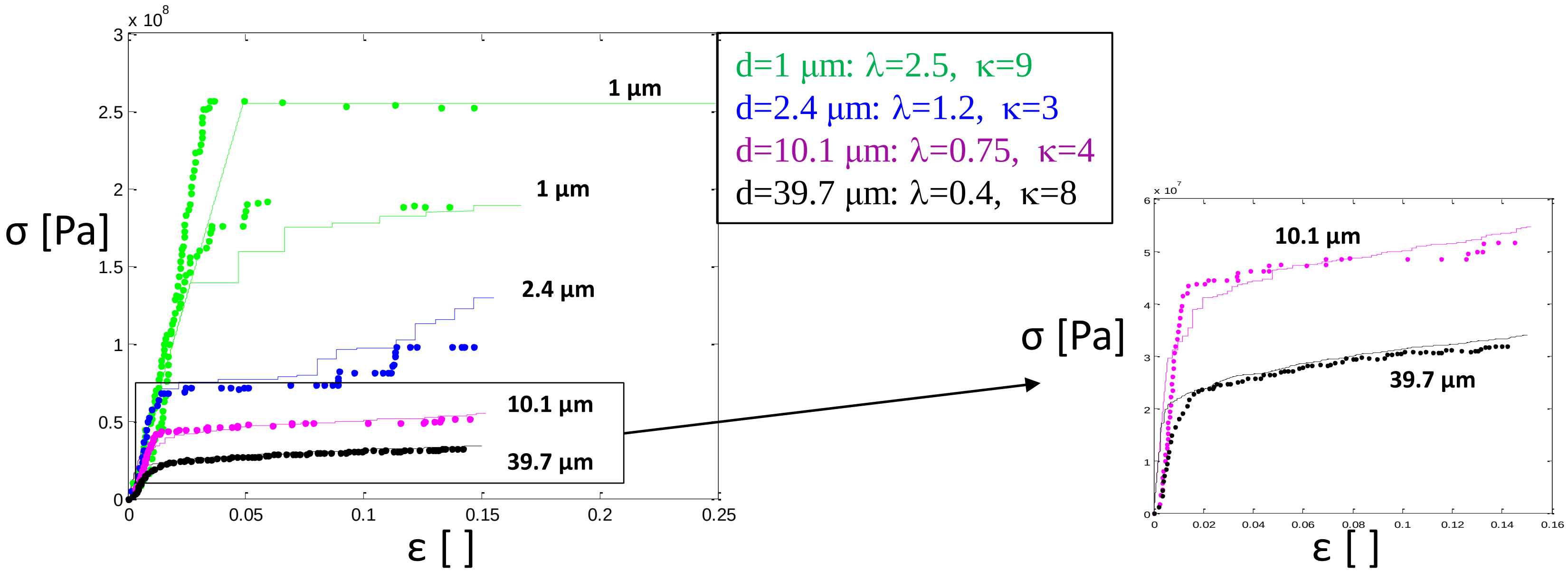
$$PDF(\delta) = \frac{\kappa}{\lambda}\left(\frac{\delta}{\lambda}\right)^{\kappa-1} e^{-(\delta/\lambda)^\kappa}; \quad \bar{\delta} = \lambda\Gamma\left[1+(1/\kappa)\right], \quad \left\langle \delta^2 \right\rangle = \lambda^2\Gamma\left[1+(2/\kappa)\right] - \bar{\delta}^2$$

- ***Cellular Automata Simulations***

  - Lattice of 6d×1 cells of size 0.5 μm× d μm (3:1 height to diameter ratio)
  - Force controlled simulation
  - Weibull distributed cell yield stress

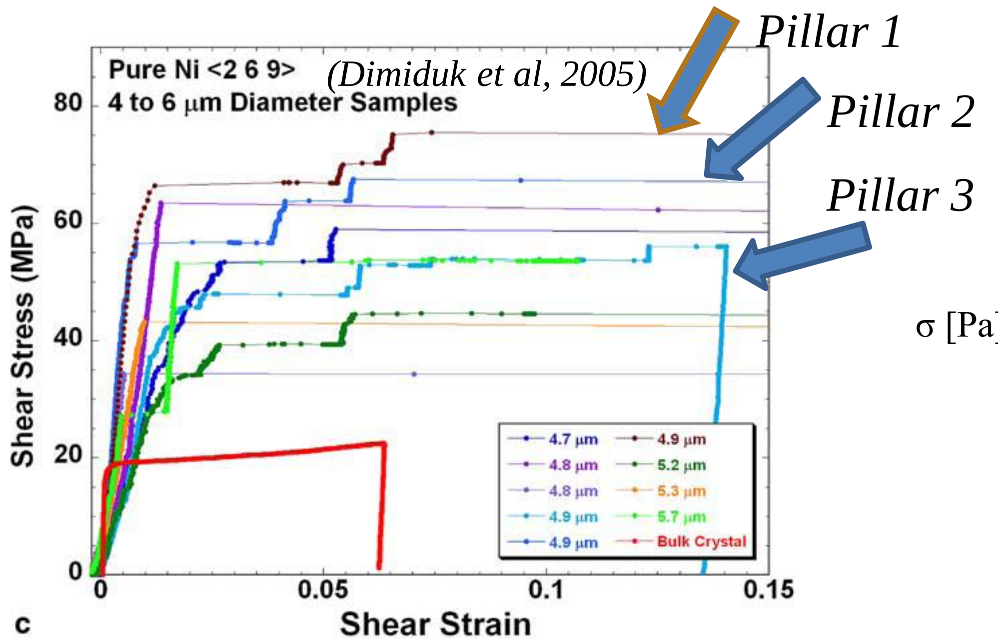
- ***Intermittent Size-dependent Micropillar Plasticity***

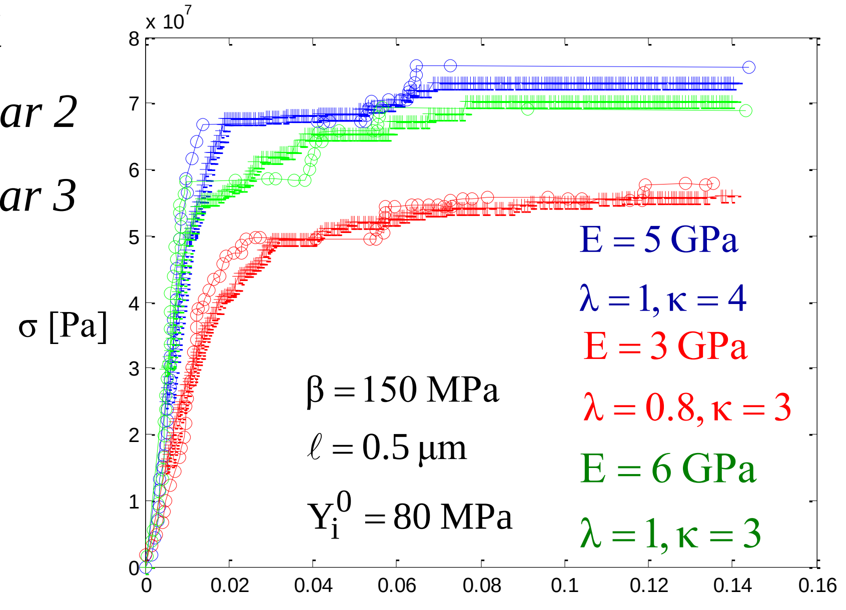
$$E = 5\,\text{GPa}; \quad \beta = 150\,\text{MPa}; \quad \ell = 0.5\,\mu\text{m}; \quad Y^0 = 80\,\text{MPa}$$

