Nano-Composite Material Properties: Homogenization Over Flow-induced Orientational Distribution

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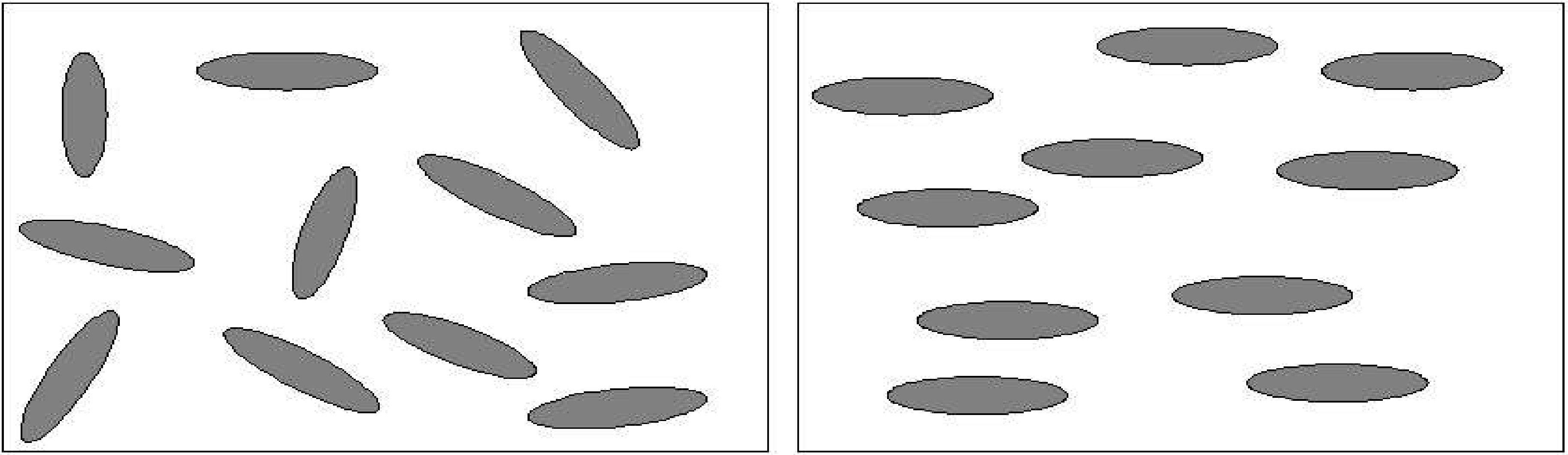
Dispersions of High Aspect Ratio Spheroids



Random oriented ellipsoids
(isotropic phase)

Aligned ellipsoids
(nematic phase)

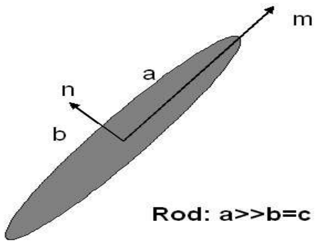
Our purpose is to develop a model which can describe the electrical (or thermal) conductivity of nano-composites due to the

- orientational distribution of the nano particle ensemble; and
- volume fractions and properties of nano inclusions and matrix, and
- geometry of the inclusions.

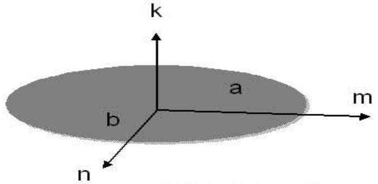
Motivation

We consider suspensions of spheroidal inclusions with *isotropic electrical conductivity* $\sigma_2\mathbf{I}$ and volume fraction θ_2 in an *isotropic matrix of electrical conductivity* $\sigma_1\mathbf{I}$.

Monodispersity: we assume spheroids have the same geometry: a, b, c are the three semi-axes, with $a \gg b = c$ for thin rods $a = b \gg c$ for platelets. The ensemble of macromolecules orients according to a probability distribution that is the central object of the Doi-Hess kinetic theory, in quiescent or flow-induced phases.



