J. Non-Newtonian Fluid Mech. 164 (2009) 17–28

Contents lists available at ScienceDirect

Journal of Non-Newtonian Fluid Mechanics

journal homepage: www.elsevier.com/locate/jnnfm

Constitutive equations for weakly entangled linear polymers

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ARTICLE INFO

Article history:
Received 12 May 2009
Received in revised form 4 July 2009
Accepted 15 July 2009

Keywords:
Constitutive equations
Mesoscopic approach
Polymer dynamics
Polymer melts
Relaxation of macromolecule
Reptation
Viscoelasticity

ABSTRACT

To interpret the viscoelastic behaviour of entangled linear polymers in terms of dynamics of a single macromolecule, we have been developing the approach, which allows one to study systematically deviations from the Rouse dynamics, when adding non-Markovian and anisotropic noise. It was shown earlier, that 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. The additional introduction of local anisotropy of mobility of particles allows one to get the results of the conventional reptation-tube model for both mobility and relaxation times of macromolecular coil and, beyond it, to estimate a transition point between weakly (the length of macromolecules $M < 10M_e$, no reptation) and strongly (the length of macromolecules $M > 10M_e$, reptation) entangled polymer systems. The adequate mesoscopic equation allows us to develop theory of different relaxation phenomena, in particular, a theory of viscoelasticity and 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.

1. Introduction

A system of macromolecules with the molecular weights (lengths) above $2M_e$, where M_e is 'the molecular weight (length) of a macromolecule between adjacent entanglements', is used to be called the system of entangled macromolecules [1–3]. To explain the empirical facts of macromolecular mobility, one has to consider two modes of motion of separate macromolecules in the systems of entangled macromolecules: diffusive isotropic and reptation anisotropic [1], which determine, as we have shown earlier [4], two kinds of systems with different predominant relaxation mechanisms of macromolecules in the system. In the strongly entangled linear polymers ($M > 10M_e$), relaxation of separate macromolecules is realised through reptation—these are systems to which the results of conventional reptation-tube theory [2] and its modifications [6–8] can be applied, while, in the weakly entangled systems ($M < 10M_e$), the reptation is absent, the relaxation of macromolecules is realised through isotropic diffusion of particles of macromolecules. Recently [4,5], we attempted to find such a formal unified equation for dynamics of individual macromolecules in the system, which could explain all peculiarities of dynamic behaviour of the system in the region above $2M_e$. Indeed, the proposed model allowed one to get a consistent interpretation of experimental data for diffusion and conformational relaxation of linear macromolecules in the systems of entangled macromolecules [5]. The proposed theory could be considered as an attempt to formalise the common knowledge about the dynamics of a macromolecule; in any case, it recovers (with some corrections) the results of the conventional reptation-tube model, that is the confinement of a macromolecule in the tube and easier (reptation) motion of the macromolecule along its contour—the features, which were envisaged originally by Edwards [9] and de Gennes [10] for entangled systems. The considered model is a non-Markovian and non-linear generalisation of the Rouse dynamics that allows one to describe stochastic dynamics of a macromolecule in an entangled system, so that, to stress the difference to the Doi–Edwards model, which operates with mean quantities, the model can be called *a model of underlying stochastic motion*.

In this paper, we intend to apply the unified equations of macromolecular dynamics for derivation of the constitutive equations of the systems. In Section 2, the fundamentals of dynamics of a macromolecule in the system of macromolecules are discussed and the linear normal modes of the system are described. We have no possibility to collect all details here: some of them can be found in other places [3–5] and in the original papers cited there. The purpose of this Section is to discuss the foundations and main features of the mesoscopic approach for both weakly and strongly entangled systems. In Section 3, linear dynamics of entangled systems will be considered in linear approximation of macromolecular dynamics. We shall not be able here to presents the results on the base of non-linear unified model and have to be restricted to a discussion of linear dynamics. The results for dynamic modulus shows that

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doi:10.1016/j.jnnfm.2009.07.003

the linear approximation of macromolecular dynamics allows us to calculate correctly terminal properties for both weakly and strongly systems, but is non-sufficient to describe adequately dynamic modulus in the whole region of frequencies. In Section 4, we shall consider, rectifying our previous results [11], constitutive relations for weakly entangled systems and discuss its consequences for two simple cases: simple shear and simple elongation. A sample of identification of a weakly entangled system is given. The Section 5 contains a discussion of the problem.

