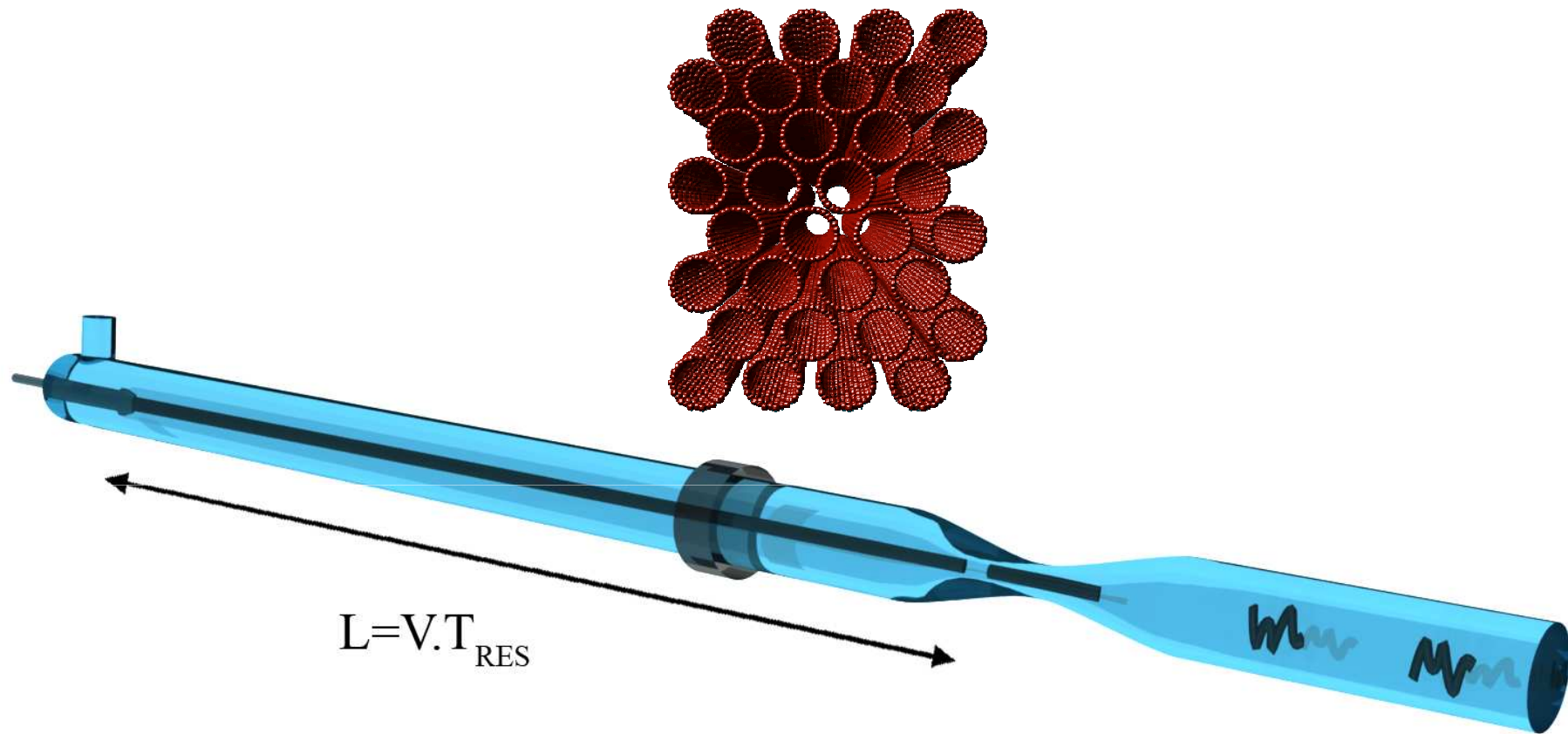


Liquid processing of carbon nanotubes



P. Poulin
Centre de Recherche Paul Pascal – CNRS Bordeaux, France

Mass production in progress : several tons/y, continuous production



Several producers around the world

Example :
Arkema Group
Pilot plant in Lacq



**BUT RESEARCH CHALLENGES ARE STILL FACED
IN PARTICULAR FOR THEIR PROCESSING**

POWDER: difficult use

Disordered

Grand. = 10.00 K X

1 μ m



EHT = 10.00 kV
WD = 7 mm

Signal A = MPSE

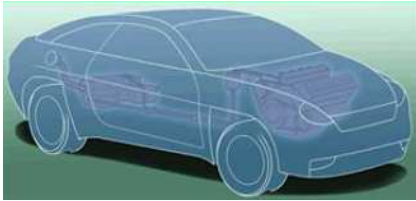
Date :13 Déc
Heure :11:24



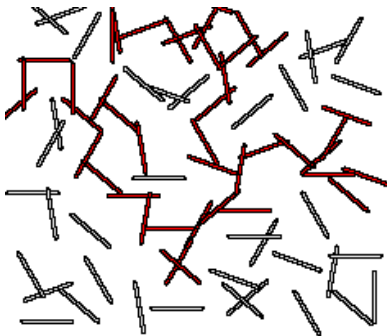
Control of spatial organization is critical to manifest CNT properties

Two opposite examples

Antistatic materials, conductive coatings, etc



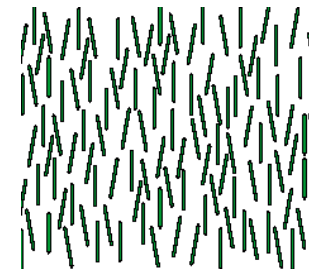
Percolation threshold at **low** concentration
Rod-like and « **unaligned** » particles to maximize the contact probability



Mechanical properties



Alignment and high concentration



Liquid crystals, Fibers

A lot of research in the field

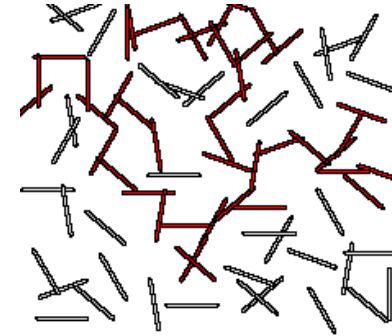
Often : Liquid Processing => Composites, Films, Fibers, etc
CNT dispersions : stability, structure



Stabilization: Functionalization, surfactants, polymers, etc
Control of interactions and chemistry are important

I - Influence of interactions on the percolation of CNT dispersions

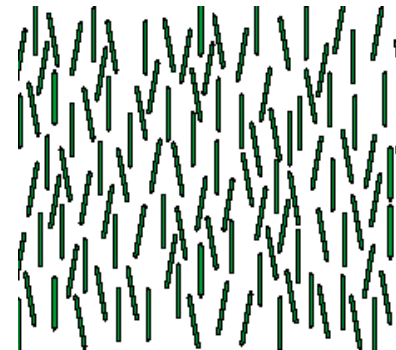
B. Vigolo, C. Coulon, M. Maugey, C. Zakri



II – Coagulation of CNT composite fibers

A route towards aligned composites

C. Mercader, A. Lucas, A. Derré, M. Maugey, C. Zakri

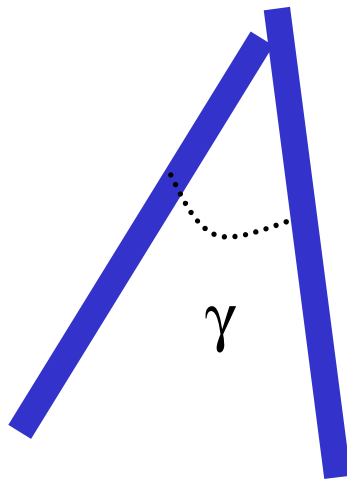


Results which hopefully can be relevant for other materials
(nanorods, whiskers, synthetic polymer fibers, natural fibers such as silk, etc)

I - Interactions and percolation of rods

No interactions : just geometrical effects
(excluded volume) to be considered

$\phi_p \rightarrow \phi_0 = d/L$, $u \rightarrow 0$ (Balberg et al. 1984, Onsager)



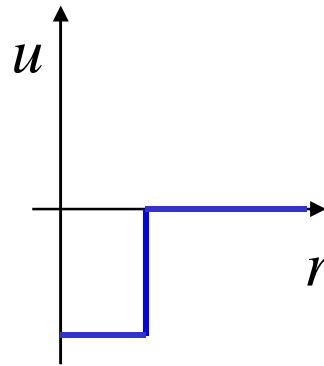
$$V_{ex} = \frac{4\pi}{3} d^3 + 2\pi L d^2 + \underline{2L^2 d \langle \sin(\gamma) \rangle}$$

High aspect ratio (nanotubes)

$$\phi_p \approx \frac{Ld^2}{V_{ex}} \approx \frac{Ld^2}{L^2 d \langle \sin(\gamma) \rangle} \approx \frac{d}{L}$$

Low percolation threshold makes nanotubes interesting
for antistatic materials, transparent conductive films, paints, EM shielding
CNTs 1% or less vs 10% or more for carbon blacks

Effect of attractive interactions ?



