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Dynamics of Rouse polymers in Maxwell fluids

Jana Tothova, Vladimir Lisy

Department of Physics, Technical University of Kosice, Slovakia

Corresponding author: Vladimir Lisy, Dept. of Physics, Faculty of Electrical Engineering
and Informatics, Technical University of Kosice, Park Komenskeho 2, 042 00 Kosice,
Slovakia, E-Mail: vladimir.lisy@tuke.sk

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Abstract

A generalization of the Rouse model of the dynamics of polymers in solution is proposed. The motion of long polymer chains is considered to be due to exponentially correlated random forces driving the polymer segments, which is a more realistic model than the approximation of white thermal noise in the standard theory. Due to the fluctuation-dissipation theorem such a model is consistent with the assumption that the solvent has weakly viscoelastic properties, which corresponds to the theory, originally proposed by Maxwell and later substantiated coming from first principles. A consequence of such approach is the appearance of “memory” in the polymer dynamics. To obtain a correct description at short times, we also include inertial effects into the consideration. Discrete and continuum models of the universal dynamics of polymer chains are built. Exact solutions are obtained for the center of mass motion of the polymer coil in the discrete variant of the theory. The time correlation functions describing the dynamics of internal modes are calculated in the continuum approximation. The results significantly differ from those in the standard Rouse theory and its later generalizations valid at long times.

Keywords

Long polymer chains, weakly viscoelastic solvent, dynamics, generalized Rouse model

1. Introduction

It is well known for a long time that the standard models of the dynamics of polymers in dilute solutions often do not correspond to experiments even for flexible polymers, for which these models have been designed [1]. Moreover, the models do not adequately describe the short-time behavior of polymer chains since they are based on Einstein´s theory of the Brownian motion, which fully neglects the inertial effects in the dynamics. The theory of the Brownian motion constitutes the basis of all models of the polymer dynamics. At present, it has been definitely proven in experiments that neither the Einstein theory, nor its Langevin generalization [2] give a good description of the experiments on Brownian particles at times smaller or comparable to the particle´s relaxation time, when the effects of inertia and memory in the dynamics play a role [3 – 6]. The original Langevin description of the chaotic motion of particles as being due to the white thermal noise [2] should be generalized to account for a nonzero correlation time of the thermal force. This force thus must be "colored" [7], which due to the fluctuation-dissipation theorem [8] means that the dynamics of driven particles displays a kind of memory [8 – 10]. The Langevin equation for the Brownian dynamics then takes a form of a stochastic integro-differential equation with a memory integral, whose kernel is associated with the time correlation function of the thermal force. In the description of the dynamics of polymer chains, such equation should be used for every of $N >> 1$ beads, on which the chain is mapped within the Rouse approach [1, 11, 12]. The problem arises how to choose a realistic thermal noise entering the equations. This force in fluids has been for the first time probed in recent experiments [6] (for their interpretation in the frame of hydrodynamic approach to the Brownian motion see [7]). 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 the present contribution 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 [13 – 17]. 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 [18, 19]. Here we use 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. Our main aim is 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.

2. Formulation of the generalized Rouse model

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 [1, 12]. 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 [20]. (Note that in fact the Rouse and Zimm models naturally join in one model [21 – 24]. This has important consequences for the interpretation of experiments on polymer solutions and the determination of polymer characteristics; however, since here we give the main attention to building a model that could reveal the role of the "colored" thermal noise, we try to keep the model simple and avoid the mentioned complications (for possible generalizations of the presented model we refer to the recent study by Fatkullin et al. [25]).

The equations of motion (projected on an axis, say x) for the nth bead in the Rouse model appear as

$$M\frac{\mathrm{d}^2 x_n}{\mathrm{d}t^2} = f_n^{fr} + f_n^{ch} + f_n, \tag{1}$$

where x_n is the projection of the radius vector $\vec{x}_n$ 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

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

with U being the total energy of interaction between the particles, given by their equilibrium Gaussian distribution in the chain [1] (for a more general approach without the use of this assumption see Ref. [25])

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

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

$$x_{n\pm 1}\left(t\right) \to x\left(t,n\right) \pm \frac{\partial x\left(t,n\right)}{\partial n} + \frac{1}{2}\frac{\partial^2 x\left(t,n\right)}{\partial n^2} + \ldots \tag{5}$$

