Nanjing Lecture 5: Introduction to deformation tensors, elasticity and integral models.

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Displacement gradient tensor and its time derivative

To begin with, we present here the time derivatives of the displacement gradient tensor and the strain tensor used in the development. The notation follows that of Bird et al. (1987). Let a material particle have coordinates x_i' $(i = 1, 2, 3)$ at time t' and x_i $(i = 1, 2, 3)$ at time t. Then, the components of the displacement gradient tensor E are defined by

$$E_{ij} = \frac{\partial x_i}{\partial x_j'} \tag{1}$$

The tensors relate to the fixed particle describing the changes from t' to t but are used without these arguments whenever no confusion can arise. The time derivative of the displacement gradient tensor is computed directly from its definition

$$\frac{\partial}{\partial t} E_{ij} = \frac{\partial}{\partial t} \frac{\partial x_i}{\partial x_j'} = \frac{\partial}{\partial x_j'} \frac{\partial x_i}{\partial t} \tag{2}$$

$$= \frac{\partial v_i}{\partial x_m} \frac{\partial x_m}{\partial x_j'} = (\nabla v)_{mi} E_{mj} \tag{3}$$

In going from the first to the second line, the velocity has been initially defined as $v_i = \partial x_i / \partial t$ of the given particle at the present position. Subsequently the chain rule has been used to obtain the derivatives with respect to the coordinates at the past time. Keep in mind also that the partial time derivative on E indicates a derivative at fixed particle that would be replaced by a substantial derivative at fixed position.

The inverse of the displacement gradient E is defined by

$$F_{ij} = \frac{\partial x_i'}{\partial x_j} \tag{4}$$

It follows from Eqs.1 and 4 that

$$E_{im} F_{mj} = \delta_{ij} \tag{5}$$

Exercise 5.1: Simple shear

Consider a simple shear deformation of shear strain γ:

$$x_1 = x_1' + \gamma x_2' \tag{6}$$

$$x_2 = x_2' \tag{7}$$

$$x_3 = x_3' \tag{8}$$

Show that

$$E_{ij} = \begin{pmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{9}$$

Note that $\det E = 1$.

Exercise 5.2: Uniaxial extension

Consider a uniaxial deformation of stretch ratio λ given by

$$x_1 = \lambda^{-1/2}\, x_1' \tag{10}$$

$$x_2 = \lambda^{-1/2}\, x_2' \tag{11}$$

$$x_3 = \lambda\, x_3' \tag{12}$$

Show that

$$E_{ij} = \begin{pmatrix} \lambda^{-1/2} & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda \end{pmatrix} \tag{13}$$

Note that $\det E = 1$.

Principle of virtual work

Imagine a material in which it is meaningful to define a Helmholtz energy that characterizes the energy involved in deformation from an equilibrium state t' to a deformed state t. This may be a polymer network or a viscoelastic material in which the relaxation process is sufficiently slow that relaxation may be neglected during the deformation from t' to t. In other words we imagine that $A = A(E_{ij})$ is the Helmholtz energy per volume and that the stress in the deformed configuration may be derived from $A(E_{ij})$. The relation follows from a two component argument. In the first component we compute the time derivative of A according to:

$$\frac{d}{dt}A = \frac{\partial A}{\partial E_{jn}} \frac{\partial E_{jn}}{\partial t} \tag{14}$$

$$= \frac{\partial A}{\partial E_{jn}} E_{in} (\nabla v)_{ij} \tag{15}$$

The second component we relate the work done on the material to the stress components, σ_{ij}. To rationalize this relation consider a small volume V. The rate at which fluid outside of V is doing work on the fluid inside V across a differential surface element dS is $n_i \sigma_{ij} v_j dS$ where n_i are the components of an outwardly directed unit vector normal to dS. The total work is obtained by integrating this expression over the entire surface. By application of the divergence theorem this amounts to

$$\int \frac{\partial}{\partial x_i} \sigma_{ij} v_j dV = \int \sigma_{ij} \frac{\partial}{\partial x_i} v_j dV + \int v_j \frac{\partial}{\partial x_i} \sigma_{ij} dV \tag{16}$$

