DILUTE SOLUTION RHEOLOGY OF FLEXIBLE MACROMOLECULES[1]

V. Lisý[2]**, J. Tóthová**[3]
Institute of Physics, P.J. Šafárik University, Jesenná 5, 041 54 Košice, Slovakia

The dynamic and viscous properties of dilute solutions of flexible polymers are studied. We come from our hydrodynamic theory of the single polymer kinetics and build the joint Rouse-Zimm model of the polymer behaviour. To take into account the presence of other polymer coils in the solution the Brinkman's porous medium approach is used. Various observable quantities such as the shear viscosity of the solution, the Huggins coefficient and the monomer mean square displacement are calculated. We also give the first description of the hydrodynamic screening as a concentration- and time-dependent effect.

Dilute solutions of flexible polymers show a number of peculiar differences with simple fluids. For example, the addition of tiny amounts of polymers to certain flows can cause enormous effects, such as the stabilization of jets and turbulent reduction. Despite a large number of applications, the reason for these phenomena is poorly understood [1]. In general, they are attributed to large elongational viscosity, while the shear viscosity of the solution, $\eta(c)$, is affected only slightly if the number of polymers per unit volume, c, is small [2]. Nevertheless, a large resistance to a stretching motion can be inferred from $\eta(c)$ [1], one of the most important rheological quantities of polymer solutions [2, 3]. The existing theories give very different results for $\eta(c)$ (see, e.g., [3, 4] and citations there). The aim of the present work was to contribute to this problem by developing a bead-spring theory of the dynamics of polymers in solution. Our approach differs from the previous ones in the following main points. First, we come from the joint Rouse-Zimm (RZ) theory [5] instead of its nondraining (Zimm) limit that is assumed to be valid at θ conditions. Next, the normal internal modes of the polymer are distributed discretely with respect to the mode number since the assumption of their continuous distribution often leads to incorrect interpretation of experiments [6]. The results of our hydrodynamic theory of polymer dynamics [6] has been adopted and, finally, the Brinkman-Debye-Bueche theory (see [7]) for the flow in porous media was used to take into account the influence of other coils on the polymer motion.

The presented theory has the following limitations. The considered time scales are $t \gg \tau_R = R^2\rho/\eta$, where R is the hydrodynamic radius of the polymer, ρ is the density, and η the viscosity

---

of the solvent. This means that the effects of hydrodynamic memory are neglected [5, 8, 9]. The distribution of the coils in solution is considered to be stationary (this is justified at least for the times $t \ll \tau_D$; the choice of this time scale is possible since always $\tau_p \ll \tau_D$, where τ_p, $p = 1, 2, 3...$, are the relaxation times of the polymer internal modes and $\tau_D = R^2/D$ is the characteristic time of the coil diffusion with the diffusion coefficient D). Our theory is restricted to θ solvents [3]; generalizations to other cases require knowledge of the equilibrium distribution of the segments when the exclude volume interactions are taken into account. Only solutions of unentangled polymers are considered. We are thus limited to concentrations of the coils $c < 1/[\eta]$, where $[\eta]$ is the intrinsic viscosity [2]. In spite of these restrictions and other ones like those that we do not consider the internal viscosity of polymers and the self-entanglements (the importance and even the reality of these effects are uncertain [2]), we believe that our results of could be of interest. In particular, we have found new expressions for rheological quantities of polymer solution, such as the viscosity of the solution, and the Huggins coefficient.

To calculate them, we need only the expressions for the relaxation rates of the polymer internal modes, $\tau_p(c)$. Within the Brinkman's theory they can be obtained from our previous results on the time-dependent hydrodynamics of noninteracting polymers [5, 8]. In the stationary case one has simply to replace the quantity $-\mathrm{i}\omega\rho/\eta$ that enters the Oseen matrix [5] with κ^2, κ^{-2} being the solvent permeability. The dependence of κ on c is given by the relation [10] $\kappa^2 = (27\sqrt{\pi}\widetilde{c}/16R_G^2)(1 + 3/4\sqrt{2}h)^{-1}$, where R_G is the gyration radius of the polymer. Here $h = 2(3N/\pi)^{1/2}b/a$ is the draining parameter determined by the radius of the bead b, the mean square distance between the beads along the chain, a, and the number of beads N. The dimensionless concentration $\widetilde{c}$ denotes the number of polymers per the volume of a sphere with the radius R_G. Then, rewriting the result [5] for the relaxation rates, we come to the c-dependent expression $\tau_p^{-1}(c) = \tau_{pR}^{-1} + \tau_{pZ}^{-1}(c)$, where τ_{pR} and $\tau_{pZ}(0) \equiv \tau_{pZ}$ are given in [3] and $\tau_{pZ}(c) = (\tau_{pZ}/2)[1 + (1 + \chi_p)^2](1 + \chi_p)^{-1}$, with $\chi_p = (N/3\pi p)^{1/2}\kappa a$. As seen from these expressions, all quantities determined by the relaxation times τ_p display the hydrodynamic screening effect: with the increase of c every polymer shows a tendency to become the Rouse one. As distinct from previous theories [3,4] where this tendency has only a qualitative character (in the sense that the dependence of τ_p on p becomes $\tau_p \sim p^{-2}$ as for Rouse polymers), in our approach as c grows the polymer tends to become the Rouse one exactly.