As usually [1, 12], 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

$$\frac{\partial x\left(t,n\right)}{\partial n} = 0, \quad n = 0, N \tag{6}$$

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

$$M\frac{\partial \upsilon\left(t,n\right)}{\partial t} + M\int_0^t \Gamma\left(t-\tau,n\right)\upsilon\left(\tau,n\right)\mathrm{d}\tau = \frac{3k_B T}{a^2}\frac{\partial^2 x\left(t,n\right)}{\partial n^2} + f\left(t,n\right). \tag{7}$$

Here $\Gamma(t) = \omega_M\omega_m\exp(-\omega_m t)$, $\omega_m = \gamma/m$, $\omega_M = \gamma/M$, and $\omega_m\omega_M = (m/M)\tau_m^{-2}$, if we denote the relaxation time as $\tau_m = m/\gamma$. For the random force we have

$$\left\langle f\left(t,n\right) f\left(t',m\right)\right\rangle = k_B T\delta_{nm}\Gamma\left(t-t'\right). \tag{8}$$

In this notation m can be understood as the mass of a Brownian particle in the standard Langevin equation $m\dot{u}(t) + \gamma u(t) = \varphi(t)$ with the Stokes friction and delta correlated (white) noise force $\varphi(t)$, with the correlation function $\left\langle \varphi(t)\varphi(t')\right\rangle = 2k_B T\gamma\delta(t-t')$. For spherical beads $\gamma = 6\pi\eta R$, with η being the dynamic viscosity of the solvent. One thus could interpret the motion of particles *M*, described by Eq. (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 $m\mathrm{d}\upsilon/\mathrm{d}t$. Its relation (8) to the memory kernel is due to Kubo´s fluctuation-dissipation theorem [8]. Note that equations similar to (7) have been already used in Ref. [26] but without the inertial term and the intrachain force written with the opposite sign (see also Ref. [27]).

3. Motion of the center of mass of the polymer coil

For the clarity of further consideration, we explicitly write down the equations of motion (1) in their discrete variant:

$$M\dot{\upsilon}_n(t)+M\int_0^t\Gamma(t-\tau)\upsilon_n(\tau)\mathrm{d}\tau=\frac{3k_BT}{a^2}\left(x_{n+1}+x_{n-1}-2x_n\right)+f_n,\quad n\neq 1,N, \tag{9}$$

$$M\dot{\upsilon}_1(t)+M\int_0^t\Gamma(t-\tau)\upsilon_1(\tau)\mathrm{d}\tau=\frac{3k_BT}{a^2}\left(x_2-x_1\right)+f_1,$$

$$M\dot{\upsilon}_N(t)+M\int_0^t\Gamma(t-\tau)\upsilon_N(\tau)\mathrm{d}\tau=\frac{3k_BT}{a^2}\left(x_{N-1}-x_N\right)+f_N.$$

For the motion of the whole coil, this set of equations can be solved exactly. If we sum up all equations, the internal forces disappear and we obtain the following equation for the motion of the polymer center of mass, $x_C=\sum x_n/N$, which is the same as the sum of *N* equations of motion for independent particles,

$$MN\dot{\upsilon}_C(t)+MN\int_0^t\Gamma(t-\tau)\upsilon_C(\tau)\mathrm{d}\tau=\sum_{n=1}^{N}f_n, \tag{10}$$

The stochastic integro-differential equation (10) is within the Gibbs statistics equivalent to the deterministic equation for the mean square displacement of the coil, $X_C(t)=\langle[x_C(t)-x_C(0)]^2\rangle$. If we denote $V_C\equiv\mathrm{d}X_C/\mathrm{d}t$, the new equation will be [28, 29] (for more details see Refs. [9, 10]; a proof of the transformation from Eq. (10) to (11) is given in [30])

$$\dot{V}_C(t)+\int_0^t\Gamma(t-\tau)V_C(\tau)\mathrm{d}\tau=\frac{2k_BT}{NM}. \tag{11}$$

Equation (11) should be solved with the evident initial conditions $X_C(0)=0$ and $V_C(0)=0$. The solution can be easily obtained using the Laplace transformation, $\tilde{V}_C(s)=\mathcal{L}\{V(t)\}$,

$$\tilde{V}_C(s)=\frac{2k_BT}{NM}\frac{1}{s_2-s_1}\left(1+\frac{\omega_m}{s}\right)\left(\frac{1}{s-s_2}-\frac{1}{s-s_1}\right),\qquad s_{1,2}=-\frac{\omega_m}{2}\left(1\mp\sqrt{1-\frac{4\omega_M}{\omega_m}}\right). \tag{12}$$

