

VISCOELASTICITY

2.1 BASIC EXPERIMENTS

Two simple and easy to grasp concepts (or *models*) describing mechanical properties of materials originated in the XVII century. One is the Newton law of liquids:¹

$$\dot{\gamma} = \frac{\sigma}{\eta} \quad [2.1.1]$$

and another is Hooke's law of solids:²

$$\varepsilon = \frac{\sigma_E}{E} \quad [2.1.2]$$

where ε – deformation, $\dot{\gamma}$ – rate of shear deformation, σ – shear stress, σ_E – tensile stress, E – elastic (or Young's) modulus, and η – viscosity.

Both equations are the simplest *rheological equations of state*, or *constitutive equations* of material. These two concepts and their further developments are discussed in detail in the subsequent chapters of this book (liquids in Chapter 3 and solids in Chapter 4). Here, we would like to present the main features of these fundamental laws, which are:

- linearity of $\varepsilon(\sigma_E)$ dependence for solids and $\dot{\gamma}(\sigma)$ dependence for liquids
- absence of time effects in $\varepsilon(\sigma_E)$ dependence for solids; deformation strictly corresponds to stress and changes immediately following stress evolution
- absence of any fixed deformation of liquids because at any stress deformations develop unlimitedly and they increase linearly with time at constant stress
- existence of a single constant characterizing properties of material – viscosity, η , for liquids and elastic modulus, E , for solids.

Many independent experimental evidences are well-known that cannot be explained within the framework of the classic theories of fluid dynamics and elasticity, based on Eqs. 2.1.1 and 2.1.2, respectively, and these are discussed in the subsequent sections.

2.1.1 CREEP (RETARDED DEFORMATION)

Let a bar of a length, l , be stretched by the force, F , as shown in Fig. 1.1.1. What happens afterwards?

Time dependencies of deformation, $\varepsilon(t)$, for the two above-mentioned classical models are shown in Fig. 2.1.1a. Deformation of liquid (Eq. 2.1.1) increases linearly with time (line N) and deformation of solid (Eq. 2.1.2) instantly increases until it reaches a definite level and then stays constant (line H) as long as an observer wishes to follow it. If the force is taken away at the time t_0 , the deformation of liquid remains at the level reached

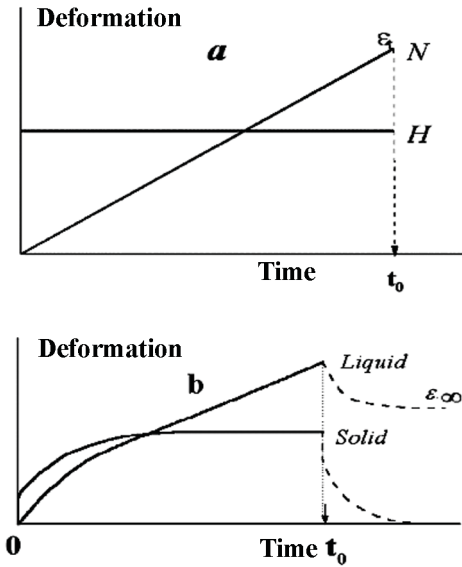


Figure 2.1.1. Development of deformation and retardation in materials of different types.

before t_0 , at the point ϵ_t , and the deformation of solid instantly disappears.

These relationships appear to be very simple, and, in fact, many real materials behave as predicted by these models. However, there are also many other materials which have different behavior. A typical illustration of such behavior is given in Fig. 2.1.1b for both liquid and solid. The main peculiarity of these curves is the delay of deformation with instantaneous application and release of forces. It is related to the initial time where a constant force acts (until the point t_0) and to *retardation*, which is the reverse of deformations (after the point t_0 at which force is removed). The difference between the pairs of curves N–Liquid and H–Solid is remarkable.

The difference between the two curves in Fig. 2.1.1a leaves no doubt about the difference in behavior of liquid and solid. This difference is not so evident in Fig.

2.1.1b because the initial parts of the curves are similar. In practice, this initial behavior continues for a long time. The difference also appears in the final parts of these curves. The comparison of the two curves in Fig 2.1.1b helps to point out differences between liquids and solids. In *liquids*: the final part of the $\epsilon(t)$ dependence is a line inclined to the coordinate axes and the liquid viscosity is responsible for its slope; after the force is removed, some residual deformation, ϵ_∞ , can always be found. In *solids*: the final part of the $\epsilon(t)$ dependence is a horizontal straight line, which is then stopped. After force is removed, deformation disappears completely and no residual deformation remains.

This difference between liquids and solids, which is very clear in the model picture, may be less definite in real practice because the processes of deformation and retardation might be very slow and an observer is never certain whether he waited long enough to reach at an unambiguous conclusion.

The phenomenon of slow development of deformations is called *creep*,³ and the effect of retardation is sometimes called *elastic recoil*.

2.1.2 RELAXATION

Let the bar drawn in Fig. 1.1.1 be stretched rapidly by a force, F , to some length and then be fixed at this new length. What is the force necessary to maintain deformation?

The answer for the two simplest models of liquid and solid is pertinent: if there is no continuation of deformation rate, the force cannot exist in liquid (Eq. 2.1.1), i.e., the force instantly drops to zero. If deformation of a solid is fixed ($\epsilon = \text{const}$), in accordance with Eq. 2.1.2 the force remains constant during any long time observation. Again, these conclusions can be very easily grasped and they are true for many real materials.

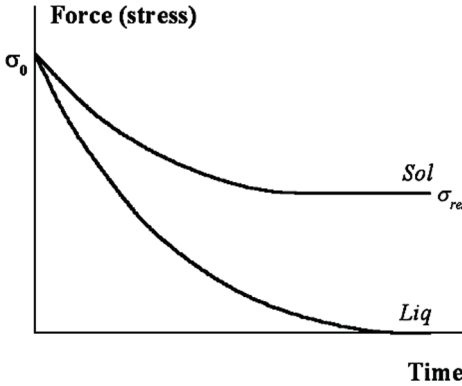


Figure 2.1.2. Stress relaxation in solids (marked as Sol) and liquids (marked as Liq).

However, many other materials have different behavior. It is possible to note a slow decay of forces (or stresses) resulting from *stress relaxation*.^{4,5} Two possible modes of relaxation are shown in Fig. 2.1.2. Stresses in liquids, after unloading, relax (sooner or later) from its initial value, σ_0 , until zero is reached because liquids cannot store stresses if they do not flow. Stresses in solids decrease after unloading from their initial value of σ_0 , but always some residual (equilibrium) stresses, σ_{res} , remain regardless of how long the relaxation continues.

This difference in behavior of materials is characteristic of definitions of liquids and solids. The model presents some uncertainties in practice because very slow relaxation may not be noticed by some impatient observers. The rate of the relaxation process is quantitatively characterized by the relaxation time.

Relaxation time - general concept in physics

The concept of relaxation has a general meaning for many physical phenomena. It is a reflection of an idea of restoration of equilibrium state from a non-equilibrium condition, regardless of the reasons which caused the departure from equilibrium. For example, this can be concentration fluctuation caused by purely statistical reasons as was considered by Maxwell. Let the equilibrium value of some physical parameter be X_0 , current value of this parameter be X , and let it be supposed that the rate of approach of equilibrium is proportional to the distance from the equilibrium. This assumption immediately leads to the following first-order kinetic equation:

$$\frac{dX}{dt} = -k(X - X_\infty) \quad [2.1.3]$$

where k is a kinetic rate constant with the dimension of reciprocal time.

The parameter X in the initial state equals to X_0 . Then, the solution of this equation is

$$\frac{X(t) - X_\infty}{X_0 - X_\infty} = e^{-kt} \quad [2.1.4]$$

Now, if $X_\infty = 0$, then the simplest form of this equation is

$$X(t) = X_0 e^{-kt} \quad [2.1.4a]$$

The last two equations describe the relaxation process, and the value of

$$\theta = k^{-1} \quad [2.1.5]$$

is called the *relaxation time*. Its value characterizes the rate of approach of the equilibrium (but not the complete time necessary to reach this equilibrium because it is infinitely large according to Eq. 2.1.4).

The exponential equation is the simplest way of quantitative description of the relaxation process, directly related to the basic concept of relaxation. In reality, the relaxation process is more complex. For example, if one places a small hot ball into a cold liquid bath, the temperature of a ball will approach the temperature of a liquid bath but the temperature evolution will be described by quite different (non-exponential) law. The general way of treating real relaxation processes using superposition of several individual exponential modes is discussed in section 2.2.

A large number of empirical equations were proposed to describe $\sigma(t)$ functions during relaxation. The Kohlrausch function⁶ is frequently used. It can be written as

$$\sigma(t) = \sigma_0 \exp[-(t/\theta_K)^n] \quad [2.1.6]$$

where σ_0 is the initial stress, θ_K is a characteristic time of the relaxation process which must not be confused with a relaxation time as defined by Eqs. 2.1.4 and 2.1.5, and n is an empirical constant. The equation of this structure is frequently used in different branches of physics for fitting experimental data.

2.1.3 FADING MEMORY

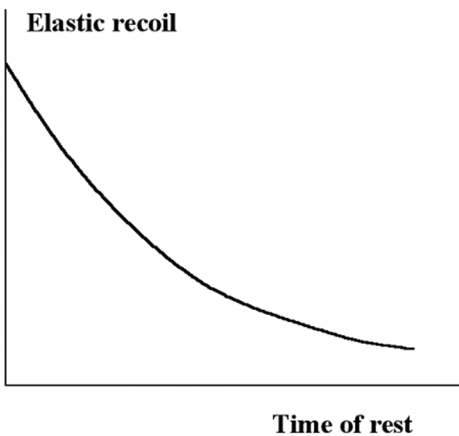


Figure 2.1.3. Fading memory – decrease of elastic recoil as a function of time delay.

Fading memory is a more general concept than creep or relaxation because it unites them both. This concept consists of the following: Let a bar be stretched, as in the case of creep and elastic recoil, but the sample is not released instantly but held for some time before the elastic recoil. In reality, the term “instantly” always is realized with some delay, depending on the skills of the experimentalist and the capabilities of the experimental technique.

What is the influence of this delay on the elastic recoil? In the case of liquid, according to Eq. 2.1.1, material instantly “forgets” its previous deformation, any current state is equilibrium, elastic recoil is absent, and, as a result, liquids are considered to have no memory.

In the case of elastic material, according to its model, Eq. 2.1.2, the time of rest has no influence on its behavior after releasing stresses. Such materials do not forget the pre-history of their deformations at all. So, their memory does not fade.

However, behavior of many real materials is intermediate. It is possible to observe a phenomenon of retarding elastic recoil by increasing the delay time (Fig. 2.1.3), i.e., it is reasonable to treat this effect in terms of the “fading memory” of the pre-history of their deformations. The reasons are quite evident: in the period preceding the elastic recoil, a relaxation partly takes place and stresses responsible for the post-effect decrease. For an observer, it appears as if the material was forgetting the pre-history of its deformations, or in other words, this is the phenomenon of fading memory.

The concept of viscoelasticity comes from the above-described experimental evidence.⁷ They demonstrate that in deformation of many real materials it is necessary to consider a combination of viscous and elastic behavior. This is very clear in a creep experiment: deformation consists of flow and an elastic (retarded) part. The same is observed from a relaxation curve because this curve reflects features of viscous liquids and elastic solids. The concept of fading memory also assumes that superposition of elastic behavior and viscous flow explains experimental facts.

2.2 RELAXATION AND CREEP – SPECTRAL REPRESENTATION. DYNAMIC FUNCTIONS

2.2.1 RETARDATION AND RELAXATION SPECTRA – DEFINITIONS

Experimental *linear* relaxation and creep functions are demonstrated here by their spectral representations. The description of viscoelastic behavior of material is the same for any geometrical mode of deformation, e.g., extension, shear, or volume changes. Therefore, no special definition concerning the geometry of deformations and type of stress are considered below.⁸ The creep and the relaxation phenomena are compared side-by-side in the table below.

Creep	Relaxation
<p>The typical creep functions are represented in Fig.2.1.1. The <i>linear</i> viscoelastic behavior in creep means that deformation, γ, at any time is proportional to the applied stress, σ_0. Based on the typical form of experimental data, the following equation for the creep curve can be written as:</p> $\gamma(t) = \sigma_0 \left[J_0 + \psi(t) + \frac{t}{\eta} \right] \quad [2.2.1]$ <p>where σ_0 is the constant stress producing creep.</p>	<p>The typical relaxation curves are represented in Fig. 2.1.2. The <i>linear</i> viscoelastic behavior in relaxation means that the stress, σ, at any time, is proportional to deformation created before relaxation. Then, based on the typical form of experimental data, the following equation for the relaxation curve can be written:</p> $\sigma(t) = \gamma_0 [G_\infty + \phi(t)] \quad [2.2.2]$ <p>where γ_0 is constant deformation, at which relaxation takes place.</p>
<p>The linearity of viscoelastic behavior is expressed by positioning the stress out of square brackets. So, the function, called <i>viscoelastic compliance</i></p> $J(t) = \frac{\gamma(t)}{\sigma_0} = J_0 + \psi(t) + \frac{t}{\eta} \quad [2.2.3]$ <p>is independent of stress and can be considered as a rheological property of matter.</p>	<p>The linearity of viscoelastic behavior is expressed by positioning the deformation out of square brackets. So, the function, called <i>viscoelastic or relaxation modulus</i></p> $G(t) = \frac{\sigma(t)}{\gamma_0} = G_\infty + \phi(t) \quad [2.2.4]$ <p>is independent of deformation and can be considered as a rheological property of matter.</p>
<p>J_0 is an <i>instantaneous compliance</i>, η is viscosity, and $\psi(t)$ is a <i>creep function</i>, which is a representation of viscoelastic behavior of sample in an experiment. These two constants, J_0 and η, and the creep function, $\psi(t)$, are characteristic parameters of material. The creep function, $\psi(t)$, is also called the <i>creep compliance</i>, J_c. It is a ratio of (creep) deformation to stress.</p>	<p>G_∞ is an <i>equilibrium modulus</i>, and $\phi(t)$ is a <i>relaxation function</i>, which is a representation of viscoelastic behavior of sample in an experiment. The constant G_∞ and the <i>relaxation function</i>, $\phi(t)$, are individual parameters of material. The relaxation function, $\phi(t)$ is also called the <i>relaxation modulus</i>, G_r. It is a ratio of (relaxing) stress to deformation.</p>
<p>The difference between solids and liquids is as follows. For a liquid $\eta < \infty$, i.e., material can flow. For solid: $\eta = \infty$, i.e., irreversible deformations are absent. This difference is clearly seen in Fig. 2.1.1. The creep function has a limit at $t \rightarrow \infty$; $\psi(\infty) < \infty$. The equilibrium elastic deformations are expressed via the <i>equilibrium shear compliance</i>, J_e</p> $J_e = J_0 + \psi(\infty) \quad [2.2.5]$	<p>The difference between solids and liquids is as follows. For liquid $G_\infty = 0$ and $\phi(\infty) = 0$ because, by definition, it is assumed that $\phi(\infty) = 0$. For solids $G_\infty > 0$. This difference is clearly seen in Fig. 2.1.1. The initial value of relaxation modulus (at $t = 0$) is called an <i>instantaneous modulus</i>, G_0, and its value is found as</p> $G_0 = G_\infty + \phi(0) \quad [2.2.6]$

Creep	Relaxation
<p>The creep function, by its physical meaning, is an increasing function of time having a definite limit. The functions of such type can <i>always</i> be represented by the following integral</p> $\psi(t) = \int_0^{\infty} J(\lambda)[1 - e^{-t/\lambda}]d\lambda \quad [2.2.7]$ <p>where λ is called a retardation time, and $J(\lambda)$ is a function of distribution of retardation times, or a <i>retardation time spectrum</i>.</p>	<p>The relaxation function, by its physical meaning, is a decreasing function of time having zero limit at $t \rightarrow \infty$. The functions of such type can be <i>always</i> presented by the following integral</p> $\varphi(t) = \int_0^{\infty} G(\theta)e^{-t/\theta}d\theta \quad [2.2.8]$ <p>where θ is called a relaxation time, and $G(\theta)$ is a function of distribution of relaxation times, or <i>relaxation time spectrum</i> as measured in shear.</p>
<p>Retardation for many materials takes place in a wide time scale, and therefore it is important to know the retardation spectrum in a wide time scale. The <i>logarithmic retardation spectrum</i>, $k(\ln\lambda)$, is commonly used and Eq. 2.2.7 is written as</p> $\psi(t) = \int_0^{\infty} k(\ln\lambda)[1 - e^{-t/\lambda}]d\ln\lambda \quad [2.2.7a]$ <p>and evidently</p> $J(\lambda) = \frac{k(\ln\lambda)}{\lambda}$	<p>Relaxation for many materials takes place in a wide time scale, and therefore it is important to know the relaxation spectrum in a wide time scale. The <i>logarithmic relaxation spectrum</i>, $h(\ln\theta)$, is commonly used and Eq. 2.2.8 is written as</p> $\varphi(t) = \int_0^{\infty} h(\ln\theta)e^{-t/\theta}d\ln\theta \quad [2.2.8a]$ <p>and evidently</p> $G(\theta) = \frac{h(\ln\theta)}{\theta}$
<p>The integral expression can be approximated by the sum of the limited number of members:</p> $\psi(t) = \sum_{i=1}^N J_i(\lambda_i)[1 - e^{-t/\lambda_i}] \quad [2.2.9]$ <p>In this formula, λ_i is a set of <i>retardation times</i> and J_i are “weights” or <i>partial compliances</i>.</p>	<p>The integral expression can be approximated by the sum of the limited number of members:</p> $\varphi(t) = \sum_{i=1}^M G_i(\theta_i)e^{-t/\theta_i} \quad [2.2.10]$ <p>In this formula, θ_i is a set of <i>relaxation times</i> and G_i are “weights” or <i>partial moduli</i>.</p>
<p>If</p> $J(\lambda) = \sum_{i=1}^N J_i\delta(\lambda - \lambda_i)$ <p>Then</p> $\int_0^{\infty} J(\lambda)[1 - e^{-t/\lambda}]d\lambda = \sum_{i=1}^N J_i[1 - e^{-t/\lambda_i}]$ <p>and the validity of Eq. 2.2.9 is evident.</p>	<p>If</p> $G(\theta) = \sum_{i=1}^M G_i\delta(\theta - \theta_i)$ <p>Then</p> $\int_0^{\infty} G(\theta)e^{-t/\theta}d\theta = \sum_{i=1}^M G_ie^{-t/\theta_i}$ <p>and the validity of Eq. 2. 2.10 is evident.</p>

Creep	Relaxation
<p>The discrete approximation helps us to understand the meaning of spectral representation of the creep function. This function is a sum (or linear superposition) of several retardation modes, each of which is characterized by its own retardation time. The distribution of the retardation times can be continuous, as written in Eq. 2.2.7 or discrete, as in Eq. 2.2.9. In both cases, the limits of distribution are not known beforehand and need to be determined from an experiment or a theoretical model.</p> <p>The simplest case of creep function is described by the single retardation time:</p> $\psi(t) = J(1 - e^{-t/\lambda}) \quad [2.2.11]$ <p>This equation for the creep function is known as the Kelvin-Voigt model.¹⁰</p> <p>The methods for finding a retardation spectrum will be discussed below, in section 2.5.3.</p>	<p>The discrete approximation helps us to understand the meaning of the spectral representation of the relaxation function. This function is a sum (or linear superposition) of several relaxation modes, each of which is characterized by its own relaxation time. The distribution of the relaxation times can be continuous, as written in Eq. 2.2.8 or discrete, as in Eq. 2.2.10. In both cases the limits of distribution are not known beforehand and need to be determined from an experiment or a theoretical model.</p> <p>The simplest case of the relaxation function is described by the single relaxation time:</p> $\phi(t) = Ge^{-t/\theta} \quad [2.2.12]$ <p>This is the Maxwell model of relaxation.</p> <p>The methods for finding a relaxation spectrum will be discussed below, in section 2.5.3.</p>

The transition from continuous spectrum to the set of discrete values, i.e., the transition for Eq. 2.2.7 to Eq. 2.2.9 or from Eq. 2.2.8 to Eq. 2.2.10, is based on the Dirac⁹ concept or the delta function.

Comments – delta-function

The delta-function, $\delta(x)$, belongs to the class of special singular functions. This is a “line” with zero width and infinite length, defined by the following equality:

$$\int_{-\infty}^{\infty} \delta(x) dx = 1$$

The main feature of this function used in many applications is its definition *via* the following functional:

$$\int_{-\infty}^{\infty} \delta(x - x_0) f(x) dx = f(x_0)$$

here $f(x)$ is any “regular” function. It means that $\delta(x - x_0)$ is defined through the above written functional which puts into conformity $\delta(x - x_0)$ to some number $f(x_0)$.

It is easily seen that presenting $J(\lambda)$ or $G(\theta)$ as a sum of delta functions defined at a set of points λ_i or θ_i , respectively, one converts the integrals as in Eqs. 2.2.7 and 2.2.8, to sums as in Eqs. 2.2.9 and 2.2.10, respectively.

It is not necessary for creep and relaxation functions, or, consequently, relaxation and retardation spectra to be the same or to be mirror reflections of each other. In fact they are not, though there is a mathematical relation between them, which will be discussed in section 2.4.

2.2.2 DYNAMIC FUNCTIONS

In order to find rheological characteristics of material it is preferable to carry out an experiment using the simplest and the easiest to interpret conditions. In section 2.2.1, the regimes of constant stress or deformation were discussed.

It is possible to propose another simple experimental scheme such as *periodic oscillation*.¹² The form of an oscillation can be arbitrary, but it is preferable to use harmonic oscillation as the basic stress (or deformation) mode. The mathematical analysis of harmonic functions is very well developed. Also, any periodic function can be represented by a sum of harmonic functions (by the Fourier integrals).

Harmonic oscillation may continue for the duration of the experiment design. The changes taking place in material are measured as a function of time. It is also important for modern experimental techniques to use harmonic oscillation in a very wide frequency domain, exceeding many (at least 6-8) decimal orders.

The discussion in this section will be limited to small deformations within the range of linear mechanical behavior of material. Such a regime of deformation is known as the dynamic mechanical studies of materials.

Similar to static experiments (e.g., measurement of creep and relaxation), dynamic experiments can be conducted in stress- or deformation-controlled modes of deformation. The interpretation of both experimental modes is similar and it will be compared in the table below.

In operation with harmonic functions, it is convenient to use mathematics of complex numbers, because it simplifies calculations.

Comments – the Euler equality

The central operation in this calculation uses the Euler theorem:

$$e^{i\omega t} = \cos(\omega t) + i \sin(\omega t)$$

where $\omega = 2\pi f$ is frequency of oscillation in rad/s, f is frequency expressed in Hz (s^{-1}), and t is time. Writing periodic function as an exponent indicates that the real or imaginary part of sum is involved in an experiment.

Stress-controlled experiment	Deformation-controlled experiment
Let stress change according to the harmonic law as $\sigma(t) = \sigma_0 e^{i\omega t} \quad [2.2.13]$ where σ_0 is the amplitude of harmonic oscillation of stresses and ω is frequency. It leads to deformation, which (in a general case) changes as $\varepsilon(t) = J_0 \sigma(t) + \gamma_0 e^{i(\omega t - \delta)} - i \frac{1}{\omega \eta} \sigma(t) \quad [2.2.15]$	Let deformation change according to the harmonic law as $\gamma(t) = \gamma_0 e^{i\omega t} \quad [2.2.14]$ where γ_0 is the amplitude of harmonic oscillation of deformations and ω is frequency. It leads to stresses which (in a general case) change as $\sigma(t) = G_0 \varepsilon(t) + \sigma_0 e^{i(\omega t + \delta)} \quad [2.2.16]$

Stress-controlled experiment	Deformation-controlled experiment
<p>This equation is equivalent of Eq. 2.2.1 with the same meaning of members. The new factor here is angle, δ, which reflects the possible delay of deformation changes which follows the oscillation of stresses. The value σ_0 is the amplitude of periodically changing deformations.</p> <p>Dividing $\gamma(t)$ by $\sigma(t)$ the equation is obtained which is equivalent to Eq. 2.2.3</p> $J^* = \frac{\gamma(t)}{\sigma(t)} = \left(J_0 + \frac{\gamma_0}{\sigma_0} \cos \delta \right) - i \left(\frac{1}{\omega \eta} + \frac{\gamma_0}{\sigma_0} \sin \delta \right) \quad [2.2.17]$	<p>This equation is equivalent of Eq. 2.2.2 with the same meaning of members. The new factor here is angle, δ, which reflects the possible delay of stress changes which follows the oscillation of deformations. The value σ_0 is the amplitude of periodically changing stresses.</p> <p>Dividing $\sigma(t)$ by $\gamma(t)$ the equation is obtained which is equivalent to Eq. 2.2.4</p> $G^* = \frac{\sigma(t)}{\gamma(t)} = \left(G_0 + \frac{\sigma_0}{\gamma_0} \cos \delta \right) + i \left(\frac{\sigma_0}{\gamma_0} \sin \delta \right) \quad [2.2.18]$
<p>The value J^* is called <i>complex shear compliance</i> and J^* can be written as a sum:</p> $J^* = (J_0 + J') - i \left(\frac{1}{\omega \eta} + J'' \right) \quad [2.2.19]$	<p>The value G^* is called <i>complex shear modulus</i> and G^* can be written as a sum:</p> $G^* = (G_0 + G') + i G'' \quad [2.2.20]$
<p>The components of the complex compliance, J' and J'', are called real and imaginary parts of the complex compliance, respectively, and are expressed as:</p> $J' = \frac{\gamma_0}{\sigma_0} \cos \delta \text{ and } J'' = \frac{\gamma_0}{\sigma_0} \sin \delta \quad [2.2.21]$	<p>The components of the complex modulus, G' and G'', are called real and imaginary parts of the complex modulus, respectively, and are expressed as:</p> $G' = \frac{\sigma_0}{\gamma_0} \cos \delta \text{ and } G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \quad [2.2.22]$
<p>The J' and J'' components of complex compliance represent deformations changing in-phase and out-phase along with stress.</p> <p>The angle δ is calculated as</p> $\tan \delta = \frac{J''}{J'} \quad [2.2.23]$	<p>The G' and G'' components of complex modulus represent stresses changing in-phase and out-phase along with deformation.</p> <p>The angle δ is calculated as</p> $\tan \delta = \frac{G''}{G'} \quad [2.2.24]$

In some applications, changes in the deformation rate are followed instead of deformation at a stress-controlled regime of deformations.

Formal rearrangements give the following result:

$$\eta^* = \frac{\sigma(t)}{\gamma(t)} = (\eta + \eta') - \eta'' \quad [2.2.25]$$

where η^* is called *complex dynamic viscosity* and its components η' and η'' are real and imaginary parts of complex dynamic viscosity, respectively. These factors are expressed as

$$\eta' = \frac{\sigma_0}{\gamma_0 \omega} \sin \delta \text{ and } \eta'' = \frac{\sigma_0}{\gamma_0 \omega} \cos \delta \quad [2.2.26]$$

The following relationships follow:

$$\eta' = \frac{G''}{\omega} \text{ and } \eta'' = \frac{G'}{\omega} \quad [2.2.27]$$

The last central equation of the theory of periodic oscillation in studies of material properties is the consequence of expressions for J^* and G^* . If constants are neglected, the following simple relationship is valid:

$$J^*G^* = 1 \quad [2.2.28]$$

Two parameters (in addition to constants) are measured in a dynamic regime of deformation at any frequency. They are components of the dynamic modulus, or components of dynamic compliance, or any of the components and the angle δ .

Dynamic measurements are carried out in the *linear* range of mechanical properties of material *when* and *if* the ratio of amplitudes of stress and deformations does not depend on amplitudes and therefore these two functions (J' , J'' or G' , G'') do not depend on σ_0 and consequently on γ_0 . This happens when deformations are small. However, the last term (linear) must be understood not in the geometrical meaning only. The amplitude of deformations may be small ($\gamma_0 \ll 1$) but sufficient to influence the structure of material. It may result in the observed changes of J^* or G^* . The latter is true, for example, in disperse systems. The deformation may exceed the characteristic size of dispersed particles or structure elements in material (which might be very small), and in this case deformations are not small in relation to the physical (structural) size, though the geometrical condition $\gamma_0 \ll 1$ is strictly fulfilled.

