

Directed Assembly of Nanostructures: Theory, Simulations and Experiments in Hard and Soft Materials

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The aim of this NIRT project is to investigate, within a unified theoretical and experimental approach, the microscopic mechanisms of field-assisted aggregation in both hard (metal alloy) and soft (colloidal) material systems. The use of external fields to direct micro- and nanostructural evolution is a very promising avenue for achieving precise control of aggregation [1,2,3] that in turn opens up new directions for fabricating novel structures. The two material systems of interest in this project are complementary. While the colloidal system is easier to probe experimentally, the atomic (or particle) interactions in some metallic systems are better characterized from a simulation point of view because of the absence of hydrodynamic interactions and complex morphologies on the particle surfaces found in the colloidal system.

Aggregation in Soft Material Systems (DNA-Mediated Colloidal Interactions)

In this thrust, we are pursuing two simultaneous efforts related to better understanding of the aggregation physics of DNA-coated micron-scale polystyrene colloids. In this system, specially designed single-stranded DNA chains are attached to the colloidal particles via a polyethylene glycol (PEG) spacer layer. The single-stranded DNA chains bind to each other via a DNA linker strand present in solution, collectively resulting in a tunable and reversible interaction (see Fig. 2). The functional form of this interaction is qualitatively similar to the well-known depletion interaction, which provides a convenient theoretical starting point.

Using this system, Crocker has recently demonstrated reversible aggregation [4]. Under appropriate driving force conditions (controlled by the temperature), the clusters exhibit close-packed structures as shown in Fig. 2(b). The reversibility of the aggregation is demonstrated in Fig. 2(c). Current efforts in this area are aimed at extending this successful result to binary systems in which two different DNA sequences 'A' and 'B' are used to coat the particles so that A and B particles have a weak attraction to each other, while A-A and B-B interactions are purely repulsive. Such binary systems have been postulated to exhibit complex phase behavior with many novel alloy structures [5].

Exploring the large phase space associated with binary systems is a formidable experimental challenge. Even in the single component system, the relatively slow dynamics associated with aggregation limit the exploration of optimal interactions and we are using this as a starting point for our complementary simulation studies. An important feature of the experimental studies is the ability to directly measure the interaction pair-potential between two colloidal particles that can be used as direct input into Monte Carlo and Brownian Dynamics simulations of the crystallization process [4]. We are implementing efficient Monte Carlo based approaches that will allow us to investigate crystallization phase diagrams as a function of pair potential features, such as well-depth and interaction range. Given the short-range of DNA-mediated interactions, we are beginning our investigations by using the hard-sphere system as a reference point. We will then map out the effects on the phase diagram that result from the DNA-mediated interactions in the single component system and then will extend this work to binary systems. In future work we will consider heterogeneous nucleation sources such as corrugated surfaces.

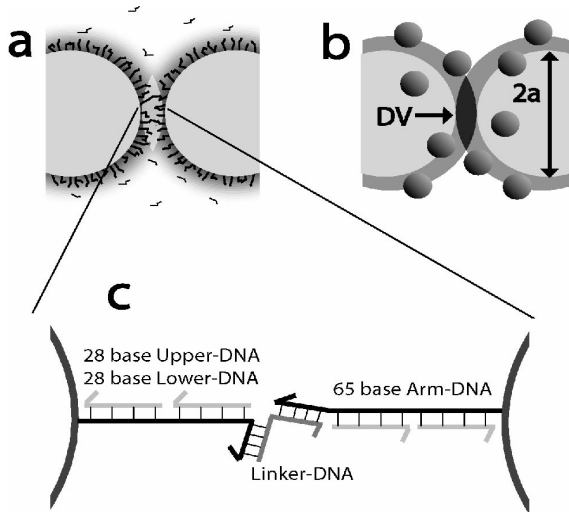


Fig. 1: Schematic representations of: (a) our DNA-mediated self-assembly system. (b) the entropic depletion attraction, which yields a similar attraction. (c) 65 nucleotide long Arm-DNA grafted to the particles. Upper-DNA and Lower-DNA provide extra persistence length. Linker-DNA allows 2 arm-DNA strands to crosslink.

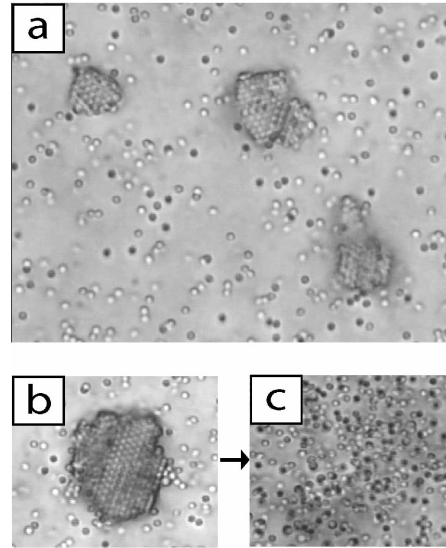


Fig. 2: (a) Close-packed crystal structures assembled using the DNA-grafted PEG-ylated particles with $\sim 4,000$ DNA/particle. When the crystallized samples were heated up to 50°C , large crystals (b) completely redispersed (c) in less than 10 seconds.

