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Variance reduced Brownian simulation of a bead-spring chain under steady shear flow considering hydrodynamic interaction effects

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To obtain numerical estimates for the properties of a model for polymers in dilute theta solutions in its long-chain limit we follow a stochastic approach to polymer kinetic theory. The model takes into account configuration-dependent hydrodynamic interaction (HI) and simplifies to the Zimm bead-spring chain model in the case of preaveraged HI, for which parameter-free ''universal ratios'' such as the ratio between radius of gyration and hydrodynamic radius are known. The Chebyshev polynomial method and a variance reduction simulation technique are used to implement an efficient Brownian dynamics simulation. We resolve the full dependence of several characteristic ratios versus both chain length and hydrodynamic interaction parameter, we extrapolate their values to determine universal behaviors, and compare with analytical and experimental results. *© 2000 American Institute of Physics.* [S0021-9606(00)51035-6]

I. INTRODUCTION

As pointed out by Kirkwood and Riseman,[1] the perturbation of the solvent flow field induced by suspended spherical particles (''beads'') leads to an additional interaction between beads, the so called hydrodynamic interaction. Incorporation of this effect into the classical Rouse model[2] for dilute polymer solutions makes the resulting model equations—containing a hydrodynamic interaction matrix—nonlinear. Predictions for some material properties were found to become much more realistic when hydrodynamic interaction is accounted for.[3,4]

In the usual discussion of HI, one linearizes the Navier–Stokes equation (NSE) and assumes that the propagation of solvent flow perturbations is infinitely fast.[5] If the beads are point particles one obtains for the perturbation of the flow at position $\mathbf{r}$: $\triangle\mathbf{v}(\mathbf{r})=\boldsymbol{\Omega}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{F}(\mathbf{r}')$, where $\mathbf{F}(\mathbf{r}')$ is the force exerted by a bead at point $\mathbf{r}'$ on the solvent, and $\boldsymbol{\Omega}(\mathbf{r})$ is the Green's function of the time-dependent linearized NSE, known as Oseen–Burgers tensor [one has to require $\boldsymbol{\Omega}(\mathbf{0})=\mathbf{0}$ in order to avoid hydrodynamic self-interaction].

The diffusion equation, sometimes referred to as Fokker–Planck equation, for the configurational distribution function $p(t,\mathbf{r}_1,\mathbf{r}_2,..,\mathbf{r}_N)$ for a chain with N beads then reads[6,4]

$$\frac{\partial p}{\partial t}=-\sum_{i=1}^{N}\frac{\partial}{\partial\mathbf{r}_i}\cdot\left(\mathbf{v}(\mathbf{r}_i)+\frac{1}{\zeta}\sum_{j}\mathbf{H}_{ij}\cdot\mathbf{F}_j\right)p+\frac{k_BT}{\zeta}\sum_{i,j}\frac{\partial}{\partial\mathbf{r}_i}\cdot\mathbf{H}_{ij}\cdot\frac{\partial}{\partial\mathbf{r}_j}p \qquad (1)$$

with the hydrodynamic interaction matrix $\mathbf{H}_{ij}\equiv\mathbf{H}(\mathbf{r}_{ij})=\delta_{ij}\mathbf{1}+\zeta\boldsymbol{\Omega}(\mathbf{r}_{ij})$. In the Itô approach, the stochastic differential (Langevin) equations of motions for bead positions $\mathbf{r}_i(t)$ $(i=1,2,..,N)$ equivalent to the Fokker–Planck equation (1) are

$$d\mathbf{r}_i=\left(\mathbf{v}(\mathbf{r}_i)+\frac{1}{\zeta}\sum_{j}^{N}\mathbf{H}_{ij}\cdot\mathbf{F}_j\right)dt+\sqrt{\frac{2k_BT}{\zeta}}d\mathbf{S}_i, \qquad (2)$$

where $d\mathbf{S}_i\equiv\Sigma_j\mathbf{B}_{ij}\cdot d\mathbf{W}_j(t)$; $\mathbf{W}$ denotes a Wiener process (Gaussian white noise vector); $\mathbf{B}$ is related to the HI matrix through the fluctuation-dissipation theorem $\mathbf{H}_{ij}=\Sigma_k^N\mathbf{B}_{ik}\cdot\mathbf{B}_{jk}^T$ and $\mathbf{F}_j$ denotes the sum of (other than hydrodynamic, i.e., spring) forces on bead j. Equation (2) is the starting point for a Brownian dynamics computer simulation, the only tool available for treating chains with hydrodynamic interactions rigorously.

