Modeling the pipeline of high performance, nano-composite materials and effective properties, I

IMA Workshop
Composites: Where Mathematics Meets Industry

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- Hong Zhou, Naval Postgraduate School

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On the Theme of this Workshop

• I have had the privilege to work with industry engineers & scientists at Hoechst Celanese Corporation in the 1990’s, then in the past 10 years many other experimental scientists & engineers

• The payoff begins when you have found resonance between experiments, technology targets, and “mathematical modeling”.

• Getting there is fun, but challenges in “soft matter & complex fluids”, which includes composites and biological systems, are grand, perhaps the grandest. They will not yield without “IMA brand” of interactions.

• So, we are thankful to the IMA for creating the atmosphere, and running the experiments.
Relationships evolve through a dance that goes something like this

- **What happens?** amazing; not off the shelf
- **Why does that happen?** build a theory based on skillful compromises that predicts what is measured, through analysis & computation (iterative, hopefully convergent, process)
- **What is possible?** A much higher level question than 2. Classify all possible outcomes! Scaling laws & phase diagrams
- **Can we engineer & control it?** Highest level

I will use this model to tell the story of nematic polymer nano-composites, whose final chapter has not been written.
Designer Molecules (particles) at low vol %

Spheroidal nano-elements

clay platelets

rods

Angstrom—100 nm scale

Multifunctional Bulk Properties

- Electrical
- Thermal
- Lightweight
- Mechanical (moduli)
- Piezoelectric sensors
- Barrier
- Self-healing
  mm—meter scale

What happens?

- Ubiquitous, micron-scale morphology
  - created in flow processing
  - between molecular and device scales
- Undetermined effects on bulk properties
Model the nano-composite pipeline

**Anticipate:** Control wrapper around 4 direct solvers

Parametrize control variables
1. Nano-element + Matrix features
2. Flow type and rate
3. Confinement effects

**Performance Properties**
- \(E\) field
- Temperature
- Strength
- Transport
- Healing

For given boundary value problems and “shaping” of the material

**Phase 2**
Quench into solid film

\[f(m,x,t)\]
Nano pdf

**Phase 3**
Effective anisotropic property tensor:
\[s(x)\]

Elliptic

Solvers + time stepper

2nd or 4th order
Why the difficulty? Conspiring factors in *nematic polymer nano-composites*

- **Nano-elements**: high-aspect-ratio rods & platelets (Carbon nanotubes, Kevlar, Vectra, TMV, spider silk, nano-clays, carbon pitch, NP resins)
- **“Rest property”**: isotropic-to-nematic (I-N) mesophase order transitions above a critical volume fraction (below $T^*$)
- **Materials engineering tradeoff**: enough “nano” for property enhancements; too much & viscosity goes ballistic…sweet spot often close to the I-N transition
- **Onsager (1949), Landau, de Gennes understood**: *orientational degeneracy of nematic equilibria implies the I-N transition is 1st order & this would be a source of inherent complexity in “weak fields”—shear versus extension-dominated deformation*
These lectures address elements of the nematic polymer, nano-composite materials pipeline.

• Lecture 1 focuses on why? & what’s possible? in flow processing. I will build a “modeling” framework to explain: Anisotropy & dynamics (longwave limit) then heterogeneity of the molecular orientational distributions, associated stored elastic stresses, and hydrodynamic feedback phenomena.

• Lecture 2: we map these predictions onto effective property tensors of nano-composites, either based on modeling results or experimental data.

• Discussion can amplify what compromises (a.k.a. sins of omission) were made that need to be built into next generation pipeline models.
Anisotropic molecular liquids: scales of relevance (apologies to chemistry friends)

Molecule scale
$L \sim nm$

Mesoscopic scale
$L \sim \mu m$

Chemical details: ongoing focus of our group

Schematic of a nematic mesophase: Experimental scale
Multi-scale descriptive variables
linking theory for flowing, anisotropic macromolecules
& experiments (& effective properties tomorrow)

• Kinetic theory: PDF $f(m,x,t)$ assigns a likelihood of the spheroidal molecule axis $m \in S^2$ at each $(x,t)$ (Doi-Hess)
• Mesoscopic theory: upscale $f \rightarrow 2^{nd}$ moment tensor $M = \langle m \otimes m \rangle$ symmetric, trace 1, frame of principal axes (directors) & principal values (order parameters) (Landau-deGennes models)
• Continuum theory: major director (Leslie-Ericksen-Frank)
• Orientation tensor $Q = M - 1/3 I$

normalized $M$, gleaned from now-standard devices
*micron-scale light scattering measurements
*normal & shear stress measurements

$Q$ & $M$ define a triaxial ellipsoid, imaged in simulations, whose shape $\Leftrightarrow$ order parameters; orientation $\Leftrightarrow$ directors
**Kinetic theory**

variable: probability distribution function \( f(m, t) \)

