

## Chapter 5

# Flow Properties of Complex Materials

### 5.1 Introduction

Every system, irrespective of its detailed nature, responds when subjected to an external source. The systems we shall consider are materials, and we are interested in the mechanical response. This response is usually referred to as anelasticity for solids and viscoelasticity for high viscosity liquids. The scientific discipline where the flow properties of materials are studied is called rheology.

In 1678 Robert Hooke developed his theory of elasticity, and in 1687 Isaac Newton proposed a relation between stress and rate of strain for liquids. For a Hookean solid a shear stress  $\sigma$  applied to the surface  $y = b$  results in an instantaneous deformation (figure 5.1).

Once the deformed state is reached there is no further movement, but the deformed state persists as long as the stress is applied. Here the strain is

$$\tan \gamma \approx \gamma = \frac{\delta x}{b}, \quad (5.1)$$

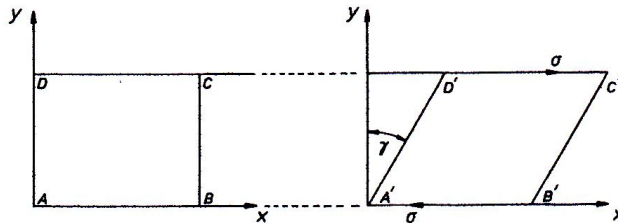


Figure 5.1: *The result of the application of a shear stress  $\sigma$  to a block of a Hookean solid. On the application of the stress the material section ABCD is deformed and becomes A'B'C'D'. Here the side AD is  $b$ ,  $DD'$  is  $\delta x$ , and  $\tan \gamma = \delta x/b$ .*

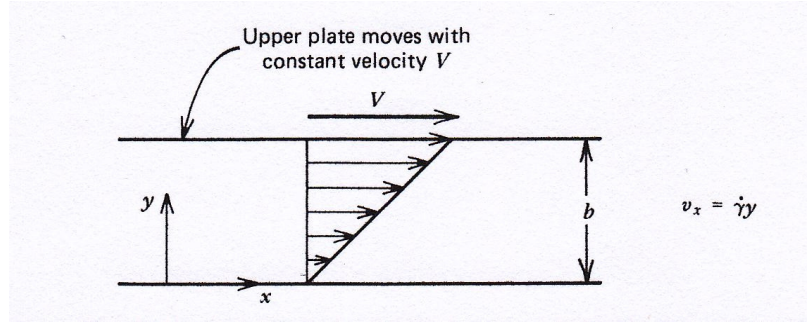


Figure 5.2: *Steady simple shear flow with shear rate  $\dot{\gamma} = V/b$ . In this flow the surfaces  $y = \text{constant}$  slide relative to one another.*

and the stress is

$$\sigma = \frac{F}{A}, \quad (5.2)$$

where  $A$  is the area of the surface at  $y = b$ . The relevant constitutive equation is

$$\sigma = G\gamma \quad (5.3)$$

where  $G$  is referred to as the rigidity modulus or shear modulus.

The corresponding situation for a liquid is the application of a force  $F$  which results in a velocity  $V$ . The shear rate is then

$$\frac{d\gamma}{dt} = \dot{\gamma} = \frac{V}{b} \quad (5.4)$$

and Newtons hypothesis is then

$$\sigma = \eta\dot{\gamma} \quad (5.5)$$

where  $\eta$  is the shear viscosity. So in a liquid a shear stress  $\sigma$  results in a flow, while in a solid it results in a deformation. In the case of a liquid the flow persists as long as the stress is applied.

In 1835 Wilhelm Weber carried out experiments on silk threads and found out that they were not perfectly elastic. Rather there was an immediate extension followed by a further lengthening with time after a load was applied. On removal of the load an immediate contraction took place, followed by a gradual further decrease in length until the original length was reached. This is an example of a solid-like material where Hooke's law cannot describe the behaviour. There are elements of flow in the deformation pattern, which look more like a liquid-like response. The term viscoelasticity is used to describe such behaviour.

A first attempt to explain such viscoelastic behaviour was proposed by Maxwell in 1867. He argued that the solid and liquid-like behaviour in (5.3) and (5.5) should be combined. For short times (5.3) should be valid and for long times (5.5). This gives  $\dot{\gamma} = \dot{\sigma}/G$  and  $\dot{\gamma} = \sigma/\eta$  respectively or when combined

$$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \quad (5.6)$$

This can be written as

$$\sigma + \frac{\eta}{G}\dot{\sigma} = \eta\dot{\gamma} \quad (5.7)$$

Another possibility is the so called Kelvin or Voigt model with the assumption

$$\sigma = G\gamma + \eta\dot{\gamma} \quad (5.8)$$

Both these and other models interpolate between short and long times.

The distinction between solid and liquid-like behaviour can be illustrated by means of the Deborah number  $D_e$  where

$$D_e = \frac{\tau}{\tau_{\text{exp}}} \quad (5.9)$$

Here  $\tau$  is a characteristic time for the material and  $\tau_{\text{exp}}$  a characteristic experimental time for the process being observed. The time  $\tau$  is infinite for an elastic solid and zero for a Newtonian viscous liquid. In practice  $\tau$  is never either infinite or zero. For water in the liquid state  $\tau$  is typically  $10^{-12}$  s, while for an oil  $\tau$  can be of order  $10^{-6}$  s, and for polymer melts used in plastic processing  $\tau$  may be as high as a few seconds. Similarly in real solids there are some residual motions like vacancy diffusion etc. The idea with the Deborah number  $D_e$  is that everything flows if you wait long enough, high  $D_e$  corresponds to solid like behaviour and low  $D_e$  to liquid like behaviour. A material can therefore appear solid-like either because it has a very long  $\tau$  or because the deformation process is very fast.

In (5.7) the Maxwell relaxation time is given by

$$\tau_M = \frac{G}{\eta} \quad (5.10)$$

and if  $\tau_M \ll 1$  (5.7) reduces to  $\dot{\sigma} = G\dot{\gamma}$  while for  $\tau_M \gg 1$  we have  $\sigma = \eta\dot{\gamma}$ , i.e.  $\tau_M$  is the characteristic time for the switching between solid-like and liquid-like behaviour.

## 5.2 The liquid state

A liquid is usually defined in the following way

A liquid is a fluid which if placed in a closed vessel at once conforms to the shape of the vessel without necessarily following the whole of its volume.  
(Rowlinson)

The first property, that it easily change its shape, distinguishes a liquid from a solid. The second property, that it is not completely filling a container but forming a free surface, distinguishes a liquid from a gas. The two properties is sufficient to identify the commonly experienced liquids such as water, alcohol and many other simple organic liquids. At sufficiently low temperatures and high pressures the material exists as a solid, at high temperatures and low pressures as a gas. The transitions between the states are marked by the phenomena of freezing and boiling, occuring at well defined temperatures.

For more complex systems like polymers and glasses, this simple definition is inadequate. At room temperature such materials often appear to be solids, apparently maintaining their shape for long times. On raising the temperature melting occurs and the

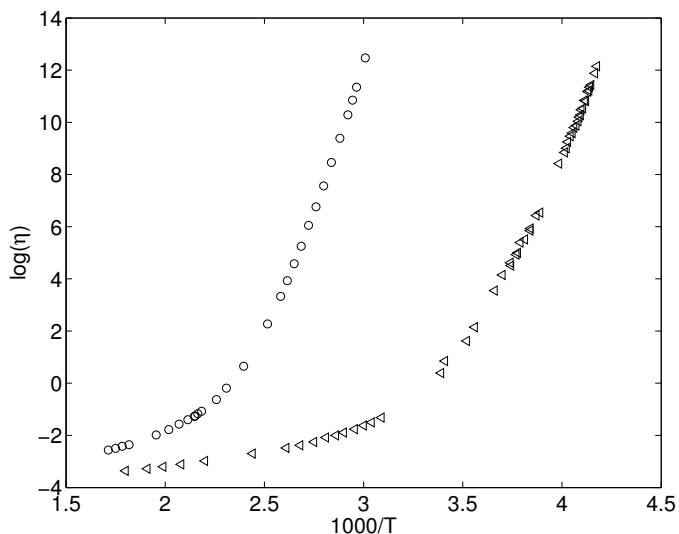


Figure 5.3:  $\log(\eta)$  versus  $1000/T$  for two typical organic liquids. The open dots show *ortho-terpenyl* and the triangle *tri- $\alpha$ naphthylbenzene*.

material flows like a liquid. However, the transition from solid to liquid does not occur at a well defined temperature, and is not accompanied by the absorption of a latent heat and the discontinuity in density or volume normally associated with the phenomenon of melting. Also in the liquid state the flow is often sluggish, the material having such a high viscosity that it is not possible for it to conform to the shape of the containing vessel except for rather long times.

Such a material, characterized by high values of viscosity and no definite melting point, is described as a supercooled liquid or when the viscosity is so high that the rate of flow is almost zero as a glass. A glass has the external appearance of a solid, but maintains the molecular structure of a liquid, lacking the long range order of a crystalline solid. The melting temperature  $T_m$  at which crystallization occurs in simple liquids, does not apply in the case of supercooled liquids, as the material stays in the liquid state as the temperature is lowered. A characteristic property of supercooled liquids is a high viscosity in the region at the freezing point, and this means that the rate of crystallization becomes very low preventing crystallization to occur if the cooling rate is sufficiently high.

A measure of the relaxation time for molecular motions is the Maxwell relaxation time  $\tau_M = \eta/G_\infty$ . Here  $G_\infty$  is the instantaneous modulus at short times or high frequencies. The value of  $G_\infty$  is found to be close to  $10^9$  Pascal (Pa) for most liquids at the glass transition, a value which is typical of the glassy state, and the temperature dependence is given by

$$\frac{1}{G_\infty} = \frac{1}{G_\infty(T_g)} + c(T - T_g)$$

where  $T_g$  denotes the glass transition temperature which is the temperature at which the viscosity is  $10^{12}$  Pa s. The viscosity has a very strong dependence on temperature that is

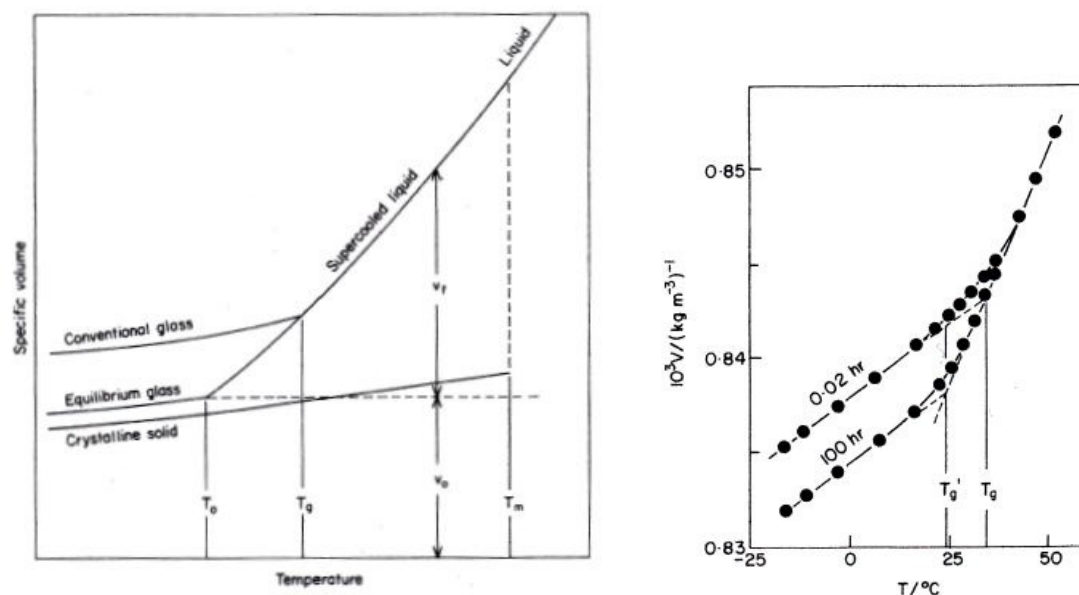


Figure 5.4: *Left: schematic variation of the specific volume with temperature for a crystalline solid, an equilibrium glass, a conventional (non-equilibrium) glass, and a liquid.  $T_m$  is the melting temperature of the crystalline solid,  $T_g$  is the conventional glass transition temperature,  $T_0$  is the transition temperature to a closed packed structure and  $v_0$  is the temperature-independent occupied volume. Taken from Plazek and Magill, *J. Chem. Phys.* **45** 3038 (1966). Right: Specific volume of amorphous polyvinyl acetate as a function of temperature. Volumes were observed at 0.02 hr and 100 hr after cooling rapidly from a high temperature.  $T_g$  and  $T_g'$  are the glass transition temperatures corresponding to these two different experimental times. Taken from Kovacs, *J. Polymer Sci.* **30** 131 (1958).*

usually given by the Vogel-Fulcher expression

$$\eta = A \exp(B/(T - T_0))$$

Consequently,  $\tau_M$  has a temperature dependence which is dominated by the viscosity the value being given approximately by

$$\tau_M = \eta \times 10^{-9} \text{s}$$

where  $\eta$  is measured in Pa s ( $\text{Ns/m}^2$ ).