Rod: a>>b=c



Platelet: a=b>>c

Electrical (Thermal) Conduction Problem

- Local Relations:

$$\vec{J}(x) = \sigma(x)\vec{E}(x), \quad \nabla \cdot \vec{J}(x) = 0, \quad \nabla \times \vec{E}(x) = 0$$

where $\vec{J}(x)$ is the electric current field (thermal flux), $\vec{E}(x) = -\nabla\phi$ is the electric field (negative of the temperature gradient filed), ϕ is the electric potential (temperature), $\sigma(x)$ is the local conductivity tensor which can be expressed as

$$\sigma(x) = (\sigma_1\chi^{(1)}(x) + \sigma_2\chi^{(2)}(x))\mathbf{I}$$

$\chi^{(i)}$ is the indicator function for phase i.

- Homogenization: The effective conductivity is defined by an averaged Ohm's Law:

$$\langle\vec{J}(x)\rangle = \sigma^e \cdot \langle\vec{E}(x)\rangle.$$

Model Problem in $\mathcal{R}^3$

The potential ϕ is governed by variable coefficient elliptic equation within and outside the ellipsoids:

$$-\nabla \cdot (\sigma(x)\nabla\phi) = f(x) \text{ in } \Omega$$

subject to the boundary conditions:

$$\begin{cases} \phi^- = \phi^+, & \text{on the phase boundary} \\ \sigma^+\partial_n\phi^+ = \sigma^-\partial_n\phi^-, & \text{on the phase boundary} \end{cases}$$

The superscripts $+$ *and* $-$ *denote its limits from the right and left to the boundary, respectively.*

Effective Conductivity Formula

The effective conductivity σ^e can be computed by a Taylor expansion in low volume fraction θ_2 (*Stratton, 1941*):

$$\sigma^e = \sigma_1 I + \theta_2(\sigma_2 - \sigma_1) \int_{S^2} E(\mathbf{m}) f(\mathbf{m}) d\mathbf{m} + O(\theta_2^2)$$

where

- $E(\mathbf{m})$ is the polarization tensor of the cell problem;
- and $f(\mathbf{m})$ is the orientational probability density function of the inclusions.

Strategy:

- simplify $E(\mathbf{m})$ for nano-composite geometry, leads to remarkable simplification of σ^e for *any* $f(\mathbf{m})$.
- use knowledge of $f(\mathbf{m})$ from kinetic, mesoscopic theory, or experimental databases.

Polarization Tensor

- Depolarization factors $L_a, L_b, L_c \geq 0$

$$L_a = \frac{abc}{2} \int_0^\infty \frac{ds}{(s+a^2)\sqrt{(s+a^2)(s+b^2)(s+c^2)}}$$

$$L_b = \frac{abc}{2} \int_0^\infty \frac{ds}{(s+b^2)\sqrt{(s+a^2)(s+b^2)(s+c^2)}}$$

$$L_c = \frac{abc}{2} \int_0^\infty \frac{ds}{(s+c^2)\sqrt{(s+a^2)(s+b^2)(s+c^2)}}$$

$$L_a + L_b + L_c = 1$$

-

$$E(\mathbf{m}) = \left[\left(1 + \left(\frac{\sigma_2 - \sigma_1}{\sigma_1} \right) L_a \right) \mathbf{mm} + \left(1 + \left(\frac{\sigma_2 - \sigma_1}{\sigma_1} \right) L_b \right) \mathbf{nn} \right.$$
$$\left. + \left(1 + \left(\frac{\sigma_2 - \sigma_1}{\sigma_1} \right) L_c \right) \mathbf{kk} \right]^{-1}$$

Exact Scaling Law

A series of observations follow from the spheroidal assumption: $L_b = L_c = (1 - L_a)/2$, and $\mathbf{mm} + \mathbf{nn} + \mathbf{kk} = \mathbf{I}$,$(\mathbf{I} + b\mathbf{mm})^{-1} = \alpha \mathbf{I} + \beta \mathbf{mm}$, $f(\mathbf{m})$ has a spherical harmonic expansion, orthogonality of spherical harmonics, and $\cdots$ we deduce:

♠

$$\begin{aligned}\sigma^e =& \sigma_1 \mathbf{I} + \sigma_1\, \theta_2 (\sigma_2 - \sigma_1) \left(\frac{2}{\sigma_2 + \sigma_1 - (\sigma_2 - \sigma_1) L_a} \mathbf{I} \right. \\ & \left. + \frac{(\sigma_2 - \sigma_1)(1 - 3L_a)}{((\sigma_1 + \sigma_2) - (\sigma_2 - \sigma_1) L_a)(\sigma_1 + (\sigma_2 - \sigma_1) L_a)} \; \mathbf{M}(f) \right) + O(\theta_2^2).\end{aligned}$$

- Only the second moment of $f(\mathbf{m})$ contributes to the leading order conductivity tensor!
- principal axes of σ^e follow from those of $\mathbf{M}$.

