Polymer Networks

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Eduardo Mendes

NanoStructured Materials (NSM)
Faculty of Applied Sciences (TNW)
Delft University of Technology (The Netherlands)

e.mendes@tudelft.nl
http://www.tudelft.nl/emendes (download updated notes here)

Part one :
Deformation of polymer networks

1. Introduction
2. Force on the single chain (Ideal and Real)
3. Models for Gels and Rubbers: The (junction) affine model
4. Other models
5. Swelling and elasticity of gels
6. Failure of classical models

Part two:
Probing deformation at small scales

1. Overview of scattering
2. Scattering by fractals
3. The semi-dilute solution (a reference system)
4. Swelling of a gel : a 3D deformation
5. Gel uniaxial deformation
6. Transient network (polymer melt)
7. Actual Research Trends

Part one :
Deformation of polymer networks

1. Introduction

Polymer Networks :

Collection of polymer chains attached to each other and percolating in the vessel in such a way that the system does not flow in the time scale of the measurement.

Polymer Networks :

"Permanent" (chemically crosslinked)

chains attached chemically to each other

"Physical" (temporary or thermoreversible)

Junctions are formed by "physical" crosslinks
- semi-crystalline polymer
- hydrophobic interactions
- triblock copolymers
- stickers

Natural rubber is being used since

3.600 years ago…. with a great function !

The Ball Game.

Many variations depending on time and culture.

- 2 to 6 players each side
- natural rubber ball from 10 to 30 cm of diameter…

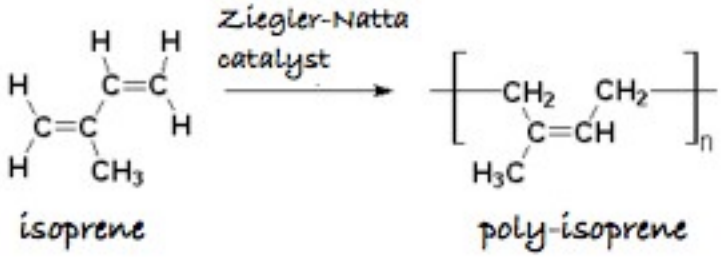
Example: « chemical » network - Natural rubber

from: http://www.agroolm.com.br/

Before crosslinking (as obtained from tree):

- linear
- Mn ~10^6 g/mol
- amorphous, T_g ~ -70°C
- not much elastic (no recovery after etretching)

(or by synthesis):



Curious Note on Ziegler-Natta reaction:

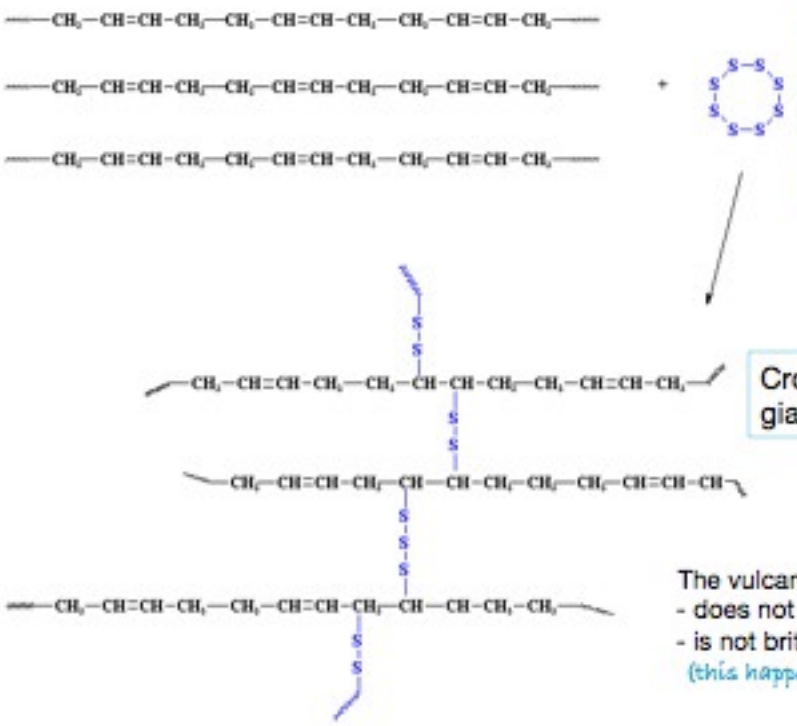
from http://pslc.ws/macrog.ss/ziegler.htm

Ziegler-Natta polymerization is a method of vinyl polymerization. It's important because it allows one to make polymers of specific tacticity. It was discovered by two scientists, and I think we can all figure out what their names were. Ziegler-Natta is especially useful, because it can make polymers that can't be made any other way, such as linear unbranched polyethylene and isotactic polypropylene. Free radical vinyl polymerization can only give branched polyethylene, and propylene won't polymerize at all by free radical polymerization. So this is a pretty important polymerization reaction, this Ziegler-Natta stuff.

So then how does it work? Something like this: Take your Ziegler-Natta catalyst, usually $TiCl_3$ or $TiCl_4$, along with an aluminum based co-catalyst, and place in the monomer at midnight on the night of the full moon. Then place the beaker on the ground in a circle of lighted candles, and then write the word "isotactic" or "syndiotactic", depending of the tacticity you desire, in runic letters on the side of the beaker with the blood of a freshly slain goat. The goat must be less than one year old, and without blemish. Then one must recite aloud the Ziegler-Natta incantation seven times, followed by the tacticity dance. If the polymerization is successful, a cold and violent wind will quickly arise and extinguish the candles, and then die away as quickly as it arose. It is important that one fast for three days before and after carrying out the ceremony. Following this little procedure usually does the trick.

Ok, so that's not really how it works, but our knowledge of how Ziegler-Natta polymerization works, and why one initiator system will work better than another is rather limited. Picking the right conditions to make a Ziegler-Natta polymerization work often feels more like magic than science. But we do know a little bit. We know that it involves transition metal catalyst, like $TiCl_3$. We also know that co-catalysts are involved, and these are usually based on group III metals like aluminum. Most of the time our catalyst/co-catalyst pair are $TiCl_3$ and $Al(C_2H_5)_2Cl$, or $TiCl_4$ with $Al(C_2H_5)_3$....

Natural rubber: crosslinking with sulphur



1839 - Charles Goodyear discovers the "vulcanization" process: he accidentally heated a mixture of rubber latex, sulfur and a little white lead box leading to a boiling stinky mixture (like a vulcan!), **crosslinking** the original latex.

Crosslinking creates (in theory) **one** giant macromolecule.

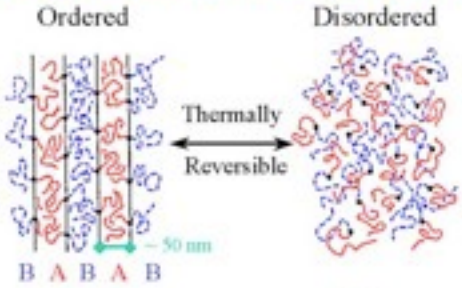
The vulcanized rubber :
- does not flow anymore (in summer)
- is not brittle anymore (in winter)

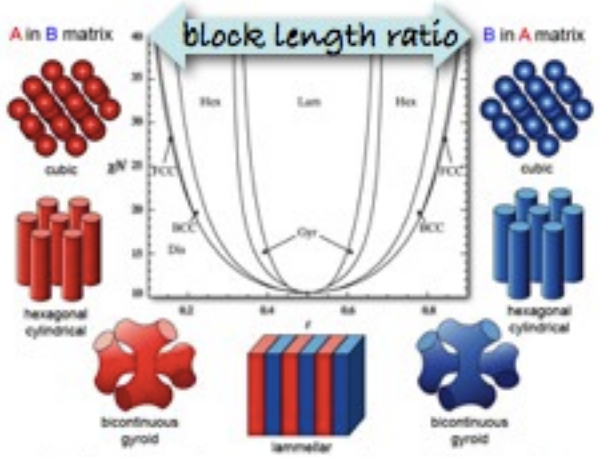
(this happened before cars needed tires)

Permanent network: covalent crosslinks

after crosslinking:
- chains cannot flow past each other upon mechanical deformation
- elastic recovery of deformation
- does not dissolve in solvents anymore (only swells)

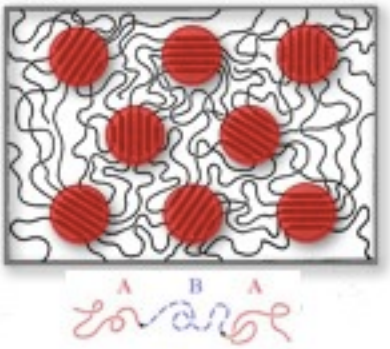
Physical Networks : many different origins





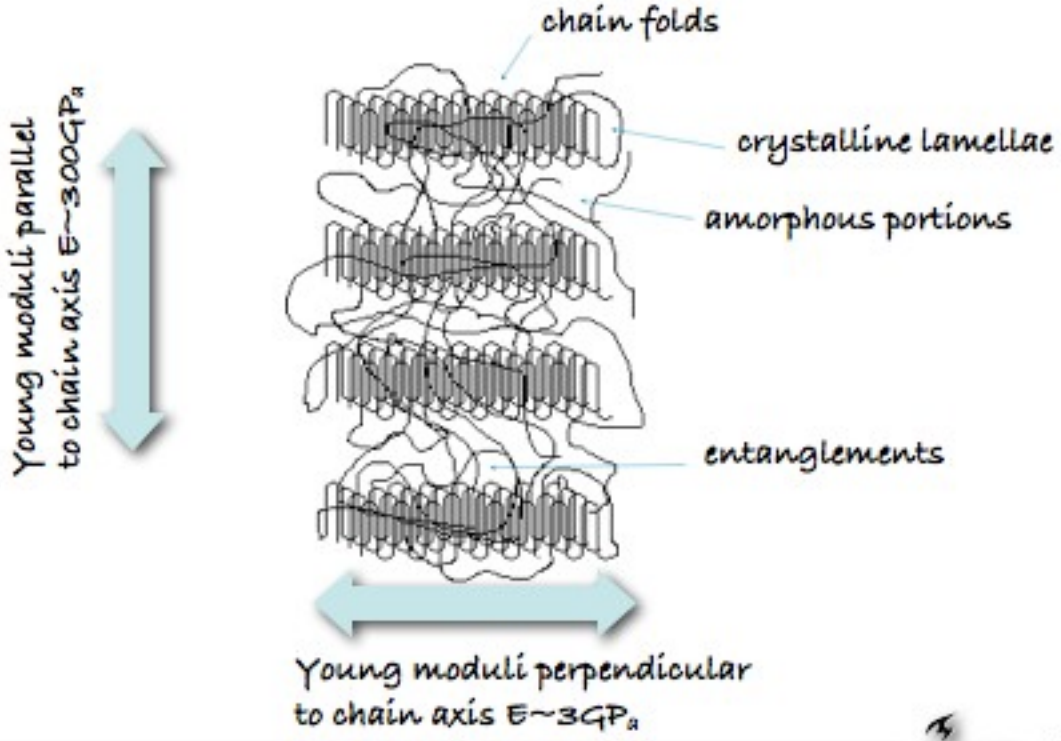
http://www.physics.nyu.edu/pine/research/nanocopoly

Triblock copolymer elastomer: midleblock above Tg at room temperature



Telechelic stickers

Physical Networks : semi-crystalline elastomers



Focus today:

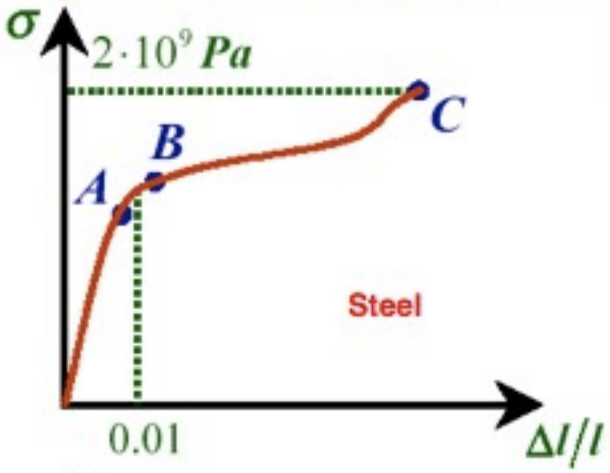
Permanent polymer networks:
(rubbers and gels)

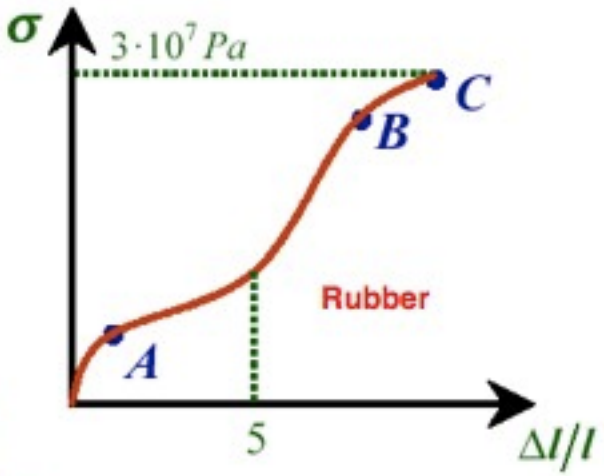
- chains attached chemically to each other
- polymer above Tg
- no crystallinity

Property :

Exhibit large elasticity:
- they can undergo large reversible deformations with relatively small applied stress.

Stress-strain curves for metals and rubbers



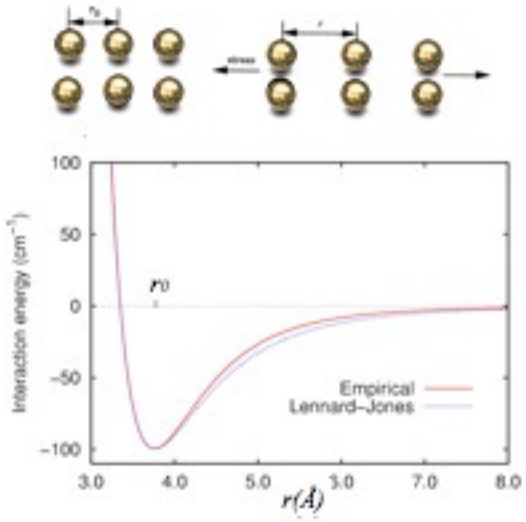


A) Upper limit for stress-strain linearity
B) Upper limit for reversibility of deformation
C) Fracture point

- Values of deformation much larger for rubbers
- Values of stress much larger for steel
- Young moduli far larger for steel (E~2 10^{11} Pa) than for rubbers (E < 10^{6} Pa)
- Linearity and reversibility easily lost for steel while very large for rubbers (reversible even in the non-linear region)
- Larger plastic deformation in steel (B to C) almost absent in rubbers

Elasticity in solids: Enthalpic origin

typical for crystalline solids – example steel wire can be streched reversibly about 1% extension.



Near the equlibrium point the potential

$$U = C(r - r_0)^2$$

Elastic force:

$$f = \frac{\partial U}{\partial r} = 2C(r - r_0)$$

Stress is

$$\sigma = \frac{f}{A} = \frac{2C}{A}(r - r_0)$$

$$= \frac{2Cr_0}{A}\frac{(r - r_0)}{r_0} = E\varepsilon$$

Hooke's law

Due to strong enthalpic contribution – Entropy is a minor factor

1. Force on a single chain

Polymer Networks :

A rubber is a liquid !

DNA dynamics simulation in 3D

Motion of a free DNA filament

time: 0.00 ms

Simulation time: 1 ms
Frames: 1000
Area: 0.32 um X 0.24 um
DNA length: 500 nm
Stick length: 50 nm

time: 0.00 ms

Simulation time: 10 ms
Frames: 1000
Area: 0.32 um X 0.24 um
DNA length: 500 nm
Stick length: 50 nm

NanoStructured Materials

Z. Farkas, I Derényi, T. Fülöp and T. Vicsek
http://angel.elte.hu/~zeno/dna/index.html

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17

DNA dynamics simulation in 3D

Motion of a free DNA filament

time: 0.00 s

Simulation time: 0.1 s
Frames: 1000
Area: 2.13 um X 1.6 um
DNA length: 10 um
Stick length: 50 nm

time: 0.00 s

Simulation time: 1 s
Frames: 1000
Area: 2.13 um X 1.6 um
DNA length: 10 um
Stick length: 50 nm

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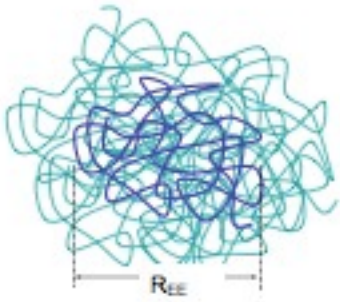
18

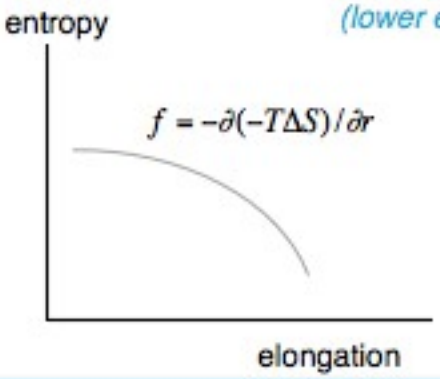
2. Force on a single chain



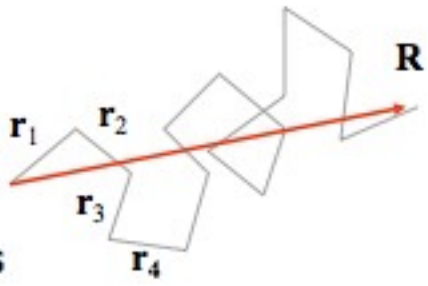
Chain in bulk

Polymers: Entropy driven elasticity

stretched chain
(lower entropy)



Random-walk



- Consider N steps of equal size, b

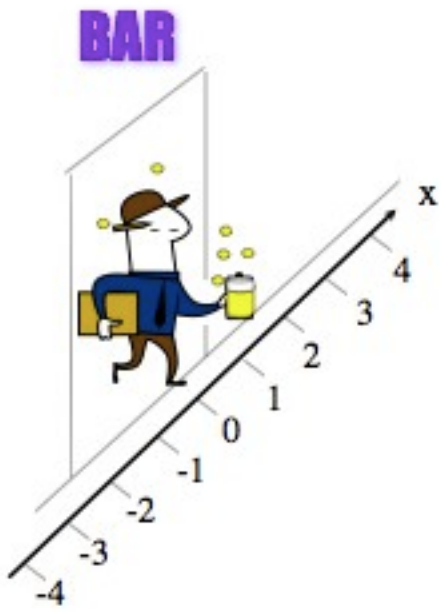
- Every step is independent of all previous ones

- Every possible conformation of an ideal chain can be mapped on a random-walk

- one random-walk trajectory = one chain conformation:

statistics of a collection of trajectories = ideal fluctuating chain statistics
(same number of states)

The drunk in a dark alley makes 4 steps (1D):



start

	N=1	N=2	N=3	N=4
X=-4	0	0	0	1
X=-3	0	0	1	0
X=-2	0	1	0	4
X=-1	1	0	3	0
X=0	0	2	0	6
X=1	1	0	3	0
X=2	0	1	0	4
X=3	0	0	1	0
X=4	0	0	0	1

W(N=4,x) = number of different trajectories finishing at x

General expression:

Note: $N = N_+ + N_-$

$x = N_+ - N_-$

number of different trajectories with N steps leading to position x

$$W(N,x) = \frac{(N_+ + N_-)!}{N_+!N_-!} = \frac{N!}{[(N+x)/2]![(N-x)/2]!}$$

Since the total number of N-steps walk is 2^N the probability of finding x after N steps is : $W(N,x) / 2^N$

After a tedious calculation:

$$P_{1d}(N,x) \cong \frac{W(N,x)}{2^N} = \frac{1}{\sqrt{2\pi N}} \exp\left(-\frac{x^2}{2N}\right)$$

since $\langle x^2 \rangle = N$

$$P_{1d}(N,x) = \frac{1}{\sqrt{2\pi < x^2 >}} \exp\left(-\frac{x^2}{2 < x^2 >}\right)$$ (for 1d)

In 3d: $$P_{3d}(N,\vec{R}) = P_{1d}(N,R_x)dR_x P_{1d}(N,R_y)dR_y P_{1d}(N,R_z)dR_z$$

a combination of independent random-walks....

