

Chapter 6

Linear Viscoelasticity

Abstract In the course-grained approximation, polymer solutions and melts can be considered as a suspension of interacting Brownian particles, which allow us to determine a general expression for the stress tensor, following a method developed in the theory of liquids (Rice and Gray in *Statistical mechanics of simple liquids* (Wiley, New York), 1965; Gray in *Physics of simple liquids*, ed by H.N.V Temperley (North Holland, Amsterdam, pp. 507–562), 1968). The general theory is specified to calculate dynamic modulus both for dilute and concentrated polymer systems. The approach allows one correctly to describe the linear viscoelastic behaviour of dilute polymer solutions over a wide range of frequencies, if the effects of excluded volume, hydrodynamic interaction, and internal viscosity are taken into account. As far as the very concentrated solutions and melts of polymers – entangled polymers – are concerned, the results for the linear approximation of macromolecular dynamics are only available now. As one can anticipate, it is not sufficient for complete description of relaxation processes in strongly entangled systems, though some relations for terminal characteristics are obtained for these systems. Remarkably, the mesoscopic theory appears to be self-consistent for entangled systems: the relaxation time of the environment is equal to the relaxation time of the entire system, which is calculated in this chapter. The intermediate scale introduced in Chapter 5 appears here once more as connected with the well-known length of a macromolecule between adjacent entanglements M_e . It casts a new light on the old terms and old theories. The pictures given earlier by different theories appear to be consistent.

6.1 Stresses in the Flow System

6.1.1 The Stress Tensor

As before, we shall consider each macromolecule either in dilute or in concentrated solution to be schematically represented by a chain of $N + 1$ Brownian

particles, so that a set of the equations for motion for the macromolecule can be written as a set of coupled stochastic equations

$$m \frac{d^2 \mathbf{r}^\alpha}{dt^2} = \mathbf{F}^\alpha + \mathbf{G}^\alpha + \mathbf{K}^\alpha + \boldsymbol{\phi}^\alpha, \quad \alpha = 0, 1, \dots, N, \quad (6.1)$$

where m is the mass of a Brownian particle associated with a piece of the macromolecule of length $M/(N+1)$, \mathbf{r}^α are the co-ordinates of the Brownian particles. The dissipative forces \mathbf{F}^α and \mathbf{G}^α acting on the particles were discussed in Chapter 2 for dilute solutions and in Chapter 3 for entangled systems.

We consider n to be the number density of macromolecular coils in the system, so that the system contains $n(N+1)$ Brownian particles in unit volume. This number is sufficiently large to introduce macroscopic variables for the suspension of Brownian particles, namely, the mean density

$$\rho(\mathbf{x}, t) = \sum_{a,\alpha} m \langle \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \rangle = m(N+1)n(\mathbf{x}, t) \quad (6.2)$$

and the mean density of the momentum

$$\rho v_j(\mathbf{x}, t) = \sum_{a,\alpha} m \langle u_j^{a\alpha} \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \rangle. \quad (6.3)$$

The angle brackets denote averaging over the ensemble of the realisation of random forces in the equations of motion of the particles. The sum in (6.2) and (6.3) is evaluated over all the Brownian particles. The double index $a\alpha$ consists of the label of a chain a and the label of a particle α in the chain.

The methods developed in the theory of liquids (Rice and Gray 1965, Gray 1968) was used by Pokrovskii and Volkov (1978a) to determine the stress tensor for the set of Brownian particles in this case. One can start with the definition of the momentum density, given by (6.3), which is valid for an arbitrary set of Brownian particles. Differentiating (6.3) with respect to time, one finds

$$\frac{\partial}{\partial t} \rho v_j = - \frac{\partial}{\partial x_i} \sum_{a,\alpha} m \langle u_i^{a\alpha} u_j^{a\alpha} \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \rangle + \sum_{a,\alpha} \left\langle m \frac{du_j^{a\alpha}}{dt} \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \right\rangle. \quad (6.4)$$

The right-hand side of equation (6.4) has to be reduced to a divergent form. To transform the second term, we use the dynamic equation (6.1), which ought to be multiplied by $\delta(\mathbf{x} - \mathbf{r}^{a\alpha})$. After summing over all the particles of the macromolecule and averaging, one uses the requirement that there is no mean volume force, that is,

$$\sum_{\alpha=0}^N \langle (\mathbf{F}^{a\alpha} + \boldsymbol{\phi}^{a\alpha}) \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \rangle = 0, \quad a = 1, 2, \dots, n. \quad (6.5)$$

So, for each macromolecular coil, one can write

$$m \sum_{\alpha=0}^N \left\langle \frac{d\mathbf{u}^{a\alpha}}{dt} \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \right\rangle = \sum_{\alpha=0}^N \langle (\mathbf{K}^{a\alpha} + \mathbf{G}^{a\alpha}) \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \rangle, \quad a = 1, 2, \dots, n.$$

Next, the formal expansion of the δ -function into a Taylor's series about the centre of mass \mathbf{q}^a of the a th macromolecule can be used, retaining only the first two terms of the expansion

$$\delta(\mathbf{x} - \mathbf{r}^{a\alpha}) = \delta(\mathbf{x} - \mathbf{q}^a) - (r_k^{a\alpha} - q_k^a) \frac{\partial}{\partial x_k} \delta(\mathbf{x} - \mathbf{q}^a).$$

So, the above formula is transformed into

$$-\frac{\partial}{\partial x_k} \sum_{\alpha=0}^N \langle (K_j^{a\alpha} r_k^{a\alpha} + G_j^{a\alpha} r_k^{a\alpha}) \delta(\mathbf{x} - \mathbf{q}^a) \rangle, \quad a = 1, 2, \dots, n.$$

Here, the sum is conducted over all the particles in a given macromolecule. Assuming that all the macromolecules are identical, and neglecting the statistical dependence of the position of the centres of mass of the macromolecules on the other co-ordinates, one obtains an expression for the second term on the right-hand side of equation (6.4) in the divergent form

$$\sum_{a,\alpha} \left\langle m \frac{du_j^{a\alpha}}{dt} \delta(\mathbf{x} - \mathbf{r}^{a\alpha}) \right\rangle = -\frac{\partial}{\partial x_k} n \sum_{\alpha=0}^N \langle K_j^{a\alpha} r_k^{a\alpha} + G_j^{a\alpha} r_k^{a\alpha} \rangle.$$

The first term on the right-hand side of (6.4) can also be rewritten in a more convenient form. One uses the definition of the mean velocity v_i and, taking only the first term of the expansion of the δ -function into account, one finds that

$$m \sum_{a,\alpha} \langle u_j^{a\alpha} u_i^{a\alpha} \delta(\mathbf{x} - \mathbf{q}^a) \rangle = nm \sum_{\alpha=0}^N \langle (u_j^\alpha - v_j)(u_i^\alpha - v_i) \rangle + \rho v_i v_j.$$

Thus, an equation, which has the sense of a law of conservation of momentum has been obtained. There is an expression for the momentum flux $\rho v_i v_j - \sigma_{ij}$ under the derivation symbol, which allows one to write down the expression for the stress tensor

$$\sigma_{kj} = -n \sum_{\alpha=0}^N [m \langle (u_j^\alpha - v_j)(u_k^\alpha - v_k) \rangle + \langle K_k^\alpha r_j^\alpha + G_k^\alpha r_j^\alpha \rangle]. \quad (6.6)$$

The assumption that the particle velocities are described by the local-equilibrium distribution yields

$$\sigma_{kj} = -n(N+1)T\delta_{jk} - n \sum_{\alpha=0}^N \langle K_j^\alpha r_k^\alpha + G_j^\alpha r_k^\alpha \rangle. \quad (6.7)$$

As was demonstrated by Pyshnograï (1994), the last term in (6.7) can be written in symmetric form, if the continuum of Brownian particles is considered incompressible. In equation (6.7), the sum is evaluated over the particles in a given macromolecule. The monomolecular approximation ensures that the stress tensor of the system is the sum of the contributions of all the macromolecules. In this form, the expression for the stresses is valid for any dynamics of the chain. One can consider the system to be a dilute polymer solution or a concentrated solution and melt of polymers. In any case the system is considered as a suspension of interacting Brownian particles.

6.1.2 Oscillatory Deformation

Experimentally a variety of quantities are used to characterise linear viscoelasticity (Ferry 1980). There is no need to consider all the characteristics of linear viscoelastic response of polymers which are measured under different regimes of deformation: in linear region, they are connected with each other. The study of the reaction of the system in the simple case, when the velocity gradients are independent of the co-ordinates and vary in accordance with the law

$$\gamma_{ik} \sim e^{-i\omega t}$$

for different deformation frequencies ω , gives a clear picture of the phenomena of linear viscoelasticity and yields important information about the relaxation processes in the system. For this case, the expression for the stress tensor can be written in the form

$$\sigma_{ik}(t) = -p\delta_{ik} + 2\eta(\omega)\gamma_{ik}(t) \quad (6.8)$$

which defines the complex viscosity coefficient – dynamic viscosity

$$\eta(\omega) = \eta'(\omega) + i\eta''(\omega).$$

Since the velocity gradient is related to the displacement gradient by the expression $\nu_{12} = -i\omega\lambda_{12}$, it follows that, instead of the dynamic viscosity, the use may be made of another characteristic – the dynamic modulus

$$G(\omega) = G'(\omega) - iG''(\omega) = -i\omega\eta(\omega). \quad (6.9)$$

The components of the above complex quantities are linked by the relation

$$G' = \omega\eta'', \quad G'' = \omega\eta'. \quad (6.10)$$

Dynamic modulus is a convenient characteristic of viscoelasticity. To analyse the results, it is convenient also to consider the asymptotic behaviour of the dynamic modulus at high and low frequencies. In the latter case

$$G(\omega) = -i\omega\eta + \omega^2\nu. \quad (6.11)$$

The expansion determines the terminal quantities: the viscosity coefficient η and the elasticity coefficient ν which, in their turn, determine the terminal relaxation time and steady-state compliance, correspondingly,

$$\tau = \frac{\nu}{\eta}, \quad J_e = \frac{\nu}{\eta^2}. \quad (6.12)$$

Both the dynamic modulus and the terminal quantities are characteristics of viscoelasticity of a system and are subject of interest of experimentalists.

Note that the dynamic modulus is the Fourier-transform of the relaxation modulus $G(t)$

$$G(\omega) = -i\omega \int_0^\infty G(t)e^{i\omega t} dt,$$

which is also often used to characterise viscoelastic behaviour on the system.

6.2 Macromolecules in a Viscous Liquid

The dilute polymer solution can be considered as a collection of non-interacting macromolecular coils suspended in a viscous liquid, the stress tensor of which is written as

$$\sigma_{ik}^0 = -p\delta_{ik} + 2\eta_s\gamma_{ik}. \quad (6.13)$$

The dynamics of a separate macromolecular coil in the viscous liquid, discussed in Chapter 2, allows one to determine the problem.

6.2.1 The Stress Tensor

To find the stress tensor, one can use equation (6.7), in which the elastic and internal viscosity forces, according to equations (2.2) and (2.25), have the form

$$K_i^\alpha = -2T\mu A_{\alpha\gamma} r_i^\gamma, \quad G_j^\alpha = -G_{\alpha\gamma}(\dot{r}_j^\gamma - \omega_{jl}r_l^\gamma).$$

This gives the expression for the stress tensor

$$\begin{aligned} \sigma_{ik} &= -nT(1 + N)\delta_{ik} \\ &+ n \sum_{\nu=0}^N [2\mu T A_{\alpha\gamma} \langle r_i^\alpha r_k^\gamma \rangle - T\delta_{ik} + G_{\alpha\gamma} (\langle \dot{r}_k^\gamma r_i^\alpha \rangle - \omega_{il} \langle r_l^\alpha r_k^\gamma \rangle)]. \end{aligned}$$

Furthermore, it is convenient to switch to normal co-ordinates (1.13). We can use the expressions for forces (2.26) to rewrite the expression for the stress tensor in normal co-ordinates

$$\begin{aligned} \sigma_{ik} = & -n(N+1)T\delta_{ik} \\ & + n \sum_{\alpha=1}^N \left[2\mu T \lambda_{\alpha} \langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle - T\delta_{ik} + \zeta \varphi_{\alpha} \left(\langle \dot{\rho}_k^{\alpha} \rho_i^{\alpha} \rangle - \omega_{kl} \langle \rho_l^{\alpha} \rho_i^{\alpha} \rangle \right) \right]. \end{aligned} \quad (6.14)$$

Here the linear terms in respect to the coefficient of internal viscosity φ_{α} have taken into account only. Averaging with respect to the velocity distribution has been assumed here. One ought to add the stresses (6.13) of carrier viscous liquid to stresses (6.14) to determine the stress tensor for the entire system, that is for the dilute solution of the polymer.

