Analyzing Neutron Specular Reflectivity

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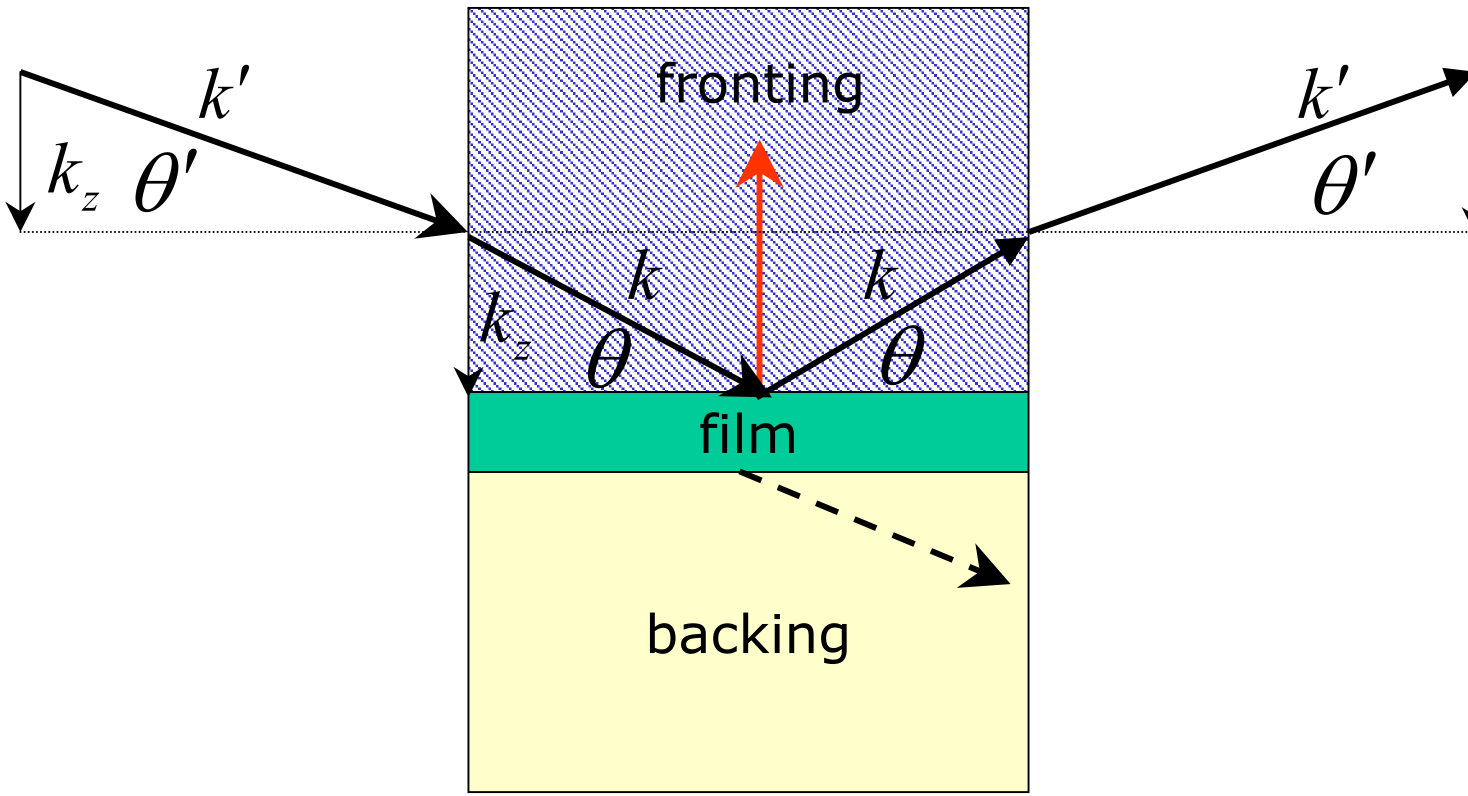
Recall:

Specular reflection: reflection $\angle$ = incidence $\angle$

$$Q_z = -2k_z = -2k\sin\theta = -2k'\sin\theta'$$



Recall:

$$\text{Reflectivity: } \mathrm{R}(Q_z) = \frac{\text{number of neutrons reflected at } Q_z}{\text{number of incident neutrons}} \leq 1$$

$$\text{Reflectivity coefficient: } \mathrm{r}(Q_z) = \frac{\text{reflected amplitude at } Q_z}{\text{incident amplitude}}$$

The reflection coefficient is a complex function:

$$\mathrm{r}(Q_z) = |\mathrm{r}(Q_z)|\, e^{i\phi(Q_z)}$$

$$\operatorname{Re} r(Q_z) = |\mathrm{r}(Q_z)| \cos\phi(Q_z), \quad \operatorname{Im} r(Q_z) = |\mathrm{r}(Q_z)| \sin\phi(Q_z)$$

What's measured $\mathrm{R}(Q_z) = |\mathrm{r}(Q_z)|^2$ What's calculated

Recall:

$$\bar{\rho}(z) = \frac{1}{S}\int \rho(x, y, z)\, dxdy = <\rho(x, y, z)>_{xy}$$

… determines the specular reflection from a film.

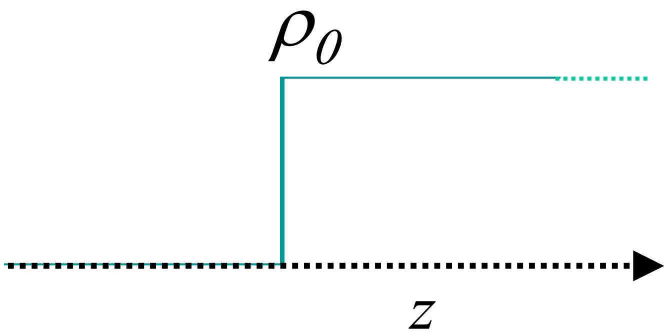
$$\text{… Now call } \bar{\rho}(z) = \underbrace{\rho(z)}_{\text{Scattering Length Density (SLD) profile}} \text{ …}$$

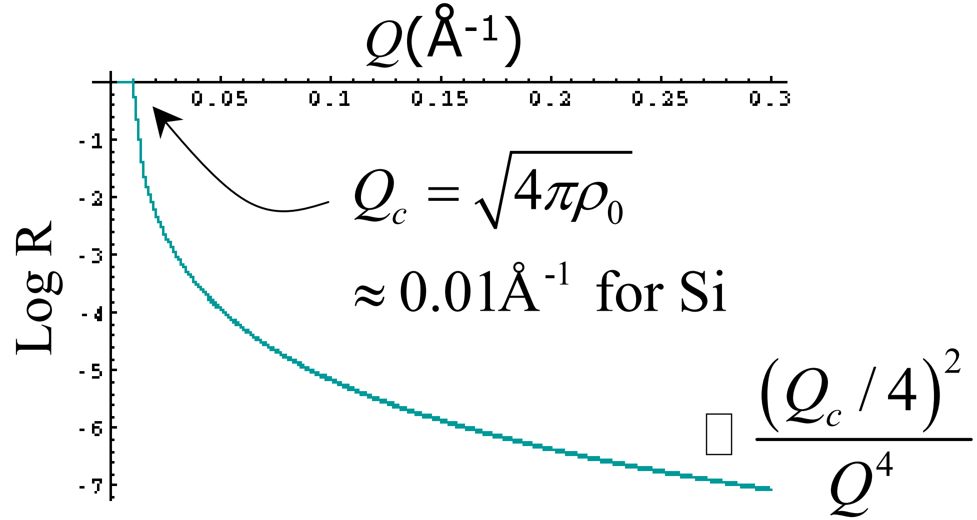
Also, since we're now in one dimension: $k_z = k,\ Q_z = Q = 2k$

$$\rho - \text{values for neutrons} = O(1)$$

$$\text{in units of } O(10^{-6}\,\text{Å}^{-2}) = O(10^{10}\text{cm}^{-2})$$

Fresnel Reflectivity:

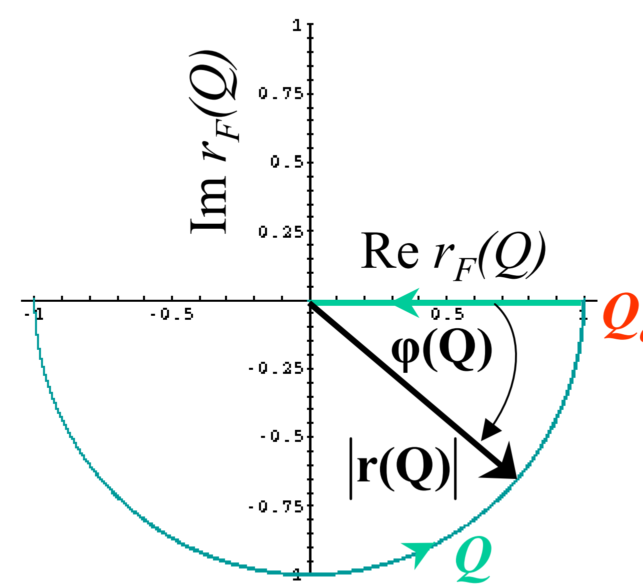




$$r_F(Q) = \frac{1-n(Q)}{1+n(Q)}, \quad n(Q) = \sqrt{1-\frac{Q_c^2}{Q^2}}$$

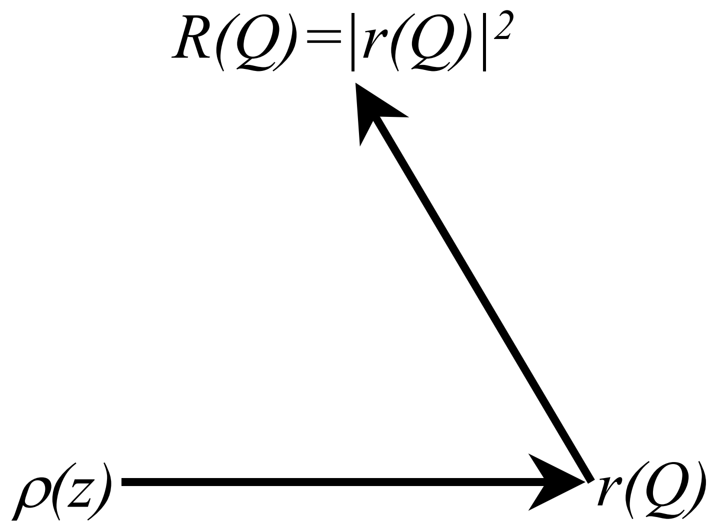
$$R_F(Q) = \left|r_F(Q)\right|^2 = \begin{cases} 1, & Q \le Q_c \\ \frac{n(Q)+n(Q)^{-1}-2}{n(Q)+n(Q)^{-1}+2}, & Q > Q_c \end{cases}$$

Argand diagram

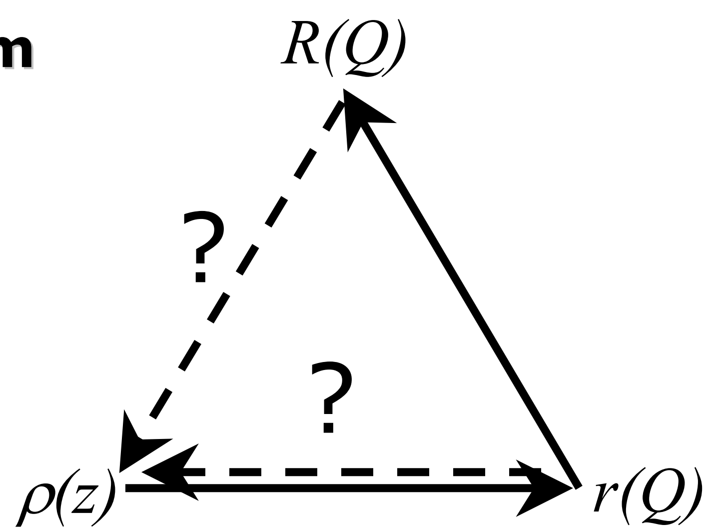


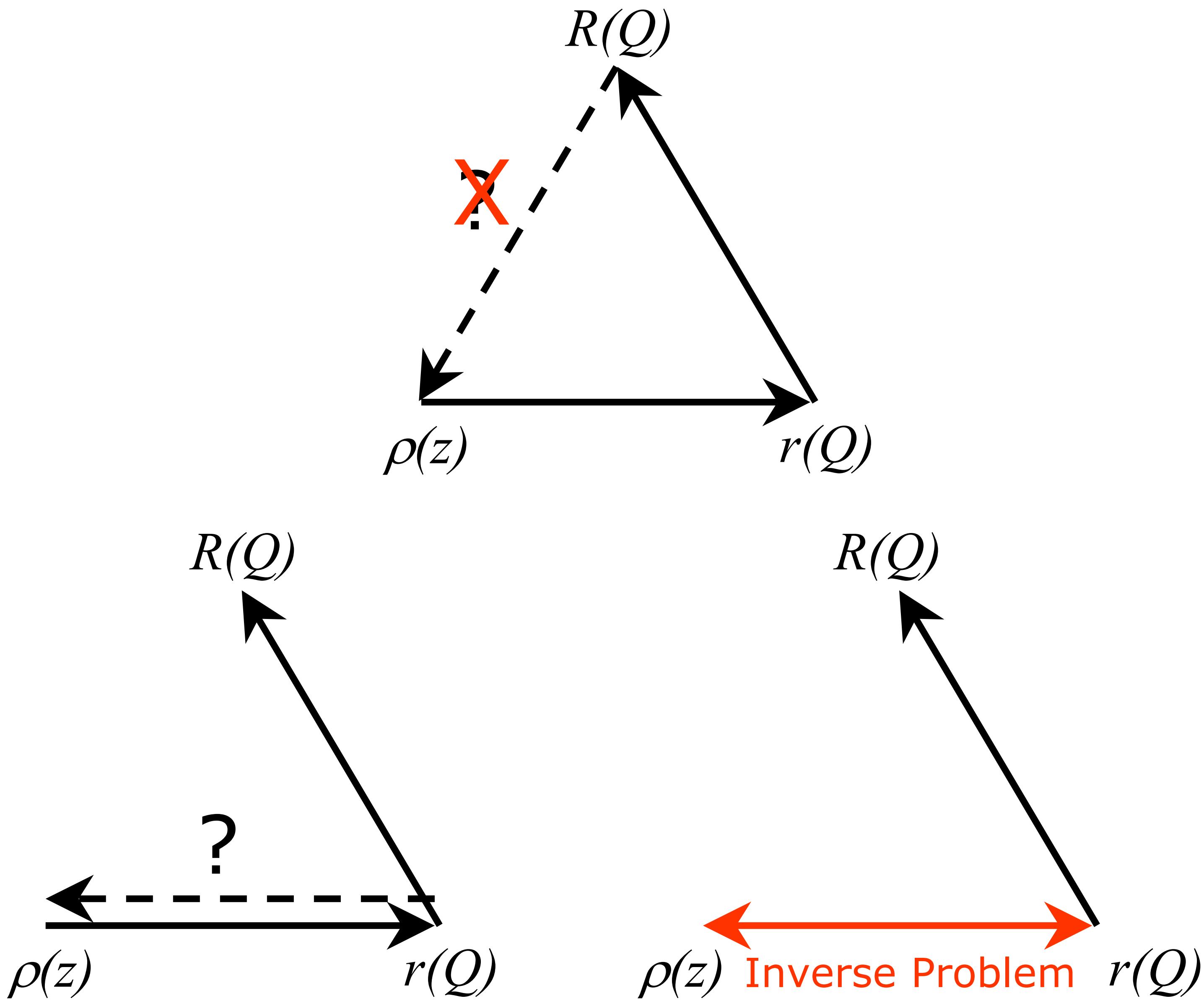
Reflectivity analysis falls into two broad problems:

