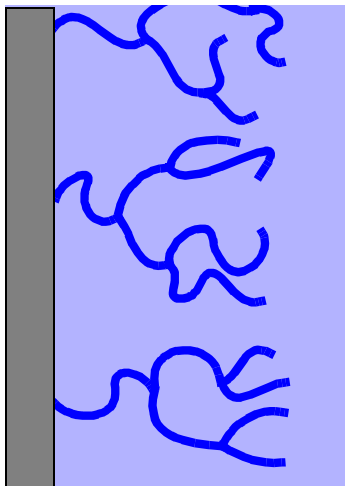
Hyperbranched Molecules:

Surfaces and Self-assembly



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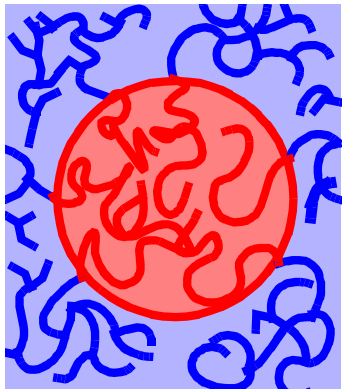
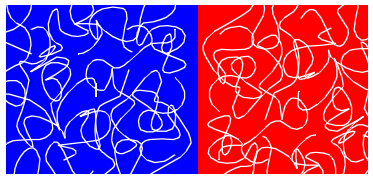


- **Stuff we want to do:**

Strengthen mixtures of plastics

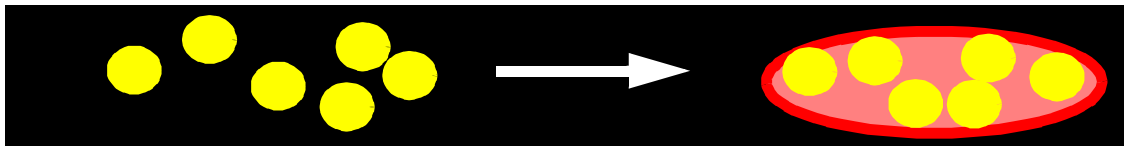


- Incompatible plastics
- Combine properties (strength, flexibility)

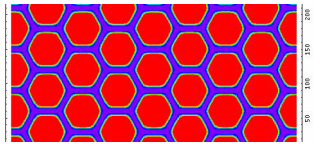
Lubricate/protect surfaces

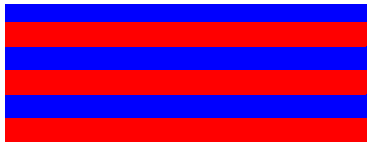
- Prevent contact
- Avoid damage

Encapsulate drugs



Create patterns

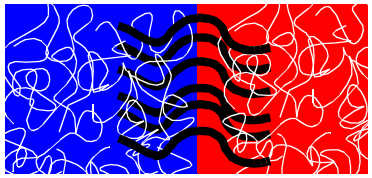




- Symmetry, scale

Stuff that can do it.

Stitching polymers: reinforce mixtures

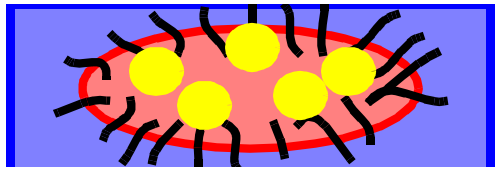


- Half blue / half red reinforces interface.

End-grafted polymers: lubrication

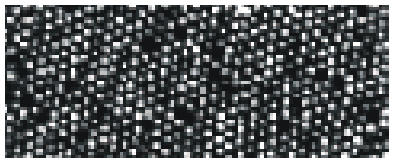
- Trapped coating
- "Osmotic" barrier

Amphiphillic polymers: housing for droplets



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

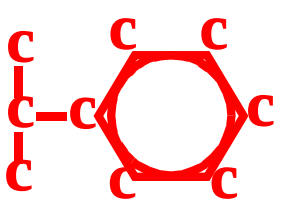
Block copolymers: templates for ordering



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

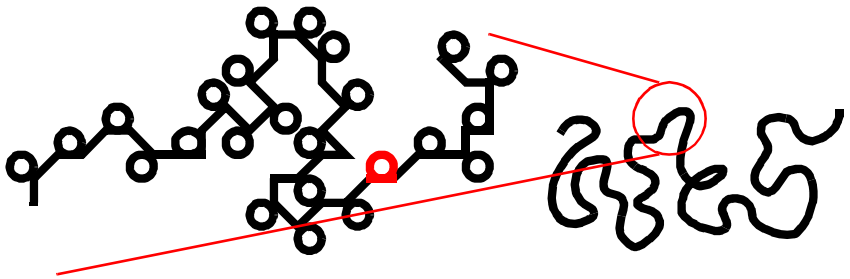
Polymers

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



Styrene
104AMU
1nm

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



Polystyrene

1000 monomers:104,000AMU

$1000nm = 1\mu m$

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

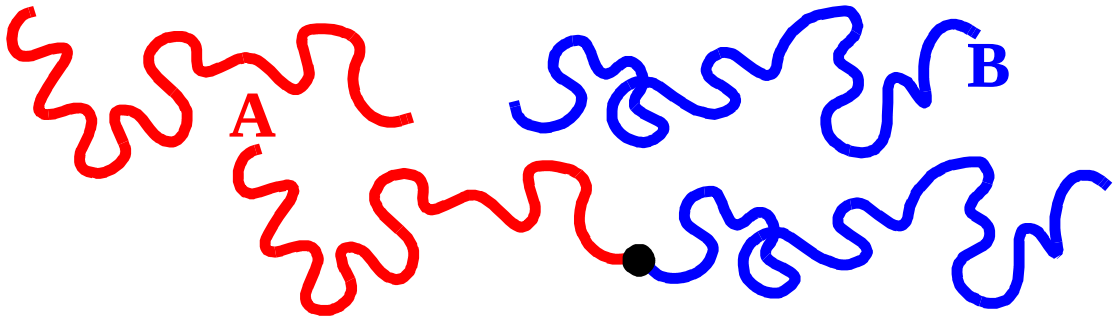
$$\Delta x \Delta p \approx (1nm)(10^5 \text{AMU} v) \approx 10^8 \frac{v}{m/s} h$$