Consider, e.g., the steady shear viscosity of the solution at weak flows. It can be calculated from the formula [2,3]

$$\eta(c) = \eta + \frac{1}{2}k_B T c \sum_{p=1}^{\infty} \tau_p(c). \tag{1}$$

In the Rouse limit (small h) we have the familiar result [3] $\eta(c) - \eta = \pi N^2 a^2 bc\eta/6$. In the Zimm limit at small concentrations [10]

$$\eta(c) - \eta = 0.425\eta c \left(Na^2\right)^{3/2} \left[1 + 0.140c \left(Na^2\right)^{3/2} + ...\right]. \tag{2}$$

The first term coincides with the known result [3]. A more general expression for the viscosity, following from eq.(1), is

$$\frac{\eta(c) - \eta}{\eta} = \frac{1}{\pi} N^2 a^2 bc \sum_{p=1}^{\infty} \frac{1}{p^2} \left(1 + \frac{2h}{\sqrt{p}} \frac{1 + \chi_p}{1 + (1 + \chi_p)^2}\right)^{-1}. \tag{3}$$

At very low concentrations when $\chi_p \ll 1$ one has

$$\frac{\eta(c) - \eta}{\eta} = \frac{1}{\pi} N^2 a^2 bc \sum_{p=1}^{\infty} \frac{1}{p^2} \left(1 + \frac{h}{\sqrt{p}}\right)^{-1}. \tag{4}$$

Due to the dependence on h the difference between this and the classical result [3] can be notable. So, for a polymer with small h the ratio of the intrinsic viscosity $[\eta]_h = \lim_{c \to 0} [\eta(c) - \eta]/(\eta c)$ at $h < 1$ (when the polymer is assumed to be the Rouse one) to that with $h = 0$ changes as a function of h from 1 to ≈ 0.55, at $h = 0.5$ being 30% smaller than in the case of a pure Rouse polymer. For a very large h the intrinsic viscosity is $[\eta]_{h \gg 1} = 3\sqrt{2/\pi} R_G^3 \zeta(3/2) = 6.253 R_G^3$, where ζ is the Riemann zeta function. Considering the viscosity normalized to this expression, one finds that even for rather large h the difference from the traditional result for the pure Zimm polymer is significant. So, at $h = 10$ it represents some 25% and is still about 10% even for h as large as 50.

One of the important rheological parameters of polymer solutions is the Huggins coefficient k_H. It can be determined from the general expression for the viscosity (2), using the intrinsic viscosity $[\eta]_h$ at zero concentration:

$$\eta(c) - \eta = [\eta]_h \eta c \left(1 + k_H [\eta]_h c + ...\right). \tag{5}$$

We find

$$k_H = \frac{3\pi}{2^{3/2}} \sum_{p=1}^{\infty} \frac{1}{p^{7/2}} \left(1 + \frac{h}{\sqrt{p}}\right)^{-2} \left(1 + \frac{3}{4\sqrt{2}h}\right)^{-1} \left[\sum_{p=1}^{\infty} \frac{1}{p^2} \left(1 + \frac{h}{\sqrt{p}}\right)^{-1}\right]^{-2}. \tag{6}$$

For large h (the Zimm case) one thus has

$$k_H = 3 \times 2^{-3/2} \pi \zeta(5/2) \zeta^{-2}(3/2) \approx 0.655. \tag{7}$$

This value differs from the literature results, see, e.g., [3] where $k_H = 0.757$; in Ref. [11] one finds $k_H = 0.6949$, and in [12] the calculations gave the value 0.3787. The Freed and Edwards theory [3] possesses an intrinsic viscosity, which is inconsistent with the Kirkwood-Riseman steady-state limit and gives the hydrodynamic screening even for infinitely dilute solutions (the discussion of this question has been given already in the paper [4]).

