Computational modeling of environmental effect and 2nd phase pinning in alloys for advanced fossil power systems

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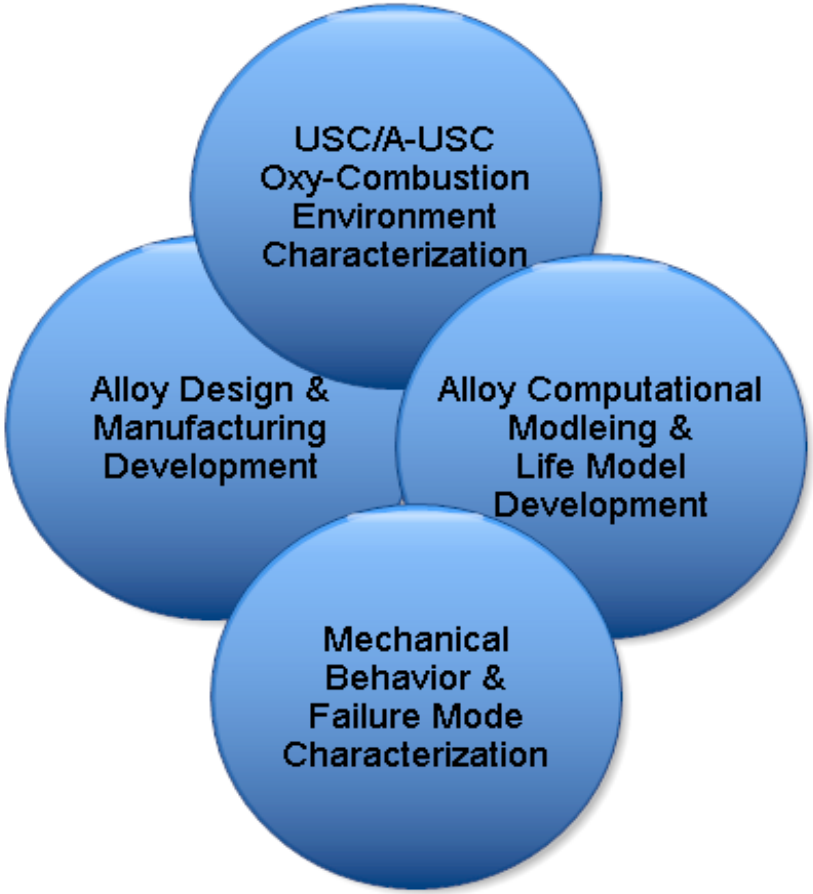
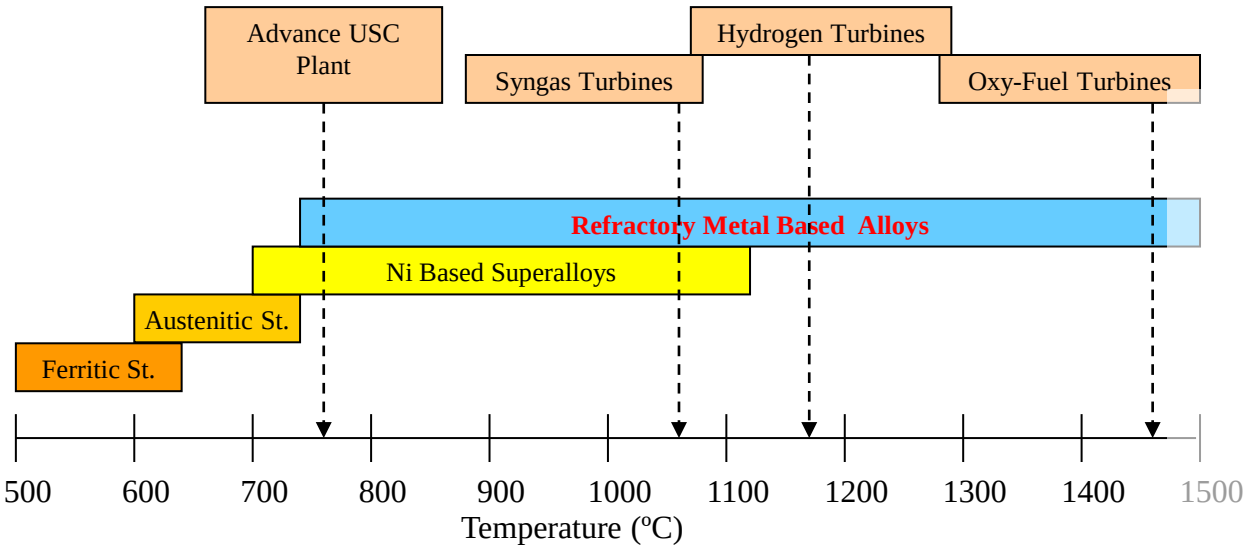
Advanced Combustion

- **Integrated multi-scale computational approach, complimented with a focused experimental program, emphasizing the design & optimization of materials for advanced combustion systems.**

  - ***Computational material design & optimization.***
  - ***Lab-scale synthesis of materials.***
  - ***Mechanical & chemical assessment of materials performance in real environments***
  - ***Simulation of component life in conventional & oxy-fuel combustion environments.***



New Energy Generating Technologies and High-Temperature Structural Materials



Advanced FE systems

- Extreme environment (corrosive,T,P)
- Components have to last 10,000's to 100,000's hours

- Lack of experience with alloy performance in these extreme conditions and times scales necessary for advanced FE systems
- Need for reliable and fast methods for predicting materials performance.
- **Integrated computational and focused experimental approach.**

Outline

- Background for Oxidation Modeling
- Oxidation Model Description
- Simulation Results for Oxidation Modeling
- Summary for Oxidation Modeling
- 2nd Phase Pinning and Grain Growth
- Summary for 2nd Phase Pinning

Dominant Oxidation Theories

- Cabrera-Mott Theory (thin-film)
- Wagner Theory (thick-film)
- Deal-Grove Theory (Silicon)

C-M Theory

- **Space charge neglected**
- Thermal electron emission or quantum tunneling effect the rate limiting process

Wagner Theory

- Transport of ions/electrons across the film (due to electrochemical potential gradient) the rate limiting process
- **Local charge neutrality** (Space charge neglected)
- **Coupled-currents assumption**

D-G Theory

- Diffusion of **neutral** species in the scale
- **Steady state** diffusion
- **Interface reaction rate** limiting or diffusion limiting process

Gaps in Existing Oxidation Theories

C-M Theory

Wagner Theory

Research Field Gap

Charge carrying metal vs Silicon

D-G Theory

Uncharged species is just a strong assumption of charge neutrality. Charge carrying or not should not cause a gap in modeling.

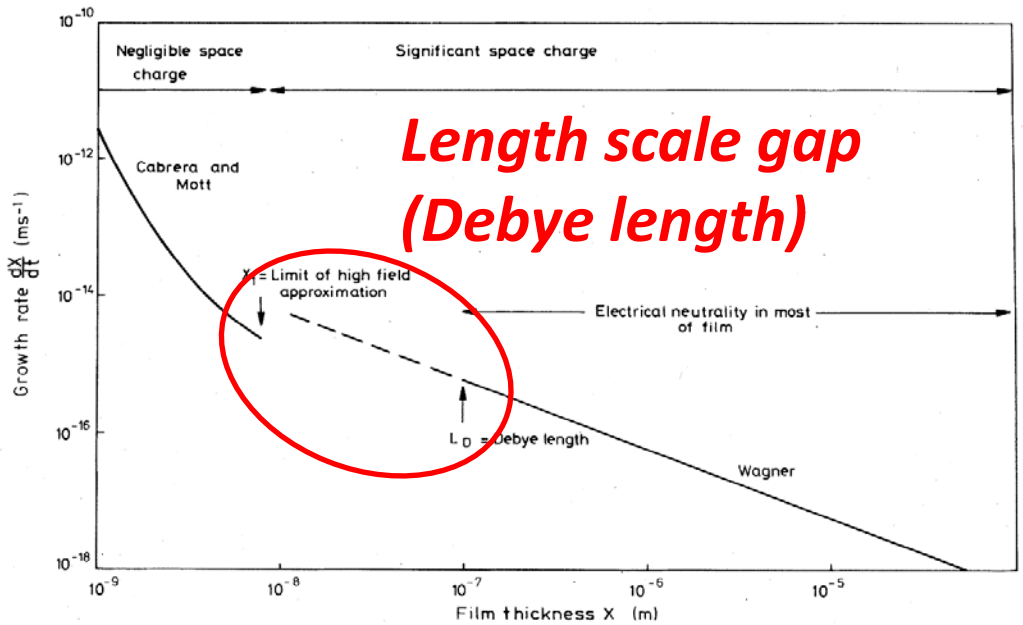
A general model should handle both!

