Modeling and simulation of soft-particle colloids under dynamic environmental gradients

UNM

Sandia National Laboratories

Intro

➢ Directed assembly of soft-particle colloids is a bottom-up production method for nano-electronics, photonic devices, sensors/assays, bio-conjugate devices, and ***functional coatings***. *In this work we direct with drying and irradiation of coatings!*

➢ Nanoparticles coated with bio-polymers are solvated and undergo hydrophilic / lithographic patterning, evaporation, irradiation processing to produce controlled nanoscale features. Colloids can also allow greater resolution in lithography.

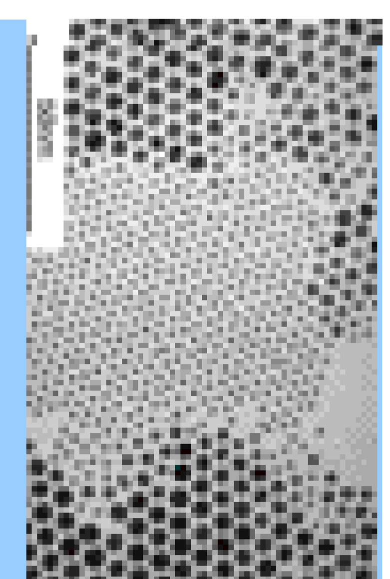
➢ Our simulation method is versatile and easily modifiable. Bio-polymer and solvent interactions are course-grained to enable micron-scale simulation box sizes. We can correlate to experiment and parametrize order in several ways.

Colloid Simulation

Outcome of *Nanoparticle Flow Project Consortium*: Production Computational Tools for

-Rheology of Nanoparticle Suspensions[1]

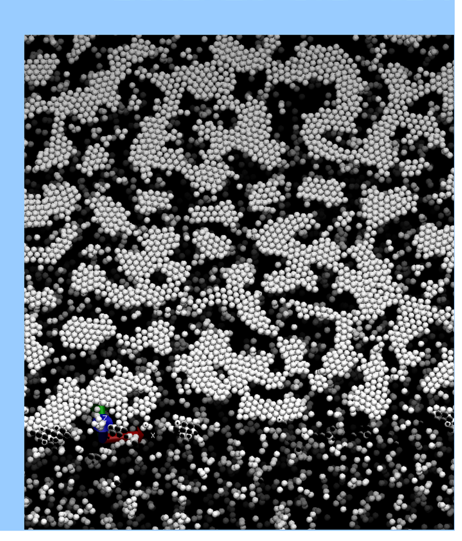
-Drying and microstructure of self-and-directed assembly.



➢ Particles: Large-scale atomic/molecular massively parallel simulator (LAMMPS) discrete element solver allows coarse-grained force-interactions and is fully scalable.

➢ Solvent: Stokesian fast lubrication expedient (Higdon and Kumar 2009), and Flory-Huggins polymer-solvent dynamics.

➢ Shearing, fast-drying, irradiation, (non-equilibrium) dynamics are enabled by new custom LAMMPS code.

