Bifurcation of Polyelectrolyte Brushes Subject to Normal Electric Fields

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CAP
May 31, 2013

Stimuli-Responsive MEMS Components

"Smart" Surfaces

- Biology abounds with mesoscopic systems that dynamically and reversably respond to environmental cues

Schematic of biological and synthetic, mechanically triggered stimuli-responsive surfaces
Credit: Wilhelm Huck, Melville Laboratory for Polymer Synthesis

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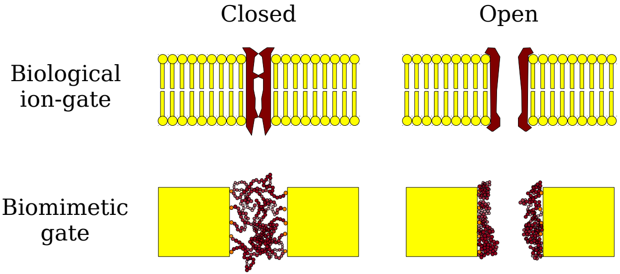
- If structures change radically with environment they can be engineered into
  - detectors
  - *gates*



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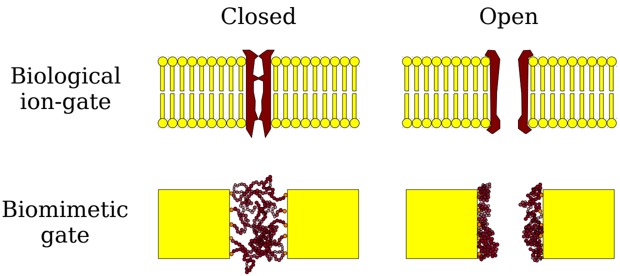

Schematic of biological and synthetic, mechanically triggered stimuli-responsive surfaces
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Charged Soft Matter as "Smart" Surfaces

Polyelectrolyte Brushes

- Different than neutral brush due to *chain-counterion complex* nature
- f is charge fraction of chain, z valency, N number of segments, H brush height, T counterion cloud thickness and Σ normalized grafting density

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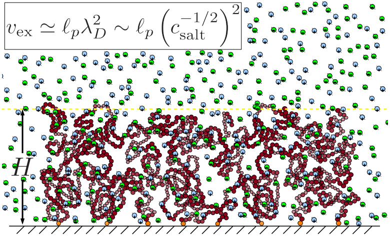
High Salt Brush

- Salt screens electrostatics so brush is effectively electro-*neutral*
  - Screening inverse to salt concentration
  - $H \sim N$
  - $H \sim \Sigma^{1/3}$



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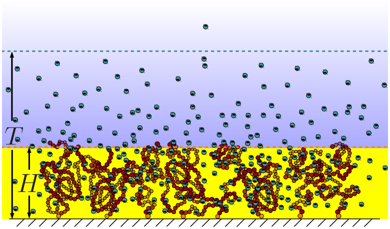
Pincus Brush (weakly charged)

- Brush is like a *thin charged film* and counterion cloud is attracted to it
  - $T \sim [\Sigma N]^{-1}$
  - $H \sim N^3$ — strong dependence
  - $H \sim \Sigma$



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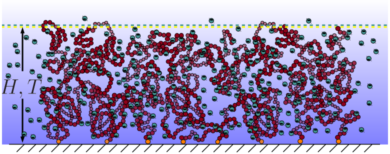
Osmotic Brush (highly charged)

- Counterions are pulled into brush (polyelectrolyte / counterion complex)
  - $T \approx H$
  - $H \sim N$
  - *H does not have Σ dependence*



Charged Soft Matter as "Smart" Surfaces
Polyelectrolyte Brushes

Osmotic Brushes as "Smart" Surfaces

- Ideal as stimuli-responsive surfaces because structure is *hyper-dependent* on environmental cues
- Favourable because form electroneutral films when unperturbed
- Easy, reproducible control over switching:
    - temperature
    - pH
    - salt

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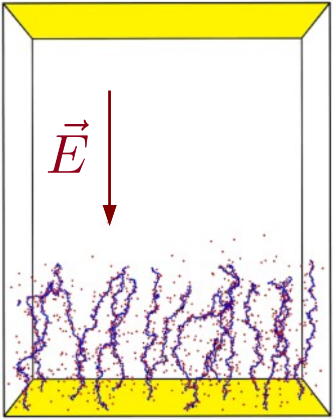
Polyelectrolyte Brushes

Osmotic Brushes as "Smart" Surfaces

- Ideal as stimuli-responsive surfaces because structure is *hyper-dependent* on environmental cues
- Favourable because form electroneutral films when unperturbed
- Easy, reproducible and *fast* control over switching:
  - temperature
  - pH
  - salt
  - *electric fields*

Langevin Dynamics

Simulations of Polyelectrolyte Brushes Subject to Normal Electric Fields



Modeling the separation of macromolecules: A review of current computer simulation methods. Electrophoresis, 30: 792-818, 2009.

