KITP Program: Physical Principles of Multiscale Modeling, Analysis and Simulation in Soft Condensed Matter

Evaporation-Induced Nanoparticle Assembly: Molecular Dynamics Studies

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U.S. DEPARTMENT OF ENERGY

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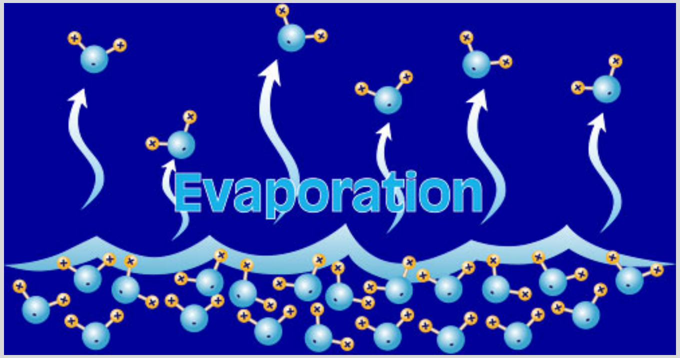
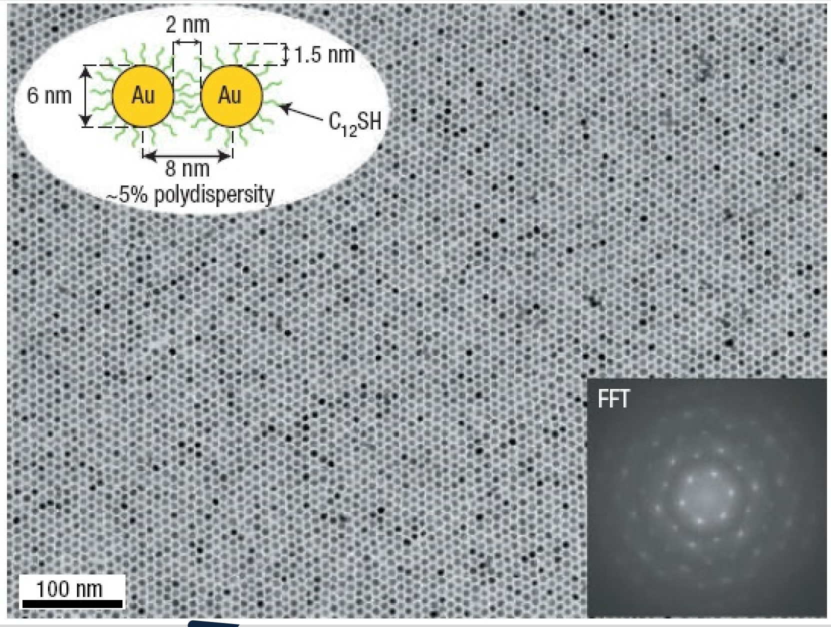
Center for Integrated Nanotechnologies

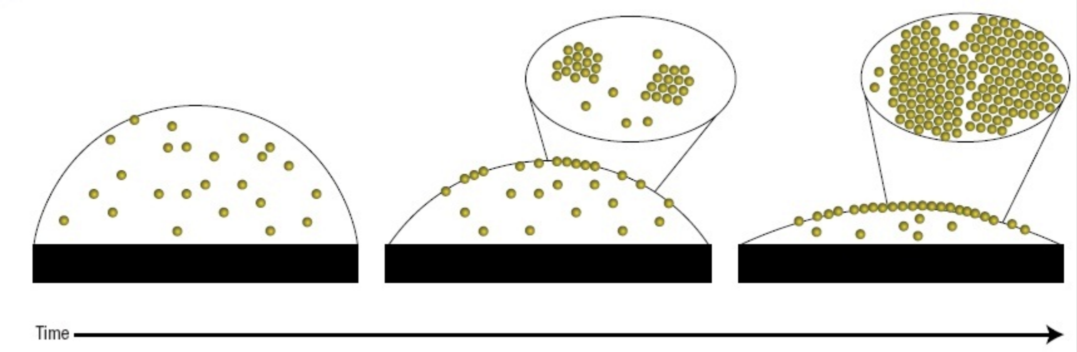
Evaporation

molecular scale



- Evaporation is everywhere
- Evaporation-induced nanoparticle-assembly is promising *"for the fabrication of technologically important ultra thin film materials for sensors, optical devices and magnetic storage media"*

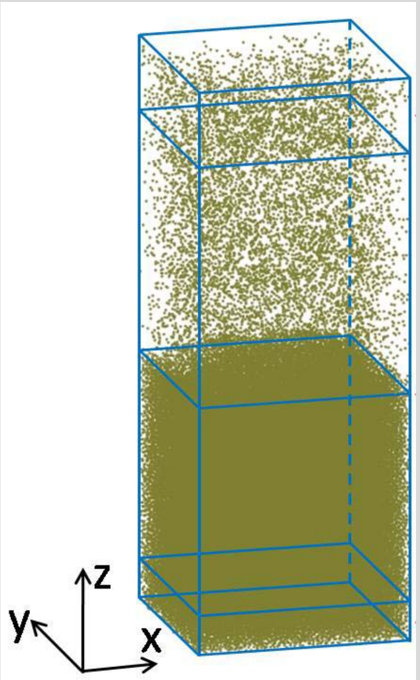


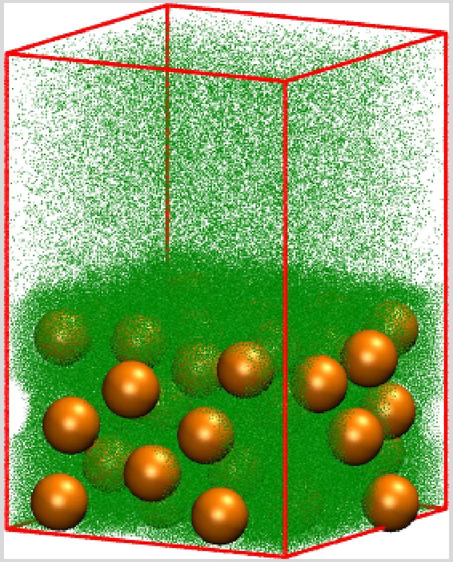


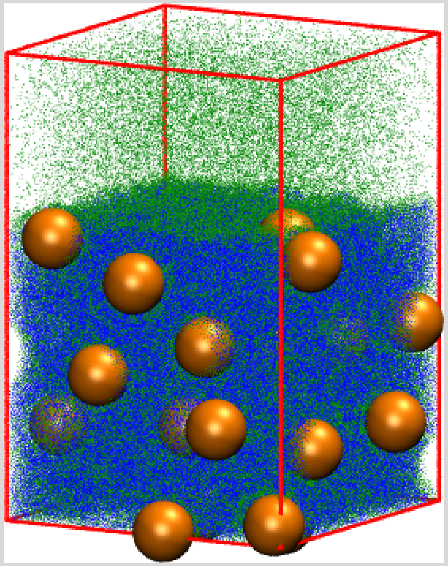
Bigioni *et al* (2006)
Nature Materials

Outline

- Evaporation of Lennard-Jones liquids (pure solvent)
- Evaporation of nanoparticle/solvent systems
- Evaporation of nanoparticle/polymer/solvent systems



