# Le leggi del disordine

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*Cavolo romano*

PhD/Postdoc
(in ordine di apparizione):

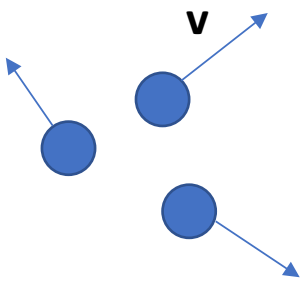
Claudio Donati,
Cristiano De Michele,
Andrea Barbieri,
Vasile Bercu,
Luca Larini,
Alistar Ottochian,
Francesco Puosi,
Oleksandr Chulkin,
Sebastiano Bernini,
Mara Barucco,
Andrea Giuntoli,
Antonio Tripodo

# Disordine :

- Disordine nelle velocita’
- Disordine nelle posizioni:
  - Liquidi
  - Polimeri
  - Solidi disordinati ( vetri, amorfi)

# Disordine nelle velocita': la distribuzione di Maxwell-Boltzmann

$$f_{MB}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{mv^2}{2kT}\right]$$




Per una storia dei contrari (Kelvin..), dei cauti (Maxwell…) e degli entusiasti (Clausius…) vedi:
Rowlinson, Mol. Phys. 2005

**NB**:
Le leggi dei sistemi disordinati sono di natura statistica

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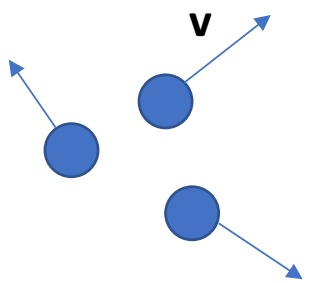


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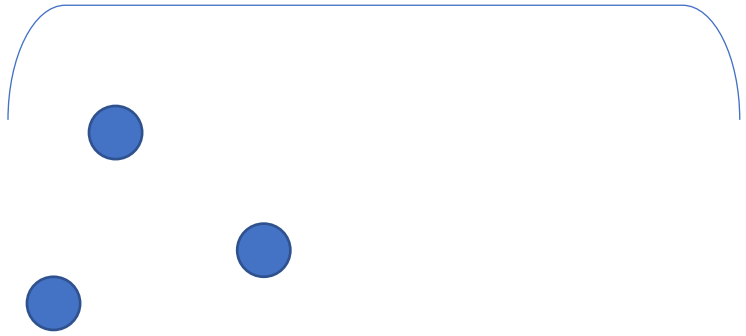

Gas ideali

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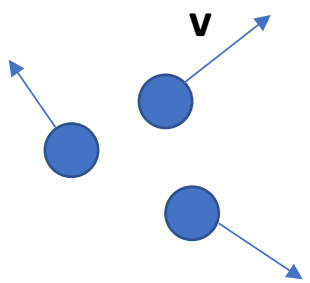


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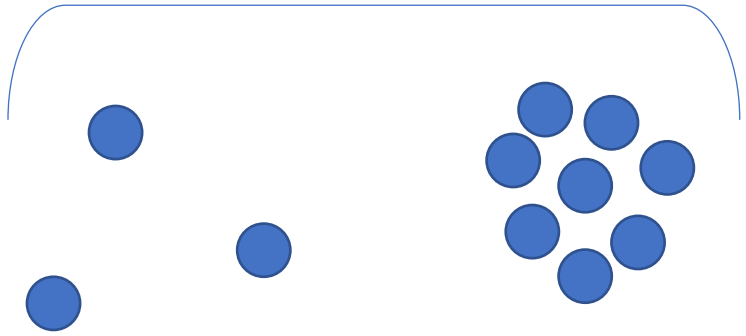

Gas ideali Liquidi

Raizen et al, Science 2010, Optics Express 2015

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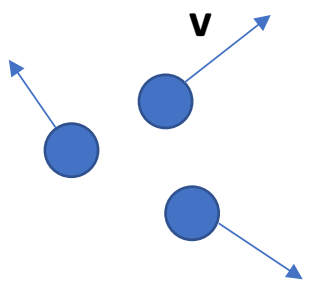


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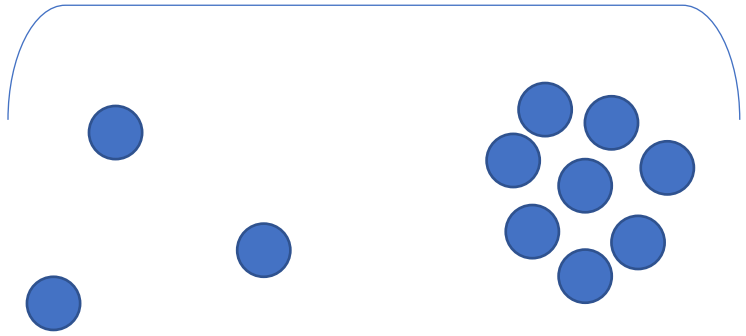

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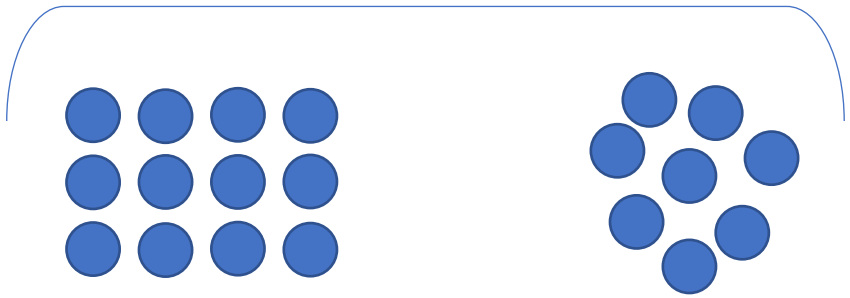
**Solidi** (mobilita' trascurabile)



Cristalli Vetri

Mohazzabi et al, 2018

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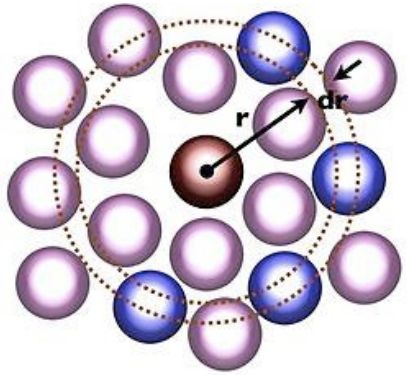
# Disordine nelle posizioni in liquidi e solidi: assenza di ordine a lungo raggio




$$dN(r) = 4 \pi \rho r^2 \mathbf{g(r)} dr$$

radial distribution function

$\lim_{r \to \infty} \mathbf{g(r)} = 1$ ;

**homogeneity**

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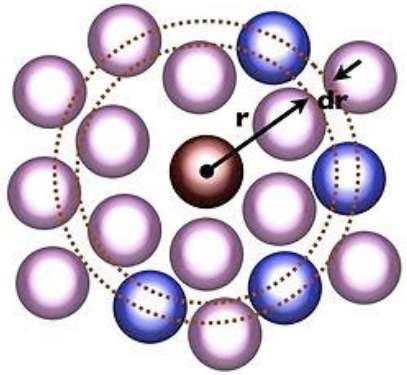


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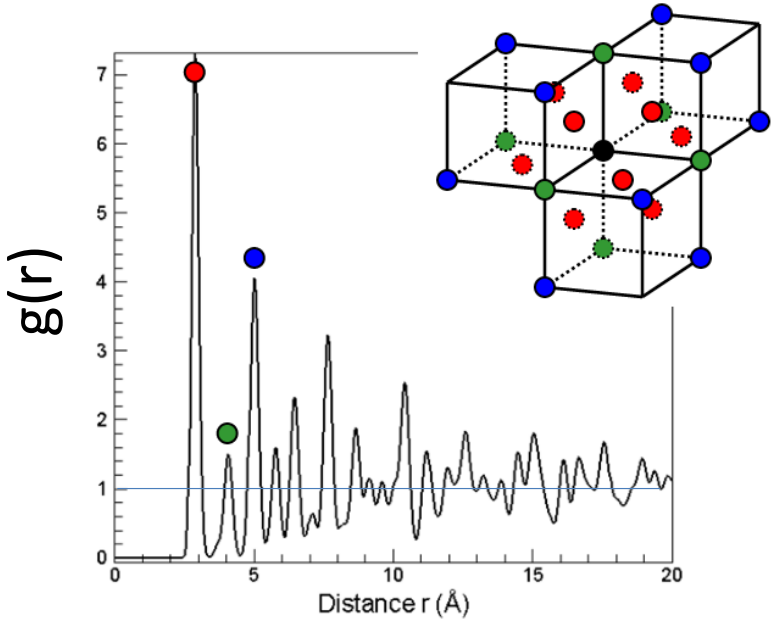
Crystalline fcc Au



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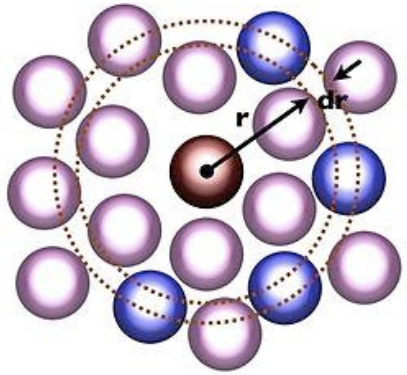


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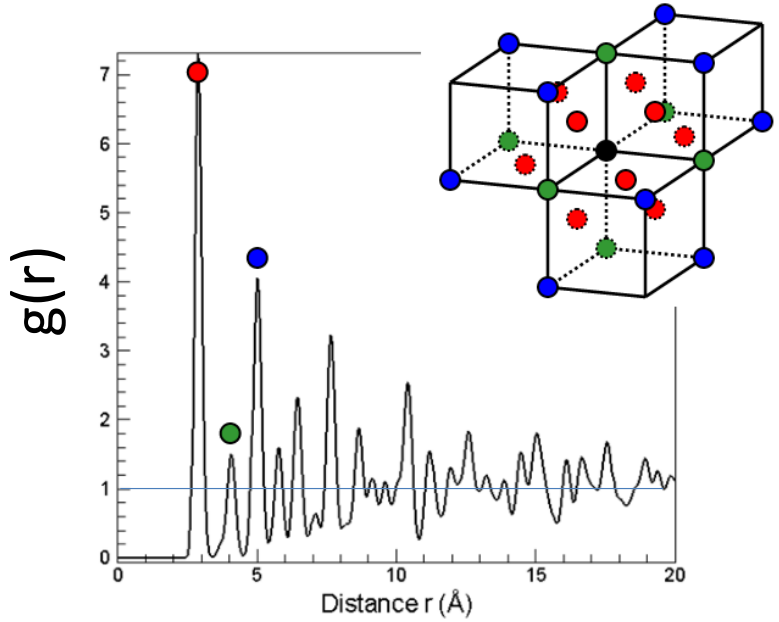
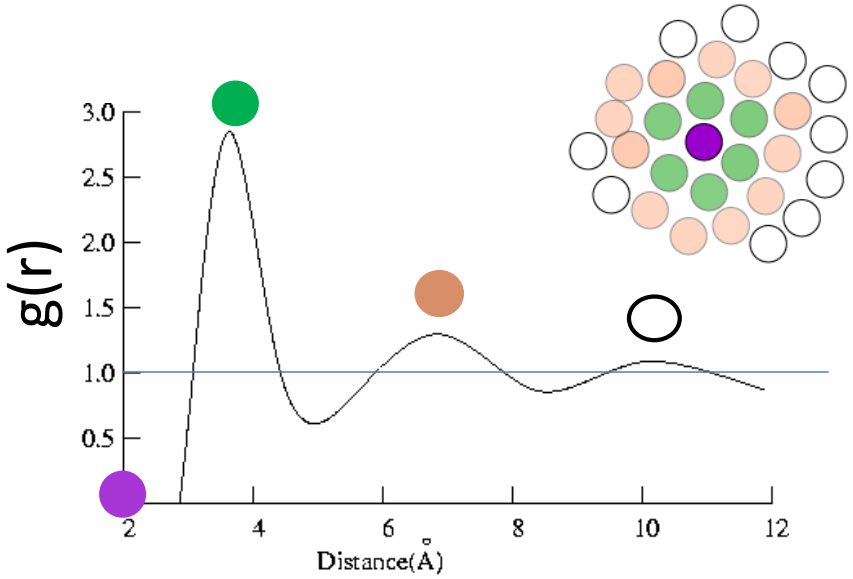



Ar (liquido) , Ar (vetro)



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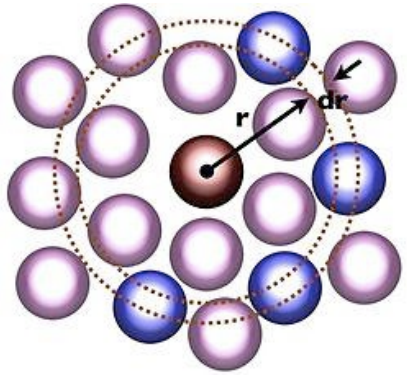


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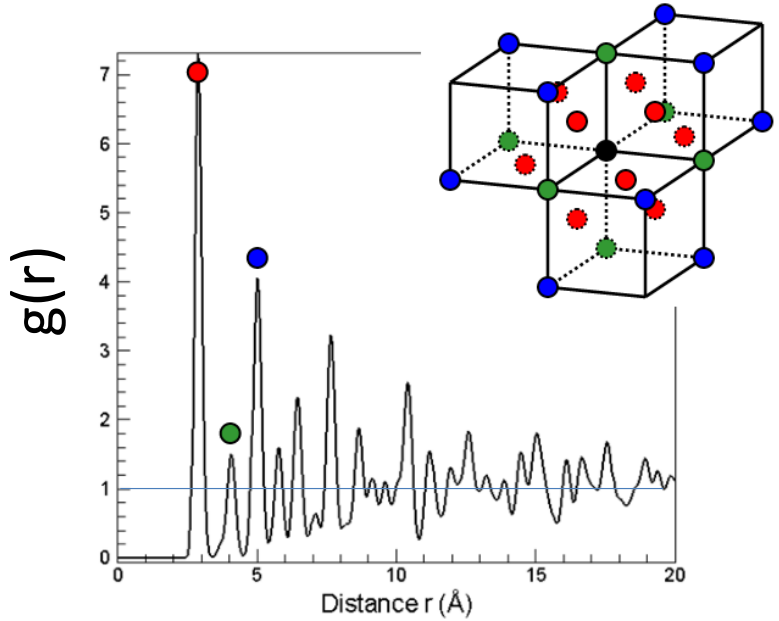


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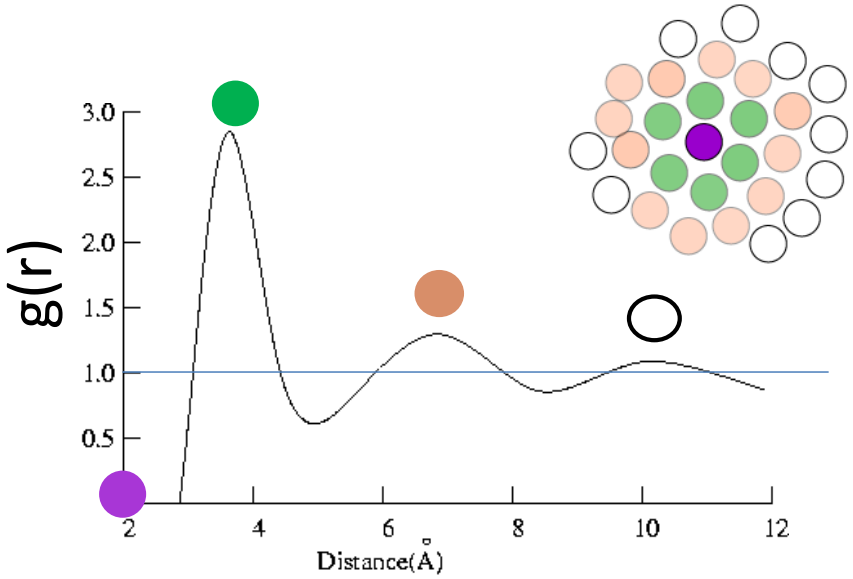
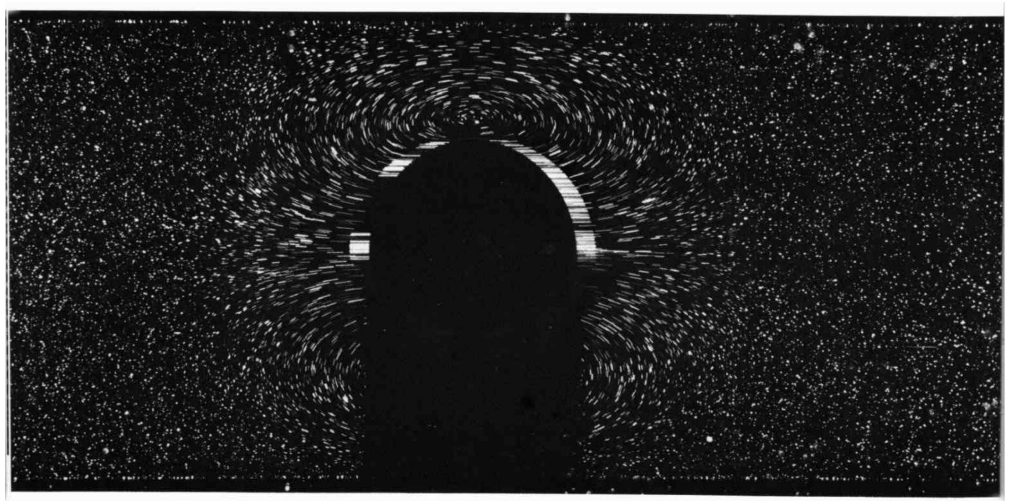
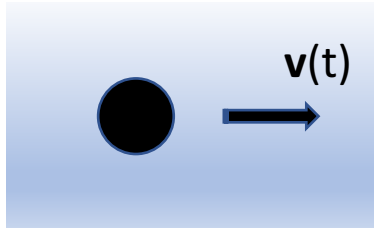



**NB**:
Sistemi spazialmente disordinati, anche con strutture molto simili possono avere mobilita' molto diverse

# Liquidi: autosimilarita’ nel tempo e nello spazio (backflow)



**9. Sphere moving through a tube at $R=0.10$, absolute motion.** In contrast to the photograph above, here the camera remains fixed with respect to the distant fluid. During the exposure the sphere has moved from left to right less than a tenth of a diameter, to show the absolute motion of the fluid. At this small Reynolds number the flow pattern, shown by magnesium cuttings in oil, looks completely symmetric fore-and-aft. *Coutanceau 1968*




Sfera macroscopica in liquido

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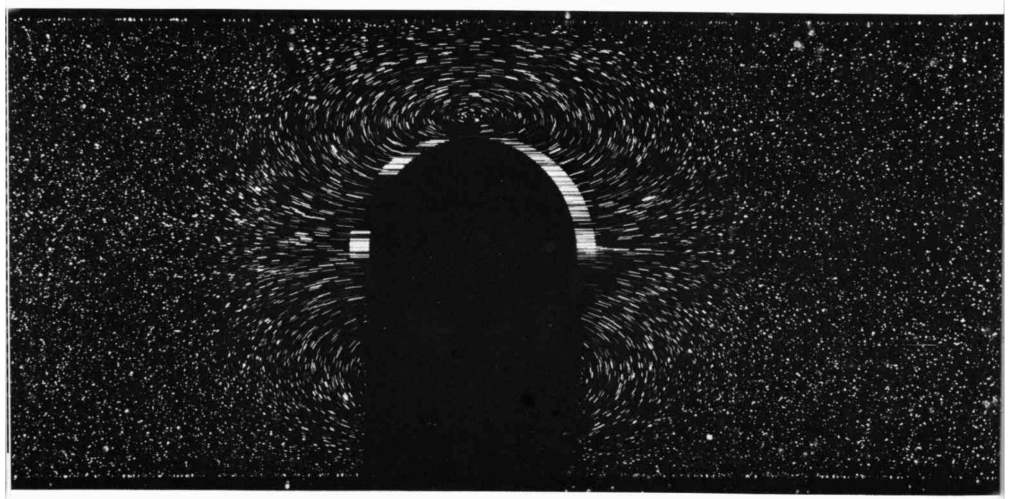

