SAND2016-4282C

Influence of Nanostructure and Environment on Nanoparticle Membrane Mechanical Properties

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Background

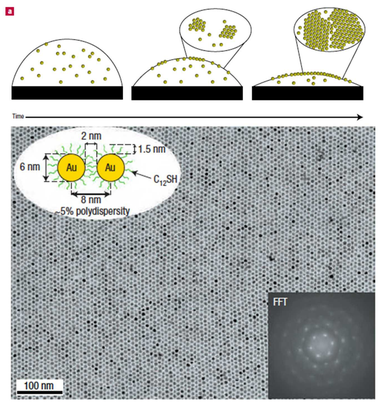
Nanoparticles (NPs) self-assemble to form structures with nanoscale features that can be used in thermal, chemical, mechanical and optical sensing or in filtration.

Experiments at Sandia and at Argonne's Center for Nanoscale Materials showed that alkanethiol-capped gold-core NPs can be assembled into two and three-dimensional arrays. Experimentally it is difficult to measure how changes in oligomer coating chemistry or in the environment, such as temperature or the presence solvent or ions, affect the local structure of assembly.

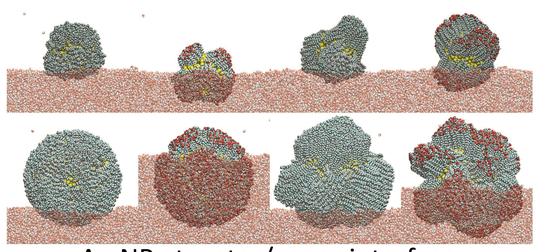
Molecular simulations are a natural tool for examining nanostructure. Work at CINT has used large-scale molecular simulations to explore the how molecular nanostructure influences assembly properties at larger scales.

Previous Experiments and Simulations

Lin and co-workers[1] at Argonne's Nanoscience Center demonstrated a reproducible way to make single-NP-thick membranes. Membranes are mechanically stable, with long-range hexagonal NP order. Strength and stiffness varies with NP core and oligomer coating composition. Membranes are stable to ~400K.



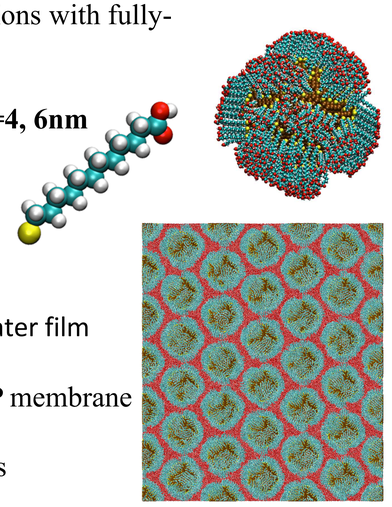
Lane and Grest[2] showed that the morphology of the NP oligomer coating could vary greatly with small changes in core size, ligand length, and solvent quality. This result suggests that NP-NP interactions at the liquid-vapor interface could also vary strongly with these parameters. The NP-NP interactions are relevant to self-assembly. Understanding NP-NP interactions is critical to understanding the membrane formation and ultimately the membrane properties.



Au NP at water/vapor interface

Simulation Model

- Molecular dynamics simulations with fully-atomistic force field
- Au NP cores with diamter **d=4, 6nm**
- **S-$(CH_2)_{n-1}$-X** ligands
  X = CH_3 or COOH
  n = 12 or 18
- NP Membrane formed on water film
- Water evaporated to form NP membrane
- Periodic and open boundaries
- Equilibrated for 20+ ns with and without water



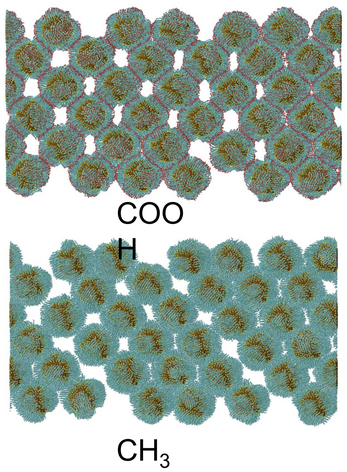
Mechanical Properties[3]

Oligomer end group influences membrane mechanical stiffness and failure strength:

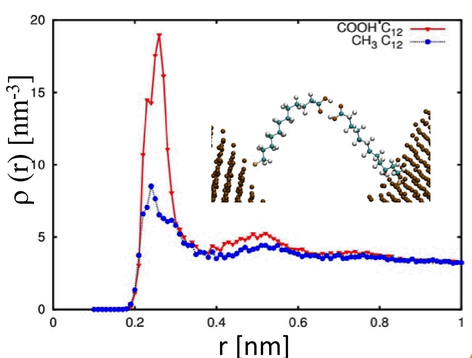
- Young's modulus > 3 GPa for X=COOH
- 50% higher than X=CH_3
- Good agreement with experiment

Stiffness and strength reduced for **d=4nm**

COOH – stiffer and stronger



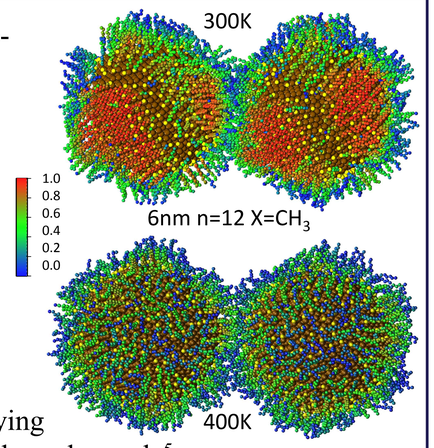
- Hydrogen bonding
  - Strong for COOH
  - Oligomer pairing between NPs
  - Accounts for end group effect on membrane stiffness



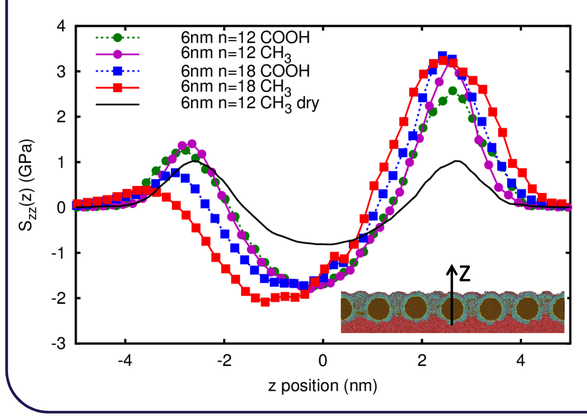
Nanostructure[3,4]

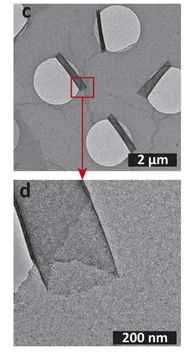
Nanostructure linked to meso- and macro-scale behavior

- Oligomer ordering
  - Highly temperature dependent
  - ~400K -> membrane rupture
  - Order correlates with Young's Modulus



- Membrane rolling
  - After formation and drying membranes with a free boundary role[5]
  - Stress asymmetric through membrane
  - Liquid-vapor interface asymmetry persists in membrane
  - Asymmetry for all core sizes and ligand lengths





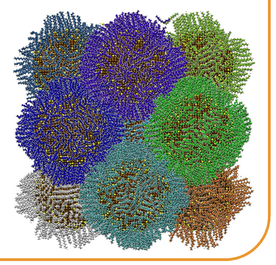
Experiment[5]

Summary & Future Work

MD simulations are ideal for studying nanoscale assembly and nanostructure. Nanostructure of 2D NP membranes due to end-group chemistry and environment is directly related to mesoscale properties.

Simulations on 3D NP FCC lattice underway

- All-atom simulations capture pressure response in NP crystal
- At high pressure deviatoric stress drives sintering to form nanowires



References

[1] T. P. Bigioni, et al., Nat. Mater. 5, 265 (2006).
[2] J. M. D. Lane and G. S. Grest, Phys. Rev. Lett. 104, 235501 (2010).
[3] K. M. Salerno, et al., Phys. Rev. Lett. 113, 1 (2014).
[4] K. M. Salerno, et al., Phys. Rev. E 91, 062403 (2015).
[5] Y. Wang, et al., Nano Lett. 15, 6732 (2015).

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