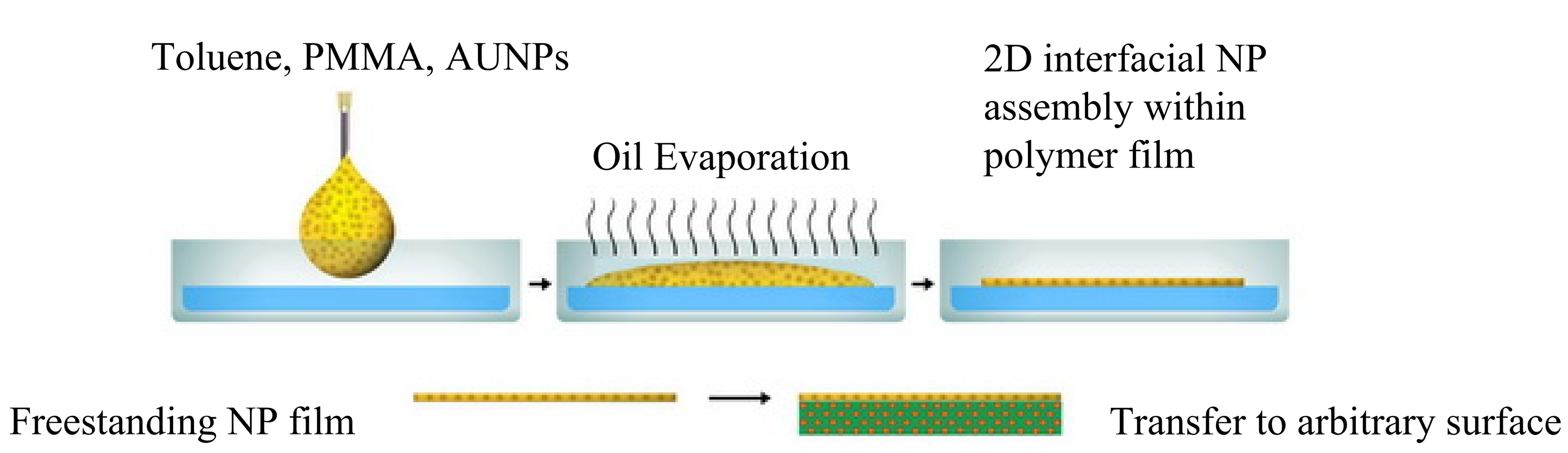


(image top right: bi-disperse nanoparticles in solution)
(image bottom right: 3D soft-particle evap. simulation)

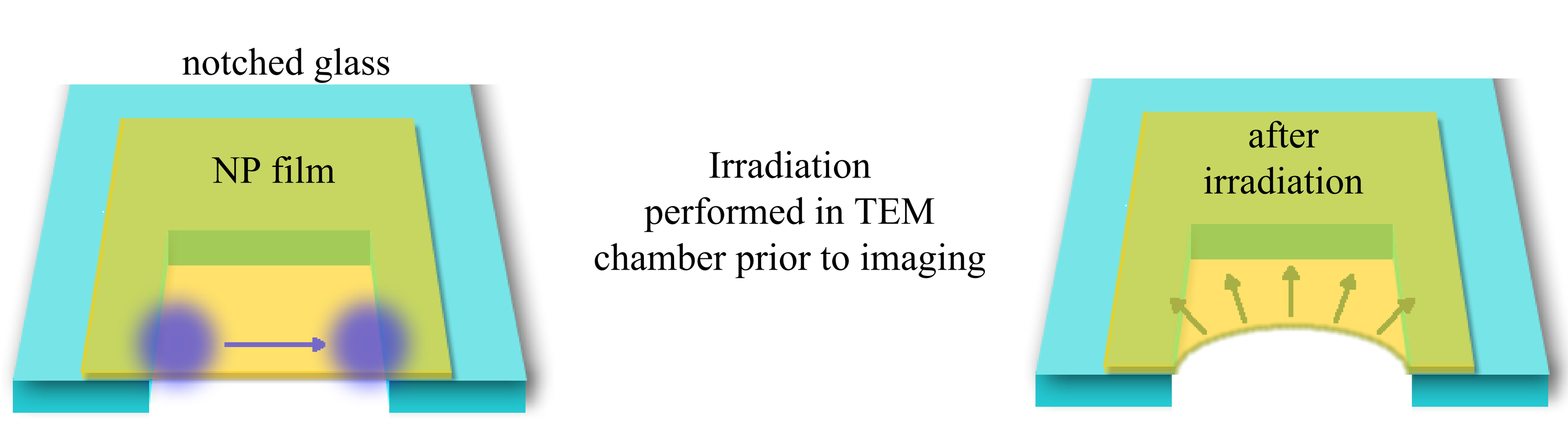
1. Peterson et al., *J. Comp. Phys* 132, 174106, p 17046-1

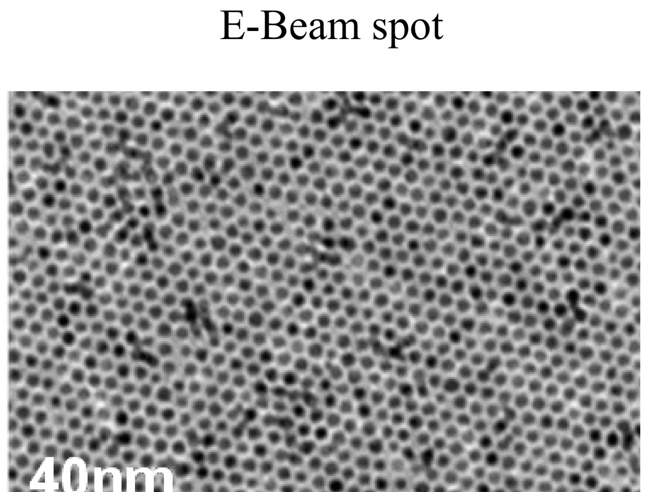
Colloid Experiment

1) Evaporation-Induced Self-Assembly (EISA) at a fluid interface[2]



