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Simulations of Nanoparticle Ordering in Polymers via Solvent Evaporation

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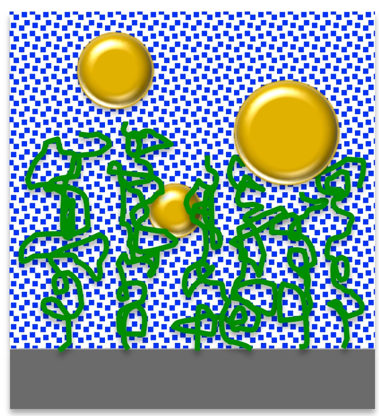
Polymer/Nanoparticle Composites

- Generally, composites are made in order to have material properties better than the components
  - Polymer film may be container for nanoparticles that possess key property
  - Responsive polymer could turn on/off nanoparticle property
- What determines the material properties?
  - Structure of composite
- How to control nanoparticle placement/distribution?
  - Interactions
  - Nonequilibrium effects (e.g. evaporation)

General system is polymer + nanoparticles + solvent

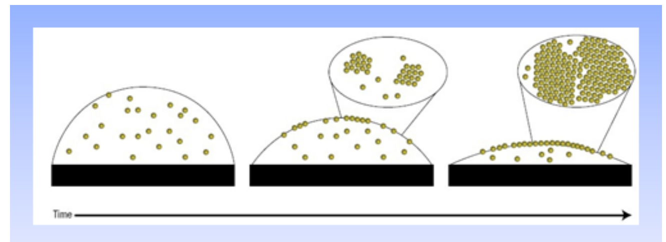


Self-Assembly of Nanoparticle Films

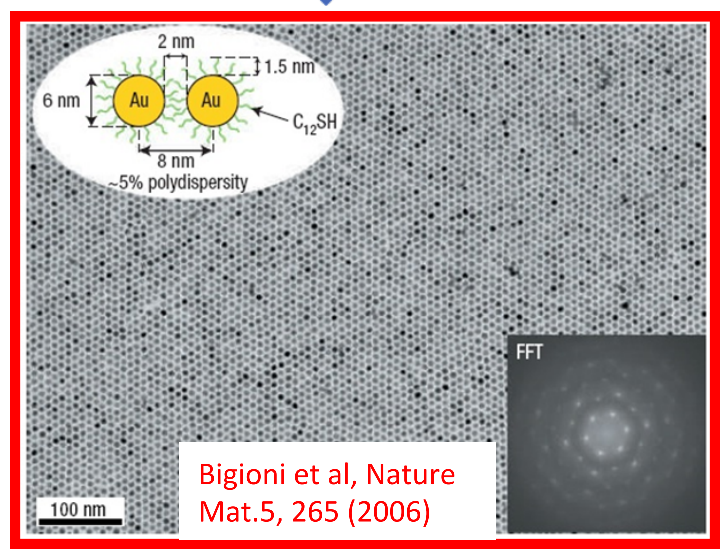
Assembly by Solvent Evaporation

- Monolayer assembly with long-range order
- Extremely strong but flexible (Young's modulus of several GPa)
- Assembled nanoparticles retaining unique properties without acting like a bulk metal

Solvent + Nanoparticles



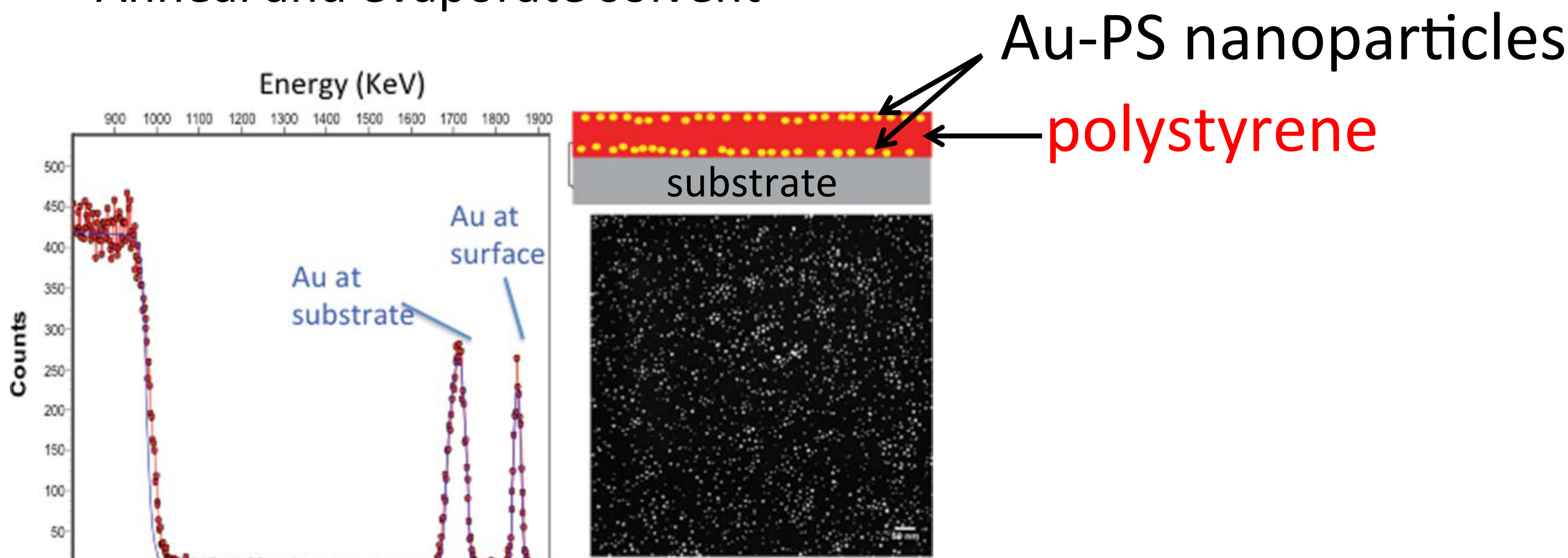
Slow evaporation of solvent



Bigioni et al, Nature Mat.5, 265 (2006)

Polymer Thin Film & Nanoparticle Composite

- Polymer thin film of polystyrene (PS)
- Gold nanoparticles with grafted PS
- Spin coat film
- Anneal and evaporate solvent



RBS

STEM image

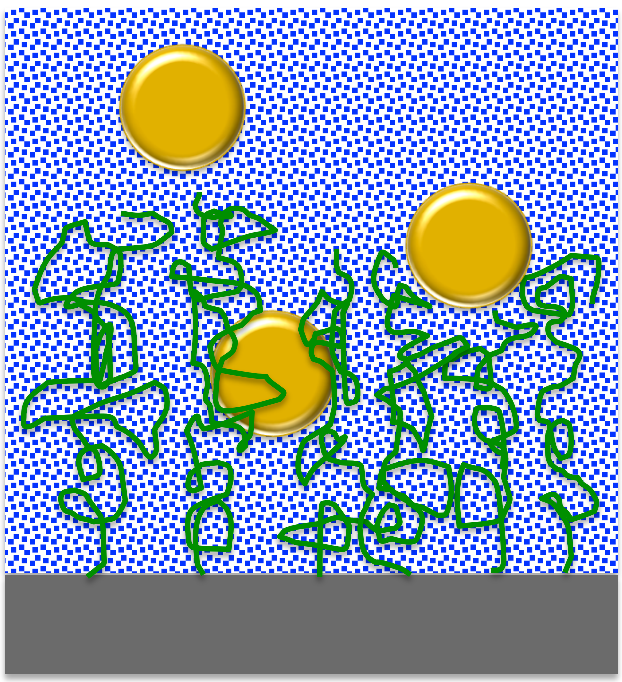
(a) (b)

Green, Soft Matter (2012)

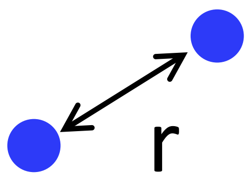
Simulation System

Polymer Brush + Nanoparticles + Solvent
- no molecular coating on nanoparticle
- effective interaction between nanoparticle and polymer or solvent
- vary strength of nanoparticle interaction
- vary brush grafting density

Where does nanoparticle go?
What conditions create an array of nanoparticles?

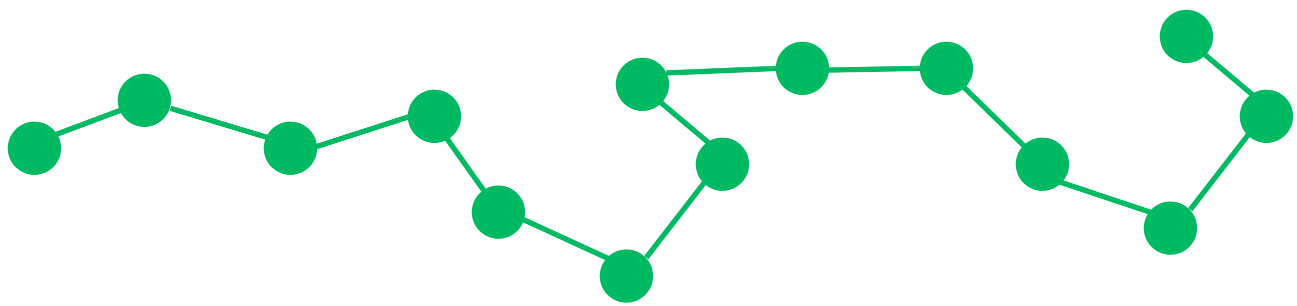


Interactions



solvent:solvent and solvent:polymer bead

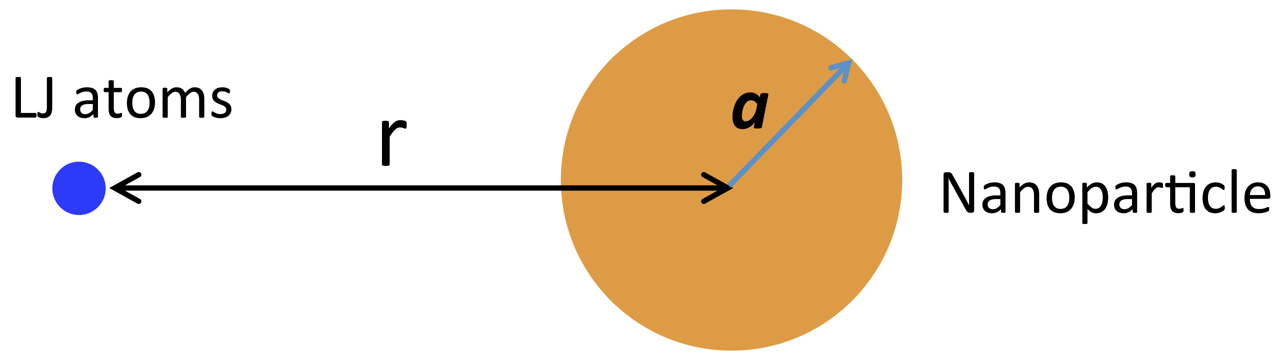
Lennard-Jones potential $$U(r) = 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{12} - \left(\frac{r}{\sigma}\right)^{6}\right]$$



polymer chains (bead-spring model)

bond potential $$U(r) = -0.5KR_0^2 \ln\left[1-\left(\frac{r}{R_0}\right)^2\right] + 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{12} - \left(\frac{r}{\sigma}\right)^{6}\right] + \varepsilon$$

