

The reptation and diffusive modes of motion of linear macromolecules

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Abstract

It is shown, that there is a length of macromolecule $M^* \approx 10M_e$, where M_e is 'the length of the macromolecule between adjacent entanglements', above which macromolecules of a melt can be considered as obstacles to motion of each other, and the macromolecules reptate. The transition to reptation mode of motion is determined by both topological restrictions and local anisotropy of motion. The investigation confirms that the reptation motion determines the molecular-weight dependence of self-diffusion coefficient of macromolecules in melts as M^{-2} .

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36.20-r Macromolecules and polymer molecules

61.25Hq Polymer solutions and melts - Diffusion

83.10.Mj Molecular dynamics, Brownian dynamics

Key words: Diffusion; Mesoscopic approach; Modified Rouse-Cerf modes; Polymer dynamics; Polymer solutions and melts; Relaxation of macromolecule; Reptation; Viscoelasticity

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Introduction. To interpret the diffusion and relaxation behaviour of macromolecules in the entangled linear polymers (polymer melts) some modelling situations were considered [1,2]. It was shown by de Gennes [1], that in the case, when motion of a macromolecule is confined with fixed obstacles, so that it is moving like a snake by reptation, the coefficient of diffusion of the mass centre of the macromolecule appears to be reciprocally proportional to its squared length. So as this law of diffusion appeared to be valid for long macromolecules in polymer melts as well, one concluded that in the polymer melts, the neighbouring macromolecules can be considered as mobile obstacles for a tagged macromolecule, which is also moving via reptation. It was a successful hypothesis, though repeatedly some discussion emerged [3], whether a macromolecule reptates in a melt and, if reptates, what is the length of macromolecule that marks the beginning of reptation.

A direct solution of the problem of simultaneous motion of many macromolecules, which could bring a certain answer to the question, whether a macromolecule reptates and under which conditions, appeared a rather difficult problem. The accurate solution is apparently available [4] only for short chains, when reptation motion is not expected. For the longer macromolecules, the most resultant approach appears to be a mean-field one, when the reaction of many surrounding macromolecules on the selected macromolecule is approximated as an average reaction of some medium, the property of which are chosen in proper way [2,5]. In the conventional reptation-tube model [2], the surrounding was schematised as a tube and the reptation of the macromolecule in the flexible tube is postulated; this allowed one to explain some effects of dynamic behaviour of polymers, but says nothing about the conditions when the tube and reptation exist. In contrast to it, the model of underlying stochastic motion [5 - 7] led to justifying the concepts of tube and reptation and allowed one to calculate an intermediate length, which has the meaning of a tube radius and/or the length of a macromolecule between adjacent entanglements, and consider effects, which are used to associate with reptation motion. The model allows one to get a consistent interpretation of experimental data connected with dynamic behaviour of linear macromolecules in the systems of entangled macromolecules with the lengths above $2M_e$ and can be used to obtain the conditions of existence of reptation motion.

Dynamics of macromolecule in entangled system. The equation for the co-ordinates r^α and velocities u^α of particles ($\alpha = 0, 1, 2, \dots, N$) of a coarse-grained polymer chain, associated with a tagged macromolecule of length M , can be written [7] as equation for the Rouse chain in presence of additional random force Φ_i^α

$$m \frac{d^2 r_i^\alpha}{dt^2} = -\zeta u_i^\alpha + \Phi_i^\alpha - 2\mu T A_{\alpha\gamma} r_i^\gamma + \bar{\phi}_i^\alpha(t), \quad (1)$$

where m is the mass of a Brownian particle associated with a piece of the macromolecule of length M/N , 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. It is known that such a representation of macromolecular dynamics was considered [8,9] as a possible description of motion of a macromolecule in entangled system. One can also note that the above equation (at $m = 0$) is identical to the Langevin equation, which was formulated [10] to study the behaviour of polymer chain in a random static field; the equation was investigated numerically by Milchev *et al* [11].

The force Φ_i^α in equations (1) can be specially designed for a chain in the entangled system, according to the equation

$$\tau \frac{d\Phi_i^\alpha}{dt} = -\Phi_i^\alpha - \zeta B H_{ij}^{\alpha\gamma} u_j^\gamma - \zeta E G_{ij}^{\alpha\gamma} u_j^\gamma + \sigma_i^\alpha(t). \quad (2)$$

