Lecture 2: Constitutive Relations

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1 Introduction

This lecture discusses equations of motion for non-Newtonian fluids. Any fluid must satisfy conservation of momentum

$$\rho \frac{D\boldsymbol{u}}{Dt} = -\nabla p + \nabla \cdot \sigma + \rho \boldsymbol{g} \tag{1}$$

where ρ is the density of the fluid, $\boldsymbol{u}$ is the velocity field, p is the pressure and σ is the deviatoric stress tensor (the trace-free component of the stress).[1] We can absorb the body force $\rho\boldsymbol{g}$ into a modified pressure, and in turn we can absorb the modified pressure into the stress giving $\rho\frac{Du}{Dt} = \nabla \cdot \sigma$. Much of the modeling in non-Newtonian fluids concentrates on finding a constitutive relation between σ and the flow velocity distribution.

The fluids we use are incompressible unless stated otherwise, so we have assumed

$$\nabla \cdot \boldsymbol{u} = 0.$$

In many practical applications of non-Newtonian fluids inertia is also negligible. So we will often use the Stokes equations:

$$\nabla \cdot \sigma = \boldsymbol{0}.$$

2 Phenomenological

2.1 Simple materials

In a simple material the stress σ depends on the deformation and the rate of deformation. To understand this relationship we begin by considering how the fluid deforms. Using a Lagrangian fluid description we follow a fluid particle in the flow. The flow $\boldsymbol{u}$ maps a material element to a new position $\boldsymbol{x}$ that depends on its initial position $\boldsymbol{X}$

$$\boldsymbol{X} \to \boldsymbol{x}(\boldsymbol{X}, t).$$

If we follow a material line element, $\delta\boldsymbol{X}$, it is stretched and rotated in the flow according to

$$\delta\boldsymbol{X} \to \delta\boldsymbol{x} = \mathsf{A} \cdot \delta\boldsymbol{X}, \qquad \mathsf{A}_{iJ} = \frac{\partial \boldsymbol{x}_i}{\partial \boldsymbol{X}_J}.$$

[1] In these notes σ is used for either the stress or just the deviatoric stress. It is usually obvious from the context.

We assume that the system is local and causal. That is, the stress at a material point depends only on the history of that material point, and the stress cannot depend on future time. This gives a functional for stress

$$\sigma(t) = \sigma\{\mathsf{A}(\tau)\}_{\tau \leq t}. \tag{2}$$

We now adopt the assumption of *material frame indifference* which states that our constitutive equation should not depend on the translation, rotation or acceleration of the frame of reference. Except in extreme cases this should be a good approximation. Thus, we should get the same result if we calculate our stress before or after rotating the frame of reference.

Consider a change of frame of reference given by

$$\boldsymbol{x}' = \mathsf{Q}(t)\boldsymbol{x} + \boldsymbol{a}(t), \tag{3}$$

with $\mathsf{Q}(t)$ a rotation matrix and $\boldsymbol{a}$ a translation vector. The stress in the new frame of reference is given by

$$\begin{aligned} \sigma' &= \sigma\,\{\mathsf{Q}(\tau)\,\mathsf{A}(\tau)\,\mathsf{Q}^T(0)\}_{\tau \leq t} \\ &\equiv \mathsf{Q}(t)\,\sigma\{\mathsf{A}(\tau)\}_{\tau \leq t}\,\mathsf{Q}^T(t). \end{aligned}$$

We require $\sigma\{\mathsf{A}\}$ to obey this identity for all $\mathsf{Q}(t)$.

2.1.1 Perfectly Elastic Materials

A perfectly elastic material responds instantaneously to an applied stress. All that matters is the present strain which depends only on the present position and the relaxed position. The history of how it arrived into its current position does not matter. The functional $\sigma\{\mathsf{A}(t)\}$ becomes a function $\sigma(\mathsf{A})$.

