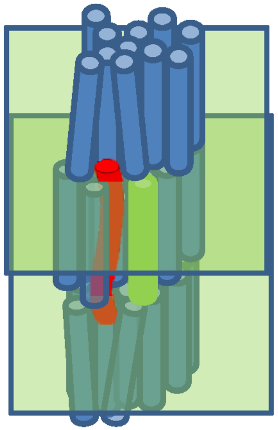


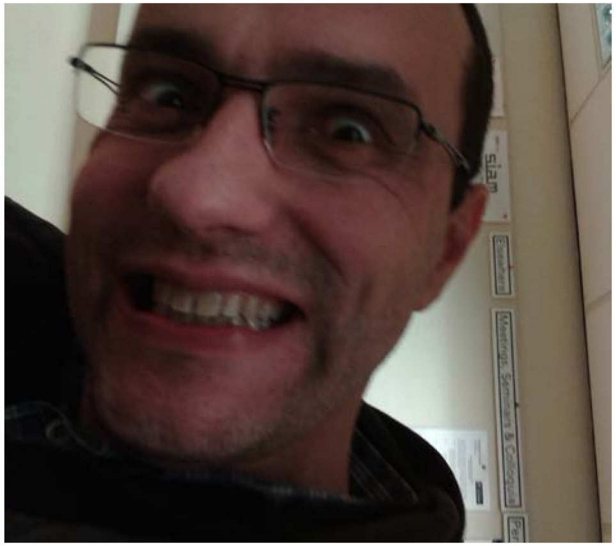
When bigger is faster: how non-commensurability in particle size favors self-diffusion in smectics.

Rotterdam, 24th of June 2018| Pavlik Lettinga

Acknowledgements

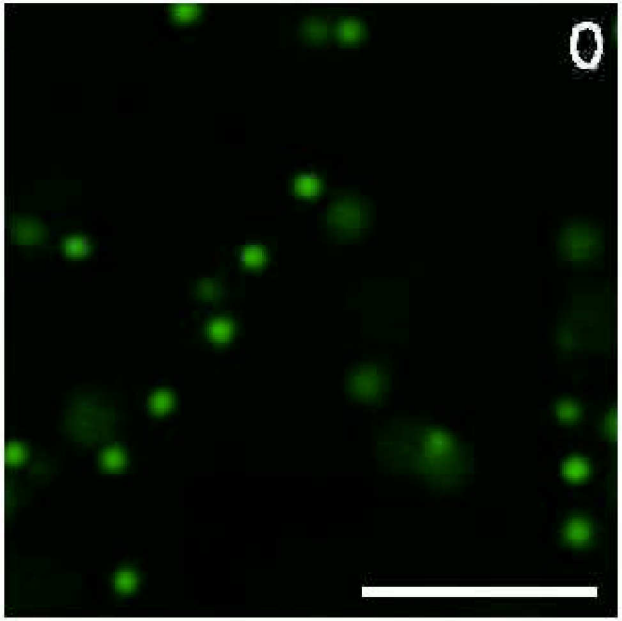
Eric Grelet

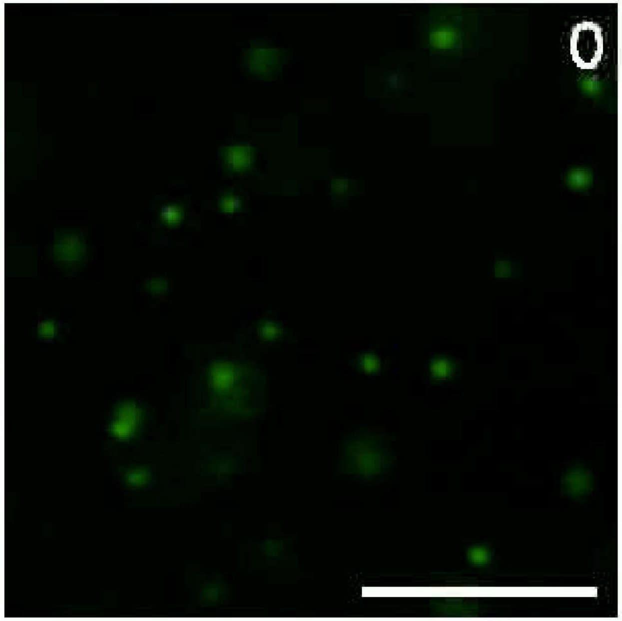
Laura Alvarez

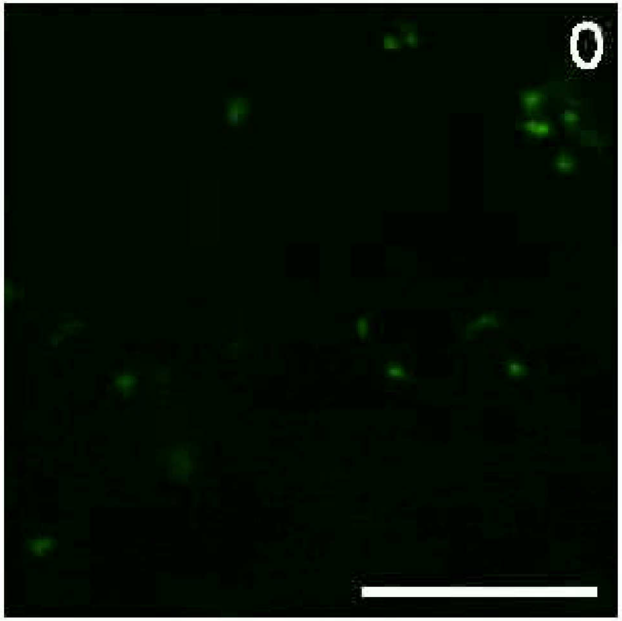


Dynamics of colloids

Dynamics of colloids







E.R. Weeks, Austin

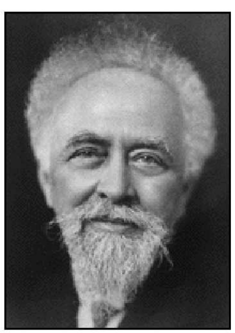
a = 1.5 μm   1.0 μm   0.5 μm

G.G. Stokes

A. Einstein

Stokes-Einstein: big is slow

$$D = \frac{RT}{N}\frac{1}{6\pi k P} = \frac{k_b T}{6\pi\eta_0 a}$$



J.B. Perrin

Mean square displacement and Self-van Hove function

$$W(t) = \frac{1}{N}\sum_{i=1}^{N}\langle[\mathbf{r}_t^2 - \mathbf{r}_0^2]\rangle$$

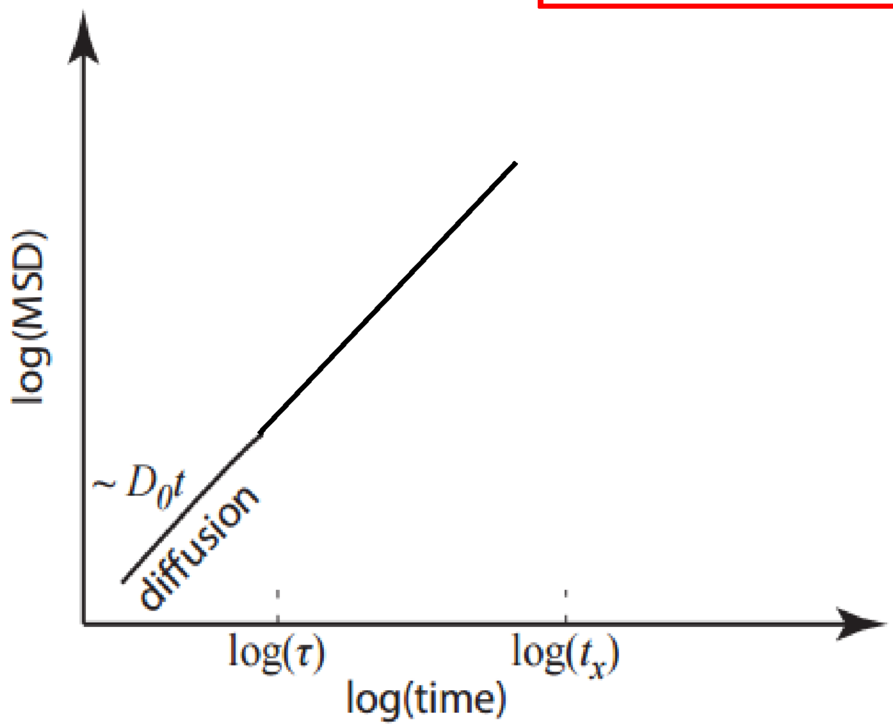
Free particles: $= 6D_0$

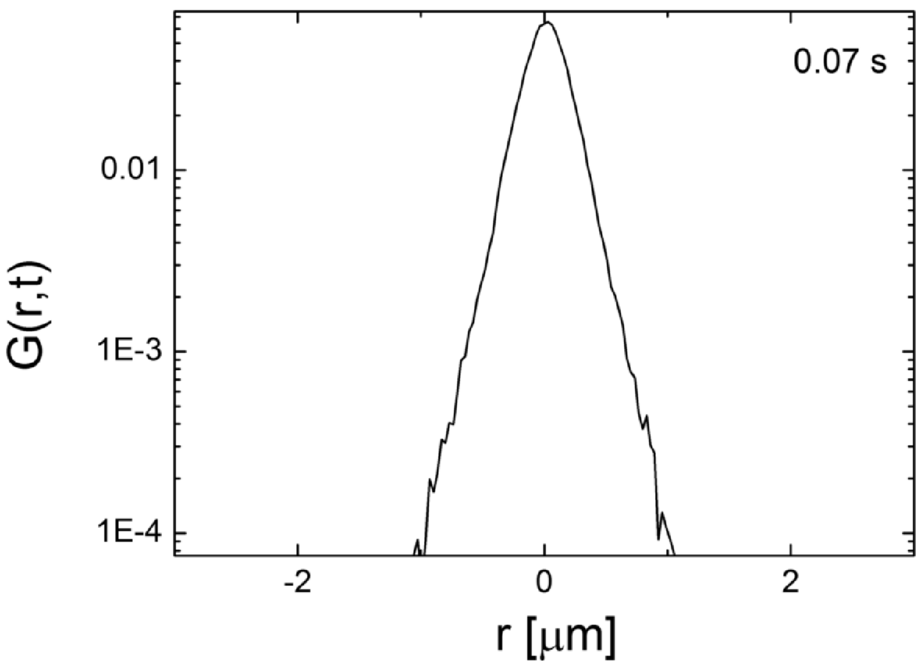
Probability for displacement r during time t :

$$G_s(t) = \frac{1}{N}\sum_{i=1}^{N}\delta[\mathbf{r} - (\mathbf{r}_i(t)) - \mathbf{r}_i(t=0))]$$

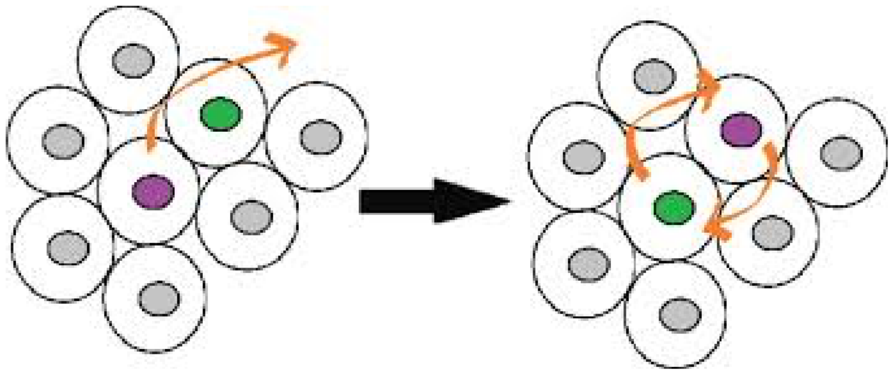
$$= (4\pi Dt)^{-3/2}\exp\left(-\frac{r^2}{4Dt}\right)$$