Direct Problem



Inverse Problem




R(Q)
?
ρ(z)
r(Q)
R(Q)
?
ρ(z)
r(Q)
R(Q)
ρ(z)
Inverse Problem
r(Q)

Uniqueness:

$\rho(z) \longleftrightarrow r(Q)$

Inverse Problem

$\rho(z) \longrightarrow r(Q)$

Direct Problem (unique)

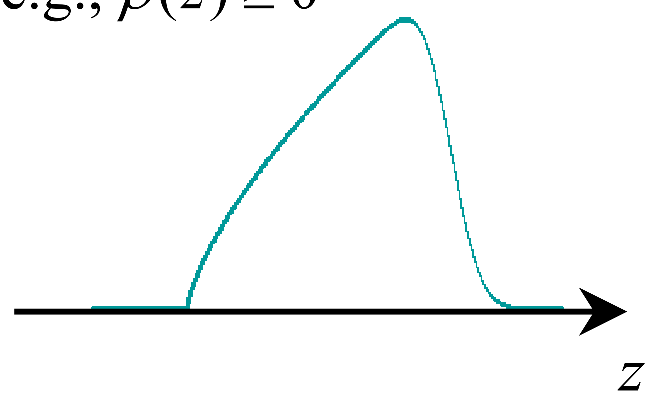
$\rho(z) \longleftarrow r(Q)$

Direct Problem (unique?)

