Time domain effects in the single-chain dynamics of semidilute and concentrated polymer solutions

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Single-chain dynamics in semidilute polymer solutions is Zimm-like on short time scales and Rouse-like on long time scales. The crossover is due to time-dependent screening of hydrodynamic interactions. We present a generalized Zimm theory for polymer dynamics in an elastic polymer network. We show that the coupled equations of motion of the polymer network–fluid system lead to a generalized Oseen tensor with a time-dependent hydrodynamic screening length. The time correlation function of the Rouse modes, monomer mean-square displacements and the single-chain dynamical structure factor are calculated.

1. Introduction

The dynamics of flexible polymers are usually discussed in the framework of the Zimm–Rouse models (Doi & Edwards, 1986; Grosberg & Khokhlov, 1994; de Gennes, 1993; Teraoka, 2002): the polymer is represented as a Gaussian chain of beads and the dynamics are given by the Langevin equation for the beads. In the Rouse model (Doi & Edwards, 1986) the solvent is not flowing. Hydrodynamic interactions are taken into account in the Zimm model (Doi & Edwards, 1986). The disturbance of the solvent velocity field due to motion of the polymer chain is investigated with the help of the linearized stationary hydrodynamic equation for an incompressible fluid. This is a Stokes approximation and it provides a way of calculating hydrodynamic interactions in suspensions and polymer solutions. In the dilute limit, it is usually sufficient to restrict oneself to the leading-order pair interaction, which decays inversely proportional to the interparticle distance r. In this case the tensor, which relates the velocity of the fluid to acting forces, is called the Oseen tensor.

While the Zimm model correctly describes the chain dynamics in dilute solution, the Rouse model applies to concentrated polymer solutions and melts where hydrodynamic interactions are screened, *i.e.* where hydrodynamic interactions become negligible between segments whose spatial distance apart is larger than hydrodynamic screening length ξ_H.

Recent computer simulations (Ahlrichs *et al.*, 2001) of single-chain motion in semidilute polymer solutions have provided evidence for a more complex dynamical scenario. In particular, the single-chain dynamic structure factor (DSF) was found to display Zimm-like behaviours for short time scales, regardless of wavenumber. The crossover to Rouse-like behaviours occurred only at later times. To arrive at a coherent theory for polymer dynamics in semidilute solutions, it is necessary to treat hydrodynamic screening as a dynamic, time-dependent phenomenon.

There are quite a number of works (Doi & Edwards, 1986; Grosberg & Khokhlov, 1994; Richter *et al.*, 1984) based on the Zimm–Rouse models. However, the precise regime of applicability of these phenomenological models is not clear. The crossover regime from one model to another needs more detailed research.

Inadequacy of the assumption of complete hydrodynamic screening was discussed by Richter *et al.* (1984), where they proposed the model of incomplete hydrodynamic screening owing to the residual viscosity of the solution, and they investigated the single-chain dynamics of linear polymers in solution over the full concentration range. The model introduced by Richter *et al.* (1984) suffers from fundamental problems: the obstacles are the mobile polymer chains themselves, whereas they are fixed in this model. Moreover, the incomplete screening model assumes that the hydrodynamic interaction should cross over to a second r^{-1} regime on very large scales, with the overall viscosity as a prefactor. For the short-time behaviour of a single chain, this model also predicts Rouse-like motion, while on larger time scales there is an additional Zimm regime. Thus, the model of incomplete screening cannot give the correct picture for all times.

In the work of Lisy *et al.* (2004), the dynamics of polymers in dilute solution was investigated for the single chain taking into account hydrodynamic memory. Another way of looking at the single-chain dynamics in polymer solutions for different time scales was to investigate the polymer dynamics in a porous medium with frequency-dependent permeability (Tchesskaya, 2003, 2005). This simple phenomenological model for polymer dynamics has led to a generalization of the Debye–Bueche–Brinkman equation resulting in an Oseen tensor with a time-dependent hydrodynamic screening length.