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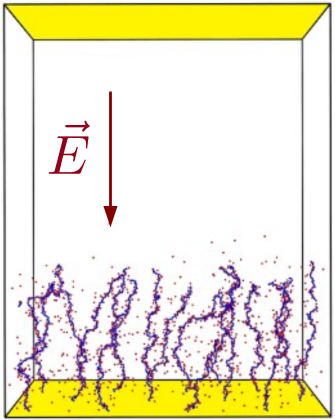


- Low Grafting Density: $\Sigma = 0.0136$
- Intermediate Grafting Density: $\Sigma = 1.11$
- High Grafting Density: $\Sigma = 11.1$

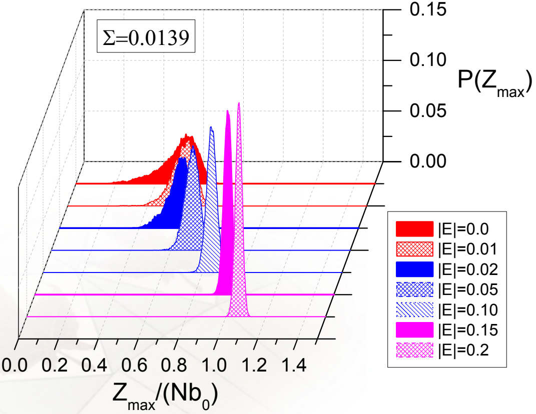
Modeling the separation of macromolecules: A review of current computer simulation methods. Electrophoresis, 30: 792-818, 2009.

Low Grafting Density

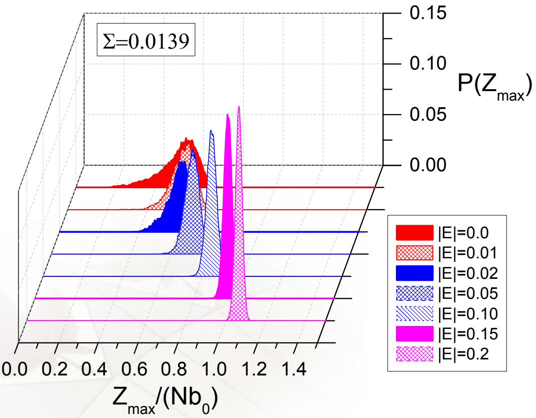
Low Grafting Density Brushes Subject to Normal Electric Fields

Low Grafting Density

Brush Height



Low Grafting Density
Brush Height

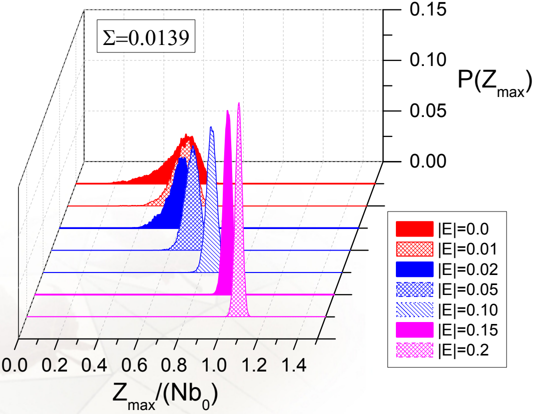


Two regimes:

- $|E| \lesssim 0.02$: Height is rather constant

Low Grafting Density

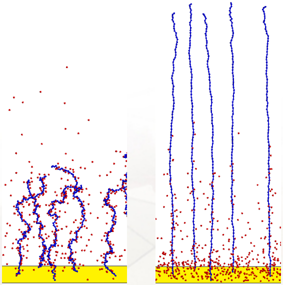
Brush Height



Two regimes:

- $|E| \lesssim 0.02$: Height is rather constant
- $|E| \gtrsim 0.02$: Height increases with increased $|E|$

