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Evaporation of Lennard-Jones Fluids and Evaporation-Induced Nanoparticle Assembly: Molecular Dynamics Studies

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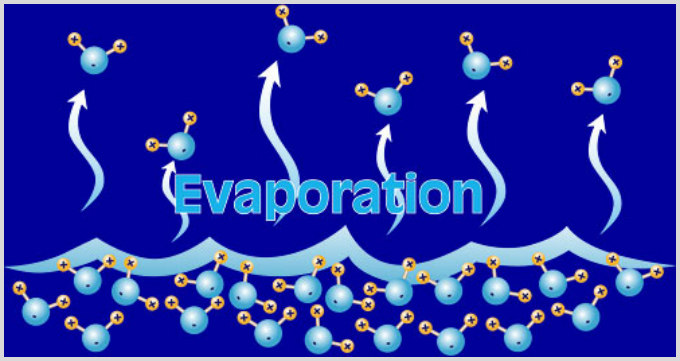
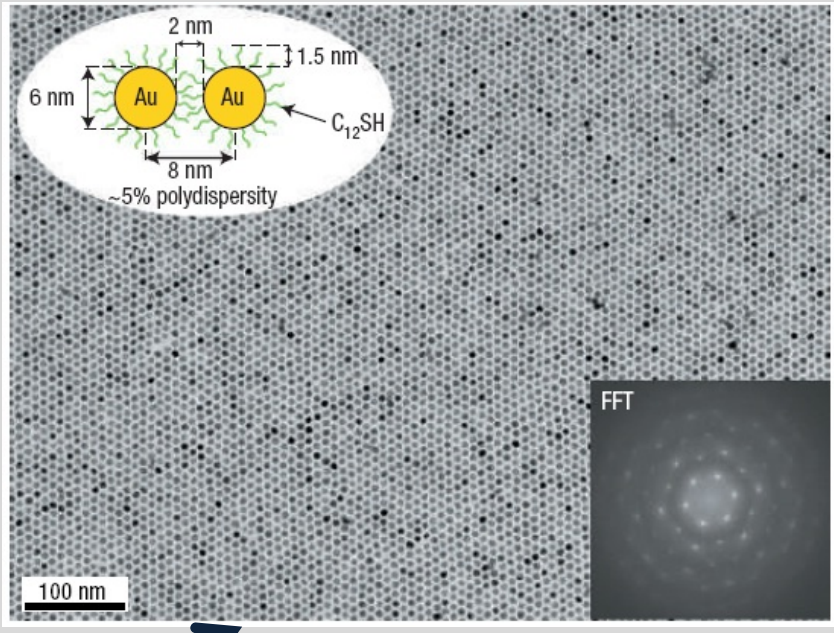
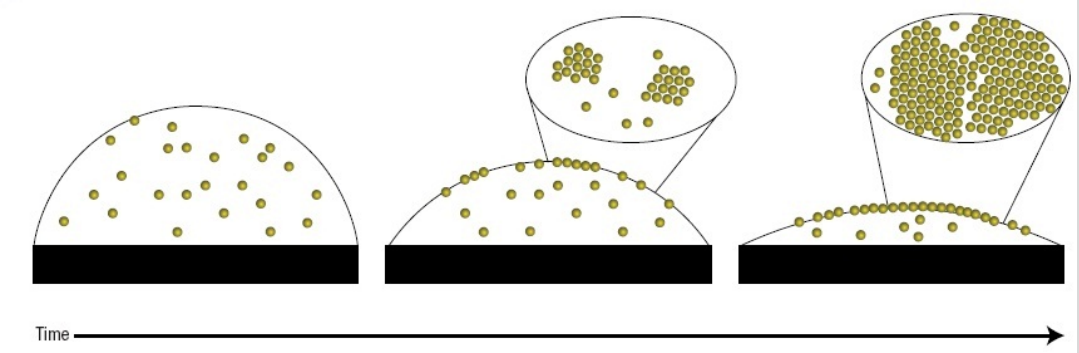
Motivation