For the freely jointed chain: $$< \vec{R}^2 >=< R_x^2 > + < R_y^2 > + < R_z^2 >= Nb^2$$

Therefore: $$< R_x^2 >=< R_y^2 >=< R_z^2 >= \frac{Nb^2}{3}$$

Finally, in spherical coordinates:

$$P_{3d}(N,R)4\pi R^2 = 4\pi\left(\frac{1}{2\pi Nb^2}\right)\exp\left(-\frac{3R^2}{2\pi Nb^2}\right)R^2 dR$$

The distribution function of a random walk is a Gaussian function

The random walk chain is often called the "Gaussian chain" or "Ideal chain".

$$R_g^2 = \frac{1}{N}\sum_{i=1}^{N}(\mathbf{R}_i - \mathbf{R}_{CM})^2 \qquad R_{CM} = \frac{1}{N}\sum_{i=1}^{N}\mathbf{R}_i$$ position of the center of mass

Ideal chain $$R_g^2 = \frac{b^2 N}{6} = \frac{\langle R^2 \rangle}{6}$$

Rod-like polymer $$R_g^2 = \frac{b^2 N^2}{12} = \frac{L^2}{12}$$

Measured by scattering techniques

Free energy of an ideal chain:

Entropy is the product of Boltzmann constant and the logarithm of the **number of states,** Ω :

S = klnΩ in the present case: $$S(N,\vec{R}) = k\ln\Omega(N,\vec{R})$$

since Ω is simply the number of conformations of a freely jointed chain

$$P_{3d}(N,\vec{R}) = \frac{\Omega(N,\vec{R})}{\int \Omega(N,\vec{R})d\vec{R}}$$

Therefore:

$$S(N,\vec{R}) = k\ln P_{3d}(N,\vec{R}) + k\ln\left[\int \Omega(N,\vec{R})d\vec{R}\right]$$

$$S(N,\vec{R}) = -\frac{3}{2}k\frac{\vec{R}^2}{Nb^2} + \frac{3}{2}k\ln\left(\frac{3}{2\pi Nb^2}\right) + k\ln\left[\int \Omega(N,\vec{R})d\vec{R}\right]$$

$$S(N,\vec{R}) = -\frac{3}{2}k\frac{\vec{R}^2}{Nb^2} + S(N,0)$$

Helmholtz Free Energy is $F(N,\vec{R}) = U(N,\vec{R}) - TS(N,\vec{R})$

But for an ideal chain, U(N,R) = 0 ! no interaction between monomers !

$$F(N,\vec{R}) = \frac{3}{2}kT\frac{\vec{R}^2}{Nb^2} + F(N,0)$$

Force on an ideal chain:

$$f_x = \frac{\partial F(N,\vec{R})}{\partial R_x} = \frac{3kT}{Nb^2}R_x \qquad \left|\vec{f}\right| = \frac{3kT}{Nb^2}R$$

To hold the fluctuating chain at a fixed R_x, would require a opposing force proportional to R !

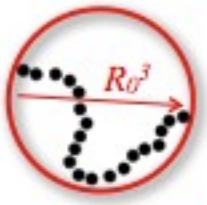
Remarks :
- force ~ R : Kind of Hooke's Law.
- force ~ kT : the hotter the harder ! (entropic spring)
- force ~1/N : shorter chains are harder to deform
- Nb^2 is a kind of average amplitude of thermal fluctuations

The Flory excluded volume chain

Athermal or good solvent : excluded volume (self-avoiding walk)

- **excluded volume swells the chain**
- **entropy loss due to deformation**

Consider N monomers of size $v=b^3$ in the volume permeated by the ideal chain $R_0=bN^{1/2}$



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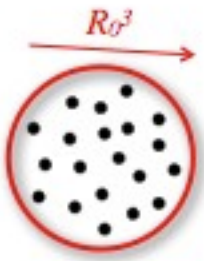


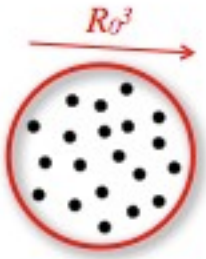
forget connectivity!

The Flory excluded volume chain

Probability of a second monomer found in the volume v of a given monomer is $v\,N/R^3$

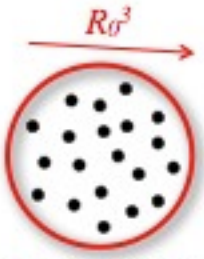
Since there are N monomers in the volume occupied by the chain, the energy cost of all contacts within the chain is $(v\,N/R^3)\,kT\,N$

$$F_{int} \sim kT\,v\,(N^2/R^3)$$



forget connectivity!

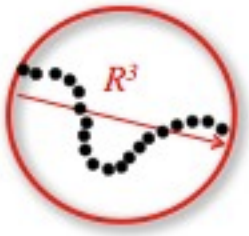
The Flory excluded volume chain



$$F_{int} \sim kT\,v\,(N^2/R^3)$$

excluded volume swells the chain

Flory's estimation of the entropic contribution of a real chain is the energy required to stretch the ideal chain to a new end-to-end distance R



$$F_{ent} \sim kT\,(R^2/Nb^2)$$

The Flory excluded volume chain

The total free energy of the Flory chain is

$$F = F_{\text{int}} + F_{ent} = kT\left(v\frac{N^2}{R^3} + \frac{R^2}{Nb^2}\right)$$

The optimum size of he Flory chain is given by

$$\frac{\partial F}{\partial R} = 0 = kT\left(-3v\frac{N^2}{R_F^4} + 2\frac{R_F}{Nb^2}\right)$$

$$R_F^5 \approx vb^2N^3$$

$$R_F \approx v^{1/5}b^{2/5}N^{3/5}$$

Flory's calculations lead to a **universal law**:

$$R \sim bN^{\nu}, \quad \nu = 3/5$$

ν =3/5 , the Flory excluded volume exponent

- is in agreement with experiment
- is very close to that calculated from sophisticated theory (0.588)

- But is a consequence of 2 fortuitous errors

  -It overestimates the contact between monomers since correlations between monomers along the chain are not taken into account.

  -The entropy used (ideal chain) overestimates the elastic energy since conformation of real chains are different form ideal ones.

Polymers in good solvent:

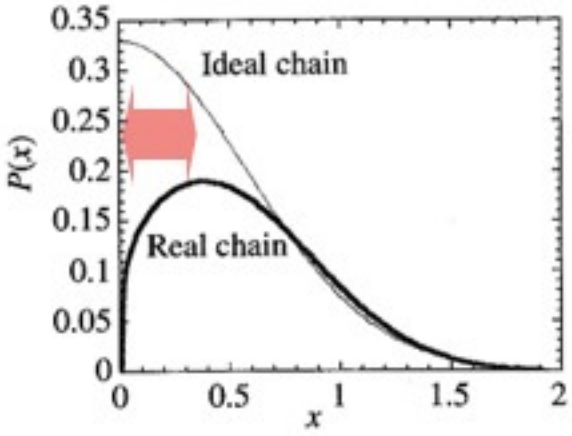
Athermal or good solvent : excluded volume (self-avoiding walk)

- excluded volume swells the chain
- entropy loss due to deformation

End-to-end distance: $R_F \approx \nu^{1/5} b^{2/5} N^{3/5}$

While in melts or θ-conditions,
Gaussian chain, end-to-end distance: $R_0 \approx b\, N^{1/2}$

End-to-end distribution of the Real chain

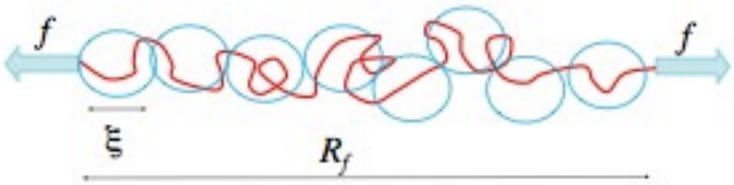


Distribution function $P(x)$ of normalized end-to-end distances $x = R/\sqrt{\langle R^2 \rangle}$. Thin curve, ideal chain; thick curve, real chain.

Ends become further apart in the real chain: chain is swollen

Ideal chain under tension: scaling approach

Stretched chain: a collection of tension blobs



Ideal chain

$$R_0 \approx bN^{1/2}$$

$$\xi \approx bg^{1/2}$$

Section of chain obeys the same statistics as whole chain

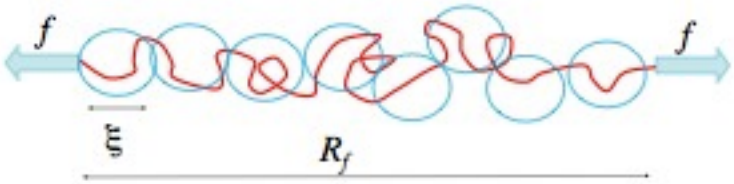
$$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^2}{\xi} \approx \frac{R_0^{\,2}}{\xi}$$

Stretched chain is a collection of aligned blobs

$$\xi \approx \frac{R_0^2}{R_f}$$

Size of "tension blob"

Stretched chain: a collection of tension blobs



Ideal chain

$$F(N,R_f) \approx kT\frac{N}{g}$$

Free energy is kT times number of blobs

Because it costs one **kT per blob** to re-direct the blob on the direction of the stretching

$$F(N,R_f) \approx kT\frac{R_f}{\xi} \approx kT\left(\frac{R_f}{R_0}\right)^2$$

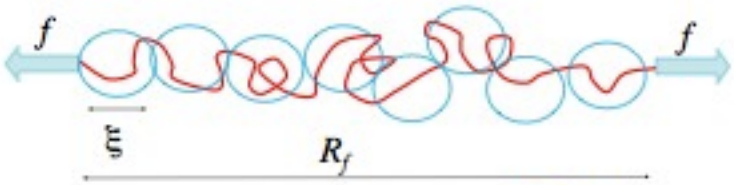
$$f \approx \frac{kT}{\xi} \approx \frac{kT}{R_0}\left(\frac{R_f}{R_0}\right)$$

Force is kT per blob !

Alternative way:
Force has to be kT per blob
(use dimensions of force)

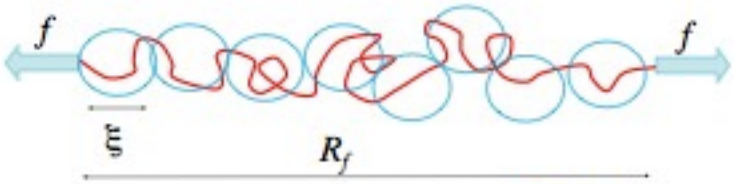
Excluded volume chain under tension

Stretched chain: a collection of tension blobs



Ideal		Real
$R_0 \approx bN^{1/2}$	Section of chain obeys the same statistics as whole chain	$R_F \approx bN^{3/5}$
$\xi \approx bg^{1/2}$		$\xi \approx bg^{3/5}$
$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^2}{\xi} \approx \frac{R_0^2}{\xi}$	Stretched chain is a collection of aligned blobs	$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^{5/3}}{\xi^{2/3}} \approx \frac{R_F^{5/3}}{\xi^{2/3}}$
$\xi \approx \frac{R_0^2}{R_f}$	Size of "tension blob"	$\xi \approx \frac{R_F^{5/2}}{R_f^{3/2}}$

Stretched chain: a collection of tension blobs



Ideal		Real
$F(N,R_f) \approx kT\frac{N}{g}$	Free energy is kT times number of blobs	$F(N,R_f) \approx kT\frac{N}{g}$
$F(N,R_f) \approx kT\frac{R_f}{\xi} \approx kT\left(\frac{R_f}{R_0}\right)^2$		$F(N,R_f) \approx kT\frac{R_f}{\xi} \approx kT\left(\frac{R_f}{R_F}\right)^{5/2}$
$f \approx \frac{kT}{\xi} \approx \frac{kT}{R_0}\left(\frac{R_f}{R_0}\right)$	Force is kT per blob	$f \approx \frac{kT}{\xi} \approx \frac{kT}{R_F}\left(\frac{R_f}{R_F}\right)^{3/2}$

In general, the free energy cost of stretching a polymer chain with equilibrium end-to-end distance

$$R_0 \approx bN^{\nu}$$

to a final end-to-end distance R_f is

$$F(N,R_f) \approx kT\left(\frac{R_f}{bN^{\nu}}\right)^{1/(1-\nu)}$$

3. Models for Gels and Rubbers: The (junction) affine model

Polymer Gels = Swollen Rubber

⇕

Dried Polymer Gel = Rubber

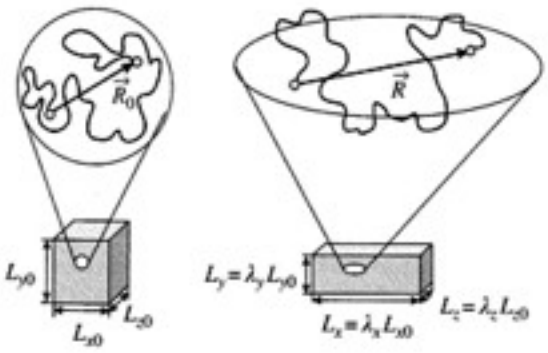
Since we know how a single chain deforms we may make models for the deformation of Gels and Rubbers

The (junction) affine model

Affine deformation

MICROscopic

MACROscopic



MACROscopic $\quad L_x = \lambda_x L_{x0}, \quad L_y = \lambda_y L_{y0} \quad \text{and} \quad L_z = \lambda_z L_{z0}.$

MICROscopic $\quad R_x = \lambda_x R_{x0}, \quad R_y = \lambda_y R_{y0} \quad \text{and} \quad R_z = \lambda_z R_{z0}.$

Entropy of undeformed chain

$$S(N,\vec{R}) = -\frac{3}{2}k\frac{\vec{R}^2}{Nb^2} + S(N,0) = -\frac{3}{2}k\frac{R_x^2+R_y^2+R_z^2}{Nb^2} + S(N,0).$$

Entropy difference between deformed and undeformed chain

$$S(N,\vec{R}) - S(N,\vec{R}_0) = -\frac{3}{2}k\frac{R_x^2+R_y^2+R_z^2}{Nb^2} + \frac{3}{2}k\frac{R_{x0}^2+R_{y0}^2+R_{z0}^2}{Nb^2}$$
$$= -\frac{3}{2}k\frac{(\lambda_x^2-1)R_{x0}^2+(\lambda_y^2-1)R_{y0}^2+(\lambda_z^2-1)R_{z0}^2}{Nb^2}.$$

For a network that contains n strands

$$\Delta S_{\text{net}} = -\frac{3}{2}\frac{k}{Nb^2}\left[(\lambda_x^2 - 1)\sum_{i=1}^{n}(R_{x0})_i^2 + (\lambda_y^2 - 1)\sum_{i=1}^{n}(R_{y0})_i^2 + (\lambda_z^2 - 1)\sum_{i=1}^{n}(R_{z0})_i^2\right]$$

Network crosslinked at the "relaxed state" the average positions in the undeformed state

$$\langle R_{x0}^2 \rangle = \frac{1}{n}\sum_{i=1}^{n}(R_{x0})_i^2 = \frac{Nb^2}{3} = \langle R_{y0}^2 \rangle = \langle R_{z0}^2 \rangle.$$

$$\sum_{i=1}^{n}(R_{x0})_i^2 = \sum_{i=1}^{n}(R_{y0})_i^2 = \sum_{i=1}^{n}(R_{z0})_i^2 = \frac{n}{3}Nb^2.$$

The entropy difference of the deformed network

$$\Delta S_{\text{net}} = -\frac{3}{2}k\frac{(\lambda_x^2 - 1)(n/3)Nb^2 + (\lambda_y^2 - 1)(n/3)Nb^2 + (\lambda_z^2 - 1)(n/3)Nb^2}{Nb^2}$$

$$= -\frac{nk}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3).$$

And its free energy (no enthalpic contribution)

$$\Delta F_{\text{net}} = -T\Delta S_{\text{net}} = \frac{nkT}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