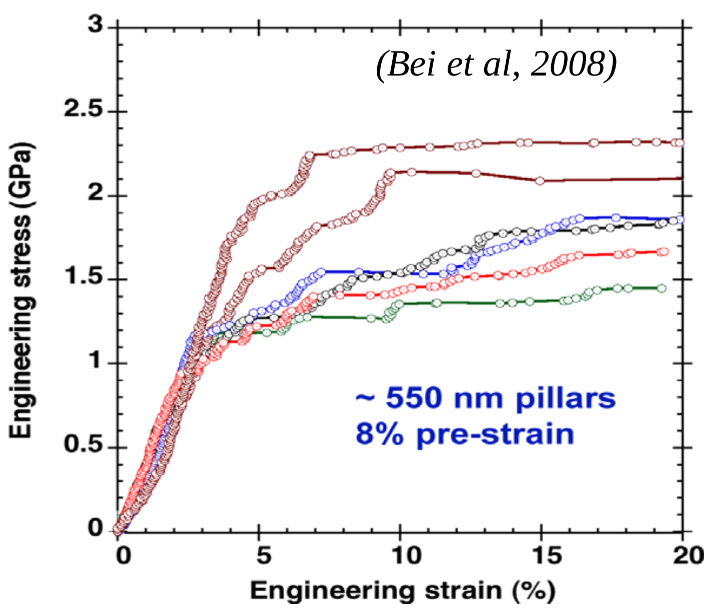


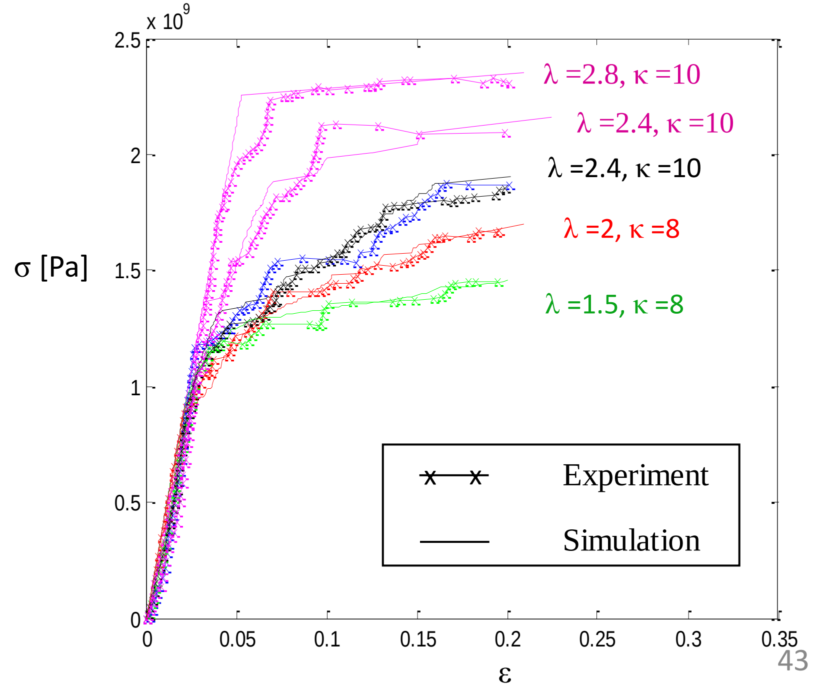
K.E. Aifantis & Konstantinidis, in progress

- *Random Response of Same Diameter Micropillars*









■ Stochasticity Information from Entropy

- ***Boltzmann-Gibbs Entropy***

$$S = -k_B \sum_i P(I) \ln P(I) ; \quad k_B = 1.38065 \cdot 10^{-23} \ J/K$$

- ***Tsallis Entropy***

$$S_q(P) = \frac{1}{q-1}\left[1 - \sum_I \left(P(I)\right)^q\right] \quad ; \quad q \neq 1 \quad : \quad \text{entropic index}$$

- Maximum entropy principle leads to q-exponential distribution

$$P\left(I\right) = \left[1 + (q-1)I\right]^{1/(1-q)}$$

- Generalization

$$\therefore \quad p\left(I\right) = A\left[1 + B(q-1)I\right]^{1/(1-q)}$$

(instead of $p\left(I\right) \sim I^{\Lambda}$ as commonly done)

Note: Using the Tsallis entropy formulation the "events" with high probability but low intensity are ***not*** *ignored, as is the case with power-law formulations*

• *Extracting Information on Randomness / PDF*

Probability of bursts of size s

$$P(s) = A\left[1+(q-1)Bs\right]^{\frac{1}{1-q}}$$

Burst size relation to local yield stress

$$s = nL\varepsilon_y^{loc} = nL\frac{\sigma_y^{loc}}{E}; \quad P\left(\sigma_y^{loc}\right) \equiv P\left(\varepsilon_y^{loc}\right)$$

(L: cell size)

Probability of bursts from n "sites"

