Abstract:
We have developed a method to produce well-defined, lithographically-designed, non-spherical colloidal particles. We demonstrate here that the formation of highly anisotropic structure in a model system of Brownian cylindrical particles can be achieved by precisely controlling DLVO and depletion interactions, as well as the surface properties of the particles.

Summary:
We developed the use of direct lithography to form colloids of well-defined, non-spherical structure (Figure 1A - [1]). By fully characterizing the relevant physical properties (size, shape, density, surface charge and structure, dielectric properties) of these new polymeric particles, we have established them as a model colloidal system for fundamental studies.

Over this past year, we have exploited this colloidal system to elucidate the roles of global shape, surface roughness, and adsorbed layers of polymers in defining particle-particle interactions (electrostatic, van der Waals, and depletion). Via characterization of the near-equilibrium, structural states of aggregates in well-defined dispersions of these particles, we have established that the degree of complementarity of both global curvature and roughness of the interacting surfaces can have significant impact on the strength of interaction. Of particular interest, we have shown that the combination of global curvature and roughness can strongly modulate interactions (both van der Waals and depletion): flat, smooth surfaces interact strongly under conditions at which curved, rough surfaces on the same particles do not.

Based on this phenomenon, we have grown extended, linear “polymers” of cylindrical particles (Figure 1B); such orientational selectivity of interactions is unusual on the colloidal scale. We have adapted a statistical thermodynamic model based on Wertheim Perturbation Theory to treat these linear aggregates. Application of this model to our experimental data allowed us to quantify the role of roughness in defining the interparticle “bond” energy (Figure 1C - [2]).

This study points to future developments in both fundamental colloid science and applications. The ability to form well-defined colloidal particles by direct fabrication opens the possibility of incorporating functional materials (e.g., silicon and III-V compound semi-conductors) and shapes that are not accessible via synthetic routes into building blocks for self-assembly. The identification of selectivity based on shape and surface roughness provides a general rule for the design of particles that could assemble into non-close packed structures. The apparent importance of roughness in our experimental system suggests that tuning this surface feature might allow one to define the selective interactions in the absence of complementarity of global shape: e.g., smooth patches on an otherwise rough sphere could act as directionally selective binding sites.

Finally, the development of well-defined dispersions of non-spherical colloids provides interesting new targets for simulations and theories of self assembly.
References:


Figure 1: Self assembly of non-spherical colloids. (A) Electron micrograph of colloids formed lithographically. (B) Optical micrograph of colloids as in (A) assembled into colloidal “polymers.” (C) Free energy of end-to-end interactions, in linear aggregates as a function of concentration of soluble polymer, (d, and ionic strength, I [mM]).