Let us note that the extra stresses arise due to the differences in the rate of diffusion \mathbf{w}^{α} of a Brownian particle and the averaged velocity of the medium \mathbf{v}^{α} at the point where the particle is located. It results in the emergence of forces

$$\mathbf{F}^{\alpha} = -\zeta(\mathbf{v}^{\alpha} - \mathbf{w}^{\alpha}).$$

Accordingly, the extra stresses after averaging can be written as

$$-n\zeta \sum_{\alpha=0}^N \langle (v_i^{\alpha} - w_i^{\alpha}) r_k^{\alpha} \rangle \quad (6.15)$$

where the angle brackets denote averaging with respect to the distribution function for the particle co-ordinates. One ought to determine the diffusion velocity \mathbf{w}^{α} to arrive at expression (6.14) for the stress tensor. Expression (6.15) was the starting point in the calculations of the extra stresses in dilute solutions of polymer in works by Cerf (1958), Kirkwood and Riseman (1948), Peterlin (1967), and Zimm (1956).

One can use equation (2.37) to obtain the other form of the stress tensor

$$\sigma_{ik} = -nT(N+1)\delta_{ik} + n\zeta \sum_{\nu=1}^N \frac{1}{2} \left[\frac{1}{\tau_{\nu}^{\parallel}} \left(\langle \rho_i^{\nu} \rho_k^{\nu} \rangle - \frac{1}{2\mu\lambda_{\nu}} \delta_{ik} \right) + 2\varphi_{\nu} \langle \rho_i^{\nu} \rho_j^{\nu} \rangle \gamma_{jk} \right] \quad (6.16)$$

where the times of relaxation τ_{ν}^{\perp} and $\tau_{\nu}^{\parallel} = (1 + \varphi_{\nu})\tau_{\nu}^{\perp}$ were defined earlier by expressions (2.30).

Note that the internal viscosity is a residual of internal relaxation process in the case, when the slow deformation is considered. In a more general case, the elastic and internal viscosity forces acting on the chain, according to equations (2.2) and (2.28), can be written as

$$K_i^{\alpha} = -2T\mu A_{\alpha\gamma} r_i^{\gamma}, \quad G_i^{\alpha} = - \int_0^{\infty} G_{\alpha\gamma}(s) (u_i^{\gamma} - \omega_{ij} r_j^{\gamma})_{t-s} ds. \quad (6.17)$$

Then, equation (6.7) gives, instead of (6.14), the expression for the stress tensor in normal co-ordinate

$$\begin{aligned} \sigma_{ik}(t) = & -n(N+1)T\delta_{ik} + n \sum_{\alpha=1}^N \left\{ 2\mu T \lambda_{\alpha} \langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle - T\delta_{ik} \right. \\ & \left. + \zeta \int_0^{\infty} \varphi_{\alpha}(s) \left(\langle \dot{\rho}_i^{\alpha}(t-s) \rho_k^{\alpha}(t) \rangle - \omega_{ii}(t-s) \langle \rho_i^{\alpha}(t-s) \rho_k^{\alpha}(t) \rangle \right) ds \right\}. \end{aligned} \quad (6.18)$$

The validity of the theory for the non-linear region is restricted by terms of the second power with respect to the velocity gradient for non-steady-state flow and by terms of the third order for steady-state flow, due to approximations described in Chapter 2, when the relaxation modes of a macromolecule were being determined.

6.2.2 Dynamic Characteristics

Let us write down first of all the stress tensor for dilute solution (6.16) as a function of the velocity gradients. We can use expressions (2.41) for moments, in order to determine the stresses with accuracy within the first-order term with respect to velocity gradients

$$\begin{aligned} \sigma_{ik} = & -p\delta_{ik} + 2\eta_s\gamma_{ik} \\ & + 2nT \sum_{\nu=1}^N \left[\frac{1-\varphi_{\nu}}{1+\varphi_{\nu}} \int_0^{\infty} \exp\left(-\frac{s}{\tau_{\nu}^{\parallel}}\right) \gamma_{ik}(t-s) ds + \varphi_{\nu} \tau_{\nu}^{\perp} \gamma_{ik} \right]. \end{aligned} \quad (6.19)$$

This equation contains two sets of relaxation times, which are defined by equations (2.30), that is,

$$\tau_{\alpha}^{\parallel} = \tau_{\alpha}^{\perp} (1 + \varphi_{\alpha}), \quad \tau_{\alpha}^{\perp} = \tau_1 \alpha^{-z\nu}, \quad \varphi_{\alpha} = \varphi_1 \alpha^{\theta}, \quad \alpha = 1, 2, \dots \ll N.$$

The exponents in the above expressions can be estimated beforehand from the dependence of the limiting values of the characteristic viscosity at low and high frequencies on the length of the macromolecule.

In the case of the oscillatory motion, equation (6.19) defines, in accordance with equation (6.8), the complex shear viscosity $\eta(\omega) = \eta' + i\eta''$ with components

$$\begin{aligned} \eta'(\omega) = & \eta_s + nT \sum_{\nu=1}^N \tau_{\nu}^{\perp} \left[\varphi_{\nu} + \frac{1-\varphi_{\nu}}{1+(\tau_{\nu}^{\parallel}\omega)^2} \right], \\ \eta''(\omega) = & nT \sum_{\nu=1}^N \frac{\omega(\tau_{\nu}^{\perp})^2}{1+(\tau_{\nu}^{\parallel}\omega)^2}. \end{aligned} \quad (6.20)$$

Figure 14 illustrates the dependence of the characteristic viscosity

$$[\eta] = \lim_{n \rightarrow 0} \frac{\eta - \eta_s}{nT}$$

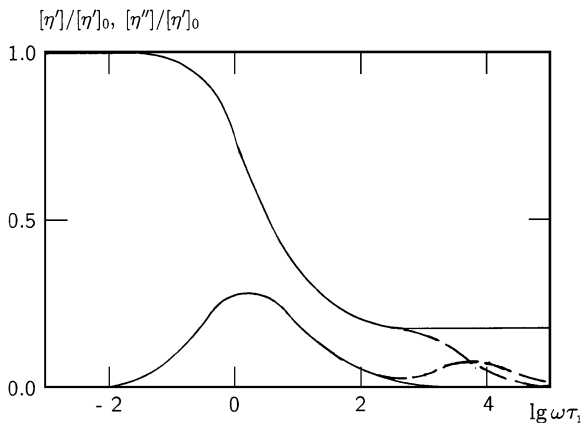


Figure 14. The components of characteristic viscosity. The real and imaginary components of characteristic viscosity have been calculated according to equations (6.20) for $z\nu = 2$, $\varphi_1 = 0.5$, $\theta = 0.5$. The dashed curves depicts the alternation of the dependencies in the case when an internal relaxation process is taking into account, whereas equations (6.28) are used at $\tau/2\tau_1 = 10^{-5}$.

as defined by equations (6.20) on the non-dimensional frequency $\tau_1\omega$ for some values of the parameters $z\nu$, φ_1 and θ which appeared in the formulae for relaxation times, introduced previously.

Equations (6.20) are followed by the expression for the characteristic dynamic modulus, components of which are

$$\begin{aligned}
 G' &= nT \sum_{\nu=1}^N \frac{(\tau_\nu^\perp \omega)^2}{1 + (\tau_\nu^\parallel \omega)^2}, \\
 G'' &= \eta_s \omega + nT \sum_{\nu=1}^N \tau_\nu^\perp \omega \left[\varphi_\nu + \frac{(1 - \varphi_\nu)}{1 + (\tau_\nu^\parallel \omega)^2} \right].
 \end{aligned}
 \tag{6.21}$$

Figure 15 demonstrates a comparison of the characteristic modulus

$$[G] = \lim_{n \rightarrow 0} \frac{G - i\eta_s \omega}{nT},$$

calculated according to equation (6.21), with the corresponding experimental values. One can note, that for certain values of the maximum relaxation time τ_1 and certain values of the exponents $z\nu$ and θ (whereas, in virtue of equation (6.27), $\theta = 2\nu - 1$), the theory satisfactorily reproduces the experimental relations for polymer solutions at infinite dilution. We may note yet again that the identifying constants are unambiguously determined by the limiting values of the characteristic viscosity and can be estimated independently.

The results (6.20) and (6.21), which are valid in the first order with respect to the coefficient of internal viscosity φ_1 , were found by Peterlin (1967).

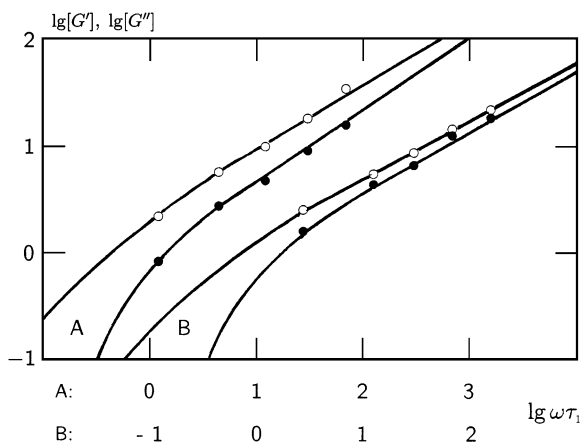


Figure 15. The components of characteristic dynamic modulus.

Frequency dependence of characteristic dynamic modulus for polystyrene solutions in decalin (A) and in toluene (B). Experimental values due to Rossers et al. (1978) (see also the last lines of Table 2) are shown by filled points (for the real part) and empty points (for the imaginary part). The theoretical curves have been plotted for $z\nu = 1.788$, $\theta = 0.788$, $\tau_1 = 2.5 \times 10^{-3}$ s for case A and for $z\nu = 1.5$, $\theta = 0.5$, $\tau_1 = 8.35 \times 10^{-4}$ s for case B. Adapted from the paper of Pokrovskii and Tonkikh (1988).

A generalisation of the theory for the case of arbitrary values of internal viscosity was done by Pokrovskii and Tonkikh (1988). We may note that the case when $\varphi_1 = 0$ and $z\nu = 2$, corresponds to an ideally flexible freely-draining macromolecule, and reproduces the relations indicated by Rouse (1953).

Thus, one may conclude that, in the region of comparatively low frequencies, the schematic representation of the macromolecule by a subchain, taking into account intramolecular friction, the volume effects, and the hydrodynamic interaction, make it possible to explain the dependence of the viscoelastic behaviour of dilute polymer solutions on the molecular weight, temperature, and frequency. At low frequencies, the description becomes universal. In order to describe the frequency dependence of the dynamic modulus at higher frequencies, internal relaxation process has to be considered as was shown in Section 6.2.4.

As an illustration, certain data characterising dilute polymer solutions are presented in Table 2.