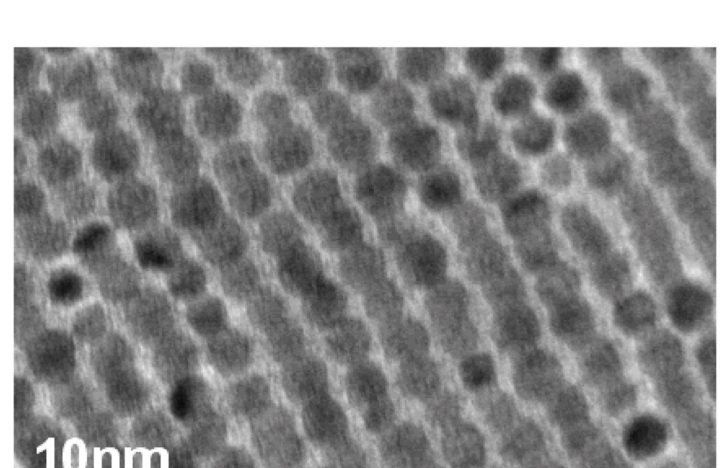
2) Directed assembly via e-beam irradiation (deformation)





NP film surface after evaporation

Nano-wire Formation via Directed Assembly



NP film surface after irradiation

2. J. Pang, S. Xiong, F. Jaeckel, Z. Sun, D. Dunphy, C.J. Brinker ", *J. Am. Chem. Soc* 2008, 130, p 3284-3285

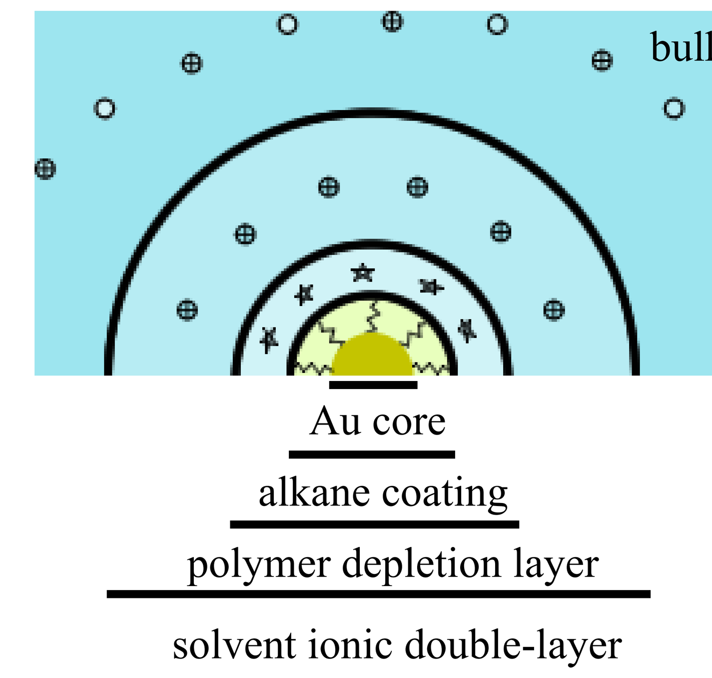
Modelling soft-particles

➢ DLVO, polymer, lubrication forces are all coarse-grained to enable multi-scale simulations much larger than DFT or molecular methods can permit.

➢ Flory-Huggins theory for polymer/solvent interactions applied to spherical polymer-coated particles by Vincent[3]. Forces derived and integrated into LAMMPS code.

➢ Specific potentials in the Vincent model:
1) bulk-polymer induced depletion
2) polymer-polymer steric repulsion
3) polymer-polymer elastic repulsion

3. B. Vincent et al., *Colloids and Surfaces* 1986, 18, p. 261-281



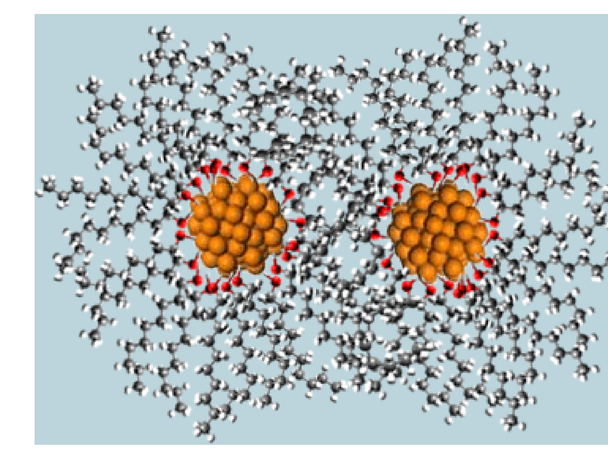
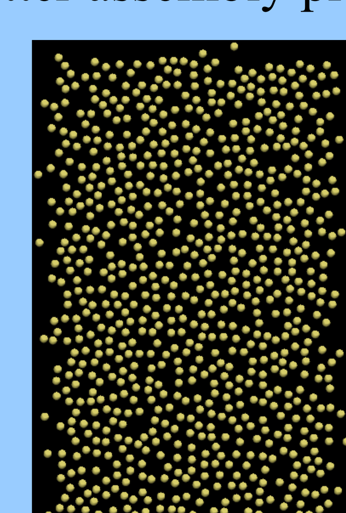