$$s^b = \varepsilon_y^b L = \left(\sigma_y^b / E\right) L$$

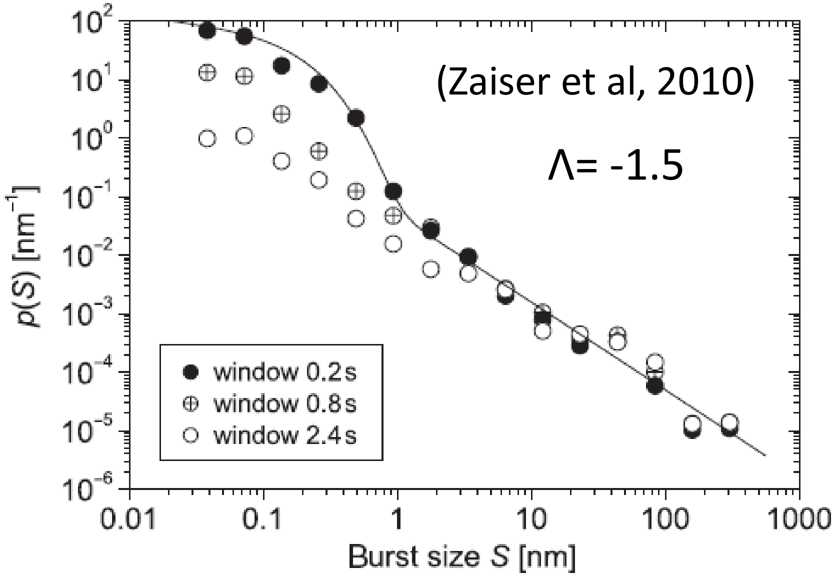
s_b : *smallest burst and yield*

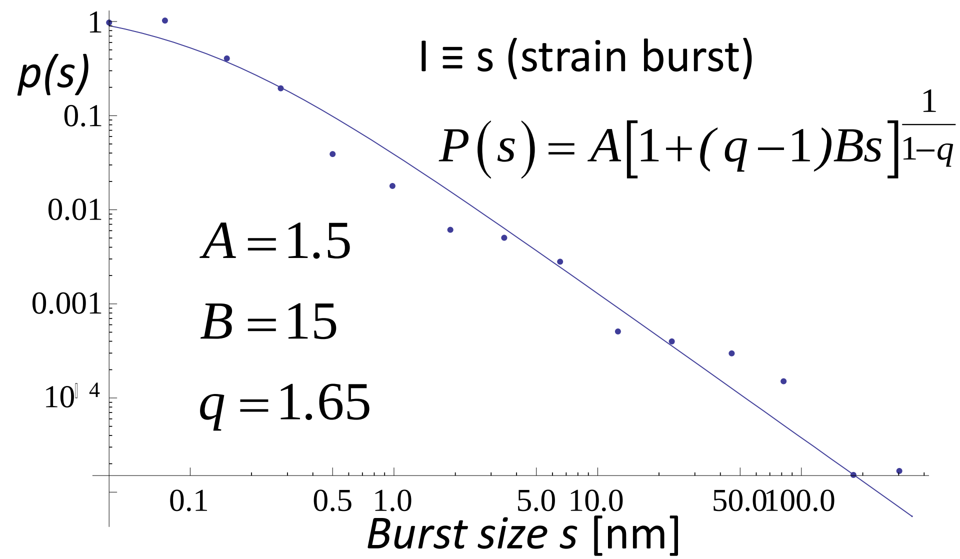
σ_y^b : *yield stress of a single "site"*

$$n = floor\left[\frac{s}{s_b}\right] = floor\left[\frac{\sigma_y^{loc}/E}{\sigma_y^b/E}\right] = floor\left[\frac{\sigma_y^{loc}}{\sigma_y^b}\right]$$

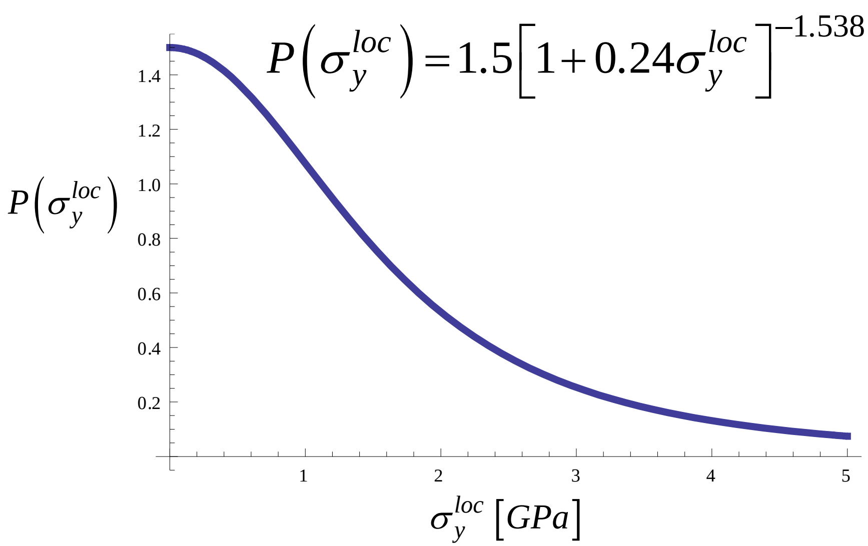
$$\therefore \quad P\left(\sigma_y^{loc}\right) = A\left[1+(q-1)Bs_b\left(\frac{\sigma_y^{loc}}{\sigma_y^b}\right)^2\right]^{1/(1-q)}$$

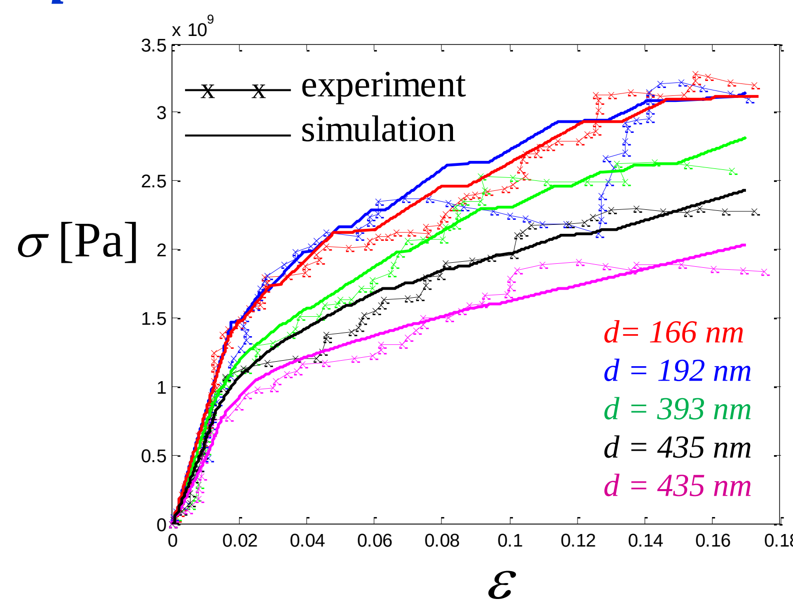
- ***Strain bursts in Mo micropillars under compression***





- ***CA simulations with input from q-statistics***





•Micropillar Compression CA Simulations

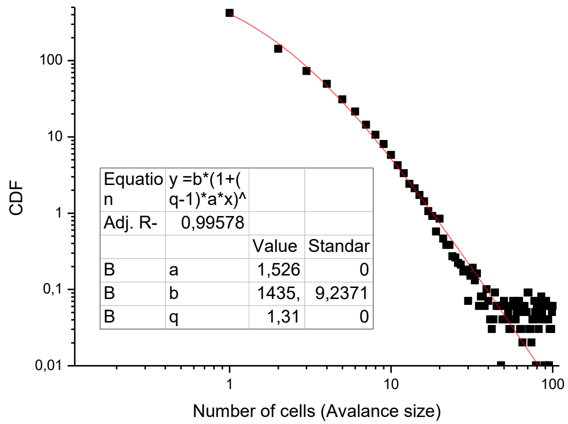
- *Constitutive relation*

$$\sigma_{EXT} - \beta\varepsilon^{p} + c\frac{d^{2}\varepsilon^{p}}{dx^{2}} = \sigma_{y}$$

