Warren Averbach analysis of XRD peak shapes:

Measuring disorder in soft organic materials

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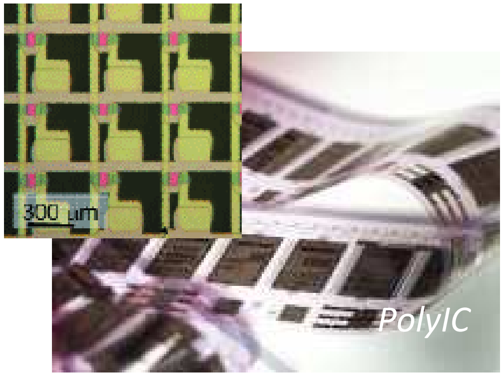
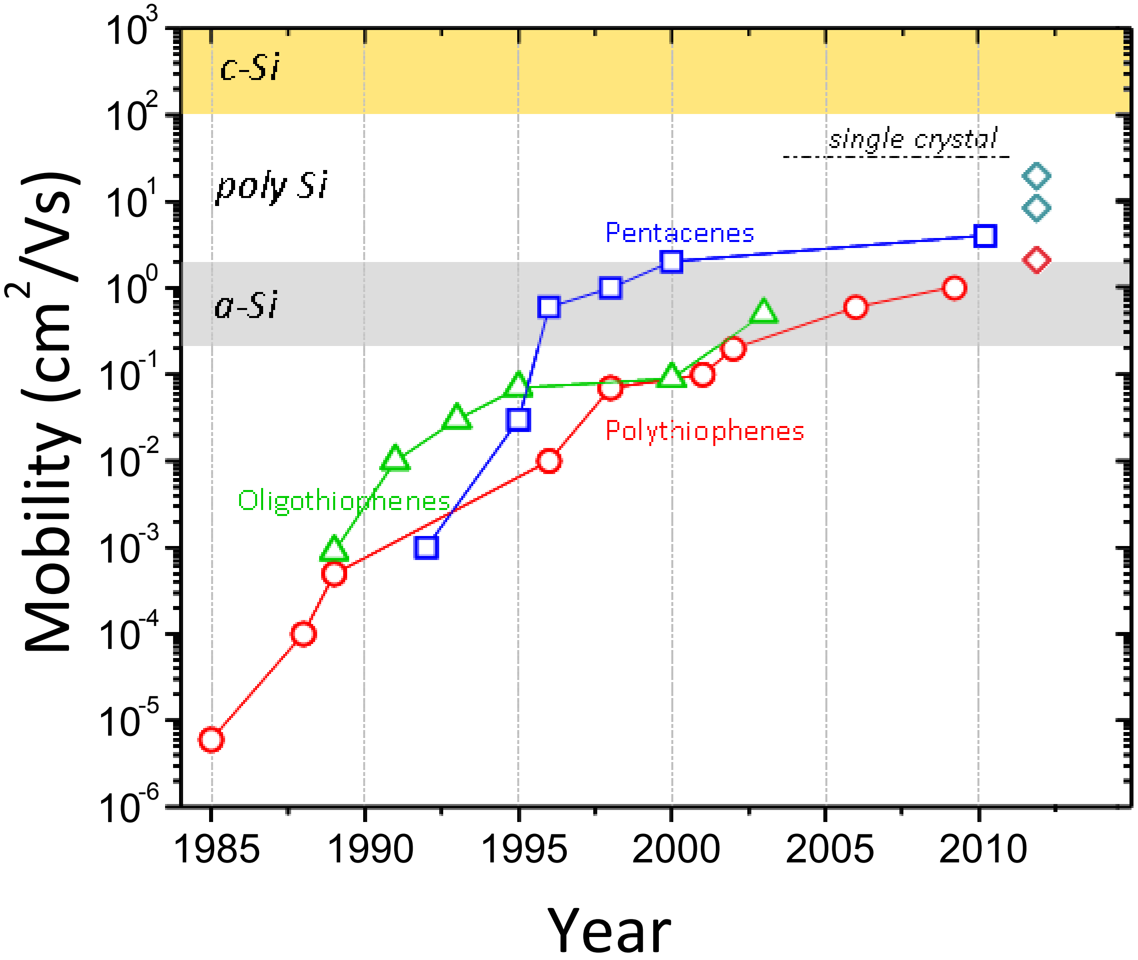
How will organic semiconductors continue improving?

Organic Thin Film Transistors (OTFTs)



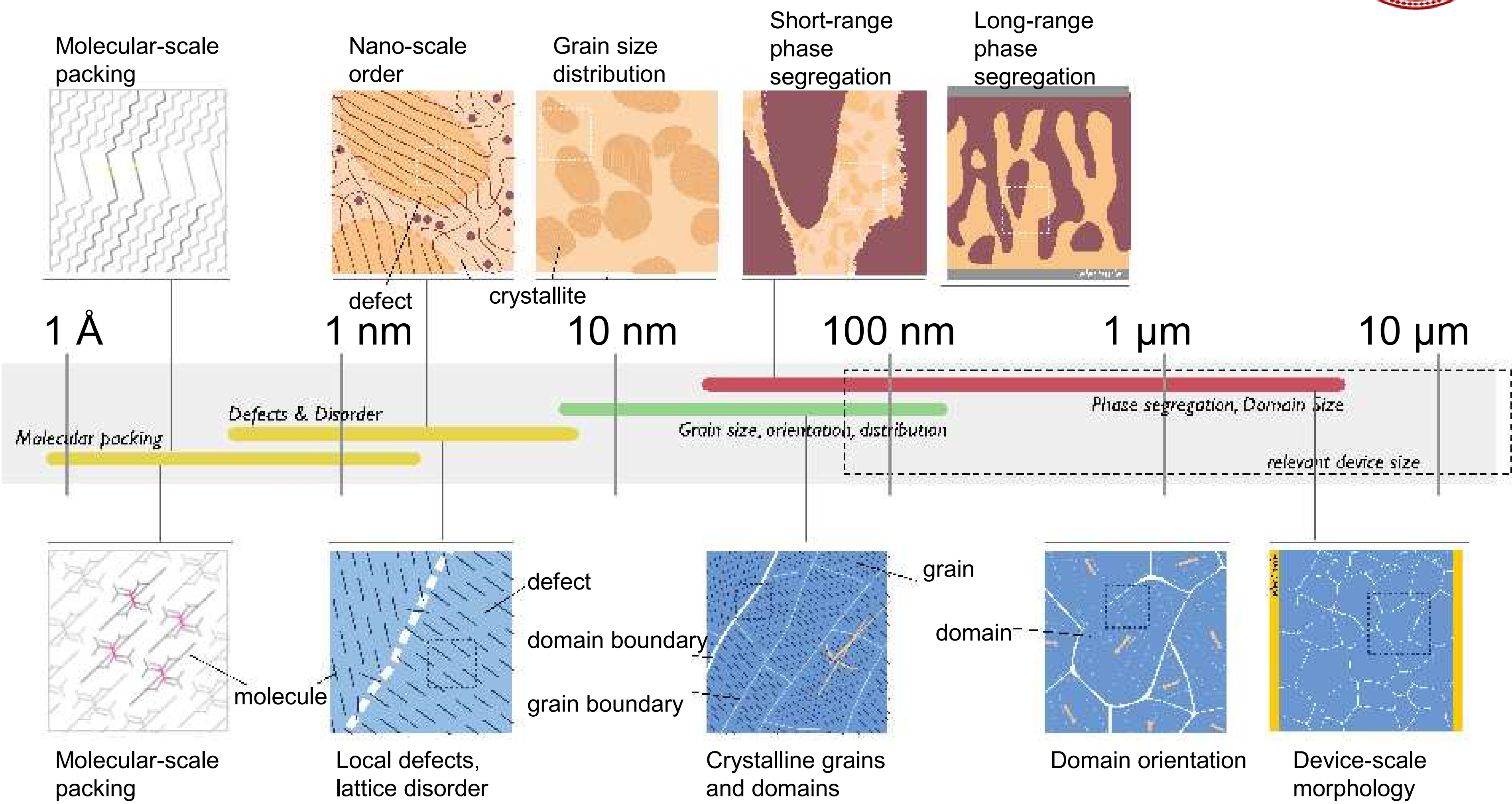
Applications:

Complementary Logic
Display Backplanes
RFID Tags
Sensors



Can we develop design rules to continue to improve performance/understanding?

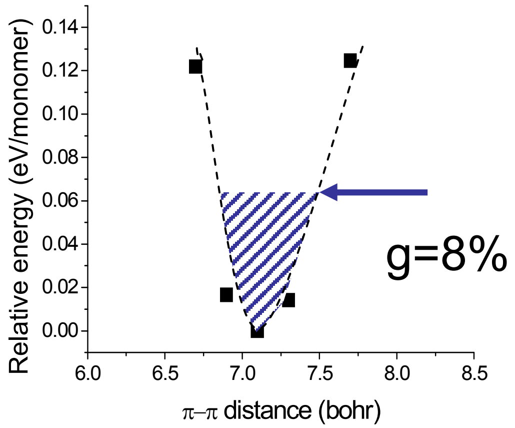
Must understand and control morphology over vast range of length scales

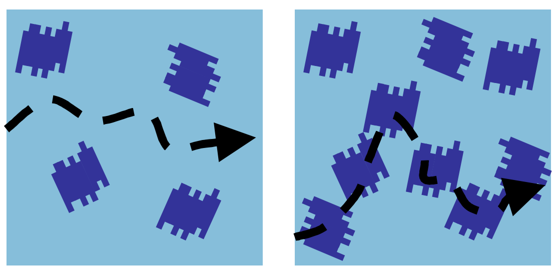


Rivnay (Chem. Rev., submitted)

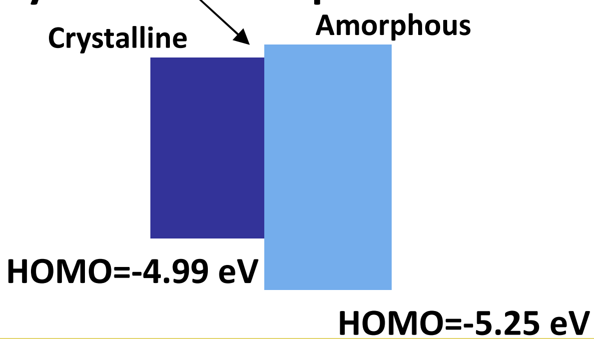
Disorder is important for organic materials

