Marginal Nature of DNA solutions

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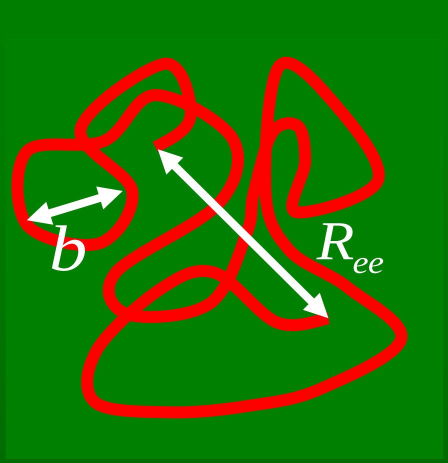
Polymer physics starts with simple intuitive models

Take into account non-idealities => drastic change in the behavior of the models => require mathematically complicated models

The intuitive models remain ideal models without real-life examples

DNA to the rescue !

Ideal Polymer – random walk in space



Measure of flexibility: *b* - Kuhn length

$$N = L/b \qquad \left\langle R_{ee}^2 \right\rangle = Nb^2 = Lb$$

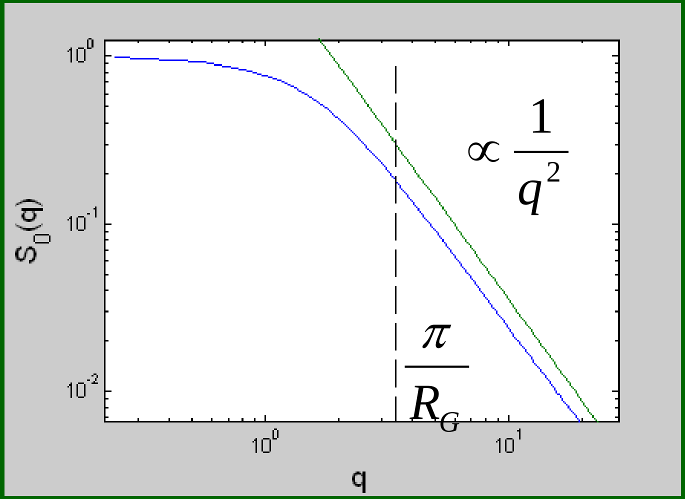
$$R_g \propto b\sqrt{N}$$

$$P\left(\vec{R}_{ee}\right) \propto \exp\left(-\frac{3R_{ee}^2}{2\left\langle R_{ee}^2 \right\rangle}\right)$$

Solution structure:

$$S_0(\vec{q}) = \frac{2}{(qR_G)^4}\left[q^2R_G^2 - 1 + \exp\left(-q^2R_G^2\right)\right]$$

Debye function



Real Polymer – self-avoiding random walk in space

excluded volume interactions (Flory)

$$\left\langle R_{ee}^{2} \right\rangle \propto N^{3/5}$$

$$r < R_G \qquad g(r) \propto \frac{n}{r^3} \propto \frac{r^{5/3}}{r^3} \propto \frac{1}{r^{4/3}}$$

$$q > \frac{\pi}{R_G}$$

BUT!!!

DNA is semiflexible polymer – nearly ideal for contour lengths:

$$L \sim \left(\frac{b}{d}\right)^2 b \sim 60\mu m$$

b – DNA Kuhn length (100 nm)
d – double helix diameter (2 nm)

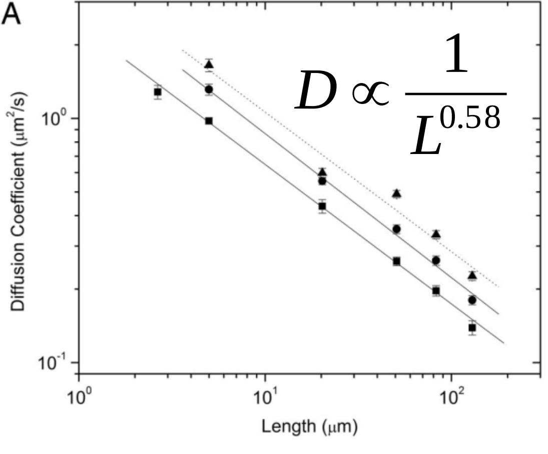
Experiments:

- 70-90s: static light scattering

  show ~30% coil (radius) expansion for 14μm DNA

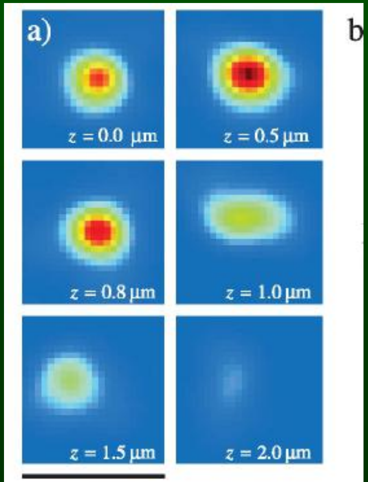
-Diffusion of single DNA molecules vs. length

