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A justification of the reptation-tube dynamics of a linear macromolecule in the mesoscopic approach

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Abstract

The paper contributes to the problem of description of relaxation behaviour of entangled linear polymers in terms of dynamics of a single macromolecule. The approach systematically studies deviations from the Rouse dynamics when adding non-Markovian and anisotropic noise. The introduction of these terms decreases in mobility and increases in relaxation times of the macromolecule in comparison with the Rouse case. An intermediate length, which has the meaning of a tube radius and/or the length of a macromolecule between adjacent entanglements, is calculated through parameters of the model. It is shown that introduction of local anisotropy of mobility of particles in the mesoscopic dynamics of generalised Cerf-Rouse modes allows one to get the effects, which used to be associated with reptation motion of the macromolecule. The devised model can be considered as a possible expansion of the conventional reptation-tube model and can be useful, for example, for formulating a consequent theory of viscoelasticity of linear polymers in entangled states.

Keywords: Diffusion; Local anisotropy; Mesoscopic approach; Modified Cerf-Rouse modes; Polymer dynamics; Polymer solutions and melts; Relaxation of macromolecule; Reptation; Neutron scattering function; Viscoelasticity

1. Introduction

To explain dynamic behaviour of polymer solutions and melts, some specifying hypotheses about the behaviour of individual macromolecules in the system were formulated. One of the hypotheses assumed that motion of the chain is essentially confined in a tube-like region made of the surrounding macromolecules [1], and the reptation motion of macromolecule inside the tube was introduced by de Gennes [2]. Based on these ideas, a very elegant model—the reptation-tube model—was elaborated by Doi and Edwards [3]. It appeared that the model perfectly (or almost perfectly) describes the phenomenon of diffusion of macromolecules in strongly entangled systems ($M > 10M_e$, where M_e is 'the length of the macromolecule between adjacent entanglements'), though, in application to viscoelasticity, the model was not so successful: the well-known long-standing discrepancies are discussed, for example, by Lodge [4]. For the long time the scholars saw a solution of the problem in expansion of the reptation-tube model, in order a generalised model could describe

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the phenomena of viscoelasticity as well. The recent discussion of improvements to the reptation-tube theory can be found, for example, in papers by Likhtman and McLeish [5] and by Park and Larson [6]. One can see, nevertheless, that the introduction of the amendments, such as the constraint-release mechanism, contour-length fluctuations, subchain stretching and so on, too numerous and elusive to be listed here in full, has not brought the desired consistent interpretation of the bulk of empirical facts.

Our intention is also to find a proper expansion of the reptation-tube model, though our starting point is different. The model, we shall consider, is designed as a non-linear generalisation of the known [7,8] stochastic dynamics of a macromolecule. To avoid misunderstanding and misinterpreting, note that we do not deny the achievements in understanding of dynamics of a separate macromolecule in an entangled system; on the contrary, looking for a unified mathematical model, we argued earlier [8] that the reptation relaxation is important for correct understanding of viscoelasticity; we needed also in incorporation of a mechanism similar to the constraint-release mechanism to describe the dynamics properly. However, there is no need in a special discussion of such effects as the contour-length fluctuations and the subchain stretching, so as they are inherently included in the basic model. We do not postulate the existence of the tube; it is enough to postulate that the surrounding of the considered chain is dynamic, something like a viscoelastic medium, which determines some restrictions on the motion of the macromolecule and allows one to introduce and calculate a dynamic intermediate length, which can be identified with the radius of the tube postulated in the conventional reptation-tube model. This study demonstrates that the introduction of local anisotropy of mobility of particles of the coarse-grained chain brings changes in mobility and relaxation times of the macromolecular coil, so that one can attain the results of the conventional reptation-tube model. The proposed theory can be considered as an attempt to formalise the common knowledge about the dynamics of a macromolecule and can be called a generalised reptation-tube theory; in any case, it does not belong to the class of theories, which deny the reptation motion of a macromolecule. One can note that the introduction of local anisotropy of mobility in a model of dynamics of a macromolecule is not a new idea. Some earlier works (see Ref. [9], for example) exploit this idea, but, in contrast to this paper, the authors used an assumption of Markovian dynamics, which could not allow to get restrictions on the lateral motion of a macromolecule. Only a combination (considered in this paper) of non-Markovian dynamics and local anisotropy allows us to reflect the dynamics of a macromolecule adequately.

The equations of dynamics of a macromolecule in the system of macromolecules are described in Section 2: the motivations and details can be found in the cited works [7,8]. Some results of simulation are considered in Section 3. The algorithm of numerical solution is described in the Appendix. The conclusion contains a discussion of the results.

2. Generalised dynamics of a macromolecule

2.1. The conventional form of dynamic equations

It is known, that every flexible macromolecule can be effectively presented as a chain of coupled Brownian particles (so-called bead and spring model). Dynamics of a probe macromolecule in an entangled system can be simplified by the assumption that the neighbouring macromolecules are described as a uniform structureless medium and all important interactions can be reduced to intramolecular interactions, so that large-scale stochastic dynamics of a single macromolecule in the entangled system can be considered as dynamics of effective Brownian particles. The situation can be considered in an approximation, which is linear to respect to velocities, while the mutual hydrodynamic interaction of the particles can be omitted, so that effective dynamics of a single chain as the dynamics of coupled Brownian particles is described by a set of the coupled stochastic equations

$$m\frac{\mathrm{d}^2 r_i^\alpha}{\mathrm{d}t^2} = -\zeta \dot{r}_i^\alpha + F_i^\alpha + G_i^\alpha - 2\mu T A_{\alpha\gamma} r_i^\gamma + \phi_i^\alpha(t), \quad \alpha = 0, 1, 2, \ldots, N, \tag{1}$$

where m is the mass of a Brownian particle associated with a piece of the macromolecule of length M/N, r^α and $\dot{r}^\alpha = u^\alpha$ are the co-ordinates and velocity of the Brownian particle and $2T\mu$ is the coefficient of elasticity of

'a 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 in Eqs. (1) are introduced by three terms, the first of which, $-\zeta u_j^\gamma$, presents the resistance from the 'monomeric' liquid, and the others, F_i^α and G_i^α present the effective forces from the neighbouring macromolecules and satisfy the equations

$$\tau \frac{\mathrm{d}(F_i^\alpha + G_i^\alpha)}{\mathrm{d}t} + F_i^\alpha + G_i^\alpha = -\zeta B H_{ij}^{\alpha\gamma} u_j^\gamma - \zeta E G_{ij}^{\alpha\gamma} u_j^\gamma, \tag{2}$$

where τ is a relaxation time of the surrounding. The force F_i^α is a force of external resistance, while the force G_i^α is a force of internal resistance with the property

$$\sum_{\alpha=0}^{N} G_i^\alpha = 0, \quad i = 1, 2, 3. \tag{3}$$

The coefficients B and E in Eq. (2) are introduced as measures of intensities of the external and internal extra dissipative forces. These coefficients are determined by the surrounding of the considered macromolecule; in particular, they depend on the length of the neighbouring macromolecules.

For the case, when Eqs. (1) and (2) are linear, as assumed, in velocities, the correlation functions of the stochastic forces in the system of Eqs. (1) can be easily determined [10] from the requirement that, at equilibrium, the set of equations must lead to well-known results (the fluctuation–dissipation theorem). It is readily seen that, according to the general rule [10],

$$\langle \phi_i^\alpha(t) \phi_k^\gamma(t') \rangle = T\zeta \left[2\delta_{\alpha\gamma}\delta_{ik}\delta(t-t') + \frac{1}{\tau}(B H_{ij}^{\alpha\gamma} + E G_{ij}^{\alpha\gamma}) \exp\left(-\frac{t-t'}{\tau} \right) \right]. \tag{4}$$

In linear, in respect of the co-ordinates, approximation [7,8], the matrixes $H_{ij}^{\alpha\gamma}$ and $G_{ij}^{\alpha\gamma}$ in Eqs. (2) and (4) are numerical matrixes (see below). A special case, when non-linearity is connected with local anisotropy of mobility, is studied in this paper.

The sources of inspiration for formulating the above equations, also as discussion of origin and physical meaning of the introduced quantities τ, B and E, can be found in our earlier publications [7,8].

2.2. A new form of dynamic equations

The random process in Eq. (1) can be represented as a sum of the two independent processes

$$\phi_i^\alpha(t) = \bar{\phi}_i^\alpha(t) + \tilde{\phi}_i^\alpha(t),$$

while the first one is a Gaussian process with the correlation

$$\langle \bar{\phi}_i^\gamma(t) \bar{\phi}_j^\mu(t') \rangle = 2T\zeta\delta_{\gamma\mu}\delta_{ij}\delta(t-t') \tag{5}$$

and the second one is not delta-correlated, but a Gaussian process as well.