Smoluchowski equation: \((\mathbf{R} = m \times \frac{\mathbf{a}}{\mathbf{m}})\)

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

Jeffery orbit for the molecule axis \( m \):
\[ \mathbf{m} = \Omega \cdot m + a[D \cdot m - D : mmm] \]

**Mesoscopic theory**

variable: orientation tensor \( Q = \int_{\|\mathbf{m}\| = 1} mmf \, d\mathbf{m} - \frac{1}{3} I \)

pre-closure equation:
\[ \frac{d}{dt} Q - \Omega \cdot Q + Q \cdot \Omega - a[D \cdot Q + Q \cdot D] = \frac{2a}{3} D - 2aD : \langle mmmm \rangle - 6D^0 \langle Q - N(Q + \frac{1}{3}) \cdot Q + NQ : \langle mmmm \rangle \rangle \]

**Continuum theory**

variable: director \( n \)

L–E model:
\[ 0 = n \times \left[ \gamma_1 \left( \frac{\mathbf{m}}{dt} + \Omega \cdot n \right) + \gamma_2 D \cdot n \right] \]

<table>
<thead>
<tr>
<th>Velocity</th>
<th>( \mathbf{v} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vorticity tensor</td>
<td>( \Omega = \frac{1}{2}(\nabla \mathbf{v} - (\nabla \mathbf{v})^T) )</td>
</tr>
<tr>
<td>Rate-of-strain tensor</td>
<td>( D = \frac{1}{2}(\nabla \mathbf{v} + (\nabla \mathbf{v})^T) )</td>
</tr>
<tr>
<td>Excluded-volume potential</td>
<td>( V = -\frac{a}{2} NkT \mathbf{mm} : \langle \mathbf{mm} \rangle )</td>
</tr>
<tr>
<td>Concentration</td>
<td>( N )</td>
</tr>
<tr>
<td>Molecular shape parameter</td>
<td>( a = \frac{r^2 + 1}{r^2 - 1} )</td>
</tr>
</tbody>
</table>

**Multiscale models for Monodomain phases & the longwave limit**

Molecular ensemble response to rotational diffusion, excluded volume, and imposed flow
Upscaling: spherical harmonic expansions & mesoscopic projections

Expansion of $f$

$$f(m, t) \approx \sum_{l=0}^{L} \sum_{m=-l}^{l} a_{l,m}(t) Y_{l}^{m}(\theta, \phi)$$

Projection onto second moments gives mesoscopic $Q$ tensor

$$Q_{xx} = -\frac{2}{3} \sqrt{\frac{\pi}{5}} a_{2,0} + \sqrt{\frac{8\pi}{15}} \Re(a_{2,2})$$

$$Q_{yy} = -\frac{2}{3} \sqrt{\frac{\pi}{5}} a_{2,0} - \sqrt{\frac{8\pi}{15}} \Re(a_{2,2})$$

$$Q_{xy} = -\sqrt{\frac{8\pi}{15}} \Im(a_{2,2})$$

$$Q_{xz} = -\sqrt{\frac{8\pi}{15}} \Re(a_{2,1})$$

$$Q_{yz} = \sqrt{\frac{8\pi}{15}} \Im(a_{2,1})$$

$\Re(\cdot)$ and $\Im(\cdot)$ represent real and imaginary part, respectively.
Intuition about scale of resolution of spherical harmonics

\[ f(m, t) \approx \sum_{l=0}^{L} \sum_{m=-l}^{l} a_{l,m}(t) Y_{l}^{m}(m) \]
What happens at rest to bulk phases?

Onsager phase diagram of quiescent hard-rod liquids

Kinetic simulations: Larson-Ottinger ’91; Faraoni et al. ’99; FWZ ’04,’05 Rheol. Acta I,II

\[ s(f) = \text{Flory order parameter} = d_1 - d_2 \]

\[ d_1, d_2 \text{ are largest eigenvalues of } M(f) \]

1. O(3) degenerate ordered phases
2. Isotropic-nematic 1\textsuperscript{st} order phase transition

Source of remarkable complexity when broken by weak (shear) flows

Nematic concentration \( N \)

Onsager, 1949
The Onsager diagram is deceptive if you don’t read the fine print:

Orientational degeneracy of nematic phases

The nematic equilibrium distribution, \( f(m) \) of kinetic theory, is invariant under rotations. Here we compute \( f(m) \) at a nematic concentration, with peak aligned with “z” axis. Then we produce another element of the \textbf{continuous group of equilibria}, \( f(Um) \), for \( U \) in \( O(3) \). FWZ, Phys Rev E 02: symmetries of kinetic and mesoscopic theory
What happens when you drive this $O(3)$-degenerate phase transition with weak fields? De Gennes: “very little is known, even less is understood”

