Molecular Modeling of Tethered Polyelectrolytes

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Outline

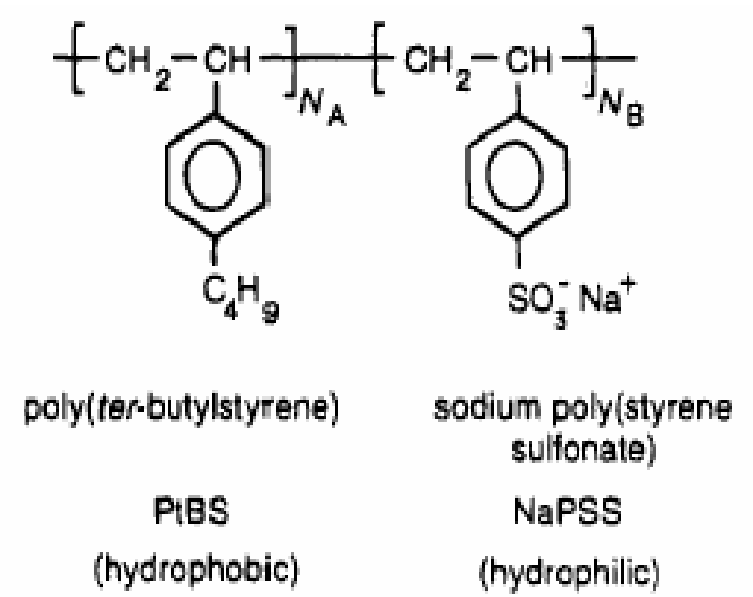
- Overview of molecular simulation and molecular modeling
- Introduction to Tethered Polyelectrolytes
- Homogeneous PEs, Tethered to 2 walls (MD)
- Homogeneous PEs, Tethered to 1 wall (MC, MF)
- End-charged PEs, Tethered to 1 wall (MC)
- End-charged PE's, Tethed to 1 wall, + colloid (MC, MF)
- Acknowledgements

Overview of simulation and molecular modeling

- A molecular model is a mathematically simplified description of the physical properties of a molecule.
- Molecular simulation is a "computer experiment" where the behavior of some collection of molecules, physically defined by a molecular model, is observed under a controlled set of parameters.
- Molecular simulation is an effective tool for modeling polymer behavior

What is a polyelectrolyte brush?

A tethered polyelectrolyte brush is a system in which polymers with electrically charged monomers are end-constrained, covalently bonded directly to a surface.



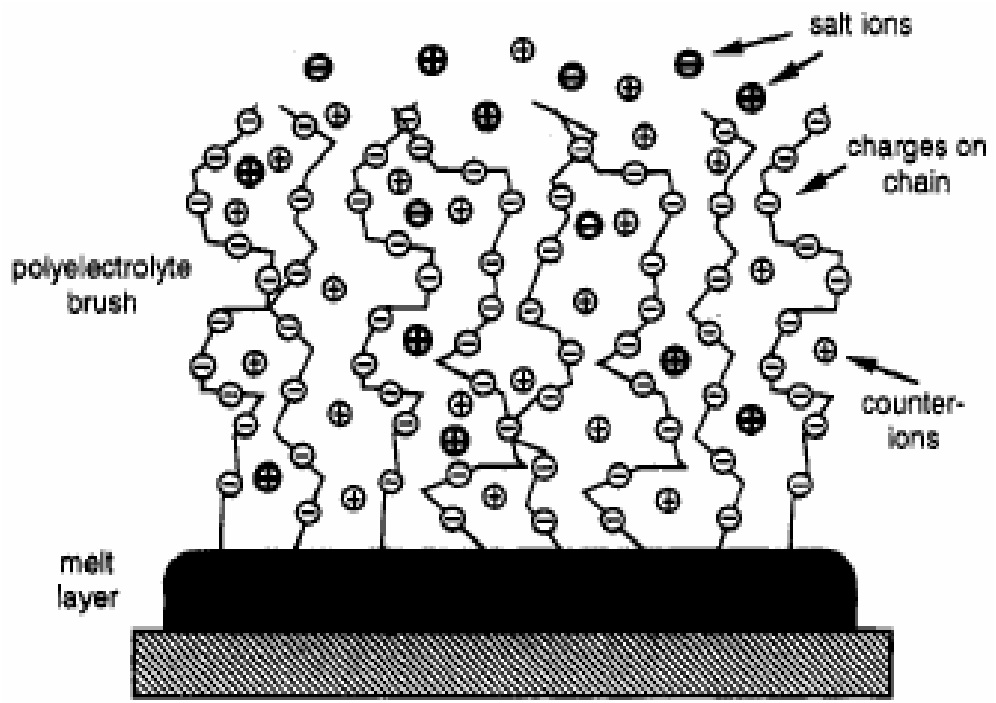
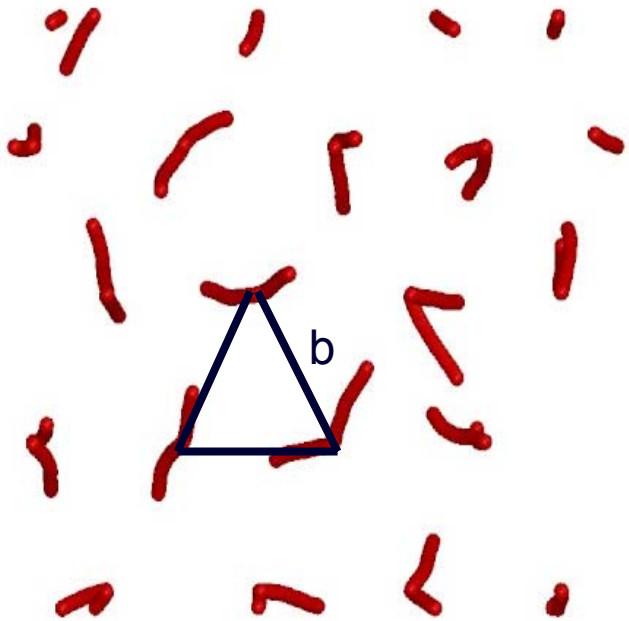


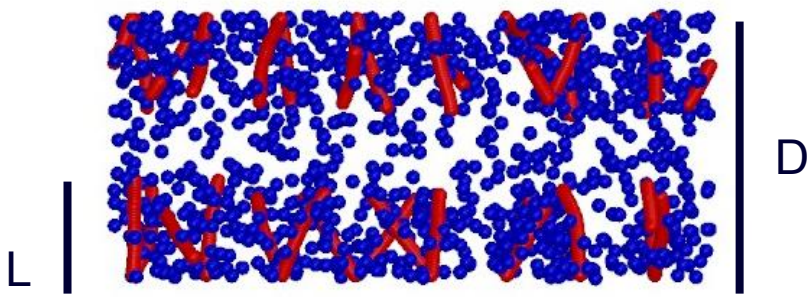
Figure Credit: C. Amiel, *et al.*, Macromolecules **28**, 3125-3134, 1995.