It's easier to melt disordered crystals

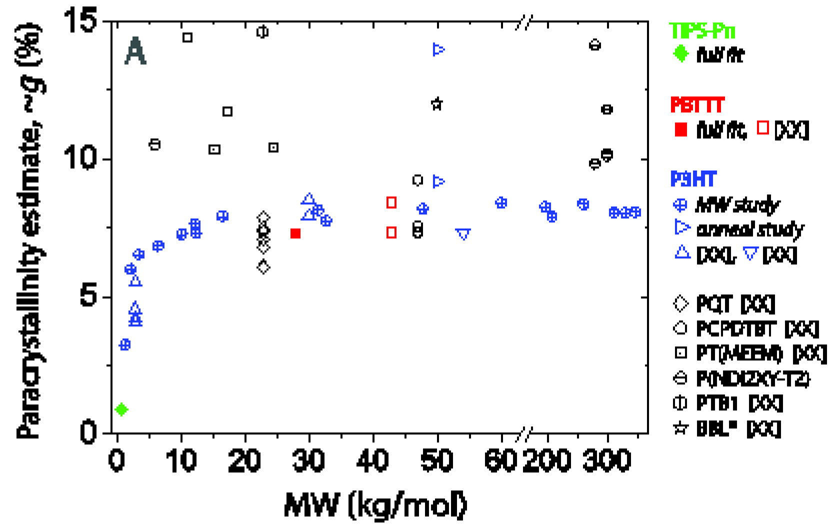


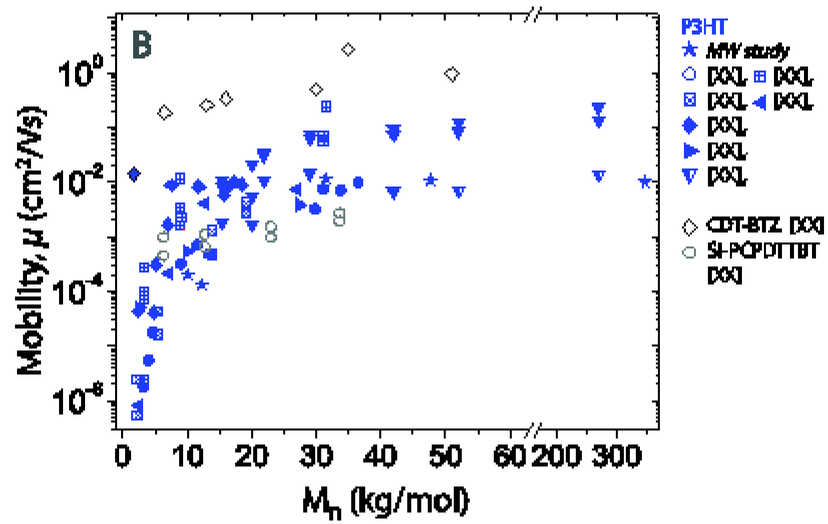


Crystalline-amorphous interface



Top performers are disordered

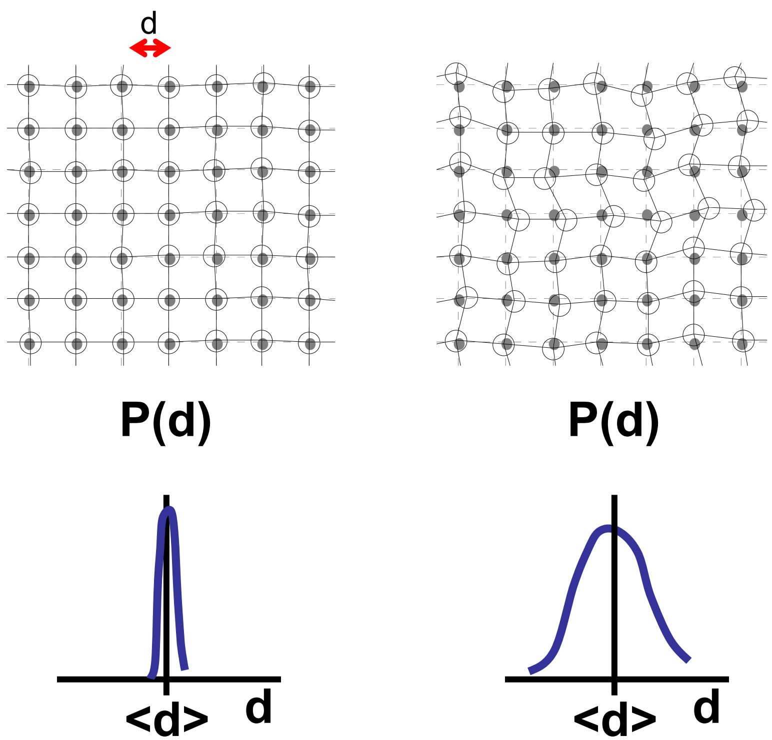




Paracrystalline parameter characterizes disorder

Δ² is the variance of interplanar spacing d: $\Delta^2 = \langle d^2 \rangle - \langle d \rangle^2$

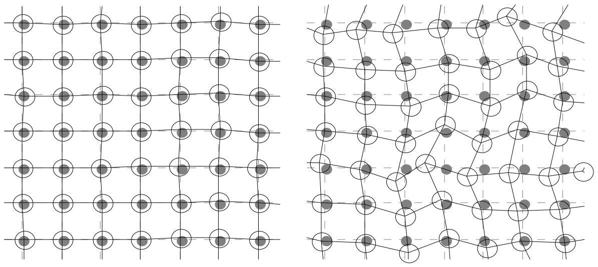
Can now define the "paracrystallinity parameter", g: $g^2 = \Delta^2 / \langle d \rangle^2$

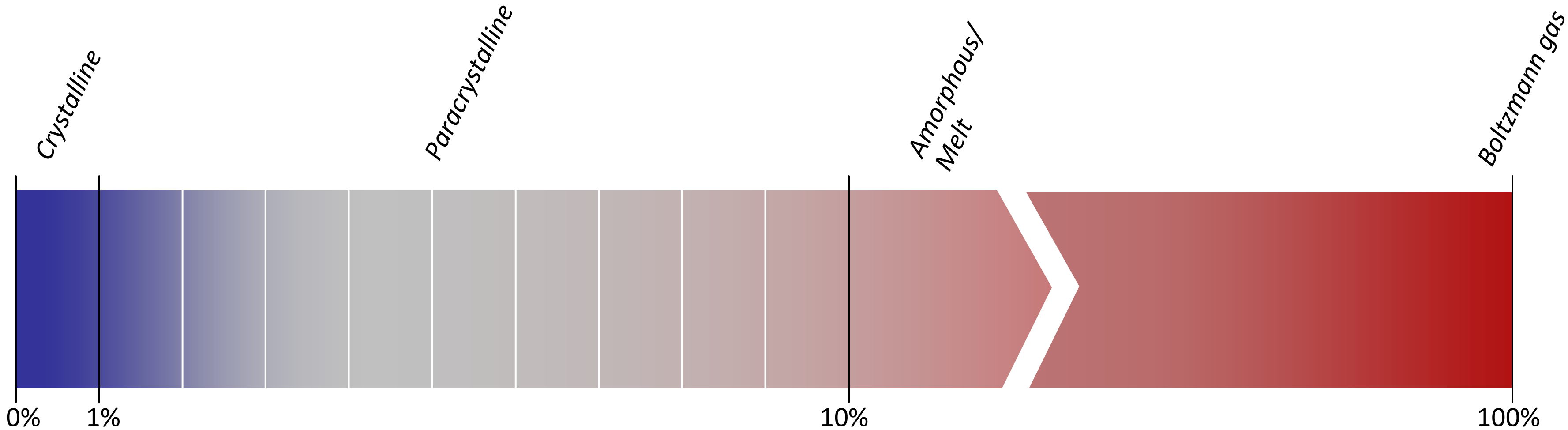


Using g to rank materials from crystalline to amorphous

Most of peak-broadening due to
paracrystalline disorder (*g*)

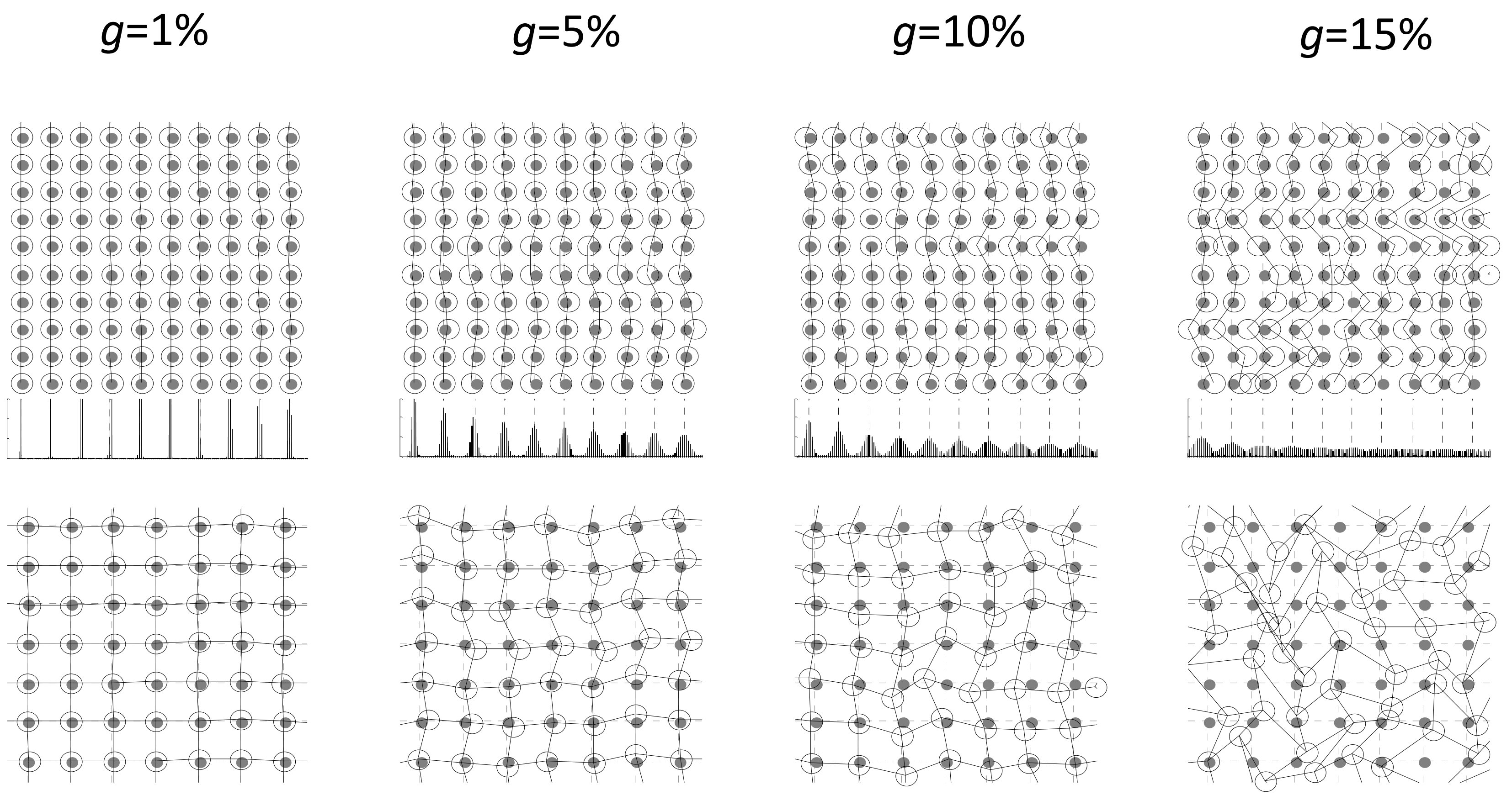
Statistical deviation from mean lattice spacing



