Electrorheological Fluids: Mechanism and its Theoretical Description

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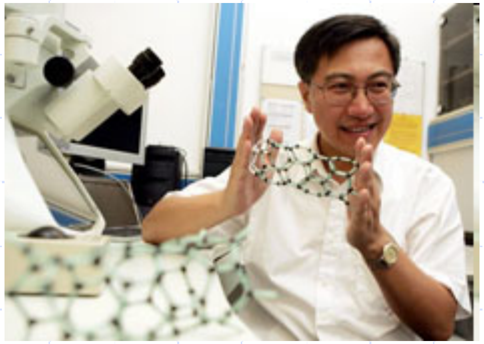


Ning Wang

Outline

Phenomenon

Mechanism

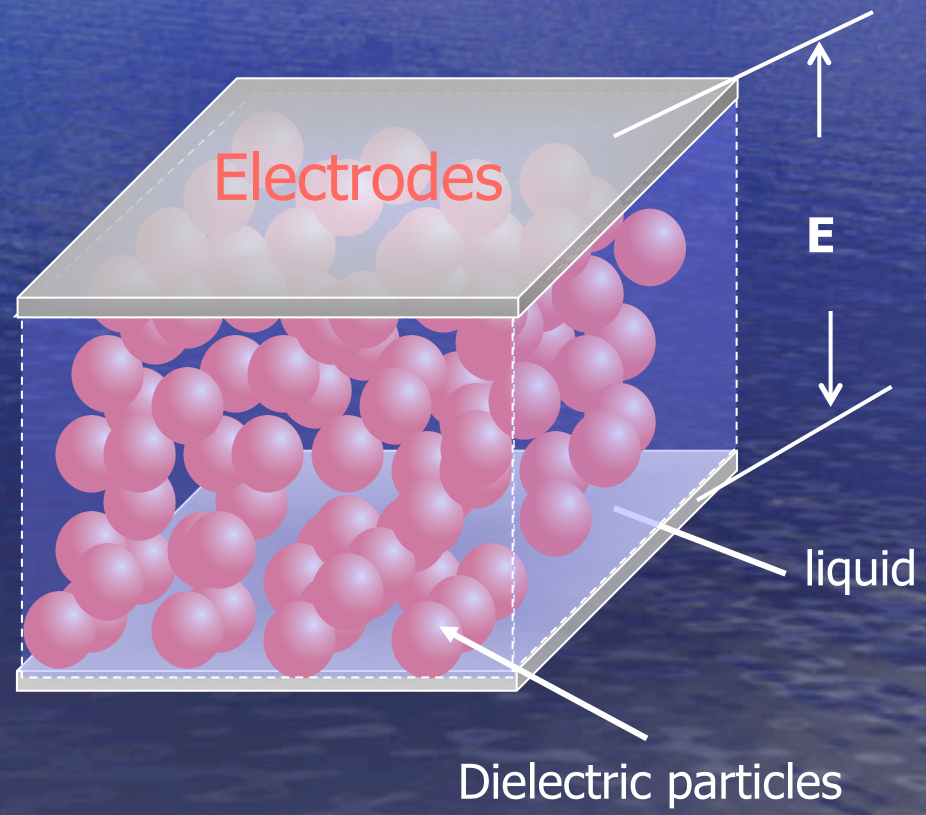
Formulation of the Simulation Approach

Predictions and Comparison with Experiments

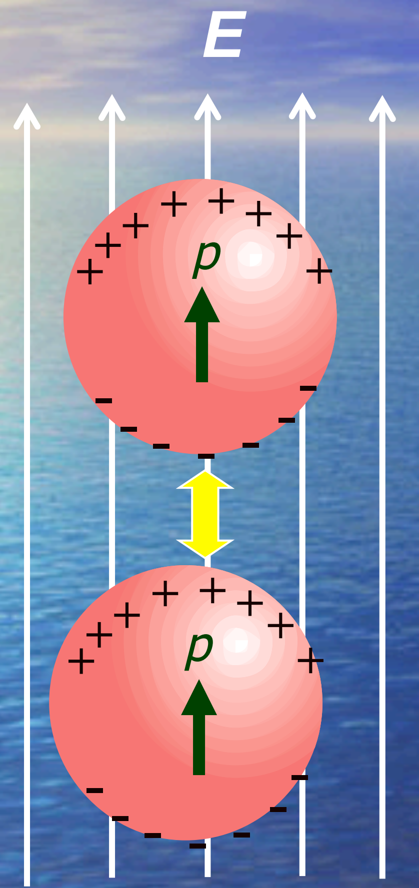
Outstanding Issue

Interaction of Nano/micro Particles with Electric Field

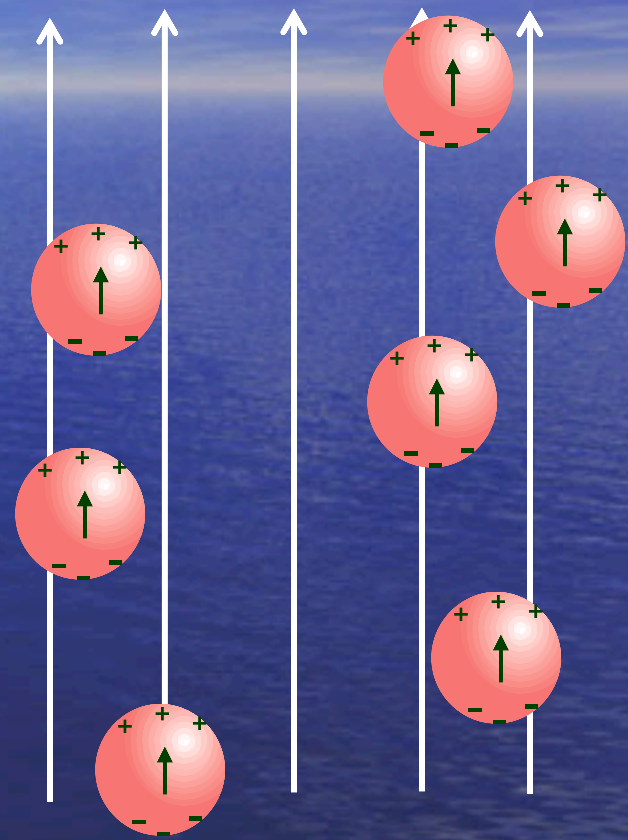
Electrorheology means changing the rheological characteristics through an electric field.
It can occur in colloids consisting of dielectric particles suspended in a nonconducting liquid.