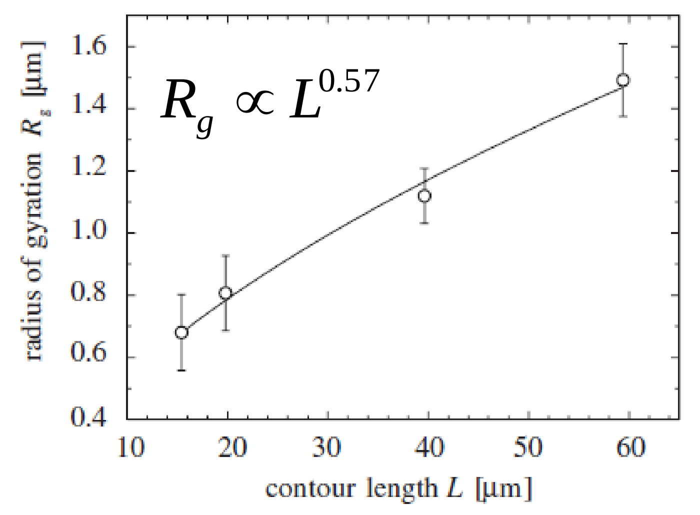
Robertson, Laib, Smith PNAS 2006



-segment distribution of end-tethered DNA

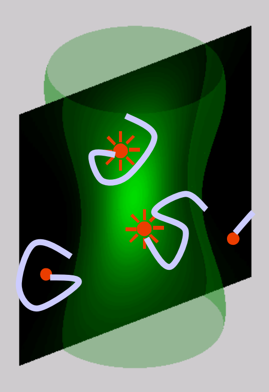
Gisler et al, PRL 2006



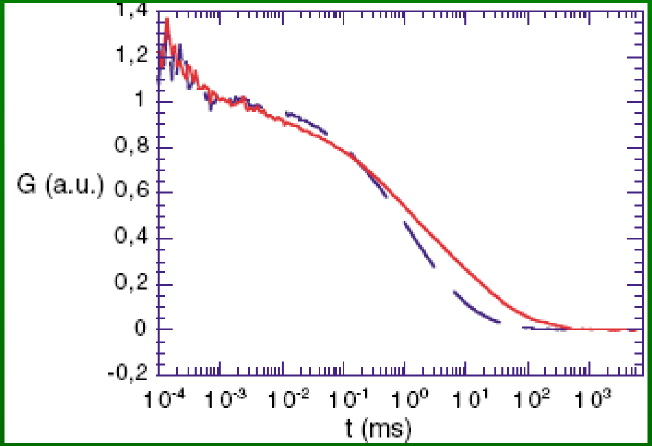


Experimental approach:

- Fluorescence Correlation Spectroscopy



$$G(t) = \frac{1}{\bar{I}^2}\frac{1}{T}\int_0^T \delta I(t')\,\delta I(t'+t)\,dt'$$



Add constant (high) scaning speed V:

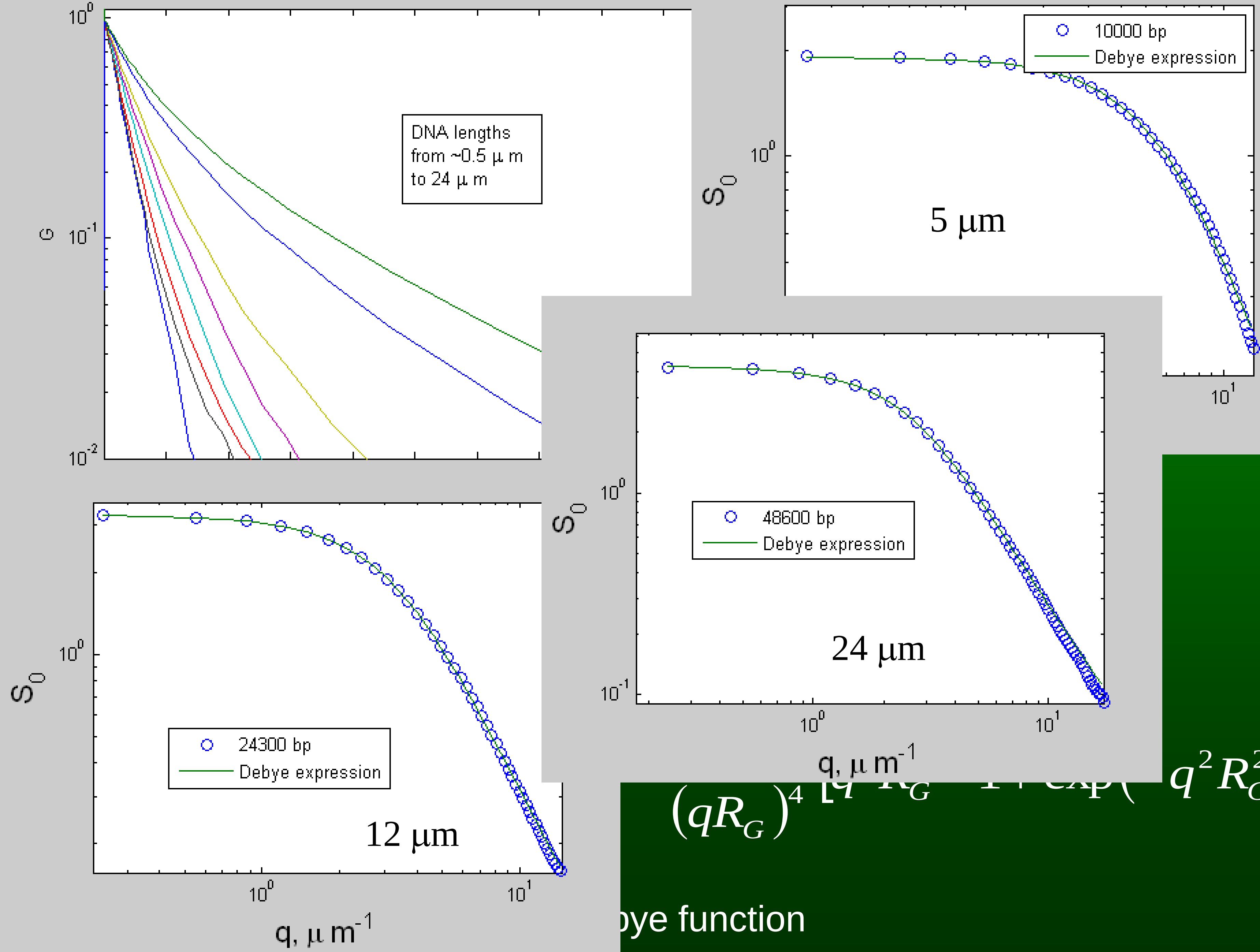
converting spatial correlations
into temporal correlations

