End-to-End Alignment of Polymer Grafted Nanorods in Polymer Thin Films by Self-Assembly

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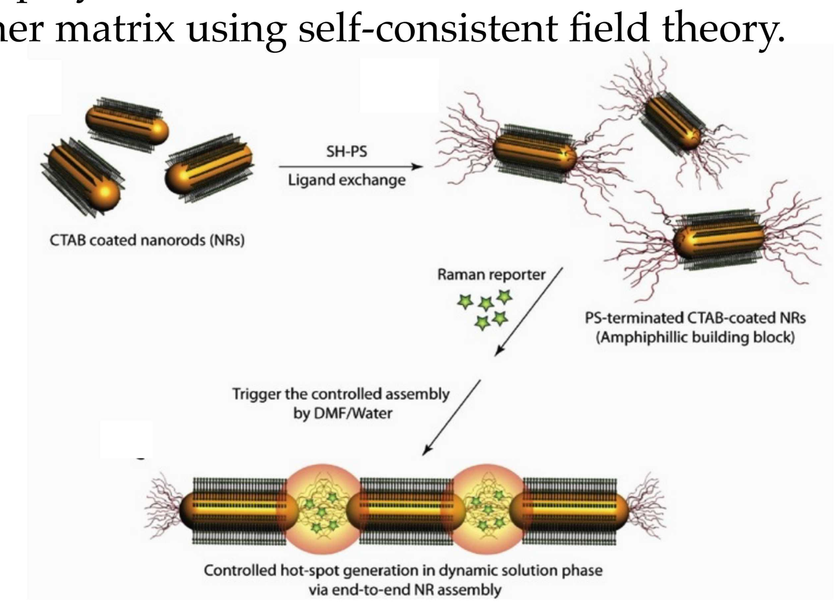
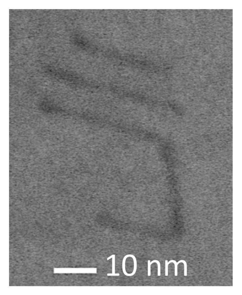
Abstract

Controllable end-to-end over side-by-side alignment of nanorods in polymer films would enable new applications, especially for metallic nanorods, where coupling of surface plasmon resonances can lead to enhanced electric fields (hot spots) between nanorod ends. To achieve end-to-end alignment, we investigate the dispersion and aggregation behavior of polymer brush-coated nanorods in a chemically identical homopolymer matrix using self-consistent field theory.



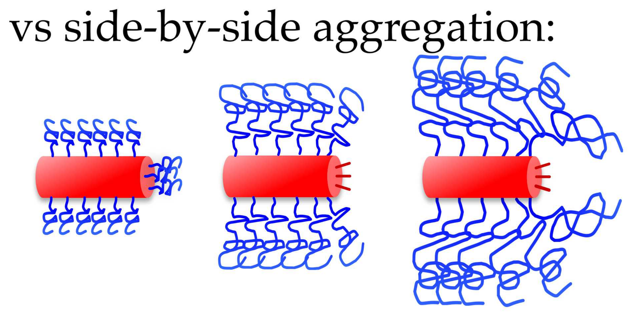
Experimental system

- CdS nanorods (5 x 28 nm)
- Grafted polystyrene (PS) brushes
- PS homopolymer matrix

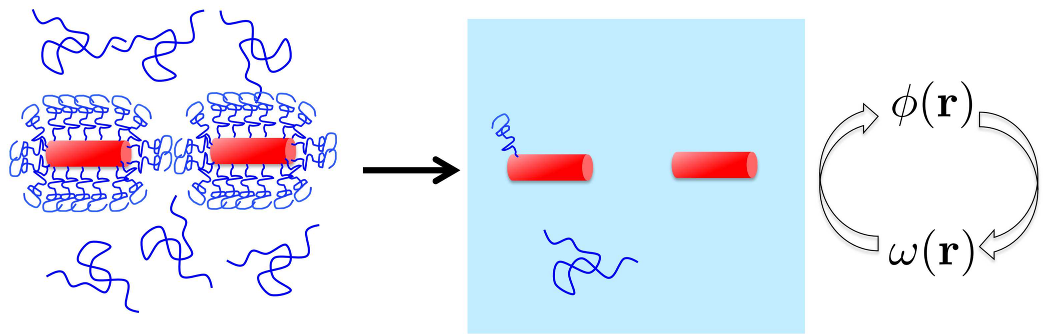


Spin-coated to an average thickness 36 nm.