The Heuristic Dipole Interaction Model



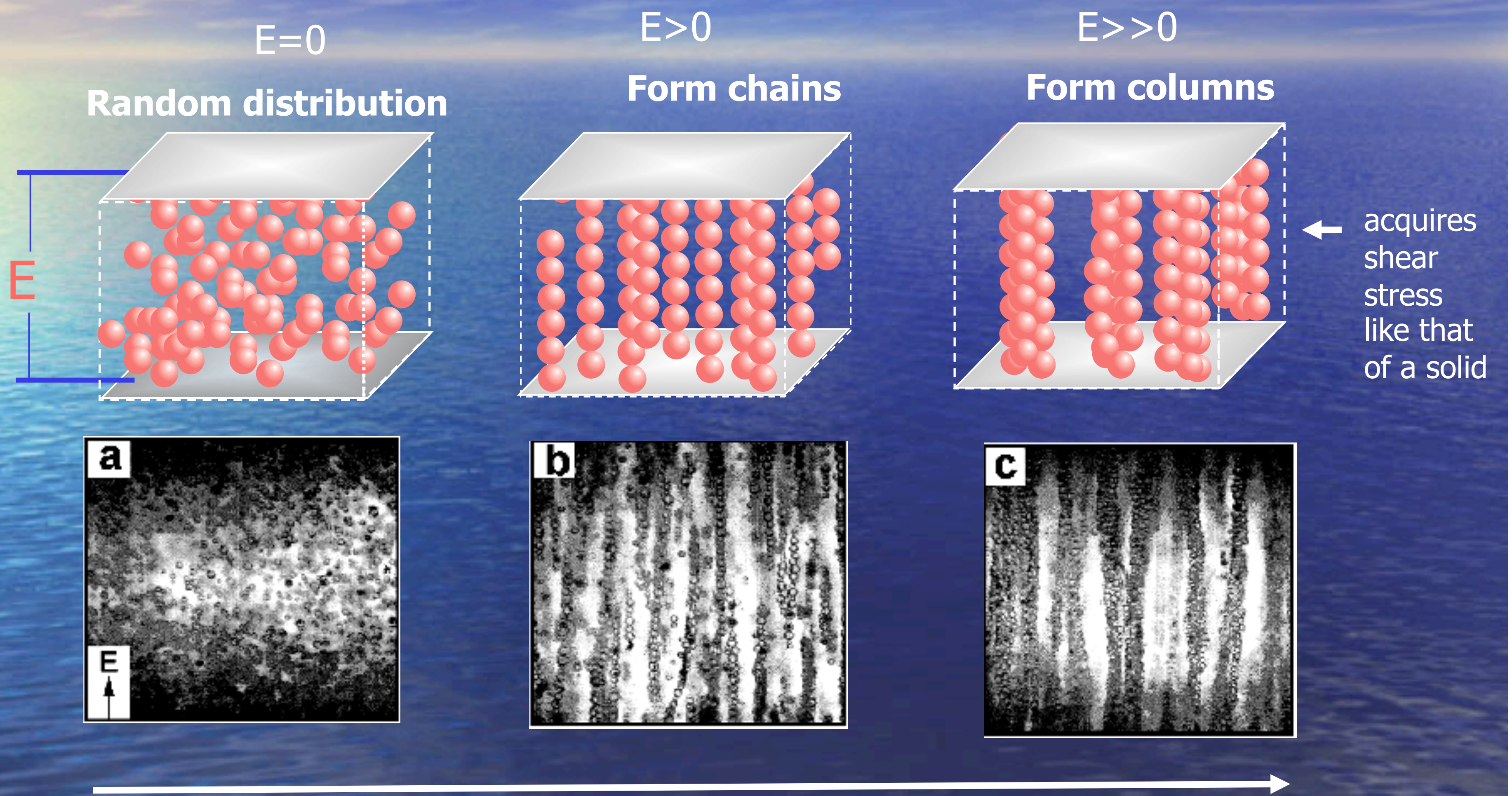
$$\vec{p} = \frac{\varepsilon_s - \varepsilon_\ell}{\varepsilon_s + 2\varepsilon_\ell} a^3 \vec{E} = \beta a^3 \vec{E}$$



Polarization induced by E-field

Chain formation

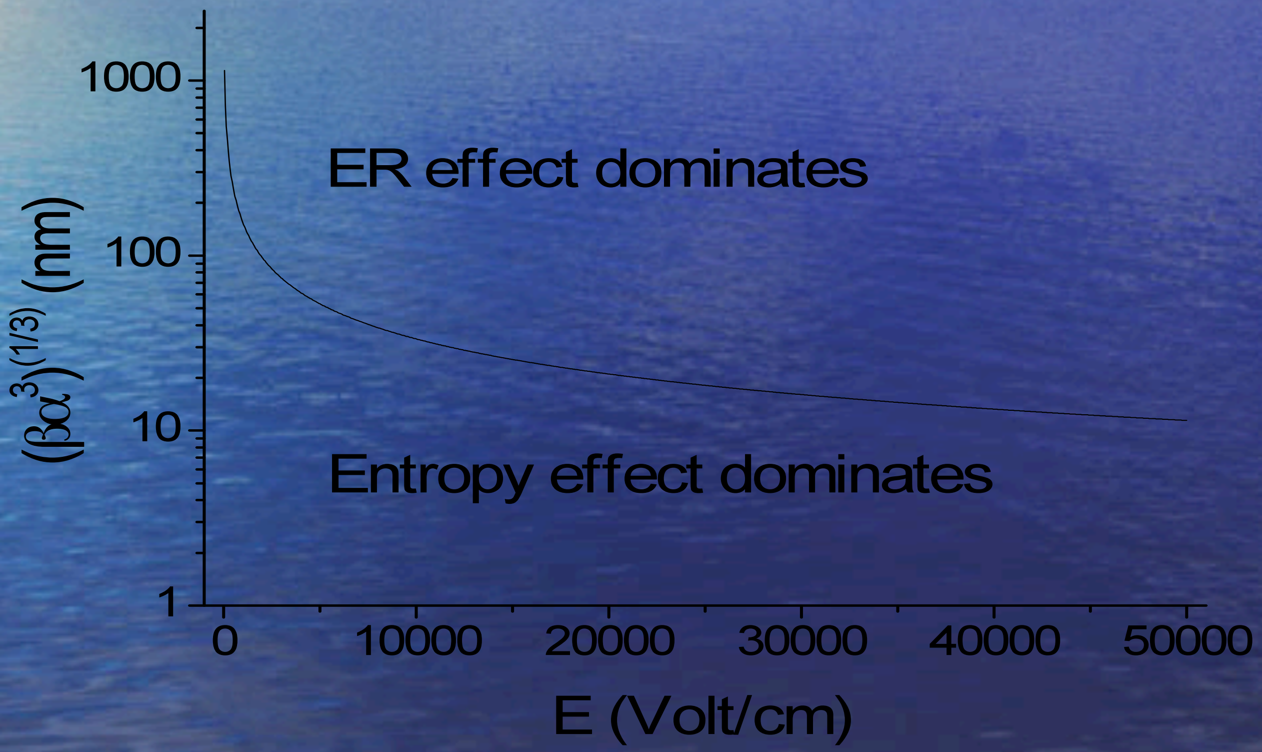
How does the ER fluid work?



~ 1-10 ms and reversible

Dependence on Particle Size

Competition between entropy and ER effect: $\vec{p} \cdot \vec{E} / k_B T = \beta a^3 E / k_B T$



Study of the ER Mechanism

- A structural transition always accompanies the rheological transformation.
  - The dipole interaction model can qualitatively explain the structural transition.

- Problems to be addressed
  - Multipole interactions are very important since the particles can be in close contact.
  - Local field effects have to be taken into account self-consistently.
  - What is the role of the conductivity (imaginary part of the dielectric constant)?
  - What is the particles' configuration in the high-field state?
  - How to calculate the shear modulus and the yield stress of the high-field state?
  - What are the upper bounds of the yield stress and the shear modulus?

Variational Formulation

- The applied electric field is always nearly DC.
- Response of the colloidal mixture is always captured by the effective dielectric constant tensor.

$$\begin{pmatrix} \overline{\varepsilon}_{xx} \overline{\varepsilon}_{xy} \overline{\varepsilon}_{xz} \\ \overline{\varepsilon}_{yx} \overline{\varepsilon}_{yy} \overline{\varepsilon}_{yz} \\ \overline{\varepsilon}_{zx} \overline{\varepsilon}_{zy} \overline{\varepsilon}_{zz} \end{pmatrix}$$

- Matrix elements of the effective dielectric constant tensor depend on the (a) volume fraction, (b) the relative ratio of the dielectric constants of the components, and (c)the *microstructure* (at high solid particle volume fractions).

Variational Formulation (continued)

- The overall electrostatic free energy is given by

  electrostatic free energy + T*(configuration entropy)

  - In the ER regime the first term dominates, given by

$$-\frac{1}{8\pi} Re\left\{\vec{E}\cdot\overleftrightarrow{\varepsilon}\cdot\vec{E}\right\} = Re\left\{-\frac{\bar{\varepsilon}_{zz}}{8\pi}E^2\right\}.$$

  - The high field ground state structure can be determined by maximizing $\bar{\varepsilon}_{zz}$ with respect to particle positions.

Calculation of $\bar{\varepsilon}_{zz}$

- Effective medium theories are the most common approach
  - Can not distinguish fine differences in the microstructure.
- Need a first-principles approach.