$$G(t) = \int_0^T F(\vec{r})\,g(\vec{r} - \vec{V}t)\,dt$$

$$\vec{R} = \vec{V}t$$

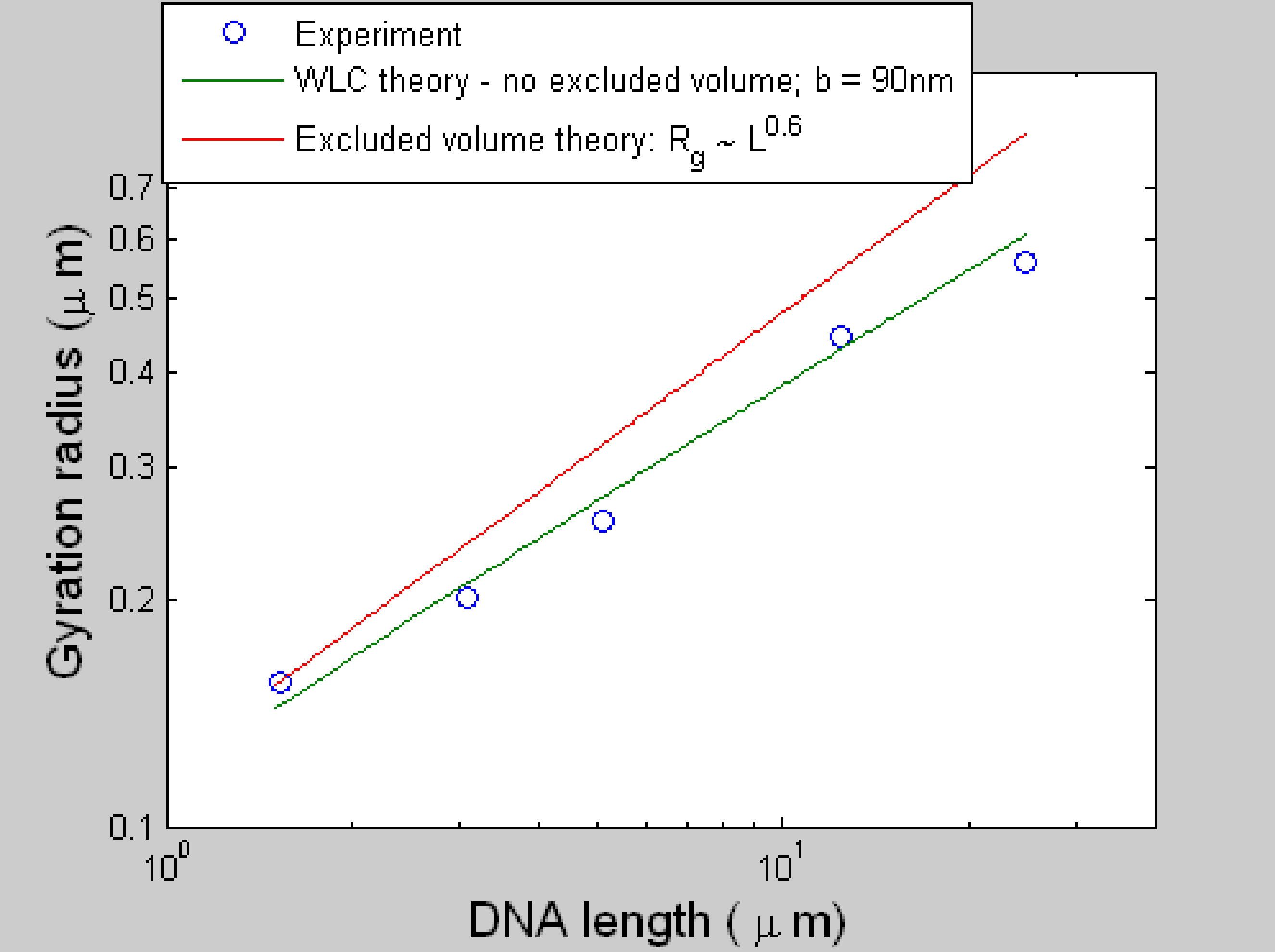
$$G(\vec{R}) = \int F(\vec{r})\,g(\vec{r} - \vec{R})\,dt$$

$$g(\vec{q}) \equiv S(\vec{q}) = \frac{G(\vec{q})}{F(\vec{q})}$$



$$(qR_G)^4\ [q\ R_G\ \ 1 + \exp(\ \ q^2R_G^2\ )]$$

bye function



No excluded volume interactions: ideal chain !!!

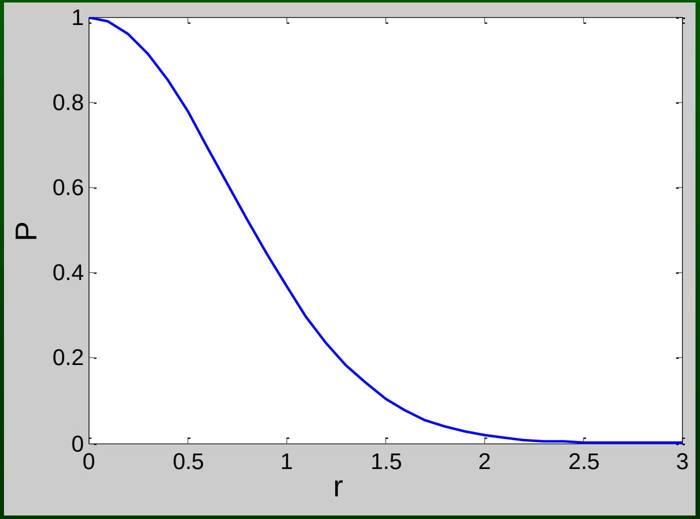
$$\frac{10^{0.6}}{10^{0.5}} \approx 1.25$$

