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Evaporation-Induced Nanoparticle Assembly: Molecular Dynamics Studies

Shengfeng Cheng and Gary S. Grest

Sandia National Laboratories, Albuquerque, NM

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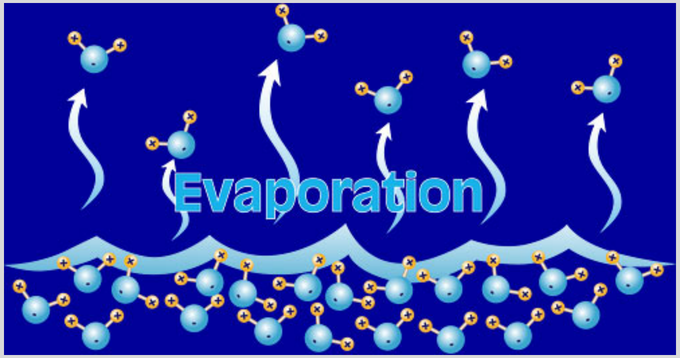
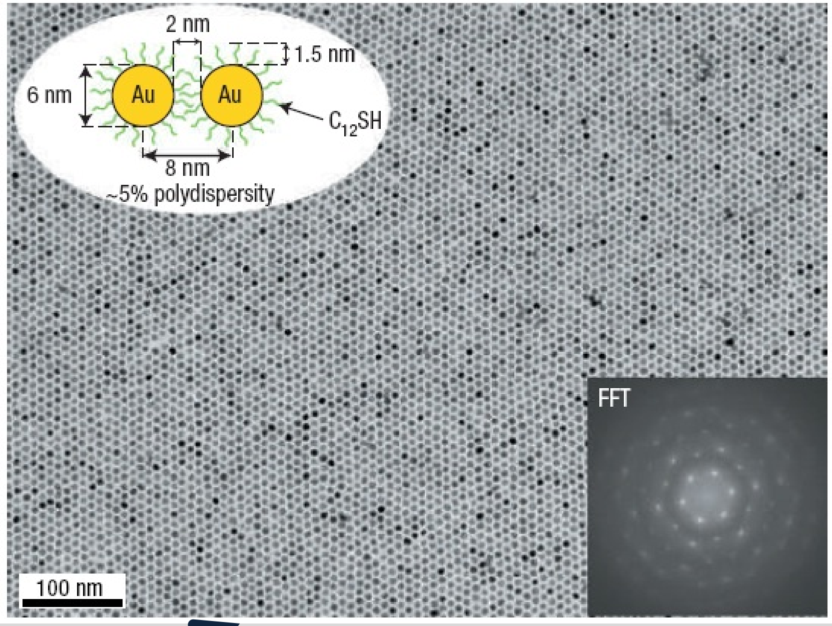
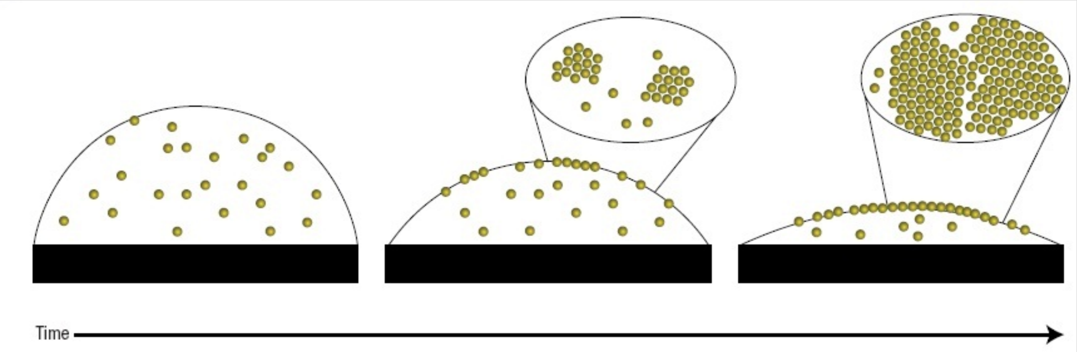
Evaporation is important and useful

