

Self-assembled chains of polymer-grafted nanorods

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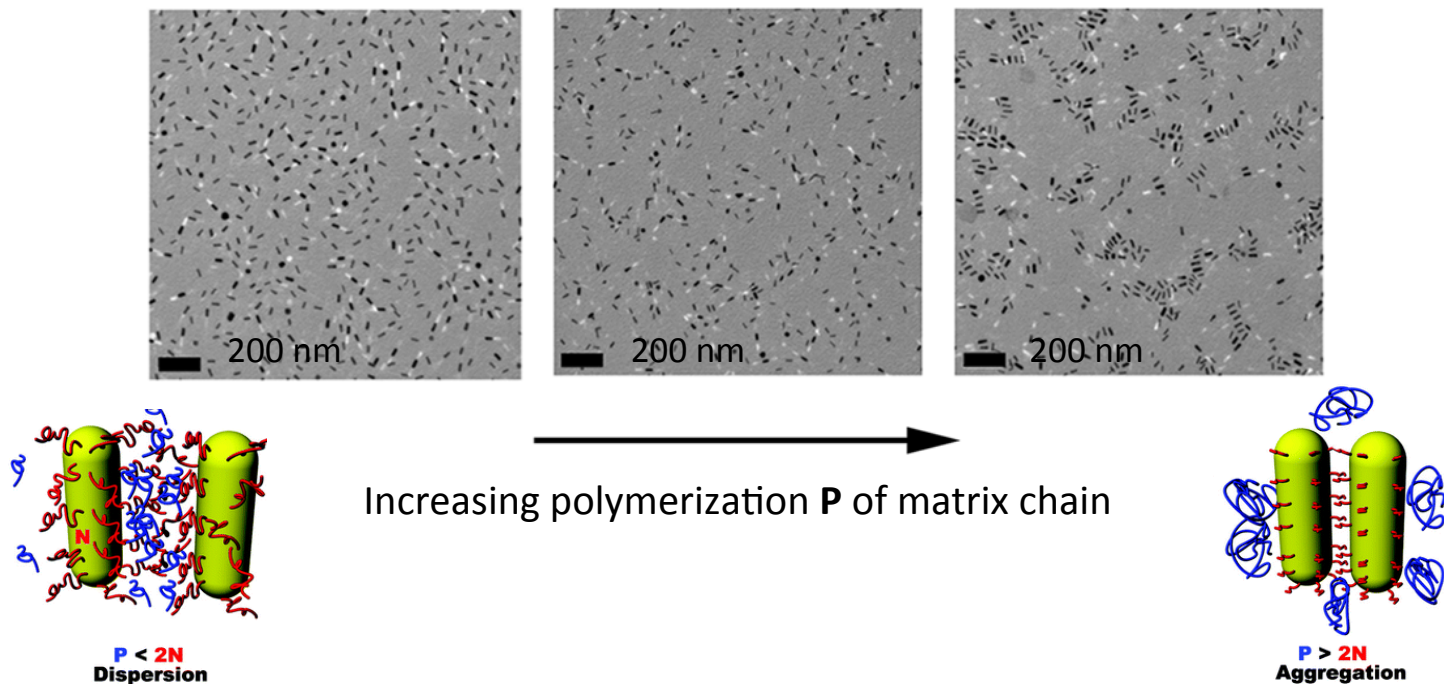
APS March Meeting
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Polymer nanocomposite thin films