Answer not so obvious

Intuitive expectations

- Attractive interactions promote aggregation => **lower** the percolation threshold (reported for spheres)
- Attractive interactions also promote alignment => lower excluded volume => **increase** percolation threshold

INTERACTIONS RAISE THE PERCOLATION THRESHOLD OF RODS

M. Grujicic et al. (2004) Computational analysis

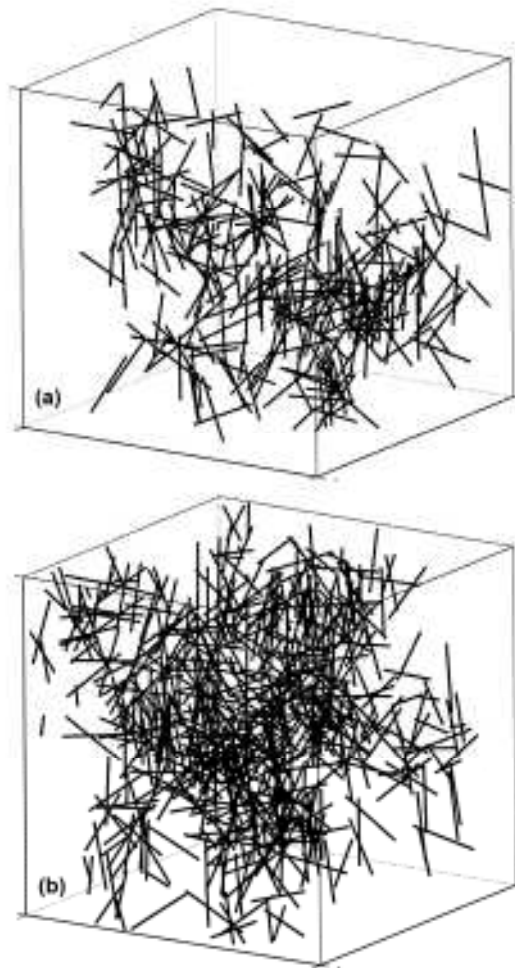


Figure 4 Typical structure of a percolating cluster in the cases of: (a) a random distribution of the SWCNTs and (b) the SWCNTs interacting via the van der Waals forces.

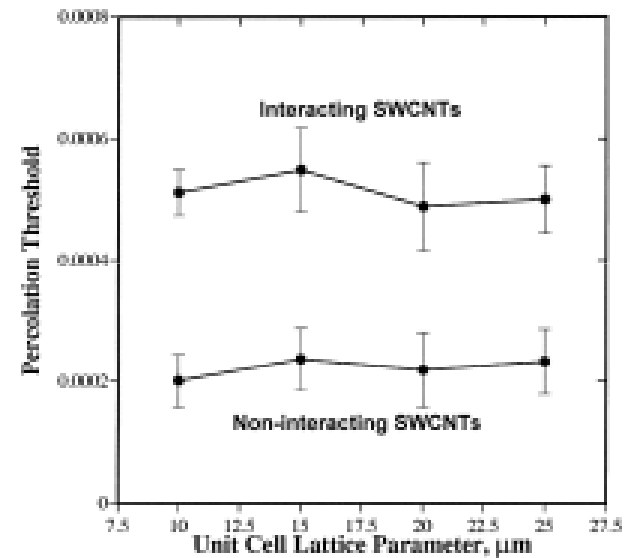


Figure 5 Effect of the unit cell size on the percolating threshold in the cases of a random distribution of the SWCNTs and the SWCNTs interacting via the van der Waals forces.

Other more recent simulations

T. Schilling, S. Jungblut, M. Miller (PRL 2007)

And theory

A. V. Kyrylyuk and P. van der Schoot (PNAS 2008)

**INTERACTIONS LOWER THE PERCOLATION
THRESHOLD OF RODS**

General approach by Coniglio et al.

Clusters formed at equilibrium : theoretically predicted

Physical clusters, Molecular clusters in imperfect Gases, Hill (1955)

Pair connectedness and cluster size, Coniglio et al. (1977)

Continuum percolation of permeable objects, Bug et al. (1986)

Distribution of clusters of interacting particles
(Not a phase separation)

Percolation threshold

Diluted systems:
$$\phi_p \approx \frac{1}{\langle \exp(-\beta u) \rangle}$$

u : potential between sticky particles, $\beta = 1/kT$
($u \neq 0$ at contact)

Lower threshold

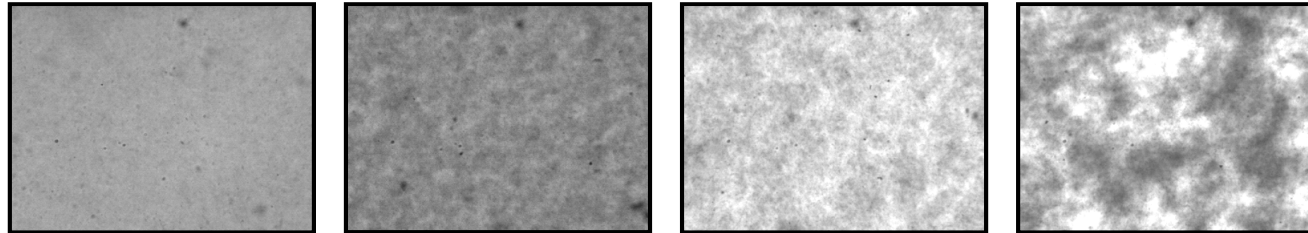
EXPERIMENTAL REPORTS FOR SPHERES (micro-emulsions)

EXPERIMENTS FOR RODS ?

EXPERIMENTAL SYSTEM Water based system where the interactions can be finely tuned (accuracy $10^{-4}kT$)

