Homodyne and Heterodyne X-ray Photon Correlation Spectroscopy in Carbon black-Filled polymers

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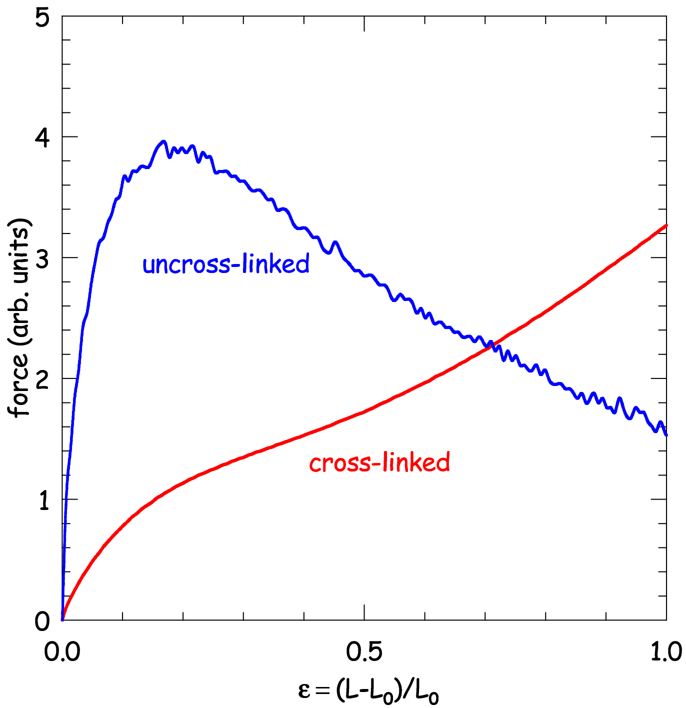
The Problem

We want to study the dynamical behaviour of filled elastomers polymers at the scale of the inclusions when submitted to a stress.

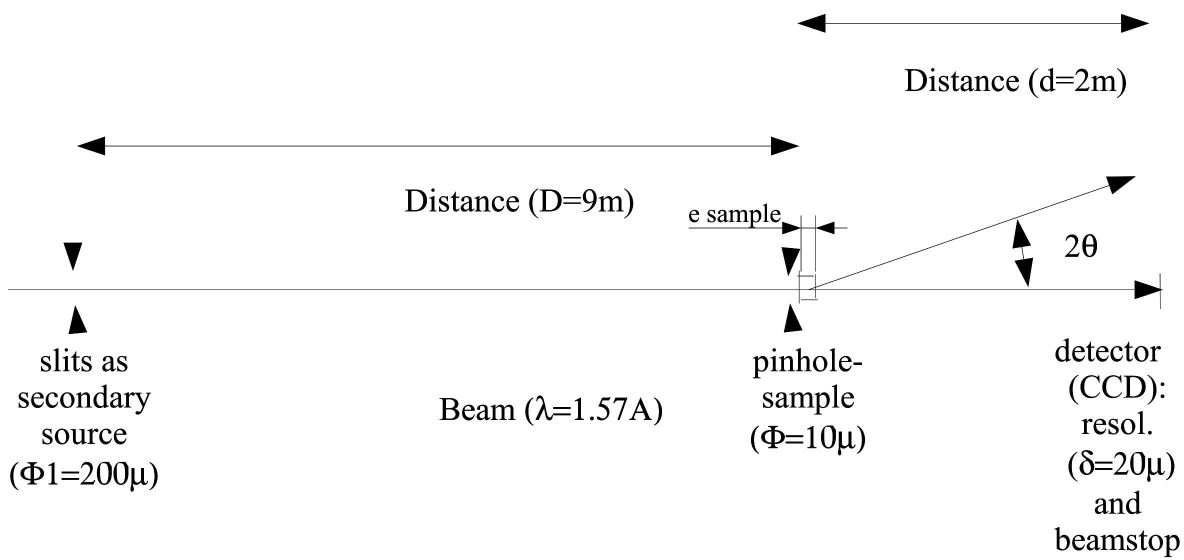
Here, carbon black dispersed in an elastomer matrix of an Ethylene-Propylene-Rubber (EPR). The Carbon black content is of the order of 20% vol, i.e. above the percolation threshold. Different mechanical behaviours are observed when a deformation is applied to the system.



If the polymer is cross-linked, the system is essentially elastic, If the polymer is not, the system is visco-elastic.

CSAXS

The time evolution of the microstructure of the sample can be studied with Coherent Small Angle X-ray Scattering (CSAXS).