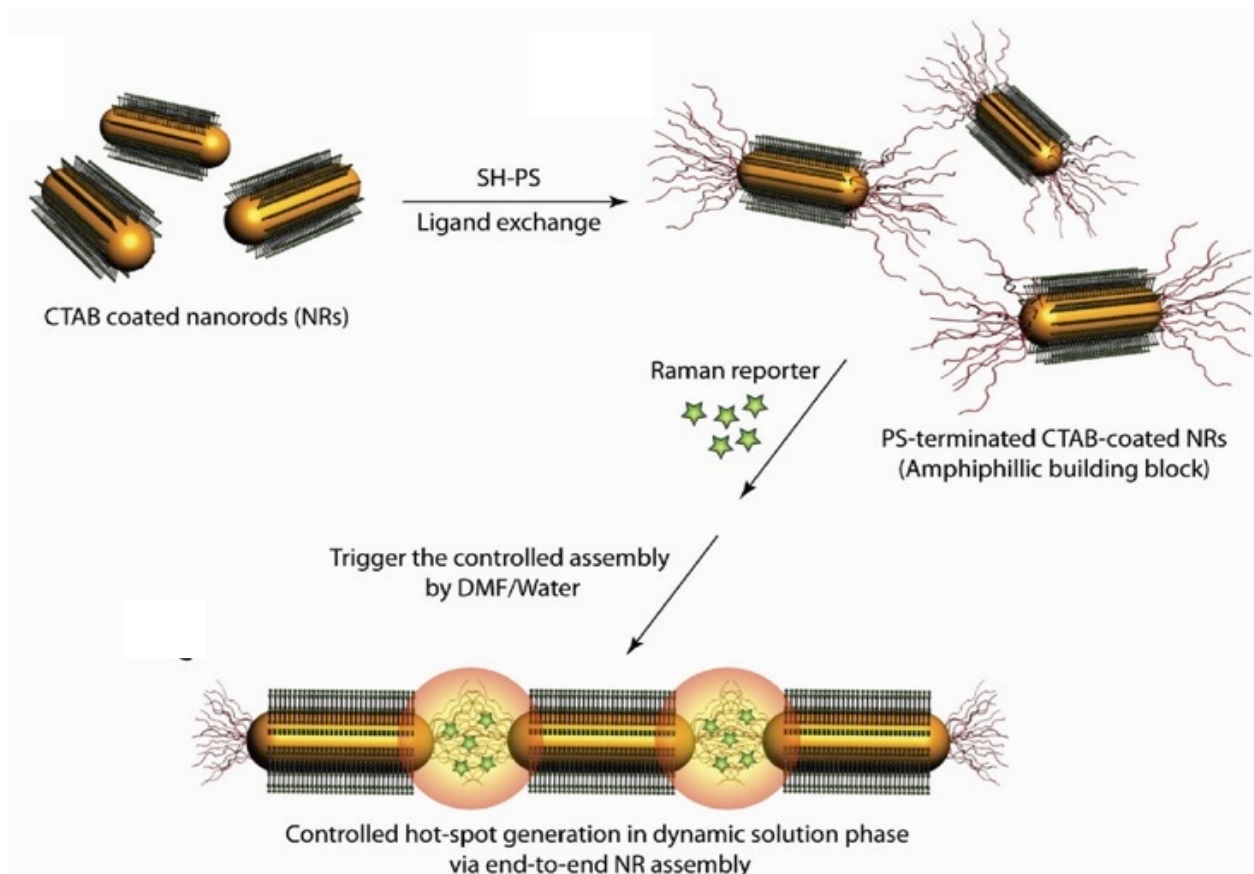
Goal: Integrate functional nanoparticles into a (functional) polymer matrix: top-down nanofabrication vs **bottom-up self-assembly**.

Use polymer brush to control nanoparticle spacing via interactions between the brush and the polymer matrix: enthalpically or **entropically**

Dispersed-to-aggregated state determined mainly by the wet-to-dry transition:

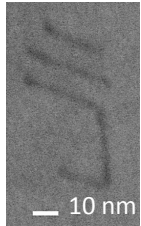
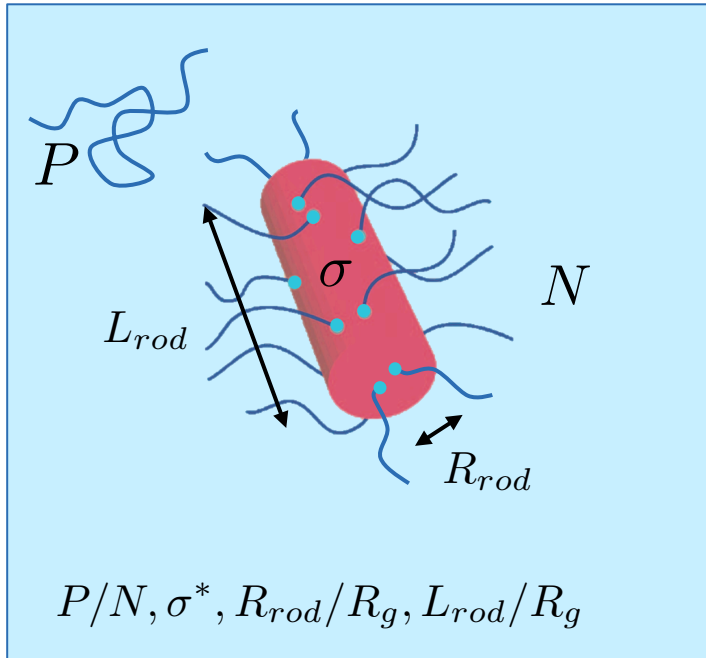


Orientational control: end-end linkage



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

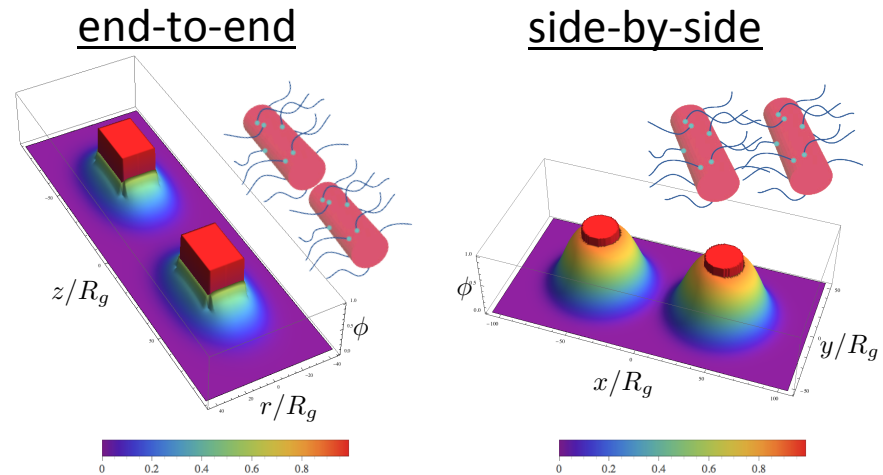
Theoretical model



Brush MW (g/mol)	R_g (nm)	R_{rod}/R_g	$\alpha = P/N$
3000	1.5	1.67	0.57 - 13.33
5300	1.95	1.28	0.47 - 13.28
11500	2.90	0.86	0.48 - 12.59

CdSe/CdS nanorods (5 x 28 nm) with PS brushes in PS matrix prepared by spin coating (average thickness 36 nm).

