Microphase Segregation of Polyelectrolyte Brushes

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Charged and Ion-Containing Polymers I

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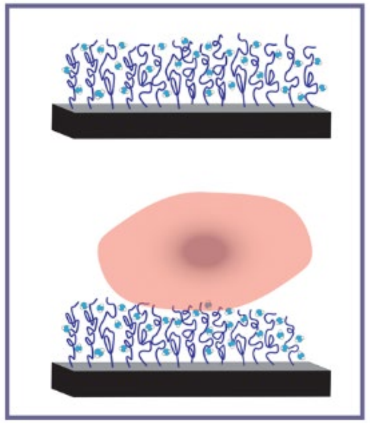
Introduction

- Polyelectrolyte brushes (PEBs) are particularly promising for interfacial modification, “smart” materials, and as model systems in biology

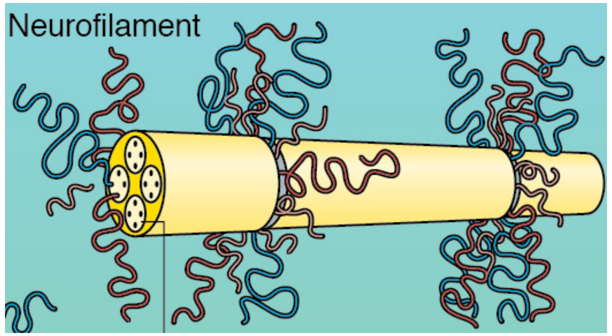


Biofouling

pH-sensitive flow valves

Lubrication

(Chen, et al., *Macromolecules*, 2017)



Aggregation mechanisms

Protein distribution

Mutation effects

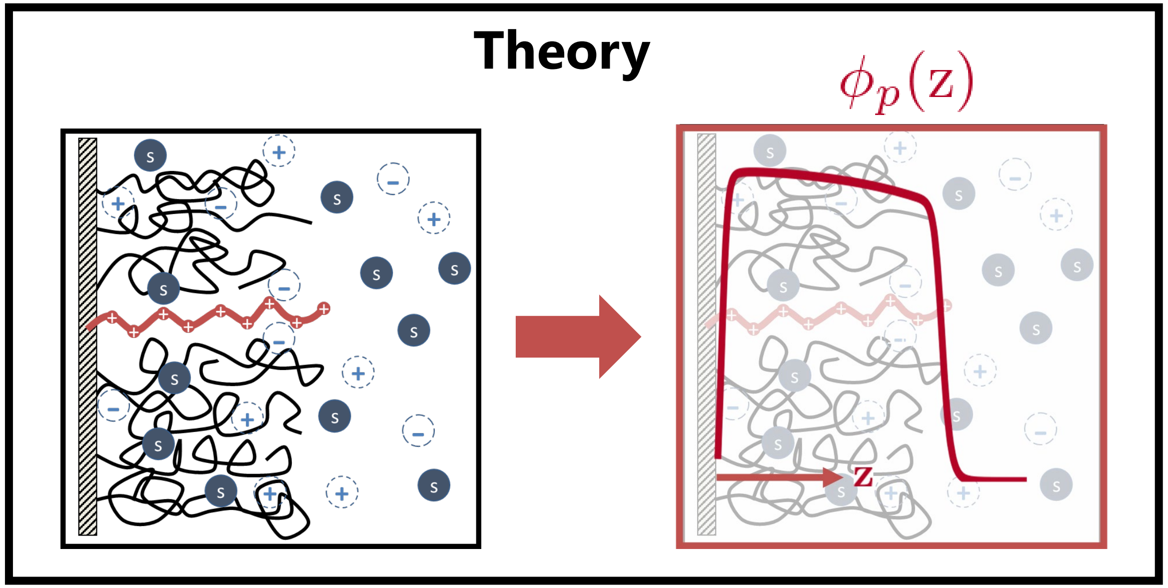
(Yuan, et. al., *J. Cell Sci.*, 2012)

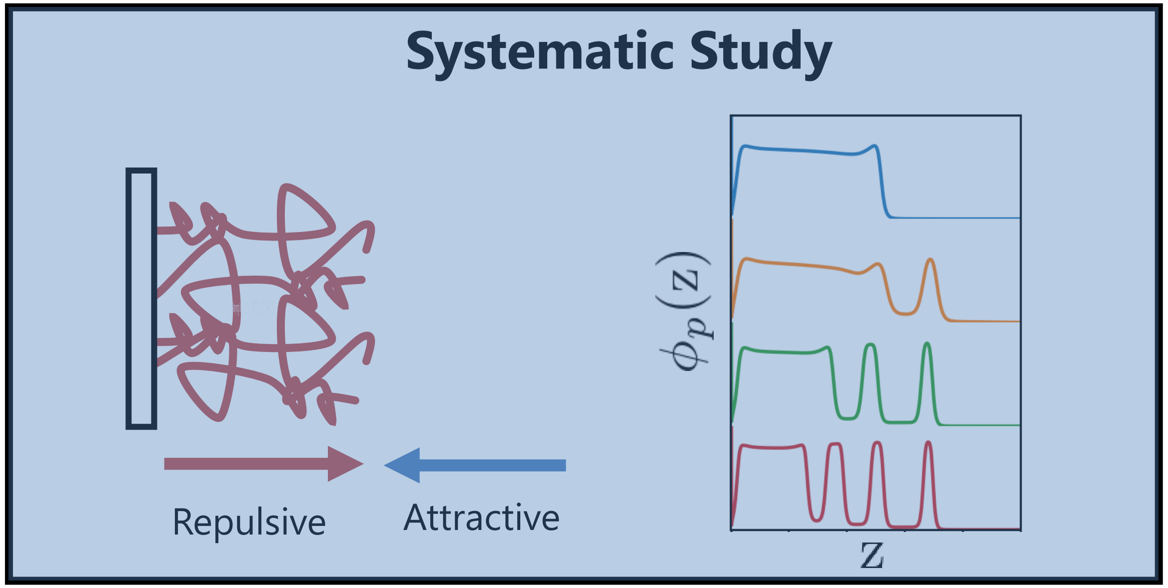
- A comprehensive understanding of the underlying physics is necessary for
  - Discovery of new conformational targets and transition mechanisms
  - Polymer design strategies for desired phenomena

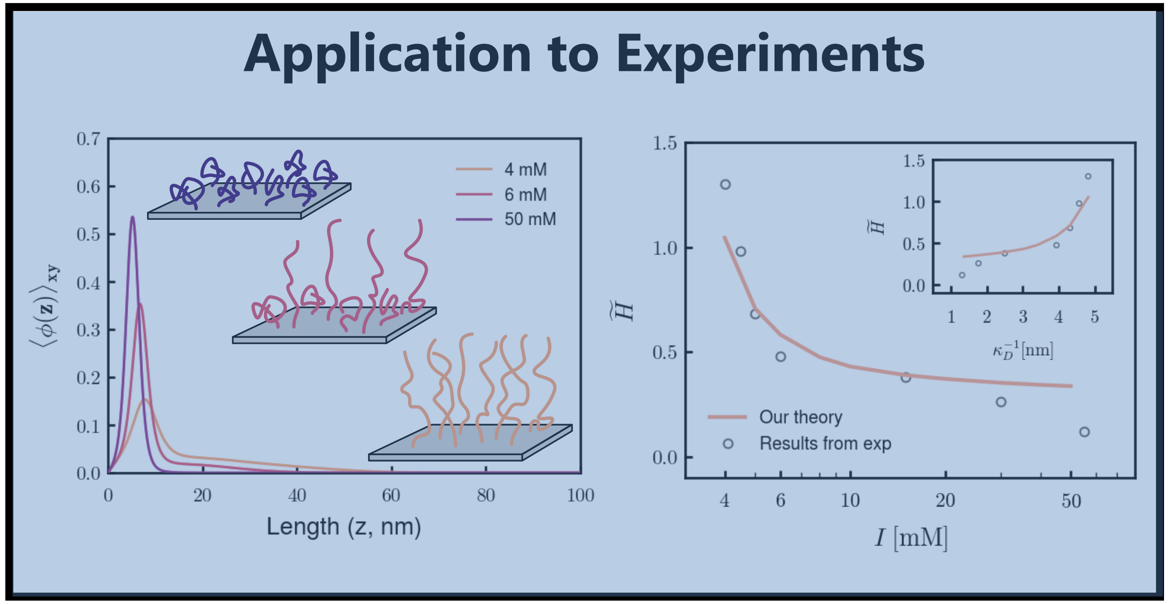
Motivation

- Theory allows for the study of mechanisms and structures throughout the entire parameter space (chain length, charge fraction, solubility, etc.)
- There has not been a systematic study of the coupling between polymer conformation and the interactions with its surroundings in PEBs
- Standard buildup from statistical mechanics allows for straightforward implementation of additional interactions, such as
  - Ion fluctuations (multivalent ions / charge inversion)
  - Excluded volume effects
  - Multi-chain interactions

