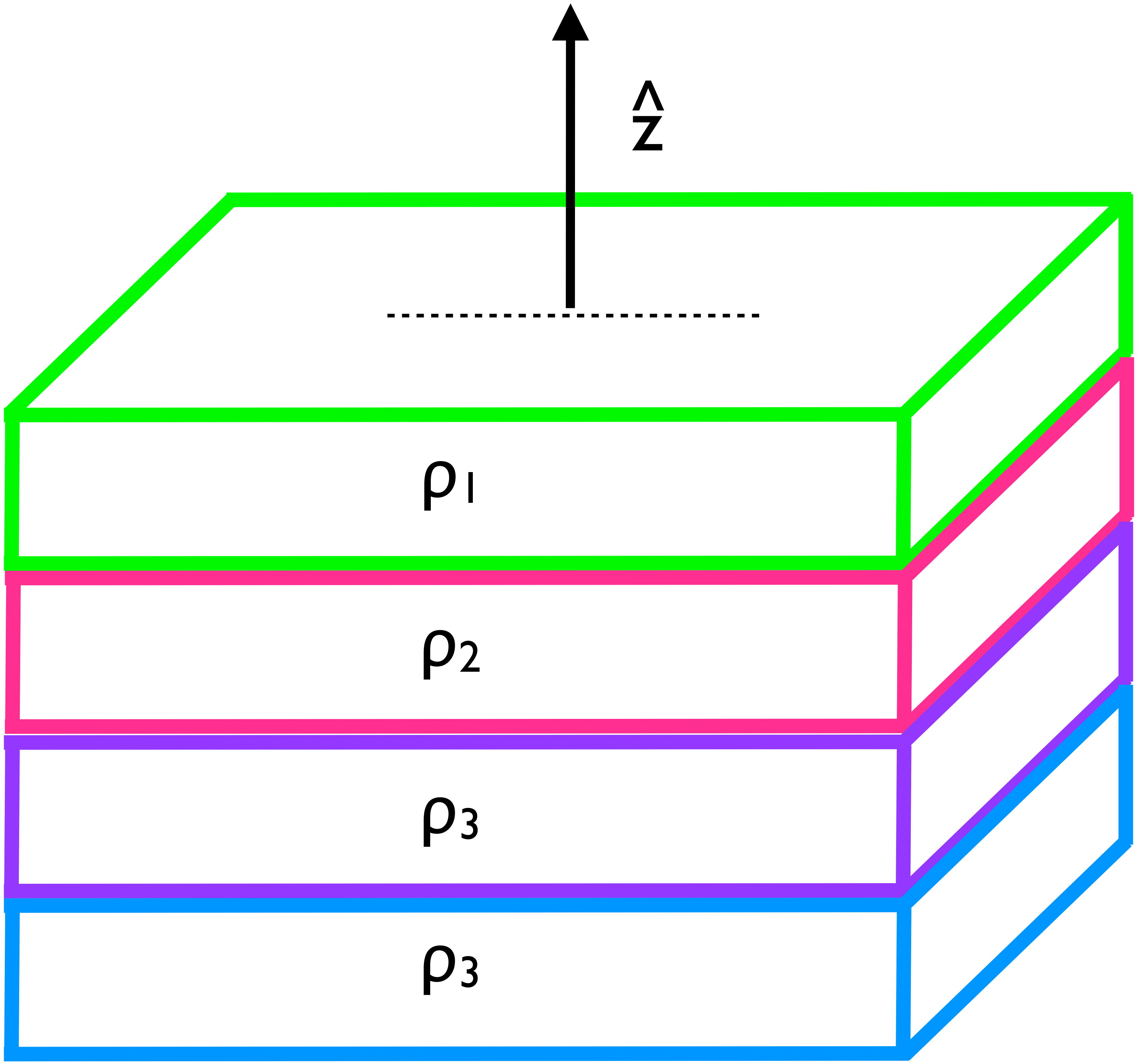
ORGANIC PHOTOVOLTAICS AND PHASE SENSITIVE NEUTRON REFLECTOMETRY

Jon Kiel, Brett Guralnick, and Michael Mackay

Brian Kirby, Brian Maranville, Frank Heinrich, Paul Kienzle, and Chuck Majkrzak

SPECULAR NR: DEPTH SENSITIVITY



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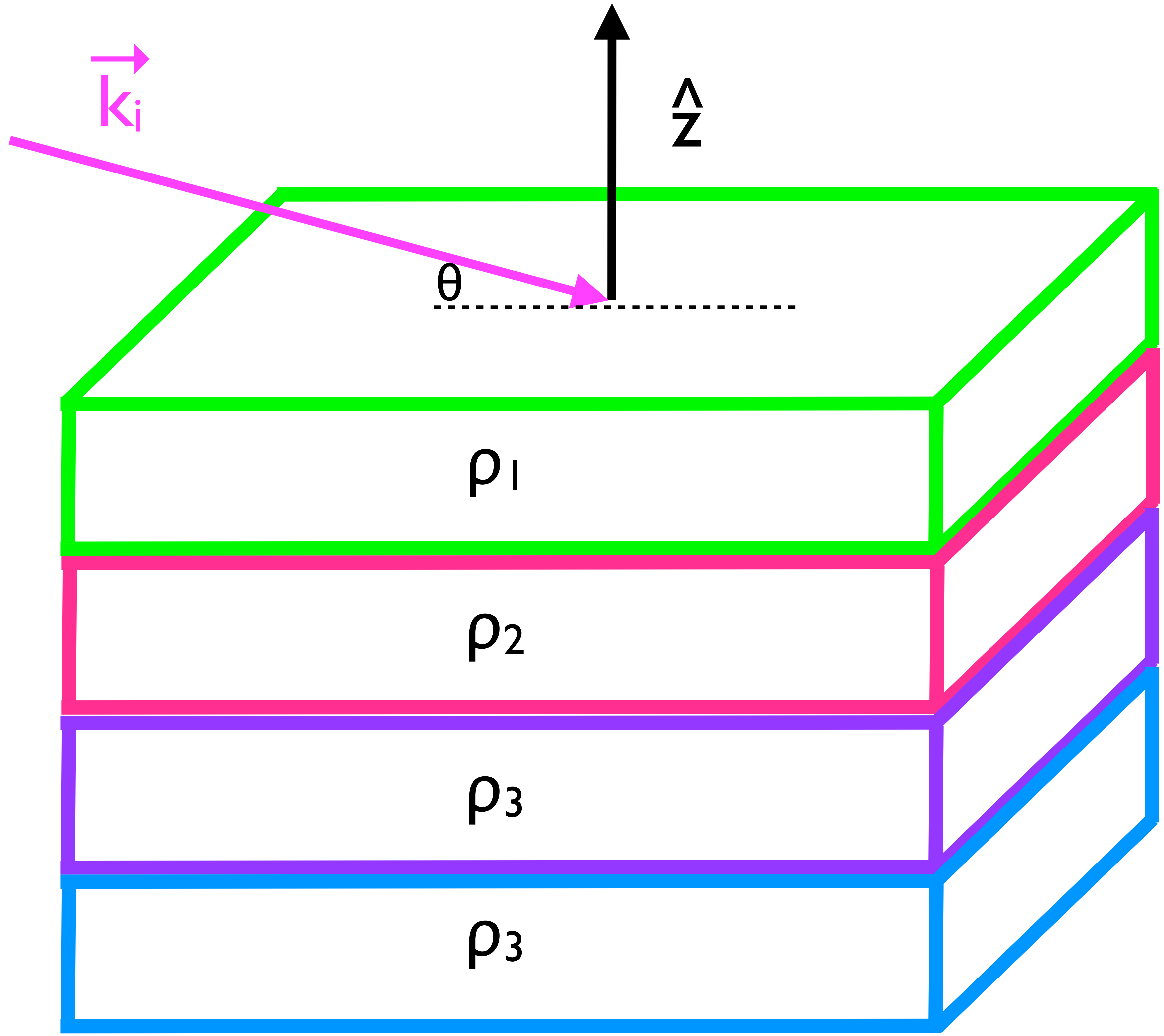

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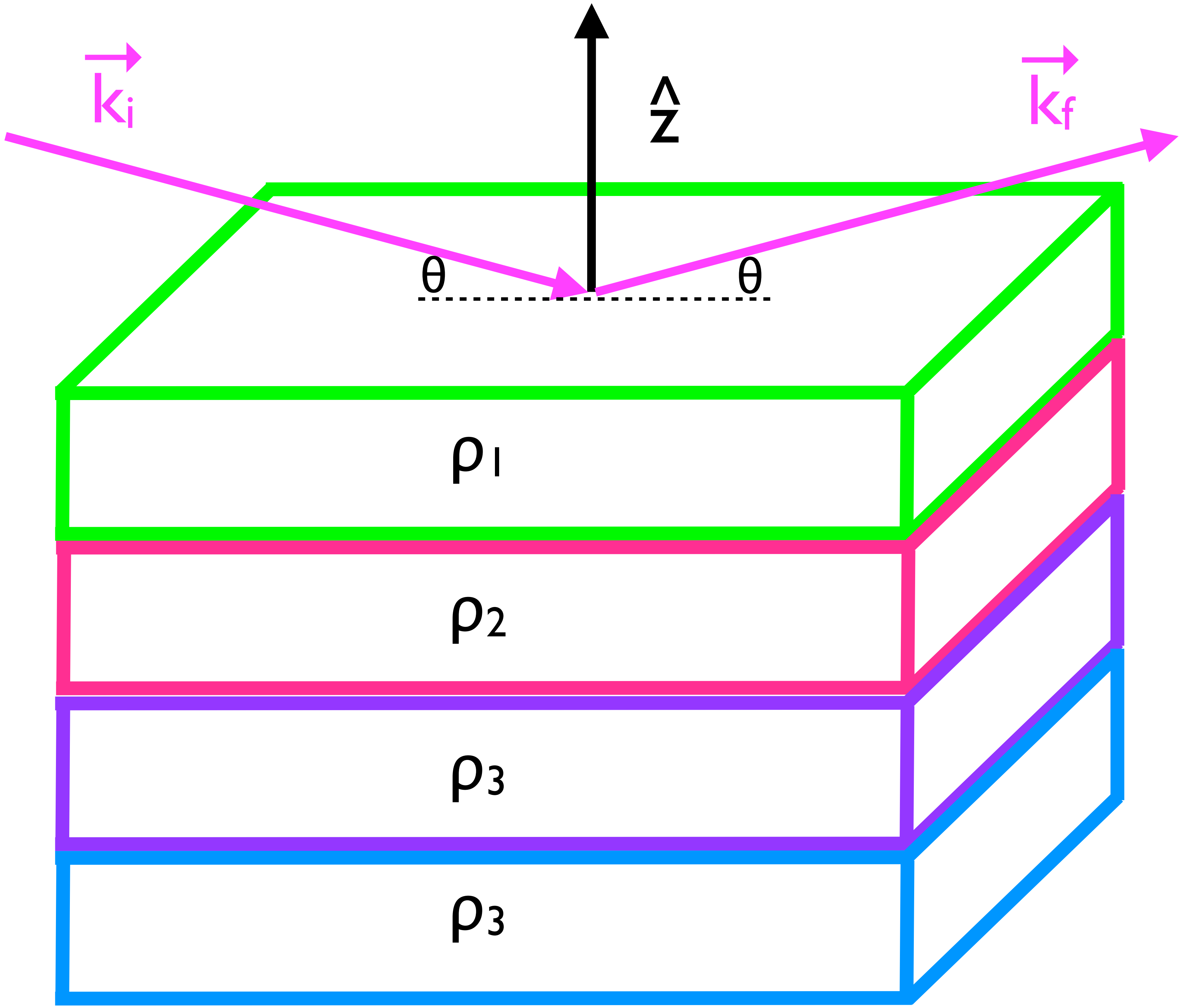
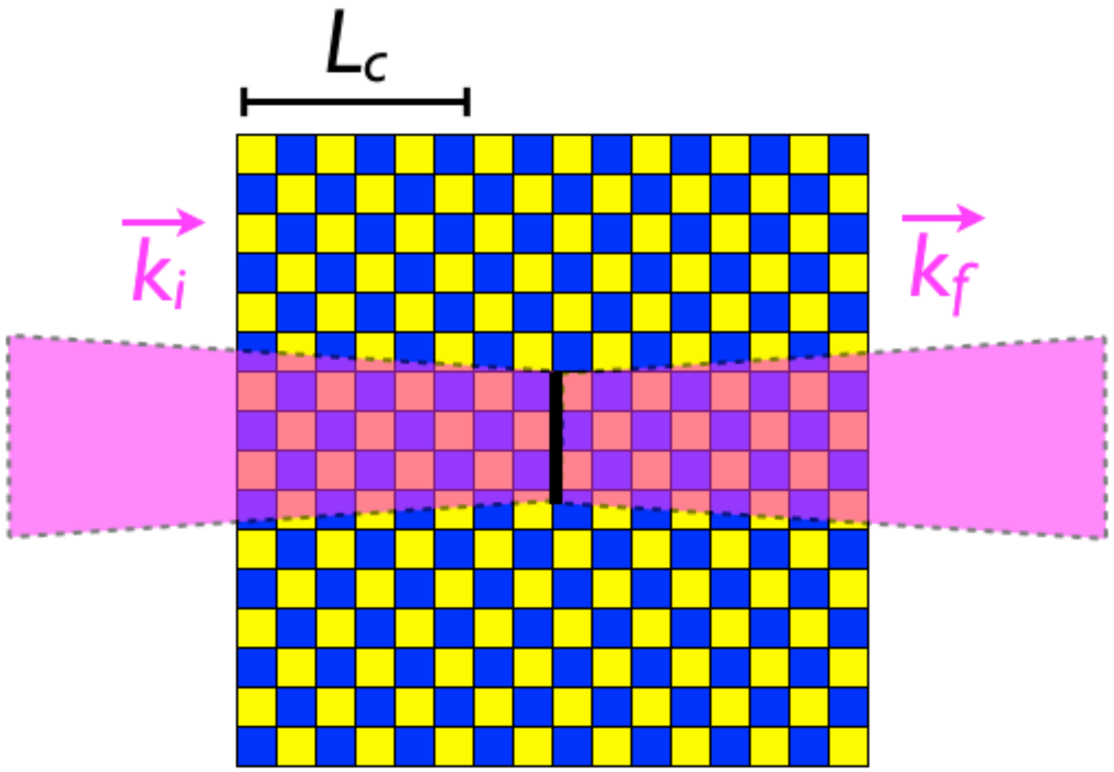


SPECULAR NR: PLANAR UNIFORMITY

For specular NR, neutron coherence length L_c (~ 10-100 μm) determines in-plane averaging. Consider domains ρ_1 and ρ_2:



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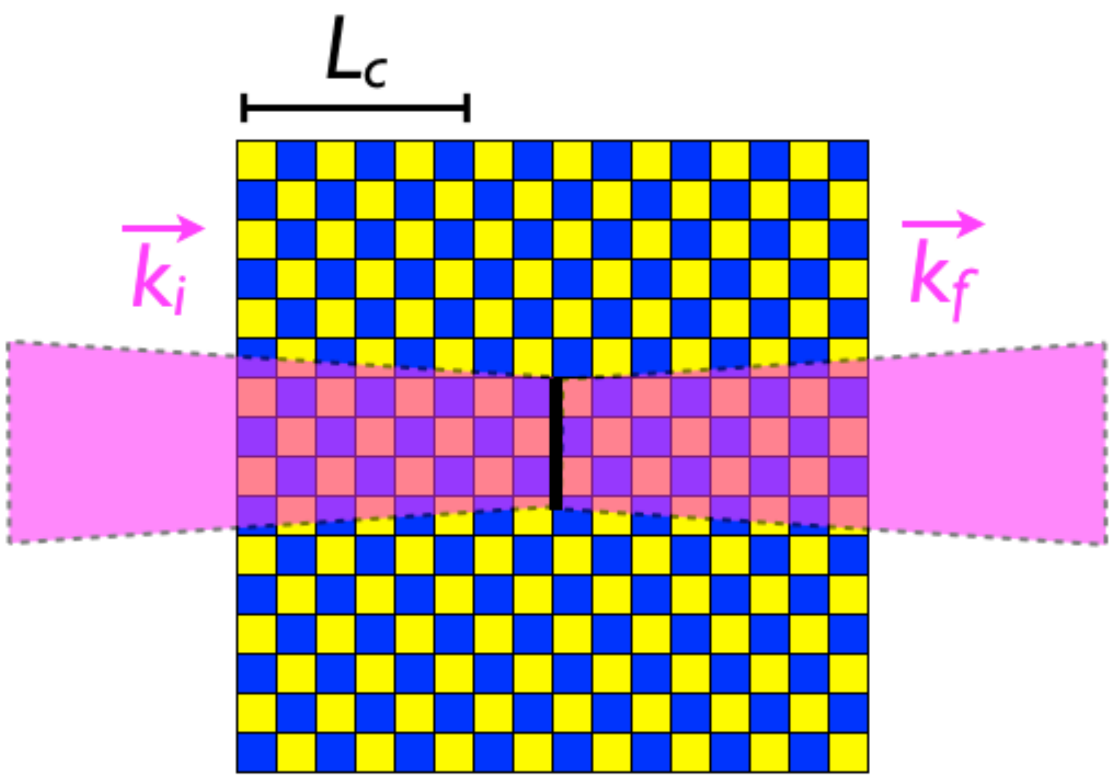
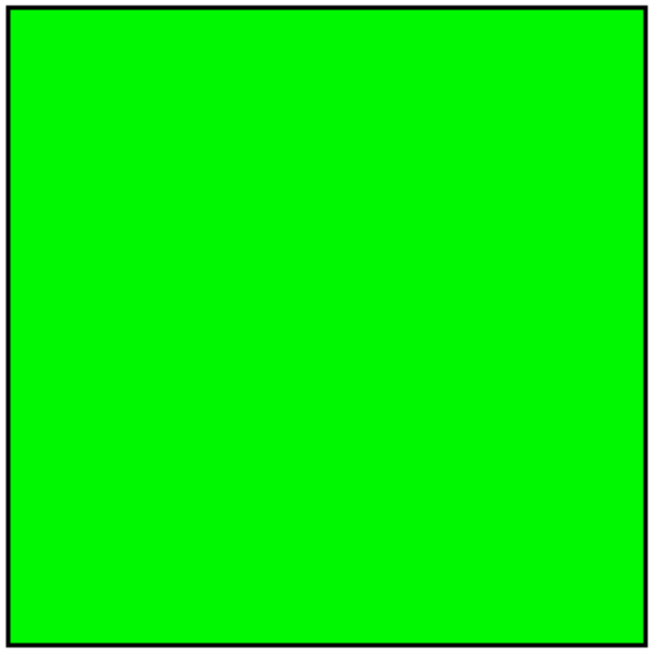


reflectivity charateristic of average ρ



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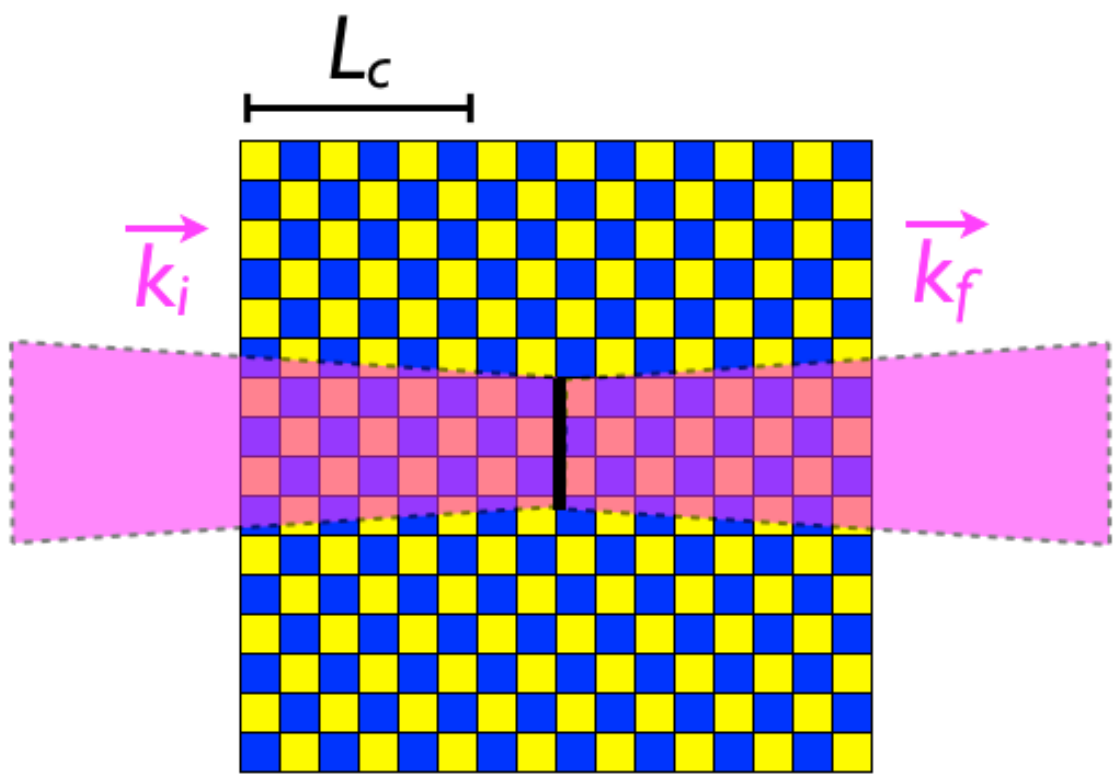