There are two possibilities for restoring a positive-semidefinite diffusion term when the assumption of point particles fails (one implicitly introduces a bead radius through Stokes monomer friction coefficient ζ): one can prevent the beads from overlapping, or one can modify the hydrodynamic Oseen–Burgers interaction tensor. In this work we use the regularization proposed by Rotne, Prager and Yamakawa,[7] i.e.,

$$\boldsymbol{\Omega}(\mathbf{r})=\frac{1}{8\pi r\eta_s}\mathbf{C}(\mathbf{r},a) \qquad (3)$$

with

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$$\mathbf{C}(\mathbf{r},a)=\left(1+\frac{2a^2}{3r^2}\right)\mathbf{1}+\left(1-\frac{2a^2}{r^2}\right)\hat{\mathbf{r}}\hat{\mathbf{r}}$$

for $a/r \leqslant 1/2$ (bead radius a) and

$$\mathbf{C}(\mathbf{r},a)=\frac{r}{2a}\left(\frac{8}{3}-\frac{3r}{4a}\right)\mathbf{1}+\frac{r^2}{8a^2}\hat{\mathbf{r}}\hat{\mathbf{r}}$$

for $a/r > 1/2$ with $\hat{\mathbf{r}} \equiv \mathbf{r}/|\mathbf{r}|$. As the ratio $a/r \rightarrow 0$, one recovers the Oseen–Burgers tensor. For the case of a homogeneous macroscopic flow, the velocity field is $\mathbf{v}(\mathbf{r})=\mathbf{k}\cdot\mathbf{r} = \gamma\mathbf{r}\cdot\mathbf{e}_y\mathbf{e}_x$ (usual Cartesian base vectors $\mathbf{e}_{x,y,z}$) with $\mathbf{k} = (\nabla\mathbf{v})^{\dagger}$. The Langevin equation (2) can not be solved in closed form. In order to obtain a tractable form, Zimm[8] replaced the random variables $\mathbf{\Omega}_{\mathbf{r}_{ij}}$ by their equilibrium (isotropic) averages, i.e., $\mathbf{H}_{ij} \rightarrow H_{ij}\mathbf{1}$ with the $N\times N$ matrix $H_{ij} = \delta_{ij}+h^*(1-\delta_{ij})\sqrt{2/|i-j|}$ and a hydrodynamic interaction parameter

$$h^* \equiv \frac{\zeta}{6\pi\eta_\mathrm{s}}\sqrt{\frac{H}{\pi k_\mathrm{B}T}}, \tag{4}$$

as introduced by Thurston and Peterlin.[9] In Eq. (4), H denotes the harmonic bead-spring coefficient. The parameter h^* can be expressed as $h^*=a_\mathrm{b}/(\pi k_\mathrm{B}T/H)^{1/2}$ which is roughly the bead radius a_b over the root-mean-square distance between two beads connected by a spring at equilibrium, hence $0<h^*<1/2$. For analytical and experimental estimates of h^* see Refs. 6,10,3. For the Zimm model $h^* = 1/4$ minimizes the effect of chain length and the very short- and long-chain limits can be elaborated analytically.

For several reasons, the long-chain limit is important. It is independent of the details of the mechanical model, and hence is a general consequence of the presence of HI and equilibrium averaged HI for the Zimm model,[11] respectively. For long chains it should be observed that h^* occurs only in the combination ζ/h^* in all material properties. Therefore, the parameter h^* has no observable effect on the material properties of long chains. Power law dependencies of various material properties on molecular weight $M \propto N$ with universal exponents are expected (see Sec. 8.2.2.1 of Ref. 12) and, from the prefactors, one can form universal ratios.[4] The universal exponents and prefactors are ideally suited for a parameter-free test of the model by means of experimental data for high molecular weight polymer solutions. In this work, we obtain estimates by extrapolation from extensive and efficient simulation. A coarse-grained molecular model represents the polymer molecules: the bead-spring chain model, i.e., N identical beads joined by $N-1$ springs with spring coefficients H. The solvent is modeled as an incompressible, isothermal Newtonian homogeneous fluid characterized by its viscosity η_s. The solution is considered to be infinitely diluted, and the problem is limited to the behavior of one single molecule. Authors of previous works either did not use the efficient decomposition method proposed by Fixman[13] or performed simulations without using a variance reduction method and therefore did not simulate sufficiently long chains. There is an increasing interest in using iterative schemes to decompose the HI matrix, e.g., Refs. 14–25. In combination with the variance reduction scheme, chain lengths comparable to real conditions (e.g., 300 persistence lengths) are now coming within reach of simulations.[26]

