Dynamics of complex fluids in external flows and fields

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External fields modify the dynamics and morphology of suspensions. For example a suspension of β-amyloid – protein, which aggregation accompanies human diseases like Alzheimer disease or amyloidosis. In quiescent fluid in room temperature there is no aggregation. However, the introduction of the shear flow triggers the aggregation. The suspension aggregates quicker with increasing shear rate up to a certain point when it begins to slow down and eventually stops. Depending on the initial concentration of the particles the fibril shaped aggregates have different properties: for small concentrations (volume fraction below 1%) they are stiff while for large concentrations they are flexible. Similar behavior can be found among other biologically relevant proteins like insulin or albumin.

There are two main approaches to the measurements in protein aggregation experiments. Both bias the sample. Direct measurement can be carried with atomic force microscope after taking a sample from the suspension. Indirect measurement involves adding thioflavin-T to the sample. The thioflavin-T binds with fibrils and shows fluorescence. The interpretation of the measurements is simple – the more fluorescence the more fibrils, even though there is now knowledge about influence of thioflavin-T on the aggregation of proteins.

This dissertation aims to understand the mechanics of the aggregation process in the shear flow. Because the aggregation appears in various biologically relevant situations it is to investigate phenomena in as general way as possible with special accent on the influence of the hydrodynamic interactions.

Hydrodynamic interactions are mediated by the medium in which particles are suspended. They depend on the position of all particles in the suspension and result from the solution of the Stokes equation. Without hydrodynamic interactions the diffusion coefficient of the particles in the suspension would be independent of the particle position. For the suspension of spherical particles it is known how to solve the Stokes equation with arbitrary precision, however the numerical complexity of solution makes it useless for biologically relevant applications. There are various approximations present, among which the most popular is the Rotne-Prager-Yamakawa approximation. It assumes that particles are spherical and interact pairwise up to the first order in scattering series. A part of this dissertation was a generalization of Rotne-Prager-Yamakawa approximation for the overlapping particles with different radii and to write down the mobility matrices for Lees-Edwards periodic boundary conditions. The latter was essential to simulate suspension in a shear flow. Since the mobility matrices for the overlapping particles are known and remain positive definite there is no need for collision tracking in order to prevent overlaps. This accelerates the simulations.

The aggregation of the Brownian spheres in the dilute limit was analyzed. The time dependent aggregation ratio has analytical solution in the case without hydrodynamic interactions and without shear flow. With hydrodynamic interactions only a stationary aggregation is known without the shear flow and in the asymptotic limit of low shear rate and in the asymptotic limit of high shear rate. In the regime where advection and diffusion are comparable numerical methods are necessary. Based on Brownian dynamics simulations a phenomenological formulas for aggregation rate in the dilute solution as function of shear rate were proposed. The results of simulations were in good agreement with theoretical predictions.

A set of simulations of aggregating spheres and linear polymers were done in non-dilute regime. Polymers were constructed from five spherical beads connected with stiff harmonic potential for extension and pending to preserve linear shape. Particles interacted with each other with Lennard-Jones potential with depth only five times deeper than the energy of thermal fluctuations. There were two major classes of simulations: including hydrodynamic interactions in Rotne-Prager-Yamakawa approximation and neglecting hydrodynamic interactions.

The simulations of the aggregating spheres for the 1% volume fraction were in a good agreement with the dilute solution model both with and without hydrodynamic interactions. For 5% volume fractions additional effects appeared, that cannot be explained with dilute model such as rapid formation of spatially extended aggregates an then breakage into smaller ones of more globular shape. It was show that there is a different scaling of diffusion coefficient of an aggregate depending on the applied model of hydrodynamic interactions.

When the shear flow is introduced to the system the aggregates manifest qualitatively different behavior depending on whether hydrodynamic interactions are present or not. Without hydrodynamic interactions aggregates are formed in fibrils elongated in the direction of the flow, whereas with hydrodynamic interactions aggregates form rotating globules which become oblate for large shear rates. The

aggregation proceeds quicker when hydrodynamic interactions are present. Thus it was shown that investigating aggregation process or any process including multiple time and length scales without hydrodynamic interactions will likely give qualitatively wrong results.

The shape and stability of aggregates was investigated further. An analytic model was proposed that explained both shape and stability of the aggregate. It was shown that in case of weakly interacting particles the stability of the aggregate grows with its size and decreases with the shear rate. The growth of stability is a result that is qualitatively different to strongly interacting particles. When stiff structure is formed, internal tensions build up with the particle size and eventually the aggregate cracks.

It was shown that described above behavior is universal in the sense of monomer shape. All the phenomena observed for spheres were also present for linear polymers. Furthermore once aggregate become big enough to cover the details of single particles the systems become indistinguishable in all aspects but stability which is higher for polymers that have multiple interaction centers. This means that the results ca be applied to multiple length and time scales thus to multiple stages of aggregation. The only restriction is that particles have to interact weakly.