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"*



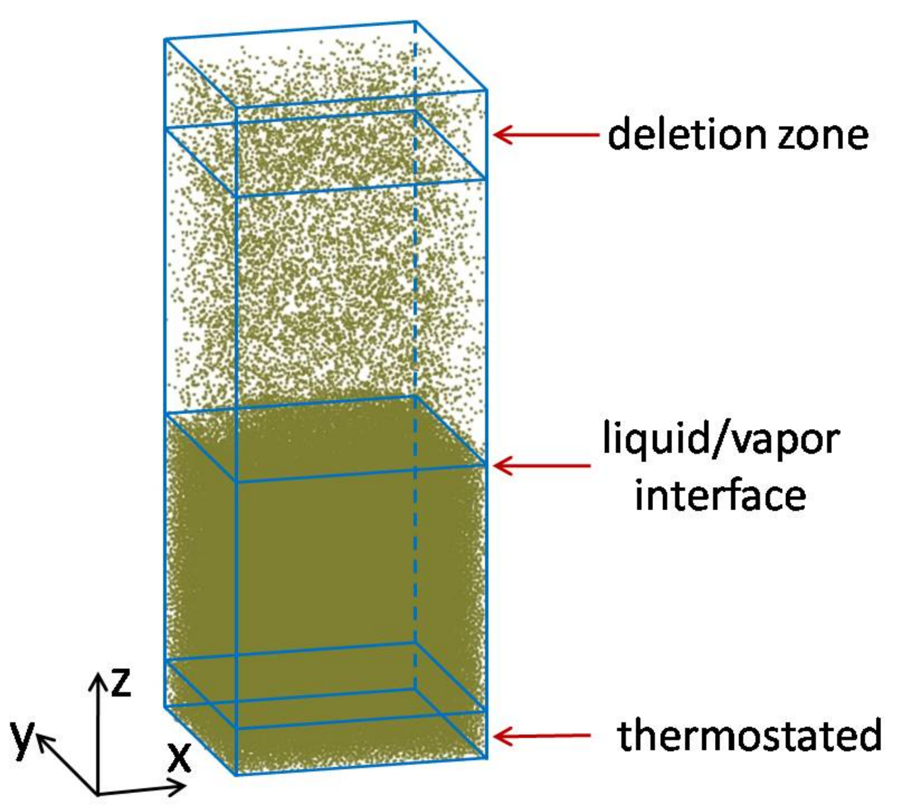


Bigioni *et al* (2006)
Nature Materials

Evaporation of Lennard-Jones Liquids: Molecular Dynamics

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

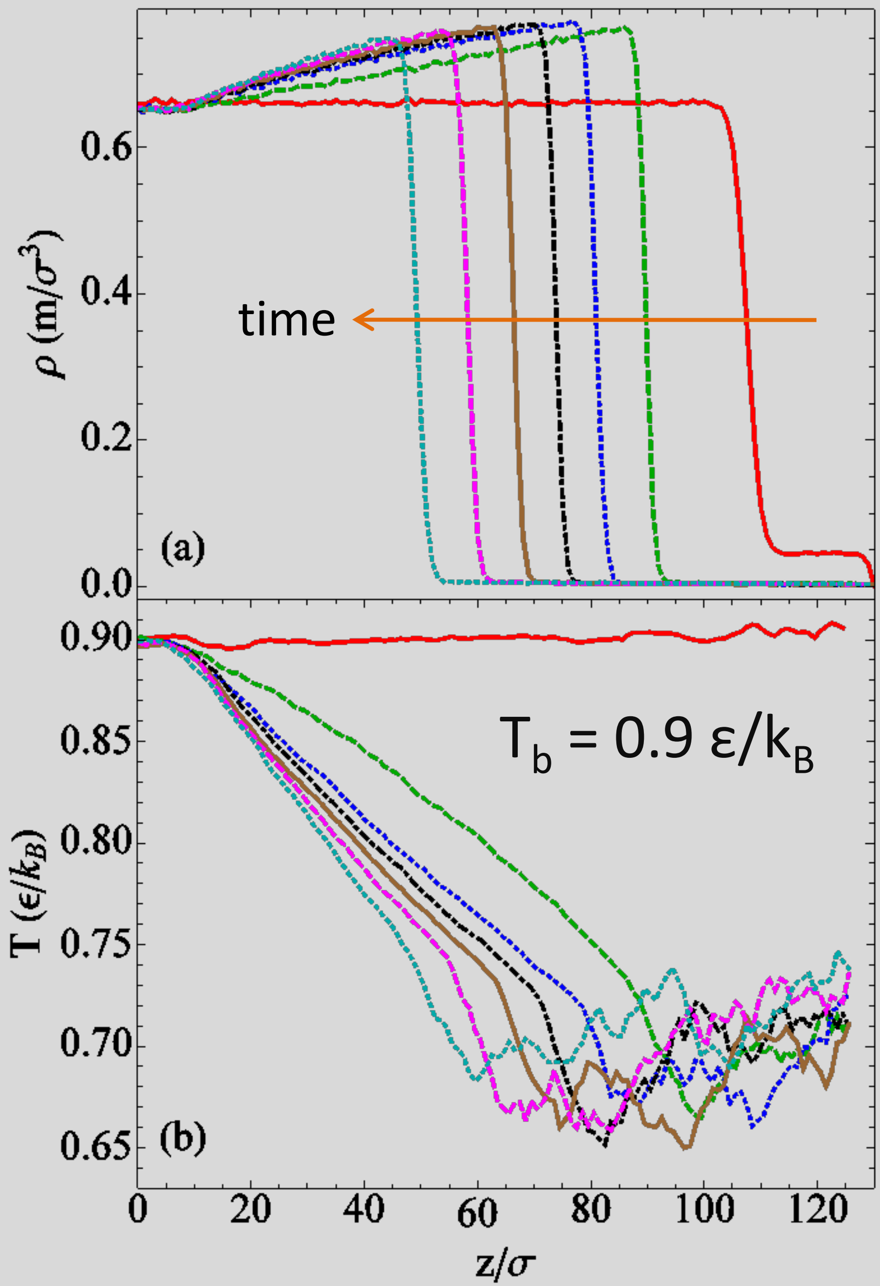
- Liquid/vapor coexistence of LJ fluids (monomers/dimers/trimers)
- Vapor atoms entering ***deletion zone*** removed at specified rates
- Vapor atoms supplied by evaporation occurring at liquid/vapor interface
- NVE simulations + thermostated thin liquid layer near confining wall
- Measuring temperature/density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

