

Screening of hydrodynamic interactions in semidilute polymer solutions: A computer simulation study

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We study single-chain motion in semidilute solutions of polymers of length $N=1000$ with excluded-volume and hydrodynamic interactions by a novel algorithm. The crossover length of the transition from Zimm (short lengths and times) to Rouse dynamics (larger scales) is proportional to the static screening length. The crossover time is the corresponding Zimm time. Our data indicate Zimm behavior at large lengths but short times. There is no hydrodynamic screening until the chains feel constraints, after which they resist the flow: “Incomplete screening” occurs in the time domain.

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The dynamics of polymer chains in solution [1,2] has been the subject of long-standing theoretical investigations, even for the simple case of flexible uncharged chains in good solvent. While in the dilute limit the validity of Zimm scaling predictions [1–4] is generally accepted, as confirmed by experiments [3,5,6] and computer simulation [7–9], the theoretical understanding becomes much more involved as soon as one considers finite concentrations [10–17]. This is so due to the complicated interplay between excluded-volume interactions, hydrodynamic interactions, and entanglements. Only for the opposite limit of dense melts, where the first two interactions are fully screened, a fair level of understanding has been achieved in terms of the Rouse or reptation model [1,18,19]. However, the details of the crossover, the underlying mechanism of the screening of hydrodynamic interactions, and the concentration dependence of the screening length have been a subject of considerable debate.

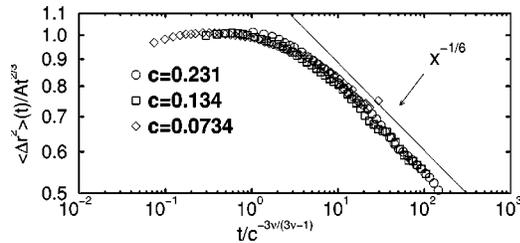
In this Rapid Communication, we present a computer simulation study which is able to contribute to the resolution of these questions. Experiments, such as light scattering [20,21] or nonequilibrium methods [22] usually focus on *collective* concentration fluctuations, while *single-chain* motions are only accessible by labeling techniques (neutron [14] or light [5] scattering). Computer simulations can in principle analyze both types of motion; however, for reasons of statistical accuracy we had to confine ourselves to single-chain motion.

We study the equilibrium fluctuations of a three-dimensional semidilute system of flexible bead-spring polymer chains with full excluded-volume interactions, coupled to a hydrodynamic background to fully take into account hydrodynamic interactions, using an efficient method which we have recently developed and tested [9]. The polymer system is simulated by Langevin stochastic dynamics, the solvent by a stochastic D3Q18 lattice Boltzmann model [23,24], and a point-particle coupling is introduced via a monomeric friction coefficient. The present work uses the same model with the same parameters but in the semidilute regime. One particular advantage, without which the study would have been unfeasible, is the fact that the lattice Boltzmann solvent does not alter the good solvent statistics of the chain conformations. We therefore first equilibrated the multichain system without the computationally expensive solvent, using a

combination of stochastic dynamics and slithering-snake Monte Carlo moves comprising several monomers (roughly one blob; see below). This run produced a set of configurations, which were afterwards coupled to the solvent. For further details of the model, we refer the reader to Ref. [9].