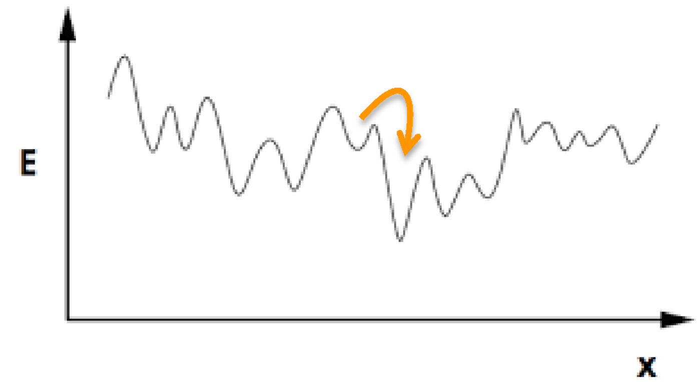
Diffusion is continuous process

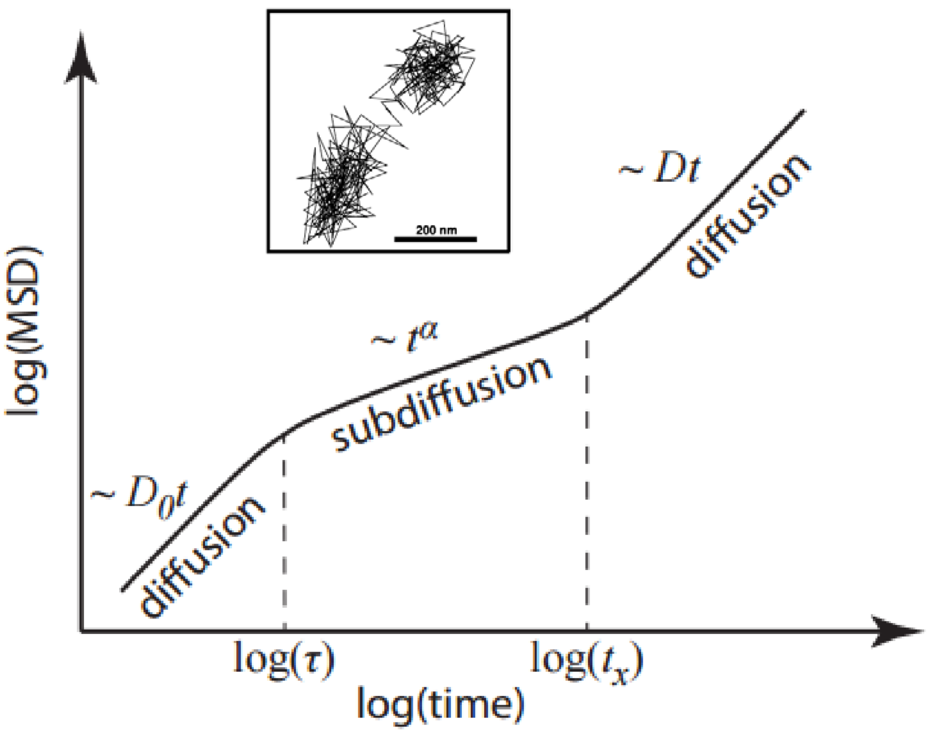


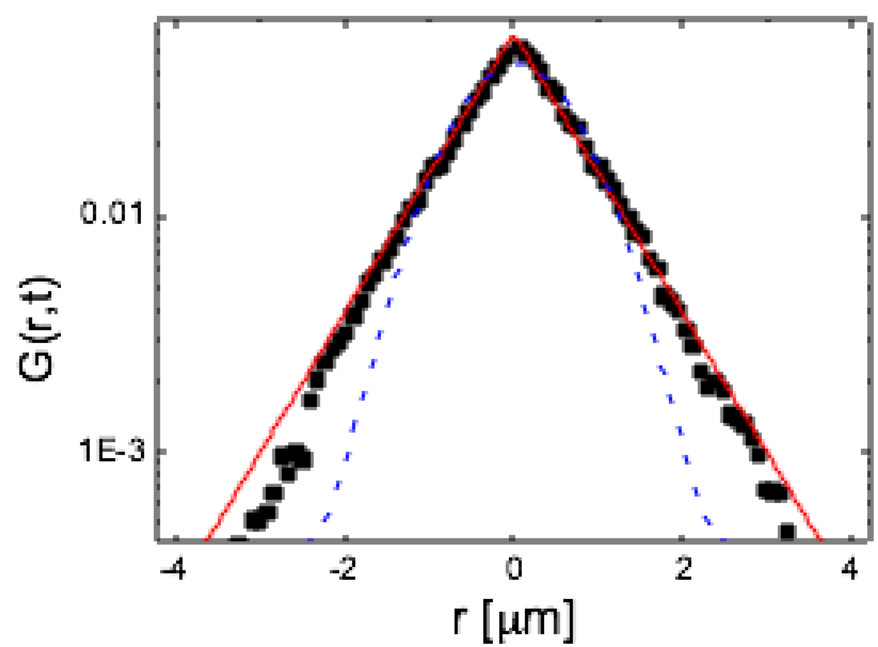


Diffusion in complex hosts: colloidal glasses



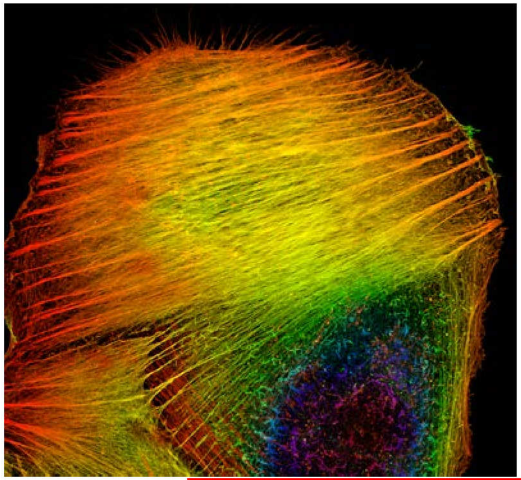


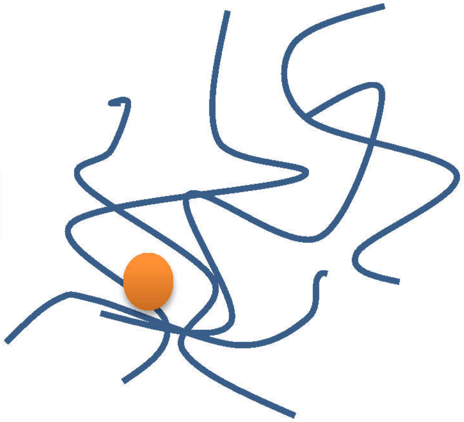




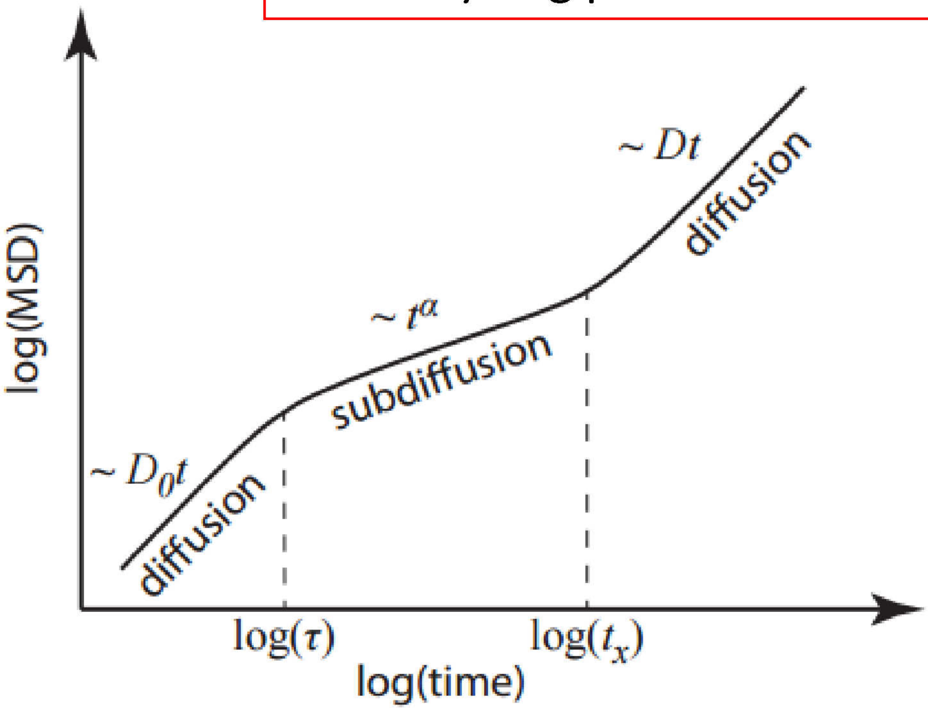
Weeks et al, Science., 2000

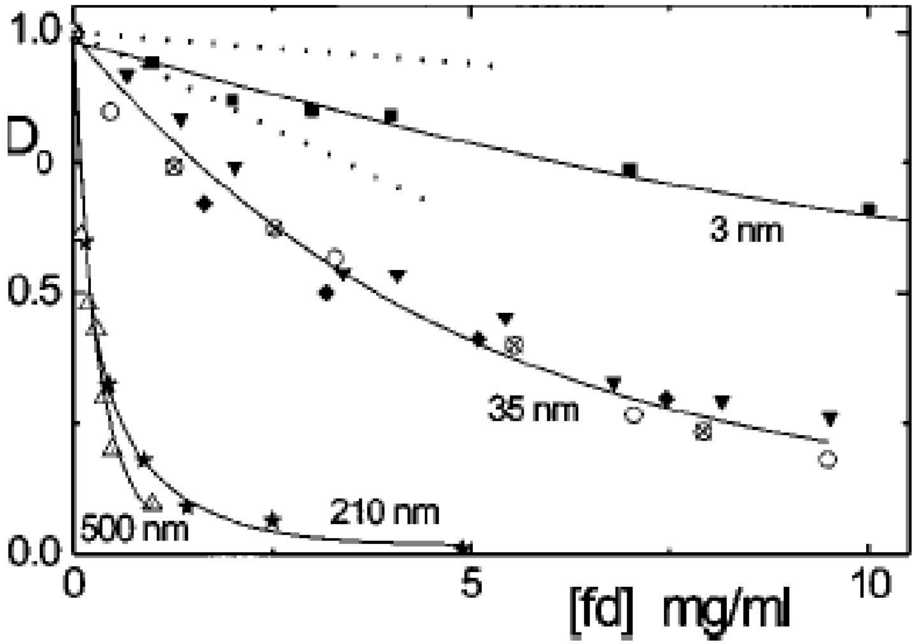
Diffusion in complex hosts: local probing of the host





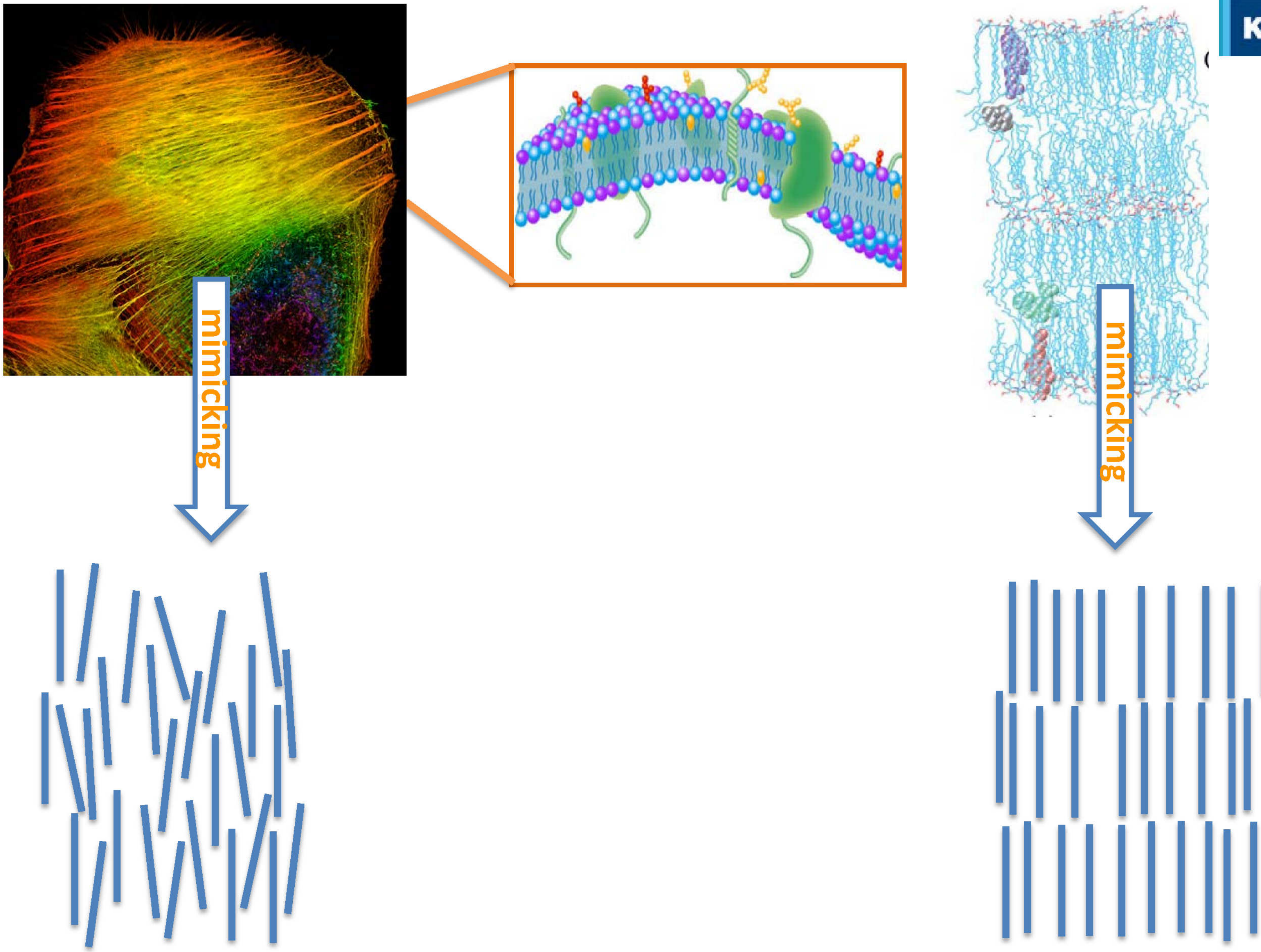
Generally: big particles are slower than small particles



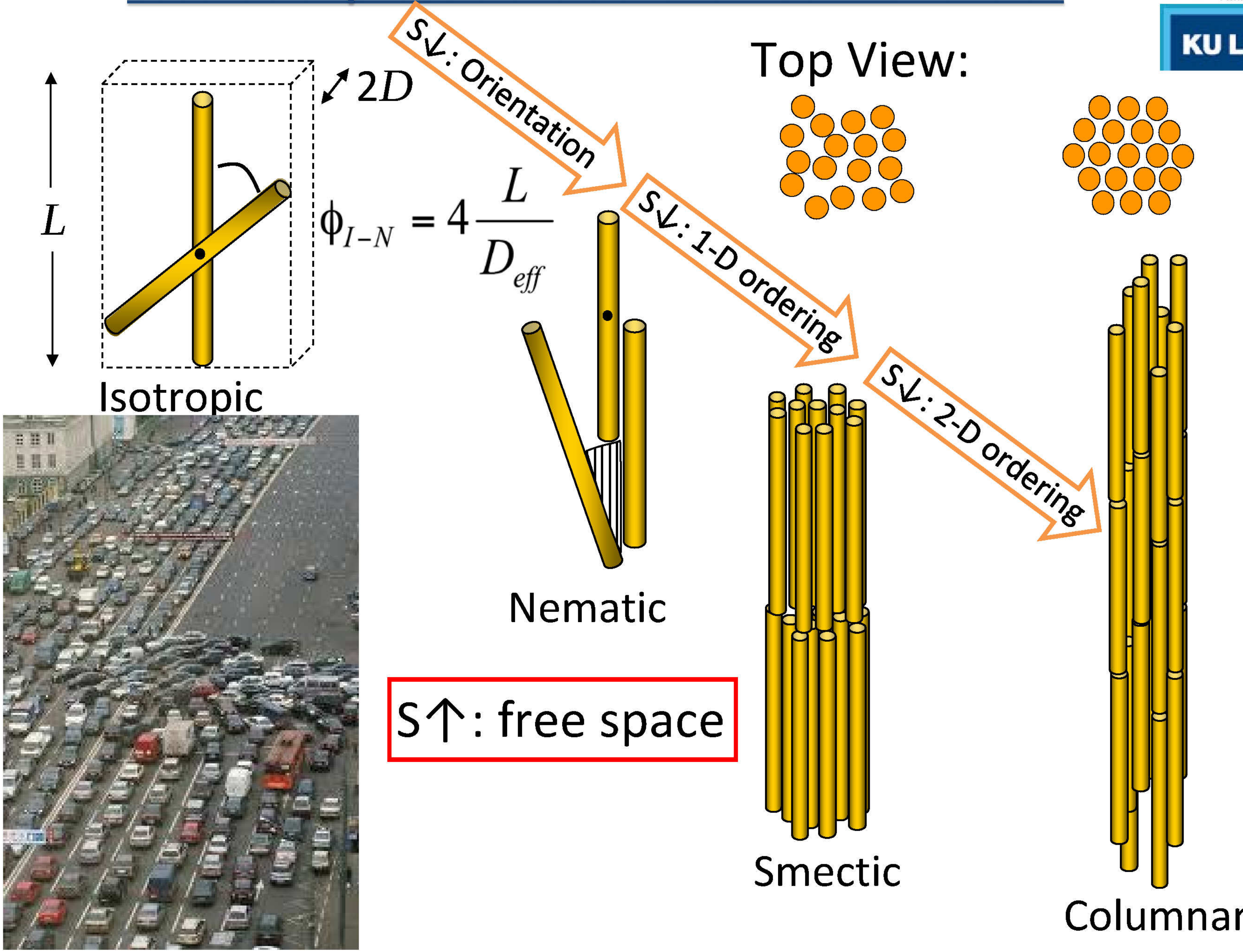


Kang et al., J. Chem. Phys. 122, 044905 (2005)

Diffusion in ordered complex hosts



Cascade of phase transitions for rod-like colloids

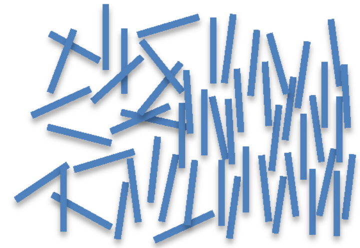


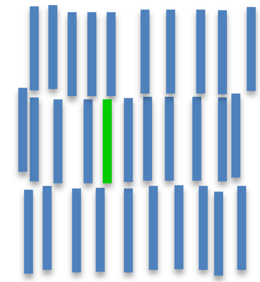
Goal

- Dynamics at increasing degree of ordering

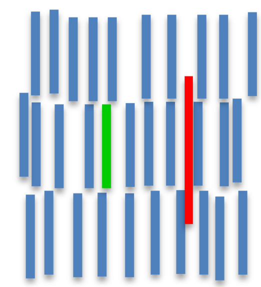
  Focus:

  I-N transition





  Smectic

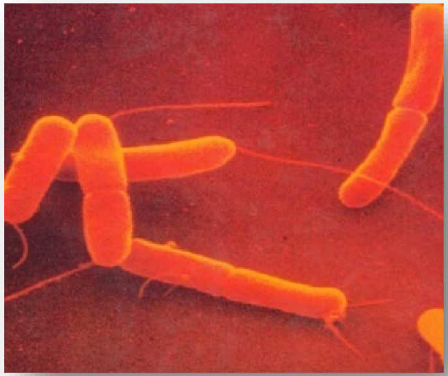


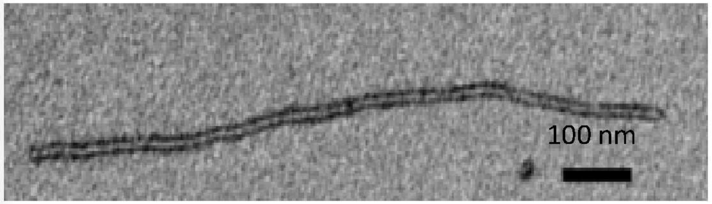
- **Size dependence of diffusion in ordered systems**

Experimental tool

- Fluorescense Video Microscopy on mono-disperse rods

Model system: bacteriophages





Genetic Modification/different phages:

system	L [µm]	L_p [µm]
fd wild type	0.88	2.8
fd Y21M	0.91	9.9
Pf1	1.96	2.8
M13k07	1.2	2.8

Labelling with red and green dye (ratio 1:10^4)