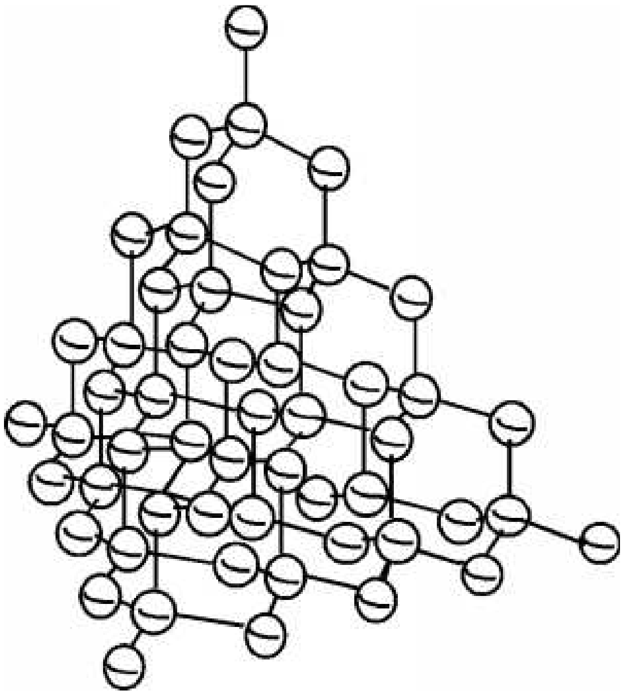


Hindeleh (J. of. Physics C, 1988)

Paracrystalline disorder: a picture

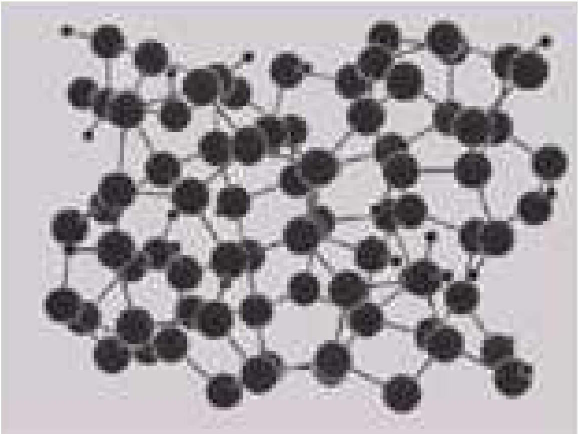


Paracrystallinity in Silicon

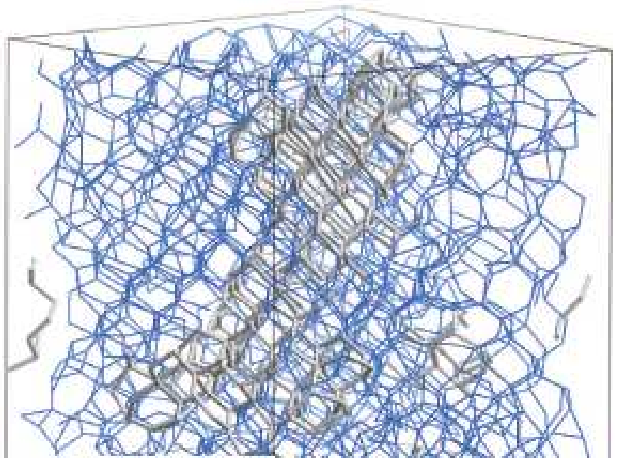


Crystalline silicon

Is this the whole story?



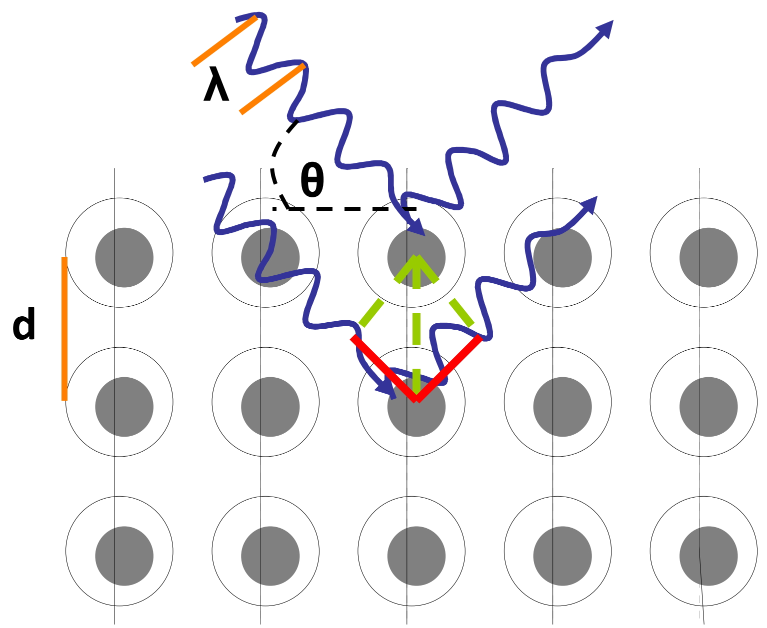
Amorphous silicon



Paracrystalline silicon

Treacy (Science, 2012)

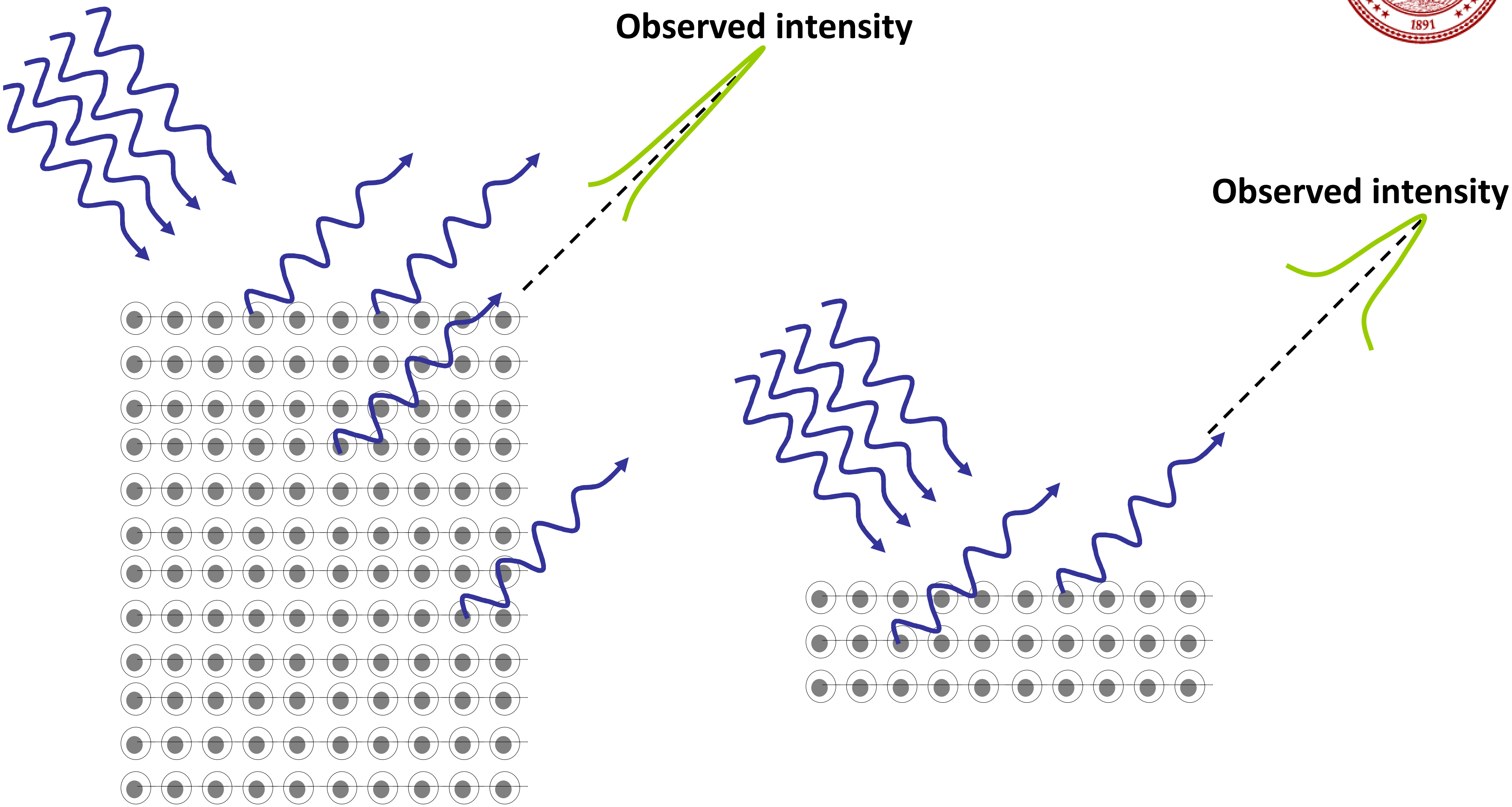
Bragg's law recap



Constructive interference happens if
$2d\sin\theta=n\lambda$

In terms of the scattering vector:
$q=4\pi\sin\theta/\lambda=Q_{rec}$

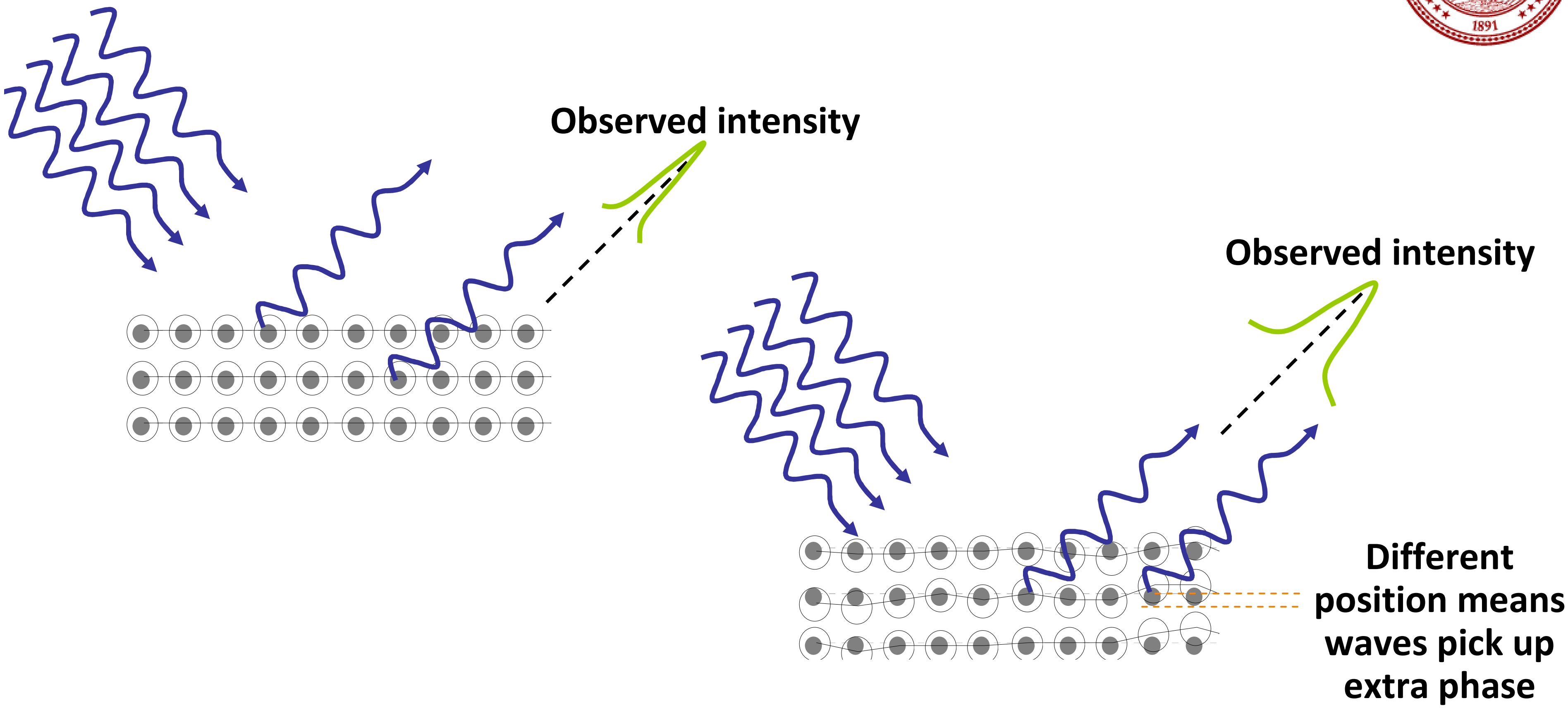
X-ray scattering is sensitive to imperfections



Finite-size crystals have nonzero breadth diffraction peaks.

