4 Microscopic dynamics

In this section we will look at the first model that people came up with when they started to model polymers from the microscopic level. It's called the **Oldroyd B** model. We will spend one double lecture to derive it and in the last lecture, look at its macroscopic (top-down) properties:

- Linear rheology
- Stress in shear
- Stress in extensional flow

4.1 The stress tensor

Remember we had the three Navier-Stokes equations (in incompressible form):

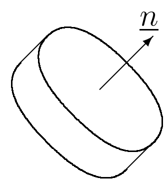
$$\underline{\nabla} \cdot \underline{u} = 0$$

This is mass conservation: integrated over a volume of space, it tells us that fluid flow in matches fluid flow out, so fluid does not accumulate in one place.

$$\rho \left(\frac{\partial \underline{u}}{\partial t} + \underline{u} \cdot \underline{\nabla u} \right) = \underline{\nabla} \cdot \underline{\underline{\sigma}}$$

$$\underline{\underline{\sigma}} = -p\underline{\underline{I}} + \eta(\underline{\nabla u} + (\underline{\nabla u})^\top)$$

In the last two equations, $\underline{\underline{\sigma}}$ is the **stress tensor**. The physical meaning of this is calculated from the force the force exerted across a small surface element with area δS and unit normal $\underline{n}$:



The force acting on the top surface of the tiny pillbox is $\underline{\underline{\sigma}} \cdot \underline{n}\, \delta S$.

4.2 Beads in a viscous fluid

Probably the simplest object you could put into a flow is a solid spherical bead. Let's look briefly at the motion of a microscopic solid sphere in a **Newtonian** fluid.

There is really only one parameter in Newtonian fluid flow (once you've made everything dimensionless): the **Reynolds number**, Re, which gives the ratio of inertial to viscous forces. If the scale of the flow is very small, then the Reynolds number is very small and we can assume it is zero. Then the governing equations are the **Stokes equations**:

$$\underline{\nabla} \cdot \underline{u} = 0 \qquad\qquad \eta \nabla^2 \underline{u} = \underline{\nabla} p.$$

There isn't time in this course to go into the details of these flows: we'll just accept one key fact. In a fluid which is otherwise at rest, a sphere of radius a, moving with constant velocity $\underline{U}$, experiences a drag force of

$$\underline{F} = -6\pi\eta a\underline{U}.$$

In the same way, a sphere moving with velocity $\underline{U}$ relative to the fluid around it experiences the same drag force.

4.3 Microscopic model

4.3.1 Bead-spring dumbbell

The dynamics of a single sphere in a viscous fluid are not very interesting. Interactions between them can be... but that's a whole other research area.

In order to model a polymer, we need something which can in some way remember the flows it has been through. We do this by creating something which can change its physical configuration as it responds to flow: then when the flow stops, its configuration is the way it carries the information about the flow history. This is exactly what real polymers do: but our model will be much simpler than real polymers.

We take two spherical beads, and connect them together with a linear spring. This is the simplest possible deformable object. The spring is intended to represent the entropic tendency of the polymer coil to end up in a random, relaxed state. So if you stretch out the coil, it will tend to recoil: the spring tends to bring the beads back together.

Now there are three effects acting on each bead:

- The spring force
- A drag force if it is moving relative to the fluid around it
- Brownian motion

We will build up the behaviour of the whole dumbbell bit by bit.

4.3.2 Separate beads in deterministic motion

Let us just look at one bead of radius a. We'll choose the radius to represent the typical size of a relaxed polymer coil. Now say it's instantaneously at a position $\underline{x}$; and suppose the other bead is instantaneously at $\underline{x} + \underline{r}$. We'll look at what it does under the action of a fluid flow and the spring force and nothing else.

Because it is very small, it has no inertia, and Newton's second law becomes a force balance: total force on our bead is zero.

The spring force pulling it towards the other bead is $\lambda\underline{r}$. λ is just a spring constant. Because it comes from thermal forces, we know its size:

$$\lambda = \frac{3kT}{a^2}$$

which also depends on the typical size of the relaxed polymer coil.

