Self-Assembly via Anisotropic Interactions.
A.C. Newton

Summary

Self-assembly, the non-dissipative spontaneous formation of structural order spans many length scales, from amphiphilic molecules forming micelles to stars forming galaxies. This thesis mainly deals with systems on the colloidal length scale where the size of a particle is between a nanometer and a micrometer. As such, this thesis focuses on the self-assembly of colloidal particles made in the laboratory forming supracolloidal structures in a capillary and making the link to proteins forming complexes or virus shells. Whereas retrosynthetic analysis gives a handle on how atoms form molecules and subsequently how molecules form even bigger molecules, similar design principles are lacking for assembling micrometer particles. Last decade has witnessed great advances in the synthesis of micrometer particle building blocks. It is currently possible to make colloids anisotropic in shape, or anisotropic in surface properties, so-called patchy particles. Patchy particles show great promise in the design of new building blocks, possibly applicable in novel functional materials. Moreover, patchy particles have also shown to be good models for globular proteins. This thesis discusses mainly two topics using advanced computer simulation techniques. The first part of this thesis deals with the extraction of an effective potential for anisotropic colloidal dumbbell particles interacting through the critical Casimir force. The second part deals with how the kinetics and mechanism of formation of simple colloidal or protein structures are influenced by changing the interaction between or the dynamics of patchy particles.

In chapter 3 a modeling study is presented to understand experiments performed on colloidal dumbbells submersed in a binary liquid which self-assemble via solvent mediated interactions when the critical point is approached, the so-called critical Casimir forces. We define a new correlation function that characterizes the local structure of anisotropic colloids. Instead of the site-site radial distribution function, important in the RISM theory for molecular liquids which we also apply to colloidal dumbbells, we define a minimum distance radial distribution function which excludes contributions of trivial neighbors that obscure the signatures of the interaction. A framework is presented where via matching experimentally obtained correlation functions to correlations functions obtained through Monte Carlo simulation using a simple model for colloidal dumbbells interacting through critical Casimir forces, an effective potential is extracted. We find that the ex-

tracted potential, even though it is based on a very simple model, can reproduce the correct morphologies as seen in microscopy images, can predict the onset of aggregation and at the same time give an explanation for the sudden collapse of a network structure made of colloidal dumbbells very near the critical point.

The second part of this thesis studies the colloidal self-assembly mechanisms and rate of (dis)assembly and thus requires the rates and pathways for all possible dissociation and association events in the kinetic network. However, on the time-scale of the dynamics of the microscopic particles, binding and certainly dissociation processes are usually rare events due to high free energy barriers caused by strong directional binding. As straightforward dynamical simulation is extremely inefficient, in chapters 4 through 6 we employed the Single Replica Transition Interface Sampling (SRTIS) algorithm to collect all possible (un)binding trajectory ensembles relevant to the patchy colloid assembly.

In chapter 4 we investigated how varying the ratio between rotational and translational diffusion influences the equilibrium kinetic network for small self-assembled clusters of colloidal patchy particles. Already for the dimerization of a 1-patch particle or a 2-patch particle an effect of the rotation is found on the formation dynamics. The (dis)association mechanism moves from a pathway along more translational degrees of freedom, to a more unconcerted pathway along rotational degrees of freedom upon increasing the rotational diffusion from ten times slower to ten times faster normal Stokes-Einstein conditions. We have also studied a tetrahedron system of a 3-patch particle where metastable states are possible. For the unconstrained tetrahedron, the entire nine-state kinetic network was sampled, and we demonstrated that a change in the rotational diffusion shifts the preferred self-assembly pathways significantly. While for low rotational diffusion the overall rate of tetrahedron formation decreased, frustrated states are avoided, leading to significantly less kinetic trapping. Including the interplay between rotational and translational diffusion in the self-assembly design of new supra-colloidal structures could open up new opportunities for controlling the bottom-top synthesis of functional materials. Moreover, this work helps to understand how rotational diffusion influences self-assembly processes in naturally occurring crowded environments such as the biological cell.

In chapter 5 the effect of multivalency is studied in the self-assembly of patchy particles. We found that multivalency has a trivial way of influencing the thermodynamics of binding and the associated kinetics, namely that for a fixed patch binding interaction the binding constant increases exponentially with the binding strength. When the bond strength is fixed, the kinetics also is very dependent of the multivalency, with dissociation rates exponentially lower with the number of bonds. Alternatively, when the total bond energy is kept constant, association and dissociation is rather independent of multivalency, although of course very dependent on the total energy. The association and dissociation mechanism however depend on the presence and nature of the intermediate states. For higher five-fold multivalency, the intermediate states are relatively avoided with respect to particles with only three bonds. Such intermediate state can lead to kinetic trapping, and malformed aggregates. We showed that the intermediates have an effect on

the overall association or dissociation process and as such the mechanism.

In chapter 6 we investigated the effect of one additional non-productive binding site on the association/dissociation rate as well as the effect of adding nonspecific isotropic interaction. The effect of the depth as well as the position of the decoy site on the binding kinetics is studied, and it is found that stronger decoy state always reduces the association as the pathway between target and decoy state is less probable than unbinding. In contrast, adding a non-specific isotropic interaction in general increases the association rate at low decoy site interaction, and the amount of reduction then does depends strongly on the position and strength of the decoy site. For weak/intermediate decoy strength, there is hardly an effect of the position, whereas for strong decoy position away from the target site, the association is suppressed. We also studied the effect of non-specific decoy binding on particles forming complexes. Adding a non-specific isotropic interaction to a multivalent particle forming a tetramer complex with an already formed trimer of particles, increases the rate of binding and dissociation at first, but when the isotropic interaction rises above 4 kT the rate lowers dramatically. This maximum in association rate also changes with concentration, shifting to higher values of nonspecific isotropic interaction. While one would think that this cluster binding is almost identical to the two particle binding with decoy, the cooperativity of binding multiple particles creates qualitative different behavior.