

# Computer Simulations of the Dynamics of Polymer Solutions

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## ABSTRACT

A method for simulating the dynamics of polymer–solvent systems is described. The fluid is simulated via lattice Boltzmann and the polymer chains via Molecular Dynamics. The two parts are coupled by a simple dissipative point–particle force, and the system is driven by Langevin stochastic forces added to both the fluid and the polymers. This method is applied to a semidilute system of chains of length  $N = 1000$ . We observe the crossover from Zimm dynamics at short length and time scales to Rouse dynamics at long length and time scales. Moreover, we find “incomplete screening”, i. e. Zimm–like behavior at short times but large length scales. This behavior can be nicely described in terms of the de Gennes picture, which explains hydrodynamic screening as a result of entanglements. An analogous simulation approach has been developed for electrostatics, where the interaction is described by a dynamic Maxwell field coupled to the system of charges. This method will be briefly outlined as well, with emphasis on the analogy between hydrodynamics and electrostatics.

## 1. Hydrodynamic Interactions: A Computational Challenge

Complex fluids like colloidal dispersions or polymer solutions are characterized by a huge difference in length scales and, even more importantly, time scales. The solvent particles are much smaller, and they relax much more quickly, than the solute. Indeed, for a single flexible polymer chain in dilute solution, the macromolecule’s relaxation time may be estimated by the scaling prediction of the Zimm model [1],

$$\tau_Z \sim \frac{\eta R^3}{k_B T}, \quad (1)$$

where  $\eta$  denotes the solvent viscosity,  $R$  the chain’s size (e. g. given by the gyration radius),  $k_B$  the Boltzmann constant, and  $T$  the absolute temperature. The underlying picture is a self–similar object relaxing on all length scales  $\lambda$ , where the corresponding relaxation time is given by  $\tau(\lambda) \sim \eta \lambda^3 / (k_B T)$ , implying a dynamic exponent  $z = 3$ . The longest relaxation time is given by the time which the object needs to move its own size, and this is in turn governed by its diffusion constant  $D$ :  $D \tau_Z \sim R^2$ . Equation 1 then follows from the fact that the chain behaves essentially like a Stokes sphere, as far as diffusion is concerned,  $D \sim k_B T / (\eta R)$ .

The important point for computer simulations is that Eq. 1 holds (approximately) for the solvent particles as well; however, the relaxation is much faster. Thus, a length scale ratio of, say, only ten would result in a chain relaxation which is

roughly one thousand times slower than that of the solvent particles, or of the monomers. Therefore simulations of polymer dynamics which aim at resolving the full spectrum of relaxation times between the monomer scale and the macromolecular scale are intrinsically expensive, and one would like to do this with a model / method which is as simple and efficient as possible.

The most striking observation is that for dilute systems there are many more solvent than solute degrees of freedom. Therefore the solvent should be reduced to its bare essentials, which are just needed to reproduce the chain dynamics correctly. The first important solvent property is the supply of thermal noise, such that one is tempted to just simulate the solute particles via Brownian Dynamics,

$$\dot{\vec{r}}_i = \frac{1}{\zeta} \vec{F}_i + \vec{f}_i, \quad (2)$$

where  $\zeta$  is the friction coefficient of monomer  $i$  at position  $\vec{r}_i$ ,  $\vec{F}_i$  the deterministic force, and  $\vec{f}_i$  the Langevin noise. However, this simple scheme does not take into account the *hydrodynamic interaction*, which is nothing but *highly correlated* motion of the Brownian particles, due to fast diffusive momentum transport through the solvent, and of paramount importance for dilute systems. These correlations are actually the reason for the Stokes-like behavior of the diffusion constant; without them one would obtain Rouse-like scaling  $D \propto N^{-1}$ , where  $N$  is the degree of polymerization. The so-called Schmidt number  $Sc = \eta_{kin}/D_m$ , i. e. the ratio between kinematic viscosity (which is the diffusion constant for momentum) and monomer diffusion coefficient, has typical values of  $10^2 \dots 10^3$  in dense fluids, and can safely be replaced by  $Sc = \infty$ . Therefore, one should replace Eq. 2 by

$$\dot{\vec{r}}_i = \sum_{ij} \overleftrightarrow{\mu}_{ij} \vec{F}_j + \vec{f}_i, \quad (3)$$

where the Langevin noise is now described by a huge correlation matrix, proportional to the mobility matrix  $\overleftrightarrow{\mu}_{ij}$ ,

$$\langle \vec{f}_i(t) \otimes \vec{f}_j(t') \rangle = 2k_B T \overleftrightarrow{\mu}_{ij} \delta(t - t'). \quad (4)$$