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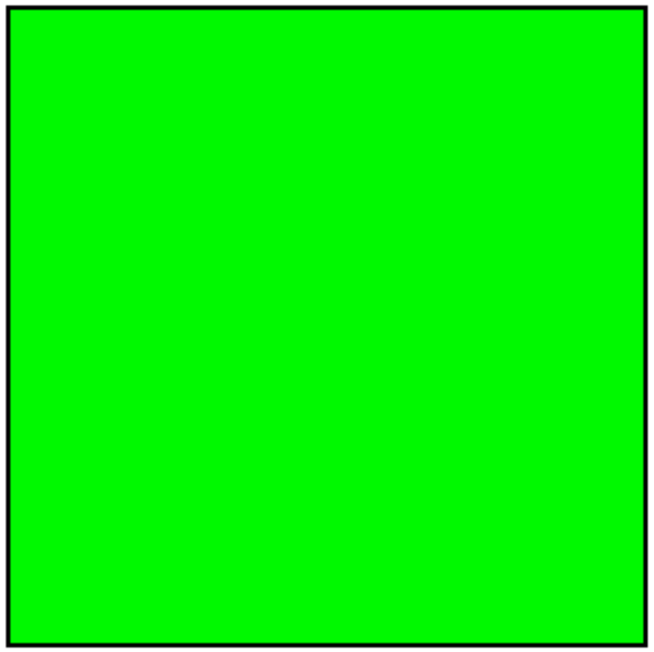

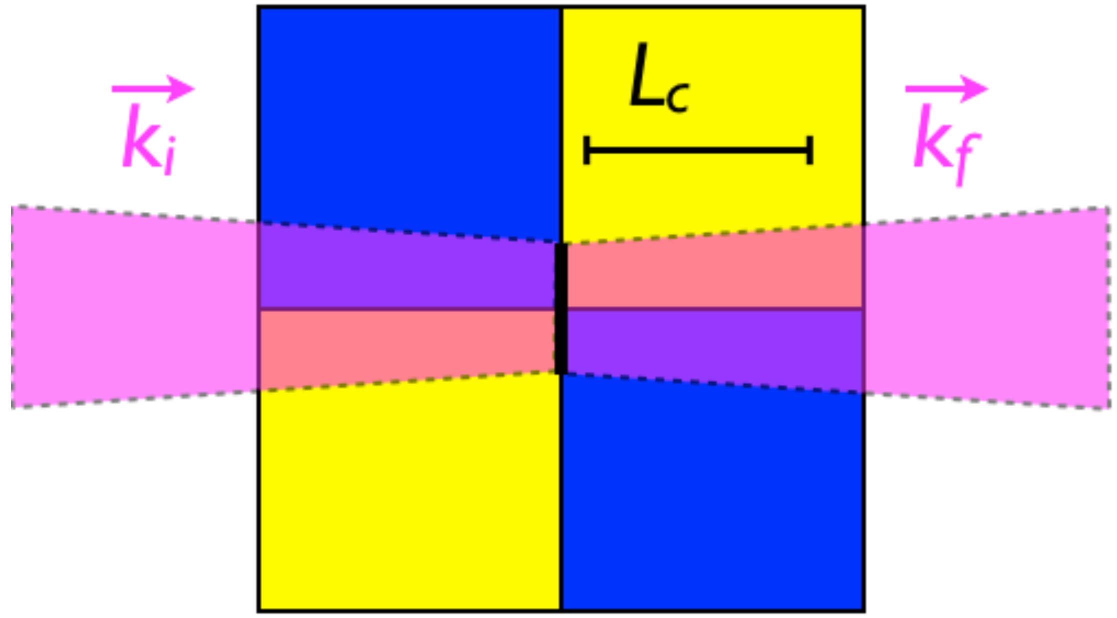

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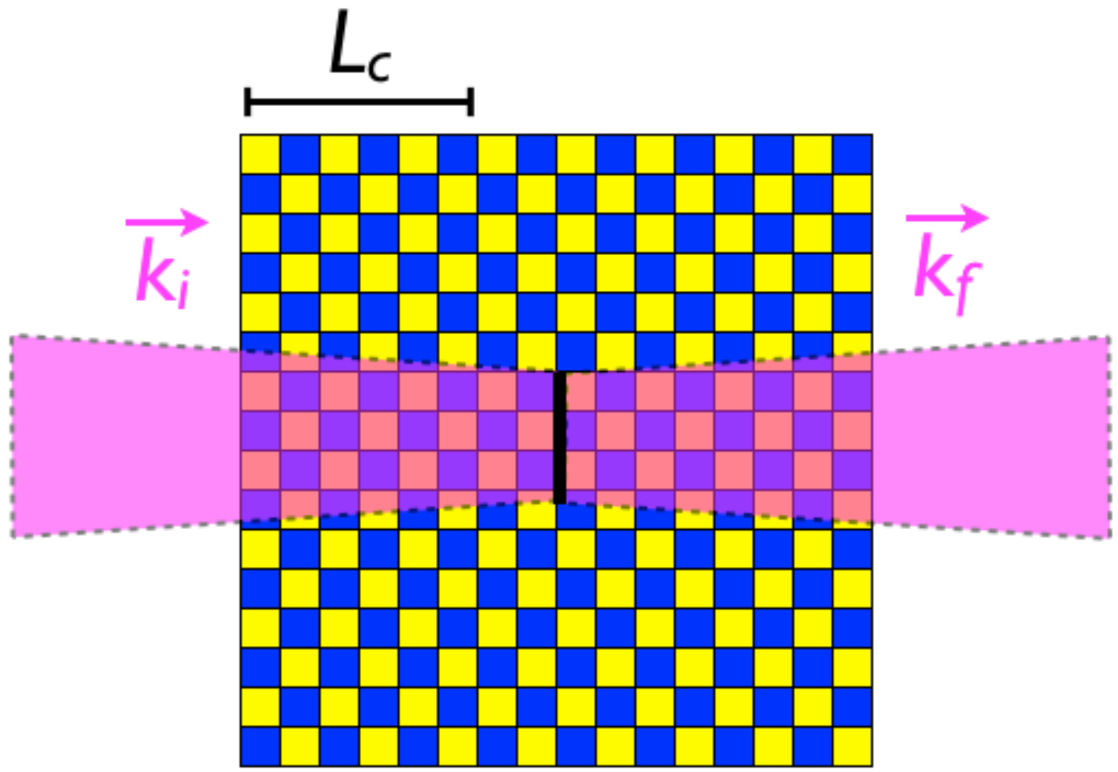

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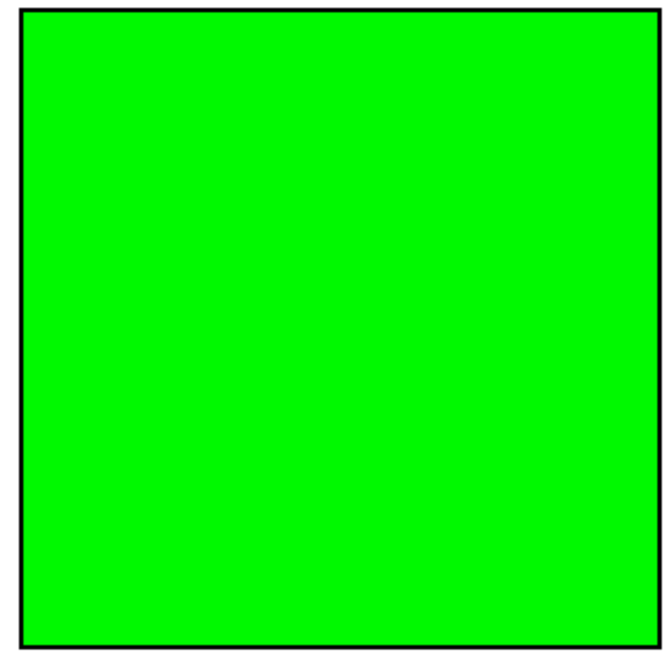
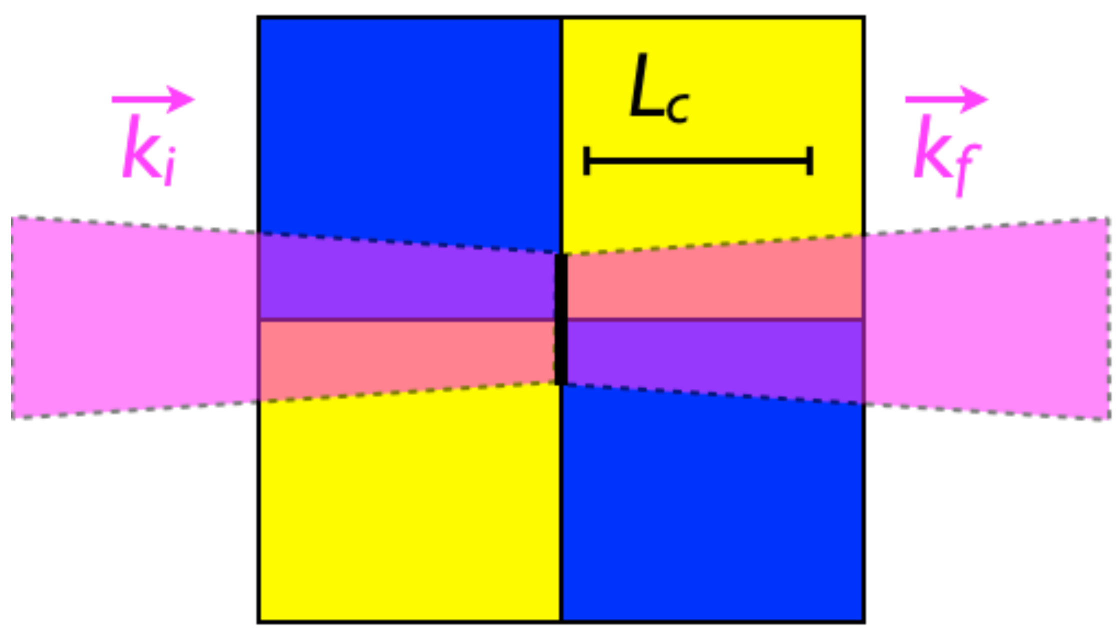
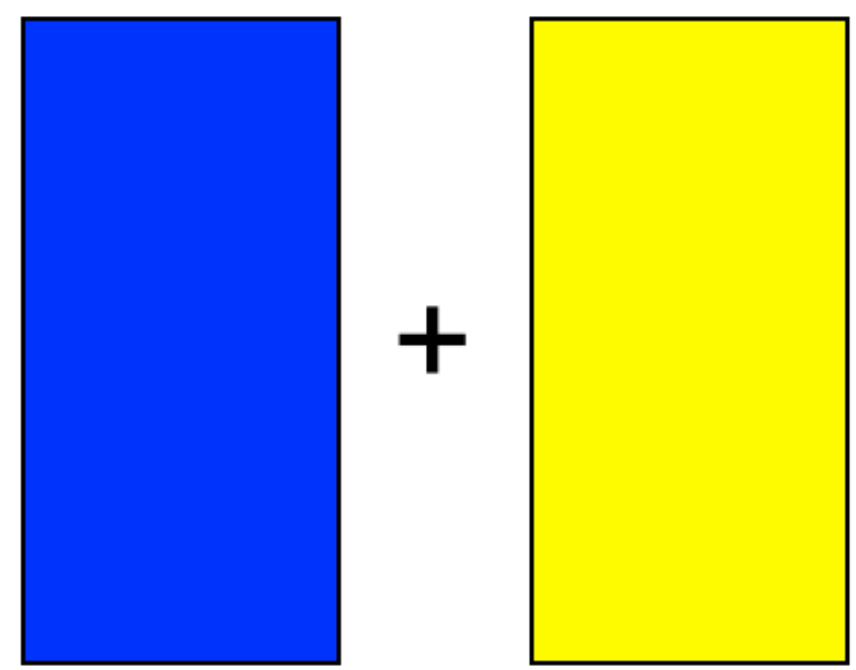




incoherent additon of two reflectivities



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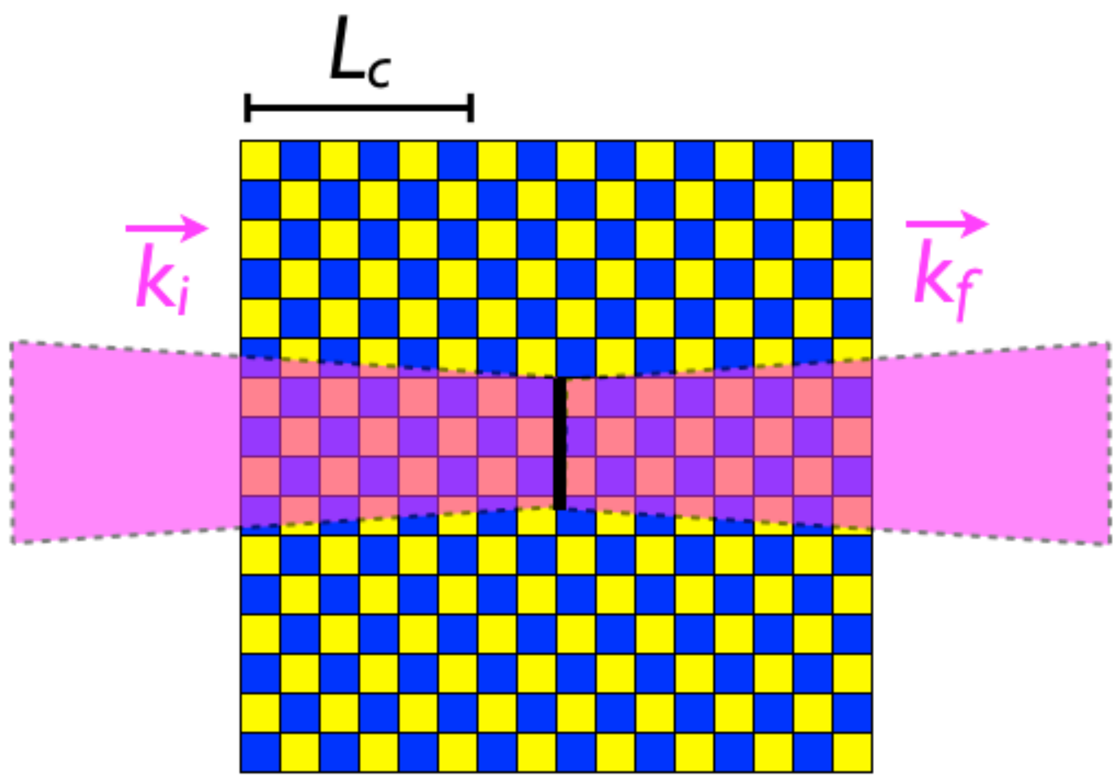

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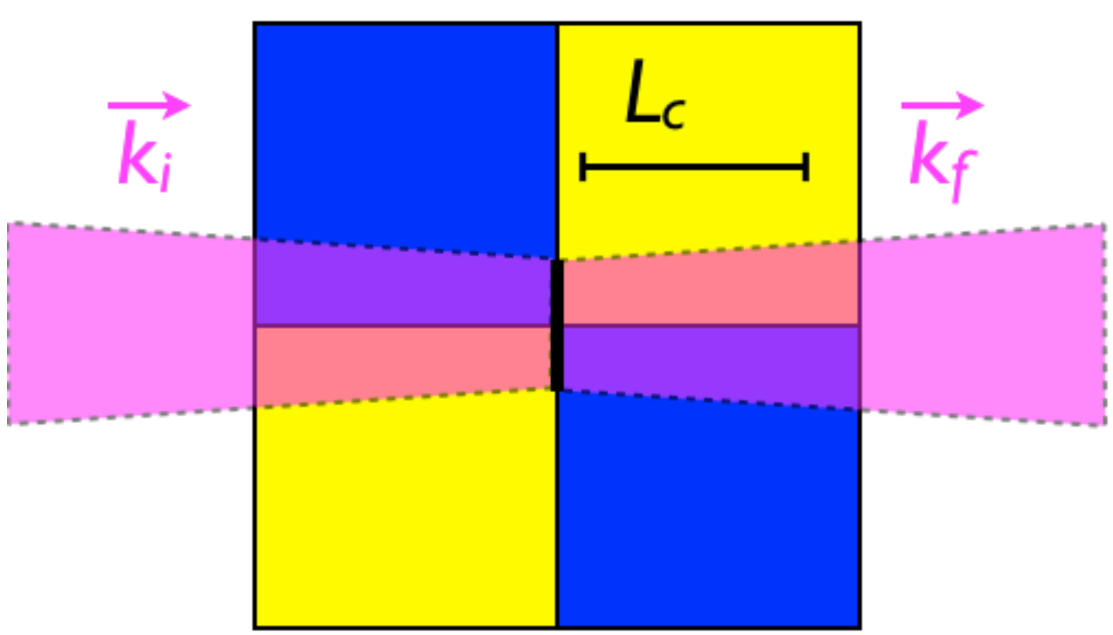

