Chapter 2
Fundamentals of Rheology

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Abstract Some important fundamental aspects of fluid mechanics and rheology are discussed. First, we examine the basis for the continuum approximation of fluids, and the formulation of equations in the continuum description. Then, we look at stress-strain rate relationships for simple shear flows of both viscous and viscoelastic fluids. The extension of the description to complex flows, which involves the decomposition of the rate of deformation tensor into fundamental components, is discussed. The conservation laws for mass and momentum, and the constitutive relations in the momentum conservation equation are derived. The simple Maxwell model for polymeric fluids, which uses the bead-spring representation of the polymer chain, is discussed.

2.1 Introduction

Rheology [1] deals with the flow of complex fluids. Fluids are different from solids, because fluids continuously deform when there is an applied stress, as shown in Fig. 2.1b, while solids deform and then stop, as shown in Fig. 2.1a. Solids are said to have an ‘elastic’ response, and can resist an applied stress, while fluids do not have an elastic response, and deform continuously under stress. The distinction between liquids and gases is less fundamental from a macroscopic point of view, even though they are very different at the molecular level. The responses of both liquids and gases to applied stresses are qualitatively similar, even though gases have a much larger deformation rate for a given applied stress than liquids. The objective of rheology is to determine the fluid flow that would be produced due to applied forces [1]. The applied forces could be of different forms. In channels and pipes, for example, the applied force is due to the pressure difference across the ends of the
pipe, as shown in Fig. 2.2a. In reactors, the applied force is due to the rotation of the impeller, as shown in Fig. 2.2b. The applied force could also be natural in origin, such as the gravitational force in falling fluid films. An applied force is necessary for causing fluid flow, because a fluid resists deformation, and this ‘fluid friction’ has to be overcome to generate a flow. The objective of rheology is to predict the flow that would result in a given equipment under the action of applied forces.

The variables used to describe fluid flow [2] are the density, the velocity (which is a vector and contains three components), the pressure and the stresses. These variables are considered as ‘continuum fields’, which are continuously varying functions in space and time. This is not an accurate picture from a microscopic point of view, of course, because actual fluids consist of molecules which exhibit random motion. However, this prediction is valid if the length scales of flow, which are macroscopic, are large compared to the intermolecular separation, and are defined as averages over volumes, which are small compared to the macroscopic volume under consideration, but large compared to molecular scales. For example, to determine the density field, consider a volume of fluid $\Delta V$ shown in Fig. 2.3a. The total number
of particles in the volume is \( N \), and the mass of a molecule is \( M \). The ‘density’ of the fluid within this volume is defined as

\[
\rho = \lim_{\Delta V \to 0} \frac{NM}{\Delta V}
\]  

(2.1)

If the volume \( \Delta V \) is of molecular scale, then there will be large fluctuations in the density, because the density will depend on whether a particle is located within the volume or not. As the volume is made larger, but is still small compared to macroscopic scales, the magnitude of the fluctuations will decrease, because the addition or subtraction of a particle will not make much difference in the total number of particles. The density will approach a constant value in this limit, as shown in Fig. 2.3b and this is the value referred to in the limiting process in the above equations. The fluctuation goes as \( 1/\sqrt{N} \), where \( N \) is the number of particles, so the magnitude of the fluctuation decreases rapidly as the number of particles is increased. When the volume is made still larger, there will be an averaging over macroscopic fluctuations in the density and velocity. This is undesirable because we are trying to capture these real fluctuations. Therefore, it is necessary to ensure that the volume taken for averaging is small compared to macroscopic scales, but still contains a large number of molecules. The average velocity, pressure and stress fields are defined in a similar manner. This process for defining macroscopic variables also has a reflection in the computational fluid dynamics method used for solving fluid flow problems. Here, the domain (flow equipment under consideration) is ‘discretized’ into little volume elements, and the continuum ‘fields’ are defined on each of these elements. In this case, it is necessary to ensure that the elements are small compared to the macroscopic scales, so that one does not average over real variations in the system, while they are large compared to molecular size.
Flow prediction has two components. The first is a knowledge of how an individual fluid element deforms in response to applied stresses, and this is called the ‘model’ for the fluid flow. In practice, the response of an individual element has to be measured using a suitable instrument. Usually, ‘rheometers’ are used to measure the relationship between stress and deformation of an individual element. However, even rheometers make measurement on definite geometries and not on an individual volume element, and so some inference is required to relate the properties of individual volume elements to the rheometer measurements. The models for fluid elements are of different types. If the internal structure of the fluid is simple, in the sense that it does not contain any long chain molecules, colloidal particles, etc., the model for the fluid is usually well described by Newton’s law of viscosity. This law states that the rate of deformation of a volume element of the fluid is proportional to the applied stress. All gases, and most low-molecular-weight fluids, follow this law. In the case of polymeric and colloidal fluids, Newton’s law of viscosity is not obeyed, and the relationship between the stress and the rate of deformation is more complicated. These fluids are called non-Newtonian fluids. The constitutive relationship between the stress and the strain rate is based on ‘rheological models’ for the fluid. These could be phenomenological, on the basis of certain invariance properties that have to be followed by fluids. Rheological models could also be based on statistical mechanics, where we start with a microscopic (molecular) description of the fluid, and use averaging to obtain the average properties. Once we have a relationship between the rate of deformation and the applied stresses, it is necessary to determine how the velocity field in the fluid varies with position and time. This is usually determined using a combination of the fluid model, called the constitutive equation, and the conservation equations for the mass and momentum. The law of conservation of mass states that mass can neither be created nor destroyed, and the law of conservation of momentum states that the rate of change of momentum is equal to the sum of the linear applied forces. These are combined with the constitutive relations to provide a set of equations that describe the variation of the fluid density and velocity fields with position and time.

There are two broad approaches for determining the velocity, density, and other dynamical quantities within the equipment of interest from a knowledge of the variation of the properties in space and time. The first is to use analytical techniques, which involve integration of the equations using a suitable mathematical technique. The second is computational, where the differential equations are ‘discretized’ and solved on the computer. We shall not go into the details of either of these solution techniques here, but merely sketch how the solution is determined for simple problems. The above solution procedure seems simple enough, and one might expect that once the fluid properties are known, the flow properties can easily be calculated with the aid of a suitable computing technique. However, there are numerous complications as listed below:

1. The constitutive properties of the fluid may not be well known. This is common in polymeric and colloidal systems, where the stress depends in a complicated way on the rate of deformation. In such cases, it is necessary to have a good understanding between the constitutive properties of the fluid and the underlying microstructure.
2. The flow may be turbulent. In a ‘laminar’ flow, the streamlines are smooth and vary slowly with position, so that the deformation of any fluid element resembles the deformation that would be observed in a test equipment which contained only that element. However, when the flow becomes turbulent, the streamlines assume a chaotic form and the flow is highly irregular. Therefore, the flow of an individual volume element does not resemble the deformation that would be observed in a test sample containing only that element. More sophisticated techniques are required to analyse turbulent flows.

3. The flow may actually be too complicated to solve even on a high-speed computer. This is especially true of complicated equipments such as extruders, mixers, fluidised beds, etc. In this case, it is necessary to have alternative techniques to handle these problems.

