

Chapter 8

Relaxation Processes in the Phenomenological Theory

Abstract This chapter contains an outline of the phenomenological theory of flow and deformation as a consequence of the conservation laws and the principles of non-equilibrium thermodynamics. We exploit the concept of internal thermodynamic variables that describe the deviation of a state of the system from equilibrium. This concept has a long history beginning with the pioneering work of Mandelstam and Leontovich (Zh. Exper. Theor. Fiziki 7:438–449, 1937) and has appeared to be useful in description of a deformable viscoelastic continuum (Coleman and Gurtin in J. Chem. Phys. 47:597–613, 1967; Pokrovskii in Polym. Mech. 6(5):693–702, 1970; Wood in The thermodynamics of fluid systems (Calendron, Oxford), 1975; Maugin in Thermomechanics of nonlinear irreversible processes (World Scientific, Singapore), 1999). The purpose of the chapter is to show how relaxation processes are included in the phenomenological theory of flow. The principles of the formulation of the phenomenological theory of viscoelasticity for any real materials are clear. In this sense, one can postulate a general phenomenological theory of viscoelasticity, which includes all known particular cases, among them those constitutive equations that are formulated on the basis of macromolecular dynamics in the previous and in the subsequent chapters. Principles of the theory, which allows classify the various phenomenological constitutive equations proposed for a viscoelastic medium, are discussed but no attempt is made to review available constitutive equations.

8.1 The Laws of Conservation of Momentum and Angular Momentum

The general form of transfer equations for a medium of arbitrary structure, including melts and solutions of polymers, is established on the basis of conservation laws of mass, momentum, angular momentum and energy (Landau and Lifshitz 1987a, Shliomis 1966).

A continuous medium is characterised by its mean density, a function of co-ordinates and time

$$\rho = \rho(\mathbf{x}, t).$$

The motion of a continuous medium is described by its velocity vector \mathbf{v} , which is a certain mean macroscopic velocity and has three components – functions of the co-ordinates and time –

$$v_i = v_i(\mathbf{x}, t), \quad i = 1, 2, 3.$$

The law of conservation of mass can be written in the form of the continuity equation

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho \mathbf{v} = 0 \quad (8.1)$$

where $\rho \mathbf{v}$ is the flux of mass density. Here and further on, the density of some quantity means the amount of this quantity in the volume unit of the medium.

The law of conservation of momentum can be written as

$$\frac{\partial(\rho v_i)}{\partial t} + \frac{\partial \Pi_{ik}}{\partial x_k} = \sigma_i$$

where $\Pi_{ik} = \rho v_i v_k - \sigma_{ik}$ is the tensor flux of momentum density, which consists of the convective flux and the stress tensor; σ_i is the density of the external forces that act on the fluid.

We can use the above relations to rewrite the law of conservation of momentum density in the form

$$\rho \left(\frac{\partial v_i}{\partial t} + v_j \frac{\partial v_i}{\partial x_j} \right) = \frac{\partial \sigma_{ik}}{\partial x_k} + \sigma_i. \quad (8.2)$$

The law of conservation of the angular momentum for the medium can be written under an assumption that there is an internal angular momentum, the density of which S_{ij} obeys the law

$$\frac{\partial S_{ij}}{\partial t} + \frac{\partial(v_l S_{ij})}{\partial x_l} + \frac{\partial g_{ijl}}{\partial x_l} = G_{ij} \quad (8.3)$$

where G_{ij} is the density of force torque which acts on the inner elements of the system, and g_{ijl} is the density of the non-convective flux of angular momentum.

No assumption was stated when equation (8.3) was written down. Without any assumption we can also formulate the law of conservation of the total angular momentum

$$\frac{\partial}{\partial t}(J_{ik} + S_{ik}) + \frac{\partial G_{ikl}}{\partial x_l} = N_{ik} + x_i \sigma_k - x_k \sigma_i \quad (8.4)$$

where $J_{ik} = -\rho(x_i v_k - x_k v_i)$ is the density of the external angular momentum, G_{ikl} is the flux of the total angular momentum, and N_{ik} is the torque density from the external volume forces.

The definition of the density of external angular momentum can be used to express, with the help of equations (8.1) and (8.2), the rate of change of the external angular momentum through the stress tensor σ_{ik}

$$\frac{\partial J_{ik}}{\partial t} + \frac{\partial}{\partial x_l} (v_l J_{ik}) = \sigma_{ki} - \sigma_{ik} - \frac{\partial}{\partial x_l} (x_i \sigma_{kl} - x_k \sigma_{il}) - x_i \sigma_k + x_k \sigma_i. \quad (8.5)$$

After summing equations (8.3) and (8.5), we obtain

$$\begin{aligned} \frac{\partial (J_{ik} + S_{ik})}{\partial t} + \frac{\partial}{\partial x_l} [(J_{ik} + S_{ik})v_l + x_i \sigma_{kl} - x_k \sigma_{il}] + g_{ikl} \\ = G_{ik} - \sigma_{ik} + \sigma_{ki} - x_i \sigma_k + x_k \sigma_i. \end{aligned}$$