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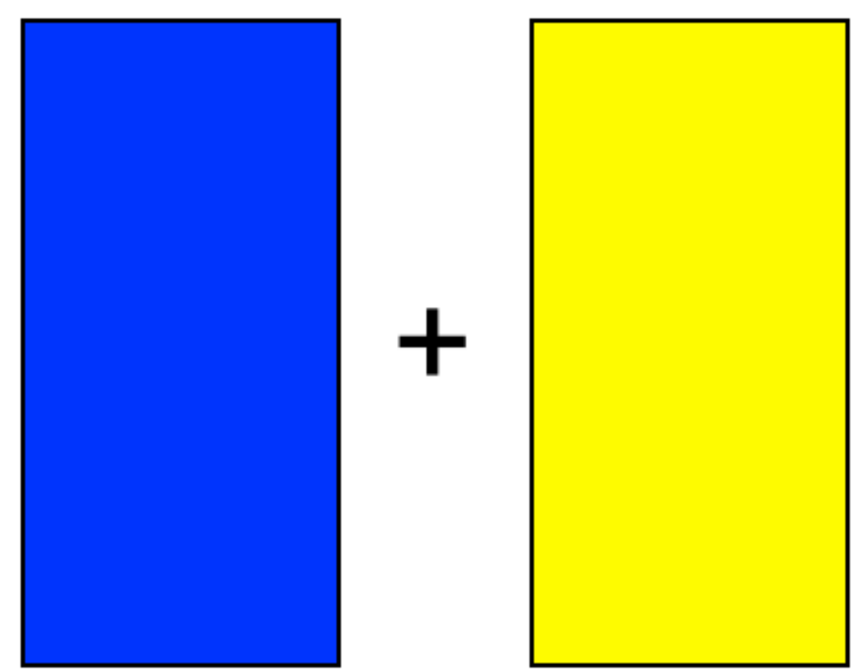
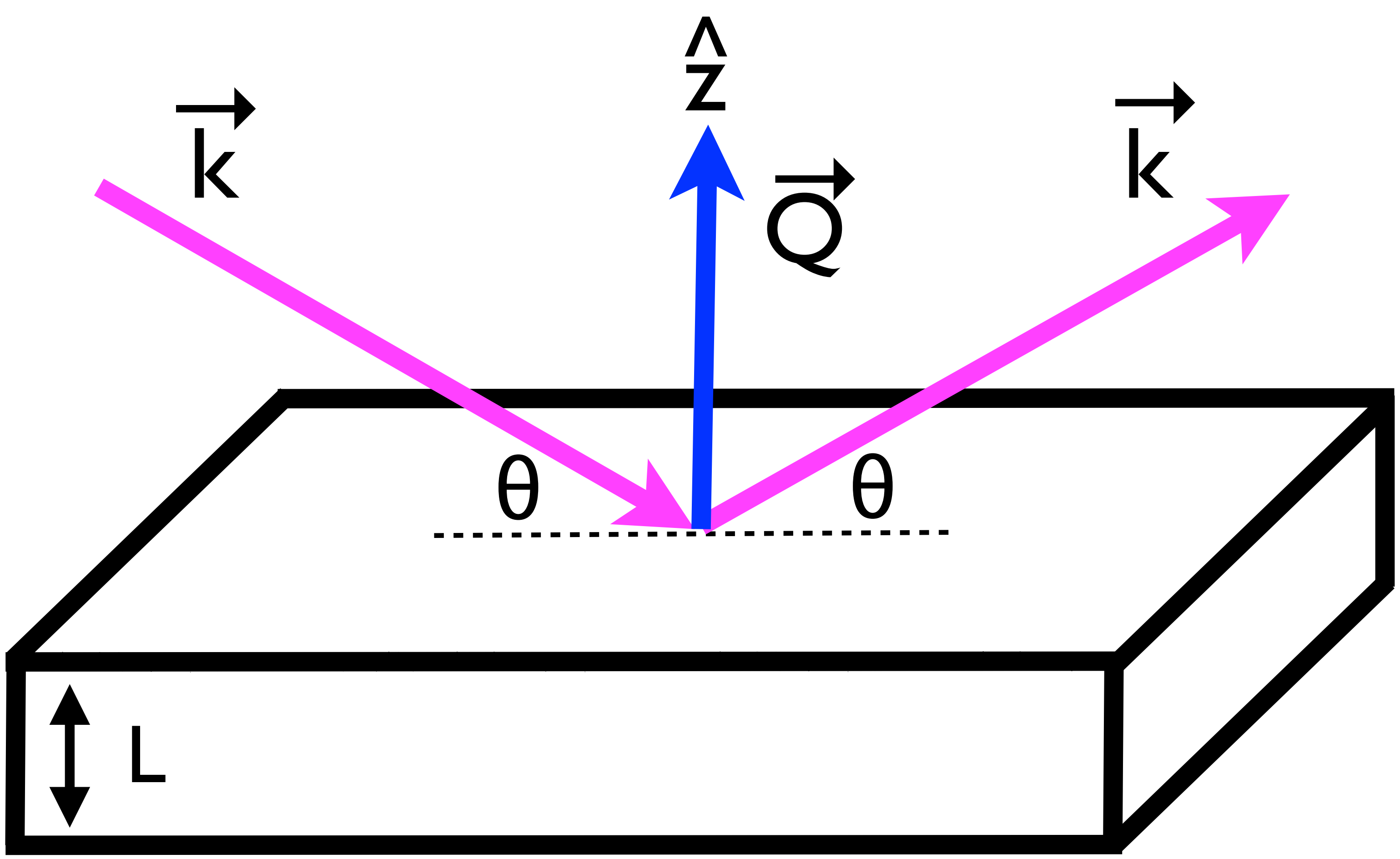


SPECULAR REFLECTOMETRY

Schrödinger wave equation

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



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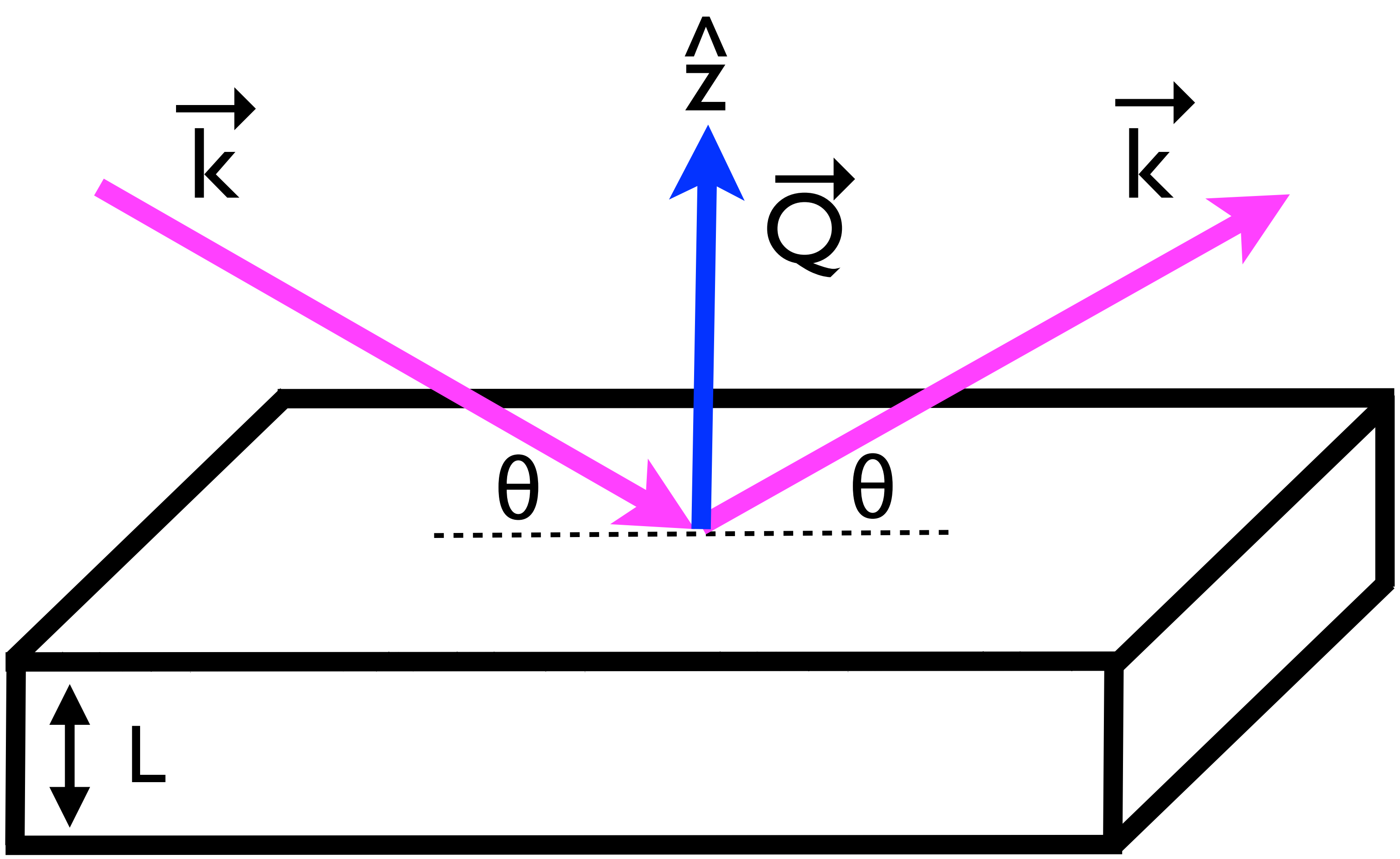
reflection amplitude

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



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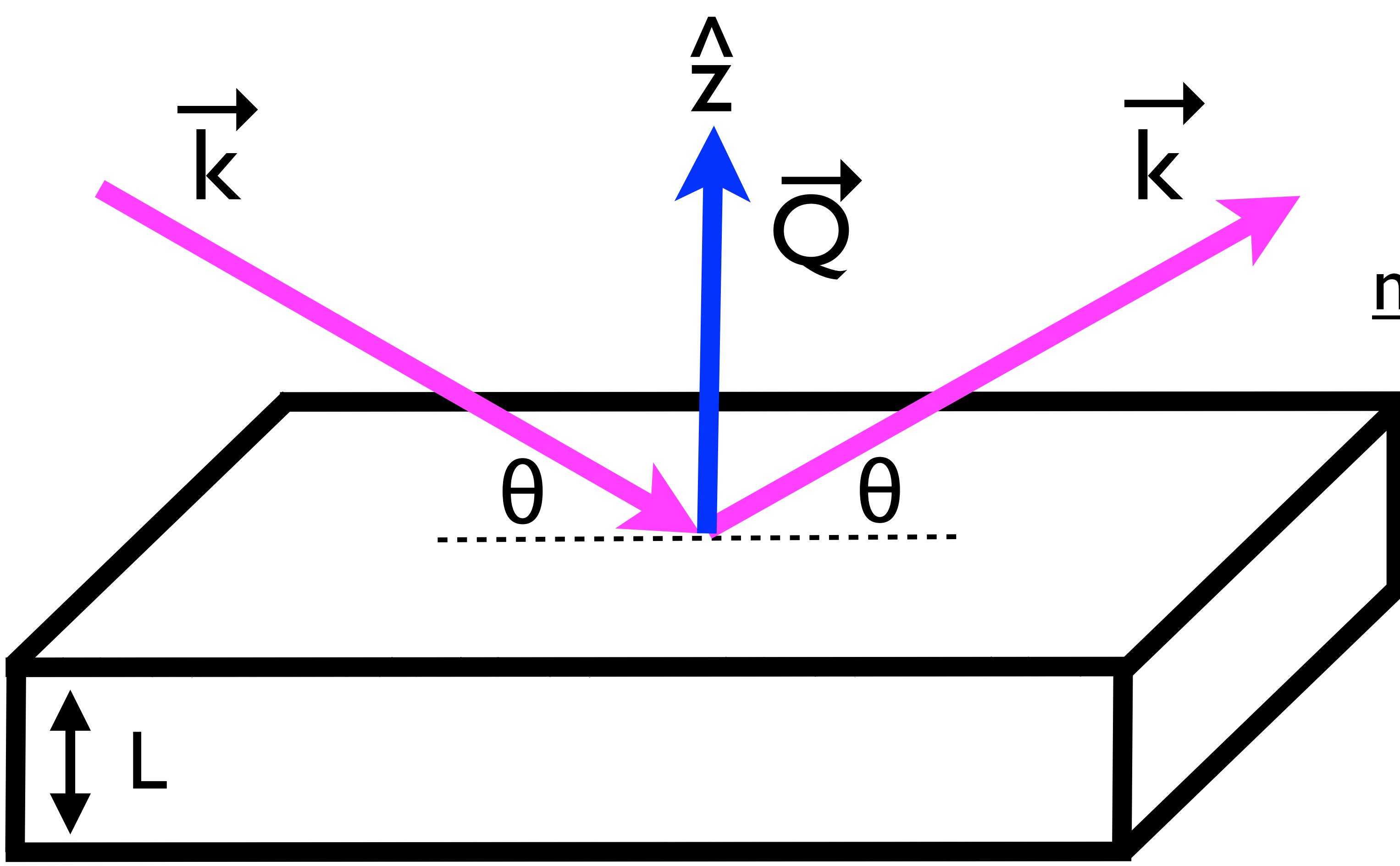

<u>measure</u>: $R(Q_z) = |r(Q_z)|^2$

SPECULAR REFLECTOMETRY

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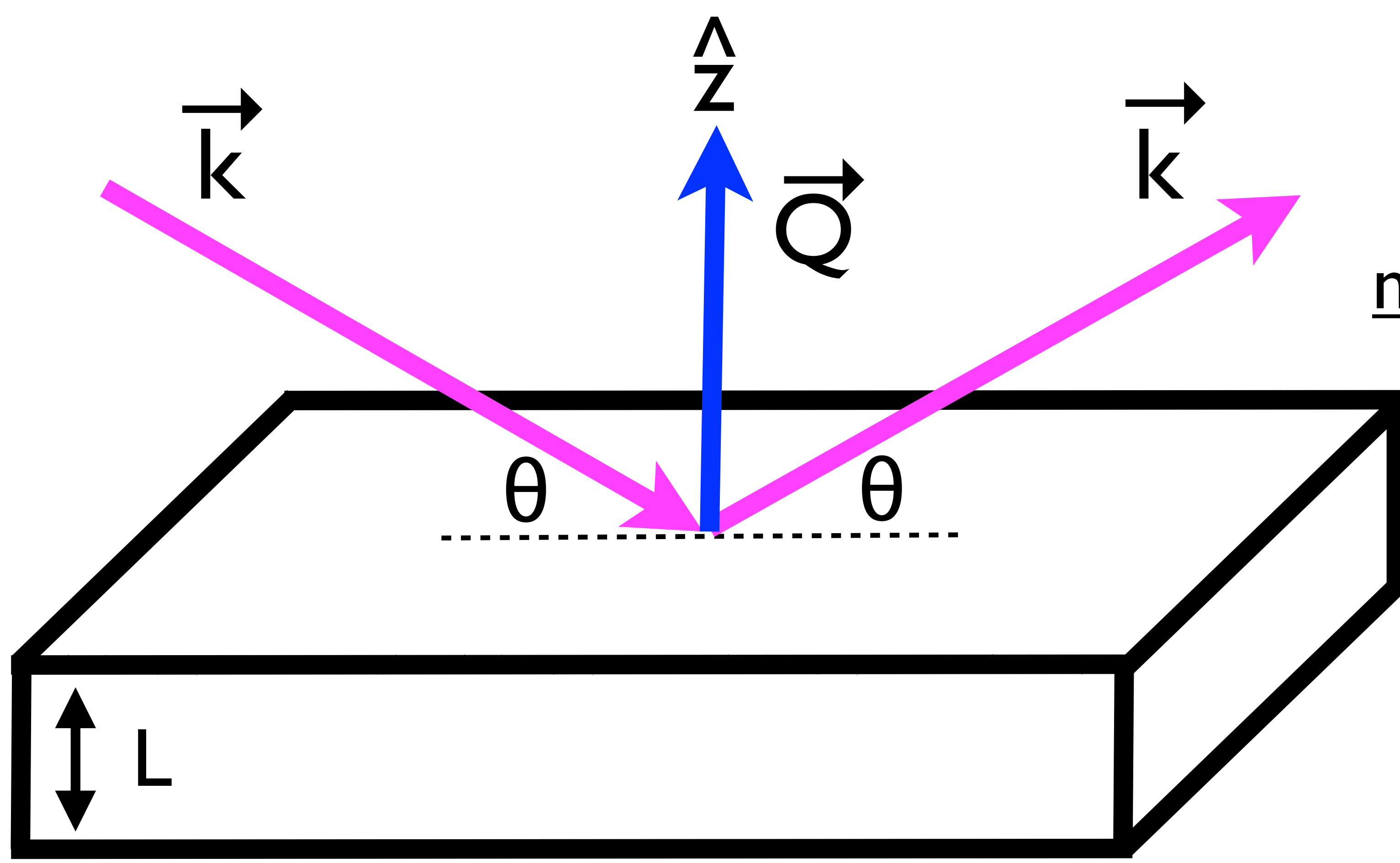

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determine: $\rho(z)$

SPECULAR REFLECTOMETRY

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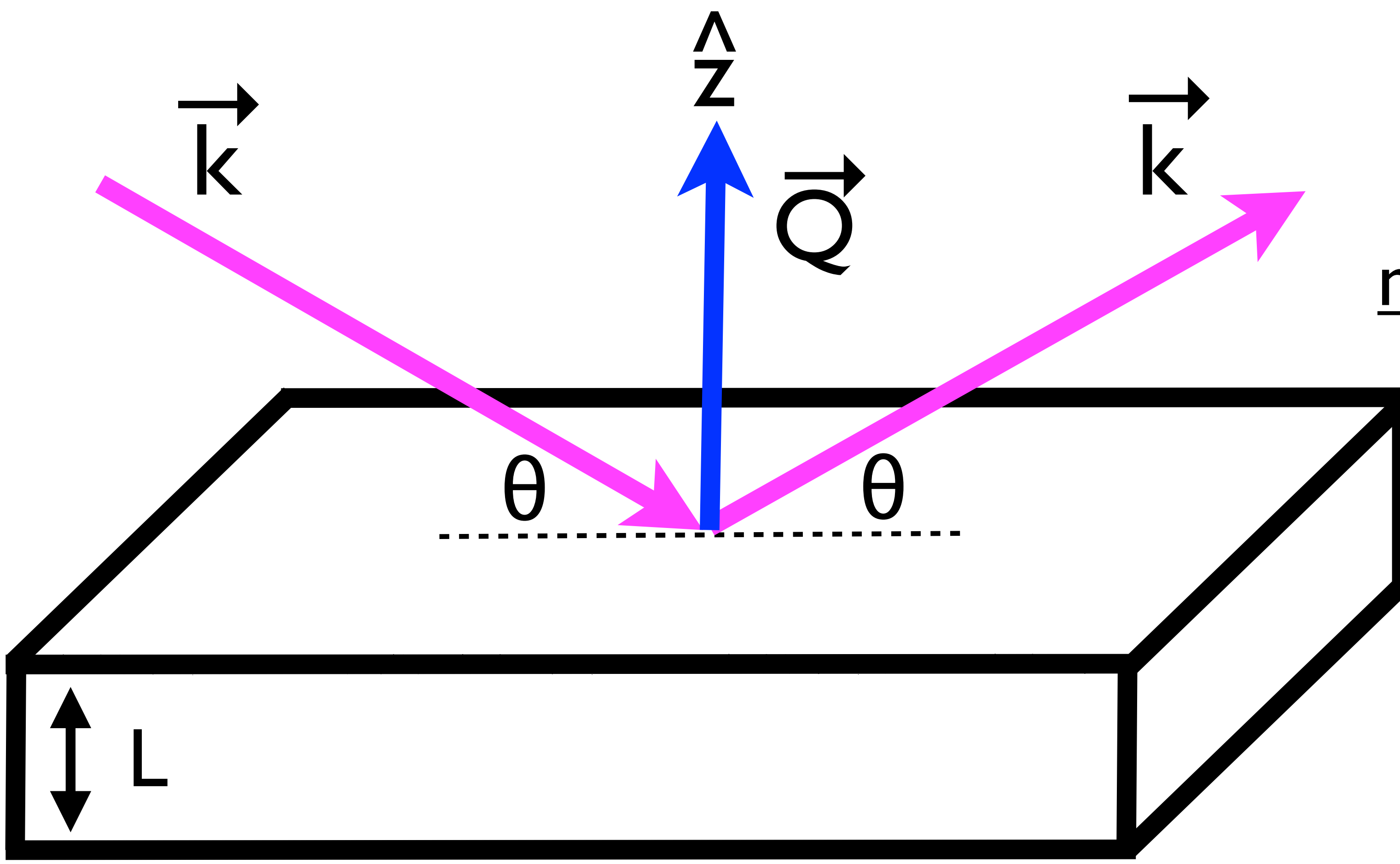