Most simple organic liquids have a viscosity at the melting point of 0.01 Pa s or less, corresponding to a relaxation time  $\tau_M \simeq 10^{-7}$  s. In order to see any viscoelastic effects higher values of the viscosity must be reached by supercooling the liquid below  $T_m$ . More complex liquids like polymers have a larger intrinsic viscosity and show viscoelastic effects even at room temperature.

The rapid variation of the viscosity with temperature is shown in figure 5.3 for two simple organic liquids. When temperature is varied by a factor two the viscosity can change 14 orders of magnitude. At the glass transition temperature the relaxation time is  $10^3$  s or about 15 minutes. Below  $T_g$  the relaxation time become very large even hundred of years, and eventually of the order of the age of the universe.

The Vogel-Fulcher expression can be derived from the concept of free volume. The specific volume  $v = 1/\rho$ , where  $\rho$  is the mass density, can be written as

$$v = v_0 + v_f$$

where  $v_f$  is the free volume and  $v_0$  is the volume associated with the liquid when in its state of closest molecular packing. The model for the viscosity is then

$$\eta = A \exp\left(B \frac{v_0}{v_f}\right)$$

Thus  $v_f$  represents the volume available in the liquid for the translational motion of molecules. When  $v_f$  is zero the viscosity becomes infinite and  $v = v_0$ . Assuming that  $v(T_0) = v_0$  for some temperature  $T_0$  and expanding around  $T_0$  we find

$$\rho = \frac{1}{v} = \rho_0 (1 - a_0(T - T_0))$$

where  $\rho_0 = 1/v_0$ . Then

$$\eta = A' \exp(B'/(T - T_0))$$

In figure 5.4 (left) we show a schematic representation of the variation of the specific volume with temperature. The temperature  $T_0$  above defines the state of closest random packing. Supercooling the liquid below the melting point  $T_m$  there is eventually a temperature  $T_g$ , the glass transition temperature, when a change of slope occurs. Above  $T_g$  the material is a liquid, below it behaves as a glass. The change in slope at  $T_g$  implies that the system falls out of equilibrium, i.e. the relaxation time for attaining equilibrium becomes longer than the experimental cooling rate. The value of  $T_g$  depends on the time scale of the experiment. If a sufficient time is allowed for equilibrium to be reached when cooling the liquid the transition occurs at a lower temperature. This effect is also shown in figure 5.4 (right) which shows the dependence of  $T_g$  on the time scale of the experiment for the polymer polyvinylacetate.

### 5.3 General concepts

In general the strain, rate of strain and the stress are tensors with elements  $\gamma_{ij}$ ,  $\dot{\gamma}_{ij}$  and  $\sigma_{ij}$  respectively ( $i, j = x, y, z$ ). In a solid we can introduce a displacement vector  $\mathbf{u}(\mathbf{r}, t)$  of a small volume element at the position  $\mathbf{r}$ , from some unperturbed reference state  $\mathbf{r}_0$

$$\mathbf{u} = \mathbf{r} - \mathbf{r}_0$$

and we then have

$$\gamma_{ij} = \nabla^i u_j + \nabla^j u_i, \quad \text{and} \quad \dot{\gamma}_{ij} = \nabla^i v_j + \nabla^j v_i \quad (5.11)$$

where  $\mathbf{v} = \dot{\mathbf{u}}$  is the velocity. The components of the stress are related to the forces acting on a surface element.

The constitutive relations are in general of the form

$$\sigma_{ij} = \sum_{kl} M_{ijkl} \gamma_{kl}$$

and

$$\sigma_{ij} = \sum_{kl} \zeta_{ijkl} \dot{\gamma}_{kl}$$

with a modulus tensor  $M_{ijkl}$  and viscosity tensor  $\zeta_{ijkl}$ .

For a simple shear experiment, like in figure 5.1, we have

$$u_x = \gamma y, \quad u_y = u_z = 0 \quad (5.12)$$

with the strain tensor

$$\vec{\gamma} = \begin{pmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (5.13)$$

and for an isotropic material the corresponding stress tensor is

$$\vec{\sigma} = \begin{pmatrix} -P & G\gamma & 0 \\ G\gamma & -P & 0 \\ 0 & 0 & -P \end{pmatrix} \quad (5.14)$$

where  $P$  is the ambient isotropic pressure. Similarly for a liquid we have

$$v_x = \dot{\gamma} y, \quad v_y = v_z = 0 \quad (5.15)$$

with the rate of strain tensor

$$\vec{\dot{\gamma}} = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (5.16)$$

and a corresponding stress tensor. In simple shear experiments we therefore write

$$\sigma_{xy} = G\gamma_{xy}, \quad \text{or simply} \quad \sigma = G\gamma$$

and similarly

$$\sigma_{xy} = \eta \dot{\gamma}_{xy}, \quad \text{or simply} \quad \sigma = \eta \dot{\gamma}.$$

## 5.4 Experimental methods

### 5.4.1 Static experiments

We will first consider the mechanical properties in a shear experiment as outlined in section 5.2. At a sufficiently small stress a linear relationship exists between the shear stress  $\sigma$  and the shear strain  $\gamma$

$$\sigma = G\gamma, \quad \gamma = J\sigma, \quad G = J^{-1} \quad (5.17)$$

Here  $G$  and  $J$  are material constants, the shear modulus and shear compliance respectively. In the absence of relaxation there is no variation of  $\gamma$  with elapsed time after the application of the stress.  $G$  and  $J$  are therefore independent of time.

### 5.4.2 Step-function experiments

In a mechanical creep experiment a stress  $\sigma_0$  is applied at time zero and then hold constyant

$$\sigma(t) = \sigma_0 \theta(t) = \begin{cases} \sigma_0 & t > 0 \\ 0 & t < 0 \end{cases} \quad (5.18)$$

Then

$$\gamma(t) = J(t)\sigma_0 \quad (5.19)$$

where

$$J(t) = J_\infty + (J_e - J_\infty)\psi(t) \quad (5.20)$$

Here  $J_\infty = J(t = 0)$  is the so called "unrelaxed" compliance for short times or high frequencies ( $\omega = \infty$ ) and  $J_e = J(t = \infty)$  the relaxed or equilibrium compliance. The retardation function  $\psi(t)$  is an increasing function with

$$\psi(0) = 0, \quad \psi(\infty) = 1$$

and alternatively we can express it in terms of a relaxation function

$$\psi(t) = 1 - \phi_J(t), \quad \phi_J(0) = 1, \quad \phi_J(\infty) = 0 \quad (5.21)$$

If instead the strain  $\gamma_0$  is applied at  $t = 0$  the stress  $\sigma(t)$  is time dependent

$$\begin{aligned} \sigma(t) &= G(t)\gamma_0 \\ G(t) &= G_\infty + (G_e - G_\infty)\phi_G(t) \end{aligned} \quad (5.22)$$

where the relaxation function satisfies  $\phi_G(0) = 1$  and  $\phi_G(\infty) = 0$ . Experimentally one finds

$$J_\infty = G_\infty^{-1}, \quad J_e = G_e^{-1} \quad (5.23)$$

Taking Laplace transforms of (5.19) and (5.22) we find

$$\gamma(z) = J(z)\sigma_0 = zJ(z)\sigma(z), \quad \sigma(z) = \frac{\sigma_0}{z} \quad (5.24)$$

and

$$\sigma(z) = G(z)\gamma_0 = zG(z)\gamma(z), \quad \gamma(z) = \frac{\gamma_0}{z} \quad (5.25)$$

where

$$J(z) = \int_0^\infty dt e^{-zt} J(t).$$

and similarly for  $G(z)$ . Therefore we have the general relation

$$\frac{\sigma(z)}{\gamma(z)} = zG(z) = \frac{1}{zJ(z)} \quad (5.26)$$

or

$$J(z)G(z) = \frac{1}{z^2} \quad (5.27)$$



Taking the inverse Laplace transform this gives

$$\int_0^t dt' J(t-t')G(t') = t \quad (5.28)$$

Also from (5.20), (5.21) and (5.22) we have

$$\begin{aligned} J(z) &= \frac{1}{z}J_\infty - (J_e - J_\infty)\phi_J(z) \\ G(z) &= \frac{1}{z}G_\infty + (G_e - G_\infty)\phi_G(z) \end{aligned} \quad (5.29)$$

which gives a general relation between the relaxation functions  $\phi_J$  and  $\phi_G$

$$[J_e - (J_e - J_\infty)z\phi_J(z)][G_\infty + (G_e - G_\infty)z\phi_G(z)] = 1 \quad (5.30)$$

When a constant stress  $\sigma_0$  is applied at  $t = 0$  and then switched off at a later time  $t_0$  one obtains a response  $\gamma(t)$ , which typically looks as in Fig. 5.5

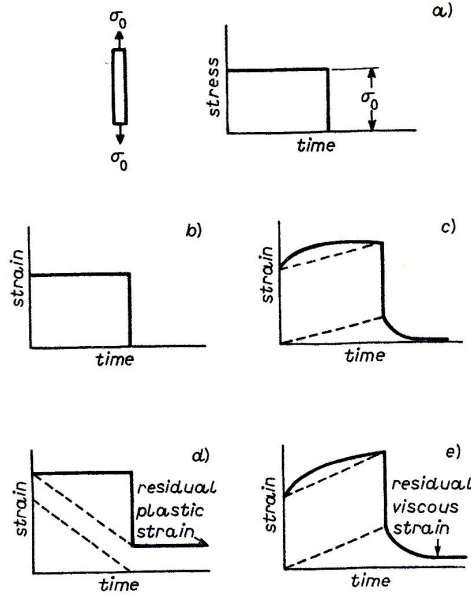


Figure 5.5: Schematic illustration of typical responses observed when a constant stress as in a) is applied: b) elastic, c) anelastic, d) partially plastic, e) viscoelastic. In the anelastic, plastic and viscoelastic cases, there is an elastic component to the total response. When the stress is removed, the elastic deformation is always recovered. In the anelastic case there is complete recovery but after a waiting time. In the plastic and viscoelastic cases there is no complete recovery.

### 5.4.3 Superposition principle

Consider a specimen to which is applied a stress  $\sigma_0$  at time  $t = 0$ . The resulting strain is given by (5.19) and (5.20)

$$\gamma(t) = [J_\infty + (J_e - J_\infty)\psi(t)] \sigma_0 \quad (5.31)$$

What can we say about the strain produced a time  $t$  by a stress applied at  $t = 0$  but which at time  $u$  ( $0 < u < t$ ) is not a constant  $\sigma_0$  but some variable stress  $\sigma(u)$ .