Nanoparticle Interactions

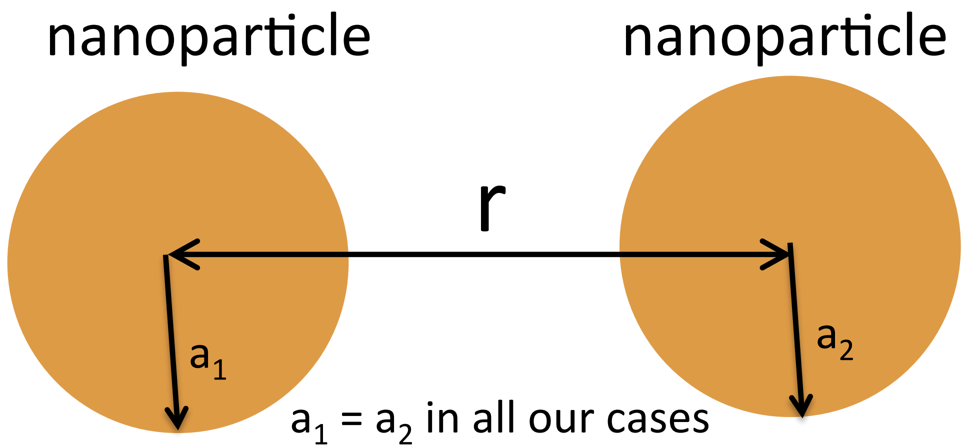


np:bead potential

$$U(r) = \frac{2}{9}\frac{a^3\sigma^3 A_{cs}}{\left(a^2 - r^2\right)^3}\left[1 - \frac{\left(5a^6 + 45a^4r^2 + 63a^2r^4 + 15r^6\right)\sigma^6}{15(a-r)^6(a+r)^6}\right]$$

- Each nanoparticle is made of uniformly distributed LJ atoms
- integrate LJ potentials to obtain np:bead or np:np interactions
- np:bead interaction strength controlled by A_{cs}

np:np interaction



NP-NP interaction strength controlled by A_{cc}

$$U = U_A + U_R$$

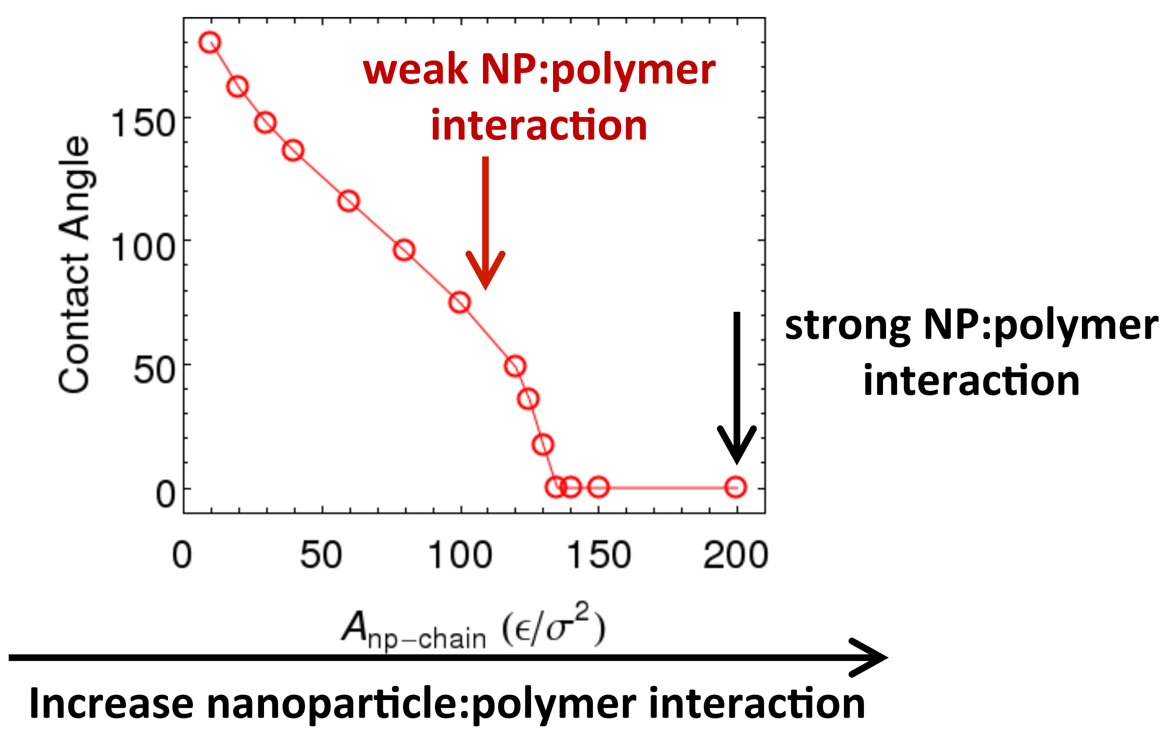
$$U_A = -\frac{A_{cc}}{6}\left[\frac{2a_1a_2}{r^2-(a_1+a_2)^2}+\frac{2a_1a_2}{r^2-(a_1-a_2)^2}+\ln\left(\frac{r^2-(a_1+a_2)^2}{r^2-(a_1-a_2)^2}\right)\right]$$

Note: range of attractive part is long!

$$U_R = \frac{A_{cc}}{37800}\frac{\sigma^6}{r}\left[\frac{r^2-7r(a_1+a_2)+6(a_1^2+7a_1a_2+a_2^2)}{(r-a_1-a_2)^7}+\frac{r^2+7r(a_1+a_2)+6(a_1^2+7a_1a_2+a_2^2)}{(r+a_1+a_2)^7}\right.$$
$$\left.-\frac{r^2+7r(a_1-a_2)+6(a_1^2-7a_1a_2+a_2^2)}{(r+a_1-a_2)^7}-\frac{r^2-7r(a_1-a_2)+6(a_1^2-7a_1a_2+a_2^2)}{(r-a_1+a_2)^7}\right]$$

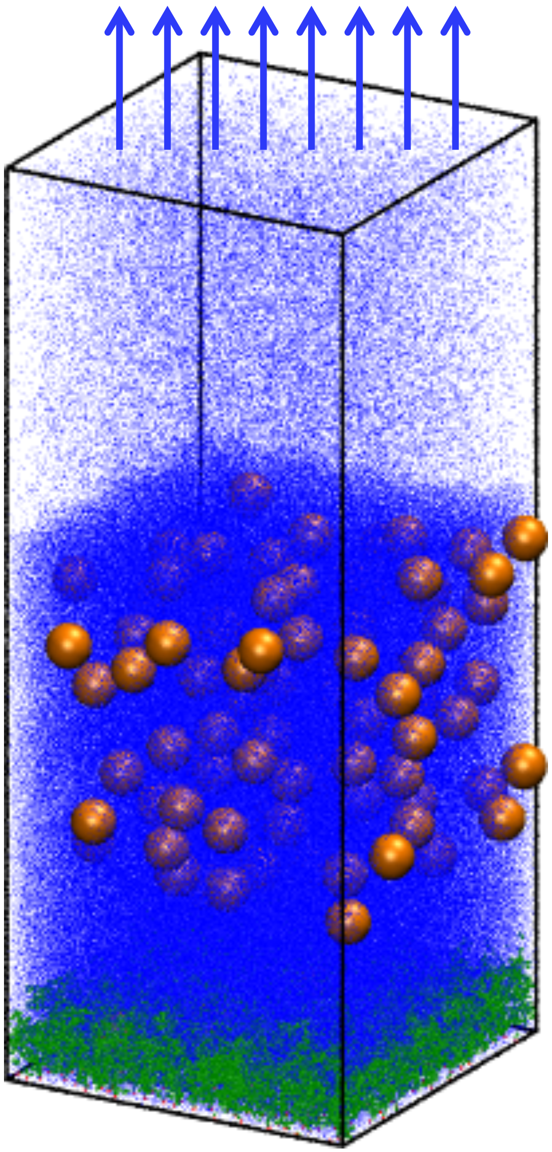
Nanoparticle:Polymer Interaction

Determine 'weak' and 'strong' Nanoparticle:Polymer strengths from contact angle simulations



Molecular Dynamics Simulations

Evaporating Solvent



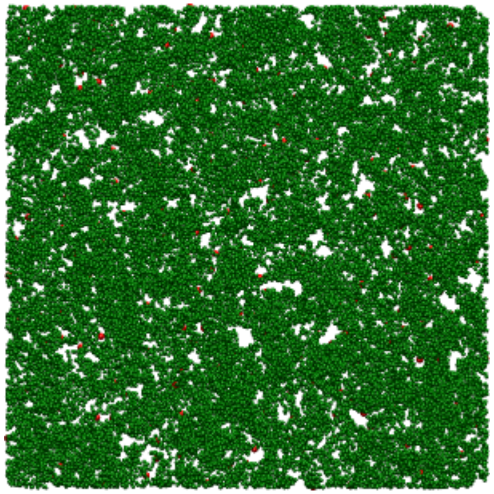
Nanoparticles/Brush

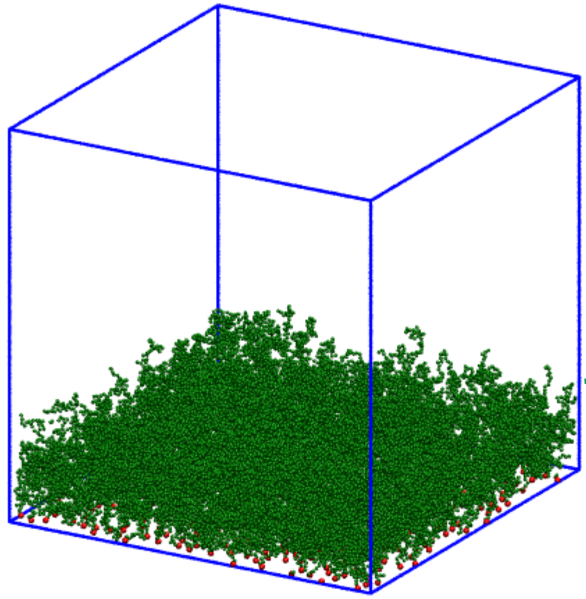
- Polymer brush with 100-bead chains
- LJ solvent in equilibrium with its vapor
- Spherical nanoparticles (D=10σ)
- Area = 100σ × 100σ
- Strong NP:solvent interaction → solvated NP
- Vary NP:brush interaction
  - A_{nb}=100ε/120ε (contact angle of 75°/30°)
  - A_{nb}=200ε (contact angle of 0°)
- Vary NP and brush densities