Depletion interaction – proportional to the concentration of additives

Nanotubes, SDS concentration \uparrow



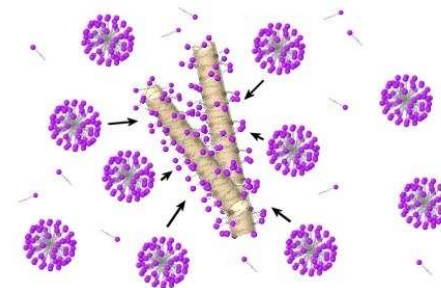
B. Vigolo et al. Science 2005

Optical micrograph 320 μ m

NO COARSENING

No macroscopic phase separation

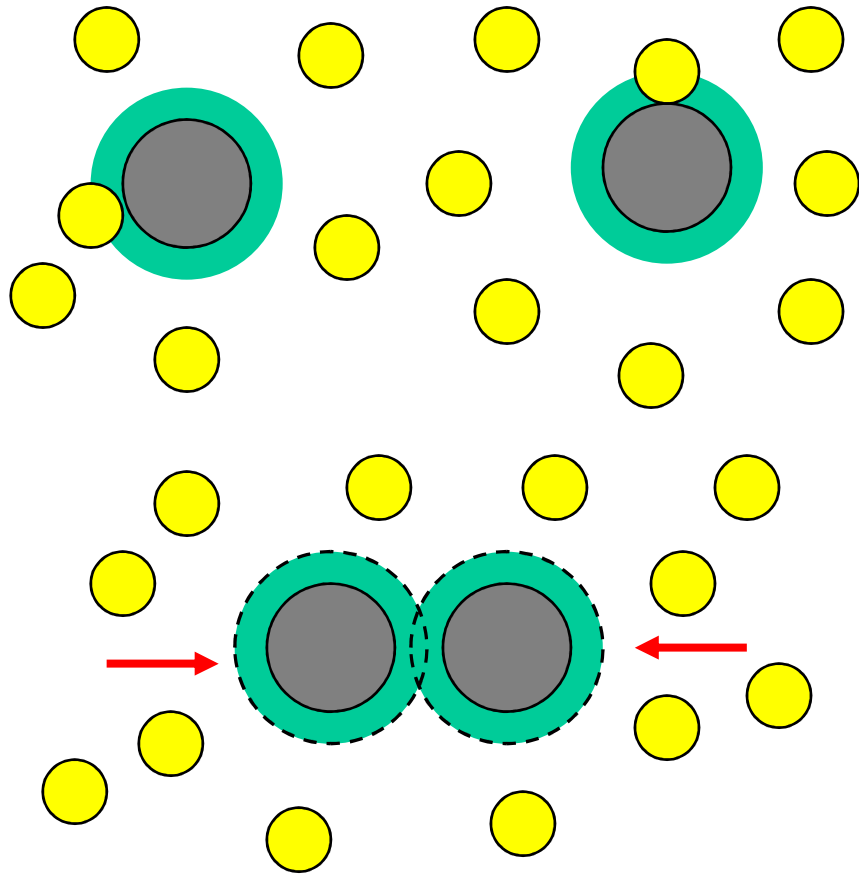
EQUILIBRIUM STATES



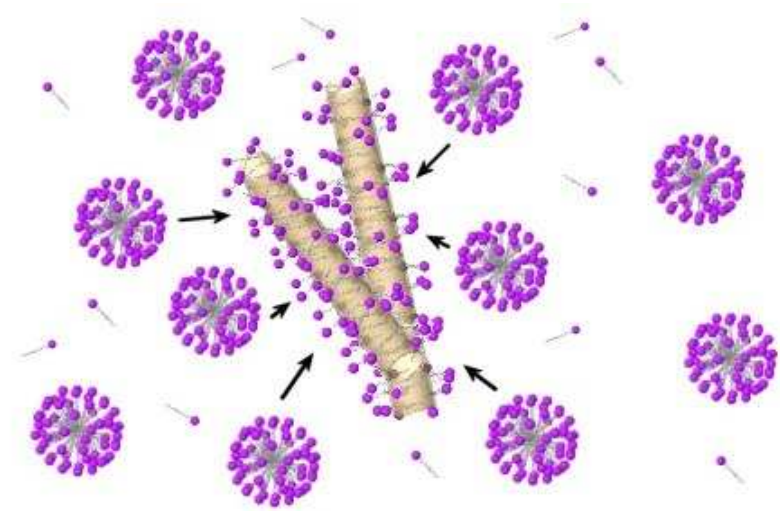
Water, SDS+ Sonication
(cut the nanotubes into smaller and straighter rod-like fragments)

Percolation characterized by dielectric spectroscopy

Depletion attraction



Overlap of excluded volumes



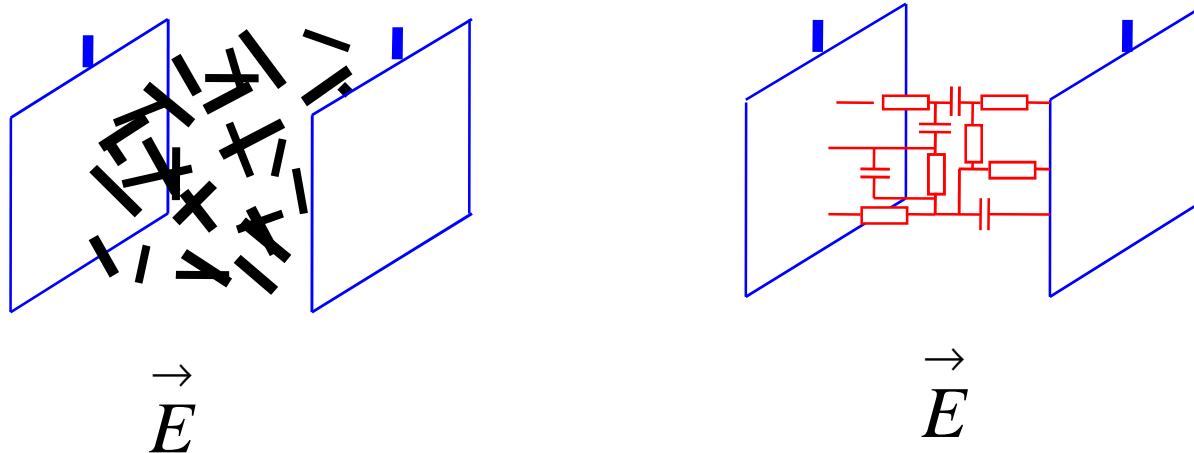
$U_{dep}(r) = -\Pi_{mic.} V_{excl.}$
Spherical particles R
in a solution of micelles of size d

$$U(r) = -\Pi_p \frac{\pi}{4} \left(R \lambda (r - R \lambda)^2 + \frac{1}{3} (r - R \lambda)^3 \right)$$

$$\lambda = 1 + \frac{2d}{R}$$

Asakura, Oosawa (1958)

Dielectric characterizations of NT suspensions

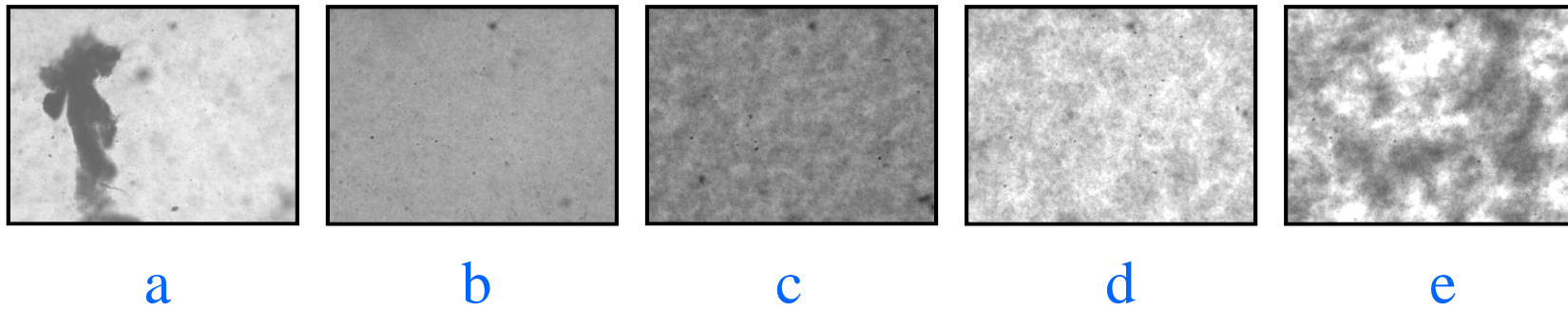
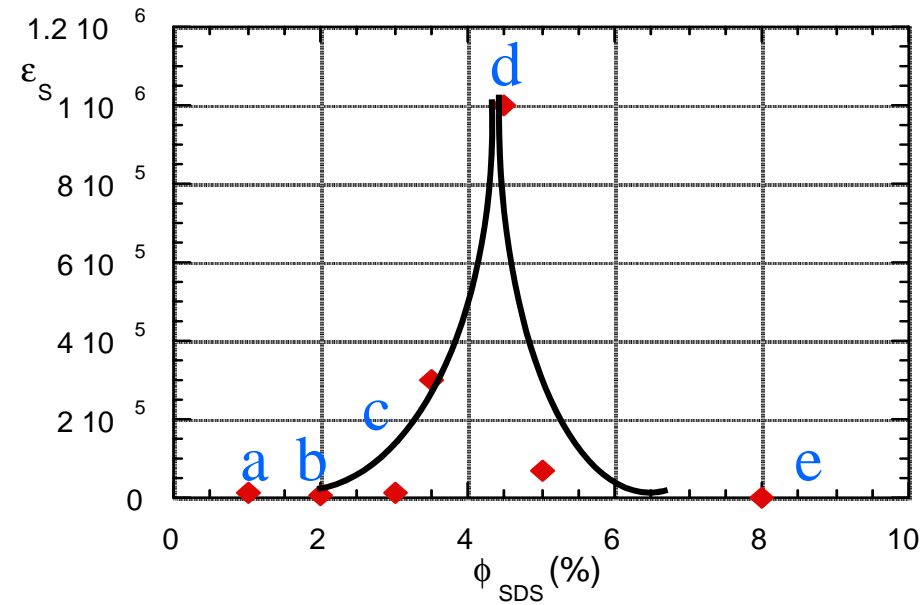


Ohm's law

$$\vec{\Omega} = (\sigma(\nu) + 2\pi j \epsilon_0 \epsilon(\nu)) \vec{E}$$

Percolation should yield a divergence of $\epsilon(0)$ at the percolation threshold

For a given CNT concentration : a corresponding SDS threshold



Low CNT concentration => greater SDS concentration needed to observe the texture and reach the threshold

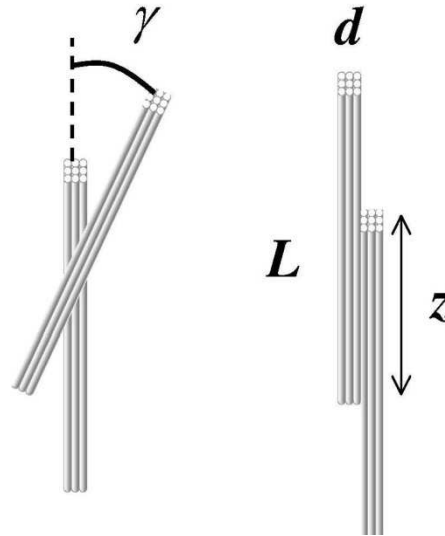
**PERCOLATION THRESHOLD OF NANOTUBES
LOWERED BY ATTRACTIVE INTERACTIONS**

Following Coniglio et al. :
Sticky nanotubes ($u \neq 0$ at contact)

$$\phi_p = \frac{2Ld^2}{\int_V \int_0^\pi \exp(-\beta u) d^3 r \sin(\gamma) d\gamma} \quad \phi_p \rightarrow \phi_0 = d/L, \quad u \rightarrow 0$$