Yes

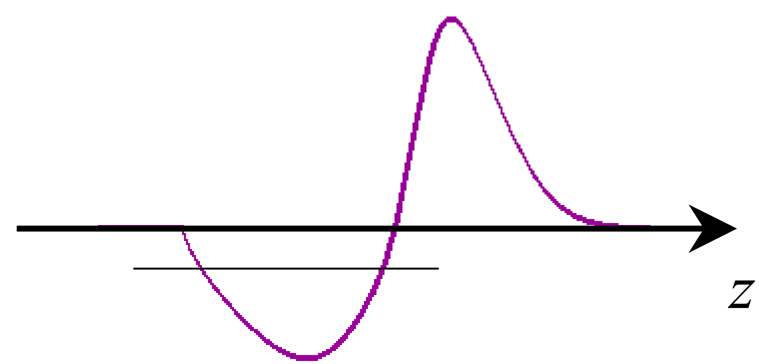
if $\rho(z)$ has no bound states

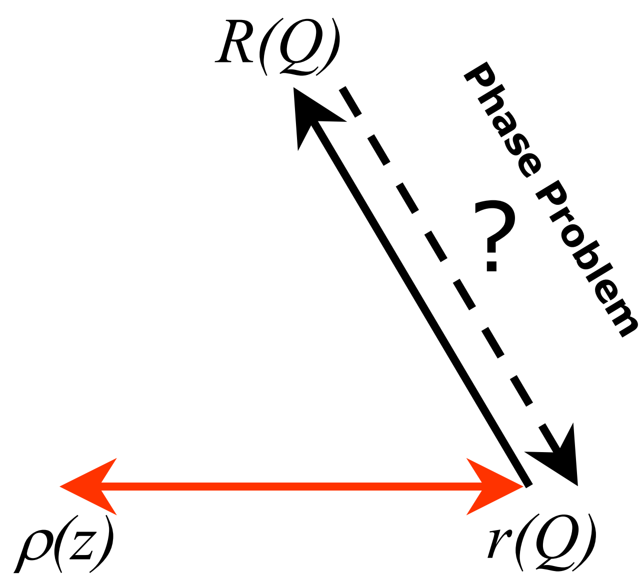
e.g., $\rho(z) \geq 0$



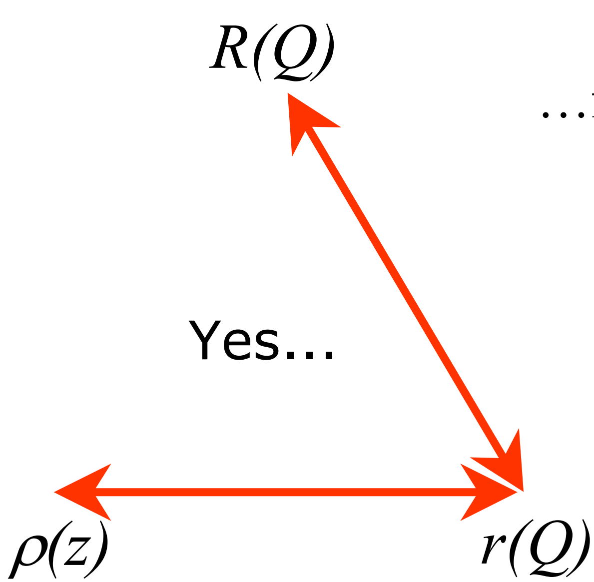
No

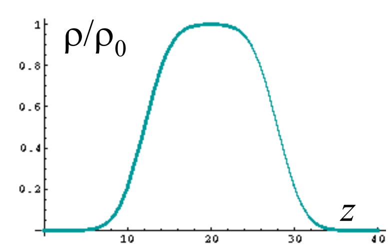
if $\rho(z)$ has bound states

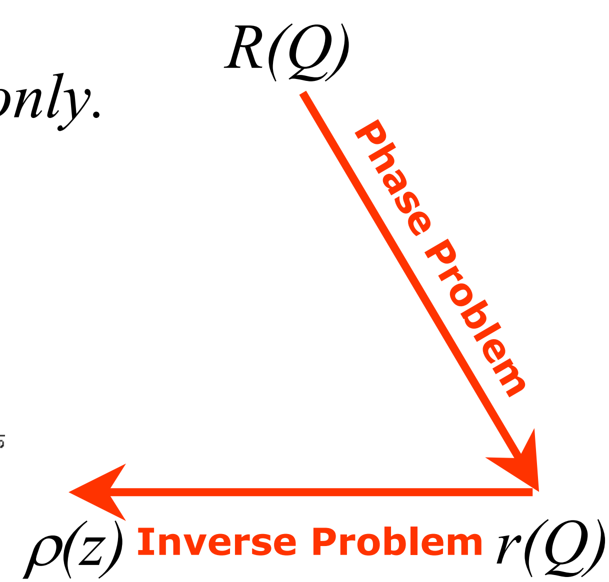




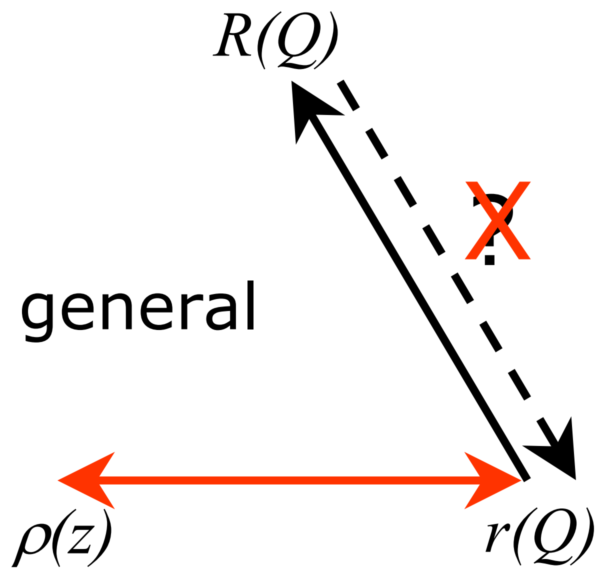
…for symmetric $\rho(z)$, *only*.







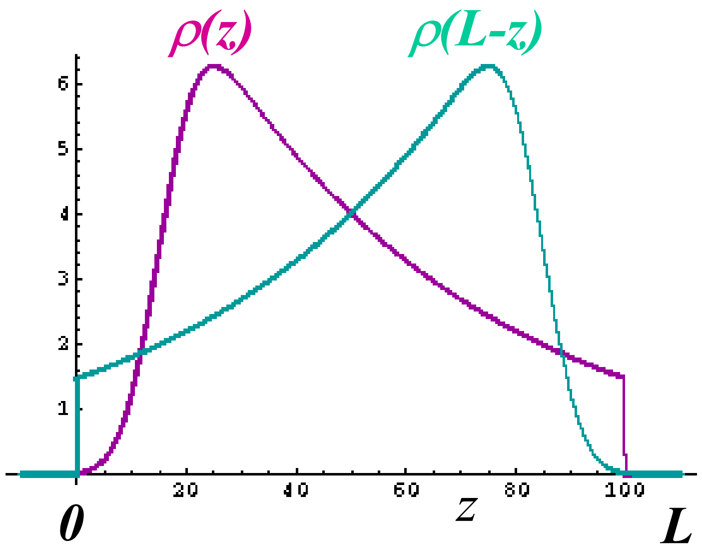
...but in general

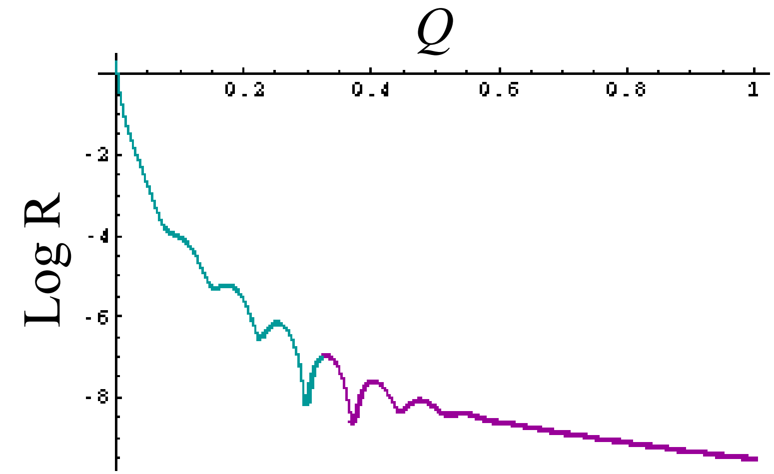


There exist families of $\rho(z)$ which produce different $r(Q)$ ... *but exactly the* same $R(Q)$; *i.e.,* which produce $r(Q)$ *having the same magnitude* but different *phases. We'*

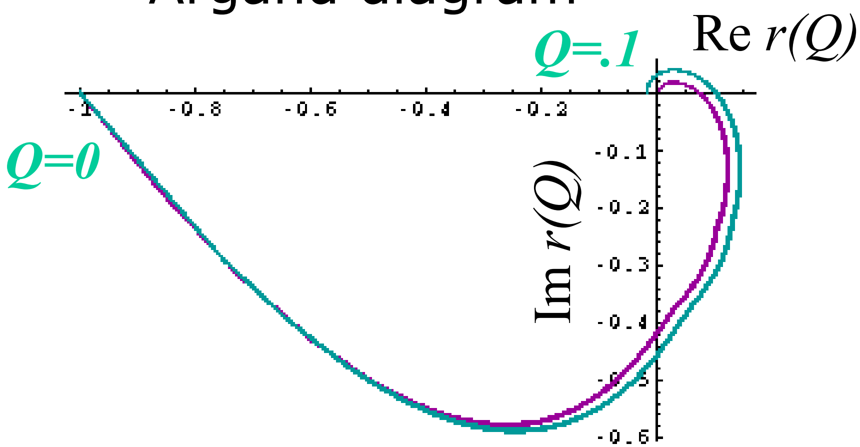
However, there are multiple measurement strategies for finding $r(Q)$, as we'll see later.

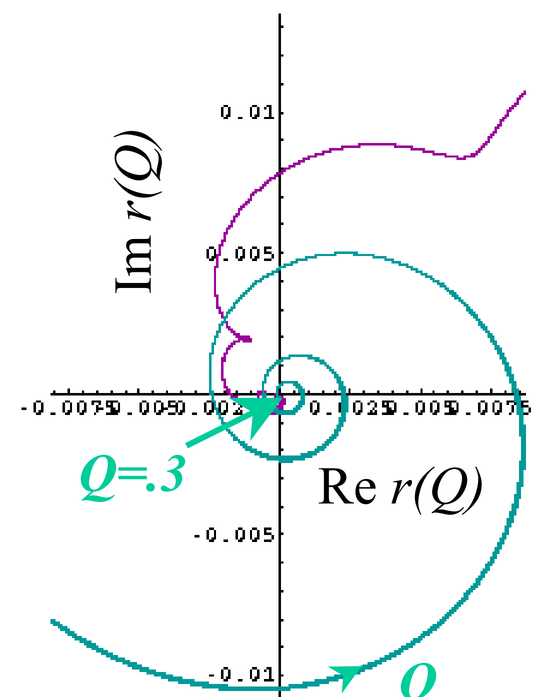
Ex. 1) Reversing $\rho(z)$:





Argand diagram





Ex. 2) Something less obvious:

For a given $r(Q)$, consider the transformation:

$$\tilde{r}(Q) = r(Q)\frac{i\kappa - Q}{i\kappa + Q}, \text{ for a real constant } \kappa \geq 0.$$

