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On the difference between weakly and strongly entangled linear polymers

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Abstract

The paper proposes an explanation of the second critical point in viscoelastic behaviour of linear polymers, position of which, according to Ferry (1980), is empirically estimated as $M^* \approx (4.6 - 12)M_e$, where M_e is the length of the macromolecule between adjacent entanglements'. The paper begins with an introduction to the dynamics of a single macromolecule in the entangled system. Diffusive and reptation mechanisms of relaxation of macromolecules are considered and compared, which allows one to introduce the division between weakly and strongly entangled systems and to calculate the dynamic transition point as $M^* \approx 10M_e$. Three types of linear polymer systems ought to be considered, according to the ratio of the length of the macromolecule M to M_e: $M < 2M_e$ – non-entangled system, $2M_e < M < 10M_e$ – weakly entangled systems and $M > 10M_e$ – strongly entangled systems. Reptation motion of macromolecules can be noticeable only in the strongly entangled systems. It is shown for these systems that contribution of reptation relaxation in low-frequency linear viscoelasticty can be neglected, while one has to take reptation relaxation into account to obtain the correct dependence of effects of the second order on the length of the macromolecule.

Keywords: Constitutive equations; Mesoscopic approach; Polymer dynamics; Polymer melts; Relaxation of macromolecule; Reptation; Time-dependent constraint release; Viscoelasticity

1. Introduction

Linear viscoelasticity is conveniently characterised by the dynamic modulus $G(\omega)$ which depends on frequency ω. To analyse the results, one also considers asymptotic behaviour of the dynamic modulus at high and low frequencies. In the latter case

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

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

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

The dependencies of the terminal characteristics on the length of macromolecules M appeared to be decisive for the classification of linear polymer solutions and melts [1,2]. The law for coefficient of viscosity, which was confirmed for all polymer system which were investigated, determines the first critical point M_c separating entangled and non-entangled systems of linear polymers

$$\eta \sim \begin{cases} M, & M < M_c, \quad \text{non} - \text{entangled systems}, \\ M^{3.4}, & M > M_c, \quad \text{entangled systems}. \end{cases} \tag{1}$$

While the above formula is valid in the whole region above $M_c \approx 2M_e$, where M_e is the length of the macromolecule between adjacent entanglements', the dependence of terminal relaxation time is different (Ferry, 1980) for weakly and strongly entangled systems and determines the second critical point M^*

$$\tau \sim \begin{cases} M^{4.4}, & M < M^*, \quad \text{weakly entangled systems}, \\ M^{3.4}, & M > M^*, \quad \text{strongly entangled systems}. \end{cases} \tag{2}$$

The data for melts of different polymers collected by Ferry [[1], p. 379, Table 13-III], while accepting $M_c \approx 2M_e$, allows us to estimate the second critical point as

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$$M^* \approx (4.6 - 12.0)M_e. \quad (3)$$

One can think that there are more recent numbers, but we believe that the above data are typical. It is remarkable that linear and non-linear viscoelastic behaviour of linear polymers with molecular weight less than a certain critical value is different from that of the system with longer macromolecules. The very existence of the transition point between weakly and strongly entangled systems can be considered as empirical fact which has to be explained.

The concept of reptation relaxation of a macromolecule was used to explain the effects of viscoelasticity in entangled polymers [3,4]. However, one can see that this theory was designed to describe a case, when $\tau/\eta \sim M^0$, $\eta \sim M^{3.4}$, that is the case of strongly entangled systems. Simultaneously, one can note that an alternative approach [5], which is based on suggestion that isotropic stochastic motion of the segments of the macromolecules is possible in an entangled system, can be applicable for weakly entangled systems. Indeed, it gives $\tau/\eta \sim M$, in accordance with the above Eqs. (1) and (2) for weakly entangled systems. Note that the alternative approach [5], at slow motion, is formally equivalent to the constraint-release theory [7] and can be considered as a formal time-dependent generalisation of the latter. Thus, one can suppose that two mechanisms of relaxation: reptation and diffusive (constraint-release) are possible in entangled systems, the transition point between weakly and strongly entangled systems is determined by the competition of these mechanisms. To calculate a position of the transition point, we compare the above mechanisms and refer to two models, while one of them imitates the basic isotropic stochastic motion of a particle among the neighbouring chains [5,6] and the other is needed to describe special motion of the macromolecule – the original non-amended Doi–Edwards model [3]. It is important that the considered models are consistent: the localisation of the macromolecule in a tube, postulated by the second model is justified by the first model [6]. The radius of the tube is calculated as a dynamic intermediate length through phenomenological parameters of the first model. Two models appear to be complementary models and one can combine the results.

The objective of the paper is to discuss a possible mechanism of transition between weakly and strongly entangled linear polymers. For consistency of the paper, the fundamentals of dynamics of a macromolecule in the system of macromolecules are discussed and the linear normal modes of the system are described in Section 2: the omitted details can be found in the monographs [4,6]. The purpose of this Section is to describe the foundations and main features of the mesoscopic approach. In Section 3, diffusion and relaxation processes in entangled systems are discussed. The division between weakly and strongly entangled systems is introduced here, and the dynamic transition point is calculated as $M^* \approx 10M_e$. Relaxation behaviour of the different systems is different: only in the strongly entangled systems effects of reptation relaxation of macromolecules can be noticeable and these are the system to which the results of theory [8] are applied. In Section 4 viscoelasticity of strongly entangled systems will be considered and will be shown that, though the reptation motion is present, contribution of the reptation branch into low-frequency linear viscoelasticity can be neglected, so that, to obtain the correct exponent 3.4 for the molecular weight scaling of the terminal relaxation time and zero-shear viscosity (Eqs. (1) and (2)), one has to refer to the constraint-release mechanism. However, one has to take reptation relaxation into account to obtain the correct dependence of effects of the second order on the length of macromolecules. Considering the dilute blends of polymers in Section 5 allows us to collect extra arguments in favour of the proposed theory. The Conclusion contains discussion of the problem and consequences for constitutive relations.

2. Modes of motion of a macromolecule in an entangled system

2.1. Modified Cerf-Rouse modes

2.1.1. Equation of motion

It is known [4,6], that every flexible macromolecule can be effectively presented as a chain of coupled Brownian particles (so called bead and spring model), and one can follow Zwanzig-Mori method described, for example, in monographs [9,10] to obtain an equation for the large-scale stochastic dynamics of the entangled system as dynamics of interacting chains of Brownian particles. The situation can be simplified more, if one use, similar to works [11–14], the projector-operator methods once more to derive a dynamic equation for a single chain in the system of entangled chains. In virtue of the results of these works, it is natural to present the anticipated dynamic equation for a chain as stochastic equation with memory function terms. Dynamics of the probe macromolecule is simplified by the assumption that the neighbouring macromolecules can be described as a uniform structureless medium and all important interactions can be reduced to intramolecular interactions. The requirements of proper covariance and of the linearity in co-ordinates and velocities determine [6] the general form of the equation for the dynamics of the single macromolecule. In the linear approximation, one can consider the situation for every Brownian particle to be isotropic and the mutual hydrodynamic interaction of the particles to be negligible, so that effective dynamics of the single chain as the dynamics of coupled Brownian particles is described by a set of coupled stochastic equations

$$\begin{aligned} m\frac{\mathrm{d}^2 r_i^\alpha}{\mathrm{d}t^2} = &-\int_0^\infty \beta(s)(\dot{r}_i^\alpha - \nu_{ij} r_j^\alpha)_{t-s}\,\mathrm{d}s \\ &- \int_0^\infty G_{\alpha\gamma}\varphi(s)(\dot{r}_i^\gamma - \omega_{ij} r_j^\gamma)_{t-s}\,\mathrm{d}s \\ &- 2\mu T A_{\alpha\gamma} r_i^\gamma + \phi_i^\alpha(t) \end{aligned} \quad (4)$$