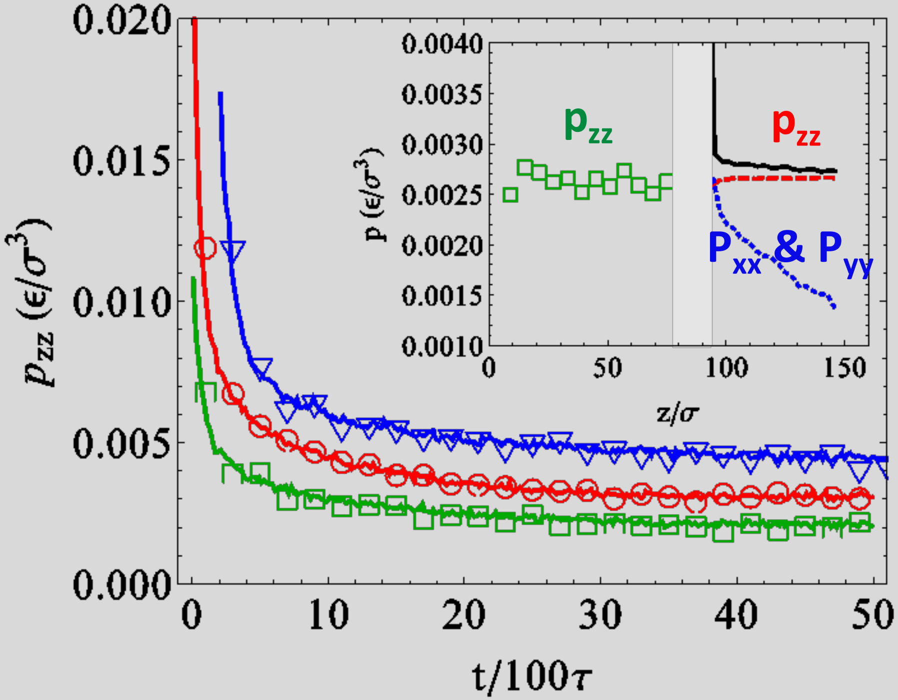


Cheng *et al*, JCP **134**, 224704 (2011)

T_b: temperature in thermostated liquid layer

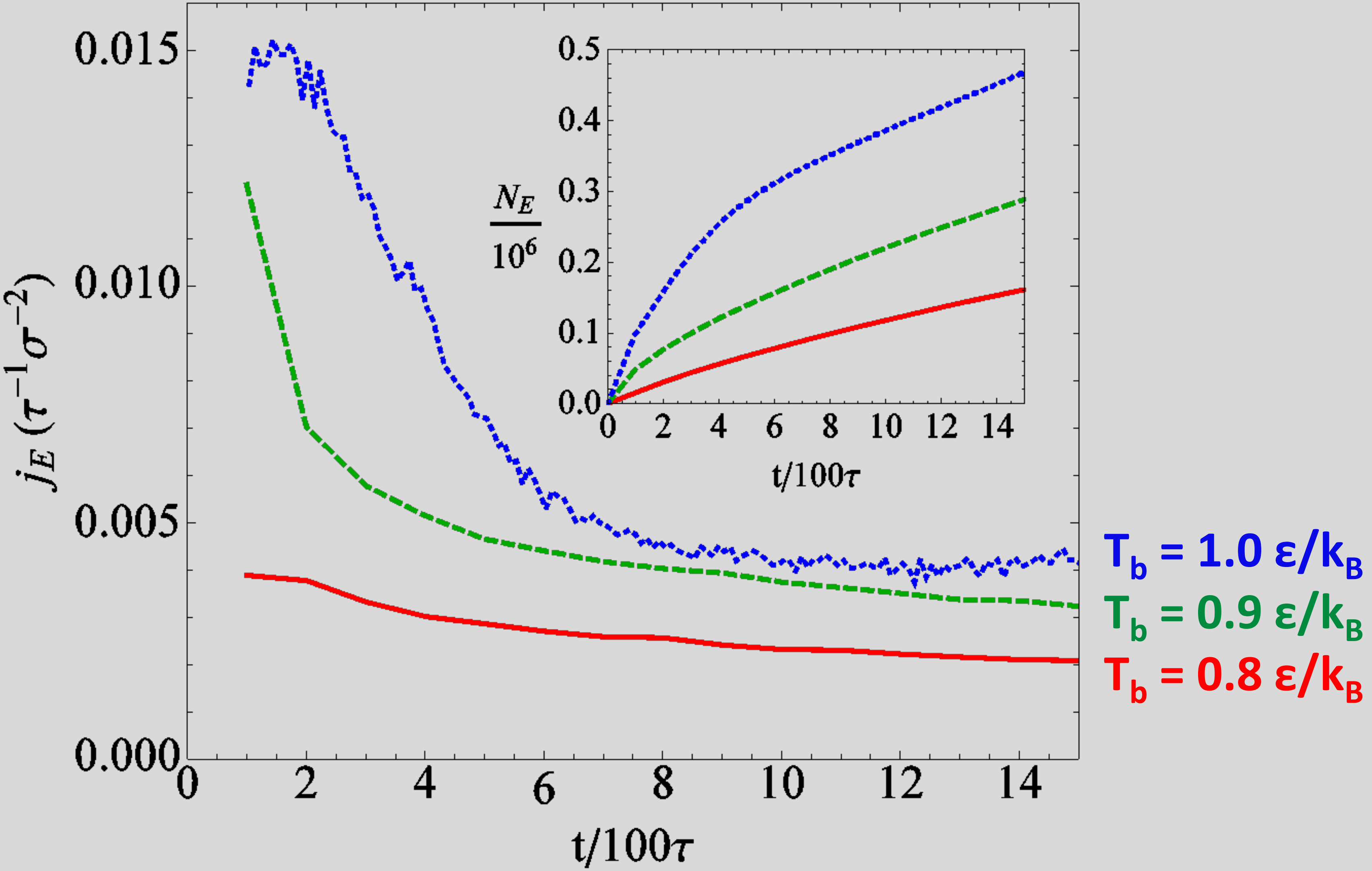
Evaporation of LJ fluids into vacuum is very fast