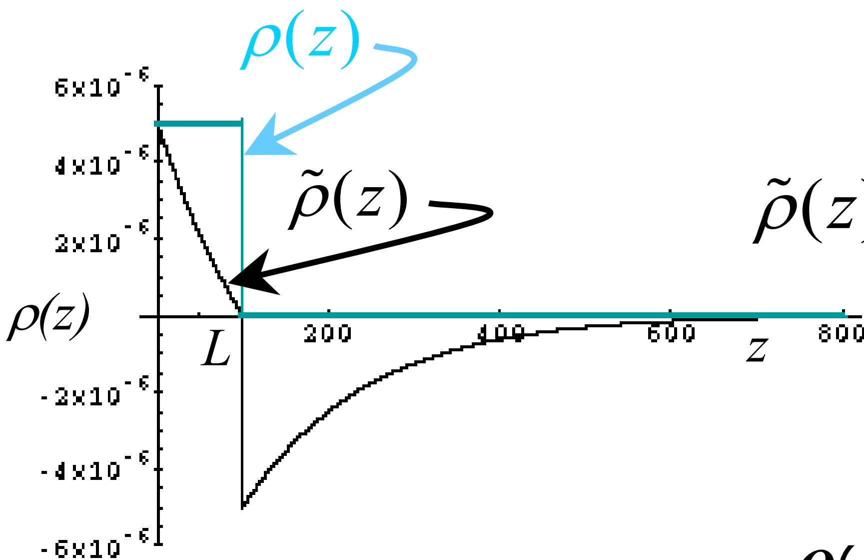
$$\text{Now } \left|\frac{i\kappa - Q}{i\kappa + Q}\right| = \frac{|i\kappa - Q|}{|i\kappa + Q|} = \frac{\sqrt{\kappa^2 + Q^2}}{\sqrt{\kappa^2 + Q^2}} = 1$$

$$\text{So } |\tilde{r}(Q)| = \left|r(Q)\frac{i\kappa - Q}{i\kappa + Q}\right| = |r(Q)|\left|\frac{i\kappa - Q}{i\kappa + Q}\right| = |r(Q)|$$

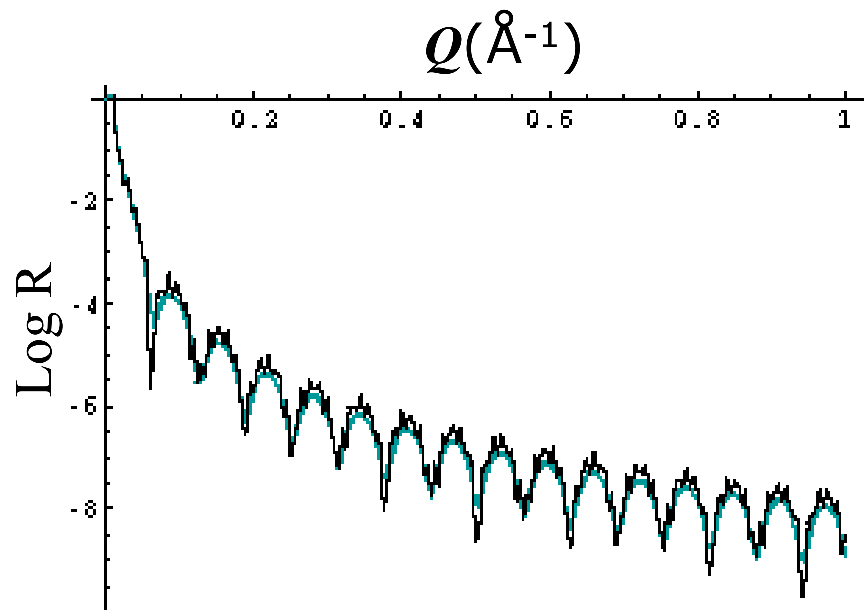
$$\text{i.e., } \tilde{r}(Q) = r(Q)\frac{i\kappa - Q}{i\kappa + Q} = |r(Q)|\,\mathrm{e}^{i\phi(Q)}\,\mathrm{e}^{i\chi(Q)} = |r(Q)|\,\mathrm{e}^{i[\phi(Q)+\chi(Q)]}$$

Is there a $\tilde{\rho}(z)$ corresponding to $\tilde{r}(Q)$?

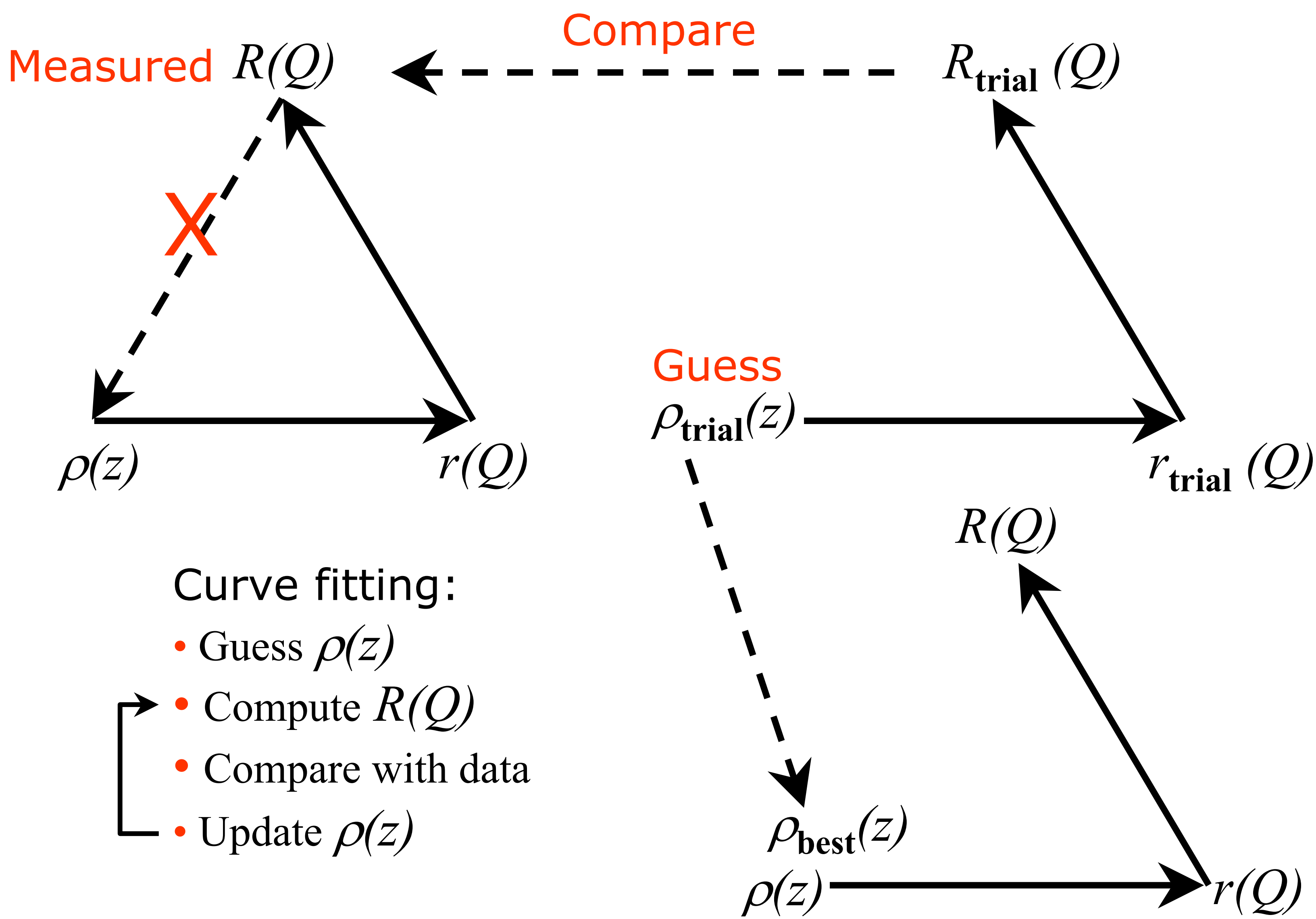
...Yes:



$$\tilde{\rho}(z) = \begin{cases} 0, & z < 0 \\ \rho_0\left(2\,\mathrm{e}^{-2\kappa z} - 1\right), & 0 \le z \le L \\ \rho_0\left(\mathrm{e}^{2\kappa L} - 1\right)\mathrm{e}^{-2\kappa z}, & L < z \end{cases}$$