An important consideration in fluid flow problems is the ‘Reynolds number’, which provides the ratio of inertial and viscous effects. Fluid ‘inertia’ refers to the change in momentum due to acceleration, while ‘viscous effects’ refers to the change in momentum due to frictional forces exerted due to fluid deformation. The Reynolds number is a dimensionless number \( Re = \frac{\rho U L}{\eta} \), where \( \rho \) and \( \eta \) are the fluid density and viscosity, \( U \) is the velocity and \( L \) is the characteristic length of the flow equipment. The Reynolds number can also be considered as a ratio between ‘convective’ and ‘diffusive’ effects, where the ‘convective’ effect refers to the transport of momentum due to the motion of fluid elements, while the ‘diffusive’ effect refers to the transport of momentum due to frictional stresses within the fluid. When the Reynolds number is small, viscous effects are dominant and the dominant mechanism of momentum transport is due to diffusion. When the Reynolds number is large, it is expected that viscous effects can be neglected. In flows of complex fluids that we will be concerned with, the Reynolds number is usually sufficiently small that inertial effects can be neglected. Therefore, these flows are mostly dominated by viscosity, and turbulence is not encountered.

### 2.2 Concept of Viscosity

Viscosity is a measure of the ‘fluid friction’ or the ‘resistance to flow’ of a liquid or a gas. This is best illustrated by considering an experiment where the gap between two parallel plates, of area \( A \) and separation \( L \), is filled with a fluid (liquid or gas). One of the plates is moved with a velocity \( U \) relative to the second stationary plate. It is of interest to determine the force required to move the upper plate at this constant velocity, as a function of the area, the velocity and the separation of the two plates. A typical situation envisaged might be as shown in Fig. 2.4. The two plates are kept at rest, and the fluid is also initially at rest. The top plate is set into motion at time \( t = 0 \) with a velocity \( U \). At the initial instant, only the fluid very close to the top plate will be in motion, while the rest of the fluid is at rest. In the long time limit, the velocity is a linear function of distance. The shear viscosity is measured in this
steady state, when the fluid velocity has become a linear function of the distance across the gap. The following can be anticipated quite easily

1. The force required is proportional to the area of the plate $A$.
2. The force is proportional to the velocity gradient, $(U/L)$.

Since the force required is proportional to the area, it is more convenient to define the ‘stress’ $\sigma$ as the (Force/unit area). This can be written as a constant times the strain rate

$$\sigma = \eta U / L.$$  \hspace{1cm} (2.2)

The coefficient of proportionality, $\eta$, is called the ‘shear viscosity’ of the fluid. As $\eta$ becomes larger, the force required for producing a given rate of deformation is larger, and there is more internal friction in the fluid. The unit of viscosity can be deduced from (2.2). The stress, which is the force per unit area, has units of Pascal or (Newton/m$^2$). The strain rate has units of $s^{-1}$, since the velocity has units of (m s$^{-1}$) and the separation has units of m. Therefore, the viscosity has units of Pa s. A knowledge of the practical range of application of the strain rate is particularly important, since the viscosity depends on the range of the strain rate and other parameters, such as the temperature and the microstructure. In this respect, the viscosity of liquids and gases have very different dependencies on the temperature and strain rate. This difference arises primarily due to the difference in the microstructure.

1. In *gases*, the molecules are separated by distances that are large compared to the molecular diameter, and they interact primarily due to intermolecular collisions. If the velocity scale is small compared to the fluctuating velocity of the molecules, and the length scale is large compared to the distance between the molecules, the viscosity of a gas is independent of the strain rate. It has a strong dependence on the temperature, however, and the viscosity of gases increases proportional to $\sqrt{T}$, where $T$ is the absolute temperature in Kelvin.

2. In *liquids*, the separation of molecules is comparable to the molecular length. Due to this, the viscosity has a strong dependence on the temperature, as well as the strain rate. The flow of a liquid takes place due to the sliding of layers of the liquid past each other, and this sliding is easier when the temperature is higher and the molecules have a higher fluctuating velocity. Thus, the viscosity typically decreases with increase in temperature. However, the dependence on the strain rate can be quite complex.
2.2.1 Temperature Dependence

The viscosity of Newtonian liquids decreases with an increase in temperature, according to an Arrhenius relationship. The reason for this kind of relationship is not quite clear. However, it is thought that relative motion between the different molecules in a fluid is due to a type of activated ‘hopping’ mechanism, and so the viscosity of a liquid also obeys an Arrhenius type behaviour.

\[ \eta = A \exp \left( -\frac{B}{T} \right), \]  

where \( T \) is the absolute temperature (Kelvin), \( A \) and \( B \) are constants of the liquids. The constant \( B \) can be determined by plotting \( \log \left( \frac{d\eta}{dT} \right) \) vs. \( \log (\eta) \), as shown in Fig. 2.5. This curve has a slope of \( B/T^2 \), where \( T \) is the absolute temperature. The temperature dependence is stronger for liquids with greater viscosity, and under normal conditions, the thumb rule is that the viscosity decreases by approximately 3% for every degree rise in the temperature. Consequently, it is important to be able to maintain a constant temperature in viscometric measurements. This is of particular importance because the shear of a liquid results in viscous heating, which could change the temperature. Therefore, in a practical measurement, care has to be taken to ensure that sufficient heat is extracted to maintain the system at a steady temperature. The viscosity of liquids increases exponentially with pressure. However, this dependence is not very strong for pressure variations of the order of a few bars, and so is usually ignored in practical applications.

2.2.2 Dependence on Shear Rate

The shear rate dependence of fluids is an important consideration, since many fluids have complex shear rate dependence. Newtonian fluids are characterised by the following behaviour:

1. The viscosity is independent of shear rate.
2. The viscosity is independent of time of shear at a constant shear rate.
3. The ‘normal stress differences’ are zero.
4. The viscosities measured by different types of deformations, such as uniaxial and biaxial extension, are proportional to each other.

Any liquid showing a deviation from this behaviour is a non-Newtonian liquid. All gases, as well as simple liquids such as water, are Newtonian liquids. Non-Newtonian liquids include all complex liquids such as suspensions, polymeric liquids, etc., which have a complex microstructure where the microstructure depends on the rate of strain of the liquid.

2.2.3 Time Effects

In most fluids which display a shear thinning, there is also a decrease of the viscosity in time at a constant strain rate. This is because of the gradual breakdown of the viscosity under stress, and is similar to the mechanism for shear thickening. There could be a recovery of the structure upon cessation of stress, and the time scale for the recovery gives the typical time for the structures to recover. This type of recovery is typically observed in polymer solutions. There are other cases where the breaking down of bonds is irreversible, such as polymer gels. Here, the viscosity will not recover after the stress has been removed. There are still other cases, such as liquid crystals, where the structures do not break down irreversibly, but the recovery time is long compared to any processing time scale. In this case also there will not be any recovery on the time scale of observation, and the change in structure will appear irreversible. Another widely used concept is the ‘yield stress’, which is the minimum stress that has to be applied for fluid flow.

However, the concept of yield stress should be used with caution, since the yield stress often depends on the time for which the stress is applied. A material which is rigid for a short duration will flow if stress is continuously applied for a much longer duration. The apparent viscosity of a fluid could also depend on the duration of the applied stress, when the strain rate is maintained a constant. In the case of thixotropic substances, the shear stress decreases with time at a constant strain rate. In contrast, the shear stress of rheopectic substances increases with time at constant shear rate.

2.3 Linear Viscoelasticity

The term ‘linear viscoelasticity’ refers to the relation between stress and deformation of a material near equilibrium usually when the deformation is small. Deformations are not usually small under conditions of processing or use, and so data obtained by linear viscoelasticity measurements often do not have direct relevance to conditions of use. However, these tests are important for two reasons. First, these tests are easier to carry out and understand than nonlinear measurements,
and the parameters obtained from linear viscoelasticity measurements are a reliable reflection of the state of the system. Second, these measurements can also be used in quality control, and any variations in quality can be easily detected by linear viscoelasticity measurements.

