

SPHERICAL POLYMER BRUSHES UNDER GOOD SOLVENT CONDITIONS:  
MOLECULAR DYNAMICS RESULTS COMPARED TO  
DENSITY FUNCTIONAL THEORY

Federica Lo Verso

Condensed Matter Theory Group, Institut für Physik Johannes Gutenberg-Universität 55099 Mainz, Germany

# SPHERICAL BRUSHES OUTLINE

- **background**

- motivations/applications, open questions

- **single spherical brush**

- model/methods

- **results** Peculiarity of the spherical brush (crossover) regime with respect to star polymers and planar brushes

Limit of applicability of Molecular Dynamics

Density Functional Theory as a possible approach to extend the accessible range of parameters

- **summary**

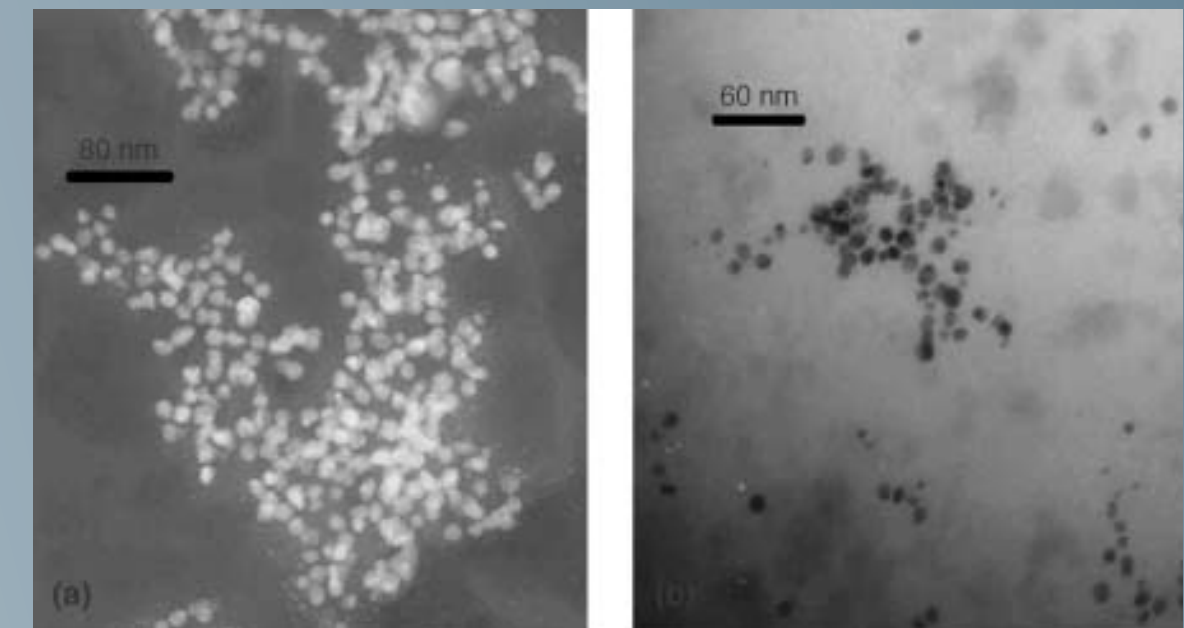
- **future work**

- Monomer Dynamics
- Interaction between spherical brushes

## BACKGROUND

- Polymer brushes play a role of great scientific and technological relevance, even beyond colloidal stabilization; the applications range from lubrication, tuning of adhesion and wetting properties, to biotechnology including protein purification, enzyme immobilization, virus capturing, improvement of biocompatibility of drugs, etc

The functionalization by polymers has been used to alter the physical characteristics of the particular nanoparticle. In the case of viral vectors, e.g., polymer functionalization tunes the biocompatibility, suppressing the binding of antibodies and conferring the nanoparticle with stealth properties. By contrast, the inorganic nanoparticles comprise materials in a form that is not normally encountered in the human body, and polymer functionalization is necessary to ensure biocompatibility.

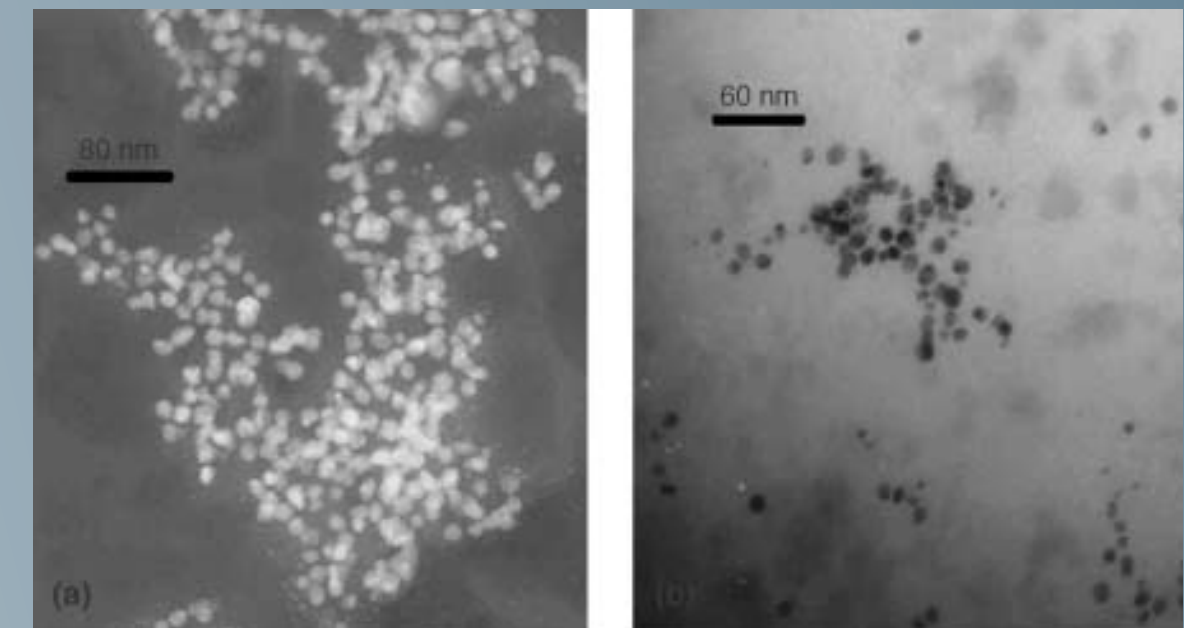


Kemp et al., WIREs Nanomed Nanobiotechnol 2010, 2 77  
Transmission electron microscopy

## BACKGROUND

- Polymer brushes play a role of great scientific and technological relevance, even beyond colloidal stabilization; the applications range from lubrication, tuning of adhesion and wetting properties, to biotechnology including protein purification, enzyme immobilization, virus capturing, improvement of biocompatibility of drugs, etc

The functionalization by polymers has been used to alter the physical characteristics of the particular nanoparticle. In the case of viral vectors, e.g., polymer functionalization tunes the biocompatibility, suppressing the binding of antibodies and conferring the nanoparticle with stealth properties. By contrast, the inorganic nanoparticles comprise materials in a form that is not normally encountered in the human body, and polymer functionalization is necessary to ensure biocompatibility.



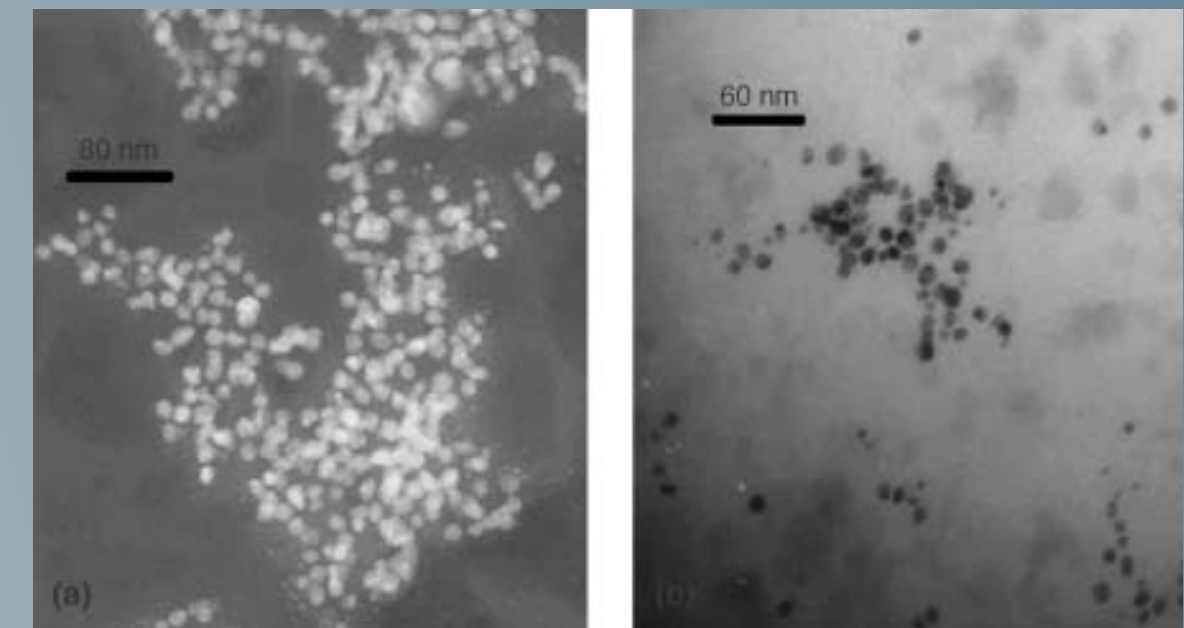
Kemp et al., WIREs Nanomed Nanobiotechnol 2010, 2:77  
Transmission electron microscopy

- For many applications (building blocks of nanocomposites, surface modification of biomolecules...) the grafting surfaces are (approximately) spherical, with a radius comparable to the linear dimensions of the grafted polymers.
  - The intermediate curvature regime, where the size of the core is comparable to the full molecule extension, has received somewhat less attention.

