Lecture 5: Microstructural studies

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1 Introduction

These two lectures will describe attempts to derive constitutive equations from "first principles." A large separation of length scales between the flow and the microstructure allows us to approximate the bulk properties of the fluid by averaging over the small scales. We begin by considering microstructure in a Newtonian solvent: first spheres, then other shapes, and finally their deformations and interactions. Moving beyond this approach, we also consider models for isolated or entangled polymers.

2 Separation of length scales

A typical length scale characterizing microstructure is $l \sim 1\,\mu$m, while the macroscopic length scale, the scale on which the flow varies, is a few orders of magnitude large, e.g., $L \sim 1\,$cm. The micro scale is large enough that the continuum approximation is valid (it works well down to about 10 nm). However, even though the length scales are separated, the time scales are comparable. Thus, we will use only space-averages (or maybe ensemble averages) but not time-averages. Another assumption is that the microscopic Reynolds number is small:

$$Re_l = \frac{\rho\dot{\gamma}l^2}{\mu} \ll 1.$$

Without this assumption it is possible to have macroscopic boundary layers smaller than the microscopic length scale. Note that the macroscopic Reynolds number $Re_L = (\rho\dot{\gamma}L^2)/\mu$ can be large or small. If Re_L is very large, then the macroscopic length scale (e.g. in boundary layers) can be comparable to the microscopic length scale and the desired separation of scales breaks down.

Our general approach to this two-scale problem has two steps. First we compute the effect of the flow on the microstructure; this is difficult and requires approximations or models. We will delay the discussion of this procedure in detail to the following sections. Once that problem is solved, we can extract the constitutive relation by averaging, which we discuss presently.

There are several ways to do this averaging. One choice, not employed here, is ensemble averaging. Another technique that we will not discuss further is homogenization; this uses asymptotic analysis to achieve the same result. Here we will use volume averaging with a representative volume V between the micro and macro scales, $l \ll V^{1/3} \ll L$. Averaging the momentum equation and neglecting micro Reynolds stresses we get

$$\overline{\rho}\left[\frac{\partial \overline{\mathbf{u}}}{\partial t} + \overline{\mathbf{u}} \cdot \nabla \overline{\mathbf{u}}\right] = \nabla \cdot \overline{\boldsymbol{\sigma}} + \overline{F}, \tag{1}$$

where $\bar{\cdot}$ denotes averaging over V. The stress tensor in the presence of particles in a Newtonian fluid is given by

$$\boldsymbol{\sigma} = -p\boldsymbol{\delta} + 2\mu \boldsymbol{E} + \boldsymbol{\sigma}^+, \tag{2}$$

where $\boldsymbol{\sigma}^+$ is the stress inside the particles, μ is the viscosity of the solvent, $\boldsymbol{E}$ is the rate of strain tensor and p is the pressure. The averages of the latter three quantities are unchanged by the microstructure up to leading order in the small parameter l/L, i.e., $\overline{p} = p + O(l/L)$, etc. Note that for general microstructure we cannot compute $\boldsymbol{\sigma}^+$ but it varies on the micro scales. The average of $\boldsymbol{\sigma}^+$ is

$$\overline{\boldsymbol{\sigma}^+} = \frac{1}{V}\int_V \boldsymbol{\sigma}^+ dV = n\left\langle \int_P \boldsymbol{\sigma}^+ dV \right\rangle, \tag{3}$$

where n is the number density of particles, $\int_P \cdot dV$ is the integral over a particle and $< \cdot >$ is the average over types of particles if needed. If the particles are considered to be rigid, the strain e inside the particle is zero. Neglecting the pressure and micro-gravity, we see that

$$\sigma^+_{ij} = \partial_k(\sigma^+_{ik} x_j) - x_j \partial_k \sigma^+_{ik} = \partial_k(\sigma^+_{ik} x_j), \tag{4}$$

where $\mathbf{x} = (x_1, x_2, x_3)$ are the space-coordinates. Then the volume integral over the particle reduces to a integral over the surface S:

$$\int_P \boldsymbol{\sigma}^+ dV = \oint_S \boldsymbol{\sigma}^+ \cdot \hat{\mathbf{n}}\, \mathbf{x}\; dA. \tag{5}$$

Thus, we need to know only the stress on the surface of the particle.

