Chapter 9
Non-Linear Effects of Viscoelasticity

Abstract Now we are in a position to formulate a system of constitutive equations for polymer systems on the basis of the mesoscopic approach, described in the previous chapters, to investigate non-linear behaviour of polymeric liquids. In the first section, the known results for dilute polymer solutions are described. The other sections contain derivation of constitutive equations for entangled systems, while the weakly $(2M_\mathrm{e} < M < M^*)$ and strongly $(2M_\mathrm{e} < M^* < M)$ entangled systems are considered separately. In the latter case, the reptation motion of macromolecules emerges. Though the reptation motion practically does not contributes to terminal properties of linear viscoelasticity of strongly entangled system, it has to be included in the consideration at higher velocity gradients to obtain the correct dependencies of non-linear effects on the length of the macromolecules. One can demonstrate how different non-linearities can be explained in terms of macromolecular dynamics. Simplifications of the many-modes constitutive equations will be considered in Sections 3. The simplest form of constitutive equations appears to be the well-known Vinogradov equation. Despite of essential simplification, the reduced forms of constitutive equation allow one to describe the non-linear effects for simple flows: shear and elongation.

9.1 Dilute Polymer Solutions

Comparison with experimental data demonstrates that the bead-spring model allows one to describe correctly linear viscoelastic behaviour of dilute polymer solutions in wide range of frequencies (see Section 6.2.2), if the effects of excluded volume, hydrodynamic interaction, and internal viscosity are taken into account. The validity of the theory for non-linear region is restricted by the terms of the second power with respect to velocity gradient for non-steady-state flow and by the terms of the third order for steady-state flow due to approximations taken in Chapter 2, when relaxation modes of macromolecule were being determined.

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9.1.1 Constitutive Relations

Many-Mode Approximation

The set of constitutive equations for the dilute polymer solution consists of the definition of the stress tensor (6.16), which is expressed in terms of the second-order moments of co-ordinates, and the set of relaxation equations (2.39) for the moments. The usage of a special notation for the ratio, namely

$$x_{ik}^{\nu} = \frac{\langle \rho_i^{\nu} \rho_k^{\nu} \rangle}{\langle \rho^{\nu} \rho^{\nu} \rangle_0} = \frac{2}{3} \mu \lambda_{\nu} \langle \rho_i^{\alpha} \rho_k^{\nu} \rangle,$$

allows us to write down these equations in more compact form

$$\begin{aligned} \sigma_{ik} &= -p\delta_{ik} + 2\eta_{\mathrm{s}}\gamma_{ik} \\ &\quad + 3nT \sum_{\nu=1}^{N} \left[\frac{1}{1+\varphi_{\nu}} \left(x_{ik}^{\nu} - \frac{1}{3}\delta_{ik} \right) + \tau_{\nu}^{\perp} \varphi_{\nu} (\gamma_{ij} x_{jk}^{\nu} + \gamma_{kj} x_{ji}^{\nu}) \right], \quad (9.1) \\ \frac{\mathrm{d}x_{ik}^{\nu}}{\mathrm{d}t} &- \omega_{ij} x_{jk}^{\nu} - \omega_{kj} x_{ji}^{\nu} \\ &= -\frac{1}{\tau_{\nu}^{\parallel}} \left(x_{ik}^{\nu} - \frac{1}{3}\delta_{ik} \right) + (1-\varphi_{\nu})(\gamma_{ij} x_{jk}^{\nu} + \gamma_{kj} x_{ji}^{\nu}) \quad (9.2) \end{aligned}$$

where $\tau_{\nu}^{\parallel} = (1+\varphi_{\nu})\tau_{\nu}^{\perp}$ and $\tau_{\alpha}^{\perp} = \tau_{\alpha}$ is an orientational relaxation time of the mode α of the macromolecular coils.

In some cases, if we consider, for example, the slow motion of a solution of very long macromolecules, the effect of internal viscosity is negligible, so that the set of constitutive equations can be simplified and written as

$$\sigma_{ik} = -p\delta_{ik} + 2\eta_{\mathrm{s}}\gamma_{ik} + 3nT \sum_{\nu=1}^{N} \left(x_{ik}^{\nu} - \frac{1}{3}\delta_{ik} \right), \quad (9.3)$$

$$\frac{\mathrm{d}x_{ik}^{\nu}}{\mathrm{d}t} = -\frac{1}{\tau_{\nu}} \left(x_{ik}^{\nu} - \frac{1}{3}\delta_{ik} \right) + \nu_{ij} x_{jk}^{\nu} + \nu_{kj} x_{ji}^{\nu}. \quad (9.4)$$

For the steady-state case, both equations (9.1)–(9.2) and (9.3)–(9.4) are followed by the steady-state form of the stress tensor

$$\sigma_{ik} = -p\delta_{ik} + 2\eta_{\mathrm{s}}\gamma_{ik} + 3nT \sum_{\nu=1}^{N} \tau_{\nu} \left(\nu_{ij} x_{jk}^{\nu} + \nu_{kj} x_{ji}^{\nu} \right). \quad (9.5)$$

This equation makes it possible to calculate stresses for low velocity gradients to within third-order terms in the velocity gradient if one knows the moments to within second-order terms in the velocity gradients. Due to the approximations, used earlier in Chapter 2, the results are applicable for small extensions of the macromolecular coil and hence for low velocity gradients: the results for the moments are valid to within second-order terms in the velocity gradients.

Single-Mode Approximation

We can see that a set of constitutive equations for dilute polymer solutions contains a large number of relaxation equations. It is clear that the relaxation processes with the largest relaxation times are essential to describe the slowly changing motion of solutions. In the simplest approximation, we can use the only relaxation variable, which can be the gyration tensor $\langle S_i S_j \rangle$, defined by (4.48), or we can assume the macromolecule to be schematised by a subchain model with two particles. The last case, which is considered in Appendix F in more detail, is a particular case of equations (9.3) and (9.4), which is followed at $N = 1, \lambda_1 = 2$,

$$\sigma_{ik} = -p\delta_{ik} + 2\eta_{\mathrm{s}}\gamma_{ik} + 3\frac{\eta - \eta_{\mathrm{s}}}{\tau}\left(\xi_{ik} - \frac{1}{3}\delta_{ik}\right), \tag{9.6}$$

$$\frac{\mathrm{d}\xi_{ik}}{\mathrm{d}t} = -\frac{1}{\tau}\left(\xi_{ik} - \frac{1}{3}\delta_{ik}\right) + \nu_{ij}\xi_{jk} + \nu_{kj}\xi_{ji}. \tag{9.7}$$

The following notations are used in the equations written above

$$\xi_{ik} = x^1_{ik}, \qquad \eta = \eta_{\mathrm{s}} + \frac{3}{2}n\zeta.$$

Equations (9.6) and (9.7) make up the simplest set of constitutive equations for dilute polymer solutions, which, after excluding the internal variables ξ_{ij}, can be written in the form of a differential equation that has the form of the two-constant contra-variant equation investigated by Oldroyd (1950) (Section 8.6).

Note once again that equations (9.6) and (9.7) determines the stresses for the completely idealised macromolecules (without internal viscosity, hydrodynamic interaction and volume effects) in dilute solutions. To remedy the unrealistic behaviour of constitutive equations (9.6) and (9.7), some modifications were proposed (Rallison and Hinch 1988; Hinch 1994).

The expressions for the stress tensor together with the equations for the moments considered as additional variables, the continuity equation, and the equation of motion constitute the basis of the dynamics of dilute polymer solutions. This system of equations may be used to investigate the flow of dilute solutions in various experimental situations. Certain simple cases were examined in order to demonstrate applicability of the expressions obtained to dilute solutions, to indicate the range of their applicability, and to specify the expressions for quantities φ_ν, which were introduced previously as phenomenological constants.

9.1.2 Non-Linear Effects in Simple Shear Flow

We shall consider the case of shear stress when one of the components of the velocity gradient tensor has been specified and is constant, namely $\nu_{12} \neq 0$.

In order to achieve such a flow, it is necessary that the stresses applied to the system should be not only the shear stress σ_{12}, as in the case of a linear viscous liquid, but also normal stresses, so that the stress tensor is

$$\left\| \begin{matrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{matrix} \right\| .$$

The shear stress σ_{12} and the differences between the normal stresses σ_{11}–σ_{22} and σ_{22}–σ_{33} are usually measured in the experiment.

For the specified in this way motion, equation (9.2) defines, as was shown in Section 2.7.2, the non-zero components of the second-order moments

$$\begin{aligned} x_{11}^{\nu} &= \frac{1}{3}\left[1 + (2+\varphi_{\nu})(\tau_{\nu}\nu_{12})^2\right], \\ x_{22}^{\nu} &= \frac{1}{3}\left[1 - \varphi_{\nu}(\tau_{\nu}\nu_{12})^2\right], \\ x_{33}^{\nu} &= \frac{1}{3}, \\ x_{12}^{\nu} &= \frac{1}{3}\tau_{\nu}\nu_{12}, \end{aligned} \tag{9.8}$$

where, in accordance with (2.27) and (2.30), for high molecular weights

$$\begin{aligned} &\varphi_{\alpha} = \varphi_1 \alpha^{\theta}, \quad \varphi_1 \sim M^{-\theta}, \quad 0 < \theta < 1, \\ &\tau_{\alpha} = \tau_1 \alpha^{-z\nu}, \quad \tau_1 \sim M^{z\nu}, \quad 1.5 < z < 2.1. \end{aligned}$$

According to the theoretical estimate of the exponent, $z\nu$ varies from 1.5 (non-draining Gaussian coil) to 2.11 (draining coil with volume interactions).

