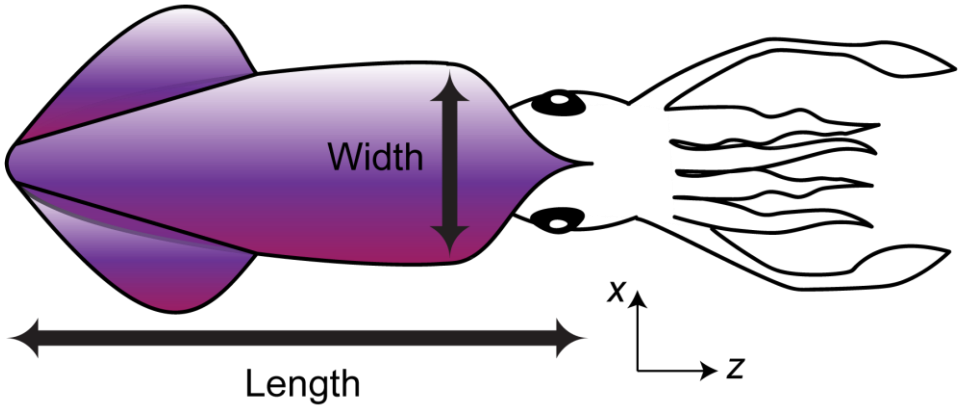
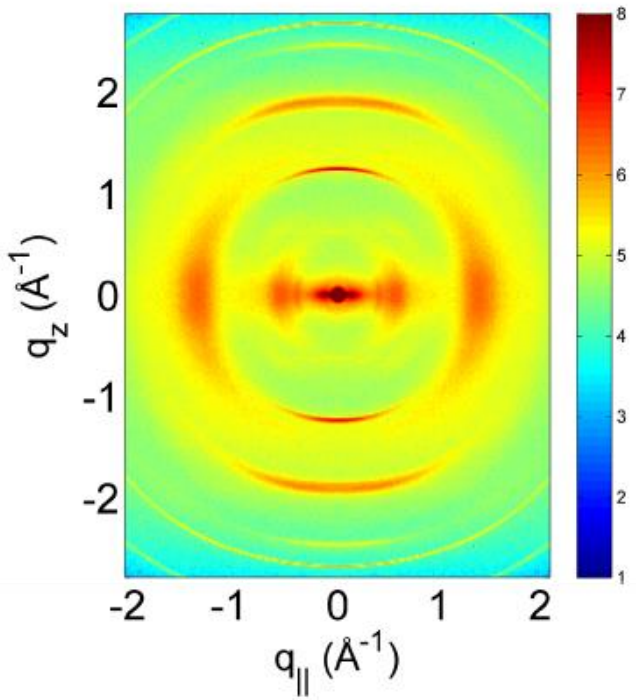




Hierarchical, Self-Similar Structure in Native Squid Pen

Fei-Chi Yang,

Robert Peters, Hannah Dies, and Maikel C. Rheinstädter

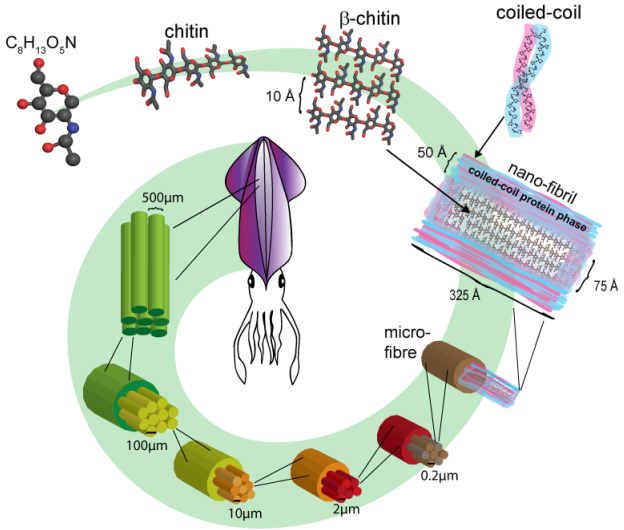
McMaster University

Soft Matter, 2014, Accepted Manuscript
DOI: 10.1039/C4SM00301B

Properties of Biomaterials

- Functionality
- Self-similarity
- Synthesis T=300K, P~1atm
- Evolution & Environmental constraints
- Hierarchy of structures.

(built from bottom-up rather than top-down)



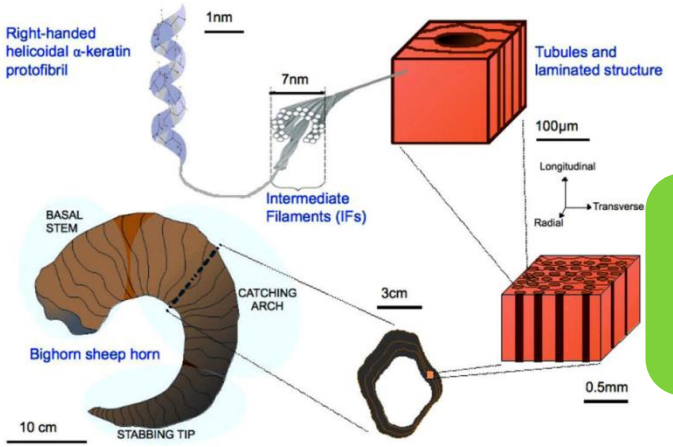
Building Blocks of Biomaterials

Protein

Material Properties

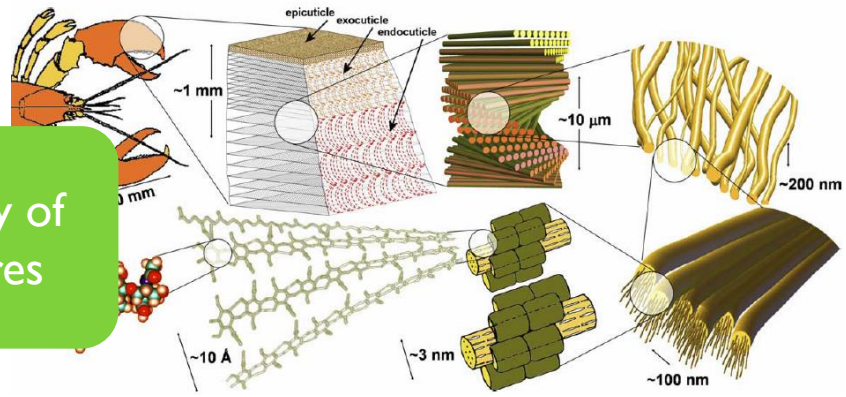
?

Hierarchy of Structures



Acta Biomaterialia 6 (2010) 319–330

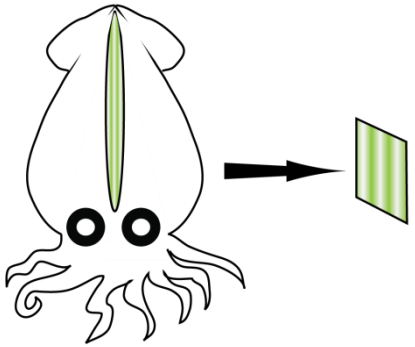
Chitin



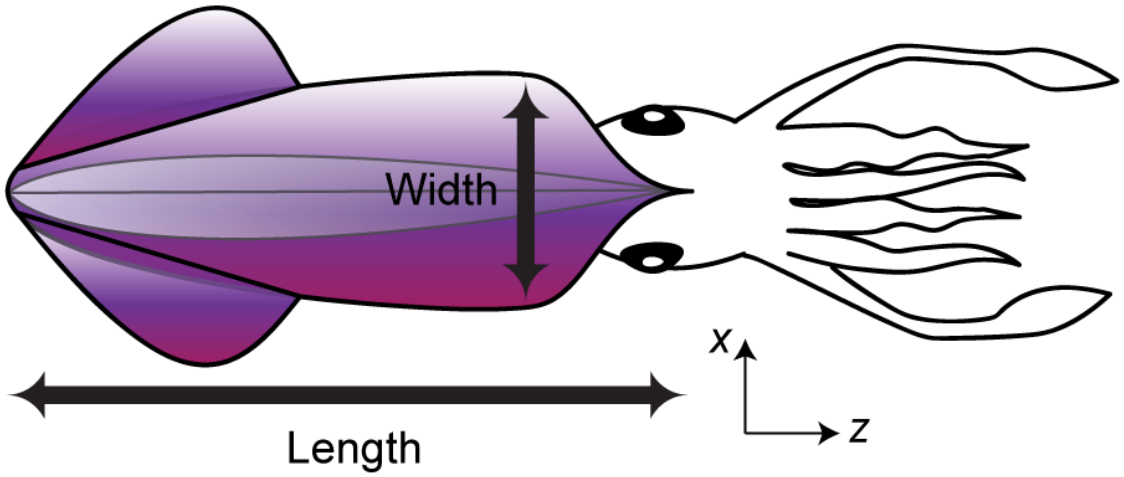
Acta Materialia 53 (2005) 4281–4292

Squid Pen

- Transparent backbone inside the squid
- Made of Protein and Chitin



Samples

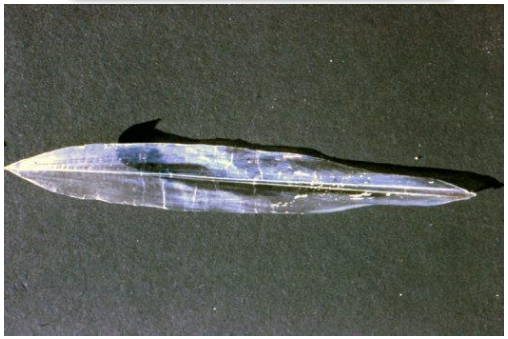


Sample	Species	Mantle Length × Width	Pen Length × Width
1	Sepioteuthis lessoniana	170 × 150 mm	180 × 20 mm
2	Uroteuthis chinensis	255 × 60 mm	240 × 40 mm

