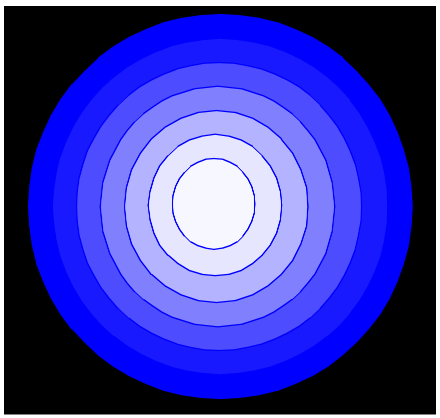
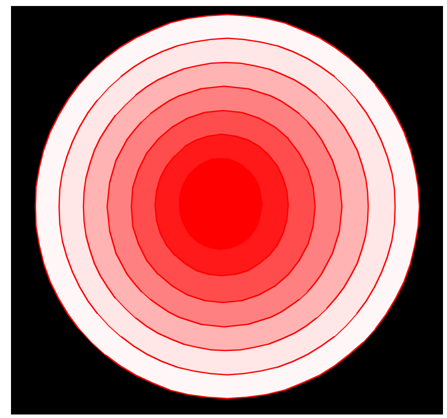
# “Hollow-core” dendrimers revisited





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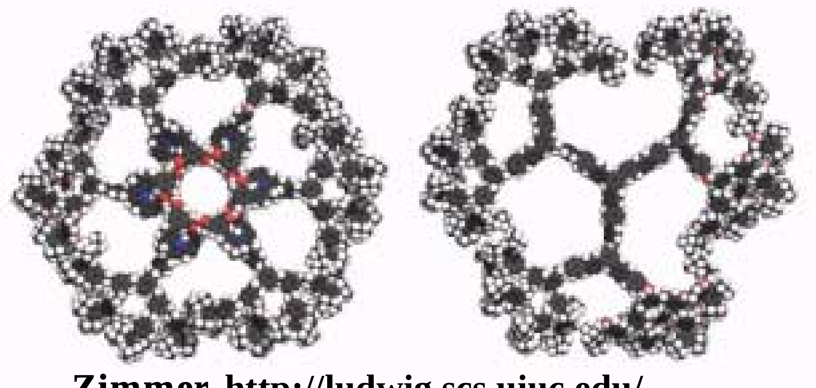
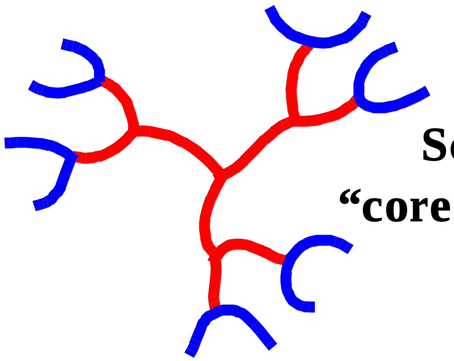
- **Dendrimers**

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



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



**Schematic, G3**
**"core-shell" copolymer**

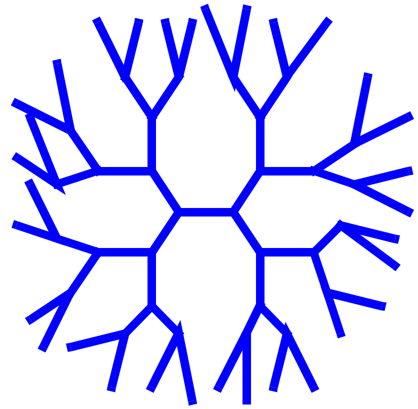
- **Complex self-organization for a single molecule**

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

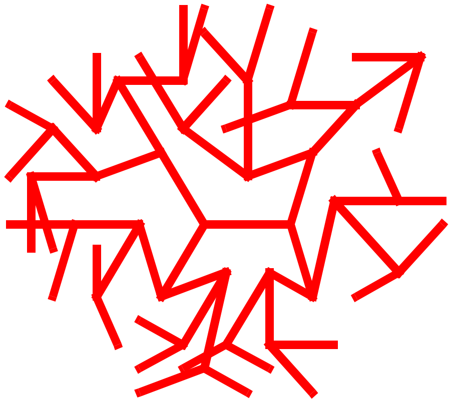
## ● Hollow or Filled Core?