We can decompose the deformation tensor A into a rotation tensor R and a stretch tensor U such that

$$\mathsf{A} = \mathsf{R} \cdot \mathsf{U} \;\text{ with }\; \mathsf{R}^T\mathsf{R} = \mathsf{I} \;\text{ and }\; \mathsf{U}^2 = \mathsf{A}^T\mathsf{A}. \tag{4}$$

Then setting $\mathsf{Q} \equiv \mathsf{R}^T$ in *material frame indifference* gives

$$\sigma\{\mathsf{A}\} = \mathsf{R}^T(t)\,f(\mathsf{U}(t))\,\mathsf{R}(t), \tag{5}$$

thus reducing the problem to determining the unknown function $f(U)$. It is convenient to express the constitutive law in erms of the potential energy$w(U)$ instead of the function f. The principal of frame indifference leads to the constitutive law. For an elastic material that is isotropic in its rest state, and has potential energy w for elastic deformations, this gives

$$\sigma = \frac{1}{\gamma}\frac{\partial w}{\partial \alpha}\,\mathsf{A}\mathsf{A}^T - \frac{1}{\gamma}\frac{\partial w}{\partial \beta}\,\mathsf{A}^{-T}\mathsf{A}^{-1} \tag{6}$$

where $\alpha = \frac{1}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)$, $\beta = \frac{1}{2}(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2})$ and $\gamma = \lambda_1^2\lambda_2^2\lambda_3^2$ (=1 if incompressible), and λ_n^2 are the eigenvalues of $\mathsf{A}^T\mathsf{A}$

2.2 Time derivative problem

In a new reference frame the stress is given by

$$\sigma' = \mathsf{Q}\sigma\mathsf{Q}^T$$

and so

$$\dot{\sigma}' = \mathsf{Q}\dot{\sigma}\mathsf{Q}^T + \dot{\mathsf{Q}}\sigma\mathsf{Q}^T + \mathsf{Q}\sigma\dot{\mathsf{Q}}^T.$$

Thus the transformation from $\dot{\sigma}$ to $\dot{\sigma}'$ does not follow the same relation as the transformation from σ to σ'. We will try to find some other derivative that does.

The new flow velocity is

$$\boldsymbol{u}' = \mathsf{Q}\boldsymbol{u} + \dot{\mathsf{Q}}\boldsymbol{x} + \dot{\boldsymbol{a}}$$

and the velocity gradient is

$$\frac{\partial \boldsymbol{u}'}{\partial \boldsymbol{x}'} = \mathsf{Q}\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{x}}\mathsf{Q}^T + \dot{\mathsf{Q}}\mathsf{Q}^T. \tag{7}$$

The velocity gradient can be separated into symmetric (strain rate) and antisymmetric (vorticity) parts The transformed strain rate is $\mathsf{E}' = \mathsf{Q}\mathsf{E}\mathsf{Q}^T$ and the transformed vorticity is $\Omega' = \mathsf{Q}\Omega\mathsf{Q}^T + \dot{\mathsf{Q}}\mathsf{Q}^T$.

Putting these elements together we can show that the co-rotational (Jaumann [1, 2]) time derivative

$$\overset{\circ}{\sigma} \equiv \frac{D\sigma}{Dt} - \Omega\cdot\sigma + \sigma\cdot\Omega \tag{8}$$

has transformation

$$\overset{\circ\prime}{\sigma'} = \mathsf{Q}\ \overset{\circ}{\sigma}\ \mathsf{Q}^T,$$

(where $\overset{\circ\prime}{\sigma'}$ denotes the co-roational derivative of the stress in the new frame of reference,) as does the co-deformational (Oldroyd [3] or upper convected) derivative

$$\overset{\triangledown}{\sigma} \equiv \frac{D\sigma}{Dt} - \nabla\boldsymbol{u}^T\cdot\sigma - \sigma\cdot\nabla\boldsymbol{u}. \tag{9}$$

Note $\overset{\circ}{\mathsf{I}} = \mathsf{0}$ but $\overset{\triangledown}{\mathsf{I}} \neq \mathsf{0}$.

The co-rotational time derivative is the rate of change as observed while rotating and translating with the fluid. The co-deformational derivative is the rate of change as observed while deforming and translating with the fluid.