Warren and Averbach (JAP, 1950 and 1952)

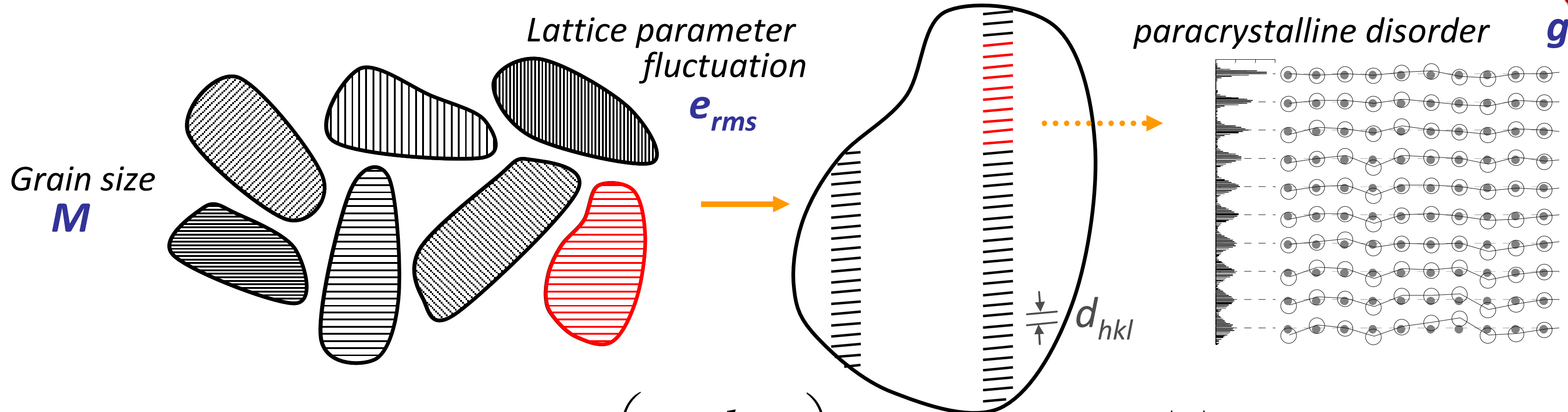
X-ray scattering is sensitive to imperfections



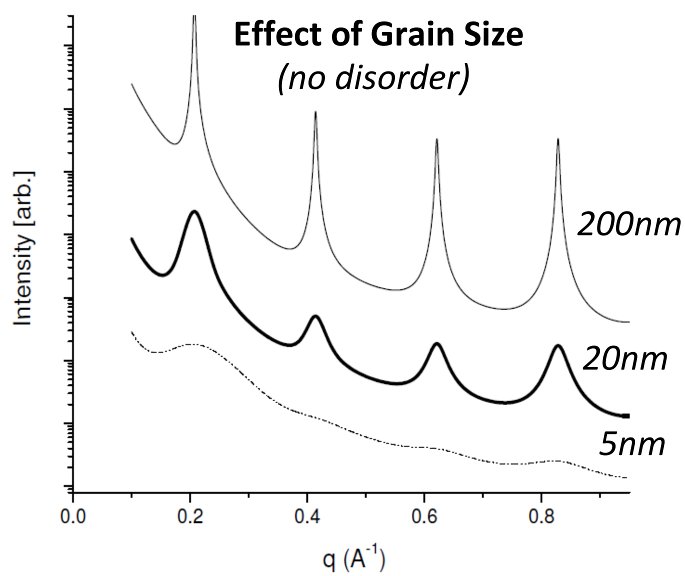
The width of a diffraction peak is increased when we add disorder to the lattice. More importantly, the peak width increases with diffraction order.

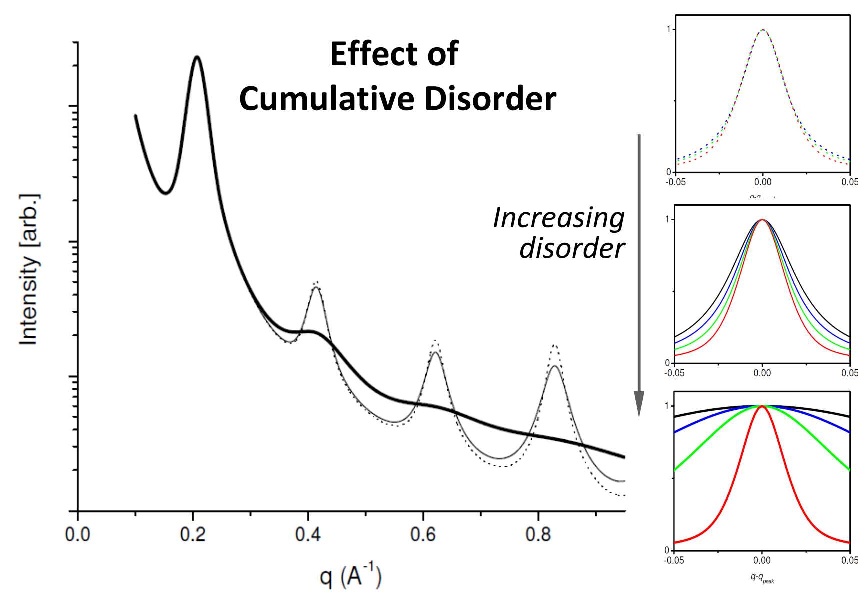
Warren and Averbach (JAP, 1950 and 1952)
Prosa et al. (Macromolecules, 1999)

Measuring disorder quantitatively using X-ray diffraction



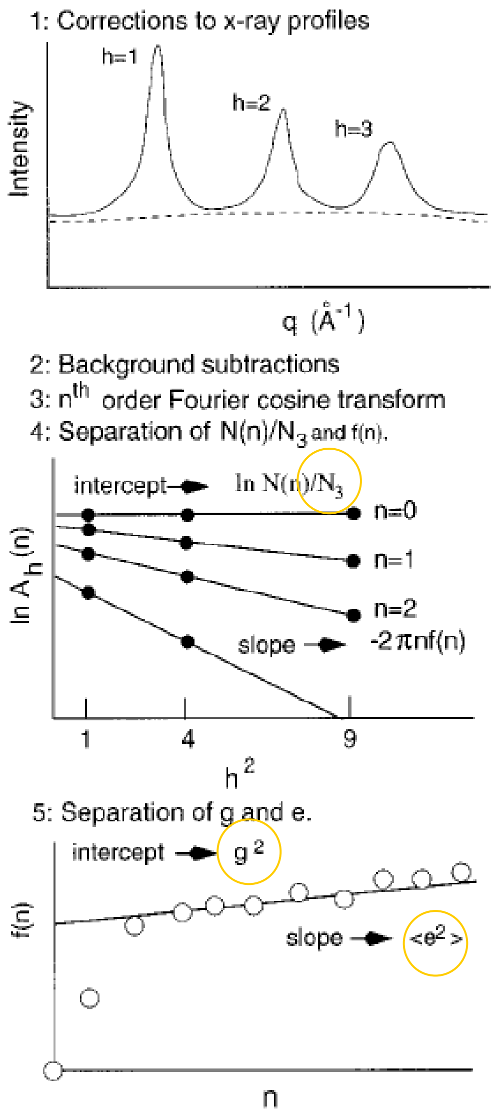
$$A_n = \left(1-\frac{d_{hkl}n}{M}\right)e^{-2\pi^2m^2ng^2}e^{-2\pi^2m^2n^2\langle e^2\rangle}$$





Warren and Averbach (JAP, 1950 and 1952)
Prosa et al. (Macromolecules, 1999)

Warren-Averbach Graphical approach



Diffraction peaks can be represented by Fourier series

$$A_m(n) = A^S(n) A_m^e(n) A_m^g(n)$$

$$\ln A_m(n) = \ln N(n)/N_3 - 2\pi^2 m^2 n f(n)$$
$$f(n) = g^2 + n\langle e^2 \rangle$$