System geometry and molecular model for MD simulation:
Homogeneous PEs tethered to 2 walls

- Two apposing surfaces separated by a distance *D*, each with 16 chains arranged in a triangular lattice with spacing *b*.
- Each polymer consists of *N* beads
- Single charge at the center of each bead
- Counterions (blue) between walls balance system so that charge neutrality is maintained
- Periodic in x and y, but not z. (slit geometry)
- We use a bead-spring model. The total energy is given by:

$$U_{total} = U_{LJ} + U_{bond} + U_{angle} + U_{Coulomb} + U_{wall}$$



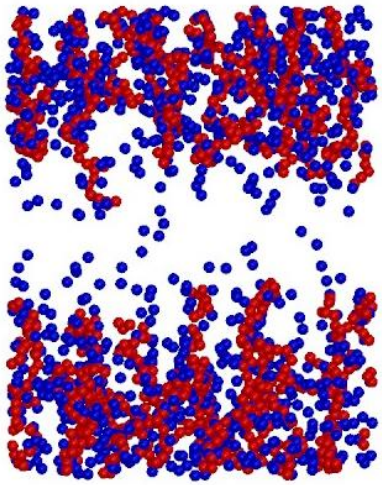


Comparing simulation parameters to experiments

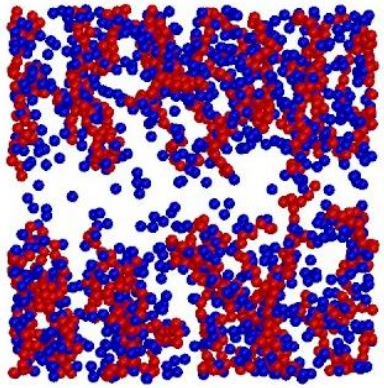
Careful attention is paid to how experimental systems map to simulation parameters.

Quantity	Variable	Exp. Range	This Simulation
Grafting Separation	b	10Å < b < 100Å	27Å < b < 87Å
Number of Monomers	N	20 < N < 2000	16 < N < 128
Charge Strength	$T^*=a/L_b$	0.38 < T^* < 1.1	$T^*=1$

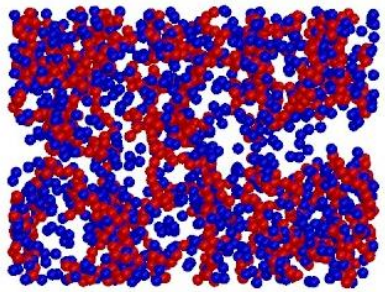
Increasing confinement



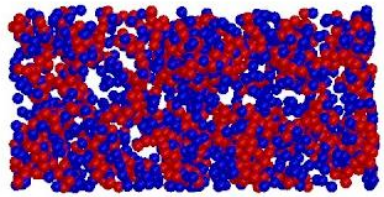
The two brushes do not overlap, and the polymers are extended.



The gap between the brushes decreases, but still, the polymers avoid contact.



At last, they are forced together, and interpenetration cannot be avoided.

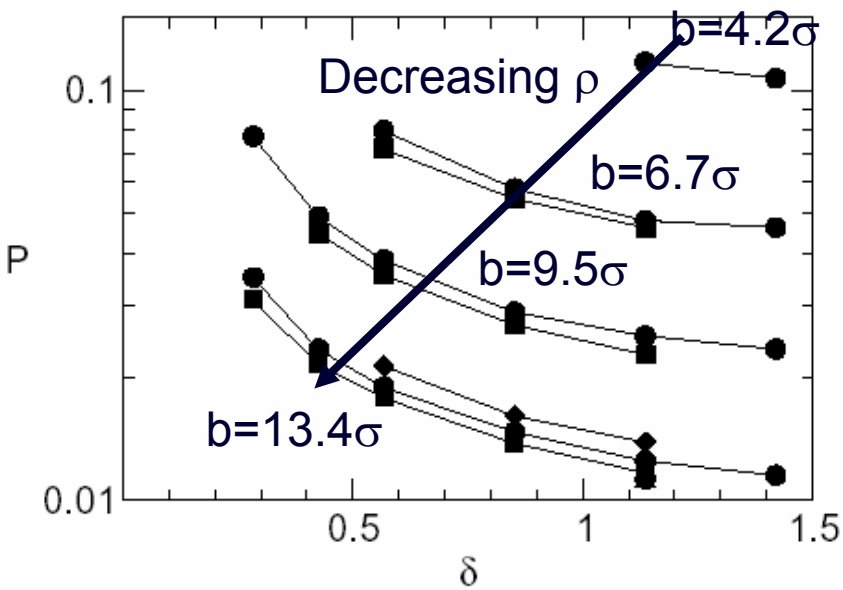


At very small gap widths, the system looks almost liquid like, with the whole space filled.