Nanoparticle 2D density: $\phi = \frac{N_{\mathrm{np}} D^2}{A}$

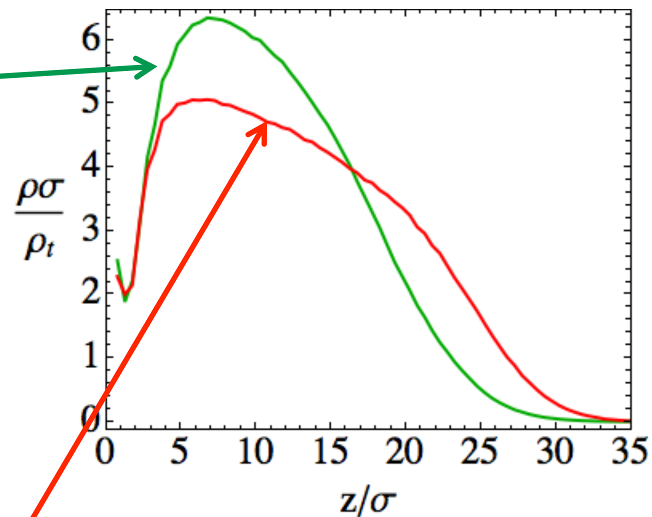
Brush Density: $\rho_b = \frac{N_{\mathrm{Brush}}}{A}$

Brush in Solvent

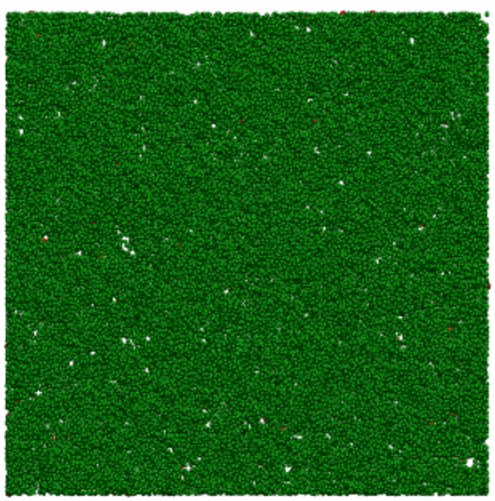


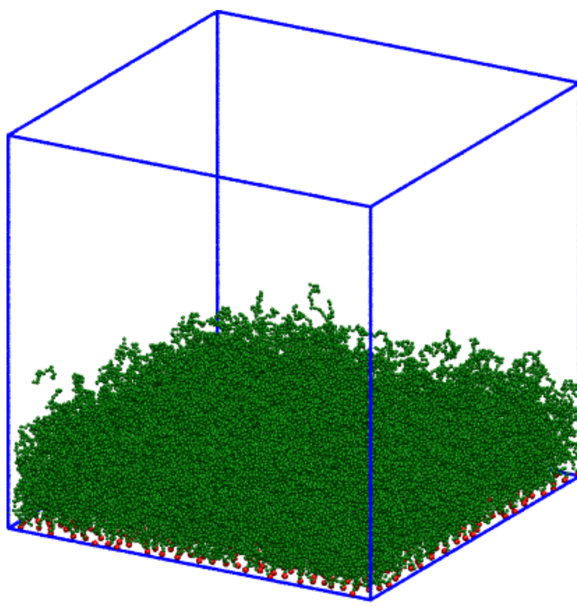


brush density = $0.04\sigma^{-2}$



Brush density normalized by 2D density of tether points



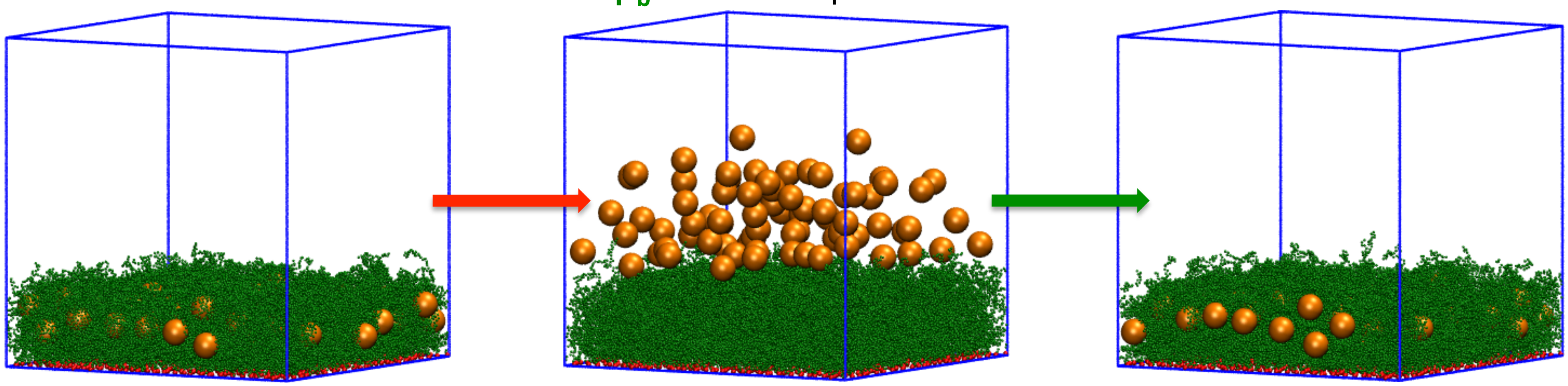


brush density = $0.08\sigma^{-2}$

Distribution of NPs: vary NP:Brush interaction

Solvent not shown

$\rho_b = 0.08$ $\phi = 0.75$



$A_{nb} = 200\ \varepsilon$	$A_{nb} = 100\ \varepsilon$	$A_{nb} = 200\ \varepsilon$
Strong interaction: NP within Brush	Reduce to weak strength: NPs release into solvent	Reset to original: NPs re-enter

Demonstrates can equilibrate nanoparticle distribution.

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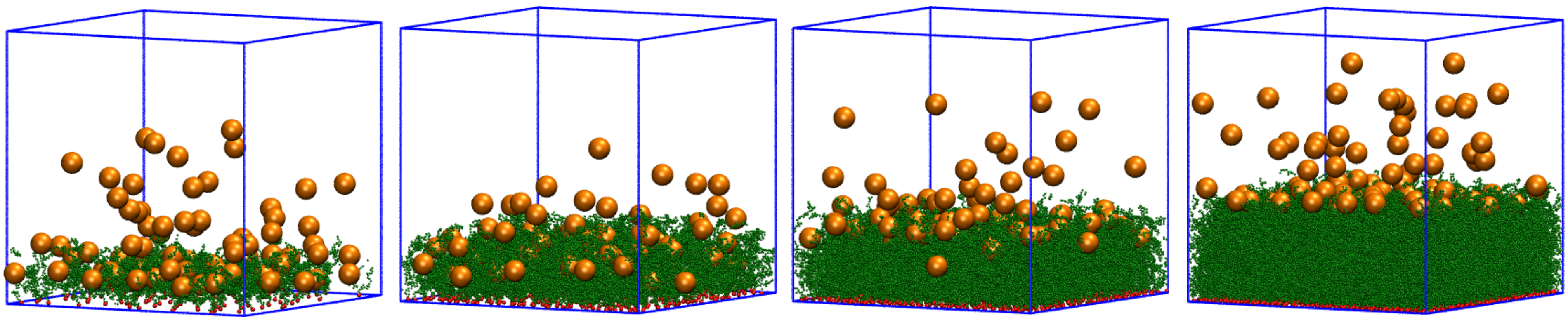
Distribution of NPs: vary Brush density

Solvent not shown

ϕ = 0.75 A_{nb} = 120 ε (weak)