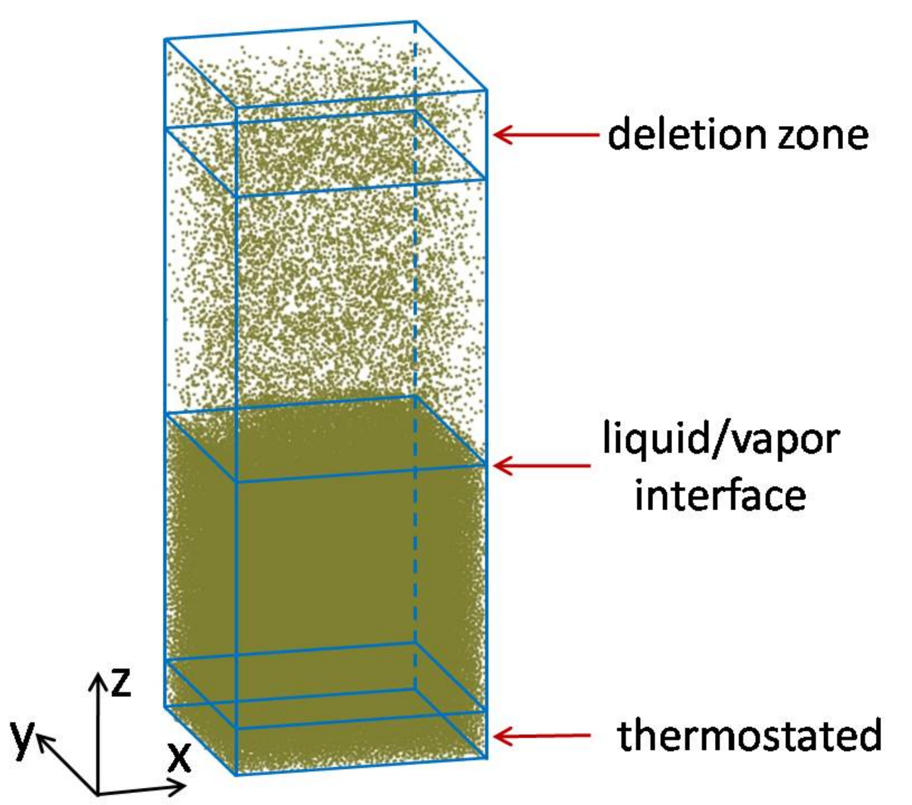




Evaporation of Lennard-Jones Liquids: Molecular Dynamics

$$V_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

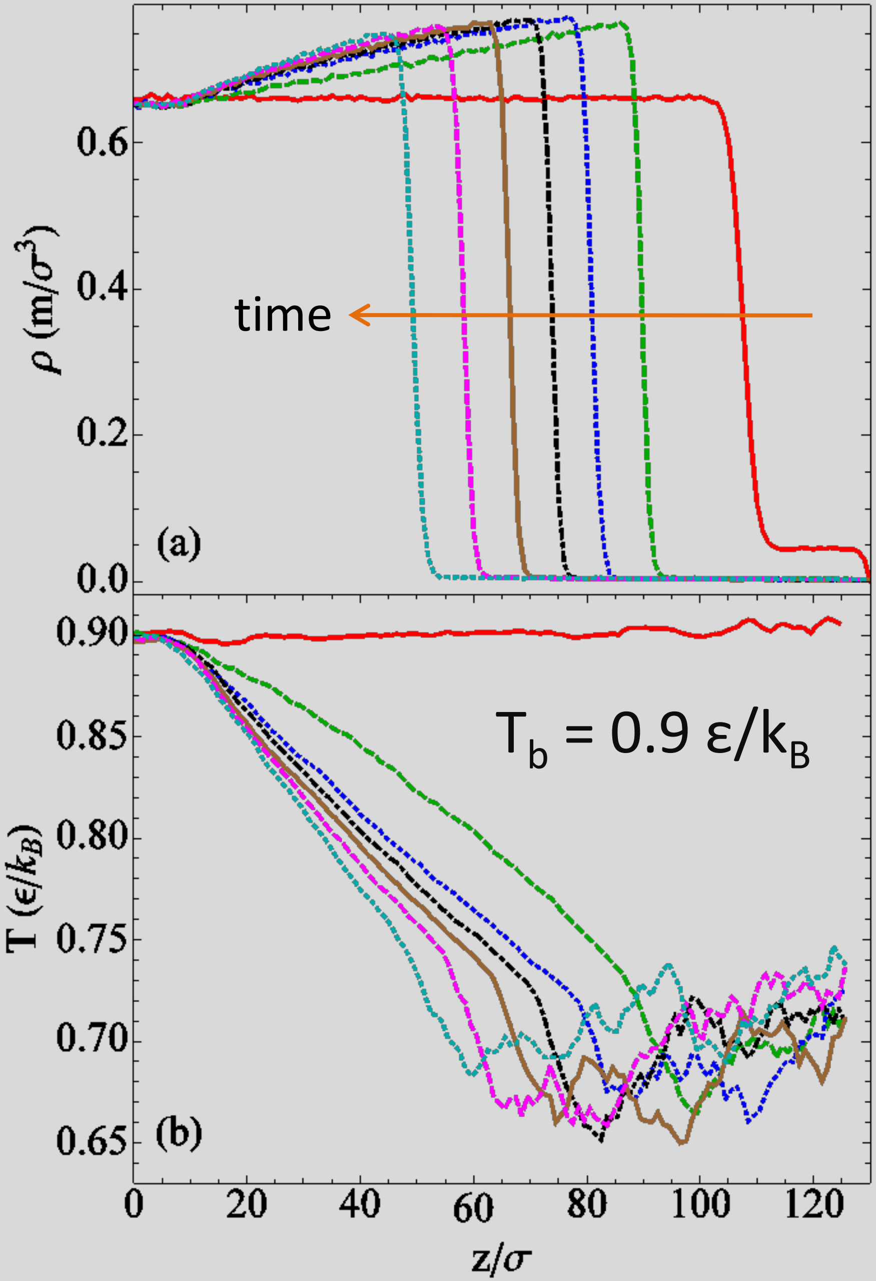
- Liquid/vapor coexistence of LJ fluids (monomers/dimers/trimers)
- Vapor atoms entering ***deletion zone*** removed at specified rates
- Vapor atoms supplied by evaporation occurring at liquid/vapor interface
- NVE simulations + thermostated thin liquid layer near confining wall
- Calculate temperature/density profiles and evaporation flux