## BACKGROUND

- Polymer brushes play a role of great scientific and technological relevance, even beyond colloidal stabilization; the applications range from lubrication, tuning of adhesion and wetting properties, to biotechnology including protein purification, enzyme immobilization, virus capturing, improvement of biocompatibility of drugs, etc

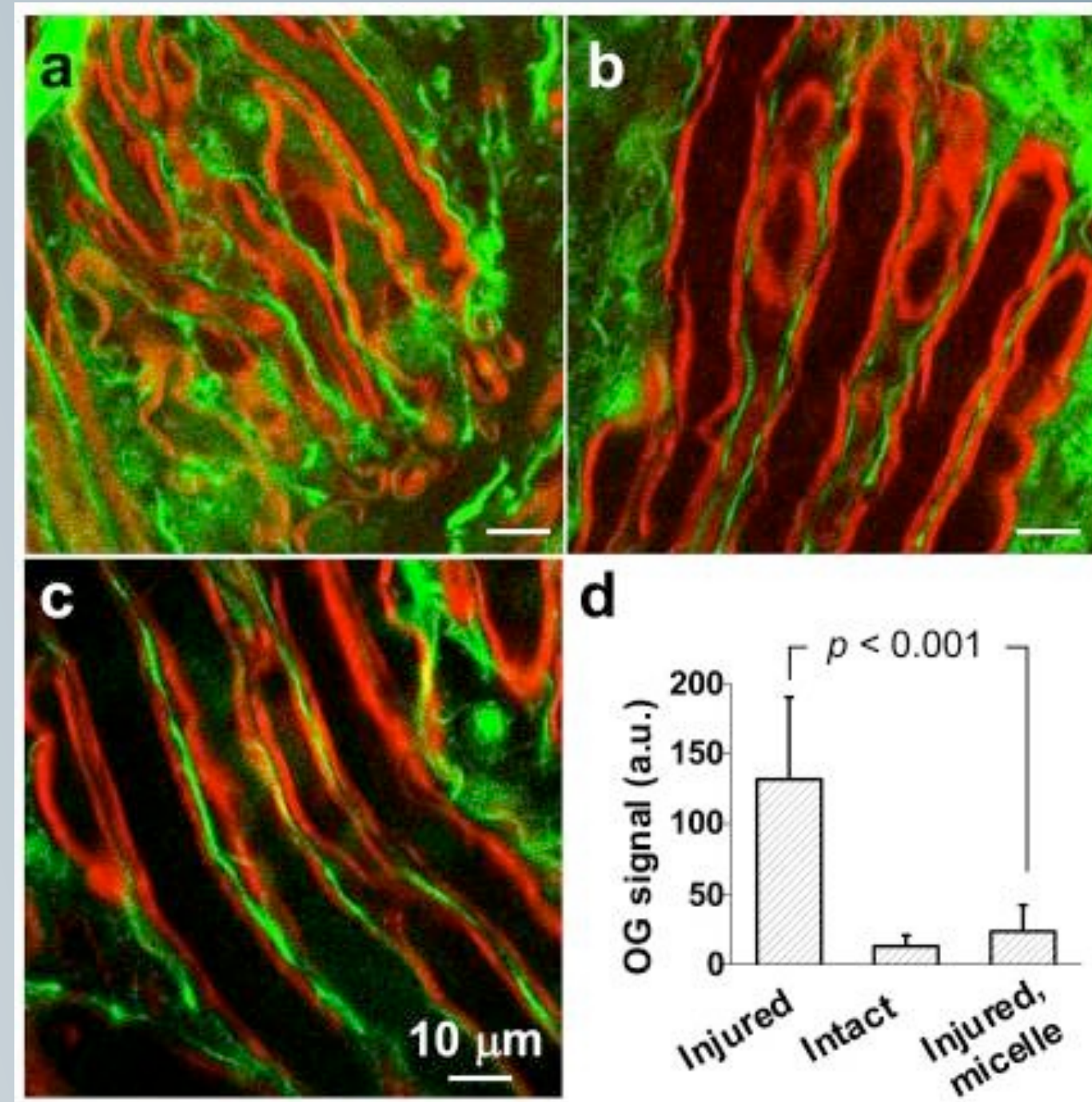
The functionalization by polymers has been used to alter the physical characteristics of the particular nanoparticle. In the case of viral vectors, e.g., polymer functionalization tunes the biocompatibility, suppressing the binding of antibodies and conferring the nanoparticle with stealth properties. By contrast, the inorganic nanoparticles comprise materials in a form that is not normally encountered in the human body, and polymer functionalization is necessary to ensure biocompatibility.



Kemp et al., WIREs Nanomed Nanobiotechnol 2010, 2:77  
Transmission electron microscopy

- For many applications (building blocks of nanocomposites, surface modification of biomolecules...) the grafting surfaces are (approximately) spherical, with a radius comparable to the linear dimensions of the grafted polymers.
  - The intermediate curvature regime, where the size of the core is comparable to the full molecule extension, has received somewhat less attention.
- Another debated aspect is related to the description of micelles in terms of spherical polymer brushes.
  - Small spherical nanoparticles with many flexible chains grafted to their surface are similar to spherical micelles, formed from asymmetric block copolymers

## BACKGROUND



Calcium influx into axons. TPEF images of Oregon Green 488 (green) and CARS images of myelin (red) show intra-axonal free  $\text{Ca}^{2+}$  level in (a) compression injured, (b) healthy, and (c) compression-injured and micelle-treated spinal cords. Images were acquired at 1 h after the compression injury. Statistical analysis is shown in (d). Without micelle treatment, the TPEF intensity from Oregon Green 488 inside the injured axons was 10 times greater than healthy axons. The intensity was only twice that of healthy axons when 0.67 mg/mL micelles were added immediately after compression injury [*Nature Nanotechnology* **5**, 80 - 87 (2010)]

# SINGLE MOLECULE: STATICS

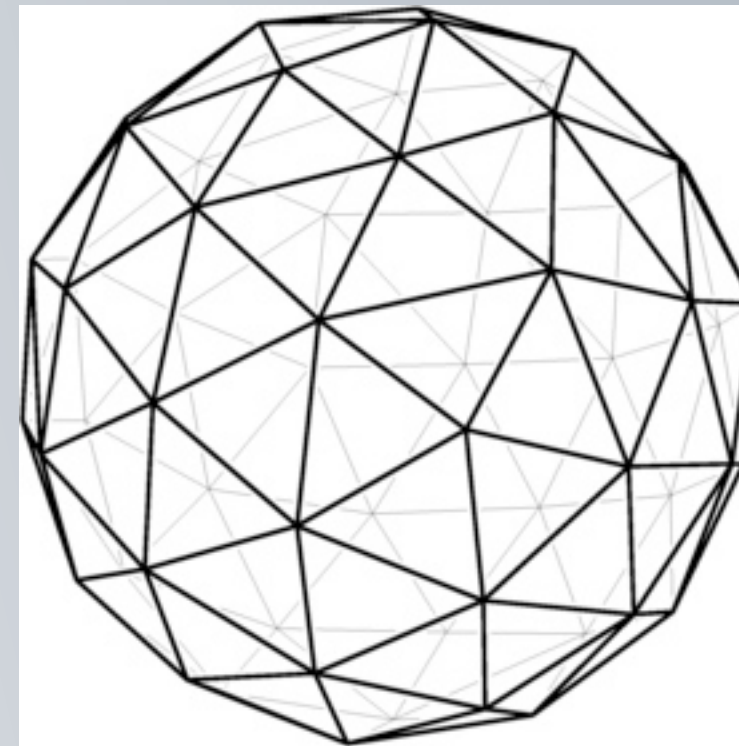
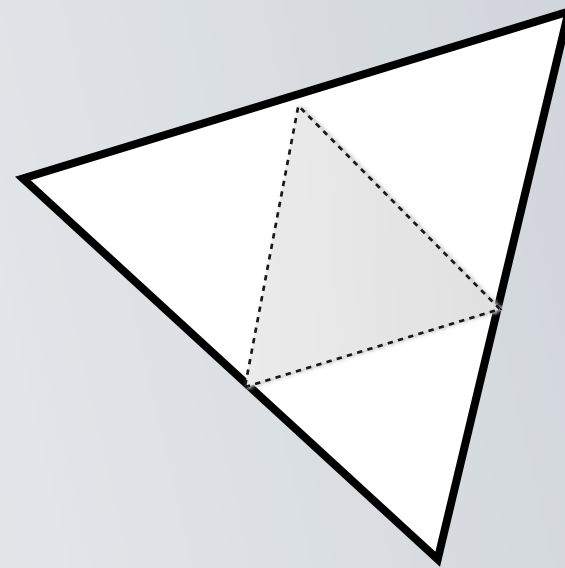
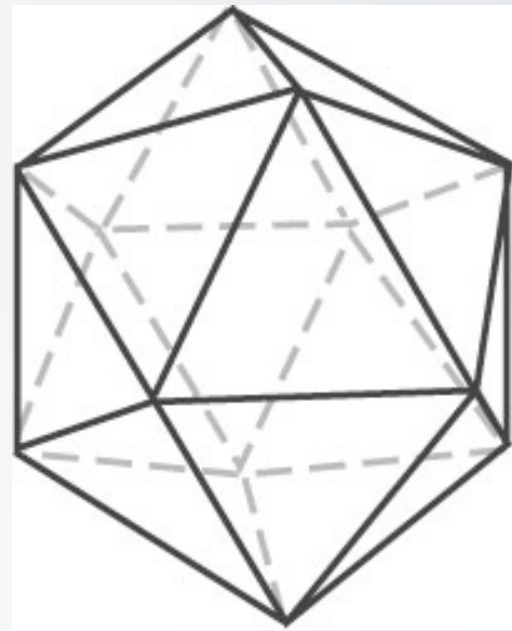
**Method:** Monomer resolved Molecular Dynamics simulation

**The molecule has  $f$  flexible chains containing  $N$  effective beads (standard Kremer-Grest model)**

FLV, S. Egorov, A. Milchev and K. Binder JCP 133, 184901 (2010)

**Model:**

The chains are grafted to sites regularly distributed on the surface of spheres (via **geodesic subdivision**);  
**grafting density  $\sigma=0.068, 0.118$  and  $0.185$**



$f=42$	$f=92$	$f=162$
$R_c=7$	$R_c=7.9$	$R_c=8.35$
$\sigma=0.068$	$\sigma=0.118$	$\sigma=0.185$

# SINGLE MOLECULE: STATICS

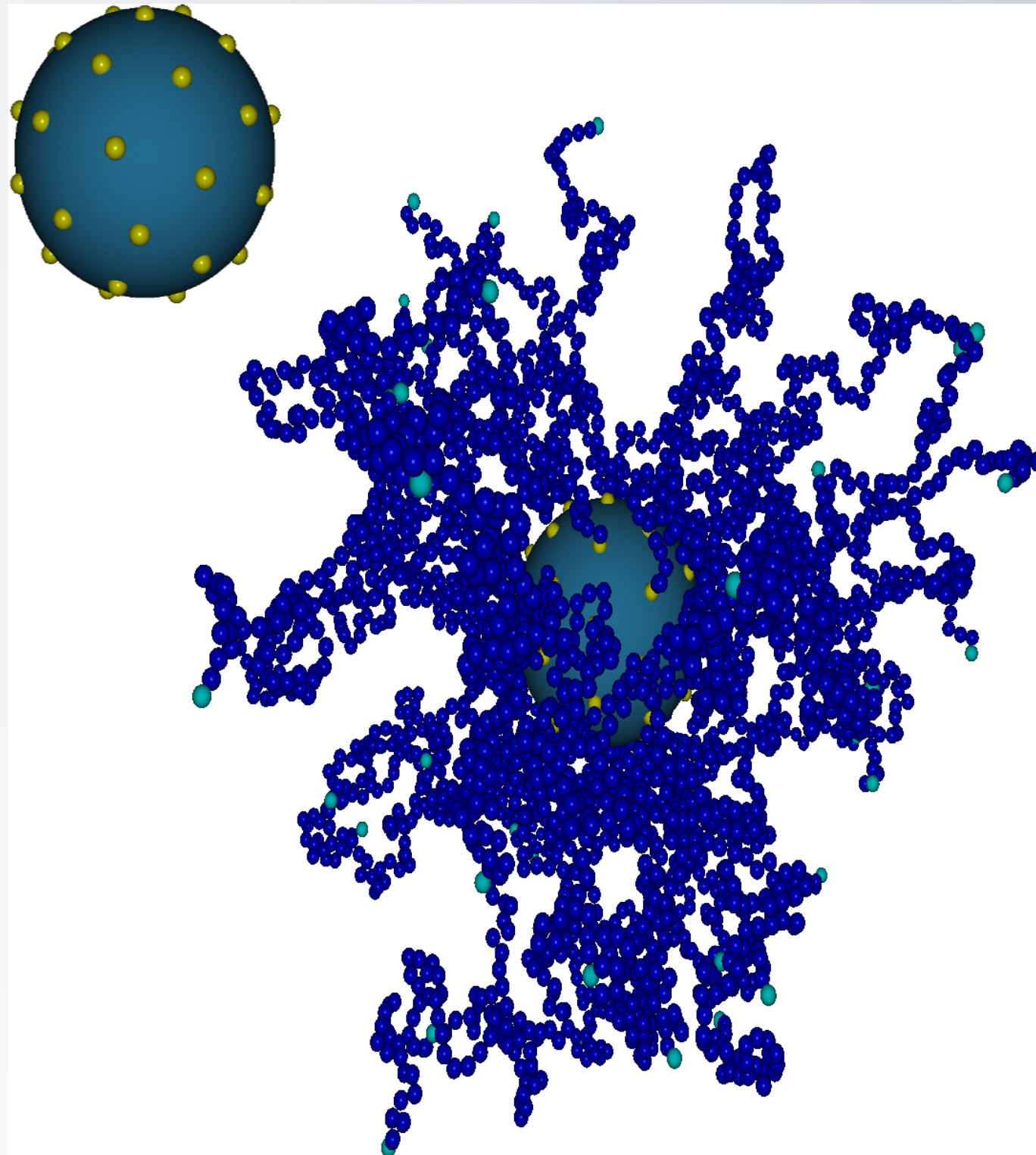
## Method: Monomer resolved Molecular Dynamics simulation