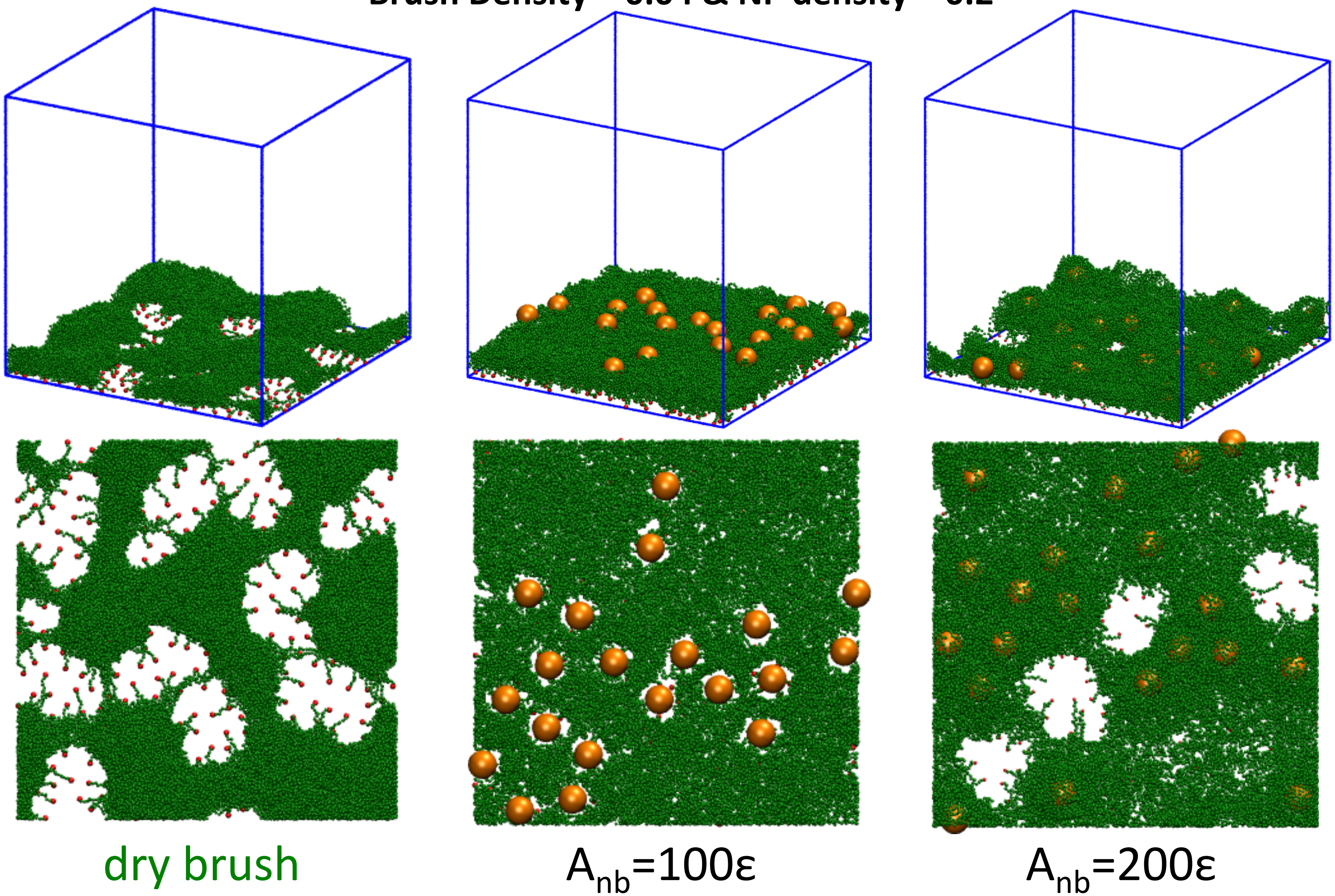
ρ_b = 0.01   0.04   0.08   0.16

1. Need sufficiently high brush density to exclude nanoparticles
2. At high brush density NPs cannot enter brush; entropic cost too high.

Thus, intermediate brush density best for mixing NPs in brush.

After Solvent Evaporation: Nanoparticles can fill voids

Brush Density = 0.04 & NP density = 0.2



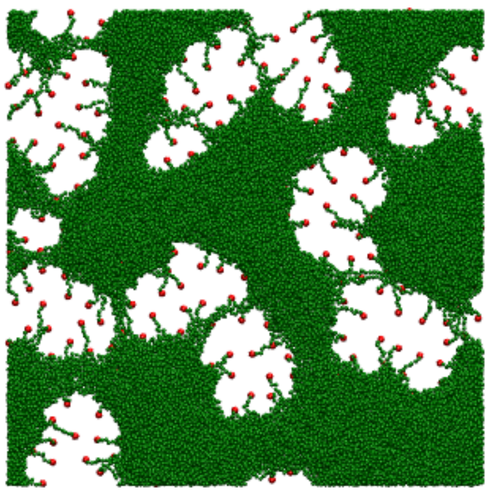
After Solvent Evaporation: Nanoparticles can fill voids

Brush Density = 0.04 & NP density = 0.2

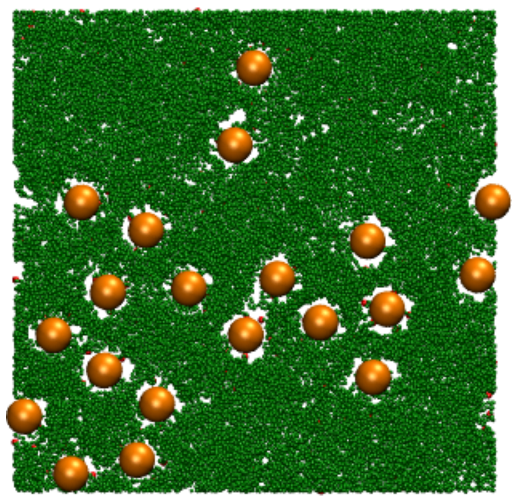
no solvent =
'poor solvent'

weak interactions &
density match =
void filling

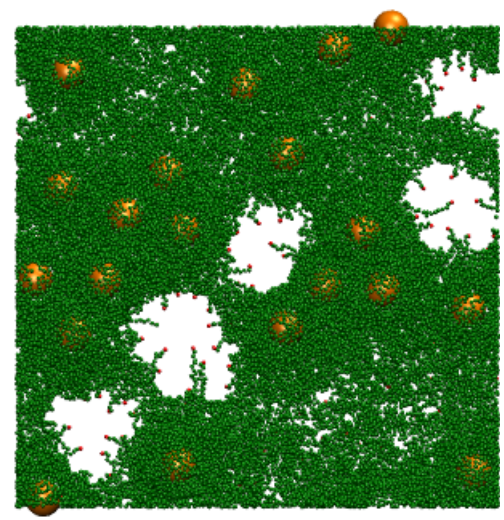
strong interactions =
NPs in brush,
not voids



dry brush



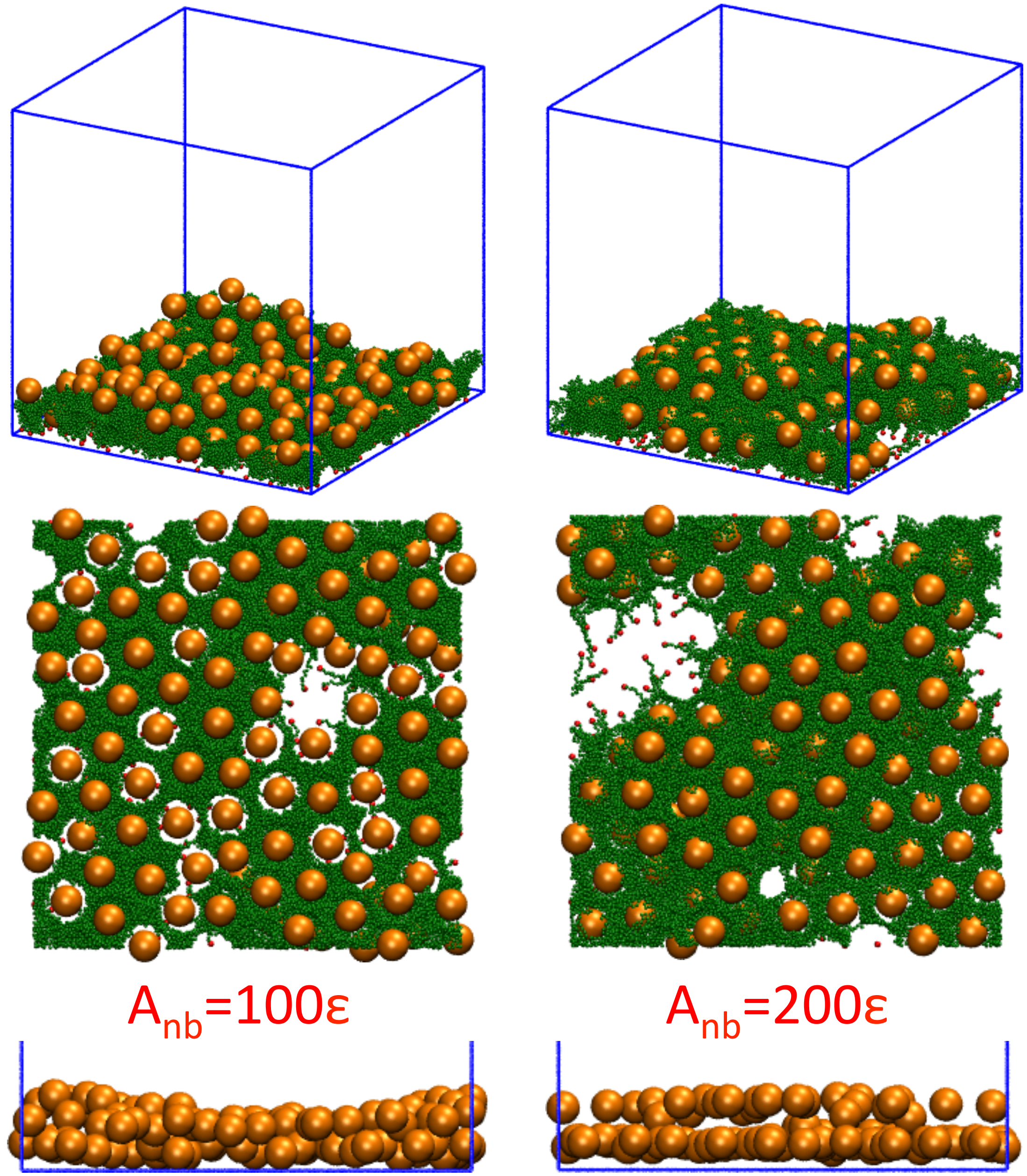
A_{nb}=100ε

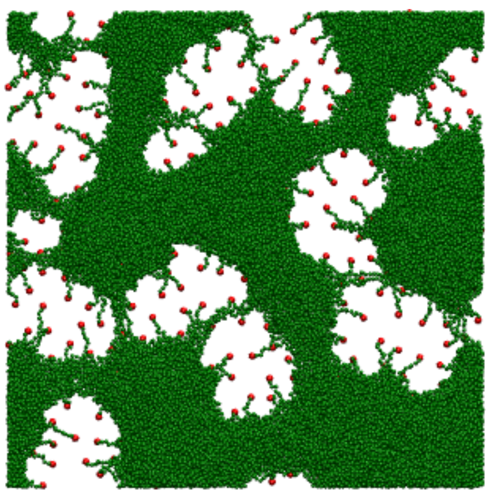


A_{nb}=200ε

Solvent Evaporation: High NP density (ϕ=1)

- Get two layers of NPs
- Weak case: not all voids filled.
- Stong case: void coalesce.