Then, equation (9.5) defines the non-zero components of the stress tensor, which makes it possible to formulate expressions for the shear viscosity and the differences between the normal stresses:

$$\eta = nT\sum_{\nu=1}^{N}\tau_{\nu}\left[1 - \varphi_{\nu}(\tau_{\nu}\nu_{12})^2\right], \tag{9.9}$$

$$\sigma_{11} - \sigma_{22} = nT\sum_{\nu=1}^{N}(\tau_{\nu}\nu_{12})^2, \tag{9.10}$$

$$\sigma_{22} - \sigma_{33} = 0. \tag{9.11}$$

It follows from equations (9.9) that the viscosity (or, what amounts to the same thing, the characteristic viscosity) is independent of the velocity gradient for flexible chains ($\varphi_1 = 0$). For chains with an internal viscosity, the viscosity diminishes with increase in the velocity gradient; the nature of the variation may be estimated. Using the known dependences of the relaxation times and coefficient of internal viscosity on molecular weight and mode label, one can obtain

$$\eta - \eta_0 \sim M^{3z\nu-\theta-1}\nu_{12}^2.$$

From empirical equation (6.27), according to which $\theta = z\nu - 1$, the dependence of the viscosity on the molecular weight can be estimated as follows

$$\eta - \eta_0 \sim M^{2z\nu}\nu_{12}^2. \tag{9.12}$$

The dependence of the first difference of normal stresses on the molecular weight follows from equation (9.10)

$$\sigma_{11} - \sigma_{22} \sim M^{2z\nu-1}. \tag{9.13}$$

In another way, this expression was obtained by Öttinger (1989b).

Experimental data and analysis of the shear-dependent viscosity for dilute solutions of polyethelene oxide in water can be found in work by Kalashnikov (1994). These data show that the deviations in reduced viscosity (9.12) at constant shear rate from initial (at $\nu_{12} \to 0$) values are the more, the more is the molecular weight of the polymer. Other empirical estimates of the exponent $z\nu$ in equation (9.12) for solutions in which the coils are nearly unperturbed yield the exponent $2z\nu \approx 3$ (Lohmander 1964; Tsvetkov et al. 1964).

We may note that it has been shown for the dumbbell (Altukhov 1986) (see Appendix F) that the combined allowance for the internal viscosity and the anisotropy of the hydrodynamic interaction leads to the appearance of a non-zero second difference between the normal stresses σ_{22}–σ_{33}. Since the internal viscosity may be estimated, for example, from dynamic measurements, this effect may serve to estimate the anisotropy of the hydrodynamic interaction in a molecular coil.

9.1.3 Non-Steady-State Shear Flow

In this section we shall continue to investigate shear motion, while, in contrast to the previous section, we shall assume that the velocity gradient depends on the time but, as before, does not depend on the space coordinate. We shall consider a simple case of ideally flexible chains, for which the stress tensor and relaxation equations are defined by equations (9.3) and (9.4).

For simple shear, equation (9.4) is followed by the set of equations for the components of the second-order moment

$$\frac{dx_{11}}{dt} = -\frac{1}{\tau}\left(x_{11} - \frac{1}{3}\right) + 2\nu_{12}x_{12},$$

$$\frac{dx_{22}}{dt} = -\frac{1}{\tau}\left(x_{22} - \frac{1}{3}\right),$$

$$\frac{dx_{33}}{dt} = -\frac{1}{\tau}\left(x_{33} - \frac{1}{3}\right), \tag{9.14}$$

$$\frac{dx_{12}}{dt} = -\frac{1}{\tau}x_{12} + \nu_{12}x_{22},$$

$$\frac{dx_{13}}{dt} = -\frac{1}{\tau}x_{13} + \nu_{12}x_{23},$$

$$\frac{dx_{23}}{dt} = -\frac{1}{\tau}x_{23}.$$

Here and henceforth in this section, the label of mode is omitted for simplicity. Consider the case when the motion with a given constant velocity gradient ν_{12} begins at time $t = 0$. Under the given initial conditions, the set of equations (9.14) has the solution

$$x_{11} = \frac{1}{3}\left[1 + 2\tau^2\left(1 - \frac{t}{\tau}\exp\left(-\frac{t}{\tau}\right) - \exp\left(-\frac{t}{\tau}\right)\right)\nu_{12}^2\right],$$

$$x_{12} = \frac{1}{3}\tau\left[1 - \exp\left(-\frac{t}{\tau}\right)\right]\nu_{12},$$

$$x_{22} = x_{33} = \frac{1}{3}; \qquad x_{13} = x_{23} = 0.$$

Now, we can determine, according to equation (9.3), the non-zero components of the stress tensor

$$\sigma_{11}(t) = -p + 2nT\sum_{\alpha=1}^{N}\tau_\alpha^2\left[1 - \frac{t}{\tau_\alpha}\exp\left(-\frac{t}{\tau_\alpha}\right) - \exp\left(-\frac{t}{\tau_\alpha}\right)\right]\nu_{12}^2,$$

$$\sigma_{12}(t) = \eta^0\nu_{12} + nT\sum_{\alpha=1}^{N}\tau_\alpha\left[1 - \exp\left(-\frac{t}{\tau_\alpha}\right)\right]\nu_{12}, \tag{9.15}$$

$$\sigma_{22}(t) = \sigma_{33}(t) = -p,$$

$$\sigma_{13}(t) = \sigma_{23}(t) = 0.$$

These expressions describe the establishment of stresses for given uniform shear motion.

9.1.4 Non-Linear Effects in Oscillatory Shear Motion

From the methodical point of view, it is very interesting to consider the non-linear terms of the stresses under oscillatory shear velocity gradients, which it is convenient to write in the complex form

$$\nu_{12} \sim e^{-i\omega t}.$$

Akers and Williams (1969), calculating non-linear terms, noticed that the stresses are real quantities, which are determined through real quantities. That is why we ought to remember that formulae always contain the real parts of complex quantities, so that one has to bear in mind that ν_{ik} means $\frac{1}{2}(\nu_{ik} + \bar{\nu}_{ik})$, where the operation of complex conjugation is denoted by the bar above the symbol.

Assuming that the flow is described by the set of equations (9.3) and (9.4), one can use equations (9.14) for arbitrary time dependence of velocity gradient, to obtain for oscillatory simple shear the solution in the form

$$\begin{aligned}
x_{11} &= \frac{1}{3}\left[1 + \frac{\tau^2|\nu_{12}|^2}{1+\omega^2\tau^2} + \frac{1}{2}\left(\frac{\tau^2\nu_{12}^2}{(1-i\omega t)(1-2i\omega t)} + \frac{\tau^2\bar{\nu}_{12}^2}{(1+i\omega t)(1+2i\omega t)}\right)\right],\\
x_{12} &= \frac{1}{6}\left(\frac{\tau\nu_{12}}{1-i\omega t} + \frac{\tau\bar{\nu}_{12}}{1+i\omega t}\right),\\
x_{22} &= x_{33} = \frac{1}{3},\\
x_{12} &= x_{23} = 0.
\end{aligned}$$

Since all non-oscillatory terms in the solution are now omitted, we shall determine the non-zero components of the stress tensor according to equation (9.3)

$$\begin{aligned}
\sigma_{12} &= \eta_{\mathrm{s}}\frac{1}{2}(\nu_{12} + \bar{\nu}_{12})\\
&\quad + nT\sum_{\alpha}\left[\frac{\tau_\alpha}{1+\omega^2\tau_\alpha^2}\frac{1}{2}(\nu_{12}+\bar{\nu}_{12}) + \frac{\omega\tau_\alpha^2}{1+\omega^2\tau_\alpha^2}\frac{i}{2}(\nu_{12}-\bar{\nu}_{12})\right],
\end{aligned} \tag{9.16}$$

$$\begin{aligned}
\sigma_{11} &= -p + nT\sum_{\alpha}\left[\frac{\tau_\alpha^2|\nu_{12}|^2}{1+\omega^2\tau_\alpha^2}\right.\\
&\quad \left. + \frac{\tau_\alpha^2(1-2\omega^2\tau_\alpha^2)\frac{1}{2}(\nu_{12}^2+\bar{\nu}_{12}^2) + 3\omega\tau_\alpha^3\frac{i}{2}(\nu_{12}^2-\bar{\nu}_{12}^2)}{1+5\omega^2\tau_\alpha^2+4\omega^4\tau_\alpha^4}\right],
\end{aligned} \tag{9.17}$$

$$\sigma_{22} = \sigma_{33} = -p.$$

Expression (9.16) determines the non-linear dynamic viscosity and dynamical modulus. The first difference of the normal stresses σ_{11}–σ_{22}, defined by expressions (9.17), oscillate with a frequency twice that of velocity gradients (Akers and Williams 1969).

9.2 Many-Mode Description of Entangled Systems

9.2.1 Constitutive Relations

Stress Tensor

The expression for the stress tensor (6.7) allows us to investigate the non-linear with respect to velocity gradient effects. We use the normal co-ordinates (1.13) to write equation (6.7) in the form

$$\sigma_{ik} = -n(N+1)T\delta_{ik} + n\sum_{\nu}\left(2\mu T\lambda_{\nu}x_{ik}^{\nu} - T\delta_{ik} - \langle\rho_k^{\nu}T_i^{\nu}\rangle\right)$$

where $T_k^{\nu} = Q_{\nu\gamma}G_k^{\gamma}$ is the transformed force of the internal viscosity determined by equation (7.4). It is convenient to use the macroscopic mean quantities

$$x_{ij}^{\alpha} = \frac{2}{3}\mu\lambda_{\alpha}\langle\rho_i^{\alpha}\rho_j^{\alpha}\rangle, \qquad u_{ij}^{\alpha} = -\frac{1}{3T}\langle\rho_j^{\alpha}T_i^{\alpha}\rangle \tag{9.18}$$

to write the stress tensor in the more compact form

$$\sigma_{ik} = -p\delta_{ik} + 3nT\sum_{\nu}\left(x_{ik}^{\nu} - \frac{1}{3}\delta_{ik} + u_{ik}^{\nu}\right). \tag{9.19}$$

The pressure p includes both the partial pressure of the gas of Brownian particles $n(N+1)T$ and the partial pressure of the carrier "monomer" liquid. We shall assume that the viscosity of the "monomer" liquid can be neglected. The variables x_{ik}^{ν} in equation (9.19) characterise the mean size and shape of the macromolecular coils in a deformed system. The other variables u_{ik}^{ν} are associated mainly with orientation of small rigid parts of macromolecules (Kuhn segments). As a consequence of the mesoscopic approach, the stress tensor (9.19) of a system is determined as a sum of the contributions of all the macromolecules, which in this case can be expressed by simple multiplication by the number of macromolecules n. The macroscopic internal variables x_{ik}^{ν} and u_{ik}^{ν} can be found as solutions of relaxation equations which have been established in Chapter 7. However, there are two distinctive cases, which have to be considered separately.

