

Simulation of the Dynamics of Polymers in Solution via a Hybrid Molecular Dynamics- Lattice Boltzmann Scheme

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Abstract. We present a novel scheme for the simulation of polymers in solution, including hydrodynamic interactions via coupling to a Lattice Boltzmann background. This is applied to a system of 50 chains of length $N = 1000$, thus allowing for the first time to study the crossover from Zimm to Rouse dynamics when the concentration is increased and the hydrodynamic interaction is screened. Our results are in agreement with de Gennes' picture, and indicate a *time-delayed* screening, which is related to the entanglement-driven screening mechanism.

An important goal in polymer physics is understanding the Brownian motion of flexible chains in solutions or dense melts. This is of immediate practical relevance for rheology, since the thermal motion of the chains also governs the thermal fluctuations of the internal stresses, which in turn, via linear-response theory, directly control the viscoelastic behavior of the fluid [1]. We are here concerned with three-dimensional polymer solutions in the dilute and semidilute regime in good solvent, in the absence of any long-range electrostatic interactions. The meaning of these terms is as follows: *Dilute* solutions are those where the concentration is so low that the individual chains have no overlap and thus assume the conformation of a self-avoiding random walk (SAW), where the typical chain extension R (for example, the root mean square end-to-end distance) scales as $R \propto N^\nu$ with $\nu \approx 0.59$, N denoting the number of monomers of the chain. The chain flexibility (conformational entropy) favors such a random conformation, while the good solvent quality leads to chain swelling relative to the random walk (RW, $R \propto N^{0.5}$) via excluded volume interactions (if the solvent were poor, the chain would rather be a collapsed dense globule, $R \propto N^{1/3}$). *Semidilute* solutions are characterized by an extremely low monomer concentration c , while nevertheless the chains are long enough to generate strong overlap. These solutions therefore have, besides the chain extension R , and the monomer size a (or persistence length, i. e. the length scale beyond which the bond vector orientations can be considered as random), another relevant length scale ξ , which can be viewed as the correlation length of concentration fluctuations (i. e. the solution is homogeneous on length scales beyond ξ), or as the typical mesh size of the temporary network formed by the chains. In the semidilute limit, $a \ll \xi \ll R$. It is well-known that, due to an entropic packing effect [2], the

excluded-volume interactions are effectively *screened* beyond the length scale ξ , such that RW statistics applies there. The concentration dependence of ξ , which is also called the “blob size”, directly results from noting that a blob contains $(\xi/a)^{1/\nu}$ monomers, i. e. $c \sim \xi^{-3}(\xi/a)^{1/\nu}$. The overall chain is a RW of blobs with $R^2 \sim \xi^2 N/(\xi/a)^{1/\nu}$.

Except for static screening, there is also the concept of *dynamic* screening, i. e. screening of hydrodynamic interactions, which induces a concentration-driven dynamic crossover from Zimm to Rouse dynamics (see below). The physics of this screening is considerably less-well understood.

The Rouse and the Zimm model both aim at the description of polymer Brownian motion. Starting from the observation that the conformational degrees of freedom are by far the slowest in the system, one writes down an overdamped Langevin equation for the monomer coordinates \mathbf{r}_i (here in a discretized form with a finite time step h), which in its most general form reads

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + \sum_j \overset{\leftrightarrow}{\mu}_{ij} \mathbf{F}_j h + \boldsymbol{\varrho}_i. \quad (1)$$

Here \mathbf{F}_j is the (effective) force acting on the j th monomer, due to interactions with other monomers (connectivity and excluded volume). $\overset{\leftrightarrow}{\mu}_{ij}$ is the mobility tensor, which describes the velocity response of monomer i to a force on monomer j . Finally, $\boldsymbol{\varrho}_i$ is the stochastic displacement of monomer i , with $\langle \boldsymbol{\varrho}_i \rangle = 0$ and

$$\langle \boldsymbol{\varrho}_i \otimes \boldsymbol{\varrho}_j \rangle = 2k_B T \overset{\leftrightarrow}{\mu}_{ij} h = 2 \overset{\leftrightarrow}{D}_{ij} h \quad (2)$$