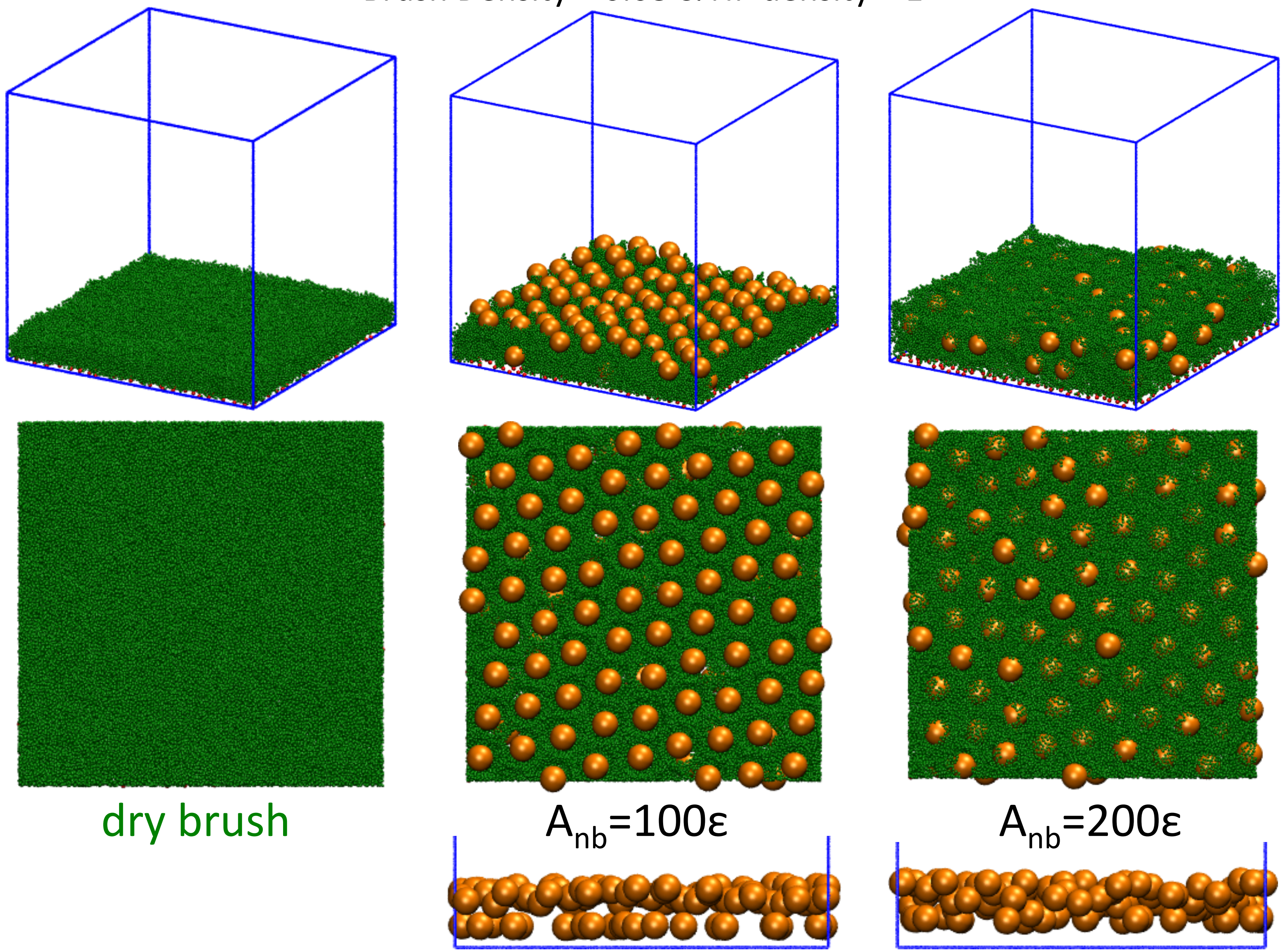




dry brush
ρ_b = 0.04

Forming Dense Arrays of Nanoparticles

Brush Density = 0.08 & NP density = 1

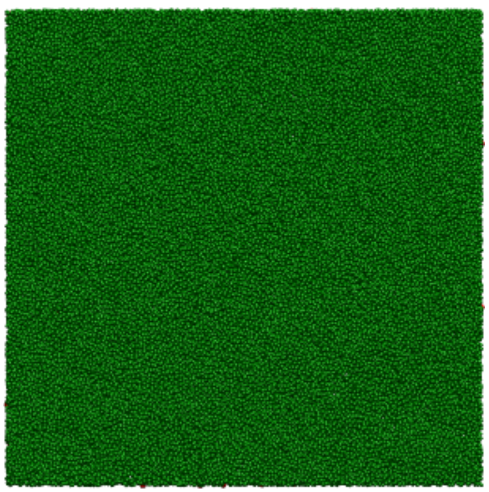


Forming Dense Arrays of Nanoparticles

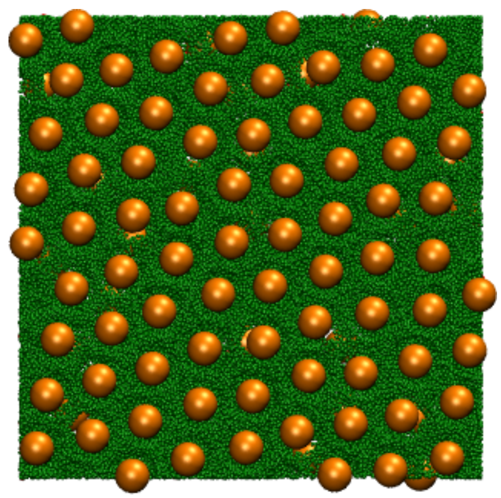
Brush Density = 0.08 & NP density = 1

two, distinct layers
top layer well ordered
& on top of brush

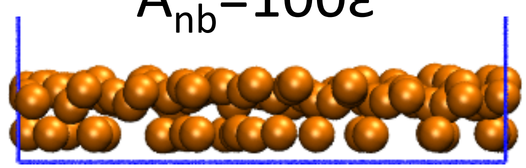
two overlapping layers
top layer immersed &
defected

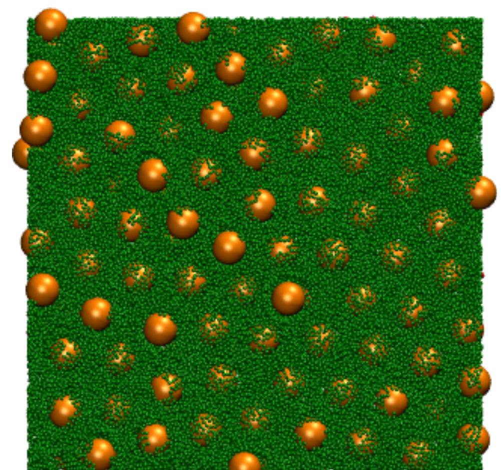


dry brush

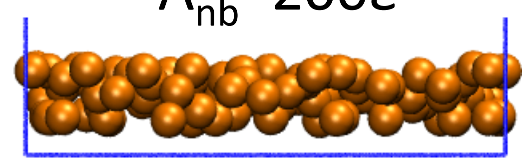


A_{nb}=100ε





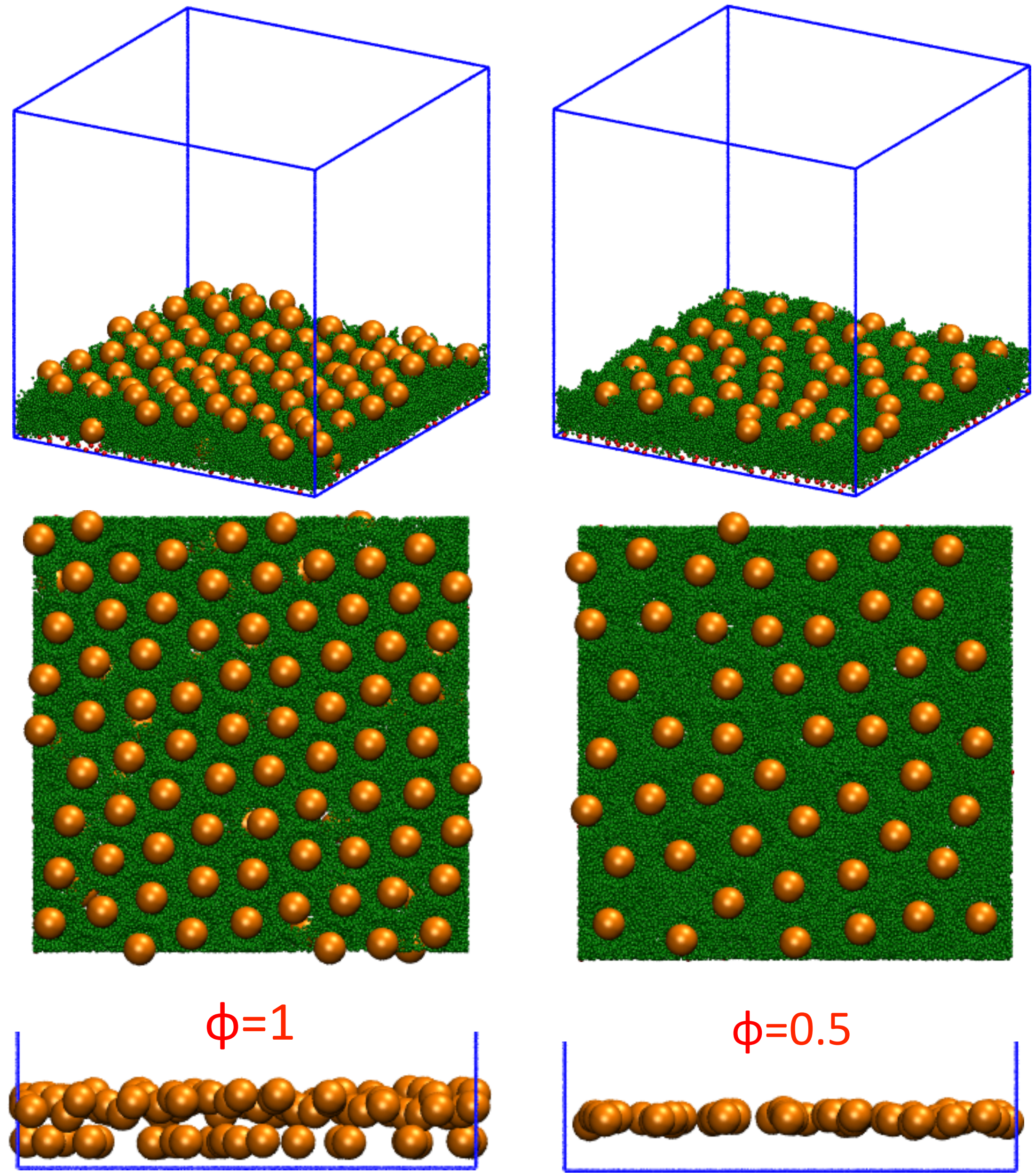
A_{nb}=200ε



Solvent Evaporation: vary NP density

Brush Density = 0.08
at A_{nb} = 100 ε

Decrease ϕ to 0.5
Not enough NPs to form monolayer.

