Dynamics of Network Fluids

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Abstract

Network fluids are structured fluids consisting of chains and branches. They are characterized by unusual physical properties, such as, exotic bulk phase diagrams, interfacial roughening and wetting transitions, and equilibrium and nonequilibrium gels. Here, we provide an overview of a selection of their equilibrium and dynamical properties. Recent research efforts towards bridging equilibrium and non-equilibrium studies are discussed, as well as several open questions.

Keywords: Network fluids, Dynamics, Non-equilibrium

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1. Introduction

Structured fluids are fluids where the particle-particle correlations extend beyond the molecular scale. Prototypical examples are suspensions of colloidal particles, where the interactions between particles lead to the formation of mesoscopic structures that determine the physical properties of the system (e.g., rheological properties). Among the structured fluids are network fluids, where the anisotropic particle interactions lead to the formation of dynamical network-like structures consisting of chains and branches that are much larger than the individual particles [1, 2]. Such fluids exhibit exotic phase diagrams, including reentrant liquid-vapor or wetting transitions and low density (empty) liquids [3, 4, 5]. Examples of network fluids include, suspensions of cross-linked polymers [6, 7], and dipolar [8, 9, 10, 11, 12], Janus [13, 14, 15, 16, 17, 18], and patchy [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 55, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51] particles.

Here, we review some of the equilibrium properties of network fluids and focus on their dynamics. We discuss both the bulk [3, 57, 58] and interfacial properties [31, 59, 13]. The manuscript is organized in the following away. The interfacial properties of network fluids are discussed in Sec. 2, including self-assembly on substrates and at interfaces. The submonolayer regime is the focus of Sec. 3. In Sec. 4, the bulk properties are discussed. Experimental and theoretical works on the use of programmed annealing cycles to overcome kinetic barriers are discussed in Sec. 5. Finally, a few concluding remarks are made in Sec. 6.

2. Interfacial properties

The equilibrium and non-equilibrium properties of network fluids close to substrates or interfaces depend on the anisotropy and strength of the interactions, the temperature, and, for non-equilibrium, the overall dynamics. In one example, combining equilibrium Monte Carlo (MC) simulations and density functional theory (DFT) for three-patch colloidal particles near a hard wall, it was found that a contact region of higher density is formed close to the wall, whose maximum density depends on the temperature and bulk density [66]. At high bulk densities, the contact density decreases monotonically with the temperature, as an increase in the bond probability favors a decrease in density, due to the formation of a low density liquid. At sufficiently low bulk densities, the dependence of the contact density on temperature has a minimum at an intermediate temperature, as for very low temperatures, the bond probability approaches unity and an ordered, fully connected, quasi-2d structure is formed near the wall that sets a lower bound for the contact density [66].

The feasibility of the equilibrium structures will depend on the dynamics of self-organization of the colloidal particles. As particles start to aggregate, mesoscopic structures are formed becoming the relevant units for the dynamics at later times. Investigations of the dynamics are non trivial as they involve a hierarchy of processes at different time and length scales [67]. The first studies of patchy colloidal particles on substrates considered the limit of irreversible bond formation, where bond breaking is neglected within the timescale of relevance [68]. Performing kinetic Monte Carlo simulations of a stochastic model, it was shown that the structures depend strongly on the mechanism of mass transport [69], number of patches [70], and flexibility of the bonds [71]. For multilayer growth, due to the irreversible nature of the aggregation, for diffusive transport the structure is fractal, resembling that of Diffusion Limited Deposition, while for ballistic transport, the structure is found to be self-affine [69].

Recent studies of the irreversible growth of patchy colloidal particles have uncovered phenomena such as rough-