The molecule has  $f$  flexible chains containing  $N$  effective beads (standard Kremer-Grest model)

FLV, S. Egorov, A. Milchev and K. Binder JCP 133, 184901 (2010)

### Model:

The chains are grafted to sites regularly distributed on the surface of spheres (via geodesic subdivision);  
grafting density  $\sigma=0.068, 0.118$  and  $0.185$



-All blue monomers are described by:

$$V_{LJ}(r) = \begin{cases} 4\epsilon_{LJ} \left[ \left( \frac{\sigma_{LJ}}{r} \right)^{12} - \left( \frac{\sigma_{LJ}}{r} \right)^6 + \frac{1}{4} \right] & \text{for } r \leq 2^{1/6}\sigma_{LJ} \\ 0 & \text{for } r > 2^{1/6}\sigma_{LJ} \end{cases}$$

purely repulsive LJ

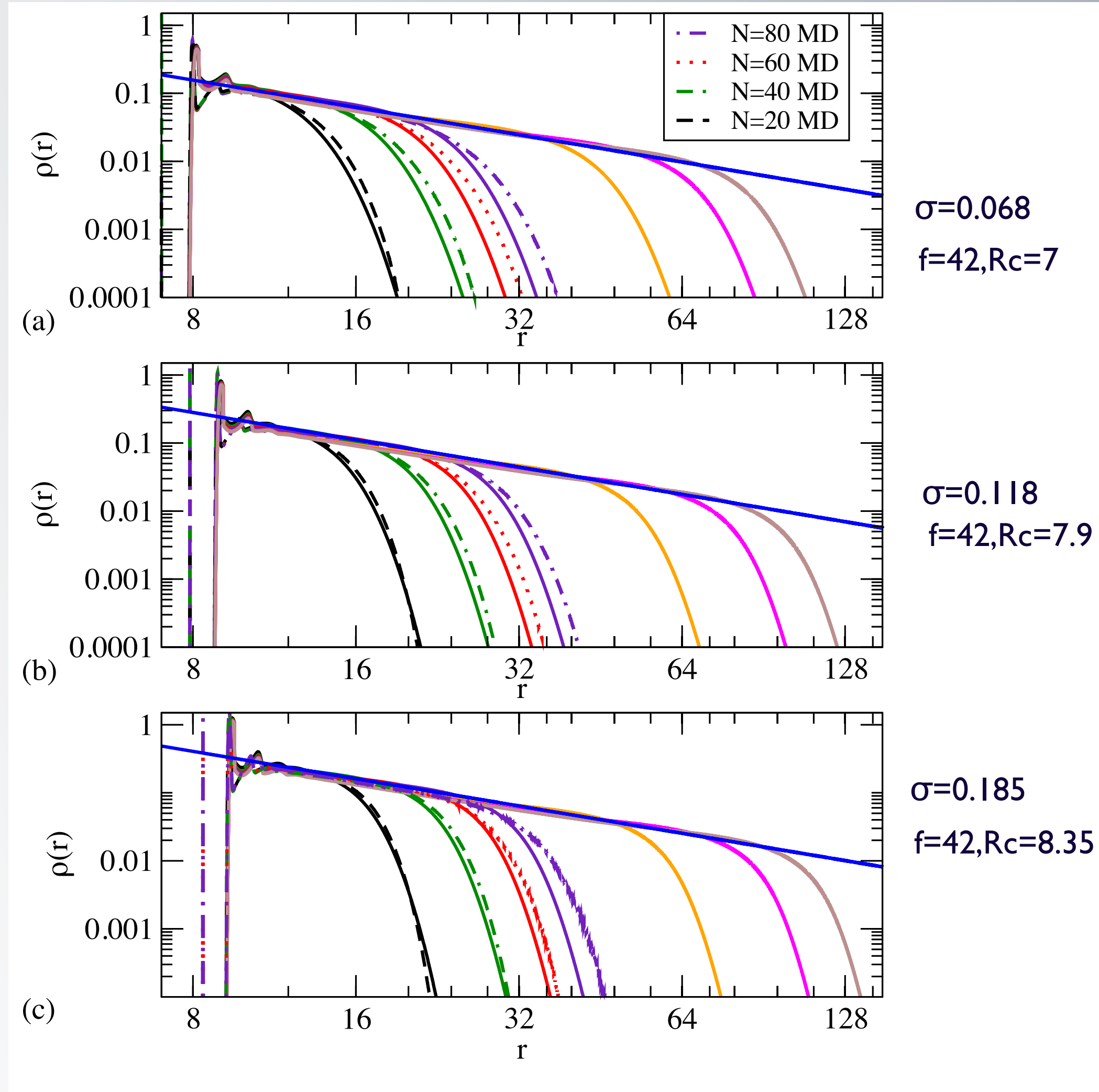
-Neighboring monomers in the same arm:  
FENE potential (connectivity of the chain)

$$V_{FENE}(r) = \begin{cases} \frac{k_{FENE}}{2} \left( \frac{R_0}{\sigma_{LJ}} \right)^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] & \text{for } r \leq R_0 \\ \infty & \text{for } r > R_0 \end{cases}$$

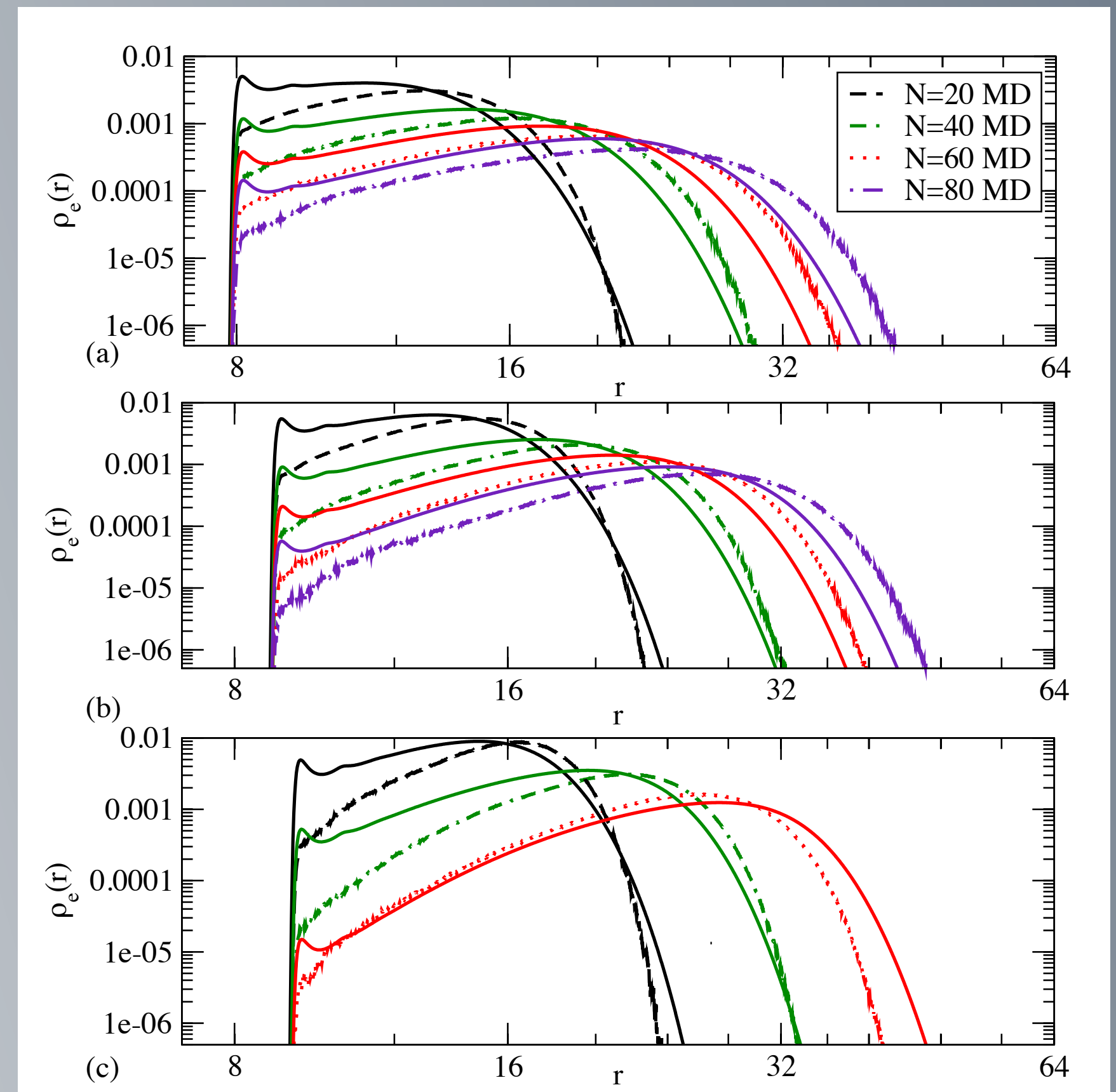
# RADIAL MONOMER DENSITY PROFILE

For  $N \geq 40$ : characteristic power law decay expected for **star polymers** with very large arms  $r^{-4/3}$

For low enough N and/or big enough radius of the internal core we expect a crossover to the flat brush limit:  
the results we obtained for  $N < 40$  evidenced a **parabolic profile**.