Gaps in Existing Oxidation Theories

G-M Theory

Moderate film thickness

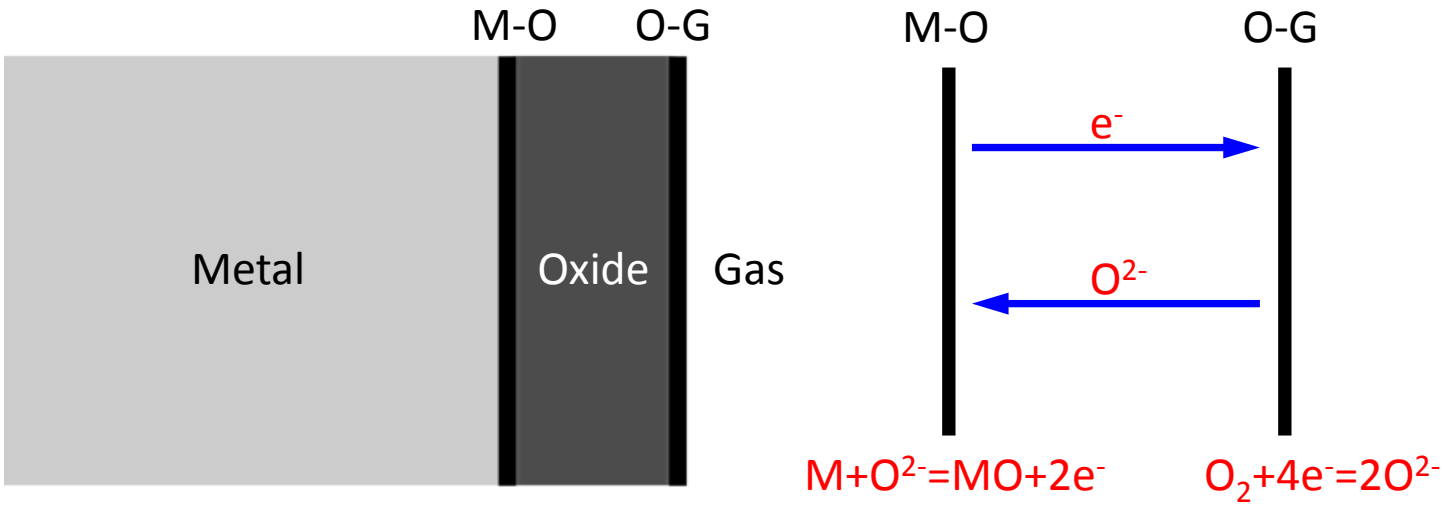
Wagner Theory



(Atkinson, *Review of Modern Physics*, 1985)

Moderate film thickness regime*:** *The coupling of space charge and ionic diffusion with long-range electrostatic interaction has to be addressed –* ***<u>a tough problem</u>*.*

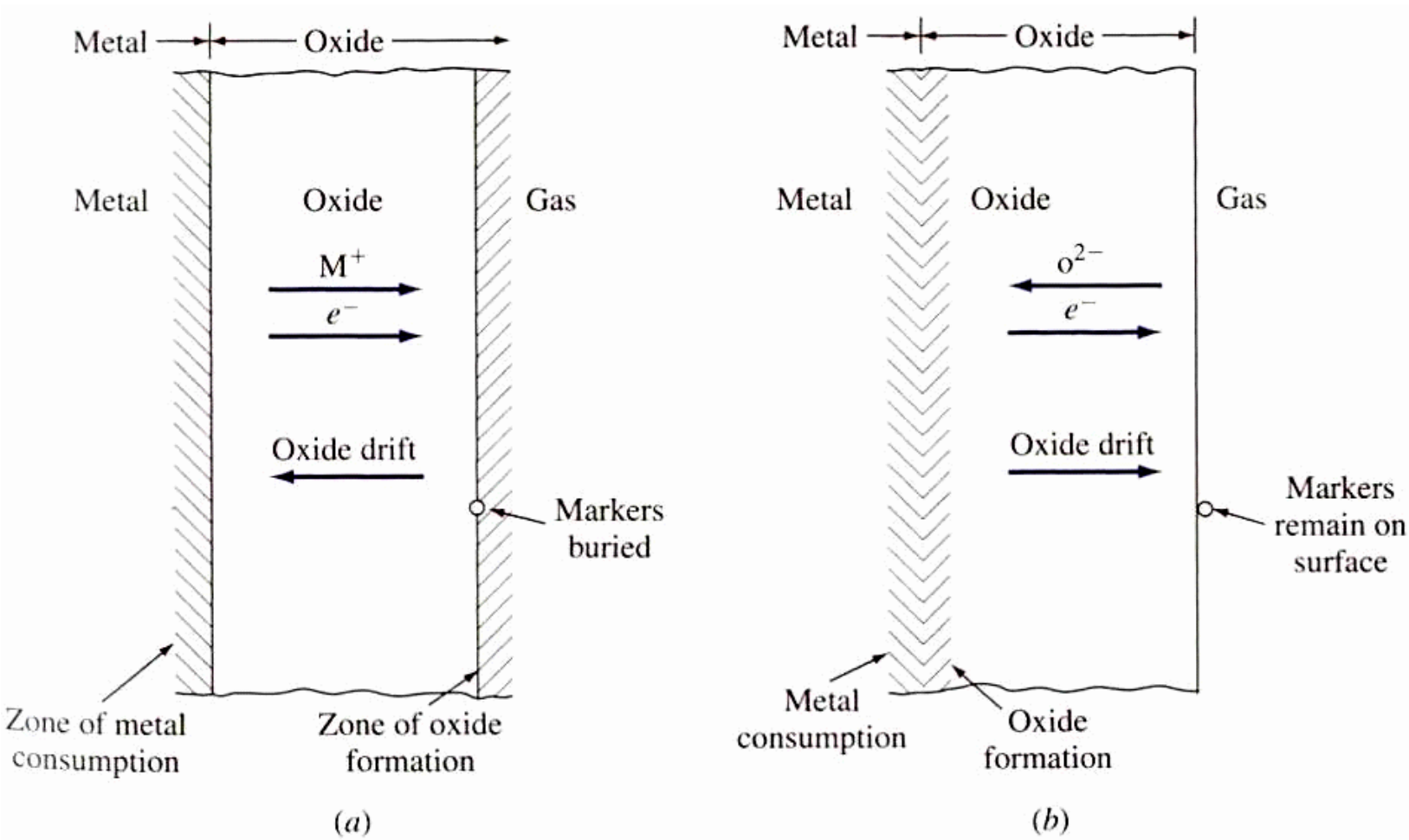
The Simplest Metal Oxidation



The coupling physics with no viable simplification

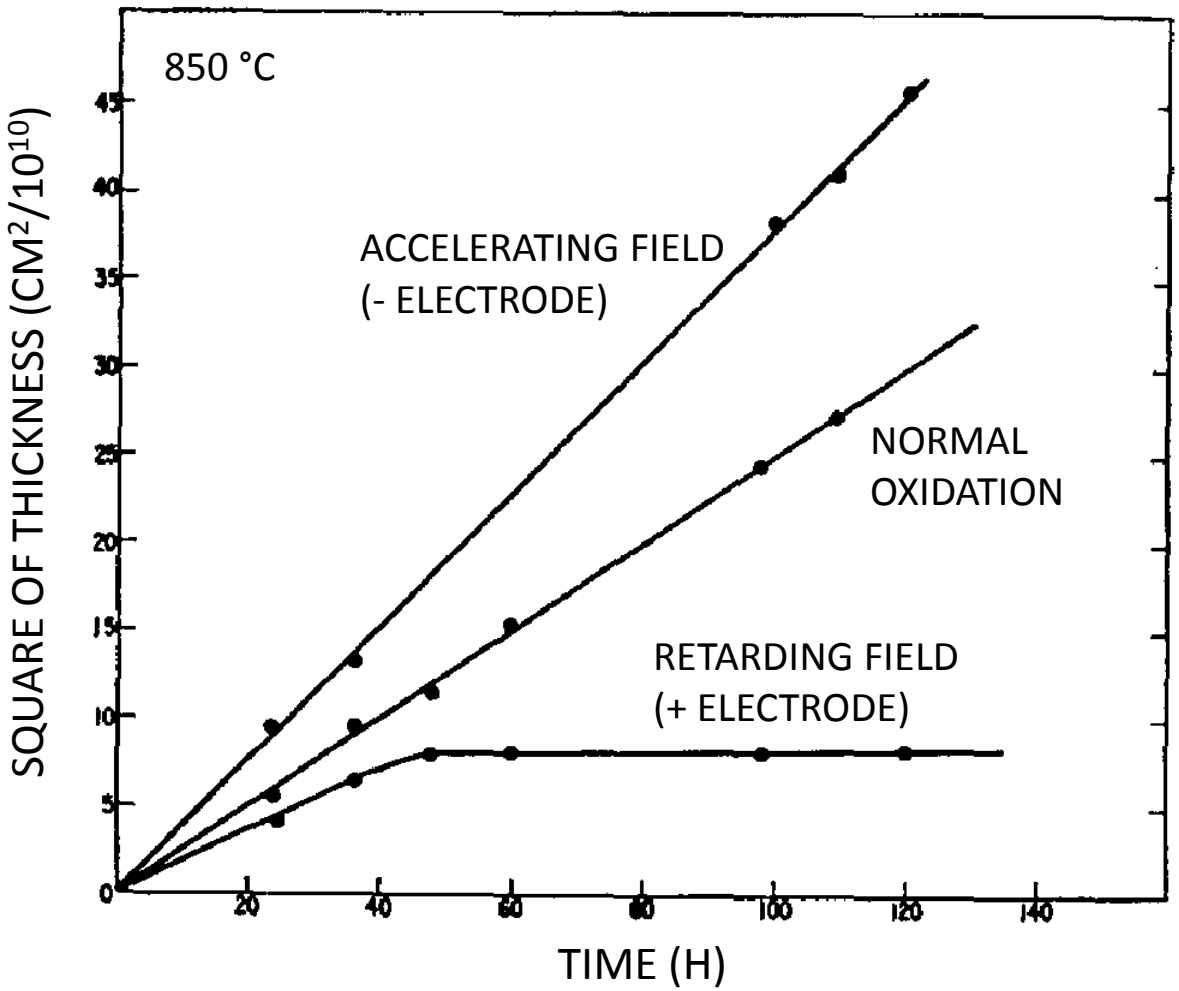
- **Chemical reaction**
- **Mass transport**
- **Charge interaction**
- **Evolving structure**
- **Evolving electric field**

The Simplest Metal Oxidation: cont.