The inversion of Eq. (12) gives

$$V_C(t)=\frac{2k_BT}{NM}\frac{1}{s_2-s_1}\left[\omega_m\left(\frac{1}{s_1}-\frac{1}{s_2}\right)+\exp(s_2t)\left(1+\frac{\omega_m}{s_2}\right)-\exp(s_1t)\left(1+\frac{\omega_m}{s_1}\right)\right]. \tag{13}$$

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

$$X_C(t)=\frac{2k_BT}{NM}\frac{1}{s_2-s_1}\left[\frac{\omega_m t}{s_1}-\left(1+\frac{\omega_m}{s_1}\right)\frac{\exp(s_1t)-1}{s_1}-(s_1\to s_2)\right]. \tag{14}$$

Let us find the asymptotic behavior of this solution. At $t\to 0$, the ballistic motion follows from (14), independently on the character of the random force,

$$X_C(t)\approx\frac{k_BT}{NM}t^2. \tag{15}$$

At long times

$$X_C(t\to\infty)=\frac{2k_BT}{NM}\left[\frac{t}{\omega_M}+\frac{1}{\omega_M}\left(\frac{1}{\omega_m}-\frac{1}{\omega_M}\right)+\dots\right], \tag{16}$$

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. (12) are $s_1\approx-\omega_M$, $s_2\approx-\omega_m$, so that

$$X_C(t)\approx\frac{2k_BT}{N\gamma}\left[t+\frac{\exp(-\omega_M t)-1}{\omega_M}\right], \tag{17}$$

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.

4. Dynamics of internal modes

It is convenient to perform further analysis of Eq. (1) in terms of the normal modes $y_p(t)$, defined by Fourier transforms

$$x(t,n)=y_0(t)+2\sum_{p=1}^{\infty}y_p(t)\cos\frac{\pi np}{N},\quad f(t,n)=f_0(t)+2\sum_{p=1}^{\infty}f_p(t)\cos\frac{\pi np}{N}, \tag{18}$$

chosen so that the boundary conditions (6) are already satisfied. The index $p = 0$ corresponds to the motion of the whole coil, and $p = 1, 2, 3,\dots$ are for the internal modes [1, 12]. Substituting (18) in Eq. (7), we obtain after multiplication by $\cos(\pi qn/N)$ and integration through n from 0 to N the following equation for y_q in the continuum approximation:

$$M\ddot{y}_q(t)+\int_0^t\Gamma(t-\tau)\dot{y}_q(\tau)\mathrm{d}\tau+3k_BT\left(\frac{\pi q}{Na}\right)^2y_q(t)=f_q(t). \tag{19}$$

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 mean square displacement for internal modes,

$$\dot{U}_q(t)+\int_0^t\Gamma(t-\tau)U_q(\tau)\mathrm{d}\tau+\omega_q^2\int_0^t U_q(\tau)\mathrm{d}\tau=\frac{k_BT}{NM}, \tag{20}$$

where

$$\omega_q^2 = \frac{3k_BT}{M}\left(\frac{\pi q}{Na}\right)^2 . \tag{21}$$

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

$$\tilde{U}_q(s) = \frac{k_BT}{NM}\frac{s+\omega_m}{s^3+\omega_m s^2+\left(\omega_m\omega_M+\omega_q^2\right)s+\omega_m\omega_q^2}, \tag{22}$$

we obtain in the time domain

$$U_q(t) = \frac{k_BT}{NM}\sum_{i=1}^{3} A_i \exp(s_i t), \tag{23}$$

$$Y_q(t) = \int_0^t U_q(t')\mathrm{d}t' = \frac{k_BT}{NM}\sum_{i=1}^{3}\frac{A_i}{s_i}\left[\exp(s_i t)-1\right]. \tag{24}$$

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 are obtained by the cyclic change 1→2→3→1) satisfy the relations

$$\sum_i \frac{A_i}{s_i} = \frac{\omega_m}{s_1 s_2 s_3} = -\frac{1}{\omega_q^2}, \qquad \sum_i A_i = 0, \qquad \sum_i A_i s_i = 1,$$

$$\sum_i A_i s_i^2 = 0, \qquad \sum_i A_i s_i^3 = -\left(\omega_m\omega_M+\omega_q^2\right), \ldots \tag{25}$$