PseudoInverse Problem (iterative direct problem):

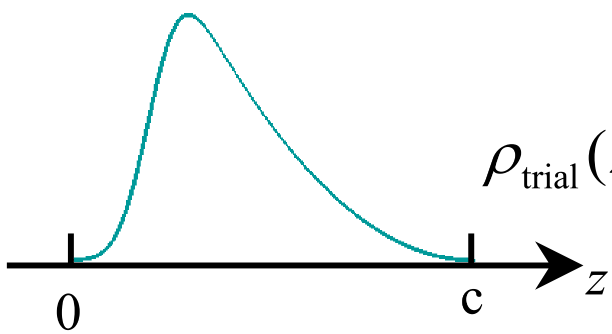


Curve fitting:

- Guess $\rho(z)$
- Compute $R(Q)$
- Compare with data
- Update $\rho(z)$

Two generic types of curve fitting:

1) Model fitting tests functions: $\rho_{\text{trial}}(z) = f(z; \underbrace{a, b, c, \ldots}_{\text{fit parameters}})$



$$\rho_{\text{trial}}(z) = a(b-z)^2[1+\text{erf}(z/c-d)]\Theta(z)\Theta(b-z)$$

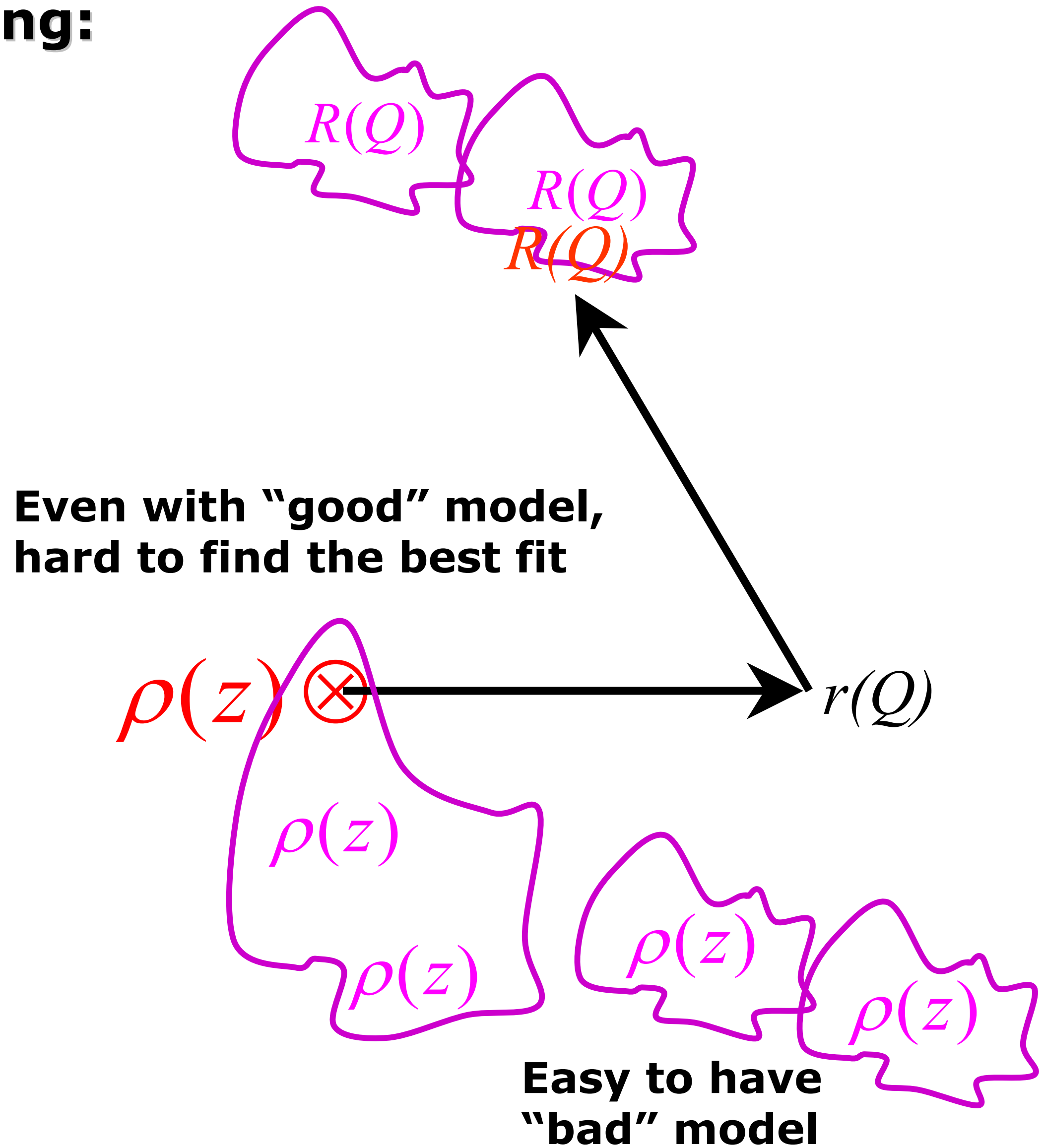
...best used to test theoretical predictions.

2) Model-independent fitting tests function spaces:

$$\rho_{\text{trial}}(z) = \sum_{n=0}^{N} \underbrace{A_n}_{\substack{\text{fit}\\\text{parameters}}} \underbrace{B_n(z)}_{\text{bases functions}} \begin{cases} \text{Fourier basis} \\ \text{B-spline basis (e.g., PBS)} \\ \vdots \end{cases}$$