Suppose that at time  $u$  the stress is changed by  $d\sigma(u)$  and that this stress increment causes a strain increment  $d\gamma(t)$  at the later time  $t$ , then

$$d\gamma(t) = [J_\infty + (J_e - J_\infty)\psi(t - u)] d\sigma(u)$$

The total strain at time  $t$  is a superposition of all the increments so that

$$\begin{aligned}\gamma(t) &= J_\infty\sigma(t) + (J_e - J_\infty) \int_{-\infty}^t \psi(t - u) \frac{d\sigma(u)}{du} du \\ &= \int_{-\infty}^t J(t - u) \frac{d\sigma(u)}{du} du\end{aligned}\quad (5.32)$$

Now, a partial integration gives

$$\begin{aligned}\int_{-\infty}^t \psi(t - u) \frac{d\sigma(u)}{du} du &= [\psi(t - u)\sigma(u)]_{-\infty}^t - \int_{-\infty}^t \frac{d\psi(t - u)}{du} \sigma(u) du = \\ \int_{-\infty}^t \frac{d\psi(t - u)}{du} \sigma(u) du &= \int_0^\infty \sigma(t - u) \frac{d\psi(u)}{du} du\end{aligned}$$

i.e. we also have

$$\gamma(t) = J_\infty\sigma(t) + (J_e - J_\infty) \int_0^\infty \sigma(t - u) \frac{d\psi(u)}{du} du \quad (5.33)$$

A similar argument gives

$$d\sigma(t) = [G_\infty + (G_e - G_\infty)\phi_G(t - u)] d\gamma(u) \quad (5.34)$$

and

$$\begin{aligned}\sigma(t) &= G_\infty\gamma(t) + (G_e - G_\infty) \int_{-\infty}^t \phi_G(t - u) \frac{d\gamma(u)}{du} du = \int_{-\infty}^t G(t - u) \frac{d\gamma(u)}{du} du \\ &= G_\infty\gamma(t) + (G_e - G_\infty) \int_0^\infty \gamma(t - u) \frac{d\phi_G(u)}{du} du\end{aligned}\quad (5.35)$$

#### 5.4.4 Dynamic experiments

If the stress is given by

$$\sigma(t) = \sigma_0 e^{i\omega t} \quad (5.36)$$

then from (5.33) we find

$$\begin{aligned}\gamma(t) &= J_\infty\sigma_0 e^{i\omega t} + (J_e - J_\infty) \int_0^\infty \sigma_0 e^{i\omega(t-u)} \frac{d\psi(u)}{du} du \\ &= \left[ J_\infty + (J_e - J_\infty) \int_0^\infty e^{-i\omega u} \frac{d\psi(u)}{du} du \right] \sigma_0 e^{i\omega t} = J^*(\omega)\sigma(t)\end{aligned}\quad (5.37)$$

Here the compliance function is

$$J^*(\omega) = J_\infty + (J_e - J_\infty) \int_0^\infty e^{-i\omega u} \frac{d\psi(u)}{du} du = J_\infty - (J_e - J_\infty) \int_0^\infty e^{-i\omega u} \frac{d\phi_J(u)}{du} du \quad (5.38)$$

We define the Laplace transform

$$\hat{J}^*(z) = J_\infty - (J_e - J_\infty) \int_0^\infty e^{-zt} \frac{d\phi_J(t)}{dt} dt \quad (5.39)$$

or for the time-dependent function

$$J^*(t) = J_\infty \delta(t) - (J_e - J_\infty) \frac{d\phi_J(t)}{dt} \quad (5.40)$$

then

$$J^*(\omega) = \hat{J}^*(z = i\omega) \quad (5.41)$$

Also

$$\hat{J}^*(z) = J_\infty - (J_e - J_\infty) \left[ z \hat{\phi}_J(z) - 1 \right] = J_e - (J_e - J_\infty) z \hat{\phi}_J(z) = zJ(z) \quad (5.42)$$

Similarly we get the frequency dependent modulus as

$$\begin{aligned} \hat{G}^*(z) &= G_e + (G_e - G_\infty) \int_0^\infty e^{-zt} \frac{d\phi_G(t)}{dt} dt = G_e + (G_e - G_\infty) \left[ z \hat{\phi}_G(z) - 1 \right] \\ &= G_\infty + (G_e - G_\infty) z \hat{\phi}_G(z) = zG(z) \end{aligned} \quad (5.43)$$

Therefore

$$\hat{J}^*(z) \hat{G}^*(z) = z^2 J(z) G(z) = 1$$

### 5.4.5 General deformations

In simple shear, the change in shape is not accompanied by any change in volume. There are other deformation geometries which are characterized by a change in volume or combined change in volume and shape. To describe the mechanical behaviour under such conditions it is necessary to introduce a more complicated constitutive equation including all components of the stress tensor.

From (5.32) we have

$$\gamma(t) = \int_{-\infty}^t J(t-u) \frac{d\sigma(u)}{du} du \quad (5.44)$$

and similarly

$$\sigma(t) = \int_{-\infty}^t G(t-u) \frac{d\gamma(u)}{du} du \quad (5.45)$$

In a general tensor notation this gives

$$\begin{aligned} \gamma_{ij}(t) &= \sum_{kl} \int_{-\infty}^t J_{ijkl}(t-u) \frac{d\sigma_{kl}(u)}{du} du \\ \sigma_{ij}(t) &= \sum_{kl} \int_{-\infty}^t G_{ijkl}(t-u) \frac{d\gamma_{kl}(u)}{du} du \end{aligned} \quad (5.46)$$

Now a general isotropic tensor have two independent components

$$T_{ijkl} = \alpha\delta_{ij}\delta_{kl} + \beta(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \quad (5.47)$$

Therefore

$$\begin{aligned} \gamma_{ij}(t) &= \int_{-\infty}^t \alpha(t-u)\delta_{ij} \sum_k \dot{\sigma}_{kk}(u)du + \int_{-\infty}^t \beta(t-u) [\dot{\sigma}_{ij}(u) + \dot{\sigma}_{ji}(u)] du \\ &= \int_{-\infty}^t \alpha(t-u)\delta_{ij} \sum_k \dot{\sigma}_{kk}(u)du + \int_{-\infty}^t 2\beta(t-u)\dot{\sigma}_{ij}(u)du \end{aligned} \quad (5.48)$$

Comparing this expression with (5.44) for  $i = x, j = y$  we find  $2\beta(t) = J(t)$ . Then we can write

$$\begin{aligned} \gamma_{ij}(t) &= \int_{-\infty}^t J(t-u) \left[ \dot{\sigma}_{ij}(u) - \frac{1}{3} \sum_k \dot{\sigma}_{kk}(u)\delta_{ij} \right] du \\ &+ \int_{-\infty}^t \frac{2}{3}B(t-u)\frac{1}{3}\delta_{ij} \sum_k \dot{\sigma}_{kk}(u)du \end{aligned} \quad (5.49)$$

where the relaxation compliance is defined as

$$B(t) = \frac{9}{2}\alpha(t) - \frac{3}{2}J(t) \quad (5.50)$$

Similarly from (5.46)

$$\begin{aligned} \sigma_{ij}(t) &= \int_{-\infty}^t G(t-u) \left[ \dot{\gamma}_{ij}(u) - \frac{1}{3} \sum_k \dot{\gamma}_{kk}(u)\delta_{ij} \right] du \\ &+ \int_{-\infty}^t \frac{3}{2}K(t-u)\frac{1}{3}\delta_{ij} \sum_k \dot{\gamma}_{kk}(u)du \end{aligned} \quad (5.51)$$

Here  $J(t)$  and  $G(t)$  are the same shear stress compliance and modulus as before.  $B(t)$  and  $K(t)$  are corresponding volumetric relaxation compliance and modulus.

If the dimensions of an isotropic cubical element are increased or decreased uniformly by application of normal forces on all faces  $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = -P$ , the hydrostatic pressure and all other stress components are zero, and the three  $\dot{\gamma}_{kk}$  are equal (5.49) and (5.51) becomes

$$\gamma_{ii}(t) = \frac{2}{3} \int_{-\infty}^t B(t-u)\dot{\sigma}(u)du = -\frac{2}{3}B(t)P \quad (5.52)$$

and

$$-P = \frac{3}{2} \int_{-\infty}^t K(t-u)\dot{\gamma}_{ii}(u)du \quad (5.53)$$

The strain is the relative change in volume

$$\frac{V - V_0}{V_0} = \left(1 + \frac{\gamma_{xx}}{2}\right) \left(1 + \frac{\gamma_{yy}}{2}\right) \left(1 + \frac{\gamma_{zz}}{2}\right) = \frac{1}{2} \sum_k \gamma_{kk} + O(\gamma^2) = \Delta_v \quad (5.54)$$

Then

$$P(t) = -K(t)\Delta_v \quad (5.55)$$

$K(t)$  is therefore termed the bulk relaxation modulus. Alternatively, if the pressure  $P$  is applied suddenly and the volume change is followed as a function of time, the creep experiment is described by

$$\Delta_v(t) = -PB(t) \quad (5.56)$$

where  $B(t)$  is the bulk creep compliance.

If an isotropic cubical element is elongated in one direction and the dimensional changes in the two mutually perpendicular directions are equal, the experiment is termed simple extension. If  $\gamma_{zz}$  is positive,  $\gamma_{xx}$  and  $\gamma_{yy}$  are equal and negative. The stresses are  $\sigma_{zz} = \sigma_T - P_a$ ,  $\sigma_{xx} = \sigma_{yy} = -P_a$ , where  $\sigma_T$  is the tensile stress resulting from the applied force and  $P_a$  is the ambient pressure.

From (5.51) we have

$$\sigma_{zz}(t) = \int_{-\infty}^t \left\{ \frac{2}{3}G(t-u) [\dot{\gamma}_{zz}(u) - \dot{\gamma}_{xx}(u)] + \frac{1}{2}K(t-u) [\dot{\gamma}_{zz}(u) + 2\dot{\gamma}_{xx}(u)] \right\} du \quad (5.57)$$

and

$$\sigma_{xx}(t) = -P_a = \int_{-\infty}^t \left\{ \frac{1}{3}G(t-u) [\dot{\gamma}_{xx}(u) - \dot{\gamma}_{zz}(u)] + \frac{1}{2}K(t-u) [2\dot{\gamma}_{xx}(u) + \dot{\gamma}_{zz}(u)] \right\} du \quad (5.58)$$

This gives

$$\sigma_{zz}(t) = \int_{-\infty}^t G(t-u) [\dot{\gamma}_{zz}(u) - \dot{\gamma}_{xx}(u)] du - P_a \quad (5.59)$$

Here  $\gamma_{zz}$  is constant but  $\gamma_{xx}$  will in general change with time. The relation between axial extension and lateral contraction for a perfectly elastic solid is specified by the Poisson ratio  $\mu$

$$\mu(t) = -\frac{\gamma_{xx}(t)}{\gamma_{zz}} = \frac{1}{2} - \frac{\gamma_{zz} + 2\gamma_{xx}}{2\gamma_{zz}} = \frac{1}{2} - \frac{\Delta_v}{\gamma_{zz}} = \frac{1 - \Delta_v/\epsilon}{2} \quad (5.60)$$

where  $\epsilon$  is the practical tensile strain  $\gamma_{zz}/2$ .

With

$$\dot{\mu}(t) = -\frac{\dot{\gamma}_{xx}(t)}{\gamma_{zz}} \quad (5.61)$$

we find

$$\sigma_{zz}(t) = \gamma_{zz}G(t) - \int_{-\infty}^t G(t-u)\dot{\gamma}_{xx}(u)du - P_a = \gamma_{zz} \left[ G(t) + \int_{-\infty}^t G(t-u)\dot{\mu}(u)du \right] - P_a \quad (5.62)$$

This gives the tensile stress

$$\sigma_T(t) = \gamma_{zz} \left[ G(t) + \int_{-\infty}^t G(t-u)\dot{\mu}(u)du \right] = \epsilon E(t) \quad (5.63)$$

where  $E(t)$  is the time-dependent Young modulus,

$$E(t) = 2 \left[ G(t) + \int_{-\infty}^t G(t-u)\dot{\mu}(u)du \right] \quad (5.64)$$

A sudden tensile stress  $\sigma_T$  produces a strain from (5.49)

$$\gamma_{zz}(t) = \frac{2}{3}J(t)\sigma_T + \frac{2}{9}B(t) [\sigma_T - 3P_a] \quad (5.65)$$

and

$$\gamma_{xx}(t) = -\frac{1}{3}J(t)\sigma_T + \frac{2}{9}B(t) [\sigma_T - 3P_a] \quad (5.66)$$

Then for  $\sigma_T \gg P_a$  we have

$$\epsilon(t) = D(t)\sigma_T \quad (5.67)$$

where

$$D(t) = \frac{1}{3}J(t) + \frac{1}{9}B(t) \quad (5.68)$$

and

$$\mu(t) = \frac{J(t) - \frac{2}{3}B(t)}{2J(t) - \frac{2}{3}B(t)} \quad (5.69)$$

## 5.5 Simple models

Having defined the various functions appearing in stress and shear experiments, we will now calculate these for some simple models.