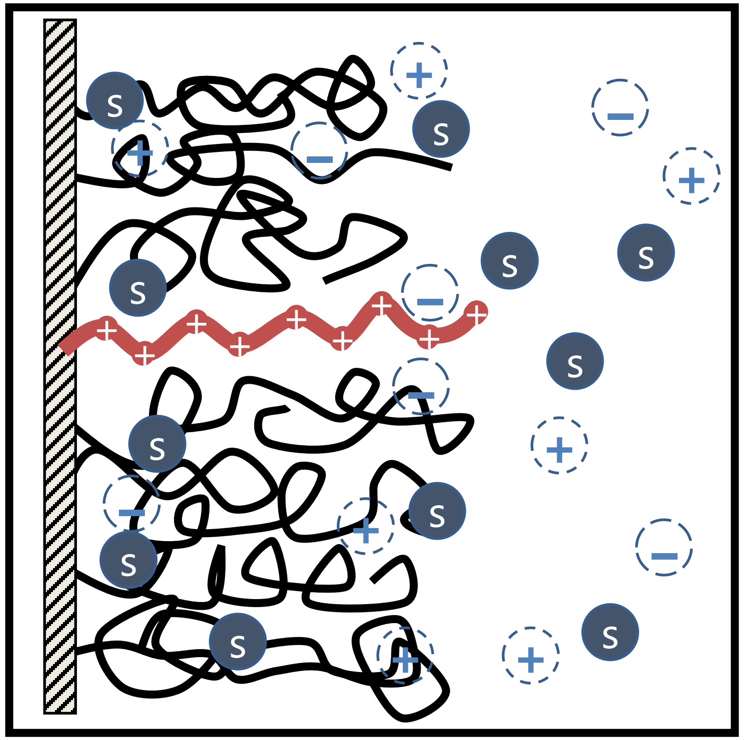
Presentation Overview







Partition Function Formulation



$\sigma\ [c/nm^2]$

$$\Xi = \int \hat{\mathrm{D}}\boldsymbol{\Gamma}\ \exp\left[-\beta(E_{elas} + E_{attr} + E_{rep} + E_{elec})\right]$$

$$\beta E_{elas} = \frac{3}{2b^2}\int_0^N ds\ \left(\frac{\partial \mathbf{R}(s)}{\partial s}\right)^2$$

Elastic entropy following Gaussian statistics

$$\beta E_{attr} = \frac{\chi}{\nu}\int d\mathbf{r}\ \hat{\phi}_p(\mathbf{r})\hat{\phi}_s(\mathbf{r})$$

Flory-Huggins short-range interactions

$$\beta E_{elec} = \frac{\beta e^2}{2}\int d\mathbf{r}\ d\mathbf{r}'\ \hat{\rho}_e(\mathbf{r})\ C(\mathbf{r},\mathbf{r}')\ \hat{\rho}_e(\mathbf{r}')$$

Electrostatic correlations

$$\beta E_{repel} = -\ln\left\{\delta[\hat{\phi}_p(\mathbf{r}) + \hat{\phi}_s(\mathbf{r}) - 1]\right\}$$

Local incompressibility

$$= \sum_{N_s,\pm=0}^{\infty} \frac{e^{\beta\mu_s N_s} e^{\beta\mu_\pm N_\pm}}{N_s!\ \nu^{N+1+N_s} N_\pm!\ \nu_\pm^{N_\pm}} \int \mathcal{D}\mathbf{R} \int \prod_{\beta=1}^{N_s} d\mathbf{r}_\beta \int \prod_{\gamma,\kappa=1}^{N_+,N_-} d\mathbf{r}_{\gamma,\kappa}\ \exp\left\{-\left[\frac{3}{2b^2}\int_0^N ds\ \left(\frac{\partial \mathbf{R}(s)}{\partial s}\right)^2 + \frac{\chi}{\nu}\int d\mathbf{r}\ \hat{\phi}_p\hat{\phi}_s - \ln\left\{\delta[\hat{\phi}_p(\mathbf{r}) + \hat{\phi}_s(\mathbf{r}) - 1]\right\} + \frac{\beta e^2}{2}\int d\mathbf{r}\ d\mathbf{r}'\ \hat{\rho}_e\ C(\mathbf{r},\mathbf{r}')\ \hat{\rho}_e\right]\right\},$$

Free Energy and SCF Equations

[Supp]

$Q_p := \nu^{-1} \int \mathrm{dz}\ q_c(\mathrm{z};\mathrm{s}) q(\mathrm{z};\mathrm{s}) \quad \forall s, \quad Q_s := \nu^{-1} \int \mathrm{dz}\ \exp(-w_s), \quad \rho_\pm := \exp\left(\beta\mu_\pm \nu_\pm^{-1} \mp Z_\pm i\psi\right)$

Free Energy (ensemble average across surface)

$$\langle F \rangle_{x,y} = -\sigma \ln Q_p - \exp(\beta\mu_s) Q_s + \frac{1}{\nu} \int \mathrm{dz}\ \chi\phi_p\phi_s - w_p\phi_p - w_s\phi_s - \eta(\phi_p + \phi_s - 1) + \int \mathrm{dz}\ \left[-\frac{\epsilon}{2}|\nabla\psi|^2 + \frac{Z_p\psi}{\nu}\alpha\phi_p - \rho_+ - \rho_- \right]$$

Functional Minimization $\quad \frac{DF}{Dw_\gamma} = 0$

Polymer Density: $\quad \phi_p = \frac{\sigma}{Q_p} \int_0^N \mathrm{ds}\ q_c(\mathrm{z};\mathrm{s}) q(\mathrm{z};\mathrm{s})$

Polymer-controlling Field: $\quad w_p = \chi\phi_s - \alpha\psi - \frac{\partial\epsilon}{\partial\phi_p}\frac{|\nabla\psi|^2}{2}\nu - \eta$

Solvent Density: $\quad \phi_s = e^{\beta\mu_s} \exp(-w_s)$

Solvent-controlling Field: $\quad w_s = \chi\phi_p - \eta$

Incompressibility: $\quad 0 = \phi_p + \phi_s - 1$

Monomer Probability: $\quad \left(\frac{\partial}{\partial s} - \frac{b^2}{6}\nabla^2 + w_p(\mathrm{z}) \right) q(\mathrm{z};\mathrm{s}) = 0$

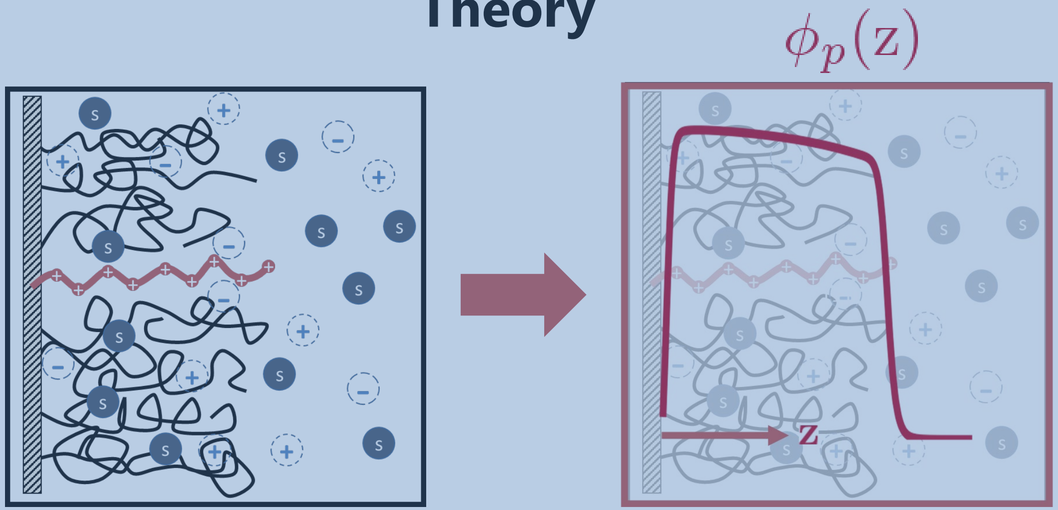
$$\begin{cases} q(\mathrm{z}=0;\mathrm{s}) = 0 \\ q(\mathrm{z}\to\infty;\mathrm{s}) = 0 \\ \begin{cases} q(\mathrm{z};\mathrm{s}=0) = \delta(z-\epsilon), \quad \epsilon \to 0 \\ q_c(\mathrm{z};\mathrm{s}=N) = 1 \end{cases} \end{cases}$$