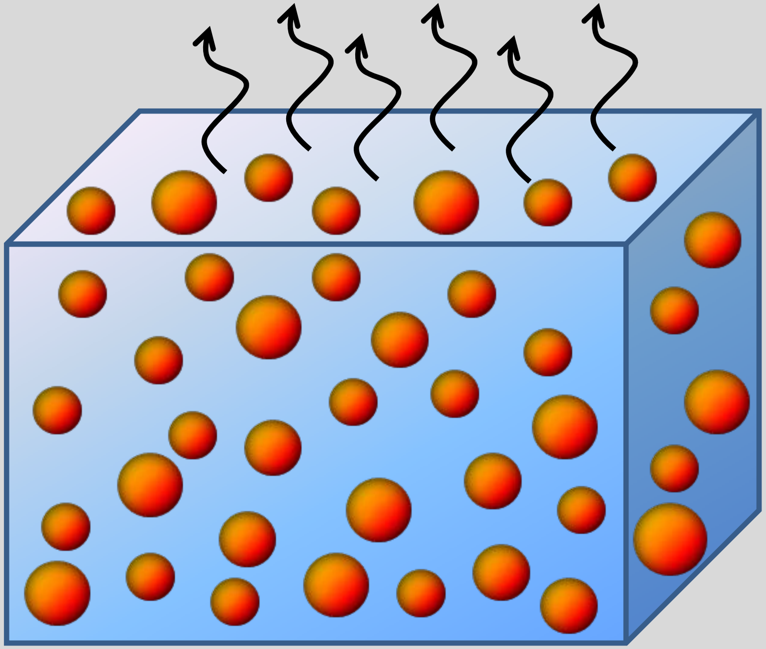
- Vapor density almost vanishes after evaporation initiated
- **Mechanical equilibrium** → liquid density enhances by 20% near interface
- **Evaporative cooling**: temperature drops near L/V interface in liquid region, but increases with distance from interface in vapor region → **L/V interface is the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

Evaporation rates decrease over time

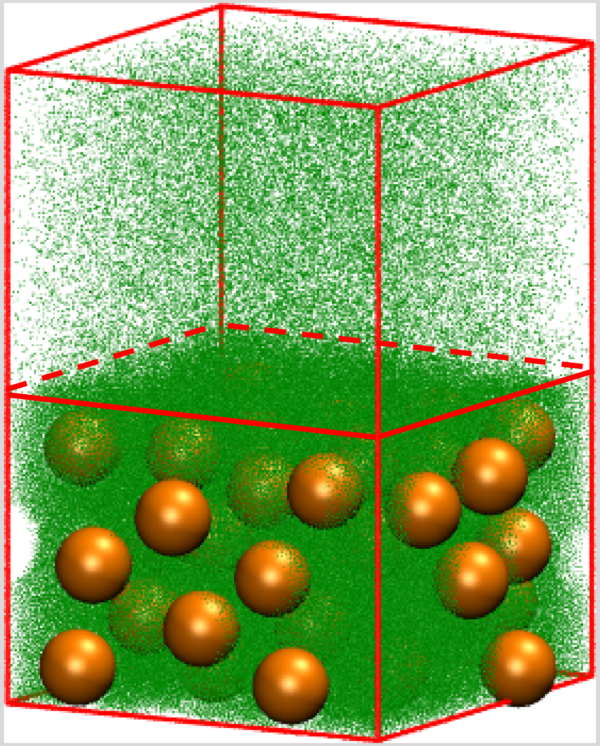


- Depletion of vapor → decrease of evaporation rates with time
- Decrease more dramatic at higher temperatures