If the bead at $\underline{x}$ is moving with velocity $\underline{U}_1$, and the fluid around it has velocity $\underline{u}(\underline{x})$, the drag force on the bead will be

$$6\pi\eta a[\underline{u}(\underline{x}) - \underline{U}_1].$$

The total force on the bead (which must be zero) is

$$\frac{3kT}{a^2}\underline{r} + 6\pi\eta a[\underline{u}(\underline{x}) - \underline{U}_1] = \underline{0}$$

so we can work out the velocity of the bead:

$$\underline{U}_1 = \frac{kT}{2\pi\eta a^3}\underline{r} + \underline{u}(\underline{x}).$$

The other bead is positioned at $\underline{x} + \underline{r}$ and the spring force on it is $-\lambda\underline{r}$ so its velocity is

$$\underline{U}_2 = -\frac{kT}{2\pi\eta a^3}\underline{r} + \underline{u}(\underline{x} + \underline{r}).$$

In the absence of Brownian motion, these two velocities tell us how the bead positions evolve:

$$\begin{aligned} \frac{\mathrm{d}\underline{x}}{\mathrm{d}t} &= \frac{kT}{2\pi\eta a^3}\underline{r} + \underline{u}(\underline{x}) \\ \frac{\mathrm{d}(\underline{x} + \underline{r})}{\mathrm{d}t} &= -\frac{kT}{2\pi\eta a^3}\underline{r} + \underline{u}(\underline{x} + \underline{r}) \end{aligned}$$

Finally we subtract the two to get the evolution of $\underline{r}$:

$$\frac{\mathrm{d}\underline{r}}{\mathrm{d}t} = -\frac{kT}{\pi\eta a^3}\underline{r} + \underline{u}(\underline{x} + \underline{r}) - \underline{u}(\underline{x})$$

Since $\underline{r}$ is microscopically small relative to the scale over which $\underline{u}$ changes, we can use a Taylor series for $\underline{u}(\underline{x} + \underline{r})$:

$$\frac{\mathrm{d}\underline{r}}{\mathrm{d}t} = -\frac{kT}{\pi\eta a^3}\underline{r} + \underline{r} \cdot \underline{\nabla u}(\underline{x})$$

which is correct up to terms of order $\underline{r}$.

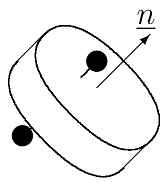
The constant $2kT/\pi\eta a^3$ is called $1/\tau$; it represents the inverse relaxation time of the dumbbell following distortion caused by the flow.

$$\frac{\mathrm{d}\underline{r}}{\mathrm{d}t} = -\frac{1}{2\tau}\underline{r} + \underline{r} \cdot \underline{\nabla u}.$$

4.3.3 Stress in the fluid

Now suppose we have a suspension containing many of these dumbbells. What will the extra stress they contribute be? Of course, the fluid they are suspended in, which has its own viscosity η, will continue to contribute a Newtonian stress; we're just looking for the **polymer extra stress**, $\underline{\underline{\sigma}}^p$.

Again, we look at the tiny surface element with area δS and unit normal $\underline{n}$. We are interested in dumbbells that cross the surface.



The force associated with a single dumbbell that crosses the surface is $\lambda\underline{r}$; how many will cross the surface?

Clearly a long dumbbell is more likely to cross the surface than a short one; and a dumbbell which is lined up with $\underline{n}$ is more likely to cross the surface than one which is perpendicular to it. If there are m dumbbells per unit volume, then we expect the number crossing our surface element to be

$$m\underline{r} \cdot \underline{n}\, \delta S.$$

Then the extra stress exerted by the dumbbells is

$$\underline{\underline{\sigma}}^p \cdot \underline{n}\, \delta S = \lambda \underline{r}(m\underline{r} \cdot \underline{n}\, \delta S) \quad \text{so} \quad \underline{\underline{\sigma}}^p = m\lambda \underline{rr} = \frac{3\pi\eta a m}{2\tau}\underline{rr}.$$

Again, we introduce a name for the new constant: this time, $G = 3\pi\eta a m/2\tau$ so that

$$\underline{\underline{\sigma}}^p = G\underline{rr}.$$

4.3.4 Adding Brownian motion

We have worked out how a dumbbell will evolve if its motion is deterministic, and the stress it will cause. But to complete the model, we need to add Brownian motion of the two beads.