Using self-consistent field theory (SCFT), we minimize the free energy and obtain polymer brush profiles:



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

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

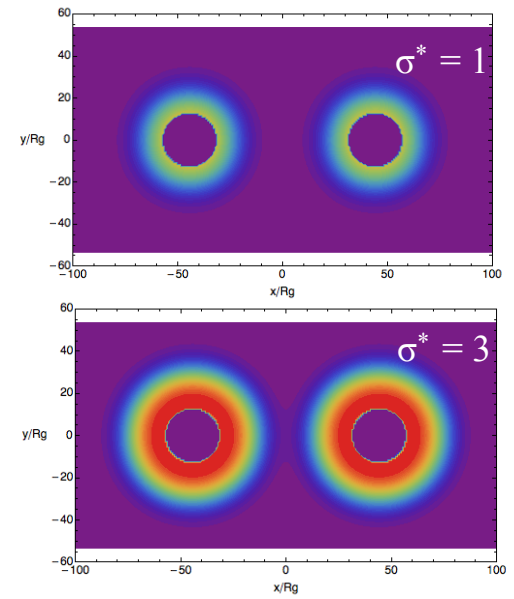
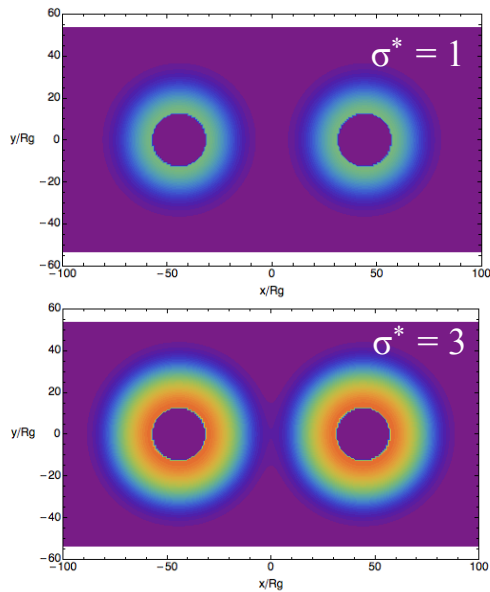
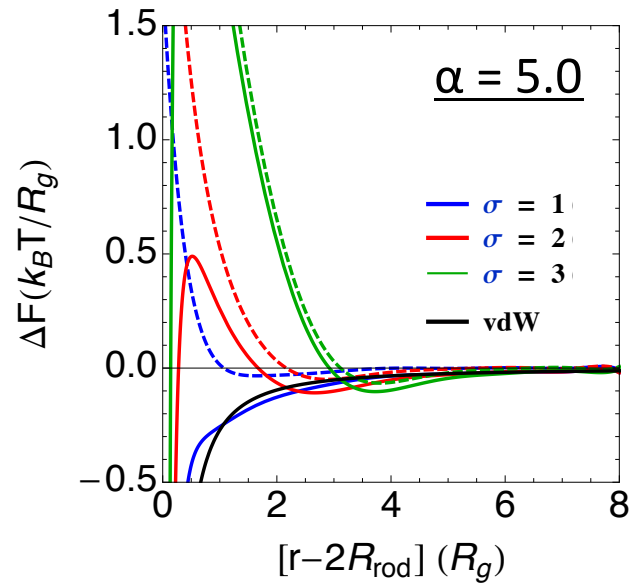
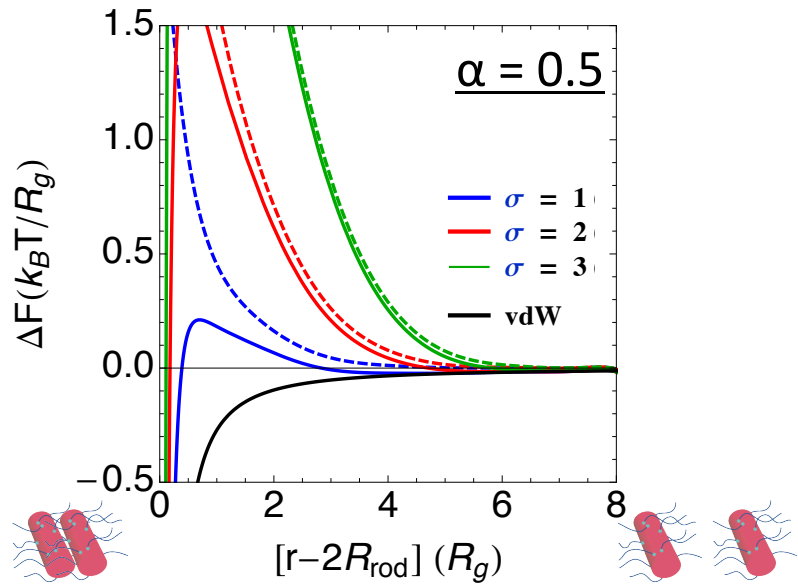
Total interaction energy is then the sum:

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

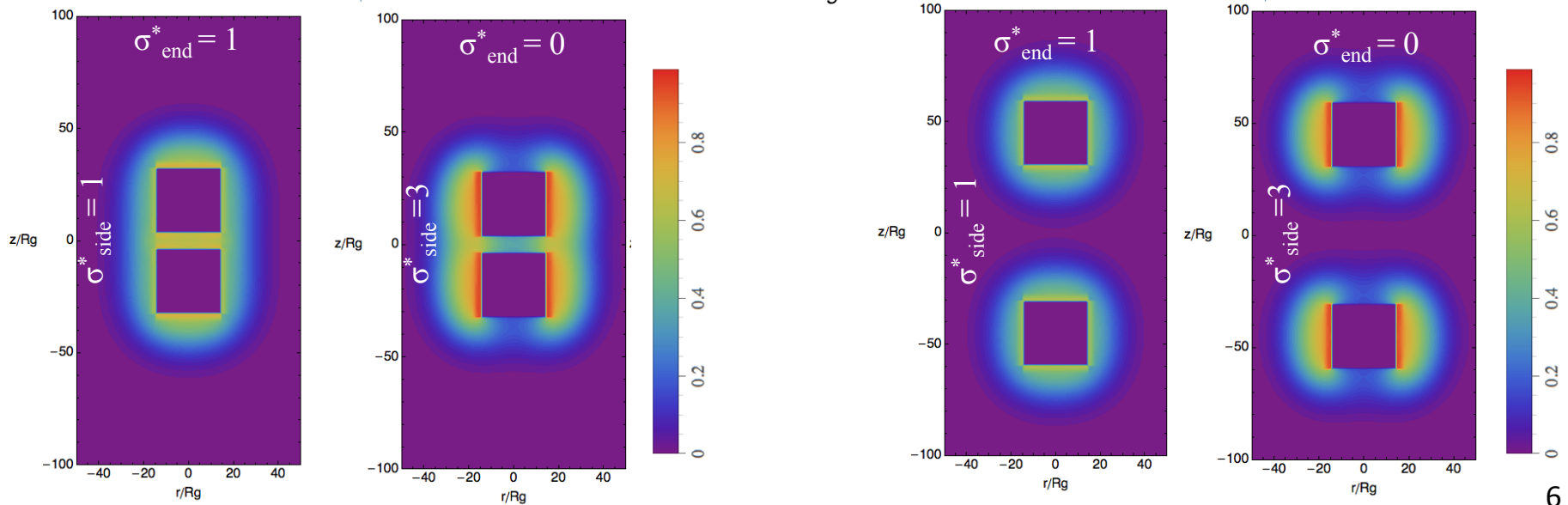
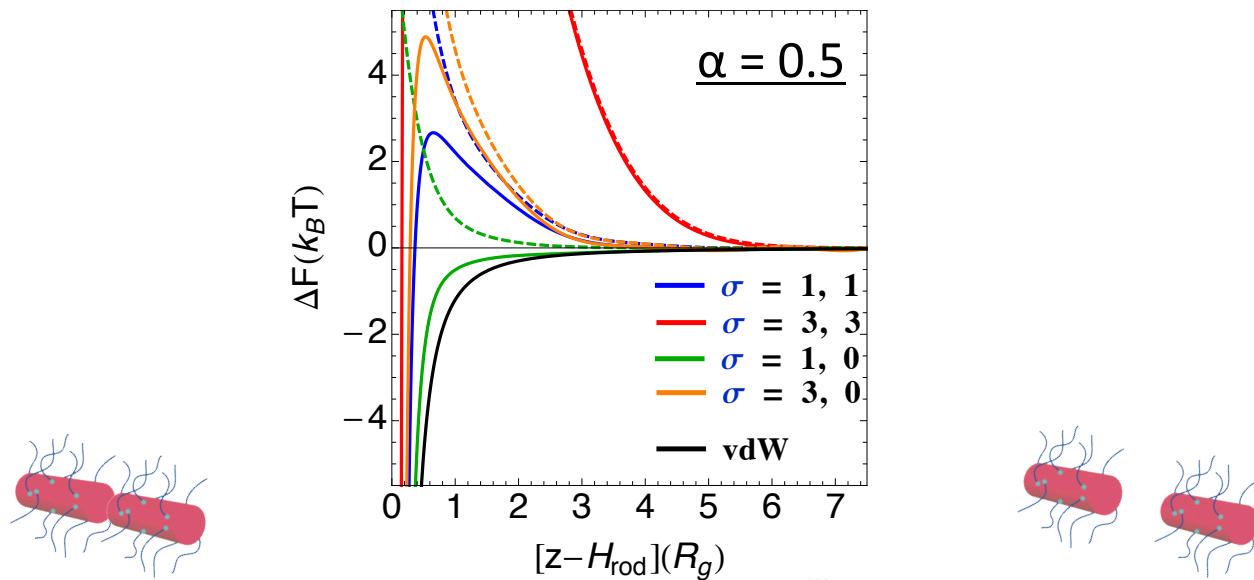
polymer chain entropy
+ excluded volume

