The effect of topology and self-avoidance on polymer configurations

Erwin Frey

LMU

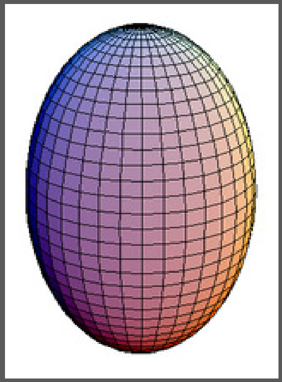
Arnold Sommerfeld Center for Theoretical Physics

Linear Polymer Chains

Typical size grows like power law (Flory)

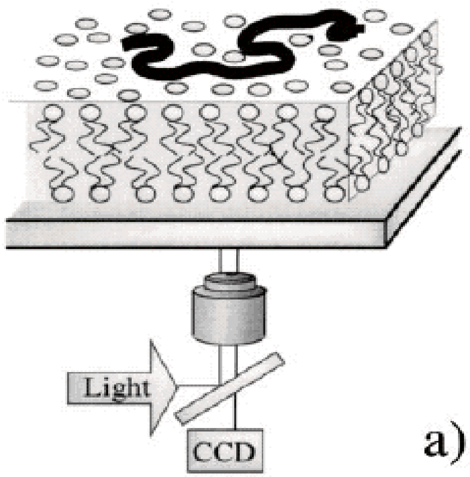
$$R_G \propto L^{3/(2+d)}$$

Typical shapes are prolate (Kuhn)

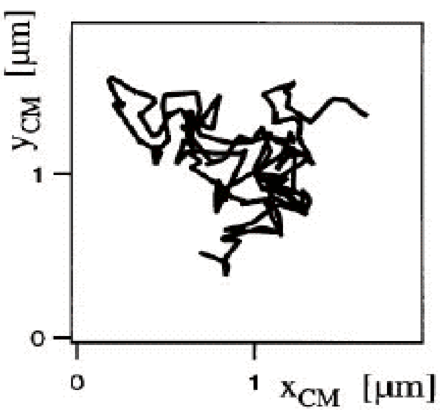


Excluded Volume Effects

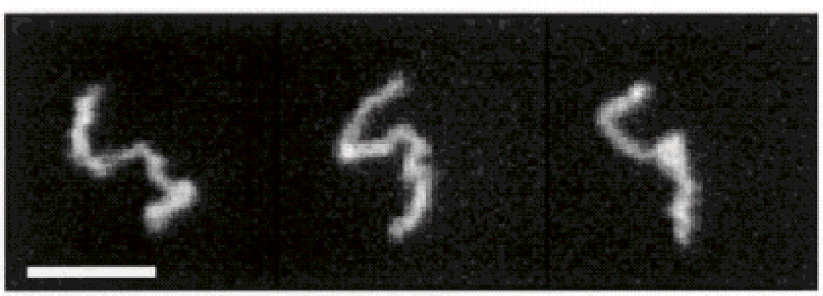
Single DNA Molecules confined to 2D



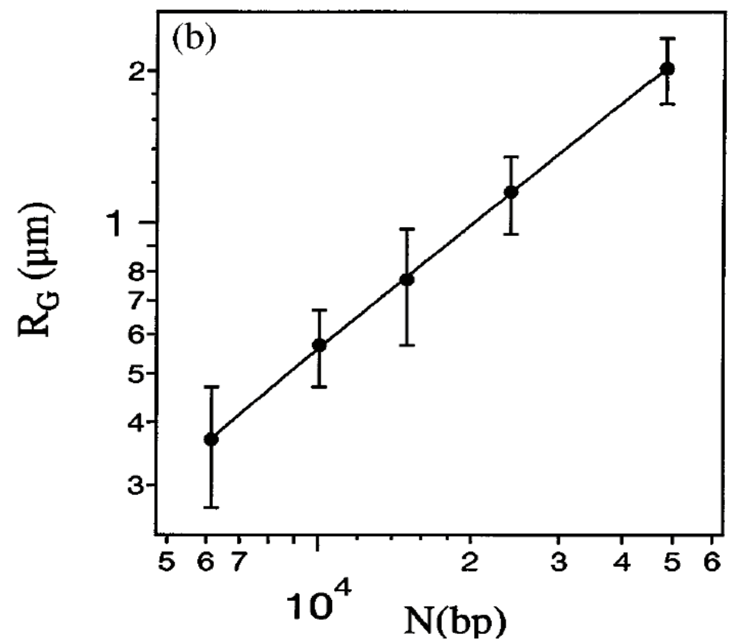
a)



c)



b)



$$R_G \propto L^{3/4}$$

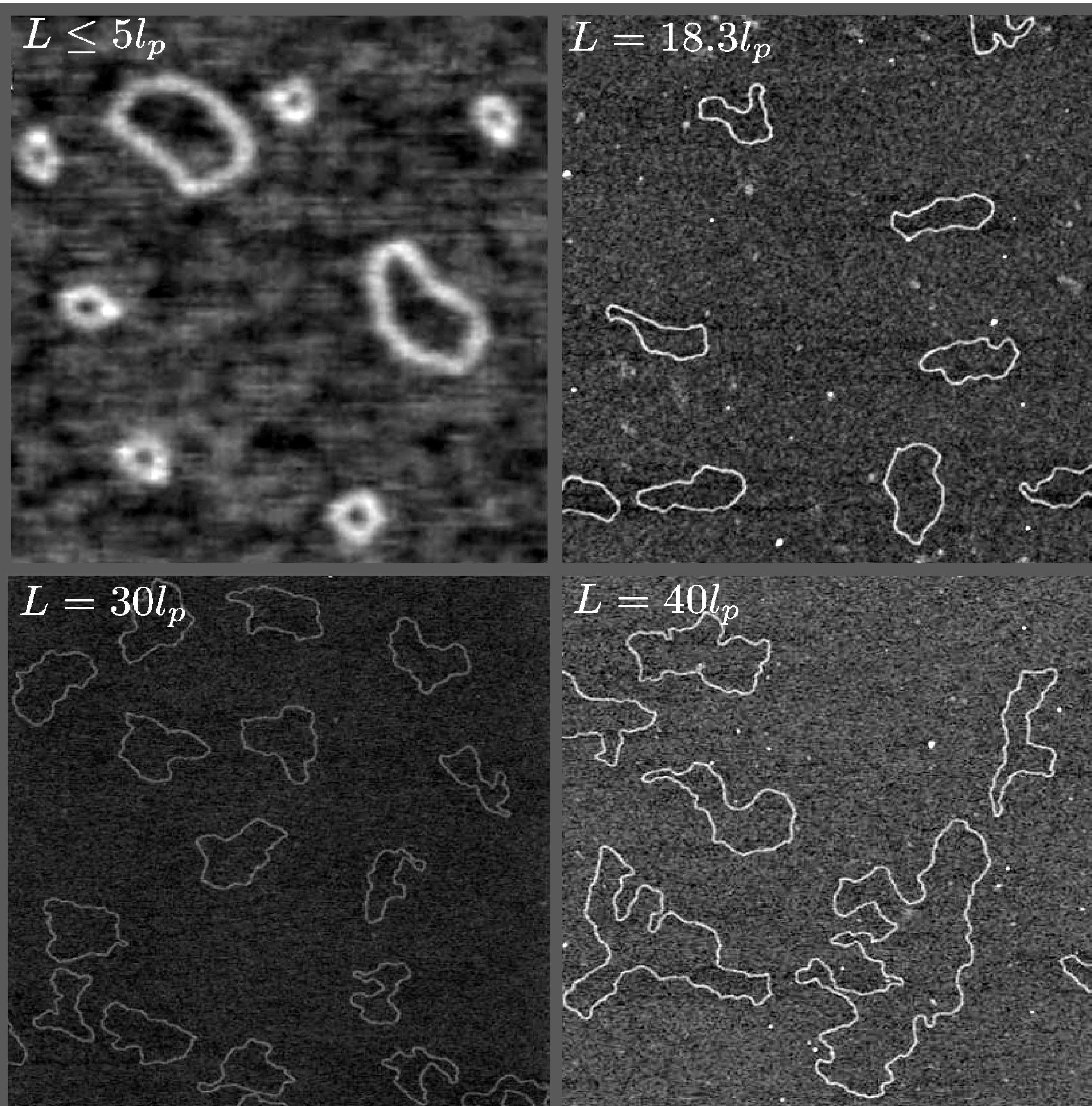
B. Maier and J.O. Rädler, PRL 82, 1911 (1999)

Circular DNA

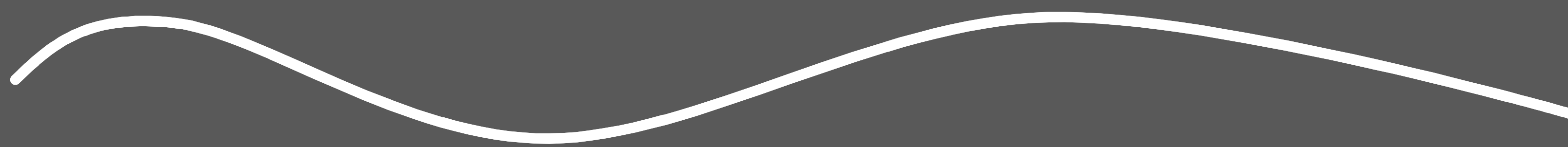
Nicked plasmids were used to generate circular DNA without superhelicity