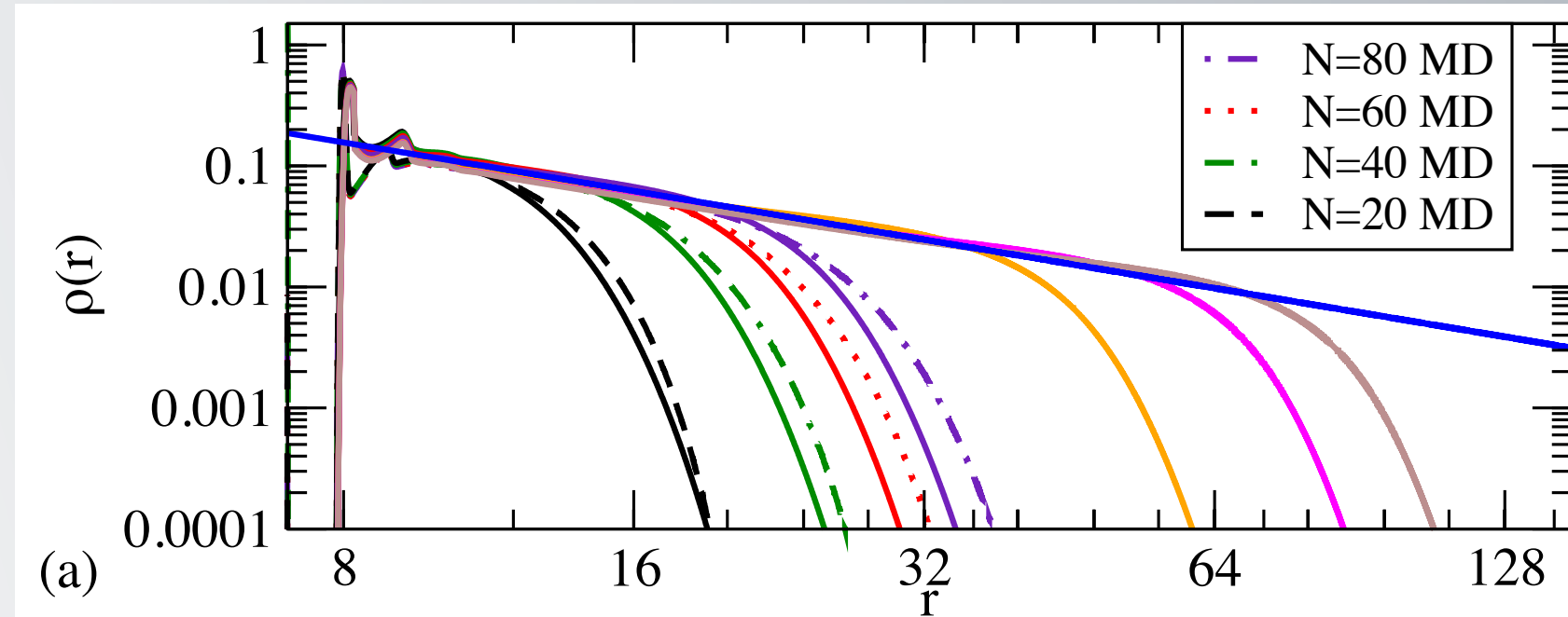
straight lines: DFT



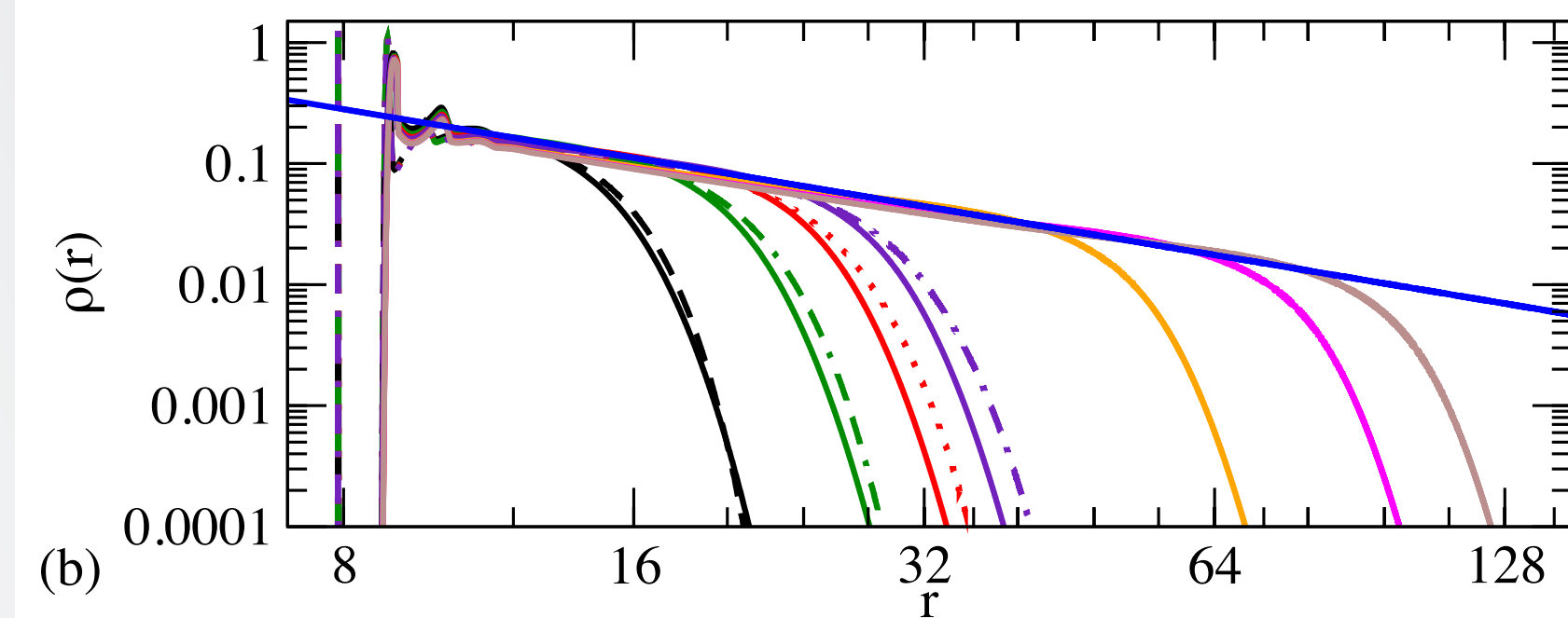
# RADIAL MONOMER DENSITY PROFILE

For  $N \geq 40$ : characteristic power law decay expected for **star polymers** with very large arms  $r^{-4/3}$

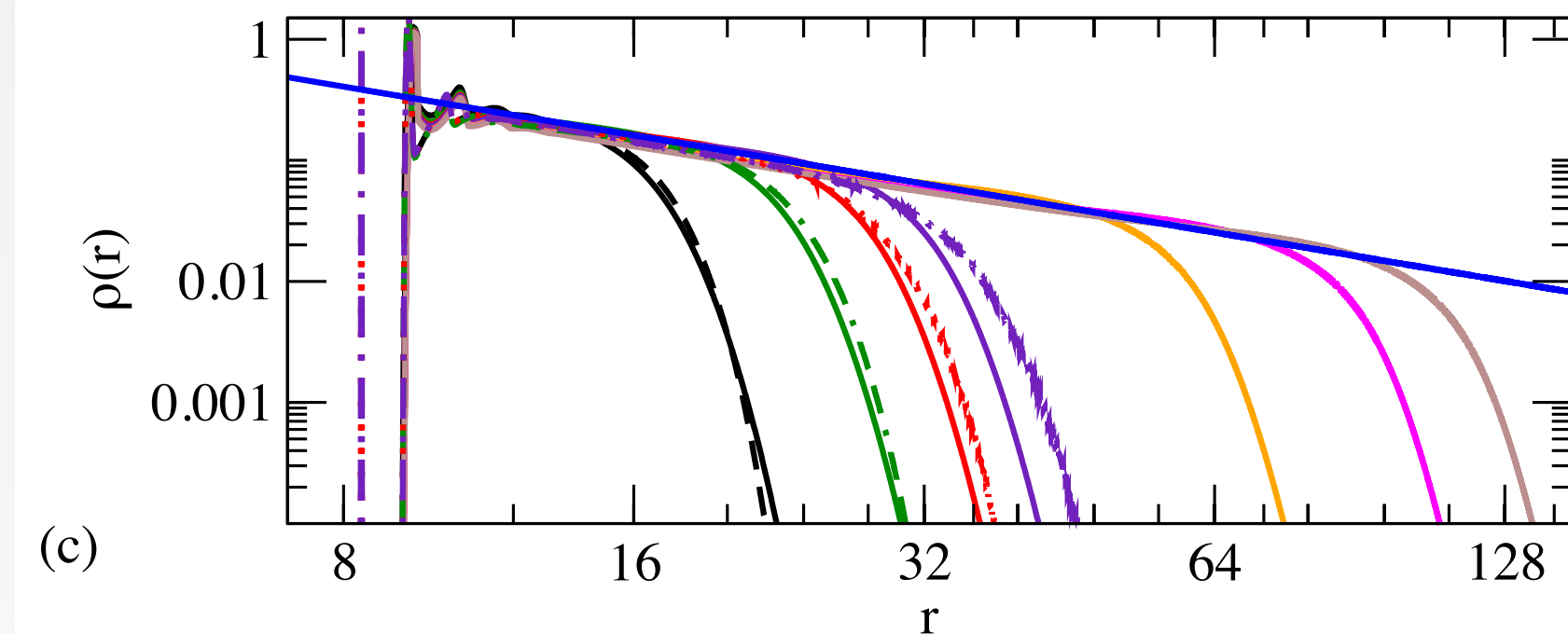
For low enough N and/or big enough radius of the internal core we expect a crossover to the flat brush limit: the results we obtained for  $N < 40$  evidenced a **parabolic profile**.