Semidilute systems are characterized by a very low monomer concentration c , which is nevertheless large enough to induce strong overlap of the coils. The static conformations are well understood [2] in terms of the “blob size” ξ_S , i.e., the typical mesh size of the temporary network. On scales below ξ_S , the chains are self-avoiding walks (SAWs) characterized by the scaling law $R \sim aN^\nu$, where a is the monomer size, R the chain extension, N the degree of polymerization, and $\nu \approx 0.59$. The concentration dependence of ξ_S results from $c \sim \xi_S^{-3} (\xi_S/a)^{1/\nu}$. On scales above ξ_S the density is homogeneous, and the excluded-volume interaction is screened, such that the chains are random walks (RWs, $R \sim aN^{1/2}$). The overall chain is thus a RW of blobs with $R^2 \sim \xi_S^2 N / (\xi_S/a)^{1/\nu}$. This picture implies that rather long chains are necessary in order to clearly observe both regimes; guided by the idea of having roughly 30 blobs of 30 monomers each available, we chose $N=1000$, and varied ξ_S by studying the concentration values $c=0.00837$, 0.0397, 0.0734, 0.134, and 0.231 for the statics, and the latter three values for the dynamics (data are always given in the Lennard-Jones unit system of Ref. [9]). The number of chains $M=50$ was kept fixed; this is large enough to ensure that even the most concentrated system does not exhibit self-overlap due to the periodic boundary conditions. Our data for the static chain conformations fully agree with the blob scaling picture [25], as did those of previous extensive Monte Carlo simulations [26,27].

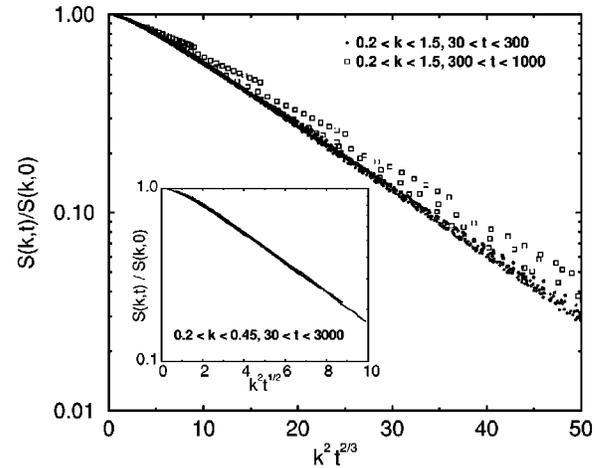
Dynamic scaling for a single chain which exhibits no special length scale except a and R implies $\tau \propto R^z$, where τ is the conformational relaxation time, and $z=3$ for the Zimm model (applicable to dilute solutions without chain overlap where hydrodynamic interactions are fully developed), while $z=4$ for the RW Rouse model (applicable to dense melts where hydrodynamic interactions are fully screened; we do not consider reptationlike slowing down, which occurs only for sufficiently long chains and/or sufficiently dense systems [28], and does not play any role for our simulation data,

FIG. 1. Scaled $\langle \Delta r^2 \rangle$ for different concentrations.

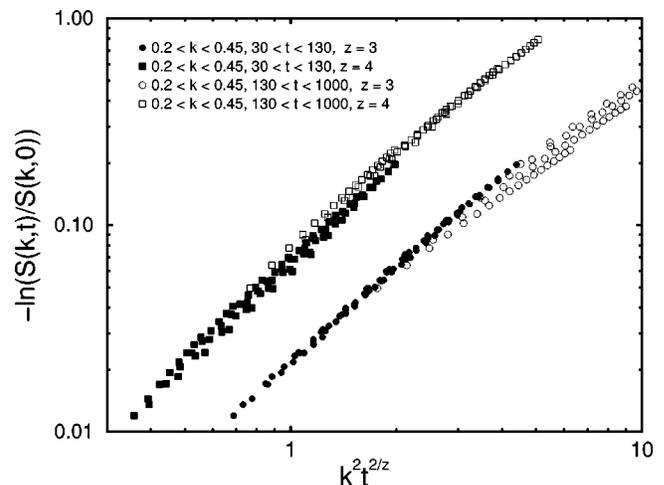
which are restricted to short times). In terms of the chain diffusion constant D this corresponds, via $D\tau \sim R^2$, to $D \propto R^{-1}$ for Zimm (chain as a Stokes sphere) and $D \propto N^{-1}$ for Rouse (monomers as independent friction centers). Furthermore, the scaling of lengths with the corresponding times implies a subdiffusive behavior for the single-monomer mean square displacement $\langle \Delta r^2 \rangle \propto t^{2/z}$, and a $k^z t$ behavior for the single-chain dynamic structure factor $S(k, t) = N^{-1} \sum_{ij} \langle \exp\{i\vec{k} \cdot [\vec{r}_i(t) - \vec{r}_j(0)]\} \rangle$ in the scaling regime of intermediate length scales (between a and R) and time scales (between τ_0 , the microscopic time for monomer relaxation, and τ).

