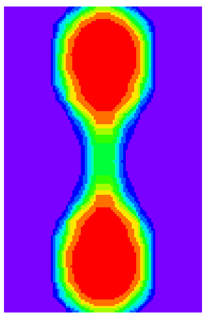
Self Assembly of Charged Polymers



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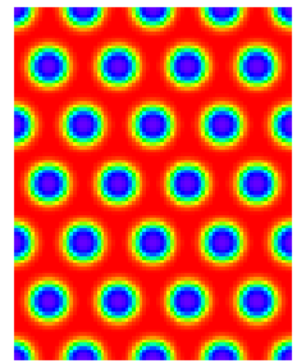
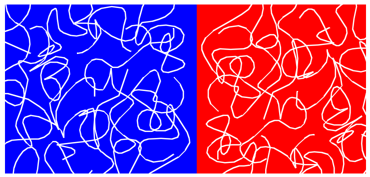


- **Stuff we want to do:**

- **Strengthen mixtures of plastics**

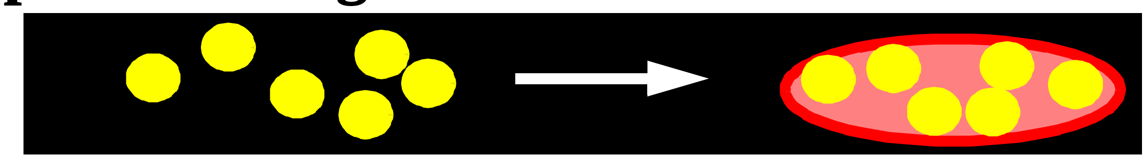


  - Incompatible plastics
  - Combine properties (strength, flexibility)

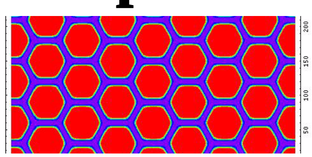
- **Lubricate/protect surfaces**

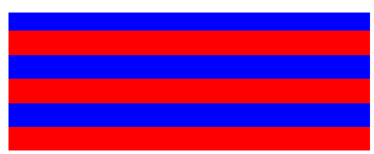
  - Prevent contact
  - Avoid damage

- **Encapsulate drugs**



- **Create patterns**

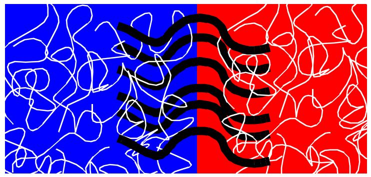




  - Symmetry, scale

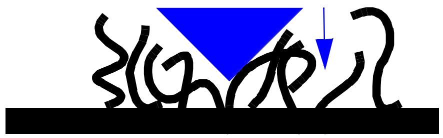
Stuff that can do it.

- **Stitching polymers: reinforce mixtures**



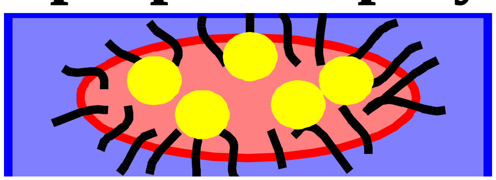
- Half blue / half red reinforces interface.

- **End-grafted polymers: lubrication**



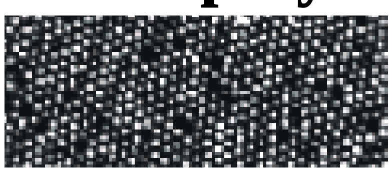
- Trapped coating
- “Osmotic” barrier

- **Amphiphillic polymers: housing for droplets**



- Polymer forms vesicles
- Release contents, pH *e.g.*

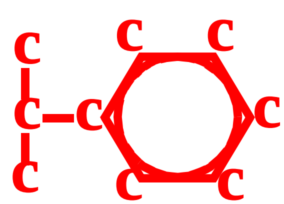
- **Block copolymers: templates for ordering**



http://www.princeton.edu/~polymer/

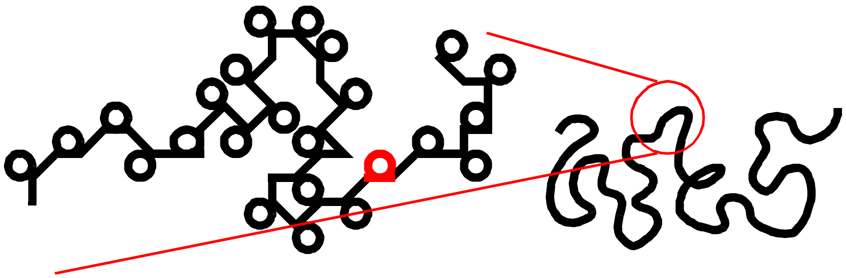
● Polymers

- ❏ **Are made of monomers...**



Styrene
104AMU
1nm

- ❏ **... strung together into huge chains...**



Polystyrene

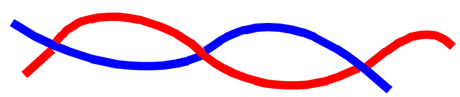
1000 monomers:104,000AMU

$1000\,nm = 1\,\mu m$

- ❏ **... which mostly ignore** $h\ldots$

$$\Delta x \Delta p \approx (1\,nm)(10^5\,\mathrm{AMU}\,v) \approx 10^8 \frac{v}{m/s} h$$