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

- Entangling, knots

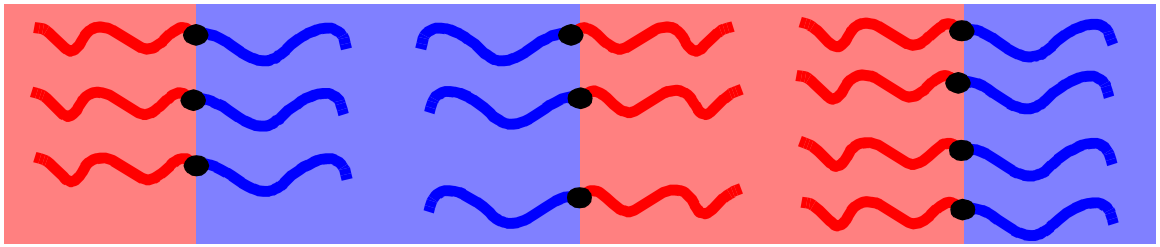
- **Block copolymers**

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



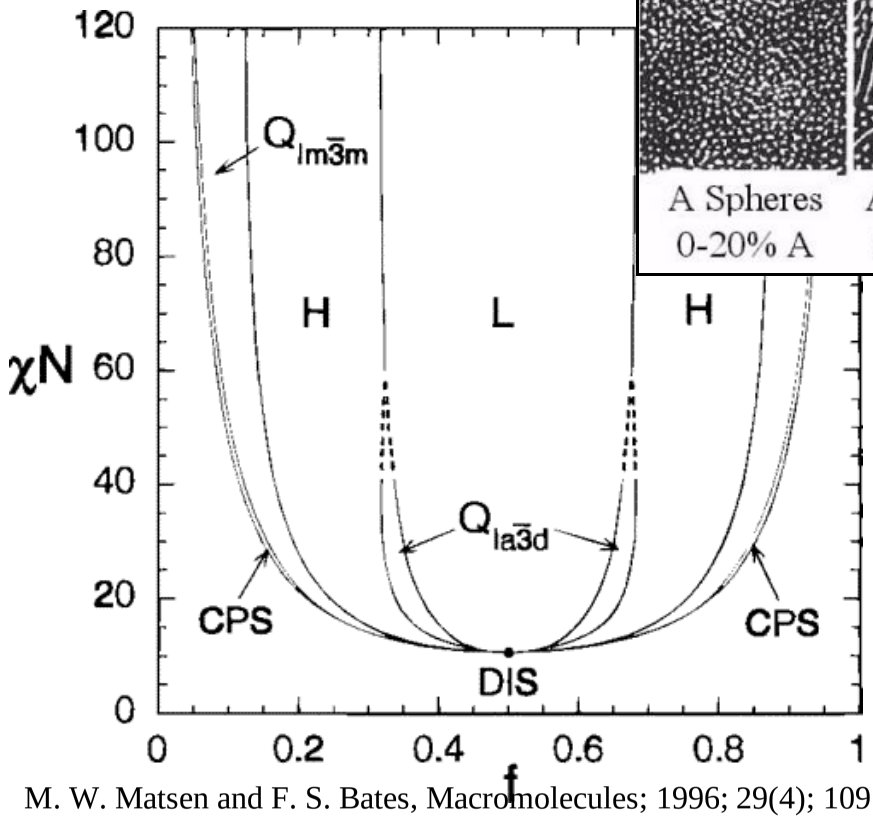
    - A-block and B-block: “diblock”

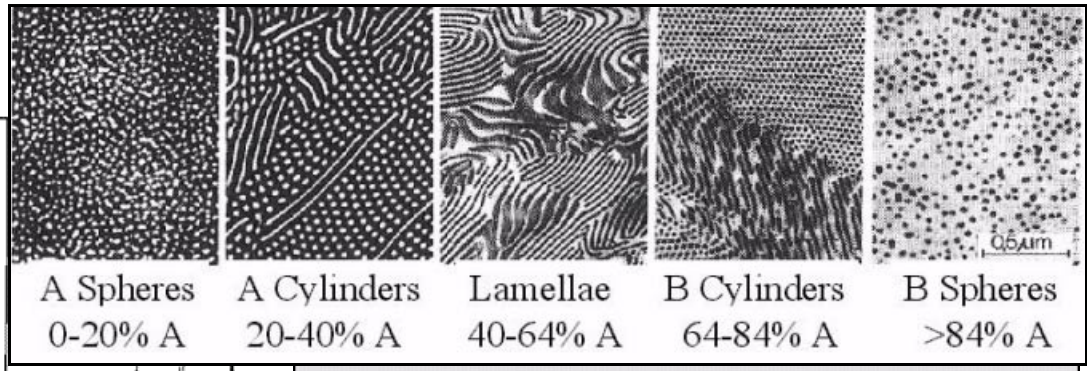
  - **Unless you break bonds, micro-scale texture happens.**

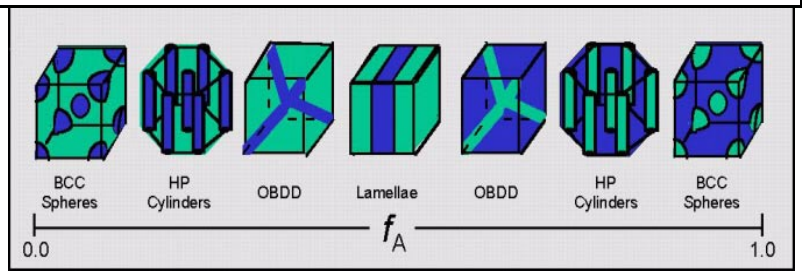


Asymmetric diblocks

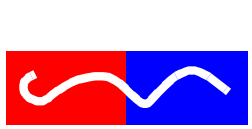
- *f*= fraction of A on molecule, controls symmetry:

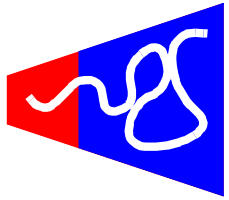






http://www.psrc.usm.edu/mauritz/block.html

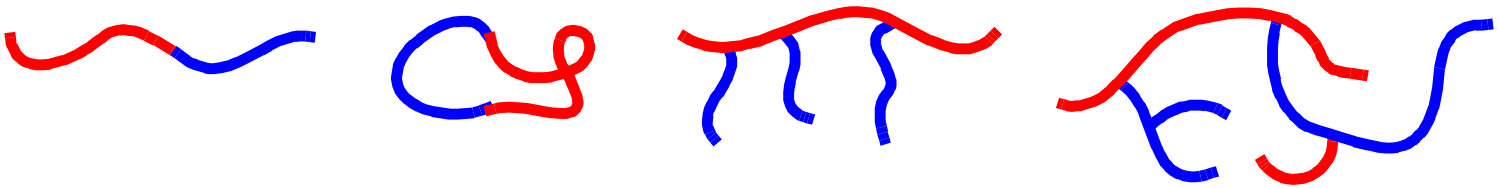




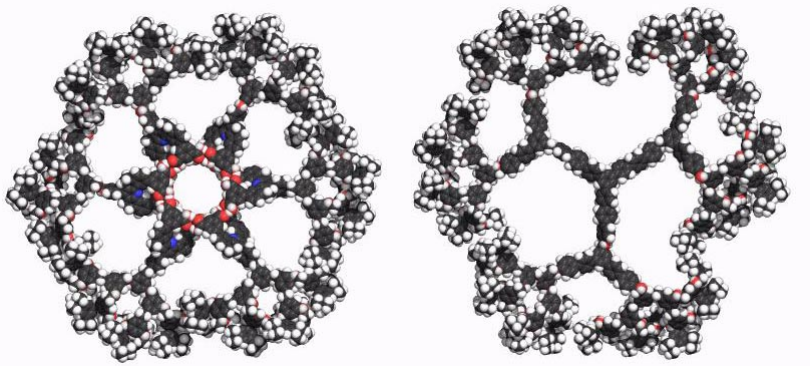
M. W. Matsen and F. S. Bates, Macromolecules; 1996; 29(4); 1091-1098.

