Microstructural studies for rheology

- Micro & macro views
- Einstein viscosity
- Rotations
- Deformations
- Interactions
- Polymers
- Others

Rotations

- Rotation of particles
- Macro stress
- Uni-axial straining
  - Extensional viscosity rods
  - Extensional viscosity disks
- Simple shear
  - Shear viscosity
- Anisotropy
- Brownian rotations
  - Macro stress
  - Viscosities
  - Closures

Rotation of particles – rigid and dilute

Spheroid: axes a, b, b, aspect ratio $r = \frac{a}{b}$.

rod $r > 1$ disk $r < 1$

Direction of axis $\mathbf{p}(t)$, unit vector.

Stokes flow by Oberbeck (1876). See Lamb. Uses ellipsoidal harmonic function in place of spherical harmonic $1/r$

$$\int_{s(\mathbf{x})}^{\infty} \frac{ds'}{\Pi_{i=1}^{3}(a_i^2 + s')^{1/2}}, \qquad \text{where} \quad \sum_{i=1}^{3} \frac{x_i^2}{a_i^2 + s(\mathbf{x})} = 1.$$

Rotation of particles

Microstructural evolution equation

$$\frac{D\mathbf{p}}{Dt} = \Omega \times \mathbf{p} + \frac{r^2-1}{r^2+1}\left[\mathbf{E}\cdot\mathbf{p} - \mathbf{p}(\mathbf{p}\cdot\mathbf{E}\cdot\mathbf{p})\right]$$

Straining less efficient at rotation by $\frac{r^2-1}{r^2+1}$.

Long rods $\frac{r^2-1}{r^2+1} \to +1$ i.e. Upper Convective Derivative $\overset{\nabla}{A}$

Flat disks $\frac{r^2-1}{r^2+1} \to -1$ i.e. Lower Convective Derivative $\overset{\triangle}{A}$

Rotation of particles

Student Exercise
Show that

$$\mathbf{p}(t) = \frac{\mathbf{q}(t)}{|\mathbf{q}(t)|} \quad \text{with} \quad \dot{\mathbf{q}} = \Omega \times \mathbf{q} + \tfrac{r^2-1}{r^2+1}\mathbf{E}\cdot\mathbf{q}$$

satisfies

$$\frac{D\mathbf{p}}{Dt} = \Omega \times \mathbf{p} + \tfrac{r^2-1}{r^2+1}\left[\mathbf{E}\cdot\mathbf{p} - \mathbf{p}(\mathbf{p}\cdot\mathbf{E}\cdot\mathbf{p})\right]$$

Hence find $\mathbf{p}(t)$ for axisymmetric extensional flow and for simple shear, starting from an arbitrary initial $\mathbf{p}(0)$.

Micro→macro link: stress

$$\overline{\sigma} = -\overline{p}I + 2\mu\mathbf{E} + 2\mu\phi\left[A(\mathbf{p}\cdot\mathbf{E}\cdot\mathbf{p})\mathbf{pp} + B(\mathbf{pp}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{pp}) + C\mathbf{E}\right]$$

with A, B, C material constants depending on shape but not size

	A	B	C
$r \to \infty$	$\frac{r^2}{2(\ln 2r - \frac{3}{2})}$	$\frac{6\ln 2r - 11}{r^2}$	2
$r \to 0$	$\frac{10}{3\pi r}$	$-\frac{8}{3\pi r}$	$\frac{8}{3\pi r}$

Rotation in uni-axial straining

$$\mathbf{U} = E(x, -\tfrac{1}{2}y, -\tfrac{1}{2}z)$$

rotates to

Aligns with stretching direction → maximum dissipation

rotates to

Aligns with inflow direction → maximum dissipation

Effective extensional viscosity for rods

$$\mu^*_{\mathrm{ext}} = \mu\left(1 + \phi\frac{r^2}{3(\ln 2r - 1.5)}\right)$$

Large at $\phi \ll 1$ if $r \gg 1$.
Now $\phi = \frac{4\pi}{3}ab^2$ and $r = \frac{a}{b}$, so

$$\mu^*_{\mathrm{ext}} = \mu\left(1 + \frac{4\pi na^3}{9(\ln 2r - 1.5)}\right)$$

so same as sphere of radius a its largest dimension (except for factor $1.2(\ln 2r - 1.5)$).
Hence 5ppm of PEO can have a big effect in drag reduction.