AFM images on mica surfaces

Witz et al. PRL (2008)



The Wormlike Chain Model



$$\mathcal{H} = \frac{\kappa}{2} \int_0^L ds \left(\frac{\partial^2 \mathbf{r}}{\partial s^2} \right)^2$$

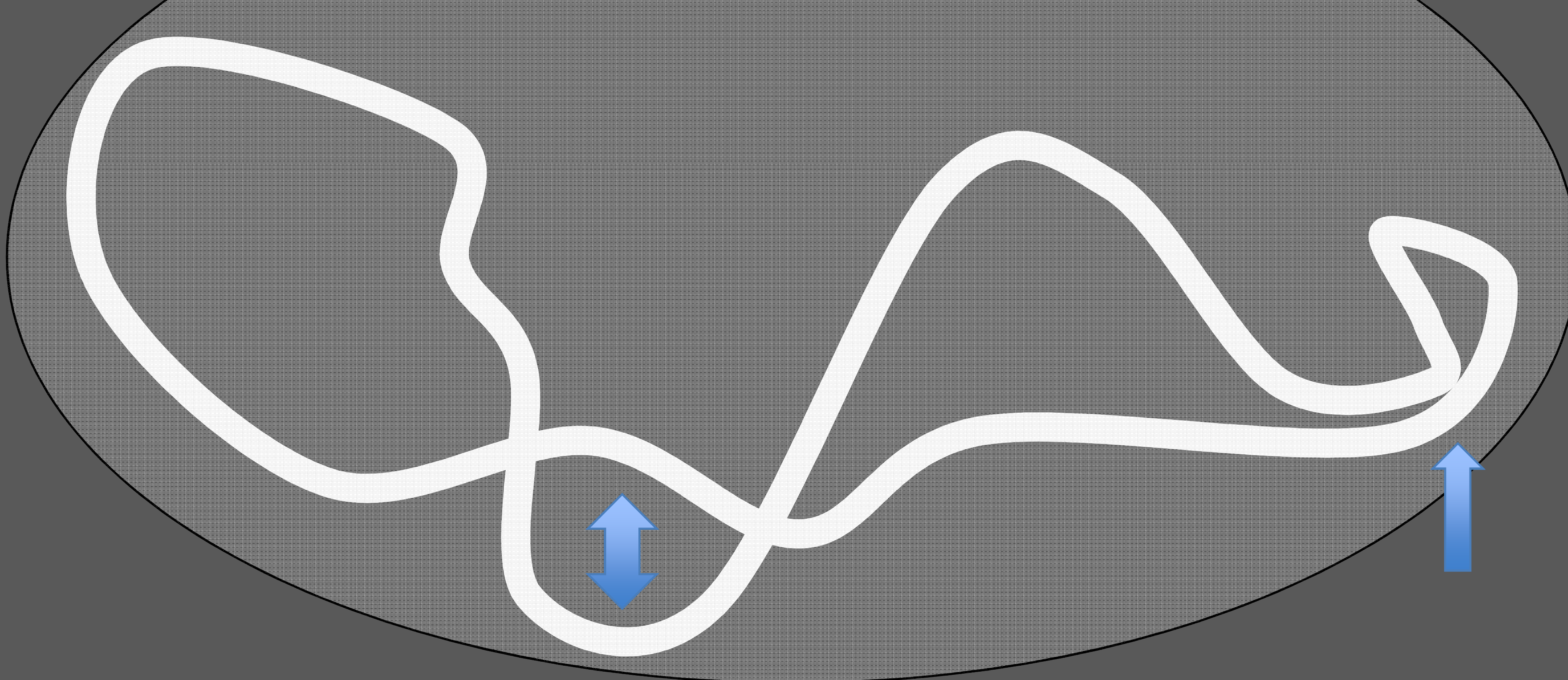
Inextensible chain: $\mid \mathbf{t}(s) \mid = \mid \partial \mathbf{r}(s) / \partial s \mid = 1$

Bending stiffness: $\kappa = l_p k_{\mathrm{B}} T$

Persistence length: $\langle \mathbf{t}(s) \mathbf{t}(s') \rangle = \exp \left[(s - s') / l_p \right]$

O. Kratky and G. Porod, Rec. Trav. Chim. **68**, 1106 (1949) ; N. Saito et al., J. Phys. Soc. Jpn. **22**, 219 (1967)

- Ring Geometry?
- Self-Avoidance?



- Tangent-Tangent Correlations
- Radius of Gyration
- Shape (Asphericity)

AFM Images of DNA Plasmids on Mica

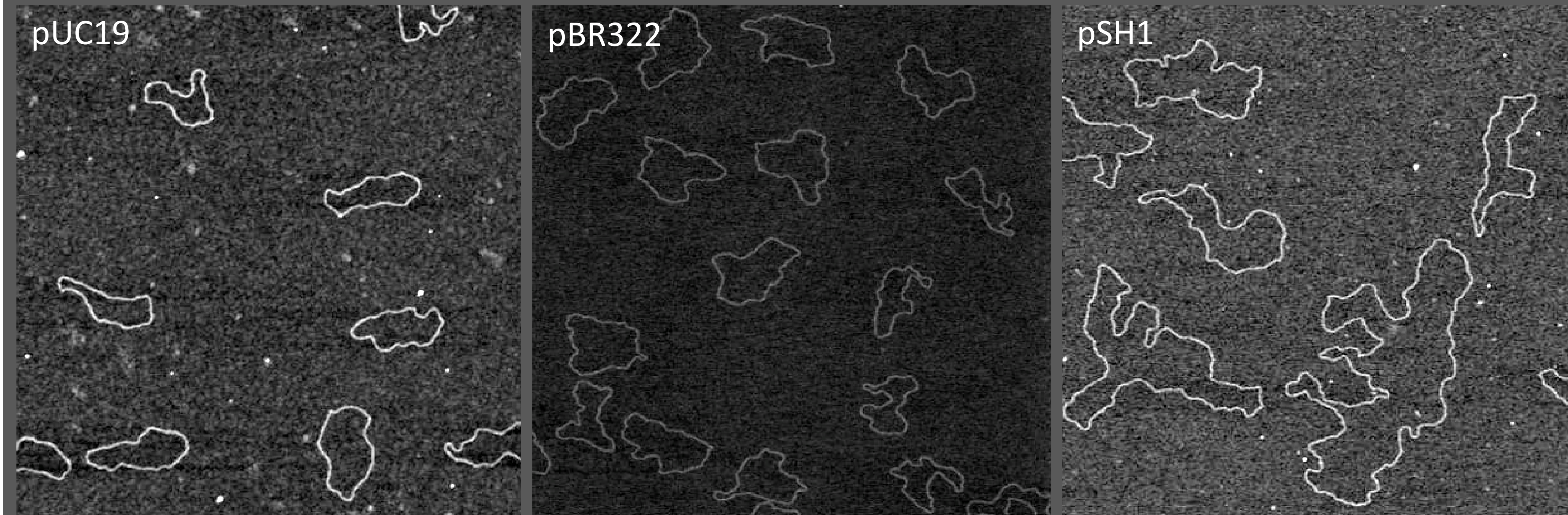


TABLE I. Properties of the investigated DNA molecules. The length L is calculated using 0.34 nm per base pair. All lengths are in nanometers.

DNA type	(bp)	L	L/ℓ_p	ℓ_p	L_{fit}	ν
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pBR322	4361	1483	30	49.1 ± 4.6	1543 ± 5	0.82 ± 0.01
pSH1	5930	2016	40	53.5 ± 4.2	2110 ± 10	0.81 ± 0.01
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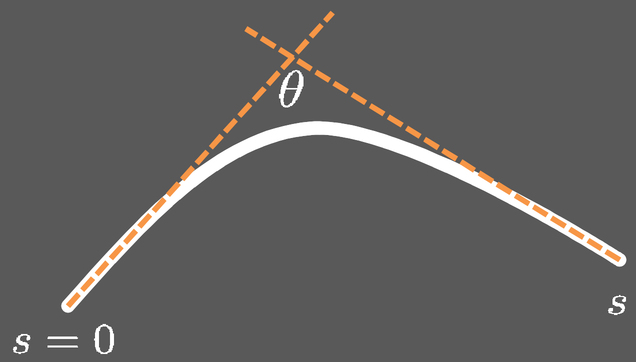
Tangent-Tangent Correlations (2D)