Significant when you have several decades in polymer lengths

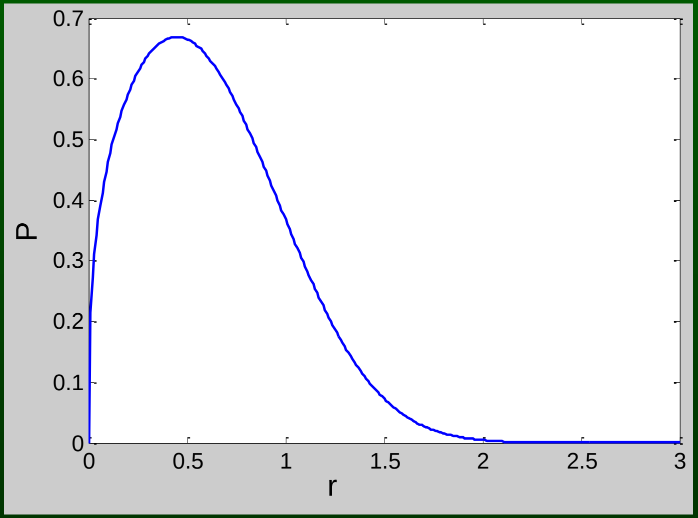
Main support for DNA ideality: Structure factor behaves as Debye function

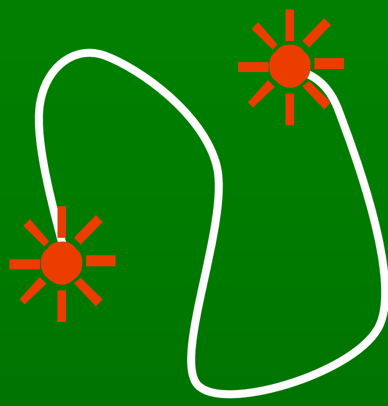
End to end distance distribution: qualitative difference in behavior

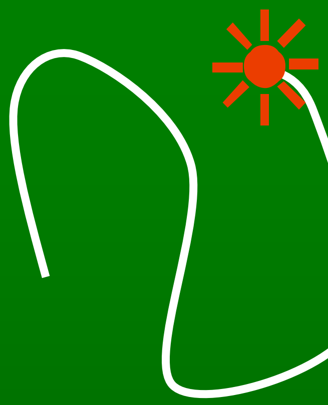
Ideal chain

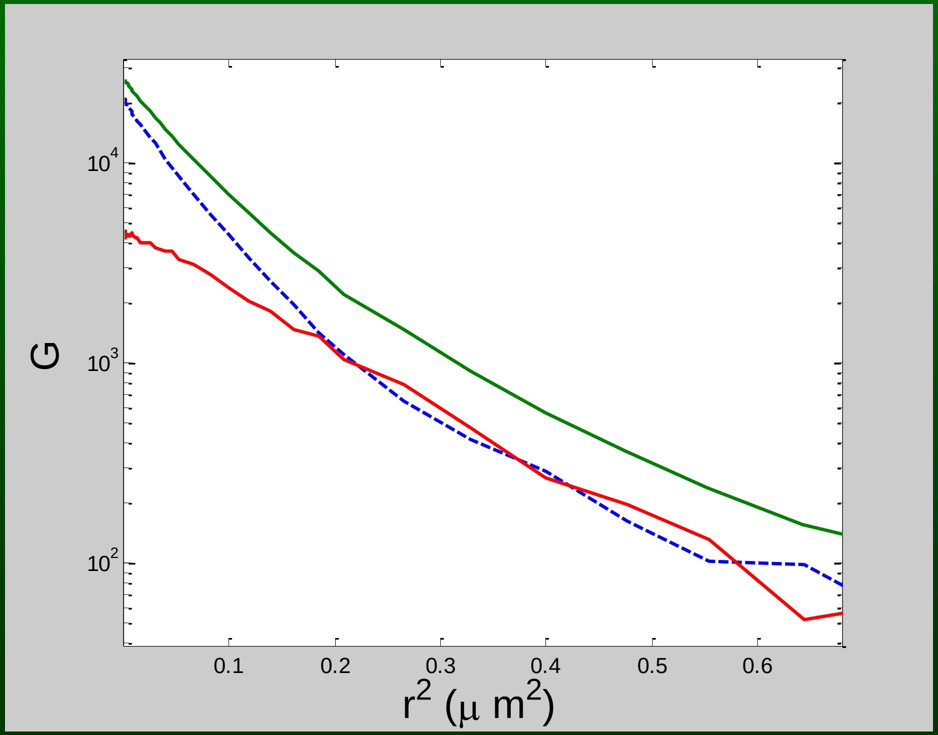


Real chain

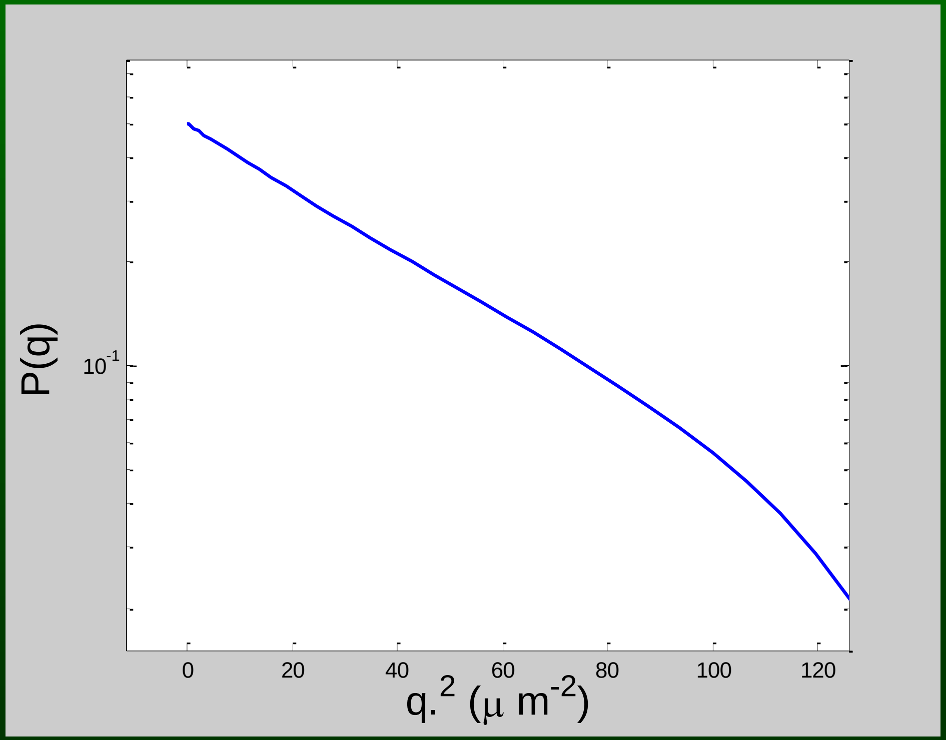








G
10^4
10^3
10^2
0.1
0.2
0.3
0.4
0.5
0.6
r^2 (μ m^2)



