acta physica slovaca vol. 65 No. 1, 1 – 64 February 2015

GENERALIZED LANGEVIN THEORY OF THE BROWNIAN MOTION AND THE DYNAMICS OF POLYMERS IN SOLUTION

Jana Tóthová[a] **and Vladimír Lisý**[a,b,1]
[a] *Department of Physics, Technical University of Košice,*
Park Komenského 2, 042 00 Košice, Slovakia
[b] *Laboratory of Radiation Biology, Joint Institute of Nuclear Research,*
141 980 Dubna, Moscow Region, Russia

Received 12 May 2015, accepted 14 May 2015

The review deals with a generalization of the Rouse and Zimm bead-spring models of the dynamics of flexible polymers in dilute solutions. As distinct from these popular theories, the memory in the polymer motion is taken into account. The memory naturally arises as a consequence of the fluid and bead inertia within the linearized Navier-Stokes hydrodynamics. We begin with a generalization of the classical theory of the Brownian motion, which forms the basis of any theory of the polymer dynamics. The random force driving the Brownian particles is not the white one as in the Langevin theory, but "colored", *i.e.*, statistically correlated in time, and the friction force on the particles depends on the history of their motion. An efficient method of solving the resulting generalized Langevin equations is presented and applied to the solution of the equations of motion of polymer beads. The memory effects lead to several peculiarities in the time correlation functions used to describe the dynamics of polymer chains. So, the mean square displacement of the polymer coils contains algebraic long-time tails and at short times it is ballistic. It is shown how these features reveal in the experimentally observable quantities, such as the dynamic structure factors of the scattering or the viscosity of polymer solutions. A phenomenological theory is also presented that describes the dependence of these quantities on the polymer concentration in solution.

PACS: 05.40.Jc, 05.10.Gg, 61.25.he, 82.35.Lr

KEYWORDS: Brownian motion, Generalized Langevin equation, Polymer solutions, Polymer dynamics, Bead-spring models, Memory effects, Scattering of light and neutrons, Viscosity of polymer solutions

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[1] E-mail address: vladimir.lisy@tuke.sk

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1 Introduction

Polymeric systems are an attractive subject of investigations in various fields of fundamental and applied science. One of the reasons is the richness of their possible structures and dynamical behavior. Understanding the properties of these systems requires knowledge of the static and dynamic properties of individual polymers in solution. For example, the slow internal dynamics of long polymer chains is the origin of viscoelasticity of dilute polymer solutions [Doi 1986, Grosberg 1989, Ferry 1964] and the natural motions of many biological macromolecules appear to be essential for their functioning [Grosberg 1997, Chou 1986]. Consequently, considerable experimental and theoretical work has been devoted to the study of polymer dynamics. Among the available theories the most popular are the bead-spring Rouse [Kargin 1948, Rouse 1953] and Zimm [1956] phenomenological models that are considered universal models of the long-time and scale dynamics. In spite of the long-standing investigations of these models, there are still problems in their applications in the interpretation of experiments, such as the dynamic light or neutron scattering [de Gennes 1967, Dubois-Violette 1967, Richter 1984, Stockmayer 1984, Balabonov 1987, Harnau 1996]. For example, the "universal" plateau in the plot of Γ/k^3 *vs.* kR_G (Γ is the first cumulant of the dynamic structure factor (DSF), k is the wave-vector transfer at the scattering, and R_G the gyration radius of the polymer) is lower than predicted in the Rouse-Zimm (RZ) theory for flexible polymers. The diffusion coefficients of the polymer coils determined from the dynamic scattering at small kR_G are lower than calculated from the theory using R_G from the static scattering data, *etc*. The origin of these discrepancies remains unclear for many years [Doi 1986, Stockmayer 1984, Balabonov 1987, Harnau 1996, Sawatari 1998, Tothova 2007a]. Besides the scattering experiments, in other methods suitable for investigations of polymer fluids still difficulties exist between the models and experiments. For example, one can find different results for the viscosity of dilute polymer solutions (see [Muthukumar 1981, 1983] and the citations there) and the observed monomer motion in single polymer chains cannot be explained by the available theories [Shusterman 2004, Winkler 2006, Tothova 2005, 2007b]. These and many other problems [Larson 2005] are the matter of continuous discussion. The development of the theory of polymer dynamics, even in the simplest case of ideal flexible polymers in dilute solutions, is thus a challenge, first of all in the soft condensed matter physics. The present work offers one possible direction of such a development, which is based on the theory of the Brownian motion (BM), significantly generalizing the commonly used Einstein theory.

During the past decade important new results have been published on the BM in fluids. First of all, it has been definitely confirmed in experiments that the classical Einstein [1905] and Langevin [1908] theories of the BM fail to describe the chaotic motion of freely buoyant mesoscopic particles in fluids, except very long times, when the theories possess the same results. This finding has, *inter alia*, significant consequences for the models of the dynamics of polymers in solution since all of them are fully based on the theory of the BM. The aim of the present paper is to review some recent studies of the polymer dynamics, coming from a generalization of the Langevin theory. As distinct from the Langevin theory, the random force driving Brownian particles will no more be "white", *i.e.* statistically uncorrelated in the time. This, in principle, gives one a possibility to describe the motion of the particles and, consequently, the kinetics of the polymer chains in solution, over all time scales – from the ballistic regime (short times) to the diffusive one at long times.

In the present paper the main attention will be given to the natural generalization of the

Rouse and Zimm (RZ) models of the polymer dynamics, which can be called the hydrodynamic RZ model. In the Einstein description (as well as in the later Ornstein-Langevin theory [Langevin 1908, Ornstein 1927]) the resistance force on the particle during its motion in the liquid is the Stokes force, which is at a given moment of time t determined by the bead velocity at the same time. This approximation is valid only for the steady motion, $i.e.$ at $t \to \infty$ [Landau 1986]. In a more general case, within the usual Navier-Stokes hydrodynamics, the friction force on the Brownian particle should be the Boussinesq force [Boussinesq 1885] called the history force since, in general, at the time t it depends on the state of the particle motion in all the preceding moments of time (for incompressible fluids $t \gg b/c$ where c is the velocity of sound and b the radius of the spherical particle). This was noted by Vladimirsky and Terletzky [1945] who have built the first hydrodynamic theory of the translational Brownian motion. For compressible fluids it was generalized in the work [Giterman 1966], and the hydrodynamic rotational Brownian motion was first considered by Zatovsky [1969]. (These investigations (reviewed in Ref. [Lisy 2004a]) remained unknown or very little known to the physical community and a long time after the appearance of the original papers their main results were rediscovered by other authors.) The hydrodynamic memory (or the so-called viscous aftereffect) is a consequence of fluid inertia. In the Brownian motion it displays in the "long-time tails" in the particle velocity autocorrelation function that became famous after their discovery in the computer experiments on simple liquids (for a review see, $e.g.$, Ref. [Schram 1998]). The tails reflect strong correlations with the initial state of the particle and persist for a long time. The time dependence of the mean square displacement (MSD) of the particle changes from the "ballistic" regime at short times to the Einstein diffusion when the MSD is proportional to t. The nondiffusive regime with the characteristic time $\tau_b = b^2\rho/\eta$ (ρ is the density of the solvent and η its viscosity) was observed in the dynamic light scattering (DLS) experiments, $e.g.$ [Boon 1976, Paul 1981, Weitz 1989]. For example, using the diffusive wave spectroscopy, the ballistic motion of polystyrene spheres with the radius $b = 0.206$ μm in aqueous solution (with the characteristic time τ_b about 0.04 μs) was observed [Weitz 1989]. The size of such particles corresponds to the hydrodynamic radius of the DNA polymer coil of a molecular weight 6×10^6 g/mol. Even much smaller particles can be now studied using various scattering techniques. One could thus expect that similar memory effects exist in the dynamics of polymers and are observable in the DLS (or neutron scattering) experiments. The corresponding generalization of the RZ theory was given in our papers [Zatovsky 2003, Tothova 2003, 2004, 2012, 2013, Lisy 2004b]. It was shown how the memory effects reveal in observable quantities, such as the dynamic structure factor of the DLS and its first cumulant. We have also derived the generalized RZ equation taking into account the effects of hydrodynamic noise, with random fluctuations of the hydrodynamic stress tensor being responsible for the noise [Lisy 2008]. As a result, the spectral properties of the random forces acting on the polymer segments are not delta-correlated and are determined by the hydrodynamic susceptibility of the solvent. Using the preaveraging approximation we related the time correlation functions of the Fourier components of the segment radius vector to the correlation functions of the hydrodynamic field created by the noise. The velocity correlation function of the center of mass of the coil has been considered in detail. At long times its behavior follows the algebraic $t^{-3/2}$ law and does not depend on the polymer parameters. This particular result exactly corresponds to that known from the theory of BM for individual rigid particles [Vladimirsky 1945]. It also agrees with the computer simulation study [Lowe 2004] and older theoretical results that take into account the inertial effects in the motion of macromolecules in solution [Jones 1980, Bonet Avalos 1991]. In the work [Jones 1980], the macromolecule was regarded as a stiff spherical particle permeable to solvent. Its interaction with the fluid was described by the Brinkman [1947a, b] (or Debye-Bueche [1948]) equations. In Ref. [Bonet Avalos 1991], a similar approach to that used in the present work has been applied, i.e., the random sources have been incorporated in the Navier-Stokes equations to account for the hydrodynamic fluctuations. The authors have obtained equations of motion for the macromolecule in solution and analyzed the influence of nonstationary fluid motion on the dynamics of Zimm polymers through time-dependent correlation functions. However, there are several differences in [Bonet Avalos 1991] from our results, which will be discussed in Section 3. Finally, a phenomenological theory was built that takes into account the presence of other polymers in dilute solution. This was done based on the mentioned Debye-Bueche-Brinkman representation of the solution as a permeable medium [Lisy 2006a, b] where the obstacles against the fluid flow are the polymer coils themselves.

Besides the hydrodynamic approach (based on the Navier-Stokes equations), the account for the memory in the RZ theories can be done in various different ways. The common problem in all the approaches is how to choose a realistic thermal noise force entering the equations of motion for the polymer segments. This force in fluids was for the first time probed in the experiments [Franosch 2011] (for their interpretation within the hydrodynamic BM see [Lisy 2013a]). It has been shown that the time correlation function of this force in incompressible fluids consists of two terms that depend on time as $t^{-1/2}$ and $t^{-3/2}$. When the fluid displays viscoelastic properties, this dependence significantly changes. In Sec. 3 we will consider a weakly viscoelastic fluid (solvent), for which the correlation function of the thermal noise exponentially decreases in the time. Such a model corresponds to the Maxwell theory of viscoelasticity, who derived the phenomenon of viscosity by assuming that the linear elastic force acting on a particle can relax in time, yielding a viscoelastic force [Maxwell 1867, Raikher 2010, Chakraborty 2011, Grimm 2011, Goychuk 2012]. It is important to note that the corresponding generalized Langevin equation describing the chaotic motion of particles in such a fluid can be derived from first principles, modeling the solvent as a thermal bath of harmonic oscillators [Allahverdyan 2002, Goychuk 2009]. We used this theory to formulate the description of the motion of polymer chains as a set of coupled Brownian particles. Another difference from the previous theories of the polymer dynamics consists in the inclusion of inertial effects into the consideration. This allowed us to give a more correct description of universal behavior of polymers than so far not only at long times, but at short times as well, and to determine how the memory affects the behavior and observable characteristics of flexible polymers.

The next section is devoted to the description of the BM, being essential in the theory of the polymer dynamics. We begin with a short history of this phenomenon, not commonly known for the scientific audience. Then we focus on a generalization of the Langevin theory of the BM and give a simple and effective method of the solution of the equations of motion for the Brownian particles, including those that lead to the so called anomalous diffusion. Linear systems and the validity of the Gibbs statistics will be assumed. Having in disposition a strong instrument for solving different tasks involving the BM of particles constituting the studied systems, we in Section 3 develop generalizations of the RZ models for the dynamics of flexible polymers in solution: the hydrodynamic model and the model of Maxwell fluid as a solvent. Various measurable quantities will be calculated, such as the dynamic structure factors, phenomenological parameters of the statistical models of long polymer chains, diffusion coefficients, viscosity of polymer solutions and others. Where it is possible, a comparison with experiments is discussed.

In Section 4 the theory is developed also for the case of nonzero concentration of polymers in solution. This is done considering the polymer solution as a porous medium and the coils as obstacles to the solvent flow.

2 Brownian motion in fluids: the Langevin-Vladimirsky theory

2.1 A few historical remarks on the Brownian motion

Mobile particles immersed in an ambient medium can undergo an irregular, unpredictable motion. It is called the Brownian motion (BM), since it is traditionally regarded as discovered by the Scottish botanist Robert Brown who was in 1827 studying pollen particles floating in water under the microscope [Brown 1828]. The physics and mathematics behind the BM is often ascribed to Einstein. In his 1905 paper (the most frequently cited one of all his works) Einstein brought to the attention of the physicists the main mathematical concepts of the BM and indirectly con?rmed the existence of molecules and atoms (at that time the atomic nature of matter was still a controversial idea). However, the true history of both the observation and theory of the BM is much more intricate. So, some scientists believe that the first description of the BM (the jittering motion of coal dust on the surface of alcohol) belongs to the Dutch physiologist Jan Ingen-Housz [1784], best known for having discovered photosynthesis. But most probably the BM was observed soon after the discovery of microscope (the early 1590s). A remarkable description of the BM of dust particles in the air is found in the philosophical poem *De rerum natura* by Titus Lucretius Carus (c. 60 BC), who uses it also as a proof of the existence of atoms [Lucretius 1994]. The title of the Lucretius' poem is a translation of the lost Epicurus' treatise *Peri fyseós*. One could find this fact as intriguing since Epicurus (341-270 BC) pursued the Democritus' atomism but softened his strong determinism by introducing the effect of randomness, due to which something new and unexpected can arise. Also the history of the mathematics of the BM is offered equivocally. It seems that the first person to describe the mathematics behind the BM was Thiele in his 1880 paper on the method of least squares [Lauritzen 2002]. This was followed independently by L. Bachelier in 1900 in his PhD thesis (under the supervision of H. Poincaré) “Théorie de la Spéculation”, in which he presented a stochastic analysis of the stock and option markets [Bachelier 1900]. Bachelier is credited with being the first person to model the stochastic process now called BM. In the rich history of the pre-Einstein theory of the BM, important contributions of Smoluchowski and Sutherland should not be forgotten. M. Smoluchowski began to study the BM around 1900 and independently of Einstein derived the formula for the MSD of the Brownian particle [Smoluchowski 1906] (with a different numerical coefficient). Sutherland [1905] prior to Einstein [1905] and even in a more general form (taking into account a possible slipping of solvent at the particle surface) derived the now famous formula for the diffusion coefficient of the Brownian particle. In addition to the mentioned paper [Einstein 1905], Einstein published four additional works on the BM. Of remarkable interest is mainly his doctoral dissertation [Einstein 1906], where he also developed (although not correctly - for corrections due to L. Hopf see [Einstein 1911]) the celebrated formula relating the viscosity of a suspension of particles to their volume fraction. The initial period of the creation of the theory culminated with the appearance of the Langevin publication [Langevin 1908] of the (according to his own words) “infinitely more simple” theory of the BM than the Einstein's one. In what follows, we give a lot of attention to the Langevin equation, one of the most used equations of all the times. We show how it can be easily solved both in its original and the generalized form that takes into account possible memory effects in the evolution of the system.

2.2 Classical Langevin equation for the Brownian motion

As distinct from Einstein [1905], who derived and solved differential equations with partial derivatives for the probability density of the Brownian particle, Langevin [1908] has simply written down the 2nd Newton's law and included in it a stochastic force that acts on the "test" particle as a result of the chaotic hits from surrounding particles. The obtained ordinary differential equation has led to the creation of the theory of stochastic processes and is still widely used to describe Markovian (memoryless) processes in different fields of physics, chemistry, biology, electrical engineering, and even in finance [Coffey 2005]. The success of this work lies in its simplicity and in the fact that the irregular "complementary" force was introduced intuitively, not mathematically, which has given a lot of space for innumerable further studies and applications (for references see, $e.g.$, the classic works [Uhlenbeck 1930, Chandrasekhar 1943, Berne 1979, Van Kampen 1981, Doi 1987, Risken 1989] and the newer monographs [Coffey 2005, Klages 2008, Mazo 2009]).

Today, the Langevin equation for the velocity $\vec{v} = \mathrm{d}\vec{r}/\mathrm{d}t$ of the Brownian particle of mass M is used in the form

$$M\dot{\vec{v}} = -\gamma\vec{v} + \sqrt{2k_BT\gamma}\vec{\xi}\,(t)\,, \tag{2.1}$$

where the random (white noise) force with zero mean has the statistical properties $\langle\xi_i(t)\xi_j(t')\rangle = \delta_{ij}\delta(t-t')$ and its intensity is $k_BT\gamma$. The friction factor γ for a spherical particle with radius R is the Stokes one, $\gamma = 6\pi\eta R$ (η is the solvent viscosity), and the diffusion coefficient of the particle represents the simplest realization of the fluctuation-dissipation theorem (FDT), $D = k_BT/\gamma$ (this formula, usually called the Stokes-Einstein relation, should carry the name of Sutherland as well [1905]). The derivation of the MSD from equation (2.1) is very simple [Langevin 1908] and can be found in many textbooks and monographs. For any of the coordinates x, y, and z it is defined as $X(t) = \langle[x(t) - x(0)]^2\rangle$. As distinct from the Einstein relation $X(t) = 2Dt$, which is valid only for "infinite" times t, equation (2.1) predicts the behavior of the particle for arbitrary time intervals:

$$X\,(t) = 2Dt\left(1 - \frac{1 - \exp\left(-t\gamma/M\right)}{t\gamma/M}\right). \tag{2.2}$$

However, it is not fully correct and equations (2.1) and (2.2) are often used to describe situations, when they are not valid. The theory that determined the range of applicability of the Langevin theory has been published only in 1945 [Vladimirsky 1945]. In this little known paper by Vladimirsky and Terletzky, the first hydrodynamic theory of the translational BM has been created (for the discussion of this work and the first theory of the hydrodynamic rotational BM [Zatovsky 1969] see [Lisy 2004a]). Below we formulate and give the solution of the "hydrodynamic Langevin equation". Our approach differs from those published so far and is, in our opinion, simpler. It is applicable to linear systems with arbitrary memory. Here we first illustrate it on the solution of the memoryless Langevin equation.

For what follows we do not need to know explicitly the time correlation functions of the random force in Eq. (2.1). In the spirit of the original Langevin paper [1908] (see also [Coffey

2005]), we just assume that the particle is in equilibrium with the medium, all directions of the random force are equivalent (so that its mean value is zero and there is no correlation between different components of ξ), and the characteristic time of correlation of the values of the Langevin force is much less than the relaxation time due to viscous friction, $\tau = M/\gamma$. If we multiply both sides of the projection of (1) onto some of the coordinate axes, say x, by the x-component of the velocity at the time $t = 0$, after the statistical averaging we obtain

$$\dot{\Phi}_x\left(t\right) = -\frac{1}{\tau}\Phi_x\left(t\right), \tag{2.3}$$

where $\Phi_x(t) = \langle \upsilon_x(t)\upsilon_x(0)\rangle$ is the velocity autocorrelation function (VAF). It has been used that the values of the random force at the time t are statistically independent on the values of velocity at the initial time $t = 0$. The solution of equation (2.3) is

$$\Phi_x\left(t\right) = \frac{k_B T}{M}\exp\left(-\frac{t}{\tau}\right). \tag{2.4}$$

The initial condition follows from the equipartition theorem: $\Phi_x(0) = \left\langle \upsilon_x^2 \right\rangle = k_B T/M$. Having the VAF, other relevant time correlation functions for the Brownian particle can be easily found. So, the time-dependent diffusion coefficient in the x direction, $D_x(t)$, is connected to the VAF by the relation $\Phi_x(t) = \mathrm{d}D_x(t)/\mathrm{d}t$, and the MSD $X(t) = \langle [x(t) - x(0)]^2\rangle$ is obtained as [Felderhof 1991, Schram 1998]

$$X\left(t\right) = 2\int\limits_0^t (t-s)\Phi_x\left(s\right)\mathrm{d}s, \tag{2.5}$$

so that $\Phi_x(t) = \ddot{X}(t)/2$. Equation (2.5) is easily obtained representing the distance a particle moves in time as an integral of its velocity $\upsilon_x(t)$,

$$x\left(t\right) - x\left(0\right) = \int\limits_0^t \upsilon_x\left(s\right)\mathrm{d}s. \tag{2.6}$$

In [Tothova 2011a, b], we used the Vladimirsky rule [1942] for the quantity

$$V_x(t) = 2\int_0^t \Phi_x(s)\mathrm{d}s = 2D_x(t) = \mathrm{d}X(t)/\mathrm{d}t\,.$$

According to this rule, the projection of equation (2.1) on the axis x must be replaced by the equation

$$\dot{V}_x = -\frac{V_x}{\tau} + \frac{2k_B T}{M}. \tag{2.7}$$

Now it is seen that this equation, established in [Vladimirsky 1942] in a quite different and much more complicated manner, simply follows from equation (2.3) by its integrating from 0 to t and taking into account the initial condition for $\Phi_x(0)$.

In the case of the now very popular generalized Langevin equation [Kubo 1966],

$$M\dot{v} + \int_0^t \Gamma\left(t-t'\right) v\left(t'\right) \mathrm{d}t' = \eta\left(t\right), \tag{2.8}$$

the Vladimirsky rule is obtained in the same way as above (the index x is now omitted and $\eta(t)$ is a colored noise force). Equation (2.8) averaged after multiplying it by $v(0)$ becomes

$$M\dot{\Phi} + \int_0^t \Gamma\left(t-t'\right) \Phi\left(t'\right) \mathrm{d}t' = 0, \tag{2.9}$$

which is equivalent to the Vladimirsky equation

$$M\dot{V} + \int_0^t \Gamma\left(t-t'\right) V\left(t'\right) \mathrm{d}t' = 2k_B T, \tag{2.10}$$

with the initial condition $V(0) = 0$. The equivalence between (2.9) and (2.10) is seen using the Laplace transformation $\tilde{V}(s) = \mathcal{L}\{V(t)\}$, $\tilde{\Phi}(s) = \mathcal{L}\{\Phi(t)\}$, and the relation $s\tilde{V}\left(s\right) = 2\tilde{\Phi}\left(s\right)$. The Laplace transformation is effective in all the problems described by equations (2.9) and (2.10), which contain the convolution integral with a memory kernel Γ. It is also of interest to include in equations (2.1) and (2.8) external forces acting on the Brownian particle. The described method is applicable in this case as well, assuming the equations remain linear [Tothova 2011a, b].

Equation (2.8) will be considered in more detail in the section devoted to the generalized Langevin equation. Next sections will concern the hydrodynamic theory of the BM.

2.3 Hydrodynamic theory of the Brownian motion

The modern period of the studies of the BM in suspensions can be related to the late sixtieth and early seventieth of the last century, when the famous long-time "tails" of the molecular VAF (persistent or long-lived correlations) have been discovered. First in the computer experiments, and later they have been confirmed theoretically and experimentally (for a review of the literature see [Lisy 2004, Tothova 2003, Lisy 2004b, 2008]). In particular, this discovery had put in doubt the commonly accepted conception on the microscopic and macroscopic properties of liquids as being characterized by very different time scales and showed real limits (broader than expected at that time) of the hydrodynamic theory. The common view on the history of this subject can be found in a number of papers, *e.g.* [Schram 1998]. However, this view almost completely forgets several substantial contributions to the theory. In some cases the principal results in the theory of

BM were rediscovered later and attributed to other authors. First of all it concerns the remarkable work [Vladimirsky 1945]. For the later development of the hydrodynamic theory of Brownian motion we again refer to the paper [Lisy 2004a]. Here we only note that the mentioned computer experiments were explained already in [Fisher 1970]. Moreover, the solution of an interesting phenomenon of the oscillations and decay of the molecular VAF observed by Rahman [1964] was proposed as early as in 1967 [Reut 1967]. The computer simulations showed the existence of long-time asymptotes (tails) $\sim t^{-3/2}$ in the VAF of a molecule in classical fluid. The discovery of these tails had far-reaching consequences on the physics of fluids and stimulated a flow of theoretical and experimental investigations of the collective correlations in liquids. The long-time tails of the correlation functions describing the translational motion of Brownian particles have similar properties as the correlation functions for individual molecules. The effects of hydrodynamic memory appeared to be important also for the rotational Brownian motion where the memory reveals in the angular velocity correlation function of the spherical particle in the long-time algebraic asymptote $\sim t^{-5/2}$, independently on the size and density of the particle [Zatovsky 1969]. Analogous results have been found later by a number of other authors (see [Lisy 2004a]).