For a semidilute system, one expects a crossover between these cases. Indeed, our data for $\langle \Delta r^2 \rangle$ do exhibit a crossover from a Zimm-like $t^{2/3}$ behavior at short times to $t^{1/2}$ at longer times. The behavior at short length and time scales is thus Zimm-like. The pure Zimm model [1] predicts that the decay rate, i.e., in the given context, the prefactor A of the law $\langle \Delta r^2 \rangle = A t^{2/3}$ should only depend on solvent viscosity and not on concentration. We nevertheless found a weak concentration dependence of A (roughly 20% within the given concentration range; see below). Figure 1 thus studies $\langle \Delta r^2 \rangle / (A t^{2/3}) = f(t/t_c)$, where t_c is the concentration-dependent crossover time, which again is the Zimm relaxation time of a dynamic crossover length (or hydrodynamic screening length), $t_c \propto \xi_H^3$, and $f(x) \propto x^{-1/6}$ for large x . We find a very good data collapse assuming that $\xi_H \propto \xi_S$ or $t_c \propto c^{-3\nu/(3\nu-1)} = c^{-2.3}$, as is done in Fig. 1. The assumptions $\xi_H \propto c^{-1}$ [10,13] and $\xi_H \propto c^{-1/2}$ [16] produced poorer collapses, in particular for the case c^{-1} . The simulation is thus consistent with the prediction of de Gennes, $\xi_H \propto \xi_S$ [11], as are experimental data [20,22] (for finite-concentration corrections, which also occur in our system, see below).

$S(k, t)$ was studied for the most dilute system, $c = 0.0734$. We prefer scaling plots of the raw data using asymptotic exponents over fits to functional forms derived from approximate theories. From $S(k, 0)$ we estimated the crossover wave number between RW and SAW as $k_c \approx 0.45$ and the scaling regime $R^{-1} \ll k \ll a^{-1}$ as $0.2 < k < 1.5$. From $\langle \Delta r^2 \rangle$ we read off $t_c \approx 10^3$; the nonuniversal regime $t < 30$ was discarded. Figures 2 and 3 show that for short times $t \ll t_c$ the decay can be described quite well by Zimm scaling, regardless of wave number, while for $t \approx t_c$ there is a simultaneous smooth crossover to Rouse dynamics for those wave numbers which have not yet fully decayed, i.e., for $k < k_c$. Note that the initial Zimm regime of these wave numbers can be easily overlooked in the representation of the inset of Fig. 2.

FIG. 2. Decay of $S(k, t)/S(k, 0)$ on length and time scales as indicated, suggesting Zimm scaling for short times (main figure) and Rouse scaling for long wavelengths (inset).

The physical picture which results from this observation is thus free Zimm motion up to the crossover time (*on all length scales*), after which screening sets in, leading to Rouse-like motion. Hence, the most important finding of our simulation is that hydrodynamic screening must necessarily be viewed as a *dynamic time-dependent phenomenon*. We consider this to be the logical consequence of the (correct) original treatment by de Gennes [11] (see below). Nevertheless, this has so far been overlooked in the literature, the main reason being that single-chain motion on length scales beyond ξ is not accessible to standard scattering experiments [20,21] which are sensitive to collective concentration fluctuations: On scales $k\xi \ll 1$ the overall solution is homogeneous, and one observes a simple diffusive decay $\exp(-D_{coop} k^2 t)$, with $D_{coop} \propto \xi^{-1}$. Accordingly, single-chain motion on scales beyond ξ was not treated explicitly in Ref. [11]. The experiments on labeled chains [5,14] produced data which are fully consistent with our view, but were interpreted

FIG. 3. $S(k, t)/S(k, 0)$ in the RW regime $0.2 < k < 0.45$ with both Zimm and Rouse scaling, using a representation that emphasizes the short-time behavior.

incorrectly (see below). The rest of the paper will be devoted to further discussion of the underlying mechanism.