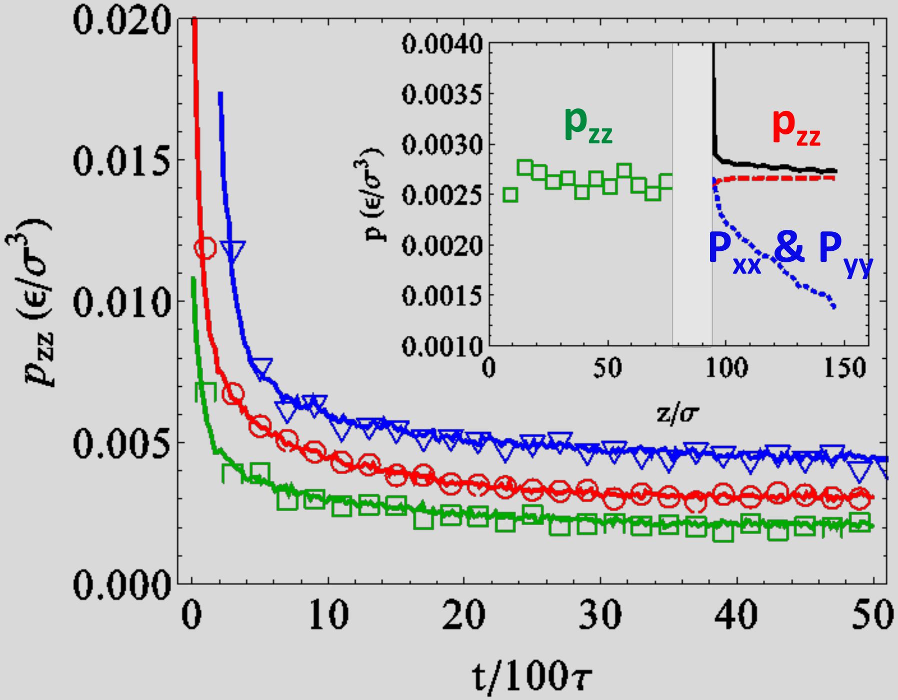


Cheng *et al*, JCP **134**, 224704 (2011)

