

# Dispersión de rayos X: De los sistemas heterogéneos a las capas delgadas

**Mari Cruz García Gutiérrez**

**Instituto de Estructura de la Materia, CSIC**

**maricruz@iem.cfmac.csic.es**



Aplicación de la radiación sincrotrón a la  
caracterización de materiales

Sevilla, 27-29 octubre 2010

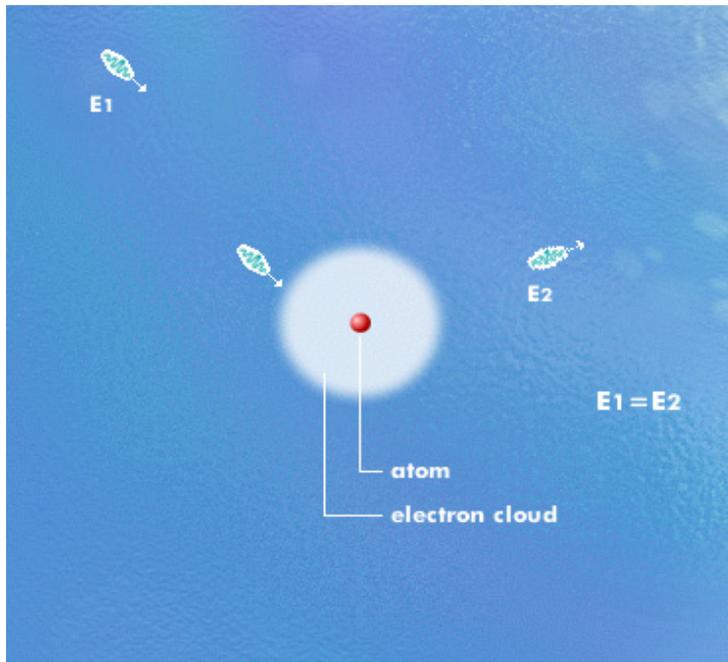


# Índice

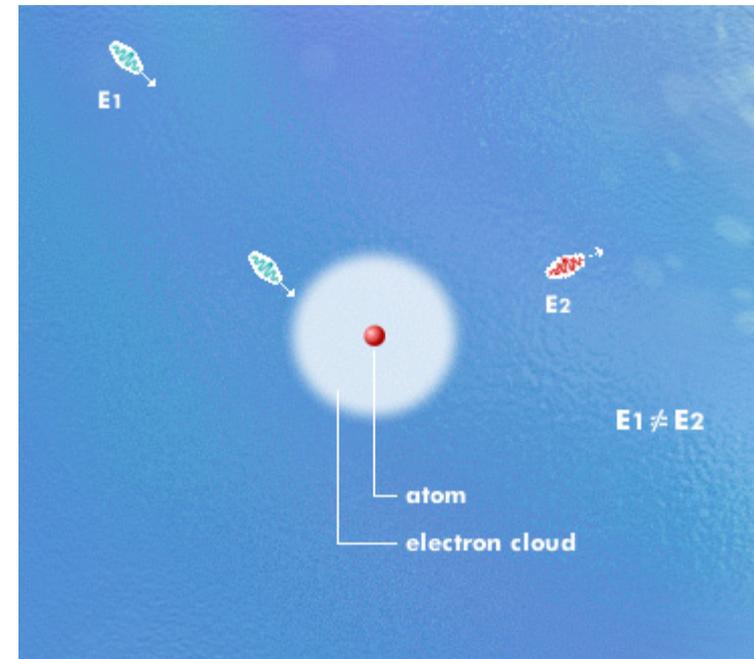
- ✓ **Nociones sobre la dispersión de rayos X**
- ✓ **Difracción de rayos X por cristales**
- ✓ **Jerarquías estructurales y técnicas**
- ✓ **Dispersión de rayos X a alto (WAXS) y bajo ángulo (SAXS)**
- ✓ **Dispersión de rayos X con microfoco ( $\mu$ WAXS y  $\mu$ SAXS)**
- ✓ **Dispersión de rayos X con incidencia rasante (GIWAXS y GISAXS)**
- ✓ **Estaciones experimentales de dispersión de rayos X en el mundo**

# Dispersión de rayos X

Dispersión elástica (dispersión Thomson)

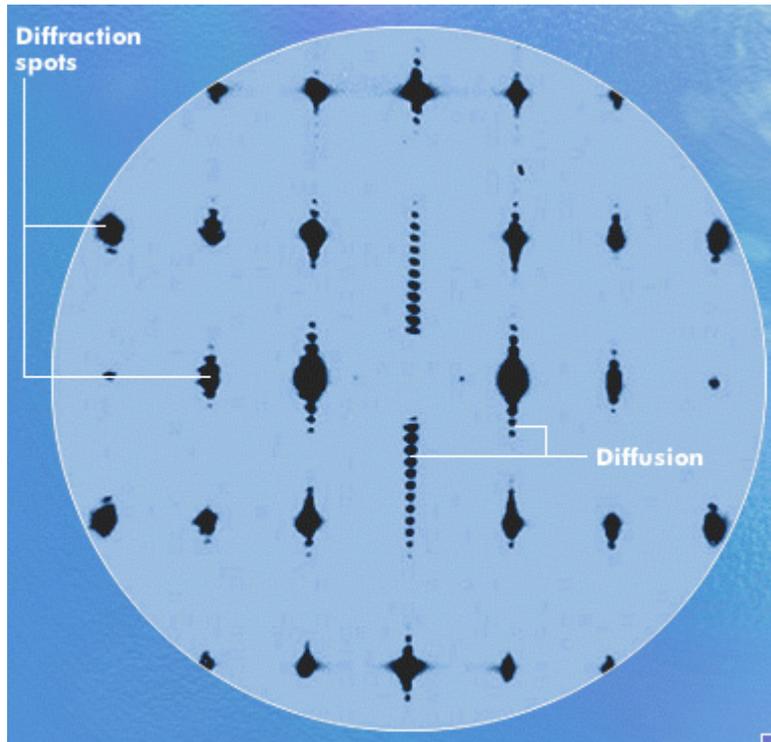


Procesos inelásticos

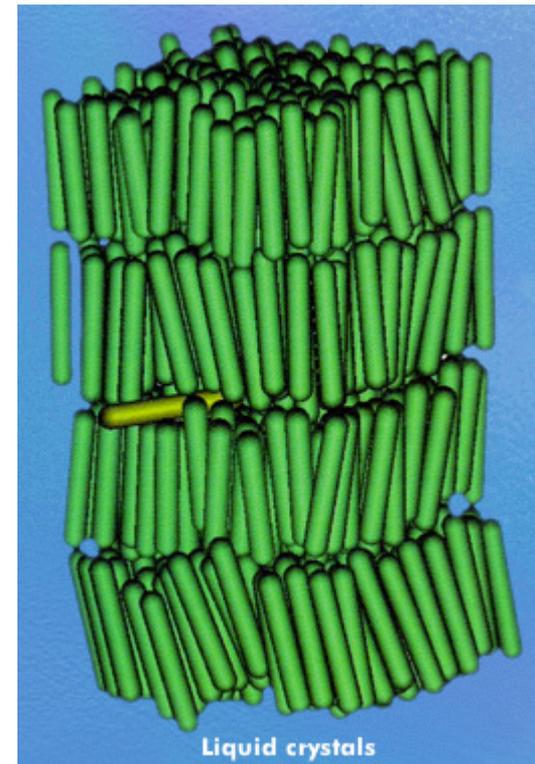


# Dispersión de rayos X

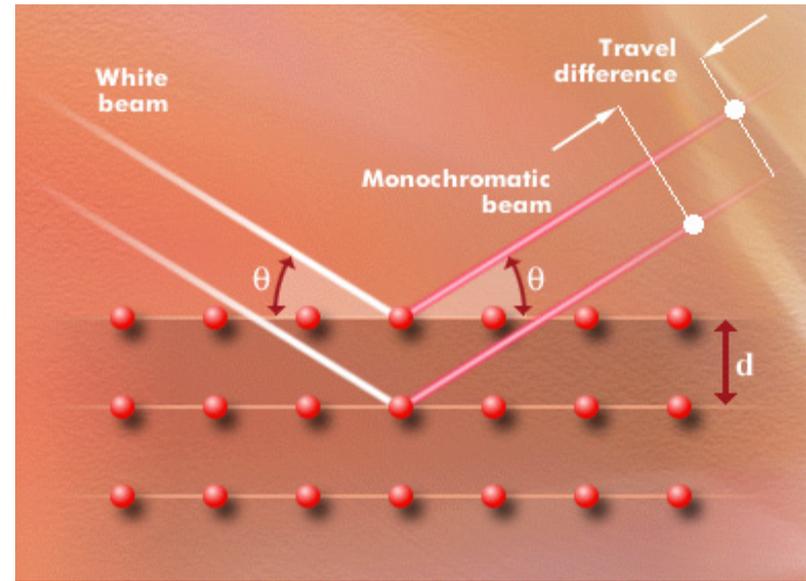
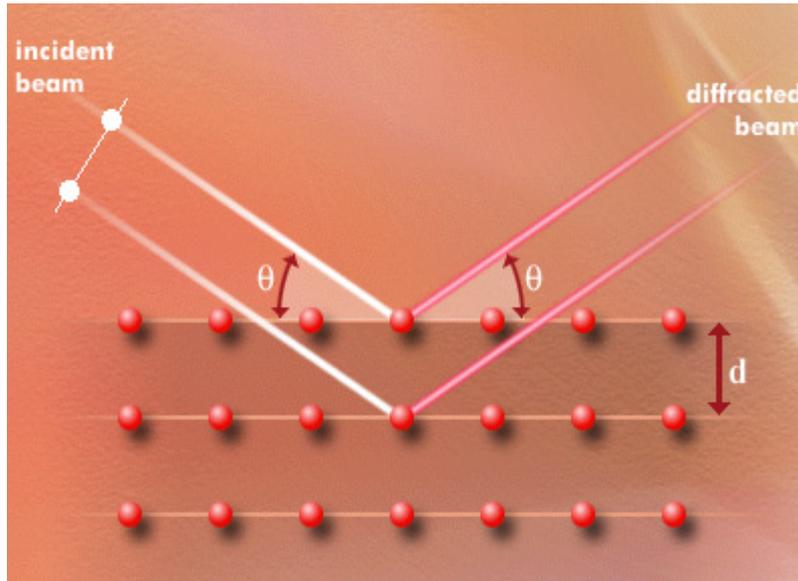
“Scattering” difuso



Materia condensada blanda



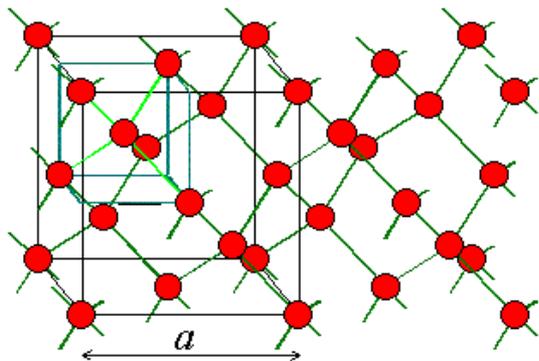
# Difracción de rayos X



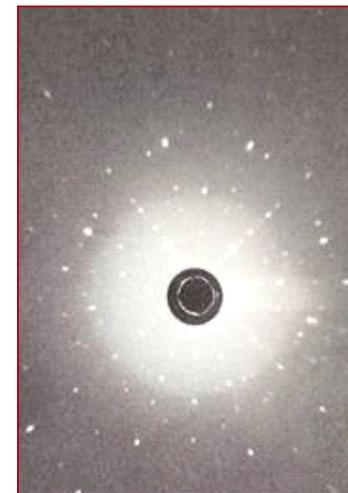
Ley de Bragg:

$$2d \sin \theta = n\lambda$$

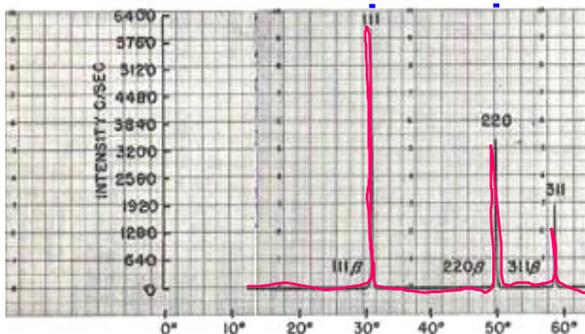
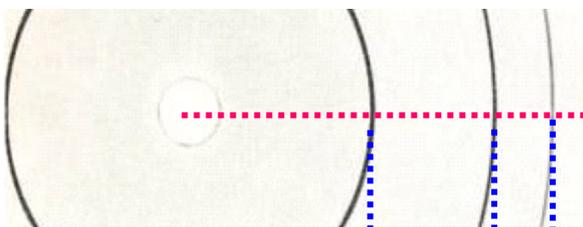
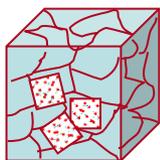
# Difracción por cristales: Silicio