Relaxation Equations for Weakly Entangled Systems

In the cases, when concentration of solution is not very high or melt consists of short macromolecules, the values of parameter χ ascend above the critical one $\chi^* \approx 0.1$. It is also implies the small values of the parameter ψ, that is

$$\chi^* < \chi < 0.3, \quad \psi \ll 1.$$

The internal variables are governed by relaxation equations (7.25) and (7.38) which are valid for the small mode numbers $\alpha^2 \ll 1/\chi$ and can be rewritten in the form

$$\begin{aligned}
&\frac{\mathrm{d}x^\alpha_{ik}}{\mathrm{d}t} - \nu_{ij}x^\alpha_{jk} - \nu_{kj}x^\alpha_{ji} \\
&\quad = -\frac{1}{2\tau_\alpha}\left(\left(x^\alpha_{ij} - \frac{1}{3}\delta_{ij}\right)b_{jk} + \left(x^\alpha_{kj} - \frac{1}{3}\delta_{kj}\right)b_{ji}\right), \qquad (9.20)
\end{aligned}$$

$$\begin{aligned}
&\frac{\mathrm{d}u^\alpha_{ik}}{\mathrm{d}t} - \omega_{ij}u^\alpha_{jk} - \omega_{kj}u^\alpha_{ji} \\
&\quad = -\left(\frac{1}{\tau}\delta_{ij} + \frac{1}{2\tau_\alpha}b_{ij}\right)u^\alpha_{jk} - \frac{1}{\tau}\frac{E}{B}\left[\left(x^\alpha_{ij} - \frac{1}{3}\delta_{ij}\right)d_{jk} - 2B\tau^{\mathrm{R}}_\alpha x^\alpha_{il}\gamma_{lj}f_{jk}\right] \\
&\qquad + \gamma_{il}u^\alpha_{lk} \qquad (9.21)
\end{aligned}$$

where the set of relaxation times is defined as

$$\tau, \quad \tau_\alpha = B\,\tau^{\mathrm{R}}_\alpha, \quad \tau^{\mathrm{R}}_\alpha = \frac{\tau^*}{\alpha^2}, \quad \alpha = 1, 2, \ldots \ll \left(\frac{1}{\chi}\right)^{1/2}. \qquad (9.22)$$

In this case, the auxiliary quantities b_{ik}, d_{ik} and f_{ik} are defined, in limits of applicability of the equations ($\alpha^2 \ll 1/\chi$, $\psi \ll 1$), in terms of the anisotropy tensors β_{jl} and ϵ_{kl} as

$$b_{ik} = \beta^{-1}_{ik}, \quad d_{ik} = \beta^{-1}_{ij}\epsilon_{kj}, \quad f_{ik} = \epsilon_{ik}. \qquad (9.23)$$

Relaxation Equations for Strongly Entangled Systems

This is a case, when the parameter χ has values less than a certain critical value χ^*, while additionally one requires that values of the parameter ψ are big, that is

$$\chi < \chi^* < 0.3, \quad \psi > 1.$$

The internal variables for this case are governed by relaxation equations (7.29) and (7.40) which are valid for the small mode numbers $\alpha^2 \ll \psi/\chi$. This is a case of very concentrated solutions and melts of polymers. Keeping only the zero-order terms with respect to the ratio B/E, the set of relaxation equations for the internal variables can be written in the simpler form

$$\begin{aligned}
&\frac{\mathrm{d}x^\alpha_{ik}}{\mathrm{d}t} - \nu_{ij}x^\alpha_{jk} - \nu_{kj}x^\alpha_{ji} \\
&\quad = -\frac{1}{2\tau^{\mathrm{rep}}_\alpha}\left(\left(x^\alpha_{ij} - \frac{1}{3}\delta_{ij}\right)b_{jk} + \left(x^\alpha_{kj} - \frac{1}{3}\delta_{kj}\right)b_{ji}\right), \qquad (9.24)
\end{aligned}$$

$$\begin{aligned}
&\frac{\mathrm{d}u^\alpha_{ik}}{\mathrm{d}t} - \omega_{ij}u^\alpha_{jk} - \omega_{kj}u^\alpha_{ji} \\
&\quad = -\frac{1}{\tau}u^\alpha_{ik} - \frac{1}{\tau}\left(x^\alpha_{ik} - \frac{1}{3}\delta_{ik} - 2B\tau^{\mathrm{R}}_\alpha x^\alpha_{il}\gamma_{lj}f_{jk}\right) + \frac{B}{E}e_{ij}\gamma_{jl}u^\alpha_{lk}, \qquad (9.25)
\end{aligned}$$

where the set of relaxation times is defined as

$$\tau, \quad \tau_\alpha^{\text{rep}} = \frac{\pi^2}{\chi}\tau_\alpha^{\text{R}}, \quad \tau_\alpha^{\text{R}} = \frac{\tau^*}{\alpha^2}, \quad \alpha = 1, 2, \ldots \ll \left(\frac{\psi}{\chi}\right)^{1/2}. \tag{9.26}$$

The auxiliary quantities b_{ik}, e_{ik} and f_{ik} are introduced in Chapter 7 to take into account the effect of the induced anisotropy of medium on the dynamics of a single macromolecule in the system. In limits of applicability of the above equations ($\alpha^2 \ll \psi/\chi,\ \psi \gg 1$), the quantities are defined in terms of the anisotropy tensors β_{jl} and ϵ_{kl} as

$$b_{ik} = \epsilon_{ik}^{-1}, \quad e_{ik} = \epsilon_{ij}^{-1}\beta_{jk}, \quad f_{ik} = \epsilon_{ij}^{-1}\beta_{jl}\epsilon_{kl}. \tag{9.27}$$

Let us remind that equation (9.24), describing the relaxation of macromolecular conformation, can be considered only as an assumed results of accurate derivation of the relaxation equation from the macromolecular dynamics.

Tensor of Anisotropy

Thus, two sets of constitutive relations are formulated. The systems of equations both (9.19)–(9.22), applicable to the weakly entangled systems, and (9.19) and (9.24)–(9.26), applicable to the strongly entangled systems, include, through equations (9.23) and (9.27), the tensors of global anisotropy

$$\beta_{ik} = (\delta_{jk} + \kappa a_{ll}\delta_{jk} + 3\beta a'_{jk})^{-1}, \qquad \epsilon_{ik} = (\delta_{jk} + \nu a_{ll}\delta_{jk} + 3\epsilon a'_{jk})^{-1},$$
$$a_{ij} = \sum_\nu \left(x_{ij}^\nu - \frac{1}{3}\delta_{ij} + u_{ij}^\nu\right), \qquad a'_{ij} = a_{ij} - \frac{1}{3}a_{ll}\delta_{ij}.$$

The set of equations both for weakly and strongly entangled systems contains only two relaxation branches and describe viscoelastic behaviour in the region of small frequencies (One can look at Fig. 17 to be convinced that essential contributions to the modulus are given by the first and the second branches in the region of small frequencies). These sets of equations are the basic constitutive relations which allow us to develop a reliable theory of non-linear effects in viscoelasticity of non-dilute polymer systems following the works by Pokrovskii and Pyshnograi (1990, 1991) and Pyshnograi (1994, 1996).

9.2.2 Linear Approximation

To calculate characteristics of linear viscoelasticity, one can consider linear approximation of constitutive relations derived in the previous section. The expression (9.19) for stress tensor has linear form in internal variables x_{ik}^ν and u_{ik}^ν, so that one has to separate linear terms in relaxation equations for the internal variables. This has to be considered separately for weakly and strongly entangled system.

Weakly Entangled Systems

In the cases, when

$$\chi^* < \chi < 0.3, \quad \psi < 1,$$

the relaxation equations (9.20) and (9.21) reduce to the simpler form

$$\begin{aligned} \frac{\mathrm{d}x_{ik}^{\alpha}}{\mathrm{d}t} &= -\frac{1}{\tau_\alpha}\left(x_{ik}^{\alpha} - \frac{1}{3}\delta_{ik}\right) + \frac{2}{3}\gamma_{ik}, \\ \frac{\mathrm{d}u_{ik}^{\alpha}}{\mathrm{d}t} &= -\frac{1}{\tau_\alpha^*}u_{ik}^{\alpha} - \frac{1}{\tau}\psi\left(x_{ik}^{\alpha} - \frac{1}{3}\delta_{ik} - \frac{2}{3}B\tau_\alpha^{\mathrm{R}}\gamma_{ik}\right) \end{aligned} \tag{9.28}$$

where the set of relaxation times is defined as

$$\tau, \quad \tau_\alpha^* = \frac{2\tau\tau_\alpha}{\tau + 2\tau_\alpha}, \quad \tau_\alpha = B\,\tau_\alpha^{\mathrm{R}}, \quad \tau_\alpha^{\mathrm{R}} = \frac{\tau^*}{\alpha^2}, \quad \alpha = 1, 2, \ldots \ll \left(\frac{1}{\chi}\right)^{1/2}.$$

Equations (9.28) have the following solutions for oscillatory motion

$$\begin{aligned} x_{ik}^{\alpha} &= \frac{1}{3}\delta_{ik} + \frac{2}{3}\,\frac{\tau_\alpha}{1 - i\omega\tau_\alpha}\gamma_{ik}, \\ u_{ik}^{\alpha} &= \frac{2}{3}\,\frac{1}{\tau}\psi\left(B\,\tau_\alpha^{\mathrm{R}} - \frac{\tau_\alpha}{1 - i\omega\tau_\alpha}\right)\frac{\tau_\alpha^*}{1 - i\omega\tau_\alpha^*}\,\gamma_{ik}. \end{aligned}$$

Then, one can make use of the expression (9.19) for the stress tensor to obtain the coefficient of dynamic modulus

$$G(\omega) = nT\sum_{\alpha}^{1/\sqrt{\chi}}\left[\frac{i\omega\tau_\alpha}{1 - i\omega\tau_\alpha} + \frac{1}{\tau}\psi\left(B\,\tau_\alpha^{\mathrm{R}} - \frac{i\omega\tau_\alpha}{1 - i\omega\tau_\alpha}\right)\frac{\tau_\alpha^*}{1 - i\omega\tau_\alpha^*}\right].$$