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<u>determine</u>: $\rho(z)$

<u>interpret</u>: $\rho = \sum_i N_i\, b_i$

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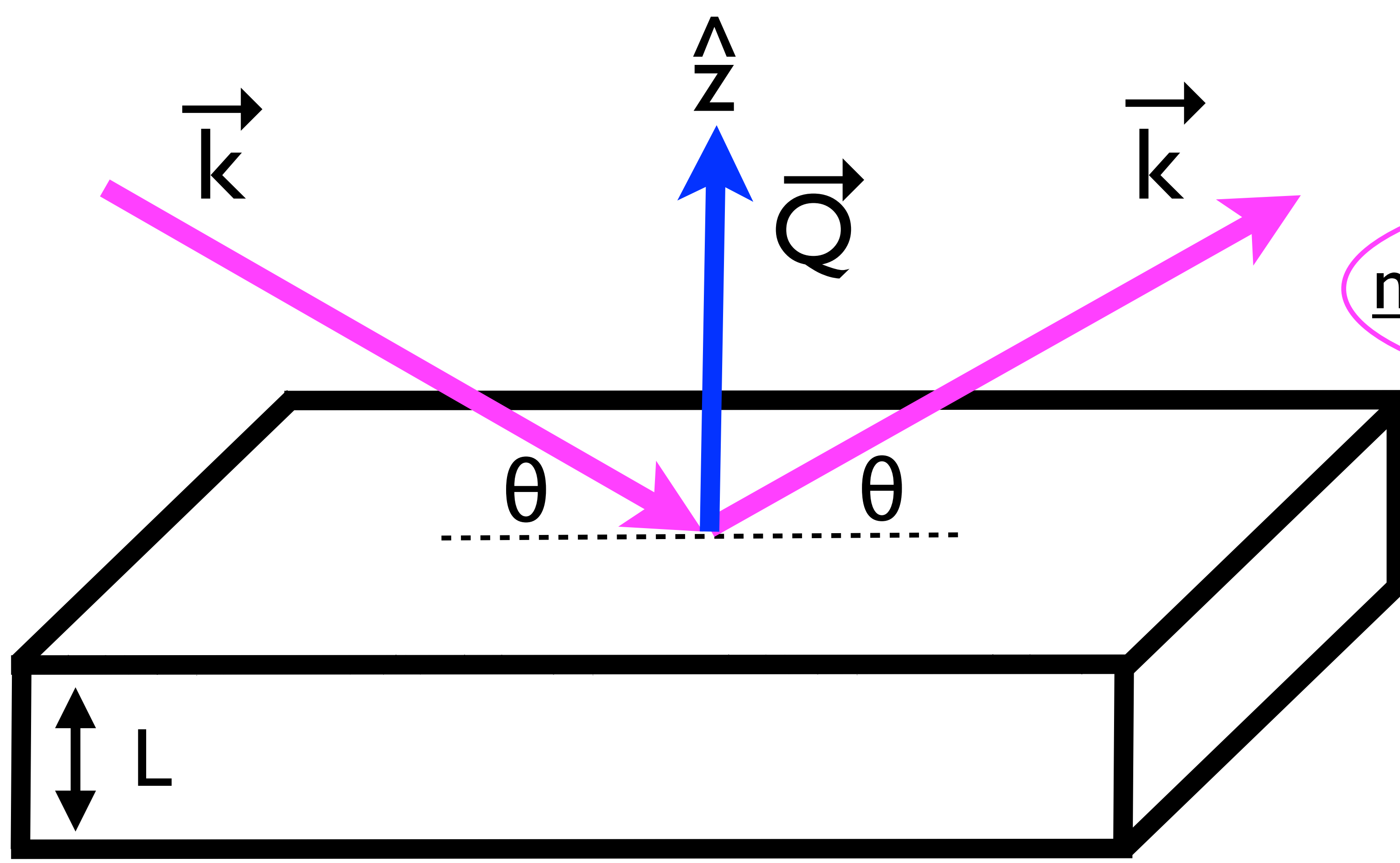

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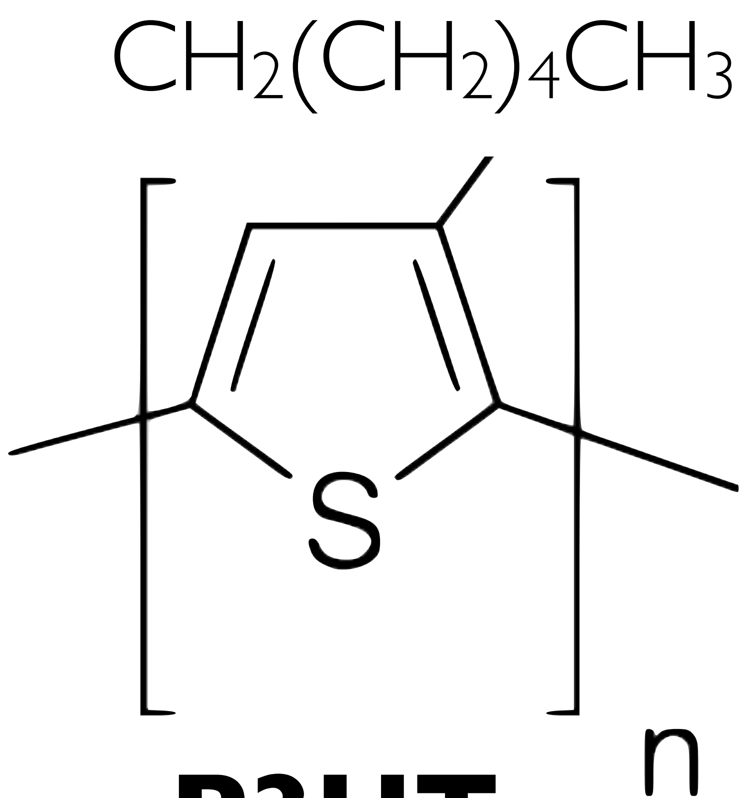
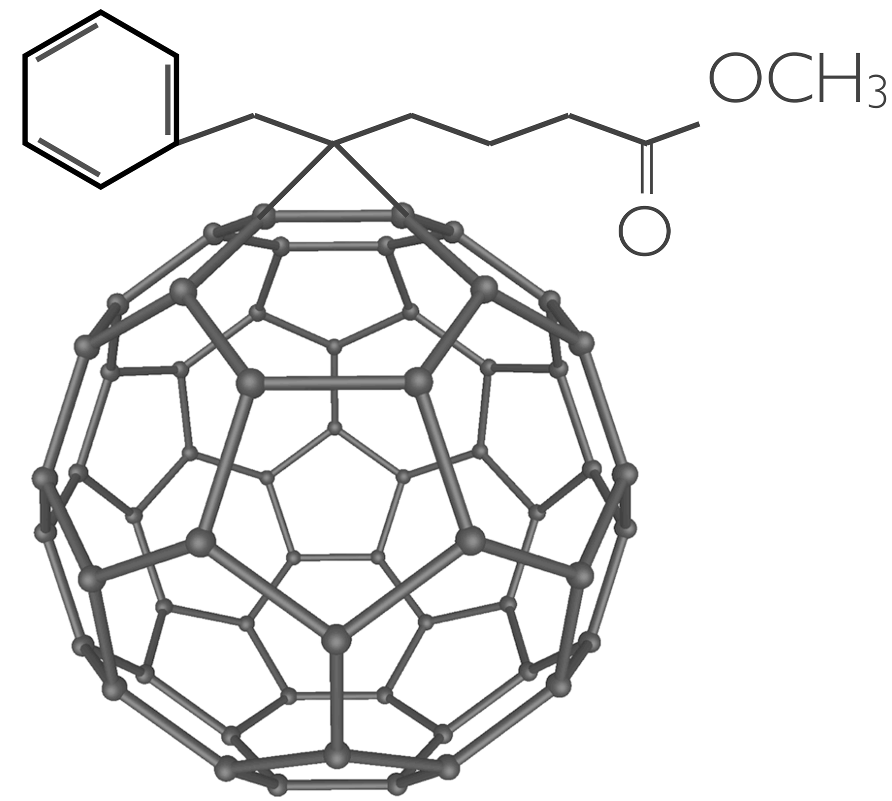
ORGANIC PHOTOVOLTAICS

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



P3HT

(poly 3-hexylthiophene)



PCBM

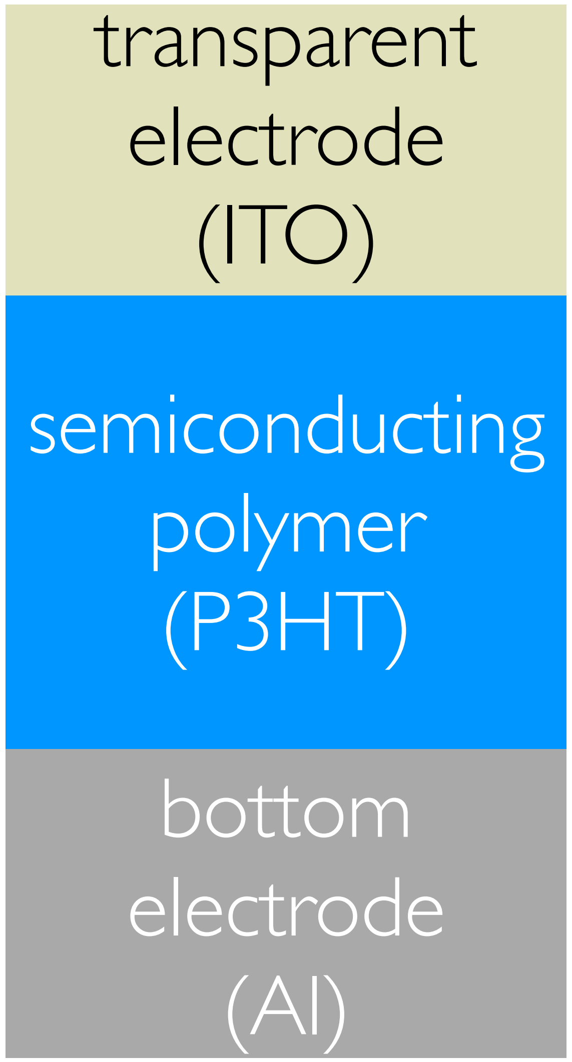
([6,6]-phenyl-C61-butyric acid methyl ester)

conducting polymer

acceptor dopant

distribution is important!

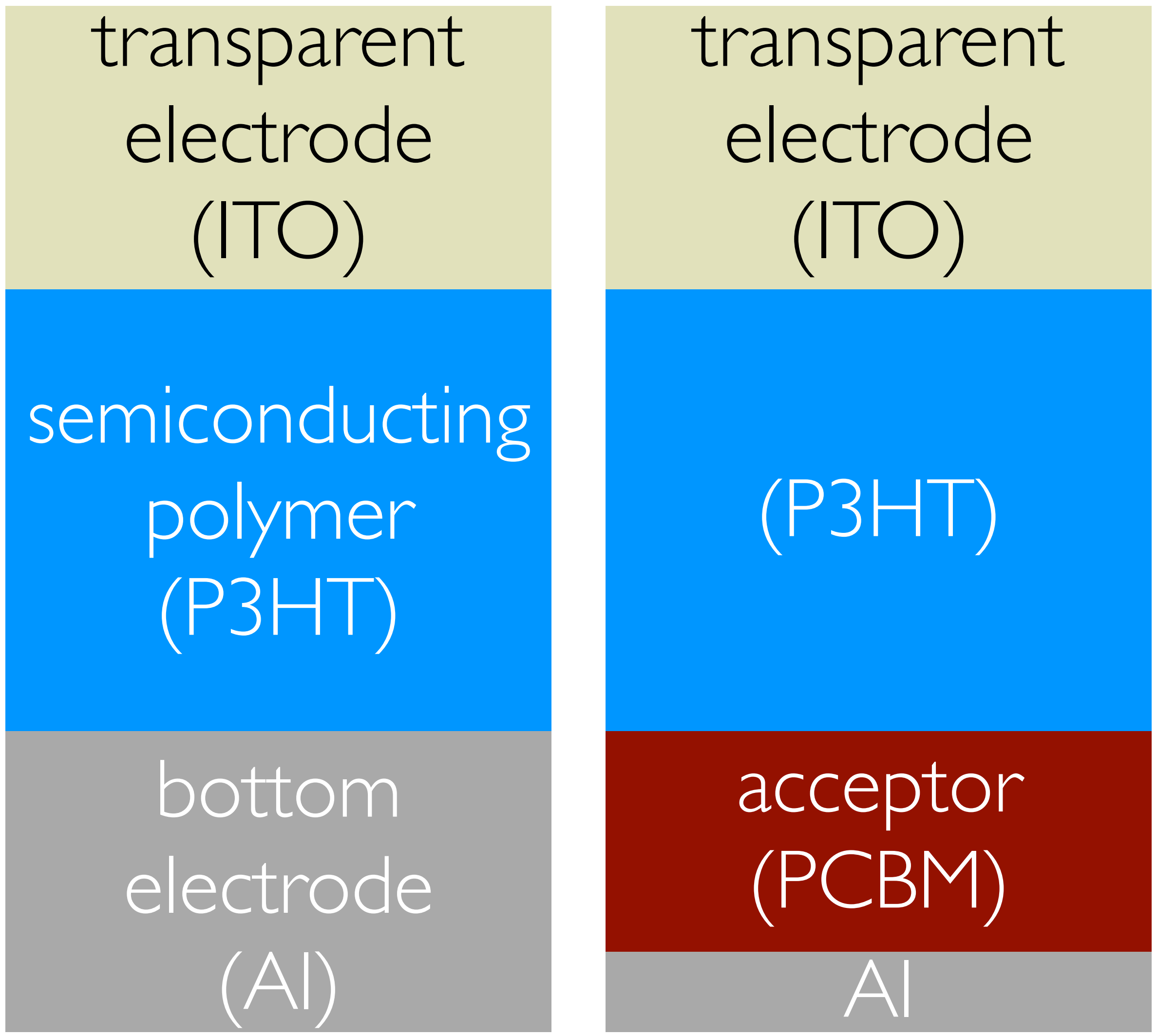
P3HT:PCBM



monolayer

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

P3HT:PCBM



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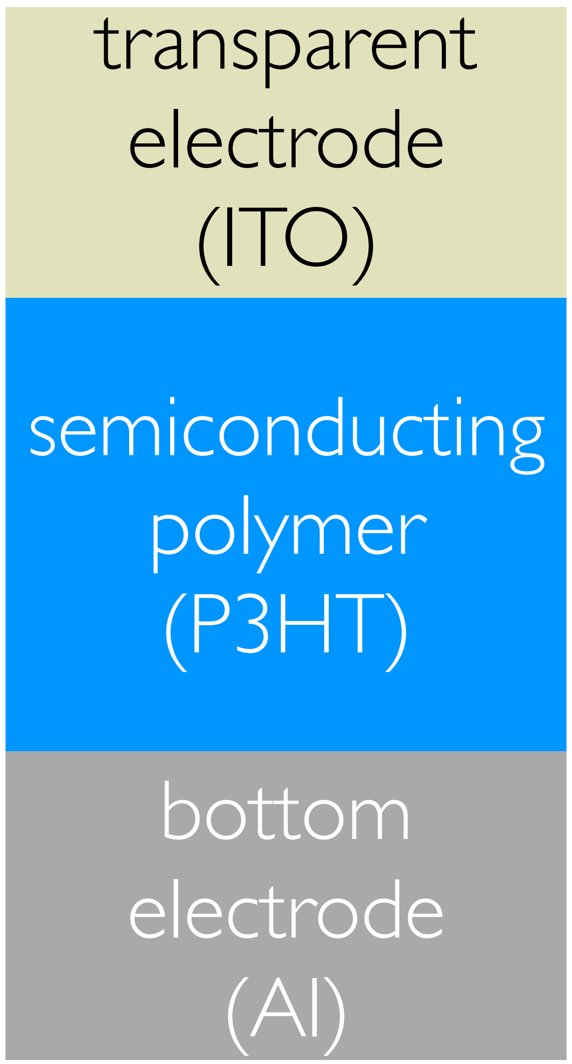
bilayer

PCBM interface inhibits recombination, but there's only one

P3HT:PCBM



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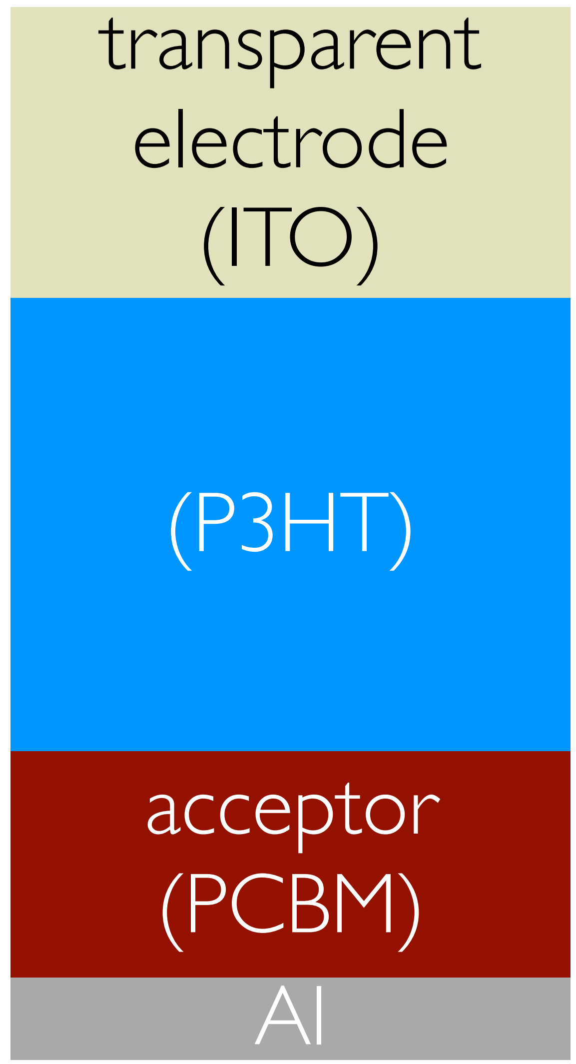