+ Extracting more information from peaks

- Prone to inaccuracies

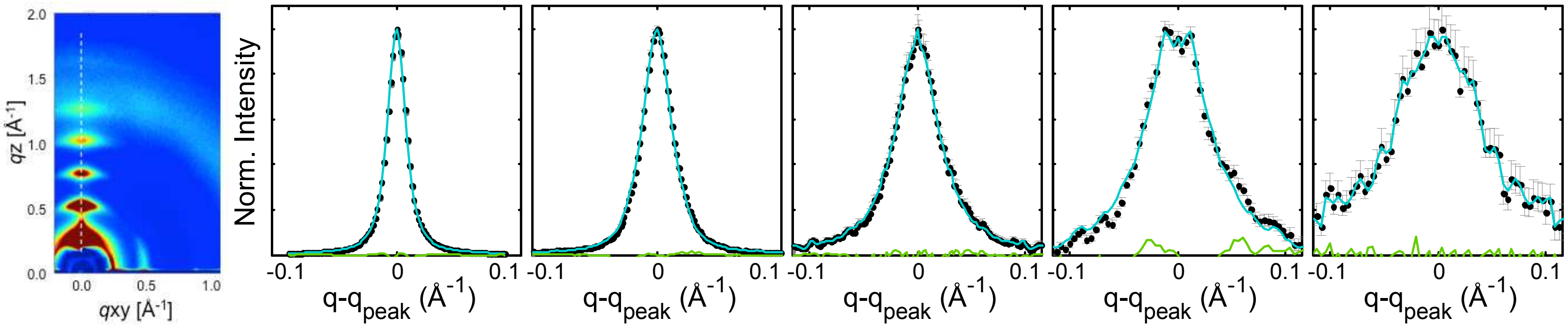
Multiple steps

Fitting lines to as few as 2-3 points

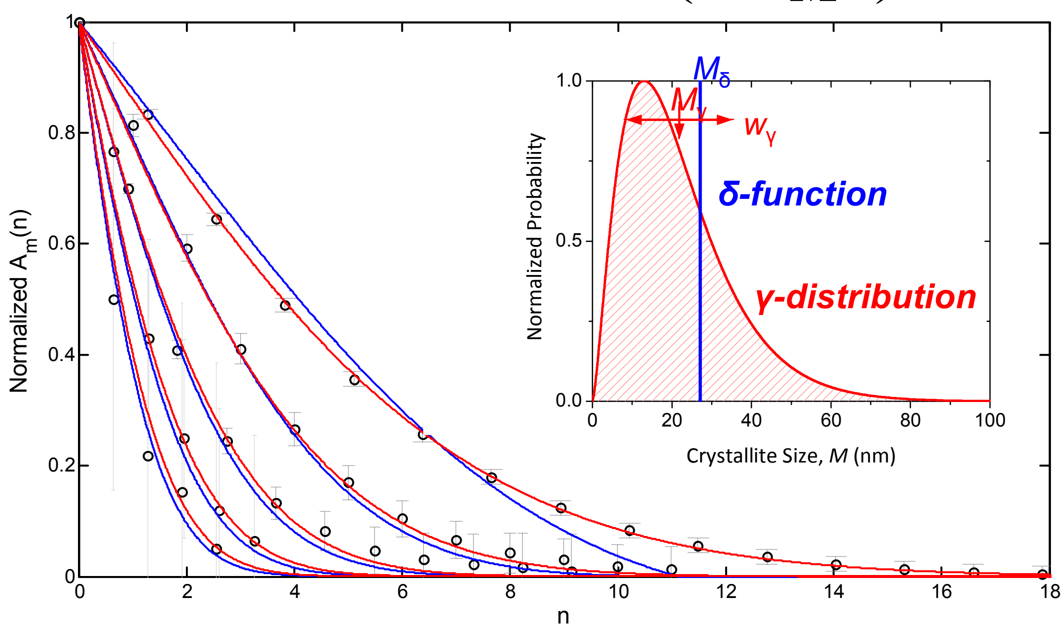
Basing fits on previous fit results

Warren (1951)
T.J. Prosa, Macromolecules (1999)

Line-shape analysis applied to Polyera N2200



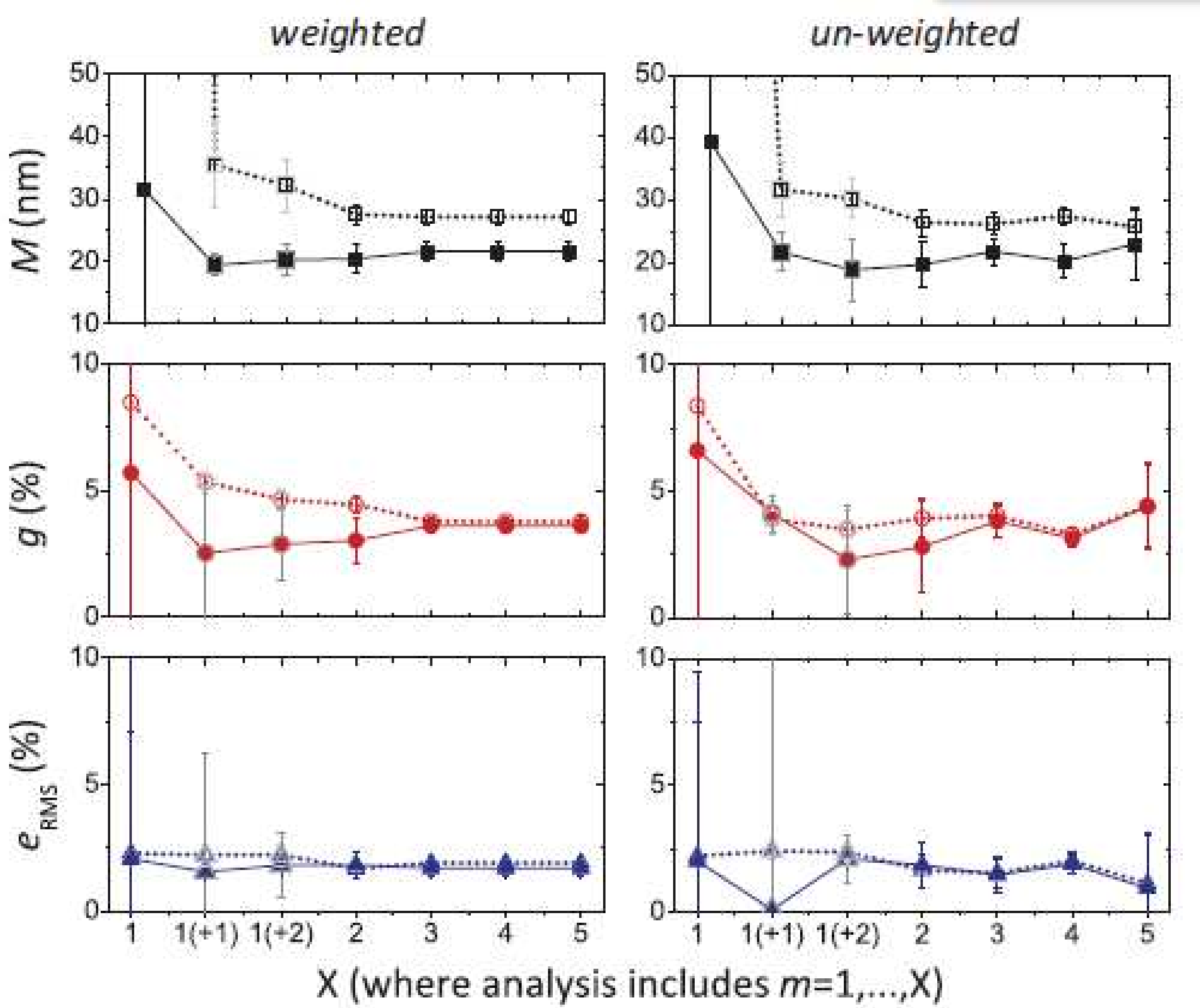
$$A_n = \left(1 - \frac{d_{hkl} n}{M}\right) e^{-2\pi^2 m^2 n g^2} e^{-2\pi^2 m^2 n^2 \langle e^2 \rangle}$$



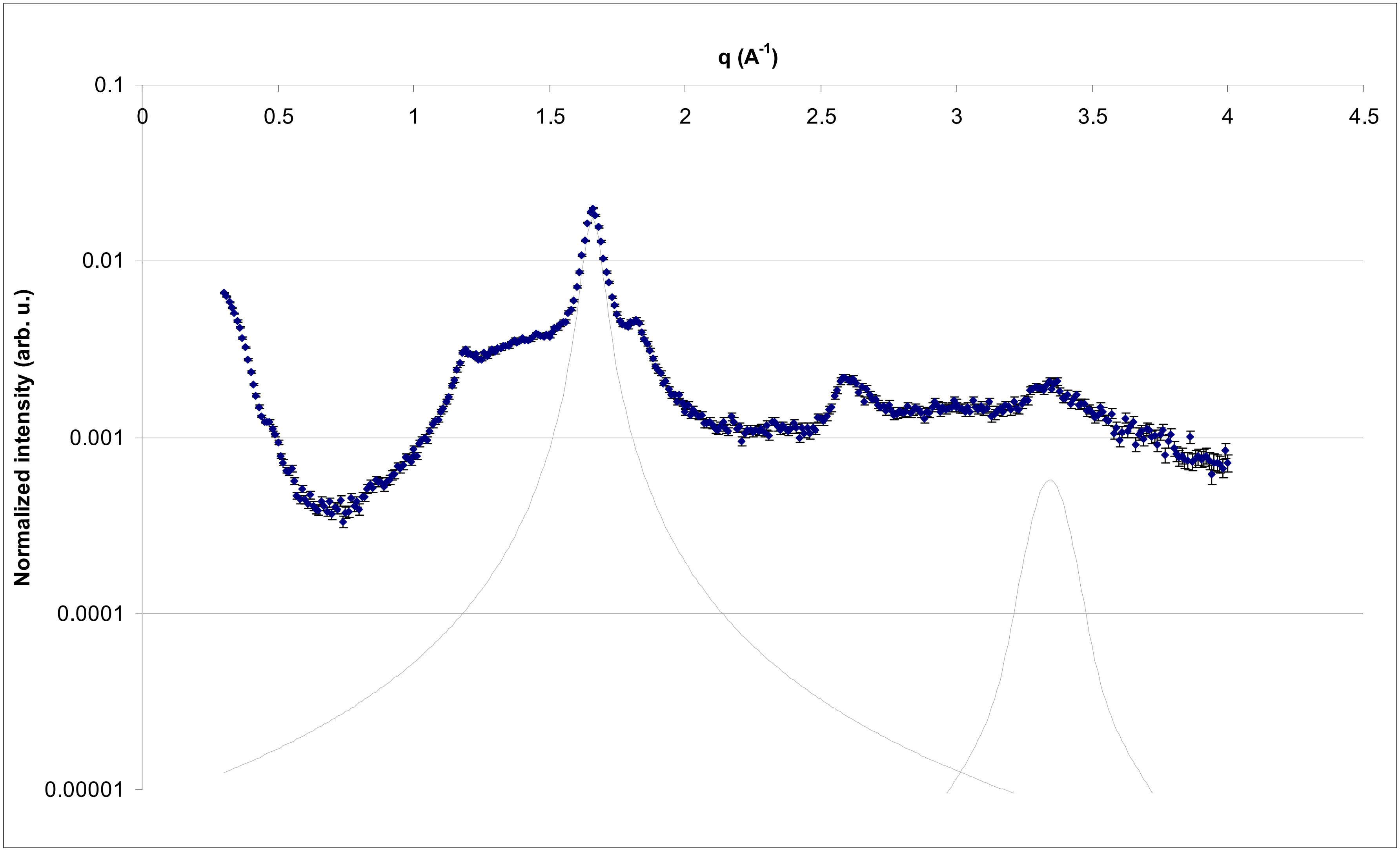
	M (nm)	g (%)	e_{rms} (%)
δ-distribution	27 ± 1	3.8 ± 0.2	1.9 ± 0.2
γ-distribution	22 ± 2 W_γ~14 nm	3.6 ± 0.2	1.7 ± 0.3

Rivnay (PRB, 2011)