Define the relative conductivity enhancement $\mathcal{E}_j$, measuring the composite principal conductivities relative to the matrix:

$$\mathcal{E}_j = \frac{\sigma_j^e - \sigma_1}{\sigma_1}$$

Doi-Hess Kinetic Theory: Orientation of Inclusions

Doi-Hess Equation for the probability density function $f(\mathbf{m}, t)$, where $\mathbf{m} \in S^2$ represents the molecule direction:

$$\frac{Df}{Dt} = \mathcal{R} \cdot [D_r(\mathbf{m}, a)(\mathcal{R}f + \frac{1}{kT} f \mathcal{R} V_{MS})] - \mathcal{R} \cdot [\mathbf{m} \times \dot{\mathbf{m}} f]$$

- $\frac{D}{Dt}(\bullet) = \frac{\partial}{\partial t} + \mathbf{v} \cdot \bigtriangledown(\bullet)$, $\mathbf{v}$ –fluid velocity.
- $\mathcal{R} = \mathbf{m} \times \frac{\partial}{\partial \mathbf{m}}$ – rotational gradient operator.
- $D_r(\mathbf{m}, \mathbf{a})$ – rotary diffusion coefficient. $a = \frac{r^2 - 1}{r^2 + 1}$ aspect ratio parameter.
- $\dot{\mathbf{m}} = \Omega \cdot \mathbf{m} + \mathbf{a}[\mathbf{D} \cdot \mathbf{m} - \mathbf{D} : \mathbf{mmm}]$ – the Jeffery orbit of ellipsoids.
- $V_{MS} = -\frac{3NkT}{2} \langle \mathbf{mm} \rangle : \mathbf{mm}$ – Maier-Saupe potential.
- $\mathbf{N} \propto \nu l^{\mathbf{2}} \mathbf{d}$ – dimensionless polymer concentration.

High Contrast Conductivity & Extreme Aspect Ratio

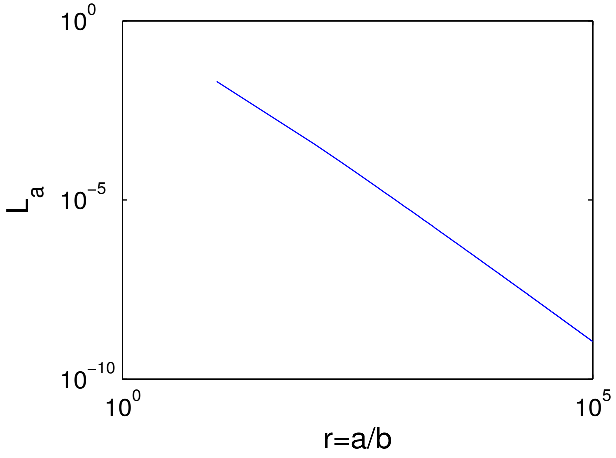
Two features specfic to nematic polymer and CNT composite:

- High contrast conductivities, where the nano-inclusion has extreme conductivity σ_2 relative to the matrix value σ_1,

$$\sigma_1/\sigma_2 \ll 1.$$

- High aspect ratio ($r \gg 1$), spheroidal nano-inclusions, satisfy $a \gg b = c$; then L_a admits the asymptotic evaluation:

$$\begin{aligned} L_a =& \frac{1-\epsilon^2}{\epsilon}\left\{\frac{1}{2\epsilon}\ln\left(\frac{1+\epsilon}{1-\epsilon}\right)-1\right\} \\ &\sim (\log(r)/r^2) + O(r^{-2}) \text{ for } r \gg 1; \\ \epsilon =& \sqrt{1-(1/r)^2}. \end{aligned}$$



Finer Estimates

Recall principal values σ_j^e of σ^e, eigenvalue d_j of $\mathbf{M}$.