Since rubbers are incompressible (constant volume upon deformation)

$$V = L_{x0}L_{y0}L_{z0} = L_xL_yL_z = \lambda_x L_{x0}\lambda_y L_{y0}\lambda_z L_{z0} = \lambda_x\lambda_y\lambda_z V.$$

$$\lambda_x\lambda_y\lambda_z = 1$$

Uniaxial deformation:

$$\lambda_x = \lambda \quad \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}.$$

Free energy difference for uniaxial deformation:

$$\Delta F_{\text{net}} = \frac{nkT}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right)$$

Force needed for deformation along x-direction

$$f_x = \frac{\partial \Delta F_{\text{net}}}{\partial L_x} = \frac{\partial \Delta F_{\text{net}}}{\partial(\lambda L_{x0})} = \frac{1}{L_{x0}}\frac{\partial \Delta F_{\text{net}}}{\partial \lambda}$$

$$= \frac{nkT}{L_{x0}}\left(\lambda - \frac{1}{\lambda^2}\right)$$

The xx component of the stress tensor is the force applied in the direction x divided by the area of the network perpendicular to the x-axis.

$$\sigma_{xx} = \frac{f_x}{L_y L_z} = \frac{nkT}{L_{x0} L_y L_z}\left(\lambda - \frac{1}{\lambda^2}\right) = \frac{nkT}{L_{x0} L_{y0} L_{z0}}\lambda\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$= \frac{nkT}{V}\left(\lambda^2 - \frac{1}{\lambda}\right) \equiv \sigma_{\text{true}}$$ (L_yL_z used; area deforms)

($L_{0y}L_{0z}$ used; original area used)

$$\sigma_{\text{eng}} = \frac{f_x}{L_{y0} L_{z0}} = \frac{nkT}{L_{x0} L_{y0} L_{z0}}\left(\lambda - \frac{1}{\lambda^2}\right) = \frac{nkT}{V}\left(\lambda - \frac{1}{\lambda^2}\right) = \frac{\sigma_{\text{true}}}{\lambda}$$

Therefore:

$$\sigma_{\text{true}} = G\left(\lambda^2 - \frac{1}{\lambda}\right)$$

$$\sigma_{\text{eng}} = G\left(\lambda - \frac{1}{\lambda^2}\right)$$

Where the elastic modulus is

$$G = \frac{nkT}{V} = \upsilon kT = \frac{\rho \Re T}{M_s}$$

$$\upsilon = \frac{n}{V} = \frac{\rho N_{Av}}{M_s}$$ Number of strands per unit volume

M_s Number average molecular mass of a strand

ρ network density (mass/unit volume)

Ideal gas !

$$p = \frac{nkT}{V}$$

Remarks :

$$\sigma = \nu k_B T\left(\lambda - \frac{1}{\lambda^2}\right)$$

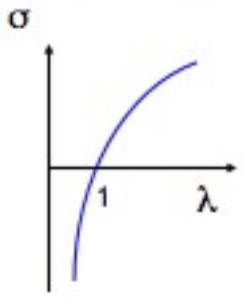
Shear Modulus
(Young modulus $E=3\nu k_B T$)

- For loosely crosslinked networks E is small since $\nu \sim 1/Na^3$(from incompressibility $\nu Na^3=1$, a^3 is the monomer volume).

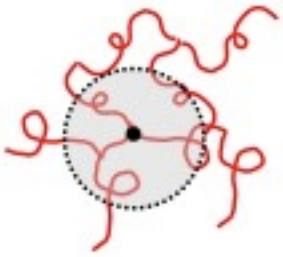
- Equation predicts modulus *and* nonlinear elasticity

- Analogous equations can be found for other deformations (shear, twist, etc…)

- Final equation independent of chain model or details.



The Phanton network model

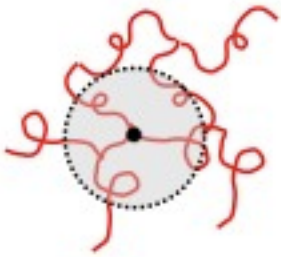


- **Junction points are allowed to fluctuate**
- **Fluctuations of junctions points are Gaussian-like**

$$G = \nu kT\,\frac{f-2}{f} = \frac{\rho \mathcal{R} T}{M_s}\left(1-\frac{2}{f}\right)$$

Where f is the functionality of the junction points (number of chains connected in a crosslink)

Phantom Network



Uses the same assumptions as in the affine model but includes Gaussian fluctuations of junctions.

For functionality $f = 4$:

$$\sigma = (\nu k_B T/2)(\lambda - 1/\lambda^2)$$

factor 1/2

Stress-strain relations :

Affine Network : $$\sigma = \nu k_B T\left(\lambda - \frac{1}{\lambda^2}\right)$$

Phantom Network: $$\sigma = \frac{\nu k_B T}{2}\left(\lambda - \frac{1}{\lambda^2}\right)$$

Meaning of factor 2 :

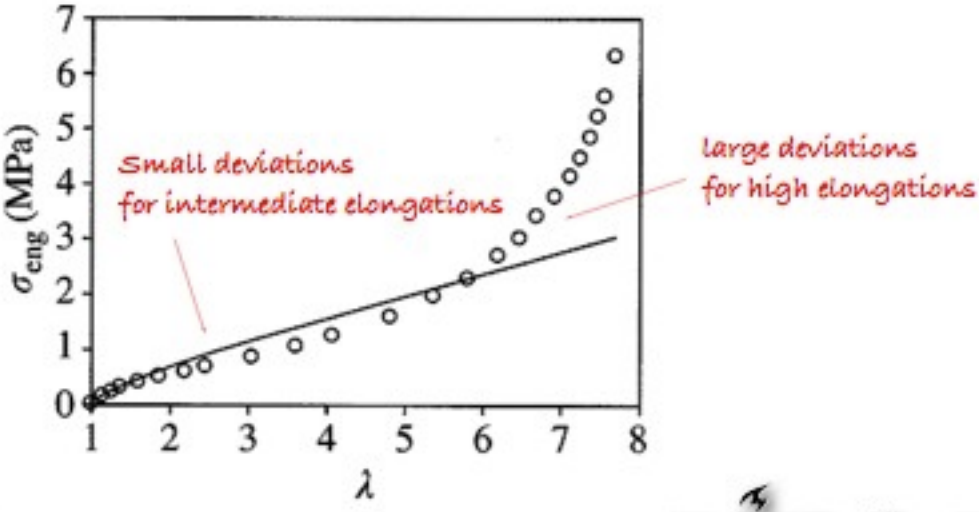
As the junctions fluctuate, the Gaussian chains of the network "look" longer as the crosslinks fluctuate as the chains themselves. Since longer chains are easier to deform, the modulus decreases.

Both models fail to predict behaviour at large elongations

4. Failure of Models

Finite extensibility

In reality chains are finite and cannot be stretched infinitely. All classical models fail to describe this that.



Deviations at high elongations: Chains behave non-Gaussian

Stress - strain relationship f(r) for non-Gaussian chains
(after tedious derivation by Kuhn) :

$$f = \left(\frac{kT}{l}\right) L^{-1}\left(\frac{r}{nl}\right) = \frac{kT}{l}\left[3\left(\frac{r}{nl}\right) + \frac{9}{5}\left(\frac{r}{nl}\right)^3 + \frac{297}{175}\left(\frac{r}{nl}\right)^5 + \frac{1539}{875}\left(\frac{r}{nl}\right)^7 + \cdots\right]$$

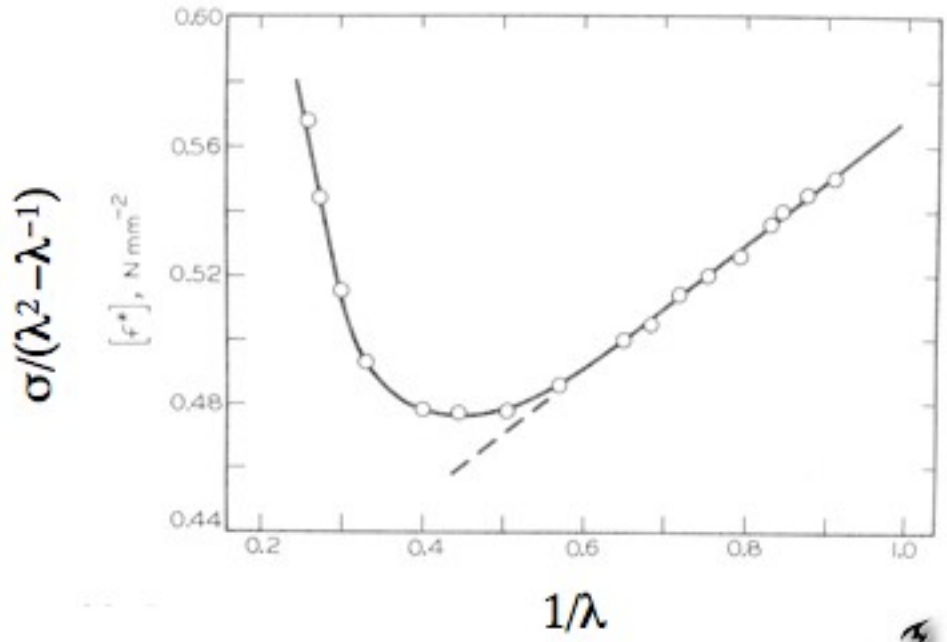
$$L(x) = \coth x - \frac{1}{x}$$

Gaussian chain recovered in the limit of small elongations :

$$f = \frac{kT}{l}\left(3\left(\frac{r}{nl}\right)\right)$$

Another Example : Natural rubber

Deviations at intermediate elongations best seen in the reduced stress representation



Mooney and Rivlin 1940's

Considering the elastomer as a continuum and basic assumptions that rubber was incompressible, isotropic in a unstrained state.

$$\sigma = 2(C_1 + \frac{C_2}{\lambda})(\lambda^2 - \frac{1}{\lambda})$$

where C_1 and C_2 are materials constant

Fits data at intermediate elongations but it is ***not*** a molecular theory

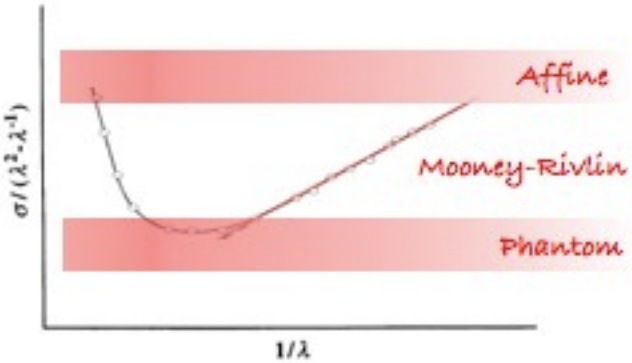
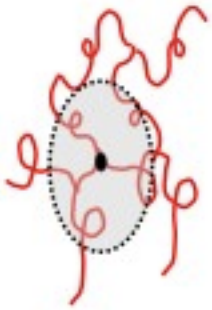


Figure 3.20 Reduced stress, $\sigma/(\lambda^2 - \lambda^{-1})$, as a function of the reciprocal strain.

Other molecular models



Erman model :
Junctions allowed to fluctuate anisotropically

Flory model :
ln F, add deformation term $\nu \ln(V/V_0) \sim \nu \ln(\lambda_x \lambda_y \lambda_z)$

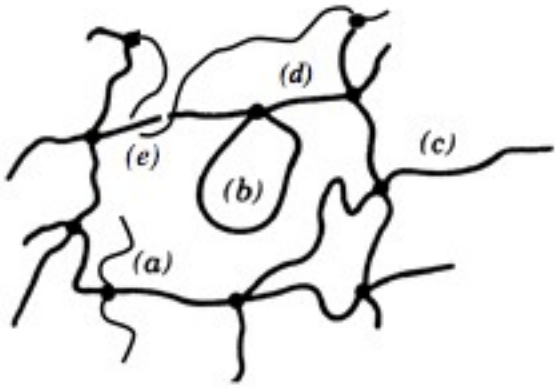
Graessley model :
Works for micronetworks.
Analogy with resistors to resolve topology.

$$\sigma = (1-2/f)\,(\nu\, k_B T)\,(\lambda - 1/\lambda^2)$$

…

Claimed reasons for failure at intermediate elongations :

real networks are ***not "chemically perfect"***



networks defects :

a) decorated chain

b) loop

c) dangling end

d) short chains

e) trapped entanglement

…

*There is a large variety of models that take that into account **local defects** :*

a) *decorated chains*
b) *loops*
c) *dangling ends*
d) *short chains*
e) *trapped entanglements*

But most use the Affine and Phantom models as starting points, and therefore incorporate the basic assumptions of those models and their weakness.

5. Swelling and elasticity of Gels

Osmotic pressure causes polymer gels swelling

⇩

Elasticity causes gel to shrink.

⇩

The free energy of a gel may be written

$$F_{gel} = F_{dilution} + F_{elastic}$$

⇩

In swelling equilibrium

$$\Pi = G$$

Semi-dilute solutions and osmotic pressure

Dilute solution $\phi < \phi^*$

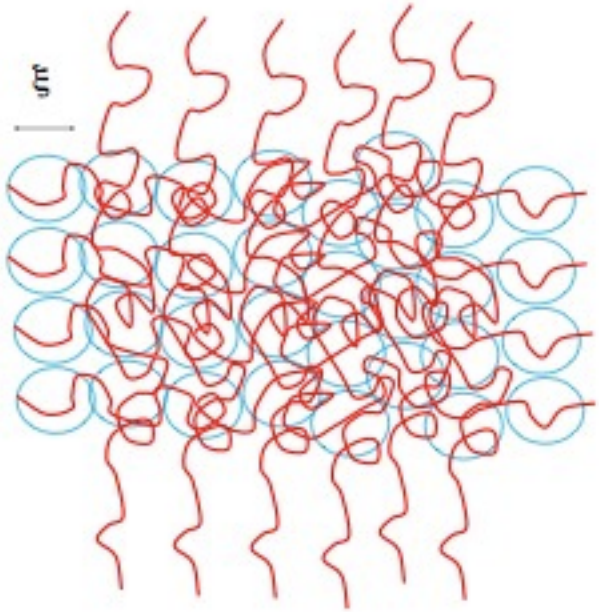
ϕ^* is the "overlapping" volume fraction
(c^* is the "overlapping" concentration)

$$\phi^* = (Nb^3)/R^3 \sim N^{(1-3\nu)}$$

In athermal good solvent

$$\phi \sim \xi^{-4/3}$$

Semi-dilute solution when $\phi > \phi^*$

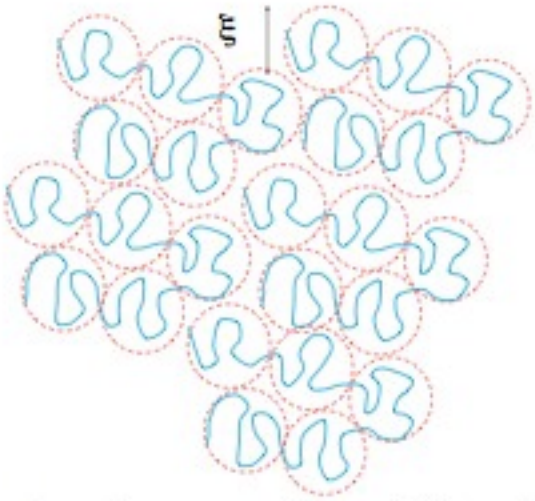


Compact collection of
uncorrelated blobs of size ξ

$$\phi \sim g(\xi) \sim \xi^{5/3} / \xi^3 \sim \xi^{-4/3}$$
for $\phi > \phi^*$

The correlation length ξ
is called the blob size

Osmotic pressure of a semi-dilute solution in athermal solvent



Osmotic pressure of a semi-dilute solution :
(des Cloiseaux law)

$$\Pi_{sol} = kT / \xi^3$$

In athermal good solvent

$$\phi \sim \xi^{-4/3}$$

$$\Pi_{sol} \sim kT\,\phi^{9/4}$$

Elasticity of Gels

It is convenient to define:

$$\phi = \frac{V_{dry}}{V}$$

Polymer volume fraction

$$V_0\phi_0 = V\phi = V_{dry}$$

"0" refers to the preparation state of the gel. Gel "remembers" the state in which chains were relaxed

$$Q \equiv \frac{V_{eq}}{V_{dry}}$$

equilibrium swelling ratio in pure solvent

$$\lambda = \left(\frac{V}{V_0}\right)^{1/3} = \left(\frac{\phi_0}{\phi}\right)^{1/3}$$

Swelling as deformation in 3D

Affine deformation : chain end-to-end distance deforms in the same manner as the macroscopic network

Assume: Swelling is affine deformation in 3D

$$\lambda = \lambda_x = \lambda_y = \lambda_z = (V/V_0)^{1/3} = (\phi/\phi_0)^{-1/3}$$

index « 0 » is for « reference (preparation) state »

$$\langle R_i^2 \rangle = \lambda_i^2 \langle R_{i0}^2 \rangle \text{ , } i=x,y,z$$

We saw that for the ideal chain : $F_{el} \approx kT \frac{R^2}{Nb^2} = kT \frac{R^2}{R_0^2}$

Where R_0 is the mean end-to-end distance of the chain in the relaxed state

Note:
here $\mathbf{R_0}$ is the average value over all configurations due to **fluctuations**

or

at T=0 the coil is collapsed into a nanosphere. At finite T it fluctuates.
$\mathbf{R_0}$ is then a kind of **amplitude of fluctuations**

"Modern form" of elastic energy of a swollen strand affinely deformed is given by (Panyukov):

$$F_{el} \approx kT\left(\frac{\lambda R_0}{R_{ref}}\right)^2$$

R_{ref} is the **mean fluctuation amplitude** of the end-to-end distance of the chain in the relaxed state (usually preparation state) In many cases, it is reasonable to assume: $R_0^2 = R_{ref}^2$.