The last equation can be compared to (8.4), which determined the relations

$$\begin{aligned} G_{ikl} &= (J_{ik} + S_{ik})v_l + (x_i \sigma_{kl} - x_k \sigma_{il}) + g_{ikl}, \\ G_{ik} &= N_{ik} + \sigma_{ik} - \sigma_{ki}. \end{aligned}$$

Then, equations (8.3) and (8.4) can be written in the form

$$\begin{aligned} \frac{\partial (J_{ik} + S_{ik})}{\partial t} + \frac{\partial}{\partial x_l} [(J_{ik} + S_{ik})v_l + x_i \sigma_{kl} - x_k \sigma_{il}] \\ = N_{ik} - x_i \sigma_k + x_k \sigma_i, \end{aligned} \quad (8.6)$$

$$\frac{\partial S_{ik}}{\partial t} + \frac{\partial}{\partial x_l} (v_l S_{ik} + g_{ikl}) = N_{ik} + \sigma_{ik} - \sigma_{ki}. \quad (8.7)$$

The set of motion equations (8.1), (8.2), (8.6) and (8.7) contains the unknown quantities σ_{ik} and g_{ikl} , which will be determined later.

Before we come to further determinations of the unknown quantities, we shall estimate here the effect of the internal angular momentum on the motion of the liquid. Let a be the characteristic size of internal structural elements, then $S_{ik} \approx \rho a v$, $\sigma_{ik} \approx \eta v/a$, where η is the viscosity coefficient. An estimate of the characteristic relaxation time of the balance of the internal and external rotation follows from equation (8.7)

$$\tau \approx \rho \frac{a^2}{\eta}.$$

For a polymer solution, $\eta \approx 10^{-2}$ P s, $\rho \approx 1$ g/cm³, and the size of macromolecular coil is $a \approx 10^{-5}$ cm, which allow us to estimate the relaxation time $\tau \approx 10^{-10}$ s. Processes with relaxation times so small are not essential when compared to other relaxation processes in polymer solutions.

For times which are much bigger than the relaxation time, the internal and external rotation are balanced, so equation (8.7) is followed by

$$\sigma_{ik} - \sigma_{ki} = -N_{ik}. \quad (8.8)$$

In this case, the stress tensor is non-symmetric, if there is an external force torque. The law of conservation of angular momentum follows from the law of conservation of momentum.

So, we shall further assume, that the internal and external rotation are balanced in polymer solutions and the stress tensor is symmetric, when there is no external force torque.

8.2 The Law of Conservation of Energy and the Balance of Entropy

We assume that there are no internal sources of energy in the liquid, so that the change of the energy density E is connected with fluxes through the surface of the volume. The law of the conservation of energy can be written in the form

$$\frac{\partial E}{\partial t} + \operatorname{div} \mathbf{q} = 0 \quad (8.9)$$

where \mathbf{q} is the flux of energy density.

The law of the conservation of energy is also known as the first principle of thermodynamics. To formulate the motion equation of a liquid, it is necessary to use the second principle of thermodynamics also, which can be written as the equation for the change of the entropy s for unit mass.

The balance equation for the entropy density has the form

$$\frac{\partial(\rho s)}{\partial t} + \operatorname{div}(\mathbf{v}\rho s + \mathbf{H}) = \Sigma$$

where \mathbf{H} is the non-convective flux of entropy density, Σ is the non-negative quantity of emerging of entropy – entropy production. This equation can be rewritten in another form

$$\rho \left(\frac{\partial s}{\partial t} + v_i \frac{\partial s}{\partial x_i} \right) + \operatorname{div} \mathbf{H} = \Sigma. \quad (8.10)$$

For systems, which are in a state of equilibrium, there is only convective transfer of entropy. This is the case of an ideal fluid, for which

$$\frac{\partial s}{\partial t} + v_i \frac{\partial s}{\partial x_i} = 0. \quad (8.11)$$

The entropy arises in systems, which can be considered as systems that are locally in equilibrium. The increase of entropy can be connected with heat production in units of volume of fluid or, in other words, with the dissipation of energy Φ .

$$\rho \left(\frac{\partial s}{\partial t} + v_i \frac{\partial s}{\partial x_i} \right) = \frac{\Phi}{T}. \quad (8.12)$$

Non-equality can be written for the case when we cannot consider the system as to be locally in equilibrium.

$$\rho \left(\frac{\partial s}{\partial t} + v_i \frac{\partial s}{\partial x_i} \right) > \frac{\Phi}{T}.$$

In this general case, equation (8.10) is valid.