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

**Hollow Core**



**Filled Core**



# ● Other theories, experiments support Filled core

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

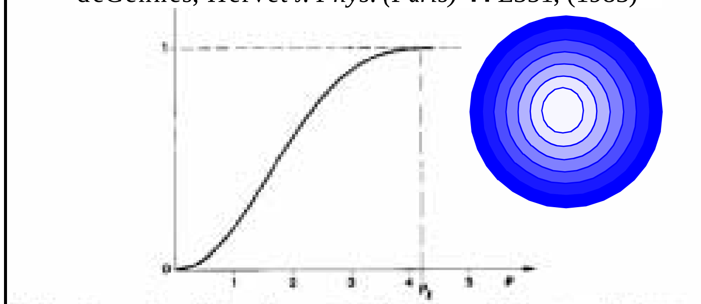


Fig. 3. — Concentration profile in starburst molecules. Notice the parabolic form at small distances ρ, and the stopping point at $\rho = \rho_t \cong 4.1$. Because of the -$NH_2$ groups present at the last generation, the physical limiting radius $R_t$ is somewhat larger than $Pa_t$ : see equation (21).

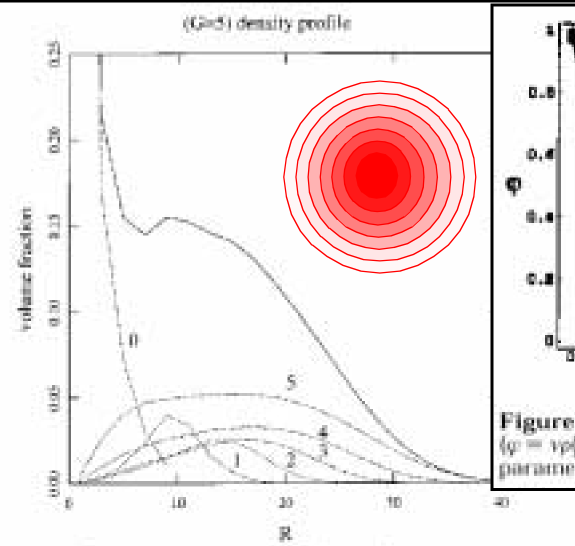



**Figure 6.** Radial density profile of the $G = 5$ model dendrimer.

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

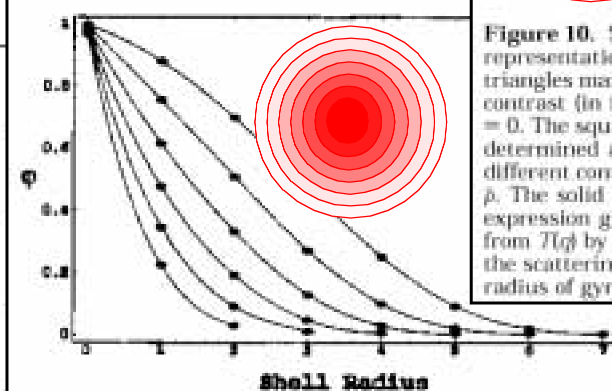



**Figure 8.** Density profile $\rho(l)$ of starbursts: volume fraction ($\varphi = v\rho(l)$) as a function of radial distance for excluded volume parameter $v' = 0.5l^3$ for starburst of generation $g = 2-7$.