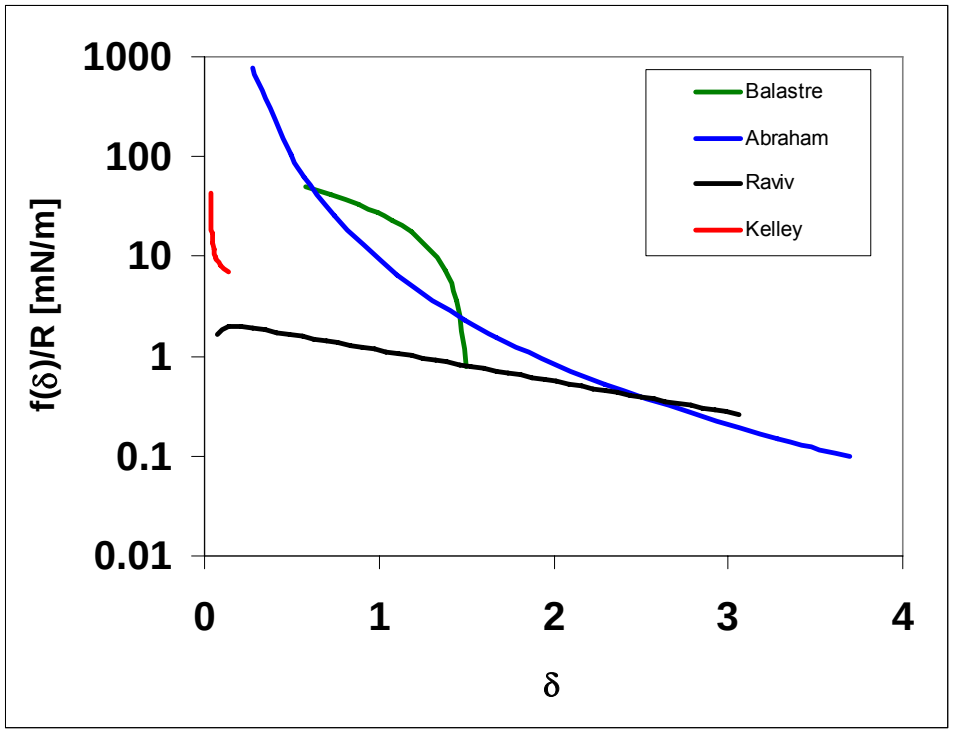
Key Finding: Experimentalists have hypothesized that an avoidance of interpenetration might be the origin of lubrication between polyelectrolyte brush surfaces. This data suggests their hypothesis might be correct.

What happens to the pressure?

Pressure vs. gap width for chains of length N=16 (♦), 32 (•), 64 (■), 96 (▲), and 128 (o). Results resemble one subset of the experimental data.



Force vs. gap width as measured with the SFA. Data from Raviv (black), Balastre (green), Abraham (blue), and Kelley (red).

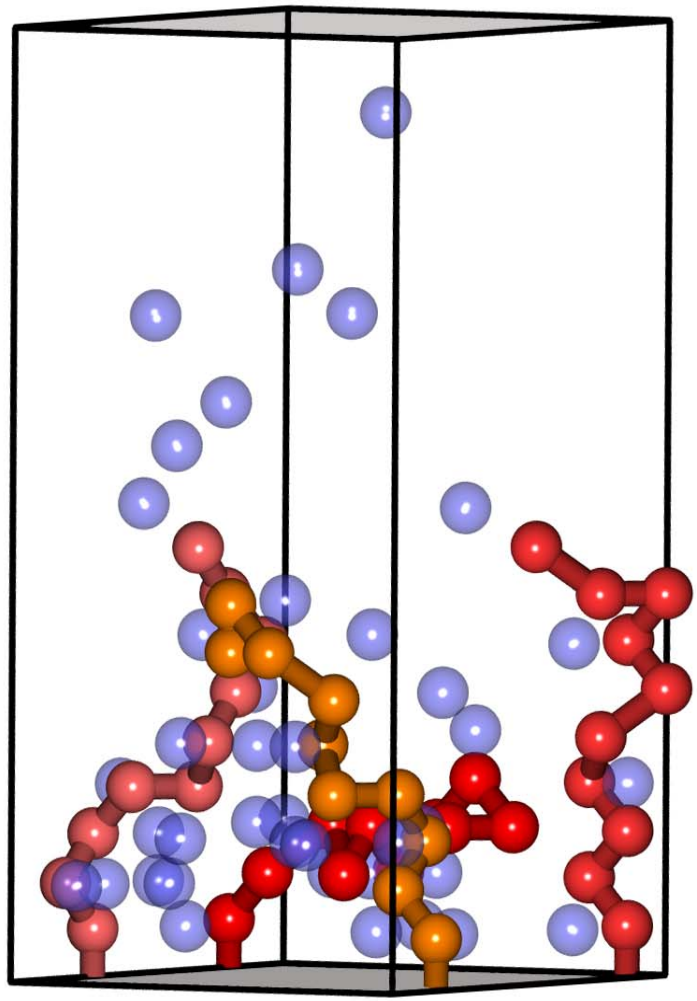


Key Finding: Pressure rises rapidly as gap width decreases

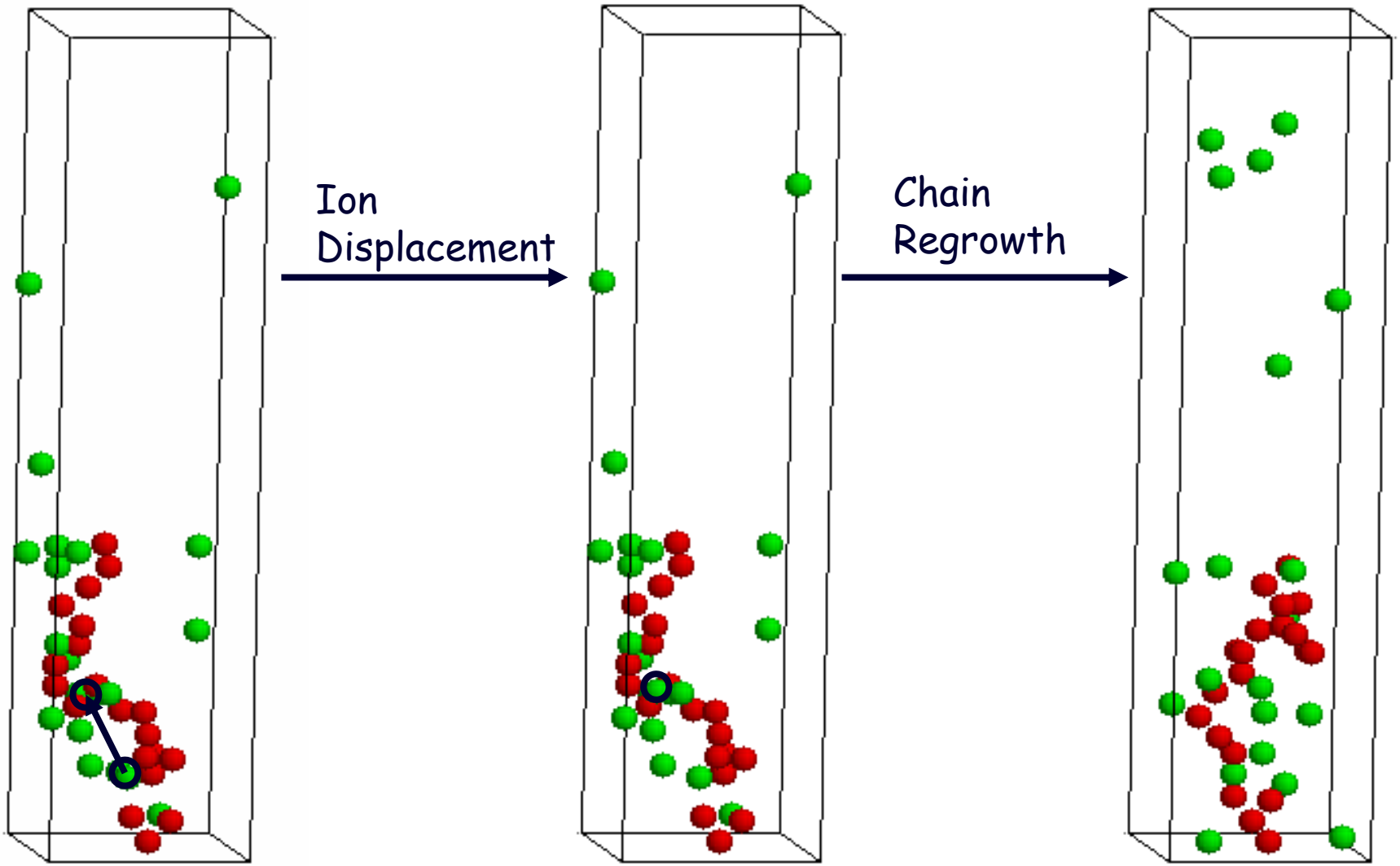
System geometry and molecular model for MC study:

Homogeneous PEs tethered to 1 wall

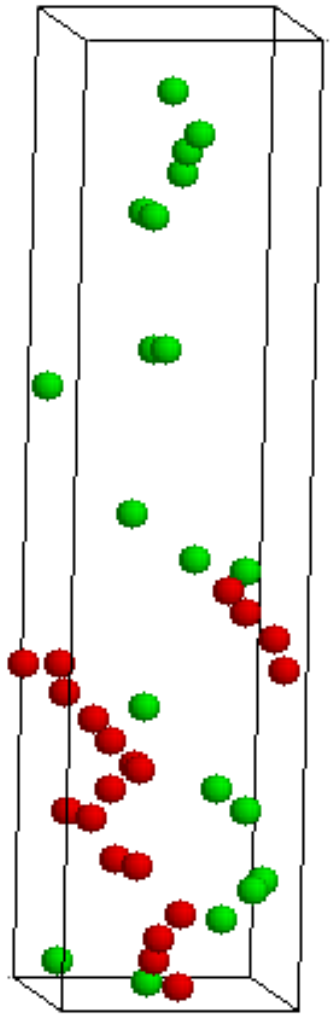
- Each polymer consists of N beads
- Single charge at the center of each bead
- System is charge neutral
- Periodic in x and y, but not z.
- Charged wall
- Geometry is a lattice
- Coulombic and exclude volume interactions only



NVT Monte Carlo simulation method

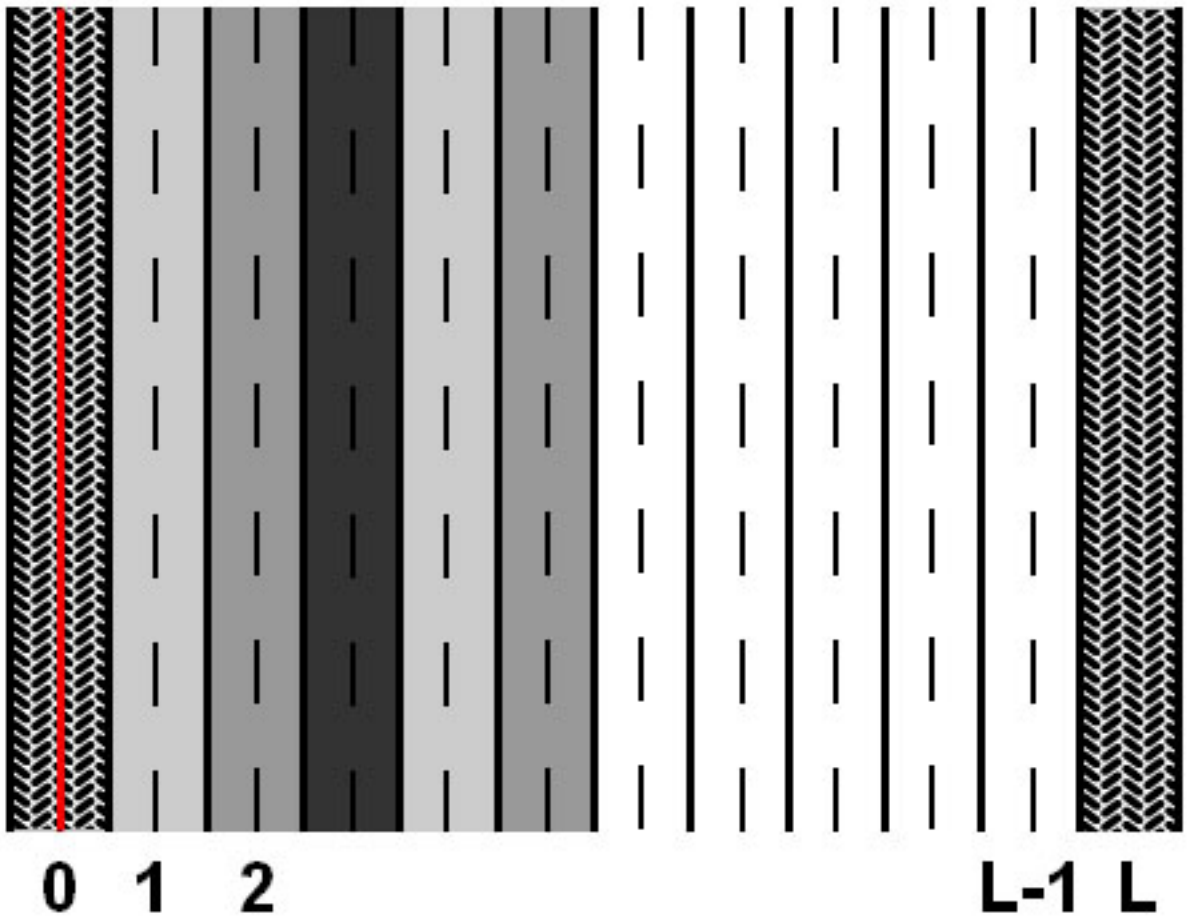


NVT Monte Carlo simulation method (N=20, T*=5.0, σ_g=0.01)