MD Model of Evaporation-Induced Nanoparticle Assembly

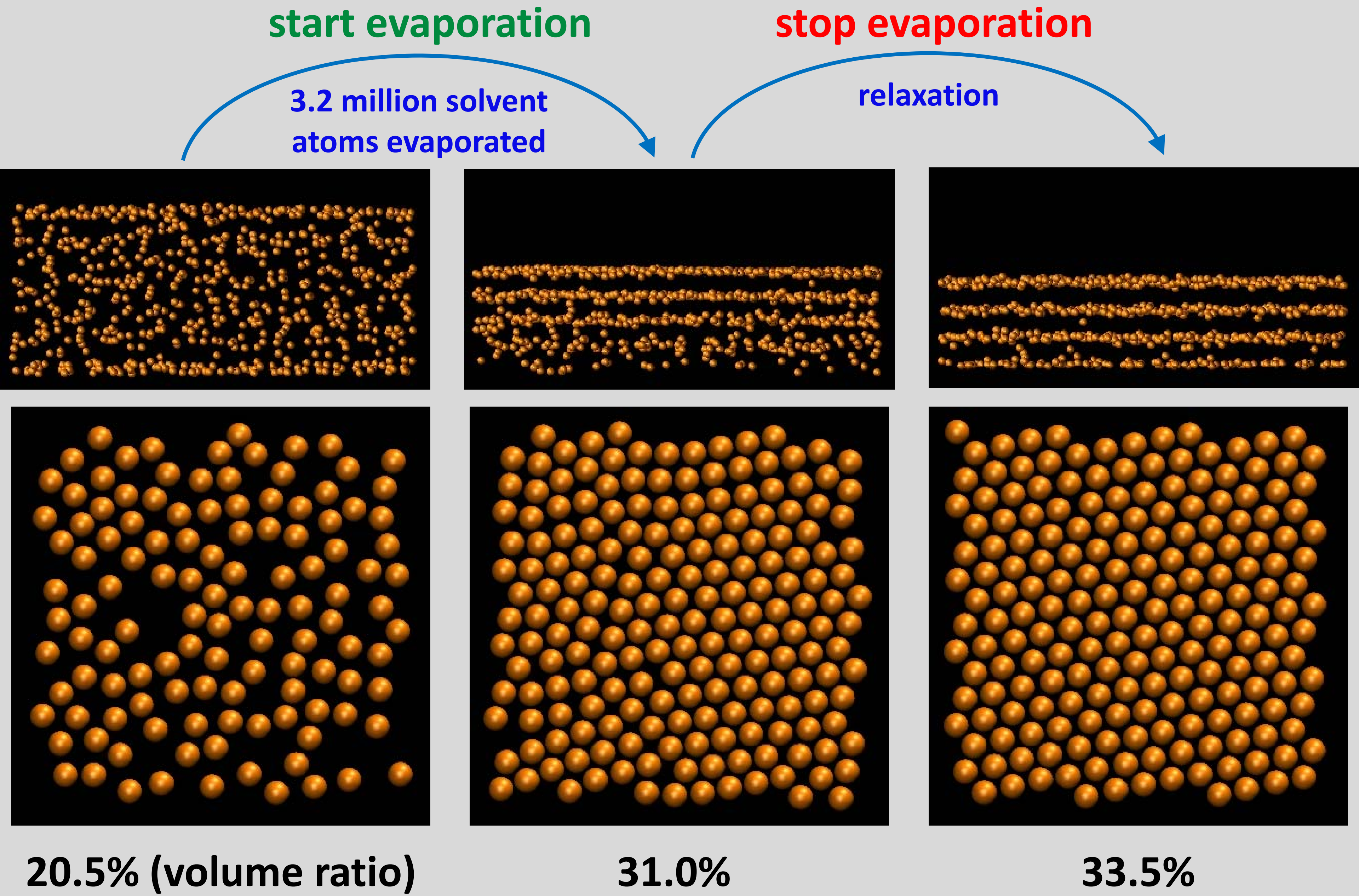


- Explicit **LJ solvent (~ 7 million)** + **668 nanoparticles (d ~ 20σ ~ 6nm)** (also 17 million solvent + 720 NPs)
- Integrated LJ potential between nanoparticles (purely repulsion), and nanoparticles and solvent (with attractions)

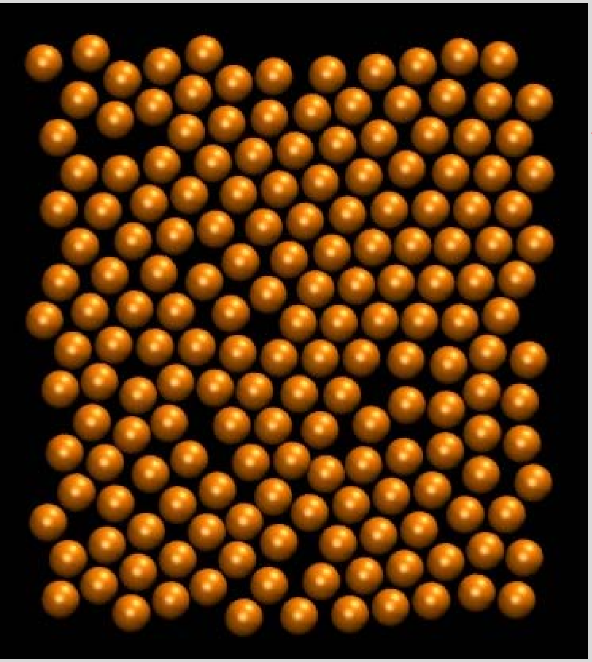


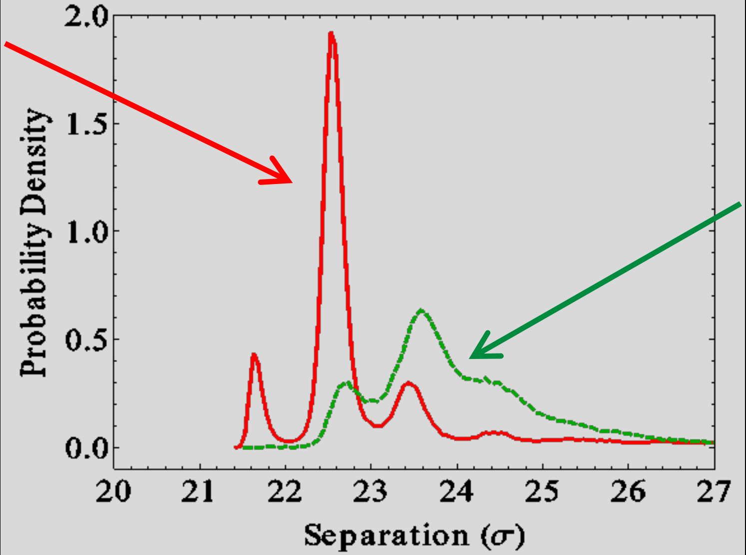
- Evaporating vapor of solvent into vacuum or at controlled rates
- Nanoparticles move toward interface but remain in solution during evaporation
- Monitor structure of nanoparticles assembled near interface