T_b: temperature in thermostated liquid layer

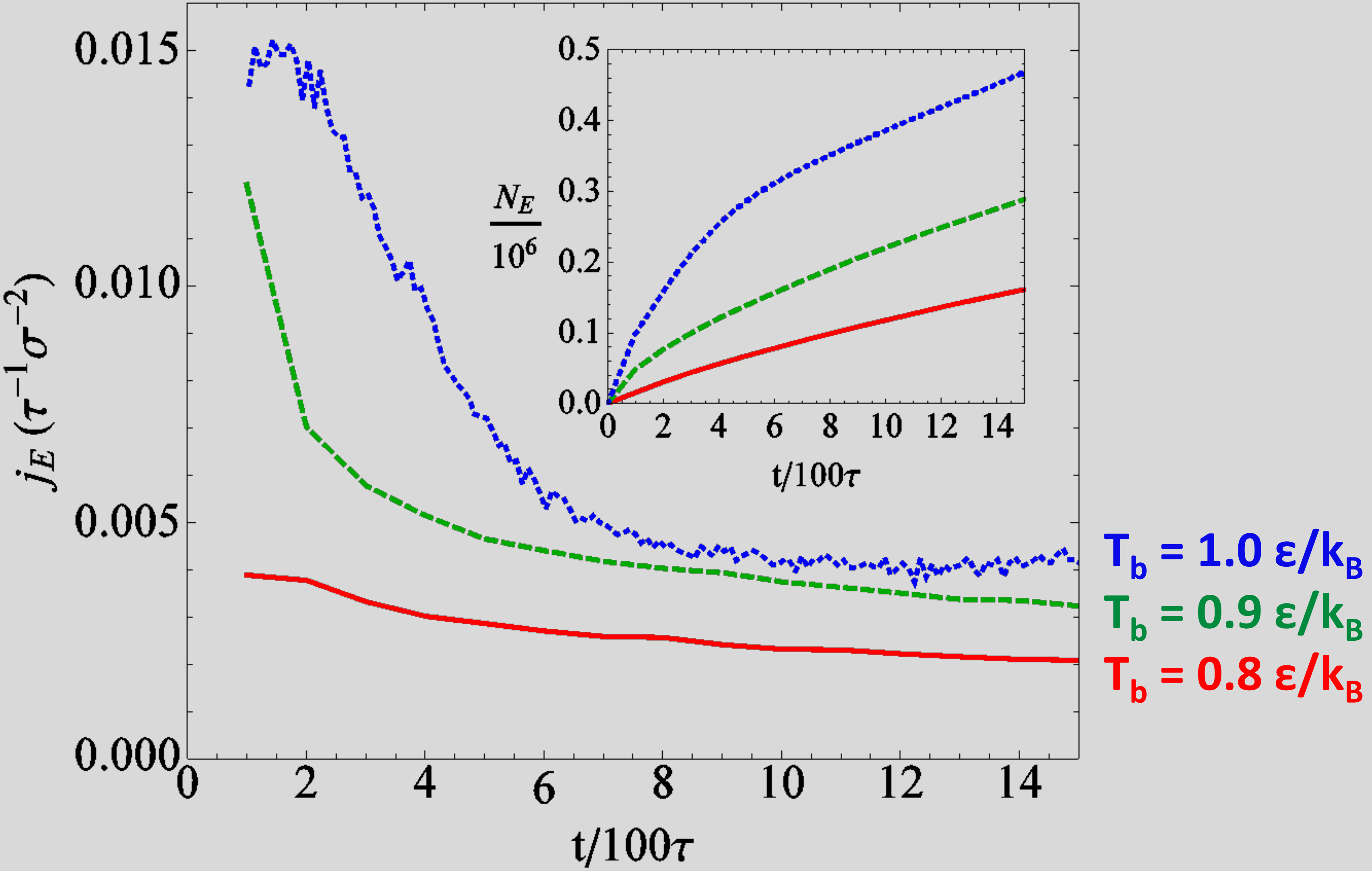
Evaporation of LJ fluids into vacuum





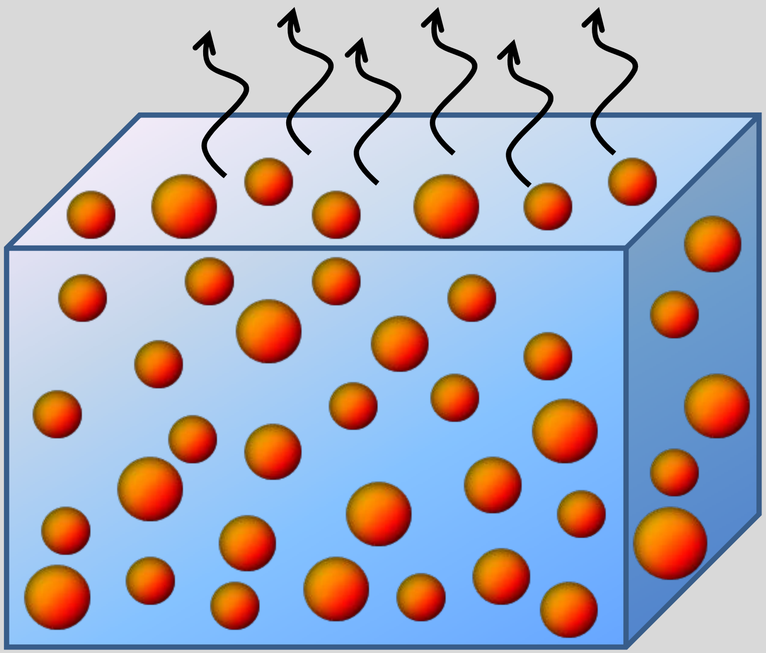
- Vapor density almost vanishes after evaporation initiated
- **Mechanical equilibrium** → liquid density enhances by 20% near interface
- **Evaporative cooling**: temperature drops near L/V interface in liquid region, but increases with distance from interface in vapor region → **L/V interface is the coolest place**

Evaporation Rates vs. Time

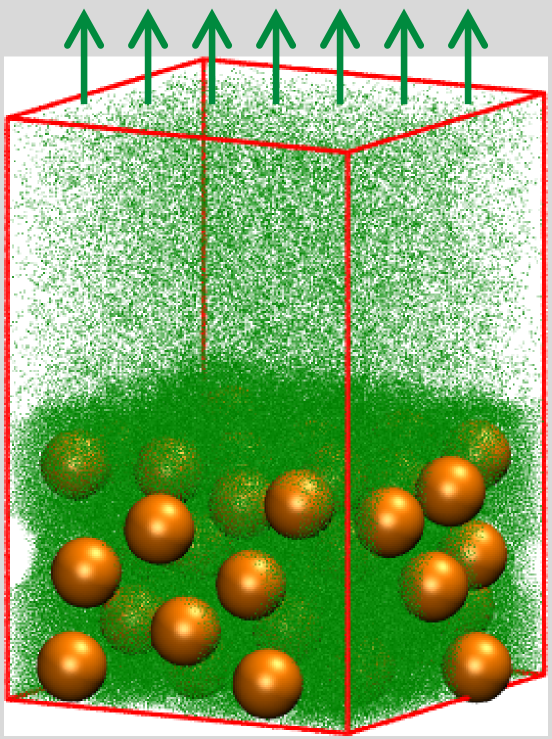


- Depletion of vapor → decrease of evaporation rates with time
- Decrease more dramatic at higher temperatures

MD Model of Evaporation of Nanoparticle/Solvent Systems

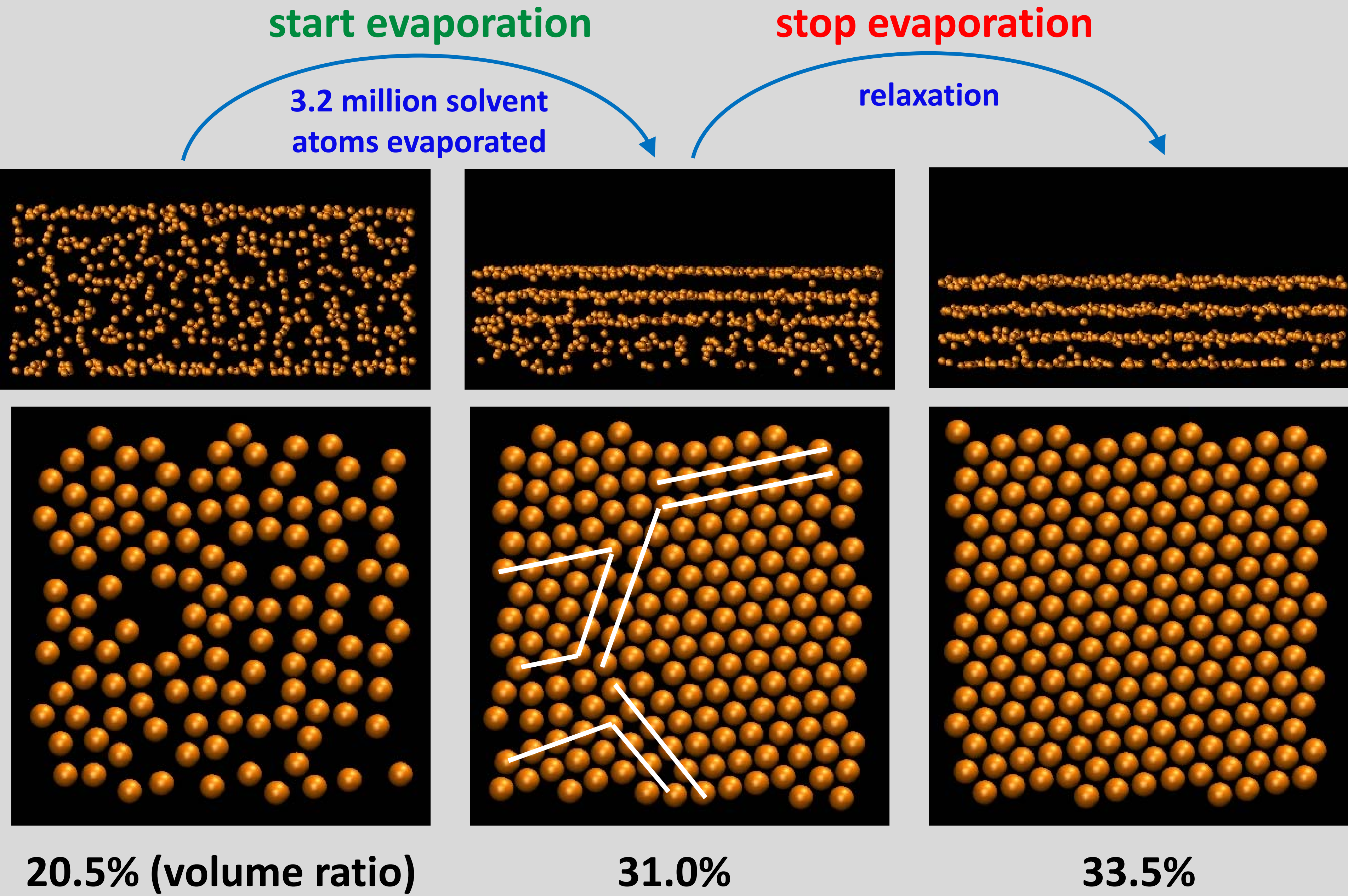


- Explicit **LJ solvent (~ 7 million)** + **668 nanoparticles (d ~ 20σ ~ 6nm)** (also 17 million solvent + 720 NPs)
- Integrated LJ potential between nanoparticles (purely repulsion), and nanoparticles and solvent (with attractions)