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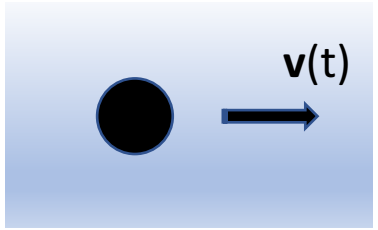


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PHYSICAL REVIEW A VOLUME 1, NUMBER 1 JANUARY 1970

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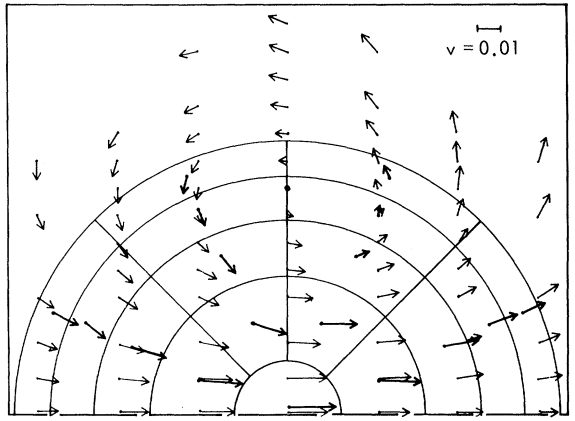
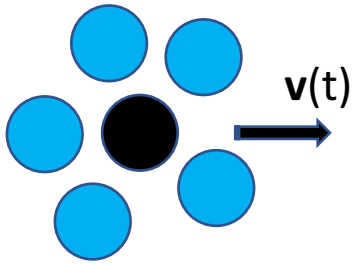
B. J. Alder and T. E. Wainwright
*Lawrence Radiation Laboratory, University of California, Livermore, California* 94550
(Received 10 July 1969)




Atomo in liquido atomico

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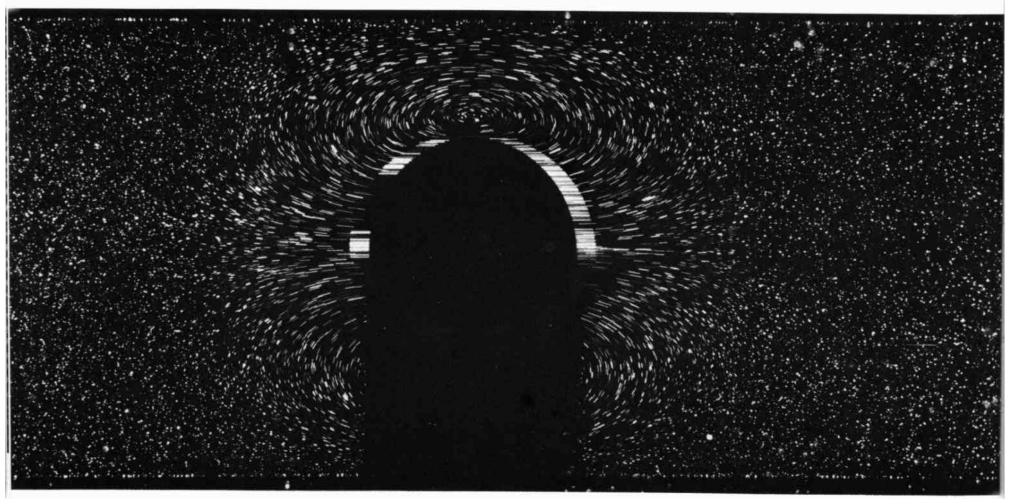

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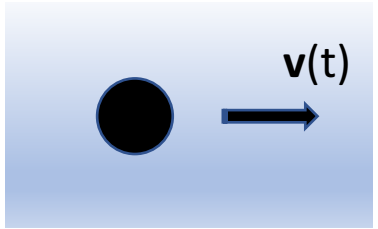


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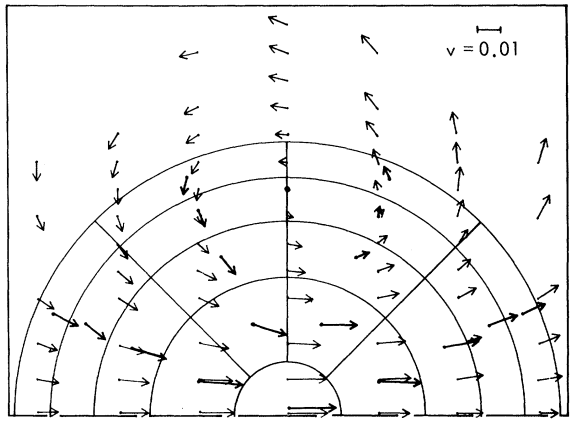


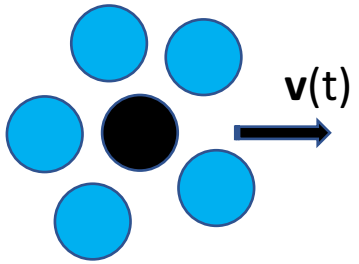


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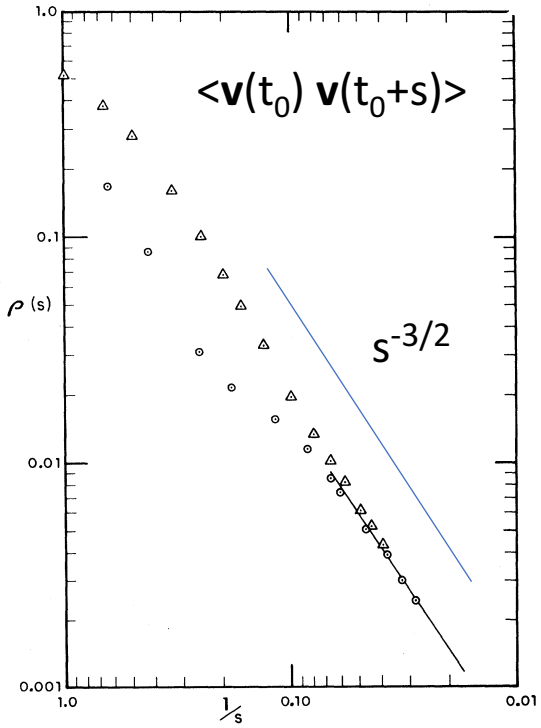
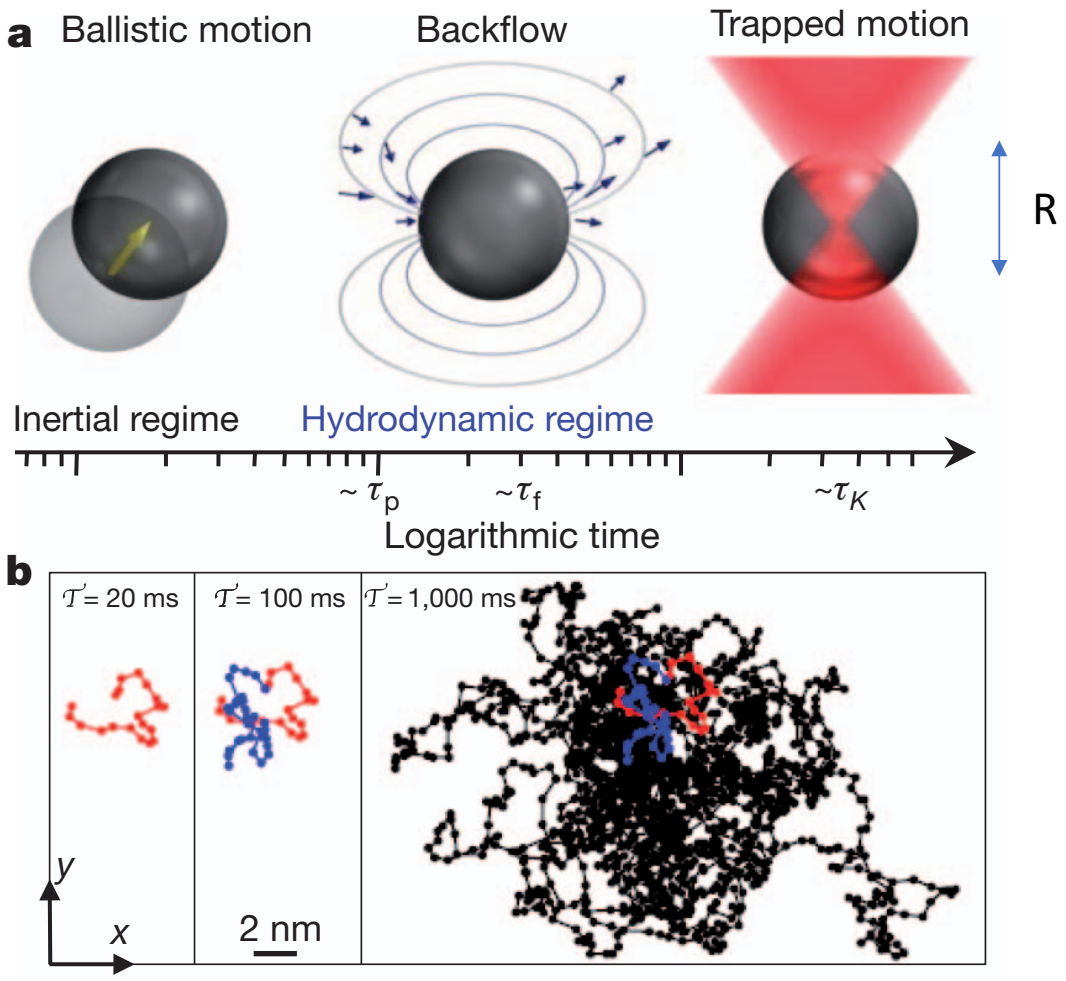



FIG. 2. Comparison of the velocity autocorrelation function $\rho(s)$ as a function of time (in terms of mean collision times $s$) between the hydrodynamic model (circles) and a 500-hard-sphere molecular-dynamic calculation (triangles) at a volume relative to close packing of 0.6 on a log–log plot. The straight line is drawn with a slope corresponding to $s^{-3/2}$. To the molecular dynamics $\rho(s)$

# Enhanced hydrodynamic anticorrelations driven by Backflow: lab-on-a-chip application

Franosch et al, Nature 2011



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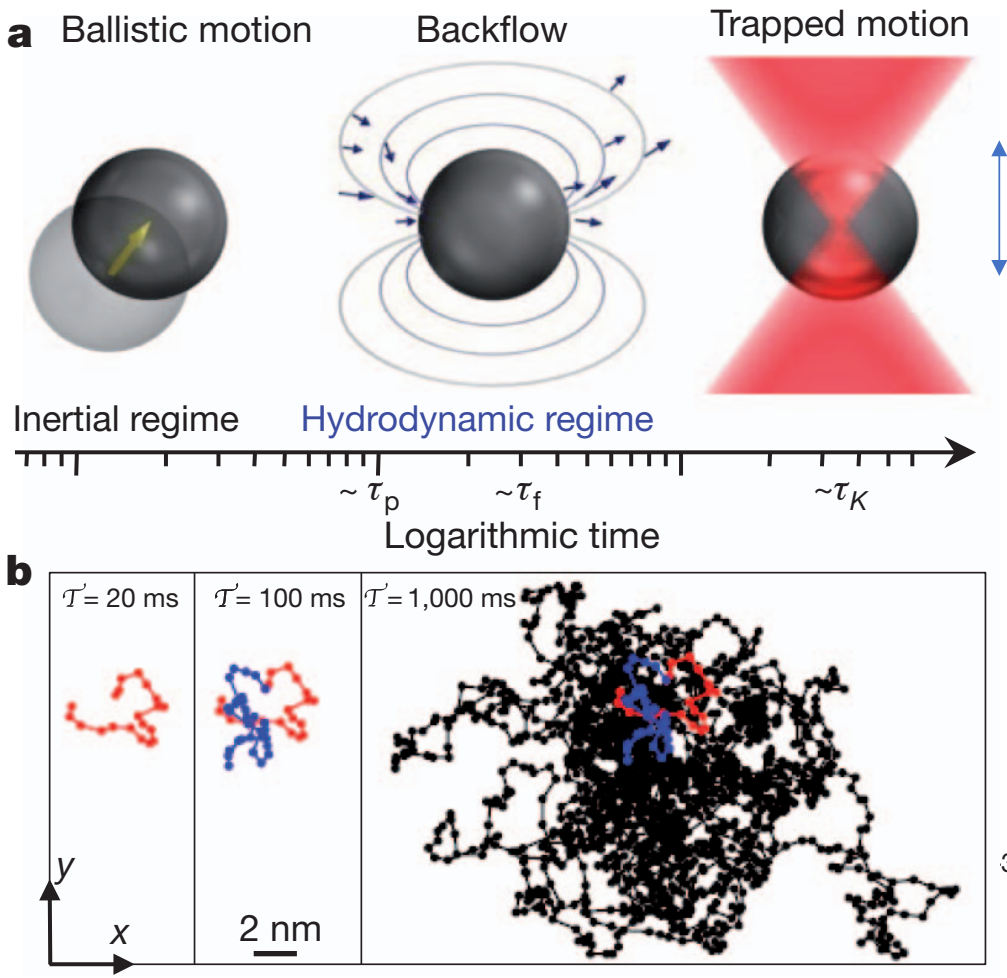
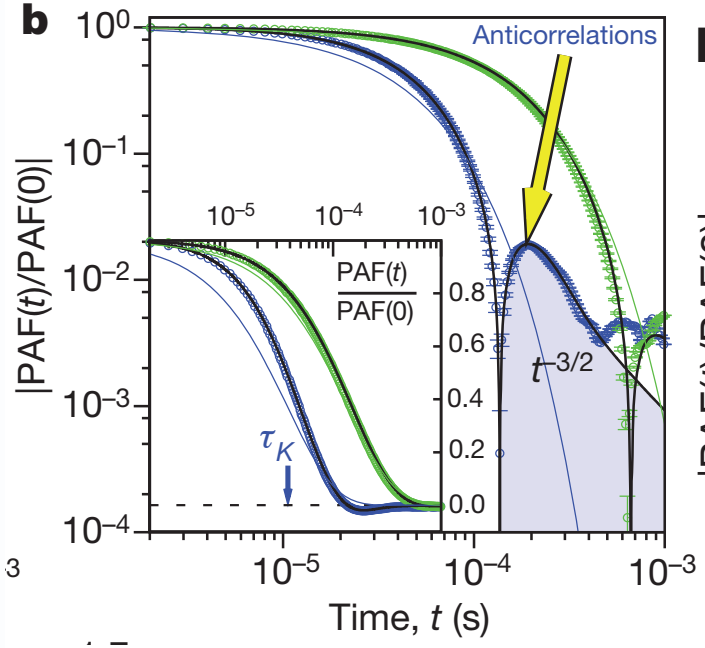
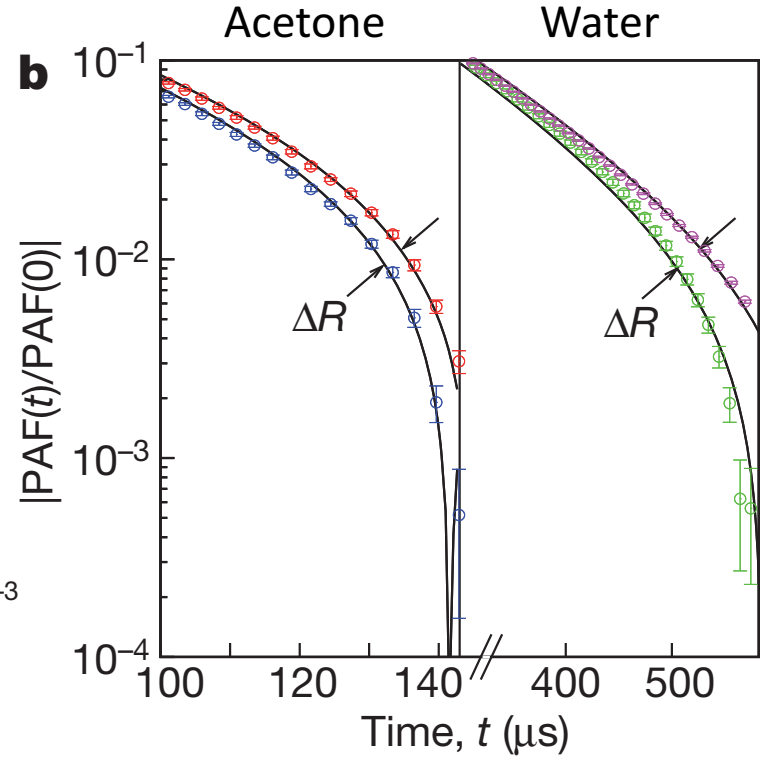



R

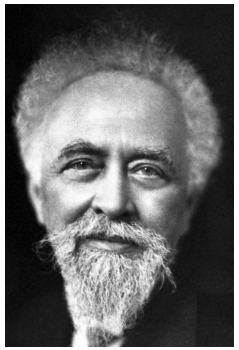
PAF(t) = <x x(t)>




ΔR/R ~ 3 %, R ~ 1μm



# Liquidi: il moto browniano e l’esistenza degli atomi



J. Perrin

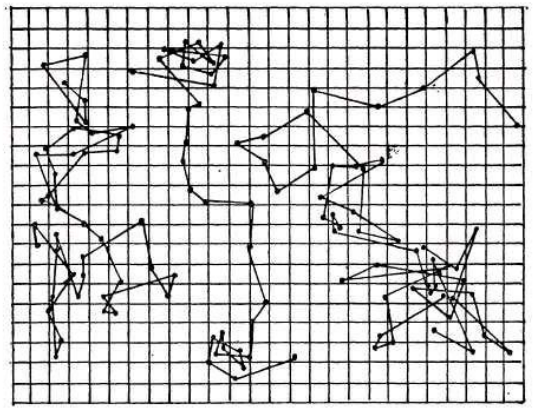
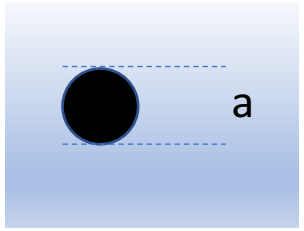


Fig. 7.