This expression can be written in standard form

$$\begin{aligned} G(\omega) = nT \times \sum_{\alpha}^{1/\sqrt{\chi}}\Bigg[&\left(1 + \psi\frac{\tau_\alpha\tau_\alpha^*}{\tau(\tau_\alpha^* - \tau_\alpha)}\right)\frac{-i\omega\tau_\alpha}{1 - i\omega\tau_\alpha} \\ &+ \frac{1}{\tau}\psi\left(B\,\tau_\alpha^{\mathrm{R}} - \frac{\tau_\alpha\tau_\alpha^*}{\tau_\alpha^* - \tau_\alpha}\right)\frac{-i\omega\tau_\alpha^*}{1 - i\omega\tau_\alpha^*}\Bigg]. \end{aligned} \tag{9.29}$$

The terms of the first and the second orders give the coefficients of viscosity and elasticity

$$\eta = nT\sum_{\alpha}^{1/\sqrt{\chi}}\left(\tau_\alpha - \psi\frac{\tau_\alpha\tau_\alpha^*}{\tau}\right) \approx \frac{\pi^2}{6}nT\tau^*B, \tag{9.30}$$

$$\nu = nT\sum_{\alpha}^{1/\sqrt{\chi}}\left(\tau_\alpha^2 - \psi\frac{\tau_\alpha\tau_\alpha^*}{\tau}(\tau_\alpha^* + \tau_\alpha)\right) \approx \frac{\pi^4}{90}nT(\tau^*B)^2. \tag{9.31}$$

Value of the dynamic modulus on the plateau can be found as $G_e = \lim_{\omega\to\infty} G(\omega)$ which gives

$$G_e = nT \sum_{\alpha}^{1/\sqrt{\chi}} 1 \approx nT\chi^{-\frac{1}{2}}. \tag{9.32}$$

It is natural that estimates (9.30)–(9.32) practically coincide with estimates (6.39) and (6.40), at $\chi \ll 1$, for corresponding quantities for a system of macromolecules in viscoelastic liquid.

Strongly Entangled Systems

In the cases, when

$$\chi < \chi^* \approx 0.1, \quad \psi > 1,$$

the internal variables are governed by relaxation equations (9.24) and (9.25) which are valid for the small mode numbers $\alpha^2 \ll \psi/\chi$. Keeping only the zero-order terms with respect to velocity gradient, the set of relaxation equations for the internal variables can be written in the simpler form

$$\begin{aligned} \frac{\mathrm{d}x_{ik}^{\alpha}}{\mathrm{d}t} &= -\frac{1}{\tau_{\alpha}^{\mathrm{rep}}}\left(x_{ik}^{\alpha} - \frac{1}{3}\delta_{ik}\right) + \frac{2}{3}\gamma_{ik}, \\ \frac{\mathrm{d}u_{ik}^{\alpha}}{\mathrm{d}t} &= -\frac{1}{\tau}u_{ik}^{\alpha} - \frac{1}{\tau}\left(x_{ik}^{\alpha} - \frac{1}{3}\delta_{ik} - \frac{2}{3}B\tau_{\alpha}^{\mathrm{R}}\gamma_{ik}\right) \end{aligned} \tag{9.33}$$

where the set of relaxation times is defined as

$$\tau, \quad \tau_{\alpha}^{\mathrm{rep}} = \frac{\pi^2}{\chi}\tau_{\alpha}^{\mathrm{R}}, \quad \tau_{\alpha}^{\mathrm{R}} = \frac{\tau^*}{\alpha^2}, \quad \alpha = 1, 2, \ldots \ll \left(\frac{\psi}{\chi}\right)^{1/2}.$$

Equations (9.33) have the following solutions for oscillatory motion

$$\begin{aligned} x_{ik}^{\alpha} &= \frac{1}{3}\delta_{ik} + \frac{2}{3}\frac{\tau_{\alpha}^{\mathrm{rep}}}{1 - i\omega\tau_{\alpha}^{\mathrm{rep}}}\gamma_{ik}, \\ u_{ik}^{\alpha} &= \frac{2}{3}\left(B\,\tau_{\alpha}^{\mathrm{R}} - \frac{\tau_{\alpha}^{\mathrm{rep}}}{1 - i\omega\tau_{\alpha}^{\mathrm{rep}}}\right)\frac{1}{1 - i\omega\tau}\gamma_{ik}. \end{aligned}$$

Then, one can make use of the expression (9.19) for the stress tensor to obtain the dynamic modulus

$$G(\omega) = nT\sum_{\alpha=1}^{\pi/\chi}\left[\frac{-i\omega\tau_{\alpha}^{\mathrm{rep}}}{1 - i\omega\tau_{\alpha}^{\mathrm{rep}}} + \left(B\,\tau_{\alpha}^{\mathrm{R}} - \frac{\tau_{\alpha}^{\mathrm{rep}}}{1 - i\omega\tau_{\alpha}^{\mathrm{rep}}}\right)\frac{-i\omega}{1 - i\omega\tau}\right]. \tag{9.34}$$

This expression, after some transformations, can be written in the standard form

$$G(\omega) = nT \sum_{\alpha=1}^{\pi/\chi} \left[\left(1 + \frac{\tau_\alpha^{\mathrm{rep}}}{\tau - \tau_\alpha^{\mathrm{rep}}} \right) \frac{-i\omega\tau_\alpha^{\mathrm{rep}}}{1 - i\omega\tau_\alpha^{\mathrm{rep}}} + \left(\frac{B\,\tau_\alpha^{\mathrm{R}}}{\tau} - \frac{\tau_\alpha^{\mathrm{rep}}}{\tau - \tau_\alpha^{\mathrm{rep}}} \right) \frac{-i\omega\tau}{1 - i\omega\tau} \right]. \tag{9.35}$$

This equation, also as equation (6.49) gives description of the frequency dependency of dynamic modulus at low frequencies (the terminal zone). Both in equation (6.49) and (9.35), the second terms present the contribution from the orientational relaxation branch, while the first ones present the contribution from the conformational relaxation due to the different mechanisms: diffusive and reptational.

The terms of the first and the second orders in expansion of expression (9.34) or (9.35) in powers of $-i\omega$ determine the coefficients of viscosity and elasticity

$$\begin{aligned} \eta &= nT \sum_{\alpha=1}^{\pi/\chi} B\,\tau_\alpha^{\mathrm{R}} = \frac{\pi^2}{6} nT\tau^* B, \\ \nu &= nT \sum_{\alpha=1}^{\pi/\chi} (B\,\tau\tau_\alpha^{\mathrm{R}} - \tau\tau_\alpha^{\mathrm{rep}}) = nT \left(\frac{\pi^2}{3} (B\tau^*)^2 \chi - \frac{\pi^4}{3} B(\tau^*)^2 \right). \end{aligned} \tag{9.36}$$

One can see that the last terms in the last relations can be omitted in comparison with the other, so that this equations reduce to equations (6.52), that is

$$\eta = \frac{\pi^2}{6} nT\tau^* B, \qquad \nu = \frac{\pi^2}{3} nT\,(B\tau^*)^2 \chi. \tag{9.37}$$

Value of the dynamic modulus on the plateau can be found as $G_e = \lim_{\omega\to\infty} G(\omega)$ which gives

$$G_e = nT \sum_{\alpha=1}^{\pi/\chi} \left(1 + \frac{B\,\tau_\alpha^{\mathrm{R}}}{\tau} \right) \approx nT \left(\frac{\pi}{\chi} + \frac{\pi^2}{12} \frac{1}{\chi} \right). \tag{9.38}$$

The contribution from the first term (reptation branch) has the same order of magnitude as the contribution from the second term at very high frequencies. However, one has to take into account that, due to distribution of relaxation times, the limit value of the first term is reached at higher frequencies than the limit value of the second term. At lower frequencies the plateau value of the dynamic modulus is determined by the second term and coincides with expression (6.52).

One can see that introduction of the reptation mechanism of conformational relaxation, instead of diffusive mechanism, does not affect the values of the terminal quantities, but, one can expect, improves the situation in the region of the minima of the loss modulus G'': reptation branch fill the gap between the orientational and the second conformational branches of relaxation times. Thus, the description with help of two relaxation branches is valid in the terminal zone and for higher frequencies close to it.

9.2.3 Steady-State Simple Shear Flow

To demonstrate the consistency of constitutive relations with experimental evidence for entangled systems, some particular cases, when the velocity gradients are known and can be assumed to be independent of time, have been investigated (Pyshnograi and Pokrovskii, 1988; Pyshnograi, 1994, 1996; Altukhov and Pyshnograi, 1995, 1996). We shall consider here steady-state shear flow of both weakly entangled system and strongly entangled system. The stress tensor is given by equation (9.19), that is

$$\sigma_{ik} = -p\delta_{ik} + 3nT\sum_{\nu}\left(x_{ik}^{\nu} - \frac{1}{3}\delta_{ik} + u_{ik}^{\nu}\right).$$

For the case of small velocity gradients, the variables x_{ik}^{α} and u_{jk}^{α} can be found in the form of an expansion in powers of velocity gradients. The first terms are defined by equations (7.28) and (7.39) for the case of weakly entangled systems ($\chi > \chi^* \approx 0.1$) and by equations (7.32) and (7.43) for the case of strongly entangled systems ($\chi < \chi^* \approx 0.1$).

Further on, we shall consider the case of shear stress when one of the components of the velocity gradient tensor has been specified and is constant, namely $\nu_{12} \neq 0$. This situation occurs in experimental studies of polymer solutions (Ferry 1980). In order to achieve such a flow, it is necessary that the stresses applied to the system should be not only the shear stress σ_{12}, as in the case of a linear viscous liquid, but also normal stresses, so that the stress tensor is

$$\begin{Vmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{Vmatrix}.$$

The shear stress σ_{12} and the differences between the normal stresses $\sigma_{11} - \sigma_{22}$ and $\sigma_{22} - \sigma_{33}$ are usually measured in the experiment (Meissner et al. 1989). The results of calculation of the stresses up to the third-order terms with respect to the velocity gradient will be demonstrated further on. For simplicity, we shall neglect the effect of anisotropy of the environment when the case of strongly entangled systems will be considered.