Approaches to controlling end-to-end vs side-by-side aggregation:
1. Bare nanorod ends
2. Comb-over effect
3. Brush, matrix, rod parameters

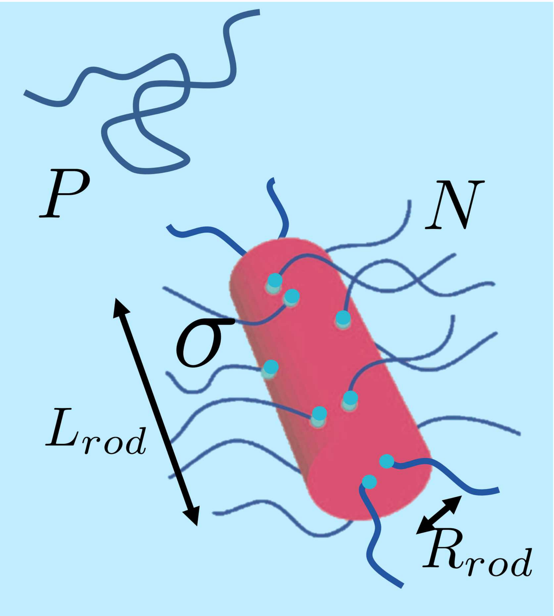


Theory and model



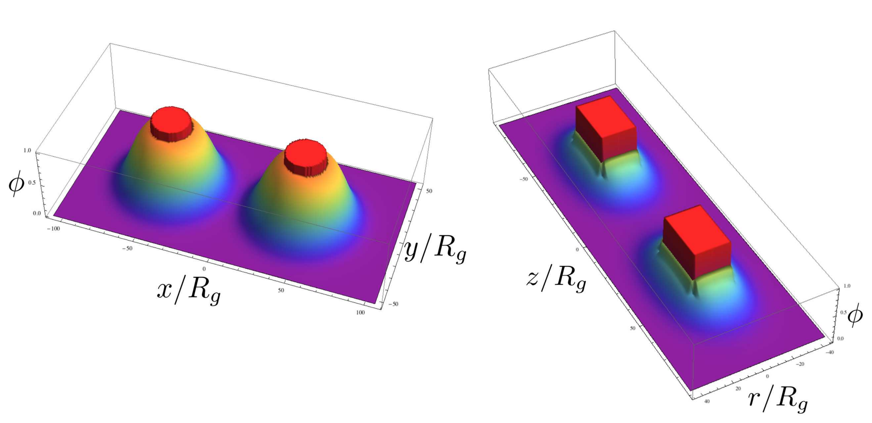
Many-body interaction   Mean-field theory

- Chain statistics determines polymer density $\phi(\mathbf{r})$ which determines external field $\omega(\mathbf{r})$ which determines chain statistics
- Mean-field approximation accurate for melts, exact as $N \to \infty$
- Free energy functional is *known*: $F[\phi^*(\mathbf{r}), \omega^*(\mathbf{r})]$



Key parameters:
- brush/matrix polymerization
- grafting density
- nanorod radius
- nanorod length

side-by-side   end-to-end



$$W(H) = -\frac{A L_{rod} R_{rod}^{1/2}}{24 H^{3/2}} \qquad W(H) = -\frac{A R_{rod}^2}{12 H^2}$$