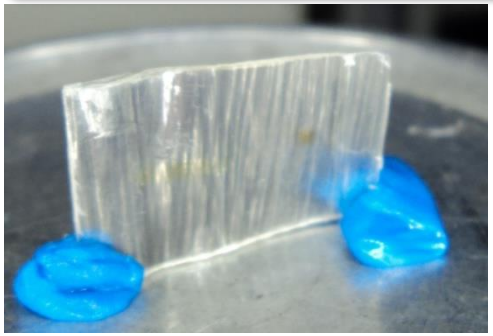
Experimental Protocol

Dissect the Squid

Take out the Pen



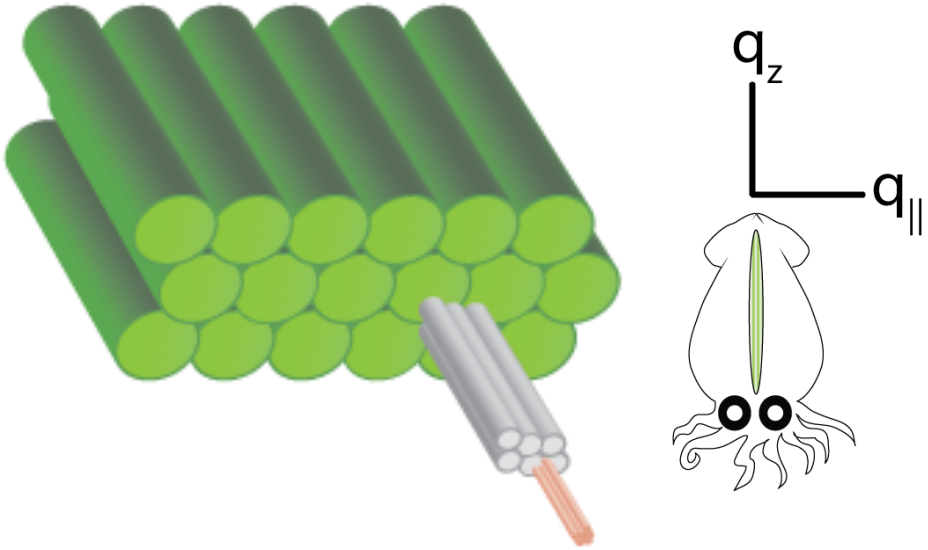
Cut a 20 × 10 mm^2 piece



Dry and store between two pieces of metal in $Mg(NO_3)_2$ (52.9±0.22% RH)

Run experiments

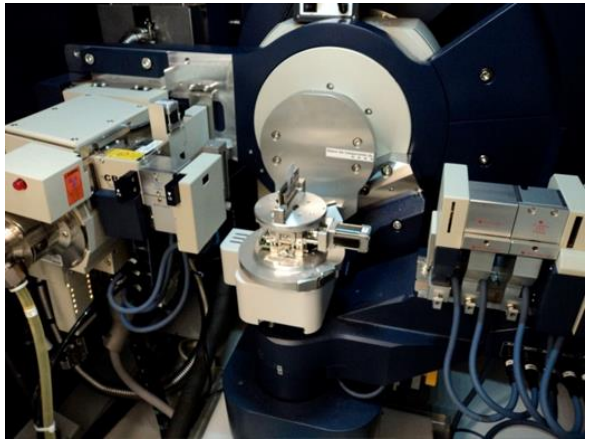
Hierarchical Order in Squid Pen

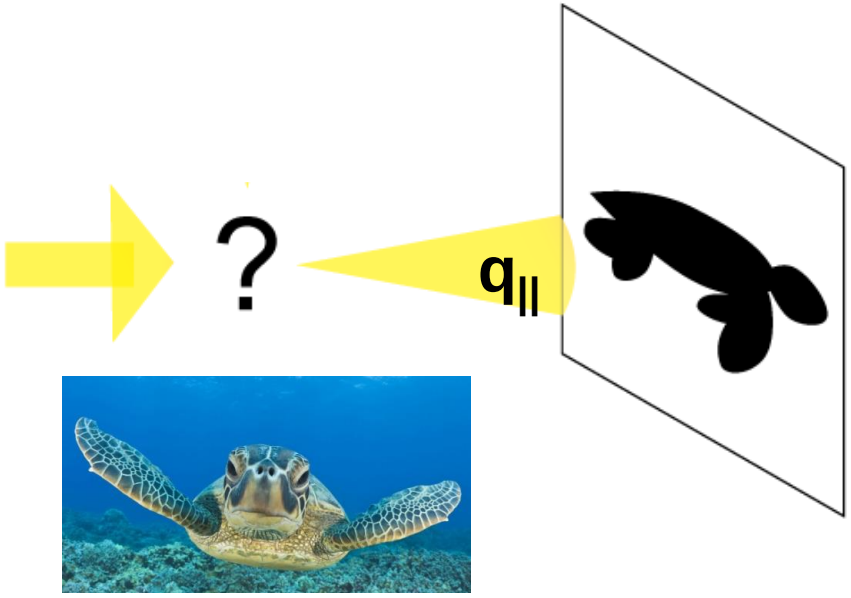


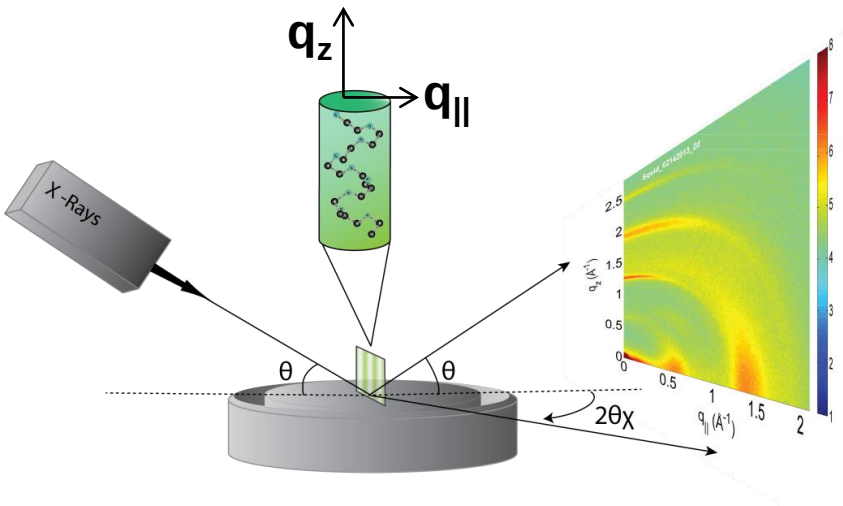
Hierarchical, Self-Similar Structure: Fibres oriented along q_z direction that covers 4 orders of magnitude.

X-Ray Diffraction: What's in the sample

Blade
(Biological Large Angle Diffraction Experiment)

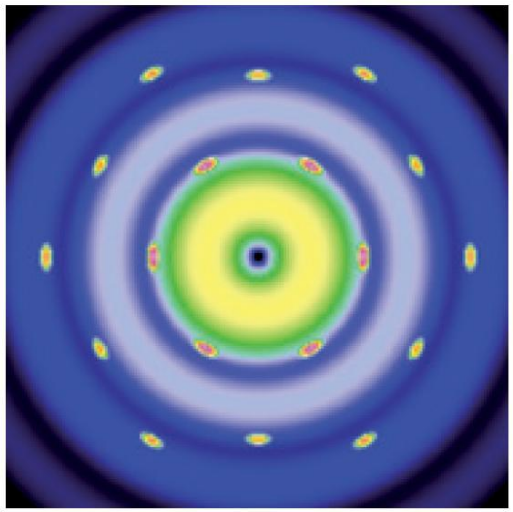


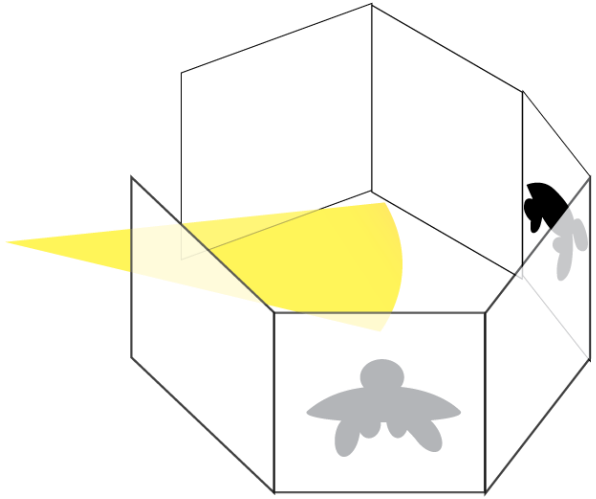




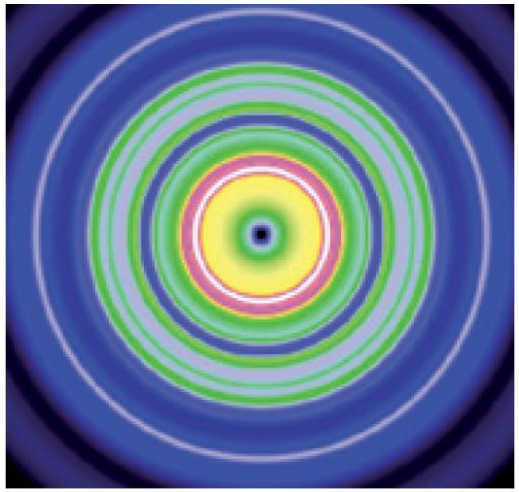
X-Ray Diffraction: How ordered is the sample