Low Grafting Density
Brush Height

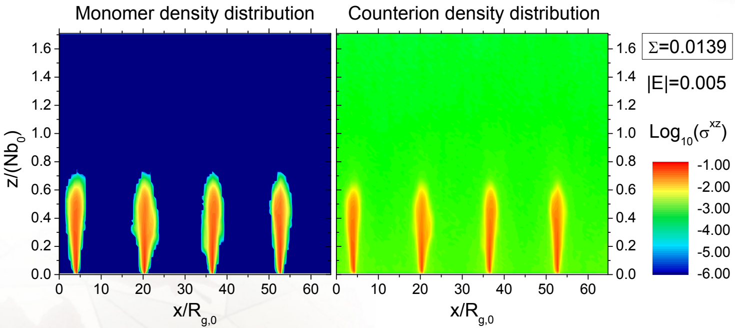


Two regimes:

- Why not a steady rise?
- What does *"critical"* $|E^*|$ arise from?

Low Grafting Density

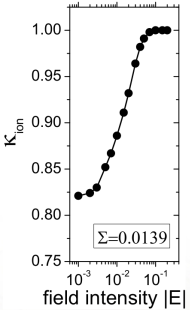
Monomer/Counterion Distributions — Low Fields



- Counterion distribution corresponds to monomer distribution
- Not perfectly electroneutral — background probability
- Low grafting density brush not quite *ideal osmotic brush*

Low Grafting Density

Counterion Confinement and Condensation



In weak field limit, 82% of counterions *confined to brush region* $(z \leq Z_{\max})$

Low Grafting Density

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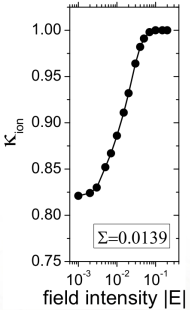
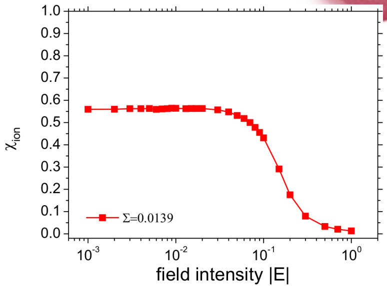
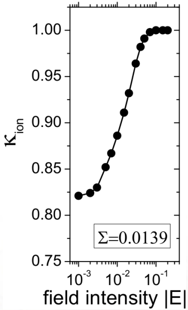


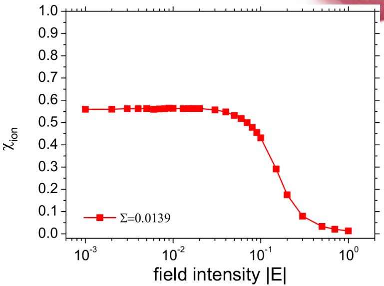


In weak field limit, 82% of counterions *confined to brush region* ($z \leq Z_{\max}$)

- 56% *condensed* (closer than λ_B to a chain)
- Manning theory for free chain predicts $\chi_{\text{ion}} = 1 - b_0/\lambda_B = 61\%$

Low Grafting Density
Counterion Confinement and Condensation





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Although not perfect, screening is effective for fields $\lesssim |E^*| \simeq 0.02$

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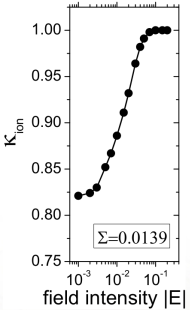

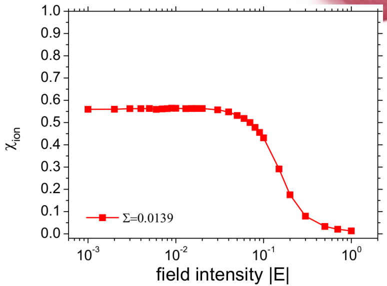

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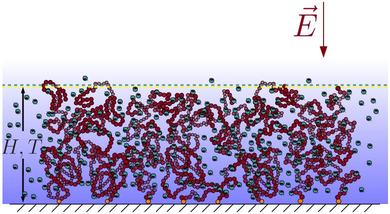
- When $|E| \ll |E^*|$, counterion and monomer distributions correspond
- When $|E| \gtrsim |E^*|$, counterions forced down thus superimposing exponential/Boltzmann distribution
- When $|E| \gg |E^*|$, positive monomers hardly perturb exponential distribution

Low Grafting Density
Critical Field

Scaling Argument

Chain stretches once energy gained by moving charge a *characteristic distance*, ℓ, is greater than $k_B T$

$$E^* e\ell \sim k_B T \qquad \rightarrow \qquad E^* \sim \frac{k_B T}{e} \frac{1}{\ell}$$



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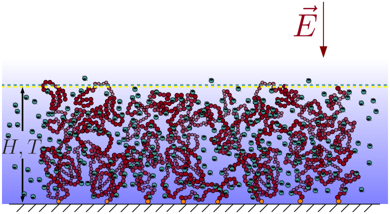

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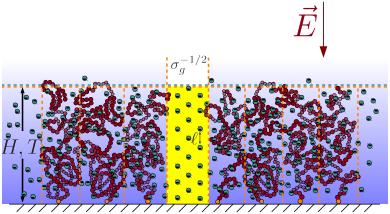
But what is the *characteristic distance*?