Frequency dependence of the dynamic modulus, $G'(\omega)$, may span over a very wide frequency range, covering many decimal orders of magnitude. Values of G' also vary in a wide range. For many polymeric substances, there is a frequency range where $G' = \text{const.}$ This is known as *plateau modulus* (in extension, E_N^0 , and in shear deformations, G_N^0), which plays an important role in mechanical characterization of materials.

The above-formulated theory of dynamic measurements can be interpreted in a graphical form as in Fig. 2.2.1. Let stresses and deformations be presented by the vectors with the lengths γ_0 and σ_0 , respectively. The vector $\dot{\gamma}$ representing the rate of deformation is also shown in the Figure 2.2.1. The vectors rotate counter-clockwise with angular velocity of ω . The angles between γ_0 and σ_0 and the axis of real numbers at any moment, t , equal to ωt and $\omega t - \delta$, respectively.

Linearity of viscoelastic properties of materials means that stretching any vector results in stretching all other vectors by the same ratio. The angle between both vectors, σ_0 and γ_0 , remains unchanged.

The projection of the stress vector on the γ_0 -vector is $\sigma_0 \cos \delta$ and the projection in the perpendicular direction is $\sigma_0 \sin \delta$. G' and G'' are the ratios of these projections on γ_0 , i.e., these ratios are the in- and out-of-phase components of G^* . The same is true for η^* with changes of terms.

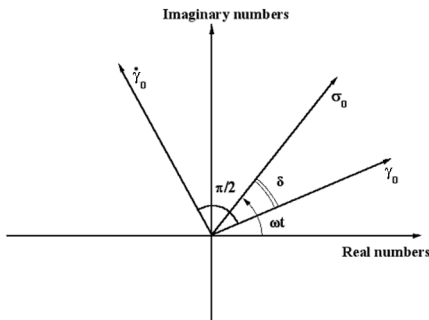


Figure 2.2.1. Graphic interpretation of oscillations in dynamic measurements of properties of viscoelastic materials.

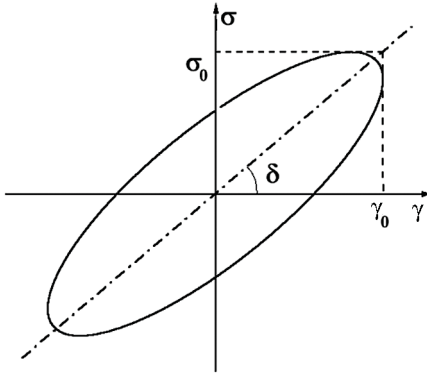


Figure 2.2.2. Graphical representation of the stress-deformation relationship in dynamic measurements of viscoelastic properties.

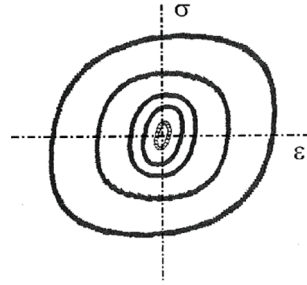


Figure 2.2.3. Several examples of Lissajou figures at different amplitudes of deformations obtained in study of concentrated emulsions. (deformation is designated, ϵ , as in the original publication). [Adapted, by permission, from T.G. Mason, P.K. Rai, *J. Rheol.*, **47**, 513 (2003)].

Another useful graphical interpretation of dynamic experiment in measurement of viscoelastic properties is based on combination of equations for stresses and deformations by excluding time as a parameter. Then, the following relationship between stress and deformation is obtained:

$$\left(\frac{\sigma}{\sigma_0}\right)^2 + \left(\frac{\gamma}{\gamma_0}\right)^2 = (\sin \delta)^2 + 2\left(\frac{\sigma}{\sigma_0}\right)\left(\frac{\gamma}{\gamma_0}\right) \cos \delta \quad [2.2.29]$$

This equation is that of an ellipse with the principal axis inclined to the abscissa by angle, δ , as represented in Fig. 2.2.2.

The exclusion of argument, t , in both dependencies, $\sigma(t)$ and $\gamma(t)$, permits building the closed curves called the *Lissajou figures* (Fig.2.2.3). These curves are not necessarily ellipses, and their shapes differ depending on deformation. Non-elliptic shape of the Lissajou figures is a reflection of non-linear behavior of material in oscillation (see section 2.8).

The area, A , of an ellipse equals:

$$A = \pi \sigma_0 \gamma_0 \sin \delta \quad [2.2.30]$$

Two limiting cases are of special interest.

1. $\delta = \pi/2$. In this case, the ellipse transforms into a circle with coordinates (σ/σ_0) and (γ/γ_0) and its area is $A = \pi \sigma_0 \gamma_0$. This case corresponds to $G' = 0$ and it means that material is a purely viscous liquid without elasticity.
2. $\delta = 0$. In this case, the ellipse degenerates into a straight line. This means that $G'' = 0$ and material becomes a purely elastic body. The area of ellipse equals zero, $A = 0$.

The representation of experimental results of stress-deformation relationships by means of an elliptic figure permits use of a simple method for calculation of angle, δ . The area of a rectangle circumscribed around an ellipse equals

$$S = 4\sigma_0 \gamma_0$$

Then, $\sin \delta$ is expressed by the ratio of the ellipse surface area to the surface area of a circumscribed rectangle as

$$\sin \delta = \left(\frac{4}{\pi} \right) \left(\frac{A}{S} \right) \quad [2.2.31]$$

This approach is used in some standards and experimental devices because the value of angle δ has important applications by itself (for example, in estimating the damping characteristics of rubbers, rubber compounds and porous materials). The angle δ can be found from a hysteresis loop (i.e., a surface area of an ellipse, as in Fig. 2.2.2) with no need to calibrate stress and deformation scales and to find σ_0 and ϵ_0 .

The graphic representation of oscillating deformation gives a physical interpretation of parameters introduced for quantitative description of results of dynamic experiment.

The work of entire oscillation cycle (gained and lost) is calculated as

$$W = \int_0^T \sigma(t) d\gamma \quad [2.2.32]$$

where $T = 2\pi/\omega$ is the duration of a single cycle of oscillations.

Direct calculation shows that this work is as follows

$$W = \pi \sigma_0 \gamma_0 \sin \delta \quad [2.2.33]$$

Eqs. 2.2.30 and 2.2.33 are identical, which means that the surface area of an ellipse is directly interpreted as the work dissipated during the cycle of oscillation. The angle δ is a relative measure of work losses. For this reason, it is called the *loss angle*. For an elastic body $\delta = 0$ (an ellipse degenerates into a straight line) and losses are absent. For a viscous liquid $\delta = \pi/2$, and consequently the losses are at maximum. By decreasing δ , and consequently decreasing viscous losses, material transits from pure viscous to pure elastic.

The introduction of values J'' and G'' into Eq. 2.2.33 leads to the following relationship:

$$W = \pi \sigma_0^2 J'' = \pi \gamma_0^2 G'' \quad [2.2.34]$$

Values of J'' and G'' are also measures of losses (heat dissipation in periodic oscillation) and therefore they are called *loss compliance* and *loss modulus*, respectively.

It is possible to show that real components of dynamic compliance and modulus, J' and G' , are measures of elasticity because energy stored (and then returned) during the cycle of oscillation is proportional to these values. Therefore J' and G' are called *storage compliance* and *storage modulus*, respectively.

In real practice, viscoelastic materials can be used in many forms and applications. Engineering products (e.g., springs) must be highly elastic (losses must be low) and they should be made out of materials having low loss angle values. This is also true of church bells. A bell continues to sound as long as the mechanical losses of material, from which it is made, are low. Shock absorbers, sound insulators, and materials for many other similar applications must possess a high dissipative function (energy), meaning that the loss angle of such materials must be as close to $\pi/2$ as possible.

The above formulated parameters are used to describe viscoelastic effects and characterize properties of real materials. However, they are not constants but functions. Just as creep and relaxation functions depend on time, the dynamic properties depend on frequency of oscillation. In representing viscoelastic properties of material, it is necessary to consider the functions $J'(\omega)$ and $J''(\omega)$, or $G'(\omega)$ and $G''(\omega)$ as permitted by equation 2.2.28. Other parameters can also be included (loss angle or dynamic viscosity). The principal conclusion is as follows: the viscoelastic properties of material, measured in a dynamic experiment, are represented by two frequency dependent functions.

2.3 MODEL INTERPRETATIONS

2.3.1 BASIC MECHANICAL MODELS

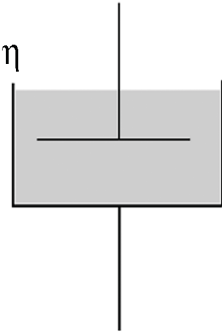


Figure 2.3.1. A dashpot as a mechanical model of a viscous (Newtonian) liquid.

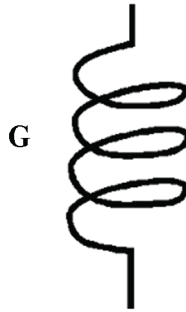


Figure 2.3.2. A spring as a mechanical model of an elastic (Hookean) solid.

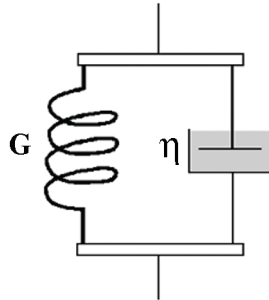


Figure 2.3.3. A spring and dashpot elements joined in parallel – a model of the Kelvin-Voigt viscoelastic liquid.



Figure 2.3.4. A spring and a dashpot element joined in series – a model of the Maxwellian viscoelastic liquid.

It is instructive and useful for better understanding the ideas of theory of viscoelasticity to illustrate some typical behaviors of viscoelastic materials by simple mechanical models.

The simplest model of viscous behavior of material is a dashpot, a piston moving inside (Fig. 2.3.1) a cylinder filled with liquid. It is supposed that the speed of movement, $V = dX/dt$, of the piston is proportional to the applied force, F :

$$F = \eta V \quad [2.3.1]$$

where X is displacement, t is time, and η is the coefficient of proportionality.

This equation is formally analogous to the basic equation for Newtonian liquid and one assumes that the speed is an analogue of the rate of deformation, the force F is an analogue of a stress, σ , and the coefficient η is an analogue of viscosity.

The simplest mechanical model of an elastic body is a spring (Fig. 2.3.2). The displacement X is proportional to the applied force, F :

$$X = \frac{F}{G} \quad [2.3.2]$$

In order to compare this equation with the standard formulation of Hooke's law, X can be treated as a relative deformation, F as an analogue of stress, and G as an analogue of the elastic modulus.

Both equations are quite trivial and do not add anything new to the initial concepts of viscous (Newtonian) liquid and elastic (Hookean) material. However, it is instructive to analyze the following mechanical models: let a spring and a dashpot elements be connected in parallel (Fig. 2.3.3) or in series (Fig. 2.3.4). These two mechanical models are compared below.

<p>Let the constant force, $F = F_0 = \text{const}$, be suddenly applied to the end of the jointed two-component model shown on Fig. 2.3.3 and continue to be applied for an unlimited time. It is easy to anticipate that both components will resist the movement, with a spring stretching and the piston slowly pulling out of a cylinder. This process continues until the spring is stretched to the length corresponding to the applied force. The movement of the piston stops at this state because the force is balanced by a spring and the force is absent at the piston. The mathematical representation of the above-mentioned statement is as follows.</p>	<p>Let the constant displacement, $X = X_0 = \text{const}$, be suddenly created at the end of the jointed two-component model shown on Fig. 2.3.4 and then fixed for an unlimited time. It is easy to anticipate that this displacement immediately stretches the spring. Then, the extended spring will pull a piston out of a cylinder and this process will continue for some time because the movement in a viscous liquid is not very fast. This process continues until the spring comes to the equilibrium state (its initial length is restored). The mathematical representation of the above-mentioned statement is as follows.</p>
<p>Total force, F, of the two-component model F is the sum of forces acting on both elements of a model:</p> $F_{\text{sp}} + F_{\text{pist}} = F$ <p>where F_{sp} is the force acting on the spring branch and F_{pist} is the force acting on the piston.</p>	<p>Total displacement, X, of the two-component model is the sum of displacements of both components</p> $X_{\text{sp}} + X_{\text{pist}} = X$ <p>where X_{sp} is the displacement of the spring and X_{pist} is the displacement of the piston. The same equality is true for the derivatives of the components and their sum</p> $\dot{X}_{\text{sp}} + \dot{X}_{\text{pist}} = \dot{X}$
<p>Now, using Eqs. 2.3.1 and 2.3.2, the last sum can be rearranged as</p> $\eta \dot{X} + GX = F_0 \quad [2.3.3]$	<p>Now, using Eqs. 2.3.1 and 2.3.2, the last sum can be rearranged as</p> $\frac{\dot{F}}{G} + \frac{F}{\eta} = 0 \quad [2.3.4]$
<p>The solution of this equation gives the time dependence of the displacement X Eq. [2.3.5] below:</p> $X(t) = X_{\infty} \left(1 - e^{-\frac{t}{\eta/G}} \right) = EF_0 \left(1 - e^{-\frac{t}{\eta/G}} \right)$	<p>The solution of this equation gives the time dependence of the force F:</p> $F(t) = F_0 e^{-\frac{t}{\eta/G}} = X_0 E e^{-\frac{t}{\eta/G}} \quad [2.3.6]$

<p>The last expression is the analogue of Eq. 2.2.11. The ratio (k/G) has the meaning of a <i>retardation time</i>. The combination of components as shown in Fig. 2.3.3 behaves like Kelvin-Voigt viscoelastic material and this is why it is called the Kelvin-Voigt model. The Kelvin-Voigt material is a solid because the application of a constant force leads to a limited displacement as for any solid body (though with delayed elasticity). The relaxation time of the Kelvin-Voigt model is absent (or to be more exact is equal to infinity). The Kelvin-Voigt model stretched by a constant force supports this force unlimitedly long due to stretching a spring which does not relax.</p>	<p>The last expression is the analogue of Eq. 2.2.12, where the ratio (k/G) has the meaning of a <i>relaxation time</i>. The combination of components as shown in Fig. 2.3.4 behaves like the Maxwell viscoelastic material and this is why it is called the Maxwell model. It is easy to see that Maxwellian material is liquid because application of a constant force leads to unlimited movement of the piston, i.e., this is a model of flow. The retardation time of the Maxwell model equals zero. The Maxwell model immediately follows the applied force due to the reaction of a spring acting without any delay.</p>
<p>Let us now join N the Kelvin-Voigt models in series to each other as shown in Fig. 2.3.5. Formal calculations show that this model's behavior can be described by Eq. 2.2.9 with N retardation times.</p>	<p>Let us now join M the Maxwell models in parallel to each other as shown in Fig. 2.3.6. Formal calculations show that this model's behavior can be described by Eq. 2.2.10 with M relaxation times.</p>

Use of the mechanical analogue models illustrates the behavior of material in different modes of deformations. As an example, dynamic functions of both models are calculated by changing the model parameters, such as the rheological characteristics, viscosity, η , and modulus, E , of components of the Kelvin-Voigt and Maxwell models.

<p>The parameters of the model and the components of the dynamic functions of the Kelvin-Voigt model are expressed as: retardation time $\lambda = \eta/G$ relaxation time $\theta = \infty$</p>	<p>The parameters of the model and the components of the dynamic functions of the Maxwell model are expressed as: relaxation time $\theta = \eta/G$; retardation time $\lambda = 0$</p>
<p>Then</p> $G'(\omega) = G \text{ \& } G''(\omega) = \omega\eta$ $J'(\omega) = \frac{1}{G} \frac{1}{1 + (\lambda\omega)^2} \text{ \& } J''(\omega) = \frac{1}{G} \frac{\omega\lambda}{1 + (\lambda\omega)^2}$ $\tan \delta = \omega\lambda \quad [2.3.7]$	<p>Then</p> $G'(\omega) = \frac{G(\omega\theta)^2}{1 + (\omega\theta)^2} \text{ \& }$ $G''(\omega) = \frac{G(\omega\theta)}{1 + (\omega\theta)^2}$ $J'(\omega) = G^{-1} \text{ \& } J''(\omega) = (\omega\theta)^{-1}$ $\tan \delta = (\omega\theta)^{-1} \quad [2.3.8]$

The comparison of the above presented results in both columns shows that the Kelvin-Voigt and the Maxwell models predict different behavior of material, in respect of retardation and relaxation times, frequency dependencies of loss tangent, etc. The Maxwell material is liquid and the Kelvin-Voigt material is solid. Using mechanical analogue models it is easy to transit from describing solid-like to liquids-like behavior and *vice versa*.

Let us assume that in a multi-component The Kelvin-Voigt model one partial modulus equals zero. Then, this component degenerates into a single viscous element, and finally it means that such multi-component system models do not have solid but liquid-like behavior, because unlimited deformations become possible.	Let us assume that in a multi-component The Maxwell model one partial viscosity is infinite. Then, this component degenerates into a single elastic element, and finally it means that such a multi-component system model is not a liquid but it has solid-like behavior, because the spring stores non-relaxing stress.
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For combinations of either the Kelvin-Voigt (Fig. 2.3.5) or the Maxwell (Fig. 2.3.6) models, the expressions for the components of the dynamic functions include sums of the same structure as the equations for the single elements.

Frequency dependencies of the components of the dynamic functions for multi-element models are

$J'(\omega) = \sum_{i=1}^N \frac{1}{G_i} \frac{1}{1 + (\omega\lambda_i)^2}$ $J''(\omega) = \sum_{i=1}^N \frac{1}{G_i} \frac{(\omega\lambda_i)}{1 + (\omega\lambda_i)^2} \quad [2.3.9]$ <p>where N is the number of elements in the model in Fig. 2.3.5 (retardation times).</p>	$G'(\omega) = \sum_{i=1}^M G_i \frac{(\omega\theta_i)^2}{1 + (\omega\theta_i)^2}$ $G''(\omega) = \sum_{i=1}^M G_i \frac{(\omega\theta_i)}{1 + (\omega\theta_i)^2} \quad [2.3.10]$ <p>where M is the number of elements in the model in Fig. 2.3.6 (relaxation times).</p>
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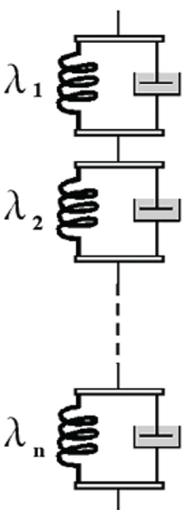


Figure 2.3.5. A combination of the Kelvin-Voigt models joined in series – a model of viscoelastic solid with a set of retardation times, λ_i .

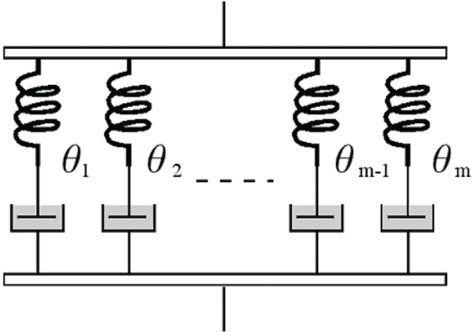


Figure 2.3.6. A combination of the Maxwell models joined in parallel – a model of viscoelastic liquid with a set of relaxation times θ_i .

Use of the model representation opens a good potential for analysis of material behavior in various deformation-stress modes.

2.3.2 COMPLICATED MECHANICAL MODELS - DIFFERENTIAL RHEOLOGICAL EQUATIONS

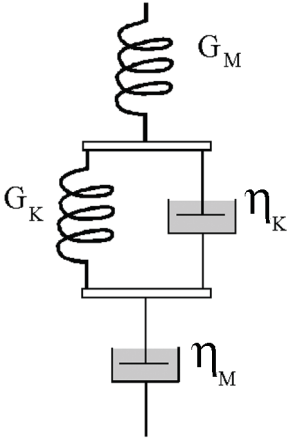


Figure 2.3.7. The Burgers model – predicting superimposed relaxation and retardation.

The Maxwell and the Kelvin-Voigt models can be joined in parallel, in series, or combinations thereof. In many applications, these models are also joined in their combinations. The combination of the Maxwell model and the Kelvin-Voigt model joined in series (known as the Burgers model¹³) is shown in Fig. 2.3.7. This combination represents a popular quantitative model of behavior of polymeric materials.

The central peculiarity of this model is the possible combination of relaxation and retardation phenomena in one material. Let us suppose that at low temperatures the “Maxwell viscosity”, η_M , is very high – a material is “frozen” – and it is possible to neglect deformations of this element. Then, the model under discussion presents a solid-like behavior due to the spring G_M . With temperatures increasing, viscosity, η_M , decreases and relaxation becomes possible. Then it is a typical relaxation-retardation behavior of a viscoelastic material. At even higher temperatures, viscosity of both components, η_M and η_K , becomes very low and the model represents the behavior of primarily viscous liquid, such as polymer melt (with a slight retardation).

The mathematical description of behavior of a model represented in Fig. 2.3.7 is based on summation of deformations of three components of the model

$$\gamma_{M, sp} + \gamma_K + \gamma_{M, pist} = \gamma$$

where γ is the total deformation, which is the sum of deformation of a Maxwellian spring, $\gamma_{M, sp}$, Maxwellian viscous element, $\gamma_{M, pist}$, and deformation of a Kelvin-Voigt element, γ_K . The direct substitutions lead to two equations:

$$\begin{cases} \frac{\dot{\sigma}}{G_M} + \frac{\sigma}{\eta_M} + \dot{\gamma}_K = \dot{\gamma} \\ \sigma = G_K \gamma_K + \eta_K \dot{\gamma}_K \end{cases}$$

Then, after excluding $\dot{\gamma}_K$ from both equations, the final rheological equation for $\gamma(\sigma)$ dependence is obtained. The structure of this dependence is of special interest. This is an equation including higher derivatives of variables:

$$k_2 \frac{d^2 \sigma}{dt^2} + k_1 \frac{d\sigma}{dt} + k_0 \sigma = l_1 \frac{d\gamma}{dt} + l_0 \gamma \quad [2.3.11]$$

where the coefficients of members of sums, k_i and l_i , are constructed from *four* rheological constants of the Burgers model.

The relaxation behavior of the Burgers model can be determined. $\sigma(t)$ is found as the solution of the *second-order differential equation*, as follows:

$$\sigma(t) = C_1 e^{-t/\theta_1} + C_2 e^{-t/\theta_2}$$

where C_1 and C_2 are constant expressed *via* k_i (or four rheological parameters of the Burgers model) and θ_1 and θ_2 are *two* independent relaxation times also expressed *via* four parameters of the Burgers model. This means that the Burgers model is equivalent to two Maxwell models joined in series. However, it is evident that the Burgers model predicts a single retardation time only.

The construction of rheological models by joining the simplest the Kelvin-Voigt and the Maxwell models in various (sometimes rather whimsical) combinations leads, in a general case, to the following *operator equation*:

$$\sum_{n=0}^N k_n \frac{d^n}{dt^n} \sigma = \sum_{m=0}^M l_m \frac{d^m}{dt^m} \gamma \quad [2.3.12]$$

where k_n and l_m are individual rheological parameters of material. Relaxation and retardation times are expressed *via* these parameters.

If material is liquid $N > M$. If it is solid $N = M$. The differential rheological model predicts the existence of a set of discrete relaxation times. Consequently, it is possible to prove that, for a model of liquid, the number of relaxation times, m , equals the number of retardation times, n , plus 1.

Differential equations are considered to be old-fashioned and they are used infrequently for presenting rheological properties of material. More popular are the integral equations derived from the superposition principle (see section 2.4).

2.3.3 NON-MECHANICAL MODELS

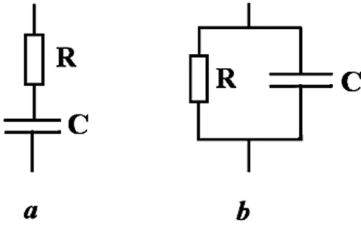


Figure 2.3.8. Combination of resistor and capacitor joined in series as an analogue of the Kelvin-Voigt solid (a) and in parallel as an analogue of the Maxwell liquid (b).

Any combination of physical elements leading to the same mathematical predictions, primarily exponential decay and growth of some variables, can be treated as an analogue model of viscoelastic rheological behavior of material.

Among them, the most interesting and useful are electrical analogue systems,¹⁴ because electrical analogue models can be easily built in a laboratory and their behavior can be followed in detail using simple experimental techniques.

In order to illustrate the electrical analogue, let us consider a circuit consisting of two elements: a resistor with resistance, R , and a capacitor with capacitance, C . Electrical charge, Q , is an analogue of mechanical deformation, current, $J = dQ/dt$, is an analogue of deformation rate and voltage, U , is an analogue of mechanical stress. Both elements can be joined in series and parallel as shown in Fig. 2.3.8.

The starting relationships for the simplest elements are:

$$\text{for a resistor:} \quad J = \dot{Q} = \frac{1}{R} U$$

for a capacitor: $Q = CU$

Then the analysis of Fig. 2.3.8 gives the following results.

<p>For a capacitor and a resistor joined in series, the total voltage, U_0, is a sum of voltages at both components:</p> $R\dot{Q} + \frac{1}{C}Q = U_0$ <p>and it is easy to show that charge increases according to the following equation:</p> $Q = Q_\infty(1 - e^{-t/RC})$ <p>where $Q_\infty = CU_0$ is the equilibrium charge of capacitor.</p>	<p>For a capacitor and a resistor joined in parallel, the total current, J, is a sum of currents in both components:</p> $\frac{U}{R} + CU = J$ <p>and it is easy to show that at $Q = \text{const}$ ($J = 0$), the voltage relaxes according to the following equation:</p> $U = U_0 e^{-t/RC}$ <p>where $U_0 = Q_0/C$, and Q_0 is the initial charge of capacitor.</p>
<p>This is a direct analogue of the Kelvin-Voigt model and the product (RC) has meaning of the retardation time.</p>	<p>This is the direct analogue of the Maxwell model and the product (RC) has meaning of the relaxation time.</p>
<p>The set of models shown in Fig. 2.3.8a joined in parallel presents an analogue of the multi-retardation time the Kelvin-Voigt model.</p>	<p>The set of models shown in Fig. 2.3.8b joined in series presents an analogue of the multi-relaxation time the Maxwell model.</p>

Electrical analogue modeling permits construction of even more complicated versions of relaxation and retardation behavior and examination of their behavior by varying the model parameters.

2.4 SUPERPOSITION – THE BOLTZMANN-VOLTERRA PRINCIPLE

2.4.1 INTEGRAL FORMULATION OF THE SUPERPOSITION PRINCIPLE

The phenomenon of fading memory can be formulated in the following way: the longer the time interval between events and their observed consequences, the weaker the influence of these events on the observed material behavior.

Mathematical formalization of this assumption means that functions connecting deformations and stresses must be decreasing and written *via* an argument $(t - t')$, where t is the actual (current) time and t' is the time at which some event took place. This formalism leads to the general formulation of a relationship between stresses and deformations.

Two principal ideas are the basis of this approach:

- the response to any event is linear
- all consequent events lead to independent responses.

This is the *principle of linear superposition* of stresses and/or deformations.¹⁵ It means that material reacts to the next action as if no former action took place. In other words, the structure and properties of the material are not changed, regardless of its deformation, and the last statement is a real physical meaning of the principle of linear superposition.

Now, let us write the above stated concept in the form of mathematical formalism. Let the initial stress, acting from the time $t = 0$, be equal σ_0 . Then, deformations immedi-

ately begin to change according to Eq 2.2.1. At some point of time, t' , let stress change by $\Delta\sigma$. The principle of linear superposition assumes that in this case, deformation changes accordingly:

$$\gamma(t) = \sigma_0 \left[J_0 + \psi(t) + \frac{t}{\eta} \right] + \Delta\sigma \left[J_0 + \psi(t - t') + \frac{t - t'}{\eta} \right] \quad [2.4.1]$$

Stress can change at any given time. For any such moment of time and any corresponding change of stress, one can add an independent term in the last equation for $\gamma(t)$.

