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REPTATION AND DIFFUSIVE MODES OF MOTION OF LINEAR MACROMOLECULES

V. N. Pokrovskii*

The Center for Ecodynamics
123290, Moscow, Russia

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It is shown that the model of underlying stochastic motion of a macromolecule leads to two modes of motion: reptative and isotropically diffusive. There is a length of a macromolecule $M^* \approx 10M_e$, where M_e is "the macromolecule length between adjacent entanglements", above which macromolecules of a melt can be regarded as obstacles to motion of each other, and the macromolecules reptate. The transition to the reptation mode of motion is determined by both topological restrictions and the local anisotropy of motion. The investigation confirms that the reptation motion determines the M^{-2} molecular-weight dependence of the self-diffusion coefficient of macromolecules in melts.

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1. INTRODUCTION

To interpret the diffusion and relaxation behavior of macromolecules in entangled linear polymers (polymer melts), some modeling situations were considered in [1, 2]. It was shown in [1] that in the case where the motion of a macromolecule is confined by fixed obstacles, such that it moves like a snake by reptation, the diffusion coefficient for the center of mass of the macromolecule is inversely proportional to its squared length. Because this law of diffusion turned out to be also valid for long macromolecules in polymer melts, it was concluded that the neighbouring macromolecules in polymer melts can be regarded as mobile obstacles for a tagged macromolecule, which also moves via reptation. It was a successful hypothesis, although some discussion repeatedly emerged [3] regarding whether a macromolecule reptates in a melt and if it does, what is the macromolecule length that marks the beginning of reptation.

A direct solution of the problem of simultaneous motion of many macromolecules, which could yield an answer to the question whether and under which conditions a macromolecule reptates turned out to be a rather difficult problem. The accurate solution is apparently available [4] only for short chains, when reptation motion is not expected. For longer macromolecules, the most efficient approach appears to be the mean-field one, when the average reaction of many surrounding macromolecules on the selected macromolecule is approximated as a reaction of some medium, whose properties are chosen in a proper way [2, 5]$^{1)}$. In the conventional reptation-tube model [2], the surrounding was schematized as a flexible tube and the reptation of the macromolecule in the tube is postulated; this allowed explaining some effects of dynamic behavior of polymers, but said nothing about the conditions under which the tube and reptation exist. On the other hand, the model of underlying stochastic motion [5–7] led to justifying the concepts of tube and reptation and allowed calculating a mean length, which has the meaning of the tube radius and/or the macromolecule length between adjacent entanglements, and considering the effects associated with reptation motion. The model allows consistently interpreting experimental data related to the dynamic behavior of linear macromolecules in the systems of entangled macromolecules with the lengths above $2M_e$, where M_e is the "macromolecule length between adjacent entanglements" [5], and can be used to obtain the conditions for the existence of reptation motion.

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*E-mail: vpok@comtv.ru

1) The preliminary version of the revised and enlarged edition of monograph [5] can be found at the page http://ecodynamics.narod.ru/polymer/content.html.

2. DYNAMICS OF A MACROMOLECULE IN AN ENTANGLED SYSTEM

The equation for the coordinates $\mathbf{r}^\alpha$ and velocities $\mathbf{u}^\alpha$ of particles ($\alpha = 0, 1, 2, \ldots, N$) of a coarse-grained polymer chain, associated with a tagged macromolecule of length M, can be written [7] as an equation for the Rouse chain in the presence of an additional random force Φ_i^α,

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

where m is the mass of a Brownian particle associated with the macromolecule piece of length M/N, $2T\mu$ is the elasticity coefficient of a "spring" between adjacent particles, and T is temperature in energy units. The matrix $A_{\alpha\gamma}$ describes the connection of Brownian particles in the entire chain. Such a representation of the macromolecular dynamics was regarded as a possible description of the motion of a macromolecule in an entangled system [8, 9]. The presence of the random force Φ_i^α means that the Rouse chain is located in some medium representing the surrounding chains of the tagged macromolecule. We also note that the above equation (at $m = 0$) is identical to the Langevin equation, which was formulated [10] to study the behavior of a polymer chain in a random static field; the equation was investigated numerically in [11].

To properly describe the dynamics of a chain in the entangled system, the random force Φ_i^α in Eq. (1) has to be not static but dynamic, with a relaxation time τ, which can be interpreted as the terminal viscoelastic relaxation time of the environment [5, 7]. The force Φ_i^α can be specially designed for a chain in the entangled system, according to the equation

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

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

The parameters B and E in Eq. (2) are introduced as measures of the external and internal resistance of the particle in a given medium, and we therefore assume that the quantities B and E are given functions of the molecular weight M_0 of macromolecules of the environment. The dependence can be specified by considering some simple heuristic models [5, 6] and/or by comparing the derived results with the available empirical evidence [5]. For example, these considerations allow identifying the dependence of one of the parameters as

$$B = \left(\frac{M_0}{2M_e}\right)^{2.4}. \qquad (3)$$

In the linear case, $H_{ij}^{\alpha\gamma}$ and $G_{ij}^{\alpha\gamma}$ are numerical matrices, but to imitate the dynamics of a macromolecule properly, we must include nonlinear terms related to the local anisotropy of mobility [7]. We thus obtain the simplest approximation