The second of the terms on the right side on the equation is the work associated with the movement of the volume as a whole. The first terms is the work associated with deformation of the volume. Assuming that there is negligible relaxation this work is the increase in the Helmholtz energy so that

$$\frac{d}{dt} A = \sigma_{ij} (\nabla v)_{ij} \tag{17}$$

This is sometimes referred to as the principle of virtual work. The desired relation for the stress is now obtained by combination of Eqs. 15 and 17:

$$\sigma_{ij} = \frac{\partial A}{\partial E_{jn}} E_{in} - p\delta_{ij} \tag{18}$$

The stress is determined only to within an additive pressure p times the unit tensor. This is because of we consider incompressible materials for which there is a constraint on the permissible deformations. (p disappears when Eq. 18 is inserted into Eq. 17).

If the free energy is known as function of the deformation gradient tensor then Eq. 18 is all that is needed to find the equivalent expression for the stress tensor. For example Doi (M. Doi, Introduction to Polymer Physics, Oxford, (1992) Eq. 3.8) gives an expression that for cross-linked networks (rubber) amounts to

$$A = \frac{1}{2}\nu_c k_B T(E_{\alpha\beta}E_{\alpha\beta}) + A_0 \tag{19}$$

where ν_c is the number density of chains between cross-links. Insertion of this expression into Eq. 10 immediately gives

$$\sigma_{ij} = \nu_c k_B T E_{in}E_{jn} - p\delta_{ij} \tag{20}$$

It may be shown that the combination $\nu_c k_B T$ is the shear modulus G (see exercise 5.3). The constitutive relation in Eq. 20 with G substituted for $\nu_c k_B T$ is called the equation for a neo-Hookean material.

$$\sigma_{ij} = GE_{in}E_{jn} - p\delta_{ij} \tag{21}$$

Exercise 5.3: Neo-Hookean material in simple shear

Use the deformation tensor from exercise 5.1 and Eq. 21 to show that in simple shear

$$\sigma_{12} = G\gamma \tag{22}$$

$$\sigma_{11} - \sigma_{22} = G\gamma^2 \tag{23}$$

$$\sigma_{22} - \sigma_{33} = 0 \tag{24}$$

Eq.22 shows that the parameter G is indeed the shear modulus.

Exercise 5.4: Neo-Hookean material in uniaxial extension.

Use the deformation tensor from Exercise 5.2 and and Eq. 21 to show that in uniaxial extension

$$\sigma_{33} - \sigma_{11} = G(\lambda^2 - \lambda^{-1}) \tag{25}$$

Let $\lambda = 1 + \epsilon$. Then show that

$$\sigma_{33} - \sigma_{11} = 3G\epsilon + \cdots \tag{26}$$

Strain tensors, strain invariants and free energy

In most situations, the free energy may be more conveniently reported in terms of stretch ratios or the so-called strain invariants. This is the object of the following section.

From E, the components of the Finger strain tensor B are defined by

$$B_{ij} = E_{in}E_{jn} \tag{27}$$

Likewise the components of the Cauchy strain tensor are defined from the components of F according to

$$C_{ij} = F_{mi}F_{mj} \tag{28}$$

The Cauchy strain and the Finger strain are symmetric and inverse to each other so that

$$C_{im}B_{mj} = \delta_{ij} \tag{29}$$

The two strain invariants I_1 and I_2 are defined as the trace of the two tensors

$$I_1 = B_{ii}, \qquad \text{and} \qquad I_2 = C_{ii} \tag{30}$$

Since the Helmholtz energy is a scalar it must there are some restrictions on way in which it can depend on the components of the displacement gradient. The simplest way to formulate this restriction for an incompressible material is to let A be a function of the two invariants, that is to let

$$A = A(I_1, I_2) \tag{31}$$

The consequence of this restriction is that the stress is expressible as a combination of the Finger and Cauchy strain. To se this insert Eq. 31 into Eq. 18. In this connection the chain rule needs to be used. It follows directly from the definitions that

$$\frac{\partial I_1}{\partial E_{ij}} = 2E_{ij} \tag{32}$$

$$\frac{\partial I_2}{\partial E_{ij}} = 2F_{mn}\frac{\partial F_{mn}}{\partial E_{ij}} \tag{33}$$