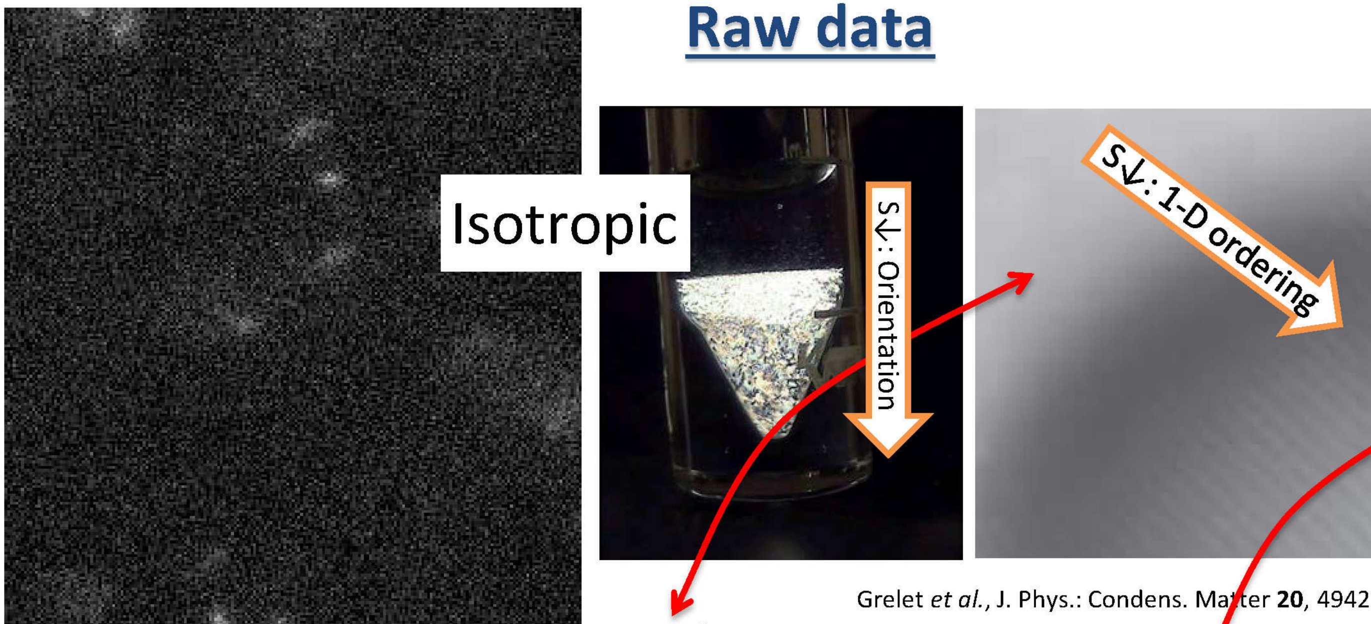
M13KO7Dylight550

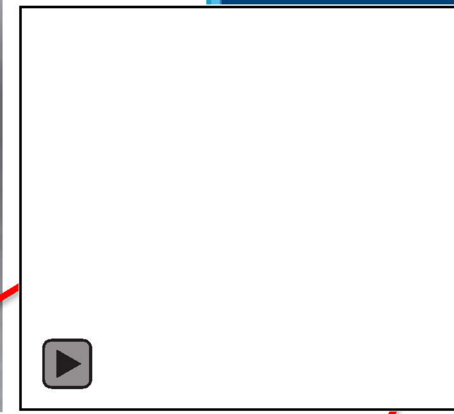
fdY21M-fdY21MAlexa488

Onsager rod: $\phi_{I\text{-}N}=4D_{eff}/L$

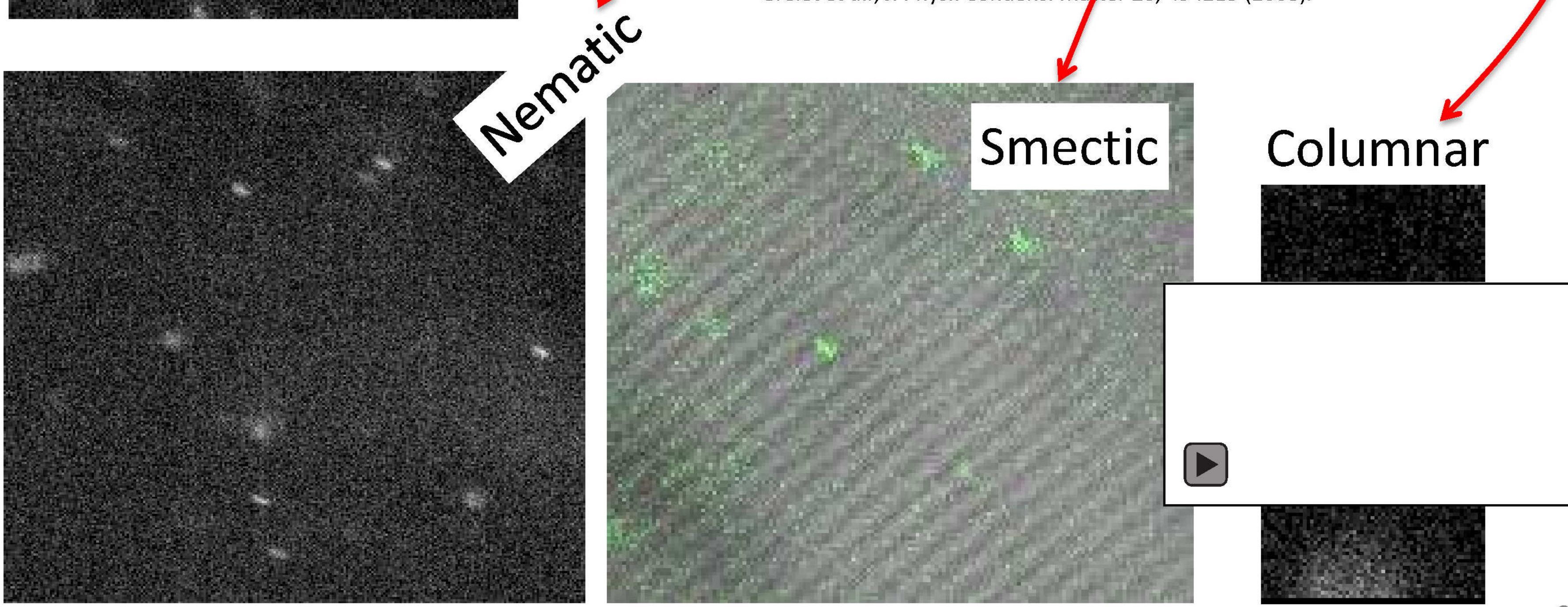
$$L_{guest}/L_{host}=1.3$$

Raw data





Grelet *et al.*, J. Phys.: Condens. Matter **20**, 494213 (2008).

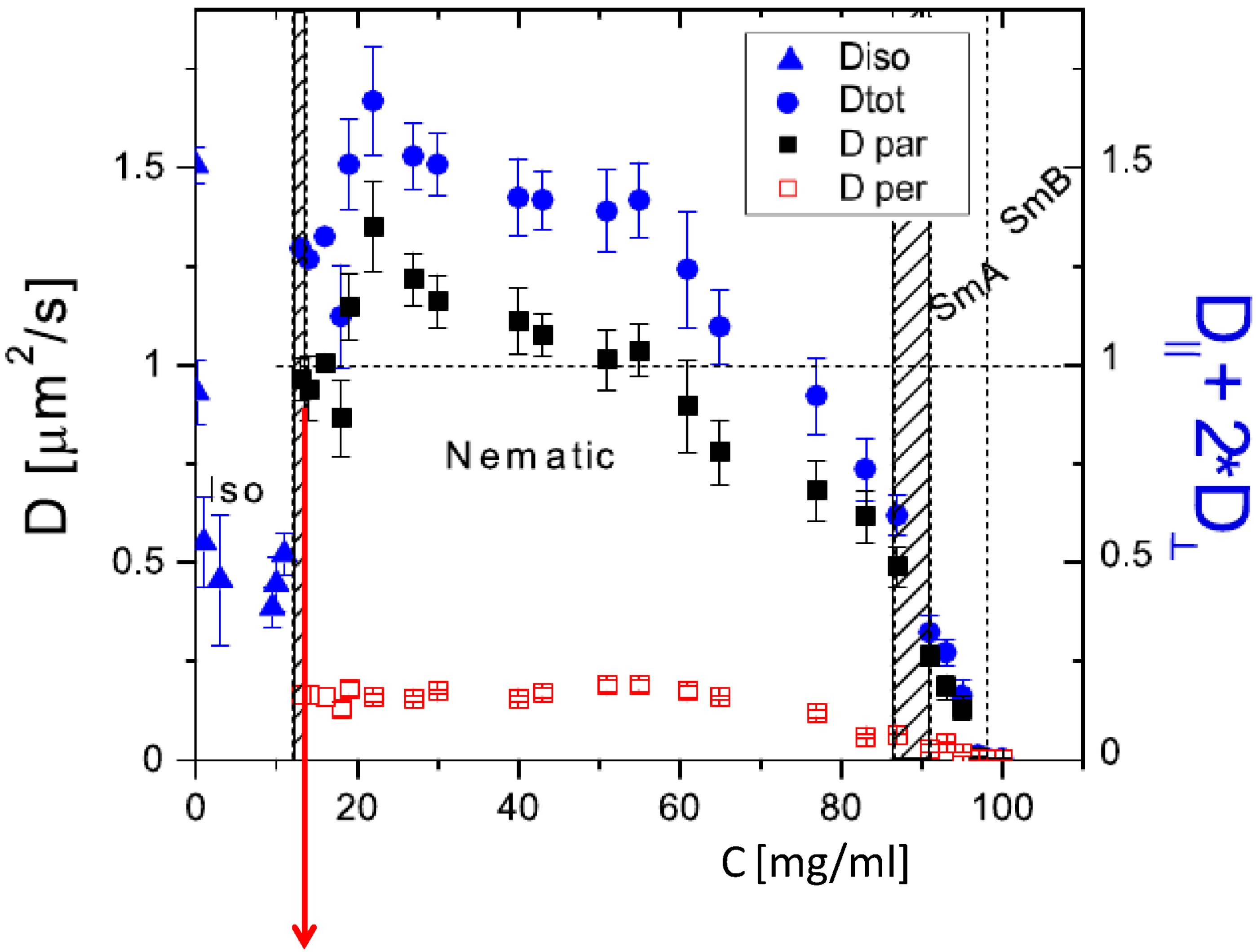


Lettinga *et al.*, Euro.Phys.Let., **71**, 692 (2005)

Lettinga, Grelet, PRL **99**, 1997802 (2007)

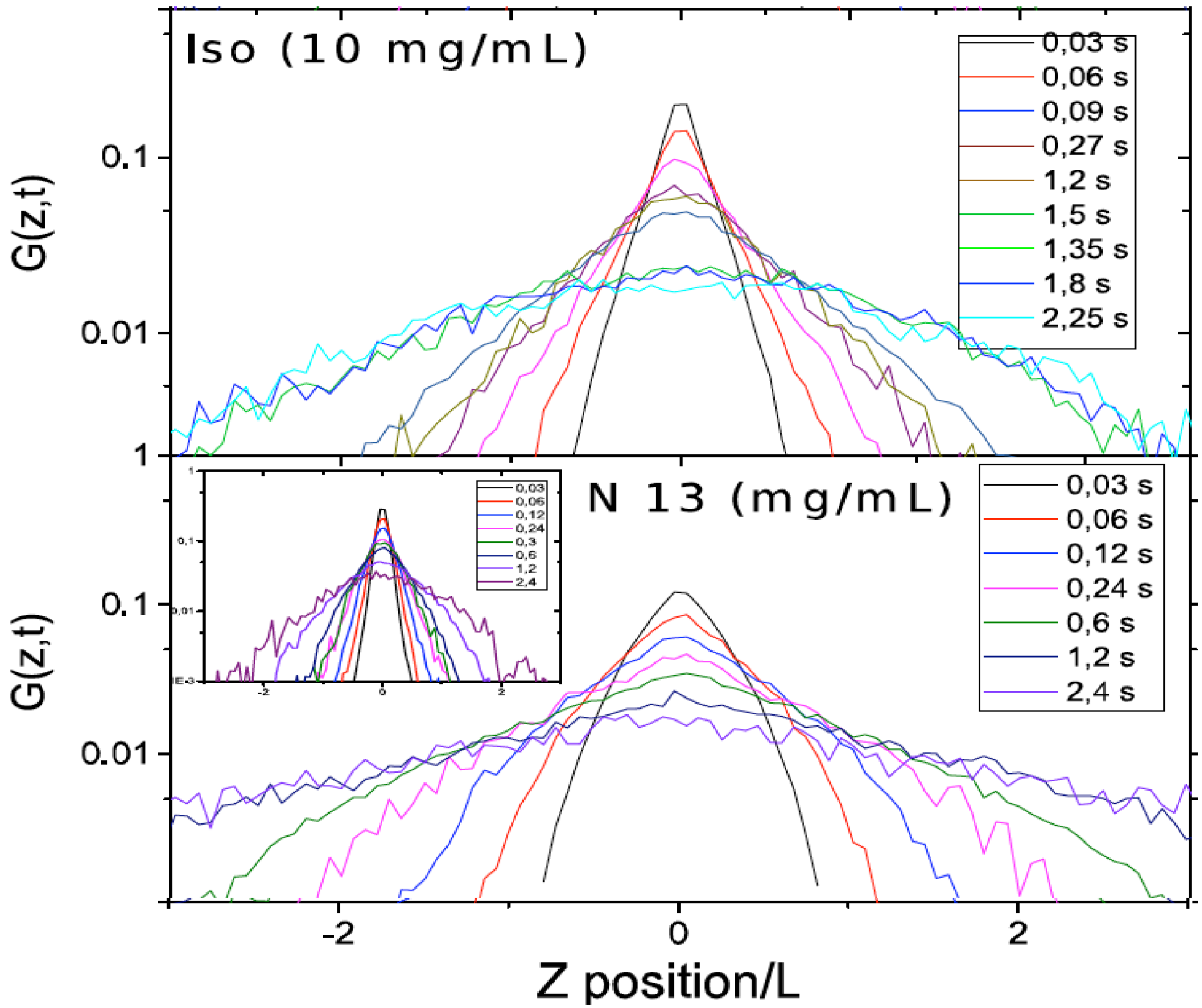
Naderi *et al.*, PRL **111**, 037801 (2013)