So as there is a thermodynamic relation between entropy and internal energy, the unknown quantities \mathbf{q} , \mathbf{H} in equations (8.9) and (8.10) can be connected with each other and also can be determined production of entropy Σ through other quantities. The density of total energy E in equation (8.9) can be represented as a sum of the kinetic energy and the thermodynamic total energy of the resting volume

$$E = \frac{1}{2} \rho v^2 + E_0. \tag{8.13}$$

In equilibrium situations, the quantity E_0 is internal thermic energy $E_0 = \rho \varepsilon$, which is directly connected with entropy s per unit of mass by relation

$$dE_0 = \rho T ds + w d\rho \tag{8.14}$$

where ε is internal energy per unit of mass, $w = \varepsilon + p/\rho$ is the enthalpy for unit mass. This relation (8.14) is followed directly from known (Landau and Lifshitz, 1969) thermodynamic relation, which connects change of internal energy ε for unit mass with specific volume v and entropy s

$$d\varepsilon = T ds - p dv. \tag{8.15}$$

In non-equilibrium situations, local states of the deformed system are described by some internal thermodynamic variables ξ^α , where the label α is used for the number of a variable and its tensor indices. All the equilibrium values of the internal variables are functions of two thermodynamic variables: for example, density and entropy

$$\xi_e^\alpha = \xi_e^\alpha(s, \rho).$$

The deviation of the thermodynamic system from the equilibrium state is described by the differences $\xi^\alpha - \xi_e^\alpha$ which are noted as ξ^α henceforth.

In non-equilibrium situations, the quantity E_0 includes also potential of internal variables (Wood 1975, Maugin 1999, Pokrovskii 2005), so that the differential of this function has the form

$$dE_0 = \rho T ds + w d\rho + \Xi_\alpha d\xi^\alpha \tag{8.16}$$

where the thermodynamic force has appeared:

$$\Xi_\alpha = \left(\frac{\partial E_0}{\partial \xi^\alpha} \right)_{s, \rho} = -T \left(\frac{\partial(\rho s)}{\partial \xi^\alpha} \right)_{T, \rho} > 0.$$

The quantities T, w and Ξ_α are functions of the variables s, ρ, ξ^α . At equilibrium, when there is no external fields, all the $\xi^\alpha = 0$, while the quantities T and w take their equilibrium values. The external field affects the internal variables, which determine the state of the system.

Now, taking relations (8.13) and (8.16) into account, we are ready to write down the rate of change of the density of the total energy of the moving fluid

$$\frac{\partial E}{\partial t} = \rho v_i \frac{\partial v_i}{\partial t} + \rho T \frac{\partial s}{\partial t} + \left(w + \frac{v^2}{2} \right) \frac{\partial \rho}{\partial t} + \Xi_\alpha \frac{\partial \xi^\alpha}{\partial t}.$$

We can use equations (8.1), (8.2) and (8.10) to transform the above expression to the equation which has the form of the law of the conservation of energy

$$\begin{aligned} \frac{\partial E}{\partial t} + \frac{\partial}{\partial x_k} \left[\rho v_k \left(w + \frac{v^2}{2} \right) - v_i (\sigma_{ik} + p \delta_{ik}) + T H_k \right] \\ = T \Sigma - (\sigma_{ik} + p \delta_{ik}) \nu_{ik} + H_i \nabla_i T + \frac{d \xi^\alpha}{dt} \Xi_\alpha \end{aligned} \quad (8.17)$$

where, as before, $\nu_{ik} = \frac{\partial v_i}{\partial x_k}$ is a tensor of the velocity gradient.

Comparison of equations (8.9) and (8.17) determines

$$\begin{aligned} q_k &= \rho v_k \left(w + \frac{v^2}{2} \right) - v_i (\sigma_{ik} + p \delta_{ik}) + T H_k, \\ \Sigma &= \frac{1}{T} \left((\sigma_{ik} + p \delta_{ik}) \nu_{ik} - H_i \nabla_i T - \frac{d \xi^\alpha}{dt} \Xi_\alpha \right). \end{aligned} \quad (8.18)$$

Internal variables ξ^α are introduced in relation (8.16) formally. However, the success of the theory depends on the proper choice of the internal variables for the considered case. Consideration of models usually helps to recognise which quantities describe the deviation of the system from its equilibrium state and which can be used as internal variables. A set of internal variables were identified in Chapter 2 for dilute polymer solutions and in Chapter 7 for polymer melts.¹

8.3 Thermodynamic Fluxes and Relaxation Processes

The laws of conservation determine the equations of fluid motion which, however, contain a few unknown quantities discussed below.

¹ Note, that a set of internal variables with labels, which take a continuous set of values, can be considered. Grmela (1985) and Jongschaap (1991) have generalised the above-written relations for this case. They showed that the values of the distribution function itself $W(\rho, t)$ in the problem of dynamics of dumbbells (see Appendix F), for example, can be considered as a set of internal variables, whereas the arguments of the function play the role of the label α with a continuous set of values ρ .