Shear Viscosity

In steady-state shear, when the only component of the velocity gradient tensor differs from zero is ν_{12}, equation (9.19) is followed by

$$\sigma_{12}^{0} = \eta_0\nu_{12}, \qquad \eta_0 = \frac{\pi^2}{6}nTB\tau^*, \qquad \chi < 0.5. \tag{9.39}$$

The third-order terms in shear stress give us the expression for the effective shear viscosity

$$\eta = \eta_0 \times \begin{cases} 1 - \left(\frac{2\pi^4}{315}\psi + \frac{2\pi^2}{15}\chi + \frac{52\pi^4}{4725}\beta + \frac{4\pi^4}{945}\kappa\right)\left(B\tau^*\nu_{12}\right)^2, & \chi > \chi^*, \\ 1 - \left(4\chi^2 - \frac{\pi^2}{15}\frac{\chi}{B} - \frac{2\pi^6}{315}\frac{1}{(\chi B)^2}\right)\left(B\tau^*\nu_{12}\right)^2, & \chi < \chi^*. \end{cases} \tag{9.40}$$

One can see that two factors lead to non-linear effects in shear, namely, the relaxation response of the surrounding (χ and ψ) and the effects associated with the change in dimensions and the shape of the macromolecular coils (β and κ). Though comparative influence of these effects does not investigated enough, one can suggest that the influence of χ and ψ is small as compared with the influence of the other parameters at $\chi > \chi^*$, while at $\chi < \chi^*$ the change of the environment (β and κ) can be neglected. The first term in the parentheses in (9.40) at $\chi < \chi^*$ dominates for the long macromolecules. The above relation, in agreement with the experimental evidence (Schreiber et al. 1963; Ito and Shishido 1972), shows that the deviation of the behaviour of the system from Newtonian starts at the shear stress which is the lesser, the larger the length of the macromolecule is. For very long macromolecules the deviation does not depend on the length of the macromolecules.

Normal Stresses

Calculation of terms of the second order reveals that normal stresses are

$$\begin{aligned} \sigma_{11} + p &= \begin{cases} nT\left(\frac{\pi^4}{45} + \frac{\pi^2}{6}\chi - \frac{\pi^4}{90}\beta\right)(B\tau^*\nu_{12})^2, & \chi > \chi^*, \\ nT\left(\frac{\pi^6}{90}\frac{1}{B\chi} + \frac{\pi^2}{6}\chi\frac{B}{E} + \frac{\pi^2}{3}\chi\right)(B\tau^*\nu_{12})^2, & \chi < \chi^*, \end{cases} \\ \sigma_{22} + p &= \begin{cases} -nT\left(\frac{\pi^2}{6}\chi + \frac{\pi^4}{90}\beta\right)(B\tau^*\nu_{12})^2, & \chi > \chi^*, \\ nT\left(\frac{\pi^6}{90}\frac{1}{B\chi} + \frac{\pi^2}{6}\chi\frac{B}{E} - \frac{\pi^2}{3}\chi\right)(B\tau^*\nu_{12})^2, & \chi < \chi^*, \end{cases} \\ \sigma_{33} + p &= 0. \end{aligned} \tag{9.41}$$

Specific characteristics of viscoelastic medium are differences of the normal stresses

$$\begin{aligned} \sigma_{11} - \sigma_{22} &= \begin{cases} nT\left(\frac{\pi^4}{45} + \frac{\pi^2}{3}\chi\right)(B\tau^*\nu_{12})^2, & \chi > \chi^*, \\ nT\frac{2\pi^2}{3}\chi\,(B\tau^*\nu_{12})^2, & \chi < \chi^*, \end{cases} \\ \sigma_{22} - \sigma_{33} &= \begin{cases} -nT\left(\frac{\pi^2}{6}\chi + \frac{\pi^4}{90}\beta\right)(B\tau^*\nu_{12})^2, & \chi > \chi^*, \\ nT\left(\frac{\pi^6}{90}\frac{1}{B\chi} + \frac{\pi^2}{6}\chi\frac{B}{E} - \frac{\pi^2}{3}\chi\right)(B\tau^*\nu_{12})^2, & \chi < \chi^*. \end{cases} \end{aligned} \tag{9.42}$$

The ratio of the first difference of the normal stresses $\sigma_{11} - \sigma_{22}$ to the square of the shear stress is an important characteristic quantity. The expressions for the steady-state modulus in the region of low velocity gradients are defined as

$$\frac{2\sigma_{12}^2}{\sigma_{11}-\sigma_{22}} = \begin{cases} \frac{5}{2}nT\left(1-\frac{15}{\pi^2}\chi\right), & \chi > \chi^*, \\ \frac{\pi^2}{12}nT\chi^{-1}, & \chi < \chi^*. \end{cases} \tag{9.43}$$

For the weakly entangled system, the steady-state modulus depends on the molecular weight of polymer as M^{-1}, while for strongly entangled system, the steady-state modulus does not depend on the molecular weight of polymer, which is consistent with typical experimental data for concentrated polymer systems (Graessley 1974). The expression for the modulus is exactly the same as for the plateau value of the dynamic modulus (equations (6.52) and (6.58))

Expressions (9.42) lead to the following relation for the ratio of the normal stresses differences

$$\frac{\sigma_{22}-\sigma_{33}}{\sigma_{11}-\sigma_{22}} = \begin{cases} -\frac{15}{2\pi^2}\chi - \frac{1}{2}\beta, & \chi > \chi^*, \\ \frac{\pi^4}{60}\frac{1}{\chi^2 B} + \frac{B}{4E} - \frac{1}{2}, & \chi < \chi^*. \end{cases} \tag{9.44}$$

This ratio depends on the molecular weight of polymer M and predicted to be negative for typical values of parameters. For the strongly entangled systems, according to equations (3.30), $B \sim M^{\delta}, \quad \chi \sim M^{-1}$, so that the ratio (9.44) approaches $-1/2$ for very long macromolecules. According to experimental evidence, the second difference of the normal stresses $\sigma_{22} - \sigma_{33}$ is negative and less than the first. The ratio has generally been reported to be in the range of -0.15 to -0.3 (Brown et al. 1995), though Faitelson (1995) found the values of the quantity for polybutadiene with narrow molecular-weight distribution to lie in the range from -0.3 to -0.45. It would be desirable to measure the ratio of differences of the normal stresses for well-characterised systems to test the validity of relation (9.44).

9.3 Single-Mode Description of Entangled System

Notwithstanding the simplifying assumptions in the dynamics of macromolecules, the sets of constitutive relations derived in Section 9.2.1 for polymer systems, are rather cumbersome. Now, it is expedient to employ additional assumptions to obtain reasonable approximations to many-mode constitutive relations. It can be seen that the constitutive equations are valid for the small mode numbers α, in fact, the first few modes determines main contribution to viscoelasticity. The very form of dependence of the dynamical modulus in Fig. 17 in Chapter 6 suggests to try to use the first modes to describe low-frequency viscoelastic behaviour. So, one can reduce the number of modes to minimum, while two cases have to be considered separately.

It is clear that at transition from many modes to a single mode, weight coefficients for mode contributions into the stress tensor have to be introduced. One has to require correspondence of some specified quantities to the same ones calculated within the many-mode theory. The procedure eliminates the arbitrariness to the choice of the weights. One can see that the following form of the stress tensor

$$\sigma_{ik} = -p\delta_{ik} + \frac{\pi^2}{2}\,nT\left(x_{ik}^1 - \frac{1}{3}\delta_{ik} + u_{ik}^1\right) \tag{9.45}$$

provides the correct form for initial coefficient of viscosity both for the weakly and strongly entangled systems.

9.3.1 Weakly Entangled Systems

Constitutive Relations

First, we refer to constitutive relations (9.19)–(9.22) which describe the behaviour of the system with moderate concentration of polymer and/or the systems with shorter macromolecules, when the characteristic parameters of the system are satisfied to conditions

$$\chi^* < \chi < 0.5, \quad \psi < 1.$$

Every mode contains two relaxation processes, described by the relaxation equations (9.20) and (9.21). One can retain one relaxation equation from each relaxation branch only, so that the two relaxation equations have to be considered

$$\begin{aligned}
&\frac{\mathrm{d}x_{ik}^1}{\mathrm{d}t} - \nu_{ij}x_{jk}^1 - \nu_{kj}x_{ji}^1 \\
&\quad = -\frac{1}{2\tau_1}\left[\left(x_{ij}^1 - \frac{1}{3}\delta_{ij}\right)b_{jk} + \left(x_{kj}^1 - \frac{1}{3}\delta_{kj}\right)b_{ji}\right],
\end{aligned} \tag{9.46}$$

$$\begin{aligned}
&\frac{\mathrm{d}u_{ik}^1}{\mathrm{d}t} - \omega_{ij}u_{jk}^1 - \omega_{kj}u_{ji}^1 \\
&\quad = -\left(\frac{1}{\tau}\delta_{ij} + \frac{1}{2\tau_1}b_{ij}\right)u_{jk}^1 - \frac{1}{\tau}\psi\left[\left(x_{ij}^1 - \frac{1}{3}\delta_{ij}\right)d_{jk} - 2B\tau_1^{\mathrm{R}}x_{il}^1\gamma_{lj}f_{jk}\right] \\
&\qquad + \gamma_{il}u_{lk}^1,
\end{aligned} \tag{9.47}$$

where the relaxation time $\tau_1 = \tau^* B$ and the auxiliary quantities are

$$\begin{aligned}
&b_{ik} = \beta_{ik}^{-1}, \qquad d_{ik} = \beta_{ij}^{-1}\epsilon_{kj}, \qquad f_{ik} = \epsilon_{ik}, \\
&\beta_{ik} = [(1-\kappa+(\kappa-\beta)a_{ll})\delta_{ik} + 3\beta a_{ik}]^{-1}, \\
&\epsilon_{ik} = [(1-\nu+(\nu-\epsilon)a_{ll})\delta_{ik} + 3\epsilon a_{ik}]^{-1}, \qquad a_{ik} = x_{ik}^1 - \frac{1}{3}\delta_{ij} + u_{ij}^1.
\end{aligned}$$

The relaxation equations (9.46) and (9.47) describe the joint non-linear relaxation of the two variables which appear to be weakly connected with each other through the term with the small quantity ψ in equation (9.47).