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

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

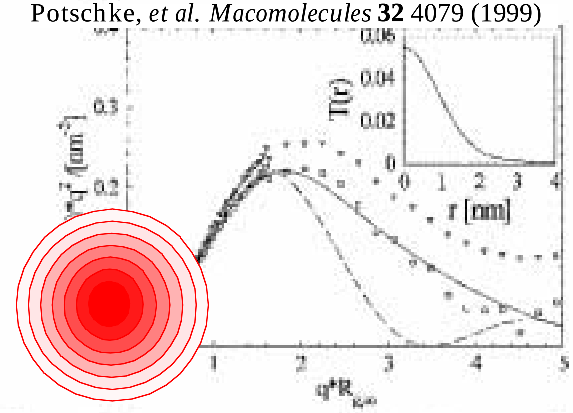


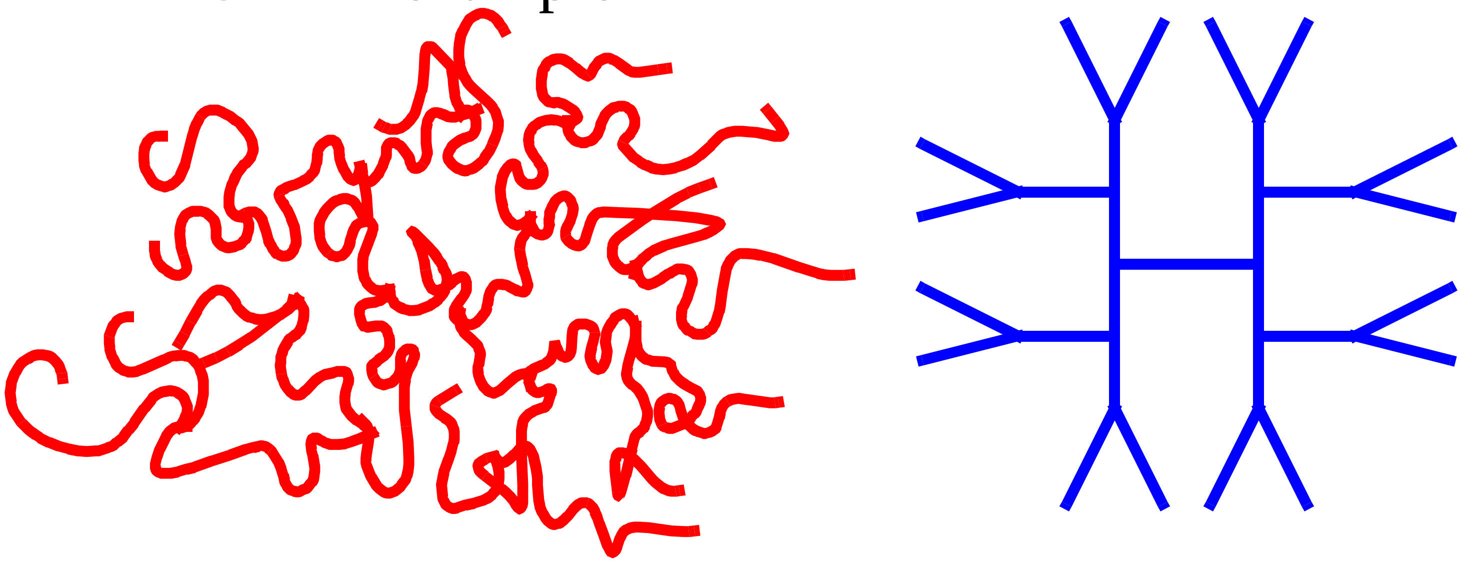

**Figure 10.** Scattering intensities of the dendrimer in Kratky representation vs magnitude of scattering vector $q$. The triangles mark the scattering intensities measured at highest contrast (in fully deuterated DMA) normalized to unity at $q = 0$. The squares give $(\bar\rho - \rho_m)^2 T^2(q)$. 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