Efforts to model and predict experimental evidence, then to map out what is possible, comprise the rest of this lecture. Start simple: what works (fiber flows). Then shear-dominated processing flows: take appropriate limits in orientation and physical space, and length and time scales, to get some handle on scaling laws. Develop scaling laws to guide simulations.
Flow-molecular interactions

Spiders instruct us to make fibers

Nematic polymer fiber theory & simulations

- progressive focusing & orientation of the molecular distribution downstream
- extension-dominated hydrodynamics uniquely breaks orientational degeneracy
- molecular orientational stresses are beneficial (suppress capillary (Rayleigh) instability)
- FWBZ papers ’95-’00; Hoechst-Celanese

But, we are greedy... beyond fibers
Films, mold-filling, ... 2d & 3d materials
Flow-phase diagram for discotic nematic polymers

Extension if $\text{Pe} > 0$
Compression if $\text{Pe} < 0$

Stable bulk morphology is biaxial; strong birefringence in every plane of measurement!

Birefringence reading clockwise from top left: regions XI, IX, VII, VI

Fix stretching rate; study increasing volume fraction of nano-platelets align toward flow axis (like pennies falling down a horn).

As concentration grows: More birefringent in planes through the flow axis, less birefringent in planes transverse to flow axis.

Ellipsoids ↔ principal axes and degrees of order

What’s possible? Fiber spinning & pure extensional flow yield steady, quantifiable anisotropic orientation & stored stresses versus volume fraction, molecular geometry, and extension rate.
The Couette cell—model system for shear-dominated flow of complex anisotropic fluids:

Imposed kinematics first (the longwave limit) then morphology due to confinement

Molecular inclusions store anisotropy and stresses between moving plates, coupled with hydrodynamic feedback and solid wall confinement
What happens? Rheological oscillators
Onsager’s nightmare: Mesophase oscillators in steady shear flow.....the cast of transient bulk attractors
Rheological oscillators in steady shear
A Kayaking Orbit of kinetic theory: A “dynamical circle of equilibria” selected from orientational degeneracy in weak shear
Period doubling route to chaos & associated normal stress differences

\[ N_2 \text{ vs. } N_1 \]

\[ N = 5.2 \]

\[ \text{Pe} = 4.07 \]

\[ \text{Pe} = 4.05 \]

\[ \text{Pe} = 4.044 \]
These bulk mesophase responses to local pure shear flow foreshadow how material properties are being “engineered” in processing; we have Simulations on structures generated in this dynamic regime
Why? What molecular & flow properties pick the response(s)? A Mesoscopic-Microscopic “Predictor-Corrector” Strategy

- **Multi-scale Symmetries**: quiescent & linear flows (scaling properties & virtual experiments)
- Rigorous analysis at mesoscopic $2^{nd}$ moment scale in weak flow limit (selection criteria)
- Closure-dependent vs robust features
- Pass to kinetic simulations to confirm robust features and resolve sensitive issues
- **Multi-scale strategy already for sheared bulk phases!** (i.e., even in the longwave limit with imposed linear flows)
Monodomain selection criteria

• Criteria for “what survives orientational degeneracy?”
  steady = fixed points     periodic = closed curves

• Attractors versus model parameters (nematic concentration \( N \), molecular aspect ratio \( r \), flow type, flow rate \( Pe \))
  - Number and type (in-plane, logrolling, out-of-plane)
  - Stability
  - Phase transitions (vs \( N \), \( r \), or \( Pe \)!)  

• From explicit constructions, predict experimental features:
  - alignment, birefringence, stresses

• Caveat: only possible in asymptotic weak flow limit
• Provides scaling properties & guides for numerical simulations into arbitrary flow regime

FWZ, J. Rheology, Jan. 2003, JNNFM, 2004
Weak-shear selection criteria vs. aspect ratio & concentration

- Parametrize orientational degeneracy
  \[ Q_0 = s_{eq}^{0,1,2} \left( \text{nn}^T - \frac{1}{3} I \right) \]
  \[ n = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \]
- Posit, \( Q = Q_0 + Pe Q_1 \), solvability for
  Solvability takes the form \( A(Q_0)Q_1 = R(Q_0) \)
  \[ A(Q_0) \leftrightarrow \text{intermolecular potential, closure - dependent} \]
  \[ R(Q_0) \leftrightarrow \text{closure - dependent} \]
- Fredholm alternative? selection criteria: which states survive from \( O(3) \) degeneracy of quiescent nematics
  \[ R(Q_0) \perp N(A^*(Q_0)) \]
Example: Doi closure