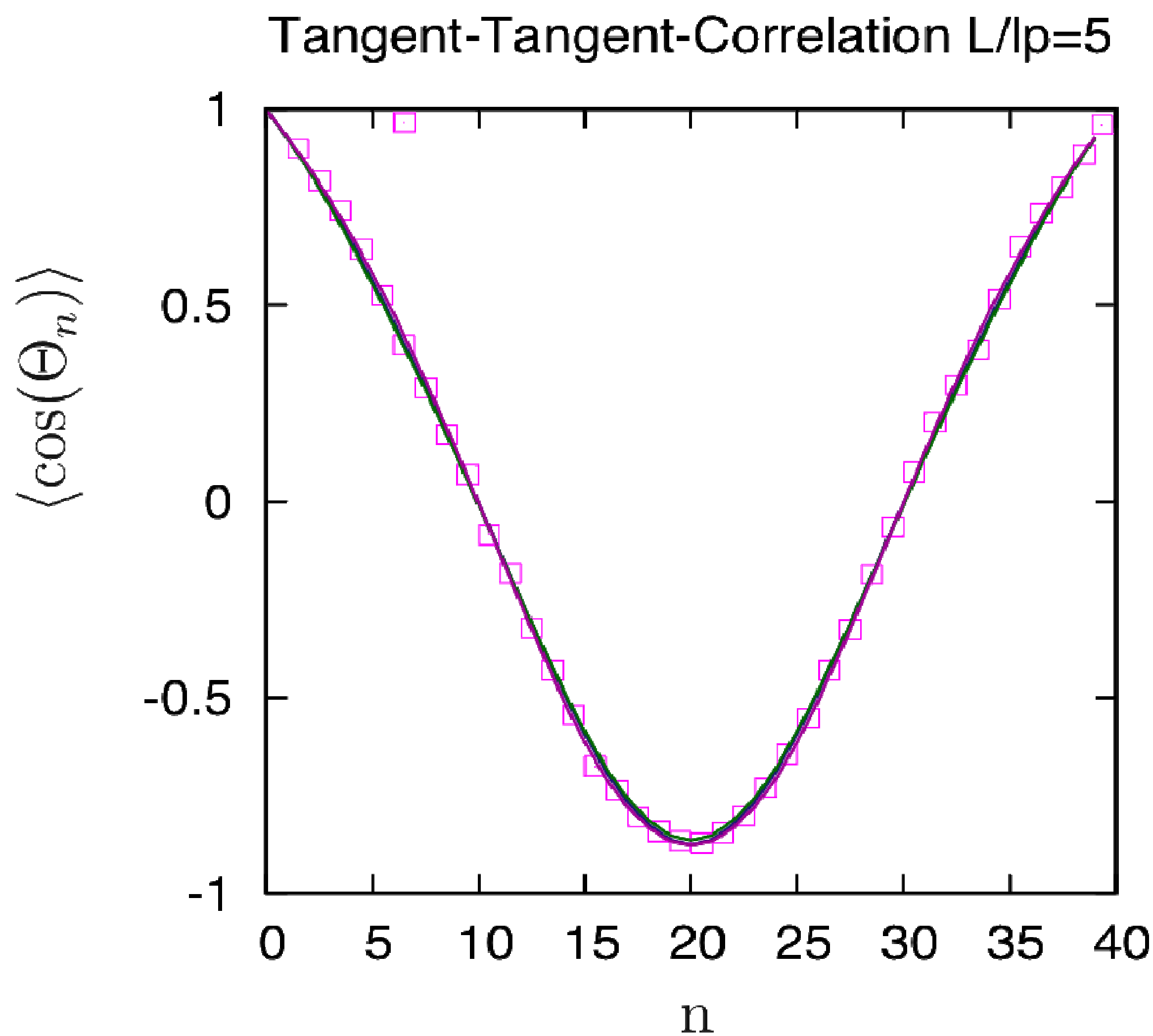


$$\langle \cos\theta(s) \rangle = \exp[-s/2l_p]$$

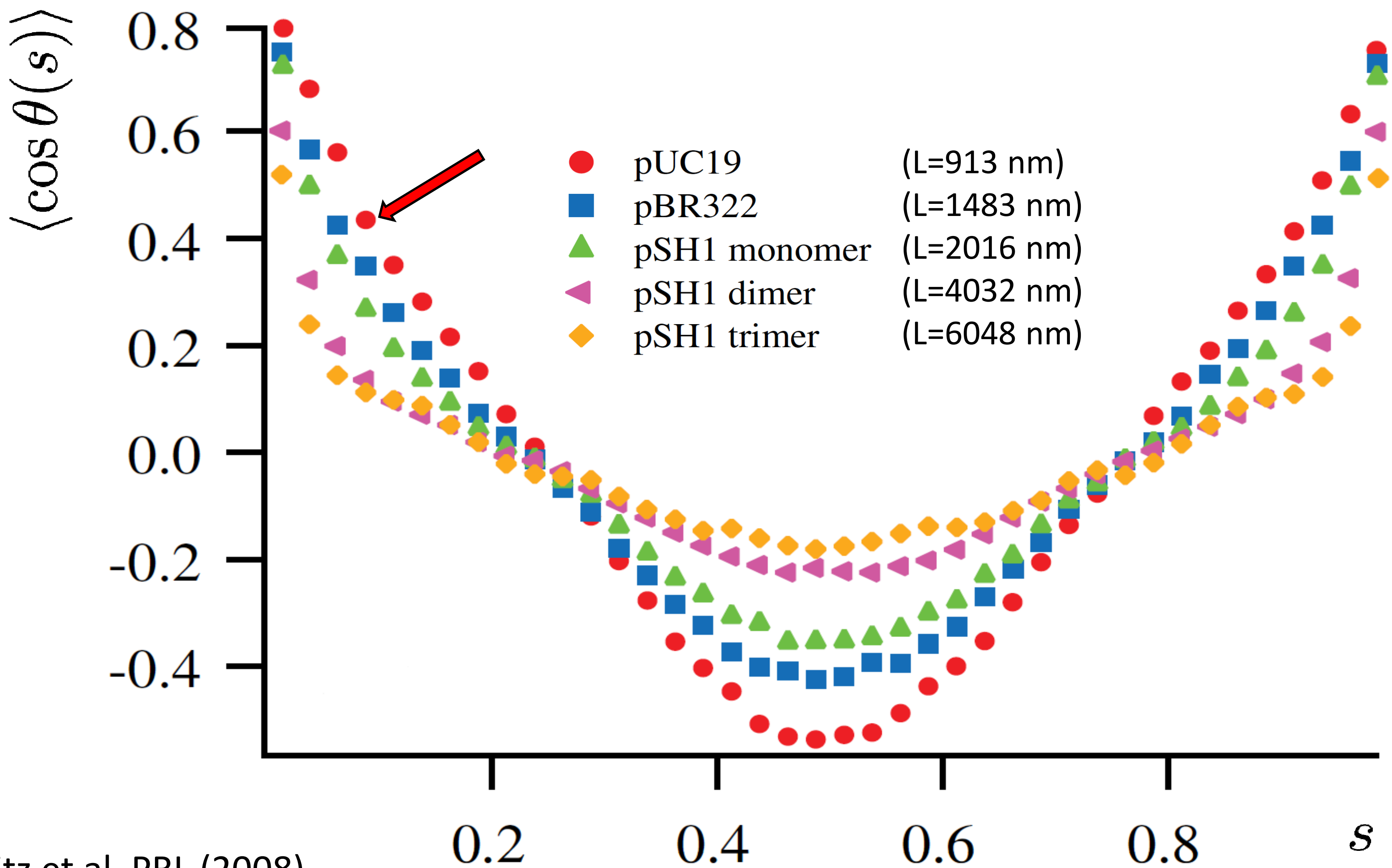
(exact for open 2D string w/out self-avoidance)

- What is the effect of ring geometry?
- What is the effect of self-avoidance?

Very Stiff Rings (Mini-circles)

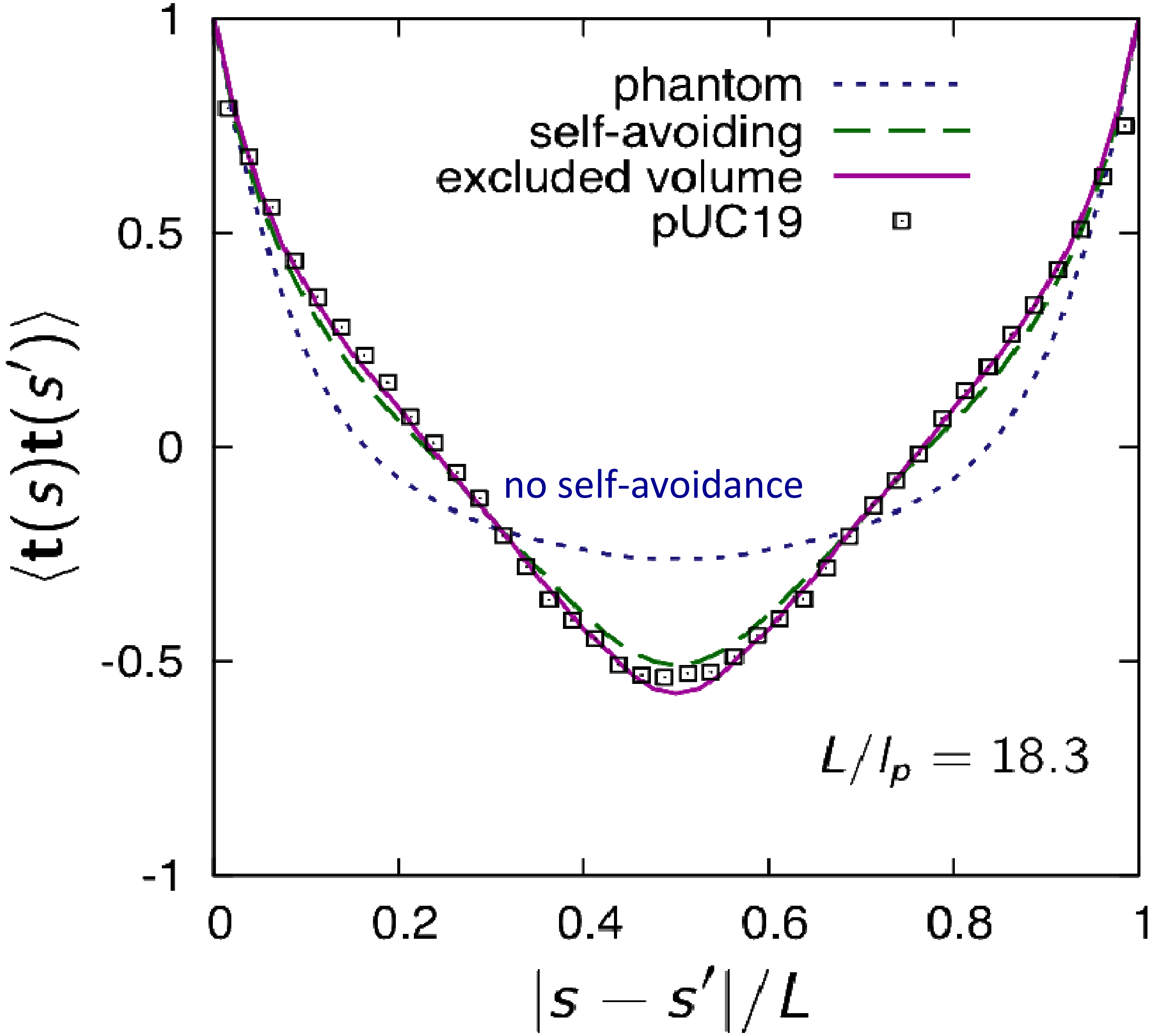


2D DNA Data (Dietler group @ EPFL)