$\sigma=0.068$   
 $f=42, R_c=7$

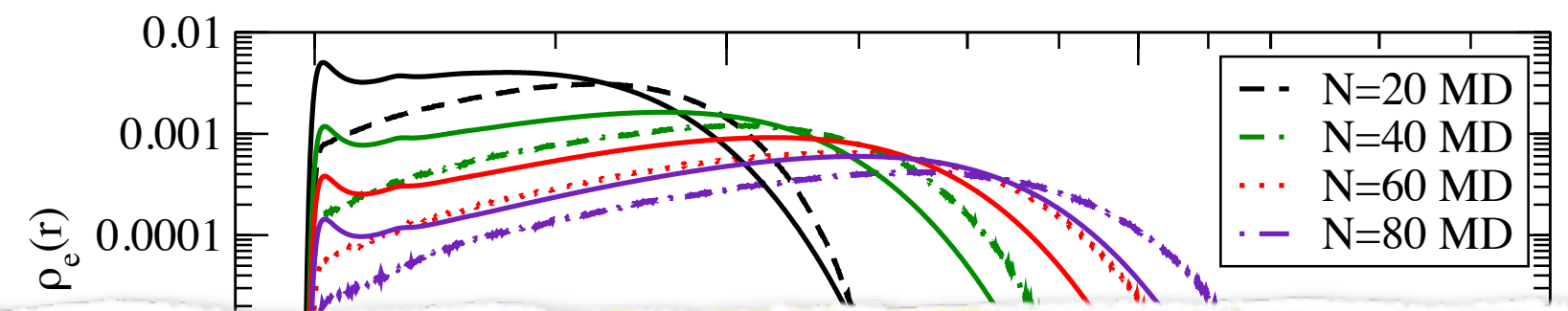


$\sigma=0.118$   
 $f=42, R_c=7.9$



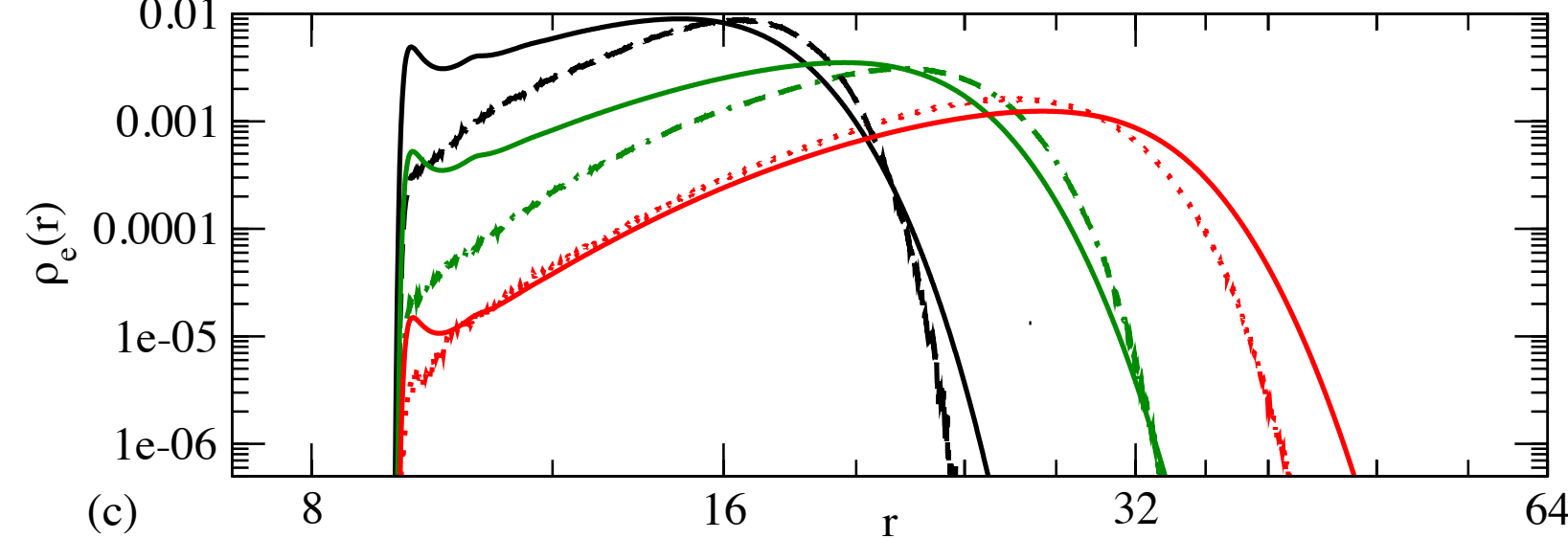
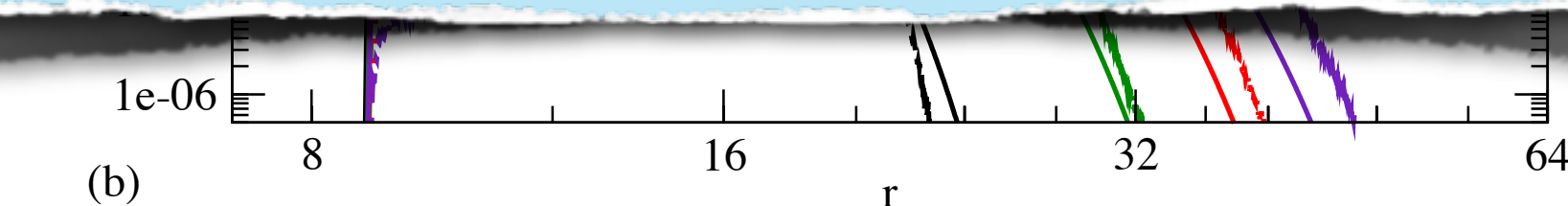
$\sigma=0.185$   
 $f=42, R_c=8.35$

straight lines: DFT



DFT reproduces the general trend of the MD results rather faithfully.

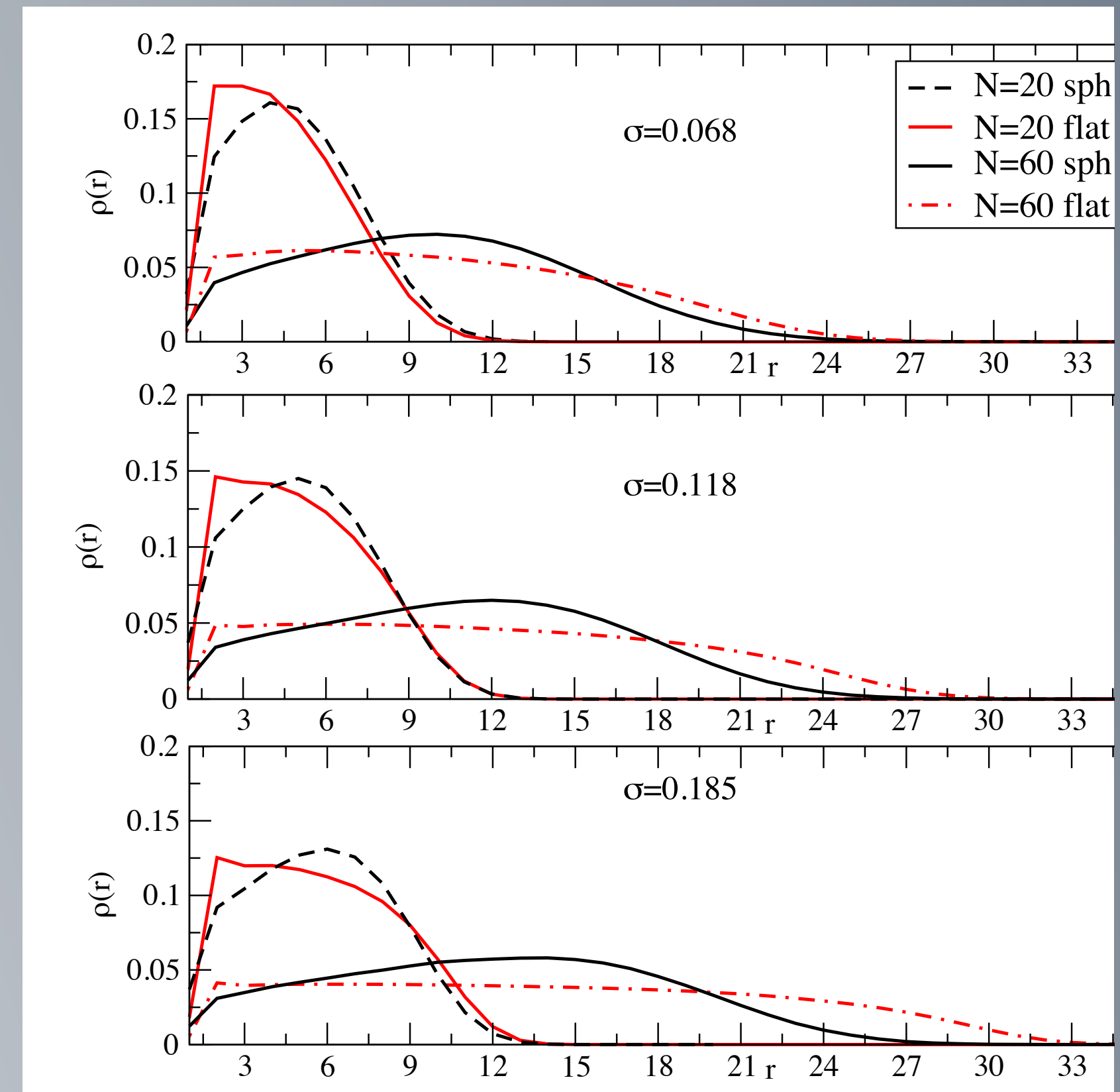
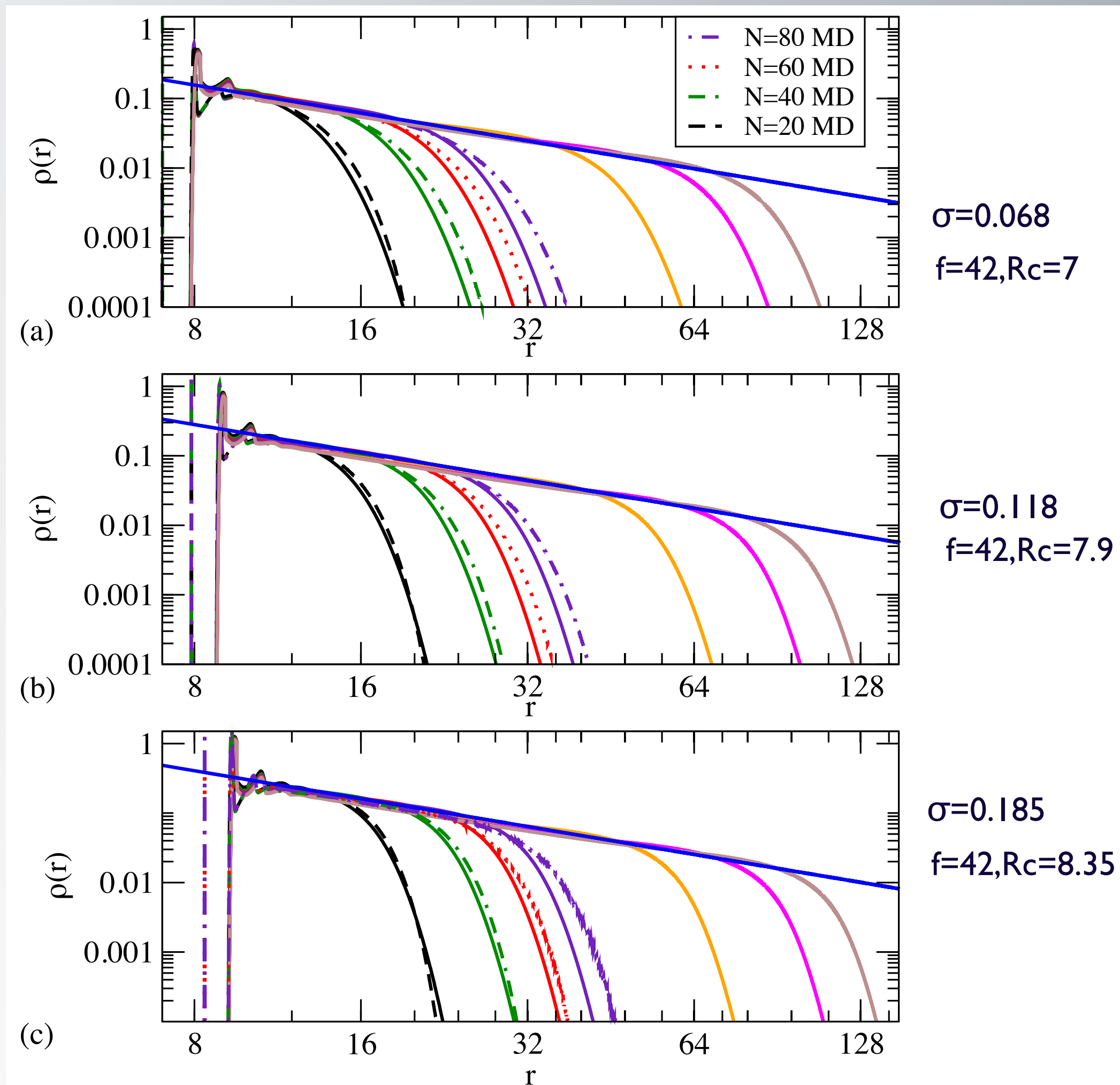
The slight discrepancy reflects the fact that DFT does not reproduce the star scaling for  $N \rightarrow \infty$ . The deviations increase with N.