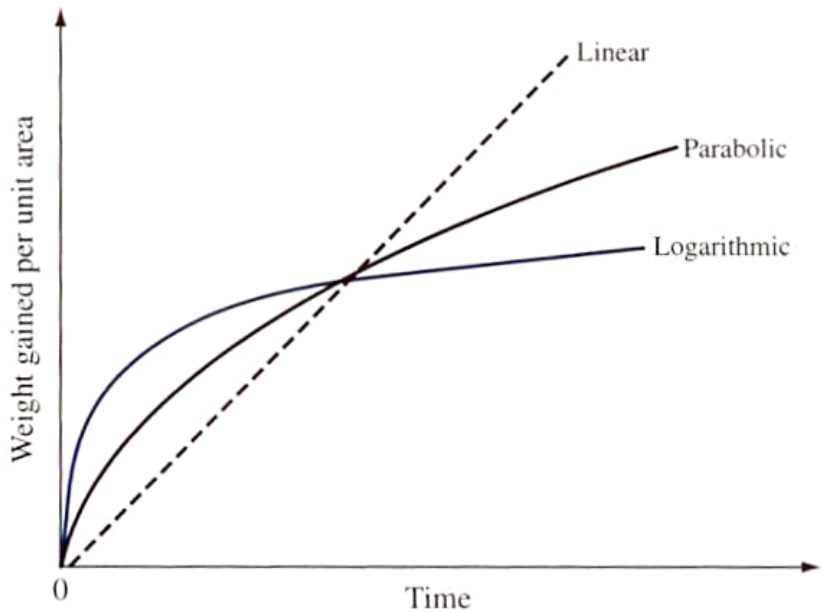
Two typical scenarios: Outward (a) vs Inward (b) Diffusion

External electric field altering silicon oxidation kinetics (Direct evidence of charge transport)



(Jorgensen P., J.C.P. 1962)

Empirical Rate Laws Observed for Metals



- **<u>Linear law</u>**: $w = k\,t$

Observed for metals at certain environments (chemical reaction to be rate limiting), e.g., Fe in $CO+CO_2$, Cr in H_2O-H_2 , Ti in H_2O; or rapid breakaway oxidation (spallation of oxide scales)

- **<u>Parabolic law</u>**: $w^2 = kt + C$

Common for metals at high temperatures with thick coherent oxides

- **<u>Logarithmic rate</u>**: $w = k \log (Ct + A)$

or **inverse logarithmic** (*1/w=A-k log(t)*) Oxidation at early stage, typically <400°C; very fast oxidation at the start, then the rate decreases to a low value

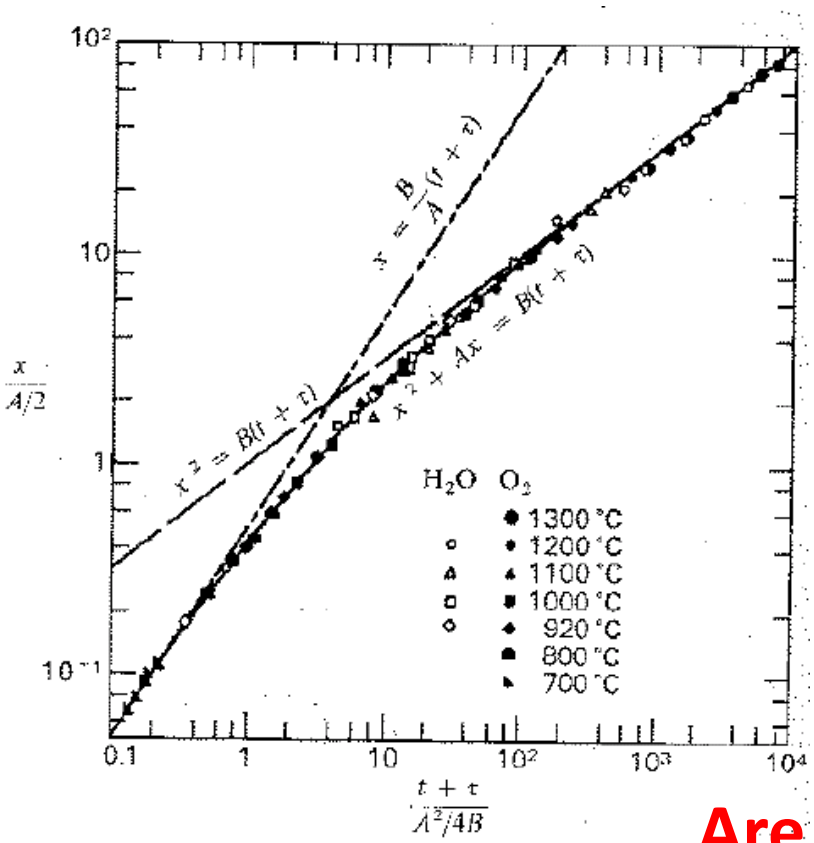
- **<u>Catastrophic at high T</u>**

Rapid exothermal reactions, oxides are volatile, e.g. Mo, W, V

w – weight gain per unit area; or oxide thickness
t – time

Reference: Goncharova, Kofstad, Birks et al

Linear-Parabolic Rate Laws Transition



Deal-Grove, J.A.P, 1965

Widely observed in metals and Si

Linear regime for the thin film
Parabolic regime when the film grows thick

D-G Theory Explanation: Interface (surface) reaction rate limiting (thin film) to diffusion through the oxide rate limiting (thick film) transition

Are the same mechanisms responsible for the transition in metals oxidation with charged species?

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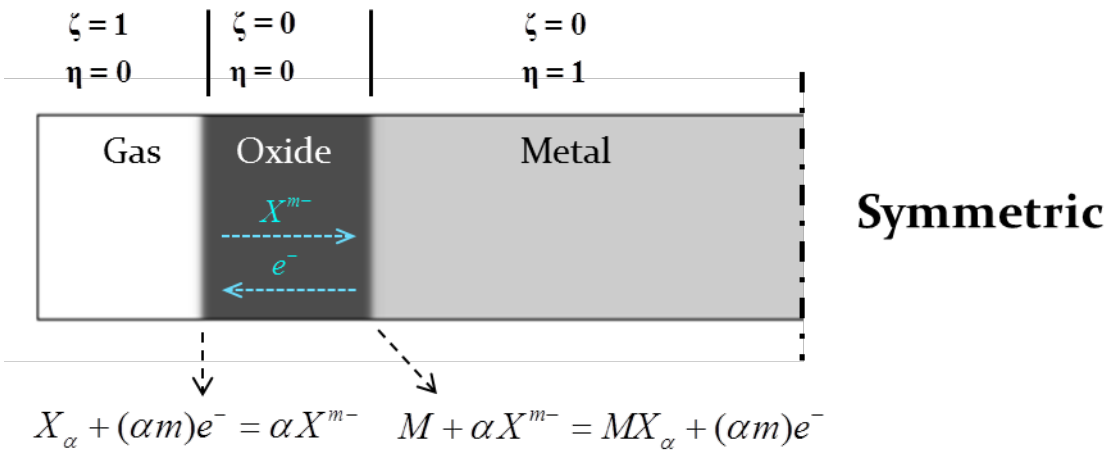
Oxidation Model Description



$$\frac{d[X^-]}{dt} = k_I p_X \left([X^-]^* - [X^-]\right)[e^-]$$

$$\frac{d[e^-]}{dt} = -k_I p_X \left([X^-]^* - [X^-]\right)[e^-]$$

$$\frac{d[X^-]}{dt} = \frac{d[M]}{dt} = -k_{II}[M][X^-]$$

$$\frac{d[e^-]}{dt} = k_{II}[M][X^-]$$

(cf. Standard Deal-Grove oxidation model)

Boundary condition:

Metal phase: electric field inside a conductor should be zero.
(large mobility electrons + background cations)