where m is the mass of a Brownian particle associated with a piece of the macromolecule of length M/N, r^α and $\dot{r}^\alpha$ are the co-ordinates and velocity of the Brownian particle and $2T\mu$ is the coefficient of elasticity of the spring between adjacent particles, T is temperature in energy units. The matrix $A_{\alpha\gamma}$ depicts the connection of Brownian particles in the entire chain. The dissipative forces are presented by two terms containing the memory function $\beta(s)$ and $\varphi(s)$. The first integral term on the right-hand side of Eq. (4) is the hydrodynamic drag force in the medium moving with mean velocity gradient ν_{ij}, so that a particle located at a point with co-ordinates r_j^α is dragged with velocity $\nu_{ij} r_j^\alpha$. The second dissipative term in Eq. (4) has a form similar to Cerf's approximation [15] of the internal viscosity force for a macromolecule in a dilute solution and, thus, represents the intramolecular resistance (kinetic stiffness). Due to the vorticity term $\omega_{il} = 1/2(\nu_{il} - \nu_{li})$, the latter term does not depend on the rotation of the macromolecular coil as a whole. The symmetrical numerical matrix $G_{\alpha\gamma}$ represents the influence of movement of the particle γ on the movement of the particle α which is considered to be small at $\gamma \neq \alpha$, so that it is expected to be almost diagonal. As an initial approximation, to express the idea of severe confinement, one can assume that the intramolecular resistance force is determined equally by all the particles of the chain, so that one has for the matrixes:

$$\mathsf{A} = \left\| \begin{array}{ccccc} 1 & -1 & 0 & \dots & 0 \\ -1 & 2 & -1 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & 1 \end{array} \right\|,$$

$$\mathsf{G} = \left\| \begin{array}{cccc} 1 & -1/N & \dots & -1/N \\ -1/N & 1 & \dots & -1/N \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ -1/N & -1/N & \dots & 1 \end{array} \right\|. \tag{5}$$

We have chosen the simplest form of the symmetric matrix $G_{\alpha\gamma}$, consistent with the requirement that the matrix must have a zero eigenvalue. This form allows the matrix $G_{\alpha\gamma}$ to be transformed into diagonal form simultaneously with matrix $A_{\alpha\gamma}$. All eigenvalues of the matrix $G_{\alpha\gamma}$, besides the zeroth one, are equal to unity, and eigenvalues of the matrix $A_{\alpha\gamma}$ for large N and small α are given by

$$\lambda_\alpha = \left(\frac{\pi\alpha}{N}\right)^2, \quad \alpha = 0, 1, 2, \dots, \ll N. \tag{6}$$

After the transformation, the system of Eq. (4) turns into a set of uncoupled equations for normal co-ordinates

$$m\frac{\mathrm{d}^2\rho_i^0}{\mathrm{d}t^2} = -\int_0^\infty \beta(s)(\dot{\rho}_i^0 - \nu_{il}\rho_l^0)_{t-s}\,\mathrm{d}s + \sigma_i^0(t), \tag{7}$$

$$\begin{aligned} m\frac{\mathrm{d}^2\rho_i^\alpha}{\mathrm{d}t^2} = &-\int_0^\infty \beta(s)(\dot{\rho}_i^\alpha - \nu_{il}\rho_l^\alpha)_{t-s}\,\mathrm{d}s \\ &-\int_0^\infty \varphi(s)(\dot{\rho}_i^\alpha - \omega_{il}\rho_l^\alpha)_{t-s}\,\mathrm{d}s \\ &- 2\mu T\lambda_\alpha\rho_i^\alpha(t) + \sigma_i^\alpha(t), \end{aligned} \tag{8}$$

where the variable ρ_i^0 is proportional to the mass centre of the macromolecular coil (diffusion mode), variables ρ_i^α, $\alpha = 1, 2, \dots, N$ describe relative positions of the particles in the coil (relaxation modes). Whatever the specification of the memory functions is, Eqs. (7) and (8) determine linear modes of motion of the macromolecule in polymer melts – the modified Cerf-Rouse modes. Note that a particular case of Eqs. (7) and (8) is a simple equation

$$m\frac{\mathrm{d}^2\rho_i^\alpha}{\mathrm{d}t^2} = -\zeta(\dot{\rho}_i^\alpha - \nu_{il}\rho_l^\alpha) - 2\mu T\lambda_\alpha\rho_i^\alpha(t) + \sigma_i^\alpha(t), \quad \alpha = 0, 1, \dots, \ll N, \tag{9}$$

which describes normal modes of motion of the macromolecule in a viscous 'monomeric' liquid. This dynamics is commonly referred to as the Rouse dynamics and independent variables ρ^α in (9) as to Rouse modes.

Statistical properties of the random thermal forces in Eqs. (7) and (8) are, as usual, defined in such a way, that the equilibrium values of the calculated quantities are the same as those already known. The scalar correlation function of the random force can be introduced

$$\langle \sigma_i^\alpha(t)\sigma_j^\gamma(t-s)\rangle = K(s)\delta_{\alpha\gamma}\delta_{ij}. \tag{10}$$

Fourier transform of the correlation function is connected with the one-side transform of memory functions

$$K(\omega) = 2TRe(\beta[\omega] + \varphi[\omega]).$$

2.1.2. *Approximation of the memory functions*

The memory functions $\beta(s)$ and $\varphi(s)$ in Eqs. (7) and (8) cannot be determined from general considerations: they could be found theoretically as correlation functions of the random force in microscopic dynamics of interacting Kuhn-Kramers chains, or, otherwise, the memory functions ought to chosen in such a way, that the final results describe empirical facts. At the moment, we have no choice as to look for empirical memory functions. However, it appears to be helpful to consider very slow and very fast deformation of the system which elucidates causes and meaning of the dissipative forces in Eq. (4).

2.1.2.1. Intramolecular friction. For a fast enough deformation (that is, before relaxation can occur), one expects that the macromolecules deform affinely, i.e., for every particle $\dot{r}_i^\alpha = \nu_{ij} r_j^\alpha$, where ν_{ij} is the velocity gradient, and r_j^α is the position in space of a particle of a chain. Under given deformation, the first term from the two terms for dissipative force in Eq. (4) is equal to zero, while the second one generates a force proportional to $\dot{r}_i^\alpha - \omega_{ij} r_j^\alpha$, where

ω_{ij} is the vorticity, or $\gamma_{ij}r_j^\alpha$, where γ_{ij} is the symmetric part of the velocity gradient, so that this force is a force of the intramolecular resistance due to the change in shape of the macromolecular coil (kinetic stiffness). As far as we consider the coarse-grained approximation, all the neighbouring chains, or, one can say, the particles of coarse-grained chains follow the deformation affinely, and there is no apparent cause for this force. To explain the emerging of the force, we have to refer to more detailed model of macromolecule – to the chain of freely-jointed rigid segments. Apparently, small parts of macromolecules cannot follow the deformation affinely, segments can only rotate, and an extra force is needed to change the direction of a segment in the case, when the segments of the other chains present around. That is why we can say that the internal resistance force for a macromolecule in a polymer melt has to be attributed to the interaction with neighbouring chains, though in the coarse-grained approximation we forget about segments, and this force is characterised by only phenomenological coefficient of internal resistance which can be denoted as ζE.

2.1.2.2. External friction. For very slow deformation of the system, when all relaxation times are less than a characteristic time of deformation, the macromolecular coil keeps its equilibrium form, so that the force of internal resistance (the second dissipative term in Eq. (4)) can be neglected, and the resistance-drag coefficient originated from the first dissipative term can be written down as ζB. The dimensionless quantity B is a measure of the increase in the friction coefficient, due to the fact that the particle is moving among neighbouring macromolecules, perturbing them. Note that this situation is equivalent to that considered earlier in molecular terms by the constraint-release theory, originated by Graessley [7] (a review of subsequent work can be found in work of Watanabe [2]), so that one can use the results [7] to estimate the molecular weight dependence of the coefficient of enhancement B.[1] The constraint-release mechanism suggests that a large-scale lateral motion of a macromolecule in an entangled system is possible due to process of release of some constraints of the probe chain and jumps some parts of the chain in lateral direction. The lifetime of constraints depends apparently on dynamics of neighbouring macromolecules, which is assumed to be the dynamics of the same type as that of the probe macromolecule, and can be considered as a characteristic of the medium in which the probe macromolecule is moving. Eventually, the consideration determines the friction coefficient of effective Brownian particle as

$$\zeta B(M_0) \sim M_0^3 \tag{11}$$

where ζ is a 'monomer' friction coefficient and $B(M_0)$ is the measure of enhancement of the friction coefficient due to the presence of neighbouring chains with the lengths M_0. It is important that this mechanism introduces the dependence of coefficient of enhancement of the friction coefficient on the length of the neighbouring macromolecules as $B(M_0) \sim M_0^3$.