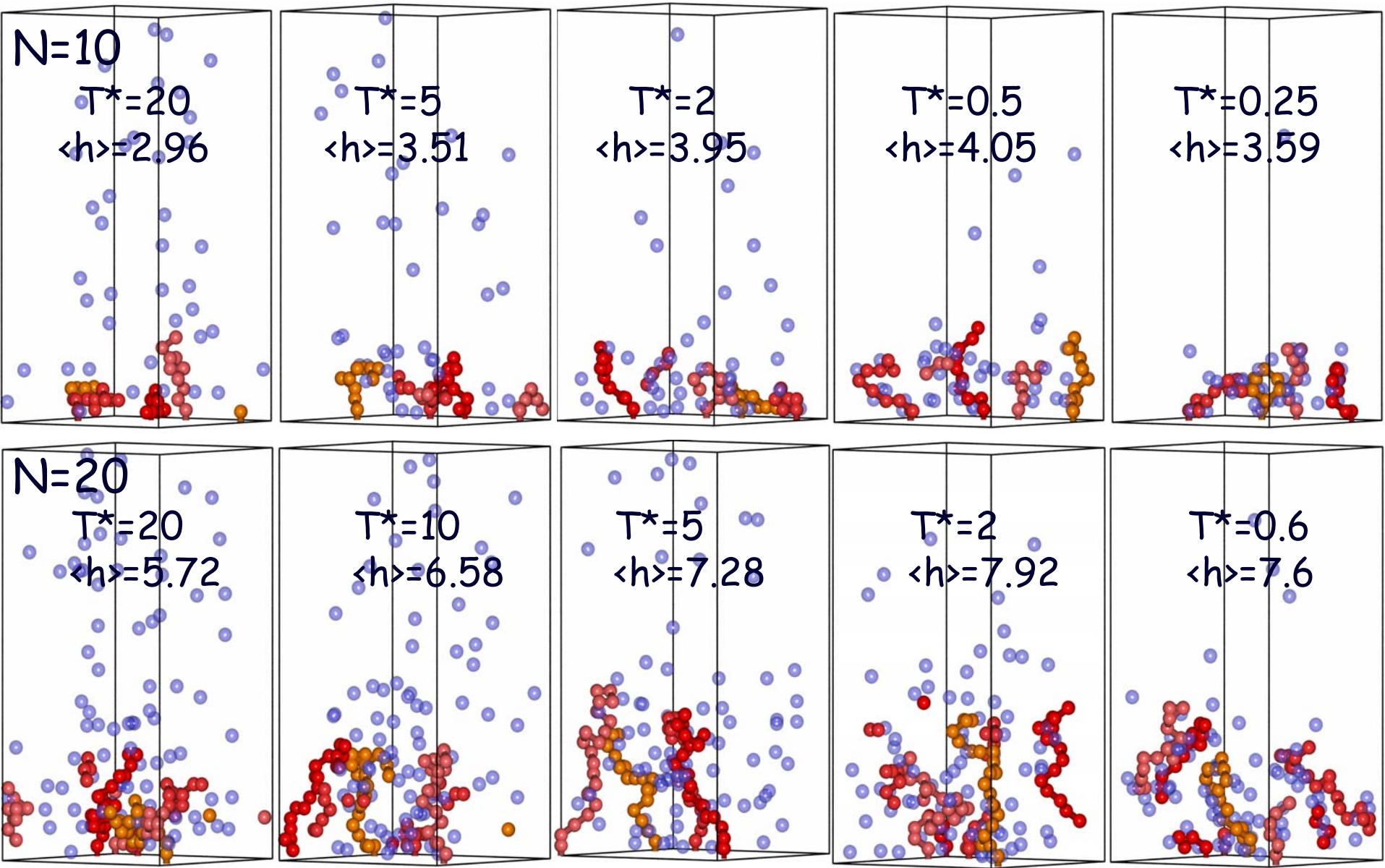
Mean-Field methodology

$$\sigma(0) = \sigma_{\pm}$$



Method of: F. Fang and I. Szleifer, J. Chem. Phys. 119, 1053 (2003).

Effect of temperature on brush height (MC simulation)