The term ‘viscoelasticity’ implies that the substance under consideration has both viscous and elastic properties. We have already discussed the meaning of the term viscosity. The term elasticity refers to solid materials, and in these cases the stress is a linear function of the strain $\gamma$ (and not the strain rate). If a solid is subjected to a stress, as shown in Fig. 2.6, the solid will undergo deformation up to a certain limit and then stop (provided the stress is less than the breaking point of the solid material, of course). This is in contrast to a liquid, which undergoes continuous deformation when a stress is applied. In Fig. 2.6, if the deformation of the solid is termed $\delta$, then the strain $\gamma$ is defined as $\gamma = (\delta/L)$, where $L$ is the thickness of the solid. The force required to produce this displacement is proportional to the cross sectional area $A$, and the stress (force per unit area) is related to the strain field by

$$\sigma = \frac{G\delta}{L}, \quad (2.4)$$

where $G$ is the ‘modulus of elasticity’. It is useful to compare the quantity ‘strain’ used in the definition of elasticity and ‘rate of strain’ used to define the viscosity. In Fig. 2.6, the velocity of the top plate is the rate of change of the displacement with time,

$$U = \frac{d\delta}{dt}. \quad (2.5)$$

Since the distance between the plates is a constant, the rate of strain is just the time derivative of the strain

$$\dot{\gamma} = \frac{d\gamma}{dt}. \quad (2.6)$$

A ‘viscoelastic’ fluid is one which has both viscous and elastic properties, i.e. where a part of the stress is due to the strain field and another part is due to the strain rate.

Next, we turn to the term ‘linear’ in the title ‘linear viscoelasticity’. Linear just means that the relationship between the stress and the strain is a linear relationship, so that if the strain is increased by a factor of 2, the stress also increases by a factor of 2. Newton’s law of viscosity and (2.4) for the elasticity are linear relationships. However, if we have a term of the form

$$\sigma = K\dot{\gamma}^n, \quad (2.7)$$
it is easy to see that if the strain is increased by a constant factor, the stress does not increase by that factor. Therefore, the relationship is nonlinear. Almost all non-Newtonian fluids have nonlinear relationships between the stress and the strain rate, and therefore they cannot be described by linear viscoelastic theories. However, a linear relationship between the stress and strain could be more complicated than Newton’s law of viscosity, and could include higher order time derivatives as well. For example,

\[
\left( A_3 \frac{d^3}{dt^3} + A_2 \frac{d^2}{dt^2} + A_1 \frac{d}{dt} + A_0 \right) \sigma = \left( B_3 \frac{d^3}{dt^3} + B_2 \frac{d^2}{dt^2} + B_1 \frac{d}{dt} + B_0 \right) \gamma
\]  

(2.8)

is a linear relationship between the stress and strain. Relations of the above form do not mean much unless we can relate them to viscous and elastic elements individually. This is the objective of linear viscoelasticity. First, consider viscous and elastic elements separately. They are usually represented diagrammatically as shown in Fig. 2.7.

The stress–strain relationships for these elements are

\[
\begin{align*}
\sigma_E &= G \gamma \\
\sigma_V &= \eta \dot{\gamma}.
\end{align*}
\]  

(2.9)

If these two elements are connected as shown in Fig. 2.8a, the total strain for the viscous and elastic elements is the same, while the total stress is the sum of the stresses due to the viscous and elastic parts.

\[
\sigma = G \gamma + \eta \dot{\gamma}.
\]  

(2.10)
This model is called the ‘Kelvin model’ for the stress–strain relationship. If a stress is suddenly applied at $t = 0$ and held constant thereafter (step stress), it is easy to show that in the Kelvin model the strain varies as

$$\gamma = (\sigma / G)(1 - \exp(-t / \tau_K)),$$

where $\tau_K = (\eta / G)$ is the ‘Kelvin time constant’. At long times, the strain attains a constant value $(\sigma / G)$, which is the strain for a solid with elasticity modulus $G$. Therefore, the Kelvin model behaves like a solid at long times.

The other way to connect the two elements is as shown in Fig. 2.8b, where the stress transmitted through the two elements is the same, while the total strain is the sum of the strains in the two elements. This type of element is called the ‘Maxwell model’. In this case, the stresses in the two elements are

$$\sigma = G\gamma_E = \eta \dot{\gamma}.$$

These two relations can easily be used to obtain the stress–strain relationship

$$\sigma + \tau_M \dot{\sigma} = \eta \dot{\gamma},$$

where $\tau_M = (\eta / G)$ is the Maxwell time constant for this model. If a constant strain rate $\dot{\gamma}$ is applied at time $t = 0$, the evolution of the strain for subsequent times is given by

$$\sigma = \eta \dot{\gamma}(1 - \exp(-t / \tau_M)).$$

At long times, we recover the Newton’s law for viscosity, and therefore the Maxwell model behaves as a fluid at long times.

It is possible to devise more complicated models with three and four parameters to represent the behaviour of viscoelastic fluids. For example, the Jeffrey’s model, shown in Fig. 2.9 is a three-parameter model which in the present notation has a constitutive relation of the form

$$\sigma + \tau_M \dot{\sigma} = \eta (\dot{\gamma} + \tau_J \dot{\gamma}).$$
Other four-parameter models, such as the four-parameter Burgers’ model, can also be devised. One can also devise ‘generalized Kelvin’ and ‘generalized Maxwell’ models, which have a large number of elements with different time constants (Fig. 2.10).

The stress–strain relationships for these models are complicated, but can be evaluated in principle from the known time constants. For example, if we start with a simple Maxwell model, the stress–strain relationship for a fluid with a varying imposed strain rate $\dot{\gamma}(t)$ is

$$\sigma(t) = \frac{\eta}{\tau_M} \int_{-\infty}^{t} \exp \left[ -\frac{(t - t')}{\tau_M} \right] \dot{\gamma}(t') dt'. \tag{2.16}$$

This can easily be extended to the ‘generalised Maxwell model’ with $n$ Maxwell elements

$$\sigma(t) = \sum_{i=1}^{n} \frac{\eta_i}{\tau_i} \int_{-\infty}^{t} \exp \left[ -\frac{(t - t')}{\tau_i} \right] \dot{\gamma}(t') dt'. \tag{2.17}$$

where $\eta_i$ and $\tau_i$ correspond to the $i$th Maxwell element. A similar relationship can be derived for the ‘generalised Kelvin model’, where the strain is determined as a
function of the applied stress. For a single Kelvin element, the relationship between 
the stress and strain is

$$\gamma(t) = \frac{1}{\eta} \int_{-\infty}^{t} \exp \left[ \frac{-(t - t')}{\tau_K} \right] \sigma(t') dt'.$$  \hspace{1cm} (2.18)

For the generalised Kelvin model, this can easily be extended to provide a relaxation 
behaviour of the form

$$\gamma(t) = \sum_{i=1}^{n} \frac{1}{\eta_i} \int_{-\infty}^{t} \exp \left[ \frac{-(t - t')}{\tau_i} \right] \sigma(t') dt'.$$  \hspace{1cm} (2.19)

The above relationships are quite easy to derive once the models for the viscoelastic 
fluid are known. However, the basic question is how does one determine the model 
from a known relationship between the stress and strain. These model relationships 
are best derived using ‘oscillatory’ measurements, where a sinusoidal oscillatory 
strain is imposed on the sample and the stress is recorded. If the strain is sufficiently 
small (linear response regime), the stress response will also have an oscillatory be-

The stress–strain relationship in this case is usually represented using a com-
plex shear modulus $G^*$, which is a function of frequency. For example, if the strain 
imposed is of the form

$$\gamma(t) = \gamma_0 \sin(\omega t).$$  \hspace{1cm} (2.20)
The stress response will be of the form

\[ \sigma(t) = G'\gamma_0 \sin(\omega t) + G''\gamma_0 \cos(\omega t), \]  

(2.21)

where \( G' \) and \( G'' \) are the real and imaginary parts of the complex modulus \( G^* \). \( G' \) is the ‘storage modulus’ which gives the response which is in phase with the imposed perturbation, and is related to the elasticity of the material. \( G'' \) is the ‘loss modulus’, which gives the response which is exactly out of phase with the imposed perturbation, and this is related to the viscosity of the material.