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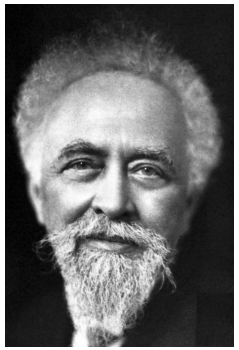

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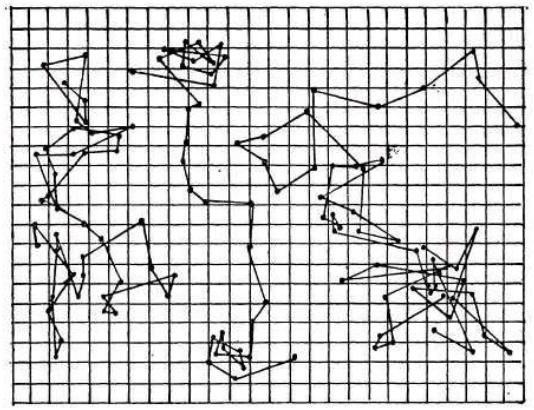

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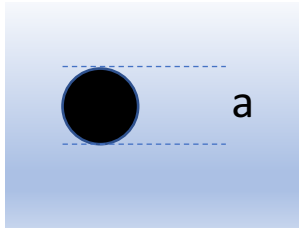


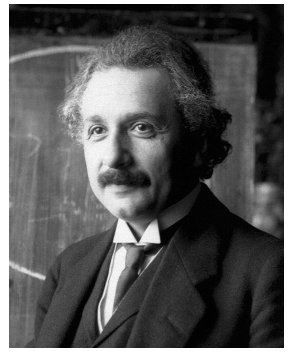

A. Einstein

Articoli 1905 (Annus Mirabilis), in ordine di invio:

- Effetto fotoelettrico (Nobel 1921)
- **Moto Browniano**
- Relativita' speciale
- $E=mc^2$

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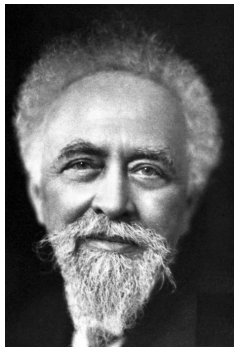

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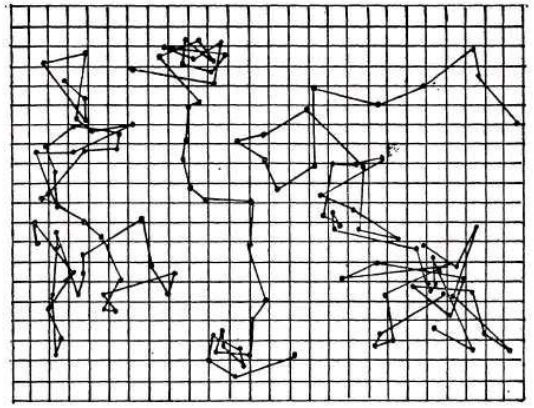

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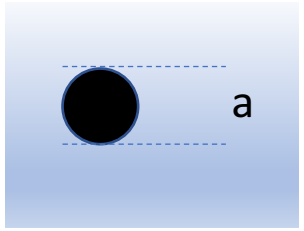


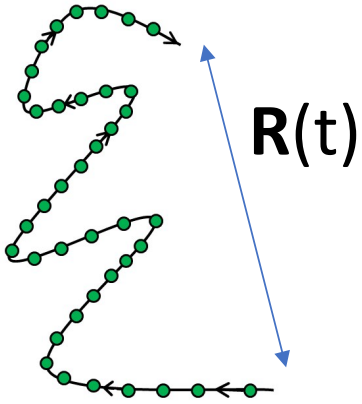


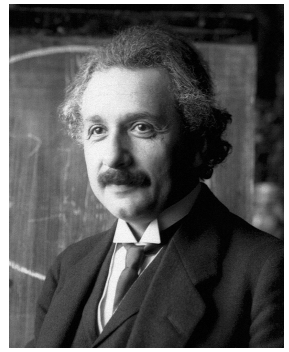

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D: coefficiente di diffusione
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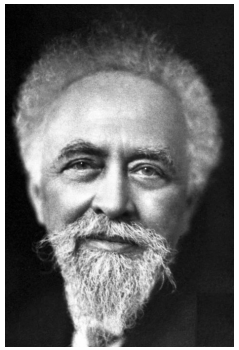
# Liquidi: il moto browniano e l'esistenza degli atomi



J. Perrin

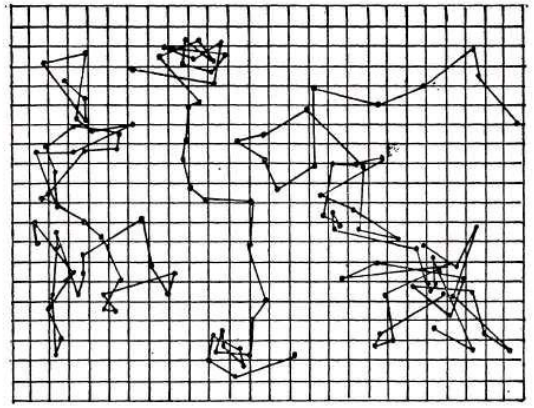
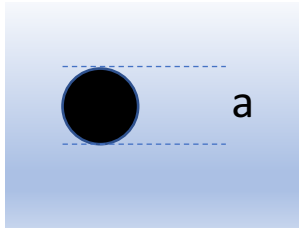
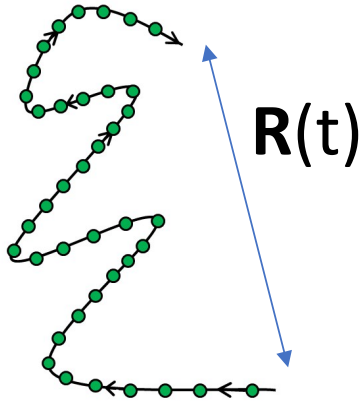
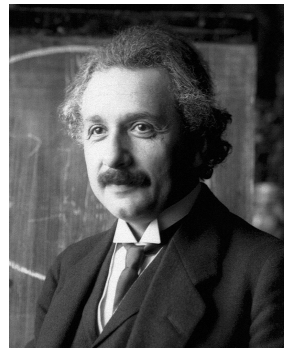


Fig. 7.



A. Einstein

Articoli 1905 (Annus Mirabilis), in ordine di invio:

- Effetto fotoelettrico (Nobel 1921)
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Legge di Stokes-Einstein

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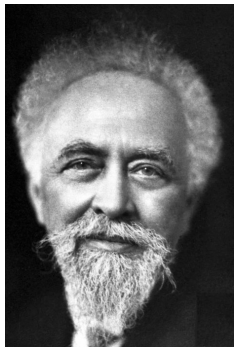
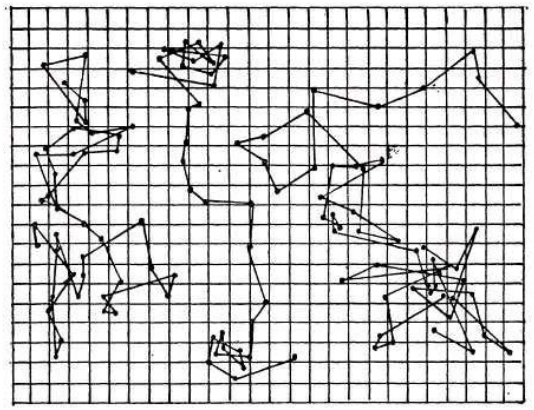


J. Perrin



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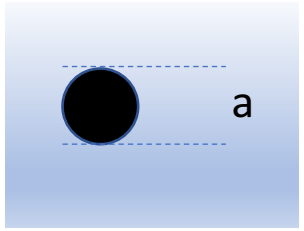


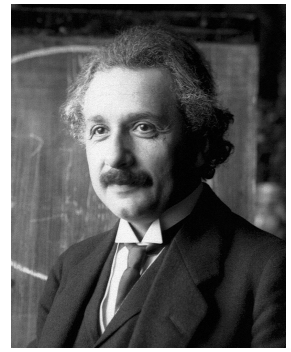

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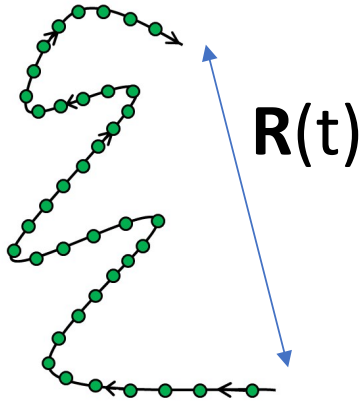


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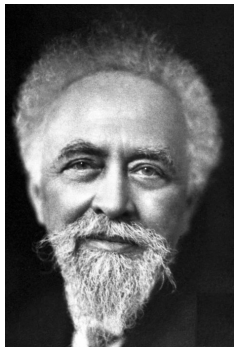
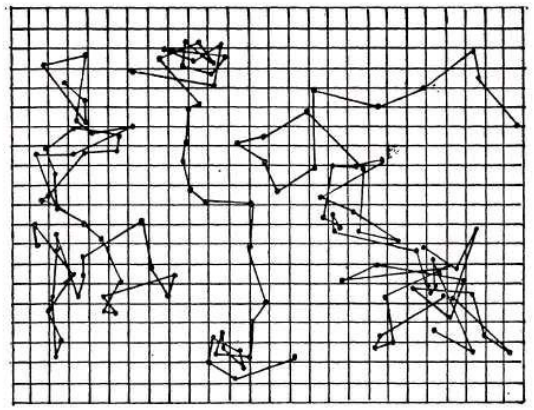


J. Perrin



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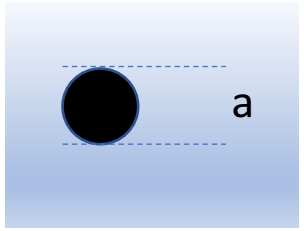
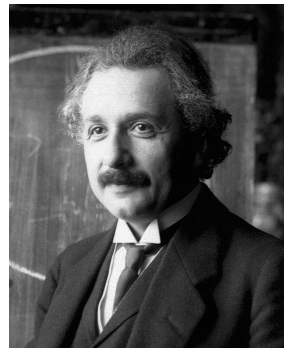
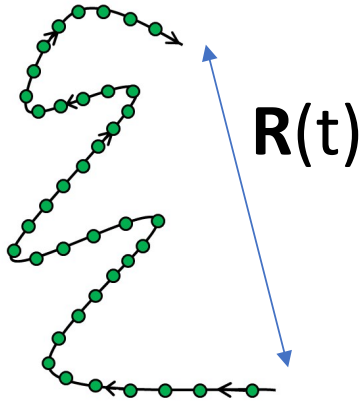


A. Einstein

Jean Baptiste Perrin, The Nobel Prize in Physics 1926
"for his work on the **discontinuous structure of matter**..."

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**During the 1880s atoms and molecules became important scientific concepts, but whether or not they actually had a physical existence was still a matter of dispute**. Jean Perrin maintained that if molecules were real, particles blended into a liquid should not all sink to the bottom but should distribute themselves throughout the liquid. In **1908** he could substantiate this through experimentation. He also substantiated Albert Einstein's theory that Brownian motion - the random movement of small particles in a liquid - was due to collisions between the particles and molecules in the liquid. ( Source: https://www.nobelprize.org/prizes/physics/1926/summary/ )

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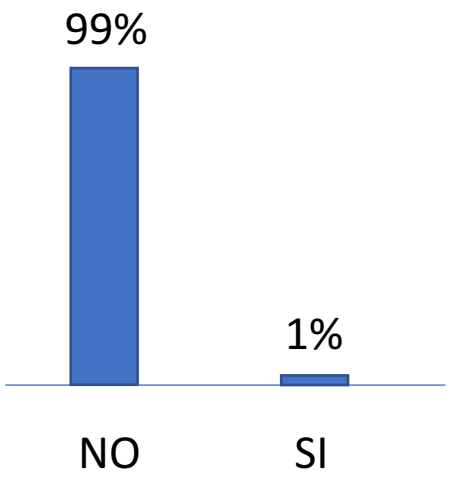
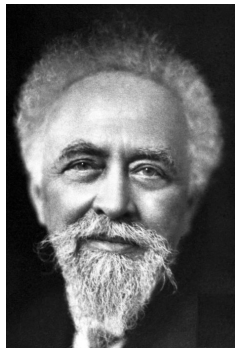
Legge di Stokes-Einstein

# Sondaggi (ventennali)….

**Domanda**: conosci Perrin ?



J. Perrin

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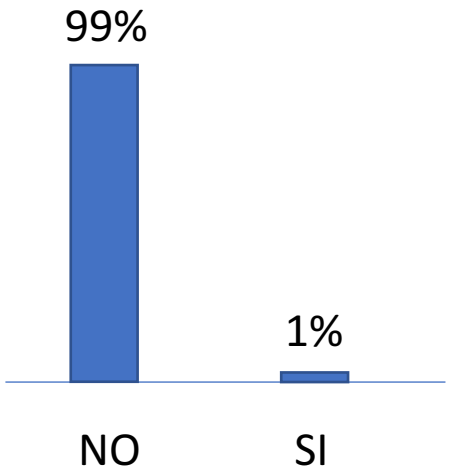
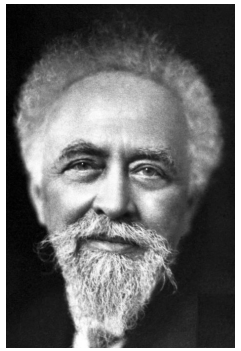
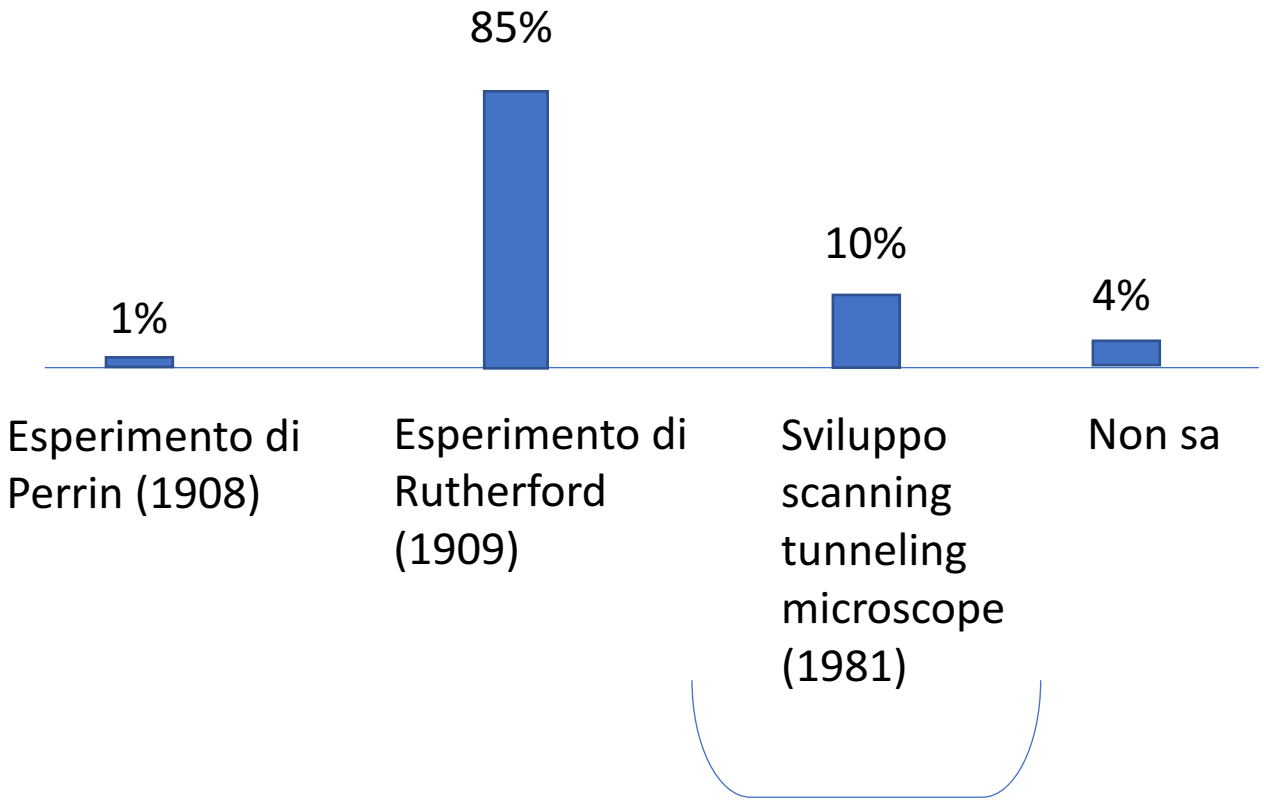


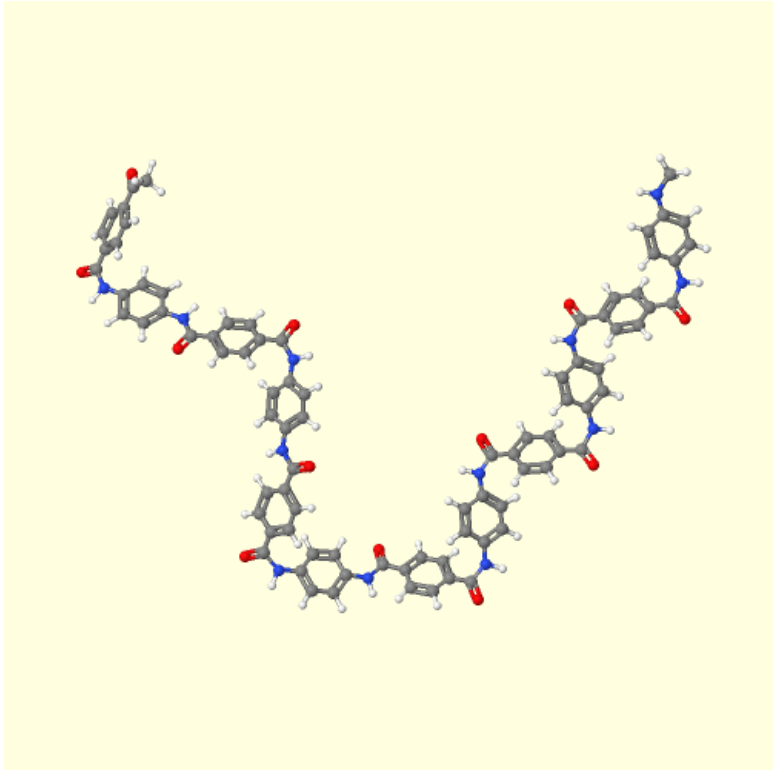
J. Perrin

**Domanda**: sai come/quando e’ stata provata l’esistenza degli atomi ?




“Se non vedo, non credo”

# Polimeri: analogia con il  moto browniano



Kevlar:
Polimero poliaramide
“bio-inspired” dalla tela dei ragni

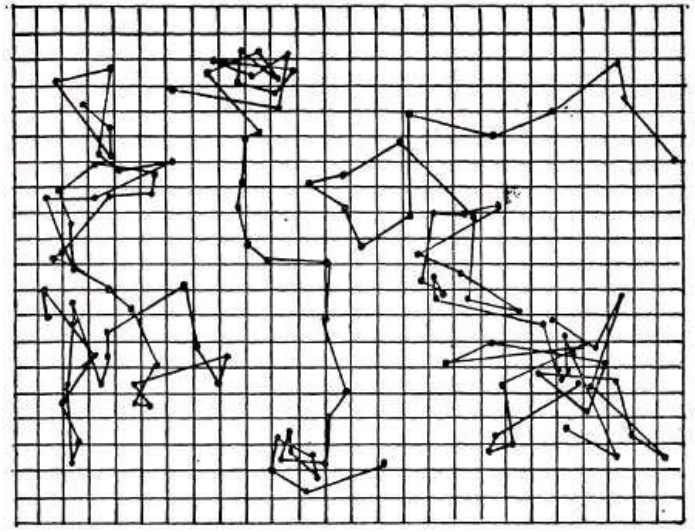
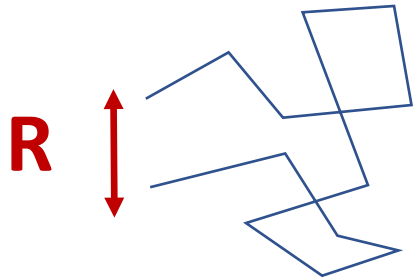


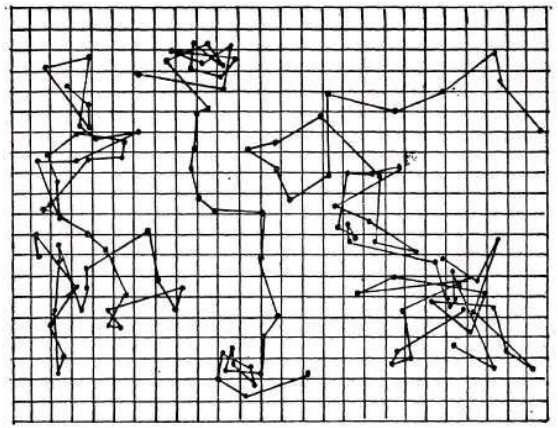
Fig. 7.