The hydrodynamic approach has essentially enriched the classical Einstein theory valid for $t \to \infty$ and showed the limitations of the later attempts to generalize it for arbitrary times. The basic idea of the work [Vladimirsky 1945] comes from the observation that the Stokes force, which is traditionally used to describe the friction that a particle experiences during its motion in a liquid, is in fact correct only at the steady flow. Within the usual (linearized) nonstationary Navier-Stokes hydrodynamics this force should be replaced by the expression [Landau 1986]

$$\vec{F}(t) = -6\pi\eta R\left\{\vec{v}(t) + \frac{\rho R^2}{9\eta}\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} + \sqrt{\frac{\rho R^2}{\pi\eta}}\int\limits_{-\infty}^{t}\frac{\mathrm{d}\vec{v}}{\mathrm{d}t'}\frac{\mathrm{d}t'}{\sqrt{t-t'}}\right\}. \tag{2.11}$$

Equation (2.11) is valid for all times, except the very short times when the compressibility effects should be taken into account. That is, for incompressible fluids the condition $t \gg R/c$, where c is the sound velocity, is required. This expression has been derived by Boussinesq in [Boussinesq 1885] (notice as a curiosity that Boussinesq was a member of the committee at the Bachelier's defense of the PhD thesis) and independently by Basset [1888]. As it should be in the nonstationary case, the Boussinesq-Basset force on the particle at the time t is determined by its velocities and accelerations in all the preceding moments of time. This phenomenon is called the viscous aftereffect or the hydrodynamic memory. It is seen from (2.11) that for fluids with the density comparable to the density of the Brownian particle (which is the usual case of freely buoyant particles) the terms additional to the Stokes one cannot be neglected since in the equation of motion for the particle they are of the same order as the inertial term.

2.4 Solution of the hydrodynamic Langevin equation

There are several ways how to solve the Langevin equation (2.1) with the Stokes force replaced by the Boussinesq force (2.11). For example, one can rewrite the problem in the Fourier transformation for the velocity,

$$\vec{v}(t) = \int_{-\infty}^{\infty} \vec{v}_\omega \exp(-\mathrm{i}\omega t)\mathrm{d}t.$$

For the force we shall have $\vec{F}_\omega = -\gamma_\omega \vec{v}_\omega$ with the frequency-dependent friction

$$\gamma_\omega = 6\pi\eta R(1 - \mathrm{i}kR - k^2R^2/9), \quad k^2 = \mathrm{i}\omega\rho/\eta, \quad \mathrm{Re}\, k > 0\,,$$

so that the transformed Langevin equation becomes $\vec{v}_\omega = \sqrt{2k_BT\gamma}(\gamma_\omega - \mathrm{i}m\omega)^{-1}\vec{\xi}_\omega$. Then we find the generalized susceptibility $\alpha(\omega)$ that connects the radius vector with the random force $\vec{f}_\omega = \sqrt{2k_BT\gamma}\vec{\xi}_\omega$. Using $\vec{v}_\omega = -\mathrm{i}\omega\vec{r}_\omega$ and the above relation between the velocity and the force, we get

$$\alpha(\omega) = -\frac{1}{(m\omega^2 + \mathrm{i}\omega\gamma_\omega)}.$$

The MSD in the x direction is obtained from the fluctuation-dissipation relation

$$X(\tau) = \frac{2k_BT}{\pi \mathrm{i}} \int_{-\infty}^{\infty} \frac{\alpha(\omega)}{\omega}(1 - \cos\omega\tau)\mathrm{d}\omega. \tag{2.12}$$

Performing the calculations is not easy but in this case it can be done exactly (even in a more general case of compressible solvents [Gitterman 1966]). In the long-time limit

$$X\,(t) \approx 2Dt\left[1 - \frac{2}{\sqrt{\pi}}\left(\frac{\tau_R}{t}\right)^{1/2} + \frac{\tau_R - \tau}{t} + \cdots\right], \tag{2.13}$$

where $\tau_R = R^2\rho/\eta$ (the characteristic vorticity time) and $\tau = M^*/\gamma$, with $M^* = M + M_s/2$, M_s being the mass of the solvent displaced by the particle.

Now we will show that the solution can be obtained very easily as follows. Based on the work [Vladimirsky 1945], instead of equation (2.1) with the force (2.11) we can solve the deterministic "equation of motion" for the quantity $V(t) = \mathrm{d}X/\mathrm{d}t$ [Lisy 2010, Tothova 2011c]

$$\dot{V}(t) + \frac{1}{\tau}\sqrt{\frac{\tau_R}{\pi}} \int_0^t \frac{\dot{V}(t')}{\sqrt{t - t'}}\mathrm{d}t' + \frac{1}{\tau}V(t) = \frac{2k_BT}{M^*}. \tag{2.14}$$

Here, the constant "force" $2k_BT$ at the right begins to act on the particle at the time $t = 0$; up to this moment the particle is at rest together with the liquid. The initial conditions are thus $V(0) = X(0) = 0$ (as seen from (2.14), it also holds $\dot{V}(0) = 2k_BT/M^*$). A simple way to solve Eq. (2.14) is to use the Laplace transformation, $\tilde{V}(s) = \mathcal{L}\{V(t)\}$. This leads to the equation

$$\tilde{V}(s) = \frac{2k_BT}{M^*}s^{-1}\left(s + \tau_R^{1/2}\tau^{-1}s^{1/2} + \tau^{-1}\right)^{-1}\,. \tag{2.15}$$

The inverse transform is found expanding the term $(...)^{-1}$ in simple fractions. If

$$\lambda_{1,2} = -(\tau_R^{1/2}/2\tau)[1 \mp \sqrt{1 - 4\tau/\tau_R}]$$

are the roots of equation $s + \tau^{-1}(\tau_R s)^{1/2} + \tau^{-1} = 0$, then

$$\tilde{V}(s) = \frac{2k_B T}{M^* s} \frac{1}{\lambda_2 - \lambda_1} \left(\frac{1}{\sqrt{s} - \lambda_2} - \frac{1}{\sqrt{s} - \lambda_1} \right), \tag{2.16}$$

so that the inverse transform yields [Abramowitz 1964]

$$\begin{aligned} V(t) = \frac{2k_B T}{M^*} \frac{1}{\lambda_2 - \lambda_1} \Bigg\{ & \frac{1}{\lambda_2} \left[\exp(\lambda_2^2 t) \mathrm{erfc}\left(-\lambda_2 \sqrt{t}\right) - 1 \right] \\ & - \frac{1}{\lambda_1} \left[\exp(\lambda_1^2 t) \mathrm{erfc}\left(-\lambda_1 \sqrt{t}\right) - 1 \right] \Bigg\}. \end{aligned} \tag{2.17}$$

The VAF obtained as $\Phi\left(t\right) = \dot{V}\left(t\right)/2$ exactly corresponds to the solutions found by Hinch [1975] by a different method, but disagrees with the earlier solution of Karmeshu [1973] due to the difference in the roots $\lambda_{1,2}$. The long-time tails in the time correlation functions of the Brownian particle have been discovered already in the mentioned paper [Vladimirsky 1945]. For the VAF at $t \to \infty$ it follows from equation (2.17) that $\Phi(t) \sim t^{-3/2}$,

$$\Phi(t) \approx \frac{k_B T}{2\sqrt{\pi} M^*} \frac{\tau \sqrt{\tau_R}}{t^{3/2}} \left[1 - \frac{3}{2} \left(1 - 2\frac{\tau}{\tau_R} \right) \frac{\tau_R}{t} + \cdots \right]. \tag{2.18}$$

The mean square displacement,

$$\begin{aligned} X\left(t\right) = 2D \Bigg\{ & t - 2\left(\frac{\tau_R t}{\pi}\right)^{1/2} + \tau_R - \tau \\ & + \frac{1}{\tau} \frac{1}{\lambda_2 - \lambda_1} \left[\frac{\exp\left(\lambda_2^2 t\right)}{\lambda_2^3} \mathrm{erfc}\left(-\lambda_2 \sqrt{t}\right) - \frac{\exp\left(\lambda_1^2 t\right)}{\lambda_1^3} \mathrm{erfc}\left(-\lambda_1 \sqrt{t}\right) \right] \Bigg\} \end{aligned} \tag{2.19}$$

obtained from (2.17) by simple integration, corresponds very well to experiments, *e.g.*, [Jeney 2005]. The long-time limit, $t \to \infty$,

$$X\left(t\right) \approx 2Dt \left\{ 1 - 2\sqrt{\frac{\tau_R}{\pi\tau}} + \frac{2}{9}\left(4 - \frac{M}{M_s}\right)\frac{\tau_R}{t} - \frac{1}{9\sqrt{\pi}}\left(7 - 4\frac{M}{M_s}\right)\sqrt{\frac{\tau_R^3}{t^3}} + \cdots \right\}, \tag{2.20}$$

agrees with (2.13). It has been definitely confirmed in [Jeney 2005] that the original Langevin solution has a very limited applicability. In fact [Vladimirsky 1945], it is true only for heavy particles in a low-density environment (such as dust particles in a gas [Blum 2006]) and simultaneously at short times or, alternatively, at long times, when it is however not necessary since the Einstein theory is valid.

2.5 Generalized Langevin-Kubo equation

In the preceding section the Langevin equation has been considered, in which the dissipative force originates from the Navier-Stokes hydrodynamics. In a variety of systems this force can be different. The used approach can be however equally applied to the solution of linear problems with any kind of memory. One needs not to take care of a concrete form of the random force driving the particles. If this force is not the delta-correlated white noise but a colored noise, the resistance force cannot be arbitrary (*e.g.*, it cannot be the Stokes one) but must obey the FDT [Kubo 1966, Balakrishnan 1979]. For example, if the equation of motion for the Brownian particle has a non-Markovian form of the so called generalized Langevin equation (2.8), the FDT dictates that the kernel Γ must be connected to the noise $\eta(t)$ (a stochastic force with zero mean) by the relation $\langle\eta(t)\eta(0)\rangle = k_BT\Gamma(t)$ (at $t > 0$). The equation for the MSD of the particle with mass M now has the form (2.10). It can be easily solved for the specific memory kernels considered in the literature so far. It also allows deriving all the properties of this kind of anomalous diffusion that have been obtained by more complicated methods. For example, taking the Laplace transformation Λ and using the initial conditions $X(0) = V(0) = 0$, we obtain for $\tilde{V}(s) = \mathcal{L}\{V(t)\}$ and $\tilde{X}(s) = \mathcal{L}\{X(t)\}$

$$\tilde{V}(s) = \frac{2k_BT}{s}\frac{1}{Ms + \tilde{\Gamma}(s)}, \qquad \tilde{X}(s) = \frac{\tilde{V}(s)}{s}. \tag{2.21}$$

It immediately follows from this equation that if at small s the kernel $\tilde{\Gamma}$ behaves as $\tilde{\Gamma} \propto s^{\nu}$ and the root MSD at long times is $X(t) \propto t^{\alpha}$, then there are two possibilities: i) if $\nu < 1$, then $\alpha = \nu + 1$, and the VAF $\Phi(t)$ decays to zero as $t \to \infty$ (this corresponds to the irreversibility condition and, consequently, the ergodicity of the variable v [Lapas 2008]), ii) if $\nu \geq 1$, then $\alpha = 2$ (ballistic motion) and $\Phi(t)$ converges to a constant as $t \to \infty$. We have sub-diffusion ($\alpha < 1$) if $\nu < 0$ and super-diffusion ($\alpha > 1$) if $\nu > 0$. The Einstein diffusion corresponds to $\nu = 0$. At short times the result is consistent with the equipartition theorem,

$$D(t) \approx k_BTt/M, \qquad X(t) \approx (k_BT/M)t^2, \qquad t \to 0 \tag{2.22}$$

independently of a concrete form of $\Gamma(t)$. Note that if $\Gamma(t) \propto t^{-\alpha}$, $0 < \alpha < 1$, the second term on the left side of equation (2.8) can be expressed through the fractional derivative ${}_0D_t^{\alpha-1}v(t)$. Equation (2.10) can be thus used also for effective solving of fractional Langevin equations for the translational BM [Lutz 2001].

Equation (2.8) does not contain regular external forces. A generalization to this case is, however, straightforward. The direct application of the method used in the previous section is possible in all cases when the deterministic force $\vec{F}_{\text{ext}}(\vec{x}, \vec{v})$ linearly depends on the dynamic variables and $\vec{F}_{\text{ext}}(0, 0) = 0$. Then, as above, one can in the generalized Langevin equation (2.8) in its vector form simply replace x_i by X_i, v_i by V_i = dX_i/dt, and η_i by $2k_BT$, $i = x$, y, z. An example of a problem of such kind can be found in [Tothova 2010]. It corresponds to the BM in an external magnetic field $\vec{B}$ (then $\vec{F}_{\text{ext}} = Q\vec{v} \times \vec{B}$) and the fluctuating colored force $\vec{\eta}$. In more complicated cases when the external force is nonlinear or if for the linear force $\vec{F}_{\text{ext}}(0, 0) \neq 0$(*e.g.*, for a particle in an external harmonic potential with a time dependent position $\vec{x}^*$ of its minimum the force will be $\vec{F}_{\text{ext}}(\vec{x}, \vec{v}) = -k(\vec{x} - \vec{x}^*)$, where k is the force constant of this potential), one can use the method of the work [Van Zon 2003] and act as follows. First, the deterministic equation (2.8) ($i.e.$, the equation without the random force) is solved for $\bar{x}_i(t)$with the appropriate initial conditions. Then the transition to the equation of the type (2.10) can be accomplished with the equation that is obtained after subtracting the deterministic equation from the original equation (2.8) with the force $\vec{F}_{\text{ext}}$. By this way one finds $X_i(t)$ for the deviation of the coordinates $x_i(t)$ from $\bar{x}_i(t)$. After finding the solution for $\bar{x}(t)$the full MSD for $x_i(t)$ is obtained as $\xi_i(t) = X_i(t) + [\bar{x}_i(t) - \bar{x}_i(0)]^2$, where we have used that $\langle x_i(t) - \bar{x}_i(t) \rangle = 0$ and the fact that the quantity $\bar{x}_i(t)$ is deterministic. We have illustrated this approach on the problem of the BM in a harmonic optical trap [Vasziova 2010]. This problem has attracted attention in connection with the attempts to validate the fluctuations theorems [Mazonka 1999, Van Zon 2003, Wang 2002]. As distinct from those works where the overdamped form of the equations of motion was considered, we proceeded with their full form, keeping $m \neq 0$. It has been shown, in particular, that the fluctuation spectrum of the VAF (obtained using the Wiener-Khinchin theorem [Van Kampen 1981]) at the $m \to 0$ limit significantly differs from the results obtained in the mentioned works. We thus suppose that it would be important to take the inertial effects into account and to consider the validity of the fluctuation theorems for all the times, not only for long times as in the cited works. Moreover, as already discussed, for Brownian particles moving in a fluid (as in the experiment [Wang 2002]), the standard Langevin equation does not represent a good model and a more correct description (for instance, the hydrodynamic Langevin-Vladimirsky model) should be used. We have applied this model to the BM of charged particles across the external magnetic field in [Tothova 2010]. A similar task for charged Brownian particle driven by exponentially correlated noise forces was considered in [Lisy 2013b, 2014].

In conclusion to this part of our review, we mentioned some problems in the BM, which for their solution need a generalization of the standard Langevin equation often used to describe situations for which it is inappropriate. We have given attention to a more general “hydrodynamic Langevin equation” and the related questions of anomalous diffusion, often described by the so called generalized Langevin equation. One of the main presented results is the method of solution of the corresponding Volterra-type integro-differential stochastic equations. Using it, a number of attractive problems from various fields of science related to the BM, including the anomalous BM) can be efficiently solved. From the applications that are currently of great interest we mention, for example, the motion of Brownian particles dragged by optical tweezers [Van Zon 2003, Li 2010], the anomalous motion of colloidal particles under the influence of various external fields [Carberry 2004, Löwen 2009], the behavior of mesoscale electric circuits in contact with the thermal bath [Garnier 2005, Allahverdyan 2002], or the motion of magnetic domain walls [Saitoh 2004]. In what follows, the generalized Langevin theory will be used to model the dynamics of polymers in dilute solutions.

3 Dynamics of polymers in solution: Generalized bead-spring models

As already mentioned in Introduction, traditional bead-spring models of the polymer dynamics are based on the Einstein theory of the BM, valid only at the times much larger than the particle's relaxation time. The reason is in neglecting the inertial and memory effects in the dynamics, which are connected to the fact that the thermal noise force driving the particles has a nonzero correlation time [Franosch 2011]. Here, we use a generalized theory of the BM to build models of the dynamics of polymers in solution. Basic stochastic equations of motion for the polymer beads will be established. First, we consider the motion of polymers in the so called Maxwell's fluids, then the models that naturally arise within the Navier-Stokes hydrodynamics and generalize the Rouse model, in which the hydrodynamic interactions (HI) are neglected (or really screened out). It is notable that the description of the motion of the polymer as a whole does not assume any concrete form of the interactions between the beads and the equilibrium conformation of the chain. In the original model the chains are Gaussian in equilibrium and only the nearest neighbors along the chain interact. To get a correct description of the short-time dynamics, inertial effects are included into the consideration. Then an attempt to include the HI into the consideration is presented. In both the cases the friction force has a form of a memory integral, so that mathematically the problem requires the solution of integro-differential stochastic equations.

3.1 Generalization of the Rouse model for polymers in Maxwell's fluids

In the standard Rouse theory an "ideal" polymer modeled as a chain with a large number of spherical beads is considered. The chain is flexible and thus coiled in solution. In equilibrium, the distribution of the beads is Gaussian. During the motion the chain remains phantom and only small deviations from the equilibrium are assumed. Every bead interacts only with its neighbors along the chain. The interaction with the solvent is through the friction force (which is the Stokes force in the traditional approach), and the bead moves due to the hits of the solvent molecules that give rise to the Langevin random force. The model aims to be universal, $i.e.$, the details of chemical structure of the polymers are neglected and only distances and times much larger than the atomic ones are considered [Doi 1986, Grosberg 1989]. Also the so called volume interactions are neglected, as well as interactions between different chains. In a more general approach these interactions and, first of all, the hydrodynamic interactions should be included in the consideration, which leads to a more sophisticated Zimm model [Zimm 1956]. (Note that in fact the Rouse and Zimm models naturally join in one model [Lisy 2004b, 2006a, Tothova 2007a, b]). This has important consequences for the interpretation of experiments on polymer solutions and the determination of polymer characteristics; however, here we give the main attention to building a model that could reveal the role of the "colored" thermal noise and try to keep the model simple and avoid the mentioned complications (for possible generalizations of the presented model we refer to the study by Fatkullin *et al.* [2010] and below in this section).

The equations of motion (projected on an axis, say x) for the nth bead ($n = 1, 2, ..., N \gg 1$) in the Rouse model appear as

$$M\frac{\mathrm{d}^2 x_n}{\mathrm{d}t^2} = f_n^{fr} + f_n^{ch} + f_n, \tag{3.1}$$

where x_n is the projection of the radius $\vec{r}_n$ of a particle of mass M, f_n^{fr} is the friction force, f_n^{ch} is the force by neighbor particles in the chain, and f_n is the random force. The force f_n^{ch} ($n \neq 1, N$) can be expressed as

$$f_n^{ch} = -\frac{\partial U}{\partial \vec{x}_n} = \frac{3k_BT}{a^2}\left(x_{n+1} + x_{n-1} - 2x_n\right), \tag{3.2}$$

where U is the total energy of interaction between the particles, given by their equilibrium Gaussian distribution in the chain [Doi 1986] (for a more general approach without the use of this assumption see [Fatkullin 2010])

$$U = \frac{3k_BT}{2a^2}\sum_{n=1}^{N-1}\left(\vec{r}_{n+1} - \vec{r}_n\right)^2 + A. \tag{3.3}$$

Here, the constant A is independent on the polymer conformation and a is the mean square distance between the particles along the chain. The first and end particles have only one neighbor, so that for them f_n^{ch} will be

$$f_1^{ch} = \frac{3k_BT}{a^2}\left(x_2 - x_1\right), \qquad f_N = \frac{3k_BT}{a^2}\left(x_{N-1} - x_N\right). \tag{3.4}$$

For processes at distances much larger than the bead radius b and for long chains ($L \gg a$), the continuum approximation is substantiated: $x_n \rightarrow x\left(n, t\right)$,

$$x_{n\pm 1}\left(t\right) \rightarrow x\left(t, n\right) \pm \frac{\partial x\left(t, n\right)}{\partial n} + \frac{1}{2}\frac{\partial^2 x\left(t, n\right)}{\partial n^2} + \cdots . \tag{3.5}$$

As usually [Doi 1986, Grosber 1989], for the first and the last bead we introduce fictitious particles with the indices 0 and $N+1$, so that $x_0 - x_1 \equiv 0$ and $x_{N+1} - x_N \equiv 0$. In the continuum approximation it is equivalent to the boundary conditions

$$\frac{\partial x\left(t, n\right)}{\partial n} = 0, \qquad n = 0, N\,. \tag{3.6}$$

For the discussed Maxwell viscoelasticity model the friction force is expressed as a convolution of the bead velocity and a memory kernel Γ, so that the final generalization of the Rouse equations in the continuum approximation reads

$$M\frac{\partial v\left(t, n\right)}{\partial t} + M\int_0^t \Gamma\left(t - \tau, n\right) v\left(\tau, n\right) \mathrm{d}\tau = \frac{3k_BT}{a^2}\frac{\partial^2 x\left(t, n\right)}{\partial n^2} + f\left(t, n\right)\,. \tag{3.7}$$

Here,

$$\begin{aligned}\Gamma(t) &= \omega_M \omega_m \exp(-\omega_m t),\\ \omega_m &= \gamma/m,\\ \omega_M &= \gamma/M,\\ \omega_m\omega_M &= (m/M)\tau_m^{-2},\end{aligned}$$

if we denote the relaxation time as $\tau_m = m/\gamma$. For the random force we have

$$\langle f(t,n)\, f(t',m)\rangle = k_B T \delta_{nm} \Gamma(t-t'). \tag{3.8}$$

In this notation m can be understood as the mass of a Brownian particle in the standard Langevin equation $m\dot{u}(t) + \gamma u(t) = \phi(t)$ with the Stokes friction and delta correlated (white) noise force $\phi(t)$, with the correlation function $\langle\phi(t)\phi(t')\rangle = 2k_B T\gamma\delta(t-t')$. For spherical beads $\gamma = 6\pi\eta b$, with η being the dynamic viscosity of the solvent. One thus could interpret the motion of particles M, described by Eq. (3.7), as being induced by other Brownian particles of mass m, whose motion is governed by the normal Langevin equation. The exponentially correlated force $f(t)$ exactly corresponds to the solution of this Langevin equation for $m\mathrm{d}v/\mathrm{d}t$. Its relation (3.8) to the memory kernel is due to Kubo's fluctuation-dissipation theorem [Kubo 1966]. Note that equations similar to (3.7) have been already used in Ref. [Fatkullin 1993] but without the inertial term and with the intrachain force written with the opposite sign (see also [Kimmich 2004]).