II. ALGORITHM

The decomposition of the diffusion matrix $\mathbf{H}$ to obtain a representation for $\mathbf{B}$ (e.g., Cholesky decomposition) for long chains is expensive and scales with N^3. A highly efficient method[13] is based on an approximation of the square root function in Chebyshev (tensor) polynomials $\mathbf{T}_k$ of the first kind, following the notation in Ref. 27,

$$\mathbf{B}=\sqrt{\mathbf{H}} \approx \sum_{k=1}^{L} c_k\mathbf{T}_{k-1}(\mathbf{H})-\frac{\mathbf{1}}{2}c_1, \tag{5}$$

where the recursive formula

$$\mathbf{T}_{k+1}(\mathbf{H})=2\,\mathbf{H}\cdot\mathbf{T}_k(\mathbf{H})-\mathbf{T}_{k-1}(\mathbf{H}) \tag{6}$$

together with $\mathbf{T}_0(\mathbf{H})=\mathbf{1}$ and $\mathbf{T}_1(\mathbf{H})=\mathbf{H}$ defines these polynomials. For a fixed L, Eq. (5) is a polynomial in $\mathbf{H}$ which approximates $\mathbf{B}$ in the interval $[-1,1]$ (concerning the eigenvalues of $\mathbf{H}$), where all the zeros of $\mathbf{T}_k$ are located. The sum can be truncated in a very graceful way, one that does yield the ‘‘most accurate’’ approximation of degree L (in a sense which can be made precise). The order L of the series affects the accuracy in the result (see also next section).

The convergence of the Chebyshev polynomial approximation requires that the eigenvalues of the matrix $\mathbf{H}$ are within the interval $[-1,1]$. Actually, this is not the case, and one introduces shift coefficients, h_a and h_b in order to apply the recursion formula to the ‘‘shifted’’ matrix $\mathbf{H}' \equiv h_\mathrm{a}\mathbf{H} + h_\mathrm{b}\mathbf{1}$ whose eigenvalues should be within the desired range. This requirement is fulfilled for $h_\mathrm{a}=2/(\Lambda_M-\Lambda_0)$, $2\,h_\mathrm{b} = -h_\mathrm{a}(\Lambda_M+\Lambda_0)$, where Λ_0 and Λ_M denote the minimum and maximum eigenvalues of the original HI matrix $\mathbf{H}$, respectively. The coefficients of the series are readily obtained by standard methods:[28,27]

$$c_j=L^{-1}\sum_{k=1}^{L} \alpha_{kj}^{L}\;\; F(a_+ + a_-\cos[\pi(k-1/2)/L]) \tag{7}$$

with the scalar function $F(x)=\sqrt{x}$, coefficients $a_+ \equiv (h_a + h_b)/2$, $a_- \equiv (h_b-h_a)/2$, and the abbreviation $\alpha_{kj}^{L} \equiv 2\cos[\pi(j-1)(k-1/2)/L]$.

Instead of calculating the square root matrix first, thus implying several time consuming matrix by matrix products for the evaluation of the polynomials of the series, and afterward its product with the random $\mathbf{W}$ vector, the desired vector is obtained directly as a result of a series of different vectors $\mathbf{V}$, recursively calculated only through less expensive matrix ($\mathbf{H}$) by vector ($\mathbf{V}$) products, i.e., one replaces $d\mathbf{S}_i$ in Eq. (2) by

$$\begin{aligned} d\mathbf{S}_i &= \left(\sum_{k}^{L} c_k\mathbf{T}_{k-1}(\mathbf{H}')-\frac{\mathbf{1}}{2}c_1\right)\cdot d\mathbf{W}_j(t) \\ &= \sum_{k}^{L} c_k\, d\mathbf{V}_{k-1}^{i}-\frac{c_1}{2}d\mathbf{W}_j . \end{aligned} \tag{8}$$

The recursion formula for $d\mathbf{V}_k^i \equiv \mathbf{T}_k(\mathbf{H}')\cdot d\mathbf{W}_i$ is immediately obtained from Eq. (6). Its evaluation requires an effort

$\propto N^2$ for every $k=1,2,..,L$. The overall computational demand of the method we use scales with $N^2 L \propto N^{9/4}$ per time step, as will be seen below.

In addition to this decomposition method a variance reduction simulation technique has been implemented to reduce the statistical error bars (see Ref. 4, p. 177). For this purpose two simulations are run in parallel, one at equilibrium, and another undergoing steady shear flow but using the same sequence of random numbers. After a certain time interval to be specified below, the desired magnitudes are sampled, and the chain simulated under steady shear flow is (periodically) reset to the state of the chain in equilibrium.

In particular, the monomer diffusion coefficient D and radius of gyration R_g are sampled from bead trajectories $\{\mathbf{r}_i(t)\}$ according to $D=\lim_{t\to\infty}(\Sigma_{i=1}^N[\mathbf{r}_i(t)-\mathbf{r}_i(0)]^2)/(6\,N\,t)$ and $R_g^2=\Sigma_i[\mathbf{r}_i-\mathbf{r}_c]^2/N$, respectively, where $\mathbf{r}_c$ denotes the center of mass of the molecule. The simulation reveals that the power law regime for monomer diffusion D will be obtained earlier than the one for the more ''global'' R_g. By analogy to classical results for the diffusion of a sphere embedded in a Newtonian liquid the hydrodynamic radius (of the corresponding sphere) is defined by $R_h=k_\mathrm{B}T/(6\pi\eta_s D)$.