Schema of a D2AM SAXS setup

Coherence conditions

One obtains speckles provided some conditions are (roughly) fulfilled:
-Transverse coherence condition:

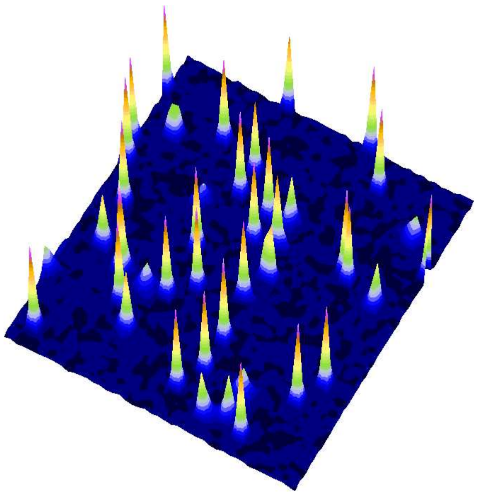
$$\epsilon \times \phi \leq \lambda \text{ } (\epsilon \leq 10\mu\text{rd}, \phi \simeq 10\mu\text{m and } \lambda \simeq 1.6\text{Å})$$

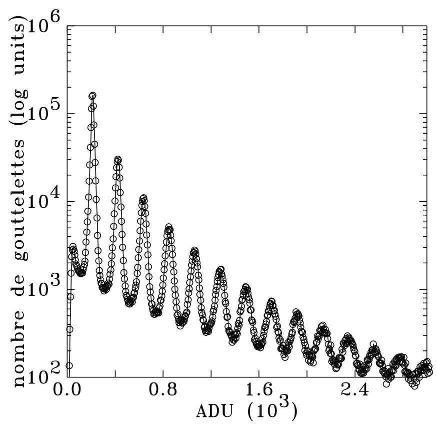
-Detection Resolution: same order of magnitude: the detector aperture should be in the 10μrd range: $20\mu m$ at about 2 m.
-Longitudinal coherence: depends on the beam monochromaticity: In SAXS, the length Λ along the beam path where scattered amplitudes interfere is essentially angle-dependent (θ is the Bragg angle):

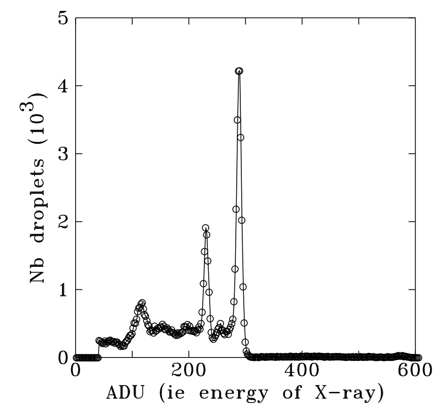
$$\Lambda \leq \lambda^2/(4\delta\lambda \times \theta^2)$$

For SAXS, for $\theta < 1 \times 10^{-2}$ rd, Λ is in the millimeters range.

Examples with DI-CCD



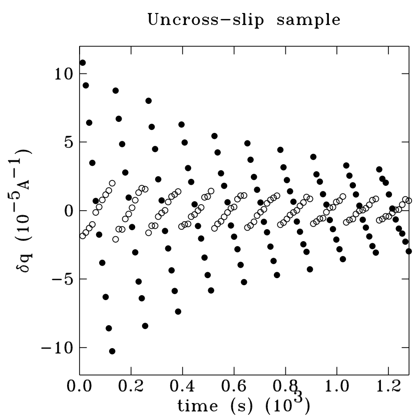


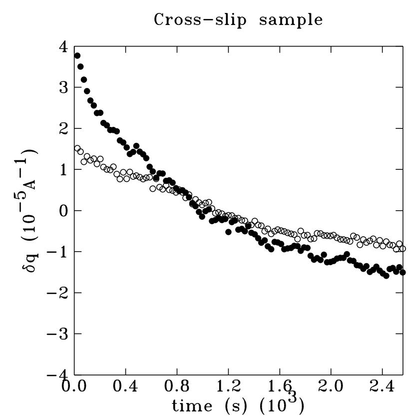


Observation of the impact of 8 KeV X-rays on a DI-CCD :(a). Distribution of the droplets total charge obtained during a series of 1000 frames, where some piling-ups occur: On can easily know the number of X-rays in one droplet (b). Energy distribution observed on a rotating anode ($Cu_{K\alpha}$) with a multlayer sample (Fe-Pd), where the $Fe_{K\alpha}$ and the Pd_L can be filtered.