In this work we propose a new generalized Zimm theory for polymer dynamics, improving the model proposed by Tchesskaya (2003, 2005). The polymer solution is modelled as an elastic polymer network immersed in the solvent. The model equations of motion are based on the equations for polymer gels (Bacri & Rajaonarison, 1979; Marqusee & Deutch, 1981; Johnson, 1982) with some simplifications. These coupled equations lead to a generalized Oseen tensor with a time-dependent hydrodynamic screening length as given in the model (Tchesskaya, 2005) and allow the crossover from Zimm-like to Rouse-like behaviour to be described not only in the spatial domain, but also in the time domain. We calculate the mean-square displacement of the single polymer chain and the DSF. We show that the introduced relaxation time of the medium has a strong influence on single-chain dynamics.

2. Generalized Zimm theory: the network–fluid model of polymer solutions

2.1. The network–fluid model

Following on the works studying the dynamics of gels [an ample review was given by Johnson (1982)], we model the polymer solution as an elastic polymer network immersed in solvent. In our model we take into account the mobility of polymer chains in the solvent relative to themselves, using a system of connected elastic and hydrodynamic equations. In the usual condition of Brownian motion, the relevant hydrodynamic equation of motion is that of low Reynolds number hydrodynamics, which assumes an incompressible fluid and negligibly small inertia of the fluid. It is correct for our problem. The coupling effect of the elastic waves of the network with the fluid motion in this two-phase system is small for the weakly perturbed and nearly incompressible fluid and network, and we only need take into account the exchange of momentum between the fluid and the network (*e.g.* Bacri & Rajaonarison, 1979). The polymer network displacements **s** due to interaction with the solvent are described by the stationary linearized equation of motion of the elastic medium with an additional term describing the frictional damping, which arises from the fluid flow through the polymer network

$$0 = \mu \Delta \mathbf{s} + (\lambda + \mu)\nabla(\nabla \cdot \mathbf{s}) - f\left(\frac{\partial \mathbf{s}}{\partial t} - \mathbf{v}\right). \quad (1)$$

Here λ and μ are the Lamé coefficients of the elastic network, **v** is the solvent fluid velocity, and f describes the exchange of momentum between the fluid and the network.

The flow of the incompressible fluid is described by the stationary linearized Navier–Stokes equation taking into account the frictional damping as in the equation of elasticity [equation (1)] and an external force $\boldsymbol{\varphi}$, acting on the solvent near each polymer segment

$$0 = -\nabla p + \eta \Delta \mathbf{v} - f\left(\mathbf{v} - \frac{\partial \mathbf{s}}{\partial t}\right) + \boldsymbol{\varphi}, \quad \nabla \cdot \mathbf{v} = 0. \quad (2)$$

The coefficients f in equations (1) and (2) are identical as required by symmetry (Marqusee & Deutch, 1981).

It is simpler to solve the Fourier transformed coupled equations (1) and (2), to give

$$v_\alpha^{\omega k} = \frac{1}{\eta k^2}\left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right)\varphi_\beta^{\omega k}\left\{1 + \frac{f}{\eta}\frac{\delta_{\alpha\beta}\mu + [\lambda + \mu + i(\lambda + 2\mu)]k_\alpha k_\beta/k^2}{\delta_{\alpha\beta}(\mu k^2 - fi\omega) + (\lambda + \mu)k_\alpha k_\beta}\right\}^{-1} \quad (3)$$

Hence

$$v_\alpha^\omega(\mathbf{r}) = \int d\mathbf{r}' H_{\alpha\beta}^\omega(\mathbf{r} - \mathbf{r}')\varphi_\beta^\omega(\mathbf{r}'), \quad (4)$$

with the Fourier transformed mobility tensor with components $\alpha, \beta = x, y, z$ given by

$$H_{\alpha\beta}^\omega(\mathbf{r}) = A^\omega \delta_{\alpha\beta} + B^\omega \frac{r_\alpha r_\beta}{r^2}. \quad (5)$$

The scalars A^ω and B^ω are determined from the equations

$$H_{\alpha\alpha}^\omega = 3A^\omega + B^\omega, \quad H_{\alpha\beta}^\omega \frac{r_\alpha r_\beta}{r^2} = A^\omega + B^\omega. \quad (6)$$

The results obtained here will be applied in the next section.