van der Waals
attraction

Side-by-side assembly

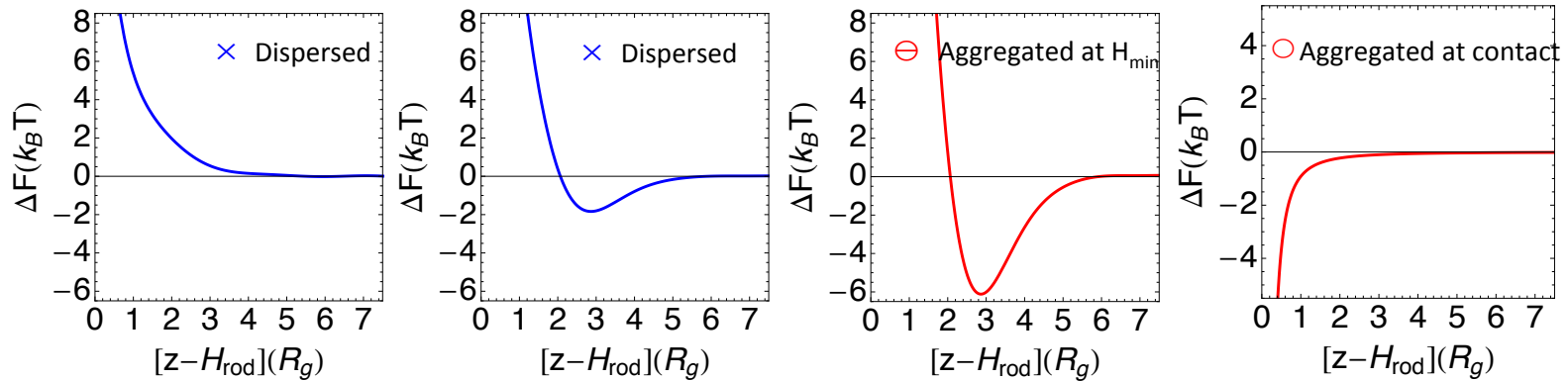


End-to-end linkage



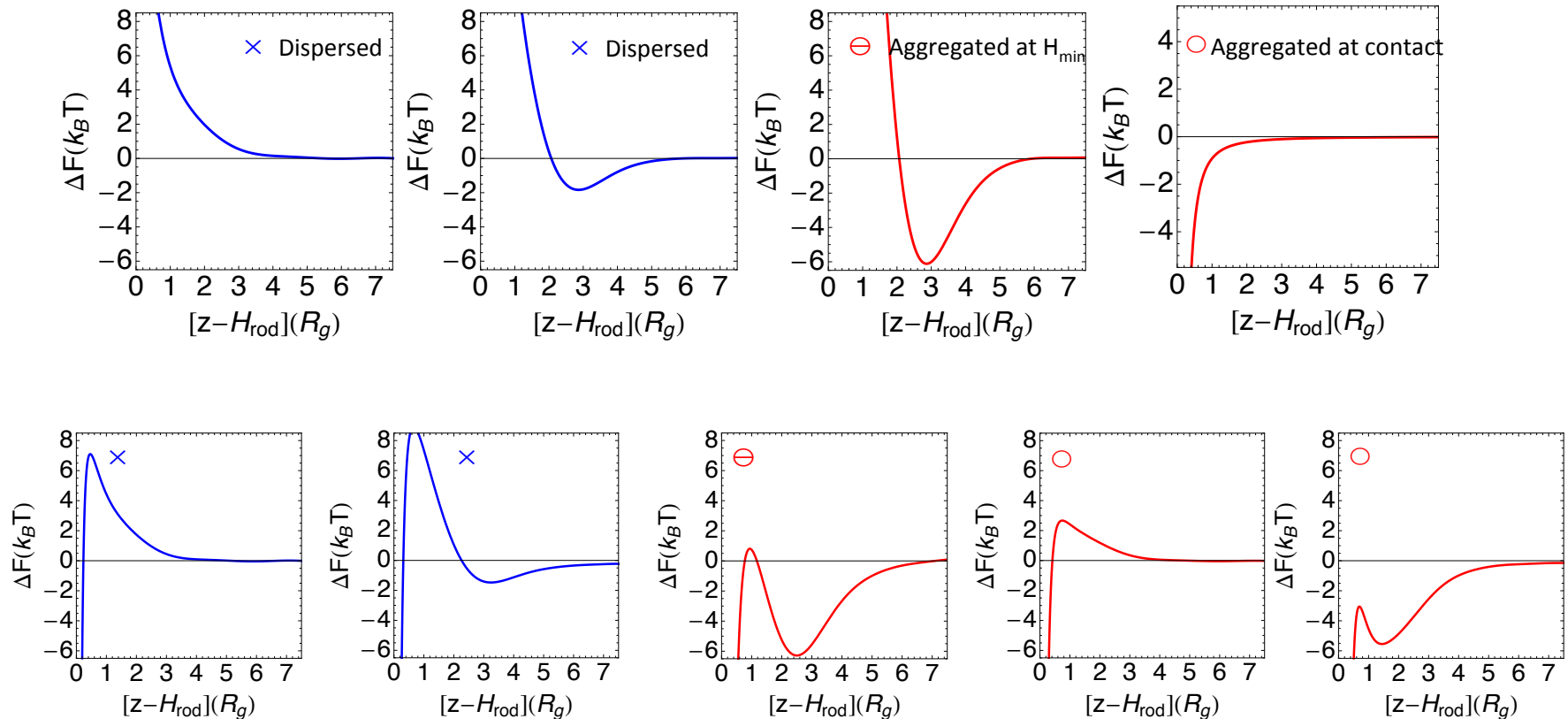
End-to-end interaction free energy

How do we determine dispersed/aggregated state?