So, $\gamma(t)$ is written as a sum:

$$\gamma(t) = \sum_i \Delta\sigma_i \left[J_0 + \psi(t - t'_i) + \frac{t - t'_i}{\eta} \right] \quad [2.4.2]$$

where $\Delta\sigma_i$ is the new change of stress added at the time t_i .

This equation shows the following:

- all stress inputs are independent, they do not interact with each other and the deformation is proportional to stress (the principle of linear superposition)
- the influence of stress changes on deformation decreases with time. If stress was applied earlier, as determined by the argument $(t - t')$ (fading memory) more changes were observed compared with the recent applied stresses.

Stress may change continuously, this leads to the final integral (instead of sum) formulation of the principle of linear superposition:

$$\gamma(t) = \int_{-\infty}^t \left[J_0 + \psi(t - t') + \frac{t - t'}{\eta} \right] d\sigma(t') \quad [2.4.3]$$

or

$$\gamma(t) = \int_{-\infty}^t \frac{d\sigma}{dt'} \left[J_0 + \psi(t - t') + \frac{t - t'}{\eta} \right] dt' \quad [2.4.4]$$

The lower limit of integration $(-\infty)$ reflects an idea that the *whole* history of deformation influences deformation at any chosen moment, t .

The analogous line of arguments can be used to describe changes in stresses, and in this case, Eq 2.2.2 is a starting point. The final result is quite similar to Eq 2.4.4, and can be written as

$$\sigma(t) = \int_{-\infty}^t \frac{d\gamma}{dt'} [G_{\infty} + \varphi(t - t')] dt' \quad [2.4.5]$$

A pair of symmetrical Eqs 2.4.4 and 2.4.5 is called the *Boltzmann-Volterra equations*.¹⁶ They form a complete mathematical formulation of the principle of linear superposition.

The integrals representing the Boltzmann-Volterra superposition principle contain the difference $(t - t')$ as an argument. The integrals of such structure are called the *hereditary integrals*, because they reflect the fading influence of pre-history of deformations on the current state of material.

The hereditary part of Eq. 2.4.5 is

$$\sigma(t) = \int_{-\infty}^t \dot{\gamma}(t') \varphi(t-t') dt' \quad [2.4.5a]$$

This expression is conveniently used in discussion of viscoelastic behavior of liquids because it is characterized by the rate of deformation. For solids, deformation by itself is the determining factor. Therefore, the Boltzmann-Volterra superposition principle is more useful in the alternative form

$$\sigma(t) = \int_{-\infty}^t \gamma(t') m(t-t') dt' \quad [2.4.6]$$

where $m(t-t')$ is called a *memory function*. Its physical meaning is equivalent to the meaning of the relaxation function in Eq. 2.4.5 because both characterize the fading influence of pre-history of deformations on the current stress state of material.

The relationship between functions $\varphi(t-t')$ and $m(t-t')$ is established from comparison of Eqs 2.4.5 and 2.4.6:

$$m(t) = \frac{d\varphi(t)}{dt} \quad [2.4.7]$$

The behavior of viscoelastic material according to the principle of superposition can

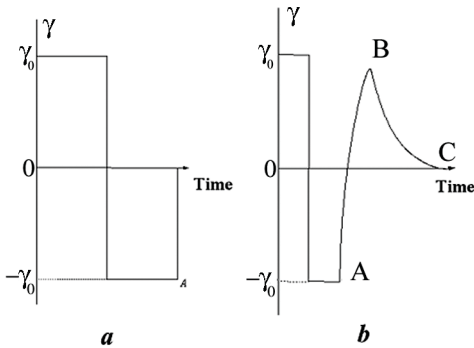


Figure 2.4.1. Deformation history created by external force (a) and the post-reaction (b) of viscoelastic material after removal of the force at the point A.

be illustrated by the following example for elastic recoil (retardation) after forced deformation of a body.

Let the history of deformations be as shown in Fig. 2.4.1a: the external force created deformation, γ_0 , and then (very rapidly) the same deformation but with the opposite sign, $-\gamma_0$, is realized. When the force was acting during two short periods of time, one could neglect partial relaxation at deformations γ_0 and $-\gamma_0$. Now, we follow what happens if at the moment A the external force is removed. An ideal elastic body immediately returns to its initial state, as shown by the vertical line from the point

A in Fig. 2.4.1a. The behavior of a viscoelastic body is quite different, as illustrated by the line ABC in Fig. 2.4.1b. Seemingly, the shape of the curve looks rather strange. Indeed, why does the deformation cross the zero line and reach point B? The first part of this line, AB, is the retardation from the second deformation, $-\gamma_0$, but the sample “remembers” that the first deformation was γ_0 and strives to restore itself to a state determined by the first deformation, γ_0 . Only after that slow (delayed) action does a return to the zero state occur.

Another very interesting (and important for technological applications) example of the influence of deformational prehistory on the behavior of material is related to the poly-

mer processing (thermoplastic and rubber compounds). During extrusion of continuous profile, a molten material moves between the screw and the barrel of an extruder, then it passes through transient channels. Finally, it is shaped in an outlet section of a die. It is desirable that the shape of the final profile is equivalent to the shape of the outlet section of the die. But the material continues to react to all deformations, which took place before the outlet section of the die. As a result, distortion of its shape occurs; therefore, the final section of the part can be different than expected. The related effects are discussed in Chapter 3.

Memory effects become complicated and sometimes rather unexpected when temperature changes during the process of deformation. In these cases, if temperature decreases, the memory of former deformations can be frozen and material looks stable (retardation times become too long for an observer). However, upon heating of an article, the frozen deformations release and one observes effects that are unusual. Many examples of memory of the previous deformation states of such kind are characteristic of applications of viscoelastic materials.

The following example can be considered to illustrate the critical case related to frozen stresses. A polymer block stores large internal (frozen) stresses due to its previous temperature-deformation pre-history. This block appears stable. However, when additional stresses are imposed during its machining (drilling, cutting or other operations) the block may disintegrate into small pieces, may even become powder. This is typical of some materials (polymers and inorganic glasses, large crystallized blocks) especially if they are cooled rapidly.

Viscoelastic materials have fading memory of the history of previous deformations. The integrals in Eqs. 2.4.4 and 2.4.5 are called hereditary integrals because they summarize events which took place before the current moment of time and are responsible for the stress (or deformation) state of material at the current moment.

The relaxation function, $\varphi(t)$, is a decreasing function. Therefore, its values are higher when the argument is smaller. It means that the changes of deformation, which happened earlier, influence stress in a lesser degree than later changes. In the first case, the value of the argument $(t - t')$ in Eq. 2.4.5, for a fixed moment of time, t , is smaller than for events which happened later because values of t' are smaller. In other words, a material continuously “forgets” what happened before and in this sense the integrals in Eqs. 2.4.4 and 2.4.5 form a model of material with “fading memory”.

It is interesting to outline the limiting cases. They are:

- liquid which “forgets” everything immediately (energy of deformation completely dissipates); in this case, the integral Eq. 2.4.5 transforms to the Newton law
- solid which “remembers” everything (energy of deformation is completely stored), and in this case, the integral Eq. 2.4.3 transforms to Hooke’s law.

2.4.2 SUPERPOSITION PRINCIPLE EXPRESSED VIA SPECTRA

Relaxation or retardation spectra can be inserted into general integral of Eqs. 2.4.4 and 2.4.5 by substitution of Eqs. 2.2.7 and 2.2.8 into Eqs. 2.4.4 and 2.4.5, respectively.

Below, this procedure is illustrated by calculations of stresses, $\sigma(t)$, developing in liquid ($E_\infty = 0$); the same will be done for deformations, $\gamma(t)$.

Substitution and the subsequent rearrangements lead to the following result:

$$\begin{aligned}
 \sigma(t) &= \int_{-\infty}^t \frac{d\gamma}{dt'} [\varphi(t-t')] dt' = \int_{-\infty}^t \frac{d\gamma(t-t')}{dt'} \left[\int_0^{\infty} G(\theta) e^{-\frac{t-t'}{\theta}} \right] dt' d\theta = \\
 &= \int_0^{\infty} G(\theta) \left[\int_{-\infty}^t \frac{d\gamma(t-t')}{dt'} e^{-\frac{t-t'}{\theta}} dt' \right] d\theta
 \end{aligned} \tag{2.4.8}$$

The expression in the square brackets is a function of t only. It permits us to analyze some typical cases of stress development in various deformation modes.

2.4.3 SIMPLE TRANSIENT MODES OF DEFORMATION

The superposition principle can be illustrated by several simple examples related to transient modes of deformation. The examples given below are based on Eqs. 2.4.5 or 2.4.6 and they relate to shear deformation.

2.4.3.1 Relaxation after sudden deformation

First of all it is necessary to define the word “sudden” for the purposes of mathematical language. This deformation mode can be formulated as

$$\sigma(t) = \gamma_0 \varphi(t) \tag{2.4.9}$$

Evidently, this is nothing else than the definition of the relaxation function expressed by Eq. 2.2.2.

From Eq. 2.4.6, the following equation for $\sigma(t)$ can be derived

$$\sigma(t) = \gamma_0 \int_0^{\infty} G(\theta) d\theta \tag{2.4.10}$$

This equation is also already known: it is Eq. 2.2.8. The initial value of the $\sigma(t)$ function divided by γ_0 equals $\varphi(0)$:

$$\frac{\sigma(t=0)}{\gamma_0} = \varphi(0) = \int_0^{\infty} G(\theta) d\theta \tag{2.4.11}$$

and this is a part of instantaneous modulus (see Eq. 2.2.4).

2.4.3.2 Developing stresses at constant shear rate

In this deformation mode $\dot{\gamma} = \dot{\gamma}_0 = \text{const}$, deformation is suddenly created at the time $t = 0$. Then it is easy to show that Eq. 2.4.5 leads to the following expression:

$$\sigma(t) = \dot{\gamma}_0 \int_0^{\infty} \varphi(x) dx \tag{2.4.12}$$

Calculations based on Eq. 2.4.8 result in the following expression for stress evolution in material with the known relaxation spectrum

$$\sigma(t) = \dot{\gamma}_0 \int_0^{\infty} \theta G(\theta) (1 - e^{-t/\theta}) d\theta \tag{2.4.13}$$

The equilibrium value of σ (at $t \rightarrow \infty$) divided by $\dot{\gamma}_0$ equals

$$\frac{\sigma(t \rightarrow \infty)}{\dot{\gamma}_0} = \int_0^\infty \varphi(x) dx = \int_0^\infty \theta G(\theta) d\theta \quad [2.4.14]$$

Viscosity at the steady state regime of flow is a physical meaning of this value.

2.4.3.3 Relaxation after steady shear flow

Let the deformation rate be $\dot{\gamma} = \dot{\gamma}_0 = \text{const}$ at $t < 0$, and, at the time $t' = 0$, deformation rate suddenly drops to zero. Here, the deformation rate is described by two members: $\dot{\gamma} = \dot{\gamma}_0 = \text{const}$ at $t' < 0$ and by means of the negative delta-function at the point $t' = 0$. After some formal rearrangements, Eq. 2.4.5 leads to the final expression for stress relaxation:

$$\sigma(t) = \dot{\gamma}_0 \left\{ \int_0^\infty \varphi(t) dt - \int_0^t \varphi(t) dt \right\} = \dot{\gamma}_0 \int_t^\infty \varphi(t) dt \quad [2.4.15]$$

The first integral term in this equation represents the equilibrium value of stress at steady flow (see Eq. 2.4.14).

The difference between Eqs. 2.4.9 and 2.4.15 (both written for “relaxation”) demonstrates that the relaxation process can be very different depending on the history of deformation prior to relaxation.

Calculations using Eq. 2.4.8 give the following result:

$$\sigma(t) = \dot{\gamma}_0 \int_0^\infty \theta G(\theta) e^{-t/\theta} d\theta \quad [2.4.16]$$

The difference between Eqs. 2.4.10 and 2.4.16 is evident.

It is also worth mentioning that Eqs. 2.4.12 and 2.4.15 as well as Eqs. 2.4.13 and 2.4.16 are mirror relations of each other.

Eqs. 2.4.4 and 2.4.5 can be used for quantitative analysis of any other arbitrary regimes of stress or deformation evolution.

2.4.3.4 Relationship between relaxation and creep functions

Eqs. 2.4.4 and 2.4.5 contain deformation and stress, and each of them can be treated as an equation for either stress or deformation. Eq. 2.4.4 determines the development of deformation for known evolution of stresses. It can be considered as an integral equation for $\sigma(t)$ if the function $\gamma(t)$ is known. The same is true for Eq. 2.4.5. Therefore, it is possible to exclude these functions by substituting, for example, the function $\gamma(t)$ from Eq. 2.4.4 to the right side of Eq. 2.4.5. After some formal mathematical rearrangements, the relationship between rheological parameters is obtained which does not contain $\gamma(t)$ or $\sigma(t)$. The resulting equation includes only constants and creep and relaxation functions in the following form:

$$G_\infty J_0 + J_0 \varphi(t) + G_\infty \left[\frac{t}{\eta} + \psi(t) \right] + \int_{-\infty}^t \varphi(t') \left[\frac{1}{\eta} + \frac{d\psi(t-t')}{d(t-t')} \right] dt' = 1 \quad [2.4.17]$$

where G_∞ is the equilibrium modulus, J_0 is the instantaneous compliance, $\psi(t)$ is the creep function, $\varphi(t)$ is the relaxation function and η is viscosity.

Eq. 2.4.17 shows that the relaxation and creep functions are not independent but related to each other by the integral equation. If one of these functions is known (measured, calculated, or assumed), the other can be found from Eq. 2.4.17. This equation formally, and rigorously, confirms that behavior of material, in different modes of deformation, is governed by the same inherent properties.

Eqs. 2.4.4 and 2.4.5 give the mathematical ground for calculation of stress-deformation relationship at any arbitrary path of material loading. The only, but very essential, limitation in application of these equations is the requirement of linearity of rheological behavior of medium, i.e., independence of all material constants and functions entered into these equations (instantaneous compliance, equilibrium modulus, viscosity, relaxation and creep functions) on stresses and deformations.

Eqs. 2.4.4 and 2.4.5 are general rheological equations of state, or constitutive equations, for viscoelastic materials. The differences in properties of various materials are hidden in the values of constants and types of viscoelastic (creep or relaxation) functions.

It is essential to remember that the above properties are related to a “point” as adapted for Newtonian liquid and Hookean solid and in general for any rheological equation of state. In order to find stress deformation distribution throughout a body, it is necessary to combine these equations with equilibrium conditions (equations of conservation, introduced in Chapter 1) and appropriate boundary conditions.

2.4.3.5 Relaxation function and large deformations

The concept of large deformation (as discussed in section 1.2) require treatment of any deformation as three-dimensional. In simple shear, it results in appearance of normal stresses, N_1 (see section 3.4.2 for more details concerning the normal stress effect in shear flow).

Shear stress evolution in a simple shear, $\sigma(t)$, proceeding with constant shear rate, $\dot{\gamma} = \text{const}$, created at the time $t = 0$ is described by Eq. 2.4.13, which is a direct consequence of Eq. 2.4.5 in which the large deformation measure is used.

The analysis of the three-dimensional problem gives the following result:¹⁷ the direct calculations lead to the following expression for the time evolution of the first difference of normal stresses:

$$N_1^+(t) = 2\dot{\gamma}^2 \int_0^t x \varphi(x) dx \quad [2.4.18]$$

where $\varphi(t)$ is a relaxation function.

Another form of equation for the transient increasing function $N_1^+(t)$ is obtained from a relaxation spectrum (instead of a relaxation function) as the characteristic of rheological properties of material. In this case the following result is obtained:

$$N_1^+(t) = 2\dot{\gamma}^2 \int_0^\infty \theta^2 G(\theta) \left[1 - e^{-t/\theta} \left(1 + \frac{t}{\theta} \right) \right] d\theta \quad [2.4.19]$$

The difference in development of shear and normal stresses (Eqs. 2.4.13 and 2.4.18 and 2.4.19, respectively) is pertinent. It is also possible to prove that regardless of the relaxation spectrum, the development of normal stresses proceeds slower than shear stresses.

Equilibrium value of the coefficient of the first difference of normal stresses¹⁸ corresponding to the regime of steady state flow is expressed *via* relaxation spectrum as

$$\Psi_1 = \frac{N_1^+(t \rightarrow \infty)}{\dot{\gamma}^2} = 2 \int_0^\infty \theta^2 G(\theta) d\theta \quad [2.4.20]$$

Relaxation of normal stresses is described by an equation which is the mirror image of Eq. 2.4.19, i.e.:

$$N_1^-(t) = 2 \dot{\gamma}^2 \int_0^\infty \theta^2 G(\theta) e^{-t/\theta} \left(1 + \frac{t}{\theta}\right) d\theta \quad [2.4.21]$$

It is possible to prove that relaxation of normal stresses always proceed slower than shear stresses.

The most important physical result of the above-mentioned derivations is that the transient behavior of normal stresses is determined by the same viscoelastic functions (relaxation function or relaxation spectrum) as the evolution of one-dimensional shear deformations (stresses).

With regard to dynamic functions, oscillating normal stresses also appear in periodically changing shear deformations.¹⁹ But deformations are changing according to the harmonic law:

$$\gamma(t) = \gamma_0 e^{i\omega t}$$

In addition to shear stresses oscillating with the same frequency and described by dynamic functions (as discussed in Section 2.2.2), normal stresses appear and are oscillating with *double* frequency. The time dependence of the first difference of normal stresses in harmonic oscillations of deformations is:

$$N_1(\omega, t) = N_{1,c}(\omega) + N_{1,osc}(\omega) e^{2i(\omega t - \delta)} \quad [2.4.22]$$

The last equation shows that normal stresses appearing in shear oscillations consist of three components: a constant steady-state component, $N_{1,c}$, depending on frequency only, in-phase and out-of-phase components of N_1 having the amplitude, $N_{1,osc}$, changing with double frequency and characterized by the retardation angle, δ .

The same formalism as for dynamic moduli in shear deformation can be introduced for oscillating normal stresses. In-phase and out-of-phase components of dynamic normal stresses can be characterized by frequency-dependent “moduli of normal stresses”. In the general case, in a *quasi-linear* mode²⁰ of shear deformations, normal stresses are described by means of the frequency-dependent coefficients

$$\Psi(\omega) = \Psi_0 + \Psi'(\omega) + i\Psi''(\omega) \quad [2.4.23]$$

The members of the sum in Eq. 2.4.21 reflect the components of the sum in Eq. 2.4.22.

It was theoretically proven and experimentally confirmed²¹ that these coefficients are not independent parameters of material but are directly related to a standard set of viscoelastic functions of materials. It means that the effect of oscillating normal stresses as well as transient changes in normal stresses are not separate properties of material but only

the consequence of its general viscoelastic behavior, whereas normal stresses appear as a second-order effect due to large deformations.

More complicated modes of deformation can also be studied on the basis of the general relationships discussed above. As an example of such complex deformation modes, where viscoelastic behavior of material is a dominating factor, sometimes the superposition of low-amplitude oscillations on steady shear flow are considered. It was demonstrated that superposition of flow changes viscoelastic behavior.²² This and other complicated cases must be treated in the framework of more general non-linear theories of viscoelastic behavior.

2.5 RELATIONSHIPS AMONG VISCOELASTIC FUNCTIONS

2.5.1 DYNAMIC FUNCTIONS – RELAXATION, CREEP, AND SPECTRA

The main goal of the theory of viscoelasticity is to establish a relationship among all functions mentioned above and used in interpretation of experimental data obtained in different deformation-stress modes.²³

In the most general form, it is done by the principle of superposition. However, it is useful to obtain some simpler relationships that are more convenient in practice.

The connection between dynamic functions, creep, and relaxation functions can be found on the basis of Eqs 2.4.4 and 2.4.5 by substituting the harmonic functions into these equations. Subsequent calculations lead to the following equations:

For the components of dynamic compliance	For the components of dynamic modulus
$J'(\omega) = \int_0^\infty \frac{\partial \psi}{\partial t} \cos \omega t dt$	$G'(\omega) = \omega \int_0^\infty \varphi(t) \sin \omega t dt$
$J''(\omega) = \int_0^\infty \frac{\partial \psi}{\partial t} \sin \omega t dt \quad [2.5.1]$	$G''(\omega) = \omega \int_0^\infty \varphi(t) \cos \omega t dt \quad [2.5.2]$

These types of equations are well known in mathematics: they are called Fourier transforms.²⁴ The structure of the inverse transformation is the same as the direct one. It is possible to rearrange Eqs. 2.5.1 and 2.5.2, treating them as equations of functions $\psi(t)$ and $\varphi(t)$. The solutions are

$\frac{\partial \psi}{\partial t} = \frac{2}{\pi} \int_0^\infty J'(\omega) \cos \omega t d\omega =$	$\varphi(t) = \frac{2}{\pi} \int_0^\infty \frac{G'(\omega)}{\omega} \sin \omega t d\omega =$
$= \frac{2}{\pi} \int_0^\infty J''(\omega) \sin \omega t d\omega \quad [2.5.3]$	$= \frac{2}{\pi} \int_0^\infty \frac{G''(\omega)}{\omega} \cos \omega t d\omega \quad [2.5.4]$

The following conclusions can be drawn from Eqs. 2.5.1-2.5.4.

- there are direct relationships between time-dependent (relaxation and creep) functions and frequency-dependent dynamic functions, thus, any of them can be calculated if the others are known

- the pair of dynamic functions (either J' and J'' or G' and G'') are, in fact, not independent but can be expressed by each other. The resulting relationships, known as the *Kronig-Kramer equations*,²⁵ are:

$J'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\alpha J''(\alpha)}{\alpha^2 - \omega^2} d\alpha$ $J''(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega J'(\alpha)}{\omega^2 - \alpha^2} d\alpha \quad [2.5.5]$	$G'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega^2 G''(\alpha)}{\alpha(\omega^2 - \alpha^2)} d\alpha$ $G''(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega G'(\alpha)}{\alpha^2 - \omega^2} d\alpha \quad [2.5.6]$
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The last pairs of relationships are the functional representations of dynamic functions via a retardation (or relaxation) spectrum. They are also based on the superposition principle, Eqs. 2.4.4. and 2.4.5, and the path of rearrangements is the same as for Eq. 2.4.8. The final results omit the constants:

$J'(\omega) = \int_0^\infty J(\lambda) \frac{1}{1 + (\omega\lambda)^2} d\lambda$ $J''(\omega) = \int_0^\infty J(\lambda) \frac{\omega\lambda}{1 + (\omega\lambda)^2} d\lambda \quad [2.5.7]$	$G'(\omega) = \int_0^\infty G(\theta) \frac{(\omega\theta)^2}{1 + (\omega\theta)^2} d\theta$ $G''(\omega) = \int_0^\infty G(\theta) \frac{\omega\theta}{1 + (\omega\theta)^2} d\theta \quad [2.5.8]$
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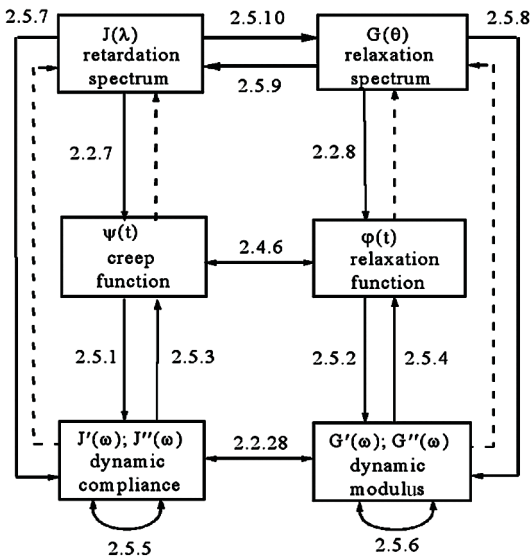


Figure 2.5.1. Interrelations between different functions used to characterize viscoelastic behavior of material in shear.

It is interesting to show the evident analogy between these equations and Eqs. 2.3.9 and 2.3.10 obtained for mechanical analogues, i.e., representing a discrete retardation (relaxation) spectrum.

The main sense of all equations given in this chapter is, first of all, to demonstrate the existence of relationships for all viscoelastic characteristics under discussion (they can be used for mutual calculations), and secondly, to emphasize the fact that all these relationships are represented by the integral equations with infinite limits.

The first point can be represented as in Fig. 2.5.1. The second point will be discussed in more detail below. The scheme in Fig.

2.5.1 represents the general structure of the theory of viscoelasticity. The solid lines are relationships and the numbers of suitable equations which were discussed above are clearly marked.

Double lines in the upper part of the scheme indicate the relationship between relaxation and retardation spectra. This relationship can be obtained by substituting the equations for the components of J' and J'' , on one hand, and G' and G'' , on the other hand, and expressed *via* spectra based on Eq. 2.2.28.

The final pair of relationships, known as the *Cross equations*, are as follows:

$$J(\lambda) = \frac{G(\theta)}{\left[G_{\infty} - \int_0^{\infty} \frac{G(x)}{(\lambda/x) - 1} dx \right]^2 + [\pi \theta G(\theta)]^2} \quad [2.5.9]$$

$$G(\theta) = \frac{J(\lambda)}{\left[J_0 - \int_0^{\infty} \frac{J(x)}{1 - (x/\theta)} dx - \frac{\theta}{\eta} \right]^2 + [\pi \lambda J(\lambda)]^2} \quad [2.5.10]$$

The functions describing one spectrum can be found from the other spectrum at $\theta = \lambda$.

The dashed lines, i.e., the methods of calculation of a retardation (relaxation) spectrum, are worth special discussion, and section 2.5.3 is specifically devoted to this subject.

2.5.2 CONSTANTS AND VISCOELASTIC FUNCTIONS

An experiment gives characteristics of material behavior. The characteristics do not change with time nor depend on frequency. These parameters, as well as viscoelastic functions, can be determined for different geometrical modes of deformations. Below, they will be related to shear.

The following constants²⁶ were introduced in the theory of viscoelasticity:

Newtonian viscosity $\eta = \sigma / \dot{\gamma}$

steady-state compliance $J_s^0 = \sigma / \gamma_{\infty}$

instantaneous elastic modulus G_0

where σ is a steady shear stress, $\dot{\gamma}$ is shear rate in steady flow, and γ_{∞} is equilibrium (stored in the state of steady flow) elastic (or recoverable) shear deformation, or *elastic recoil*.²⁷

Theoretical analysis made within the framework of the linear theory of viscoelasticity leads to the following relationships between a relaxation spectrum and the above listed constants.

The *zero moment* of a relaxation spectrum is an instantaneous modulus

$$G_0 = \int_0^{\infty} G(\theta) d\theta \quad [2.5.11]$$

(compare with Eq. 2.4.11).

The *first moment* of a relaxation spectrum is viscosity:

$$\eta_0 = \int_0^\infty \theta G(\theta) d\theta \quad [2.5.12]$$

(compare with Eq. 2.4.14).

Steady-state shear compliance is calculated *via* the moments of a relaxation spectrum in the following way:

$$J_s^0 = \frac{\int_0^\infty \theta^2 G(\theta) d\theta}{\left[\int_0^\infty \theta G(\theta) d\theta \right]^2} \quad [2.5.13]$$

The last equation is directly related to the expression of the coefficient of normal stresses (see section 3.4.2) calculated as the *second moment* of the relaxation spectrum

$$\Psi_1 = 2 \int_0^\infty \theta^2 G(\theta) d\theta \quad [2.5.14]$$

(compare with Eq. 2.4.20).

Then, comparing the last two equations, one comes to the *Lodge equation*:²⁸

$$J_s^0 = \frac{\Psi_1}{2\eta_0^2} \quad [2.5.15]$$

where η_0 and Ψ_1 are initial values of viscosity and the coefficient of the first difference of normal stresses, respectively, i.e., these values are determined in the domain of linear viscoelastic behavior of material.