βw_\perp

Adhesion between
two perpendicular **bundles**
in contact



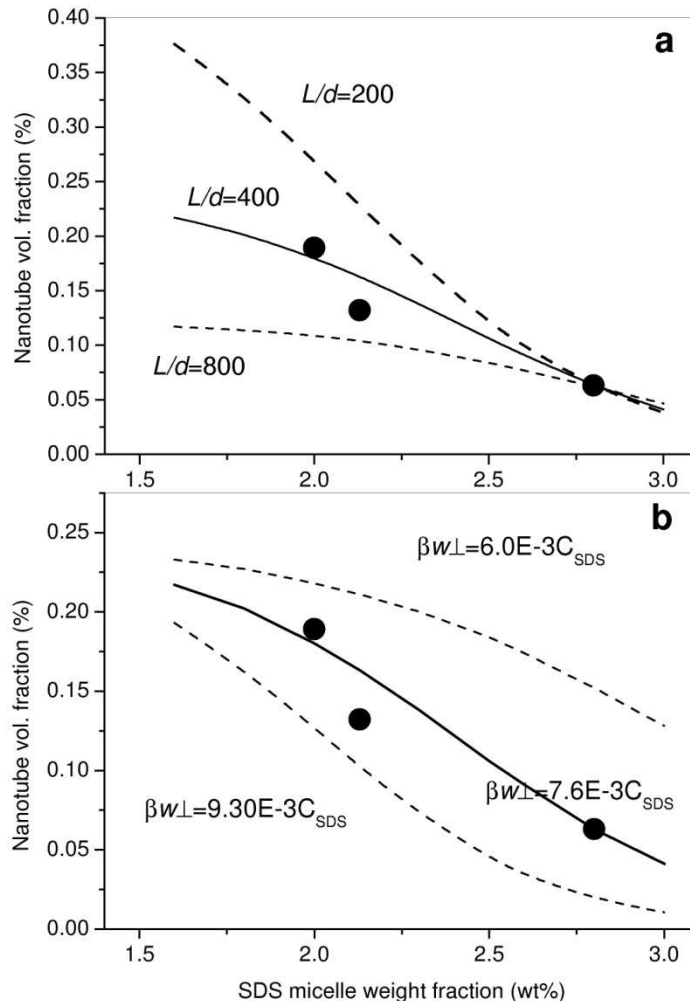
$$\sin(\gamma_c) = \frac{d}{L}$$

Following Grosberg and Khokhlov (1981) and
van der Schoot and Odijk (1992)
Second virial coefficient of rigid polymers

$$I = 2L^2 d \int_{\gamma_c}^{\pi/2} \exp\left(\frac{\beta w_\perp}{\sin(\gamma)}\right) \sin(\gamma) d\gamma + 4d^2 \int_0^L \exp\left(\frac{\beta w_\perp}{d} z\right) dz$$

→ 2 parameters L/d and βw_\perp

**We can not choose any numbers to fit
the values of the percolation threshold
(SW HiPco bundles in SDS solution)**



$L/d \sim 400$

$$\beta w_{\perp} = 7.6 \cdot 10^{-3} C_{SDS}$$

*We deduce the contact area and
thereby the diameter of the
bundles*

$\Rightarrow d \sim 3 \text{ nm}$

w_{\perp} varies by $0.006kT$
Percolation threshold
decreased by a factor 3
(6000 kT with micro rods)

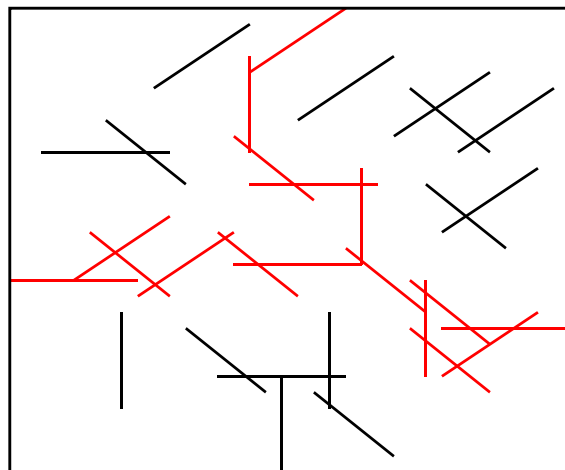
REASONABLE FACTORS

B. Vigolo *et al.* Science 2005

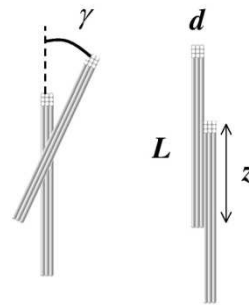
Different expected structures as a function of the interaction strength

$$I = 2L^2 d \int_{\gamma_c}^{\pi/2} \exp\left(\frac{\beta w_{\perp}}{\sin(\gamma)}\right) \sin(\gamma) d\gamma + 4d^2 \int_0^L \exp\left(\frac{\beta w_{\perp}}{d} z\right) dz$$

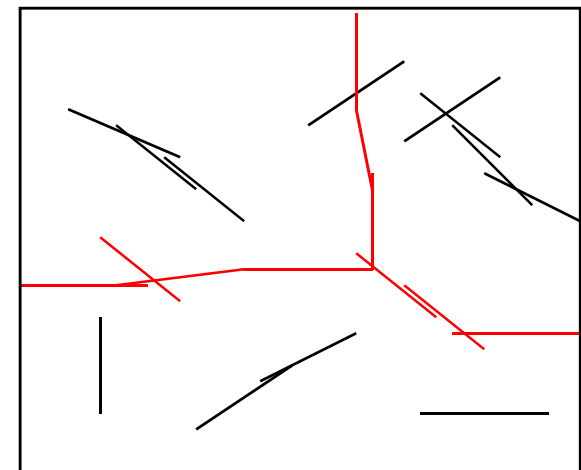
Weak interactions ↙



Completely random structure



↘ Strong interactions



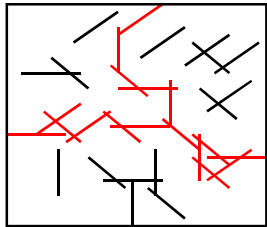
Lower threshold and more rods parallel

Interaction and percolation of rods

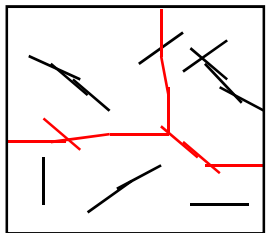
Opportunity to **lower** the percolation threshold: important for applications.

But this is not the end of the story :

CONSEQUENCES ON PHYSICAL PROPERTIES ?



Conductivity in composites is dominated by the density and nature of the contacts between the conducting inclusions.



Less, but more effective, electrical contacts
⇒ **Better conductivity and less material ?**

A positive answer would good news for applications

II- NANOTUBE FIBERS

More concentrated and aligned CNTs

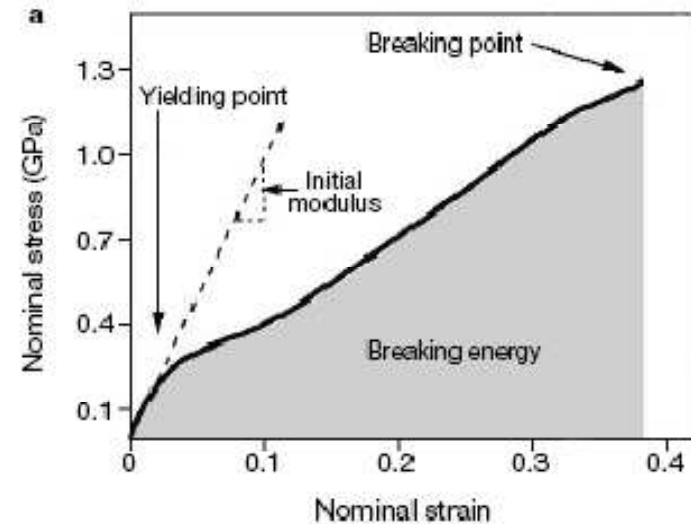
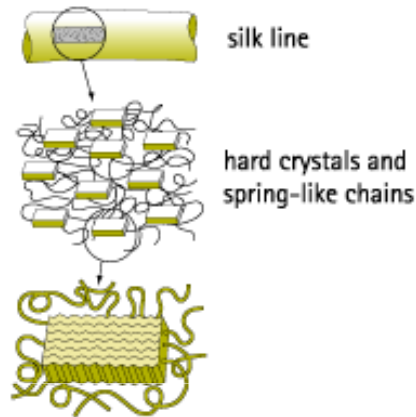
Properties of polymers are enhanced when they are processed into fibers
Fibers easy to process : textiles, cables, electrodes, composites, etc