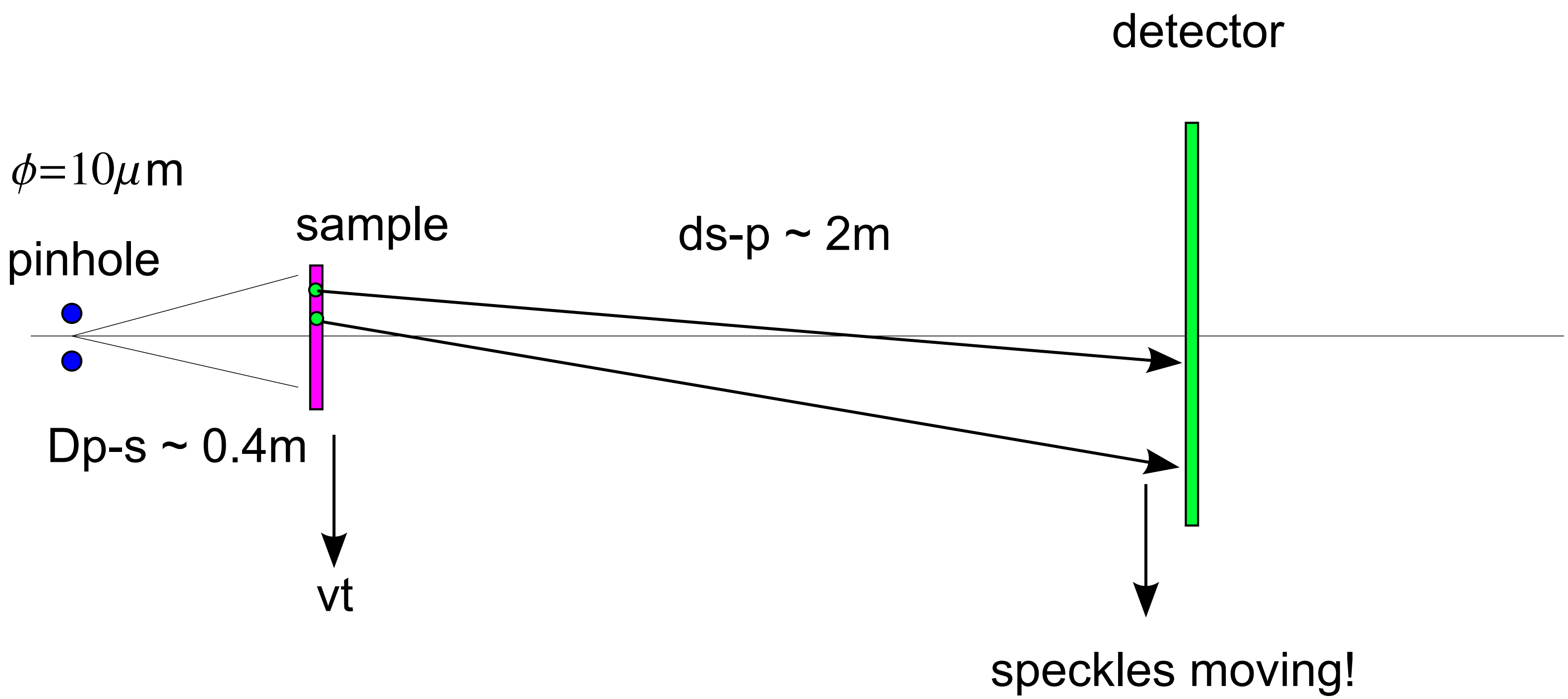
homodyne

Both systems have been studied by “in situ” stretching in a CSAXS measurement at D2AM (French CRG BM2 at ESRF).
After a 10% deformation, only the transversal movement of the speckle pattern is observed. This can be estimated by comparing the average pattern with the successive frames. A displacement of 4×10^{-5} corresponds to one pixel of our detector.





q-variations of the speckle patterns after a 10% deformation



Homodyne observation of movement shift out of the detector:

$$\delta l = \frac{d_{s-p}}{D_{p-s}} \times vt$$

sample movement

We work at the beginning of the Far-Field position:

$$D_{p-s} = 0.4m \geq \phi^2/(2\lambda) = 0.3m$$

The beam divergence is:

$$\epsilon \simeq \lambda/\phi$$

For a sample movement of vt, the scattering at the $\vec{q}$ is now observed at a different pixel of the CCD at a distance d:

$$\delta q = \frac{2\pi}{\lambda} \times \frac{vt}{D_{p-s}} = \frac{2\pi}{\lambda} \times \frac{\delta l}{d}$$

so that:

$$\delta l_{det} \simeq \frac{d_{s-d}}{D_{p-s}} \times vt$$

Speckle Dynamics

In this experience, only the flowing of the sample was observed. We want both fluctuations and sample movement: Heterodyning!

Setup for heterodyning:
We pile the moving sample and a reference with a total thickness small enough vs longitudinal coherence length. For SAXS, it may be one centimeter! The beam is crossing the hybrid sample.
By studying correlations, one is able to observe both flowing (sample velocity v) and fluctuations.
Reference: Bern and Pecora (1976)

Obtaining correlations

One fi rst averages over experimental time:

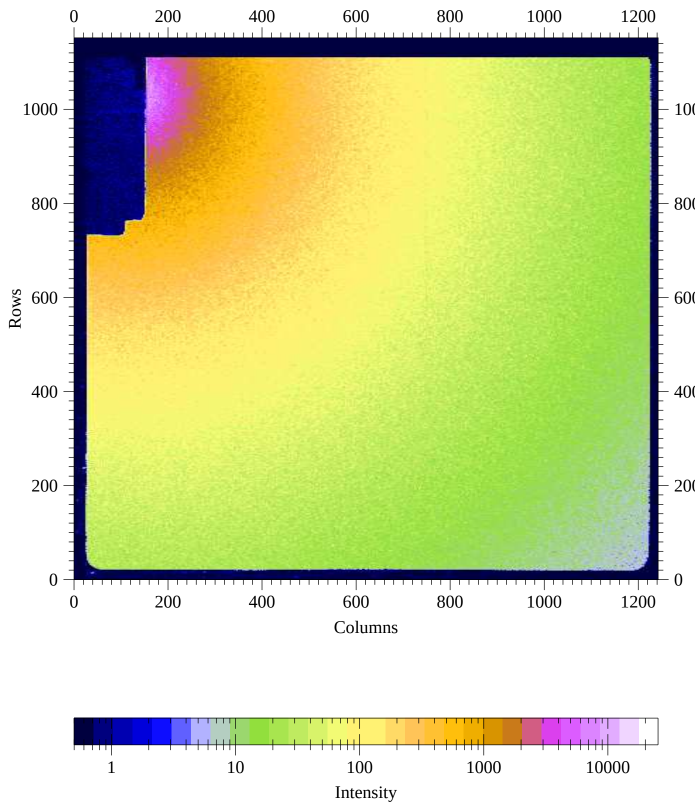
$$< I(\vec{q}, t + t')I(\vec{q}, t') >_{t'}$$