We simply add a standard 3D Brownian motion (i.e. each of the x, y, z components is a Brownian motion) to the evolution of the vector $\underline{r}$:

$$\underline{dr} = \left(-\frac{1}{2\tau}\underline{r} + \underline{r} \cdot \underline{\nabla u}(\underline{x})\right) dt + \tau^{-1/2}\underline{dB_t}$$

We have chosen $\tau^{-1/2}$ as the coefficient for two reasons: it has the correct dimension; but also because (as we will see later) this leads to a dumbbell with no flow having a natural length of 1.

Because we eventually want to work out the extra stress, we then define the **conformation tensor**

$$\underline{\underline{A}}(\underline{x},t) = \mathbb{E}\left[\underline{r}(\underline{x},t)\underline{r}(\underline{x},t)\right]$$

which will give us

$$\underline{\underline{\sigma}}^p = G\underline{\underline{A}}.$$

Now we use the first-step method (see GM01 part 1). As we take a time-step dt, the position $\underline{x}$ of our dumbbell will move to

$$\underline{x} + \underline{dx} = \underline{x} + \underline{u}(\underline{x})dt.$$

So when we take our time-step, we get

$$\begin{aligned}
\underline{\underline{A}}(\underline{x}+\underline{u}(\underline{x})dt, t+dt) &= \mathbb{E}\left[(\underline{r}+\underline{dr})(\underline{r}+\underline{dr})\right] \\
&= \mathbb{E}\left[\underline{r}\,\underline{r} + \underline{r}\,\underline{dr} + \underline{dr}\,\underline{r} + \underline{dr}\,\underline{dr}\right] \\
\underline{\underline{A}}(\underline{x}+\underline{u}(\underline{x})dt, t+dt) &= \mathbb{E}\left[\underline{r}\,\underline{r}\right] + \mathbb{E}\left[\underline{r}\,\underline{dr}\right] + \mathbb{E}\left[\underline{dr}\,\underline{r}\right] + \mathbb{E}\left[\underline{dr}\,\underline{dr}\right]
\end{aligned}$$

Now let's look at these four terms separately. As usual, we only keep terms up to order dt.

$$\begin{aligned}
\mathbb{E}\left[\underline{r}\,\underline{r}\right] &= \underline{\underline{A}}(\underline{x},t) \\
\mathbb{E}\left[\underline{r}\,\underline{dr}\right] &= \mathbb{E}\left[\underline{r}\left(\left(-\frac{1}{2\tau}\underline{r} + \underline{r}\cdot\underline{\nabla u}(\underline{x})\right)dt + \tau^{-1/2}\underline{dB}_t\right)\right] \\
&= \mathbb{E}\left[\underline{r}\left(\left(-\frac{1}{2\tau}\underline{r} + \underline{r}\cdot\underline{\nabla u}(\underline{x})\right)dt\right)\right] \\
&= -\frac{1}{2\tau}\underline{\underline{A}}dt + \underline{\underline{A}}\cdot\underline{\nabla u}dt \\
\mathbb{E}\left[\underline{dr}\,\underline{r}\right] &= \mathbb{E}\left[\left(\left(-\frac{1}{2\tau}\underline{r} + \underline{r}\cdot\underline{\nabla u}(\underline{x})\right)dt + \tau^{-1/2}\underline{dB}_t\right)\underline{r}\right] \\
&= \mathbb{E}\left[\left(\left(-\frac{1}{2\tau}\underline{r} + \underline{r}\cdot\underline{\nabla u}(\underline{x})\right)dt\right)\underline{r}\right] \\
&= -\frac{1}{2\tau}\underline{\underline{A}}dt + (\underline{\nabla u})^\top\cdot\underline{\underline{A}}dt \\
\mathbb{E}\left[\underline{dr}\,\underline{dr}\right] &= \mathbb{E}\left[\left(\left(-\frac{\underline{r}}{2\tau} + \underline{r}\cdot\underline{\nabla u}\right)dt + \tau^{-1/2}\underline{dB}_t\right)\left(\left(-\frac{\underline{r}}{2\tau} + \underline{r}\cdot\underline{\nabla u}\right)dt + \tau^{-1/2}\underline{dB}_t\right)\right] \\
&= \mathbb{E}\left[\left(\tau^{-1/2}\underline{dB}_t\right)\left(\tau^{-1/2}\underline{dB}_t\right)\right] \\
&= \tau^{-1}\underline{\underline{I}}dt
\end{aligned}$$