The relationship between the complex modulus and the material parameter in the viscoelastic models is best illustrated using the Maxwell model. If the perturbation is of the form given in (2.20), the strain rate is

\[ \dot{\gamma} = \frac{d\gamma}{dt} = \gamma_0 \omega \cos(\omega t), \]  

(2.22)

When this is substituted into the Maxwell model, a first order differential equation is obtained, which can be solved to give

\[ \sigma = \frac{\eta \omega \gamma_0}{1 + \omega^2 \tau^2} (\omega \tau \sin(\omega t) + \cos(\omega t)). \]  

(2.23)

Therefore, the storage and loss moduli are given by

\[ G' = \frac{\eta \tau \omega^2}{1 + \omega^2 \tau^2}, \]

\[ G'' = \frac{\eta \omega}{1 + \omega^2 \tau^2}. \]  

(2.24)

The shapes of the storage and loss moduli ‘spectra’ are a function of frequency. The storage modulus decreases proportional to \( \omega^2 \) in the limit of low frequency, and attains a constant value at high frequency. The loss modulus decreases proportional to \( \omega \) at low frequency, and proportional to \( \omega^{-1} \) at high frequency. A parameter often quoted in literature is the ‘loss tangent’ \( \tan \delta \), which is defined as

\[ \tan \delta = \frac{G''}{G'}. \]  

(2.25)

This provides the ratio of viscous to elastic response. This goes to infinity proportional to \((1/\omega)\) at low frequency, indicating that the response is primarily viscous at low frequency. At high frequency, this goes to zero as \((1/\omega)\) indicating that the response is dominated by elasticity at high frequency. The above formalism can easily be extended to the generalised Maxwell model, for example. The storage and loss
moduli in this case are related to the time constants and viscosities of the individual Maxwell elements.

\[
G' = \sum_{i=1}^{n} \frac{G_i \tau_i^2 \omega^2}{1 + \omega^2 \tau_i^2},
\]

\[
G'' = \sum_{i=1}^{n} \frac{\eta_i \omega}{1 + \omega^2 \tau_i^2},
\]

(2.26)

where \(G_i\), \(\eta_i\) and \(\tau_i\) are the parameters in the equations for the individual Maxwell elements.

The shape of the storage and loss modulus curves is useful for deducing quantitative information about the relaxation times in the substance. For example, the loss modulus \(G''\) has a peak when \(\omega = (1/\tau)\) for a Maxwell fluid with a single time constant. For a generalised Maxwell fluid with two elements, for example, there are two peaks at \(\omega = (1/\tau_1)\) and \(1/(\tau_2)\) in the loss modulus spectrum. This implies that there are two rheological relaxation mechanisms in the system, and provides their time constants. This could be used to deduce the structure of these fluids. We will examine this a little further while dealing with specific fluids.

2.4 Kinematics

This is the subject of the description of motion, without reference to the forces that cause this motion. Here, we assume that time and space are continuous, and identify a set of particles by specifying their location at a time \((x_0, t_0)\). As the particles move, we follow their positions as a function of time \(\{x, t\}\). These positions are determined by solving the equations of motion for the particles, which we have not yet derived. Thus, the positions of the particles at time \(t\) can be written as

\[
x(t) = x(x_0, t).
\]

(2.27)

Note that \(x\) and \(t\) are independent variables; we can find the location of the particle only if the initial location \(x_0\) is given. Further, we can also express the (initial) position of the particles at time \(t_0\) as a function of their (final) positions at \(t\):

\[
x_0(t_0) = x_0(x, t_0).
\]

(2.28)

2.4.1 Lagrangian and Eulerian Descriptions

The properties of the fluid, such as the velocity and temperature can be expressed in two ways. One is called the ‘Lagrangian description’, which is a natural extension
Fig. 2.12  Eulerian and Lagrangian descriptions of variables in a fluid

of solid mechanics, where attention is focused on a set of particles in the flow with initial position $\mathbf{x}_0$, and the evolution of the properties of these particles as they move through space is determined, as shown in Fig. 2.12. For example, the temperature in Lagrangian variables is given by

$$T = T(\mathbf{x}_0, t). \quad (2.29)$$

The positions of the particles can be expressed in the Lagrangian variables as noted below.

$$\mathbf{X} = \mathbf{X}(\mathbf{x}_0, t). \quad (2.30)$$

In the ‘Eulerian description’, the positions of the properties of the fluid are expressed with reference to positions fixed in space. For example, the velocity and temperature fields are

$$\mathbf{u} = \mathbf{u}(\mathbf{x}, t) \quad (2.31)$$

$$T = T(\mathbf{x}, t). \quad (2.32)$$

The position vector in Eulerian variables is simply the particle position.

In order to illustrate the Lagrangian viewpoint, let us take a simple example. Consider a simple linear flow between two flat plates of length $L$ separated by a distance $H$, with the upper plate moving at a constant velocity $V$. Neglecting entrance effects, the fluid velocity is given by

$$u_x = U(z/H) \quad (2.33)$$

$$u_y = 0 \quad (2.34)$$

$$u_z = 0. \quad (2.35)$$

In addition, the fluid is being heated on the right and cooled on the left, so that there is a constant temperature gradient

$$T = T_0 + T_1 x. \quad (2.36)$$
The velocity and temperature as specified above are Eulerian, because they are referenced to a fixed coordinate. To obtain the Lagrangian description, we consider a fluid particle with initial position \(x_0, y_0, z_0\). The velocity of this particle is given by:

\[
\begin{align*}
u_x &= U(z_0/H) \\
u_y &= 0 \\
u_z &= 0.
\end{align*}
\] (2.37)
(2.38)
(2.39)

The velocity of the fluid particle remains constant as the particle moves through the channel, and is independent of time. The particle position is a function of time, however, and is given by

\[
\begin{align*}
x &= x_0 + t U(z_0/H) \\
y &= y_0 \\
z &= z_0.
\end{align*}
\] (2.40)
(2.41)
(2.42)

From the equation for the temperature profile along the length of the channel, we can obtain the Lagrangian form of the temperature profile as well:

\[
T = T_0 + T_1 x = T_0 + T_1 [x_0 + t U(z_0/H)].
\] (2.43)

This gives the Lagrangian form of the particle position, velocity and temperature for the simple flow that we have considered. For more complex flows, it is very difficult to obtain the Lagrangian description of the particle motion, and this description is not often used.