Gas phase: Diffusing species are prohibited to enter

Governing Equations

		Reaction	Diffusion + Electromigration
[X-]:	$\frac{\partial c_1}{\partial t} =$	$K_I p_X \Lambda_\zeta c_2(\bar{c}_1 - \tilde{c}_1) - K_{II}\Lambda_\eta \tilde{c}_1$	$+\nabla\cdot(D_1\nabla c_1) - \frac{e}{k_B T}\nabla\cdot(D_1 c_1 z_1 \mathbf{E})$
[e-]:	$\frac{\partial c_2}{\partial t} =$	$-K_I p_X \Lambda_\zeta c_2(\bar{c}_1 - \tilde{c}_1) + K_{II}\Lambda_\eta \tilde{c}_1$	$+\nabla\cdot(D_2\nabla c_2) - \frac{e}{k_B T}\nabla\cdot(D_2 c_2 z_2 \mathbf{E})$
[c+]:	$\frac{\partial c_3}{\partial t} =$		$\nabla\cdot(D_3\nabla c_3) - \frac{e}{k_B T}\nabla\cdot(D_3 c_3 z_3 \mathbf{E})$
[M]:	$\frac{\partial \eta}{\partial t} =$	$-K_V K_{II}\Lambda_\eta \tilde{c}_1$	$+M_\eta \nabla^2\left(\partial f/\partial\eta - \beta\nabla^2\eta\right)$

$$\tilde{c}_i = (1 + \kappa_G \zeta + \kappa_M{}^{(i)}\eta)c_i$$

$$\Lambda_\eta = \eta^p(1-\eta)^q, \quad \Lambda_\xi = \xi^p(1-\xi)^q$$

$$F(\eta) = \int\left[f(\eta) + \frac{1}{2}\beta|\nabla\eta|^2\right]dV$$

The electric field, satisfying Poisson's equation, is solved by **an efficient numerical scheme** for arbitrary **dielectric heterogeneity**

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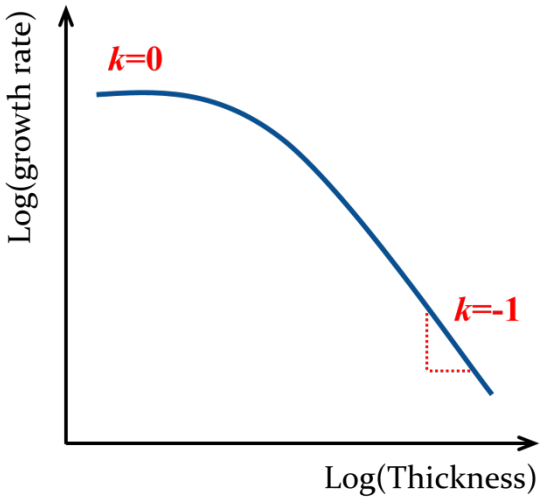
Results: Linear-Parabolic Transition in Kinetics



(expected plot on a log-log plot)

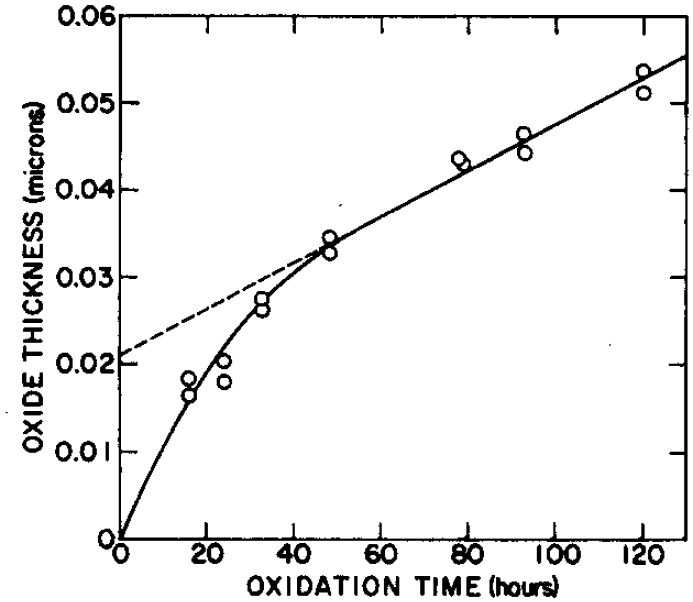


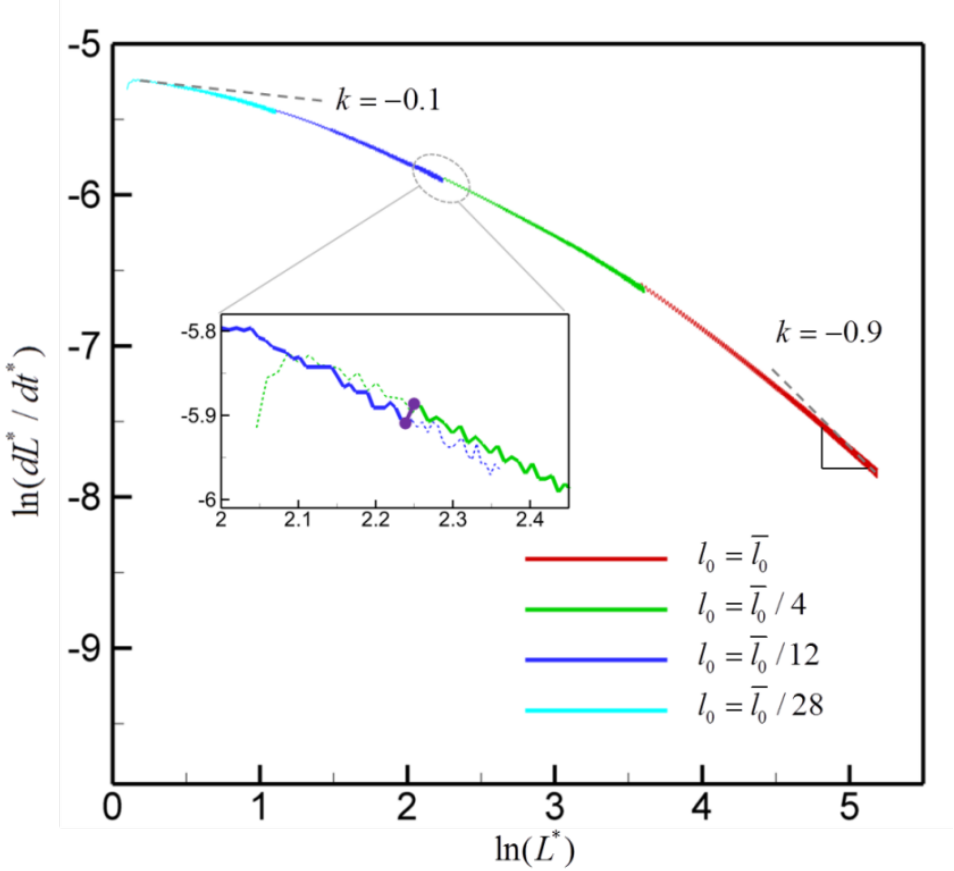
FIG. 6. Oxidation of silicon in dry oxygen at 700°C.

Deal & Grove, J.A.P. 1965: assume steady state diffusion, without considering electric field

Can we capture the transition without any *a prior* assumptions?

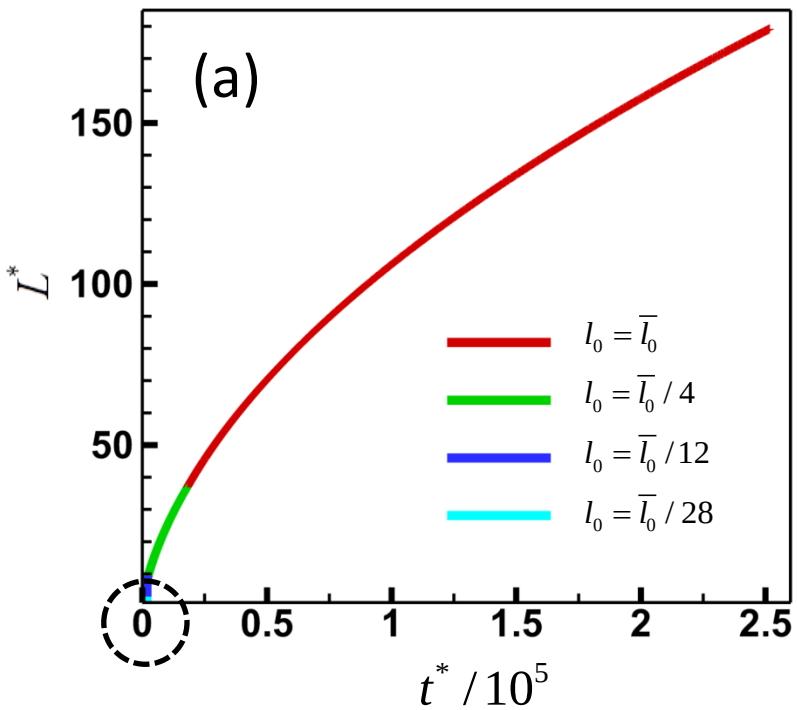
Multiscale Simulation: Linear-Parabolic Transition

❖ Reproducing classical Deal-Grove reaction-diffusion model (analytical) with explicit consideration of charge transport