Strain-Directed Aggregation in Hard Material Systems (Metal Alloys)

The interaction between lattice strain and diffusion and aggregation of atoms is a highly promising avenue for control of the evolution of the microstructure in hard crystalline materials. We are studying this process using coupled experimental and theoretical approaches. Our experimental system has now been designed and is shown schematically in Fig. 3. The key steps include: (1) deposition of a thin alloy film on a hard substrate, (2) deposition of a hard tungsten ‘capping’ layer on top of the alloy film or a bulk alloy sample, (3) heating the sample above the solvus temperature into single phase region, (4) applying a patterned load to the sample, (5) quenching to form aggregates in desired arrangements, and (6) aging to form nano-precipitates.

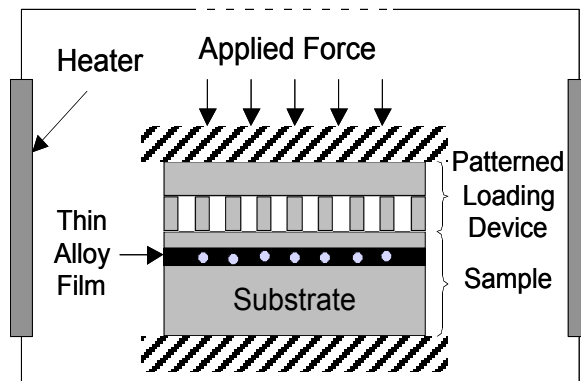


Fig. 3: Idealization of apparatus for imposing patterned stress fields on a thin metallic alloy layer.

Based on phase diagram analysis of microstructure and the requirements for epitaxial deposition, we have chosen five candidate aluminum alloy systems: Al-Mn, Al-Cu, Al-Mg, Al-Si, and Al-Ag. We now have an operational dual head sputtering system for deposition of metal alloy films, and have purchased Al-Ag sputter targets for thin film alloy deposition, sapphire and rock salt substrates, as well as a tungsten target for the capping layer. As part of our industrial

outreach efforts we are also pursuing the procurement of highly pure bulk samples of these five alloy systems from Alcoa for performing complementary studies such as four-point bending experiments. These will allow us to produce uniform strain fields to identify the basic relationships between strain and aggregation.

The processed films will be characterized initially with Orientation Imaging Microscopy (OIM). This is a scanning electron microscopy (SEM) based method. The samples will also be compositionally analyzed using X-ray fluorescence and electron energy loss spectroscopy. We have identified suitable furnaces for the thermal processing and found the expected loading required to create aggregates without inducing plastic deformation. We are in the process of designing a spring-loaded clamping device to apply loads in this range.

Computational work in this area has been focused on the development of physically realistic continuum phase-field models. An example of phase-field model results for an idealized representation of our experimental system is shown in Fig. 4, in which eight loading points are applied to an initially homogeneous thin-film. The snapshots show the increasing tendency for the solute to aggregate in the regions immediately below the compressively stressed areas (yellow and red regions).

Once the basic mechanistic representations of the aggregation physics have been captured, the phase-field models will be interfaced with large scale empirical molecular dynamics simulations and Density Functional Theory calculations to provide more realistic continuum representations that can then be compared directly with experimental measurements.

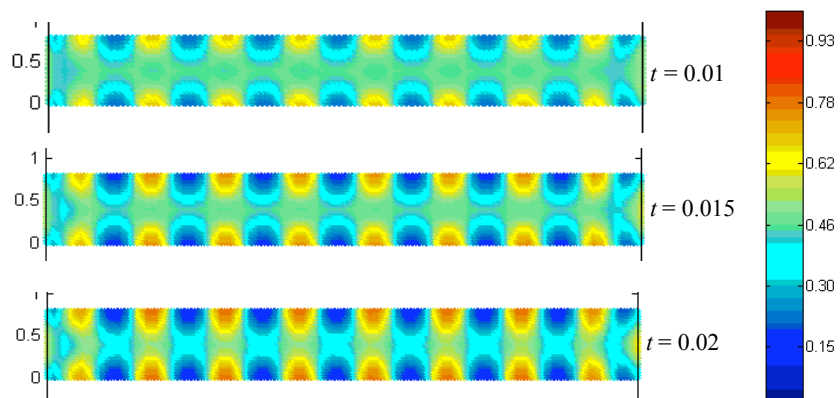


Fig. 4: Phase-field model predictions for a solute aggregation under patterned loading. The behavior is driven by elastic interactions between the solute-lattice mismatch and the applied field.

We are in the process of consolidating existing results from this project, relevant literature, and contact information for the project personnel into a dedicated website.

References

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