3 Suspension of Rigid Spheres

The simplest case of a microstructure is that of a dilute suspension of inert, rigid spheres. This highly idealized case was studied originally by Einstein in 1906, although his method involved subtracting two divergent integrals to get the right answer! The problem is to solve the Stokes flow around a sphere of radius a with prescribed linear flow far away. We also require that there be no net force and couple. The governing equations are

$$\nabla \cdot \mathbf{u} = 0 \tag{6}$$

$$\mathbf{0} = -\nabla p + \mu \nabla^2 \mathbf{u} \tag{7}$$

for $r > a$ with boundary conditions

$$\mathbf{u} = \mathbf{V} + \boldsymbol{\omega} \times \mathbf{x}, \text{ on } r = a, \tag{8}$$

$$\mathbf{u} = \mathbf{U} + \mathbf{x} \cdot \nabla \mathbf{U},\ r \to \infty, \tag{9}$$

where $\mathbf{U} + \mathbf{x} \cdot \nabla\mathbf{U}$ is the prescribed flow at infinity, $\boldsymbol{\omega}$ is the vorticity and $\mathbf{V}$ the velocity on the surface of the particle, to be determined using the force- and couple-free conditions

$$\mathbf{F} = \oint_{r=a} \boldsymbol{\sigma} \cdot \mathbf{n} dA = \mathbf{0} \tag{10}$$

$$\mathbf{G} = \oint_{r=a} \mathbf{x} \times \boldsymbol{\sigma} \cdot \mathbf{n} dA = \mathbf{0}. \tag{11}$$

We split $\nabla\mathbf{U}$ into symmetric strain rate $\mathbf{E}$ and antisymmetric vorticity $\boldsymbol{\Omega}$, i.e.,

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

The conditions (10)-(11) imply that the particle translates with the mean flow $\mathbf{V} = \mathbf{U}$ and rotates with the mean vorticity $\boldsymbol{\omega} = \boldsymbol{\Omega}$. The flow field and the pressure field is

$$\mathbf{u} = \mathbf{U} + \boldsymbol{\Omega} \times \mathbf{x} + \mathbf{E} \cdot \mathbf{x} - \mathbf{E} \cdot \mathbf{x}\frac{a^5}{r^5} - \frac{5}{2r^2}\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x}\left(\frac{a^3}{r^3} - \frac{a^5}{r^5}\right)\mathbf{x} \tag{12}$$

$$p = -5\mu a^3(\mathbf{x} \cdot E\mathbf{x})/r^5. \tag{13}$$

Evaluating the stress on the surface of the particle

$$\boldsymbol{\sigma} \cdot \mathbf{n}|_{r=a} = \frac{5}{2}\frac{\mu}{a}\mathbf{E} \cdot \mathbf{x} \tag{14}$$

and integrating

$$\oint \boldsymbol{\sigma} \cdot \mathbf{n} dA = 5\mu\mathbf{E} \cdot \frac{4\pi}{3}a^3 \tag{15}$$

gives an average stress

$$\overline{\boldsymbol{\sigma}} = -p\boldsymbol{\delta} + 2\mu\mathbf{E} + 5\mu\mathbf{E}\varphi = -p\boldsymbol{\delta} + 2\mu^*\mathbf{E} \tag{16}$$

where $\varphi = 4\pi n a^3/3$ is the fraction of volume occupied by the spheres and

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

is the Einstein viscosity due to the presence of the spheres in the liquid. This result does not depend on the type of flow or the size of individual particles, only their volume fraction.

4 Suspension of Rigid Spheroids

Now consider a dilute suspension of rigid particles that are not spherical. The next simplest class of particles are spheroids which are ellipsoids with semi-axes a, b and b. The aspect ratio of the spheroid is $r = a/b$. For $r > 1$, this is a prolate spheroid with the two equal axes being shorter than the unique axis, while for $r < 1$ this is an oblate spheroid with the two equal axes being longer. As in the previous section, in order to determine the effect of these particles on the flow, we will determine the stress contribution of one particle and then average over the number of particles per unit volume to get the macroscopic stress contribution.

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

Table 1: Material constants A, B and C for suspensions of rigid spheroids.

Considering Stokes flow around a spheroid we are lead to an evolution equation for a unit vector $\mathbf{p}$ in the direction of the axis of symmetry

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

where $\dot{()}$ is the material time derivative of $()$ and $\mathbf{\Omega}$ is the vorticity of the flow at infinity. The solution of Stokes flow around a spheroid was obtained by Oberbeck in 1876 [1]. For a given $\mathbf{p}$ we can integrate the stress around the boundary of the particle and get an expression for the macroscopic stress due to a volume fraction φ of spheroids

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

with A, B, and C constants depending only on the shape of the particles. For the limits of slender rods and flat disks the values of A, B and C are given in table 1.