3.2 Center of mass motion of Rouse polymers: exact solution

Let us explicitly write down the equations of motion (3.1) in their discrete variant:

$$\begin{aligned}&M\dot{v}_n(t) + M\int_0^t \Gamma(t-\tau)\, v_n(\tau)\, \mathrm{d}\tau = \frac{3k_BT}{a^2}(x_{n+1}+x_{n-1}-2x_n) + f_n, \quad n \neq 1,\, N,\\ &M\dot{v}_1(t) + M\int_0^t \Gamma(t-\tau)\, v_1(\tau)\, \mathrm{d}\tau = \frac{3k_BT}{a^2}(x_2 - x_1) + f_1,\\ &M\dot{v}_N(t) + M\int_0^t \Gamma(t-\tau)\, v_N(\tau)\, \mathrm{d}\tau = \frac{3k_BT}{a^2}(x_{N-1} - x_N) + f_N.\end{aligned} \tag{3.9}$$

For the motion of the whole coil, this set of equations can be solved exactly. Summing up all equations, the internal forces, as expected, disappear and one obtains the following equation for the motion of the polymer center of mass, $x_C = \sum_n x_n/N$, which is the same as the sum of N

equations of motion for independent particles,

$$MN\dot{v}_C\,(t) + MN\int\limits_0^t \Gamma\,(t-\tau)\,v_C\,(\tau)\,\mathrm{d}\tau = \sum_{n=1}^{N} f_n, \tag{3.10}$$

The stochastic integro-differential equation (3.10) is within the Gibbs statistics equivalent to the deterministic equation for the MSD of the coil, $X_C(t) = \langle [x_C(t) - x_C(0)]^2 \rangle$. If we denote $V_C = \mathrm{d}X_C/\mathrm{d}t$, the new equation will be [Tothova 2011a, c] (for the proof of the transformation from Eq. (3.10) to (3.11) see [Tothova 2011b])

$$\dot{V}_C\,(t) + \int\limits_0^t \Gamma\,(t-\tau)V_C\,(\tau)\,\mathrm{d}\tau = \frac{2k_BT}{NM}. \tag{3.11}$$

Equation (3.11) should be solved with the evident initial conditions $X_C = V_C = 0$. The solution can be easily obtained using the Laplace transformation, $\tilde{V}_C(s) = \mathcal{L}\{V(t)\}$,

$$\begin{aligned}\tilde{V}_C\,(s) &= \frac{2k_BT}{NM}\frac{1}{s_2-s_1}\left(1+\frac{\omega_m}{s}\right)\left(\frac{1}{s-s_2}-\frac{1}{s-s_1}\right),\\ s_{1,2} &= -\frac{\omega_m}{2}\left(1\mp\sqrt{1-\frac{4\omega_M}{\omega_m}}\right).\end{aligned} \tag{3.12}$$

The inversion of Eq. (3.12) gives

$$V_C\,(t) = \frac{2k_BT}{NM}\frac{1}{s_2-s_1}\left[\left(\frac{\omega_m}{s_1}-\frac{\omega_m}{s_2}\right)+\exp\left(s_2t\right)\left(1+\frac{\omega_m}{s_2}\right)-\exp\left(s_1t\right)\left(1+\frac{\omega_m}{s_1}\right)\right]. \tag{3.13}$$

For the MSD $X_C\,(t) = \int_0^t V_T\,(\tau)\mathrm{d}\tau$ one finally obtains

$$X_C\,(t) = \frac{2k_BT}{NM}\frac{1}{s_2-s_1}\left[\frac{\omega_m t}{s_1}-\left(1+\frac{\omega_m}{s_1}\right)\frac{\exp\left(s_1t\right)-1}{s_1}-(s_1\to s_2)\right]. \tag{3.14}$$

Let us find the asymptotic behavior of this solution. At $t \to 0$, the ballistic motion follows from (3.14), independently on the character of the random force,

$$X_C\,(t) \approx \frac{k_BT}{NM}t^2. \tag{3.15}$$

At long times we obtain

$$X_C\,(t\to\infty) = \frac{2k_BT}{NM}\left[\frac{t}{\omega_M}+\frac{1}{\omega_M}\left(\frac{1}{\omega_m}-\frac{1}{\omega_M}\right)+\cdots\right]. \tag{3.16}$$

The original Rouse result should be obtained at zero relaxation time of the random force. In this case $\omega_m \to \infty$ and the roots $s_{1,2}$ after Eq. (3.12) are $s_1 \approx -\omega_M$, $s_2 \approx -\omega_m$, so that

$$X_C\left(t\right) \approx \frac{2k_BT}{N\gamma}\left[t + \frac{\exp\left(-\omega_M t\right) - 1}{\omega_M}\right], \tag{3.17}$$

which still gives corrections to the Rouse expression. Only at $M \to 0$ ($\omega_M \to \infty$) the classical result $X_C(t) = 2k_BT/N\gamma$ is recovered.

3.3 Dynamics of internal modes

It is convenient to perform further analysis of Eq. (3.1) in terms of the normal modes $y_p(t)$, defined by the Fourier transforms

$$\begin{aligned} x\left(t,n\right) &= y_0\left(t\right) + 2\sum_{p=1}^{\infty} y_p\left(t\right)\cos\frac{\pi n p}{N}, \\ f\left(t,n\right) &= f_0\left(t\right) + 2\sum_{p=1}^{\infty} f_p\left(t\right)\cos\frac{\pi n p}{N}, \end{aligned} \tag{3.18}$$

chosen so that the boundary conditions (3.6) are already satisfied. The index $p = 0$ corresponds to the motion of the whole coil, and $p = 1, 2, 3, ...$ are for the internal modes. Substituting (3.18) in Eq. (3.7), we obtain after multiplication by $\cos(\pi q n/N)$ and integration through n from 0 to N the following equation for y_q in the continuum approximation:

$$M\ddot{y}_q\left(t\right) + \int_0^t \Gamma\left(t-\tau\right)\dot{y}_q\left(\tau\right)\mathrm{d}\tau + 3k_BT\left(\frac{\pi q}{Na}\right)^2 y_q\left(t\right) = f_q\left(t\right). \tag{3.19}$$

It can be again transformed to a deterministic equation for $U_q \equiv \mathrm{d}Y_q/\mathrm{d}t$, where $Y_q(t) = \langle[y_q(t) - y_q(0)]^2\rangle$ is the MSD for internal modes,

$$\dot{U}_q\left(t\right) + \int_0^t \Gamma\left(t-\tau\right)U_q\left(\tau\right)\mathrm{d}\tau + \omega_q^2\int_0^t U_q\left(\tau\right)\mathrm{d}\tau = \frac{k_BT}{NM}, \tag{3.20}$$

where

$$\omega_q^2 = \frac{3k_BT}{M}\left(\frac{\pi q}{Na}\right)^2. \tag{3.21}$$

Using the Laplace transformation $\tilde{U}_q(s) = \mathcal{L}\{U_q(t)\}$,

$$\tilde{U}_q\left(s\right) = \frac{k_BT}{NM}\frac{s+\omega_m}{s^3 + \omega_m s^2 + \left(\omega_m\omega_M + \omega_q^2\right)s + \omega_m\omega_q^2}, \tag{3.22}$$

we obtain in the time domain

$$U_q\left(t\right)=\frac{k_BT}{NM}\sum_{i=1}^{3}A_i\exp\left(s_it\right), \tag{3.23}$$

$$Y_q\left(t\right)=\int\limits_0^t U_q\left(t'\right)\mathrm{d}t'=\frac{k_BT}{NM}\sum_{i=1}^{3}\frac{A_i}{s_i}\left[\exp\left(s_it\right)-1\right]. \tag{3.24}$$

Now s_i are the roots of cubic equation

$$s^3+\omega_m s^2+\left(\omega_m\omega_M+\omega_q^2\right)s+\omega_m\omega_q^2=0.$$

The parameters A_i

$$A_1=(s_1+\omega_m)(s_1-s_2)^{-1}(s_1-s_3)^{-1},$$

(and A_2, A_3 obtained by the cyclic change $1\to 2\to 3\to 1$) satisfy the relations

$$\begin{aligned}
&\sum_i\frac{A_i}{s_i}=\frac{\omega_m}{s_1s_2s_3}=-\frac{1}{\omega_q^2},\\
&\sum_i A_i=0,\\
&\sum_i A_is_i=1,\\
&\sum_i A_is_i^2=0,\\
&\sum_i A_is_i^3=-\left(\omega_m\omega_M+\omega_q^2\right),\\
&\quad\vdots
\end{aligned} \tag{3.25}$$

Using these relations, the asymptotic behavior of the solution (3.24) is as follows:

$$Y_q\left(t\right)=\frac{k_BT}{2NM}t^2\left(1-\frac{\omega_m\omega_M+\omega_q^2}{12}t^2+...\right),\qquad t\to 0, \tag{3.26}$$

$$Y_q\left(t\right)\approx\frac{k_BT}{NM\omega_q^2}\left[1-\exp\left(-\frac{\omega_q^2t}{\omega_M}\right)\right],\qquad t\to\infty. \tag{3.27}$$

At $t\to 0$ we thus have the ballistic behavior $Y_q(t)\approx k_BTt^2/(2NM)$.

If the correlation time τ_m of the random force tends to zero, the classical solution [Rouse 1953] should be recovered,

$$\psi_p\left(t\right) = \left\langle y_p\left(0\right) y_p\left(t\right)\right\rangle = \frac{1}{2} D_C \tau_p \exp\left(-t/\tau_p\right), \tag{3.28}$$

where $Y_p(t) = 2[\psi_p(0) - \psi_p(t)]$, $D_C = k_B T/\gamma$ is the diffusion coefficient of the coil, and

$$\tau_p = \frac{N^2 a^2 \gamma}{3\pi^2 k_B T p^2}, \qquad p \geq 1, \tag{3.29}$$

are the well-known Rouse relaxation times for the internal modes [Rouse 1953, Doi 1986, Grosberg 1989]. The result (3.28) can be obtained from our solution (3.24) at $\tau_m \to 0$

$$Y_q\left(t\right) = \frac{k_B T}{NM} \frac{1}{s_2 - s_1} \left(\frac{1}{s_1} - \frac{1}{s_2} + \frac{\exp(s_2 t)}{s_2} - \frac{\exp(s_1 t)}{s_1}\right), \tag{3.30}$$

where the roots s_i are now

$$2s_{1,2} = -\omega_M \left[1 \mp \sqrt{1 - 4\omega_q^2 \omega_M^{-2}}\right], \tag{3.31}$$

only when $M \to 0(\omega_M \to \infty)$, *i.e.*, for a chain of overdamped oscillators. In this case

$$Y_q\left(t\right) \approx \frac{k_B T}{NM\omega_q^2} \left\{1 - \exp\left[-\frac{3k_B T}{\gamma}\left(\frac{\pi q}{Na}\right)^2 t\right]\right\} \to \frac{k_B T}{NM\omega_q^2} = \frac{N}{3}\left(\frac{a}{\pi q}\right)^2, \quad t \to \infty, \tag{3.32}$$

which coincides with Eq. (3.28).

3.4 Possible experimental verification of the generalized Rouse model

The question arises how the features predicted in the previous paragraph could be checked in experiments. Besides the scattering experiments, widely used in the studies of polymer dynamics, the NMR techniques are often very useful. It has been shown by Fatkullin *et al.* [Fatkullin 2010] that intermolecular dipole-dipole (d-d) interactions can strongly affect or even dominate NMR experiments probing the polymer dynamics at sufficiently low frequencies. Interpretations of proton NMR data, in which the role of such interactions was neglected, should therefore be revisited in this aspect, using an appropriate theoretical model describing the spin-lattice relaxation in polymer systems. To validate or invalidate theoretical models on the basis of experiments, the key problem is to have in disposition a theoretically calculated physical quantity that is experimentally measurable. In the case of polymers studied by NMR methods it is difficult to find a correspondence between the theory and a suitable experimental technique. Basically, such correspondence has been established in a series of works by Kimmich, Fatkullin, and collaborators, beginning from Ref. [Fatkullin 1993] (see also [Kimmich 2004, Fatkullin 2010] and refs. therein). The experimental method developed for the purpose to study the polymer relaxation times up to the times when the usual diffusometry with the magnetic field gradients begins to be applicable, is the field-cycling NMR relaxometry. At high frequencies this technique can be supplemented with the spin-lattice relaxation measurements with the use of conventional NMR spectrometers [Kimmich 2004]. The method allows investigating the fluctuations of d-d couplings between identical spins (most often the proton ones). Mathematically, these interactions are described through the time correlation functions of the spin Hamiltonian H_d: the inverse spin-lattice relaxation time $1/T_1$ is determined as a Fourier transform of the correlator $\langle H_d(t)H_d(0)\rangle$. The problem how to relate the measured relaxation time to the polymer characteristics has been resolved in [Fatkullin 1993]. If the polymer is modeled as a chain of segments located at positions $\vec{r}_n$, T_1 is in the continuum approximation connected to the fluctuations of $\vec{r}_n(t)$ according to the formula

$$\frac{1}{T_1} \propto \int\limits_{-\infty}^{\infty} \left\langle \vec{b}(t,n)\vec{b}(0,n)\right\rangle^2 \exp(-\mathrm{i}\omega t)\mathrm{d}t, \tag{3.33}$$

where $\vec{b}(t,n) = \partial\vec{r}(t,n)/\partial n$. All the remaining depends on the model used in the description of the polymer dynamics. Using the model described in the previous sections, the spin-lattice relaxation time of polymers can be expressed through the correlator $\psi_p(t)$ of the normal modes y_p (see Eq. (3.28)) as

$$\frac{1}{T_1} \propto \frac{36\pi^4}{N^4} \int\limits_{-\infty}^{\infty} \mathrm{d}t \left(\sum_{p>0} p^2 \psi_p\left(t\right)\right)^2 \exp\left(-\mathrm{i}\omega t\right). \tag{3.34}$$

The general formula for the spin-lattice relaxation rate has the form [Kimmich 2004]

$$\frac{1}{T_1} \propto \frac{18}{N^5} \left(\frac{\pi^2 k_B T}{M}\right)^2 \int\limits_{0}^{\infty} \mathrm{d}t \left(\sum_{p>0}\sum_{i=1}^{3} C_i(p) \exp\left(s_i t\right)\right)^2 \cos\left(\omega t\right), \tag{3.35}$$

where C_i are constants depending on the characteristic relaxation times of the problem and the Kuhn length a. The evaluation of (3.35) can be done numerically for given parameters. Various approximate results are analytically reachable. In the long-time limit we obtain T_1 independent on the segment mass M,

$$\frac{1}{T_1} \propto \frac{2a^4}{N^2} \int\limits_{0}^{\infty} \mathrm{d}t \left[\sum_{p>0} \exp\left(-\frac{t}{\tau_p}\right)\right]^2 \cos\omega t, \tag{3.36}$$

with the Rouse relaxation times τ_p (3.29). This equation can be expressed exactly through the elliptic integrals. At low frequencies ($\omega\tau_1 \ll 1$) a very simple result follows from (3.36): the relaxation time T_1 does not depend on N at all, and is proportional to $k_BT/a^6\gamma$.

Thus, whereas in the standard theory the chaotic motions of beads ending long polymer subchains and thus the motion of the whole coil are assumed to be due to the white thermal noise, here a phenomenological Rouse model is proposed when this noise exponentially correlates in time. This is a simple but microscopically substantiated generalization [Schweitzer 1989, Allahverdyan 2002, Kimmich 2004, Goychuk 2009], which corresponds to the friction in Maxwell's weakly viscoelastic fluids [Maxwell 1867, Raikher 2010, Chakraborty 2011, Grimm 2011, Goychuk 2012]. The polymer dynamics in such solvents shows memory and has been described by a generalized Langevin equation of Kubo's type [Kubo 1966], in which also the inertial term has been taken into account. We solved these equations both for the motion of the center of mass of the coil and for its internal normal modes. The results considerably differ from the previous ones and reduce to the known formulas at long times when the correlation time of random forces and also the masses of the bead converge to zero. We believe that at present these findings could be tested, $e.g.$, in the light or neutron scattering experiments or NMR relaxometry. Memory effects and the correlation properties of thermal noise have been recently probed on optically trapped Brownian particles [Franosch 2011, Jannasch 2011]. Similar experiments could be done also with polymer coils. In particular, the transition to the diffusive motion of the coils could be detected. It would be interesting also because at short times the predicted here ballistic motion should not depend on specific properties of the thermal noise. Various other generalizations of the Rouse model with nonmoving solvent are possible. For example, the conformational statistics of the chains can be non-Gaussian, which will change the forces between the beads [Fatkullin 2010], the volume interactions should be taken into account, the chains can overlap, *etc*. The Rouse model is expected to fairly describe the dynamic characteristics of polymer systems in which hydrodynamic interactions can be neglected. For dilute solutions, however, these interactions should necessarily be taken into account. This significantly complicates the consideration, since along with the equations of motion for polymer beads the hydrodynamic equations for the solvent must be solved. This will be the subject of the next paragraph.

3.5 Hydrodynamic generalization of the Rouse model: Brownian motion of polymer coils

The details of the classical theories of the dynamics of large numbers of spherical beads forming chains in dilute solutions at theta conditions (when the repulsive effects of the volume interactions are cancelled by the attractive forces between the polymer segments, and the polymer coils behave like ideal chains forming random coils) can be found in Ref. [Yamakawa 2001]. For more references and a generalization of the Rouse model to an exponentially correlated thermal noise see the previous paragraph. Here, to reveal the role of the inertial and memory effects we also begin with the Rouse theory as the simplest bead-spring model that even in its generalized form allows to obtain exact analytical solutions. The starting equation of motion for the nth bead is (3.1). In the original model this distribution is assumed Gaussian, and the monomers interact only with their nearest neighbors. The friction force is the Stokes one (then, due to the FDT, the random force is delta-correlated in the time), the inertial term is neglected, and the continuum approximation in n is used. Then Eq. (3.1) is transformed to a diffusion-type equation with the diffusion coefficient $D = k_BT/N\gamma(\gamma = 6\pi\eta b$ is the friction factor for a particle with radius b in a fluid with viscosity η). Below this model is generalized in all the mentioned points. We do no assumption on the forces $\vec{f}_n^{ch}$. Instead of the Stokes friction, the resistance force naturally arises from the linearized Navier-Stokes and continuity equations for incompressible fluids as a memory force (2.11), which can be written in the form [Tothova 2011a, c]

$$\vec{f}_n^{fr}(t) = -\gamma\vec{\upsilon}_n(t) - M_s\dot{\vec{\upsilon}}_n(t) - 6\left(M_s\gamma/2\pi\right)^{1/2}\int_0^\infty \dot{\vec{\upsilon}}_n\left(t-\beta^2\right)\mathrm{d}\beta, \tag{3.37}$$

where $\vec{\upsilon}_n = \mathrm{d}\vec{r}_n/\mathrm{d}t$ is the bead velocity and M_s is the mass of the solvent displaced by the bead. The model can be modified by inclusion of internal friction independent on the solvent viscosity [Samanta 2013], however, it does not affect the center of mass motion of the chain considered here, and we will not take it into account.

Let us sum up all equations of motion (3.1) from $n = 1$ to N. It is important that independently of a concrete model the sum of internal forces is zero. The resulting equation will be

$$M^*N\frac{\mathrm{d}\upsilon_T}{\mathrm{d}t} + \gamma N\upsilon_T + 6NR^2(\pi\rho\eta)^{1/2}\int_{-\infty}^t \frac{\mathrm{d}\upsilon_T(\tau)}{\mathrm{d}\tau}\frac{\mathrm{d}\tau}{\sqrt{t-\tau}} = f, \tag{3.38}$$

where $M^* = M + M_s/2$, $f = \sum f_n$, and $\upsilon_T = \sum \upsilon_n/N$ is the velocity of the polymer center of inertia (CI). Using the approach presented in [Tothova 2011a, b], one can write down solutions for all relevant time correlation functions describing the motion of the polymer CI. So, its VAF $\Phi_T(t) = \langle\upsilon_T(0)\upsilon_T(t)\rangle$ exactly corresponds to the VAF of a Brownian particle with the mass M^*N:

$$\Phi_T(t) = \frac{k_BT}{M^*N(\lambda_2-\lambda_1)}\left\{\lambda_2\exp(\lambda_2^2t)\mathrm{erfc}\left(-\lambda_2\sqrt{t}\right) - \lambda_1\exp(\lambda_1^2t)\mathrm{erfc}\left(-\lambda_1\sqrt{t}\right)\right\}. \tag{3.39}$$

This result can be obtained also as a particular case of a more general problem considered in the next section, if there the HI is absent; due to this we omit here the details of its calculation. In Eq. (3.39) $\lambda_{1,2} = -(\tau_R^{1/2}/2\tau)[1 \mp \sqrt{1-4\tau/\tau_R}]$, where the time $\tau_R = R^2\rho/\eta$ characterizes the loss of memory in the dynamics (ρ is the density of the solvent). At $t \to \infty$ the VAF contains a long-time tail $\sim t^{-3/2}$:

$$\Phi_T(t) \approx k_BT\tau\sqrt{\tau_R}\left[1 - 3\left(1/2 - 3\tau/\tau_R\right)\tau_R/t + ...\right]/2\sqrt{\pi}M^*t^{3/2}$$

($\tau = M^*/\gamma$ is the usual Brownian relaxation time). In experiments, the MSD $X_T(t) = \langle[x_T(t) -x_T(0)]^2\rangle$ is measured. It is calculated according to the formula $X_T(t) = 2\int_0^t (t-s)\Phi_T(s)\mathrm{d}s$ [Schram 1998] and, in addition to the classical result, at long times it contains a $t^{1/2}$term:

$$X_T(t) \approx (2k_BTt/N\gamma)\left[1 - 2(\tau_R/\pi t)^{1/2} + \cdots\right].$$

At short times that cannot be described by the original theory $X_T(t) \approx (k_B T/M^* N)t^2$. The velocity autocorrelation function, $\Phi_T(t) = \langle v_T(0) v_T(t)\rangle = (\mathrm{d}^2/2\mathrm{d}t^2) X_T(t)$, was zero in the Rouse model; now it contains long-time tails, the longest-lived of which decays as $\sim t^{-3/2}$.

