SAND2016-2939C

Orientational Control of Polymer Grafted Nanorods

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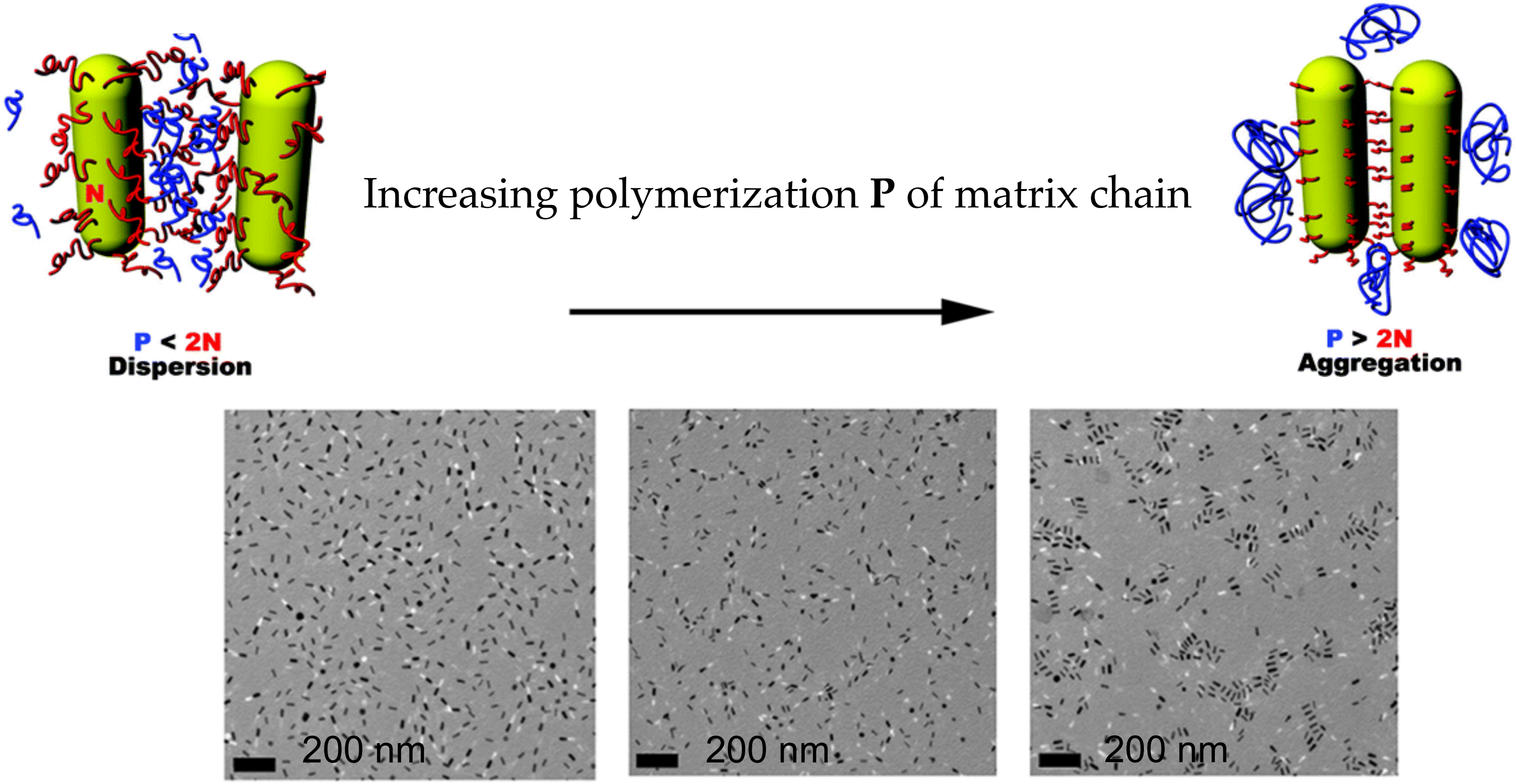
MRS Spring Meeting
March 30, 2016