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"*



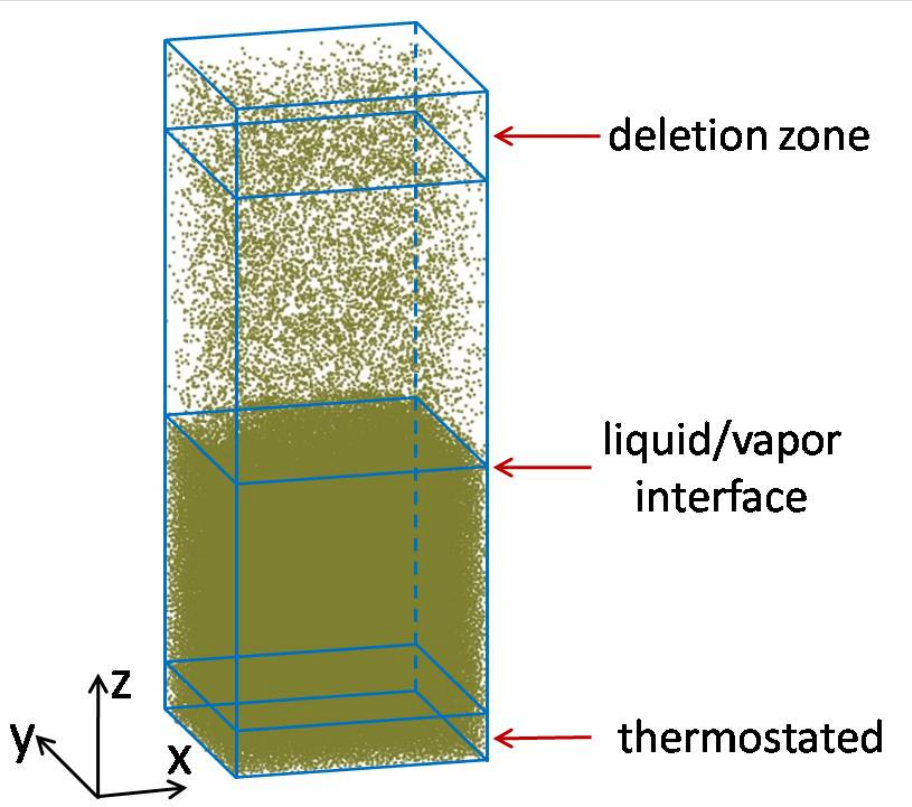


Bigioni *et al* (2006)
Nature Materials

Evaporation of Lennard-Jones Liquids: Molecular Dynamics

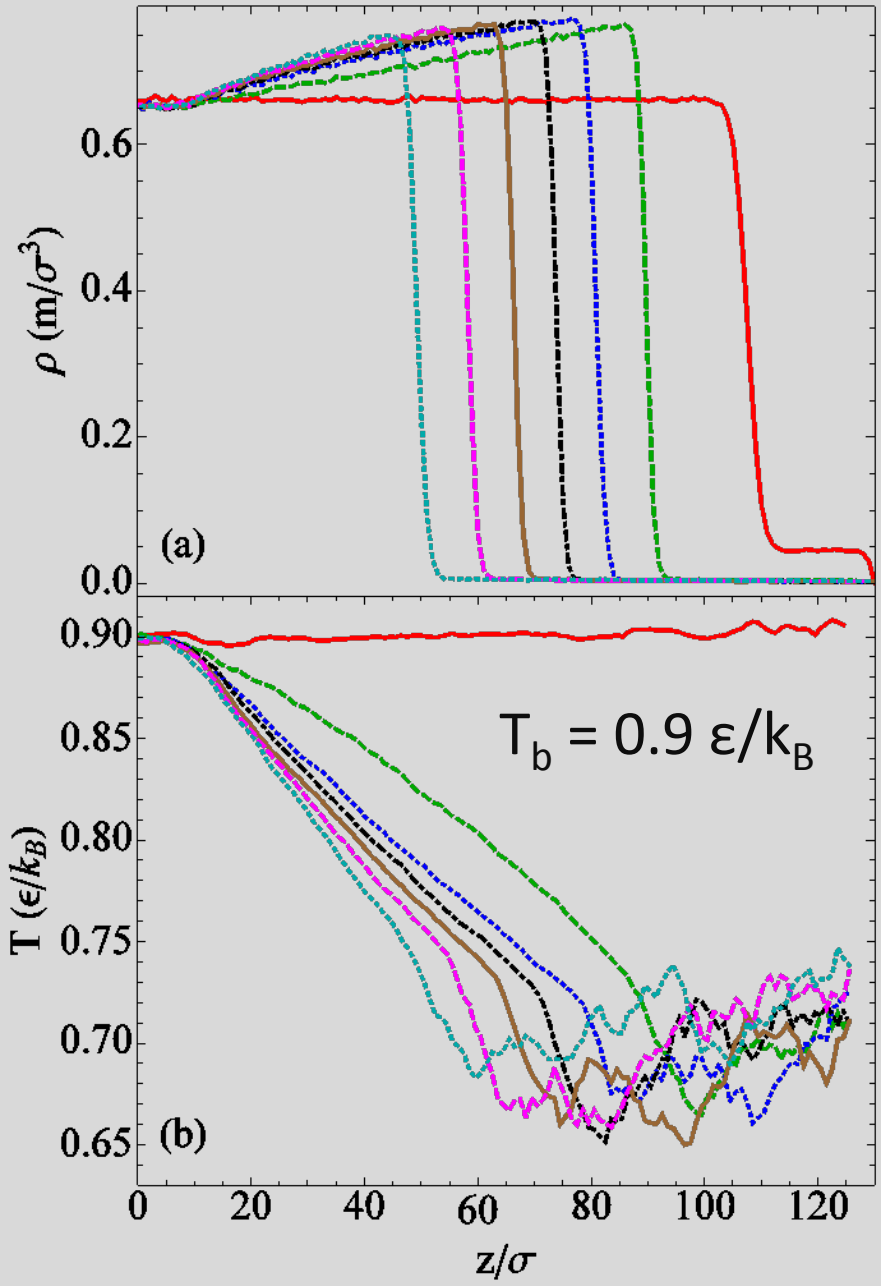
$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- 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



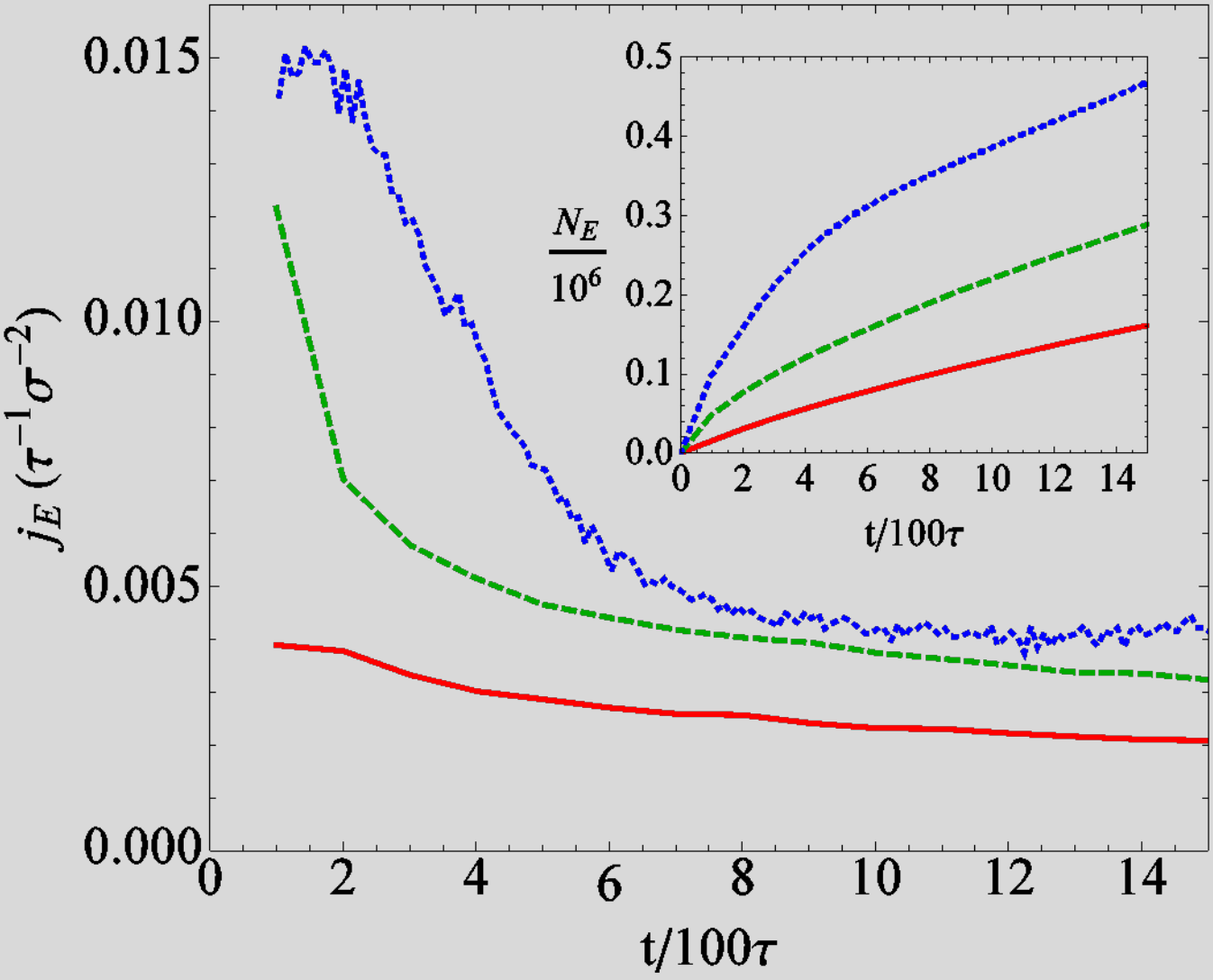
Cheng *et al*, JCP (submitted)

Density and Temperature Profiles: Evaporation into Vacuum



- Vapor density almost vanishes after evaporation initiated
- Liquid density enhances by ~ 20% near L/V interface
- 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: Time Dependence



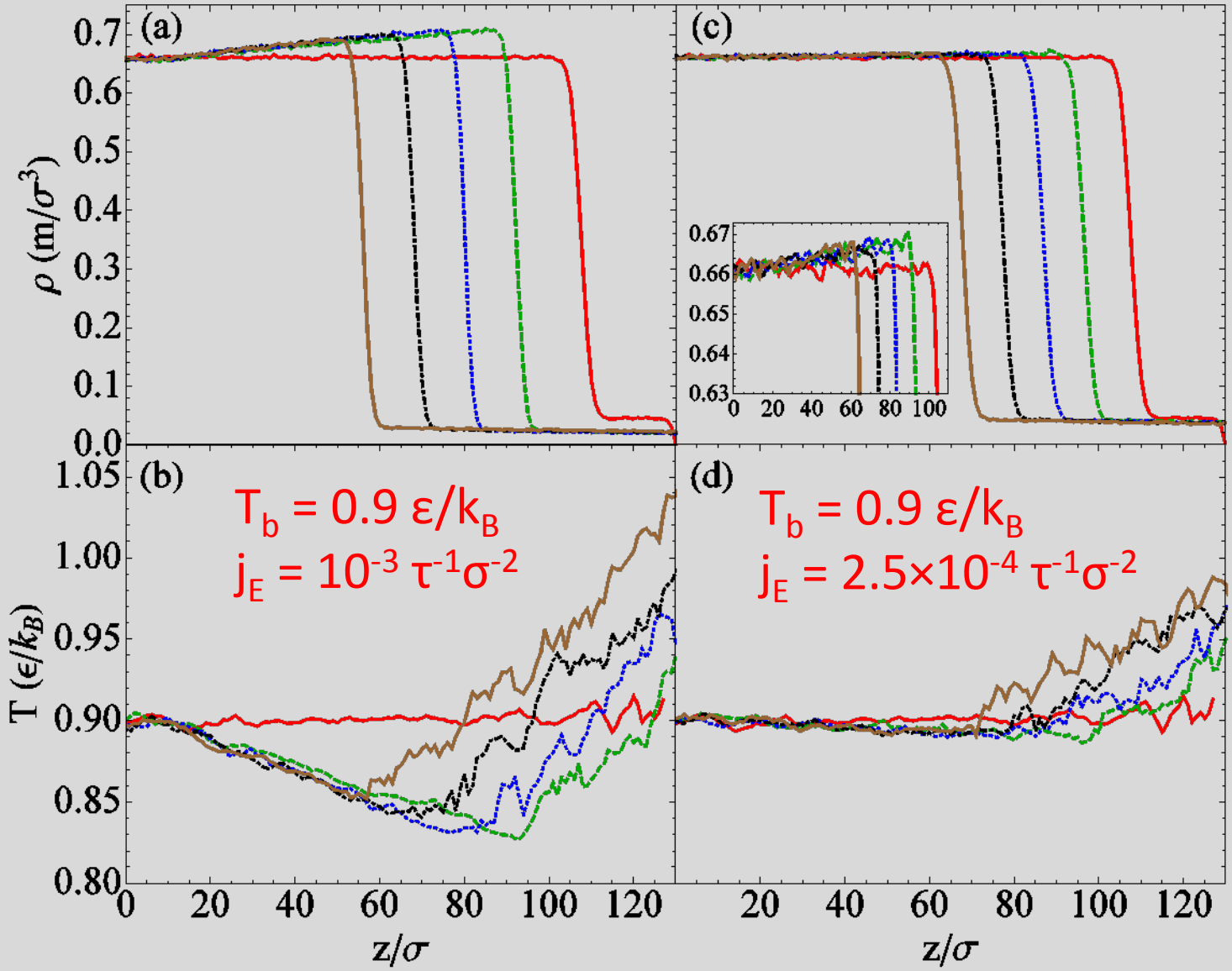
$T_b = 1.0\ \varepsilon/k_B$

$T_b = 0.9\ \varepsilon/k_B$

$T_b = 0.8\ \varepsilon/k_B$

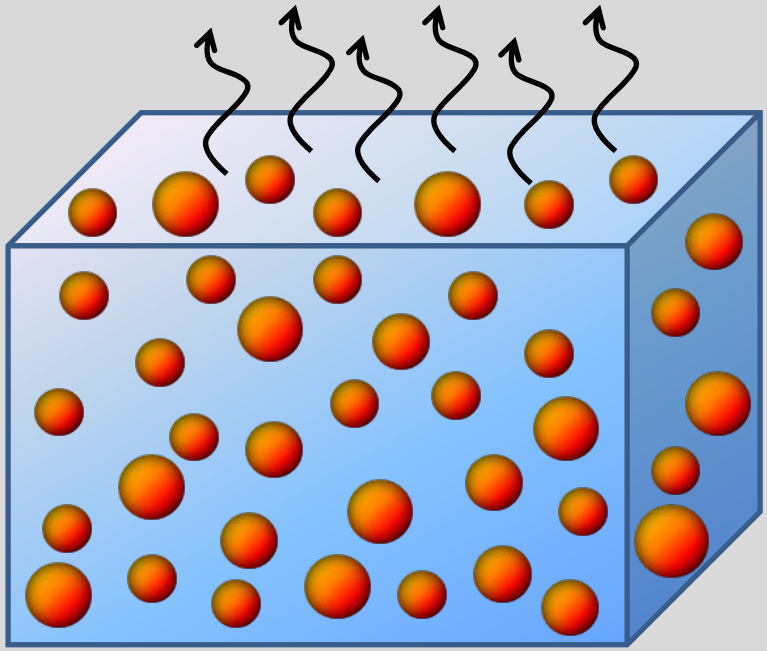
- Depletion of vapor → decrease of evaporation rates with time
- Decrease more dramatic at higher temperatures

Density and Temperature Profiles: Controlled Evaporation Rates



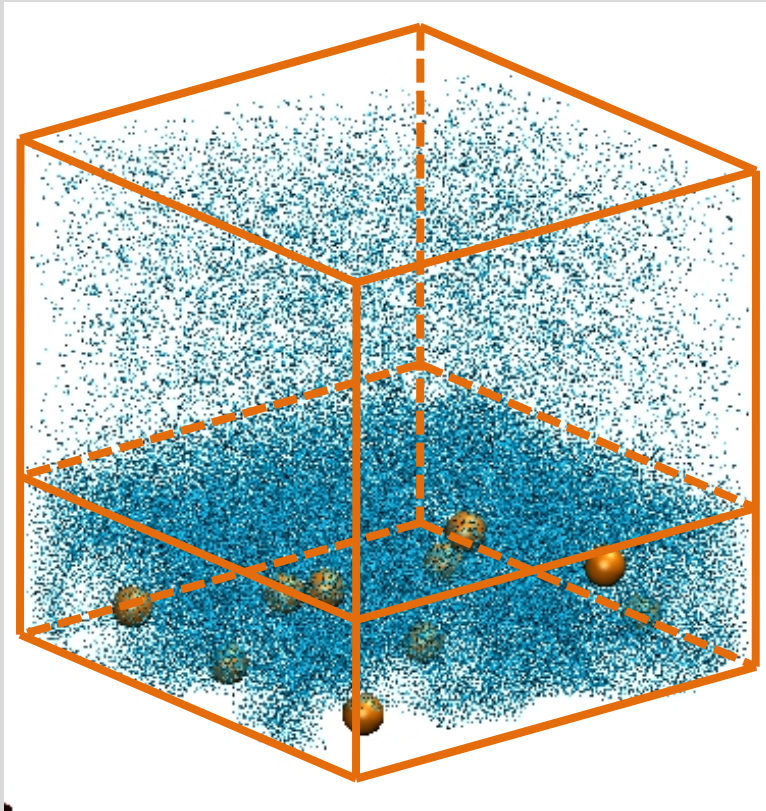
- **Lower evaporation rates → less changes in ρ and T near L/V interface**

Evaporation-Induced Nanoparticle Assembly: MD Model

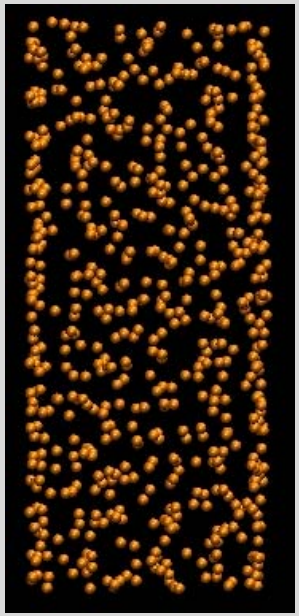


- Explicit LJ solvent (~ 7 million) + 668 nanoparticles (d ~ 20σ ~ 6nm)
- Integrated LJ potential between nanoparticles, and nanoparticles and solvent

- Evaporating vapor of solvent
- Nanoparticles move toward interface but remain in solution during evaporation
- Measure structure of nanoparticles assembled near interface