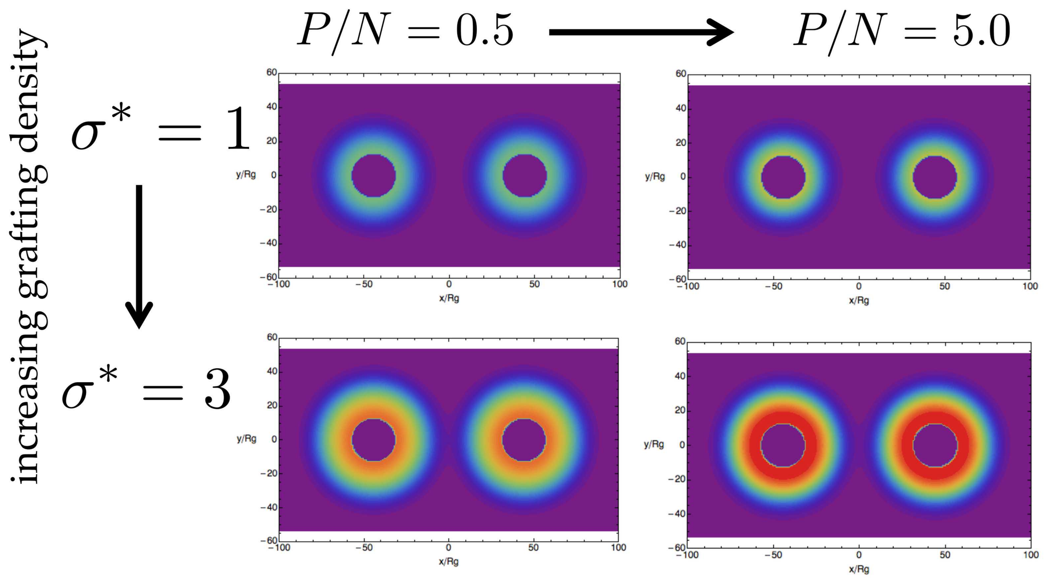
Total interaction energy:

$$F_{tot}(H) = F(\phi(\mathbf{r}), \xi(\mathbf{r}); H) + W(H)$$

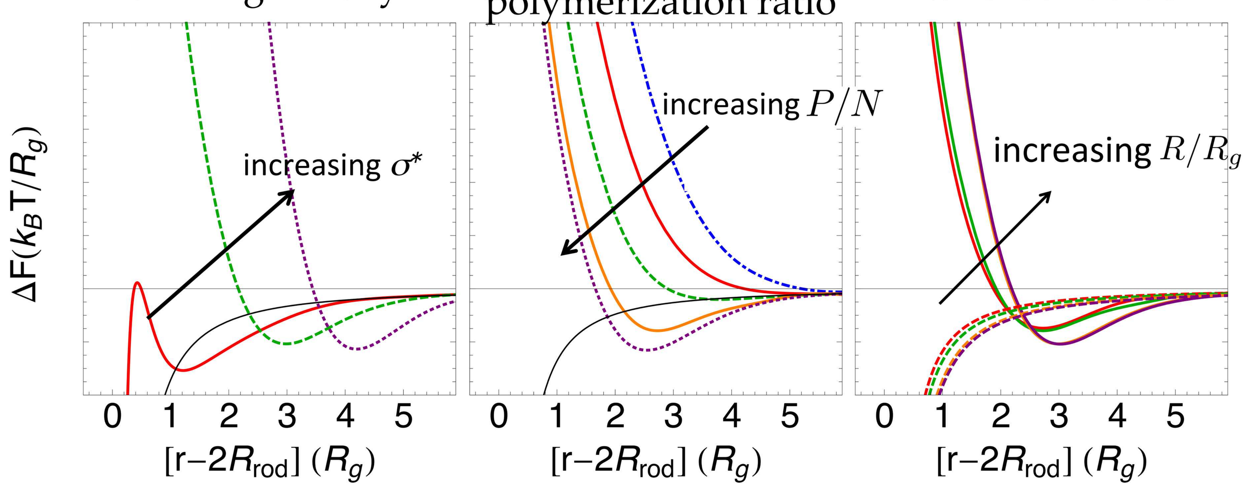
Results: side-by-side alignment

Side-by-side brush profiles

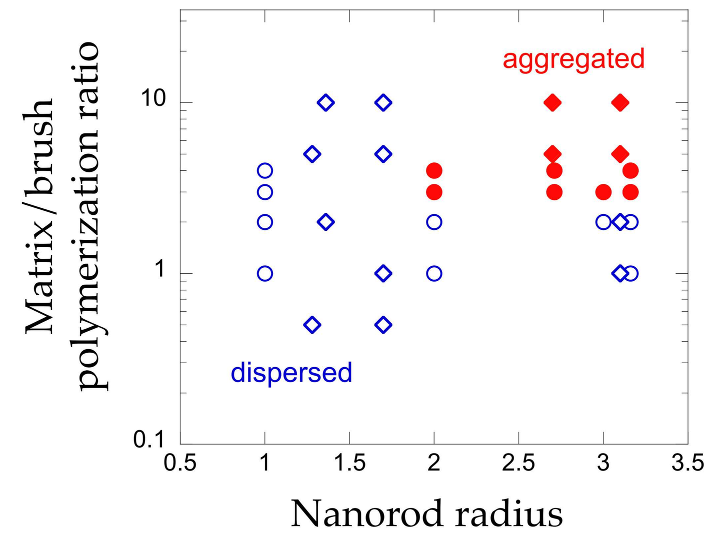
increasing matrix/brush polymerization ratio
$P/N = 0.5$ → $P/N = 5.0$