2.2. A generalization of the Zimm model

We start from the Zimm model and, first of all, give a short description of this model. The equation of motion of the nth polymer segment (bead) is written in the form without inertia effects, which are unnecessary for usual thermal motion and

$$0 = \mathbf{f}_n^{\mathrm{ch}} + \mathbf{f}_n^{\mathrm{fr}} + \mathbf{f}_n^{\mathrm{r}}, \quad (7)$$

where $\mathbf{f}_n^{\mathrm{ch}} = -\partial u/\partial \mathbf{x}_n$ is the force from the neighbouring beads along the chain, $\mathbf{x}_n$ is the position vector of the nth chain segment. The interaction energy between the chain segments is $u = 3k_{\mathrm{B}}T/(2a^2)\sum_{n=1}^{N-1}(\mathbf{x}_{n+1} - \mathbf{x}_n)^2$, where a is the mean-square distance between the neighbouring beads, $\mathbf{f}_n^{\mathrm{fr}}$ is the friction force acting on the bead during its motion in the solvent. In the Zimm model

$$\mathbf{f}_n^{\mathrm{fr}} = -\xi\left[\frac{\partial \mathbf{x}_n}{\partial t} - \mathbf{v}(\mathbf{x}_n)\right] \quad (8)$$

with the solvent velocity $\mathbf{v}(\mathbf{x}_n)$ at the location of the nth segment. The friction coefficient for a spherical bead of radius b is $\xi = 6\pi\eta b$, where η is the solvent viscosity. The random force is denoted by $\mathbf{f}_n^{\mathrm{r}}$.

The external force $\boldsymbol{\varphi}$ per unit volume, acting on the solvent near $\mathbf{x}_n$ is given by

$$\boldsymbol{\varphi}(\mathbf{x}, t) = \sum_n\left(-\frac{\partial u}{\partial \mathbf{x}_n} + \mathbf{f}_n^{\mathrm{r}}\right)\delta(\mathbf{x} - \mathbf{x}_n). \quad (9)$$

The equation of motion of the nth polymer segment [equation (7)] can be rewritten taking into account equations (8) and (4). After this, in the continuum limit, equation (7) has a Zimm-like form, and in Fourier representation we have

$$-i\omega x_\alpha^\omega(n) = \int_0^N dm\, H_{\alpha\beta nm}^\omega\left[\frac{3k_{\mathrm{B}}T}{a^2}\frac{\partial^2 x_\beta^\omega(m)}{\partial m^2} + f_\beta^\omega(n)\right]. \quad (10)$$

Here $H_{\alpha\beta nm}^\omega = H_{\alpha\beta}^\omega(x_n - x_m)$ for $m \neq n$, and $H_{\alpha\beta nm}^\omega = \delta_{\alpha\beta}/\xi$ for $m = n$.

Because of the dependence $H_{\alpha\beta nm}^\omega$ on **r**, *i.e.* on $x_n - x_m$, equation (10) is nonlinear, and to solve it we preaverage (Doi & Edwards, 1986) the mobility tensor. The preaveraging of $H_{\alpha\beta nm}^\omega$ over the equilibrium distance distribution function yields

$$\langle H_{\alpha\beta}^\omega(x_m - x_n)\rangle_0 = \left(\frac{3}{2\pi a^2|m - n|}\right)^{3/2}\int d\mathbf{r}\exp\left(-\frac{3}{2a^2}\frac{r^2}{|m - n|}\right)$$
$$\times \left[A^\omega(r)\delta_{\alpha\beta} + B^\omega(r)\frac{r_\alpha r_\beta}{r^2}\right]$$
$$= \frac{\delta_{\alpha\beta}}{6\pi\eta}\frac{1}{1 - i\omega t_{\mathrm{m}}}\left\langle\frac{1}{r}\left[\exp(-r/\xi_{\mathrm{H}}) - i\omega t_{\mathrm{m}}\right]\right\rangle_0. \quad (11)$$