2.1.2.3. Concept of microviscoelasticity. In the case, when one applies the coarse-grained approximation for the description of chains, each particle of the chain can be considered as moving in a liquid, which represents a dense system made of the interacting rigid Kuhn segments. The effective medium has properties of relaxing liquid; thus, the concept of microviscoelasticity, instead of the concept of microviscosity in the case of dilute solutions, can be introduced. The times of relaxation of the surrounding medium are times of relaxation of the mean orientation of segments. In a dense system of long linear macromolecules, the motion of a separate segment is determined strongly by its environment, being weakly dependent on its position in the chain. The simplest case assumes that one chooses the single time τ, so that one has the law of relaxation for mean orientation of segments

$$\frac{\mathrm{d}\langle e_i e_k\rangle}{\mathrm{d}t} = -\frac{1}{\tau}\left(\langle e_i e_k\rangle - \frac{1}{3}\delta_{ik}\right) \tag{12}$$

This assumption allows us to write down simple expressions for the one-sided Fourier transforms of the memory functions

$$\beta[\omega] = \zeta\left(1 + \frac{B}{1 - i\omega\tau}\right), \quad \varphi[\omega] = \frac{\zeta E}{1 - i\omega\tau}, \tag{13}$$

where ζ is the monomer friction coefficient. One needs to introduce some characteristics of the environment, B the measure of the increase of friction due to interaction with the neighbouring macromolecules, and E is the measure of intramolecular resistance (internal viscosity). One can see that the above speculation is nothing more as an assumption that the environment of a Brownian particle is characterised by the only relaxation time and the quantities B and E are phenomenological (mesoscopic) characteristics of the dynamics of a single macromolecule in the system of interacting macromolecules. With comparison with results of molecular theories (as above), the meaning of introduced parameters can be elucidated. Thus, one can assume that the parameter B in Eq. (13) is a function of the length of the neighbouring macromolecules in the form

$$B \sim M^\delta. \tag{14}$$

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[1] One can note that, at slow motion, the constraint-release theory determines formally the dynamics of a probe macromolecule as a Rouse dynamics (of the form of Eq. (9)), which can be attributed to as a certain 'static' method of consideration. However, as it was noted recently by Schieber et al. [16], the process of constraint release is developing in time and one needs in time scale τ of the matrix to describe the process, so that the theory ought to be generalised for this case. One can consider the stochastic model (4) as a formalisation (for slow motion) and generalisation of constraint-release mechanisms which can be regarded as the time-dependent constraint-release model.

One can consider the index δ to be an empirical index in the theory, which has, as we see in Section 4, the empirical values 2.4 - 3 in accordance with the theoretical estimate 3 due to the constraint-release theory. An alternative estimation of the index, from friction of moving overlapping coils [6], gives an estimate of the index > 2.

2.1.3. *Mobility of a macromolecule*

It is known that the macromolecule in a viscous liquid (dilute solution) moves as a Brownian particle and its mean square displacement is given by the standard expression

$$\langle \Delta q^2 \rangle = 6D_0 t, \quad D_0 \sim M^{-1} \tag{15}$$

where D_0 is the coefficient of the diffusion of the macromolecular coil in viscous liquid which is inversely proportional to the length of macromolecule M for freely draining coils.

So as the co-ordinate q of mass centre of macromolecular coil is proportional to the zeroth normal co-ordinate ρ^0, it is not difficult to calculate [6], using Eqs. (7) and (13), the mean square displacement of the centre of mass of a macromolecule in entangled system

$$\langle \Delta q^2 \rangle = 6D_0 \frac{\tau}{B}\left(\frac{t}{\tau} + 1 - \mathrm{e}^{-tB/\tau}\right). \tag{16}$$

where D_0 has the same meaning as in the previous formula. The displacement as a function of the ratio t/τ has a plateau which is the longer, the longer the macromolecule. The value of the function on the plateau can be taken as a definition of an intermediate length

$$\xi^2 = 6D_0 \frac{\tau}{B} \tag{17}$$

Up to intermediate length ξ the macromolecule diffuses as a particle in viscous fluid. For long times of observation $t \gg \tau$, the mean displacement of the particle is unrestricted and is proportional to time, so that the diffusion coefficient can be determined from Eqs. (15) and (16) as

$$D = D_0 B^{-1} \sim M^{-1-\delta}. \tag{18}$$

2.1.4. *Relaxation times*

To calculate relaxation times, one considers equilibrium correlation function of normal co-ordinates

$$\langle \rho_i^\alpha(t)\rho_k^\alpha(t-s)\rangle_0 = M_\alpha(s)\delta_{ik}$$

The angle brackets denote the averaging over the ensemble of the realisation of the random forces in a dynamic equation.

In the simplest case – macromolecule in a viscous liquid – one can use the Rouse modes (9) to determine the equilibrium correlation function as

$$M_\alpha(t) = \frac{1}{2\mu\lambda_\alpha}\exp\left(-\frac{t}{2\tau_\alpha^{\mathrm{R}}}\right). \tag{19}$$

There are many internal relaxation modes, so that one has a set of relaxation times

$$\tau_\alpha^{\mathrm{R}} = \tau^*/\alpha^2, \quad \tau^* = \frac{\zeta N\langle R^2\rangle}{6\pi^2 T} \sim M^2, \quad \alpha = 1, 2, \ldots \ll N. \tag{20}$$

where ζ is the friction coefficient of a Brownian particle ($\zeta \sim N^{-1}$), M is the length or the molecular weight of the macromolecule, $\langle R^2\rangle$ is the mean squared end-to-end distance of the macromolecule and τ^* is the largest relaxation time of the macromolecule – a characteristic Rouse relaxation time.

For the modified Cerf-Rouse dynamics (8), an equilibrium correlation function can be found [6] after simple calculations

$$M_\alpha(t) = \frac{1}{2\mu\lambda_\alpha}\left[S_\alpha^+ \exp\left(-\frac{t}{2\tau_\alpha^+}\right) - S_\alpha^- \exp\left(-\frac{t}{2\tau_\alpha^-}\right)\right] \tag{21}$$

where

$$S_\alpha^\pm = \frac{\tau_\alpha^{\mathrm{R}}(1+B+E) - \tau_\alpha^\mp}{\tau_\alpha^+ - \tau_\alpha^-},$$

$$2\tau_\alpha^\pm = \tau_\alpha \pm (\tau_\alpha^2 - 2\tau\tau_\alpha^{\mathrm{R}})^{1/2},$$

$$\tau_\alpha^+ = \tau_\alpha - \frac{\tau\tau_\alpha^{\mathrm{R}}}{2\tau_\alpha}, \qquad \tau_\alpha^- = \frac{\tau\tau_\alpha^{\mathrm{R}}}{2\tau_\alpha}.$$

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

$$\chi = \frac{\tau}{2B\tau^*}$$

In contrast to the original Rouse modes, the modified Cerf-Rouse modes of a macromolecule in an entangled system give two conformation relaxation branches τ_α^+ and τ_α^-. We shall consider the situation at $B \gg 1$ which allows us to neglect the branch of small relaxation times. The largest relaxation times decreases monotonically from $\tau^*(B+E)$ till $\tau/2$, when the mode number increases. Further on, we are going to compare the relaxation times for small mode numbers, so that it is convenient to use the asymptotic formula

$$\tau_\alpha^+ = (B+E)\tau_\alpha^{\mathrm{R}}, \quad \tau_\alpha^{\mathrm{R}} = \frac{\tau^*}{\alpha^2},$$
$$\alpha = 1, 2, \ldots, \ll \left(\frac{1+E/B}{\chi}\right)^{1/2} \tag{22}$$