In a simple extensional flow, rod-like particles will align with the stretching direction of the flow, the orientation that maximizes dissipation. For disk-like particles the axis of symmetry will align with the compression direction which is also the orientation of that shape that maximizes the dissipation of the flow. For rods and disks (the limits $r \to \infty$ and $r \to 0$) we can compute from this flow an effective extensional viscosity for dilute suspensions. If $\varphi \ll 1$ and $r \gg 1$ then

$$\mu^*_{\text{ext}} = \mu \left(1 + \varphi \frac{r^2}{3(\ln 2r - 3/2)} \right)$$

and if we substitute the definition of $\varphi = 4\pi n a b^2/3$ where n is the number of particles per unit volume then we get

$$\mu^*_{\text{ext}} = \mu \left(1 + \frac{4\pi n a^3}{9(\ln 2r - 3/2)} \right)$$

which is the same viscosity that we would get from a suspension of rigid spheres of radius a, apart from a factor that varies only logarithmically in r. Since a is the largest dimension of the spheroid, this explains why very small concentrations of polymers which are very long can have large effects on the characteristics of the flow. In the case of disks rather than rods

$$\mu^*_{\text{ext}} = \mu \left(1 + \varphi \frac{10}{3\pi r} \right) = \mu \left(1 + \frac{10 n b^3}{a} \right).$$

In a simple shear flow, these spheroidal particles do not approach a steady state, but instead tumble in the flow, spending some time aligned with the flow and then flipping relatively quickly to the opposite orientation again aligned with the flow. The effective shear viscosities can be computed for rods,

$$\mu^*_{\text{shear}} = \mu \left(1 + \varphi \frac{8}{25} \frac{r}{\ln r}\right),$$

and for disks,

$$\mu^*_{\text{shear}} = \mu \left(1 + \varphi \frac{31}{10}\right),$$

where the exact effective shear viscosities depend on the distribution of all of the particles in the flow over all of the possible tumbling orbits. Even this very simple model of rigid, asymmetric particles can explain a situation where $\mu^*_{\text{shear}} \ll \mu^*_{\text{ext}}$ that is typical of many non-Newtonian fluids (for Newtonian fluids $\mu_{\text{ext}} = 3\mu_{\text{shear}}$). We also see that there are three measures of concentration for the rods:

$$\begin{aligned} \varphi r^2 &= na^3 && \text{for } \mu^*_{ext}, \\ \varphi r &= na^2 b && \text{for } \mu^*_{shear}, \\ \varphi &= nab^2 && \text{for permeability.} \end{aligned}$$

One feature of non-Newtonian fluids that cannot be explained by these simple models is the relaxation of the fluid back to a basic state over a particular time-scale. One way to add this feature of relaxation to this model is to allow the rods and disks to execute Brownian motion on a particular time-scale, $1/6D_{\text{rot}}$ given by

$$\begin{aligned} D_{\text{rot}} &= kT \left(8\pi\mu a^3\right)^{-1} && \text{for spheres,} \\ D_{\text{rot}} &= kT \left(\frac{8\pi\mu a^3}{3(\ln 2r - 3/2)}\right)^{-1} && \text{for rods} \\ \text{and } D_{\text{rot}} &= kT \left(8\mu b^3/3\right)^{-1}, && \text{for disks.} \end{aligned}$$

Then instead of writing down an evolution equation for the orientation vector $\mathbf{p}$, we write down the Fokker-Planck equation for the probability density $\mathcal{P}(\mathbf{p}, t)$

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

where $\dot{\mathbf{p}}$ is as before from the deterministic model. Then we can compute an average stress by averaging not only over all of the particles in a volume, but also over the distribution $\mathcal{P}$. If we write $\langle \cdot \rangle = \int_{|\boldsymbol{p}|=1} \cdot \mathcal{P} d\mathbf{p}$ then the average stress due to rigid spheroids is

$$\sigma = -p\mathbf{I} + 2\mu\mathbf{E} + 2\mu\varphi \left[A\mathbf{E} : \langle \mathbf{pppp} \rangle + B\left(\mathbf{E} \cdot \langle \mathbf{pp} \rangle + \langle \mathbf{pp} \rangle \cdot \mathbf{E}\right) + C\mathbf{E} + F D_{\text{rot}} \langle \mathbf{pp} \rangle\right],$$

where there is now a new material constant F for the entropic stress ($F = 3r^2/(\ln 2r - 1/2)$ for rods, $F = 12/(\pi r)$ for disks). The equations for $\langle \mathbf{pp} \rangle$ and $\langle \mathbf{pppp} \rangle$ involve even higher order moments leading to an infinity hierarchy of equations. Different closures can be used to solve this problem. Some commonly used closures assume $\langle \mathbf{pppp} \rangle$ to be a function of $\langle \mathbf{pp} \rangle$.

Notes by Neil Burrell and Amit Apte

References

[1] H. Oberbeck, "über stationäre flussigkeitsbewegungen mit berücksichtigung der inneren reibung," Crelles Journal **81**, 62 (1876).