(this formulation also to mimic "**memory**" of the preparation state)

Chain number density $\nu=\phi/(Nb^3)$ times elastic free energy per chain

$$G(\phi) \approx \nu kT\left(\frac{\lambda R_0}{R_{ref}}\right)^2 \approx \frac{kT\phi}{Nb^3}\left(\frac{\lambda R_0}{R_{ref}}\right)^2$$

R_{ref} is the **mean fluctuation amplitude** of the end-to-end distance of the chain in the relaxed state

In a θ-solvent:

- chain end-to-end distance R independent of ϕ
- fluctuations of R also independent of ϕ

$$R_{ref}^2 \approx R_0^2 \approx b^2 N$$

swelling is deformation in 3D for ideal chain: $R = \lambda R_0 \rightarrow \phi^{-1/3}$
in the relaxed state: $R_{ref} = R_0 \rightarrow \phi_0^{-1/3}$

$$G^{\theta}(\phi) \approx \frac{kT\phi}{Nb^3}\lambda^2\left(\frac{R_0}{R_{ref}}\right)^2 \approx \frac{kT\phi}{Nb^3}\left(\frac{\phi_0}{\phi}\right)^{2/3} \approx \frac{kT\phi_0^{2/3}}{Nb^3}\phi^{1/3}$$

(James and Guth)

In an athermal (good) solvent:

$$G(\phi) \approx \frac{kT\phi}{Nb^3}\left(\frac{\lambda R_0}{R_{ref}}\right)^2 \approx \frac{kT\phi}{Nb^3}\left(\frac{\phi_0}{\phi}\right)^{2/3}\left(\frac{\phi}{\phi_0}\right)^{(2\nu-1)/(3\nu-1)} \approx \phi_0^{0.44}\phi^{0.56}$$

with

$$R_0 \approx bN^{1/2}\phi_0^{-(\nu-1/2)/(3\nu-1)}$$

$$R_{ref} \approx bN^{1/2}\phi^{-(\nu-1/2)/(3\nu-1)}$$

R_0 is the end-to-end distance of a chain with N monomers in semi-dilute regime and polymer volume fraction ϕ.

Note: these models use a general "harmonic elastic term" for the elastic energy, exponent "2" in the deformation

$$G^{\theta}(\phi) \approx \frac{kT\phi}{Nb^3}\lambda^2\left(\frac{R_0}{R_{ref}}\right)^2$$

and introduce the chain statistics only via the ratio "R_0/R_{ref}".

Equilibrium swelling in pure solvent

Free energy of a gel :

$F_{gel} = F_{dilution} + F_{elastic}$

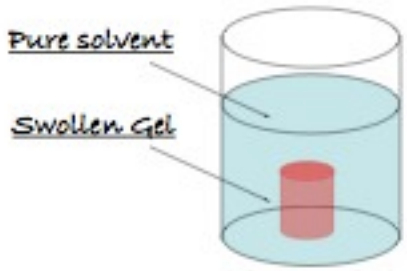
using $\Pi(\phi) = \phi\frac{\partial\tilde{F}}{\partial\phi} - \tilde{F}$ *« ~ » = per unit volume*

Osmotic Pressure of a Gel :

$$\Pi_{gel}(\phi) = \Pi_{sol}(\phi) - G(\phi)$$

$$\Pi_{gel}(\phi) = P_0\phi^{9/4} - gG(\phi)$$

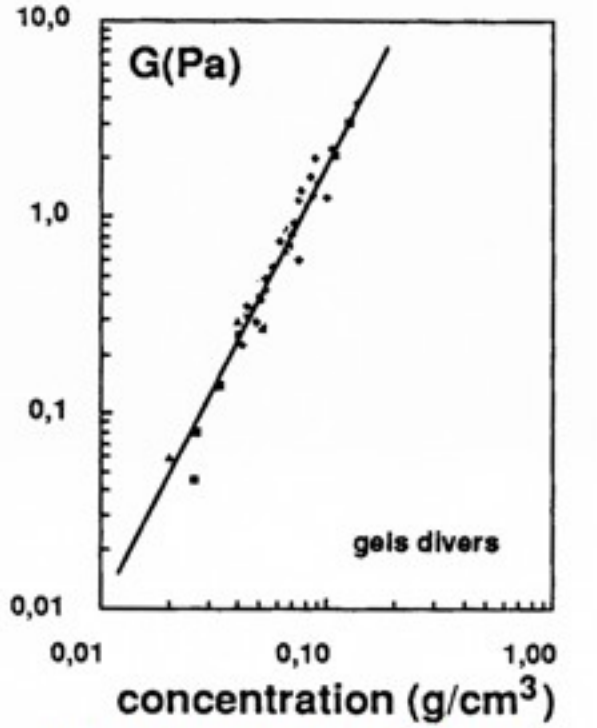
Gel in equilibrium swelling in pure solvent



Swelling equilibrium in pure solvent:

$$\Pi_{gel}(\phi_e) = 0$$

$G(\phi_e) \sim \phi_e^{9/4}$



Elastic moduli of gels of different origins swollen to equilibrium in pure solvent. The law $G(\phi_c) \sim \phi_c^{9/4}$ is observed

Part two: Probing deformation at small scales

Form now on we will focus on two points :

*A) **Test the basic assumptions of classical models** (also used by other models)*

*B) **Study a new class of defects,** not taken into account by classical or scaling models.*

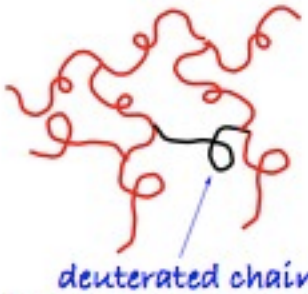
These "mesoscopic" defects are intrinsic to the randomness of the crosslinking process and therefore, always present , even in a "chemically perfect" network.

6. Failure of classical elasticity theory

Swelling a rubber with solvent is to a 3D deformation

⇩

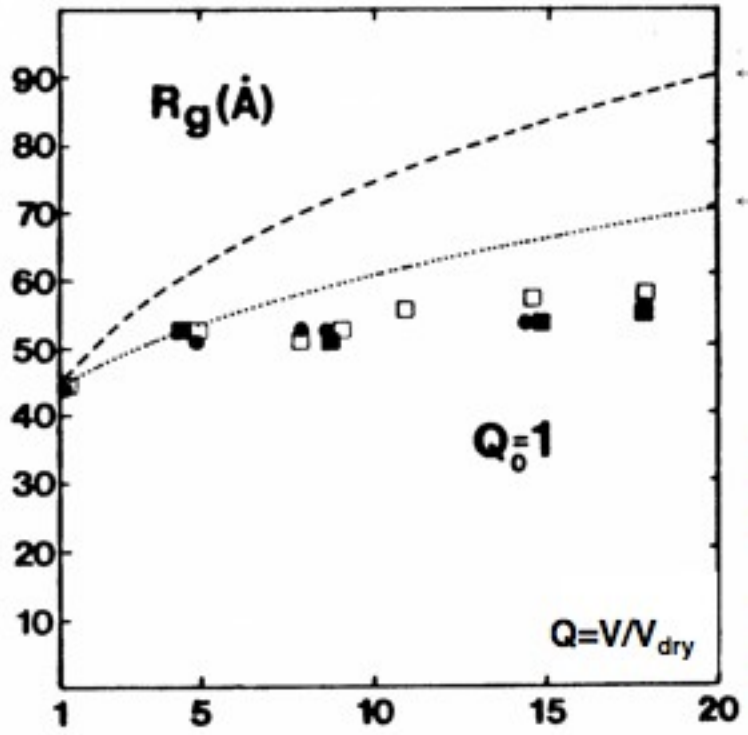
Chains are stretched in 3D : $R = \lambda R_0$



Selective labelling :
***only** few individual labelled chains in a gel made by end-linking are visible in the experiment. They appear as diluted in space since all others are invisible.*

Using small angle neutron scattering (SANS) one can measure Rg of individual chains with degree of swelling…

(Rg scales in the same way as R with concentration)



← Affine network

$$\frac{R_g}{R_{g0}} = \left(\frac{\left(\frac{Q}{Q_0}\right)^{2/3} + 1}{2} \right)^{1/2}$$

← Phantom network

$$\frac{R_g}{R_{g0}} = \left(\frac{\left(\frac{Q}{Q_0}\right)^{2/3} + 3}{4} \right)^{1/2}$$

Rg of individual chains almost do not vary with degree of swelling !!

No apparent stretching of chains !!!

Variation of the radius of gyration of a labelled chain in a gel for different swelling degrees Q = volume/ dry volume.

c* theorem :

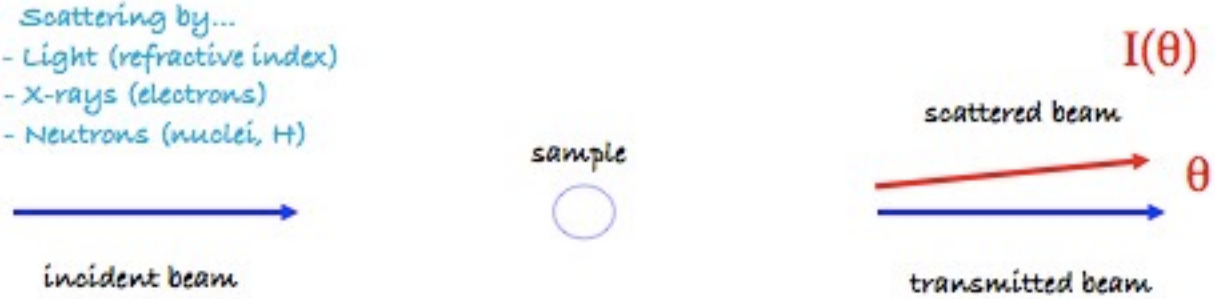
« gels synthesized at c* exhibits a correlation length variation with concentration that is similar to semi-dilute solution. »

Or simply,

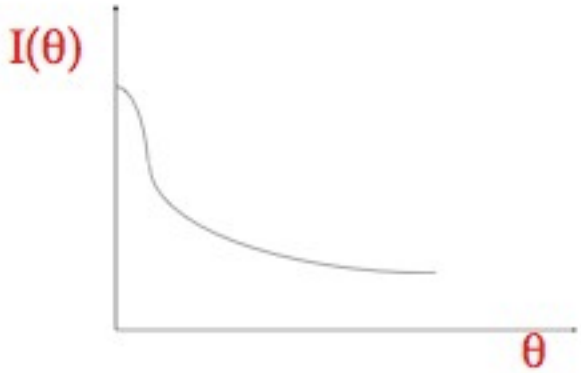
« the correlation length varies with concentration in a gel in a similar manner as in a semi-dilute solution. »

1.Overview of Scattering

Scattering by...
- Light (refractive index)
- X-rays (electrons)
- Neutrons (nuclei, H)

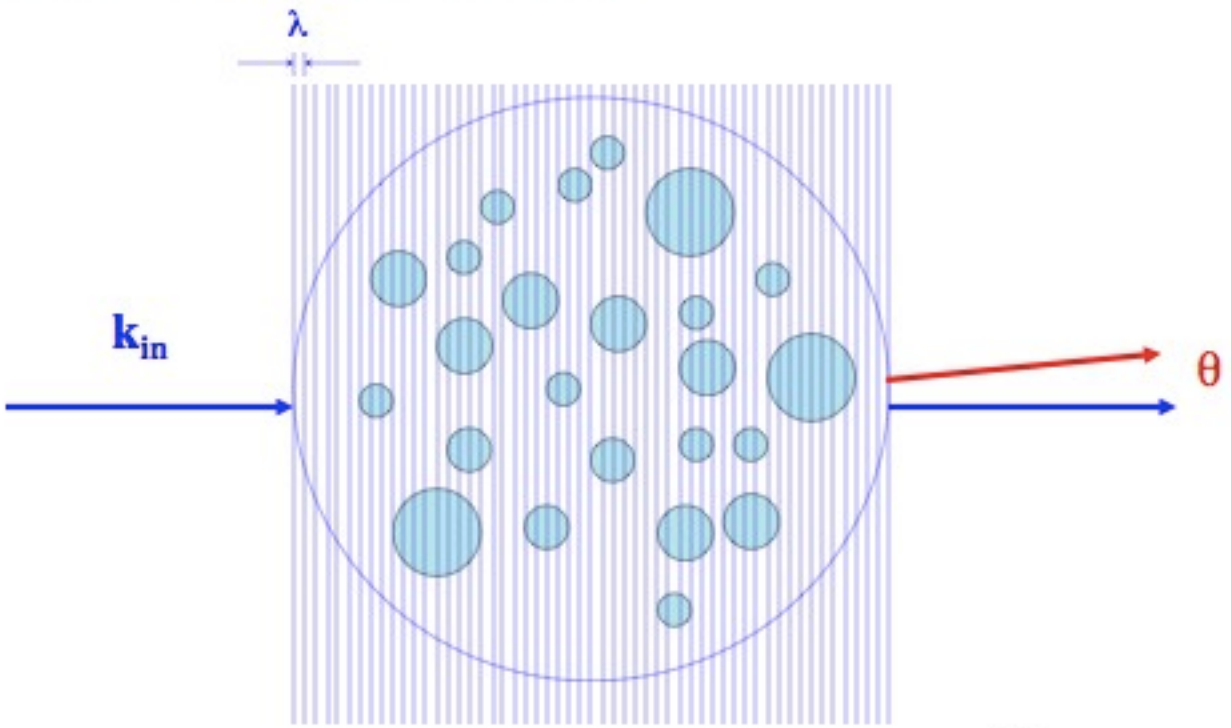


"The" Advantage of Neutrons
"contrast selectivity"
(such as the measurement of Rg of a chain in a gel)

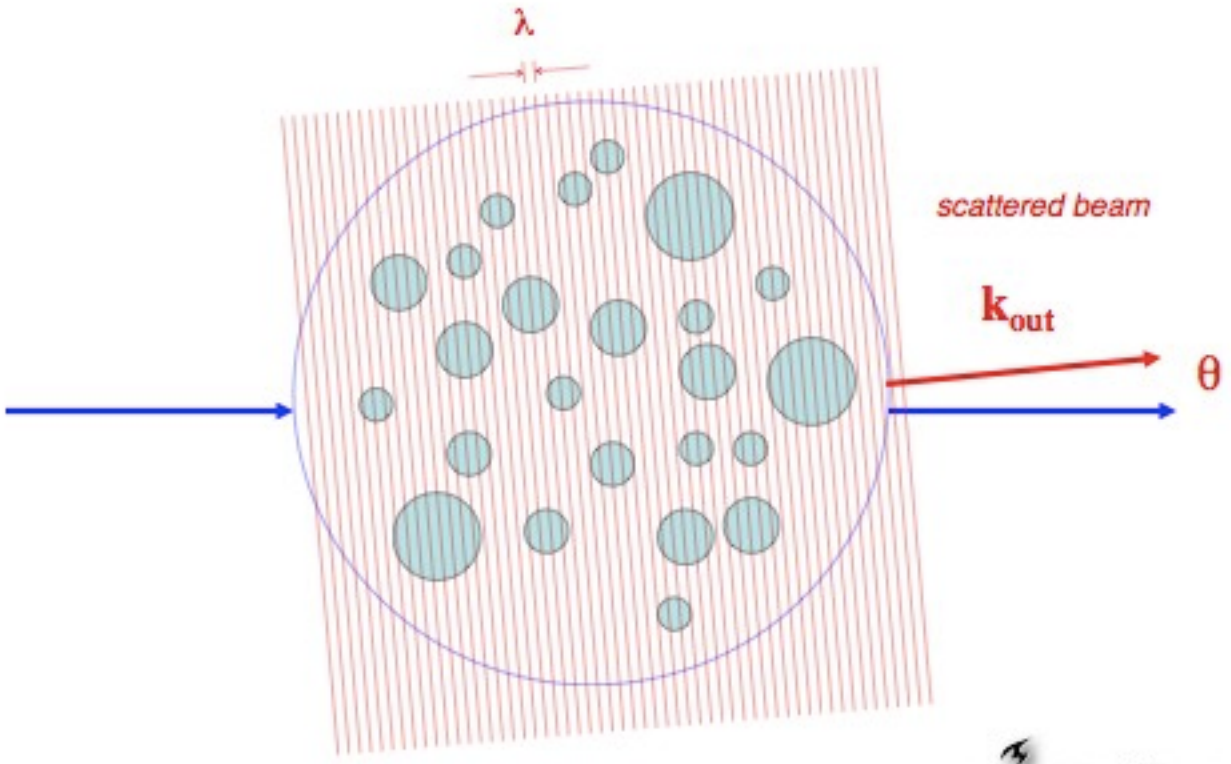


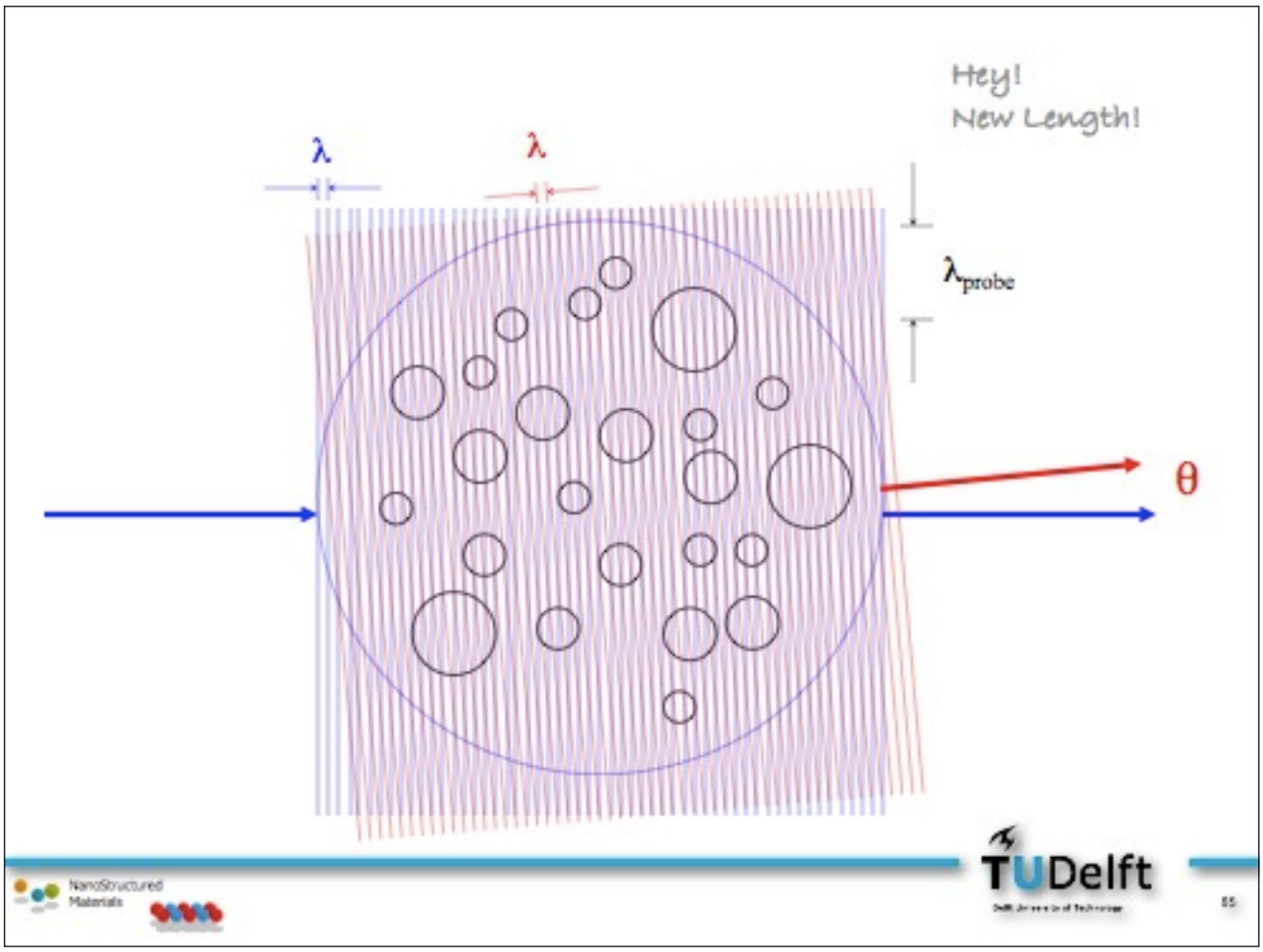
A lot of information here !