## RADIAL MONOMER DENSITY PROFILE

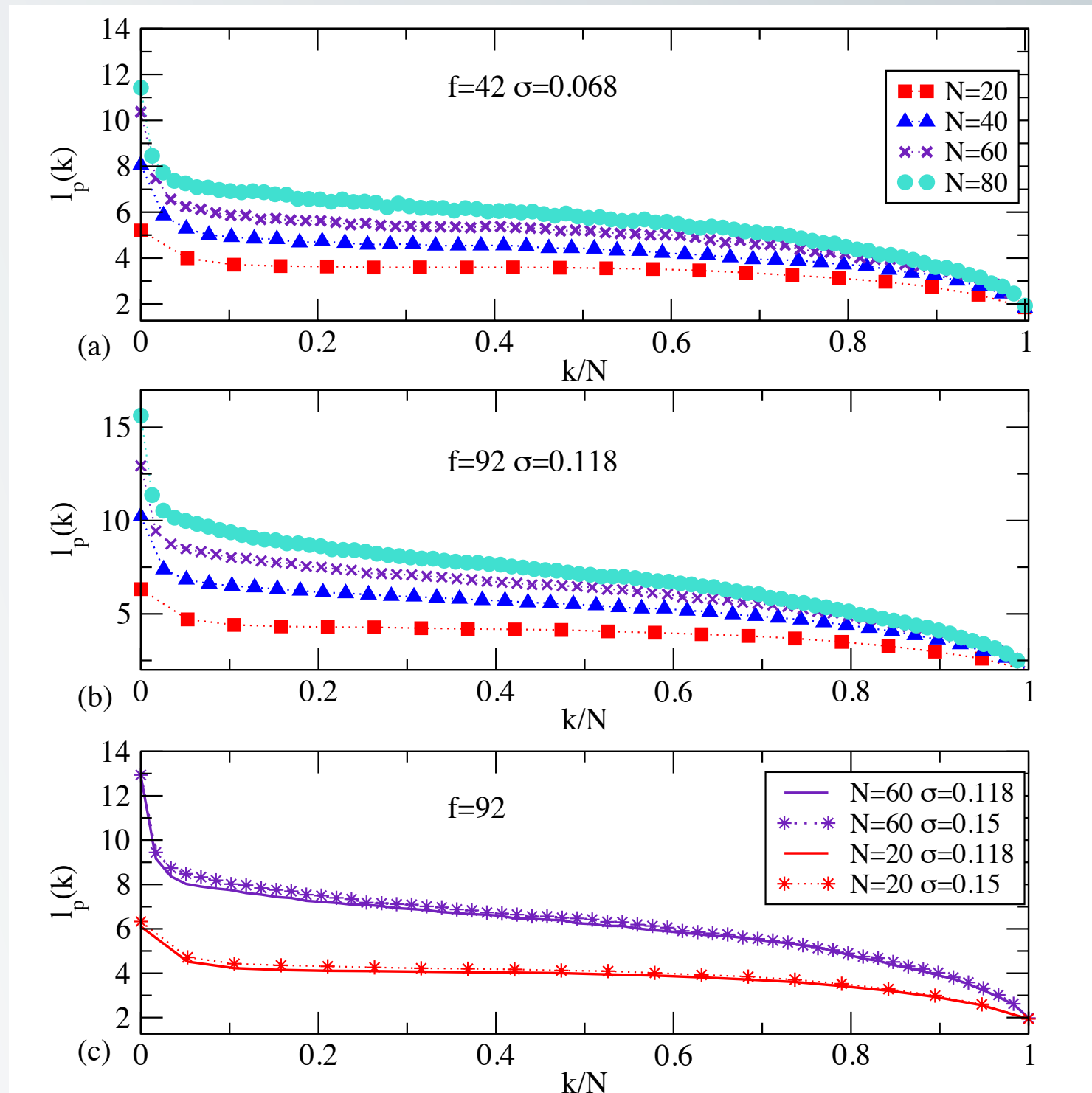
For  $N \geq 40$ : characteristic power law decay expected for **star polymers** with very large arms  $r^{-4/3}$

For low enough N and/or big enough radius of the internal core we expect a crossover to the flat brush limit:  
the results we obtained for  $N < 40$  evidenced a **parabolic profile**.



For  $N=20$  the differences between the profiles for flat and spherical brushes are rather minor

# Local stretching of the chains



$$l_p(k)/r_{bond} = \langle \mathbf{a}_k \mathbf{R}_e / |\mathbf{a}_k|^2 \rangle$$

$$\mathbf{a}_k = \mathbf{r}_k - \mathbf{r}_{k-1}, k = 1, \dots, N$$

$\vec{r}_k$  is the position of the  $k$ 'th monomeric unit along a chain, starting with  $k=0$  at the grafting site.

not quantitative informations but..

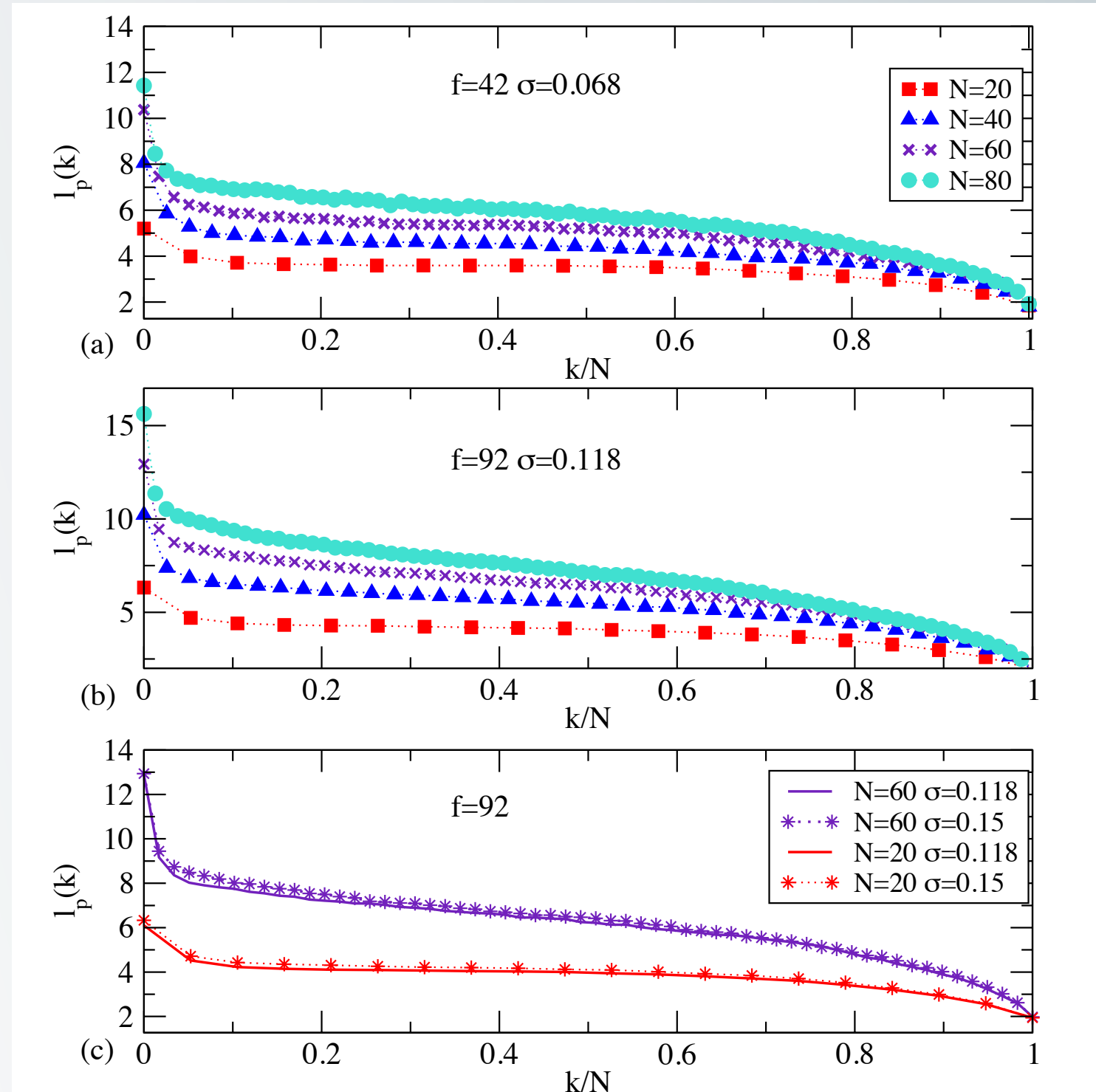
informations on the relative orientation of bond vectors, correlated with the end-to-end vector orientation

[H. P. Hsu, W. Paul, and K. Binder, Macromolecules, 43, 3094 (2010)]

Behavior mostly controlled by the excluded volume interactions between the monomers of the single chain

# Local stretching of the chains

# Structure factor from the spherical brush and spherically averaged scattering intensity from single arms



$$l_p(k)/r_{bond} = \langle \mathbf{a}_k \mathbf{R}_e / |\mathbf{a}_k|^2 \rangle$$

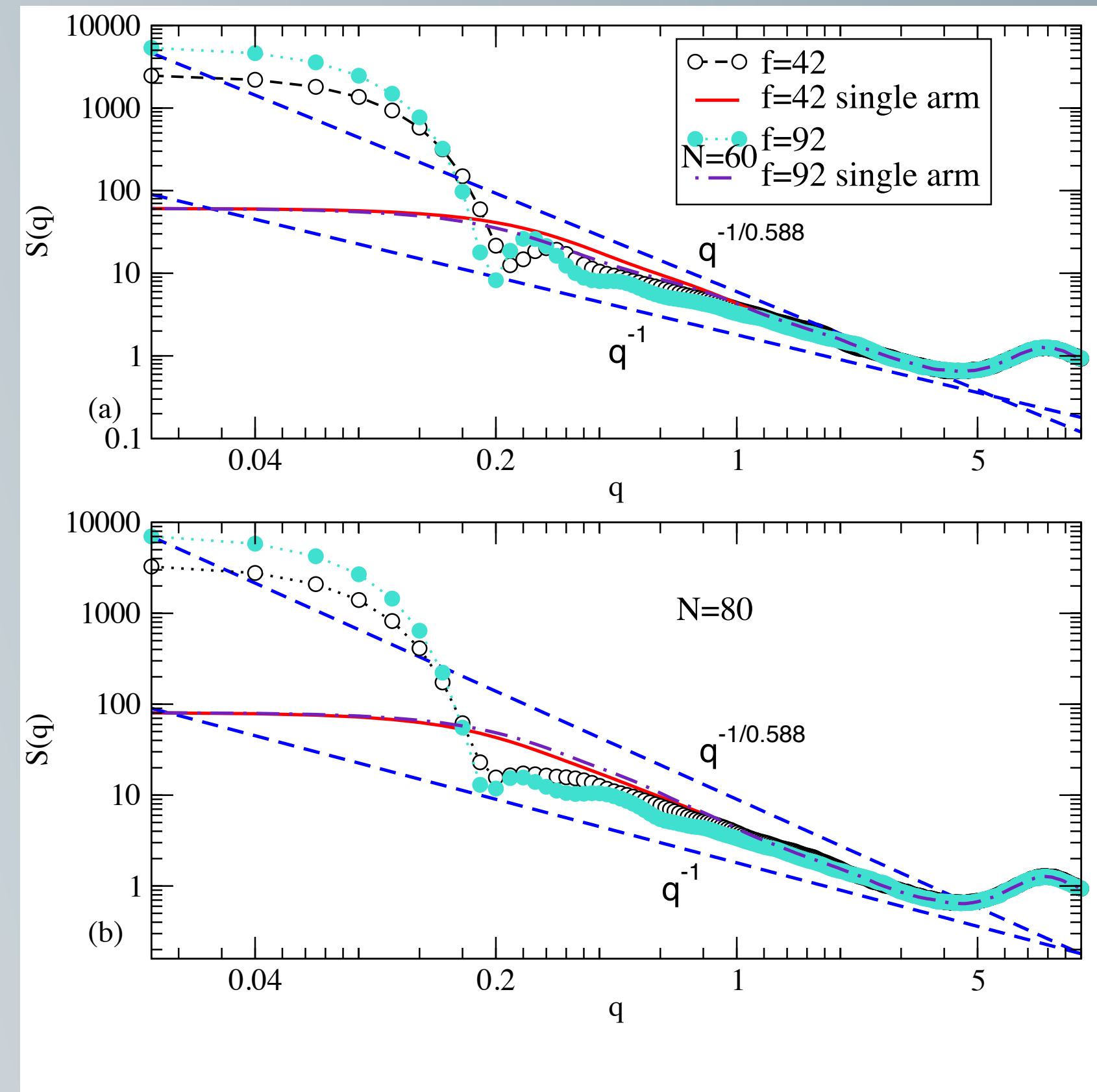
$$\mathbf{a}_k = \mathbf{r}_k - \mathbf{r}_{k-1}, \quad k = 1, \dots, N$$

$\vec{r}_k$  is the position of the k'th monomeric unit along a chain, starting with k=0 at the grafting site.

not quantitative informations but..  
 informations on the relative orientation of bond vectors, correlated with the end-to-end vector orientation

[H. P. Hsu, W. Paul, and K. Binder, Macromolecules, 43, 3094 (2010)]

Behavior mostly controlled by the excluded volume interactions between the monomers of the single chain



The structure factor for the full spherical brush resembles the scattering from a compact sphere @ small q,  
 exhibits a minimum, (roughly @  $1/R_c$ )  
 the maximum at larger q is more and more washed out as N increases.