**VARIOUS APPROACHES AND
VARIOUS NANOTUBE FIBERS REPORTED IN THE LITTÉRATURE**

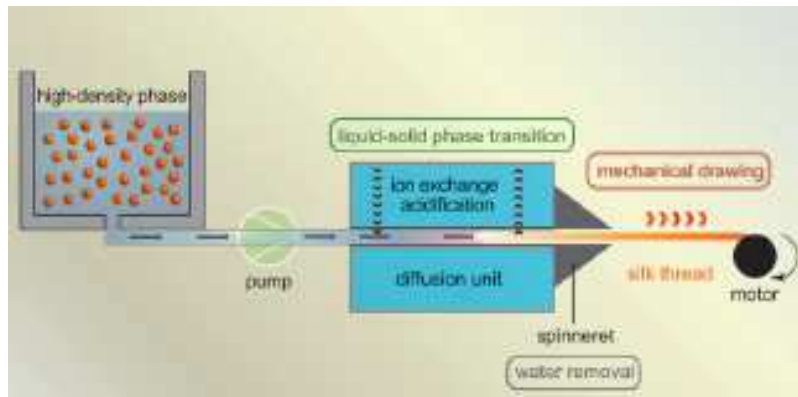
INCLUDING LIQUID PROCESSING

Several strong natural and synthetic fibers are spun via liquid processing

Silk : coagulation of proteins (mechanisms are still debated)
 « nanocomposite » structure with giant toughness



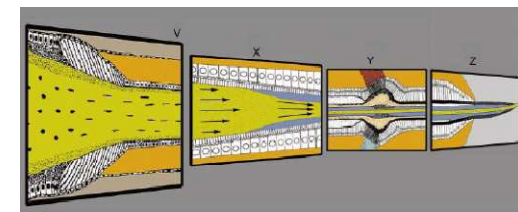
Very high toughness



Biomimetic spinning

Spider Silk: From Soluble Protein to Extraordinary Fiber

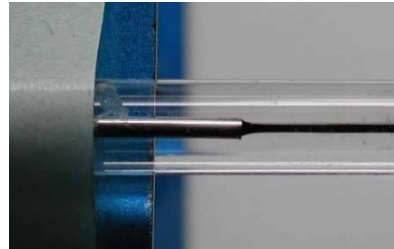
M. Heim, D. Keerl, T. Scheibel, *Angw. Chem.* 2009



Liquid crystalline spinning of spider silk

Vollrath and Knight *Nature* 2001

CONTINUOUS WATER BASED COAGULATION SPINNING IN CO-FLOWING STREAMS

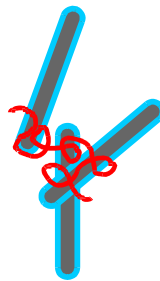
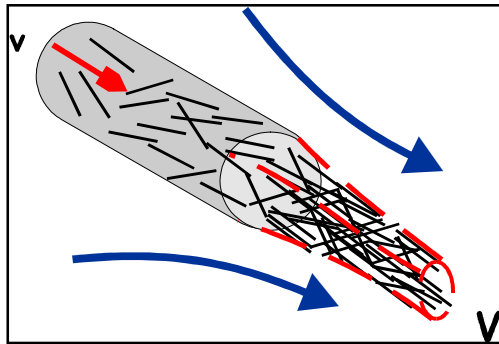


Dispersion
SONICATION

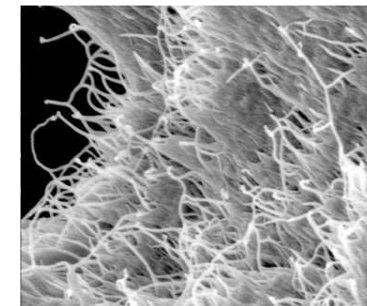
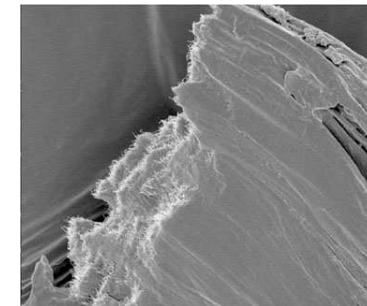
Coagulation

Powder

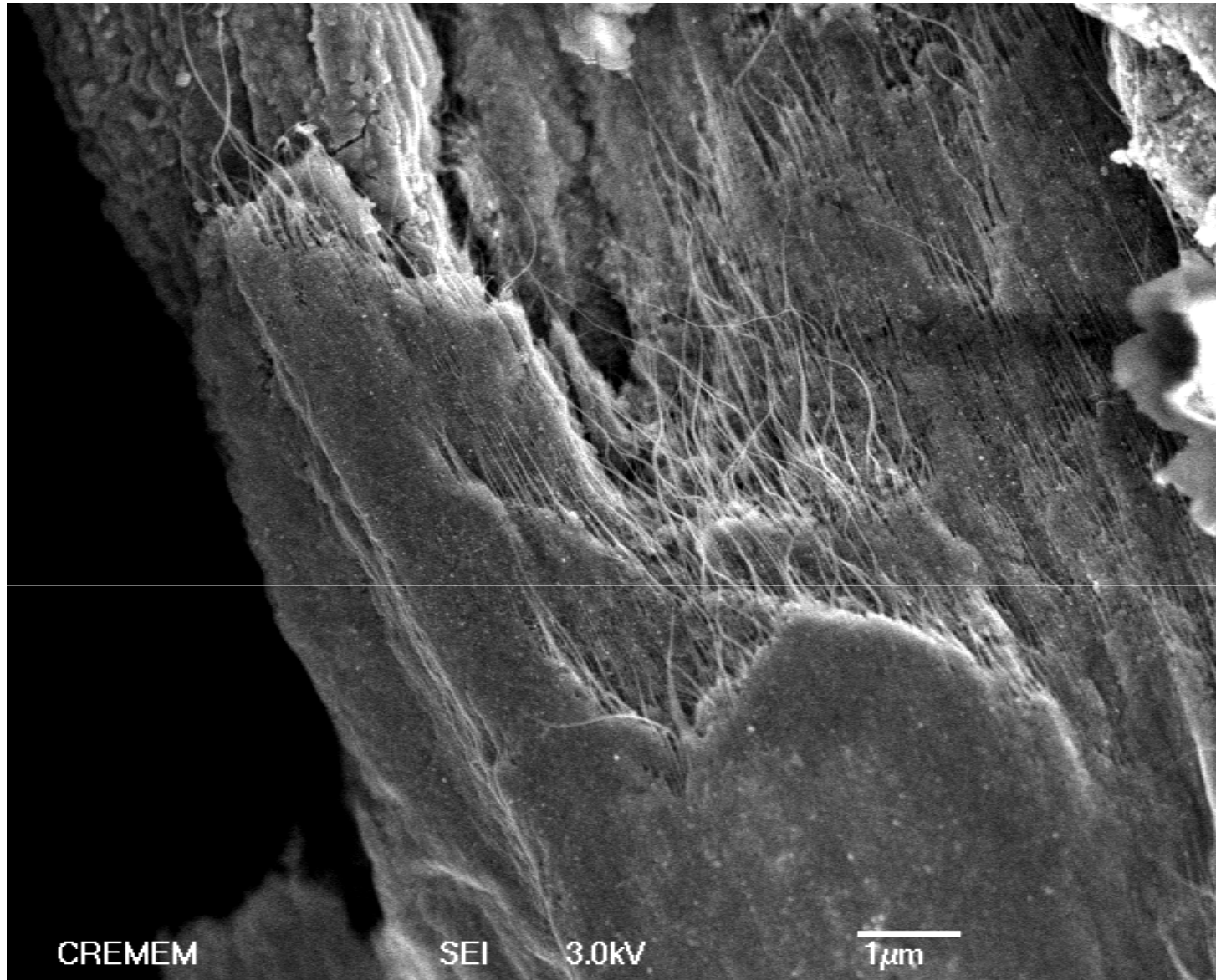
Fiber



Fiber cross section
10-100 microns



Coagulation upon injection of a
CNT dispersion in the co-flowing
stream of a polyvinyl alcohol (PVA) solution
(bridging coagulation)