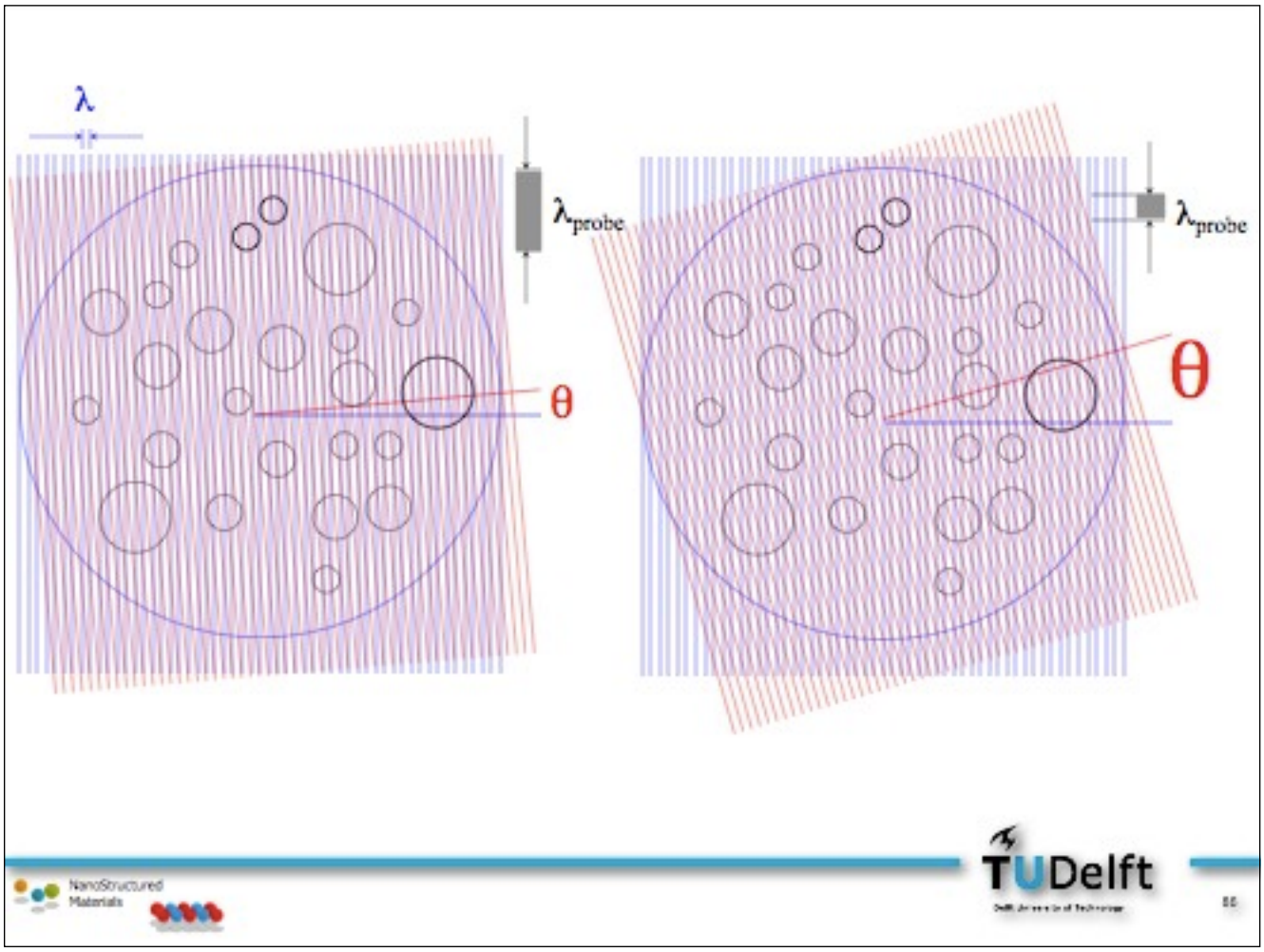
Principle :
Coherent Scattering (plane waves as usual!!)



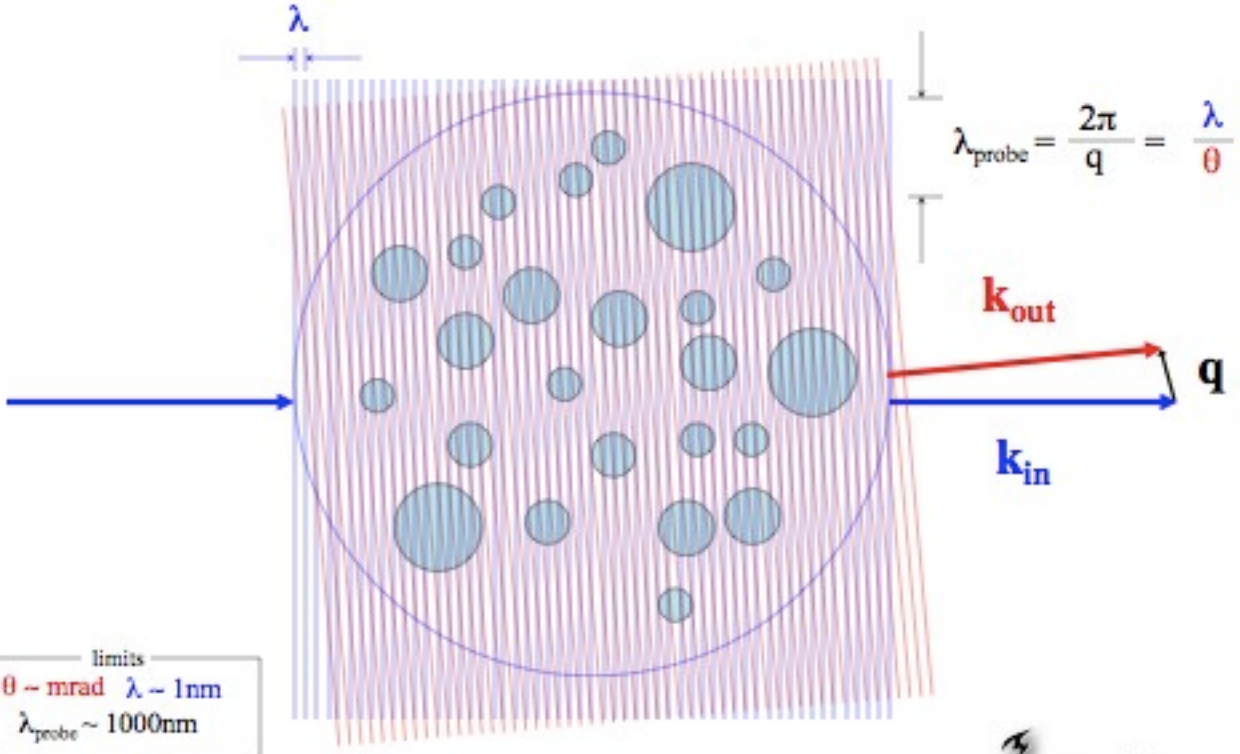
- scattered wave is also plane




Hey!
New Length!
λ
λ
λprobe
θ

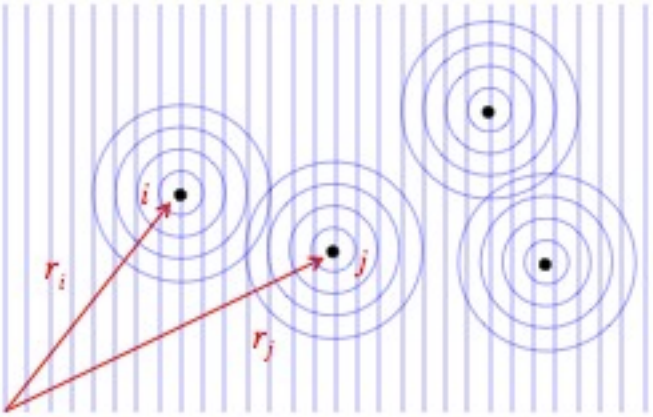

λ
λprobe
θ
λprobe
θ

$q=k_{out}-k_{in}$ $q=2k_0\sin(\theta/2) \sim k_0\theta$



limits
θ ~ mrad λ ~ 1nm
λ_{probe} ~ 1000nm

The scattering function

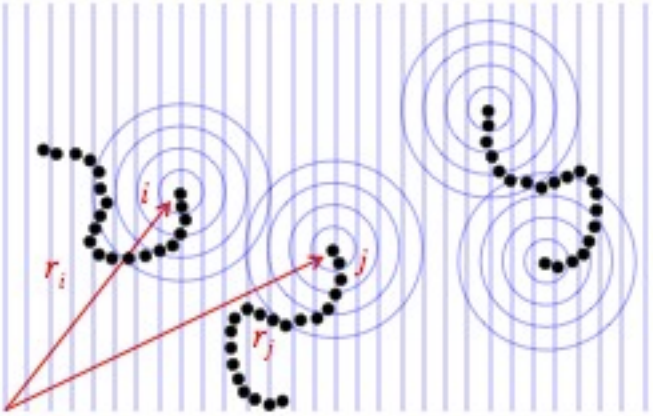


$$I(q)=\sum_{i,j}^{N_p} b_i\, b_j e^{iq(\mathbf{r}_i-\mathbf{r}_j)}$$

i and j are scattering centers

Incident neutrons

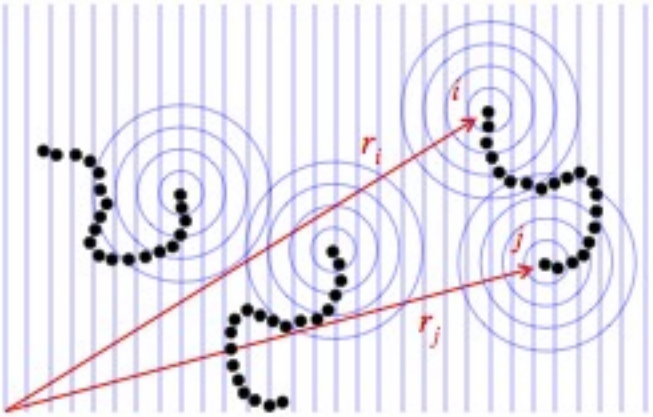
The scattering function



$$I(q)=\sum_{i,j}^{N_p} b_i\, b_j e^{iq(\mathbf{r}_i-\mathbf{r}_j)}$$

i and j are scattering centers
that can belong to different objects

The scattering function



$$I(q)=\sum_{i,j}^{N_p} b_i\, b_j e^{iq(\mathbf{r}_i-\mathbf{r}_j)}$$

i and *j* are scattering centers
that can belong to same object

$$I(q)=\sum_{i,j}^{N_p} b_i\, b_j e^{iq(\mathbf{r}_i-\mathbf{r}_j)}$$

rearranging the summation

$$I(q) = N_P(\Delta\rho)^2 P(q)S(q)$$

form factor (intra-object)

structure factor (inter-object)

2. Scattering by Fractals

Example : Sierpinski gasket

Interesting properties :

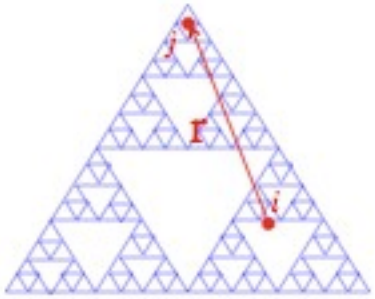
- Self similarity
(object looks the same at different scales)

- "Fractal" mass distribution :

$$M(r) \sim r^D$$

$D \sim 1.584$ For the Sierpinski gasket (not 3 !)

Scattering function : form factor P(q)



$$P(q) = \sum_{i,j same object} b_i b_j e^{i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)}$$

$$P(q) \sim \int g(r) e^{iqr} d^3 r$$

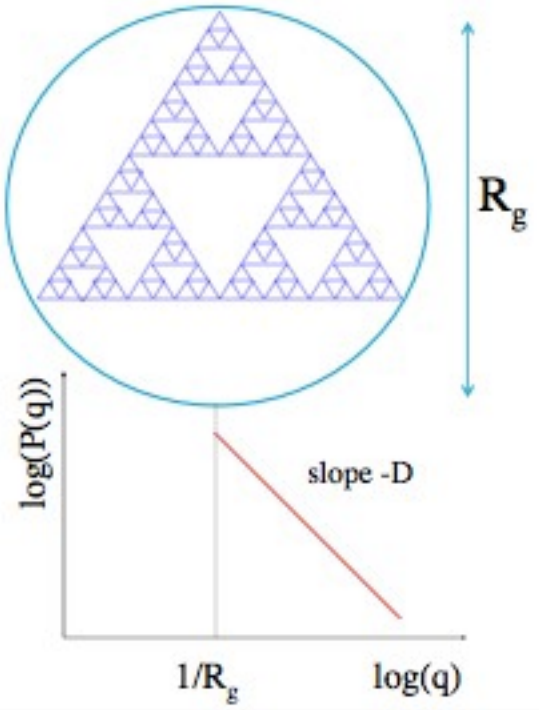
i, j on the object

$$g(r) \sim |r|^{D-d}, D = 1.584, d = 3$$

probability of finding scattering sites at j given i

Scattering function : (wide angles = short distances)

$q > 1/R_g$



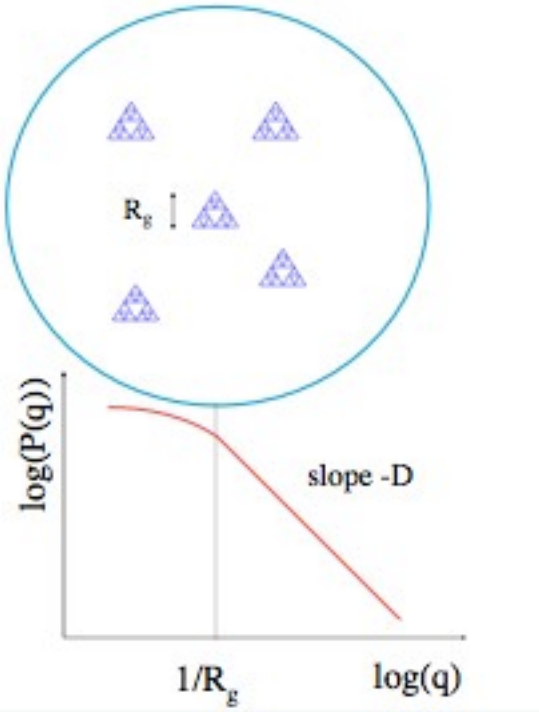
fractal

$$M(r) \sim r^D$$

$$P(q) \sim q^{-D}$$

Scattering function : (small angles = large distances)

$q << 1/R_g$



$$P(q) \sim \sum_{i,j}^{N_p} b_i\, b_j\, e^{iqr}$$ qr<<1

$$P(q) = \frac{1}{1+q^2\xi^2}$$

$$3\xi^2 = R_g = \frac{1}{2N_p^2} \sum_{i,j}^{N_p} r_{ij}^2$$

scattering by uncorrelated objects (blobs) of size ξ << 1/q

Other objects :

rod		$D = 1$	
Sierpinski gasket		$D = 1.584$	
Gaussian chain		$D = 2$	$Rg \sim N^{1/2}$ $M \sim R^2$
excluded volume chain		$D = 5/3$	$Rg \sim N^{3/5}$ $M \sim R^{5/3}$
branched aggregates		$D = ...$	

Polymers in dilute regime : (uncorrelated objects!)