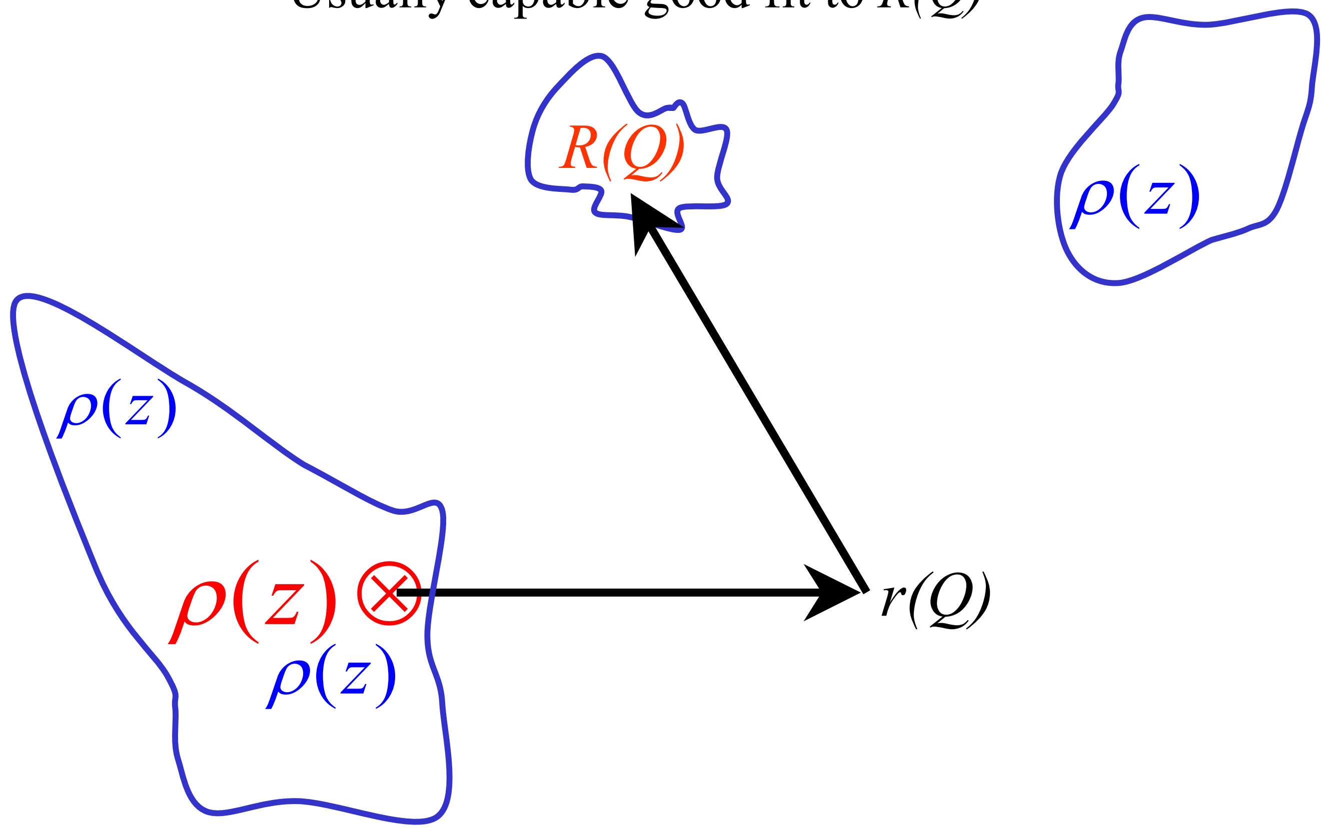
...best used to find sets of $\rho(z)$ consistent with data; not good for "finding" specific functional form.

1) Model fitting:



2) Model-independent fitting:

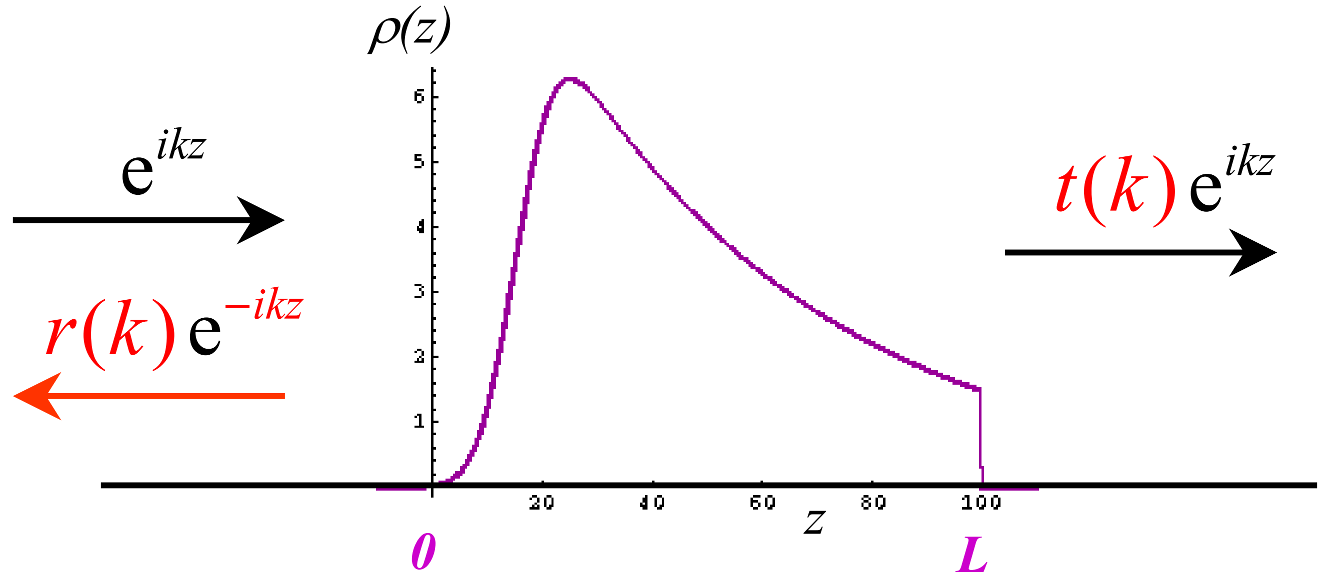
Usually capable good fit to *R(Q)*



Direct Problem

$$\rho(z) \rightarrow r(Q)$$

1) ***How to calculate reflectivity***
2) ***Some properties of r(Q)***



$$-\frac{d^2\psi(z,k)}{dz^2}+4\pi\rho(z)\psi(z,k)=k^2\psi(z,k)$$

$$\psi(z,k)=e^{ikz}+r(k)e^{-ikz}$$

for $z<0$

$$\psi(z,k)=t(k)e^{-ikz}$$

for $z>L$

$$\psi(z,k)=?$$

for $0\le z\le L$

$$-\frac{d^2\psi(z,k)}{dz^2}+4\pi\rho(z)\psi(z,k)=k^2\psi(z,k)$$

Exact: $$r(k)=\frac{4\pi}{2ik}\int_0^L e^{ikz}\rho(z)\underbrace{\psi(z,k)}_{\text{exact wavefunction}}dz$$

$$r_{BA}(k)=\frac{4\pi}{2ik}\int_0^L e^{ikz}\rho(z)\{\psi(z,k)\rightarrow e^{ikz}\}dz$$

$$=\frac{4\pi}{2ik}\int_0^L e^{2ikz}\rho(z)dz=\frac{4\pi}{iQ}\int_0^L e^{iQz}\rho(z)dz$$

Note: $r_{BA}(Q)\rightarrow\infty$ as $Q\rightarrow 0$ (bad)

Transfer Matrix:

$$\left.\begin{matrix} \psi(z,k) \\ \dfrac{d\psi(z,k)}{kdz} \end{matrix}\right\} \quad \overset{z=L}{\begin{pmatrix} 1 \\ i \end{pmatrix}} t(k)\,\mathrm{e}^{ikL} = \mathbf{M}(k,L) \overset{z=0}{\begin{pmatrix} 1+r(k) \\ i(1-r(k)) \end{pmatrix}}$$

$$\mathbf{M}(L,k) = \begin{pmatrix} A(L,k) & B(L,k) \\ C(L,k) & D(L,k) \end{pmatrix}, \quad AD - BC = 1$$

$$\frac{d\mathbf{M}(z,k)}{dz} = \begin{pmatrix} 0 & 1 \\ \dfrac{4\pi\rho(z)}{k} - k & 0 \end{pmatrix} \mathbf{M}(z,k), \quad \mathbf{M}(0,k) = \mathbf{1}$$