# Analogia tra moto browniano e polimeri lineari: quale moto browniano ?

**RW**




$$\langle R^2 \rangle \propto N$$



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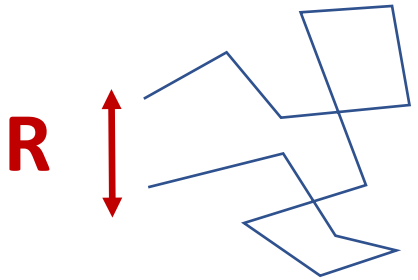


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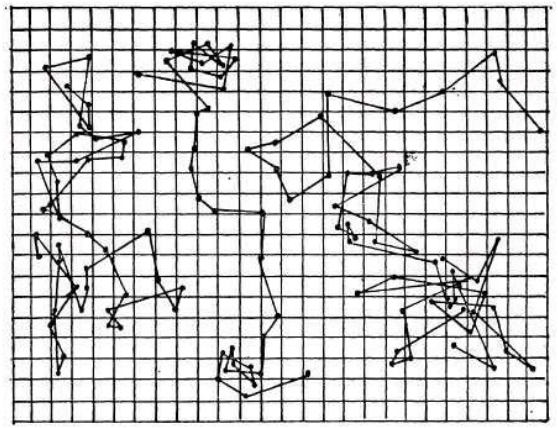
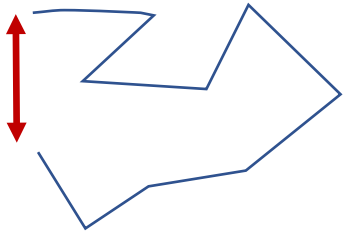


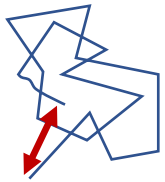
Fig. 7.

**RW autoevitante**



$$\langle R^2 \rangle \propto N^{6/5}$$

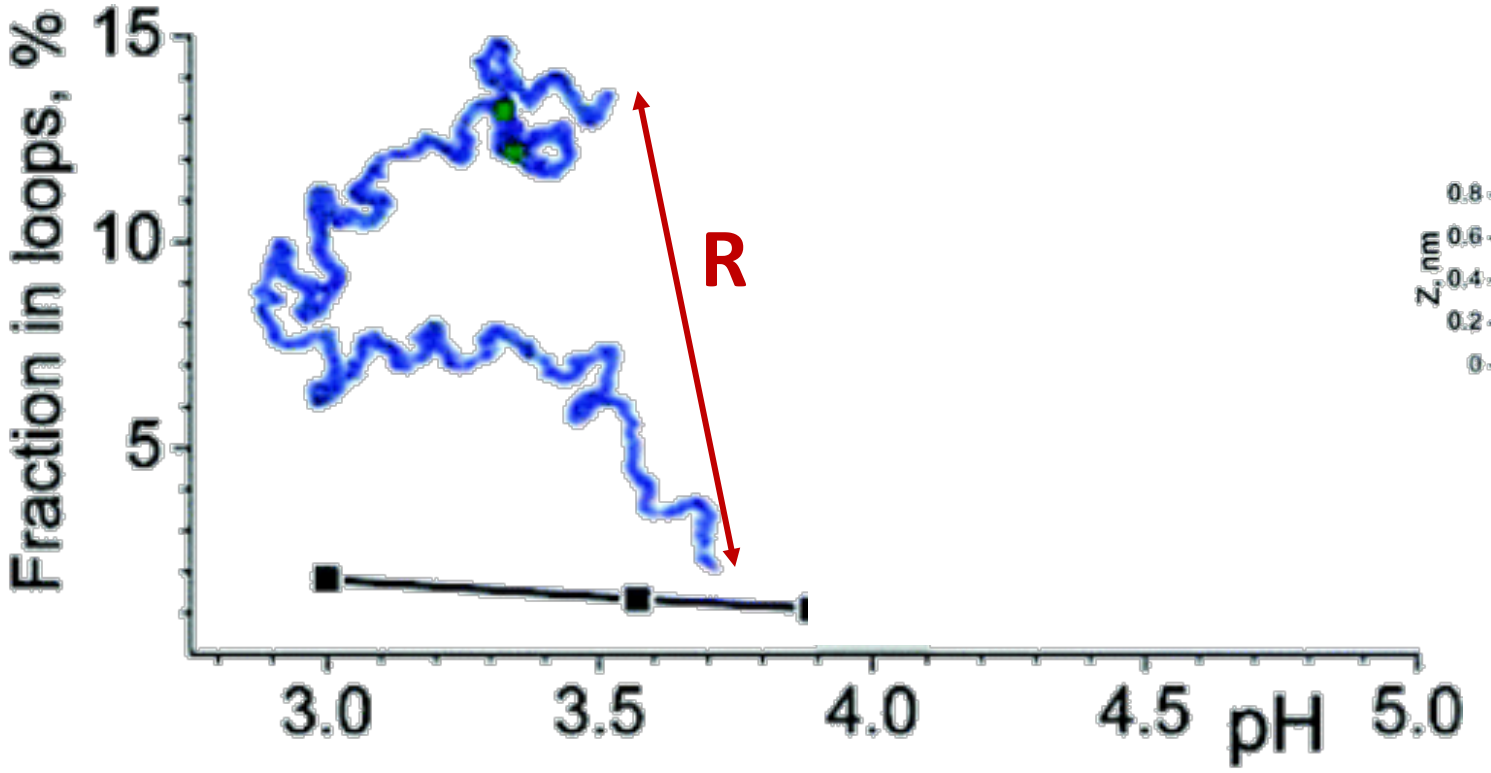
**Globulo**

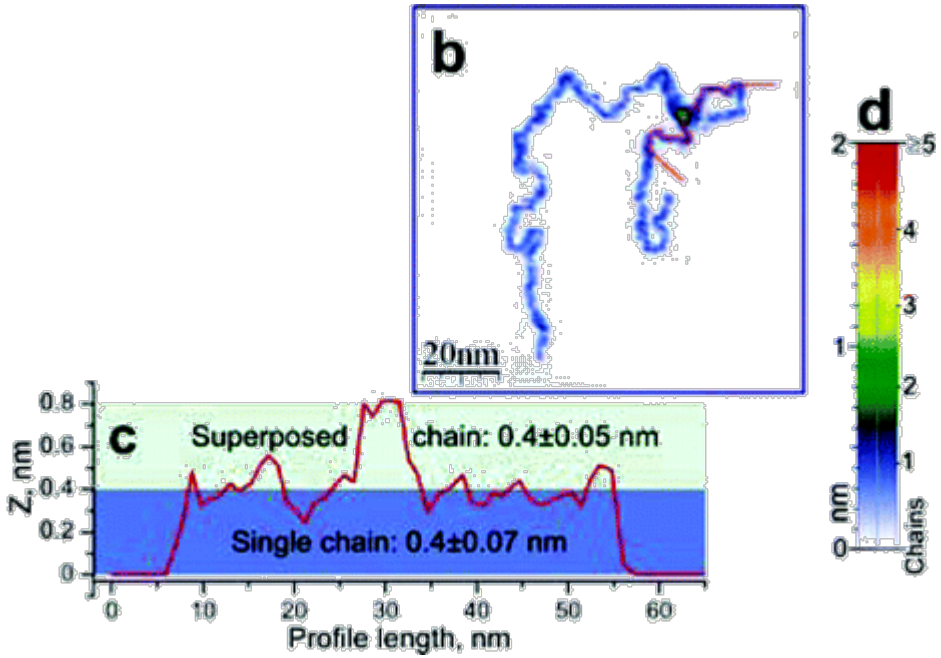


$$\langle R^2 \rangle \propto N^{2/3}$$

# Transizione “coil-globule” di singola catena: un esempio di transizione disordine-disordine

**RW autoevitante**




**Singola** macromolecola di poly(2-vinylpyridine) depositata su mica in soluzione acquosa e visualizata con AFM (Roiter and Minko, JACS 2005)

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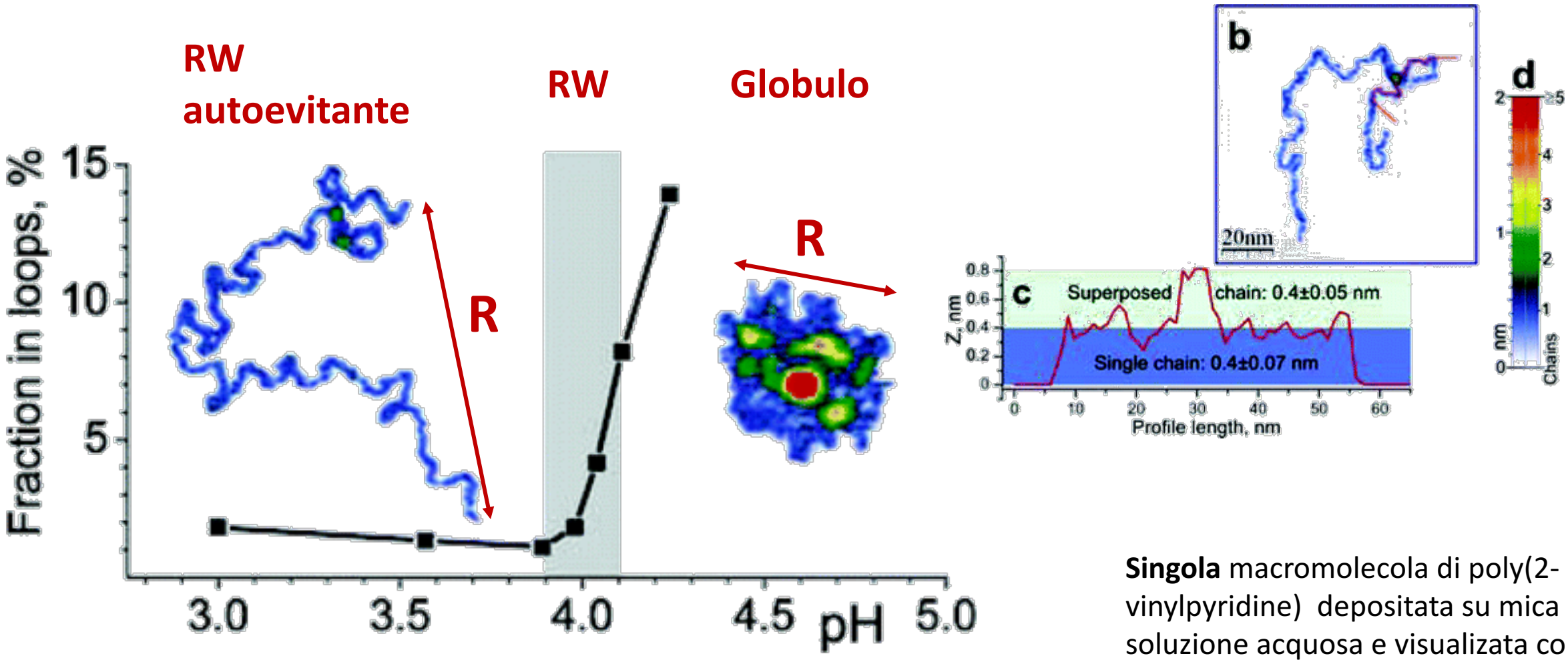


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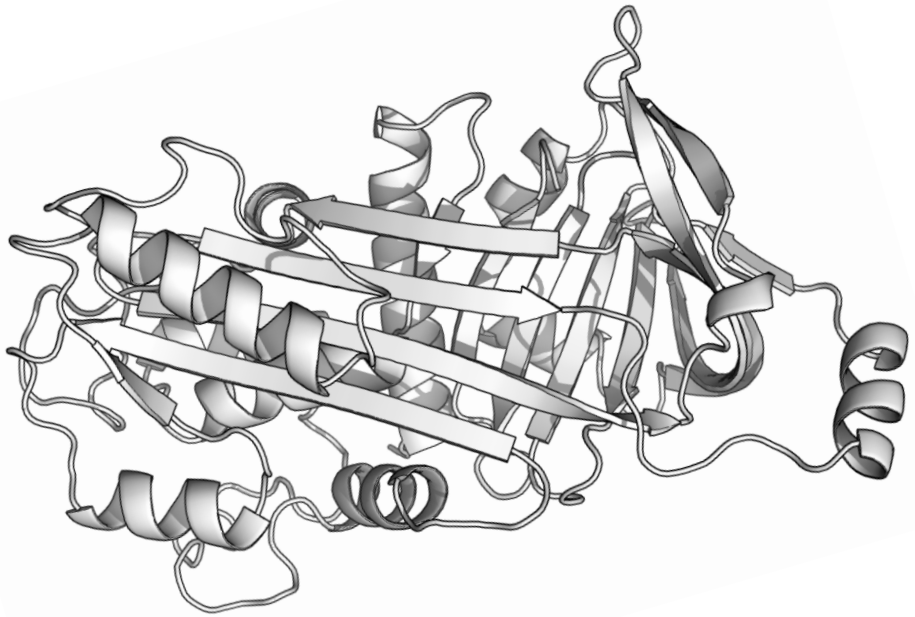
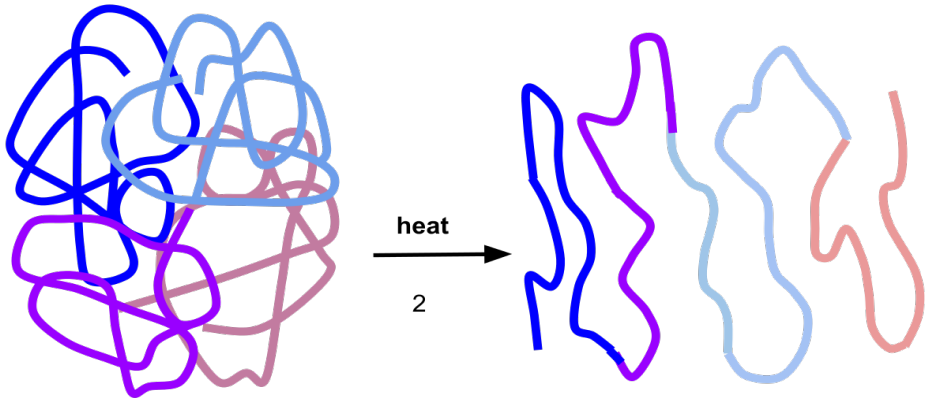
# Transizione “coil-globule” di singola catena : analogia con la denaturazione delle proteine

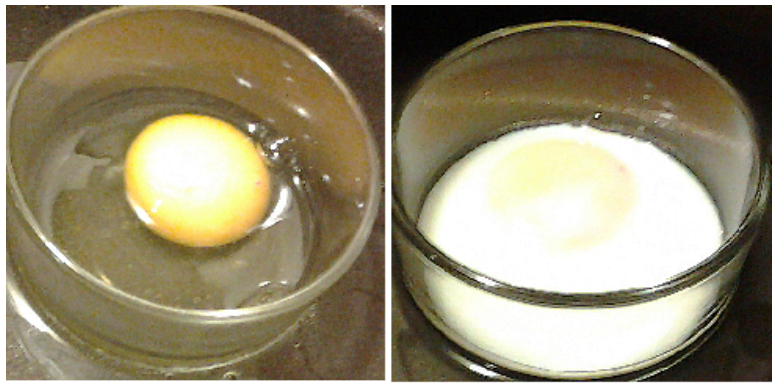


**Ovalbumina**
Notare forma globulare

**Proteina Folded (globulare): funziona**

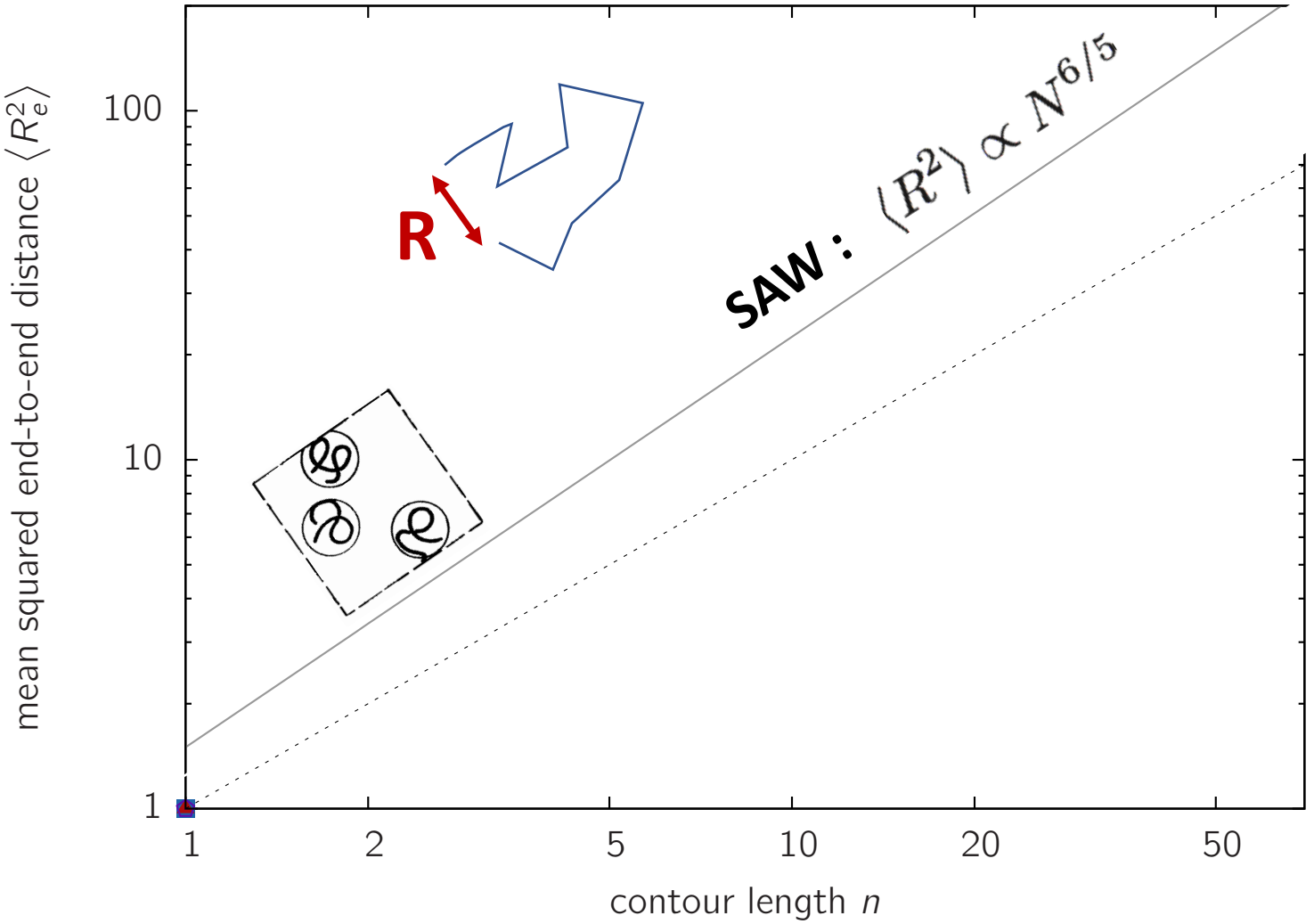
**Proteina Unfolded: non funziona**



L’ ovalbumina, se riscaldata, diventa insolubile

Il disordine <u>semplifica</u> la vita: polimeri come RW se ad <u>alta</u> concentrazione in buon solvente