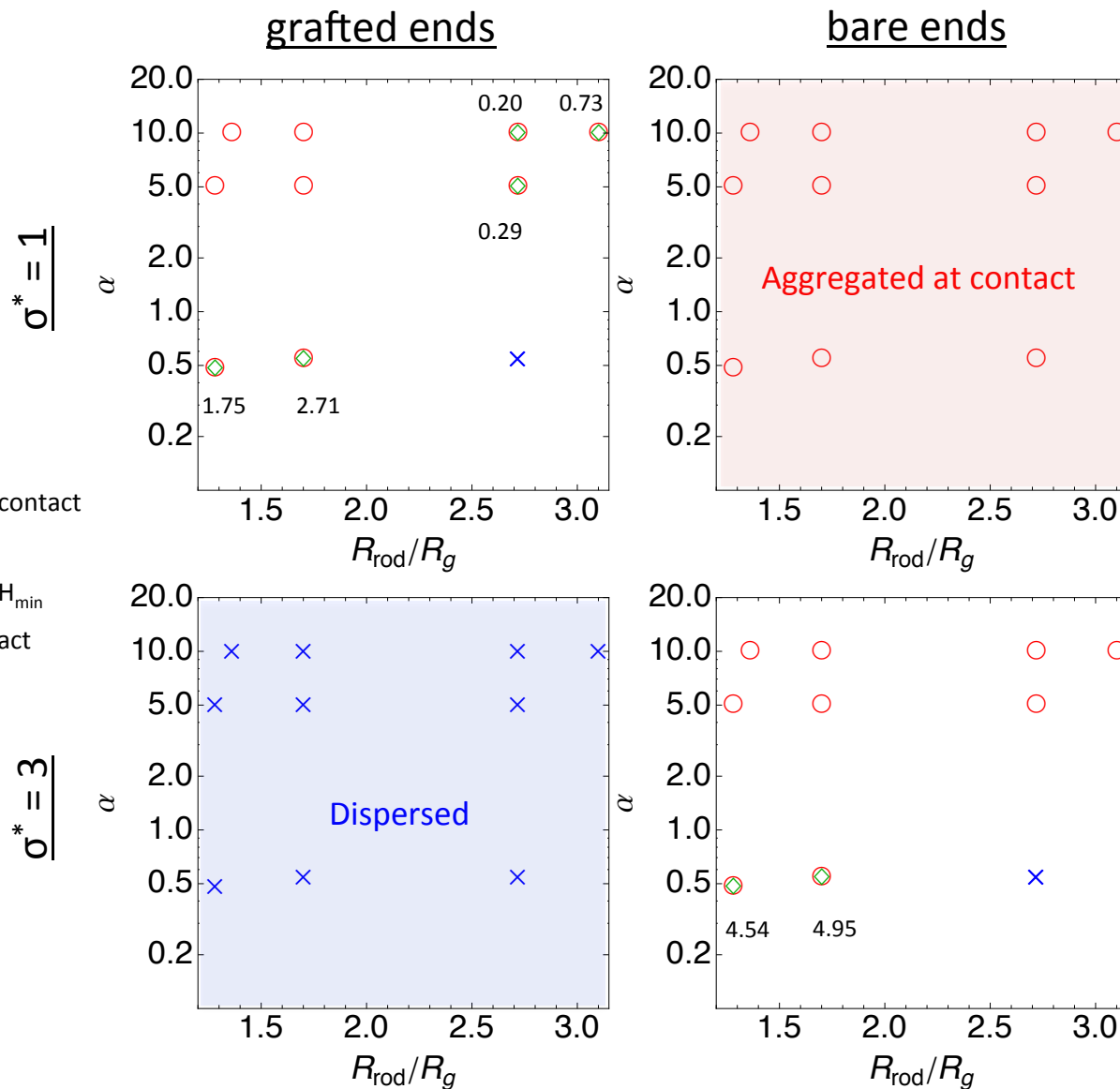


End-to-end interaction free energy