It is convenient to introduce new variables, so that expression (9.45) for the stress tensor can be written in the form

$$\sigma_{ik} = -p\delta_{ik} + 3\frac{\eta_0}{\tau_0}\left(\xi_{ik} - \frac{1}{3}\delta_{ik}\right), \quad \xi_{ik} = x_{ik}^1 + u_{ij}^1, \tag{9.48}$$

where one retains the previous definitions of the shear viscosity η_0 and define the relaxation time τ_0 as

$$\eta_0 = \frac{\pi^2}{6}nT\tau^* B, \qquad \tau_0 = \tau^* B.$$

The set of relaxation equations in the single-mode approach (9.46) and (9.47) can be written in different approximations. One can see, that in zero approximation ($\psi = 0$), the relaxation equations (9.46) and (9.47) appear to be independent. The expansion of the quantity u_{ik}^1 in powers of velocity gradient begins with terms of the second order (see equation (7.39)), so that, according to equation (9.47), the variable u_{ik}^1 is not perturbed in the first and second approximations at all and, consequently, can be omitted at $\psi = 0$. In virtue of $\psi \ll 1$, the second variable has to considered to be small in any case and can be neglected with comparison to the first variable, so that the system of equations can be written in a simpler way. In the simplest case, relaxation equation (9.46) in terms of the new variables ξ_{jk} can be rewritten as

$$\begin{aligned}\frac{\mathrm{d}\xi_{ik}}{\mathrm{d}t} - \nu_{ij}\xi_{jk} - \nu_{kj}\xi_{ji} = &-\frac{1}{\tau_0}\,[1 + (\kappa - \beta)(\xi_{ss} - 1)]\left(\xi_{ik} - \frac{1}{3}\delta_{ik}\right)\\ &-\frac{1}{\tau_0}\,3\beta\left(\xi_{ij} - \frac{1}{3}\delta_{ij}\right)\left(\xi_{jk} - \frac{1}{3}\delta_{jk}\right).\end{aligned} \tag{9.49}$$

One may note that the system of constitutive relations (9.48)–(9.49), which were derived and investigated by Pyshnograi et al. (1994), Pyshnograi (1996), Altukhov and Pyshnograi (1996), is a particular case of a set of the phenomenological constitutive equations (8.30)–(8.31).

Steady-State Simple Shear Flow

The expressions for stresses in simple shear flow are followed constitutive relations (9.48)–(9.49). With accuracy up to the third-order terms with respect to velocity gradient ν_{12} one has

$$\begin{aligned}&\sigma_{12} = \eta\nu_{12}, \qquad \frac{\eta}{\eta_0} = 1 - \frac{1}{3}(2\kappa + 7\beta)(\tau_0\nu_{12})^2,\\ &\sigma_{11} - \sigma_{22} = 2\eta_0\tau_0\nu_{12}^2 = 2\frac{\tau_0}{\eta_0}\,\sigma_{12}^2,\\ &\sigma_{22} - \sigma_{33} = -\beta\eta_0\tau_0\nu_{12}^2 = -\beta\frac{\tau_0}{\eta_0}\,\sigma_{12}^2.\end{aligned} \tag{9.50}$$

In the region of the higher velocity gradient, the viscosity coefficient η and the coefficients of normal stresses as functions of velocity gradients were calculated (Golovicheva et al. 2000) for different values of the parameters β and κ. The relations for simple shear flows are typical for polymer solutions of moderate concentration.

Constitutive relations (9.48)–(9.49) determine certain amendments to known expressions for flow of viscous liquid through the long channels. The results are available (Erenburg and Pokrovskii 1981; Altukhov and Pyshnograi 1996) for flow between parallel planes with the gap h and for flow through a round tube with the radius R, correspondingly

$$Q = \frac{A}{12\eta_0} h^3 \left(1 + \frac{1}{20} \left(\frac{Ah\tau_0}{\eta_0} \right)^2 (2\kappa + 7\beta) \right),$$

$$Q = \frac{\pi A}{8\eta_0} R^4 \left(1 + \frac{1}{6} \left(\frac{AR\tau_0}{\eta_0} \right)^2 (2\kappa + \beta) \right).$$

In these expressions, Q is the volume rate and $A = p/L$ is gradient of pressure along the channels.

One can concluded that the constitutive relations (9.48)–(9.49) do indeed approximate the behaviour of systems containing long macromolecules.

9.3.2 Strongly Entangled Systems

Constitutive Relations

In this case, when

$$\chi < \chi^* < 1, \quad \psi > 1,$$

the expression (9.45) for the stress tensor can be used in the previous form

$$\sigma_{ik} = -p\delta_{ik} + \frac{\pi^2}{2} nT \left(x_{ik}^1 - \frac{1}{3}\delta_{ik} + u_{ik}^1 \right). \tag{9.51}$$

Now, one can refer to constitutive relations (9.19) and (9.24)–(9.26) and, as in previous case, one can keep one relaxation equation from each relaxation branch only, so that one has two relaxation equations in the following form to be considered

$$\begin{aligned} &\frac{\mathrm{d}x_{ik}^1}{\mathrm{d}t} - \nu_{ij} x_{jk}^1 - \nu_{kj} x_{ji}^1 \\ &\quad = -\frac{1}{2\tau_1^{\mathrm{rep}}} \left[\left(x_{ij}^1 - \frac{1}{3}\delta_{ij} \right) b_{jk} + \left(x_{kj}^1 - \frac{1}{3}\delta_{kj} \right) b_{ji} \right], \end{aligned} \tag{9.52}$$

$$\begin{aligned} &\frac{\mathrm{d}u_{ik}^1}{\mathrm{d}t} - \omega_{ij} u_{jk}^1 - \omega_{kj} u_{ji}^1 \\ &\quad = -\frac{1}{\tau} u_{ik}^1 - \frac{1}{\tau} \left(x_{ik}^1 - \frac{1}{3}\delta_{ik} - 2B\tau^* x_{il}^1 \gamma_{lj} f_{jk} \right) + \frac{B}{E} e_{ij} \gamma_{jl} u_{lk}^1 \end{aligned} \tag{9.53}$$

where the auxiliary quantities are

$$b_{ik} = \epsilon_{ik}^{-1}, \qquad e_{ik} = \epsilon_{ij}^{-1}\beta_{jk}, \qquad f_{ik} = \epsilon_{ij}^{-1}\beta_{jl}\epsilon_{lk},$$

$$\beta_{ik} = [(1-\kappa+(\kappa-\beta)a_{ll})\delta_{ik}+3\beta a_{ik}]^{-1},$$

$$\epsilon_{ik} = [(1-\nu+(\nu-\epsilon)a_{ll})\delta_{ik}+3\epsilon a_{ik}]^{-1}, \qquad a_{ik} = x_{ik}^1 - \frac{1}{3}\delta_{ij} + u_{ij}^1.$$

In linear case, the dependence of the tensors β_{ik} and ϵ_{ik} on the anisotropy tensor can be neglected, and all the above quantities become the unit matrixes.

Equations (9.52) and (9.53) describe the non-linear relaxation processes, which are featured, in particular, by the anisotropy of relaxation which means that in a deformed system, different components of the tensors x_{ik}^1 and u_{ik}^1 relax at different rates. The change of the second variables depends on the first one, so that the two variables of each mode are closely connected with each other.

One considers the anisotropy of environment to give a small contribution to the terms of the second order and higher with respect to velocity gradient, so that it can be neglected for the beginning, and relaxation equations (9.52) and (9.53) take simpler forms

$$\frac{\mathrm{d}x_{ik}^1}{\mathrm{d}t} - \nu_{ij}x_{jk}^1 - \nu_{kj}x_{ji}^1 = -\frac{1}{\tau_1^{\mathrm{rep}}}\left(x_{ij}^1 - \frac{1}{3}\delta_{ij}\right), \tag{9.54}$$

$$\frac{\mathrm{d}u_{ik}^1}{\mathrm{d}t} - \omega_{ij}u_{jk}^1 - \omega_{kj}u_{ji}^1$$
$$= -\frac{1}{\tau}u_{ik}^1 - \frac{1}{\tau}\left(x_{ik}^1 - \frac{1}{3}\delta_{ik} - 2B\tau^* x_{il}^1\gamma_{lk}\right) + \frac{B}{E}\gamma_{il}u_{lk}^1. \tag{9.55}$$

The set of equations (9.51)–(9.53) or (9.51) and (9.54)–(9.55) makes up the set of constitutive equations of strongly entangled system in the single-mode approximation.

Linear Viscoelasticity

In linear case, one can rewrite the relaxation equations (9.54)–(9.55) in the form

$$\begin{aligned}\frac{\mathrm{d}x_{ik}^1}{\mathrm{d}t} &= -\frac{1}{\tau_1^{\mathrm{rep}}}\left(x_{ik}^1 - \frac{1}{3}\delta_{ik}\right) + \frac{2}{3}\gamma_{ik},\\ \frac{\mathrm{d}u_{ik}^1}{\mathrm{d}t} &= -\frac{1}{\tau}u_{ik}^1 - \frac{1}{\tau}\left(x_{ik}^1 - \frac{1}{3}\delta_{ik} - \frac{2}{3}\tau^* B\gamma_{ik}\right).\end{aligned} \tag{9.56}$$

These equations have the following solutions for oscillatory motion

$$x_{ik}^1 = \frac{1}{3}\delta_{ik} + \frac{2}{3}\,\frac{\tau_1^{\mathrm{rep}}}{1 - i\omega\tau_1^{\mathrm{rep}}}\gamma_{ik},$$

$$u_{ik}^1 = \frac{2}{3}\left(\tau^* B - \frac{\tau_1^{\mathrm{rep}}}{1 - i\omega\tau_1^{\mathrm{rep}}}\right)\frac{1}{1 - i\omega\tau}\,\gamma_{ik}.$$

Then, one can make use of the expression for the stress tensor from (9.51), to obtain the coefficient of dynamic viscosity

$$\eta(\omega) = \frac{\pi^2}{6}\,nT\left[\frac{\tau_1^{\mathrm{rep}}}{1 - i\omega\tau_1^{\mathrm{rep}}} + \left(\tau^* B - \frac{\tau_1^{\mathrm{rep}}}{1 - i\omega\tau_1^{\mathrm{rep}}}\right)\frac{1}{1 - i\omega\tau}\right]. \tag{9.57}$$

At $\omega = 0$, this expression reduces to the steady-state viscosity coefficient

$$\eta = \frac{\pi^2}{6}nT\tau^* B.$$

Expression (9.57) leads to an expression for the dynamic modulus $G(\omega) = -i\omega\eta(\omega)$, from which the value on the plateau can be found

$$G_e = \lim_{\omega\to\infty} G(\omega) = \frac{\pi^2}{6}\,nT\left(\frac{\tau^* B}{\tau} + 1\right) \approx \frac{\pi^2}{12}\,nT\chi^{-1}.$$

Thus, one can see that the single-mode approximation allows us to describe linear viscoelastic behaviour, while the characteristic quantities are the same quantities that were derived in Chapter 6. To consider non-linear effects, one must refer to equations (9.52) and (9.53) and retain the dependence of the relaxation equations on the anisotropy tensor.