(fluctuation-dissipation theorem). Rouse and Zimm model differ with respect to their assumptions concerning $\overset{\leftrightarrow}{\mu}_{ij}$. The Rouse model simply assumes that the stochastic displacements are uncorrelated, $\overset{\leftrightarrow}{\mu}_{ij} = \mu_0 \overset{\leftrightarrow}{1} \delta_{ij}$, while the Zimm model takes into account that in dilute solutions there occurs fast diffusive momentum transport through the solvent which introduces *correlations*, which can be approximately calculated within the framework of low Reynolds number hydrodynamics:

$$\overset{\leftrightarrow}{\mu}_{ij} = \mu_0 \delta_{ij} \overset{\leftrightarrow}{1} + (1 - \delta_{ij}) \frac{1}{8\pi\eta r_{ij}} \left(\overset{\leftrightarrow}{1} + \hat{r}_{ij} \otimes \hat{r}_{ij} \right), \quad (3)$$

where η denotes the solvent viscosity. The Coulomb-like $1/r$ interaction is genuinely long-ranged, and thus places the Zimm model into a different dynamic universality class than the Rouse model. Starting from the scaling assumption that the internal relaxation of the conformation of a single test chain happens on the same time scale τ as the time needed for the chain to move its own size, one easily derives the scaling laws $\tau \propto R^z$ with $z = 3$ for the Zimm model (regardless of chain statistics) and $z = 2 + 1/\nu$ (i. e. $z = 4$ for the RW case) for Rouse dynamics. It is important to note that Zimm motion

can in essence be viewed as the motion of a Stokes sphere with size R . The exponent z then shows up in the sub-diffusive behavior of the single-monomer mean square displacement, $\langle \Delta r^2 \rangle \propto t^{2/z}$ for $a^2 \ll \langle \Delta r^2 \rangle \ll R^2$, corresponding to $\tau_{\text{mic}} \ll t \ll \tau$, where τ_{mic} is the “microscopic” time scale associated with single-monomer motion. Similarly, one has for the single-chain dynamic structure factor

$$S(k, t) = N^{-1} \sum_{ij} \langle \exp \{i\mathbf{k} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))\} \rangle \propto k^{-1/\nu} f(k^z t) \quad (4)$$

for $R^{-1} \ll k \ll a^{-1}$ and $\tau_{\text{mic}} \ll t \ll \tau$ (note that the prefactor $k^{-1/\nu}$ gives direct information on the chain statistics and can be used to distinguish the RW and SAW regimes in semidilute solutions – RW for $k\xi \ll 1$, SAW for $k\xi \gg 1$). For further details, see [1].

It is known from experiments and simulations that Zimm dynamics applies for dilute solutions, while Rouse dynamics holds for dense systems as long as the chains are short enough to prevent reptation [1]. Therefore the hydrodynamic interactions must be unimportant, or screened, in dense melts, while in semidilute solutions there is a crossover. The physical mechanism is, strictly spoken, unknown. In our opinion, it is most probably the microscopic mechanism of momentum transfer: While in dilute solutions the momentum in essence propagates linearly (more precisely, according to the solution of the Stokes equation), this cannot happen in dense melts: Here, a chain-chain collision in essence leads to propagation *along the backbone*, due to the connectivity forces. This induces a randomization and effective removal of the dynamic correlations.

A simplistic picture of screening arises from the notion of *Darcy flow*. Here, one considers a random array of *fixed* obstacles of concentration c , through which the solvent flows. Assigning a friction coefficient ζ to each obstacle, one arrives at a modified Stokes equation

$$\varrho \frac{\partial \mathbf{u}}{\partial t} = \eta \nabla^2 \mathbf{u} - \zeta c \mathbf{u}, \quad (5)$$

where ϱ denotes the solvent mass density. This yields a modified hydrodynamic interaction $\exp(-r/\xi_H)/r$ with $\eta \xi_H^{-2} = \zeta c$, i. e. a screening length whose scaling ($\xi_H \propto c^{-1/2}$) differs from that of the static length ($\xi \propto c^{-\nu/(3\nu-1)}$). De Gennes [3] has however argued that, apart from prefactors, ξ_H and ξ should *coincide*. The physical essence of this argument is based on the observations that (i) the polymer chains *move*, and thus one cannot use a picture of fixed obstacles; that (ii) Zimm chains behave like rigid Stokes spheres, and thus *exactly oppositely* as fixed obstacles (i. e. embedded in the flow); and that (iii) the *entanglements*, i. e. the strong coupling of the chain to the temporary matrix, prevent unrestrained Zimm motion and rather tend to confine the blobs. Thus the physical objects which actually serve as obstacles to generate Darcy-type flow are the blobs. However, Stokes’ law implies