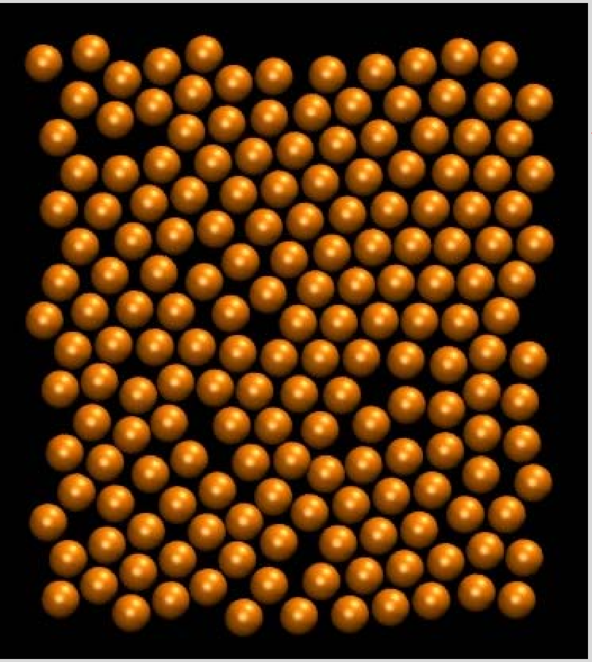


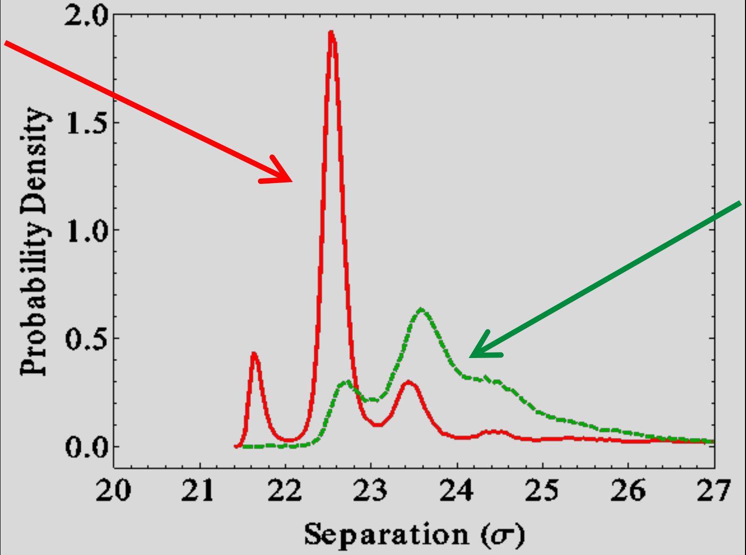
- Strong nanoparticle/solvent interaction → a layer of solvent atoms around each np
- Evaporate vapor of solvent into vacuum or at controlled rates
- Nanoparticles move toward interface but remain in solution during evaporation

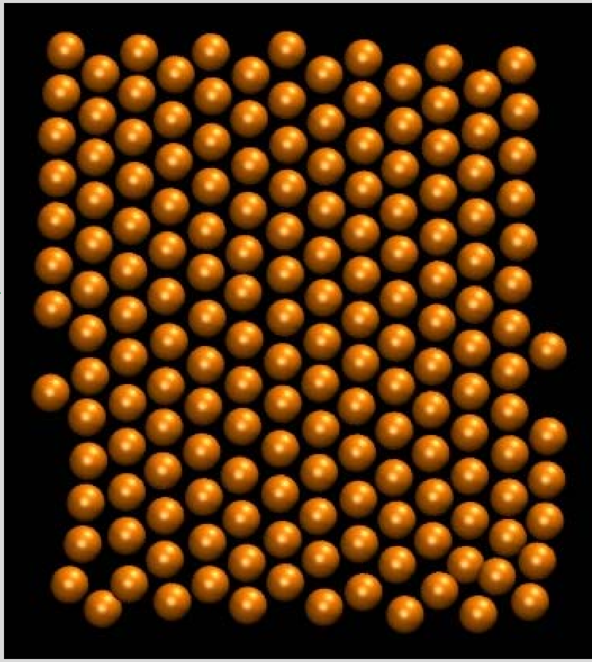
Evaporation-Induced Nanoparticle Assembly



Effect of Evaporation Rate on Assembly Quality





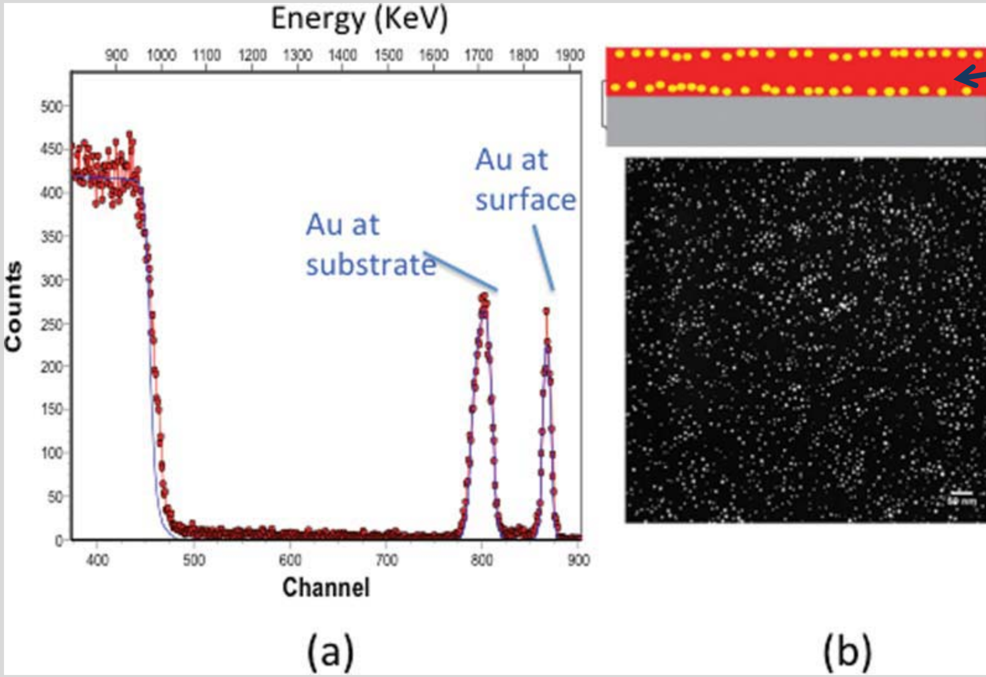


Evaporation into Vacuum

Evaporation at Fixed Rate

- Initial (final) rate into vacuum about 100 (6) times of the fixed rate
- Averaged rate into vacuum about 10 times of the fixed rate
- Slower evaporation → higher quality of assembly (enough time to adjust when evaporate slowly) → optimum rate for best quality?
- Separations smaller and more peaked (1, 2, 3… liquid layers between particles) at faster evaporation