- **Architecture controls properties**

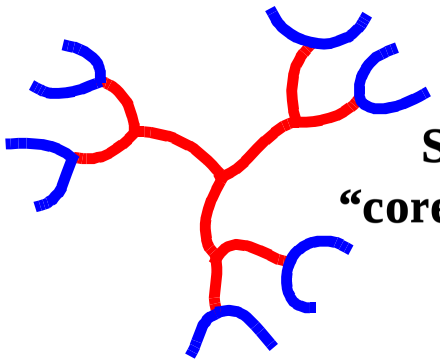
  - **Diblocks, composition fraction is only control**
  - **Chain topology is also something to consider:**



  - **“Starburst” dendrimers**



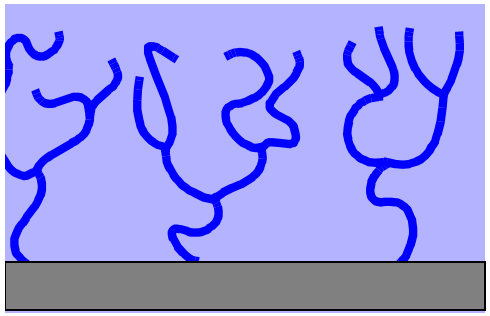
Zimmer, http://ludwig.scs.uiuc.edu/



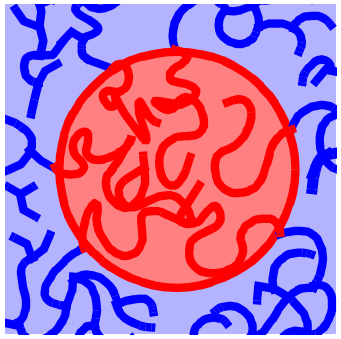
Schematic, G3
“core-shell” copolymer

Outline

- **Introduction**
  - Polymers, block copolymers, architectures
- **Dendrimer brush**



- **Dendrimer copolymers**



- **Conclusions**

- **Lots of polymers jammed together**

$F = conformation + insertion$

- **Stretching (conformation) energy depends on just the red chain**
- **Insertion energy depends on what the neighboring chains are doing**
- **Insertion energy must be found consistent with what all the other chains are doing**

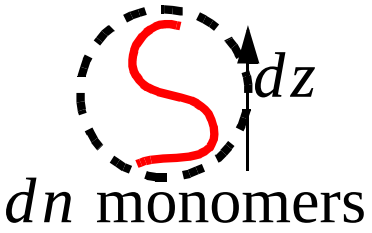
- **Self-consistent polymer brush**

  - **Anchored polymers**

  - **To insert red polymer:**

$$F[z(n)] = \int_0^N \left[\frac{1}{2} \left| \frac{dz}{dn} \right|^2 + P(z(n)) \right] dn$$

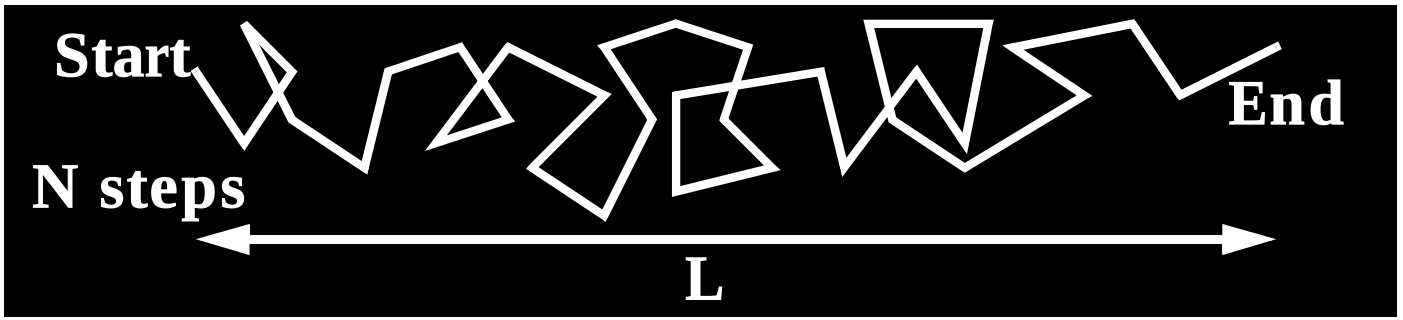
Stretching **Insertion**



  - **Insertion, ok but why is stretching quadratic?**

- **Stretching energy is quadratic**

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



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

$$force \propto L$$

Double F, go twice as far

$$force \propto 1/N$$

More steps, less force

  - **Work = force *distance:** $\left(\frac{L}{N}\right)L = \left(\frac{L}{N}\right)^2 N$

  - **Generalization for non-uniform stretching**

Single-chain self-consistent field

- Lots of polymers jammed together

$$F[z(n)] = \int_0^N \left[\frac{1}{2} \left| \frac{dz}{dn} \right|^2 + P(z(n)) \right] dn$$

- **Stretching** is exact for the **red** test chain.
- **Insertion** energy averaged over conformations of all other chains
- **Insertion** energy must be found consistent with what all the other chains are doing

Classical mechanics

- **Single-chain free energy $\Leftrightarrow$ Lagrangian**

$$F[z(n)] = \int_0^N \left[\frac{1}{2} \left| \frac{dz}{dn} \right|^2 + P(z(n)) \right] dn$$

Time, t, is equivalent to "monomer number",n

$$S[z(t)] = \int_0^T \left[\frac{m}{2} \left| \frac{dz}{dt} \right|^2 - V(z(t)) \right] dn$$

Minimize F, extremize S

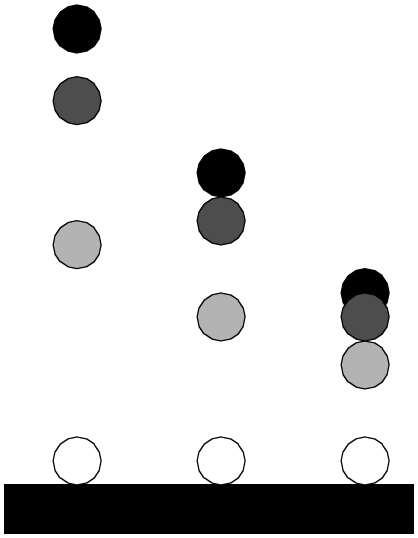
Ground state approx for F

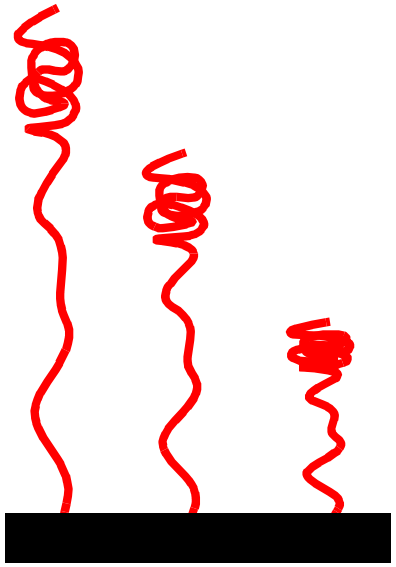
- **Potential $V(z)$ must have an "equal-time" property.**
  - If particle is released from rest, at a time T it will arrive at z=0, regardless of where it started.