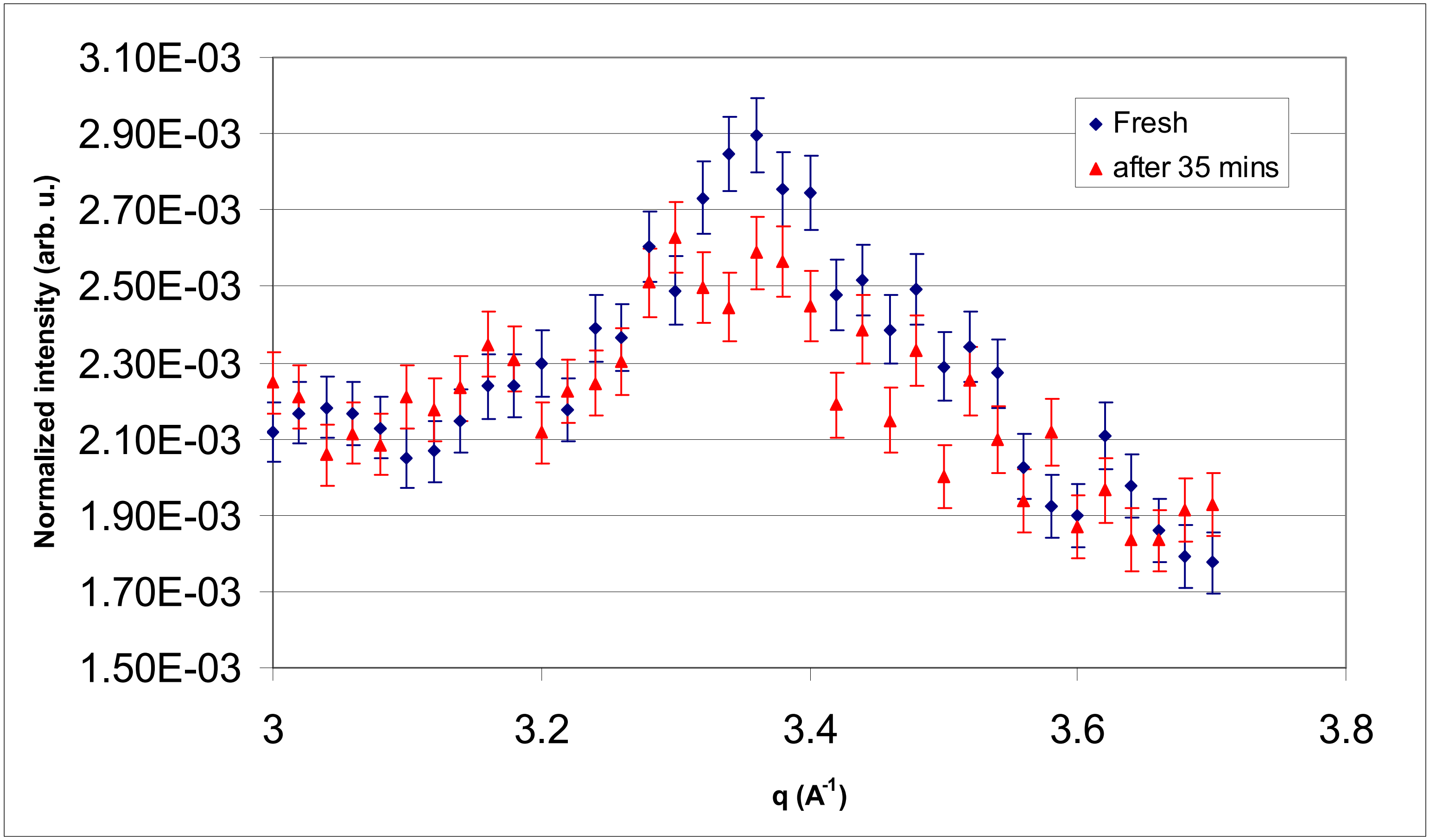
Fits converge quickly with more data



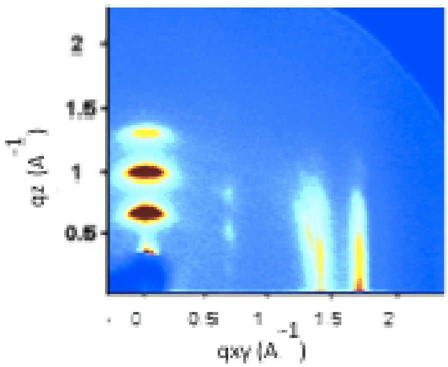
Data is not always that nice

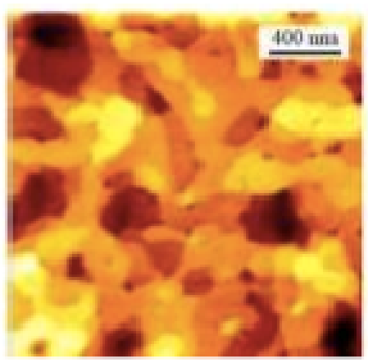


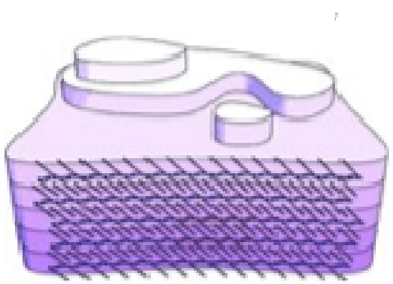
Beam damage is something to be aware of



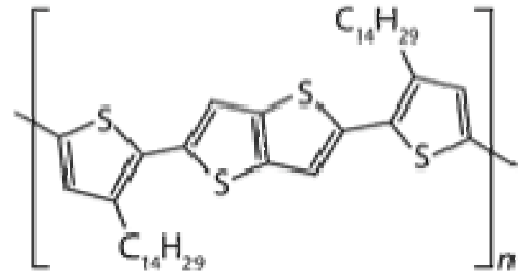
A model system for anisotropic disorder: PBTTT

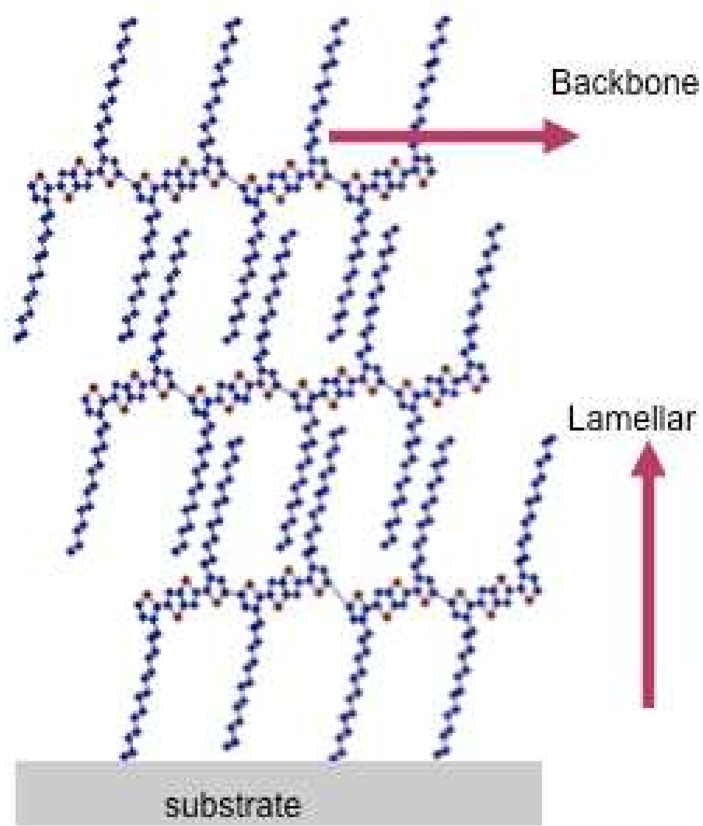


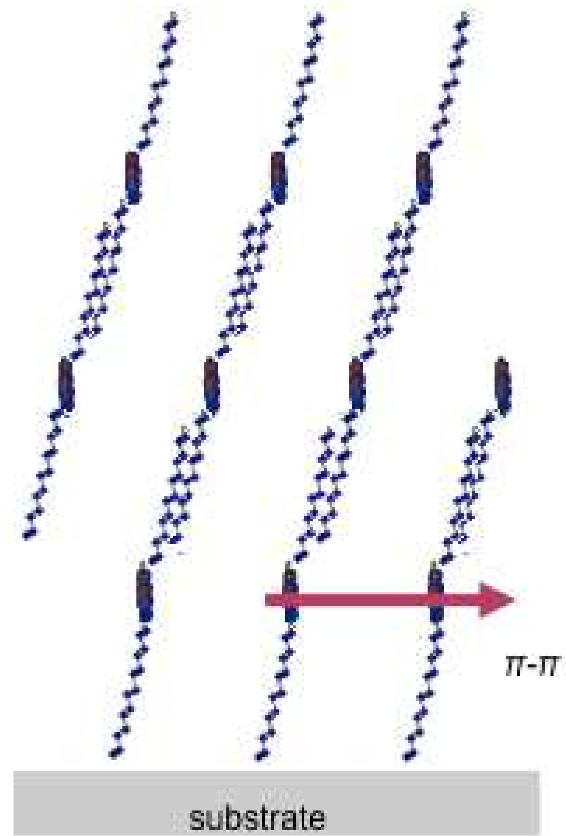




PBTTT:

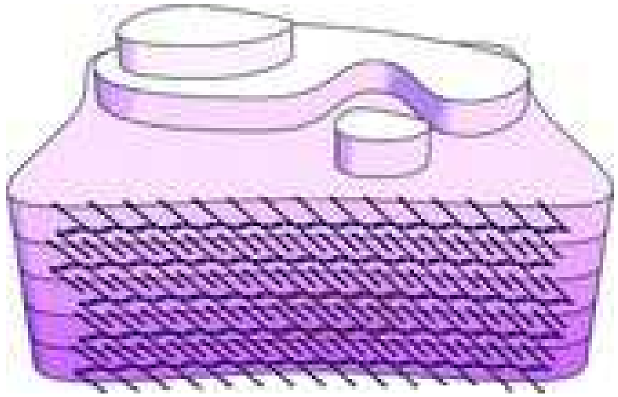


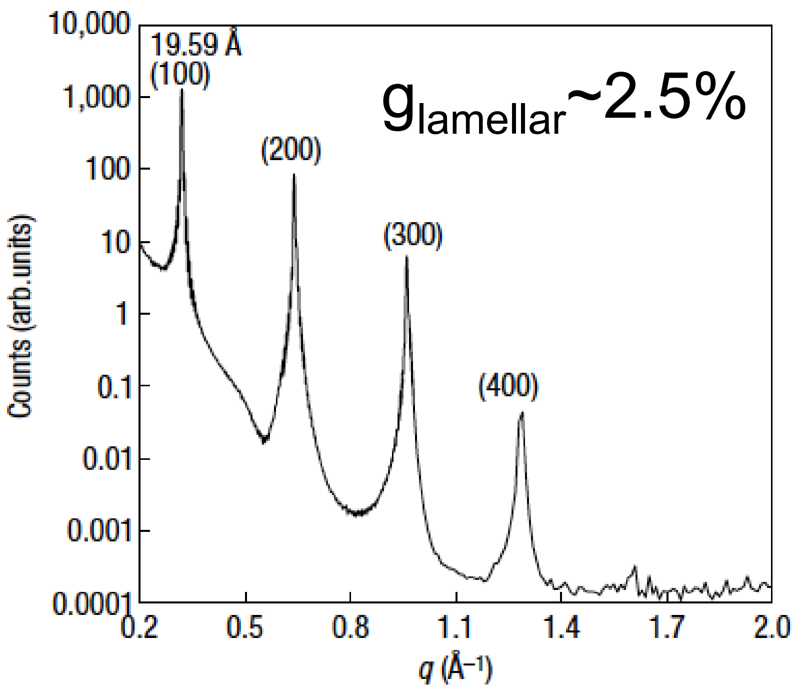


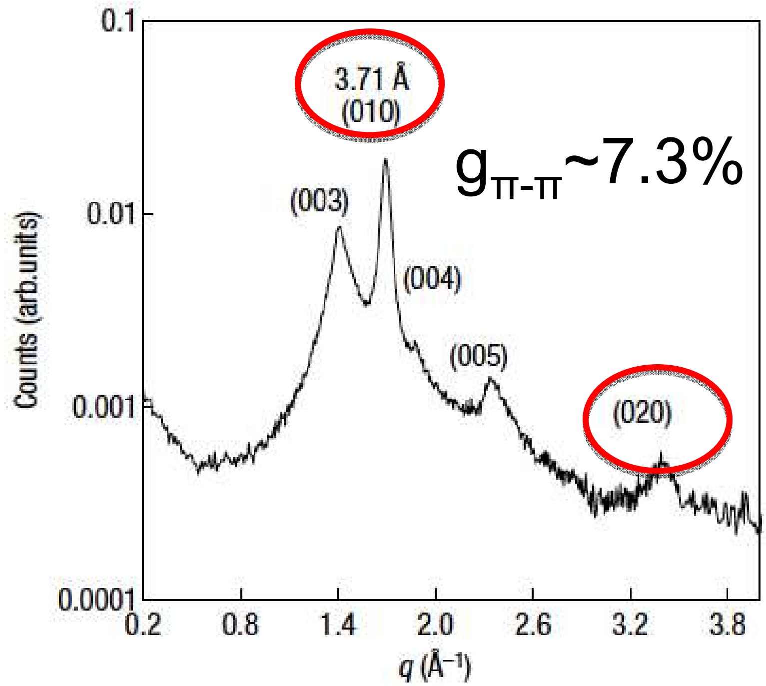


Chabinyc (JACS, 2007), Wang (Adv. Mat., 2010)
Delongchamp (Adv. Mat., 2011)