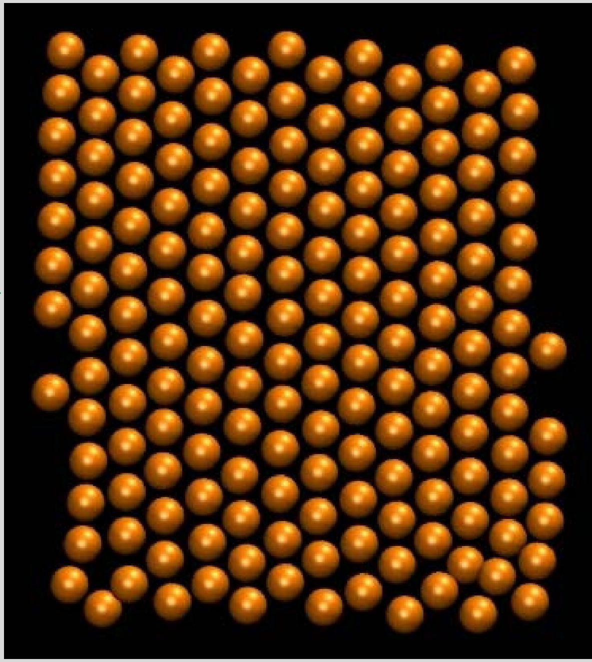
Nanoparticles assemble near interface during evaporation



Assembly quality is better at slower evaporation rates







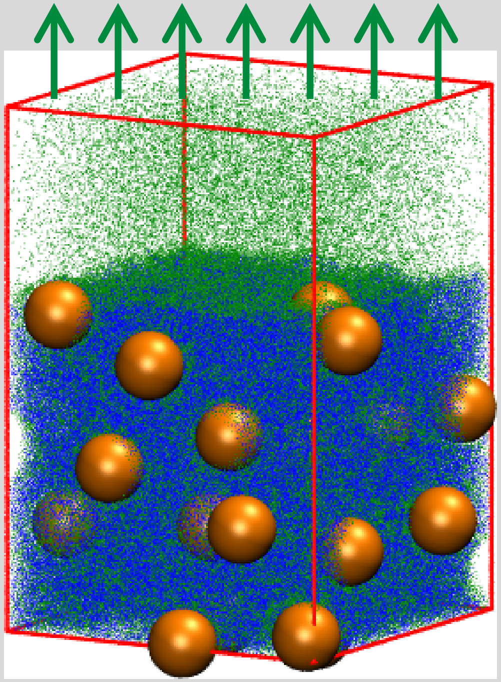
Evaporation into Vacuum

Evaporation at Fixed Rate

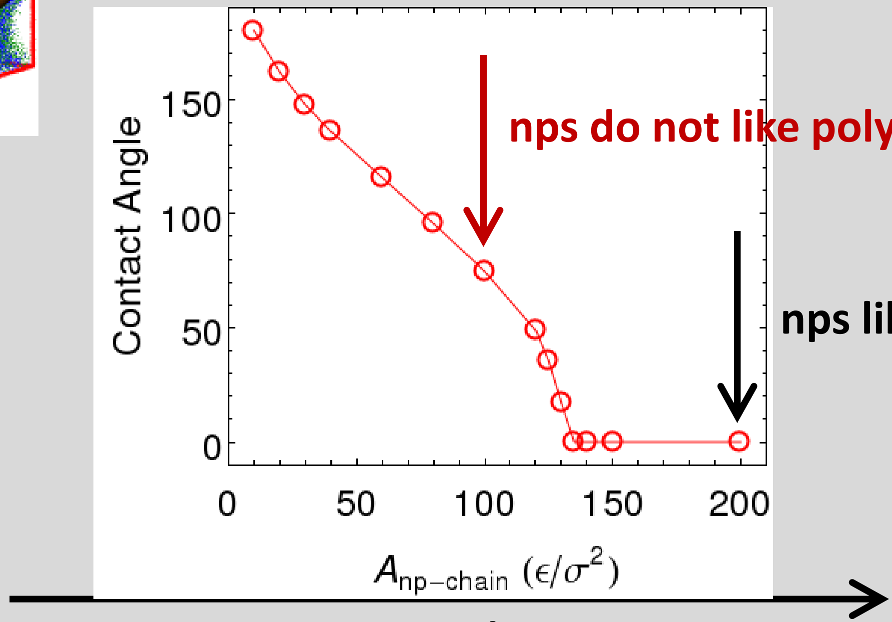
- **Initial (final) rate into vacuum about 100 (6) times of the fixed rate**
- **Averaged rate into vacuum about 10 times of the fixed rate**
- **Slower evaporation → higher quality of assembly (enough time to adjust when evaporate slowly) → optimum rate for best quality?**
- **Separations smaller and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