We also need to look at the left-hand side term.

$$\begin{aligned}
\underline{\underline{A}}(\underline{x}+\underline{u}(\underline{x})dt, t+dt) &= \underline{\underline{A}}(\underline{x}+\underline{u}(\underline{x})dt, t+dt) - \underline{\underline{A}}(\underline{x}, t+dt) + \underline{\underline{A}}(\underline{x}, t+dt) \\
&= (\underline{u}dt\cdot\underline{\nabla})\underline{\underline{A}} + \underline{\underline{A}}(\underline{x}, t+dt) \\
&= (\underline{u}dt\cdot\underline{\nabla})\underline{\underline{A}} + \underline{\underline{A}}(\underline{x}, t+dt) - \underline{\underline{A}}(\underline{x},t) + \underline{\underline{A}}(\underline{x},t) \\
&= (\underline{u}\cdot\underline{\nabla})\underline{\underline{A}}dt + \frac{\partial\underline{\underline{A}}}{\partial t}dt + \underline{\underline{A}}(\underline{x},t)
\end{aligned}$$

Putting these all together gives:

$$\left(\frac{\partial \underline{\underline{A}}}{\partial t} + (\underline{u}\cdot\underline{\nabla})\underline{\underline{A}}\right)dt = -\frac{1}{2\tau}\underline{\underline{A}}dt + \underline{\underline{A}}\cdot\underline{\nabla u}dt - \frac{1}{2\tau}\underline{\underline{A}}dt + (\underline{\nabla u})^{\top}\cdot\underline{\underline{A}}dt + \frac{1}{\tau}\underline{\underline{I}}dt$$

$$\frac{\partial \underline{\underline{A}}}{\partial t} + (\underline{u}\cdot\underline{\nabla})\underline{\underline{A}} - \underline{\underline{A}}\cdot\underline{\nabla u} - (\underline{\nabla u})^{\top}\cdot\underline{\underline{A}} = -\frac{1}{\tau}\left(\underline{\underline{A}} - \underline{\underline{I}}\right)$$

and the polymer extra stress is

$$\underline{\underline{\sigma}}^{p} = G\underline{\underline{A}}.$$

The terms on the left-hand side of the $\underline{\underline{A}}$ equation are called the **co-deformational time derivative** because they represent what happens to a line element that is deforming with the flow.

We have now derived the **Oldroyd-B equations**:

$$\begin{gathered}
\underline{\nabla}\cdot\underline{u} = 0\\
\rho\left(\frac{\partial \underline{u}}{\partial t} + \underline{u}\cdot\underline{\nabla u}\right) = \underline{\nabla}\cdot\underline{\underline{\sigma}}\\
\underline{\underline{\sigma}} = -p\underline{\underline{I}} + \eta\left(\underline{\nabla u} + (\underline{\nabla u})^{\top}\right) + G\underline{\underline{A}}\\
\frac{\partial \underline{\underline{A}}}{\partial t} + (\underline{u}\cdot\underline{\nabla})\underline{\underline{A}} - \underline{\underline{A}}\cdot\underline{\nabla u} - (\underline{\nabla u})^{\top}\cdot\underline{\underline{A}} = -\frac{1}{\tau}\left(\underline{\underline{A}} - \underline{\underline{I}}\right)
\end{gathered}$$

In the final lecture we will see how the fluid corresponding to these equations behaves.