Eq. 2.5.15 can also be written in another form:

$$\sigma_{11} - \sigma_{22} = 2\sigma\gamma_\infty \quad [2.5.16]$$

where γ_∞ is ultimate recoil (complete elastic deformation stored during steady shear flow).

All three principal characteristics of steady rheological behavior of liquid are expressed *via* different moments of the relaxation spectrum, *zero for instantaneous modulus, the first for Newtonian viscosity, and the second for elastic properties* (equilibrium compliance and normal stresses).

The theory also gives some useful “limiting” expressions. If $G'(\omega)$ and $G''(\omega)$ have been measured in a wide frequency range, it could be proven that, at sufficiently low frequencies, G' is expected to be proportional to ω^2 , and G'' to ω . Then the following limits are valid:

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega} \quad [2.5.17]$$

and

$$J_s^0 = \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{[G''(\omega)]^2} \quad [2.5.18]$$

Sometimes another equation is used instead of Eq. 2.5.18:

$$J_s^0 = \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{[G'(\omega)]^2 + [G''(\omega)]^2} \quad [2.5.18a]$$

Because at low frequencies $G'' \gg G'$, Eq. 2.5.18a degenerates to Eq. 2.5.18.

The last useful relationship is the consequence of the equation for Ψ_1 . It is easily seen that

$$\Psi_1 = \lim_{\omega \rightarrow 0} \frac{2G'(\omega)}{\omega^2} \quad [2.5.19]$$

The above formulated integral expressions, Eqs. 2.5.1-2.5.8, can also be written in adequate forms if integrals are replaced by sums. This is reasonable if a continuous spectrum, entering the integral equations, is replaced by a discrete spectrum (discrete distribution of relaxation modes), found by treating experimental data (see section 2.5.3). In this case a function $G(\theta)$ is given by the set of pairs $\theta_i - g_i$.

One more interesting relationship is from a relaxation curve measured after steady shear flow, $\sigma(t)$, as expressed by Eq. 2.4.2 (with consequent change in symbols). The area under a relaxation curve, S , is calculated as

$$S = \int_0^\infty \sigma(t) dt = \dot{\gamma} \int_0^\infty \theta^2 G(\theta) d\theta \quad [2.5.20]$$

where $\dot{\gamma}$ is shear rate at steady flow.

The last integral is exactly the expression for the coefficient of the first normal stress difference, Ψ_1 , (Eq. 2.4.20), and therefore the following equality is valid:

$$\Psi_1 = \frac{2S}{\dot{\gamma}} \quad [2.5.21]$$

The physical meaning of this equation is evident: the area under the relaxation curve, as well as the coefficient of normal stresses, are the measures of stored elastic energy.

2.5.3 CALCULATION OF A RELAXATION SPECTRUM

2.5.3.1 Introduction – general concept

A relaxation spectrum,²⁹ by definition, is a function defined by Eq. 2.2.8, which is well known in mathematics as the *Laplace transform*.³⁰ The theory says that any decreasing function (such as a relaxation function) can be represented by the Laplace integral. The theory also permits finding $G(t)$ if a function $\phi(t)$ is known in an *analytical form in the whole range* of its argument, i.e., from zero to infinity. However, if one refers not to mathematics but to a *practical* determination of a relaxation spectrum based on an *experimental grounds*, at least two principal difficulties appear and the roots of these difficulties are as follows:

- first, no experiment can be performed “from zero to infinity”, neither in time scale nor in frequency scale; and therefore what the contribution of absent ranges of the experimental scale (outside of the “*experimental window*”) is to the results of calculations is unknown and cannot be estimated
- second, no experiment gives the absolutely correct measured value, but only within some experimental confidence, and the influence of the experimental error on the results of calculations, especially considering that the integral transforms are non-linear, is uncertain and can be large.

Therefore, it is necessary to refuse attempts to find an unambiguous and rigorous answer to the question as to how to find the function $G(t)$ if a function $\varphi(t)$ has been measured. Then, it is necessary to state the meaning of the determined relaxation spectrum. The answer depends on a goal: why are we interested in finding a relaxation spectrum?

First, a relaxation spectrum appears as a mathematical image and only this is the complete and full definition of a spectrum. In this case, a spectrum is treated as some *fitting function* reflecting viscoelastic properties of material. This function, found in one experiment, can be used in solving different problems related to any arbitrary deformation modes.

According to this concept, a relaxation spectrum can be found from experimental data by some procedures, based on the integral equations discussed in the previous sections of this chapter. This is essentially the *inverse problem*.

Problems of such kind are usually treated as *ill-posed* or incorrect, because determination of a function by solving an integral equation leads (in principle) to ambiguous results strongly and uncertainly depending on slight perturbation of the experimentally measured function. It is quite evident that any limited set of experimental data, known within some limits of error, can be fitted by many independent ways.

There are several approximate methods useful in applications. These methods will be considered below. This attitude to a relaxation spectrum as some fitting function is the only one close to today's understanding of the problem. Indeed, the final result of numerous attempts to find the “true” relaxation spectrum was summarized in the following way: the problem of line spectrum determination is essentially a curve fitting procedure and “no line spectrum – produced by whatever method – is ever the *true* spectrum”.³¹ In this sense, the choice of an algorithm for determining a relaxation spectrum is a “personal preference rather than objective definition”.³² Moreover, it was proven that different approximations, based on various fitting procedures and resulting in different forms of a relaxation spectrum, lead to very close predictions concerning viscoelastic behavior of material.³³

Second, another attitude to a relaxation spectrum determination is based on the modeling molecular movements in material (consisting, for example, of individual macromolecules, their aggregates or supermolecular structures) and treating these movements in terms of a set of relaxation times (i.e., a relaxation spectrum).

Obviously, a relaxation spectrum reflects molecular movements. However, this statement is nothing more than the general idea in the first approach, but it leads to unique and unambiguous predictions in the second approach, and, within the framework of an accepted model, any relaxation mode has definite physical meaning. This concept will be discussed in more detail in section 2.7.

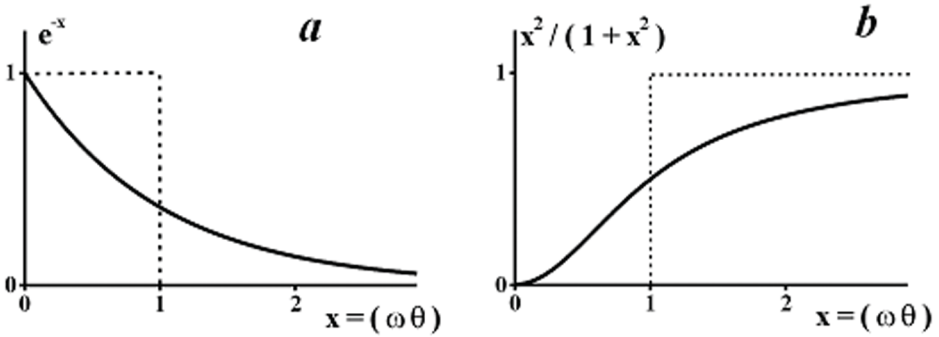


Figure 2.5.2. Approximations of some kernels of integral transforms by step functions: for a relaxation function (a) and for dynamic modulus (b).

Then, if a form of relaxation mode is known beforehand (from a molecular model), it is easy to calculate any viscoelastic function which is then compared with independent experimental data.

In this approach a relaxation spectrum is not a pure mathematical image but any mode of a spectrum has a quite clear physical meaning, and the problem of relaxation spectrum determination transforms from an inverse mathematical problem to a *semi-inverse* problem.

2.5.3.2 Kernel approximation – finding a continuous spectrum

It is noticeable from any of the integral transforms including a relaxation spectrum that a kernel of all equations is a quickly decreasing function of its argument. The exponential function, e^{-x} , entering Eq. 2.2.18, decreases in comparison with its initial value (at $x = 0$) by 10 times already at $x = 2.3$. A function $x^2/(1+x^2)$ entering Eq. 2.5.8, increases from its initial value (at $x = 0$) by 10 times at $x = 3$. Analogous conclusions can be made for other kernels of integral transforms. The character of some kernel functions is shown in Fig. 2.5.2.

It is possible to make the following approximations of the kernel functions:

$$e^{-x} = \begin{cases} 1, & x \leq 1 \\ 0, & x > 1 \end{cases}; \quad \frac{x^2}{1+x^2} = \begin{cases} 0, & x \leq 1 \\ 1, & x > 1 \end{cases} \quad [2.5.22]$$

These approximations are also shown in Fig. 2.5.1 by dotted lines.

It can be anticipated that small values of kernels strongly diminish the input of the part of an integral with small values of a kernel and it is reasonable to neglect this part in calculating a viscoelastic function. Using these approximations, the integral transforms are easily solved in an analytical form and the final results are as follows.

The first level approximation of Eq. 2.2.8 is:

$$G(\theta) \cong -\frac{d\phi(t)}{dt} \text{ at } \theta = t \quad [2.5.23]$$

Analogous approach to Eq. 2.5.8 gives the following final result:

$$G(\theta) \cong \omega^2 \frac{dG(\omega)}{d\omega} \text{ at } \theta = \omega^{-1} \quad [2.5.24]$$

The higher level approximations can also be obtained by the same method. Similar ideas are used for calculations of a retardation spectrum.

The approach based on kernel approximations was very popular in the pre-computer era, because they are quite simple to handle and do not require time-consuming calculations.³⁴ However, today the latter argument is not important and the methods based on kernel approximations are practically not used, being replaced by computer methods utilizing a spectrum represented by a set of discrete lines.

2.5.3.3 Computer-aided methods for a discrete spectrum

2.5.3.3.1 The direct method³⁵

According to this method it is assumed that a unique continuous spectrum describes the viscoelastic behavior of material. However, this spectrum is discretized and it is presented as a set of independent relaxation modes, though both (continuous and discrete spectra) are considered as equivalent.

This is the direct method for searching a relaxation spectrum, which is supposed to exist in the form of a set of discrete lines, $G_i - \theta_i$. The values of $G_i - \theta_i$ are used for calculating the experimentally observed functions (let it be $G'_{\text{exp}}(\omega)$ and $G''_{\text{exp}}(\omega)$). These values are varied and the calculated values of $G'_{\text{cal}}(\omega)$ and $G''_{\text{cal}}(\omega)$ are compared with experimental values. The deviation of the results of approximation (in varying $G_i - \theta_i$) from experimental data is estimated by the *functional of errors*, E . It can be calculated in different manners but the simplest and the most evident form of this functional is

$$E = \frac{1}{2M} \sqrt{\sum_{n=1}^M \left[\left(\frac{G'_{\text{exp},n} - G'_{\text{calc},n}}{G'_{\text{exp},n}} \right)^2 + \left(\frac{G''_{\text{exp},n} - G''_{\text{cal},n}}{G''_{\text{exp},n}} \right)^2 \right]} \quad [2.5.25]$$

The subscript symbol, n , shows that this result relates to the n -th experimental point and the total number of these points is M .

The general computer-aided procedure consists of minimization of functional of errors, which, according to Eq. 2.5.25, is nothing else than a standard average deviation. This procedure results in a set of parameters $G_i - \theta_i$ for the best fit of experimental data.

Two important points are taken into account in an algorithm of calculations:

- initial independence of $2M$ parameters; the search for a minimum is a non-linear problem by its nature
- obtaining the best fit of experimental data with a minimum number of modes (the latter allows authors to call their approach a *parsimonious model*).

Authors say that the discrete relaxation modes are not meaningful by themselves and can be replaced by other sets of pairs of $G_i - \theta_i$. So, the method does not give the unique or unambiguous solution of the problem. However, a continuous spectrum obtained from this

set of parameters “certainly is a meaningful representation of the macromolecular dynamics”.

2.5.3.3.2 Method of linearization³⁶

This method is based on representation of experimental dependencies (either $G'(\omega)$ and $G''(\omega)$, or a relaxation curve determined inside an experimental window) by the expansion series using increasing powers of ω . The unknown values are the coefficients of series. Contrary to the procedure described above, the search for these parameters by minimizing the functional of errors (such as Eq. 2.5.25 or any other) is a linear problem by itself and therefore this problem has a unique solution.

The result of the computer-aided calculations is also a set of discrete modes. The set of relaxation modes obtained by this method is different than that obtained by the direct method discussed above. None of these modes has any definite physical meaning, but they adequately represent viscoelastic properties of materials.

The advantage of this method is in unambiguity of results, since there is only a single minimum of linear functional of errors.

2.5.3.3.3 Semi-inverse method³⁷

The freedom of choice of relaxation modes permits presetting the distribution of relaxation times along the frequency (or time) scale. This distribution can be arbitrary. However, for simplicity, it is preferable to establish certain rules for the choice of relaxation times. As an example, the relaxation time distribution can be expressed as

$$\log \theta_n = \log \theta_{\max} + Cn \quad [2.5.26]$$

where n is an ordinary number of a relaxation mode and C is a step. The equidistant distribution in log-scale is proposed. The other possible distribution of relaxation times is proposed in the form of the power law:

$$\theta_n = 3\theta_{\max}/n^{-\alpha} \quad [2.5.27]$$

where θ_{\max} is the initial value of the distribution, n is an ordinary number of relaxation modes, and α is an arbitrary factor.

Experimental data are always known for a limited “window” of frequency range, from ω_{\min} to ω_{\max} . However, it does not mean that the distribution must also be limited to the same range. For computation purposes it is preferable to take the maximum value of the relaxation time beyond the upper limit of frequencies, i.e., it is reasonable to take $\theta_{\max} > \omega_{\min}^{-1}$ and θ_{\min} can be less than ω_{\max}^{-1} .

This does not mean that we may determine the relaxation spectrum beyond the boundaries of the experimental window: the choice of θ_{\max} is important for the method of fitting the experimental data.

The preliminary choice of the relaxation time distribution makes the calculations much easier because determination of spectrum degenerates into a linear problem that is necessary to find the weights of relaxation modes (partial moduli) only, satisfying the condition of minimizing the standard deviation or other measures of fitting errors.

2.5.3.3.4 Regularization method³⁸

This is a particular case of a more general approach to solving the Fredholm integral equations of the first kind. All inverse problems of searching for a relaxation (retardation) spectrum belong to these equations. One of the most popular general method is based on

the Tikhonov regularization.³⁹ The method is based on minimization of the following functional $V(\lambda)$ (omitting the constants), which is somewhat more of a general expression than the standard average deviation as in Eq. 2.5.25:

$$V(\lambda) = \sum_{i=1}^N \frac{1}{\sigma_i^2} \left\{ g_i^\sigma - \left[\int K(t-\tau) G(\ln \theta) d \ln \tau \right] \right\}^2 + \lambda (L|E|)^2 \quad [2.5.28]$$

Here g_i^σ is a measured value of the experimental function (let it be a relaxation function or elastic modulus) determined with some error, or noise, σ ; $K(t-\tau)$ is a kernel as in formulas for an experimental function; $G(\theta)$ is a relaxation spectrum (argument is used in a logarithmic scale because an experimental window covers several decimal orders of time or frequency changes); N is the number of experimental points.

The second, new term in Eq. 2.5.28, $\lambda L|E|$, reflects the idea of smoothing the calculated function. Here, λ is a *regularization parameter* and $L|E|$ is an arbitrary operator, usually it is the second derivative of the function $G(\ln \theta)$. Introducing this term leads to minimization of undesirable oscillations of unknown function.

The regularization method is a rigorous way of searching a relaxation spectrum. Appropriate software gives a powerful method of the computer-aided solution of the problem under discussion.

However, the above-cited remark that “no line spectrum – produced by whatever method – is ever the true spectrum” is still valid. And again, it is necessary to stress that different approximations based on various fitting procedures can lead to very close predictions concerning viscoelastic behavior of material as described in this chapter.

2.6 VISCOELASTICITY AND MOLECULAR MODELS

2.6.1 MOLECULAR MOVEMENTS OF AN INDIVIDUAL CHAIN

Viscoelastic (or relaxation) properties are very important characteristics of polymeric materials in the form of dilute solutions, melts, or solids. The origin of viscoelasticity is attributed to molecular movement of polymeric chains. Some macro-models were constructed to explain the nature of relaxation phenomenon in polymer substances and to predict the distribution of relaxation times in real materials.

The relaxation phenomenon is caused by molecular movement of a polymer chain. These movements change conformations of flexible macromolecular chains. The transition between different conformations proceeds in time and these transitions are of a relaxation nature.

The model of macromolecular movement is visualized by simple viscoelastic elements described in section 2.3. Here, basic ideas and principal conclusions, useful in rheological applications, are briefly discussed. Mathematical calculations are not included because they belong to the field of polymer physics rather than rheology.⁴⁰



2.6.1.1 A spring-and-bead model (“free draining chain”)

Figure 2.6.1. A spring-and-bead model (free-draining coil).

Fig. 2.6.1 shows a model of a macromolecular chain called a *spring-and-bead*

model.⁴¹ This model predicts viscoelastic or relaxation behavior due to the combination of viscous resistance and elastic recoil. The elements of the model are not directly related to atoms in a macromolecular chain: the model represents an image of some peculiarities of chain deformation. This model is also called a model of a free-draining chain, because an effect of intramolecular interactions (between different elements of a model) is neglected.

A chain contains $(N + 1)$ identical beads and N identical springs. Resistance to the displacement of the n -th bead is expressed as the product of viscosity of a surrounding medium and its velocity, $\eta(du_n/dt)$. In this case “viscosity” is some measure of the intermolecular interaction between a macromolecule and a surrounding liquid. Force acting on every i -th string is the product of its modulus, G , by relative displacement of its ends: $G(u_n - u_{n-1})$. Analogous equations are written for every chain element. Then, as a result of accurate calculations, the expression for displacement of the chain end under constant force, F_0 , is given by:

$$U(t) = \frac{F_0 t}{\eta(N + 1)} + F_0 \sum_{n=1}^N G_n (1 - e^{-t/\lambda_n}) \quad [2.6.1]$$

The first term expresses a continuous movement of a chain under constant force (“flow”), and the second term represents the retarded deformation as in any viscoelastic model element discussed in section 2.3. The partial moduli, G_n , are calculated via constants of the model.

$$G_n = \frac{1}{2G(N + 1)} \left[\cot \frac{n\pi}{2(N + 1)} \right]^2 \quad [2.6.2]$$

The constants λ_n in Eq. 2.6.1 are retardation times expressed by

$$\lambda_n = \frac{\eta}{4G} \left[\sin \frac{n\pi}{2(N + 1)} \right]^2 \quad [2.6.3]$$

The existence of set of identical elements joined in a chain leads to appearance of a retardation (and relaxation) spectrum by itself. The number of lines in a spectrum (number of retardation times) is determined by the number of elements in the chain.

A long chain, consisting of many elements ($N \gg 1$) can be analyzed. The range of retardation times is determined by the boundary values of minimum, λ_{\min} , and maximum, λ_{\max} , retardation times, respectively. Calculations show that

$$\lambda_{\min} \approx \frac{1}{4} \left(\frac{\eta}{G} \right) \quad [2.6.4]$$

and

$$\lambda_{\max} \approx \frac{(N + 1)^2}{\pi^2} \left(\frac{\eta}{G} \right) \quad [2.6.5]$$

The minimum retardation time is practically independent of the full length of chain because quick relaxation movements occur inside the chain segments. The maximum retardation time is proportional to N^2 , i.e., it increases with its molecular mass.

There is only a single independent retardation time and all others can be expressed by it. The n -th retardation time (in the range of long retardation times, $n < 5$) is expressed as

$$\lambda_n = \lambda_{\max} n^{-2} \quad [2.6.6]$$

A retardation spectrum represented by the pairs G_n - λ_n is discrete.⁴² If N is sufficiently large, summation can be replaced by integration in order to obtain a continuous spectrum. Then, the following formula for a relaxation spectrum can be obtained:

$$G(\theta) = K\theta^{-3/2} \quad [2.6.7]$$

This formula is valid within the limits from λ_{\min} to λ_{\max} . Sometimes a logarithmic form of a relaxation spectrum, $h(\ln\theta)$, is used (see Eq. 2.2.8a). Then

$$h(\ln\theta) = K\theta^{-1/2} \quad [2.6.8]$$

The constant K is found from any integral characteristic of spectrum (see section 2.5.2).

Molecular theory helps to express the model constants by parameters which have physical meaning. Elasticity of macromolecules originates from their Brownian movement and therefore the elastic modulus, G_e , is written as

$$G_e = akTN \quad [2.6.9]$$

where k is the Boltzmann constant, T is the absolute temperature, N is a factor depending on concentration (number of chains in a unit volume) and a is some front-factor close to one. It is easy to show that

$$G_e = \frac{3G}{N}$$

and finally

$$G = \frac{1}{3}akTN^2 \quad [2.6.10]$$

A value of “viscosity” entering the molecular model is expressed as

$$\eta = \frac{\eta_0 - \eta_s}{N} \quad [2.6.11]$$

where η_0 is viscosity of solution, η_s is viscosity of solvent, i.e., the value of η is decrement of viscosity (increase of viscosity) caused by the presence of a macromolecule in a solution related to a unit volume.

After some evident rearrangements, the following formula for maximum retardation time is obtained:

$$\lambda_{\max} \approx \frac{3(\eta_0 - \eta_s)}{\pi^2 N k T} \quad [2.6.12]$$

and all other times can be calculated from a spectrum using Eq. 2.6.6. Eq. 2.6.12 relates relaxation times of macromolecular movements to macroscopic parameters of a polymer system.

The following features of a spring-and-bead model need to be mentioned:

- this model relates to very dilute solution without taking into account intermolecular interaction, but based on the analysis of behavior of an individual polymer chain
- this is a linear model, i.e., it predicts linear viscoelastic behavior of solution
- relaxation properties of dilute polymer solutions can be predicted from macroscopic properties of liquid
- the whole relaxation spectrum is defined through a single relaxation time, i.e., all relaxation modes are not independent but are the consequence of movement of identical “sub-molecules”.

2.6.1.2 Model of a non-draining coil⁴³

This is the same model as the spring-and-bead model discussed above, but it is supplemented by intramolecular interactions inside the chain. It means that in contrast to the above-discussed models, this model takes into account perturbations of the flow field in liquid due to the presence of foreign particles in it. This concept leads to another method of calculation of a force acting on every bead in a chain. Without discussion of details of calculations, the following main theoretical results for a model of a non-draining coil are of interest:

- maximum relaxation time in this model, θ_{\max}^Z , is expressed in the same manner as in the spring-and-bead-model, though with a different front-factor
- all other relaxation times are not independent but can be found within the framework of a model
- the distribution of relaxation times is different than in the spring-and-bead-model (more narrow), though the differences are not very large
- new relaxation time distribution results in slightly different predictions concerning experimentally observed functions, primarily $G'(\omega)$ and $G''(\omega)$.

The difference in predictions of the $G'(\omega)$ and $G''(\omega)$ functions in both theories permits to compare them with experimental data in a wide frequency range. The following theoretical predictions are obtained from both models. In the low frequency range, both models give practically identical predictions for $G'(\omega)$ and $G''(\omega)$ dependencies. However, in the high frequency range, a spring-and-bead model predicts that $G'(\omega)$ must coincide with $[G'' - \omega\eta_s]$ where η_s is viscosity of solvent and the slope of both functions (in log-log scale) equals 1/2. The model of non-draining chains predicts that $[G'' - \omega\eta_s]$ exceeds G' by $\sqrt{3}$ times and the slope of both functions is 2/3.

The intermediate case of partial draining was examined by many authors.⁴⁴ This model, regardless of the details of calculation, leads to predictions lying in between the results of calculations of the two above mentioned theories.

It is difficult to make accurate experimental measurements which permit us to evaluate different theoretical predictions. This is because measurements have to be made for

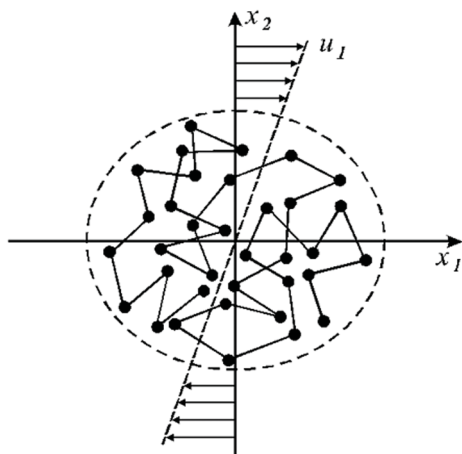


Figure 2.6.2. A model of rotating macromolecular coil.

statistical coil. If this coil is placed in a shear field, forces appear which tilt a position of any element of a coil from its equilibrium state (Fig. 2.6.2). As a result, a restoring force appears and this force tends to push an element back to its equilibrium state. This effect is modeled by a spring resistance and resistance of a bead to a medium. The behavior of a macromolecular coil is modeled by a set of Maxwellian elements, attached to the center of mass of a coil.

Rotation of a macromolecular coil with respect to the center of mass in a shear field results in some additional loss of energy (energy dissipation) and this is equivalent to an increase in apparent viscosity.

Calculations based on this model lead to the following conclusions:

- the maximum retardation time calculated from this model equals to $2\lambda_{\max}$, which is found using Eq. 2.6.12
- the dependence of apparent viscosity on shear rate is the same as the dependence of dynamic viscosity on frequency, $\eta'(\omega)$, assuming that shear rate equals frequency,⁴⁸ i.e., the theory predicts linear viscoelastic behavior with simultaneous shear-rate dependence of viscosity in shear flow
- as in any other molecular theory, all other relaxation times can be expressed by the maximum relaxation time, i.e., all relaxation modes are interrelated.

2.6.2 RELAXATION PROPERTIES OF CONCENTRATED POLYMER SOLUTIONS AND MELTS

The intermolecular interaction, which is certainly present in concentrated polymer solutions and melts, is simulated by friction of beads moving through a viscous medium in all models concerning individual chains. This may be insufficient in modelling relaxation properties of concentrated solutions and melts where every chain interacts with other long chains. There are several more or less realistic models which represent these cases.

2.6.2.1 Concept of entanglements

The concept of *entanglements* assumes that every long chain interacts with other chains, and it is necessary to account for restrictions to motion of an individual chain caused by

very dilute solutions (formally for infinitely dilute solutions), the use of “monodisperse” polymers, and the use of correct and unique measure of molecular interaction in such solutions. However, several very accurate experimental studies were carried out and they confirmed the principal conclusions of the model predictions.⁴⁵ If a “good” solvent is taken, the viscoelastic behavior of solution is described by a model of a free-draining chain, and if a “theta-solvent” is taken, the results of the measurements are much closer to predictions of the model of a non-drained chain.⁴⁶

2.6.1.3 Model of a rotating coil⁴⁷

A polymer molecule in a solution forms a

molecular movements of other chains. This idea was first introduced in the model of entangled ropes:⁴⁹ pulling one rope from a bundle inevitably leads to movement of all other ropes and the force of pulling depends on the length of ropes and their number. Though the idea of this approach was rather clear, quantitative predictions of theory were not so adequate.

Later, the idea of entanglements was developed on the basis of a model of a single free-draining chain, and subsequent principal steps were related to the law of frictions of the beads of a chain. There were numerous versions of the friction law, and some of the most popular are discussed below.

2.6.2.2 Two-part distribution of friction coefficient

The coefficient of friction, f , of beads moving in a viscous medium depends on the length of a chain. The law of friction was assumed to be as follows:⁵⁰

$$f = f_0 = \text{const} \quad [2.6.13a]$$

for short portions of a chain, where f_0 is the same constant as in the model of a free-draining chain, i.e., short segments of chain between entanglements are treated as free-draining chains, and

$$f = f_0(M/M_e)^{2.4} \quad [2.6.13b]$$

for long chains, where M is molecular mass of an entire chain and M_e is average molecular mass of a chain segment between equivalent entanglements.

The idea of increasing resistance to movement due to the presence of macromolecular entanglements is expressed in this model very clearly and leads to appearance of a spectrum of long relaxation times.

The power factor 2.4 is chosen arbitrarily because of the need to use a power law for the dependence of viscosity on molecular mass (it is well known that the universal rule $\eta \propto M^{3.4}$ is applicable – see Chapter 3).