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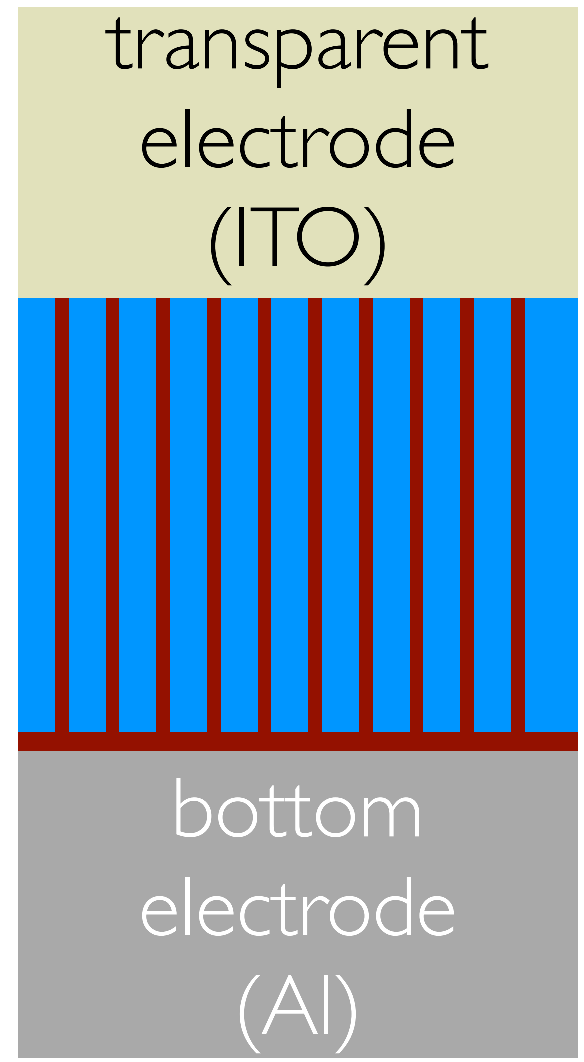
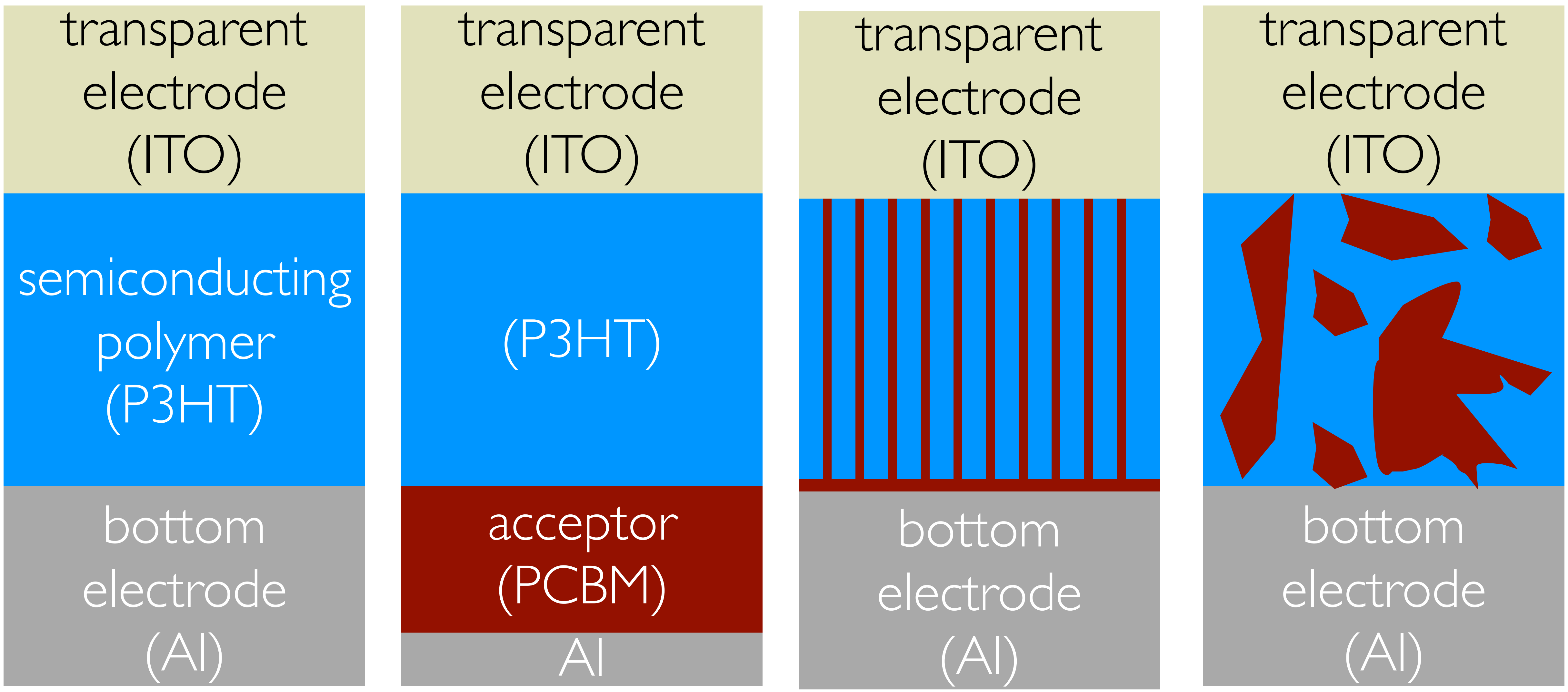


comb

ideal, but difficult to engineer

P3HT:PCBM



monolayer

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bilayer

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comb

ideal, but difficult to engineer

bulk heterojunction

best geometry so far - how does is the PCBM distributed?

ELECTRON CONTRAST

J. W. Kiel et. al, *Soft Matter* **6**, 641 (2010).

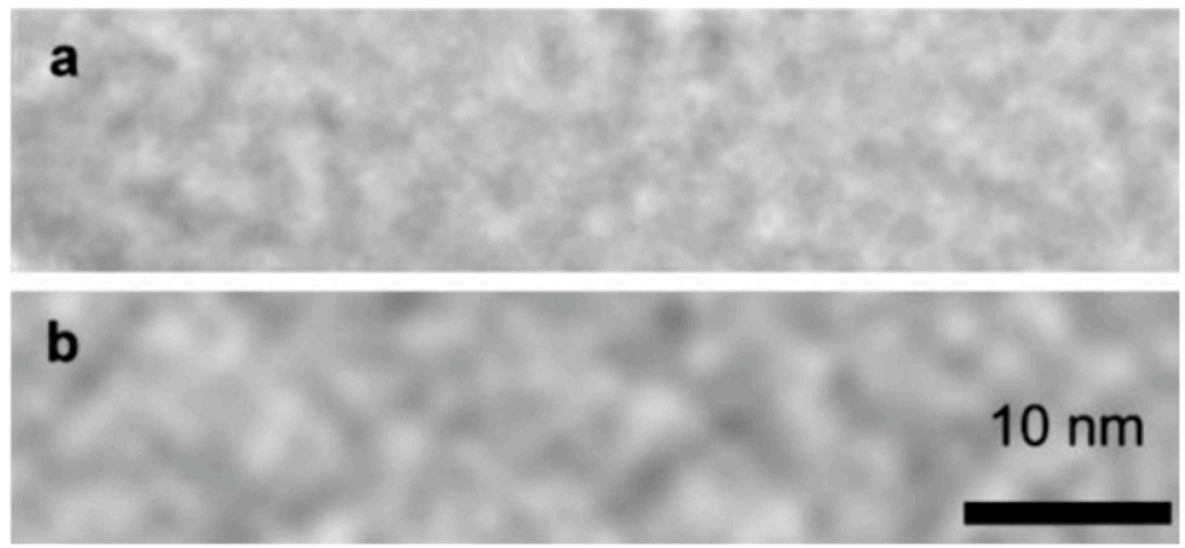
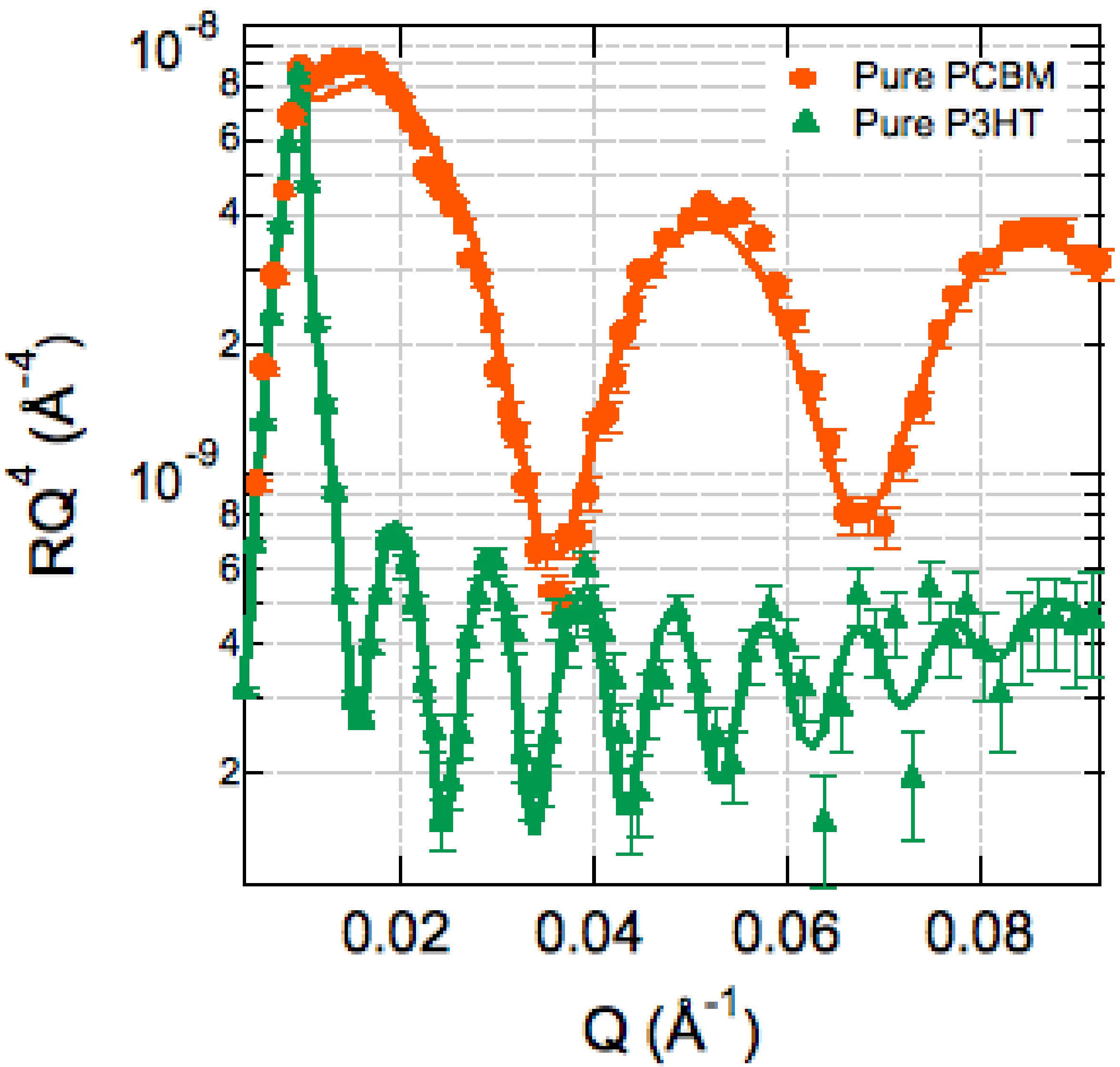
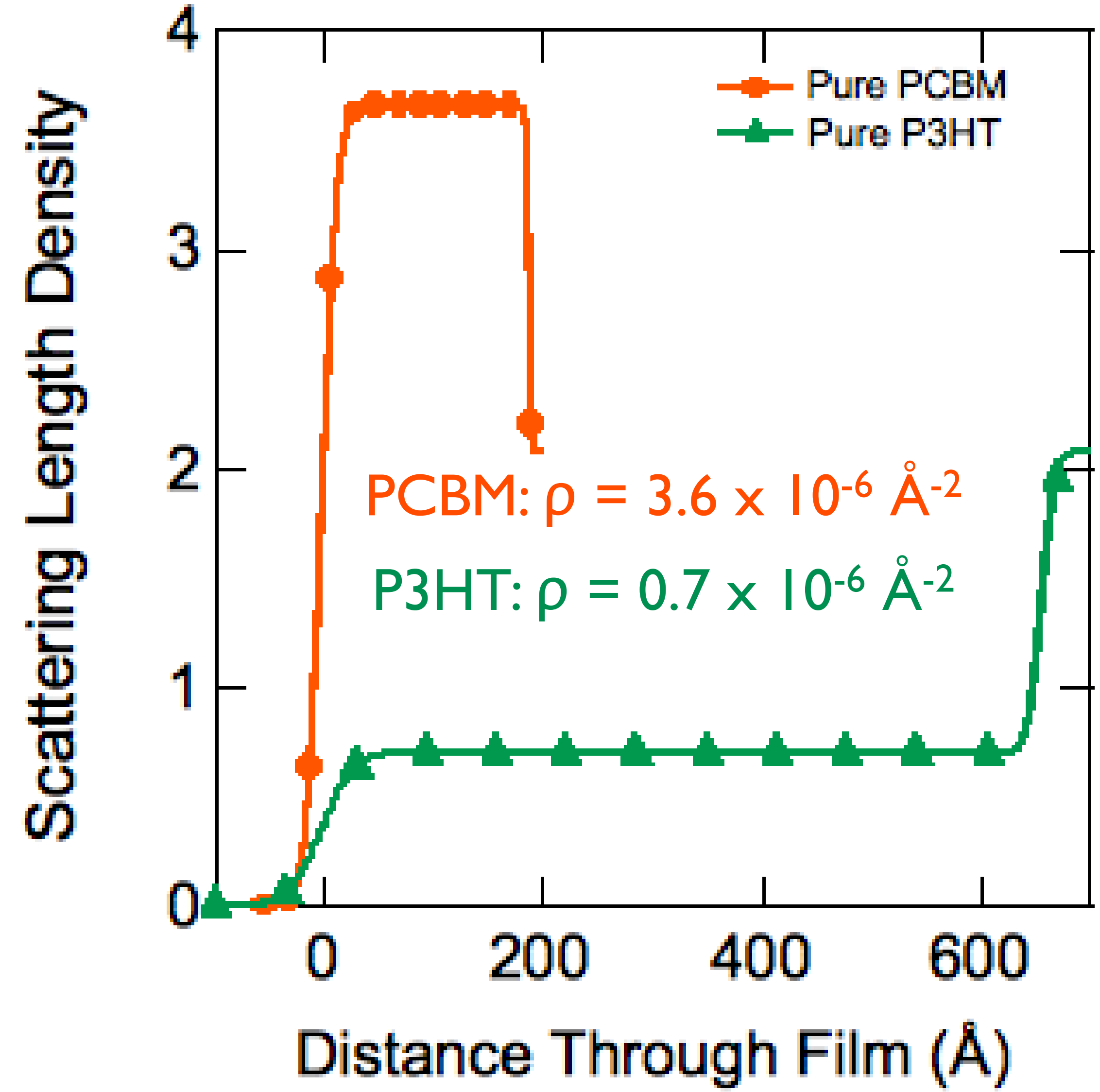


Fig. 1 Defocused transmission electron microscopy cross-sectional images of polymer samples prepared by ultramicrotomy shows little difference for a variety of materials. A 1 : 1 by weight PCBM : P3HT blend (a) and pure polystyrene (b) both have lighter and darker regions demonstrating the difficulty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

NEUTRON CONTRAST

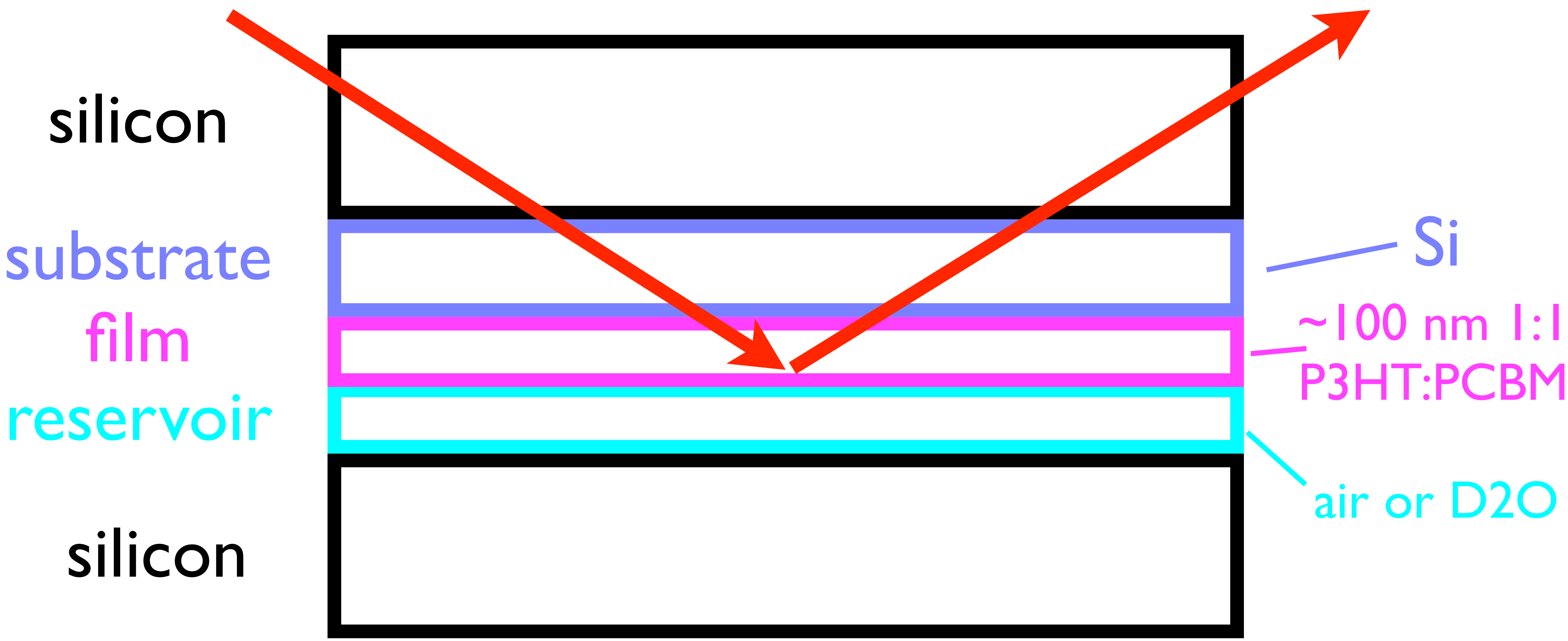
J. W. Kiel, et al., *J. Phys. Chem.* **133**, 074902 (2010)