Solvability conditions:

\[ r_1 \perp \text{Null}(A^{adj}), \quad r_2 \perp \text{Null}(A^{adj}) \]

where,

\[ A \bullet Q_1 = Q_1 - N(M_0 \bullet Q_1 + Q_1 \bullet Q_0) + N(Q_0 : M_0 Q_1 + (Q_1 : M_0 + Q_0 : Q_1) M_0) \]

\[ O(Pe) : \quad r_1 = \Omega \bullet Q_0 - Q_0 \bullet \Omega + a(D \bullet Q_0 + Q_0 \bullet D) + \left( \frac{2}{3} D - D : M_0 M_0 \right) \]

\[ O(Pe^2) : \quad r_2 = \Omega \bullet Q_1 - Q_1 \bullet \Omega + a(D \bullet Q_1 + Q_1 \bullet D) - 2a(D : M_0 Q_1 + D : M_1 M_0) \]

\[ + N Q_1 \bullet Q_1 + N((Q_1 : M_0 + Q_0 : Q_1) Q_1 + Q_1 : Q_1 M_0) \]

Synopsis:

- 5 dimensional, linear, variable-coefficient systems
- which we solve for O, D of simple shear explicitly
- extension to any planar flow by “symmetry”

All persistent steady states in the weak shear limit vs. molecule aspect ratio and nematic concentration & phase transitions, steady and unsteady!

Existence of Steady states

| I   | FA0, FA+(1,2), FA(1,2), LR+ |
| II  | FA0, FA-(1,2), LR+-          |
| III | FA0, LR+-                   |
| Solid | FA0, OS+(1,2), LR+-       |
| Dashe | FA0, OS_(1,2), LR+-        |
| Dotted | FA0, OS-(3,4), LR+-     |

Stable states

| FA     | Flow aligning |
| LR     | Log-rolling   |
| OS     | Out-of-plane  |
| +,-    | Quiescent branches |
| 1,2,3,4 | Number of survived |
Steady-unsteady phase transition diagnostic: mesoscopic Leslie “tumbling parameter”
Sensitivity to Closure Rule (FWZ)

Leslie-Ericksen theory
\[ \lambda_L = \frac{1 + \alpha_3}{\alpha_2}, \quad \text{where } a_2, a_3 \text{ correspond to Leslie viscosities.} \]

Kuzuu-Doi theory
\[ \lambda_L = \frac{2S_2}{dU_0} \langle g \frac{dU}{d\theta} \rangle \]
\[ \lambda_{L}^{Doi} = \frac{a(s + 2)}{3s}, \quad \lambda_{L}^{RT} = \frac{a(4 + 2s - s^2)}{6s}, \]
\[ \lambda_{L}^{HL1} = \frac{a(6 + s + 8s^2)}{15s}, \quad \lambda_{L}^{LdeG} = \frac{6 + 5a}s {15s} \]

- \( \lambda_{L}^{Doi} \rightarrow 3 \) simultaneous phase transition phenomena
- Details vary with closure, some phenomena are robust
- Have to pass to kinetic theory
Downscaling to Kinetic PDF “survivors” in weak shear:
\[ a=1, \ Pe=0.1 \] using AUTO

[Forest, Zhou and Wang, RheoActa 04]
Bifurcations vs Flow Rate at a fixed nematic concentration all orbits, stable and unstable

Why 7 states at Onset of flow?
FW 03 Rheol Acta
Virtual Bifurcations versus Molecular Aspect Ratio

N=6, Pe=5 in FA regime when r=3, 1/3

Forest & Wang, '03, Rheol Acta
Shear-driven mesoscopic flow-phase diagram:
numerical continuation software (AUTO)
Doi closure; Forest & Wang, ’03, Rheol. Acta

What’s possible?

Data compression:
Mesoscopic
stable solution
space! + all
phase transitions

Shear rate

Nematic concentration
Molecular-scale kinetic theory: robust vs closure-sensitive behavior

- FWZ series of papers show unacceptable dependence on closure rule, and we have yet to couple confinement and structure!
- Kinetic theory reveals “origins” of stress signatures for steady-unsteady shear driven, phase transitions (Kiss & Porter experiments in 1980’s)
- I.e., how would you know if you resonate one of these attractors, and if you experience a transition?