Expression for production of entropy (8.18) can be now compared with the general results of non-equilibrium thermodynamics, which are known for both non-stationary and stationary cases. It is obvious, that last term in the right-hand side of relation (8.18) corresponds to a non-stationary case and includes the equation of change of internal variables that is relaxation equation. The first two terms in formula (8.18) correspond to a stationary case and should be considered as the products of thermodynamic fluxes and thermodynamic forces (it is possible with any multipliers). When the internal variables are absent, we should write a relation between the fluxes and forces in the form

$$\begin{aligned}\sigma_{ij} + p\delta_{ij} &= f_{ij}(\nu_{js}, \nabla_l T), \\ -H_i &= H_i(\nu_{js}, \nabla_l T).\end{aligned}$$

At small gradients, the right parts of these relations can be expanded in a power series. In linear approximation of a parity for the anisotropic environment one gets

$$\begin{aligned}\sigma_{ik} + p\delta_{ik} &= \eta_{ikjs}\nu_{js} + L_{ikj}\nabla_j T, \\ -H_i &= \bar{L}_{ijs}\gamma_{js} + A_{ij}\nabla_j T.\end{aligned}$$

Here one can take advantage of the Onsager principle, that is equate factors at cross members.

In situations when internal relaxation processes cannot be neglected, it is necessary to include in consideration relaxation equation for internal variables, and we write down

$$\begin{aligned}\sigma_{ij} + p\delta_{ij} &= f_{ij}(\nu_{js}, \nabla_l T, \xi^\gamma), \\ -H_i &= H_i(\nu_{js}, \nabla_l T, \xi^\gamma), \\ -\frac{d\xi^\alpha}{dt} &= g^\alpha(\nu_{js}, \nabla_l T, \xi^\gamma).\end{aligned}\tag{8.19}$$

One can note that the diffusion of the internal variables, i.e. the diffusion of structural elements at non-homogeneous distribution of the values of internal variables, is neglected here. Otherwise, the quantities $\frac{\partial^2 \xi^\alpha}{\partial x_i \partial x_l}$ must be added to the set of arguments of the right-hand side functions in (8.19). We shall not discuss this situation henceforth.

It is known, that thermodynamic forces are functions of internal variables (not speaking about other thermodynamic variables)

$$\Xi_\alpha = \Xi_\alpha(\xi^\gamma),\tag{8.20}$$

so that relations (8.19) can be understood in such a way, that the quantities

$$\frac{1}{T}(\sigma_{ik} + p\delta_{ik}), \quad -\frac{1}{T}H_i, \quad -\frac{1}{T}\frac{d\xi^\alpha}{dt}$$

are functions of the thermodynamics forces

$$\nu_{ik}, \quad \nabla_i T, \quad \Xi_\alpha.$$

The application of general thermodynamic theory can be considered, first, in linear approximation. In practice, it is sufficient for the most part of applications. We can use our usual notations for symmetric and antisymmetric tensors of the velocity gradients

$$\gamma_{ij} = \frac{1}{2}(\nu_{ij} + \nu_{ji}), \quad \omega_{ij} = \frac{1}{2}(\nu_{ij} - \nu_{ji})$$

and divide the stress tensor into symmetric and antisymmetric parts, to write the fluxes as quasi-linear function of the forces

$$\begin{aligned} \frac{1}{2}(\sigma_{ik} + \sigma_{ki} + 2p\delta_{ik}) &= \eta_{ikjs}\gamma_{js} + K_{ikjs}\omega_{js} + L_{ikj}\nabla_j T + M_{ik\alpha}\xi_\alpha, \\ \frac{1}{2}(\sigma_{ik} - \sigma_{ki}) &= \bar{K}_{ikjs}\gamma_{js} + N_{ikjs}\omega_{js} + \bar{C}_{ikj}\nabla_j T + \bar{D}_{ik\alpha}\xi_\alpha, \\ -H_i &= \bar{L}_{ijs}\gamma_{js} + C_{ijs}\omega_{js} + A_{ij}\nabla_j T + G_{i\alpha}\xi_\alpha, \\ -\frac{d\xi^\alpha}{dt} &= \bar{M}_{\alpha js}\gamma_{js} + D_{\alpha js}\omega_{js} + \bar{G}_{\alpha i}\nabla_i T + P_{\alpha\gamma}\xi_\gamma. \end{aligned} \quad (8.21)$$

The matrix coefficients in (8.21) depend on the thermodynamic variables, which, in the case under discussion, are pressure p or density ρ (we can choose any of them, so as there exist an equation of state, connecting these variables), temperature T and internal variables ξ^α . The coefficients can be expanded into series near equilibrium values of internal variables. Zero-order terms of expansions of the components of the matrices in a series of powers of the internal variables are connected due to the Onsager principle (Landau and Lifshitz 1969) by some relations

$$\bar{K}_{jsik}^0 = K_{ikjs}^0, \quad \bar{C}_{ikj}^0 = -C_{jik}^0, \quad \bar{L}_{jik}^0 = -L_{ikj}^0.$$

The bars over letters denote matrices, which are obtained from the original matrices (without bars) by simple transformation. Note once more that these relations are valid for equilibrium values. Further on we shall be interested in non-linear relations, so we consider all matrices to depend on the internal variables.