### 2.4.2 Substantial Derivatives

Next, we come to the subject of the time derivatives of the properties of a fluid flow. In the Eulerian description, we focus only on the properties as a function of the positions in space. However, note that the positions of the fluid particles are themselves a function of time, and it is often necessary to determine the rate of the change of the properties of a given particle as a function of time, as shown in Fig. 2.12. This derivative is referred to as the Lagrangian derivative or the substantial derivative:

\[
\frac{DA}{Dt} = \left\{ \frac{dA}{dr} \right\}_{x_0},
\] (2.44)

where \(A\) is any general property, and we have explicitly written the subscript to note that the derivative is taken in the Lagrangian viewpoint, following the particle...
positions in space. For example, consider the substantial derivative of the temperature of a particle as it moves along the flow over a time interval $\Delta t$:

$$\frac{D T}{D t} = \lim_{\Delta t \to 0} \left[ \frac{T(x + \Delta x, t + \Delta t) - T(x, t)}{\Delta t} \right]$$

$$= \lim_{\Delta t \to 0} \left[ \frac{T(x + u\Delta t, t + \Delta t) - T(x, t)}{\Delta t} \right]. \quad (2.45)$$

Taking the limit $\Delta t \to 0$, and using chain rule for differentiation, we obtain

$$\frac{D T}{d t} = \frac{\partial T}{\partial t} + u_x \frac{\partial T}{\partial x} + u_y \frac{\partial T}{\partial y} + u_z \frac{\partial T}{\partial z}$$

$$= \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T, \quad (2.46)$$

where

$$\nabla = e_x \frac{\partial}{\partial x} + e_y \frac{\partial}{\partial y} + e_z \frac{\partial}{\partial z} \quad (2.47)$$

is the gradient operator. The relation between the Eulerian and Lagrangian derivatives for the problem just considered can be easily derived. In this example, the Eulerian derivative of the temperature field is zero, because the temperature field has attained steady state. The substantial derivative is given by

$$\frac{D T}{D t} = \mathbf{u} \cdot \nabla T = u_x \frac{\partial T}{\partial x} = (U_z/H)T_1. \quad (2.48)$$

This can also be obtained by directly taking the time derivative of the temperature field in the Lagrangian description.

### 2.4.3 Decomposition of the Strain Rate Tensor

The ‘strain rate’ tensor refers to the relative motion of the fluid particles in the flow. For example, consider a differential volume $dV$, and two particles located at $x$ and $x + \Delta x$ in the volume, separated by a short distance $\Delta x$. The velocities of the two particles are $u$ and $u + \Delta u$. The relative velocity of the particles can be expressed in tensor calculus as

$$d\mathbf{u} = (\nabla \mathbf{u}) \cdot \Delta \mathbf{x}, \quad (2.49)$$

where $\nabla \mathbf{u}$ is the gradient of the velocity, which is a second-order tensor. In matrix notation, this can be expressed as:

$$\begin{pmatrix} d\mathbf{u}_x \\ d\mathbf{u}_y \\ d\mathbf{u}_z \end{pmatrix} = \begin{pmatrix} \frac{\partial u_x}{\partial x} & \frac{\partial u_x}{\partial y} & \frac{\partial u_x}{\partial z} \\ \frac{\partial u_y}{\partial x} & \frac{\partial u_y}{\partial y} & \frac{\partial u_y}{\partial z} \\ \frac{\partial u_z}{\partial x} & \frac{\partial u_z}{\partial y} & \frac{\partial u_z}{\partial z} \end{pmatrix} \begin{pmatrix} dx \\ dy \\ dz \end{pmatrix}. \quad (2.50)$$
The second-order tensor, $\nabla u$, can be separated into two components, a symmetric and an antisymmetric component, $S + A$, which are given by

$$S = \frac{1}{2} (\nabla u + (\nabla u)^T)$$

$$A = \frac{1}{2} (\nabla u - (\nabla u)^T).$$

The antisymmetric part of the strain rate tensor represents rotational flow. Consider a two-dimensional flow field in which the rate of deformation tensor is antisymmetric,

$$\begin{pmatrix} \Delta u_x \\ \Delta u_y \end{pmatrix} = \begin{pmatrix} 0 & -a \\ a & 0 \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \end{pmatrix}. \quad (2.53)$$

The flow relative to the origin due to this rate of deformation tensor is shown in Fig. 2.13a. It is clearly seen that the resulting flow is rotational, and the angular velocity at a displacement $\Delta r$ from the origin is $a \Delta r$ in the anticlockwise direction.

$$\Delta u = \frac{1}{2} \Delta x \times \omega. \quad (2.54)$$

Fig. 2.13 Velocity fields due to the isotropic (a), antisymmetric (b) and symmetric traceless (c) parts of the rate of deformation tensor.
where $\times$ is the cross product, and the vorticity $\omega$ is

$$\omega = \nabla \times \mathbf{u}. \quad (2.55)$$

The symmetric part of the stress rate tensor can be further separated into two components as follows:

$$\mathbf{S} = \mathbf{E} + \frac{1}{3} (S_{xx} + S_{yy} + S_{zz}), \quad (2.56)$$

where $\mathbf{E}$ is the symmetric traceless part of the strain tensor, $\mathbf{I}$ is the identity tensor,

$$\mathbf{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (2.57)$$

and $(1/3)\mathbf{I}(S_{xx} + S_{yy} + S_{zz})$ is the isotropic part. ‘Traceless’ implies that the trace of the tensor, which is $E_{xx} + E_{yy} + E_{zz}$, is zero. The symmetric traceless part, $\mathbf{E}$, is called the ‘extensional strain’, while the isotropic part, $(1/3)\mathbf{I}(S_{xx} + S_{yy} + S_{zz})$, corresponds to radial motion. Note that the isotropic part can also be written as

$$\frac{1}{3} (S_{xx} + S_{yy} + S_{zz}) = \frac{1}{3} \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) = \frac{1}{3} \nabla \cdot \mathbf{u}. \quad (2.58)$$

Thus, the isotropic part of the rate of deformation tensor is related to the divergence of the velocity. The velocity difference between the two neighbouring points due to the isotropic part of the rate of deformation tensor is given by

$$\begin{pmatrix} \Delta u_x \\ \Delta u_y \end{pmatrix} = \begin{pmatrix} s & 0 \\ 0 & s \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \end{pmatrix}. \quad (2.59)$$

The above equation implies that the relative velocity between two points due to the isotropic component is directed along their line of separation, and this represents a radial motion, as shown in Fig. 2.13b. The radial motion is outward if $s$ is positive, and inward if $s$ is negative. The symmetric traceless part represents an ‘extensional strain’, in which there is no change in density and no solid body rotation. In two dimensions, the simplest example of the velocity field due to a symmetric traceless rate of deformation tensor is

$$\begin{pmatrix} \Delta u_x \\ \Delta u_y \end{pmatrix} = \begin{pmatrix} s & 0 \\ 0 & -s \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \end{pmatrix}. \quad (2.60)$$

The relative velocity of points near the origin due to this rate of deformation tensor is shown in Fig. 2.13c. It is found that the fluid element near the origin deforms in
such a way that there is no rotation of the principal axes, and there is no change in the total volume. This type of deformation is called ‘pure extensional strain’ and is responsible for the internal stresses in the fluid.

The symmetric traceless part of the rate of deformation tensor also contains information about the extensional and compressional axes of the flow. A symmetric tensor of order $n \times n$ has $n$ eigenvalues which are real, and $n$ eigenvectors which are orthogonal. The sum of the eigenvalues of the tensor is equal to the sum of the diagonal elements. Therefore, for the symmetric traceless rate of deformation tensor, the sum of the eigenvalues is equal to zero. This means that, in two dimensions, the two eigenvectors are equal in magnitude and opposite in sign. In three dimensions, the sum of the eigenvalues of the tensor is equal to zero. If $E_v$ is the column of the normalised eigenvectors of the symmetric traceless tensor $E$,

$$
E_v = \left( \begin{array}{c} e_{v1} \\ e_{v2} \\ e_{v3} \end{array} \right),
$$

and if the eigenvalues are $\lambda_1$, $\lambda_2$ and $\lambda_3$, then the tensor can be written as

$$
E_v^{-1} E E_v = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}.
$$

Also, the eigenvectors satisfy the equation $E_v^{-1} = E_v^T$. Equation (2.62) can be interpreted as follows. The difference in velocity between two neighbouring locations due to the deviatoric part of the rate of deformation tensor is

$$
\begin{pmatrix} \Delta u_x \\ \Delta u_y \\ \Delta u_z \end{pmatrix} = E \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}.
$$