Further development of this model can be found in many publications, and in particular in a model of two chains sliding at the points of junctions.⁵¹ The restriction to movement is due to interaction in some entanglement points, where the friction is determined by a new parameter of model – coefficient of sliding, δ . For a chemically cured network (with permanent crosslinks) $\delta = 0$; for free-draining chains moving independently from each other $\delta = 1$.

The concept of two-part relaxation spectrum is very useful and was explored in many other molecular models.

2.6.2.3 Non-equivalent friction along a chain

It is possible that the coefficient of friction of beads is changing along a macromolecular chain. The coefficient of friction distribution can also be represented by the following rule:⁵²

$$f = f_0 \frac{L}{N} (1 + |q|)^b \quad [2.6.14]$$

where L is the chain length, N is the number of entanglement points, q and b are constants determining the character of friction coefficient distribution along chain. The power factor

$b = 2.4$ is assumed to fit the standard viscosity vs. molecular mass dependence ($\eta \propto M^{3.4}$).

Other versions of the same approach were also discussed based on different distribution of the friction law along a chain.⁵³

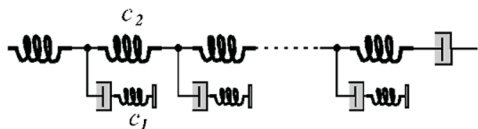


Figure 2.6.3. A model of viscoelastic interaction in an entanglement.

2.6.2.4 Viscoelastic entanglements

The basic idea in this approach is the assumption that a surrounding medium exerts (*via* entanglements) not only a viscous drag but an elastic resistance as well.⁵⁴ Each entanglement is treated by

means of a spring-bead interaction as shown in Fig. 2.6.3. The original model of such kind was proposed in some versions differing in magnitudes of elastic spring rigidity C_1 and C_2 .⁵⁵

This model predicts some interesting relationships between viscoelastic parameters of materials. The following expression for steady state (equilibrium) compliance, J_s^0 , gives a good correlation with experimental data:

$$J_s^0 = \frac{\alpha_1 E}{1 + \alpha_2 E} \quad [2.6.15]$$

where α_1 and α_2 are constants, and E is the number of entanglements per macromolecule, i.e., its value is proportional to the full length of a chain.

The model of viscoelastic junctions was developed in several publications.⁵⁶ It gives realistic predictions of the viscoelastic behavior of polymer melts.

2.6.2.5 Rubber-like network

It is reasonable to suppose that macromolecules form temporary junctions (entanglements) with different characteristic lifetimes and/or propensities to slide at these junctions. A portion of chain between two neighboring knots can be long enough to treat molecular movement of each portion as a free-draining chain, as discussed above. The junctions of chains can also be permanent. This is the case of cured rubber because no sliding occurs in crosslinks. In the other limiting case, chains are moving without “noticing” each other: this is a case of very dilute solutions. However, in numerous intermediate cases it is necessary to take into account interactions between macromolecules, which form temporary junctions. It is a case of concentrated solutions and melts.

The central equation of the model of rubber-like network is an expression for the concentration of junctions between two different chains a and b :⁵⁷

$$N(t - t') = \sum_{a, b} L_{a, b} e^{-(t - t')/\theta_{a, b}} \quad [2.6.16]$$

where $L_{a, b}$ is the rate of formations of junctions between chains a and b ; $\theta_{a, b}$ is the rate constant characterizing the breakdown of junctions; this constant can be treated as the characteristic relaxation time of the corresponding junctions. The argument of the function $N(t - t')$ is typical for all hereditary processes discussed in the theory of viscoelasticity.

The stresses acting on the network chains at each instance of time are proportional to the value of N changing with time. This is the reason why the memory function, entering

the constitutive equation, can have very different forms depending on the kinetic parameters of the model.

It is important that the values $L_{a,b}$ and $\theta_{a,b}$ are not specified in the original theory because it gives freedom of selection of these factors for fitting experimental data.

The initial version of the rubber-like network can be modified in different directions. It is possible to assume that the distance between neighboring junctions is not constant but described by Gaussian or some other distribution. It is also possible to suppose that the kinetics of formation and breakdown of knots depend on stress; this is a natural way for introducing non-linear effects in viscoelasticity.

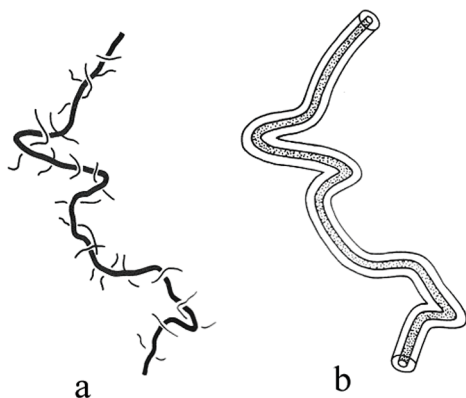


Figure 2.6.4. A “tube” (reptation) model.

chain backbone, creating strong resistance to movements at distances longer than the characteristic cross-section of a macromolecule. This can be represented by a slightly modified scheme as shown in Fig. 2.6.4b; this is a “tube” model.⁵⁸ The effect of topological constraints is similar to that of a macromolecule placed into a tube of the same configuration as the chain. According to this model it is assumed that the long range motions of a chain are allowed essentially along its own length only. This type of motion resembles a displacement of a snake and was called reptation, and the model is also called a *reptation model*.⁵⁹

Fig. 2.6.4b shows that the reptation model does not include special points of interactions (e.g., “beads”, as in some of the above mentioned models) but operates with characteristic dimensions: length of a chain, L , and the diameter of a tube, d . The reptation model considers two different relaxation processes – rapid with a characteristic time θ_e (“equilibration time”) which takes place inside a tube, and a characteristic time θ_d related to diffusion process of the tube renewal. Evidently, for long chains $\theta_d \gg \theta_e$. The model predicts the existence of two groups of relaxation times. For times $t < \theta_e$, relaxation processes are the same as in the model of an individual chain.

According to the initial version of the reptation model, the characteristic (terminal) relaxation time, θ_d , and viscosity are proportional to the cube of the molecular mass. This high value of the exponent reflects strong intermolecular interactions (entanglements), though even this exponent’s value is lower than the experimental value of the exponent close to 3.5.

2.6.2.6 “Tube” (reptation) model

Modern approach to the modeling of relaxation behavior of concentrated polymer solutions (and melts) also utilizes the concept of restriction of molecular movement of an individual chain due to intermolecular entanglements. However, the model represents these restrictions in a different way without localization of these entanglements. Fig. 2.6.4a shows a single macromolecule (solid line) and numerous other macromolecules which prevent its movement in the direction perpendicular to the

It was also shown⁶⁰ that the theory permits calculation of characteristic relaxation time, θ_d , using measured rheological parameters:

$$\theta_d = \frac{10}{\pi^2} \eta_0 J_s^0 \quad [2.6.17]$$

where η_0 is Newtonian viscosity and J_s^0 is the steady state (equilibrium) compliance.

The reptation model is the most widely used (in different modifications) for interpretation of experimental results in studies of viscoelastic properties of concentrated polymer solutions and melts. However, the predictions of theory, though they correctly reflect some principal features of relaxation properties of long-chain polymers, are more qualitative than quantitative. Possibly, it is due to some oversimplifications of the real molecular movements. In particular, the theory predicts a very narrow relaxation spectrum, while real relaxation spectra are much wider.

The attempts to improve the reptation model were based on the concept of “*double reptation*”⁶¹ or including the entanglements (in addition to a contour tube) as superimposing restrictions to molecular movements.⁶² It is known that the presence of long branching in a macromolecule leads to significant problems in the framework of a tube model, because reptations, as they are described in the basic model, become impossible. This special case of a tube model required further development and was discussed in the so-called “pom-pom” macromolecules.⁶³ It was shown that branching leads to some special features of viscoelastic properties, and it is especially important for extension.⁶⁴

2.6.2.7 Some conclusions

Summarizing the above discussion of molecular models, it is possible to make the following conclusions regarding numerous mechanical macromolecular models proposed for description of viscoelastic properties of concentrated polymer solutions and melts.

- all models are based on sets of mechanical elements, which can be joined in numerous arbitrary combinations; this allows one to vary theoretical predictions concerning experimentally observed functions; indeed, all models give a possibility to calculate viscoelastic properties, in particular $G'(\omega)$ and $G''(\omega)$ dependencies, which can be compared with experimental data
- relaxation spectra of concentrated solutions or melts are assumed to consist of the sum of two parts – rapid relaxation time, obeying the same distribution as for a free-draining chain, and a slow relaxation time distribution; the latter reflects the existence of intermolecular interactions (“entanglements”); any model includes some arbitrary (“free”) scaling parameters.

A complete molecular model should describe the following principal and general experimental facts, such as:

- viscosity depends on molecular mass (MM) as $\eta \sim MM^\alpha$, where α is of the order of 3.5
- existence of the plateau value, G_N^0 , on the frequency dependence of dynamic storage modulus, the length of this plateau depends on MM
- independence of steady state compliance on MM
- the empirical rule: $J_s^0 G_N^0 \approx 2$

- it is very desirable that the theory correctly predicts the frequency dependencies of G' and G'' in a wide frequency range.

2.6.3 VISCOELASTICITY OF POLYDISPERSE POLYMERS

Any molecular theory initially operates with molecules of equal length. But real polymers are polydisperse, i.e., all polymers are mixtures of molecules of different length and the latter is characterized by molecular-mass distribution (MMD).

About MMD

MMD is characterized by the function $w(M)$, where dw is the mass share of the fraction with molecular mass, MM , from M to $(M + dM)$. MMD, by its physical sense, is discrete because the values of MM change discretely. However, it is convenient to neglect this and to treat MMD as continuous due to small steps in argument of a distribution. In many cases, it is useful to operate with some average values of MMD:

$$\text{number-average MM: } \bar{M}_n = \int_0^{\infty} \frac{w(M)}{M} dM$$

$$\text{weight-average MM: } \bar{M}_w = \int_0^{\infty} w(M) dM$$

$$\text{z-average MM: } \bar{M}_z = \int_0^{\infty} Mw(M) dM$$

$$\text{z+1-average MM: } \bar{M}_{z+1} = \int_0^{\infty} M^2 w(M) dM$$

and so on. The lower boundary in these integrals is rather formal because MM cannot equal zero.

According to the tube model, the θ_d for monodisperse polymers is determined by Brownian motion (or diffusion) of a macromolecule as a whole. However, if a contour tube is formed by shorter molecules (as in a polydisperse polymer) the tube renewal happens in a shorter time scale and it provides an additional relaxation mechanism with relaxation times being different in comparison with θ_d .⁶⁵ It means that a relaxation spectrum of a polydisperse polymer is not a simple mixture of relaxation times of the fractions forming MMD of a polydisperse polymer.

The central problem, when passing from a monodisperse polymer to polydisperse samples, is in the construction of a “*mixing rule*”, i.e., formulation of a law of summarizing inputs of different fractions that will match observed viscoelastic properties. It relates to the integral constants, as well as to the relaxation spectrum itself.

The principal and applied interests were concentrated on the most easily measured parameters, such as Newtonian viscosity, η_0 , steady state compliance, J_s^0 , plateau modulus, G_N^0 , coefficient of normal stresses, Ψ , the crossover frequency, ω_c (the frequency at which $G' = G''$), curvature of a flow curve (see Chapter 3), and so on.

Numerous publications have proven that in viscosity calculations the following mixing rule is valid in many cases:⁶⁶

$$\eta_0 = K \bar{M}_w^\alpha \quad [2.6.18]$$

where the scaling parameter, α , is commonly accepted as $\alpha = 3.4 - 3.5$, though it is possible to meet other values, from 3.2 to 3.9. The presence of low-MM fractions and branching affects the value of α . The pre-factor K depends on the molecular structure and temperature, and it is not a subject of this discussion.

This equation is assumed to be valid for high-molecular mass polymers, where the whole MMD lies above some critical value of MM, M_c .

A very impressive illustration of the $\eta_0(\bar{M}_w)$ dependency is shown in Fig. 2.6.5 and some other examples are presented in Chapter 3 (Fig. 3.3.2) and in Chapter 6 (Figs. 6.2.1 and 6.2.2). Numerous experimental data show that, in many cases, Eq. 2.6.18 is valid in changing viscosity by 6-8 decimal orders. However, corrections to Eq. 2.6.18 are sometimes needed. More general equation for (MM, MMD) looks as follows⁶⁷

$$\eta_0 = K \bar{M}_w^\alpha \left(\frac{\bar{M}_w}{\bar{M}_n} \right)^b \left(\frac{\bar{M}_z}{\bar{M}_w} \right)^c \quad [2.6.19]$$

where $b \approx 0.24$; $c \approx 0.44$.

Steady state compliance, J_s^0 , depends primarily on higher average MM. The following equation is commonly used:⁶⁸

$$J_s^0 = k \frac{\bar{M}_{z+1} \bar{M}_z}{\bar{M}_w \bar{M}_n} \quad [2.6.20]$$

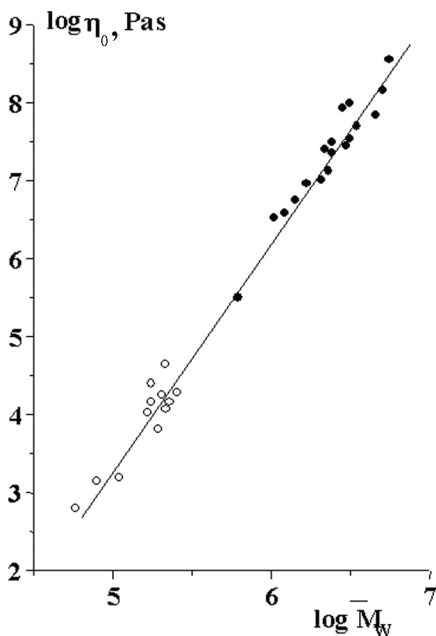


Figure 2.6.5. Viscosity-MM dependence for polyethylenes. The unfilled circles refer to the data taken from literature. The filled circles are the original data of the author of the publication. [Adapted, by permission, from M.T. Shaw, *Polym. Eng. Sci.*, 17, 266 (1977)].

where k is an empirical constant.

Many publications support the existence of strong dependence of steady state compliance on higher average values of MMD. These two examples (for viscosity and steady state compliance) demonstrate that different rheological parameters depend mainly on various average values of MM. It is rather difficult to expect that some very general law of mixing can be easily written, and formulation of the rule of mixing is still a serious challenge to molecular theories of polydisperse polymers.

It is also worth mentioning that the experimental curves of monodisperse polymers are quite smooth. The same is true for the majority of industrial polydisperse polymers. However, from the experience with the mixtures of two monodisperse polymers as a model of polydisperse sample, it appears that both fractions behave – to some extent – as independent, and sometimes it is possible to suspect that they are not completely miscible. Then, the relaxation properties of both fractions are separated as in Fig. 2.6.6 and give clear separate peaks. The short relaxation side of the spectrum

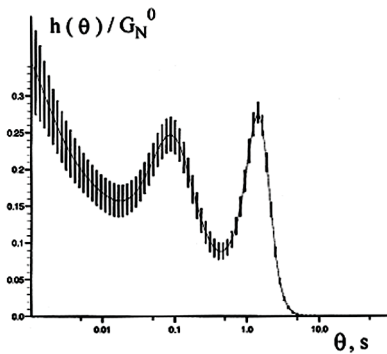


Figure 2.6.6. A logarithmic relaxation spectrum (normalized by the plateau modulus, G_N^0) of the mixture of two monodisperse polystyrene samples: 80% of polymer with $M=177 \cdot 10^3$ and 20% of a polymer with $M=60 \cdot 10^3$. Bars show possible errors of calculations. [Adapted, by permission, from W. Thimm et al., *J. Rheol.*, **44**, 429 (2000)].

seems the same for both fractions. Then, it is reasonable to think that the smooth spectrum of polydisperse polymers is a consequence of superposition of numerous peaks responsible for each fraction.

The mixing rules for polydisperse polymers discussed in modern literature⁶⁹ are based on some molecular model arguments. They are usually obtained empirically and confirmed in experiments made with a rather limited number of polymers. Though there is some degree of independence in the rheological behavior of fractions in a mixture, it is commonly assumed that relaxation properties of fractions entering a mixture are modified as a result of intermolecular interaction. A rather general form of the mixing rule, which reflects this phenomenon, was formulated for a relax-

ation function, $G(t)$, in the following form:⁷⁰

$$\frac{G(t)}{G_N^0} = \left(\int_0^\infty F^{1/\beta}(t, m) \frac{w(m)}{m} dm \right)^\beta \quad [2.6.21]$$

where $m = M/M_0$ is reduced MM, M_0 is MM of a monomer unit in a polymer chain, $m_e = M/M_e$ and M_e is average MM between two neighboring entanglements. This value is found as:

$$M_e = \frac{\rho RT}{G_N^0} \quad [2.6.22]$$

and G_N^0 is the plateau modulus value, ρ is the density, R is the universal gas constant, and T is the absolute temperature.

The function $F(t, m)$ in Eq. 2.6.21 reflects the effect of mixing and the scaling factor originates from a molecular model of mixing: for the reptation model $\beta = 1$ ("linear mixing rule") and for a model of double reptation $\beta = 2$ ("quadratic mixing rule"). In some publications, a model combining linear and quadratic mixing rules was also discussed.⁷¹

The central point of the formulation of the mixing rule is the form of the kernel $F(t, m)$ reflecting the mutual influence of different fractions in a polydisperse polymer.⁷² Based on very accurate experimental data for polystyrene and statistical comparison of different kernels it was found⁶⁹ that the best fit can be achieved with $\beta = 3.84 \pm 0.1$ and the kernel represented by:

$$F(t, m) = e^{-t/\theta_0(m)} \quad [2.6.23]$$

where the maximum (terminal) relaxation time θ_0 is related to MM by the standard scaling law:

$$\theta_0 = km^\alpha \quad [2.6.24]$$

and the scaling exponent $\alpha \approx 3.5$ (more exactly, for polystyrene $\alpha = 3.67$).

This mixing rule (with β close to the standard value of 3.5) is more realistic than the theoretical values of β (1 or 2), because it directly connects with a natural rule of mixing in calculating viscosity through \bar{M}_w as in Eq. 2.6.18. Viscosity is calculated from

$$\eta_0 = [w(M_i)M_i^{1/\alpha}]^\alpha \quad [2.6.25]$$

It is worth mentioning that the final results of calculations, at least in cases of some polymers with moderately wide MMD, show that viscosity is not very sensitive to the choice of the scaling factor (3.5 or another). It is also difficult to verify which coefficient is correct.⁷³

The high value of the scaling factor (~ 3.5) in comparison with the lower theoretical value (1 or 2) may be explained by difficulties in estimation of the relaxation spectrum responsible for slow relaxation processes.⁷⁴ Eq. 2.6.21 includes relaxation modes for fractions with $m > m_e$ only. A measured relaxation spectrum includes all types of molecular movements and can be treated as consisting of two parts: for $m < m_e$ and $m > m_e$. Then, the whole spectrum, $F(\theta)$, is a sum:

$$F(\theta) = F_{\text{entangl}}(\theta) + F_{\text{rapid}}(\theta) \quad [2.6.26]$$

Only the first part (entanglement effect) is used in Eq. 2.6.21, but not the second term that reflects the rapid molecular movements occurring between neighboring links. It was shown⁷³ that the scaling factor in Eq. 2.6.21 appears close to 2 if rapid molecular movements are included, as predicted by the double reptation (entanglement) model.

The concept of relationship between MMD and relaxation properties of polymer is viewed from two perspectives. First is a mixing rule, which permits calculation of viscoelastic properties of polydisperse polymers. The solution is hidden in Eq. 2.6.21 with appropriate choice of exponent β and kernel $F(t, m)$. Second is determination of MMD based on the results of rheological measurements made in the range of linear viscoelastic behavior. It is not important whether relaxation curve or frequency dependence of dynamic moduli are used for this purpose.

It is also necessary to find function $w(m)$ included in Eq. 2.6.21, i.e., from a mathematical point of view to solve the first kind of the Fredholm integral equation.

Some necessary preliminary steps are required in this method. First of all, a mixing rule must be known, i.e., the kernel should be written in an analytical form and the scaling factor β selected. Different types of kernel are used. From a practical point of view it may not be important which kernel is selected. Usually, the simpler it is, the more convenient it is to make calculations, but even complicated forms can be handled by modern computer techniques). Then, it is necessary to formulate how MMD will be determined.

The first task involves determination of the MMD parameters, assuming that its shape is known *a priori*. The function $w(m)$, is substituted into Eq. 2.6.21 and the results of calculations are compared with experimental data. The MMD parameters are fitting factors found by standard procedure. In industrial synthesis, the shape of MMD is determined by the process chemistry. Studies usually follow changes in MMD caused by varia-

tion of technological conditions. Finding MMD of an unknown sample is more complex. More reliable results are obtained from unimodal MMD, i.e., MMD has a single maximum. However, some multi-modal materials MMD are prepared and used for technological applications and laboratory experiments and these materials are difficult to study.

Based on Eq. 2.6.21 the following analytical equation was obtained,^{69,73} which helps to determine MMD using measured relaxation spectrum:

$$w(M) = \frac{1}{\beta} \left(\frac{\alpha}{G_N^0} \right)^{1/\beta} h_{\text{ent angl}}(m) \left[\int_{m_e}^{\infty} \frac{h_{\text{ent angl}}(m')}{m'} dm' \right]^{\frac{1}{\beta}-1} \quad [2.6.27]$$

where $h_{\text{ent angl}}$ is a logarithmic relaxation spectrum related to the entanglement relaxation modes only, i.e., obtained as written in Eq. 2.6.25 after extraction of part related to rapid relaxation processes, m' is a variable of integration, and M is molecular weight. The spectrum $h_{\text{ent angl}}$, as a function of m , is determined in the following way

$$h_{\text{ent angl}}(m) = h_{\text{ent angl}}[\theta(m)] \quad [2.6.28]$$

in accordance with Eq. 2.6.24. All other constants entering this equation are the same as above. The relaxation spectrum used for calculations related to the molecular mass is in the range of $m > m_e$.

An example of final results of MMD calculations is shown in Fig. 2.6.7. The rheological method gives realistic behavior of MMD including positions of peaks for bimodal samples. The correspondence between MMD and relaxation properties of a sample does exist.

2.7 TIME-TEMPERATURE SUPERPOSITION. REDUCED (“MASTER”) VISCOELASTIC CURVES

2.7.1 SUPERPOSITION OF EXPERIMENTAL CURVES

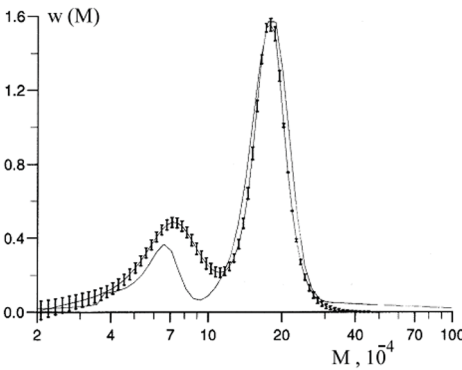


Figure 2.6.7. Results of calculation of MMD (bars show the limits of errors of calculation) in comparison with experimental data (solid line found by chromatographic method). The same sample as in Fig. 2.6.6. [Adapted, by permission, from W. Thimm et al., *J. Rheol.*, **44**, 429 (2000)].

In real experimental or technological practice, frequency dependence of elastic modulus can be measured for a limited frequency range because of limitations of experimental techniques. Let the frequency be from ω_1 to ω_2 . This range is sometimes called an experimental window. Measurements can be carried out at different temperatures. The experimental data for a linear high-molecular mass polymer are presented by a set of curves, as shown in the vertical column on the left side of Fig. 2.7.1. The curves 1-2, 3-4,..., 15-16 relate to different temperatures decreasing from lower to upper curves. The curves in the column might have some practical interest, but they do not show a broader picture.

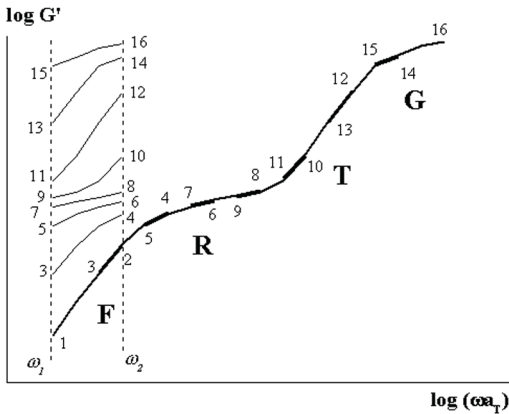


Figure 2.7.1 An example of experimental dependencies of $G'(\omega)$ measured at different temperatures (vertical column at the left part of the figure) and construction of the reduced (master) curve of dependence $G'(\omega)$ in the wide frequency range. Qualitative illustration.

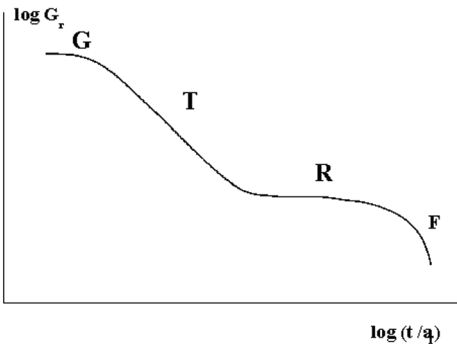


Figure 2.7.2. Relaxation modulus as a function of a reduced time. Qualitative illustration.

the master curves by the same numbers as those used at the ends of the initial curves. For an illustration, the overlapping portions of neighboring curves are shown by doubled lines (they would not superimpose completely, but, in fact, the points of both curves lie on the same curve).

An analogous curve for relaxation modulus is shown in Fig. 2.7.2. The characteristic zones (domains) of viscoelastic behavior are marked in these curves. Their explanation can be found below.

It is assumed that the reduced curve has the same shape in the whole temperature range, though changing the temperature of reduction, or *reference temperature*, leads to shift of the curve along the $\log \omega$ scale. Temperature dependence of this shift is expressed by the function $\log a_T(T)$.

They do not represent the general picture of frequency dependence on the modulus, because the frequency range from ω_1 to ω_2 is narrow. An interesting question arises as to what happens with a modulus beyond the experimental window.

It was noticed that the time (or frequency) dependencies of viscoelastic properties, measured at different temperatures, are similar in their shape though shifted along the time (frequency) axis.⁷⁷ In practice, it is sufficient to see that the boundary parts of curve are similar, and then it is assumed that the whole curve should be similar too. Then, it is reasonable to suspect that each curve can be

extended beyond the range of its real measured values with conservation of the shape which is general for all curves. In this approach it is supposed that each curve is shifted along the frequency scale and the distance between the curves, a_T , depends on temperature.

Based on this concept the initial (experimental) curves can be *superimposed* by shifting all curves to one arbitrarily chosen as the base curve. The resulting *reduced* (or *master*) curve⁷⁸ is shown in Fig. 2.7.1 by a solid line and the position of initial curves are marked along

This master curve is related to the reduction temperature (which is the largest of the examined intervals in the example under discussion). The method permits us to obtain the viscoelastic curves in the frequency range which is much wider than the experimental window of initial experimental curves. The reduced curve contains more information than any initial curve obtained at a single temperature. It is now a standard method of treating experimental data obtained at different temperatures but with the narrow frequency (time) windows.

The method of reduced variables helps to exceed direct experimental capabilities of any measuring device. Frequency (or time) dependence of any viscoelastic function can be obtained for a broader range.