$\overleftrightarrow{\mu}_{ij}$  can be calculated from hydrodynamics [1] with various degrees of accuracy (Oseen-Tensor, Rotne-Prager-Tensor, etc.); the leading-order Oseen correlations are long-ranged, decaying like  $1/r$ . The Oseen tensor is nothing but the Green's function of the Stokes equation, in close analogy to electrostatics, where the Coulomb potential is the Green's function of the Poisson equation. This matrix has been a severe obstacle to Brownian dynamics simulations, since simple algorithms to treat it scale as  $N^3$ , where  $N$  is the number of Brownian particles. Recent progress has reduced this to roughly  $N \log N$  [2]; however, this complicated method has not yet found widespread use.

The “mesoscopic” approach instead resolves this problem by *keeping* the solvent degrees of freedom, but reducing them to just a means of momentum transport. Different methods (Navier-Stokes, Dissipative Particle Dynamics [3], Multi-Particle Collision Dynamics [4], lattice Boltzmann (LB) [5]) have been invented and implemented, and in the author's opinion they are all very similar both in terms

of philosophy and (probably) computational efficiency. Space restrictions do not permit to describe any of these here. For complex fluids, one then couples one such method to a particle description of the solute, making sure that the overall momentum is conserved. An important point is that the solvent should be *structureless*, in order to make sure that the static equilibrium properties of the solute are the same with and without solvent, such that the latter can be discarded for equilibration.

The method developed in our group [6] is based upon a simple LB description for the solvent, coupled dissipatively to a bead–spring system to describe polymers. The latter is described by the equation of motion

$$m\ddot{\vec{r}}_i = \vec{F}_i - \zeta \left( \dot{\vec{r}}_i - \vec{u}(\vec{r}_i) \right) + \vec{f}_i, \quad (5)$$

where  $\vec{f}_i$  is a standard Langevin noise, while  $\vec{u}(\vec{r}_i)$  is the solvent velocity at the particle’s position, obtained via linear interpolation from the surrounding lattice sites. The LB part is subjected to a fluctuating Langevin stress tensor, and external forces coming from the Brownian particles (these forces are determined via interpolating back onto the lattice, plus the condition that the overall momentum should be conserved). This system satisfies the fluctuation–dissipation theorem, and faithfully represents hydrodynamic interactions on sufficiently large length and time scales. The Schmidt number can be chosen as rather large (roughly  $0.5 \times 10^2$ ), by using a suitably large value for  $\zeta$ .

## 2. Hydrodynamic Screening in Semidilute Polymer Solutions

A semidilute polymer solution (in good solvent) is characterized by the so-called “blob size”  $\xi$  [7], which marks the onset of chain–chain interactions, and which governs *both* the static crossover from self–avoiding walk (SAW) statistics at small length scales to random walk (RW) statistics at large length scales, *and* the dynamic crossover from Zimm dynamics for small length scales to Rouse dynamics at large length scales. This latter crossover, which is usually referred to by the term “hydrodynamic screening”, had been poorly understood. An important landmark was the observation by de Gennes [8] that the screening is due to *entanglements*, which, in the present context, should however not be viewed as topological confining interactions as in reptation theory [1], but rather as the presence of chain–chain collisions. In this picture, the blobs are viewed as “hooked up” in a temporary gel, such that they provide Darcy–type friction to the solvent flow. Thus the viscous stress  $\eta \nabla^2 \vec{u}$  in the Stokes equation should be augmented by an additional term  $-\zeta_{blob} c_{blob} \vec{u}$ , where  $\zeta_{blob}$  is the friction constant of a blob, and  $c_{blob}$  the concentration of blobs. However, since  $c_{blob} \sim \xi^{-3}$ , and  $\zeta_{blob} \sim \eta \xi$  (Stokes), this term can also be written as  $(\eta/\xi^2) \vec{u}$ . Balancing this against the viscous stress, one finds a hydrodynamic screening length  $\sim \xi$ . Therefore, there are no hydrodynamic correlations beyond the length scale  $\xi$ , such that the dynamics should be Rouse–like there.