Calculation of $\bar{\varepsilon}_{zz}$ (continued)

- We use the Bergman-Milton representation of $\bar{\varepsilon}_{zz}$, which can be derived as follows.

$$\nabla \cdot \vec{D} = 0 \Rightarrow \nabla \cdot \varepsilon \nabla \phi = 0$$

$$\varepsilon = \varepsilon_s \eta(\vec{r}) + \varepsilon_\ell (1 - \eta(\vec{r}))$$

$$= \varepsilon_\ell \left[1 - \frac{(\varepsilon_\ell - \varepsilon_s)}{\varepsilon_\ell} \eta(\vec{r}) \right]$$

$$\eta(\vec{r}) = \begin{cases} 1 & \text{for } \vec{r} \text{ inside component 1} \\ 0 & \text{otherwise} \end{cases}$$

Calculation of $\bar{\varepsilon}_{zz}$ (continued)

$$\nabla \cdot \left[1 - \frac{1}{s}\eta(\vec{r})\right]\nabla\phi = 0, \qquad \Rightarrow \qquad \nabla^2\phi = \frac{1}{s}\nabla\cdot\eta(\vec{r})\nabla\phi$$

where $s = \varepsilon_\ell / (\varepsilon_\ell - \varepsilon_s).$ $\quad s \le 0 \quad or \quad s > 1$

$$\phi = z - \frac{1}{s}\int d\vec{r}\,'G(\vec{r},\vec{r}\,')\nabla'\cdot(\eta(\vec{r}\,')\nabla'\phi(\vec{r}\,')) = \phi_0 + \frac{1}{s}\Gamma\phi$$

$$\phi_0 = z$$

$$\Gamma = \frac{1}{V}\int d\vec{r}\,'\eta(\vec{r}\,')\nabla' G_0(\vec{r}-\vec{r}\,')\cdot\nabla'$$

Note: Γ contains only geometric information

$G_0(\vec{r}-\vec{r}\,') = 1/4\pi|\vec{r}-\vec{r}\,'|$ denotes the Green's function for the Laplace equation, and V the sample volume.

Calculation of $\bar{\varepsilon}_{zz}$ (continued)

The formal solution to $\varphi = z + s^{-1}\Gamma\varphi$, given the condition of $\Delta V / \ell = E = -1 = -\partial\phi / \partial z$ in the z direction, is

$$\phi = \left[(1 - \frac{1}{s}\Gamma)^{-1}\right] z = s\frac{z}{s - \Gamma},$$

it becomes possible to write the effective dielectric constant as

$$\bar{\varepsilon}_{zz} = \frac{1}{V}\int d\vec{r}\left[\varepsilon_2(1-\eta(\vec{r})) + \varepsilon_1\eta(\vec{r})\right]\frac{\partial\phi(\vec{r})}{\partial z} = \varepsilon_2\left(1 - \frac{1}{V}\int d\vec{r}\,\frac{1}{s}\eta(\vec{r})\frac{\partial\phi(\vec{r})}{\partial z}\right)$$

- By defining the inner product operation as

$$\langle\phi|\psi\rangle = \int d\vec{r}\,'\eta(\vec{r}\,')\nabla'\phi^* \cdot \nabla'\psi,$$

$$\bar{\varepsilon}_{zz} = \varepsilon_2\left[1 - \frac{1}{s}\langle z|\varphi\rangle\frac{1}{V}\right] = \varepsilon_2\left[1 - \frac{1}{V}\langle z|(s-\Gamma)^{-1}|z\rangle\right].$$

Calculation of $\bar{\varepsilon}_{zz}$ (continued)

From Eqs. (2) and (3), it follows that the effective dielectric constant is given by the Bergman-Milton representation:

- $$\frac{\bar{\varepsilon}_{zz}}{\varepsilon_2} = 1 - \frac{1}{V}\sum_{n,m}\langle z|\varphi_n\rangle\left\langle\varphi_n\left|\frac{1}{s-\Gamma}\right|\varphi_m\right\rangle\langle\varphi_m|z\rangle$$

$$= 1 - \frac{1}{V}\sum_n \frac{|\langle z|\varphi_n\rangle|^2}{s-s_n} = 1 - \sum_n \frac{f_n^z}{s-s_n}$$

- f_n^z, s_n are real numbers

  s_n is in the range of [0,1]

  $\Gamma\phi_n = s_n\phi_n$

  - The formalism is similar for coated particles.

Calculation of $\bar{\varepsilon}_{zz}$ (continued)

Under an electric field, the ER fluid is always a two-phase composite: a columnar phase and a liquid phase.

Hence

$$\bar{\varepsilon}_{zz} = \frac{p}{p_{col}} \bar{\varepsilon}^{zz}_{col} + \left(1 - \frac{p}{p_{col}}\right) \varepsilon_{\ell} .$$

The computational task is mainly focused on the calculation of $\bar{\varepsilon}^{zz}_{col}$.

Computational Formalism

- Use local basis functions $\chi_{\ell m}(\vec{r}-\vec{R}) = f_\ell(|\vec{r}-\vec{R}|)Y_{\ell m}(\theta,\phi)$ which are the local eigenfuctions of the $\mathbf{\Gamma}$ operator. These eigenfunctions can be obtained analytically.

- Obtain the matrix elements $\hat{\Gamma}_{\ell' m',\ell m}(\vec{R}-\vec{R}') = \langle \chi_{\ell' m'}(\vec{r}-\vec{R}') | \hat{\Gamma} | \chi_{\ell m}(\vec{r}-\vec{R}) \rangle$

- Define the operator $\hat{\Gamma}^{(0)}_{\ell m,\ell' m'} = \sum_{\vec{R}} \hat{\Gamma}_{\ell m,\ell' m'}(\vec{R})$ (microgeometry of the spheres' arrangement enters here). Then the (global) eigenfunction of the $\hat{\Gamma}^{(0)}$ operator is expressible as

$$\varphi_u^{(0)} = \sum_u \varphi_{\ell m}^{(u)} \chi_{\ell m} \quad .$$

Computational Formalism (continued)

- Then

$$\sum_{\ell',m'}\left(\delta_{\ell\ell'}\delta_{mm'}-\frac{1}{s_u}\hat{\Gamma}^{(0)}_{\ell m,\ell'm'}\right)\varphi^{(u)}_{\ell m}=0\,.$$

and

$$\bar{\varepsilon}^{zz}_{col}=\varepsilon_\ell\left(1-\frac{1}{V}\sum_u\frac{|\langle z|\varphi_u\rangle|^2}{s-s_u}\right)=\varepsilon_\ell\left(1-\frac{1}{V}\sum_{\vec{R},\ell,m}\sum_u\frac{|\langle z|\chi_{\ell m}\rangle\langle\chi_{\ell m}|\varphi^{(0)}_u\rangle|^2}{s-s_u}\right)$$

$$=\varepsilon_\ell\left(1-\frac{N}{V}\sum_u\sum_{\ell m}\frac{|z_{\ell m}\varphi^{(u)}_{\ell m}|^2}{s-s_u}\right)=\varepsilon_\ell\left(1-p_{col}\sum_u\frac{|\varphi^{(u)}_{10}|^2}{s-s_u}\right)$$

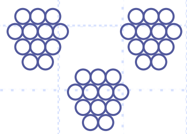
.