3.6 Inclusion of the hydrodynamic interactions

The inclusion of HI brings serious difficulties in the description of polymer dynamics [Yamakawa 2001, Samanta 2013]. First, one has to calculate the velocity of the solvent in the place of nth bead due to the motion of other beads, $v(\vec{r}_n)$, and then to determine the friction force through $\mathrm{d}\vec{r}_n/\mathrm{d}t - v(\vec{r}_n)$. To do this, the hydrodynamic equations for the solvent must be solved. The Navier-Stokes equation contains an additional force density $\vec{\varphi}(\vec{r}) = -\sum_n \vec{f}_n^{fr}(\vec{r}_n)\delta(\vec{r}-\vec{r}_n)$ reflecting the force from the beads on the solvent [Doi 1986, Grosberg 1989]. The solution for $\vec{v}(\vec{r})$ is expressed through a nonstationary Oseen tensor$H_{\alpha\beta}(\vec{r}, t)$ (see the next paragraph for its calculation). Since the tensor depends on coordinates, the incorporation of $H_{\alpha\beta}$into the equations of motion makes the problem nonlinear. A number of approximations, some of them hardly controllable, is thus needed to get analytical solutions of the generalized Zimm equation for the components of the beads' position vectors, $r_{n\alpha}$, $\alpha = x, y, z$. In the Fourier representation the equation for $r_{n\alpha} = \int_{-\infty}^{\infty} \mathrm{d}\omega \, r_{n\alpha}^\omega \exp(-i\omega t)$ reads

$$-i\omega r_{n\alpha}^\omega = \psi_{n\alpha}^\omega (\gamma^\omega)^{-1} + \sum_\beta \sum_{m\neq n} H_{\alpha\beta}^\omega(\vec{r}_n - \vec{r}_m)\psi_{m\beta}^\omega, \tag{3.40}$$

where

$$\begin{aligned}
&\psi_{n\alpha}^\omega = f_{n\alpha}^{ch,\omega} + f_{n\alpha}^\omega + M^*\omega^2 r_{n\alpha}^\omega \,, \\
&\gamma^\omega = \gamma[1 + \chi b + (\chi b/3)^2] \,, \\
&\chi = \sqrt{-\mathrm{i}\omega\rho/\eta}, \qquad (\mathrm{Re}\chi > 0).
\end{aligned}$$

It was used that the Fourier transform of the friction force (3.37) is $\vec{f}_n^{fr,\omega} = -\gamma^\omega \vec{v}_n^\omega$. Now we go to the continuum approximation, in which the internal forces, assuming Gaussian equilibrium distribution of the beads, become $\vec{f}_n^{ch} \to 3k_B T a^{-2}\partial^2\vec{r}(t,n)/\partial n^2$($a$ is the mean square distance between the neighboring beads along the chain). After the linearization of the problem by preaveraging of the Oseen tensor over this distribution, Eq. (3.40) contains only the diagonal terms with $\beta = \alpha$ and can be solved expanding the position vector in normal modes, $\vec{r}^\omega(n) = \vec{r}_T^\omega + 2\sum_{p=1}^\infty \vec{r}_p^\omega \cos(\pi np/N)$. The same expansion for the stochastic force is $f_{n\alpha}^\omega = f_\alpha^\omega + 2\sum_{p=1}^\infty f_{\alpha p}^\omega \cos(\pi np/N)$. Summing up equations (3.40) we obtain

$$\begin{aligned}
&-i\omega N\gamma^\omega r_{T\alpha} = M^* N\omega^2 r_{T\alpha} + N f_\alpha^\omega + 2\sum_n \sum_{p=1}^\infty f_{\alpha p}^\omega \cos\frac{\pi np}{N} \\
&+ \gamma^\omega \sum_{m\neq ?} \sum_{p=1}^\infty h^\omega(n-m) \left[M^*\omega^2 r_{m\alpha}^\omega + f_{m\alpha}^\omega - \frac{6k_B T}{a^2} r_{\alpha p}^\omega \left(\frac{\pi p}{N}\right)^2 \cos\left(\frac{\pi pm}{N}\right)\right].
\end{aligned} \tag{3.41}$$

In the continuum approximation the sum over n is replaced by the integral $\int_0^N \mathrm{d}n\,(.)$. Let us denote $h_p^\omega = \int_0^N \mathrm{d}n \int_0^N \mathrm{d}m\, h^\omega(n-m)$. Then the equation for $r_{T\alpha}^\omega$ reads

$$\begin{aligned} &- r_{T\alpha}^\omega \left[i\omega N + M^* \omega^2 \left(\frac{N}{\gamma^\omega} + h_0^\omega \right) \right] \\ &= \left(\frac{N}{\gamma^\omega} + h_0^\omega \right) f_\alpha^\omega + 2 \sum_{p=1}^\infty f_{\alpha p}^\omega h_p^\omega + \sum_{p=1}^\infty r_{\alpha p}^\omega h_p^\omega \left[2m\omega^2 - \frac{6k_BT}{a^2} \left(\frac{\pi p}{N} \right)^2 \right]. \end{aligned} \tag{3.42}$$

At this moment we neglect the small terms containing h_p^ω with $p > 0$. The possibility to do this was proven in Ref. [Grosberg 1989] at $\omega = 0$. Here ω is nonzero but small since the long times are considered, which allows us to adopt this approximation. For h_0^ω an exact expression has been found, see (3.56). We thus obtain the following equation that relates the coordinate of the CI to the random force:

$$r_{T\alpha}^\omega = \alpha(\omega)\, f_\alpha^\omega = - \left[M^* \omega^2 + i\omega \left(\frac{h_0^\omega}{N} + \frac{1}{\gamma^\omega} \right)^{-1} \right]^{-1} f_\alpha^\omega. \tag{3.43}$$

Now one can use the FDT to calculate the time correlation functions describing the motion of the polymer CI. For the diffusion, *e.g.*, along the axis x, the MSD of the coil, $X_T(t) = 2\langle x_T(0)x_T(0) - x_T(0)x_T(t)\rangle$ ($x_T = r_{T\alpha}$) is determined through the susceptibility $\alpha(\omega)$ in Eq. (3.43) as [Lisy 2004b]

$$\begin{aligned} X_T(t) &= \frac{2k_BT}{\pi i} \int_{-\infty}^{\infty} \frac{\alpha(\omega)}{\omega} (1 - \cos\omega\tau)\, \mathrm{d}\omega \\ &= \frac{2k_BT}{\pi} \int_{-\infty}^{\infty} \frac{Im\alpha(\omega)}{\omega} (1 - \cos\omega\tau)\, \mathrm{d}\omega. \end{aligned} \tag{3.44}$$

The calculation of this quantity, or the velocity autocorrelation function, is just a technical work. Here we give the long-time limit for the MSD, obtained as an asymptotic expansion of $X_T(t)$ for the Zimm polymers with strong HI ($h_0^0\gamma \gg N$)

$$X_T(t) \approx 2D_Z \left[t - \sqrt{\frac{3N\rho}{32\eta}} \sqrt{t} + \cdots \right] = 2D_Z t \left[1 - \frac{2}{\sqrt{\pi}} \sqrt{\frac{\tau_R}{t}} + \cdots \right], \tag{3.45}$$

where $D_Z = k_BTh_0^0N^{-2} = 8k_BT/3\sqrt{6\pi^3N}\eta a$ is the diffusion coefficient known from the Zimm theory, and R in $\tau_R = R^2\rho/\eta$ is now the hydrodynamic radius of the coil [Doi 1986, Grosber 1989]. Similarly to the Rouse model with hydrodynamic memory, $X_T(t)$ at long times contains additional (to the Einstein term $\sim t$) contributions, the leading of which is $\sim \sqrt{t}$. As illustrated in Fig. 3.1, the convergence to the classical result is very slow. For arbitrary strengths

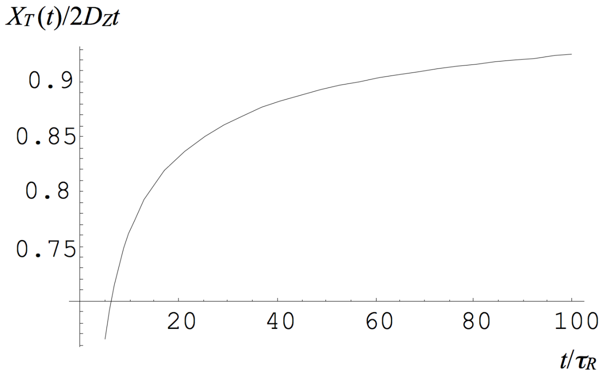

Fig. 3.1. MSD of a polymer coil calculated from Eq. (3.45) shows a slow convergence to the classical result from the Zimm theory, $X_T(t) = 2D_Z t$.

of the HI the diffusion coefficient of the coil contains both the Rouse and Zimm contributions, $D_C = D_Z + D_R$ [Lisy 2004b], where $D_R = k_B T/N\gamma$.

Note that the MSD found earlier in Ref. [Bonet Avalos 1991] must be corrected: at long times the main terms of the MSD are the Einstein term $\sim t$ and the longest-lived tail, which is negative and proportional to $t^{1/2}$ instead of the positive $\sim t^{3/2}$ [Bonet Avalos 1991]. Figure 1 in that work also does not correspond to the correct solution: with growing t the MSD should slowly approach the Einstein limit valid for infinitely long times.

3.7 Nonstationary Oseen tensor

We put the evaluation of the Oseen tensor in this separate section to make the previous part more readable, and also because of the importance of the result: to our knowledge the below obtained analogue of the Oseen tensor is the most general one obtained in the literature so far. It could find applications in various problems of the physics of suspensions.

To take the hydrodynamic interactions into account, the equation of motion (3.1) with the friction force (3.37) has to be solved together with the hydrodynamic (Navier-Stokes and continuity) equations for the macroscopic velocity of the liquid,

$$\rho \frac{\partial \vec{v}}{\partial t} = -\nabla p + \eta \Delta \vec{v} + \vec{\varphi}, \quad \mathrm{div} \vec{v} = 0. \tag{3.46}$$

Here p is the pressure. The quantity $\vec{\varphi}$ has the meaning of an external force per unit volume [Grosberg 1989]. Here

$$\vec{\varphi}\left(\vec{r}\right) = -\sum_n \vec{f}_n^{\,fr}\left(\vec{r}_n\right) \delta\left(\vec{r} - \vec{r}_n\right). \tag{3.47}$$

The hydrodynamic equations are solved using the Fourier transformation (FT)

$$\vec{v}_k^\omega = (2\pi)^{-4} \int \mathrm{d}\vec{r}\mathrm{d}t \exp\left[i\left(\vec{k}\vec{r} + \omega t\right)\right] \vec{v}\left(\vec{r}, t\right). \tag{3.48}$$

The solution,

$$\vec{v}_k^\omega = \frac{1}{k^2\eta - i\omega\rho}\left[\vec{\varphi}_k^\omega - \frac{\vec{k}}{k^2}\left(\vec{k}\vec{\varphi}_k^\omega\right)\right], \tag{3.49}$$

can be in the $\vec{r}$-representation, for any of the component α (x, y, or z), written in the form

$$v_\alpha^\omega\left(\vec{r}\right) = \int \mathrm{d}\vec{r}' \sum_\beta H_{\alpha\beta}^\omega\left(\vec{r} - \vec{r}'\right)\varphi_\beta^\omega\left(\vec{r}'\right). \tag{3.50}$$

The inverse transform, using (3.42), is

$$v_\alpha\left(\vec{r}, t\right) = -\frac{1}{2\pi}\sum_{m,\beta}\int_{-\infty}^{t} \mathrm{d}t'\, H_{\alpha\beta}\left(\vec{r} - \vec{r}_m, t - t'\right) f_{m\beta}^{fr}\left(\vec{r}_m\right). \tag{3.51}$$

The Fourier transform of the Oseen tensor

$$H_{\alpha\beta}^\omega\left(\vec{r}\right) = \frac{1}{(2\pi)^3\eta}\int \frac{\mathrm{d}\vec{k}}{k^2 - i\omega\rho/\eta}\left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right)\exp\left(-i\vec{k}\vec{r}\right) \tag{3.52}$$

can be expressed as

$$H_{\alpha\beta}^\omega\left(\vec{r}\right) = A\delta_{\alpha\beta} + B\frac{r_\alpha r_\beta}{r^2}. \tag{3.53}$$

After the integration in (3.52) we obtain

$$\begin{aligned} A &= \frac{1}{8\pi\eta r}\left[\exp(-y) - y\left(\frac{1-\exp(-y)}{y}\right)''\right], \\ B &= \frac{1}{8\pi\eta r}\left[\exp(-y) + 3y\left(\frac{1-\exp(-y)}{y}\right)''\right]. \end{aligned} \tag{3.54}$$

Here $y = r\chi$, $\chi = \sqrt{-\mathrm{i}\omega\rho/\eta}$, (Re $\chi > 0$), and the prime denotes the differentiation with respect to y. Equations (3.53) and (3.54) can be used also in different problems on the dynamics of suspensions.

If the equilibrium distribution of the beads is Gaussian,

$$P\left(r_{nm}\right)=\left(\frac{3}{2\pi a^{2}\left|n-m\right|}\right)^{3/2}\exp\left(-\frac{3}{2a^{2}}\frac{r_{nm}^{2}}{\left|n-m\right|}\right),\quad \vec{r}_{nm}\equiv\vec{r}_{n}-\vec{r}_{m}, \tag{3.55}$$

the preaveraging of the tensor (3.53) consists in replacing it with the mean value over this distribution,

$$\begin{aligned}\left\langle H_{\alpha\beta nm}^{\omega}\right\rangle_{0}&=\left\langle A\left(r_{nm}\right)\delta_{\alpha\beta}+B\left(r_{nm}\right)\frac{r_{nm\alpha}r_{nm\beta}}{r_{nm}^{2}}\right\rangle\\&=\frac{\delta_{\alpha\beta}}{6\pi\eta}\left\langle\frac{1}{r_{nm}}\exp\left(-\chi r_{nm}\right)\right\rangle=\delta_{\alpha\beta}h^{\omega}\left(n-m\right).\end{aligned} \tag{3.56}$$

The result of integration is

$$\begin{aligned}&h^{\omega}\left(n-m\right)=\left(6\pi^{3}\left|n-m\right|\right)^{-1/2}\left(\eta a\right)^{-1}\left[1-\sqrt{\pi}z\exp\left(z^{2}\right)\operatorname{erfc}\left(z\right)\right],\\&z\equiv\chi a\sqrt{\left|n-m\right|/6},\end{aligned} \tag{3.57}$$

where erfc (.) is the complementary error function. It is seen that the effective interaction between the beads decreases with the distance between the beads as

$$h^{\omega}\left(n-m\right)\approx\sqrt{\frac{3}{2\pi^{2}}}\frac{1}{-i\omega\rho a^{2}\left|n-m\right|^{3/2}},\quad\left|n-m\right|\to\infty, \tag{3.58}$$

$i.e.$, more rapidly than in the case without memory [Grosberg 1989] when the function h at large $|n-m|$ behaves as $\sim|n-m|^{-1/2}$.

Using (3.57), the integral $h_{p}^{\omega}=\int_{0}^{N}dn\int_{0}^{N}dm\,h^{\omega}\left(n-m\right)\cos\left(\pi pm/N\right)$ can be evaluated. To describe the CI motion of the coil only its $p=0$ value is needed, when

$$h_{0}^{\omega}=\frac{2N}{\pi\eta a^{2}\chi}\left\{1-\frac{2}{\sqrt{\pi}R_{G}\chi}-\frac{1}{\left(R_{G}\chi\right)^{2}}\left[\exp\left(R_{G}^{2}\chi^{2}\right)\operatorname{erfc}\left(R_{G}\chi\right)-1\right]\right\} \tag{3.59}$$

($R_{G}=a\sqrt{N/6}$ is the gyration radius connected to the hydrodynamic radius R as $R_{G}=\frac{8}{3}R/\sqrt{\pi}$). At $\omega\to0$ we have

$$h_{0}^{\omega}\approx\frac{8N^{3/2}}{3\eta a\sqrt{6\pi^{3}}}\left(1-\frac{3\sqrt{\pi}}{8}R_{G}\chi+\cdots\right), \tag{3.60}$$

and when $\omega\to\infty$,

$$h_{0}^{\omega}\approx\frac{2N}{\pi\eta a^{2}\chi}\left(1-\frac{2}{\sqrt{\pi}R_{G}\chi}+\frac{1}{\left(R_{G}\chi\right)^{2}}+\cdots\right). \tag{3.61}$$

To consider the internal modes of the polymer (see below this task in the continuum approximation), the matrix

$$h_{pq}^{\omega} = \frac{1}{N^2} \int\limits_0^N \mathrm{d}n \int\limits_0^N \mathrm{d}m \, h^{\omega}\left(n-m\right) \cos\frac{\pi p n}{N} \cos\frac{\pi p m}{N} \tag{3.62}$$

will be needed ($p, q > 0$). One can act similarly as in [Grosberg 1989] and use the rapid decrease of $h^{\omega}\left(n-m\right)$ with the increase of $|n-m|$, Eq. (3.58). The non-diagonal components of the matrix are small, and for the diagonal ones we found

$$h_{pp}^{\omega} \approx \frac{1}{\pi\eta\, a\sqrt{3\pi N p}} \frac{1+\chi_p}{1+\left(1+\chi_p\right)^2}, \qquad \chi_p = \sqrt{\frac{N}{3\pi p}}\chi a. \tag{3.63}$$

This result will be used also in Section 4 when the influence of other polymers in solution on the dynamics of our chosen "test" polymer will be discussed.

Note that the theory presented in this review is based on the hydrodynamics of incompressible fluids, which is applicable only for times much larger than b/c (b is the radius of the particle and c is the velocity of sound). In the theory of the Brownian motion this causes problems with the equipartition theorem (the so called Ehrenfest's paradox, explained already in the work [Vladimirsky 1945], see also [Schram 1998]. A generalization of the above formulas for the Oseen tensor is thus of interest. Instead of (3.46), now we have to solve the nonstationary Navier-Stokes equations [Landau 1986],

$$\begin{aligned} \rho_0 \frac{\partial \vec{v}}{\partial t} &= -\vec{\nabla} p + \eta \Delta \vec{v} + (\zeta + \frac{\eta}{3})\vec{\nabla}\mathrm{div}\vec{v} + \vec{\varphi}, \\ \frac{\partial \rho}{\partial t} &= -\rho_0 \mathrm{div}\vec{v} \\ \vec{\nabla} p &= c_0^2 \vec{\nabla}\rho \end{aligned} \tag{3.64}$$

where ρ_0 is the equilibrium density of the solvent and η and ζ are the viscosity coefficients. The solution for the velocity field can be again expressed through Eq. (3.50) and the Oseen tensor will have the form (3.53). However, the coefficients A and B from (3.54) change. They contain additional terms A_l and B_l, respectively, which are determined from the equations [Lisy unpublished]

$$\begin{aligned} 3A_l + B_l &= \frac{-\mathrm{i}\omega}{4\pi c^2 \rho_0 r} \exp\left(-\lambda\right), \\ A_l + B_l &= \frac{(\mathrm{i}\omega/c)^2}{8\pi\rho_0 c} \left(\frac{1-\exp\left(-\lambda\right)}{\lambda}\right)'', \end{aligned} \tag{3.65}$$

where $\lambda = \mathrm{i}\omega r/c$, $c = \sqrt{c_0^2 - \mathrm{i}\omega\nu_l}$, and $\nu_l = (4\eta/3 + \zeta)/\rho_0$. To our knowledge, Eq. (3.53) with (3.54) and (3.65) represents the most general expression for Oseen tensor in the literature.

3.8 Internal modes in the model with hydrodynamic interactions

In the continuum approximation for long chains, Eq. (3.40) linearized by preaveraging the Oseen tensor as shown in the previous section becomes

$$\begin{aligned} -\mathrm{i}\omega\vec{r}^{\omega}(n) = {} & \frac{1}{\gamma^{\omega}}\left[\frac{3k_BT}{a^2}\frac{\partial^2\vec{r}^{\omega}(n)}{\partial n^2} + M^*\omega^2\vec{r}^{\omega}(n) + \vec{f}^{\omega}(n)\right] \\ & + \int\limits_0^N \mathrm{d}m\, h^{\omega}(n-m)\left[\frac{3k_BT}{a^2}\frac{\partial^2\vec{r}^{\omega}(m)}{\partial m^2} + M^*\omega^2\vec{x}^{\omega}(m) + \vec{f}^{\omega}(m)\right]. \end{aligned} \tag{3.66}$$

This equation can be solved with the help of the Fourier transform in the variable n, taking into account the boundary conditions at the ends of the chain (3.6):

$$\vec{r}^{\omega}(n) = \vec{y}_0^{\omega} + 2\sum_{p=1}^{\infty}\vec{y}_p^{\omega}\cos(\pi np/N).$$

The inverse transformation yields the following equation for the Fourier components $\vec{y}_p^{\omega}$:

$$\vec{y}_p^{\omega} = \frac{\vec{f}_p^{\omega}}{-\mathrm{i}\omega\Xi_p^{\omega} - M^*\omega^2 + K_p}, \tag{3.67}$$

where we have denoted

$$\Xi_p^{\omega} = \frac{\gamma^{\omega}}{1 + (2-\delta_{p0})\,N\xi^{\omega}h_{pp}^{\omega}}, \qquad K_p = \frac{3\pi^2k_BT}{N^2a^2}p^2, \qquad p = 0,1,2,\ldots \tag{3.68}$$

The matrix h_{pp}^{ω} is defined by (3.62). In obtaining Eq. (3.67) we have already taken into account that the nondiagonal elements of the matrix are small in comparison with the diagonal ones and can be in the first approximation neglected. This “diagonalization approximation” has been proven in the case without memory [Doi 1986, Grosberg 1989]. In our case it should be substantiated by numerical calculations. However, since we are interested in the long-time properties of the chain, where only small corrections to the classical results are expected, the approximation is reasonable. The obtained equation (3.67) can be investigated as it is usually done in the theory of the Brownian motion using the FDT [Giterman 1966, Landau 1976] or the correlation properties of the forces $\vec{f}_p^{\omega}$ [Schram 1998, Tothova 2003, Lisy 2004b],

$$\left\langle f_{p\alpha}^{\omega}f_{q\alpha}^{\omega}\right\rangle = \frac{k_BT}{(2-\delta_{p0})\,\pi N}\mathrm{Re}\;\Xi_p^{\omega}\delta_{\alpha\beta}\delta_{pq}\delta(\omega+\omega'). \tag{3.69}$$

Equation (3.67) then yields the following expression for the time correlation function of the

Fourier components $y_{\alpha p}(t)$:

$$\begin{aligned}\psi_p\left(t\right) &= \left\langle y_{\alpha p}\left(0\right) y_{\alpha p}\left(t\right)\right\rangle \\ &= \frac{k_B T}{\left(2-\delta_{p0}\right)\pi N}\int\limits_{-\infty}^{\infty} \mathrm{d}\omega\, \cos\omega t \frac{\mathrm{Re}\,\Xi_p^{\omega}}{\left|-\mathrm{i}\omega\Xi_p^{\omega} - M^{*}\omega^2 + K_p\right|^2},\end{aligned} \tag{3.70}$$

in agreement with the FDT [Landau 1976]. Another form of Eq. (3.70) is

$$\psi_p\left(t\right) = \frac{k_B T}{\pi i}\int\limits_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{\omega}\alpha_p\left(\omega\right)\cos\omega t, \tag{3.71}$$

where $\alpha_p(\omega)$ is a generalized susceptibility. The use of the Kramers-Kronig dispersion relation [Landau 1976] immediately gives the initial value $\psi_p(0) = k_B T(2NK_p)^{-1}$, $p > 0$. Equation (3.70) represents the solution of the hydrodynamic Rouse-Zimm model, within the approximations described, for the Fourier amplitudes of the correlation functions of the positions of beads. Knowing $\psi_p(t)$, other correlation functions of interest can be found from (3.70), *e.g.*, the VAF and the MSD [Schram 1998]:

$$\begin{aligned}&\phi_p\left(t\right) = \left\langle v_{\alpha p}\left(0\right) v_{\alpha p}\left(t\right)\right\rangle = -\frac{\mathrm{d}^2\psi_p\left(t\right)}{\mathrm{d}t^2}, \\ &\left\langle \Delta y_p^2\left(t\right)\right\rangle = 2\left[\psi_p\left(0\right) - \psi_p\left(t\right)\right].\end{aligned} \tag{3.72}$$

In the steady-state limit and when the inertial effects are not considered, $\omega = 0$ and $M = 0$ have to be put in Eq. (3.68). Then the internal modes ($p \neq 0$) relax exponentially,

$$\psi_p\left(t\right) = \frac{k_B T}{2NK_p}\exp\left(-\left|t\right|/\tau_p\right), \tag{3.73}$$

with the relaxation times τ_p. The relaxation rates can be expressed in the form

$$\frac{1}{\tau_p} = \frac{1}{\tau_{pR}} + \frac{1}{\tau_{pZ}} \tag{3.74}$$

(the indices R and Z stay for the Rouse and Zimm limits), where

$$\tau_{pR} = \frac{2N^2 a^2 b\eta}{\pi k_B T p^2}, \qquad \tau_{pZ} = \frac{\left(\sqrt{N}a\right)^3\eta}{\left(3\pi p^3\right)^{1/2} k_B T}. \tag{3.75}$$

Usually only the limiting (Rouse or Zimm) cases are considered. The applicability of a specific model is controlled by the so-called draining parameter $h = 2\sqrt{3N/\pi}\frac{b}{a}$ that indicates whether the hydrodynamic interaction in solution is strong ($h \gg 1$, then the dynamics is of the Zimm type) or not ($h \ll 1$, the Rouse dynamics). For the diffusion of the coil as a whole the corresponding "draining parameter" is $D_Z/D_R = 4\sqrt{2}h/3$ (see Section 3.6). For the internal modes the draining parameter depends on the mode number p: $h(p) = \tau_{pR}/\tau p_Z = h/\sqrt{p}$. Due to this, beginning from some p, all the higher internal modes become the Rouse modes. In general, the polymer is not a pure Zimm or Rouse one; the polymer dynamics should always possess features of both the models. This should be taken into account (but is often neglected) in the determination of the phenomenological model parameters (N, a, b) from experiments. For example, in the experiments [Shusterman 2004] the motion of the individual monomer within the polymer coils has been observed for the first time using the fluorescence correlation spectroscopy. The measured MSD of the monomer was fitted by the Rouse and Zimm limits assuming continuous distribution of the internal relaxation modes. In this approximation the MSD is proportional to $t^{1/2}$ and $t^{3/2}$in the Rouse and Zimm case, respectively [Dubois-Violette 1967, de Gennes 1967]. It was concluded that the double-stranded DNA surprisingly follows the Rouse-type dynamics in spite of the common belief that the behavior of this polymer is close to the Zimm-type dynamics. However, coming from the "joint" Rouse-Zimm theory described above, with the discrete internal modes, it can be shown that this conclusion is misleading and the long DNA's behave predominantly as the Zimm polymers [Tothova 2005, 2007b].