Electrostatic Potential: $\quad \frac{d}{dz}\left(\epsilon \frac{d}{dz}\psi\right) = \pm\frac{Z_\pm}{\nu}\exp\left(\beta\mu_\pm \mp Z_\pm\psi\right) + \frac{Z_p}{\nu}\alpha\phi_p$

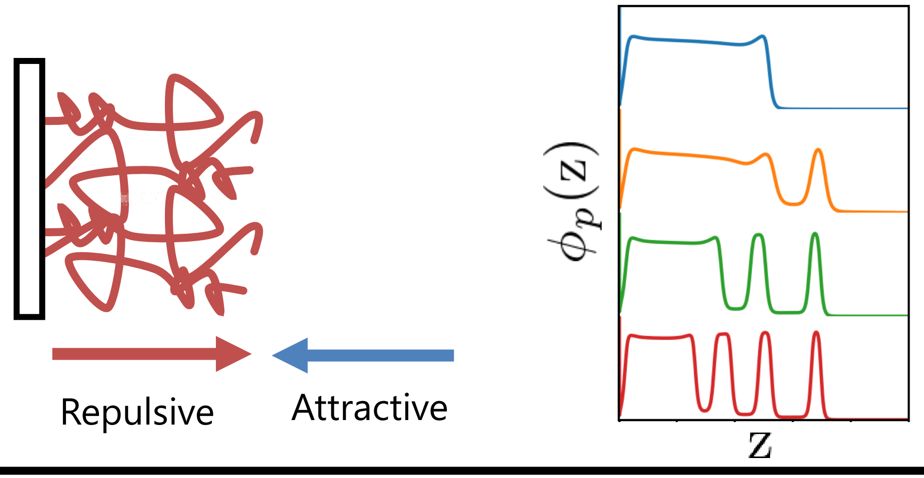
$$\begin{cases} \psi(z\to\infty) = 0 \\ \left.\frac{d\psi}{\mathrm{dz}}\right|_{\mathrm{z}=0} = \sigma_s \end{cases}$$

Presentation Overview

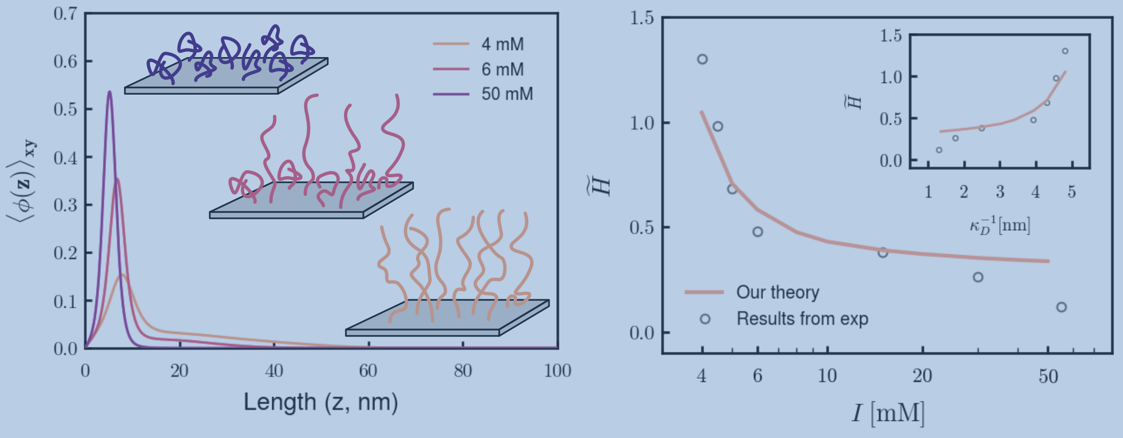
Theory



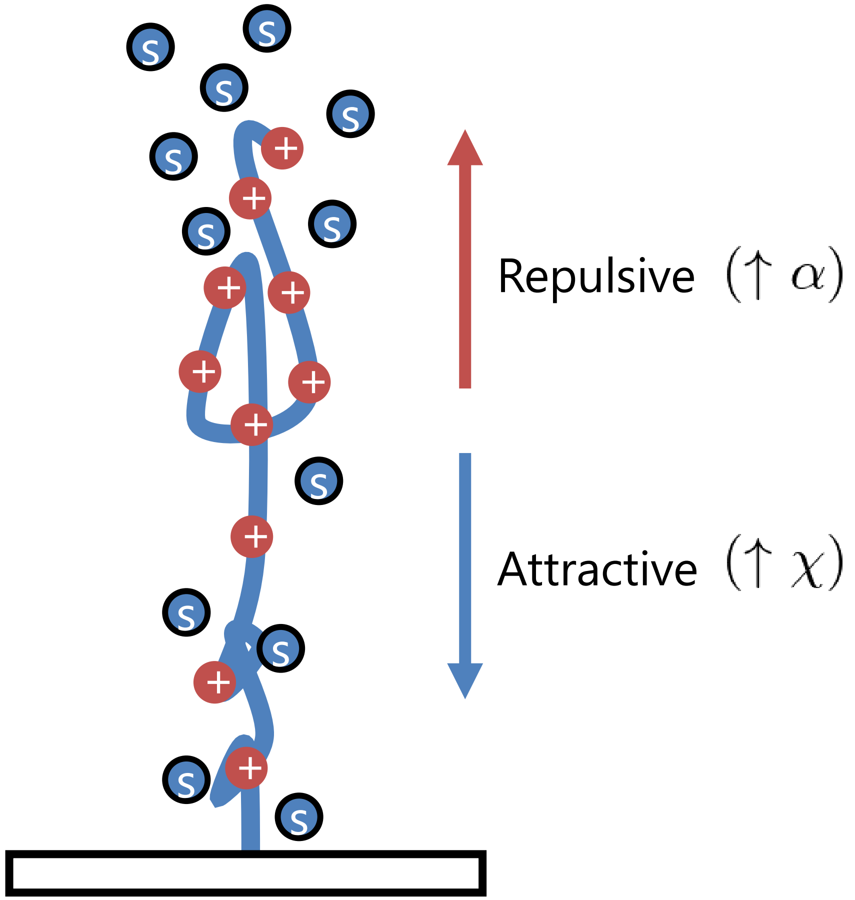
Systematic Study



Application to Experiments



Number of layers tunable with polymer charge fraction



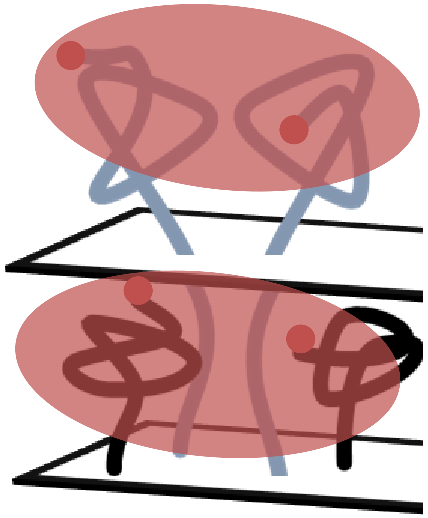
ϕ_p Vol. fraction

α Smeared charge

χ Flory-Huggins

Chain organization within brush is deducible by SCFT

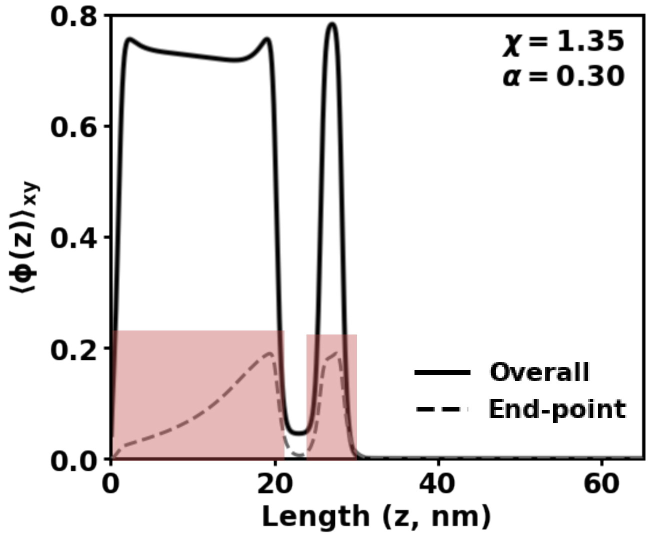
Two candidates with identical *averaged* density profiles