Equation (11) defines the hydrodynamic screening length $\xi_{\mathrm{H}} = \xi_{\mathrm{H}}^0(1 - i\omega t_{\mathrm{m}})^{-1/2}$, $t_{\mathrm{m}} = 3\eta/L$ is the relaxation time of the elastic network, and $L = 4\mu + \lambda + i(2\mu + \lambda)$. In the case $t_{\mathrm{m}} = 0$, ξ_{H} reduces to the rigid medium limit $\xi_{\mathrm{H}}^0 = \{(f/n)[L/(4\mu + \lambda)]\}^{-1/2}$. Note, that equations (5) and (6) reduce to the Oseen tensor (Doi & Edwards, 1986) for the special case $\xi_{\mathrm{H}} \to \infty$.

Further, for ease of calculation we will examine an incompressible medium. In this case we obtain $L = 4\mu + \lambda$, and parameters dependent on L are reduced to $\xi_{\mathrm{H}}^0 = (\eta/f)^{1/2}$, $t_{\mathrm{m}} = 3\eta/(2\mu)$.

The solution of equation (10) can be found in the form of a superposition of Rouse modes

$$\mathbf{x}_n^\omega = \mathbf{y}_0^\omega + 2\sum_{p=1}^\infty \mathbf{y}_p^\omega \cos\frac{\pi pn}{N},$$
$$\mathbf{y}_p^\omega = \frac{1}{N}\int_0^N dn \cos\frac{\pi pn}{N}\mathbf{x}_n^\omega, \quad p = 0, 1, 2\ldots. \quad (12)$$

Hence, equation (10) simplifies to

$$-i\omega y_{p\alpha}^{\omega} = \sum_{q=0}^{\infty} h_{\alpha\beta pq}^{\omega}\left(-\frac{6\pi^2 k_B T q^2}{Na^2}y_{q\beta}^{\omega} + f_{q\beta}^{\omega}\right), \tag{13}$$

where the mobility tensor expressed in Rouse modes is

$$h_{\alpha\beta pq}^{\omega} = \frac{1}{N^2}\int_0^N dn \int_0^N dm \cos\frac{\pi pn}{N}\cos\frac{\pi qm}{N}\langle H_{\alpha\beta nm}^{\omega}\rangle_0. \tag{14}$$

The mobility tensor [equation (11)] is diagonal over Cartesian indices α,β after averaging and is only dependent on $|n-m|$. It is easy to show that the interactions between the beads disappear according to the law $h(n-m) \propto |n-m|^{-1/2}$, as in Grosberg & Khokhlov (1994), for the Zimm model. The matrix $h_{\alpha\beta pq}^{\omega}$ is diagonal dominant in indices p,q, i.e. $\sim\delta_{pq}$. Consequently, we neglect the off-diagonal components and approximate the mobility tensor by

$$h_{\alpha\beta pq}^{\omega} = \frac{\delta_{\alpha\beta}\delta_{pq}}{\lambda_p^{\omega}}, \, (p \neq 0), \tag{15}$$

$$\frac{1}{\lambda_p^{\omega}} = \sigma\frac{\xi_H^0}{\eta a^2 \pi N}\frac{1}{1-i\Omega\tau_m}\left[\frac{1+\tilde\sigma}{1+(1+\tilde\sigma)^2} - i\Omega\frac{\tau_m}{2}\right]. \tag{16}$$

Here $\tilde\sigma = \sigma\sqrt{1-i\Omega\tau_m}$ is a dimensionless function of ξ_H and the Rouse index p. The prefactor $\sigma = (a/\xi_H^0)(N/3\pi p)^{1/2}$ is the reduced wavelength of the pth Rouse mode, because the local motion of N/p Rouse chain segments corresponds to the motion with a length-scale of the order of $a(N/p)^{1/2}$. $\tau = t/t_c$ is the time normalized to the characteristic polymer time $t_c = 3\pi\eta(\xi_H^0)^3/(2k_BT)$, which specifies the single-chain polymer dynamics in a rigid medium. As evident from the expression, t_c is defined by medium properties; $\Omega = \omega t_c$ is the dimensionless frequency, $\tau_m = t_m/t_c$ is the normalized relaxation time of the elastic network.