To describe the dynamics of chain in entangled system properly, the random force Φ_i^α in the equations has to be not static, but dynamic, with relaxation time τ , which can be interpreted as terminal viscoelastic relaxation time of the environment [5, 7]. The parameters B and E are introduced as measures of external and internal resistance. In the linear case, studied in details earlier [5], the matrixes $H_{ij}^{\alpha\gamma}$ and $G_{ij}^{\alpha\gamma}$ are numerical matrixes, but to imitate the dynamics properly, one has to include non-linear terms connected with local anisotropy of mobility [7], so that one can get the simplest approximation

$$\begin{aligned} H_{ij}^{\alpha\gamma} u_j^\gamma &= u_i^\alpha - \frac{3}{2} a_e \left(e_i^\alpha e_j^\alpha - \frac{1}{3} \delta_{ij} \right) u_j^\alpha, \\ G_{ij}^{\alpha\gamma} u_j^\gamma &= \frac{1}{N} \left\{ (N+1) \left[u_i^\alpha - \frac{3}{2} a_i \left(e_i^\alpha e_j^\alpha - \frac{1}{3} \delta_{ij} \right) u_j^\alpha \right] \right. \\ &\quad \left. - \sum_{\gamma=0}^N \left[u_i^\gamma - \frac{3}{2} a_i \left(e_i^\gamma e_j^\gamma - \frac{1}{3} \delta_{ij} \right) u_j^\gamma \right] \right\}, \end{aligned}$$

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

$$e_i^0 e_j^0 = e_i^N e_j^N = \frac{1}{3} \delta_{ij}, \quad (3)$$

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 to linear form.

The model is formulated in such a form, that the derived results do not dependent on number N of particles of coarse-grained chain. The dependence on the length of macromolecule is introduced through the parameters B and E , which can be identified by comparison of the derived results with the available empirical evidence [5]. The results for linear viscoelasticity, for an example, allow us to identify one of the parameters as

$$B = \left(\frac{M}{2M_e} \right)^{2.4}. \quad (4)$$

The random processes $\bar{\phi}_i^\gamma$ and σ_i^γ in the stochastic equations (1) and (2) relate to the dissipative terms due to the dissipation-fluctuation theorem [12].

The transition point. The model (1) - (3) allows one to study systematically deviations from the Rouse dynamics when adding non-Markovian and anisotropic noise. The introduction of specific form of non-Markovian dynamics leads to emerging of an intermediate length, which has the meaning of a tube radius and/or the length of a macromolecule between adjacent entanglements [5]. The introduction of local anisotropy of mobility of particles allows one to get the effects, which used to be associated with reptation motion of the macromolecule [7]. The described model of underlying stochastic motion of a macromolecule leads to the two modes of motion, which alternatively determine two kinds of systems: weakly entangled systems ($M < M^*$), in which the local anisotropy of motion does not affect isotropic stochastic motion of particles of macromolecules, and strongly entangled linear polymers ($M > M^*$) [7]. In the latter region, the model provides the confinement of a macromolecule in 'a tube' and easier (reptation) motion of the macromolecule along its contour – the features, which were envisaged by Edwards [13] and de Gennes [1] for the entangled systems.

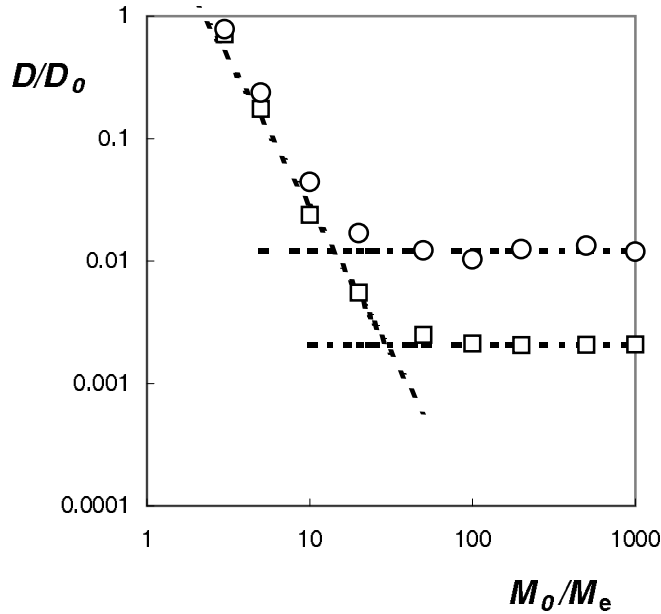


Figure 1. **Coefficient of diffusion of a macromolecule.**

Each point shows value of the ratio of asymptotic values of the displacement of a macromolecule for large times to values of displacement for the Rouse case of a macromolecule of length $25M_e$ among macromolecules with different lengths M_0 . The values of the parameter of local anisotropy are 0.3 for the circles and 0.1 for the squares. The slope of the dashed lines is -2.4 for short macromolecules and 0 for long ones, so that the simulation determines the point of transition between diffusive and reptation modes of motion.