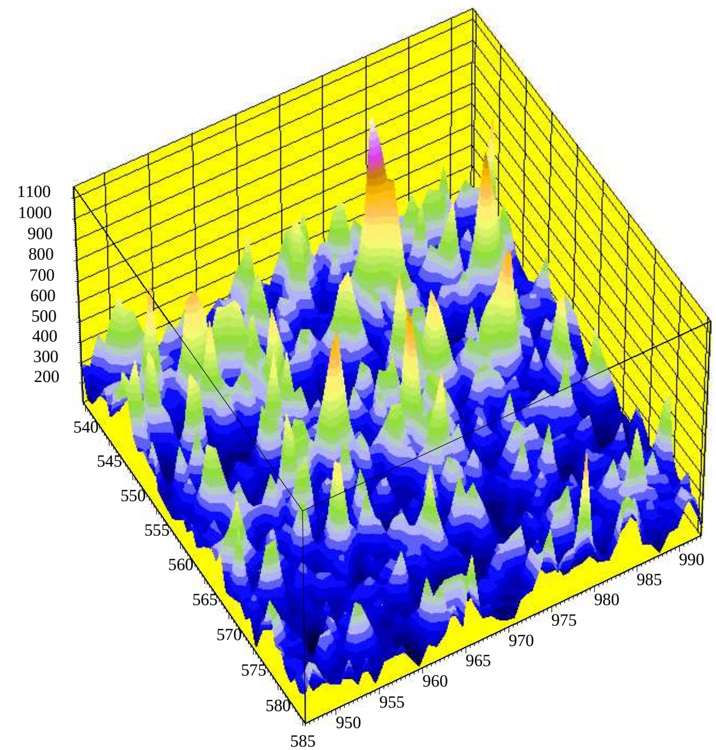
For each pixel of wavevector $\vec{q}$. Not enough statistics! One carries out also an average over a suitable $\vec{q}$ domain D_q:

$$\gamma(t, q) =< I(q, t + t)I(q, t) >_q / < I(q, t) >_q^2$$

EXPERIMENT CARRIED OUT AT THE IMMCAT BEAMLINE OF APS (ARGONNE, ILLINOIS)

Typical images





Typical scattering obtained from 500 frames, 0.25s each (above) and a small region (50*50 pixels) of the previous image

Directional

Correlations were fi tted by means of the equation:

$$g_2(q,\phi,t) = 1+\beta(1-x)^2 + 2x(1-x)\beta\cos(\omega t)\gamma(t/\tau(q)) + x^2\beta\gamma^2(t/\tau(q)) \quad (1)$$

where x is the degree of mixing:

$$x_\Delta = \langle\langle I_s\rangle_t\rangle_{\vec{q}\in\Delta}/(\langle\langle I_r + \langle I_s\rangle_t\rangle_{\vec{q}\in\Delta}). \quad (2)$$

$\beta(1-x)^2$ is the static coherence from the reference sample, the second term is the interference between the two samples, and $x^2\beta$ corresponds to the homodyne dynamic part from fluctuating sample

Fits

We found that the relaxation $\gamma(t/\tau)$ can be written:

$$\gamma(t/\tau) = \exp(-(t/\tau)^{1.66})$$

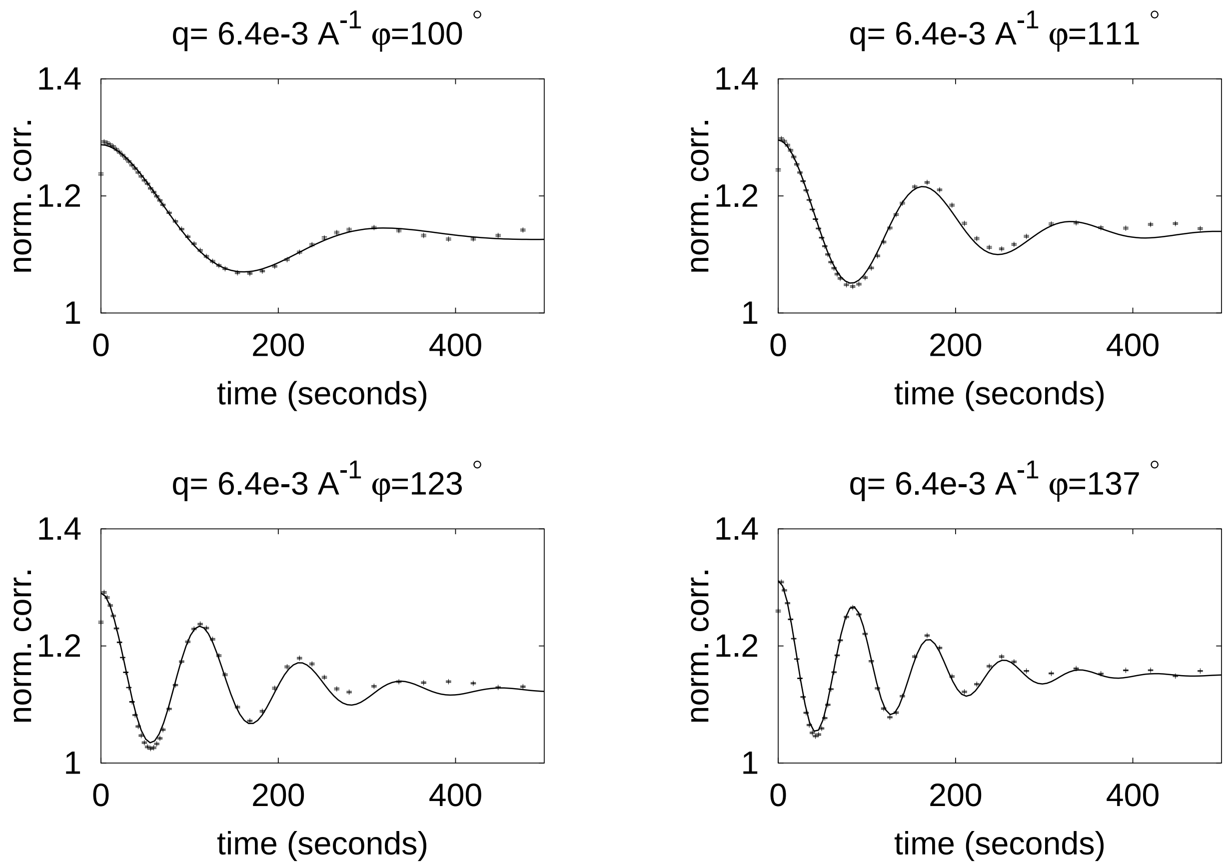
$\tau(q)$ corresponds to the fluctuations in the sample. The exponent $\mu \simeq 1.66$ seems necessary to take account of data.

The oscillating behaviour $\cos(\omega t)$, where: $\omega = qv\cos(\phi)$, is the phase shift introduced by the sample movement in the amplitude diffracted by the reference.

The domains for calculating the q-averages must be selected both from the value of $|\vec{q}|$- and from that of $\cos(\phi)$.

Typical fits: various angles ϕ

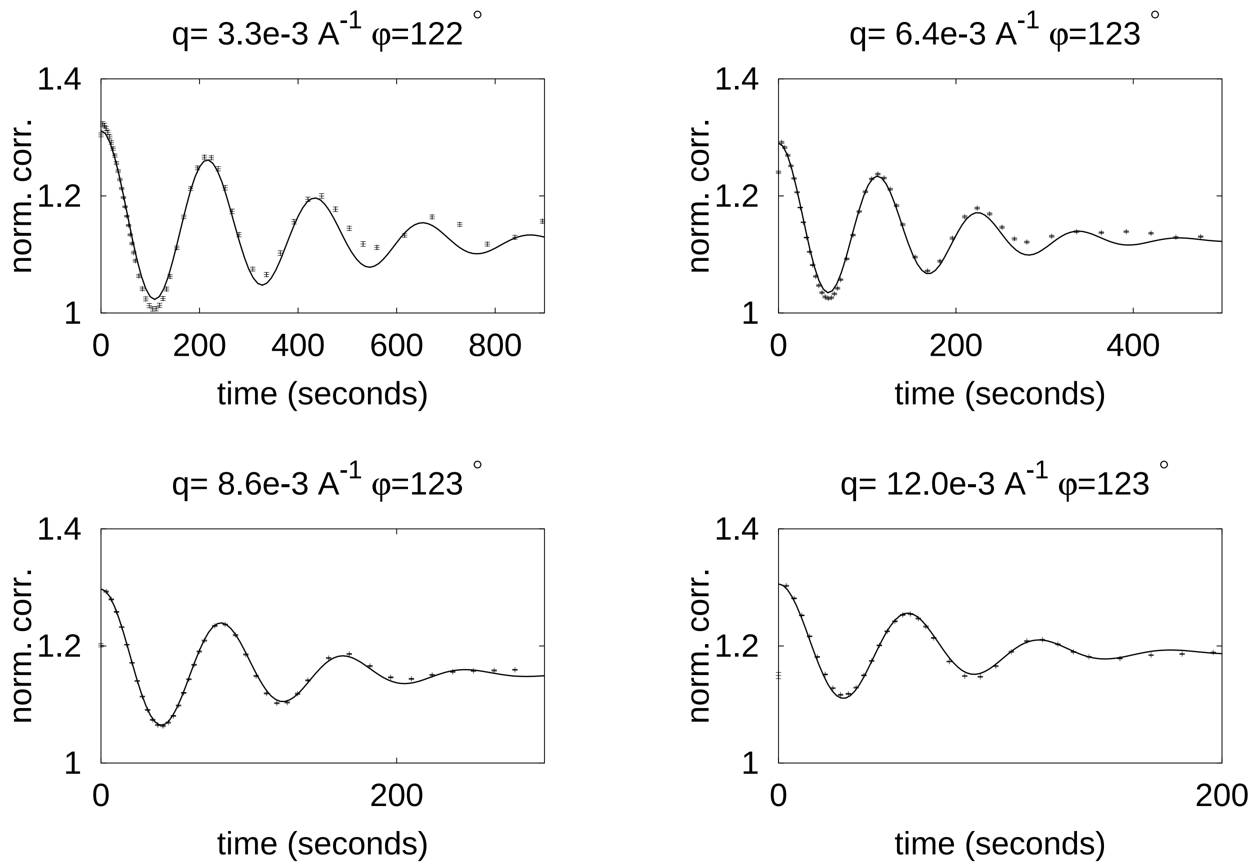
$$\gamma(q,\phi,t) = 1 + \beta_0 + \beta_1 \times \exp(-(t/\tau(q))^{\mu}) \times \cos(\omega t)$$