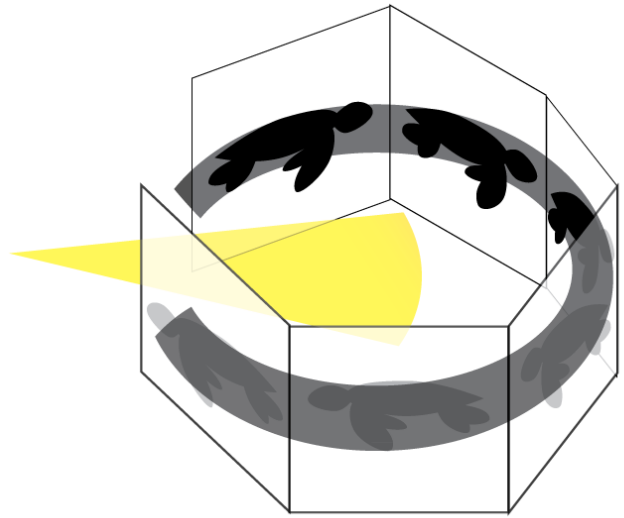
Completely Ordered





Randomly Oriented





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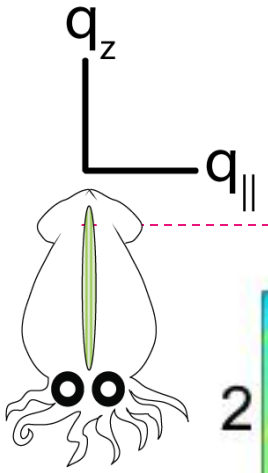
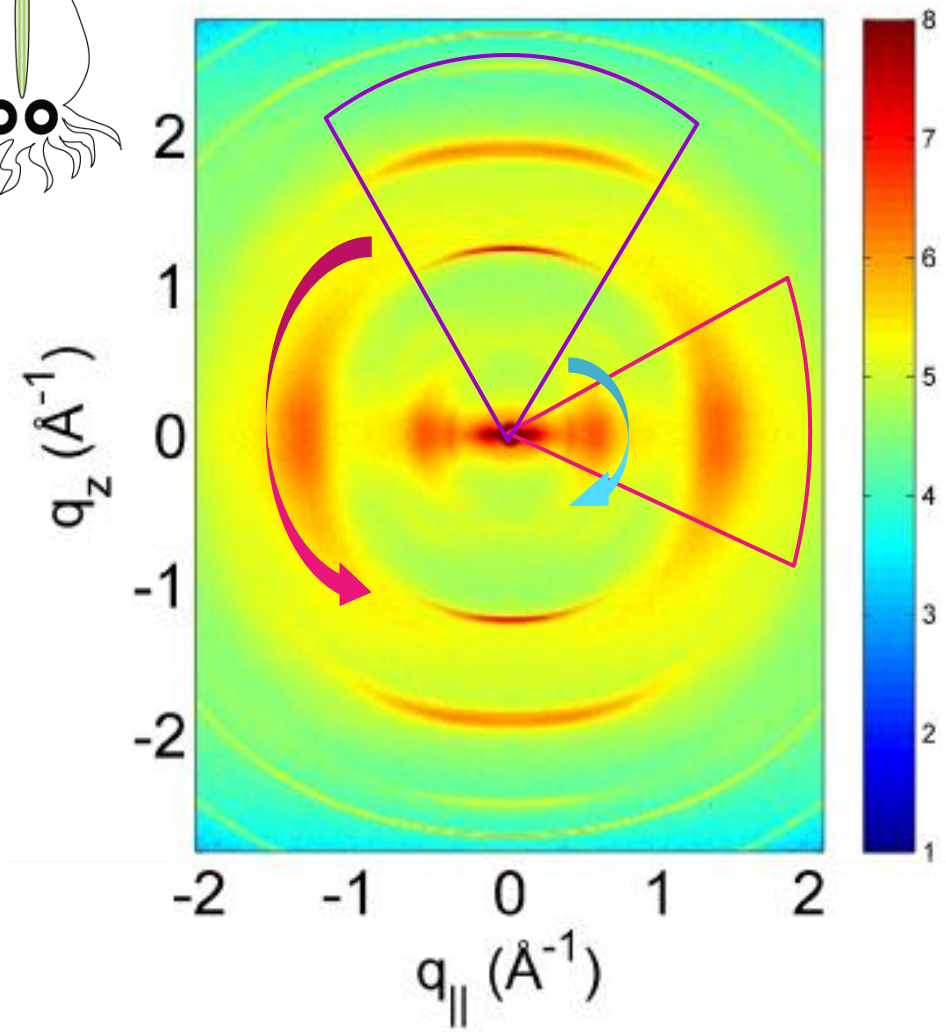
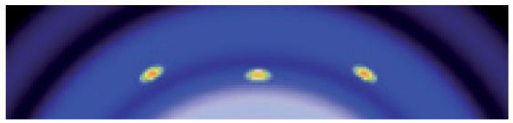
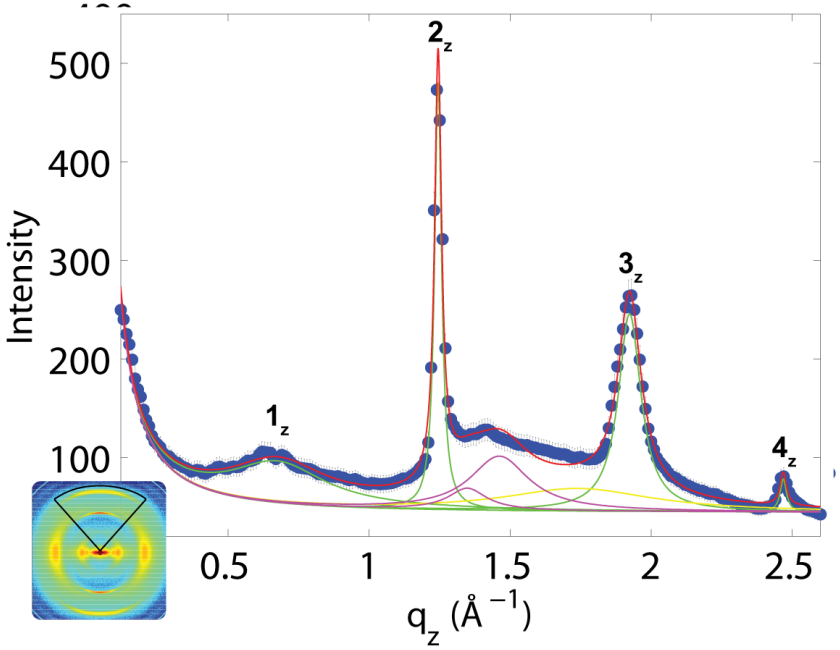
X-Ray Data

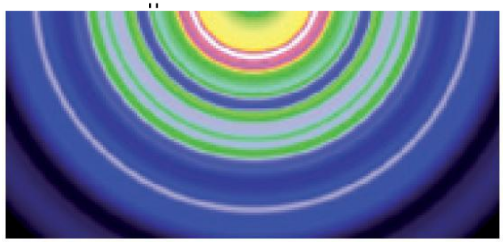








Oriented



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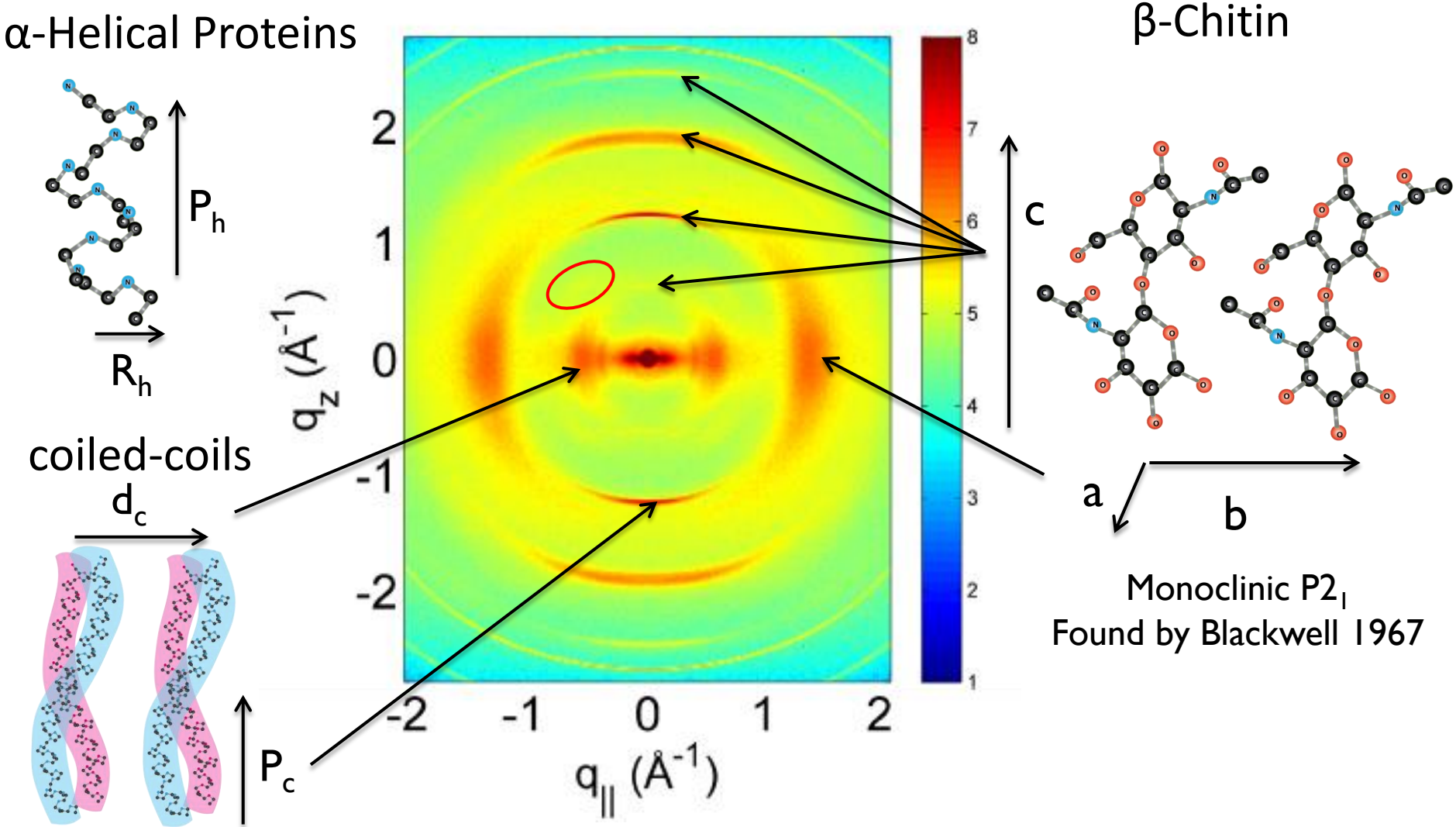
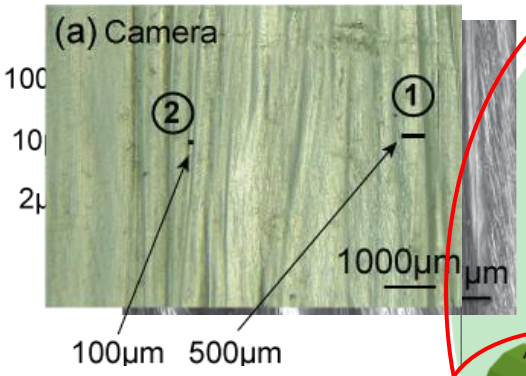
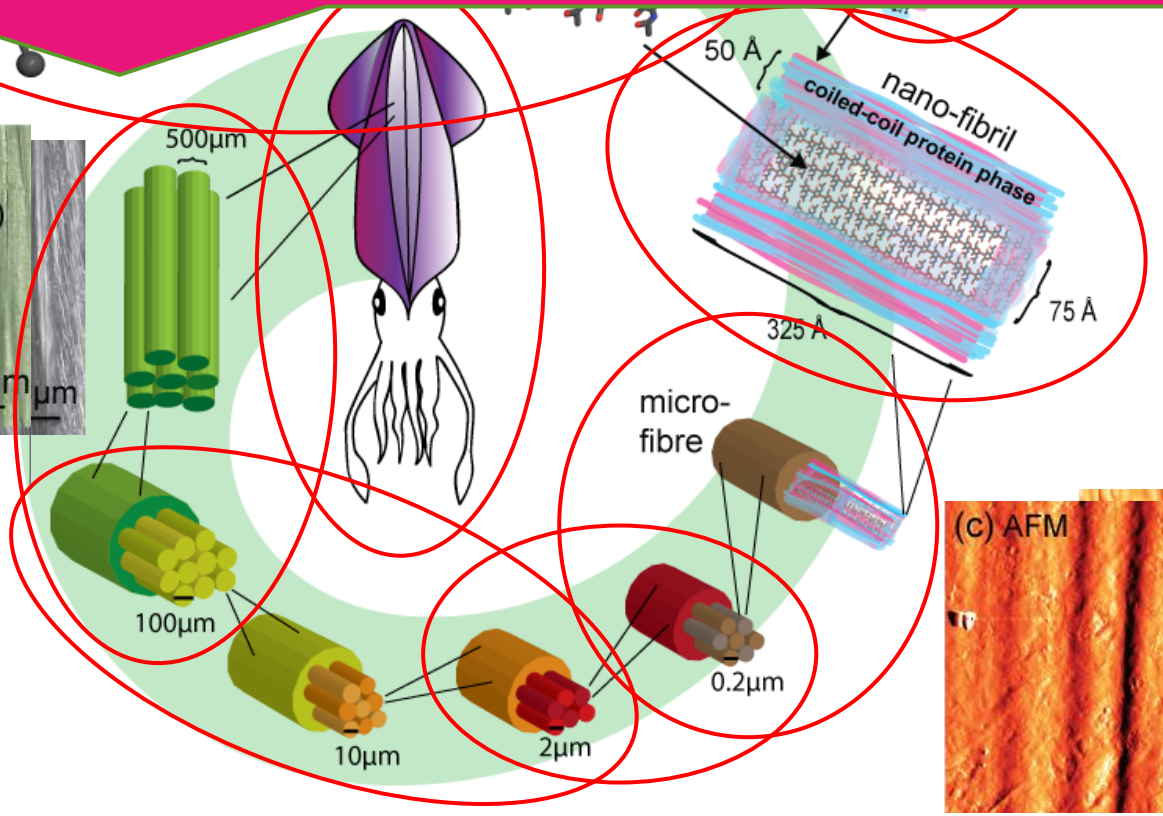
X-Ray Data