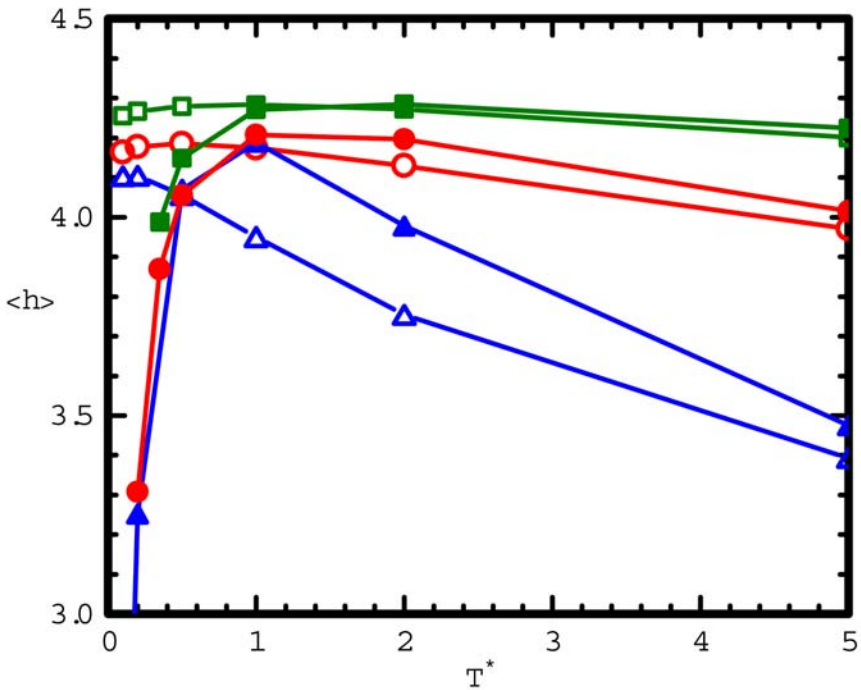


Effect of T* on brush height: Comparison of MF and MC for N=10 and N=20

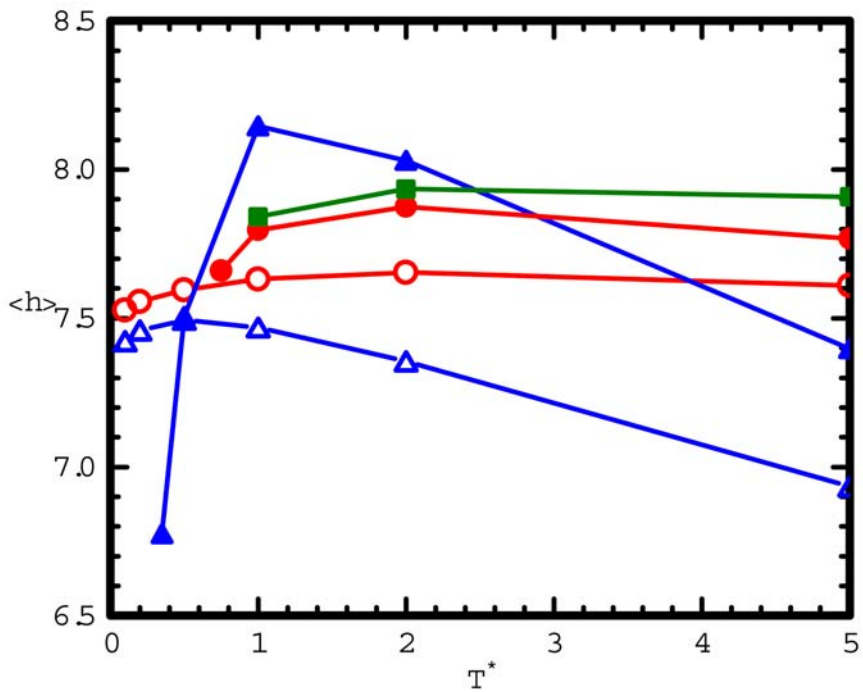
σ=0.01, MF, Blue Δ
σ=0.04, MF, Red ○
σ=0.08, MF, Green □

σ=0.01, MC, Blue ▲
σ=0.04, MC, Red ●
σ=0.08, MC, Green ■

N=10



N=20



Key Finding: Brush height increases slowly with grafting density, MF fails at T*< 1

What is an end-charged brush?

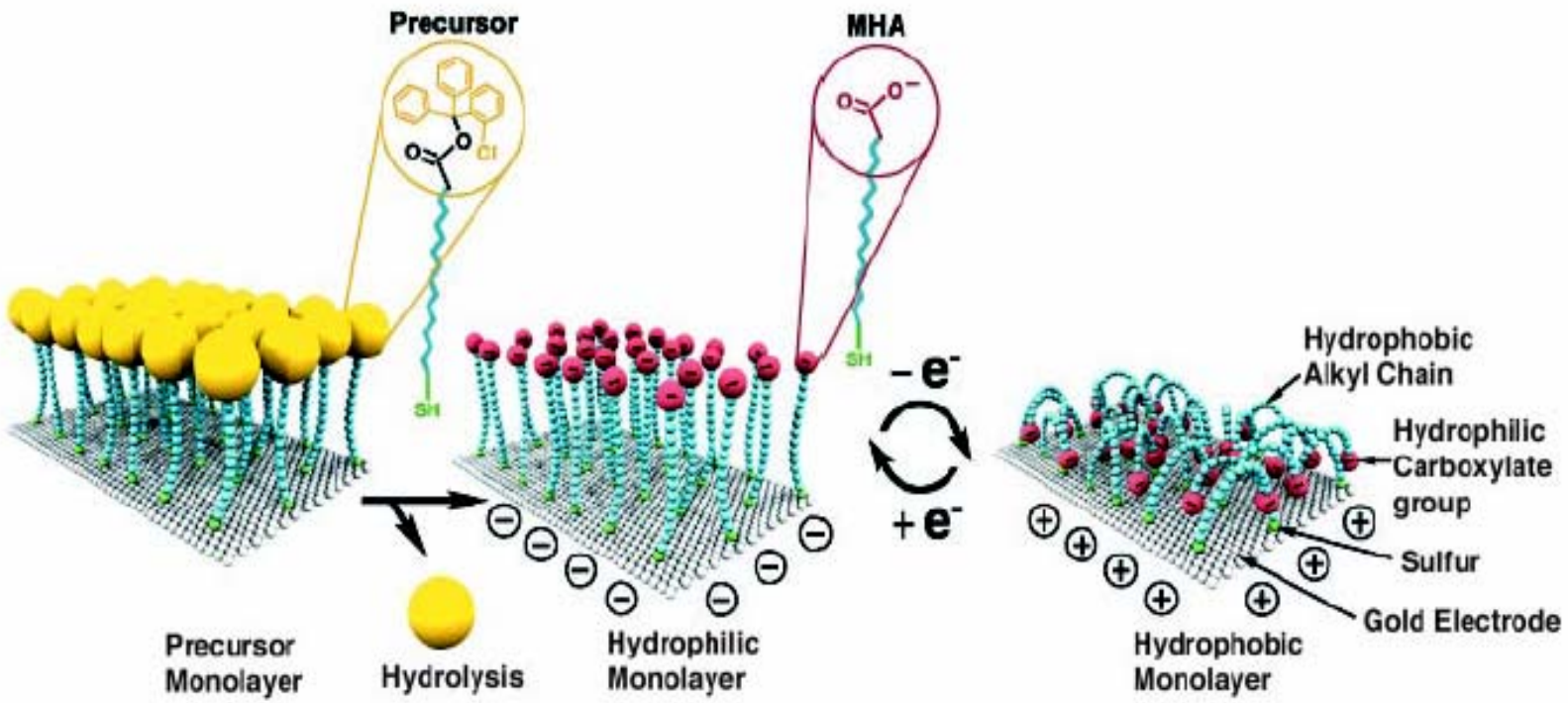
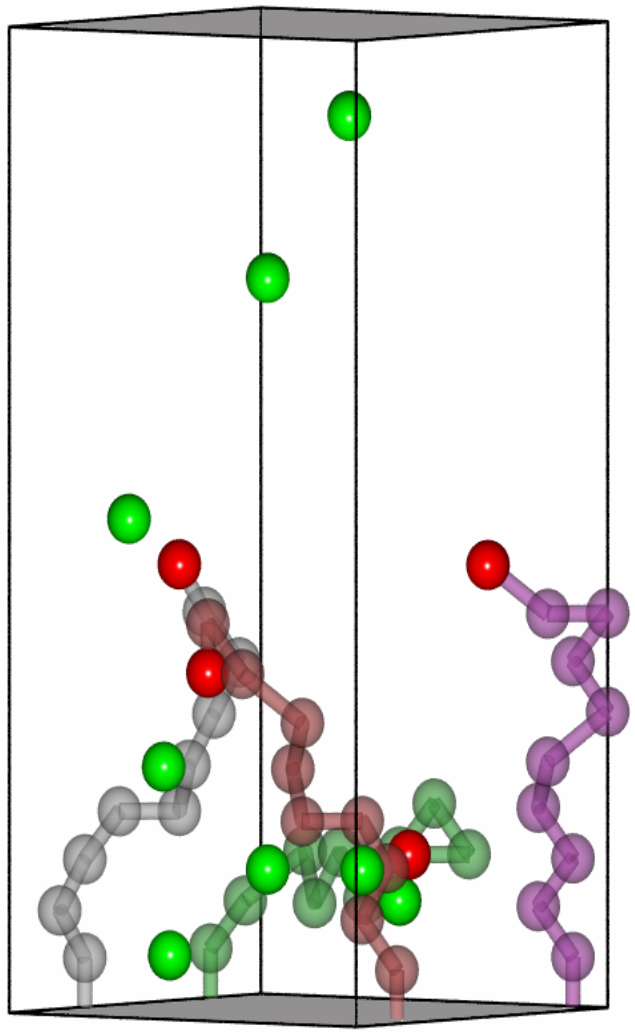