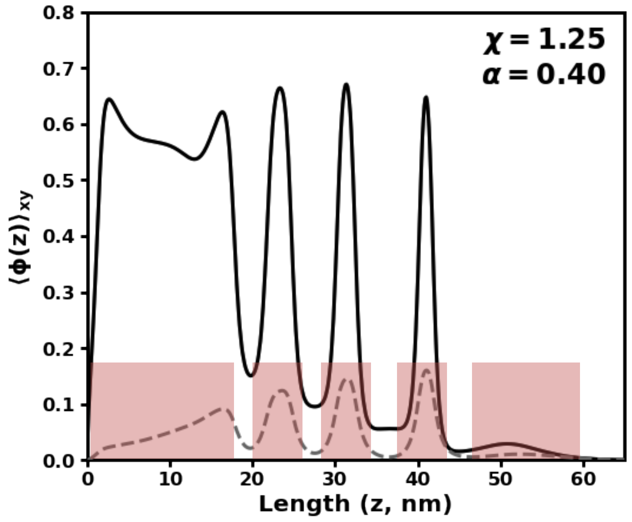
"Locked-in-layer"

"Locked-in-layer" minimizes elastic penalty with mushroom conformations

Energetic cost of segregation scales with the "stem" traversing layers



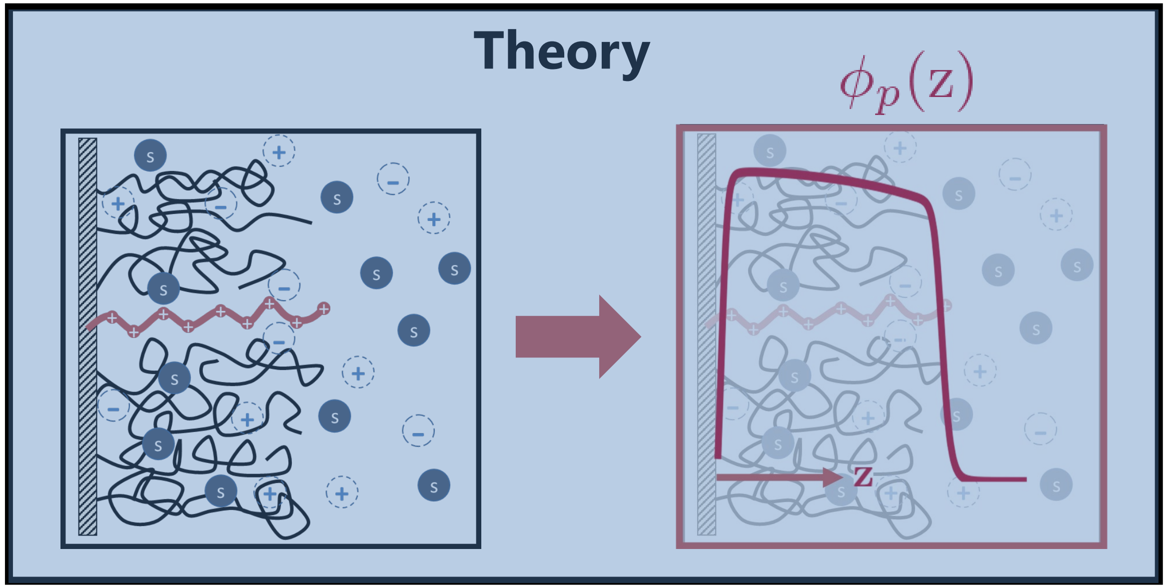
2 condensed

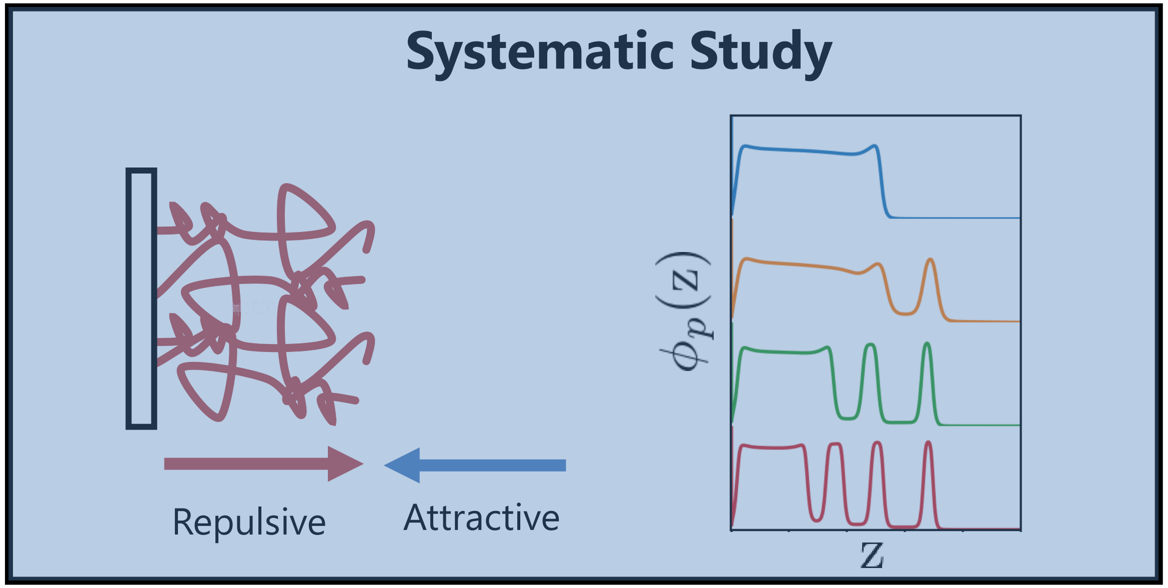


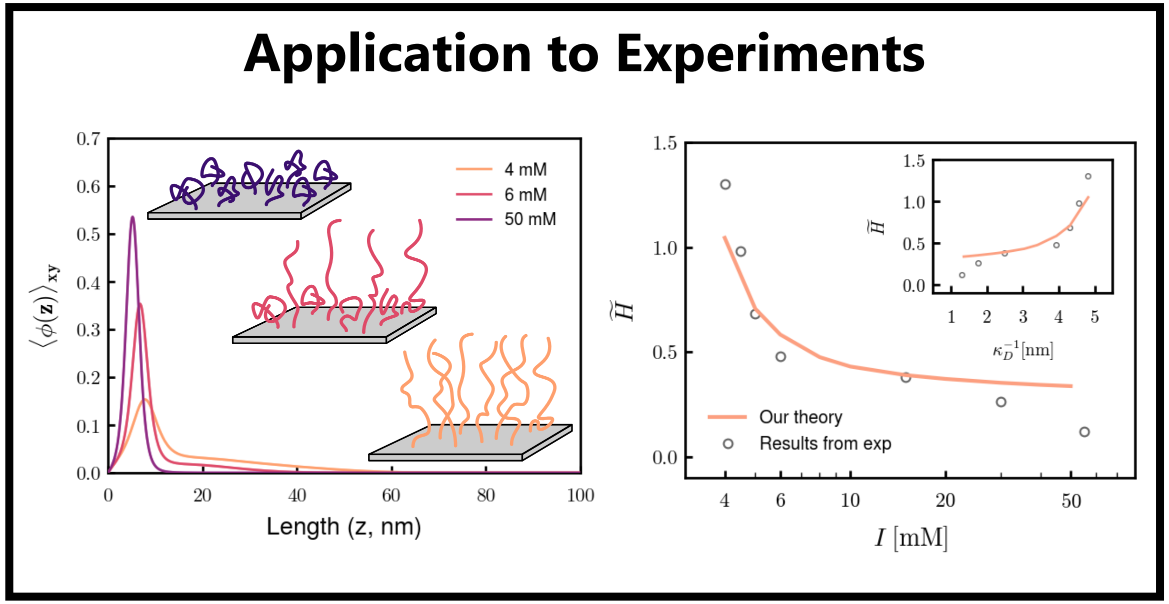
4 condensed + 1 dilute

(Endpoint densities x 30)