P(q)
10^{-1}
0
20
40
60
80
100
120
q.^{2} (μ m^{-2})

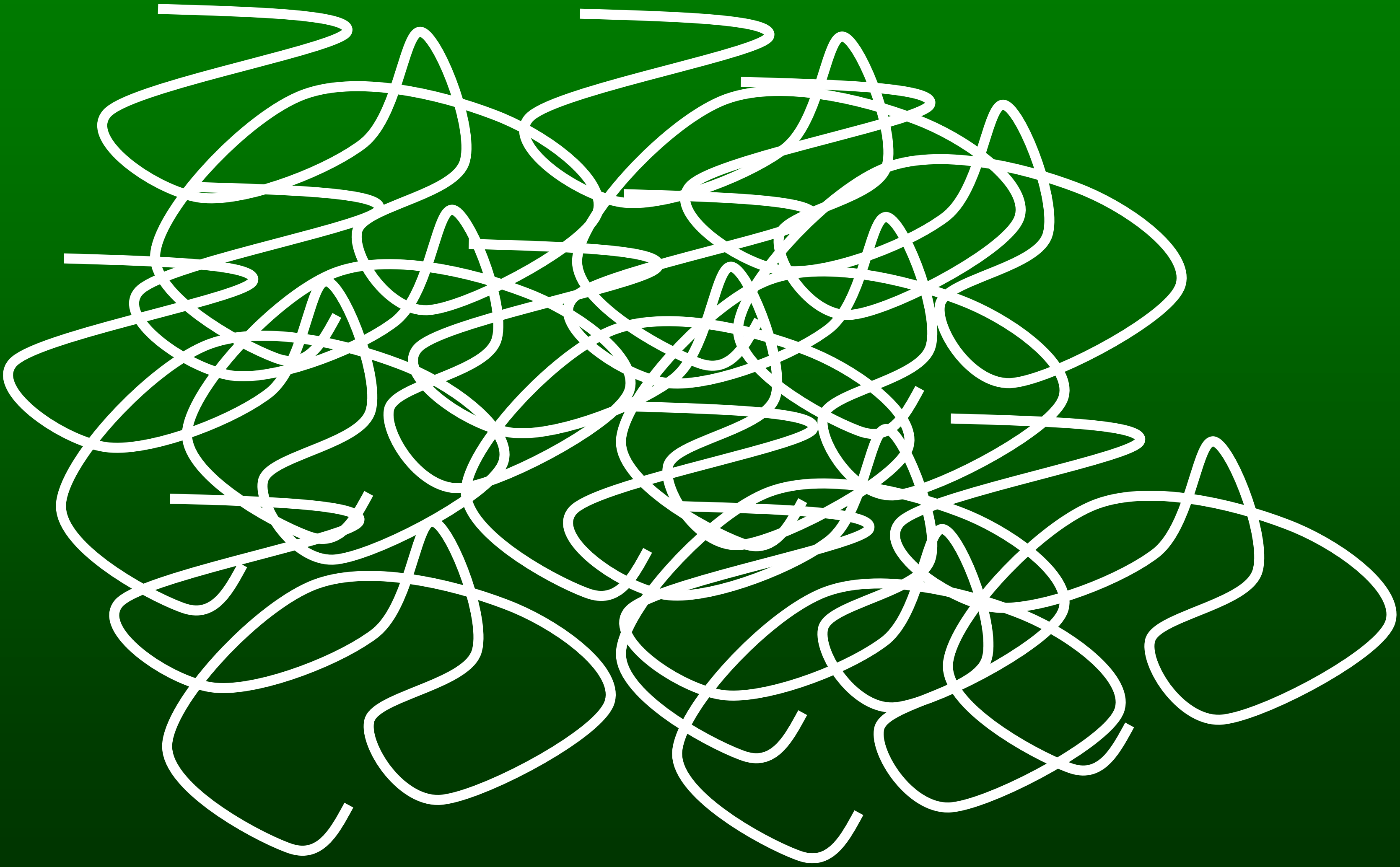
Dilute regime: DNA

$c < c^*$ (overlap concentration)

Semi-dilute regime: DNA

$c > c^*$ (overlap concentration)

$$c^* \sim {}^{1}\!/_{R_{ee}^3}$$



Screening (Edwards, 1975):
similar to Debye-Hückel theory of electrostatic screening

in dilute solution

$$g(r) \propto \frac{1}{r}$$

$$S_0(\vec{q}) \propto \frac{1}{q^2}$$

in semi-dilute solution (perturbation theory)

$$g(r) \propto \frac{1}{r}\exp\left(-r/\xi\right)$$

$$S(\vec{q}) \propto \frac{1}{1+(q\xi)^2} = \frac{1}{1+\xi^2/S_0(q)}$$

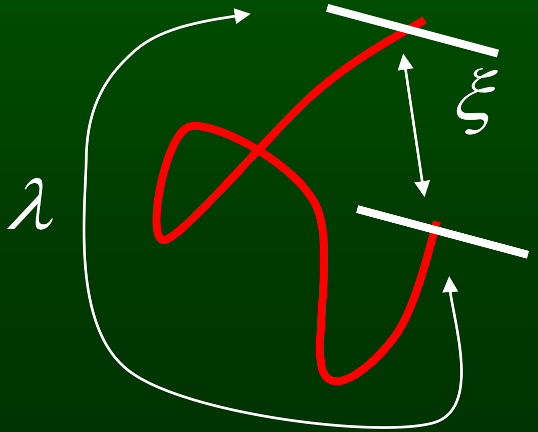
Dependence of screening length on concentration