Bohn, Heermann 2018

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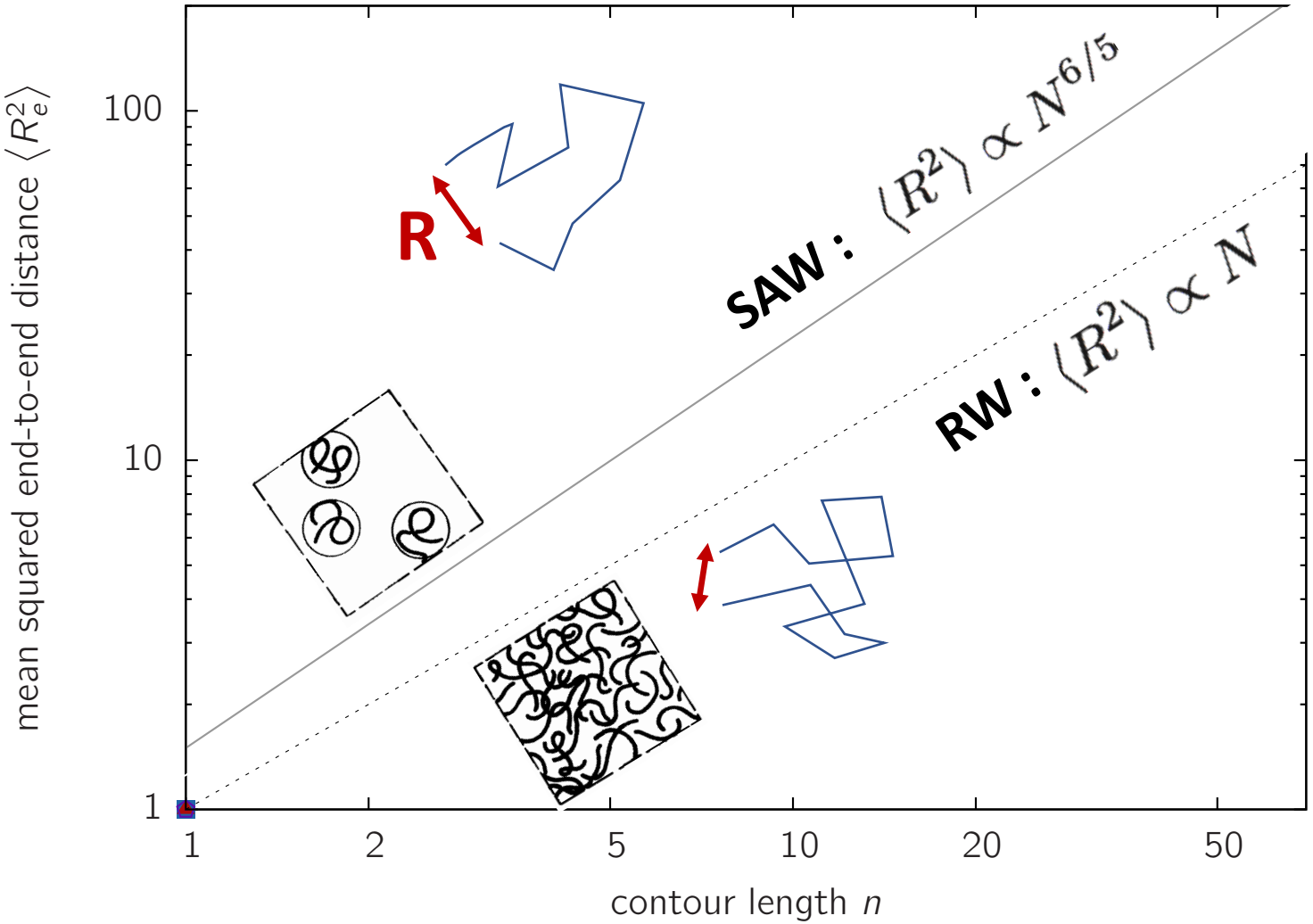


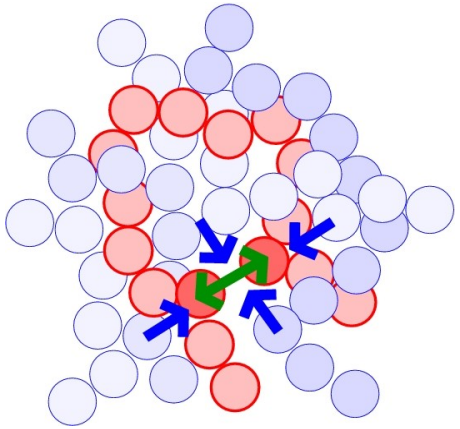

In soluzioni polimeriche ad **alta concentrazione** si verifica la mutua cancellazione degli opposti effetti di:

- Volume escluso
- Pressione osmotica

Bohn, Heermann 2018

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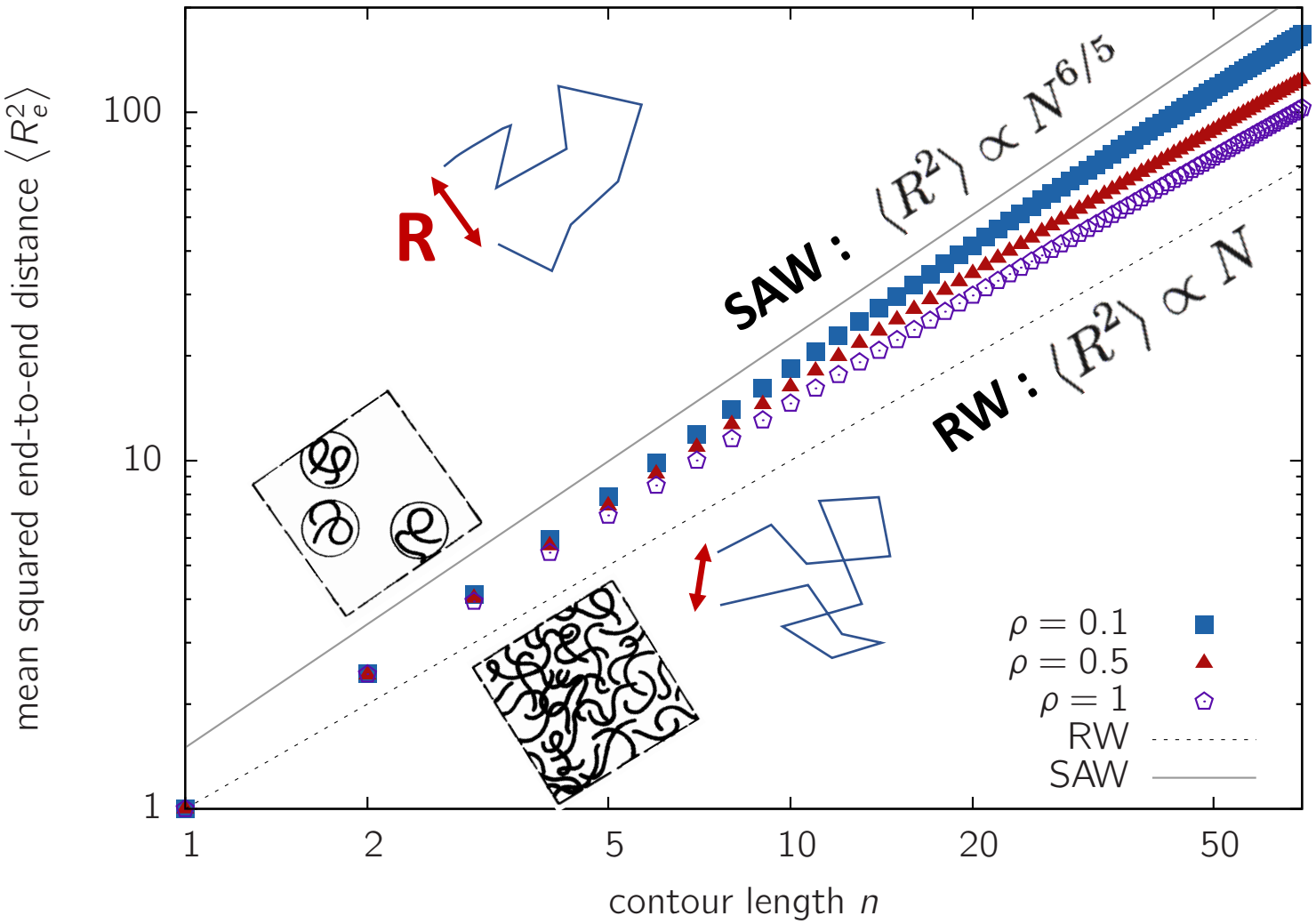


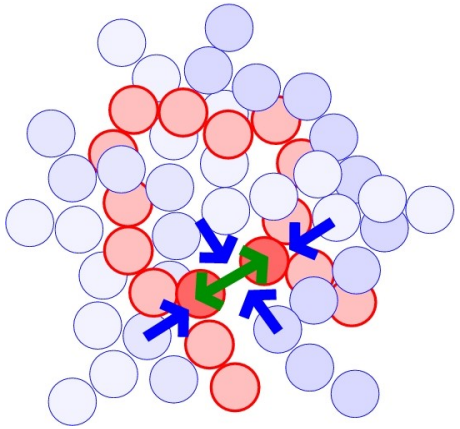

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Bohn, Heermann 2018

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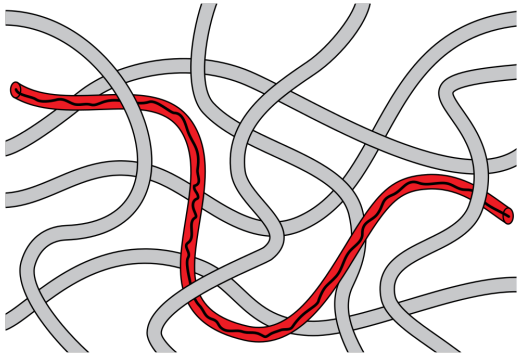

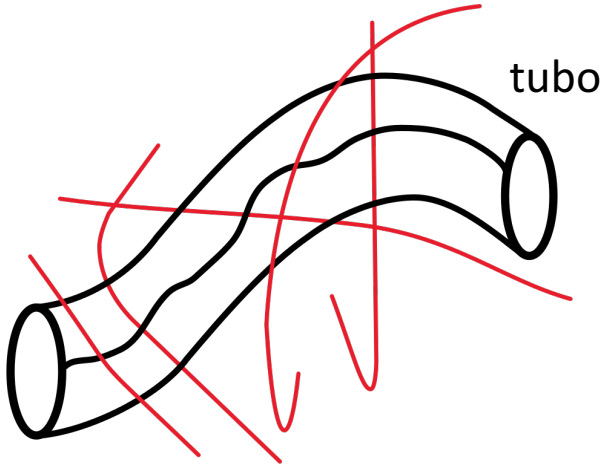


S. Edwards

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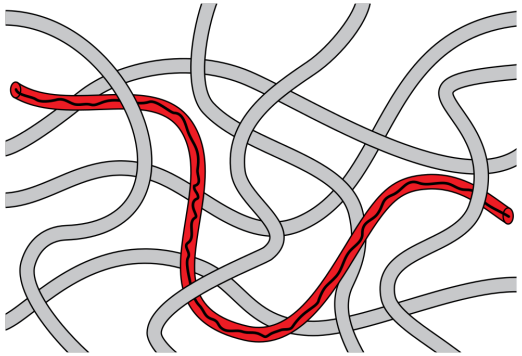
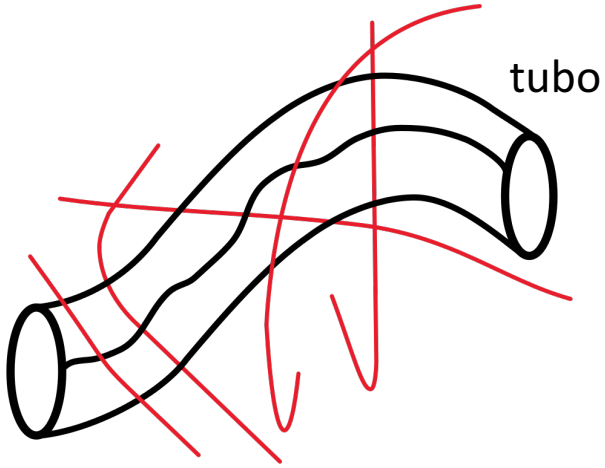
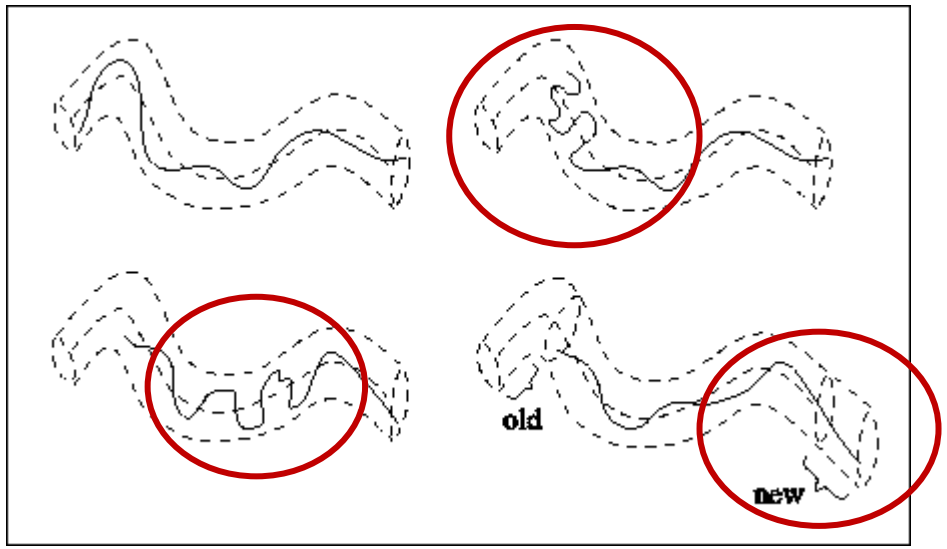





S. Edwards

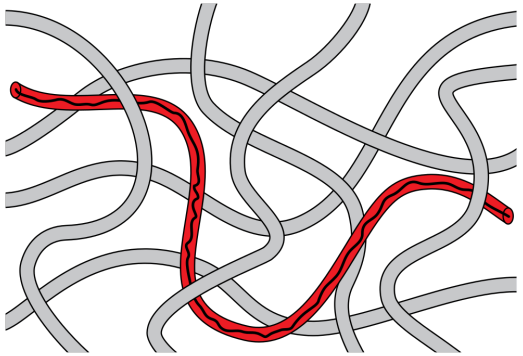
P.G. De Gennes, Nobel (Fisica) 91

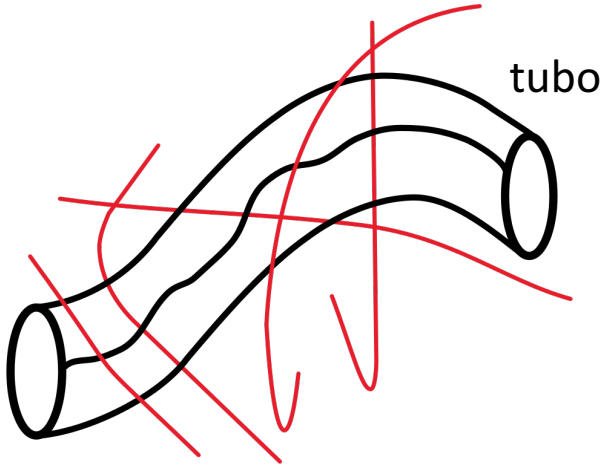



Moto di reptazione di un polimero nel tubo costituito dai suoi vicini

# Il disordine semplifica la vita: polimeri come serpenti in un tubo se ad alta concentrazione





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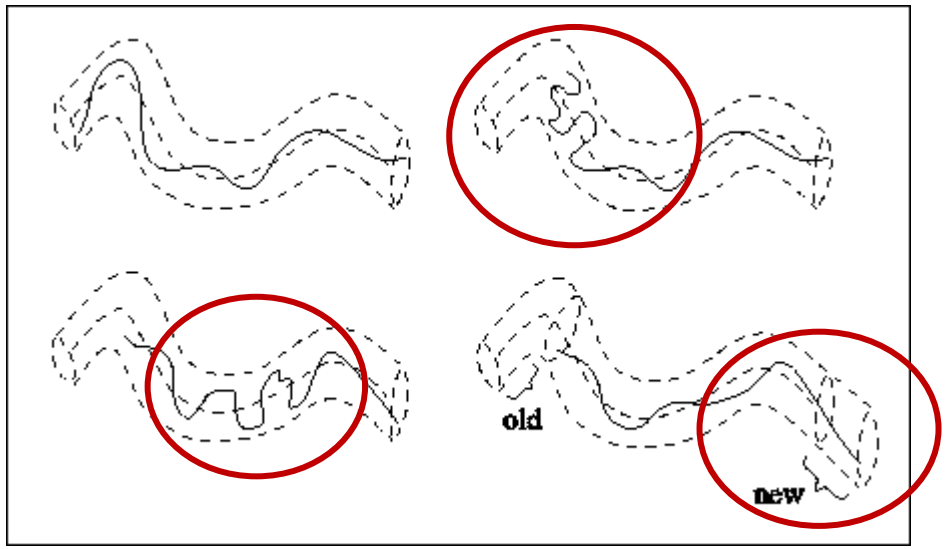
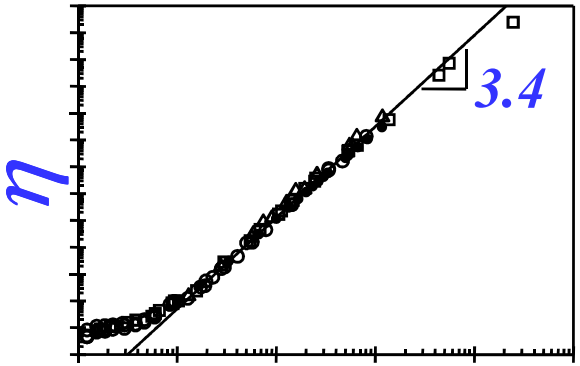



Moto di reptazione di un polimero nel tubo costituito dai suoi vicini

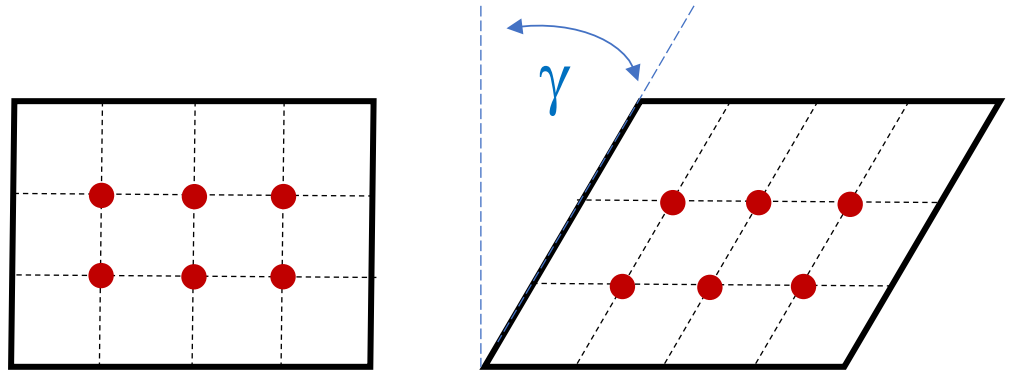
Scaling **universale** della viscosita' con la lunghezza della catena polimerica



# Solidi disordinati (vetri): non-affinita' e disomogeneita' elastica

$$\mathbf{R} = \mathbf{R}_0 + \mathbf{u}$$

Deformazione affine (omogenea)

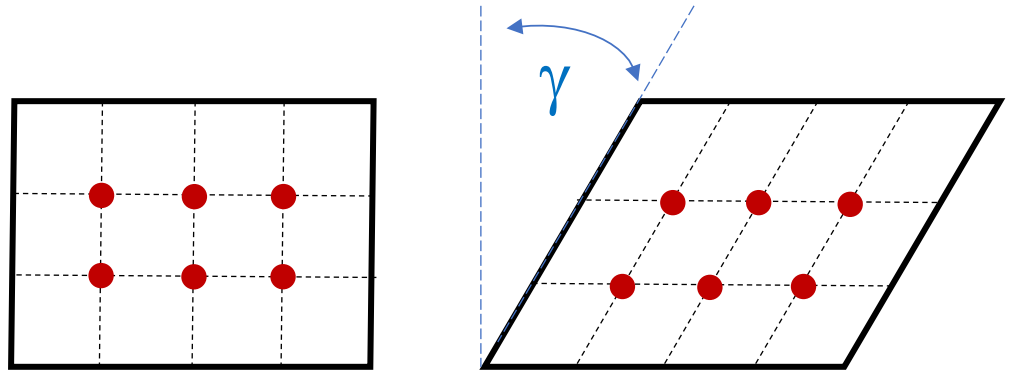



$$\begin{cases} u_x = \gamma\, y \\ u_y = 0 \end{cases}$$

# Solidi disordinati (vetri): non-affinita' e disomogeneita' elastica

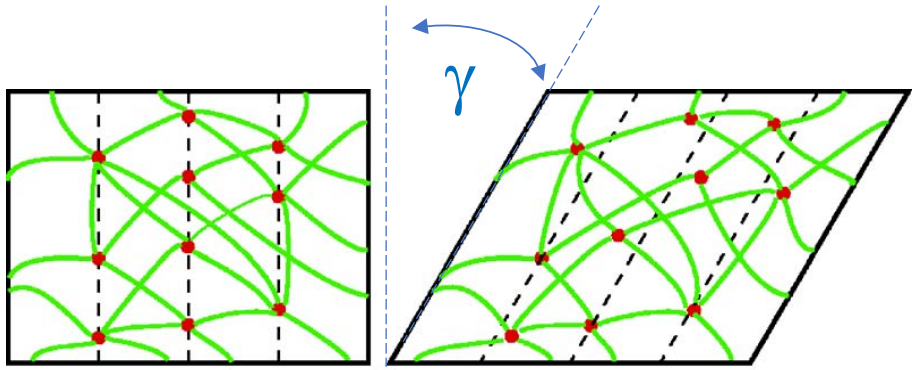
$$\mathbf{R} = \mathbf{R}_0 + \mathbf{u}$$