The Rouse limit assumes that the HI contribution to the quantity Ξ_p^ω from Eq. (3.68) is negligible for all ω (cf. Section 3.5). Accordingly, the subsequent equations change only by the substitution $\Xi_p^\omega \approx \gamma^\omega$. This case is considered in detail in our work [Tothova 2003]. To get analytical results for the motion of the whole coil ($p = 0$), in the Rouse limit one can adapt the results of the hydrodynamic theory of the Brownian motion of one particle (usually the work [Hinch 1975] is cited). In the Rouse model the friction force on the coil is just a sum of the forces on individual beads (since the solvent is nonmoving). The results for one bead and that for the whole coil thus differ only by the factor $1/N$. In the case $p \neq 0$ ($K_p \neq 0$) the integral in Eq. (3.70) can be represented through the inverse Laplace transform [Schram 1998]. The integrand is then expanded into a sum of elementary fractions, for which the Laplace transforms are known. This allows one to express the searched integral in a closed form through the error functions. The asymptotic expansions are then derived using known properties of these functions. The long-time asymptote for the function $\psi_p(t)$ has the form

$$\psi_p(0) - \psi_p(t) = \frac{k_B T}{2NK_p}\left\{1 + \frac{1}{2\sqrt{\pi}}\frac{\tau_{pR}\sqrt{\tau_b}}{t^{3/2}}\left[1 + 3\frac{\tau_{pR}}{t} + \cdots\right]\right\}. \tag{3.76}$$

Comparing these formulas with the results of the Rouse theory, it is seen that for the internal modes ($p \geq 1$) the value $\psi_p(0) = k_B T/(2NK_p)$ is the same as in the original model. The time dependence of at short times of the function $\psi_p(t)$ is different, now $\sim t^2$. A difference reveals also in the long-time dependence of other time correlation functions of the coordinates and velocities of the polymer segments in the Fourier representation. The inclusion of the hydrodynamic memory leads to the relaxation of the internal modes that differs from the traditional exponential decay of the correlation functions $\psi_p(t)$ and $\phi_p(t)$. This is reflected in the long-time tails of these functions. Half a century ago the discovery of the tails of the molecular VAF in simple liquids (by means of computer experiments [Rahman 1964, Alder 1967]) has led to enormous number of investigations in the field of the statistical theory of liquids and in the theory of Brownian motion

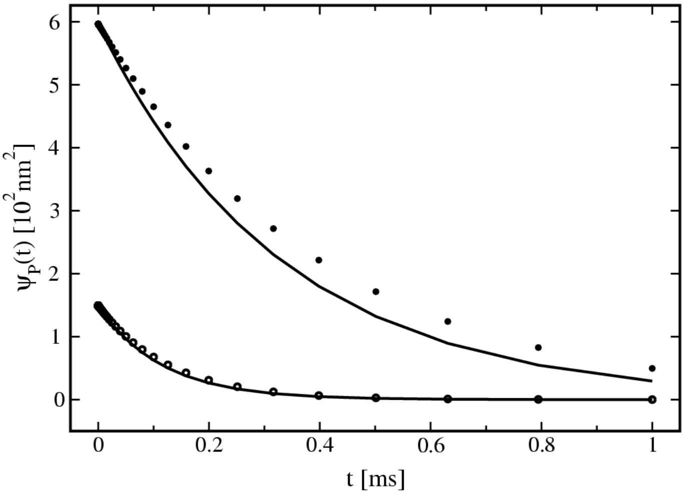

Fig. 3.2. Correlation functions $\psi_p(t)$ calculated from Eq. (3.70). The filled circles correspond to the lowest internal mode p = 1, the open ones are for $p = 3$. The lines correspond to exponential relaxation according to Eq. (3.73). The parameters for the single stranded DNA (6700 bases) have been obtained by us optimizing the RZ theory to the data from [Shusterman 2004] ($N = 422$, $a = 9.15$ nm, $b = 4.56$ nm). The solvent characteristics were $\eta = 0.69$ mPa·s, $\rho = 10^3$ kg/m^3, and $T = 310$ K.

[Schram 1998]. We believe that similar peculiarities found here could stimulate new studies in the dynamics of polymers, first of all by means of computer simulations.

The algebraic long-time tails are predicted also for the correlation functions in the Zimm limit, when the HI are strong. In this case we have from Eq. (3.68)

$$\Xi_p^\omega \approx \frac{1}{(2-\delta_{p0})\,Nh_{pp}^\omega}\,. \tag{3.77}$$

However, the inertial effects of the viscous solvent are still included into the consideration. The Oseen matrix (3.62) can be calculated with any degree of precision, $e.g.$, for $p = 0$ we have the exact result (3.63). If $p \neq 0$, in the main approximation the result (3.63) for diagonal components should be used. Equations (3.68) and (3.70) then give for long times (small ω) [Lisy 2004b]

$$\frac{\psi_p(t)}{\psi_p(0)} \approx -\frac{2^9}{45\pi^3}\sqrt{\frac{2}{\pi}}\left(1+\frac{16}{3\pi^2 p}\frac{\tau_R}{\tau_{pZ}}\right)\frac{1}{p^3}\frac{\tau_{pZ}\tau_R^{3/2}}{t^{5/2}}, \tag{3.78}$$

where $p \geq 1$, and τ_{pZ} is the Zimm relaxation time (3.75).

Figures 3.2 and 3.3 show examples of the numerical calculations of relevant correlation functions with no assumption on the validity of a specific, Rouse or Zimm, limit. The calculations done from Eq. (3.70) illustrate the peculiarities of the polymer dynamics with the inertia effects included into the consideration.

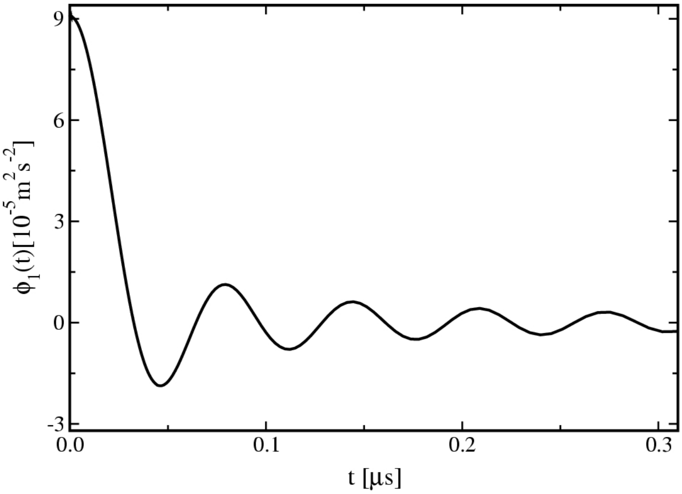

Fig. 3.3. Velocity autocorrelation function for the $p = 1$ internal mode and the same parameters as in Fig. 3.2. In the previous Zimm theory $\phi_1(t) < 0$ and relaxed exponentially. The corresponding curve is on the graph indistinguishable from 0.

3.9 Time scales in the polymer dynamics

The motion of an individual polymer in solution, from its microscopic origin to macroscopically observable phenomena, can be characterized by several very different time and length scales. The traditional approach to the polymer dynamics based on the Einstein theory of the Brownian motion is appropriate at "infinite" times. It might seem that the Langevin theory [Langevin 1908] that includes the inertial effects into the consideration can be used to describe the Brownian motion of free and massive Brownian particles of radius b (and the polymer dynamics) for any times. However, as we have already mentioned, this theory, giving the same results as Einstein's theory at long times, possesses good results at short times only when the density ρ_B of the particles is much larger than that of the surrounding fluid, ρ. For the usual case of neutrally buoyant particles both the times are comparable and the effects of fluid inertia should be taken into account at such time scales. This was shown in Ref. [Vladimirsky 1945], where the hydrodynamic theory of the Brownian motion has been developed for the first time. This theory constitutes the bases of the models presented in this paper. The inclusion of the inertial terms in the equations of motion for polymer segments allows describing the short time dynamics of the polymers with the characteristic time $\tau_B = M/\gamma$. The exponential relaxation of the Brownian particles would hardly be observable for such short times. However, the friction force in the form of the memory integral leads to a different relaxation due to which the Einstein diffusion regime is approached very slowly, with the characteristic time $\tau_R = R^2\rho/\eta = 9\rho\tau_B/2\rho_B$. As it is seen from Eq. (3.45), which has the same form for a Brownian particle and a polymer coil with R being its hydrodynamic radius, even for the times t as large as $100\tau_R$ the MSD constitutes only some 90% of the Einstein's MSD. The dynamics differs also due to the increase of the effective mass of the particle. These features are present in the considered dynamics of the polymer chains as well.

There are several other time scales inherent to the presented models. As in the Langevin theory of the Brownian motion, the time scale ($\sim 10^{-12}$ s) characterizing the collisions between the BP and the molecules of solvent must be much smaller than all other characteristic times. Then the collisions can be considered as a stochastic noise. The size of the beads R must be large enough to consider the solvent as a continuum. The solvent is described by the linearized hydrodynamic equations for incompressible fluids, so that we are restricted to the times much larger than the sound traversal time $\tau_s = R/c$, where c is the speed of sound. (For particles with $R \sim 100$ nm in water at room conditions, τ_s is less than 10^{-10} s.) The vorticity time $\tau_R = R^2\rho/\eta$ should be much larger than τ_c and τ_s. For a typical polymer coil with radius $R \sim 100$ nm this is well satisfied ($\tau_R \sim 10^{-8}$ s) but if R is a bead radius in the Rouse model, this phenomenological parameter can be so small that there will be no reason to consider the inertial and memory effects in the polymer dynamics. Our model in its full formulation thus requires b much larger than the atomic dimensions, and the vorticity time much larger than τ_c. If these conditions are not satisfied, the model applies to such long times that instead of the Boussinesq force we should again use the Stokes force as in the classical theory. Due to this the memory effects will play no role in the Rouse limit. However, they are still present in the general case. It is well seen in the Zimm limit when the non-diffusive motion of the polymer is characterized by the time scale τ_R determined by the radius of the whole polymer R. The simplest variant of our theory thus consists in replacing γ^ω (see Eq. (3.40)) by γ so that Ξ_p^ω in Eq. (3.68) and further becomes $\Xi_p^\omega = \xi\left[1 + (2 - \delta_{p0})\, N\gamma h_{pp}^\omega\right]^{-1}$.

Using the above characteristic time scales one can classify the regimes in the Brownian motion or in the polymer dynamics and judge about their importance for the observed quantities. For example, the known Ehrenfest's paradox [Vladimirsky 1945] (the initial value of the VAF in incompressible fluid is in disagreement with the equipartition theorem) is explained as follows. In the time scale τ_c the VAF of the Brownian particle decays from the equipartition value k_BT/M to $k_BT/(M + M_s/2)$ through emission of sound waves. It is interesting that for longer times the VAF not only decays but is an oscillating function of time. Such a behavior is characteristic for a single molecule in a liquid [Rahman 1964] and can be qualitatively explained as a result of the collective elastic reaction of the surrounding molecules to the motion of the particle [Reut 1967]. A similar relaxation occurs for the VAF $\phi_p(t)$ of the internal modes of our polymer as a result of the effective interaction between the beads (see Fig. 3.3). Note that in the previous Zimm model $\phi_p(t) < 0$ and monotonically converges to zero.

3.10 Memory effects in the scattering of light and neutrons by polymer coils

The quasielastic scattering of light or neutrons from a polymer coil in dilute solution is described by the Van Hove function (the intermediate scattering function or the dynamic structure factor (DSF)) of an individual coil [Doi 1986, Grosberg 1989],

$$G\left(\vec{k},t\right) = \frac{1}{N}\sum_{m,n}\left\langle \exp\left\{i\vec{k}\left[\vec{r}_n(t) - \vec{r}_m(0)\right]\right\}\right\rangle, t > 0. \tag{3.79}$$

Here $\vec{k}$ is the wave-vector change at the scattering and $\vec{r}_n(t)$ is the position of the nth bead at the time t. Since $\vec{r}_n(t) - \vec{r}_m(0)$ is a linear function of the Gaussian random force, the distribution of this quantity is also Gaussian [Doi 1986],

$$\left\langle \exp\left\{ i\vec{k}\left[\vec{r}_n(t) - \vec{r}_m(0)\right]\right\}\right\rangle = \exp\left\{ -\frac{k^2}{2}\left\langle \left[r_n(t) - r_m(0)\right]^2\right\rangle\right\}, \tag{3.80}$$

where r_n is the projection of $\vec{r}_n$ on the vector $\vec{k}$. After the transition to the Fourier representation as in Eq. (3.18) we obtain

$$G(k,t) = \frac{1}{N}\sum_{nm}\exp\left[-k^2\Phi_{nm}(t)\right], \tag{3.81}$$

where

$$\begin{aligned}\Phi_{nm}(t) = \psi_0(0) - \psi_0(t) + 2\sum_{p=1}^{\infty}\Bigg[\psi_p(0)\left(\cos^2\frac{\pi mp}{N} + \cos^2\frac{\pi np}{N}\right)& \\ - 2\psi_p(t)\cos\frac{\pi mp}{N}\cos\frac{\pi np}{N}\Bigg]&, \qquad (3.82)\\ \psi_0(0) - \psi_0(t) = \frac{1}{2}\left\langle\left[y_0(t) - y_0(0)\right]^2\right\rangle&, \\ \psi_{p\ge 1} = \left\langle y_p(t)\, y_p(0)\right\rangle&.\end{aligned}$$

In the Rouse and Zimm models without the hydrodynamic memory the correlation functions ψ_p describing the internal motion are exponential, $\psi_p \sim \exp(-t/\tau_p)$, which is essentially used in the evaluation of the Van Hove function [Doi 1986, Grosberg 1989]. The internal modes contribute practically only at large kR (R is the radius of the coil) and at small $\psi_p(0) - \psi_p(t)$, which implies $t \ll \tau_p$, since in other cases the Van Hove function is too small.

Let us consider now the situation when the hydrodynamic memory is taken into account.

3.10.1 Long time approximation of the dynamic structure factor

Although at long times the memory effects are small, we shall dwell on this case which is useful from the methodical point of view and also for the study of the kinetics of individual monomers, *e.g.*, by fluorescence correlation spectroscopy (FCS) [Shusterman 2004, Tothova 2007b]. For the interpretation of the FCS measurements only the time dependence of the studied correlation functions is important - the measured MSD of a monomer does not depend on the scattering vector k. Here this corresponds to the consideration of the time dependence of the function (3.82). The time behavior of the whole DSF, however, essentially depends on the region of the employed scattering vectors. Taking into account that $\psi_p(0)$ from Eq. (3.70) is $\psi_p(0) = Na^2/6\pi^2p^2$, Eq. (3.82) can be rewritten in the form

$$\begin{aligned}\Phi_{nm}(t) = R^2\frac{t}{\tau_D}\left[1 - \frac{2}{\sqrt{\pi}}\left(\frac{\tau}{t}\right)^{1/2} + ...\right]& \\ + \frac{128}{(3\pi)^3}R^2\sum_{p=1}^{\infty}\frac{1}{p^2}\left[\cos^2\frac{\pi mp}{N} + \cos^2\frac{\pi np}{N} - 2\frac{\psi_p(t)}{\psi_p(0)}\cos\frac{\pi mp}{N}\cos\frac{\pi mp}{N}\right]&.\end{aligned} \tag{3.83}$$

Here $\tau = \tau_b = b^2\rho/\eta$ for the Rouse model, in the Zimm case $\tau = \tau_R = R^2\rho/\eta$, and τ_D is the characteristic diffusion time of the whole coil ($\tau_D = R^2/D$, the time during which the object of radius R moves on the distance R). It is seen from (3.83) that at times $t \sim \tau_D$ both the terms on the right hand side are important. The first term begins to dominate for the times longer than τ_D, and when $t \gg \tau_D$, the scattering is fully determined by the diffusion of the coil as a whole. This holds for *all values* of the scattering vectors. When $t \ll \tau_D$, the diffusion term becomes negligibly small and the contributions of internal modes prevail. Again, this is true independently on the values of k. The memory effects in the FCS thus could be revealed only at short times (if we are interested in the polymer internal motion) or at long times (for the motion of the whole polymer). However, since the characteristic time of the non-diffusive motion is negligibly small compared to the diffusion time, $\tau_R \ll \tau_D$, the hydrodynamic memory has no effect on the diffusion contribution to the MSD of an individual monomer. For the dynamic scattering experiments the consideration must be carried out more carefully. So, as will be shown below, the motion of the whole polymer can be studied also at short times, assuming the scattering vectors k are small enough.

Let us return to the expression for the Van Hove function (3.81),

$$\begin{aligned} G(k,t) &= \frac{1}{N}\exp\left\{-k^2\left[\psi_0(0)-\psi_0(t)\right]\right\} \\ &\times \sum_{nm}\exp\left\{-\frac{Na^2k^2}{3\pi^2}\sum_{p=1}^{\infty}\frac{1}{p^2}\left[\cos^2\frac{\pi np}{N}+\cos^2\frac{\pi mp}{N}-2\frac{\psi_p(t)}{\psi_p(0)}\cos\frac{\pi mp}{N}\cos\frac{\pi np}{N}\right]\right\}. \end{aligned} \tag{3.84}$$

The sums with cosines squared are known [Prudnikov 1981] so that for the sum in this expression we have

$$\begin{aligned} \sum_{mn}\exp\{...\} &\approx \exp\left(-\frac{Na^2k^2}{9}\right)\sum_{mn}\exp\left[-\frac{Na^2k^2}{6}\left(\frac{m^2+n^2}{N^2}-\frac{m+n}{N}\right)\right] \\ &\times\left[1+\frac{2Na^2k^2}{3\pi^2}\sum_{p=1}^{\infty}\frac{1}{p^2}\frac{\psi_p(t)}{\psi_p(0)}\cos\frac{\pi mp}{N}\cos\frac{\pi np}{N}\right]. \end{aligned} \tag{3.85}$$

In the continuum approximation the sums over m and n are replaced by integrals. Using the fact that only small quantities $Na^2k^2/6 = R_G^2k^2 \ll 1$ are relevant for our consideration (in the opposite case the DSF becomes very small), after the integration we obtain

$$\begin{aligned} G(k,t) &\approx N\exp\left\{-k^2\left[\psi_0(0)-\psi_0(t)\right]\right\}\exp\left(-\frac{Na^2k^2}{36}\right) \\ &\times\left[1+\frac{2}{27}\left(\frac{Na^2k^2}{\pi^2}\right)^3\sum_{p=1}^{\infty}\frac{\psi_p(t)}{\psi_p(0)}\frac{1}{p^6}\cos^2\frac{\pi p}{2}\right]. \end{aligned} \tag{3.86}$$

The lowest mode that contributes in this approximation is $p = 2$. Taking into account that for the Rouse and Zimm models the quantity $\psi_p(t)/\psi_p(0)$ depends on p as p^{-2} and $p^{-9/2}$, respectively, there is no reason to keep the higher modes, so that Eq. (3.86) can be rewritten in a more compact form,

$$G\left(k,t\right)\approx N\exp\left\{-k^{2}\left[\psi_{0}\left(0\right)-\psi_{0}\left(t\right)\right]\right\}\exp\left[-\frac{Na^{2}k^{2}}{36}\left(1-\frac{N^{2}a^{4}k^{4}}{24\pi^{6}}\frac{\psi_{2}\left(t\right)}{\psi_{2}\left(0\right)}\right)\right].\tag{3.87}$$

Substituting here the solutions for the corresponding correlation functions ψ_p and the solution for the diffusion of the coil as a whole, we obtain the Van Hove function for the considered models. However, at the studied conditions not only the second exponential can be simply replaced by unity but also the first exponential practically does not differ (at the considered long times) from $\exp(-k^2Dt)$, *i.e.*, the memory effects could not be observed.

3.10.2 Large scattering vectors

Consider now large wave-vector transfers at the scattering, $kR_G \gg 1$. At this case the internal motion of the polymer is usually expected to be observed. Our analysis of Eq. (3.70) (see Fig. 3.2 for illustration) shows that the internal modes relax practically exponentially, as in the classical models. The derivation of the DSF thus can almost exactly repeat the calculations known from the literature [de Gennes 1967, Dubois-Violette 1967, Doi 1989]. For exponentially relaxing internal modes, $\psi_p(t) = \psi_p(0)\exp(-t/\tau_p)$, Eq. (3.82) can be rewritten as follows:

$$\begin{aligned}\Phi_{nm}\left(t\right)&=\psi_{0}\left(0\right)-\psi_{0}\left(t\right)+\frac{a^{2}}{6}\left|m-n\right|\\&+\frac{2Na^{2}}{3\pi^{2}}\sum_{p=1}^{\infty}\frac{1}{p^{2}}\left[1-\exp\left(-t/\tau_{p}\right)\right]\cos\frac{\pi mp}{N}\cos\frac{\pi np}{N},\end{aligned}\tag{3.88}$$

where the second term comes from the sum

$$\sum_{p=1}^{\infty}\frac{1}{p^{2}}\left(\cos\frac{\pi mp}{N}-\cos\frac{\pi np}{N}\right)^{2}=\frac{\pi^{2}}{2N}\left|m-n\right|.$$

The consideration can be limited to the times $t \ll \tau_p$ since the DSF becomes very small in other cases. The product of cosines is represented through a sum of cosines with the arguments $p\pi(n+m)/N$ and $p\pi(n-m)/N$. Since the sum is dominated by large p, for which the first cosine changes the sign very rapidly, its contribution becomes very small. The remaining term is evaluated by converting the sum over p to the integral. Then in the DSF from Eq. (3.81) the sum over n and m is replaced by the double integral [Doi 1986]. The approximate result for the Rouse case is

$$G\left(k,t\right)=\frac{12}{k^{2}a^{2}}\exp\left\{-k^{2}\left[\psi_{0}\left(0\right)-\psi_{0}\left(t\right)\right]\right\}\int_{0}^{\infty}\mathrm{d}u\,\exp\left[-u-\sqrt{\Gamma t}\,h\left(\frac{u}{\sqrt{\Gamma t}}\right)\right],\tag{3.89}$$

where Γ is the so called first cumulant to the DSF,

$$\Gamma = \frac{k_B T}{12\gamma} k^4 a^2 = \frac{1}{2} D k^4 R_G^2. \tag{3.90}$$

Here γ is the friction coefficient of one bead and the second equality is expressed through the diffusion coefficient of the Rouse coil and the gyration radius. The function $h(u)$ is

$$h\left(u\right) = \frac{2}{\pi} \int\limits_0^\infty \mathrm{d}x \frac{\cos\left(xu\right)}{x^2} \left[1 - \exp\left(-x^2\right)\right]. \tag{3.91}$$

When $\Gamma t \gg 1$ (for "short times" $t \ll \tau_p$ it is possible if $1/\Gamma \ll \tau_p$, *i.e.*, if $6\pi/k^2a^2 \ll N/p$), the integral in Eq. (3.89) is further simplified to the stretched exponential $\sim \exp\left(-2\sqrt{\Gamma t/\pi}\right)$ [Doi 1986].