9.3.3 Vinogradov Constitutive Relation

It is important to have a simple but reliable constitutive relations to investigate flows of polymer liquids in different appliances of complex geometrical forms. Now we can take one more step to simplify the set of constitutive equations (9.48)–(9.49), which approximate the behaviour of polymer liquid in the region of the applicability of the relation: $\chi^* < \chi < 0.5$, $\psi < 1$. Let us note that these conditions define the systems, which can easily flow in the devices.

One can assume that the anisotropy of the relaxation process can be neglected. This means that, in relaxation equation (9.49), we equate to zero the parameter β, but retain the parameter κ, so that the set of constitutive equations can be rewritten as follows

$$\begin{gathered}\sigma_{ij} = -p\delta_{ij} + 3\frac{\eta}{\tau}\left(\xi_{ij} - \frac{1}{3}\delta_{ij}\right),\\ \frac{\mathrm{d}\xi_{ij}}{\mathrm{d}t} - \nu_{il}\xi_{lj} - \nu_{jl}\xi_{li} = -\frac{1}{\tau}\left(\xi_{ij} - \frac{1}{3}\delta_{ij}\right), \qquad \tau = \frac{\tau_0}{1 + \kappa(\xi_{ss} - 1)}.\end{gathered} \tag{9.58}$$

The relaxation time τ can be considered to be a function of the first invariant of the tensor of additional stresses

$$D = 3(\xi_{ss} - 1) = \frac{\tau_0}{\eta_0}(\sigma_{ss} + 3p). \tag{9.59}$$

The quantity η in set (9.58) represents the shear viscosity coefficient and depends on the invariant of the anisotropy tensor in the same way as the relaxation time

$$\frac{\eta}{\eta_0} = \frac{\tau}{\tau_0} = \left(1 + \frac{1}{3}\kappa D\right)^{-1} = \phi(D). \tag{9.60}$$

The suffix zero signifies the initial values of the relevant quantities (at $D \to 0$).

One can see that the set of constitutive equations (9.58)–(9.60) contains two rheological parameters: the initial shear viscosity η_0 and the initial relaxation time τ_0, as well as a single non-dimensional parameter κ.

In this and in the next sections, we shall demonstrate the consequences of the simplified description for shear and extension motions in order to understand the applicability of the approach. We shall deal with uniform steady-state motions for which we have, from (9.58), the expression for the stress tensor

$$\sigma_{ij} + p\delta_{ij} = 3\eta(\nu_{il}\xi_{lj} + \nu_{jl}\xi_{li}). \tag{9.61}$$

For the simple shear flow, the only one component of the velocity gradient tensor differs from zero, namely, $\nu_{12} \neq 0$. The shear stress and the differences of the normal stresses are defined by equation (9.61) as

$$\begin{aligned} \sigma_{12} &= \eta\nu_{12}, \\ \sigma_{11} - \sigma_{22} &= 2\eta\tau\nu_{12}^2, \\ \sigma_{22} - \sigma_{33} &= 0. \end{aligned} \tag{9.62}$$

The first equation of the set (9.62) confirms that η is the coefficient of shear viscosity, which can be estimated according to the rule

$$\eta = \frac{\sigma_{12}}{\nu_{12}}. \tag{9.63}$$

We may note that the function $\phi(D)$, which is introduced by relation (9.60), can be excluded from expressions (9.62) which leads to a relation between normal and shear stresses

$$\sigma_{11} - \sigma_{22} = 2\frac{\tau_0}{\eta_0}\sigma_{12}^2. \tag{9.64}$$

This relation can be used to estimate the value of the shear modulus η_0/τ_0. Measurement of the first difference of normal stresses allows us to evaluate the relaxation time

$$\tau = \frac{\sigma_{11} - \sigma_{22}}{2\sigma_{12}\nu_{12}}. \tag{9.65}$$

TABLE 3. Characteristics of the sample systems

System	T °C	c %	$\frac{\eta_0}{\tau_0} \cdot 10^{-4}$ dyn cm^{-2}	η_0 P	τ_0 s	No. on Fig. 19
Polyisobutylene	22	100	4.8	$1.7 \cdot 10^7$	354	1
$M = 7 \cdot 10^4$ *	40	100	4.6	$3.46 \cdot 10^6$	77.8	2
Blend of 62% low density polyethylene and 38% high density polyethylene**	170	100	3.1	$1.41 \cdot 10^6$	45	3
Low density polyethylene**	170	100	5.6	$4.2 \cdot 10^5$	7.5	4
Solution of polyacrylamide in the mixture glycerine–water (1:1)***	25	1.5	0.038	$1.8 \cdot 10^4$	47	5
Solution of poly (ethylene oxide) in the mixture glycerine–water (1:2) + 11% isopropanol***	25	3.0	0.02	$1 \cdot 10^4$	50	6

* Fikhman et al. (1970); ** Weinberger and Goddard (1974)
*** Pokrovskii et al. (1973)

Equations (9.63)–(9.65) were used, in fact, to evaluate the shear viscosity coefficient and the relaxation times which reveal the nature of dependence on the velocity gradient ν_{12} or shear stress σ_{12} (Isayev 1973). It is convenient to consider the shear viscosity coefficient and the relaxation time as a generalised function of the first invariant of the tensor of additional stresses

$$D = \frac{\tau_0}{\eta_0}(\sigma_{ss} + 3p) = 2\left(\frac{\tau_0}{\eta_0}\sigma_{12}\right)^2 = 2\Gamma^2. \tag{9.66}$$

It is remarkable that the dependencies of the non-dimensional quantities η/η_0 and τ/τ_0 on the non-dimensional argument $\tau_0\nu_{12}$ or $(\tau_0/\eta_0)\sigma_{12}$ are universal. The dependencies are not essentially effected by the temperature, the molecular weight, and the concentration and chemical nature of the polymers (Isayev 1973).

Despite the apparent deficiency of description (9.58) when applied to a real system, we may note that the set of constitutive equations (9.58)–(9.60) represent qualitatively the behaviour of concentrated polymer solutions and melts under shear. The set of equations include two material constants which are the individual characteristics of the system, namely, the initial shear viscosity and the initial relaxation time, which depend on the temperature, the molecular weight of polymer, and its concentration in the system. As an illustration, the estimation of the material constants for some systems are shown in Table 3. The returning to the fuller approximation (equations (9.48)–(9.49)) improves the description, as has been shown by Pyshnograi et al. (1994).

The constitutive equations (9.58)–(9.60) were derived as a consequent simplification of general equations, discussed in Section 9.2.1, so that one can conclude which assumptions have to be introduced to obtain the equations. We may note that, before this consequent derivation, the considered constitutive equations (9.58)–(9.60) were formulated (Vinogradov et al. 1972b; Phan-Thien and Tanner 1977) and used for the investigation of simple (Pokrovskii and Kruchinin 1980) and complex (Altukhov et al. 1986; Erenburg and Pokrovskii 1981) flows of polymeric liquids. The constitution equations named in honour of one of the pioneer investigator of polymer rheology G.V. Vinogradov.

It is important to note that the constitutive equation (9.58)–(9.60) belong to the class of the rare equations which are Hadamard and dissipative stable (Kwon and Leonov 1995).

9.3.4 Relation between Shear and Elongational Viscosities

Consider the case of applying the system (9.58)–(9.60) to description of uniaxial deformation with the constant elongational velocity gradient ν_{11}. The elongational viscosity coefficient λ is determined as the ratio of the extensional stress σ to the elongational velocity gradient. We shall calculate, according to Pokrovskii and Kruchinin (1980), the ratio between the coefficients of elongational and shear viscosity, namely, the quantity λ/η for a polymer liquid.[1]

For uniform uniaxial elongational deformation along axis 1, the tensor of the velocity gradients, taking into account the condition of incompressibility, can be written in the form

$$\nu_{ik} = \begin{Vmatrix} \nu_{11} & 0 & 0 \\ 0 & -\frac{1}{2}\nu_{11} & 0 \\ 0 & 0 & -\frac{1}{2}\nu_{11} \end{Vmatrix} .$$

If we exclude the pressure from the relation for the stresses (9.58) under the considered uniaxial deformation, we can obtain an expression for the extensional stress

$$\sigma = 3\frac{\eta}{\tau}(\xi_{11} - \xi_{22}) = 3\eta(2\xi_{11} - \xi_{22})\nu_{11} \tag{9.67}$$

where, in a steady-state case,

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[1] The earlier history of the investigation of elongational flow can be found in the monograph by Petrie (1979).