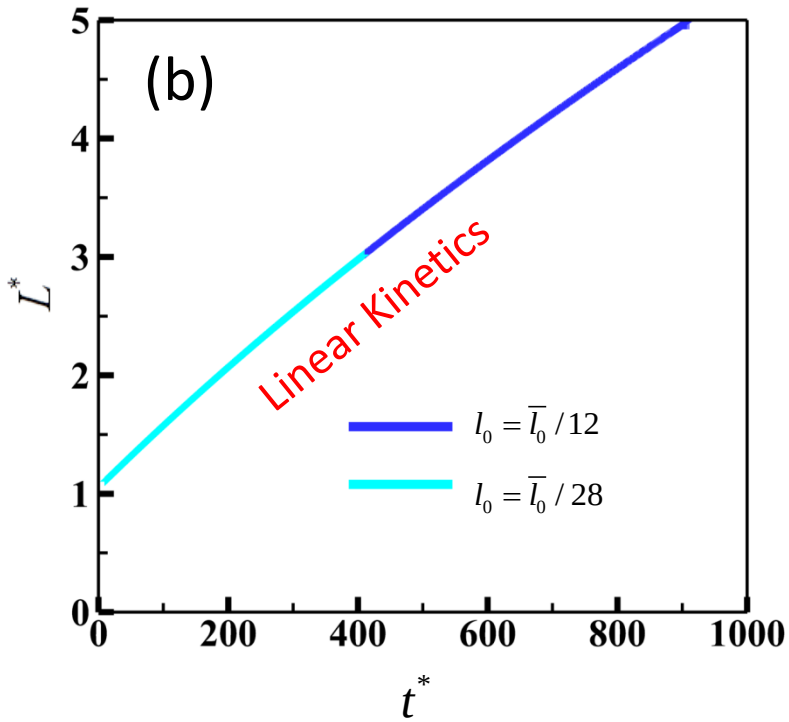


- **Four different simulations at 4 length scales are combined together**
- **Resembling 'relay-race game' in track and field**
- **Excellent agreements at the "exchange of baton" zones**
- **Continuous linear to parabolic transition**

Multiscale Simulation: Linear-Parabolic Transition

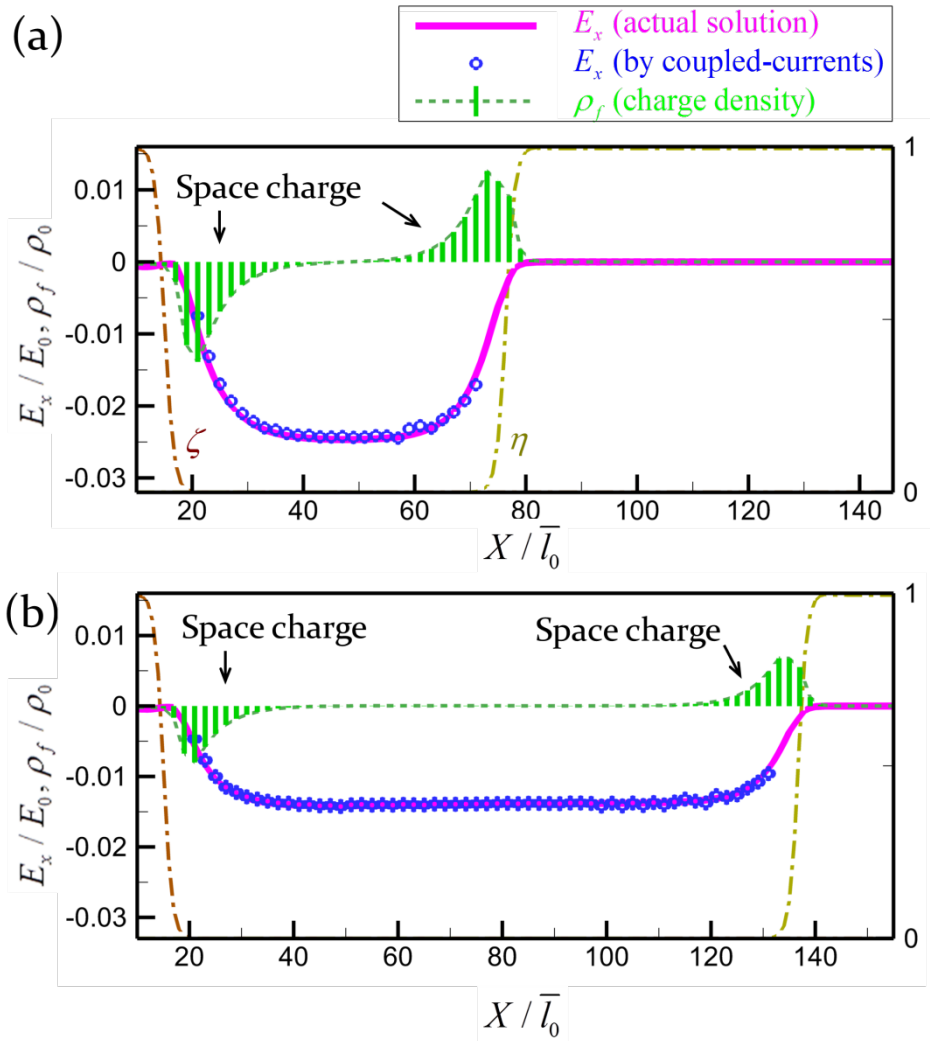


Overall growth kinetics



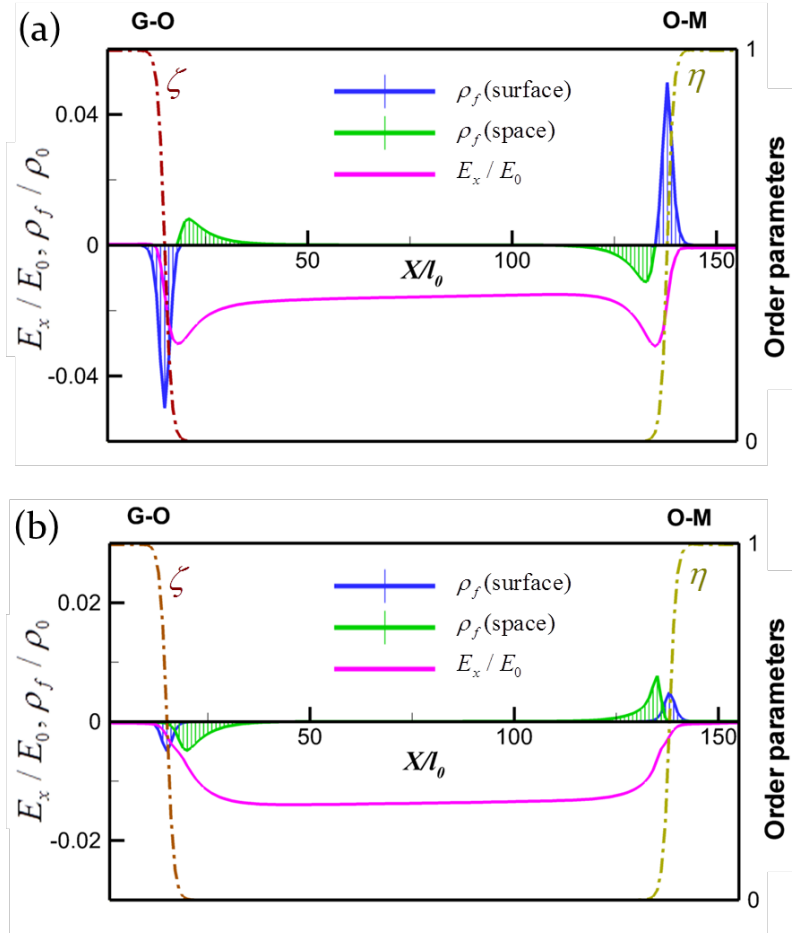
Initial stage growth kinetics

Simulated space charge and electric field distribution (c.f. Wagner theory)



- Charge neutrality is satisfied in bulk area outside the diffuse layers (a few times of Debye length)
- Coupled-currents assumption is satisfied except for the interface zones
- Electric field in bulk oxide has finite magnitude
- Electric field magnitude decreases with increasing film thickness

Electric field distribution with excess surface charge (mild influence on oxidation kinetics)



$$\rho_f^{(s)} = \sigma_I \zeta(1-\zeta) + \sigma_{II}\eta(1-\eta)$$

- Space charge only partially screens surface charge even there exists significant surface charge
- Space charge may enhance surface charge with weak surface charge
- Mean electric field in the bulk zone is stable and of finite magnitude - responsible for mediating different mobilities of ions; different from conventional Debye screening
- Coupling between electrostatic interaction, mass diffusion and chemical reaction is inseparable

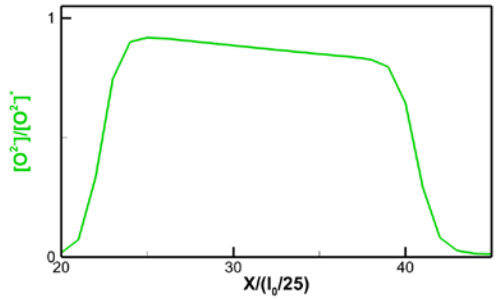
Interfaces with Environment Characterization Task

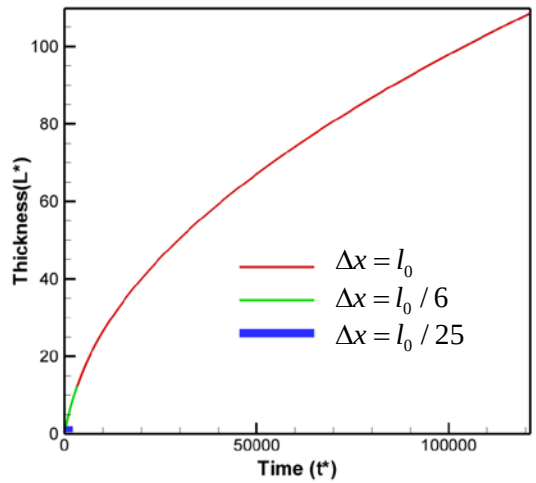
- Diffusivity Data
- Solubility Data

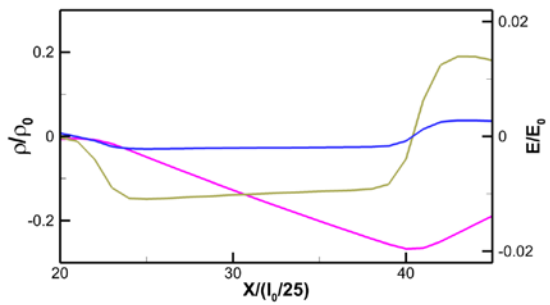
Provide Input

Oxidation Modeling

Validate Kinetics







Characterization Task Provide Critical Input Data for Oxidation Modeling and Validate Predicted Kinetics

Summary

- Developed a phase-field oxidation model. The model takes into account reaction-diffusion and charge interactions, which is the key to explain the kinetics in an intermediate length scale (nm to µm).
- The continuous linear-parabolic transition is captured by computer simulation, compared to the standard Deal-Grove model. The local charge neutrality condition of Wagner theory is asymptotically satisfied at thick film stage. - Unified explanation for Wagner theory and Deal-Grove theory.