From the beginning of application of the method of reduced variables, it was recognized that shifting viscoelastic curves is based on the concept of the same temperature dependence of all relaxation times of material. This can be illustrated by an example of relaxation spectrum for an individual macromolecular chain. Let the frequency dependencies of $G'(\omega)$ and $G''(\omega)$ be described by Eq. 2.3.10 and the distribution of relaxation times as per Eq. 2.6.6. Then, after substitution, the following equations can be obtained:

$$G'(\omega) = \sum_{n=1}^M G_n \frac{(\omega\theta_n)^2}{1 + (\omega\theta_n)^2} = \sum_{n=1}^M G_n \frac{(\omega\theta_{\max})^2}{n^2 + (\omega\theta_{\max})^2} \quad [2.7.1a]$$

$$G''(\omega) = \sum_{n=1}^M G_n \frac{(\omega\theta_n)}{1 + (\omega\theta_n)^2} = \sum_{n=1}^M G_n \frac{n(\omega\theta_{\max})}{n^2 + (\omega\theta_{\max})^2} \quad [2.7.1b]$$

(In these equations the dummy index, i , used in Eq. 2.3.10, is changed to n , in order not to confuse the index with the imaginary unit).

It is immediately seen that G' and G'' are the functions of the single dimensionless argument, $\omega\theta_{\max}$, and temperature dependence of modulus is completely described by the temperature dependence of the relaxation time θ_{\max} . Then, the frequency dependencies of G' and G'' measured in a wide temperature range as a function of the dimensionless argument ($\omega\theta_{\max}$) should form a single master curve.

Frequency can be replaced by time with the same argumentation and the single dimensionless argument in this case is (t/θ_{\max}) . The same conclusion concerning construction of a general master curve from the experiments performed at different temperatures is true for any viscoelastic curve – creep, relaxation, etc. It is also true of a relaxation spectrum itself, which can be treated as a function of the single reduced parameter (θ/θ_{\max}) .

Above, it was tacitly assumed that the coefficient G_n does not depend on temperature. This is not correct. This parameter is proportional to the factor ρT , where ρ is density and T is the absolute temperature. It is necessary to introduce a factor of vertical shift equal to $\rho T/\rho_0 T_0$. The values with zero-index are related to a reference temperature. The origin of this correction factor is explained in the theory of rubbery elasticity because the value G_n has a meaning of rubbery modulus of material in extension (compare with Eq. 2.6.22 rearranged for G_N^0). However, this correction factor is small and becomes important only in the domain of rubbery behavior of polymeric material where the frequency dependence of modulus is rather weak.

The construction of the master curve is based on the following general assumptions: all relaxation times are characterized by the same temperature dependence (possibly due to the common mechanism of material relaxation) and it is possible to neglect the temperature correction factor for G_n . Then, it is reasonable to suppose that the opposite conclusion is also valid: temperature superposition becomes impossible if different temperature dependencies exist for various relaxation times, or there are different relaxation mechanisms characterized by various temperature dependencies. The latter conclusion is the general principal limitation of application of the method of frequency (time) superposition.

Numerous experimental evidences confirm that the time superposition method is valid for linear polymers and their solutions but the method is not valid in the following cases:

- mixtures of different polymers characterized by their own relaxation spectra with their own temperature dependences of relaxation times
- branched polymers: relaxation processes in long branches can be different than in the backbone chain
- materials with inherent supermolecular structure, which can change with changing temperature
- block copolymers
- materials with properties changing with time (during an experiment), for example because of slow chemical reactions.

One must be careful in applying the superposition method to unknown materials because doubt is always there as to whether the master curve reflects the physical reality in the very wide frequency range. New relaxation mechanisms may appear at very low or very high frequencies.

The temperature shift factor, a_T , is a function of current temperature, T , and the reference temperature, T_0 . Using the definition of viscosity as the integral measure of a relaxation spectrum, it is easy to show that a_T can be calculated as the ratio of viscosities at temperatures T and T_0 :

$$a_T = \eta(T)/\eta(T_0) \quad [2.7.2]$$

Temperature dependence of viscosity can be expressed by any standard method, in particular by the Arrhenius equation:⁷⁹

$$\frac{\eta(T)}{\eta(T_0)} = \exp \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad [2.7.3]$$

where E_a is an activation energy of the relaxation processes (and viscous flow), T_0 is some arbitrary chosen reference temperature, and R is the universal gas constant.

The Williams-Landel-Ferry (WLF) equation is another popular expression of temperature dependence of relaxation times:⁸⁰

$$\log a_T = \frac{-C_1^0(T - T_0)}{C_2^0 + (T - T_0)} \quad [2.7.4]$$

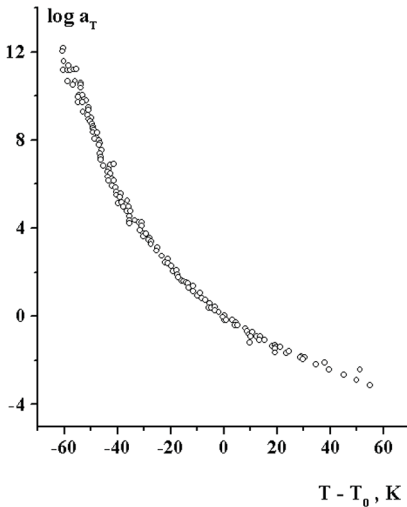


Figure 2.7.3. Temperature dependence of relaxation times, expressed as the ratio of relaxation times as a function of temperature difference according to the Williams-Landel-Ferry. Points present experimental data for 17 different polymeric systems.

It is interesting to notice that $T_0 \approx T_g + 50$ (T_g is the glass transition temperature), then, for many polymers, C_1^0 and C_2^0 are universal constants having the following values: $C_1^0 \approx 7.60$ and $C_2^0 \approx 227.3$.

The classical illustration of the $\log a_T$ dependence on temperature decrement, reproduced in many editions, is presented in Fig. 2.7.3. The average line that is drawn through these points is described by the WLF equation with the universal values of the constant. The relationship is true for an enormous range of 16 decimal orders of a_T values.

Using any of these equations, it is easy to see that by changing the temperature it is possible to vary a_T , and consequently the reduced time (frequency) by many decimal orders. It allows one to broaden the range of the argument up to 10-15 decimal orders. Such results cannot be obtained by direct measurements but only by the method of reduced variables. Direct experiments in a narrower frequency range, carried out for different polymer materials by many authors, confirmed that the superposition gives realistic data coinciding with those obtained by direct measurements.

The dependence of relaxation modulus in reduced variables (in this case, it is reduced time scale) is similar to the frequency dependence of a dynamic modulus, but it is a mirror reflection of the latter (compare the curves in Figs 2.7.1 and 2.7.2). Curves of both types contain the same physical information on viscoelastic properties of materials under investigation.

Experimental data for “almost” monodisperse (polymers with very narrow MMD) polybutadiene sample, presented in form of master curves, are given in Fig. 2.7.4 for $G'(\omega)$ and $G''(\omega)$. This figure shows the relative position of the components of dynamic modulus as well as the existence of a “cross-over” point – the frequency at which $G' = G''$. The second important example based on real experimental data is presented in

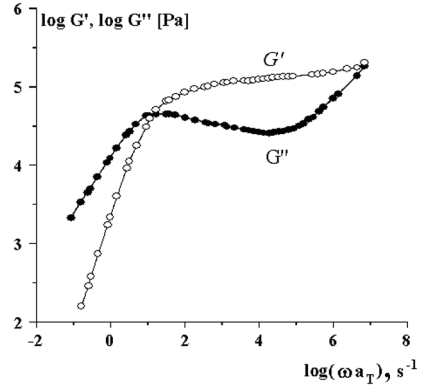


Figure 2.7.4. Frequency dependencies of the dynamic storage and loss moduli reduced to 28°C. Initial experimental data were obtained in the temperature range from -70 to 28°C. Sample is a monodisperse polybutadiene, $M = 9.7 \cdot 10^4$. [Adapted, by permission, from M. Baumgaertel et al., *Rheol. Acta*, **31**, 75 (1992)].

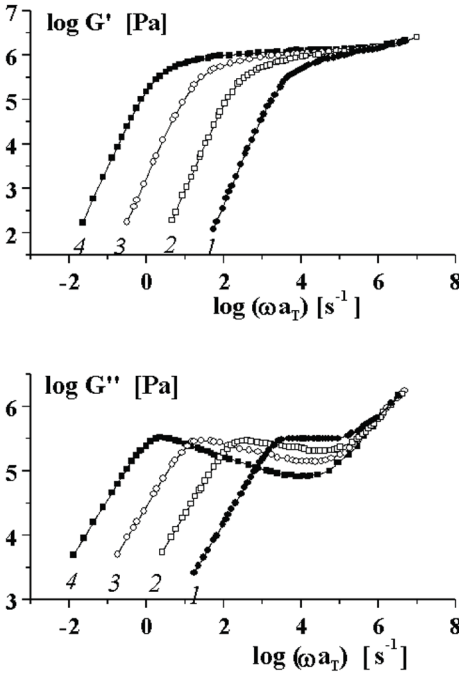


Figure 2.7.5. Frequency dependencies of the dynamic storage and loss moduli reduced to 28°C for monodisperse polybutadienes of different MM: $2.07 \cdot 10^5$ (1); $4.41 \cdot 10^5$ (2); $9.7 \cdot 10^5$ (3); $20.1 \cdot 10^5$ (4). Initial experimental data were obtained in the temperature range from -70 to 28°C. [Adapted, by permission, from M. Baumgaertel et al., *Rheol. Acta*, **31**, 75 (1992)].

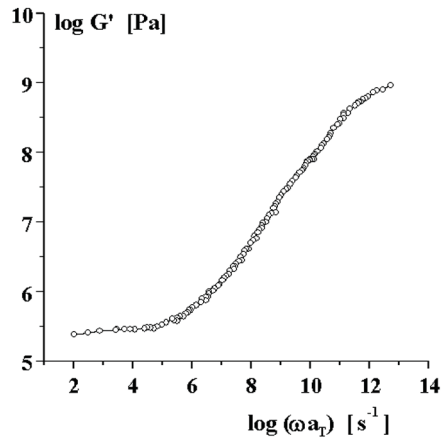


Figure 2.7.6. Frequency dependence of dynamic storage modulus in the transition zone (from rubbery to glassy state) for NBS polyisobutylene at a reference temperature of 25°C. [Adapted, by permission, from E. Catsiff, A.V. Tobolsky, *J. Colloid Sci.*, **10**, 375 (1955)].

Fig. 2.7.5 for the dependencies $G'(\omega)$ and $G''(\omega)$ related to the homologous series of polymers – materials having identical structure but with different chain lengths. These curves demonstrate the influence of MM on the range of frequencies where relaxation phenomena are observed.

Analogous experimental data were observed and published for various polymers and they form the basis for general conclusions concerning physical properties of polymeric materials. These conclusions are summarized in the following section.

2.7.2 MASTER CURVES AND RELAXATION STATES

Qualitative curves, as well as the results of experimental observations, show that there are several typical and very general features of the viscoelastic curves.

First of all, there are four characteristic domains (or zones) on the viscoelastic curves, designated by the letters F, R, T and G on the curves of Figs. 2.7.1 and 2.7.2. Real experimental data presented in Figs 2.7.4 and 2.7.5 show that only F and R zones and the transition to the T zone can be observed, even in the frequency range covering 9 decimal orders. However, other experimental data for different polymeric samples are shown in Fig. 2.7.6. These data can be treated as supplementary to Figs 2.7.4 and 2.7.5, because they start from the same level of modulus as in Figs 2.7.4 and 2.7.5. The curve in Fig. 2.7.6 covers the R, T and initial portion of G zones. These domains spread over 12 decimal orders of frequency.

Combining experimental data of these figures, one can see the full range of relaxation covering about 20 decimal orders of frequency and a range of modulus from 10^2 to 10^{10} Pa. Based on real numerical values of the storage modulus, the physical sense of different domains, marked in Figs 2.7.1 and 2.7.2 as F, R, T and G is given below.

F – is a flow zone. In the frequency range corresponding to this domain a material is treated as liquid. Storage modulus is considerably small ($G' \ll G''$). In the limiting case (at $\omega \rightarrow 0$) $G' \propto \omega^2$ and $G'' \propto \omega$, and it corresponds to the relaxation process determined by the maximum relaxation time, θ_{\max} . The relaxation processes in this zone is governed by the chain movement as a whole as described by the reptation model and the model of entanglements, as discussed in section 2.6.

R – is a rubbery zone. In the frequency range corresponding to this domain, material behaves like rubber. For rubbers and rubber-like materials, storage modulus is constant and its plateau value lies between 10^5 – 10^7 Pa, depending on the chain rigidity. The transition from F to R zone is arbitrary and can be attributed to the maximum of G'' or the cross-over frequency. For real rubbers (cured polymers with permanent network of chemical bonds) the F zone disappears and the R zone, corresponding to equilibrium storage (rubbery) modulus, continues to unlimited low frequencies, formally to steady (or equilibrium) state of deformations. Adding solvent to a rubbery material (plasticization) decreases the plateau values of the modulus, and adding of a solid filler increases its value.

Relaxation process in the R zone cannot be observed, even in the wide time interval (as seen from plateau of relaxation modulus in Fig. 2.7.2). It is interesting to mention that the influence of the length of molecular chain is important in the F zone only. The transition from F to R zone also depends on MM. The position of the $G''(\omega)$ dependence in the F zone is determined by viscosity and therefore it is proportional to $M^{3.5}$. It is seen (Fig. 2.7.5) that the plateau end in the high frequency region does not depend on MM. It is easily proven that the plateau width is proportional to $M^{3.5}$.

T – is a transition zone. In the frequency range corresponding to this domain, properties of material, determined by its modulus, resemble leather materials and therefore this zone is sometimes called the leather-like zone. It is a wide domain (Fig. 2.7.6) and relaxation properties here are determined by small-scale molecular motions of the portion of chains between entanglements. It is a different relaxation mechanism than in the F and R zones and, possibly, their temperature dependencies may be different. Therefore, it is necessary to be careful in applying the superposition method over all relaxation states of a material.

G – is a glassy zone, and the behavior of material at very high frequencies resembles the deformation of glass. It is reflected by the high values of the modulus (about 10^9 – 10^{10} Pa) characteristic for inorganic and organic glasses and independent of the modulus values on frequency, i.e., it is possible to think that frequencies in this domain are so high that all relaxation processes are absent.⁸¹

The main and principal conclusion obtained from application of the time (frequency)-temperature superposition method consists of a statement that the same values of modulus can be reached by changing either temperature or frequency. It means that the question: what is the state of this material? must be substituted by another, more accurate question: how does material behave under these conditions (frequency)?, i.e., at the fixed temperature the same material can behave in very different manner either like liquid (at

very prolonged intervals of observation or at very low frequencies), like a rubber (if duration of observation or frequency corresponds to the rubbery plateau), like a leather (if frequency is positioned in the glass transition zone), or like a glass (if frequencies are very high).

This conclusion is very important for numerous applications of viscoelastic polymeric materials, because their properties can be estimated in one frequency domain and the application can be related to quite different conditions. Then, one may encounter such effects as glassy behavior of rubber articles – they break as fragile material at high frequencies, a behavior not expected from rubbers (for example, aircraft tires at high speed of landing in winter may break due to high frequencies of glassy state deformation, though they are safe at the same temperature based on the result of a static or low frequency experiment). Polymer melts at high shear rates cannot flow, due to forced transition into rubbery state (see section 3.6).

The success of application of the time-temperature superposition method in numerous examples urged investigators to propose an analogous method for various phenomena. For example, time of aging depends on temperature. Then, it was proposed to accelerate the experiments of aging by temperature increase and extrapolating results of such experiments to lower temperatures as a basis for predicting material behavior for long periods of time at lower temperatures. The acceleration of relaxation processes can be reached by adding a solvent; then the results of experiments with polymer-solvent systems are used for predicting the behavior of materials at other concentrations of a solvent or without it (this is a method of time-concentration superposition), and so on. Sometimes, this approach gives quite positive and useful results. However, this is not a universal method and one ought to be sure that the method of superposition used reflects the physical effects caused by relaxation phenomena.

Generally speaking, it is a dangerous practice to extend any of these methods for predicting beyond more than, say, one decade of time.

2.7.3 “UNIVERSAL” RELAXATION SPECTRA

There were a number of attempts to propose some “universal” functions for describing viscoelastic properties (primarily, a relaxation spectrum). The main difficulty in approximation of real experimental data is caused by the polydisperse nature of real polymers. In reality, then, the relaxation spectrum of polydisperse material is achieved by superposition of relaxation properties of different fractions. This means that no “universal” spectrum exists for polymer with arbitrary MMD because polymers with different MMD are different materials.

Indeed, one meets with two separate problems: describing relaxation properties of individual fractions and combining these properties in their mixing. This problem is discussed in section 2.6 based on molecular models of relaxation properties of a polymer chain.

It is necessary to divide the general problem of searching a relaxation spectrum into two parts. First, these are relaxation properties in the F and R zones and second in T zone.

All these problems are actively discussed in modern rheological literature, because their solution gives a chance to find general methods for calculating viscoelastic properties of real polymeric materials. Existing molecular models do not give a realistic (close to an experiment) representation of the relaxation spectrum, even for a monodisperse poly-

mer. That is why it is important to propose at least an empirical approximation to experimental data.

Concerning monodisperse polymers, the general solution was proposed for relaxation behavior in the F and R zones.⁸² This “universal” relaxation spectrum is described by the function:

$$G(\theta) = G_0 \left[\left(\frac{\theta}{\theta_0} \right)^{-n} + \left(\frac{\theta}{\theta_{\max}} \right)^m \right] \quad [2.7.5]$$

where G_0 is constant, m and n are empirical parameters of a spectrum, and θ_0 and θ_{\max} are minimum and maximum boundary values of relaxation spectrum for F and R zones.

The relaxation spectrum in the T zone is regarded as caused by movements of short portions of a macromolecular chain. In the first approximation, these movements can be described by the spring-and-bead model (see section 2.6).

The problem of summation of inputs of relaxation properties of different fractions into a relaxation spectrum of polydisperse polymers is also discussed in section 2.6. However, it is worth mentioning that at the moment this problem is far from a clear understanding and quantitative description.

In conclusion to this section, it is worth mentioning that many relaxation properties of polymers are successfully treated in the framework of some “universal” equations. For example, it is true for temperature dependence of relaxation times (Eq. 2.7.4), “universal” form of a relaxation spectrum (Eq. 2.7.5), regardless of the chemical nature of a polymer chain. It is reasonable to suspect that it is not coincidental but it reflects the basic peculiarity of relaxation properties of polymers: movement of long flexible chains interacting with their surrounding; in this concept the primary role is played by geometrical restrictions to the Brownian movement, and in the first approximation, these restrictions do not depend on details of the chemical structure of a chain.

2.8 NON-LINEAR EFFECTS IN VISCOELASTICITY

2.8.1 EXPERIMENTAL EVIDENCES

There is ample experimental evidence, which clearly demonstrates that all concepts discussed in the previous section are related to the limiting cases of low deformations (or low deformation rates). The increase of deformation or deformation rate immediately leads to non-linear effects which are characteristics of all real technological materials. Thus, the linear viscoelastic behavior should be considered as the limit of generalization of viscoelastic properties.

Below, the principal experimental evidences of non-linear behavior of viscoelastic materials are discussed.

2.8.1.1 Non-Newtonian viscosity

Viscosity appears in the linear theory of viscoelasticity as the first moment of a relaxation spectrum, according to Eq. 2.5.12. By this definition, it is expected that viscosity is constant, i.e., does not depend on shear rate or stress. This regards Newtonian viscosity according to the definition of Eq. 2.1.1. However, it is well known (and this is one of the basic effects of rheology) that viscosity of numerous liquids is not constant but depends on conditions of flow such as shear rates, $\eta(\dot{\gamma})$, or shear stresses, $\eta(\sigma)$. This effect is known

as non-Newtonian behavior of liquids. Non-Newtonian flow is a non-linear effect not described within the framework of the linear theory of viscoelasticity.

The theoretical and applied meaning of non-Newtonian behavior of liquids is complex. Therefore, a separate chapter of this book is devoted to non-Newtonian flow and these effects are further discussed in Chapter 3.

The same is valid for the coefficient of normal stresses, determined in the theory of viscoelasticity as the second moment of a relaxation spectrum. According to Eq. 2.5.14, the coefficient of normal stresses is also a material constant. However, this is not true for all real viscoelastic liquids. In fact, the coefficient of normal stresses depends on shear rate, $\Psi_1(\dot{\gamma})$. This non-linear phenomenon will be discussed in more detail in Chapter 3, along with viscosity.

2.8.1.2 Non-Hookean behavior of solids

According to the linear theory of viscoelasticity, the elastic modulus depends on time (or frequency), but not on stress or deformation. In fact, the elastic modulus of many real materials depends on deformation in static conditions (regardless of time effects). This non-Hookean behavior is a main non-linear phenomenon characteristic of solids. This is of fundamental significance for rheology and non-linear elastic behavior of solids is discussed in Chapter 4.

2.8.1.3 Non-linear creep

The creep function in the linear viscoelasticity limit is, by definition, independent of stress. But the real behavior of mechanical properties of material is more complex. A typical and general example of mechanical behavior of viscoelastic behavior of material at different constant stresses is shown in Fig. 2.8.1 by creep functions (ratios of deformation to stress applied), $\psi(t)$. At low stresses, σ_1 in this example, the limit of $\psi(t)$ at $t \rightarrow \infty$ exists. The same creep function (in the limits of experimental errors) is observed for the

range of low stresses, at least at $\sigma < \sigma_1$. This is the linear limit of viscoelastic behavior of material.

The increase of stress results in deviation from the linear limit, and at stress σ_2 the creep function grows approximately linearly in time, i.e. the *stationary* regime is observed. At higher stresses, σ_3 , deformation increases with acceleration; this is an *unsteady* regime of creep, which ends with rupture of the sample.

It is interesting to mention that in the initial part of deformations all curves coincide, i.e., at low deformations (or at times shorter than some “critical” value t^*) the behavior of material at any stress is linear.

It is seen from the scheme in Fig. 2.8.1, that this critical time t^* depends on the applied stress. Real experimental data

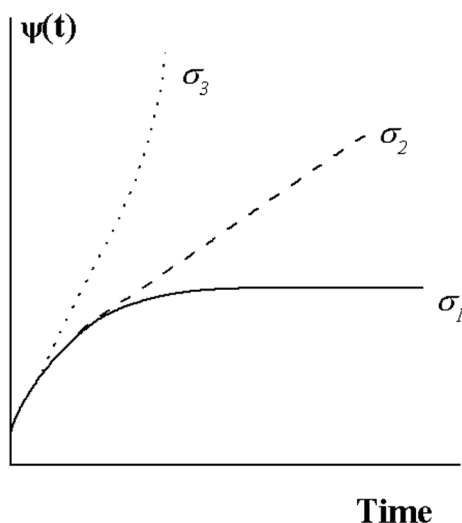


Figure 2.8.1. Creep function at different stresses ($\sigma_1 < \sigma_2 < \sigma_3$). Qualitative picture.

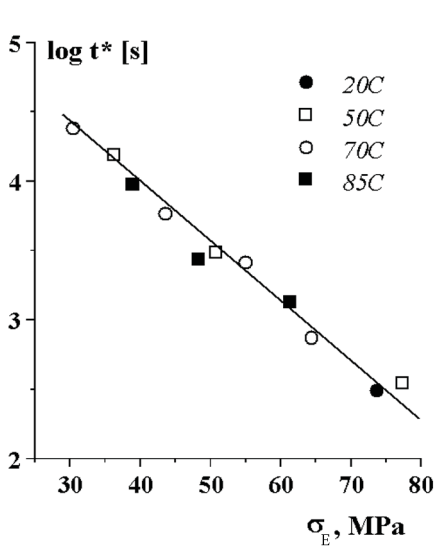


Figure 2.8.2. Dependence of the “critical” time corresponding to the limit of linear viscoelastic behavior on stress in extension of polycarbonate at different temperatures. [Adapted, by permission, from A.Ya. Malkin, A.E. Teishev, M.A. Kutsenko, *J. Appl. Polym. Sci.*, **45**, 237 (1992)].

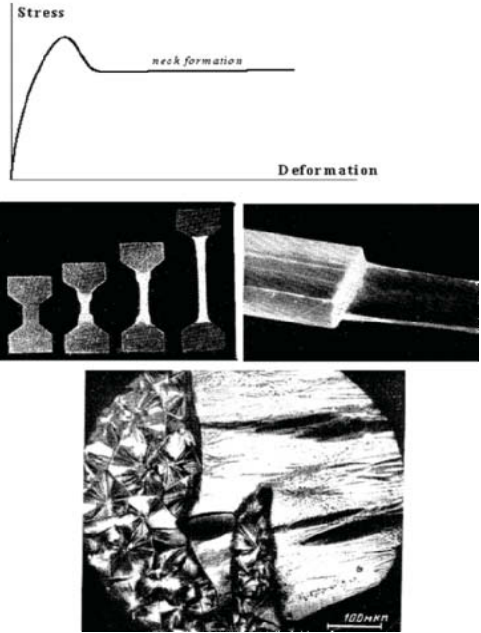


Figure 2.8.3. Neck formation at the transition from isotropic to oriented state of a polymeric material (lower photograph was made by G.P. Andrianova).

illustrating this dependence are shown in Fig. 2.8.2 for extension of a solid plastic. It is seen that, in the range of stresses increasing by about 2.5 times, the limit of linearity, t^* , decreases by 2 decimal orders, i.e., by 100 times. It demonstrates that the non-linearity limit is a very strong function of stresses. In Fig. 2.8.2, t^* is exponentially dependent on stress. Such strong dependence of the limit of linearity on stress is valid for the whole domain of non-linear behavior of viscoelastic materials.

Experimental data of the type shown in Fig. 2.8.1 can be treated in the following manner: up to $t/t^* \approx 1$, the behavior of material obeys the laws of linear viscoelasticity and at $t > t^*$ a correction ought to be introduced, which is a function of stress and the ratio $t/t^*(\sigma)$. Even this simple example demonstrates that the description of non-linearity of mechanical properties of material is complex, because the stress factor enters in two different manners – limiting the boundary of linearity and determining the form of the deformation vs. the stress curve. This becomes even more complex in transition to three-dimensional deformations because invariants must be used instead of unidimensional deformations and stresses.

However, this problem can be solved on the basis of fitting experimental data with a suitable analytical expression giving the formal (phenomenological) representation of non-linearity. This is true for homogeneous deformations of material. In reality, creep (for example in extension of solid viscoelastic materials) is even more complex, due to the effects of instability of deformations.

The most well known example of instability is the formation of a neck (the effect of *necking*). This effect is illustrated in Fig. 2.8.3 and it consists of sudden transition from homogeneous extension to a jump-like transit from the wide to the narrow section of a sample. This figure shows a graphical representation of stress vs. deformation, necking development (the middle part of a sample with a bright strip is a neck), and a microscopic picture of changes (lower part of the picture clearly shows that necking is the transition from an isotropic structure to oriented state of material).

Extension appears here not as the homogeneous decrease of the cross-section of the sample but as the co-existence of two different parts of sample and the continuous decrease of the length of the wide part and increase of sample length because of increase in the length of the narrow part. This transition is typical of any polymer, either crystalline or amorphous. In fact, this is a kind of phase transition, from homogeneous to oriented. It is also possible that macromolecules and their assemblies exist in two distinct states.

In the formulation of laws of non-linear behavior of viscoelastic materials, it is necessary to include some critical states and effects of instability at some specific conditions. These effects may be treated as phase non-linearity, and these phenomena are not restricted to solid materials only.

2.8.1.4 Non-linear relaxation

According to the principles of the linear theory of viscoelasticity, a relaxation function (or relaxation modulus) does not depend on deformation and time at which dependence of stresses is measured. The same is true for relaxation after sudden cessation of steady flow at different shear rates. Eq. 2.4.15 shows that the ratio of relaxing stress, $\sigma(t)$, to deformation rate, $\dot{\gamma}$, or to its initial value, σ_0 , which equals $\eta\dot{\gamma}_0$, does not depend on shear rate but on time only. Then, one would expect that the experimental points obtained for relaxation

after flow at different shear rates, presented in coordinates σ/σ_0 - t , lie on the same curve.