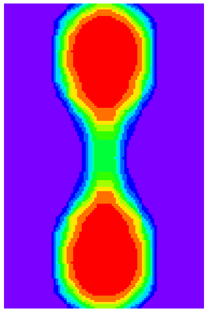
- ❏ **... and are all tangled up.**



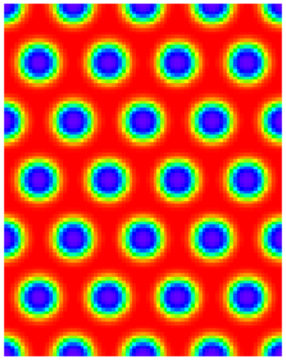
☛ Entangling, knots

- **Outline:**

- **Single-chain self-assembly "folding"**

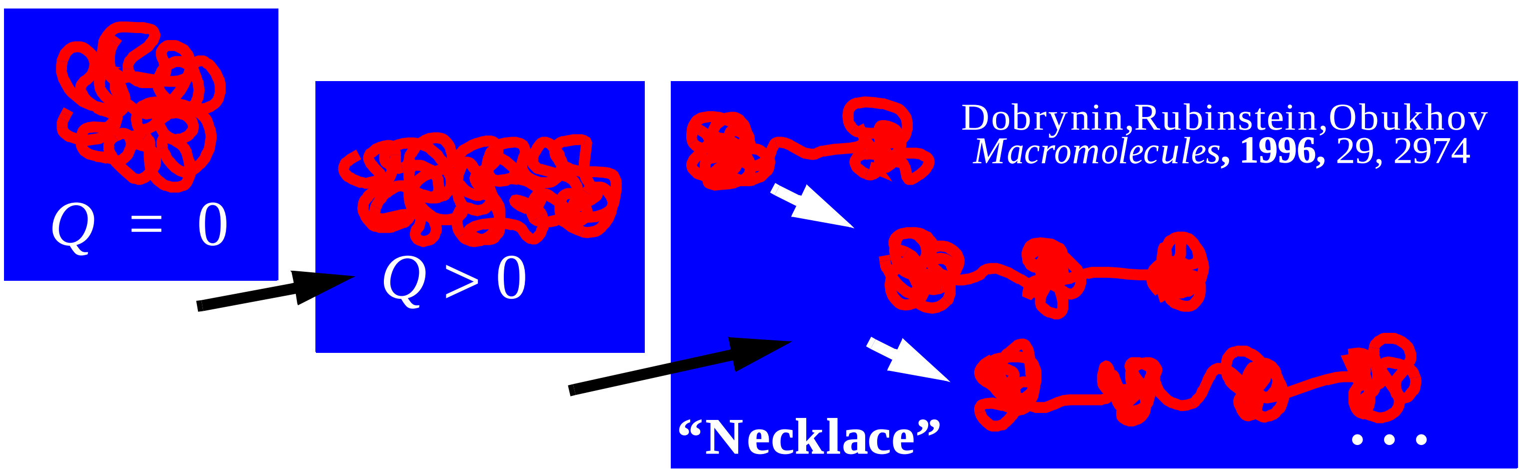


- **Many-chain "super-structures"**



- **Polyelectrolyte, poor solvent**

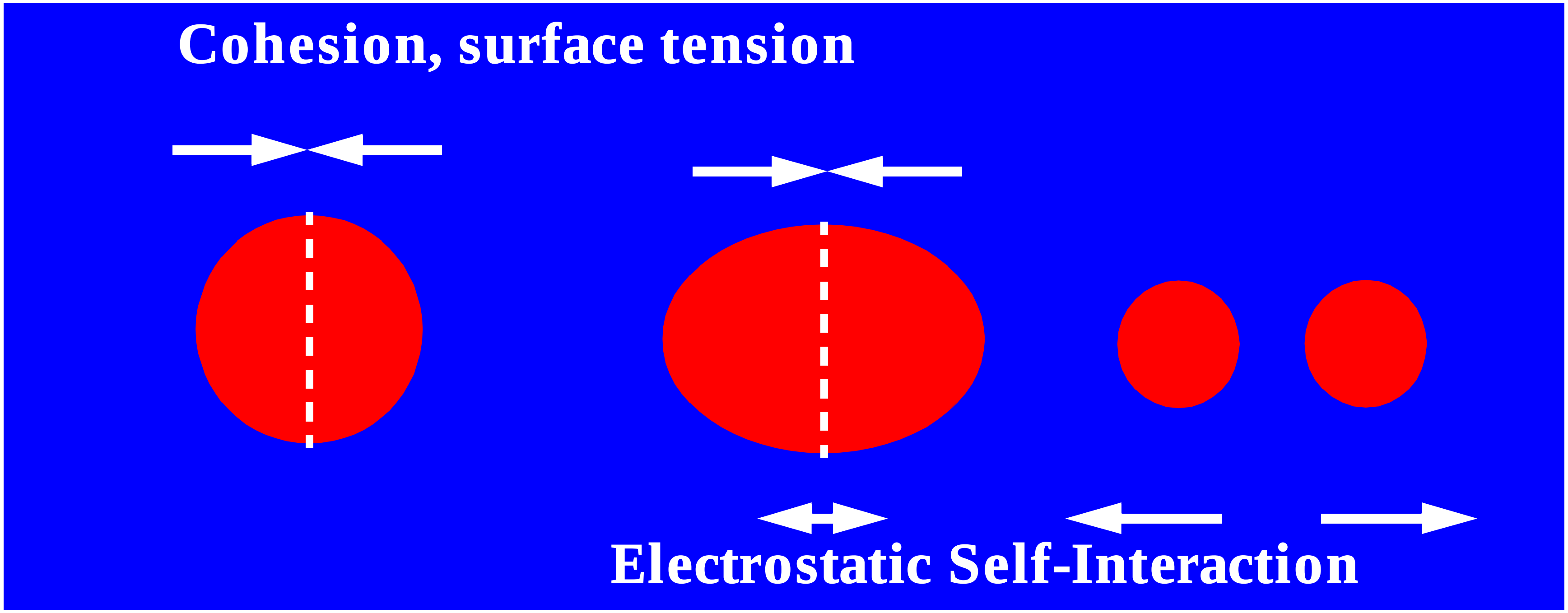
- **Fixed charge** $Q = \alpha N$ **on a flexible polymer,** N **monomers.**
- **Poor solvent:**
  - Q, N control conformation.



- **Cascade of transitions.**

- **Instability for Charged Oil Drop**

- **Lord Rayleigh:**

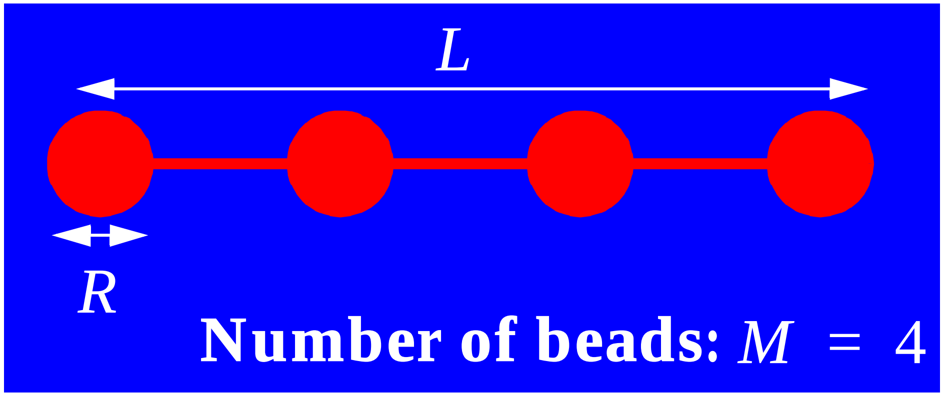


- **If charge exceeds threshold, surface tension can’t maintain the droplet.**

- **Chain *CAN’T* break up.**

- **Cartoon theory for *chain***

- **Free energy of necklace conformation:**



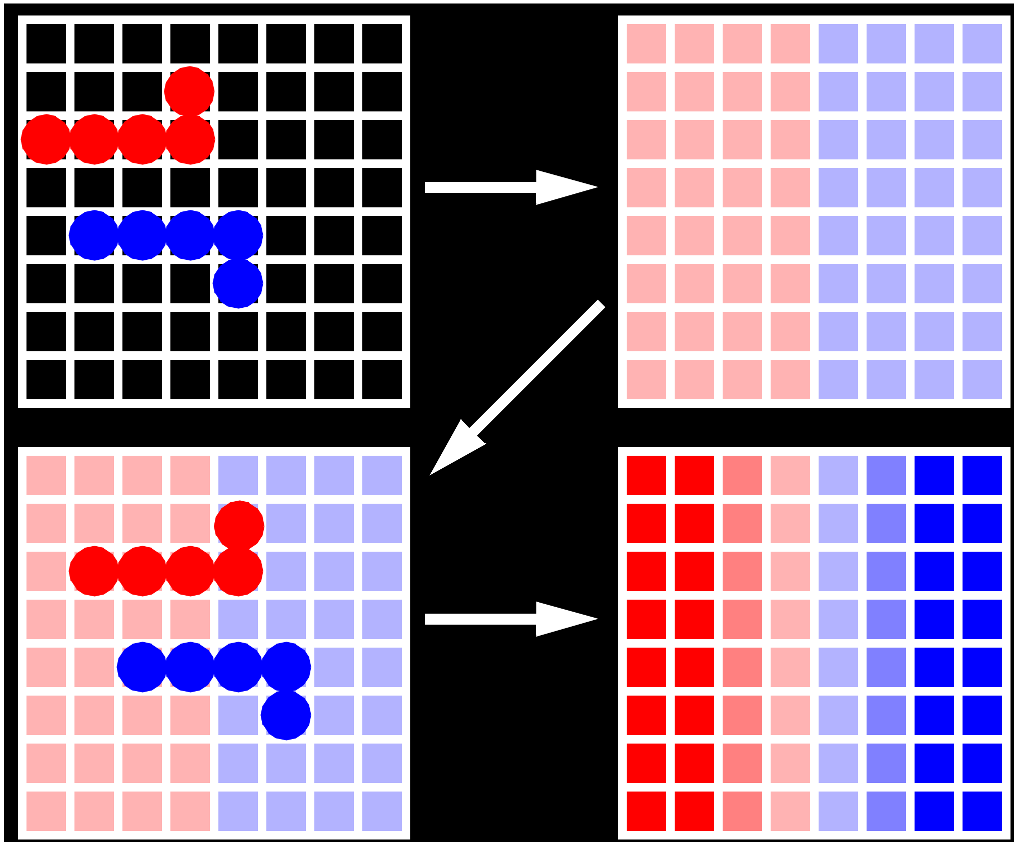
$$F = M\left(\gamma R^2 + \left(\frac{Q}{M}\right)^2 R^{-1}\right) + L\gamma + \frac{Q^2}{L}$$

- **Predicts transitions from 1 to 2 to ...**

● Self-consistent Lattice Model

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

❑ Lattice model

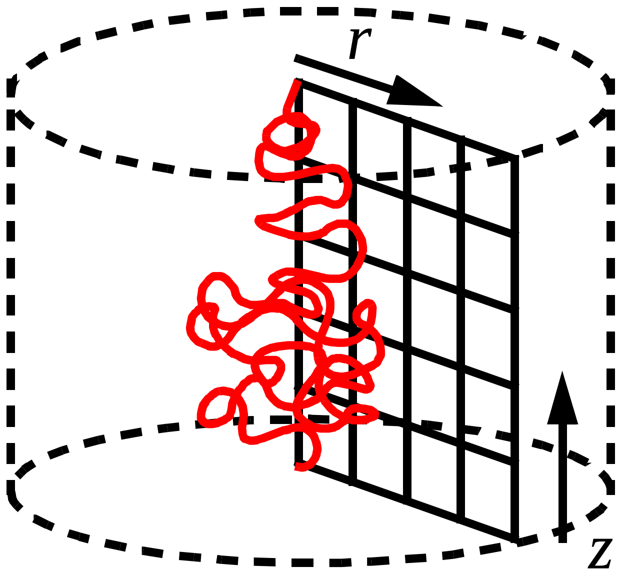


1. Start with empty lattice
2. Throw down polymers at random
3. Calculate average monomer densities
4. Regrow the chains
5. Recalculate the monomer densities
6. Repeat

❑ Azimuthal symmetry, *cylindrical* lattice.

- **2-D Cylindrical lattice**

- **Azimuthal symmetry:**

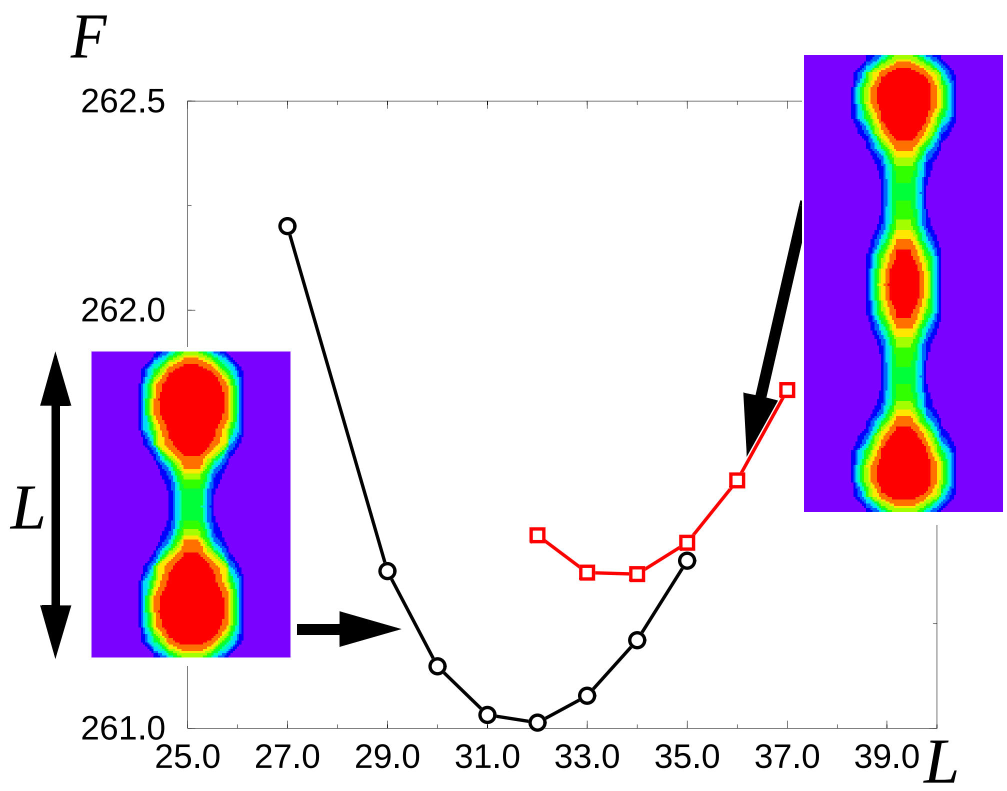


- r,z label annular section of three dimensional space.
- Polymer is held at center of top and bottom plate "bridging"
- Electrostatics, surface energy, chain connectivity are all accounted for