Close to the spherical surface where the chain are more stretched the curve approach the power law straight line typical of rigid molecules (stretched chains)

These data clearly resemble quantitatively experimental scattering data from spherical micelles

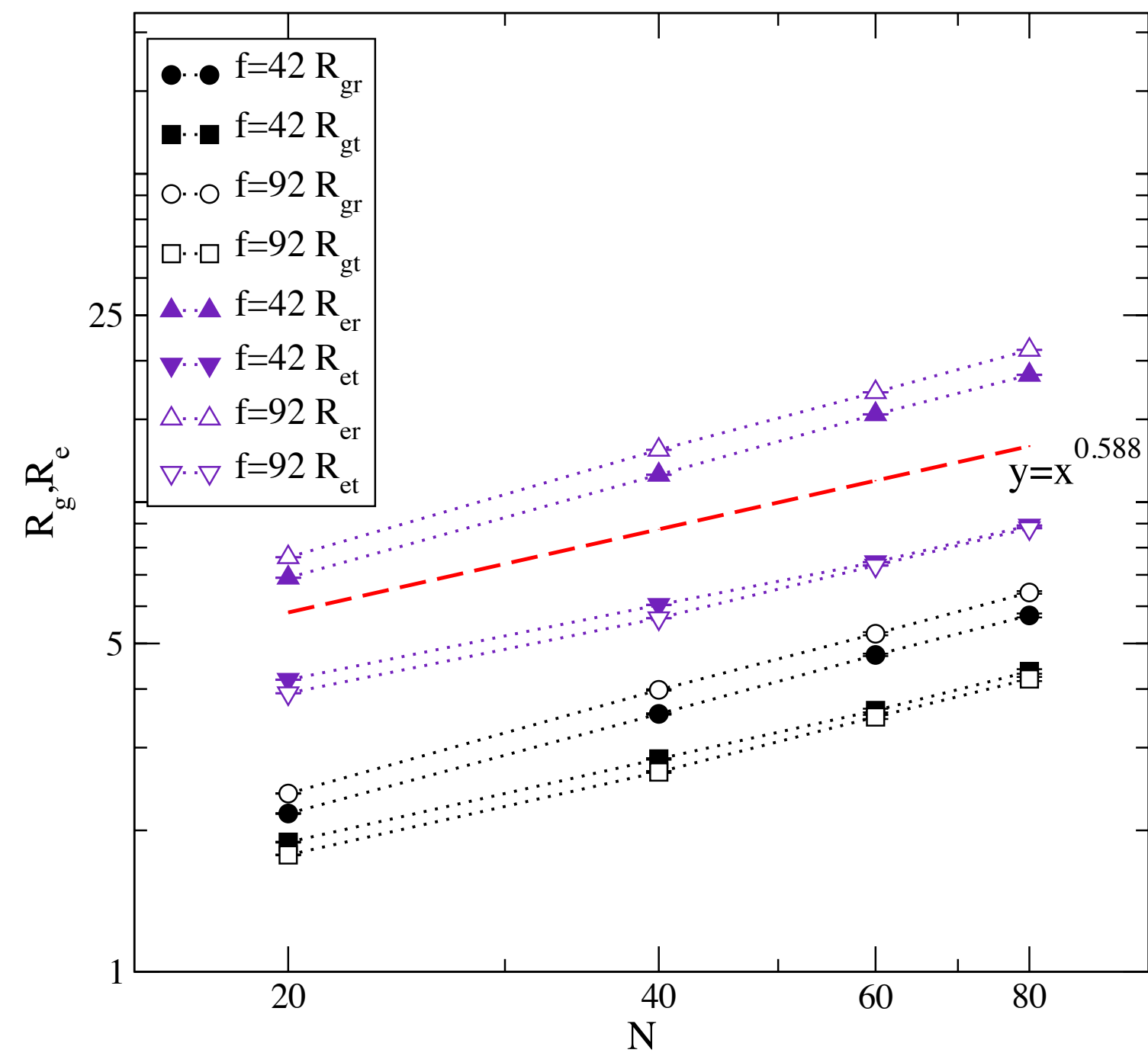
## Mean square radius and end-to-end distance components in radial and tangential directions versus N.

The tangential components decrease with increasing  $f$  in agreement with the increase of the stretching of the chains with the grafting density.

Note that all the chain linear dimensions still scale with chain length according to the standard excluded volume power law.

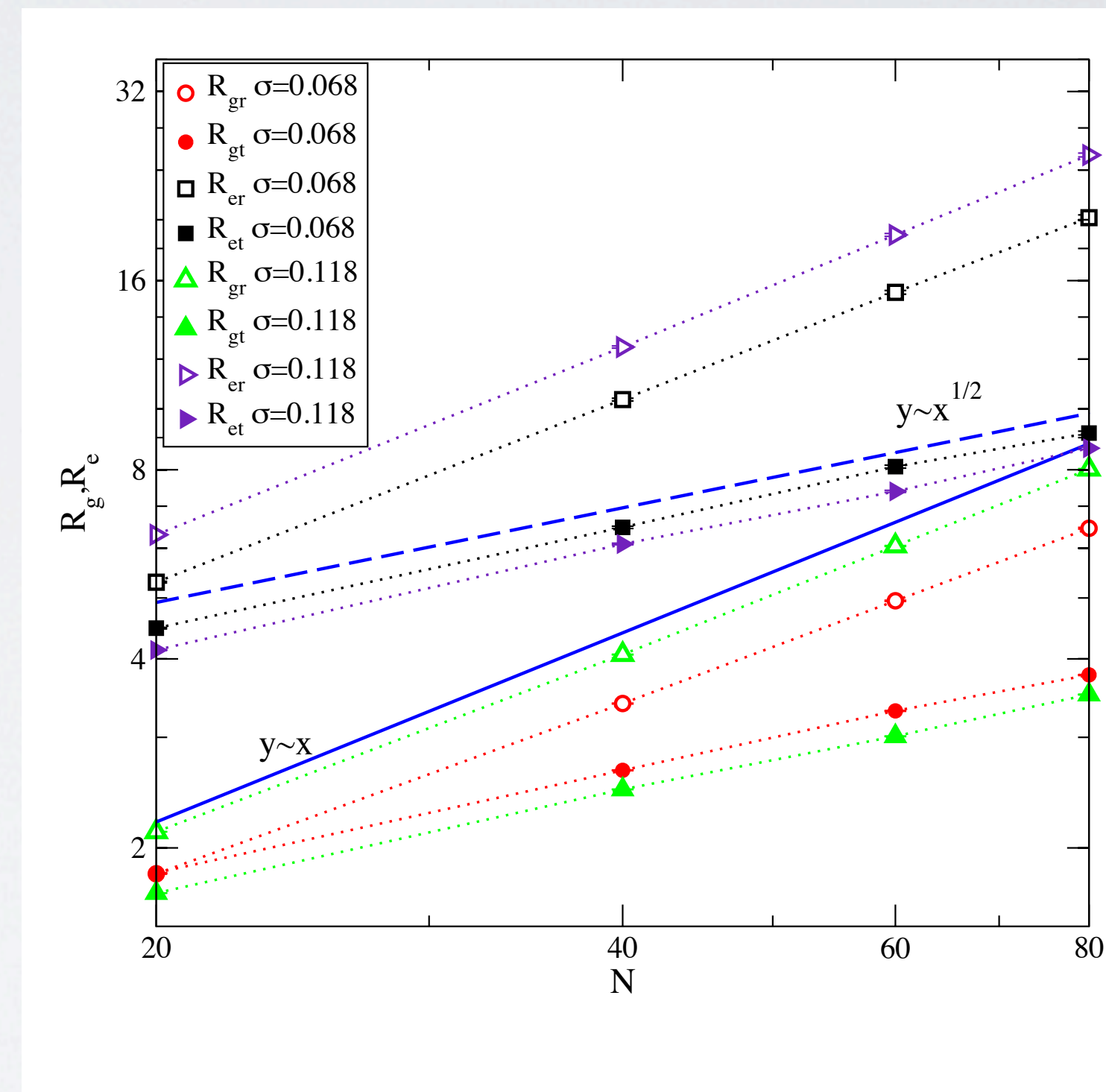
Neither the scaling relation for star polymers  $\langle R_{gr}^2 \rangle \propto \langle R_{er}^2 \rangle \propto N^{2\nu} f^{1-\nu}$

nor for chains in planar brushes in the strong stretching limit  $\langle R_{gz}^2 \rangle \propto \langle R_{ez}^2 \rangle \propto N^2 \sigma^{2/3}$  describes our numerical results perfectly .



$R_{gr}$  and  $R_{gt}$  same order of magnitude

There exists a very extended regime of gradual crossover from the planar brushes to the star polymer limit



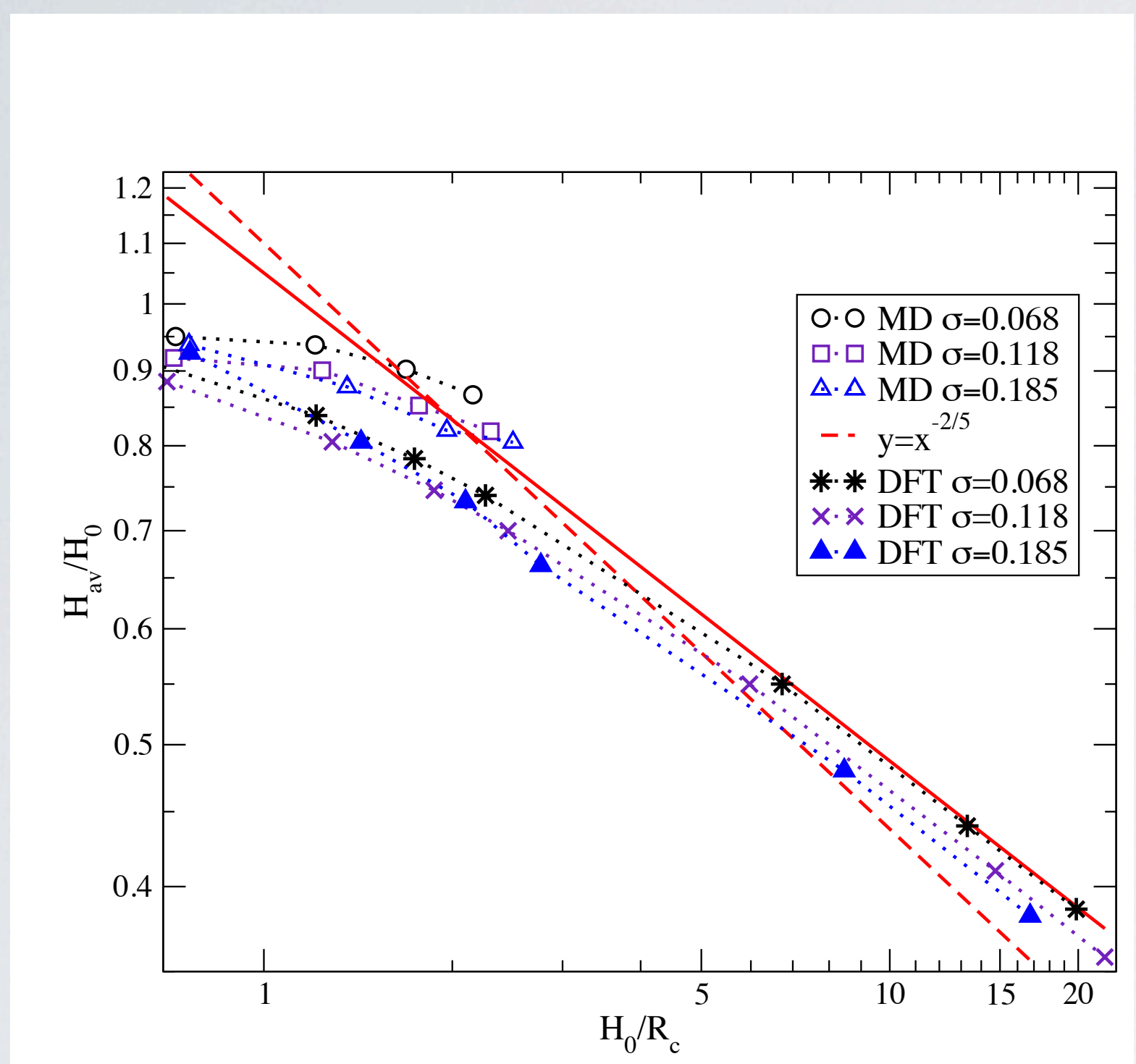
\*Daoud and J. P. Cotton, J. Phys. (Paris), 43, 531 (1982), S.T. Milner, T.A. Witten, and M. E. Cates, Macromolecules, 21, 2610 (1988)