It is convenient to introduce the variable

$$\Phi_i^\alpha = F_i^\alpha + G_i^\alpha + \tilde{\phi}_i^\alpha(t),$$

so that the system of Eqs. (1) and (2) can be written as

$$\begin{aligned} m\frac{\mathrm{d}^2 r_i^\alpha}{\mathrm{d}t^2} &= -\zeta u_i^\alpha + \Phi_i^\alpha - 2\mu T A_{\alpha\gamma} r_i^\gamma + \bar{\phi}_i^\alpha(t), \\ \tau\frac{\mathrm{d}\Phi_i^\alpha}{\mathrm{d}t} &= -\Phi_i^\alpha - \zeta B H_{ij}^{\alpha\gamma} u_j^\gamma - \zeta E G_{ij}^{\alpha\gamma} u_j^\gamma + \sigma_i^\alpha(t). \end{aligned} \tag{6}$$

The first one of the above equations represents Langevin equation for the Rouse chain in the presence of the extra random force Φ_i^α. One can note that this equation (at $m = 0$) is identical to the Langevin equation, which was formulated [11] to study the behaviour of polymer chain in a random static field; the equation was investigated numerically by Milchev et al. [12]. However, the force Φ_i^α in Eqs. (6) is not static one and can be specially designed for a chain in the entangled system, according to the second equation.

The random process in the last stochastic equation from set (6) is related to the above introduced random force by equation

$$\sigma_i^\gamma = \tilde{\phi}_i^\gamma + \tau \frac{\mathrm{d}}{\mathrm{d}t} \tilde{\phi}_i^\gamma \tag{7}$$

and is specified below for two cases.

2.2.1. Linear approximation

In the linear case, the matrixes $H_{ij}^{\alpha\gamma}$ and $G_{ij}^{\alpha\gamma}$ are numerical matrixes, satisfying the requirement (3), so that the simplest forms can be written as

$$H_{ij}^{\alpha\gamma} u_j^\gamma = u_i^\alpha, \quad G_{ij}^{\alpha\gamma} u_j^\gamma = \frac{1}{N} \left\{ (N+1) u_i^\alpha - \sum_{\gamma=0}^{N} u_i^\gamma \right\} = G^{\alpha\gamma} u_i^\gamma. \tag{8}$$

where $G^{\alpha\gamma}$ is a component of the numerical matrix

$$\mathsf{G} = \begin{Vmatrix} 1 & -1/N & \cdots & -1/N \\ -1/N & 1 & \cdots & -1/N \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ -1/N & -1/N & \cdots & 1 \end{Vmatrix}. \tag{9}$$

Then, if the relation

$$\langle \sigma_i^\gamma(t) \sigma_j^\mu(t') \rangle = 2T\zeta (B\delta_{\gamma\mu} + EG^{\gamma\mu}) \delta_{ij} \delta(t - t') \tag{10}$$

is satisfied, the following relation, according to Eq. (7), is valid for the random force correlator

$$\langle \tilde{\phi}_i^\gamma(t) \tilde{\phi}_j^\mu(t') \rangle = \frac{T\zeta}{\tau} \left(B\delta_{\gamma\mu} + EG^{\gamma\mu} \right) \delta_{ij} \exp\left(-\frac{t - t'}{\tau} \right). \tag{11}$$

The sum of expressions (5) and (11) is a particular form of the random-force correlation function (4) for this case.

2.2.2. A non-linear approximation: local anisotropy

The relations of the previous section are valid for the simple case, when there is neither global nor local anisotropy, that is the particles have spherical forms and the medium is isotropic. For the case, when the local anisotropy is taken into account, relations (8) ought to be generalised as

$$H_{ij}^{\alpha\gamma} u_j^\gamma = u_i^\alpha - \frac{3}{2} a_\mathrm{e} \left(e_i^\alpha e_j^\alpha - \frac{1}{3} \delta_{ij} \right) u_j^\alpha,$$

$$G_{ij}^{\alpha\gamma} u_j^\gamma = \frac{1}{N} \left\{ (N+1) \left[u_i^\alpha - \frac{3}{2} a_\mathrm{i} \left(e_i^\alpha e_j^\alpha - \frac{1}{3} \delta_{ij} \right) u_j^\alpha \right] - \sum_{\gamma=0}^{N} \left[u_i^\gamma - \frac{3}{2} a_\mathrm{i} \left(e_i^\gamma e_j^\gamma - \frac{1}{3} \delta_{ij} \right) u_j^\gamma \right] \right\},$$

$$e_i^\alpha = \frac{r_i^{\alpha+1} - r_i^{\alpha-1}}{|\boldsymbol{r}^{\alpha+1} - \boldsymbol{r}^{\alpha-1}|}, \quad \alpha = 1, 2, \ldots, N-1,$$

$$e_i^0 e_j^0 = e_i^N e_j^N = \frac{1}{3} \delta_{ij}, \tag{12}$$

where a_e and a_i are parameters of local anisotropy introduced in such a way, that positive values of the parameters correspond to increase in mobility along the contour of the chain. For the linear case, when on average $e_i^\alpha e_j^\alpha = (1/3)\delta_{ij}$, one returns from Eqs. (12) to relations (8).

For this case of local anisotropy, relation (10) ought to be written as

$$\langle \sigma_i^{\gamma}(t)\sigma_j^{\mu}(t')\rangle = 2T\zeta(B H_{ij}^{\gamma\mu} + E G_{ij}^{\gamma\mu})\delta(t-t'), \tag{13}$$

where the matrixes $H_{ij}^{\gamma\mu}$ and $G_{ij}^{\gamma\mu}$ are defined by Eqs. (12) and have the form

$$H_{ij}^{\alpha\gamma} = \delta_{\alpha\gamma}[\delta_{ij} - \tfrac{3}{2}a_{\mathrm{e}}(e_i^{\gamma}e_j^{\gamma} - \tfrac{1}{3}\delta_{ij})],$$

$$G_{ij}^{\alpha\gamma} = G^{\alpha\gamma}[\delta_{ij} - \tfrac{3}{2}a_{\mathrm{i}}(e_i^{\gamma}e_j^{\gamma} - \tfrac{1}{3}\delta_{ij})]. \tag{14}$$

2.3. Parameters of the problem

So, dynamics of a single macromolecule in an entangled system is defined by the system of non-linear Eqs. (5), (6), (12) and (13), which contain some phenomenological (mesoscopic) parameters. In addition to characteristic relaxation time of the Rouse theory

$$\tau^* = \frac{\zeta N\langle R^2\rangle}{6\pi^2 T} = \frac{\zeta N^2}{4\pi^2\mu T} \sim M^2, \tag{15}$$

where $\langle R^2\rangle$ is the end-to-end distance of the macromolecule, some quantities have appeared to specify the influence of the neighbouring macromolecules on the behaviour of the tagged macromolecule.

The linear case ($a_{\mathrm{e}} = 0,\ a_{\mathrm{i}} = 0$) of the above equations was investigated thoroughly [7,8], which allows one to identify the parameters τ, B and E due to the available empirical results for linear viscoelasticity of linear polymers. Indeed, the expressions for the coefficients of viscosity, terminal viscoelastic relaxation time and the plateau value of dynamic modulus for the system of strongly entangled macromolecules are calculated as

$$\eta = \frac{\pi^2}{6} nT\tau^* B, \quad \tau = 2B\tau^*\chi, \quad G_{\mathrm{e}} = \frac{\pi^2}{12} nT\chi^{-1}, \tag{16}$$

where n is a number of macromolecules in unit of volume. The terminal relaxation time τ coincides with the postulated relaxation time, which means that the system is characterised by self-consistency. Relations (16) allow one to interpret the parameter χ as

$$\chi = \frac{\pi^2}{12}\frac{M_{\mathrm{e}}}{M} \approx \frac{M_{\mathrm{e}}}{M},$$

where M is the length of a macromolecule and M_{e} is the length of a part of a macromolecule between adjacent entanglements, and to consider the dimensionless quantity $\chi = \tau/(2B\tau^*)$ to be a parameter of the system instead of the quantity τ. Taking the above relation into account, the experimental evidence for viscosity allows one to define the parameters B as a function of the parameter χ

$$B = (2\chi)^{-2.4}, \quad \chi < 0.5. \tag{17}$$

The measure of internal resistance E of a macromolecule is small for weakly entangled systems and is as big as $E = B\pi^2/\chi$ for long macromolecules ($\chi \ll 0.1$ or $M \gg 10M_{\mathrm{e}}$), but the exact dependence in the intermediate region is not known. For estimation of the measure of internal resistance for the values from $M = 2M_{\mathrm{e}}$ up to $635M_{\mathrm{e}}$, one can use the simple approximate formula

$$\psi = \frac{E}{B} = (1/\chi - 2)^2/64. \tag{18}$$

The non-linear case ($a_{\mathrm{e}} \neq 0,\ a_{\mathrm{i}} \neq 0$) of Eqs. (4), (5), (11) and (12) is an object of study in this work. To estimate the effect of introduction of local anisotropy, we shall use the standard procedure of numerical integration, implementation of which to the considered problem is described in Appendix A. We shall calculate some characteristic quantities, which allows us to identify the parameters of local anisotropy a_{e} and a_{i}.