The needed derivative in Eq. 33 is obtained from Eq. 4 as

$$\frac{\partial F_{mp}}{\partial E_{ij}} = -F_{mi}F_{jp} \tag{34}$$

By combination of Eqs. 18,31,32,33 and 34 it follows that

$$\sigma_{ij} = 2\frac{\partial A}{\partial I_1}B_{ij} - 2\frac{\partial A}{\partial I_2}C_{ij} - p\delta_{ij} \tag{35}$$

Either Eq.18 or Eq.35 may be useful in a given situation. The classical theory for rubber elasticity corresponds to $A = (1/2)nk_BTI_1$, where n is the number density of network strands, k_B Boltzmanns constant, and T the absolute temperature.

Exercise 5.5: Strain tensors in simple shear

For the simple shear in exercise 5.1, show that the Finger and Cauchy tensors are

$$B_{ij} = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{36}$$

$$C_{ij} = \begin{pmatrix} 1 & -\gamma & 0 \\ -\gamma & 1+\gamma^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{37}$$

Mooney-Rivlin materials. The expression above is a remarkably good prediction of the modulus and also a fair approximation of the needed non-linear relation between f and λ. To obtain a better approximation of the non-linear behavior, Mooney and Rivlin proposed the following expression,

$$\bar{A} = C_1I_1 + C_2I_2 + \bar{A}_0(V,T)$$

Here again $\bar{A}_0(V,T)$ designates a contribution to the free energy that depends only on specific volume and temperature but is independent of the deformation

Exercise 5.5: Mooney Rivlin plot:

Show that the stress in uniaxial extension corresponding to the Mooney Rivlin expression is

$$\sigma_{zz} - \sigma_{xx} = 2C_1(\lambda^2 - \lambda^{-1}) + 2C_2(\lambda - \lambda^{-2})$$

or that

$$\frac{\sigma_{zz} - \sigma_{xx}}{\lambda^2 - \lambda^{-1}} = 2\,C_1 + 2\,C_2\,\lambda^{-1}$$

Show further that $(\sigma_{zz} - \sigma_{xx})/(\lambda^2 - \lambda^{-1})$ plotted as function of $1/\lambda$ should be a straight line. The intersection with $1/\lambda = 1$ is the modulus $G = 2C_1 + 2C_2$ and the slope is $2C_2$. Such a plot is denoted a Mooney-plot. An example of a Mooney plot for cross-linked PDMS networks is given in R. Hansen, A.L. Skov and O. Hassager, Phys. Rev. E **77**, 011802 (2008).

Integral constitutive equation Several models for viscoelastic liquids are derived from Eq. 35.Most well known is the class of BKZ models given by

$$\sigma_{ij} = \int_{t'=\infty}^{t} M(t-t') \left(\frac{\partial W}{\partial I_1} B_{ij} - \frac{\partial W}{\partial I_2} C_{ij} \right) dt' - p\delta_{ij} \tag{38}$$

Here M is the linear viscoelastic memory function and W is a function of the strain invariants. The original version of the Doi-Edwards model for entangled polymers comes out in the form of a BKZ model (both the form with independent alignment and without independent alignment).

The simple Lodge rubber-like liquid model corresponds to $W = I_1$ but keeping the memory function general. If furthermore we specialize to a single exponential memory function we obtain the integral from of the Upper-Convected Maxwell (UCM) model,

$$\sigma_{ij} = \int_{t'=\infty}^{t} \frac{\eta_0}{\lambda^2} e^{(-t-t')/\lambda} B_{ij} dt' \tag{39}$$

where η_0 is a viscosity parameter and τ a time constant.