A. Choice of parameters

In order to reproduce the results to be reported in the subsequent section we first present a choice of parameters for the particular system under study. It will be outlined how to confirm the validity of the approximations; a price one has to pay when using the efficient series expansion method.

Simulation runs were performed for a series of chain lengths N and hydrodynamic interaction parameters h^*. For all results shown, which were averaged over three independent runs, the total simulation time divided by the longest relaxation time λ_1^Zimm of the Zimm model is 60.000 for every run, where the approximate expression $\lambda_1^\mathrm{Zimm}\approx 1.22\lambda_H N^{3/2}/(h^*\pi^2)$ (Ref. 4) has been used for convenience, with $\lambda_\mathrm{H}\equiv\zeta/(4H)$. In the course of the variance reduction method positions were reset periodically at $t/\lambda_1^\mathrm{Zimm}=5,10,15,..$. The shear rate chosen for the purpose of this work has to be small compared to the inverse maximum relaxation time but as large as possible, we use $\gamma\lambda_1^\mathrm{Zimm}=1/4$. Few runs have been performed at smaller rates, the results agree with the presented data within the available precision. An integration time step of $\triangle t=\lambda_H$ serves to obtain results for all chain lengths with the desired accuracy. The eigenvalues Λ_0 and Λ_M have been estimated during the course of the simulation, at every 100th integration time step. We found that $2\Lambda_0>\Lambda_0^\mathrm{Zimm}$ and $\Lambda_M<2\Lambda_M^\mathrm{Zimm}$ serve as ''efficient'' (see discussion below) lower and upper bounds for the eigenvalue spectrum, where the quantities indexed by ''Zimm'' denote the exact results obtained from the equilibrium averaged HI matrix.

Also, we obtained an approximate expression (within 5% for $M\geqslant 5$, $h^*\leqslant 0.5$) for the exact result, which is

$$\Lambda_0^\mathrm{Zimm}\approx 1-1.71h^*,\quad \Lambda_M^\mathrm{Zimm}\approx 1+\pi N^{1/2}h^*. \tag{9}$$

By using these approximations we avoid calculating the eigenvalues of the HI matrix during production runs. With increasing shear rate the spectrum of eigenvalues is slightly shifted toward larger values, and merely unchanged for the low shear rates investigated. The Chebyshev series was taken up to the order $L=(\Lambda_M/\Lambda_0)^{1/2}+1$, where L takes the corresponding (truncated) integer value, in order to obtain 0.01 error. This finding is in agreement with Table I of Ref. 13. To summarize, and to ensure the full reproducibility of our results, we use $\Lambda_0=(1-1.71h^*)/2$, $\Lambda_M=2(1+\pi N^{1/2}h^*)$, $L=(\Lambda_M/\Lambda_0)^{1/2}+1$, and the relaxation time for the variance reduction method $\lambda_1=1.22N^{3/2}/(h^*\pi^2)$ (in reduced units). The total CPU time required for a single time step therefore scales with $\mathrm{CPU_{step}}\propto N^2\times L\propto N^{9/4}$, the one for a single run scales with $\lambda_1^\mathrm{Zimm}\times\ \mathrm{CPU_{step}}\propto N^{15/4}$, since L varies with N through Eq. (9). On the other hand, the convergence of the Chebyshev approximation is best for $\Lambda_M\Lambda_0=1$, i.e, for h^* close to zero and 1/2, respectively. Finally, we have chosen the simulated chain lengths such that they are equidistant on a $1/\sqrt{N}$ scale, i.e., for the current simulations we choose $N=4,5,6,8,10,13,18,26,41,73,169$ (plus a maximum feasible chain length of $N=254$) in view of the expected dependences of universal numbers versus chain length [see Figs. 1(a)–1(d)].

The only simulation parameters are hence N and h^*, all other parameters are fixed according to the above procedure. If an approximation favoring the accuracy of either global or local motions is wanted, this can be achieved by further overestimating Λ_0 or underestimating Λ_M, respectively.