3. Some results of simulation and discussion

The introduction of local anisotropy can be helpful for description of the behaviour of a macromolecule in the systems with well developed entanglements restricting the lateral motion of the macromolecule. Apparently, there is a such molecular weight M^* of linear polymer—a transition point, above which ($M > M^*$) a macromolecule moves among the neighbouring macromolecules via reptation mechanism. This point is defined theoretically [8] as a solution of the equation $2\chi B(\chi) = \pi^2$, which, taking empirical dependence (17) into account, gives $M^* \approx 10M_e$. The transition point can be estimated empirically as a position of a point, in which the molecular-weight dependencies of relaxation times and coefficient of diffusion change drastically. Examining empirical data of different scholars on diffusion of macromolecules, Wang [13] showed, that, for both melts and solutions of linear polymers (with a few exceptions, among them hydrogenated polybutadiene—hPB), there is a point $M^* = 10M_e$ dividing regions of different dependences of self-diffusion coefficient on molecular weight, while in the region of higher molecular weights the reptation law of diffusion with index -2 is valid. It was also noted earlier [14], that 'if there is a *nonuniversal* crossover to an exponent of -2.0, for hPB it occurs at or beyond $M/M_e \approx 10^2$, whereas for PS and PDMS it might occur near $M/M_e \approx 10$'. So, one can consider that for linear polymers, as a rule, there is a point about $M^* = 10M_e$, where the mechanisms of mobility change, while the reptation mechanism of mobility dominates above the transition point $M^* = 10M_e$ (or in the formulation, which has no exceptions: below the value $\chi^* = 0.1$).

Thus, the examination of empirical data [13] confirms the theoretical estimate of the transition point as $M^* \approx 10M_e$, and one needs in some non-zero values of the coefficients of local anisotropy to obtain empirical dependences of diffusion and relaxation times in the region above the point $10M_e$. In contrast to the above, some scholars [4,14] assume that the transition point coincides with the entanglement point $2M_e$ and, considering the data for the whole region above $2M_e$, find the empirical law of molecular-weight dependence of self-diffusion coefficient with the index about -2.3, thus, calling in question the well-established reptation law with the index -2. However, to estimate a real empirical value of the index in the reptation law of diffusion, one needs much longer macromolecules and, in any case, one has to exclude the transition interval below $10M_e$. Note also that the measurements of diffusion of labelled chains in a melt matrix of much higher molecular weight (tracer diffusion) show the index -2 [13].

3.1. Mobility of a macromolecule

The mean square displacement of the centre of mass of a macromolecule in a viscous liquid under the simplest assumptions (the Rouse case) is described as

$$\Delta(t) = 6D_0 t, \quad D_0 = \frac{T}{N\zeta} \sim M^{-1}, \tag{19}$$

where D_0 is the coefficient of diffusion of the macromolecular coil. In a complicated case, when a macromolecule is moving among the neighbouring macromolecules via reptation mechanism, mobility of the macromolecule is described by the Doi–Edwards model [3,15]. The dependence of the mean square displacement of the centre of mass of a macromolecule on the time, in the symbols used in this paper, can be written as

$$\Delta(t) = \begin{cases} 6D_0 t, & t < \tau_e, \\ 4\xi^2 \left(\dfrac{D_0}{\langle R^2 \rangle} t \right)^{1/2}, & \tau_e < t < \tau^*, \\ 6Dt, & t > \tau^*, \end{cases} \tag{20}$$

where D_0 is the coefficient of diffusion of the macromolecular coil in a 'monomer' viscous liquid, τ^* is the characteristic Rouse relaxation time defined by Eq. (15), $\tau_e = (4\pi^2/3)(\xi^4/\langle R^2 \rangle^2)\tau^*$ is an entanglement time, ξ is the radius of the tube, which is considered to be identical to the intermediate length emerged in the model of generalised Cerf-Rouse modes and $\langle R^2 \rangle$ is the mean square end-to-end distance of the macromolecule. The last

line of relations (20) defines the coefficients of diffusion of the macromolecule via the reptation mechanism

$$D = D_0 \frac{4}{3} \frac{\xi^2}{\langle R^2 \rangle} \approx D_0 \frac{\xi^2}{\langle R^2 \rangle} \sim M^{-2}. \tag{21}$$

The reptation mechanism of mobility was specially invented [2] to describe the molecular-weight dependence of the coefficient of diffusion of a macromolecule in entangled systems correctly. As an example, dependence (20) for a polymer with the length $M = 25M_e$ is depicted in Fig. 1 by dashed lines.

Looking at relations (20), one can think that the changes of the exponent occur in the vicinity of the points τ_e and τ^*. Indeed, it is easily seen that the position of the first crossing practically coincides with the entanglement relaxation time τ_e, while the position of the second one is essentially different from the characteristic relaxation time τ^*, as one can see also in Fig. 1. It can be estimated as

$$t \approx \frac{3}{2} \pi^2 \tau^*. \tag{22}$$

Relations (20) ought to be corrected, in order to eliminate, at least, the internal inconsistency.

A complementary picture is given by the linear model of generalised Cerf-Rouse modes. The mean square displacement of the centre of mass of a macromolecule, calculated as the zeroth normal co-ordinate ρ^0, for the above model (1)–(4) with linear approximation (8) is defined as

$$\Delta(t) = 6D_0 \frac{\tau}{B} \left(\frac{t}{\tau} + 1 - e^{-tB/\tau} \right), \quad D_0 = \frac{T}{N\zeta} \sim M^{-1}. \tag{23}$$

Fig. 1 contains the results of calculations for the displacement of a macromolecule of the length $M = 25M_e$ (value of parameter $\chi = 0.04$) for this mechanism. 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 is defined as

$$\xi^2 = \frac{6T\tau}{N\zeta B} = 6D_0 \frac{\tau}{B}. \tag{24}$$

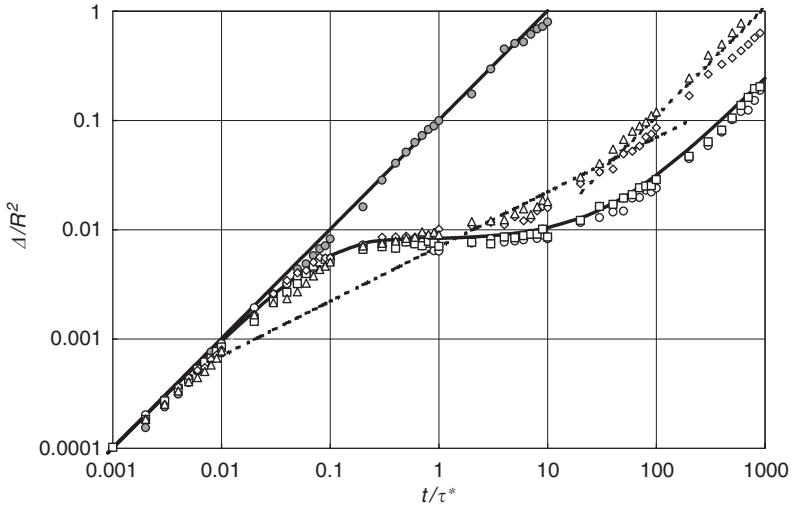

Fig. 1. Displacement of macromolecule vs. time. The solid straight line, accompanied by the filled circles—the results of numerical solution of Eqs. (A.3) and (A.4) at $\Phi_i^\alpha = 0$, depicts the analytical result for the Rouse dynamics. The solid curve represents the other analytical results—the displacement for a macromolecule of length $M = 25M_e$ ($\chi = 0.04$) in an isotropic situation calculated according to Eq. (23) with corresponding (according to relations (17) and (18)) values of parameters $\psi = 8.27$ and $B = 429$. The two dashed straight lines depict the asymptotic results for the displacement $\Delta \sim t^{1/2}$ and $\Delta \sim t$ according to Eq. (20). The open symbols present the results of simulation for the above values of parameters ψ and B and values of parameters of local anisotropy $a_e = 0$, $a_i = 0$ (circles); $a_e = 0$, $a_i = 0.3$ (squares); $a_e = 0.3$, $a_i = 0$ (diamonds) and $a_e = 0.3$, $a_i = 0$ (triangles, $\psi = 0$ in this case).

For large times of observation $t \gg \tau$, the mean displacement of the macromolecule, according to Eq. (23), is unrestricted and proportional to time with the coefficient of diffusion

$$D = D_0 B^{-1} \sim M^{-3.4}. \tag{25}$$

The introduction of local anisotropy in the model of generalised Cerf-Rouse modes changes the situation: mobility of the macromolecular coil increases as can be seen in Fig. 1, so that one can choose a particular value of the coefficient of local anisotropy of external resistance in order to obtain the correspondence with the reptation-tube model. The results of estimation of coefficient of self-diffusion due to simulation for macromolecules with different lengths are shown in Fig. 2. The introduction of local anisotropy practically does not affect the coefficient of diffusion below the transition point M^*, the position of which depends on the coefficient of local anisotropy. For strongly entangled systems ($M > M^*$), the value of the index -2 in the reptation law is connected only with the fact of confinement of macromolecule, and does not depend on the value of the coefficient of local anisotropy. At the particular value $a_e = 0.3$, the simulation reproduces the results of the conventional reptation-tube model (see Eq. (21)) and corresponds to the typical empirical situation ($M^* = 10 M_e$).