Exercise 5.6: Start-up of simple shear flow for UCM - integral version Consider start-up of constant shear flow as follows:

$$v_1 = H(t)\dot{\gamma} x_2 \tag{40}$$
$$v_2 = 0 \tag{41}$$
$$v_3 = 0 \tag{42}$$

5.6-1 Show that the displacement functions are now given by Eqs.6-8 with

$$\gamma(t,t') = \begin{cases} \dot{\gamma} t & \text{for} \quad -\infty < t' < 0 \\ \dot{\gamma}(t-t') & \text{for} \quad 0 < t' < t \end{cases} \tag{43}$$

5.6-2 Show that

$$\sigma_{12} = \eta[1 - \exp(-t/\lambda)]\dot{\gamma} \tag{44}$$
$$\sigma_{11} - \sigma_{22} = 2\eta\lambda[1 - (1 + t/\lambda)\exp(-t/\lambda)]\dot{\gamma}^2 \tag{45}$$
$$\sigma_{22} - \sigma_{33} = 0 \tag{46}$$

Time derivatives of strain tensors and differential constitutive equations The time derivative of the Finger strain tensor follows directly from its definition and the derivative of the displacement gradient tensor.

$$\frac{\partial}{\partial t} B_{ij} = (\nabla v)_{mi} E_{mn} E_{jn} + E_{in} (\nabla v)_{mj} E_{mn} \tag{47}$$
$$= (\nabla v)_{mi} B_{mj} + B_{im} (\nabla v)_{mj} \tag{48}$$

In particular this implies that

$$\frac{\partial}{\partial t} I_1 = 2(\nabla v)_{mn} B_{mn} \tag{49}$$

Now consider a non-dimensional second order tensor defined by

$$Q_{ij} = \frac{1}{\lambda} \int_{-\infty}^{t} e^{-(t-t')/\lambda} B_{ij} dt' \tag{50}$$

In molecular theories this is the molecular configuration tensor for the Maxwell model. For Gaussian springs, the the stress in the Maxwell model maybe written in terms of Q simply as

$$\sigma_{ij} = GQ_{ij} - p\delta_{ij} \tag{51}$$

where the modulus $G = \eta_0/\lambda$. However Q as defined in Eq.50 is also the solution to the equation

$$\frac{\partial}{\partial t}Q_{ij} - (\nabla v)_{mi}Q_{mj} - Q_{im}(\nabla v)_{mj} = -\frac{1}{\lambda}(Q_{ij} - \delta_{ij}) \tag{52}$$

Hence we may also define the UCM model by the equations 51 and 52. This latter definition is the differential form of the Maxwell equation.
There are a number of properties of the upper convected Maxwell model that must be kept in mind. The most important one may be the fact that it predicts an unbounded increase of the stress in uniaxial extensional flow at stretch rates larger than one half the time-constant τ. To see this consider the flow given by $(v_x, v_y, v_z) = (-x/2, -y/2, z)\dot{\epsilon}$. By inserting this into Eq. 52 one obtains the following evolution equation for Q,

$$\begin{pmatrix} \dot{Q}_{xx} & 0 & 0 \\ 0 & \dot{Q}_{yy} & 0 \\ 0 & 0 & \dot{Q}_{zz} \end{pmatrix} + \begin{pmatrix} (\dot{\epsilon} + \lambda^{-1})Q_{xx} & 0 & 0 \\ 0 & (\dot{\epsilon} + \lambda^{-1})Q_{yy} & 0 \\ 0 & 0 & (-2\dot{\epsilon} + \lambda^{-1})Q_{zz} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{1}{\tau} \tag{53}$$

where the dots on the components of Q the first terms indicate time-derivatives. In particular it appears that the evolution equation for Q_{zz} predicts unbounded growth for $\dot{\epsilon} > 1/2\lambda$. This corresponds to an unlimited amount of molecular stretching in the Rouse model.