- **Only one “equal-time” potential will do**

  - **Harmonic Oscillator**

$$z(t) = z_o \cos\omega t \qquad z(n) = z_o \cos\omega n$$



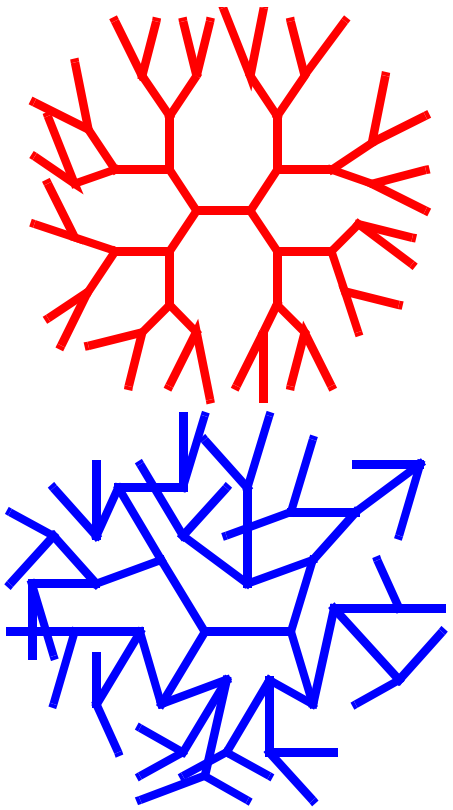


$$V(z) = \frac{1}{2}\omega^2 z^2 \qquad P(z) = const. - \frac{1}{2}\omega^2 z^2$$

  - **Strong constraint from self-consistency**

- **What has to change for branched grafts?**

  - **deGennes, single dendrimers**
    - Hollow core
    - Tips all exposed
  - **Lescanec, single dendrimers**
    - Core filled, backfolded
    - Ends distributed
  - **Where are the ends?**
  - **Where are ends for a brush of dendrimer?**



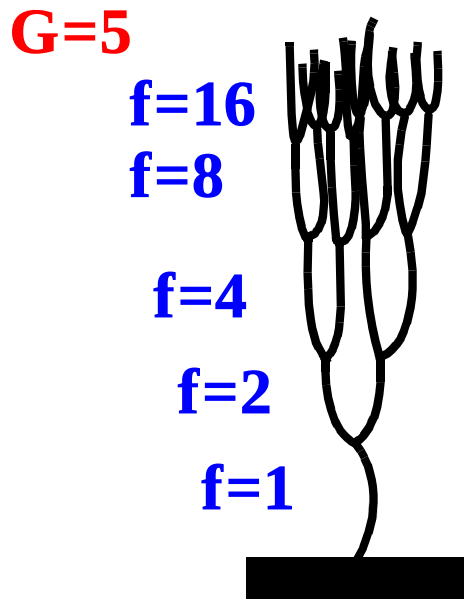
- **Classical analog for dendrimer brush**

  - **Single-chain free energy:**

Generations

$$F[z(n)] = \int_0^{GN} f(n)\left[\frac{1}{2}\left|\frac{dz}{dn}\right|^2 + P(z(n))\right]dn$$

Number of equivalent branches

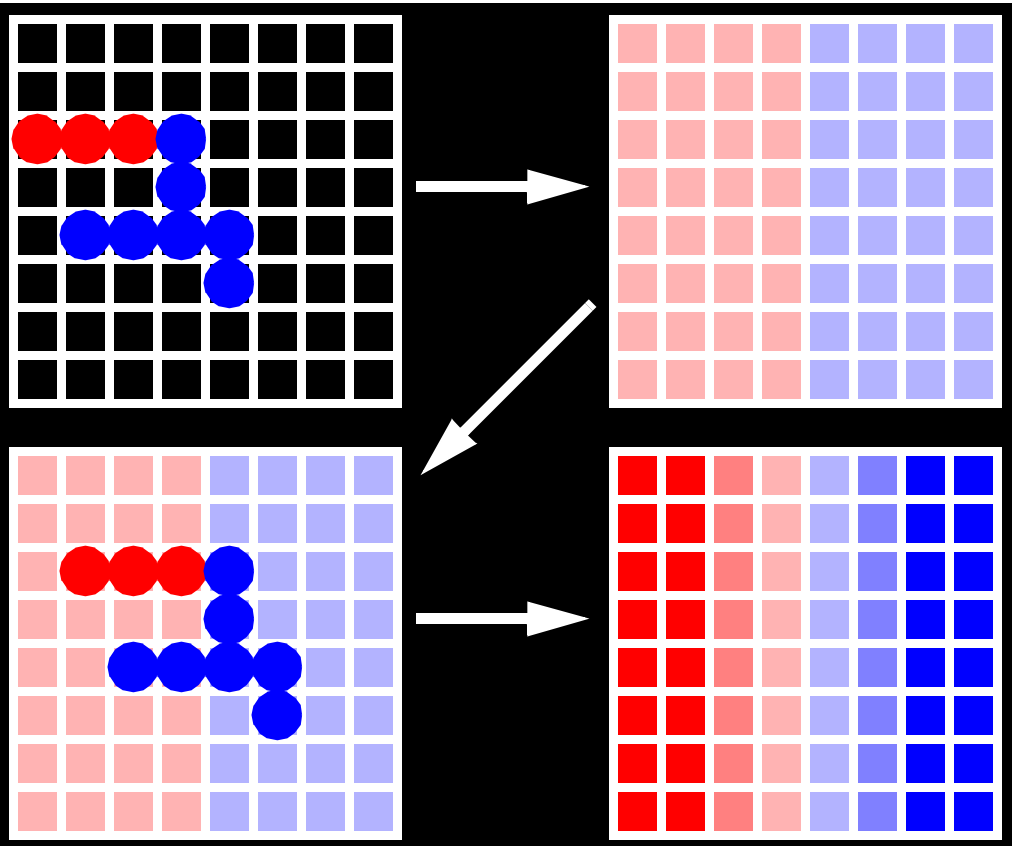


  - **Time-dependent “mass”, in a time-dependent potential.**

Clues from numerical work.

