Chapter 7: Microstructural studies for rheology

- To calculate the flow of complex fluids, need governing equations,
- in particular, the constitutive equation relating stress to flow and its history.
- Either 'ad hoc', such as Oldroyd-B differential equation and BKZ integral equation,
- Or look at microstructure for highly idealised systems and derive their constitutive equations.
- Most will be suspensions of small particles in Newtonian viscous solvent.

Microstructural studies for rheology

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

Micro & macro views

- Separation of length scales
- Micro $\leftrightarrow$ Macro connections
- Case of Newtonian solvent
- Homogenisation

Separation of length scales

Essential

$$\text{Micro} \quad \ell \ll L \quad \text{Macro}$$

$$\text{Micro} = \text{particle } 1\mu m \qquad \text{Macro} = \text{flow, } 1cm$$

- Micro and Macro time scales similar
- Need ℓ small for small micro-Reynolds number
  $Re_\ell = \frac{\rho\gamma\ell^2}{\mu} \ll 1$,
  otherwise possible macro-flow boundary layers $\not\ll \ell$
  But macro-Reynolds number $Re_L = \frac{\rho\gamma L^2}{\mu}$ can be large
- If $\ell \not\ll L$, then non-local rheology

Two-scale problem $\ell \ll L$

- Solve microstructure – tough, must idealise
- Extract macro-observables – easy

Here: suspension of particles in Newtonian viscous solvent

1. Macro→micro connection

- Particles passively move with macro-flow $\mathbf{u}$
- Particles actively rotate, deform & interact with macro-shear $\nabla\mathbf{u}$

both needing $Re_\ell \ll 1$.

2. Micro→macro connection

Macro = continuum = average/smear-out micro details

E.g. average over representative volume V with $\ell \ll V^{1/3} \ll L$

$$\overline{\sigma} = \frac{1}{V}\int_V \sigma \, dV$$

Also ensemble averaging and homogenisation

To be used in averaged = macro momentum equation

$$\overline{\rho}\left[\frac{\partial\overline{\mathbf{u}}}{\partial t} + \overline{\mathbf{u}}\cdot\nabla\overline{\mathbf{u}}\right] = \nabla\cdot\overline{\sigma} + \overline{F}$$

NB micro-Reynolds stresses $\overline{(\rho\mathbf{u})'\mathbf{u}'}$ small for $Re_\ell \ll 1$.

Reduction for suspension with Newtonian viscous solvent

Write:

$$\sigma = -pI + 2\mu e + \sigma^+$$

with pressure p, solvent viscosity μ, strain-rate e,
and σ^+ non-zero only inside particles.

Average:

$$\overline{\sigma} = -\overline{p}I + 2\mu\overline{e} + \overline{\sigma^+}$$

with

$$\overline{\sigma^+} = \frac{1}{V}\int_V \sigma^+ \, dV = n\left\langle \int_{\text{particle}} \sigma^+ \, dV \right\rangle_{\text{types of particle}}$$

with n number of particles per unit volume

Reduction for suspension with Newtonian viscous solvent 2

Inside rigid particles $e = 0$, so $\sigma^+ = \sigma$.

Also $\sigma_{ij} = \partial_k(\sigma_{ik}x_j) - x_j\partial_k\sigma_{ik}$, ignoring gravity $\partial_k\sigma_{ik} = 0$, so

$$\int_{\text{particle}} \sigma^+ \, dV = \int_{\text{particle}} \sigma \cdot n \, x \, dA$$

so only need σ on surface of particle. (Detailed cases soon.)

Hence

$$\overline{\sigma} = -\overline{p}I + 2\mu\overline{e} + n\int_{\text{particle}} \sigma \cdot n \, x \, dA$$

Integral called 'stresslet', is the force-dipole strength of the particle.

Homogenisation: asymptotics for $\ell \ll L$

Easier transport problem to exhibit method

$$\nabla \cdot k \cdot \nabla T = Q$$

with k & Q varying on macroscale x and microscale $\xi = x/\epsilon$,

Multiscale asymptotic expansion

$$T(x;\epsilon) \sim T_0(x,\xi) + \epsilon T_1(x,\xi) + \epsilon^2 T_2(x,\xi)$$

Homogenisation 2

ϵ^{-2}:

$$\partial_\xi k \partial_\xi T_0 = 0$$

$$\text{i.e.} \quad T_0 = T(x)$$

Thus T varies only slowly at leading order, with microscale making small perturbations.