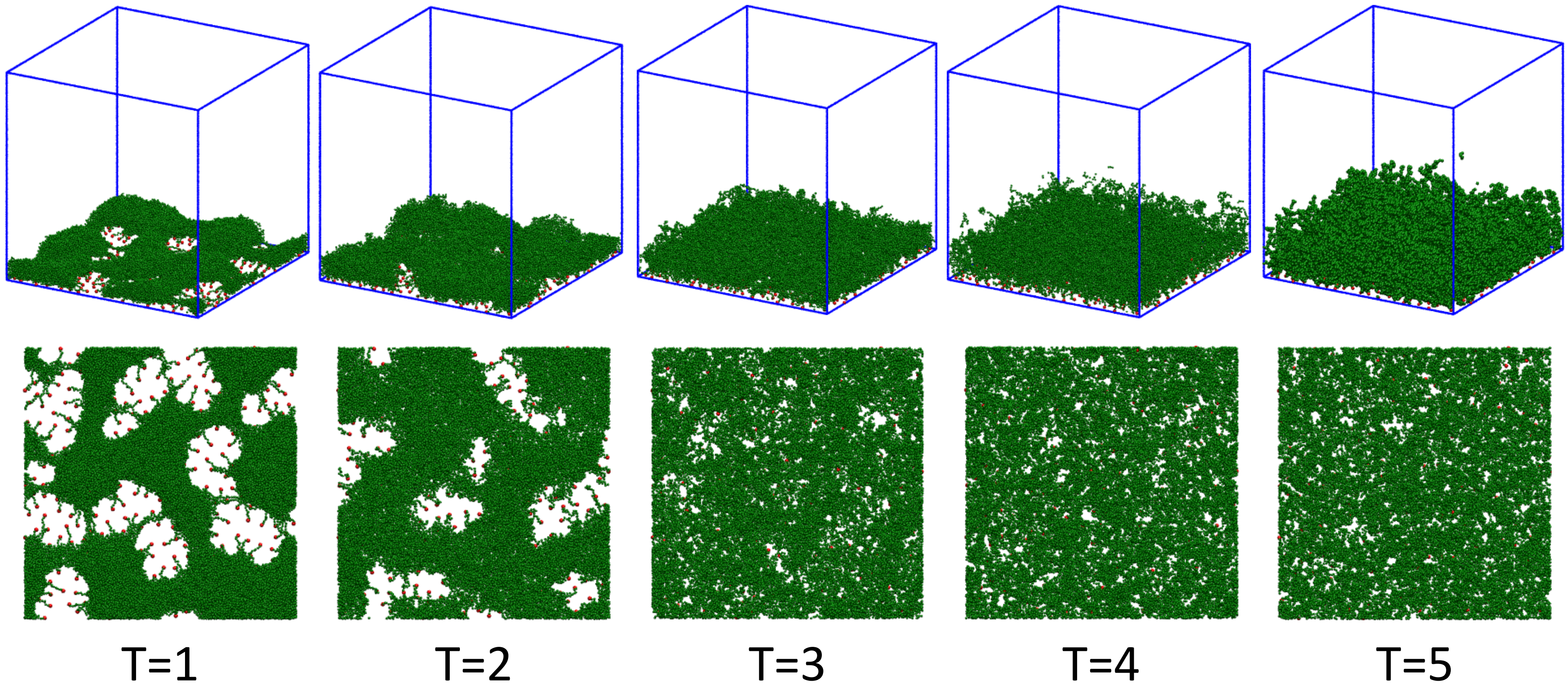


Summary

MD simulations of Nanoparticles in Polymer Brush with Solvent Evaporation

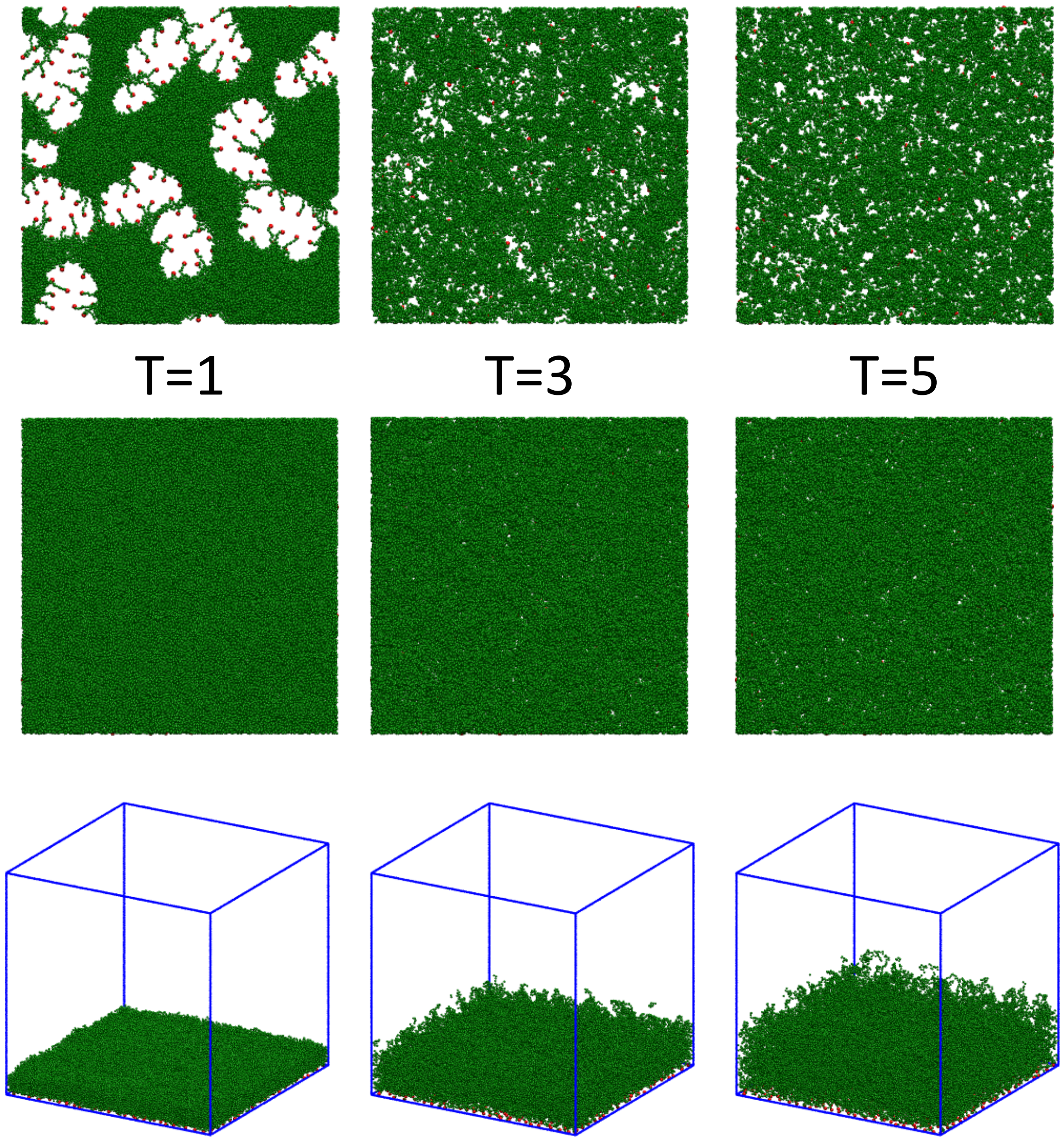
- We can achieve equilibrated dynamics of nanoparticles in brush & solvent
- Best nanoparticle ordering for high-density brush with weak nanoparticle:brush interaction
- Weakly interacting nanoparticles tend to reside on brush surface
- Strongly interacting nanoparticles tend to reside within brush
- Interesting behavior of nanoparticles filling voids at low brush density

Dry Brush at Low Density



- Temperature unit ε/k_B
- Number of chains: 400 → brush density 0.04σ^{-2} (experimental range: 0 ~ 0.2σ^{-2})
- Chain length: 100 beads
- Brush more uniform at higher T (but we will work at T=1)

Dry Brush at High Density

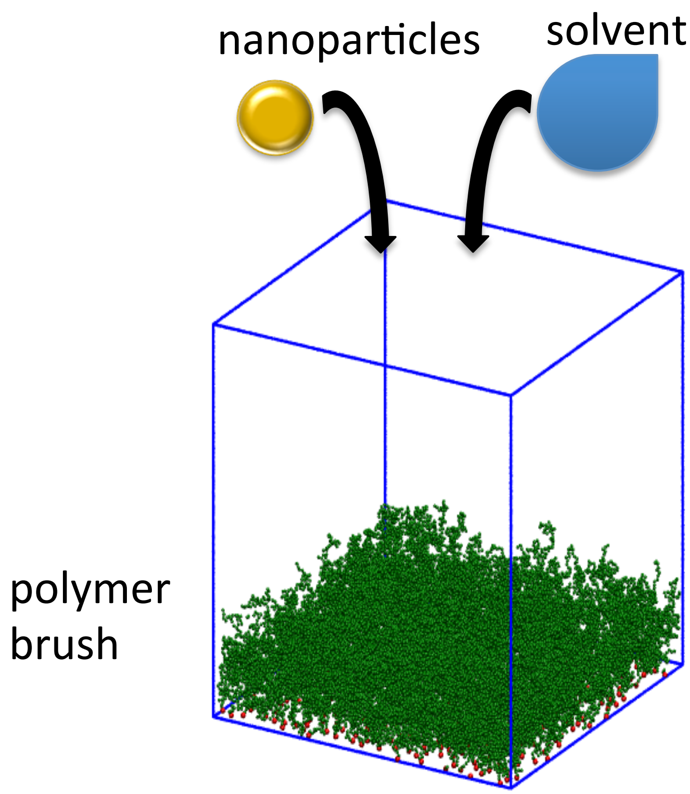


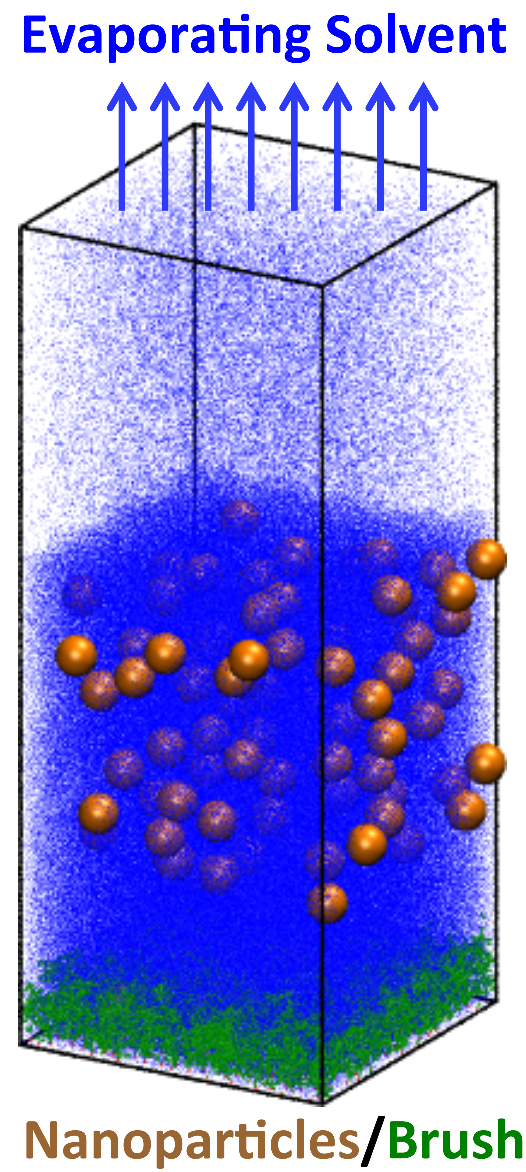
- brush density $0.04\sigma^{-2}$

- brush density $0.08\sigma^{-2}$
- Very uniform brush

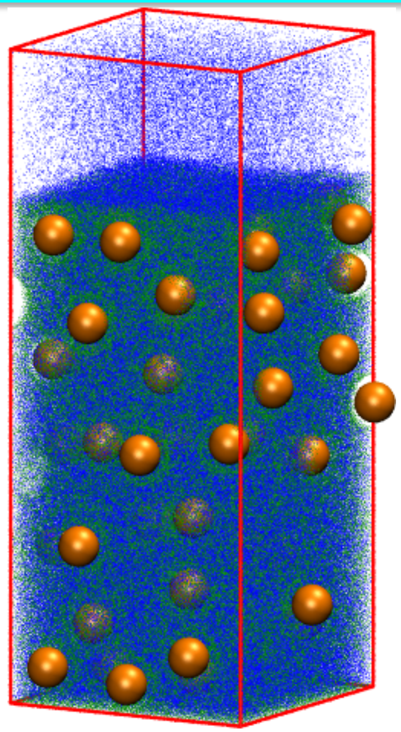
Molecular Dynamics Simulations

- System:
  - LJ solvent (~3 million)
  - 100-bead polymer chains (~ 3 million beads)
  - 200 Nanoparticles with D=20σ
- Starting volume fractions: polymer = 45%   NP = 10%
- Evaporation: remove vapor at top
- Vary NP:solvent interaction strength