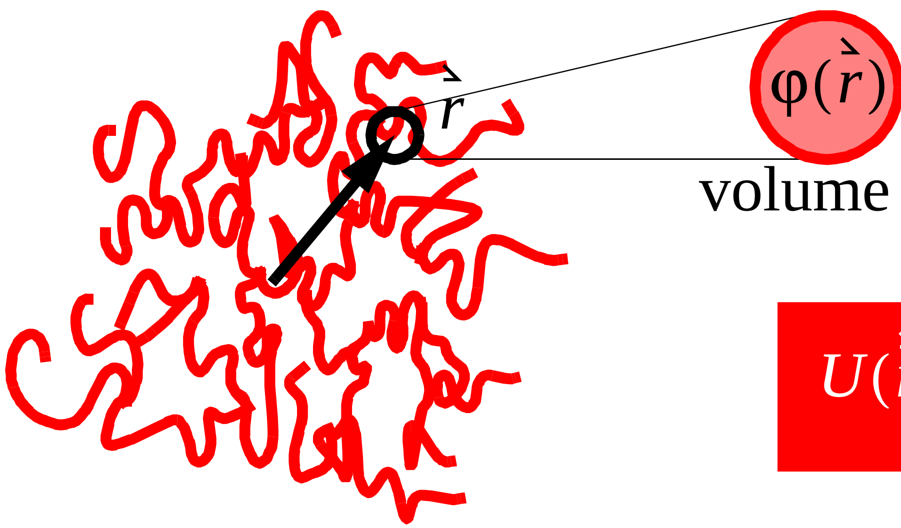


- **Excluded volume and chain entropy are the only effects in the Hervet and deGennes calculation**

- **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 $\vec{r}$

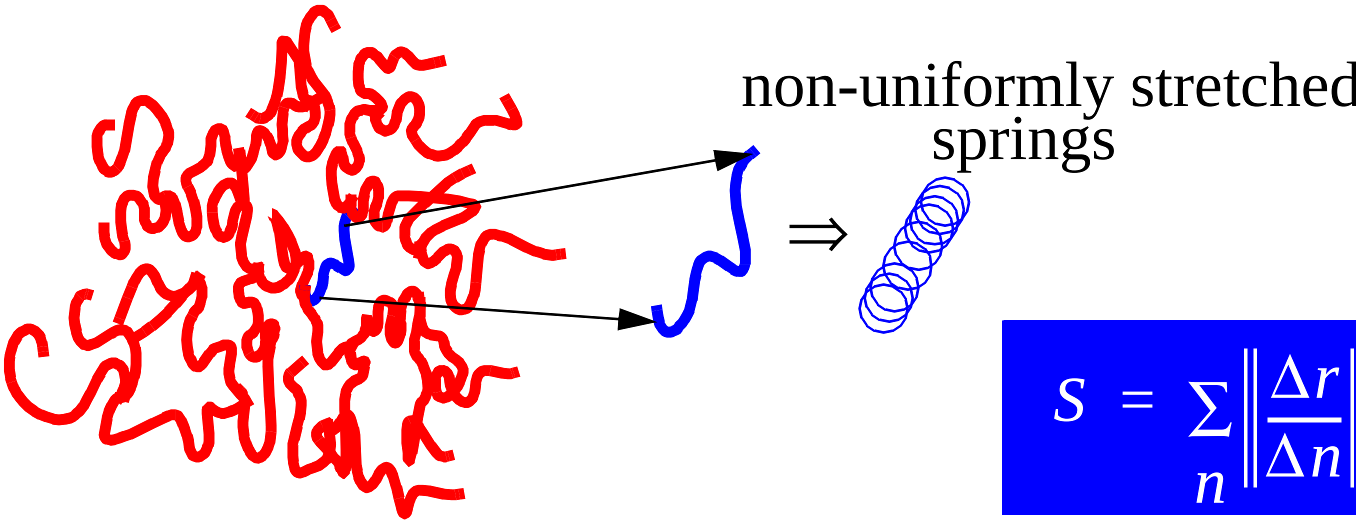
$$\boxed{U(\vec{r}) = v_o \varphi(\vec{r})}$$