Figure Credit: Joerg Lahann, et. al., "A Reversibly Switching Surface," *Science*, 2003, 299, 371-374.

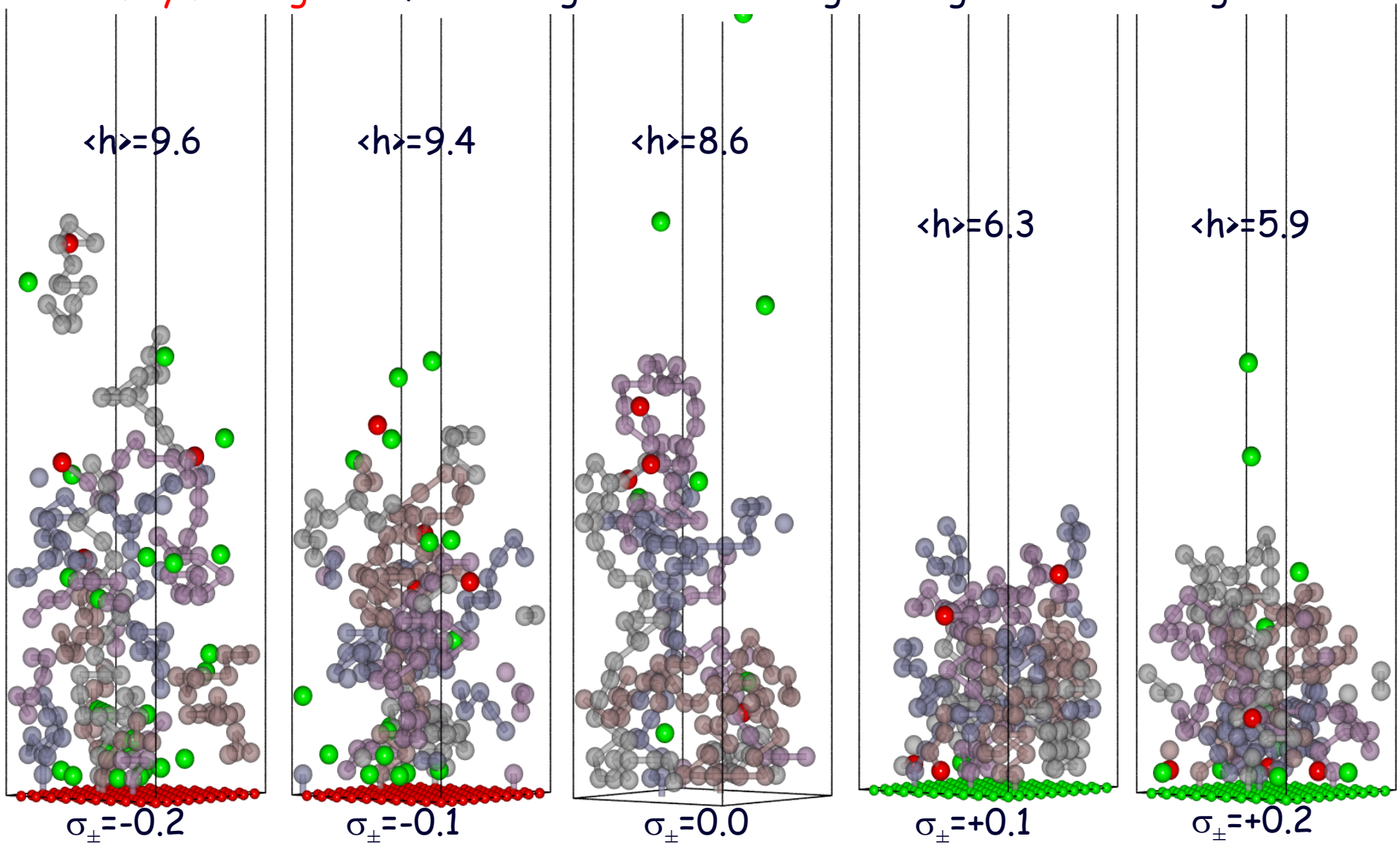
System geometry and molecular model for MC simulation:
End-charged PEs tethered to 1 wall

- Each polymer consists of N beads
- Charge only on end-bead (-2e)
- System is charge neutral
- Periodic in x and y, but not z.
- Charged wall
- Geometry is a lattice
- Coulombic and excluded volume interactions only