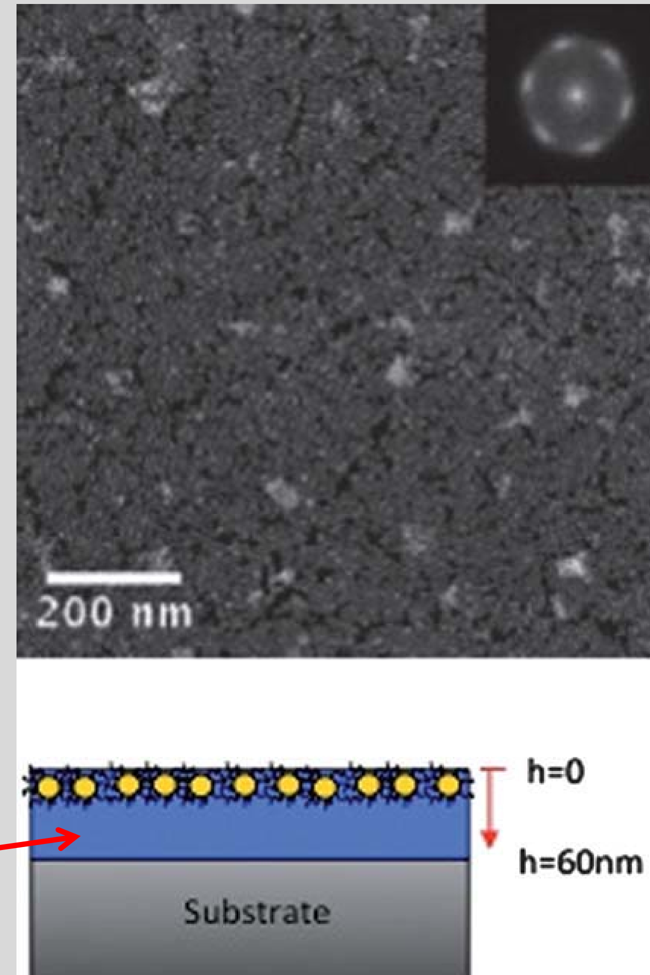
Polymer/Nanoparticle Composite



polystyrene

Green et al. Soft Matter (2012)

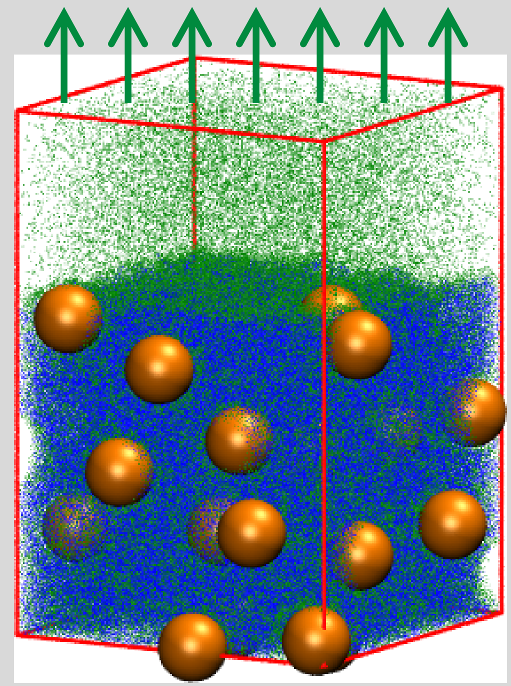
Green et al. ACS Nano (2008)