3 Exact approximations

3.1 Linear viscoelasticity

Linear viscoelasticity is valid in the limit where $\mathsf{A}^T\mathsf{A} \approx \mathsf{I}$. The most general form of the history-dependent linear constitutive law is

$$\sigma(t) = \mathsf{R}(t)\int_0^\infty G(s)\ \left(\mathsf{A}^T\mathsf{A}\right)^{\cdot}\ (t-s)ds\ \mathsf{R}^T(t). \tag{10}$$

This is a co-rotational time integral. $G(s)$ represents the elastic memory. It is the Fourier transform of the frequency dependent elastic modulus $G^*(w)$ defined in section 3.3 of Lecture 1. For a Newtonian fluid $G(s) = \delta(s)$ and for an elastic solid, $G(s) = 1$.

For simple shear with shear rate $\dot{\gamma}$

$$\sigma(t) = \int_0^\infty G(s)\dot{\gamma}(t-s)ds \tag{11}$$

and since for steady shear $\dot{\gamma}$ is constant, the steady shear viscosity is given by $\int_0^\infty G(s)ds$.

3.2 Second order fluid

The second order fluid is derived through a retarded motion expansion and is valid for slow, weak flows. Considerable care must be used because this model can have instabilities in regimes where it doesn't apply (*e.g.*, high frequency), and these regimes can arise from poorly chosen boundary conditions.

The stress is Newtonian with small terms added:

$$\begin{aligned} \sigma &= -p\mathsf{I} + 2\mu\mathsf{E} - 2\alpha_1\overset{\triangledown}{\mathsf{E}} + \alpha_2\mathsf{E}\cdot\mathsf{E} \\ \mu &= \int_0^\infty G(s)ds \\ \alpha_1 &= \int_0^\infty s\,G(s)ds. \end{aligned} \tag{12}$$

In simple shear the second order fluid has constant viscosity $\mu = \int_0^\infty G(s)ds$ and normal stress differences $N_1 = \sigma_{yy} - \sigma_{xx} = 2\alpha_1\dot{\gamma}^2$, $N_2 = \sigma_{zz} - \sigma_{yy} = -\frac{1}{4}\alpha_2\dot{\gamma}^2$, where x denotes the flow direction, y is the velocity gradient direction.

In uniaxial extensional flow the viscosity is

$$\mu_{\text{ext}} = \mu + (\alpha_1 + \frac{1}{4}\alpha_2)\dot{\epsilon}, \tag{13}$$

where $\dot{\epsilon}$ is the elongation rate.

4 Semi-empirical models

Many fluids are too non-linear to be described by the linear viscoelastic or slightly non-linear second order models discussed above. For these fluids there are no exact solutions or exact approximations and other models must be considered.

4.1 Generalized Newtonian Fluid

The generalized Newtonian fluid follows the same equations as the Newtonian fluid but the viscosity depends on the shear rate $\dot{\gamma} = \sqrt{2\mathsf{E}:\mathsf{E}}$. As for Newtonian fluids, the stress depends only on the instantaneous flow and not the flow history. The constitutive law is

$$\sigma = -p\mathsf{I} + 2\mu(\dot{\gamma})\mathsf{E}. \tag{14}$$

The generalized Newtonian models were developed to fit experimental data and the form of $\mu(\dot{\gamma})$ is usually derived empirically. Some common expressions used to fit data are:

- Power Law [4]

$$\mu(\dot\gamma) = k\dot\gamma^{n-1}, \tag{15}$$

  where k and n are fit parameters.

- Carreau, Yasuda, Cross [5, 6, 7]

$$\mu(\dot\gamma) = \mu_\infty + (\mu_0 - \mu_\infty)[1 + (\lambda\dot\gamma)^a]^{\frac{n-1}{a}} \tag{16}$$

  where μ_0 and μ_∞ are the viscosities at the limits of zero and infinite shear rate, respectively; a, n, and λ are fit parameters.