### 5.5.1 Maxwell model

The shear stress in a liquid subjected to a step function of applied shear strain rises immediately to a value determined by the instantaneous modulus, and then decays steadily as the liquid flows and takes up new configuration. For a step function  $\gamma(t) = \gamma_0\theta(t)$  we have  $\dot{\gamma}(t) = \gamma_0\delta(t)$ , where  $\delta(t)$  is Diracs delta-function. In the Maxwell model (5.7) we find in this case

$$\dot{\sigma} + \frac{1}{\tau_M}\sigma = G_\infty\gamma_0\delta(t), \quad t > 0$$

where  $\gamma_0$  is the magnitude of the shear strain. The solution is

$$\sigma(t) = G_\infty\gamma_0e^{-t/\tau_M}$$

The stress relaxation modulus is therefore

$$G(t) = \frac{\sigma(t)}{\gamma_0} = G_\infty e^{-t/\tau_M}$$

The stress decay exponentially with time, the Maxwell relaxation time  $\tau_M$  being the time at which the stress is reduced to  $1/e$  of its original value.

The converse experiment, in which a step function of stress is applied and the variation of strain at time is observed is known as creep. In this case  $\sigma(t) = \sigma_0\theta(t)$  and  $\dot{\sigma}(t) = \sigma_0\delta(t)$ . The Maxwell model is

$$\dot{\gamma} = \frac{1}{\eta}\sigma_0 + \frac{1}{G_\infty}\sigma_0\delta(t), \quad t > 0$$

and the response in this case is

$$\gamma(t) = \sigma_0\frac{t}{\eta} + \frac{\sigma_0}{G_\infty}$$

The creep function is

$$J(t) = \frac{\gamma(t)}{\sigma_0} = J_\infty + \frac{t}{\eta}$$

For sinusoidal variations of stress and strain with frequency  $\omega$  (5.7) becomes

$$\sigma + i\omega\tau_M\sigma = i\omega\eta\gamma$$

The complex modulus then becomes

$$G^*(\omega) = \frac{\sigma}{\gamma} = \frac{i\omega\eta}{1 + i\omega\tau_M} = \frac{\omega^2\eta\tau_M + i\omega\eta}{1 + (\omega\tau_M)^2}$$

The complex compliance for the Maxwell model is similarly given by

$$J^*(\omega) = \frac{\gamma}{\sigma} = \frac{1 + i\omega\tau_M}{i\omega\eta} = J_\infty - i\frac{1}{\omega\eta}$$

### 5.5.2 The Voigt model

For the Voigt model, a step function in the applied strain, gives

$$\sigma = G_\infty\gamma_0 + \eta\gamma_0\delta(t)$$

and so

$$G(t) = \frac{\sigma}{\gamma_0} = G_\infty + \eta\delta(t)$$

This expression is however not very informative. The utility of the Voigt model lies mainly in the response to a step function of the stress

$$\dot{\gamma} + \frac{1}{\tau_M}\gamma = \frac{1}{\eta}\sigma_0, \quad t > 0$$

with the solution

$$\gamma(t) = \sigma_0 \frac{1}{G_\infty} \left(1 - e^{-t/\tau_M}\right)$$

The creep function is then

$$J(t) = \frac{\gamma}{\sigma_0} = J_\infty \left(1 - e^{-t/\tau_M}\right).$$

The oscillatory response is obtained with sinusoidal variations of stress and strain

$$\sigma = i\omega\eta\gamma + G_\infty\gamma$$

The complex modulus becomes

$$G^*(\omega) = \frac{\sigma}{\gamma} = i\omega\eta + G_\infty$$

The more useful response is the complex compliance

$$J^*(\omega) = \frac{\gamma}{\sigma} = \frac{1}{i\omega\eta + G_\infty} = J_\infty \frac{1}{1 + i\omega\tau_M} = J_\infty \frac{1 - i\omega\tau_M}{1 + (\omega\tau_M)^2}$$

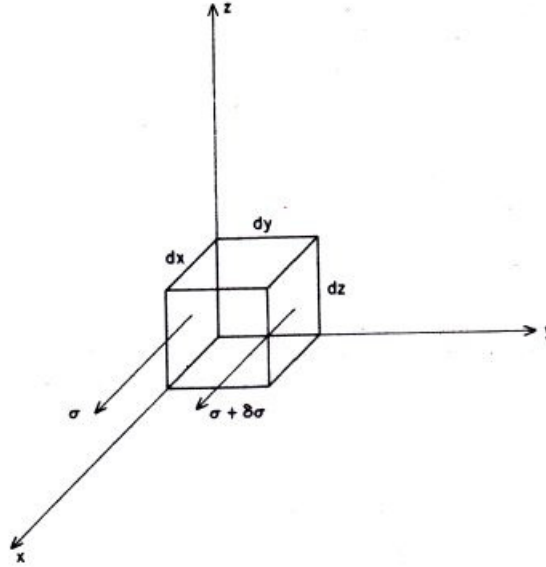


Figure 5.6: Shear stress on a small volume element of the material.

### 5.5.3 Propagation of waves in liquids

Let's consider the oscillatory responses in more details. In many of the techniques used for measuring the viscoelastic properties of liquids, a plane shear wave is propagated into the liquid. The motion will be assumed to be sinusoidal with the displacement in the  $x$ -direction and the wave propagating in the  $y$ -direction. The wave fronts are parallel to the  $x - z$  plane. Considering a small volume element of sides  $dx$ ,  $dy$  and  $dz$  as shown in figure 5.6 we have the net shear stress

$$(\sigma + \delta\sigma)(y + dy) - \sigma(y) = \frac{\partial\sigma}{\partial y}dy$$

The force on the element in the  $x$ -direction is

$$F = \left( \frac{\partial\sigma}{\partial y} dy \right) dx dz = \frac{\partial\sigma}{\partial y} dV$$

where  $dV$  is the volume of the element. Newtons equation for the element is then

$$\begin{aligned} \rho dV \frac{\partial^2 u}{\partial t^2} &= \frac{\partial\sigma}{\partial y} dV \\ \rho \frac{\partial^2 u}{\partial t^2} &= \frac{\partial\sigma}{\partial y} \end{aligned}$$

Here  $\rho$  is the mass-density and  $u = x - x_0$  denotes the displacement of the element in the  $x$  direction due to the applied force.



The shear stress  $\sigma$  and the shear strain  $\gamma = \partial u / \partial y$  are related by the shear modulus  $\sigma = G\gamma$ . Inserting this into the equation of motion gives

$$\frac{\partial^2 u}{\partial t^2} = \frac{G}{\rho} \frac{\partial^2 \gamma}{\partial y^2}$$

which gives the wave equation for shear wave propagation in the  $y$  direction. Assuming the displacement varies sinusoidally with time and space

$$u(y, t) = u_0 \exp [i(\omega t - ky)]$$

we find a solution for  $\omega = ck$  where the velocity of propagation is  $c = \sqrt{G/\rho}$ . This solution is appropriate for a Hookean solid where the stress varies in phase with the strain. In a liquid we rather have  $\sigma = \eta \dot{\gamma} = i\omega\eta\gamma$  so that

$$G(\omega) = \frac{\sigma}{\gamma} = i\omega\eta$$

then we have

$$k = \omega \sqrt{\frac{\rho}{G(\omega)}} = \sqrt{\frac{\omega\rho}{i\eta}} = (1 - i) \sqrt{\frac{\omega\rho}{2\eta}}$$

Inserting this into the solution above we find

$$u(y, t) = u_0 \exp \left[ -\sqrt{\frac{\omega\rho}{2\eta}} y \right] \exp \left[ i\omega \left( t - \sqrt{\frac{\omega\rho}{2\eta}} y \right) \right]$$

and the wave travels with a phase velocity  $c = \sqrt{(2\omega\eta/\rho)}$  and is damped with a damping constant  $\alpha = \sqrt{(\omega\rho/2\eta)}$ .

In a viscoelastic material the modulus can have both a real and imaginary component  $G^*(\omega) = G'(\omega) + iG''(\omega)$ . From measurements of the velocity and damping of a shear wave one can extract  $G^*(\omega)$ . The quantity which is most easily measured is the mechanical shear impedance defined as

$$Z_L = -\frac{\sigma}{\partial u / \partial t}$$

The velocity is  $\partial u / \partial t = i\omega u$  and the shear stress is

$$\sigma = G^*(\omega) \frac{\partial u}{\partial y} = G^*(\omega) [-iku] = -i\omega \sqrt{\rho G^*(\omega)} u$$

Thus

$$Z_L = R_L + iX_L = \frac{i\omega \sqrt{\rho G^*(\omega)} u}{i\omega u} = \sqrt{\rho G^*(\omega)}$$

or

$$Z_L^2(\omega) = \rho G^*(\omega)$$

The components of the complex modulus can therefore be obtained from the components of the impedance

$$\begin{aligned} G'(\omega) &= \frac{1}{\rho} [R_L^2(\omega) + X_L^2(\omega)] \\ G''(\omega) &= \frac{1}{\rho} 2R_L(\omega)X_L(\omega) \end{aligned} \quad (5.70)$$

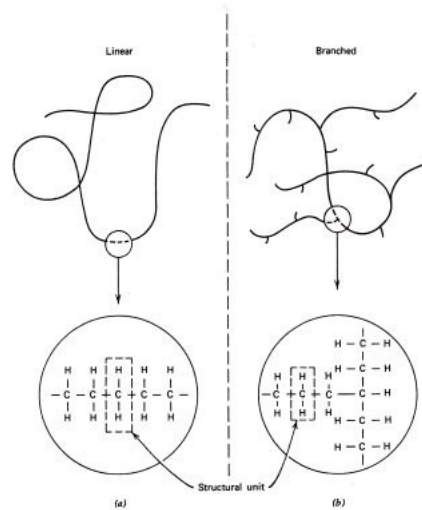


Figure 5.7: Schematic picture of long polymer molecules.

## 5.6 Experimental results

### 5.6.1 Creep and relaxation experiments

In stress relaxation and creep measurements the experimental time scale is in the range  $10^{-2}$  to  $10^3$  s. These techniques therefore necessitate measurements being made on liquids having viscosities in the range  $10^7$  to  $10^{12}$  Pa s if viscoelastic effects are to be observed. Consequently, the measurement must be made at, or near, the glass transition temperature of the liquid. Alternatively complex liquids like polymers with a high viscosity are used for these type of measurements. A schematic picture of polymers with and without side groups is shown in figure 5.7.

Figure 5.8 show representative examples of the time dependence of  $J(t)$  for eight different polymer solutions. The various symbols refer to:

**I** a dilute polymer solution

**II** an amorphous polymer of low molecular weight

**III** an amorphous polymer of high molecular weight

**IV** an amorphous polymer of high molecular weight with long side groups

**V** an amorphous polymer of high molecular weight below its glass transition temperature

**VI** a lightly cross-linked amorphous polymer

**VII** a very lightly cross-linked amorphous polymer

**VIII** a highly crystalline polymer

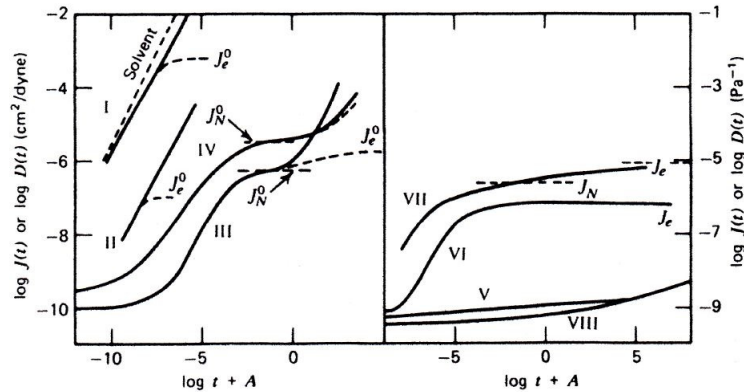


Figure 5.8: The creep function plotted logarithmically for eight typical polymer systems. Viscoelastic liquids are shown in the left part and anelastic solids on the right. The creep function  $J(t)$  is plotted except for curves VI and VIII which show results for simple extension  $D(t)$ . The dashed curves represent the creep after subtraction of a flow contribution  $t/\eta_0$  where  $\eta_0$  is the solvent viscosity. The solvent for the dilute solution in example I is also shown as a dotted line. Taken from Ferry "Viscoelastic properties of polymers."