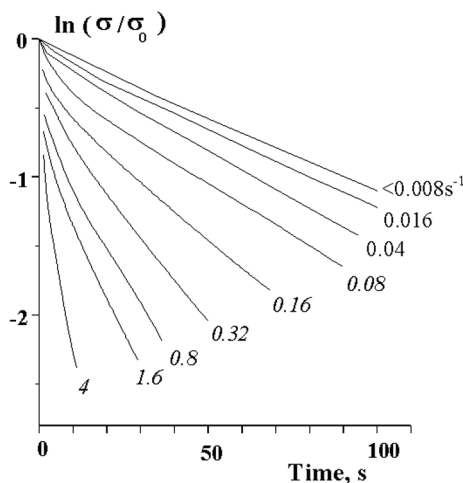


Figure 2.8.4. Shear stress relaxation after sudden cessation of steady flow at different shear rates for polyisobutylene with $MM = 1 \cdot 10^5$ at 20°C .

The reality appears much more complex, as shown in Fig. 2.8.4 for sudden cessation of steady shear flow. The linear domain is only a limiting case of very low shear rate, and the higher the shear rate before relaxation, the faster the relaxation. The viscoelastic behavior of material in the wide range of deformation conditions is strongly non-linear. It is more a characteristic of viscoelastic properties of material than the limiting linear case. The increase in stress (that is equivalent to increase in shear rate) leads to acceleration of relaxation as a general rule for non-linear behavior.

The analogous situation is observed with normal stresses (Fig. 2.8.5): relaxation

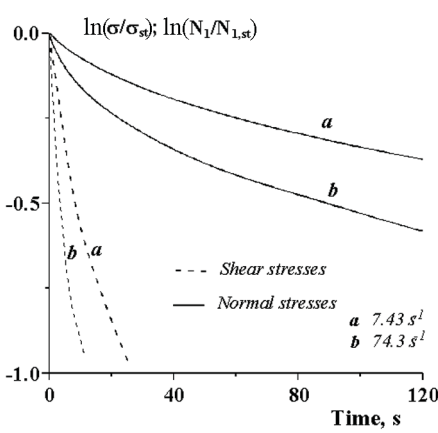


Figure 2.8.5. Relaxation of stresses after cessation of steady shear flow for butyl rubber at 25°C.

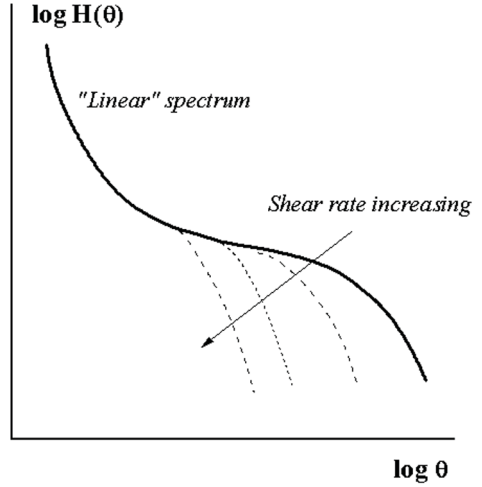


Figure 2.8.6. Changes in a relaxation spectrum induced by increase in shear rate. Qualitative picture.

of shear stresses is much faster than relaxations of normal stresses. Increase in shear rate, which precedes relaxation, accelerates relaxation of shear and normal stresses.

Based on these (and many other analogous) experimental data it is reasonable to suppose that the increase of deformation rate results in suppressing slow relaxation processes.⁸⁴ In other words, at high deformation rates slow relaxation modes do not have enough time to be realized. Formally, this phenomenon can be discussed in terms of the dimensionless parameter, $\dot{\gamma}\theta$: viscoelastic effects can be observed when values of this parameter are of the order of 1. The increase of deformation rates results in a shift of the boundary of relaxation times, which are still active in a relaxation spectrum of material, to lower relaxation times (i.e., faster relaxation processes).

Fig. 2.8.6 shows that the increase in deformation rate leads to a shift of high relaxation times of a relaxation spectrum. This effect should be taken into account in formulation of the rheological equation of state, describing a non-linear behavior of real viscoelastic materials.

The relaxation spectrum shortening can be expressed by simple equations relating to its integral characteristics, such as viscosity and coefficient of normal stresses. The influence of deformation rate on shear flow depends on the relationship between shear rate and relaxation time. Then, it is possible to assume that the following equations are the generalization of Eqs. 2.5.12 and 2.5.14, respectively:

$$\eta(\dot{\gamma}) = \int_0^{\infty} \theta G(\theta, \dot{\gamma}\theta) d\theta \quad [2.8.1]$$

$$\Psi_1(\dot{\gamma}) = 2 \int_0^{\infty} \theta^2 G(\theta, \dot{\gamma}\theta) d\theta \quad [2.8.2]$$

These equations are valid for the steady-state flow, demonstrating that non-Newtonian behavior is due to a change in relaxation spectrum of a flowing liquid induced by intensive shearing.

In light of this experimentally established fact the question arises how the initial relaxation spectrum $H(\theta)$ at low shear rates corresponding to the Newtonian behavior shifts with an increase of the shear rate corresponding to the non-Newtonian behavior. This question is closely related to the generalized (invariant) representation methodology of non-Newtonian viscosity that was developed in many papers.⁸⁵⁻⁸⁸ In particular, it was proposed^{85,86} that the shear rate dependence of the apparent viscosity of concentrated polymer solutions can be represented in an invariant form by plotting the ratio of η/η_{in} , where η is the apparent viscosity and η_{in} is the initial Newtonian viscosity, as a function of the product $\theta_{in}\dot{\gamma}$, where θ_{in} is the initial (characteristic) relaxation time at low shear rates. The following invariant representation was obtained:

$$\eta = \frac{\eta_{in}}{1 + (\theta_{in}\dot{\gamma})^{0.75}} \quad [2.8.3]$$

Later,⁸⁷ it was found that the shear rate dependence of the apparent viscosity for a wide range of bulk industrial polymer melts can be represented by plots of η/η_{in} as a function of $\eta_{in}\dot{\gamma}$. This function was found to be independent of a temperature. It was fitted to the following equation:

$$\eta = \frac{\eta_{in}}{1 + A_1(\eta_{in}\dot{\gamma})^{0.355} + A_2(\eta_{in}\dot{\gamma})^{0.72}} \quad [2.8.4]$$

Plots of η/η_{in} versus $\eta_{in}\dot{\gamma}$ or $\theta_{in}\dot{\gamma}$ were found to strongly depend on the polydispersity of polymers.

Subsequently, it was established⁸⁸ that the generalized invariant form can only be established for the shear rate dependence of the apparent relaxation time, $\theta = N_1/\sigma_{12}\dot{\gamma}$ when plotted in coordinates of θ/θ_{in} versus $\theta_{in}\dot{\gamma}$. This generalized plot for various polymer melts and their concentrated solution is shown in Fig. 2.8.7. This data were fitted to

$$\theta = \frac{N_1}{\sigma_{12}\dot{\gamma}} = \frac{\theta_{in}}{1 + 0.3(\theta_{in}\dot{\gamma})} \quad [2.8.5]$$

as indicated in Fig. 2.8.7 by the solid line. Clearly, this quantitative representation collaborates with schematics shown in Fig. 2.8.6 indicating that an increase of the shear rate leads to a shift of the relaxation spectrum to lower relaxation times with this process being universal for polymer melts and their concentrated solutions. However, it should be noted that a deviation from this universal behavior was found to occur in the case of low molecular weight polymer melts and dilute polymer solutions.⁸⁷

Such an invariant representation can also be obtained for the frequency dependence of dynamic properties of polymer melts and solutions in linear range of their behavior. In particular, Fig. 2.8.8 shows a master curve of the ratio of relaxation times determined by a value of $2G'/(G''\omega\theta_{in})$ as a function of the product of a frequency and initial relaxation time, $\theta_{in}\omega$. The solid line in this figure corresponds to the following equation:

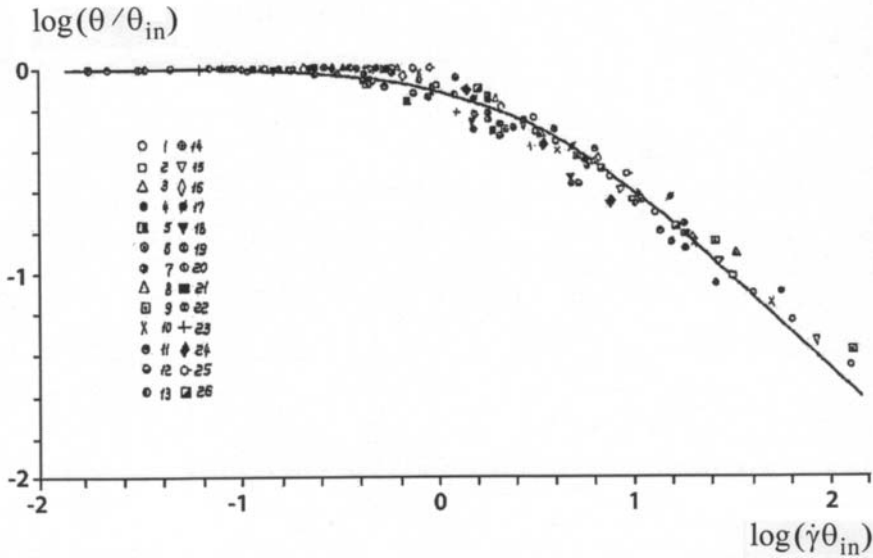


Figure 2.8.7. Master curve for apparent relaxation time for polymer melts of different molecular weights and molecular weight distributions and their solutions (symbols and numbers next to them indicate various polymers). Initial relaxation time and materials: (1) 400 s, polyisobutylene (PIB), 22°C; (2) 100 s, PIB, 40°C; (3) 20 s, PIB, 60°C; (4) 5.7 s, PIB, 80°C; (5) 2.2 s, PIB, 100°C; (6) 0.04 s, polystyrene in decalin (PS-D), 25°C, 18.4 vol%; (7) 0.58 s, PS-D, 29 vol%; (8) 3.4 s, PS-D, 38 vol%; (9) 41.7 s, PS-D, 46.6 vol%; (10) 400 s, PS-D, 57.3 vol%; (11) 52.5 s, polybutadiene, $M_w=1.52 \times 10^5$, $M_w/M_n=1.1$, 22°C; (12) 0.026 s, polybutadiene ($M_w=2.4 \times 10^5$, $M_w/M_n=1.1$) in α -methylnaphthalene (PBD-N), 22°C, 10 vol%; (13) 1.32 s, PBD-N, 30 vol%; (14) 81.2 s, PBD-N, 50 vol%; (15) 2.75 s, poly(methylmethacrylate) in diethyl phthalate, 30°C, 5 wt%; (16) 2.14 s, PIB in tetralin, 25°C, 12 wt%; (17) 0.155 s, PS in toluene (PS-T), 9 wt%; (18) 0.048 s, PS-T, 15 wt%; (19) 4.8 s, PS-T, 20.1 wt%; (20) 0.076 s, PS in chlorinated diphenyl (PS-CD), 27°C, 13 wt%; (21) 0.224 s, PS-CD, 16 wt%; (22) 0.32 s, polydimethylsiloxane (PDMS), $M_w=4.68 \times 10^5$, $M_w/M_n=1.29$, 20°C; (23) 0.045 s, PDMS, $M_w=9.71 \times 10^4$, $M_w/M_n=1.18$; (24) 1.82 s, polyethylene (PE), 150°C, 1.4×10^3 Pas; (25) 9.55 s, PE, 8×10^3 Pas; (26) 226 s, PE, 2.5×10^5 Pas. [Adapted, by permission, from A. I. Isayev, *J. Polym. Sci., Polym. Phys.*, **11**, 2123 (1973)].

$$\theta = \frac{2G'}{G''\omega} = \frac{\theta_{in}}{1 + 0.3(\theta_{in}\dot{\gamma})} \quad [2.8.6]$$

It is seen that the right-hand side of this equation coincides with that of Eq. 2.8.5 at $\omega = \dot{\gamma}$. Therefore, the dependence of relaxation time in the steady state flow at various shear rates corresponding to the nonlinear region of behavior is similar to that of the oscillatory flow at small amplitudes corresponding to the linear region of behavior.

2.8.1.5 Non-linear periodic measurements

Within the framework of linear theory of viscoelasticity, dynamic modulus (its both components G' and G'') does not depend on amplitude of deformations. However, if the amplitude of deformation is increased, two possible situations occur:

- the response is still harmonic but the stress/deformation ratio becomes amplitude dependent
- harmonic deformation leads to periodic but inharmonic response in stress, and *vice versa*.

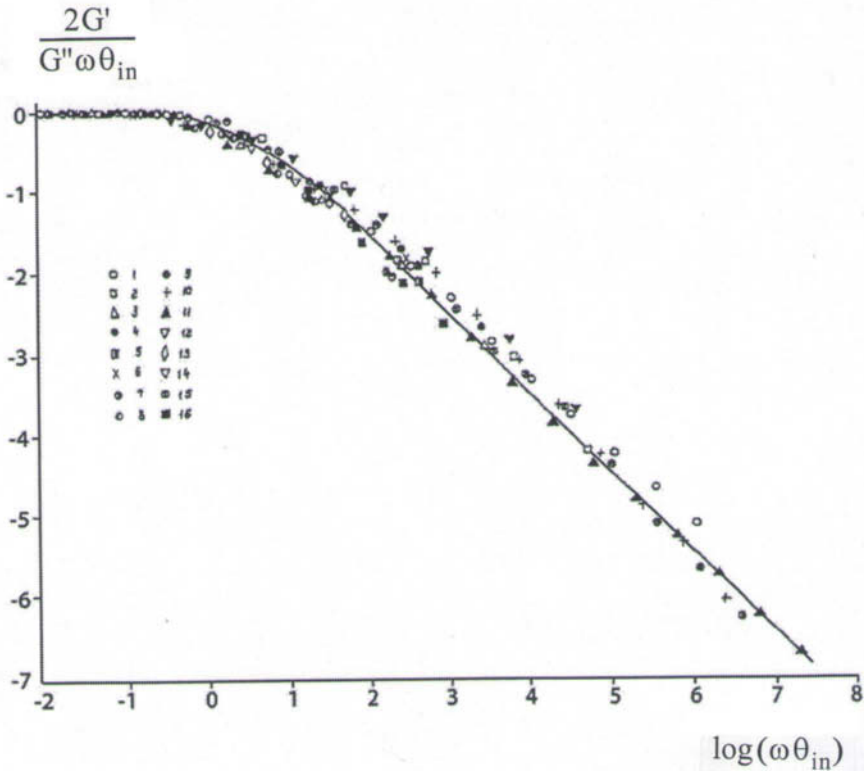


Figure 2.8.8. Master curve for apparent relaxation time of polymer melts of different molecular weights and molecular weight distributions and their concentrated solutions (symbols and numbers next to them indicates various polymers). Initial relaxation time and materials: (1) 107 s, PIB NBS in decalin, 25°C, 20 wt%; (2) 0.55 s, PS S-111, 190°C; (3) 27.6 s, PIB in cetane, 2 wt%; (4) 27 s, PMMA, $M_w=1.91 \times 10^5$, $M_w/M_n=1.26$; (5) 0.04 s, PMMA, $M_w=5.21 \times 10^4$, $M_w/M_n=1.39$; (6) 3.24 s, PMMA mixture, $M_w=1.43 \times 10^5$, $M_w/M_n=1.23$ and $M_w=8.01 \times 10^4$, $M_w/M_n=1.59$, 220°C; (7) 0.0178 s, PIB ($M_w=8.4 \times 10^5$) in mineral oil, 25°C, 2 wt%; (8) 0.0025 s, PS in Arochlor (PS-A), $M_v=2.67 \times 10^5$, 25°C, 10 wt%; (9) 0.02 s, PS-A, 20 wt%; (10) 24 s, PS, $M_v=5.18 \times 10^6$, 200°C; (11) 400 s, PIB, 22°C; (12) 0.316 s, PIB in cetane (PIB-C), $M_w=10^6$, 25°C, 8.7 wt%; (13) 0.069 s, PIB-C, 5.4 wt%; (14) 6170 s, PS, $M_w=5.81 \times 10^5$, $M_w/M_n=1.06$, 160°C; (15) 3720 s, mixture of PS, $M_w=5.81 \times 10^5$, $M_w/M_n=1.06$, $M_w=5.87 \times 10^4$, $M_w/M_n=0.94$ and $M_w=8.9 \times 10^3$, $M_w/M_n=1.01$; (16) 0.276 s, PIB in mineral oil, 25°C, 4 wt%. [Adapted, by permission, from A. I. Isayev, *J. Polym. Sci., Polym. Phys.*, **11**, 2123 (1973)].

These two cases are characteristic of a non-linear behavior of material at large deformations. First of all, it is necessary to make some comments concerning the term “large” deformations. In continuum mechanics, deformations become large when they approach 1 (100%). This leads to the effects of *geometrical* non-linearity. However, the structure of material can be destroyed at much lower deformation. This is characteristic of materials containing particles of filler. Displacement comparable with the size of solid particles may lead to destruction of the initial structure and change the mechanical properties of material. This is the case of *physical* non-linearity, and in this case deformations can be very small, for example, a few percent.

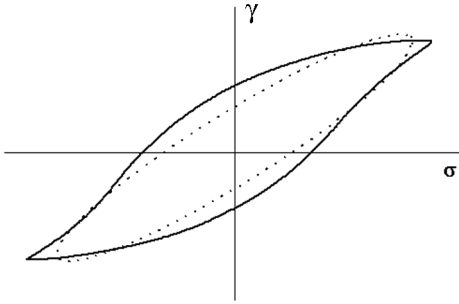


Figure 2.8.9. Hysteresis loops for a linear viscoelastic material (dots) and non-linear viscoelastic behavior (solid curve).

If response to harmonic deformations is also a harmonic stress evolution, then the definitions of the components of dynamic modulus are the same as in the linear theory of viscoelasticity.

However, if the response is non-harmonic, it appears that it is necessary to introduce some different definitions for the components of (complex) elastic modulus. These “new” generalized definitions are based on the physical meaning of both G' and G'' from Eq. 2.2.34. According to this equation, G'' is the measure of energy dissipation during the cycle of oscillations.

Let us come back to Fig. 2.2.2. The area of the hysteresis loop corresponds to the dissipation energy. In the non-linear domain, the hysteresis loop can also be measured, though it can be non-elliptic in shape (Fig. 2.8.9 is an example of real experimental data analogous to Fig. 2.2.3). Its surface area corresponds to energy losses and it gives the ground for calculating loss modulus, G'' . So, “conventional” or apparent loss modulus is calculated from Eq. 2.2.34. The next step is calculation of loss angle, δ , based on the hysteresis loop using Eq. 2.2.30 or Eq. 2.2.31. Apparent storage modulus, G' , is calculated by means of Eq. 2.2.24.

The above-mentioned calculations of the apparent G' and G'' values in the non-linear domain are not the only method. Other ways can also be proposed. It is possible to decompose the non-harmonic wave to a series of harmonics and to take the main harmonic. Then, G' and G'' are calculated in a similar way as in linear theory, but based on the main harmonic only.

It is also possible to decompose the response non-linear signal into several harmonics at different frequencies and to calculate modulus for these higher harmonics. The Fourier analysis of non-harmonic signals is well known and can also be applied.⁸⁹ In these different ways, it is possible to find G' in the range of non-linear viscoelastic behavior of material and evaluate its amplitude dependence of G' (see Fig. 2.8.10). Data are given for two polymer samples having different MM but with the same content of solid filler. Analogous curves can be easily drawn for G'' as a function of the amplitude of deformations, though in the latter case the influence of the amplitude on modulus is not so extensive.

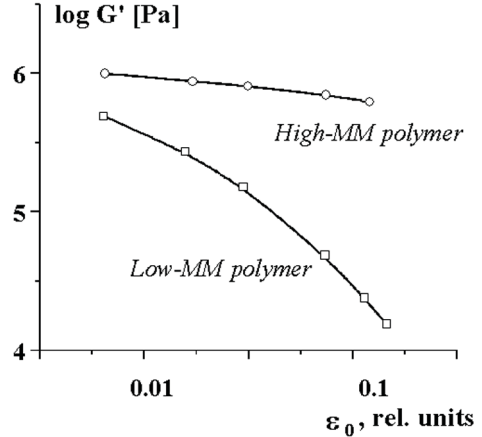


Figure 2.8.10. Amplitude dependence of the storage modulus (measured in oscillatory shear deformations) for carbon black filled polyisobutylene at frequency of 63 s^{-1} ; ϵ_0 – amplitude of deformation.

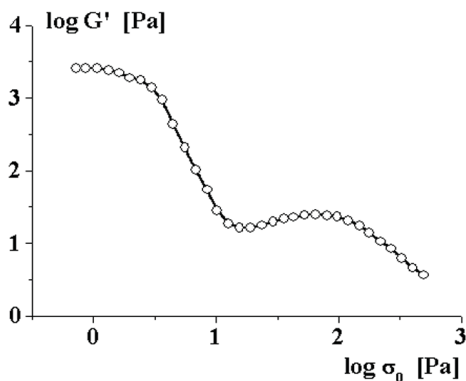


Figure 2.8.11. Amplitude dependence of the elastic modulus in oscillatory amplitude sweep test of a suspension of PMMA spheres in low-molecular-mass PDMS at a frequency of 6.28 s^{-1} . Average diameter of the particles is $5 \text{ }\mu\text{m}$ and concentration is 0.45. [Adapted, by permission, from L. Heymann, S. Peukert, N. Aksel, *J. Rheol.*, **46**, 93 (2002)].

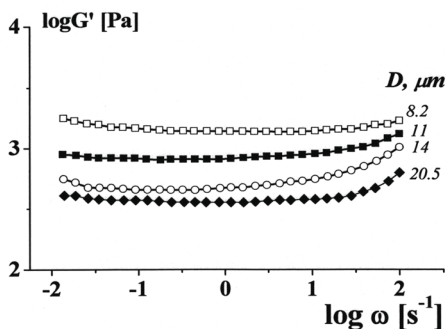


Figure 2.8.12. Frequency dependencies of the storage modulus for highly concentrated emulsions with varying droplet size at constant concentration.

The meaning of the term “large” deformations varies with polymer properties. Elasticity of the matrix in dispersion of high-MM polymer makes the decrease of modulus a slower process, while in the case of inelastic binder the transition to a non-linear region is rapid. In the latter case, it is difficult to establish the boundaries of linearity because even small deformations lead to non-linear effects (the decrease of apparent modulus). This is due to changes in the filler-matrix interphase even at very small deformations. This is a typical behavior of a low viscosity matrix. It is difficult to measure their real linear viscoelastic properties because they easily manifest physical non-linear effects at small deformations.

The effect of non-linearity at large periodic deformations was often observed for multi-component systems such as emulsions or suspensions. It was repeatedly demonstrated that the increase of deformation (or stress) amplitude results in several decades of modulus drop (see Fig. 2.8.11). In the low-amplitude range, suspensions behave as Hookean solids, whereas at high shear stress amplitude they show a Newtonian fluid behavior.⁹⁰ This effect is explained by degradation of their structure induced by high stresses.

For highly concentrated emulsions the linear-to-non-linear transition at large deformations looks rather expressive.⁹¹ At low deformations these emulsions behave like a quasi-solid substance. The reflection of this behavior is an independence of elastic modulus on frequency in a wide frequency range. An example presented in Fig. 2.8.12 demonstrates that this is true in the frequency range exceeding 4 decimal orders.

However, an increase of the deformation amplitude leads to a decrease of the storage modulus and the growth of the loss modulus (Fig. 2.8.13). Point A in this Figure is the limit of linearity defined by elastic modulus, and point B is the deformation amplitude at which $G' = G''$. At higher deformation amplitudes emulsion behaves in a liquid-like manner that is opposite to the domain of low amplitudes.

The transition from the solid-like to liquid-like behavior is explained by the transformation of the initial (related to the static state) emulsion structure. Then it is possible to

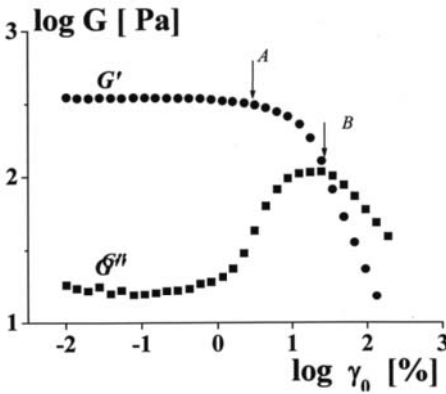


Fig. 2.8.13 Amplitude dependencies of storage and loss moduli for highly concentrated emulsion. Concentration of an internal phase 92%. Frequency 1 Hz.

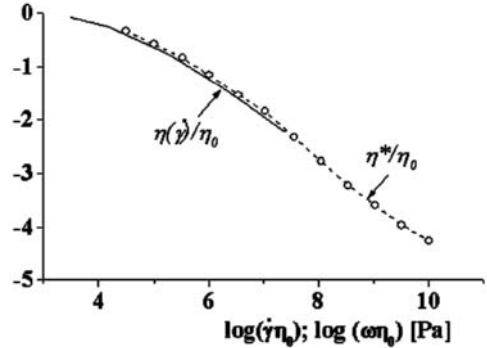


Figure 2.8.14. Correlation between dynamic viscosity and apparent viscosity for polyisobutylene (experimental data were obtained at different temperatures and reduced to 22°C). [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, Yu.G. Yanovsky, E.A. Dzyura, V.F. Shumsky, V.G. Kulichikhin, *Rheol. Acta*, **8**, 490 (1969)]

see the analogy between behavior of a solid-like medium at low deformations and properties measured at low shear rates with the similar transition observed at large deformations and large shear rates. In both cases, the linear-to-non-linear transition was observed. However, the quantitative criterion of the transition in both cases can be different due to the difference in the mechanics of shearing.⁹²

2.8.2 LINEAR – NON-LINEAR CORRELATIONS

An interesting phenomenon was elucidated from comparison of linear and non-linear viscoelastic properties of polymeric materials. It was found that functions $|\eta^*|(\omega)$ and $\eta(\dot{\gamma})$ practically coincide, i.e., $|\eta^*| = \eta$ if $\omega = \dot{\gamma}$. Here $|\eta^*|$ is the absolute value of the complex dynamic viscosity. The first of these functions is characteristic of linear viscoelastic properties of material, whereas the second one is a non-linear function (apparent viscosity dependence on shear rate). This correlation is called the *Cox-Merz rule*⁹³ and an example of such correlation is presented in Fig. 2.8.14.

Analogous correlation exists between the dependencies $2G'(\omega)/\sin\delta$ and $N_1(\dot{\gamma})$ at the same condition of comparison ($\omega = \dot{\gamma}$).⁹⁴

The existence of very close correlation between linear viscoelastic and non-linear viscous (apparent viscosity) and elastic (normal stresses) properties is clearly seen if one presents experimental data using dimensionless variables – $\tan\delta$ and the ratio $2\sigma/N_1$ as functions of the same arguments $\omega = \dot{\gamma}$ (Fig. 2.8.15).

Other correlation was established between transient shear and normal stresses (see section 3.5.1) and shear rate dependence of apparent viscosity and coefficient of normal stresses (known as the *Gleissle mirror relations*).⁹⁵

Based on these correlations, it appears possible to widen the experimental window beyond the limits of direct measurements.

2.8.3 RHEOLOGICAL EQUATIONS OF STATE FOR NON-LINEAR VISCOELASTIC BEHAVIOR

Non-linear viscoelastic behavior means absence of linear proportionality between input and response, for example, between stresses and deformations. From the physical point of view, the non-linearity means:

- absence of superposition of consequent actions
- energetic exchange among different relaxation modes.

This is directly opposite to linear behavior, for which all relaxation modes are independent and superposition of different actions is true.

One can distinguish three basic reasons for non-linearity:⁹⁶

- *geometrical* (or *weak*) non-linearity is caused by large deformations; in this case a relaxation spectrum is not changed
- *physical* (or *strong*) non-linearity is caused by forced-induced structure rearrangements; in this case a relaxation spectrum is continuously changed because of increase in deformation (deformation rates or stresses)
- *thermodynamic* (or *rupture*) non-linearity is caused by deformation-induced phase or relaxation transitions; in this case a relaxation spectrum is changed rapidly at the point of transition.