When $h \to 0$ (the Rouse case), the Huggins coefficient approaches zero as $k_H \approx 2\pi h \zeta(7/2) \times \zeta^{-2}(2)$ and when h grows, k_H slowly converges to the Zimm limit (7). The difference from this limit is significant in a broad region of h, with the maximum ≈ 1.27 of the function k_H/k_{HZimm} at $h = 3$, and with $k_H/k_{HZimm} \approx 1.15$ for $h = 20$.

In connection with the unresolved problem of the dynamic nature of hydrodynamic screening in polymer solutions [13], it is of interest to consider the time-dependent quantities describing the polymer behaviour. Among such quantities, the relaxation modulus, which determines the shear stress at shear flows can be easily studied since it is given simply by a sum of exponentials containing the relaxation times τ_p [2, 3]. Here we shall briefly focus on simplest (but observable [14]) motion of the end monomer in a chain and calculate its mean square displacement (MSD). The MSD part due to internal modes is [6]

$$\left\langle r^2(t) \right\rangle_{int} = (4Na^2/\pi^2) \sum_{p=1}^{\infty} p^{-2} \left[1 - \exp\left(-t/\tau_p\right)\right]. \tag{8}$$

As already shown, with growing c every polymer tends to behave as a Rouse one, which is due to the decrease of the Zimm contribution to τ_p^{-1}. The time dependence of the screening is well displayed considering, e.g., the ratio of the Rouse part of the MSD (i.e. that if the polymer was the pure Rouse one, $h = 0$) to the total MSD in the joint RZ model. This function, $\langle r^2(t)\rangle_{int,R}/\langle r^2(t)\rangle_{int}$, depends on the draining parameter h, the concentration c, and the time. With growing t the above relation converges to unity showing the transition to the Rouse behaviour. For example, at a concentration $\widetilde{c} = 0.1$ and $h = 10$ we have $\langle r^2(t)\rangle_{int,R}/\langle r^2(t)\rangle_{int} \approx 0.75$ at $t = \tau_R$; at $t = 2\tau_R$ the difference from the Rouse MSD is only 10%, and at $t = 5\tau_R$ the initially Zimm polymer becomes indistinguishable from the Rouse one. When the same relation is considered as a function of $\widetilde{c}$ for different times, one sees that the tendency to approach the Rouse limit with the increase of $\widetilde{c}$ becomes more expressed as t growths. At longer times the polymer behaves as the Rouse one already at small concentrations.

In conclusion, our theory yields several predictions for experiments in which rheological characteristics of dilute polymer solutions are probed. The difference from some previous results, e.g., on the viscosity or Huggins coefficient are notable. We have also suggested the first description of the time dependence of the tendency to hydrodynamic screening in such systems and demonstrated it on the single monomer motion; this effect could be studied experimentally as in Ref. [14] or by computer simulations similarly as in Ref. [13].

References

[1] A. Lindner, J. Vermant, D. Bonn: *Physica A* **319** (2005) 125

[2] R.G. Larson: *J. Rheol.* **49** (2005) 1

[3] M. Doi, S.F. Edwards: *The Theory of Polymer Dynamics*, Clarendon, Oxford, 1986

[4] M. Muthukumar: *J. Phys. A: Math. Gen.* **14** (1981) 2129

[5] V. Lisy, J. Tothova, A.V. Zatovsky: *J. Chem. Phys.* **121** (2004) 10699

[6] J. Tothova, B. Brutovsky, V. Lisy: *Czech. J. Phys.* **55** (2005) 221

[7] P. Debye, A.M. Bueche: *J. Chem. Phys.* **16** (1948) 573

[8] A.V. Zatovsky, V. Lisy: *J. Mol. Liq.* **105** (2003) 289

[9] J. Tothova, V. Lisy, A.V. Zatovsky: *J. Chem. Phys.* **119** (2003) 13135

[10] V. Lisy, J. Tothova, A.V. Zatovsky: submitted to *Cond. Matt. Phys.*

[11] M. Muthukumar: *J. Chem. Phys.* **79** (1983) 4048

[12] M. Muthukumar, K.F. Freed: *Macromolecules* **11** (1978) 843

[13] P. Ahlrichs, R. Everaers, B. Dünweg: *Phys. Rev. E* **64** (2001) 040501

[14] R. Shusterman, S. Alon, T. Gavrinyov, O. Krichevsky: *Phys. Rev. Lett.* **9** (2004) 048303