Oscillating behaviour of the normalised correlations for various angles at $q = 6.4 \times 10^{-3}$ Å^{-1} observed during relaxation of the cross-slip sample after 100% elongation

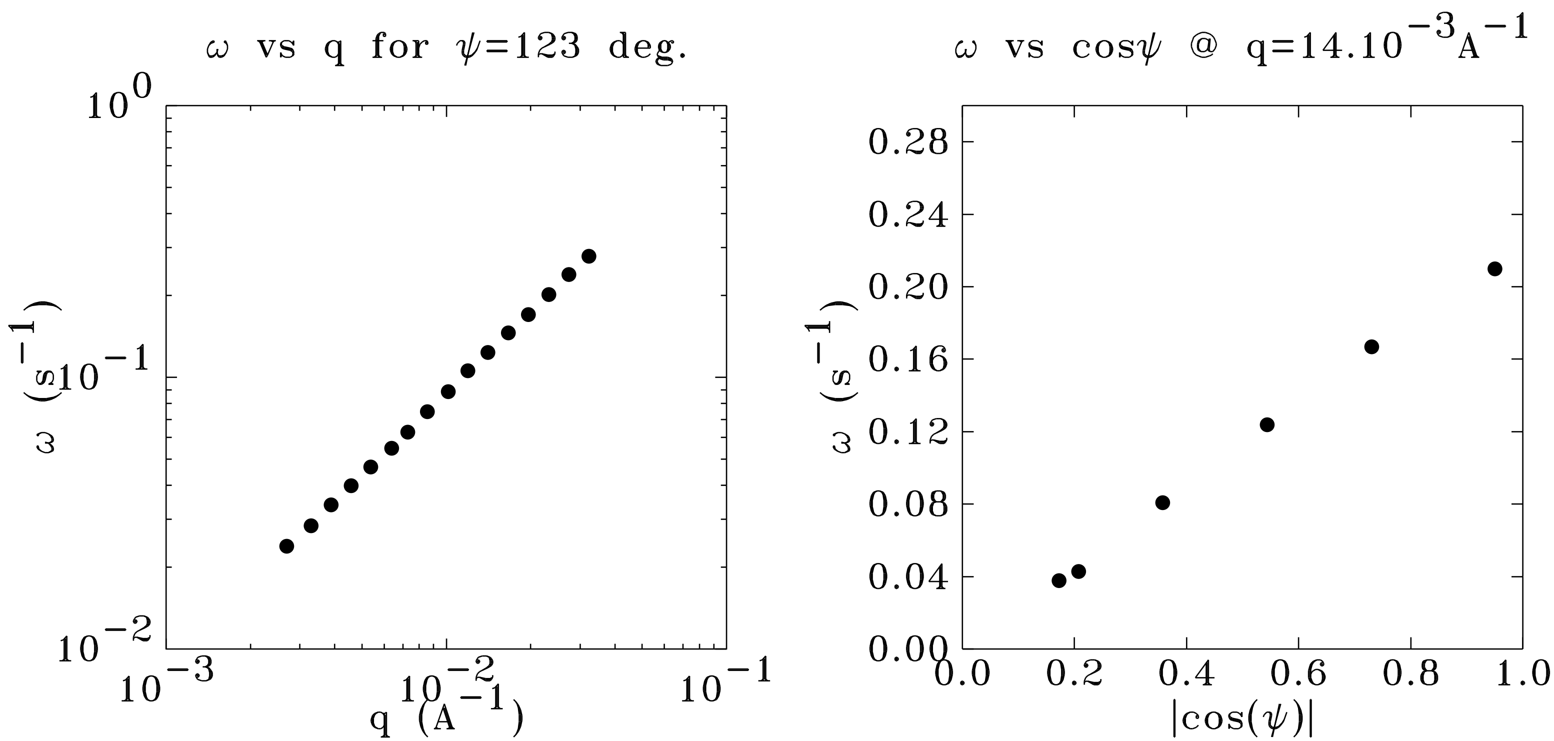
Typical fits: various q-values

$$\gamma(q, \phi, t) = 1 + \beta_0 + \beta_1 \times \exp(-(t/\tau(q))^{\mu}) \times \cos(\omega t)$$



Oscillating behaviour of the normalised correlations for the same angle ($\phi = 122\,\mathrm{deg}$) at various q-values observed during relaxation of the cross-slip sample after 100% elongation