Evolution equations for molecular stretch

In the closing we briefly mention how models with stretch variables fit into the continuum picture. Motivated by a search for constitutive equations with finite stress several authors have introduced the notion of molecular stretch and an upper limit to the stretch. As an example we consider the model by McLeish and Larson. In this model a separate evolution equation is proposed for the molecular stretch $\lambda_s(t)$:

$$\frac{\partial \lambda_s}{\partial t} = \lambda_s(\nabla v)_{mn}S_{mn} - \frac{1}{\tau_s}(\lambda_s - 1) \quad \text{for } \lambda_s < q \tag{54}$$

The stretch variable λ_s cannot exceed a maximum value q (governed by the number of long-chain branches off the main chain backbone). In Eq. 54, τ_s is a separate stretch relaxation time-constant ($\tau_s \ll \lambda$) and the tensor S is a normalized orientation tensor defined by

$$S_{ij} = \frac{Q_{ij}}{Q_{nn}} \tag{55}$$

and the stress is

$$\sigma_{ij} = 3G\lambda_s^2 S_{ij} \tag{56}$$

The tensor Q may be defined either Eq. 50 or by 52.
The non-linear properties of the Pom-Pom model may be categorized according to the two Weissenberg numbers defined as $\text{Wi} = \lambda\dot{\gamma}$ and $\text{Wi}_R = \tau_s\dot{\gamma}$ where $\dot{\gamma}$ is a representative deformation rate. In the following we consider start-up flow from equilibrium. Three regimes may be considered:
1: $\text{Wi} \ll 1$: In this situation the Pom-Pom model just reproduces linear viscoelasticity.
2: $\text{Wi}_R \ll 1 \ll \text{Wi}$: In this situation the solution to Eq. 54 remains simply $\lambda = 1$. Then the stress may be written as:

$$\sigma_{ij} = 3G\frac{\int_{t'=-\infty}^{t} e^{(t-t')/\tau}B_{ij}(t,t')dt'}{\int_{t'=-\infty}^{t} e^{(t-t')/\tau}I_1(t,t')dt'} \tag{57}$$

The non-linear properties of this equation are similar to the Doi-Edwards equation.
3: $1 \ll \mathrm{Wi}_R$ ($\ll$ Wi): In this situation there is no relaxation either in the evolution equation for Q nor in the evolution equation for λ. The evolution equation for Q gives just the Finger strain tensor so that

$$S_{ij} = \frac{B_{ij}}{I_1} \tag{58}$$

Moreover we neglect the relaxation term in Eq 54. Then the equation may be shown to have the following solution:

$$\lambda^2 = I_1/3 \tag{59}$$

Here I_1 is taken from the equilibrium state to the deformed state. Consequently the stress may be written as

$$\sigma_{ij} = \begin{cases} GB_{ij} & I_1 \le 3q^2 \\ 3Gq^2 B_{ij}/I_1 & I_1 > 3q^2 \end{cases} \tag{60}$$

For strains smaller than $I_1 = 3q^2$, the model is equivalent to a neo- Hookean material in the network theory of rubber elasticity. During rapid stretching deformations, the topological junction points along the chain serve effectively as permanent physical cross links in the material which efficiently transmit the stress as in a vulcanized rubber. At larger strains, $I_1 > 3q^2$, branch-point withdrawal becomes important and the stress acting on the central links of the chain becomes sufficient to disentangle the arms of the pom-pom from the surrounding melt.
Reference:
B.B. Bird, R.C. Armstrong and O. Hassager, Dynamics of Polymeric Liquids, vol. I, Fluid Mechanics, Wiley (1987).
T.C.B. McLeish and R.G. Larson: Molecular constitutive equations for a class of branched polymers: The pom-pom polymer, J. Rheol. **42** 1 (1998).