In the simple case when all the internal variables are scalar quantities, the state of the system is isotropic, all the matrix coefficients in (8.21) are expressed in unit matrices, and the relations (8.21) take the simpler form, which can be easily written for every given set of internal variables.

In rheological terms, equations (8.20) and (8.21) make up a set of constitutive relations of the system. Together with equations (8.1), (8.2) and (8.10), they determine the equations of motion of the system.

We should pay special attention to the last relation in (8.20), which is a relaxation equation for the variable ξ^α . One can find examples of relaxation equations in Section 2.7 for dilute solutions of polymers and in Chapter 7 for concentrated solutions and melts of polymers. The presence of internal variables and equations for their change are specific features of the liquids we consider in this monograph.

8.4 The Principle of Relativity for Slow Motions

The form of the above-written relations (8.21) can be specified more by applying some restrictions which follow from the assumption that the motion of structural elements of medium does not change very rapidly, so that the following relation is valid

$$\frac{u\rho a}{\eta} \ll 1. \tag{8.22}$$

Here, a is the characteristic size of the structural element, ρ is the density, which is approximately equal to 1 g/cm^3 , η is the effective viscosity coefficient of the medium which is 10^{-2} – 10 P s, and u is the characteristic velocity of motion of the particle, which is not more than the mean thermal velocity $(T/m)^{1/2}$. It is easy to see that, at room temperature and with the above values of the parameters, condition (8.22) is valid if $a \gg 10^{-7}$ – 10^{-6} cm.

As is well known, the equations of mechanics are covariant with the Galileo transform. This can be also said about relations (8.19) and (8.21). In the case, when the motions of the internal particles are slow (in the sense discussed above), we can state that a stronger principle is valid. It says that all the processes run in the same way and, consequently, should be described by similar equations in all the co-ordinate frames which are connected to each other by the transform

$$x_i = a_{ik}x'_k + c_i \tag{8.23}$$

where an orthogonal tensor a_{ik} and a vector c_i are arbitrary functions of time. In contrast to the Galileo principle, the above principle, which is also called the principle of material objectivity (Coleman and Nolle 1961), is valid for the cases when the forces of inertia can be neglected.

Let us consider the restriction imposed on the form of the transfer equations by the discussed principle. It is easy to see that, when transformation (8.23) is applied to the co-ordinates, the tensor of velocity gradients transforms as

$$\nu_{ik} = a_{il}a_{kj}\nu'_{lj} + \dot{a}_{il}a_{kl}.$$

The superscript point denotes differentiation with respect to time.

The symmetrical tensor of velocity gradient transforms as a tensor, which does not depend on time

$$\gamma_{ik} = a_{il}a_{kj}\gamma'_{lj}. \tag{8.24}$$

The antisymmetrical tensor transforms in the following way

$$\omega_{ik} = a_{il}a_{kj}\omega'_{lj} + \dot{a}_{il}a_{kl}. \tag{8.25}$$

Let us now turn to the internal variables. We can consider that one of the internal variables is a tensor of arbitrary rank and transforms as the co-ordinates do, that is, contravariantly

$$\xi_{ik\dots l} = a_{ij}a_{ks} \dots a_{ln}\xi'_{js\dots n}.$$

Differentiating the tensor with respect to time, we find that

$$\frac{d\xi_{ik\dots l}}{dt} = \dot{a}_{ij}a_{pj}\xi_{pk\dots l} + \dot{a}_{kj}a_{pj}\xi_{ip\dots l} + \dots + \dot{a}_{lj}a_{pj}\xi_{ik\dots p} + a_{ij}a_{ks} \dots a_{ln} \frac{d\xi'_{js\dots n}}{dt}.$$

We can define the expression $\dot{a}_{il}a_{kl}$ from (8.25) to rewrite the last expression in the form

$$\begin{aligned} & \frac{d\xi_{ik\dots l}}{dt} - \omega_{ip}\xi_{pk\dots l} - \omega_{km}\xi_{im\dots l} - \dots - \omega_{ln}\xi_{ik\dots n} \\ &= a_{ij}a_{ks} \dots a_{ln} \left(\frac{d\xi'_{is\dots n}}{dt} - \omega'_{jq}\xi'_{qs\dots n} - \omega'_{sq}\xi'_{jq\dots n} - \dots - \omega'_{nq}\xi'_{js\dots q} \right). \end{aligned}$$

We can see that the combination

$$\frac{D\xi_{ik\dots l}}{Dt} = \frac{d\xi_{ik\dots l}}{dt} - \omega_{ip}\xi_{pk\dots l} - \omega_{km}\xi_{im\dots l} - \dots - \omega_{ln}\xi_{ik\dots n} \quad (8.26)$$

transforms as a tensor, which is independent of time. Expression (8.26) is called the Jaumann derivative of tensor $\xi_{ik\dots l}$ with respect to time.