Our simulation data [9] show that this picture needs to be completed in terms of time scales. Though the Darcy picture of screening by the blobs turns out

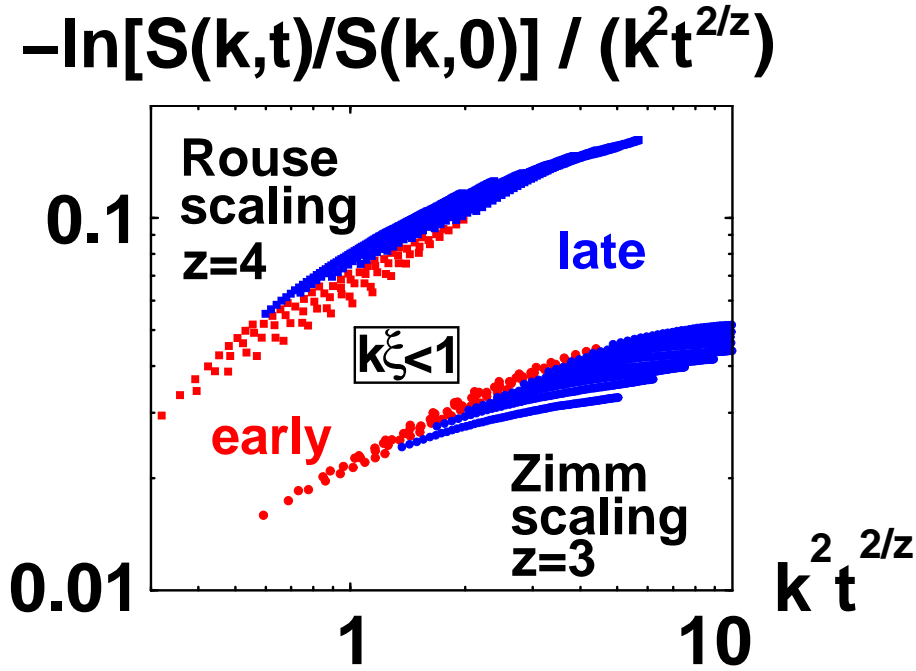


Figure 1: Single-chain dynamic structure factor  $S(k, t)$  for a semidilute polymer solution (replotted data of Ref. [9]). The wave numbers  $k$  are restricted to the regime  $k\xi < 1$ , such that only correlations beyond the blob size are probed. For pure Zimm scaling, the structure factor should be just a function of  $k^2 t^{2/3}$ , while it should only depend on  $k^2 t^{1/2}$  for pure Rouse scaling. The early and late times refer to those which are smaller or larger than  $\tau_\xi$ .

to be essentially correct, one nevertheless needs to take into account that the entanglements are not felt before the blob relaxation time  $\tau_\xi \sim \eta\xi^3/(k_B T)$ , which is the average waiting time until a chain-chain collision occurs. Before this time, an initial “kick” will just propagate throughout the system, and just drag the chains along. Therefore, the hydrodynamic interactions are *unscreened* on time scales below  $\tau_\xi$ , even on large length scales well beyond  $\xi$ . This completes the de Gennes picture, and explains the experimental observation of “incomplete screening” [10] in a straightforward way.

It should also be mentioned that this study was quite non-trivial with respect to computational demands: In order to resolve the SAW-RW crossover, and the Zimm-Rouse crossover, we needed roughly thirty blobs per chain, plus roughly thirty monomers per blob, such that we needed to simulate 50 chains of length 1000 in a box containing  $88^3$  LB lattice sites. This is the smallest system one can study for this problem.

### 3. Maxwell Equations Molecular Dynamics (MEMD)

For hydrodynamic interactions, we started from the observation that the  $1/r$  Oseen tensor is just the Green’s function of a dynamic field theory (hydrodynamics) in its