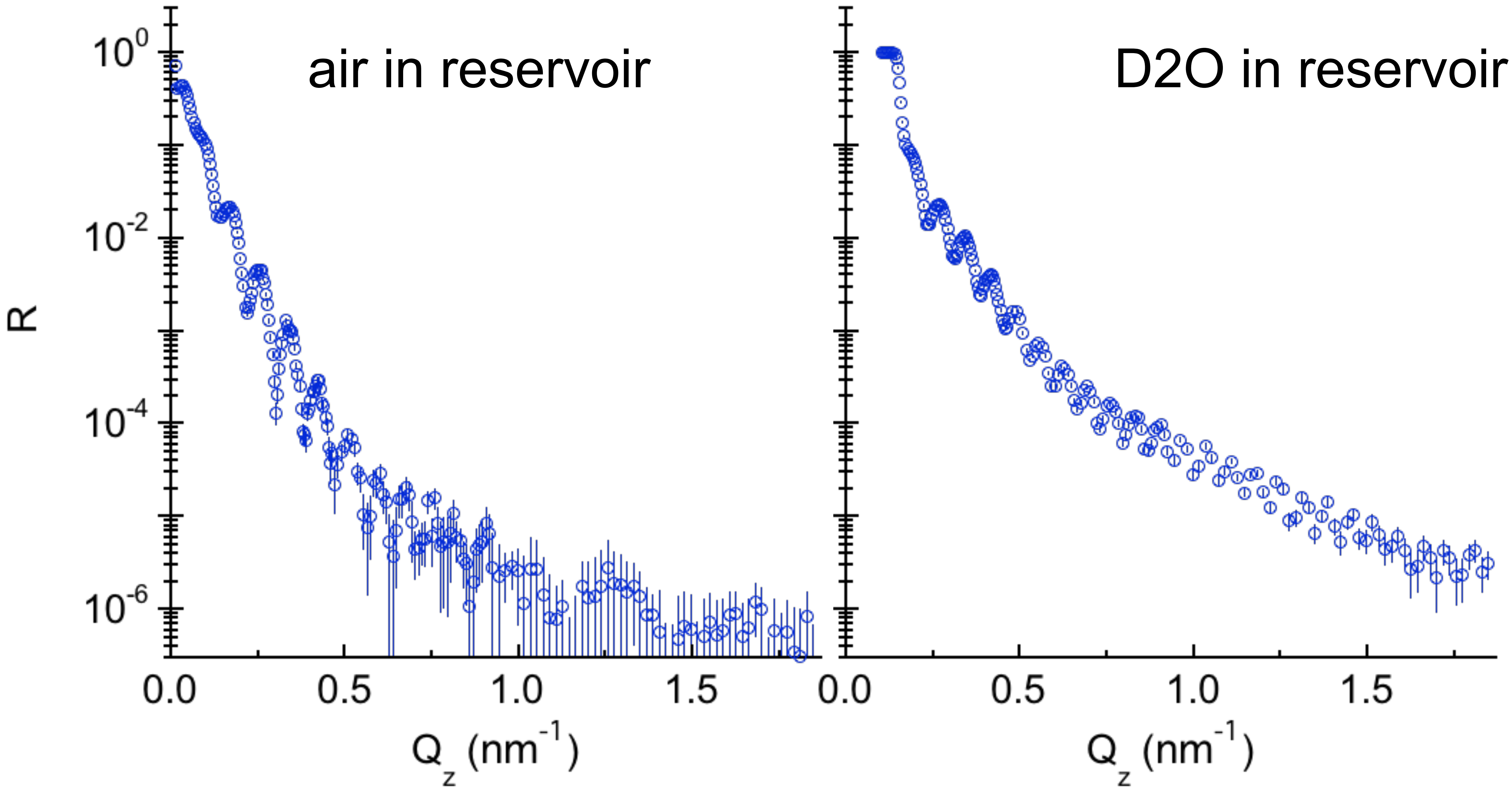


CONTRAST VARIATION VIA BACKING MEDIUM

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



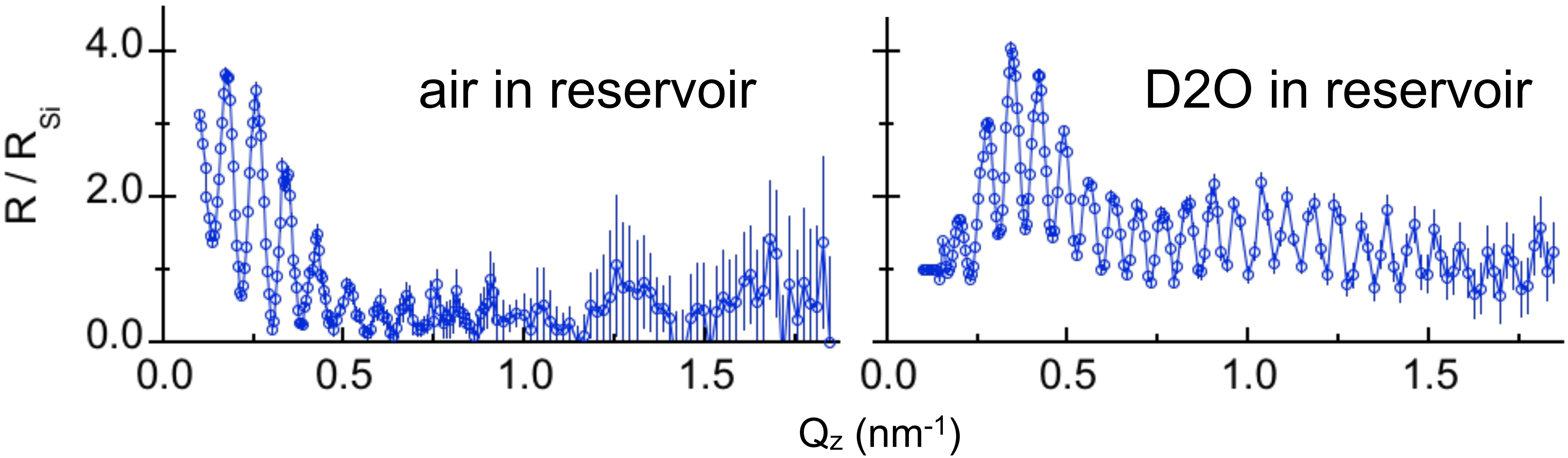
R vs. Qz



air in reservoir
D2O in reservoir
R
10^{0}
10^{-2}
10^{-4}
10^{-6}
0.0
0.5
1.0
1.5
Q_z (nm^{-1})

INVERSION

reflectivities



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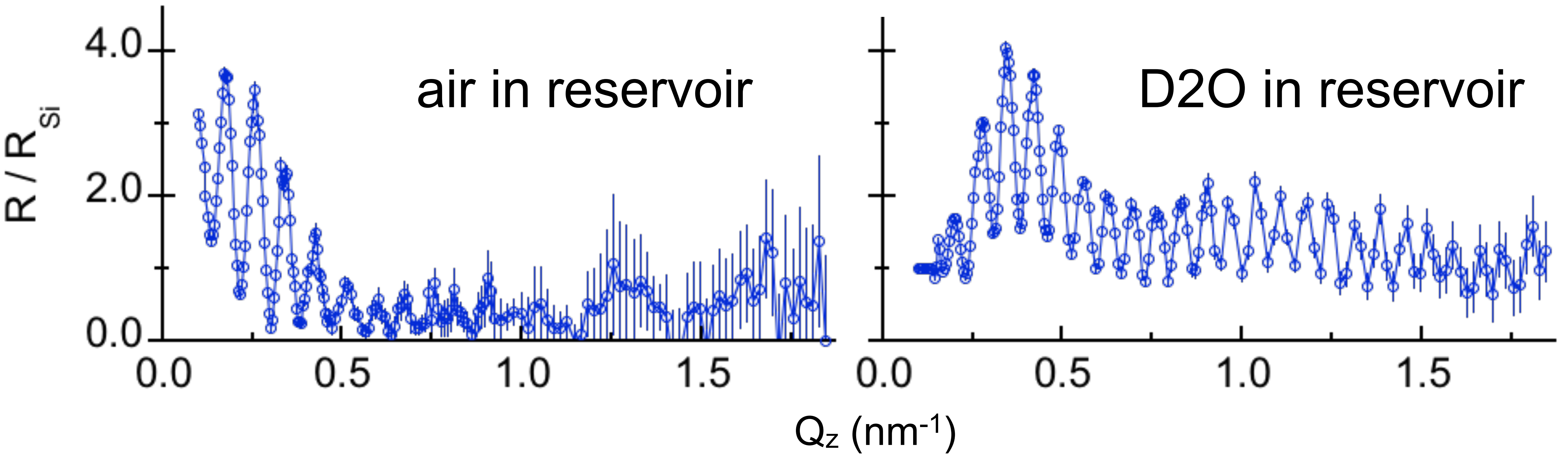

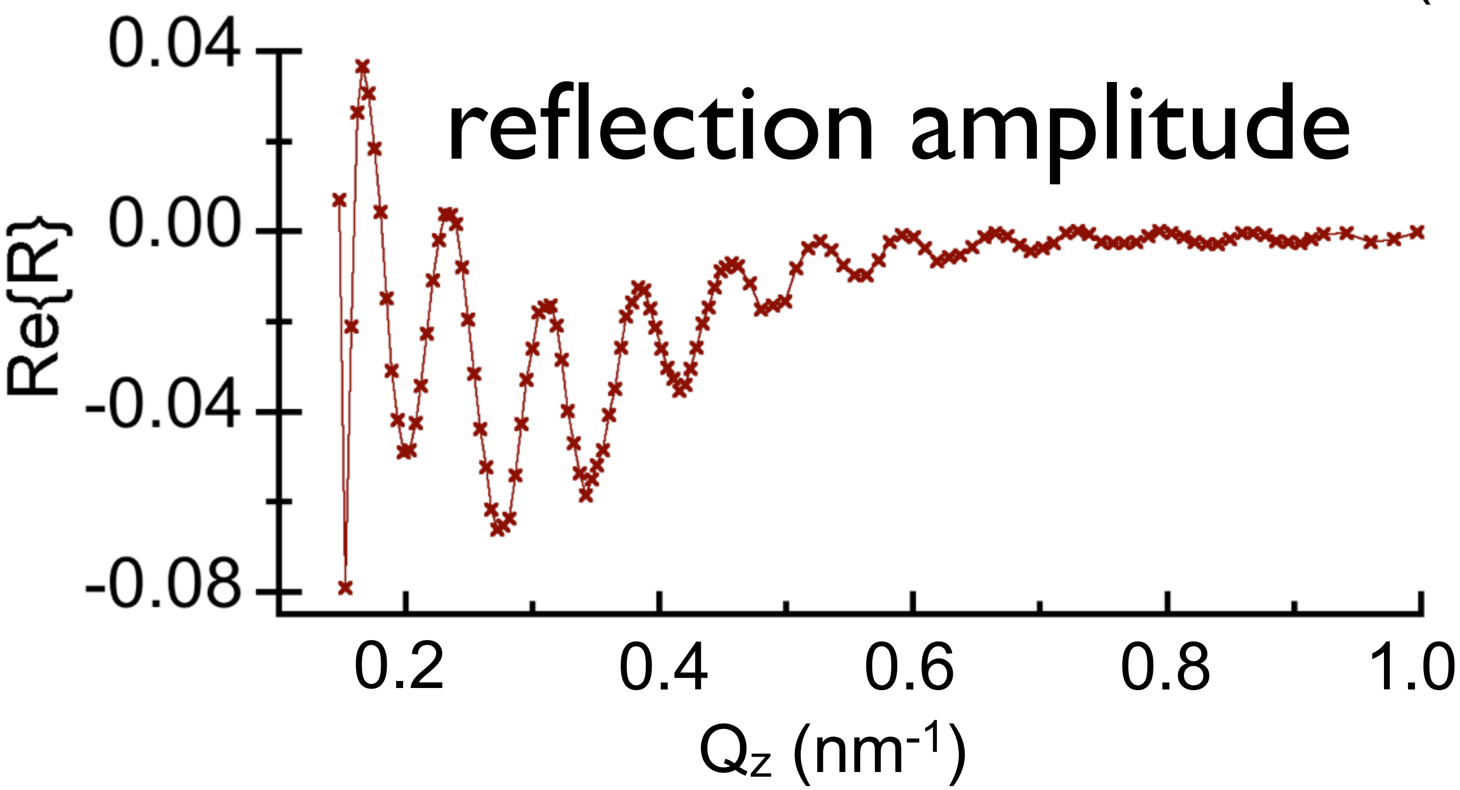

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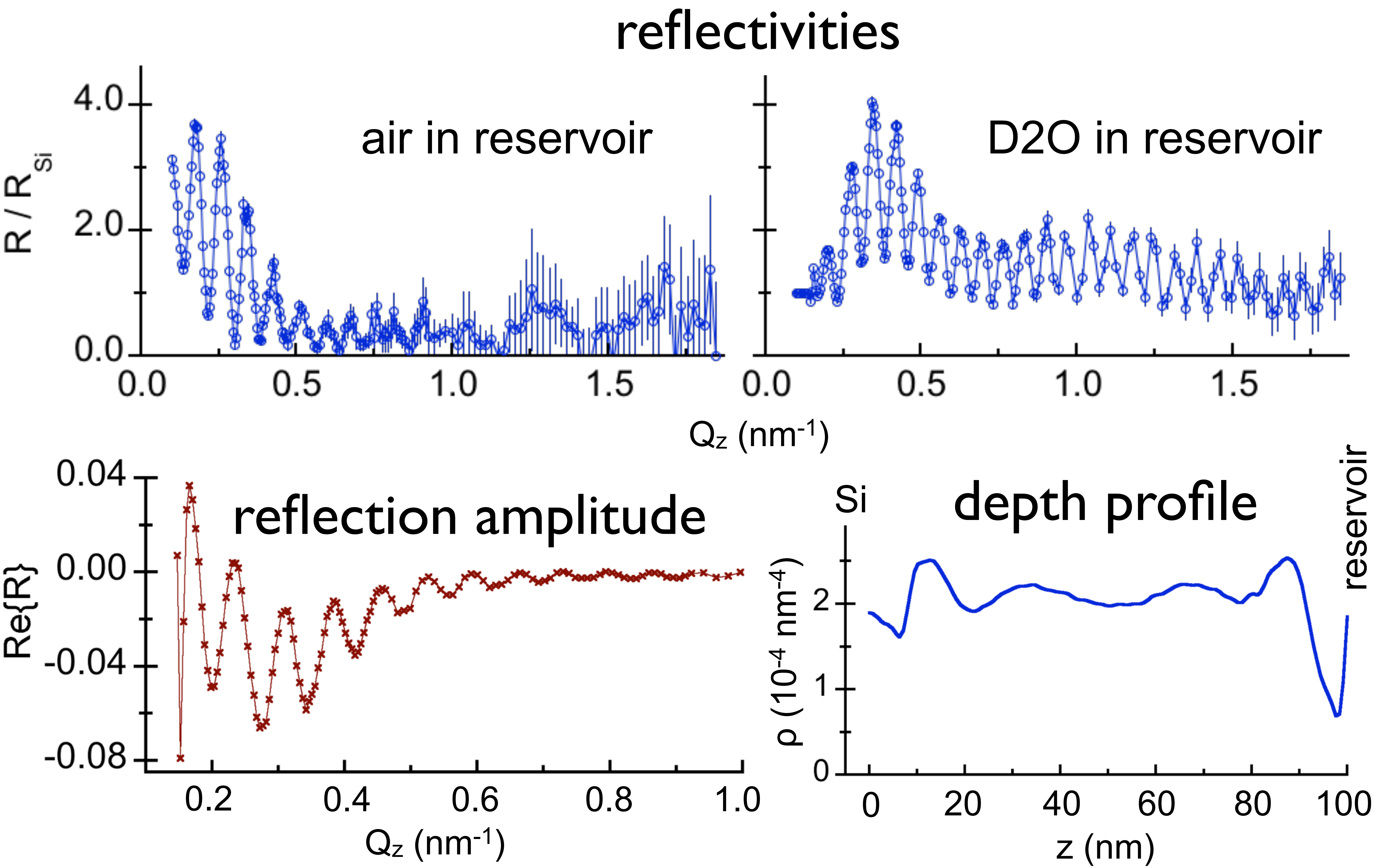
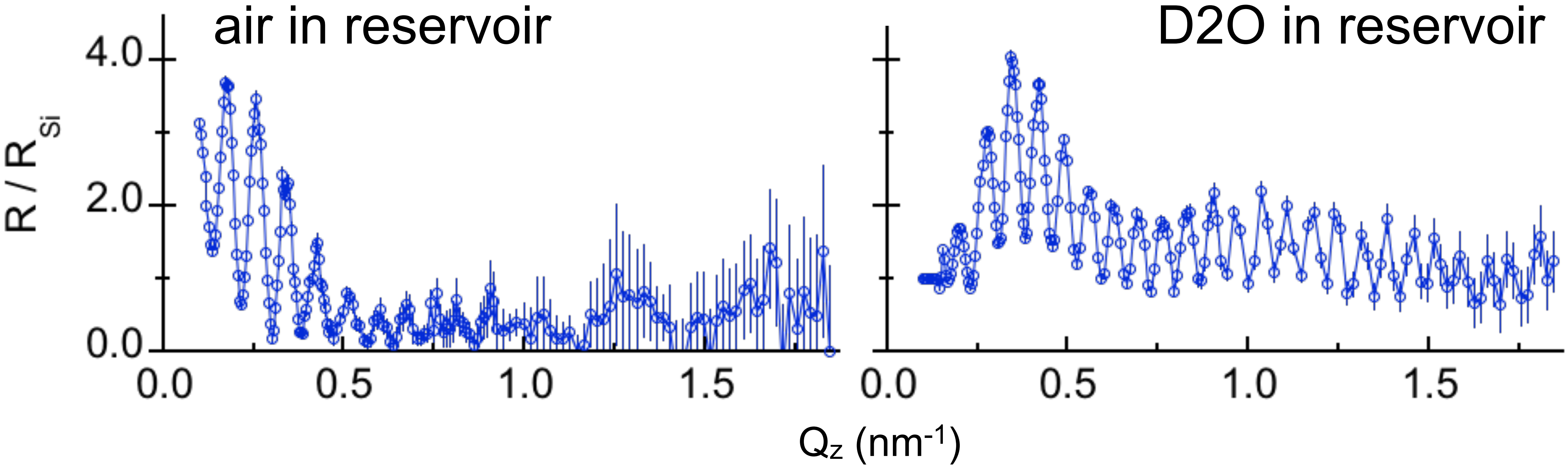


reflectivities
air in reservoir
D2O in reservoir
R / R_Si
4.0
2.0
0.0
0.0
0.5
1.0
1.5
Qz (nm-1)
reflection amplitude
Re{R}
0.04
0.00
-0.04
-0.08
0.2
0.4
0.6
0.8
1.0
Qz (nm-1)
Si
depth profile
reservoir
ρ (10-4 nm-4)
0
1
2
0
20
40
60
80
100
z (nm)