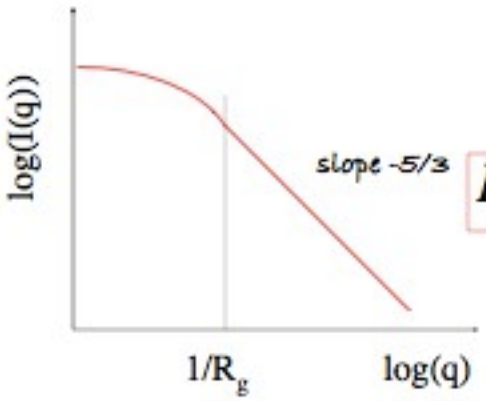
$$I(q) \sim P(q)S(q) \qquad S(q) \sim 1$$

form factor (intra-object)

structure factor (inter-object)

$$I(q) \sim \frac{N_p \phi}{1 + q^2 \xi^2}$$

$\xi = \sqrt{3} R_g$

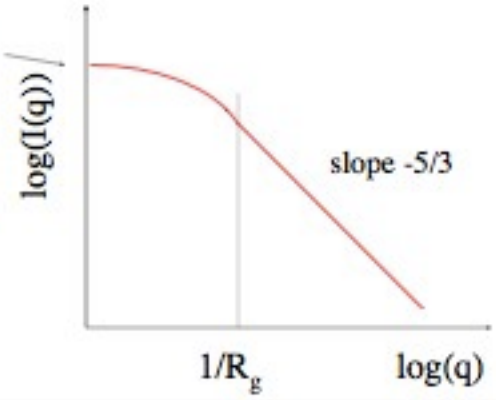


$$I(q) \sim \phi q^{-D}$$

Polymers in dilute regime :

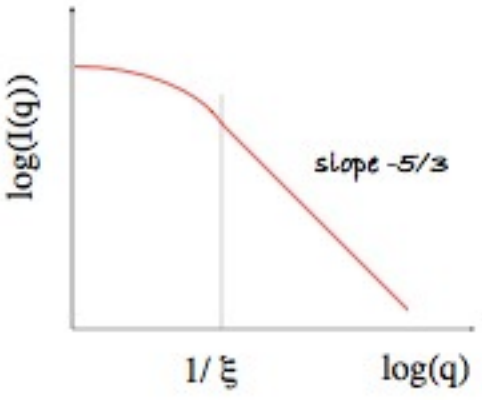
I(0) = $N_p\phi$ = # of scattering centres in one uncorrelated object (N_p)
x
# of scattering objects (ϕ) per unit volume.

$$I(q) \sim \frac{N_p \phi}{1+q^2\xi^2}$$



3. The semi-dilute solution (a reference system)

$$I(q) \sim \frac{\phi^{-0.31}}{1+q^2\xi^2}$$



$$I(q) \sim \phi q^{-5/3}$$

$$I(0) \sim N_p \frac{M_p}{V} = N_p \phi \sim \xi^D \phi$$

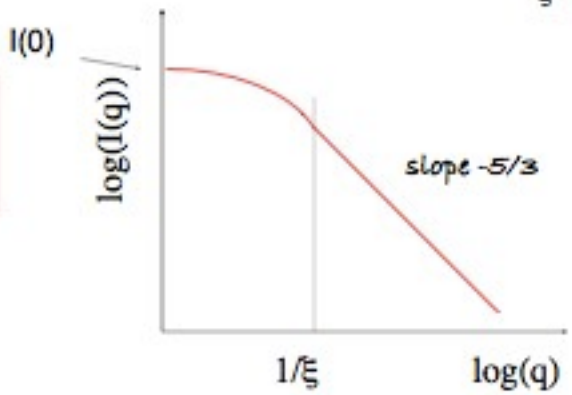
$\phi^{-0.31}$ → number of blobs x number of scatterers per blob

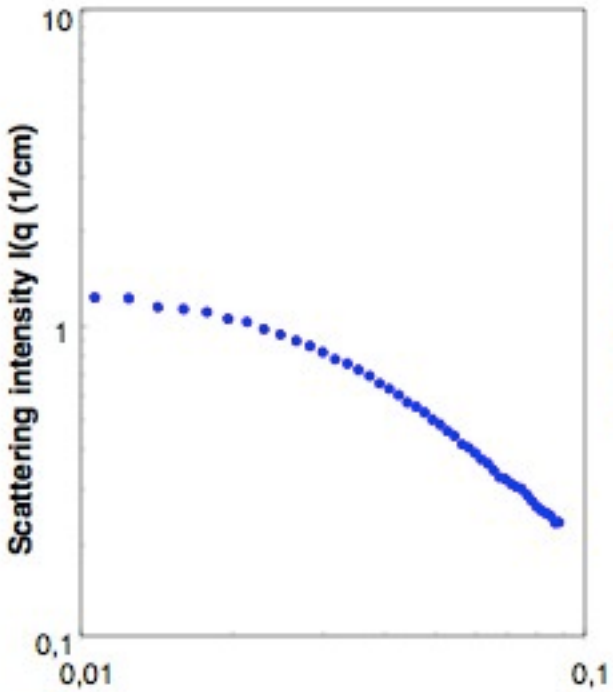
scattering by uncorrelated blobs of size ξ << 1/q

Polymers in semi-dilute regime :

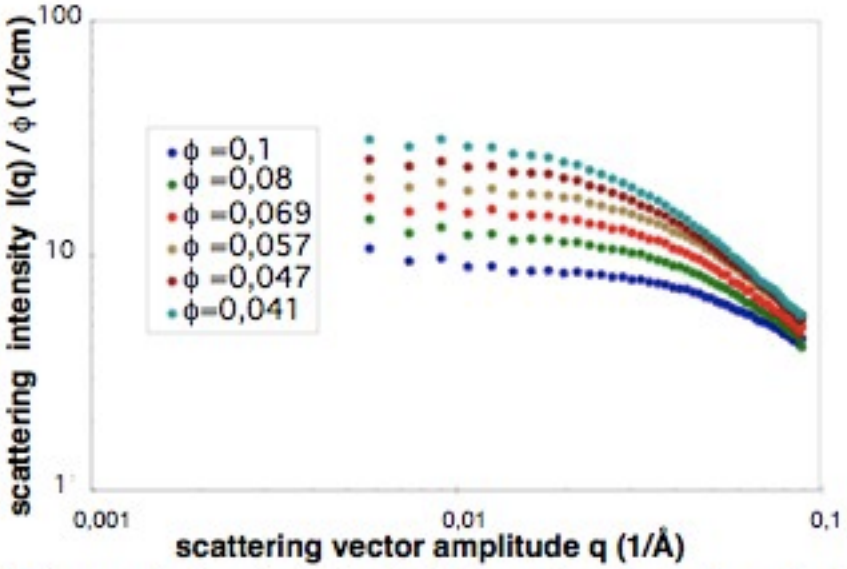
$I(0) = \xi^D \phi =$ # of scattering centres in one uncorrelated object (in one blob) ξ^D
x
# of scattering objects (ϕ) per unit volume.

$$I(q) \sim \frac{\phi^{-0.31}}{1+q^2\xi^2}$$





scattering intensity of a semi-dilute solution of polystyrenene in deuterated toluene at a volume fraction of ϕ=0,041



750K Polystyrene chains in deuterated toluene at various volume fractions

note:

The ***relative*** intensity ***increases*** with the ***dilution*** of the SD solution.
This is a consequence of disentenglement of polymer chains upon dilution due to the dilution of fractal interspersed objects.

4. Swelling of a gel : a 3D deformation

Classical elasticity theories :

swelling is stretching of chains in 3D

-deformation implies loss of fractality (scattering expressed in mass of deformed blob M_ξ = constant)

For q<<1/ξ (Guinier regime) :

$$I(q) \sim \frac{\phi M_\xi}{1+q^2\xi^2} \qquad I(0) \sim \phi$$

-Due to affiness, the correlation length of gel should vary as $\xi \sim \phi^{-1/3}$

-exponent -5/3 should decrease due to stretching of chains for q > 1/ξ

C* network :

swelling is unfolding the network like in a semi-dilute solution

-Scattering for q<<1/ξ (Guinier regime) as in SD solution :

$$I(q) \sim \frac{\phi^{-0.31}}{1+q^2\xi^2} \qquad I(0) \sim \phi^{-0.31}$$

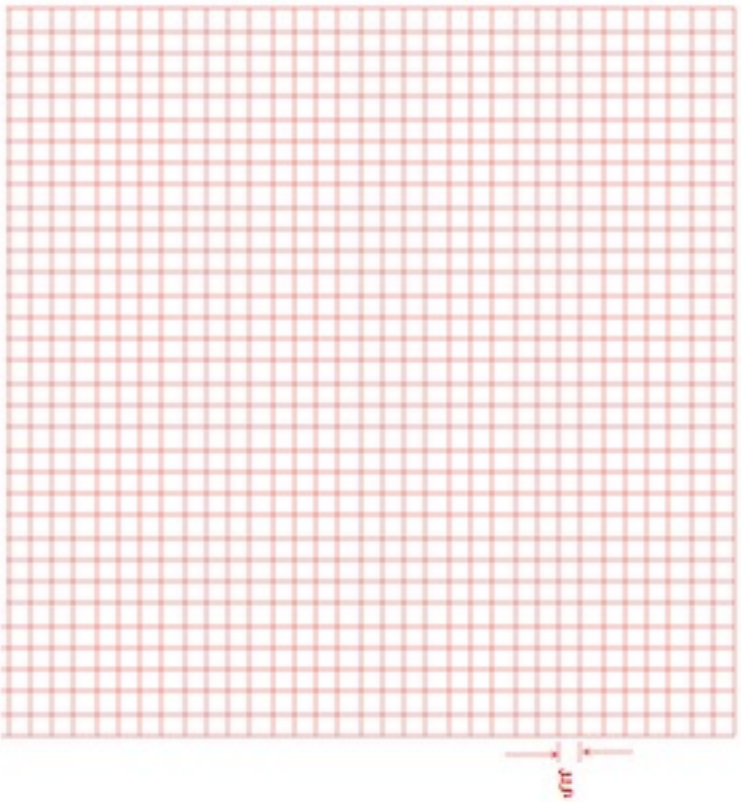
-correlation length is postulated to vary as in a SD solution $\xi \sim \phi^{-0.77}$

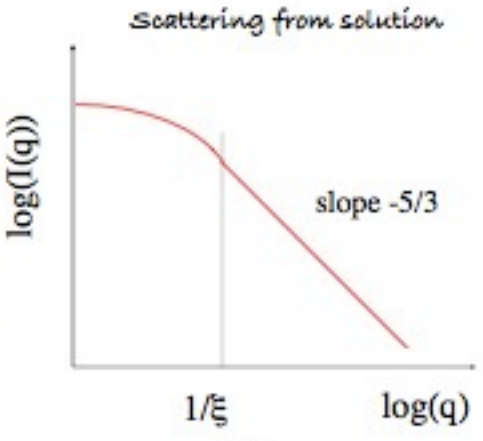
-exponent -5/3 observed for q > 1/ξ.

First, consider the sacattering of a gel at the preparation (reference) state.

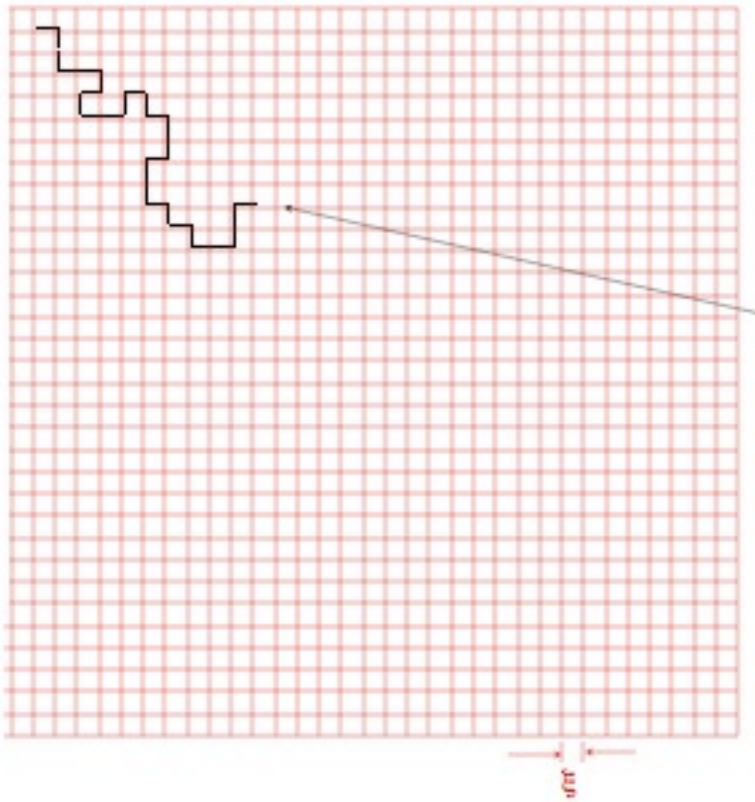
Gel formed from random crsslinking of a semi-dilute solutiuon.

Semi-dilute polymer solution mapped on a lattice

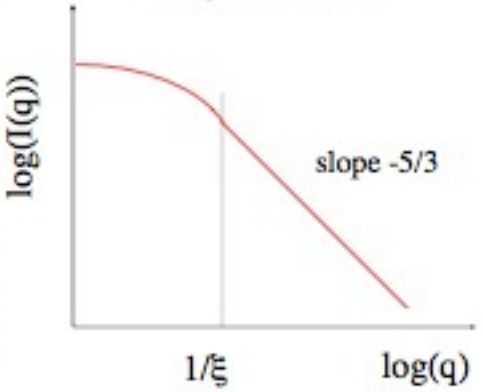




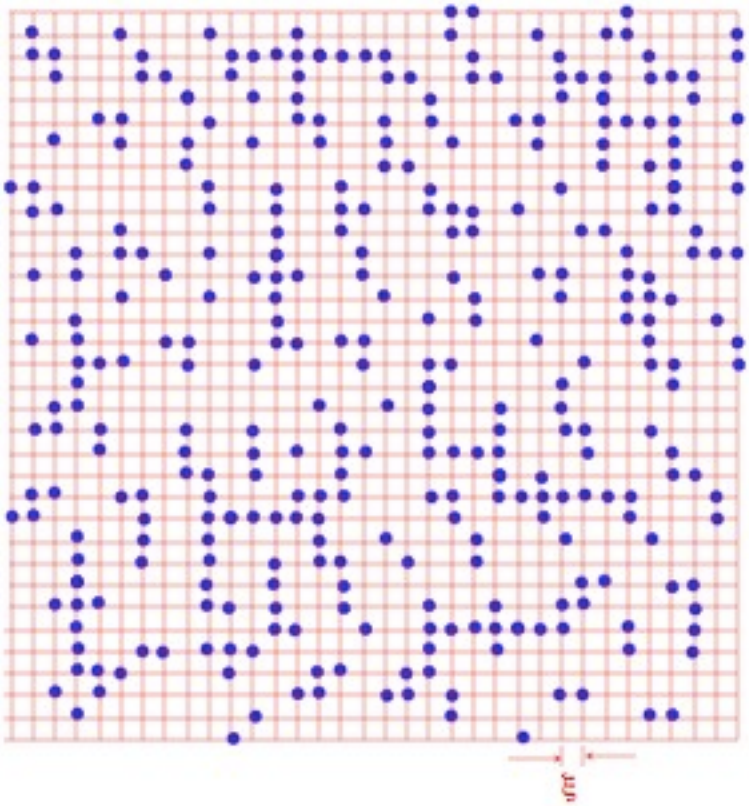
Semi-dilute polymer solution mapped on a lattice



One chain in Semi-dilute polymer solution



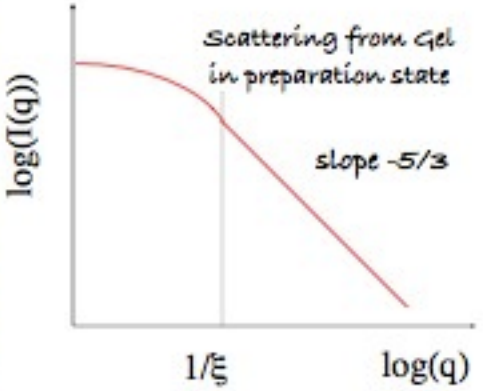
Chemically crosslinked semi-dilute polymer solution = statistical gel

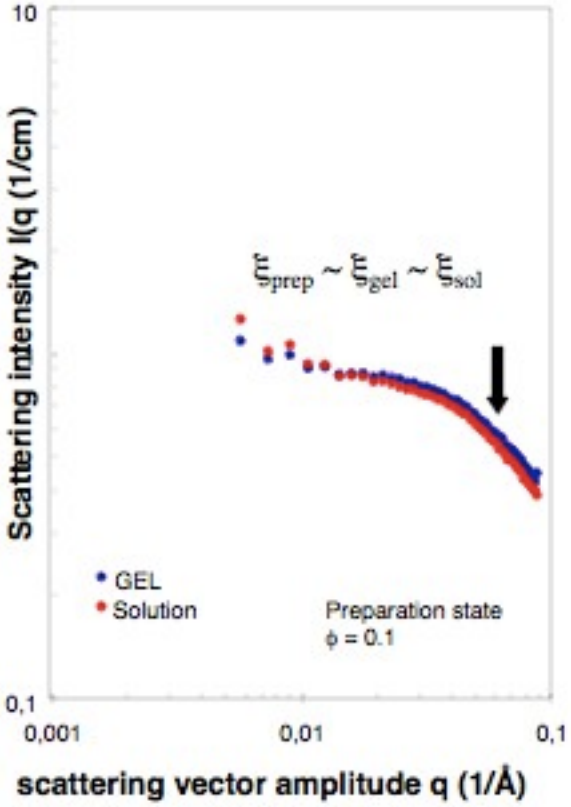


RANDOM
Crosslinking Points
added instantaneously

(Invisible to scattering)

Scattering from Gel in preparation state



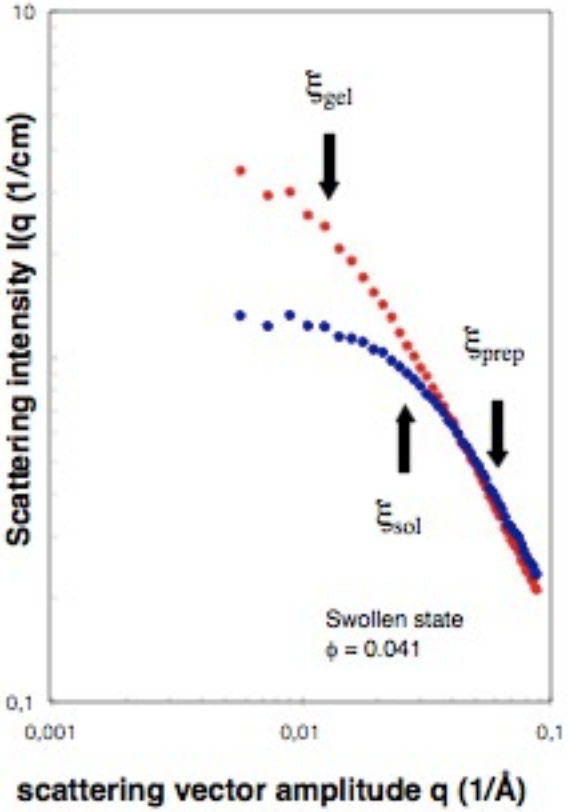


Preparation state :

Spectra of both, gel and solution coincide almost perfectly : no influence of addition of crosslinking points to the solution.