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

Lattice model

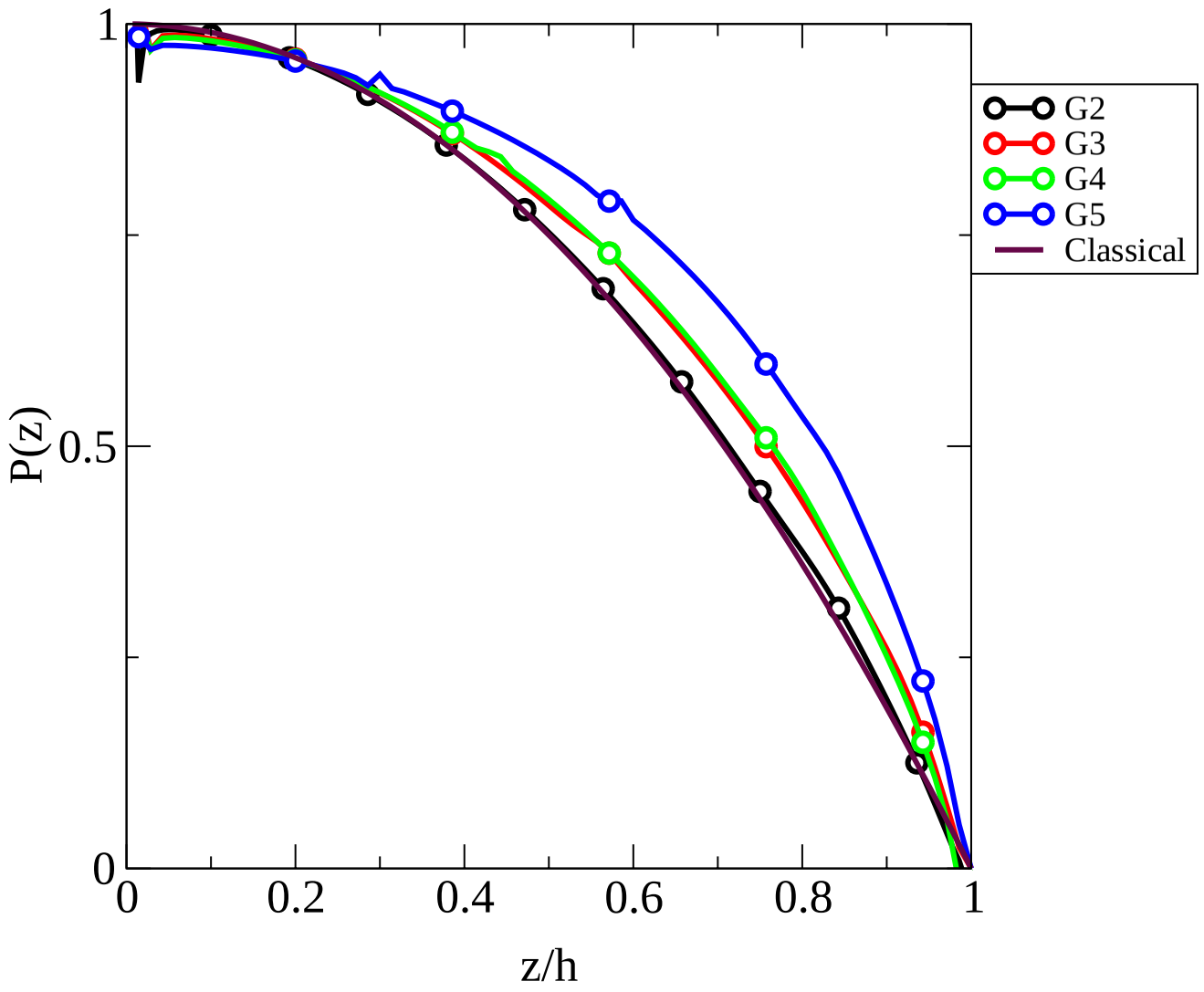


1. Start with empty lattice
2. Throw down copolymers at random
3. Calculate average monomer densities
4. Regrow the chains
5. Recalculate the monomer densities
6. Repeat

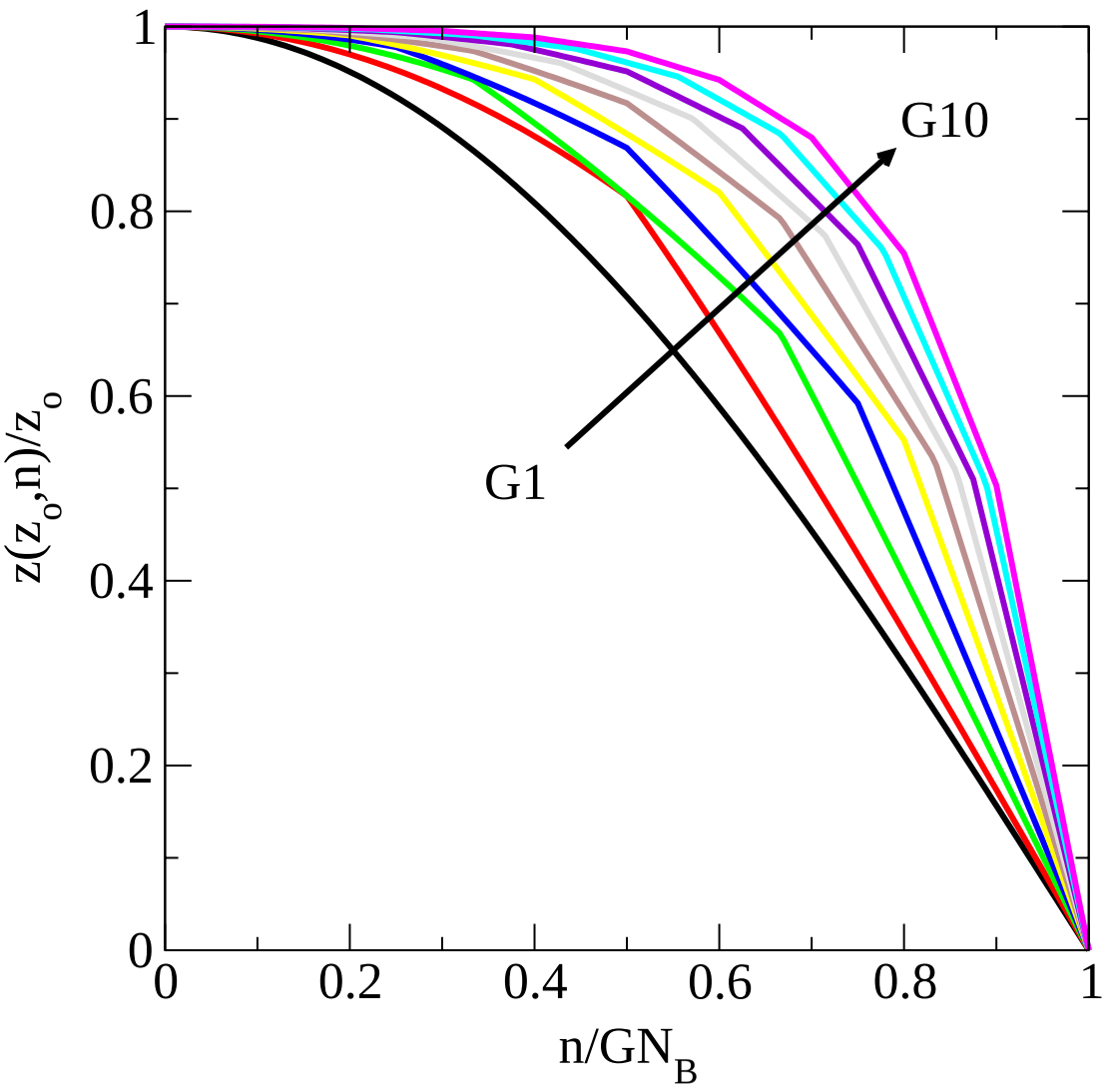
No "ground state" assumption!

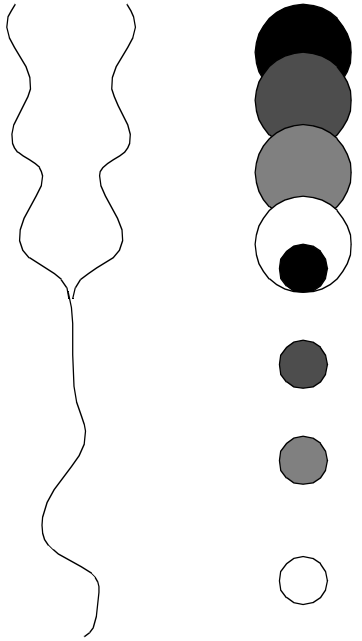
What are potentials for G1-5?