  F-Wang-R. Zhou I, II Rheologica Acta ’04, ‘05
Kinetic monodomain phase diagram of attractors versus vol % and shear rate

\[ a = 1 \]

- 13 separate regions
- 8 different attractors

<table>
<thead>
<tr>
<th>Region</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Flow-aligned steady</td>
</tr>
<tr>
<td>II</td>
<td>Out-of-plane steady</td>
</tr>
<tr>
<td>IV</td>
<td>chaos</td>
</tr>
<tr>
<td>V</td>
<td>Tumbling/logrolling</td>
</tr>
<tr>
<td>VI</td>
<td>Tilted kayaking</td>
</tr>
<tr>
<td>IX</td>
<td>Kayaking</td>
</tr>
<tr>
<td>XI</td>
<td>Wagging &amp; logrolling</td>
</tr>
<tr>
<td>XII</td>
<td>logrolling</td>
</tr>
</tbody>
</table>

- Region 1
- Region II
- Region IV
- Region V
- Region VI
- Region IX
- Region XI
- Region XII

- Region 9
- Region 11
- Region 12
First & second order phase transitions between regions: **bifurcation city**

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Bifurcation type</th>
<th>Attractor transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI-II</td>
<td>Hopf</td>
<td>$K_2^{+,-}$ to $OS^{+,-}$</td>
</tr>
<tr>
<td>IV-VI</td>
<td>periodic doubling</td>
<td>chaos to $K_2^{+,-}$</td>
</tr>
<tr>
<td>XII-V</td>
<td>periodic doubling</td>
<td>unstable to stable $T$, LR remains</td>
</tr>
<tr>
<td>XII-IX</td>
<td>Hopf</td>
<td>LR to $K_1$</td>
</tr>
<tr>
<td>IX-XIII</td>
<td>periodic doubling</td>
<td>unstable to stable $T$, $K_1$ remains</td>
</tr>
<tr>
<td>XI-VIII</td>
<td>Hopf</td>
<td>LR to $K_1$, $W$ remains</td>
</tr>
<tr>
<td>VIII-VII</td>
<td>transcritical</td>
<td>TW to $K_2$, $K_1$ remains</td>
</tr>
<tr>
<td>VII-VI</td>
<td>saddle-node</td>
<td>$K_1$ disappears, stable $K_2^{+,-}$ remain</td>
</tr>
<tr>
<td>VIII-X</td>
<td>saddle-node</td>
<td>$K_1$ disappears, stable $W$ remains</td>
</tr>
<tr>
<td>X-I</td>
<td>Hopf</td>
<td>$W$ to $FA$</td>
</tr>
<tr>
<td>VII-III</td>
<td>periodic doubling</td>
<td>stable $K_2^{+,-}$ to chaos</td>
</tr>
<tr>
<td>III-IV</td>
<td>saddle-node</td>
<td>$K_1$ disappears, chaos continues</td>
</tr>
</tbody>
</table>
Stress signatures!

First and second normal stress differences N1 and N2, and the shear stress for the wagging W and Kayaking K2 solutions. The concentration is N=4.85.
Signs of normal stress differences
Vs. Attractor Type; note W and K2+/-
Co-exist with K1, as do OS+/-.

The issue of “strength” of bi-stable attractors becomes relevant (X. Zheng, F-W-Z, RheoActa ‘05)
How long does it take to reach an attractor from experimental initial conditions?

<table>
<thead>
<tr>
<th>Stable state</th>
<th>FA</th>
<th>K₁</th>
<th>W</th>
<th>K₂</th>
<th>OS</th>
<th>LR</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₁</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>±</td>
<td>+</td>
</tr>
<tr>
<td>N₂</td>
<td>-</td>
<td>±</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>+</td>
</tr>
</tbody>
</table>
Passing from shear to other linear flows—toward film processing

- Arbitrary laminar 2d planar flows
- Models for film tenters, four roll mills etc
- Correspondence principle of kinetic theory & inherited by Q tensor closures: FWZ & Choate, JNNFM ’04
- Pure shear code w/ variable aspect ratio maps out all laminar 2d planar flows: parallel processing
- Robustness of chaotic shear response to extensional flow components: FWZ, Phys. Rev. Letters ’04
Devices to explore planar flows combining shear and extension: 4 roll mill, G.I. Taylor
A simple observation of an underlying symmetry in the coupling of orientation & flow

Since the shape parameter of the molecule $a$ enters only in product with $\mathbf{D}$, we can adjust the flow and the molecule shape simultaneously, without changing the distribution $f$

\[
\frac{\partial f}{\partial t} = R \cdot \left( D_a (m) \left( R f + \frac{1}{k_B T} f R V \right) \right) - R \cdot (m \times mf)
\]

\[
m = \Omega \cdot m + \left((a \cdot \mathbf{D}) \cdot m - (a \cdot \mathbf{D}) : \mathbf{mm} \right)
\]

\[
R = m \times \frac{\partial}{\partial m} \text{ is the rotational gradient}
\]

\[
D_r(m) = \begin{cases} 1, & \text{if } m' = 1 \\ \int_{\|m'\|=1} \|m \times m'\| f(m') \end{cases}
\]
“Finesse” monodomain response in linear, planar flows from pure shear! PRE 2002; JNNFM 2004; PRL 2004