In the Zimm case the DSF is obtained in the same way [Dubois-Violette 1967]. The quantity Γ is now

$$\Gamma = \frac{k_B T}{6\pi\eta} k^3 \tag{3.92}$$

and

$$h\left(u\right) = \frac{2}{\pi} \int\limits_0^\infty \mathrm{d}x \frac{\cos\left(xu\right)}{x^2} \left[1 - \exp\left(-\frac{x^{3/2}}{\sqrt{2}}\right)\right]. \tag{3.93}$$

For $\Gamma t \gg 1$ (which is possible if $(kN^{1/2}a/p^{1/2})^3 \gg 60$, or $(kR_G)^3 \gg 4p^{3/2}$) the DSF in the Zimm model was

$$G\left(k, t\right) \approx G\left(k, 0\right) \exp\left[-1.35 \left(\Gamma t\right)^{2/3}\right]^{.} \tag{3.94}$$

For large scattering vectors the diffusion term in DSF is usually neglected [Doi 1986]. In the case of Rouse model (for the solution in the form of the stretched exponential) it is possible when the time-dependent ratio

$$\zeta_R = \frac{k^2 D t}{2\left(\Gamma t/\pi\right)^{1/2}} = \frac{\left(\pi \Gamma t\right)^{1/2}}{\left(k R_G\right)^2} = \frac{1}{p}\sqrt{\frac{t}{\pi \tau_p}}$$

is much smaller than unity. Analogously, in the Zimm case the diffusion contribution in Eq. (3.94) can be neglected in comparison with the contribution from internal modes, if

$$\zeta_Z = \frac{1}{N^{1/2}a}\left(\frac{k_BTt}{\eta}\right)^{1/3} \approx \frac{0.7}{\sqrt{p}}\left(\frac{t}{\tau_p}\right)^{1/3} \ll 1.$$

It is seen from the last two expressions that even if t/τ_p is relatively small, the ratio between the diffusion contribution and the lowest internal mode can be notable (if $t/\tau_p \sim 10^{-2}$ in the Zimm case, the diffusion contribution differs only some 15% from the contribution due to the first internal mode). Note that one should be careful with the use of the elegant solutions in the form of the stretched exponentials. In fact, these are rather crude approximations valid in a restricted time interval. For instance, applying such solutions in the determination of the character of the monomer dynamics in the FCS experiments [Shusterman 2004], the dynamics of the double-stranded DNA motion in water solution has been characterized as being of the Rouse type (the observed monomer MSD followed the $t^{1/2}$ law). However, a closer look at the validity of this approximation has revealed that the assumption of the continuous distribution of the internal modes (in the mode numbers p) fails for the experimental times. For the studied times the monomer MSD calculated as $\sim t^{1/2}$ was from 20% to one order larger than the MSD found using the correct (discrete in p) distribution of the polymer normal modes [Tothova 2007b]. In such cases the identification of the polymer dynamics based on the $t^{1/2}$ ("Rouse") or $t^{2/3}$ ("Zimm") has obviously no value.

3.10.3 Small scattering vectors

In the classical monograph [Doi 1986] this case is considered as follows. In the exponent in Eq. (3.81) only the diffusion term ($-k^2Dt$) is considered and the other terms are neglected assuming that their magnitudes are smaller than k^2Na^2. However, as seen from Eq. (3.83), all the terms in the exponential equally depend on k and only the time dependence is essential for their comparison. In spite of this the result for $G(k,t) \sim \exp(-k^2Dt)$ is correct. This can be shown by the direct calculation of the DSF, similarly as it was done above. For all range of k these calculations are complicated but the desired result can be obtained by a simpler way, calculating the initial decay rate of the DSF. In fact, since we are interested in the behavior of the DSF at short times where the influence of the memory is expected, the DSF can be approximated by the expression

$$G(k,t) = G(k,0)\exp(-\Gamma t). \tag{3.95}$$

The decay rate Γ can be calculated rigorously [Akcasu 1976, Doi 2003]. For $kR_G \ll 1$ the result is $\Gamma = k^2D$ and $G(k,0) \to N$ as $k \to 0$. In the Zimm model D in this expression is not the true long-time diffusion coefficient but the Kirkwood diffusion coefficient [Doi 1986, Liu 2003]. Within the linearization approximation these coefficients are equal and we will not distinguish them.

The difference between our approach and the original theory (if the relaxation of the internal modes is assumed to be exponential) is in the replacement of the factor $\exp(-k^2Dt)$ by the exponential $\exp\{-k^2[\psi_0(0) - \psi_0(t)]\}$. Then the DSF at short times and small k is expressed as

$$G(k,t) \approx G_{RZ}(k,0)\exp\left\{-k^2\left[\psi_0(0) - \psi_0(t) - Dt\right] - \Gamma t\right\}, \tag{3.96}$$

where G_{RZ} and Γ have the same meaning as in the previous Rouse and Zimm theories. Below the first cumulant will be considered in more detail. Equation (3.96) can be used in estimations of the effects of hydrodynamic memory on the DSF at short times.

3.10.4 Experimental time resolution and the first cumulant to the DSF

Every dynamic scattering experiment is characterized by the shortest accessible time. The existence of a finite resolution time has a significant role in the analysis of the data. As already mentioned in this work, there are discrepancies between the theoretical and experimental values of the first cumulant. According to [Balabonov 1987], the differences are caused by the principal underestimating of the first cumulant, which is due to the experimental resolution in the time. Let us assume that a measured time correlation function is a sum of exponential functions with the relaxation times $1/\Gamma_n$ and the amplitudes A_n. Then the observed first cumulant will be

$$\bar{\Gamma}_{\mathrm{exp}}= \sum\nolimits_n A_n\Gamma_n \exp\left(-\Gamma_n\Delta\tau\right)\Big/\sum\nolimits_n A_n \exp\left(-\Gamma_n\Delta\tau\right), \tag{3.97}$$

where $\Delta\tau$ is the time resolution. When $\Gamma_n\Delta\tau \ll 1$, after the expansion to the first order in $\Delta\tau$ we get

$$\bar{\Gamma}_{\mathrm{exp}} \approx \bar{\Gamma}\left[1+\frac{\bar{\Gamma}^2-\overline{\Gamma^2}}{\bar{\Gamma}^2}\bar{\Gamma}\Delta\tau\right], \tag{3.98}$$

where $\bar{\Gamma}_n \equiv \bar{\Gamma}$ and $\overline{\Gamma_n^2} \equiv \overline{\Gamma^2}$. Usually (*e.g.*, for polydisperse systems) the difference $\bar{\Gamma}^2 - \overline{\Gamma^2}$ is smaller than or of order $\bar{\Gamma}^2$ so that $\bar{\Gamma}_{\mathrm{exp}} \approx \bar{\Gamma}$, which is the result that we would obtain from the experiments at $\Delta\tau = 0$. However, the inequality $\Gamma_n\Delta\tau \ll 1$ does not hold for all the internal modes. Due to this the situation is quite different in the case of polymer coils. Equation (3.98) thus does not follow from (3.97). Using $\bar{\Gamma}_{\mathrm{exp}} = \bar{\Gamma}$, we introduce in the analysis an error, which has been estimated in the work [Balabonov 1987] (see also [Tsunashiva 1983]) as $\bar{\Gamma}_{\mathrm{exp}} - \bar{\Gamma} \approx \left(\bar{\Gamma}\Delta\tau\right)^{1/3}\bar{\Gamma}$. However, this estimation was done for the case of large scattering vectors; it is thus inapplicable for large-time motion and small scattering vectors, $kR \ll 1$. In the latter case the role of the internal modes is negligible and only the diffusion of the coil determines the Van Hove function. We thus argue that the reason for the observed discrepancy between the theory and experiment has a deeper origin. Probably it is due to the fact that the results describing the scattering on the coil are 1) not applicable in the limit $t \longrightarrow 0$, and 2) even if the time resolution $\Delta\tau$ is relatively large, for polymer coils with large radii R, $\Delta\tau$ can be not enough large in the sense that the polymer motion already follows the long-time regime predicted by the original Rouse-Zimm theory. There is a transition regime between the short-time behavior (which is very different from that in the Rouse-Zimm models) and the long-time behavior of the correlation functions that determine the DSF $G(k,t)$. Even for the times t ¿¿$\Delta\tau$ there are still long-time tails in $G(k,t)$, which make it different from the scattering function of the diffusion type, $\sim \exp(-k^2Dt)$. As a result, the DSF decays more slowly in the time, which could lead to an experimentally observed (apparent) diffusion coefficient that is smaller than the value D, predicted by the RZ theory. The situation is similar to that in the experiments on the Brownian motion of rigid particles, see, *e.g.*, Ref. [Weitz 1989].

Since the effects of the hydrodynamic memory on the relaxation of the polymer internal modes can hardly be observed (the time dependence of the correlation functions for these modes only very slightly differs from that in the traditional RZ theory), one could try to reveal these effects in the diffusion of the coil as a whole. In this case the memory effects seem to be not only measurable but could contribute to some of the existing problems between the theory and experiment.

As is well known, the diffusion of the polymer as a whole is observed at small scattering vectors, $kR \ll 1$, when the DSF can be approximated by the function

$$G\left(k,t\right) = G\left(k,0\right) \exp\left\{-k^2 \left[\psi_0\left(0\right) - \psi_0\left(t\right)\right]\right\}. \tag{3.99}$$

The first cumulant that characterizes the decay rate of the DSF at $t \to 0$, and is defined as [Doi 1986]

$$\Gamma = -G\left(k,0\right)^{-1} \left[\mathrm{d}G\left(k,t\right)/\mathrm{d}t\right]_{t=0}, \tag{3.100}$$

can be written in the form

$$\Gamma = k^2 \frac{\mathrm{d}}{\mathrm{d}t}\left[\psi_0\left(0\right) - \psi_0\left(t\right)\right], \qquad t \to 0, \tag{3.101}$$

and expressed through the time-dependent diffusion coefficient $D(t) = -\mathrm{d}\psi_0(t)/\mathrm{d}t$ [Schram 1998]. The function $\psi_0(t)$ can be found using Eq. (3.70) or the subsequent results for the Rouse and Zimm models. Another way is to evaluate Γ directly from the expression for the DSF.

In the traditional Rouse model the DSF is calculated from Eq. (3.81). The static structure factor (SSF) can be from this equation expressed as

$$G\left(k,0\right) = \frac{1}{N}\sum_{nm} \exp\left\{-\frac{Na^2k^2}{3\pi^2}\sum_{p=1}^{\infty}\frac{1}{p^2}\left(\cos\frac{\pi mp}{N} - \cos\frac{\pi np}{N}\right)^2\right\}. \tag{3.102}$$

We use $Na^2 = 128R^2/(3\pi)$, and the relation between the hydrodynamic and gyration radii, $R_G = 8R/(3\sqrt{\pi})$, $R_G^2 = a^2N/6$. The sum in the exponent is $\pi^2\left|n-m\right|/\left(2N\right)$ [Prudnikov 1981]. As usually in the continuum approximation, the summation through n and m is replaced by the integration from 0 to N, so that for the SSF one obtains [Doi 1986]

$$G\left(k,0\right) = \frac{2N}{\left(kR_G\right)^2}\left\{1 - \frac{1}{\left(kR_G\right)^2}\left[1 - \exp\left(-k^2R_G^2\right)\right]\right\}. \tag{3.103}$$

Since the internal modes relax exponentially, $\psi_p(t) = \psi_p(0)\exp(-t/\tau_p)$, $p > 0$, and for the Einstein diffusion of the whole coil, the quantity $\mathrm{d}\Phi_{nm}(t)/\mathrm{d}t$ in Eqs. (3.81) and (3.82) is

$$\left(\frac{\mathrm{d}\Phi_{nm}\left(t\right)}{\mathrm{d}t}\right)_{t=0} = D\left[1 + 2\sum_{p=1}^{\infty}\cos\frac{\pi mp}{N}\cos\frac{\pi np}{N}\right], \tag{3.104}$$

where we have used $\psi_p(0)/\tau_p = D/2$. The time derivation of the DSF can be expressed in the form

$$\left(-\frac{\mathrm{d}G}{\mathrm{d}t}\right)_{t=0} = \frac{k^2}{N}\sum_{nm}\left(\frac{\mathrm{d}\Phi_{nm}(t)}{\mathrm{d}t}\right)_{t=0}\exp\left(-k^2R_G^2\left|n-m\right|/N\right). \tag{3.105}$$

Calculating the sum we again convert it to the integral. The integral is easily found noting that the quantity in the square brackets in Eq. (3.104) is proportional to the delta function of the difference $(m-n)$,

$$N\delta(n-m) = 1 + 2\sum_{p=1}^{\infty}\cos\frac{\pi np}{N}\cos\frac{\pi mp}{N},$$

represented through the orthonormal set of functions in the interval from 0 do N,

$$\psi_p(n) = \sqrt{2-\delta_{p0}}\cos\frac{\pi np}{N}, \quad p = 0,\, 1,\, 2, ...$$

Instead of Eq. (3.105) we thus have

$$-\left.\frac{\partial G}{\partial t}\right|_{t=0} = k^2D\int_0^N \mathrm{d}n\int_0^N \mathrm{d}m\,\delta(n-m)\exp\left(-\frac{k^2R_G^2}{N}\left|n-m\right|\right) = k^2ND \tag{3.106}$$

and the first cumulant from Eq. (3.100) is

$$\frac{\Gamma}{k^2D} = \frac{1}{2}\frac{x^2}{x+\exp(-x)-1}, \qquad x = (kR_G)^2. \tag{3.107}$$

The limiting cases of this expression are well known [Doi 1986, Grosberg 1989]

$$\begin{aligned} \frac{\Gamma}{k^2D} &\approx 1 + \frac{x}{3} + ..., \qquad x \to 0, \\ \frac{\Gamma}{k^2D} &\approx \frac{x}{2}, \qquad x \gg 1. \end{aligned} \tag{3.108}$$

The first cumulant in the Rouse model does not reflect the internal dynamics of the polymer coil.

In the Zimm case we proceed analogously as above; the difference is only in the diffusion coefficient D and in the relaxation times τ_p (3.75). At large kR_G again Eq. (3.105) is used, now with

$$\left(\frac{\mathrm{d}\Phi_{nm}(t)}{\mathrm{d}t}\right)_{t=0} = 2D\left[1 + \frac{3}{2\sqrt{2}}\sum_{p=1}^{\infty}\frac{1}{\sqrt{p}}\cos\frac{\pi mp}{N}\cos\frac{\pi np}{N}\right]. \tag{3.109}$$

This expression is integrated with the factor $\exp(-k^2 R_G^2 \left|n-m\right|/N)$, due to which the main contribution is given by $n \approx m$. If the summation is replaced by integration [Dubois-Violette 1967], one arrives at the result

$$-\left.\frac{\partial G}{\partial t}\right|_{t=0} \approx \frac{3\sqrt{\pi}}{4}\frac{kDN}{R_G}. \tag{3.110}$$

Using the expression for the SSF (3.103) at large kR_G, $G(k,0) \approx 2N(kR_G)^{-2}$, the well-known "$k^3$ law" is obtained for the first cumulant when the HI is taken into account:

$$\Gamma \approx \frac{k_B T}{6\pi\eta}k^3. \tag{3.111}$$

At small wave-vector transfers, $kR_G \ll 1$, the cumulant is, as in the Rouse model, $\Gamma = k^2 D$.

3.10.5 The first cumulant in the model with hydrodynamic memory

When the hydrodynamic memory is taken into account, the first cumulant Γ, defined by Eq. (3.100) identically equals to zero. Indeed, the time derivative of the DSF from Eq. (3.81) is (at $t = 0$)

$$G'\left(k,0\right) = -\frac{k^2}{N}\sum_{mn}\Phi'_{mn}\left(0\right)\exp\left[-k^2\Phi_{mn}\left(0\right)\right]. \tag{3.112}$$

When we express $\Phi_{mn}(t)$ through the correlation functions of the normal modes, *i.e.*, through the MSD of the coil ($p = 0$) and the functions $\psi_{p\geq 1}\left(t\right)$ describing the internal modes, and take into account that

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\psi_0\left(0\right) - \psi_0\left(t\right)\right]_{t=0} = 0 \tag{3.113}$$

(remind that, as distinct from the linear time dependence in the previous models, the MSD is at short times $\sim t^2$), we obtain

$$\Phi'_{mn}\left(0\right) = -4\sum_{p=1}^{\infty}\psi'_p\left(0\right)\cos\frac{\pi mp}{N}\cos\frac{\pi np}{N}. \tag{3.114}$$

In the classical theory [Doi 1986] $\psi'_p\left(0\right)$ is nonzero. Now $\psi'_p\left(0\right) = 0$, as easily seen from Eq. (3.70). Due to this also $\Phi'_{mn}\left(0\right)$ and $G'\left(k,0\right)$ equal to zero; consequently, $\Gamma = 0$. The fact that in experiments the first cumulant is nonzero can be explained as follows. Every experiment has its "time zero". It is given by the experimental resolution in the time. The time $t = 0$, used in the theory, does not exist in experimental situations. Any experiment is able to monitor the polymer dynamics only beginning from some time t_0. The theoretical results are thus applicable for the times t larger than t_0. While the time-dependent diffusion coefficient $D(t) = -\mathrm{d}\psi_0(t)/\mathrm{d}t$ is zero for $t = 0$, at $t_0 > 0$ we have a nonzero diffusion coefficient. With the time growing our result for the DSF will approach the classical one and for enough long times the two results cannot be distinguished. Thus, for poor experimental resolution (large t_0) our results will be very close to the classical ones. Better the experimental resolution, larger the deviation of our theory from the prediction for the first cumulant in the previous theory. Since the classical results are in our theory approached very slowly in the time, we believe that the deviations could be experimentally accessible. There are two questions to be answered. First, whether the time resolution in the current experiments allows to detect these deviations, and second, whether the theory is able to resolve the existing discrepancies with experiment, mentioned in Introduction. As to the first question, at least the non-diffusive motion of the whole polymer should be observable. For a typical polymer 100 nm in radius, in water solution at room conditions, the characteristic time of the ballistic motion is $\tau_R \sim 10$ ns and the transition to the diffusive regime is very slow. In the current scattering experiments the sampling times are on the level of tenths μs, but can be an order shorter [Hohenadl 1999]. Even much shorter times are accessible by the neutron spin echo technique [Monkenbusch 2003]. For some of the experiments in which the ballistic motion of small rigid spheres has been successfully observed see Refs. [Boon 1976, Paul 1981, Weitz 1989]. Before answering the second question we have to calculate the DSF and the first cumulant as they follow from our hydrodynamic theory.

The relaxation of the internal modes will be assumed indistinguishable from the exponential relaxation in the previous theory, $\psi_p(t) \sim \exp(-t/\tau_p)$. In this case the time derivative of the DSF (3.81) is

$$\begin{aligned}\frac{\partial G}{\partial t} = \frac{k^2}{N}\sum_{mn}\left\{\frac{\mathrm{d}}{\mathrm{d}t}\psi_0(t) - 4\sum_{p=1}^{\infty}\frac{\psi_p(0)}{\tau_p}e^{-t/\tau_p}\cos\frac{\pi np}{N}\cos\frac{\pi mp}{N}\right\} \\ \times\exp\left(-k^2R_G^2\left|n-m\right|/N\right),\end{aligned} \tag{3.115}$$

and for the first cumulant (3.100) we find at $t = t_0$

$$\frac{\Gamma}{k^2D} = -\frac{1}{k^2DG(k,0)}\left.\frac{\partial G}{\partial t}\right|_{t=t_0} \approx -\frac{1}{D}\left.\frac{\mathrm{d}}{\mathrm{d}t}\psi_0(t)\right|_{t=t_0} - 1 + \frac{N}{G(k,0)}. \tag{3.116}$$

In the Rouse limit the last term in this equation is $x^2\left(x-1+\exp(-x)\right)^{-1}/2$, $x = \left(kR_G\right)^2$, and the first term in the classical theory was equal to 1. When t_0 increases, the contribution of the first two terms decreases. Similarly, in the Zimm limit we obtain

$$\Gamma = -k^2D\left\{1 - D^{-1}\left.\frac{d}{dt}\left[\psi_0(0)-\psi_0(t)\right]\right|_{t=t_0}\right\} + \Gamma_Z, \tag{3.117}$$

where $\Gamma_Z(k)$ is the cumulant in the original Zimm theory. In general, we have that in the case of “ideal” experiment, with t_0 = 0, the hydrodynamic memory would lower the measured cumulant by the quantity $-k^2D$. In the case of small kR_G, when the pure diffusion is observed, the cumulant would be zero. Since $t_0 \neq 0$, the cumulants are nonzero but their values are smaller than in the traditional theory. The importance of this effect could be judged by a detailed comparison with experiments.

The first cumulant of long flexible polymers in θ solutions was experimentally studied in a number of works. One of the most detailed studies is the work by Sawatari *et al.* [1998], which probably supports our view on the dynamics of individual polymers. Whereas most of the investigations have been devoted to the confirmation of the universal behavior of Γ as a function of the scattering vector k, the mentioned work tests the dependence of $\eta\Gamma/k_BTk^3$ on kR_G in the "k^3 region" for different polymers. Indeed, it has been found that the cumulants differ for different polymers, even if they have large molecular weights. This is in agreement with the theoretical prediction [Yoshizaki 1997], the theory is however not able to explain quantitatively the data for an individual polymer.

It is not very surprising that the "universal" region is in fact not universal (*i.e.*, that the Zimm plot $\eta\Gamma/k_BTk^3$ on kR_G depends on the system polymer – solvent). Such universality requires the existence of a "pure" Zimm polymer while the dynamics of every polymer, within the standard bead-spring model, reveals at the same time properties of both the Zimm and Rouse polymers. Different polymers are thus described (in addition to the parameters entering the Zimm model) by different phenomenological friction coefficients for one bead that could be the reason for the observed nonuniversality [Tothova 2007b]. The importance of the work [Sawatari 1998] is also in the detailed investigation of the following two problems in the experimental determination of the first cumulant. First, it is known that the determination of $\Gamma(k)$ is sensitive to the experimental sampling time [Stockmayer 1984]. It seems also that it depends on the choice of the method of its evaluation from the data. For us both these problems are important since the effect of hydrodynamic memory is detectable first of all at short times, on the level of the shortest resolution times in the usual light scattering experiments. In the experiments [Sawatari 1998] solutions of polystyrene and poly(methylmethacrylate) of large molecular weights were studied by the static and dynamic light scattering. The diffusion coefficients of the observed polymer coils have been compared to their gyration radii. The values of D were always smaller than the corresponding Kirkwood values for the Zimm model ($D_Z = 8k_BT/3\sqrt{6\pi^3N}\eta a$, see Eq. (3.45)). The DSF was determined from the normalized autocorrelation function of the scattered light, $g^{(2)}(t)$, as $G(k,t) \propto g^{(2)}(t) - 1$. In our approach the measured function $g^{(2)}(t)$ corresponds to

$$\ln\left[g^{(2)}(t) - 1\right] = \text{const} + k^2\left\{D_Ct - \left[\psi_0(0) - \psi_0(t)\right]\right\} + \ln G(k,t)\,, \tag{3.118}$$

if G is understood as the DSF in the previous Rouse-Zimm theory. The additional second term on the right, which disappears at long times, determines the deviation from the value expected within the previous theory. The differences can be detected only at small sampling times. Experimental results are in qualitative agreement with our predictions. Really, the measured values of ln $[g^{(2)}(t) - 1]$ obtained with the sampling time $t_0 = 0.5$ μs were slightly larger than the DSF values in the region of its decay at short times, found with a longer $t_0 = 2$ μs. The reason for this difference was unclear for the authors [Sawateri 1998] (note that for a different polymer, using closer sampling times, the difference in the values of $g^{(2)}(t)$ was smaller). The observed difference is small (since the used times t_0 are still rather long compared to the characteristic time τ_R, which we have assumed for the longest polymer to be $\tau_R \sim 10^{-8}$ s). Although the quantitative comparison with the experiment requires a precise treatment of the experimental data using the above derived expression for the DSF, the noted observations support our theory. As to the first cumulant Γ determined from $g^{(2)}(t)$ by the extrapolation of (1/2)ln $[g^{(2)}(t) - 1]$ to $t = 0$, only the data for $t > 5$ μs have been considered in the determination of Γ, and the diffusion coefficient was measured with the sampling time 22-27 μs, $i.e.$, far out of the region of our main interest. The observed deviations from the values $\eta\Gamma/k_BTk^3 = 1/6\pi$ and D expected in the frame of the Zimm theory were small, of order of 10%. The memory effects do not persist at such long times (for the considered situation our theory predicts corrections to the Zimm results for Γ and D on the level of 2% and 1%, respectively), but another reasons can play a role ($e.g.$, the mentioned combined Rouse-Zimm behavior of the polymers, or the approximate character of the used expressions in the region of relatively small ($2 < kR_G < 7$) scattering wave vectors). It thus seems that the hydrodynamic memory alone cannot give a satisfactory solution of the long-standing puzzles discussed in Introduction.