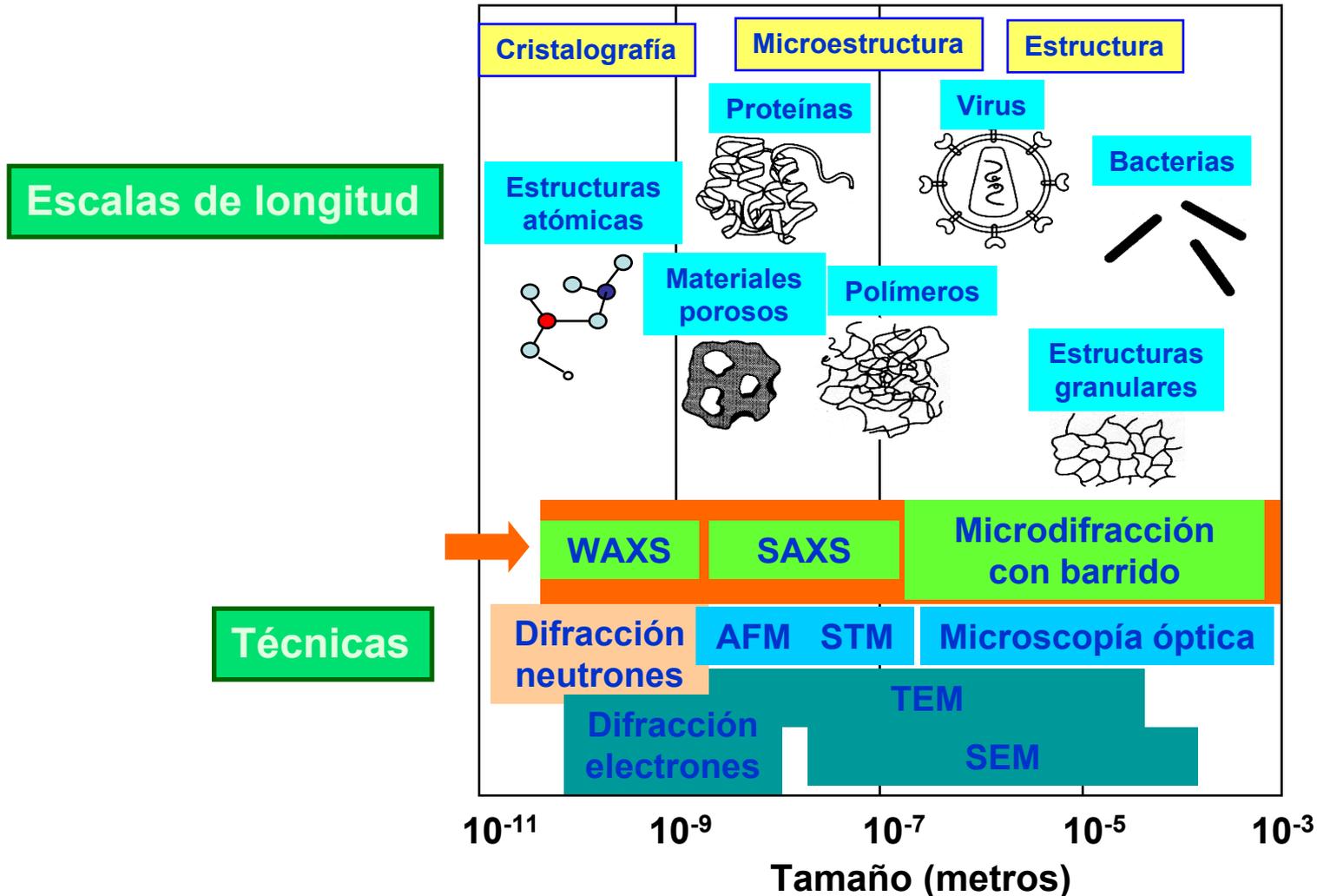
## Monocrystal



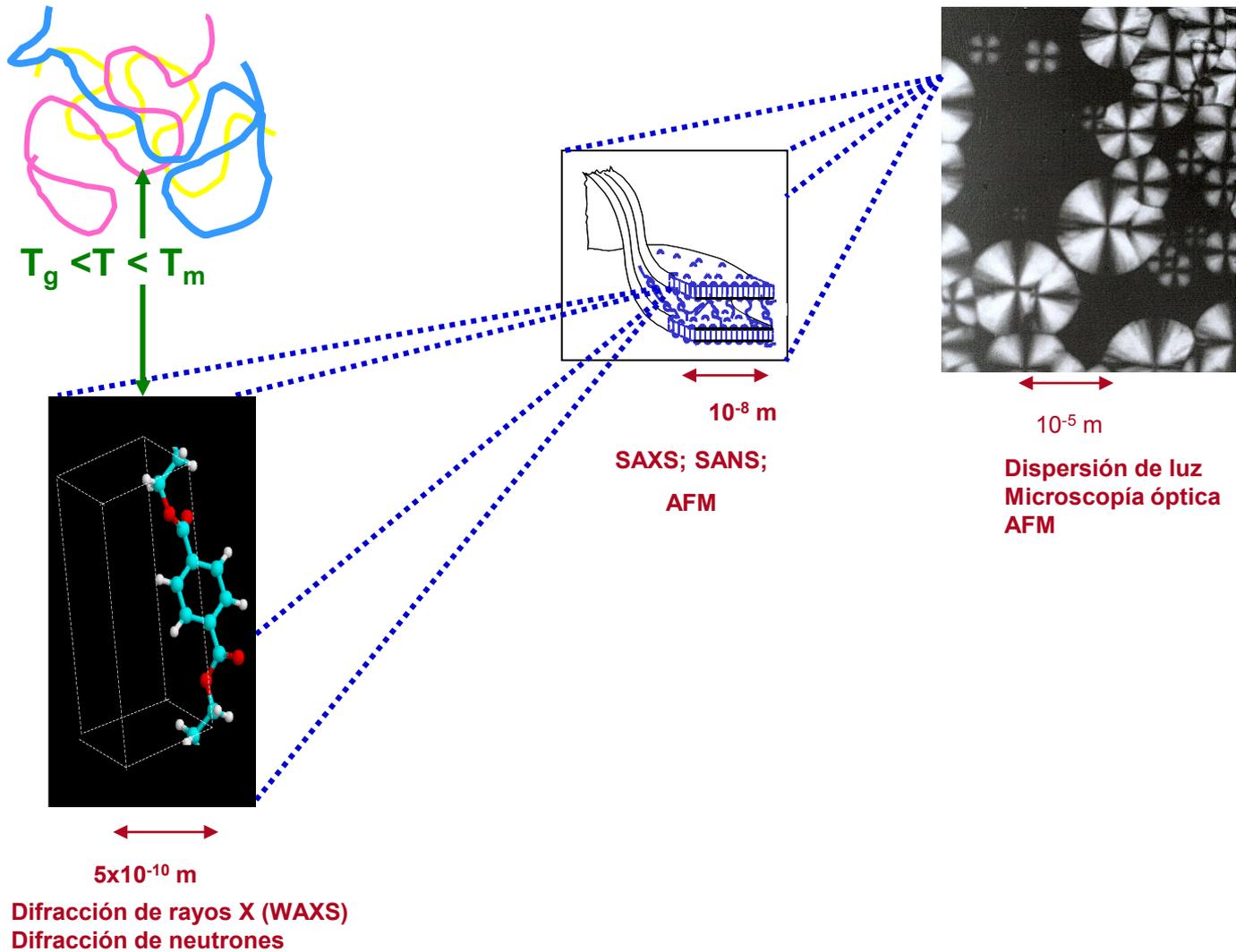
## Policristal



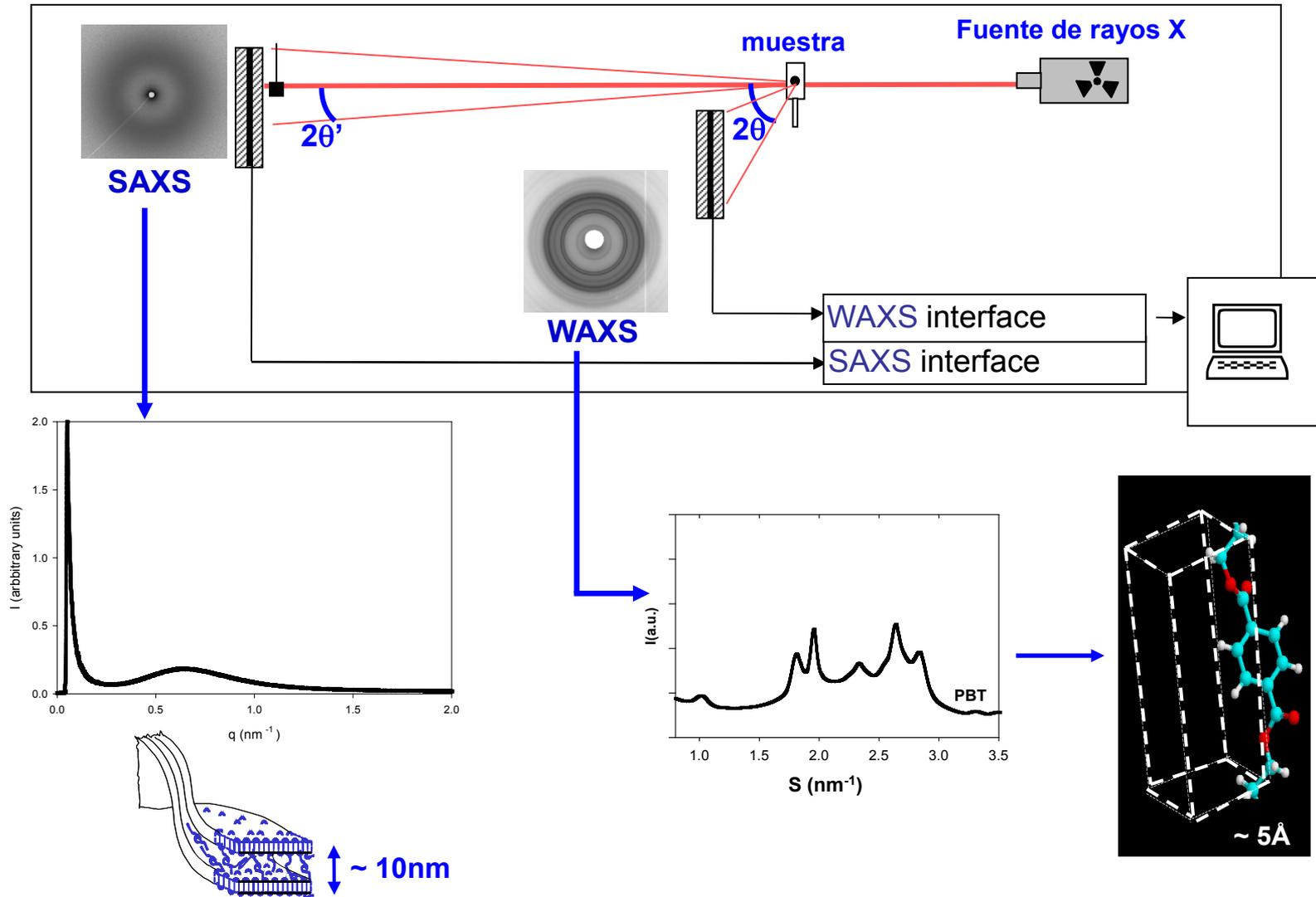
# Jerarquías Estructurales



# Jerarquías Estructurales: Cristalización de polímeros

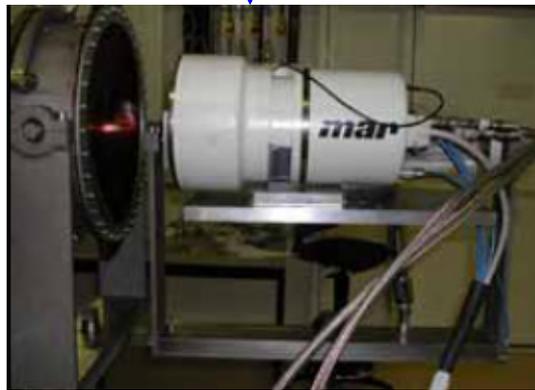
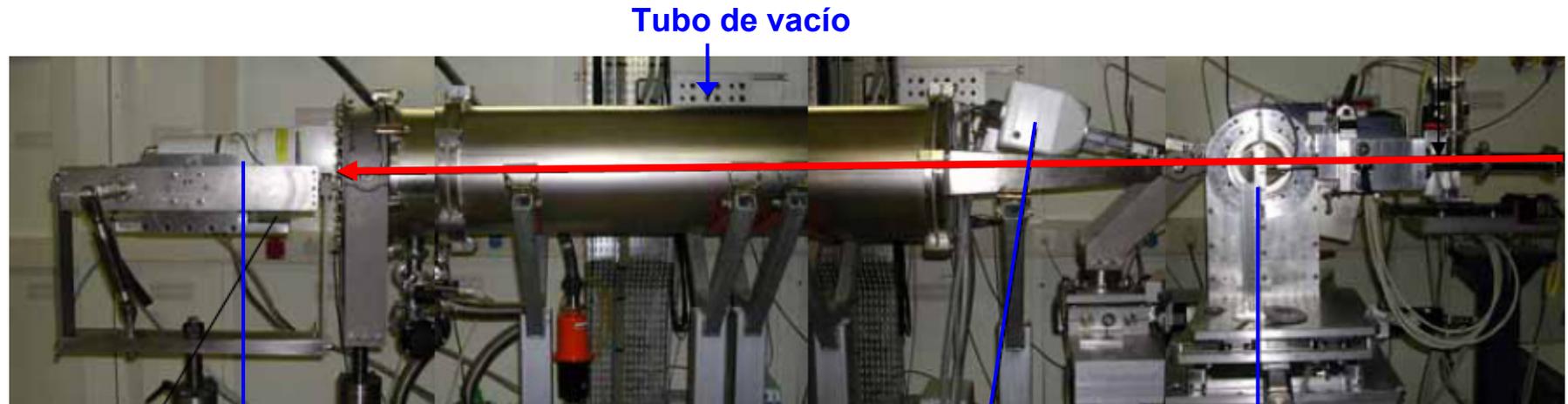