Doi-Hess kinetic theory and its mesoscopic closures allow one to trade off the extensional flow component for a renormalized molecular aspect ratio (sometimes even imaginary!). All solutions, indeed bifurcations and entire phase diagrams, for the four-parameter flow-liquid system follow from a two parameter solution space — a shear rate and a modified aspect ratio parameter.

\[ \nabla \mathbf{v} = \begin{bmatrix} p_1 & p_2 & 0 \\ p_3 & -p_1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \]

\[ \nabla \mathbf{v}_{\text{shear}} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \]
Correspondence principle: extrapolating from pure shear to linear planar flows by varying molecular aspect ratio

If $f(m, t)$ solves the Smoluchowski Equation, or if $Q$ solves the tensor equation, for aspect ratio parameter $a$ and Peclet number $Pe$, then $f(Um, t)$, or $\overline{Q} \equiv UQU^T$, solves the equation with aspect ratio

$$\bar{a} = \omega a, \text{ with } \omega = \frac{\sqrt{4p_1^2 + (p_2 + p_3)^2}}{p_2 - p_3},$$

and with orthogonal matrix of rotation in the plane of flow

$$U = \begin{pmatrix}
\cos \delta & \sin \delta & 0 \\
-\sin \delta & \cos \delta & 0 \\
0 & 0 & 1
\end{pmatrix}$$

where the angle $-\pi / 2 < \delta \leq \pi / 2$ solves

$$\cos 2\delta = \frac{p_2 + p_3}{\sqrt{4p_1^2 + (p_2 + p_3)^2}}, \quad \sin 2\delta = \frac{-2p_1}{\sqrt{4p_1^2 + (p_2 + p_3)^2}}.$$
First introduce an orthogonal change of coordinates

\[
U = \begin{pmatrix}
\cos\delta & \sin\delta & 0 \\
-\sin\delta & \cos\delta & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

where the angle $-\pi / 2 < \delta \leq \pi / 2$ solves

\[
\cos 2\delta = \frac{p_2 + p_3}{\sqrt{4p_1^2 + (p_2 + p_3)^2}}, \quad \sin 2\delta = \frac{-2p_1}{\sqrt{4p_1^2 + (p_2 + p_3)^2}}
\]

This rotation does not effect the vorticity of the flow

\[
U \Omega U^T = \Omega
\]

However, this judicious choice of coordinates transforms $\mathbf{D}$ to the form of a the rate-of-strain of a shear flow but multiplied by a scalar $\omega$.

\[
U DU^T = U((p_2 + p_3)\bar{\mathbf{D}}_{\text{shear}} + 2p_1\mathbf{D}_{\text{extension}})U^T = Pe \omega \bar{\mathbf{D}}_{\text{shear}}
\]

\[
\omega = \frac{\sqrt{4p_1^2 + (p_2 + p_3)^2}}{p_2 - p_3}
\]
Streamlines for various linear flows

Shear Flows

\[ p_1 = 0, \ p_2 = 1, \ p_3 = 0 \]

General Linear Planar Flows

\[ p_1 = 1, \ p_2 = 4, \ p_3 = 1 \]
\[ p_1 = 1, \ p_2 = 4, \ p_3 = -1 \]
Kinetic Bifurcation Diagram

Predicted bifurcation diagram for the projection of $f$ onto the spherical harmonic function $Y_{20}$ created for pure shear with $N=6$, and $a=1$.

This correspondence principle says that this diagram generated for pure shear should apply to the two parameter $(d, ?)$ family of general linear flow-molecule systems given by

$$p_1 = -\frac{1}{2} \omega Pe \sin 2\delta, \quad p_2 = \frac{1}{2} (\omega \cos 2\delta + 1) Pe$$

$$a = \frac{1}{\omega}$$
Robustness of chaotic & oscillatory monodomain
Attractors to aspect ratio, vol %, shear vs extension strength
Transition from bulk homogeneous phase response to structure

- All this work so far was the longwave limit for imposed linear flows! Are we having fun yet?
- We are now poised to address what happens from a pristine equilibrium mesophase when we confine it and drive the anisotropic composite liquid.
- “Structure happens” in the conflict between bulk preferred response & plate anchoring.
- These lectures address drag-driven flows, we also explore pressure-driven flows.
Structure in shear cells: leaving the longwave limit
mesoscopic 2nd moment models & full kinetic simulations
We are looking for lengthscale genesis, propagation, interactions…. & “structure attractors”