- In mean-field sense, ℓ is average distance between charges

$$\ell \sim \left(\frac{H\sigma_g^{-1}}{N}\right)^{1/3}$$



Low Grafting Density

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Scaling Result

$$E^* \sim \frac{k_B T}{e}\left(\frac{N\sigma_g}{H}\right)^{1/3}$$

$$\sim \Sigma^{1/3}$$

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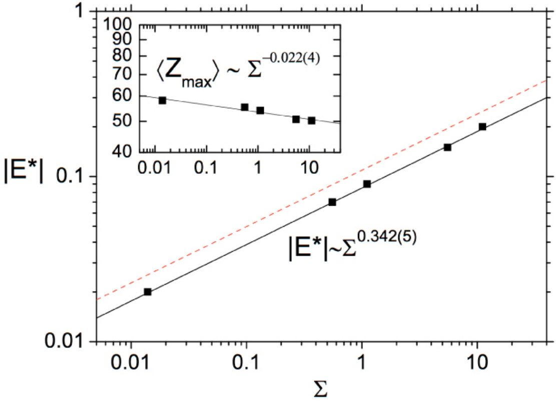

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$$E^* \sim \frac{k_B T}{e} \left(\frac{N \sigma_g}{H} \right)^{1/3}$$

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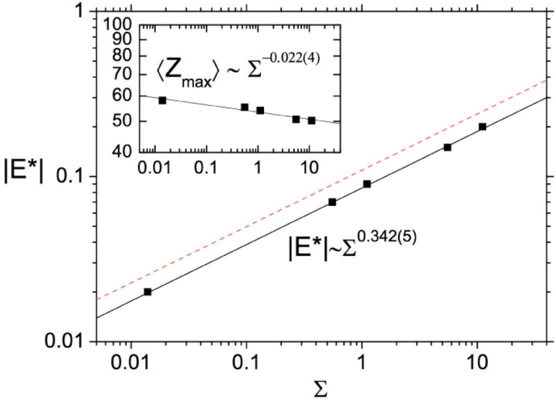
- If $H = H(\Sigma)$ (as observed) then $E^* \sim \Sigma^{0.341}$.



Low Grafting Density
Conclusion

Conclusion About Low Grafting Density:

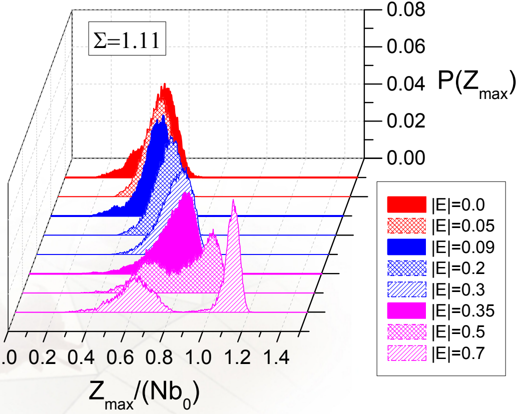
- There are two regimes:
  - $|E| < |E^*|$: brush height is constant
  - $|E| > |E^*|$: brush height increases
- $E^* \sim \Sigma^{1/3}$

Structure of polyelectrolyte brushes subject to normal electric fields.
Langmuir, 29(7): 2359-2370, 2013.