Deformazione affine (omogenea)




$$\begin{cases} u_x = \gamma\, y \\ u_y = 0 \end{cases}$$

Deformazione non-affine (disomogenea)



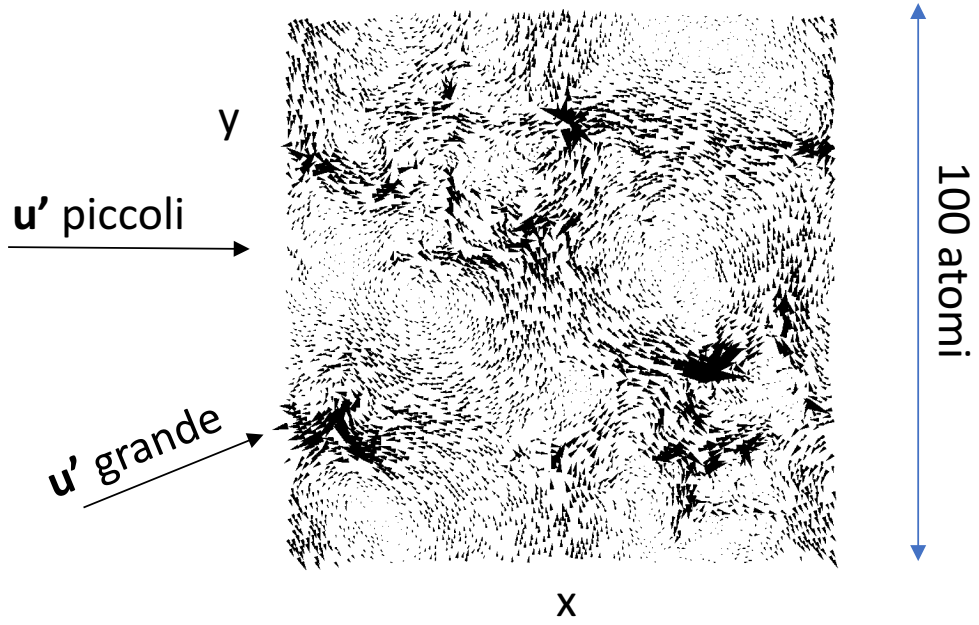

$$\begin{cases} u_x = \gamma\, y + u'_x \\ u_y = u'_y \end{cases}$$

# Solidi disordinati (vetri): non-affinita' e disomogeneita' elastica

$$\mathbf{R} = \mathbf{R}_0 + \mathbf{u}$$

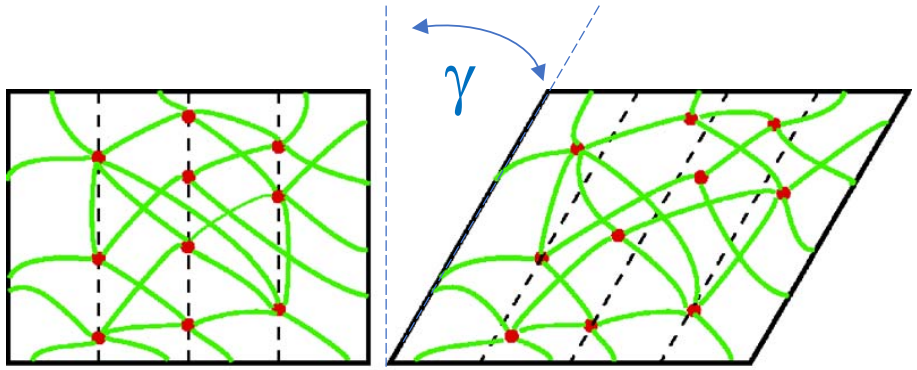
Mappa della deformazione non affine

**Vortici !** Come nella turbolenza…




Lennard-Jones glass (MD)
Tanguy et al, PRB 2002:

Deformazione non-affine (disomogenea)

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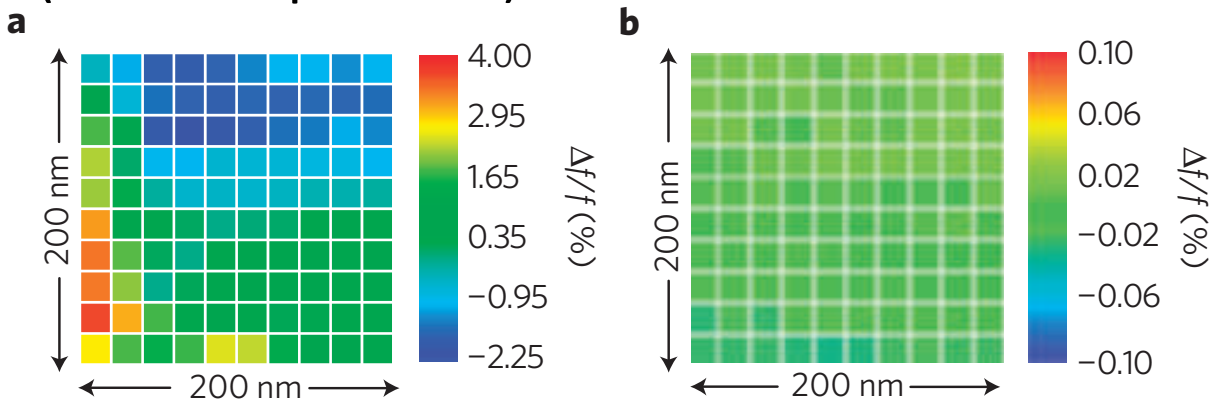
Mappa del modulo elastico locale di PdCuSi (microscopia AFM)

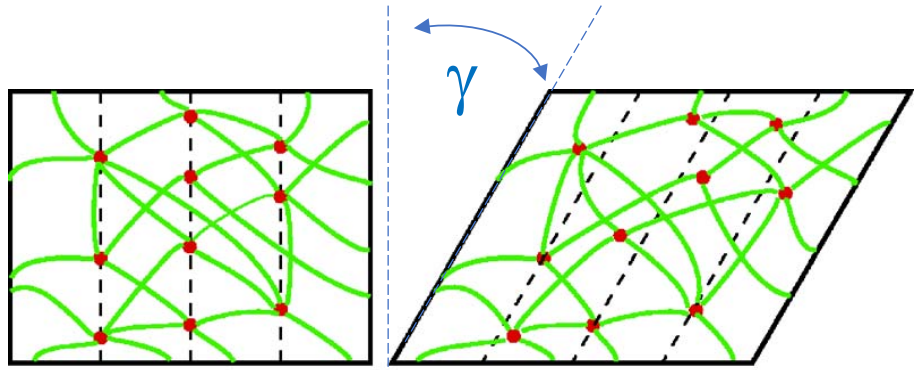



Vetro

Cristallo

Wagner et al, Nature Mat 2011

Deformazione non-affine (disomogenea)

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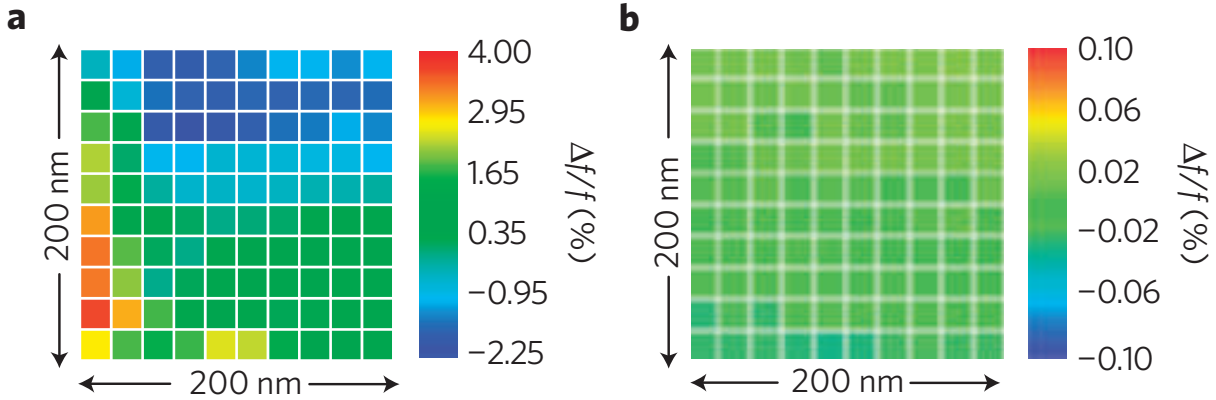
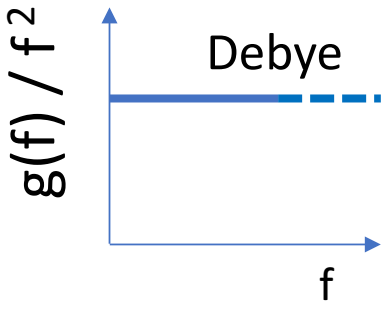



Vetro

Cristallo

Distribuzione modi acustici g(f)




Cristallo

Wagner et al, Nature Mat 2011

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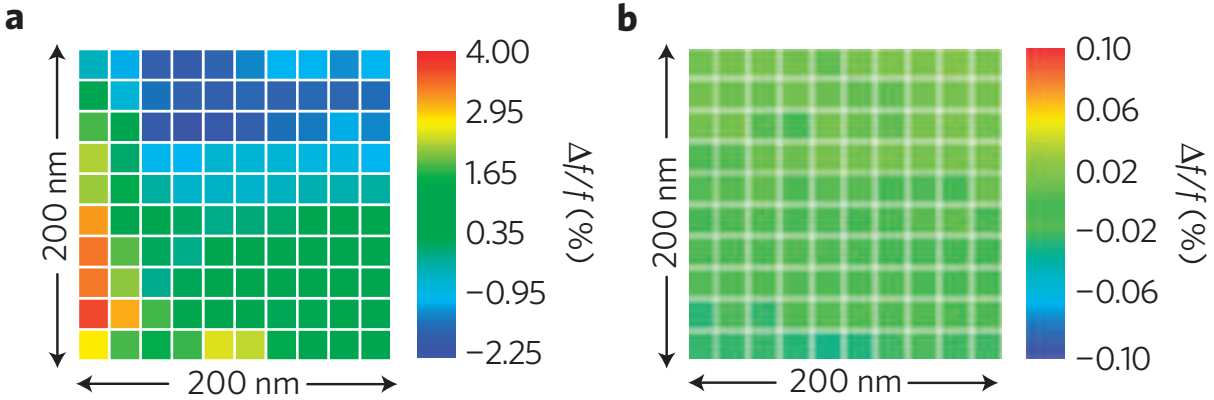
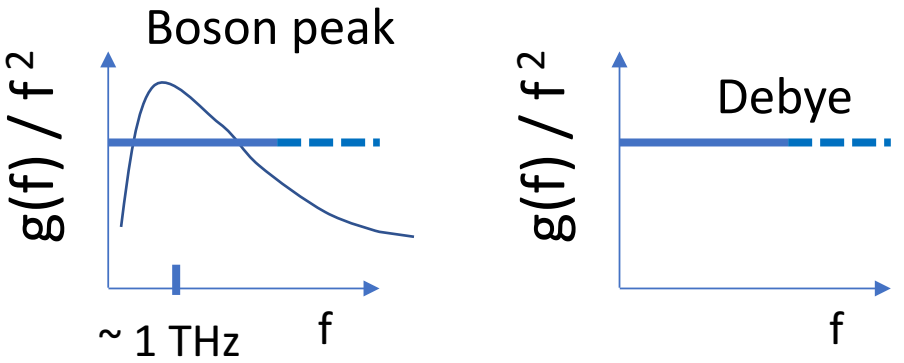



Vetro Cristallo

Distribuzione modi acustici g(f)

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Wagner et al, Nature Mat 2011

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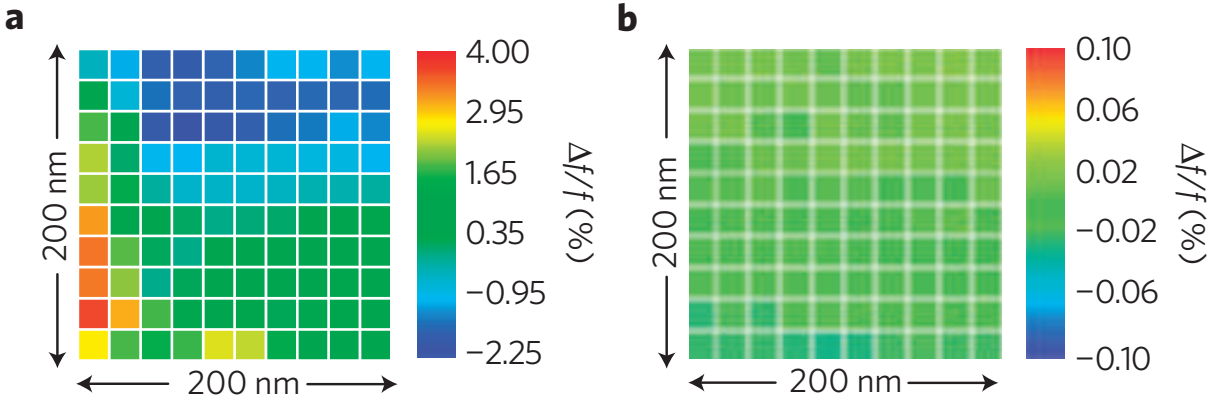


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Wagner et al, Nature Mat 2011

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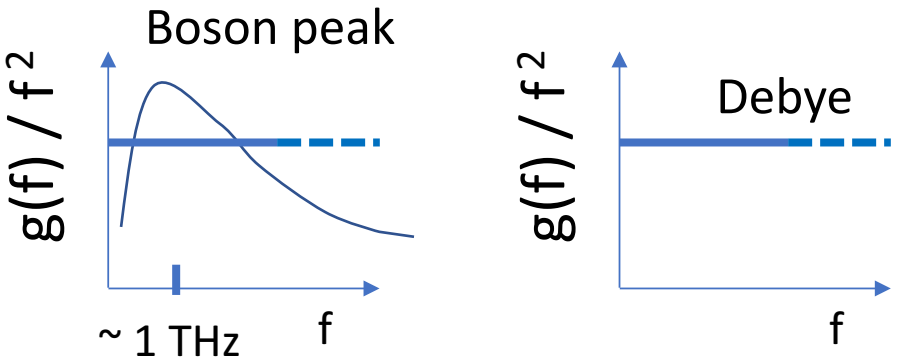
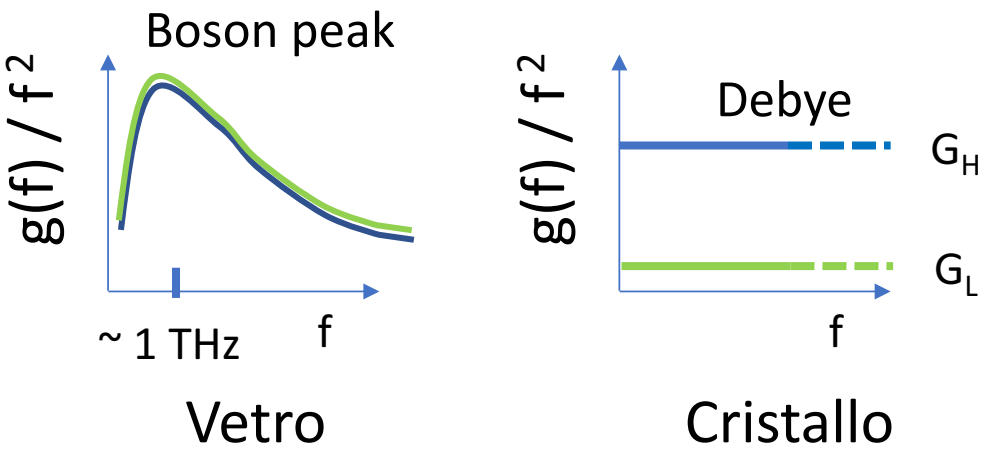



Vetro Cristallo

f ~ 1 THz → λ ~ 1 nm. **Domanda**: Il vetro e' omogeneo come un cristallo sulla scala di ~ 1 nm ?

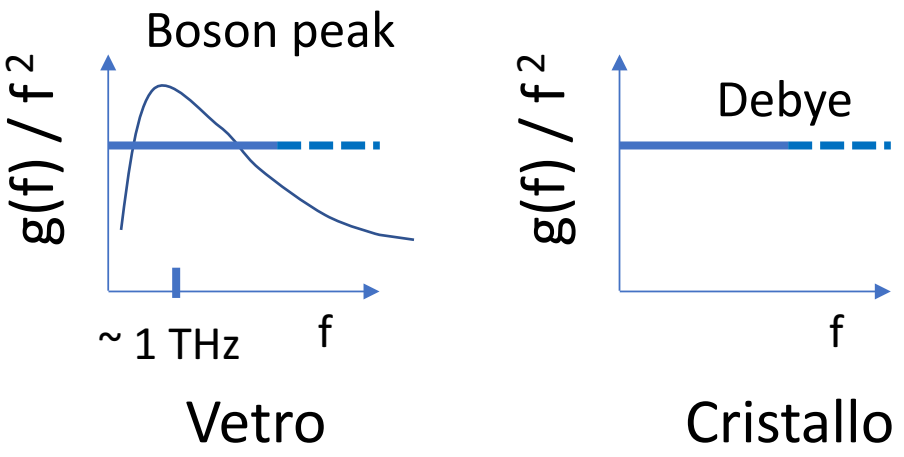
# Solidi disordinati (vetri): modi vibrazionali acustici e disomogeneita' elastica

**No**, se il vetro e' a "bassa connettivita'"




Giuntoli, DL, PRL 2018

Distribuzione modi acustici g(f)

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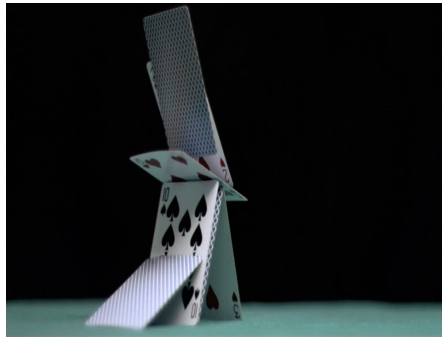
# Solidi disordinati (vetri): modi vibrazionali acustici e disomogeneita' elastica

"Boson peak" -> eccesso di **modi a bassa frequenza ("soffici")** rispetto ai cristalli -> instabilita', dissipazione e plasticita'

Presenza di modi soffici

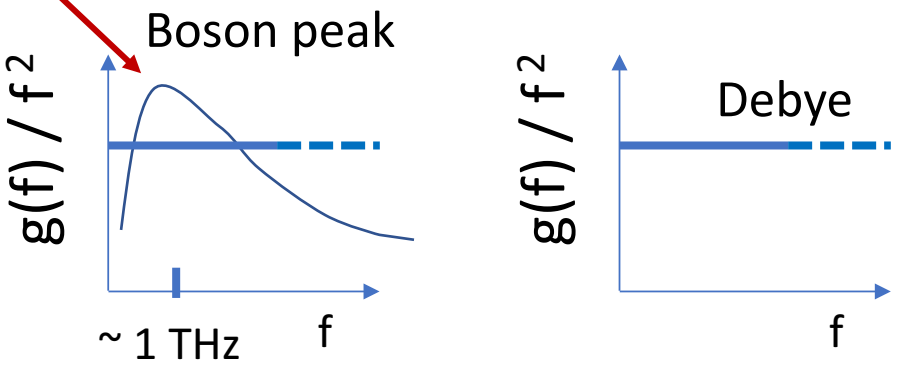


Assenza di modi soffici

ponteggio

Perche' me ne devo preoccupare ?