Witz et al. PRL (2008)

pUC19 (*L=913nm*)



with topological self-avoidance

with excluded volume
d=0.13 l_p

Ring Geometry (3D)

(no self-avoidance)

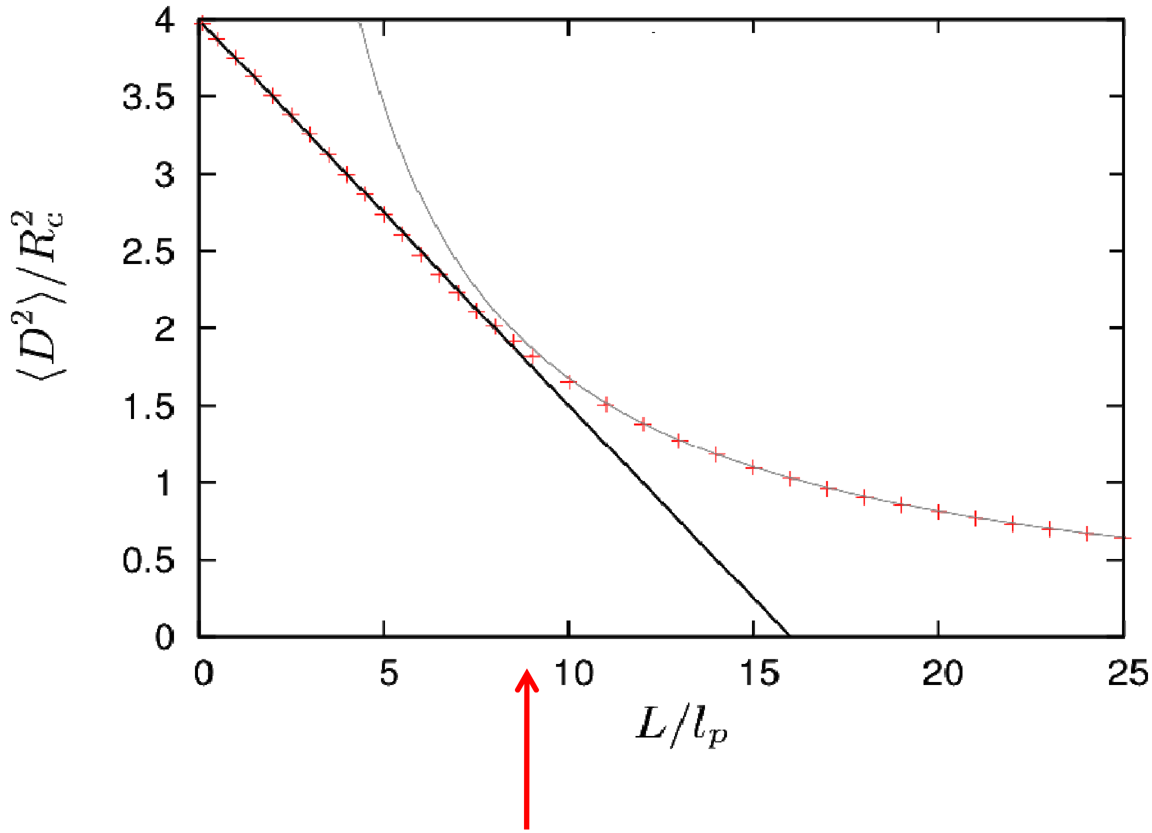
Mean-Square Diameter

Stiff regime:

$$\langle D^2 \rangle = \left(\frac{L}{\pi}\right)^2 \left(1 - \frac{1}{16}\frac{L}{l_p}\right)$$

Flexible regime:

$$\langle D^2 \rangle \propto \left(\frac{L}{l_p}\right)^{-1}$$



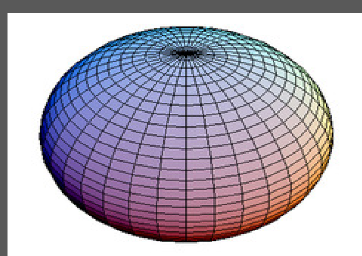
K. Alim and E. Frey, Eur. Phys. J. E 24, 185–191 (2007)

What is the shape of a polymer ring?

Radius of gyration (shape) tensor:

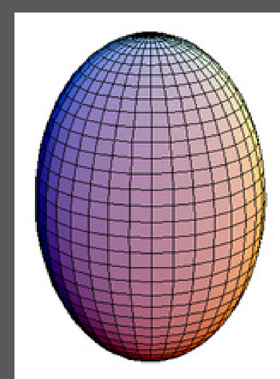
$$Q_{ij} = \frac{1}{L}\int ds\, r_i(s) r_j(s) - \frac{1}{L}\int ds\, r_i(s)\ \frac{1}{L}\int ds\, r_j(s)$$

$$\rightarrow \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$



$\lambda_1 \approx \lambda_2 \gg \lambda_3$

oblate



$\lambda_1 \gg \lambda_2 \approx \lambda_3$

prolate

Radius of gyration ("size")

$$R_G^2 = \mathrm{Tr}\, Q = \lambda_1 + \lambda_2 + \lambda_3$$

Traceless shape tensor:

$$\hat{Q}_{ij} = Q_{ij} - \frac{1}{3}\mathrm{Tr}\, Q\, \delta_{ij} = Q_{ij} - \bar{\lambda}\, \delta_{ij}$$

Asphericity:

$$\mathrm{Tr}\, \hat{Q}^2 = \sum_{i=1}^{3} (\lambda_i - \bar{\lambda})^2$$

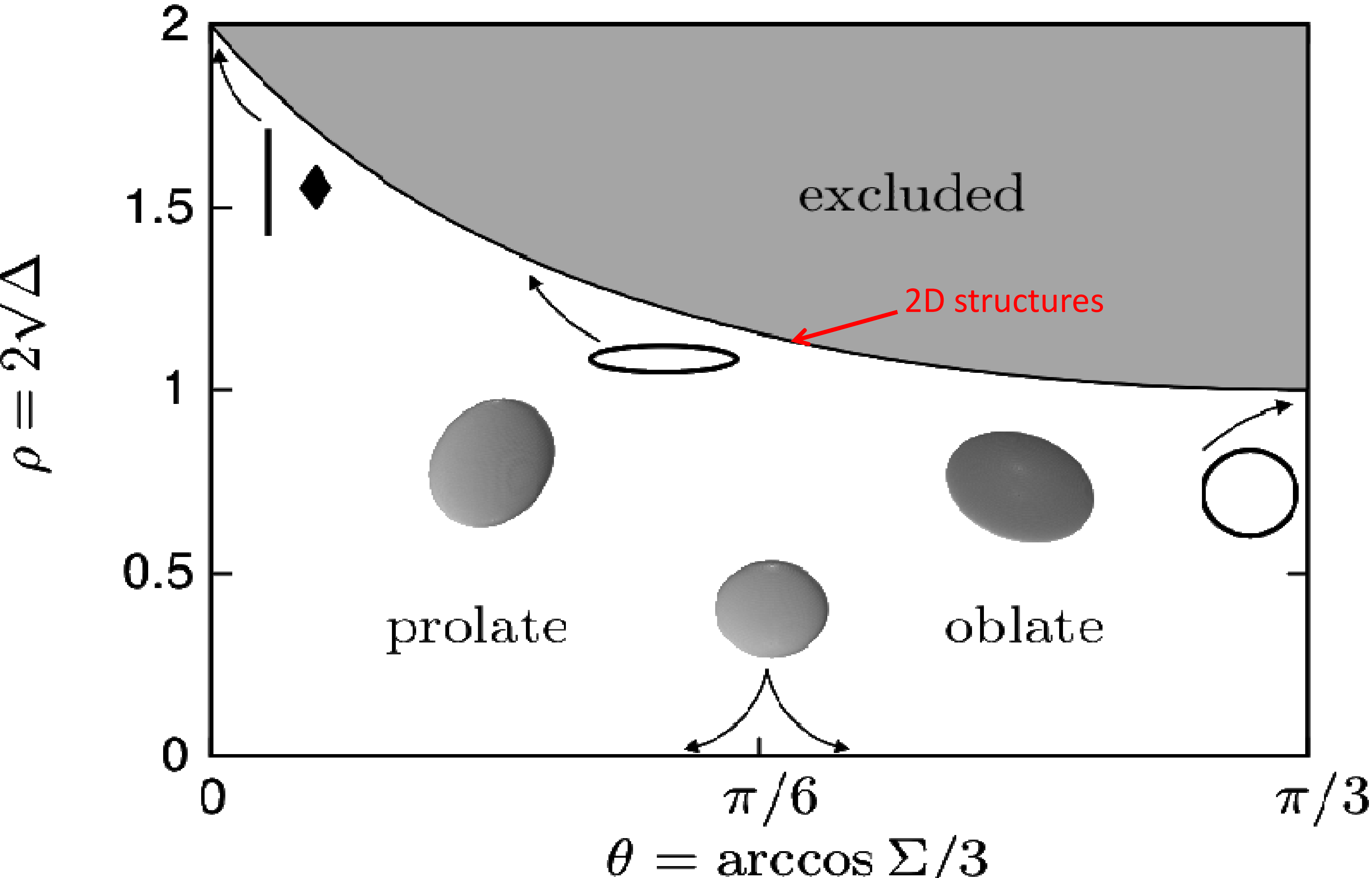
= rescaled variance measuring the deviation from a sphere