From which we obtain

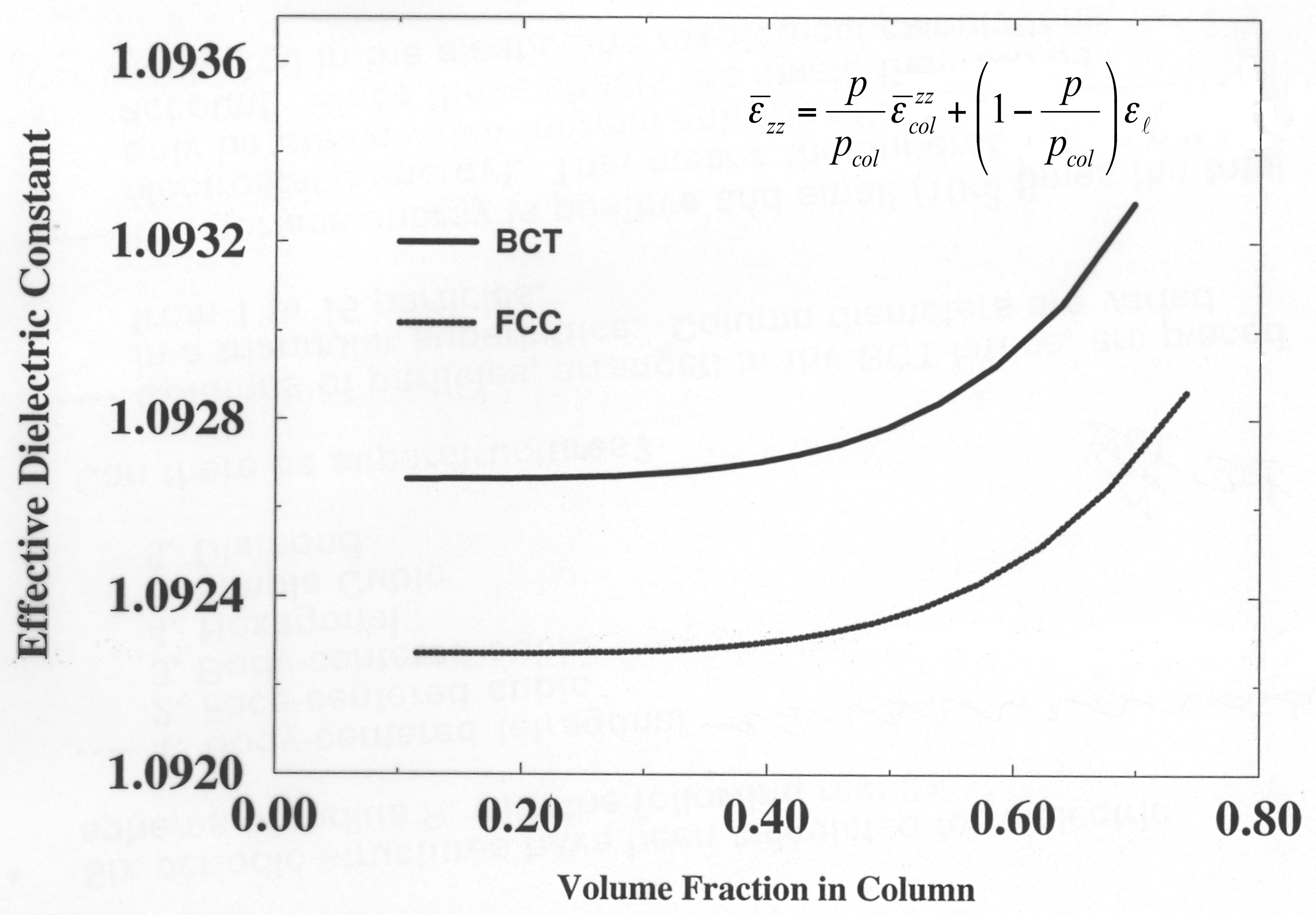
$$\bar{\varepsilon}_{zz}=\frac{p}{p_{col}}\bar{\varepsilon}^{zz}_{col}+\left(1-\frac{p}{p_{col}}\right)\varepsilon_\ell\,.$$

The Search for the Maximum $\bar{\varepsilon}_{zz}$

- Six periodic structures have been calculated for dielectric spheres of radius R, with the following results:
  - 1. Body-centered tetragonal
    2. Face-centered cubic
    3. Body-centered cubic
    4. Hexagonal
    5. Simple Cubic
    6. Diamond
- Can there be superstructures?
  - Columns of particles, arranged in the BCT lattice, are placed in a triangular superlattice. Column diameters are varied from 1 to 15 particles.



  - The surface energy is positive and small (10^{-3} times the total electrostatic energy). That means the superstructure can only be stable when thermal entropy effects are taken into account. Since these effects are small, they will be neglected in the elastic and rheological calculations.

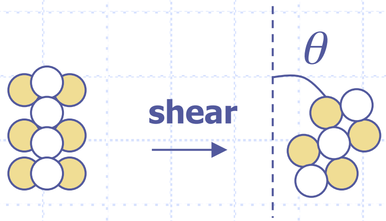


$\bar{\varepsilon}_{zz} = \frac{p}{p_{col}} \bar{\varepsilon}^{zz}_{col} + \left(1 - \frac{p}{p_{col}}\right) \varepsilon_{\ell}$
BCT
FCC
Effective Dielectric Constant
1.0936
1.0932
1.0928
1.0924
1.0920
0.00
0.20
0.40
0.60
0.80
Volume Fraction in Column

Shear Modulus Calculation

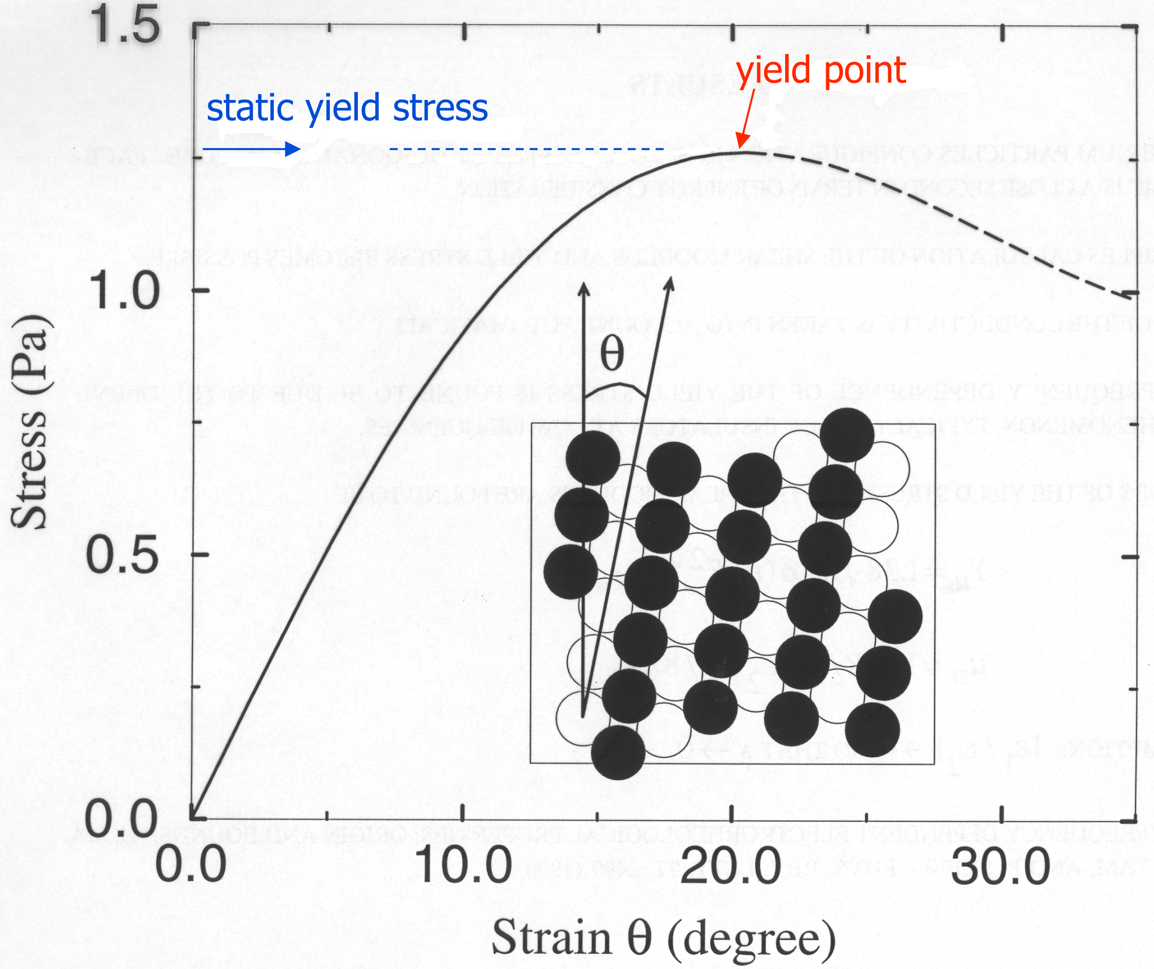
- To calculate elastic and rheological properties, it is necessary to perturb away from the electrostatic ground state.
  - Shearing not only tilt the *c*-axis away from the electric field direction by an angle θ, but also distort the lattice constants *c* and *a* by

