From intermolecular interactions to self-assembly, phase behaviour and rheology in colloids: a bottom-up approach

A number of macromolecular and (bio)colloidal systems have emerged as potential candidates to be used as building-blocks in the synthesis of materials by design. The ultimate goal is to achieve a perfect control over the internal architecture of the material, and its final properties, by tuning the physico-chemical interactions among building blocks (e.g. charge, weak attractive interactions, directional anisotropic interactions etc.). Biological molecules such as DNA and proteins are most studied as candidate building blocks due to the high selectivity of the intermolecular interactions and the variety of physic-chemical parameters they offer for the structural tuning. However, a big fundamental question remains in the background of these important experimental efforts: is there a unifying framework that can guide us from the judicious choice of the microscopic parameters to the final multi-scale structure and properties?

In this talk I will present a possible answer to this question, based on a bottom-up approach that involves a nonequilibrium description of molecular self-assembly. Microscopic intermolecular interactions control the emergence of mesoscopic structures through self-assembly. The large-scale structure in turn controls the macroscopic mechanical behaviour of the colloidal/macromolecular system. Connecting this hierarchy of levels into a single bottom-up framework is challenging. Master kinetic equations are used as a general tool to describe the emergence of mesoscopic structures in time, for different physico-chemical conditions. A single topological parameter, in terms of a multi-fractal dimension, can be implemented in the master equations. A unifying framework is thus obtained which enables us to predict which type of aggregate morphology emerges from a certain molecule under given physico-chemical conditions. The analytical scheme has been successfully tested on the self-assembly of insulin where different (amyloid) aggregates, such as filaments rather than giant micelles (spherulites) or amorphous structures, are formed depending on charge, salt and pH conditions [1].

The solutions to the master equations can be used within linear viscoelasticity to infer the distribution of relaxation time scales in the system. A bridge is therefore built between the molecular-level self-assembly process and the rheological response, which can be predicted [2]. This approach retrieves power-law rheology at the gelation transition, in a fully bottom-up manner. It provides a theoretical description which for the first time is in good agreement with experiments on attractive colloids with tunable attraction energy [3]. Also, it naturally bridges chemical gelation and physical gelation in a single framework as limiting cases.
The approach can be extended also to field-induced self-assembly and gelation, such as shear-induced aggregation/gelation processes [4] which are of great importance for the chemical industry.

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