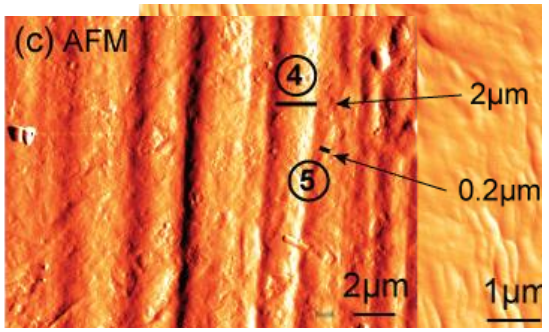

α-Helical Proteins
P_h
R_h
coiled-coils
d_c
P_c
q_z (Å^{-1})
$q_{||}$ (Å^{-1})
β-Chitin
c
a
b
Monoclinic $P2_1$
Found by Blackwell 1967

Connecting the Dots

~90% of the α-coils and β-chitin crystallites are oriented along the fibre-axis





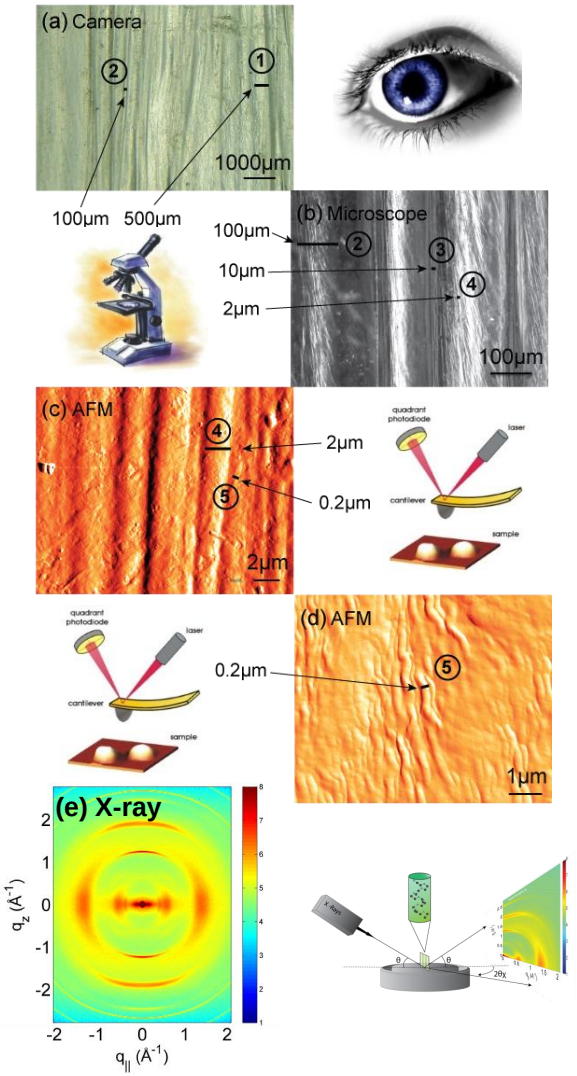


Summary

- It's interesting and inspiring to study the properties of biomaterials

- Protein and Chitin are two common building blocks of biomaterials

- Squid pen has at least 7 levels of hierarchical structures from millimeters to the molecular level, determined by combing microscope, AFM, x-ray diffraction techniques



Acknowledgements

Laboratory for Membrane and Protein Dynamics

Ontario

NSERC CRSNG

National Research Council of Canada

McMaster University

Canada Foundation for Innovation

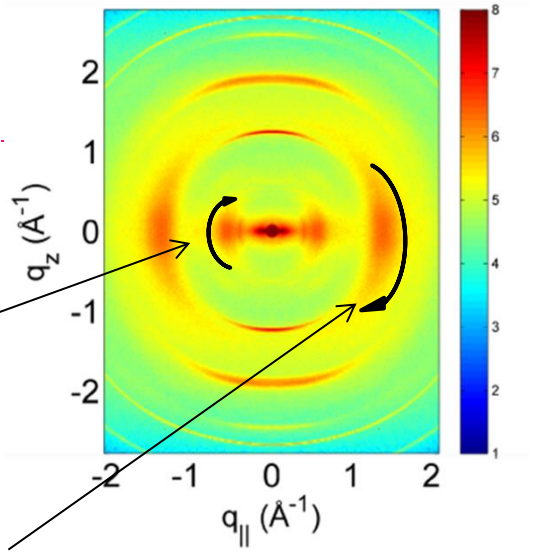
Fondation canadienne pour l'innovation

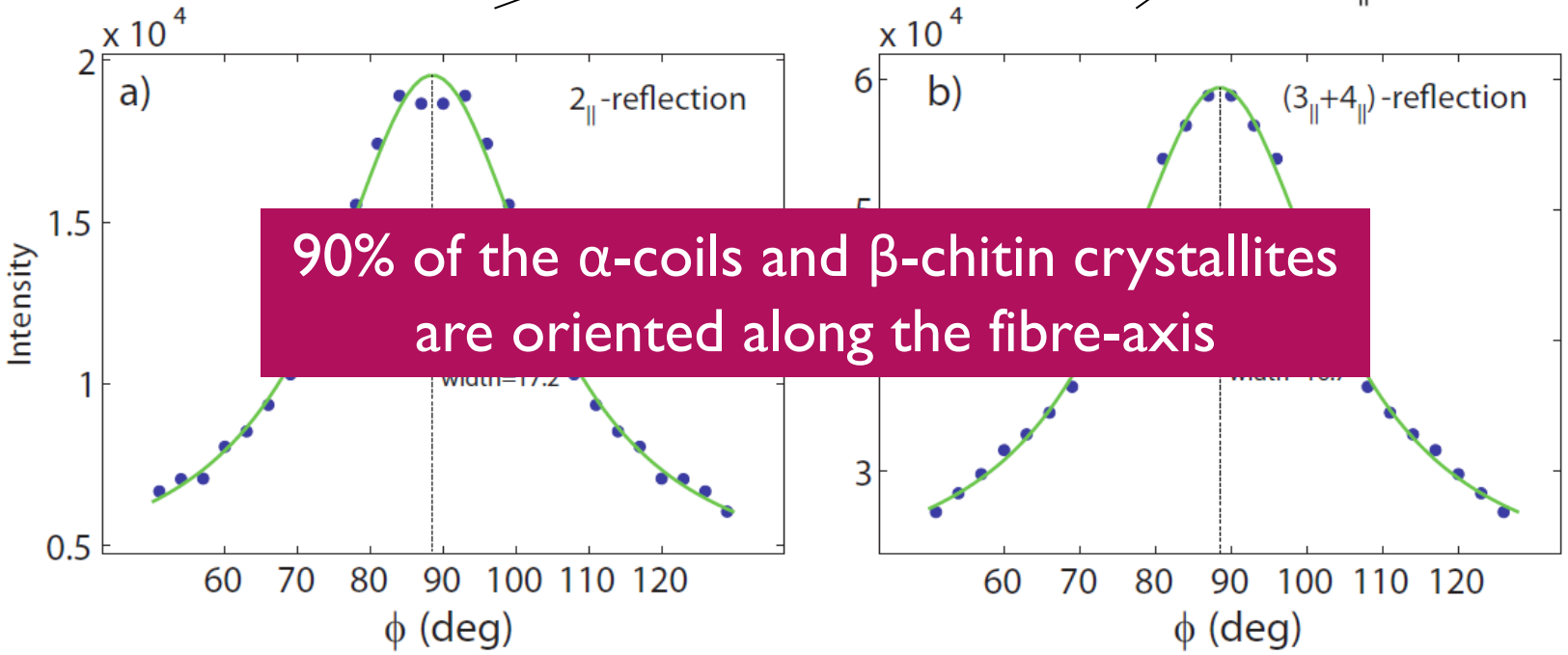
Backup Slides

Degree of Orientation

Orientational Order Parameter

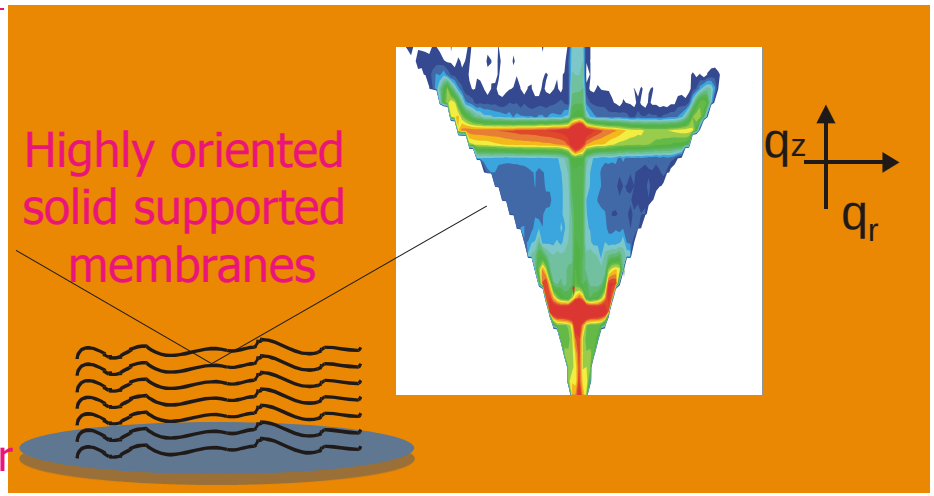
$$S = \frac{3 < cos^2(\varphi) > -1}{2}$$