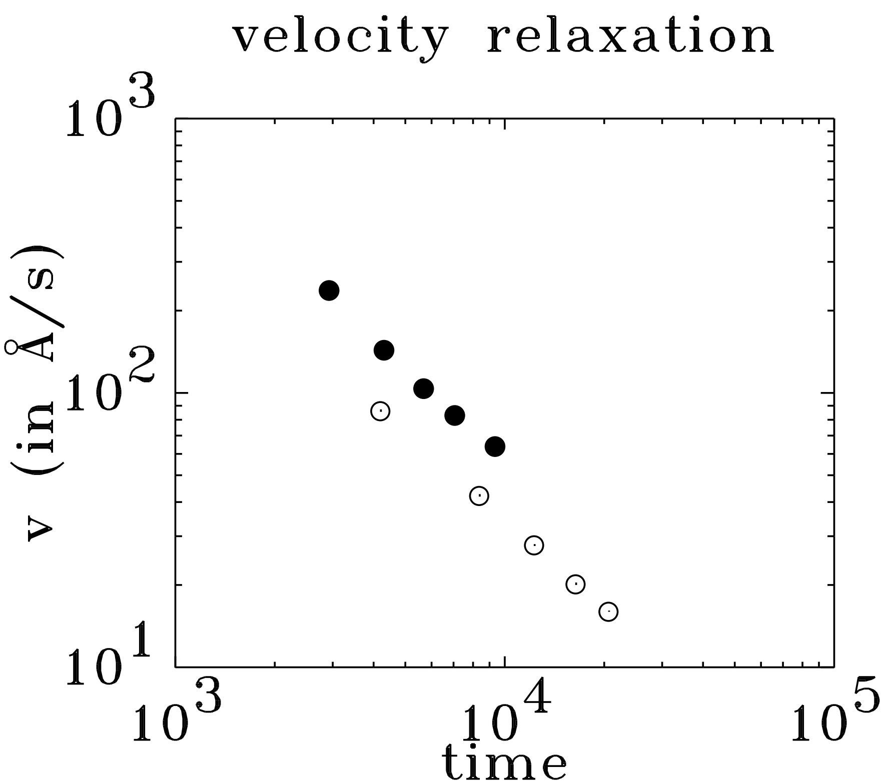
Scaling



Scaling of $\omega(q, \phi)$ for the relaxation of the cross-linked system, after 20000s. The relation: $\omega = vq\cos(\phi)$ is verifi ed, with $v = 1.5$nm/s

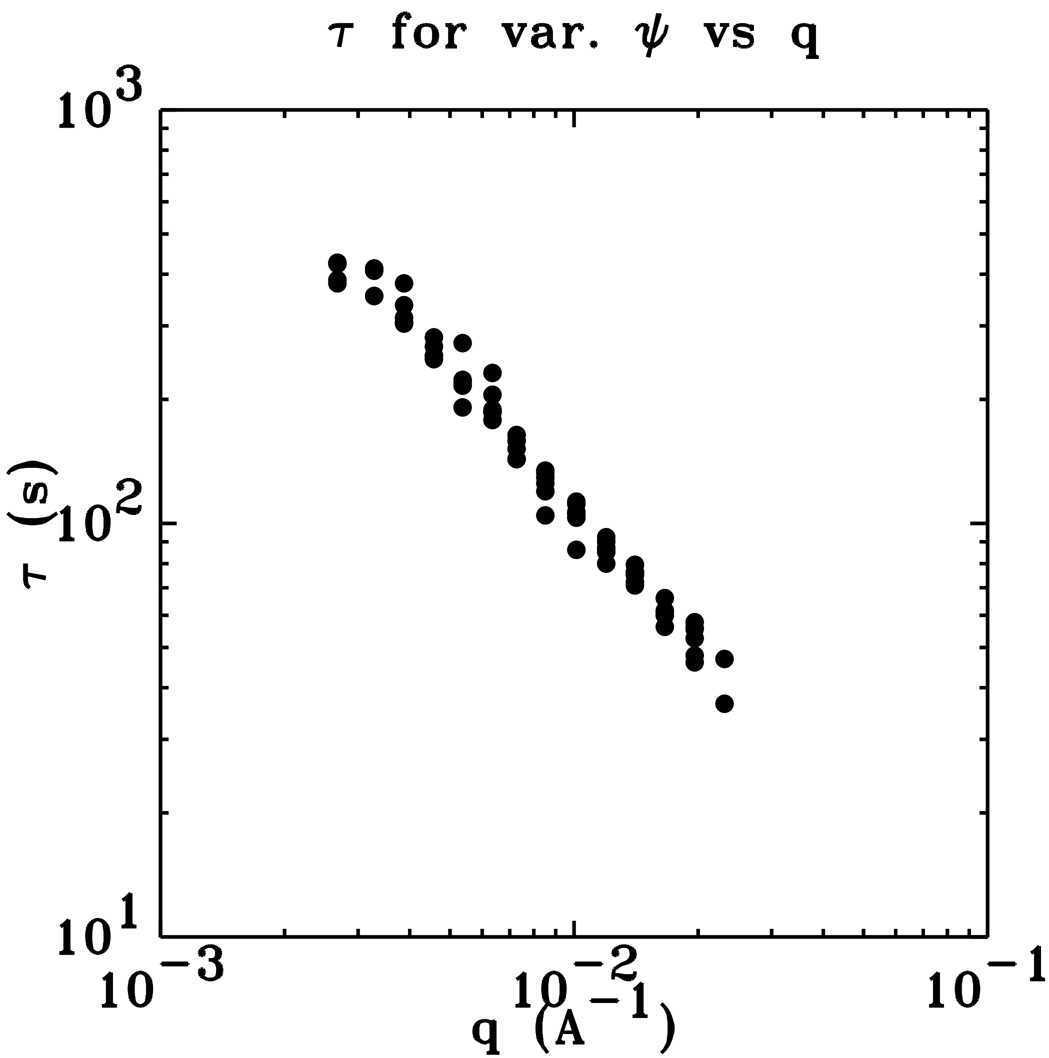
Velocities

Very long relaxation process in both cases (cross-linked and un-cross liked). Velocities down to $\simeq 15$Å/s.