This can be rewritten, using (2.62), as

$$
\begin{pmatrix} \Delta u_x \\ \Delta u_y \\ \Delta u_z \end{pmatrix} = E_v \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} E_v^{-1} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}.
$$

If we define a new co-ordinate system

$$
\begin{pmatrix} \Delta x' \\ \Delta y' \\ \Delta z' \end{pmatrix} = E_v^{-1} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix},
$$
and velocity
\[
\begin{pmatrix}
\Delta u_x' \\
\Delta u_y' \\
\Delta u_z'
\end{pmatrix} = \mathbf{E}_v^{-1}
\begin{pmatrix}
\Delta u_x \\
\Delta u_y \\
\Delta u_z
\end{pmatrix}.
\]
(2.66)
then the equation for the velocity difference between two neighbouring locations becomes
\[
\begin{pmatrix}
\Delta x' \\
\Delta y' \\
\Delta z'
\end{pmatrix} = \begin{pmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{pmatrix}
\begin{pmatrix}
\Delta u_x' \\
\Delta u_y' \\
\Delta u_z'
\end{pmatrix}.
\]
(2.67)

The operations in (2.65) and (2.66) are just equivalent to rotating the coordinate system. Equation (2.67) indicates that in this rotated coordinate system, the differences in velocity are directed along the axes of the rotated coordinate system. Since the sum of the three eigenvalues is zero, there are three possibilities for the signs of the three eigenvalues. If two of the eigenvalues are positive and one is negative, then there is extension along two axes and compression along one axis, as shown in Fig. 2.14a. This is called biaxial extension. If one of the eigenvalues is positive and the other two are negative, then there is compression along two axes and extension along one axis, as shown in Fig. 2.14b. This is called uniaxial extension. If one of the eigenvalues is zero, then there is extension along one axis, compression along the second and no deformation along the third axis. This is called plane extension, as shown in Fig. 2.13c.

### 2.5 Conservation of Mass

The conservation of mass simply states that mass cannot be created or destroyed. Therefore, for any volume of fluid,
\[
\begin{pmatrix}
\text{Rate of mass accumulation} \\
\text{IN}
\end{pmatrix} = \begin{pmatrix}
\text{Rate of mass} \\
\text{OUT}
\end{pmatrix}.
\]
(2.68)
Consider the volume of fluid shown in Fig. 2.15. This volume has a total volume \( \Delta x \Delta y \Delta z \), and it has six faces. The rate of mass in through the face at \( x \) is \( (\rho u_x) |_{x} \Delta y \Delta z \), while the rate of mass out at \( x + \Delta x \) is \( (\rho u_x) |_{x+\Delta x} \Delta y \Delta z \). Similar expressions can be written for the rates of mass flow through the other four faces. The total increase in mass for this volume is \( \frac{\partial}{\partial t} \). Therefore, the mass conservation equation states that

\[
\Delta x \Delta y \Delta z \frac{\partial \rho}{\partial t} = \Delta y \Delta z [(\rho u_x) |_{x} - (\rho u_x) |_{x+\Delta x}]
+ \Delta x \Delta z [(\rho u_y) |_{y} - (\rho u_y) |_{y+\Delta y}]
= \Delta x \Delta y [(\rho u_z) |_{z} - (\rho u_z) |_{z+\Delta z}].
\] (2.69)

Dividing by \( \Delta x \Delta y \Delta z \), and taking the limit as these approach zero, we get

\[
\frac{\partial \rho}{\partial t} = - \left( \frac{\partial (\rho u_x)}{\partial x} + \frac{\partial (\rho u_y)}{\partial y} + \frac{\partial (\rho u_z)}{\partial z} \right).
\] (2.70)

The above equation can often be written using the substantial derivative

\[
\frac{\partial \rho}{\partial t} + \left( u_x \frac{\partial \rho}{\partial x} + u_y \frac{\partial \rho}{\partial y} + u_z \frac{\partial \rho}{\partial z} \right) = -\rho \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right).
\] (2.71)
The left side of the above equation is the substantial derivative, while the right side can be written as

\[
\frac{D\rho}{Dt} = -\rho(\nabla \cdot \mathbf{u}). \tag{2.72}
\]

The above equation describes the change in density for a material element of fluid, which is moving along with the mean flow. A special case is when the density does not change, so that \(D\rho/Dt\) is identically zero. In this case, the continuity equation reduces to

\[
\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0. \tag{2.73}
\]

This is just the isotropic part of the rate of deformation tensor, which corresponds to volumetric compression or expansion. Therefore, if this is zero, it implies that there is no volumetric expansion or compression, and if mass is conserved, then the density has to be a constant. Fluids that obey this condition are called ‘incompressible’ fluids. Most fluids that we use in practical applications are incompressible fluids; in fact, all liquids can be considered incompressible for practical purposes. Compressibility effects only become important in gases when the speed of the gas approaches the speed of sound, 332 m s\(^{-1}\).

### 2.6 Conservation of Linear Momentum

The conservation of linear momentum is a consequence of Newton’s second law of motion, which states that the rate of change of momentum in a differential volume is equal to the total force acting on it. The momentum in a volume \(V(t)\) is given by

\[
P = \int_{V(t)} dV \rho \mathbf{u}, \tag{2.74}
\]

and Newton’s second law states that the rate of change of momentum in a moving differential volume is equal to the sum of the applied forces,

\[
\frac{DP_t}{Dt} = \frac{d}{dt} \int_{V(t)} dV \left( \rho \mathbf{u} \right) = \text{Sum of forces.} \tag{2.75}
\]

Here, note that the momentum conservation equation is written for a moving fluid element. In a manner similar to the mass conservation equation, the integral over a moving fluid element can be written in an Eulerian reference frame as

\[
\int_{V(t)} dV \left( \frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) \right) = \text{Sum of forces.} \tag{2.76}
\]

The forces acting on a fluid are usually of two types. The first is the body forces, which act on the bulk of the fluid, such as the force of gravity, and the surface forces,
which act at the surface of the control volume. If \( \mathbf{F} \) is the body force per unit mass of the fluid, and \( \mathbf{R} \) is the force per unit area acting at the surface, then the momentum conservation equation can be written as

\[
\int_{V(t)} dV \left( \frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla(\rho \mathbf{u} \mathbf{u}) \right) = \int_{V(t)} dV \mathbf{F} + \int_{S} dS \mathbf{R},
\]

where \( S \) is the surface of the volume \( V(t) \).

To complete the derivation of the equations of motion, it is necessary to specify the form of the body and surface forces. The form of the body forces is well known—the force due to gravity per unit mass is just the gravitational acceleration \( g \), while the force due to centrifugal acceleration is given by \( \omega^2 R \)., where \( \omega \) is the angular velocity and \( R \) is the radius. The form of the surface force is not specified a-priori however, and the ‘constitutive equations’ are required to relate the surface forces to the motion of the fluid. But before specifying the nature of the surface forces, one can derive some of the properties of the forces using symmetry considerations.