$$c/R = 2/\cos\theta, \qquad a/R = [8-(c^2/2R^2)]^{1/2}$$



- For θ small, $\bar{\varepsilon}(\theta)$ may be expanded about its optimal value as

$$\frac{\bar{\varepsilon}(\theta)}{\varepsilon_2} = \frac{\bar{\varepsilon}(0)}{\varepsilon_2} - \frac{1}{2}\mu\theta^2 + --$$



static yield stress
yield point
1.5
1.0
0.5
0.0
Stress (Pa)
0.0
10.0
20.0
30.0
Strain θ (degree)
θ

Bounds on Electrorheological Properties

- ER properties depend sensitively on the magnitude of s. The lowest structural pole s_n=0 is for touching spheres. As s approaches zero, enhancement in electrorheological properties results.
  - $$\frac{\bar{\varepsilon}_{zz}}{\varepsilon_\ell} = 1 - \sum_n \frac{f_n^z}{s - s_n};$$
    $$s = \frac{\varepsilon_\ell}{\varepsilon_\ell - \varepsilon_s}$$
- To construct physical bounds for the yield stress and the shear modulus:
  (1) Let $|\varepsilon_s / \varepsilon_\ell| \to \infty. \Rightarrow s = 0$
  (2) The surfaces of the two spheres of radius R can not be closer to each other than 2 δ.
  - The upper bounds that result:

    Static yield stress $< 1.4\sqrt{R/\delta} * (|\varepsilon_\ell| E^2 / 8\pi).$

    Shear modulus $< 1.9(R/\delta) * (|\varepsilon_\ell| E^2 / 8\pi).$

    For R=20 microns, δ =1 Angstrom, E=1 KV/mm, and ε_ℓ =2.5 we have static yield stress <8KPa and shear modulus <11MPa.

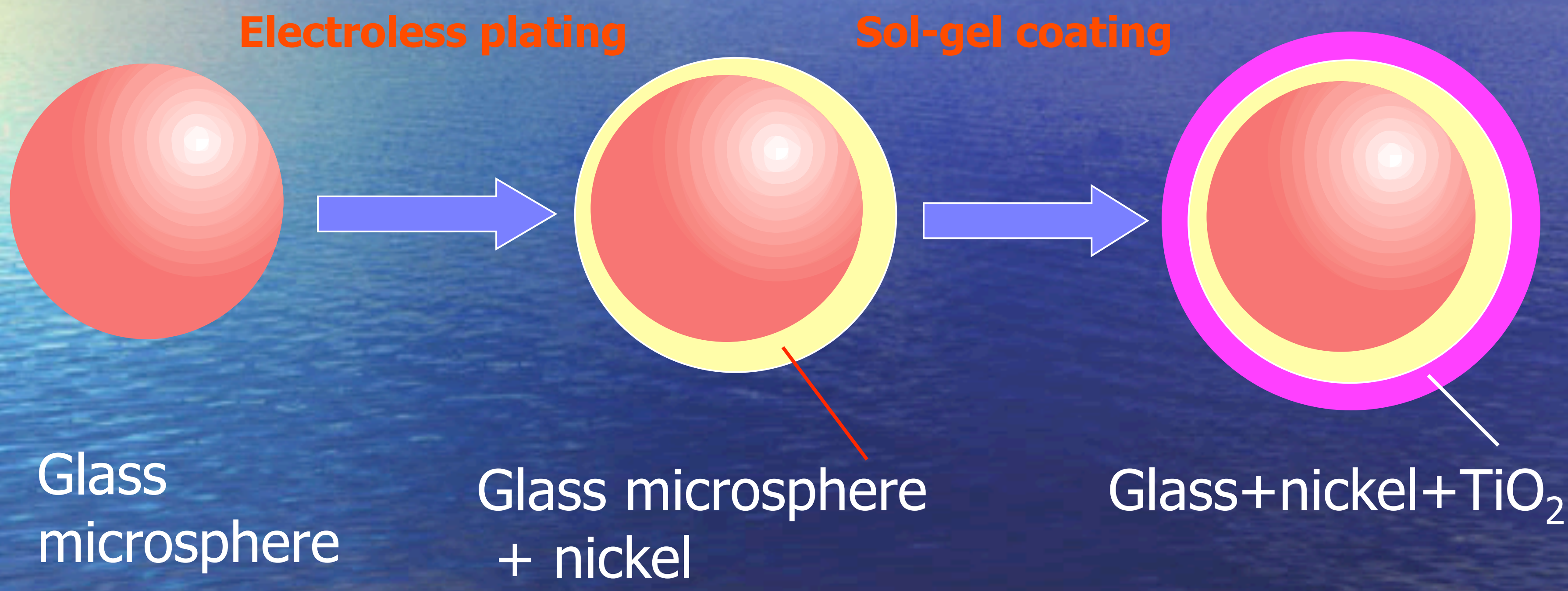
Heuristic Derivation of the $\sqrt{R/\delta}$ Upper Bound Form

- Mutual capacitance between two perfectly conducting spheres of radius R and surface to surface separation δ :
  - $C \sim ln\frac{R}{\delta}$ for $R >> \delta$
  - When the line joining the centers of the two spheres is tilted by θ with respect to the electric field,

    $\delta' \approx \delta + R\theta^2$ for $small\ \theta$ $\Rightarrow$ $\theta = \sqrt{\frac{\delta' - \delta}{R}}$
  - Shear stress $\propto -\frac{\partial C}{\partial \theta} \propto \frac{R}{\delta'}[(\delta' - \delta)/R]^{1/2}$, which peaks at $\delta' = 2\delta$
  - Therefore yield stress $\propto \sqrt{\frac{R}{\delta}}$