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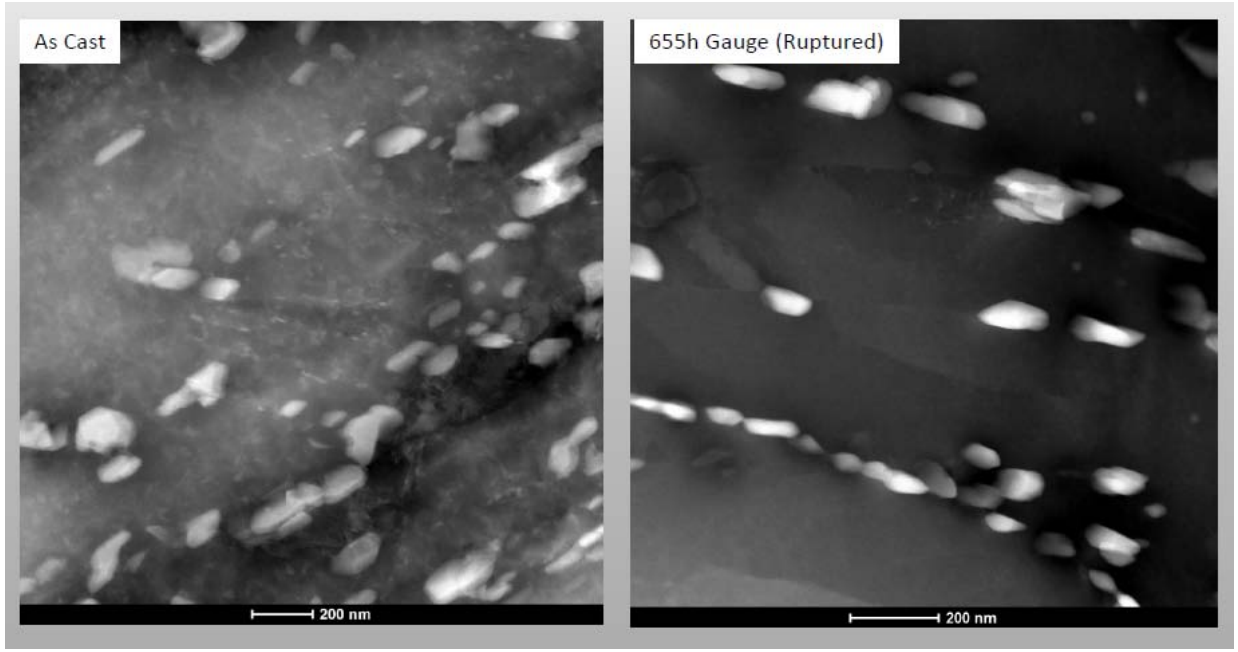
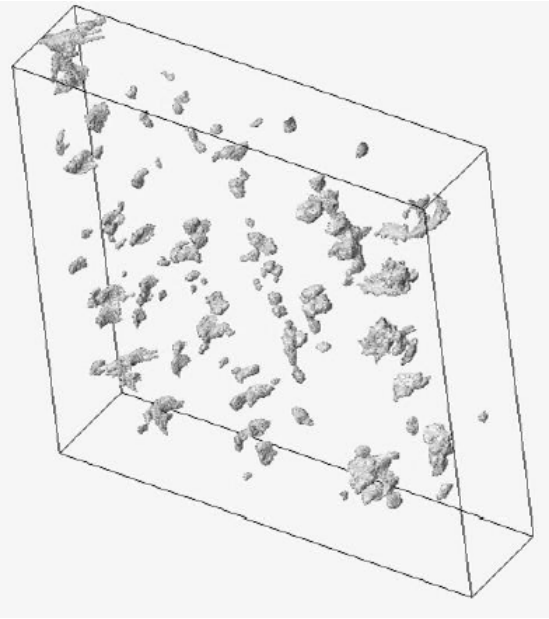
2nd Phase Pinning



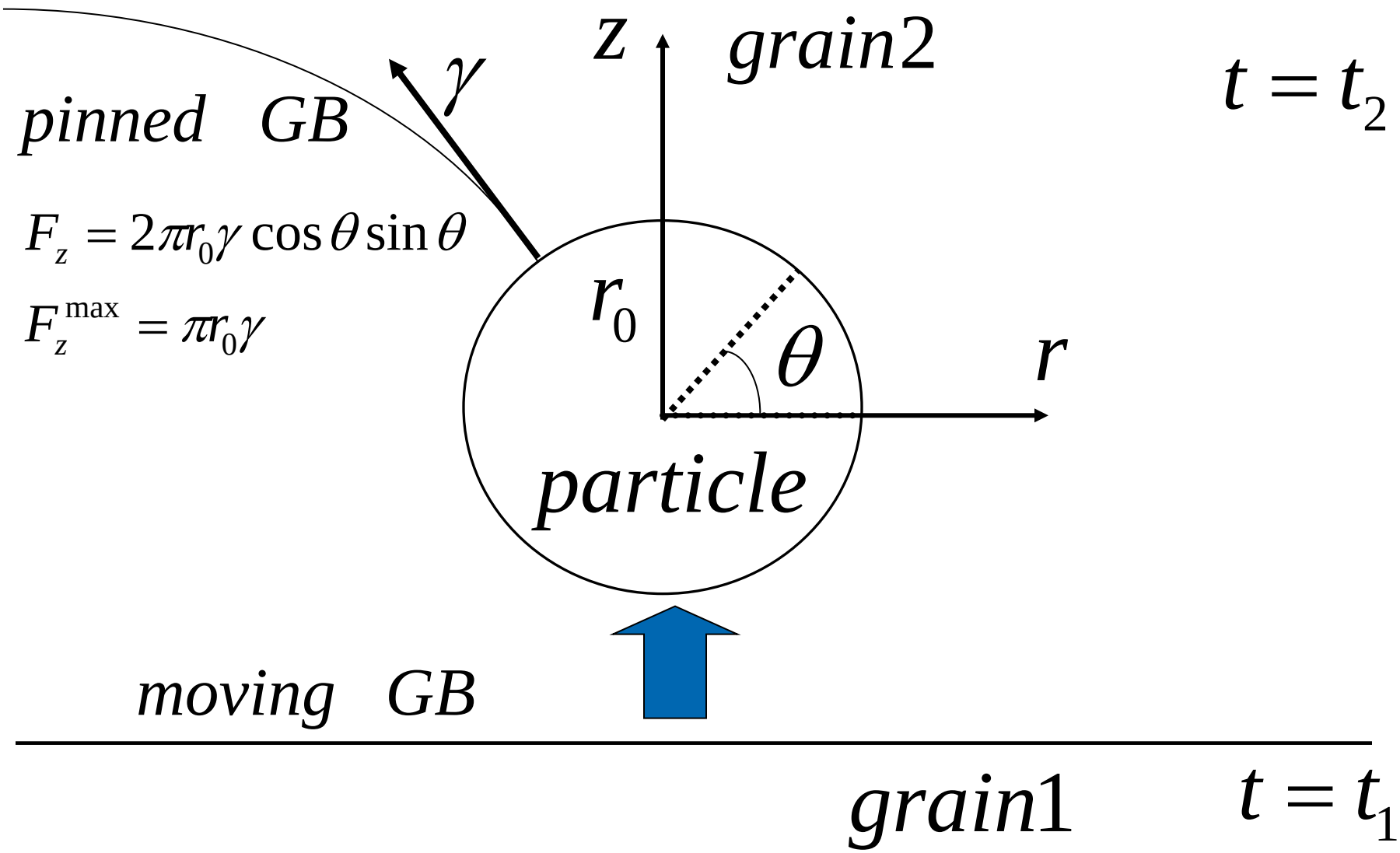


Carbide Precipitations in 9Cr Steel (left) and

3D reconstructed M23C6 in COST B2 steel (right)