# Dispersión de rayos X a alto (WAXS) y bajo ángulo (SAXS)



# Estación experimental de WAXS y SAXS

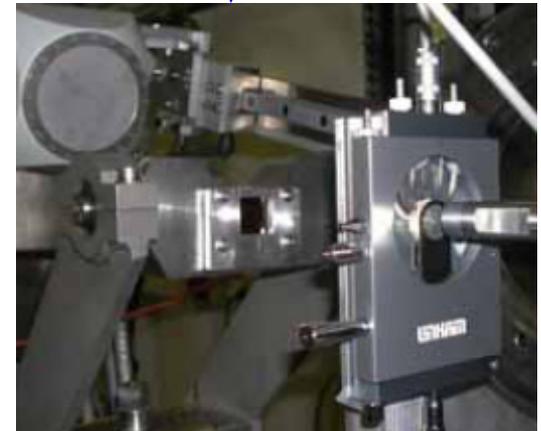
Línea española (BM16) en el ESRF



Detector SAXS



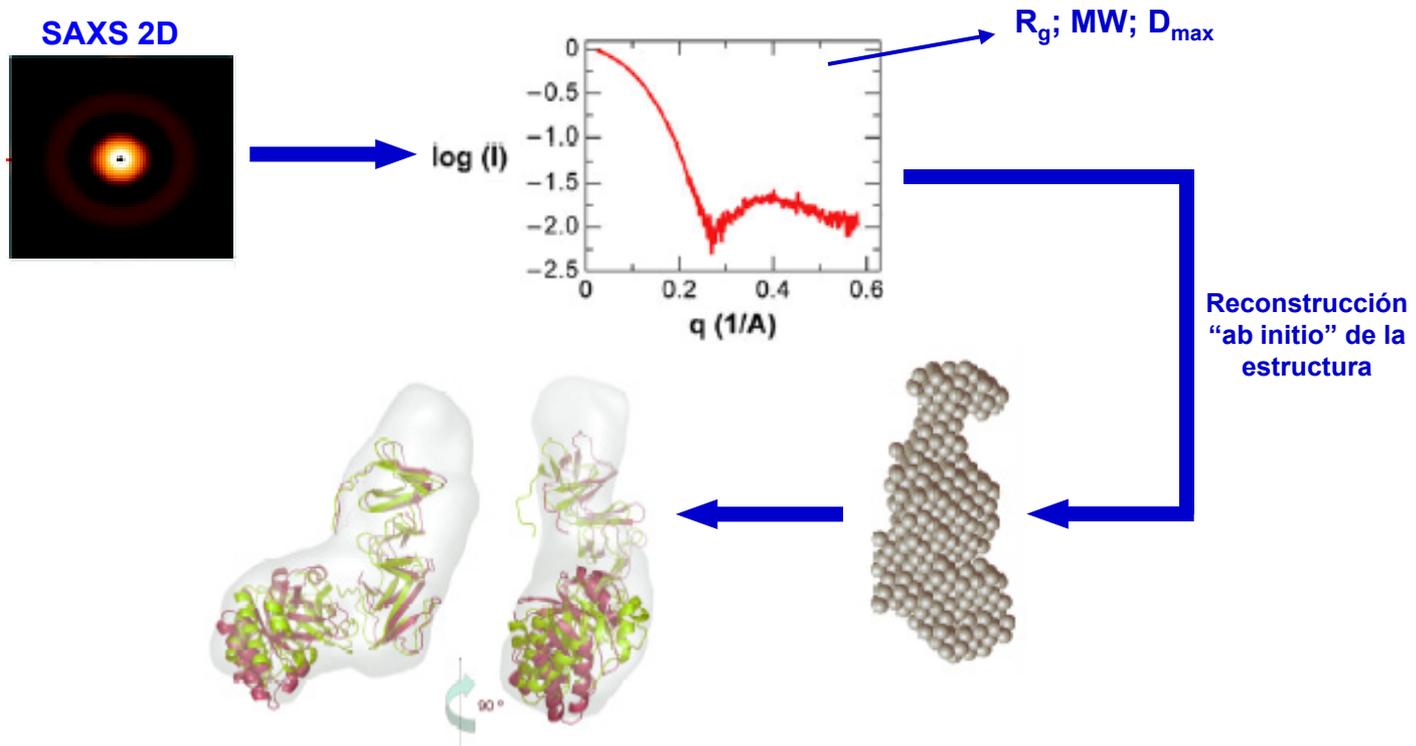
Detector WAXS



Entorno de muestra

# Aplicaciones de la dispersión de rayos X

# Proteínas en disolución

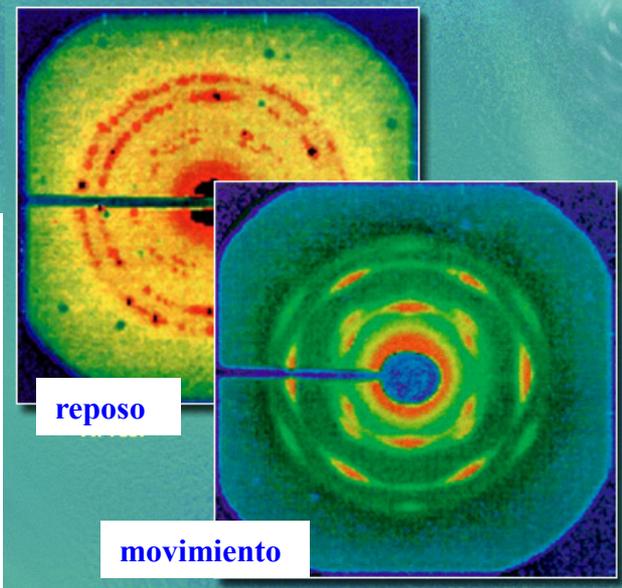
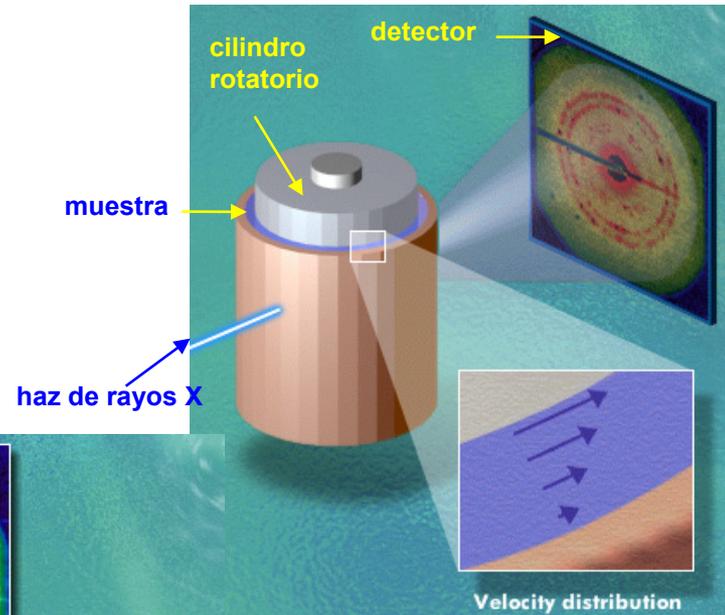
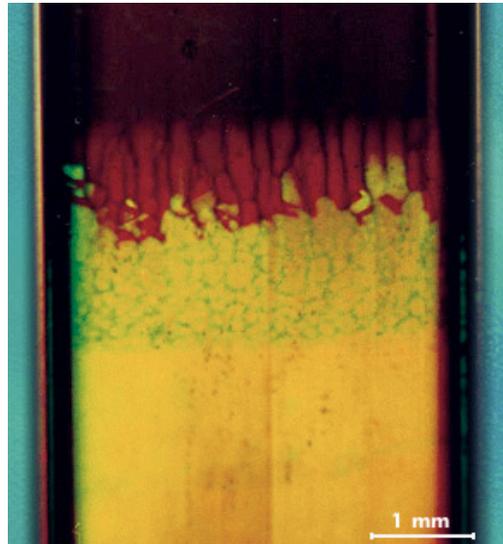


- PX: Gran cantidad de proteínas no pueden cristalizar
- NMR: Limitación para estudiar proteínas de gran tamaño
- SAXS: Proteínas en condiciones fisiológicas y bajo perturbaciones físicas y químicas en tiempo real

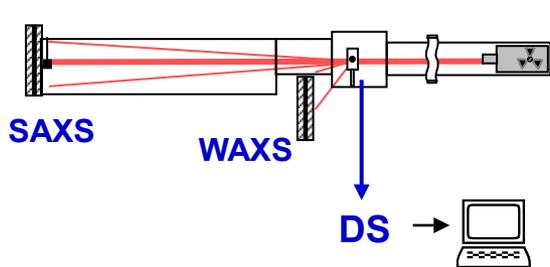
R.M. Buey *et al.* Lecture Notes in Physics 776, Springer (2009)

# Sistemas coloidales

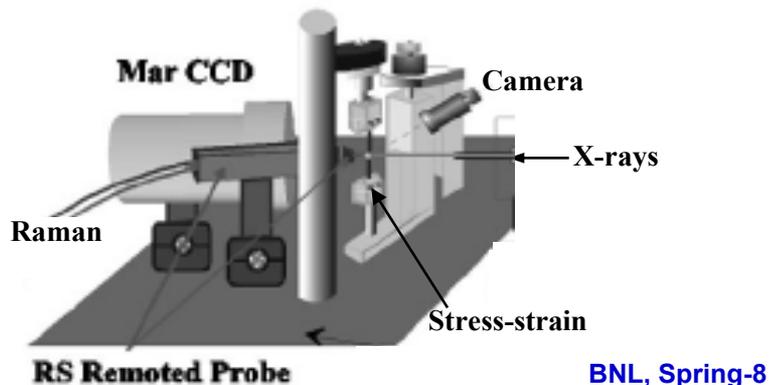
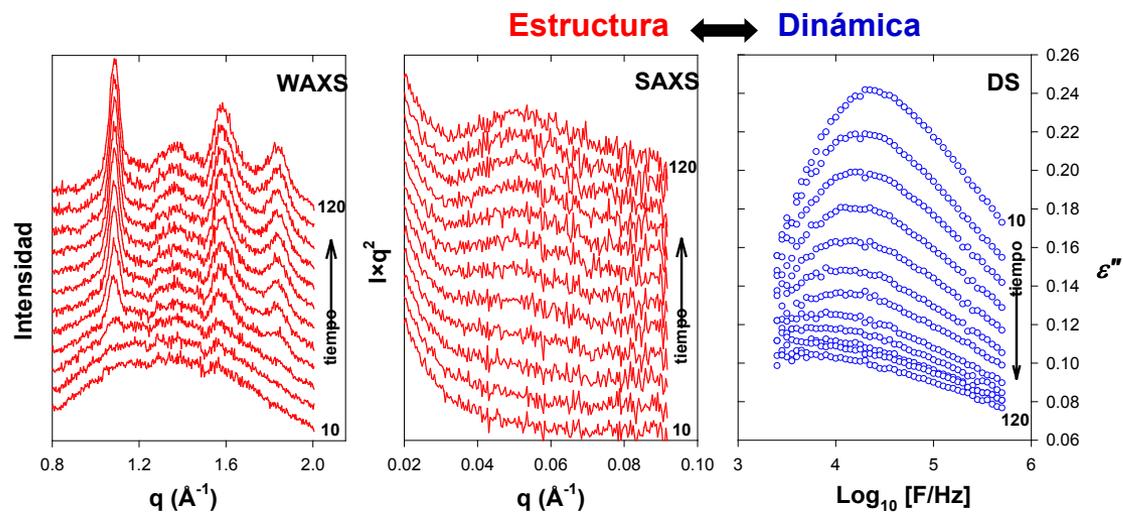
PS en metanol



# Técnicas simultáneas

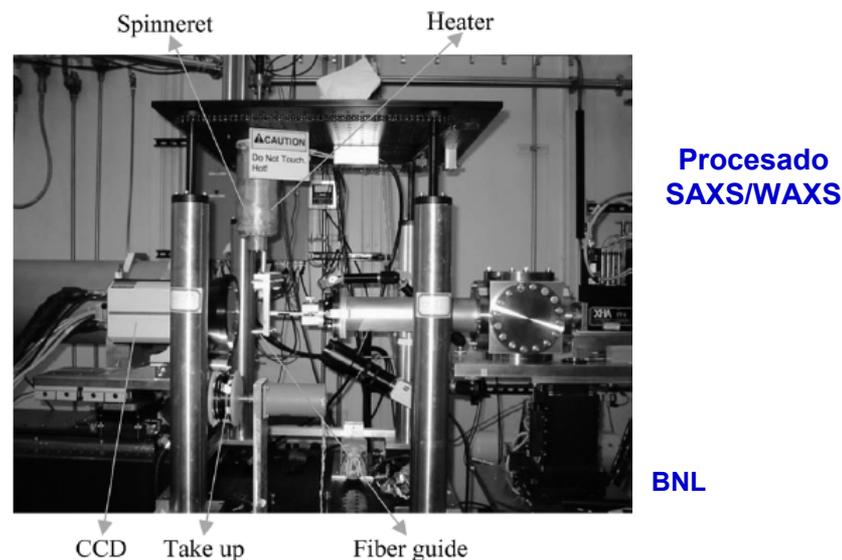


I Sics et al, *Rev. Sci. Instrum.* 71,1733 (2000)



Deformación  
SAXS/WAXS  
Raman

Información complementaria sobre evolución estructural de la cadena molecular tanto en la fase amorfa, mesofase y fase cristalina.