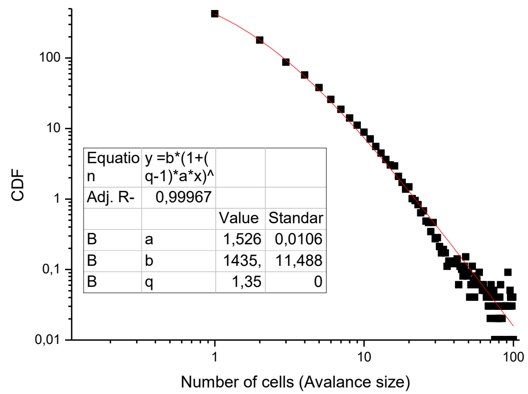
- *Avalanche probability distribution*

$$P(s) = A\left[1+(q-1)Bs\right]^{\frac{1}{1-q}}$$

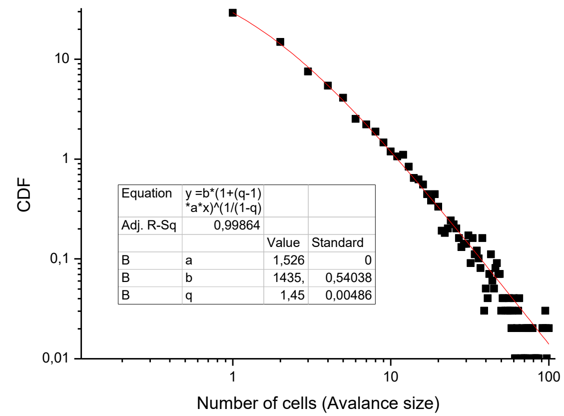
- *Avalanche size distributions for varying* $c = \beta\ell^{2}$



$c = 0.75mN \rightarrow q = 1.3$

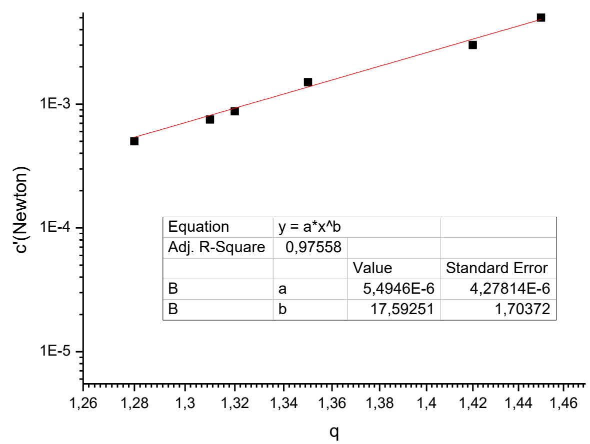


$c = 1.75mN \rightarrow q = 1.35$



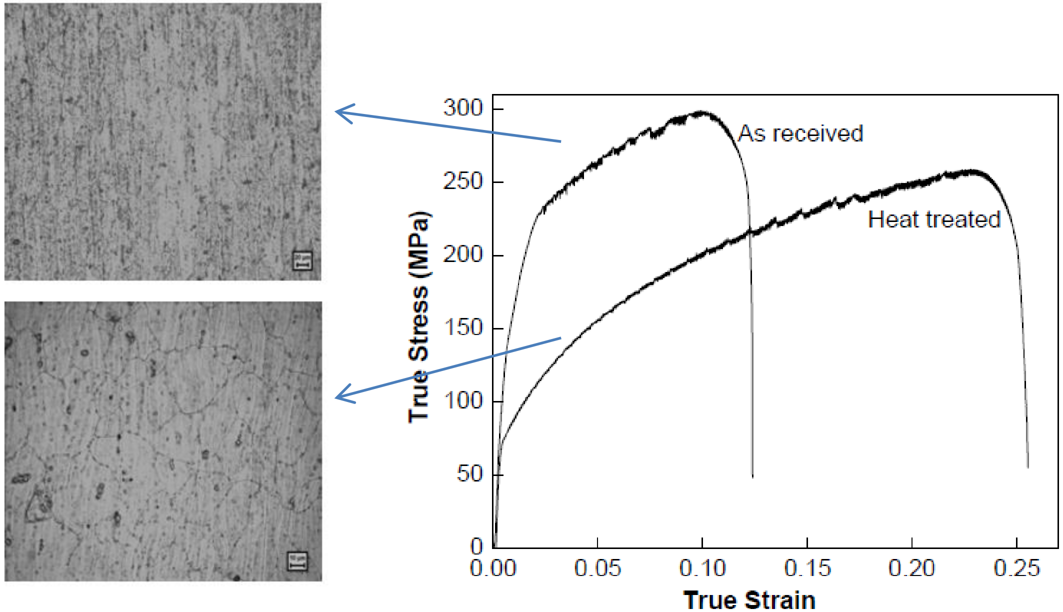
$c = 5mN \rightarrow q = 1.45$

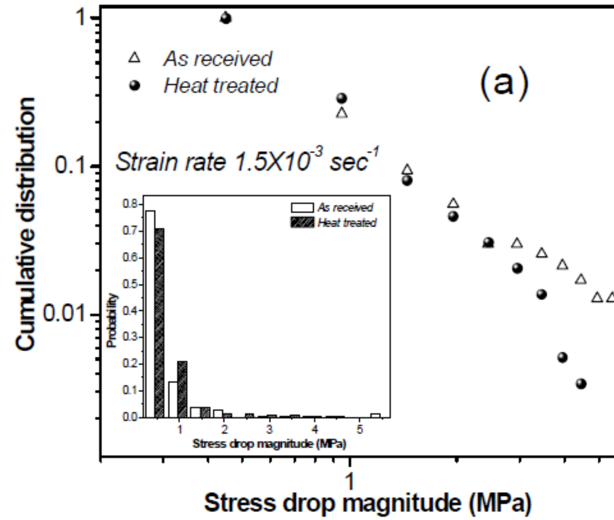
$\therefore \quad c = c_{0}q^{k}\ ; \quad c_{0} = 5.5\ \mu N, k = 17.6$



• PLC Effect in Al-2.5%Mg Alloy

- *Chatterjee et al, 2010*

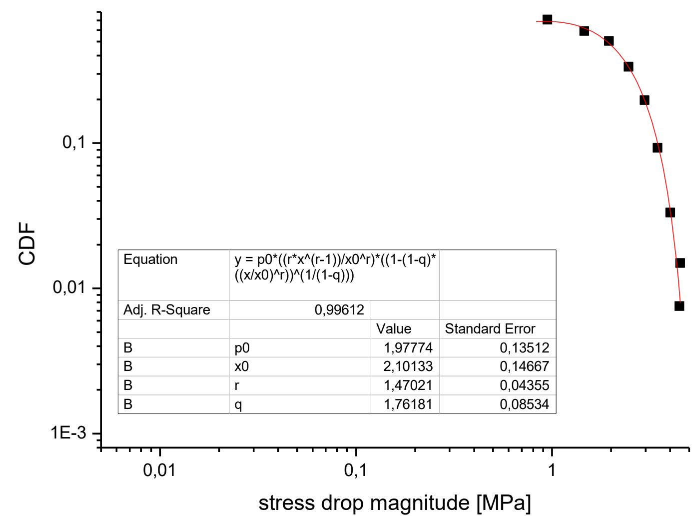




- *Tsallis q-Statistics*

$$P(s) = p_0 \frac{r x^{r-1}}{x_0^r} \left[1 + (q-1) \left(\frac{x}{x_0} \right)^r \right]^{\frac{1}{1-q}}$$

$$q = 1.76,\ p_0 = 1.97,\ x_0 = 2.1,\ r = 1.47$$



Equation	y = p0*((r*x^(r-1))/x0^r)*((1-(1-q)*((x/x0)^r))^(1/(1-q)))		
Adj. R-Square	0,99612		
		Value	Standard Error
B	p0	1,97774	0,13512
B	x0	2,10133	0,14667
B	r	1,47021	0,04355
B	q	1,76181	0,08534