- Yield fluids: the fluid flows only above some critical stress σ_y.
  - Bingham [8]

$$\mu = \begin{cases} \infty & \text{if } |\sigma| < \sigma_\mathrm{y} \\ \mu_0 + \dfrac{\sigma_y}{\dot\gamma} & \text{if } |\sigma| > \sigma_\mathrm{y} \end{cases}$$

  - Herschel Bulkley

$$\mu = \begin{cases} \infty & \text{if } |\sigma| < \sigma_y \\ k\dot\sigma^{n-1} + \dfrac{\sigma_y}{\dot\gamma} & \text{if } |\sigma| > \sigma_y \end{cases}$$

4.2 The Oldroyd-B and FENE Models

The Oldroyd-B model [3] is one of the simplest models that includes the history of the flow. We use the following equation for the evolution of the deviatoric stress,

$$\sigma + \lambda_1 \overset{\triangledown}{\sigma} = 2\mu(\mathsf{E} + \lambda_2 \overset{\triangledown}{\mathsf{E}}), \tag{17}$$

where λ_1 is the relaxation time and λ_2 is the retardation time. For a given pressure p, the Oldroyd-B model often appears in an equivalent form for the total stress:

$$\sigma = -p^*\mathsf{I} + 2\mu^*\mathsf{E} + \frac{G}{\tau}\mathsf{A} \tag{18}$$

$$\overset{\triangledown}{\mathsf{A}} = -\frac{1}{\tau}(\mathsf{A} - \mathsf{I}) \tag{19}$$

where $p^* = p + 2(1 - \lambda_2/\lambda_1)\mu/\lambda_1$, $G = 2(1 - \lambda_2/\lambda_1)\mu$, $\tau = \lambda_1$ and $\mu^* = \lambda_2\mu/\lambda_1$. The Oldroyd-B model reduces to Upper Convective Maxwell (UCM) when $\lambda_2 = 0$ and viscous Newtonian when $\lambda_2 = \lambda_1$.

In simple shear an Oldroyd-B fluid has constant viscosity $\mu = G/2 + \mu^*$ and the normal stresses are

$$N_1 = 2\mu(\lambda_1 - \lambda_2)\dot\gamma^2, \qquad N_2 \equiv 0. \tag{20}$$

The uniaxial extensional viscosity is

$$\mu_\mathrm{ext} = \frac{\mu(1 - \lambda_2\dot\epsilon - 2\lambda_1\lambda_2\dot\epsilon^2)}{(1 - \lambda_2\dot\epsilon)(1 + \lambda_1\dot\epsilon)}. \tag{21}$$

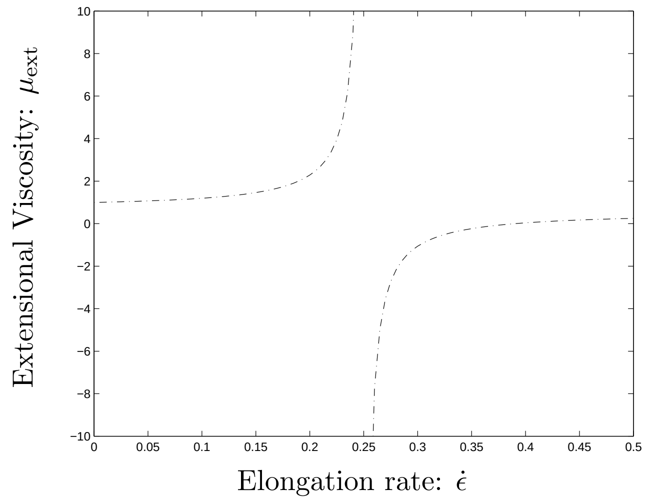

Figure 1: The extensional viscosity for $\lambda_1 = 2,\ \lambda_2 = 1$. The extensional viscosity is negative for elongation rates slightly above $1/2\lambda_1$.

This gives negative viscosities at some elongation rates (figure 1) which is unphysical. This happens because the Oldroyd-B model is derived using Hooks Law springs which are infinitely extensible.