The force acting on a surface will, in general, depend on the orientation of the surface, and will be a function of the unit normal to the surface, in addition to the other fluid properties:

\[
\mathbf{R} = \mathbf{R}(\mathbf{n}).
\]

We can use symmetry considerations to show that the force is a linear function of the unit normal to the surface. If we consider a surface dividing the fluid at a point \( P \), then the forces acting on the two sides of the surface have to be equal according to Newton’s third law. Since the unit normals to the two sides are just the negative of each other, this implies that

\[
\mathbf{R}(-\mathbf{n}) = -\mathbf{R}(\mathbf{n}).
\]

This suggests that the surface force could be a linear function of the normal:

\[
\mathbf{R} = \mathbf{T} \cdot \mathbf{n}.
\]

where \( \mathbf{T} \) is a ‘second-order tensor’. That this is the case can be shown using Cauchy’s theorem. Consider a tetrahedron with three surfaces located along the three co-ordinate axes, with lengths \( \Delta x \), \( \Delta y \) and \( \Delta z \), as shown in Fig. 2.16. In the limit as three lengths go to zero, the density and velocity in the region can be taken as constants. The integral momentum conservation equation then becomes

\[
\left( \frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla(\rho \mathbf{u} \mathbf{u}) \right) \Delta V
\]

\[
= \mathbf{F} \Delta V + \mathbf{R}(\mathbf{n}) \Delta S + \mathbf{R}(-\mathbf{e}_x) \Delta S_x + \mathbf{R}(-\mathbf{e}_y) \Delta S_y + \mathbf{R}(-\mathbf{e}_z) \Delta S_z,
\]

where \( \mathbf{e}_x, \mathbf{e}_y \) and \( \mathbf{e}_z \) are the unit vectors in the three directions, \( S_x, S_y \) and \( S_z \) are the surfaces perpendicular to \( \mathbf{e}_x, \mathbf{e}_y \) and \( \mathbf{e}_z \), respectively, and \( \mathbf{R}(\mathbf{n}) \) is the force acting
at the surface with outward unit normal \( \mathbf{n} \). In the limit as the lengths of the sides \( \Delta x, \Delta y, \Delta z \) go to zero, the inertial terms and the body forces, which are proportional to the volume \( \Delta x \Delta y \Delta z \), become much smaller than the terms proportional to the surface area, and therefore,

\[
\mathbf{R}(\mathbf{n}) \Delta S = \mathbf{R}(\mathbf{e}_x) \Delta S_x + \mathbf{R}(\mathbf{e}_y) \Delta S_y + \mathbf{R}(\mathbf{e}_z) \Delta S_z. \tag{2.82}
\]

The areas along the three axes are related to the area of the triangular plane as

\[
\Delta S_x = n_x \Delta S \quad \tag{2.83}
\]
\[
\Delta S_y = n_y \Delta S \quad \tag{2.84}
\]
\[
\Delta S_z = n_z \Delta S. \quad \tag{2.85}
\]

Using this relation, we get

\[
\mathbf{R}(\mathbf{n}) = n_x \mathbf{R}(\mathbf{e}_x) + n_y \mathbf{R}(\mathbf{e}_y) + n_z \mathbf{R}(\mathbf{e}_z). \tag{2.86}
\]

This is exactly of the same form as

\[
\mathbf{R}(\mathbf{n}) = \mathbf{T} \cdot \mathbf{n}. \tag{2.87}
\]

In matrix form, this can be written as

\[
\begin{pmatrix}
R_x \\
R_y \\
R_z
\end{pmatrix} =
\begin{pmatrix}
T_{xx} & T_{xy} & T_{xz} \\
T_{yx} & T_{yy} & T_{yz} \\
T_{zx} & T_{zy} & T_{zz}
\end{pmatrix}
\begin{pmatrix}
n_x \\
n_y \\
n_z
\end{pmatrix}.
\tag{2.88}
\]

The tensor \( \mathbf{T} \) is called the ‘stress tensor’, and it has nine components. The component \( T_{xx} \) is the force per unit area in the \( x \) direction acting at a surface whose unit normal is in the \( x \) direction, the component \( T_{xy} \) is the force per unit area in the \( x \) direction acting at a surface whose unit normal is in the \( y \) direction, and so on.
Therefore, the tensor has two physical directions associated with it; the first is the
direction of the force and the second is the direction of the unit normal to the surface
at which the stress is measured.

Using the stress tensor, the conservation equation is given by

\[ \int_{V(t)} dV \left( \frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) \right) = \int_{V(t)} dV \mathbf{F} + \int_{S} dS \mathbf{T} \cdot \mathbf{n}. \]  

(2.89)

This can be further simplified using the divergence theorem:

\[ \int_{V(t)} dV \left( \frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) \right) = \int_{V(t)} dV \mathbf{F} + \int_{S} dV \nabla \cdot \mathbf{T}. \]  

(2.90)

Since the above equation is valid for any differential volume in the fluid, the inte-
grand must be equal to zero:

\[ \left( \frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) \right) = \mathbf{F} + \nabla \cdot \mathbf{T}. \]  

(2.91)

The above equation can be simplified using the mass conservation equation:

\[ \rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \nabla \mathbf{u} \right) = \mathbf{F} + \nabla \cdot \mathbf{T}. \]  

(2.92)

An additional property of the stress tensor, which is obtained from the angular
momentum equation, is that the stress tensor is symmetric. That is, \( T_{xy} = T_{yx}, \)
\( T_{xz} = T_{zx} \) and \( T_{yz} = T_{zy} \) in (2.88).

2.7 Constitutive Equations for the Stress Tensor

Just as we had earlier separated the strain rate tensor into an antisymmetric traceless
part, a symmetric part and an isotropic part, it is conventional to separate the stress
tensor into an isotropic part and a symmetric traceless ‘deviatoric’ part:

\[ \mathbf{T} = -\rho \mathbf{I} + \mathbf{\sigma}, \]  

(2.93)

where \( p \) is the pressure in the isotropic pressure in the fluid, \( p = -(1/3)(T_{xx} +
T_{yy} + T_{zz}) \), and \( \mathbf{\sigma} \) is the second-order ‘deviatoric’ stress tensor which is traceless,
\( (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = 0 \). In the absence of fluid flow, the deviatoric part of the stress
tensor \( \mathbf{\sigma} \) becomes zero, and the pressure field is related to the local density of the
system by a thermodynamic equation of state.

The shear stress, \( \sigma \), is a function of the fluid velocity. However, the stress cannot
depend on the fluid velocity itself, because the stress has to be invariant under a
‘Galilean transformation’ i.e., when the velocity of the entire system is changed by
a constant value. Therefore, the stress has to depend on the gradient of the fluid velocity. In a ‘Newtonian fluid’, we make the assumption that the stress is a linear function of the velocity gradient. In general, the linear relation can be written as

$$\sigma = \eta \cdot \nabla \mathbf{u}, \quad (2.94)$$

where \(\eta\) is a fourth order tensor. Here \(\Delta \mathbf{u}\) is not a frame invariant measure. This tensor is a property of the fluid.

In an isotropic fluid, there is no preferred direction in space, and therefore, the tensor \(\eta\) should be independent of direction. In this case, it can be shown that the relationship between the stress and strain rate is of the form

$$\sigma = \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T - (2/3)\mathbf{I} \nabla \mathbf{u}), \quad (2.95)$$

where \(\eta\) is the ‘coefficient of viscosity’ of the fluid. This can also be expressed in terms of the rate of strain tensor:

$$\sigma = 2\eta \mathbf{E}, \quad (2.96)$$

where \(\mathbf{E}\) is the symmetric traceless part of the rate of deformation tensor.

The above constitutive equation was derived for a Newtonian fluid with the assumption that the shear stress is a linear function of the strain rate. However, the stress could be a non-linear function of the strain rate in complex fluids such as polymer solutions,

$$\sigma = f(\mathbf{E}). \quad (2.97)$$

Since \(E_{ij}\) is a frame indifferent tensor, any tensor that can be written as

$$\sigma = \text{scalar} \times \mathbf{E} \quad (2.98)$$

satisfies the conditions of frame indifference. There are three frame indifferent scalars that can be constructed from the tensor \(\nabla \mathbf{u}\):

$$I_1 = \nabla \cdot \mathbf{u} \quad I_2 = \mathbf{E} : \mathbf{E} \quad I_3 = \text{Det}(\mathbf{E}). \quad (2.99)$$

Therefore, any constitutive relation that can be written in the form

$$\sigma = \eta (I_1, I_2, I_3) \mathbf{E} \quad (2.100)$$

would satisfy the requirements of material frame indifference. Of these frame-indifferent scalars, \(I_1 = 0\) for an incompressible fluid.