Using them, the asymptotic behavior of the solution (24) is easily found:

$$Y_q(t) = \frac{k_BT}{2NM}t^2\left(1-\frac{\omega_m\omega_M+\omega_q^2}{12}t^2+\ldots\right), \quad t\to 0, \tag{26}$$

$$Y_q(t) \approx \frac{k_BT}{NM\omega_q^2}\left[1-\exp\left(-\frac{\omega_q^2 t}{\omega_M}\right)\right], \quad t\to\infty. \tag{27}$$

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 old solution [11] should be recovered,

$$\psi_p(t) = \left\langle y_p(0)\,y_p(t)\right\rangle = \frac{1}{2}D_C\tau_p\exp\left(-t/\tau_p\right), \tag{28}$$

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

$$\tau_p = \frac{N^2 a^2 \gamma}{3\pi^2 k_B T p^2}, \quad p \geq 1, \tag{29}$$

are the well-known Rouse relaxation times for the internal modes [11, 1, 12]. The result (28) can be obtained from our solution (24) at $\tau_m \to 0$

$$Y_q(t) = \frac{k_B T}{NM} \frac{1}{s_2 - s_1} \left(\frac{1}{s_1} - \frac{1}{s_2} + \frac{\exp(s_2 t)}{s_2} - \frac{\exp(s_1 t)}{s_1} \right), \tag{30}$$

with the roots s_i

$$2s_{1,2} = -\omega_M \left[1 \mp \left(1 - 4\omega_q^2 \omega_M^{-2} \right)^{1/2} \right], \tag{31}$$

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

$$Y_q(t) \approx \frac{k_B T}{NM\omega_q^2} \left\{ 1 - \exp\left[-\frac{3k_B T}{\gamma} \left(\frac{\pi q}{Na} \right)^2 t \right] \right\} \to \frac{k_B T}{NM\omega_q^2} = \frac{N}{3} \left(\frac{a}{\pi q} \right)^2, \quad t \to \infty, \tag{32}$$

which coincides with Eq. (28).

5. Spin-lattice relaxation of Rouse polymers

The question arises how the obtained features 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. [31] 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 were 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 a correspondence has been established in a series of works by Kimmich, Fatkullin, and collaborators, beginning from Ref. [26] (see also [27, 31] 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 [27]. 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 [26]. If the polymer is modeled as a chain of segments located at positions $\vec{x}_n$, T_1 is in the continuum approximation connected to the fluctuations of $\vec{x}_n(t)$ according to the formula

$$\frac{1}{T_1} \propto \int_{-\infty}^{\infty} \left\langle \vec{b}(t,n)\vec{b}(0,n) \right\rangle^2 \exp(-\mathrm{i}\omega t)\mathrm{d}t\,, \tag{33}$$

where $\vec{b}(t,n) = \partial\vec{x}(t,n)/\partial n$. 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. (28)) as

$$\frac{1}{T_1} \propto \frac{36\pi^4}{N^4} \int_{-\infty}^{\infty} \mathrm{d}t \left(\sum_{p>0} p^2 \psi_p(t) \right)^2 \exp(-\mathrm{i}\omega t)\,. \tag{34}$$

The general formula for the spin-lattice relaxation rate has the form [27]

$$\frac{1}{T_1} \propto \frac{18}{N^5} \left(\frac{\pi^2 k_B T}{M} \right)^2 \int_0^{\infty} \mathrm{d}t \left(\sum_{p>0} \sum_{i=1}^{3} C_i(p) \exp(s_i t) \right)^2 \cos(\omega t)\,, \tag{35}$$

where C_i are constants depending on the characteristic relaxation times of the problem and the Kuhn length a. The evaluation of (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,

$$\frac{1}{T_1} \propto \frac{2a^4}{N^2} \int_0^{\infty} \mathrm{d}t \left[\sum_{p>0} \exp\left(-\frac{t}{\tau_p} \right) \right]^2 \cos\omega t\,, \tag{36}$$

with the Rouse relaxation times τ_p (29). This equation can be expressed exactly through the elliptic integrals. At low frequencies ($\omega\tau_1 << 1$) a very simple result follows from Eq. (36): the relaxation time T_1 does not depend on N at all, and is proportional to $k_B T/a^6\gamma$.

6. Conclusions

In this study we have developed the phenomenological Rouse model of the dynamics of flexible polymers in solutions. 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. We considered a simple but microscopically substantiated generalization [27, 33] when this noise exponentially correlates in time, which corresponds to the friction in Maxwell´s weakly viscoelastic fluids. The polymer dynamics in such solvents shows memory and has been described by a generalized Langevin equation of Kubo´s type, 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 mass 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 [6, 33]. 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 [25], 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 our further study.

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