The Oldroyd-B model can be reformulated to eliminate the negative viscosity. Assuming that the microstructure is not infinitely extensible, we get

$$\overset{\triangledown}{\mathsf{A}} + \frac{f}{\tau}(\mathsf{A} - \mathsf{I}) = 0 \tag{22}$$

for some function $f(\mathsf{A})$. The stress σ is then

$$\tau = -p\mathsf{I} + 2\mu_s \mathsf{E} + \frac{Gf}{\tau}(\mathsf{A} - \mathsf{I}). \tag{23}$$

Occasionally f appears only in Equation (22) and not in (23).

The FENE (finitely extensible nonlinearly elastic) modification keeps A from growing too fast by setting

$$f = \frac{L^2}{L^2 - \operatorname{trace} \mathsf{A}}, \tag{24}$$

where L represents a nondimensional length scale for the stretching of the microstructure. The more A stretches, the stiffer it becomes.

4.3 Other Consititutive Equations

Below are a few of the many other costitutive equations, which are derived to match experimental data.

- The White-Metzner model [9] is used for shear-thinning fluids. It is a modified Maxwell model that allows incorporation of experimental data on viscosity as a function of shear rate. The deviatoric stress is given by

$$\sigma + \frac{\mu(\dot\gamma)}{G}\overset{\triangledown}{\sigma} = 2\mu(\dot\gamma)\mathsf{E}. \tag{25}$$

The shear thinning viscosity $\mu(\dot\gamma)$ often follows a power-law.

- The Giesekus model [10] adds quadratic nonlinearity and divides the deviatoric stress into a solvent contribution (σ_s) and a polymer contribution (σ_p).

$$\begin{aligned}\sigma &= \sigma_s + \sigma_p\\ \sigma_s &= \mu_s\mathsf{E}\\ \sigma_p + \lambda_1\overset{\triangledown}{\sigma}_p + \frac{\alpha\lambda_1}{\mu_p}\sigma_p^2 &= 2\mu_p\mathsf{E}\end{aligned}$$

- The PTT (Phan-Thien-Tanner) model [11] is similar to Giesekus but has a different nonlinear term

$$\begin{aligned}\sigma &= \sigma_s + \sigma_p\\ \sigma_s &= \mu_s\mathsf{E}\\ \sigma_p + \lambda_1\overset{\triangledown}{\sigma}_p + \left[\exp\left(\frac{\lambda_1}{\mu_p}\operatorname{trace}\sigma_p\right) - 1\right]\sigma_p &= 2\mu_p\mathsf{E}\end{aligned}$$

- The Kay-Bernstein-Kearsly-Zappa (K-BKZ) equation [12] combines linear viscoelasticity and nonlinear elasticity via a memory integral constitutive law:

$$\sigma = \int_0^\infty \dot G(s)\left[\frac{\partial w}{\partial\alpha}(\tilde{\mathsf{A}}\tilde{\mathsf{A}}^T - 1) - \frac{\partial w}{\partial\beta}(\tilde{\mathsf{A}}^{-T}\tilde{\mathsf{A}}^{-1} - 1)\right] ds \tag{26}$$

where $\tilde{\mathsf{A}} \equiv \mathsf{A}(t)\mathsf{A}^{-1}(s)$, and w, α and β are as in Section 2.1.1.
In simple shear

$$\mu = \int_0^\infty \dot G(s)\left(\frac{\partial w}{\partial\alpha} + \frac{\partial w}{\partial\beta}\right) ds,$$

while in extension

$$\mu_{\text{ext}} = \int_0^\infty \dot G(s)\left[\frac{\partial w}{\partial\alpha}(e^{2\dot\epsilon s} - e^{-\dot\epsilon s}) + \frac{\partial w}{\partial\beta}(e^{\dot\epsilon s} - e^{-2\dot\epsilon s})\right] ds.$$

The Wagner model [13] is a special case of the K-BKZ model with

$$\frac{\partial w}{\partial\beta} = 0\ (N_2 = 0) \text{ and } \frac{\partial w}{\partial\alpha} = e^{-k\sqrt{\alpha - 3 + \theta(\beta-\alpha)}}.$$

- One can choose σ_p to be the sum of several components each of which has its own relaxation time. This allows us to introduce multiple relaxation times into most of the above models.

Notes by Joel C. Miller and Alison Rust

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