- **Variations in 2D, but real 3D structures (highly symmetric).**

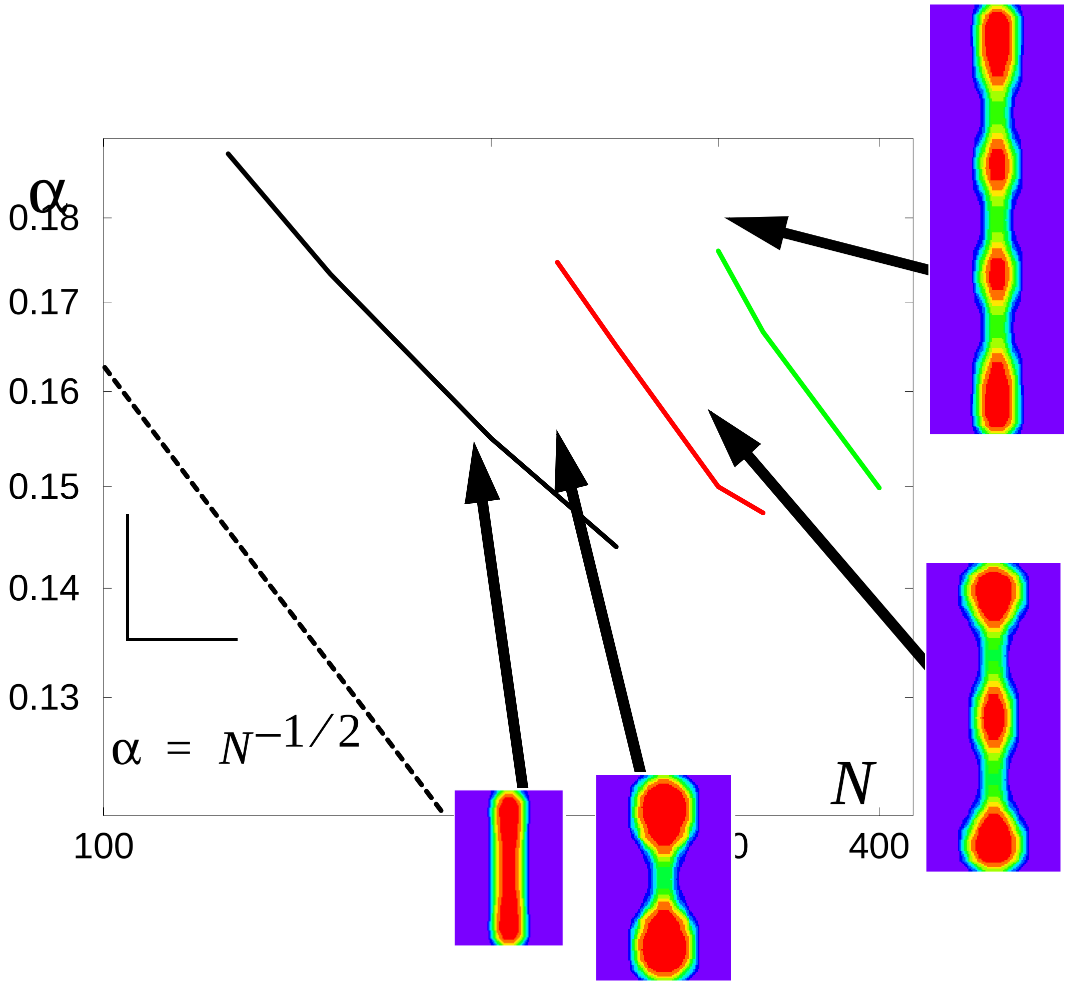
- **Compare structures:**

- **At fixed** N, α **vary** L **to find equilibrium structures.**
  - $N = 250, \alpha = 0.16, \chi = 2.0$:



  - L_{eq} minimizes F. **Possible experiment.**

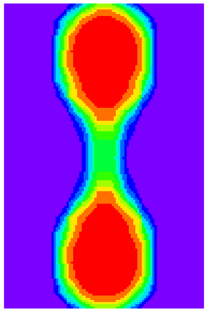
- **Diagram of states:**



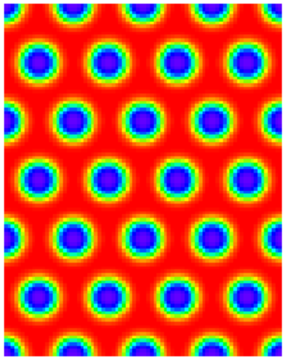
- **“Folded” conformations.**

- **Outline:**

- **Single-chain self-assembly "folding"**

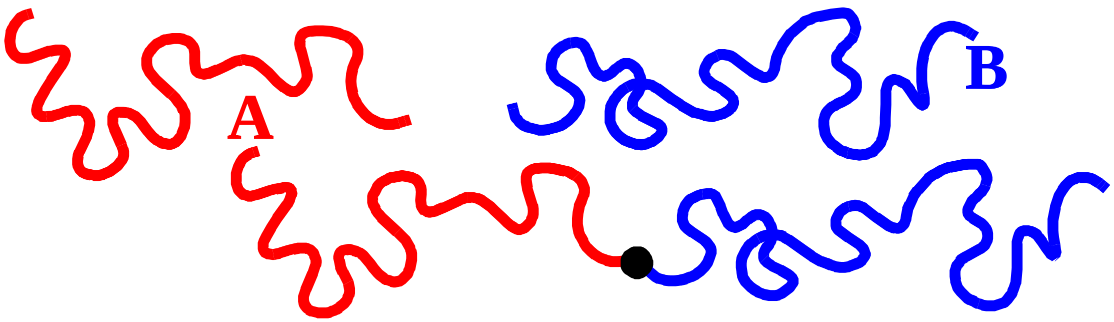


- **Many-chain "super-structures"**



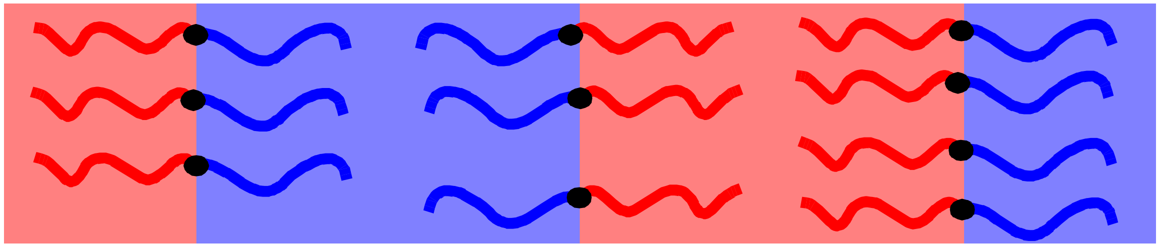
Block copolymers

- Two kinds of monomers strung together.



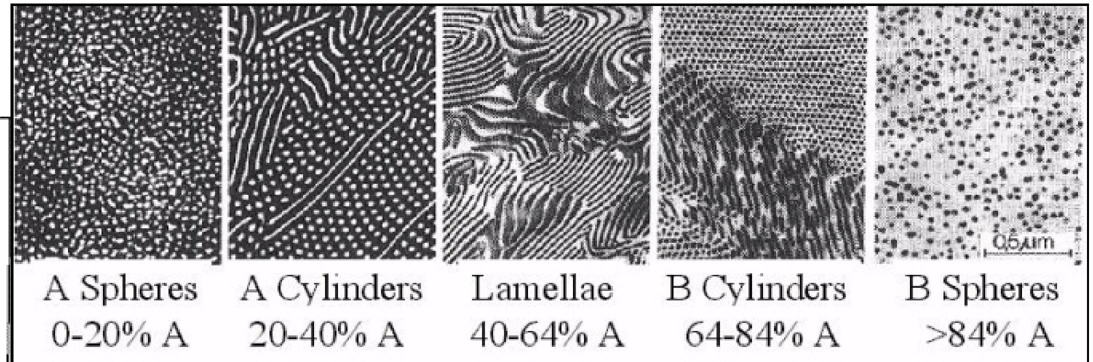
- A-block and B-block: "diblock"

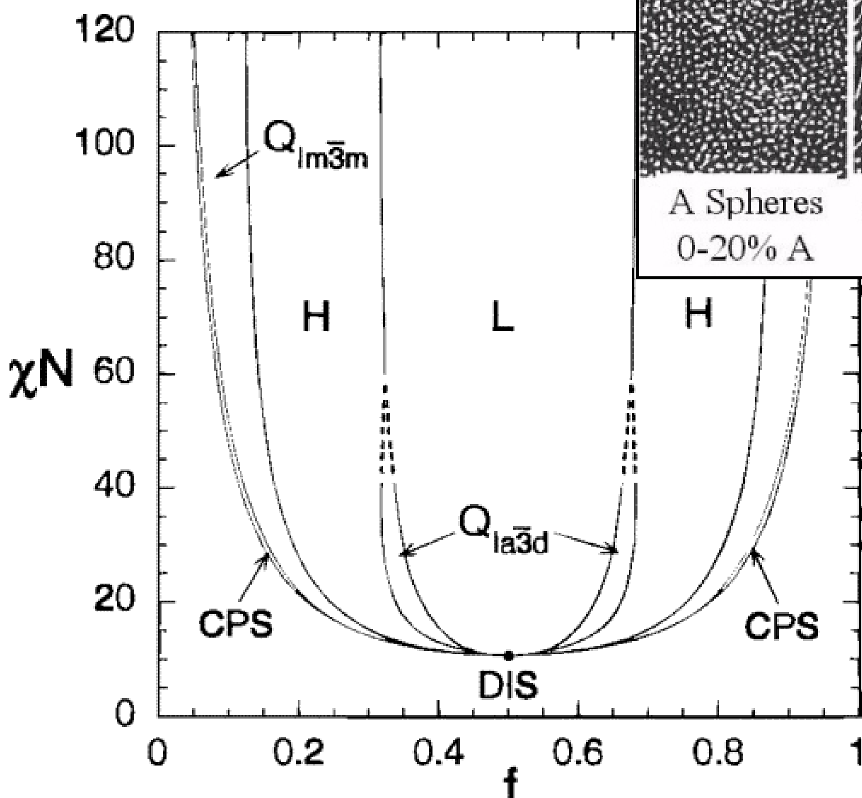
- Unless you break bonds, micro-scale texture happens.



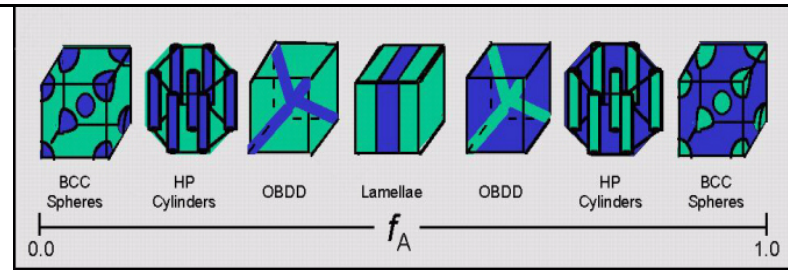
● Asymmetric diblocks

- *f* = **fraction of A on molecule, controls symmetry:**

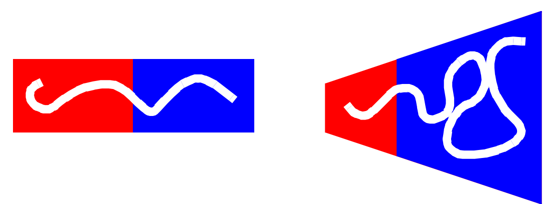




M. W. Matsen and F. S. Bates, *Macromolecules*; 1996; **29(4)**; 1091.



http://www.psrc.usm.edu/mauritz/block.html



Coarse-grained Free Energy for Diblocks

- **Local interactions for order parameter** $\varphi = \varphi_A - \varphi_B$

$$F_{\text{local}}[\varphi] = \int \left[\frac{t}{2}\varphi^2 + \frac{k}{2}\nabla\varphi \bullet \nabla\varphi + \varphi^4 \right] dx$$

- **Long-ranged interactions**

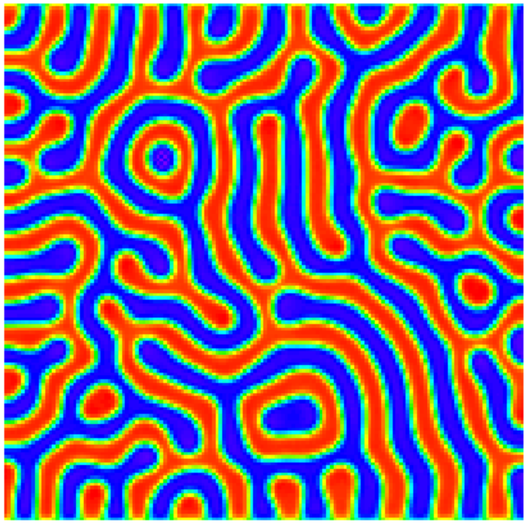
$$F_{\text{long-range}}[\varphi] = \int dx \int dx' B\varphi(x)G(x, x')\varphi(x')$$

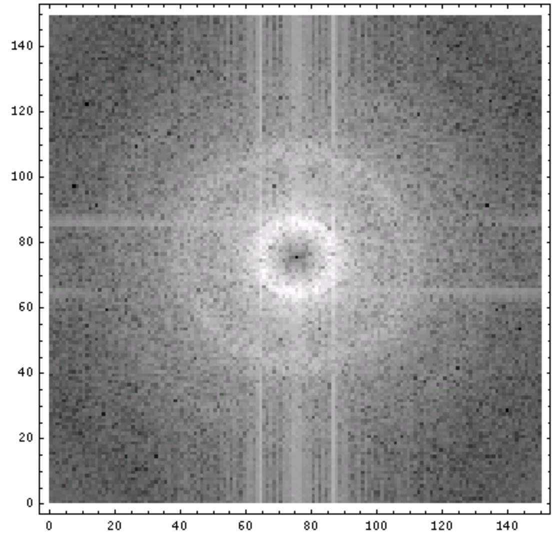
  - Ohta and Kawasaki:

$$\nabla_x^2 G(x, x') = -\delta(x - x')$$

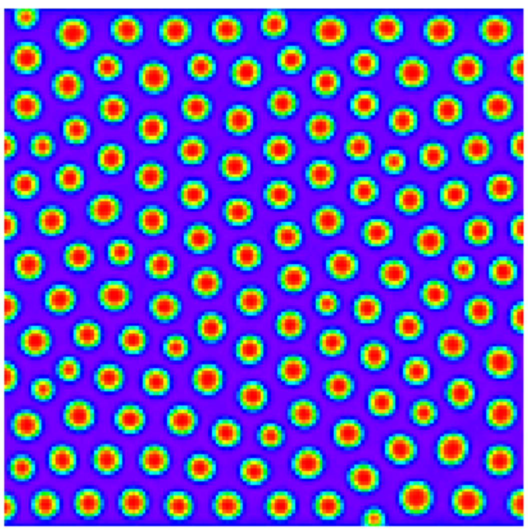
- **Formally, same as electrostatics.**
  - A monomers negative, B monomers positive

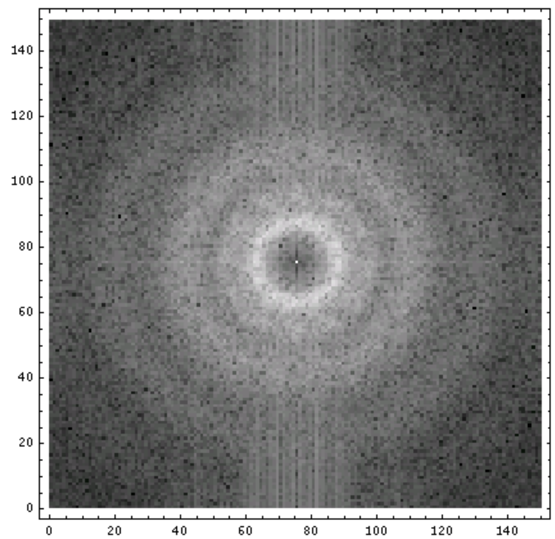
● Minimizing F gives diblock-like structures





- Cahn-Hilliard dynamics
- Lamellar phase
- Scattering

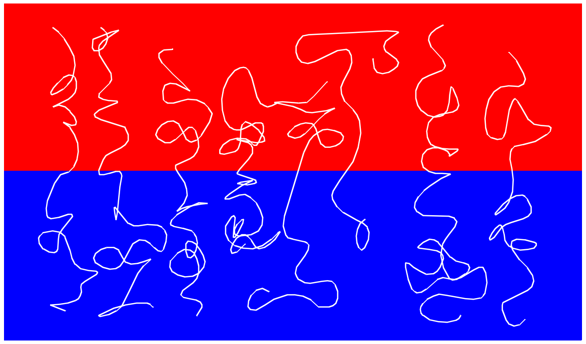


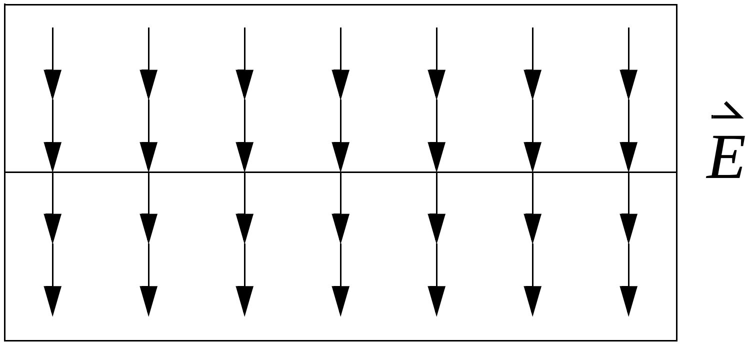


- Cylinder phase
- Scattering

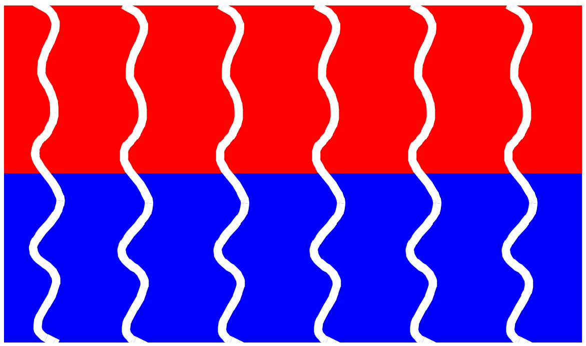
- **Electrostatic analogy for Diblocks**

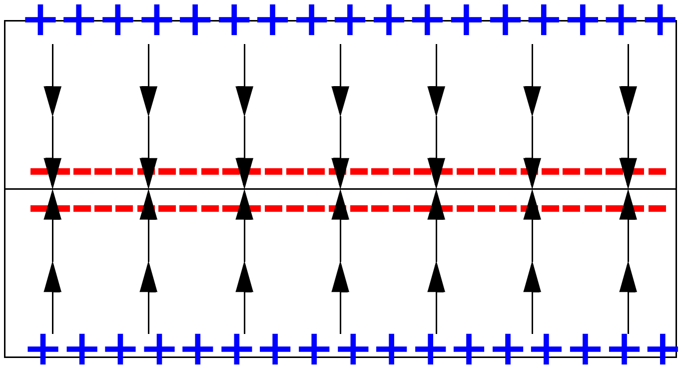
- **Elastic energy ⇔ Electrostatic self-energy**
- **Semenov, chain stretching similar to electric field:**





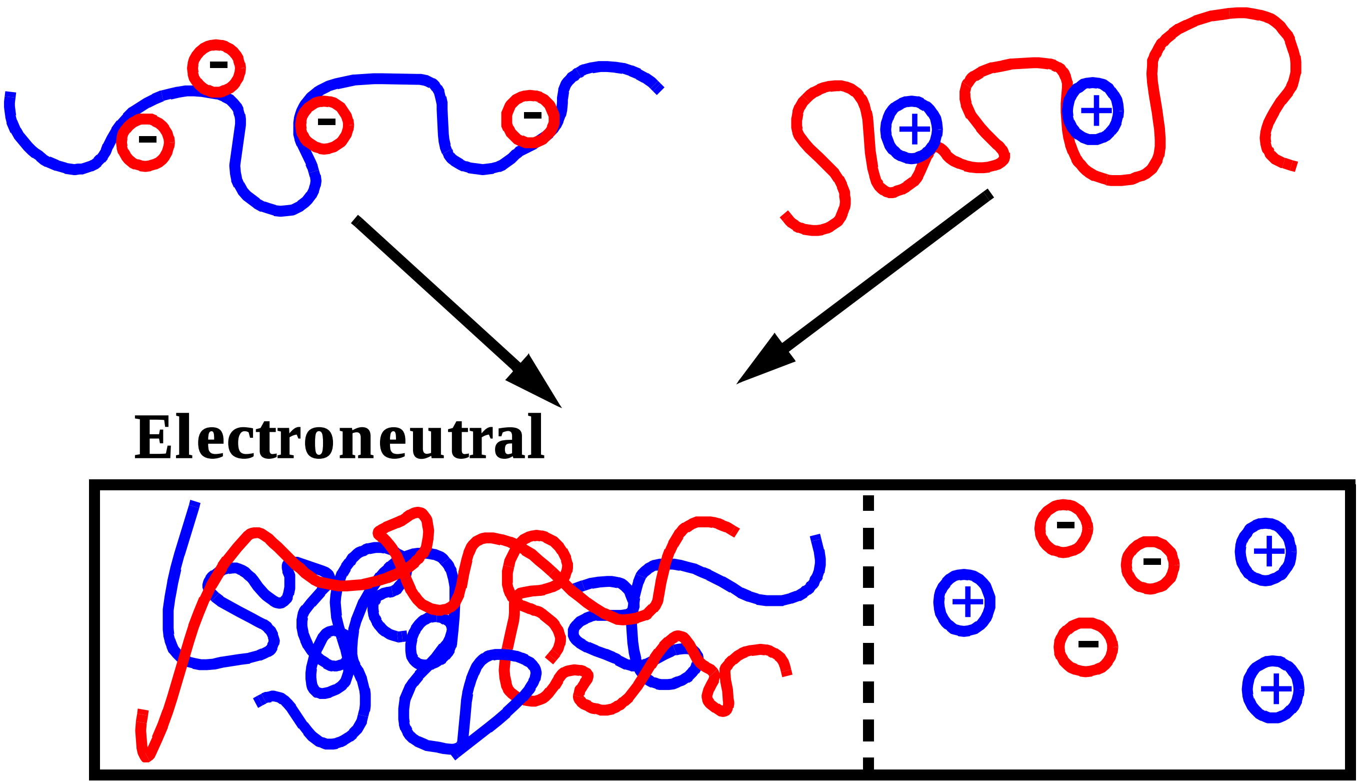
- **Alexander, deGennes, and elaborations**





- **Blend of polyelectrolytes:**

- **Polycation and polyanions mixed together:**



- **Poly-salt melt... what might it do. Phase separate?**

- **Blend to consider**

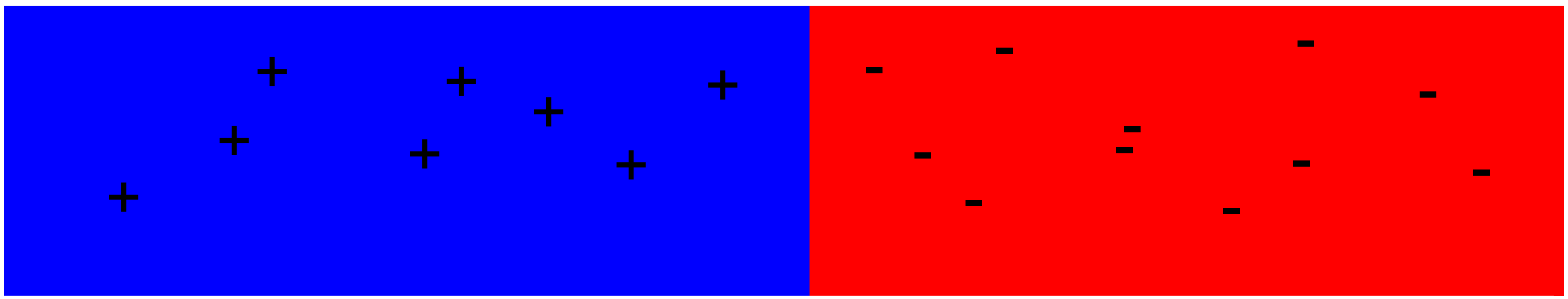
- **Let both chains have the same number of monomers (can be relaxed...)**
- **Let the CHARGE/monomer on the majority component be fixed.**
- **Electroneutrality then relates the CHARGE/ monomer of minority component to composition:**

$$0 = \rho_A f + \rho_B (1 - f)$$

- **Minority chain is more strongly charged than majority chain... synthetic chemistry.**

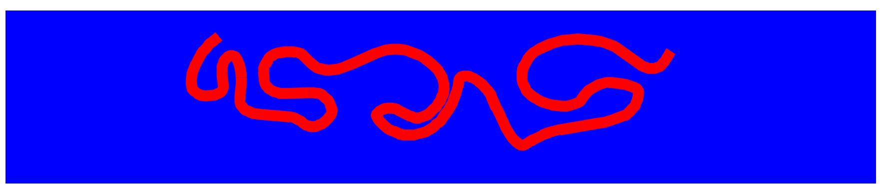
- **Can expect a mesophase.**

- **Phase separation: huge electrostatic costs**



"Collecting like charges"

- **Single phase: huge specific interactions**



N red monomers: total cost χ N

● RPA for Disordered Phase

- **Locate linear instability of the uniform phase.**

$$(\varphi_A + \varphi_B = 1) \Rightarrow \varphi_A = f + \varphi,\ \varphi_B = (1-f) + \varphi$$

f = fraction of A monomers in system

- **Collective scattering function for order parameter**

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

$$\alpha = \frac{\delta^2 F}{\delta\varphi^2}$$ giving thermal response for fluctuations of φ

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

- **Enforces incompressibility, chain architecture**

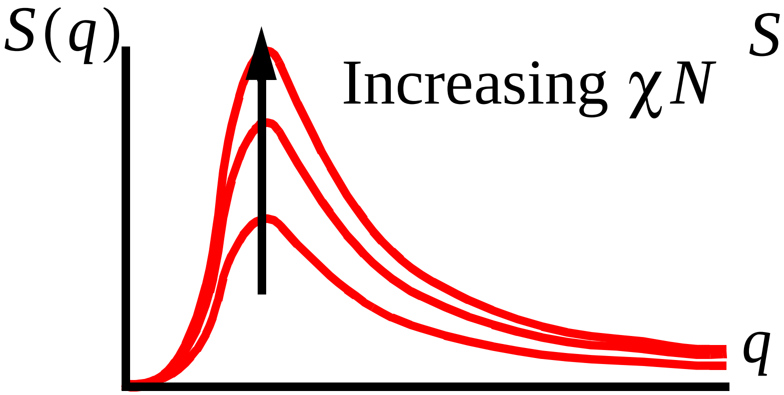
● RPA cont.

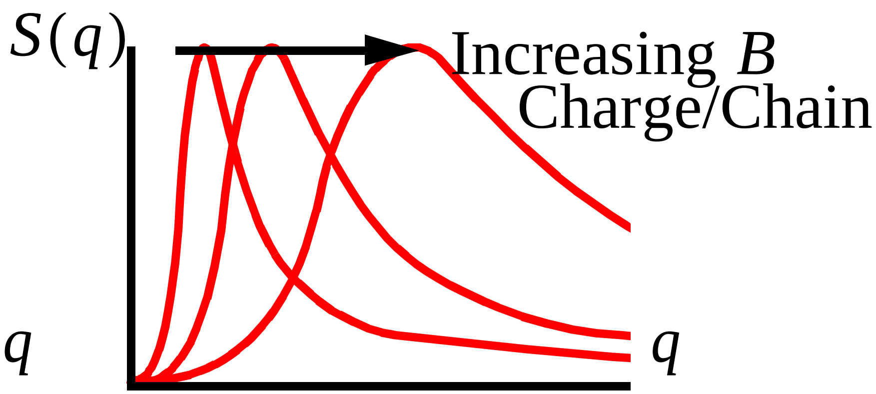
❑ **Single-chain scattering functions:**

$S_A = f g_d(q, N)$ Debye scattering from Gaussian chain

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

❑ **Typical scattering function:**



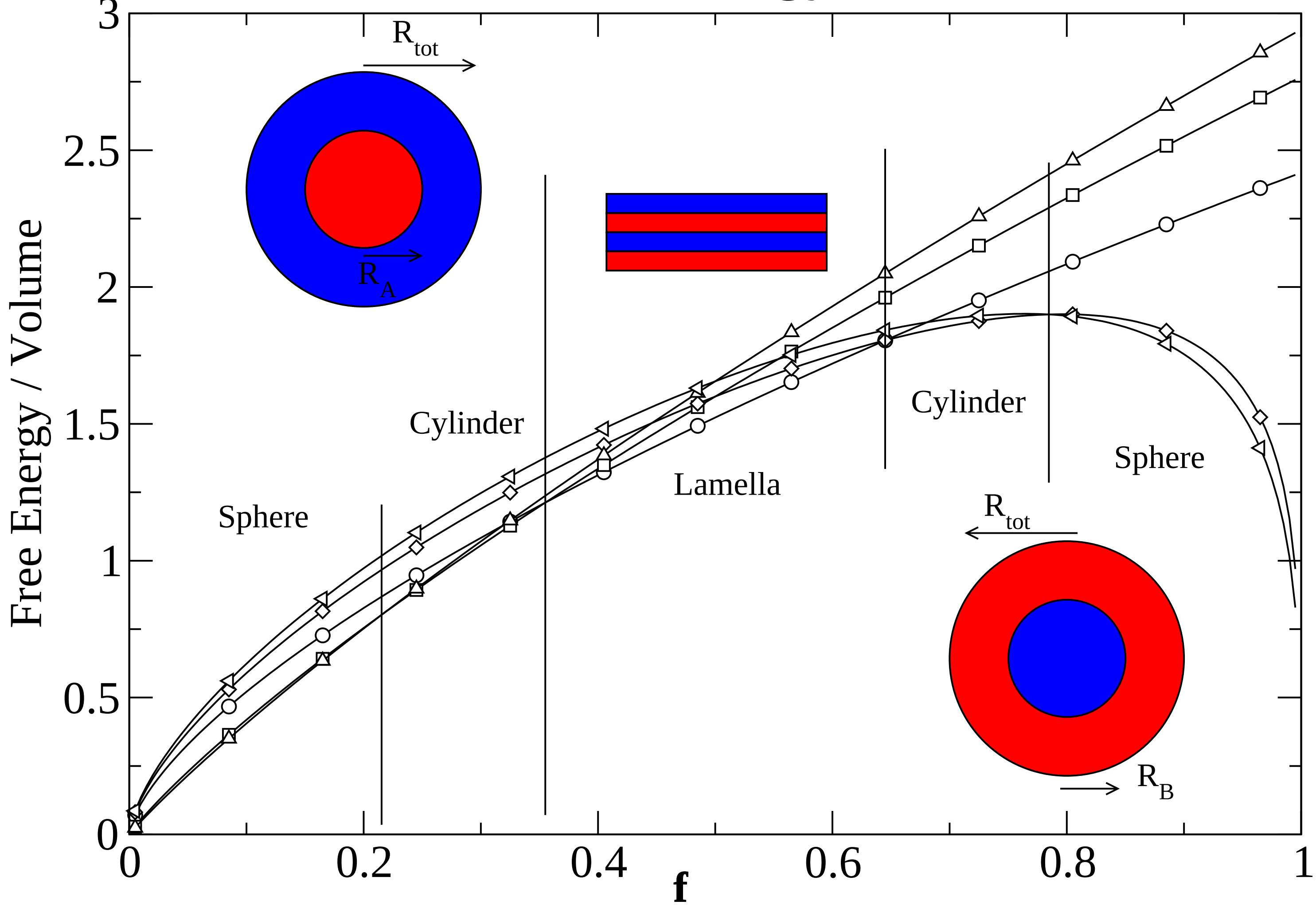


❑ **Peak diverges when**

$$(\chi N)_{spin} = \frac{1}{2f(1-f)} + N\sqrt{\frac{\pi B}{3f(1-f)^3}}, \qquad N\sqrt{B} = \text{charge/chain}$$

- **Strong-Segregation Limit**

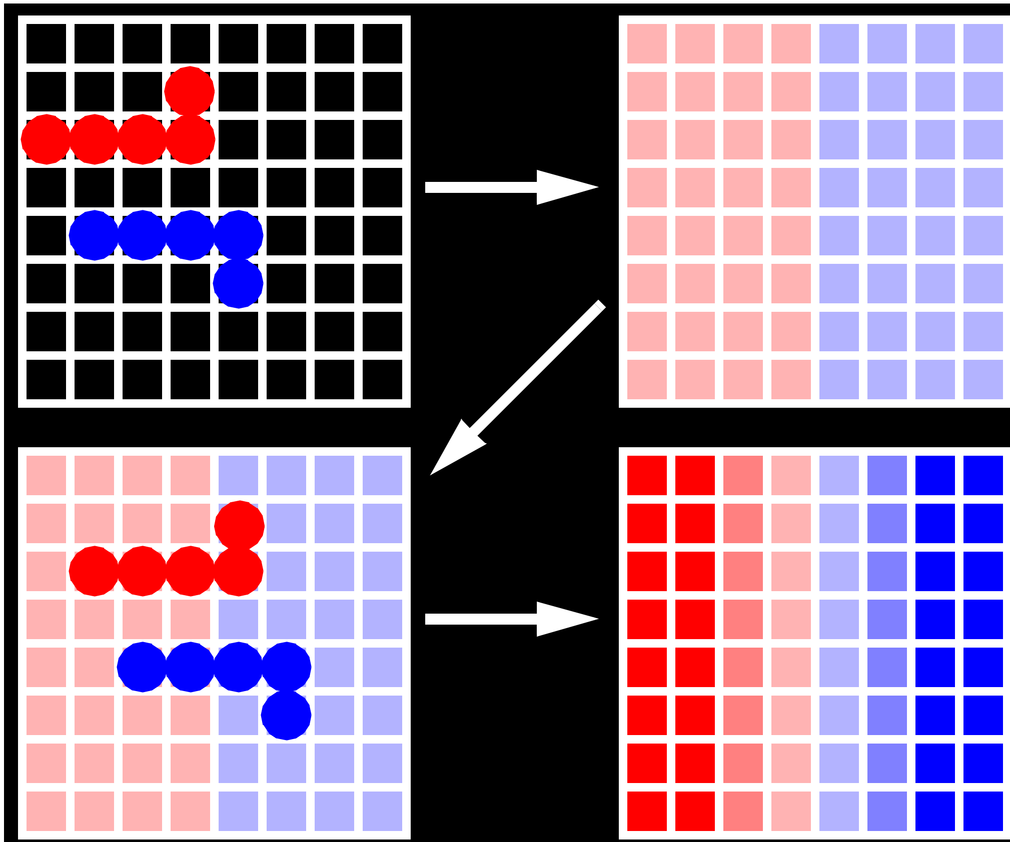
- **Just a balance of surface energy and electrostatics**



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:**

$$\nabla^2\varphi \Rightarrow \varphi(x, y+1) + \varphi(x, y-1) + \varphi(x+1, y) + \varphi(x-1, y) - 4\varphi(x, y)$$

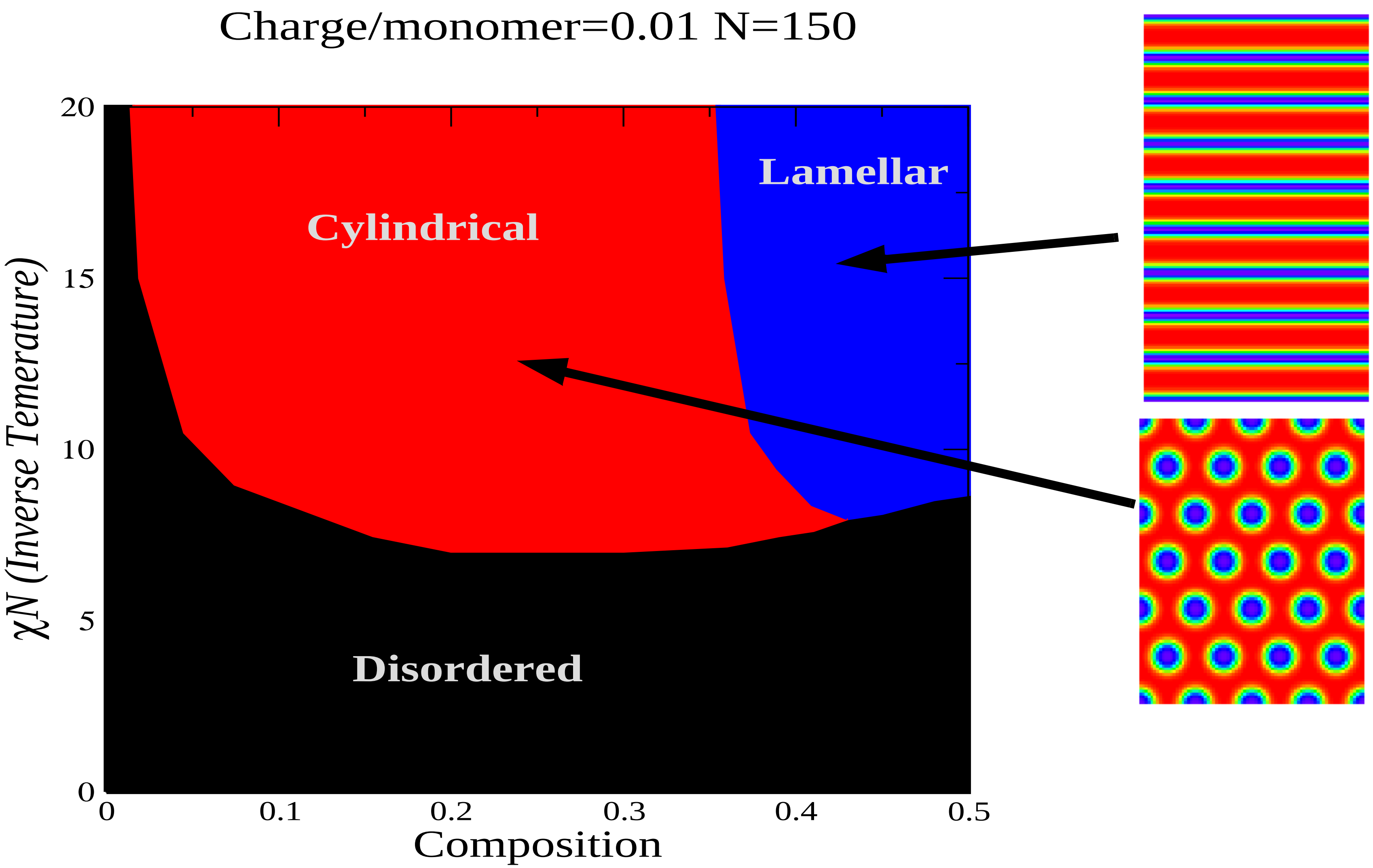
- **Gauss' Law discretized:**

$$\nabla^2\Phi = 4\pi(\rho_A\varphi_A + \rho_B\varphi_B)$$

- **Solve for Φ, electrostatic potential, involves inverting a linear operator on the lattice**

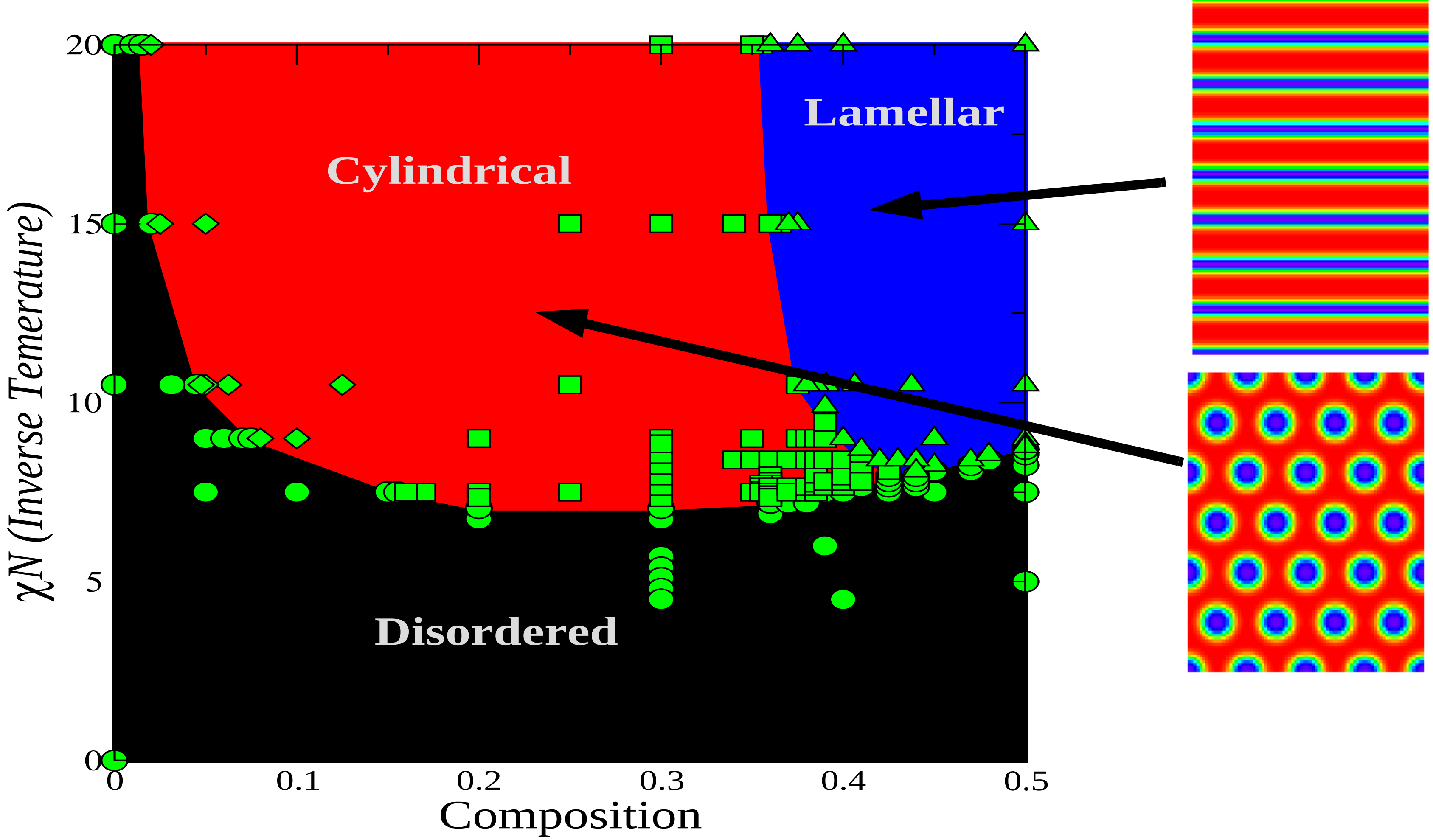
- **Solved numerically at each iteration by direct inversion.**

- **Microphases (just like block copolymers)**

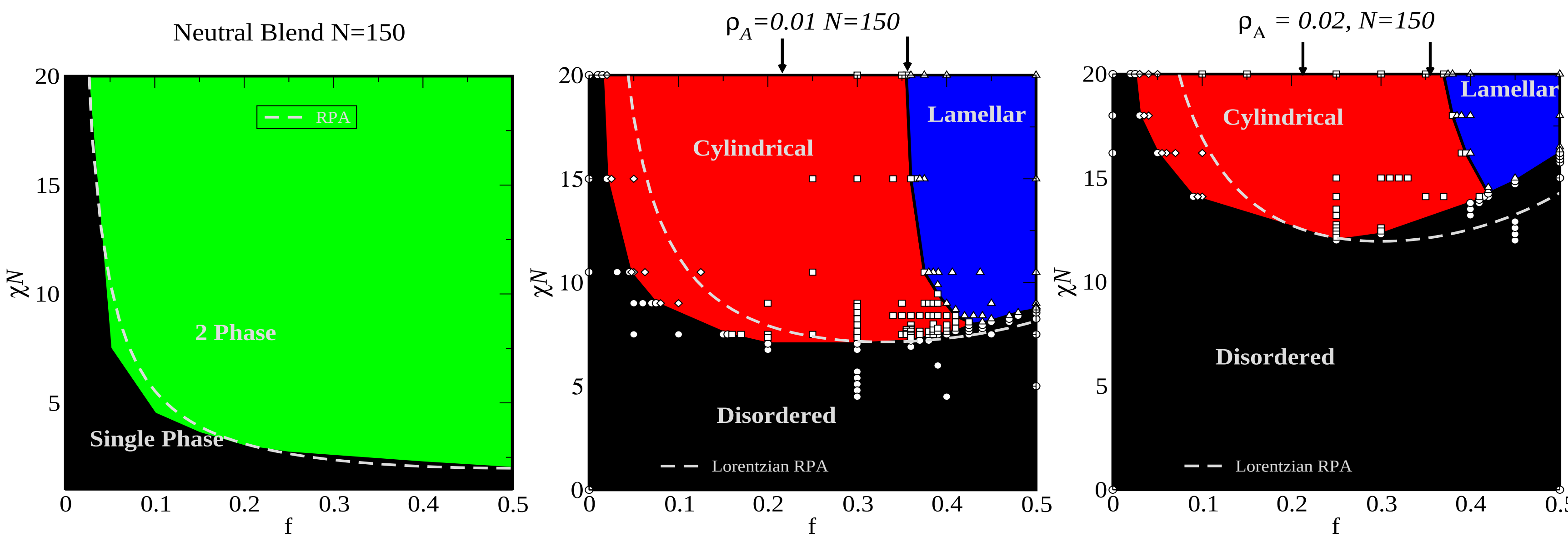


- **Microphases (just like block copolymers)**

Charge/monomer=0.01 N=150



● Charge compatibilizes the blend

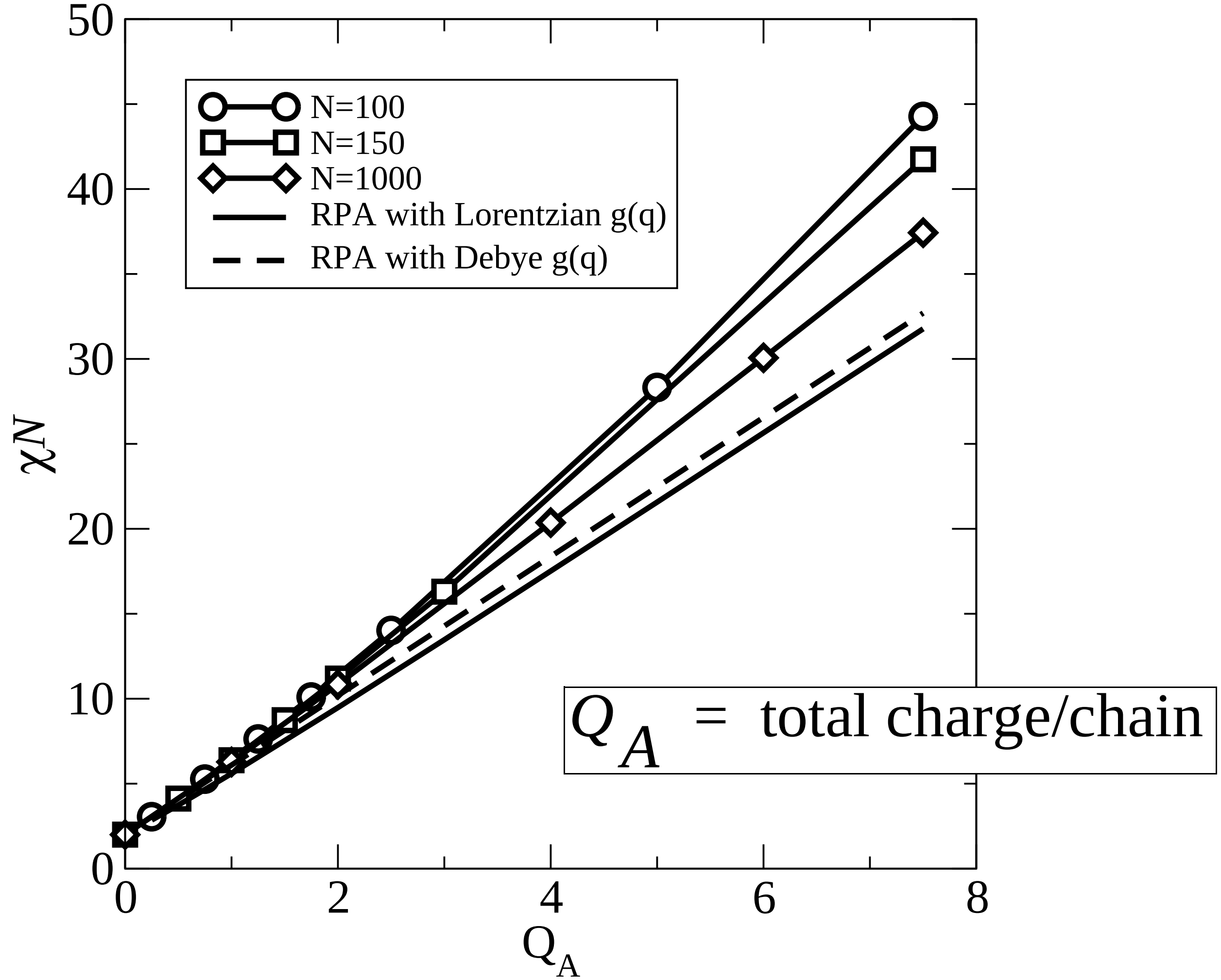


Increasing charge →

- ❑ **Simple architectures (just homopolymers) but complex patterns.**
- ❑ **Long-range vs. short-range, generic physics.**

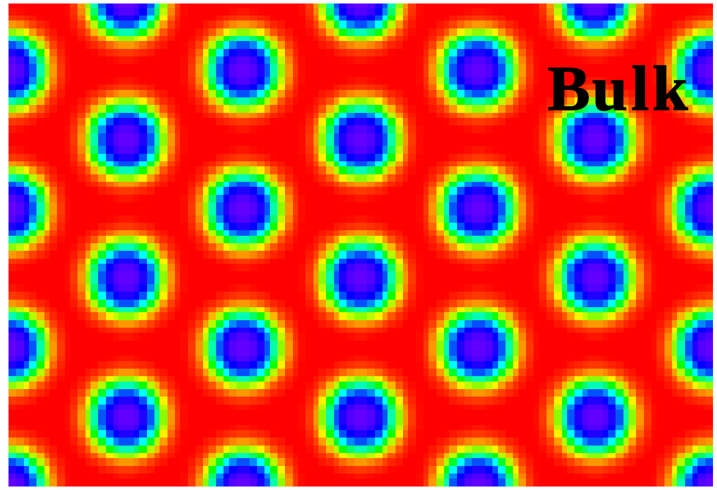
- **Comparison, SCF RPA**

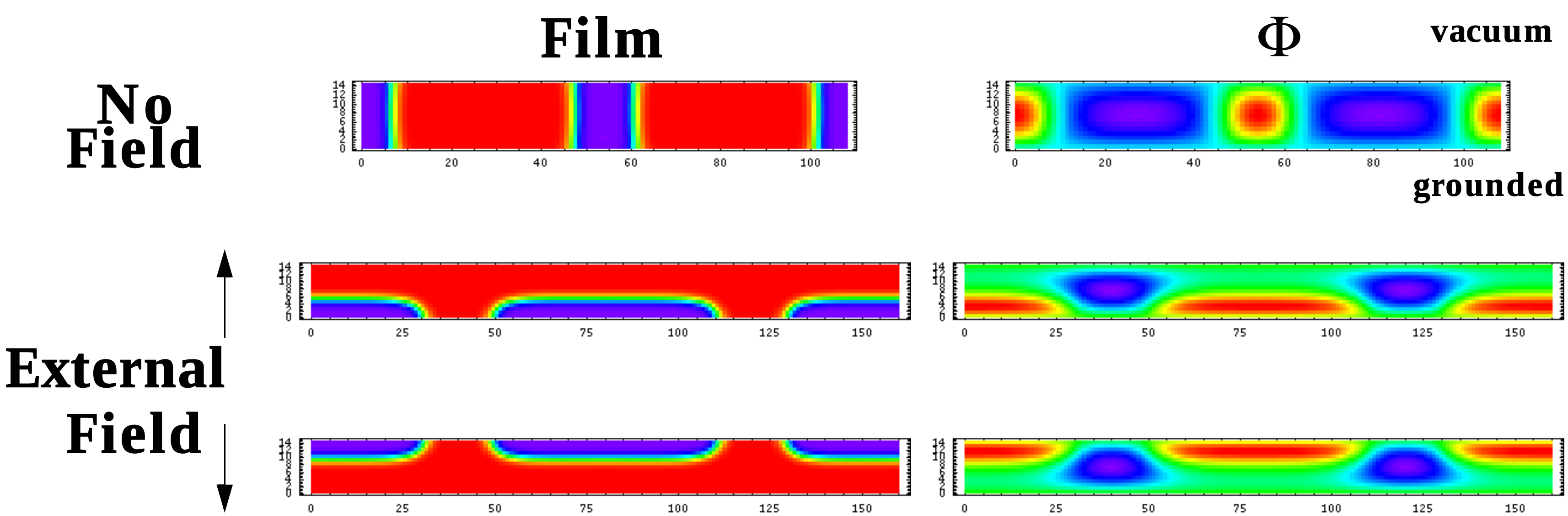
- **Disordered-Lamellar transition for $f = 1/2$:**



• Films

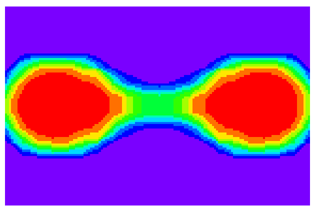
- Lower surface held at a constant potential
- Upper surface is vacuum
- Confinement and external field controls morphology



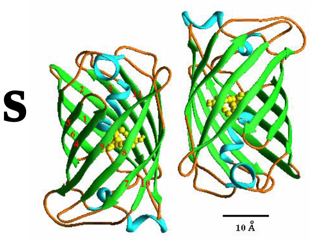


Conclusions

- Single-molecule “beads” generic folding problem



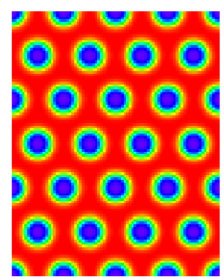
Other foldings

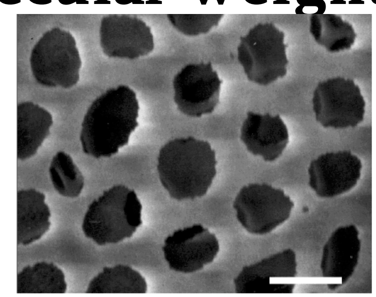


http://www.bioc.rice.edu/Bioch/Phillips/gfpbio.html

- Charged blends make microphases Length scale controlled by charge/chain not molecular weight

  - Photonic crystals?





Imhof and D.J. Pine, Advanced Materials 10, 697-700 (1998).

- Charge-separated layers, Polymer LED’s