2. Dynamics of a macromolecule in an entangled system

It is known [2,3], that every flexible macromolecule can be effectively presented as a chain of coupled Brownian particles (so called bead and spring model). To reduce the problem of many interacting chains, one can follow Zwanzig–Mori method, described, for example, in monographs [12,13] to derive a dynamic equation for a single chain in a system of entangled chains. A direct solution of the problem of simultaneous motion of many macromolecules, which could bring an answer, appeared to be a rather difficult problem. As far as we know, accurate results are available only for short chains [14], when reptation motion is not expected. Considering longer macromolecules, one can refer to the Mori–Zwanzig projector operator technique, as a possible foundation of the approach, and say that it is natural to present the anticipated dynamic equation for a chain as stochastic equation with memory function terms. The dynamics of a probe macromolecule in an entangled system can be simplified by the assumption that the neighbouring macromolecules are described as a uniform non-structural 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.

2.1. A non-Markovian form of dynamic equations

To present a general form of the equation of dynamics of a probe macromolecule in an entangled system [3], 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:

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

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 coordinates 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 and has the form:

$$\mathrm{A} = \begin{vmatrix} 1 & -1 & 0 & \ldots & 0 \\ -1 & 2 & -1 & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & 0 & \ldots & 1 \end{vmatrix}. \tag{2}$$

The dissipative forces in Eq. (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:

$$\tau\left(\frac{\mathrm{d}F_i^\alpha}{\mathrm{d}t} - \omega_{il}F_l^\alpha\right) + F_i^\alpha = -\zeta B H_{ij}^{\alpha\gamma}(u_j^\gamma - \nu_{jl} r_l^\gamma), \tag{3}$$

$$\tau\left(\frac{\mathrm{d}G_i^\alpha}{\mathrm{d}t} - \omega_{il}G_l^\alpha\right) + G_i^\alpha = -\zeta E G_{ij}^{\alpha\gamma}(u_j^\gamma - \omega_{jl} r_l^\gamma) \tag{4}$$

where τ is a relaxation time of effective medium surrounding every particle. The simplest case assumes that one chooses the single time of relaxation. The introduced relaxation time τ coincides with the terminal viscoelastic relaxation time, which means that the theory is characterized by self-consistency. The matrixes $H_{ij}^{\alpha\gamma}$ and $G_{ij}^{\alpha\gamma}$ in Eqs. (3) and (4) determine the mutual influences on motion of the particles of the chain. In Section 2.3, a few particular choices of the matrixes will be discussed.

The force F_i^α is a 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 force G_i^α is a force of internal resistance with the property:

$$\sum_{\alpha=0}^{N} G_i^\alpha = 0, \quad i = 1, 2, 3. \tag{5}$$

This force, defined by Eq. (4), represents the intramolecular resistance (kinetic stiffness) of the coil and, due to the vorticity term $\omega_{il} = 1/2(\nu_{il} - \nu_{li})$, does not depend on the rotation of the macromolecular coil as a whole.

The above dynamic equations were designed [3] to describe effects in entangled systems, that is in the systems consisting of macromolecules of length $M > 2M_\mathrm{e}$, where M_e is 'the length of the macromolecule between adjacent entanglements', though in the case, when $B = 0$ and $E = 0$, the considered equations describe the Rouse dynamics of macromolecule in a viscous liquid. For entangled systems, the coefficients B and E in Eqs. (3) and (4) are introduced as measures of intensities of the external and internal extra dissipative forces, connected with the neighbouring macromolecules. The dependence of the quantity B on the length of macromolecules can be estimated [4] by using simple picture of overlapping coils [15] or the constraint-release mechanism [16]. In either case the dependence of the quantity on the length of neighbouring macromolecules M_0 (it is helpful for the analysis to distinguish this from the length M of the probe macromolecule, even if all of them are equal) can be approximated as a power function:

$$B \sim M_0^\delta. \tag{6}$$

The estimates determine value of the index 2 or 3, but the empirical value, according to dependence of the coefficient of viscosity on the length of macromolecules, is $\delta = 2.4$. The measure of internal resistance E of a macromolecule is small for entangled systems of short macromolecules, but, for long macromolecules, the quantity has an asymptotic dependence:

$$E \sim M_0^\delta M. \tag{7}$$

For the considered, linear in velocities, case, the correlation functions of the stochastic forces in the system of Eq. (1) can be easily determined 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 [17]:

$$\langle \phi_i^\alpha(t)\phi_k^\gamma(t')\rangle = T\zeta\left[2\delta_{\alpha\gamma}\delta_{ik}\delta(t-t') + \frac{1}{\tau}(B H_{ij}^{\alpha\gamma} + E G_{ij}^{\alpha\gamma})\exp\left(-\frac{t-t'}{\tau}\right)\right]. \tag{8}$$