Dilute requires $na^3 \ll 1$, but extension by Batchelor to semi-dilute $\phi \ll 1 \ll \phi r^2$

$$\mu^*_{\mathrm{ext}} = \mu\left(1 + \frac{4\pi na^3}{9\ln\phi^{-1/2}}\right)$$

Effective extensional viscosity for disks

$$\mu^*_{\text{ext}} = \mu\left(1 + \phi\frac{10}{3\pi r}\right) = \mu\left(1 + \frac{10nb^3}{9}\right)$$

where for disks b is the largest dimension

(always the largest for Stokes flow).

No semi-dilute theory, yet.

Behaviour in simple shear

$$\mathbf{U} = (\gamma y, 0, 0)$$

rotates to

Rotates to flow direction → minimum dissipation

rotates to

Rotates to lie in flow → minimum dissipation

Both Tumble: flip in $1/\gamma$, then align for r/γ ($\delta\theta = 1/r$ with $\dot{\theta} = \gamma/r^2$)

Effective shear viscosity

Jeffery orbits (1922)

$$\begin{aligned} \dot{\phi} &= \tfrac{\gamma}{r^2+1}(r^2\cos^2\phi + \sin^2\phi) \\ \dot{\theta} &= \tfrac{\gamma(r^2-1)}{4(r^2+1)}\sin 2\theta \sin 2\phi \end{aligned}$$

Solution with orbit constant C.

$$\tan\phi = r\tan\omega t, \quad \omega = \tfrac{\gamma r}{r^2+1}, \quad \tan\theta = Cr(r^2\cos^2\phi + \sin^2\phi)^{-1/2}$$

Effective shear viscosity Leal & H (1971)

$$\mu^*_{\text{shear}} = \mu\left(1 + \phi\begin{cases} 0.32r/\ln r & \text{rods} \\ 3.1 & \text{disks}\end{cases}\right)$$

numerical coefficients depend on distribution across orbits, C.

Remarks

Alignment gives $\mu^*_{\text{shear}} \ll \mu^*_{\text{ext}}$

This material anisotropy leads to anisotropy of macro flow.

Important to Turbulent Drag Reduction

Three measures of concentration of rods

$$\begin{cases} \phi r^2 \doteq na^3 & \text{for} \quad \mu^*_{\text{ext}} \\ \phi r \doteq na^2 b & \text{for} \quad \mu^*_{\text{shear}} \\ \phi \doteq nab^2 & \text{for permeability} \end{cases}$$

Brownian rotations – for stress relaxation

Rotary diffusivity: for spheres, rods and disks

$$D_{\rm rot} = kT \Big/ 8\pi\mu a^3, \quad kT \Big/ \frac{8\pi\mu a^2}{3(\ln 2r - 1.5)}, \quad kT \Big/ \tfrac{8}{3}\mu b^3$$

NB largest dimension, again
After flow is switched off, particles randomise orientation in time $1/6D \quad \sim 1$ second for $1\mu m$ in water.

State of alignment: probability density $P(\mathbf{p}, t)$ in orientation space $=$ unit sphere $|\mathbf{p}| = 1$.
Fokker-Plank equation

$$\frac{\partial P}{\partial t} + \nabla\cdot(\dot{\mathbf{p}} P) = D_{\rm rot} \nabla^2 P$$

$\dot{\mathbf{p}}(\mathbf{p})$ earlier deterministic.

Average stress over distribution P

Averaged stress

$$\sigma = -pI + 2\mu E + 2\mu\phi[AE : \langle\mathbf{pppp}\rangle + B(E\cdot\langle\mathbf{pp}\rangle + \langle\mathbf{pp}\rangle\cdot E) + CE + FD_{\rm rot}\langle\mathbf{pp}\rangle]$$

Last $FD_{\rm rot}$ term is entropic stress.
Extra material constant $F = 3r^2/(\ln 2r - 0.5)$ for rods and $12/\pi r$ for disks.
Averaging

$$\langle\mathbf{pp}\rangle = \int_{|\mathbf{p}|=1} \mathbf{pp} P \, dp$$

Solve Fokker-Plank: numerical, weak and strong Brownian rotations

Extensional and shear viscosities

Small
strain-hardening
↕ Orientation effects
Large
shear-thinning

Also $N_1 > 0$,
N_2 small < 0.