2.1.5. *Localization of macromolecule*

A more detailed analysis shows [6] that, at $E/B \gg 1$, the mean displacement of every Brownian particle in a chain

$$\Delta_\alpha(t) = \sum_{i=1}^{3}\langle[r_i^\alpha(t) - r_i^\alpha(0)]^2\rangle_0, \quad \alpha = 0, 1, \ldots, N.$$

is restricted: the particle does not go further that a certain distance for a time τ/B. The fulfillment of the relation

$$\frac{E}{B} = \frac{\pi^2}{\chi} \tag{23}$$

ensures the existence of universal (independent on the length of a macromolecules) intermediate length ξ, defined by Eq. (17). The parameter χ introduced in the previous Subsection is, in fact, the ratio of the squared diameter of the intermediate length to the mean squared end-to-end distance of the macromolecule

$$\chi = \frac{\tau}{2B\tau^*} = \frac{\pi^2}{8}\frac{(2\xi)^2}{\langle R^2\rangle} \approx \frac{(2\xi)^2}{\langle R^2\rangle} \sim M^{-1}. \tag{24}$$

For observation times $t \ll \tau$, the small-scale motion of the particles confined to the scale ξ can take place, and the large scale chain conformation is frozen. Up to intermediate length ξ the macromolecule diffuses as a particle in viscous fluid. The displacement of every particle of the chain is restricted; the macromolecule remains near its original position for some time – localization effect. It looks like unbounded lateral motion of a macromolecule is suppressed due to the entanglement of the probe macromolecule with its many neighbouring coils which, as can be believed, effectively constitutes a “tube”. One can regard 2ξ as the diameter of a tube within which the macromolecule moves freely. However, in fact, one needs no temporary knots, no entanglements, no tube to explain dynamics of polymer systems. The immediate consequence of the modified Cerf-Rouse dynamics of a macromolecule is emerging of a certain intermediate length ξ which is connected with the relaxation time of interacting segments τ.

One can note that the existence of the intermediate length in entangled polymers can be considered as a reliable fact due to neutron spectroscopy experiments [17].

2.2. Reptation modes

The motion of the Brownian particles of the chain, described by linear Eq. (4), is essentially restricted by forces of external and internal resistance which make difficult for the macromolecule to change large-scale conformation. However, these forces do not appear at motion of particles of the chain along its contour. Coherent motion of the particles of the chain along its contour is consistent with topological integrity of macromolecules, the macromolecule moves like a snake – this is the reptation motion.

2.2.1. Doi–Edwards model

To model the reptation motion of the macromolecule, it is necessary to introduce the anisotropy of the mobility for every particle (bead) in the considered coarse-grained model of a macromolecule. The scalar quantity B in formula (12) ought to be substituted by a tensor quantity for each particle of the chain to make mobility of a particle along the axis of a macromolecule bigger than mobility in the perpendicular direction, so that the entire macromolecule can move more easily along its contour. The introduction of anisotropy of the particle mobility makes the dynamic equation non-linear, which introduces difficulties for analysis. However, in this case one can exaggerate anisotropy of mobility, assuming that unbounded lateral motion of particles is completely suppressed due to the presence of many neighbouring macromolecules. By this way, one comes to a very elegant linear model of reptating macromolecules proposed by Doi and Edwards [3]. The diameter of ‘tube’, within which the macromolecule moves as a particle in a viscous liquid, is postulated in Doi–Edwards model [3,4]. But, it is natural to identify the radius of ‘the tube’ in Doi–Edwards model with the emerged in previous model intermediate length ξ. We use a special symbol for the radius of the tube ξ, because the original diameter of the tube, postulated by Doi and Edwards [4], is slightly different from the quantity 2ξ.

As before, we shall consider a chain consisting of $N+1$ Brownian particles to be a proper schematisation of a macromolecule but, following Doi and Edwards [3], we assume that the distance between adjacent particles along the chain is constant and equal to ξ, so that the arbitrary number of particles satisfies the condition

$$N\xi^2 = \langle R^2\rangle. \tag{25}$$

The states of the macromolecule can be considered in points of time in a time interval Δt, so that the stochastic motion of Brownian particles of the chain can be described by the equation for the particle co-ordinates

$$\begin{aligned}
\boldsymbol{r}^0(t+\Delta t) &= \frac{1+\phi(t)}{2}\boldsymbol{r}^1(t) + \frac{1-\phi(t)}{2}[\boldsymbol{r}^0(t)+\boldsymbol{v}(t)],\\
\boldsymbol{r}^\nu(t+\Delta t) &= \frac{1+\phi(t)}{2}\boldsymbol{r}^{\nu+1}(t) + \frac{1-\phi(t)}{2}\boldsymbol{r}^{\nu-1}(t), \quad \nu = 1,2,\ldots,N-1,\\
\boldsymbol{r}^N(t+\Delta t) &= \frac{1+\phi(t)}{2}[\boldsymbol{r}^N(t)+\boldsymbol{v}(t)] + \frac{1-\phi(t)}{2}\boldsymbol{r}^{N-1}(t)
\end{aligned} \tag{26}$$

where $\phi(t)$ is a random quantity, which takes the values $+1$ or -1, and $\boldsymbol{v}(t)$ is a vector of constant length ξ and random direction, so that

$$\begin{aligned}
&\langle\phi(t)\phi(u)\rangle = \delta_{tu}, \quad \langle\phi(t)\rangle = 0,\\
&\langle\boldsymbol{v}(t)\boldsymbol{v}(u)\rangle = \delta_{tu}\xi^2, \quad \langle\boldsymbol{v}(t)\rangle = 0.
\end{aligned} \tag{27}$$

The set of Eq. (26) describes the stochastic reptation motion of a chain. The “head” and the “tail” particles of the chain can choose random directions. Any other particle follows the neighbouring particles in front or behind. The smaller the time interval Δt the quicker moves the chain. Clearly, the time interval can not be an arbitrary quantity and is specified by Doi and Edwards as

$$\Delta t = \frac{\zeta N}{2T}\xi^2 \tag{28}$$

2.2.2. Mobility of macromolecule

Reptation of macromolecules was specially invented to describe long-time dependence of the diffusion coefficient of macromolecules on their length. Indeed, one can directly obtain the well known [4] results from Eqs. (26) and (27)

$$\langle \Delta q^2 \rangle = 6 D_0 \frac{\xi^2}{\langle R^2 \rangle} t, \tag{29}$$

where D_0 is the coefficient of the diffusion of the macromolecular coil in 'monomer' viscous liquid $D_0 \sim M^{-1}$, ξ is an intermediate length and $\langle R^2 \rangle$ is the mean squared end-to-end distance of the macromolecule.

2.2.3. *Relaxation times*

It is not difficult to obtain an expression for the correlation function $M_\alpha(t)$ and estimate times of relaxation due to the reptation mechanism. According to Doi and Edwards [[4], p. 196], equilibrium correlation function is written as

$$M_\alpha(t) = \frac{1}{2\mu\lambda_\alpha} \exp\left(-\frac{t}{2\tau_\alpha^{\text{rep}}}\right), \tag{30}$$

$$\tau_\alpha^{\text{rep}} = \frac{\zeta \xi^2 N^3}{2\pi^2 T} \frac{1}{\alpha^2} = \frac{3\langle R^2 \rangle}{\xi^2} \frac{\tau^*}{\alpha^2} = \frac{3}{2} \frac{\pi^2}{\chi} \frac{\tau^*}{\alpha^2}, \quad \alpha = 1, 2, \ldots, \ll N. \tag{31}$$

The time behaviour of the equilibrium correlation function is described by a formula which is identical to formula for a chain in viscous liquid (Eq. (19), while the Rouse relaxation times are replaced by the reptation relaxation times.

3. Weakly and strongly entangled systems

One of the two models, considered in the previous Section, successfully imitates the basic isotropic stochastic motion of the particles of the chain among the neighbouring chains, while the other is needed to describe special motion of the macromolecule – the original non-amended reptation-tube model [3]. One can expect that reptation motion could emerge as non-linear effect from the 'correct' model. Instead of a single non-linear unknown equation, we have to use two sets of linear equations stitching up the results. We consider these two models as complementary models and combine the results, unless a unified 'correct' model is available.