Side-by-side interaction energies

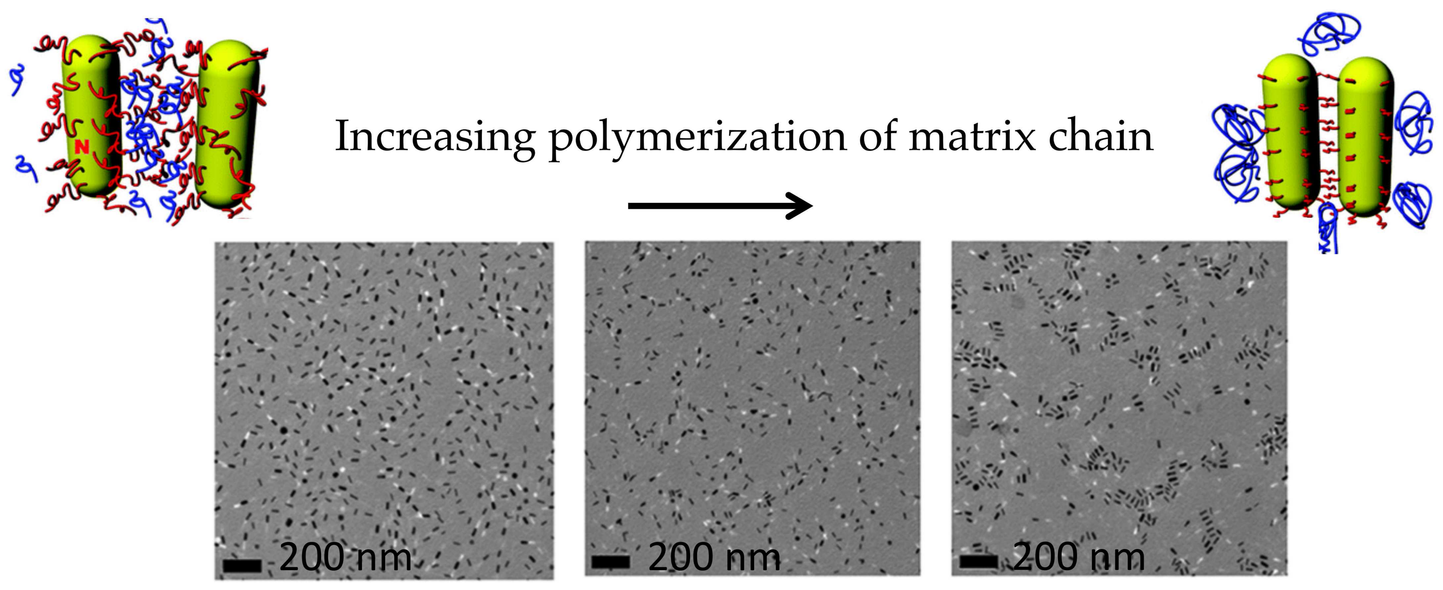


Side-by-side dispersion map



Total interaction energy: $E_{total} = L\Delta F(H) + W_{side}(H)$

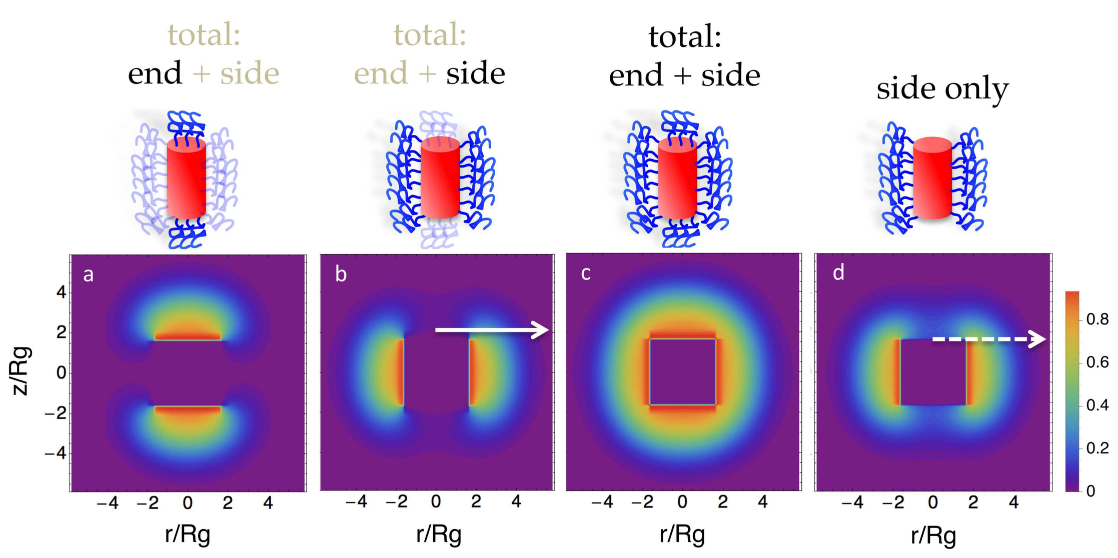
Aggregation when: $|E_{min}| > 5kT$



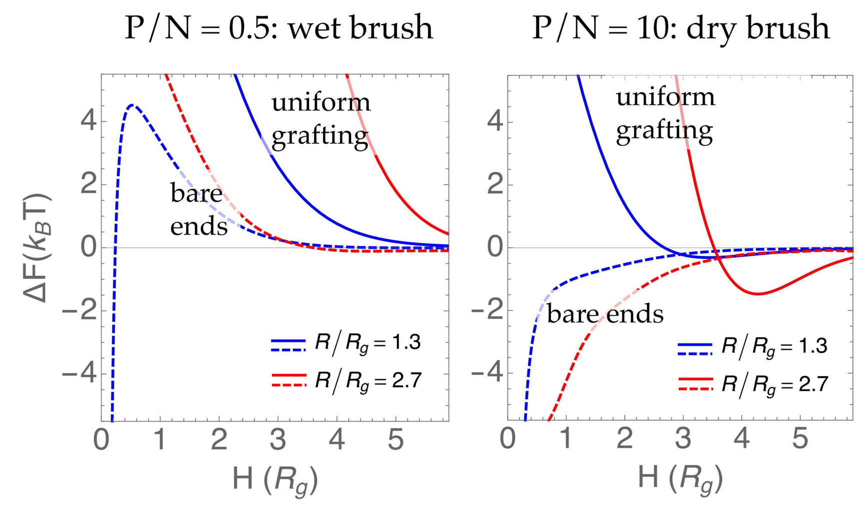
- Excellent agreement with our previous DFT calculations
- Brush transitions from 'wet' to 'dry' as a function of three key parameters: grafting density, matrix/brush ratio, nanorod radius
- Short ranged van der Waals attraction required for agreement with experimental observations for aggregation