There are plenty of covariant derivatives of the tensor $\xi_{ik\dots l}$ among which the Jaumann derivative has the simplest form. Indeed, expressions (8.24) and (8.25) are followed by the relation

$$\dot{a}_{il}a_{kl} = \omega_{ik} + \kappa\gamma_{ik} - a_{is}a_{kj}(\omega'_{sj} + \kappa\gamma'_{sj})$$

where κ is the arbitrary constant. We can use this relation to introduce derivatives, which are generalisations of (8.26).

Covariant tensors can be considered in a similar way.

8.5 Constitutive Relations for Non-Linear Viscoelastic Fluids

One can now return to the set of transfer equations (8.20) and (8.21), to which the discussed principle of covariance can be applied. The new form of the equations which is covariant under transformation (8.23) is written as follows

$$\begin{aligned} \frac{1}{2}(\sigma_{ik} + \sigma_{ki} + 2p\delta_{ik}) &= \eta_{ikjs}\gamma_{js} + L_{ikj}\nabla_j T + M_{ik\alpha}\xi_\alpha, \\ \frac{1}{2}(\sigma_{ik} - \sigma_{ki}) &= \bar{D}_{ik\alpha}\xi_\alpha, \\ -H_i &= \bar{L}_{ijs}\gamma_{js} + A_{ij}\nabla_j T + G_{i\alpha}\xi_\alpha, \\ \frac{D\xi^\alpha}{Dt} &= \bar{M}_{\alpha js}\gamma_{js} + \bar{G}_{\alpha i}\nabla_i T + P_{\alpha\gamma}\xi_\gamma, \end{aligned} \quad (8.27)$$

where the Jaumann derivative is noted as

$$\frac{D\xi^\alpha}{Dt} = \frac{d\xi^\alpha}{dt} + D_{\alpha js}\omega_{js}.$$

For every given tensor ξ^α , this expression can be compared to (8.26) which determines the matrix $D_{\alpha js}$ and, consequently, in linear approximation, matrix $\bar{D}_{ik\alpha}$ in relations (8.27).

The set of relations (8.27) determines the fluxes as quasi-linear functions of forces. The coefficients in (8.27) are unknown functions of the thermodynamic variables and internal variables. We should pay special attention to the fourth relation in (8.27) which is a relaxation equation for variable ξ^α . The viscoelastic behaviour of the system is determined essentially by the relaxation processes. If the relaxation processes are absent (all the $\xi^\alpha = 0$), equations (8.27) turn into constitutive equations for a viscous fluid.

One can see that the equations of motion for a viscoelastic fluid can always be written, when a set of internal relaxation variables is given, however, a set of internal variables cannot be determined in the frame of phenomenological theory and equations (8.27) cannot be specified any more without extra assumptions.

As an example, we shall consider a simpler case of the isothermal motion of a liquid without the external volume forces and without the external volume force torque, so that equations (8.27) acquire the form

$$\begin{aligned} \sigma_{ik} + p\delta_{ik} &= \eta_{ikjs}\gamma_{js} + M_{ik\alpha}\xi_\alpha, \\ -\frac{D\xi^\alpha}{Dt} &= \bar{M}_{\alpha js}\gamma_{js} + P_{\alpha\gamma}\xi_\gamma. \end{aligned} \tag{8.28}$$

The set of internal variables ξ^γ is usually determined when considering a particular system in more detail. For concentrated solutions and melts of polymers, for example, a set of relaxation equation for internal variables were determined in the previous chapter. One can see that all the internal variables for the entangled systems are tensors of the second rank, while, to describe viscoelasticity of weakly entangled systems, one needs in a set of conformational variables x_{ik}^α which characterise the deviations of the form and size of macromolecular coils from the equilibrium values. To describe behaviour of strongly entangled systems, one needs both in the set of conformational variables and in the other set of orientational variables u_{ik}^α which are connected with the mean orientation of the segments of the macromolecules.