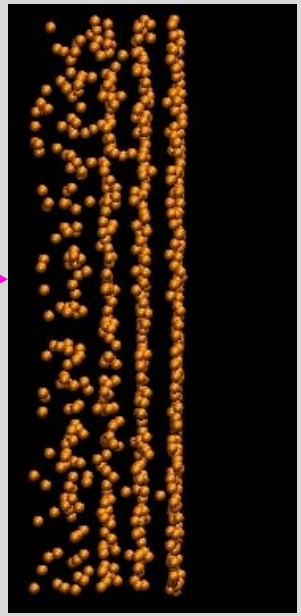


Nanoparticle Assembly: Solvent Evaporating into Vacuum

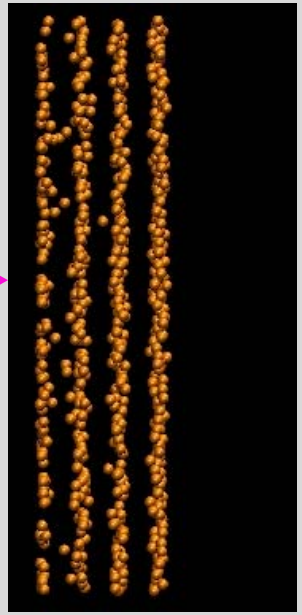


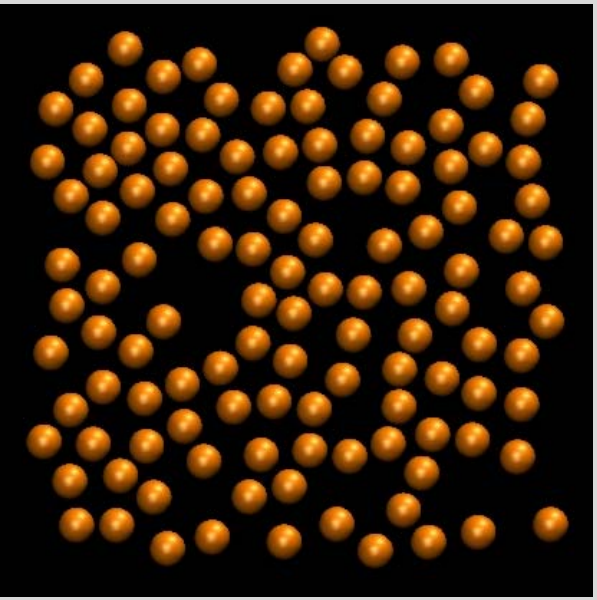
start Evaporation

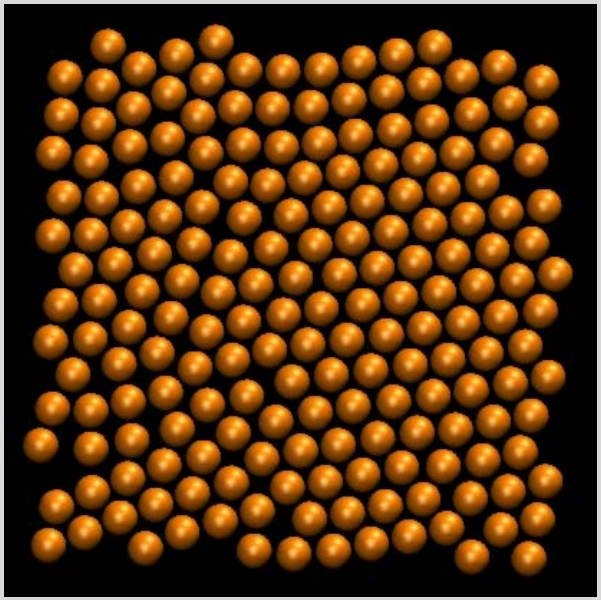
3.2 million solvent atoms evaporated

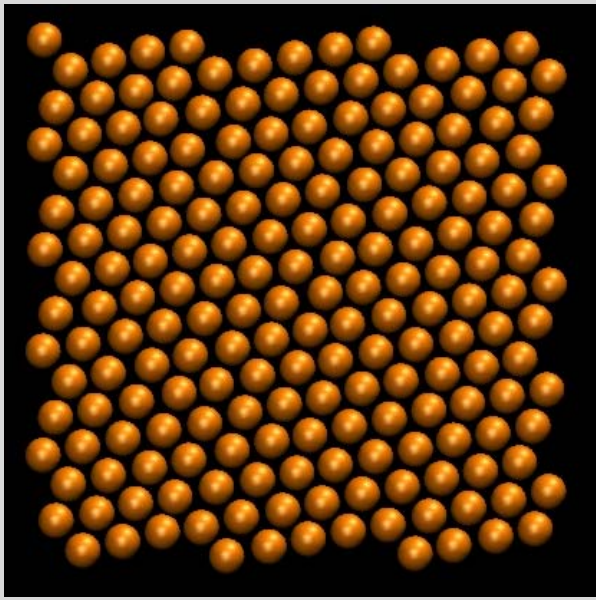


stop evaporation







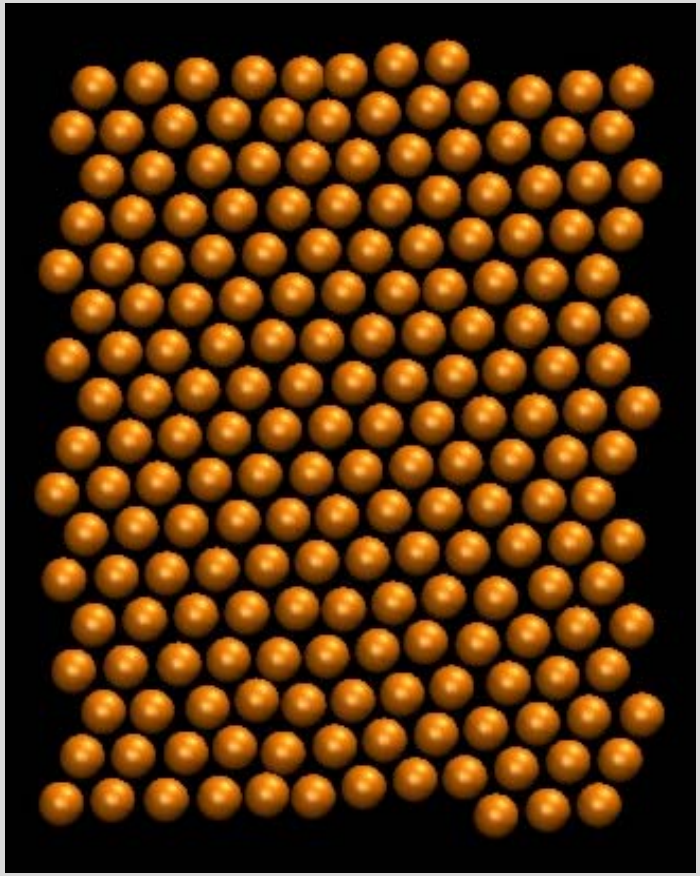


20.5% (volume ratio)