Polymer nanocomposite thin films

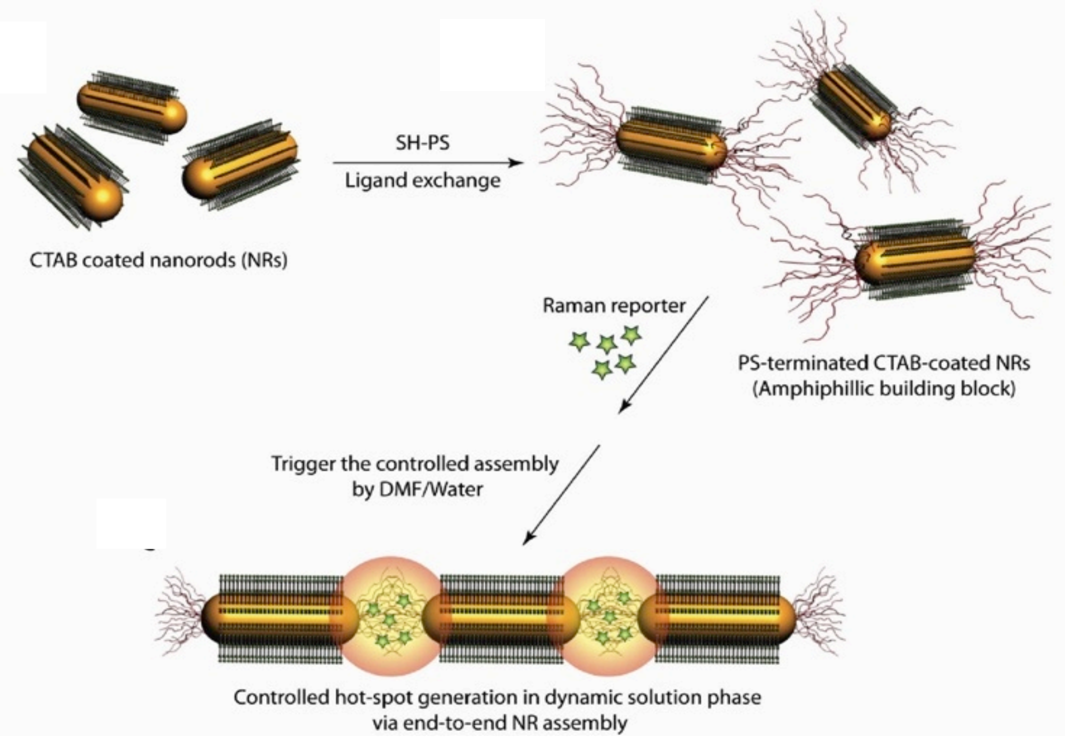
Goal: Integrate functional nanorods into a (functional) polymer matrix

Use polymer brush to control nanorod spacing via interactions between the brush and the polymer matrix



Hore MJA, Frischknecht AL, and Composto RJ, *ACS MacroLetters* (2011)

Orientational control: end-end linkage



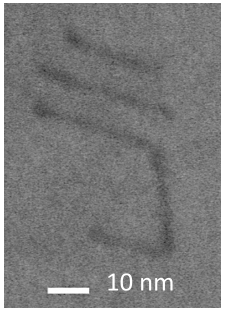
Can we preferentially obtain end-end assembly via an entropically controlled system of chemically identical brush/matrix polymers?

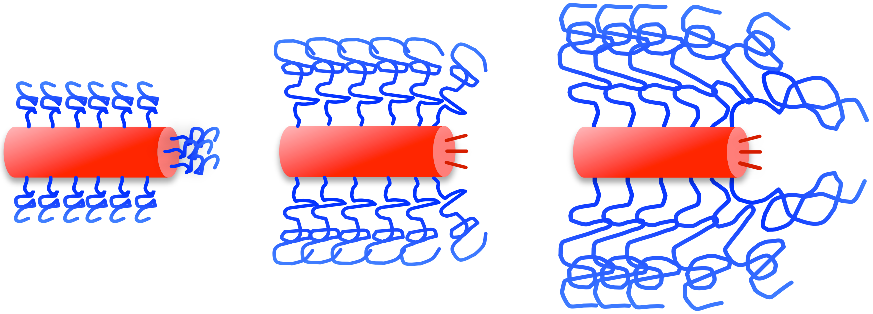
Lee A, et al., *JACS* (2011)

Experimental system

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

Spin-coated to an average thickness 36 nm.