MSDs and diffusion rates

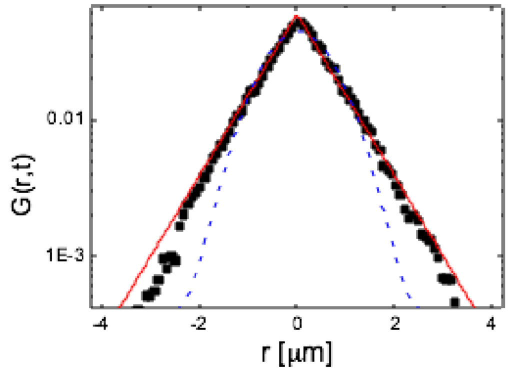


➢ Signature increase entropy

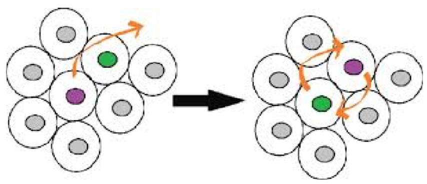
Dynamics around I-N transition



Remember:



for



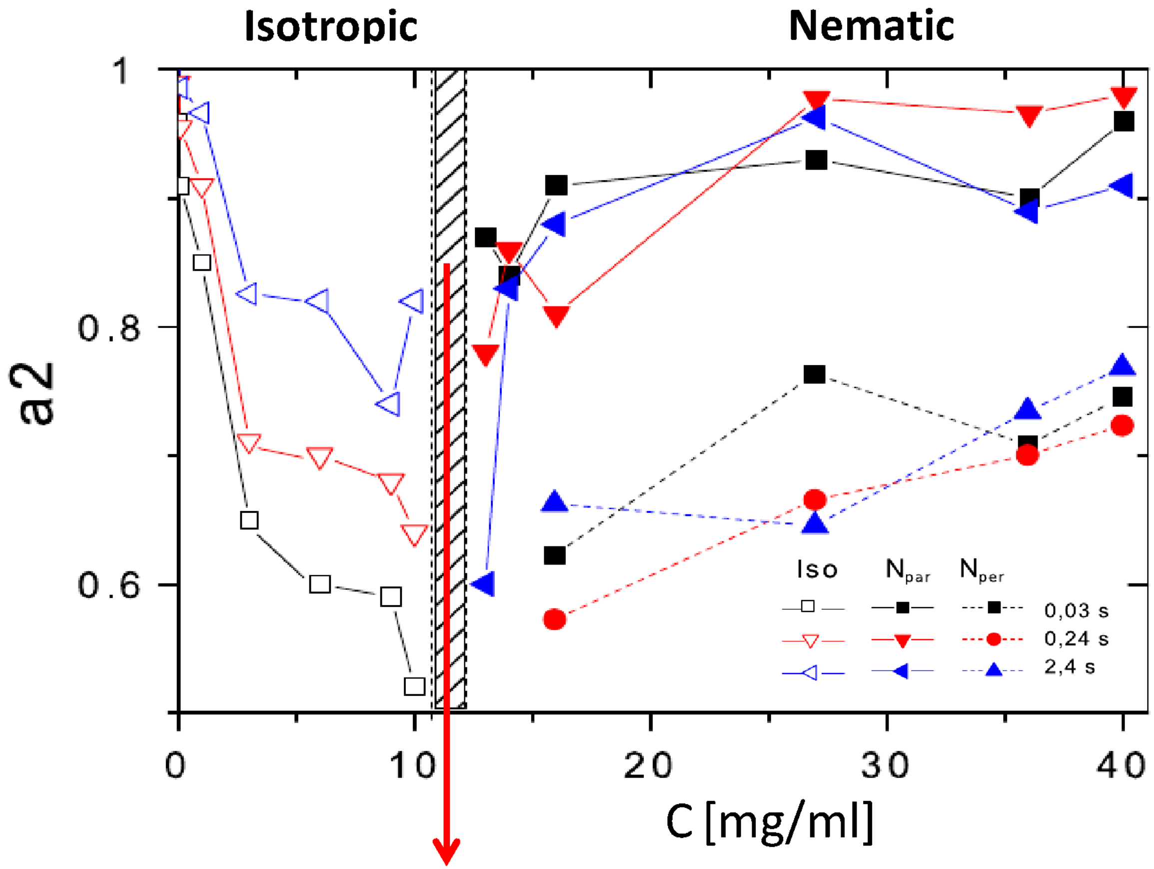
Dynamics around I-N transition

Analysis of the **Self-Van Hove function:**

$$Ln(G(z,t)) = a_0 - a_1(\triangle x^2)^{a_2}$$

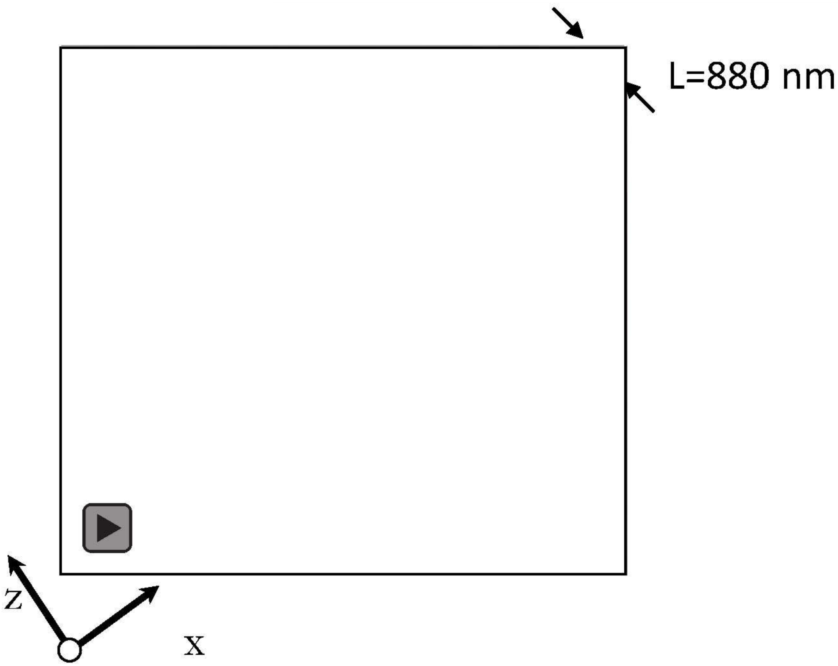
$a_2=1$ Gaussian

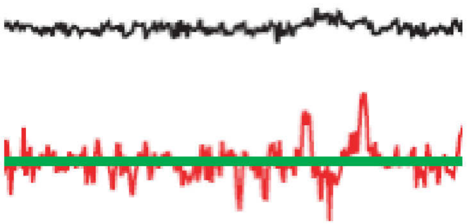
$a_2=0.5$ Lèvy-flight

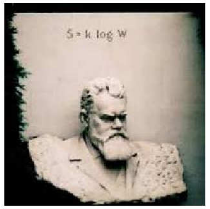


➢ I-N transition: glassy to Gaussian

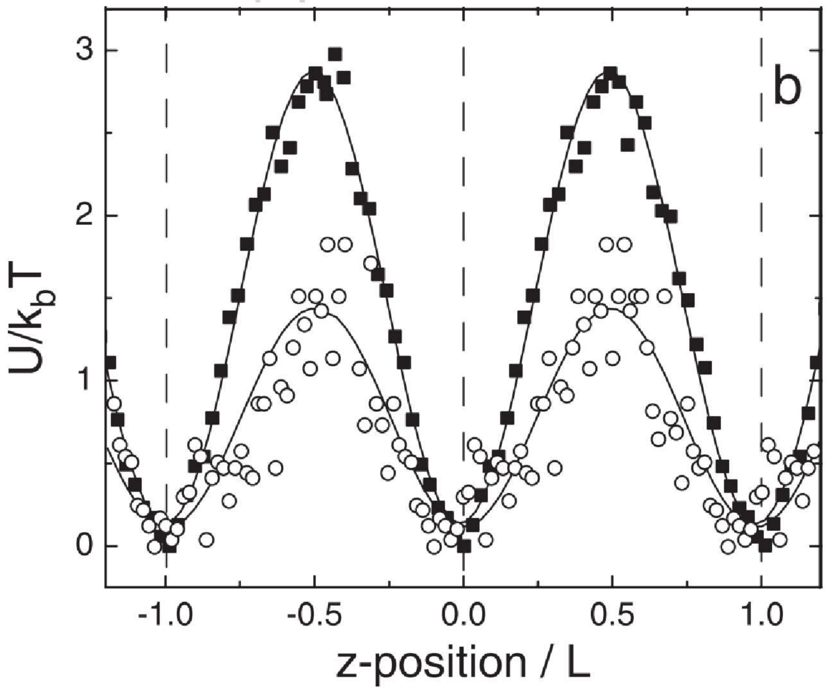
Quantized Brownian motion in smectics



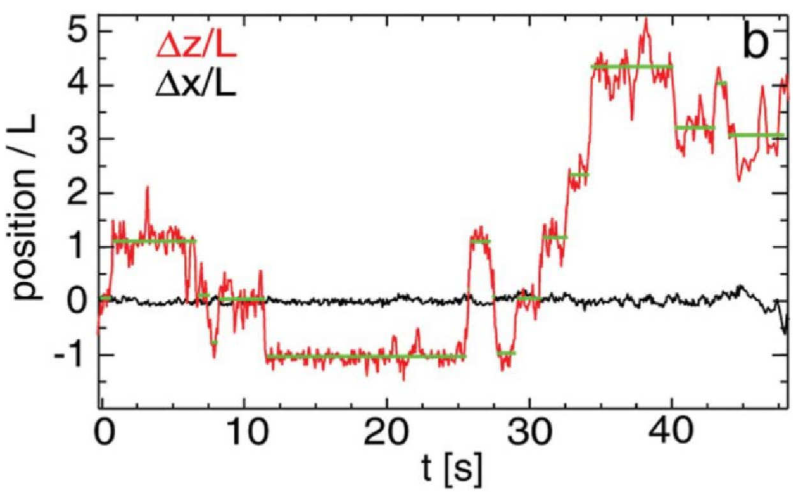




$$P(z) = e^{-U_{layer}(z)/kT}$$



Find jumps in trajectories:



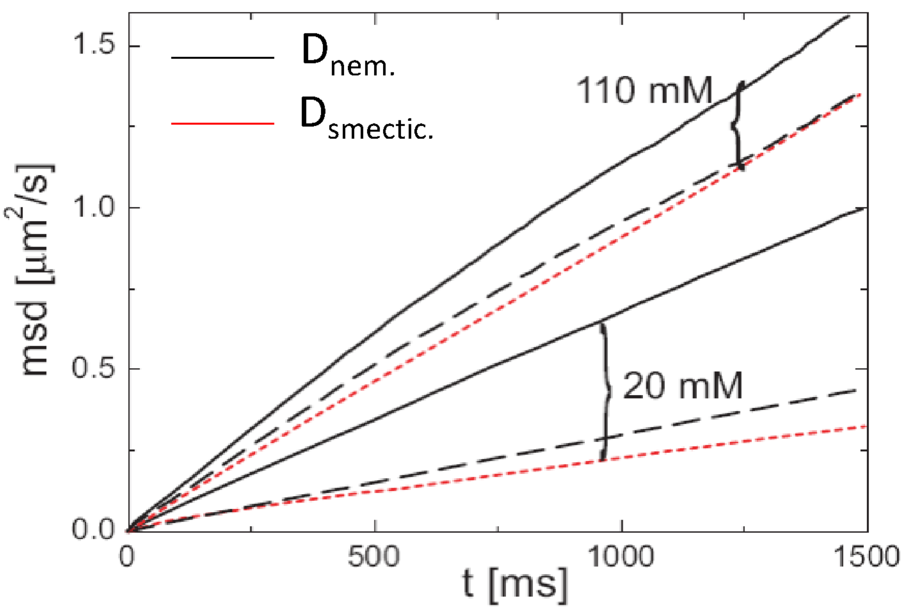
Open: 110 mM

Solid: 20mM

Quantized Brownian motion in smectics

Mean square displacement through layers

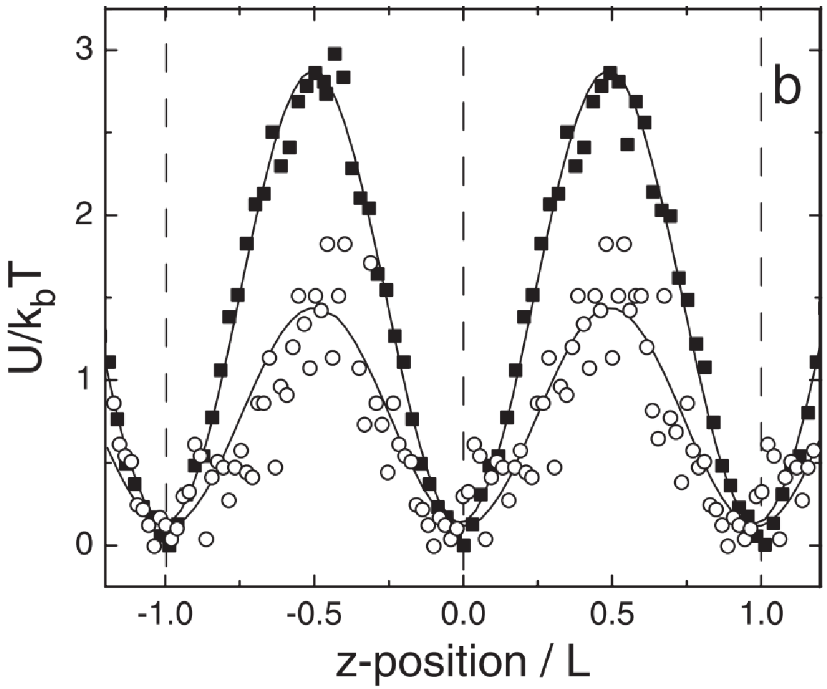
$$D = \frac{D_0}{\langle e^{-U_{layer}(z)/kT} \rangle \langle e^{U_{layer}(z)/kT} \rangle}$$



DIFFUSION COEFFICIENT FOR A BROWNIAN PARTICLE IN A PERIODIC FIELD OF FORCE

Physica **90A** (1978) 229–244

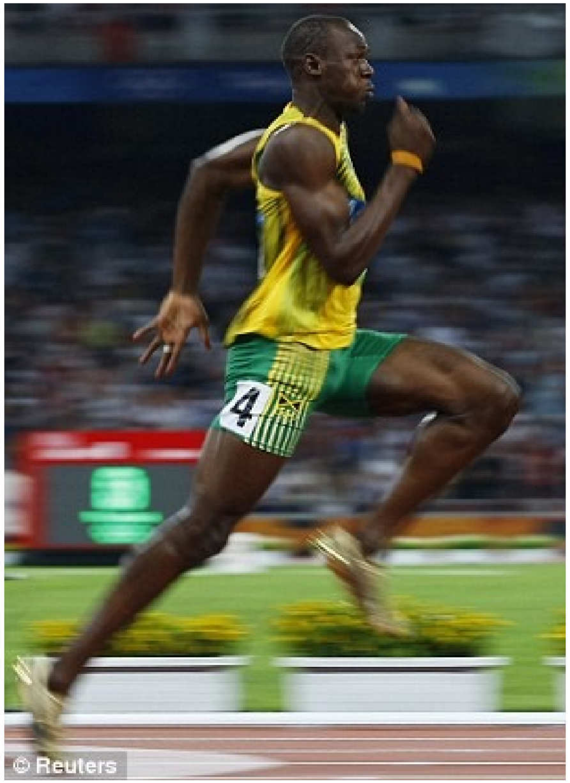
R. FESTA and E. GALLEANI d'AGLIANO



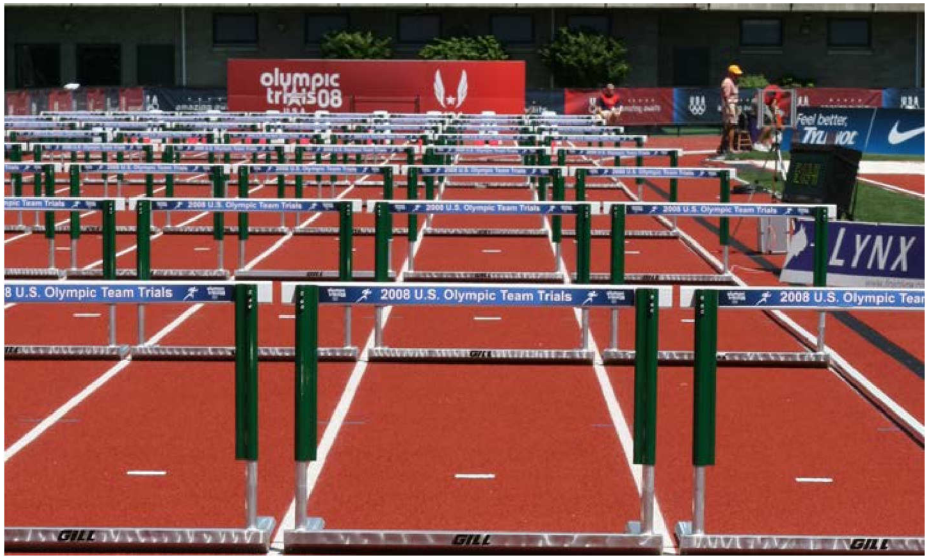
- Diffusion in Smectic = jumping in 1D periodic potential

Lettinga and Grelet, PRL, 2007

Quantized Brownian motion in smectics: so...