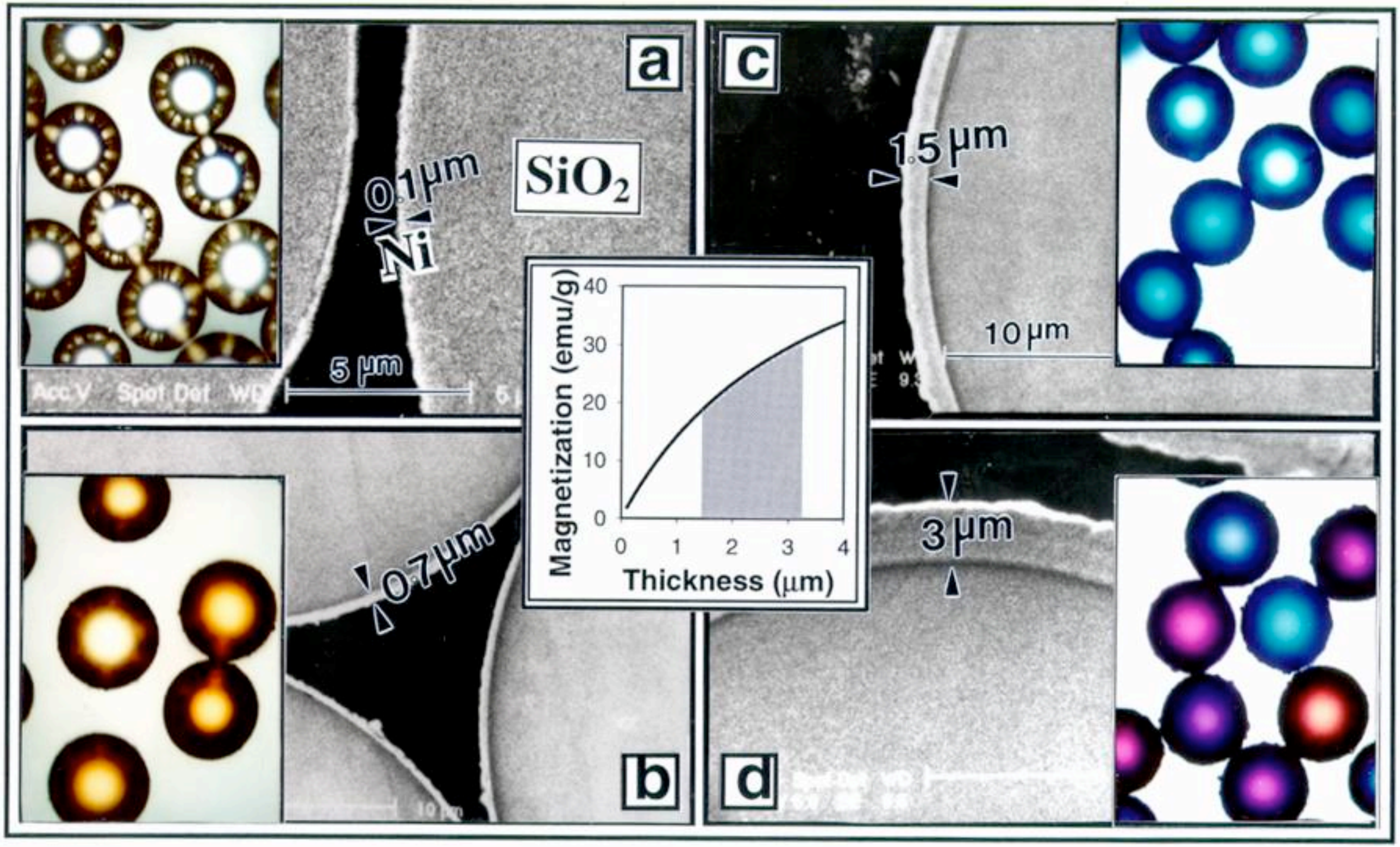
Idea of Surface Coating

- **Directly derived from theoretical upper bound**



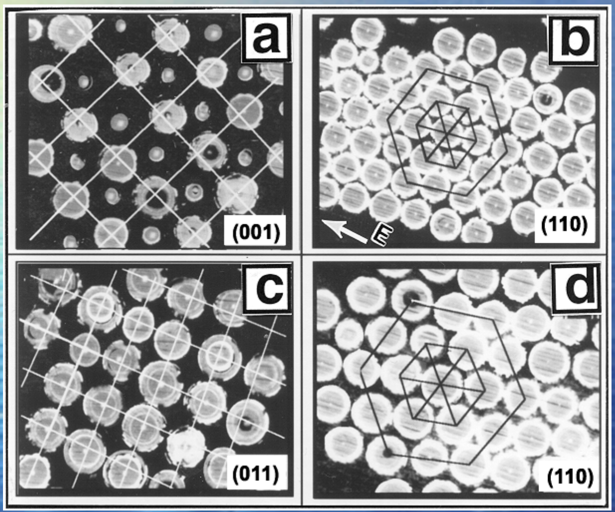
Use coated spheres to verify the ground state structure as well as the upper bound predictions

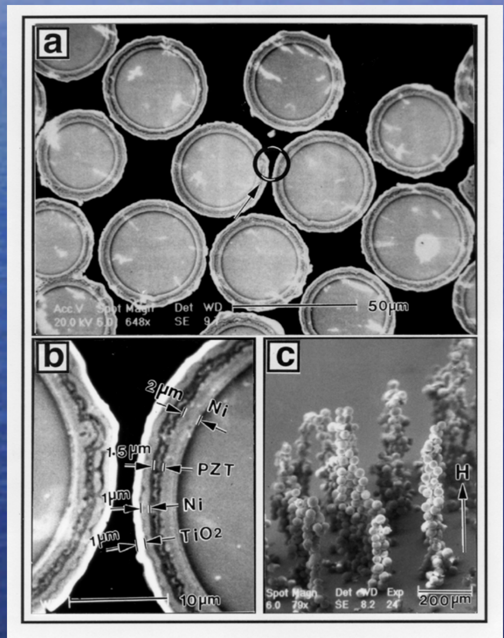
Coated Microspheres Fabrication

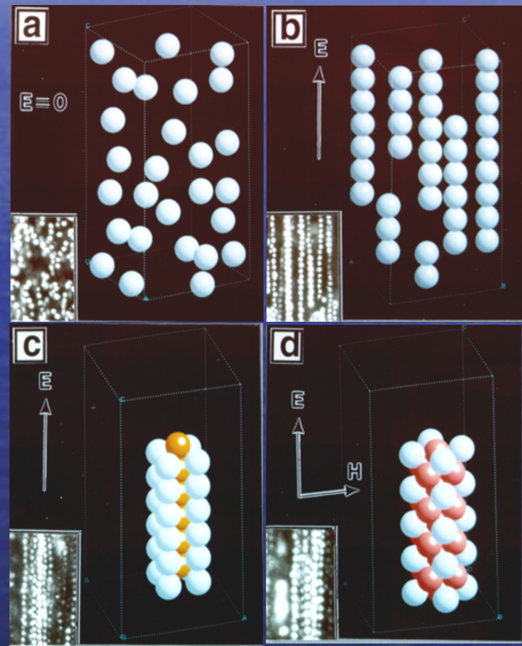


Structures of ER Suspensions Using Coated Microspheres

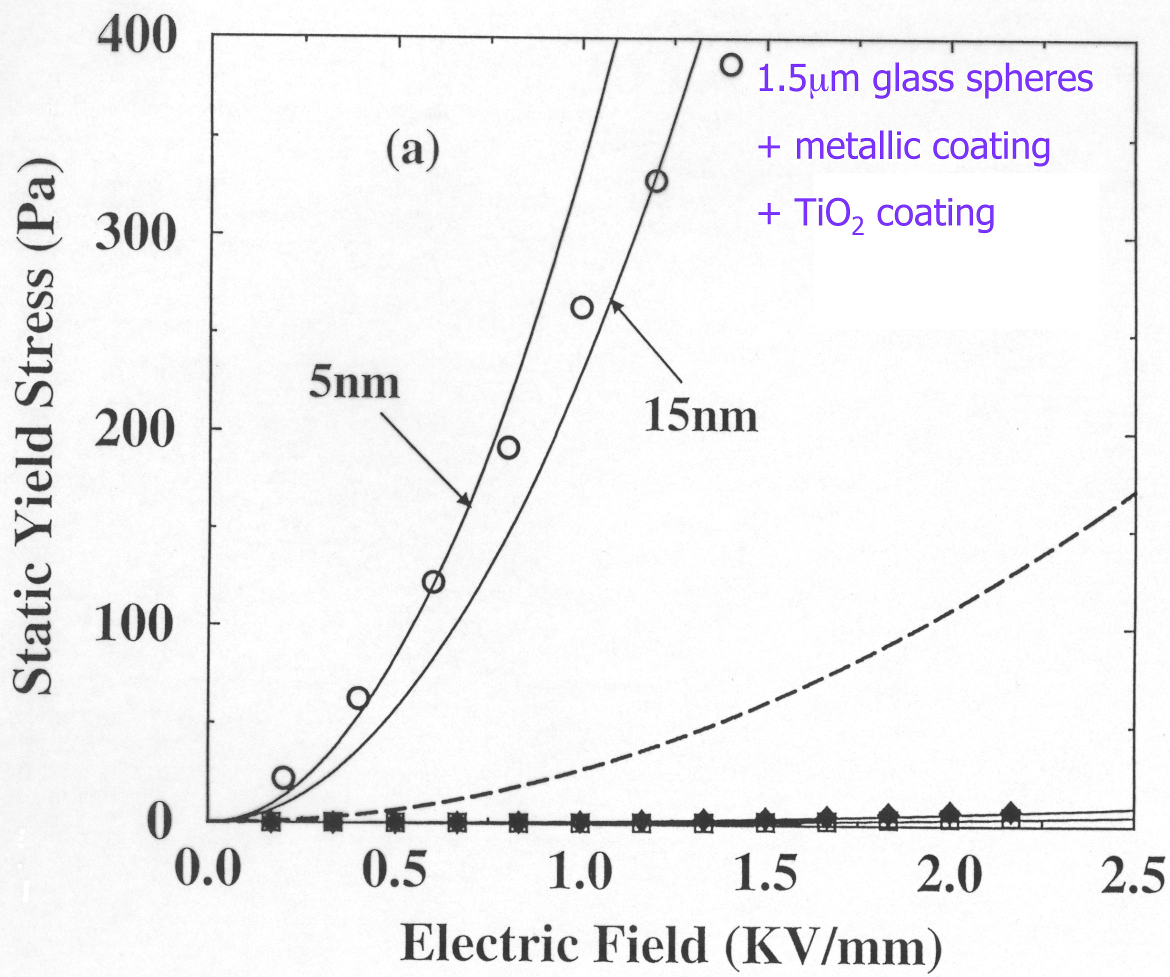
SEM cross-sectional images



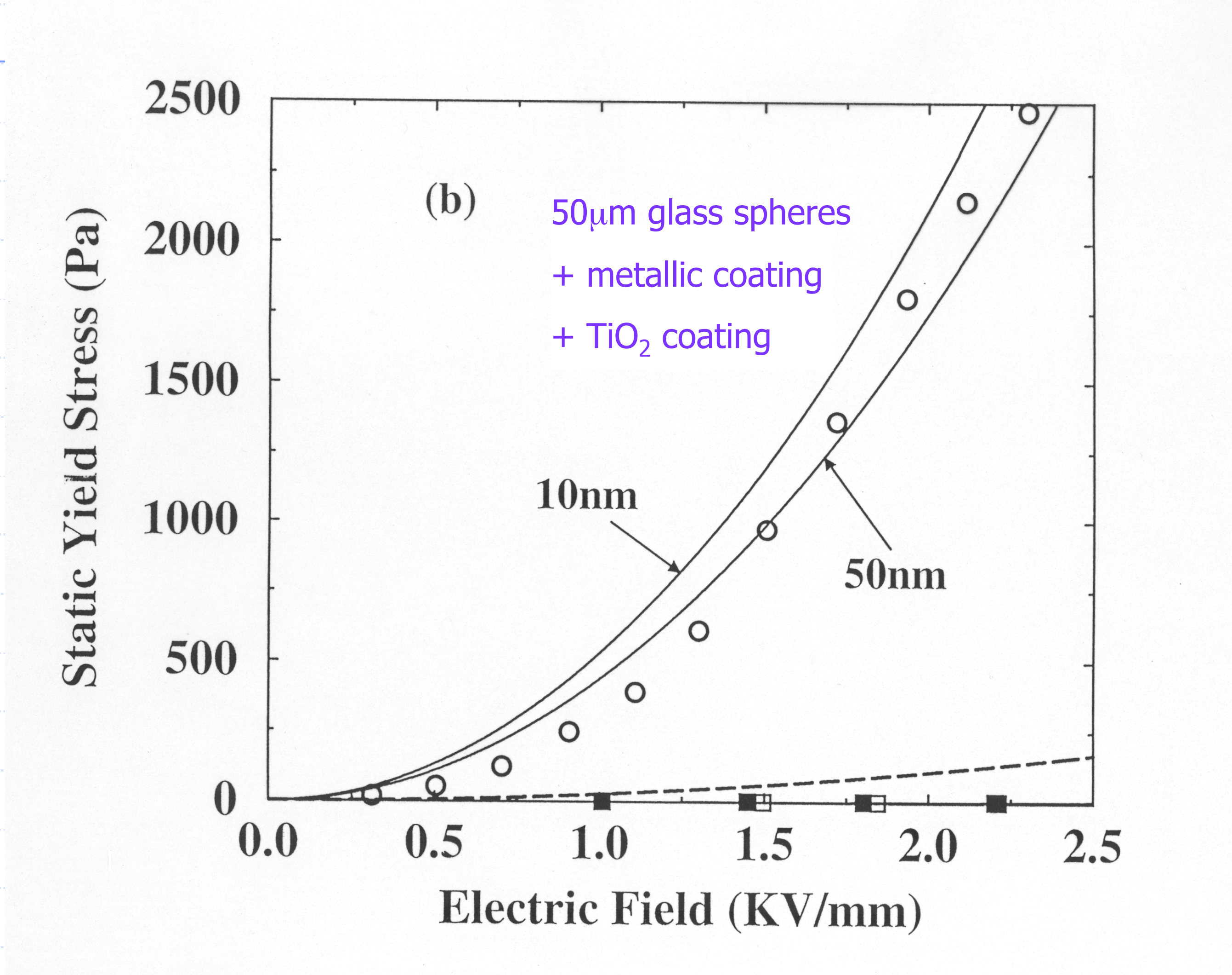




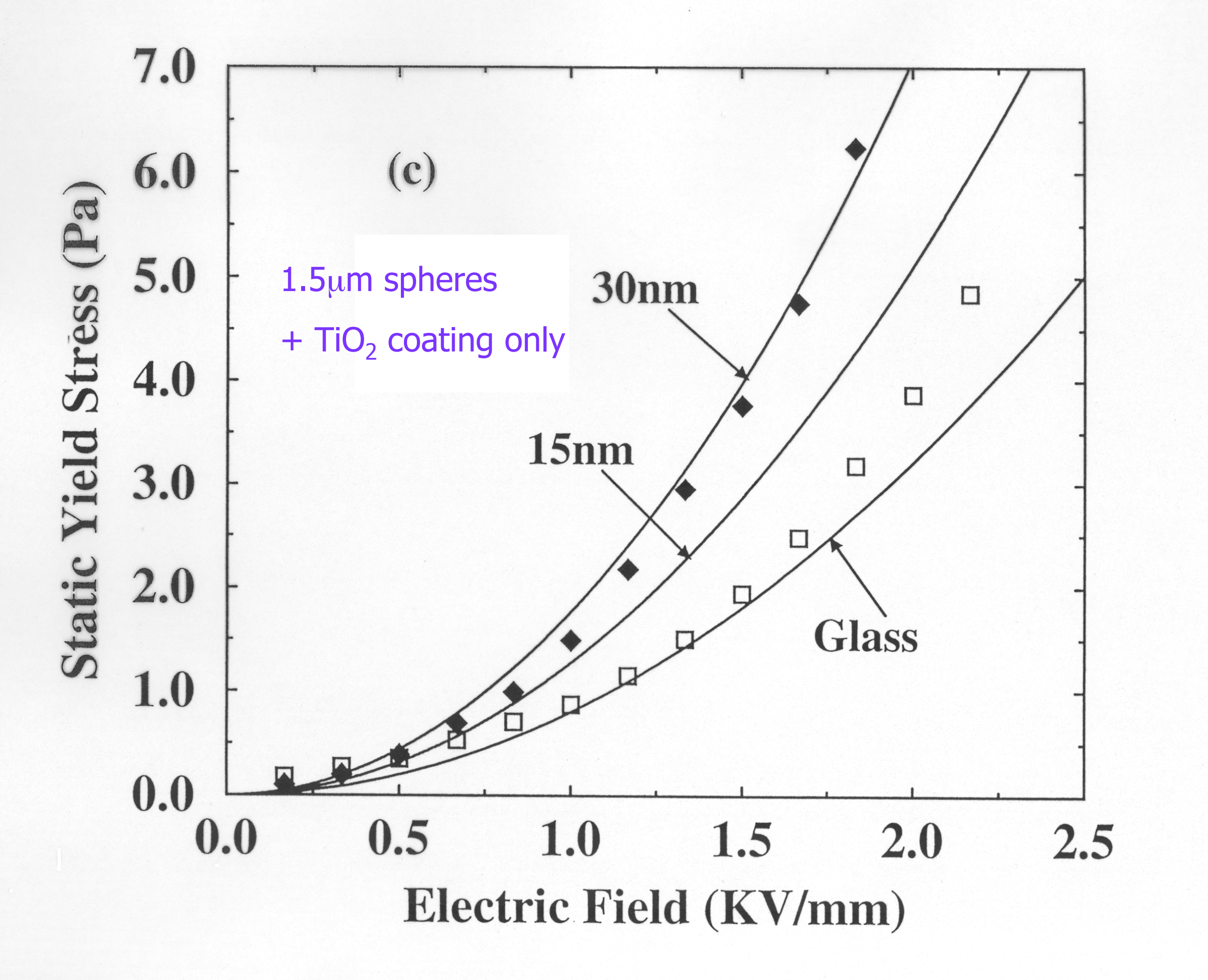
BCT-FCC transition



400
300
200
100
0
0.0
0.5
1.0
1.5
2.0
2.5
Static Yield Stress (Pa)
Electric Field (KV/mm)
(a)
5nm
15nm
1.5μm glass spheres
+ metallic coating
+ TiO2 coating



(b)
50μm glass spheres
+ metallic coating
+ TiO2 coating
10nm
50nm
Static Yield Stress (Pa)
2500
2000
1500
1000
500
0
0.0
0.5
1.0
1.5
2.0
2.5
Electric Field (KV/mm)

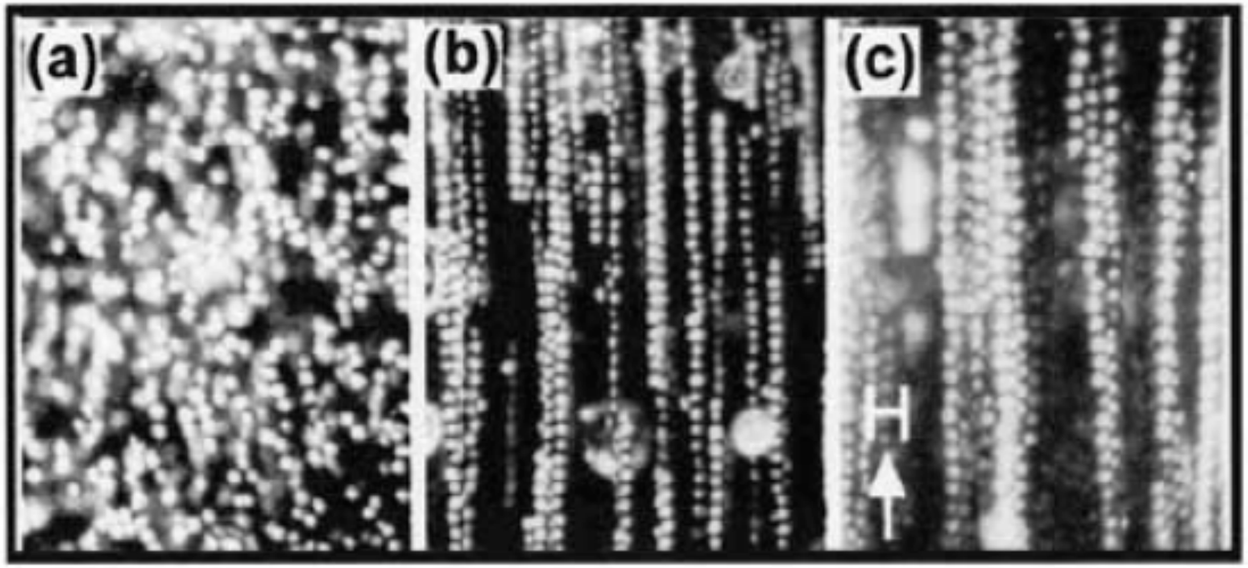


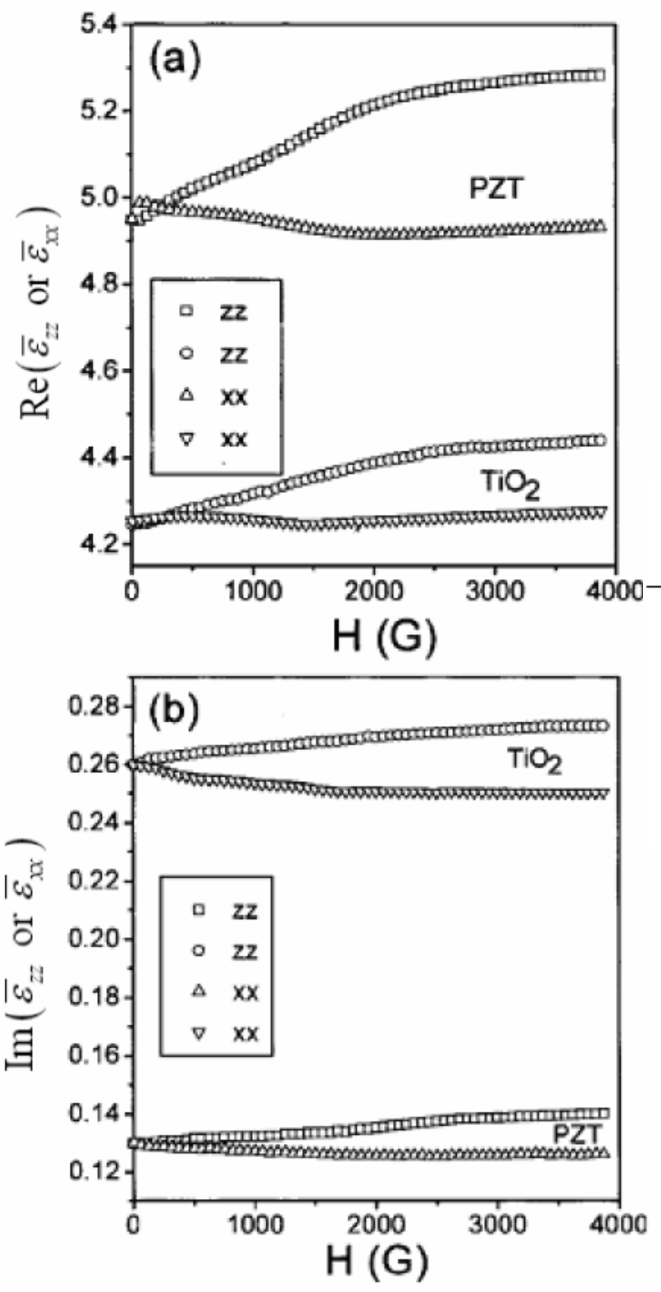
Static Yield Stress (Pa)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(c)
1.5μm spheres
+ TiO2 coating only
30nm
15nm
Glass
0.0
0.5
1.0
1.5
2.0
2.5
Electric Field (KV/mm)

To Verify the Nonlinearity of the Electrical Response

(Dielectric constant $\bar{\varepsilon}_{zz}$ increases with column formation)

To facilitate the electrical measurement, magnetic field was used to induce the column formation.





Structure		Theory		Experiment	
		Re($\bar{\varepsilon}$)	Im($\bar{\varepsilon}$)	Re($\bar{\varepsilon}$)	Im($\bar{\varepsilon}$)
Random		Fitted	Fitted	4.95	0.13
PZT coating	*zz*	5.67	0.23	5.29	0.14
	xx	4.75	0.11	4.94	0.12
Random		Fitted	Fitted	4.26	0.26
TiO_2 coating	*zz*	4.56	0.37	4.44	0.28
	xx	4.15	0.23	4.25	0.25

Issue Still Remaining to be Resolved

Question: Why is there a threshold field?

- Basic idea: Energy landscape is not smooth. Many metastable states.
- The variance of the energy landscape fluctuations is electric field dependent.

Work ongoing, in collaboration with

Ken Golden and Ben Murphy

Reference

Annual Review of Fluid Mechanics 44, 143-174 (2012)

Thanks for Your Attention!