To simplify the situation, one can keep only one internal variables with the smallest number from each set, that is x_{ik}^1 and u_{ik}^1 . It allows one to specify equations (8.28) for this case and to write a set of constitutive equations for two internal variables – the symmetric tensors of second rank. The particular case of general equations are equations (9.24)–(9.27) – constitutive equations for strongly entangled system of linear polymer. For a weakly entangled system, one can keep a single internal variable to obtain an approximate

description of viscoelastic behaviour of the system. To consider this case in more details, we specify equations (8.28) for a single internal variable – the symmetric tensor of the second rank and rewrite relations (8.28) as follows

$$\begin{aligned} \sigma_{ik} + p\delta_{ik} &= \eta_{ikjs}\gamma_{js} + M_{ikjs}\xi_{js}, \\ -\frac{D\xi_{ij}}{Dt} &= \bar{M}_{ijls}\gamma_{ls} + P_{ijls}\xi_{ls}. \end{aligned} \tag{8.29}$$

In a more general case, we do not know the dependencies of the matrices in (8.29) on the internal variable, so one can rewrite relations (8.29) in the form

$$\begin{aligned} \sigma_{ik} + p\delta_{ik} &= \eta_{ikjs}\gamma_{js} + \bar{\sigma}_{ik}(\xi_{pq}), \\ -\frac{D\xi_{ij}}{Dt} &= \bar{M}_{ijls}(\xi_{pq})\gamma_{ls} + \phi_{ij}(\xi_{pq}). \end{aligned} \tag{8.30}$$

The tensor functions in (8.30) can be written in a general form, according to the rules described, for example, for the arbitrary tensor function in the book by Green and Adkins (1960)

$$\begin{aligned} \bar{\sigma}_{ik} &= \sigma_0\delta_{ik} + \sigma_1\xi_{ik} + \sigma_2\xi_{il}\xi_{lj}, \\ \phi_{ik} &= \phi_0\delta_{ik} + \phi_1\xi_{ik} + \phi_2\xi_{il}\xi_{lk} \end{aligned} \tag{8.31}$$

where the coefficients σ_i and ϕ_i ($i = 0, 1, 2$) are functions of the three invariants of the tensor ξ_{il}

$$I_1 = \sum_{i=1}^3 \xi_{ii}, \quad I_2 = \frac{1}{2} \sum_{i,j} (\xi_{ij}\xi_{ji} - \xi_{ii}\xi_{jj}), \quad I_3 = |\xi_{ij}|.$$

The relations (8.30) and (8.31) make up a general form for a non-linear single-mode constitutive relation. To specify the constitutive equation for a given system, one ought to determine the unknown function in (8.31) relying on experimental evidence. A particular form of relation (8.30) and (8.31), called canonical form (Leonov 1992), embraces many empirical constitutive equations (Kwon and Leonov 1995). One can obtain the canonical form of constitutive relation (Leonov 1992), if one neglects the viscosity term in the stress tensor (8.30), which is quite reasonable for polymer melts, and put an additional assumption on matrix \bar{M}

$$\bar{M}_{ijls} = -\frac{1}{2}\kappa(\xi_{il}\delta_{js} + \xi_{js}\delta_{il} + \xi_{is}\delta_{jl} + \xi_{jl}\delta_{is})$$

where κ is a numerical parameter, usually taken as ± 1 or 0 . One can look at equations (9.48) and (9.49) in the next chapter as particular case of system (8.30) and (8.31) as well.

Let us note that, according to Godunov and Romenskii (1972) and Leonov (1976), the internal variable ξ_{ij} can be considered to be a second-rank tensor

of the recoverable strain. This statement changes neither definition (8.16) of the thermodynamic force Ξ_{ls} , nor the form of equations (8.30), but it does specify the form of the unknown functions and matrices in (8.30). In this case, a form of matrix M_{ikjs} can be determined, taking the relation between the stress tensor and the strain tensor (given by formula (B.7) of Appendix B) into account. Some simplification can be also achieved, because one has for an incompressible continuum an extra condition

$$|\xi_{ij}| = 1.$$

In this case, one has only two invariants of the internal tensor, which makes the general relations for the tensor functions simpler. However, it does not mean that the final relations will be simpler. We can see later (see Section 9.3.5) that there is a relation between the recoverable strain and the deformation of macromolecular coil (see formula (9.75)), so a transfer from one formalism to the other can be performed and the results of the two approaches can be compared.

8.6 Different Forms of Constitutive Relation

All the constitutive relation that we have discussed in this chapter include some relaxation equations for the internal tensor variables which ought to be considered to be independent variables in the system of equations for the dynamics of a viscoelastic liquid.

However, in the earlier times, the constitutive relation for a viscoelastic liquid were formulated when the equations for relaxation processes could not be written down in an explicit form. In these cases the constitutive relation was formulated as relation between the stress tensor and the kinetic characteristics of the deformation of the medium (Astarita and Marrucci 1974).

In this section, we shall show that the constitutive relation with internal variables is followed by two types of constitutive relations which do not include internal variables. For the sake of simplicity, we shall consider the simplest set of equations

$$\sigma_{ik} + p\delta_{ik} = 3\frac{\eta}{\tau} \left(\xi_{ik} - \frac{1}{3}\delta_{ik} \right), \quad (8.32)$$

$$\frac{d\xi_{ik}}{dt} - \nu_{ij}\xi_{jk} - \nu_{kj}\xi_{ji} = -\frac{1}{\tau} \left(\xi_{ik} - \frac{1}{3}\delta_{ik} \right) \quad (8.33)$$

where the coefficient of viscosity η and the time of relaxation τ are functions of the invariants of the internal tensor variable ξ_{ik} .