So, at a certain value of the coefficient of anisotropy of the external local resistance, the Doi–Edwards theory and the proposed in this paper consideration give the coinciding dependences for $t > (3)(2)\pi^2\tau^*$. Moreover, the theories give practically identical results for the region between points $t \approx \tau^*$ and $t \approx (3)(2)\pi^2\tau^*$, as one can see in Fig. 1. However, the dependences in the intermediate region below $t \approx \tau^*$ are different, and the theories present different physical pictures of diffusion for the intermediate times. According to the proposed theory, a macromolecule begins to feel the environment, when the mean squared displacement, independently on the length of macromolecules of the system, reaches the value

$$\Delta(t) = \xi^2. \tag{26}$$

The deviation of the displacement of a macromolecule from the Rouse behaviour is conventionally considered as a sign of the presence of the entanglements with the neighbouring macromolecules, and the above picture corresponds to the conventional image of the tube as a tube, the diameter of which does not depend on the

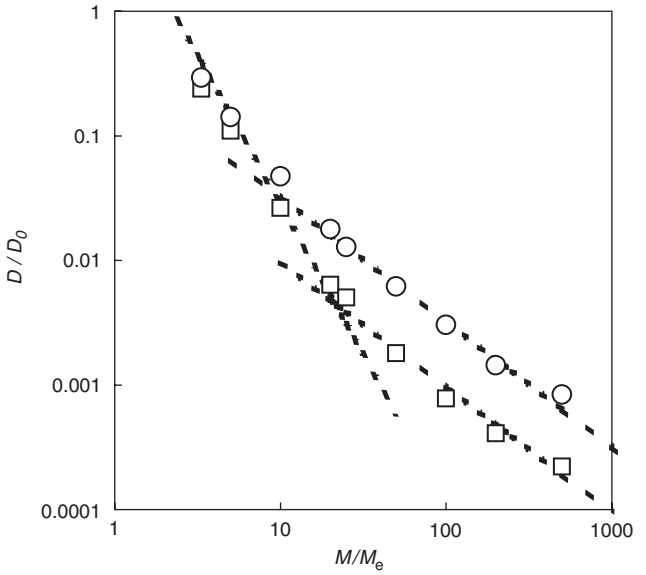

Fig. 2. Coefficient of self-diffusion of a macromolecule. Each point is calculated as the ratio of asymptotic values of the displacement of a macromolecule for large times (see an example of dependence in Fig. 1) to values of displacement for the Rouse case at corresponding values of the parameters B and the values of the other parameters: $\psi = 0$, $a_e = 0.3$, $a_e = 0$ (the circles) and $\psi = 0$, $a_e = 0.1$, $a_e = 0$ (the squares). The slope of the dashed lines is -2.4 for short macromolecules and -1 for long ones, so that the simulation gives the well-known dependence $D \sim M^{-2}$ for coefficient of self-diffusion of macromolecules in strongly entangled systems.

length of macromolecules. In the Doi–Edwards theory, a macromolecule begins to feel the environment at the mean square displacement, which decreases as M^{-1} as the length of macromolecules of the system increases,

$$\Delta(t) = 6D_0\tau_e, \quad \tau_e = \frac{4\pi^2}{3}\frac{\xi^4}{\langle R^2\rangle^2}\,\tau^* \sim M^0. \tag{27}$$

In this case, we have to imagine that the neighbouring entanglements are parted by a distance, which decreases when the length of macromolecules increases. Though this image seems to contradict to the conventional picture of the phenomenon, the decisive sentence must be said by experiment. Nevertheless, one can propose possible corrections to relations (20), which can, for example, have the following approximate form:

$$\Delta(t) = \begin{cases} 6D_0 t, & t < \pi^2\dfrac{\xi^2}{\langle R^2\rangle}\,\tau^*, \\ \xi^2, & \pi^2\dfrac{\xi^2}{\langle R^2\rangle}\,\tau^* < t < \tau^*, \\ 4\xi^2\left(\dfrac{D_0}{\langle R^2\rangle}\,t\right)^{1/2}, & \tau^* < t < \frac{3}{2}\pi^2\tau^*, \\ 6Dt, & t > \frac{3}{2}\pi^2\tau^*. \end{cases} \tag{28}$$

These relations are valid for the strongly entangled systems, when the length of macromolecule $M > 10M_e$. The available [16] molecular-dynamics numerical experiments deal with macromolecules of shorter lengths and can be used neither to confirm nor to reject these relations, also as original relations (20).

3.2. Mobility of the particles of a chain

To find an analytical expression for the mean square displacement $\Delta_\alpha(t)$ of the αth particle of the chain in linear approximation, it is convenient to transform expression

$$\Delta_\alpha(t) = \langle[\boldsymbol{r}^\alpha(t) - \boldsymbol{r}^\alpha(0)]^2\rangle$$

to normal co-ordinates and to separate the zeroth normal co-ordinate, so that one has the relation

$$\Delta_\alpha(t) = \Delta(t) + 2\sum_{\gamma=1}^{N} Q_{\alpha\gamma}Q_{\alpha\gamma}(\langle\boldsymbol{\rho}^\gamma(0)\boldsymbol{\rho}^\gamma(0)\rangle - \langle\boldsymbol{\rho}^\gamma(t)\boldsymbol{\rho}^\gamma(0)\rangle), \tag{29}$$

where the transformation matrix $Q_{\alpha\gamma}$ is given by Eq. (A.13). The displacement of the centre of mass of the macromolecule $\Delta(t)$ in this approximation is defined by Eq. (23), and the equilibrium correlation functions in the overdamped regime ($m = 0$) are provided [7] by relations

$$\langle\rho_i^\alpha(t)\rho_k^\alpha(0)\rangle = \frac{\delta_{ik}}{2\mu\lambda_\alpha}\left[S_\alpha^+\exp\left(-\frac{t}{2\tau_\alpha^+}\right) - S_\alpha^-\exp\left(-\frac{t}{2\tau_\alpha^-}\right)\right], \tag{30}$$

$$S_\alpha^\pm = \frac{\tau_\alpha^R(1+B+E) - \tau_\alpha^\mp}{\tau_\alpha^+ - \tau_\alpha^-}, \quad 2\tau_\alpha^\pm = \tau_\alpha \pm \left(\tau_\alpha^2 - 2\tau\tau_\alpha^R\right)^{1/2},$$

$$\tau_\alpha = \frac{\tau}{2} + \tau_\alpha^R(1+B+E) = \tau^* B\left(\chi + \frac{1}{\alpha^2}(1+E/B)\right), \quad \chi = \frac{\tau}{2B\tau^*}. \tag{31}$$

The modified Cerf–Rouse modes of a macromolecule in an entangled system determine two conformation relaxation branches τ_α^+ and τ_α^-.

As an example, the time dependences of the displacement of the mass centre and the central particle of a chain, due to Eqs. (23) and (29), are shown in Fig. 3 alongside with the results of simulation for certain values of the parameters. The dependences are characterised by the different mobility for short and long times of observation. The displacement of any particle of the chain is similar to the displacement of the entire macromolecule. The difference between analytical and simulation results in the region of large times is

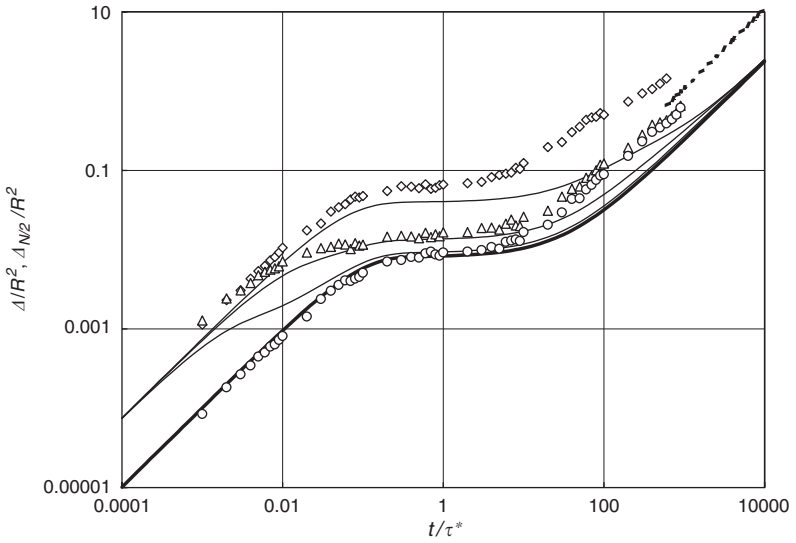

Fig. 3. Displacement of the central particle of a chain. The results for a macromolecule of the length $M = 25M_e$ ($\chi = 0.04$, $B = 429$). Analytical results available in the linear approximation are depicted for displacement of the centre of mass by the thick solid line and for displacement of the central particle of the chain by the thin lines for different values of ψ: 0 (the top curve), 8.27 and 30. The points show the results of numerical calculation of the displacement of the centre of mass (circles) and the central particle of the chain at the above values of the parameter B, values $a_e = 0.3$, $a_i = 0$ and different values of ψ: $\psi = 0$ for the diamonds and $\psi = 8.27$ for the triangles. In the region of big times, the simulation results approach the dashed line—the displacement due to the reptation-tube theory.

connected solely with the influence of the parameter of local anisotropy. The mobility of the mass centre of a macromolecule is not affected by the forces of internal resistance, in particular, by the coefficient ψ. However, the mobility of the separate particles of the chain depends on the coefficient of internal resistance ψ. One can see in Fig. 3 that the displacement of the central particle of the chain is the closer to the displacement of the mass centre, the bigger the coefficient of internal resistance ψ. The increase in internal resistance is followed by increase in confinement of particles of the chain. It means that, at $E/B \gg 1$, the mean displacement of every Brownian particle in a chain is severely restricted: the particle does not go further that the distance ξ for a time τ/B, and the macromolecule appears to be effectively localised, so that relation (24) can be taken, indeed, as a definition of the radius of the tube postulated in the Doi–Edwards model. 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.