Presentation Overview







Framework provides structural and mechanistic information for an IDP-derived brush

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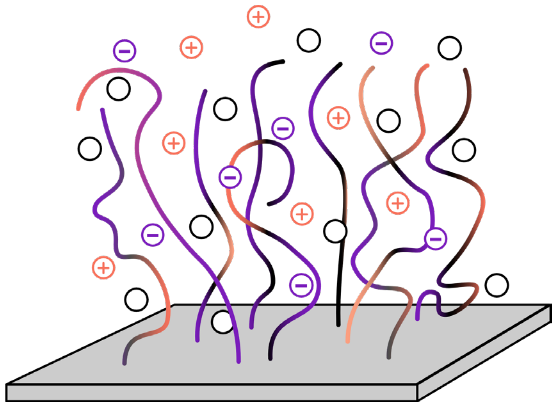
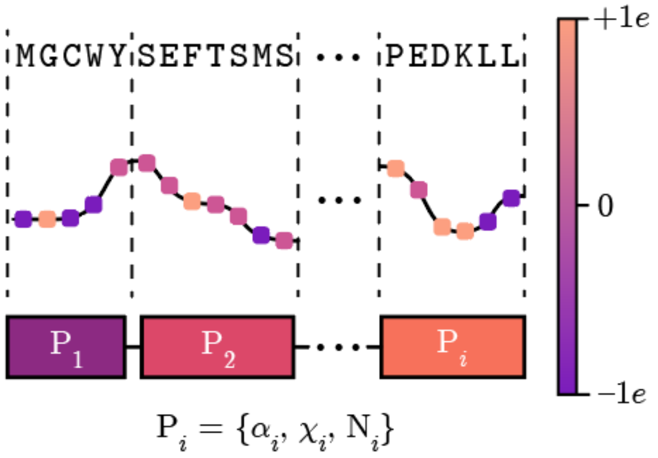
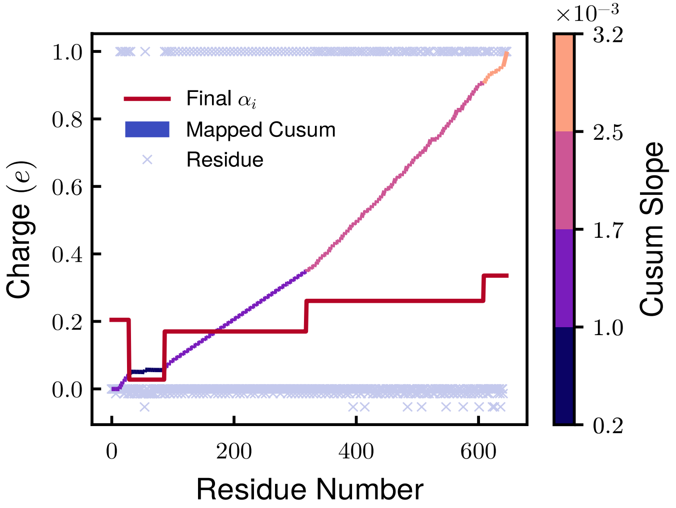
Neurofilament Heavy (NFH) chain