One should notice, that the given bounds for the eigenvalue range are specific for the problem under study. In general, one has to ensure that the degree of violation of the fluctuation-dissipation theorem (with respect to an elegible matrix norm) is small enough to obtain exact moments of the distribution function with a desired accuracy, e.g., along the lines indicated in Ref. 14 in order to prevent a direct calculation of eigenvalues. At least concerning our study, the elegant computational method used by Fixman[13] proved to serve as a basis to obtain ''efficient'' bounds (Λ_0,Λ_M) for eigenvalues. Our expressions for bounds are found to be comparable to those obtained with his method, for the particular shear rates studied. His estimate of the range of the eigenvalues of $\mathbf{H}$ is also furnished by a simple physical argument and does not require diagonalization or averaging of $\mathbf{H}$. If two nearby beads experience a force in the same direction the induced perturbations of the velocity field will have a large degree of coherence and thus add up to a larger perturbation. If on the other hand the forces are in opposite directions the induced perturbations will cancel out to a large extent. Since beads which are neighbors along the chain are likely to be also closed neighbors in space an estimate for the largest and smallest eigenvalues is obtained by using a force vector which equal absolute forces for all beads as a test-vector $\mathbf{F}_i=p^i\mathbf{F}$ $(i=1,N)$ with an arbitrary $\mathbf{F}$ to form a Rayleigh quotient[29,30] $\Sigma_{i,j}\mathbf{F}_i^T\cdot\mathbf{H}_{ij}\cdot\mathbf{F}_j/\Sigma_k\mathbf{F}_k^T\cdot\mathbf{F}_k$, which serves as a measure for the lower $(p=-1)$ and upper $(p=+1)$ bounds, respectively. To compensate for deviations of these estimates from the true values of the largest and smallest eigenvalues of $\mathbf{H}$ one takes[13] a somewhat larger interval for the shifted Chebyshev polynomials.[30] For the same reason a