Diagram of Alkanethiolated AUNPs

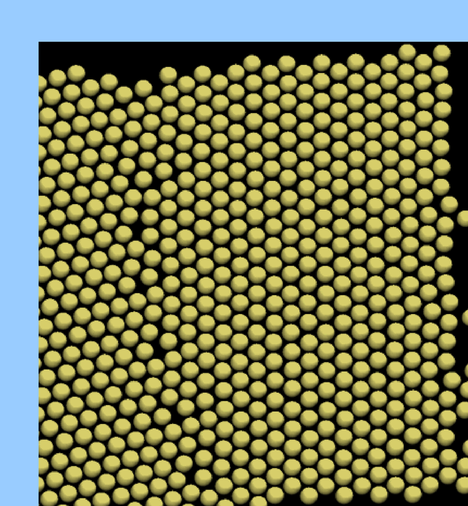
Results

➢ 2D / 3D runs with up to 13K particles performed on the "nano" linux cluster at the UNM Center for Advanced Research Computing. Average simulation time O(ms), run time O(hrs).

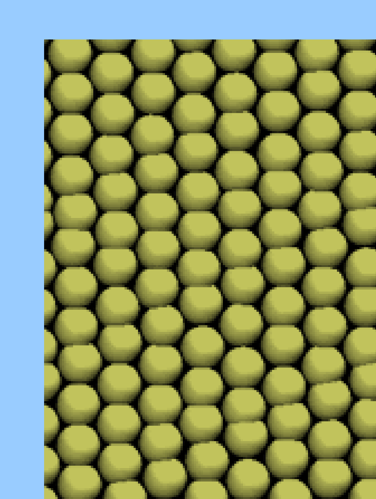
➢ Nanoscale lines nearly identical to experiment were produced in simulation, underlying key parameters were revealed and new experimental methods for better assembly proposed.



2D equilibration



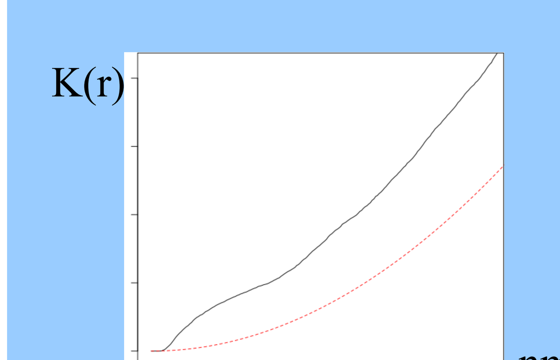
2D evaporation



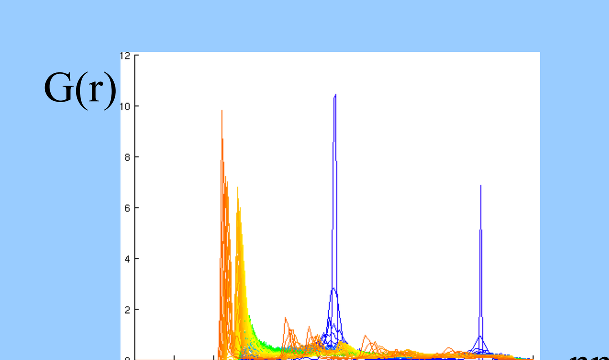
2D irradiation

➢ Order parametrization methods include clustering / spatial distribution analysis, GISAXS, coordinate visualizations.

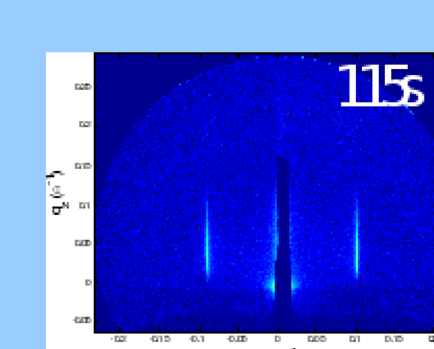
➢ Statistical methods from microbiology can be applied. We are also working on generating simulated GISAXS intensity plots from LAMMPS output files.



Ripley's K (clustering)



Spatial distribution over time



GISAXS intensity

Conclusion

➢ We have extended LAMMPS to model soft-particle colloids and demonstrated matching between simulation and experiment.

➢ DEM simulation can yield insight into physical processes and provide guidance for improving experimental methods.

➢ New research directions include extending code for explicit surface interactions, new solvent / polymer materials for experiments, and new ideas for lithographic patterning and irradiation experiments.

Ryan Molecke, Shisheng Xiong (University of New Mexico Nanoscience and Microsystems Dept.)
C. Jeffrey Brinker, P. Randall Schunk (Sandia National Laboratories, University of New Mexico Chemical & Nuclear Engineering Dept.)