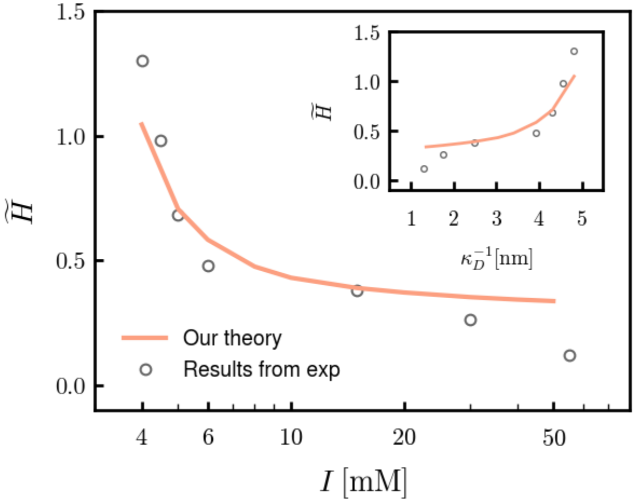


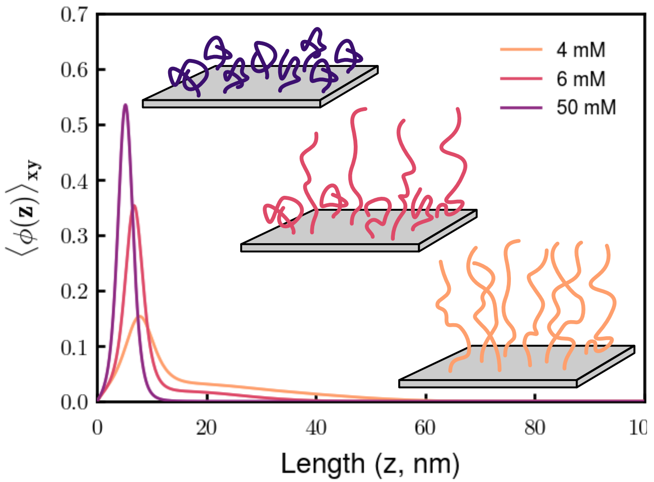
Coarse-graining



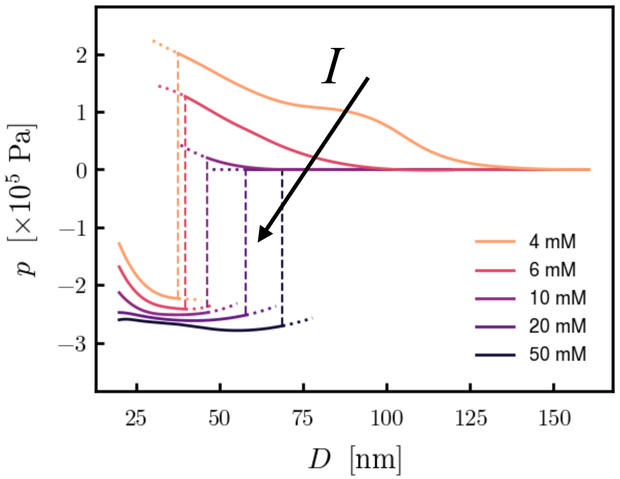


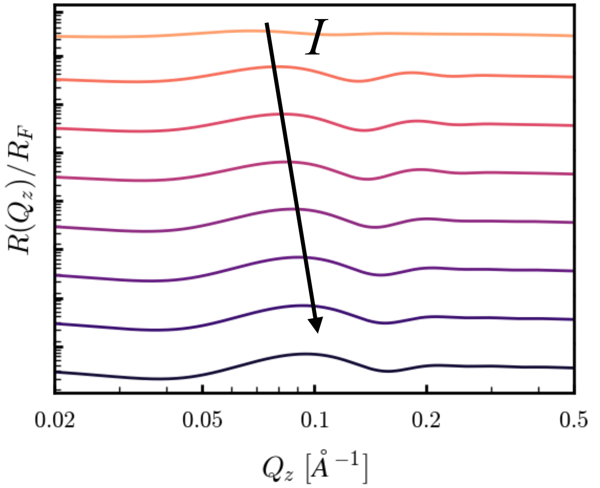
Experimental Comparison





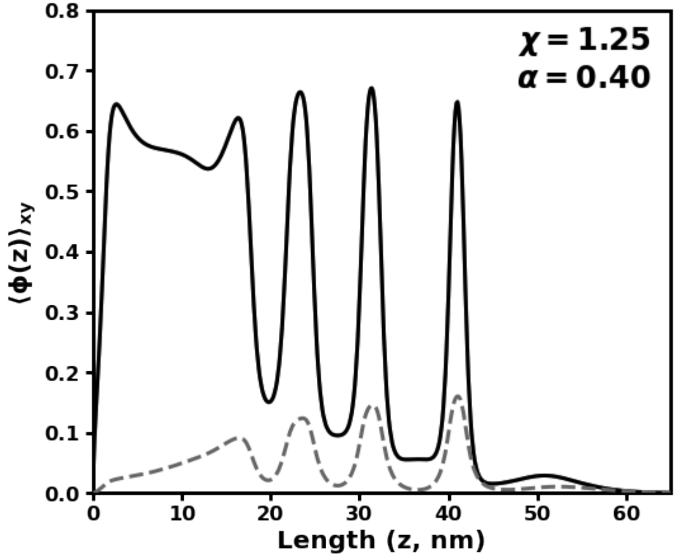
Beyond Experiments

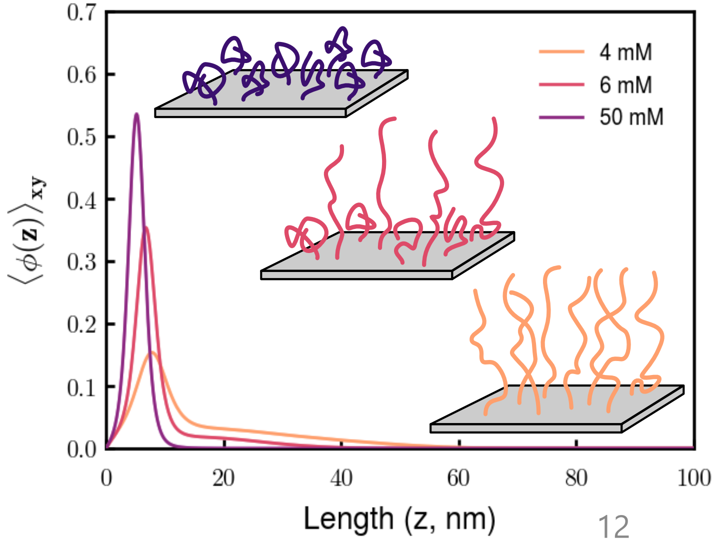




Conclusions

- SCFT accurately describes the coupled interactions within PEBs and provides experimentally inaccessible information
- High charge fraction facilitates microphase segregation in PEBs
  - Each layer as subsequent mushroom conformations ("locked-in-layer" model)
- IDP brush derived from NFH is well-described by our model
  - Polymer density profiles
  - Predicted characterization spectra
    - Reflectivity and brush-brush force





Acknowledgements

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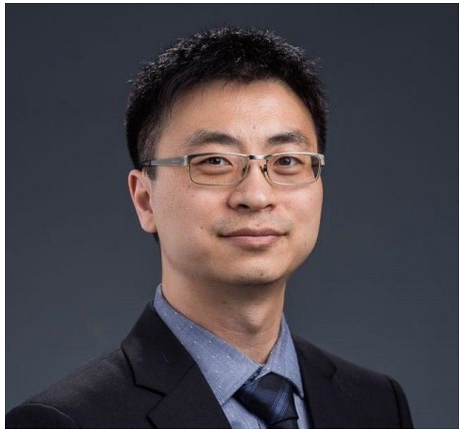
  - Luofu Liu
  - Dr. Chao Fang
  - Ian Woolsey



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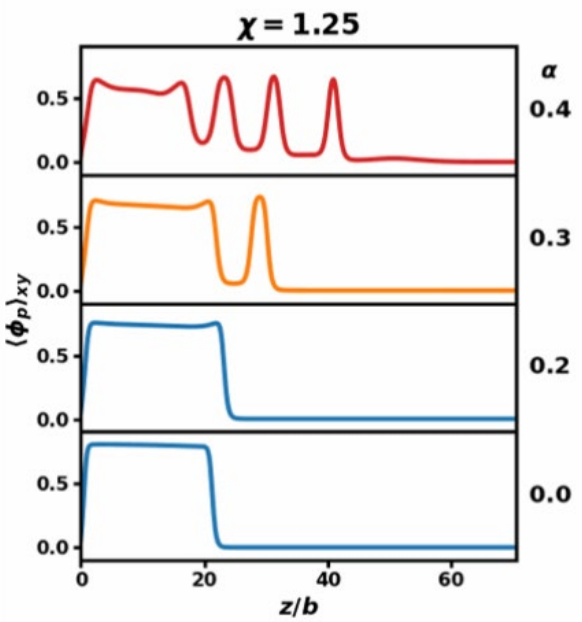
Thank you!



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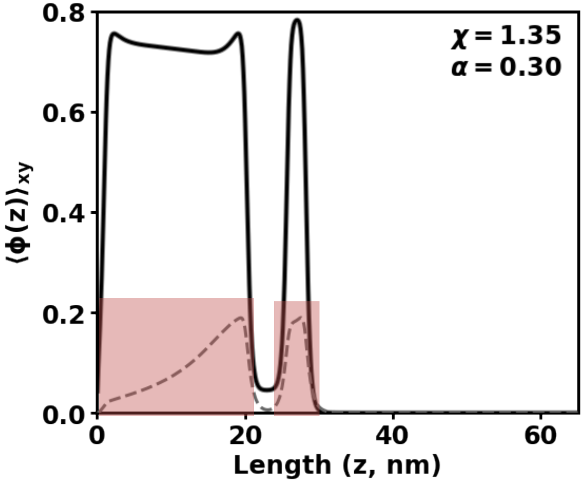
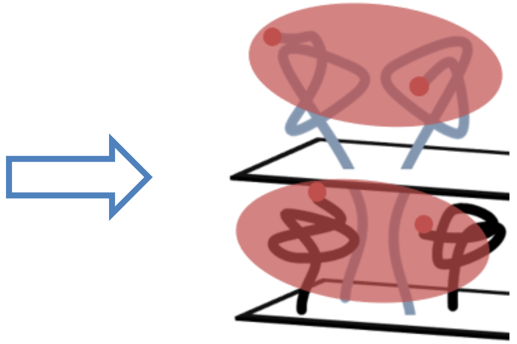
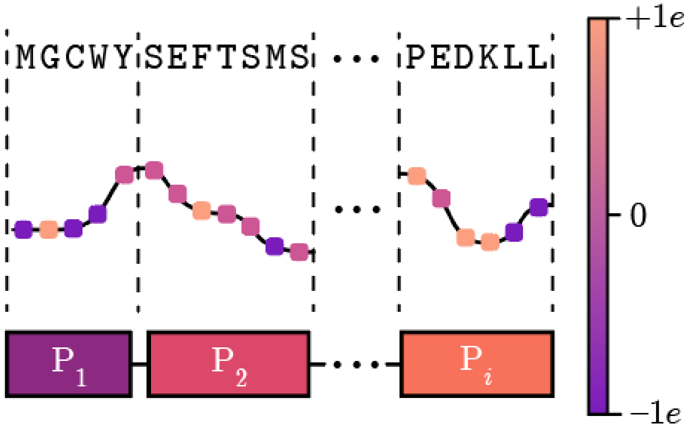


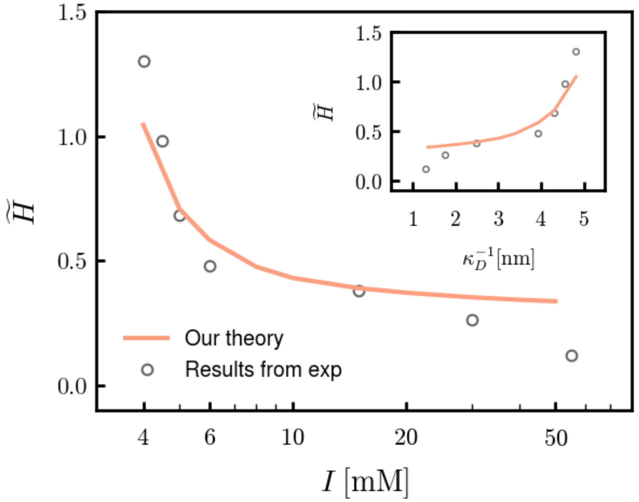


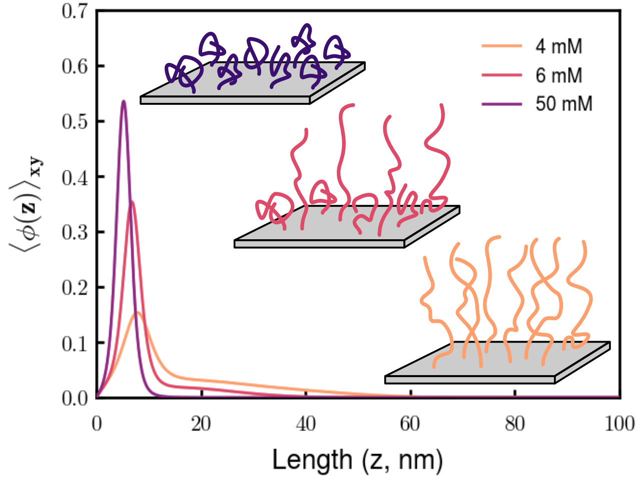
"Locked-in-layer"