3.1. *Diffusion of macromolecule*

For long times of observation $t \gg \tau$, there are two competitive mechanisms of mobility of macromolecule: due to motion through the sea of segments (constraint-release mechanism) and due to reptation. The diffusion coefficient can be defined due to Eqs. (19) and (29) as

$$D = D_0 \left(\frac{1}{B} + \frac{\xi^2}{\langle R^2 \rangle} \right).$$

The combination of the relations for diffusion defines a point of changing of mechanisms of mobility by relation $\chi B = \pi^2/2$, so that one can write

$$D = D_0 \times \begin{cases} B^{-1} \sim M^{-1-\delta}, & 2\chi B < \pi^2, \quad \text{no reptation} \\ 2\pi^{-2}\chi \sim M^{-2}, & 2\chi B > \pi^2, \text{reptation} \end{cases}. \tag{32}$$

where D_0 is the coefficient of the diffusion of the macromolecule in a viscous monomeric liquid. The transition point between weakly and strongly entangled systems will be estimated in Section 3.3 where experimental evidence on the transition point also will be discussed.

3.2. *Conformational relaxation*

The mean size and shape of the macromolecular coil in a deformed system are described by the non-equilibrium correlation functions

$$\langle \rho_i^\alpha(t) \rho_k^\alpha(t) \rangle, \quad \langle \rho_i^\alpha(t) \rho_k^\alpha(t) \rangle_0 = \frac{1}{2\mu\lambda_\alpha} \delta_{ik},$$

where the angle brackets denote averaging over the ensemble of realisation, while the subscript zero denotes the equilibrium situation. As an internal variable, it is convenient to use the dimensionless quantity

$$x_{ij}^\alpha = \tfrac{2}{3}\mu\lambda_\alpha \langle \rho_i^\alpha \rho_j^\alpha \rangle, \quad (x_{ij}^\alpha)_0 = \tfrac{1}{3}\delta_{ij}.$$

In the overdamped regime ($m = 0$), the mean sizes of the macromolecule relax to equilibrium values according to the law

$$\frac{\mathrm{d}}{\mathrm{d}t} x_{ik}^\alpha = -\frac{1}{\tau_\alpha} \left(x_{ik}^\alpha - \frac{1}{3}\delta_{ij} \right) \tag{33}$$

One has to take into account that the relaxation times τ_α includes contributions from the diffusive and reptation mechanism of relaxation

$$\frac{1}{\tau_\alpha} = \frac{1}{\tau_\alpha^+} + \frac{1}{\tau_\alpha^{\text{rep}}}.$$

The two mechanisms of relaxation compete and one has to compare the different conformational relaxation branches of the macromolecule coil which are defined by relations (22) and (31). Considering that for the strongly entangled systems $E > B$ and for the weakly entangled systems $E < B$, one can compare the above relations for relaxation times at $E = B$ to conclude that the reptation mechanism predominates at $4\chi B > \pi^2/3$, so that the conformational relaxation times for entangled system can be written as

$$\tau_\alpha = \begin{cases} B\tau_\alpha^{\text{R}} \sim M_0^\delta M^2, & (4/3)\chi B < \pi^2, \quad \text{no reptation} \\ (\pi^2/\chi)\tau_\alpha^{\text{R}} \sim M_0^0 M^3, & (4/3)\chi B > \pi^2, \quad \text{reptation} \end{cases} \tag{34}$$

It is convenient to distinguish 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. Note that the top line in Eq. (34), at $\delta = 3$ restores the result of the constraint-release theory [7], while the bottom line presents the results of reptation dynamics.

3.3. *Transition point between weakly and strongly entangled systems*

The conditions determining a point of transition to emerging of reptation motion of macromolecules are slightly different for diffusion (relations 32) and for relaxation (relations 34). It is possible to believe, taking some arbitrariness in the definition of the relaxation transition point into account, that these conditions coincides, so that one has a single dynamic transition point between weakly and strongly entangled systems, determined by equation

$$\chi B = \frac{1}{2}\pi^2$$

To find out a dynamic transition point χ^*, which separates the strongly entangled ($\chi < \chi^*$) and weakly entangled ($\chi > \chi^*$) systems, one can consider the quantity B to be a function of χ which, in virtue of relations (14), (24) and (47), can be written as power function

$$B = (2\chi)^{-\delta}, \quad \chi < 0.5 \tag{35}$$

It is not difficult then to find a solution of the Eq. (35), taking into account the empirical value $\delta \approx 2.4$, and to estimate the position of the transition point

$$\chi^* \approx 0.1 \quad \text{or} \quad M^* \approx 10M_e. \tag{36}$$

It is remarkable that there is a region between M_c and M^* in which the entangled system can be considered differently from the region of macromolecular lengths above M^*. The empirical results (2) and (3) confirm the position of the transition point next to $10M_e$, which can be interpreted as the transition point between weakly and strongly entangled systems, and determine the difference in relaxation behaviour for the two types of entangled systems. The comparison between empirical and theoretical results shows that, while the molecular-weight dependencies of relaxation times for weakly entangled systems (the top lines in Eqs. (2) and (34)), at $\delta = 2.4$ coincide, there is disagreement between the results (the bottom lines in Eqs. (2) and (34)) for the strongly entangled systems. However, one can note that Eq. (2) determine the terminal relaxation time of viscoelasticity, whereas Eq. (34) determines conformational relaxation time of macromolecules, and the comparison shows that these relaxation times are not identical. In fact, as one can see in the next Section, they are different for strongly entangled system.

Data on diffusion of linear polymers also demonstrate the existence of the region of weakly entangled systems. Data of different scholars, collected by Watanabe [2], directly demonstrate the existence of the two critical points. The first critical point, $M_c \approx 2M_e$, determines the transition between non-entangled and entangled systems. The position of the second transition point can be estimated from the data for diffusion of polybutadiene molecule [[2], p. 1333] as $M^* \approx 10M_e$, while the slope of the dependence in the region between M_c and M^* can be approximated as 3.4 which gives, according to Eq. (32), an estimate $\delta = 2.4$.

4. Viscoelasticity of strongly entangled systems

It is well known [4] that, when viscoelastic behaviour of the entangled system is considered on the base of the reptation dynamics, one obtains the following relations for coefficient of viscosity and terminal relaxation time

$$\eta \sim M^3, \qquad \tau \sim M^3.$$

The small deviation of the derived value of the exponent 3 from the empirical value 3.4 gave rise to hopes that some improvements of the reptation dynamics could bring the correct result. However, to appreciate this result properly, one has to distinguish 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 derived coefficient of viscosity and terminal relaxation time do not depend on the length of neighbouring macromolecules, so that the result of the Doi–Edwards approach [4] can be written for terminal relaxation time as

$$\tau \sim M_0^0 M^3 \tag{37}$$

The effect of lengths of the probe and neighbouring macromolecules can be separated experimentally by investigating dilute blends of polymers (see Section 5). The data, reported by Watanabe [[2], p. 1353] show that, in contrast to Eq. (37), terminal relaxation time depends on the molecular weight of neighbouring macromolecules, whereas the exponent in the dependence on the length of a probe macromolecules is less than 3. One can say that result (37) qualitatively contradicts to empirical data, this is a major problem encountered the Doi–Edwards theory based on the reptation dynamics, and modification of reptation dynamics (contour length fluctuation model, for example) could not recover the empirical relation. One has to pay attention to alternative mechanism of relaxation via constraint release and its possible generalisations.

In this situation, we chose to apply to the modified Cerf-Rouse modes to calculate the characteristics of viscoelasticity. One can note that chains with intramolecular resistance (which assumably are chains in an entangled system as described in Section 2.1) have two branches of relaxation times: conformational (reptation for the case of strongly entangled systems) and orientational (or transverse). Using the dynamics (4) to calculate stresses in the system of strongly entangled macromolecules, one takes into consideration both conformational and orientational branches of relaxation. Viscoelastic behaviour of the system is determined by interplay of the two relaxation branches (at low frequencies; one has to take into account the other relaxation branches to consider the higher frequencies).