Nature of asphericity:

$$\mathrm{Det}\, \hat{Q} = (\lambda_1 - \bar{\lambda})(\lambda_2 - \bar{\lambda})(\lambda_3 - \bar{\lambda})$$

= „counting the signs“ measures the nature of deviation from sphere

J. Aronovitz and D. Nelson, J. de Phys. **47**, 1447 (1986)



(asphericity) $\Delta = \frac{3}{2}\frac{Tr\ \hat{Q}^2}{(Tr\ \hat{Q})^2}$

(nature of asphericity) $\Sigma = \frac{4Det\ \hat{Q}}{(\frac{2}{3}Tr\ \hat{Q}^2)^{3/2}}$

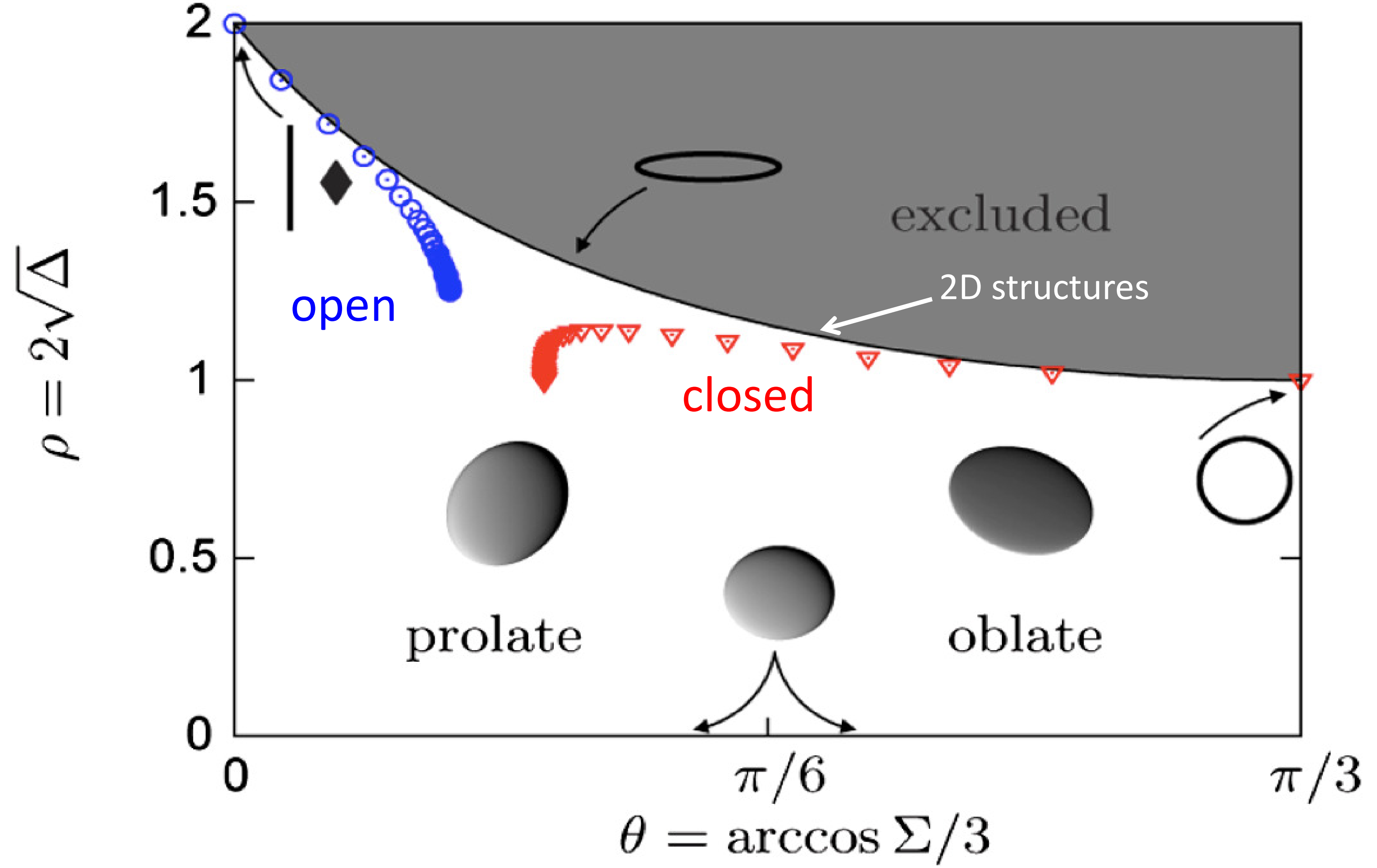
Results for Random Coils

(Diehl & Eisenriegler, 1989)

$$\langle \Delta \rangle_{\mathrm{ring}} \approx 0.25 \qquad \langle \Sigma \rangle_{\mathrm{ring}} \approx ?$$

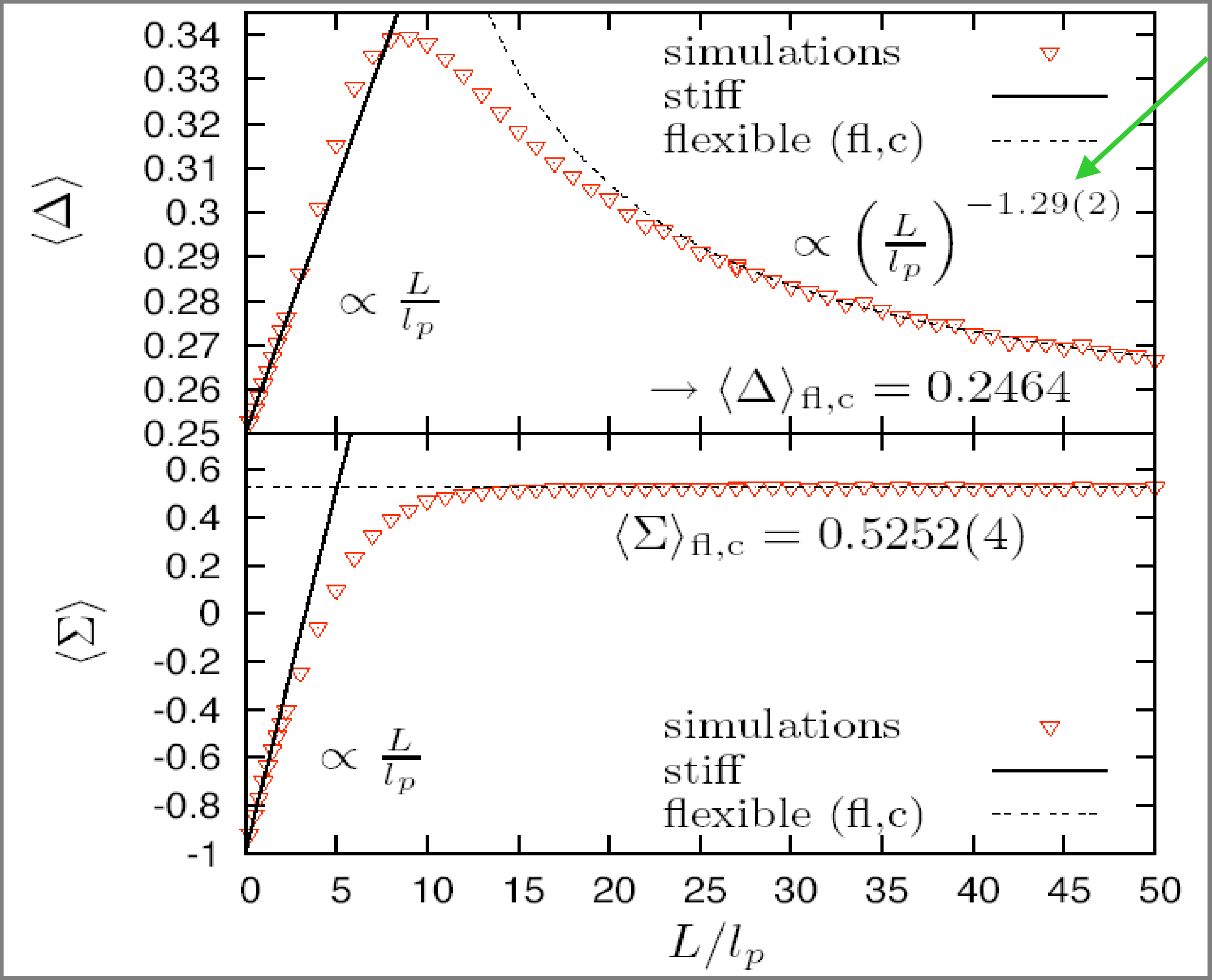
(Cannon et al., 1991)

$$\langle \Delta \rangle_{\mathrm{open}} \approx 0.40 \qquad \langle \Sigma \rangle_{\mathrm{open}} \approx 0.75$$