- **Equal time potential is still harmonic**



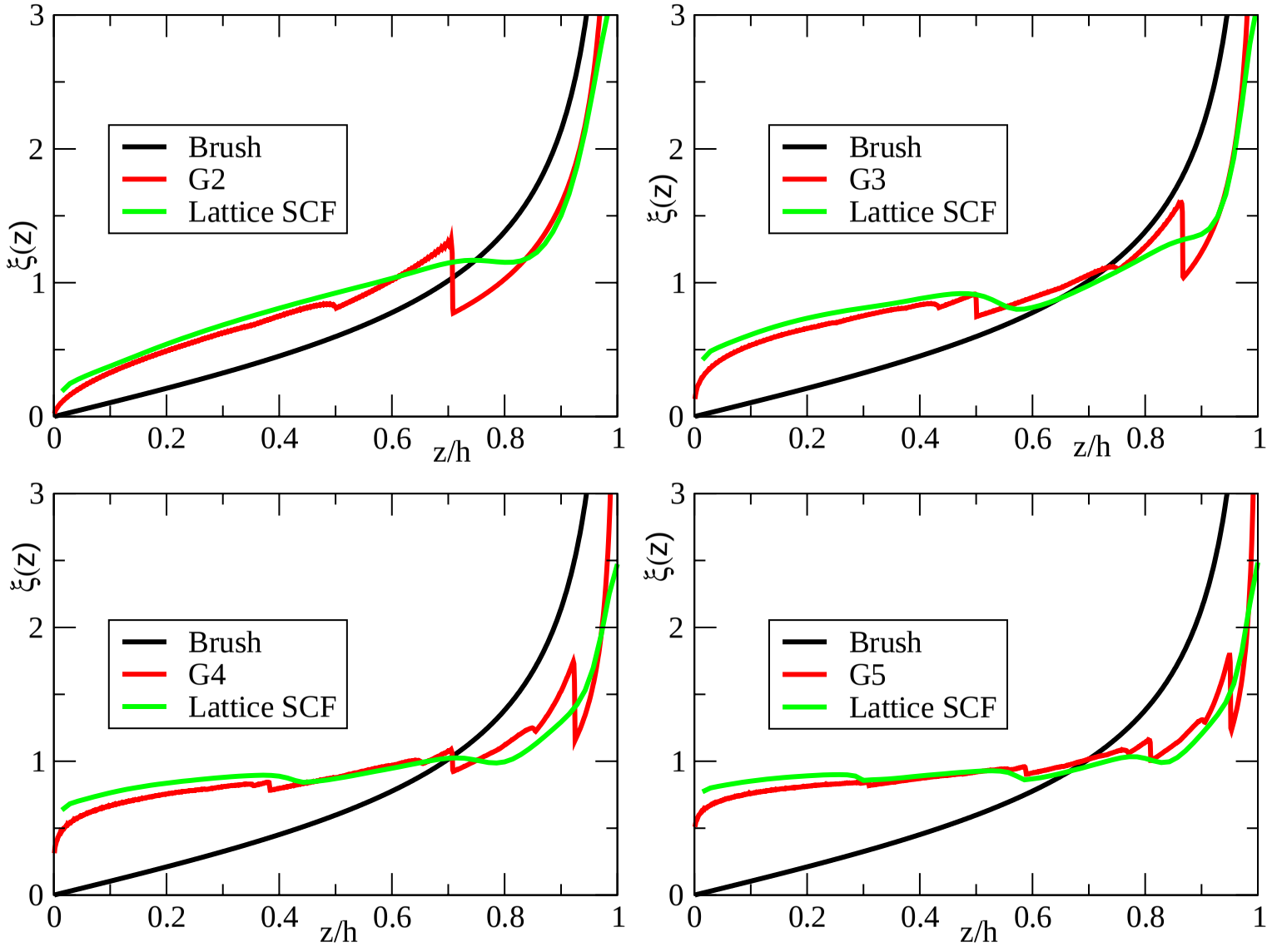
Trajectory depends on G





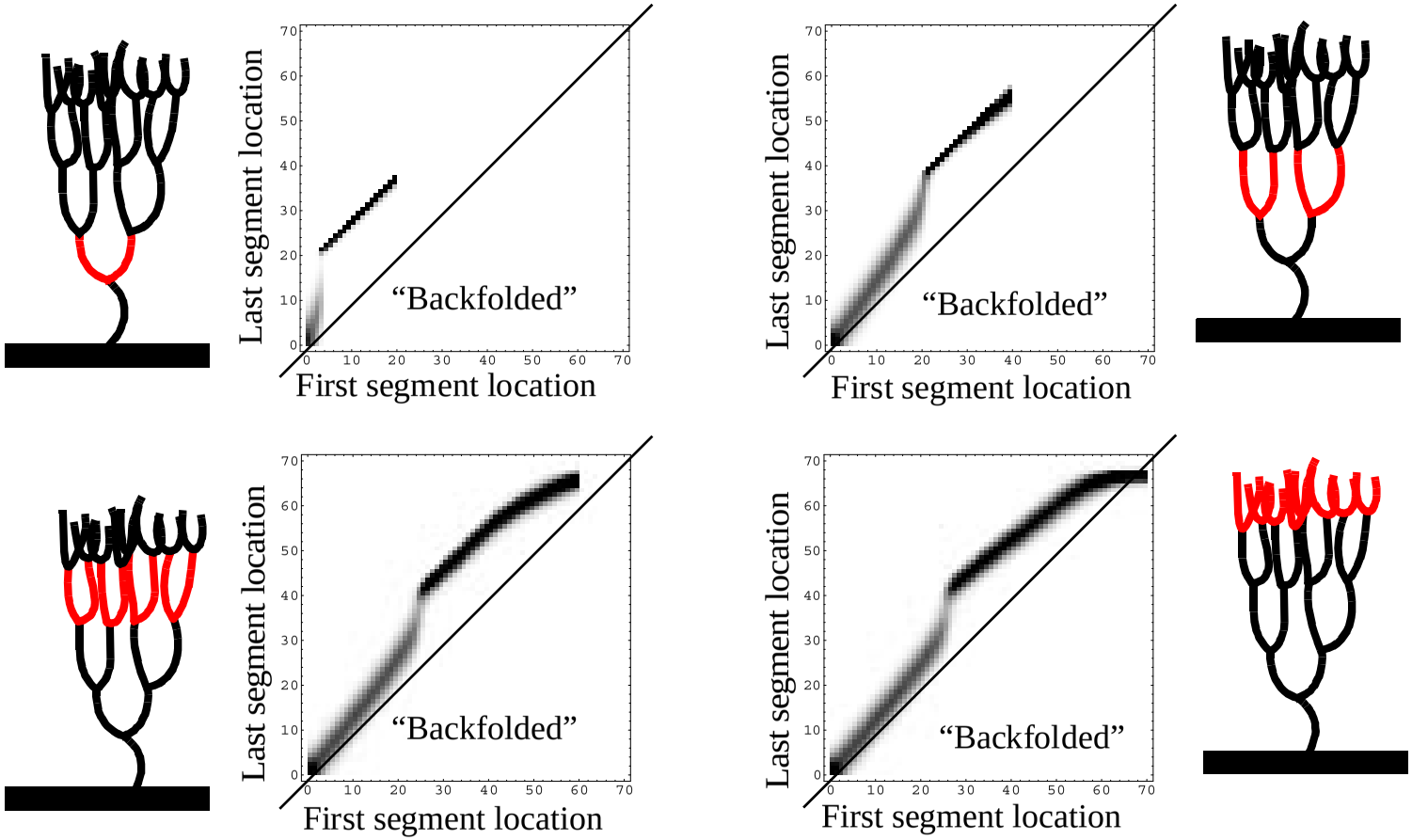
Mass gets cut in half
Momentum conserved
Velocity doubles!
Stretching doubles!