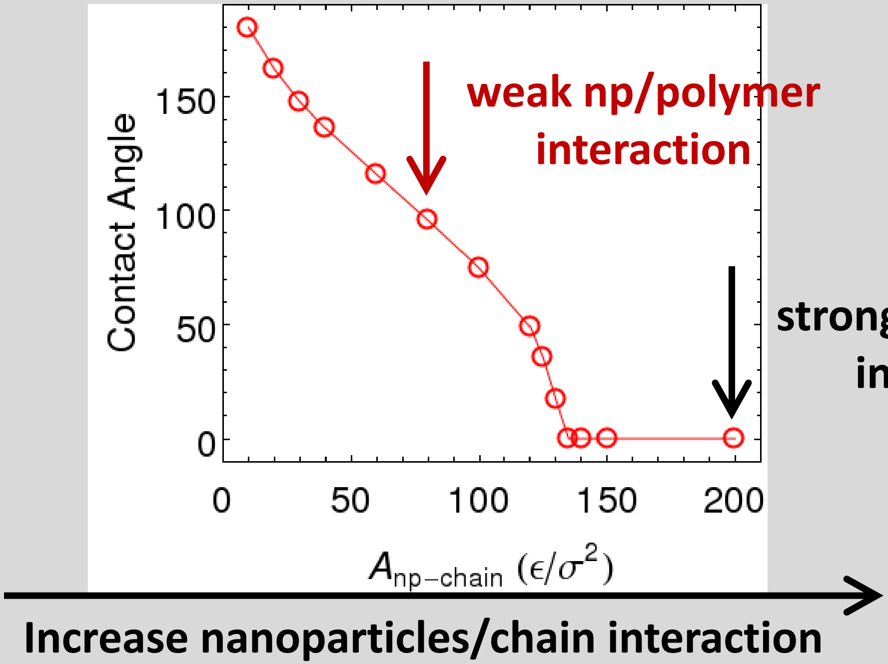
PMMA film

Nanoparticle/Polymer/Solvent Systems

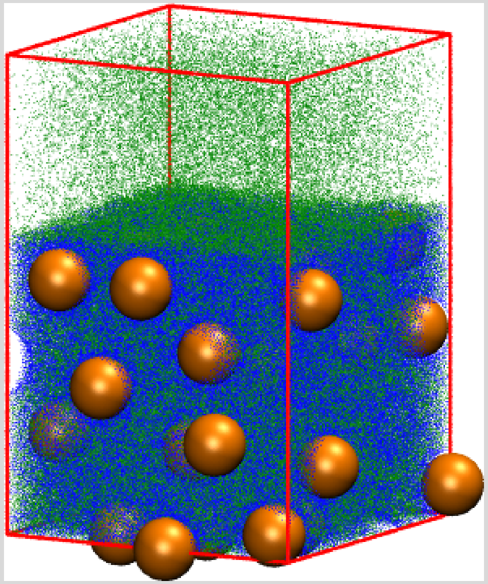
Evaporating solvent



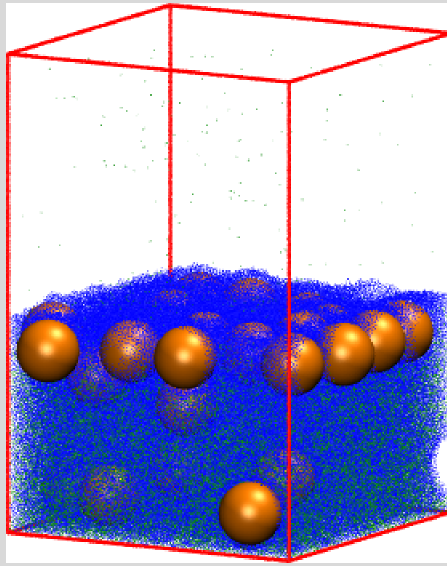
- **LJ solvent (~ 3 million)** + **100-bead polymer chains (~ 3 million monomers)** + **nanoparticles (200)**
- FENE bonds for polymer chains
- Strong np/solvent interaction → np solvated
- Starting volume % of **polymer: 45%** **nps: 10%**



Strong Nanoparticle/Polymer Interaction

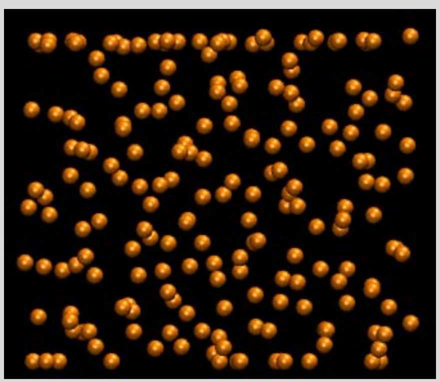


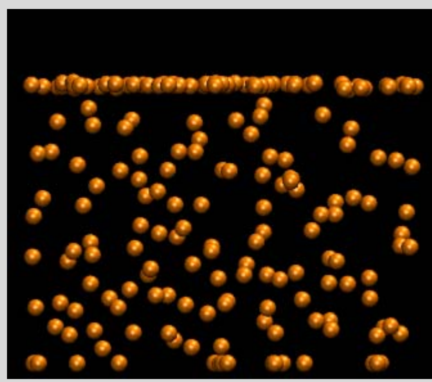
before evaporation



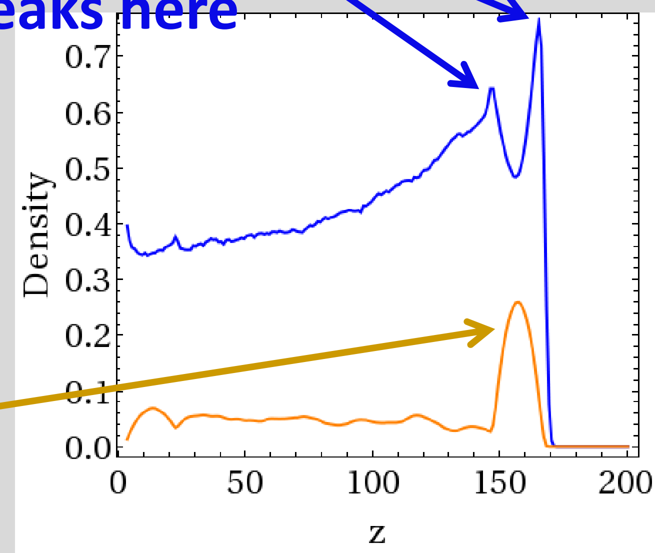
during evaporation

- **Nanoparticles accumulate near liquid/vapor interface**
  -- polymer chain density is highest