4.1. Constitutive relations

4.1.1. Stress tensor

Method of Rice and Gray [18] was used to calculate the stress tensor of the system as a stress tensor of the suspension of Brownian particles [6]. The result for the system governed by dynamics (4) can be conveniently written, using two sets of macroscopic internal variables, in the compact form

$$\sigma_{ik} = -p\delta_{ik} + 3nT\sum_{\nu}\left(x_{ik}^{\nu} - \frac{1}{3}\delta_{ik} + u_{ik}^{\nu}\right). \tag{38}$$

where n is the number density of macromolecules. The first set of variables x_{ij}^{α} – conformational variables – characterises the mean size and shape of the macromolecular coils in a deformed system, while the second set of variables u_{ij}^{α} – orientational variables (the name is justified earlier [[6], p. 126]) – is associated with stresses induced by internal resistance forces of macromolecules. 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. According to the mesoscopic approach, the stress tensor 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.

4.1.2. Relaxation equations

The macroscopic internal variables x_{ik}^{ν} and u_{ik}^{ν} can be found as solutions of relaxation equations which are different for weakly and strongly entangled system. After simple operations over dynamic Eq. (8), one can obtain [6] a set of relaxation equations for the internal variables, which, for strongly entangled systems, can be written in the form

$$\frac{\mathrm{d}x_{ik}^{\alpha}}{\mathrm{d}t} - \nu_{ij}x_{jk}^{\alpha} - \nu_{kj}x_{ji}^{\alpha} = -\frac{1}{\tau_{\alpha}^{\mathrm{rep}}}\left(x_{ij}^{\alpha} - \frac{1}{3}\delta_{ij}\right), \tag{39}$$

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

where the set of relaxation times is defined as

$$\tau, \quad \tau_{\alpha}^{\mathrm{rep}} = \frac{\pi^2}{\chi}\tau_{\alpha}^{\mathrm{R}}, \quad \tau_{\alpha}^{\mathrm{R}} = \frac{\tau^*}{\alpha^2}, \quad \alpha = 1, 2, \ldots \ll \frac{\pi}{\chi}. \tag{40}$$

Some approximations were introduced in Eqs. (39). The times of relaxation for orientational variables u_{ik}^{α}, strictly speaking, slightly depend on the number of the mode, but this dependence is ignored here. Conformational relaxation times are considered to be reptation relaxation times. In Eq. (39) and later, notation for the symmetric and antisymmetric velocity gradient tensors are used

$$\gamma_{il} = \tfrac{1}{2}(\nu_{il} + \nu_{li}), \quad \omega_{il} = \tfrac{1}{2}(\nu_{il} - \nu_{li}).$$

4.2. Linear effects of viscoelasticity

The set of Eqs. (38)–(40) allows us to calculate stresses at any given velocity gradients. To characterize linear viscoelasticity and calculate dynamic modulus, we consider oscillatory motion with gradient of velocity

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

Keeping only the first-order terms with respect to velocity gradient, the set of relaxation Eq. (39) for the internal variables can be written in the simpler form

$$\frac{\mathrm{d}x_{ik}^{\alpha}}{\mathrm{d}t} = -\frac{1}{\tau_{\alpha}^{\mathrm{rep}}}\left(x_{ik}^{\alpha} - \frac{1}{3}\delta_{ik}\right) + \frac{2}{3}\gamma_{ik}.$$

$$\frac{\mathrm{d}u_{ik}^{\alpha}}{\mathrm{d}t} = -\frac{1}{\tau}u_{ik}^{\alpha} - \frac{1}{\tau}\left(x_{ik}^{\alpha} - \frac{1}{3}\delta_{ik} - \frac{2}{3}B\tau_{\alpha}^{\mathrm{R}}\gamma_{ik}\right)$$

where the set of relaxation times is defined by Eq. (40).

These equations. have the following solutions for oscillatory motion

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

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

Then, one can make use of the expression (38) for the stress tensor to obtain the coefficient of dynamic viscosity

$$G(\omega) = nT\sum_{\alpha=1}^{\pi/\chi}\left[\frac{-i\omega\tau_{\alpha}^{\mathrm{rep}}}{1 - i\omega\tau_{\alpha}^{\mathrm{rep}}} + \left(B\tau_{\alpha}^{\mathrm{R}} - \frac{\tau_{\alpha}^{\mathrm{rep}}}{1 - i\omega\tau_{\alpha}^{\mathrm{rep}}}\right)\frac{-i\omega}{1 - i\omega\tau}\right]. \tag{41}$$

The first terms under the sum in this relation presents the direct contribution of the reptation relaxation. Having evaluated, these terms give us the results of Doi–Edwards theory.

The terms of the first and the second orders in expansion of expression (41) in powers of $-i\omega$ give, correspondingly, the coefficients of viscosity and elasticity

$$\eta = nT\sum_{\alpha=1}^{\pi/\chi}B\tau_{\alpha}^{\mathrm{R}} = \frac{\pi^2}{6}nT\tau^*B \sim M_0^{\delta}M \tag{42}$$

$$\nu = nT\sum_{\alpha=1}^{\pi/\chi}(B\tau\tau_{\alpha}^{\mathrm{R}} - \tau\tau_{\alpha}^{\mathrm{rep}}) = nT\left(\frac{\pi^2}{3}(B\tau^*)^2\chi - \frac{\pi^4}{3}B(\tau^*)^2\right) \approx \frac{\pi^2}{3}nT(B\tau^*)^2\chi \tag{43}$$

The terminal viscoelastic relaxation time

$$\tau = \frac{\nu}{\eta} = 2B\tau^* \chi \sim M_0^{\delta} M. \tag{44}$$

appears to be equal to the relaxation time which was introduced to characterise the medium surrounding the probe macromolecule. Thus, for the strongly entangled systems, the theory is self-consistent and this confirms the statement of Section 2.1.2 that chains of Brownian particles can be considered as moving independently in a liquid made of interacting Kuhn segments.

One can see that, in contrast to relation (37), terminal time of relaxation (44) depends on the length of both a probe macromolecule M and neighbouring macromolecules M_0, which is consistent with experimental data (see the next section). The estimate of exponent δ, according to the constraint-release theory, is 3, while the empirical value $\delta \approx 2.4$ can be found at the comparison expressions (42) and (44) with empirical relations (1) and (2) for strongly entangled systems. However, the assumption that there is hydrodynamic interaction between Brownian particles of the probe macromolecule changes the dependencies (42) and (44) in such a way, that empirical value of exponent δ would be more that 2.4 and closer to 3 in accordance with the constraint-release estimates. The presence or absence of hydrodynamic interaction can be discovered experimentally by measuring the characteristic quantities for dilute blends of linear polymers (see Section 5.2).

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

$$G_e = nT \sum_{\alpha=1}^{\pi/\chi} \left(1 + \frac{B\tau_\alpha^{R}}{\tau} \right) \approx nT \left(\frac{\pi}{\chi} + \frac{\pi^2}{12} \frac{1}{\chi} \right) \tag{45}$$

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, the difference in the distribution of relaxation times determines that the plateau from the reptation branch is reached at much higher frequencies than from the orientational branch, so that, for the strongly entangled systems, one can approximate dynamic modulus on the plateau as

$$G_e = \frac{\pi^2}{12} nT\chi^{-1} \sim M^0. \tag{46}$$

This relation allows one to introduce the interpretation of the parameter χ as

$$\chi = \frac{\pi^2}{12} \frac{M_e}{M} \approx \frac{M_e}{M}. \tag{47}$$

In the case of strongly entangled systems, conformational relaxation is realized through reptation mechanism, though the main contribution into linear viscoelasticity of the system came from relaxation of orientational variables. To describe linear viscoelasticity at low frequencies, one can neglect conformational relaxation, whatever the mechanism is realized, at all.

4.3. *The second order effects*

Though we do not need practically in the conformational branch to describe linear viscoelasticity, it appears to be impossible to describe correctly experimental situation in the non-linear region avoiding conformational, exactly reptation relaxation. We shall illustrate this on the example of shear 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

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

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. The results of calculation of the stresses up to the second-order terms with respect to the velocity gradient will be demonstrated further on.