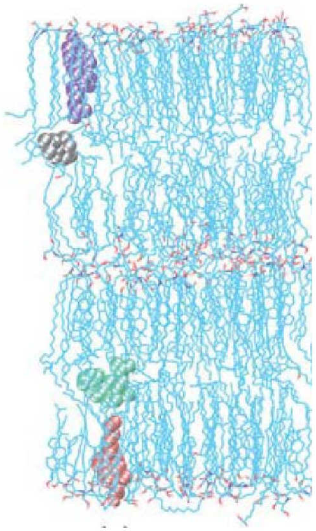


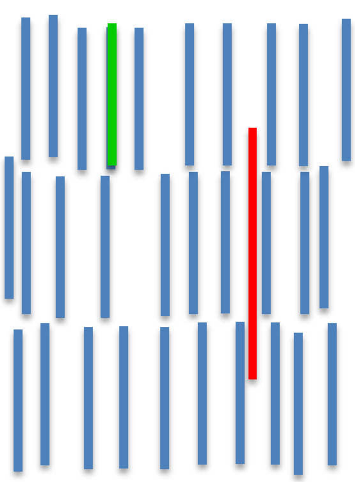
+



=

Diffusion of non-commencurate rods in smectic phase

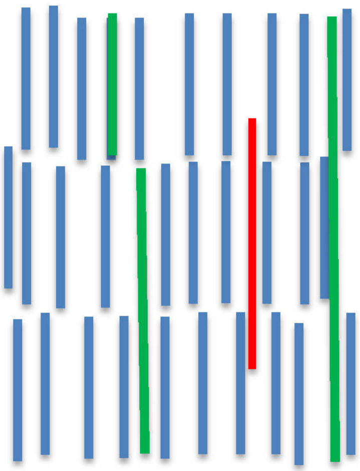


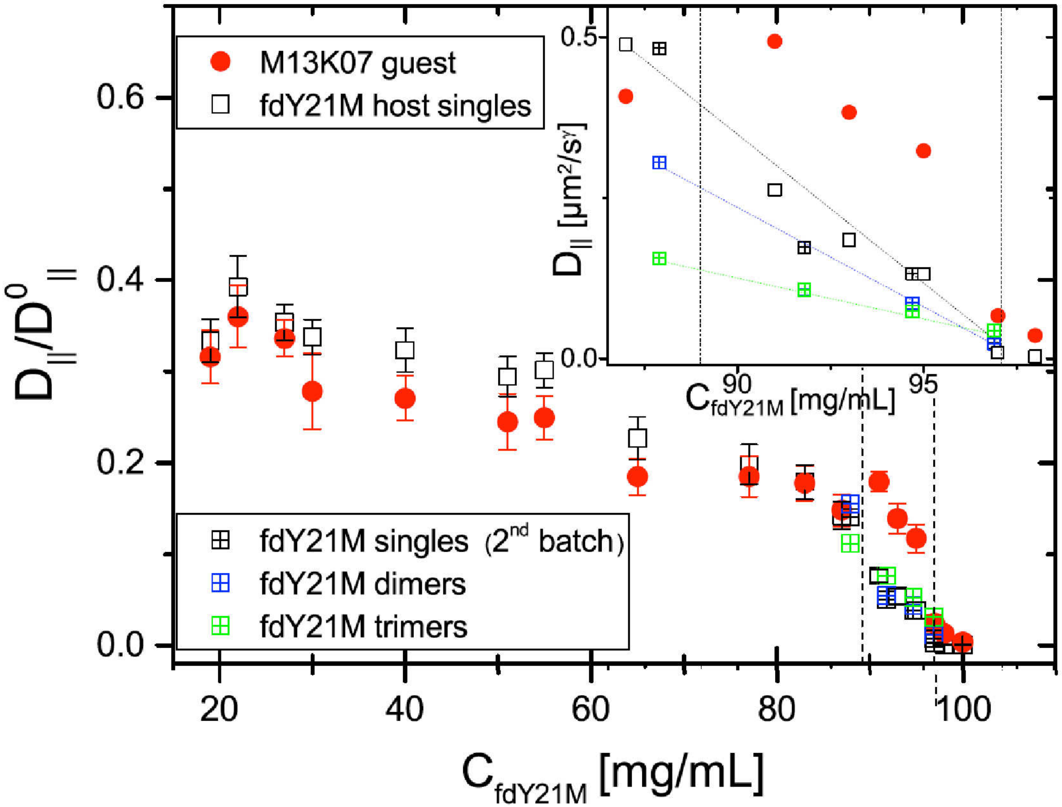


Alvarez, Lettinga, Grelet, PRL **118**, 178002 (2017)

Diffusion of non-commencurate rods in smectic phase

Longer is faster!





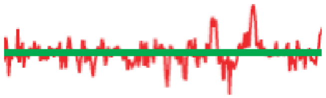
$$D = \frac{R\,T}{N}\,\frac{1}{6\,\pi\,k\,P} = \frac{k_b T}{6\pi\eta_0 a}$$

Diffusion of non-commencurate rods in smectic phase

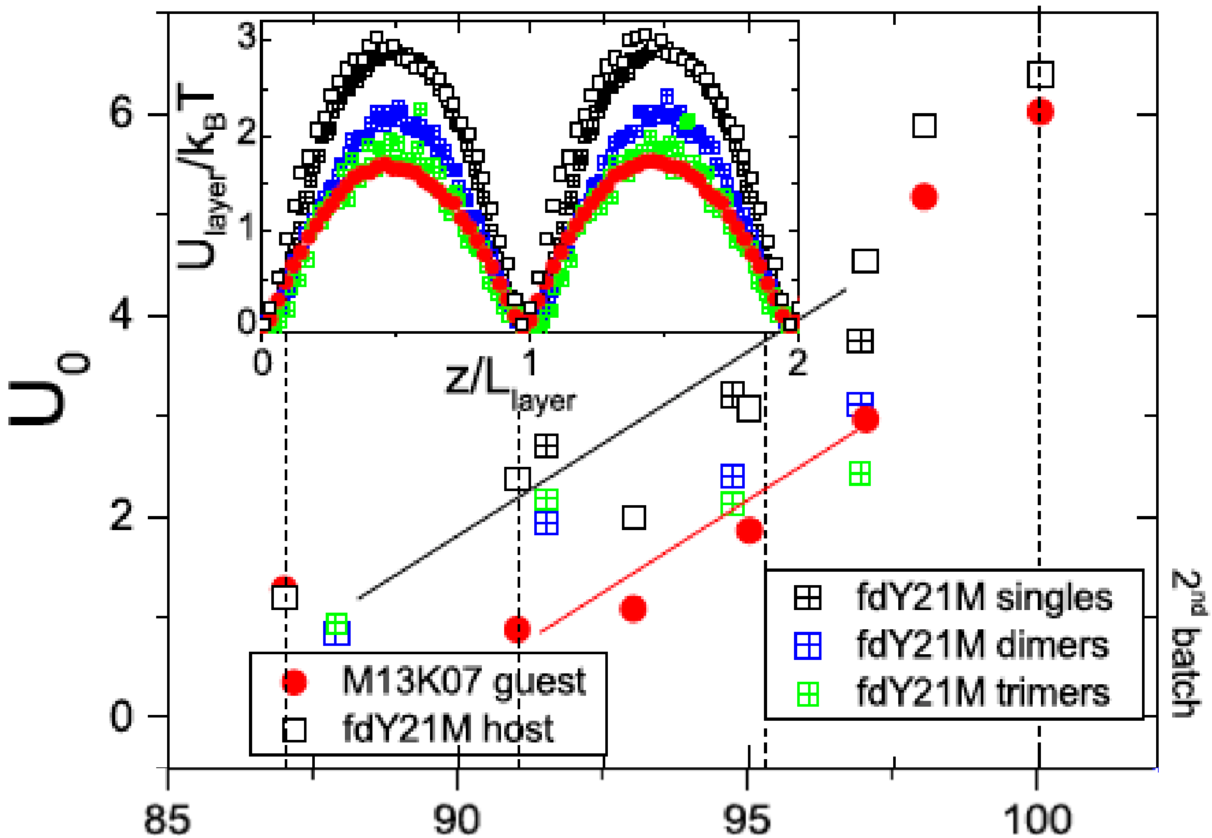
JÜLICH FORSCHUNGSZENTRUM
KU LEUVEN

Longer is faster!

…when size of particle does not fit length scale potential



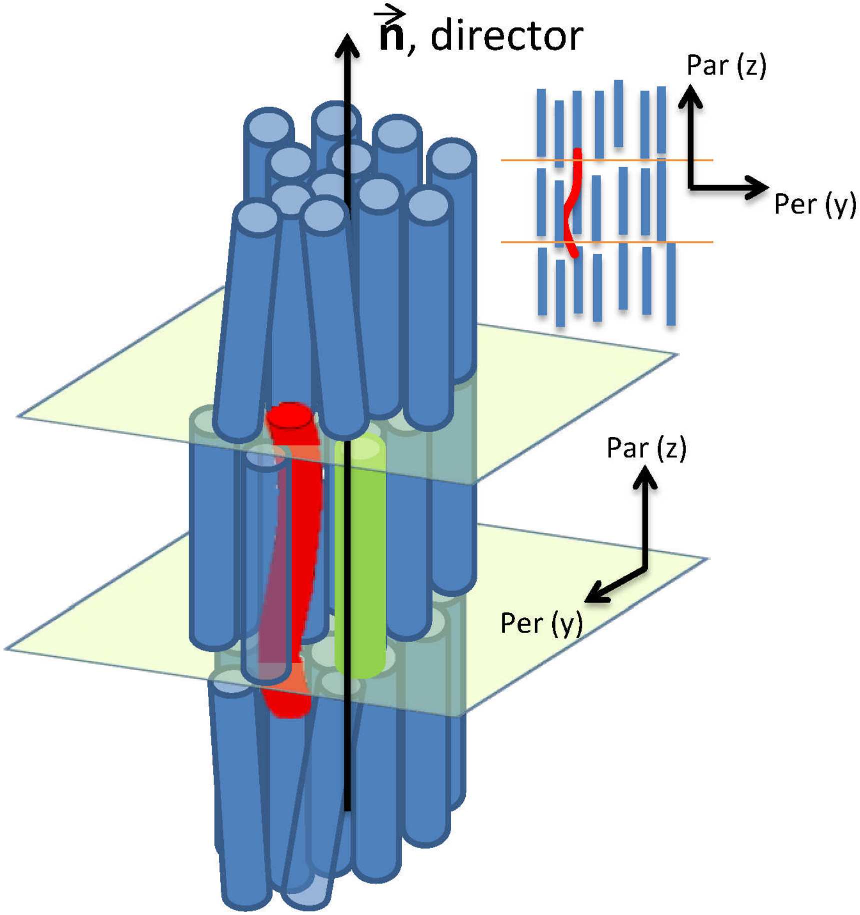
$$P(z) \sim \exp[-U_{\text{layer}}(z)/k_B T].$$

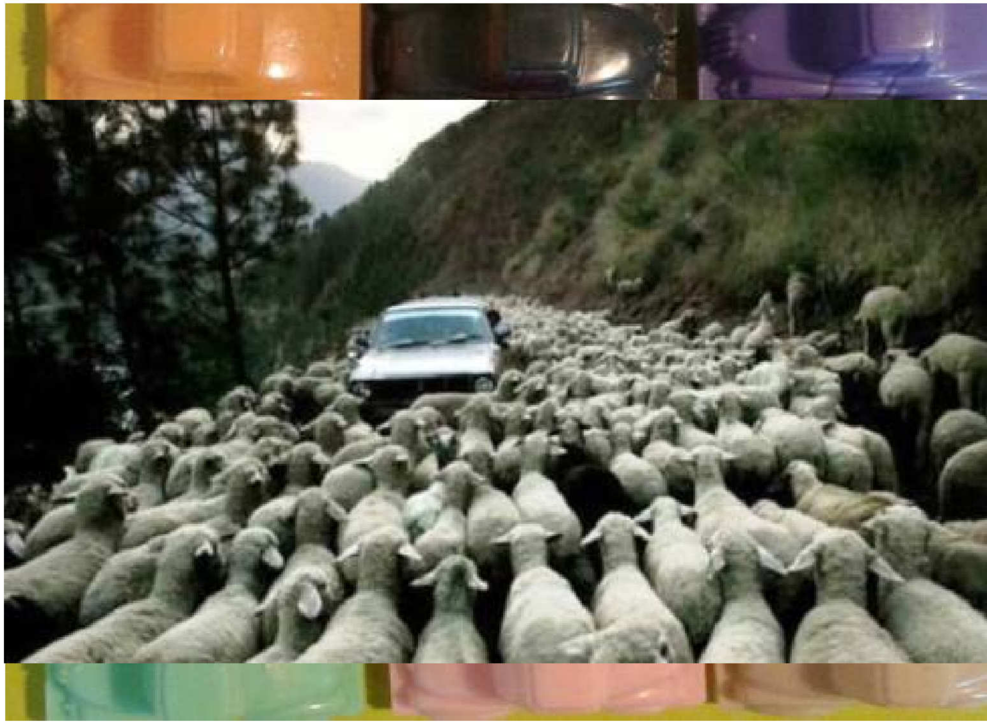


Diffusion of non-commencurate rods in smectic phase

Longer is faster!

...when size of particle does not fit length scale potential





Create free accesible volume

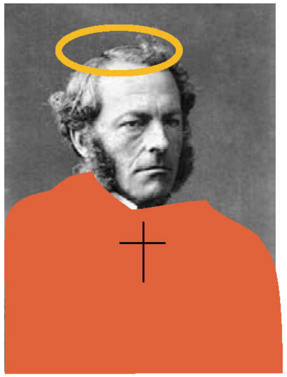
Vacancy needed to jump

Conclusions

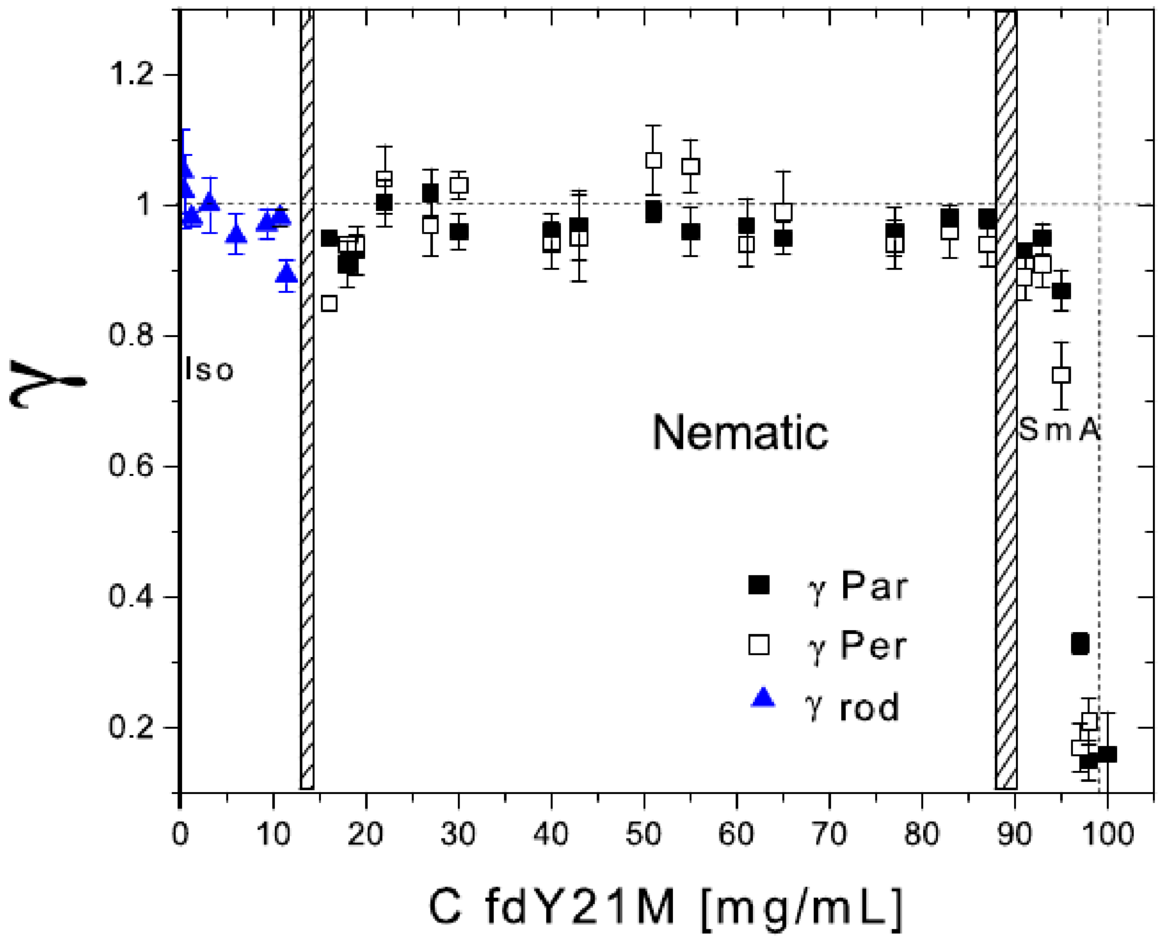
- Phase Transitions:
  Glassy dynamics before transition, Gaussian after transition