When measuring a function like  $J(t)$  one can in general vary different control-parameters like temperature  $T$ , mass density  $\rho$  or molecular weight  $M_w$ . The curves in figure 5.8 are so called master curves, which are obtained after rescaling the data for  $J(t)$  in an appropriate way. The scaling property of the data are illustrated in figures 5.9-5.10. In figure 5.9 we show the creep function for a polymeric system (poly cis-isoprene) plotted against time for ten different temperatures.

In figure 5.10a we show the same data shifted in time by an appropriate factor  $a_T$ . In this plot all data shown in figure 5.9 collapse onto a single so called master curve. This curve is shown as curve IV in figure 5.8. The scaling time  $a_T$  used to collapse the data is shown in figure 5.10b. The temperature dependence of  $a_T$  is the same as the viscosity  $\eta$  and given by the Vogel-Fulcher expression

$$a_T = t_0 \exp(E/k_B(T - T_0))$$

where  $E$  is a characteristic barrier height.

The typical time dependence of  $G(t)$  is shown in figure 5.11 for the same systems as shown in figure 5.8.

### 5.6.2 Dynamic experiments

A knowledge of the variation with temperature of both the viscosity and the shear modulus  $G_\infty$  enables experimental data obtained over a range of temperatures and frequencies to be plotted in normalized form. The measured values of the components of the complex shear impedance, plotted as  $R_L/(\rho G_\infty)^{1/2}$  and  $X_L/(\rho G_\infty)^{1/2}$  against  $\omega\eta/G_\infty$ , are shown

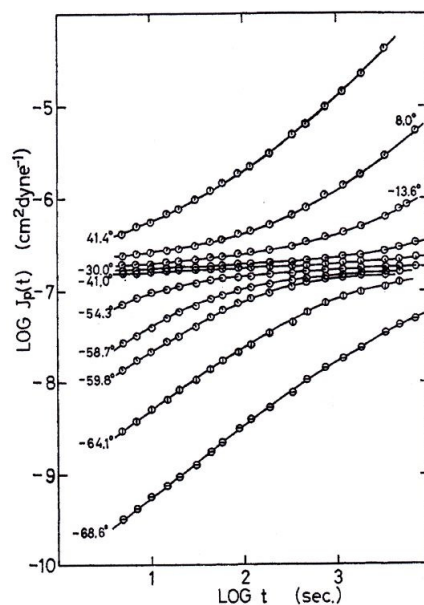


Figure 5.9: The creep function  $J(t)$  for poly(*cis-isoprene*) plotted logarithmically versus time for ten temperatures as indicated. Taken from Nemoto *et. al* *Macromolecules* **4** 215 (1971).

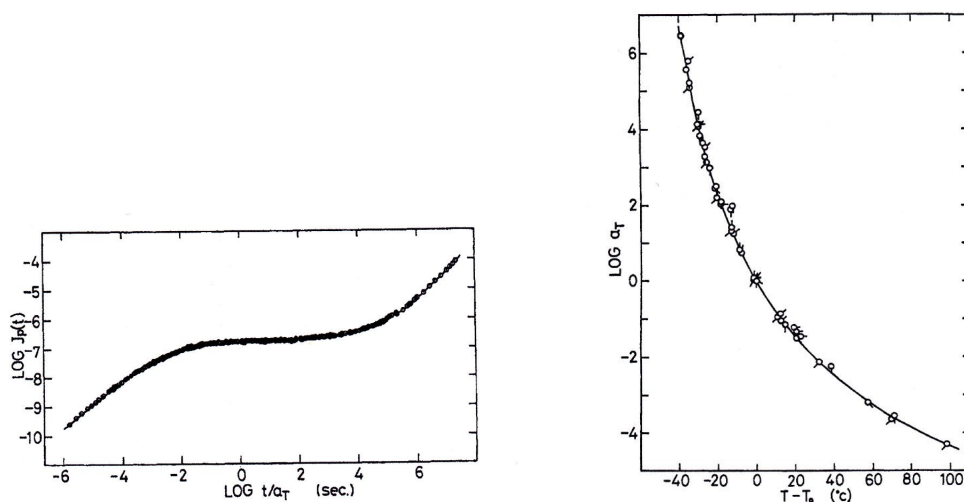


Figure 5.10: Left: The same data as in figure 5.9 rescaled onto a master curve obtained by shifting the curves along the time axis by a factor  $a_T$ . Right: Semilogarithmic plot of the scaling factor  $a_T$  plotted against  $T - T_0$  where  $T_0$  is a reference temperature.

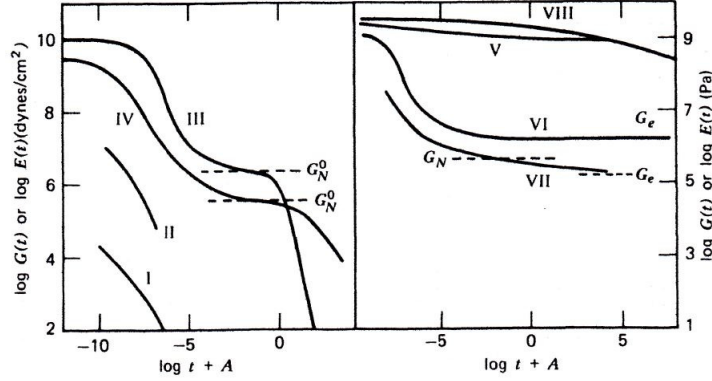


Figure 5.11: Relaxation modulus  $G(t)$  for the eight polymers shown in figure 5.8

in figure 5.12 for a large number of organic liquids. As can be seen all data fall on two master curves. The behaviour given by these two curves is found in a large number of pure liquids, among which there are wide differences in molecular structure and composition.

The variation with frequency of the components of the mechanical impedance can be described by an empirical equation shown as full curves in figure 5.12. The expression in given in terms of the complex compliance and has the form

$$J^*(\omega) = J_\infty \left[ 1 + \frac{1}{i\omega\tau_M} + 2 \left( \frac{1}{i\omega\tau_M} \right)^{1/2} \right]$$

From this expression one can then calculate  $Z_L$  via the relation

$$Z_L^2 = \rho G^*(\omega) = \frac{\rho}{J^*(\omega)}$$

The stress function corresponding to this empirical expression has the Laplace-transform

$$J(z) = J_\infty \left[ \frac{1}{z} + \frac{1}{z^2\tau_M} + \frac{2}{z} \left( \frac{1}{z\tau_M} \right)^{1/2} \right]$$

which gives the time-dependence

$$J(t) = J_\infty \left[ 1 + \frac{t}{\tau_M} + \frac{1}{\sqrt{\pi}} \left( \frac{t}{\tau_M} \right)^{1/2} \right] \quad (5.71)$$

In figure 5.14 we show typical results for the real and imaginary parts of the complex modulus

$$G^*(\omega) = G'(\omega) + iG''(\omega).$$

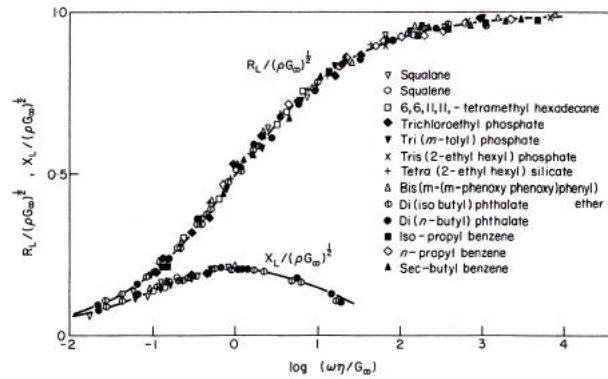


Figure 5.12: Normalized plots of  $R_L / (\rho G_\infty)^{1/2}$  and  $X_L / (\rho G_\infty)^{1/2}$  against  $\omega \eta / G_\infty$  for a number of supercooled liquids. From Lamb, *Proc. Insr. Mech. Eng.* **182**, Pt. 3A, 293 (1967).

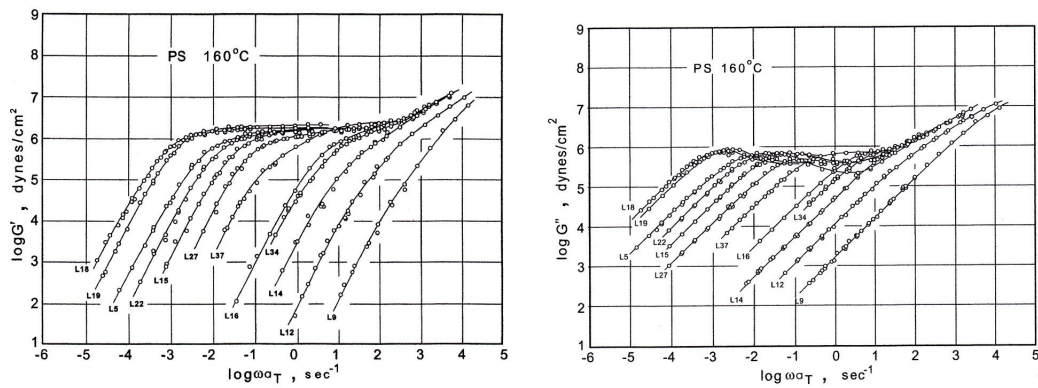


Figure 5.13: Real and imaginary parts of the frequency dependent modulus for polystyrene melts. Molecular weight ranges from  $M_w = 8.9 \times 10^3$  (L9) to  $M_w = 5.8 \times 10^5$  (L18). Taken from Onogi et. al *Macromolecules* **3**, 109 (1970).

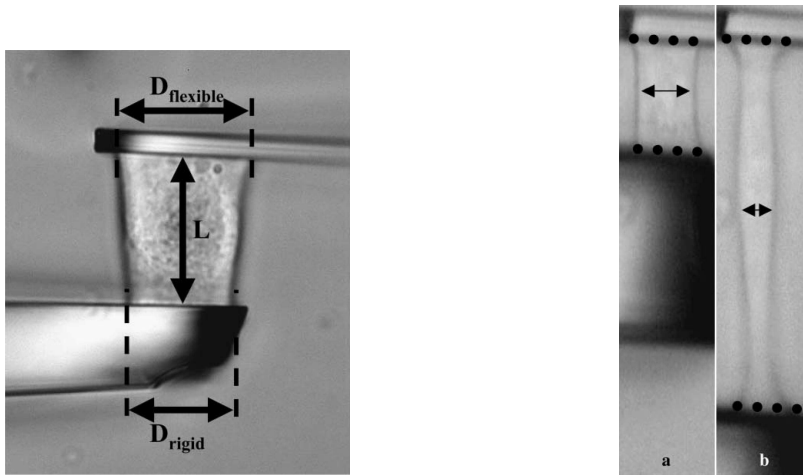


Figure 5.14: *Left: Experimental setup with cell between the microplates. Cell-length  $L$  and contact diameters are indicated. Right: Shapes of a stretched cell at (a)  $\gamma \approx 1$  and (b)  $\gamma \approx 6$ . Whereas apparent contact diameters (dots) decrease slightly at high strain, the mean cell diameter parallel to the microplates (arrows) is nearly decreased by a factor of 2.*

### 5.6.3 Biorheology

Uniaxial stretching experiments on cells has been performed in many recent experiments. Below we show experiments performed by Desprat et. al (Biophysical Journal **88** 2224 (2005)). The cell is captured between two glass-plates, and these are then separated by an applied force. The resulting elongation of the cell is then measured. The experimental setup is shown in figure 5.14 and in figure 5.15 is a schematic representation of the setup.

From the relation

$$L_0 + D(t) = L(t) + \delta(t)$$

where  $L(t)$ ,  $D(t)$ , and  $\delta(t)$  are the cell length, the rigid plate displacement and the flexible-plate deflection at time  $t$ , we obtain the strain

$$\gamma(t) = \frac{L(t) - L_0}{L_0} = \frac{D(t) - \delta(t)}{L_0}$$

The experimental results for the strain as a function of time is shown in figure 5.16 The experimental results show that the strain  $\gamma$  is well represented by two power laws

$$\gamma(t) \propto At^a$$

where the exponent  $a = 0.2$  up to 100 s whereafter there is a relatively sharp crossover to a new exponent  $a' = 0.5$ .