SIMULTANEOUS FITTING



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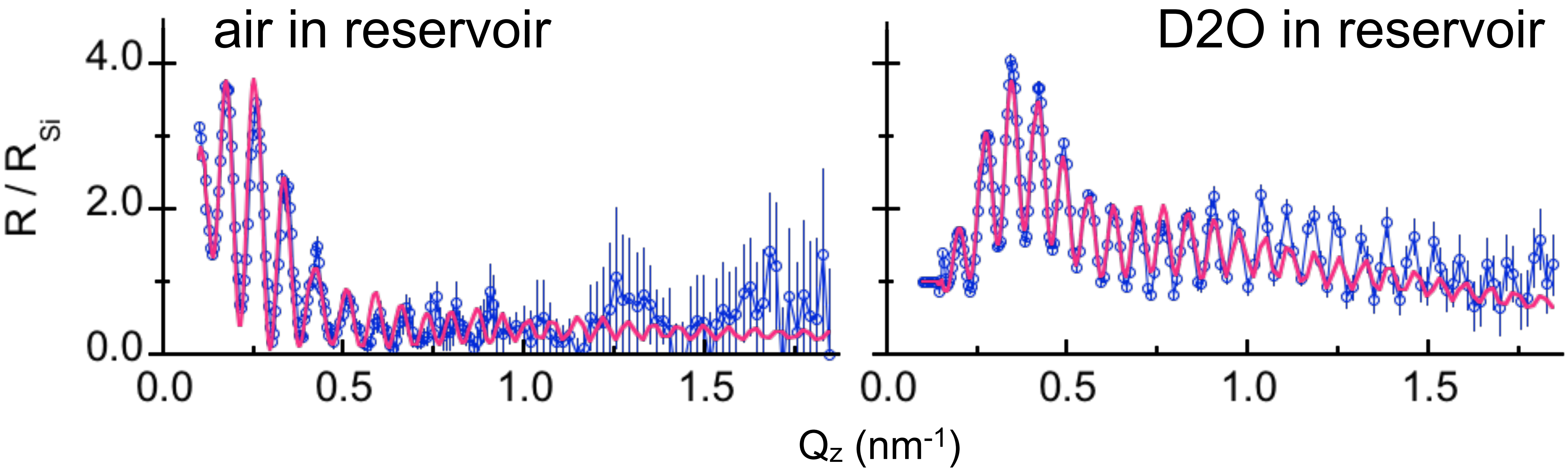

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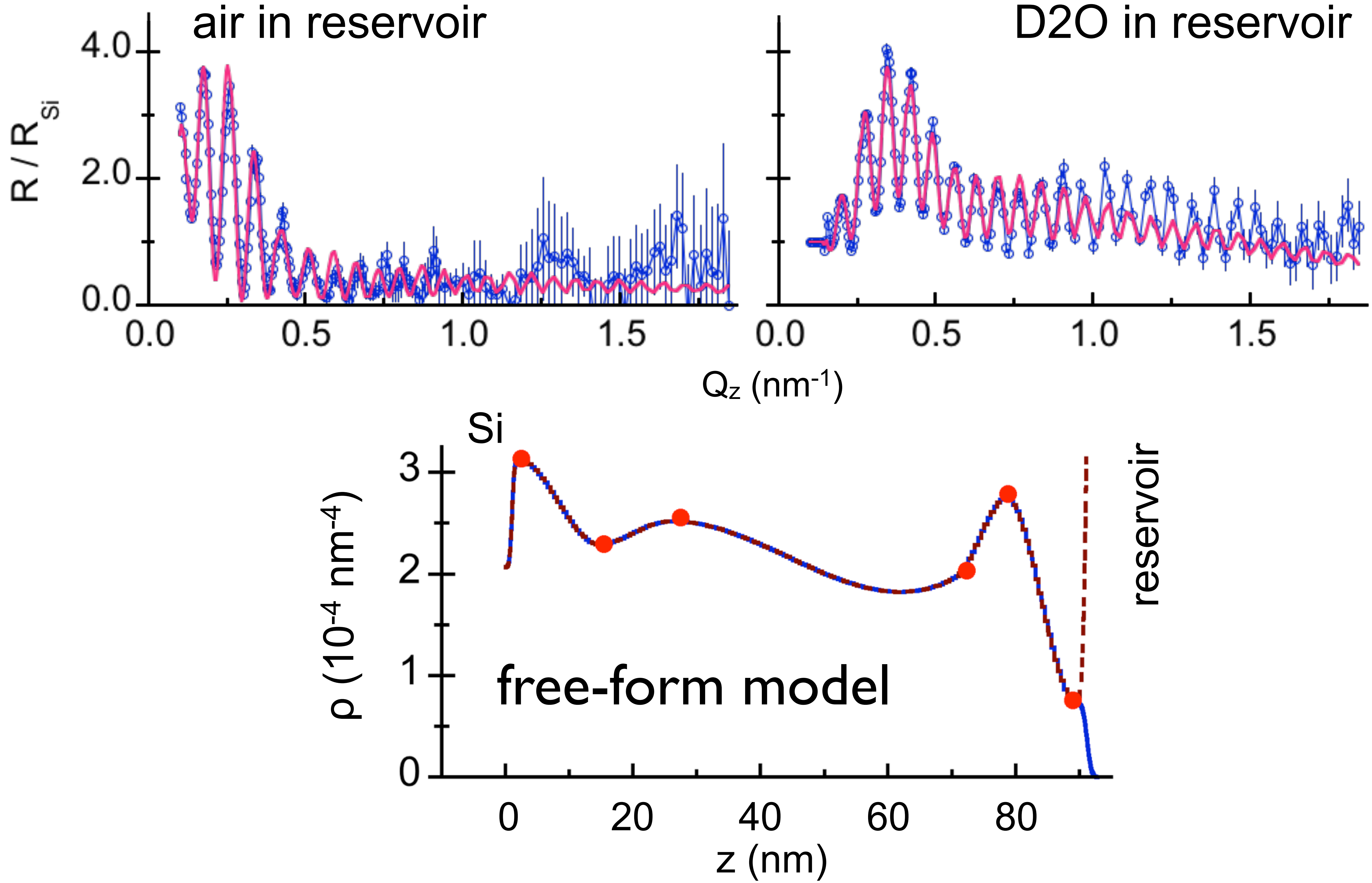
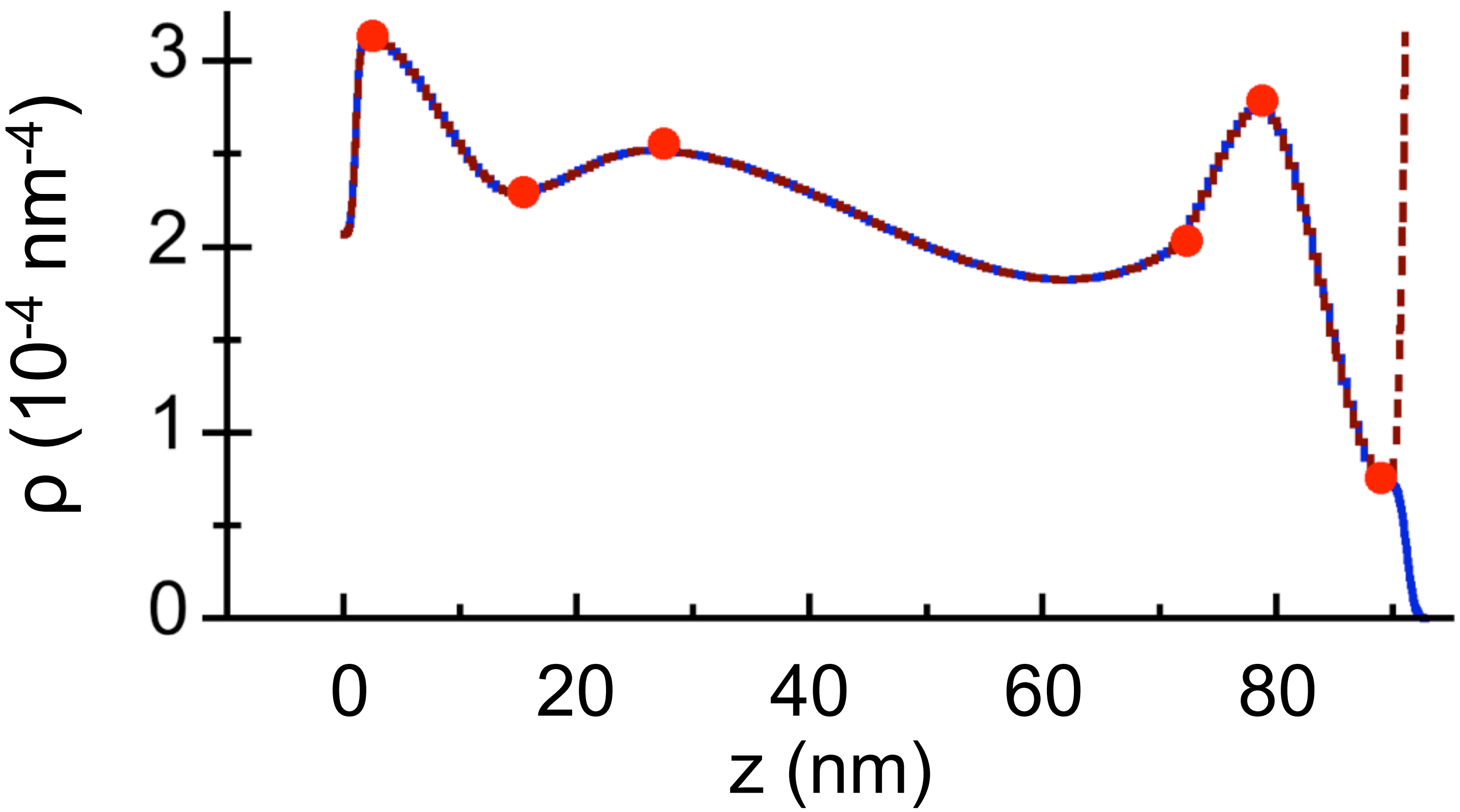


INTERPRETATION



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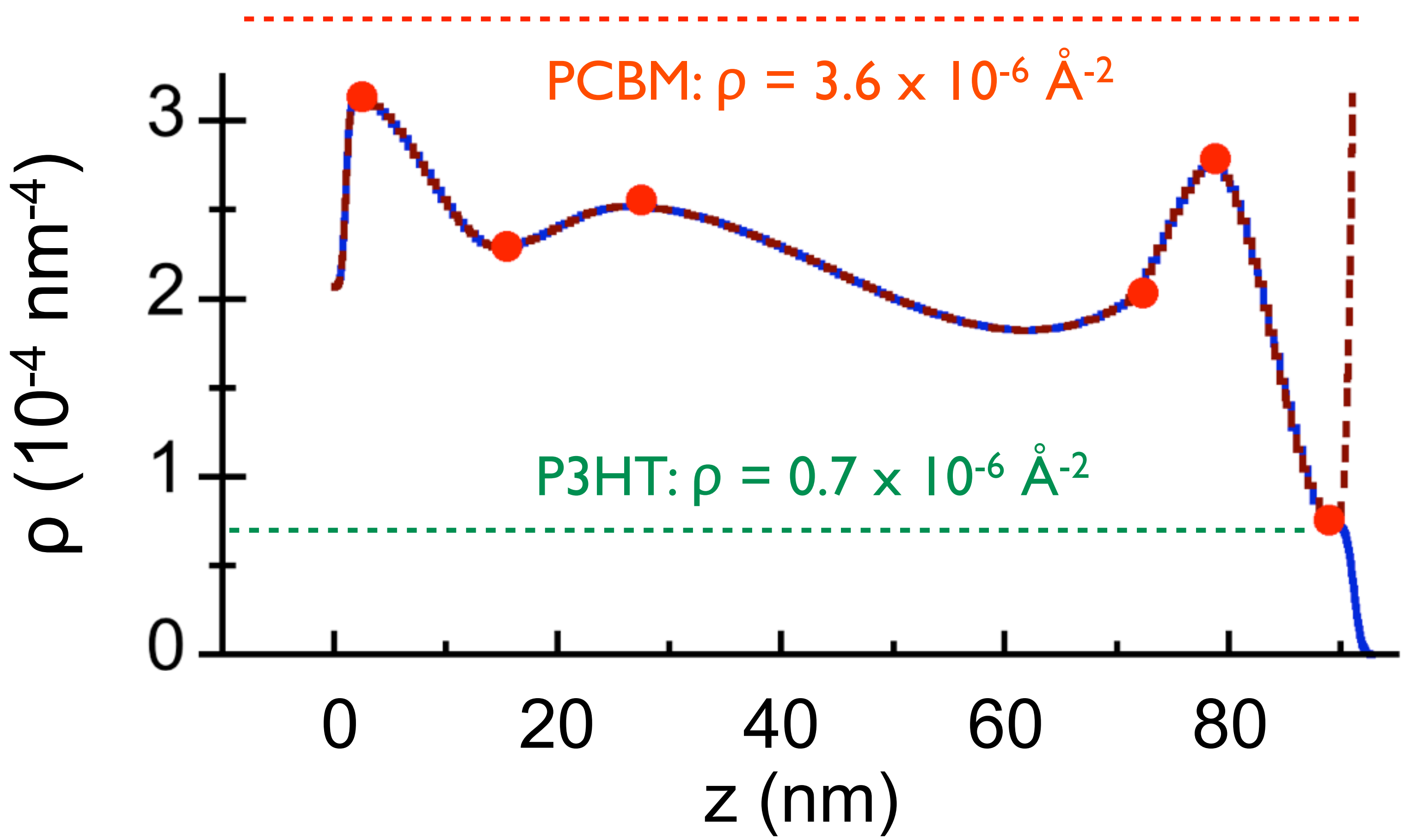

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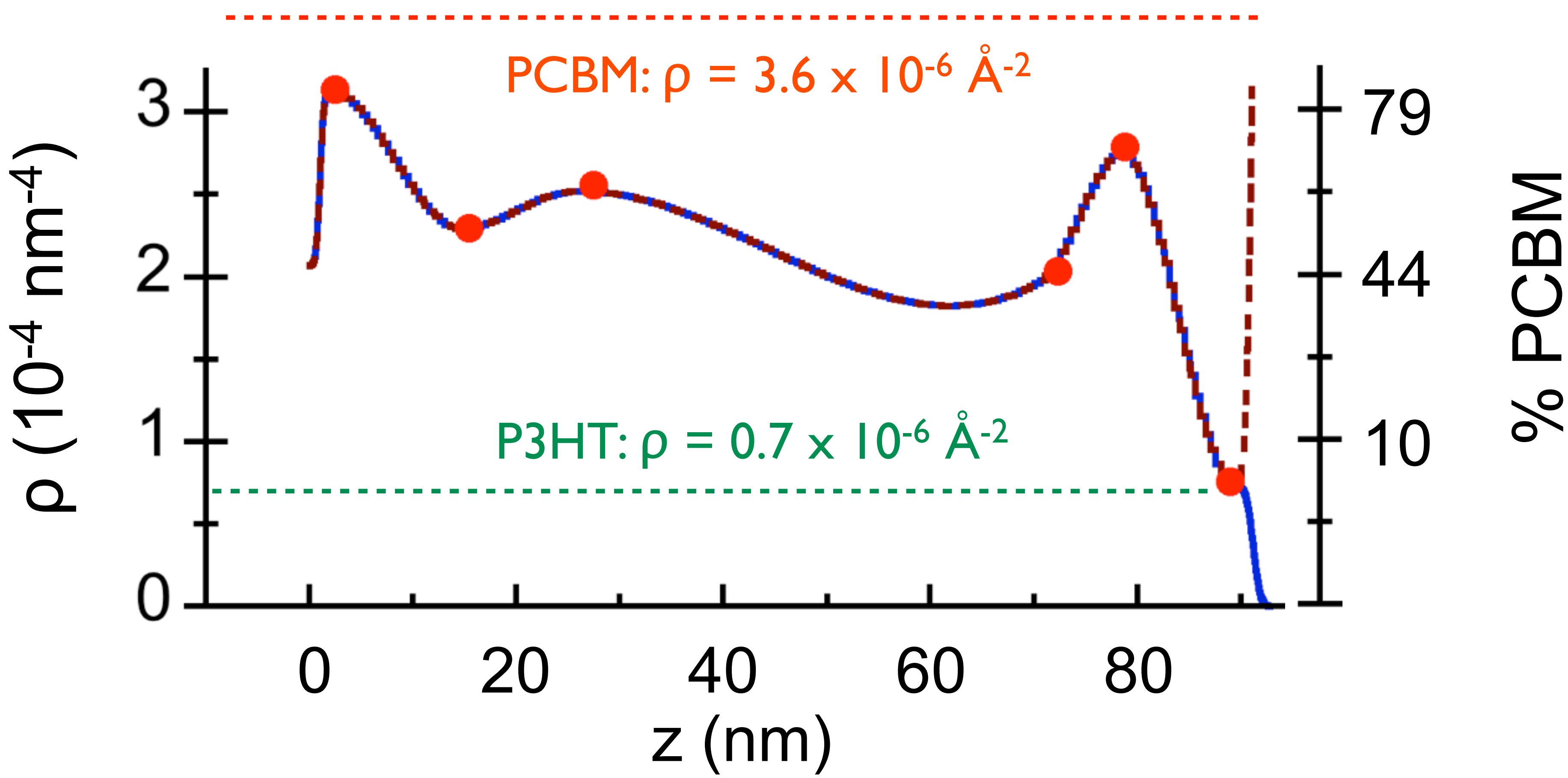