III. NANODIFFUSION

[Gradient Diffusion at the Nanoscale]

■ Double Diffusivity / Diffusion in Nanopolycrystals

$$\frac{\partial \rho_\alpha}{\partial t} + \mathrm{div}\mathbf{j}_\alpha = \mathrm{c}_\alpha \qquad \mathrm{div}\mathbf{T}_\alpha = -\mathbf{f}_\alpha$$

$$\{\mathbf{T}_\alpha,\ \mathbf{f}_\alpha,\ \mathrm{c}_\alpha\} \longrightarrow \{\rho_\alpha,\ \mathbf{j}_\alpha,\ \ldots\};\ \ \alpha = 1,2$$

- ***Simplest Model***

$$\mathbf{T}_\alpha = -\pi_\alpha \rho_\alpha \mathbf{1} \quad ; \quad \mathbf{f}_\alpha = \alpha_\alpha \mathbf{j}_\alpha \quad ; \quad \mathrm{c}_\alpha = (-1)^\alpha [\kappa_1 \rho_1 - \kappa_2 \rho_2]$$

$$\frac{\partial \rho_1}{\partial t} = \mathrm{D}_1 \nabla^2 \rho_1 - (\kappa_1 \rho_1 - \kappa_2 \rho_2) \quad , \quad \frac{\partial \rho_2}{\partial t} = \mathrm{D}_2 \nabla^2 \rho_2 + (\kappa_1 \rho_1 - \kappa_2 \rho_2)$$

- ***Solution***

$$\rho_1 = e^{-\kappa_1 t} \mathrm{h}_1(\mathrm{x}, \mathrm{D}_1 \mathrm{t}) + \frac{\sqrt{\kappa_2}}{\mathrm{D}_1 - \mathrm{D}_2} e^{\lambda t} \int_{D_2 t}^{D_1 t} e^{-\mu \xi} [\mathrm{A}_1 \mathrm{h}_1(x,\xi) + \mathrm{A}_2 \mathrm{h}_2(x,\xi)] \mathrm{d}\xi$$

$$\dot{\mathrm{h}}_\alpha = \nabla^2 \mathrm{h}_\alpha \quad ; \quad \mathrm{A}_1 = \sqrt{\kappa_1} \left(\frac{\xi - \mathrm{D}_2 \mathrm{t}}{\mathrm{D}_1 \mathrm{t} - \xi} \right)^{1/2} \mathrm{I}_1(\eta) \quad ; \quad \mathrm{A}_2 = \sqrt{\kappa_2}\, \mathrm{I}_2(\eta)$$

$$\lambda = \frac{\kappa_1 D_2 - \kappa_2 D_1}{D_1 - D_2} \quad , \quad \mu = \frac{\kappa_1 - \kappa_2}{D_1 - D_2} \quad , \quad \eta = \frac{2\sqrt{\kappa_1 \kappa_2}}{D_1 - D_2} \left[(D_1 t - \xi)(\xi - D_2 t) \right]^{1/2}$$

- ***Uncoupling / Higher-order Diffusion Equation***

$$\frac{\partial \rho}{\partial t} + \tau \frac{\partial^2 \rho}{\partial t^2} = D\nabla^2 \rho + \bar{D}\frac{\partial}{\partial t}\nabla^2 \rho - E\nabla^4 \rho$$

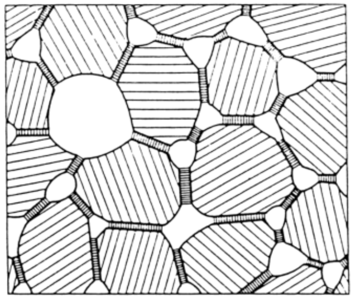
$$\tau = (\kappa_1 + \kappa_2)^{-1} \;,\; D = \tau(\kappa_1 D_2 + \kappa_2 D_1) \;,\; \bar{D} = \tau(D_1 + D_2) \;,\; E = \tau D_1 D_2$$

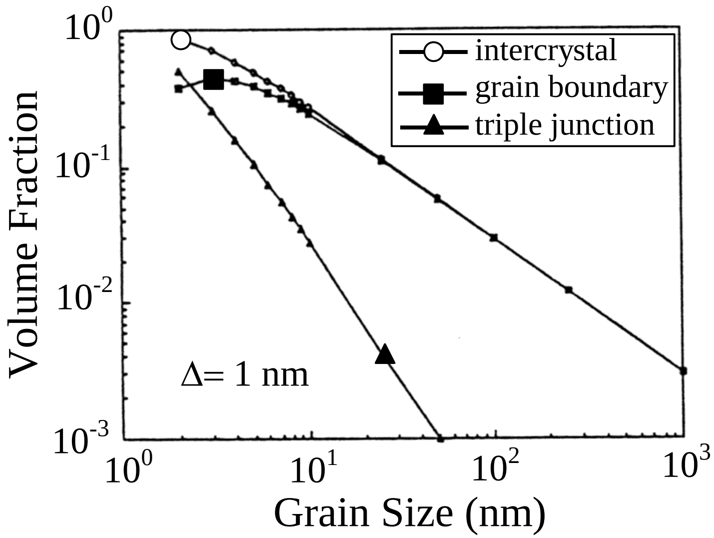
$$t \to \infty \Rightarrow \frac{\partial \rho}{\partial t} = D\nabla^2 \rho \quad ; \quad D = D_{eff} = \frac{\kappa_2}{\kappa_1 + \kappa_2} D_1 + \frac{\kappa_1}{\kappa_1 + \kappa_2} D_2$$