Homogenisation 3

ϵ^{-1}:

$$\partial_\xi k \partial_\xi T_1 = -\partial_\xi k \partial_x T_0$$

Solution T_1 is linear in forcing $\partial_x T_0$, details depending on $k(\xi)$:

$$T_1(x,\xi) = A(\xi)\partial_x T_0$$

Homogenisation 4

ϵ^0:

$$\partial_\xi k \partial_\xi T_2 = Q - \partial_x k \partial_x T_0 - \partial_\xi k \partial_x T_1 - \partial_x k \partial_\xi T_1$$

Secularity: $\langle \text{RHS} \rangle = 0$ else $T_2 = O(\xi^2)$ which contradicts asymptoticity. (Periodicity not necessary.)
Hence

$$0 = \langle Q \rangle - \partial_x \langle k \rangle \partial_x T_0 - \partial_x \langle k \frac{\partial A}{\partial \xi} \rangle \partial_x T_0$$

Hence macro description

$$\nabla k^* \nabla T = Q^* \qquad \text{with} \quad k^* = \left\langle k + k \frac{\partial A}{\partial \xi} \right\rangle \quad \text{and} \quad Q^* = \langle Q \rangle$$

Homogenisation 5

NB: Leading order T_0 uniform at microlevel, with therefore no local heat transport

NB: Micro problem forced by ∇T_0. Need to solve

$$\nabla \cdot k \nabla \cdot T_{\text{micro}} = 0$$
$$T_{\text{micro}} \to x \cdot \nabla T_0$$

Solution

$$T_{\text{micro}} = (x + \epsilon A) \nabla T_0$$

Hence heat flux

$$\langle q \rangle = \langle k \nabla T_{\text{micro}} \rangle = \langle k + \epsilon k \nabla A \rangle \, \nabla T_0$$

Micro & macro views

- Separation of length scales
- Micro $\leftrightarrow$ Macro connections
- Case of Newtonian solvent
- Homogenisation

Microstructural studies for rheology

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

Einstein viscosity

Simplest – can show all details.

Highly idealised – many generalisations

- Spheres – no orientation problems
- Rigid – no deformation problems
- Dilute and Inert – no interactions problems

Micro problem

- Isolated rigid sphere
- force-free and couple-free
- in a general linear shearing flow $\nabla\overline{U}$
- Stokes flow

Stokes problem for Einstein viscosity

$$\nabla\cdot\mathbf{u}=0 \quad \text{in} \quad r>a$$
$$0=-\nabla p+\mu\nabla^2\mathbf{u} \quad \text{in} \quad r>a$$

$$\mathbf{u}=\mathbf{V}+\omega\times\mathbf{x} \quad \text{on} \quad r=a \quad \text{with} \quad V,\omega \text{ consts}$$
$$\mathbf{u}\to\overline{U}+\mathbf{x}\cdot\nabla\overline{U} \quad \text{as} \quad r\to\infty$$

$$\mathbf{F}=\int_{r=a}\sigma\cdot n\,dA=0,\qquad \mathbf{G}=\int_{r=a}\mathbf{x}\times\sigma\cdot n\,dA=0$$

Split general linear shearing flow $\nabla\overline{U}$ into symmetric strain-rate $\mathbf{E}$ and antisymmetric vorticity $\Omega\times$, i.e.

$$\mathbf{x}\cdot\nabla\overline{U}=\mathbf{E}\cdot\mathbf{x}+\Omega\times\mathbf{x}$$

NB: The vorticity vector $=\nabla\times\mathbf{u}=2\Omega$.

NB: Stokes problem is linear and instantaneous Student Ex

Solution of Stokes problem for Einstein viscosity

- $\mathbf{F}=0$ gives $\mathbf{V}=\overline{U}$, i.e. translates with macro flow S.Ex
- $\mathbf{G}=0$ gives $\omega=\Omega$, i.e. rotates with macro flow S.Ex

Then S.Ex

$$\mathbf{u}=\overline{U}+\mathbf{E}\cdot\mathbf{x}+\Omega\times\mathbf{x}-\mathbf{E}\cdot\mathbf{x}\frac{a^5}{r^5}-\mathbf{x}\frac{5(\mathbf{x}\cdot\mathbf{E}\cdot\mathbf{x})}{2r^2}\left(\frac{a^3}{r^3}-\frac{a^5}{r^5}\right)$$
$$p=-5\mu\frac{(\mathbf{x}\cdot\mathbf{E}\cdot\mathbf{x})a^3}{r^5}$$

Evaluate viscous stress on particle Student Ex

$$\sigma\cdot n\big|_{r=a}=\frac{5\mu}{2a}\mathbf{E}\cdot\mathbf{x}$$

Evaluate particle contribution to macro/average stress

$$\int_{\text{particle}}\sigma\cdot n\,\mathbf{x}\,dA=5\mu\mathbf{E}\frac{4\pi}{3}a^3$$

Result for Einstein viscosity (1905)

$$\overline{\sigma}=-\overline{p}I+2\mu\mathbf{E}+5\mu\mathbf{E}\phi \quad \text{with volume fraction} \quad \phi=n\frac{4\pi}{3}a^3$$

Hence effective viscosity

$$\mu^*=\mu\left(1+\frac{5}{2}\phi\right)$$

- Result independent of type of flow – shear, extensional
- Result independent of particle size – OK polydisperse
- Einstein used another averaging of dissipation which would not give normal stresses with $\sigma:E=0$, which arbitrarily cancelled divergent integrals (hydrodynamics is long-ranged)