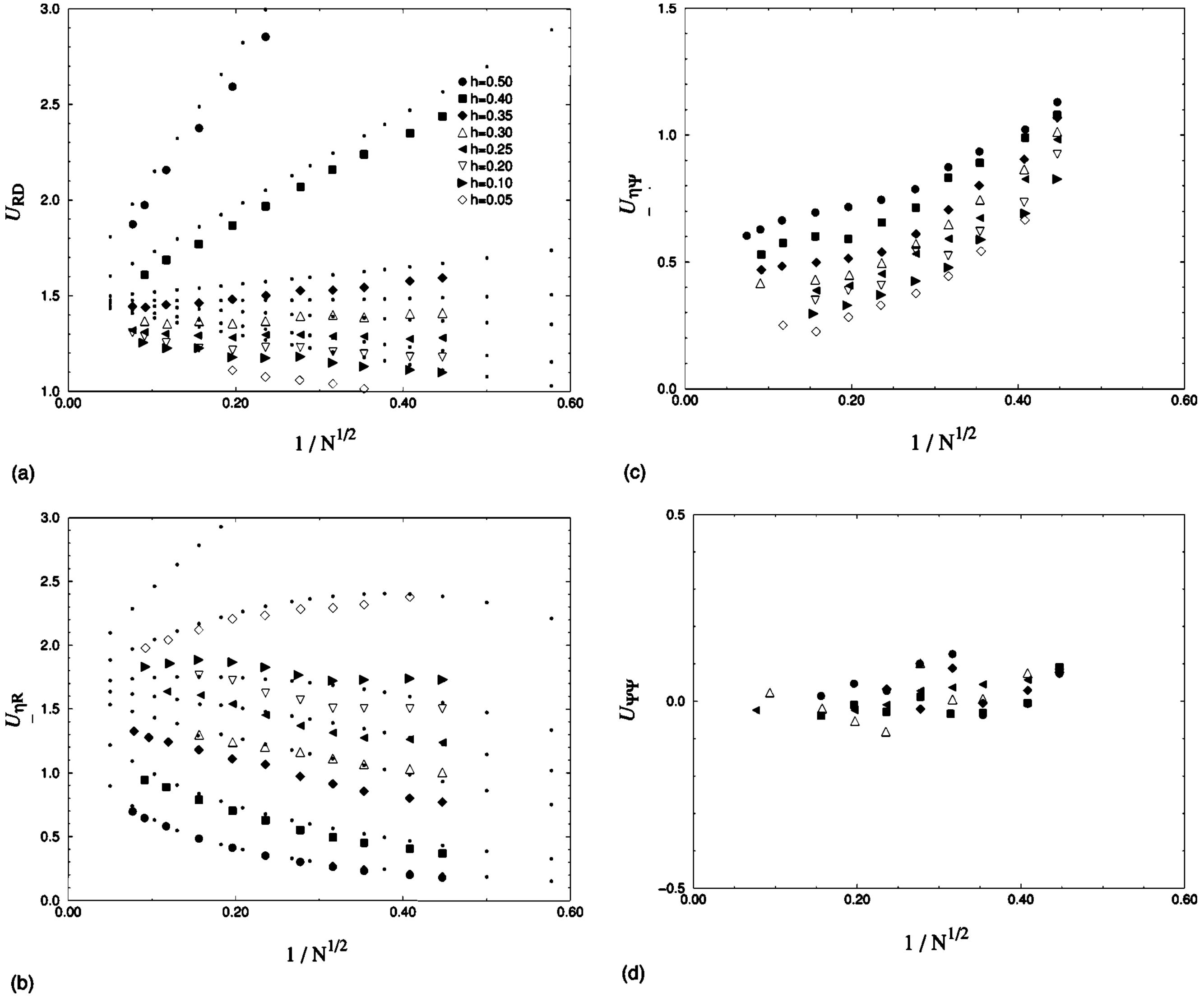

FIG. 1. The ratios (a) U_{RD}, (b) $U_{\eta\mathrm{R}}$, (c) $U_{\Psi\eta}$ and (d) $U_{\psi\psi}$ as defined in Eq. (10) vs the inverse square root of chain length for different values of the HI interaction parameter h^*. As a reference, results for the Zimm model are also shown (small dots). By extrapolation to $N\rightarrow\infty$ the universal ratio is obtained (see Table I). Apparently, U_{RD} depends linearly on $1/\sqrt{N}$.

factor 2 had been introduced above between Zimm eigenvalues and simulation parameters.

In the context of this study, the terminus ''efficient'' implies that the bounds are not strict, since overlap of particles may occur. The degree of overlap, in turn, can be reduced by increasing the shear rate. For our setting, which exhibits a rather moderate choice for the number of terms L, i.e., the polynomial degree of the approximation Eq. (5), it has been observed, that the violation of the fluctuation dissipation theorem is weak[31] and that the overall convergence and reproducibility of extracted averages is good, *independent* of the values for chain length and hydrodynamic interaction parameter. It has to be regarded as a compromise, cf. Ref. 27. Results which we obtained by using Rayleigh quotients (plus the factor of 2) agree with those to be presented in the following section (within 3% error).

On a 500 MHz alpha processor our code needs ca. 10^{-4} seconds per step for $N=20$. The performance increases regularly with the value of N. On the Cray SV1 of the ETH Zürich we get 86 MFlops for $N=30$, 156 for $N=128$, and 184 for $N=254$, which is very close to the theoretical maximum. This indicates nearly optimal use of the vector architecture for our algorithm.

III. RESULTS AND DISCUSSION

The most interesting theoretical predictions for experimentally accessible quantities are those independent of any physical parameters.

In the limit of infinitely long chains the Zimm model predicts a diffusion coefficient D_h, radius of gyration R_g and a spectrum of relaxation times $\lambda_j^{\mathrm{Zimm}}$ $(j=\{1,2,\ldots\})$:[4,32] $\lim_{N\rightarrow\infty} D_h = c h^* k_B T/(\zeta\sqrt{N})$, $\lim_{N\rightarrow\infty} R_g = (N k_{\mathrm{B}} T/2H)^{1/2}$, and $\lim_{N\rightarrow\infty} \lambda_j^{\mathrm{Zimm}} = c_j (N/j)^{2/3} \zeta/(4h^* H \pi^2)$ with $c_1 = 1.22$ and $c_j = 2\pi j/(2\pi j - 1)$ for $j>1$.[33]

Having established these relationships for the Zimm model one can construct and define a number of universal ratios for experimentally accessible quantities:

TABLE I. Previous analytical, experimental, numerical, as well as novel results for universal ratios in the zero shear rate limit. E.g., Fixman estimated $U_{\mathrm{RD}}=1.42$ (Ref. 41) but could not estimate $U_{\eta\mathrm{R}}$ due to the slow convergence of rheological properties η (and also $\Psi_{1,2}$). The asterisk marks results obtained *taking into account* excluded volume. The estimates of de la Torre *et al.* and Bernal *et al.* were obtained by extrapolation from their results for $h^*=1/4$ Ref. 45. The following abbreviations for computational methods are used: BD (Brownian dynamics), MD (Molecular dynamics), MC (Monte Carlo).