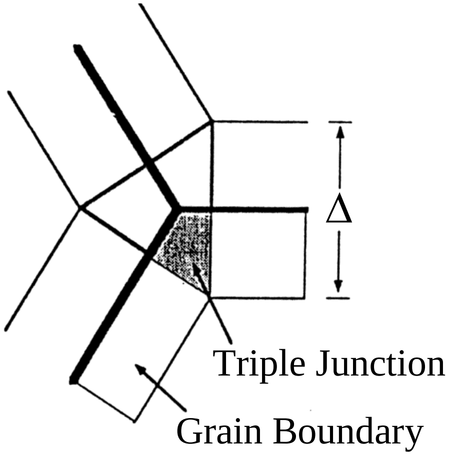
$$= f\, D_1 + (1 - f) D_2$$

- ***Observations / Experiments***

- *Grain boundary space*

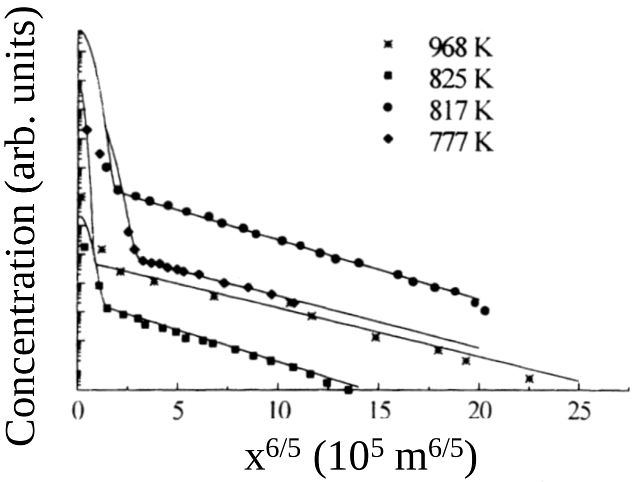




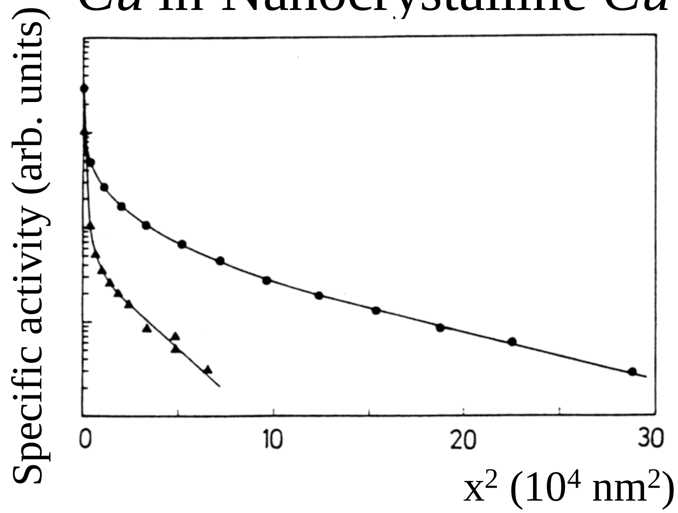


• *Diffusion Penetration Profiles*

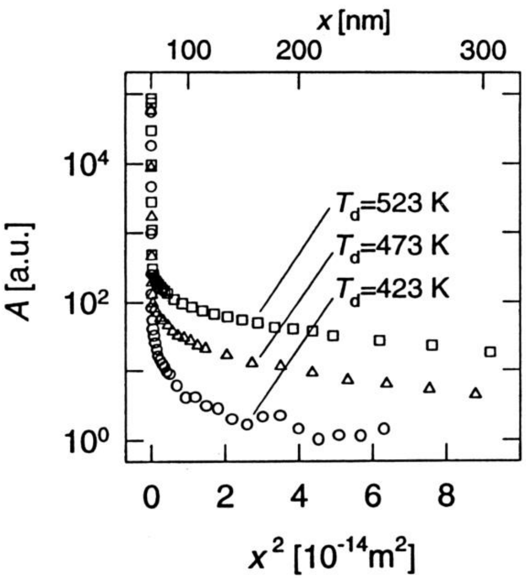
^{64}Cu in Polycrystalline Cu



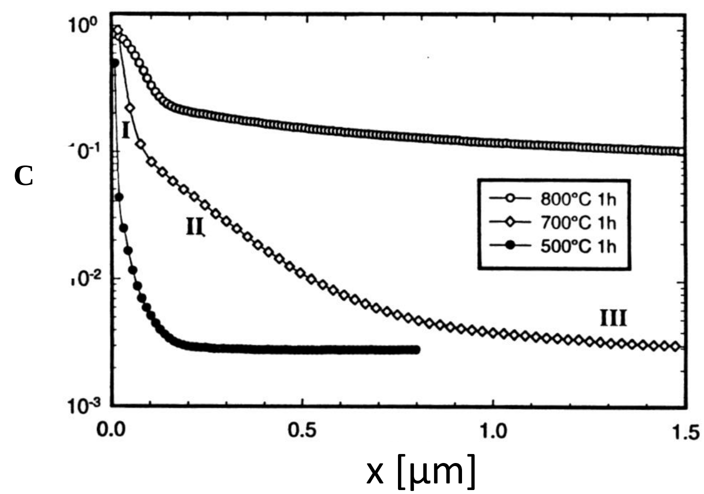
^{67}Cu in Nanocrystalline Cu



^{59}Fe in compacted $n-Pd$

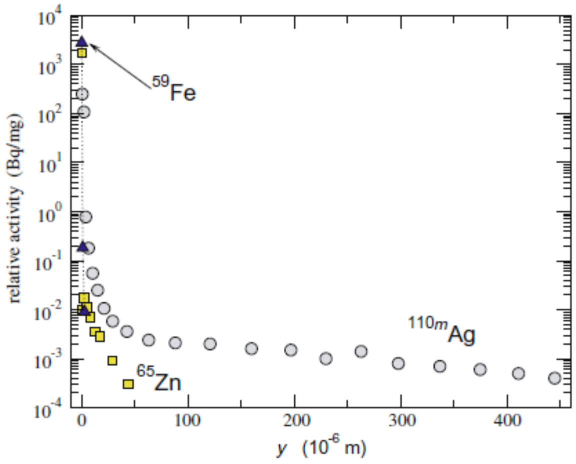


^{18}O in nano ZrO_2

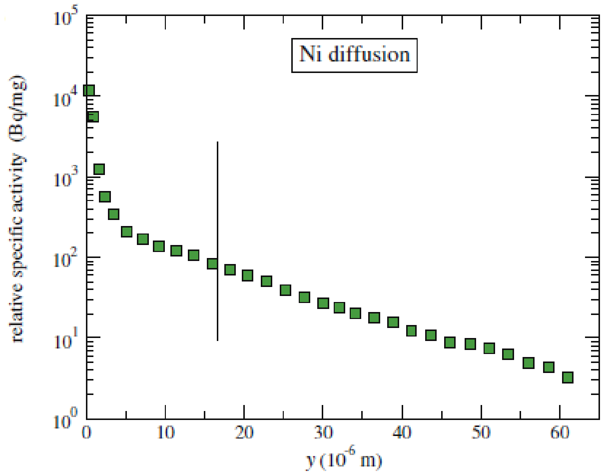


• More Recent Data: Divinski et al 2009, 2010

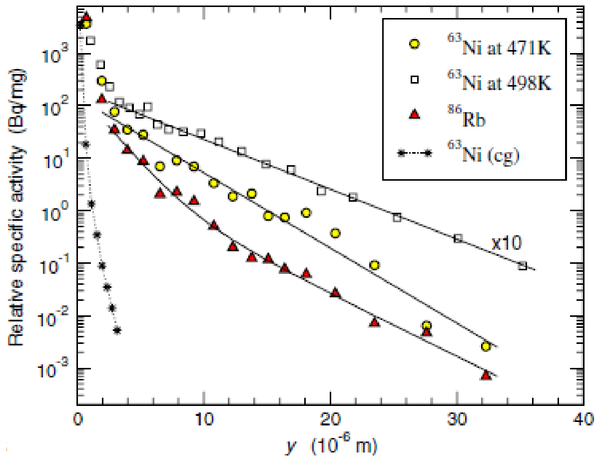
^{110m}Ag, ^{65}Zn, ^{59}Fe in UFG Cu-1wt%Pb