$$\lambda = gb \qquad \xi^2 = gb^2$$

$$g = \frac{1}{cv}$$

$$\lambda \approx \frac{b}{cv} = \frac{\xi^2}{b}$$

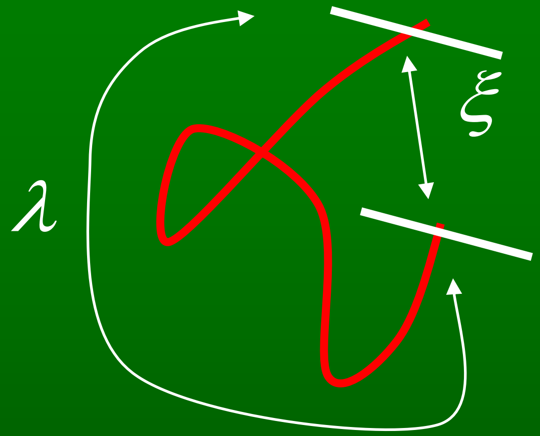
$$\xi \approx \frac{b}{(cv)^{1/2}}$$



Screening – scaling theory (deGennes, Pincus)

$$c = \frac{g}{\xi^3} \qquad \xi \propto g^{3/5}$$

$$\xi \propto \frac{1}{c^{3/4}}$$



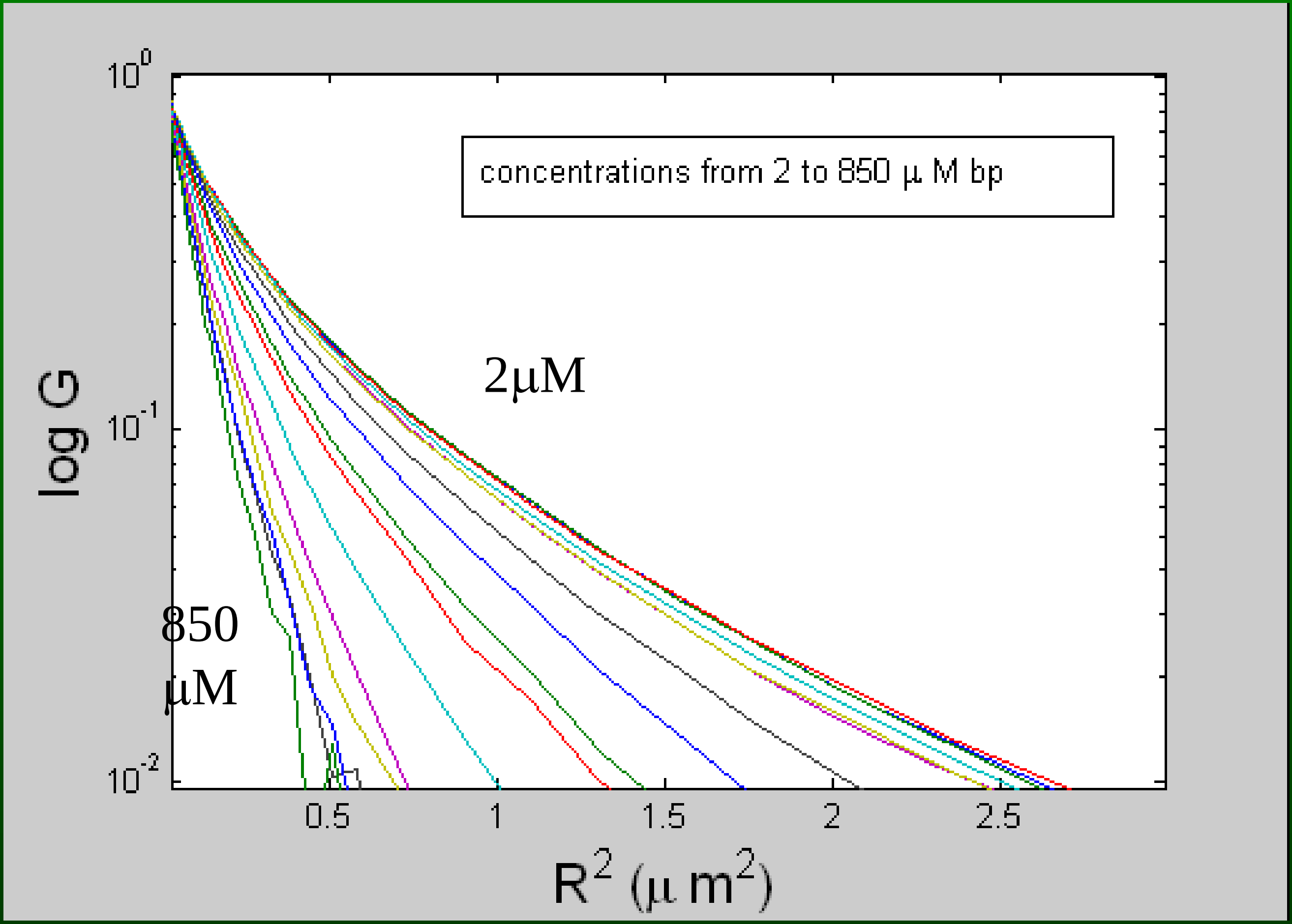
What to expect for DNA?

