

**HYDRODYNAMICS OF POLYMER SOLUTIONS WITHIN THE JOINT ROUSE-ZIMM THEORY<sup>1</sup>****J. Tóthová<sup>2</sup>, B. Brutovský<sup>3</sup>, V. Lisý<sup>4</sup>***Institute of Physics, P.J. Šafárik University, Jesenná 5, 041 54 Košice, Slovakia*

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The dynamics of polymers in dilute solutions is described within the joint Rouse-Zimm (RZ) theory, in which the Z and R models correspond to infinitely large and small draining parameter. The equation of motion for a “test” polymer in the solution is solved together with Brinkman’s hydrodynamic equations for the solvent. The solvent flow is disturbed by other coils and is “frozen” as the concentration of polymers grows, which indicates the hydrodynamic screening. We give the description of the effect of concentration on the motion of the whole coil as well as on the relaxation of its internal modes.

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Polymer solutions represent a cross-disciplinary field, borrowing wide spectra of theoretical tools from physics and chemistry. For physicists, understanding the configuration and dynamics of long polymer chains has been a significant source of problems within statistical physics from the 1950’s onwards. One of the reasons why physicists were drawn to the problem is the universality of polymer properties [1]. What they considered to be the most fundamental questions turned out to be insensitive to the details of the chemistry of the chains. Within the time and length scales much exceeding the atomic ones universal theories well describing the main features in the polymer behaviour have been built. Among them the most used are the Rouse (R) and Zimm (Z) models in which the polymer is represented as a chain of beads under Brownian motion [2]. The present work was inspired by the difficulties that still exist between the theory and experiments. Some discrepancies, e.g., with the light and neutron scattering data, remain unclear for decades [3]. We have developed the R and Z models in several aspects. First, in the frame of the Navier-Stokes (NS) hydrodynamics, we have taken into account the inertial effects in the dynamics of the polymer segments and the solvent. This allowed us to predict several peculiarities in the polymer dynamics, such as the non-exponential relaxation of its internal modes and the nondiffusive motion of the coil at short times [3]. At “long” times,  $t \gg R^2 \rho / \eta$  ( $R$  is the hydrodynamic radius of the coil,  $\rho$  is the solvent density, and  $\eta$  its viscosity), the difference from

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<sup>1</sup>Presented at 15-th Conference of Czech and Slovak Physicist, Košice, Slovakia, September 5–8, 2005<sup>2</sup>E-mail address: tothova@upjs.sk<sup>3</sup>E-mail address: bru@seneca.science.upjs.sk<sup>4</sup>E-mail address: lisy@upjs.sk

Einstein's diffusion of the coil, the so-called long-time tail, has been confirmed in computer experiments [4]. However, the found effects cannot entirely explain deviations between the theory in the stationary limit and experiments. To our opinion, a weak point in the description of the observed dynamics of polymers in dilute  $\theta$  solutions is in the use of the Z model. This model is just a limiting case of a more general theory joining the two, R and Z, models. The latter one applies in the case of large "draining parameter"  $h$  [2]. In general, every polymer carries features of both the R and Z behaviour, the relative roles of which are specified by  $h$ . Next, we do not assume the continuous distribution of internal modes with the mode number [5]. This also leads to differences from the previous results on the time behaviour of polymers. Finally, to take into account the interaction between the polymers through hydrodynamic forces, we use the Brinkman's (or Debye-Bueche) modification of the NS equation for the flow in porous media [6, 7].

In the Brinkman's theory the polymer is considered as a porous medium permeable to the solvent. In our approach the entire solution is such a medium with coils being obstacles to the solvent flow. Then in the NS equation a term  $-\kappa^2\eta\vec{v}$  has to be added, where  $\kappa^{-2}$  is the solvent permeability. This term has a meaning of the average force acting on the liquid in an element of volume  $dV$ , provided the average number of polymers per unit volume is  $c$ ; then  $\kappa^2\eta = cf$ , where  $f$  is the friction factor on one coil. Thus, for an incompressible solvent ( $\nabla\vec{v} = 0$ ) we have to solve the equation

$$\rho\frac{\partial\vec{v}}{\partial t} = -\nabla p + \eta\Delta\vec{v} - \kappa^2\eta\vec{v} + \vec{\varphi}. \quad (1)$$