# In order to study the crossover of the average brush height from the flat brush limit to the spherical one

we follow  
by defining

C. M. Wijmans and E. B. Zhulina, Macromolecules, 26, 7214 (1993)

$$H_{av}^2 = \int_{R_c}^{\infty} r^2 dr \rho(r) (r - R_c)^2 / \int_{R_c}^{\infty} r^2 dr \rho(r) \quad H_0^2 = \int_0^{\infty} \rho(z) z^2 dz / \int_0^{\infty} dz \rho(z)$$



Log-log plot of the normalized brush height  $H_{av}/H_0$  versus the normalized inverse radius  $H_0/R_c$ .

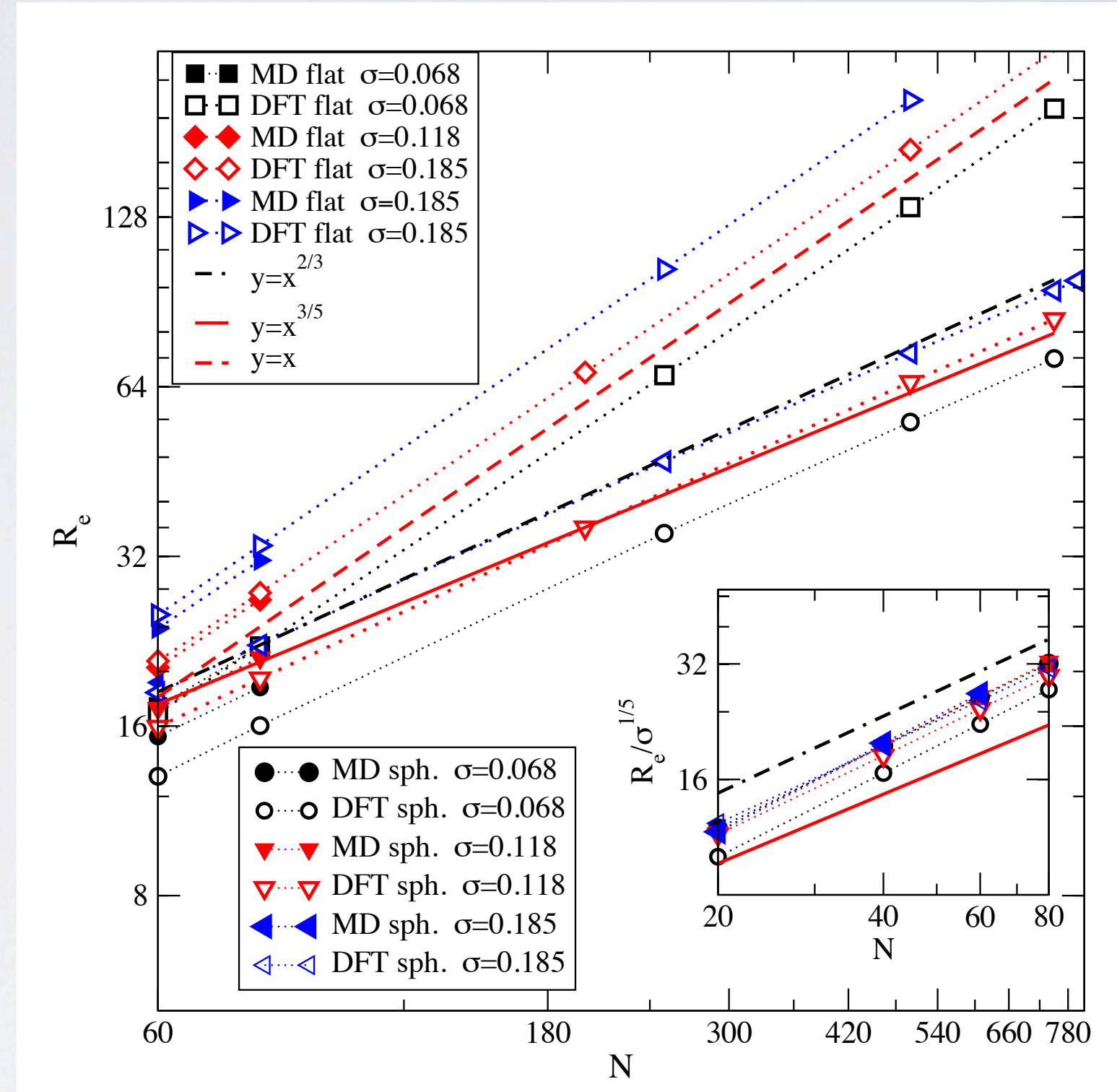
The theoretical asymptotic slope predicted from SCFT (-2/5) is shown as a broken straight line.

The DFT results converge to a power law with slope of minus one third (full straight line)

DFT data can easily be taken to  $H_0/R_c \sim 20$ , using chain lengths up to  $N=750$ , which would be inaccessible for our MD study.

The DFT results, do reach an asymptotic power law inconsistent with  $H_{av} \propto H_0^{3/5} R_c^{2/5} \propto \sigma^{1/5} N^{3/5} R_c^{2/5}$ .

We lack an explanation as to why DFT predicts a star polymer scaling  $R_{star} \propto N^{2/3}$



These discrepancies are also apparent when we study the end-to-end distance:

DFT is less useful for spherical brushes than for flat brushes, overestimating the chain stretching in spherical brushes for large  $N$  systematically.

## Analysis of conformation and structural properties of spherical brushes (crossover regime)

In order to clarify the origin of the inhomogeneous stretching of the chains, and the development of multiple relevant length scales we calculated the local persistence length, the structure factor of the chain and full molecule as well as the radial and tangential components of the  $R_g$  and  $R_e$ .

✓ The main conclusion here is that there exists an extended regime of gradual crossover between star polymer and flat brush behavior.

The crossover extends over several decades in this variable, in order to cover both star polymer scaling and flat brush scaling relations.

✓ In the regime of parameters investigated the structure of the brush is mostly driven by the intrachain excluded volume interactions.

The chain lengths and total number of chains grafted to the spherical core particle are in a similar range as for typical micelles in experimental studies.

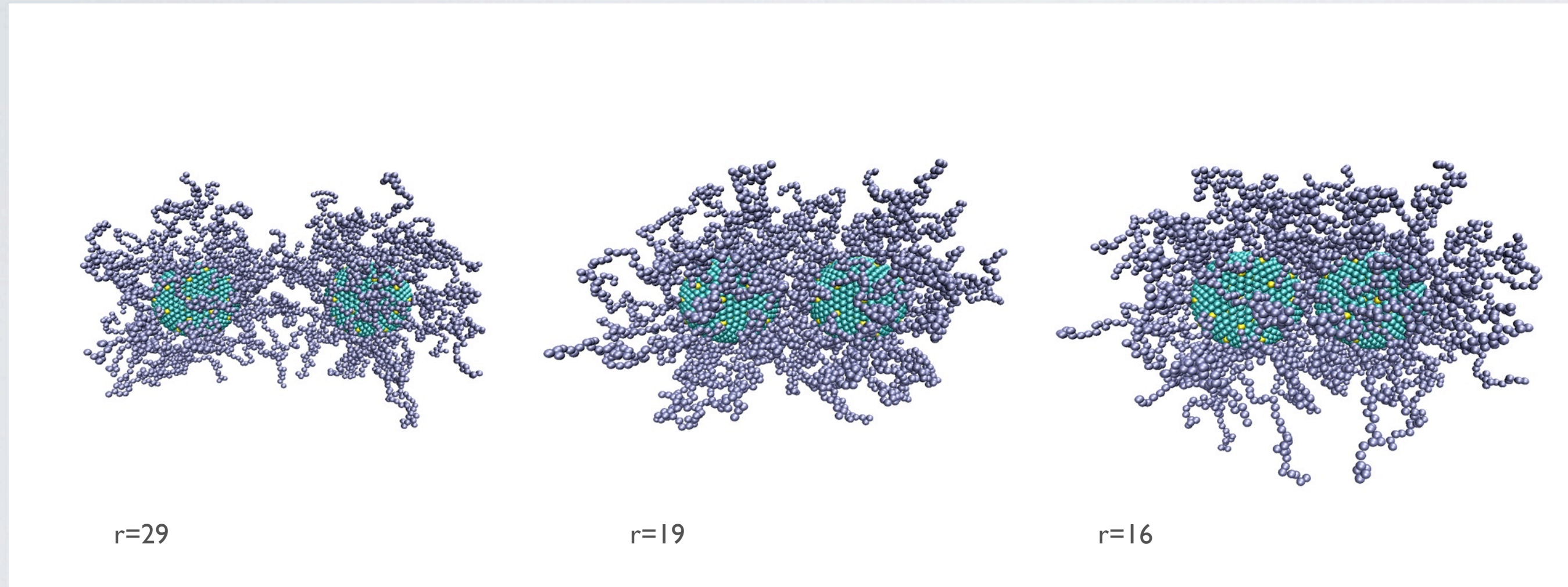
✓ DFT is a possible alternative method and open up the possibility to extend the range of parameters investigated. Nevertheless the theory does not reproduce exactly the star polymer scaling.

## Next...

The main idea here is to get a deep understanding of how polymers grafted on spherical surfaces affect the adsorption of proteins under different biological circumstances.

To move some steps in this direction we plan

- to consider the interaction between two spherical brushes (effective force, radial distribution functions...)  
as well as among one single spherical brush and nanoparticles of different size (density profiles, conformations)



- to study the dynamics of monomers (MSD, dynamic structure factor...)
- to change the quality of the solvent (comparison with experiments, Robert Graf NMR work)

## THANKS TO:

K. Binder

&

Leonid Yelash (interacting sph. brushes)

A. Milchev and S. Egorov (DFT and flat brushes)

Thank you!!!