Pattern-forming electroneutral blends of charged polymers

Galen T. Pickett

Department of Physics and Astronomy,
California State University Long Beach
Asymmetric diblocks

\[ f = \text{fraction of A on molecule, controls symmetry:} \]

\[ Q_{\text{im} \bar{3} \text{m}} \]

\[ Q_{\text{la} \bar{3} \text{d}} \]


http://www.psrc.usm.edu/mauritz/block.html
Coarse-grained Free Energy for Diblocks

- Local interactions
  \[ F_{\text{local}}[\varphi] = \int \left[ \frac{t}{2} \varphi^2 + \frac{k}{2} \nabla \varphi \cdot \nabla \varphi + \varphi^4 \right] dx \]

- Long-ranged interactions
  \[ F_{\text{long-range}}[\varphi] = \int dx \int dx' B \varphi(x) G(x, x') \varphi(x') \]
  
  - Ohta and Kawasaki:
    \[ \nabla^2 \varphi G(x, x') = -\delta(x - x') \]

- Formally, same as electrostatics.
  
  - A monomers negative, B monomers positive
Minimizing $F$ gives diblock-like structures

- Cahn-Hilliard dynamics
- Lamellar phase Scattering
- Cylinder phase Scattering
- Electrostatic analogy for Diblocks

  - Elastic energy $\Leftrightarrow$ Electrostatic self-energy
  - Semenov, chain stretching similar to electric field:

- Alexander, deGennes, and elaborations
- Blend of polyelectrolytes:

  - Polycation and polyanions mixed together:

  ![Electroneutral](image)

  - Poly-salt melt... what might it do. Phase separate?
Blending to consider

- Let both chains have the same number of monomers (can be relaxed...)
- Let the CHARGE/monomer on the majority component be fixed.
- Electroneutrality then relates the CHARGE/monomer of minority component to composition:
  \[ 0 = \rho_A f + \rho_B (1 - f) \]
- Minority chain is more strongly charged than majority chain... synthetic chemistry.
- Can expect a mesophase.

- Phase separation: huge electrostatic costs

- "Collecting like charges"

- Single phase: huge specific interactions

  $N$ red monomers: total cost $\chi N$
Locate linear instability of the uniform phase.

$\phi_A + \phi_B = 1 \Rightarrow \phi_A = f + \phi, \phi_B = (1-f) + \phi$

$f = \text{fraction of A monomers in system}$

Collective scattering function for order parameter

$S^{-1} \left[ q \right] = S_A^{-1} + S_B^{-1} + \alpha$

$\frac{\delta^2 F}{\delta \phi^2} \text{ giving thermal response for fluctuations of } \phi$

$F \left[ \phi \right] = \chi \phi(1-\phi) + \frac{2\pi B}{q(1-f)} \phi^2$

$\alpha = \frac{2}{2\pi B} \frac{\delta^2 F}{\delta \phi^2}$

Enforces incompressibility, chain architecture
- **RPA cont.**
  - **Single-chain scattering functions:**
    
    \[
    S_A = fg_d(q, N) \quad \text{Debye scattering from Gaussian chain}
    \]

    \[
    g_d(q, N) \approx \frac{N}{1 + (Nq^2)/12} \quad \text{Lorentzian approximation}
    \]

  - **Typical scattering function:**

  - **Peak diverges when**
    
    \[
    (\chi N)_{\text{spin}} = \frac{1}{2f(1-f)} + N \sqrt{\frac{\pi B}{3f(1-f)^3}}, \quad N\sqrt{B} = \text{charge/chain}
    \]
- **Strong-Segregation Limit**

- **Just a balance of surface energy and electrostatics**
Self-consistent Lattice Model

Fleer, Cohen, Scheutjens, Cosgrove, Vincent, Polymers at Interfaces Chapman and Hall, London 1993

Lattice model

1. Start with empty lattice
2. Throw down polymers at random
3. Calculate average monomer densities
4. Regrow the chains
5. Recalculate the monomer densities
6. Repeat

Charged blend, lattice electrostatics.
Lattice Electrostatics

- Discretize Laplacian:
  \[ \nabla^2 \varphi \Rightarrow \varphi(x, y + 1) + \varphi(x, y - 1) + \varphi(x + 1, y) + \varphi(x - 1, y) - 4\varphi(x, y) \]

- Gauss’ Law discretized:
  \[ \nabla^2 \Phi = 4\pi(\rho_A \varphi_A + \rho_B \varphi_B) \]

- Solve for \( \Phi \), electrostatic potential, involves inverting a linear operator on the lattice

- Solved numerically at each iteration by direct inversion.
● Microphases (just like block copolymers)

Charge/monomer=0.01 N=150

- Disordered
- Cylindrical
- Lamellar
Microphases (just like block copolymers)

\[ \chi N \text{ (Inverse Temperature)} \]

Composition

Charge/monomer=0.01 N=150

Cylindrical

Lamellar

Disordered
- Charge compatibilizes the blend

Increasing charge

- Simple architectures (just homopolymers) but complex patterns.
- Long-range vs. short-range, generic physics.
Comparison, SCF RPA

Disordered-Lamellar transition for $f = 1/2$:

$Q_A = \text{total charge/chain}$
Films

- Lower surface held at a constant potential
- Upper surface is vacuum
- Confinement and external field controls morphology

[Diagram showing film behavior with and without external field]
● Conclusions

- Charged blends make microphases
- Length scale controlled by charge/chain not molecular weight
  - Photonic crystals?
- Self-assembly of charge-separated layers, with lateral patterns.
- External controls