Here  $p$  is the pressure and  $\vec{\varphi}$  is the density of the force from the beads of the studied polymer on the solvent [8],

$$\vec{\varphi}(\vec{x}) = -\sum_n \vec{f}_n^{fr}(\vec{x}_n) \delta(\vec{x} - \vec{x}_n). \quad (2)$$

In this expression  $\vec{x}_n$  is the bead position and  $\vec{f}_n^{fr}$  is the friction force on the  $n$ th bead. Another forces acting on the beads are  $\vec{f}_n^{ch}$ , which is due to the neighbouring beads along the chain [8], and  $\vec{f}_n$ , the random force due to the motion of the solvent molecules. Thus, for a chosen "test" polymer the equation of motion of its  $n$ th bead is

$$M\frac{d^2\vec{x}_n(t)}{dt^2} = \vec{f}_n^{fr} + \vec{f}_n^{ch} + \vec{f}_n, \quad (3)$$

where  $M$  is the bead mass. To take into account the hydrodynamic interaction between the beads the force  $\vec{f}_n^{fr}$  should be expressed relatively to the solvent velocity  $\vec{v}$  in the place of the  $n$ th bead,  $\vec{f}_n^{fr} = -\xi[d\vec{x}_n/dt - \vec{v}(\vec{x}_n)]$ . The friction coefficient on the bead with radius  $b$  is  $\xi = 6\pi\eta b$ . This equation holds for steady flows. In a more general case with the hydrodynamic memory [3] the Stokes force should be replaced by the Boussinesq one and eq. (3) has to be solved together with the nonstationary equation (1) for the macroscopic velocity of the solvent.

It is difficult to solve the above formulated problem since the polymer chains are mobile. However, restricting ourselves to the times much shorter than  $\tau_D = R^2/D$ , which is the characteristic time of the coil diffusion with the diffusion coefficient  $D$ , the concentration  $c$  can be assumed constant. The equations then describe the motion of one bead in the solvent with an

effective influence of other coils on the motion of the solvent flow. This problem can be transformed to that already solved in [3, 9]. The velocity field can be expressed through the Oseen tensor preaveraged over the equilibrium (Gaussian) distribution of the beads,

$$\langle H_{\alpha\beta} \rangle_0 = \delta_{\alpha\beta} \langle \exp(-\kappa r)/r \rangle_0. \quad (4)$$

The tensor describes how a perturbation is transferred through the fluid so that the quantity  $1/\kappa$  can be (for small  $\kappa r$ ) considered as a hydrodynamic screening length. Using the solution for  $\langle H_{\alpha\beta} \rangle_0$ , the generalized RZ equation has been found [3]. It was solved in the continuum approximation with the help of the Fourier transformation (FT) in  $n$ ,  $\vec{x}(n) = \vec{y}_0 + 2 \sum_{p \geq 1} \vec{y}_p \cos(\pi n p/N)$  ( $N$  is the number of the beads in one polymer) that takes into account the boundary conditions at the ends of the chain [8]. Then, using the inverse FT and the fluctuation-dissipation theorem, the time correlation functions  $\psi_p(t) = \langle y_{\alpha p}(0) y_{\alpha p}(t) \rangle$  of the normal modes can be obtained ( $\alpha = x, y, z$ ). The index  $p = 0$  determines the mean square displacement of the whole coil, and the polymer internal modes are numbered with  $p > 0$ . For an individual polymer in the steady-state limit  $\psi_0(0) - \psi_0(t) = Dt$  with  $D = k_B T (1/N\xi + h_{00}) = D_R + D_Z$  ( $R$  and  $Z$  stay for the R and Z limits [2] and  $h_{pp}$  is for the Oseen matrix [3]). This matrix has been found in [3] solving eq. (1) (with  $\kappa = 0$ ) in the FT with respect to the time. In our stationary case but with  $\kappa \neq 0$  one can simply adopt that solution by replacing  $-i\omega\rho$  with  $c/f$  so that  $h_{pp}$  now depends on  $c$ . Then the diffusion coefficient, determined through  $h_{00}$ , is

$$D = D_R + D_Z(c), \quad (5)$$

( $D_Z(0) = D_Z$ ) and consists of the R (independent on the presence of other polymers) and the Z contributions. The latter one can be expressed in the form  $D_Z(c) = D_Z f(c)$  where

$$f(c) = \frac{3\sqrt{\pi}}{4\chi} \left[ 1 - \frac{2}{\sqrt{\pi}\chi} + \frac{1}{\chi^2} (1 - \exp \chi^2 \operatorname{erfc} \chi) \right] \quad (6)$$