3.3. Conformational relaxation

The rates of relaxation $\tau_\gamma(t)$ at the moment t, or, in other words, the current relaxation times of the macromolecular coil can be directly calculated as

$$\tau_\gamma(t) = -\frac{1}{2}\left(\frac{\mathrm{d}\,\log(M_\gamma(t)/M_\gamma(0))}{\mathrm{d}t}\right)^{-1}, \quad \gamma = 1, 2, \ldots, N, \tag{32}$$

where $M_\gamma(t) = \langle \boldsymbol{\rho}^\gamma(0)\boldsymbol{\rho}^\gamma(t)\rangle/3$ is an equilibrium correlation function of the normal co-ordinate γ.

For the modified Cerf-Rouse dynamics (1)–(4) in linear approximation (8), the equilibrium correlation functions are given by Eqs. (30), which contain two conformation relaxation times τ_α^+ and τ_α^- for every mode. The largest relaxation times

$$\tau_\alpha^+ \approx \frac{\tau}{2} + \tau_\alpha^{\mathrm{R}}(1 + B + E), \quad \alpha = 1, 2, 3, \ldots \tag{33}$$

have appeared to be unrealistically large for strongly entangled systems, whereas the reptation-tube model gives reasonable estimates of relaxation times. According to Doi and Edwards [15, p. 196], the time behaviour

of the equilibrium correlation function $M_\alpha(t)$ is described by a formula which is identical to the formula for a chain in viscous liquid, while the Rouse relaxation times are replaced by the reptation relaxation times

$$M_\alpha(t) = \frac{1}{2\mu\lambda_\alpha}\exp\left(-\frac{t}{2\tau_\alpha^{\mathrm{rep}}}\right), \tag{34}$$

$$\tau_\alpha^{\mathrm{rep}} = \frac{\zeta\xi^2 N^3}{2\pi^2 T}\frac{1}{\alpha^2} = \frac{3\langle R^2\rangle}{\xi^2}\frac{\tau^*}{\alpha^2} = \frac{3}{2}\frac{\pi^2}{\chi}\frac{\tau^*}{\alpha^2} \sim M^3, \quad \alpha = 1, 2, \ldots, \ll N, \tag{35}$$

where ζ is the friction coefficient of a Brownian particle, 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 in 'monomer' liquid—characteristic Rouse relaxation time.

The linear normal co-ordinates appear to be useful also in the considered non-linear case, though, in this case, the modes are connected with each other. The rates of relaxation for the first and the third modes, which are calculated from correlation functions (30) and (34) for the chain with $M = 25M_e$, are depicted in Fig. 4 by solid and dashed lines, correspondingly. The simulation of linear case reproduces (with large scattering, so as the changes of the correlation functions in this region are small) the theoretical dependence of the relaxation rates on the current time. The introduction of the local anisotropy of external resistance alone does not affect the relaxation times, in contrast to the local anisotropy of the internal resistance. The latter provokes changes of the largest relaxation times of the macromolecular coil, which is the bigger the bigger the coefficient of the local anisotropy of external resistance. Asymptotic values of the relaxation times are estimated for each case as the mean values of the numbers of the rate of relaxation in the interval from $0.7\,\tau^*$ to $10\,\tau^*$. A particular choice of the coefficients $a_e = 0.3$ and $a_i = 0.06$ determines the value $\tau_1 = 417\tau^*$ for the relaxation time of the first mode, which is close to the reptation relaxation time $370\,\tau^*$. The calculated relaxation times of the third mode: $\tau_3 = 315\,\tau^*$ is a few times as much as the corresponding reptation relaxation time $41.1\,\tau^*$, which indicates that the dependence of the relaxation times on the mode label is apparently different from the law (35). It is clearly seen in Fig. 5, where the dependence of the relaxation times of the first six modes of a macromolecule on the coefficient of internal anisotropy is shown. The relaxation times of different modes are getting closer to each

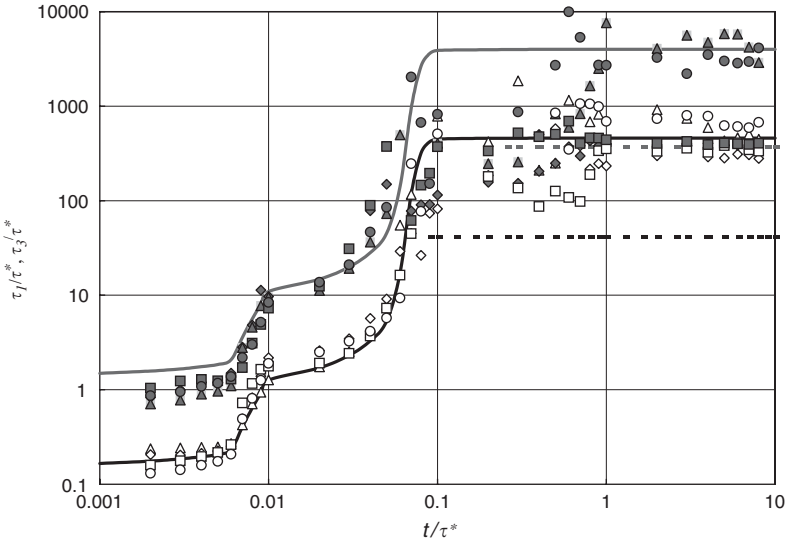

Fig. 4. The rate of relaxation of a macromolecule. The rates of relaxation of the first and the third modes of a macromolecule, estimated, due to relations (32), for the macromolecule of length $M = 25M_e$ ($\chi = 0.04$, $B = 429$, $\psi = 8.27$). The results derived from analytical correlation function (30) are depicted by solid lines. By straight dashed lines, the values of the relaxation times due to the Doi–Edwards model are presented. The filled (for the first mode) and empty (for the third mode) points depict the results of simulation for above values of parameters ψ and B and values of parameters of local anisotropy $a_e = 0$, $a_i = 0$ (circles); $a_e = 0$, $a_i = 0.3$ (triangles); $a_e = 0$, $a_i = 0.1$ (diamonds) and $a_e = 0.3$, $a_i = 0.06$ (squares).

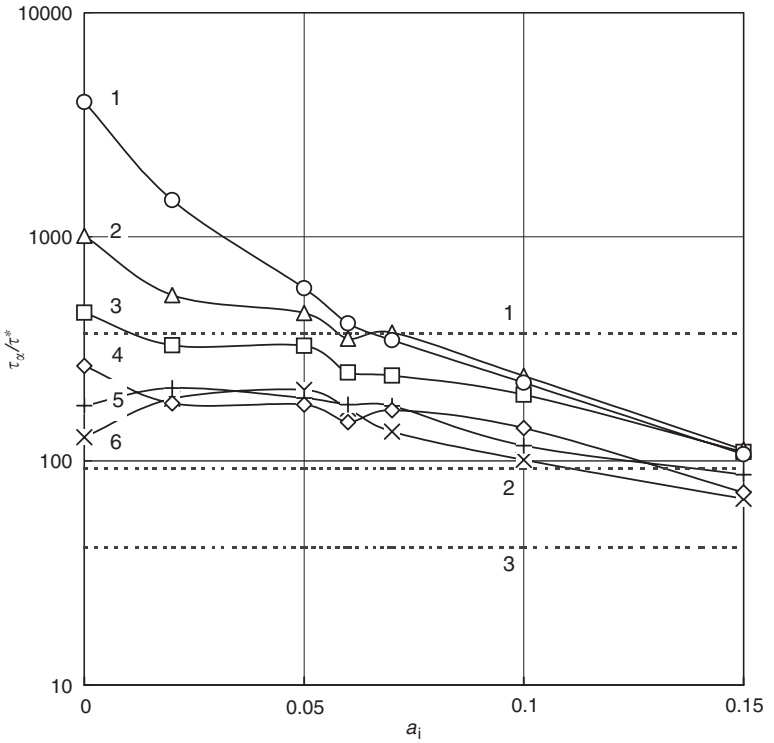

Fig. 5. The relaxation times vs. internal anisotropy. Each point is calculated as the asymptotic value of the rate of relaxation for large times (see examples of dependences in Fig. 4) for a macromolecule of length $M = 25M_e$ ($\chi = 0.04$, $B = 429$, $\psi = 8.27$) with the value of the coefficient of external local anisotropy: $a_e = 0.3$. The dashed lines reproduce the values of the relaxation times of the macromolecule due to the reptation-tube model. The labels of the modes are shown at the lines.

other with increase of the coefficient of internal anisotropy. The values of the largest relaxation time of the first mode for different molecular weights are shown in Fig. 6.The results demonstrate a drastic decrease in values of the largest relaxation times for strongly entangled systems induced by introduction of local anisotropy. The position of the transition point depends on the coefficient of internal anisotropy and is independent on the diffusion transition point discussed in Section 3.1. It can be estimated [8], due to measurements of viscoelastic properties, as $M^* \approx (4.6 - 12.0)M_e$, which corresponds to values of the coefficient of internal anisotropy 0.05–0.15 at the value of the coefficient of external anisotropy $a_e = 0.3$. The evaluation of relaxation times could not be done with great accuracy in this investigation, so that the dependence of relaxation times both on the mode label and on the length of macromolecules remains to be studied. A more detailed investigation of effects of the local anisotropy on the relaxation processes might require developing special methods and is left for the future.