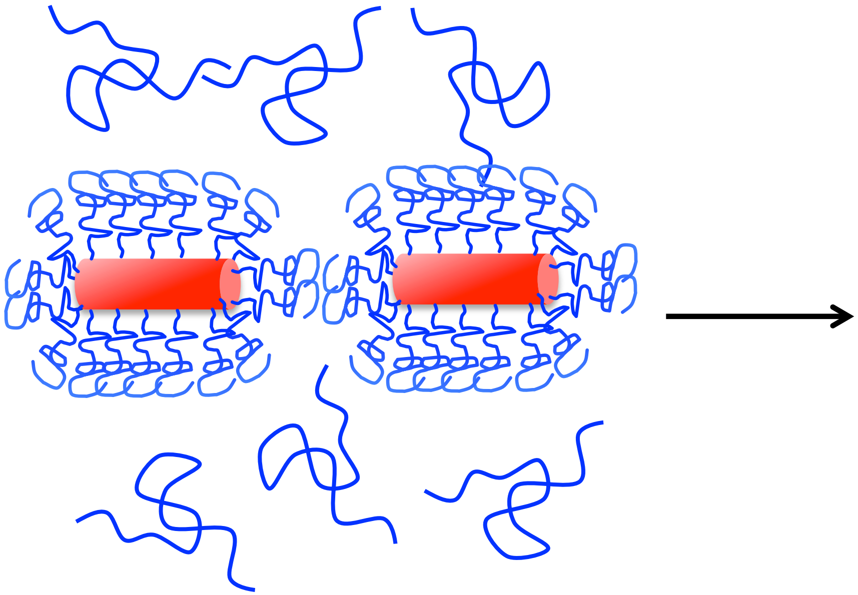




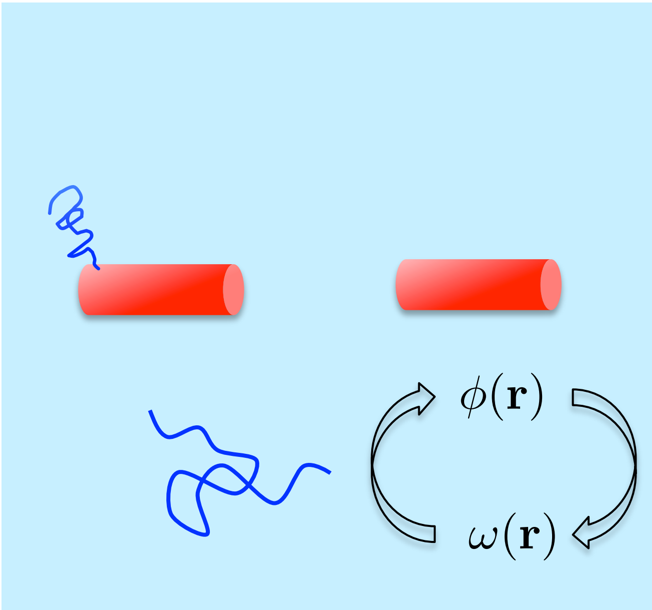
Controlling end-to-end vs side-by-side aggregation:

1. Bare nanorod ends
2. Comb-over effect
3. Brush, matrix, rod parameters

Self-consistent field theory



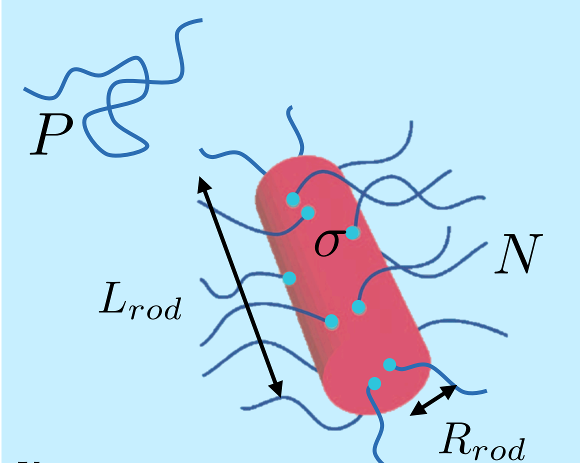
Many-body interaction



Mean-field theory

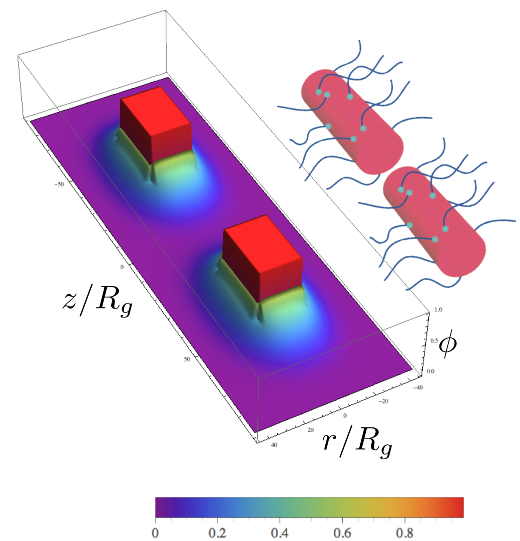
- Chain statistics determines polymer density $\phi(\mathbf{r})$ which determines external field $\omega(\mathbf{r})$ which determines chain statistics
- Mean-field approximation accurate for melts, exact as $N \to \infty$
- Free energy functional is *known:* $F[\phi^*(\mathbf{r}), \omega^*(\mathbf{r})]$

SCFT model



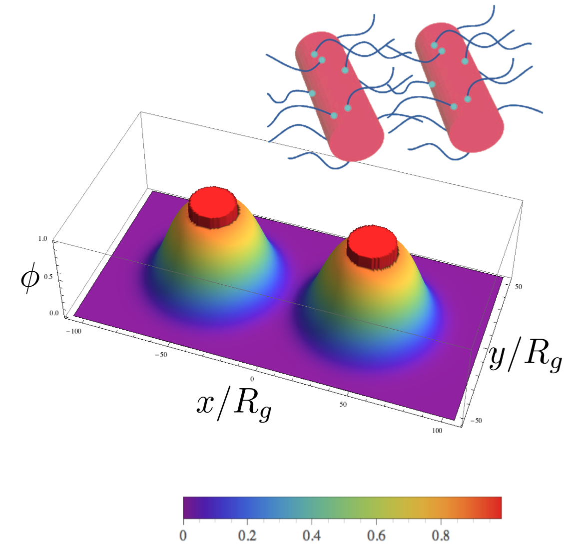
Key parameters:
- brush/matrix polymerization
- grafting density
- nanorod radius
- nanorod length

end-to-end



$$W(H) = -\frac{AR_{rod}^2}{12H^2}$$

side-by-side



$$W(H) = -\frac{AL_{rod}R_{rod}^{1/2}}{24H^{3/2}}$$

Total interaction energy is then the sum:

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

Side-by-side brush profiles

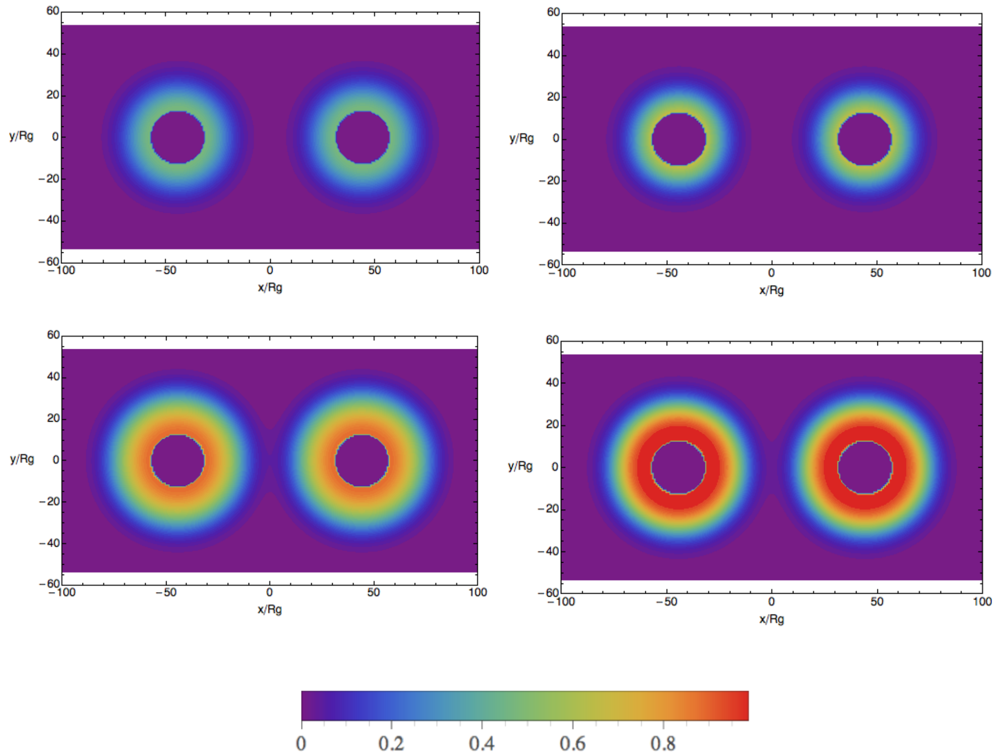
increasing matrix/brush polymerization ratio