(asphericity) $\Delta = \frac{3}{2}\frac{Tr\ \hat{Q}^2}{(Tr\ \hat{Q})^2}$ (nature of asphericity) $\Sigma = \frac{4 Det\ \hat{Q}}{(\frac{2}{3}Tr\ \hat{Q}^2)^{3/2}}$

The average shape parameters



power law

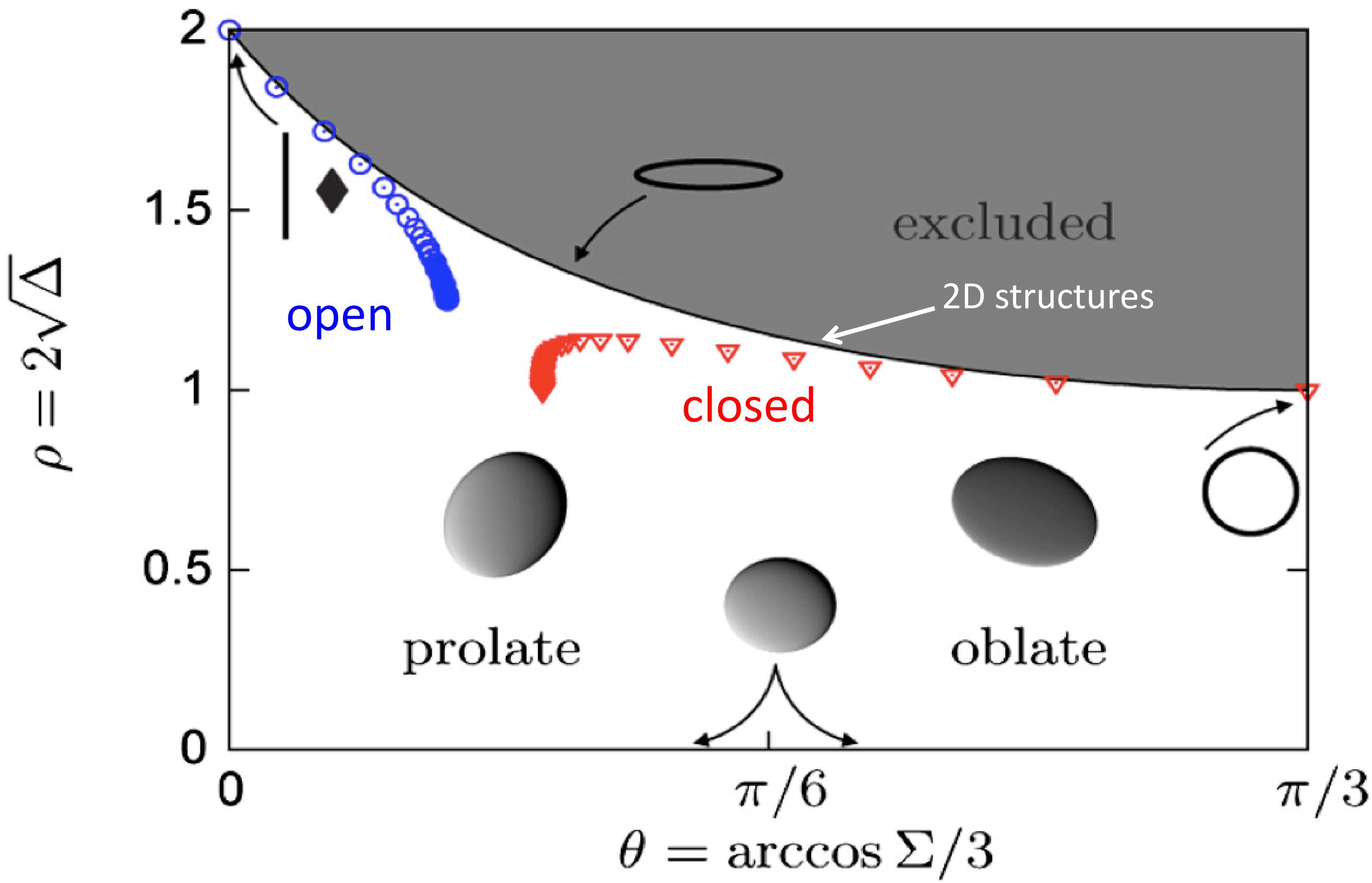
oblate

prolate

stiff

flexible

K. Alim and E. Frey, PRL 99, 198102 (2007)



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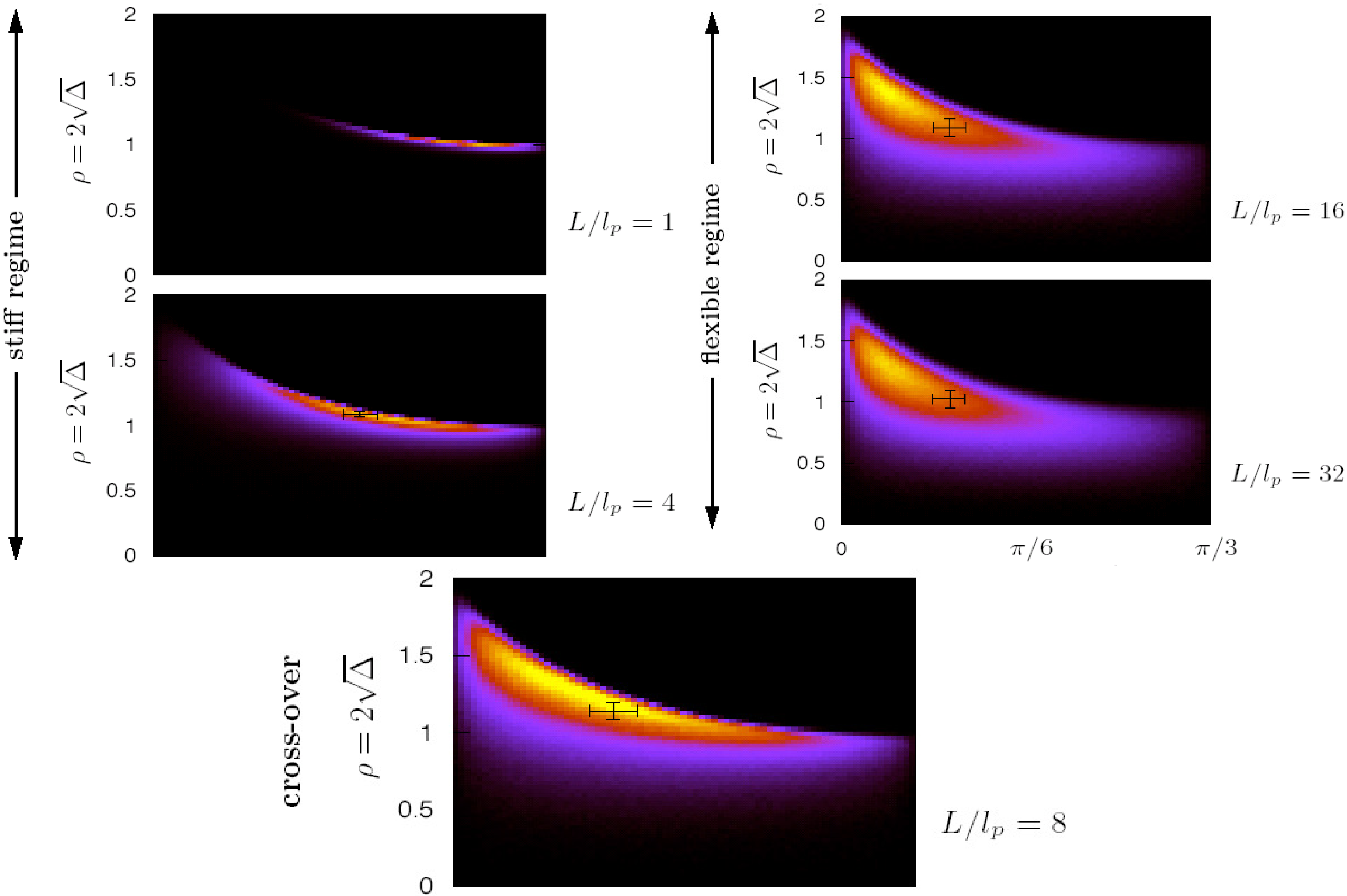


