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BROWNIAN DYNAMICS SIMULATIONS OF COLLOIDAL PARTICLES AND POLYMER CHAINS WITH HYDRODYNAMIC INTERACTIONS

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This thesis presents the development, implementation, and results of numerical simulations carried out to investigate the behavior of complex fluid dynamic systems in the field of polymer and colloid science.

In the first study, Brownian Dynamics (BD) simulations have been employed to investigate the process of ultrasound-induced scission of polystyrene polymer chains, provide a comparison of the chain breakage caused by extensional flows and ultrasound, and develop a quantitative model of the process. The results of a typical simulation of fracture kinetics of polymer chains in elongational flow show that the rate of scission follows a sigmoidal trend on molecular weight, fitted with a 3 parameters semi-empirical model, the coefficients of which depend on the shear rate according to power laws. During ultrasonication, central scission occurs only for highly stretched configurations, and longer chains often result in broader distributions and partially uncoiled conformations. The scission mechanism follows the model suggested by Okkuama and Hirose and is consistent with experimental results.

In the second and third study, the aggregation dynamics of colloidal particles exposed to shear flows and gravitational fields have been investigated by means of BD simulations with long-range Hydrodynamic interactions among the particles, modeled with RPY tensor applying the PSE algorithm. It has been observed that long-range hydrodynamic interactions are essential to capture the fast aggregation rates induced by the increase in sedimentation rate of clusters with increasing mass, which manifests with an explosive-like cluster growth after a given induction time. It was also observed that, as the Pèclet Number increases (i.e., the intensity of the sedimentation), the anisotropy of the resulting clusters decreases, suggesting that denser clusters with spherical-like morphology are formed due to cluster breakage and restructuring. In shear flows, the increase in Péclet number (i.e., in the shear rate), leads to an overall increase in the aggregation rate and the formation of large aggregates that, for sufficiently high volume fractions, rapidly grow, leading to either breakup and restructuring phenomena or percolation of the system. In some cases, a bimodal distribution of the cluster population was observed. Our simulations further indicate that at the highest Péclet, the aggregation dynamics is independent of the energy barrier and entirely controlled by shear. A comparison with a simple BD method reveals that neglecting long range hydrodynamic interactions leads to a substantial underestimation of the aggregation rate.

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