Figure 1: Plane shear flow geometry. Non-slip boundary condition for the velocity and the boundary anchoring for the orientation tensor are prescribed at the boundaries. A schematic major director windup is shown across the shearing cell for a tangential anchoring.
Mesoscopic model equations for nano-composite structure development in flow processing

\[
\frac{dv}{dt} = \nabla \cdot (-pI + \tau), \quad \text{DMG potential}
\]

\[
\tau = \left( \frac{2}{Re} + \mu_3 \right)D + a \alpha F'(Q)
\]

\[
+ \frac{a\alpha}{3E_r} \left\{ \Delta Q : Q(Q + \frac{I}{3}) - \frac{1}{2}(\Delta QQ + Q\Delta Q) - \frac{1}{3} \Delta Q \right\}
\]

\[
+ \frac{a}{3E_r} \left\{ \frac{1}{2}(Q\Delta Q - \Delta QQ) - \frac{1}{3}(\nabla Q : \nabla Q - \nabla\nabla Q : Q) \right\}
\]

\[
+ \mu_1 \left\{ (Q + \frac{I}{3})D + D(Q + \frac{I}{3}) \right\} + \mu_2 D : Q \left( Q + \frac{I}{3} \right),
\]

\[
\nabla \cdot v = 0,
\]

\[
\frac{d}{dt} Q = \Omega Q - Q\Omega + a \left[ DQ + QD \right] + \frac{2a}{3}D - 2aD : Q(Q + \frac{I}{3})
\]

\[
- \frac{1}{\Lambda} \left\{ F'(Q) + \frac{1}{3E_r} \left[ \Delta Q : Q(Q + \frac{I}{3}) - \frac{1}{2}(\Delta QQ + Q\Delta Q) - \frac{1}{3} \Delta Q \right] \right\},
\]

where

\[
F'(Q) = (1 - N/3)Q - NQ^2 + NQ : Q(Q + I/3),
\]

Plus confinement conditions on flow & anchoring
Idealized 1-d model of flow-mesophase structure: onset, evolution & correlations

• 1-d in space, in the gap dimension, not usually imaged!

• **two flow components:** primary flow, vorticity directions \( v = (v_x(y,t), 0, v_z(y,t)) \)

• mesoscopic orientation tensor \( Q(y,t) \) or PDF

• **Macro-mesoscale coupling & confinement & phase transitions:** what more can you ask for in a model!!
Aspects of molecular mesostructure induced during laminar processing

- **Scales?** What picks them? In what features of the orientational distribution? (directors, spread/focusing of the PDF? ….)

- **Can we predict and control variability** due to:
  - processing conditions (device scales and confinement conditions, flow type, strength)
  - molecular properties (geometry, size (mol.wt.), concentration, distortional elasticity potential, solvent-molecule compatibility, flexibility….)


Structure scaling laws due to Confinement--bulk motion interactions

- Doi-Marrucci-Greco model with distortional elasticity \( (L_{\text{elasticity}}) \) (nonlinear elliptic operator)

- Nondimensionalize flow-nematic equations

\[
De = \frac{\text{bulk flow rate}}{\text{nematic relaxation rate}} = \frac{h}{v_0} D_r^0
\]

\[
Er = \frac{8}{N} \left( \frac{h}{L_{\text{elasticity}}} \right)^2 De
\]

\[
2h = \text{gap-width}
\]

\[
\pm v_0 = \text{plate-speeds}
\]

\[
\psi_0 = \text{orientation anchoring angle}
\]

- Slow plate limit ➔
- Exact solvability
Self-consistent flow-molecular orientation structures

\[ Q = Q^{(0)} + D e Q^{(1)} + O(D e^2) \]

\[ Q^{(1)} = \text{Err} (y^2 - 1) Q_1 + \left( \frac{\cosh(By)}{\cosh(B)} - 1 \right) Q_2 + \left( \frac{\cosh(Dy)}{\cosh(D)} - 1 \right) Q_3 \]

where

\[ Q_1 = -\frac{9 s}{2(2 + s)} (1 - \lambda L \cos 2\psi_0) \begin{pmatrix} \sin 2\psi_0 & \cos 2\psi_0 & 0 \\ \cos 2\psi_0 & -\sin 2\psi_0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

\[ Q_2 = \frac{\alpha (1 - s)^2 (1 + 2s)}{36s} \sin 2\psi_0 \begin{pmatrix} 1 - \cos 2\psi_0 & \sin 2\psi_0 & 0 \\ -\sin 2\psi_0 & 1 + \cos 2\psi_0 & 0 \\ 0 & 0 & -2 \end{pmatrix} \]

\[ Q_3 = -\frac{\alpha (4s - 1)}{4N (3N - 8)s} \sin 2\psi_0 \begin{pmatrix} 1 + 3 \cos 2\psi_0 & \sin 2\psi_0 & 0 \\ \sin 2\psi_0 & 1 - 3 \cos 2\psi_0 & 0 \\ 0 & 0 & -2 \end{pmatrix} \]
Read off structure scaling properties parametrized by device and molecular conditions

- Recover Marrucci scaling law, $E_r^{-1/2}$, of continuum theory, but now in boundary layers solely due to molecular elasticity
- Non-uniform structure that spans the entire shear gap, dominated by nematic/director distortions, $E_r^{-1}$ mean scaling law
- Strong sensitivity to plate anchoring!
- Already enough for textures; guide numerical simulations out of asymptotic to realistic regimes
Numerical continuation studies: Resonating new flow-nematic structures as asymptotics fails.