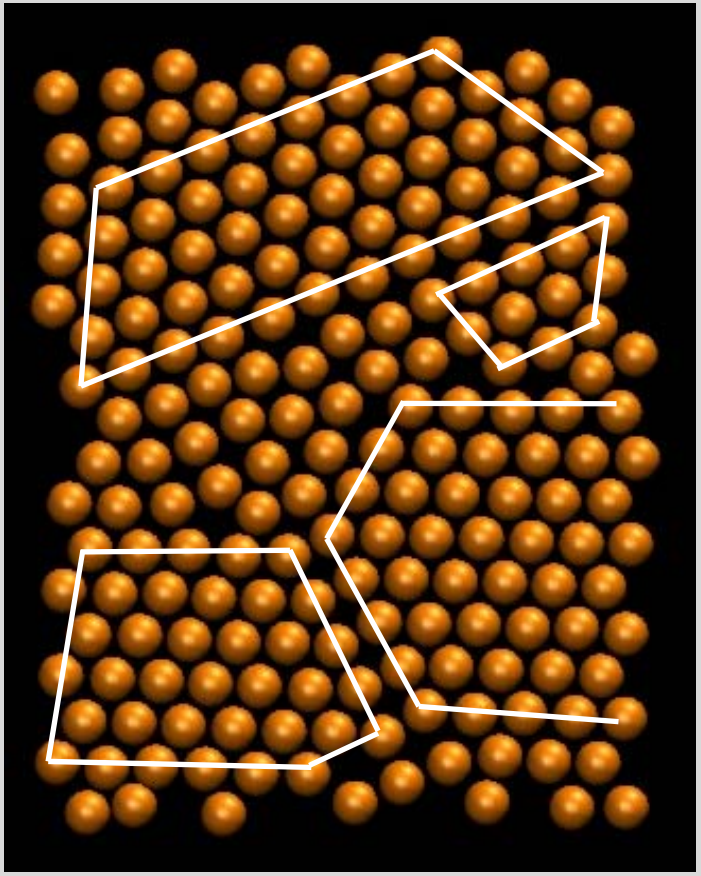
31.0%

33.5%

Effect of Evaporation Rates on Assembly Quality



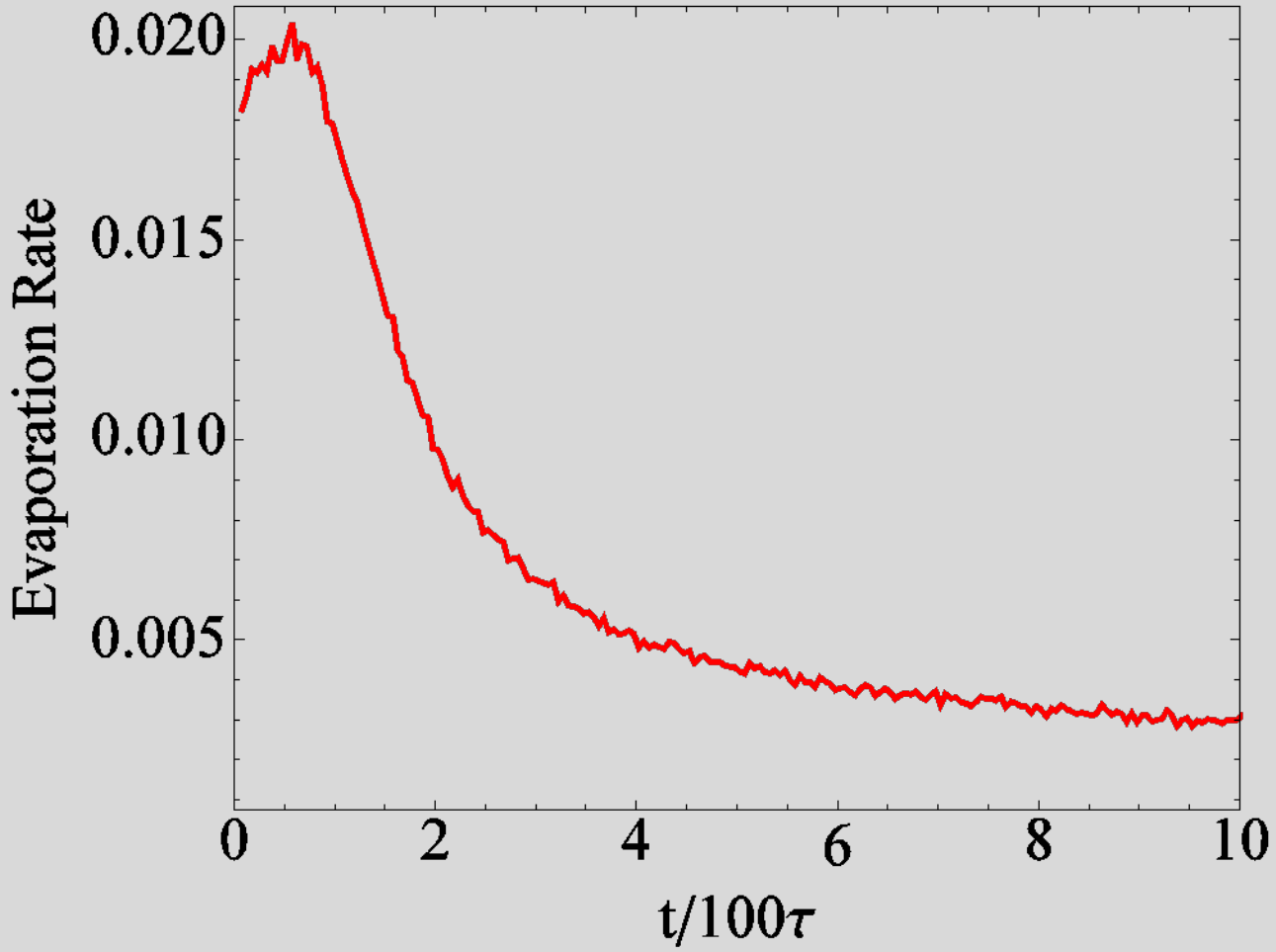
Evaporation into Vacuum



Evaporation at Fixed Rate

- **Initial evaporation rate into vacuum about 20 times of the fixed rate**
- **Averaged rate into vacuum about twice of the fixed rate**
- **Faster evaporation → higher quality of assembly (consistent with experimental observation)**

Quick Slowing-down of Evaporation: Nanoparticle Blockage



- **Evaporation rate drops by an order of magnitude quickly:**
  → Depletion of vapor
  → Blockage of nanoparticles assembling near the liquid/vapor interface

Conclusions

- Liquid/vapor interface is the coolest place during evaporation
- Liquid density enhanced near the liquid/vapor interface → effect large for LJ fluids but might be less dramatic for real liquids
- Nanoparticles assemble near the liquid/vapor interface during evaporation
- Faster evaporation rate leads to higher quality assembly
- Assembly of nanoparticles near the liquid/vapor interface slows down the evaporation rate dramatically compared to neat solvent

All simulations were done with LAMMPS developed at SNL