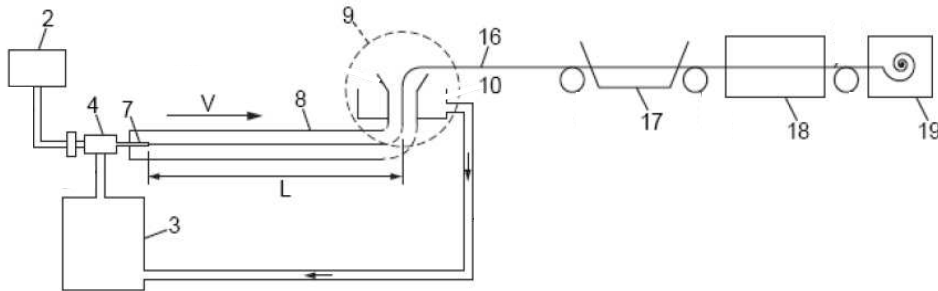
Aligned, nanocomposite structure (PVA-CNT)
High toughness, Electrically conductive, Shape memory with large generation of stress
Microelectrodes for biofuel cells (F. Gao *et al.* (CRPP) Nature Comm. 2010,
A. Dalton *et al.* Nature 2003 560J/G (UTD), P. Miaudet *et al.* (CRPP) Science 2007)

In all cases: natural or wet spun synthetic fibers

**Wet fiber spinning =
transformation from a liquid to a solid state
in a short time**

**Spinning lines and process optimization
are needed for the production of such fibers**
Important for the production rate, robustness of the process...

Challenge :
In-situ characterization of the **fiber solidification ?**
(induced by salts, coagulation, solvent, etc)
How the strength evolves with time ?

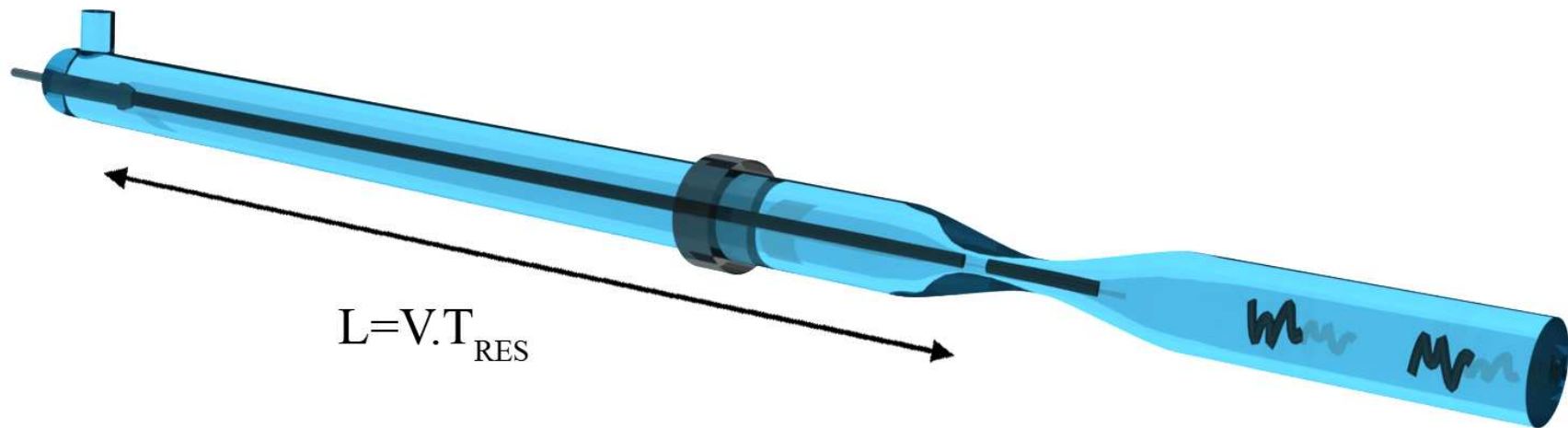


MILLIFUIDIC EXPERIMENTS

FOR

FIBER « MACRO » SPINNING

... and scale-up

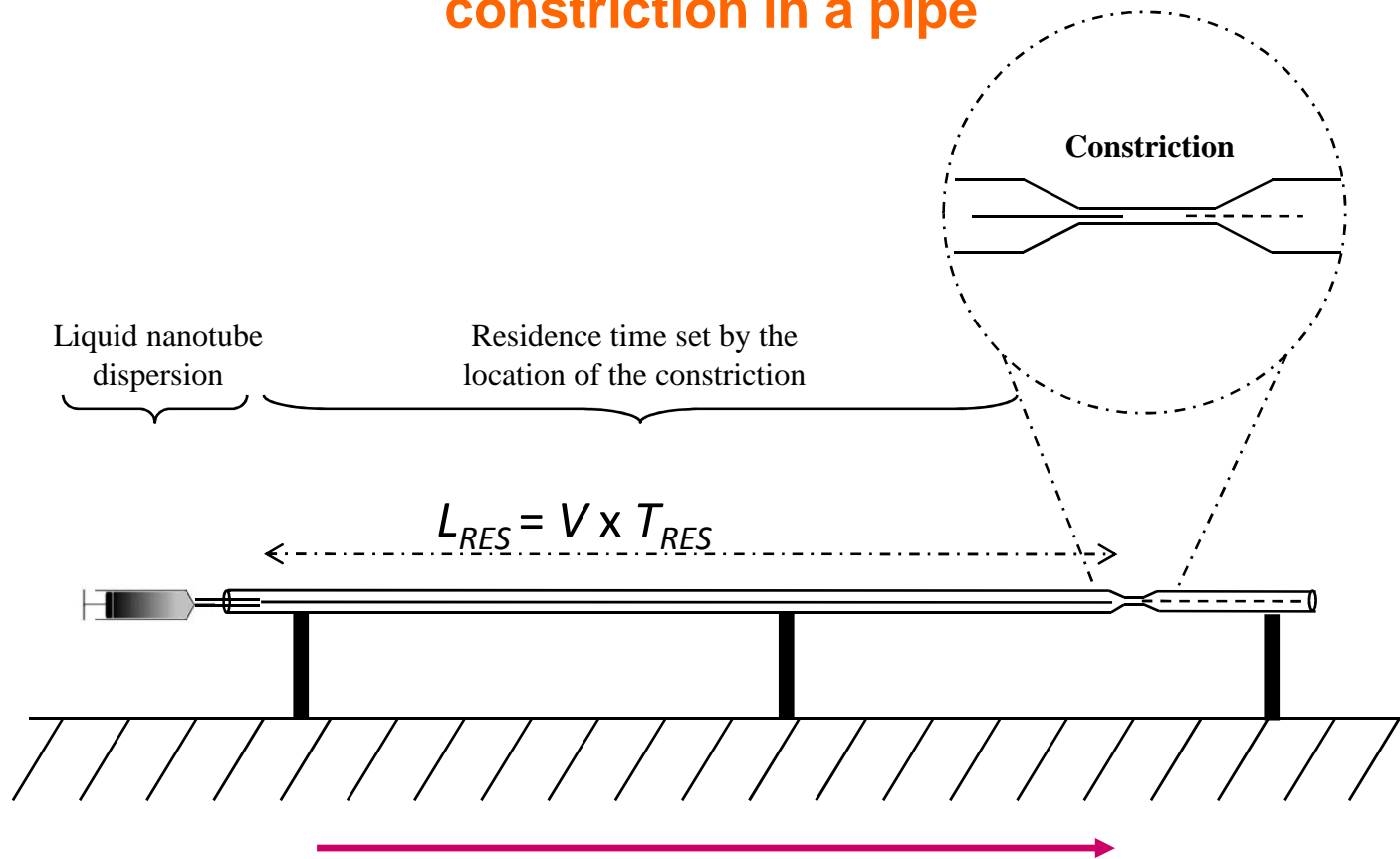


Polymer chains can be broken at the molecular level in an extensional flow
(even though not directly visualizable)

CAN WE DO THE SAME FOR A MACROSCOPIC FIBER ?