For calculation of shear viscosity and normal stresses, we use Eq. (38) for the stress tensor and relaxation Eq. (39). To the first approximation with respect to the velocity gradient ν_{12}, one determines the only component of the stress tensor — the shear stress

$$\sigma_{12}^0 = \eta_0 \nu_{12}, \qquad \eta_0 = \tfrac{\pi^2}{6} nTB\tau^*, \qquad \chi < 0.5 \tag{48}$$

The terms of the second order allow us to determine normal stresses and calculate the measurable quantities – differences of the normal stresses

$$\sigma_{11} - \sigma_{22} = \tfrac{2\pi^2}{3} nT\chi\,(B\tau^*\nu_{12})^2, \tag{49}$$

$$\sigma_{22} - \sigma_{33} = nT \left(\frac{\pi^6}{90} \frac{1}{\chi B} + \frac{1}{3}\chi^2 - \frac{\pi^2}{3}\chi \right) (B\tau^*\nu_{12})^2$$

The two quantities are used to characterise the system: the steady-state modulus and the ratio of the normal stresses differences, correspondingly,

$$\frac{2\sigma_{12}^2}{\sigma_{11} - \sigma_{22}} = \frac{\pi^2}{12} nT\chi^{-1} \sim M^0 \tag{50}$$

$$\frac{\sigma_{22} - \sigma_{33}}{\sigma_{11} - \sigma_{22}} = \frac{\pi^4}{60} \frac{1}{\chi^2 B} + \frac{1}{2\pi^2}\chi - \frac{1}{2} \tag{51}$$

The steady-state modulus (50) does not contain the unknown function $B(M)$ and, in accordance with experimental data [1,19] for strongly entangled system ($M > 10M_e$), does not depend on the molecular weight of the polymer, while the expression for the modulus is exactly the same as for the plateau value of the dynamic modulus (Eq. (46)). Note that, if one neglect the reptation relaxation branch or chose another dependence for the rate of reptation relaxation instead of the law $\tau^{\mathrm{rep}} \sim M^3$, one would obtain quite different dependence of the steady-state modulus (50) on molecular weight. This confirms that reptation motion is needed for description of non-linear viscoelasticity, while the law of the reptation relaxation $\tau^{\text{rep}} \sim M^3$ is not needed in any amendments.

5. Viscoelasticity of dilute blends

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 single macromolecule among the neighbouring macromolecules [20]. The change in the stress produced by the small amount of macromolecules of another length 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.

5.1. Relaxation of probe macromolecule

Consider a system consisting of linear polymer with molecular weight M_0 and a small impurity of a similar polymer with a different molecular weight M. We shall assume that the amount of the high-molecular-weight additive is so small that its molecules do not interact with each other. The matrix is characterized by the characteristic length M_e – the length of macromolecule between adjacent entanglements. It is convenient to use the characteristic parameters for the macromolecules of the matrix and the additive, which, respectively, are

$$\chi_0 \approx \frac{M_\text{e}}{M_0}, \qquad \chi \approx \frac{M_\text{e}}{M}. \tag{52}$$

Apart of relaxation due to constraint-release mechanism, the probe macromolecule relaxes due to reptation. The two relaxation mechanisms compete and to uncover which mechanism of relaxation of a probe macromolecules of the additive is realised, one has to compare the relaxation times from (34) to obtain the condition for realisation of reptation relaxation

$$2\chi B(\chi_0) > \pi^2 \tag{53}$$

In the case when $M = M_0$, this relation define the critical length M^* which divides weakly (macromolecules do not reptate) and strongly (macromolecules reptate) entangled systems. Similar to the procedure in Section 3.3, one can find that the characteristic parameters in the point, where the mechanism of relaxation of macromolecules of the additive changes, are connected by relation

$$\chi = 2^{\delta-1}\pi^2\chi_0^\delta \tag{54}$$

This relation can be rewritten in terms of the lengths of macromolecules as

$$\frac{MM_\text{e}^{\delta-1}}{M_0^\delta} = \frac{1}{2^{\delta-1}\pi^2} \tag{55}$$

One can see that, at $\delta = 3$, the left-hand side of the relation coincides with the Struglinski-Graessley parameter [21] which, as one can easily calculate, has critical value 0.024 for $\delta = 3$ and 0.04 for $\delta = 2.4$. Relation (55), at $M = M_0$, is an identity for critical values $M^* \approx 10$ at $\delta = 2.4$ or $M^* \approx 7.3$ at $\delta = 3$.

For the matrix of short macromolecules, when $M_0 < M^*$, the transition point for a probe macromolecule of the additive is also situated in the short-length region, so that the macromolecules of the additive, which are longer than M_0 or M^*, do not reptate. However, if the matrix is made of macromolecules, for which $M_0 > M^*$, there is a region between M^* and

$$M^{**} = \frac{M_0^\delta}{2^{\delta-1}\pi^2 M_\text{e}^{\delta-1}} \tag{56}$$

in which a probe macromolecule of the additive reptates. However, the macromolecules of additive longer that M^{**} do not reptate in the matrix of shorter macromolecules with $M_0 > M^*$, so that one has to discuss two cases: non-reptating and reptating macromolecules.

5.2. Characteristic quantities

The system contains n_0 matrix macromolecules and n impurity macromolecules per unit volume and can be characterised by dynamic modulus $G(\omega)$. The increase in 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

$$G(\omega) - G_0(\omega) = n\left(g(\omega) - \frac{M}{M_0}g_0(\omega)\right) \tag{57}$$

where $g(\omega)$ and $g_0(\omega)$ are the contributions to the dynamic modulus from a single macromolecule of the impurity and the matrix, respectively. Further on, we consider low frequencies for which

$$G(\omega) \approx -i\omega\eta - \nu\omega^2, \quad G_0(\omega) \approx -i\omega\eta_0 - \nu_0\omega^2.$$

We shall assume that the macromolecules of the matrix are long enough, so that, according to the Eqs. (42) and (43), one has for coefficients of viscosity and elasticity

$$\eta_0 = \frac{\pi^2}{6}n_0T\tau_0^*B,$$

$$\nu_0 = \begin{cases} \dfrac{\pi^4}{90}n_0T(\tau_0^*B)^2, & M_0 < M^*, \\[2ex] \dfrac{\pi^2}{3}n_0T(\tau_0^*B)^2\chi_0, & M_0 > M^*, \end{cases} \tag{58}$$

where $n_0 \sim M^{-1}$ is the number of the matrix macromolecules per unit volume and $\tau_0^* \sim M_0^2$ is the characteristic Rouse relaxation time of the macromolecules of the matrix.

The contribution of n macromolecules of the additive into the coefficients of viscosity and elasticity of the blend are defined as

$$\eta = \frac{\pi^2}{6} nT\tau^* B, \qquad \nu = \begin{cases} \dfrac{\pi^4}{90} nT(\tau^* B)^2, & M > M^{**}, \\ \dfrac{\pi^2}{3} nT(\tau^* B)^2 \chi, & M < M^{**}, \end{cases} \tag{59}$$

where $\tau^* \sim M^2$ is the characteristic Rouse relaxation time of the macromolecules of the additive. Note that, while the relaxation time τ^* is a function of M, the quantity B has to be considered as a function of M_0.