4 Joined Rouse-Zimm model in the steady-state limit

The theory presented in the previous sections is developed for a single polymer chain or very dilute solutions and does not contain any dependence on other polymers in solution. Now our aim is to show that the above results can be relatively simply generalized to take into account the presence of other polymer coils through their finite concentration in solution. We shall focus on dilute polymer solutions where the coils are well separated. That is, we do not consider semidilute and dense solutions with the chains strongly overlapping each other, so that the polymers lose their individualities. Even for very dilute polymer solutions still problems exist in understanding, $e.g.$, the viscosity behavior of such solutions [Larson 2005, Yang 2005, Tothova 2014, 2015]. In what follows we shall give an outline of a phenomenological theory of the diffusion of the polymer as a whole and the relaxation of its internal modes in the case when other chains in the solution affect the flow of the solvent. The results are interesting also because they imply the screening of the HI and the transition between the Zimm and Rouse dynamics of the "test" polymer. These effects are well revealed in semidilute and dense polymer solutions (see [Richter 1984, Ahlrichs 2001] and references there) but qualitatively they are displayed already in the theories for dilute solutions [Doi 1986].

The discussed screening of the HI can be described within our model just because it naturally joins the Rouse and Zimm theories. Due to the importance of this point, we first give a substantiation of this joining, absent in the popular monographs [Doi 1986, Grosberg 1989].

4.1 Substantiation of joining the Rouse and Zimm models

The basic equation within the bead-spring models of polymer dynamics, in the steady-state limit, is the equation of motion for the position vector of the bead [Doi 1986, Grosberg 1989],

$$\frac{\mathrm{d}\vec{r}_n}{\mathrm{d}t} = \frac{1}{\gamma}\left(\vec{f}_n^{ch} + \vec{f}_n\right) + \vec{v}\left(\vec{r}_n\right). \tag{4.1}$$

Here, $\vec{f}_n^{ch}$ is the force on the nth bead from the neighboring beads, $\vec{f}_n$ is the random force due to the motion of the molecules of solvent, $\vec{v}\left(\vec{r}_n\right)$ is the velocity of the solvent, and γ is the friction coefficient (for a spherical particle $\gamma = 6\pi\eta b$, where η is the solvent viscosity and b is the bead radius. As distinct from the theory by Rouse [1953], where the solvent is nonmoving ($v = 0$), Eq. (4.1) takes into account the HI [Zimm 1956]. Within the Zimm theory the velocity field $\vec{v}\left(\vec{r}_n\right)$ is expressed through the Oseen tensor $\widehat{H}$,

$$\frac{\mathrm{d}\vec{r}_n}{\mathrm{d}t} = \frac{1}{\gamma}\left(\vec{f}_n^{ch} + \vec{f}_n\right) + \sum_{m\neq n} \widehat{H}\left(\vec{r}_n - \vec{r}_m\right)\left(\vec{f}_m^{ch} + \vec{f}_m\right). \tag{4.2}$$

In the sum $m \neq n$ since $\vec{v}\left(\vec{r}_n\right)$in the point n is created by all other $N-$ 1 beads in the chain except the nth one. If one, following [Grosberg 1989], formally defines the Oseen tensor for $n = m$ as $\widehat{H}_{nn} = \delta_{nm}/\gamma$, the summation in (4.2) can be extended to all n, m to include the first term on the right. Usually the continuum approximation with respect to n is used,$\vec{r}_n\left(t\right) \to \vec{r}\left(t,n\right)$. After this step, however, the term $\sim \gamma^{-1}$ disappears. One should require that the Zimm model generalizes the simpler Rouse model. If we act as described above, this is not the case: the two models are independent. Moreover, imagine that in the Rouse model (with $v = 0$) we lose in the continuum approximation the term $\sim \gamma^{-1}$ in (4.1); the model would become meaningless. Thus, to generalize the Rouse model, we have in the continuum approximation to keep the $\sim \gamma^{-1}$ term in (4.2). The $m = n$ term in the sum can be defined arbitrarily since it will not influence the integration. As a result, the Rouse-Zimm equation in the continuum limit should be

$$\frac{\partial \vec{r}\,(t,n)}{\partial t} = \frac{1}{\gamma}\left[\vec{f}^{ch}\,(t,n) + \vec{f}\,(t,n)\right] + \int\limits_0^N \mathrm{d}m\widehat{H}\,(n,m)\left[\vec{f}^{ch}\,(t,m) + \vec{f}\,(t,m)\right]. \tag{4.3}$$

Depending on the polymer parameters, the model gives the description of the polymer behavior more close to the Rouse or Zimm dynamics. In general, however, both terms on the right side of Eq. (4.3) should be kept in consideration. After this correction of the method described in the monograph [Grosberg 1989], one can follow the standard way and obtain, in particular, the spectrum of polymer internal modes in theta solutions. The relaxation rates of these modes have a particularly simple form (3.74) with the limiting relaxation times given by Eq. (3.75). The quantity $h(p) = \tau_{pR}/\tau_{pZ} = h/\sqrt{p}$, with the draining parameter $h = 2\sqrt{3N/\pi}\frac{b}{a}$, indicates the strength of HI, $i.e.$, whether the internal dynamics is of the pure Zimm ($h \gg 1$) or Rouse ($h \ll 1$) type. For the diffusion of the coil as a whole we have $D_Z/D_R = 4\sqrt{2}h/3$ (see Section 3.6).

4.2 Dynamics of a test polymer in the presence of other polymers in solution: Screening of hydrodynamic interactions

The presence of other polymers in solution (with a concentration c) can be taken into account as follows [Lisy 2006a]. The equation of motion for the nth bead of a "test" polymer is (3.1) with the HI introduced in Sec. 3.6 should be completed with the equation

$$\vec{f}_n^{fr} = -\gamma\left[\frac{\mathrm{d}\vec{r}_n}{\mathrm{d}t} - \vec{v}\,(\vec{r})\right], \tag{4.4}$$

where $\vec{r}_n$ is the radius vector of the bead. This expression holds in the case of steady flows. In a more general case taking into account the hydrodynamic memory, the force (4.4) should be replaced by the Boussinesq force (3.37) and (3.1) has to be solved together with the nonstationary hydrodynamic equations for the macroscopic velocity of the solvent. To take into account the presence of other polymers in solution, we use the Brinkman [1947a, b] (or the Debye-Bueche [1948]) theory in which the polymer is considered as a porous medium. In our approach all the solution is such a medium permeable to the solvent flow. Then in the right hand side of the Navier-Stokes equation a term $-\kappa^2\eta\vec{v}$ has to be added. This term corresponds to the average value of the force acting on the liquid in an element of volume $\mathrm{d}V$, provided the average number of polymers in solution per $\mathrm{d}V$ is c; then $\kappa^2\eta = cf$. Thus,

$$\rho\frac{\partial \vec{v}}{\partial t} = -\nabla p + \eta\Delta\vec{v} - \kappa^2\eta\vec{v} + \vec{\phi}. \tag{4.5}$$

Here, $\vec{\phi}$ is the density of the force from the polymer beads on the liquid,

$$\vec{\phi}\left(\vec{r}\right) = -\sum_n \vec{f}_n^{fr}\left(\vec{r}_n\right)\delta\left(\vec{r}-\vec{r}_n\right). \tag{4.6}$$

Solving this equation is a difficult problem since the polymer coils are moving. However, in the first approximation small and slow changes of the concentration $c(t)$ around its equilibrium value can be neglected. The beads are obviously much more mobile than the whole coils of long polymer chains ($N \gg 1$). This is seen comparing the bead diffusion coefficient $D_b = k_B T/(6\pi b\eta)$ with the diffusion coefficient of the coil in the Zimm ($D_Z = 8k_B T/[3(6\pi^3 N)^{1/2}a\eta]$) or Rouse ($D_R = k_B T/(6\pi N b\eta)$) limits [Doi 1986]. In the latter case $D_R/D_b = 1/N$, and for the Zimm polymers $D_Z/D_b \approx 3.7b/(a\sqrt{N})$. The flow of the solvent created by the motion of beads is thus much faster than the motion of the coils, which determines the changes of $c(t)$.

Eqs. (3.1) and (4.4)–(4.6) describe the motion of one bead in the solvent, when the obstacles (other coils) influence the solvent flow. This problem can be transformed to that solved in [Zatovsky 2003, Lisy 2004b]. The velocity field in the Fourier representation in the time is given by Eq. (3.50) expressed through an analogue of the Oseen tensor (3.53) from Sec. 3.7., now with $y = r\chi$ and $\chi^2 = \kappa^2 - \mathrm{i}\omega\rho/\eta$. In the particular case $\omega = 0$ and for permeable solvents when $\kappa = 0$, the Oseen tensor coincides with the known result of Zimm [1956, Doi 1986]. The preaveraging of the Oseen tensor over the equilibrium (Gaussian) distribution of the beads gives Eqs. (3.56) and (3.57). In the continuum approximation with respect to the variable n, the new Rouse-Zimm equation (3.66) contains only the diagonal terms. Taking into account the boundary conditions at the ends of the chain, the Fourier transformation in n yields equations (3.67) and (3.68) with the Oseen matrix h_{pp}^{ω} from (**??** and (3.63) with $\chi_\omega = \sqrt{N/6}\chi a$ and $\chi_p = \sqrt{N/(3\pi p)}\chi a$ (but now χ depending on κ). Then the time correlation functions for the normal modes are determined by Eq. (3.70). In the stationary limit $\omega = 0$ so that $\chi = \kappa$. Then the preaveraged Oseen tensor (3.53) is

$$\left\langle H_{\alpha\beta}^{\omega}\right\rangle_0 = \frac{\delta_{\alpha\beta}}{6\pi\eta}\left\langle\frac{e^{-\chi r}}{r}\right\rangle_0. \tag{4.7}$$

The quantity $1/\kappa$ can be thus for small κr considered as the screening length. Let us first focus on the motion of the center of inertia of the polymer.

For an individual polymer ($p = 0$ in Eq. (3.70))

$$\psi_0\left(0\right) - \psi_0\left(t\right) = Dt \tag{4.8}$$

with $D = D_R + D_Z$. Now, instead of Eq. (3.63) we have h_{00}^0 with $\chi_0 = \kappa R_G$ ($R_G = \sqrt{Na^2/6}$), D depends on the concentration of the coils c,

$$D\left(c\right) = D_Z\left(c\right) + D_R, \qquad D_Z\left(0\right) = D_Z, \tag{4.9}$$

and consists of the Rouse (independent on the presence of other polymers) and the Zimm contributions. The latter one can be expressed in the form

$$D_Z\left(c\right) = D_Z\left(0\right) f\left(c\right), \tag{4.10}$$

where $f(c)$ is a universal function for every polymer:

$$f\left(c\right) = \frac{3\sqrt{\pi}}{4\chi_0}\left[1 - \frac{2}{\sqrt{\pi}\chi_0} - \frac{1}{\chi_0^2}\left(\exp\chi_0^2\,\mathrm{erfc}\chi_0 - 1\right)\right]. \tag{4.11}$$

The dependence of the permeability on c can be estimated as follows. The friction coefficient in the quantity $\kappa^2 = cf/\eta$ from Eq. (4.5) is determined from the Einstein-Stokes relation $D = k_B T/f$. Then

$$\kappa^2 = \frac{27\sqrt{\pi}}{16}\frac{\tilde{c}}{R_G^2}\left(1 + \frac{3}{4\sqrt{2}h}\right)^{-1}. \tag{4.12}$$

The quantity $\tilde{c} = 4\pi R_G^3 c/3$ denotes the number of polymers per volume of a sphere with radius R_G. The values of κ and χ_0 depend on (remember that if $h \gg 1$, the dynamics is of the Zimm type and for $h \ll 1$ we have the free-draining Rouse limit). With the increase of c the Zimm term decreases and for large c (small permeability κ, when $\chi_0 \gg 1$) it becomes $\sim 1/\sqrt{c}$,

$$D_Z\left(c\right) \approx \frac{2k_B T}{\pi\eta N a^2}\frac{1}{\kappa}. \tag{4.13}$$

The realistic case of small c corresponds to $\chi_0 = \kappa R_G \ll 1$ when

$$D_Z\left(c\right) = k_B T h_{00}^0\left(c\right) = D_Z\left(0\right)\left(1 - \frac{3}{8\sqrt{\pi}}\kappa R_G + \cdots\right). \tag{4.14}$$

The c-dependent correction to $D_Z(0)$ is proportional to $\sqrt{c}$ and differs from other results ($e.g.$ [Zhao 2005], where this correction is $\sim c$). When the polymer is free, the type of its diffusion depends only on the draining parameter h. With the growing c, the polymer changes its behavior to the diffusion with the exactly Rouse coefficient D_R.

In the stationary case and at $\kappa = 0$ the diagonal elements of the Oseen matrix are [Doi 1986] $h_{pp}^0\left(0\right) = \left(12\pi^3 N p\right)^{-1/2}\left(\eta a\right)^{-1}$. Now $h_{pp}^0\left(c\right)$ from Eq. (3.63) depends on c. The internal modes (3.70) relax exponentially,

$$\psi_p\left(t\right) = \frac{k_B T}{2NK_p}\exp\left(-\left|t\right|/\tau_p\right), \tag{4.15}$$

and their relaxation rates consist of the Rouse and Zimm contributions as in Eq. (3.74), but now the Zimm part is c-dependent:

$$\frac{1}{\tau_p\left(c\right)} = \frac{1}{\tau_{pR}} + \frac{1}{\tau_{pZ}\left(c\right)}. \tag{4.16}$$

Here τ_{pR} and $\tau_{pZ}(0) \equiv \tau_{pZ}$ are given by Eq. (3.75) and

$$\tau_{pZ}(c) = \frac{1}{2}\tau_{pZ}(0)\,\frac{1+(1+\chi_p)^2}{1+\chi_p}, \tag{4.17}$$

which at $c \to 0$ behaves as

$$\tau_{pZ}(c) = \tau_{pZ}(0)\left(1+\frac{N}{6\pi p}\kappa^2 a^2 - \cdots\right), \tag{4.18}$$

and as $c \to \infty$ one has

$$\tau_{pZ}(c) \approx \frac{1}{2}\tau_{pZ}(0)\,\chi_p = \frac{\left(Na^2\right)^2\eta}{6\pi k_B T p^2}\kappa. \tag{4.19}$$

4.3 Steady state viscosity

Viscosity is the most important property that determines the flow characteristics of the fluid. Using the above calculated relaxation times τ_p, the steady state viscosity of the solution can be calculated from the formula [Larson 2005]

$$\eta(c) = \eta + \frac{1}{2}k_B T c \sum_{p=1}^{\infty}\tau_p(c). \tag{4.20}$$

In the Rouse limit Eq. (4.20) yields the known result [Doi 1986], $\eta(c) = \eta + \pi N^2 a^2 b c\eta/6$. In the Zimm case at low c

$$\begin{aligned}\frac{\eta(c)-\eta}{\eta} &= \frac{c}{2\sqrt{3\pi}}\left(Na^2\right)^{3/2}\sum_{p=1}^{\infty}p^{-3/2}\left[1+\frac{\sqrt{6\pi}}{16p}c\left(Na^2\right)^{3/2}+\cdots\right]\\ &= 0.425c\left(Na^2\right)^{3/2}\left[1+0.140c\left(Na^2\right)^{3/2}+\ldots\right],\end{aligned} \tag{4.21}$$

where the first term corresponds to the known formula [Doi 1986]). In our theory, the most general expression for the viscosity is

$$\frac{\eta(c)-\eta}{\eta c} = \frac{N^2 a^2 b}{\pi}\sum_{p=1}^{\infty}\frac{1}{p^2}\left(1+\frac{2h}{\sqrt{p}}\frac{1+\chi_p}{1+(1+\chi_p)^2}\right)^{-1} \tag{4.22}$$

At very low c when $\chi_p \ll 1$, we have for the so called intrinsic viscosity

$$[\eta]_h = \frac{\eta(c)-\eta}{\eta c} = \frac{1}{\pi}N^2 a^2 b\sum_{p=1}^{\infty}\frac{1}{p^2}\left(1+\frac{h}{\sqrt{p}}\right)^{-1}. \tag{4.23}$$

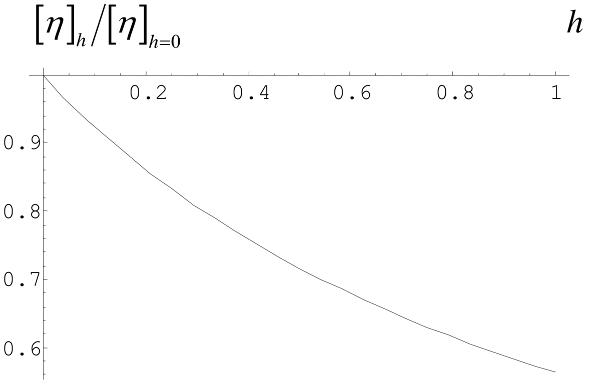

Fig. 4.1. Viscosity normalized to its Rouse limit as a function of $h < 1$ when the polymer is assumed to be the Rouse one.

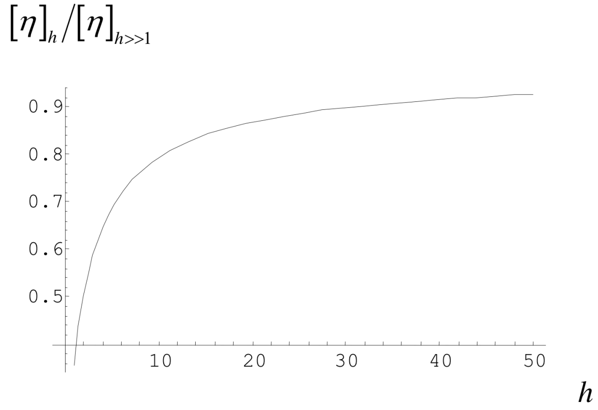

Fig. 4.2. The same as in Fig. 4.1 for very large h (the Zimm polymer).

Due to the dependence on h the difference between $[\eta]_h$ and the classical results can be notable. For a Rouse polymer with small h this is illustrated by Fig. 4.1. In Fig. 4.2, $[\eta]_{h\gg 1} \sim 1/h$ is the intrinsic viscosity of the Zimm polymer when $[\eta(c) - \eta]/\eta = 2.61N^2a^2bc/(\pi h)$. It is seen that even for $h \approx 10$ the difference from the classical result is $\sim 20\%$.

Using the above results, the Huggins coefficient k_H [Doi 1986], which is one of the most often determined quantities in viscosimetry measurements, can be found. From the general expression for the viscosity (4.22), the Huggins equation is

$$\frac{\eta\left(c\right) - \eta}{\eta c} = \left[\eta\right]\left(1 + k_H\left[\eta\right]c + \cdots\right), \tag{4.24}$$

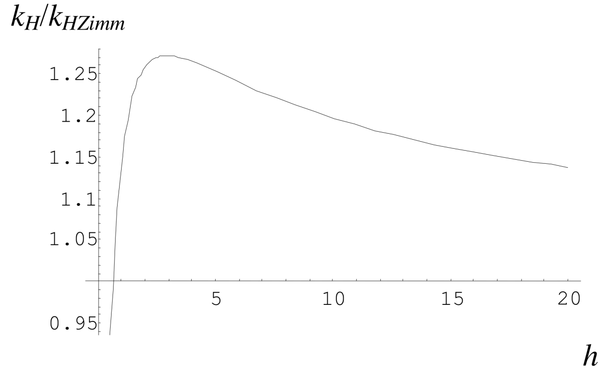

Fig. 4.3. Huggins coefficient normalized to its Zimm limit.

where

$$k_H = \pi h \left(1 + \frac{4\sqrt{2}h}{3}\right)^{-1} \left[\sum_{p=1}^{\infty} \frac{1}{p^2}\left(1+\frac{h}{\sqrt{p}}\right)^{-1}\right]^{-2} \sum_{p=1}^{\infty} \frac{1}{p^{7/2}}\left(1+\frac{h}{\sqrt{p}}\right)^{-2} \tag{4.25}$$

In Fig. 4.3, the Huggins coefficient related to its Zimm limit is shown. It is seen that with the growing h, k_H slowly approaches k_{HZimm}. The difference is significant in a broad region of h. For large h we find

$$[\eta]_\infty = \frac{N^{3/2}a^3}{2\sqrt{3\pi}} \sum_{p=1}^{\infty} p^{-3/2} = 3\sqrt{\frac{2}{\pi}} R_G^3 \zeta\left(\frac{3}{2}\right) \approx 6.253 R_G^3, \tag{4.26}$$

where ζ is the Riemann zeta function. In this case

$$k_{HZimm} = 3\pi 2^{-5/2} \zeta\left(5/2\right) \zeta^{-2}\left(3/2\right) \approx 0.3275. \tag{4.27}$$

Note that in Ref. [Tothova 2015] the steady-state shear viscosity of low-concentrated Poly(2-ethyl-2-oxazoline) (PEOX) aqueous solutions was measured near the presumed theta temperature using the falling ball viscometry technique. The experimental data possessed the Huggins coefficient $k_H = 0.418$ at $T = 20\,^\circ$C. Within the joined Rouse-Zimm model this value of k_H corresponds to the maximum of the peak in Fig. 4.3 at $h = 2.92$.

The result (4.27) differs from the literature results (*e.g.*, Doi and Edwards [1986] give the value 0.757, in [Muthukumar 1981] one finds the value 0.6949, *etc.* As discussed in [Muthukumar 1981, 1983], the theory [Freed 1974, 1975], possesses $[\eta]$ which is inconsistent with the Kirkwood and Riseman [1948] limit and gives the hydrodynamic screening even for infinitely dilute solutions. According to [Freed 1975], the screening cannot be described if the preaveraging approximation is employed for the HI; as shown here, this is not true. Finally, in the opposite Rouse limit when $h \to 0$, k_H approaches zero as $k_H \approx \pi h \zeta(3.5)\zeta^{-2}(2) \approx 1.3h$.