Hydrodynamic interaction is the presence of long-range correlations in the stochastic displacements of a system of Brownian particles, caused by fast diffusive momentum transport through the surrounding fluid. They can be calculated by solving the stationary Stokes equation around a system of spheres [29], resulting in a complicated multipole expansion which contains many-body terms representing the multiple scattering of the flow. In the dilute limit, however, it is sufficient to just consider the leading-order pair interaction, which decays like r^{-1} , where r is the interparticle distance (Oseen tensor). Conversely, *screened* hydrodynamic interactions are described by a Yukawa-like decay $r^{-1} \exp(-r/\xi_H)$ defining the hydrodynamic screening length ξ_H . Such an interaction occurs for Darcy flow through a porous medium, where *fixed* frictional obstacles with friction constant ζ exert a force $-\zeta \vec{u}$ on the flow with velocity \vec{u} . Denoting the obstacle concentration with c , the flow is described, on scales beyond the typical interparticle distance, by a modified Stokes equation $\rho \partial \vec{u} / \partial t = \eta \nabla^2 \vec{u} - \zeta c \vec{u}$, where ρ is the fluid density and η the viscosity. This implies $\eta \xi_H^{-2} = \zeta c$.

The simplest approach to hydrodynamic screening in polymer solutions just replaces the r^{-1} Oseen interaction by a screened Yukawa-like interaction, leading to uncorrelated displacements of monomers whose distance exceeds ξ_H . The resulting motion of the chain is Zimm-like on short length and time scales and Rouse-like on length scales beyond ξ_H for all times [14]. The Darcy flow thus produces the desired crossover.

Unfortunately, this picture generates as many questions as it answers. In particular, the obstacles must be the *mobile* polymer chains themselves, whereas strict Darcy flow requires *fixed* obstacles. Moreover, momentum is present and being transported infinitely far in polymeric as well as in simple fluids. This fundamental conceptual difficulty was recognized by Richter *et al.* [14]. In their “incomplete screening” model they proposed that the hydrodynamic interaction should cross over to a second r^{-1} regime on very large scales, but with the *overall* viscosity as a prefactor. For the single-chain short-time behavior this model also predicts Rouse-like motion. However, this regime is now restricted to length scales $\xi_H \ll k^{-1} \ll \xi_H \eta_{\text{solution}} / \eta_{\text{solvent}}$. On larger scales there is an additional Zimm regime. Richter *et al.* [14] used this to interpret the mixture of Rouse- and Zimm-like signals in their scattering data. Similar arguments were used by Martin [5], who observed Zimm scaling on all length scales in the initial decay rate of dynamic light scattering of labeled chains.

The simple model and the more refined version by Richter *et al.* [14] are at variance with both our data and our theoretical arguments for the short-time behavior; see below. It should be noted that the “incomplete screening” model must have fundamental conceptual difficulties, since η_{solution} appears in the short-time dynamics, although η_{solution} is established only on time scales beyond the overall chain relaxation.

It is therefore clear that a consistent theoretical description has to study the dynamics of the coupled polymer-solvent system. The first attempt by Freed and Edwards [10] considered a multiple scattering series of the flow around the monomers, which is in spirit somewhat similar to the multipole expansion of Ref. [29]. After some approximations an effective Darcy equation results, with $\xi_H \propto c^{-1}$. Later this scheme was shown to be inadequate; in Ref. [12] it was *proven* that a system of *phantom* chains (which do not interact with each other, but to which the original approach [10] should apply as well) *does not exhibit any hydrodynamic screening whatsoever*. This absence of screening is consistent with recent computer simulation results on colloidal suspensions, for which the problem is under intensive debate, too [30].

