SPECULAR NR: DEPTH SENSITIVITY

\[ \rho_1, \rho_2, \rho_3 \]
SPECULAR NR: DEPTH SENSITIVITY

\[ \rho_1 \]

\[ \rho_2 \]

\[ \rho_3 \]
SPECULAR NR: DEPTH SENSITIVITY

\[ \rho_1 \]

\[ \rho_2 \]

\[ \rho_3 \]

\[ \vec{k}_i \rightarrow \vec{k}_f \]

\[ \theta \]

\[ \theta \]

\[ \lambda \]

\[ Z \]
For specular NR, neutron coherence length $L_c$ ($\sim 10-100 \, \mu m$) determines in-plane averaging. Consider domains $\rho_1$ and $\rho_2$: 

\[ \vec{k}_i \quad \text{and} \quad \vec{k}_f \]
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Incoherent addition of two reflectivities.
For specular NR, neutron coherence length $L_c \sim 10-100 \mu m$ determines in-plane averaging. Consider domains $\rho_1$ and $\rho_2$:

- The desired case for specular NR is achieved when the coherence length $L_c$ is greater than the spatial variations in the reflectivity $\rho$.

- The reflectivity characteristic of the average reflectivity $\rho$ is obtained by incoherent addition of two reflectivities.
Schrödinger wave equation

\[- \frac{\partial^2 \Psi(k_z, z)}{\partial z^2} + 4\pi \rho(z) \Psi(k_z, z) = k_z^2 \Psi(k_z, z)\]
SPECTRAL REFLECTOMETRY

Schrödinger wave equation

\[- \frac{\partial^2 \Psi(k_z,z)}{\partial z^2} + 4\pi \rho(z) \Psi(k_z,z) = k_z^2 \Psi(k_z,z)\]

reflection amplitude

\[r(Q) = \frac{4\pi}{iQ} \int_0^L \Psi(k_z,z) \rho(z) e^{ikz} dz\]
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Measure:

\[R(Q_z) = |r(Q_z)|^2\]
SPECULAR REFLECTOMETRY

Schrödinger wave equation

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measure: \( R(Q_z) = |r(Q_z)|^2 \)

determine: \( \rho(z) \)
Schrödinger wave equation:
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Measure:
\[R(Q_z) = |r(Q_z)|^2\]

Determine:
\[\rho(z)\]

Interpret:
\[\rho = \sum_i N_i b_i\]
SPECULAR REFLECTOMETRY

Schrödinger wave equation

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determine: \(\rho(z)\)

interpret: \(\rho = \sum_i N_i b_i\)
ORGANIC PHOTOVOLTAICS

Michael Mackay, Jon Kiel, Brett Guralnick, U. Delaware

$\text{CH}_2(\text{CH}_2)_4\text{CH}_3$

$\text{CH}_2$-$\text{CH}_2$-$\text{CH}_3$

P3HT

(poly 3-hexylthiophene)

PCBM

([6,6]-phenyl-C61-butyric acid methyl ester)

cconducting polymer

acceptor dopant

distribution is important!
P3HT:PCBM

monolayer

100 nm to absorb all the light, but excitons recombine in < 10 nm
P3HT:PCBM

**monolayer**
- 100 nm to absorb all the light, but excitons recombine in < 10 nm

**bilayer**
- PCBM interface inhibits recombination, but there’s only one
P3HT:PCBM

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**Comb**
- Ideal, but difficult to engineer
P3HT:PCBM

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- PCBM interface inhibits recombination, but there's only one

**Comb**
- Ideal, but difficult to engineer

**Bulk Heterojunction**
- Best geometry so far - how does the PCBM distributed?

**Fig. 1** Defocused transmission electron microscopy cross-sectional images of polymer samples prepared by ultramicrotomy shows little difference for a variety of materials. A 1 : 1 by weight PCBM : P3HT blend (a) and pure polystyrene (b) both have lighter and darker regions demonstrating the difficulty in interpreting such images.
NEUTRON CONTRAST


PCBM: $\rho = 3.6 \times 10^{-6}$ Å$^{-2}$
P3HT: $\rho = 0.7 \times 10^{-6}$ Å$^{-2}$
CONTRAST VARIATION VIA BACKING MEDIUM

NCNR wet cell with “mock” bulk heterojunction:
~ 100 nm 1:1 P3HT:PCBM spin coated on Si
$R$ vs. $Q_z$