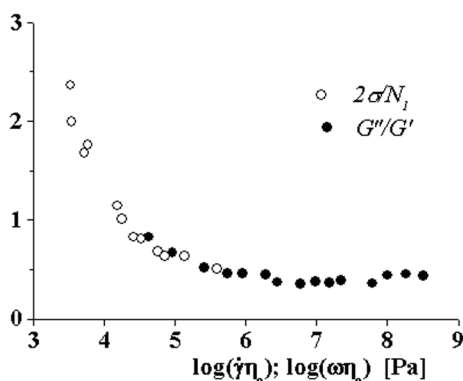


Figure 2.8.15. Correlation between dimensionless linear and non-linear characteristics of a polymer melt (polyisobutylene at 22 and 60°C reduced to 22°C).

It is noteworthy that, due to very different reasons of non-linear behavior of real materials, it is *a priori* impossible to expect to build a universal rheological equation of state for various materials. That is why it is reasonable to emphasize here an introduction to the non-linear theory as opposed to the theory of non-linear viscoelasticity. Quantitative description of non-linear effects, i.e., the building block of the rheological equation of state (or constitutive equation), is expected to be different due to a variety of mechanisms of non-linearity, which depend on the material under deformation, its structure, and a method of sample loading. It is unlikely that a constitutive equation will be derived based on

some general concepts, but the description of non-linear behavior must be based on experimental (empirical) arguments.

However, several very general principles can be formulated:⁹⁷

- stress state at time, t , is completely determined by the pre-history of deformation, i.e., it is a function of current time, t , and previous times, t'
- stress state at a point is determined by deformations in the infinitesimal surroundings of this point, but not in an entire body
- a rheological equation of state must not depend on the choice of the coordinate system

- there is no preferable configuration of the body structure, i.e., a rheological equation of state is equivalent for all points inside material
- memory of previous deformations is fading.

A great number of liquids, for which these rules are satisfied are called *simple liquids*.

These principles must be taken into account to formulate the rheological equations of state, i.e., relationships between stresses and deformations. Different modes of deformation should give a consistent solution of rheological equations of state.⁹⁸ This establishes the limitations in formulation of rheological equations of state but does not show a way of constructing suitable constitutive equations within the framework of these limitations. Every general invariant formulation is possible. But such an approach is too broad, and it is difficult to construct an equation which satisfies several practical rules:

- material constants and/or functions entering an equation of state should be determined using a set of simple experiments and it should be unambiguous within the framework of these experiments
- these constants (and/or functions) should be sufficient for prediction of the behavior of material in any arbitrary mode of deformation
- it is desirable that the structure of a constitutive equation be convenient for applied calculations (this is not a severe limitation with the availability of modern computer techniques)
- it is desirable that constants (or functions) entering a rheological equation of state are related to the molecular (structure) parameter of material; it is not necessary to limit the task by a phenomenological approach and apply a constitutive equation to a particular dynamic problem only.

In constructing rheological equations of state for viscoelastic materials, it is reasonable to pay attention to the inherent analogy between mechanical properties of rubbery solids (which cannot flow due to existence of a network of chemical bonds) and elastic liquids (which can flow because of limited lifetime of fluctuating entanglements – physical bonds). The nature of elasticity is the same in both cases and it is primarily the conformational rearrangement of segments of long flexible chains. It means that the same measures of large (finite) deformations should be used for a flowing liquid in formulating the phenomenological constitutive equation, as for rubbers. This is the Cauchy-Green tensor, C_{ij} , and the Finger tensor, C_{ij}^{-1} , which is inverse to the previous one, as was discussed in section 1.2.

Elastic effects in the range of large deformations are expressed *via* an elastic potential function, W , depending on the invariants of deformations: $W(I_1, I_2)$. For an incompressible material, the third invariant of the deformation tensor equals 1 (compare with Eq. 1.2.16) and it is not included as an argument for the elastic potential. The physical meaning of the function W is “energy stored in a material as a result of deformations”. Chapter 4 of this book is devoted to a much more detailed discussion of this function because it determines the behavior of solid materials. In this place, only one remark is important: it is very likely that this function is the same for rubbery solids and elastic liquids. This idea is widely used in formulation of constitutive equations for elastic materials of any type. Among many others, the following phenomenological rheological equation of state (or models) became popular in modern rheological literature.

2.8.3.1 The K-BKZ model

The following constitutive equation can be written in a general form:⁹⁹

$$\sigma_{ij} = 2 \int_{-\infty}^t \left(\frac{\partial \tilde{W}}{\partial I_1} C_{ij}^{-1}(t, t') - \frac{\partial \tilde{W}}{\partial I_2} C_{ij}(t, t') \right) dt' \quad [2.8.7]$$

where $\tilde{W}(I_1, I_2)$ is a function of invariants I_1 and I_2 of the tensors C_{ij} and C_{ij}^{-1} .

The elastic potential is assumed to be time-dependent not only *via* time dependency of deformations but additionally through the memory function:

$$\tilde{W}(I_1, I_2) = m(t - t') W(I_1, I_2) \quad [2.8.8]$$

where the memory function $m(t - t')$ reflects the concept of fading (decreasing) influence of previous deformation; $W(I_1, I_2)$ is an elastic potential function which is supposed to be the same for elastic deformations of a material of any kind (i.e., liquids and rubbers).

Combining Eqs. 2.8.7 and 2.8.8 leads to a *factorable K-BKZ model*, where memory and finite deformation effects are separated. The structure of this equation supposes that relaxation spectrum (represented by the memory function) is determined in the linear viscoelastic domain and it is unaffected by deformations. The non-linearity appears as a result of large deformations.

It was shown that the K-BKZ model correctly describes many special rheological effects in various modes of deformation.¹⁰⁰ It was noticed that “in the choice of $W(I_1, I_2)$ lies the art of fitting rheological data”.¹⁰¹ For adequate fitting of real experimental results complicated forms of the function $W(I_1, I_2)$ are needed. Simple potential functions, for example, the Mooney-Rivlin function (cf. Chapter 4), are not satisfactory in this case.

For fitting results of experiments carried out not only in shear but also in elongation deformation, the following form of the potential function was used:¹⁰²

$$W = \frac{3}{2\xi} \ln \left[1 + \frac{(I - 3)\xi}{3} \right] \quad [2.8.9]$$

where:

$$\xi = C_0 + C_2 \arctan \left[\frac{C_1(I_2 - I_1)^3}{1 + (I_2 - I_1)^2} \right]$$

$$I = 2 + (1 - \alpha)(I_1 - 3) + [1 + 2\alpha(I_2 - 3)]^{1/2}$$

and C_0 , C_1 , C_2 , and α are empirical numerical parameters.

Complicated equations are unlikely to be used in practical applications, though they present a rather general view of constitutive equations for elastic liquids.

2.8.3.2 The Wagner models

The direct analogy between elasticity of rubbers and flow of polymeric systems is the ground for several versions of the W-models.¹⁰³ In its initial form of an W-I model,¹⁰⁴ it

was suggested that large deformations influence a relaxation spectrum and a constitutive equation of state has the following general form:

$$\sigma_{ij} = \int_{-\infty}^t M(t-t'; I_1, I_2) C_{ij}^{-1} dt' \quad [2.8.10]$$

where M is a non-linear memory function dependent on invariants of the deformation tensor. The comparison of Eq. 2.8.10 with the K-BKZ model shows that the W-I model does not contain the Cauchy-Green tensor of deformations. The next simplification of dividing of the memory function into the product of a linear member and the “function of influence”:

$$M(t-t'; I_1, I_2) = m(t-t')h(I_1, I_2) \quad [2.8.11]$$

where the memory function $m(t-t')$ is determined in the range of linear viscoelasticity, and the function $h(I_1, I_2)$ is called the damping function, and the latter can be treated as the consequence of influence of deformations on viscoelastic behavior of material.

The final equation of the W-I model

$$\sigma_{ij} = \int_{-\infty}^t m(t-t')h(I_1, I_2)C_{ij}^{-1} dt' \quad [2.8.12]$$

can be considered as a very special case of a factorable K-BKZ model, where

$$\frac{\partial W}{\partial I_2} = h(I_1, I_2) \text{ and } \frac{\partial W}{\partial I_1} = 0$$

Another more general the W-model (called the W-II model) contains two measures of finite deformations:¹⁰⁵

$$\sigma_{ij} = \int_{-\infty}^t m(t-t')h(I_1, I_2)[(1-\beta)C_{ij}(t, t') - \beta C_{ij}^{-1}(t, t')]dt' \quad [2.8.13]$$

This equation can also be treated as a simplified version of the K-BKZ equation, and again the damping function, $h(I_1, I_2)$, plays central role in the W-model.

Several experimental investigations were carried out in order to find the analytical expression for a damping function. It is an empirical function and it is preferable to choose the simplest possible form of it. Based on some experimental data, the following expression for $h(I_1, I_2)$ was found:¹⁰⁶

$$h(I_1, I_2) = [1 + \alpha(I - 3)]^{-1}, \text{ where } I = \beta I_1 + (1 - \beta)I_2$$

The values α and β in these equations are empirical numerical parameters.

The W-models can be explained (at least on a semi-quantitative level) by some molecular model arguments.¹⁰⁷ This leads to a “universal” form of the calculated damping function, which is shown in Fig. 2.8.16 in comparison with the most reliable experimental data of several authors. It is seen that the “theoretical” damping function correctly represents the main peculiarities of experimental data.

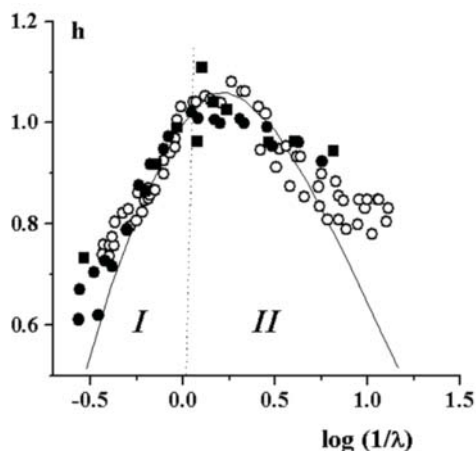


Figure 2.8.16. Experimental (various symbols correspond to data of three groups of authors obtained for different rubbers) and theoretical (line) damping factor, h . I – domain of elongation; II – domain of compressions. [Adapted, by permission, from M.H. Wagner, J. Schaefer, *J. Rheol.*, **37**, 643 (1993)]

This search for “universality” of viscoelastic properties of polymers reflects the fundamental idea of analogy of behavior of any long chain flexible polymer macromolecules. It is supposed that the presence of such a molecular structure by itself explains the main features of viscoelastic behavior, whereas details of molecular (chemical) structure are of secondary value only. This concept can be satisfactory for qualitative explanations, but it is rather difficult to use “universal” viscoelastic functions to compare different polymers, having differences in chemical structure important for technological applications.

2.8.3.2 The Leonov model¹⁰⁸

The Leonov model belongs to the state variable theories that use irreversible thermodynamics as the basis for its development.¹⁰⁹ Presently, it plays an important

role in rheological literature. It has been used for some realistic modeling of polymer processing. The Leonov model is based on a hypothesis that the rubbery state (where equilibrium elastic deformations have been stored) is the internal thermodynamic equilibrium state in flow of viscoelastic fluids. Any deviation from this state causes non-equilibrium. In contrast to the KBZ and Wagner models, this model is of differential type. Its original derivation was based on irreversible thermodynamics and the classical potential function of the network theory of elasticity (see section 4.4). In recent years, other potential functions were also proposed. Irreversible thermodynamics supplies the necessary relationship between the dissipative part of the strain rate and the dissipative part of the stress. This constitutive model is derived from the thermodynamic idea that the stress in flowing polymers is related to the stored elastic energy. The theory operates with multi-relaxation modes for Maxwell fluid, each having relaxation time, θ_k , modulus, G_k , and the elastic strain tensor (the Finger measure) in each mode, C_k , that is dependent of the strain rate tensor, D , according to the following equation:

$$C_k^\nabla - C_k(D - D_k^p)C_k = 0 \quad [2.8.14]$$

with

$$C_k^\nabla = C_k + \omega \dot{C}_k - \dot{C}_k \omega$$

being a Jaumann tensor derivative with respect to time, where ω is the vorticity tensor (see section 1.3). In Eq. 2.8.14, the quantity D_k^p is the irreversible strain rate tensor that is determined from the following equation:

$$D_k^p = \frac{1}{2G_k\theta_k} \left[\left(C_k - \frac{1}{3} I_{k,1} \delta \right) W_{k,1}^s - \left(C_k^{-1} - \frac{1}{3} I_{k,2} \delta \right) W_{k,2}^s \right] \quad [2.8.15]$$

with

$$2W_k^s = W_k(I_{k,1}, I_{k,2}) + W_k(I_{k,2}, I_{k,1})$$

$$W_{k,j} = \frac{\partial W_k}{\partial I_{k,j}}, I_{k,1} = \text{tr} C_k, I_{k,2} = \text{tr} C_k^{-1} \quad [2.8.16]$$

In Eqs. 2.8.15 and 2.8.16, $I_{k,1}$, $I_{k,2}$ are the first and second invariants of C_k , and W_k is the elastic potential. In the simplest case, W_k is taken according to the classical potential function of the network theory of elasticity (Eq. 4.4.10). In the model under discussion

$$W_k = G_k(I_{k,1} - 3)$$

The stress tensor, σ , is determined from the following equation:

$$\sigma = 2\eta_0 s D + 2 \sum_{k=1}^N (W_{k,1} C_k + C_k^{-1} W_{k,2}) \quad [2.8.17]$$

where η_0 is Newtonian viscosity of the fluid, s is a rheological parameter lying between 0 and 1. Models such as Eq. 2.8.17 were developed by Mooney and later used by Philippoff.⁹⁹ The elastic strain tensor is determined from the kinematics of the flow that can be shear, elongation, biaxial stretching or other viscometric or non-viscometric flows. By solving the governing equation, Eq. 2.8.14, one can find values of the elastic strain tensor components and then various components of the stress tensor. In a simple shear flow, the stress tensor for a N-mode of the Leonov model is given by

$$\sigma = \eta_0 s \dot{\gamma} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + 2 \sum_{k=1}^N G_k \begin{bmatrix} C_{11,k} & C_{12,k} & 0 \\ C_{12,k} & C_{22,k} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad [2.8.18]$$

The tensor components of the elastic strain tensor are governed by the following system of equations:

$$\frac{dC_{11,k}}{dt} - 2C_{12,k} \dot{\gamma} + \frac{1}{2\theta_k} (C_{11,k}^2 + C_{12,k}^2 - 1) = 0$$

$$\frac{dC_{12,k}}{dt} - 2C_{22,k} \dot{\gamma} + \frac{1}{2\theta_k} (C_{11,k} + C_{12,k}) C_{12,k} = 0 \quad [2.8.19]$$

$$C_{11,k} C_{22,k} - C_{12,k}^2 = 1$$

In this system of equations, the last equation is obtained based on the incompressibility condition that $\det C_k = 1$. This system of equations can be solved for a given value of

the shear rate, $\dot{\gamma}$, and then the shear stress, σ_{12} , the first, N_1 , and second, N_2 , differences of normal stresses can be found from Eq. 2.8.18.

The model parameters required for fluid under consideration can be obtained from the measurements of G' and G'' for oscillatory shear deformations in the linear range of behavior in the wide frequency range or by measuring flow curve (shear stress vs. shear rate) in a wide range of shear rates.¹¹⁰ These data can then be fitted to equations for the discrete relaxation spectra using known methods of nonlinear regression (see section 2.5.3). Then, these parameters can be utilized to describe various time-dependent rheological experiments for viscometric and non-viscometric flow¹¹¹ or applied to polymer processing operation to calculate dynamics and kinematics of the process.¹¹² The available scientific literature contains various examples of successful utilization of this model. The advantage of the Leonov model is that to determine model parameters it requires measurements on viscoelastic fluid in the linear range of its behavior only. Then these parameters are used to describe the fluid nonlinear behavior.

2.8.3.4 The Marrucci models

Marrucci proposed a number of molecular models for description of rheological behavior of polymer melts and solutions of flexible chain and liquid crystalline polymers. For the flexible chain polymers and solutions, Marrucci used a multi-mode Maxwell model with the convected derivative for the evolution of stress tensor dependent on the first the Rivlin-Erickson strain rate tensor.¹¹³ The moduli and relaxation times of each mode of the model were assumed to be related to structural evolution parameters governed by the first order differential equation containing an adjustable parameter. The model provides a realistic prediction of many fundamental rheological experiments in many flow situations. Predictions in step shear are not in agreement with experimental observations since the structure does not evolve from equilibrium before beginning stress relaxation. Marrucci has also made important contributions to the rheology of polymer melts by incorporating chain stretch and convective constraint release (CCR) in constitutive models.¹¹⁴ In the field of liquid crystals and liquid crystalline polymers, Marrucci explained the source of the negative first normal stress difference that appears in shearing flows of nematic polymers as being due to director tumbling.¹¹⁵ Also, the viscosity of liquid crystalline polymers in the nematic phase at low shear rates is known to depend on shear rates and does not approach a Newtonian plateau. In this regard, Marrucci has proposed a theory for the structure of defects in liquid crystals that can be applied to their flow.¹¹⁶ His theory explains this non-linear effect as the result of large distortions of the LCP polydomain (the defect structure). The defects play a leading role in LCP behavior at low shear rates by acting as pseudo-walls for director anchoring.

2.8.4 COMMENTS – CONSTRUCTING NON-LINEAR CONSTITUTIVE EQUATIONS AND EXPERIMENT

Initial information necessary for constructing a non-linear constitutive equation is the correct description of the linear viscoelastic behavior of material, which is the evident limit of the non-linear range. After that, it is necessary to move beyond this limit and know something about non-linear properties of material.

The non-linearity might be introduced by two different ways.

First, it is possible to measure *elastic properties* of a sample and then to propose an elastic potential function. This determines the limit of the non-linear domain corresponding to stationary states of stored elastic deformations at different stresses.

Second, it is possible to measure the *flow curve*, i.e., the dependence between shear stresses and shear rates at different stationary states of flow.

Both characteristics of material correspond to the non-linear domain additive to a linear relaxation spectrum.

However, a great field of possibilities lies between these experimental borders, and different versions of constitutive equations can be written which degenerate to these boundary conditions – linear relaxation spectrum in the small deformations limit and steady states at different stresses at $t \rightarrow \infty$.

In search of the equation for this field, two general problems need to be solved:

- time dependent (transient) behavior of material
- three-dimensional generalization of experimental data.

The simplest way to take into account time effects is to use the factorable non-linear equations, as was discussed above. In this approach, a linear memory function is assumed to apply (without any changes) to the domain of the non-linear viscoelastic behavior. If it appears to be insufficient for fitting experimental data, a more complicated concept must be used. One of them is introducing some arbitrary dependence of a relaxation spectrum on stress or deformation rate. For example, it can be the mathematical description of the picture illustrated in Fig. 2.8.6. If one supposes that non-linearity is the consequence of some structural process, it is reasonable to introduce a kinetic equation describing this process. In this approach, the structure is characterized by a generalized parameter, X . The kinetic equation for X is written as

$$\frac{dX}{dt} = -k_- X^n + k_+ X^m \sigma^\epsilon \quad [2.8.20]$$

where k_- and k_+ are kinetic constants, m , n , and ϵ are empirical parameters, and σ is stress.

It is also assumed that various rheological properties (for example, apparent viscosity) depend on the structure parameter, X . Many experimental data can be fitted on the basis of this equation by choice of the appropriate values of constants.

Three-dimensional generalization of experimental data obtained in a unidimensional experiment is achieved by introducing invariants of stress and deformation tensors instead of the components of these tensors.

The value of any approach to generalization of initial experimental data is to be checked against independent experiments, because no universal recipe exists on how to do it.

The experimental possibilities are usually restricted by limitations of use of standard or slightly modified experimental devices (see Chapter 5). According to modern practice and traditions, the following schemes of experiments are regularly used for construction and verification of non-linear constitutive equations.

Shear

- Flow in a simple shear. Shear stresses in steady state characterize apparent viscosity; however, pre-stationary stress evolution gives additional information about the transient behavior of material

- Shear stress relaxation; different versions of the relaxation process are possible to observe: relaxation after steady shear flow, relaxation after different moments at the pre-stationary stage of deformation
- Superposition of small-amplitude harmonic deformations on steady flow; the results of measurements characterize the changes in a relaxation spectrum induced by shearing. The direction of oscillations can be parallel or normal to direction of flow
- Two-step deformations. In the time interval $0 - t_1$, deformation is γ_1 and then deformation increases in a jump-like manner to $\gamma_2 > \gamma_1$; multi-step changes of deformation can be also used
- Large-amplitude periodic deformations
- Up-and-down sweeping of shear rate with measurement of a hysteresis loop
- Normal stress measurements including the pre-stationary part of the transient curve, determination of the steady state values of the coefficient of normal stresses and normal stress relaxation
- Non-linear creep and elastic recoil measurements; elastic recovery can be free or constrained by hard walls of an apparatus
- Flow through different channels, primarily with a simple cross-section (capillary flow)

Extension

- Uniaxial extension; evolution of stresses using different modes of deformation characterizes the combination of flow and elastic properties in this geometry of deformation, which is quite different than shear
- Two-dimensional (biaxial) extension. The rates of deformation in two normal directions can be the same (equibiaxial extension) or different

A more complicated experimental technique can also be used and sometimes is used for constructing constitutive equations and search of material functions and constants of an experimental material (sample).

In performing the experimental study of material and use of experimental data for constructing a constitutive equation of this material, it is useful to have in mind the answer to the following question: What is the final goal of this study?

When considering the simplest linear materials (Newtonian liquid and Hookean solid), two answers to these questions exist. First, the constants (viscosity and Young's modulus) are the material parameters and different materials can be compared by values of these parameters. Second, these constants are used in solving different boundary static and/or dynamic problems.

The first answer is invalid for non-linear materials, because constitutive equations of state are different for different materials, even if their structures are very similar. Therefore, it is uncertain which constants or material functions must be used for comparison. Besides, it is not necessary to know the complete complicated form of a constitutive equation: in order to compare two materials it is enough to compare some constants measured under well defined conditions.

However, the second answer is valid – a constitutive equation is necessary for solving different boundary problems. The former discussion shows (though conclusion is disappointing) that no universal rheological equation of state for non-linear viscoelastic

materials exists. It is *possible* to make a vast set of experiments and as a result to build a possible constitutive equation for this material. It takes a lot of time and effort. If it is an important material, widely used in different applications. However, in many cases (judging from numerous publications) it is not so, and constructing a constitutive equation appears to be the final goal of research.

In constructing rheological equations of state, it is reasonable to have in mind the goal of this operation. Actually, two approaches can be pursued. First, based on some very general principles, one may try to formulate a global concept, which describes numerous experimental facts. Such an “absolute” theory might appear to be too complicated and require a lot of independent experiments for determination of material constants and functions entering the equation of state. As a result, such a theory appears inconvenient and in many cases a lot of effort is spent to investigate the validity of a theory itself.

Second, it is possible to propose a rather simple model which is convenient in application. But one has to remember that such a model is limited by its origin only and can be applied within the framework of the basic assumptions used for its construction. So, in many applications, it is possible to neglect elastic effects and to solve different technological problems, e.g., in predicting transportation characteristics of material, through tubes using the model of non-Newtonian inelastic liquid. Even the simplest power-law model of viscous properties is not the worst in this case.

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C.A. Coulomb (1736-1806) – French engineer and physicist, one of the founders of electrostatics, invented the precise torsional balance and established the law of friction of solids.
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stresses are marked as σ and σ_E , respectively, moduli of shear and extension are G and E , and compliance in shear and extension are J and D , respectively. In this and the following chapters of the book both types of symbols will be used. In this chapter, the notation related to shear will be used primarily.

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QUESTIONS FOR CHAPTER 2

QUESTION 2-1

For Maxwellian liquid with a relaxation time θ , what is the residual stress (in comparison with the initial stress σ_0), if the process of stress relaxation continues for duration of time $t = 2\theta$?

QUESTION 2-2

For a solid material with rheological properties described by the Kelvin-Voigt model, with a retardation time λ , what is the time necessary to reach 95% of its equilibrium (limiting) value?

QUESTION 2-3

Viscoelastic properties of liquid are described by two relaxation modes: the first with modulus G_1 and a relaxation time $\theta_1 = 1$ s and the second with modulus G_2 and a relaxation time $\theta_2 = 100$ s. Describe the evolution of stress in time. How do relaxation curves look if a linear time-scale and a logarithmic stress scale are used?

Additional question

What is the value of an equilibrium stress in this case?

QUESTION 2-4

Explain why the value θ_K , entering the Kohlrausch function, Eq. 2.1.6 is not a relaxation time. How do you find relaxation times for this relaxation function?

QUESTION 2-5

Analyze the evolution of deformations in the following loading history: stress σ_0 was applied at the time $t = 0$; then additional stress σ_1 was added at the time t_1 and finally at the time t^* both stresses were taken away. The material is a linear viscoelastic solid.

Additional question

What will be the final deformation at $t \rightarrow \infty$?

QUESTION 2-6

What is the shape of the frequency dependencies of the components of dynamic modulus for Maxwellian liquid?

QUESTION 2-7

An experimental relaxation curve was approximated with the sum of three exponential functions with the following parameters:

$$G_1 = 2 \cdot 10^3 \text{ Pa}, \theta_1 = 100 \text{ s}; G_2 = 10^4 \text{ Pa}, \theta_2 = 20 \text{ s}; G_3 = 10^5 \text{ Pa}, \theta_3 = 6 \text{ s}.$$

What is the viscosity of this liquid?

QUESTION 2-8

Eq. 2.3.11 and its solution show that the Burgers model describes the behavior of a material with two relaxation times. The same behavior is represented by two parallel Maxwell elements with their relaxation times $\theta_1 = \eta_1/G_1$ and $\theta_2 = \eta_2/G_2$ where η_1 and G_1 are the viscosity and elastic modulus of the first and η_2 and G_2 of the second Maxwell elements joined in parallel. Calculate the values of the constants of the Burgers model expressed *via* constants of the two Maxwell elements.

QUESTION 2-9

Is it possible to measure dynamic modulus using non-harmonic periodic oscillations? How this is done?

QUESTION 2-10

In measuring a relaxation curve, it is assumed that the initial deformation is set instantaneously. In fact, it is impossible, and a transient period always exists. Estimate the role of this period for a single-relaxation mode ("Maxwellian") liquid.

QUESTION 2-11

Application of the theory of large deformations to a linear viscoelastic body leads to the following equation for the time evolution of the first normal stress difference, $N_1^+(t)$, at constant shear rate, $\dot{\gamma} = \text{const}$:

$$N_1^+(t) = 2\dot{\gamma}^2 \int_0^t t' \varphi(t') dt' \quad (\text{Can you prove this equation?})$$

Calculate the function $N_1^+(t)$ for an arbitrary relaxation spectrum, $G(\theta)$.

Additional question 1

Find the $N_1(t)$ dependence for stress relaxation after a sudden cessation of steady flow. Compare the rates of relaxation of shear and normal stresses.

Additional question 2

For a single-mode viscoelastic liquid with relaxation time, θ , calculate the relative residual shear and normal stresses after relaxation continuing for time 4θ .

QUESTION 2-12

Explain the procedure of transition from a discrete to a continuous relaxation spectrum (from Eq. 2.6.6 to Eqs. 2.6.7 and 2.2.8).

QUESTION 2-13

Let a small solid dead-weight of mass m be attached to a rod at its end and the rod is fixed at the other end. Some initial displacement from the equilibrium position of the weight (deforming the rod) was created by an applied force, and then the force was ceased.

Analyze the movement of the weight after the force is ceased. Is it possible to find the components of dynamic modulus of a rod material following the movement of a weight?

Comment

A rod can be of different length and cross-section. Not specifying the sizes and the geometrical form of a rod, the latter is characterized by the value of a “form-factor” k .

Answers can be found in a special section entitled Answers.