Rouse modes are orthogonal and related to the acting force by the relations

$$y_{p\alpha}^{\omega} = \alpha_p(\omega)f_{p\alpha}^{\omega}, \ \ \alpha_p(\omega) = \frac{1}{-i\omega\lambda_p^{\omega} + \gamma_p}, \ \ \gamma_p = \frac{6\pi^2 k_B T}{Na^2}p^2, \tag{17}$$

where $\alpha_p(\omega)$ is the generalized susceptibility of a system.

Now we have derived all necessary results in order to calculate measurable observables.

3. The mean-square displacement and the dynamical structure factor

In the following, we calculate observables which characterize the chain dynamics: Rouse-mode time-correlation functions, monomer mean-square displacements and the dynamic structure factor. In all cases, we will be interested in the time and length-scale dependence of the cross over from Zimm to Rouse-like behaviour.

From the fluctuation–dissipation theorem (Landau & Lifshits, 1980), which relates the susceptibility of a system to the action of a perturbing force with the fluctuations of the quantity, we can obtain the time correlation function of the amplitudes of the pth Rouse mode $y_p(t)$

$$\psi_p(t) = \langle y_p(t)y_p(0)\rangle = \frac{k_B T}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{\omega}\exp(-i\omega t)\text{Im}\frac{1}{-i\omega\lambda_p^{\omega}+\gamma_p}, \tag{18}$$

and, after the replacement of p by σ and normalization $\psi_\sigma(0) = 1$,

$$\psi_\sigma(\tau) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{d\Omega}{\Omega}\exp(-i\Omega\tau)\text{Im}\left\{-i\Omega\sigma^3(1-i\Omega\tau_m) \times \right.$$
$$\left. \left[2/\left(2\{(1+\tilde\sigma)/[1+(1+\tilde\sigma)^2]\} - i\Omega\tau_m\right)+1\right]\right\}^{-1}. \tag{19}$$

The exact solution of equation (19) is complicated to find, and therefore, we present limiting cases of equation (19) known from the literature. In the case $\tau_m = 0$, equation (19) reduces to the rigid medium limit $\exp(-t/\tau_\sigma)$ with the relaxation time τ_σ of the internal modes $(p > 0)$

$$\tau_\sigma = t_c\sigma^3\frac{1+(1+\sigma)^2}{1+\sigma}. \tag{20}$$

For $\xi_H^0 \rightarrow \infty$, τ_σ becomes the Zimm relaxation time $(\eta a^3 N^{3/2})/[(3\pi)^{1/2}k_BTp^{3/2}]$. The relaxation time τ_σ reduces to the Rouse relaxation time $(N^2 a^2\xi)/(3\pi^2 k_B Tp^2)$ in the case of $\xi_H^{\min} = a^2/12b$.

The mean-square displacement of the nth segment can be calculated from equation (12) as

$$\langle[\mathbf{x}(t,n) - \mathbf{x}(0,n)]^2\rangle = \langle[\mathbf{y}_0(t) - \mathbf{y}_0(0)]^2\rangle$$
$$+ 4\sum_{p=1}^{\infty}\cos^2\left(\frac{\pi pn}{N}\right)\langle[\mathbf{y}_p(t) - \mathbf{y}_p(0)]^2\rangle. \tag{21}$$

In the following, we do not consider the diffusion of the centre of mass of polymer chains, instead, we concentrate on the mean-square displacement of a single segment for times less than the longest Rouse relaxation time, $\tau_1^R = \xi N^2 a^2/(3\pi^2 k_B T)$. In this case the normalized mean-square displacement of the segment can be calculated in the continuum limit of relaxation modes (Grosberg & Khokhlov, 1994).