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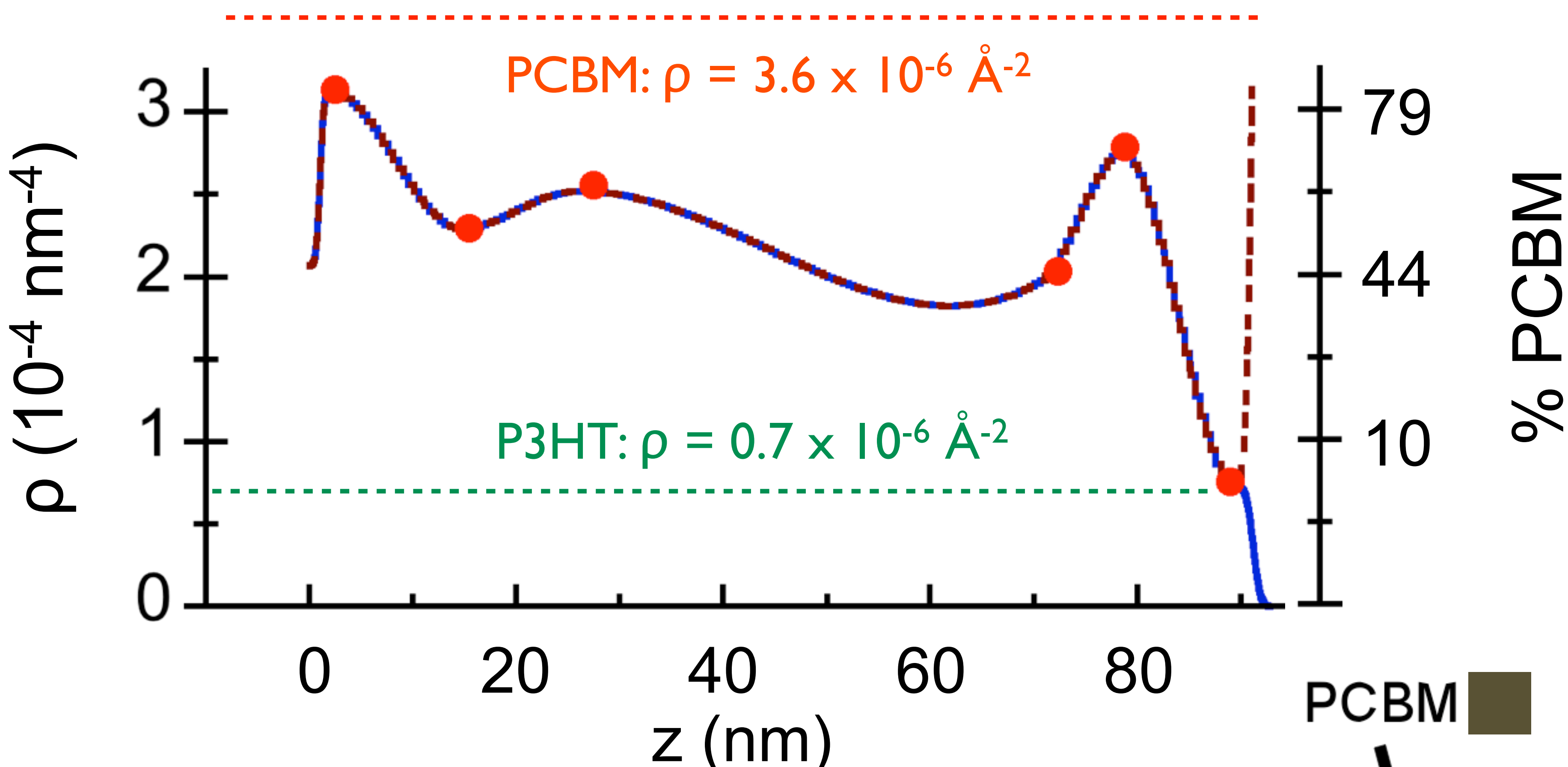
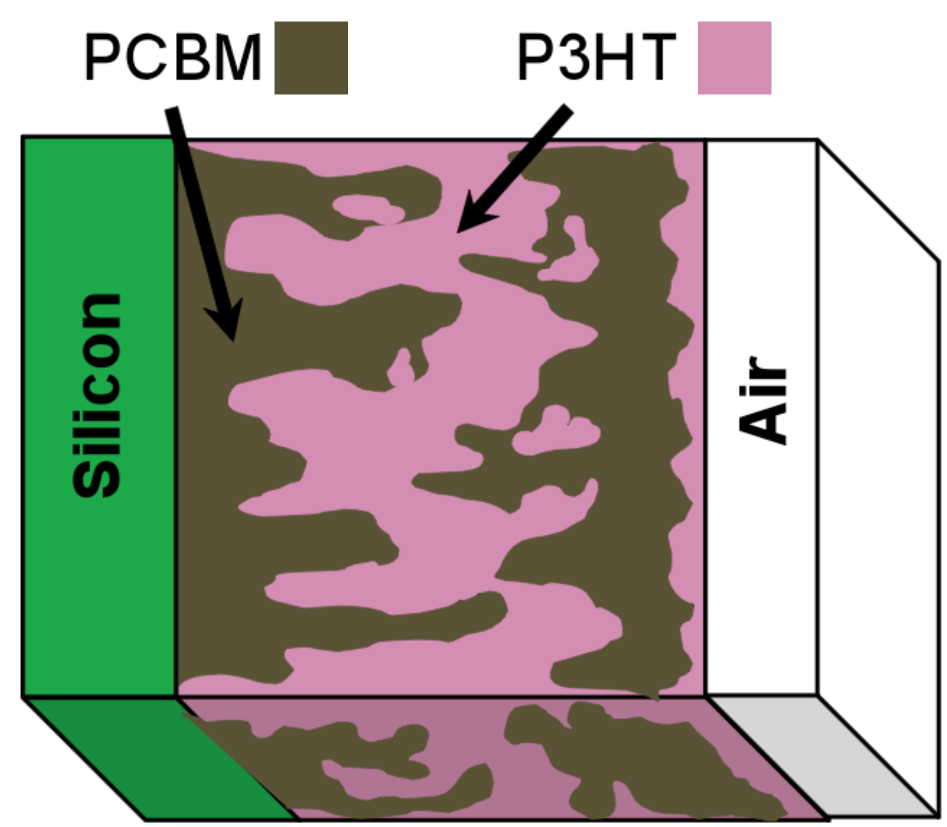
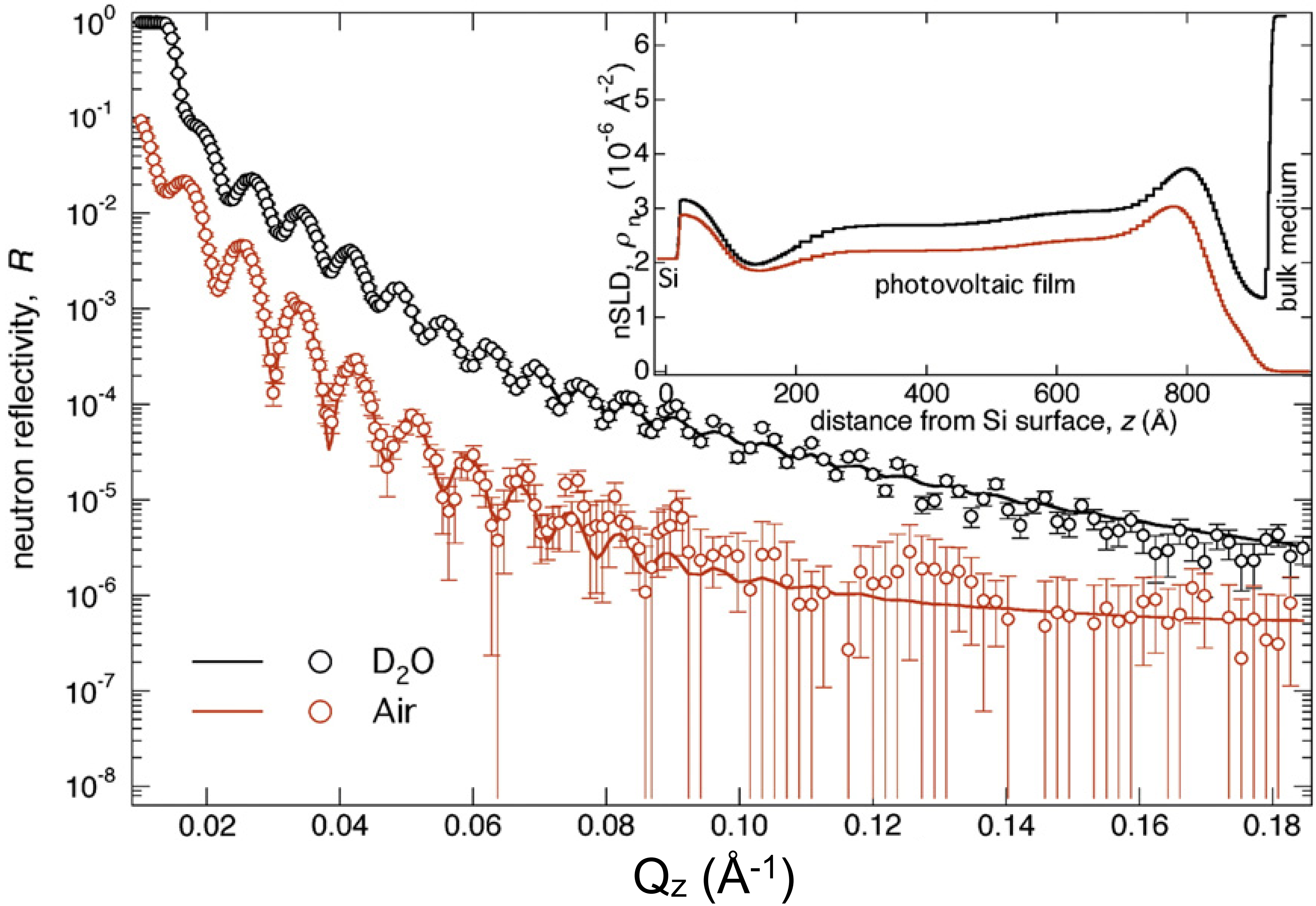




excess PCBM at the interfaces

WHAT IF IT LEAKED?



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

$\rho_N = \sum_i N_i b_i$

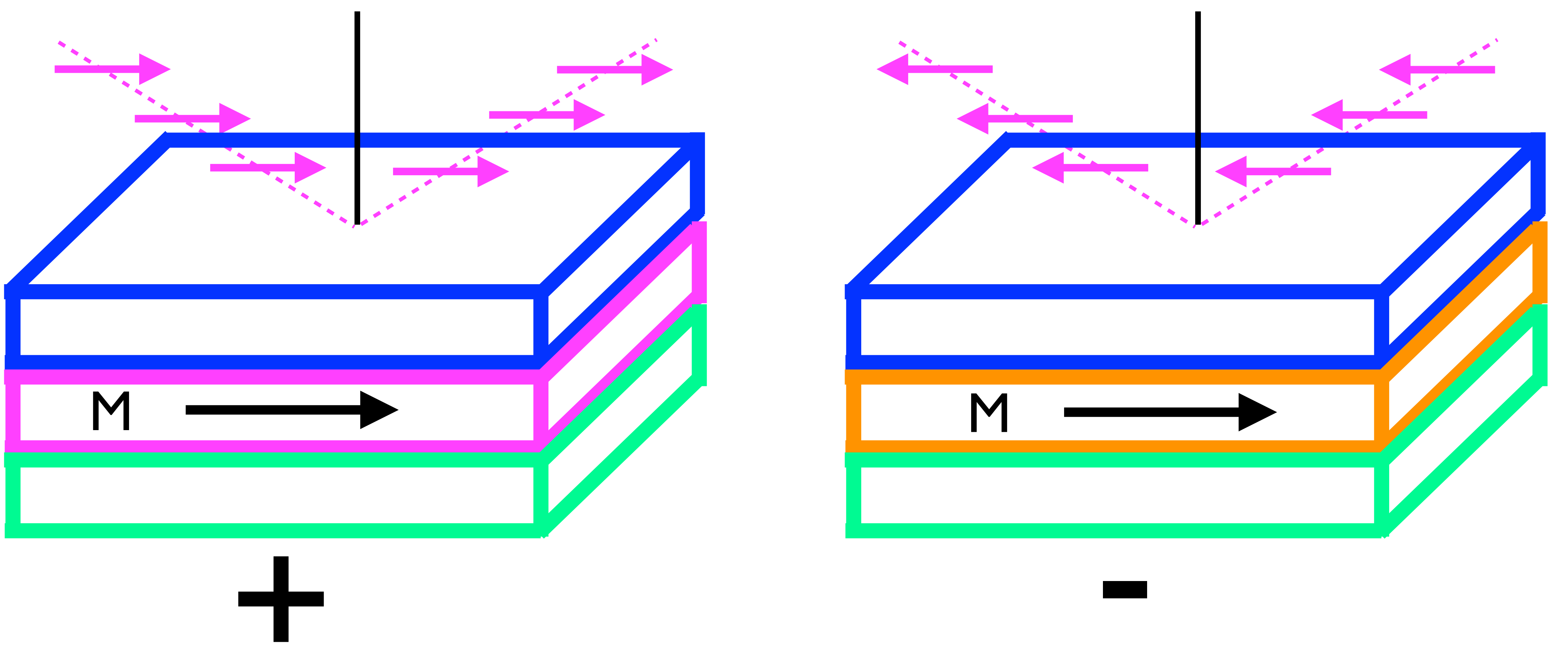
nuclear component

$\rho_M = C\,M$

magnetic component

M: magnetization

$C = 2.853 \times 10\text{-}9\ kA^{-1}\ m\ Å^{-2}$

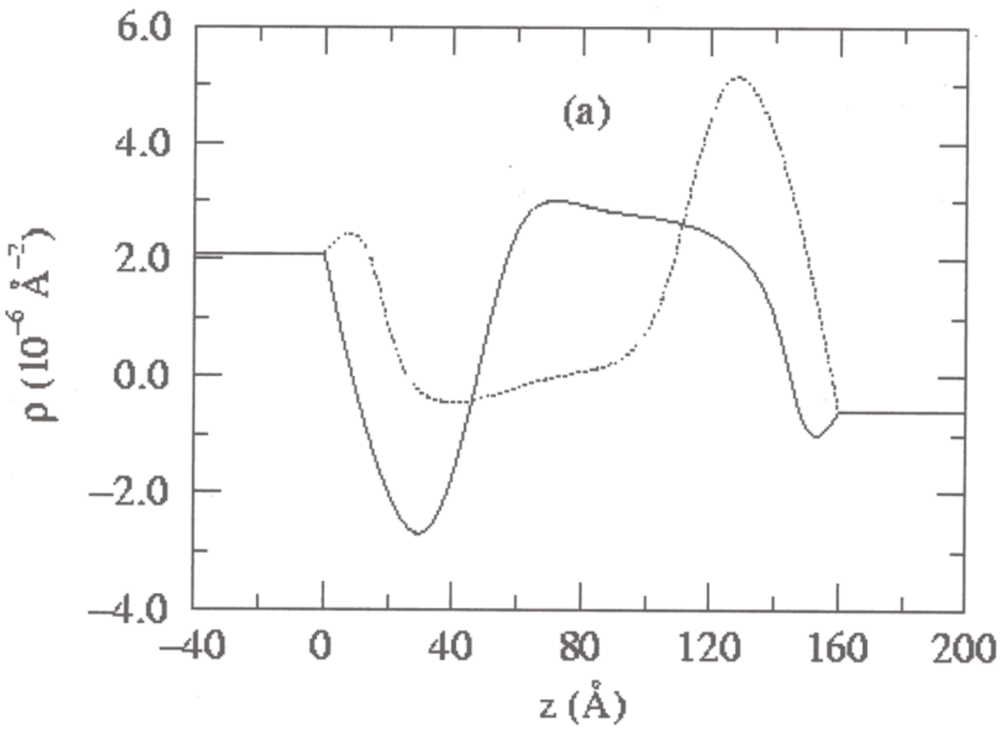


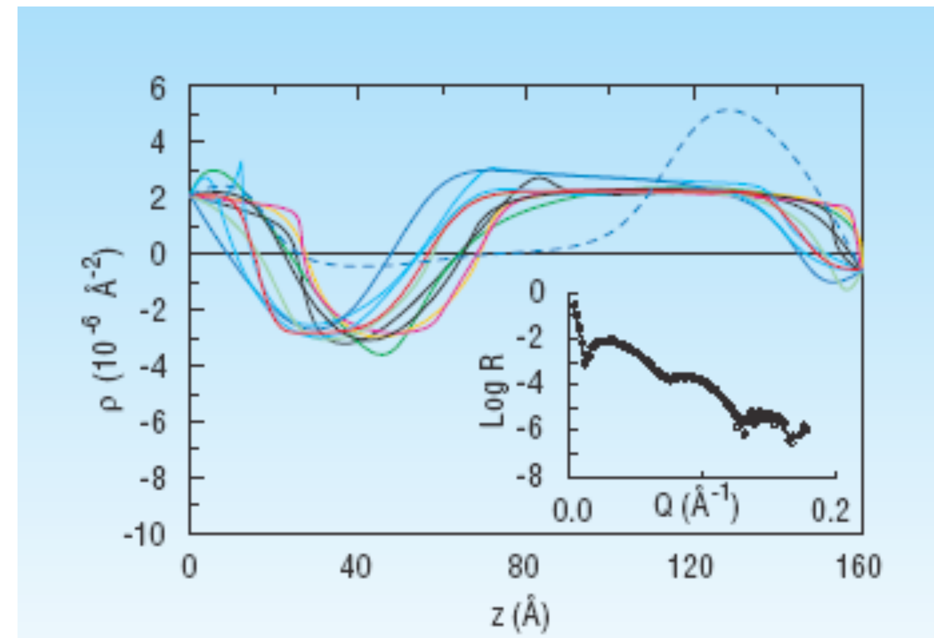
<u>buried magnetic reference layer for contrast variation</u>

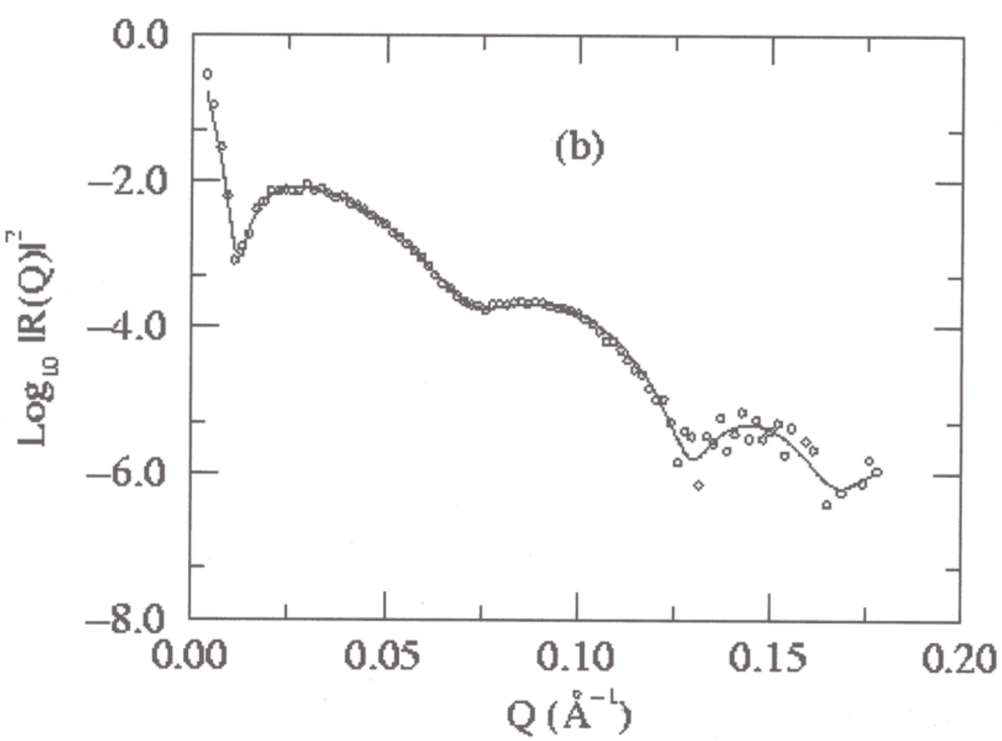
SUMMARY

- specular NR: $\rho(z)$ from $|r(Q_z)|^2$ - not unique
- recover information with contrast variation
  - variable reservoirs, magnetic reference layers...
    - C. F. Majkrzak, et al., *Langmuir* **19**, 7796 (2003)
    - S. A. Holt, et al., *Soft Matter* **5**, 2576 (2009)
  - inversion OR simultaneous model fitting
    - C. F. Majkrzak, et al. *Langmuir* **25**, 4154 (2009)
    - DiRefl, NCNR inversion software
    - Refl1D, NCNR simultaneous fitting software
- phase sensitive NR of P3HT:PCBM bulk heterojunction
  - increased PCBM at the interfaces - not ideal...
    - J. W. Kiel, et al., *Soft Matter* **6**, 641 (2010)
    - J. W. Kiel, et al., *J. Phys. Chem* **133**, 074902 (2010)
    - B. J. Kirby, et al. *Current Opinion in Colloid & Interface Science* **17**, 44 (2012)
- publications, software, online calculators, contact info
  - http://www.ncnr.nist.gov/programs/reflect/

FOR EXAMPLE...


(a)
6.0
4.0
2.0
0.0
−2.0
−4.0
ρ (10⁻⁶ Å⁻²)
−40
0
40
80
120
160
200
z (Å)


6
4
2
0
-2
-4
-6
-8
-10
ρ (10⁻⁶ Å⁻²)
0
40
80
120
160
z (Å)
Log R
0
-2
-4
-6
-8
0.0
0.2
Q (Å⁻¹)


(b)
0.0
−2.0
−4.0
−6.0
−8.0
Log₁₀ |R(Q)|²
0.00
0.05
0.10
0.15
0.20
Q (Å⁻¹)