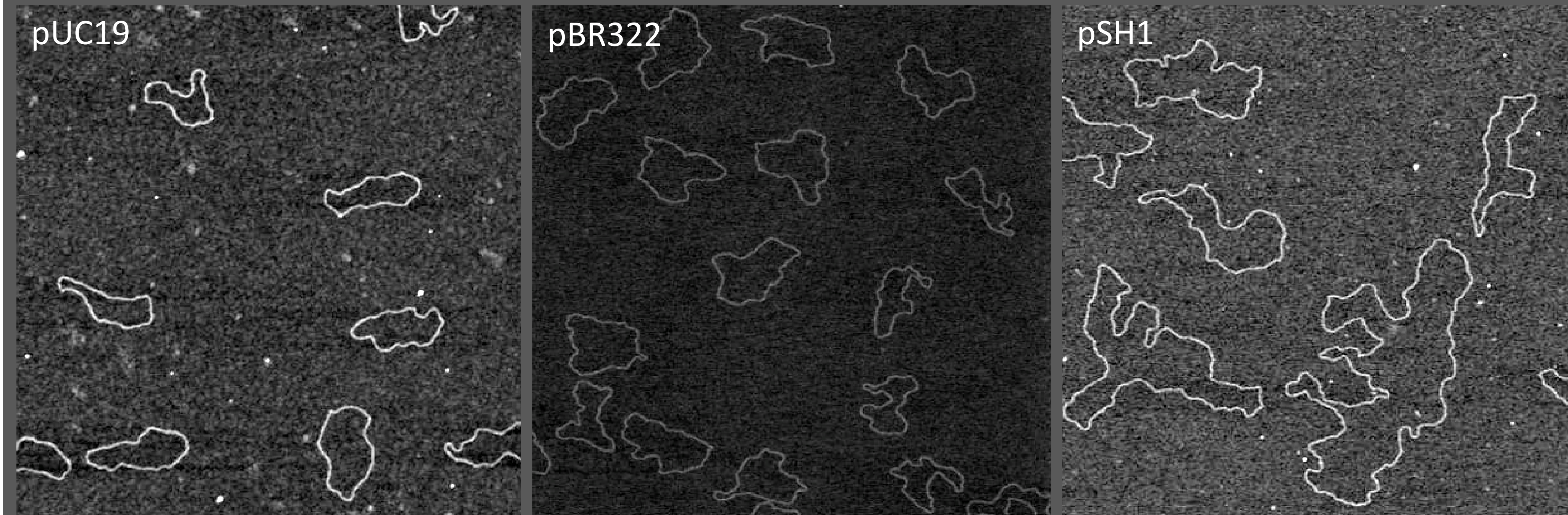
stiff regime
flexible regime
cross-over
$\rho = 2\sqrt{\Delta}$
$L/l_p = 1$
$L/l_p = 4$
$L/l_p = 16$
$L/l_p = 32$
$L/l_p = 8$
0
0.5
1
1.5
2
0
$\pi/6$
$\pi/3$

- Rings are stiff and oblate for $L \leq 4l_p$
- For $L \approx 8l_p$ the shape distribution is extremely broad: planar and crumpled conformations are equally likely.
- Shape distributions for flexible $L \geq 16l_p$ polymers are also very broad: mean and most likely value are not the same.
- Shape changes discontinuously as one cuts a polymer ring!

Ring Geometry (2D)

(the effect of self-avoidance)

AFM Images of DNA Plasmids on Mica



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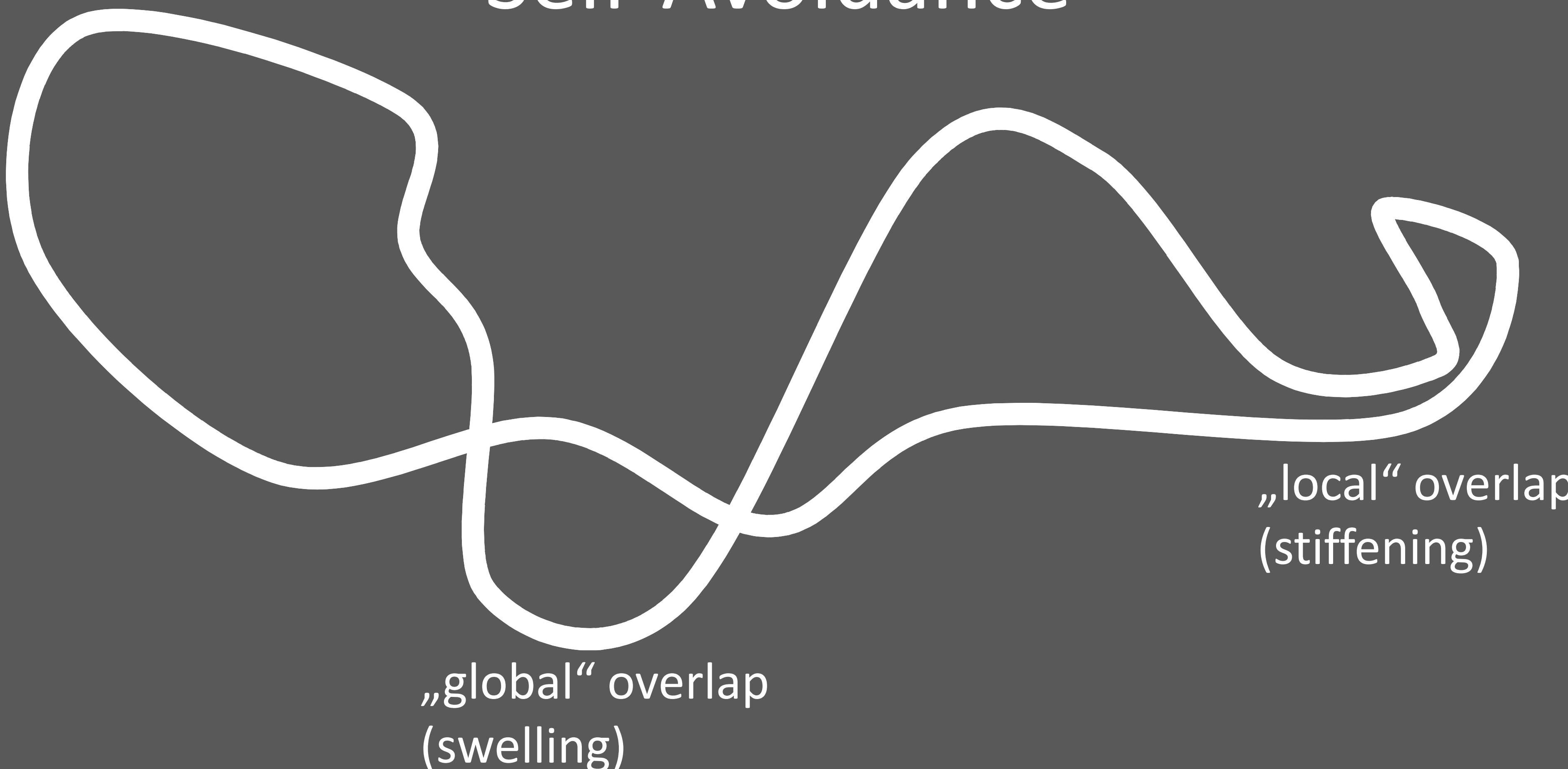
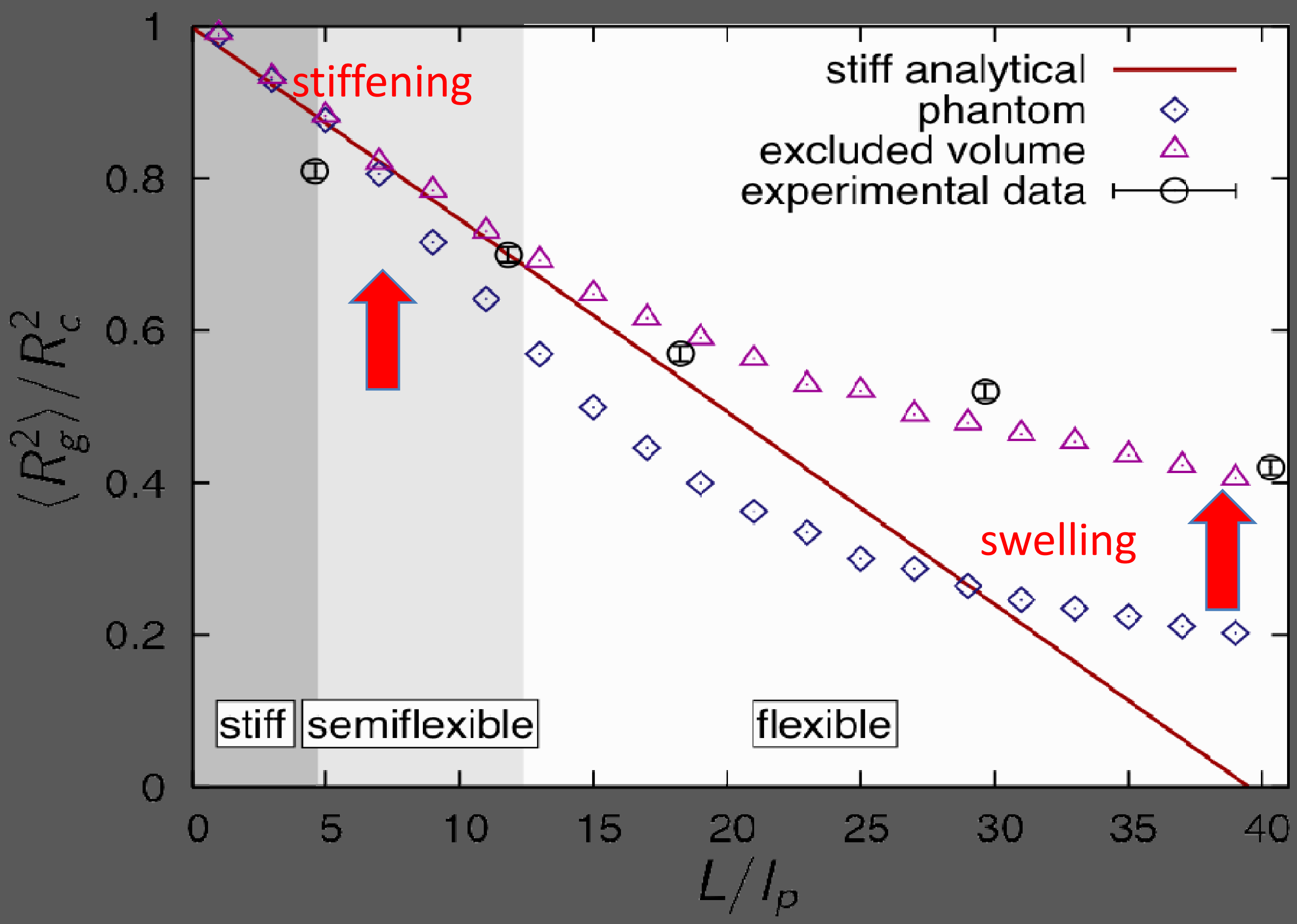
Self-Avoidance