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$$\text{For } \frac{L_a}{\sigma_2/\sigma_1} \gg 1 \left\{ \begin{array}{lcl} \sigma^e & = & \sigma_1 \mathbf{I} + \dfrac{\sigma_1\theta_2}{L_a}\mathbf{M} + O(\theta_2\sigma_1)\mathbf{I} + \mathbf{O}(\boldsymbol{\theta_2\sigma_1})\mathbf{M} + \mathbf{O}(\boldsymbol{\theta_2^2}), \\ \mathcal{E}_j & = & \dfrac{\sigma_j^e - \sigma_1}{\sigma_1} = \dfrac{\theta_2}{L_a} d_j + O(\theta_2), \quad j = 1, 2, 3. \end{array} \right.$$

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$$\text{For } \frac{L_a}{\sigma_2/\sigma_1} \sim 1 \left\{ \begin{array}{lcl} \sigma^e & = & \sigma_1 \mathbf{I} + \dfrac{\theta_2\sigma_2}{1 + \dfrac{L_a}{\sigma_1/\sigma_2}}\mathbf{M} + O(\theta_2\sigma_1)\mathbf{I} + O(\theta_2\sigma_1)\mathbf{M} + O(\theta_2^2), \\ \mathcal{E}_j & = & \dfrac{\theta_2(\sigma_2/\sigma_1)}{1 + \dfrac{L_a}{\sigma_1/\sigma_2}} d_j + O(\theta_2), \quad j = 1, 2, 3. \end{array} \right.$$

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$$\text{For } \frac{L_a}{\sigma_2/\sigma_1} \ll 1 \left\{ \begin{array}{lcl} \sigma^e & = & \sigma_1 \mathbf{I} + \theta_2\sigma_2 \mathbf{M} + O(\theta_2\sigma_1)\mathbf{I} + O(\theta_2\sigma_1)\mathbf{M} + O(\theta_2^2), \\ \mathcal{E}_j & = & \theta_2(\sigma_2/\sigma_1)\, d_j + O(\theta_2), \quad j = 1, 2, 3. \end{array} \right.$$

Application I :σ^e in quiescent isotropic regime

For isotropic phases, $f = \dfrac{1}{4\pi}, \mathbf{M}(f) = \dfrac{\mathbf{I}}{3}$, then the effective conductivity tensor is:

$$\sigma^e = \sigma_1 + \frac{\sigma_1\,\theta_2\,(\sigma_2-\sigma_1)(\sigma_2+5\sigma_1+3(\sigma_2-\sigma_1)L_a)}{3(\sigma_2+\sigma_1-(\sigma_2-\sigma_1)L_a)(\sigma_1+(\sigma_2-\sigma_1)L_a)}\mathbf{I}+\mathbf{O}(\theta_\mathbf{2}^\mathbf{2}).$$

A specific system first: For $\dfrac{L_a}{\sigma_2/\sigma_1} \gg 1$

$$\clubsuit\left\{\begin{array}{ccl} \sigma^e & \approx & \sigma_1(1+\dfrac{\theta_2}{3L_a})\mathbf{I}, \\ \mathcal{E}^{iso} & \approx & \dfrac{\theta_2}{3L_a}. \end{array}\right.$$

- The effective conductivity tensor σ^e is isotropic; only the principal value is modified proportional to θ_2 with prefactor $(3L_a)^{-1}$.
- The relative enhancement $\mathcal{E}^{iso}$ is linear in θ_2 with prefactor $(3L_a)^{-1}$.

|| :Anisotropy—σ^e in quiescent nematic phases

- Exact formulas for $f(\mathbf{m})$ do not exist, except for $N \to \infty$ (Onsager, 1949, Constantin *et al*, 2004).
- Alternatively, introduce second moment closure and orientation tensor $\mathbf{Q} = \mathbf{M} - \frac{\mathbf{I}}{3}$ from Doi-Hess theory; $\mathbf{Q} = s(\mathbf{nn} - \frac{\mathbf{I}}{\mathbf{3}})$, where

$$d_1 - d_2 = s = \frac{1}{4}\left(1 + 3\sqrt{1 - \frac{8}{3N}}\right) \text{ for } N > \frac{8}{3}$$

is the uniaxial order parameter for the stable nematic phase.