The closure problem

- Second moment of Fokker-Plank equation

$$\frac{D}{Dt}\langle\mathbf{pp}\rangle - \Omega\cdot\langle\mathbf{pp}\rangle\langle\mathbf{pp}\rangle\cdot\Omega$$
$$= \tfrac{r^2-1}{r^2+1}\left[E\cdot\langle\mathbf{pp}\rangle + \langle\mathbf{pp}\rangle\cdot E - 2\langle\mathbf{pppp}\rangle : E\right] - 6D_{\rm rot}\left[\langle\mathbf{pp}\rangle - \tfrac{1}{3}I\right]$$

  Hence this and stress need $\langle\mathbf{pppp}\rangle$, so an infinite hierarchy.
- Simple 'ad hoc' closure

$$\langle\mathbf{pppp}\rangle : E = \langle\mathbf{pp}\rangle\langle\mathbf{pp}\rangle : E$$

- Better: correct in weak and strong limits

$$= \tfrac{1}{5}\left[6\langle\mathbf{pp}\rangle\cdot E\cdot\langle\mathbf{pp}\rangle - \langle\mathbf{pp}\rangle\langle\mathbf{pp}\rangle : E - 2I(\langle\mathbf{pp}\rangle^2 : E - \langle\mathbf{pp}\rangle : E)\right]$$

- New idea Brownian fields: simulate many random walks in orientation space for each point of the complex flow.

Deformations

- Emulsions
  - Rupture
  - Theories
  - Numerical
- Flexible thread
- Double layer

Emulsions - deformable microstructure

Reviews: Ann. Rev. Fluid Mech. Rallison (1984), Stone (1994)

- Dilute – single drop, volume $\frac{4\pi}{3}a^3$
- T = surface tension (in rheology σ and γ not possible)
- Newtonian viscous drop μ_{int}, solvent μ_{ext}

Rupture if $\mu_{\text{ext}} > \frac{T}{Ea}$ (normally)

$\xrightarrow{\text{time}}$ $\xrightarrow{\text{time}}$

Irreversible reduction in size to $a_* = T/\mu_{\text{ext}}E$, as coalescence very slow.

Rupture in shear flow

$$\frac{T}{\mu_{\text{ext}}Ea}$$

$$\frac{\mu_{\text{int}}}{\mu_{\text{ext}}}$$

Experiments: de Bruijn (1989) (=own), Grace (1982)

Theories: Barthes-Biesel (1972), Rallison (1981), Hinch & Acrivos (1980)

Rupture difficult if $\mu_{\text{int}} \ll \mu_{\text{ext}}$

Too slippery. Become long and thin. Rupture if

$$\mu_{\text{ext}}E > \frac{T}{a}\begin{cases} 0.54\,(\mu_{\text{ext}}/\mu_{\text{int}})^{2/3} & \text{simple shear} \\ 0.14\,(\mu_{\text{ext}}/\mu_{\text{int}})^{1/6} & \text{extension} \end{cases}$$

but tip-streaming with mobile surfactants (makes rigid end-cap)

$$\mu_{\text{ext}}E > \frac{T}{a}0.56$$

Rupture difficult is simple shear if $\mu_{\mathrm{int}} > 3\mu_{\mathrm{ext}}$

- If internal very viscous ($\mu_{\mathrm{int}} \gg \mu_{\mathrm{ext}}$),
  - then rotates with vorticity,
  - rotating with vorticity, sees alternative stretching and compression,
  - hence deforms little.
- If internal fairly viscous ($\mu_{\mathrm{int}} \gtrsim 3\mu_{\mathrm{ext}}$),
  - then deforms more,
  - if deformed, rotates more slowly in stretching quadrant,
  - if more deformed, rotates more slowly, so deforms even more, etc etc
- until can rupture when $\mu_{\mathrm{int}} \leq 3\mu_{\mathrm{ext}}$

Theoretical studies: small deformations

Small ellipsoidal deformation

$$r = a\,(1 + \mathbf{x}\cdot\mathbf{A}(t)\cdot\mathbf{x} + \quad \text{higher orders})$$