Application to IDP



$P_i = \{\alpha_i, \chi_i, N_i\}$





Supplemental Slides

- Full partition function
- NFH pressure dilute-coex transition mechanism
- NFH coarse-graining parameters (and H formula)
- Henderson-Hasselbalch
- SCFT Flowchart
- Reflectivity master equation
- Block-polymer SCFT equations

Full Partition Function

$$\Xi = \int \hat{\mathrm{D}}\boldsymbol{\Gamma} \ \exp\left[-\beta(E_{elas} + E_{attr} + E_{rep} + E_{elec}) \right]$$

(Subscripts) s : Solvent; p : Polymer; e : Charged

(Indices) β : Solvent; γ : Cation; κ : Anion

$$\beta E_{elas} = \frac{3}{2b^2}\int_0^N ds \left(\frac{\partial \mathbf{R}(s)}{\partial s}\right)^2$$

Elastic entropy following Gaussian statistics

$$\beta E_{attr} = \frac{\chi}{\nu}\int d\mathbf{r} \ \hat{\phi}_p(\mathbf{r})\hat{\phi}_s(\mathbf{r})$$

Flory-Huggins short-range interactions

$$\beta E_{elec} = \frac{\beta e^2}{2}\int d\mathbf{r} \ d\mathbf{r}' \ \hat{\rho}_e(\mathbf{r}) \ C(\mathbf{r},\mathbf{r}') \ \hat{\rho}_e(\mathbf{r}')$$

Electrostatic correlations

$$\beta E_{repel} = -\ln\{\delta[\hat{\phi}_p(\mathbf{r}) + \hat{\phi}_s(\mathbf{r}) - 1]\}$$

Local incompressibility

Particle Operators

$$\hat{\phi}_s := \nu_s \sum_{\beta=1}^{N_s} \delta(\mathbf{r} - \mathbf{r}_\beta)$$

$$\hat{\phi}_p := \nu_p \int_0^N ds \ \delta(\mathbf{r} - \mathbf{R}(s))$$

$$\hat{\rho}_e := \pm Z_\pm \sum_{\gamma,\kappa=1}^{N_\pm} \delta(\mathbf{r} - \mathbf{r}_{\gamma,\kappa}) + \frac{\alpha Z_p}{\nu}\hat{\phi}_p$$

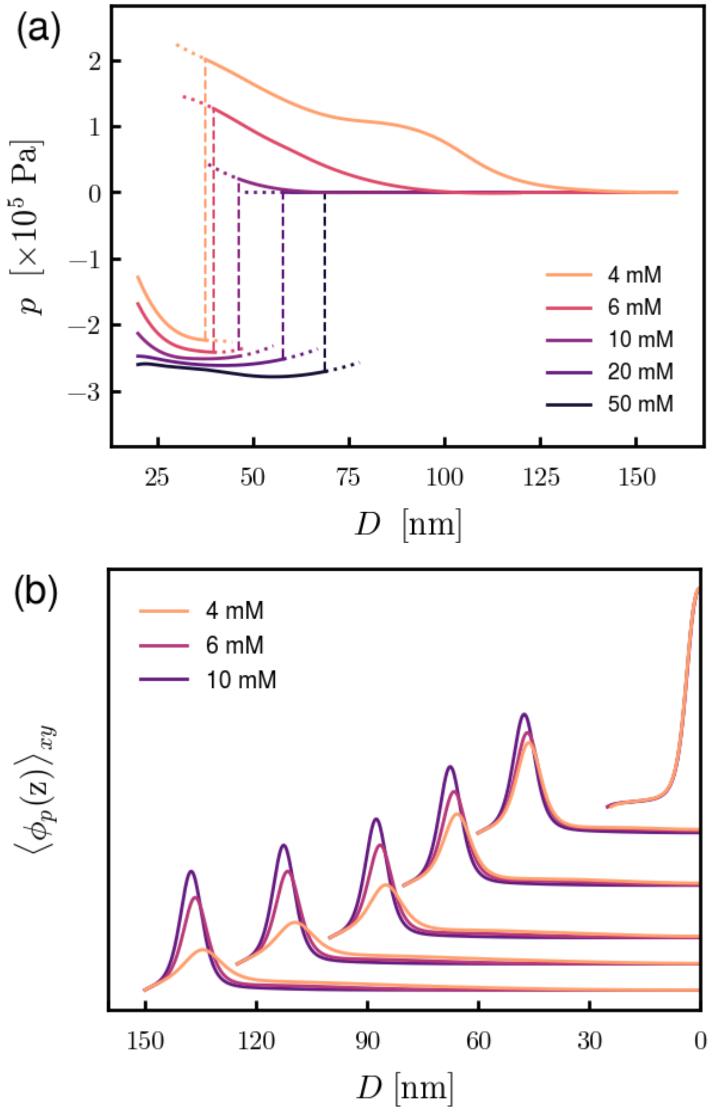
Coulomb Operator

$$-\nabla\cdot\left[\epsilon(\mathbf{r})\nabla C(\mathbf{r},\mathbf{r}')\right] := \delta(\mathbf{r}-\mathbf{r}')$$

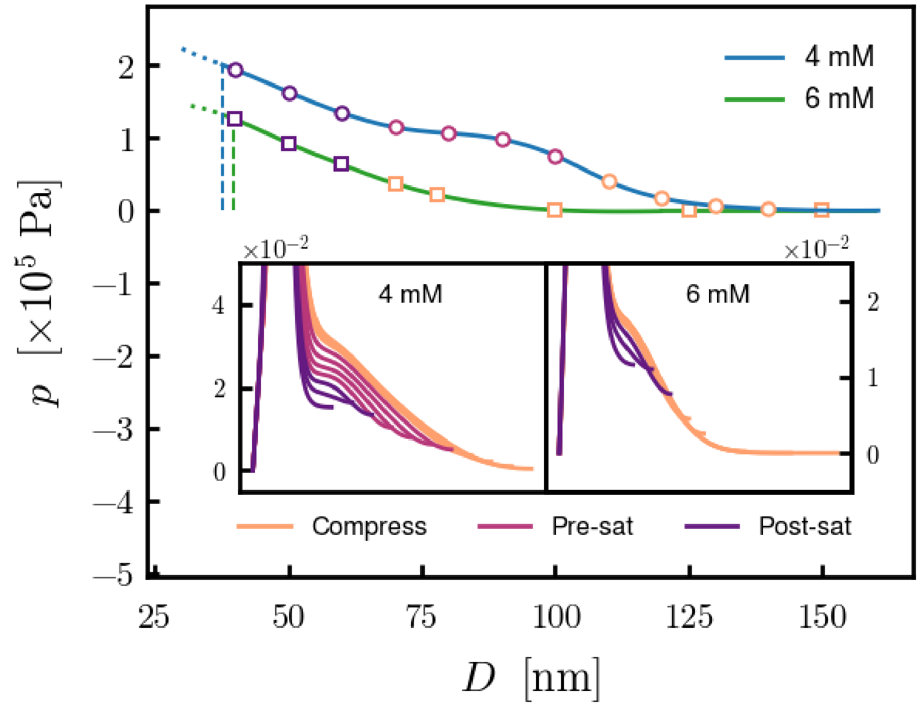
$$= \sum_{N_s,\pm=0}^{\infty} \underbrace{\frac{e^{\beta\mu_s N_s} e^{\beta\mu_\pm N_\pm}}{N_s! \ \nu^{N+1+N_s} N_\pm! \ \nu_\pm^{N\pm}}}_{\text{Semicanonical Ensemble}} \int \mathcal{D}\mathbf{R} \int \prod_{\beta=1}^{N_s} d\mathbf{r}_\beta \int \prod_{\gamma,\kappa=1}^{N_+,N_-} d\mathbf{r}_{\gamma,\kappa} \ \exp\left\{ -\left[\frac{3}{2b^2}\int_0^N ds \left(\frac{\partial \mathbf{R}(s)}{\partial s}\right)^2 \right.\right.$$

$$\left.\left. + \frac{\chi}{\nu}\int d\mathbf{r} \ \hat{\phi}_p\hat{\phi}_s - \ln\{\delta[\hat{\phi}_p(\mathbf{r}) + \hat{\phi}_s(\mathbf{r}) - 1]\} + \frac{\beta e^2}{2}\int d\mathbf{r} \ d\mathbf{r}' \ \hat{\rho}_e \ C(\mathbf{r},\mathbf{r}') \ \hat{\rho}_e \right]\right\} \ ,$$