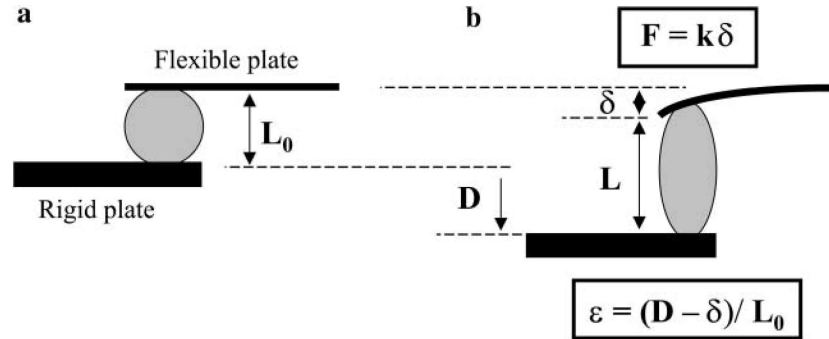


Figure 5.15: Schematic representation of a constant-rate of change experiment. (a) Initial state with a cell of length  $L_0$ . (b) The rigid plate is moved at a constant rate (the displacement  $D$  is proportional to the time  $t$ ). Both the cell length  $L(t)$  and the flexible plate deflection  $\delta(t)$  are continuously varying and their values are geometrically related.

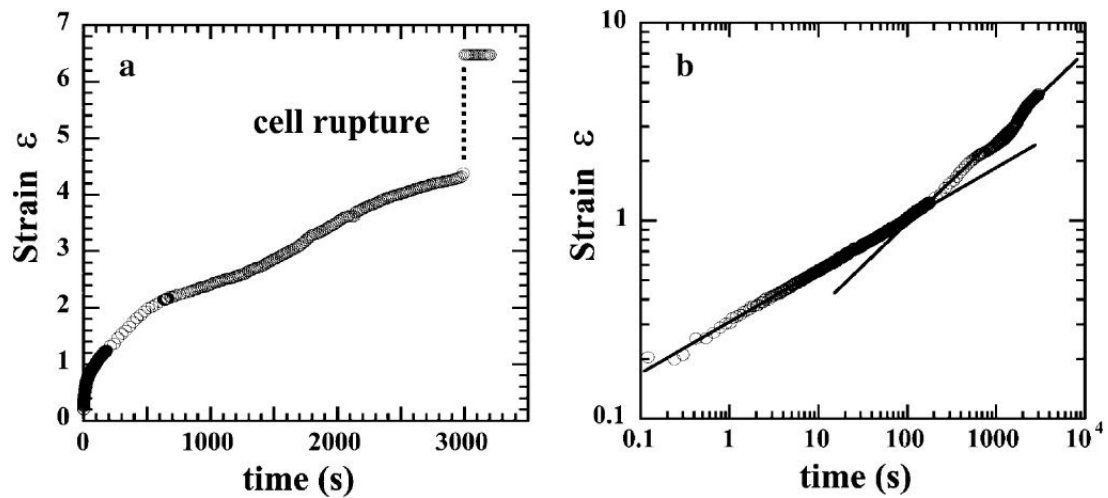


Figure 5.16: Strain data illustrating the typical behaviour of a living cell submitted to a constant force. (a) The lin-lin plot showing the cell rupture at  $\approx 50$  min. (b) The log-log plot emphasizing the existence of two different regimes.



### 5.6.4 Summary

Clearly the experimental results shown above for various viscoelastic systems, molecular liquids, polymers and cells, are much more complex than the predictions of the simple models outlined above. Therefore one has to find more refined theories to explain these results. In particular the experiments show nontrivial scaling behaviour, stretching i.e. spectra or time-functions which decay much slower than an exponential function. To explain this behaviour is therefore a challenge, and in the next section we will develop a microscopic theory to explain these results.

## 5.7 Linear response

The mechanical response of a system as described by  $J^*(\omega)$  can be analysed with the application of linear response theory. In the presence of an external stress  $\sigma^{\text{ext}}(t)$  the Hamiltonian of the system takes the form

$$\mathcal{H} = \mathcal{H}_0 - V \sum_{ij} \gamma_{ij} \sigma_{ij}^{\text{ext}}(t) \quad (5.72)$$

where  $V$  is the volume of the specimen. The unperturbed Hamiltonian  $\mathcal{H}_0$  involves the internal dynamical variables of the system. These dynamical variables are in classical mechanics expressed in terms of generalized coordinates and corresponding momenta  $\{q_i, p_i\}$ , ( $i = 1, \dots, N$ ), where  $N$  is the number of degrees of freedom. These coordinates constitute the phase-space  $\Gamma = \{q_i, p_i\}$ . In the absence of  $\sigma^{\text{ext}}(t)$  the system is taken to be in thermal equilibrium at some temperature  $T$  and is characterized by an equilibrium density matrix or distribution function

$$\varrho_{\text{eq}} = \frac{1}{Z} e^{-\beta \mathcal{H}_0}, \quad Z = \int e^{-\beta \mathcal{H}_0} d\Gamma, \quad \beta = \frac{1}{k_B T} \quad (5.73)$$

where  $d\Gamma = \prod_{i=1}^N dq_i dp_i$ . When  $\sigma^{\text{ext}}(t)$  is applied this equilibrium is disturbed, and there will be a time-dependent distribution function evolving in time as

$$\frac{\partial \varrho}{\partial t} = [\mathcal{H}, \varrho(t)]_{\text{PB}} \quad (5.74)$$

Here the Poisson-bracket between two dynamical variables  $A$  and  $B$  is defined as

$$[A, B]_{\text{PB}} = \sum_{i=1}^N \left[ \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right]$$

We are interested in the time evolution of the strain, where

$$\langle \gamma_{ij}(t) \rangle = \int \gamma_{ij} \varrho(t) d\Gamma \quad (5.75)$$

To obtain the linear response we write

$$\varrho(t) = \varrho_{\text{eq}} + \delta \varrho(t)$$

Inserting this and (5.72) for the Hamiltonian into (5.74) we get

$$\begin{aligned}
\frac{\partial}{\partial t} \delta \varrho(t) &= [\mathcal{H}_0 + \mathcal{H}_{\text{ext}}(t), \varrho_{\text{eq}} + \delta \varrho(t)]_{\text{PB}} \\
&= [\mathcal{H}_0, \varrho_{\text{eq}}]_{\text{PB}} + [\mathcal{H}_0, \delta \varrho(t)]_{\text{PB}} + [\mathcal{H}_{\text{ext}}(t), \varrho_{\text{eq}}]_{\text{PB}} + [\mathcal{H}_{\text{ext}}(t), \delta \varrho(t)]_{\text{PB}} \\
&= [\mathcal{H}_0, \delta \varrho(t)]_{\text{PB}} + [\mathcal{H}_{\text{ext}}(t), \varrho_{\text{eq}}]_{\text{PB}} + \dots \\
&= -i\mathcal{L}\delta \varrho(t) + [\mathcal{H}_{\text{ext}}(t), \varrho_{\text{eq}}]_{\text{PB}}
\end{aligned} \tag{5.76}$$

Here we have used that  $[\mathcal{H}_0, \varrho_{\text{eq}}]_{\text{PB}} = 0$  and only kept terms to linear order in  $\mathcal{H}_{\text{ext}}$ . The Liouville operator is defined via  $-i\mathcal{L}A(t) = [\mathcal{H}_0, A(t)]_{\text{PB}}$  for some dynamical variable  $A(t)$ . The solution for  $\delta \varrho(t)$  is

$$\delta \varrho(t) = \int_{-\infty}^t e^{-i\mathcal{L}(t-u)} [\mathcal{H}_{\text{ext}}(u), \varrho_{\text{eq}}]_{\text{PB}} du = -V \sum_{kl} \int_{-\infty}^t e^{-i\mathcal{L}(t-u)} [\gamma_{kl}(u), \varrho_{\text{eq}}]_{\text{PB}} \sigma_{kl}^{\text{ext}}(u) du \tag{5.77}$$

But

$$[\gamma_{kl}(u), \varrho_{\text{eq}}]_{\text{PB}} = \sum_{i=1}^N \left[ \frac{\partial \gamma_{kl}}{\partial q_i} \frac{\partial \varrho_{\text{eq}}}{\partial p_i} - \frac{\partial \gamma_{kl}}{\partial p_i} \frac{\partial \varrho_{\text{eq}}}{\partial q_i} \right] = -\beta [\gamma_{kl}(u), \mathcal{H}_0]_{\text{PB}} \varrho_{\text{eq}} = -\beta \dot{\gamma}_{kl} \varrho_{\text{eq}} \tag{5.78}$$

Then from (5.75) we have

$$\begin{aligned}
\langle \gamma_{ij}(t) \rangle &= \langle \gamma_{ij} \rangle_{\text{eq}} + \beta V \sum_{kl} \int_{-\infty}^t \langle \gamma_{ij} e^{-i\mathcal{L}(t-u)} \dot{\gamma}_{kl} \rangle_{\text{eq}} \sigma_{kl}^{\text{exp}}(u) du \\
&= -\beta V \sum_{kl} \int_{-\infty}^t \langle \dot{\gamma}_{ij}(t) \gamma_{kl}(u) \rangle_{\text{eq}} \sigma_{kl}^{\text{exp}}(u) du
\end{aligned} \tag{5.79}$$

where we used the fact that in equilibrium there is no strain, that the equilibrium state is stationary  $\langle A(t)\dot{B}(t') \rangle = -\langle \dot{A}(t)B(t') \rangle$  and

$$\gamma_{ij}(t) = e^{i\mathcal{L}t} \gamma_{ij} \tag{5.80}$$

Now for a step experiment

$$\sigma_{kl}^{\text{exp}}(t) = \begin{cases} \sigma_{kl}^0 & t > 0 \\ 0 & t < 0 \end{cases} \tag{5.81}$$

we have from (5.79) and (5.32)

$$\langle \gamma_{ij}(t) \rangle = -\beta V \sum_{kl} \int_0^t \langle \dot{\gamma}_{ij}(t) \gamma_{kl}(u) \rangle_{\text{eq}} du \sigma_{kl}^0 = \sum_{kl} J_{ijkl}(t) \sigma_{kl}^0 \tag{5.82}$$

i.e. the creep tensor is in linear response given by

$$J_{ijkl}(t) = -\beta V \sum_{kl} \int_0^t \langle \dot{\gamma}_{ij}(t) \gamma_{kl}(u) \rangle_{\text{eq}} du = \beta V [\langle \gamma_{ij} \gamma_{kl} \rangle_{\text{eq}} - \langle \gamma_{ij}(t) \gamma_{kl}(u) \rangle_{\text{eq}}] \tag{5.83}$$

Similarly for an applied stress equal to

$$\sigma_{kl}^{\text{ext}}(t) = \sigma_{kl} e^{i\omega t} \quad (5.84)$$

we have

$$\begin{aligned} \langle \gamma_{ij}(t) \rangle &= -\beta V \sum_{kl} \int_{-\infty}^t \langle \dot{\gamma}_{ij}(t) \gamma_{kl}(u) \rangle_{\text{eq}} \sigma_{kl}^0 e^{i\omega u} du \\ &= -\beta V \sum_{kl} \int_{-\infty}^t e^{-i\omega(t-u)} \langle \dot{\gamma}_{ij}(t) \gamma_{kl}(u) \rangle_{\text{eq}} du \sigma_{kl}^{\text{ext}}(t) \\ &= -\beta V \sum_{kl} \int_0^\infty e^{-i\omega u} \langle \dot{\gamma}_{ij}(u) \gamma_{kl}(0) \rangle_{\text{eq}} du \sigma_{kl}^{\text{ext}}(t) \end{aligned} \quad (5.85)$$

and so the compliance is

$$\begin{aligned} J_{ijkl}^*(\omega) &= -\beta V \sum_{kl} \int_0^\infty e^{-i\omega u} \langle \dot{\gamma}_{ij}(u) \gamma_{kl}(0) \rangle_{\text{eq}} du \\ &= \beta V \sum_{kl} \left[ \langle \gamma_{ij} \gamma_{kl} \rangle_{\text{eq}} - i\omega \int_0^\infty e^{-i\omega u} \langle \gamma_{ij}(u) \gamma_{kl}(0) \rangle_{\text{eq}} du \right] \end{aligned} \quad (5.86)$$

From linear response theory we obtain microscopic expressions for the creep function and compliance expressed in terms of the strain-strain equilibrium correlation function. The next task is to find approximate expression for this function.