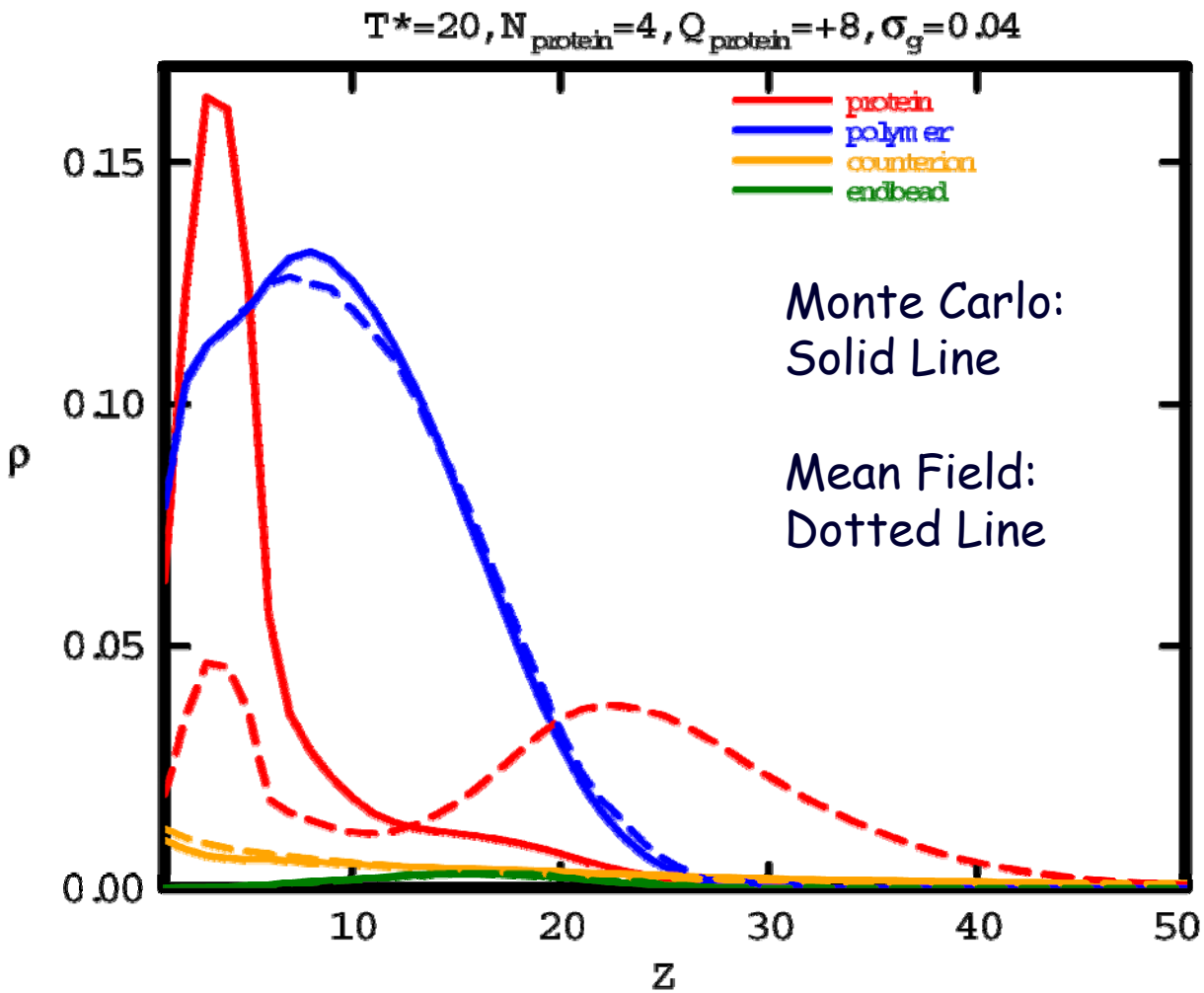


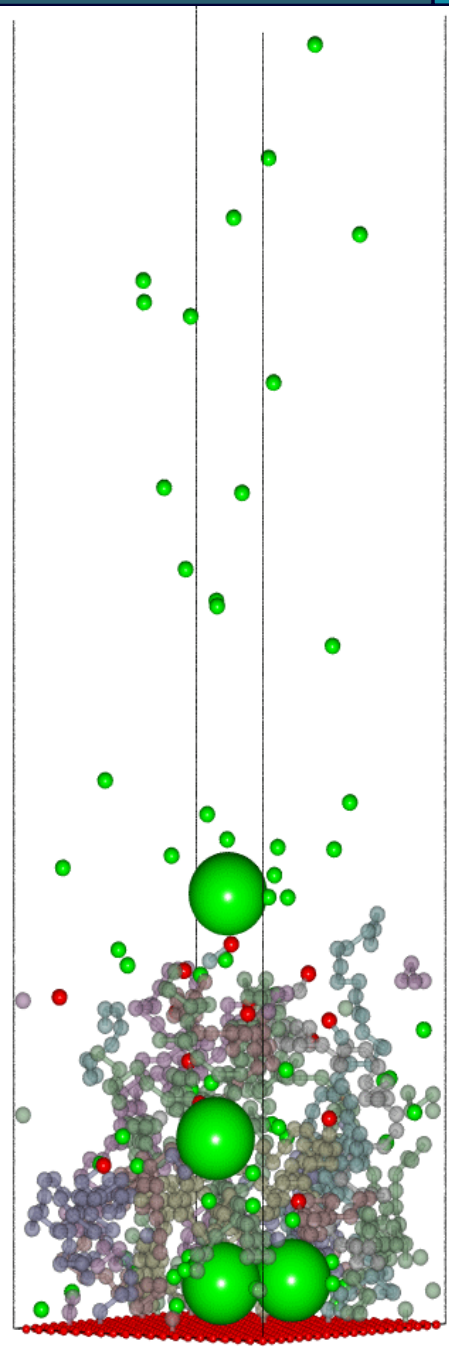
Effect of surface charge: N=50, σ_g=0.04, T*=2

Key Finding: Surface charge can cause large changes in brush height



Particle adsorption





MC? MF? MD? Which is best?

- MD easily and frequently adapted for parallel use. MC and MF are not.
- MC and MD are faster at low densities than high densities. But, MF increases in accuracy as density rises.
- MC and MD can access strongly-charged (low T*) regimes, MF cannot do so accurately.
- MC and MF adaptable to a lattice. Lattice use speeds electrostatics, but lattice itself is another approximation.
- MF can access the longest chain lengths. Of the 3, MC has the hardest time with long chain lengths

Key Finding: All three methods are important for understanding tethered PEs

Acknowledgements

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- Prof. Panagiotopoulos group for helpful discussions

Questions