● Distribution of chain ends changes



- **Do the ends fold back into the brush?**

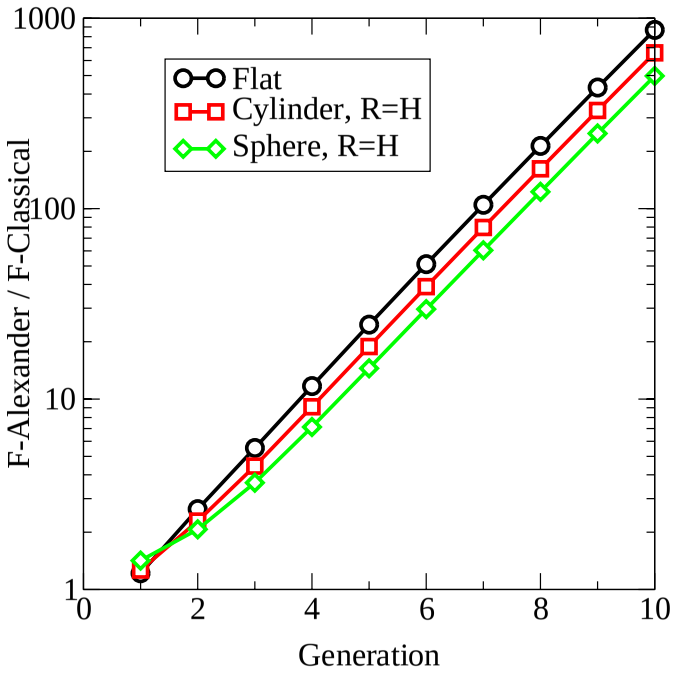
G5 dendrimer

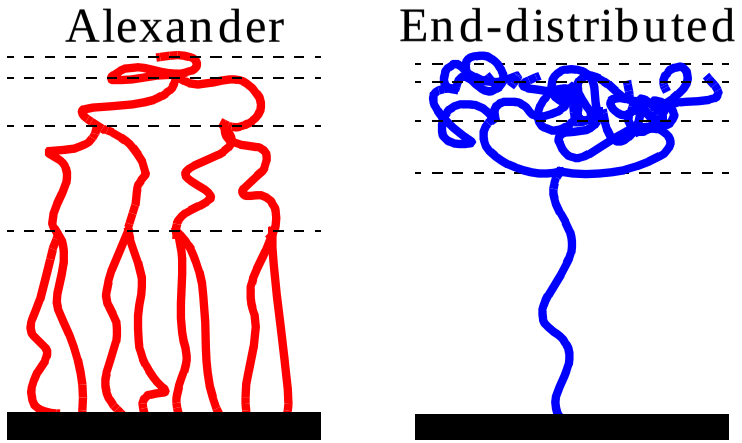


- **Filled core yes, backfolding no**

Alexander deGennes Model

Gross overestimation of stretching:



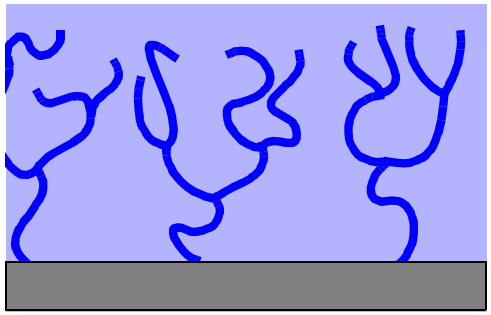


- Alexander, most branched part of chain is most stretched
- End-distributed, least branched part of chain is most stretched

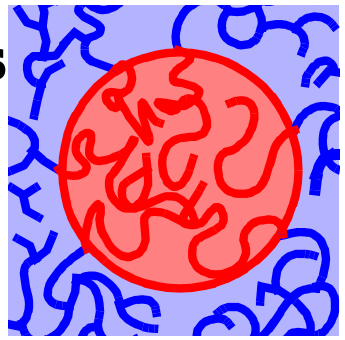
End-confining radically alters brush layer.

Outline

- **Introduction**
  - Polymers, block copolymers, architectures
- **Dendrimer brush**



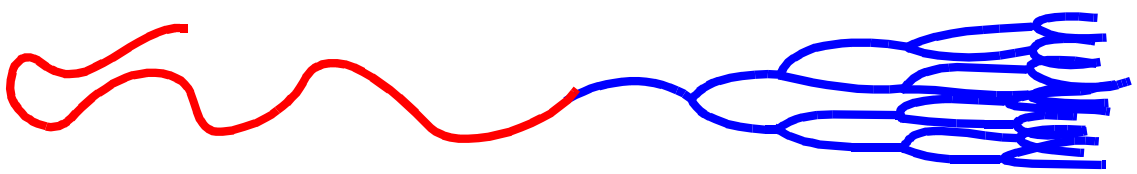
- **Dendrimer copolymers**



- **Conclusions**

- **Flexible-dendrimer copolymers**

  - **Easy to synthesize**

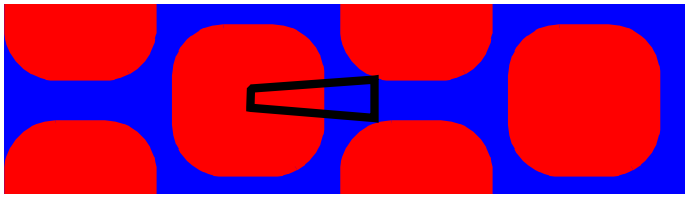


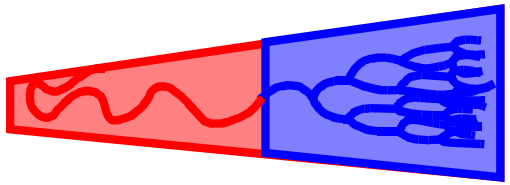
    - Extra tail added to dendrimer

  - **Should bias phase diagrams**

    - Extra branchings splay outwards

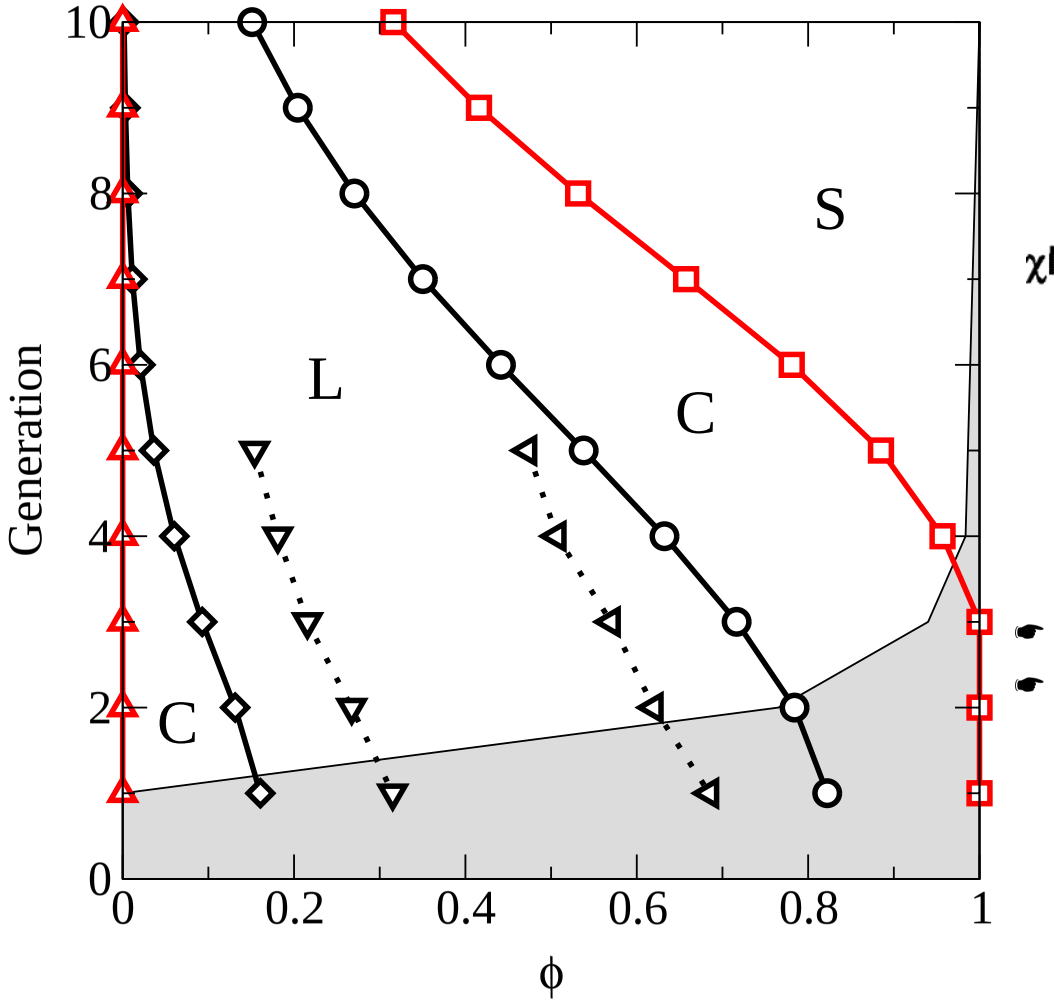
  - **Micro segregated domains: 2 stacked brushes**