- Air in reservoir
- D2O in reservoir
INVERSION

reflectivities

air in reservoir

D2O in reservoir

reflection amplitude
INVERSION

reflectivities

air in reservoir

D2O in reservoir

reflection amplitude

depth profile

\[ R / R_{Si} \]

\[ Q_z (\text{nm}^{-1}) \]

\[ \rho (10^{-4} \text{ nm}^{-1}) \]

\[ z (\text{nm}) \]
SIMULTANEOUS FITTING

air in reservoir

\[ \frac{R}{R_{\text{Si}}} \]

\[ Q_z \text{ (nm}^{-1}) \]

D2O in reservoir

\[ \frac{R}{R_{\text{Si}}} \]
SIMULTANEOUS FITTING

air in reservoir

D2O in reservoir

\( \frac{R}{R_{\text{Si}}} \)

\( Q_z \) (nm\(^{-1}\))
SIMULTANEOUS FITTING

air in reservoir

D2O in reservoir

$\rho (10^{-4} \text{ nm}^{-4})$

$z (\text{nm})$

free-form model
\( \rho (10^{-4} \text{ nm}^{-4}) \)

\( z ('n\text{m}) \)
INTERPRETATION

PCBM: $\rho = 3.6 \times 10^{-6} \text{ Å}^{-2}$

P3HT: $\rho = 0.7 \times 10^{-6} \text{ Å}^{-2}$
**INTERPRETATION**

PCBM: \( \rho = 3.6 \times 10^{-6} \text{ Å}^{-2} \)

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INTERPRETATION

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excess PCBM at the interfaces
WHAT IF IT LEAKED?

A change could conceivably involve diffusion of water into any voids that might have been produced in the PV film during the spin-coating deposition process as solvent evaporated. Upon subsequent exposure to the D$_2$O aqueous reservoir, which is the reference backing medium in one of the two composite systems required for the PSNR method, some amount of D$_2$O might have diffused into such voids. Although a number of successive NR scans were performed to check for this possibility, the practical minimum time scale for repeating a complete scan was of the order of hours. Thus, if diffusion occurred in a sufficiently short enough time period, it could go unnoticed.

To investigate the possibility that water had diffused at a faster rate, another simultaneous fit of the two composite system reflectivity data sets for the PV film has been performed here (using the same GARe program used originally), but with different constraints imposed. Specifically, this condition was that a given constant fraction of a presumed void volume in the film contain air in one composite film system and D$_2$O in the other.

Fig. 9. Schematic illustration of the terpolymer–phospholipid membrane mimic supported on a polyelectrolyte cushion adsorbed on the substrate. Fig. 1 of Perez-Salas et al. [44].

Fig. 8. Composite system reflectivity data (symbols), identical to that in previous figures, but with independent rather than simultaneous fits (lines) of the two composite system NR data sets, each with a different backing medium. The two resultant and slightly different SLD depth profiles for the putatively common PV film (shown in the inset) might be attributed to diffusion of water into PV film voids when placed adjacent to and in contact with the water reservoir which served as the second backing medium. Although, once again, the principal result regarding the enhanced concentration of PCBM at the interfaces remains unchanged, the lower chi-squared values obtained for the independent fitting, compared to those for the simultaneous constrained procedure, indicate that the diffusion of water into the film may indeed occur at some level. See text for further discussion.
A POLARIZED BEAM CAN DO A LOT OF THINGS...

for magnetization parallel to neutron spin:

\[ \rho^\pm = \rho_N \pm \rho_M \]

**spin-dependent sld**

\[ \rho_N = \sum_i N_i b_i \]

**nuclear component**

\[ \rho_M = C M \]

**magnetic component**

- **M**: magnetization
- **C**: 2.853 x 10^-9 kA^-1 m Å^-2

*buried magnetic reference layer for contrast variation*
SUMMARY

• specular NR: $\rho(z)$ from $|r(Qz)|^2$ - not unique

• recover information with contrast variation
  - variable reservoirs, magnetic reference layers...
  - inversion OR simultaneous model fitting
    - DiRefl, NCNR inversion software
    - ReflID, NCNR simultaneous fitting software

• phase sensitive NR of P3HT:PCBM bulk heterojunction
  - increased PCBM at the interfaces - not ideal...

• publications, software, online calculators, contact info
FOR EXAMPLE...