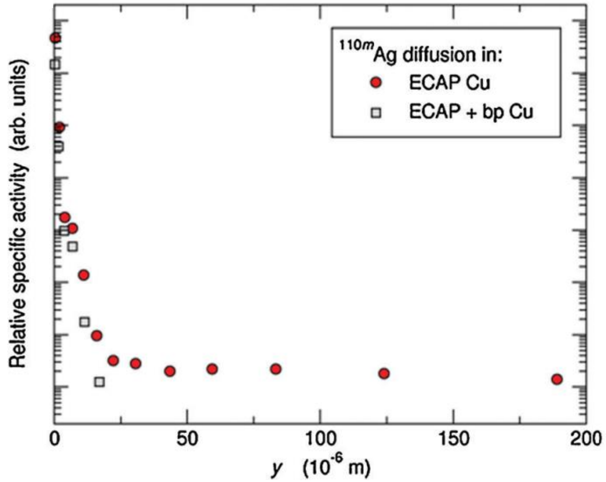
^{63}Ni in UFG Cu-1wt%Pb



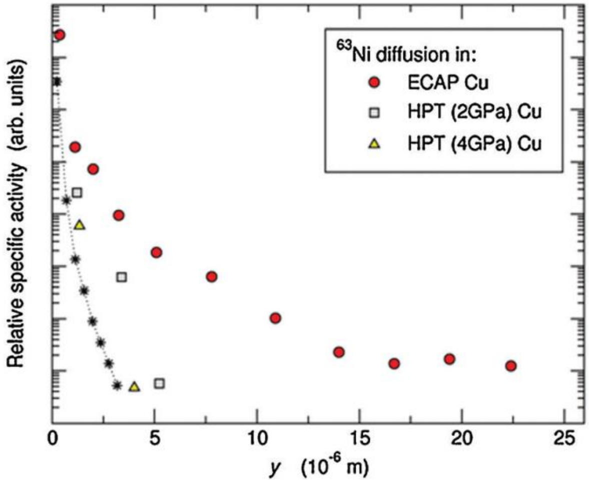
^{63}Ni in UFG Cu & cg Cu
^{86}Rb in UFG Cu



^{110m}Ag in ECAP Cu &ECAP+bp Cu



^{63}Ni in ECAP Cu & HPT Cu



IV. NANOCHEMOELASTICITY
[Gradient Chemoelasticity at the Nanoscale]

- ***Concentration/Mass Balance***

$\dot{c} + \nabla \cdot \boldsymbol{j} = 0$; c … concentration of chemical species; $\boldsymbol{j}$…flux

- ***Stress/Force Balance***

$\nabla \cdot \boldsymbol{T} = 0$; $\boldsymbol{T}$ … stress

- ***Free Energy***

$$\psi = \hat{\psi}\left(\boldsymbol{E}, \nabla(\text{tr}\,\boldsymbol{E}), c, \nabla c\right)$$

$\boldsymbol{E} = \frac{1}{2}\left[\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T\right] - \bar{c}\boldsymbol{M}$ …infinitesimal chemostrain tensor

$\boldsymbol{M}$…lattice mismatch tensor of the two phases; $\bar{c} = c / c_{\max}$ $(0 \le \bar{c} \le 1)$

- ***Spinodal Decomposition Governing PDEs***
  - Spinodal gap $\rightarrow$ homogeneous concentrations become linearly unstable
  - Linear perturbations: $\begin{cases} c(\boldsymbol{x},t) = c_o + \varepsilon\tilde{c}(\boldsymbol{x},t) \\ \boldsymbol{u}(\boldsymbol{x},t) = \boldsymbol{u_o}(\boldsymbol{x}) + \varepsilon\tilde{\boldsymbol{u}}(\boldsymbol{x},t) \end{cases}$

$\boldsymbol{u_o}(\boldsymbol{x})$ …displacement satisfying kinematic PDEs when $c(\boldsymbol{x},t) = c_o = const. \neq 0$

$$\left.\begin{aligned} & G\nabla^2\tilde{\boldsymbol{u}} + (\lambda+G)\nabla(\nabla\cdot\tilde{\boldsymbol{u}}) - (2G+3\lambda)(\ell_\varepsilon^2/3)\nabla^2\left[\nabla(\nabla\cdot\tilde{\boldsymbol{u}})\right] - (2G+3\lambda)\bar{M}_o\nabla\left(\tilde{c} - \ell_\varepsilon^2\nabla^2\tilde{c}\right) = \boldsymbol{o} \\ & \dot{\tilde{c}} = g_2(c_o)\nabla^2\tilde{c} - g_3(c_o)\nabla^4\tilde{c} - g_6(c_o)\left[\nabla^2(\nabla\cdot\tilde{\boldsymbol{u}}) - \ell_\varepsilon^2\nabla^4(\nabla\cdot\tilde{\boldsymbol{u}})\right] \end{aligned}\right\}$$

  - Finite 1D System: $\tilde{c}(x,t) = \hat{c}e^{\omega t}\cos\left(\frac{n\pi}{L}x\right);\ \tilde{u}(x,t) = \hat{u}e^{\omega t}\sin\left(\frac{n\pi}{L}x\right)$

    Uniform concentrations are unstable when

$$f''(c_o) < -\frac{\kappa\ell_\varepsilon^2\left(\frac{\pi}{L}\right)^4 + 12G\bar{M}_o^2\left[1+\ell_\varepsilon^2\left(\frac{\pi}{L}\right)^2\right] + 3\kappa\frac{2G+\lambda}{2G+3\lambda}\left(\frac{\pi}{L}\right)^2}{3\left(\frac{2G+\lambda}{2G+3\lambda}\right) + \ell_\varepsilon^2\left(\frac{\pi}{L}\right)^2}$$

- ***Constitutive Equations***

  – *Stress*

$$\boldsymbol{T} = \frac{\partial \hat{\psi}}{\partial \boldsymbol{E}} - (\nabla \cdot \boldsymbol{\tau})\mathbf{1} \;\; ; \qquad \boldsymbol{\tau} = \frac{\partial \hat{\psi}}{\partial \nabla(\mathrm{tr}\, \boldsymbol{E})}$$

  – *Flux*

$$\boldsymbol{j} = -c\boldsymbol{B}\nabla \mu; \quad \mu = \frac{\partial \hat{\psi}}{\partial c} - \nabla \cdot \boldsymbol{\xi} - \frac{\partial \hat{\psi}}{\partial \boldsymbol{E}} \cdot \bar{\boldsymbol{M}}; \quad \boldsymbol{\xi} = \frac{\partial \hat{\psi}}{\partial \nabla c} - \frac{\partial \hat{\psi}}{\partial \nabla(\mathrm{tr}\, \boldsymbol{E})}(\mathrm{tr}\, \bar{\boldsymbol{M}})$$

  – *Free Energy*

$$\hat{\psi}\left(\boldsymbol{E}, \nabla(\mathrm{tr}\, \boldsymbol{E}), c, \nabla c\right) = f(c) + \frac{1}{2}\nabla c \cdot \boldsymbol{K}\nabla c + \frac{1}{2}\boldsymbol{E} \cdot \boldsymbol{\mathcal{C}}\boldsymbol{E} + \frac{1}{2}\nabla(\mathrm{tr}\, \boldsymbol{E}) \cdot \boldsymbol{H}\nabla(\mathrm{tr}\, \boldsymbol{E})$$