Courtesy of Mitsu Murayama at VirginiaTech

Zenner Particle Pinning Theory

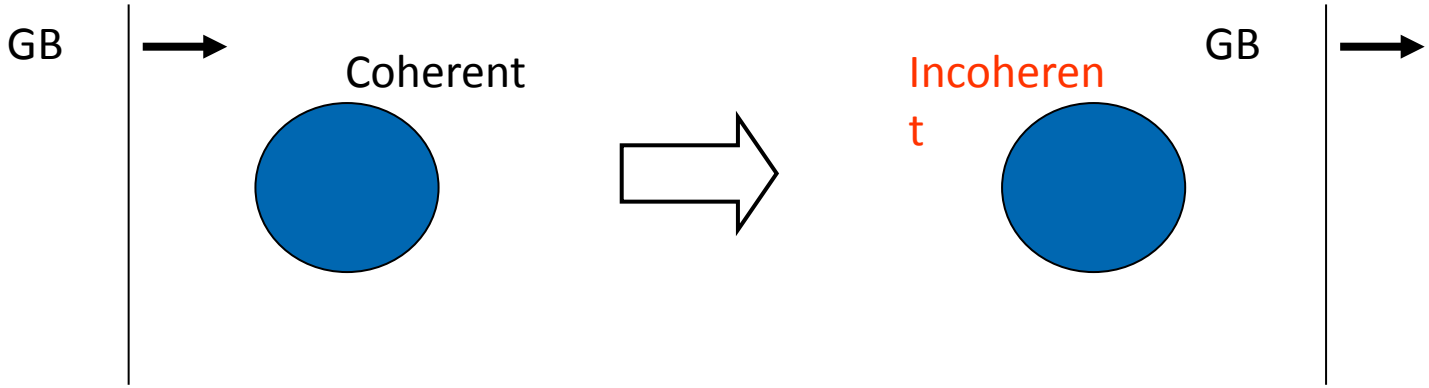


$$F_z = 2\pi r_0 \gamma \cos\theta \sin\theta$$

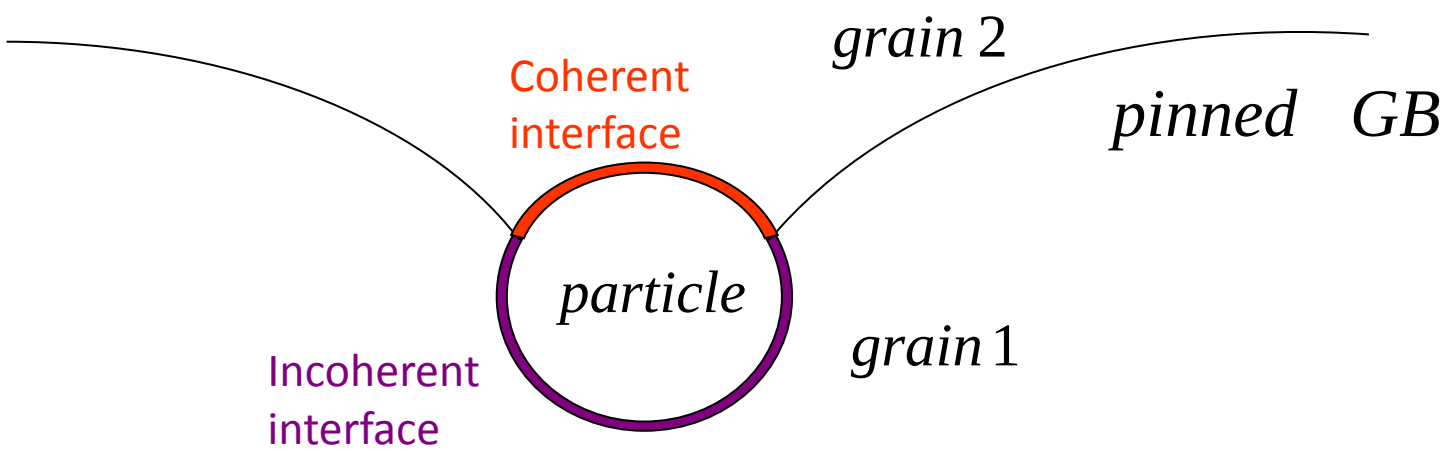
$$F_z^{\max} = \pi r_0 \gamma$$

Lattice coherency of pinning particles

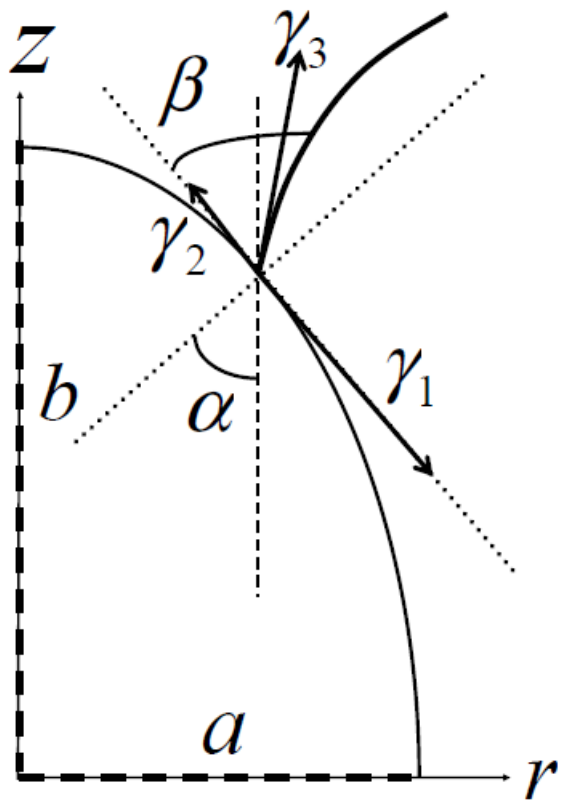
Coherency loss



Surface energy ~ $\gamma_{inc} / \gamma_{coh} \geq 5 \quad \gamma_{gb} \sim \gamma_{inc}$



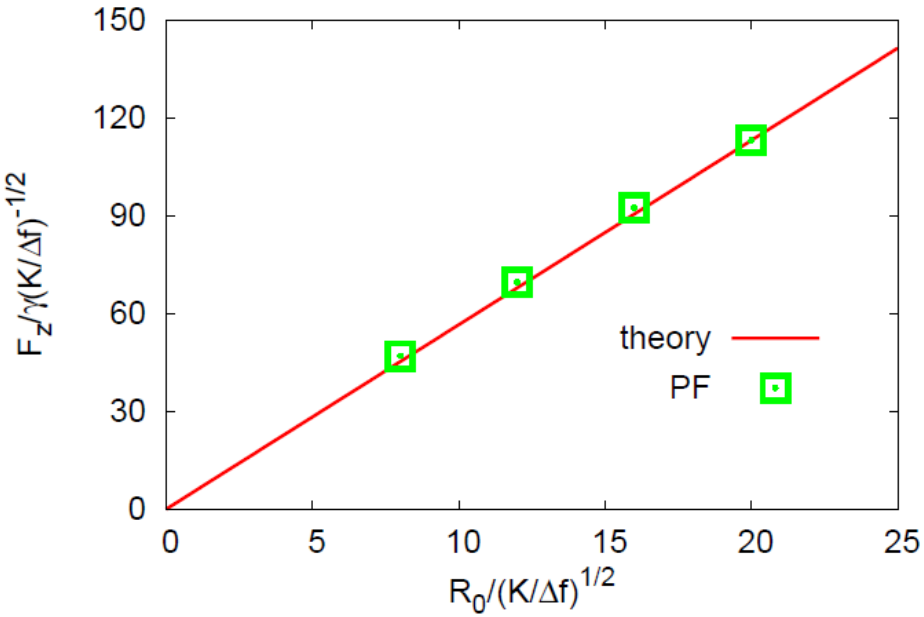
Pinning Force for an Ellipsoid Particle

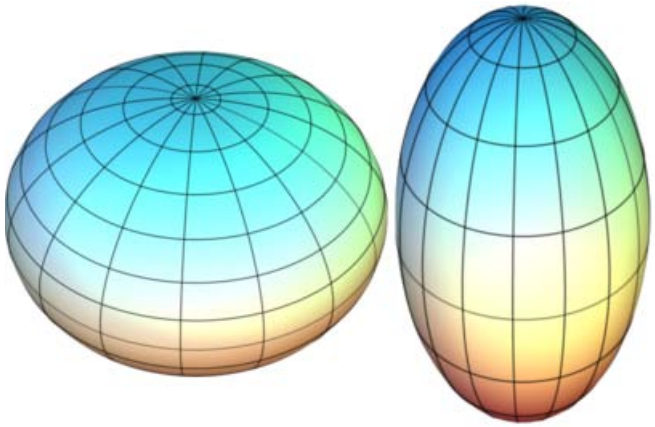


$$F_z = 2\pi\gamma_3 a\varepsilon \frac{\sin\alpha\cos[\alpha-(\pi/2-\beta)]}{\sqrt{\cos^2\alpha(1-\varepsilon^2)+\varepsilon^2}}$$

