Charge Inversion & Layer-by-Layer Assembly of Flexible Polyelectrolytes

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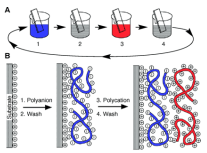
1. Polyelectrolytes (PE)

PE are charged polymers

PE are important materials

- Can be soluble in water
- Can be adsorbed onto charged surfaces

PE Layer-by-Layer (LBL) Assembly



Decher, **Science, 277**, 1232 (1997)

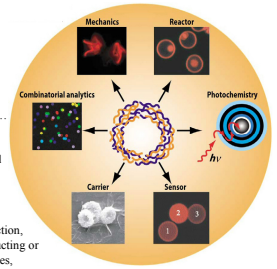
PE are difficult to study

- Both long-range (Coulomb) and short-range (excluded volume) interactions present in the system

Why Layer-by-Layer (LBL) Assembly ?

- Simple, fast, cheap
- Self-healing
- Versatile
  - ✓ **Synthetic PE:** conducting & light-emitting polymers, reactive polymers, polymeric complexes, polymeric dyes, …
  - ✓ **Natural PE:** DNA, RNA, proteins, viruses, …
  - ✓ **Charged nano-particles and platelets, …**
- Potential Applications

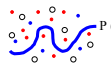
surface modification, enzyme immobilization, gene transfection, separation membranes, conducting or light-emitting devices, batteries, optical data storage, controlled particle and catalyst preparation, etc.



Peyratout and Dahne, **Angew. Chem. Int. Ed., 43**, 3762 (2004)

2. Theoretical Formalism

Field Theory for Model PE System



P (=A,B,…)

- solvent molecule (S)
- cation (+)
- anion (–)

- Ions from salt = counterions from P
- Ions have no volume
- Monovalent system
- All P segments have the same density ρ_0 as S
- All P segments have the same statistical segment length a

$\exp(-\mathcal{H}_0-\mathcal{H}_1-\mathcal{H}_2)$ $k_BT=1$ — Canonical ensemble

$\mathcal{H}_0$ = elastic energy of Gaussian Chains

$\mathcal{H}_1$ = short-range interaction energy described by χ parameters

$\mathcal{H}_2$ = pure Coulomb interaction energy

Incompressibility at everywhere and Overall charge neutrality

Partition function: $\mathcal{Z}=\int\prod_j\left(\mathcal{D}\phi_j\mathcal{D}\omega_j\right)\mathcal{D}\psi\mathcal{D}\eta\exp(-\mathcal{F})$

Self-Consistent Field Theory

Mean-field (saddle-point) approximation:

$$\frac{\delta\mathcal{F}}{\delta\omega_j(\mathbf{r})}=0 \Rightarrow \text{Quadratures evaluating } \phi_j(\mathbf{r}) \text{ (and modified diffusion equations)}$$

Poisson-Boltzmann equation

$$\frac{\delta\mathcal{F}}{\delta\psi(\mathbf{r})}=0 \Rightarrow \phi_E(\mathbf{r})=-\frac{1}{N_0}\nabla\bullet\left[\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})\right]$$

$$\frac{\delta\mathcal{F}}{\delta\phi_j(\mathbf{r})}=0 \Rightarrow \textit{Linear} \text{ equations that relate } \omega_j(\mathbf{r}) \text{ to other fields}$$

$$\frac{\delta\mathcal{F}}{\delta\eta(\mathbf{r})}=0 \Rightarrow \text{Incompressibility}$$

Position-dependent dielectric constant:

$$\varepsilon(\mathbf{r})=\sum_P\varepsilon_P\phi_P(\mathbf{r})+\varepsilon_S\phi_S(\mathbf{r})$$

ε_P (ε_S): dielectric constant of pure P (S)

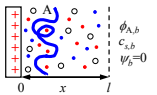
Wang et al., **JPC B, 108**, 6733 (2004); **109**, 9855 (2005)

Normalization : $R_g=a\sqrt{N_0/6}$, $\mathbf{r}/R_g\to\mathbf{r}$, $\frac{3k_BT\varepsilon(\mathbf{r})}{2\pi\rho_0e^2a^2}\to\varepsilon(\mathbf{r})$

$\phi_j(\mathbf{r})$: normalized (by ρ_0) density field for component j (j = P,S,+,–)
$\omega_j(\mathbf{r})$: conjugate field interacting with j
$\eta(\mathbf{r})$: conjugate field imposing incompressibility
N_0: chain length used for normalization
$\varepsilon(\mathbf{r})$: dielectric constant
$\psi(\mathbf{r})$: electrostatic potential (in units of k_BT/e)
e: elementary charge

3. PE Adsorption and Charge Inversion

Model System for PE Adsorption



Modified diffusion equation:

$$\frac{\partial q_A(x,s)}{\partial s}=\frac{\partial^2 q_A}{\partial x^2}-\omega_A(x)q_A$$

$$q_A(x,s=0)=1$$

At $x=0$:

$$\frac{\partial q_A}{\partial x}=d^{-1}q_A,\quad \frac{d\psi}{dx}=-\frac{\sqrt{N_0}}{\varepsilon}\sigma_{SF}$$

At $x=l$:

$$\frac{\partial q_A}{\partial x}=0,\quad \frac{d\psi}{dx}=0$$

Parameters in the model:

N	chain length of PE;
p	degree of ionization of PE;
σ_{SF}	surface charge density;
$c_{s,b}$	bulk salt concentration;
$\phi_{A,b}$	bulk polymer concentration;
χ	Flory-Huggins parameter between PE and solvent;
d^{-1}	for short-range interactions between surface and polymers, >0 for repulsive and <0 for attractive;
l	system size;
ε	(uniform) dielectric constant;

Charge distribution: smeared.

Parameters	Dimensionless Values	Values in Real Units
T		300 K
a ($\rho_0=a^{-3}$)		5 Å
ε	0.343	80
l	7~175	42~1050 nm
$\phi_{A,b}$	1~100 ×10^{-5}	0.133~13.3 mM
$c_{s,b}$	0~0.1	0~1.33 M
σ_{SF}	0~0.2	0~5.22×10^{-2} C/m^2
p	0~1	
χ	0~1	
d^{-1}	–10~∞	

Ground-State Dominance Approximation

$$\text{PB Eq.:}\ \frac{d^2\psi}{dx^2}=\frac{N_0}{\varepsilon}\left[p\phi_A-\left(c_{s,b}+p\phi_{A,b}\right)e^{-\psi}+c_{s,b}e^{\psi}\right]$$

$$\text{GSDA}\Rightarrow\frac{d^2\sqrt{\phi_A}}{dx^2}=N_0\left[\ln\frac{1-\phi_{A,b}}{1-\phi_A}-2\chi\left(\phi_A-\phi_{A,b}\right)-p\psi\right]\sqrt{\phi_A}$$

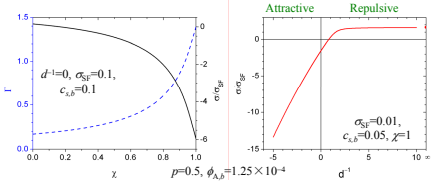
At $x=0$: $\frac{d\sqrt{\phi_A}}{dx}=d^{-1}\sqrt{\phi_A}$

$\Gamma\equiv\sqrt{N_0}\int_0^\infty\left[\phi_A(x)-\phi_{A,b}\right]dx$ ($\Gamma<0$: Depletion; $\Gamma>0$: Adsorption)

$\sigma=\sigma_{SF}-p\Gamma$ ($\sigma<0$: Charge inversion; $\sigma/\sigma_{SF}<-1$: Strong charge inversion)

Wang, **Macromolecules, 38**, 8911 (2005)

Conditions for Strong Charge Inversion



Poor solvent for polymer backbone, high salt concentration, attractive or indifferent surface for polymers, and oppositely charged surface and polyelectrolytes are *all* needed to obtain strong charge inversion.

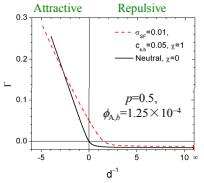
PE at High $c_{s,b}$ ≈ Neutral Polymers in Good Solvent

With several approximations, we get

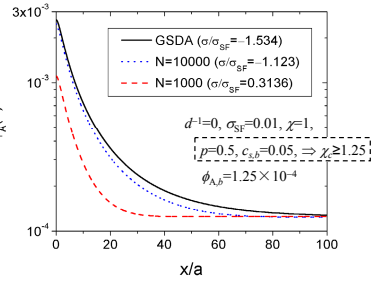
$$\Gamma=\sqrt{\frac{2\phi_{A,b}}{v_{eff}}}\left[\sqrt{1+\frac{\left(d_{eff}^{-1}\right)^2}{2N_0v_{eff}\phi_{A,b}}}-1-d_{eff}^{-1}\sqrt{\frac{1}{2N_0v_{eff}\phi_{A,b}}}\right],$$

where $v_{eff}=v+\frac{p^2}{c_b}$, $v=1-2\chi$,

$$d_{eff}^{-1}=d^{-1}-\frac{\sqrt{N_0}p\sigma_{SF}}{c_b},\quad c_b=2c_{s,b}+p\phi_{A,b}.$$



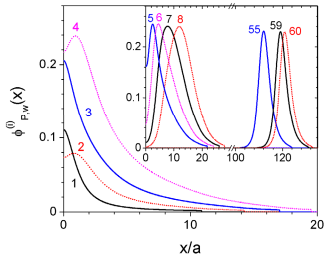
GSDA *vs.* SCFT



4. PE Layer-by-Layer Assembly

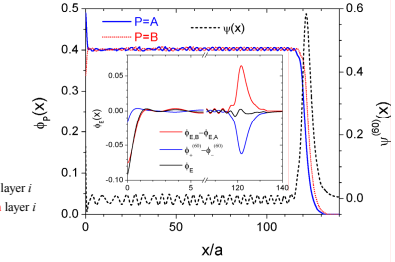
σ_{SF}=0.1, d^{-1}=0, v_A=–1, v_B=1, p_P=0.5, χ_{PS}=1, χ_{AB}=0 , $c_{s,b}$=0.05, $\phi_{P,b}$=7.5×10^{-4}

Layer Profiles



$$P=\begin{cases}A & \text{for odd layer } i\\ B & \text{for even layer } i\end{cases}$$

Three-Zone Structure

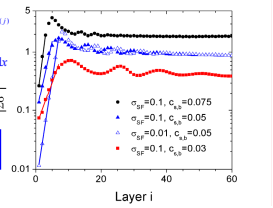


Charge Inversion & Film Growth

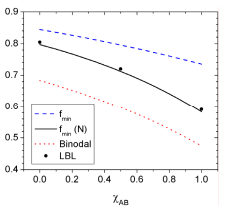
$$\Sigma\sigma^{(i)}=\sigma_{SF}+p_P\sum_{j=1}^{i}v_P\Gamma^{(j)}$$

$$\Gamma^{(j)}\equiv\sqrt{N_0}\int_0^\infty\phi_{P,v}^{(j)}(x)dx$$

$\Sigma\sigma^{(i)}<0$ for odd i
$\Sigma\sigma^{(i)}>0$ for even i



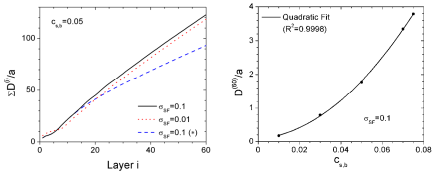
Polymer Density in Multilayer



$$f=\frac{\phi}{N_P}\ln\frac{\phi}{2}+(1-\phi)\ln(1-\phi)+\chi_{PS}\phi(1-\phi)+\chi_{AB}\frac{\phi^2}{4}+\left(p_P\phi+2c_{s,b}\right)\ln\frac{p_P\phi+2c_{s,b}}{2}$$

where $\phi=2\phi_A=2\phi_B$, $N_P\to\infty$.

Layer Thickness



$$\Sigma D^{(i)}=\frac{2R_g\int_0^l x\left[\sum_{j=1}^{i}\phi_{P,v}^{(j)}(x)\right]dx}{\sum_{j=1}^{i}\Gamma^{(j)}}$$

$$D^{(60)}=\Sigma D^{(60)}-\Sigma D^{(59)}$$

5. Summary

- We have applied a self-consistent field theory to flexible polyelectrolytes (PE) on flat surfaces. The ground-state dominance approximation was used to explore the large parameter space involved.
- Strong charge inversion is found for relatively long PE on oppositely charged, attractive surfaces in poor solvent at high salt concentrations.
- Our modeling on the layer-by-layer assembly process captures its qualitative features. Further work to refine the modeling and to compare with experimental results is undergoing.