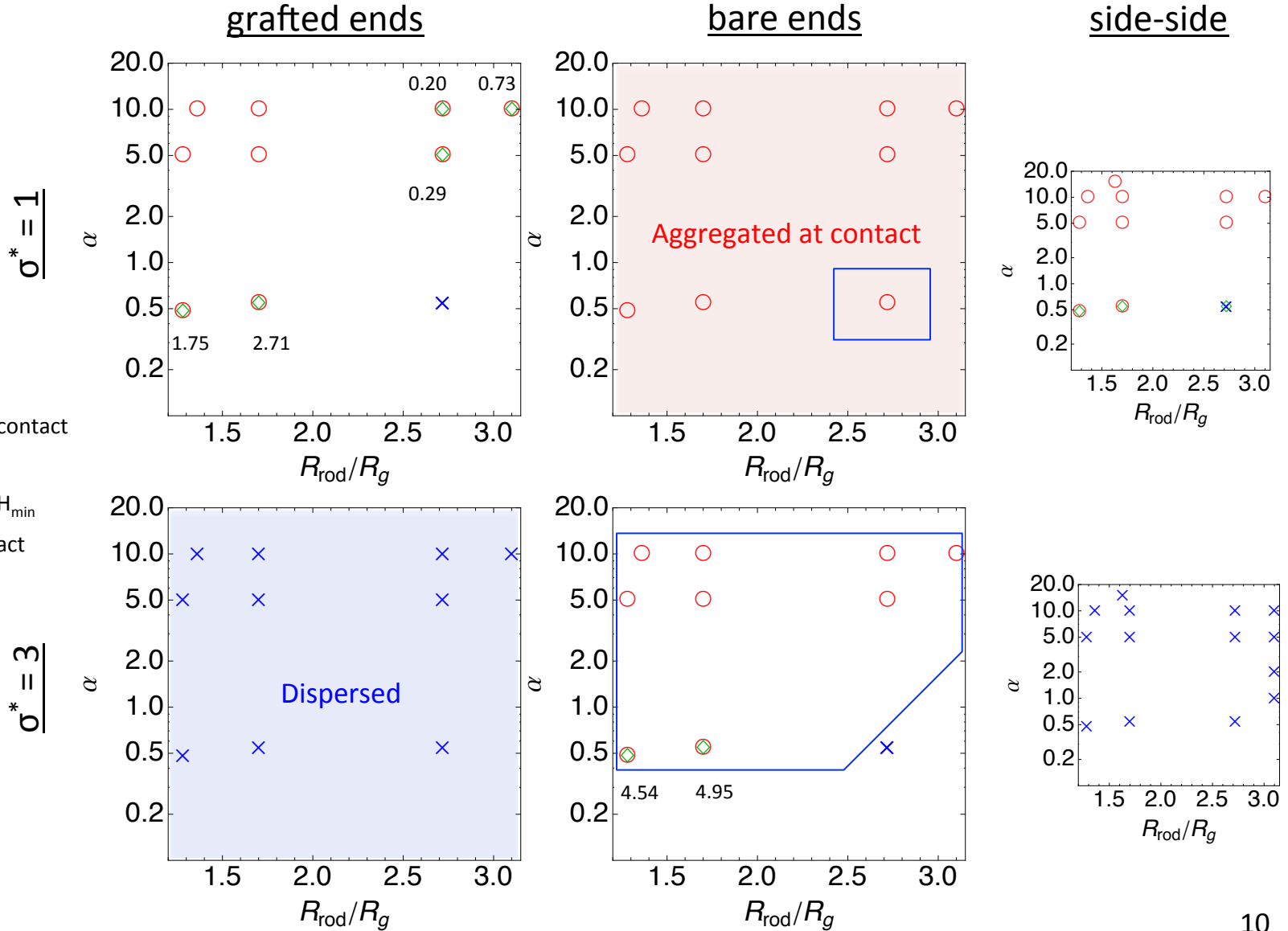
How do we determine dispersed/aggregated state?