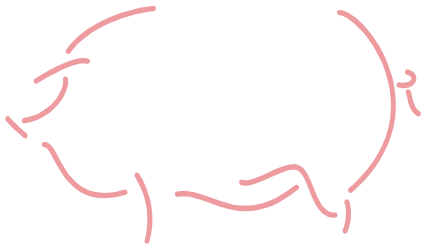


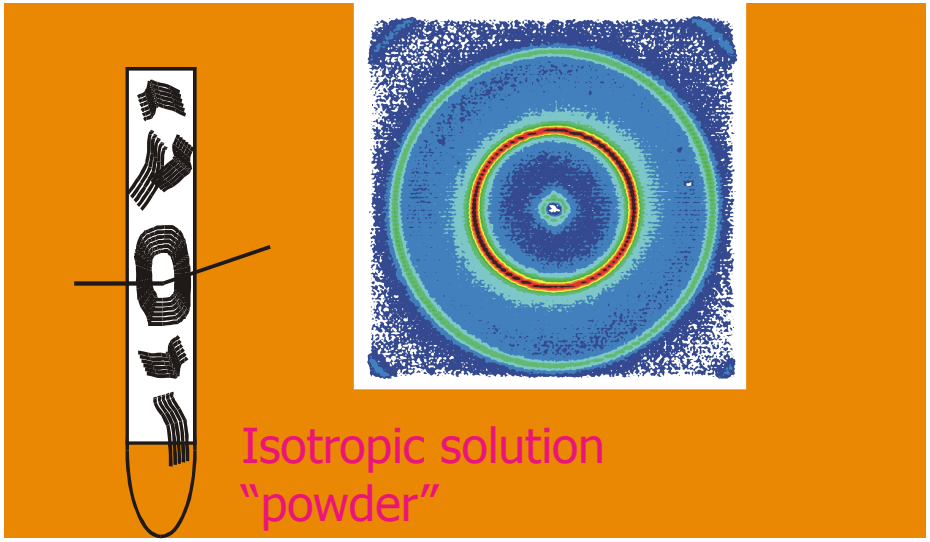


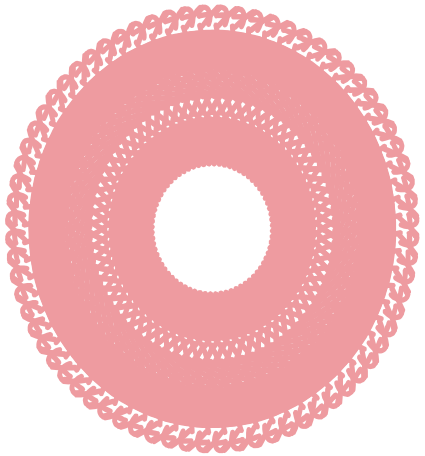
90% of the α-coils and β-chitin crystallites are oriented along the fibre-axis

Scattering from aligned phases





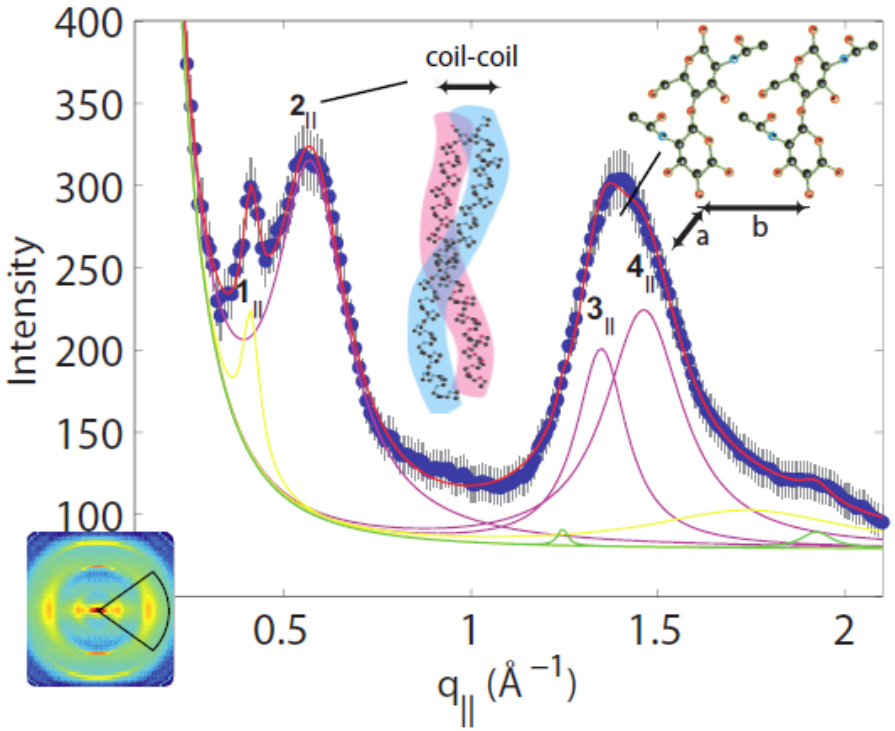


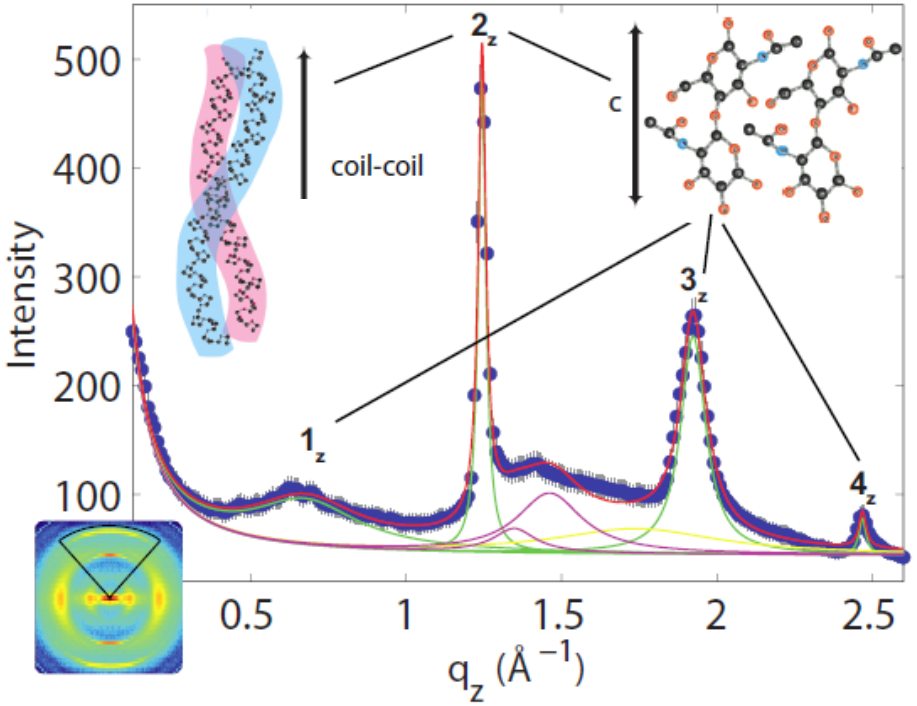


Structure Mapping

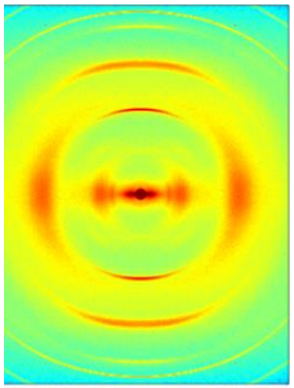
	Position ($Å^{-1}$)	Width ($Å^{-1}$)	α-coils	β-chitin
$1_{\|\|}$	0.41	0.03	Kapton Window	
$2_{\|\|}$	0.57	0.12	(100)	-
$3_{\|\|}$	1.35	0.08	-	(020)
$4_{\|\|}$	1.46	0.13	-	(110)

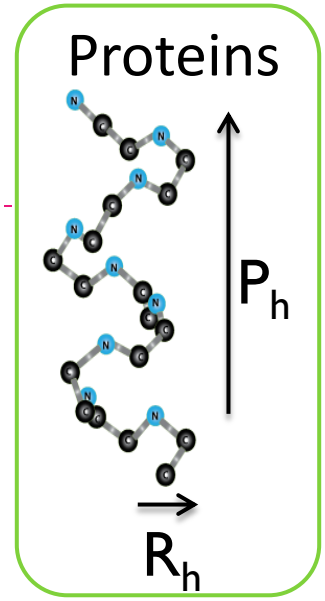
	Position ($Å^{-1}$)	Width ($Å^{-1}$)	α-coils	β-chitin
1_z	0.68	0.21	-	(001)
2_z	1.24	0.01	(001)	(002)
3_z	1.92	0.05	-	(003)
4_z	2.47	0.01	-	(004)

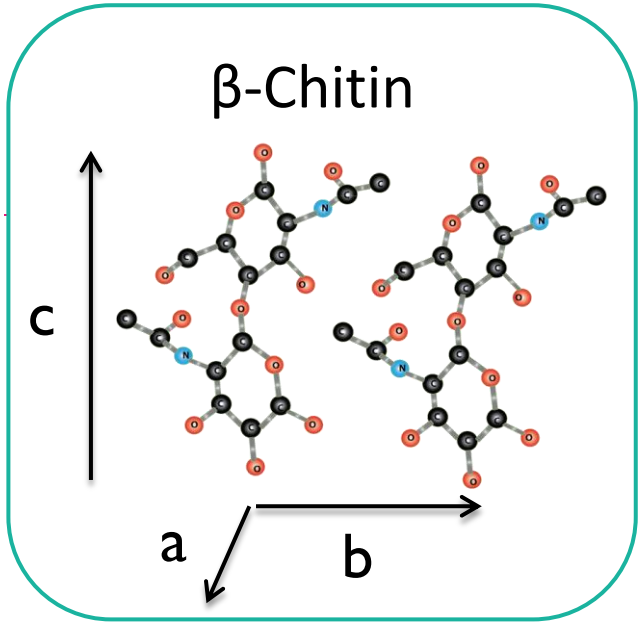




Structural Parameters







Sample	Order Parameter	R_h (Å)	P_h (Å)	Protein Layer Thickness (Å)
1	92.0%	3.70	7.85	23
2	86.9%	3.27	10.47	13

Sample	Order Parameter	a (Å)	b (Å)	c (Å)	γ	Crystallite size(Å)
1	92.3%	5.15	9.32	10.15	97.5°	65
2	87.5%	5.24	9.40	9.24	97.5°	74

Scattering from α-helices

$$q_{\|} = \frac{5\pi}{8 R_h}$$

$$q_z = \frac{2\pi}{P_h}$$

$$L_h = \frac{P_h N_h}{n_h}$$

$$\Delta q_z \cong \frac{5.57}{2 N_h \Delta h} = \frac{5.57}{2 L_h}$$

R_h radius the of α-helices

P_h pitch the of α-helices

N_h numbers of atoms

n_h numbers of atoms per pitch

Δq_z the peak width in HWHM

Scattering from β-chitin

q_{hkl} for monoclinic lattice

$$q_{hkl}^2 = \frac{4\pi^2}{\sin^2\gamma}\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2\sin^2\gamma}{c^2} - \frac{2hk\cos\gamma}{ab}\right)$$

$$q_{(002)}^2 = \frac{4\pi^2}{\sin^2\gamma}\left(\frac{2^2}{c^2}\right)$$

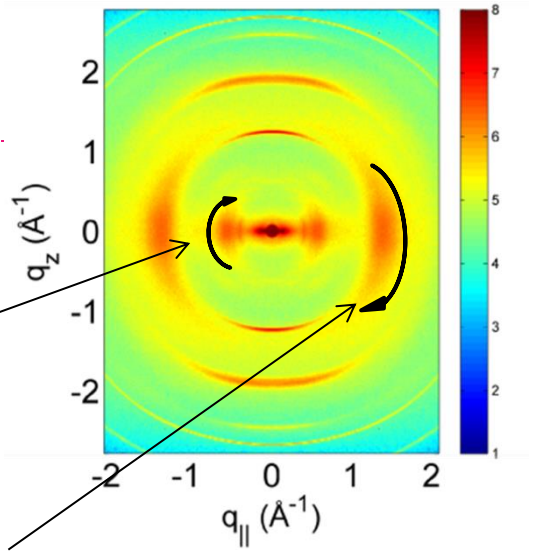
$$q_{(200)}^2 = \frac{4\pi^2}{\sin^2\gamma}\left(\frac{2^2}{b^2}\right)$$