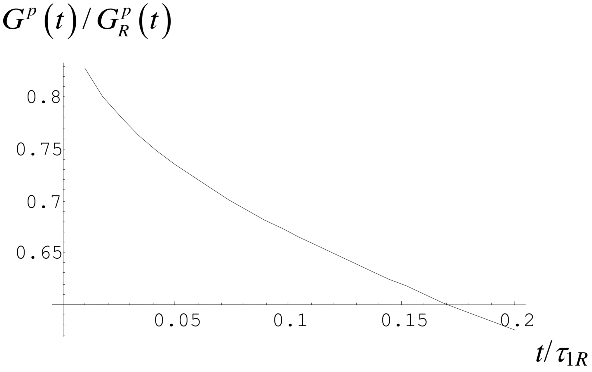

Fig. 4.4. Relaxation modulus G^p as a function of t at $h = 1$.

Another important quantity is the relaxation modulus G that determines the shear stress at shear flows $\upsilon_x(\vec{r}, t) = \zeta(t) r_y$, $\upsilon_y = \upsilon_z = 0$ [Doi 1986, Grosberg 1989],

$$\sigma_{xy}(t) = \eta\zeta(t) + \int\limits_{-\infty}^{t} \mathrm{d}t' G^p(t - t')\zeta(t') = \int\limits_{-\infty}^{t} \mathrm{d}t' G(t - t')\zeta(t') \,. \tag{4.28}$$

Having solved the chain dynamics, G is calculated from the equation

$$G^p(t) = k_B T c \sum_{q=1}^{\infty} \exp(-2t/\tau_q). \tag{4.29}$$

Figure 4.4 illustrates the time behavior of G^p at $c = 0$ related to its Rouse limit. With the growing t the difference from the Rouse result becomes significant even at small h. So, when $t/\tau_{1R} \approx 10$ and $h = 1/100$, this difference is about 20%.

Figure 4.5 illustrates how $G^p(t)$ differs from the pure Zimm limit. At very short times the difference is significant even for large h. With the increase of t, G^p becomes closer to its Zimm limit; however, the transition to the Rouse behavior at long times is observed, as shown in Fig. 4,6. For the chosen $h = 10$, the difference from the Zimm modulus is always larger than 10%.

4.4 Monomer mean square displacement

Similar results can be obtained for other quantities, like the complex modulus, the dynamic structure factor of the test polymer [Tothova 2007a], or the MSD of a monomer within an isolated coil. The latter quantity can be observed using the fluorescence correlation spectroscopy [Shusterman

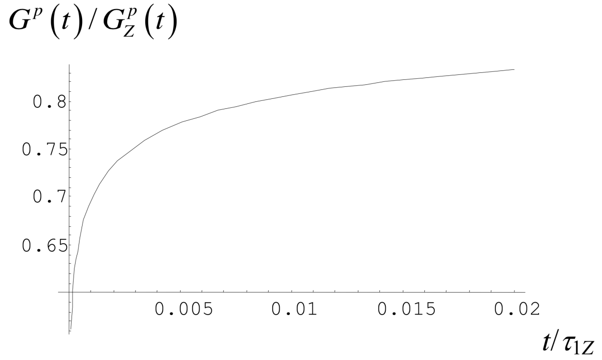

Fig. 4.5. Short-time behavior of the relaxation modulus related to its Zimm limit. The draining parameter is $h = 10$.

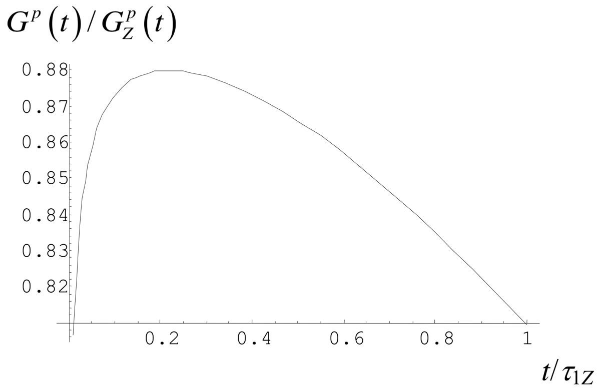

Fig. 4.6. The same as in Fig. 4.3 at longer times.

2004]. The internal modes of the polymer contribute to the MSD of its end monomer as follows [Tothova 2007a]:

$$\left\langle r^2(t)\right\rangle_{\text{int}} = \frac{4Na^2}{\pi^2}\sum_{p=1}^{\infty}\frac{1}{p^2}\left[1-\exp\left(-\frac{t}{\tau_p(c)}\right)\right]. \tag{4.30}$$

The numerical calculations using this expression are given in Fig. 4.7. We relate the Rouse MSD (at $h = 0$) to the Rouse-Zimm MSD at $h = 10$ to show how this function changes depending on the time at a relatively low concentration (one coil in the volume $10 \times \frac{4}{3}\pi R_G^3$). It is seen that at long times the behavior of the polymer, which was initially predominantly of the Zimm type, changes to the Rouse-like type.

More detailed calculations are given in [Tothova 2007b] for a single polymer coil and in

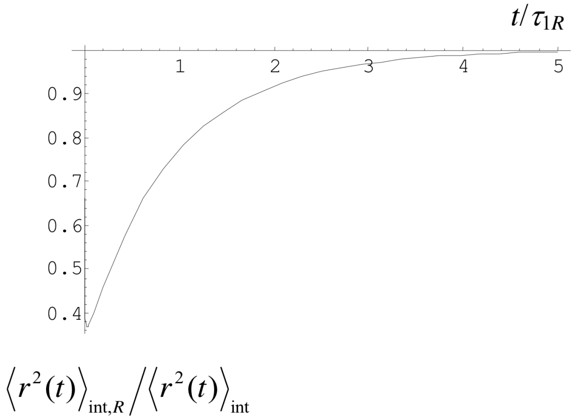

Fig. 4.7. Relation of the Rouse MSD (at $h = 0$) to the Rouse-Zimm MSD at $h = 10$ and $\tilde{c} = 0.1$ as a function of t/τ_{1R}. With the growing t the polymer tends to behave as a Rouse one.

[Tothova 2007a], where the influence of other coils is considered. These results can be summarized as follows: every polymer at very short times at any concentration c behaves as the Rouse one since HI do not yet affect the dynamics. At longer times, the HI take effect and the polymer begins to move in the Zimm regime. Then, due to the screening of HI, the polymer behavior turns again to the Rouse-like one.

5 Summary

The aim of this review was to present a natural generalization of the popular Rouse and Zimm theories of the dynamics of flexible polymers in solution by taking into account the hydrodynamic memory (the viscous aftereffect), which is a consequence of fluid inertia. This generalization has led to several interesting peculiarities in the time correlation functions describing the polymer motion, which are accessible in experiments or by computer simulations. When the memory of the viscous solvent is taken into account, the time behavior of these functions essentially differs from that in the original theory. In particular, the mean square displacement of the polymer coil is at short times proportional to t^2, instead of $\sim t$. At long times it contains additional (to the Einstein term) contributions, the so called long-time tails. It is not surprising that these results are similar to the results that follow from the hydrodynamic generalization of the Langevin theory of the Brownian motion and have been during the last decade overwhelmingly confirmed experimentally. The theory of the Brownian motion constitutes a basis for any theory of the dynamics of polymers in solution. Due to this we began our review with the description of the Brownian motion. We mentioned some problems that are not correctly treated in the literature as it is, for example, with the standard Langevin equation, sometimes used to describe situations for which it is inappropriate. We have given attention to the more general "hydrodynamic Langevin equation" and related questions of anomalous diffusion, often described by the so called generalized Langevin equation. One of the main results to be mentioned is the method of solution of the corresponding Volterra-type integro-differential stochastic equations. The method allows efficient solution of a number of problems related to the Brownian motion, including the anomalous diffusion. Here it was applied to the problems of the dynamics of polymer solutions. In order to have a possibility to compare the theory with experiments, we have calculated the dynamic structure factor (DSF) of the polymer coil in various scattering regimes. We have determined the corresponding first cumulants for the Rouse and Zimm polymers. The relation between our theory and experiments is discussed in detail. The measured values of the diffusion coefficients and the first cumulants to the polymer DSF are smaller than it has been predicted by the previous theory. We have shown that our results are, at least qualitatively, in agreement with the experimental observations. The importance of our results for the description of the experiments can be however judged only after a detailed analysis of the experimental data. We discuss that such a comparison should come from the joint Rouse-Zimm model, instead of its limiting cases as it is usually done. The model was generalized also to take into account the influence of other coils in dilute theta solution on the dynamics of the test polymer. This was done within the phenomenology in which the solution is considered as a permeable medium, where the obstacles to the solvent flow are the polymer coils themselves. At sufficiently large concentrations of the coils the flow is effectively frozen and the polymer behaves as the Rouse chain even if the draining parameter is large. This hydrodynamic screening is not only concentration-dependent but the type of the polymer dynamics changes in the time as well. The found peculiarities could be investigated using computer simulation methods and experimentally, $e.g.$, by the dynamic light or neutron scattering. While in the case of the internal modes the differences from the original theory could hardly be observed, the "ballistic" motion of the center of inertia of the polymer should be experimentally accessible.

Acknowledgement

This work was supported by the Slovak Ministry of Education Agency for the Structural Funds of the EU within the projects NFP 26220120021 and 26220120033, and by the Grant VEGA 1/0348/15.

References

Abramowitz, A., Stegun, I. A. Handbook of Mathematical Functions. National Bureau of Standards: Washington, DC, 1964

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

Akcasu, A. Z., Gurol, H. *J. Polym. Sci. Polym. Phys. Ed.* **14** (1976) 1

Alder, B. J., Wainwright, T. E. *Phys. Rev. Lett.* **18** (1967) 988

Allahverdyan, A. E., Nieuwenhuizen, Th. M. *Phys. Rev. B* **66** (2002) 115309

Bachelier, L. *Ann. Ecole Normale Supériore* **17** (1900) 21

Balabonov, S. M. Ivanova, M. A., Klenin, S. I., Lomakin, A. V., Molotkov, V. A. , Noskin, V. A. *Biophysics* (Moscow) **32** (1987) 933

Balakrishnan, V. *Pramana* **12** (1979) 301

Basset, A. B. *Phil. Trans. R. Soc. London A* **179** (1888) 43

Berne, B. J., Pecora, R. *Dynamic Light Scattering with Applications to Chemistry, Biology, and Physics*. Wiley: New York, 1979

Blum, J., Bruns, S., Rademacher, D., Voss, A., Willenberg, B., Krause, M. *Phys. Rev. Lett.* **97** (2006) 230601

Bonet Avalos J., Rubí J. M., Bedeaux D. *Macromolecules* 24 (1991) 5997

Boon, J. P., Bouiller, A. *Phys. Lett. A* **55** (1976) 391

Boussinesq, J. *C.R. Acad. Sci. Paris* **100** (1885) 935

Brinkman, H. C. *Appl. Sci. Res. A* **1** (1947a) 27

Brinkman, H. C. *Physica* **13** (1947b) 447

Brown, R. *Edinb. New Philos. J.* **5** (1828) 358

Carberry, D. M., Reid, J. C., Wang, G. M., Sevick, E. M., Searles, D. J., Evans, D. J. *Phys. Rev. Lett.* **92** (2004) 140601

Chakraborty, D. *Eur. Phys. J. B* **83** (2011) 375

Chandrasekhar, S. *Rev. Mod. Phys.* **15** (1943) 1

Chou, K. C. *Biophys. Chem.* **25** (1986) 105

Coffey, W. T., Kalmykov, Yu. P., Waldron, J. T. *The Langevin Equation. With Applications to Stochastic Problems in Physics, Chemistry and Electrical Engineering*. World Scientific: New Jersey, 2005

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

de Gennes, P.-G. *Physics* **3** (1967) 37

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

Doi, M. *Introduction to Polymer Physics*. Clarendon: Oxford, 2003

Dubois-Violette, E., de Gennes, P.-G. *Physics* **3** (1967) 181

Einstein, A. *Ann. Phys.* **17** (1905) 549

Einstein, A. *Ann. Phys.* **19** (1906) 289

Einstein, A. *Ann. Phys.* **34** (1911) 591

Fatkullin, N. F., Kimmich, R., Weber, H. W. *Phys. Rev. E* **47** (1993) 4600

Fatkullin, N. F., Shakirov, T. M., Balakirev, N. A. *Polymer Sci. Ser. A* **52** (2010) 72

Felderhof, B. U. *Physica A* **175** (1991) 114

Ferry, J. D. *Viscoelastic Properties of Polymers*. Wiley: New York, 1964

Fisher, I. Z. *Zhur. Eksp. Teor. Phys.* **61** (1971) 1647

Franosch, Th., Grimm, M., Belushkin, M., Mor, F. M., Foffi, G., Forro, L., Jeney, S. *Nature* **478** (2011) 85

Freed, K. F., Edwards, S. F. *J. Chem. Phys.* **61** (1974) 3626

Freed, K. F., Edwards, S. F. *J. Chem. Phys.* **62** (1975) 4032

Giterman, M. Sh., Gertsenshtein, M. E. *Zhur. Eksp. Teor. Fiz.* **50** (1966) 1084

Goychuk, I. *Phys. Rev. E* **80** (2009) 046125

Goychuk, I. *Fluct. Noise Lett.* **11** (2012) 1240009

Grimm, M., Jeney, S., Franosch, Th. *Soft Matter* **7** (2011) 2076

Grosberg, A. Yu., Khokhlov, A. R. *Statistical Physics of Macromolecules*. Nauka: Moscow, 1989

Grosberg, A. Yu., Khokhlov, A. R. *Giant Molecules*. Academic Press: San Diego, e.a., 1997

Harnau, L., Winkler, R., Reineker, P. *J. Chem. Phys.* **104** (1996) 6355

Hinch, E. J. *J. Fluid Mech.* **72** (1975) 499

Hohenadl, M., Storz, T., Kirpal, H., Roy K., Merkel, R. *Biophys. J.* **77** (1999) 2199

Ingen-Housz, J. *Vermischte Schriften Physisch-Medizinschen Inhalts*. C. P. Wappler: Vienna, 1784

Jannasch, A., Mahamdeh, M., Schäffer, E. *Phys. Rev. Lett.* **107** (2011) 228301

Jeney, S., Lukic, B., Tischer, C., Kulik, A. J., Forro, L., Florin, E.-L. *Phys. Rev. Lett.* **95** (2005) 160601

Jones, R. B. *Physica A* **101** (1980) 389

Kargin, V. A., Slonimskii, G. L. *Dokl. Akad. Nauk SSSR* **62** (1948) 239

Karmeshu, *J. Phys. Soc. Jpn.* **34** (1973) 1467

Kimmich, R. Fatkullin, N. *Adv. Pol. Sci.* **170** (2004) 1

Kirkwood, J. G., Riseman, J. *J. Chem. Phys.* **16** (1948) 565

Klages, R., Radons, G., Sokolov, I. M. (Eds.) *Anomalous Transport: Foundations and Applications*. Wiley-VCH: Berlin, 2008

Kubo, R. Rep. *Prog. Phys.* **29** (1966) 255

Landau, L. D., Lifshitz, E. M. *Statistical Physics*. Nauka: Moscow, 1976

Landau, L. D., Lifshitz, E. M. Hydrodynamics. Nauka: Moscow, 1986

Langevin P. *C. R. Acad. Sci. (Paris)* **146** (1908) 530

Lapas, L. C., Morgado, R., Vainstein, M. H., Rubí, J. M., Oliveira, F. A. *Phys. Rev. Lett.* **101** (2008) 230602

Larson, R. G. *J. Rheol.* **49** (2005) 1

Lauritzen, S. L. *Thiele: Pioneer in Statistics*. Oxford University Press: New York, 2002

Li, T., Kheifets, S., Medellin, D., Raizen, M. G. *Science* **328** (2010) 1673

Lisy, V., Tothova, J. *arXiv: cond-mat*/0410222 (2004a)

Lisy, V., Tothova, J. ,Zatovsky, A.V. *J. Chem.Phys.* **21** (2004b) 10699

Lisy, V., Tothova, J., Zatovsky, A. V. *Cond. Mat. Phys.* **9** (2006a) 95

Lisy, V., Tothova, J. *Acta Phys. Slov.* **56** (2006b) 185

Lisy, V., Tothova, J., Zatovsky, A. V. *J. Stat. Mech.: Theory and Exp.* **5(1)** (2008) 1

Lisy, V., Tothova, J. *arXiv*:1006.1060 [cond.mat-stat.mech] (2010)

Lisy, V., Tothova, J., Glod, L. *Int. J. Thermophys.* **34** (2013a) 629

Lisy, V., Tothova, J. *Transport Theory and Stat. Phys.* **42** (2013b) 365

Lisy, V., Tothova, J. *Acta Phys. Pol. A* **127** (2014) 413

Lisy, V., Vlasenko, D. S., Zatovsky, A. V. (unpublished work)

Liu, B., Dünweg, B. *J. Chem. Phys.* **118** (2003) 8061
Lowe C. P., Bakker A. F., Dreischor M. W. *Europhys. Lett.* **67** (2004) 397
Löwen, H. *J. Phys: Condens. Matter* **21** (2009) 474203
Lucretius, *On the Nature of the Universe*. Transl. Latham R. E. Penguin Books: London, 1994
Maxwell, J. C. *Phil. Trans. R. Soc. Lond.* **157** (1867) 49
Mazo, R M. *Brownian Motion. Fluctuations, Dynamics, and Applications*. Oxford University Press: New York, 2009
Mazonka, O., Jarzynski, C. *arXiv:cond-mat/*991212 (1999)
Monkenbusch, M. In *Neutron Spin Echo Spectroscopy*. F. Mezei, Ed., p. 246-267. Springer: Berlin, 2003
Muthukumar, M. *J. Phys. A: Math. Gen.* **14** (1981) 2129
Muthukumar, M. *J. Chem. Phys.* **79** (1983) 4048
Ornstein, L. *Zeitschrift f. Phys.* **41** (1927) 848
Paul, G. L., Pusey, P. N. *J. Phys. A: Math. Gen.* **14** (1981) 3301
Prudnikov, A. P., Brychkov, Yu. A., Marichev, O. I. *Integrals and Series*. Nauka: Moscow, 1981
Raikher Yu. L., Rusakov, V. V. *J. Exp. Theor. Phys.* **111** (2010) 883
Rahman, A. *Phys. Rev. A* **136** (1964) 405
Reut, L. S., Fisher, I. Z. *Ukr. Phys. J.* **12** (1967) 1695
Richter, D., Binder, K., Ewen, B., Stühn, B. *J. Phys. Chem.* **88** (1984) 6618
Risken, H. *The Fokker-Planck Equation: Methods of Solutions and Applications*. Springer- Verlag: Berlin, 1989
Rouse, P. E. *J. Chem. Phys.* **21** (1953) 1272
Saitoh, E., Miyajima, H., Yamaoka, T., Tatara, G. *Nature* **432** (2004) 203
Samanta, N., Chakrabarti, R. *Chem. Phys. Lett.* **582** (2013) 71
Sawatari, N., Yoshizaki, T., Yamakawa, H. *Macromolecules* **31** (1998) 4218
Schram, P. P. J. M., Yakimenko, I. P. *Physica A* **260** (1998) 73
Schweitzer, K. S. *J. Chem. Phys.* **91** (1989) 5802
Shusterman, R., Alon, S., Gavrinyov, T., Krichevsky, O. *Phys. Rev. Lett.* **92** (2004) 048303
Smoluchowski, M. *Ann. Phys.* **21** (1906) 772
Stockmayer, W. H., Hammouda, B. *Pure Appl. Chem.* **56** (1984) 1372
Sutherland, W. *Phil. Mag.* **9** (1905) 781
Tothova, J., Lisy, V., Zatovsky, A.V. *J. Chem.Phys.* **119** (2003) 13135
Tothova, J., Brutovsky, B., Lisy, V. *Laser Phys.* **14** (2004) 1511
Tothova, J., Brutovsky, B., Lisy, V. *Czech. J. Phys.* **55** (2005) 221
Tothova, J., Brutovsky, B., Lisy, V. *Acta Phys. Slov.* **56** (2006) 189
Tothova, J., Brutovsky, B., Lisy, V. *Laser Phys.* **17** (2007a) 443
Tothova, J., Brutovsky, B., Lisy, V. *Eur. Phys. J. E* **24** (2007b) 61
Tothova, J., Lisy, V. *Acta Phys. Pol. A* **118** (2010) 1051
Tothova, J., Vasziova, G., Glod, L., Lisy, V. *Eur. J. Phys.* **32** (2011a) 645
Tothova, J., Vasziova, G., Glod, L., Lisy, V. *Eur. J. Phys.* **32** (2011b) L47
Tothova, J., Lisy, V. *diffusion-fundamentals.org* **15** (2011c) 1
Tothova, J., Lisy, V. *diffusion-fundamentals.org* **17** (2012) 1
Tothova, J., Lisy, V. *diffusion-fundamentals.org* **19** (2013) 1
Tothova, J., Lisy, V. *e-Polymers* **13** (2013) 243
Tothova, J., Timko, M., Kopcansky, P., Lisy, V. *Int. J. Thermophys.* **35** (2014) 2150

Tothova, J., Paulovicova, K., Lisy V. *Int. J. Polymer Sci.* **vol. 2015** (2015) 690136

Tsunashiva Y., Nemoto N. *J. Polym. Sci., Polym. Lett. Ed.* **21** (1983) 531

Uhlenbeck, G. J., Ornstein, L. S. *Phys. Rev.* **26** (1930) 823

Van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*. North Holland: Amsterdam, 1981

Vasziova, G., Tothova, J., Glod, L., Lisy, V. *J. Electr. Eng.* **61** (2010) 252

Vladimirsky, V. V. *Zhur. Eksp. Teor. Fiz.* **12** (1942) 199

Vladimirsky, V. V., Terletzky, Ya. P. *Zhur. Eksp. Teor. Fiz.* **15** (1945) 258

Wang, G. M., Sevick, E. M., Mittag, E., Searles, D. J., Evans, D. J. *Phys. Rev. Lett.* **89** (2002) 050601

Weitz, D. A., Pine, D. J., Pusey, P. N., Tough, R. J. A. *Phys. Rev. Lett.* **16** (1989) 1747

Winkler, R. G., Keller, S., Rädler, J. O. *Phys. Rev. E* **73** (2006) 041919

Yamakawa, H. *Modern Theory of Polymer Solutions*. Harper&Row: New York, 2001

Yang, H., Yan, Y., Zhu, P., Li, H., Zhu, Q., Fan, Ch. *Eur. Polymer J.* **41** (2005) 329

Yoshizaki, T., Osa, M., Yamakawa, H. *J. Chem. Phys.* **106** (1997) 2828

Zatovsky, A.V. *Izvestia VUZ, Fizika* **10** (1969) 13

Zatovsky, A.V., Lisy, V. *J. Mol. Liq.* **105** (2003) 289

Zhao, H., Beckham, W., Ricks, H. L., Bunz, U. H. F. *Polymer* **46** (2005) 4839

Zimm, B. H. *J. Chem. Phys.* **24** (1956) 269

Jana Tóthová graduated in biophysics at the Faculty of Science, P. J. Šafárik University in Košice, Slovakia, where she was then employed as a researcher. In 2005 she defended her PhD thesis and in 2013 became Associate Professor at the Faculty of Electrical Engineering and Informatics, Technical University of Košice. Here she works from 2009 at the Department of Physics. Her main interests are in the field of spectral and thermodynamic properties of bio-macromolecules, their interaction with different agents, and rheology of nanofluids and polymer solutions.

Vladimír Lisý graduated at the Department of Theoretical Physics, Odessa State University, Ukraine. He worked at the Faculty of Science, P. J. Šafárik University in Košice, Slovakia, and from 2006 as a professor of physics at the Technical University in Košice. In the period 1982-1990 he was a researcher at the Bogolyubov Laboratory of Theoretical Physics, JINR, Dubna, Russia. There he in 1988 defended his PhD in theoretical and mathematical physics. Currently he is a deputy director of the Laboratory of Radiation Biology at the JINR. His interests are in the field of modeling and spectroscopy of macromolecules and soft condensed matter theory, particularly in the complex fluids phenomenology.