Intermediate Grafting Density

Intermediate Grafting Density Brushes Subject to Normal Electric Fields

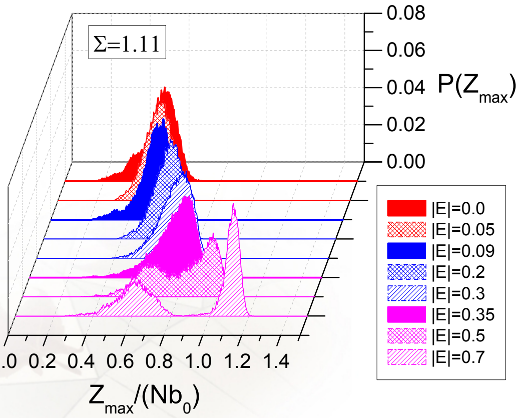
Intermediate Grafting Density
Brush Height



Three regimes:

Intermediate Grafting Density

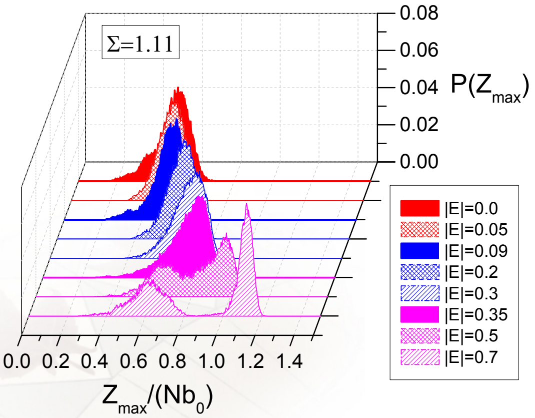
Brush Height



Three regimes:

- Height constant at low fields $|E^*| \simeq 0.09$
- Height increases at intermediate fields

Intermediate Grafting Density
Brush Height



Three regimes:

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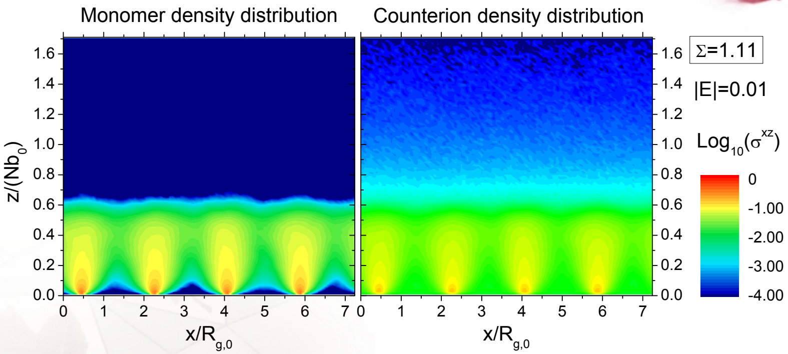
- Height increases at intermediate fields
- Splitting at *second critical field* $|E^{**}| \simeq 0.35$

Intermediate Grafting Density

Monomer/Counterion Distributions — Low Fields



- At intermediate densities brush is closer to ideally *osmotic*
- Most (97% in zero field) counterions reside within brush
- More homogeneous and effectively electroneutral

Intermediate Grafting Density

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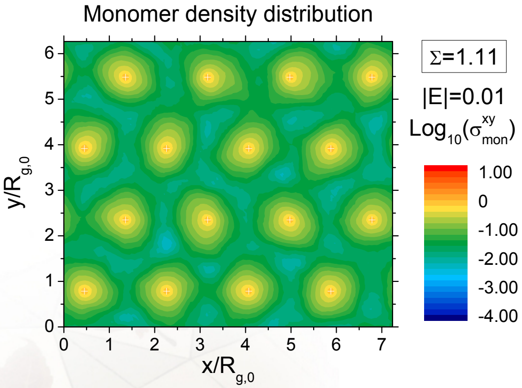

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Intermediate Grafting Density

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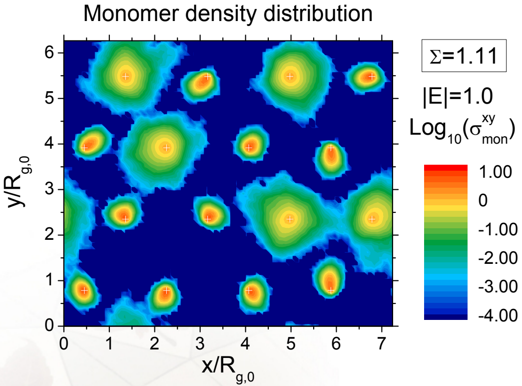