## 5.8 The Voigt model and Langevin equation

From (5.83) and (5.86) we find that the creep function and the compliance are connected to equilibrium fluctuations in the strain. In order to calculate the correlation function  $\langle \gamma(t) \gamma(0) \rangle$  we can apply a simple stochastic model. We consider a simple shear stress so that the tensor character disappears. In the absence of any stress, the strain is  $\gamma = 0$ . When a stress  $\sigma(t)$  is present the strain is given by  $G\gamma(t) = \sigma(t)$  where the constant  $G$  is related to the relaxed modulus. Here  $\sigma(t)$  is the total stress made up of the applied stress  $\sigma^{\text{exp}}(t)$  plus an internal fluctuating stress. The latter, analogous to the force exerted on a particle undergoing Brownian motion by the surrounding medium, consists of a random part  $\sigma_r(t)$  and a frictional or systematic part  $\sigma_s(t)$ . For the latter we take  $\sigma_s(t) = -\eta\dot{\gamma}(t)$ , which is the simplest model of dissipation, and implies that the retarding stress is directly proportional to the instantaneous strain rate. The equation of motion of the fluctuating strain is therefore

$$G\gamma(t) + \eta\dot{\gamma}(t) = \sigma^{\text{ext}}(t) + \sigma_r(t) \quad (5.87)$$

This is a Langevin equation for the random variable  $\gamma(t)$  driven by  $\sigma^{\text{ext}}(t)$  and the random internal stress  $\sigma_r(t)$ . The Voigt model is recovered from (5.87) by taking an average with respect to the noise  $\sigma_r(t)$  using that  $\langle \sigma_r(t) \rangle = 0$ . This gives

$$G\langle \gamma(t) \rangle + \eta\langle \dot{\gamma}(t) \rangle = \sigma^{\text{ext}}(t) \quad (5.88)$$

The solution of this equation gives

$$\begin{aligned}\langle \gamma(t) \rangle &= \frac{1}{\eta} \int_{-\infty}^t e^{-\frac{G}{\eta}(t-u)} \sigma^{\text{ext}}(u) du = \frac{1}{G} \sigma^{\text{ext}}(t) - \frac{1}{G} \int_{-\infty}^t e^{-\frac{G}{\eta}(t-u)} \frac{d\sigma^{\text{ext}}(u)}{du} du \\ &= \frac{1}{G} \int_{-\infty}^t \left[ 1 - e^{-\frac{G}{\eta}(t-u)} \right] \frac{d\sigma^{\text{ext}}(u)}{du} du\end{aligned}$$

Therefore, in this model the creep function becomes

$$J(t) = \frac{1}{G} \left[ 1 - e^{-t/\tau_M} \right], \quad \tau_M = \frac{\eta}{G} \quad (5.89)$$

and the compliance

$$J^*(\omega) = \frac{1}{\eta} \int_0^\infty e^{-i\omega t} e^{t/\tau_M} dt = \frac{1}{\eta} \frac{1}{i\omega + 1/\tau_M} = \frac{1}{i\omega\eta + G} \quad (5.90)$$

The parameters  $G$  and  $\eta$  in this model can now be related to equilibrium fluctuations. From (5.83) and (5.89) we have

$$J(t) = \beta V \langle \gamma^2 \rangle_{\text{eq}} \left[ 1 - \frac{\langle \gamma(t)\gamma(0) \rangle_{\text{eq}}}{\langle \gamma^2 \rangle_{\text{eq}}} \right] = \frac{1}{G} \left[ 1 - e^{-t/\tau_M} \right] \quad (5.91)$$

Therefore

$$\begin{aligned}\frac{1}{G} &= \beta V \langle \gamma^2 \rangle_{\text{eq}} \\ \frac{\eta}{G} &= \int_0^\infty \frac{\langle \gamma(t)\gamma(0) \rangle_{\text{eq}}}{\langle \gamma^2 \rangle_{\text{eq}}} dt\end{aligned} \quad (5.92)$$

The latter relation is obtained by requiring that the area under  $J(t)$  should be reproduced by the model (5.89).

A simple generalization of the Voigt model can be obtained if we assume the constitutive relation

$$\sigma_s(t) = - \int_{-\infty}^t \eta(t-u) \dot{\gamma}(u) du \quad (5.93)$$

where  $\eta$  is a generalized friction or viscosity. The corresponding stochastic equation now reads

$$G\gamma(t) + \int_{-\infty}^t \eta(t-u) \dot{\gamma}(u) du = \sigma^{\text{ext}}(t) + \sigma_r(t) \quad (5.94)$$

Then the average strain satisfies the equation

$$G\langle \gamma(t) \rangle + \int_{-\infty}^t \eta(t-u) \langle \dot{\gamma}(u) \rangle du = \sigma^{\text{ext}}(t) \quad (5.95)$$

For an oscillatory stress and corresponding strain

$$\sigma^{\text{ext}}(t) = \sigma_0 e^{i\omega t}, \quad \gamma(t) = \gamma_0 e^{i\omega t}$$

this gives

$$G\gamma(t) + i\omega\eta(\omega)\gamma(t) = \sigma^{\text{ext}}(t) \quad (5.96)$$

and the compliance

$$J^*(\omega) = \frac{1}{G + i\omega\eta(\omega)} \quad (5.97)$$

Comparing this with (5.86) gives

$$J^*(\omega) = \beta V \langle \gamma^2 \rangle \left[ 1 - i\omega \int_0^\infty e^{-i\omega u} \frac{\langle \gamma(u)\gamma(0) \rangle}{\langle \gamma^2 \rangle} du \right] = \frac{1}{G + i\omega\eta(\omega)} \quad (5.98)$$

With  $\beta V \langle \gamma^2 \rangle = 1/G$  this gives

$$\int_0^\infty e^{-i\omega u} \frac{\langle \gamma(u)\gamma(0) \rangle}{\langle \gamma^2 \rangle} du = \frac{\eta(\omega)}{G + i\omega\eta(\omega)} \quad (5.99)$$

The dissipative kernel  $\eta$  is determined by the random internal stress  $\sigma_r(t)$ , via the fluctuation-dissipation theorem. With  $\sigma^{\text{ext}} = 0$  we get from (5.94)

$$\gamma(\omega) = J^*(\omega)\sigma_r(\omega)$$

Multiplying with the complex conjugate and taking an average we find

$$\langle |\gamma(\omega)|^2 \rangle = |J^*(\omega)|^2 \langle |\sigma_r(\omega)|^2 \rangle$$

So

$$\int_0^\infty e^{-i\omega t} \langle \gamma(t)\gamma(0) \rangle du = |J^*(\omega)|^2 \int_0^\infty e^{-i\omega t} \langle \sigma_r(t)\sigma_r(0) \rangle du \quad (5.100)$$

From (5.98) we have

$$\text{Im}J^*(\omega) = -\beta V \omega \text{Re} \int_0^\infty e^{-i\omega t} \langle \gamma(t)\gamma(0) \rangle du$$

and so

$$\frac{1}{\beta V \omega} \frac{\text{Im}J^*(\omega)}{|J^*(\omega)|^2} = \text{Re} \int_0^\infty e^{-i\omega t} \langle \sigma_r(t)\sigma_r(0) \rangle du$$

or since

$$\frac{1}{\omega} \frac{\text{Im}J^*(\omega)}{|J^*(\omega)|^2} = \text{Im} \left[ \frac{1}{\omega J^*(\omega)} \right] = -\text{Re} \left[ \frac{1}{i\omega J^*(\omega)} \right] = -\text{Re} \eta(\omega) \quad (5.101)$$

Therefore

$$\text{Re} \eta(\omega) = \beta V \text{Re} \int_0^\infty e^{-i\omega t} \langle \sigma_r(t)\sigma_r(0) \rangle du$$

Equality of the real parts implies also the equality of the imaginary parts due to Kramers-Kronig relations, and therefore the equality of the functions themselves, i.e.

$$\eta(t) = \beta V \langle \sigma_r(t)\sigma_r(0) \rangle \quad (5.102)$$

This is just the fluctuation-dissipation theorem for this particular model.

## 5.9 General linear response

We begin with a system in equilibrium at  $t = -\infty$ , that is described by a Hamiltonian  $\mathcal{H}_0$ . The equilibrium is disturbed by the application of a space- and time-dependent stress that alters the Hamiltonian to

$$\mathcal{H} = \mathcal{H}_0 - \sum_{kl} \int_V d\mathbf{r}' \gamma_{kl}(\mathbf{r}') \sigma_{kl}(\mathbf{r}', t) \quad (5.103)$$

where  $V$  is the volume of the sample, and  $k, l$  refers to Cartesian components. As in section 5.4 we can calculate the linear response

$$\langle \gamma_{ij}(\mathbf{r}, t) \rangle = \langle \gamma_{ij}(\mathbf{r}) \rangle_{\text{eq}} - \beta \sum_{kl} \int_{-\infty}^t du \int_V d\mathbf{r}' \langle \dot{\gamma}_{ij}(\mathbf{r}, t) \gamma_{kl}(\mathbf{r}', u) \rangle_{\text{eq}} \sigma_{kl}(\mathbf{r}', u) \quad (5.104)$$

The equilibrium average of the strain may be taken to be zero. If the equilibrium distribution of defects causing the strain is uniform throughout the sample the strain  $\gamma$  is independent of the coordinate  $\mathbf{r}$ .

In a creep experiment, a time-dependent stress is applied from  $t = 0$  onwards. From (5.104) we obtain

$$\begin{aligned} \langle \gamma_{ij}(\mathbf{r}, t) \rangle &= -\beta \sum_{kl} \int_0^t du \int_V d\mathbf{r}' \langle \dot{\gamma}_{ij}(\mathbf{r}, t) \gamma_{kl}(\mathbf{r}', u) \rangle_{\text{eq}} \sigma_{kl}(\mathbf{r}') \\ &= \beta \sum_{kl} \int_V d\mathbf{r}' \left[ \langle \gamma_{ij}(\mathbf{r}, 0) \gamma_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \langle \gamma_{ij}(\mathbf{r}, t) \gamma_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \right] \sigma_{kl}(\mathbf{r}') \end{aligned} \quad (5.105)$$

This gives us the creep function

$$J_{ijkl}(\mathbf{r}t; \mathbf{r}'0) = \beta \left[ \langle \gamma_{ij}(\mathbf{r}, 0) \gamma_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} - \langle \gamma_{ij}(\mathbf{r}, t) \gamma_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \right] \quad (5.106)$$

In a dynamical experiment we have the applied stress field

$$\sigma_{kl}(\mathbf{r}t) = \sigma_{kl}(\mathbf{r}) e^{i\omega t}$$

Then

$$\langle \gamma_{ij}(\mathbf{r}, t) \rangle = \sum_{kl} \int_V d\mathbf{r}' J_{ijkl}^*(\mathbf{r}\mathbf{r}', \omega) \sigma_{kl}(\mathbf{r}'t)$$

with the compliance

$$\begin{aligned} J_{ijkl}^*(\mathbf{r}\mathbf{r}', \omega) &= -\beta \int_0^\infty du e^{-i\omega t} \langle \dot{\gamma}_{ij}(\mathbf{r}, t) \gamma_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \\ &= \beta \left[ \langle \gamma_{ij}(\mathbf{r}, 0) \gamma_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} - i\omega \int_0^\infty dt e^{-i\omega t} \langle \gamma_{ij}(\mathbf{r}, t) \gamma_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \right] \end{aligned} \quad (5.107)$$

## 5.10 Viscoelasticity

Anelasticity is the simplest form of time-dependent mechanical behaviour. It is exhibited by a wide variety of solids, especially crystalline materials with defects, under low stress levels. For anelastic materials there is a unique equilibrium relation between stress and strain. Under a constant stress, the strain creeps from zero to a saturation value. The system can be regarded as relaxing from one equilibrium configuration to another.