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

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

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

$$e_i^0 e_j^0 = e_i^N e_j^N = \frac{1}{3}\delta_{ij}, \qquad (4)$$

where a_{ext} and a_{int} are the local anisotropy parameters introduced such that positive values of the parameters correspond to an increase in mobility along the contour of the chain. In the linear case, with $e_i^\alpha e_j^\alpha = (1/3)\delta_{ij}$ on average, we return to the linear form studied in detail previously [5].

The model in (1)–(4) is formulated such that the derived results are independent of the number N of particles of a coarse-grained chain, but depend on the length of a probe macromolecule M. The parameters of the model are combined to form the characteristic quantities [5, 7]

$$\chi = \frac{\tau}{2\tau^* B} \sim M^{-1}, \quad \tau^* = \frac{\zeta N^2}{4\pi^2 \mu T} \sim M^2. \qquad (5)$$

3. THE TRANSITION POINT

The model in (1)–(4) allows systematically studying deviations from the Rouse dynamics when adding non-Markovian and anisotropic noise. Figure 1 shows an example of calculation of the squared centre-of-mass displacement Δ of a macromolecule as a function of time. At $\Phi_i^\alpha = 0$, Eq. (1) determines the well-known Rouse dynamics of a macromolecule, which in particular provides the diffusion coefficient

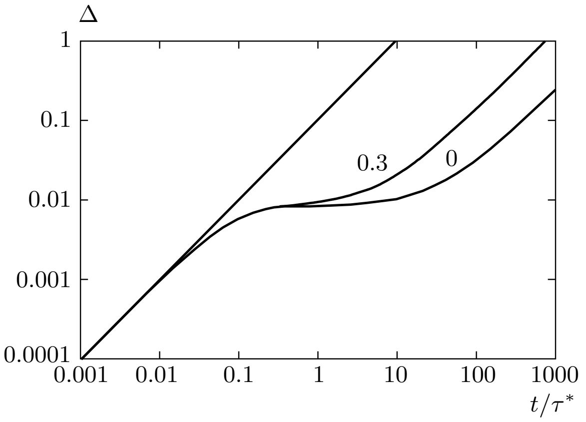

Fig. 1. Displacement of a macromolecule in time. The straight line depicts the analytic result for the Rouse dynamics. The solid curves represent the results for the displacement for a macromolecule of length $M = 25M_e$ among similar macromolecules in accordance with system (1)–(4) with the parameter values $B = 429$ and $\chi = 0.04$. The local anisotropy parameter values a_{ext} are shown at the curves. Internal resistance (parameters E and a_{int}) does not affect mobility of a macromolecular coil

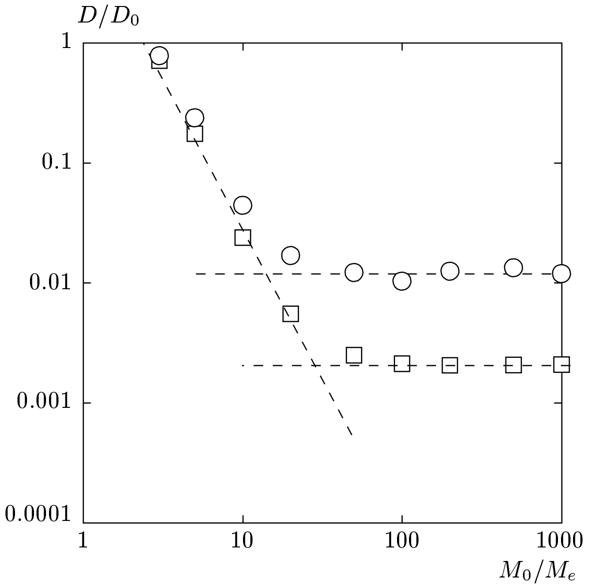

Fig. 2. Diffusion coefficient of a macromolecule. Each point shows a value of the ratio of asymptotic values of the displacement of a macromolecule for large times to values of the displacement for the Rouse case of a macromolecule of length $25M_e$ among macromolecules with different lengths M_0. The local anisotropy parameter value is 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, and hence the simulation determines the point of transition between the diffusive and reptation modes of motion

$$D_0 = \frac{T}{N\zeta} \sim M^{-1}. \tag{6}$$

In the linear case, with $a_{ext} = a_{int} = 0$, Eqs. (1)–(4) determine the large-time diffusion coefficient [5]