6.2.3 Initial Intrinsic Viscosity

In the study of the linear response, it is convenient to consider quantity independent of concentration and viscosity – the characteristic (intrinsic) viscosity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_s}{c\eta_s} \quad (6.22)$$

TABLE 2. Characteristics of dilute polymer solutions

System	T °C	ρ_s g cm ⁻³	η_s P	$M \cdot 10^{-5}$	$[\eta]$ cm ³ g ⁻¹	$\tau_1 \cdot 10^4$ s
Polystyrene in decalin*	16	0.8868	0.0295	8.6	76	0.35
Polystyrene in di-2-ethyl-hexylphthalate*	22	0.9827	0.678	8.6	—	7.59
Polystyrene in α -chloronaphthalene*	25	1.195	0.0315	8.6	197	1.26
Polystyrene in arochlor 1232*	25	1.269	0.142	8.6	183	3.98
Polystyrene in arochlor 1232*	25	1.269	0.142	4.1	111	1.2
1.4-Polybutadiene in chloronaphthalene**	25	—	0.0312	2.2	200	0.26
1.4-Polybutadiene in chloronaphthalene**	25	—	0.0312	9.1	510	2.75
1.4-Polybutadiene in decalin**	25	—	0.0245	9.1	510	2.14
Poly- α -methylstyrene in α -chloronaphthalene***	25	—	0.0315	14.3	252	2.0
Poly- α -methylstyrene in decalin***	25	—	0.0245	14.3	135	0.79
Polystyrene in decalin****	15	0.887	0.0287	180	300	23
Polystyrene in toluene****	20	0.867	0.0059	180	3100	69

* Johnson et al. (1970); ** Osaki et al. (1972a); *** Osaki et al. (1972b); **** Rossers et al. (1978).

where η_s is the viscosity of the solvent and $c = nMN_A^{-1}$ is the weight concentration of the polymer ($N_A =$ Avogadro number).

The limit of the characteristic viscosity at low frequencies, according to (6.20), is defined as

$$[\eta']_0 = \frac{nT}{c\eta_s} \sum_{\alpha=1}^N \tau_{\alpha}^{\perp} = \frac{nT}{c\eta_s} \zeta(z\nu)\tau_1 \quad (6.23)$$

where $\zeta(x)$ is Riemann's zeta-function. This quantity makes it possible to estimate the role of the volume effects and of the hydrodynamic interaction in the dynamics of the macromolecule, which influence the dependence of the quantity under discussion on the molecular weight (the length of the macromolecule)

$$[\eta']_0 = KM^{z\nu-1}. \quad (6.24)$$

Theoretical estimates of the quantity $z\nu - 1$ are in the range from 0.5 (non-draining Gaussian coil), to 1.11 (draining coil with excluded-volume interaction). A compilation of empirical values of K and of the power exponents for different polymers and different solvents may be found in the literature (Flory 1969, Tsvetkov et al. 1964). The empirical values of the exponent $z\nu - 1$ do not exceed 0.9, which indicates significant impermeability of the macromolecular coil in a flow. We may note that once a relation of type (6.24)

has been established for a certain polymer, it can be used to determine the molecular weight of the polymer from the characteristic viscosity (Flory 1969, Tsvetkov et al. 1964). If the value of the index $z\nu$ is known, equation (6.23) allows us to estimate the value of the largest relaxation time τ_1 .

For a non-draining coil, the characteristic viscosity defined by equation (6.23) can be expressed in the form

$$[\eta']_0 = \Phi \frac{\langle S^2 \rangle^{3/2}}{M} \quad (6.25)$$

where $\langle S^2 \rangle$ is the average square of the radius of inertia of the coil, while the experimental value of the constant Φ (called the Flory constant) according to Flory (1969)

$$\Phi = (2.66 \pm 0.1) \times 10^{23} \text{ mol}^{-1}.$$

Equation (6.25) makes it possible in this case to interpret a dilute solution of macromolecules as a suspension of solid non-deformable spheres with a radius close to the mean square radius of inertia.

The initial characteristic viscosity defined by equation (6.23) is seen to be independent of the characteristics of intramolecular friction, but this is a consequence of the simplifying assumptions. It has been shown for a dumbbell (Al-tukhov 1986) that, when account of the internal viscosity and the anisotropy of the hydrodynamic interaction is taken simultaneously, the characteristics of these quantities enter into the expression for a viscosity of type (6.23). This result must be revealed also by the subchain model when account is taken of the anisotropy of the hydrodynamic interaction.

6.2.4 On the Effect of Internal Viscosity

The characteristic viscosity (6.22) is of special interest in the study of the influence of intramolecular friction on the dynamics of a macromolecule in a viscous liquid. At $\omega \rightarrow \infty$, characteristic viscosity can be written as

$$[\eta']_\infty = \frac{nT}{c\eta_s} \sum_{\alpha=1}^N \tau_\alpha^\perp \varphi_\alpha = \frac{nT}{c\eta_s} \zeta(z\nu - \theta) \tau_1 \varphi_1 \quad (6.26)$$

where $\zeta(x)$ is Riemann's zeta-function.

Experimental studies indicate (Cooke and Matheson 1976, Noordermeer et al. 1975) that the limiting characteristic viscosity for a given polymer-homologous series is independent of the length of macromolecule and the type of solvent. Taking into account that $\tau_1 \sim M^{z\nu}$, $n \sim M^{-1}$ and $\varphi_1 \sim M^{-\theta}$, one can find the relation

$$\theta - z\nu + 1 = 0 \quad (6.27)$$

which follows from equation (6.26) and from the fact that the limiting characteristic viscosity is independent of the length of macromolecule.

The independence of the limiting characteristic viscosity on the type of solvent means that φ_1 is independent of the viscosity of the solvent, that is the dimensional characteristic of the ‘internal’ friction of the macromolecule $\zeta\varphi_1$ is proportional to the viscosity of the solvent and the “internal” friction is not solely internal. The conclusion that the solvent contributes significantly to the intramolecular viscosity was reported by Schrag (1991), and was dubbed as the “solvent modification effect”.

The fact that the value of the characteristic viscosity at high frequencies is not zero indicates the existence of intramolecular (taking into account the solvent molecules) relaxation processes with relaxation times smaller than the reciprocal of the frequency of the measurement. The true limiting value is naturally zero and experiments sometimes reveal a step at a frequency ω which indicates the occurrence of a relaxation process with a relaxation time $\tau \sim \omega^{-1}$ which is compatible to the times of the deformation of a system. This phenomenon may be described by including the relaxing intramolecular viscosity, as it was done by Volkov and Pokrovskii (1978).

One uses expression (6.18) for the stress tensor in which the memory function can be chosen in the simplest way

$$\varphi_\alpha(s) = \frac{\varphi_\alpha}{\tau} \exp\left(-\frac{s}{\tau}\right),$$

where φ_α is a coefficient of the intramolecular viscosity which can be defined by relation (2.27), for example. Then, we use the results of Chapter 4 for the correlation functions to write down the stresses for oscillatory deformation and to find an expression for the coefficient of dynamic viscosity

$$\begin{aligned} \eta(\omega) = & \eta_s + nT \sum_{\alpha=1}^N \left(\frac{\tau_\alpha^+ - \tau_\alpha^-}{\tau_\alpha^+ - \tau_\alpha^-} \right)^2 \left[\frac{\tau_\alpha^+ \tau_\alpha^+ [1 - i\omega(\tau_\alpha^+ - \tau_\alpha^+)]}{\tau_\alpha^+ 1 - i\omega\tau_\alpha^+} \right. \\ & - \frac{\tau_\alpha^+ + \tau_\alpha^-}{\tau_\alpha^+} \frac{\tau_\alpha^+ - \tau_\alpha^+}{\tau_\alpha^+ - \tau_\alpha^-} \frac{\tau_\alpha^0 [1 - i\omega(\tau_\alpha^0 - \tau_\alpha^+)]}{1 - i\omega\tau_\alpha^0} \\ & \left. + \frac{\tau_\alpha^-}{\tau_\alpha^+} \left(\frac{\tau_\alpha^+ - \tau_\alpha^+}{\tau_\alpha^+ - \tau_\alpha^-} \right)^2 \frac{\tau_\alpha^- [1 - i\omega(\tau_\alpha^- - \tau_\alpha^+)]}{1 - i\omega\tau_\alpha^-} \right], \end{aligned} \quad (6.28)$$

where the relaxation times are defined by

$$\begin{aligned} 2\tau_\alpha^\pm &= \tau_\alpha \pm \left(\tau_\alpha^2 - 2\tau\tau_\alpha^\pm \right)^{1/2}, & \tau_\alpha^\pm &= \frac{\tau_1}{\alpha^{z\nu}}, \\ \tau_\alpha &= \frac{\tau}{2} + \tau_\alpha^\pm (1 + \varphi_\alpha), & \tau_\alpha^0 &= \frac{2\tau_\alpha^- \tau_\alpha^+}{\tau_\alpha^+ + \tau_\alpha^-}. \end{aligned} \quad (6.29)$$

In the case, when one neglects the relaxation time of the intramolecular process,

$$\begin{aligned} \tau_\alpha &\rightarrow \tau_\alpha^\parallel = \tau_\alpha^\pm (1 + \varphi_\alpha), \\ \tau_\alpha^+ &\rightarrow \tau_\alpha^\parallel, \quad \tau_\alpha^- \rightarrow 0, \quad \tau_\alpha^0 \rightarrow 0 \end{aligned}$$

and expressions (6.28) reduce to the equation for dynamic viscosity

$$\eta(\omega) = \eta_s + nT \sum_{\alpha=1}^N \tau_{\alpha}^{\perp} \frac{1 - i\omega(\tau_{\alpha}^{\parallel} - \tau_{\alpha}^{\perp})}{1 - i\omega\tau_{\alpha}^{\parallel}} \quad (6.30)$$

which has the components (6.20).

Figure 14 illustrates the dependence of the viscosity on the frequency, while taking into account the intramolecular relaxation process with a relaxation time τ according to expression (6.28). It may be hoped that the study of intramolecular relaxation processes from a phenomenological point of view will promote the establishment of the detailed mechanism of the rapid relaxation processes in polymers, although there is no doubt that more detailed models of the macromolecule studied, for example, by Gotlib et al. (1986), Priss and Popov (1971), Priss and Gamlitski (1983) must be used at high frequencies. These models make it possible to describe the small-scale motions of the chain.

6.3 Macromolecules in a Viscoelastic Liquid

One of the first attempts to find a molecular interpretation of viscoelastic behaviour of entangled polymers was connected with investigation of the dynamics of a macromolecule in a form of generalised Rouse dynamics (Pokrovskii and Volkov 1978a; Ronca 1983; Hess 1986). It formally means that, instead of assumption that the environment of the macromolecule is a viscous medium, Brownian particles of the chain are considered moving in a viscoelastic liquid with the stress tensor

$$\sigma_{ij}^0 = -p\delta_{ij} + 2 \int_0^{\infty} \eta_s(s) \gamma_{ij}(t-s) ds. \quad (6.31)$$

The generalised Rouse dynamics is proved to be not sufficient for consistent explanation of viscoelastic behaviour of entangled polymers, but appears to be interesting from methodological point of view.

6.3.1 The Stress Tensor

To obtain the expression for the stress tensor for the set of Brownian particles suspended in a viscoelastic liquid, we use equation (6.7), in which the elastic and internal viscosity forces are specified in Section 3.2

$$K_i^{\alpha} = -2T\mu A_{\alpha\gamma} r_i^{\alpha}, \quad G_i^{\alpha} = 0.$$

It is convenient to write the stress tensor (6.7) in terms of normal coordinates:

$$\sigma_{ik}(t) = -n(N+1)T\delta_{ik} + nT \sum_{\alpha=1}^N (2\mu\lambda_{\alpha} \langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle - \delta_{ik}). \quad (6.32)$$

Expression (4.17) for non-equilibrium moments allows us to determine the stress tensor for a dilute suspension of macromolecular coils in the linear viscoelastic liquid

$$\sigma_{ik} = -p\delta_{ik} + 2 \int_0^\infty \left(\eta(s) + nT \sum_{\alpha=1}^N 2\mu\lambda_\alpha \mu_\alpha(s) M_\alpha(s) \right) \gamma_{ik}(t-s) ds. \quad (6.33)$$

Expressions (4.28) and (4.29) allow us to write the functions

$$\begin{aligned} \mu_\nu(t) &= T_\nu^+ \exp\left(-\frac{t}{2\tau_\nu^+}\right) - T_\nu^- \exp\left(-\frac{t}{2\tau_\nu^-}\right) - R(t), \\ M_\nu(t) &= \frac{1}{2\mu\lambda_\nu} \left[T_\nu^+ \exp\left(-\frac{t}{2\tau_\nu^+}\right) - T_\nu^- \exp\left(-\frac{t}{2\tau_\nu^-}\right) \right], \end{aligned}$$

where

$$T_\nu^\pm = \frac{\tau_\nu^R(1+B) - \tau_\nu^\mp}{\tau_\nu^+ - \tau_\nu^-}.$$

In accordance with definitions (4.26) the relaxation times are defined as

$$2\tau_\nu^\pm = \tau_\nu \pm \sqrt{\tau_\nu^2 - 2\tau\tau_\nu^R}, \quad \tau_\nu = \frac{\tau}{2} + \tau_\nu^R(1+B), \quad \tau_\nu^R = \frac{\tau^*}{\alpha^2}.$$

In equation (6.33), the stresses in the moving viscoelastic liquid (6.31) are added to the stresses in the continuum of Brownian particles. When the equations of motion are formulated, we have to take into account the presence of the two interacting and interpenetrating continuous media formed by the viscoelastic liquid carrier and the interacting Brownian particles that model the macromolecules. However, the contribution of the carrier in the case of a concentrated solution is slight, and we shall ignore it henceforth.

