"Self Assembly of Magnetic Nanostructures and Related Enabling Technologies" (NSF 0103587). PI: Weili Luo, University of Central Florida (UCF), Co-PI: Zeev Rosenzweig (Univ. of New Orleans), David Tomanek (Michigan State University), Aniket Bhattacharya (UCF), Kevin Belfield (UCF).

This multi-disciplinary project unites researchers from physics, chemistry, and biology to work synergistically on a coherent project that involves one basic concept, the development and synthesis of novel materials from self-assembled magnetic nanostructures whose configuration and/or functions can be tuned and controlled by external fields. We will demonstrate that, by understanding physical mechanism of self-assembly and field-controlled phenomena and by bringing together two frontiers of the new century---the nanoscale science and the field of soft matter, we will be able to develop functional materials that enable new technologies ranging from memory devices, drug delivery agents, field-controllable nanomachines, magnetically actuatable polymers, and other liquid, gel, or solid devices.

In the past one and half years after we got NSF NIRT grant, we have synthesized new magnetic nanostructures and engaged in studying physical properties of them. Both experiments and computer simulations were performed. Here we give a summary to our preliminary results.

A. Experiments: One of the main challenges in synthesizing and studying the self-assembled magnetic nanostructures is to understand and control the coating by surfactants or polymers on the solid nanoparticle surface. In the past, very little *direct* information is known about the *grafting number*, defined as the number of surfactant molecules adsorbed per surface area on the nanoparticle, which is responsible for the repulsion between particles, thus the stability of the nanocolloids that are precursors for many self-assembled nano- to mesoscopic structures. We investigated the effect of coating process as function of the adsorption temperature and the concentration of surfactant by using a modified co-precipitation method, where the Fe_3O_4 precipitates formed in the presence of the surfactants. We found that that the grafting number of surfactant-coated nanoparticles can be *designed* to improve the stability of magnetic nanocolloids or biocompatible magnetic fluids [1].

The different coating with a polymerizable surfactant shells was also studied [2]. Their suspension in a particular fluid is promoted by the adsorption or reaction of steric or electrostatic stabilizers, which are appropriate for the particular medium. Critical to the success of these magnetic fluids is the development of the steric stabilizers, which must prevent the coagulation of the metal particles. The "anchor" block of a tri-block polymer surfactant is designed to strongly adsorb onto the particle surface, and the "tail" block extends outward into the fluid, which prevents aggregation of the particles. Cyano groups have an established affinity for metal particles and can serve as a suitable functionality in an "anchor" block.

The understanding of the adsorption of organic molecules on the surface of magnetic nanoparticles helps to develop the next level of hierarchy of the self-assembled structures. We hypothesized that coating the clusters with a phospholipid bilayer will improve their stability and structural integrity and make it possible to use them for triggered drug release in aqueous media and biological fluids. We have used different synthetic techniques to prepare the bilayer coated submicron magnetic clusters:

a) Encapsulation of the synthesized clusters in liposomes by dialysis [3].
b) Direct coating of the magnetic clusters with phospholipids[4]

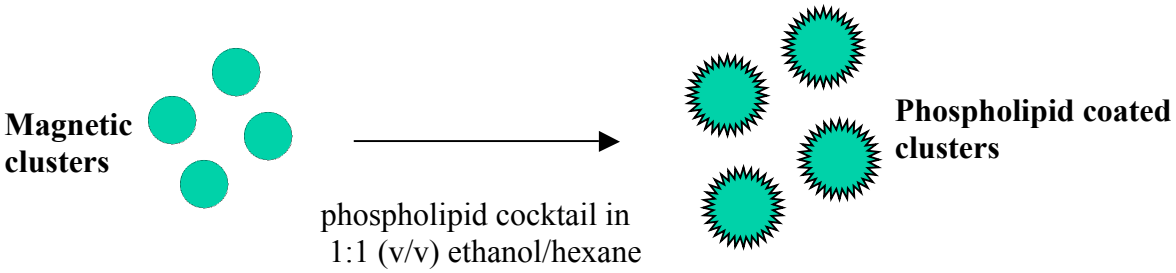


Fig.1

c) biocompatible magneto-vesicles with two different surfactants

We have used two surfactants DOPE and DDAB to prepare vesicles and magneto-vesicles (vesicle with a magnetic core). This structure is designed to specifically work in human body so can be used as drug delivery agent without harmful effect [5].

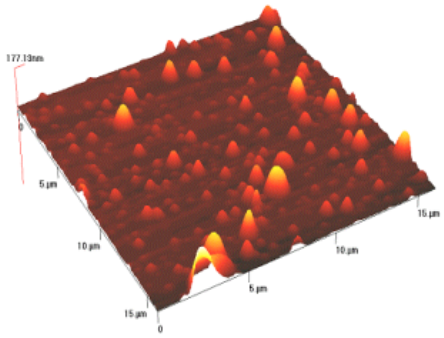


Fig. 2. AFM image of magneto-vesicle.

B. Computer simulations: Simulation can provide deeper and fundamental understanding of complex structures that arise in the context of ferro-colloid self-assembly. Three aspects magnetic colloids have been studied by simulation.

1). Polymer depletion interaction between a colloid particle and a wall: In order to tailor patterns of various colloidal aggregates, which is a key thrust component of this project, it is rather important to know the effective interaction among different segments. We carried out dynamic MC simulation[i] to find that for large colloid particle and polymer size ratio the effective force between the colloid particle and the wall is attractive as depicted below [6].

2) Role of head group geometry in amphiphilic-colloid aggregates [7, 8]**:**

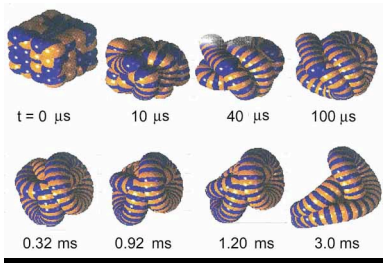
The second part of our studies deals with head group geometry of the amphiphile affects the self-assembly of surfactant-colloid aggregates. The simulation is designed to mimic the actual experiment. For larger head groups we find that the appearance of the Critical Micelle Concentration (CMC) is much sharper. We also find that the addition of a screened Coulomb (SC) interaction among the heads only produces a narrower cluster distribution and effectively raises the CMC to that of a higher temperature.

We have also studied the cluster distribution and the shape of each cluster for a variety of different combination of chain lengths, concentration, and head group geometries and corresponding cluster size distribution was found.

3). Magnetic field effect on self-assembly of magnetic nanoparticles [9, 10, 11].

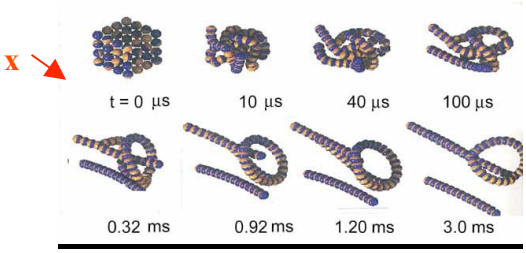
The initial configuration for the MD simulation was a 4x4x4 crystal structure of magnetic dipole particles with a random spin orientation. The structural evolution is represented by snap-shots, for different values of the applied field. In the following, the field is applied along the x-direction.

No external magnetic field



The system becomes stabilized as a double-ring like structure, when there is no magnetic field.

H = 100 Gauss



We find that there are structural transitions from rings to chains, depending on the strength of the external field. When exposed to a very high magnetic field (1000 Gauss, above), the system prefers to be a multi-chain structure, consistent with experimental results.

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