Indeed, we can obtain a relation between the stress tensor and the velocity gradient tensor if we exclude tensor ξ_{ij} from the set of equations (8.32)–(8.33). This can be done in two different ways.

Firstly, from equation (8.32), we can define the tensor ξ_{ij} which can be inserted into the second equation of (8.33). As a result, we obtain a differential equation for the extra stresses

$$\frac{d\tau_{ik}}{dt} - \nu_{ij}\tau_{jk} - \nu_{kj}\tau_{ji} = -\frac{1}{\tau}(\tau_{ik} - 2\eta\gamma_{ik}), \quad \tau_{ik} = \sigma_{ik} + p\delta_{ik}. \tag{8.34}$$

The quantities τ and η in equation (8.34) depend on the invariants of the tensor τ_{ik} in accordance with equation (8.32). We ought to note that the behaviour of a non-linear viscoelastic liquid in a non-steady state would be different, if a dependence of the material parameters τ and η on the tensor velocity gradients or on the stress tensor is assumed. This is a point which is sometimes ignored. In any case, if τ and η are constant, equation (8.34) belongs to the class of equations introduced and investigated by Oldroyd (1950).

The linear case of relation (8.34) is the Maxwell equation (see, Landau and Lifshitz 1987b, p. 36).

$$\frac{d(\sigma_{ik} + p\delta_{ik})}{dt} + \frac{1}{\tau}(\sigma_{ik} + p\delta_{ik}) = 2\frac{\eta}{\tau}\gamma_{ik} \tag{8.35}$$

where, as before, τ is the relaxation time, and η is the coefficient of shear viscosity. There are different generalisations of equations (8.34) and (8.35) (Astarita and Marrucci 1974).

On the other hand, we can imagine that a solution of equation (8.33) can be found. Below, the solution is written for uniform flow with accuracy up to the second-order terms with respect to the velocity gradient

$$\begin{aligned} \xi_{ik} = & \frac{1}{3}\delta_{ik} + \int_0^\infty \exp\left(-\frac{s}{\tau}\right) \gamma_{ij}(t-s) ds \\ & + \int_0^\infty \exp\left(-\frac{s}{\tau}\right) \int_0^\infty \exp\left(-\frac{u}{\tau}\right) \\ & \times [\nu_{ij}(t-s)\gamma_{jk}(t-s-u) - \nu_{kj}(t-s)\gamma_{ji}(t-s-u)] du ds. \end{aligned}$$

Then, the solutions should be inserted into equation (8.32), which determines the stress tensor as a function of the tensor of the velocity gradient in the previous moments of time. The linear term has the form

$$\sigma_{ij} = -p\delta_{ij} + 2\frac{\eta}{\tau} \int_0^\infty \exp\left(-\frac{s}{\tau}\right) \gamma_{ik}(t-s) ds. \tag{8.36}$$

A generalisation of (8.36) for the case of many relaxation processes can easily be found. In the simplest case of uniform motion one has

$$\sigma_{ik} = -p\delta_{ik} + 2 \int_0^\infty \eta(s)\gamma_{ik}(t-s) ds. \tag{8.37}$$

The memory function $\eta(s)$ can be calculated if a set of internal variables are given.

In general case, the stress tensor ought to be written as

$$\sigma_{ik} + p\delta_{ik} = Y_{s=0}^{\infty}[\nu_{jk}(t-s), \gamma_{lm}(t)]. \quad (8.38)$$

Instead of velocity gradients, displacement gradients can be used in relation (8.38). In this form, relations of the kind (8.38) are established on the basis of the phenomenological theory of so-called simple materials (Coleman and Nolle 1961). To put the theory into practice, function (8.38) should be, for example, represented by an expansion into a series of repeated integrals, so that, in the simplest case, one has the first-order constitutive relation (8.37). Let us note that the first person who used functional relations of form (8.38) for the description of the behaviour of viscoelastic materials was Boltzmann (see Ferry 1980).

Another form of the relation for slow motions can be obtained from equation (8.38). We can expand the velocity gradients in (8.38) into series in powers of time near the moment t . The zeroth terms of the expansion determine a viscous liquid. The next terms take viscoelasticity into account. This description is local in time.

One can see that there are several forms for the representation of the constitutive relation of a viscoelastic liquid. Of course, we ought to say that all the types of constitutive relation we discussed in this section are equivalent. We can use any of them to describe the flow of viscoelastic liquids. However, the description of the flow of a liquid in terms of the internal variables allows one to use additional information, if it is available, about microstructure of the material, and, in fact, appears to be the simplest one for derivation and calculation. We believe that the form, which includes the internal variables, reflects a deeper penetration into the mechanisms of the viscoelastic behaviour of materials. From this point of view, all the representations of deformed material can be unified and classified.