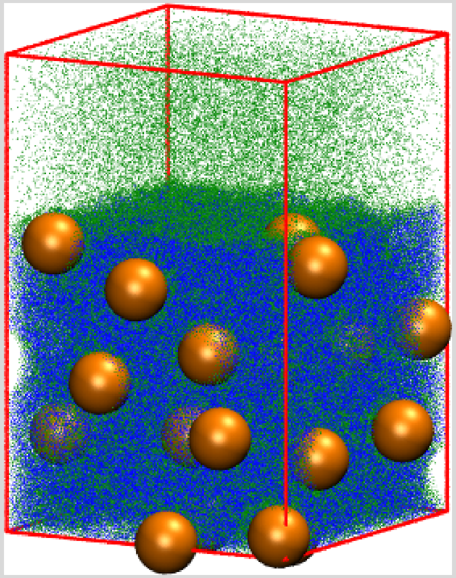


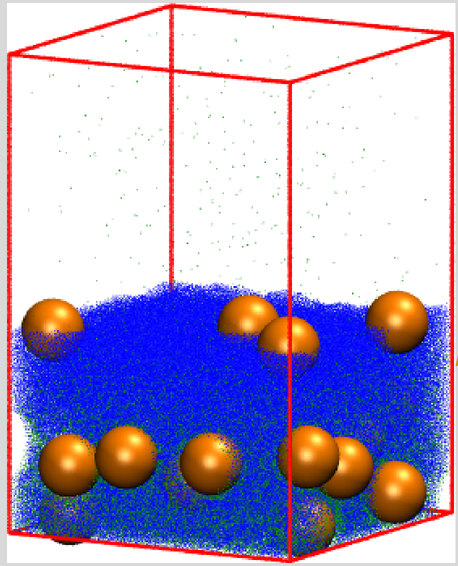
polymer density peaks here



nanoparticle accumulation

Weak Nanoparticle/Polymer Interaction

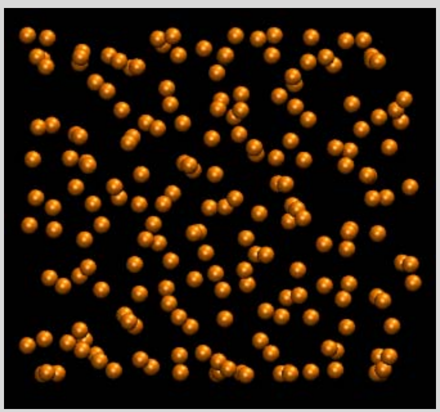


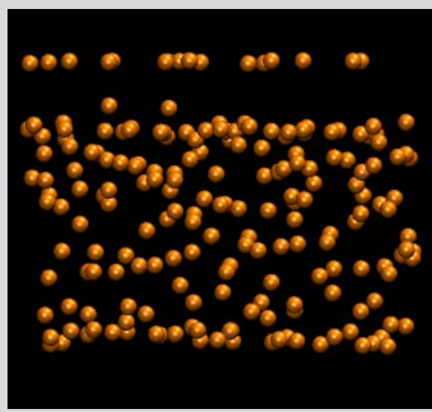


- ❑ Nanoparticle depletion in dense polymer layer near liquid/vapor interface

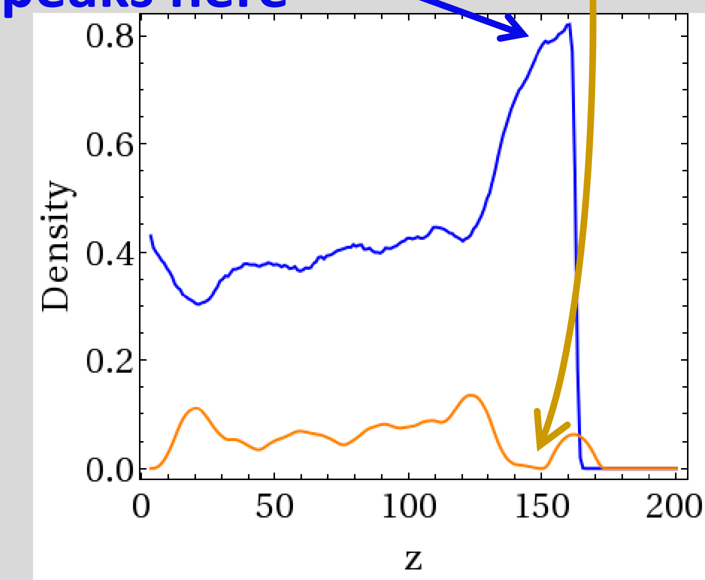
before evaporation

during evaporation

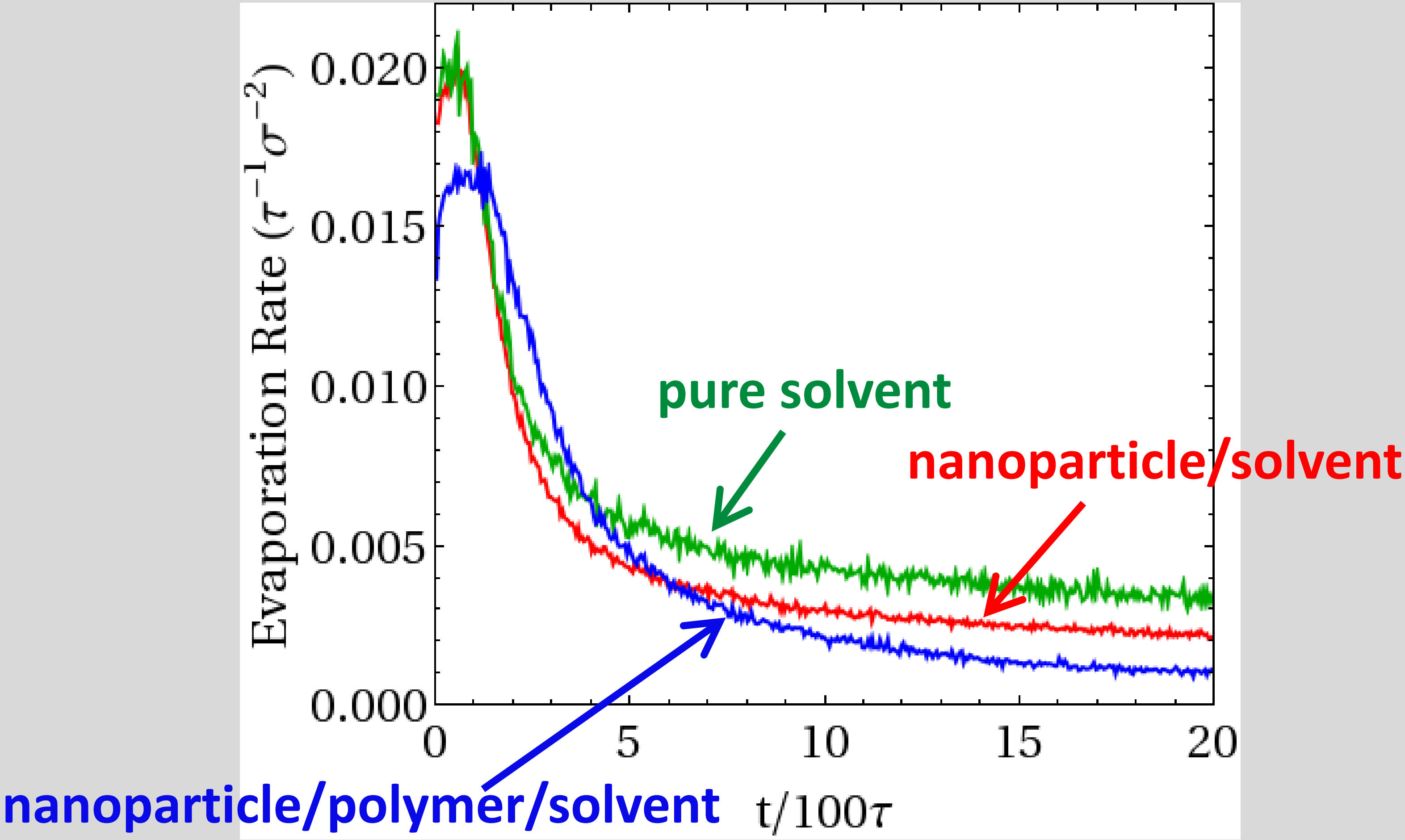




polymer density peaks here



Effect of Nanoparticle/Polymer on Evaporation Rate



- **Evaporation rate drops by an order of magnitude quickly**
  - ❑ **Depletion of vapor**
  - ❑ **Blockage of nanoparticles/polymers near liquid/vapor interface**
    → evaporation rate drops faster compared to neat solvent

Conclusions

Evaporation of pure liquids:

- Interface is the coolest place
- Mechanical equilibrium and evaporative cooling → liquid density enhanced near interface

Evaporation of nanoparticle/solvent systems:

- Nanoparticles assemble into hexagonal lattice near interface
- Slower evaporation rate → higher quality assembly

Evaporation of nanoparticle/polymer/solvent systems:

- Nanoparticles accumulate/deplete near interface depending on nanoparticle/polymer interactions
- Accumulation of nanoparticles/polymers near interface slows down evaporation