Non-Newtonian flow feedback correlated with molecular elasticity, not nematic distortions.
Macroscopic-mesoscopic steady-state structure correlations (unpublished, FWZZ): here we find a temporal-to-spatial “kayaking” transference

Material property layering:
structure correlation is with secondary vorticity generation
not the “imposed” shear flow
Dynamic structure formation in steady processes:
midgap tumbling layer with finite oscillations near
plates & defect core fluctuations
Mesoscopic Simulations of Spatio-temporal Morphology with flow feedback

Er=10,000
De=7
Tangential anchoring

A: major director
B: axial velocity
C: degree of orientation
D: shear stress
Higher $Er$

Mesoscopic codes

$Er=100,000$
$De=7$
Tangential anchoring

Finer scale structure
Transient morphology

A: major director
B: velocity
C: degree of orientation
D: $\tau(xy)$
Full kinetic structure simulations: Spherical harmonic expansion for orientational configuration space

- **Galerkin expansion**

  \[ f(m, x, t) = \sum_{l=0}^{L} \sum_{m=-l}^{l} a_{l,m}(x, t) Y_l^m(m) \]  

  spherical harmonic basis functions:

  \[ Y_l^m(m) = P_l^m(\cos \theta) e^{im \phi} \]

  \( P_l^m \): Legendre polynomials

- **Amplitude functions:**

  \[ a_l^m(x, t) = \int_{||m||=1} f(m, x, t)(Y_l^m(m))^* dm \]

Smoluchowski equation is transformed to a system of PDEs for heterogeneous simulations, ODEs for monodomains

SIAM Multiscale Modeling & Simulations, ’05, ZFW
Er=500, De=1, Probe effect of normal anchoring: Creation of internal dynamic structure layer
$E_r = 500$, $D_e = 6$, normal anchoring: Probe effects due to increasing the plate (processing) speed

Timescales & extent of dynamic structure region change!
Transition to defect-laden attractors associated with transient structures & spatial T-W transition

Left: Evolution of the peak orientation angle of LCPs in the middle of the plate gap for the TW attractor Er=500, De=4.
Right: Evolution of the peak alignment angle for several positions near the plates. At the plates, the amplitude is zero. It increases as the distance to the plates increases until to the defect core.
Blowup of defect cores: local space-time crashing of Flory order parameter of the PDF, signaling complete defocusing of orientational distribution.

Tangential plate anchoring

Normal plate anchoring

Order parameter $s$ for the TW attractor for $Er = 500, De = 4$. The defect cores are sharp spots where $s$ drops precipitously toward 0. Top: parallel anchoring. Bottom: normal anchoring.
Structure phase diagram: steady – unsteady morphology transitions
Imposed linear shear, in-plane orientational PDFs

What’s possible?
In-plane configuration space
1-d physical space
Imposed kinematics

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Table 1: In-plane structure attractors and phase transitions for 3 decades of Deborah number (De) and Ericksen number (Er). ES and VS stand for elastic (E) and viscous (V) dominated steady (S) states. T or W indicates a transient structure in which the peak orientation axis at each height between the plates either oscillates with finite amplitude (wagging) or rotates continuously (tumbling).

SIAM Multiscale Modeling & Simulations, ’05, in revision
Chaotic structure regime (to be submitted)
full kinetic flow-molecular simulations

Post processing of major director dynamic heterogeneity

Polar angle
Azimuthal angle

UPSHOT: spatial coherence with temporal chaos
Stored normal stress differences & shear stress in chaotic structure attractor:
Time series of major director at different film heights

From left to right,
1st row $y=0.08,0.3,0.34$
2nd row $y=0.42,0.5,0.6$
3rd row $y=0.62,0.8,1$

$Y$ is the distance to the Plate.
Degree of orientation, $s$, and flow feedback in primary flow component

$S = d_1 - d_2$

Velocity $v_x$

These results are to be submitted to PRL within a month.
Anisotropy, Dynamics, & Heterogeneity of Nematic Polymer Shear-driven Flows

• Now that we have mapped out part of the answers to “What is possible?”, it is natural to ask how these features of nematic polymer inclusion ensembles map to effective properties.

• Lecture 2 to follow is based on very recent results, primarily by my student Xiaoyu Zheng, with skillful guidance of Rob Lipton. We marry results of Hong & Ruhai Zhou, Qi Wang to homogenization theory.