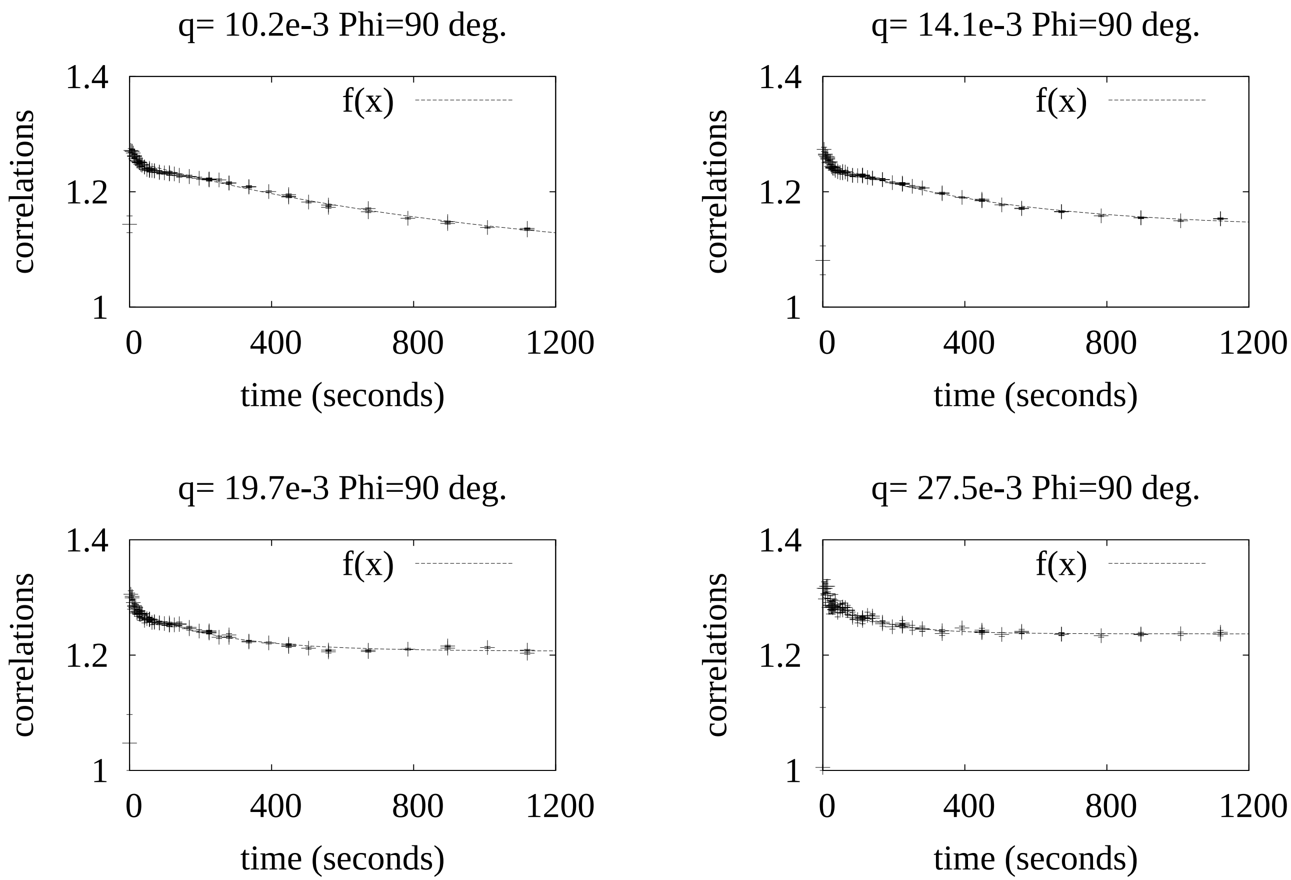
Relaxation of the uncrossed-slip (open circles) and of the crossed slip sample (close circles).

Relaxation



dirPer

The fluctuations in the direction perpendicular to flowing have an exponential behaviour in a very narrow domain of ϕ (about 1 degree).



Correlations observed in the direction $\phi = 90\,\mathrm{deg}$, for q-values where exponentials are roughly obtained

conclusion

1. Heterodyning works!
2. The heterodyning method seems promising fot this type of studies.
3. We only observed “recovery” after a 100% elongation
4. The simple model of relaxation of Bern and Peccora does not explain the relaxations observed.

$$\gamma(t) = 1 + \beta_0 + \beta_1 \times \exp(-Dq^2 t) \times \cos(qv\cos(\phi)t)$$

5. We can use this method for the study of defromation of opaque samples (metals..)