We investigate the case of very dilute blends and introduce the characteristic quantities

$$[\eta] = \lim_{c \to 0} \frac{\eta_b - \eta_0}{c\eta_0}, \quad [\nu] = \lim_{c \to 0} \frac{\nu_b - \nu_0}{c\nu_0}, \tag{60}$$

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

To calculate the quantities $\eta_b - \eta_0$ and $\nu_b - \nu_0$, we use Eqs. (58) and (59). Taking all the above into account, one can calculate expressions for the increase of viscosity and elasticity, assuming that $M > M^*$, and find expressions for the characteristic quantities in the form

$$\eta_b - \eta_0 = \frac{\pi^2}{6} nT\tau^* B \left(1 - \frac{M_0}{M}\right), \tag{61}$$

$$\nu_b - \nu_0 = \begin{cases} \dfrac{\pi^4}{90} nT(\tau^* B)^2 \left(1 - \dfrac{M_0^3}{M^3}\right), \\ \qquad M_0 < M^*, \\ \dfrac{\pi^2}{3} nT(\tau^* B)^2 \dfrac{M_e}{M} \left(1 - \dfrac{M_0^2}{M^2}\right), \\ \qquad M_0 > M^*, M < M^{**}, \\ \dfrac{\pi^4}{90} nT(\tau^* B)^2 \left(1 - \dfrac{30}{\pi^2} \dfrac{M_e M_0^2}{M^3}\right), \\ \qquad M_0 > M^*, M > M^{**}. \end{cases}$$

Using the above relations and Eq. (60), one finds that for $M \gg M_0$

$$[\eta] \sim M_0^{-1} M, \quad [\nu] \sim \begin{cases} M_0^{-3} M^3, & M_0 < M^*, \\ M_0^{-2} M^2, & M_0 > M^*, M < M^{**} \\ M_0^{-2} M^3, & M_0 > M^*, M > M^{**}. \end{cases} \tag{62}$$

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

$$[\eta] \sim M_0^0 M^0, \quad [\nu] \sim M_0^0 M^0, \quad M_0 > M^* \tag{63}$$

Results (62) and (63) do not depend upon any choice of the dependence of B on the length (molecular weight) of macromolecules.

The results [22] of empirical investigation of viscoelastic behaviour of dilute blends of polymers allow us to estimate [20] characteristic quantities for polybutadiene by the dependencies

$$[\eta] \sim M_0^{-0.8} M^{0.5}, \quad [\nu] \sim M_0^{-(1.8 \to 2.2)} M^{1.3 \to 3.0}. \tag{64}$$

The comparison of the theoretical formulas (62) with the experimental ones (64) shows the consistency of the results, though the absolute values of indexes in formula for characteristic viscosity has appeared to be less that 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 [22]) does not allow one to say whether there are any certain deviations from relations (62) or not. If relations (64) are confirmed, it could mean that there are some unaccounted issues (intrachain 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.

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 (62) and (63) for characteristic quantities for dilute blends of linear polymers. However, the dependence of the quantity B on M_0 or, in other terms, the value of exponent δ can be recovered due to empirical data. To estimate this dependence, one can consider the terminal relaxation time

$$\tau = \frac{\nu_b - \nu_0}{\eta_b - \eta_0}$$

and use Eq. (61) to obtain for $M > M^*$

$$\tau \sim \begin{cases} B(M_0) M^2, & M_0 < M^*, \\ B(M_0) M, & M_0 > M^*, M < M^{**} \\ B(M_0) M^2, & M_0 > M^*, M > M^{**}. \end{cases} \tag{65}$$

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

Watanabe ([2], p. 1354) has deducted 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

$$\tau \sim M_0^3 M^2, \tag{66}$$

while also for polystyrene/polystyrene blends, [23] found different values of indexes (2.3 instead of 3 and 1.9 instead of 2); the difference is discussed by Watanabe ([2], p. 1356).

No empirical relation, similar to relation (66), is available for strongly entangled systems, but, as it can be seen in plots of the paper [2], that the value of the first index are less that 3 in this case. It is possible that situation is different for weakly and strongly entangled systems, so that values of the index in formula (66) could be different for these two types of systems.

Comparing formulae (65) and (66) allows one to estimate the dependence of coefficient of enhancement on the lengths of macromolecules as

$$B \sim M_0^3, \tag{67}$$

that is $\delta = 3$, in contrast with previous estimate of the index, due to Eq. (42) for viscosity, 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 empirical value of the index, due to Eq. (42)), could be closer to 3, but, in this case, value of the second index in Eq. (65) must be less.

There is some contradiction of empirical result (66) with the reliable results for monodisperse ($M_0 = M$) system. Indeed, taking result (67) into account, the terminal relaxation time (44) can be written as

$$\tau \sim \begin{cases} M^5, & M < M^* \\ M^4, & M > M^* \end{cases} \tag{68}$$

To provide the correspondence to the empirical dependencies of viscosity and terminal relaxation time on the molecular length (relation 1 and 2), the sum of the two indexes in Eq. (66) 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 M^* and M^{**}. One can think that the further empirical investigation of viscoelasticity of dilute blends could shed more light on the dynamics of macromolecules in entangles systems.

6. Conclusion

The combined consideration of the two models of macromolecular dynamics allows us, first of all, to distinguish weakly entangled (length of macromolecules $M < 10M_e$) and strongly entangled (length of macromolecules $M > 10M_e$) systems. While one needs only in modified Cerf-Rouse modes to explain effects of viscoelasticity in weakly entangled systems, the combination of two models of macromolecular dynamics (unless one has a generalized model) ought to be used for consistent explanation of linear and non-linear effects of viscoelasticity in strongly entangled linear polymers. To consider viscoelasticity of strongly entangled system, one has to take into account that two branches of relaxation times of macromolecules (deformational, reptation in this case, and orientational) exist. The interplay of the two branches determines viscoelastic behaviour of the system. The conformational (reptation) relaxation appears to be very important for description the effects of viscoelasticity of the second and higher orders.

The discussed mechanisms of relaxation processes allow us to formulate constitutive equations for linear polymers which, due to the difference of mechanisms of relaxation, appear to be different for the two types of systems. The constitutive relations derived in our previous paper [[5], Eqs. (48), (50)–(52)], in which effects of reptation were not considered at all, can be used to describe viscoelastic flows of weakly entangled system. The case of strongly entangled systems is considered in this paper and appears to be the simplest one. The constitutive relations (38)–(40) contains, apart of the conventional characteristic Rouse relaxation time τ^*, the three mesoscopic parameters introduced in the macromolecular dynamic Eq. (4): τ, B and E. Due to requirement of correspondence of the derived results to empirical situations, the parameters can be defined as

$$E = B\frac{\pi^2}{\chi}, \quad \chi \ll 0.1,$$

$$B = (2\chi)^{-\delta}, \quad \chi < 0.5 \tag{69}$$

where δ is an index independent on the length of the macromolecules (typical value $\delta \approx 2.4$). So, it has appeared that the dynamics of the system of very long macromolecules ($M \gg 10M_e$) is controlled by the only dynamic parameter χ which has the direct physical meaning as the ratio of the square of the double intermediate length (the diameter of 'the tube') to the mean square end-to-end distance of the macromolecule $\langle R^2 \rangle$ or the inverse number of 'entanglements' for the macromolecule M/M_e

$$\chi = \frac{\tau}{2B\tau^*} \approx \begin{cases} (2\xi)^2/\langle R^2 \rangle, \\ M_e/M \end{cases} \tag{70}$$

The description of the phenomena might appear to remain qualitative, so as there are apparently many points, where the description of the modes can be improved. The mesoscopic effective-field approach itself is needed in proper microscopic justification. Apart of empirical justification, the considered scheme can be justified or rejected, if the problem of direct derivation a single-chain equation for a system of interacting macromolecules is solved. The approaches to the problem [11–14] demonstrate the possibility of reducing many-chain problem to a single-chain problem and of evaluating the memory function in the single-chain equation through the intermolecular correlation functions and structural dynamic factor of the system of interacting Brownian particles. Unfortunately, more detailed comparison has appeared to stumble, first of all, over the unjustified simplification of the starting point in the cited works. As an initial point was chosen not a microscopic picture of interacting atoms or, at least, rigid Kuhn segments of the macromolecules, but picture of the interacting particles of the coarse-grained chains. The preliminary switch to coarse-grained chains does not allow to calculate the contribution to the memory function from a short-range interaction between atoms of different subchains of the coarse-grained chains (what makes up ‘segment carrier liquid with non-zero relaxation time’ in phenomenological theory). There is no evidence that the contribution to the memory function from interaction of the internal parts of subchains can be disregarded due either to the level of the quantity or to value of relaxation times. On the contrary, the phenomenological approach demonstrates that the contribution of the direct interaction of Brownian particles of the coarse-grained chains can be neglected in the first approximation. Nevertheless, one can believe that the developed methods [11–14] can be helpful to bring a microscopic justification of a single-macromolecule equation in the entangled systems. This is a really fundamental problem in polymer physics.

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