	U_{RD}	$U_{\eta\mathrm{R}}$	$U_{\Psi\eta}$	$U_{\Psi\Psi}$	$U_{\eta\lambda}$	$U_{\Psi S}$
Theory						
Rouse (Ref. 2)	$\propto N^{-1/2}$	$\propto N^{+1/2}$	0.8	0	1.645	$\propto N$
Zimm (Ref. 8)	1.479 34	1.664 25	0.413 865	0	2.39	20.1128
Gaussian approx. (Ref. 35)	—	1.213(3)	0.560(3)	−0.0226(5)	1.835(1)	14.46(1)
Twofold normal Zimm (Ref. 35)	—	1.210(3)	0.5615(3)	−0.0232(1)	1.835(1)	14.42(1)
Öttinger (Ref. 10)	—	1.377(1)	0.6096(1)	−0.0130(1)	—	20.29(1)
Oono *et al.** (Ref. 36)	1.56(1)	—	—	—	—	—
Öttinger* (Ref. 37)	—	—	0.6288(1)	—	—	10.46(1)
Experiment						
Schmidt *et al.* (Ref. 38)	1.27(6)	—	—	—	—	—
Miyaki *et al.* (Ref. 39)	—	1.49(6)	—	—	—	—
Bossart *et al.* (Ref. 40)	—	—	0.64(9)	—	—	—
Bossart *et al.** (Ref. 40)	—	—	0.535(40)	—	—	—
Simulation						
Fixman (Ref. 41) (BD)	1.42(8)	—	—	—	—	—
de la Torre *et al.* (Ref. 42) (BD)	1.28(11)	1.47(15)	—	—	2.0	—
Rubio *et al.* (Ref. 43) (MC)	—	$>1.36(5)$	—	—	—	—
Garcia Bernal *et al.** (Ref. 44) (BD)	1.48(15)	1.11(10)		—	—	—
Aust *et al.** (Ref. 46) (MD)	1.41(6)	—	—	—	—	—
This work (BD)	1.33(4)	1.55(6)	0.45(7)	0.05(4)	—	19(2)

$$\begin{aligned}
U_{\mathrm{RD}} &\equiv \frac{R_g}{R_h} \equiv \frac{6\pi\eta_s D_h R_g}{k_B T},\\
U_{\eta\mathrm{R}} &\equiv \lim_{c\to 0} \frac{\eta_p}{c\,\eta_s (4\pi R_g^3/3)} \xrightarrow{\text{Zimm}} \frac{9}{2}\,\frac{U_{\eta\lambda} D_h \lambda_1^{\mathrm{Zimm}}}{U_{\mathrm{RD}} R_g^2},\\
U_{\Psi\eta} &\equiv \lim_{c\to 0} \frac{c k_{\mathrm{B}} T \Psi_1}{\eta_p^2},\\
U_{\Psi\Psi} &\equiv \frac{\Psi_2}{\Psi_1},\\
U_{\eta\lambda} &\equiv \lim_{c\to 0} \frac{\eta_p}{c k_{\mathrm{B}} T \lambda_1} \xrightarrow{\text{Zimm}} \frac{\lambda_\eta}{\lambda_1} = \frac{\Sigma_j \lambda_j}{\lambda_1} = \frac{\pi^{5/2}}{4[\Gamma(3/4)]^2 c_1},\\
U_{\Psi S} &\equiv \frac{k_{\mathrm{B}} T \Psi_1}{c\,\eta_s^2 R_g^6} = U_{\Psi\eta} U_{\eta\mathrm{R}}^2 (4\pi/3)^2.
\end{aligned} \tag{10}$$

The quantity U_{RD} is the ratio between radius of gyration and hydrodynamic radius, the latter quantity can be actually measured experimentally in a dynamic experiment, e.g., by observing the relaxation time of the dynamic scattering function $S(q,t)$ for small momentum transfers $qR_g \ll 1$. The quantity $U_{\eta\mathrm{R}}$ is a measure for the specific polymer contribution η_p to the reduced shear viscosity, $U_{\Psi\eta}$ gives the ratio between first viscometric function and squared polymer contribution to the shear viscosity, $U_{\Psi\Psi}$ is the ratio between the second and first viscometric function, $U_{\eta\lambda}$ reflects the proportionality between η_p and the longest relaxation time. For the Zimm model one infers $U_{\eta\lambda}$ from $\eta_p/ck_{\mathrm{B}}T=\Sigma_j\lambda_j$. Finally, $U_{\Psi S}$ is introduced for convenience. It is a combination of two other characteristic ratios. From these ratios one can, for example, eliminate the unspecified proportionality coefficients in the ''blob'' theory of polymer statistics.[34]

The universal ratios predicted by the Zimm model in its long-chain limit are collected in Table I. These numbers serve as reference values for the exact result without preaveraging procedure. Our estimates for the exact long-chain limit are extrapolated from the data shown in Figs. 1(a)–1(d). The polymer contribution to the stress tensor and radius of gyration needed to analyze universal ratios listed in Table I have been calculated directly from bead trajectories. An independent discussion about relaxation times for this system, needed to determine $U_{\eta\lambda}$ can be found in Ref. 42. As for the Zimm model, our simulation results reveal that the radius of gyration converges more fast to its long-chain limit than the hydrodynamic radius. A sample time series for accumulated data is shown in Fig. 2. The results are basically summarized in Table I, together with theoretical, experimental and earlier findings. Sample simulation parameters are listed in Table II.