6.3.2 Dynamic Characteristics

We are studying the simple case, when the viscoelastic carrier liquid is characterised by the dynamic viscosity

$$\eta_s(\omega) = \eta_s + \frac{\eta_s B}{1 - i\omega\tau} \quad (6.34)$$

where η_s and τ are the coefficient of viscosity and the relaxation time of the carrier liquid. The equation of dynamics of a single macromolecule in a viscoelastic liquid has the form (3.11) in which, for this case, the memory functions are determined by the transforms

$$\beta[\omega] = \zeta + \frac{\zeta B}{1 - i\omega\tau}, \quad \varphi[\omega] = 0.$$

In this case, expression (6.33) for an oscillatory shear gradient gives the dynamic modulus of the system

$$G(\omega) = G_s(\omega) - nT \sum_{\nu=1}^N i\omega \mathcal{L}\{\mu_\nu^2(s)\}$$

where $\mathcal{L}\{\mu_\nu^2(s)\}$ is the Laplace transform of the functions $\mu_\nu^2(s)$.

When calculating the Laplace transform, one finds an enhancement of the dynamic modulus due to the macromolecular coils in the viscoelastic liquid

$$G(\omega) = nT \sum_{\alpha=1}^N \left[(T_\alpha^+)^2 \frac{-i\omega\tau_\alpha^+}{1 - i\omega\tau_\alpha^+} - 2T_\alpha^+ T_\alpha^- \frac{-i\omega\tau_\alpha^0}{1 - i\omega\tau_\alpha^0} + (T_\alpha^-)^2 \frac{-i\omega\tau_\alpha^-}{1 - i\omega\tau_\alpha^-} \right]. \quad (6.35)$$

The dynamic modulus of the suspension of non-interacting macromolecular coils is determined by three sets of relaxation times

$$\tau_\alpha^+, \quad \tau_\alpha^-, \quad \tau_\alpha^0 = \frac{2\tau_\alpha^+ \tau_\alpha^-}{\tau_\alpha^+ + \tau_\alpha^-} \approx 2\tau_\alpha^-. \quad (6.36)$$

Further on we shall consider the case of large values of parameter B , when the first terms in the expansion of the relaxation times in powers of the quantity $1/B$ are

$$\tau_\alpha^+ \approx \tau_\alpha^R B (1 + \chi\alpha^2) \left[1 - \frac{2\chi\alpha^2}{B(1 + \chi\alpha^2)^2} \right], \quad (6.37)$$

$$\tau_\alpha^- \approx \frac{2\tau^* \chi}{1 + \chi\alpha^2}, \quad \chi = \frac{\tau}{2\tau^* B}. \quad (6.38)$$

At large values of B , the whole set of relaxation times can be divided into two sets: large relaxation times τ_α^+ and small relaxation times τ_α^- and τ_α^0 , while the times τ_α^+ are B times the largest times from the set τ_α^- and τ_α^0 .

One can see that the frequency dependence of the dynamic modulus is determined by two parameters B and χ

$$G(\omega) = nT f(\omega\tau^*, B, \chi).$$

Before we discuss the frequency dependencies of the dynamic modulus, which are shown in Fig. 16 for typical values of parameters, we shall find expressions for the characteristic quantities at $B \gg 1$. The latter assumption allows us to use expressions (6.36)–(6.38) and to define

$$T_\nu^+ \approx \frac{\tau_\nu^R B}{\tau_\nu^+ - \tau_\nu^-}, \quad T_\nu^- \approx \frac{\tau_\nu^R B \chi \alpha^2}{\tau_\nu^+ - \tau_\nu^-}.$$

Expressions for viscosity η , elasticity ν and the real value of the dynamic modulus on the intermediate plateau, when $\tau_\alpha^+ \gg \frac{1}{\omega} \gg \tau_\alpha^-$, follow from formula (6.35)

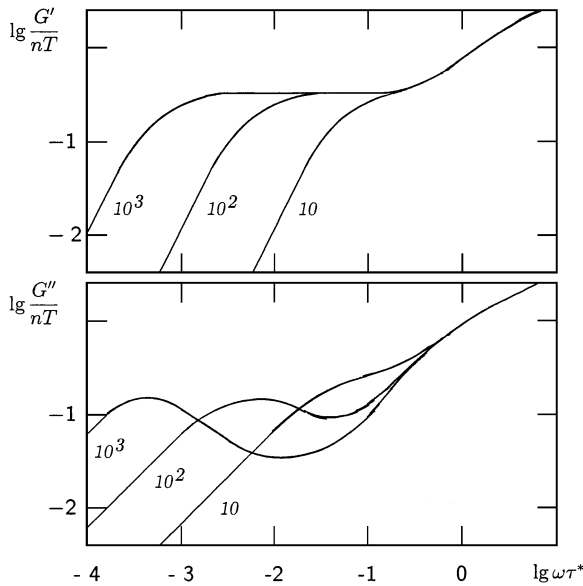


Figure 16. Macromolecules in a viscoelastic liquid. The real and the imaginary components of dynamical modulus of a dilute suspension of macromolecules in a viscoelastic liquid are calculated at values of B shown at the curves and at $\chi = 1$. Adapted from the paper of Pokrovskii and Volkov (1978a).

$$\eta = nT\tau^*B \sum_{\alpha=1}^N \frac{1}{\alpha^2(1 + \chi\alpha^2)},$$

$$\nu = nT(\tau^*B)^2 \sum_{\alpha=1}^N \frac{1}{\alpha^4},$$

$$G_e = nT \sum_{\alpha=1}^N \frac{1}{(1 + \chi\alpha^2)^2}.$$

The replacement of the sums by integrals allows us to estimate the characteristic quantities at $N \rightarrow \infty$. One can find that the elasticity does not depend on the parameter χ

$$\nu = \frac{\pi^4}{90} nT(\tau^*B)^2. \tag{6.39}$$

The viscosity and dynamic modulus value for the plateau can be estimated at large and small values of χ

$$\begin{aligned} \eta &\approx \frac{\pi^4}{90} nT\tau^* B\chi^{-1}, & G_e &\approx \frac{\pi^4}{90} nT\chi^{-2}, & \chi &\gg 1, \\ \eta &\approx \left(\frac{\pi^2}{6} - \frac{\pi}{2}\chi^{1/2} \right) nT\tau^* B, & G_e &\approx \frac{\pi}{4} nT\chi^{-1/2}, & \chi &\ll 1. \end{aligned} \quad (6.40)$$

Now, we can try to relate the above results to the experimental data on the viscoelasticity of concentrated solutions of polymers. For the systems of long macromolecules, the estimated values of parameter χ are small. Having used expressions (6.40) for this case, one can evaluate the terminal relaxation time of the system

$$\bar{\tau} = \frac{\nu}{\eta} = \frac{\pi^2}{15} \tau^* B, \quad (6.41)$$

which, due to the requirement of assumed self-consistency, ought to coincide with the given relaxation time τ . This requirement, in virtue of definition (6.38), determines the self-consistent value of the parameter

$$\chi = \frac{\tau}{2\tau^* B} = \frac{\pi^2}{30} \approx 0.33. \quad (6.42)$$

In the alternative case of large values of χ one can use the upper line of equation (6.40) to calculate the terminal relaxation time of the system, which coincides with the given relaxation time in order of magnitude

$$\bar{\tau} = \frac{\nu}{\eta} = \frac{\tau}{2}.$$

The suspension of dilute macromolecular coils in a viscoelastic liquid is suitable for the interpretation of results on the viscoelasticity of concentrated systems with macromolecules, which are not long ($M \approx M_e$). This case was carefully investigated by Leonov (1994). He has confirmed the possibility of a self-consistent description for a system of very short macromolecules.

6.4 Entangled Macromolecules

Investigation of viscoelastic behaviour of linear polymer solutions and melts shows that there are universal laws for dependencies of the terminal characteristics on the length of macromolecules, which allows to interpret these phenomena on the base of behaviour of a single macromolecule in the system of entangled macromolecules (Ferry 1980, Doi and Edwards 1986). The validity of the mesoscopic approach itself rests essentially on the fundamental experimental fact that quantities that characterise the behaviour of a polymer system have a well-defined unambiguous dependence on the length of the macromolecule.

The dependence of the characteristics on molecular weight was used for the classification of the systems (Ferry 1980; Graessley 1974; Watanabe 1999).

The law for coefficient of viscosity, which was unambiguously established by Fox and Flory (1948) for polystyrene and polyisobutylene and confirmed for many polymer system investigated later (Berry and Fox 1968, Ferry 1980), determines the first critical point $M_c \approx 2M_e$ separating entangled and non-entangled systems of linear polymers

$$\eta \sim \begin{cases} M, & \text{non-entangled systems, } M < M_c, \\ M^{3.4}, & \text{entangled systems, } M > M_c. \end{cases} \quad (6.43)$$

While the law with index 3.4 for viscosity is valid in the whole region above M_c , the dependence of terminal relaxation time is different for weakly and strongly entangled systems (Ferry 1980) and determines the second critical point M^*

$$\tau \sim \begin{cases} M^{4.4}, & \text{weakly entangled systems, } M < M^*, \\ M^{3.4}, & \text{strongly entangled systems, } M > M^*. \end{cases} \quad (6.44)$$

The data for melts of different polymers collected by Ferry (1980, p.379, Table 13-III) allows us to estimate the second critical point¹ M^* . Assuming that $M_c = 2M_e$, one has

$$M^* \approx (4.6-12.0)M_e.$$

The critical value of molecular weight can be identified with the transition point between weakly and strongly entangled systems, the position of which was estimated in Sections 4.2.3 and 5.1.2 as

$$M^* \approx 10M_e.$$

The difference in the molecular-weight dependence of the terminal relaxation time can be attributed to the change of the mechanisms (diffusive and reptation, correspondingly) of conformational relaxation in these systems. Further on in this section, we shall calculate dynamic modulus and discuss characteristic quantities both for weakly and strongly entangled systems.

6.4.1 The Stress Tensor

To calculate the characteristics of viscoelasticity in the framework of mesoscopic approach, one can start with the system of entangled macromolecules, considered as a dilute suspension of chains with internal viscoelasticity moving in viscoelastic medium, while the elastic and internal viscosity forces, according to equations (3.4)–(3.6) and (3.8), have the form

$$K_i^\alpha = -2T\mu A_{\alpha\gamma} r_i^\alpha, \quad G_i^\alpha = -G_{\alpha\gamma} \int_0^\infty \varphi(s)(u_i^\gamma - \omega_{ij} r_j^\gamma)_{t-s} ds.$$

¹ To avoid many subscripts, instead of Ferry's symbol M'_c for the second critical point, I use the symbol M^* .