Distribuzione modi acustici g(f)




Vetro

Cristallo

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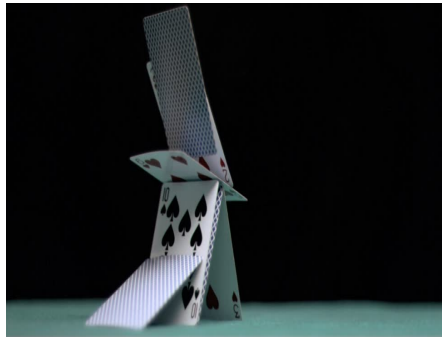

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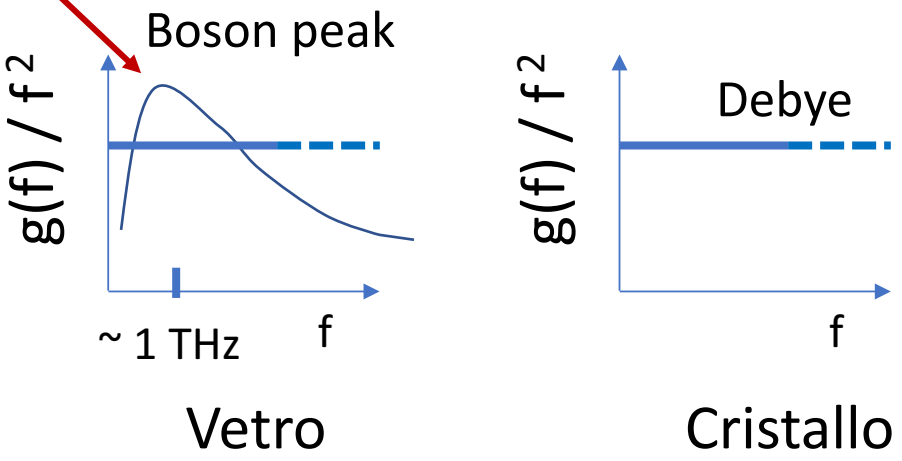

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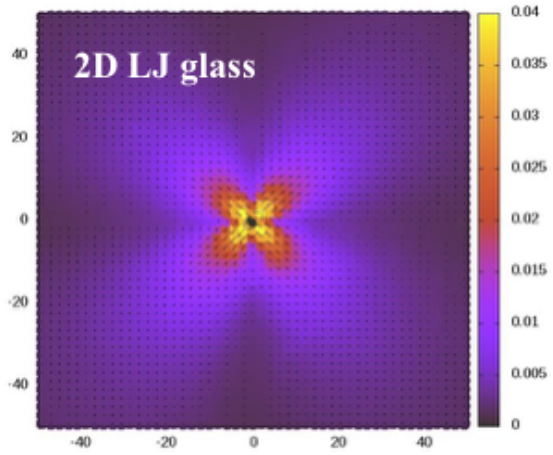
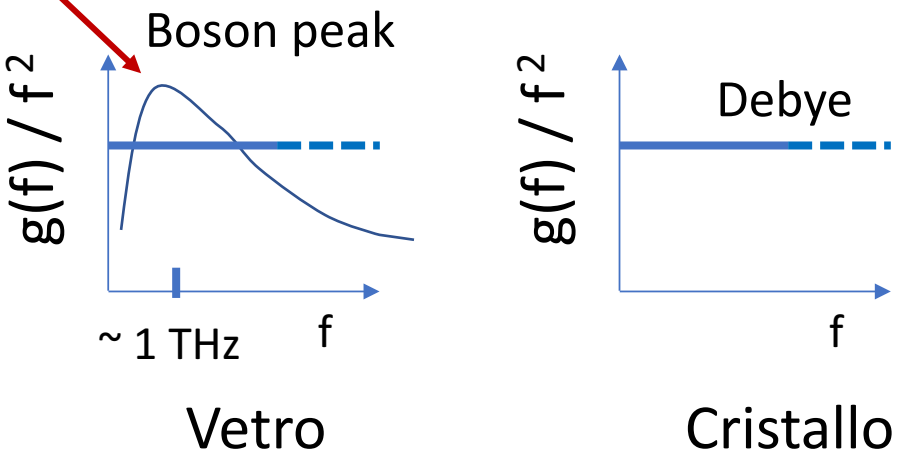
Valanga di eventi **plastici**
F. Puosi (unpublished)

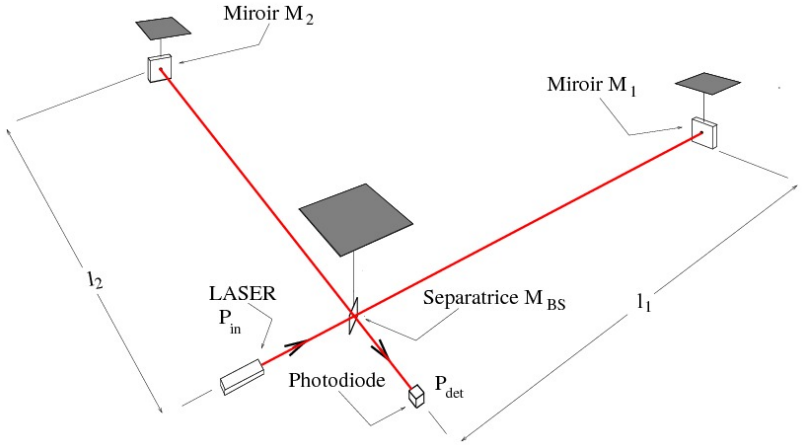



Evento **plastico** quadrupolare
F. Puosi et al, PRE 2014

Distribuzione modi acustici g(f)



Interferometro VIRGO
per la rivelazione di
onde gravitazionali




F. Puosi, DL, S. Capaccioli, D. Pisignano and F. Fidecaro

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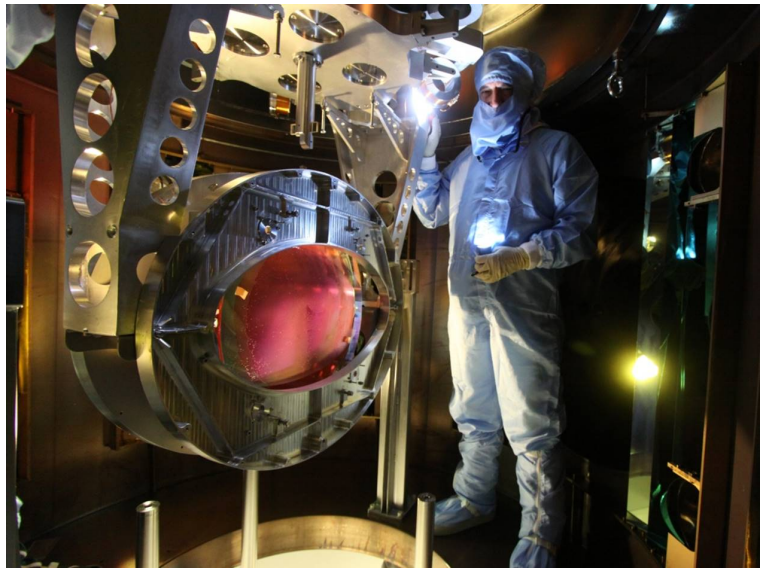
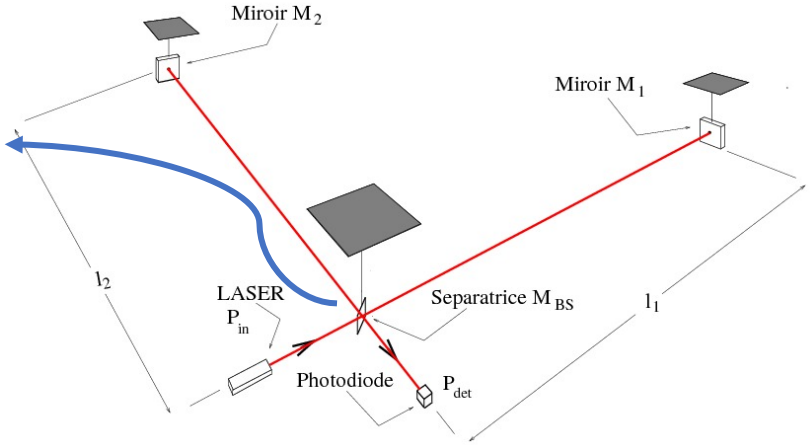


Beam splitter ( 34 kg, 55 cm ø)

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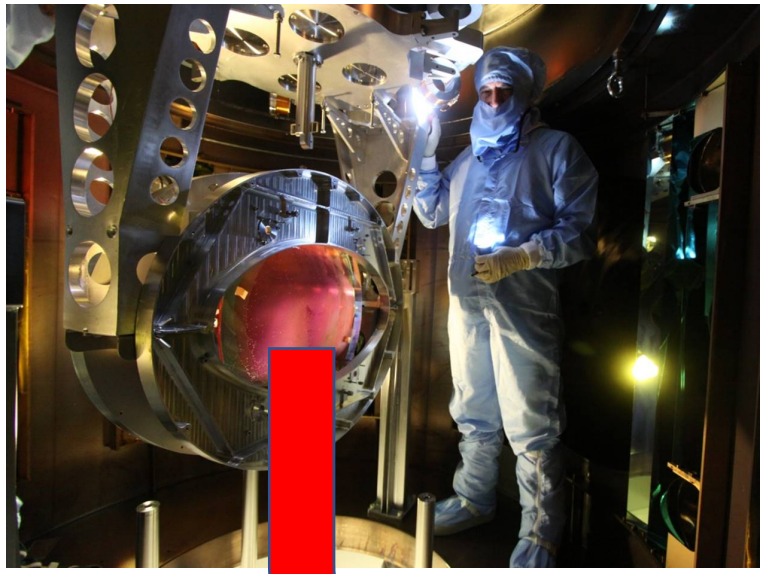
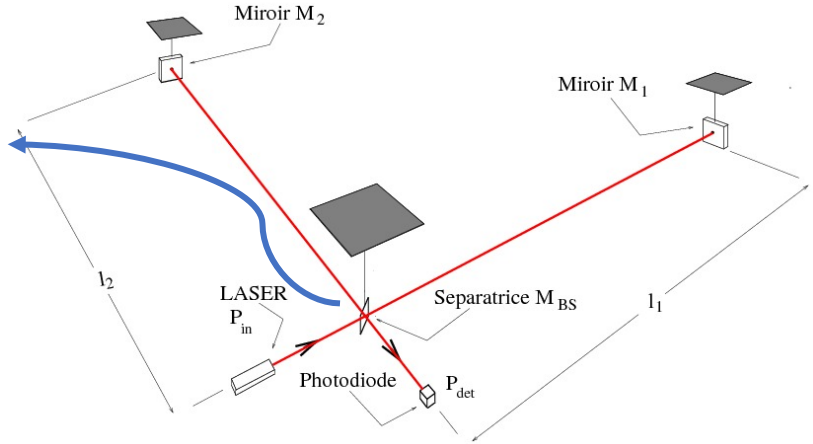
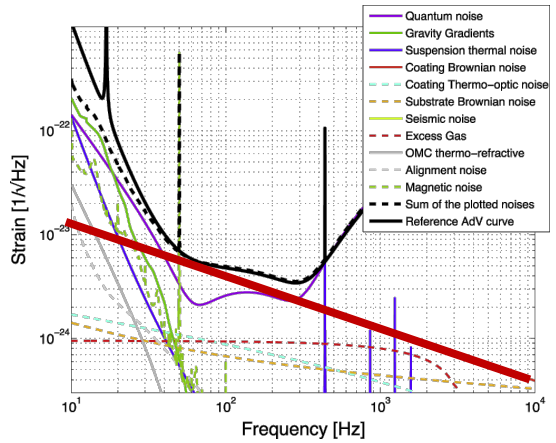


Beam split[illegible] 34 kg, 55 cm ø)




**<u>Obiettivo</u>**:
Spettroscopia dinamico-meccanica *in-silico*
per la riduzione del rumore termico
negli specchi (solidi disordinati) dell' interferometro

F. Puosi, DL, S. Capaccioli, D. Pisignano and F. Fidecaro

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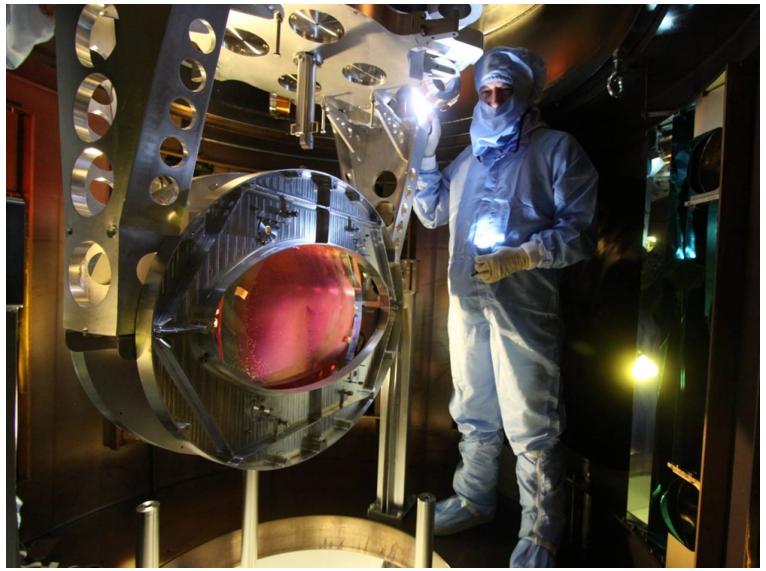
onde gravitazionali



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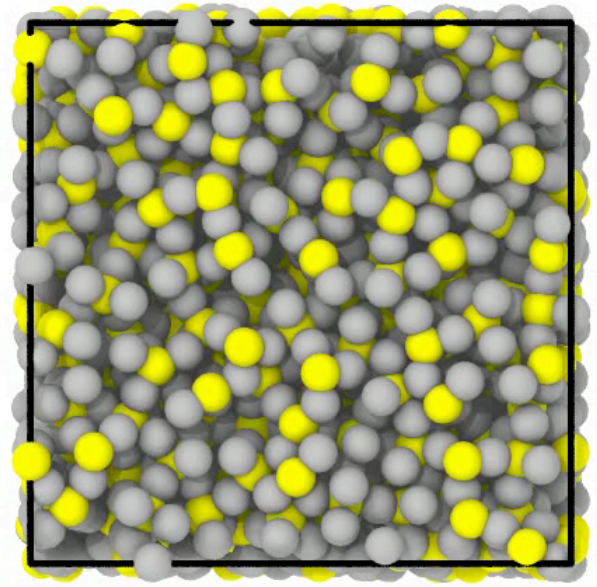


Deformazione di $Ta_2O_5$

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Spettroscopia dinamico-meccanica *in-silico*
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F. Puosi, DL, S. Capaccioli, D. Pisignano and F. Fidecaro

# Conclusioni:

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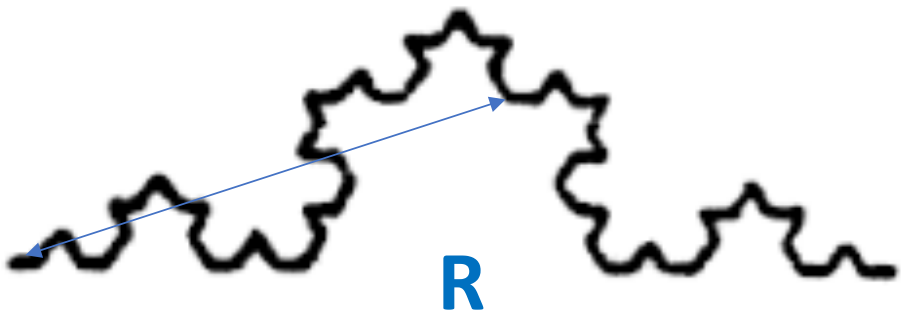
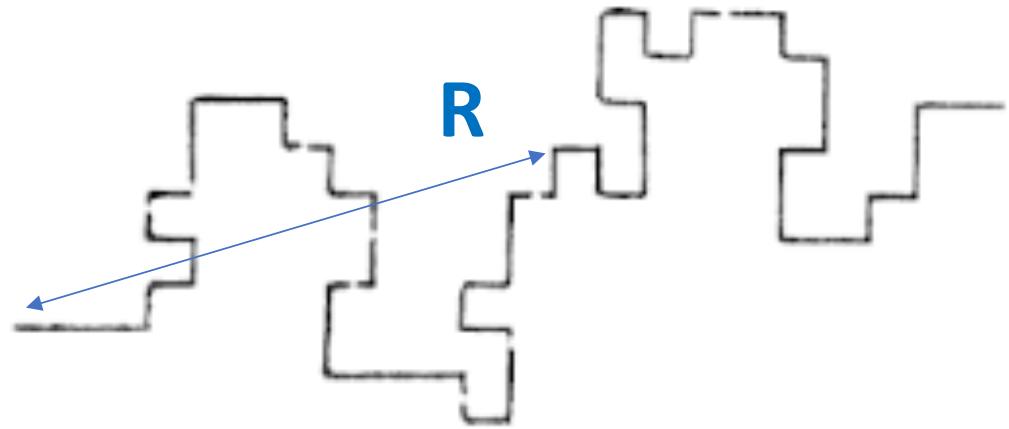
- I sistemi disordinati:
  - Aiutano a scoprire l'esistenza degli atomi,
  - Danno una mano a cercare onde gravitazionali.

# **Κόσμος (** kósmos ) : ordine, universo (Pitagora)

- Scala microscopica: ordine
- Scala meso- e macro-scopica: disordine (passaggio graduale)
  - Statistica
    - Multiscala (lunghezza, tempo):
    - **Correlazioni** tra scale causati da vincoli, moti cooperativi -> Autosimilarita', autoaffinita'
    - **Correlazioni** spaziali: impaccamento
    - Correlazioni temporali: polimeri (esistono modi come in teoria piccole oscillazioni o cristallo armonico?)
    - Isteresi: dipendenza dalla storia: fuori equilibrio, memoria (elasticita'), perdita di memoria (viscosita')
    - Viscoelasticita'




Deterministic fractal: curva di Koch

Statistical fractal : self-avoiding random walk

$R = n^{\alpha}$

$\alpha = \log 3 / \log 4 \sim 0.79$

$< R^2 >^{1/2} = n^{\alpha}$

$\alpha = 3/5 = 0.6$

# Moto browniano, Einstein, Perrin e l'esistenza degli atomi

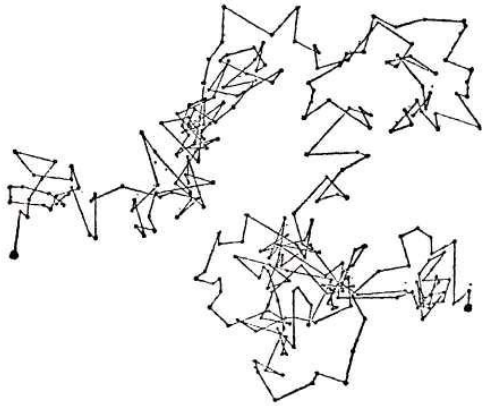
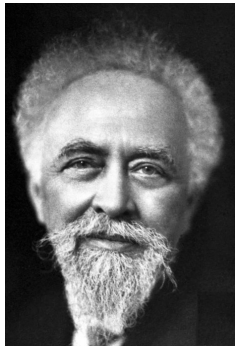
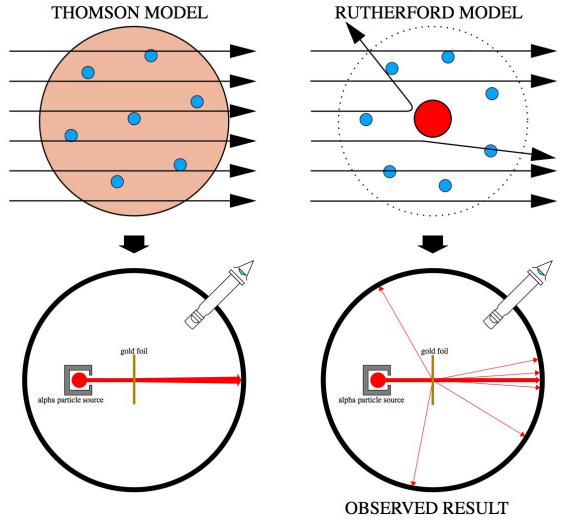


Fig. 8.