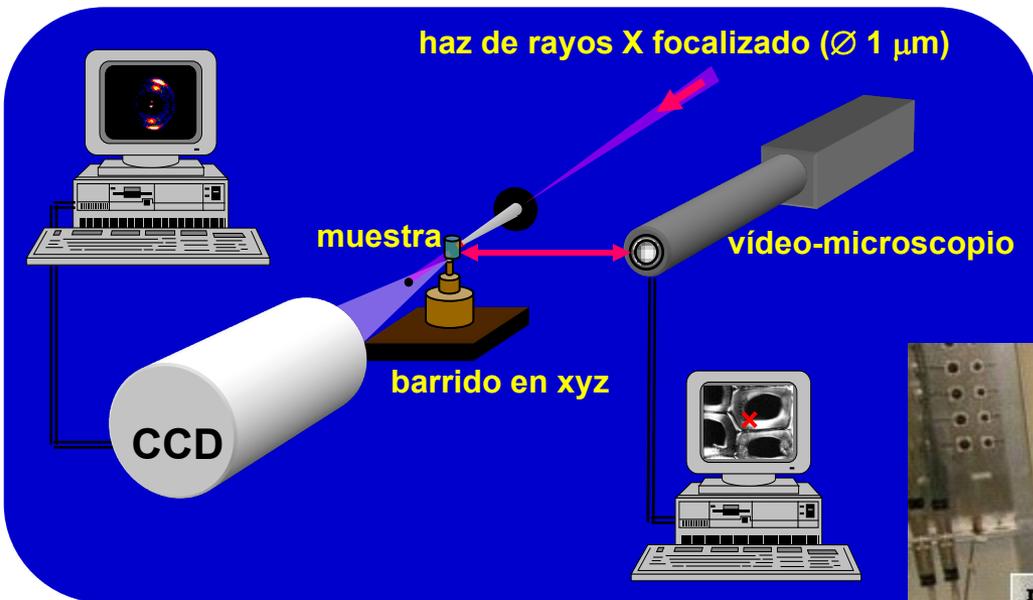


S. Ran et al, *Rev. Sci. Instrum.* 74, 3087 (2003)

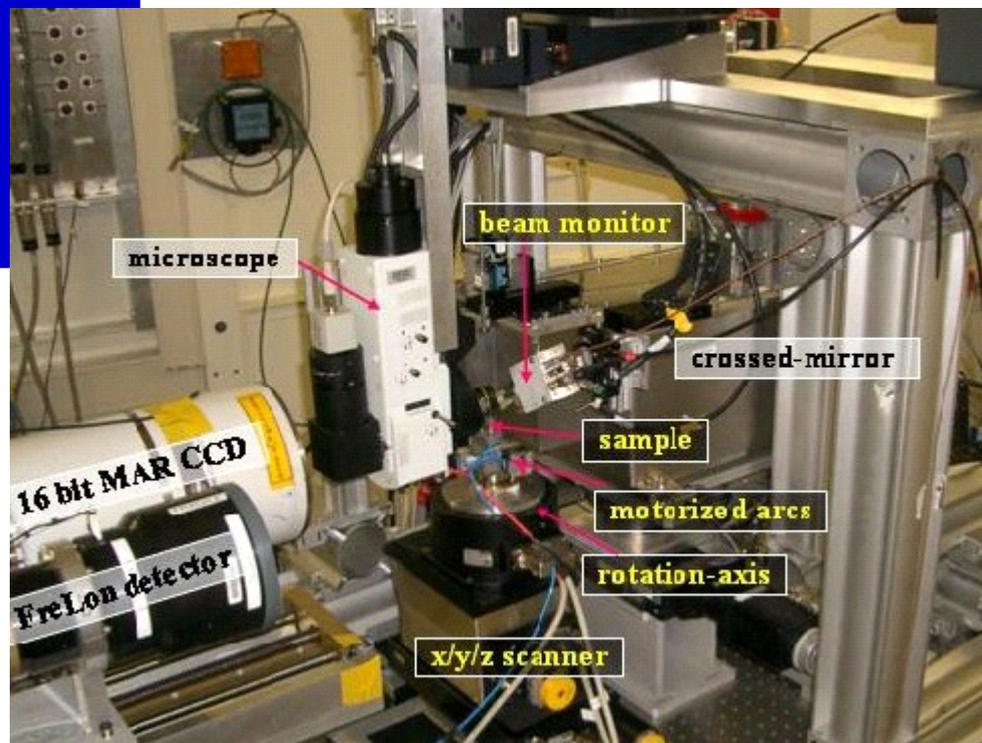
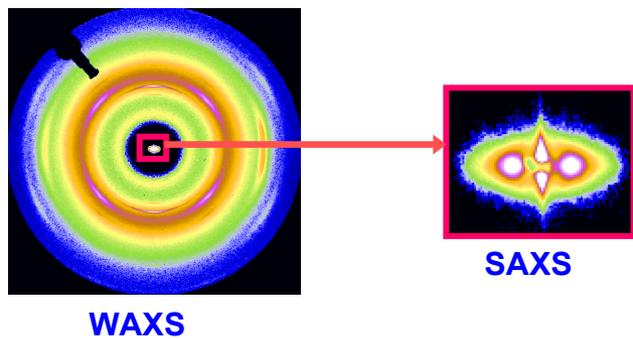
S. Ran et al, *Colloid Polym. Sci.* 282, 802 (2004)

# Dispersión de rayos X con microfoco

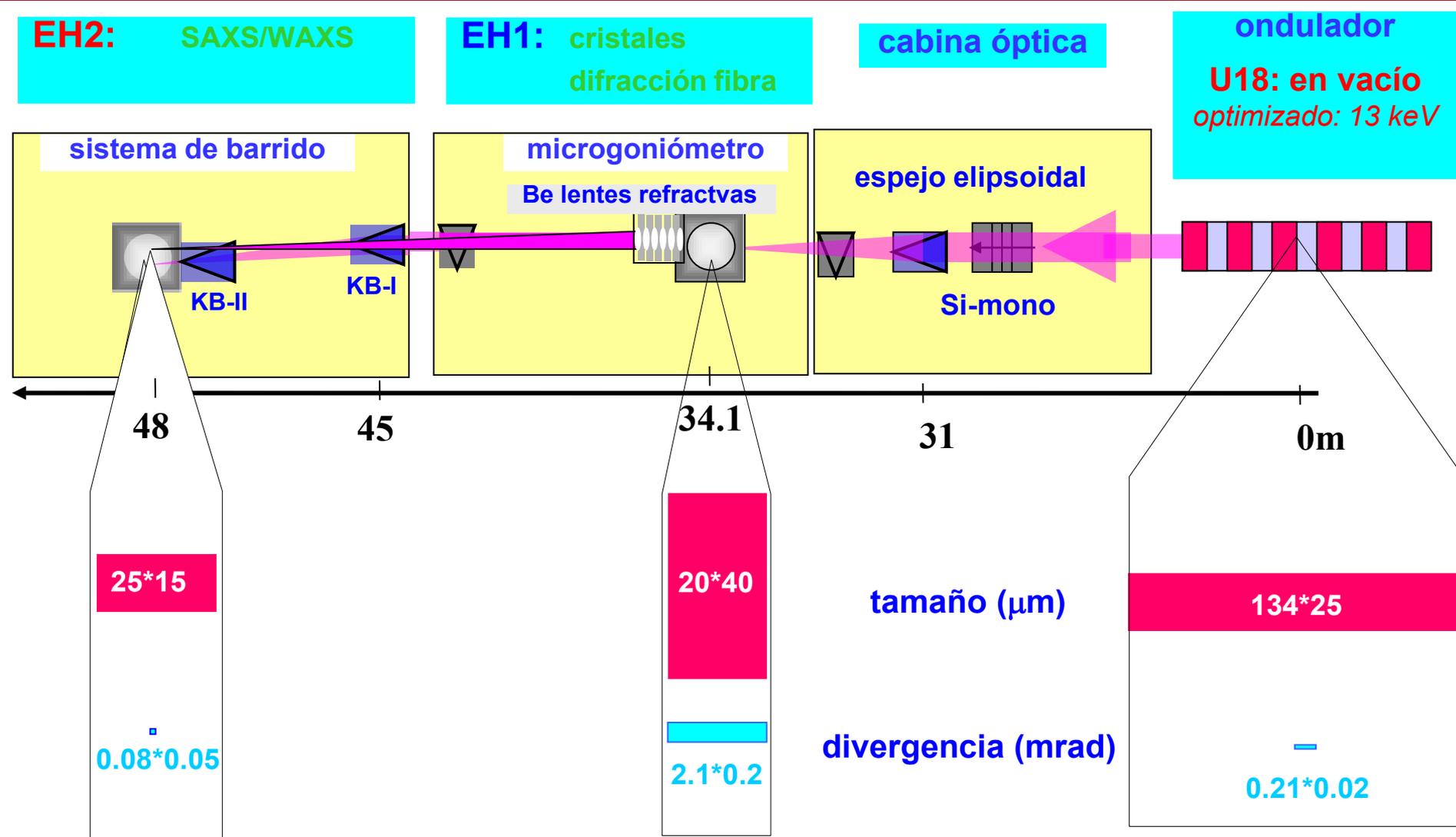
# Dispersión de rayos X con microfoco



Sistema de barrido @ ID13 (ESRF)



# Evolución de la línea de microfoco ID13 (@ESRF)



# Microfoco → Nanofoco (ID13@ESRF)

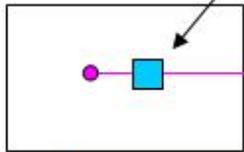
nanofocus optics: mirror/refractive...

microfocus optics: mirror/refractive...