For calculation, it is convenient to write the stress tensor (6.7) in terms of normal co-ordinates in the following form:

$$\begin{aligned} \sigma_{ik}(t) = & -n(N+1)T\delta_{ik} + nT \sum_{\alpha=1}^N \left\{ 2\mu\lambda_{\alpha} \langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle - \delta_{ik} \right. \\ & \left. + \frac{1}{T} \int_0^{\infty} \varphi(s) \left(\langle \dot{\rho}_i^{\alpha}(t-s) \rho_k^{\alpha}(t) \rangle - \omega_{il}(t-s) \langle \rho_l^{\alpha}(t-s) \rho_k^{\alpha}(t) \rangle \right) ds \right\}. \end{aligned} \quad (6.45)$$

The contribution of the carrier segment liquid in the case of a concentrated solution is slight, and we shall ignore it henceforth. The contribution of separate macromolecules, which is presented by the terms under the sum in the above equation, can be divided into two parts. The first terms describe external frictions due to connectivity of the particles, while the integral terms present stresses due to intramolecular resistance of the coils. The last can be interpreted, remembering the speculation in Section 3.3.3, as stresses emerging at orientation of separate Kuhn segments in dense medium among the other segments. Let us note that expression (6.45) can be considered as a generalisation of the known (Cerf 1958, Peterlin 1967) expressions for stress in dilute solutions of polymers with internal viscosity. Indeed, if $\varphi(s) \sim \delta(s)$, expression (6.45) for the stress tensor reduces to (6.14).

The expression (6.45) for the stress tensor can be applied to both weakly and strongly entangled systems, but, let us note, that the macromolecular dynamics is different in these cases. We use the expression (6.45) to calculate the stress tensor for entangled systems in linear approximation of macromolecular dynamics. Using expressions for moments (4.17), (4.20) and (4.21) one obtains

$$\begin{aligned} \sigma_{ik}(t) = & -p\delta_{ik} + 2nT \sum_{\alpha=1}^N \left\{ \int_0^{\infty} 2\mu\lambda_{\alpha}\mu_{\alpha}(s)M_{\alpha}(s)\gamma_{ik}(t-s)ds \right. \\ & + \frac{1}{2T} \int_0^{\infty} \varphi(s) \int_0^{\infty} [\mu_{\alpha}(u+s)\dot{M}_{\alpha}(u) \\ & \left. + \dot{\mu}_{\alpha}(u)M_{\alpha}(u+s)]\gamma_{ik}(t-s-u)du ds \right\}. \end{aligned} \quad (6.46)$$

The mesoscopic analysis, similar to truly phenomenological analysis, includes some mesoscopic parameters in final expressions for the stress tensor and for viscoelastic characteristics and assumes the necessity of investigation on the base of more specified models of the system. Some theories were based on the image of the structure of polymer systems as a network with temporary knots (entanglements) (Ferry et al. 1955; Lodge 1956; Chompff and Duiser 1966; Chompff and Prins 1968). Those attempts helped us to understand some features of polymer dynamics. A recent work by Schieber et al. (2003) gives us an example of a very detailed picture of flowing entangled polymer system.

6.4.2 Dynamic Modulus and Relaxation Branches

There are plenty of measurements of dynamic modulus of nearly monodisperse polymers starting with pioneering works of Onogi et al. (1970) and Vinogradov et al. (1972a). The more recent examples of the similar dependencies can be found in papers by Baumgaertel et al. (1990, 1992) for polybutadiene and for polystyrene and in paper by Pakula et al. (1996) for polyisoprene.

To calculate the dynamic modulus, we turn to the expression for the stress tensor (6.46) and refer to the definition of equilibrium moments in Section 4.1.2, while memory functions are specified by their transforms as

$$\beta[\omega] = \zeta + \frac{\zeta B}{1 - i\omega\tau}, \quad \varphi[\omega] = \frac{\zeta E}{1 - i\omega\tau}. \quad (6.47)$$

It means, according to the speculations in Chapter 3 that the environment of the chosen macromolecule is considered a viscoelastic medium, and, in addition, the internal resistance or the internal viscosity is taken into account. The latter was not considered in the previous section.

We are calculating dynamic modulus and characteristic quantities for entangled systems, when the linear approximation of dynamic equation is used.

The Case of Low Frequencies

To begin with, let us consider the simple case, when ζ can be neglected in comparison to ζB in equations (6.47), which can be done, if one considers low-frequency properties of the systems with long macromolecules – the strongly entangled systems. In this case, according to (4.32) and (4.33), we have

$$\begin{aligned} \mu_\alpha(s) &= \frac{B\tau_\alpha^R}{\tau_\alpha} \exp\left(-\frac{s}{2\tau_\alpha}\right) - \frac{B\tau_\alpha^R}{\tau_\alpha} R(s), \\ M_\alpha(s) &= \frac{1}{2\mu\lambda_\alpha} \left[\frac{(B+E)\tau_\alpha^R}{\tau_\alpha} \exp\left(-\frac{s}{2\tau_\alpha}\right) + \frac{\tau}{2\tau_\alpha} R(s) \right], \\ \dot{\mu}_\alpha(s) &= -\frac{B\tau_\alpha^R}{\tau_\alpha} \frac{1}{2\tau_\alpha} \exp\left(-\frac{s}{2\tau_\alpha}\right) + \frac{2B\tau_\alpha^R}{\tau_\alpha} \delta(s), \\ \dot{M}_\alpha(s) &= -\frac{1}{2\mu\lambda_\alpha} \left[\frac{(B+E)\tau_\alpha^R}{\tau_\alpha} \frac{1}{2\tau_\alpha} \exp\left(-\frac{s}{2\tau_\alpha}\right) + \frac{\tau}{\tau_\alpha} \delta(s) \right] \end{aligned}$$

where $\tau_\alpha^R = \tau^*/\alpha^2$ are the Rouse relaxation times and

$$\tau_\alpha = \frac{\tau}{2} + \tau_\alpha^R(B+E).$$

Under oscillatory motion, the stress tensor (6.46) gives us an expression for the dynamic modulus

$$G(\omega) = nT \sum_{\alpha} \frac{(\tau_{\alpha}^R)^2 B(B+E)}{\tau_{\alpha}} \times \left[\frac{-i\omega}{1-i\omega\tau_{\alpha}} + \frac{-i\omega 2E\tau_{\alpha}^R}{2\tau_{\alpha} + \tau - 2i\omega\tau\tau_{\alpha}} - \frac{-i\omega 2E\tau_{\alpha}^R}{(2\tau_{\alpha} + \tau - 2i\omega\tau\tau_{\alpha})(1-i\omega\tau_{\alpha})} \right].$$

We can introduce a new set of relaxation times

$$\tau_{\alpha}^* = \frac{2\tau\tau_{\alpha}}{2\tau_{\alpha} + \tau} \quad (6.48)$$

and, after some rearrangement, write an expression for the dynamic modulus in the standard form

$$G(\omega) = nT \sum_{\alpha} \left(\frac{\tau_{\alpha}^R}{\tau_{\alpha}} \right)^2 B \left(B \frac{-i\omega\tau_{\alpha}}{1-i\omega\tau_{\alpha}} + E \frac{\tau_{\alpha}}{\tau} \frac{-i\omega\tau_{\alpha}^*}{1-i\omega\tau_{\alpha}^*} \right), \quad (6.49)$$

where for small α and large B , we have

$$\tau_{\alpha} \gg \tau_{\alpha}^*, \quad \tau_{\alpha}^* \approx \tau.$$

One can, thus, see that, at low frequencies, the viscoelastic behaviour of the system is determined by two sets of relaxation times, or, we can say also, by two relaxation branches. The first term in (6.49) is determined by relaxation of conformation of the macromolecule. The second term in (6.49), as will be shown in the next chapter, is connected with orientational relaxation processes.

Note that the first and the second terms in (6.49) at $\omega \rightarrow \infty$ have the orders of magnitudes $nT\psi^{-2}$ and $nT\chi^{-1}$, respectively. The ratio of the quantities is very small for systems of long macromolecules, so that the contribution of the first, conformation branch to the linear viscoelasticity is negligibly small at $\chi \ll \chi^*$. Note also that, for strongly entangled systems, at $\chi \ll \chi^*$ or $M \gg M^*$, as it was shown in Section 4.2.3, conformational relaxation cannot be occurred via the diffusive mechanism (considered here), but via the reptation mechanism, so that the first term in equation (6.49) ought to be replaced by other term, for example, in the form

$$nT \sum_{\alpha=1}^{\pi/\chi} \frac{-i\omega p_{\alpha} \tau_{\alpha}^{\text{rep}}}{1-i\omega\tau_{\alpha}^{\text{rep}}}, \quad \tau_{\alpha}^{\text{rep}} = \frac{\pi^2}{\chi} \frac{\tau^*}{\alpha^{0.5}}.$$

Though the reptation relaxation times are defined by equation (4.37), the weights p_{α} of the contributions of separate relaxation processes remain unknown, and in fact, the replacement is forbidden, so that we prefer, as an initial approximation, to consider evaluation of dynamic modulus without any modification.

The Case of Higher Frequencies

To extend the theory for higher frequencies, we have to consider the general case, when the micro-viscoelasticity is given by (6.47). Using equations (4.28) and (4.29), after some rearrangement, one can find the dynamic modulus

$$G(\omega) = nT(-i\omega) \sum_{a=1}^5 \sum_{\alpha} \frac{p_{\alpha}^{(a)} \tau_{\alpha}^{(a)}}{1 - i\omega \tau_{\alpha}^{(a)}} \quad (6.50)$$

where the times of relaxation and the corresponding weights are given by the following expressions

$$\begin{aligned} \tau_{\alpha}^{(1)} &= \tau_{\alpha}^{+} = \frac{1}{2} \left(\tau_{\alpha} + \left(\tau_{\alpha}^2 - 2\tau\tau_{\alpha}^{\text{R}} \right)^{1/2} \right), \\ \tau_{\alpha}^{(2)} &= \frac{2\tau\tau_{\alpha}^{+}}{\tau + 2\tau_{\alpha}^{+}}, \quad \tau_{\alpha}^{(3)} = \frac{2\tau_{\alpha}^{+}\tau_{\alpha}^{-}}{\tau_{\alpha}^{+} + \tau_{\alpha}^{-}}, \quad \tau_{\alpha}^{(4)} = \frac{2\tau\tau_{\alpha}^{-}}{\tau + 2\tau_{\alpha}^{-}}, \\ \tau_{\alpha}^{(5)} &= \tau_{\alpha}^{-} = \frac{1}{2} \left(\tau_{\alpha} - \left(\tau_{\alpha}^2 - 2\tau\tau_{\alpha}^{\text{R}} \right)^{1/2} \right), \\ p_{\alpha}^{(1)} &= T_{\alpha}^{+} S_{\alpha}^{+} \left(1 - \frac{2E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{+} - \tau} \right), \\ p_{\alpha}^{(2)} &= S_{\alpha}^{+} \frac{E\tau_{\alpha}^{\text{R}}}{\tau} + T_{\alpha}^{+} S_{\alpha}^{+} \frac{2E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{+} - \tau} - (T_{\alpha}^{+} S_{\alpha}^{-} + T_{\alpha}^{-} S_{\alpha}^{+}) \frac{2E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{-} - \tau}, \\ p_{\alpha}^{(3)} &= (T_{\alpha}^{+} S_{\alpha}^{-} + T_{\alpha}^{-} S_{\alpha}^{+}) \left(\frac{E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{+} - \tau} + \frac{E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{-} - \tau} - 1 \right), \\ p_{\alpha}^{(4)} &= -S_{\alpha}^{-} \frac{E\tau_{\alpha}^{\text{R}}}{\tau} + T_{\alpha}^{-} S_{\alpha}^{-} \frac{2E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{-} - \tau} - (T_{\alpha}^{+} S_{\alpha}^{-} + T_{\alpha}^{-} S_{\alpha}^{+}) \frac{E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{+} - \tau}, \\ p_{\alpha}^{(5)} &= T_{\alpha}^{-} S_{\alpha}^{-} \left(1 - \frac{2E\tau_{\alpha}^{\text{R}}}{2\tau_{\alpha}^{-} - \tau} \right). \end{aligned}$$

Expression (6.50) for the dynamic modulus includes now five relaxation branches and generalises formula (6.49) for higher frequencies.