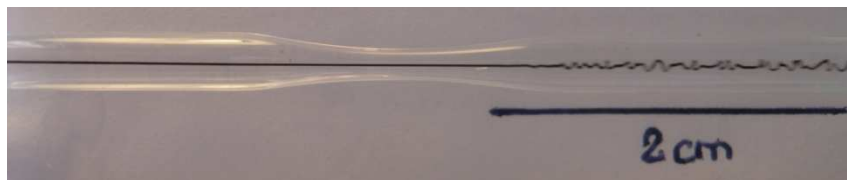
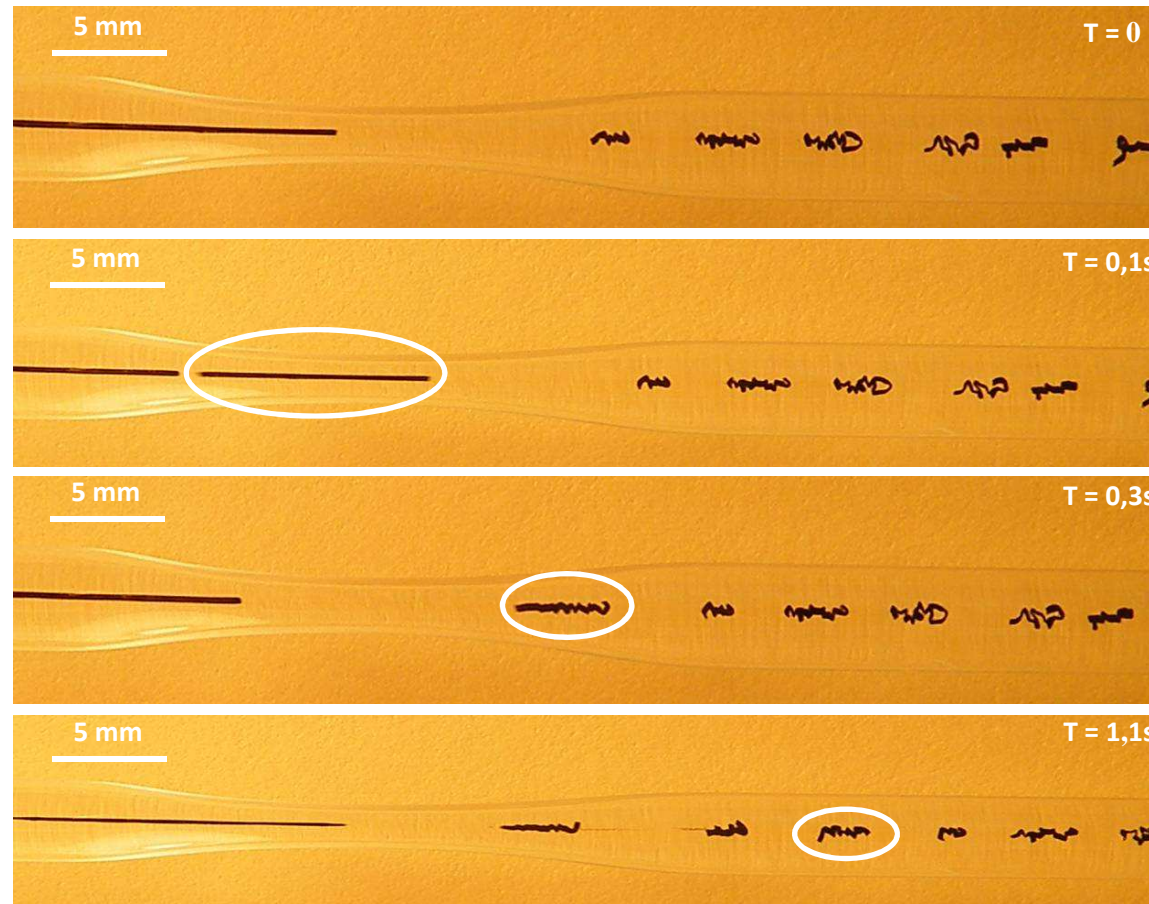
and by the way directly visualize the scission of chains in extensional flows

**Extensional flow can be simply achieved by using a diameter
constriction in a pipe**



Fiber solidification proceeds along the line

The forming fibers are indeed broken when they are not yet sufficiently strong
(residence time is too short)

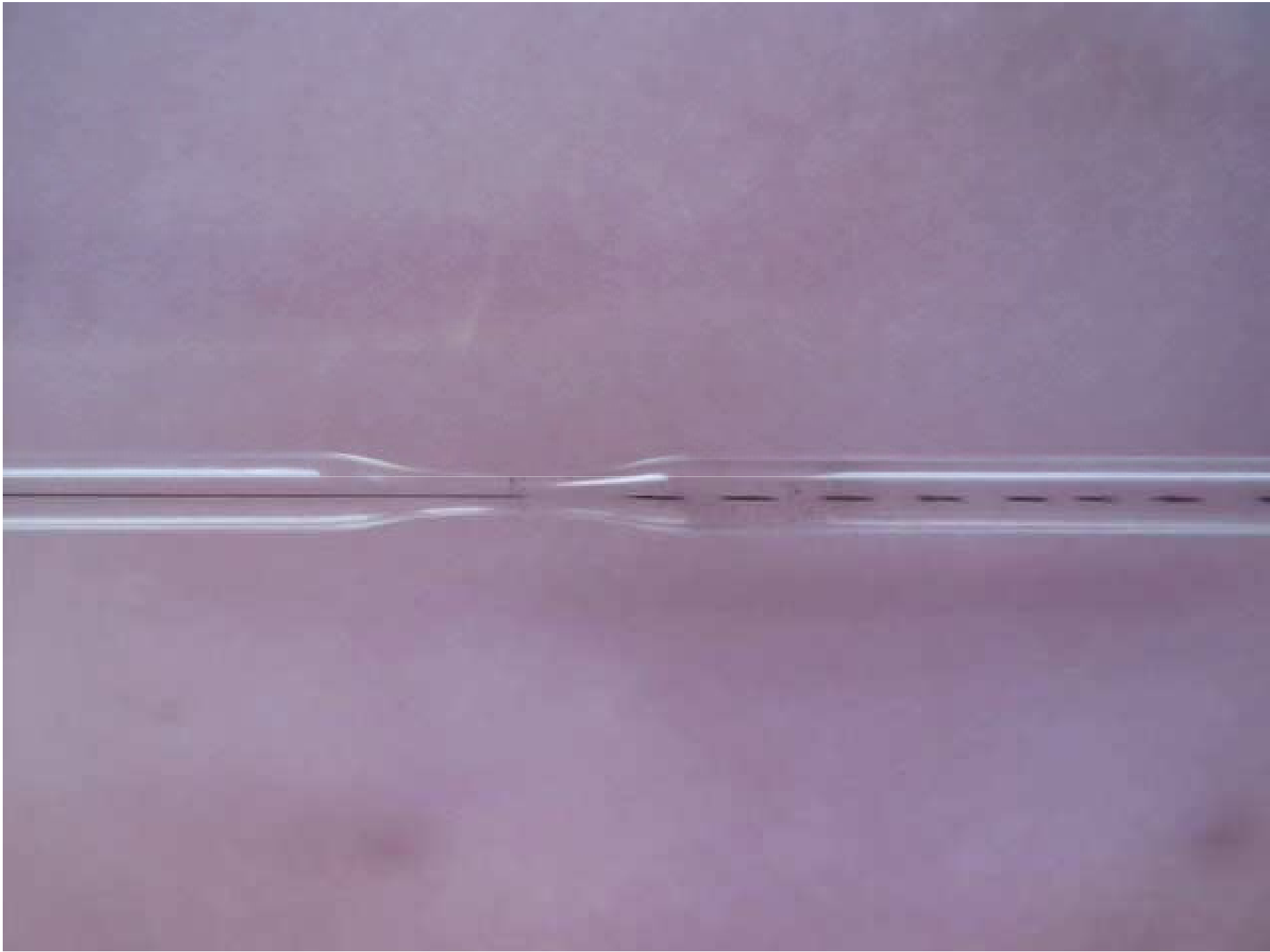


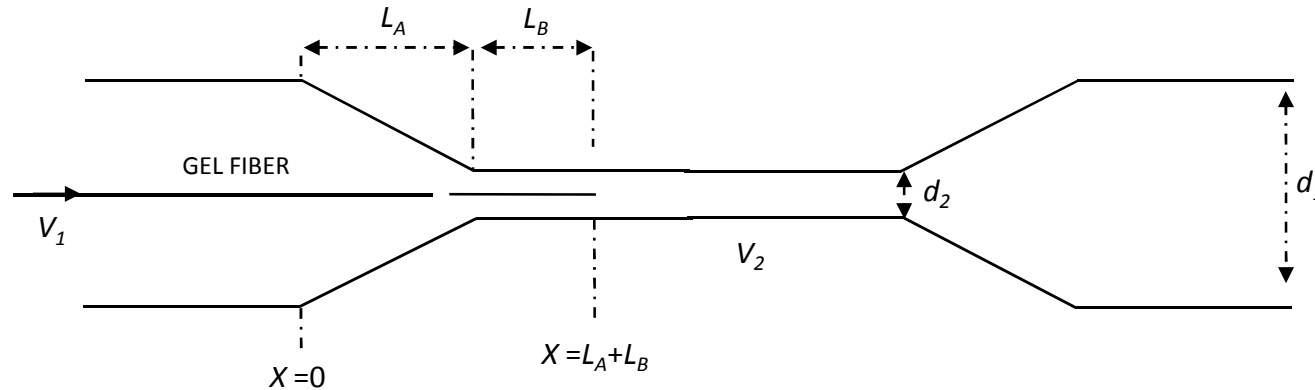
For a longer residence time, the fiber passes through the constriction without breaking.
(far from the injection point)