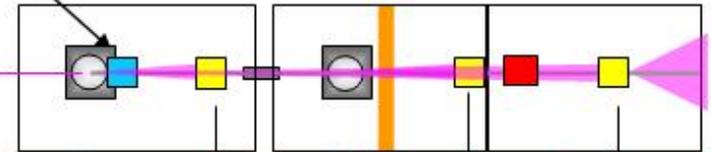
**Optical Hutch**

“nanohutch”

“microhutch”

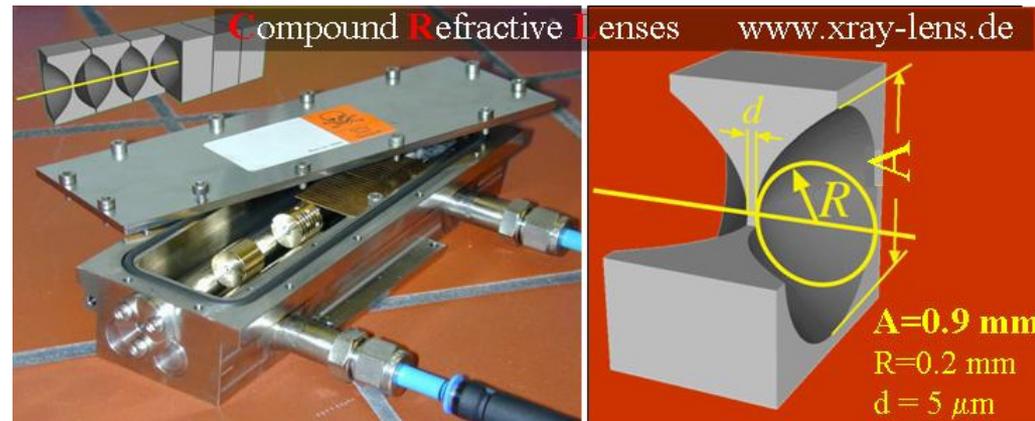
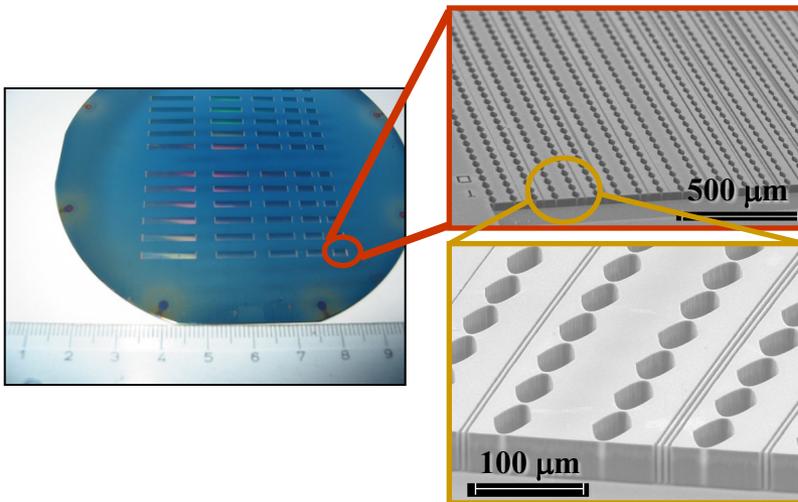


**Diámetro ≈ 50 nm**

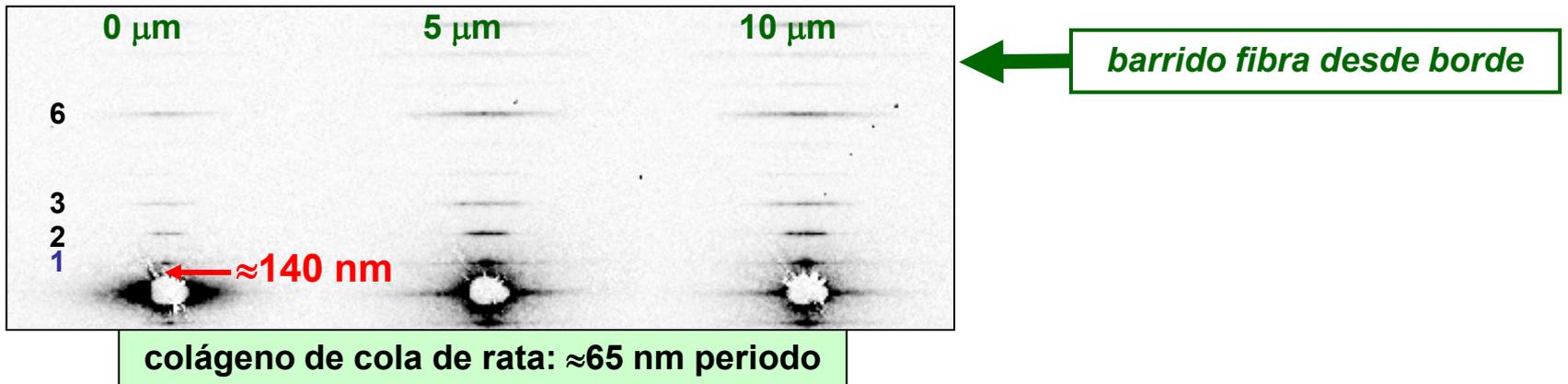
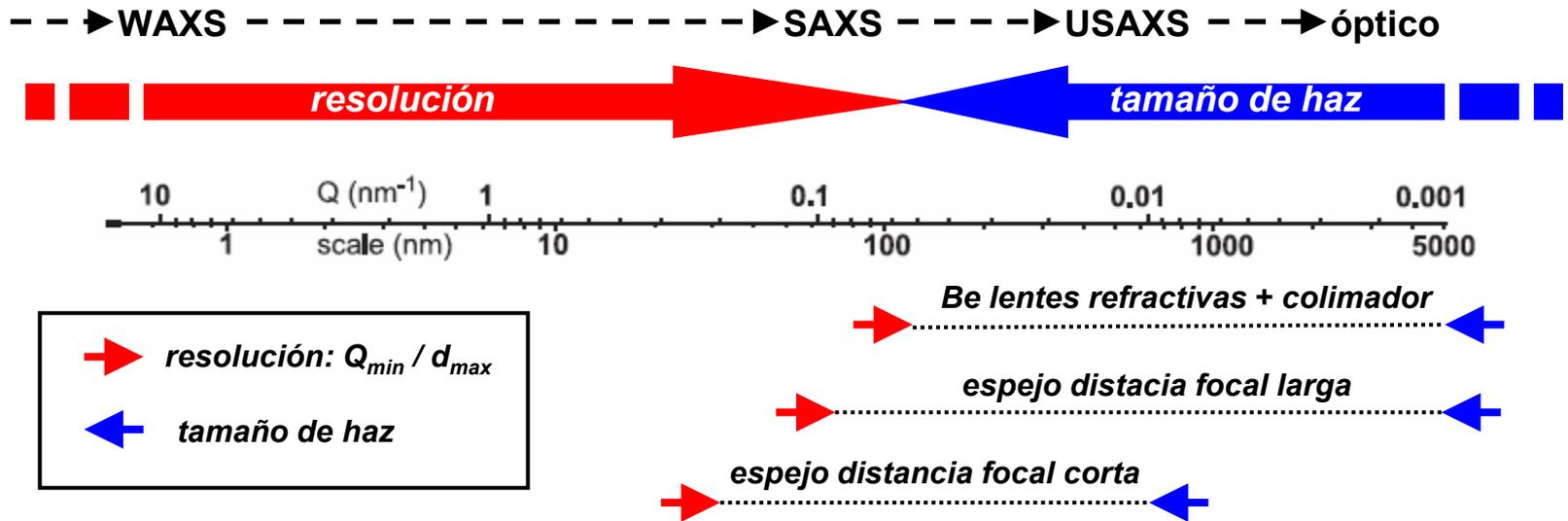


100 (meters from undulator source)

48 CRLs  
33 CRLs  
28 m CRLs

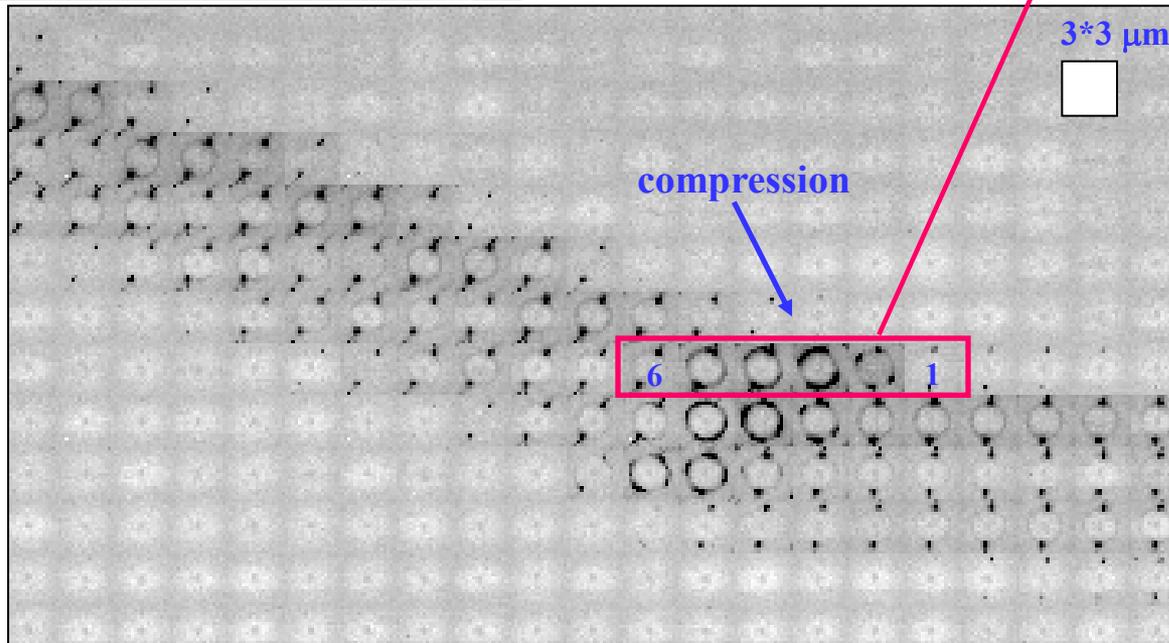
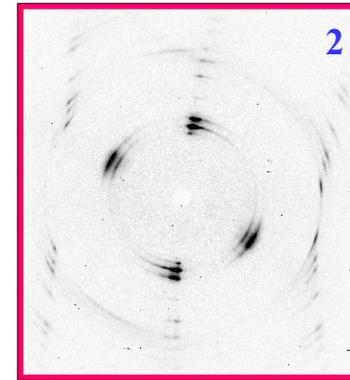
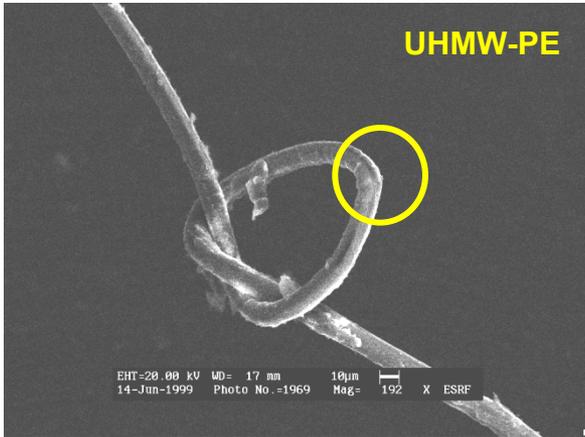


# Resolución vs. tamaño de haz



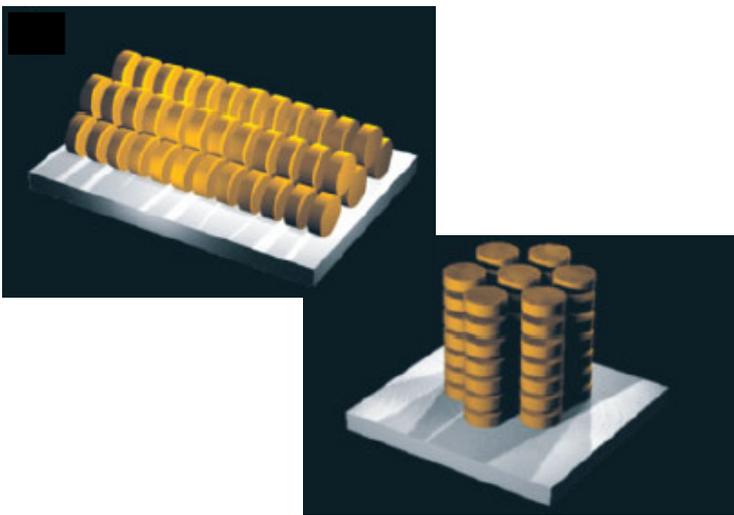
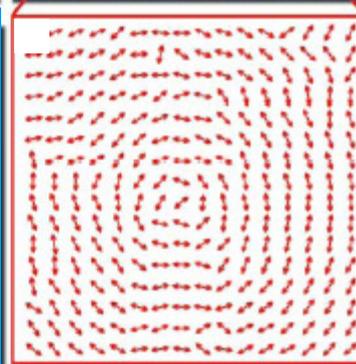
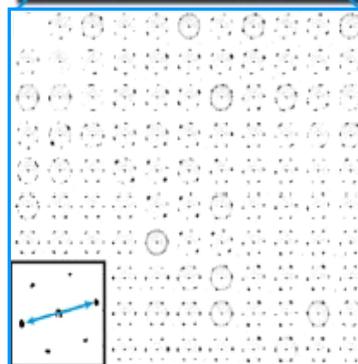
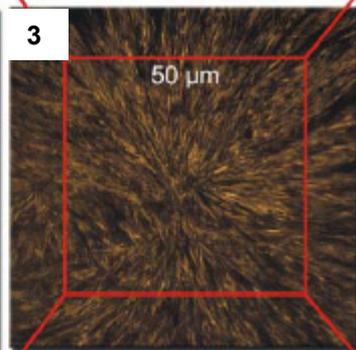
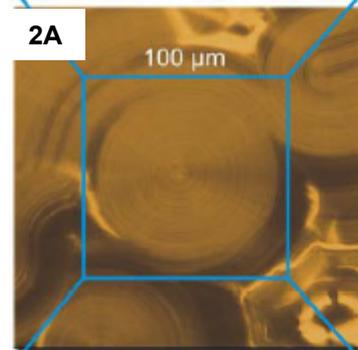
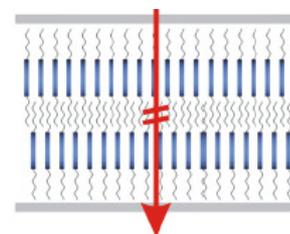
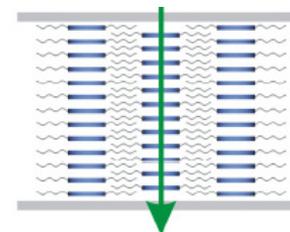
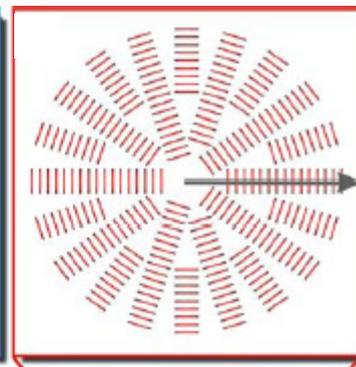
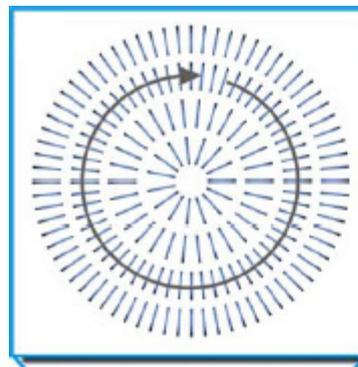
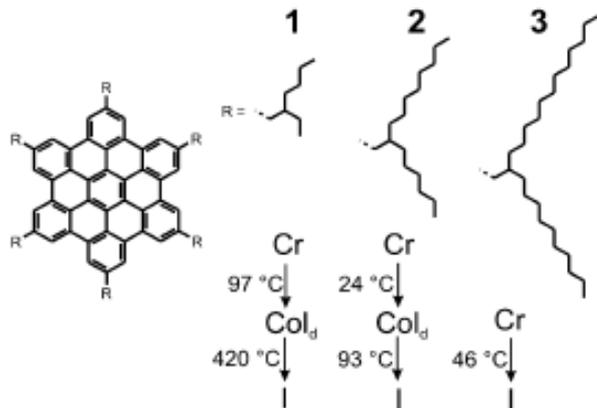
# Aplicaciones de la dispersión de rayos X con microfoco