NFH pressure dilute-coex transition



4 mM vs. 6 mM mechanisms



NFH Coarse-graining parameters

Table 1: NFH Charge and Hydrophobicity Distribution

Block	Residues	α_i	χ_i
1	[0, 28]	0.204967	1.586207
2	[29, 87]	0.027801	1.434483
3	[88, 319]	0.170493	2.113793
4	[320, 609]	0.261110	1.534483
5	[610, 647]	0.336030	0.989474

Vol. frac to height

$$\widetilde{H} = \frac{2\int_0^\infty \mathrm{dz}\ \phi_p z}{H^* \int_0^\infty \mathrm{dz}\ \phi_p},$$

Kuhn's length and monomer volume:

- b = 3.00 nm
- v = 1.30 nm^3

Henderson-Hasselbalch

AA	pKa	pKb
D (Aspartic Acid)	3.65	
E (Glutamic Acid)	4.25	
K (Lysine)		10.53
R (Arginine)		12.48
H (Histidine)		6.00

$$\mathrm{Kb} = \frac{[\mathrm{HB}][\mathrm{OH}^-]}{[\mathrm{B}^-]} \qquad \mathrm{Ka} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$\mathrm{pH} - \mathrm{pKa} = \log_{10} \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$14 = \mathrm{pH} + \mathrm{pOH}$$

$$\alpha = -\frac{[\mathrm{A}^-]}{[\mathrm{A}^-] + [\mathrm{HA}]} = -\frac{1}{1 + [\mathrm{HA}]/[\mathrm{A}^-]}$$

SCFT Build-up — Flowchart

PDE Solve (for iteration k)

$$\left(\frac{\partial}{\partial s} - \frac{b^2}{6}\nabla^2 + w_p^{\mathbf{k-1}}\right)\underline{q(z;s)}^{\mathbf{k}} = 0$$

$$-\nabla\cdot(\epsilon\underline{\nabla\psi}^{\mathbf{k}}) = Z_+\underline{\rho_+}^{\mathbf{k}} - Z_-\underline{\rho_-}^{\mathbf{k}} + \frac{Z_p}{\nu}\sum_{i=1}^{K}\alpha_i\phi_i^{\mathbf{k-1}}$$

Propagate (using PDE solutions)

$$\phi_i = \frac{\sigma}{Q_p}\int_{N_{i-1}}^{N_i} \mathrm{ds}\; \underline{q_c(z;s)}\,\underline{q(z;s)} \quad \forall i \in [1, K]$$

$$w_s = \sum_{i=1}^{K}\chi_i\phi_i - \eta$$

$$\phi_s = e^{\beta\mu_s}\exp(-w_s)$$

$$w_i = \chi_i\phi_s - \alpha_i\underline{\psi} - \frac{\partial\epsilon}{\partial\phi_p}\underline{\frac{|\nabla\psi|^2}{2}}\nu - \eta \quad \forall i \in [1, K]$$

Check (for self-consistency)

$$\max_{j\in[1\ldots N_z]}\left(\sum_{i=1}^{K}\phi_i(j) - \phi_s(j) - 1\right) < \text{Thresh}$$

$$\left[\sum_{\gamma}(w_\gamma^{\mathbf{k}} - w_\gamma^{\mathbf{k-1}})^2 \Big/ \sum_{\gamma}(w_\gamma^{\mathbf{k}})^2\right] < \text{Thresh}$$

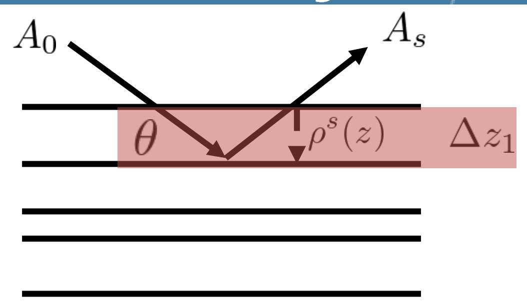
Update (if not satisfied)

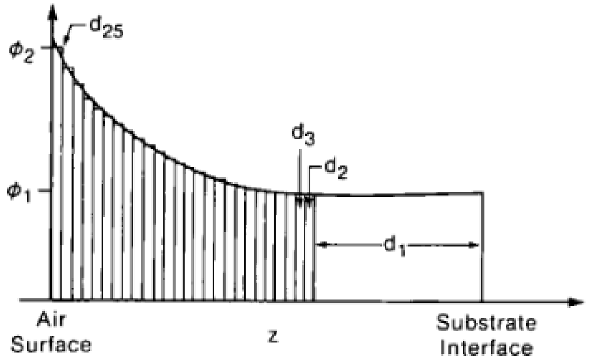
Anderson Mixing $\quad w_\gamma^{\mathbf{k+1}} = f(w_\gamma^{\mathbf{k}}, w_\gamma^{\mathbf{k-1}})$

Simple Mixing $\quad w_\gamma^{\mathbf{k+1}} = f(w_\gamma^{\mathbf{k}}, F^{\mathbf{k}}, \phi_p^{\mathbf{k}}, \phi_s^{\mathbf{k}}, F^{\mathbf{k-1}})$

Notation slightly incorrect but changed for clarity. w^{k} = f(w^{k+1/2}, w^{k-1}), where w^{k+1/2} is from SCFT calculations (\phi remains ^{k})

Reflectivity Master Equation Derivation





A_s	Scattered amplitude
A_0	Incident amplitude
λ	Wavelength
$\rho^s(z)$	Scattering density proflile
θ	Incident angle
$k_{z,0}$	Scattering vector

$$\frac{A_s}{A_0} = C\frac{\lambda\rho^s(z)\,\Delta z}{\sin\theta} = C\frac{4\pi}{k_{z,0}}\rho^s(z)\,\Delta z.$$

"missing" length dimension

C =i ; from integration over all area elements at z

Continuous density profile (Reimann sum analogue)

$$R(k_{z,0}) = \left|\frac{4\pi i\bar{\rho}^s}{k_{z,0}}\int \rho(z)\,\underline{\exp(2ik_{z,0}z)}\,dz\right|^2.$$

Phase factor for interference: $r = r_{0,1} + r_{1,2}e^{iq_{z,1}d_1} + r_{2,3}e^{i(q_{z,1}d_1+q_{z,2}d_2)} + \dots$

Integration by parts

$$R(k_{z,0}) = \frac{(4\pi\bar{\rho}^s)^2}{k_{z,0}^4}\left|\int \rho'(z)\exp(2ik_{z,0}z)\,dz\right|^2,$$

Qz notation, non-normalized density, Fresnel reflectivity

$$R(Q_z) = R_F\left|\frac{1}{\rho_e(z\rightarrow\infty)}\int dz\,\frac{d\rho_e}{dz}\exp(iQ_z z)\right|^2$$

Block copolymer PDEs

- Mean-field Poisson-Boltzmann Equation

$$-\frac{d}{dz}\left(\epsilon\frac{d}{dz}\psi\right) = Z_+\rho_+ - Z_-\rho_- + \frac{Z_p}{\nu}\sum_{i=1}^{K}\alpha_i\phi_i$$

$$\begin{cases} \psi(z \to \infty) = 0 \\ \left.\dfrac{d\psi}{dz}\right|_{z=0} = 0 \end{cases}$$

- Modified Diffusion Equation

$$\left(\frac{\partial}{\partial s} - \frac{b^2}{6}\nabla^2 + w_p(z)\right) q(z;s) = 0\,,$$

$$\text{where } w_p(z) = \begin{cases} w_1(z) & \text{for } s = [0, N_1] \\ \vdots & \\ w_K(z) & \text{for } s = [N_{K-1}, N_K] \end{cases}$$

$$\begin{cases} q(z = 0; s) = 0 \\ q(z \to \infty; s) = 0 \\ q(z; s = 0) = \delta(z - \epsilon), \quad \epsilon \to 0 \end{cases}$$