$$\clubsuit\, \frac{L_a}{\sigma_2/\sigma_1} \gg 1 \begin{cases} \sigma_1^e = \sigma_{max}^e = \sigma_1 + \dfrac{\theta_2\,\sigma_1}{3\,L_a}(1+2s), \\ \sigma_2^e = \sigma_3^e = \sigma_{min}^e = \sigma_1 + \dfrac{\theta_2\,\sigma_1}{3\,L_a}(1-s). \end{cases}$$

Explicit decomposition of enhancements:$\mathcal{E}_{max} = \dfrac{\theta_2}{3\,L_a} + \dfrac{2\,s\,\theta_2}{3\,L_a} = \mathcal{E}^{iso} + \mathcal{E}^{nema}$.

III : σ^e in Shear-induced isotropic regime

Asymptotic solution of Smoluchowski equation in weak shear flow (FWZ, JNNFM, 2004)

$f = \frac{1}{\sqrt{4\pi}}(f_0 + Pe f_1 + O(Pe^2))$, where $f_0 = \frac{1}{\sqrt{4\pi}}$, $\quad f_1 = \frac{i}{2}\sqrt{\frac{5}{6}}\frac{a}{N-5}(Y_2^2 - Y_2^{-2})$

$$\mathbf{M}(f(\mathbf{m})) = \begin{pmatrix} \frac{1}{3} & -\frac{Pe}{6(N-5)} & \\ -\frac{Pe}{6(N-5)} & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix},$$

principal axes $\vec{n_1} = (1,1,0), \vec{n_2} = (0,0,1), \vec{n_3} = (1,-1,0)$.
so the effective conductivity tensor is an anisotropic tensor with three difference principal values

$$\clubsuit \frac{L_a}{\sigma_2/\sigma_1} \gg 1 \begin{cases} \sigma^e_{max} = \sigma_1(1 + \frac{\theta_2}{3\,L_a}) + \frac{Pe\,\theta_2\,\sigma_1}{6\,(5-N)\,L_a} = \sigma_1 + \sigma_1(\mathcal{E}^{iso} + \mathcal{E}^{iso}_{Pe}), \\ \sigma^e_{vorticity} = \sigma_1(1 + \frac{\theta_2}{3\,L_a}) = \sigma_1 + \sigma_1\mathcal{E}^{iso}, \\ \sigma^e_{min} = \sigma_1(1 + \frac{\theta_2}{3\,L_a}) - \frac{Pe\,\theta_2\,\sigma_1}{6\,(5-N)\,L_a} = \sigma_1 + \sigma_1(\mathcal{E}^{iso} - \mathcal{E}^{iso}_{Pe}). \end{cases}$$

IV :σ^e in shear perturbed, flow-aligned nematic phase

$$\mathbf{Q} = s(\mathbf{nn} - \frac{\mathbf{I}}{3}) + Pe\left[\frac{c_1}{2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + c_2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} + c_3\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}\right] + O(P$$

$$\clubsuit \begin{cases} \sigma^e_{max} \approx \sigma_1 + \dfrac{\theta_2\sigma_1}{3\,L_a}\left(1 + 2s + \chi(a,\theta_2)Pe\right), \\ \sigma^e_{vorticity} \approx \sigma_1 + \dfrac{\theta_2\sigma_1}{3\,L_a}\left(1 - s - \chi(a,\theta_2)Pe\dfrac{s+2}{3(1+2s)}\right), \\ \sigma^e_{min} \approx \sigma_1 + \dfrac{\theta_2\sigma_1}{3\,L_a}\left(1 - s - \chi(a,\theta_2)Pe\dfrac{5s+1}{3(1+2s)}\right). \end{cases}$$