Intermediate Grafting Density

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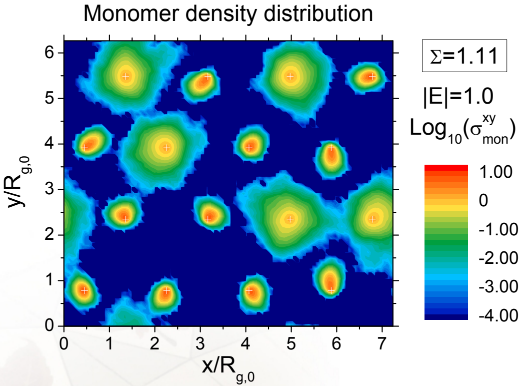
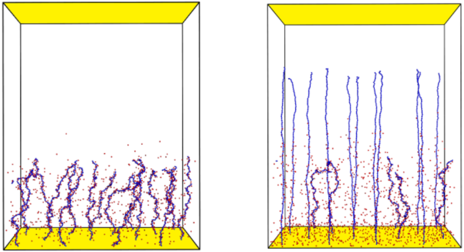


- The population bifurcates into
  - few unstretched chains
  - many highly stretched chains

Intermediate Grafting Density
Brush Height – Bifurcation

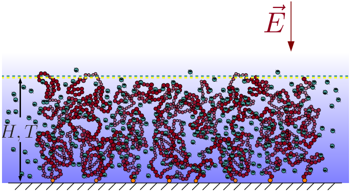


- Why does *bifurcation* occur at $|E^{**}|$?

Intermediate Grafting Density
Critical Field

Scaling Argument

Second critical field $|E^{**}|$ is the minimum for which



Intermediate Grafting Density
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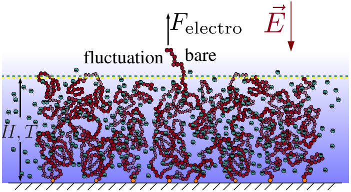
Second critical field $|E^{**}|$ is the minimum for which $F_{\mathrm{electro}} = zqE$ on segment that has fluctuated out of the protective counterion cloud

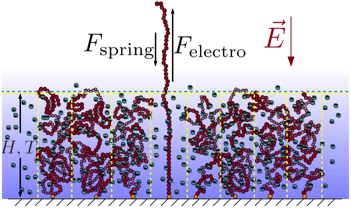


Intermediate Grafting Density

Critical Field

Scaling Argument

Second critical field $|E^{**}|$ is the minimum for which $F_{\text{electro}} = zqE$ on segment that has fluctuated out of the protective counterion cloud is greater than the elastic restoring force $F_{\text{spring}} = H/Na^2$



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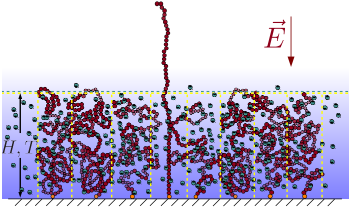
$$zqE^{**} \sim \frac{H}{Na^2}$$

$$\boxed{E^{**} \sim \frac{1}{qa}\left(\frac{f}{z^3}\right)^{1/2}} = const.$$

since $H \simeq Na\,(f/z)^{1/2}$ in an osmotic brush.



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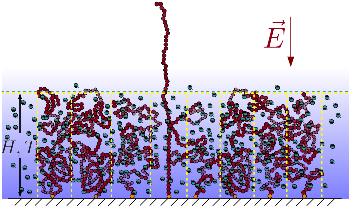


since $H \simeq Na\,(f/z)^{1/2}$ in an osmotic brush.

- E^{**} is not predicted to scale with Σ, nor N

Intermediate Grafting Density
Conclusion

Conclusion About Intermediate Grafting Density:

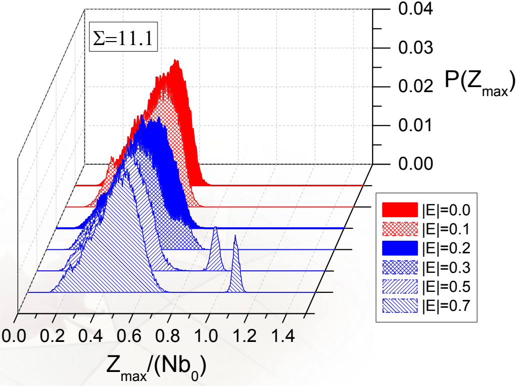
- There are three regimes:
  - $|E^{*}| < |E|$: brush height is constant
  - $|E^{*}| < |E| < |E^{**}|$: brush height increases
  - $|E^{**}| < |E|$: brush *bifurcates*
- $|E^{**}| \sim \Sigma^{0}$

High Grafting Density

High Grafting Density Brushes Subject to Normal Electric Fields

High Grafting Density

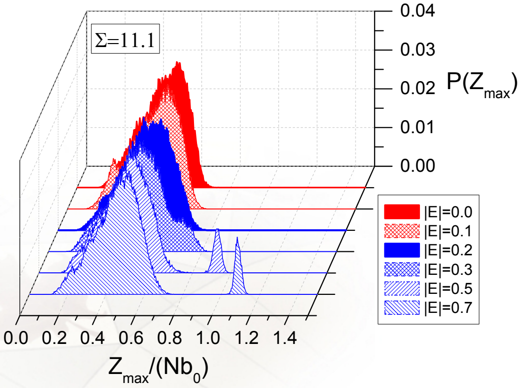
Immediate Bifurcation



Bifurcates but . . .