$$D = D_0 B^{-1} \sim M_0^{-2.4} M^{-1}, \tag{7}$$

where M and M_0 are respectively the lengths of the probe macromolecule and macromolecules of the environment. Introducing a local anisotropy of the mobility of particles, which could be related to induction of the reptation mode of motion of the macromolecule [7], leads to an increase in the large-time diffusion coefficient (Fig. 1). The method of simulation described in [7] is used to study mobility of a macromolecule in the medium made up of similar macromolecules of equal or different lengths, which allows calculating the diffusion coefficient of a 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 the mobility of the macromolecule is independent of the properties of the environment (Fig. 2). In this case, macromolecules of the environment make up topological obstacles, which are similar to fixed obstacles for the macromolecule, which therefore turns out to be effectively confined [7] to "a tube" whose radius ξ is calculated in terms of model (1)–(4) as

$$\xi^2 = D_0 \frac{\tau}{B}. \tag{8}$$

In the region above the point M^*, the described model leads to the known [2] law for self-diffusion of the macromolecular coil, as illustrated in Fig. 3. A value of the local anisotropy coefficient can be chosen such that the position of the transition point in the case of self-diffusion coincides with the typical experimental value $M^* \approx 10M_e$ [13]. By virtue of the universal topological structure, the melts of linear polymers seem to be characterized by the universal value of the local anisotropy coefficient in accordance with the picture developed in [14]. Figure 4 shows that the position of transition points depends on the lengths of both diffusing and matrix macromolecules.

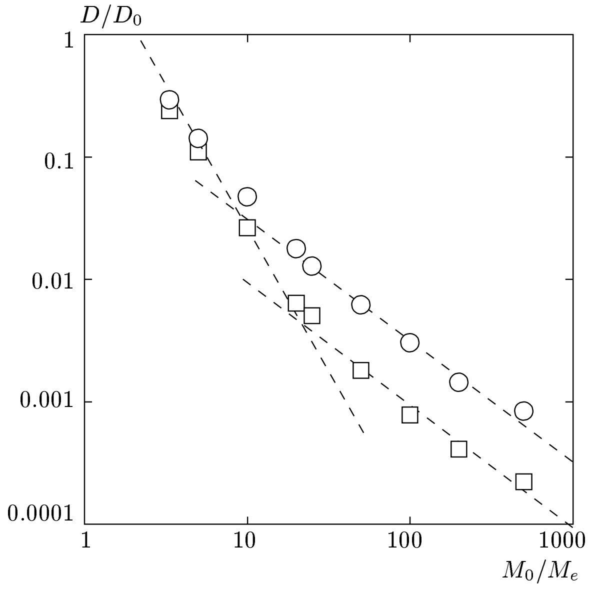

Fig. 3. Self-diffusion coefficient of a macromolecule. Each point shows a value of the ratio of asymptotic values of the displacement of a macromolecule for large times to values of the displacement for the Rouse case of a macromolecule of different lengths among macromolecules with the same lengths. The local anisotropy parameter value is 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, and hence the simulation gives the well-known dependence $D \propto M^{-2}$ for coefficient of self-diffusion of macromolecules above the point of transition

4. CONCLUSION

The described model of the underlying stochastic motion of a macromolecule leads to 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 macromolecules, and systems of strongly entangled linear polymers ($M > M^*$). For the latter, the model provides the confinement of a macromolecule in "a tube" and easier (reptation) motion of the macromolecule along its contour — the features envisaged by Edwards [15] and de Gennes [1] for entangled systems. The considered model allows demonstrating that the existence of the reptation mode of motion is determined by both topological restrictions and local anisotropy of motion, and stating that rather long macromolecules can indeed be regarded as obstacles to the motion of a probe macromolecule. This investigation also confirms that the reptation motion determines the M^{-2} universal molecular-weight dependence of the self-diffusion coefficient of melt. However, estimating the empirical value of the index in the reptation law of diffusion requires measuring the mobility of a macromolecule above the transition point.

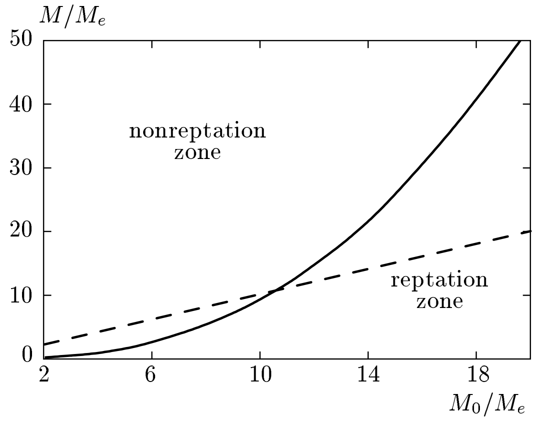

Fig. 4. Alternative modes of motion of a macromolecule. The realization of a certain mode of motion of a macromolecule among other macromolecules depends on the lengths of both the diffusing macromolecule and the macromolecules of the environment. The positions of transition points between two modes are depicted by a solid line. The dashed line marks the systems with macromolecules of equal lengths

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