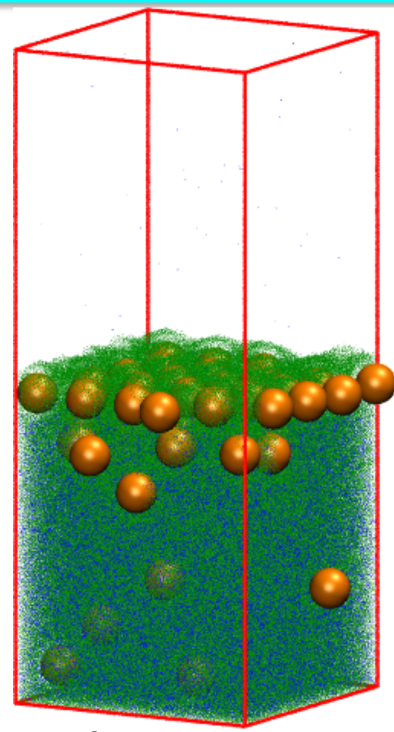




Nanoparticles in Polymer Film after Evaporation



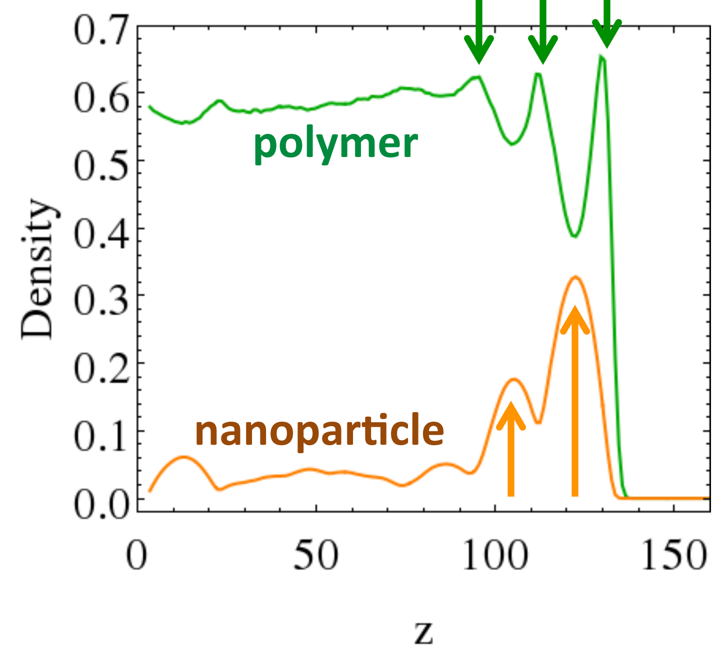
before evaporation

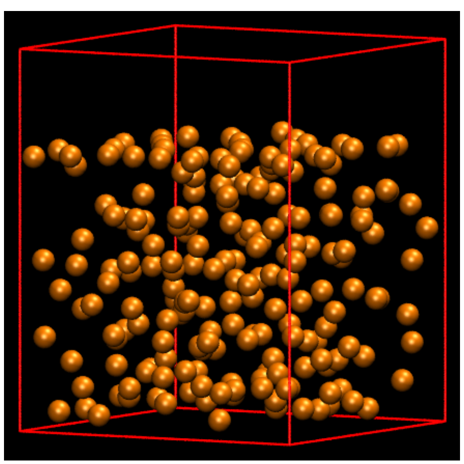


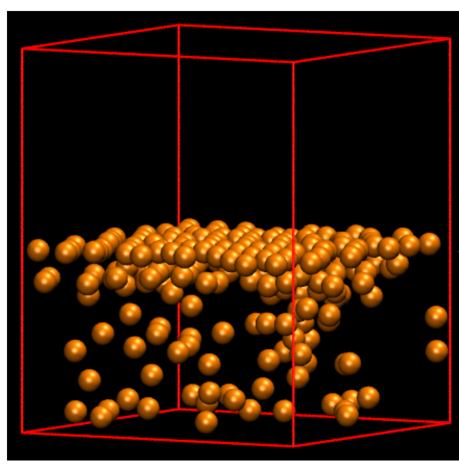
72% solvent evaporated

Nanoparticles accumulate near liquid/vapor interface

– polymer chain density is highest

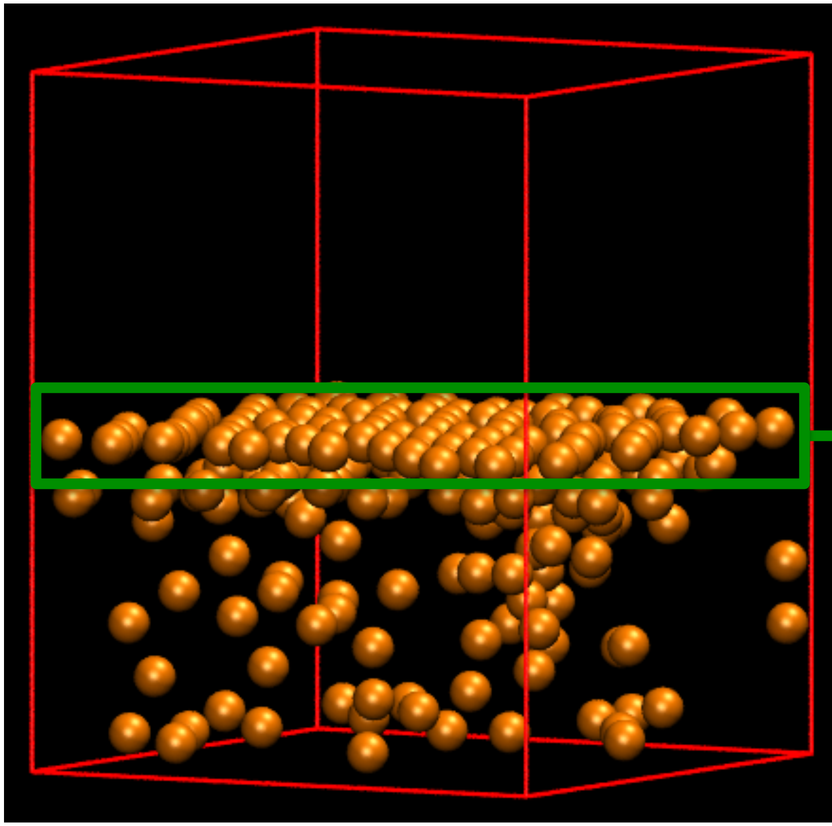




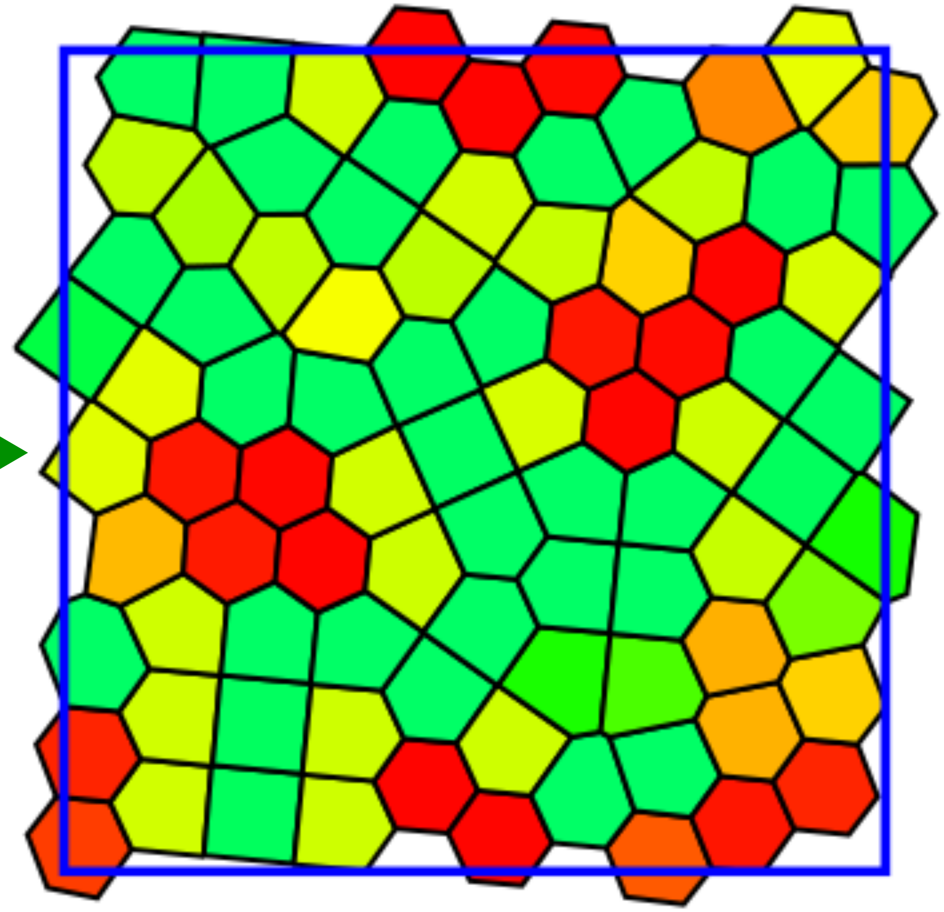


higher polymer density

Packing in Top Layer with Strong NP:Polymer Interaction



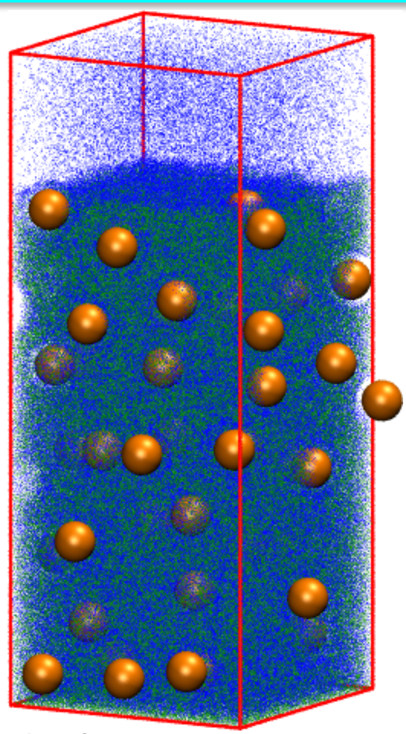
with 72% solvent evaporated



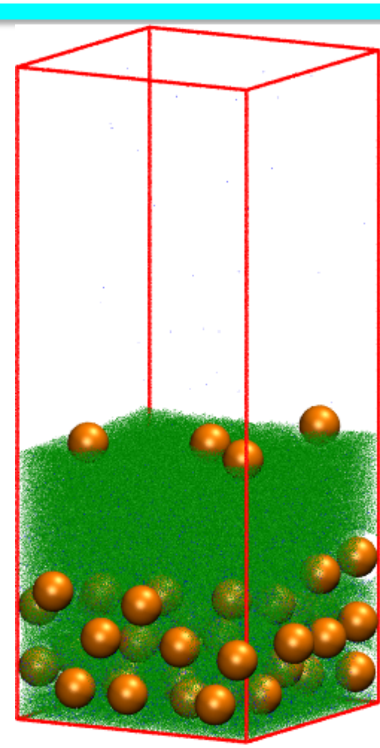
Nanoparticle packing:

- Number of neighbors: 4/5/6
- 4 neighbors: square
- 6 neighbors: hexagonal

Weak Nanoparticle:Polymer Interaction

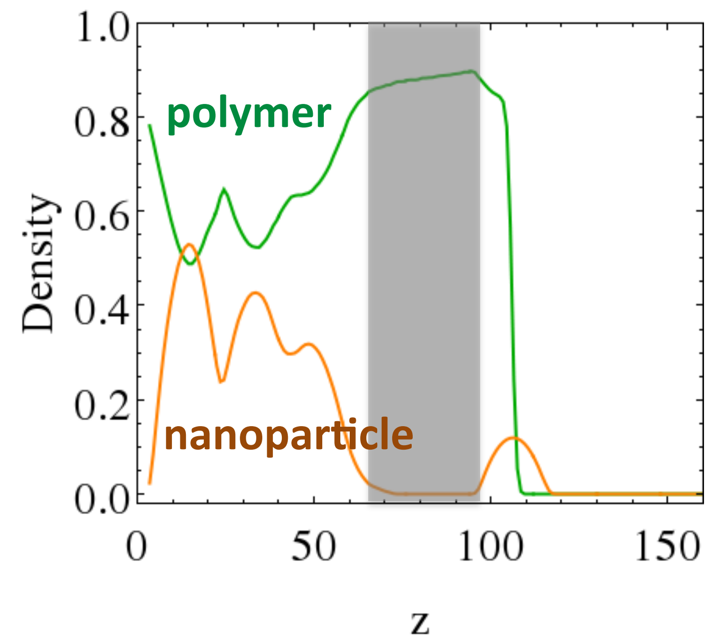


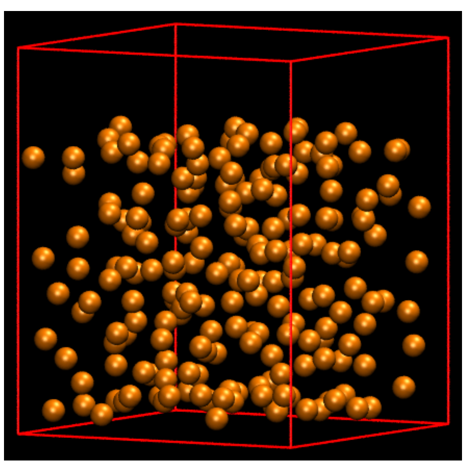
before evaporation

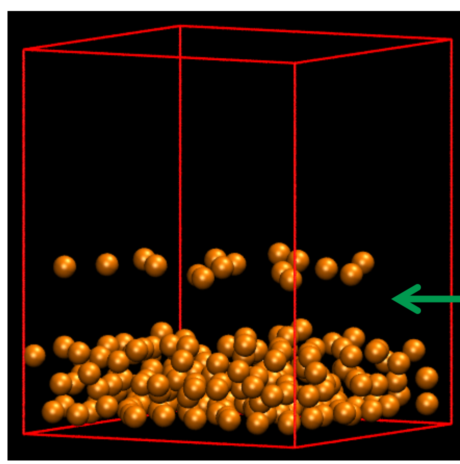


97% solvent evaporated

Nanoparticle depletion in dense polymer layer near liquid/vapor interface



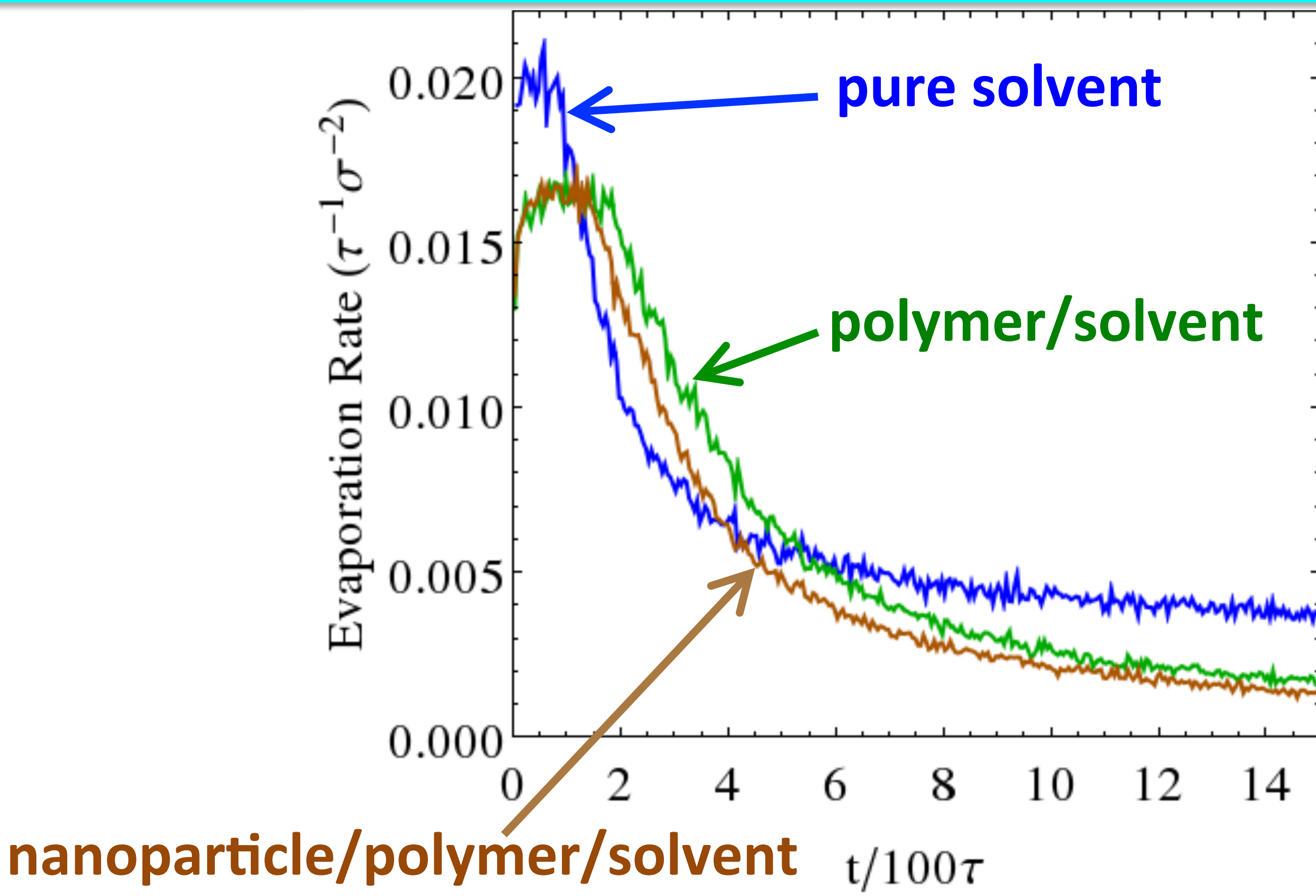




higher polymer density

No nanoparticles

Effect of Nanoparticle/Polymer on Evaporation Rate



- Evaporation rate decreases with time quickly
  - Depletion of vapor
  - Evaporative cooling
  - Blockage of nanoparticles/polymers near liquid/vapor interface
    → evaporation rate decreases faster with more blockers