- Diffusion in smectic phase:
  Discontinuous, quantized jumps through 1-d periodic potential

- Longer not always slower!
  Particle size helps crossing Smectic Potentials:
  Not commensurated in the Smectic ordering potentials



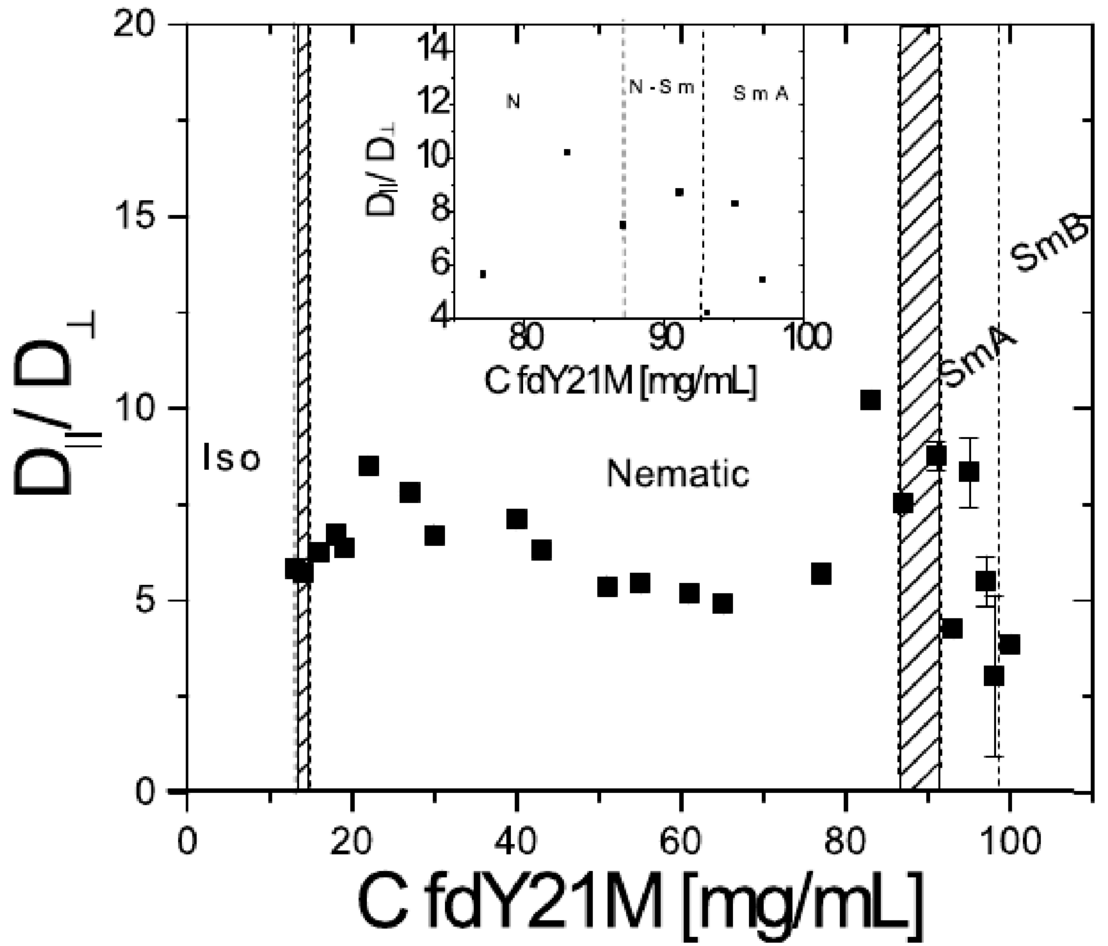

Diffusivity parameter



Dynamics at the phase transition: diffusion ratio

JÜLICH FORSCHUNGSZENTRUM

KU LEUVEN



Hydro-Dynamics of rod-like colloids

JÜLICH FORSCHUNGSZENTRUM

KU LEUVEN

MOUVEMENT BROWNIEN D'UN ELLIPSOIDE (I).
DISPERSION DIÉLECTRIQUE POUR DES MOLÉCULES ELLIPSOIDALES

Par Francis PERRIN.
(Institut H. Poincaré et Institut Ed. de Rothschild, Paris).

Sommaire. — Extension de la théorie du mouvement brownien de translation et de rotation au cas d'une particule ellipsoïdale quelconque. Application à l'étude de la dispersion diélectrique pour des molécules polaires ellipsoïdales en milieu liquide.

F. Perrin, J..Physique, **7**, (1934)

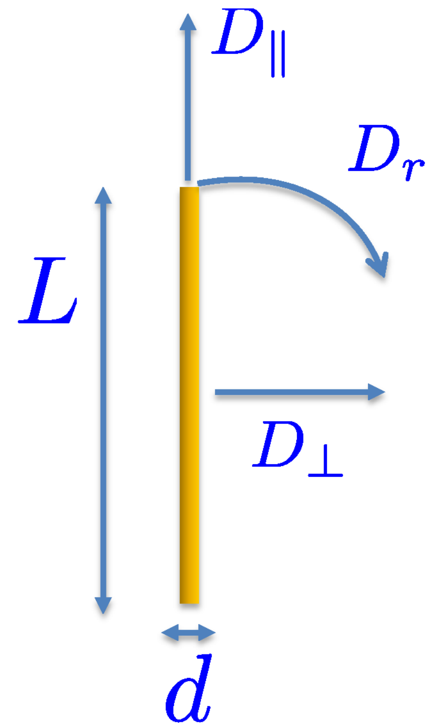
Acad.oct.15
Verhandelingen der Koninklijke Nederlandse
Akademie van Wetenschappen, Afdeeling
Natuurkunde / 1
Burgers,J.L.
16, 4: 1938

ON THE MOTION OF SMALL PARTICLES OF ELONGATED FORM.
SUSPENDED IN A VISCOUS LIQUID.

$$D^{\perp}=\frac{D_0}{4\pi}(\ln p \cdot)$$

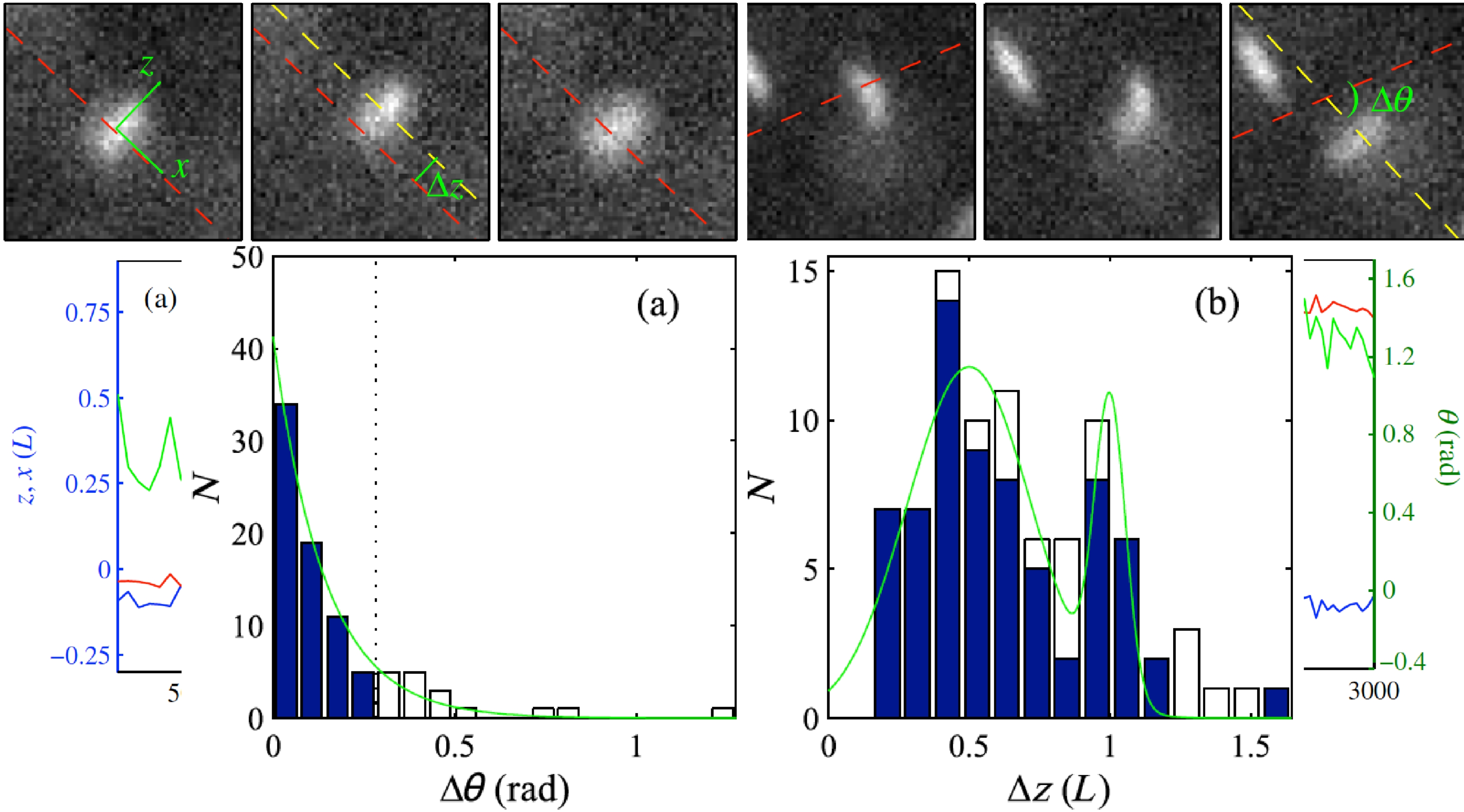
$$D^{\parallel}=\frac{D_0}{2\pi}(\ln p \cdot)$$

$$D^{r}=\frac{3D_0}{\pi L^2}(\ln p \quad)$$



$$p = L/d$$

Dynamics in the columnar phase

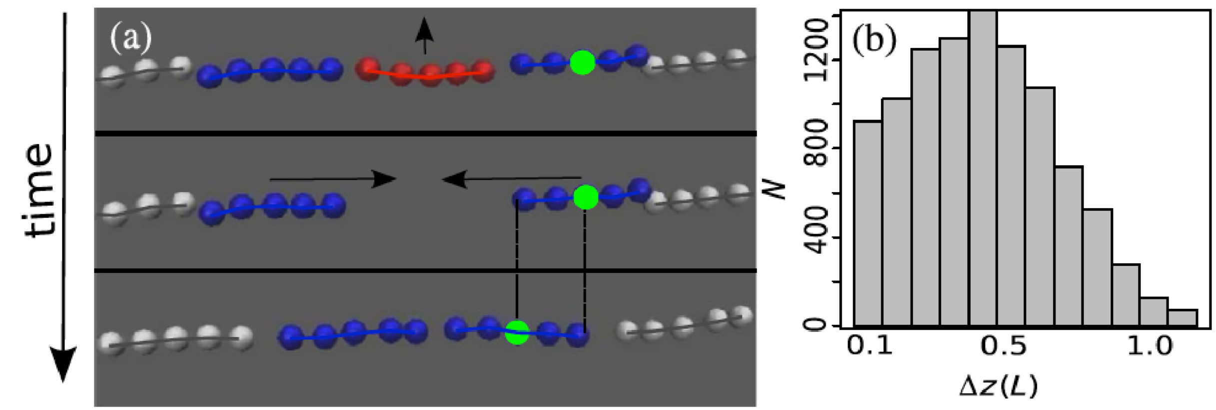


Half-jumps!!!

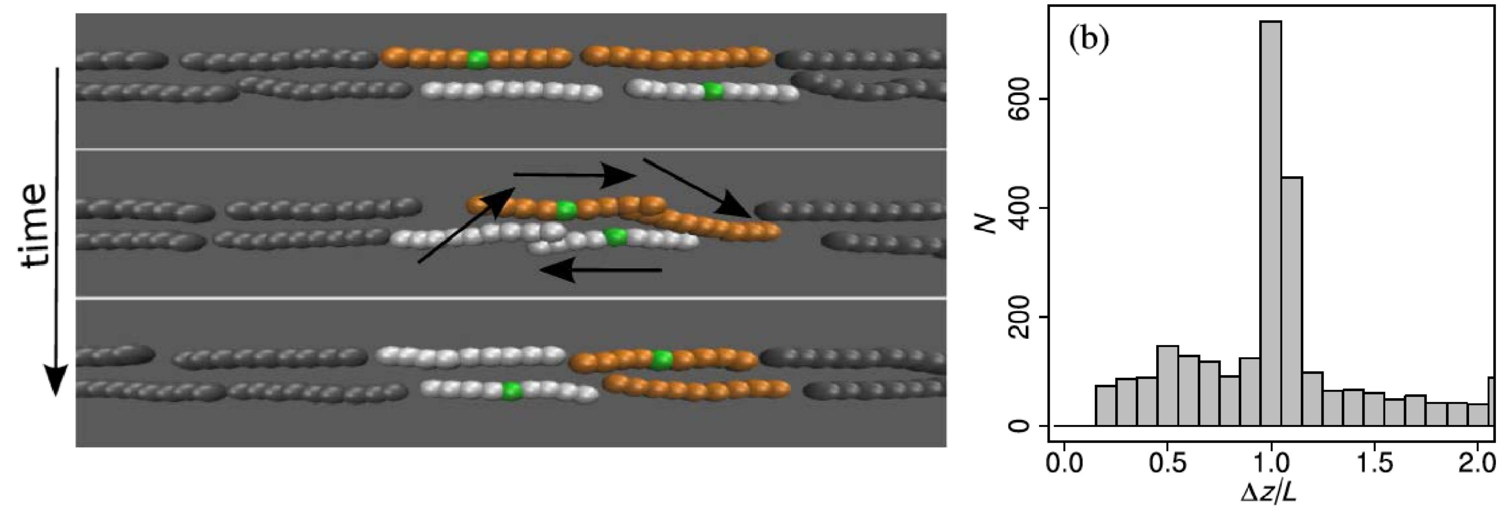
Time scale huge compared to the N and Sm

Dynamics in the columnar phase

Half-jump in columnar phase: scenario?

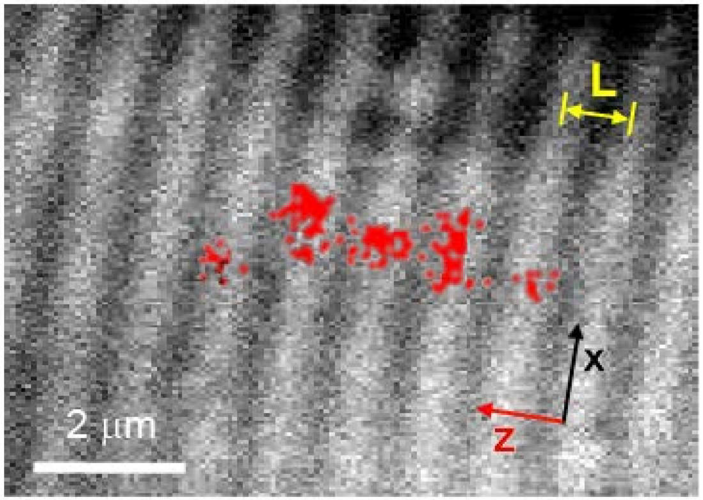


Tonks gas…



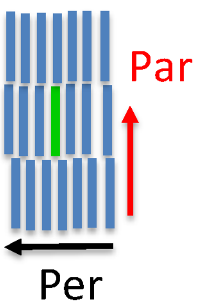
Effect of stiffness

Enhanced Diffusion in layer!

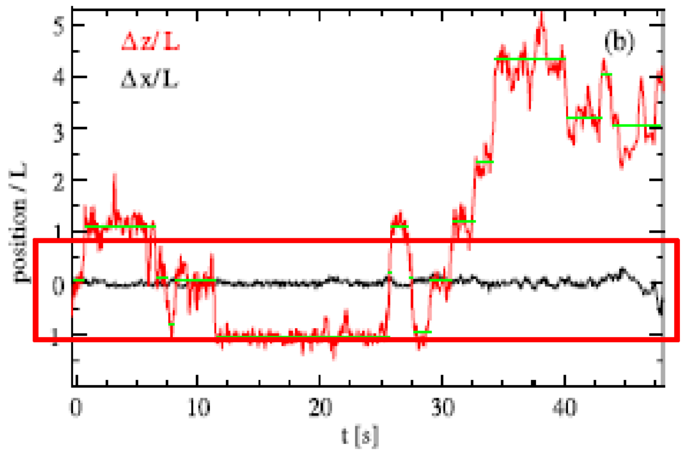


Effect of stiffness

Enhanced Diffusion in layer!