The situation is illustrated in Fig. 17, which contains experimental values of dynamic shear modulus for polystyrenes with different molecular weights and theoretical dependences calculated according to equation (6.50) and presented by the solid lines. This comparison illustrates insufficiency of linear approximation for macromolecule dynamics to describe the effects of linear viscoelasticity of entangled systems. For polymers with the length $M > 10M_e$ – strongly entangled systems, the most essential contribution is given by the second relaxation branch, that is the orientation relaxation branch with relaxation times close to τ , which determines terminal characteristics (see the next section). The largest conformational relaxation times, contribution of which are shown by the dashed lines, have appeared to be unrealistically large for strongly entangled systems in linear approximation of macromolecular dynamics. It was shown (see Section 4.2.2) that introduction of local anisotropy

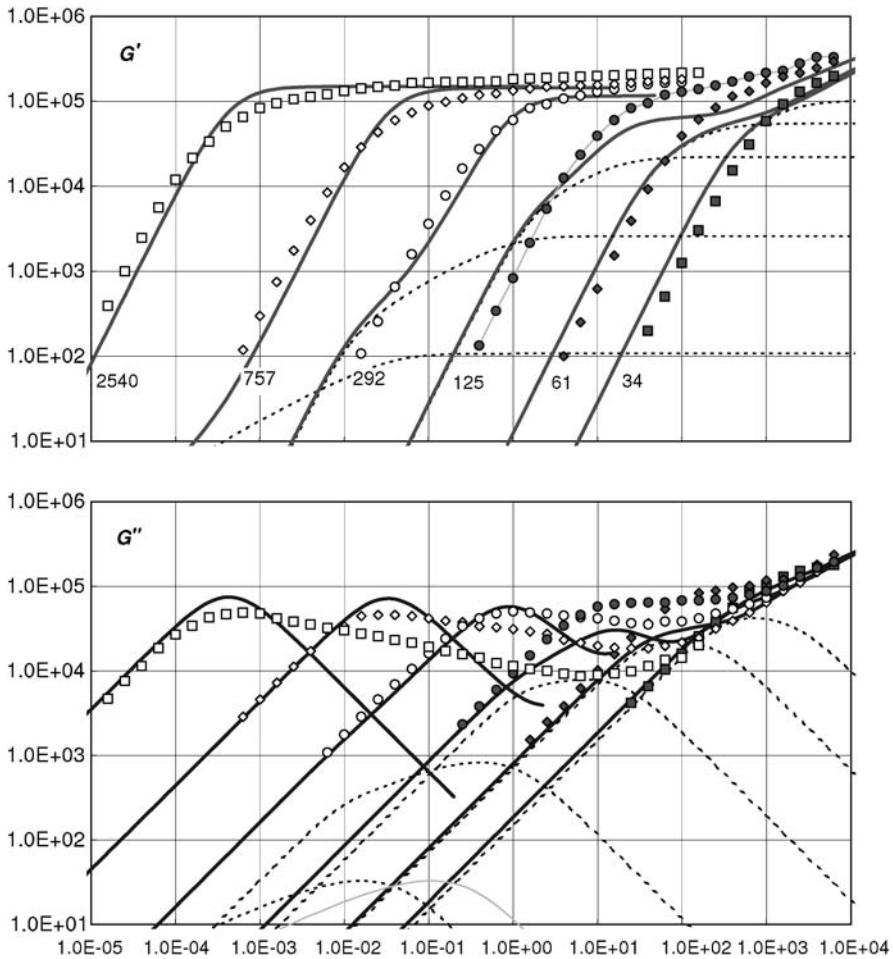


Figure 17. Dynamic modulus of typical polymers.

The experimental points (taken from the review by Watanabe 1999) are due to the measurements of Schausberger et al. (1985) for polystyrenes. The numbers indicate the lengths of macromolecules $10^{-3} \cdot M$. The reference temperature is $T = 180^\circ \text{C}$, $G'_e = 2 \times 10^5 \text{ Pa}$. The length between entanglement is $M_e = 16000$, so that the theoretical dependences, shown by the solid lines, are calculated for the numbers of entanglements per macromolecule $Z = 2.125, 3.813, 7.813, 18.25, 47.31, 158.75$, which induce, according to relations (3.17), (3.25) and (3.29), the corresponding values of parameters χ , B , and E . The separate contributions from the conformational relaxation branches are shown by dashed lines.

of mobility helps one to improve the situation: the largest relaxation times decrease when the coefficient of local anisotropy increases. However, one can see that the contribution of the conformational reptation branch into dynamic mod-

ulus appears to be negligible for the high-molecular-weight polymers in the region of low frequencies, so that, whichever mechanism of conformational relaxation is realised, the second branch gives a good approximation of terminal quantities for the strongly-entangled systems. The remaining branches merge and form a group of slow relaxation times. The absence of non-linear terms in the macromolecular dynamics affects also the behaviour in the transition region about $M \approx 10M_e$. The difference between theoretical and empirical results for polymers with length $M < 10M_e$ – weakly entangled systems, can be also connected, in particular, by polydispersity of polymers, which is larger for low-molecular weight samples, than for high-molecular weight ones.

One can see that the approximation of the theory, based on the linear dynamics of a macromolecule, is not adequate for strongly entangled systems. One has to introduce local anisotropy in the model of the modified Cerf-Rouse modes or use the model of reptating macromolecule (Doi and Edwards 1986) to get the necessary corrections (as we do in Chapters 4 and 5, considering relaxation and diffusion of macromolecules in entangled systems). The more consequent theory can be formulated on the base of non-linear dynamic equations (3.31), (3.34) and (3.35).

6.4.3 Self-Consistency of the Mesoscopic Approach

One can notice that the dissipative terms in the dynamic equation (3.11) (taken for the case of zero velocity gradients, $\nu_{ij} = 0$) have the form of the resistance force (D.3) for a particle moving in a viscoelastic liquid, while the memory functions are (with approximation to the numerical factor) fading memory functions of the viscoelastic liquid. The macromolecule can be considered as moving in a viscoelastic continuum. In the case of choice of memory functions (3.15), the medium has a single relaxation time and is characterised by the dynamic modulus

$$G_s(\omega) = \frac{-i\omega\eta_s}{1 - i\omega\tau}, \quad G_e = \lim_{\omega \rightarrow \infty} G(\omega) = \frac{\eta_s}{\tau}$$

where τ is the correlation time introduced in (3.15), and η_s is a constant. One can say that the written dynamic modulus characterises the micro-viscoelasticity.

On the other hand, the properties of the system as a whole can be calculated and the macroscopic dynamic modulus can be determined. Here the question of the relation between the postulated micro-viscoelasticity and the resulting macro-viscoelasticity appears. The answer requires a properly formulated self-consistency condition. Simple speculations show that equality of the micro- and macro-viscoelasticity cannot be obtained. Nevertheless, it is natural to require the equality of relaxation times of micro- and macro-viscoelasticities. It will be shown in this section that this condition can be satisfied.

First, we shall consider in detail the characteristic quantities: the viscosity coefficient η and the elasticity coefficient ν , defined by expansion (6.11), and the value of the dynamic modulus on the plateau G_e . The latter can be calculated as the limiting value of the modulus at frequencies satisfying the relation

$$\tau_\alpha^- < \omega^{-1} < \tau_\alpha^+ \approx \tau.$$

The estimation of the main terms of expansion of dynamic modulus (6.49) determine the expressions for the terminal quantities

$$\begin{aligned} G_e &= nT \sum_{\alpha=1}^N \frac{2\chi\alpha^2 + \psi(\chi\alpha^2 + 1 + \psi)}{2\chi\alpha^2(\chi\alpha^2 + 1 + \psi)^2}, \\ \eta &= nT\tau^*B \sum_{\alpha=1}^N \left(\frac{1}{\alpha^2(\chi\alpha^2 + 1 + \psi)} + \frac{\psi}{\alpha^2(2\chi\alpha^2 + 1 + \psi)} \right), \\ \nu &= nT(\tau^*B)^2 \sum_{\alpha=1}^N \frac{2\chi\psi(\chi\alpha^2 + 1 + \psi)}{\alpha^2(2\chi\alpha^2 + 1 + \psi)}. \end{aligned}$$

A preliminary estimate of χ which, according to (5.8), can be interpreted as the ratio of the square of the tube diameter $(2\xi)^2$ to the mean square end-to-end distance $\langle R^2 \rangle_0$, shows that $\chi \ll 1$ for strongly entangled systems. For large N , this enables us to replace summation by integration and, according to the rules of Appendix G, to obtain expressions for the characteristic quantities

$$\begin{aligned} G_e &= nT \left[\frac{\pi^2}{12} \frac{\psi}{\chi(1+\psi)} + \frac{\pi}{8} \frac{2-\psi}{(1+\psi)^{3/2}} \chi^{-1/2} \right], \\ \eta &= nT\tau^*B \left[\frac{\pi^2}{6} - \frac{\pi}{2} \left(\frac{\chi}{1+\psi} \right)^{1/2} \right], \\ \nu &= nT(\tau^*B)^2 \left[\frac{\pi^2}{3} \frac{\chi\psi}{1+\psi} - \frac{\pi}{2} \left(\frac{2\chi}{1+\psi} \right)^{3/2} 2\psi \right]. \end{aligned} \quad (6.51)$$

These expressions are valid for arbitrary ψ and small χ . We can then distinguish between two cases, namely: for systems consisting of very long molecules in the almost complete absence of the solvent (strongly entangled systems) we have $\psi \gg 1$, whereas $\psi \ll 1$ for a concentrated system consisting of not very long macromolecules (weakly entangled systems). In the latter case expressions (6.51) at $\psi = 0$ are identical to expressions (6.39) and (6.40). Here, we shall consider the former case, when $\psi \gg 1$ and find from (6.51) the zeroth-order terms in power of ψ^{-1} .

$$G_e = \frac{\pi^2}{12} nT\chi^{-1}, \quad \eta = \frac{\pi^2}{6} nT\tau^*B, \quad \nu = \frac{\pi^2}{3} nT(\tau^*B)^2\chi. \quad (6.52)$$

One can note that the relaxation times of the second branch are very close to each other, so that the frequency dependence of the modulus could be

approximated by a expression with the single relaxation time determined by the relation

$$\bar{\tau} = \frac{\eta}{G_e} = 2\tau^* B\chi = \tau.$$

The relaxation time that we have determined may be referred to as the terminal viscoelastic relaxation time; it is equal to the relaxation time which was introduced to characterise the medium surrounding the chosen macromolecule. Thus, for $\psi \rightarrow \infty$, the theory is self-consistent and this confirms the statement of Section 3.1.1 that chains of Brownian particles are moving independently in a liquid made of interacting Kuhn segments.

The condition of self-consistency, as a requirement of the identity of the times of relaxation of macro- and micro-viscoelasticity, gives the following relation for the first-order terms in power of ψ^{-1} of expansion of (6.51)

$$\psi = \frac{4\pi^2}{9} \frac{1}{\chi}. \quad (6.53)$$

This relation is practically identical to relation (5.17).

Equation (6.52) and the experimental data allow us to estimate the parameters of the theory χ and τ^*B which can be also estimated directly by other methods discussed in Chapter 5. So, the consistency of the theory can be tested.

6.4.4 Modulus of Elasticity and the Intermediate Length

Initially, the elasticity of concentrated polymer systems was ascribed to the existence of a network in the system formed by long macromolecules with junction sites (Ferry 1980). The sites were assumed to exist for an appreciable time, so that, for observable times which are less than the lifetime of the site, the entangled system appears to be elastic. Equation (1.44) was used to estimate the number density of sites in the system. The number of entanglements for a single macromolecule $Z = M/M_e$ can be calculated according to the modified formula

$$G_e = nT \frac{M}{M_e} \quad (6.54)$$

where n is the density of the number of macromolecules and T is temperature in energy unit.