Correlation lengths practically the same at the preparation state, ξ_{prep}

C* theorem verified at the preparation concentration.



Swollen state :

Large excess of scattering of gel with respect to solution of SAME CONCENTRATION.

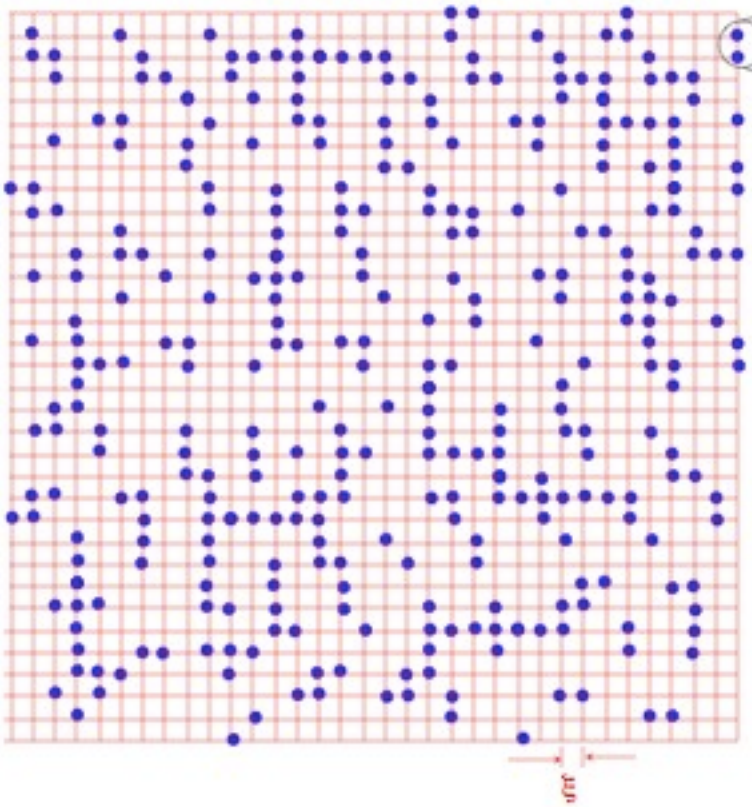
Correlation length larger in Gel
C theorem NOT verified at concentrations smaller than the preparation one.*

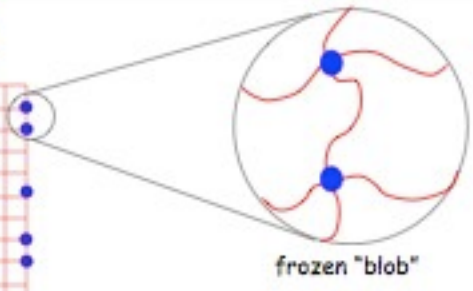
Spectra of both, gel and solution coincide almost perfectly at high q values :

NO APPARENT STRETCHING OF CHAINS !!!
(if present, it is very small)

Classical elasticity, as before, incompatible to data.

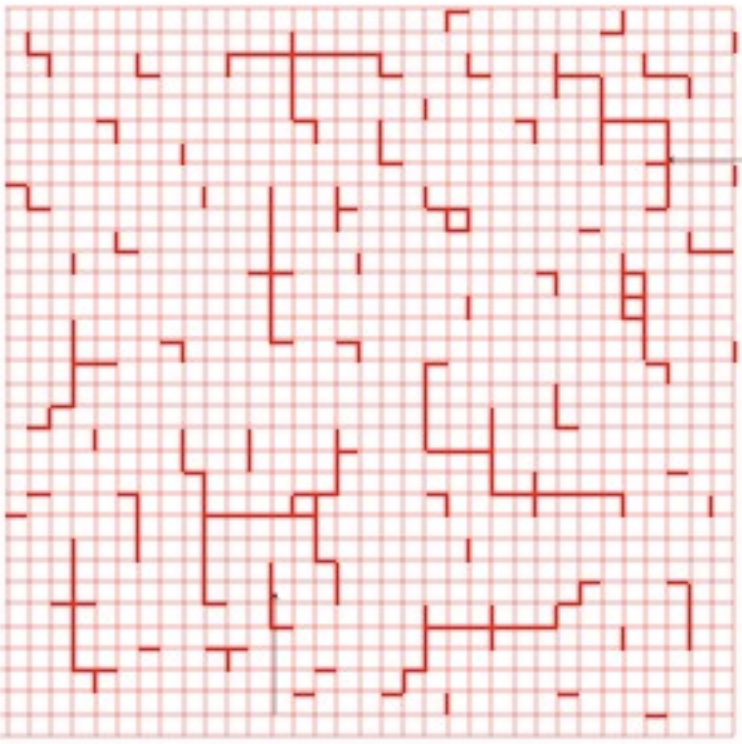
Explanation of large correlation length in gel





Frozen blobs can't slide and desintersperse as in a semi-dilute solution

J. Bastide, F. Boué, E. Mendes, F. Zielinski, M. Buzier, G. Beinert, R. Oeser, C. Lartigue Proceedings of "Networks 91", Moscow 1991. Dusek and Kuchanov Eds., VSP, The Netherlands p.119 -145 (1992).

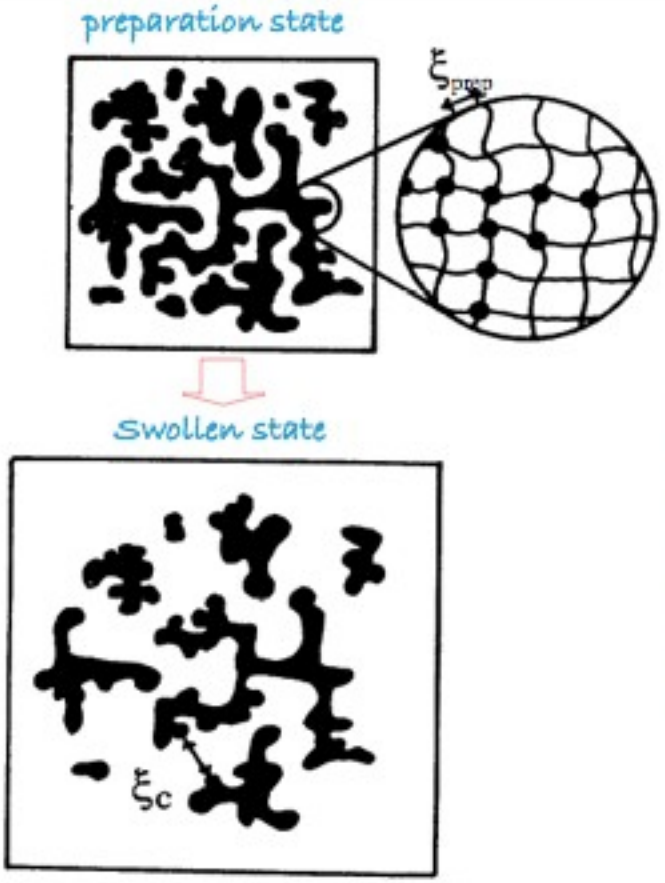


Crosslinking forms "Hard Zones" of frozen blobs (they are difficult to swell or deform)

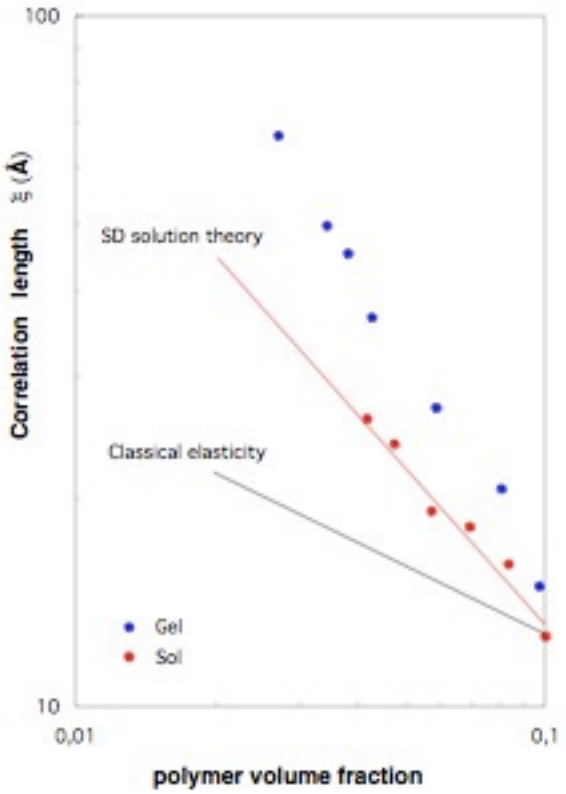
Hard Zones are Branched and interspersed

"FRACTAL HARD ZONES"

Swelling reveals the dilution of hard branched zones and the correlation length measured in scattering is the maximum distance between them.



Swelling reveals the dilution of hard branched "fractal" zones and the correlation length measured in scattering is the maximum distance between them.



The correlation length from swollen gel is far larger than that of the solution of SAME CONCENTRATION, revealing fluctuations of polymer concentration not present in solution :

The gel swells in a HETEROGENEOUS MANNER

not predicted by any classical theory or the c* theorem.

E. Mendes, P. Li ndner, M. Buzier, F. Boue, J. Bastide
Phys. Rev. Lett. 66(12), 1595 (1991).

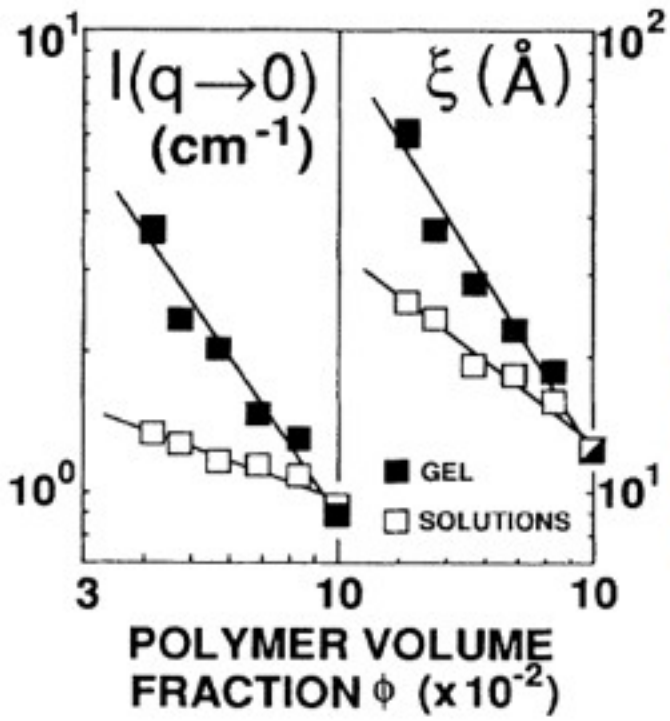


FIG. 4. Correlation lengths ξ and zero-angle extrapolated intensities vs polymer volume fraction for a given gel at different swelling degrees and for a series of semidilute solutions. Apparent exponents: gel, $I(0) \sim \phi^{-1.5}$ and $\xi \sim \phi^{-1.65}$; solutions, $I(0) \sim \phi^{-0.37}$ and $\xi \sim \phi^{-0.78}$.

The same holds for the variation of intensity scattered at q=0 : large excess of scattering from gel with respect to semi-dilute solution ***not*** predicted by any classical theory or the c* theorem.

For this particular gel it is observed :

$I(0) \sim \phi^{-1.5}$
$\xi \sim \phi^{-1.65}$

For semi-dilute solutions

$I(0) \sim \phi^{-0.37}$
$\xi \sim \phi^{-0.78}$
(very close to predictions)

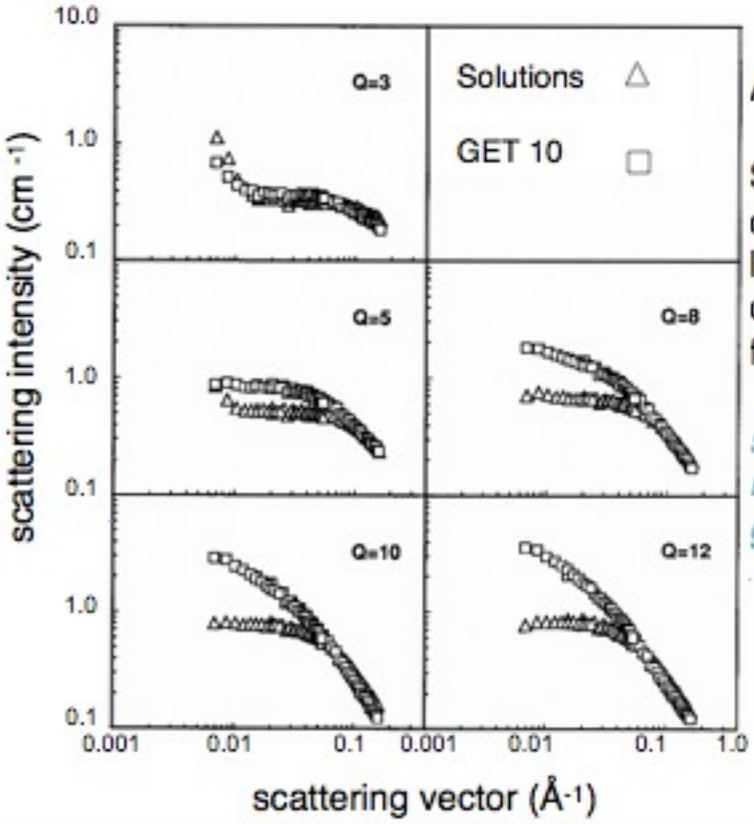
The observed exponents are indeed predicted by a theoretical model of percolation of blobs that describes swelling as the dilution of fractal interspersed hard zones.

Question :

Is this effect only observed networks crosslinked from semi-dilute soltuions ?

Answer :

No, it seems to be a general effect. Polymer networks *always* deform heterogeneously.

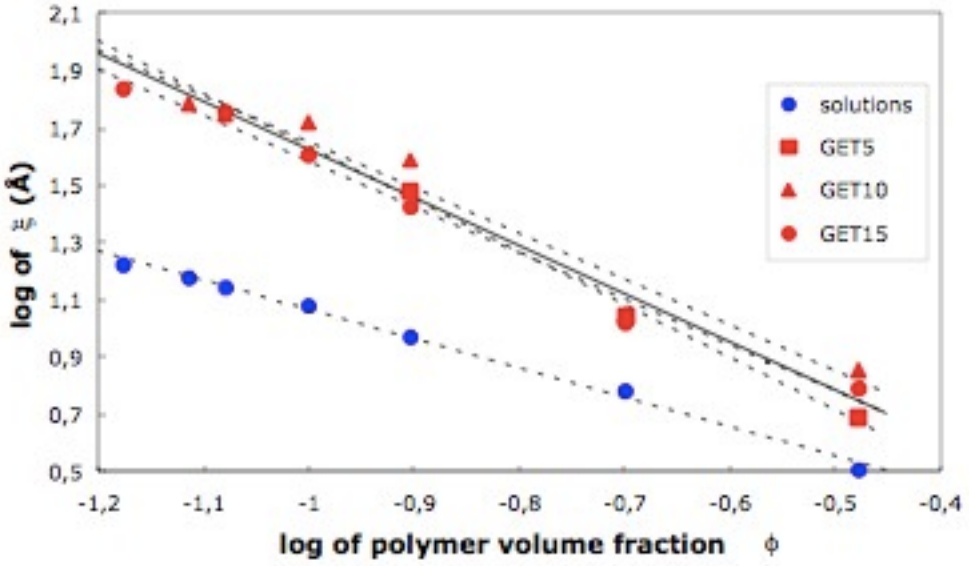


Another example :

Same kind of behaviour observed for swelling of end-linking networks of very well defined chains exhibiting very few defects

spectroscopy on crosslinking reveals up to 98% of the end-link groups reaction took place !

Structure of Trifunctional End-link Gels Studied by SANS
E. Mendes, A. Hakiki, J. Herz, F. Boue, J. Bastide
Macromolecules, 37 (7), 2643-2649 (2004)



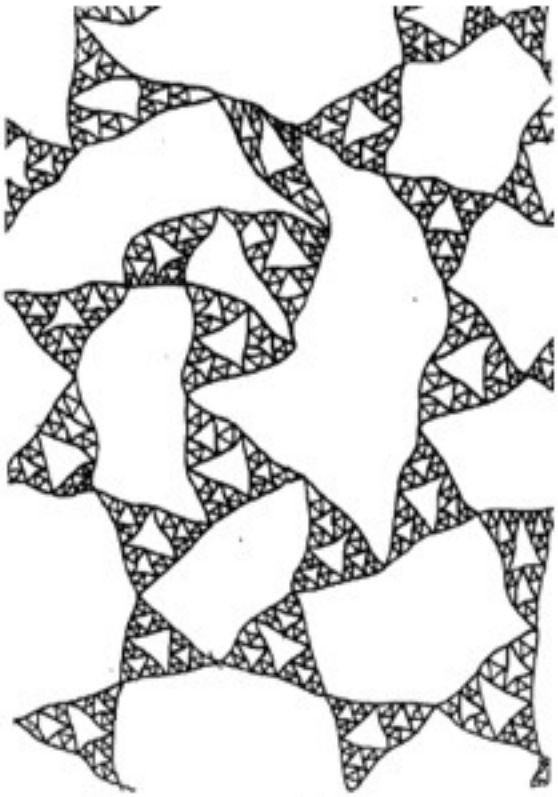
Same variation of the correlation length in with concentration for end-linking gel as that for the gel crosslinked from semi-dilute solution !!