Viscoelasticity is a more complicated type of mechanical behaviour. Here there is no unique equilibrium relationship between stress and strain, meaning that permanent or irrecoverable plastic deformation is induced by an applied stress. A host of materials under diverse conditions display viscoelasticity. Polymers provide a prime example. Diffusion creep in metals at high temperatures is another. The chief difficulty in a fundamental theoretical analysis of viscoelasticity is that the system does not approach a new equilibrium state once it is perturbed from its initial equilibrium by an applied stress. Typically, a constant stress applied for a time  $t$  produces a strain that becomes proportional to  $t$  for large values of  $t$ , i.e. the correlation function  $\langle \gamma(t)\gamma(0) \rangle \simeq t$  for  $t \rightarrow \infty$ . Thus means that one cannot define the spectrum via the Fourier transform in the usual manner. Also in a viscoelastic medium there is no microscopic expression for the strain, since the displacements of the particles become arbitrarily large. However like the velocity of a Brownian particle, the rate of strain is a well defined variable with a microscopic definition. Also

$$\gamma_{ij}(\mathbf{r}t) = \int_0^t du \dot{\gamma}_{ij}(\mathbf{r}u)$$

and so from (5.107)

$$\begin{aligned} J_{ijkl}^*(\mathbf{r}\mathbf{r}', \omega) &= \beta \int_0^\infty du e^{-i\omega u} \langle \gamma_{ij}(\mathbf{r}, u) \dot{\gamma}_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \\ &= \beta \int_0^\infty du e^{-i\omega u} \int_0^u dv \langle \dot{\gamma}_{ij}(\mathbf{r}, v) \dot{\gamma}_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} = \frac{\beta}{i\omega} \int_0^\infty du e^{-i\omega u} \langle \dot{\gamma}_{ij}(\mathbf{r}, u) \dot{\gamma}_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \end{aligned} \quad (5.108)$$

So the Laplace transform is

$$J_{ijkl}^*(\mathbf{r}\mathbf{r}', z) = \frac{\beta}{z} \int_0^\infty du e^{-zu} \langle \dot{\gamma}_{ij}(\mathbf{r}, u) \dot{\gamma}_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \quad (5.109)$$

and from (5.42) we find the corresponding creep function

$$J_{ijklk}(\mathbf{r}\mathbf{r}', z) = \frac{\beta}{z^2} \int_0^\infty du e^{-zu} \langle \dot{\gamma}_{ij}(\mathbf{r}, u) \dot{\gamma}_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \quad (5.110)$$

These relations are valid for both anelastic and viscoelastic materials.

The problem is then to calculate the rate of strain correlation function. A simple stochastic model is the Maxwell model where

$$\dot{\gamma}(t) = \frac{1}{\eta} \sigma(t) + \frac{1}{G} \dot{\sigma}(t)$$

and where  $\sigma$  is the internal fluctuating stress. Then

$$\begin{aligned}\langle \dot{\gamma}(t)\dot{\gamma}(0) \rangle &= \left\langle \left[ \frac{1}{\eta}\sigma(t) + \frac{1}{G}\dot{\sigma}(t) \right] \left[ \frac{1}{\eta}\sigma(0) + \frac{1}{G}\dot{\sigma}(0) \right] \right\rangle \\ &= \frac{1}{\eta^2}\langle \sigma(t)\sigma(0) \rangle + \frac{1}{G^2}\langle \dot{\sigma}(t)\dot{\sigma}(0) \rangle\end{aligned}\quad (5.111)$$

where we used the stationary condition  $\langle \dot{\sigma}(t)\sigma(0) \rangle = -\langle \sigma(t)\dot{\sigma}(0) \rangle$ . Taking the Fourier transform of (5.111) this gives

$$S_{\dot{\gamma}}(\omega) = \left[ \frac{1}{\eta^2} + \frac{\omega^2}{G^2} \right] S_{\sigma}(\omega)$$

where  $S_x(\omega)$  denotes the spectral function for variable  $x$ . Assuming a white noise spectrum for the stress  $S_{\sigma}(\omega) = \text{const.}$  introduces difficulties due to the  $\omega^2$  term above, since the spectrum  $S_{\dot{\gamma}}(\omega)$  would diverge as  $\omega \rightarrow \infty$ . The simplest assumption is therefore a Gaussian Markov process for  $\sigma(t)$

$$\langle \sigma(t)\sigma(0) \rangle = \langle \sigma^2 \rangle e^{-\lambda t}$$

and therefore

$$S_{\sigma}(\omega) = \frac{\langle \sigma^2 \rangle \lambda}{\omega^2 + \lambda^2}$$

Then

$$S_{\dot{\gamma}}(\omega) = \left[ \frac{1}{\eta^2} + \frac{\omega^2}{G^2} \right] \frac{\langle \sigma^2 \rangle \lambda}{\omega^2 + \lambda^2}$$

From the spectrum  $S_{\dot{\gamma}}(\omega)$  we can calculate the rate of strain correlation function. Alternatively from (5.111) we directly find

$$\langle \dot{\gamma}(t)\dot{\gamma}(0) \rangle = \left[ \frac{1}{\eta^2} - \frac{\lambda^2}{G^2} \right] \langle \sigma^2 \rangle e^{-\lambda t}$$

From this we get the compliance for this model

$$J^*(t) = \beta V \int_0^t du \langle \dot{\gamma}(u)\dot{\gamma}(0) \rangle = \beta V \left[ \frac{1}{\eta^2} - \frac{\lambda^2}{G^2} \right] \frac{\langle \sigma^2 \rangle}{\lambda} \left[ 1 - e^{-\lambda t} \right]$$

and the creep function

$$J(t) = \beta V \left[ \frac{1}{\eta^2} - \frac{\lambda^2}{G^2} \right] \frac{\langle \sigma^2 \rangle}{\lambda} \left[ t - \frac{1}{\lambda} \left( 1 - e^{-\lambda t} \right) \right]$$

We see that  $J(0) = 0$  and for  $t \rightarrow \infty$

$$J(t) = \beta V \left[ \frac{1}{\eta^2} - \frac{\lambda^2}{G^2} \right] \frac{\langle \sigma^2 \rangle}{\lambda} t$$



## 5.11 Microscopic treatment

From (5.109) and (5.110) we have the expressions

$$J_{ijkl}^*(\mathbf{r}t; \mathbf{r}'0) = \beta \int_0^t du \langle \dot{\gamma}_{ij}(\mathbf{r}, u) \dot{\gamma}_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \quad (5.112)$$

and

$$J_{ijklk}(\mathbf{r}t; \mathbf{r}'0) = \beta \int_0^t du (t-u) \langle \dot{\gamma}_{ij}(\mathbf{r}, u) \dot{\gamma}_{kl}(\mathbf{r}', 0) \rangle_{\text{eq}} \quad (5.113)$$

Here the strain tensor is defined via

$$\gamma_{ij}(\mathbf{r}t) = \nabla^i u_j(\mathbf{r}t) + \nabla^j u_i(\mathbf{r}t)$$

and the rate of strain tensor

$$\dot{\gamma}_{ij}(\mathbf{r}t) = \nabla^i v_j(\mathbf{r}t) + \nabla^j v_i(\mathbf{r}t)$$

In a viscoelastic medium the strain is not well defined since there is no reference state, while the rate of strain tensor can be expressed in terms of the momentum density or mass current

$$\rho(\mathbf{r}t)\mathbf{v}(\mathbf{r}t) = \mathbf{j}_M(\mathbf{r}t)$$

where  $\rho(\mathbf{r}t)$  is the mass density. In linear order we have

$$\mathbf{v}(\mathbf{r}t) = \frac{1}{\rho} \mathbf{j}_M(\mathbf{r}t)$$

and  $\rho$  is the average mass density. The momentum density  $\mathbf{j}_M(\mathbf{r}t)$  has a microscopic correspondence in terms of particle positions and velocities

$$\mathbf{j}_M(\mathbf{r}t) = \sum_{i=1}^N m_i \mathbf{v}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t))$$

where the positions and velocities can eventually be expressed in terms of the relevant generalized coordinates  $\{q_i, p_i\}$ . If we introduce the Fourier transform

$$\dot{\gamma}_{ij}(\mathbf{r}t) = \int \frac{d\mathbf{q}}{(2\pi)^3} e^{-i\mathbf{q}\cdot\mathbf{r}} \dot{\gamma}_{ij}(\mathbf{q}t)$$

where

$$\dot{\gamma}_{ij}(\mathbf{q}t) = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \dot{\gamma}_{ij}(\mathbf{r}t) = -\frac{i}{\rho} \left[ q^i j_M^j(\mathbf{q}t) + q^j j_M^i(\mathbf{q}t) \right]$$

Then the rate of strain correlation function can be written

$$\begin{aligned} & \langle \dot{\gamma}_{ij}(\mathbf{r}t) \dot{\gamma}_{kl}(\mathbf{r}'0) \rangle = \\ &= -\frac{1}{\rho^2} \int \frac{d\mathbf{q}}{(2\pi)^3} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{q}\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}'} \langle \left[ q^i j_M^j(\mathbf{q}t) + q^j j_M^i(\mathbf{q}t) \right] \left[ k^k j_M^l(\mathbf{k}0) + k^l j_M^k(\mathbf{k}0) \right] \rangle \\ &= -\frac{1}{\rho^2} \int \frac{d\mathbf{q}}{(2\pi)^3} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{q}\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}'} \left\{ q^i k^k \langle j_M^j(\mathbf{q}t) j_M^l(\mathbf{k}0) \rangle + q^i k^l \langle j_M^j(\mathbf{q}t) j_M^k(\mathbf{k}0) \rangle \right. \\ &+ \left. q^j k^k \langle j_M^i(\mathbf{q}t) j_M^l(\mathbf{k}0) \rangle + q^j k^l \langle j_M^i(\mathbf{q}t) j_M^k(\mathbf{k}0) \rangle \right\} \end{aligned} \quad (5.114)$$

For a translationally invariant system we must have

$$\langle j_M^j(\mathbf{q}t) j_M^l(\mathbf{k}0) \rangle = \langle j_M^j(-\mathbf{k}t) j_M^l(\mathbf{k}0) \rangle \delta(\mathbf{q} + \mathbf{k}) = C_{jl}(\mathbf{k}t) \delta(\mathbf{q} + \mathbf{k})$$

where  $C_{ij}(\mathbf{k}t)$  is the current-current correlation function. For an isotropic system we also have

$$C_{ij}(\mathbf{k}t) = \hat{k}^i \hat{k}^j C_\ell(kt) + \left[ \delta_{ij} - \hat{k}^i \hat{k}^j \right] C_t(kt)$$

where  $C_\ell$  and  $C_t$  denotes the longitudinal and transverse current-correlation functions. Inserting these results into (5.114) we find

$$\begin{aligned} \langle \hat{\gamma}_{ij}(\mathbf{r}t) \hat{\gamma}_{kl}(\mathbf{r}'0) \rangle &= \frac{1}{\rho^2} \int \frac{d\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} q^2 \left\{ 4\hat{q}^i \hat{q}^j \hat{q}^k \hat{q}^l [C_\ell(qt) - C_t(qt)] \right. \\ &\quad \left. + \left[ \hat{q}^i \hat{q}^k \delta_{jl} + \hat{q}^i \hat{q}^l \delta_{jk} + \hat{q}^j \hat{q}^k \delta_{il} + \hat{q}^j \hat{q}^l \delta_{ik} \right] C_t(qt) \right\} \end{aligned} \quad (5.115)$$

From (5.109) we then find

$$\begin{aligned} J_{ijkl}^*(\mathbf{r}\mathbf{r}'; z) &= \frac{\beta}{\rho^2} \frac{1}{z} \int \frac{d\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} q^2 \left\{ 4\hat{q}^i \hat{q}^j \hat{q}^k \hat{q}^l [C_\ell(qz) - C_t(qz)] \right. \\ &\quad \left. + \left[ \hat{q}^i \hat{q}^k \delta_{jl} + \hat{q}^i \hat{q}^l \delta_{jk} + \hat{q}^j \hat{q}^k \delta_{il} + \hat{q}^j \hat{q}^l \delta_{ik} \right] C_t(qz) \right\} \end{aligned} \quad (5.116)$$

For a homogeneous deformation we have

$$J_{ijkl}^*(z) = \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' J_{ijkl}^*(\mathbf{r}\mathbf{r}'; z)$$

The problem is therefore to calculate the longitudinal and transverse current correlation functions. This task will be performed in the next chapter within the Mori-Zwanzig formulation.