$$c = \frac{g}{\xi^3} \qquad \xi \propto g^{1/2}$$

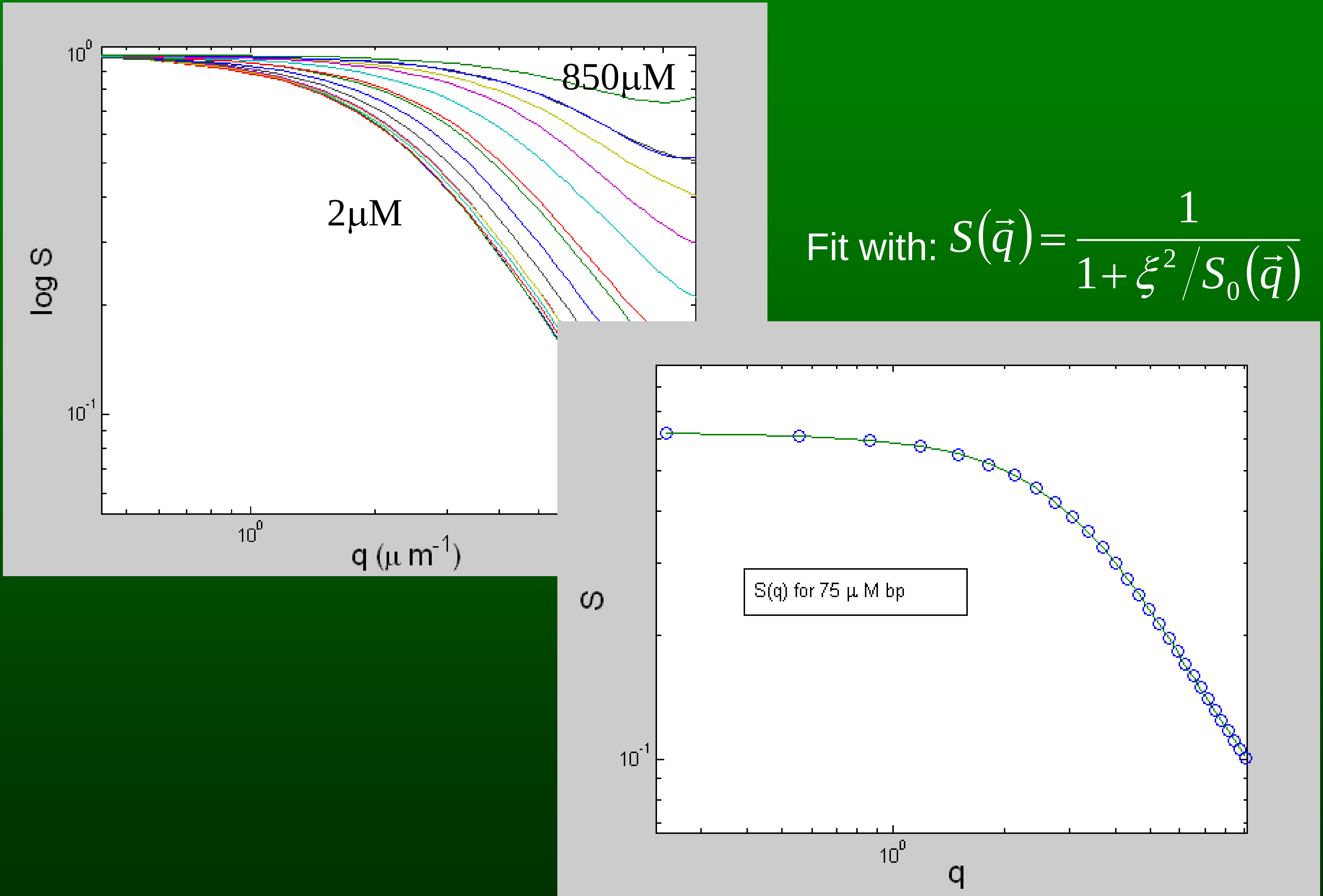
$$\xi \propto \frac{1}{c}$$ -?

FCS correlation function vs DNA concentration

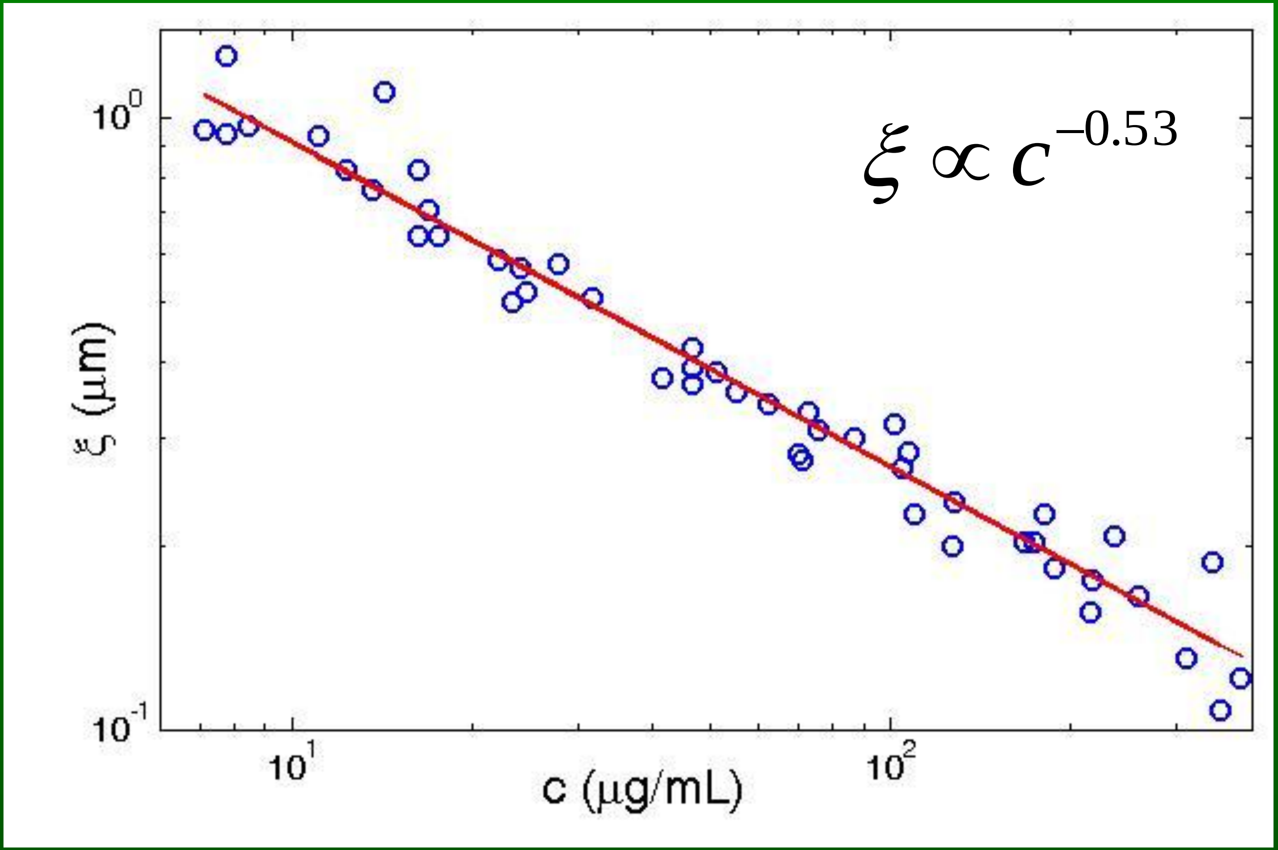
(*Eyal Shafran, Alon Yaniv & O.K, PRL 104128, 2010*)