$P/N = 0.5$ → $P/N = 5.0$

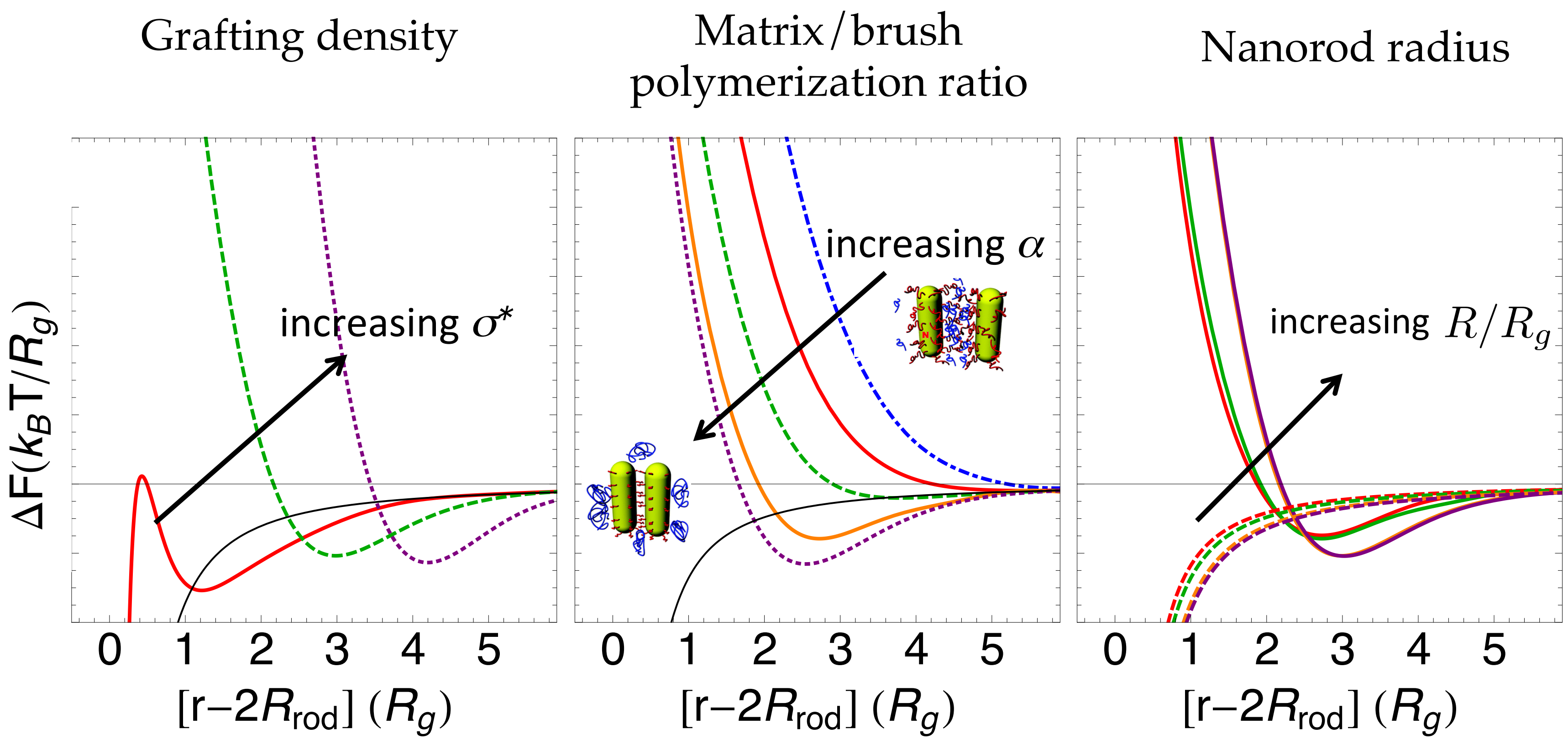
$\sigma^* = 1$

increasing grafting density

$\sigma^* = 3$

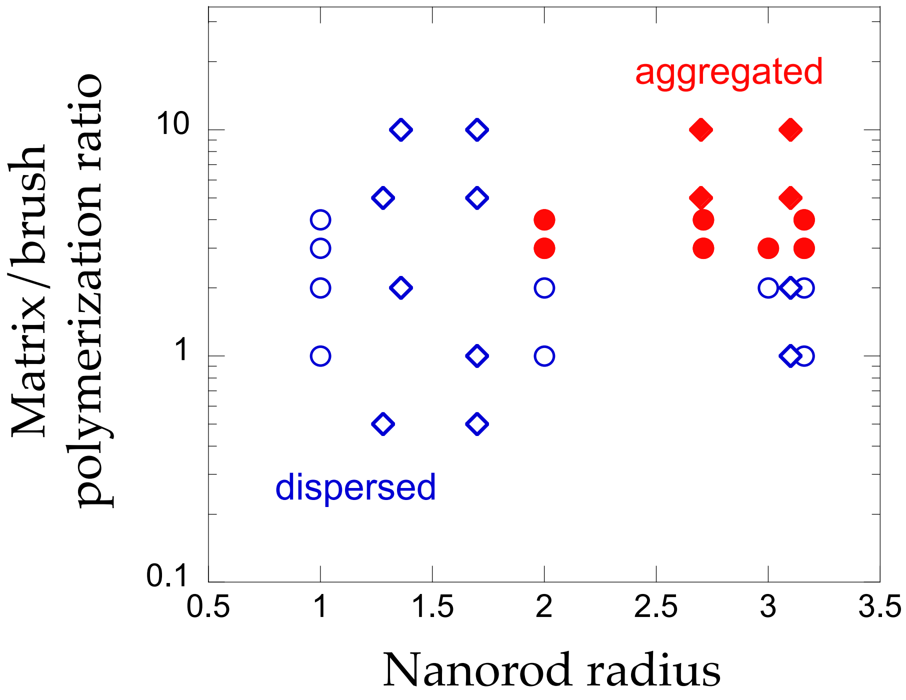


Side-by-side interaction energies



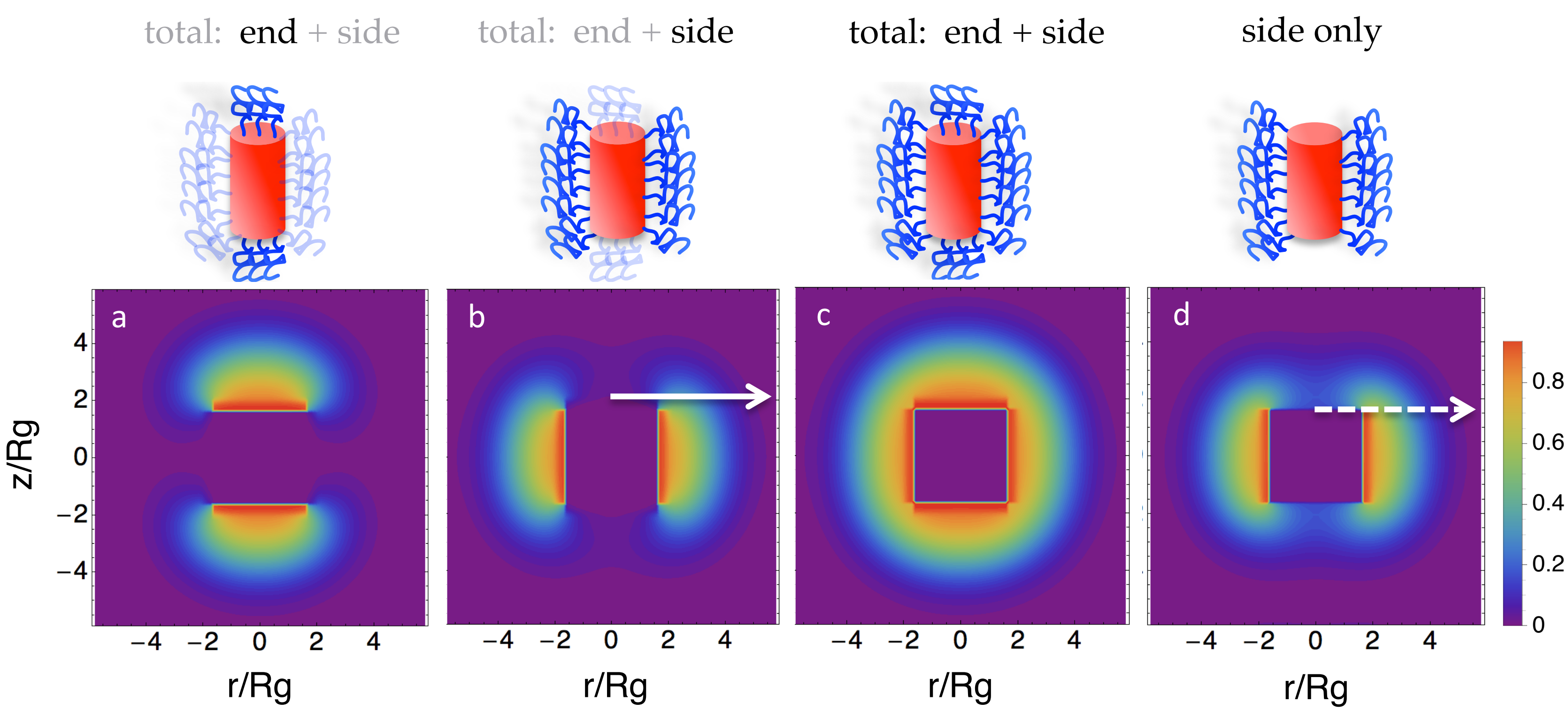
Side-by-side dispersion maps