The length of a macromolecule between adjacent entanglements M_e is used as an individual characteristic of a polymer system. Table 1 contains values of M_e for certain polymer systems. The more complete list of estimates of the quantity M_e can be found in work by Aharoni (1983, 1986). One can compare expressions (6.52) and (6.54) for the value of the modulus on the plateau to see that the length of a macromolecule between adjacent entanglements M_e is closely connected with one of the parameters of the theory

$$\chi = \frac{\pi^2}{12} \frac{M_e}{M}. \quad (6.55)$$

We should note, recalling the interpretation of χ as the ratio of the doubled intermediate length to the size of the coil discussed previously (formula (5.8)), that the length M_e , determined in the usual way, is actually related to the intermediate length ξ . Expression (6.52) can be rewritten in a form which is identical to the relation by Doi and Edwards (1986)

$$G_e = \frac{2}{3}nT \frac{\langle R^2 \rangle}{(2\xi)^2}.$$

Note that the squared diameter of the Doi-Edwards tube relates to our intermediate length as follows

$$d^2 = \frac{6}{5}(2\xi)^2. \quad (6.56)$$

The intermediate length (tube diameter) 2ξ can be estimated from the modulus with the aid of the above equations. Comparison of values of the intermediate length found from dynamic modulus and from neutron-scattering experiments was presented by Ewen and Richter (1995). They found the values to be close to each other, though there is a difference in the temperature dependence of the values of intermediate length found by different methods.

Although a network is not present in a concentrated solution, there exists a characteristic length, which had earlier been assumed the distance between neighbouring network sites. The characteristic length is a dynamic one. There are no temporary knots in a polymer system, though there is a characteristic time, which is the lifetime of the frozen large-scale conformation of a macromolecule in the system. So, the conceptions of intermediate length and characteristic time are based on deeper ideas and are reflected in the theory.

6.4.5 Concentration and Macromolecular Length Dependencies

Thus in the mesoscopic approximation or, in other words, in the mean-field approximation, the dynamic shear modulus of the melt or the concentrated solution of the polymer (strongly entangled systems) is represented by a function of a small number of parameters

$$G(\omega) = nTf(\tau^*\omega, B, \chi). \quad (6.57)$$

In this case, one assumes that $B \gg 1$, and, hence, it follows that $\tau > \tau^*$, which fact imposes certain restrictions on χ , so that $1/B < \chi \ll 1$. For these values of B and χ , the theory is found to be self-consistent for $\psi \gg 1$, so that once again, as was shown in Section 6.4.3, the formulae for the dynamic modulus lead to expressions for the characteristic quantities

$$\begin{aligned} \eta &= \frac{\pi^2}{6}nT\tau^*B, & \tau &= 2\tau^*B\chi, \\ \nu &= \frac{\pi^2}{3}nT(\tau^*B)^2\chi, & G_e &= \frac{\pi^2}{12}nT\chi^{-1}. \end{aligned} \quad (6.58)$$

Experiments reveal that the dynamic modulus and the characteristic quantities (6.58) depend on the polymer concentration c and length M of the macromolecule (Ferry 1980), and these dependencies are implied through the parameters of the theory.

In accordance with equations (1.33) and (4.25) we can write

$$n \sim \frac{c}{M}, \quad \tau^* \sim \frac{\zeta_0 M^2 C_\infty}{T} \quad (6.59)$$

where ζ_0 is the monomer friction coefficient and C_∞ is a quantity connected with the temperature dependence of the size of a macromolecular coil (see Section 1.1). The values of parameter C_∞ , which reflects the thermodynamic rigidity of the macromolecule, are given for different polymers in tables of the monographs by Flory (1969) and by Tsvetkov et al. (1964).

The mesoscopic parameters χ and B , as was shown earlier in Section 3.3.4, can be written as functions of a single argument, which can now be rewritten as

$$n\langle R^2 \rangle^{3/2} \sim C_\infty^{3/2} c M^{1/2}. \quad (6.60)$$

This allows one to write the dependencies of the characteristic quantities on the concentration of polymer and on the thermodynamic rigidity, if the dependence on molecular weight of the macromolecule, for example, is known. With help of the result of Section 3.3.4 (see formulae (3.30)), one can obtain for the strongly entangled systems

$$\begin{aligned} \eta &\sim \zeta_0 C_\infty^{3\delta+1} c^{2\delta+1} M^{\delta+1}, & \nu &\sim \zeta_0^2 C_\infty^{3\delta-1} c^{4\delta-1} M^{2\delta+2}, \\ G_e &\sim T C_\infty^3 c^3 M^0, & \tau &\sim \frac{1}{T} \zeta_0 C_\infty^{3\delta-2} c^{2\delta-2} M^{\delta+1}. \end{aligned} \quad (6.61)$$

These equations allow one to establish various relations between the characteristic quantities, while the only index δ ought to be evaluated empirically. The data obtained for almost monodisperse samples of polymer melts of different molecular weight allows one to evaluate for high molecular weights $\delta = 2.4$ (Berry and Fox 1968, Ferry 1980). Empirical estimate corresponds to the coarse theoretical estimation in Section 3.3.2, according to which $\delta = 2$ or $\delta = 3$. The molecular-weight dependencies of other quantities in (6.61) are typical for high-molecular-weight polymers: $G_e \sim M^0$, the dependence of η and of τ on the length of a macromolecule is the same (Ferry 1980).²

² The reptation-tube model, being used for interpretation of viscoelastic behaviour of the system, has allowed to obtain (Doi and Edwards 1986) the relation for terminal characteristics

$$\eta \sim M^3, \quad \tau \sim M_0^0 M^3.$$

The small deviation of the derived value of the index 3 from the empirical value 3.4 (see equations (6.43) and (6.44)) gave rise to the hopes that some improvements of the model could bring the correct results, at least, for strongly entangled systems. However, it appeared that the results delivered by the model far from empirical results (6.43) and (6.44) more, than one could earlier imagine (Altukhov et al. 2004). To appreciate these results

At the comparison of concentration dependencies of the characteristic quantities (6.61) with experimental determinations, one has to remember that effect of excluded volume was not taken into account in equations (6.61), which allow us to say only about qualitative correspondence. The behaviour of the initial viscosity is the most widely studied (Poh and Ong 1984, Takahashi et al. 1985). The concentration dependence of the viscosity coefficient in the “melt-like” region can be represented by a power law (Phillips 1995). The index can be found to be approximately $2\delta + 1$, in accordance with (6.61). There are some differences in the behaviour of polymer solutions, which are connected with different behaviour of macromolecular coils at dilution.

One should note once again that the above discussion and expressions are valid only for very long macromolecules and in the limit of very high concentrations. For semi-dilute solutions, the analysis should also include another non-dimensional parameter (see Sections 1.5 and 1.6), but then the results would become more complicated.

6.4.6 Frequency–Temperature Superposition

The dependence of the characteristic quantities (6.58) on temperature is mainly determined by the monomer friction coefficient ζ_0 , which depends on temperature, concentration, and (for small M) of molecule length (Berry and Fox 1968). The dependencies were recently discussed by Tsenoglou (2001). The monomer friction coefficient ζ_0 is a material characteristic of the system, its value is strongly determined by chemical structure of macromolecule as was shown for polybutadiene by Allal et al. (2002).

The value of the coefficient of friction is connected with relative motion of small portions of the macromolecule, so that its temperature dependence is similar to that found for low-molecular-weight liquids, and can be written in the following form at temperatures much higher than the glass transition point

$$\zeta_0 \sim \exp \frac{U}{T} \quad (6.62)$$

where U is the activation energy that depends on the molecular weight (for small M), on the concentration, and also on the temperature, if the temperature range in which the viscosity is considered is large. Near the glass transition point T_g , we have

properly, one has to consider the terminal relaxation time, distinguishing the probe macromolecule (with molecular weight or length M) and the neighbouring macromolecules (with the length M_0), even if all of them are equal. The reptation relaxation time, derived by Doi and Edwards, does not depend on the length of neighbouring macromolecules, which strongly contradicts to empirical evidence (see Section 6.5.3, equation (6.78)). The numerous attempts to improve the situation were controversial, so that there is a strong conviction that the Doi-Edwards model does not provide the first or even zero approximation to the theory of viscoelasticity of entangled system, though the reptation motion itself exists and influences effects of viscoelasticity as will be discussed later in this chapter and in Chapter 9.

$$\zeta_0 \sim \exp \left[\frac{A}{f_g - \alpha(T - T_g)} \right] \quad (6.63)$$

where A is an individual parameter, f_g is the volume fraction of free volume, and α is the expansion coefficient of the liquid. Quantities A and f_g are practically independent of the concentration and molecular weight, so that the dependence of ζ_0 on c and M is determined by the dependence of T_g on these quantities.

We note that, since the parameters B and χ are practically independent of temperature, the shape of the curves showing G/nT as a function of the non-dimensional frequency $\tau^*\omega$ does not change as the temperature increases, so that we can make a superposition using a reduction coefficient obtained from the temperature dependence of the viscosity.

To determine the procedure for the reduction, we shall write down the dynamic modulus at two different temperatures, one of which is a reference temperature T_{ref} and the other is an arbitrary temperature T ,

$$\begin{aligned} G(\omega, T_{\text{ref}}) &= nT_0 f(\tau_{T_{\text{ref}}}^* \omega, B, \chi), \\ G(\omega, T) &= nT f(\tau_T^* \omega, B, \chi). \end{aligned}$$

One can consider the parameters B and χ to be independent of the temperature and change the argument in the first line in such a way as to exclude the non-dimensional function. Then we write down the rule for reduction as

$$G(a_T \omega, T_{\text{ref}}) = \frac{\rho_{T_{\text{ref}}} T_{\text{ref}}}{\rho_T T} G(\omega, T), \quad (6.64)$$

where the shift coefficient is given by

$$a_T = \frac{\tau_T^*}{\tau_{T_{\text{ref}}}^*} = \frac{T_{\text{ref}} (C_{\infty}^{3\delta} \rho_{T_{\text{ref}}}^{2\delta+1})_{T_{\text{ref}}}}{T (C_{\infty}^{3\delta} \rho_T^{2\delta+1})_T} \frac{\eta_T}{\eta_{T_{\text{ref}}}}. \quad (6.65)$$

The above expressions confirm the known (Ferry 1980) method of reducing the dynamic modulus measured at different temperatures to an arbitrarily chosen standard temperature T_{ref} , while offering a relatively insignificant improvement on the usual shift coefficient

$$a_T = \frac{T_{\text{ref}} \rho_{T_{\text{ref}}} \eta_T}{T \rho_T \eta_{T_{\text{ref}}}}.$$

6.5 Dilute Blends of Linear Polymers

The change in the stress produced by the small amount of macromolecules of another kind is, clearly, determined by the dynamics of the non-interacting impurity macromolecules among the macromolecules of another length, so that this case is of particular interest from the standpoint of the theory of the

viscoelasticity of linear polymers. By studying a mixture of two polymers, one of which is present in much smaller amounts, – a dilute blend, one has a unique opportunity to obtain direct information about the dynamics of a chosen single macromolecule among the neighbouring macromolecules (Pokrovskii and Kokorin 1984).

6.5.1 Relaxation of Probe Macromolecule

Consider a system consisting of linear polymer with molecular weight M_0 and a small additive of a similar polymer with another molecular weight M . We shall assume that the amount of the additive is so small that its molecules do not interact with each other. The matrix is characterised by two characteristic length: M_e – the length of macromolecule between adjacent entanglements and $M^* \approx 10M_e$ – the critical length dividing weakly (macromolecules of the matrix do not reptate) and strongly (macromolecules of the matrix do reptate) entangled systems. To uncover which mechanism of diffusion and relaxation of a probe macromolecules of the additive is realised, one can consider, following the speculations in Sections 4.2.3 and 5.1.2, the competition between the diffusive and reptation mechanisms of motion of a macromolecule of the additive to obtain the condition for realisation of reptation mechanism

$$2\chi(Z)B(Z_0) > \pi^2, \quad (6.66)$$

where Z_0 and Z are the lengths of macromolecules of the matrix and the additive, respectively, in units of M_e . The function $\chi(Z_0, Z)$ and $B(Z_0)$ are given by equations (3.17) and (3.25). Taking these equation into account, one can find from equation (6.66) that the lengths of the macromolecules of the matrix and the macromolecule of the additive in the point, where the mechanism of relaxation of macromolecules of the additive changes, are connected by relation

$$\frac{M}{M_e} = \frac{1}{3 \cdot 2^{1+\delta}} \left(\frac{M_0}{M_e} \right)^\delta. \quad (6.67)$$

If $\delta = 2.5$, this relation reduces to equation

$$\frac{M}{M_e} = 0.03 \left(\frac{M_0}{M_e} \right)^{2.5}, \quad (6.68)$$

which is identity at $M = M_0 \approx 10M_e$, in accordance with the results of Section 5.1.2.