# Mecanismos de deformación



C. Riekkel, M.C. García-Gutiérrez, *et al.*;  
*Anal. & Bioanal. Chem.* 376, 594 (2003)

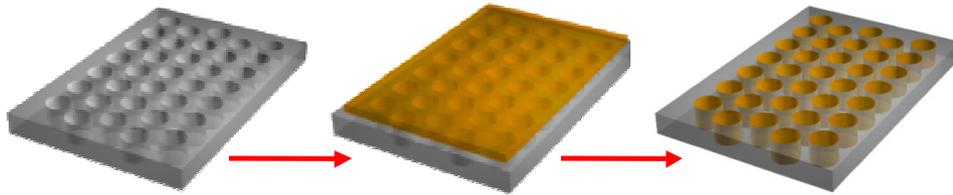
# Cristales Líquidos discoidales: Propiedades semiconductoras



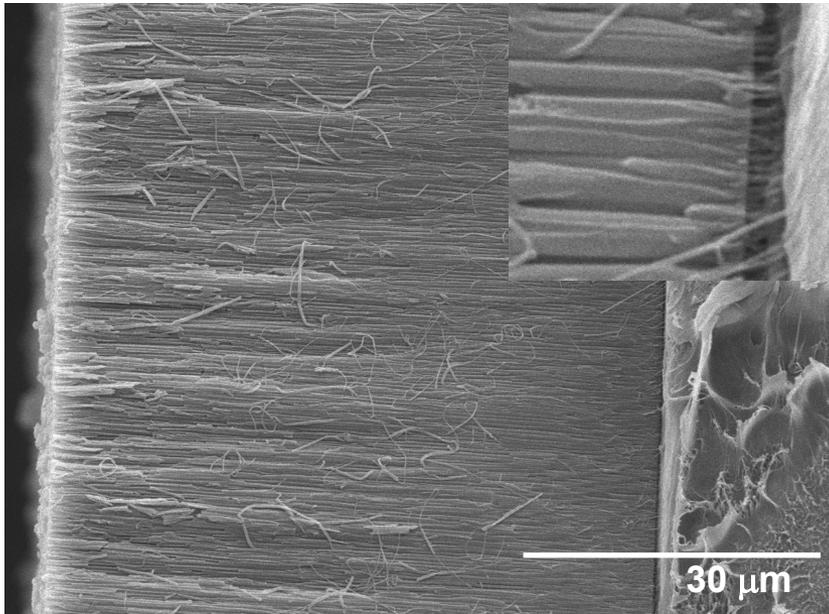
M. Kastler *et al.* *Adv. Mater.* 18, 2255 (2006)

# Efectos de confinamiento en nanofibras poliméricas

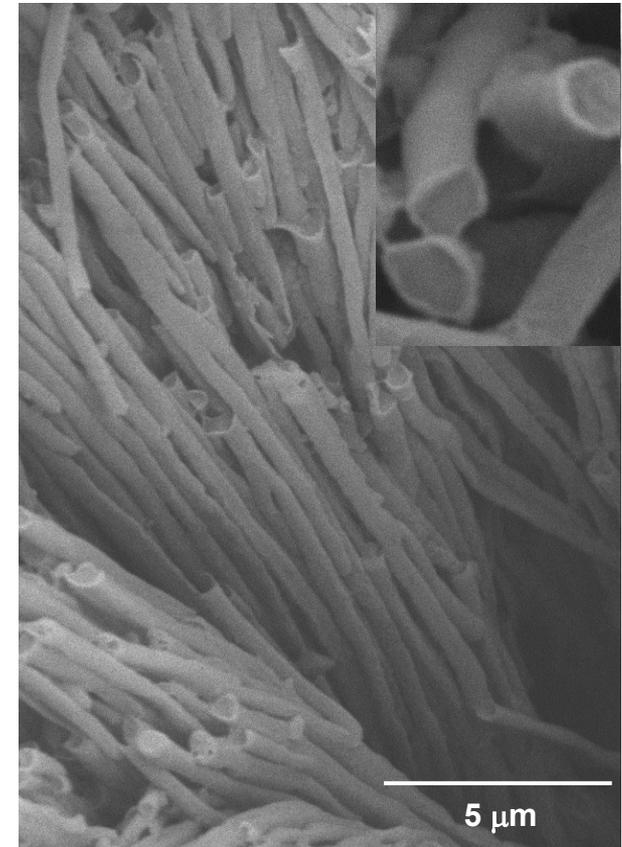
AAO Membrane + solution (30wt% PVDF-Dimethylacetamide)



SEM

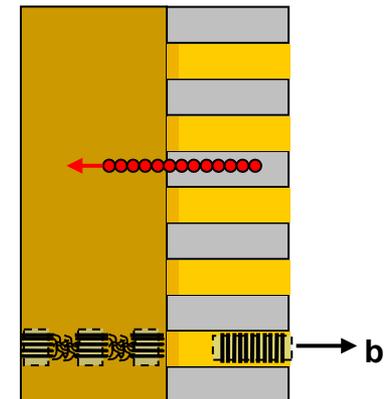
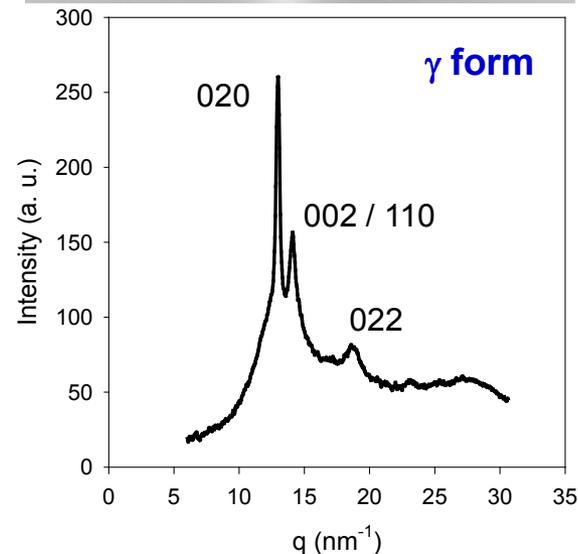
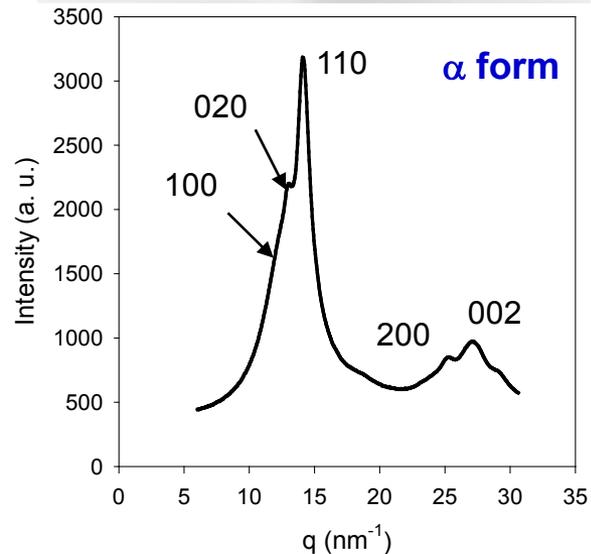
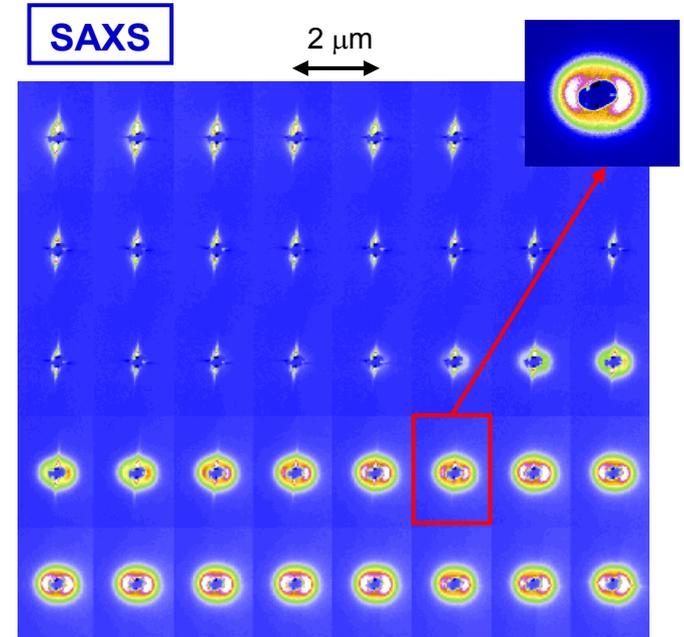
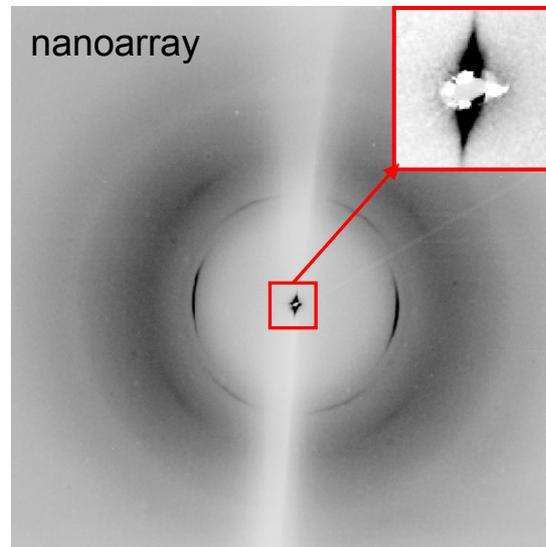
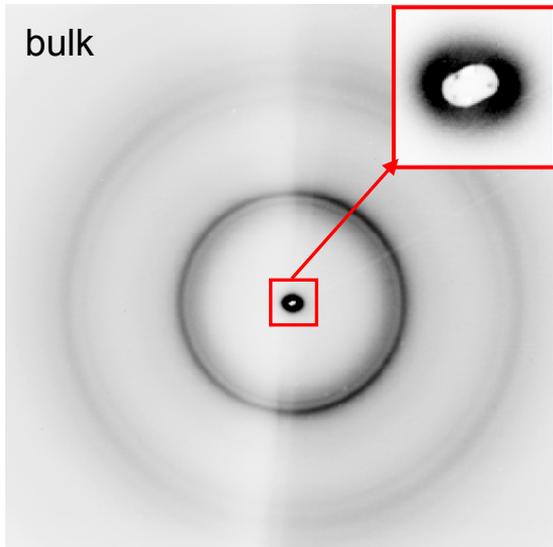


PVDF nanofibers



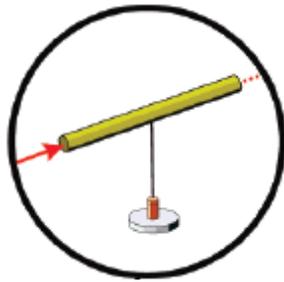
“Confinement-induced one-dimensional ferroelectric polymer arrays” M.C. García-Gutiérrez, *et al.*; *Nano Letters* 10, 1472 (2010)