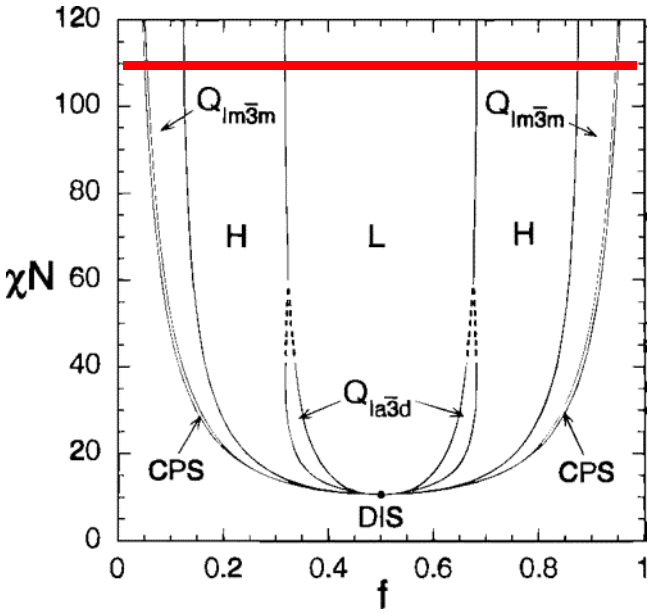


  - **Branched block resides on convex side of domains**

● Phase diagram



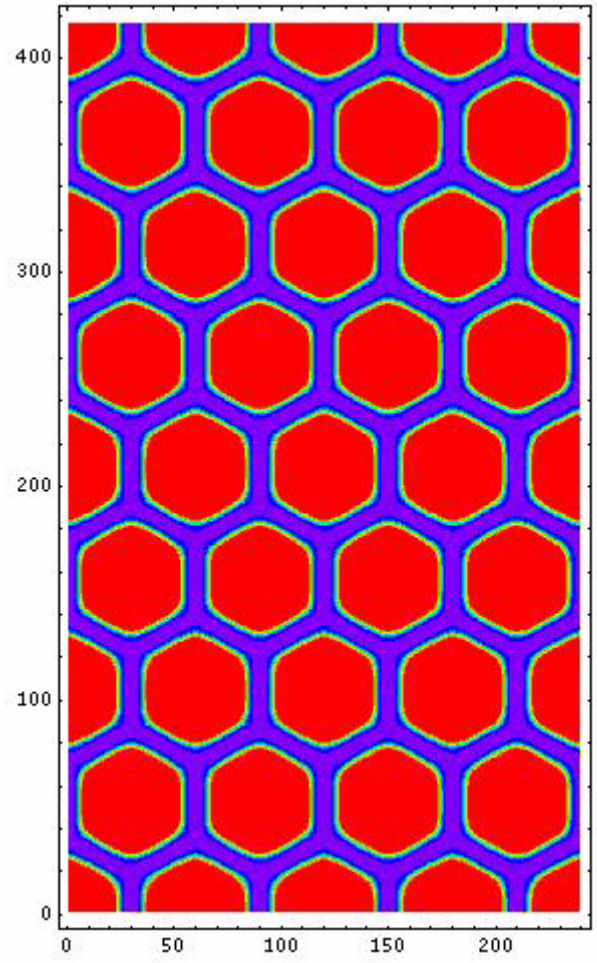
Dendrimer calculation

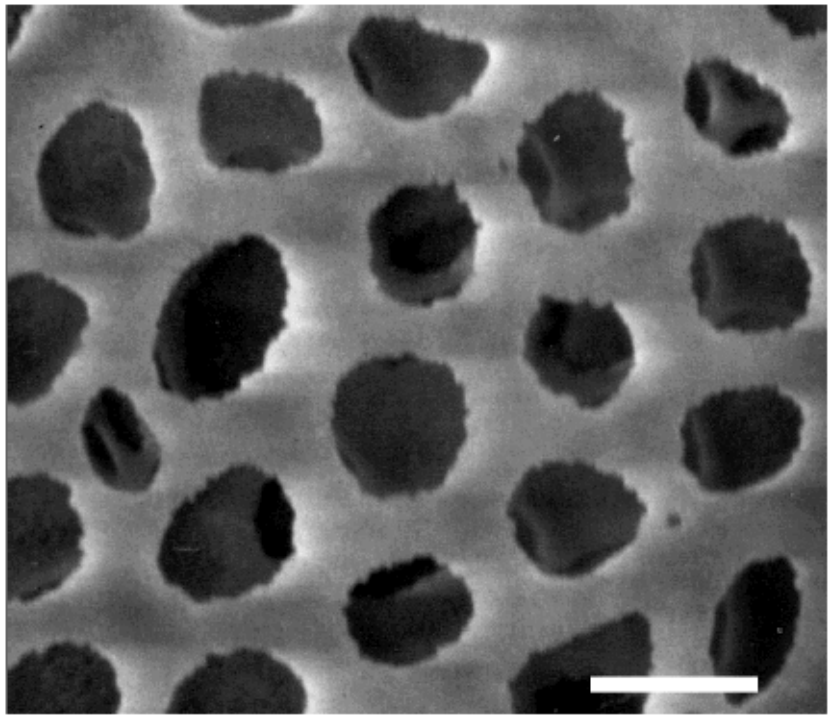


- Asymmetric diagram
- Agrees qualitatively with an Alexander model calculation:

Frischkneckt and Fredrickson, *Macromolecules* **1999** *32* 6831

● Numerical lattice calculations



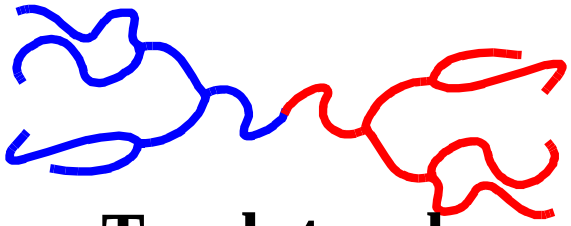


Ti foam photonic band gap forerunner

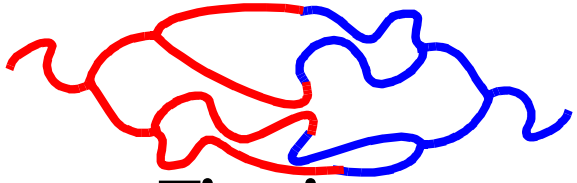
Imhof and D.J. Pine, Advanced Materials 10, 697-700 (1998).

- **Conclusions**

  - **Surfaces coated with dendrimers**
    - Ends are buried, distributed
    - Don’t fold back, (poplars, not willows)
  - **Dendrimer copolymers**
    - Shift phase boundaries
    - Photonics?
  - **Dendrimer-dendrimer block copolymers**



Trunk-trunk



Tip-tip