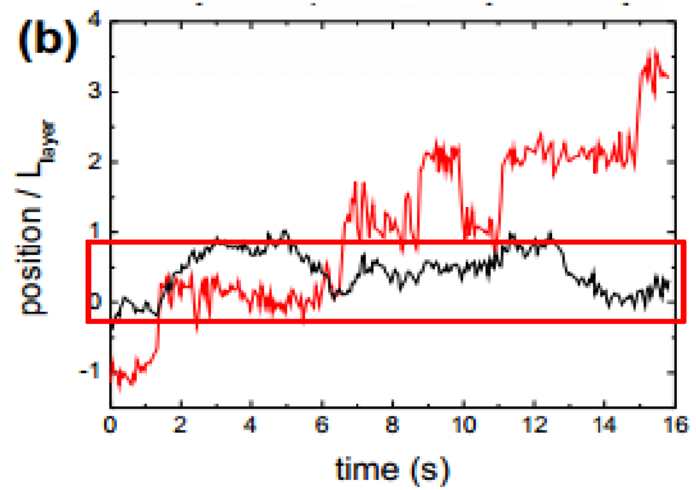
fd wt virus



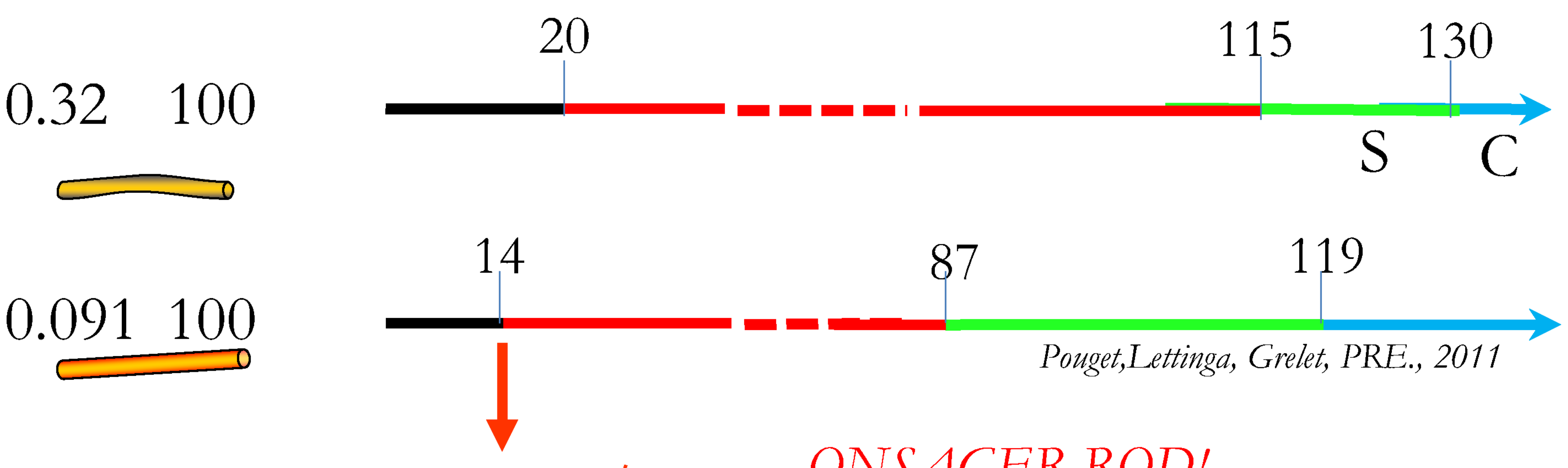
M.P. Lettinga,E. Grelet, Phys. Rev. Lett. 99, 1997802 (2007)

E.Grelet, J. Phys. Condens. Matter 20, 494213 (2008)

fdY21M (Stiffer)



E. Pouget, Physical Review E, 84,41704 (2011)



Effect of stiffness

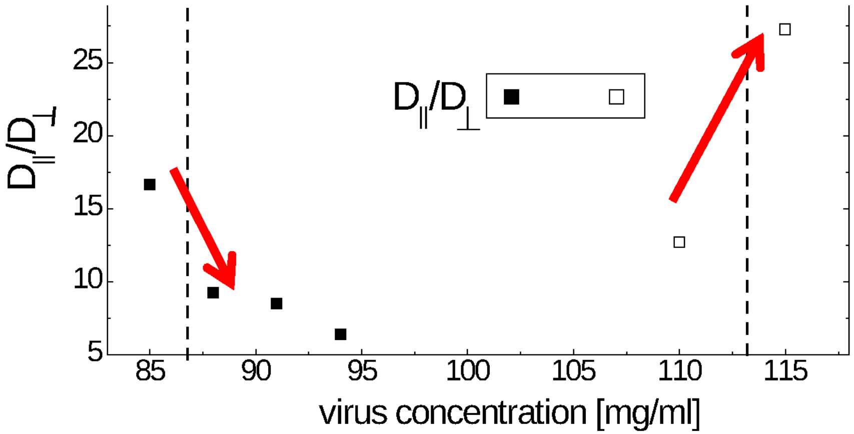
$N\text{-}Sm_{stiff}$ $N\text{-}Sm_{flexible}$

- **Origin of disappearing smectic phase?**

- Residence time set by potential barrier set by concentration

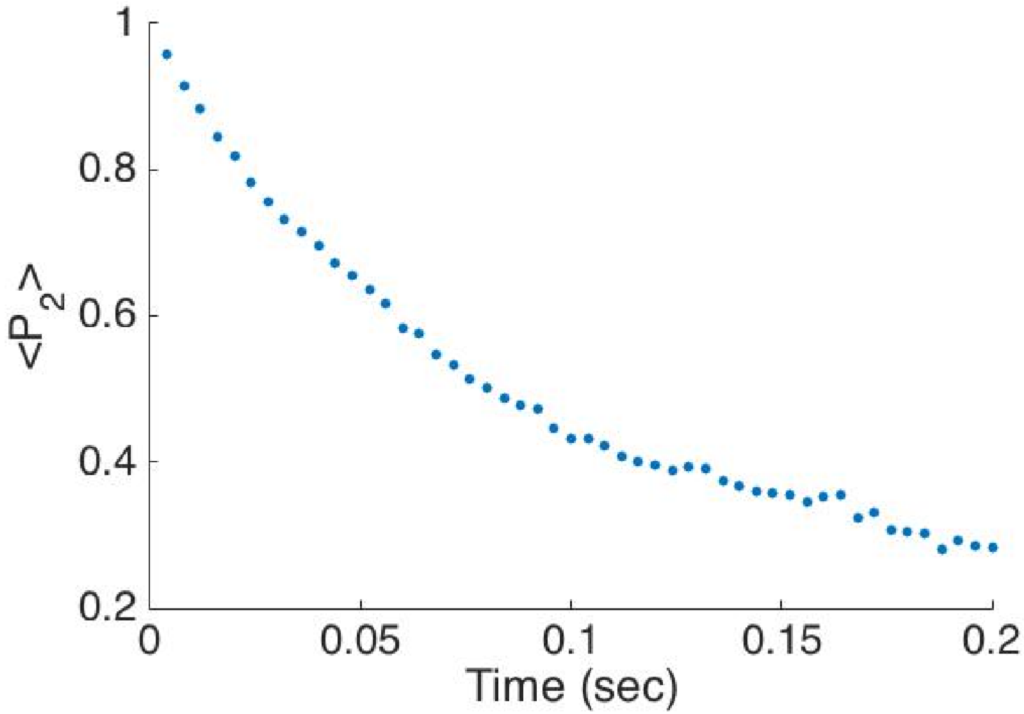
- Stiff rods diffuse within layer
  Flexible rods (almost) don 't.

- Anisotropy in diffusion
  - Decreases for Stiff rods
  - Increase for Flexible rods after N-Sm.



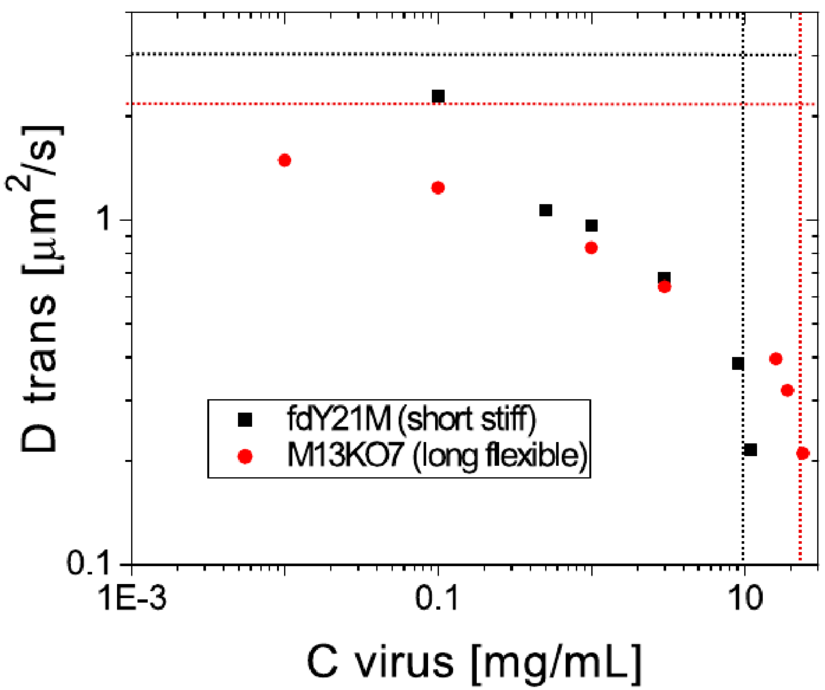
Pouget,Lettinga, Grelet, PRE., 2011

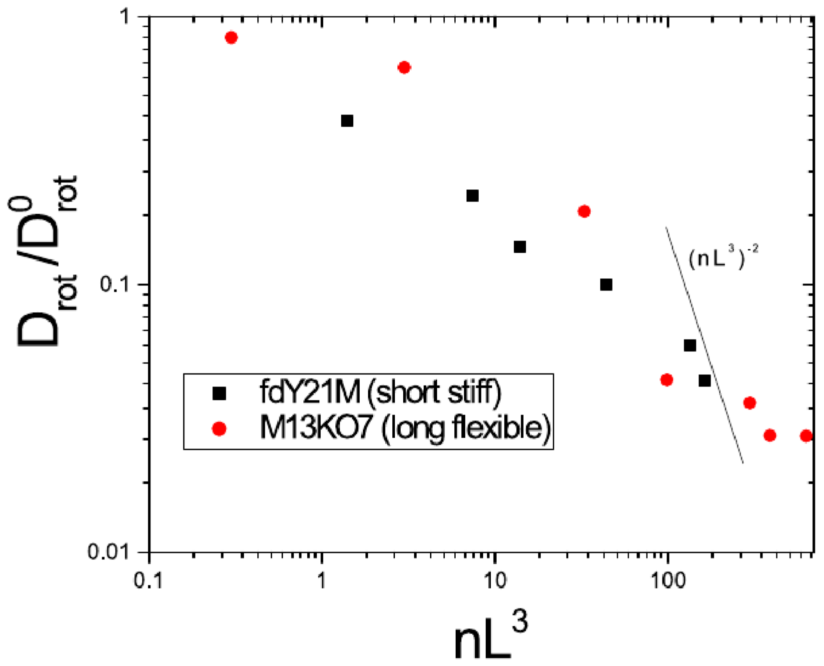
Rotational Diffusion at infinite dilution