$$\cos\beta = \frac{\gamma_1-\gamma_2}{\gamma_3}$$

Comparison with Theory for Spheroid Particles

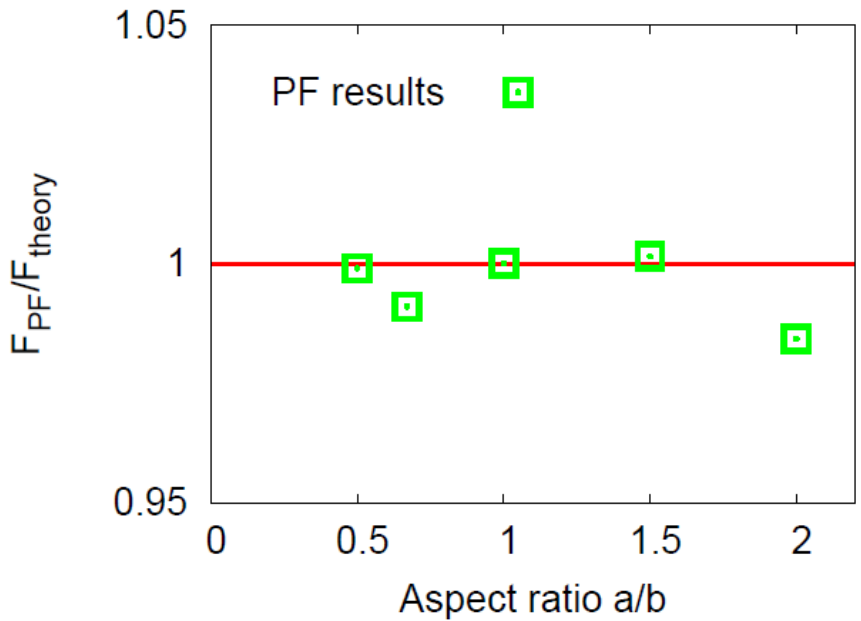




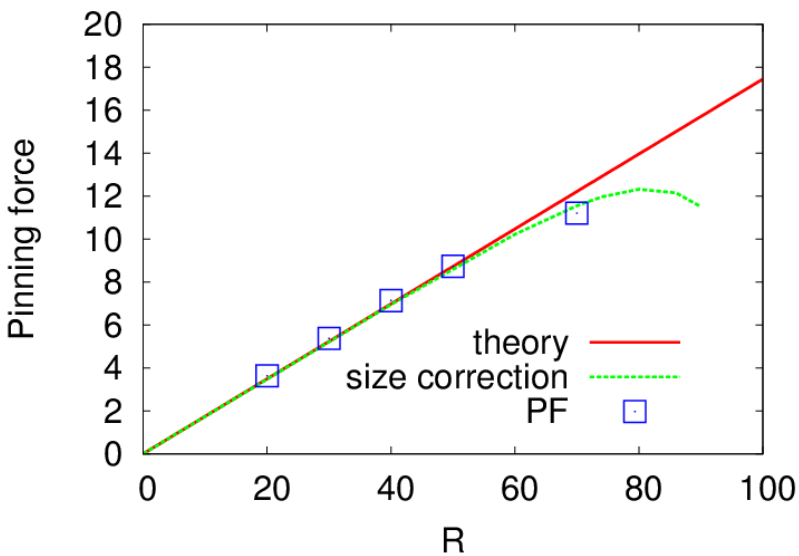
Spheriod particles

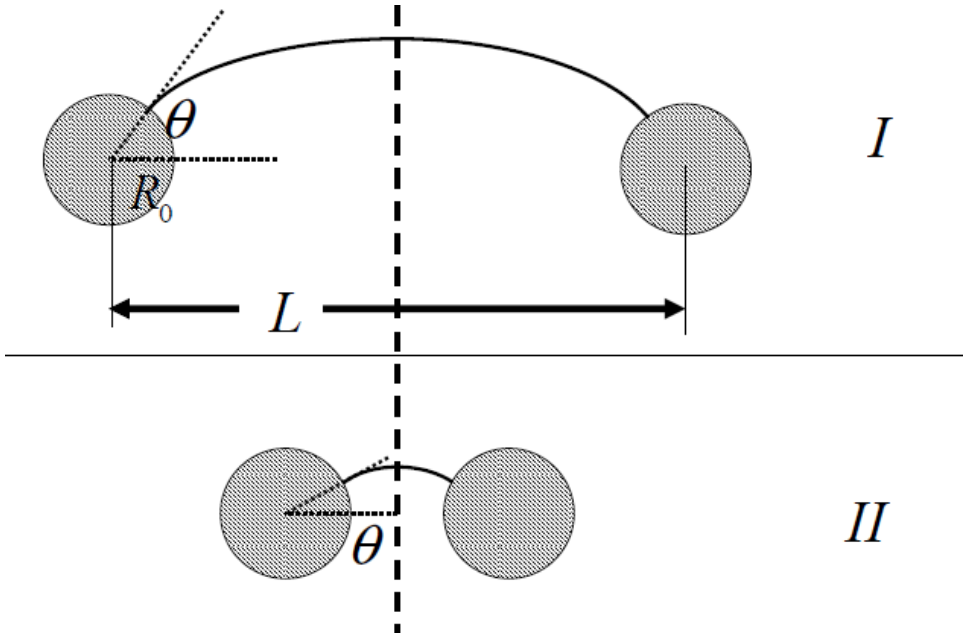
$$F_z^{theory} = \pi r_0 \gamma_{gb}(1+\cos\alpha)$$

$$\cos\alpha = \frac{\gamma_{inc} - \gamma_{coh}}{\gamma_{gb}}$$



Particle Spacing (volume fraction) Effect





Well separated:

$$L >> 2R$$

$$\theta^{\max} = \pi / 4$$

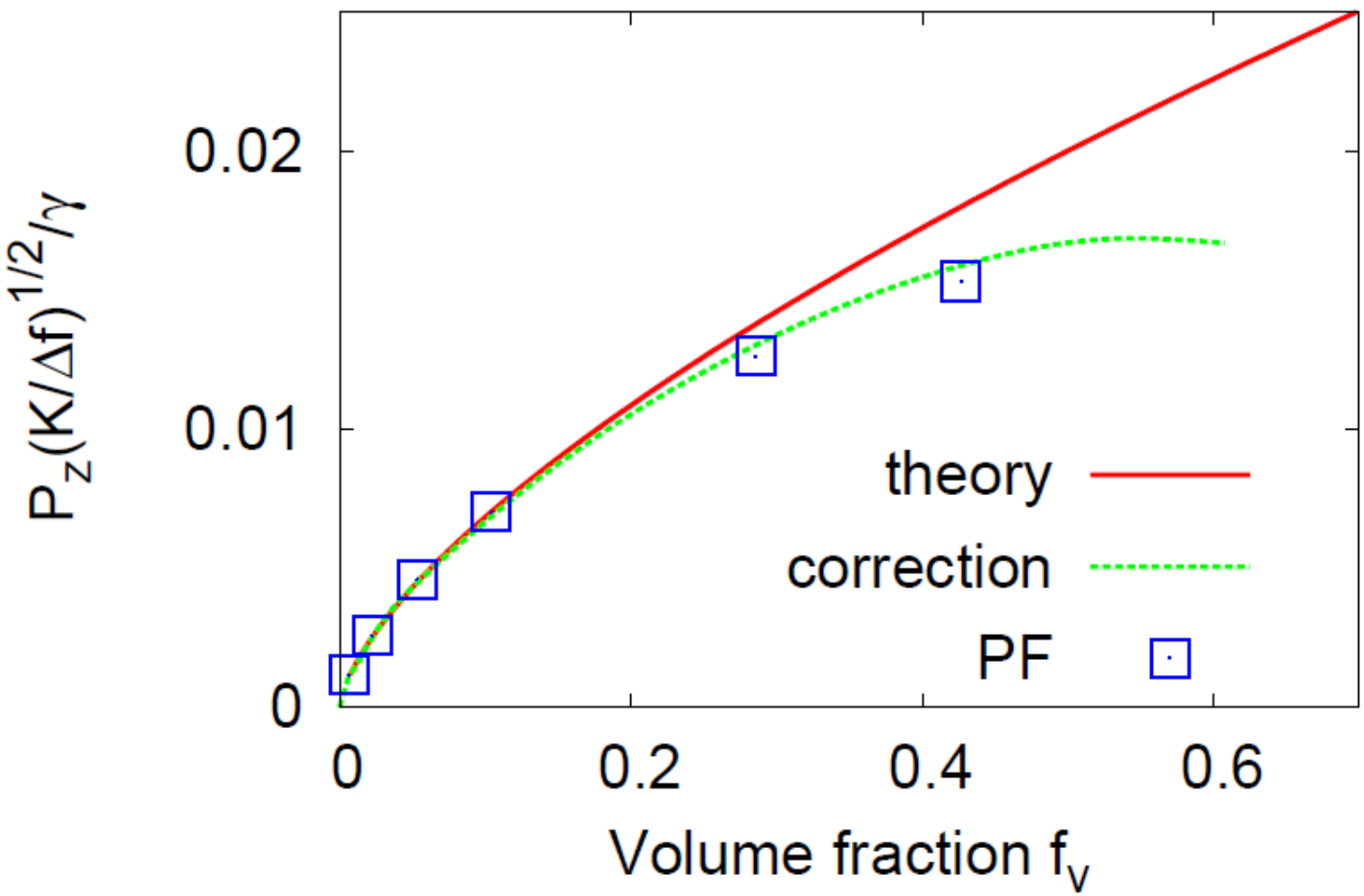
Close neighbor:

$$L \sim 2R$$

$$\theta^{\max} < \pi / 4$$

Cannot reach maximum pinning angle due to the constraint of inter-particle surface shape

Volume Fraction Effect for Spherical Particles



Smaller pinning force from close neighboring particles

Summary

- First quantitative evaluation for coherent particle pinning force
- New piece of particle pinning theory with spheroid
- Theoretical prediction of large volume fraction pinning force confirmed by Phase-field simulations

Future works

- Misfit strain effect for coherent/incoherent interface
- Grain growth modeling with pinning particles

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