is a ‘‘universal’’ function depending only on  $\chi = (N/6)^{1/2} \kappa a$  with  $a$  being the mean square distance between the beads along the chain. The dependence of the permeability on  $c$  is estimated as follows. The friction coefficient in  $\kappa^2 = cf/\eta$  from eq. (1) can be determined using the Einstein relation  $D = k_B T/f$ . In such a picture

$$\kappa^2 = \frac{27\sqrt{\pi}}{16} \frac{\tilde{c}}{R_G^2} \left( 1 + \frac{3}{4\sqrt{2}h} \right)^{-1}. \quad (7)$$

Then the values of  $\kappa$  and  $\chi$  depend on the draining parameter  $h = 2(3N/\pi)^{1/2} b/a$  (if  $h \gg 1$ , the dynamics is of the Z type, for  $h \ll 1$  we deal with the R polymers). The quantity  $\tilde{c} \equiv 4\pi R_G^3 c/3$  denotes the number of polymers per the volume of a sphere with the gyration radius  $R_G$ . With the increase of  $c$  the Z term decreases and for large  $c$  (small permeabilities when  $\chi \gg 1$ ) it becomes  $\sim 1/\sqrt{c}$ . The realistic case of small  $c$  corresponds to  $\chi = \kappa R_G \ll 1$  when

$$D_Z(c) = D_Z \left( 1 - \frac{3}{8\sqrt{\pi}} \kappa R_G + \dots \right). \quad (8)$$

The  $c$ -dependent correction to  $D_Z$  is thus  $\sim \sqrt{c}$  and differs from other results (cf. [10] and citations there, where this correction is  $\sim c$ ). The behaviour of a free polymer depends on  $h$ . If

the polymer was initially (at  $c = 0$ ) the Z one (large  $h$ ), with growing  $c$  its behaviour changes to the diffusion with the R coefficient  $D_R$ .

The relaxation times of the internal modes are calculated from the diagonal elements of the Oseen matrix. In the stationary case at zero concentration ( $\kappa = 0$ ) they are well known [2]. Now the internal modes relax exponentially as in previous theories,  $\psi_p(t) \propto \exp(-|t|/\tau_p)$ , but are affected by  $c$ . Their relaxation rates consist of the R contribution and the  $c$ -dependent Z part,

$$\tau_p^{-1}(c) = \tau_{pR}^{-1} + \tau_{pZ}^{-1}(c), \quad (9)$$

where  $\tau_{pR}$  and  $\tau_{pZ}(0) \equiv \tau_{pZ}$  are given in [2] and

$$\tau_{pZ}(c) = \frac{1}{2} \frac{1 + (1 + \chi_p)^2}{1 + \chi_p} \tau_{pZ}, \quad (10)$$

with  $\chi_p = (N/3\pi p)^{1/2} \kappa a$ . At  $c \rightarrow 0$  we have  $\tau_{pZ}(c) = \tau_{pZ} (1 + N\kappa^2 a^2 / 6\pi p - \dots)$  and as  $c \rightarrow \infty$ , one finds  $\tau_{pZ}(c) \approx \tau_{pZ} \chi_p / 2 = (Na^2)^2 \eta \kappa / (6\pi k_B T p^2)$ . Note that for the internal modes the draining parameter depends on the mode number  $p$ :  $h(p) = \tau_{pR} / \tau_{pZ} = h / \sqrt{p}$ . The ‘‘universal’’ dependence of  $\tau_{pZ}(c) / \tau_{pZ}$  on  $\chi_p$  (10) indicates that with the growing  $c$  every polymer shows a tendency to become (as distinct from the previous theories) *exactly* the R one.

In conclusion, coming from our earlier results on the hydrodynamic theory of the polymer dynamics, we have built a model that is able to predict new results on the fundamental characteristics of the universal behaviour of flexible polymers in dilute solutions. The found quantities could be verified (with the necessary account for the draining parameter) in standard experiments, such as viscosimetry or dynamic light and neutron scattering on unentangled polymers in dilute  $\theta$  solutions. Finally, note that the transition between the Zimm and Rouse regimes can be viewed also as a time-dependent process [11]. In our theory this is a natural consequence of the discrete distribution of internal modes and is clearly seen, e.g., in the motion of an individual monomer within the polymer coil [12].

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