3.4. Quasi-elastic neutron scattering

Empirical evidence of the confinement of particles of the chain is provided by neutron scattering from specially prepared samples of polymers [17,18]. In a reasonable approximation, the scattering function on a single macromolecule can be calculated as

$$S(\boldsymbol{k}, t) = \frac{1}{N+1} \sum_{\alpha,\gamma} \exp\left(-\frac{1}{6} k^2 \sum_{i=1}^{3} \langle (r_i^\alpha(t) - r_i^\gamma(0))^2 \rangle \right). \tag{36}$$

The double sum in Eq. (36) is evaluated over all Brownian particles of the macromolecule. In the above equation, $\boldsymbol{k}$ is the vector in the direction of the scattering, having the length $k = (4\pi/\lambda)\sin(\theta/2)$, where λ is the

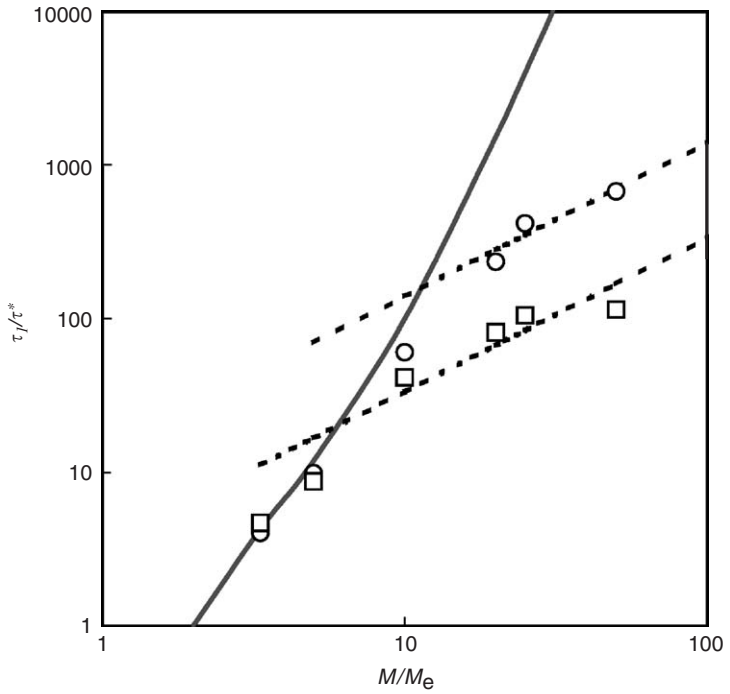

Fig. 6. The largest relaxation time of a macromolecule. Each point is calculated as the asymptotic value of the rate of relaxation for large times (see examples of dependences in Fig. 4) for different molecular weights with corresponding values of the parameters B and ψ. The values of the coefficients of local anisotropy are: $a_e = 0.3$, $a_i = 0.06$ for the circles and $a_e = 0.3$, $a_i = 0.15$ for the squares. The solid line depicts the analytical results for linear approximation. The dashed lines with the slope 1 reproduce the well-known dependence $\tau_1 \sim M^3$ for the relaxation time of macromolecules in strongly entangled systems.

wavelength of particles of a initial beam and θ is the scattering angle. If one excludes the correlation between particles with different labels, scattering function (36) takes the form

$$S(\boldsymbol{k}, t) = \frac{1}{N+1} \sum_{\alpha=0}^{N} \exp\left(-\frac{1}{6} k^2 \Delta_\alpha(t)\right), \tag{37}$$

where the mean square displacement $\Delta_\alpha(t) = \langle[\boldsymbol{r}^\alpha(t) - \boldsymbol{r}^\alpha(0)]^2\rangle$ of the particle α is determined by expression (29).

The scattering function (37) is shown in Fig. 7 by the dashed lines. There are no available analytical results for function (36), the dependences, shown in Fig. 7 by solid lines, are obtained by simulation for $a_e = 0$, $a_i = 0$. The scattering functions are close to each other, in both cases they are characterised by a step or a plateau, which exists at large values of the parameter of internal resistance ψ. The value of the function on the plateau depends also on the external and internal local anisotropy, however, at typical values (see the previous Sections) of coefficients $a_e = 0.3$, $a_i = 0.1$, the effect is small. One can easily see that all the properties of functions $\Delta_\alpha(t)$ in Fig. 3 are reflected in the scattering functions: the step in the scattering functions (Fig. 7) corresponds to the plateau on the curve of the displacement of the particles (Fig. 3). For very long macromolecules, the value of the scattering function in the plateau region is connected directly with the intermediate length ξ

$$S(k, t) = \exp\left(-\frac{1}{6} k^2 \xi^2\right), \quad \frac{\tau}{B} < t < \tau. \tag{38}$$

The step on the scattering function, which is revealed in empirical observations [17,18], is apparently connected with confinement of the macromolecule in 'the tube', and is an effect of the first order in respect to co-ordinates in the equations of macromolecular dynamics. The introduction of the terms of higher order,

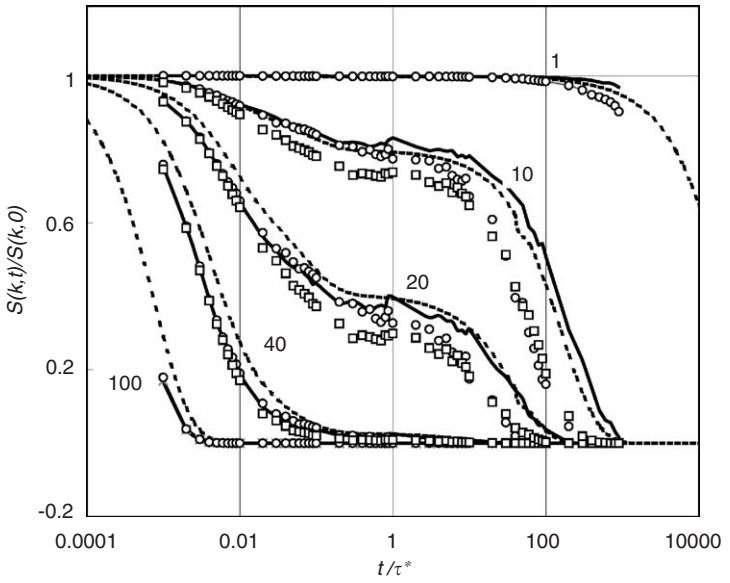

Fig. 7. Scattering function of a macromolecule. The results for a macromolecule of the length $M = 25M_e$ ($\chi = 0.04$, $B = 429, \psi = 8.27$). The analytical results due to Eq. (37), in which $\Delta_x(t)$ is taken as Eqs. (29)–(21), are shown by dashed lines. The solid lines and points show the results of calculation of function (36) due to the simulation for the above values of parameters B and ψ and for values $a_e = 0$, $a_i = 0$ (solid lines), $a_e = 0.3$, $a_i = 0$ (open circles) and $a_e = 0.3$, $a_i = 0.3$ (open squares). The values of k are shown at the curves.

describing the motion of the macromolecule along its axis (the reptation motion), gives the corrections to the dependence in the region of large times.

4. Conclusion

Thus, one can see that a possible extension of the conventional reptation-tube model of macromolecular dynamics can be formulated as the Rouse model in the presence of a random dynamic force. The generalised model provides the confinement of a macromolecule in the tube and easier (reptation) motion of the macromolecule along its contour—the features, which were envisaged by Edwards [1] and de Gennes [2] for the entangled systems. The results of the conventional reptation-tube model for both mobility and relaxation times of macromolecular coil follow from the generalised model at particular choice of the parameters of the model. It does not mean, of course, that the particles of the chain are moving in the way prescribed by the conventional reptation-tube model. Both the radius of the tube and the positions of the particles in the Doi–Edwards model are, in fact, mean quantities from the point of view of the considered model of underlying stochastic motion. The radius of the tube of the conventional reptation-tube theory is interpreted as the mean displacement of the particles of the chain in the plateau region—this is an intermediate length ξ, connected with the correlation time τ (Eq. (24)), and the mean positions of selected particles can be calculated on the base of dynamic equations (5), (6), (12) and (13) to establish a complete correspondence to the conventional reptation-tube model. The direct introduction of the mean quantities to describe dynamics of macromolecule led to the oversimplified, mechanistic model, which is believed [4] to work well for very long macromolecules ($M \gg 10M_e$), but needs in amendments (the constraint-release mechanism, contour-length fluctuations and so on) to describe the behaviour of shorter macromolecules, while the model is not applicable below the transition point ($M < 10M_e$) at all [8]. In contrast to it, the generalised model is relevant to the systems of macromolecules with the lengths above $2M_e$. Whereas one needs only in isotropic stochastic motion to explain dynamic effects in weakly entangled systems (the length of macromolecules $M < 10M_e$), the introduction of local anisotropy of motion, which leads to motion of the macromolecule along its contour (the reptation

motion), is necessary for consistent explanation of dynamic effects in strongly entangled linear polymers (the length of macromolecules $M > 10M_e$).