With the knowledge of the correlation function of normal coordinates it is possible to find the mean-square displacement, which is defined for each mode as $\langle\Delta y_p^2(t)\rangle = 2[\psi_p(0) - \psi_p(t)]$. Thus, the normalized mean-square displacement of the segment is calculated by the expression

$$\langle\Delta X^2\rangle = \pi\int_0^{\infty} d\sigma\,\sigma[\psi_\sigma(0) - \psi_\sigma(\tau)]. \tag{22}$$

The integral sum is cut off at $\sigma_{\max}(\tau)$, and its behaviour changes from the Zimm to Rouse-like, when $\sigma_{\max}(\tau) = \sigma_{\text{crossover}}(\tau)$, i.e. the length scale goes down to hydrodynamic screening and affects the modes.

The results of the numerical evaluation of equation (22) are represented in Fig. 1 for different relaxation times (τ_m) of the network–fluid system. In all of the cases there is a crossover from Zimm to Rouse-like behaviour, but the shape of the curves is strongly affected. The crossover comes later for the 'softer medium' (higher τ_m). It is possible to identify two regimes in the time scale for the mean-square displacement of the polymer segment: a Zimm-like behaviour on time scales $a^2\rho/\eta \ll t \ll t_m, \tau_1^R$ and a Rouse-like behaviour on scales $a^2\rho/\eta, t_m \ll t \ll \tau_1^R$. From Fig. 1, we can observe that the crossover time t^* of the mean-square displacement is directly proportional to τ_m. In our model, $\tau_m = 0$ implies that the crossover from Rouse-like motion to Zimm-like motion for the monomer mean-square displacement can be obtained only in the limit $\tau \rightarrow 0$. Therefore, the time of crossover is determined by the relaxation time of the medium.

The results obtained are in qualitative agreement with computer simulations (Ahlrichs et al., 2001).
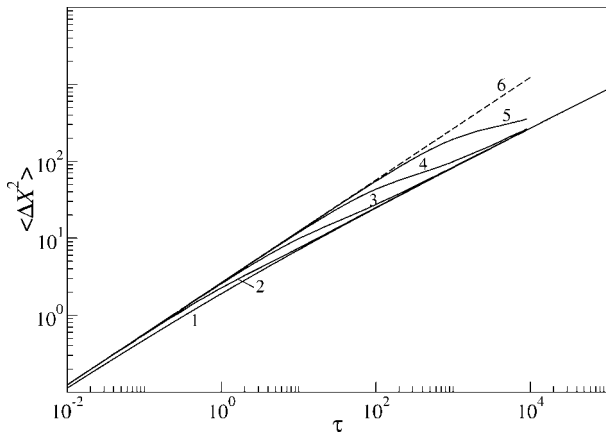
Figure 1
Time dependence of the normalized mean-square displacement. Lines 1–5 correspond to $\tau_m = 0$ (rigid medium), 1, 10^1, 10^2, and 10^3, respectively. The dashed line denotes Zimm-like behaviour.

Figure 2
Solid lines are the time dependence $S(Q, \tau)/S(Q, 0)$ for $\tau_m = 1$. Lines 1–4 correspond to $Q = 0.5, 1, 5, 10$. Dotted and dashed lines denote the Zimm-like and the rigid model behaviour, respectively.

Further, we consider the DSF, which is defined as

$$S(q, t) \equiv \frac{1}{N}\sum_{n,m}\left\langle\exp\{i\mathbf{q}[\mathbf{x}_n(t) - \mathbf{x}_m(0)]\}\right\rangle$$
$$\simeq \frac{1}{N}\sum_{n,m}\exp\left\{-\frac{q^2}{6}\left\langle\left[\mathbf{x}_n(t) - \mathbf{x}_m(0)\right]^2\right\rangle\right\}, \quad (23)$$

where $\mathbf{q}$ is the scattering vector of modulus q. Second equation (23) is derived assuming Gaussian distribution.