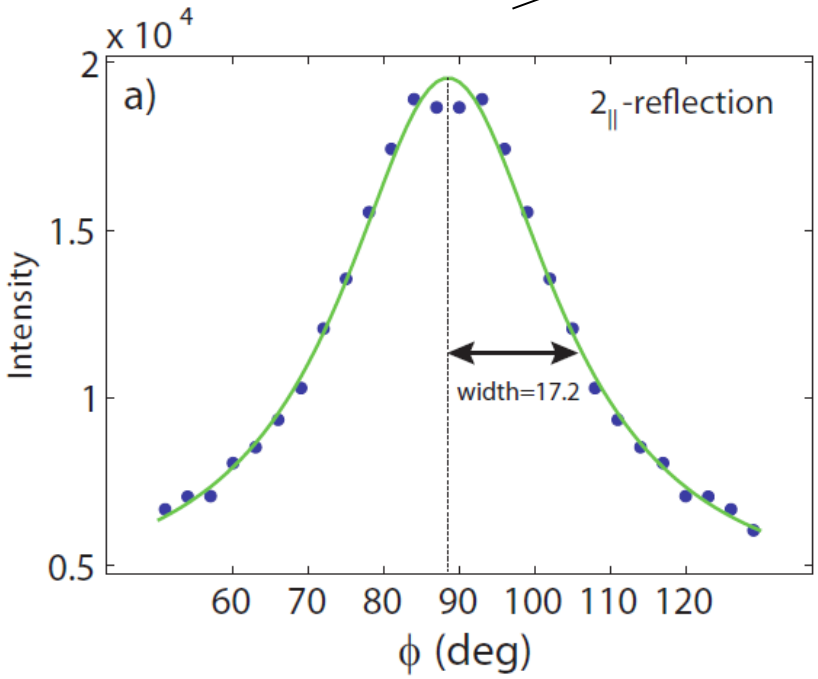
$$q_{(110)}^2 = \frac{4\pi^2}{\sin^2\gamma}\left(\frac{1^2}{a^2} + \frac{1^2}{b^2} - \frac{2\cdot 1\cdot 1\cos\gamma}{ab}\right)$$

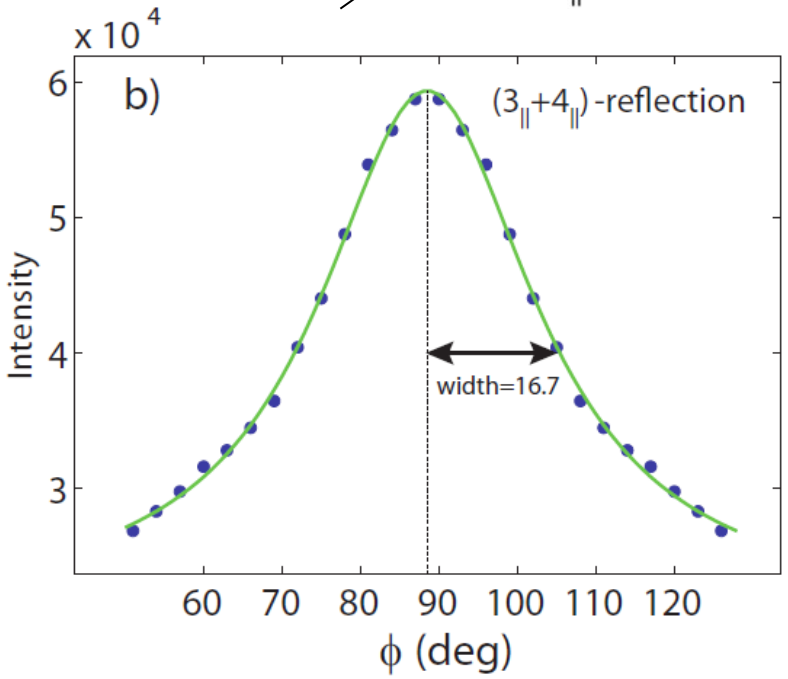
Degree of Orientation

Orientational Order Parameter

$$S = \frac{3 < cos^2(\varphi) > -1}{2}$$

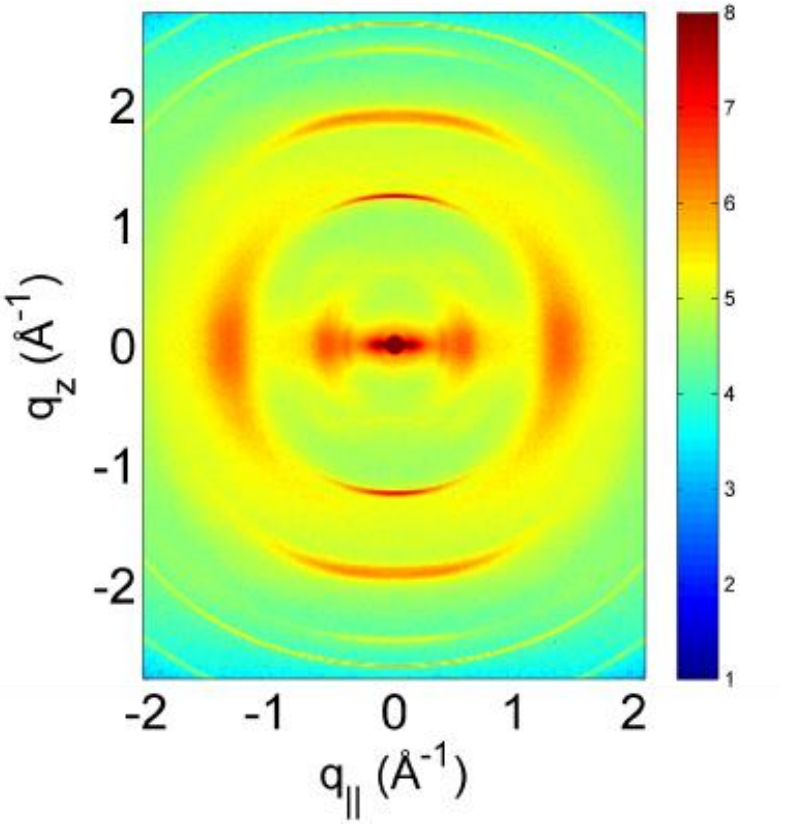






Scattering Experiments in Disordered Systems

- Few Bragg peaks; no long-ranged order
- Broadening of Bragg peaks
- Occurrence of 'Forbidden' Bragg peaks

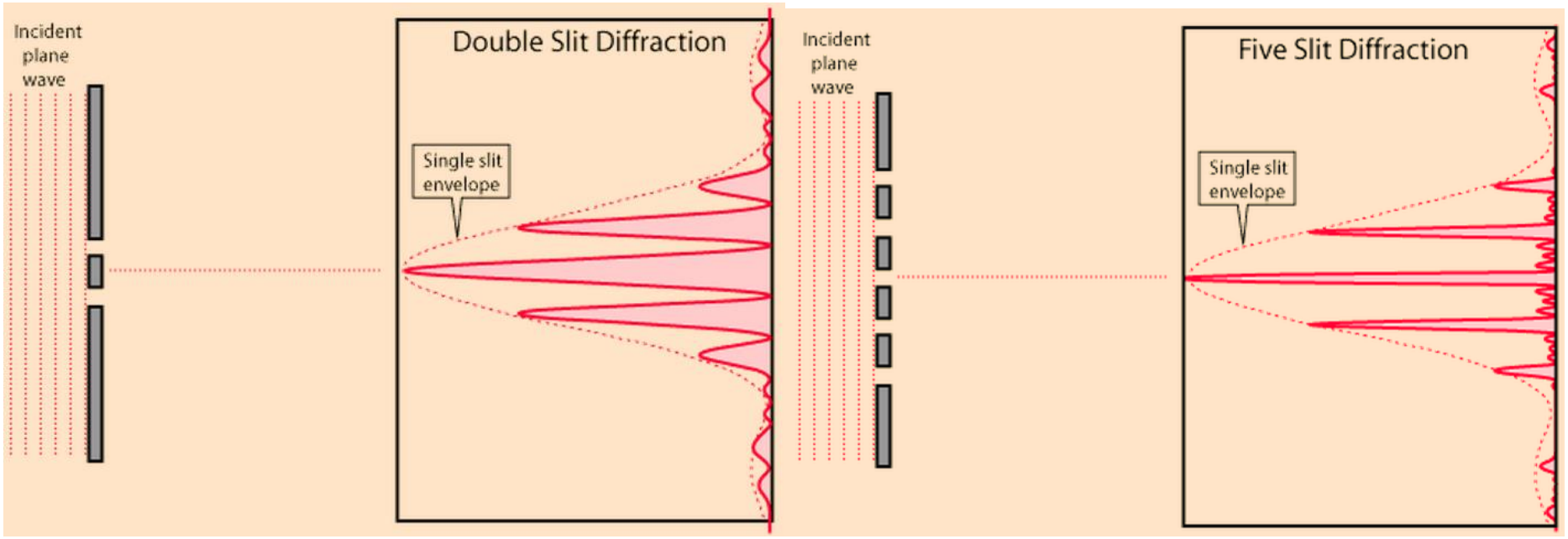


Broadening of Bragg Peaks

- Scherrer's Equation

$$L = \frac{K\lambda}{B\cos\theta}$$

L: crystallite size
λ: wavelength
B: width of the diffraction peaks in radians
θ: Bragg angle