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

- **What is the correct** $U$**, or** $\varphi$**?**

## ● Chain entropy

- **Gaussian chain segments:**

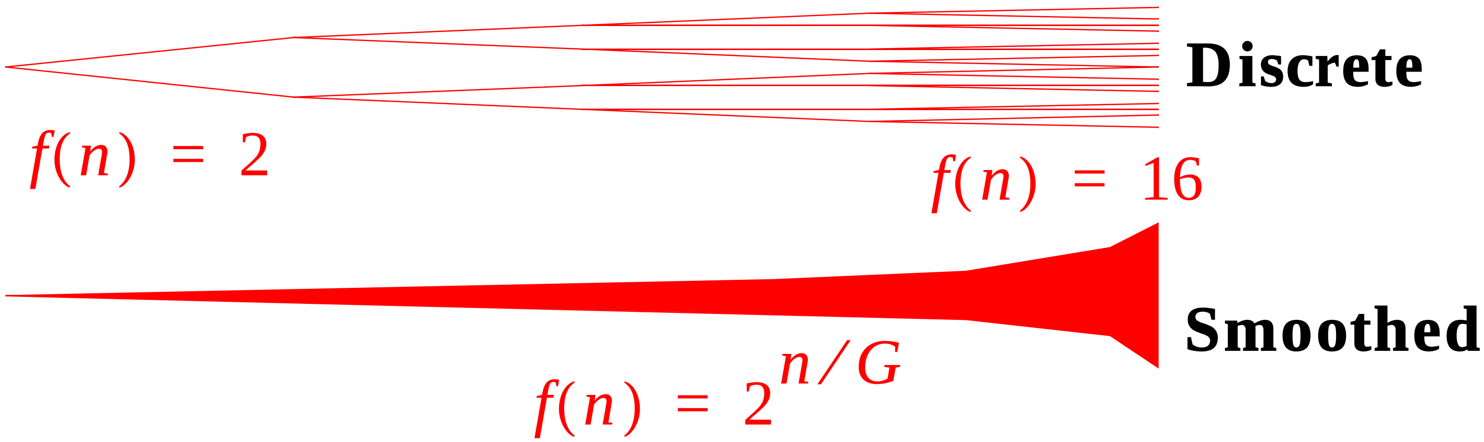



$$S = \sum_n \left\| \frac{\Delta r}{\Delta n} \right\|^2$$

- **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**

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

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

- **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.**

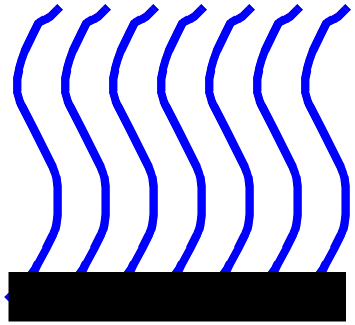
- **Source of Hollow-core.**

- **Gives a nonlinear ODE to solve numerically:**

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