For the large wavevector regime, when $q^2 N a^2 \gg 1$, we can restrict our consideration to the time region $t \ll \tau_1^R$, since $S(q, t)$ becomes very small for $t \gg \tau_1^R$. In this regime we can neglect the diffusive motion of the chain as a whole, and look only at the internal modes of the polymer chain.

In this case, following the same procedures like those given in Doi & Edwards (1986) and using solutions of the network–fluid model, we obtain for the DSF

$$S(Q, \tau)/S(Q, 0) = \int_0^\infty du\, \exp\left\{-u - \frac{2}{\pi}Q^2\int_0^\infty d\sigma[\psi_\sigma(0)\right.$$
$$\left. - \psi_\sigma(\tau)]\sigma\cos\left(\frac{2u}{Q^2\sigma^2}\right)\right\}, \quad (24)$$

where $Q = q\xi_H^0$, $u = q^2|n - m|a^2/6$.

In the limit $\tau_m = 0$, equation (24) simplifies to

$$S(Q, t)/S(Q, t) = \int_0^\infty du\, \exp\left\{-u - \frac{2}{\pi}Q^2\int_0^\infty d\sigma\, \sigma\right.$$
$$\left. \times \cos\left(\frac{2u}{Q^2\sigma^2}\right)[1 - \exp(-t/\tau_\sigma)]\right\}, \quad (25)$$

which corresponds to the DSF for the rigid model (Richter *et al.*, 1984).

Equation (24) leads to the Zimm result for short time scales and to the Rouse limit result of the rigid medium (Richter *et al.*, 1984) for long time scales in the same way as for the discussed mean-square displacement due to the mobility of the polymer medium.

It follows from Equation (25), partly a Zimm regime for the rigid model, that when the wavelength is smaller than the static screening length $\xi_H^0 \gg q^{-1}$, so the wavevector is larger than the characteristic distance between obstacles. In the opposite case, when $\xi_H^0 \ll q^{-1}$, the Rouse regime is obtainable for the model of Richter *et al.* (1984). In
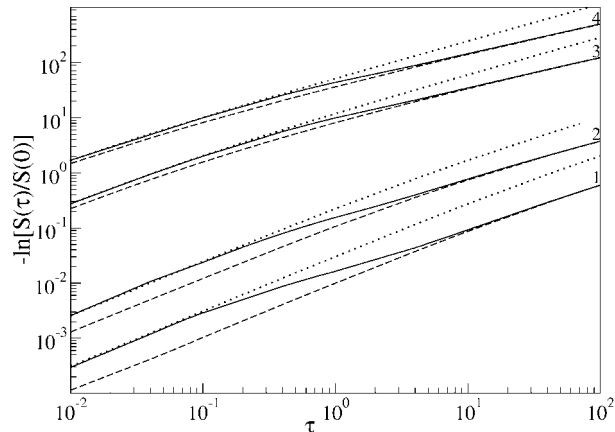
the rigid model, the condition $q\xi_H^0 \ll 1$ defines the regime of Rouse-like behaviour for all times and the condition $q\xi_H^0 \gg 1$ defines the regime of Zimm-like behaviour for short times and the Rouse-like one for large times. Thus, the rigid model does not produce correct results in the time domain. Our screening length, ξ_H, is a time-dependent parameter in contrast to the rigid model, the crossover from the Zimm motion to the Rouse-like one is present both for different length scales and for different time scales in cases of non-rigid network–fluid media.

Calculation results of the DSF for different values of Q from equation (24) are presented in Fig. 2. The time of crossover region widens with a decrease of Q. As shown in the figure, there is only the Rouse-like regime for the rigid model on length scales beyond the hydrodynamic screening length, while our model gives the crossover between the Zimm and Rouse regimes under changes of time over all length scales.