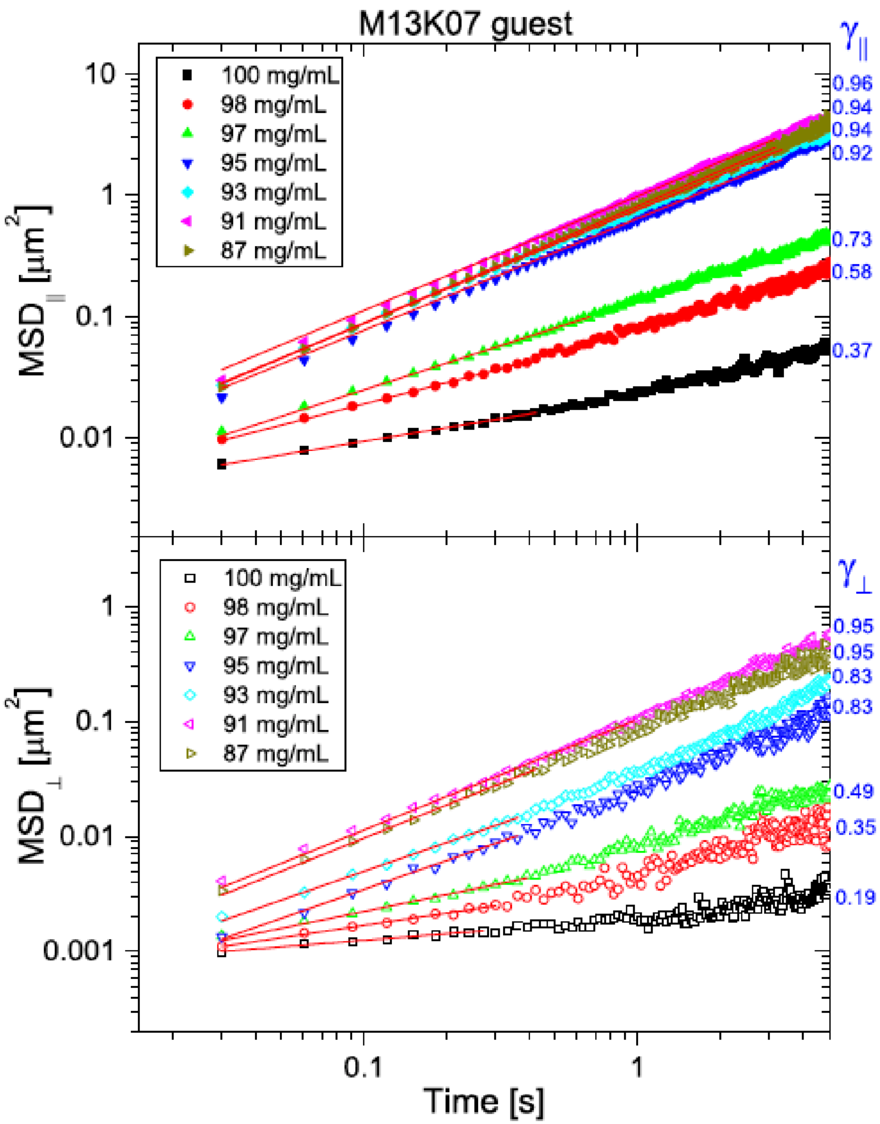
Rotational Diffusion in isotropic phase

Effect of flexibility and length in Isotropic Diffusion



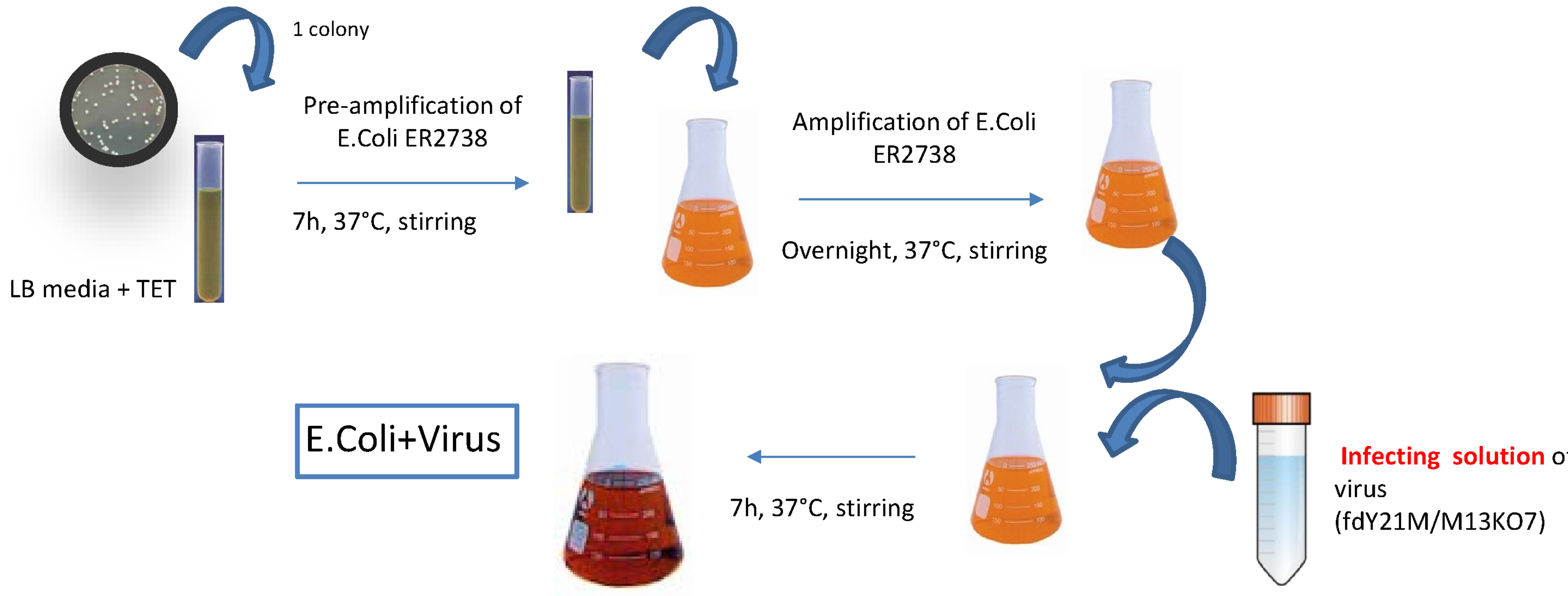


Diffusion of non-commencurate rods in smectic phase

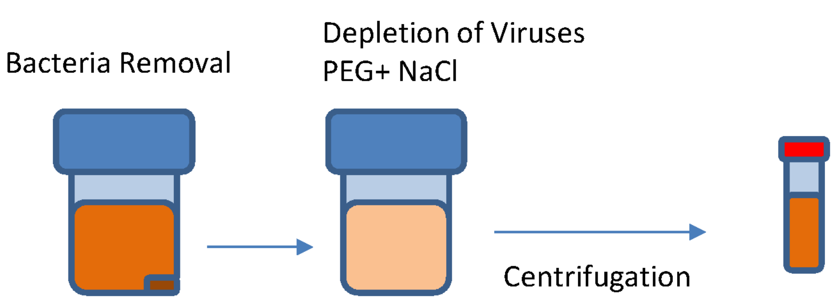


Production of the viruses and purification

1. Production



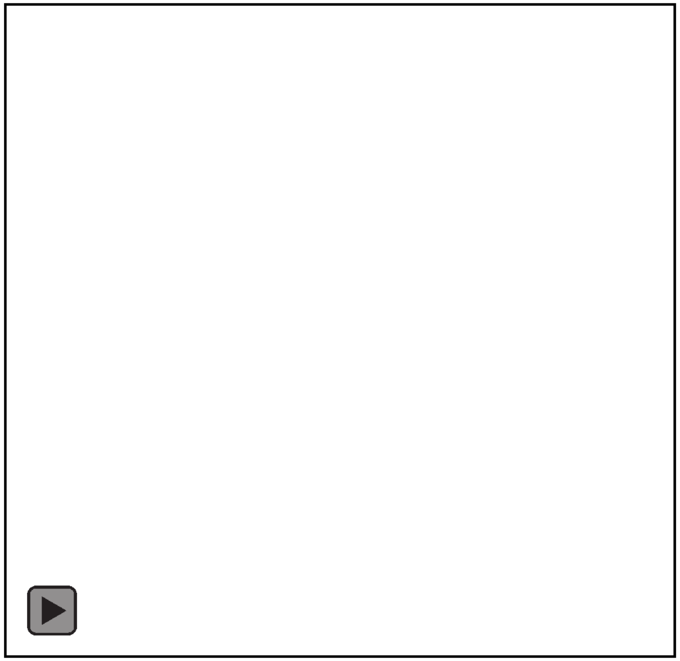
2. Purification

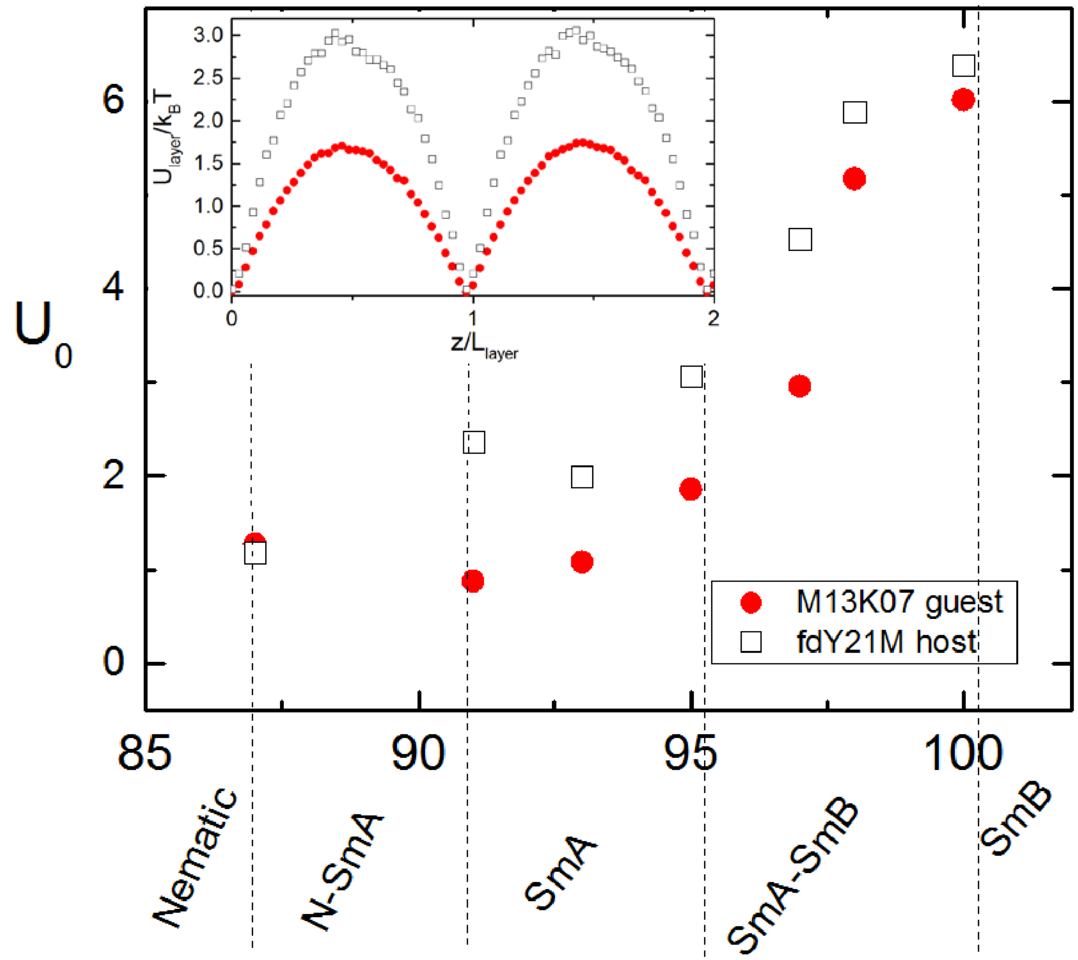


-Final purification by centrifugation
-Concentration of the sample by Ultra Centrifugation
-Dialized against TrisHCl 20 mM pH=8.2

No fit

Longer is faster!

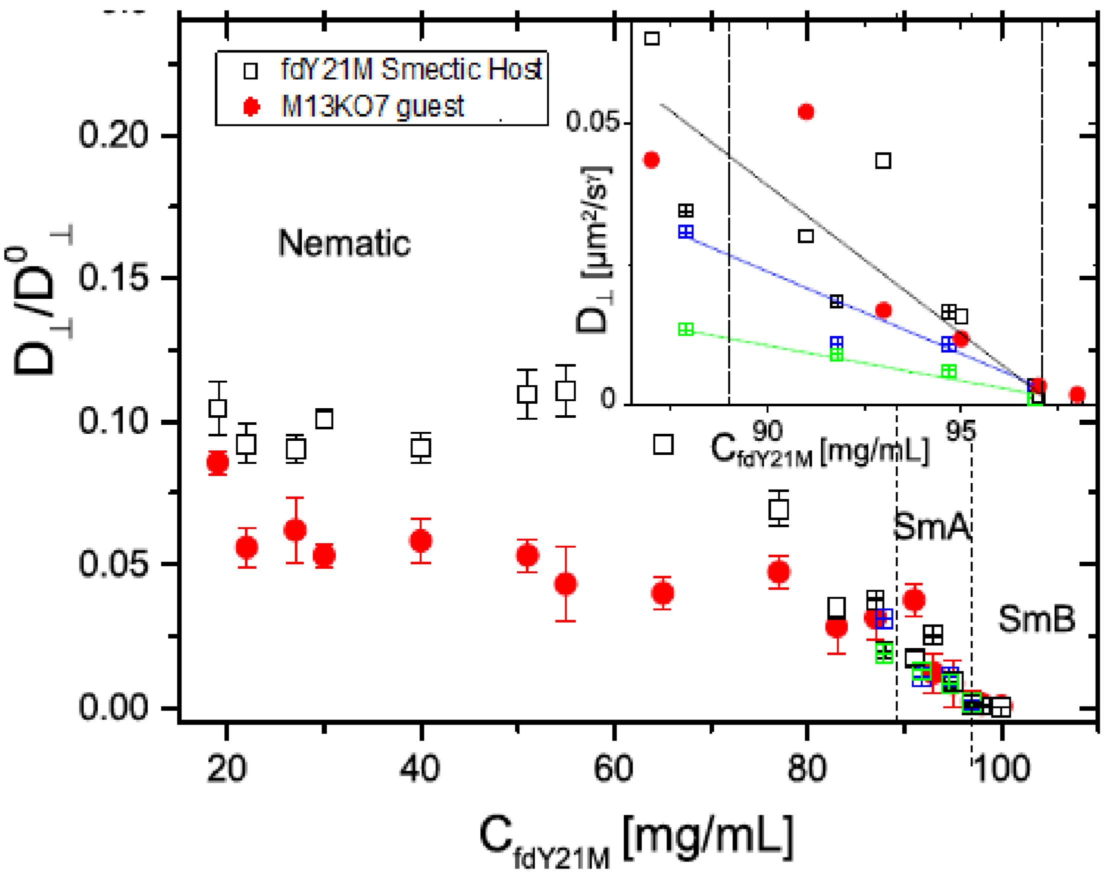


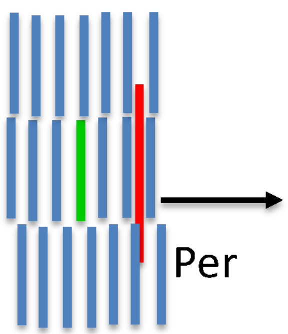


Alvarez et al PRL 2017

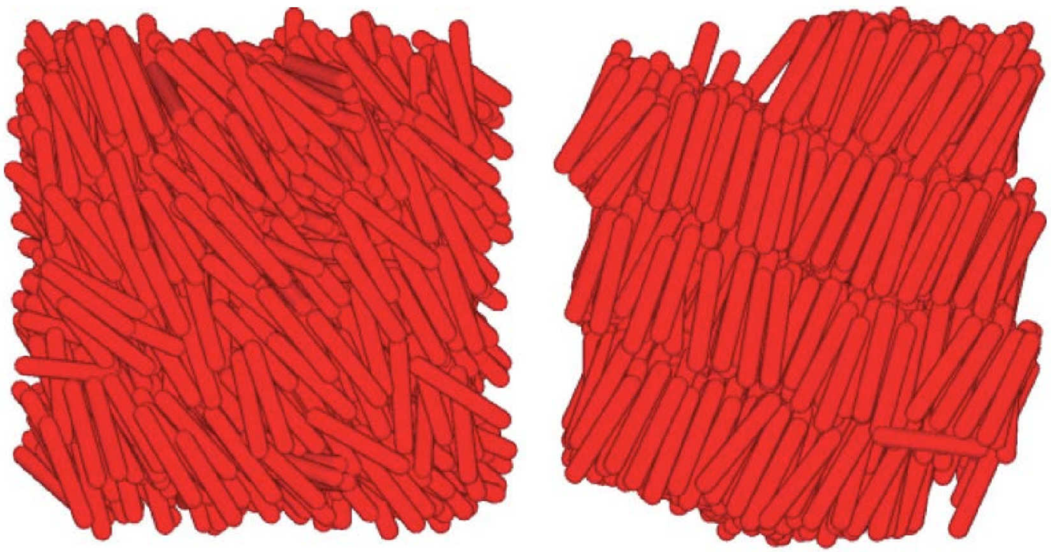
Dynamics of the guest particle: Mean Square Displacement

$$MSD = \frac{1}{N}\sum_{i=1}^{N}|r_i(t) - r_i(0)|^2 \qquad MSD = 2Dt^{\gamma}$$





Literature



Patti and Cuentas, ORE, 86, 011403 (2012)

Short-Time Dynamic Signature of the Liquid–Crystal–Glass Transition in a Suspension of Charged Spherical Colloids

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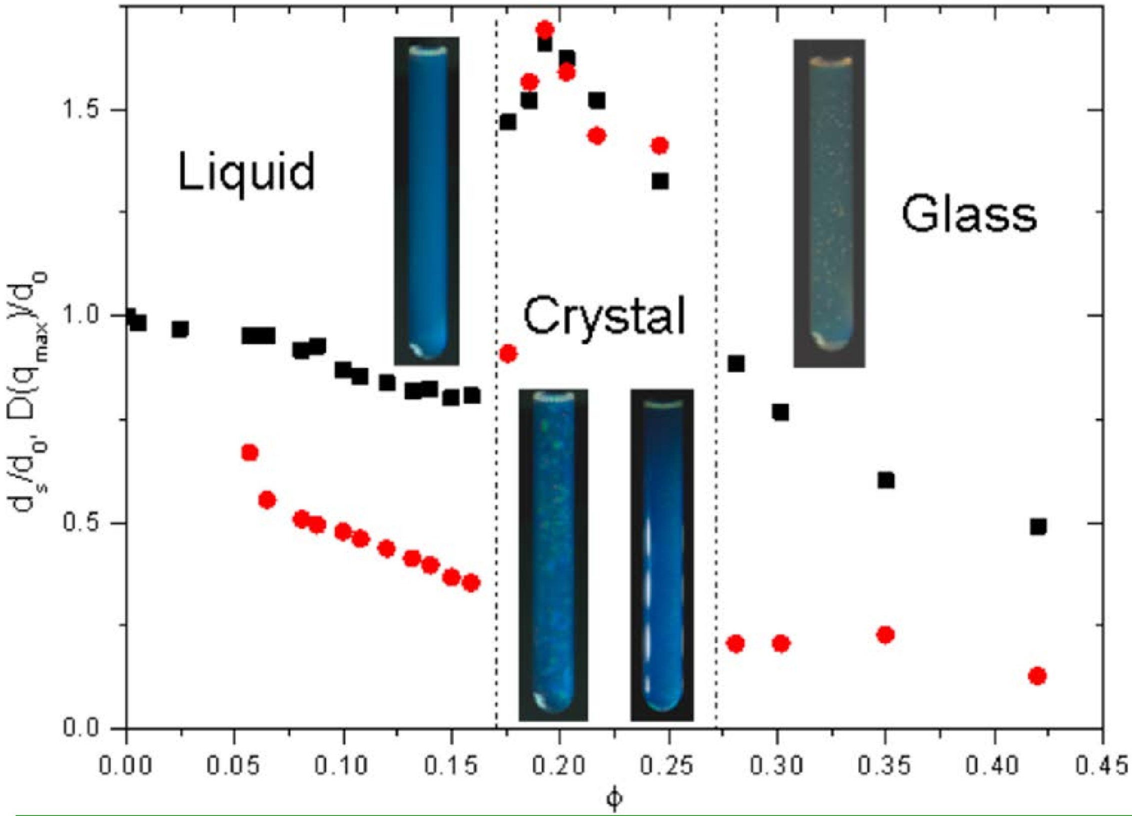

"Of some interest in this connection is the fact that the high g(O') states seem to be characterized by relatively free diffusion, while in the low g(u) states diffusion is much restricted."