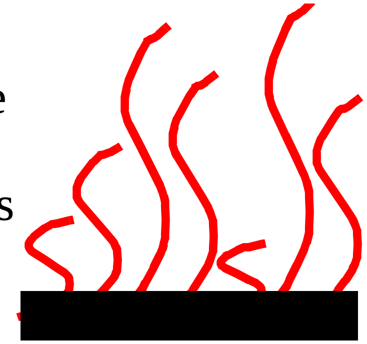
- **Polymer and Dendrimer Brush**

- **Polymer brush, no branchings:**

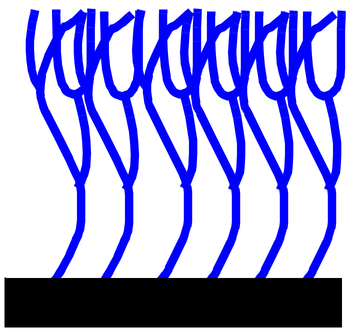


- φ is constant
- Tips segregated
- Scaling
- Not self-consistent

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



- **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:**

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

- **Harmonic potential is only self-consistent choice possible with**

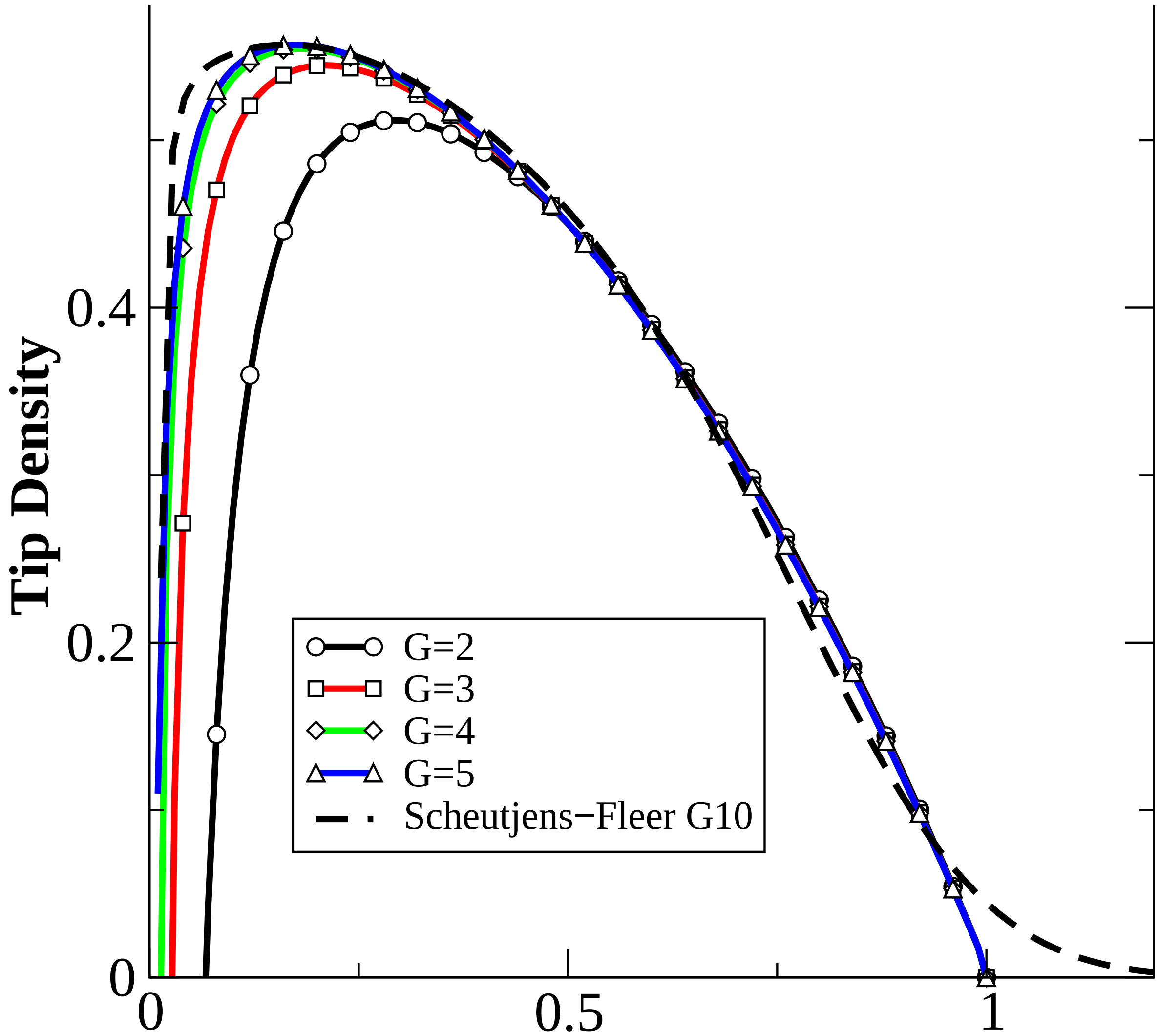
$$r(GN) = 0 \qquad\qquad r(0) = r_o$$

- Trajectory always uses up GN monomers to get to the core
- Trajectory can start off anywhere in the dendrimer