In Ref. 6 the leading corrections to the limit of infinitely long chains have been estimated in the framework of a generalized Zimm model for dilute polymer solutions. They are of the following form:

$$U_i(h^*,N) = \tilde{U}_i + \frac{c_i}{\sqrt{N}}\left(\frac{1}{h_i^*} - \frac{1}{h^*}\right) \tag{11}$$

for $i \in \{\mathrm{RD}, \eta\mathrm{R}, \mathrm{etc.}\}$. A careful analysis of the simulation data yielded the following results for the coefficients defined through Eq. (11):

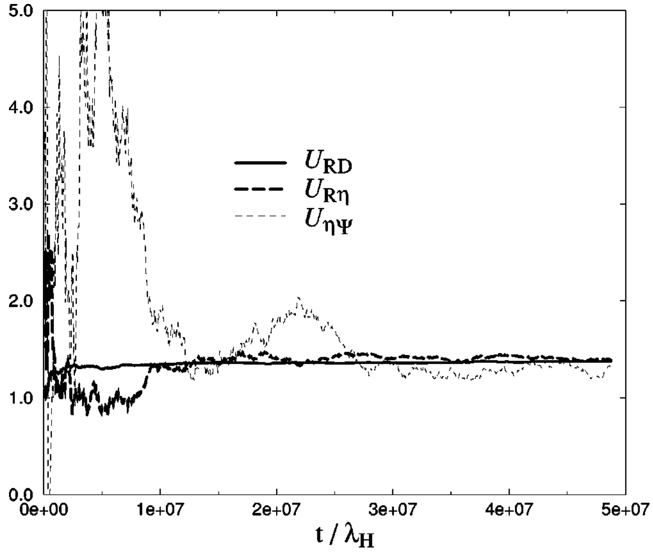

FIG. 2. Sample time series of accumulated averages for the ratios U_{RD}, $U_{\eta R}$ and $U_{\Psi\eta}$ for $N = 120$ and $h^* = 0.20$.

$$\begin{aligned}
&\tilde{U}_{\mathrm{RD}} = 1.33 \pm 0.05, \quad c_{\mathrm{RD}} = -0.49, \quad h^*_{\mathrm{RD}} = 0.267,\\
&\tilde{U}_{\eta\mathrm{R}} = 1.55 \pm 0.04, \quad c_{\eta\mathrm{R}} = 1.9, \quad h^*_{\eta\mathrm{R}} = 0.250,\\
&\tilde{U}_{\Psi\eta} = 0.29 \pm 0.1, \quad c_{\Psi\eta} = -0.20, \quad h^*_{\Psi\eta} = 0.261,\\
&\tilde{U}_{\Psi\Psi} = 0.05 \pm 0.1, \quad c_{\Psi\Psi} = 0.05, \quad h^*_{\Psi\Psi} = 0.247.
\end{aligned} \tag{12}$$

As expected from Ref. 6 the values h_i^* for which the leading order corrections are absent do not coincide for the various functions U_i. Since the functions Eq. (11) for a given i and different HI parameters appear as a set of converging straight lines in the representations of raw data in Figs. 1(a)–1(d) it is obvious that the data for U_{RD} is represented better by the expression Eq. (11) than the data for the remaining universal ratios, for the set of finite chain lengths under study.

TABLE II. The table contains static simulation parameters for a number of chain lengths N and hydrodynamic interaction parameters h^* (see Sec. II A) which allow to reproduce the results. As discussed in the text, simulations with small condition number L possess the highest efficiency due to algorithmic convergence. Methods for estimating eigenvalues Λ_0, Λ_M during the coarse of the simulation are discussed in the text; γ denotes shear rate.

N	h^*	Λ_0	Λ_M	L	γ
10	0.05	0.46	2.99	3	0.0122
10	0.1	0.41	3.99	4	0.0122
10	0.2	0.33	5.97	5	0.0122
10	0.25	0.29	6.97	5	0.0122
10	0.3	0.24	7.96	6	0.0122
10	0.4	0.16	9.95	8	0.0122
10	0.5	0.073	11.9	13	0.0122
20	0.25	0.29	9.02	6	0.003 08
50	0.25	0.29	13.1	7	0.000 493
100	0.25	0.29	17.7	8	0.000 123
200	0.05	0.46	6.44	4	0.000 030 8
200	0.25	0.29	24.2	10	0.000 030 8
200	0.5	0.073	46.4	26	0.000 030 8

IV. CONCLUSIONS

We have investigated the universal behavior of linear polymers in dilute theta solutions at small shear rates by Brownian dynamics simulations. Hydrodynamic interactions are treated with an efficient algorithm proposed by Fixman, for which the increase of computing time with chain length is governed by the exponent 9/4. With modern computers and variance reduction techniques, chain lengths up to $N = 254$ have been reached and, with careful extrapolation techniques, the universal predictions for the diffusion coefficient and the viscosity with error bars of less than 3% and 4%, respectively, have been obtained. The results for the normal-stress coefficients are much less reliable: The error bar for the first normal-stress coefficient is some 30%, the sign for the much smaller second normal-stress coefficient is inconclusive.

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