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



$|E_{min}| > 5kT$

Total brush profiles



End-to-end aligned nanorods

non-interacting

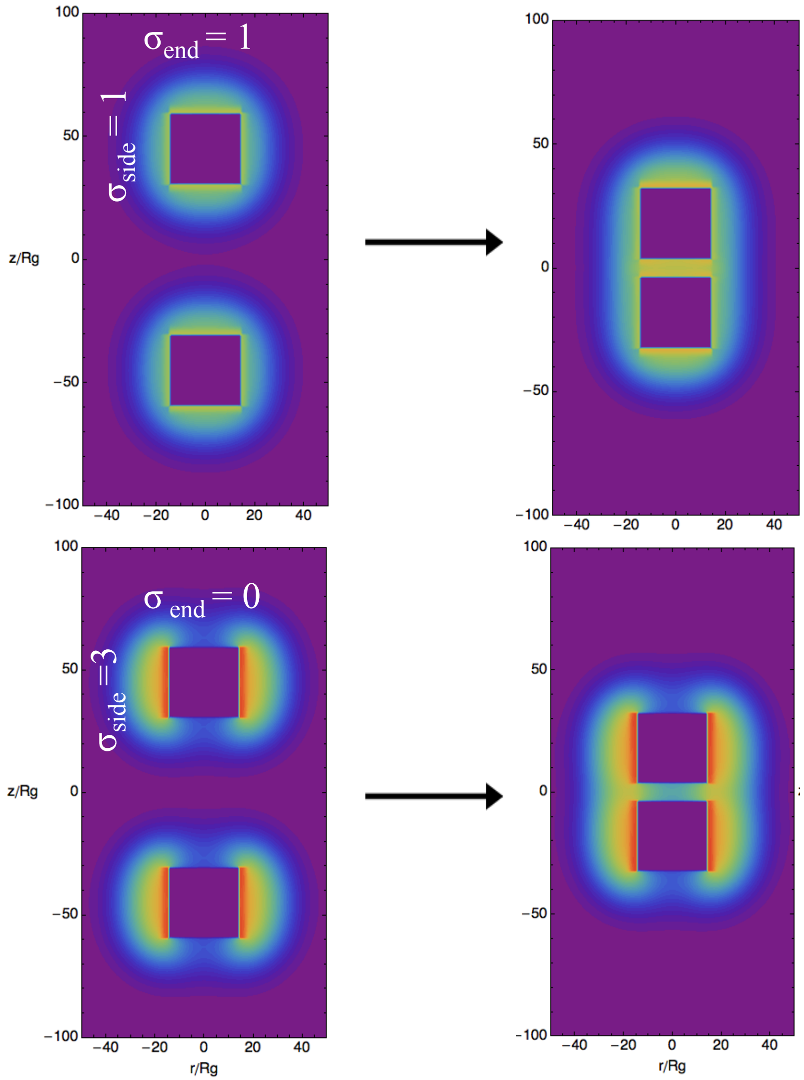
end-linked

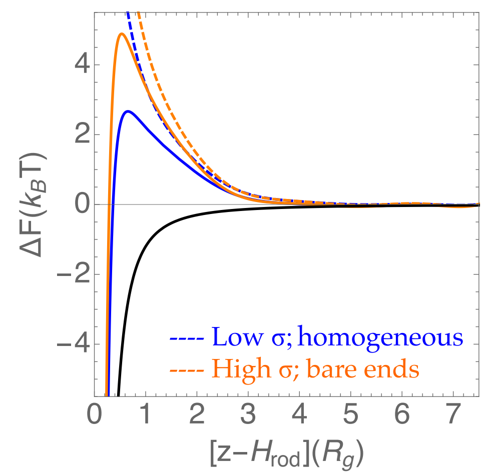
Low grafting density

P/N = 0.5