‘Forbidden’ Bragg Peaks

Completely Disorder
S=0

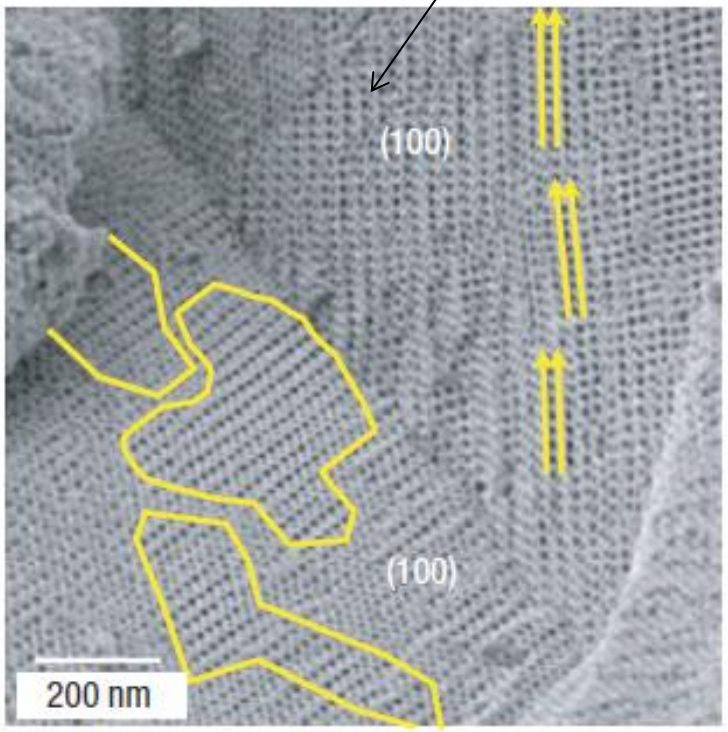
increase order

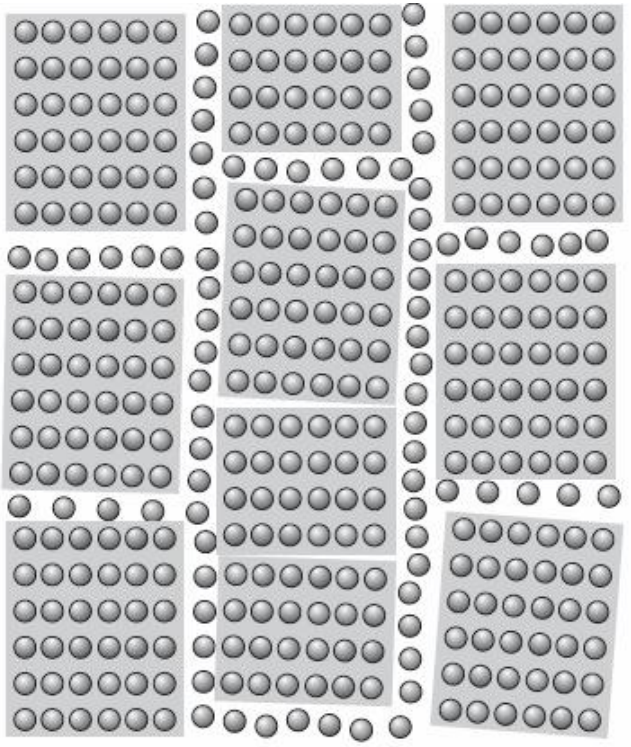
Completely Order
S=0.99

Forster et al. *Nature Materials*.VOL 6. 888-893 (2007)

‘Forbidden’ Bragg Peaks

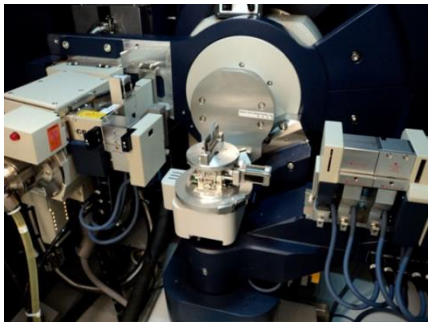
Deviations from ‘perfect’ structure where domains meet

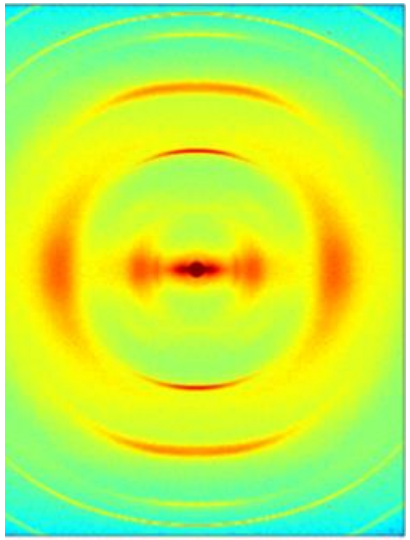




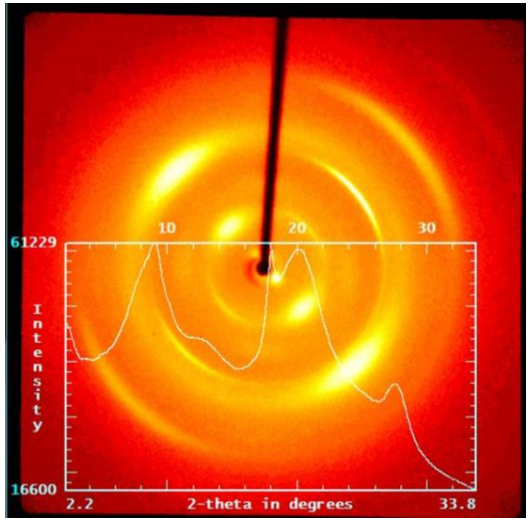
Comparison of Different Setups

Blade
(Point detector)

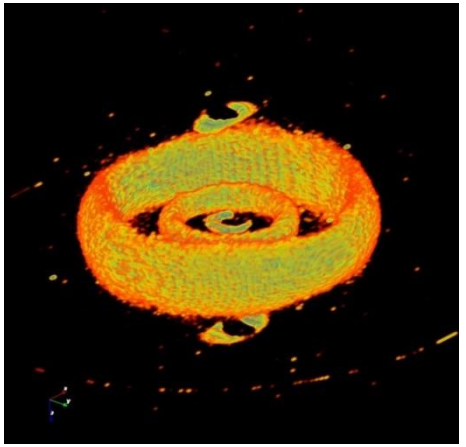


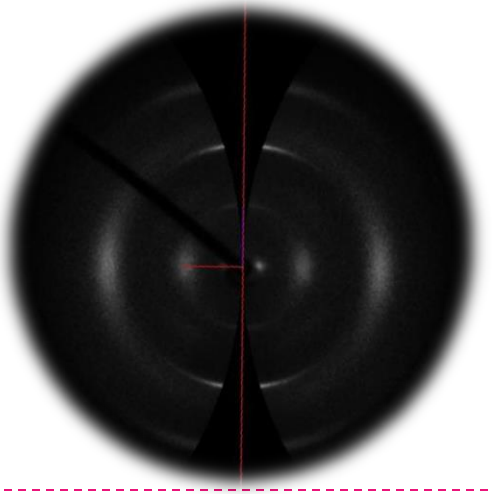


Single Crystal Diffraction
(SCD):



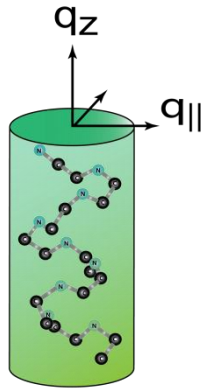
Texture and Residual Stress Analyses
(XRD^3)