$E^{*}(\Sigma) = E^{**}$ at high Σ

High Grafting Density
Immediate Bifurcation

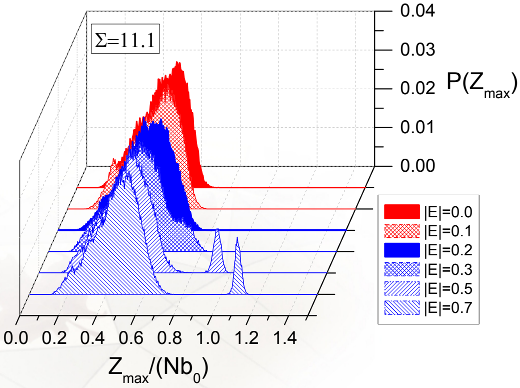


Bifurcates but . . .

$E^* (\Sigma) = E^{**}$ at high Σ

- Increasing Σ increases E^*
- but E^{**} nearly constant
- Therefore, *immediate* bifurcation at high Σ

High Grafting Density
Immediate Bifurcation



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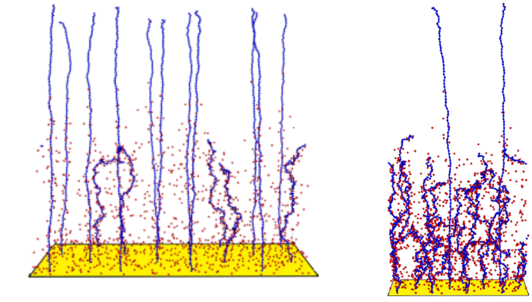
Fully stretched chains now the *minority*

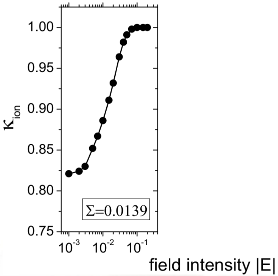
High Grafting Density
Minority

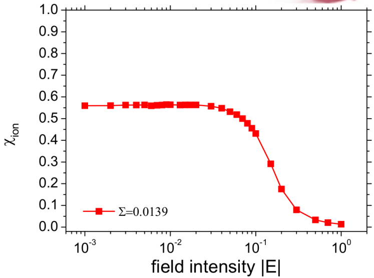


- When $|E| > |E^{**}|$:
  Majority stretched if $\Sigma = 1.11$ but *minority* stretched if $\Sigma = 11.1$
- Why are more relaxed and unstretched compared to intermediate Σ?

High Grafting Density

Increased Counterion Confinement and Condensation





- In weak fields and low grafting density, 82% of counterions *confined* to brush

- In weak fields and low grafting density, 56% of counterions condensed

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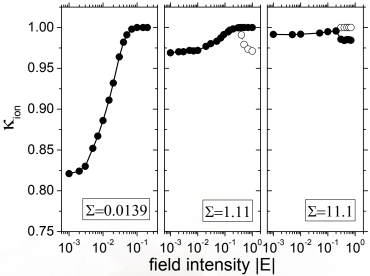

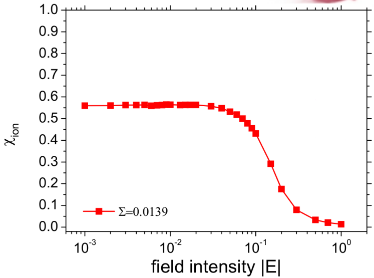

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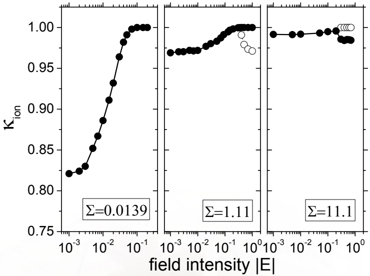