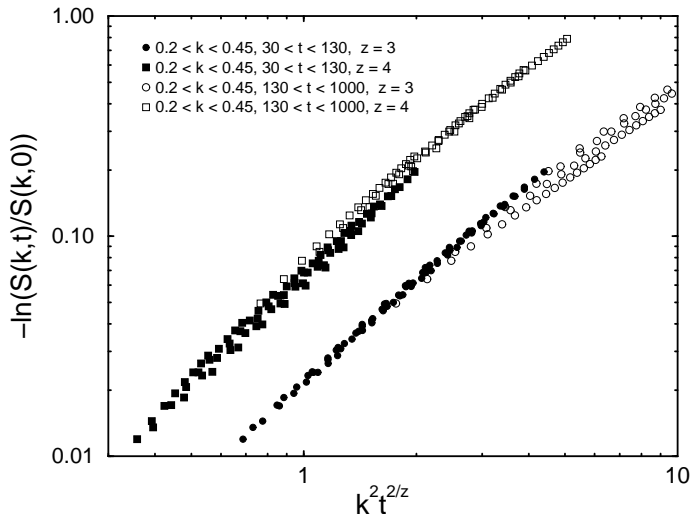


Fig. 1. $(S(k, t)/S(k, 0))$ in the RW regime $0.2 < k < 0.45$ with both Zimm and Rouse scaling, using a representation which emphasizes the short-time behavior

that the blob friction coefficient is $\sim \eta\xi$, while the blob concentration is ξ^{-3} . Thus, using the analogous reasoning as for fixed obstacles, one obtains

$$\eta\xi_H^{-2} \sim \eta\xi\xi^{-3} \sim \eta\xi^{-2}. \quad (6)$$

Furthermore, this picture necessarily implies that screening is an intrinsically *dynamic* phenomenon with a *time delay* before screening comes into play. This has so far not been noticed in such an explicit fashion. On time scales below the crossover time, which is just the Zimm relaxation time of a blob, $t_c \propto \xi^3$, a single test chain will simply not feel the surrounding chains. They just contribute to the overall flow. Only after t_c , the entanglements become (on average) important, such that the chain can no longer follow the flow. After that, there is a substantial velocity difference, which generates a counter flow or Darcy-type screening. The consequence is that the dynamics is Zimm-like as long as $t \ll t_c$, *regardless of length scales*, i. e. even for the RW regime $k\xi \ll 1$ (in the SAW regime $k\xi \gg 1$, i. e. within the blob, this is obvious). For $t \gg t_c$, the dynamics crosses over to Rouse-like motion; on these time scales the semidilute solution can be viewed as a Rouse melt of blobs.

Our large-scale simulation [4], which is the first to be able to study the dynamic crossover between Zimm and Rouse, supports these arguments. For the first time, the described time delay was not only observed, but also interpreted within the outlined picture. In our opinion, previous experiments, which indicated Zimm behavior on long length scales [5,6], have been interpreted incorrectly by not taking the time dependence properly into account. Thus we believe that a reasonably consistent description of hydrodynamic

screening has been obtained. Figure 1 shows $S(k, t)/S(k, 0)$, with k restricted to the RW regime, for both Zimm ($k^2 t^{2/3}$) and Rouse ($k^2 t^{1/2}$) scaling. Clearly there is a time-dependent crossover from Zimm to Rouse.

Our simulation method [7] is based on the following considerations: In order to resolve both the SAW and the RW regime, we need rather long chains. Guided by the idea that we should have at least 30 blobs of 30 monomers each available, we chose $N = 1000$. Furthermore, the desired blob size defines the concentration, while the condition of avoiding “wrap-back” conformations gives us the minimum size of the required periodic box, and the number of chains. We thus simulated a system of 50 chains. Directly implementing (1) is impossible for 5×10^4 Brownian particles, since in every time step one has to calculate the square root of a matrix of that size. We therefore explicitly simulate the solvent degrees of freedom. Doing this via Molecular Dynamics (i. e. by introducing many solvent particles around the chains) is again exceedingly difficult: Firstly, we found that Molecular Dynamics is roughly a factor of 20 slower than our algorithm [7], which is based upon coupling the polymer system to a stochastic Navier-Stokes background. More important, however, is the fact that the surrounding particles introduce a slight change in the chain conformations, compared to “vacuum”, while the Navier-Stokes background does not. Therefore, our approach allows us to equilibrate the polymer system *without* the solvent, and to use efficient Monte Carlo moves (slithering-snake moves on the scale of the blob) for that purpose. Only *after* equilibration the polymer system is coupled to the solvent, such that from then on the short-time regime of the dynamics can be studied. It was thus possible to observe the crossover from Zimm to Rouse, while running the polymer plus solvent system beyond the overall chain relaxation time would simply have been much too expensive. Our practical implementation uses the Lattice Boltzmann method as the Navier-Stokes equation solver. The lattice constant roughly matches the bond length, such that our largest lattice contains 88^3 sites. The coupling is purely dissipative, and based upon introducing a monomer friction coefficient. For further details of the method, and our results, see [4,7].

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