High grafting density; bare ends

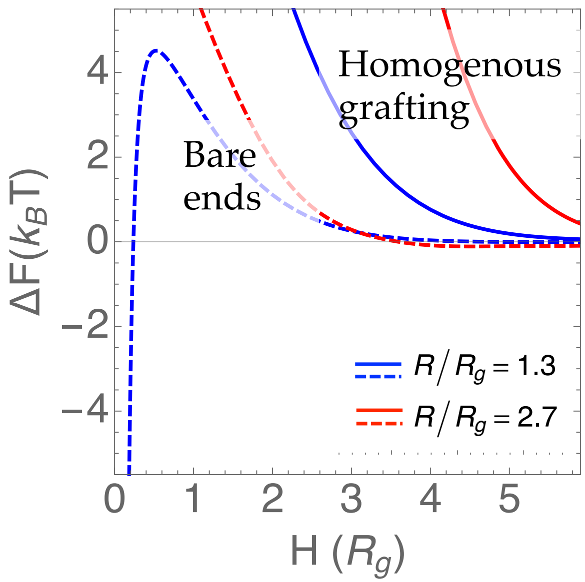
P/N = 0.5



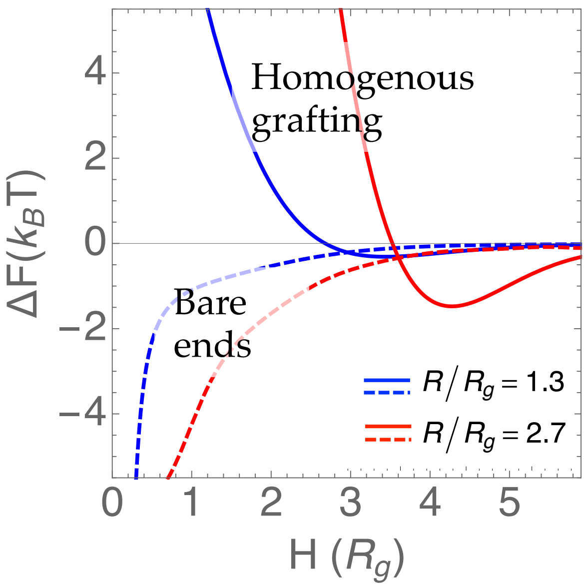


End-to-end interaction energies

P/N = 0.5: wet brush
High grafting density



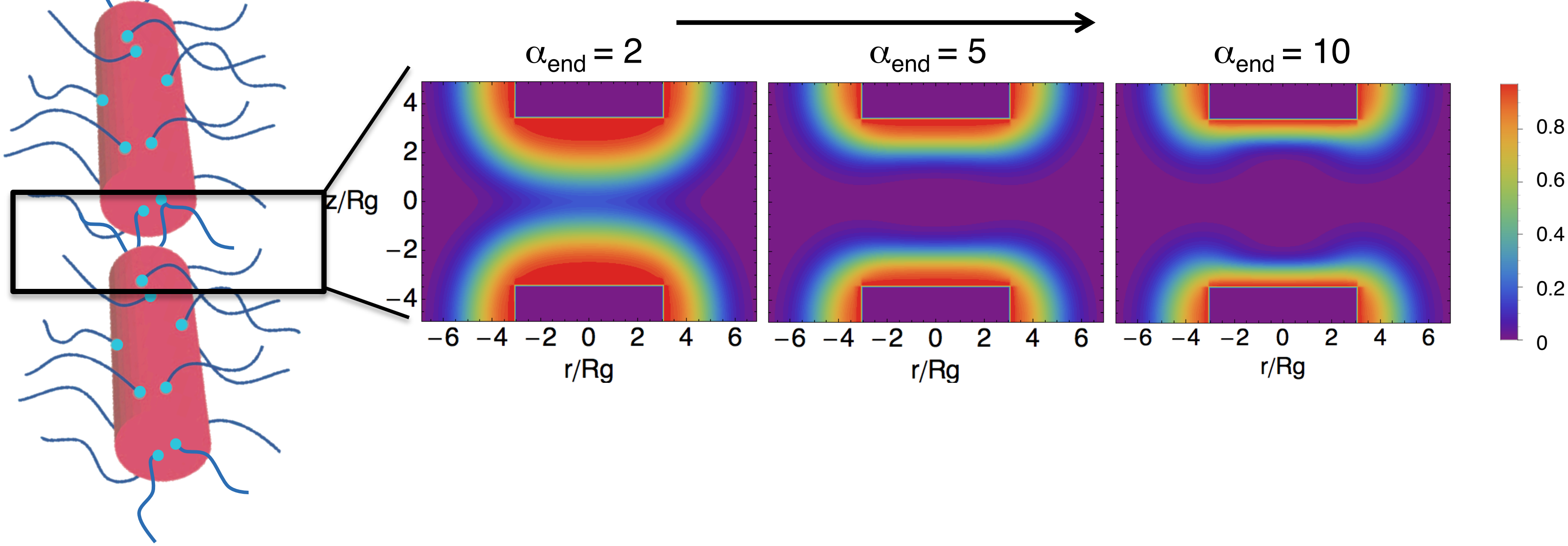
P/N = 10.0: dry brush
High grafting density