Topological self-avoidance & Excluded volume (finite thickness)

Radius of Gyration



F. Drube, K. Alim et al. (preprint) arXiv:0906.3991

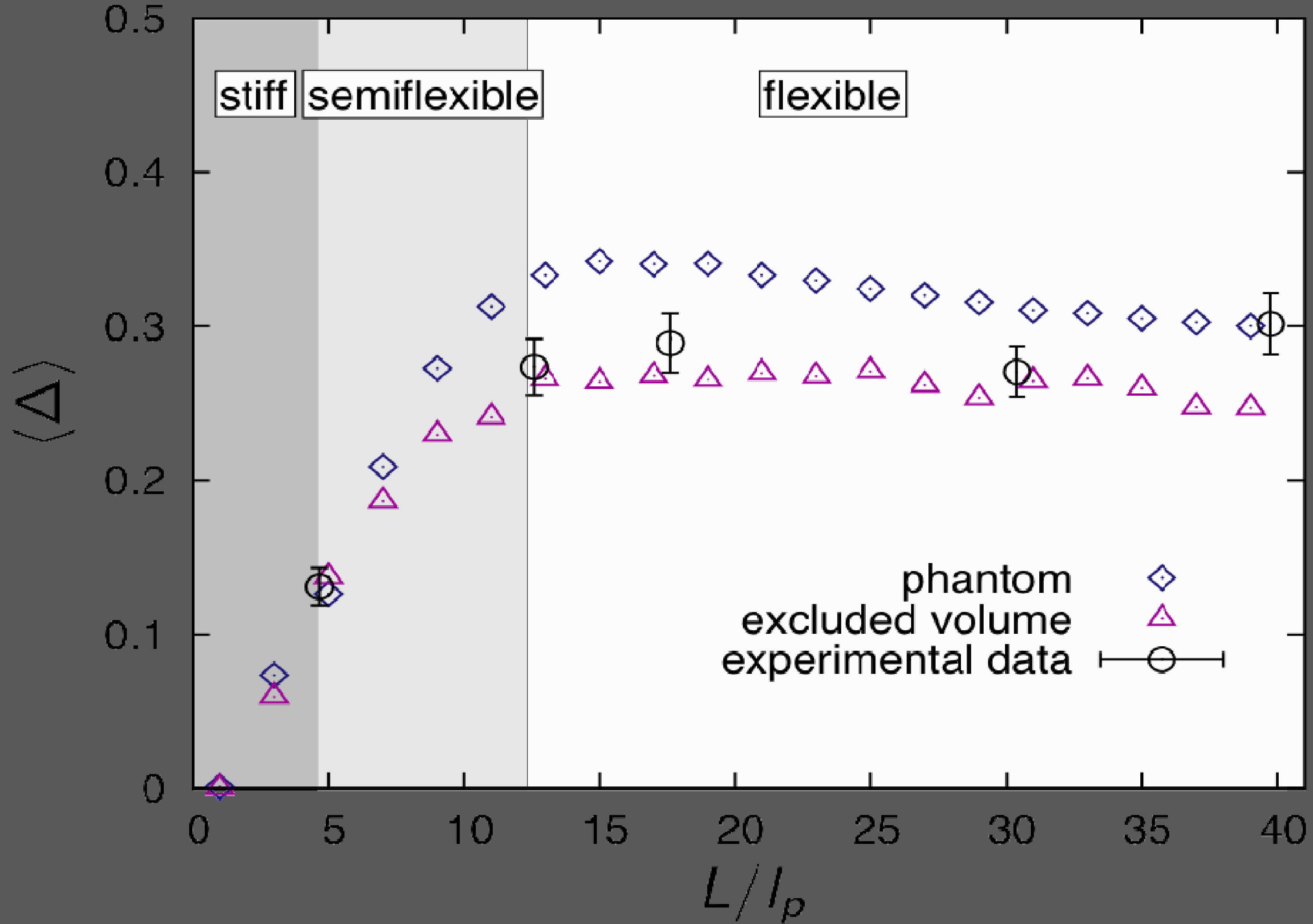
Excluded volume leads to effective stiffening up to $L = 15\ l_p$
(„local“ contacts?)

Excluded volume leads to significantly stronger swelling than topological self-avoidance
(„global“ contacts?)

Good agreement with experimental data of Dietler group for DNA on Mica surfaces for $d = 0.13\ l_p$

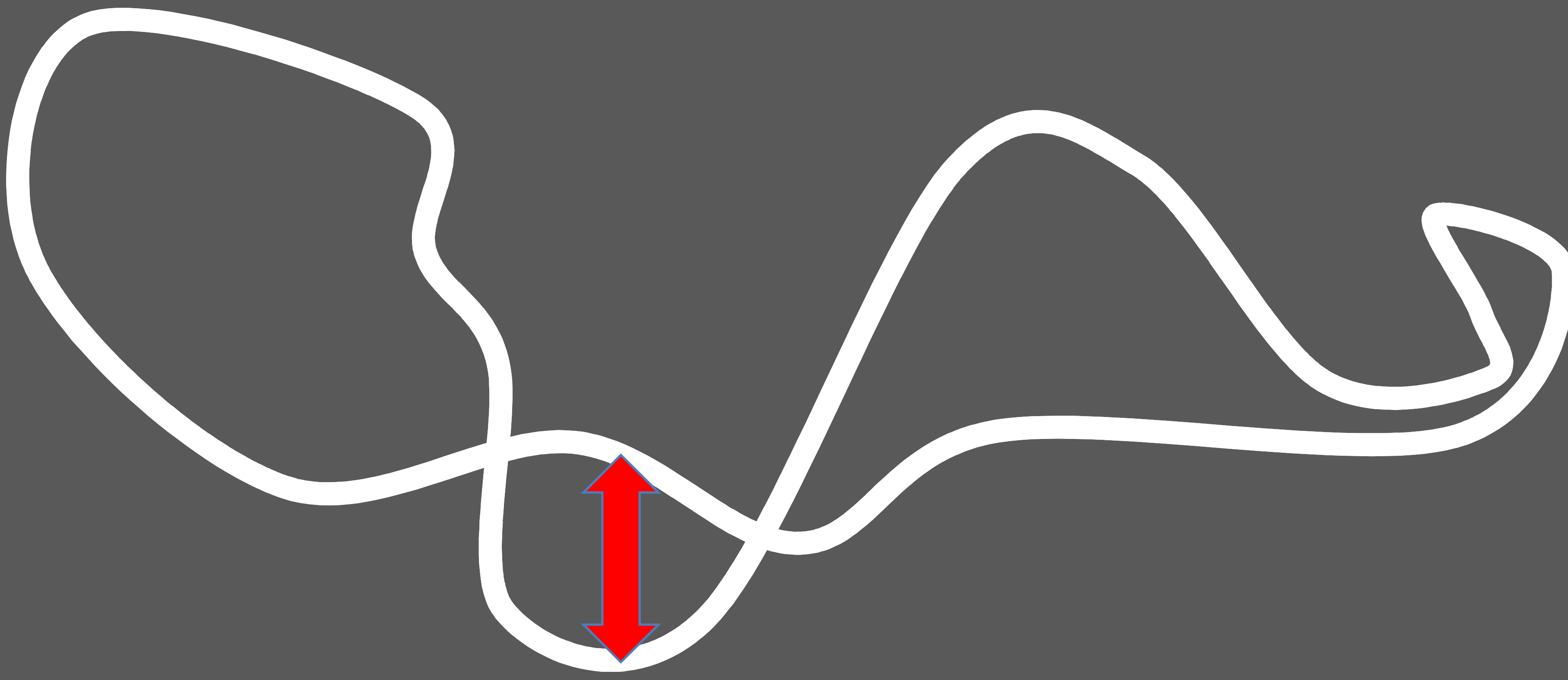
Is swelling affine (isotropic)?

Asphericity



F. Drube, K. Alim et al. (preprint) arXiv:0906.3991

Excluded volume leads to significantly reduced asphericity, i.e. to non-affine swelling



Summary & Outlook

- Shapes of 3D polymer rings strongly depend on L/l_p
- Self-avoidance alters shape and size of 2D polymer rings

LMU

Karen Alim
Fabian Drube

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Guillaume Witz
Giovanni Dietler