J. Perrin, 1912

73. Parfaite irrégularité de l'agitation.






Einstein (1905)

$k_B = 6 \pi a D \eta / T$

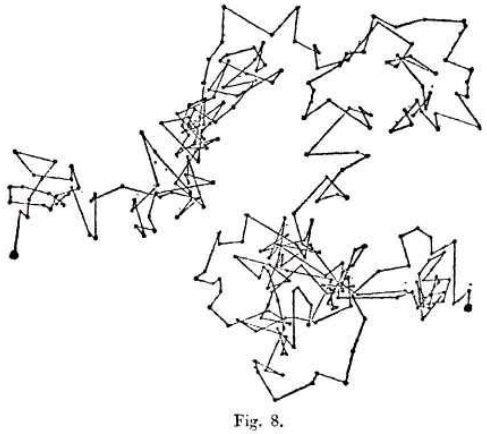
$\langle \Delta r^2 \rangle = 6 D t$

Jean Baptiste Perrin, The Nobel Prize in Physics 1926
"for his work on the discontinuous structure of matter..."

L' esperimento di Rutherford (anche detto esperimento di Geiger e Marsden) fu un esperimento effettuato per sondare la struttura dell'atomo eseguito da Hans Wilhelm Geiger e Ernest Marsden nel **1909**

**During the 1880s atoms and molecules became important scientific concepts, but whether or not they actually had a physical existence was still a matter of dispute**. Jean Perrin maintained that if molecules were real, particles blended into a liquid should not all sink to the bottom but should distribute themselves throughout the liquid. In **1908** he could substantiate this through experimentation. He also substantiated Albert Einstein's theory that Brownian motion - the random movement of small particles in a liquid - was due to collisions between the particles and molecules in the liquid. ( Source: https://www.nobelprize.org/prizes/physics/1926/summary/ )

# Liquidi: il moto browniano

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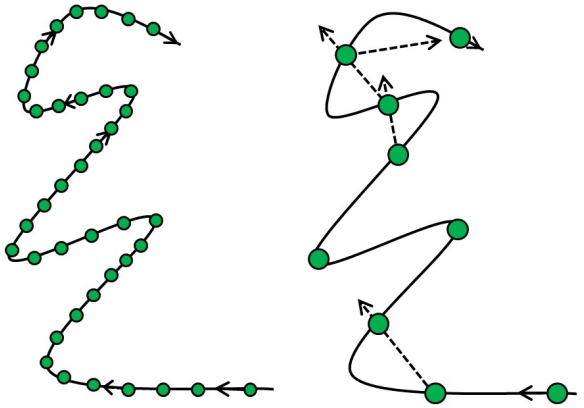
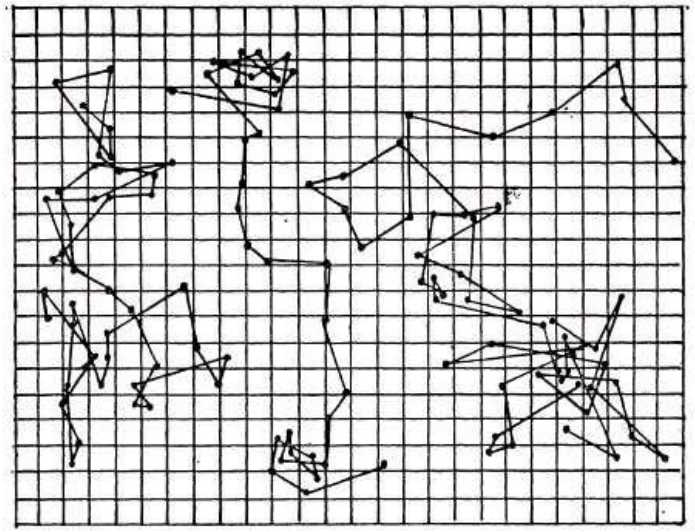
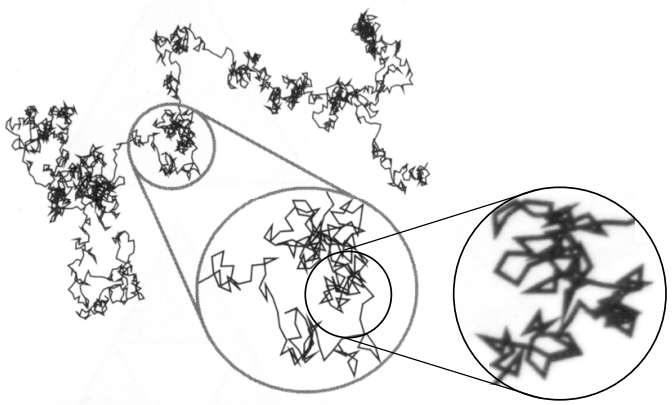
J. Perrin, 1912



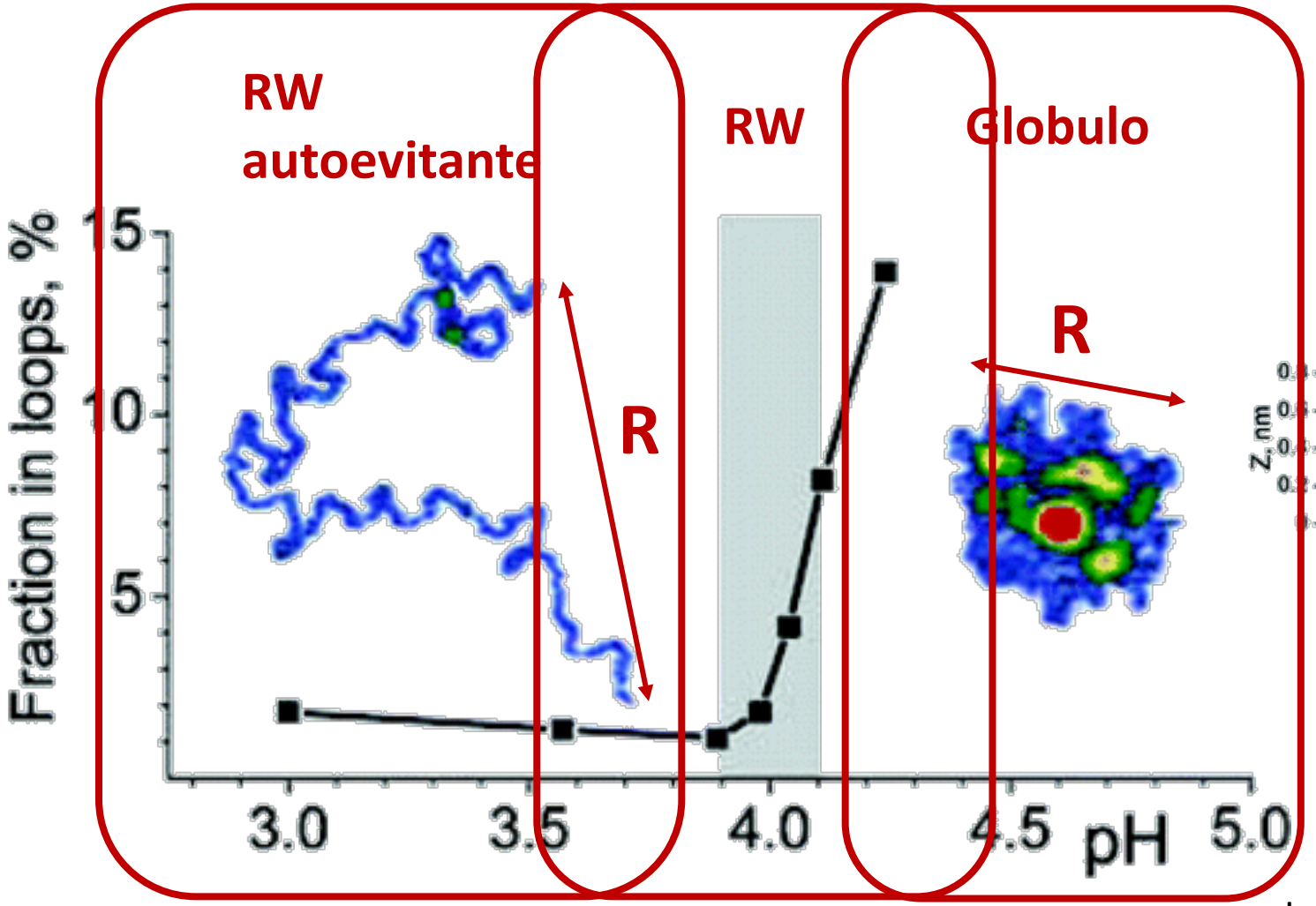
Traiettoria reale

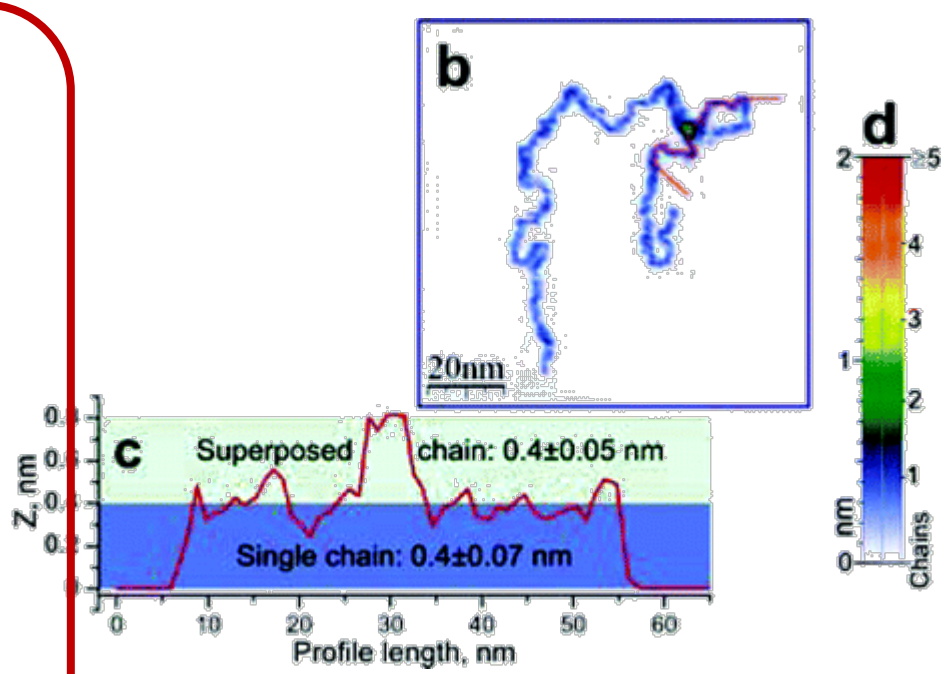
Traiettoria campionata



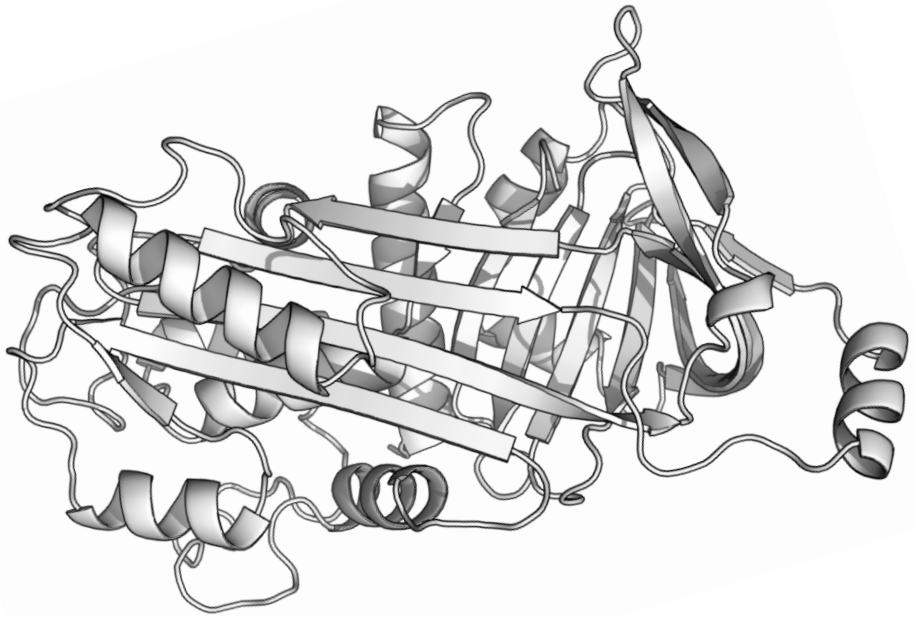
# Transizione “coil-globule” di singola catena: un esempio di transizione disordine-disordine




poly(2-vinylpyridine) su mica in soluzione acquosa
Roiter and Minko, JACS 2005

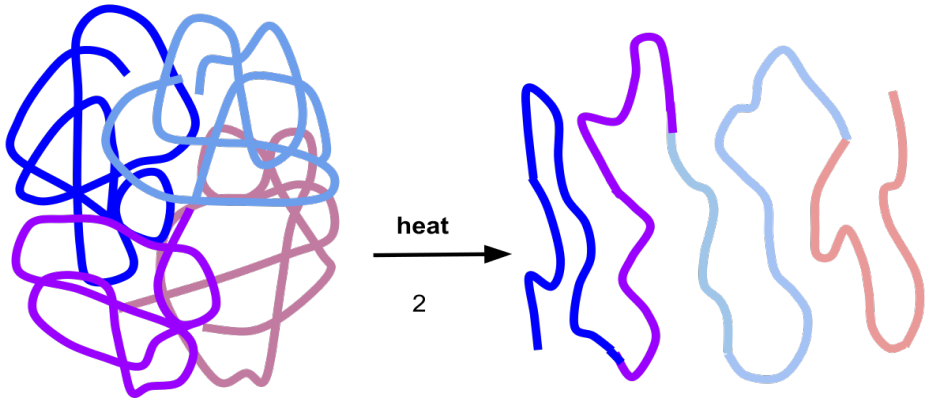
# Transizione “coil-globule” di singola catena : analogia con la denaturazione delle proteine

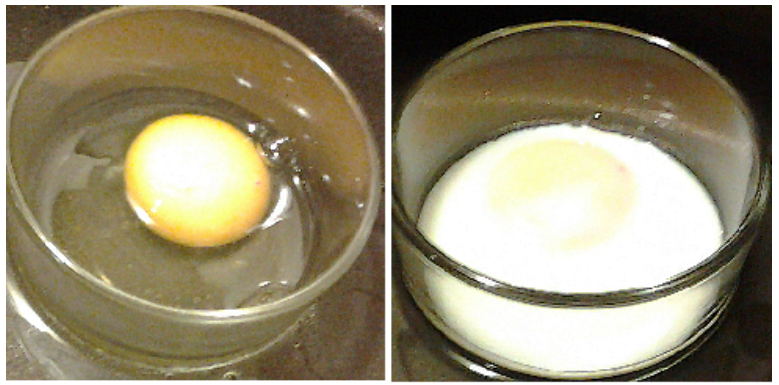


**Ovalbumina**
Notare forma globulare

**Proteina Folded (globulare): funziona**

**Proteina Unfolded: non funziona**



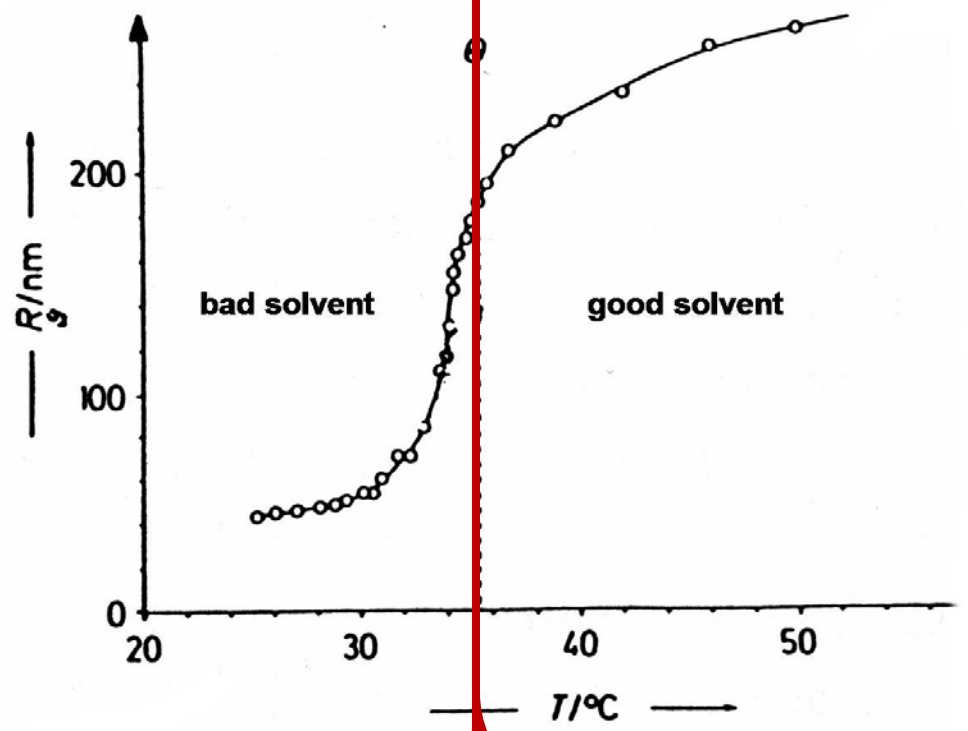



L’ ovalbumina, se riscaldata, diventa insolubile

# Transizione “coil-globule”: analogia con la denaturazione delle proteine

**Globulo**

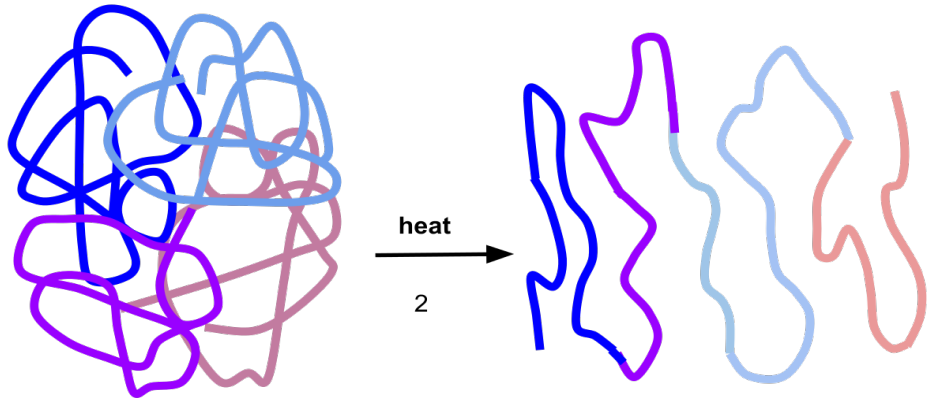
**RW autoevitante**

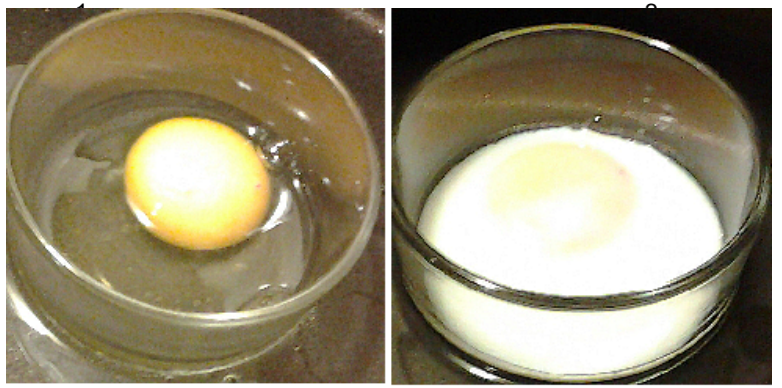



Polistirene in cicloesano

**Proteina Folded: funziona**

**Proteina Unfolded: non funziona**



L’ albumina, se riscaldata, diventa insolubile