- Homogeneous grafting: side-by-side aggregation observed over end-to-end
- Nanorods with bare bare end caps: aggregation at contact predicted

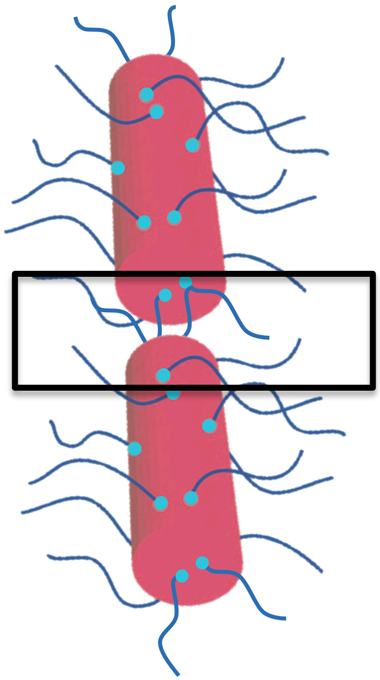
Tuning end-to-end separation

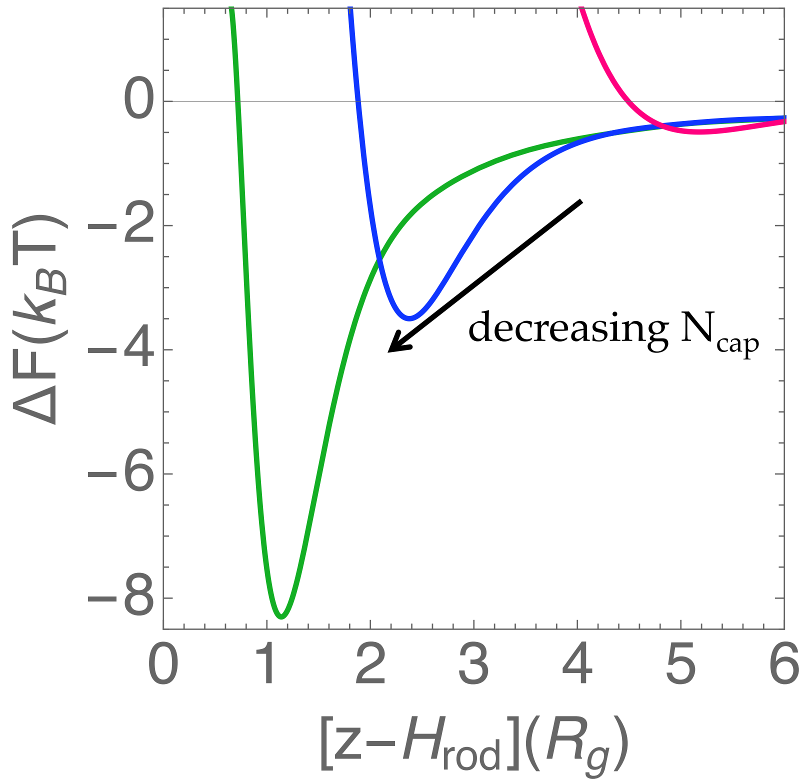
decreasing N_{cap} at constant N_{side} and P



High grafting density, $\sigma = 3$
P/N (side) = 5
$R_{rod}/R_g = 3.1$

Tuning end-to-end separation





High grafting density, σ = 3
P/N (side) = 5
R_{rod}/R_g = 3.1

Conclusions

- Side-by-side aggregation predicted for homogeneously-grafted nanorods
- Finite size of end caps leads to interesting combover effects and end-to-end behavior
- End-to-end linked nanorods achievable by independently varying side/end brush molecular weight
- The gap, and therefore the field enhancement, is tunable

Acknowledgements
Boris Rasin
Dr. Robert Ferrier
Russell Composto
Amalie Frischknecht

Harry S. Truman Fellowship