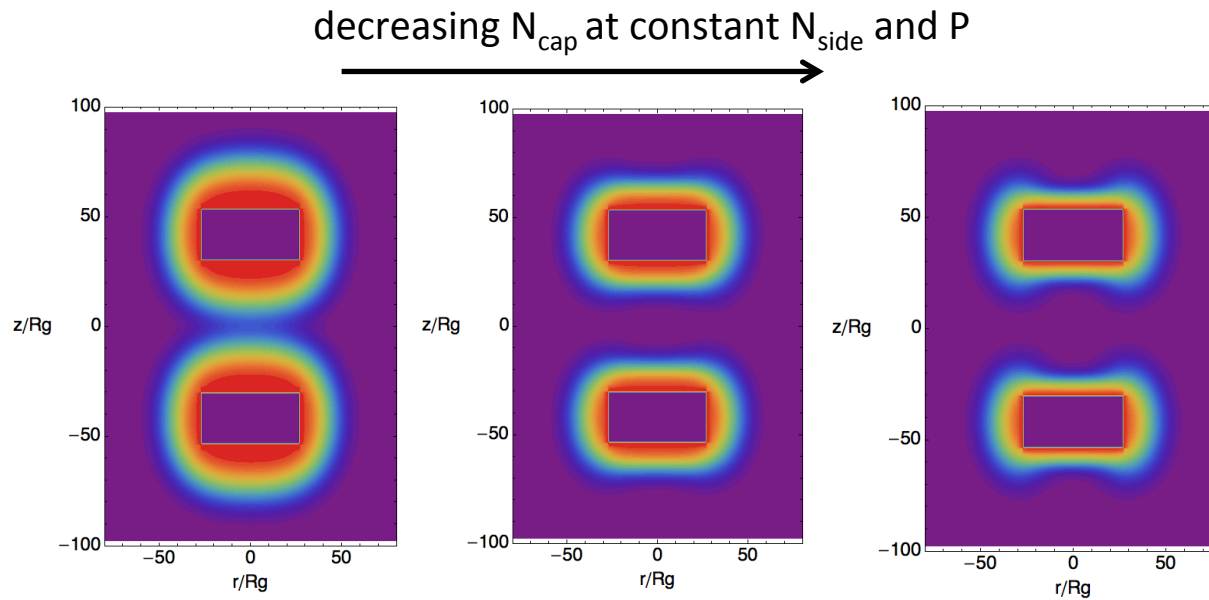
End-to-end dispersion maps



End-to-end dispersion maps

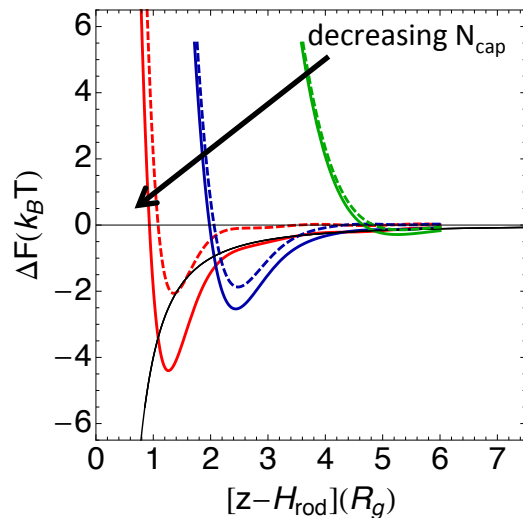
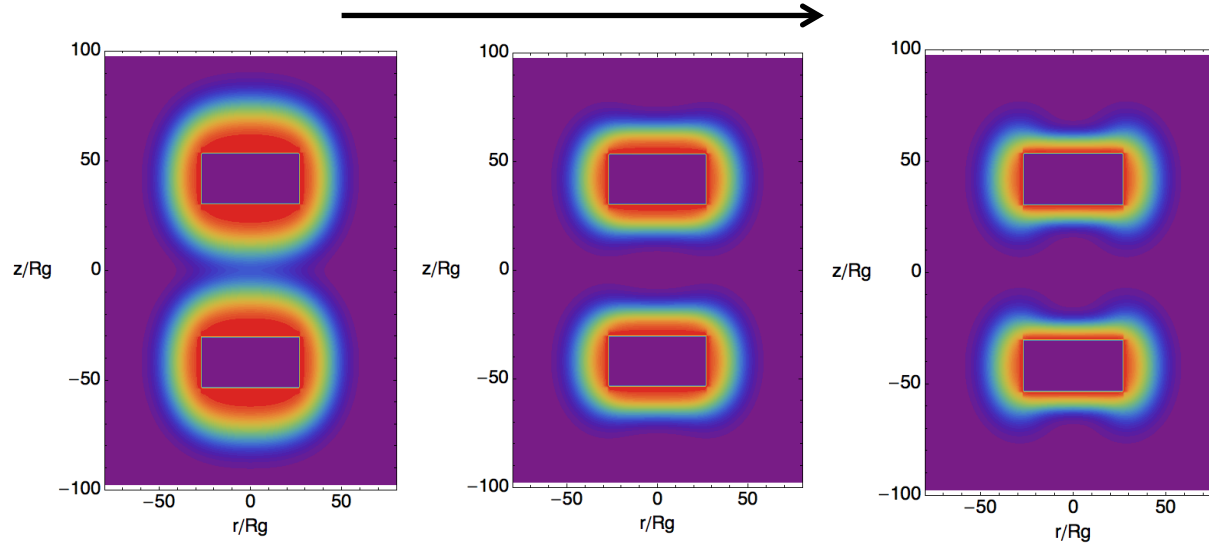


Can we control end-to-end separation?

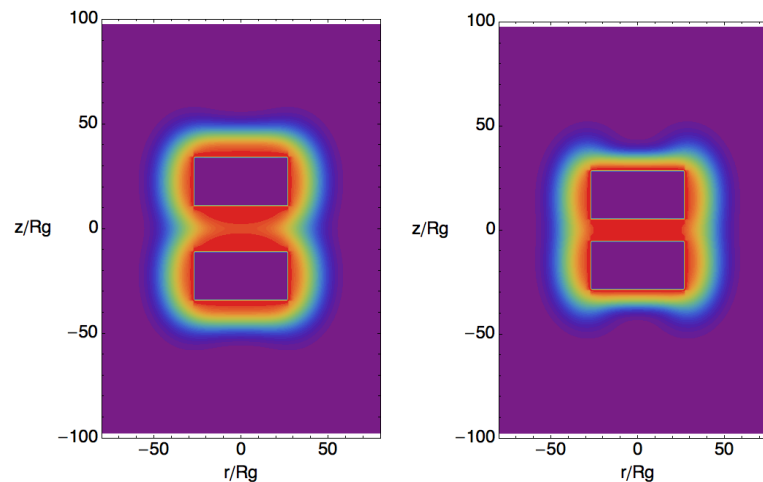


Can we control end-to-end separation?

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



At the minimum:



Acknowledgements

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Fellowship