# Efectos de confinamiento en nanofibras poliméricas

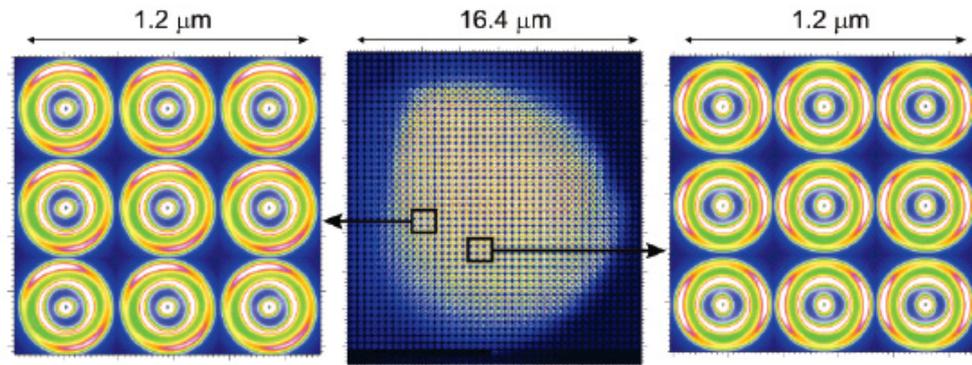


# Aplicaciones diversas

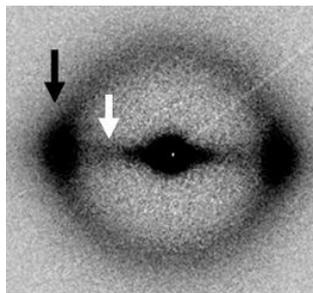
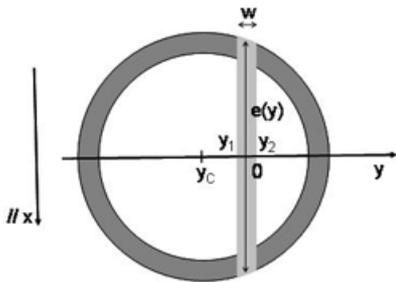
“Probing the internal structure of high-performance fibers by on-axis scanning diffractometry” R. Davies *et al. Macromolecules* 40, 5038 (2007)



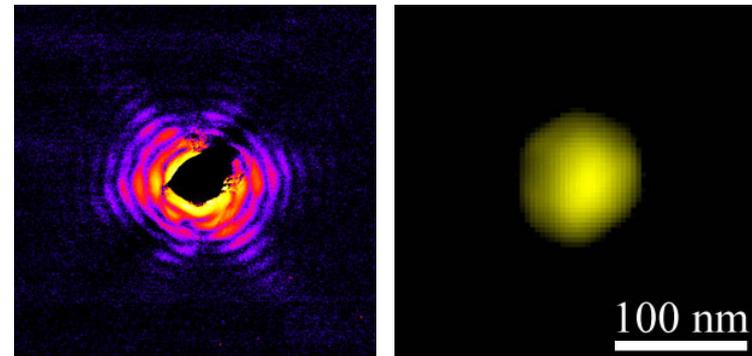
Tamaño de haz =  
500nm



“X-ray microdiffraction study of SWCNT alignment across a fiber” V. Pichot *et al. EPL* 79, 46002 (2007)



“Coherent X-ray diffraction imaging with nanofocus illumination”  
C.G. Schroer *et al. PRL* 101, 090801 (2008)

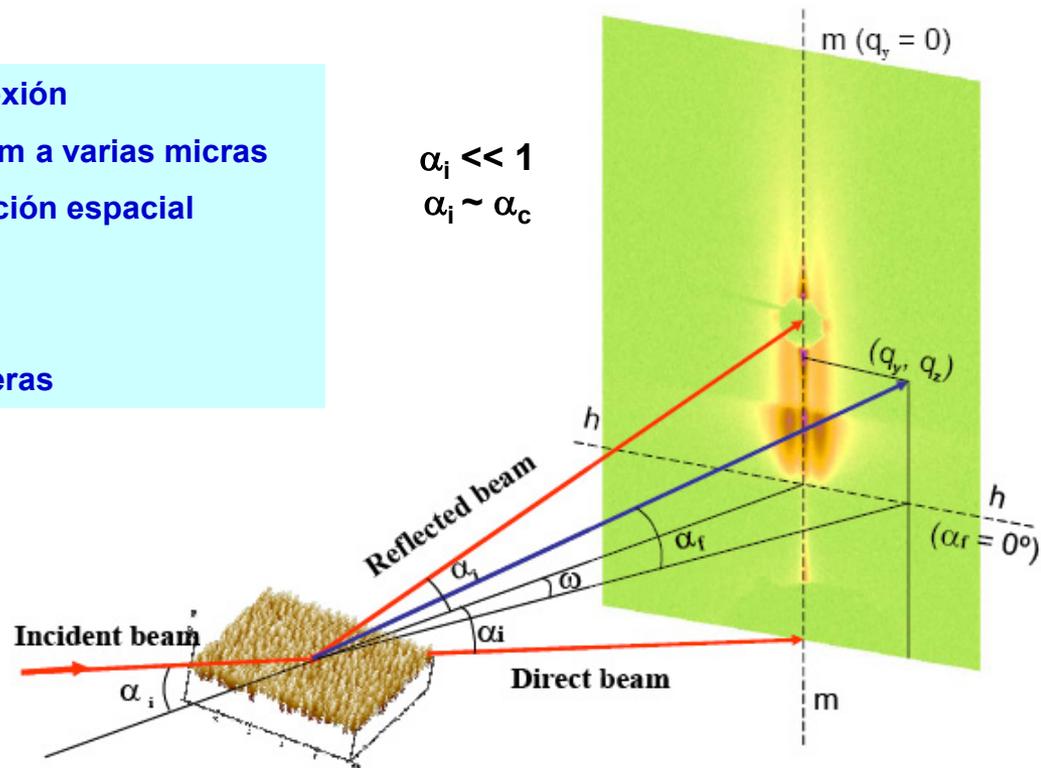
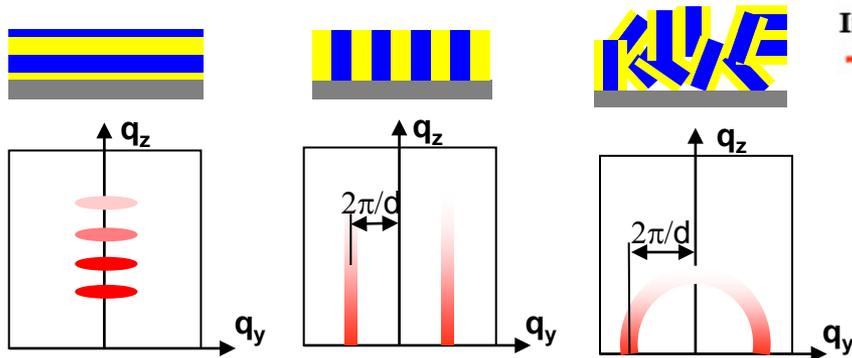


Tamaño de haz  
< 100 nm

# Dispersión de rayos X con incidencia rasante

# Dispersión de rayos X con incidencia rasante

- GIWAXS/GISAXS → análogo WAXS/SAXS en reflexión
- Rango de escalas de longitud: desde los Angstrom a varias micras
- Estructura y morfología: tamaño, forma y ordenación espacial
- Sensibilidad en profundidad (estructura interna)
- Información promedio del área iluminada (~ cm<sup>2</sup>)
- Experimentos en tiempo real y diferentes atmósferas



$$\alpha_i \ll 1$$

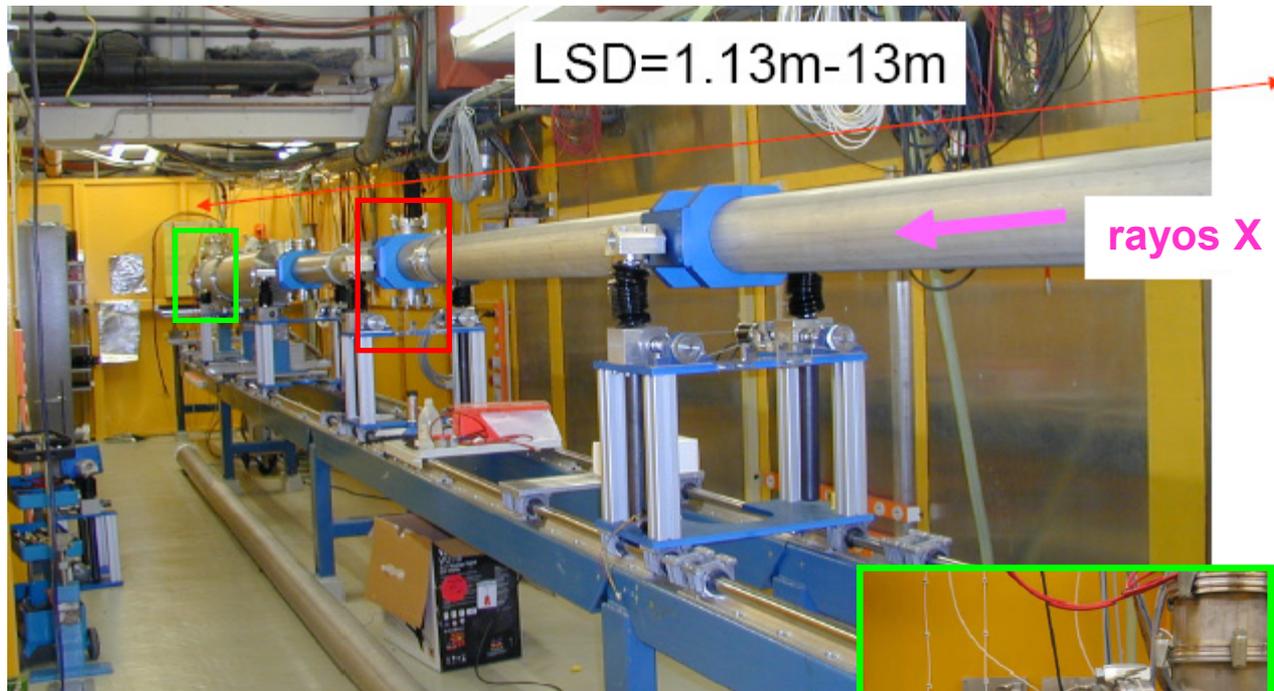
$$\alpha_i \sim \alpha_c$$

$$q_z = 2\pi/\lambda \sin(\alpha_i + \alpha_f)$$

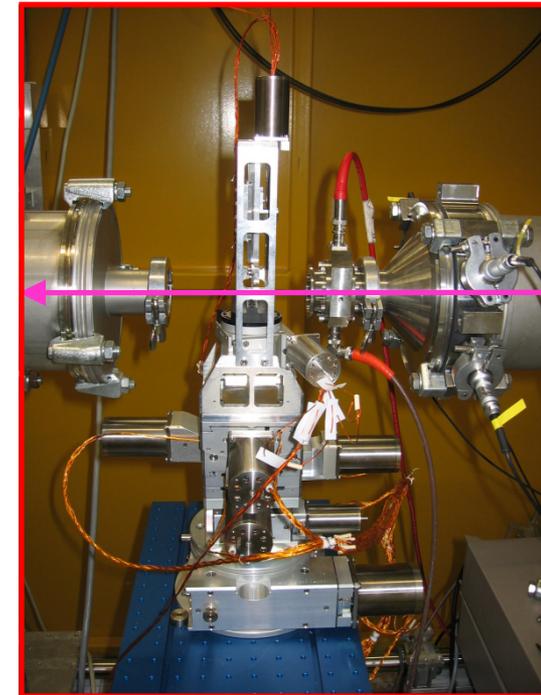
$$q_y = 2\pi/\lambda \sin(\omega) \cos(\alpha_f)$$