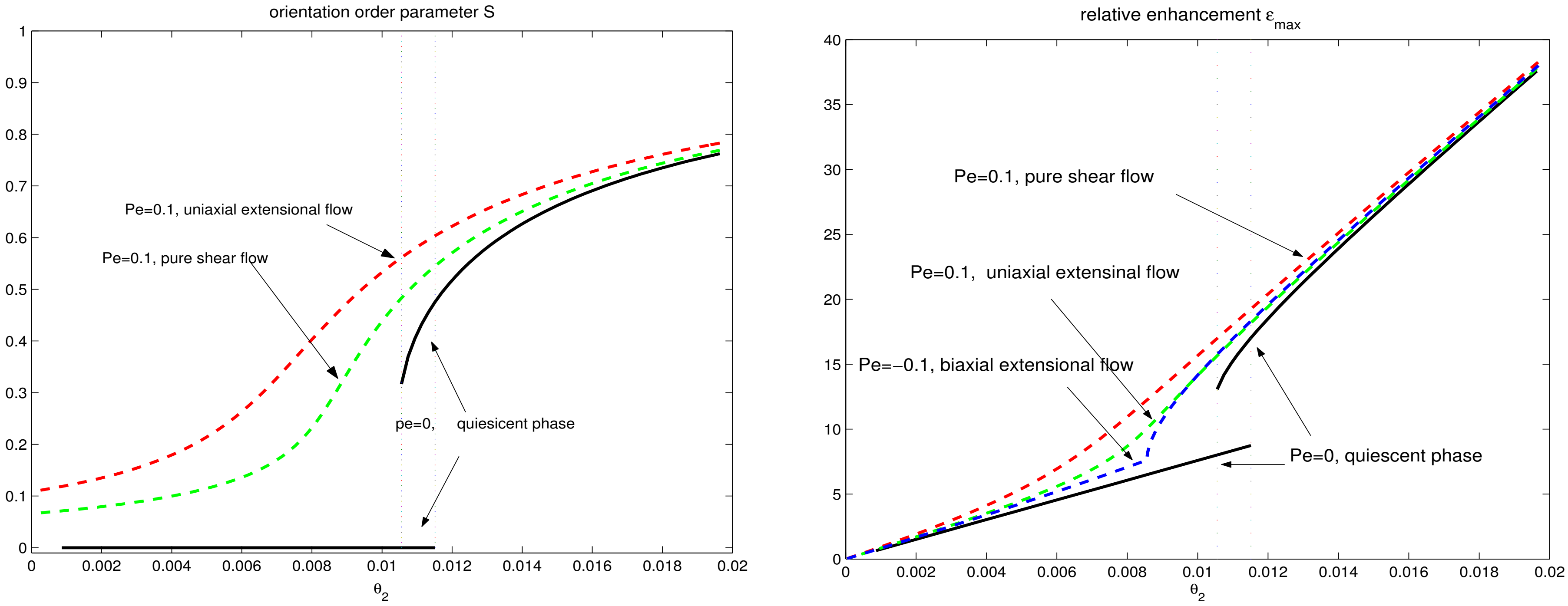
where

$$\chi(a,\theta_2) = \frac{a\,(1-s)^2\,(1+2s)^2\,\sin 2\phi_L}{s\,(4s-1)}.$$

Decomposition:

$$\mathcal{E}_{max} = \frac{\theta_2}{3\,L_a}\left(1 + 2s + \chi(a,\theta_2)Pe\right) = \mathcal{E}^{iso} + \mathcal{E}^{nema} + \mathcal{E}^{nema}_{Pe}$$

Illustrations



axial extension, pure shear, planar extention, quiescent.

- Left figure: order parameter S vs. volume fraction θ_2 from Doi-Hess Theory.
- Right figure: relative enhancement $\mathcal{E}_{max}$ vs. volume fraction θ_2.

Conclusions from Volume Averaging Theorem

- Enhancements have explicit decomposition $\mathcal{E} = \mathcal{E}^{iso} + \mathcal{E}^{nema} + \mathcal{E}_{Pe}$.
- High contrast $\dfrac{\sigma_2}{\sigma_1} \gg 1$ and high aspect ratio $r \gg 1$ are sufficient to overwhelm the low volume fraction $\theta_2 \ll 1$.
- The principal axes of σ^e follow those of the second moment $\mathbf{M}(f)$.
- Conductivity enhancements inherits the hysteresis of the isotropic-nematic phase transition, and inherits the complex multi-stability, limit cycles and steady PDFs of sheared mesophases.

Next

Experimental data suggests percolation dominates volume averaging for electrical properties. I am currently developing this theory.

Thanks for your attention!