Stokes flow with help of computerised algebra manipulator

$$\frac{D\mathbf{A}}{Dt} - \Omega\cdot\mathbf{A} + \mathbf{A}\cdot\Omega = 2k_1\mathbf{E} + k_5(\mathbf{A}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{A}) + \dots - \frac{T}{\mu_{\mathrm{ext}}a}\,(k_2\mathbf{A} + k_6(\mathbf{A}\cdot\mathbf{A}) + \dots)$$

$$\sigma = -pI + 2\mu_{\mathrm{ext}}\mathbf{E} + 2\mu_{\mathrm{ext}}\phi\big[k_3\mathbf{E} + k_7(\mathbf{A}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{A}) + \dots - \frac{T}{\mu_{\mathrm{ext}}a}(k_4\mathbf{A} + k_8(\mathbf{A}\cdot\mathbf{A}) + \dots\big]$$

with k_n depending on viscosity ratio, $\lambda = \mu_{\mathrm{int}}/\mu_{\mathrm{ext}}$,

$$k_1 = \frac{5}{2(2\lambda+3)}, \qquad k_2 = \frac{40(\lambda+1)}{(2\lambda+3)(19\lambda+16)}$$
$$k_3 = \frac{5(\lambda-1)}{3(2\lambda+3)}, \qquad k_4 = \frac{4}{2\lambda+3}$$

k_1 inefficiency of rotating by straining

Inefficiency of rotating by straining

Student Exercise

Consider the constitutive equation

$$\sigma = -pI + 2\mu_0 E + GA$$
$$\frac{DA}{Dt} - \Omega\cdot A + A\cdot\Omega - \alpha\,(E\cdot A + A\cdot E) = -\frac{1}{\tau}\,(A - I)\,,$$
$$\text{in flow} \quad u = (\Omega + E)\cdot x.$$

Solve for σ in steady simple shear, finding the shear viscosity and normal stress differences.

Find the condition on the parameters for the shear stress to be a monotonic increasing function of the shear-rate (non-shear-banding).

Theoretical studies: small deformations 2

Equilibrium shapes before rupture

extension   shear   internal circulation, tank-treading

Rheology before rupture

Small strain-hardening, small shear-thinning, $N_1 > 0$, $N_2 < 0$.

Repeated rupture leaves $\mu^* \cong$ constant.

Einstein: independent of size of particle, just depends on ϕ.

Form of constitutive equation

$$\frac{d}{dt}(\text{state}) \quad \& \quad \sigma \qquad \text{linear in} \quad \mathbf{E} \quad \& \quad \frac{T}{\mu_{\mathrm{ext}}a}$$

Numerical studies: boundary integral method

deformation angle

σ_{xy} N_1, N_2

Different λ. No rupture for $\lambda = 5$ (*)

Flexible thread – deformable microstructure

Position $\mathbf{x}(s,t)$, arc length s, tension $T(s,t)$
Slender-body theory with 2:1 drag $\perp$:$\|$, S.Ex

$$\dot{\mathbf{x}} = \mathbf{x}\cdot\nabla\mathbf{U} + T'\mathbf{x}' + \tfrac{1}{2}T\mathbf{x}''$$

Inextensibility $|\mathbf{x}'| \equiv 1$ gives S.Ex

$$T'' - \tfrac{1}{2}(\mathbf{x}'')^2 T = -\mathbf{x}'\cdot\nabla\mathbf{U}\cdot\mathbf{x}' \quad \text{and } T = 0 \text{ at ends}$$

Snap straight

H 76

Electrical double layer on isolated sphere

– another deformable microstructure

- Charged colloidal particle.
- Solvent ions dissociate,
- forming neutralising cloud around particle.
- Screening distance Debye κ^{-1}, with $\kappa^2 = \Sigma_i n_i z_i^2 e^2/\epsilon kT$.
- In flow, cloud distorts a little
- $\longrightarrow$ very small change in Einstein $\frac{5}{2}$.

Interactions

- Hydrodynamic
  - Dilute
  - Experiments
  - Numerical
- Electrical double-layer
  - Concentrated
- van der Waals
- Fibres
- Drops
  - Numerical

Hydrodynamic interactions for rigid spheres

Hydrodynamic: difficult long-ranged
Rigid spheres : two bad ideas

Dilute – between pairs (mostly)

Reversible (spheres + Stokes flow) $\rightarrow$ return to original streamlines

But minimum separation is $\frac{1}{2}\,10^{-4}$ radius $\rightarrow$ sensitive to roughness (typically 1%) when do not return to original streamlines.