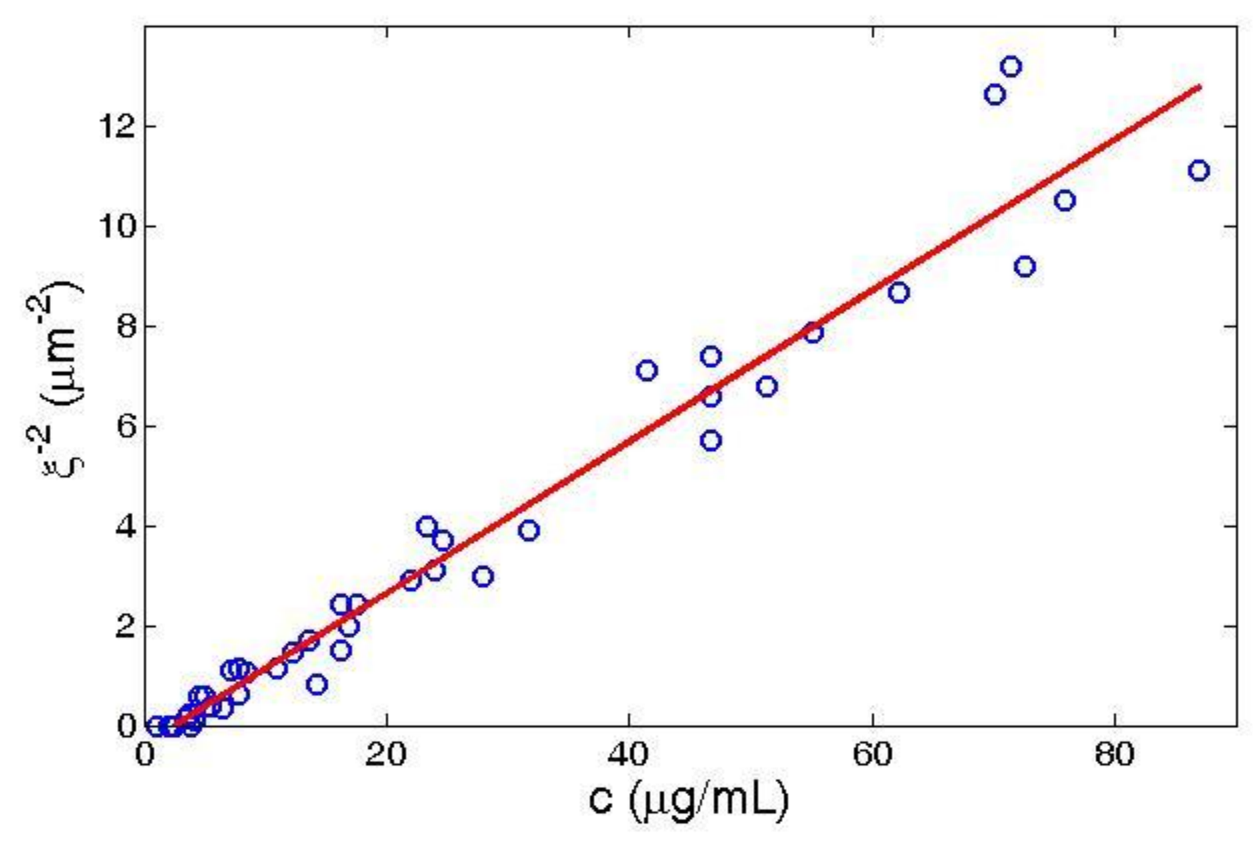
Static stucture function vs DNA concentration



Fit with: $S(\vec{q}) = \dfrac{1}{1 + \xi^2 / S_0(\vec{q})}$



Not ~$c^{-3/4}$ and not ~c^{-1} ,
close to ~$c^{-1/2}$ predicted by Edwards



$$\xi \propto c^{-1/2}$$

$$\xi^{-2} \propto c$$

~ according to mean-field of Edwards

$$\xi^2 \sim \frac{b^2}{cv} \qquad \frac{d\xi^{-2}}{dc} = \frac{v}{b^2} \approx \frac{b^2 d}{b^2} = d \qquad d \approx 3.5 nm$$

Joanny, Schaeffer, Pincus (1980):

In polymer physics we usually distinguish three types of solvents with respect to the interactions between monomers (second virial coefficient v):

$$\# collisions \sim \frac{v\sqrt{N}}{b^3}$$

strong excluded volume interactions – good solvents: $\xi \sim c^{-3/4}$

weak exluded volume interactions– marginal solutions: $\xi \sim c^{-1/2}$

no interactions ($v = 0$) – θ solvents: $\xi \sim c^{-1}$

Attractive interaction ($v < 0$) – bad solvents: irrelevant here

DNA:

-Nearly ideal polymer in dilute solutions
-Nearly mean-field polymer in semidilute solutions

All due to stiffness

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And thank you for your attention!