Equation (6.68) determines a critical length M^* , above which macromolecules of the additive do not reptate. The dependence of M^*/M_e on M_0/M_e , according to the above equation at $\delta = 2.5$, is depicted in Fig. 18 by solid line. For the matrix of short macromolecules, when $M_0 < 10M_e$, the transition point is situated in the short-length region, so that the macromolecules of the additive, which are shorter than M_0 but longer than M^* ,

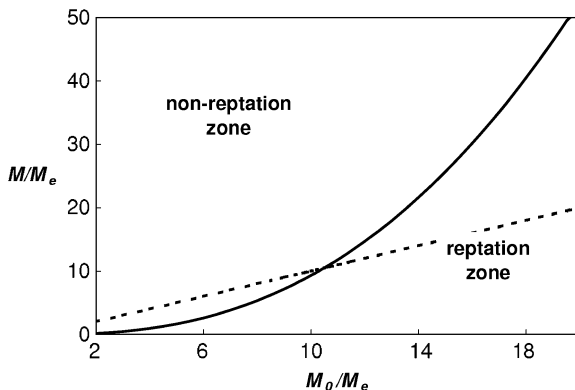


Figure 18. Alternative modes of motion of a macromolecule.

The realisation of a certain mode of motion of a macromolecule among other macromolecules depends on the lengths of both diffusing macromolecule and macromolecules of the environment. The solid line M^* divides the dilute blends into those, in which macromolecules of the additive can reptate, and those, where no reptation occurs. The dashed line marks the systems with macromolecules of equal lengths.

do not reptate. However, if the matrix consists of macromolecules, for which $M_0 > 10M_e$, there is a region between $10M_e$ and M^* in which a probe macromolecules of the additive reptate. However, the macromolecules of additive longer than M^* do not reptate in the matrix of shorter macromolecules with $M_0 > 10M_e$. One has to discuss two cases: non-reptating and reptating macromolecules.

6.5.2 Characteristic Quantities

The considered system contains n_0 macromolecules of the matrix and n macromolecules of the additive per unit volume and can be characterised by dynamic modulus $G(\omega)$. The medium, in which the macromolecules of the additive move, is a system consisting of a linear polymer of molecular weight M_0 , which is characterised by the modulus $G_0(\omega) = -i\omega\eta_0(\omega)$. The change of dynamic modulus, taking into account the fact that some of the macromolecules of the matrix have been replaced by impurity macromolecules, can be written as

$$G(\omega) - G_0(\omega) = n \left(g(\omega) - \frac{M}{M_0} g_0(\omega) \right) \quad (6.69)$$

where $g(\omega)$ and $g_0(\omega)$ are the contributions to the dynamic modulus, respectively, from a single macromolecule of the impurity and the matrix, which can be easily found from the derived expressions. We shall consider the case of low frequencies, for which the dynamic modulus can be written in the form of the expansion given by (6.11), and introduce the characteristic quantities

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{c\eta_0}, \quad [\nu] = \lim_{c \rightarrow 0} \frac{\nu - \nu_0}{c\nu_0}, \quad (6.70)$$

which are apparently functions of the length (or molecular weight) of the macromolecules of the matrix and the additive. The index 0 refers to the matrix and c is the impurity concentration.

To calculate the characteristic quantities both for the matrix and for the additive, we use equation (6.39), if $\psi \ll 1$, or (6.52), if $\psi \gg 1$. We shall assume that the macromolecules of the matrix are long enough, so that one can write, taking also relations (6.69) into account, for coefficients of viscosity and elasticity

$$\eta_0 = \frac{\pi^2}{6} n_0 T \tau_0^* B, \quad \nu_0 = \begin{cases} \frac{\pi^4}{90} n_0 T (\tau_0^* B)^2, & M_0 < 10M_e, \\ \frac{\pi^2}{3} n_0 T (\tau_0^* B)^2 \chi_0, & M_0 > 10M_e. \end{cases} \quad (6.71)$$

To choose a formulae for calculation the contributions of macromolecules of the additive, one have to estimate value of ψ , which, according to equation (3.29) depends on both macromolecules of the matrix and macromolecules of the additive. One can consider that the conditions of reptation correspond also to the big values of ψ , which is realised at $M < M^*$, and the case $M > M^*$ corresponds to the small values of ψ , so that one can write expressions for coefficients of viscosity and elasticity of the system of independent macromolecules of the additive suspended in the matrix as

$$\eta = \frac{\pi^2}{6} n T \tau^* B, \quad \nu = \begin{cases} \frac{\pi^4}{90} n T (\tau^* B)^2, & M > M^*, \\ \frac{\pi^2}{3} n T (\tau^* B)^2 \chi, & M < M^*. \end{cases} \quad (6.72)$$

In equations (6.71) and (6.72), the quantities B and τ_0^* are considered as functions of M_0 , and the characteristic relaxation time of the macromolecules of the additive τ^* as a function of M .

Taking all this into account, one can find increments of viscosity and elasticity in the form

$$\eta - \eta_0 = \frac{\pi^2}{6} n T \tau^* B \left(1 - \frac{M_0}{M} \right),$$

$$\nu_b - \nu_0 = \begin{cases} \frac{\pi^4}{90} n T (\tau^* B)^2 \left(1 - \frac{M_0^3}{M^3} \right), & M_0 < 10M_e, \quad M > M_0, \\ \frac{\pi^2}{3} n T (\tau^* B)^2 \frac{M_e}{M} \left(1 - \frac{M_0^2}{M^2} \right), & M_0 > 10M_e, \quad M < M^*, \\ \frac{\pi^4}{90} n T (\tau^* B)^2 \left(1 - \frac{30}{\pi^2} \frac{M_e M_0^2}{M^3} \right), & M_0 > 10M_e, \quad M > M^*. \end{cases} \quad (6.73)$$

Using the above relations and equations (6.58), one finds that for $M \gg M_0$

$$[\eta] \sim M_0^{-1} M, \quad [\nu] \sim \begin{cases} M_0^{-3} M^3, & M_0 < 10M_e, \\ M_0^{-2} M^2, & M_0 > 10M_e, \quad M < M^*, \\ M_0^{-2} M^3, & M_0 > 10M_e, \quad M > M^*. \end{cases} \quad (6.74)$$

On the other hand, when $M \ll M_0$ (this condition excludes the case $M_0 < 10M_e$) the characteristic quantities are negative and are independent of the length of the matrix and of the impurity macromolecules

$$[\eta] \sim M_0^0 M^0, \quad [\nu] \sim \begin{cases} M_0^0 M^0, & M_0 < 10M_e, \\ M_0^{-1} M^0, & M_0 > 10M_e. \end{cases} \quad (6.75)$$

Results (6.74) and (6.75) do not depend upon any choice of the dependence of B on the length (molecular weight) of the macromolecule.

The viscoelastic behaviour of dilute blends of polymers of different length and narrow molecular weight distributions was investigated experimentally for polybutadiene by Yanovski et al. (1982) and by Jackson and Winter (1995) and for polystyrene by Watanabe and Kotaka (1984) and Watanabe et al. (1985) (the results can be found in the work by Jackson and Winter (1995)). The results for polybutadiene were approximated by Pokrovskii and Kokorin (1984) by the dependencies

$$[\eta] \sim M_0^{-0.8} M^{0.5}, \quad [\nu] \sim M_0^{-(1.8 \rightarrow 2.2)} M^{1.3 \rightarrow 3.0}. \quad (6.76)$$

The comparison of the theoretical formulas (6.74) with the experimental ones (6.76) shows the consistency of the results, though the absolute values of indexes in formula for characteristic viscosity has appeared to be less than theoretical value 1. Unfortunately, the accuracy of original empirical data (in fact, the required linear dependence of quantities on concentration had never been reached in the work by Yanovski et al. 1982) does not allow one to say whether there are any certain deviations from relations (6.74) or not. If relations (6.76) are confirmed, it could mean that there are some unaccounted issues (intra-chain hydrodynamic interaction, for example), which would decrease in values of the index. Apparently, one needs in extra experimental data for different polymer systems in both weakly and strongly entangled states to analyse the situation in more details. Nevertheless, the above results confirm that the contribution of the orientational relaxation branch of a macromolecule in an entangled system dominates over the contribution of the reptation relaxation branch in phenomena of linear viscoelasticity. Otherwise, by considering the competing mechanism of relaxation – the reptation of the macromolecules, one would apparently have, following Daoud and Gennes (1979), instead of relation (6.74), the other expression for characteristic viscosity of blends for $M \gg M_0$

$$[\eta] \sim M_0^{-3} M^3 \quad (6.77)$$

which deviates from empirical evidence (6.76) more than relations (6.74).

6.5.3 Terminal Relaxation Time

It was assumed that the quantity B is a function of M_0 , but, luckily, one does not need in expression for explicit dependence to obtain the final results (6.74)

and (6.75) for characteristic quantities for dilute blends of linear polymers. However, the dependence of the quantity B on M_0 can be recovered due to empirical data. To estimate this dependence, one can consider terminal relaxation time

$$\tau = \frac{\nu - \nu_0}{\eta - \eta_0}$$

and use equations (6.73) to obtain for $M > M^*$

$$\tau \sim \begin{cases} B(M_0)M^2, & M_0 < 10M_e, \\ B(M_0)M^2, & M_0 > 10M_e. \end{cases} \quad (6.78)$$

The first line is valid for the case when matrix is a weakly entangled matrix, the second line – a strongly entangled matrix.

Watanabe (1999, p.1354) has deduced that, according to experimental data for polystyrene/polystyrene blends, when the matrix is a weakly entangled system, terminal time of relaxation depends on the lengths of macromolecules as

$$\tau \sim M_0^3 M^2, \quad (6.79)$$

while also for polystyrene/polystyrene blends, Montfort et al. (1984) found different values of indexes (2.3 instead of 3 and 1.9 instead of 2); the difference is discussed by Watanabe (1999, p.1356). No empirical relation, similar to relation (6.79), is available for strongly entangled matrices, but, as it can be seen in plots of the paper (Watanabe 1999), that the value of the first index are less than 3 in this case. It is possible that situation is different for weakly and strongly entangled matrices, so that values of the index in formula (6.79) could be different for these two types of systems.

The comparing formulae (6.78) and (6.79) allows one to estimate the dependence of coefficient of enhancement on the lengths of macromolecules as

$$B \sim M_0^3, \quad (6.80)$$

that is $\delta = 3$, in contrast with previous estimate of index as 2.4. The last value of the index, as discussed in the end of the previous subsection, is followed the suggestion that hydrodynamic interaction inside macromolecular coils is ignored. One cannot exclude that this index could be greater, but, in this case, value of the second index in equation (6.79) must be less.

The empirical result (6.80) does not correspond to the reliable results for monodisperse ($M_0 = M$) system well. Indeed, taking result (6.80) into account, the terminal relaxation time (6.58) can be written as

$$\tau \sim \begin{cases} M^5, & M < 10M_e, \\ M^4, & M > 10M_e. \end{cases} \quad (6.81)$$

To provide the validity of empirical dependencies of viscosity and terminal relaxation time on the molecular length (relations (6.43) and (6.44)), the sum

of the two indexes in equations (6.81) must have value 4.4 in the case, when the matrix is a weakly entangled system, and value 3.4, when the matrix is a strongly entangled system with macromolecular length M between $10M_e$ and M^* .

6.5.4 A Final Remark

The investigation of viscoelasticity of dilute blends confirms that the reptation dynamics does not determine correctly the terminal quantities characterising viscoelasticity of linear polymers. The reason for this, as has already been noted, that the reptation effect is an effect due to terms of order higher than the first in the equation of motion of the macromolecule, and it is actually the first-order terms that dominate the relaxation phenomena. Attempts to describe viscoelasticity without the leading linear terms lead to a distorted picture, so that one begins to understand the lack of success of the reptation model in the description of the viscoelasticity of polymers. Reptation is important and have to be included when one considers the non-linear effects in viscoelasticity.