- **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 $G \geq 5$:**

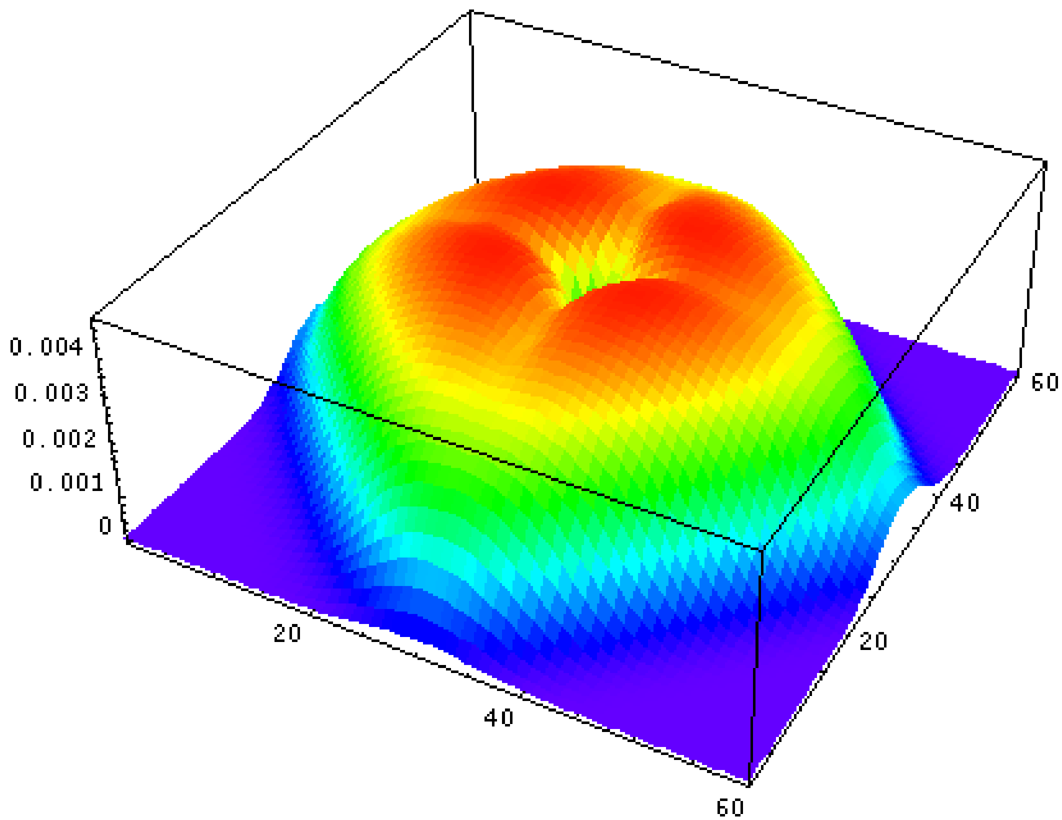



Zook, Pickett *Phys. Rev. Letts*, in press 2003.

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

- **Interesting Structures Not in Theory**

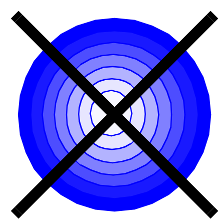
- **Short spacers give distinctly non-parabolic density/ density of tips:**
- **N=4, G=8, 2D Scheutjens and Fleer calculation**

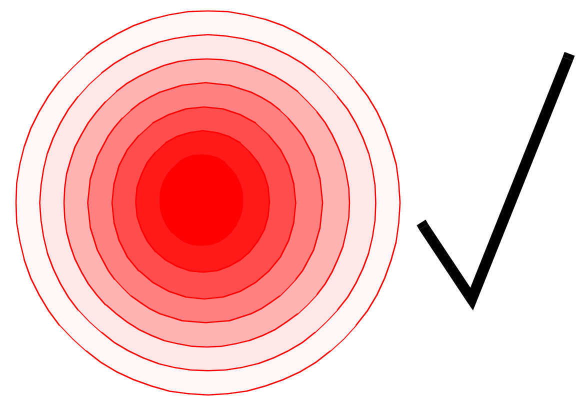



- Tip density shows internal structure, void near center.
- NOT the "long-chain, Gaussian limit" of the analytic theory.
- Excluded volume and topology of chain

## 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.





- Support: Research Corporation, Petroleum Research Fund.