Formation of uniformly long fragments

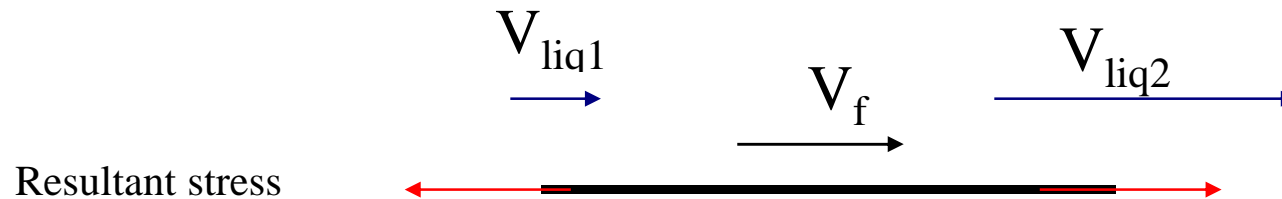
The length of the fragments increases with the residence time:
the fibers is getting stronger with the residence time.







The fiber breaks because of the hydrodynamic friction it experiences due to velocity differences of the fiber from the surrounding fluid.



Following the literature on the scission of polymer chains in extensional flow:

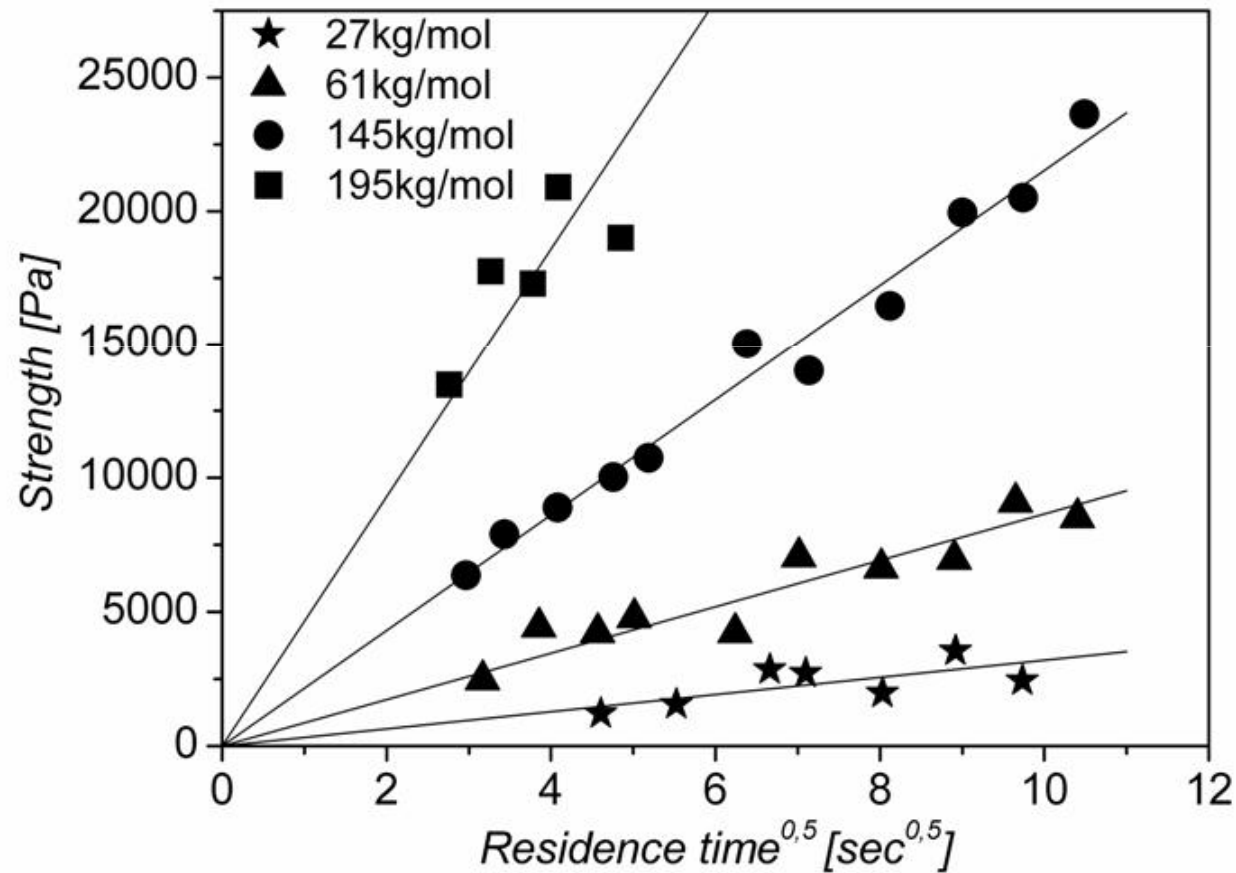
Odell et al., *J. Chem. Phys.* **1988**, 88
(6), 4022

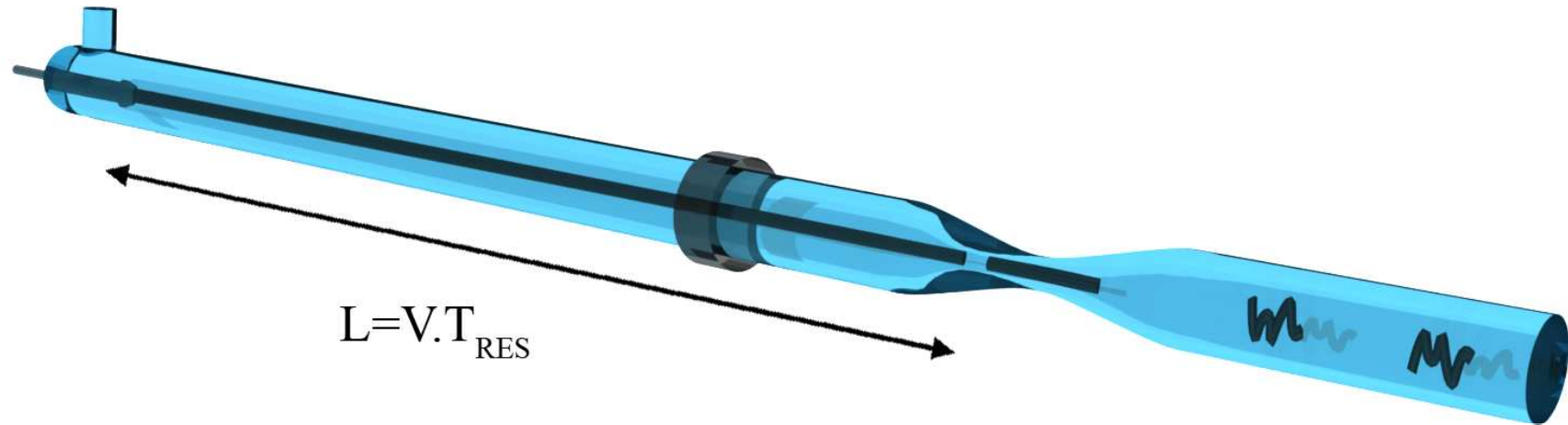
$$\sigma = 8\mu V_2 X_R \left[\left(\frac{L_B + L_A \frac{d_2}{d_1}}{L_A + L_B} \right) + \left(\frac{L_A \frac{d_2^2}{d_1^2}}{X_R \left(1 - \frac{d_2}{d_1} \right) - L_A} \right) \right] / D_F^2$$

By measuring the length of the fragments and knowing the flow conditions one can estimate the strength of the gel fiber.

Example

PVA with different molecular weights : small chains diffuse more rapidly but yield weaker fibers => High molecular weights are preferable.
(not initially obvious because faster coagulation rates are desirable)





Helpful to optimize the processing of new nanotube fibers
(in progress : tests of salts, cross-linkers, etc...)

**We hope that it can also be potentially useful for developing new synthetic fibers
or better knowing the formation of natural fibers ?**

C. Mercader *et al.* to appear in PNAS 2010





Summer retreat of the CRPP nanotube group
C. Mercader (Fiber solidification), C. Zakri, M. Maugey, A. Derré, S. Moisan

Not on the picture
CNT fibers: A. Lucas, P. Miaudet
Percolation: B. Vigolo, C. Coulon

P. van der Schoot (Eindhoven), M. Pasquali (Rice Univ)

THANKS FOR YOUR ATTENTION