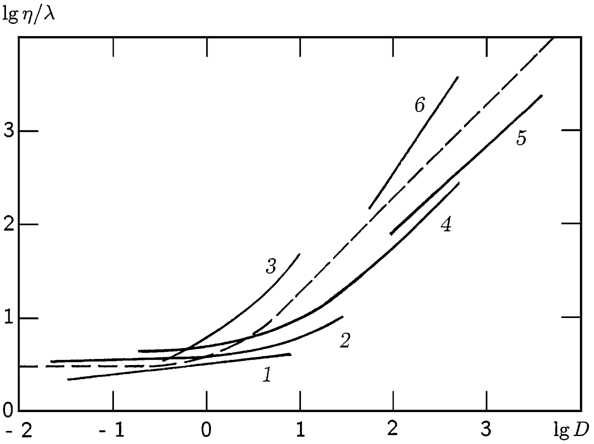

Figure 19. The ratio of elongational to shear viscosities
The theoretical dependence of the ratio of elongational to shear viscosity coefficients on the invariant of the additional stress tensor is calculated according to equation (9.71) and depicted by the dashed curve. The solid curves represent experimental data for systems listed in Table 3. Adapted from the paper of Pokrovskii and Kruchinin (1980).

$$\xi_{ii} = \frac{1}{3}\left(1 + \frac{2\tau\nu_{ii}}{1 - 2\tau\nu_{11}}\right), \quad i = 1, 2, 3. \tag{9.68}$$

The above formulae determine the elongational viscosity coefficient

$$\lambda = \frac{3\eta}{1 - \tau\nu_{11} - 2(\tau\nu_{11})^2}. \tag{9.69}$$

The viscosity coefficients η and λ are functions of the first invariant of the tensor of additional stresses

$$D = \frac{\tau_0}{\eta_0}(\sigma_{ii} + 3p).$$

When relations (9.67) and (9.68) are used, the invariant can be expressed in terms of the elongational velocity gradient or extensional stress

$$D = 2\frac{\lambda}{\eta}(\tau\nu_{11})^2 = 2\frac{\eta}{\lambda}\left(\frac{\tau_0}{\eta_0}\sigma\right)^2. \tag{9.70}$$

By eliminating the velocity gradient from relations (9.69) and (9.70) we can obtain an expression for the ratio of the coefficients of elongational and shear viscosity

$$\frac{\lambda}{\eta} = 3 + \frac{5}{4}D + \left(\frac{3}{2}D + \frac{9}{16}D^2\right)^{1/2}. \tag{9.71}$$

The ratio of the coefficients is a function of the invariant D which, for shear motion, has the form

$$D = 2\left(\frac{\tau_0}{\eta_0}\sigma_{12}\right)^2 . \tag{9.72}$$

The expression for D in the case of uniaxial deformation is easily obtained from equations (9.70) and (9.71)

$$D = -\frac{3}{2} - \frac{1}{2}\frac{\tau_0}{\eta_0}\sigma + \frac{1}{2}\left(9 + 6\frac{\tau_0}{\eta_0}\sigma + 9\left(\frac{\tau_0}{\eta_0}\sigma\right)^2\right)^{1/2} . \tag{9.73}$$

It should be noted that, when deriving this expression, we assumed that η and λ are functions of the invariant D, but we did not use a specific form of this function.

The applicability of relation (9.71) to a real polymer system was discussed in works by Pokrovskii et al. (1973); Pokrovskii and Kruchinin (1980); Pyshnograi et al. (1994). Figure 19 represents the experimental values of the ratio λ/η depending on the invariant D for the polymer systems, listed in Table 3, in comparison with the universal theoretical curve calculated according to equation (9.71). The experimental results can be seen to have a definite scatter relative to the theoretical curve; this can be ascribed to both natural experimental errors and the necessity of improving the theoretical calculation by appealing to the fuller set of constitutive relations (9.48)–(9.49). In the former case a variation of β in (9.49) leads to a set of λ/η vs D curves (Pyshnograi et al. 1994).

However, the observed consistency of the experimental and theoretical appraisals can be considered as surprisingly satisfactory. Both these results and the results of the previous section point to the possibility of employing the Vinogradov constitutive equations (9.58)–(9.60) for qualitative investigations of non-uniform flows of polymer liquids.

9.3.5 Recoverable Strain

One of the prominent features of polymeric liquids is the property to recover partially the pre-deformation state. Such behaviour is analogous to a rubber band snapping back when released after stretching. This is a consequence of the relaxation of macromolecular coils in the system: every deformed macromolecular coil tends to recover its pre-deformed equilibrium form. In the considered theory, the form and dimensions of the deformed macromolecular coil are connected with the internal variables x_{ij}^{α} which have to be considered when the tensor of recoverable strain is to be calculated. Further on, we shall consider the simplest case, when the form and dimensions of macromolecular coils are determined by the only internal tensor ξ_{ij}. In this case, the behaviour of the polymer liquid is considered to describe by one of the constitutive equations (9.48)–(9.49) or (9.58).

To determine the tensor of recoverable strains, we have to equate the stress tensor for a deformed polymer network (given in the simplest case by equation (1.43)) with the elastic part of the stress tensor for a polymer liquid, given in the general case by equation (9.19) or, in the simplified case by equation (9.48). The latter case leads to the relation

$$G\lambda_{ij}\lambda_{kj} = 3\frac{\eta_0}{\tau_0}\xi_{ik} - \left(\frac{\eta_0}{\tau_0} - G\right)\delta_{ik} \tag{9.74}$$

where G is the shear modulus and λ_{ij} is the tensor of recoverable displacement, such that $\Lambda_{ik} = \lambda_{ij}\lambda_{kj}$ is the tensor of recoverable strains. The latter quantities are discussed in Appendix B.

To determine the shear modulus and the tensor of recoverable strains, we calculate the determinants of the left-hand and right-hand sides of equation (9.74). Taking into account the incompressibility of the polymer liquid, i.e. relation $|\lambda_{ij}\lambda_{kj}| = 1$, we obtain

$$G^3 = 27\left(\frac{\eta_0}{\tau_0}\right)^3\left[\varXi_3 - \frac{1}{3}\left(1 - \frac{G\tau_0}{\eta_0}\right)\varXi_2 + \frac{1}{9}\left(1 - \frac{G\tau_0}{\eta_0}\right)^2\varXi_1\right]$$

where the invariants of the tensor ξ_{ij} are introduced as follows

$$\varXi_1 = \sum_{i=1}^{3}\xi_{ii}, \qquad \varXi_2 = \frac{1}{2}\sum_{i,j}(\xi_{ij}\xi_{ji} - \xi_{ii}\xi_{jj}), \qquad \varXi_3 = |\xi_{ij}|.$$

We consider these invariants independent of each other, so that we can determine the shear modulus and the tensor of recoverable strains

$$G = 3|\xi_{ls}|^{1/3}\frac{\eta_0}{\tau_0}, \qquad \lambda_{ij}\lambda_{kj} = \delta_{ik} + |\xi_{ls}|^{-1/3}\left(\xi_{ik} - \frac{1}{3}\delta_{ik}\right). \tag{9.75}$$

As the expansion of the invariants into series with respect to the velocity gradients do not contain terms of even order, one can directly see the correctness of the above expressions with accuracy at least up to third-order terms with respect to the velocity gradient.

As an example, we shall consider simple shear when $\nu_{12} \neq 0$, and find components of the tensor of the recoverable displacement gradients $\lambda_{12}, \lambda_{11}, \lambda_{22}, \lambda_{33}$; the components of the tensor ξ_{il} are calculated from the relaxation equations (9.49) or (9.58). In this case the matrix of the deformation tensor is determined as follows

$$\Lambda = \begin{Vmatrix} \lambda_{11}^2 + \lambda_{12}^2 & \lambda_{22}\lambda_{12} & 0 \\ \lambda_{22}\lambda_{12} & \lambda_{22}^2 & 0 \\ 0 & 0 & \lambda_{33}^2 \end{Vmatrix}. \tag{9.76}$$

Further on we shall consider the simple case when the relaxation equation is given by equation (9.58) and we shall assume the shear motion to be a steady-state one. So, we have the expressions

$$\begin{aligned}&\xi_{11} = \frac{1}{3}(1 + 2\mathit{\Gamma}^2), \qquad \xi_{12} = \frac{1}{3}\mathit{\Gamma}, \qquad \xi_{22} = \xi_{33} = \frac{1}{3},\\ &\xi_{13} = \xi_{23} = 0\end{aligned} \tag{9.77}$$

where $\mathit{\Gamma} = \tau\nu_{12} = \frac{\tau_0}{\eta_0}\sigma_{12}$.

Now, equations (9.75) allow us to calculate the shear modulus and the deformation tensor. With approximation up to the third-order terms with respect to the velocity gradient, we obtain

$$G = \frac{\eta_0}{\tau_0}\left(1 + \frac{1}{3}\mathit{\Gamma}^2\right), \tag{9.78}$$

$$\mathit{\Lambda} = \begin{Vmatrix} 1 + \frac{5}{3}\mathit{\Gamma}^2 & \mathit{\Gamma}\left(1 - \frac{1}{3}\mathit{\Gamma}^2\right) & 0 \\ \mathit{\Gamma}\left(1 - \frac{1}{3}\mathit{\Gamma}^2\right) & 1 - \frac{1}{3}\mathit{\Gamma}^2 & 0 \\ 0 & 0 & 1 - \frac{1}{3}\mathit{\Gamma}^2 \end{Vmatrix}. \tag{9.79}$$

After comparing expressions (9.76) and (9.79), we obtain the components of the recoverable displacement tensor

$$\lambda_{11} = 1 + \frac{1}{3}\mathit{\Gamma}^2, \qquad \lambda_{22} = \lambda_{33} = 1 - \frac{1}{6}\mathit{\Gamma}^2, \qquad \lambda_{12} = \mathit{\Gamma}\left(1 - \frac{1}{6}\mathit{\Gamma}^2\right). \tag{9.80}$$

In accordance with the experimental data (Ferry 1980), the shear modulus increases as the velocity gradient increases and the recoverable shear deformation λ_{12} deviates from proportionality to the velocity gradient.

We may note here that the sets of constitutive equations (9.48)–(9.49) or (9.58) can be reformulated, taking into account the established connection between the internal variable ξ_{ij} and the recoverable deformation tensor (equation (9.75)), so that the constitutive equations would include the tensor of recoverable deformation as an internal variable. In fact, such constitutive equations were obtained independently (Godunov and Romenskii 1972; Leonov 1976; Prokunin 1989). Therefore, two interpretations of the internal variables and two formalisms are equivalent, but, nevertheless, one of them appears to be simpler.