Results: end-to-end alignment

Total brush profiles



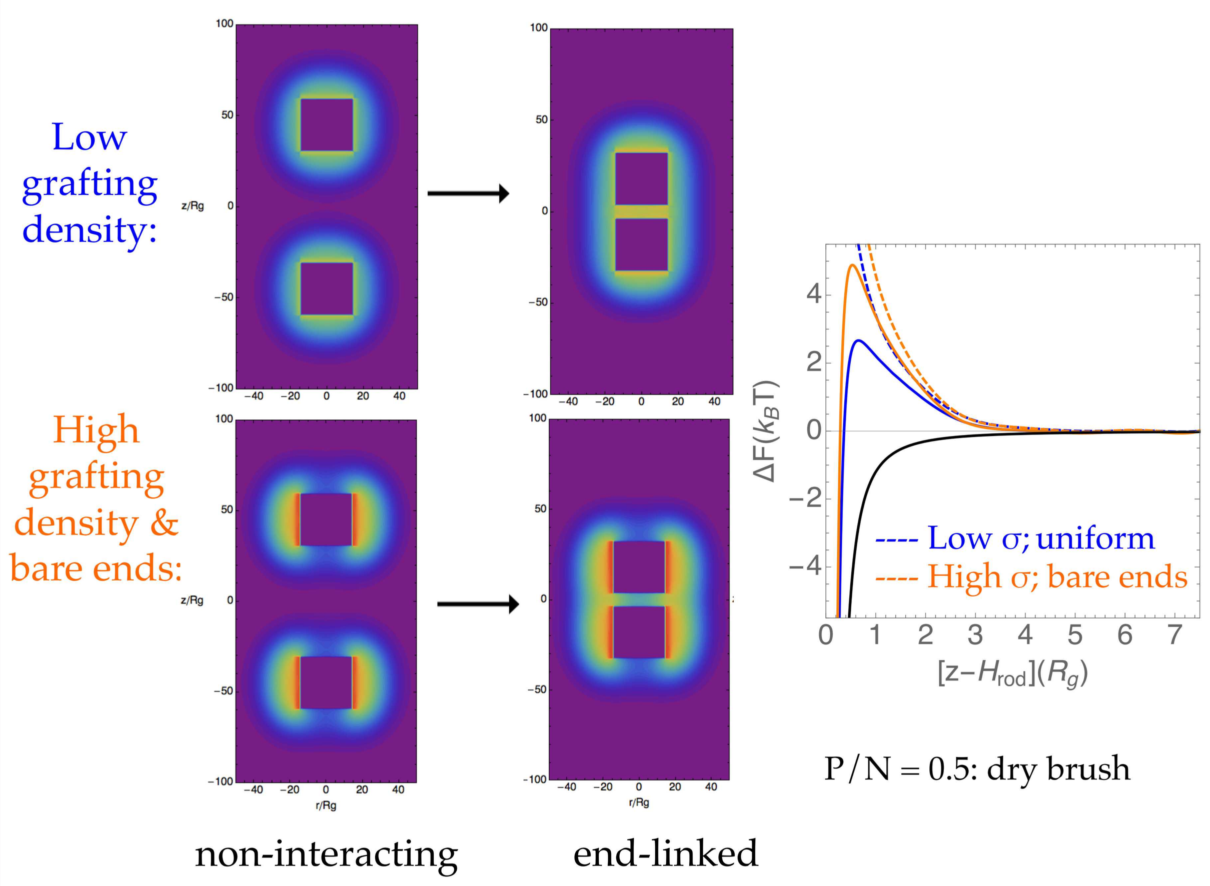
Side-by-side interaction energies



- Uniform grafting: side-by-side aggregation observed over end-to-end
- Bare end caps: aggregation at contact predicted

High grafting density

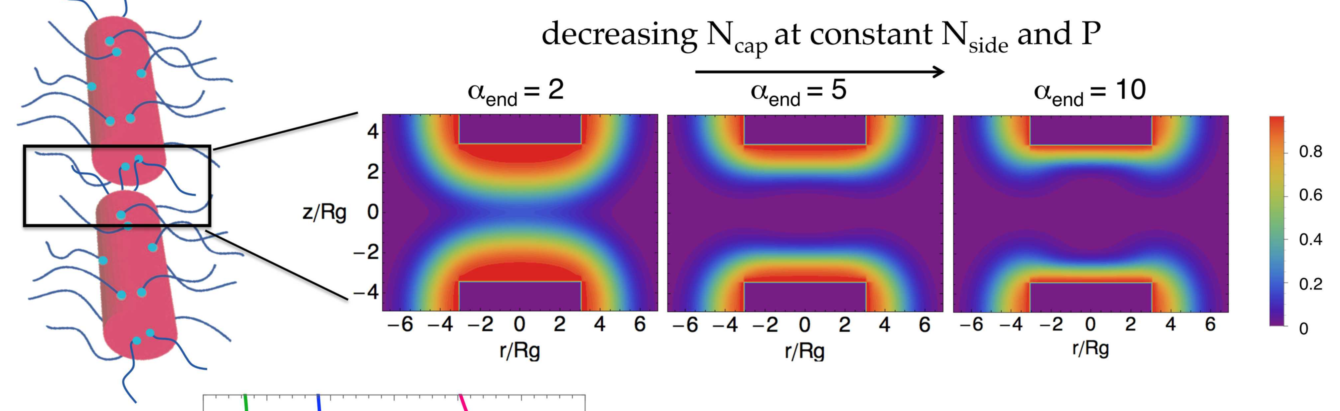
Combover effect

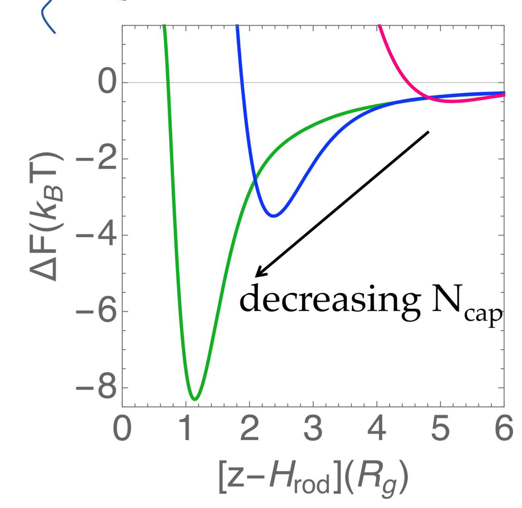


P/N = 0.5: dry brush

Tuning end-to-end separation

decreasing N_{cap} at constant N_{side} and P





- End-to-end linked nanorods achievable by independently varying side/end brush molecular weight
- The gap, and therefore the field enhancement, is tunable

Frischknecht, A. L.; Hore, M. J. A.; Ford, J.; Composto, R. J. Macromolecules **2013**, 46, 2856.
Ting, C. L.; Composto, R. J., Frischknecht, A. L. *Macromolecules* **2016**, 49, 1111.

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