The generalised description contains, apart of the conventional characteristic Rouse relaxation time τ^* and the three mesoscopic parameters introduced earlier in the linear macromolecular dynamics: τ, B and E, two more parameters characterising the local anisotropy of mobility. While the first three parameters were identified due to the requirement of correspondence of the derived results to empirical situations, the parameters of the local anisotropy can be identified due to the requirement of correspondence of the derived results to the results of the Doi–Edwards theory. The developed description does not require specific hypotheses; it is a sort of phenomenological (mesoscopic) description, which allows one to get a consistent interpretation of experimental data connected with dynamic behaviour of linear macromolecules in both weakly and strongly entangled polymer systems in terms of a few phenomenological (or better, mesoscopic) parameters. The adequate mesoscopic equation allows us to develop theory of different relaxation phenomena (diffusion, viscoelasticity, optical birefringence, neutron scattering, dielectric relaxation and so on) and, in particular, 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 entangled systems. Apart of empirical justification, the mesoscopic effective-field approach itself is needed in proper microscopic justification. The characteristics of reptation motion can be also deduced from geometrical and topological aspects of macromolecular dynamics [19,20], so that the parameters of the theory eventually could be linked with details of structure of entangled systems. It was convincingly shown by simulating the behaviour of the systems numerically, that the intermediate length correlates with characteristics of topology [21]. One can believe that the developing methods [19,20,22,23] can be helpful to bring a microscopic justification of a single-macromolecule equation in the entangled systems.

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Appendix A. Method of simulation

A.1. Dimensionless form of dynamic equations

It is convenient to use the time scale τ^* and the length scale $R = \langle R^2 \rangle^{0.5}$ to define dimensionless variables by the relations

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{1}{\tau^*}\frac{\mathrm{d}}{\mathrm{d}s},$$

$$r_i^\alpha = RR_i^\alpha,$$

$$u_i^\alpha = \frac{R}{\tau^*}U_i^\alpha,$$

$$F_i^\alpha + G_i^\alpha + \tilde{\phi}_i^\alpha(t) = \frac{\zeta R}{\tau^*}\Phi_i^\alpha,$$

so that the system of Eqs. (5), (6), (12) and (13) for macromolecular dynamics can be written in the form

$$\frac{\mathrm{d}R_i^\alpha}{\mathrm{d}s} = U_i^\alpha,$$

$$\frac{m}{\zeta\tau^*}\frac{\mathrm{d}U_i^\alpha}{\mathrm{d}s} = -U_i^\alpha + \Phi_i^\alpha - \frac{N^2}{2\pi^2}A_{\alpha\gamma}R_i^\gamma + \bar{f}_i^\alpha(s),$$

$$2\chi B\,\frac{\mathrm{d}\Phi_i^\alpha}{\mathrm{d}s} = -\Phi_i^\alpha - BH_{ij}^{\alpha\gamma}U_j^\gamma - EG_{ij}^{\alpha\gamma}U_j^\gamma + \tilde{f}_i^\alpha(s),$$

$$\bar{f}_i^\alpha(s) = \frac{\tau^*}{\zeta R}\,\bar{\phi}_i^\alpha(\tau^* s), \quad \tilde{f}_i^\alpha(s) = \chi B\,\frac{\mathrm{d}\tilde{\phi}_i^\alpha}{\mathrm{d}s} + \tilde{\phi}_i^\alpha(s),$$

$$\langle \bar{f}_i^\gamma(s)\bar{f}_j^\mu(s')\rangle = \left(\frac{\tau^*}{\zeta R}\right)^2 \langle \bar{\phi}_i^\gamma(\tau^* s)\bar{\phi}_j^\mu(\tau^* s')\rangle = \frac{N}{3\pi^2}\,\delta_{\gamma\mu}\delta_{ij}\delta(s-s'), \tag{A.1}$$

$$\langle \tilde{f}_i^\gamma(s)\tilde{f}_j^\mu(s')\rangle = \frac{N}{3\pi^2}\,B(H_{ij}^{\gamma\mu} + \psi G_{ij}^{\gamma\mu})\delta(s-s'). \tag{A.2}$$

The inertial effects can be neglected ($m = 0$), so that the above system of equations can be simplified

$$\frac{\mathrm{d}R_i^\alpha}{\mathrm{d}s} = U_i^\alpha,$$

$$\frac{\mathrm{d}\Phi_i^\alpha}{\mathrm{d}s} = \frac{1}{2\chi B}(-\Phi_i^\alpha - BH_{ij}^{\alpha\gamma}U_j^\gamma - EG_{ij}^{\alpha\gamma}U_j^\gamma + \tilde{f}_i^\alpha(s)),$$

$$U_i^\alpha = \Phi_j^\alpha - \frac{1}{2}\,\frac{N^2}{\pi^2}\,A_{\alpha\gamma}R_j^\gamma + \bar{f}_j^\alpha(s). \tag{A.3}$$

To satisfy relations (A.1) and (A.2), the random processes have to be given as

$$\bar{f}_i^\gamma(s) = \left(\frac{N}{3\pi^2}\right)^{1/2}\bar{g}_i^\gamma(s),$$

$$\tilde{f}_i^\gamma(s) = \left(\frac{N}{3\pi^2}B\right)^{1/2}\left\{(A_\mathrm{e}\delta_{ij} + C_\mathrm{e}e_i^\gamma e_j^\gamma)\tilde{g}_{\mathrm{e}j}^\gamma(s) + \frac{\sqrt{\psi}}{N}\left[(1+N)(A_\mathrm{i}\delta_{ij} + C_\mathrm{i}e_i^\gamma e_j^\gamma)\tilde{g}_{\mathrm{i}j}^\gamma(s) - \sum_{\alpha=0}^{N}(A_\mathrm{i}\delta_{ij} + C_\mathrm{i}e_i^\alpha e_j^\alpha)\tilde{g}_{\mathrm{i}j}^\alpha(s)\right]\right\},$$

$$A_\mathrm{e} = \sqrt{1 + a_\mathrm{e}/2}, \quad C_\mathrm{e} = -A_\mathrm{e} + \sqrt{1 - a_\mathrm{e}},$$

$$A_\mathrm{i} = \sqrt{(1+a_\mathrm{i})N/2(1+N)}, \quad C_\mathrm{i} = -A_\mathrm{i} + \sqrt{(1-a_\mathrm{i})N/(1+N)}, \tag{A.4}$$

where $\bar{g}_i^\gamma(s)$, $\tilde{g}_{\mathrm{e}j}^\gamma(s)$ and $\tilde{g}_{\mathrm{i}j}^\gamma(s)$ are independent Gaussian random processes with the dispersions equal to unity.

A.2. Algorithm of numerical calculations

We use the simplest method (the Eyler method, with the step of integration h) to solve Eqs. (A.3) numerically

$$R_i^\alpha(s+h) = R_i^\alpha(s) + hU_i^\alpha,$$

$$\Phi_i^\alpha(s+h) = \Phi_i^\alpha(s) + \frac{h}{2\chi}\left(-\frac{1}{B}\,\Phi_i^\alpha - H_{ij}^{\alpha\gamma}U_j^\gamma - \psi G_{ij}^{\alpha\gamma}U_j^\gamma + \Delta\tilde{f}_i^\alpha(s)\right),$$

$$U_i^\alpha = \Phi_j^\alpha - \frac{N^2}{2\pi^2}\,A_{\alpha\gamma}R_j^\gamma + \Delta\bar{f}_j^\alpha(s). \tag{A.5}$$

The random forces are defined here as

$$\Delta\bar{f}_j^\alpha(s) = \frac{1}{h}\int_s^{s+h}\bar{f}_j^\alpha(u)\,\mathrm{d}u, \quad \Delta\tilde{f}_j^\alpha(s) = \frac{1}{hB}\int_s^{s+h}\tilde{f}_j^\alpha(u)\,\mathrm{d}u.$$

Calculating the dispersions of the random processes $\Delta\bar{f}_j^{\alpha}(s)$ and $\Delta\tilde{f}_i^{\alpha}(s)$, one has to take into account relations (A.1) and (A.2) for the random forces in the continuous case, so that in the discrete approach one has

$$\langle\Delta\bar{f}_i^{\gamma}(s)\Delta\bar{f}_j^{\mu}(s')\rangle = \frac{N}{3\pi^2 h}\,\delta_{\gamma\mu}\delta_{ij}\delta(s-s'), \tag{A.6}$$

$$\langle\Delta\tilde{f}_i^{\gamma}(s)\Delta\tilde{f}_j^{\mu}(s')\rangle = \frac{N}{3\pi^2 hB}(H_{ij}^{\gamma\mu}+\psi G_{ij}^{\gamma\mu})\delta(s-s'). \tag{A.7}$$

