Hydrodynamic Interactions

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It is well-known that the dynamics of dilute polymer solutions is strongly influenced by hydrodynamic interactions, i.e. long-range dynamic correlations mediated by fast momentum transport through the solvent. For dilute polymer solutions of non-overlapping molecules, the internal relaxations are described by the single-chain Zimm model, which is confirmed by both scattering experiments and simulations. A similarly well-established fact is the Rouse-like behavior of dense melts (assuming that the chains are not too long such that no reptation occurs). The difference between Rouse and Zimm behavior is that hydrodynamic interactions are taken into account only in the latter. This means that there is a concentration-driven screening-out of the hydrodynamic correlations. Early it was understood that this must have to do with frictional resistance of the polymer system against the flow. For intermediate concentrations, in particular for semi-dilute solutions where the monomer concentration is low but the chains nevertheless strongly overlap, there is a crossover, which was not very well understood. An important milestone was the observation by de Gennes that the screening lengths for excluded-volume interactions and hydrodynamic interactions are identical (except for prefactors – this is the so-called “blob size”). Hydrodynamic screening was therefore mainly discussed solely in terms of length scales. However, neutron spin echo experiments, probing the dynamics of single labeled chains had observed the phenomenon of “incomplete screening”, i.e. an unexplained presence of Zimm-like signals for rather large length scales beyond the blob size. By means of a large-scale computer simulation using the method briefly sketched in the article „Computational Physics“, we were able to accurately calculate the single-chain dynamic structure factor in the semidilute regime, and, from these data, to elucidate the mechanism. A discussion in terms of only length scales is insufficient; rather one has to take into account both length and time scales. We found clear indication for Zimm-like behavior on length scales beyond the blob size, but restricted to the short-time regime below the blob relaxation time, which is essentially given by the time the blob needs to move its own size. The physical picture is that for short times the flow can spread throughout the system in an unhindered fashion, just pulling the polymers along. However, after the blob relaxation time, the system starts to feel that it is a temporary gel, and offers frictional resistance. This is fully consistent with the de Gennes picture, and completes it, while at the same time explaining the neutron spin echo results in a natural way.

Schematic representation of the mechanism of hydrodynamic interactions in polymer solutions: A moving monomer generates a flow field around itself, which propagates much faster than itself (momentum transport instead of particle transport). Other monomers feel this flow field, such that their dynamics becomes strongly correlated.
For dilute systems, we used accurate Monte Carlo and Brownian Dynamics simulations to clarify some questions of detail concerning the Zimm model. On the one hand, we estimated the universal limiting ratio between gyration radius and hydrodynamic radius for excluded-volume chains as 1.59, in excellent agreement with renormalization-group calculations. This analysis required to clarify the nature of the corrections to scaling.

Furthermore, we addressed the issue of the difference between short-time and long-time diffusion coefficient, which had been a subject of considerable debate (not even the sign of the correction remained undisputed). By large-scale Brownian dynamics, we could quantitatively verify the correctness of Fixman’s theory for the first time, and at the same time explain why previous simulations had failed to do so.

Normalized single-chain dynamic structure factor in a semidilute polymer solution, on length scales beyond the blob size, plotted such that data collapse occurs for either Zimm scaling ($z=3$, short times), or Rouse scaling ($z=4$, long times).

REFERENCES: