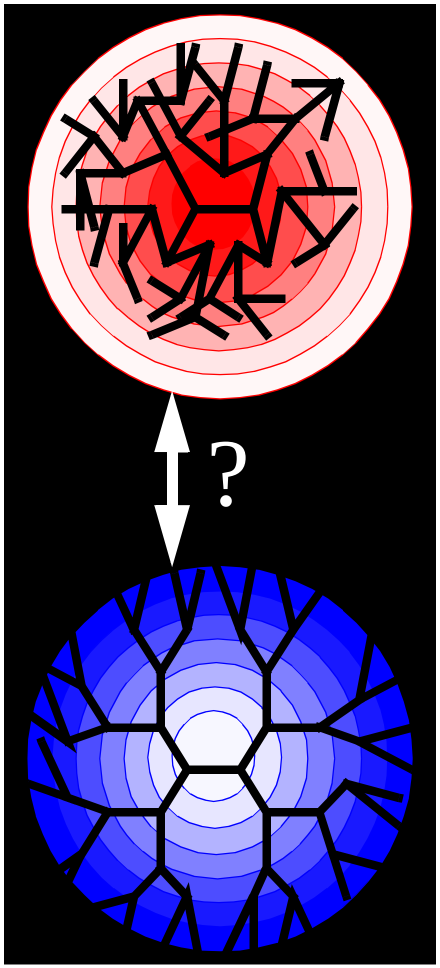

Self-Consistent Field Methods in Polymer Physics

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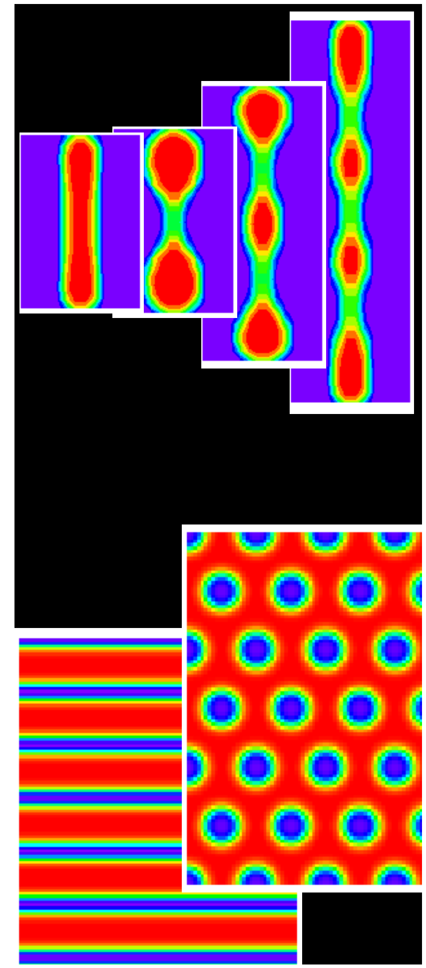
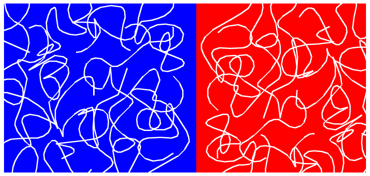
Department of Physics and Astronomy,

California State University Long Beach



- **Stuff we want to do:**

- **Strengthen mixtures of plastics**

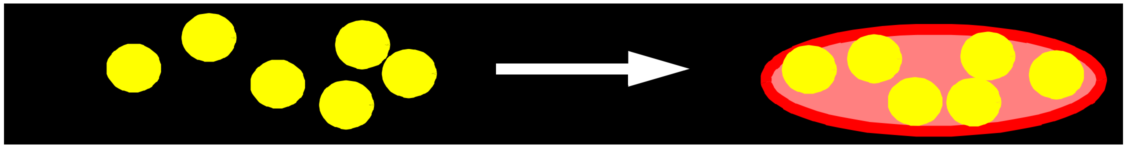


  - Incompatible plastics
  - Combine properties (strength, flexibility)

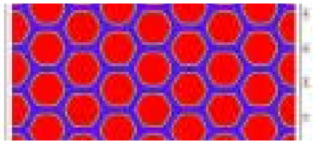
- **Lubricate/protect surfaces**

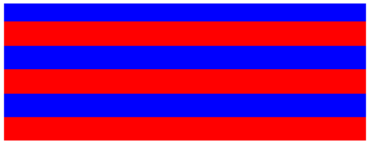
  - Prevent contact
  - Avoid damage

- **Encapsulate drugs**



- **Create patterns**

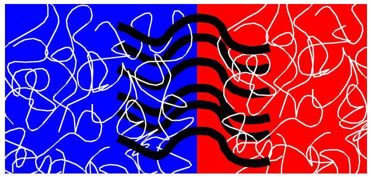




  - Symmetry, scale

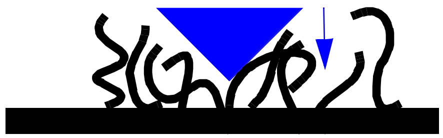
● Stuff that can do it.

- **Stitching polymers: reinforce mixtures**



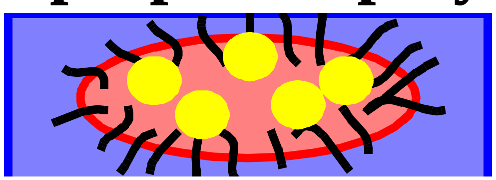
- Half blue / half red reinforces interface.

- **End-grafted polymers: lubrication**



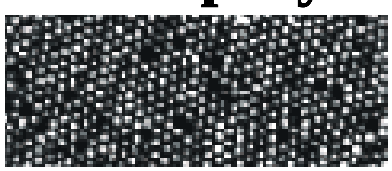
- Trapped coating
- “Osmotic” barrier

- **Amphiphillic polymers: housing for droplets**



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

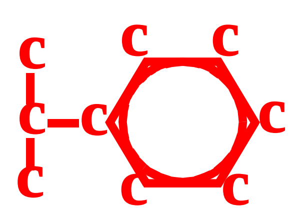
- **Block copolymers: templates for ordering**



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

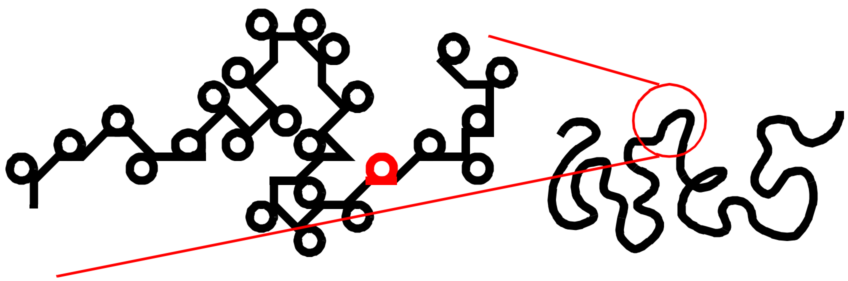
• Polymers

- **Are made of monomers...**



Styrene
104AMU
1nm

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



Polystyrene

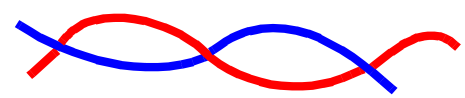
1000 monomers:104,000AMU

$1000 nm = 1 \mu m$

- **... which mostly ignore** h...

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

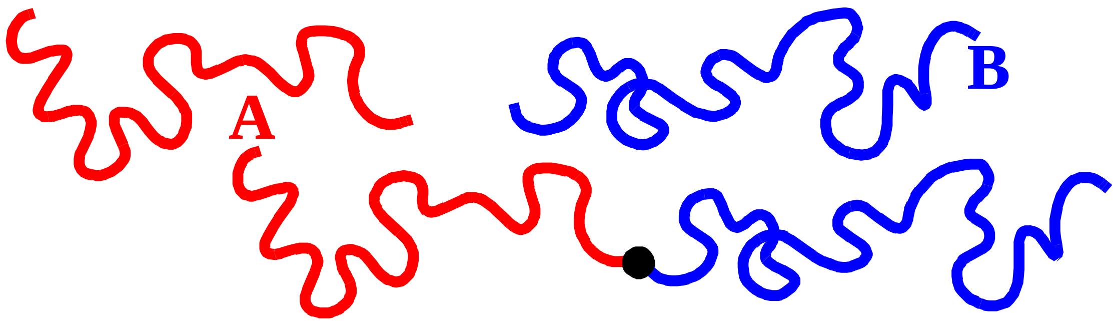
- **... and are all tangled up.**



☞ Entangling, knots

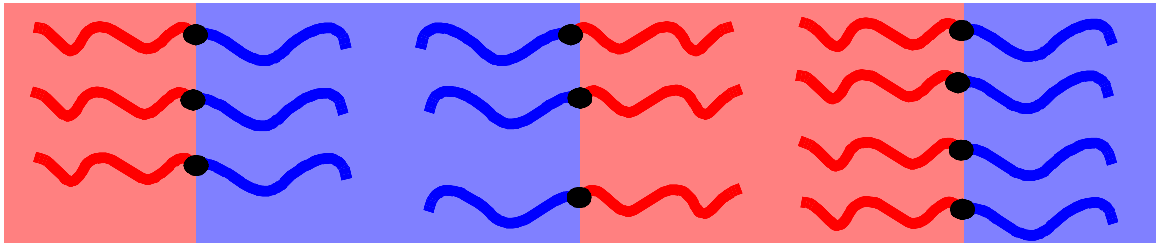
- **Block copolymers**

- **Two kinds of monomers strung together.**



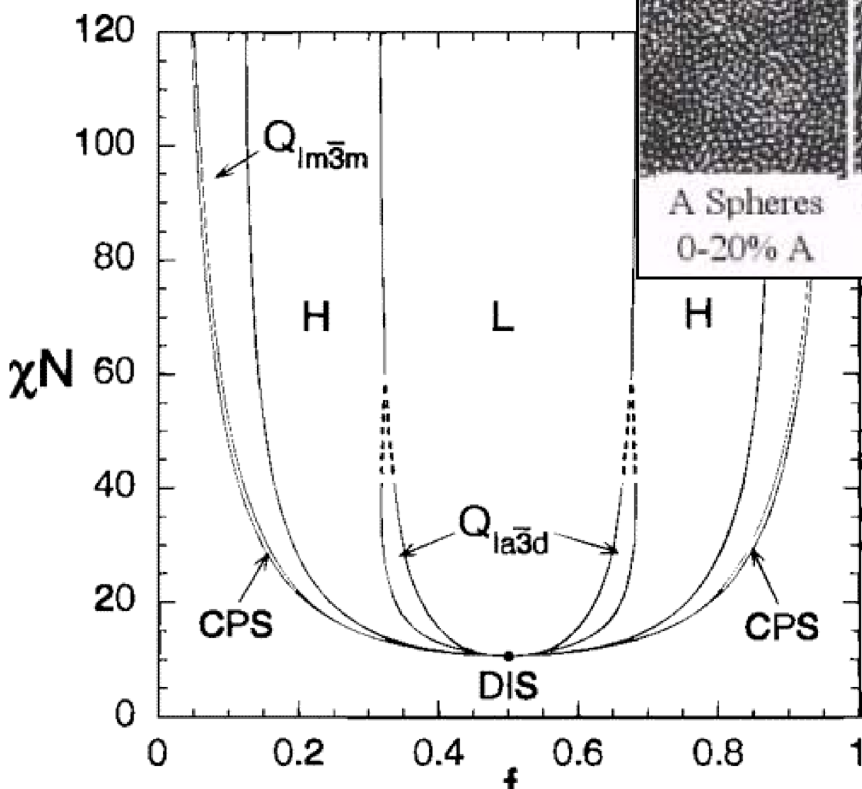
  - A-block and B-block: “diblock”

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

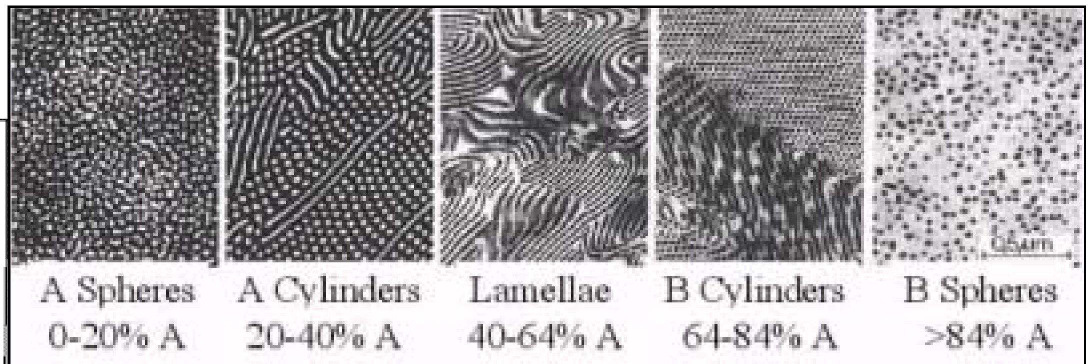


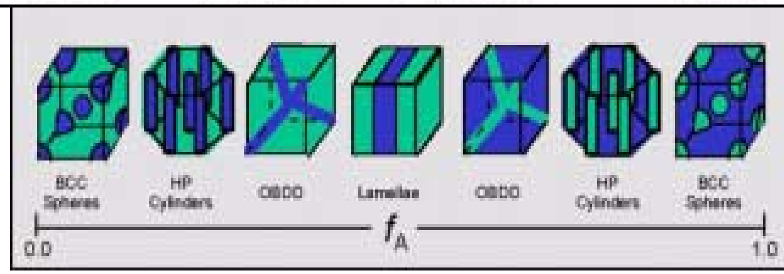
● Asymmetric diblocks

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

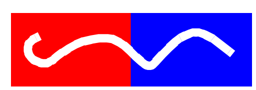


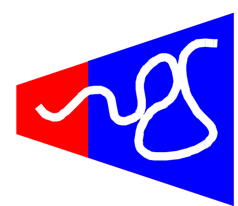
M. W. Matsen and F. S. Bates, Macromolecules; 1996; 29(4); 1091-1098.





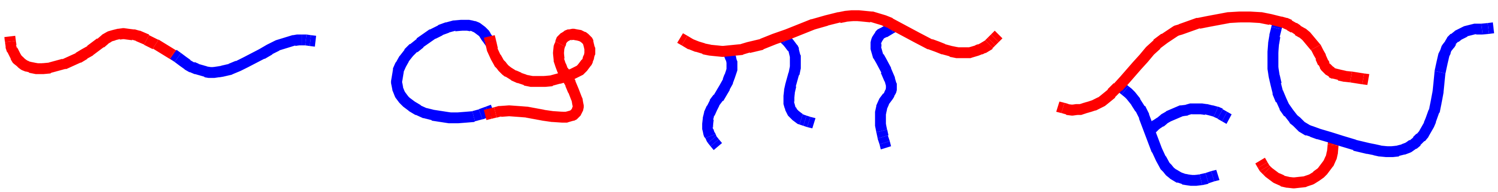
http://www.psrc.usm.edu/mauritz/block.html



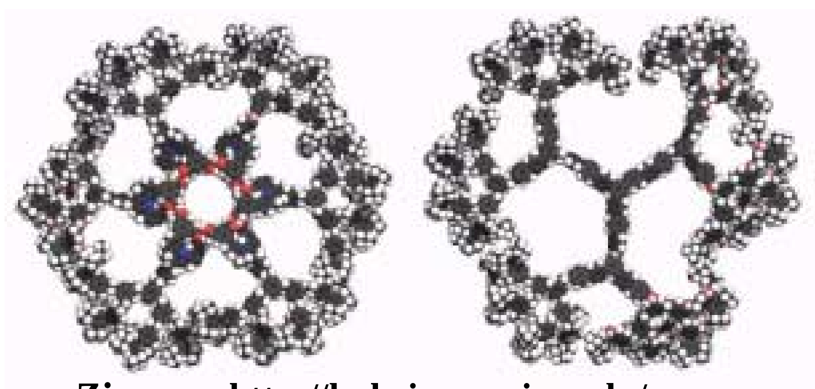


- **Architecture controls properties**

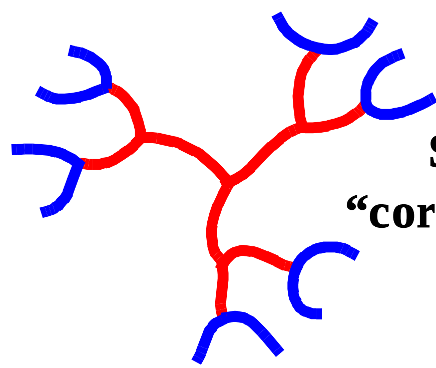
- **Diblocks, composition fraction is only control**
- **Chain topology is also something to consider:**



- **“Starburst” dendrimers**



Zimmer, http://ludwig.scs.uiuc.edu/



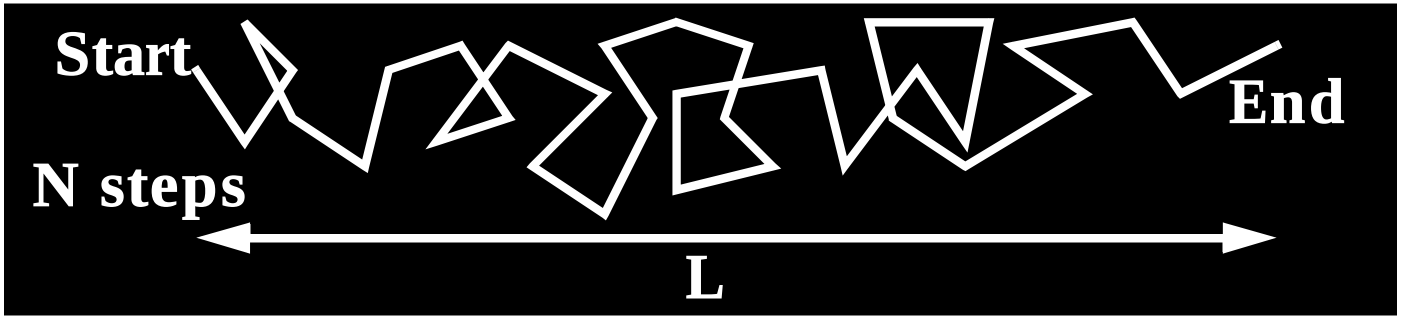
Schematic, G3
“core-shell” copolymer

Outline

- Self-consistent field treatment of complex polymer mixtures
- Applied to dendrimers
- Applied to charged polymers
- Conclusions

- ## Self-Consistent Field

- **Random walk, N steps covering an end-end distance L. How much free energy to bias it?**



- **Apply a force F to each link.**

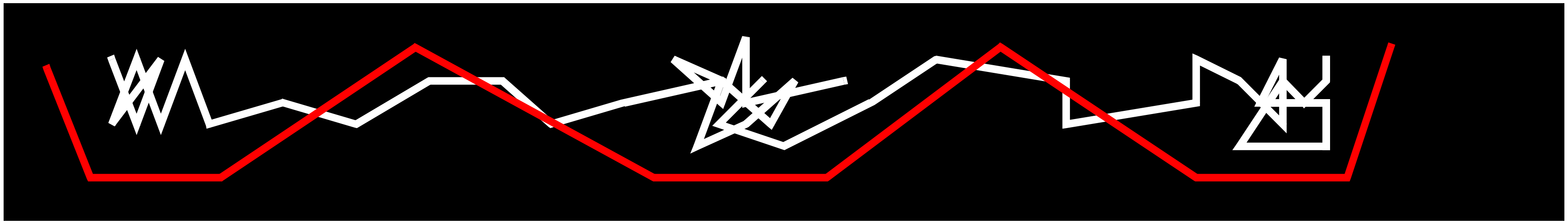
$$force \propto L \qquad\qquad force \propto 1/N$$

Double F, go twice as far **More steps, less force**

- **Work = force *distance:** $\left(\frac{L}{N}\right)L = \left(\frac{L}{N}\right)^2 N$
- **In all:** $S = \int dn \left(\frac{\mathrm{d}l}{\mathrm{d}n}\right)^2$ **, non-uniform stretching.**

- **Random walk in a field**

- **Field biases walk, statistics:**

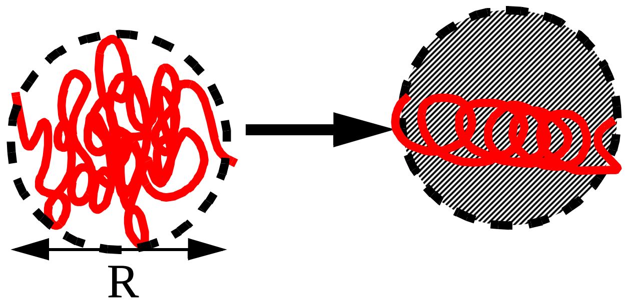


- **Walks are biased toward lower values of monomer chemical potential:** $U(r)$

- **Choose** $U(r)$ **to match some property of the surrounding material**
  - E.g. $U(r) \approx \varphi(r)$, monomer volume fraction, polymer solution.
  - $\varphi(r) \approx$ probability that one of the surrounding biased walks has a monomer at r

- **One polymer by itself, excluded volume**

- **Random walk in a potential:**



- Chain crossings result in an outward pressure
- Chain entropy pulls surface in: effective surface tension:

$$\gamma \approx \frac{(R/N)}{R}$$

- Balance:

$$\frac{\gamma}{R} = \Delta P$$

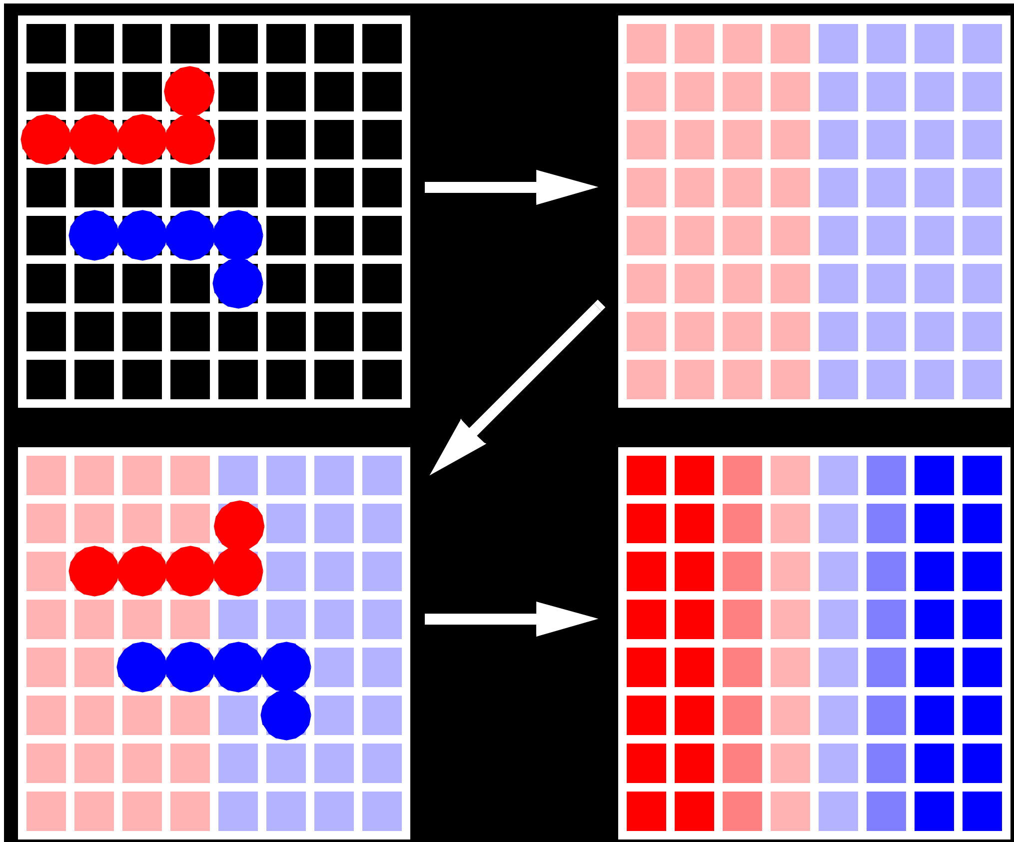
- **Relate ΔP to polymer properties:**
  - 2nd virial approach gives SAW scaling of Flory:

$$\Delta P = c^2 = \frac{N^2}{R^6} \longrightarrow \frac{1}{R}\frac{1}{N} = \frac{N^2}{R^6} \longrightarrow R = N^{3/5}$$

- # Numerical self-consistent lattice calculations

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

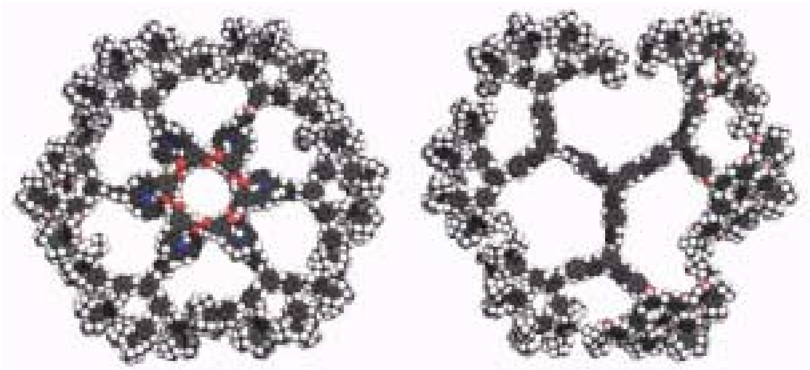
- **Dendrimers, charged blend, lattice electrostatics.**

- **Outline**

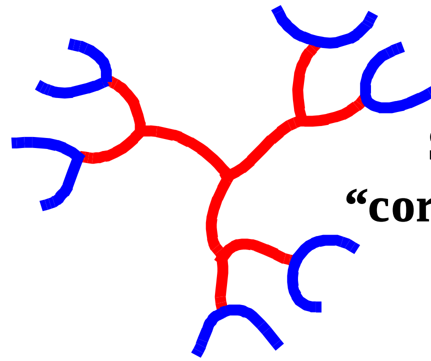
- **Self-consistent field treatment of complex polymer mixtures**
- **Applied to Dendrimers**
- **Applied to charged polymers**
- **Conclusions**

- **Dendrimers**

- **Proliferation of tips on a single molecule:**



Zimmer, http://ludwig.scs.uiuc.edu/



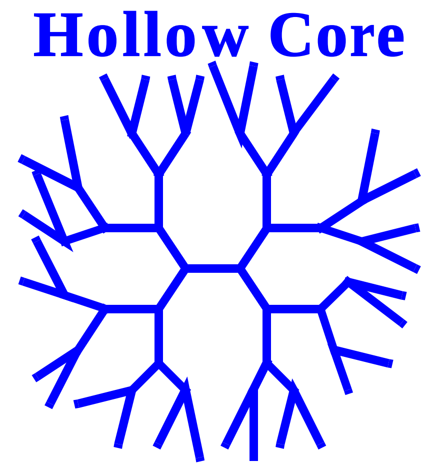
Schematic, G3
"core-shell" copolymer

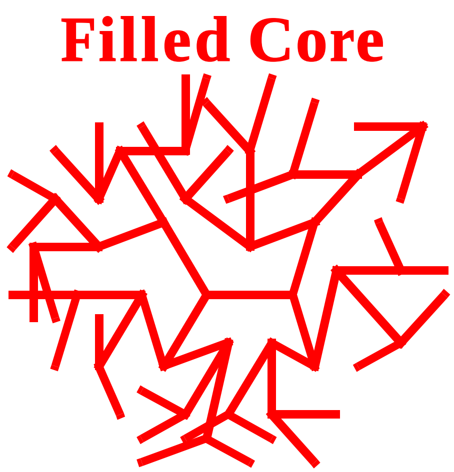
- **Complex self-organization for a single molecule**

- **Applications depend on**
  - Monomer density
  - Location of tips

Hollow or Filled Core?

- **Hervet and deGennes**
  - Long, flexible spacers
  - Tips segregate spontaneously
  - Drug delivery
- **Lescanec and Muthukumar**
  - Short spacer simulation
  - Tips dense in center
  - Monomers dense in center





● Other theories, experiments support Filled core

deGennes, Hervet *J. Phys. (Paris)* **44** L351, (1983)

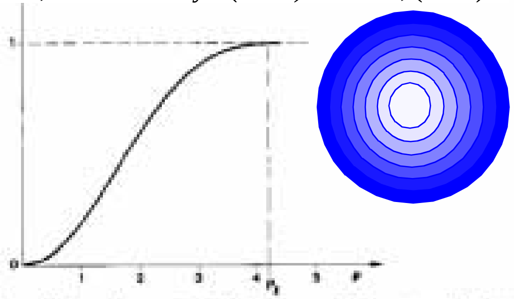


Fig. 3. — Concentration profile in starburst molecules. Notice the parabolic form at small distances ρ, and the stopping point at $\rho = \rho_1 \cong 4.1$. Because of the -NH_2 groups present at the last generation, the physical limiting radius R_1 is somewhat larger than $Pa\rho_1$: see equation (21).

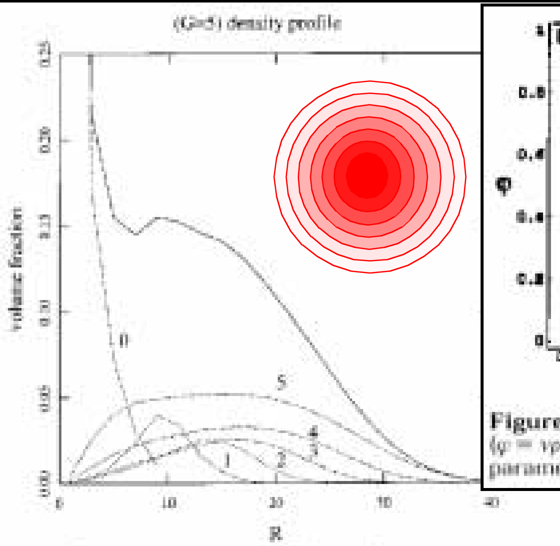


Figure 6. Radial density profile of the $G = 5$ model dendrimer.

Mansfield, *Macromolecules* **33** 8043 (2000).

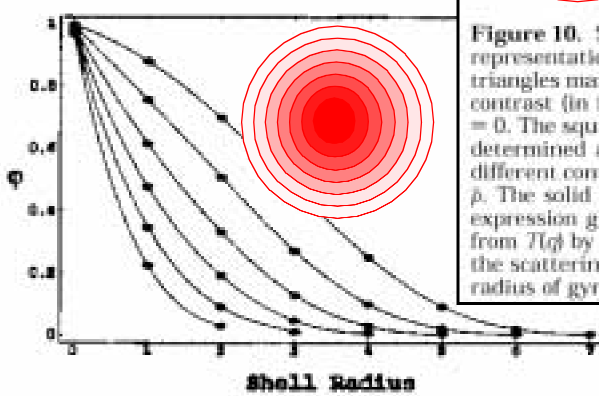


Figure 8. Density profile $\rho(j)$ of starbursts: volume fraction ($\varphi = v\rho(j)$) as a function of radial distance for excluded volume parameter $v' = 0.5l^3$ for starburst of generation $g = 2-7$.

Boris, Rubinstein *Macromolecules* **29** 7251 (1996)

Potschke, *et al.* *Macomolecules* **32** 4079 (1999)

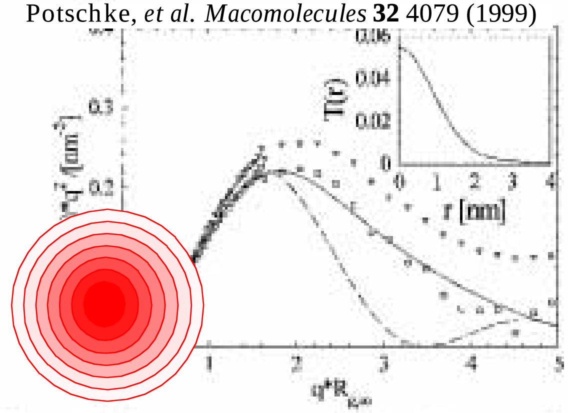


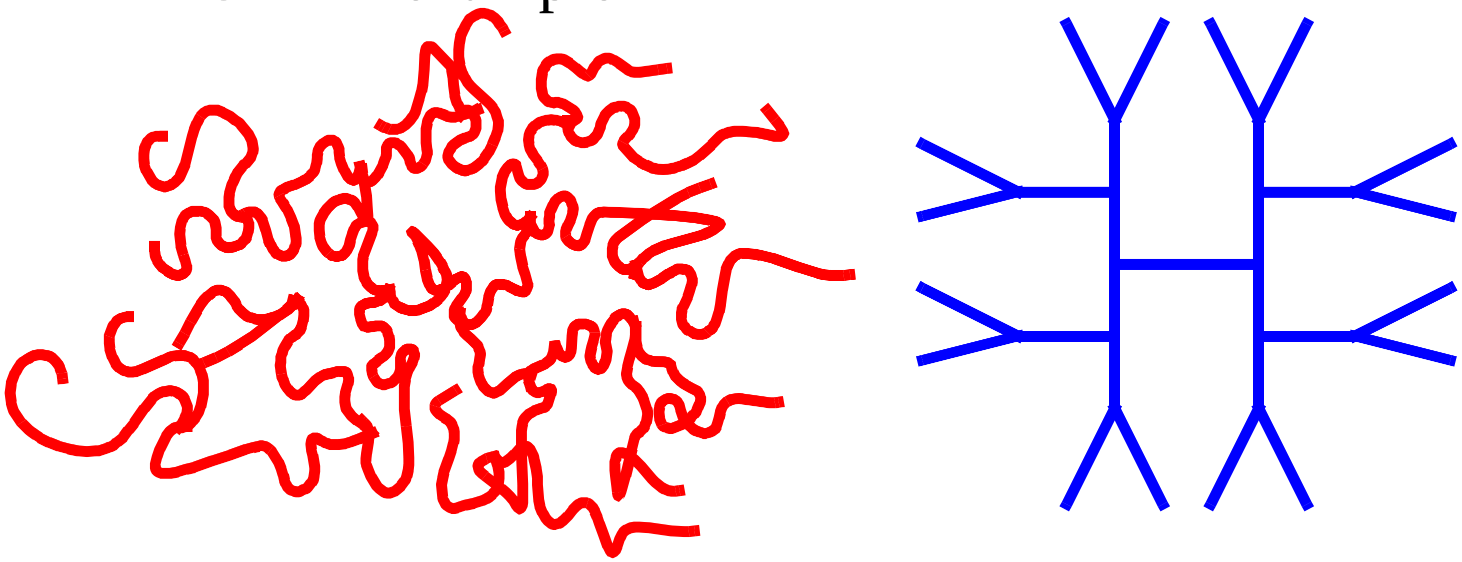
Figure 10. Scattering intensities of the dendrimer in Kratky representation vs magnitude of scattering vector q. The triangles mark the scattering intensities measured at highest contrast (in fully deuterated DMA) normalized to unity at $q = 0$. The squares give $(\bar{\rho} - \rho_m)^2 T^2(q)$. The latter part has been determined according to eq 8 from measurements taken at different contrast using the average scattering length density $\bar{\rho}$. The solid line gives the best fit of the latter term by the expression given by eq 21. The inset displays $T(r)$ obtained from $T(q)$ by Fourier inversion of eq 21. The dashed line gives the scattering intensity of a homogeneous sphere having the radius of gyration $R_{g,\infty}$.

❑ **Look at hollow-core model again**

- **a-la Hervet and deGennes:**

- ***G* generations, flexible spacers of *N* monomers**

  $G = 4$ example

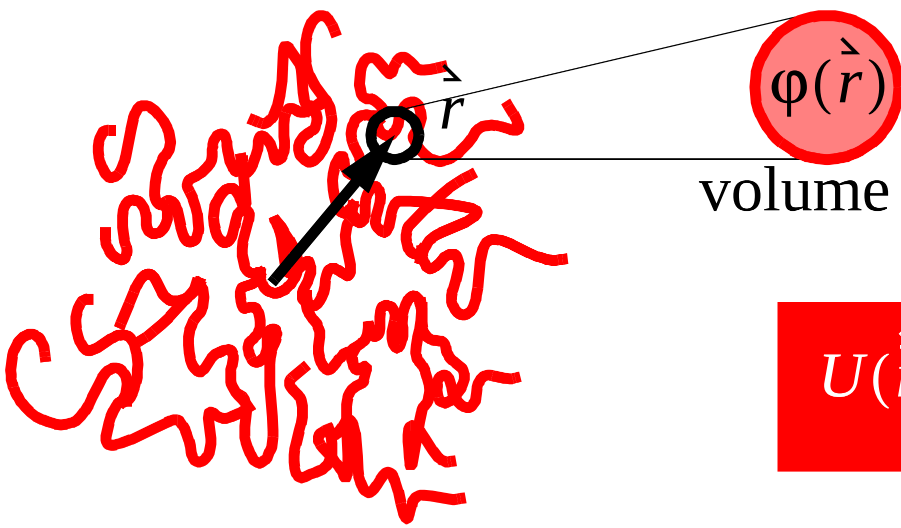


- **Excluded volume and chain entropy are the only effects in the Hervet and deGennes calculation**

- **Excluded volume:**

- **2nd virial, mean-field approach:**

Energy to insert a monomer at $\vec{r}$: $U(\vec{r})$



ensemble average
volume fraction of monomers at $\vec{r}$

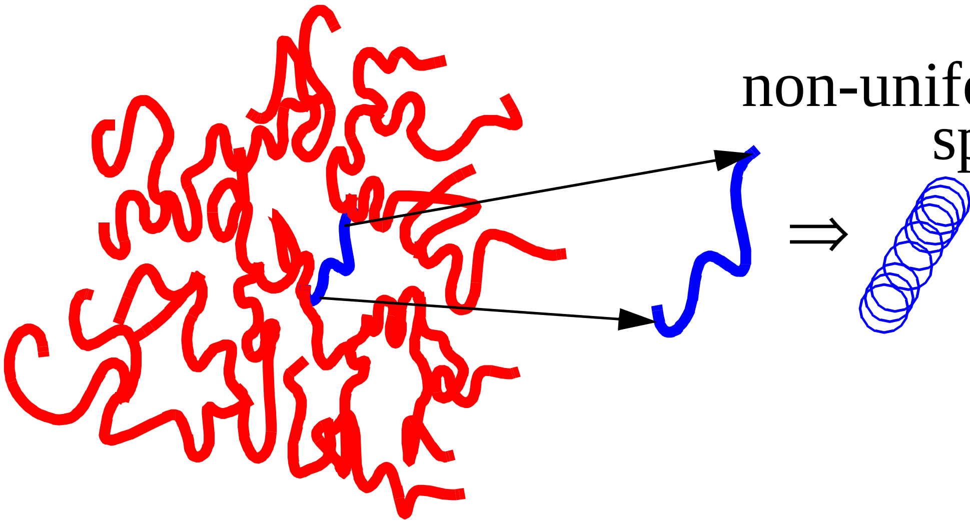
$$\boxed{U(\vec{r}) = v_o \varphi(\vec{r})}$$

- **Total excluded volume free energy:** $E = \sum_n U(\vec{r}_n)$

- **What is the correct** U**, or** φ**?**

Chain entropy

- **Gaussian chain segments:**

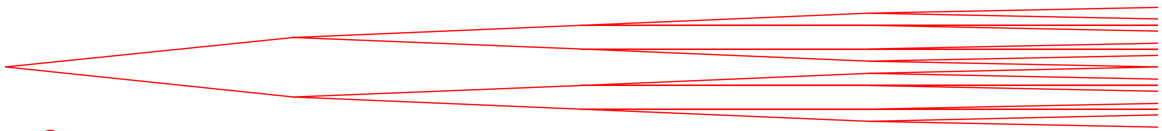


$$S = \sum_n \left\| \frac{\Delta r}{\Delta n} \right\|^2$$

- **Total free energy:** $F = E + S = \sum_n \left(\left\| \frac{\Delta r}{\Delta n} \right\|^2 + v_o \varphi(\vec{r}) \right)$
  - Self-consistent loop: Find $\vec{r}(n)$ minimizing $F[r]$, find $\varphi(\vec{r})$, repeat.

- **Further Approximations**

- **Chemical index n and weighting factor $f(n)$:**



- **Free energy, saddle point**

$$F[r] = \int_0^{GN} f(n)\left[\left\|\frac{dr}{dn}\right\|^2 + v_o \varphi(r)\right] dn$$

$$-\frac{d}{dn}\left[f(n)\frac{dr}{dn}\right] + f(n)\frac{d\varphi}{dr} = 0 \qquad \Rightarrow \frac{d^2r}{dn^2} - b\frac{dr}{dn} + v_o\frac{d\varphi}{dr} = 0$$

- **Minimizing F gives an ordinary differential eq.**

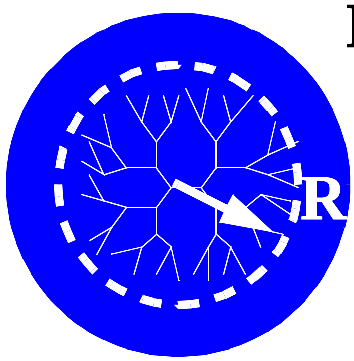
- **But, still need $\varphi(r)$**

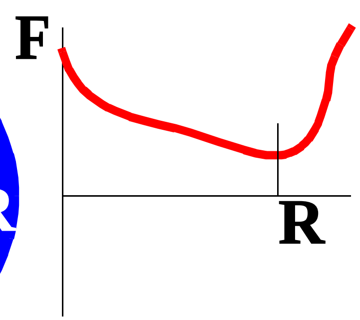
- **Hervet and deGennes make an approximation:**

$$\varphi \approx \frac{f(n)}{dr/dn}$$

- Multiply number of equivalent chain segments by
- Monomer density along a single stretched strand
- BUT, need a unique $r(n)$

- **Ok...**



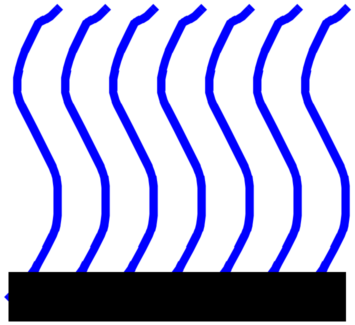


- **... if a single chain conformation dominates F.**

- **Gives $\varphi(r)$ growing strongly out to edge of dendrimer.**

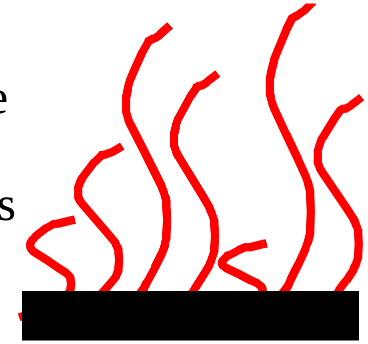
- **Polymer and Dendrimer Brush**

- **Polymer brush, no branchings:**

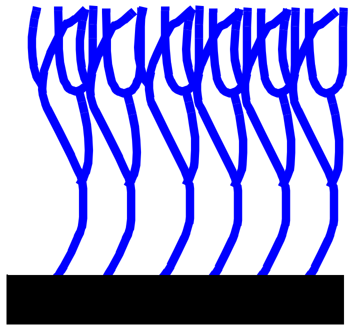


- φ is constant
- Tips segregated
- Scaling
- Not self-consistent

- φ is parabolic
- Ends everywhere
- Self-consistent
- Monodispersity is key constraint
- F is uniform



- **Dendrimer brush quite similar:**



- φ is large at free surface
- Tips segregated
- Scaling
- Not self-consistent

- φ is still parabolic
- Ends everywhere, concentrated at grafting surface
- Self-consistent
- Monodispersity is key constraint

- **Parabolic φ, densest at grafting surface.**

- **Parabolic $\varphi(r)$ is Correct for Dendrimers**

- **1st order Linear ODE to solve:**

$$\frac{d^2 r}{dn^2} - b\frac{dr}{dn} + v_o r(n) = 0$$

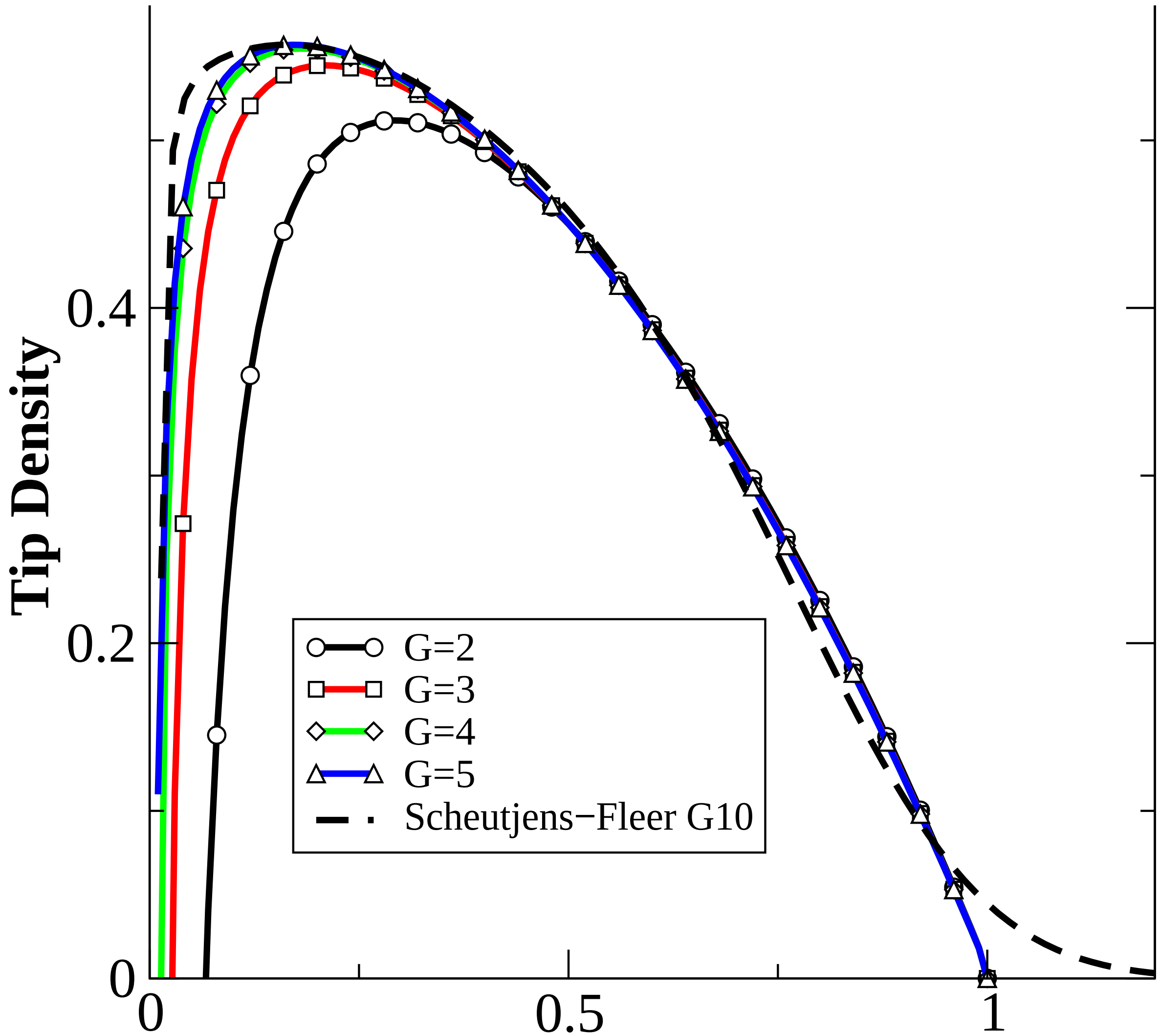
- **Given $r(n)$ satisfying this ODE, with $r(0) = R, r'(0) = 0$ can calculate restricted free energy:**

$$F[R] = \int_0^{GN} f(n)\left[\left\|\frac{dr}{dn}\right\|^2 + v_o\varphi(r)\right]dn = \text{constant}$$

- **Dendrimer conformation is a result of many nearly degenerate conformations, spreading the tips from the center out to the edge**

- **Results**

- **End density calculated self-consistently for $G \geq 5$:**

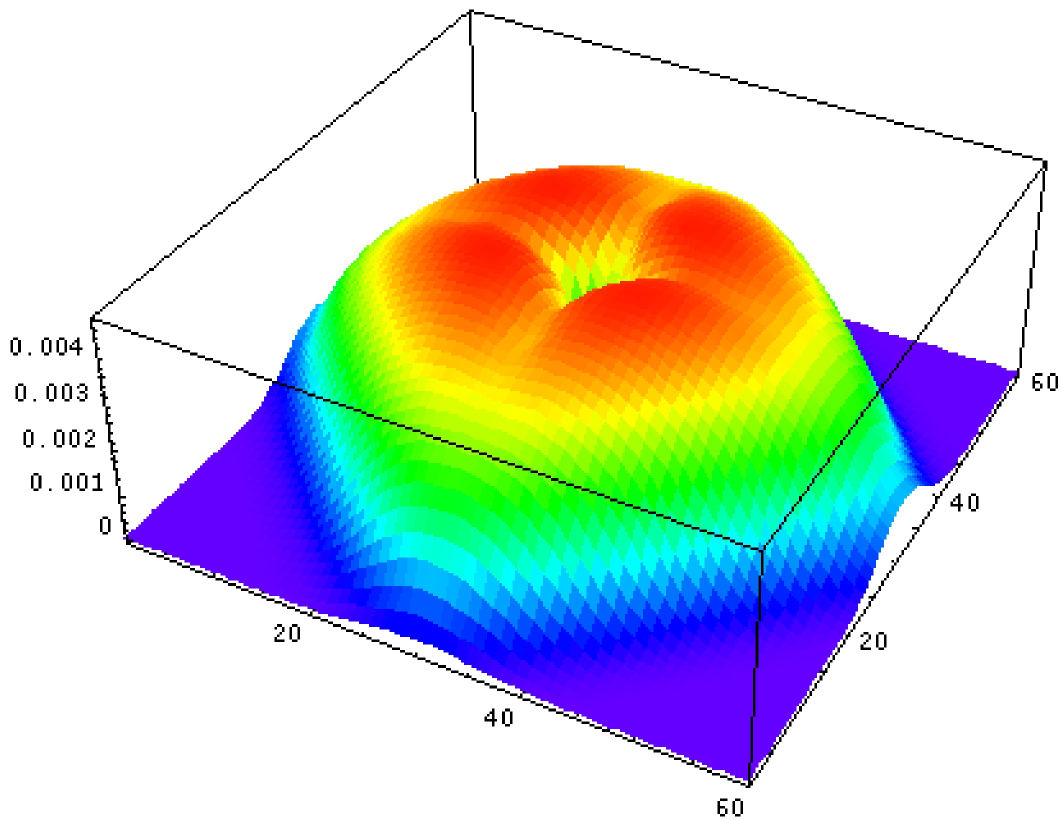


Zook, Pickett *Phys. Rev. Letts*, in press 2003.

http://www.csulb.edu/~gpickett/zook.pdf

- **Interesting Structures Not in Theory**

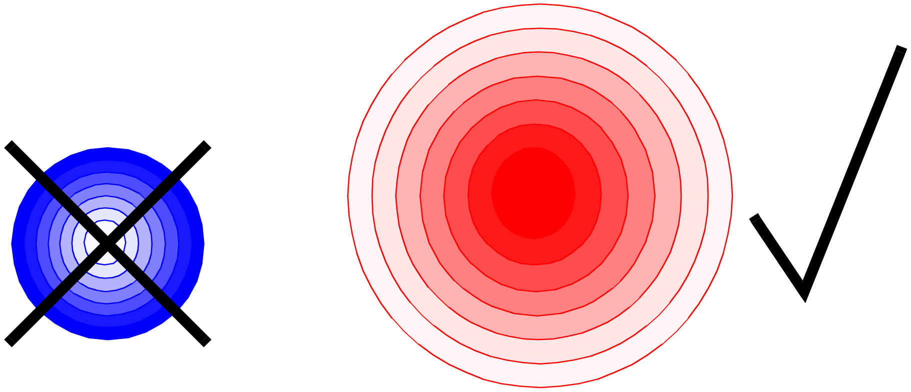
- **Short spacers give distinctly non-parabolic density/ density of tips:**
- **N=4, G=8, 2D Scheutjens and Fleer calculation**



- Tip density shows internal structure, void near center.
- NOT the "long-chain, Gaussian limit" of the analytic theory.
- Excluded volume and topology of chain

Conclusion

- Hervet and deGennes model predicts Filled Core, not hollow core, when assumptions are relaxed.
- All simulations give filled core.
- Experiments, too.
- Filled core is IT.

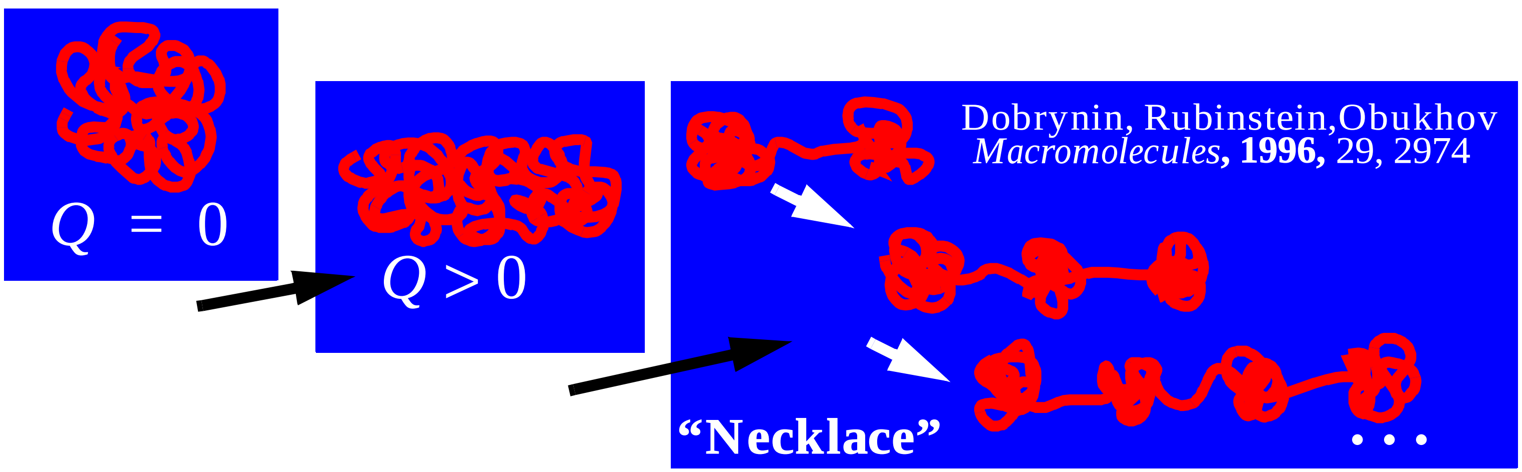


Outline

- Self-consistent field treatment of complex polymer mixtures
- Applied to Dendrimers
- Applied to charged polymers
- Conclusions

- **Polyelectrolyte, poor solvent**

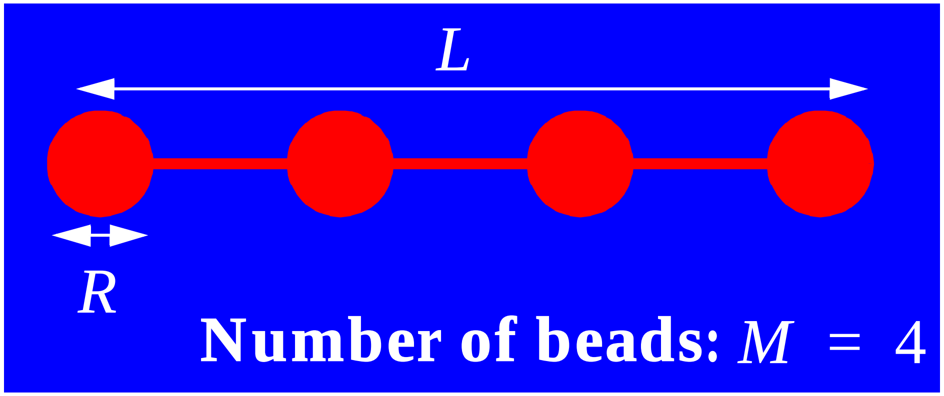
- **Fixed charge** $Q = \alpha N$ **on a flexible polymer,** N **monomers.**
- **Poor solvent:**
  - Q, N control conformation.



- **Cascade of transitions.**

Cartoon theory

- **Free energy of necklace conformation:**

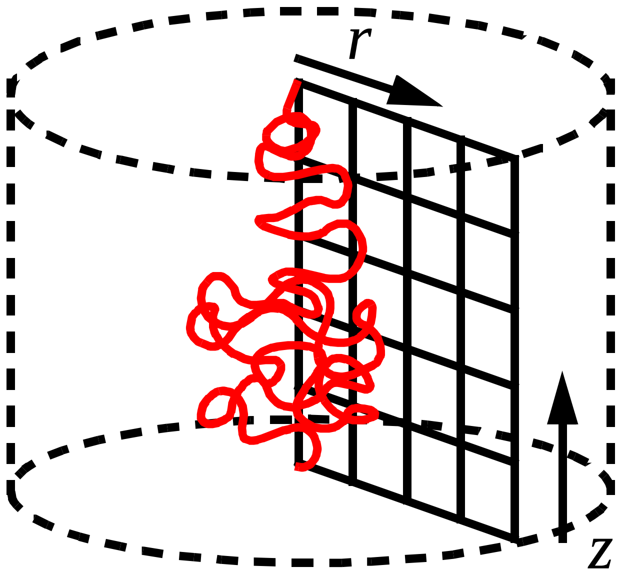


$$F = M\left(\gamma R^2 + \left(\frac{Q}{M}\right)^2 R^{-1}\right) + L\gamma + \frac{Q^2}{L}$$

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

- **2-D Cylindrical lattice**

- **Azimuthal symmetry:**

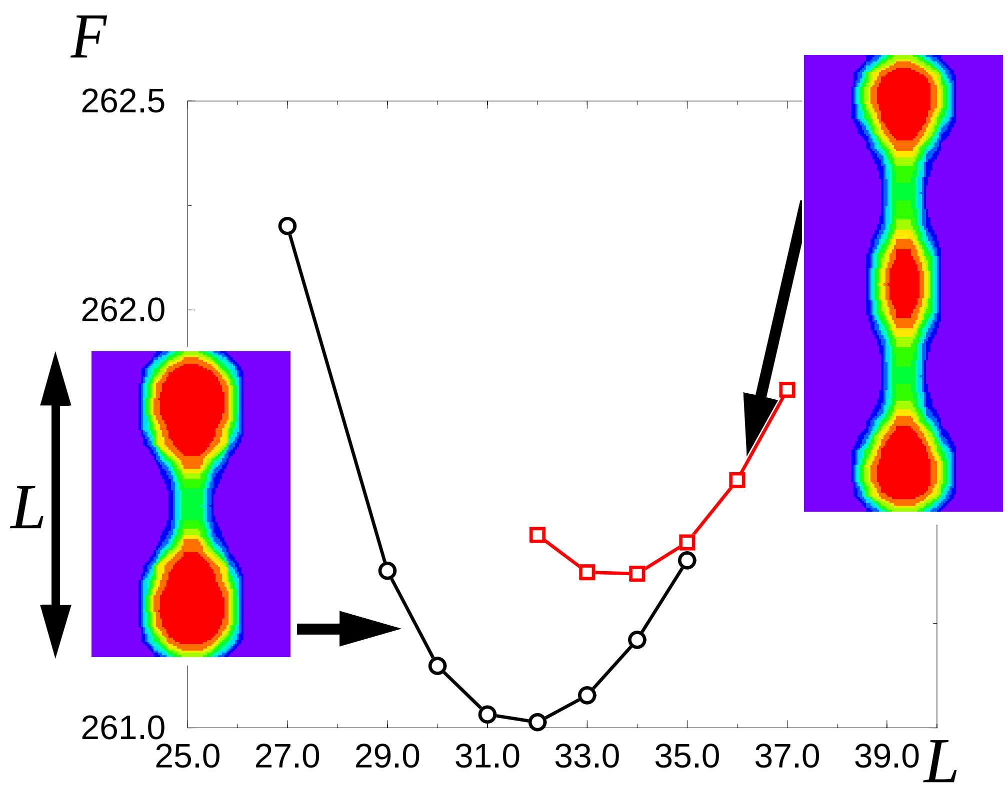


- r,z label annular section of three dimensional space.
- Polymer is held at center of top and bottom plate “bridging”
- Electrostatics, surface energy, chain connectivity are all accounted for

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

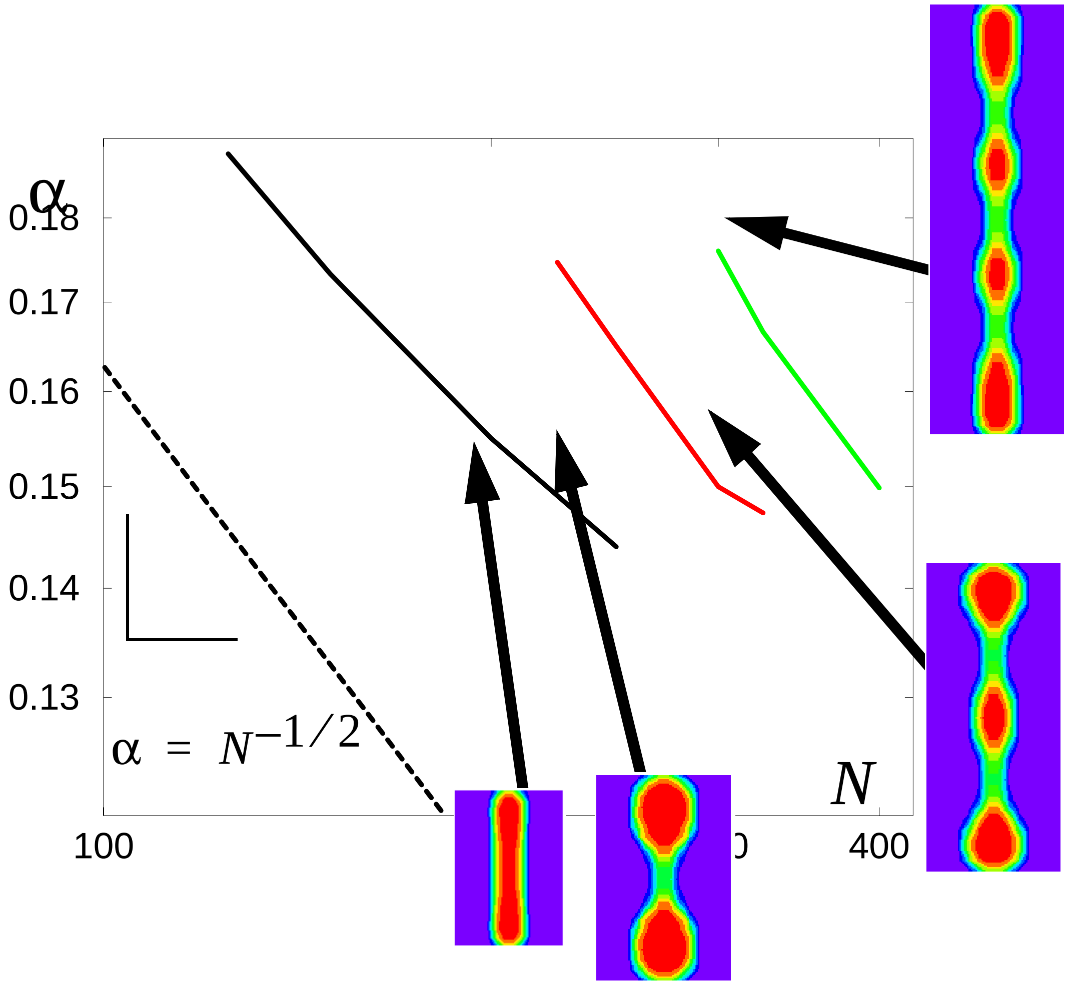
- **Compare structures:**

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



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

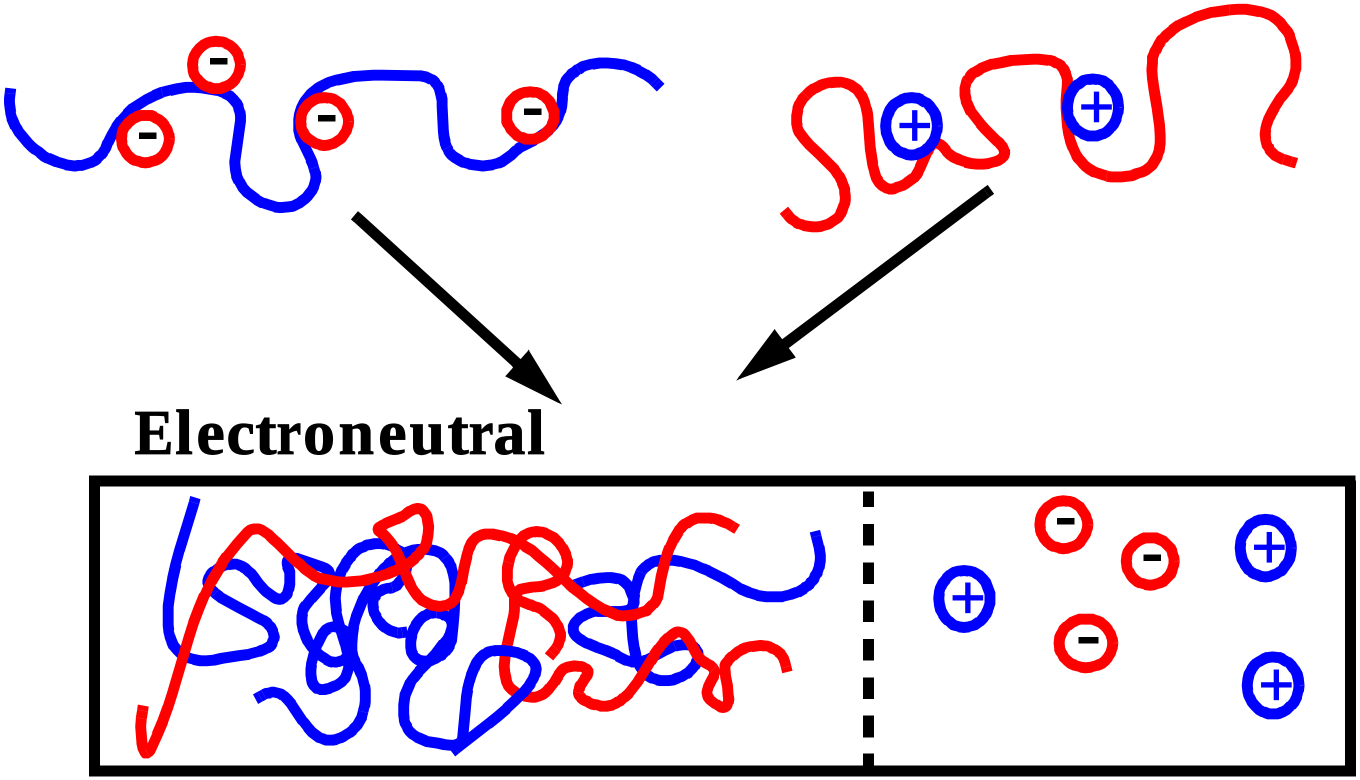
● Diagram of states:



❑ **“Folded” conformations.**

- **Blend of polyelectrolytes:**

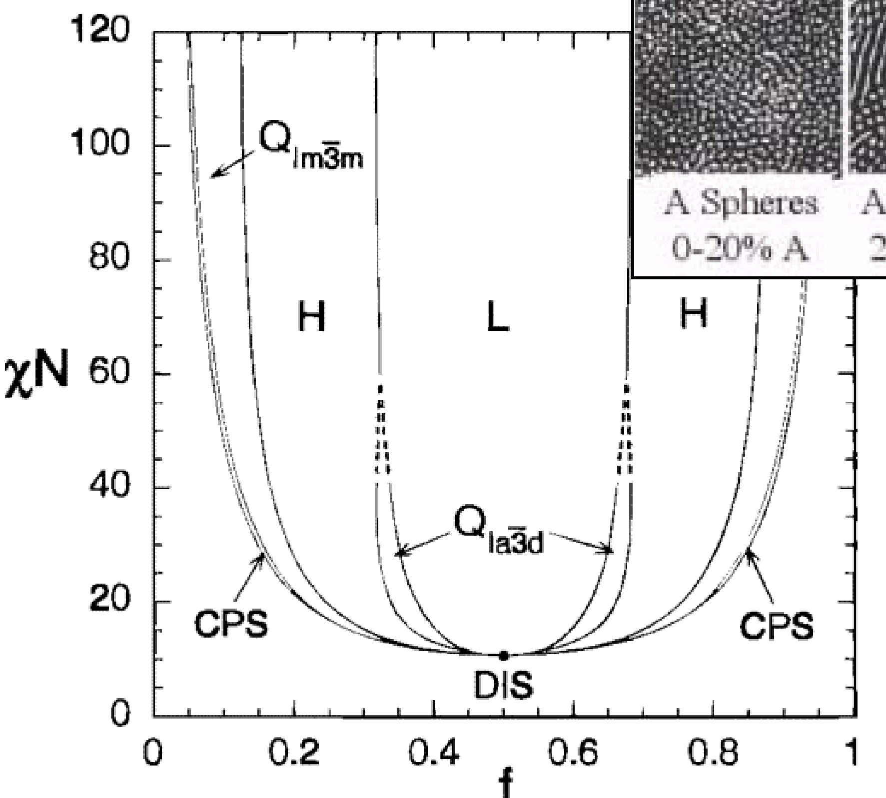
- **Polycation and polyanions mixed together:**

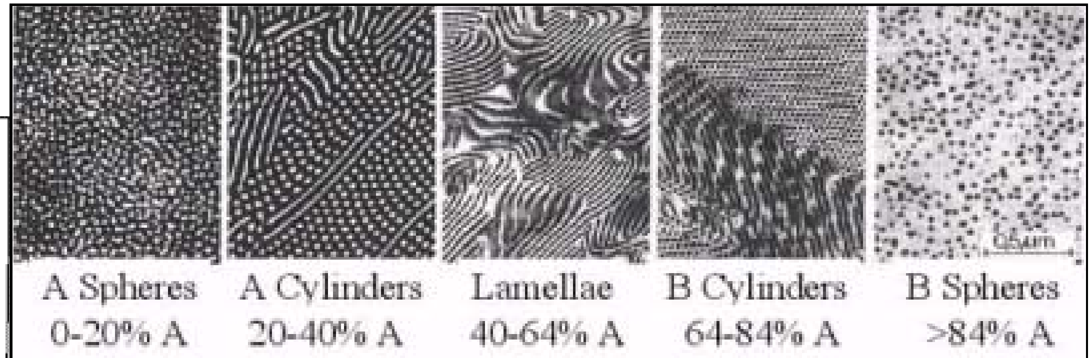


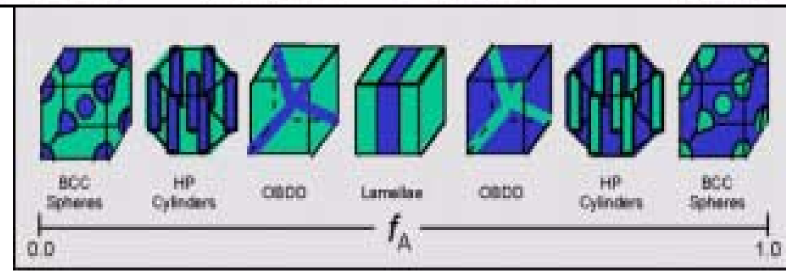
- **Poly-salt melt... what might it do. Phase separate?**

- **Asymmetric diblocks**

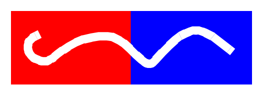
- ***f*= fraction of A on molecule, controls symmetry:**

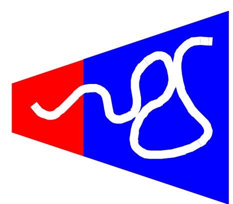






http://www.psrc.usm.edu/mauritz/block.html





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

Coarse-grained Free Energy for Diblocks

- **Local interactions**

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

- **Long-ranged interactions**

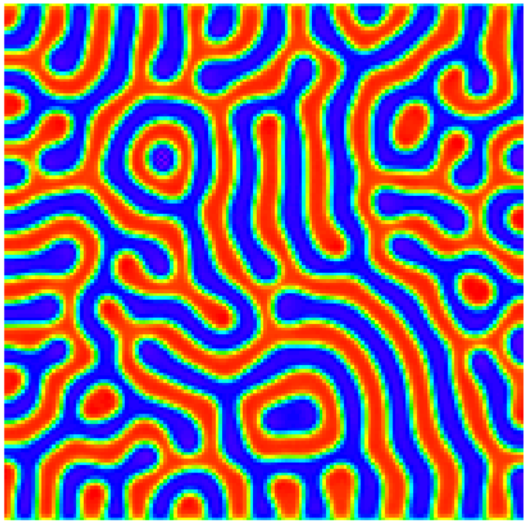
$$F_{\text{long-range}}[\varphi] = \int dx \int dx' B\varphi(x)G(x, x')\varphi(x')$$

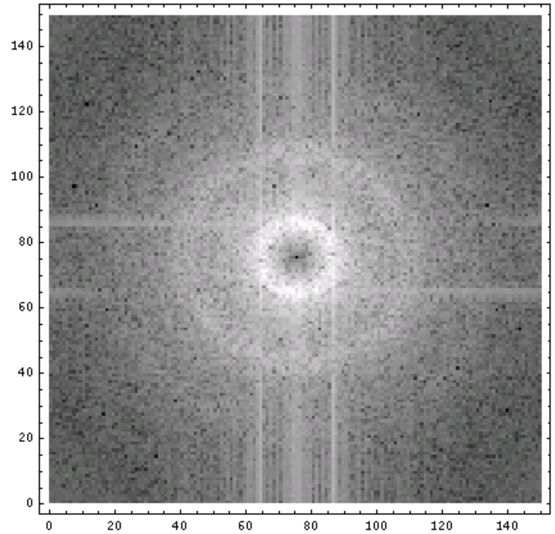
  - Ohta and Kawasaki:

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

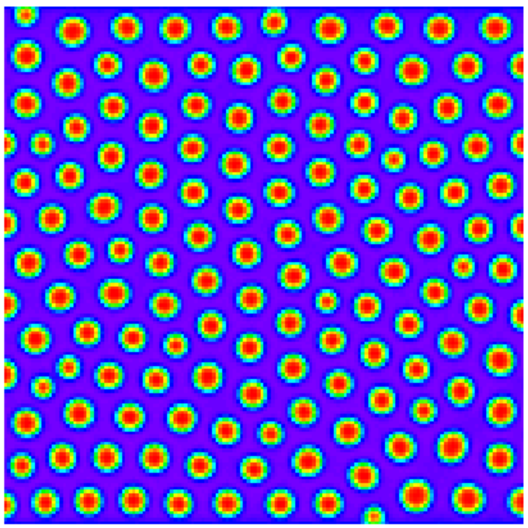
- **Formally, same as electrostatics.**
  - A monomers negative, B monomers positive

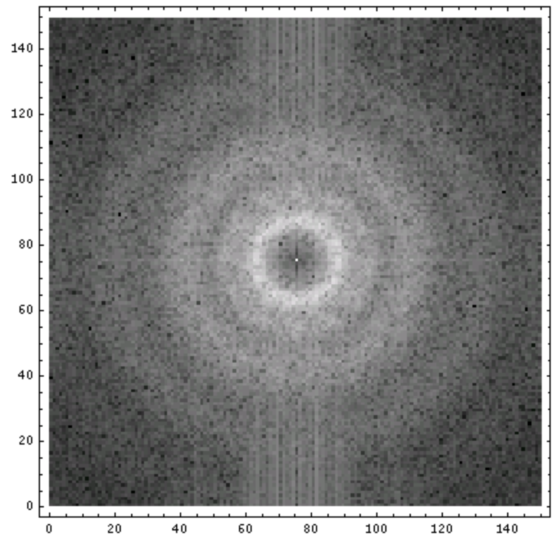
● Minimizing F gives diblock-like structures





- ☛ Cahn-Hilliard dynamics
- ☛ Lamellar phase
- ☛ Scattering

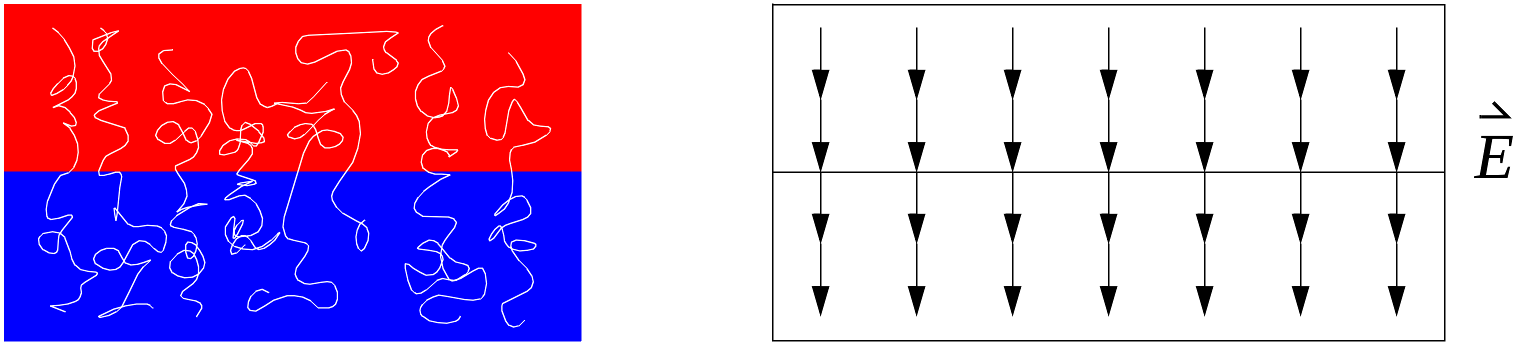




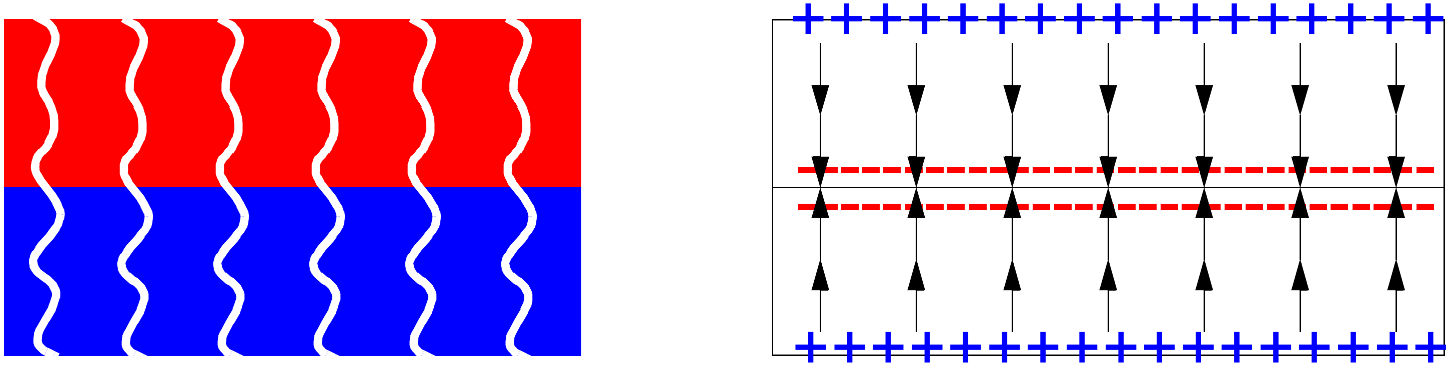
- ☛ Cylinder phase
- ☛ Scattering

- **Electrostatic analogy for Diblocks**

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



- **Alexander, deGennes, and elaborations**



- **Blend to consider**

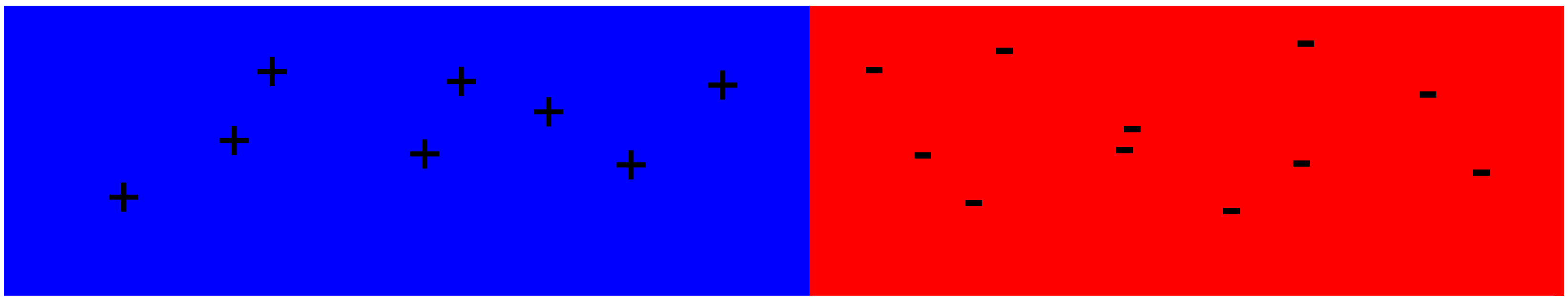
- **Let both chains have the same number of monomers (can be relaxed...)**
- **Let the CHARGE/monomer on the majority component be fixed.**
- **Electroneutrality then relates the CHARGE/ monomer of minority component to composition:**

$$0 = \alpha_A f + \alpha_B (1 - f)$$

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

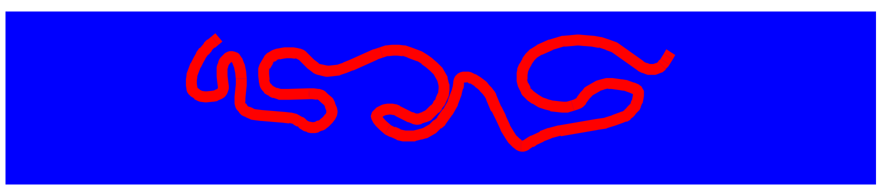
- Can expect a mesophase.

- Phase separation: huge electrostatic costs



"Collecting like charges"

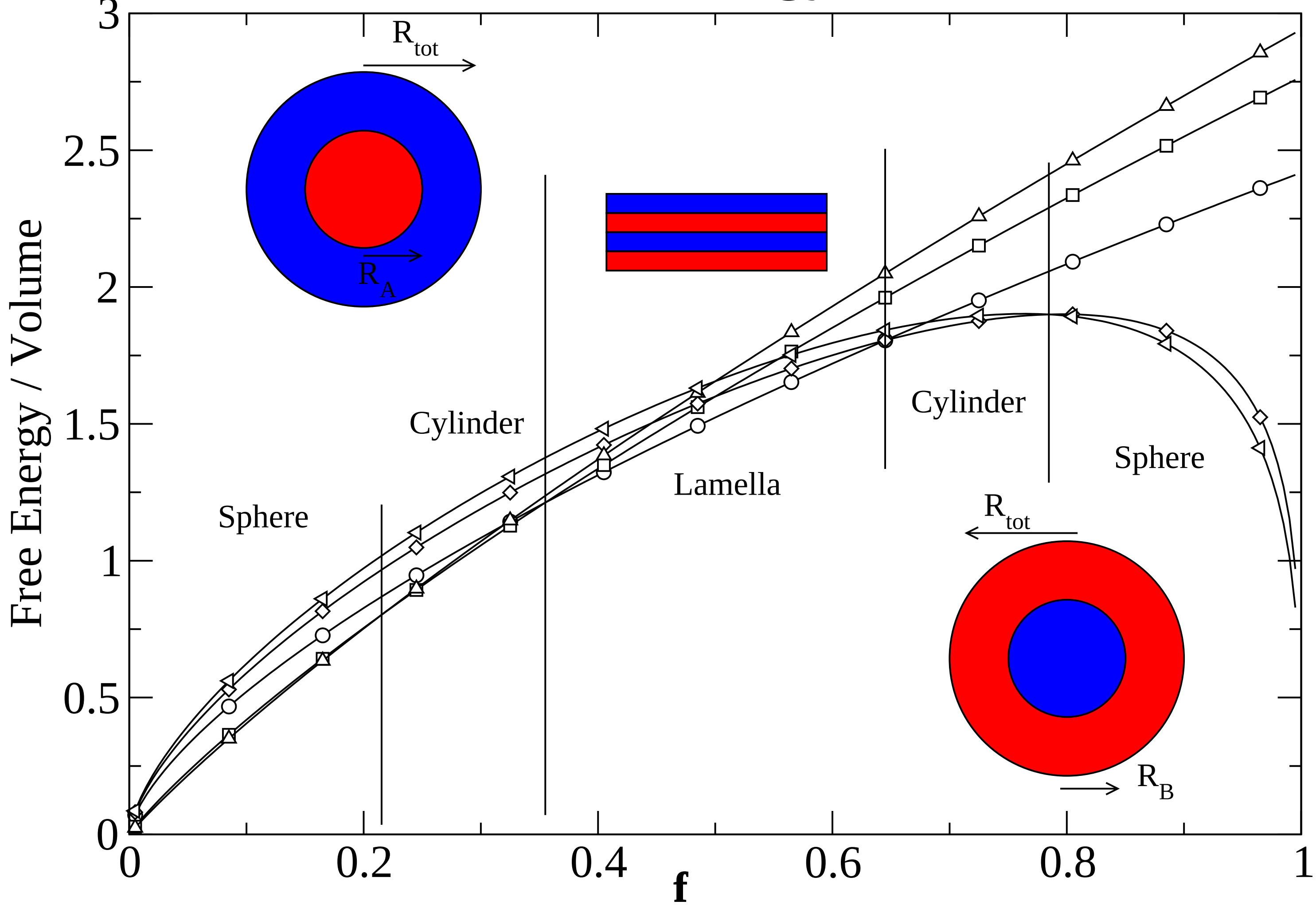
- Single phase: huge specific interactions



N red monomers:
total cost χ N

● Strong-Segregation Limit

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



Lattice Electrostatics

- **Discretize Laplacian:**

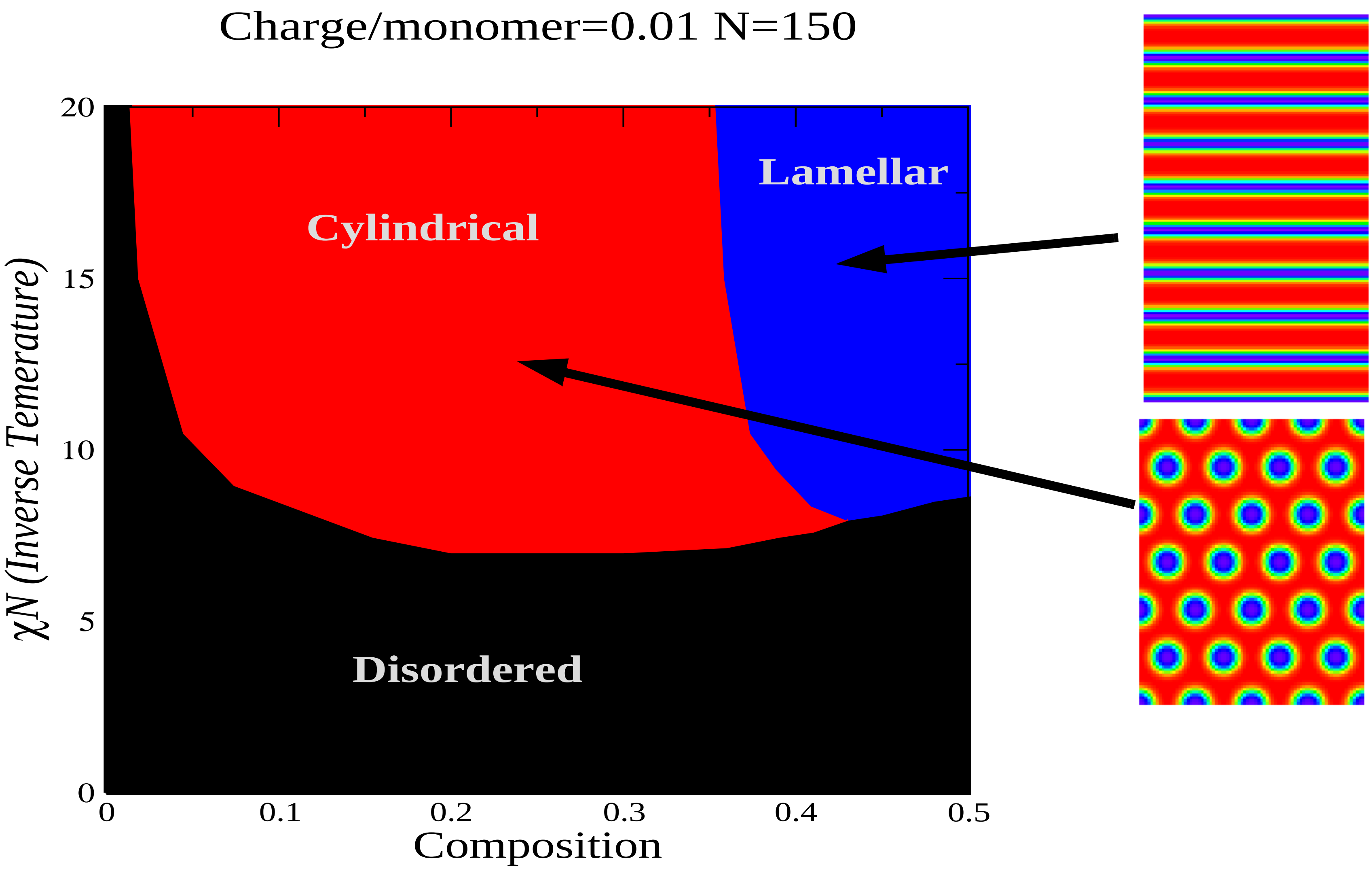
$$\nabla^2\varphi \Rightarrow \varphi(x, y+1) + \varphi(x, y-1) + \varphi(x+1, y) + \varphi(x-1, y) - 4\varphi(x, y)$$

- **Gauss' Law discretized:**

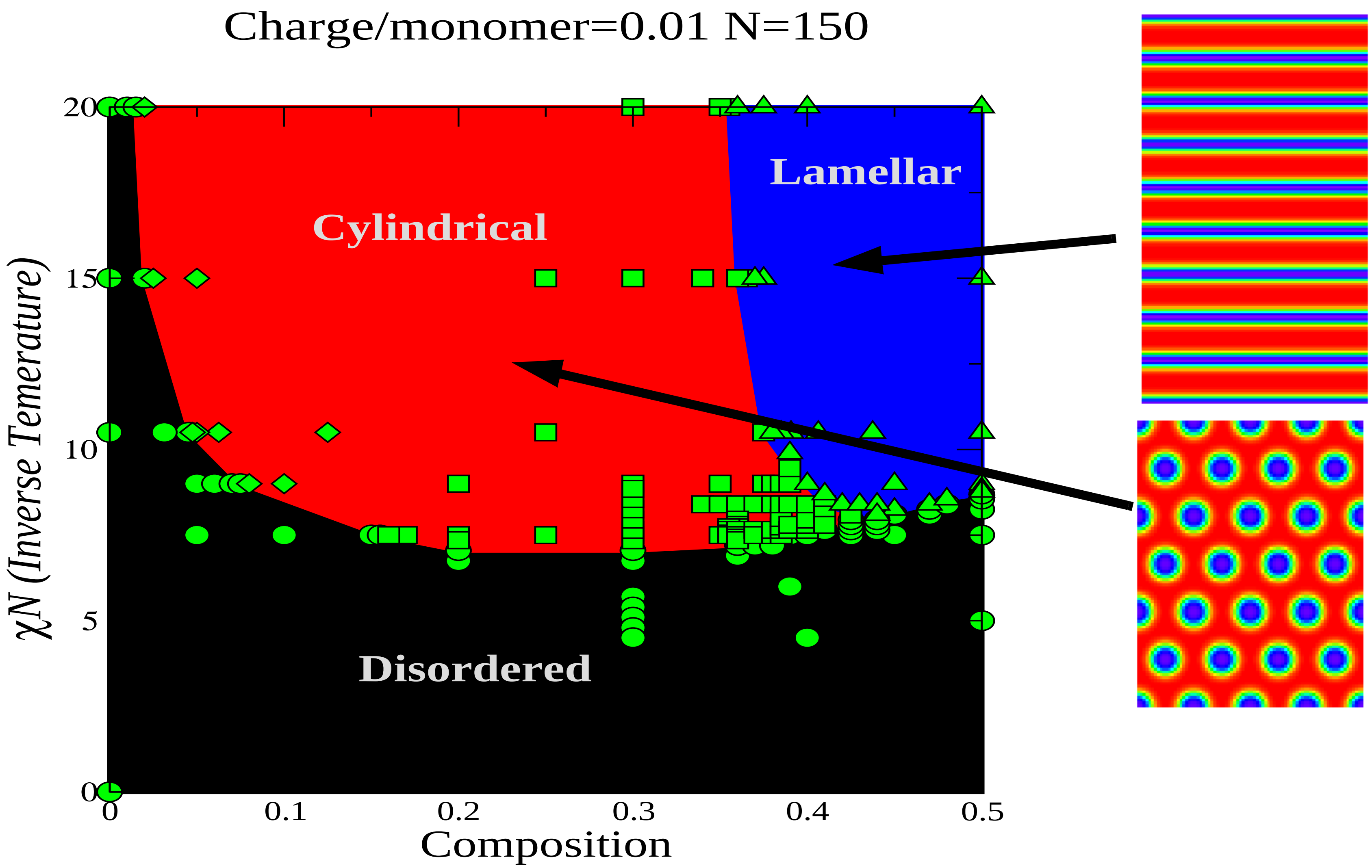
$$\nabla^2\Phi = 4\pi(\rho_A\varphi_A + \rho_B\varphi_B)$$

- **Solve for Φ, electrostatic potential, involves inverting a linear operator on the lattice**
- **Solved numerically at each iteration by direct inversion.**

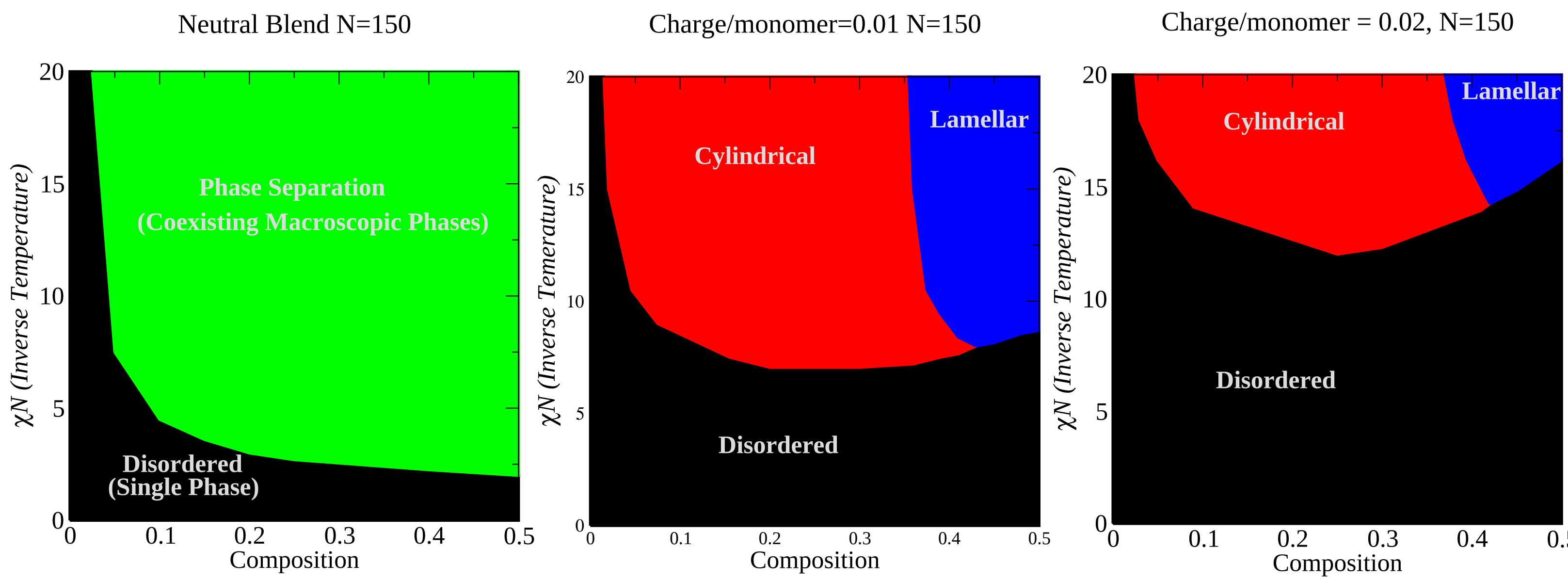
- **Microphases (just like block copolymers)**



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



- **Charge compatibilizes the blend**

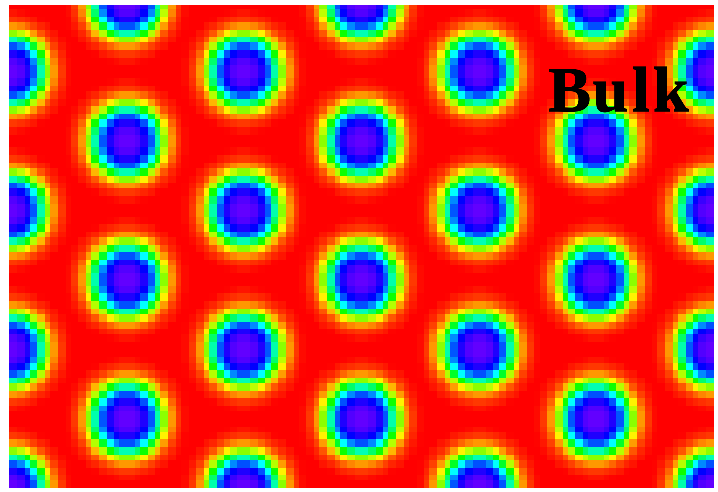


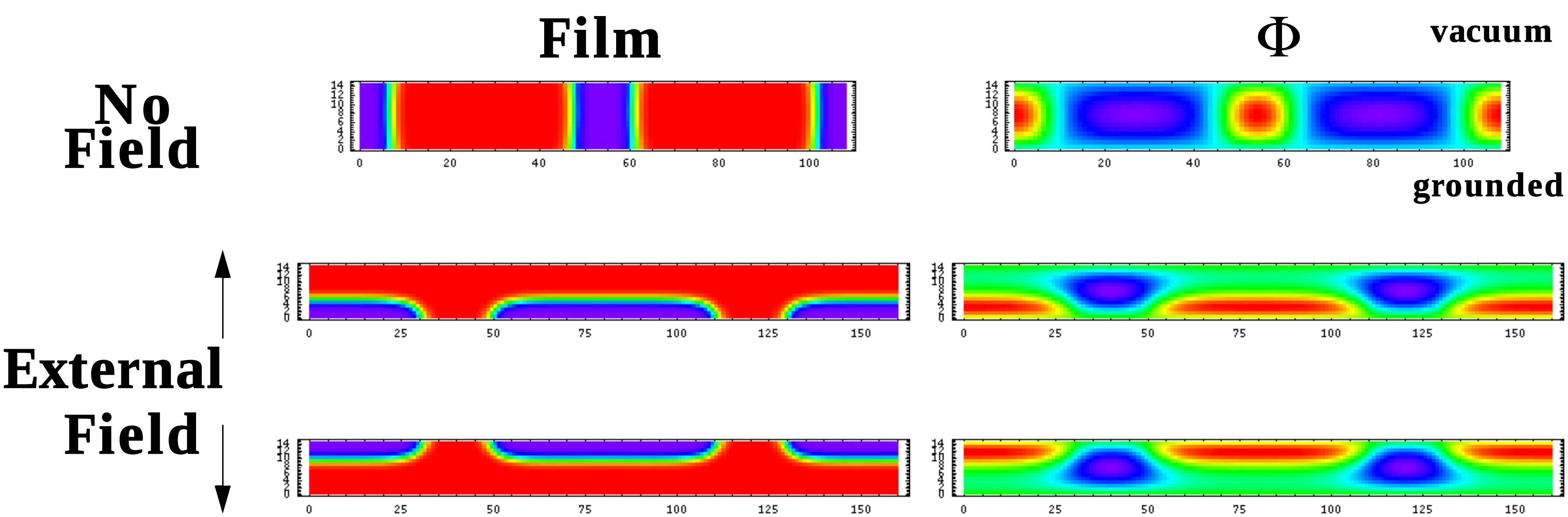
Increasing charge →

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

Films

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





Conclusions

- **Dendrimers**
  - Can’t rely on excluded volume and entropy for drug delivery, need something more specific
- **Single charged chains**
  - Single-chain self-consistent treatment lacks a priori assumptions, points toward clean experiment
- **Charged blends**
  - Dynamic control and pattern formation