Nanoparticle/Polymer/Solvent Systems

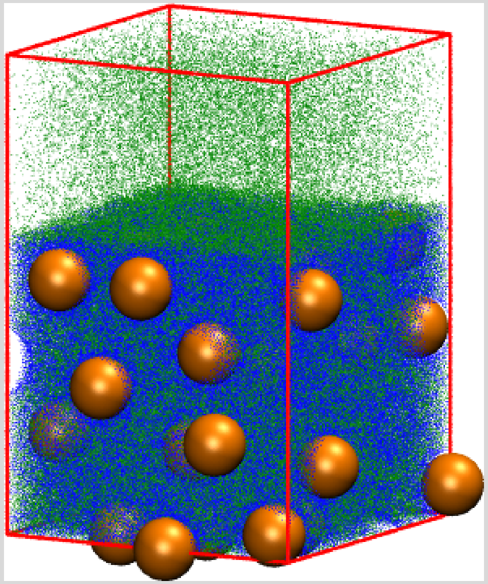
Evaporating solvent



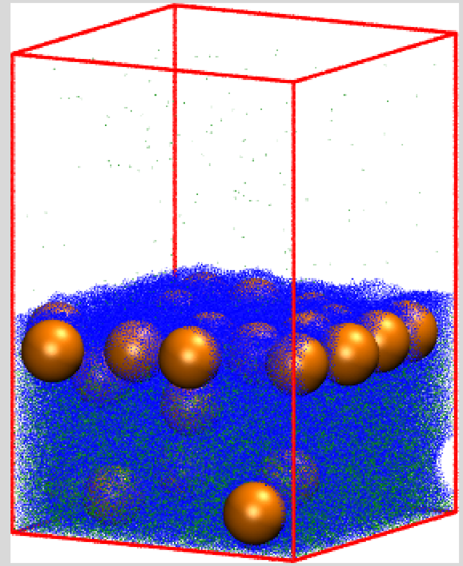
- **LJ solvent (~ 3 million) + 100-bead polymer chains (~ 3 million monomers) + nanoparticles (200)**
- FENE bonds for polymer chains
- Interactions by LJ/integrated-LJ potentials
- Starting volume % of polymer: 45%
- Starting volume % of nps: 10%



If nanoparticles like polymer chains

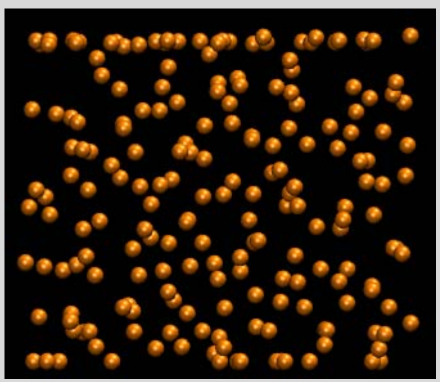


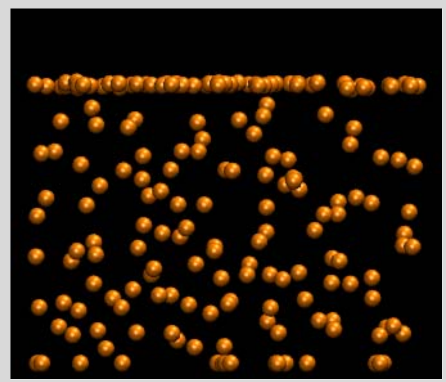
before evaporation



after evaporation

lateral view

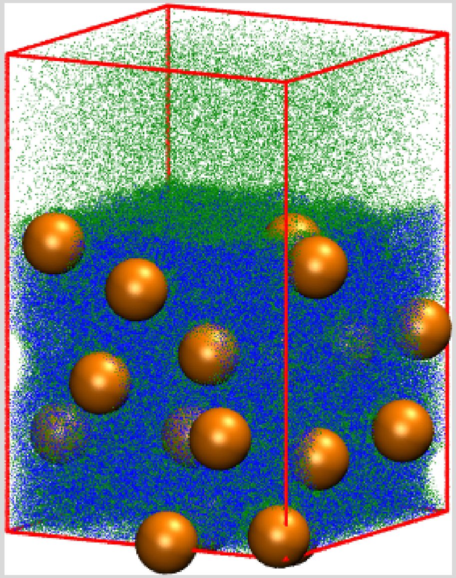




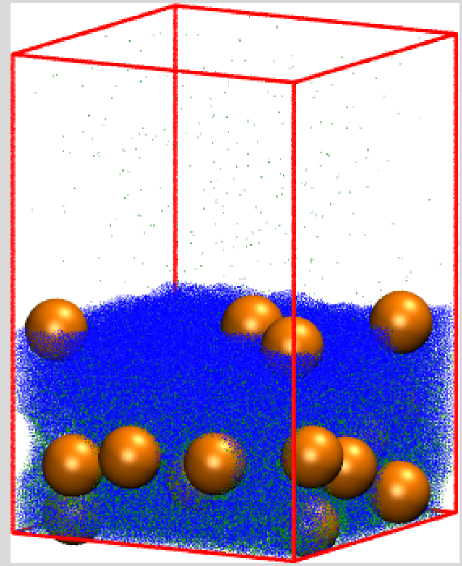
polymer density peaks here ←

Nanoparticles accumulate near liquid/vapor interface, where polymer chains are more concentrated