A method of simulation, described earlier [7], is used to study mobility of a macromolecule in the medium made up of similar macromolecules of equal or different lengths, which allows us to calculate coefficient of diffusion of macromolecule at large times. Considering diffusion of a macromolecule of length $25M_e$ among macromolecules with different lengths shows that there is a critical length M^* , above which mobility of the macromolecule is independent on the properties of the environment (Fig. 1.). In this case, the macromolecules of the environment make up topological obstacles, which are

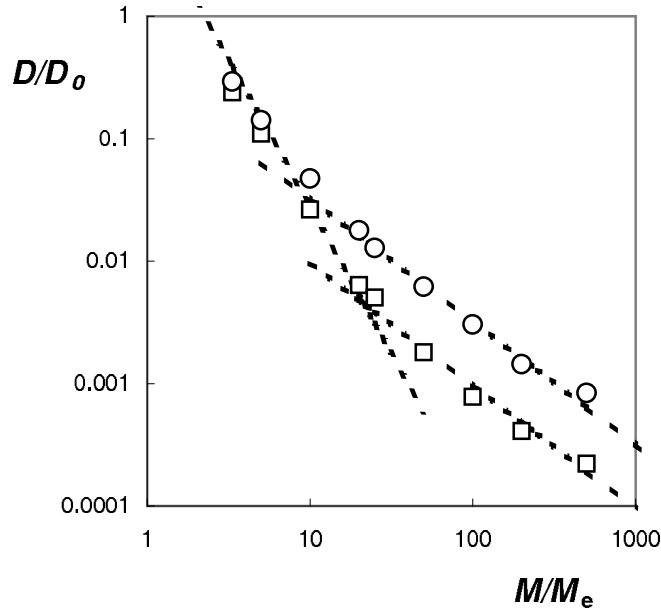


Figure 2. **Coefficient of self-diffusion of a macromolecule.**

Each point shows value of the ratio of asymptotic values of the displacement of a macromolecule for large times to values of displacement for the Rouse case of a macromolecule of different lengths among macromolecules with the same lengths. The values of the parameter of local anisotropy are 0.3 for the circles and 0.1 for 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 above the point of transition.

similar to fixed obstacles for the considered macromolecule. In the region above the point M^* , the described model leads to the known [2] law for self-diffusion of macromolecular coil, as it is illustrated in Fig. 2. One can choose such a value of coefficient of local anisotropy, that the position of transition point for the case of self-diffusion coincides with typical experimental [14] value $M^* \approx 10M_e$. In virtue of universal topological properties, the melts of linear polymers seem to be characterised by the universal value of coefficient

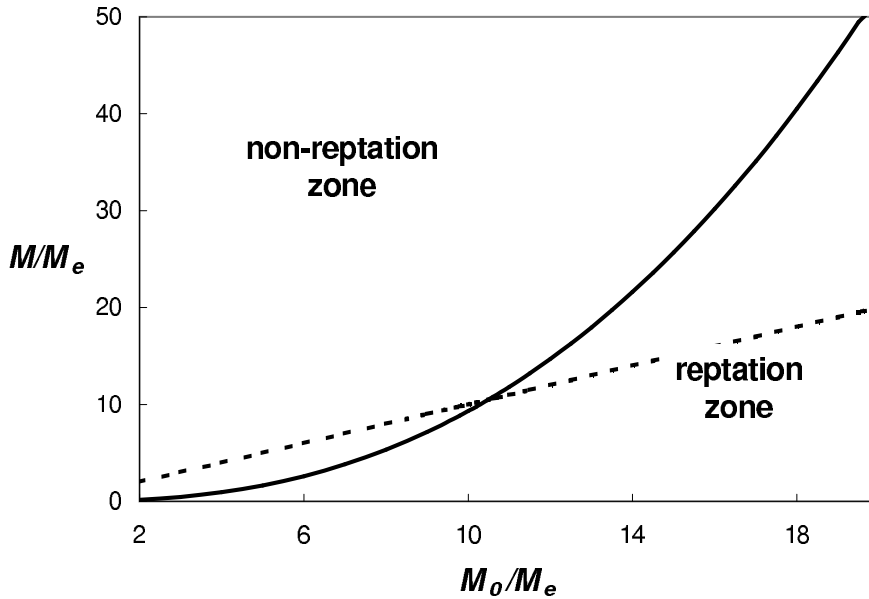


Figure 3. **Alternative modes of motion of a macromolecule.**

The realisation of a certain mode of motion of a macromolecule among other macromolecules depends on the lengths of both diffusing macromolecule and macromolecules of the environment. The positions of transition points between two modes are depicted by solid line. The dashed line marks the systems with macromolecules of equal lengths.

of local anisotropy in accordance with the picture developed by Kholodenko [15]. Figure 3 shows that the position of transition point depends on the lengths of both diffusing and matrix macromolecules.

The considered model of underlying stochastic motion allows one to demonstrate that the transition to reptation mode of motion is determined by both topological restrictions and local anisotropy of motion and to state that rather long macromolecules can be, indeed, considered as obstacles to motion of a probe macromolecule. This investigation confirms also that the reptation motion determines the molecular-weight dependence of self-diffusion coefficient of melt as M^{-2} . However, to avoid confusion, estimating an empirical value of the index in the reptation law of diffusion, one has to measure mobility of macromolecule above the transition point.

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