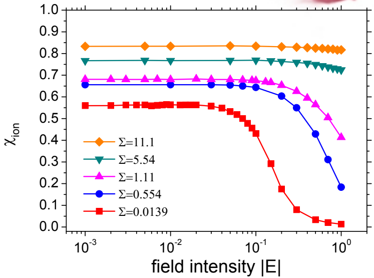

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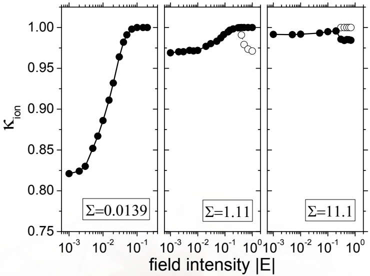

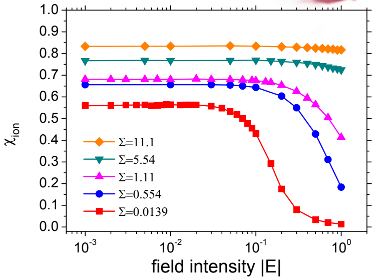

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Assuming local neutrality becomes more accurate at higher grafting densities.

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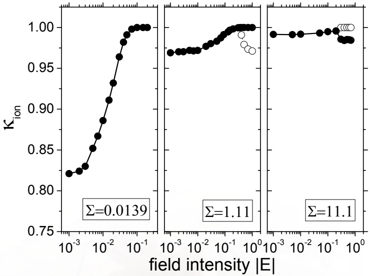

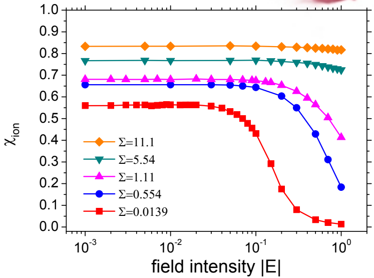

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Assuming local neutrality becomes more accurate at higher grafting densities.

Less chains bare and liable to be fully stretched.

High Grafting Density
Conclusion

Conclusion About High Grafting Density:

- At high grafting densities, $|E^*| = |E^{**}|$
- Fully stretched population becomes minority

Structure of polyelectrolyte brushes subject to normal electric fields.
Langmuir, 29(7): 2359-2370, 2013.

Conclusion

Potential Applications of Bifurcating Brushes

Original Motivation:

Polyelectrolyte brushes as field controlled gates

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- Control flow resistance
- Filtration by number of rods
- Control the surface friction
- Utilizing polyampholytes or end-labeled chains may allow choosing which chains stretch
- *Fishing* – the tethering and subsequent trapping within the interior of the brush of analytes by alternating fields

Can slip walls improve field-flow fractionation or hydrodynamic chromatography?
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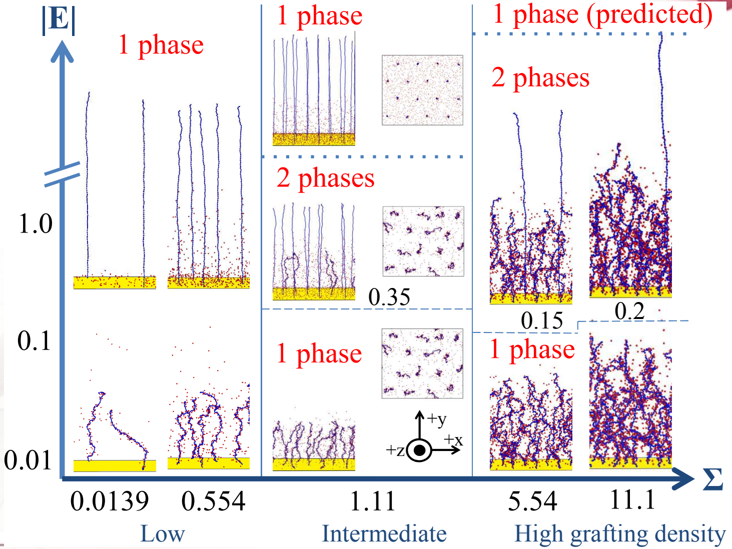
- Henk de Haan
- Martin Bertrand
- Yuguo Tao
- David Sean
- Zheng Ma

Webpages

- Gary Slater: `www.science.uottawa.ca/~gslater`
- Tyler Shendruk: `www.tnshendruk.com`

Recapitulation

Structure of *highly charged* polyelectrolyte brushes in the *no-salt* limit, subject to *normal electric fields*:



Structure of polyelectrolyte brushes subject to normal electric fields. Langmuir, 29(7): 2359-2370, 2013.