Comparison of theoretical and experimental results over the full time range presents difficulties. Experimental data (Richter *et al.*, 1984) for the DSF were limited to within 10^{-9}–10^{-8} s both for Zimm and Rouse results, because the aim of that research was to investigate the single-chain polymer dynamics over the full concentration range, but on the same time scale. Meanwhile, the crossover from the Zimm-to Rouse-like dynamics is stretched in time for one degree at least. As mentioned above, a Zimm-like behaviour takes place in the range $a^2\rho/\eta \ll t \ll t_m, \tau_1^R$. For $a = 6$, $b = 3$ Å, $\eta = 0.29$ cP, $T = 373$ K, $N = 1000$ and $\rho \sim 1$ g cm^{-3} the evaluation of left and right limits of this range gives $a^2\rho/\eta \sim 10^{-12}$ s and $\tau_1^R \simeq 4 \times 10^{-6}$ s, correspondingly. A Rouse-like behaviour is present for times in the range $a^2\rho/\eta, t_m \ll t \ll \tau_1^R$. Our assessed value of the crossover time is $t_m \simeq 8 \times 10^{-9}$ s. It is consistent with t_c and is situated within the bounds of the Zimm- and Rouse-like ranges. For estimated t_m and $\eta = 0.29$ cP we obtain $\mu = 5.4$ N cm^{-2} which is over a range of experimental data for 5% polymer gels (Tanaka *et al.*, 1973), and is one order of magnitude greater than for the cylindrical polymer gel (Sasaki, 2004). For calculated results $0.5 < Q < 1$ with $q = 0.053$ Å^{-1}, we have $9.4 < \xi_H^0 < 18.9$ Å, which is in good agreement for experimental data for an 18% polymer solution (Richter *et al.*, 1984). But the friction coefficient calculated from ξ_H^0 gives $f \sim 10^6$ N s cm^{-4} which corresponds to 5% polymer gels (Tanaka *et al.*, 1973) and the cylindrical polymer gel (Sasaki, 2004). Although it is essential to consider the difference between investigated media in these three experimental works. In fact, the room temperature shear modulus of polymers in solutions

and the friction constant are highly concentration dependent and, therefore, it is probably not correct to compare these parameters with experimental results because the concentration dependence is not discussed in the present work.

4. Conclusions

This work presents a phenomenological theory for the single-chain dynamics in semidilute and concentrated polymer solutions based on the description of the solution as the network–fluid model with strong friction between the fluid motion and polymer network. Our aim is to obtain an improved description of the crossover from the Zimm-like to the Rouse-like chain dynamics, taking into account the movability of the polymer network–fluid system, which describes the mobile chain segments relative to each other, and allows us to describe the crossover from Zimm to Rouse-like behaviour on time scales.

At the beginning, we expanded the phenomenological theory of single-chain dynamics of semidilute and concentrated polymer solution by considering the model of the polymer solution system which represents the mobile polymer chains themselves. We followed the logic of the Zimm model of single-chain dynamics of a polymer solution, but took into account the screening of the hydrodynamic interaction by using the elastic network–fluid system, which includes the influence of the fluid on the network and *vice versa*. Inclusion of the polymer medium mobility gave rise to the time dependence of the mobility tensor and, as a consequence, the time-dependent hydrodynamic screening length.

Our model allowed us to describe the crossover from Zimm-like to Rouse-like behaviour not only in spatial domain, but also in time domain. The last case cannot be captured by the rigid model (Richter *et al.*, 1984). The introduced relaxation time of the network–fluid system was associated with the crossover time in our model.

In the second part of our paper we calculated the mean-square displacement. This showed that Zimm motion is present on all length scales up to the crossover time, and goes to Rouse-like motion after screening of hydrodynamic interactions. The DSF is described by the Zimm model for short times and by the Rouse model for large times,

regardless of the wavenumber. This result agrees with the simulation study (Ahlrichs *et al.*, 2001). Whereas the rigid medium model (Richter *et al.*, 1984) leads to Zimm-like motion on short length and time scales, and to Rouse-like motion on length scales beyond hydrodynamic screening length for all times.

In accordance with previous results (Ahlrichs *et al.*, 2001; de Gennes, 1976), the generalized phenomenological theory presented of the single-chain polymer dynamics shows that the principal mechanism for hydrodynamic screening is a dynamic phenomenon.

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