If nanoparticles do not like polymer chains

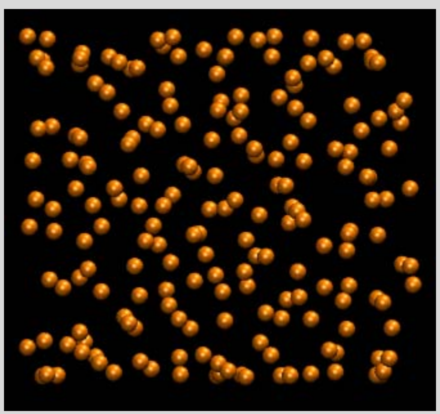


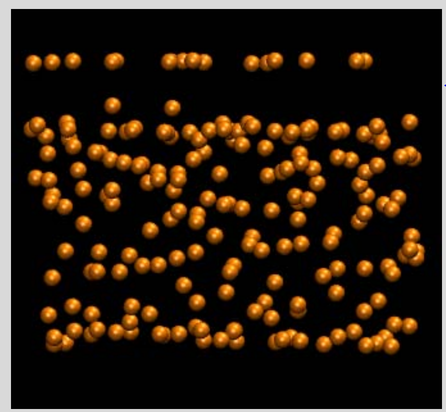
before evaporation



after evaporation

lateral view

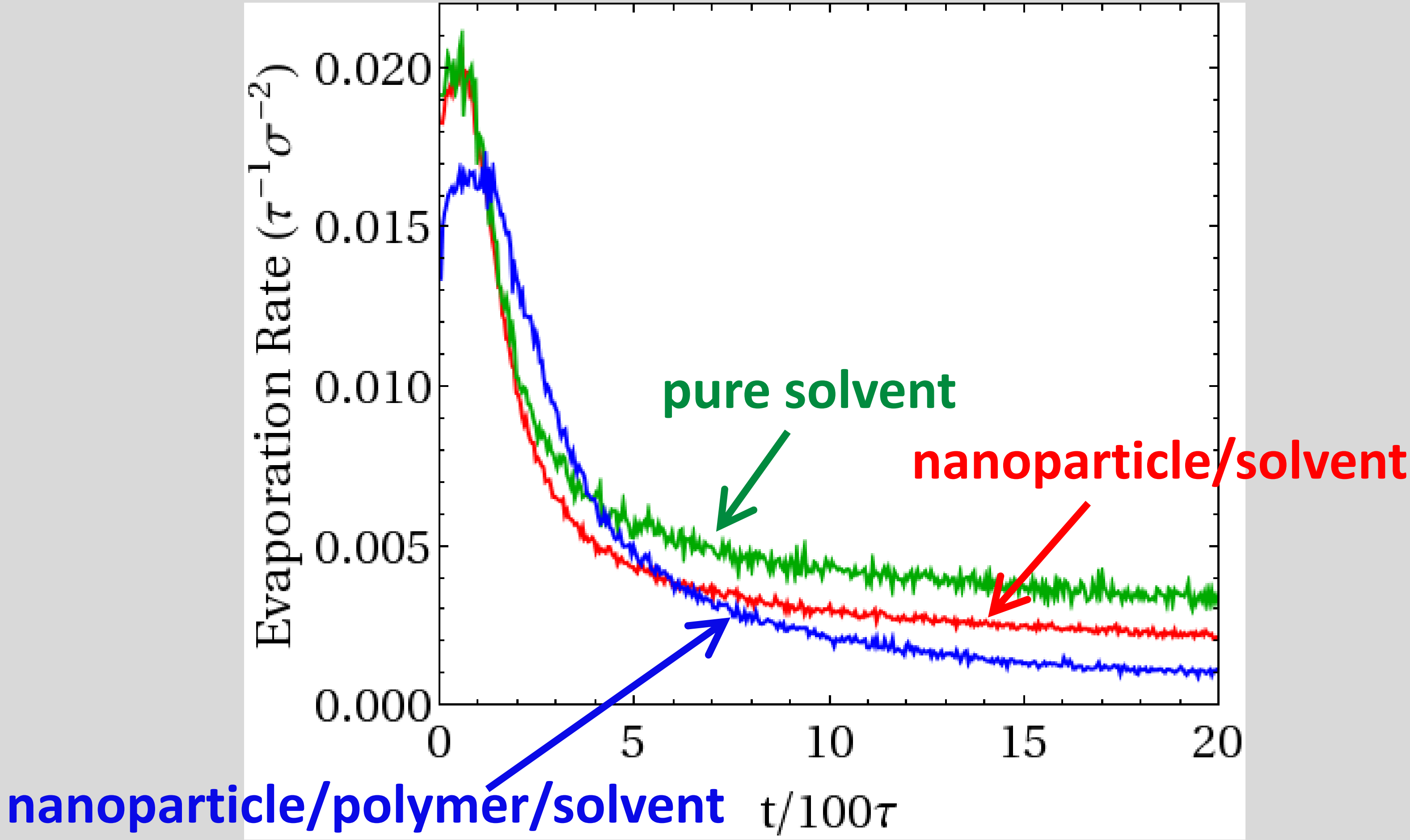




polymer density peaks here

- Some nanoparticles straddle liquid/vapor interface
- Depletion of nanoparticles in dense polymer layer near liquid/vapor interface

Nanoparticles assembled at interface block evaporation



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

Conclusions

Evaporation of pure liquids:

- Liquid/vapor interface is the coolest place during evaporation
- Mechanical equilibrium and evaporative cooling → liquid density enhanced near the liquid/vapor interface → effect large for LJ fluids but might be less dramatic for real liquids

Evaporation of nanoparticle/solvent systems:

- Nanoparticles assemble into hexagonal lattice near the liquid/vapor interface during evaporation
- 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 liquid/vapor interface slows down the evaporation rate compared to neat solvent

All simulations were done with LAMMPS developed at SNL (http://lammps.sandia.gov)