- ***Illustrative Example: Regular Solution Model***

$$f(c) = \mu^0 c + \underbrace{R\vartheta c_{\max}\left[\bar{c}\ln\bar{c} + (1-\bar{c})\ln(1-\bar{c})\right]}_{\text{Entropy of mixing for an ideal solution}} + \underbrace{R\vartheta c_{\max}\left[\alpha\bar{c}(1-\bar{c})\right]}_{\text{Deviation from ideality. Energetic interactions of mixing}}$$

$\bar{c} = c / c_{\max}$ $(0 \le \bar{c} \le 1)$, μ^0…a reference value of the chemical potential

R…universal gas constant, ϑ…absolute temperature

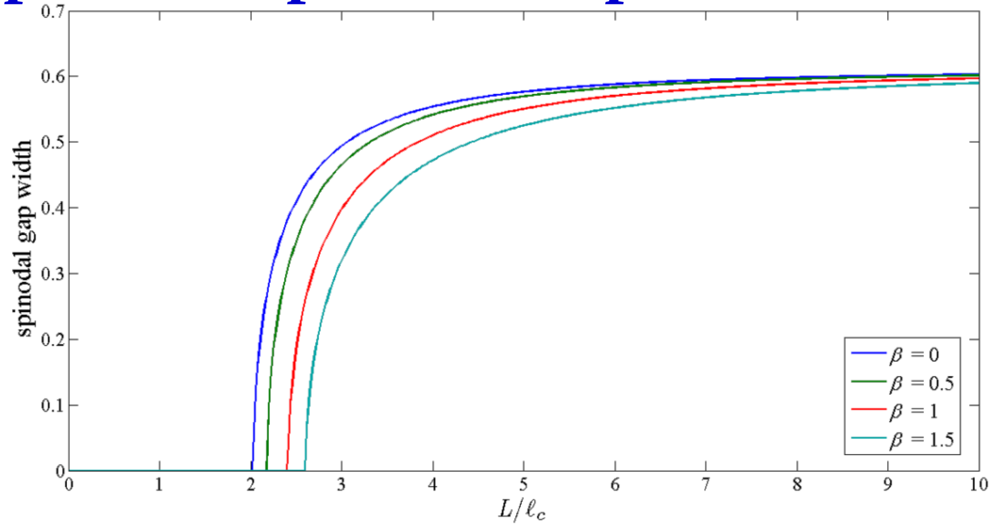
$\alpha > 2 \rightarrow f(c)$ is non-convex with two cells $\rightarrow$ spinodal decomposition

$\ell_c^2 = \kappa c_{\max} / R\vartheta$

$\therefore$ **Size Effects on Spinodal Gap Width**

$$w = \left\{ \frac{\left[2\alpha - 4 - \pi^2\left(\frac{\ell_c}{L}\right)^2\right]\left[3\frac{2G+\lambda}{2G+3\lambda} + \pi^2\left(\frac{\ell_\varepsilon}{L}\right)^2\right] - 12\frac{GM_o^2}{R\vartheta c_{\max}}\left[1+\pi^2\left(\frac{\ell_\varepsilon}{L}\right)^2\right]}{\left[2\alpha - \pi^2\left(\frac{\ell_c}{L}\right)^2\right]\left[3\frac{2G+\lambda}{2G+3\lambda} + \pi^2\left(\frac{\ell_\varepsilon}{L}\right)^2\right] - 12\frac{GM_o^2}{R\vartheta c_{\max}}\left[1+\pi^2\left(\frac{\ell_\varepsilon}{L}\right)^2\right]} \right\}^{1/2}$$

- ***Size – dependent Spinodal Gap Width***



Size effect on the spinodal gap width for different values of the internal lengths ratio β

- Spinodal range is more narrow as the specimen size decreases
- For sufficiently small values of L there is no spinodal region at all
- $$\lim_{L\to\infty} w = \left\{ \frac{6(\alpha-2)\left(\dfrac{2G+\lambda}{2G+3\lambda}\right) - 12\dfrac{GM_o^2}{R\vartheta c_{\max}}}{6\alpha\left(\dfrac{2G+\lambda}{2G+3\lambda}\right) - 12\dfrac{GM_o^2}{R\vartheta c_{\max}}} \right\}^{1/2} \cong 0.611$$

V. NANO DEFECT KINETICS
[Gradient Defect Kinetics at the Nanoscale]

- ***The W–A Model:*** $(\rho_i)_t = I(\rho_i, \rho_j) + D_i \nabla^2 \rho_i$

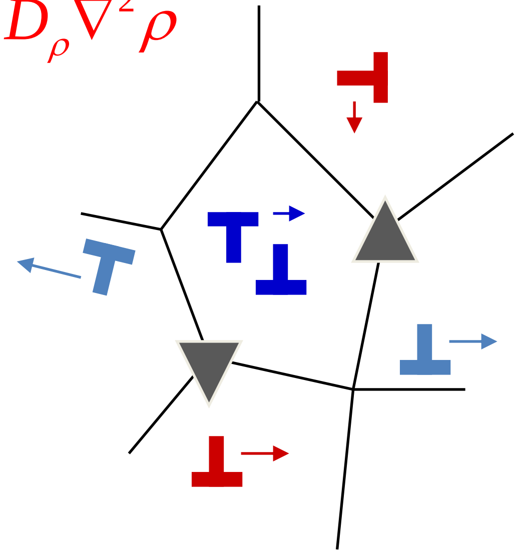
- ***Application to Nanopolycrystals***

$$\rho_t = A_\rho \rho - B_\rho \rho^2 - C_0 \frac{\rho}{d} + C_3 \rho\varphi + \omega M \vartheta + N \frac{\psi}{d} + D_\rho \nabla^2 \rho$$

$$\varphi_t = A_\varphi \rho - B_\varphi \rho^2 - C_4 \rho\varphi - K\varphi + D_\varphi \nabla^2 \varphi$$

$$\psi_t = C_1 \frac{\rho}{d} + A_\psi \psi - B_\psi \psi^2 + D_\psi \nabla^2 \psi$$

$$\vartheta_t = C_2 \frac{\rho}{\omega d^2} - P_1 \rho\vartheta - P_2 \psi\vartheta - G\vartheta + D_\vartheta \nabla^2 \vartheta$$



ρ – mobile dislocations in the grain interior

φ – low-mobility (immobile) dislocations (dipoles)

ϑ – immobile junction disclinations

ψ – grain boundary sliding dislocations

- ***Twinning in Nanopolycrystals***

$$\rho_t = A_\rho \rho - A_1 \rho^2 - B_1 \rho \xi + F_1 \theta \xi - G_1 \theta \xi \rho - K_1 \rho \phi + N_1 \theta \phi + D_\rho \frac{\partial^2 \rho}{\partial x^2}$$

$$\theta_t = B_2 \rho \xi + G_2 \theta \xi \rho + K_2 \rho \phi - R \theta^2 + D_\theta \frac{\partial^2 \theta}{\partial x^2}$$

$$\phi_t = E_0 \theta - K_3 \rho \phi - N_2 \theta \phi$$

$$\xi_t = A_2 \rho^2 - F_2 \theta \xi$$

ρ – mobile dislocations
ϑ – disclination dipoles (twin fronts)
ϕ – twin lamellae
ξ – sessile Lomer-Cotrell dislocations