It is easy to see that, the expressions for the random forces have to be similar to relations (A.4), that is

$$\Delta\bar{f}_i^{\gamma}(s) = \left(\frac{N}{3\pi^2 h}\right)^{1/2}\bar{g}_i^{\gamma}(s), \tag{A.8}$$

$$\Delta\tilde{f}_i^{\gamma}(s) = \left(\frac{N}{3\pi^2 hB}\right)^{1/2}\left\{(A_{\mathrm{e}}\delta_{ij}+C_{\mathrm{e}}e_i^{\gamma}e_j^{\gamma})\tilde{g}_{\mathrm{e}j}^{\gamma}(s) + \frac{\sqrt{\psi}}{N}\left[(1+N)(A_{\mathrm{i}}\delta_{ij}+C_{\mathrm{i}}e_i^{\gamma}e_j^{\gamma})\tilde{g}_{\mathrm{i}j}^{\gamma}(s) - \sum_{\alpha=0}^{N}(A_{\mathrm{i}}\delta_{ij}+C_{\mathrm{i}}e_i^{\alpha}e_j^{\alpha})\tilde{g}_{\mathrm{i}j}^{\alpha}(s)\right]\right\}. \tag{A.9}$$

To solve the system of Eqs. (A.5), initial values of the co-ordinates and the extra random force has to be chosen. We accept that

$$R_i^0(0) = 0,$$

$$R_i^{\alpha}(0) = R_i^{\alpha-1}(0) + \frac{1}{(3N)^{0.5}}\,g_i^{\alpha},\quad \alpha = 1,2,\ldots,N,\quad i = 1,2,3, \tag{A.10}$$

$$\Phi_i^{\alpha}(0) = 0,\quad \alpha = 0,1,2,\ldots,N,\quad i = 1,2,3, \tag{A.11}$$

where g_i^{α} is a Gaussian random process with dispersion equal to unity.

As a result of calculation, one has the positions of the particles

$$R_i^{\alpha}(s),\quad \alpha = 1,2,\ldots,N,\quad i = 1,2,3,\quad s = 0,h,2h,3h,\ldots\ .$$

To analyse the phenomena of diffusion and relaxation, it is convenient also to use the normal co-ordinates defined as

$$\rho_i^{\gamma}(s) = Q_{\alpha\gamma}R_i^{\alpha}(s),\quad \gamma = 0,1,2,\ldots,N,\quad i = 1,2,3. \tag{A.12}$$

The transformation matrix Q is assumed orthogonal and normalised. In this case, the components of the transformation matrix are defined as

$$Q_{\alpha\gamma} = \left(\frac{2-\delta_{0\gamma}}{N+1}\right)^{1/2}\cos\frac{(2\alpha+1)\gamma\pi}{2(N+1)}. \tag{A.13}$$

Note that steady-state situations are investigated, so that the end-to-end distance $\langle R^2\rangle$ and the mean gyration radius

$$S^2 = \frac{1}{1+N}\sum_{\alpha=0}^{N}\sum_{i=1}^{3}(R_i^{\alpha}-Q_i)^2,\quad Q_i = \frac{1}{1+N}\sum_{\alpha=0}^{N}R_i^{\alpha} \tag{A.14}$$

must be constant on average. The mean kinetic energy for one degree of freedom also must be constant

$$\frac{1}{3(1+N)}\sum_{\alpha=0}^{N}\sum_{i=1}^{3}U_i^{\alpha}U_i^{\alpha}\sim const. \tag{A.15}$$

The above conditions allow one to monitor whether the fluctuation–dissipation relations are valid during calculations.

A.3. The mean quantities

The calculated co-ordinates allow us to estimate mean value of any, depended on co-ordinates, quantity. For example, the displacements of the mass centre of the macromolecule and each particle of the chain are calculated as

$$\Delta(t) = \langle R^2 \rangle \sum_{i=1}^{3} \langle [Q_i(s) - Q_i(0)]^2 \rangle, \tag{A.16}$$

$$\Delta_\alpha(t) = \langle R^2 \rangle \sum_{i=1}^{3} \langle [R_i^\alpha(t) - R_i^\alpha(0)]^2 \rangle, \quad \alpha = 0, 1, \ldots, N, \tag{A.17}$$

where the centre of mass of the chain Q_i is proportional, according to Eqs. (A.12) and (A.14), to the normal co-ordinate corresponding to the zeroth eigenvalue (the diffusion mode)

$$Q_i(s) = \left(\frac{1}{1+N}\right)^{1/2} \rho_i^0(s) = \frac{1}{1+N} \sum_{\alpha=0}^{N} R_i^\alpha(s), \quad i = 1, 2, 3. \tag{A.18}$$

The results of simulation of different quantities are shown in Figs. 1–6. The calculations are fulfilled for the number of subchains $N = 10$ at the step of integration $h = 0.001$, the number of realisations was different from 100 to 10,000 in different cases. The results for the entire chain do not depend on the arbitrary number N of subchains, though mobility of separate particle of the chain depends on the number N of subchains as N^{-1}.

References

[1] S.F. Edwards, Statistical mechanics with topological constraints. I, Proc. Phys. Soc. 91 (1967) 513–519.
[2] P.G. De Gennes, Reptation of a polymer chain in the presence of fixed obstacles, J. Chem. Phys. 55 (1971) 572–579.
[3] M. Doi, S.F. Edwards, Dynamics of concentrated polymer systems. Part 1. Brownian motion in the equilibrium state, J. Chem. Soc.: Faraday Trans. II 74 (1978) 1789–1801.
[4] T.P. Lodge, Reconciliation of the molecular weight dependence of diffusion and viscosity in entangled polymers, Phys. Rev. Lett. 83 (16) (1999) 3218–3221.
[5] A.E. Likhtman, T.C.B. McLeish, Quantitative theory for linear dynamics of linear entangled polymers, Macromolecules 35 (2002) 6332–6343.
[6] S.J. Park, R.G. Larson, Tube dilation and reptation in binary blends of monodisperse linear polymers, Macromolecules 37 (2004) 597–604.
[7] V.N. Pokrovskii, The Mesoscopic Theory of Polymer Dynamics, Kluwer Academic Publishers, Dordrecht, 2000.
[8] Yu.A. Altukhov, V.N. Pokrovskii, G.V. Pyshnograi, On the difference between weakly and strongly entangled linear polymers, J. Non-Newtonian Fluid Mech. 121 (2004) 73–86.
[9] H. Giesekus, Stressing behaviour in simple shear flow as predicted by a new constitutive model for polymer fluids, J. Non-Newtonian Fluid Mech. 12 (3) (1983) 367–374.
[10] B. Dünweg, Langevin methods, in B. Dünweg, D.P. Landau, A. Milchev (Eds.), Computer Simulations of Surfaces and Interfaces, Proceedings of the NATO Advanced Study Institute/ Euroconference, Albena, Bulgaria, September 2002, Kluwer Academic Publishers, Dordrecht, 2003, pp. 77–92.
[11] G. Migliorini, V.G. Rostiashvili, T.A. Vilgis, Polymer chain in a quenched random medium: slow dynamics and ergodicity breaking, Eur. Phys. J. B 33 (2003) 61–73.
[12] A. Milchev, V.G. Rostiashvili, T.A. Vilgis, Dynamics of a polymer in a quenched random medium: a Monte Carlo investigation, Europhys. Lett. 66 (2004) 384–390.
[13] S.-Q. Wang, Chain dynamics in entangled polymers: diffusion versus rheology and their comparison, J. Polym. Sci. Part: B Polym. Phys. 41 (2003) 1589–1604.
[14] H. Tao, T.P. Lodge, E.D. von Meerwall, Diffusivity and viscosity of concentrated hydrogenated polybutadiene solutions, Macromolecules 33 (2000) 1747–1758.
[15] M. Doi, S.F. Edwards, The Theory of Polymer Dynamics, Oxford University Press, Oxford, 1986.
[16] W. Paul, G.D. Smith, Structure and dynamics of amorphous polymers: computer simulation compared to experiment and theory, Rep. Prog. Phys. 67 (2004) 1117–1185.
[17] J.S. Higgins, J.E. Roots, Effect of entanglement on the single-chain motion of polymer molecules in melt samples observed by neutron scattering, J. Chem. Soc.: Faraday Trans. II 81 (1985) 757–767.

[18] D. Richter, B. Farago, L.J. Fetters, J.S. Huang, B. Ewen, C. Lartique, Direct microscopic observation of the entanglement distance in a polymer melt, Phys. Rev. Lett. 64 (1990) 1389–1392.
[19] A.L. Kholodenko, Reptation theory: geometrical and topological aspects, Macromol. Theory Simul. 5 (1996) 1031–1064.
[20] A.L. Kholodenko, T.A. Vilgis, Some geometrical and topological problems in polymer physics, Phys. Rep. 298 (5–6) (1998) 251–370.
[21] R. Everaers, S.K. Sukumaran, G.S. Grest, C. Svaneborg, A. Sivasubramanian, K. Kremer, Rheology and microscopic topology of entangled polymeric liquids, Science 303 (2004) 823–826.
[22] V.G. Rostiashvili, M. Rehkopf, T.A. Vilgis, The Hartree approximation in dynamics of polymeric manyfolds in the melt, J. Chem. Phys. 110 (1) (1999) 639–651.
[23] N.F. Fatkullin, R. Kimmich, M. Kroutieva, The twice-renormalised Rouse formalism of polymer dynamics: segment diffusion, terminal relaxation, and nuclear spin-lattice relaxation, J. Exp. Theor. Phys. 91 (2000) 150–166.