PBTTT appears very ordered in the direction perpendicular to the substrate





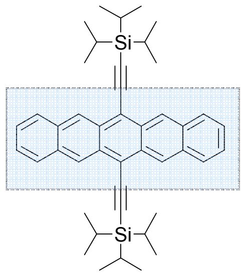


Delongchamp (Adv. Mat., 2011)

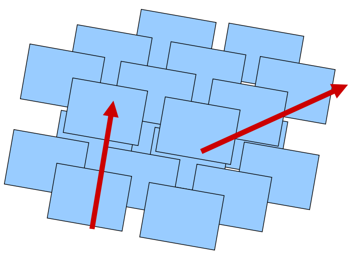
High performing materials vary in paracrystallinity

Small Molecule

TIPS-Pentacene



μ_{FET}≈0.5-5 cm^2/Vs



In plane
[100] direction

M:	47 ± 7 nm
g:	0.9 ± 0.6 %
e_{rms}:	≈ 0 %

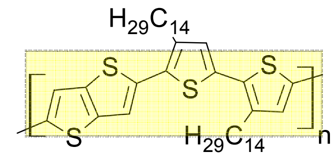
Out of plane
[001] direction

M:	55 ± 8 nm
g:	≈ 0%
e_{rms}:	≈ 0 %

Polymer

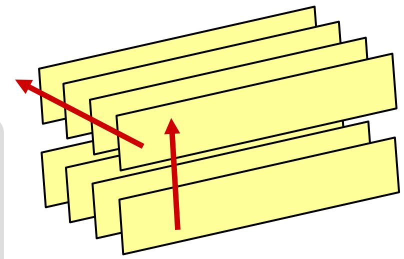
PBTTT

μ_{FET}≈0.1-1 cm^2/Vs



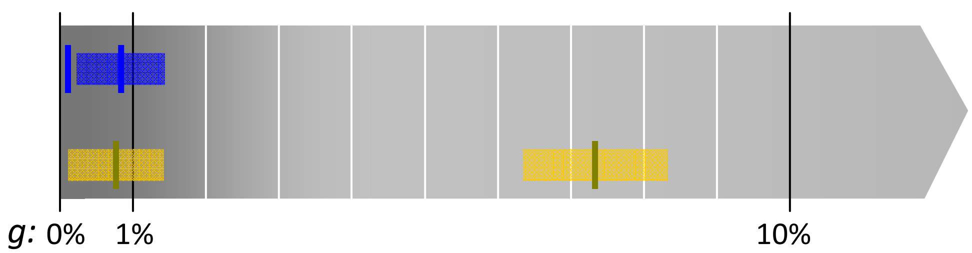
In plane
[010], π-stacking

M:	34 ± 7 nm
g:	2.6 ± 1.4 %
e_{rms}:	1.3 ± 0.6 %



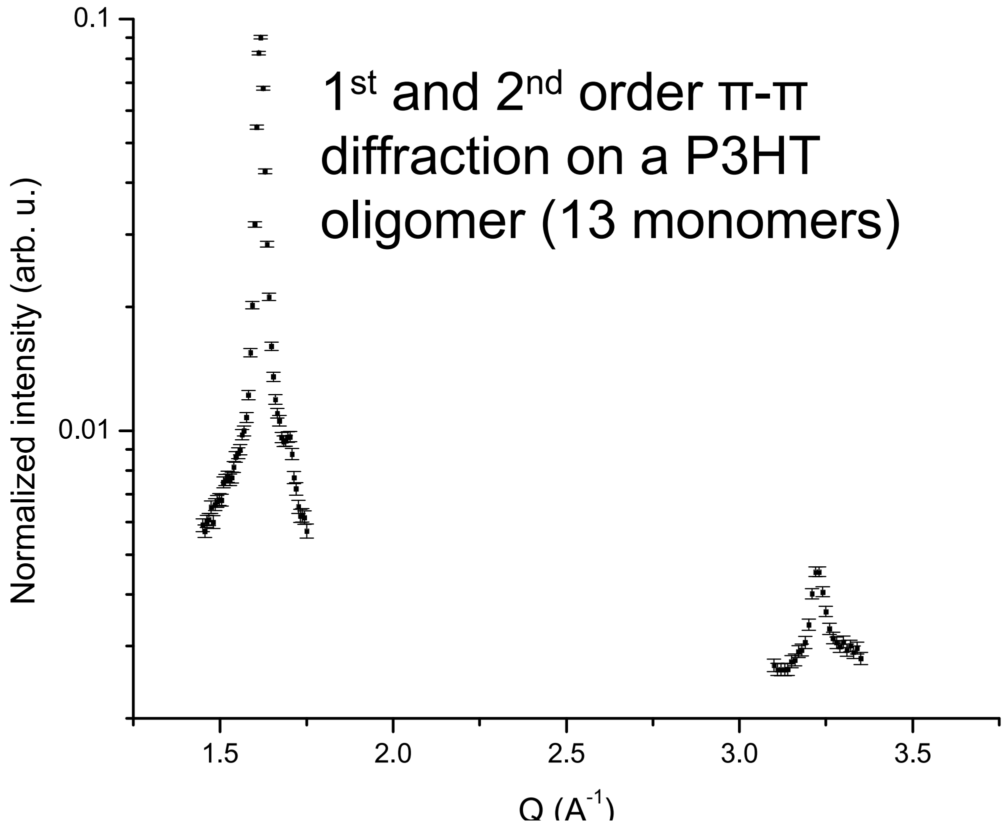
Out of plane
[100], lamellar-stacking

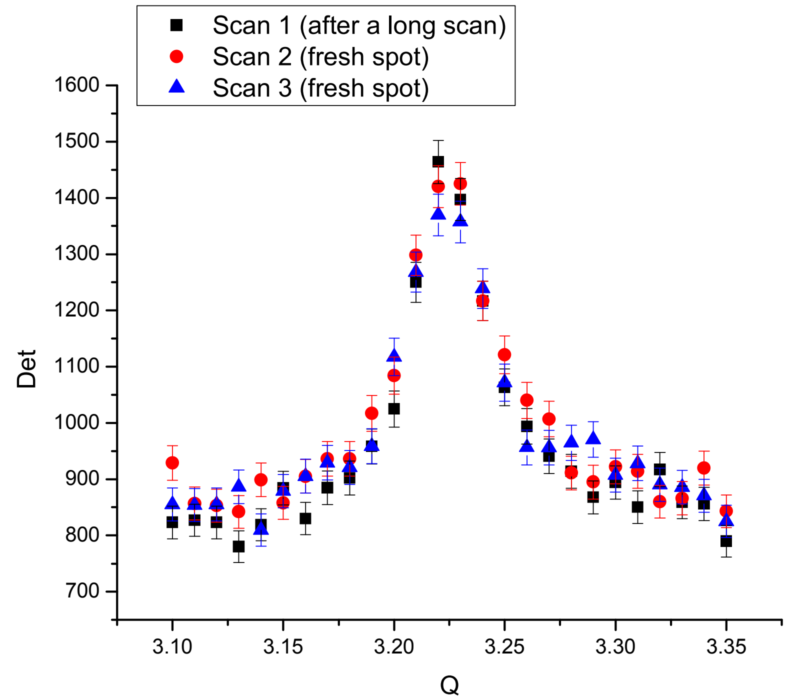
M:	n/a
g:	7.3 ± 0.7 %
e_{rms}:	0.9 ± 0.6 %



Noriega (in preparation)

Shortcuts are sometimes OK, sometimes not





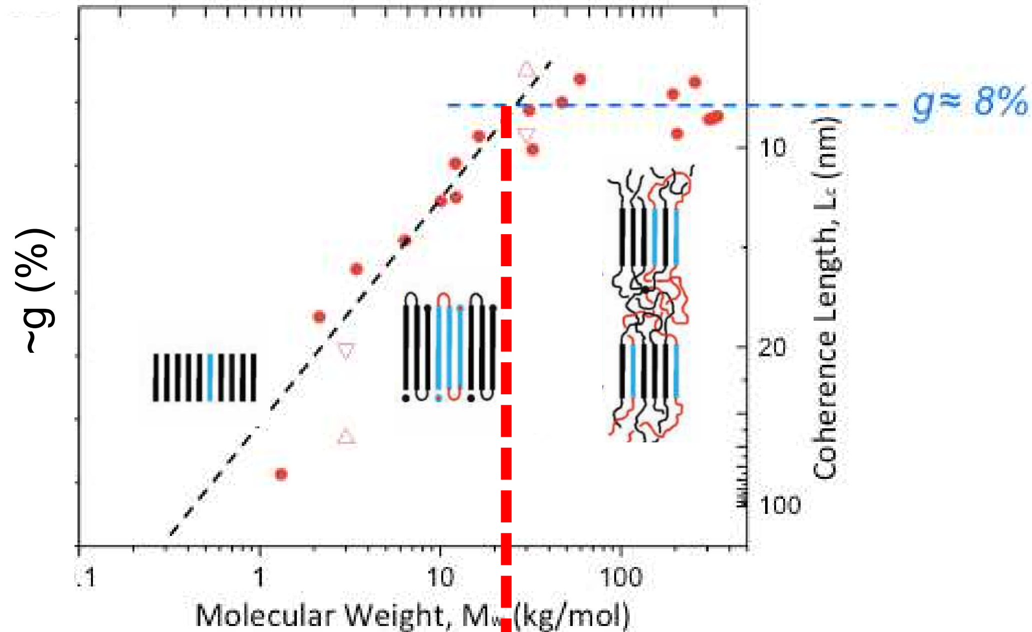
$$g = \sqrt{\frac{\Delta_q}{2\pi q_o}}$$