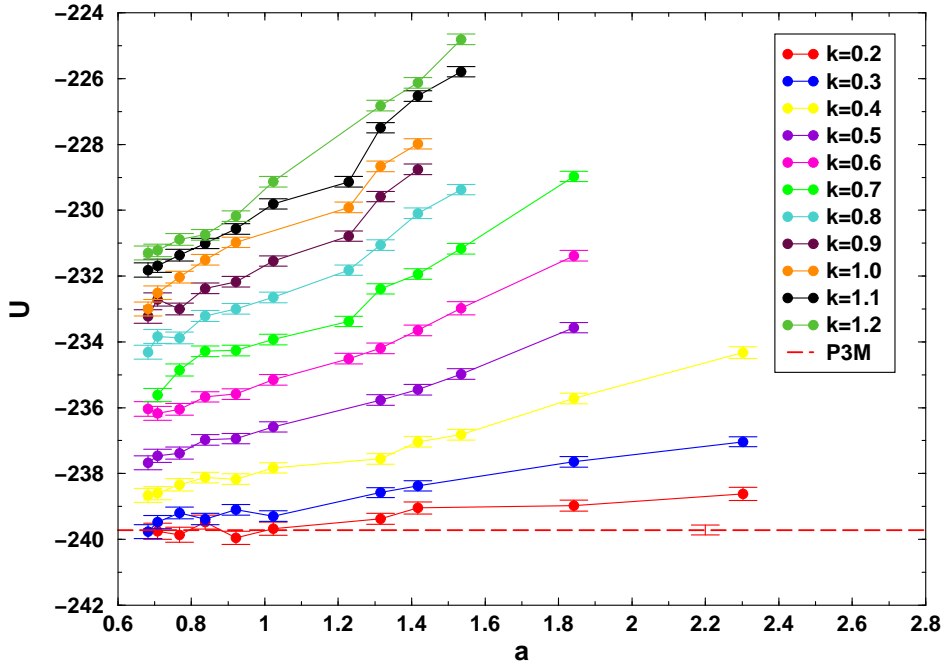


Figure 2: Electrostatic energy of a system of 4000 particles interacting via purely repulsive Lennard–Jones (LJ) interactions, and electrostatics. The Bjerrum length  $l_B = e^2/(4\pi\epsilon_0 k_B T)$  has the value 2.5 in units of the LJ parameter, which also defines the unit of length for the lattice spacing  $a$  (parameter of the abscissa), and the screening parameter  $\kappa$  of the artificial Yukawa field theory. The density has the rather small value  $10^{-2}$ . In the continuum limit  $a \rightarrow 0$ , the results all converge to the exact value, which was obtained by accurate P<sup>3</sup>M simulations.

quasistatic limit, and that we can construct an efficient algorithm by going back to the original dynamic field theory, i. e. by coupling the Brownian particles to the Navier–Stokes velocity field, such that the interaction comes about by propagation of the latter. Nothing prevents us from applying the same philosophy to the Coulomb interaction between charged particles, which we couple straightforwardly to a propagating Maxwell field. This idea has been put forward by A. Maggs, and also pursued by us [11] (see also references in there). Since the approach has been described in detail in Ref. [11], we wish to be brief, and just outline the main features:

- (i) Again the charges move in continuum space, while the electric and magnetic fields live on a simple–cubic lattice. (ii) The charges are linearly interpolated onto the nodes of the lattice, while current density  $\vec{j}$ , electric field  $\vec{E}$ , and magnetic vector potential  $\vec{A}$  are objects associated with the connecting links. (iii) This scheme allows a natural and straightforward discretization of the Maxwell equations. (iv) The discrete analogs of the continuity equation, and Gauss’ law, are satisfied within machine accuracy. (v) The equations of electrostatics  $\nabla \cdot \vec{E} = \rho/\epsilon_0$ ,  $\nabla \times \vec{E} = 0$  can be mapped onto a variational problem, where the electrostatic field energy  $(\epsilon_0/2) \int d^3\vec{r} \vec{E}^2$  is minimized under the constraint of Gauss’ law. This is analogous

to quantum–mechanical density functional theory, where the density functional needs to be minimized. (vi) Replacing the minimization by some Hamiltonian dynamics is exactly the approach of Car and Parrinello; MEMD can be shown to be formally very close related, with  $1/c^2$  ( $c$  speed of light) an adjustable mass–like parameter, whose value is irrelevant for the static averages in thermal equilibrium, while  $c/v \approx 20$  ( $v$  particle velocity) seems to be sufficient to also obtain reasonable dynamics. (vii) The distribution of particles onto lattice sites introduces an unphysical self–interaction, which however can be approximately (within time step errors) subtracted, using the appropriate lattice Green’s function. (viii) A combination with an artificial Yukawa–type field theory allows us to use the same trick as for Ewald sums, i. e. the interactions are evaluated directly in real space for short distances, while the Maxwell field propagation ensures proper Coulomb interactions on the larger length scales. (ix) With this trick, it is possible to treat dilute systems with a rather coarse grid, such that the method does not suffer from inefficiency even in this limit. (x) Preliminary benchmarks seem to indicate that the method is quite competitive with conventional electrostatics solvers like P<sup>3</sup>M, while having very advantageous properties with respect to scaling, parallelizability, and ease of implementation.

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