Precursor chain weight
GET5 ~ 5K
GET10 ~10K
GET 15 ~15K

How is it possible that a « chemically perfect » polymer network swells in a heterogeneous manner ?

A mathematical example : the Sierpinski end-linking gel.

Each strand is a real chain and the fractal network could fold to shrink and swell.



Conclusions on gel swelling :

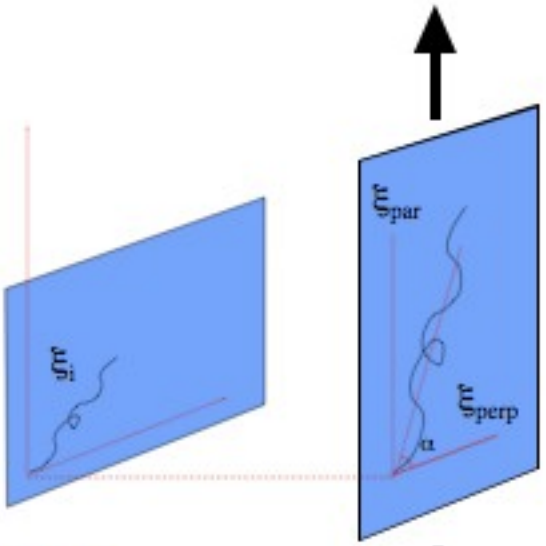
- **no apparent stretching of chains** (swelling is non-affine)

- classical theories or c* theorem can't describe scattering data

- polymer conc. fluctuations at scales larger than the mesh size (heterogeneities) revealed by swelling

DEFORMATION AT MICROSCOPIC SCALES IS HETEROGENEOUS

5. Gel uniaxial deformation



chain in a polymer network

affinely deformed chain

Affine deformation :

correlation lengths vary as :

$\xi_{par} = \lambda\, \xi_i$ and $\xi_{per} = \lambda^{-1/2}\, \xi_i$

with
ξ_i any initial isotropic length

and
ξ_{par} and ξ_{per} correlation lengths in parallel and perpendicular direction to the deformation.

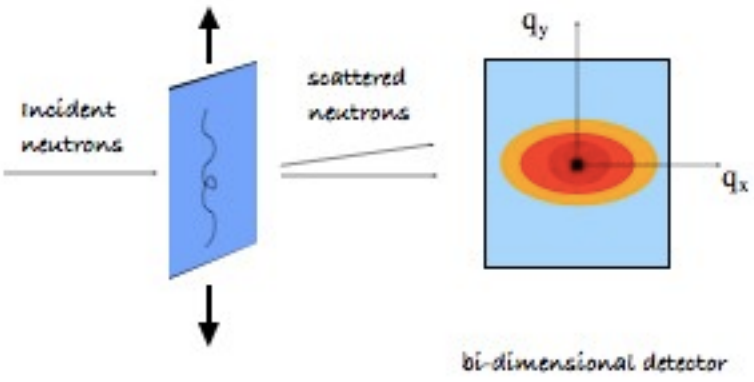
At any angle α :

$\xi(\alpha)^2 = \lambda \cos^2\alpha + \lambda^{-1} \sin^2\alpha$

Affine deformation :

$$I(q) \sim \frac{\phi M_{\Xi}}{1 + q^2 \xi(\alpha)^2}$$

$$\xi(\alpha)^2 = \lambda^2 \cos^2 \alpha + \lambda^{-1} \sin^2 \alpha$$



Intensity in parallel direction ***decreases*** with elongation ratio λ.

Intensity in perpendicular direction ***increases*** with elongation ratio λ.

Isointensity curves on a bi-dimensional detector have the form of ***ellipses*** *with long axis perpendicular to elongation.*

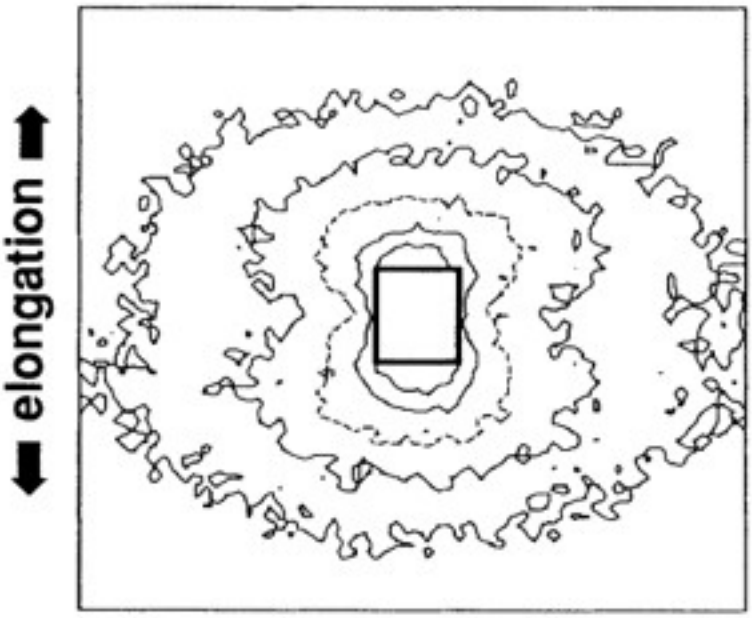
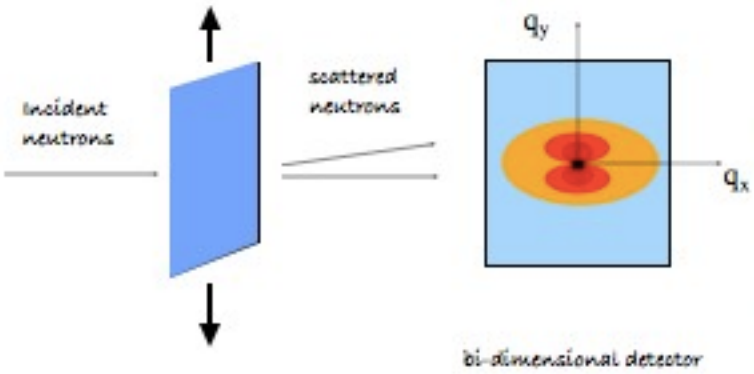


FIG. 5. Experimental isointensity curves for a gel submitted to a uniaxial elongation by a factor $\lambda = 1.5$. The rectangle in the center indicates the limits of the beamstop. Range of scattering-vector amplitude: $0.006\ \text{Å}^{-1} < q < 0.044\ \text{Å}^{-1}$.



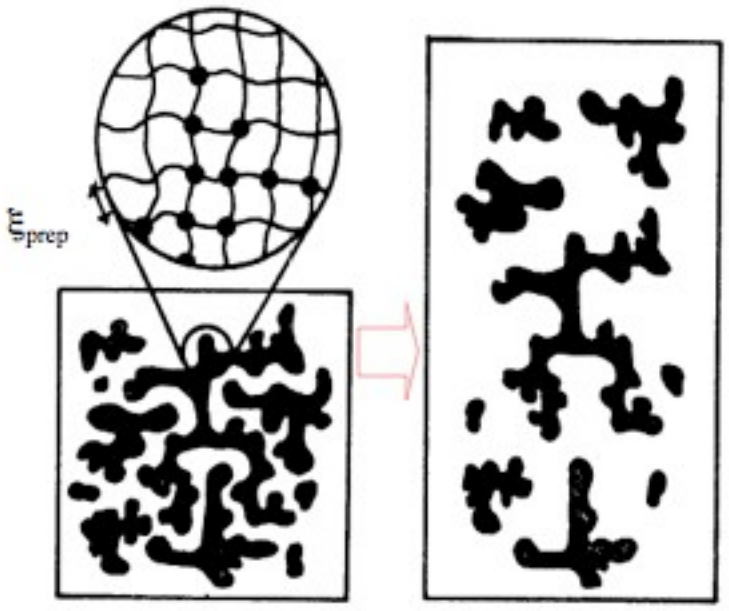
Real experiment on elongated swollen gel

Intensity in parallel direction ***increases*** with elongation ratio λ.

Intensity in perpendicular direction ***decreases*** with elongation ratio λ.

Isointensity curves on a bi-dimensional detector have the form of ***butterflies*** *with long axis parallel to elongation.*

They are inscribed into ellipses at higher q's.



Uniaxially elongated network

Explanation of butterfly patterns :

Stretching desintersperse hard branched "fractal" zones in the direction parallel to elongation leading, in that direction, to an increase of scattering correlation length.

The inverse is observed in the perpendicular direction.

Conclusions on gel stretching :

- **chains are stretched to some extent** (observation of ellipses)

- deformation is non-affine

- classical theories can't describe scattering at very small angles **(butterflies)**

- polymer conc. fluctuations at scales larger than the mesh size (heterogeneities) revealed along the stretching direction

- Butterflies interpreted as « **dilution of hard zones** » in the elongation direction and concentration of hard zones in the perpendicular direction.

DEFORMATION AT MICROSCOPIC SCALES IS HETEROGENEOUS

Remarks on butterfly patterns :

- butterfly patterns are also observed in the scattering of deformed rubbers.

- bimodal polymer melt containing free deuterated chains also exhibit butterfly patterns. (a transient polymer network !!!)

- semi-dilute solutions of very long chains also exhibit butterfly scattering patterns under shear.

- in a polyelectrolyte gel, the presence of electric charges seems to homogenize the network : electrostatics wins over mesoscopic heterogeneities

Message :

As long as there is ***randomness*** on the crosslinking process, deformation will be highly ***heterogeneous*** in polymer networks.

Heterogeneities seem to be the "***dominant defect***". At mesoscopic scales, heterogeneities play a major role on the deformation/swelling of the network.

In swelling, classical elasticity theories can't describe data since no stretching of chains is observed. C* theorem also fails, since a larger correlation length than that of a semi-dilute solution of same concentration is observed in the gel.

In stretching, chains are stretched to some extent (ellipses at high q's) but the deformation is heterogeneous (butterflies at small q's).

The relation between the observed correlation length, chain stretching and the elastic modulus is still to be written.

7. Actual Research Trends

Classic : ***football, tires, shoes, adhesives, composites, membranes, coatings, paintings…***

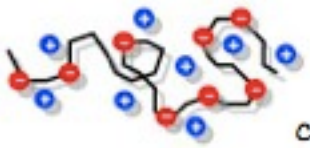
commodity

Contemporary : ***electronics, optics, contact lenses, biomaterials, tissue engineering, drug delivery, artificial muscles, smart systems, sensing, actuators…***

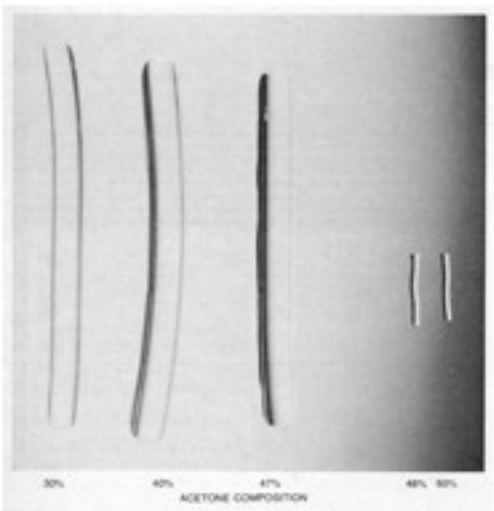
functional (passive and active)

Example :

Polyelectrolyte gel.



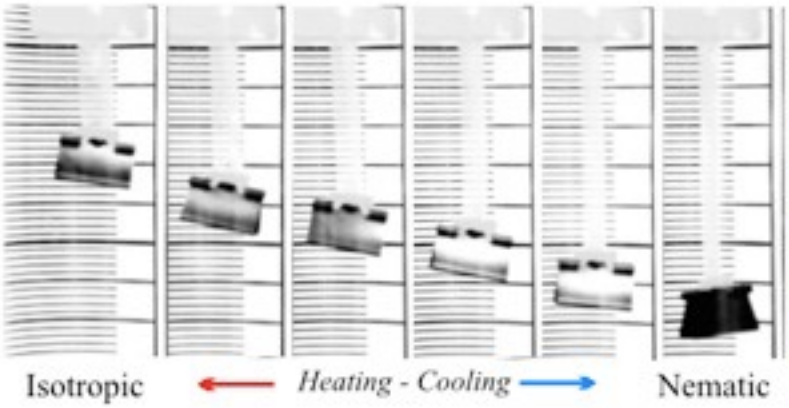
Covalent crosslinks



Function: exhibits volume phase transition with different external parameters such as temperature change, solvent quality change, Ph change, etc

Applications:
Supper-absorbents,
Drug delivery micro gels
Separation membranes
Actuators (muscles)
…

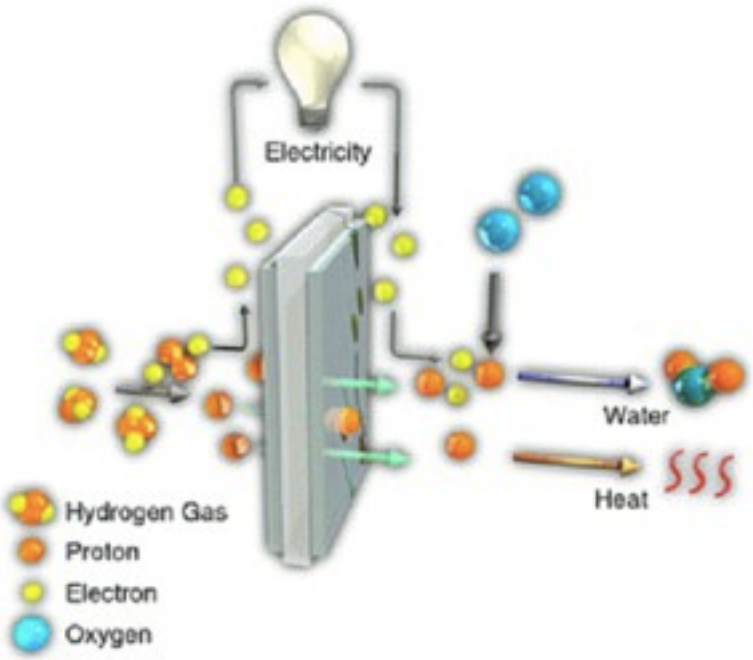
Example : Liquid crystal elastomer



Weight lifting by liquid crystal elastomer

Function:
Mechanical response (shape change) to electric fields, temperature change, light
…
Applications:
Optical devices
Coatings
Actuators
…

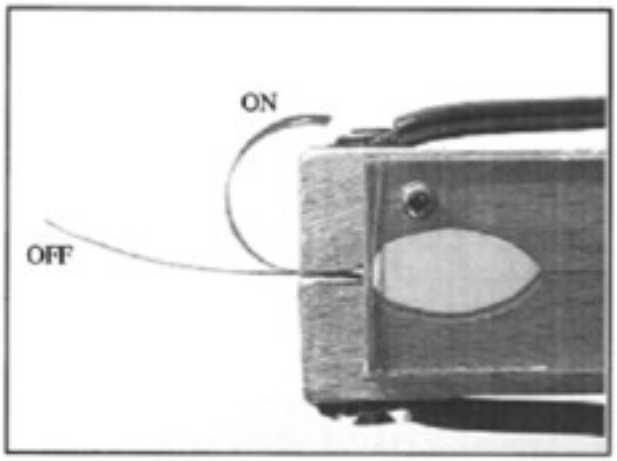
Example : Fluorinated polyelectrolyte networks



Function:
Proton(H^+) conduction
And Wetability
(while heat resistance)

Applications:
Fuel cell membranes
Separation membranes
…

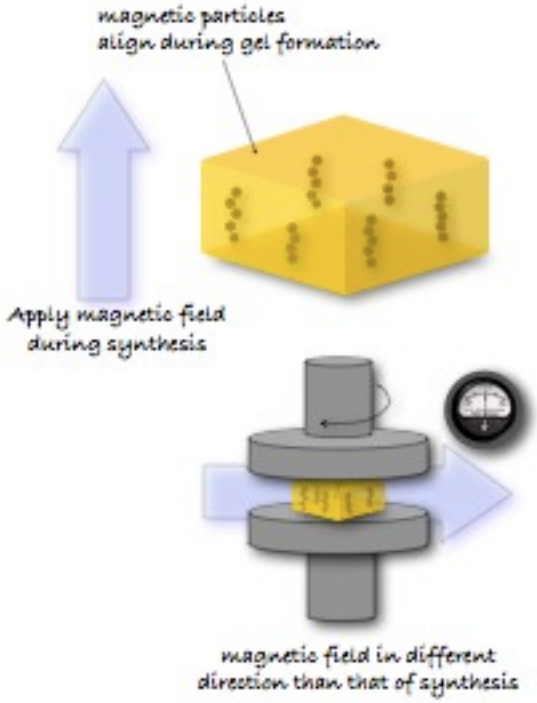
Example : Electroactive Elastomer

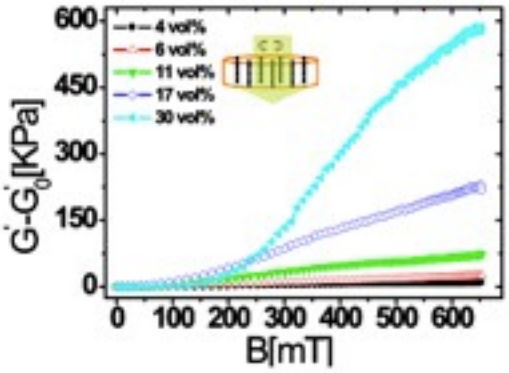


Function:
Shape change under electric field (bending, AND stretching)

Applications:
Artificial muscle
Actuators
Micropumps
…

Example : Magnetic Gels





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