$g_{estimate}$~4.7%

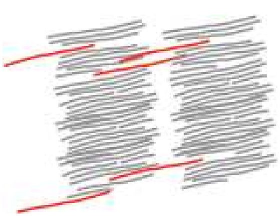
g_{full}~2.7±0.6%

M_{full}~18 nm

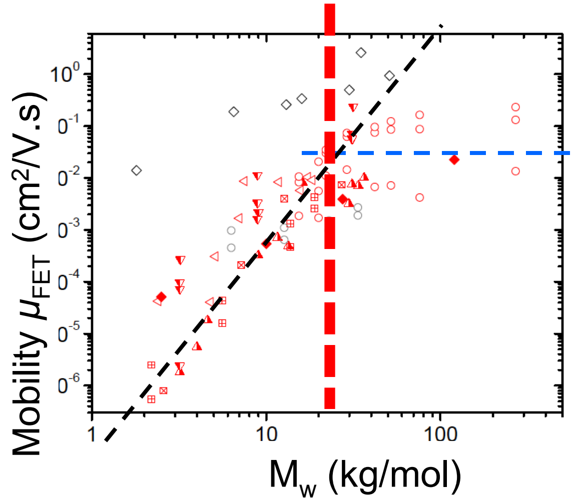
Molecular-weight dependence of disorder is related to transport in P3HT



limited by connectivity

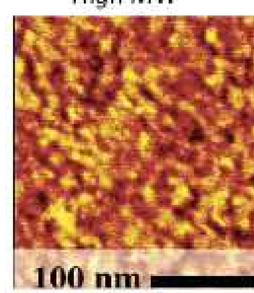


Low MW



limited by paracrystallinity

High MW



Noriega (in preparation)

Potential Sources of Disorder

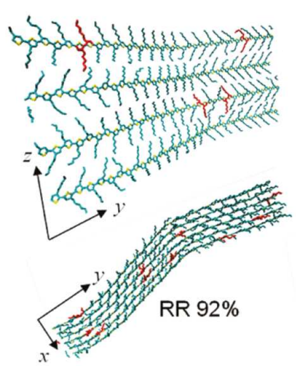
Extrinsic

<u>Impurities</u>

catalysts, degradation impurities, additives

<u>Polydispersity</u>

broad distribution of chain lengths



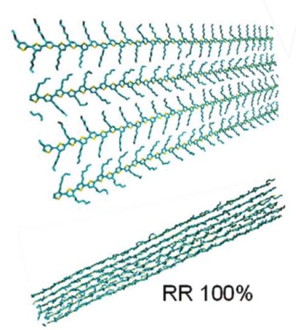
Regioregularity <u>defects</u>

Intrinsic

Side chain-induced

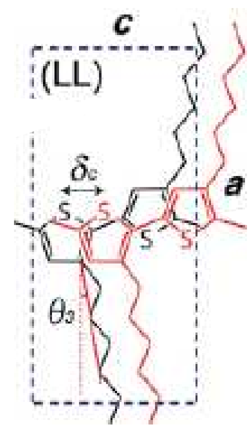
Alkyl chain (or side chain) <u>disorder</u>

Even for perfectly RR chains, side chains may cause perturbation in local packing



Chain entanglement dependent

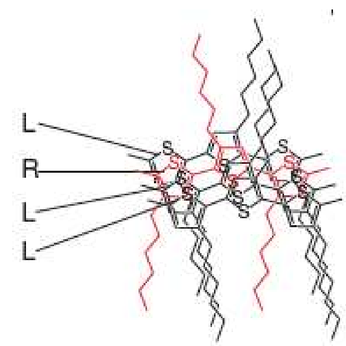
<u>Torsion from entanglement</u>



Poor <u>lateral stacking</u>

Can cause repulsion and vary π-stacking

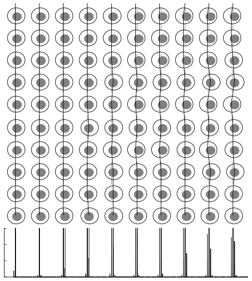
Stacking <u>Faults</u>



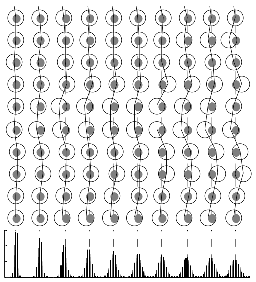
McMahon (J. Phys. Chem., 2011), Xie (PRB, 2011)

Paracrystalline disorder creates electronic traps

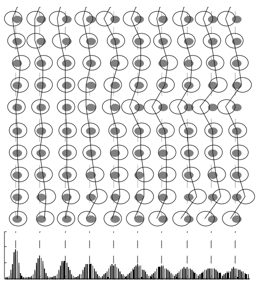
g=1%



g=5%

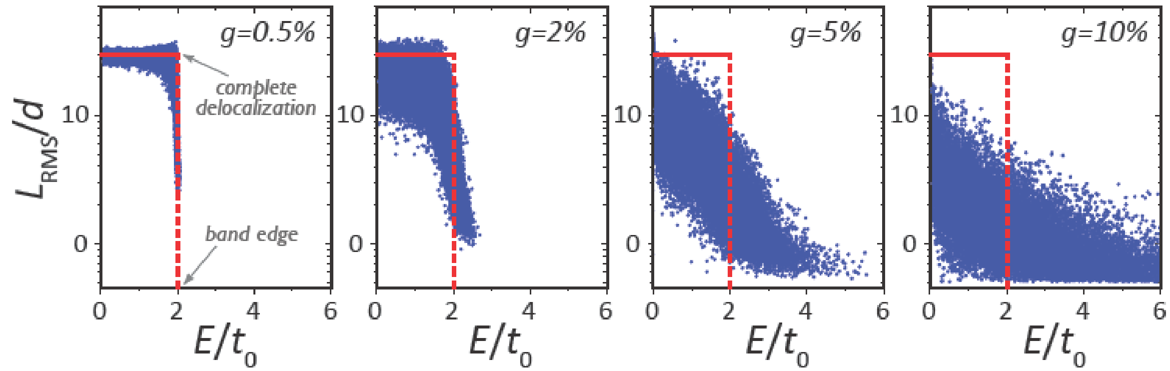


g=10%



Modeling inter-chain disorder in PBTTT pi-stacks:

Localization length vs. energy

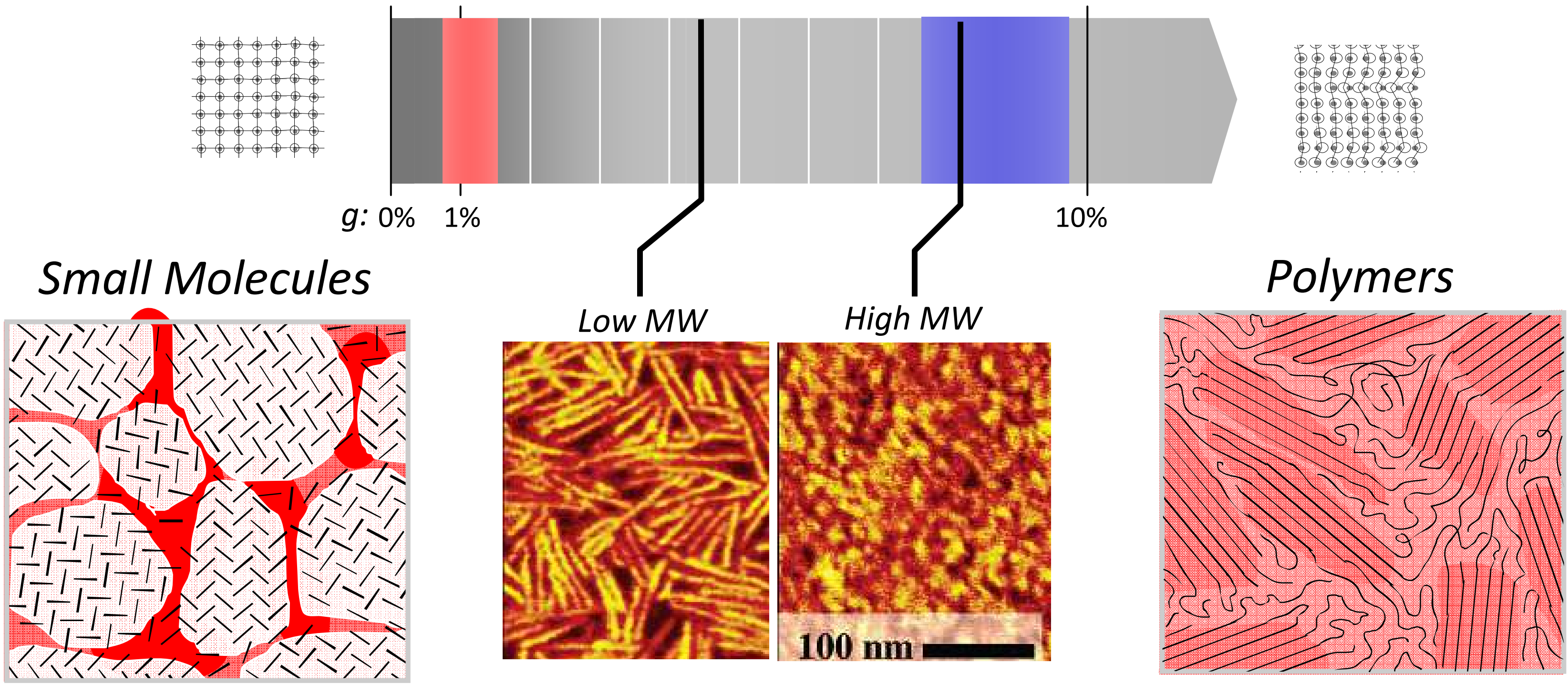


Tail states are highly localized, but for higher disorder, even states within the band become more localized

Large disorder causes localization (traps) and creates deep tail states.

Noriega (in preparation)

Macromolecules can span transport regimes



Grain boundaries dominate performance

Disorder within crystallites prevalent; complicates analysis

Conclusions – round 1

- Synchrotron-based XRD allows to quantify lattice disorder.

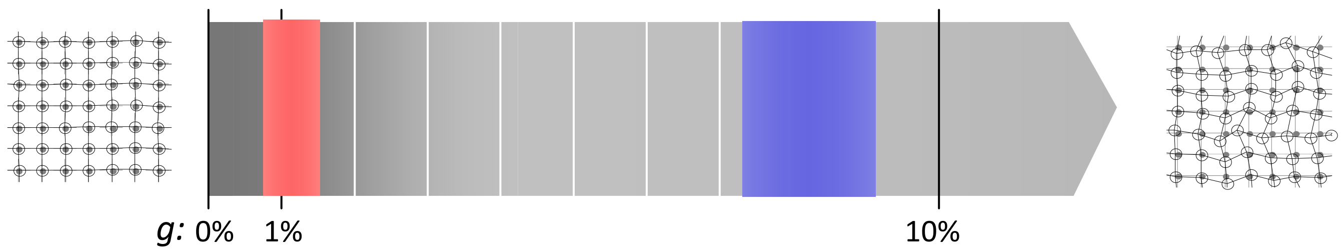
- Tradeoff between good statistics and beam damage.

- Every little thing counts toward making your life easier when it comes to data analysis: align the film, use the right scattering geometry, etc.

Conclusions – round 2

- Disorder at all length-scales affect transport in organic semiconductors.

- Lattice disorder can be described as a continuous scale, it can be quantified.



- Most (all until now) high Mw, **high mobility** polymers are disordered in the π-π stacking direction.

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Palo Alto Research Center
John Northrup

Imperial College
Martin Heeney
Iain McCulloch
Natalie Stingelin

Polyera Corp.
Antonio Facchetti

Nat. Inst. of Standards and Technology
Joe Kline

Northwestern Univ.
Tobin Marks