With respect to hydrodynamic screening in polymer solutions we can thus draw the following conclusions: (i) the presence of higher-order terms of the multipole expansion [29] at finite concentrations of scattering centers does not lead to screening; (ii) such terms cannot be of any importance in the semidilute limit, where one can reach arbitrarily small monomer concentrations c , while still keeping the chains at strong overlap; (iii) as this “colloidal” mechanism of screening does not apply, the underlying physics must rather be polymer-specific; and (iv) the mechanism must lead to a time-delayed screening. (i)–(iii) were noted before [12], while (iv), to our knowledge, has not yet been spelled out explicitly.

Concerning the short-time behavior, we note that the semidilute system is governed by a Kirkwood diffusion equation [1], with a *pure Oseen-type* r^{-1} diffusion tensor, which describes the short-time diffusive behavior, and a force term due to connectivity, excluded volume, and entanglements. Within this formalism, it can be shown rigorously [1] that the initial decay rates of correlation functions are *only* governed by the diffusion tensor and the statistics of the chain conformations. In particular, considering the initial decay rate of the single-chain structure factor [3], one obtains the *same* formula as for an isolated chain in solvent; the effect of the other chains is merely the modification of the conformations. Zimm chains, however, have always $z=3$ independently of chain statistics; the initial decay rate is given by $\Gamma(k) \sim (k_B T / \eta) k^3$, while the fractal dimension only enters the prefactor [1]. For systems in the semidilute limit we thus conclude, in accordance with our simulation results and the experimental data by Martin [5], that for short times the single-chain dynamics is Zimm-like, *independently of length scales*.

In his pioneering 1976 paper [11] de Gennes noticed that the decisive mechanism for screening is the connectivity and the strong coupling to the temporary matrix (expressed in terms of an elastic gel, which is physically more appropriate than a rigid porous medium): After the time needed for a blob to move its own size, which is the blob’s Zimm time t_c , the chain will, on average, feel the constraints by the temporary matrix. From then on it is unable to follow the flow, but rather lags behind, and starts to produce Darcy-type frictional resistance. As the blob can be envisioned as a Stokes sphere with radius ξ and friction coefficient $\sim \eta \xi$, the ob-

stacles which produce the Darcy flow are not the monomers but rather the blobs. Hence, the hydrodynamic screening length is given by $\eta\xi_H^{-2} \sim \eta\xi_S c_{blob} \sim \eta\xi_S \xi_S^{-3}$, i.e., the hydrodynamic screening length is, apart from prefactors, *identical* to the static screening length, $\xi_H \propto \xi_S$. This argument [11] makes the picture fully self-consistent. On length scales beyond ξ , and time scales beyond t_c , the semidilute solution is just a Rouse melt of blobs, while the conformations within the blobs are already fully relaxed. In the Rouse regime, momentum transport is no longer described by a simple Navier-Stokes equation. Rather, it occurs mainly along the chain backbones, due to the connectivity forces. This results in a very efficient randomization of a locally applied “kick.”

It should be noted that our simulated system deviates somewhat from that ideal scenario. The most dilute system has a density of 9% of a typical dense melt, and thus one must expect that higher-order terms in the multipole expansion [29] do play a role. We believe that these are the main source of the c dependence of the prefactor of the initial $t^{2/3}$ law in $\langle \Delta r^2 \rangle$. We expect finite size effects [8,9] with respect

to the linear box size L to be rather small, since for our data $(kL)^{-1} < 0.06$.

To summarize, we have presented a computer simulation study which was able to study the dynamic crossover from Zimm to Rouse behavior in semidilute polymer solutions. This was made possible by an algorithm whose essential feature is the replacement of the solvent by a Navier-Stokes background, which is coupled dissipatively to the monomers. Our results are fully consistent with the scaling picture of de Gennes [11], and emphasize the fact that hydrodynamic screening is a dynamic effect which becomes relevant only after the crossover time. Incomplete screening thus indeed occurs; however, not on large length scales [14], but on short time scales. Any theoretical description which builds upon a screened hydrodynamic interaction depending only on distance, but disregards the time dependence, cannot describe the phenomena correctly.

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