# Estación experimental de SAXS y GISAXS

Línea BW4 en HASYLAB, Hamburgo



Entorno de muestra

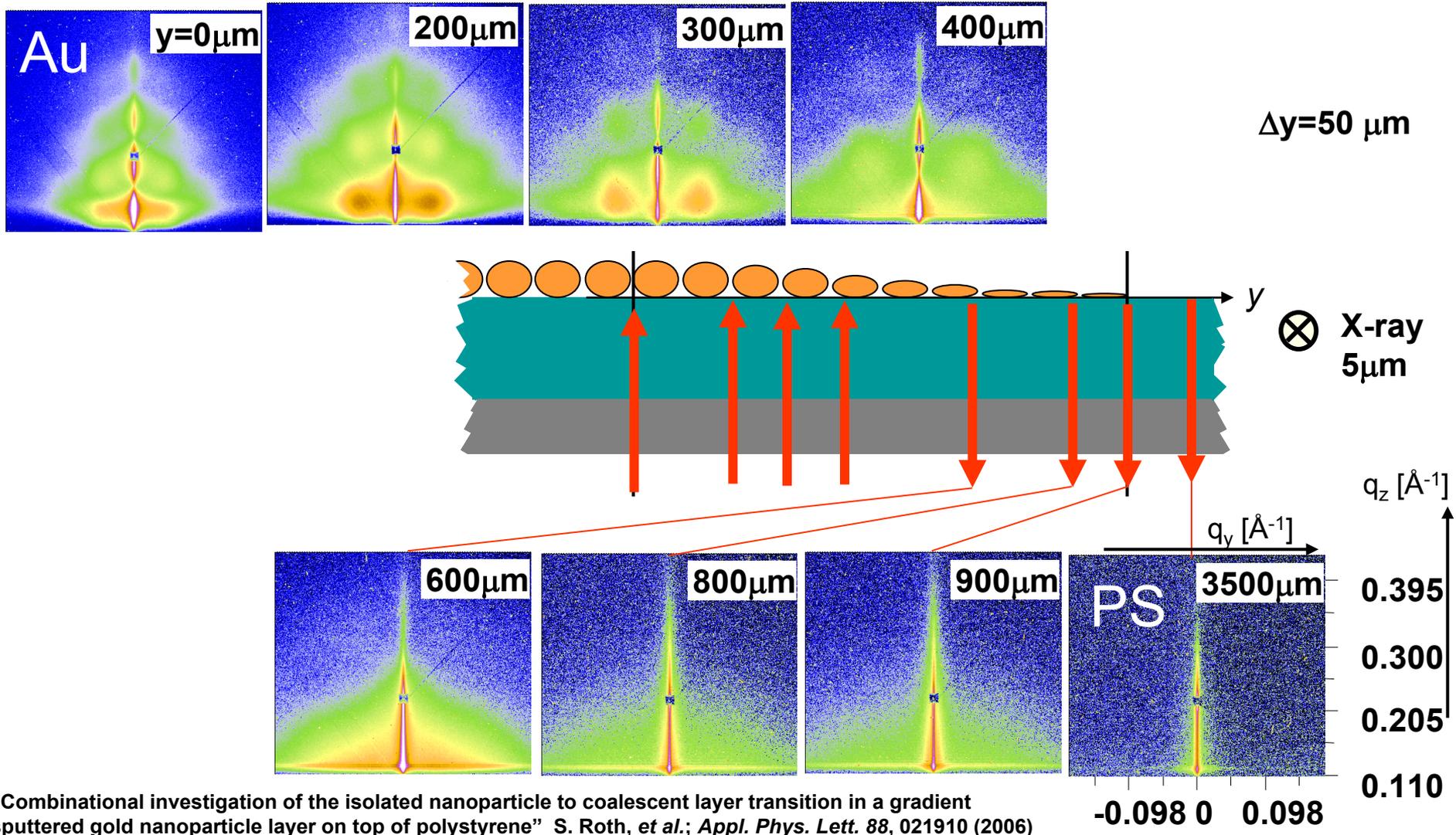


Detector



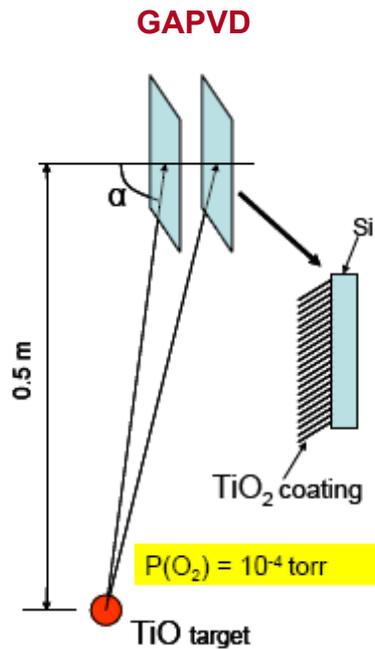
# **Aplicaciones de la dispersión de rayos X con incidencia rasante**

# Nanopartículas



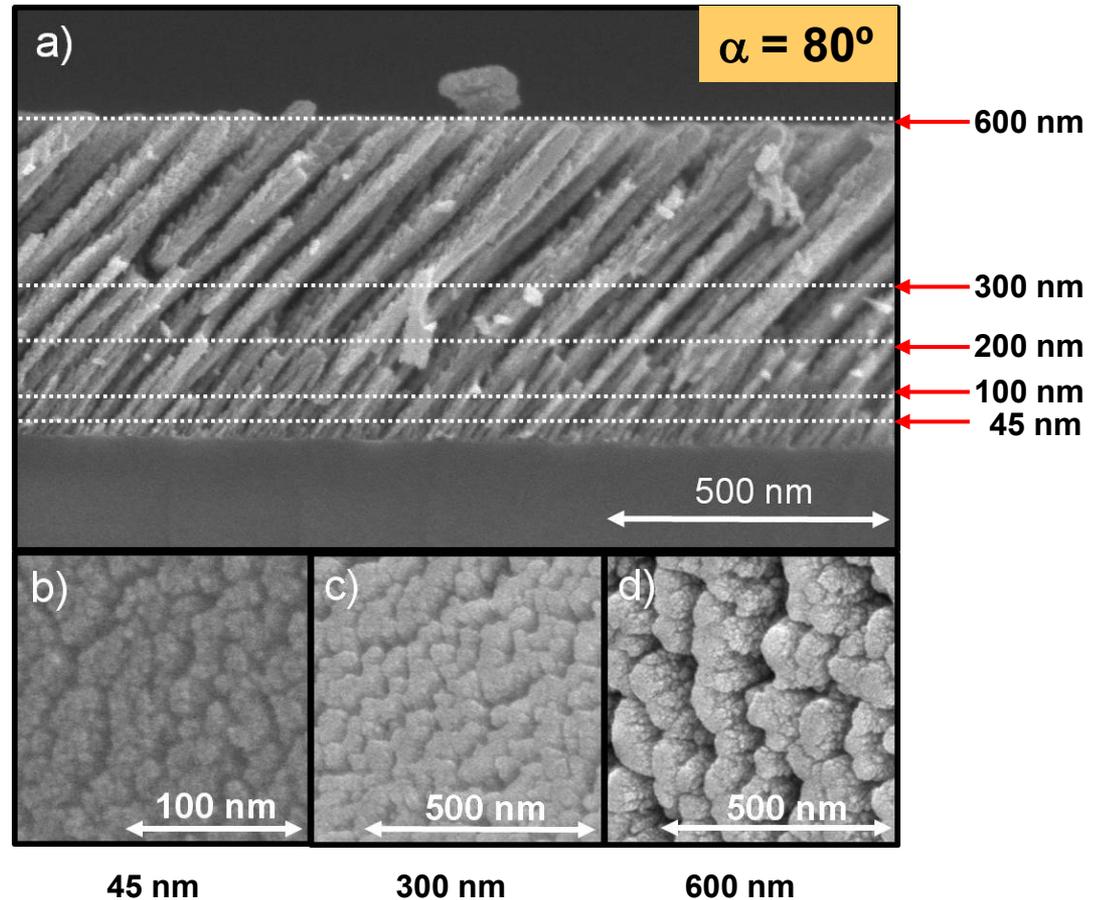
“Combinational investigation of the isolated nanoparticle to coalescent layer transition in a gradient sputtered gold nanoparticle layer on top of polystyrene” S. Roth, et al.; *Appl. Phys. Lett.* 88, 021910 (2006)

# Películas delgadas con morfología columnar



“Structure of glancing incidence deposited TiO<sub>2</sub> thin films as revealed by GISAXS” L. González-García, et al.; *ChemPhysChem* 11, 2205 (2010)

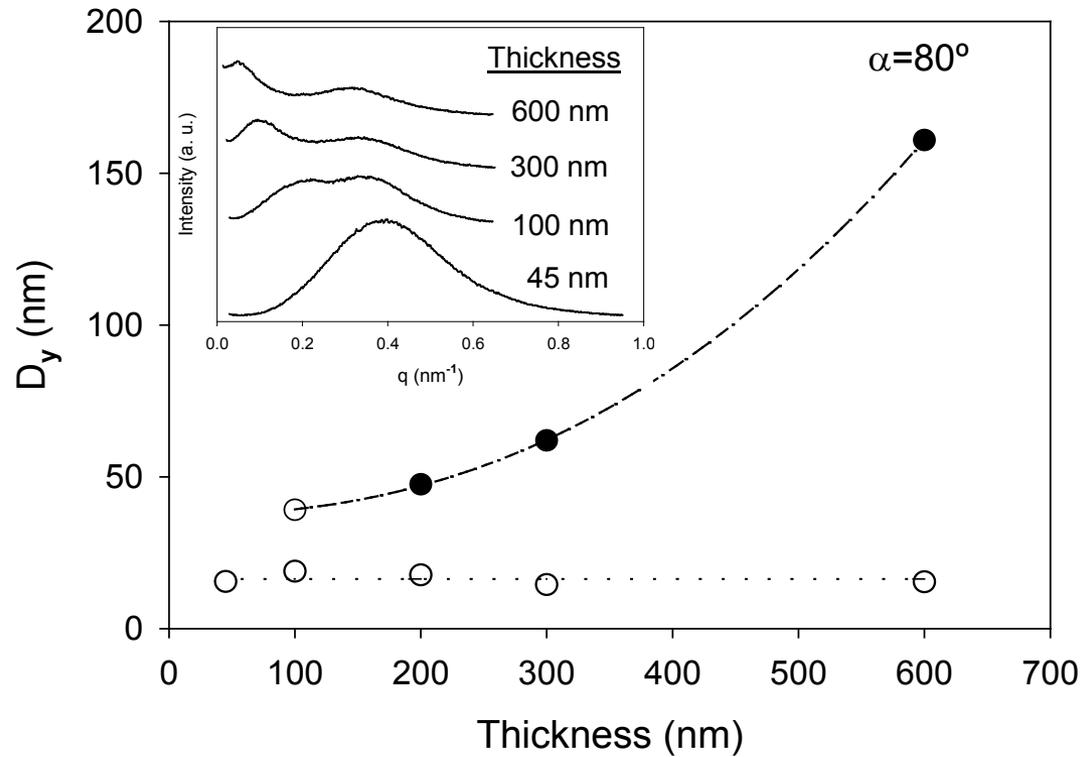
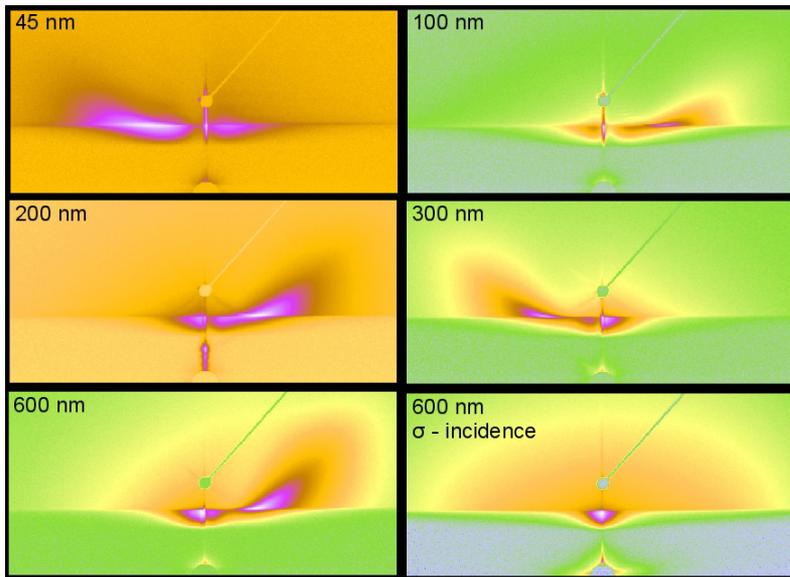
## SEM



# Películas delgadas con morfología columnar

## GISAXS

$$D_y = 2\pi/q_y^{max}$$



# **Estaciones experimentales de dispersión de rayos X en el mundo**

# Líneas de dispersión de rayos X



- **Europa:** - ESRF: ID2, ID10, ID13, BM16, BM26  
- Soleil: SWING  
- Diamond: I22  
- HASYLAB: BW4  
- BESSY:  $\mu$ Spot  
- Elettra: BL5.2L
- **América:** - APS: 1-ID, 8-ID, 18-ID  
- ALS: 7.3.3
- **Asia:** - Spring-8: BL08B2, BL40B2, BL45XU

# Sincrotrón español (ALBA)



## 7 líneas aceptadas 1ª fase

- Soft X-ray beam-line for polarisation-dependant spectroscopies and microscopies.
- Beam-line for electron and soft X-ray emission spectroscopies.
- High-resolution powder diffraction beam-line.
- High brilliance XAS (X-ray absorption Spectroscopy) beam-line.
- Beam-line for non-crystalline diffraction in life and materials sciences with microfocus option.
- Beam-line for macromolecular crystallography.
- Beam-line for X-ray microscopy.

**Proposal for a beamline on  
Non Crystalline Diffraction for Life and Material Sciences  
with Modular Microfocus Option on ALBA**

December 2004

[www.cells.es/Beamlines/NCD](http://www.cells.es/Beamlines/NCD)

# Bibliografía

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