The constitutive equation for the stress tensor can be inserted into the momentum conservation equation to obtain

$$\partial_t \rho + \partial_i (\rho \mathbf{v}_i) = 0$$

$$\rho \partial_t \mathbf{v}_i + \rho \mathbf{v}_j \partial_j \mathbf{v}_i = -\partial_i p + \eta (\partial^2 \mathbf{v}_i - (2/3)\partial_i \partial_j \mathbf{v}_j). \quad (2.101)$$
These are the Navier–Stokes mass and momentum conservation equations. For an incompressible fluid, where the density is a constant in both space and time, the Navier–Stokes equations have a particularly simple form:

\[
\begin{align*}
\partial_t v_i &= 0 \\
\partial_t v_i + v_j \partial_j v_i &= -\rho^{-1} \partial_i p + \nu \partial_j^2 v_i, \\
\end{align*}
\]  

(2.102)

where \( \nu = (\eta/\rho) \) is the kinematic viscosity.

### 2.8 Polymer Conformation

The most widely studied non-Newtonian fluids are polymer solutions and polymer melts. A polymer is a molecule with high molecular weight obtained by covalently bonding a large number of units or monomers, so that the linear length of the molecular is large compared to the molecular diameter. Polymers can be thought of as long flexible strings, and have many interesting properties because of their linear nature. In solutions and in melts, they are in a highly coiled state, as shown in Fig. 2.17. In solutions and melts, these springs are in a highly coiled state.

A useful physical picture is obtained if we consider these strings as undergoing a random walk [3]. The random walk proceeds in steps of equal length, called the ‘Kuhn segment length’ (which is a few times larger than the monomer size), with a random change in direction after each step. The average end-to-end distance of a random walk with \( N \) steps increases proportional to \( \sqrt{N} \). Therefore, one would expect the linear size of a polymer molecule to increase proportional to \( N^{1/2} \), where \( N \) is the number of monomers, if the molecule is accurately described by a random walk. However, in real solutions, there is an additional factor which comes into play, which is that the polymer molecule cannot cross itself. Due to this, the radius of gyration of a polymer molecule actually increases with a slightly higher power, \( N^{0.58} \).

If we assume a simple random walk model, then the average end-to-end distance of a polymer molecule increases proportional to \( N^{1/2} \), where \( N \) is the number of Kuhn segments. The probability of finding a configuration with a particular end-to-end distance can be evaluated from entropic arguments, based on the number of configurations corresponding to this end-to-end distance. Based on simple arguments

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**Fig. 2.17** (a) A polymer molecule and (b) the bead–spring representation of the polymer molecule
for a Gaussian chain, it can be inferred the probability that the end-to-end distance is \( x \) is proportional to \( \exp\left(-x^2/(Nl^2)\right) \), where \( l \) is the Kuhn segment length and \( N \) is the number of Kuhn segments. This is equivalent to a probability of the form \( \exp(-E_x/kT) \), where the energy \( E_x \) for a molecule with end-to-end distance \( x \) is \( E_x = (2kT/Nl^2)x^2 \). If we consider the factor \( (2kT/Nl^2) \) as a spring constant \( k_n \), then the energy penalty is of the form \( E_x = (k_n x^2/2) \). This is just the stretching energy of a spring with spring-constant \( k_n \). This leads to a still simpler bead–spring representation of a molecule, which is a linear spring between two beads which has a spring constant \( k_n \), as shown in Fig. 2.17.

In the bead–spring model, the stress due to the polymers is expressed in terms of the second-order conformation tensor, and has a very simple form,

\[
\mathbf{T}^p = c_p k_n \mathbf{x x} = c_p k_n \mathbf{Q},
\]

where the term on the right contains the tensor product of the end-to-end displacement vector \( \mathbf{x} \), and \( c_p \) is the polymer concentration. The tensor \( \mathbf{Q} = \mathbf{x x} \) is referred to as the ‘polymer conformation tensor’, which basically provides information about the state of stretch of the polymers. Here, we have a situation where the local flow field affects the polymers by stretching and rotating them, and the state of stretch of the polymers provides an additional component of the stress which in turn affects the flow field. Therefore, in a fluid-dynamical description, it is necessary to have coupled equations for both the flow field and the conformation tensor of the polymers.

In the equation for the conformation tensor of the polymer, there are terms corresponding to the stretching and bending of the polymers due to the imposed flow, and there is a ‘spring’ force which tends to reduce the polymer conformation back to its equilibrium state. From the Gaussian approximation for the polymer end-to-end distance, the conformation tensor \( \mathbf{Q}^{eq} \) at equilibrium is an isotropic tensor with no preferred direction,

\[
\mathbf{Q}^{eq} = \frac{kT}{k_n} \mathbf{I}.
\]

The simplest equation for the conformation tensor states that the polymer tends to relax back to its equilibrium conformation with a time constant,

\[
\frac{\mathcal{D} \mathbf{Q}}{\mathcal{D} t} = -\frac{\mathbf{Q} - \mathbf{Q}^{eq}}{\tau}.
\]

There are two new terms introduced above, the relaxation time \( \tau \) and the ‘upper convected’ derivative \( (\mathcal{D} / \mathcal{D} t) \) on the left. First, the upper convected derivative is defined as

\[
\frac{\mathcal{D} \mathbf{Q}}{\mathcal{D} t} = \frac{\partial \mathbf{Q}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{Q} - \mathbf{Q} \cdot \nabla \mathbf{u} - (\nabla \mathbf{u})^T \mathbf{Q}.
\]

The first two terms on the right side are just the substantial derivatives, but the ‘upper convected’ derivative contains two additional terms. In our earlier discussion,
we noted that the substantial derivative is a derivative in a reference frame moving
with the local fluid mean velocity. In a similar manner, the ‘upper convected’ deriv-
ative also contains terms due to the local rotation of fluid elements at a point. Since
the rotation of the fluid elements will tend to rotate any bead–spring dumbbells im-
mersed in the fluid, this rotation is included in the substantial derivative. Therefore,
the upper convected derivative is a derivative in a reference frame moving and ro-
tating with the local fluid element. On the right side of (2.106), the time constant
\( \tau = (\xi/k_n) \) is the ratio of the spring constant and a ‘friction coefficient’ \( \xi \), which
represents the force exerted on the beads due to the fluid flow past the beads. If the
fluid is flowing with a velocity \( v \) past the beads, the force exerted can be written
as \( F = -\xi v \) in the linear approximation. The ratio of this frictional force and the
spring constant is the time constant.

Once the value of \( Q \) is known, then (2.103) can be used to evaluate the polymer
stress, which is then inserted into the momentum conservation equation of the fluid,
\[
\rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \eta \nabla^2 \mathbf{u} + \nabla \mathbf{T}^p. \tag{2.107}
\]
The polymer stress is usually written in an alternate, but completely equivalent, form
to (2.103),
\[
\mathbf{T}^p = \frac{\eta_p k_n}{\tau k T} (Q - Q^{eq}), \tag{2.108}
\]
where \( \eta_p = (c_p k T \tau) \) is the polymer viscosity, and the only difference between the
(2.108) and (2.103) is that we have removed the isotropic part proportional to \( Q^{eq} \).
(2.107) and (2.108) constitute the upper convected Maxwell model for a polymeric
fluid.

References

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