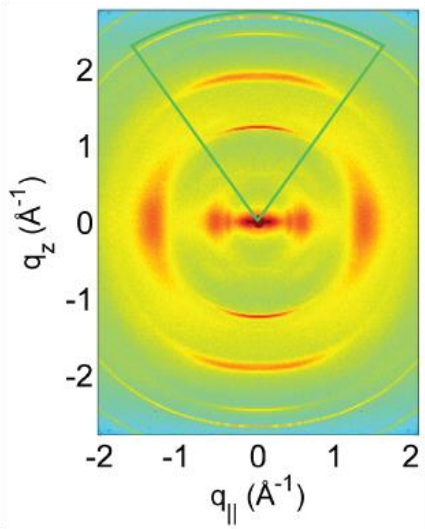


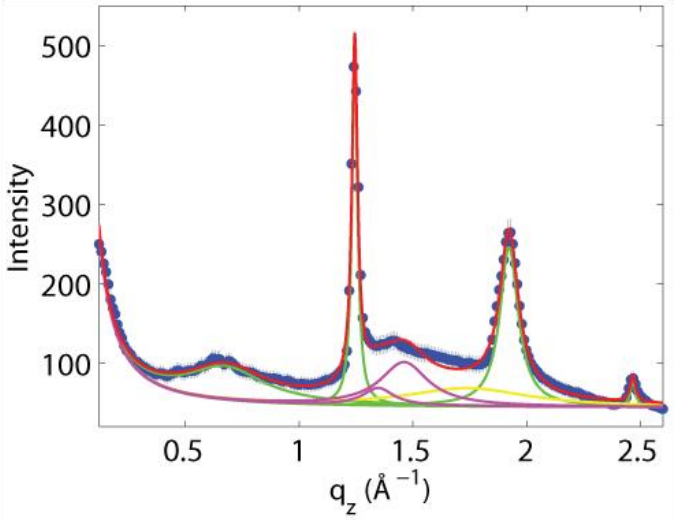


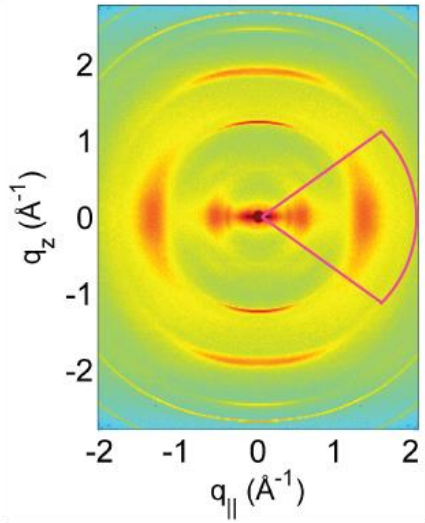
Data Analysis

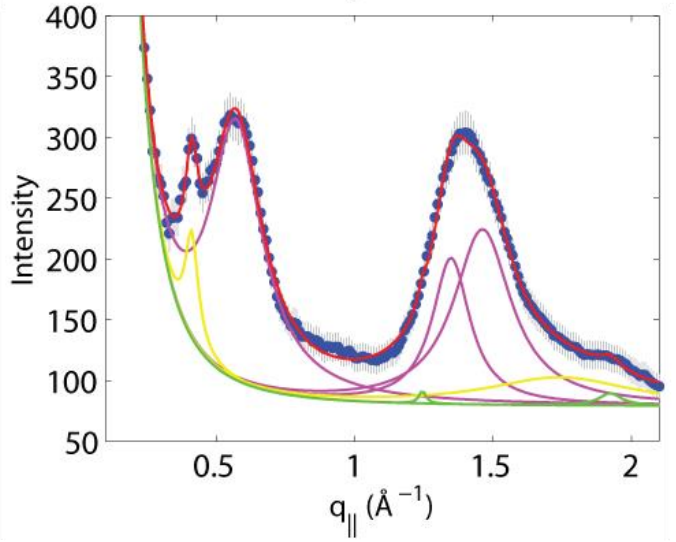
- q_z features
- $q_{||}$ features







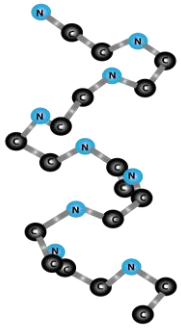




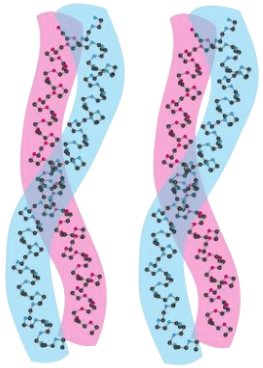
Biological Building Blocks

Protein

α Helix



coiled coils

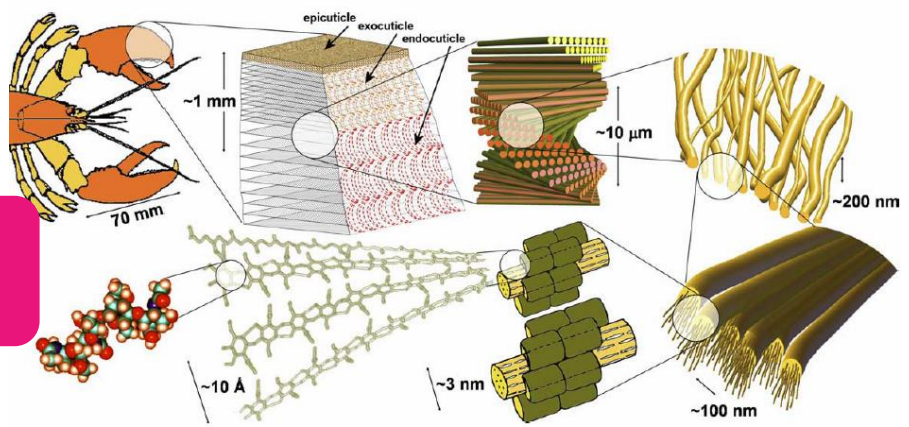


Material Properties

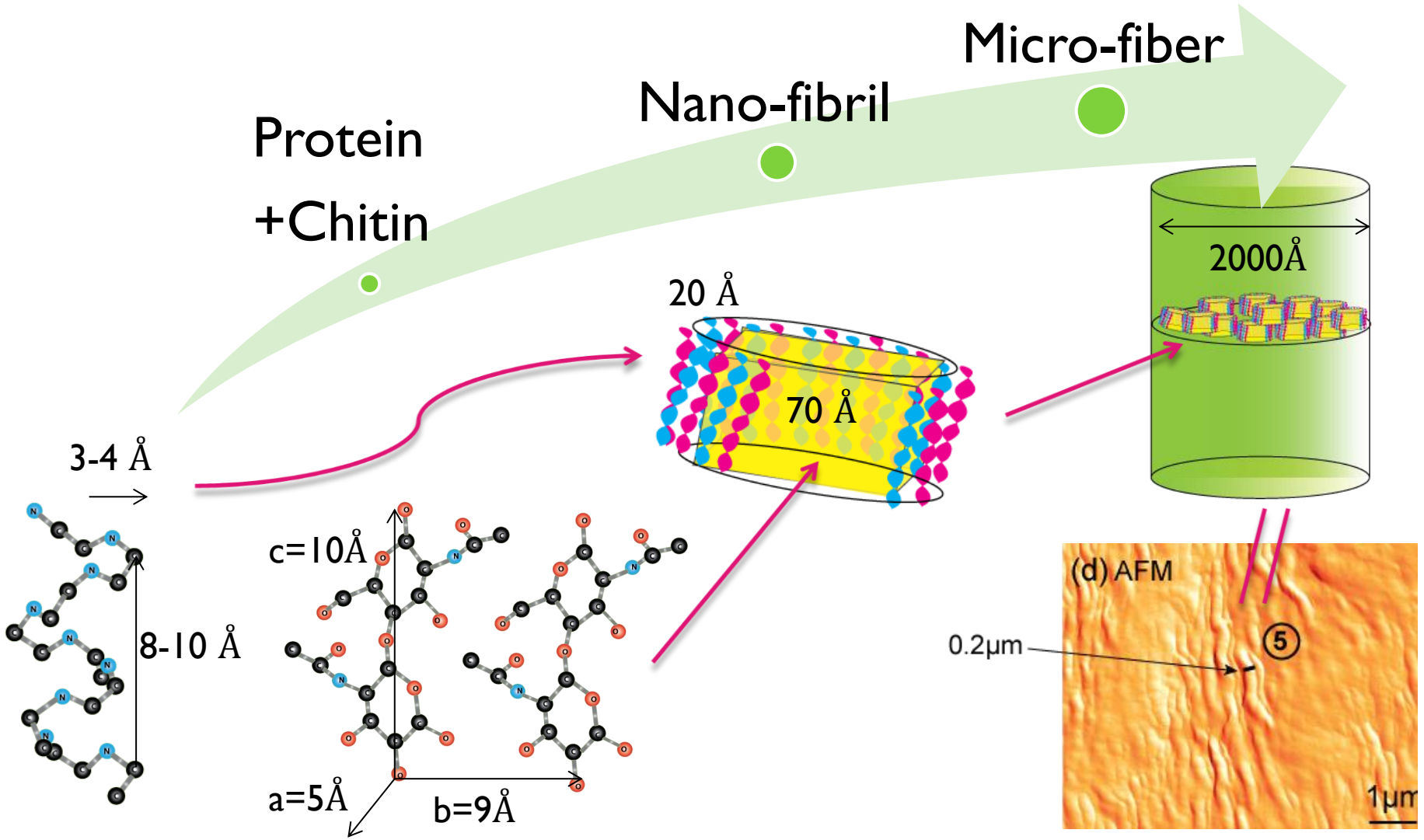
?

Molecular Structures

Chitin



Nanostructure



Building Blocks of Biomaterials

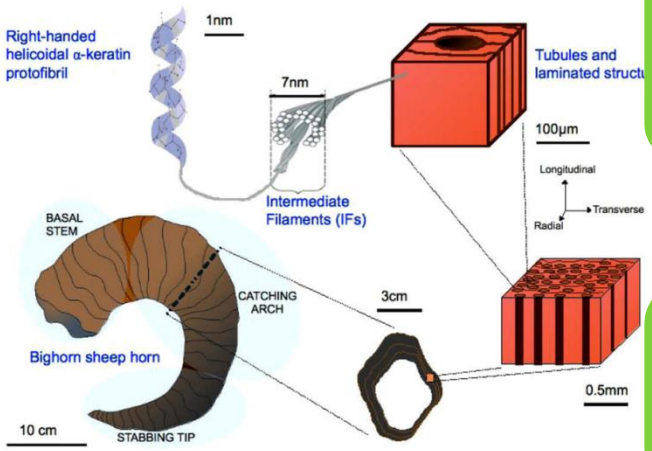
Protein

Material Properties

?

Chitin

Hierarchical Organizations



Acta Biomaterialia 6 (2010) 319–330

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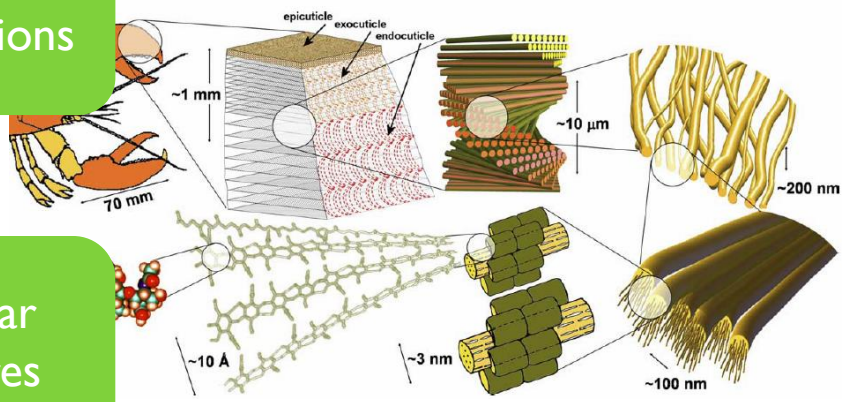
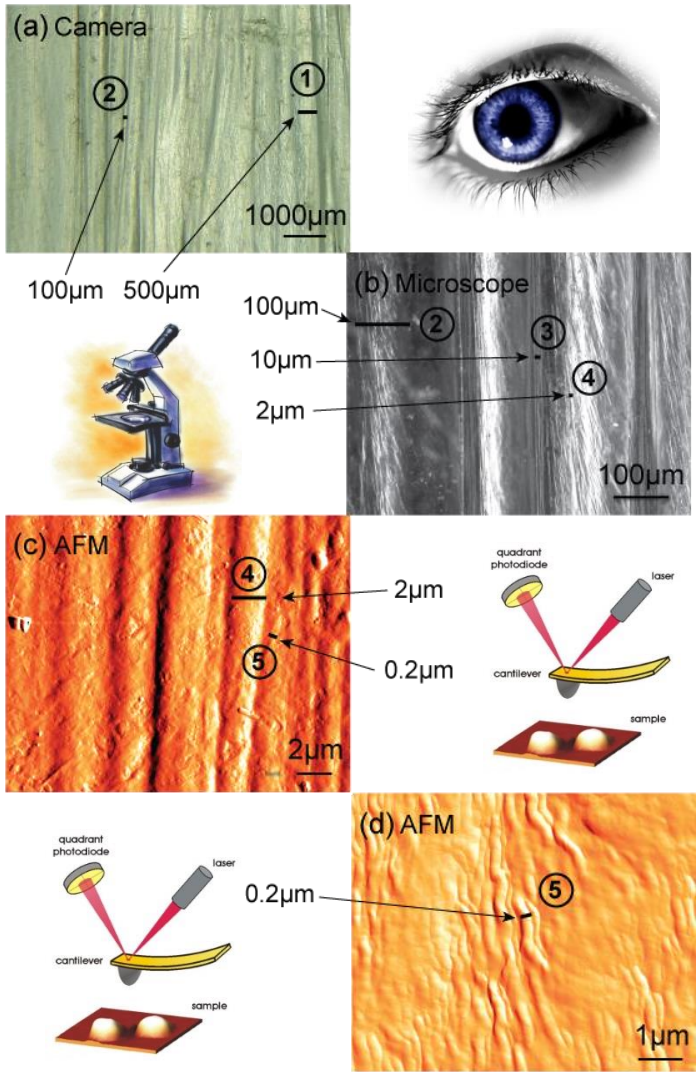
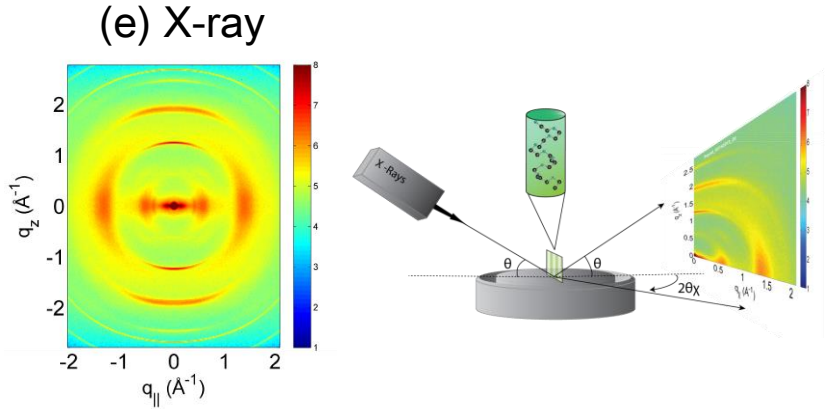
Molecular Structures



Acta Materialia 53 (2005) 4281–4292

Summary





Squid pen is a biomaterial which follows the hierarchical, self-similar structure ranging from millimeters to the molecular level