Summing dilute interactions

Divergent integral from $\nabla \mathbf{u} \sim \dfrac{1}{r^3}$
Need renormalisation: Batchelor or mean-field hierarchy.

$$\mu^* = \mu \left[1 + 2.5\phi + 6.0\phi^2\right]$$

- 6.0 for strong Brownian motion
- 7.6 for strong extensional flow
- $\cong$ 5 for strong shear flow, depends on distribution on closed orbits

Small strain-hardening, small shear-thinning

Test of Batchelor ϕ^2 result

$$\mu^* = \mu \left[1 + 2.5\phi + 6.0\phi^2\right]$$

$\leftarrow \mu_0$

slope 6.0

Einstein 2.5$\rightarrow$

$\mu_\infty \rightarrow$

Russel, Saville, Schowalter 1989

Experiments – concentrated

Effective viscosities in shear flow

μ_0

μ_∞

$\mu a^3\gamma/kT$

ϕ

Russel, Saville, Schowalter 1989

Stokesian Dynamics

– (mostly) pairwise additive hydrodynamics

Jamming/locking – clusters across the compressive quadrant

Brady & Bossis (1985)

Fragile clusters if include soft repulsion or Brownian motion

Stokesian Dynamics 2

Effective viscosity in shear flow

Foss & Brady (2000)

'Stokesian Dynamics' Brady & Bossis
Ann. Rev. Fluid Mech. (1988)

Electrical double-layer interactions

Interaction distance r_*:

$$6\mu\mu a\gamma r_* = \frac{\epsilon\zeta^2 a^2\kappa}{r_*} e^{-\kappa(r_*-2a)}$$

$$\mu_* = \mu\left(1 + 2.5\phi + 2.8\phi^2\left(\frac{r_*}{a}\right)^5\right)$$

ϕ^2 coefficient as function of $\frac{r_*}{a}$

$$\left(\frac{r_*}{a}\right)^5 = \text{velocity} \quad \gamma r_*$$

$\times$ force distance $\quad r_*$

$\times$ volume $\quad \phi\left(\frac{r_*}{a}\right)^3$

Experiments – concentrated

Stress as function of shear-rate at different pH.
Suspension of $0.33\mu m$ aluminium particles at $\phi = 0.3$

Ducerf (Grenoble PhD 1992)

Note yield stress very sensitive to pH

Interactions – van der Waals

Attraction $\to$ aggregation
$\to$ gel (conc) or suspension of flocs (dilute)

Possible model of size of flocs R

- Number of particles in floc $N = \left(\frac{R}{a}\right)^d$, d = 2.3?
- Volume fraction of flocs $\phi_{\text{floc}} = \phi \left(\frac{R}{a}\right)^3$
- Collision between two flocs
- Hydro force $6\pi\mu R\gamma R$ = Bond force $F_b \times$ number of bonds $N\frac{a}{R}$
- Hence $\phi_{\text{floc}} = \phi \frac{F_b}{6\pi\mu a^2 \gamma}$
- So strong shear-thinning and yields stress $\phi F_b / a^2$.

Breakdown of structure in rheology $\mu(\gamma)$

Interactions – fibres

Cannot pack with random orientation if

$$\phi r > 1$$

leads to spontaneous alignment, nematic phase transition

Note extensional viscosity $\propto \phi r^2$ can be big while random, but shear viscosity $\propto \phi r$ is only big if aligned.

Disk not random if $\phi \frac{1}{r} > 1$.

Interactions – drops

- No jamming/locking of drops (cf rigid spheres)
  - small deformation avoid geometric frustration
  - slippery particle, no co-rotation problems
- Faster flow $\to$ more deformed $\to$ wider gaps in collisions
- Deformed shape has lower collision cross-section

  so 'dilute' at $\phi = 0.3$, blood works!

Numerical studies: boundary integral method

$\phi = 0.3$, $Ca = \mu_{\text{ext}} \gamma a / T = 0.3$ $\lambda = 1$, $\gamma t = 10$,
12 drops, each 320 triangles.

Numerical studies: boundary integral method 3

deformation angle

σ_{xy} N_1, N_2

$\lambda = 1$, different $\phi = 0, 0.1, 0.2, 0.3$. Effectively dilute at $\phi = 0.3$.

Numerical studies: boundary integral method 4

Reduced cross-section for collisions

into flow