$\therefore\ \rho(z)$ determines $\mathbf{M}(L,k)$

$\mathbf{M}(L,k)$ is real if $\rho(z)$ is real

From now on: $A(L,k) = A(k) = A$, etc.

$$r = \frac{B + C + i(D - A)}{B - C + i(D + A)}$$

$$= -\frac{\alpha - \beta + 2i\gamma}{\alpha + \beta + 2}$$

$$\alpha = A^2 + C^2$$

$$\beta = B^2 + C^2$$

$$\gamma = AB - CD, \quad \gamma^2 = \alpha\beta - 1$$

$$\mathrm{Re}\, r = \frac{\beta - \alpha}{\alpha + \beta + 2}, \quad \mathrm{Im}\, r = \frac{-2\gamma}{\alpha + \beta + 2}$$

$$R(k) = \left| r(k) \right|^2 = \frac{\Sigma - 2}{\Sigma + 2},$$

$$\Sigma = \alpha + \beta$$

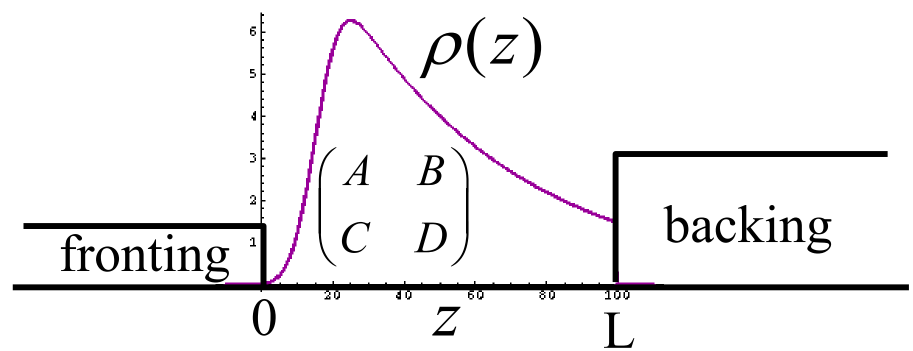
One can show… for "most" $\rho(z)$:

- $\mathrm{Re}\, r(0) = -1$
- $\mathrm{Im}\, r(0) = 0$ (i.e., phase of $r(0) = -\pi$)
- $\lim_{k \to \infty} r(k) = 0$

With non-vacuum fronting and backing, the forms remain the same:

$$r = -\frac{\tilde{\alpha} - \tilde{\beta} + 2i\tilde{\gamma}}{\tilde{\alpha} + \tilde{\beta} + 2} \qquad R(k) = \left| r(k) \right|^2 = \frac{\Sigma - 2}{\Sigma + 2}, \ \Sigma = \tilde{\alpha} + \tilde{\beta}$$

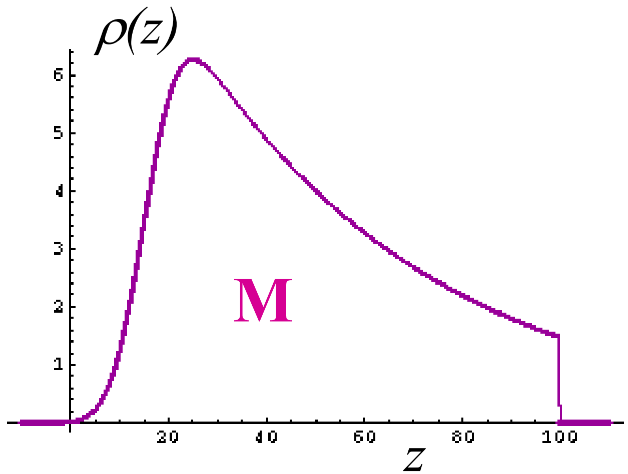
$$\tilde{\alpha} = \frac{n_b}{n_f} A^2 + \frac{1}{n_f n_b} C^2$$

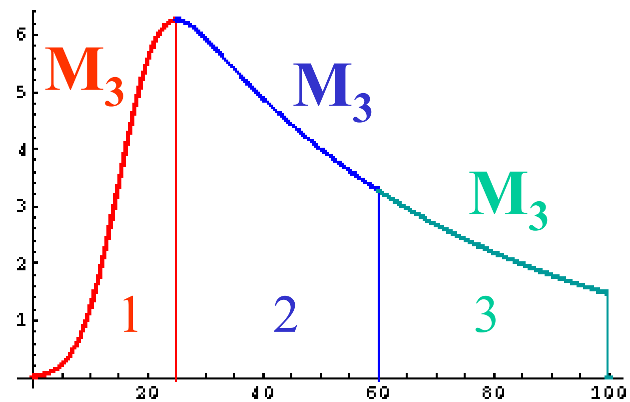


$$\tilde{\beta} = n_f n_b B^2 + \frac{n_f}{n_b} C^2$$

$$\tilde{\gamma} = n_b AB - \frac{1}{n_b} CD, \quad \tilde{\gamma}^2 = \tilde{\alpha}\tilde{\beta} - 1 \qquad n_i(k) = \sqrt{1 - \frac{4\pi\rho_i}{k^2}}, \quad i = f, b$$

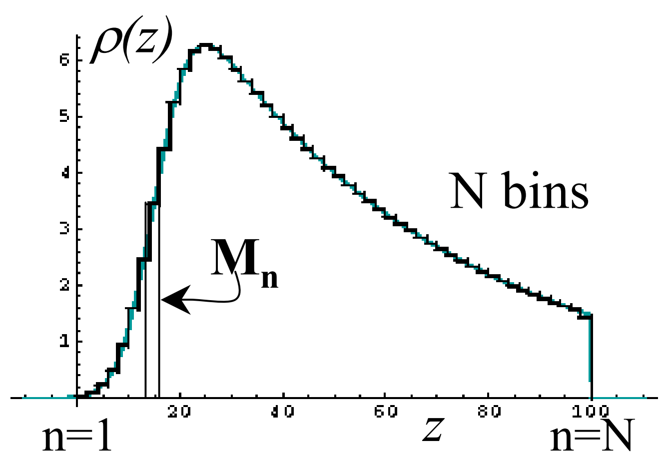
Decomposition property of M:





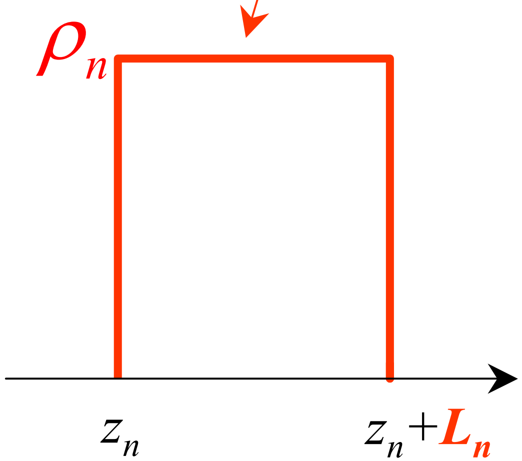
$$\mathbf{M} = \mathbf{M}_3\mathbf{M}_2\mathbf{M}_1$$

Rectangular Rendering:



$$\mathbf{M} = \mathbf{M}_N \cdots \mathbf{M}_n \cdots \mathbf{M}_2\mathbf{M}_1$$

$$\mathbf{M} = \mathbf{M}_N \cdots \mathbf{M}_n \cdots \mathbf{M}_2 \mathbf{M}_1$$

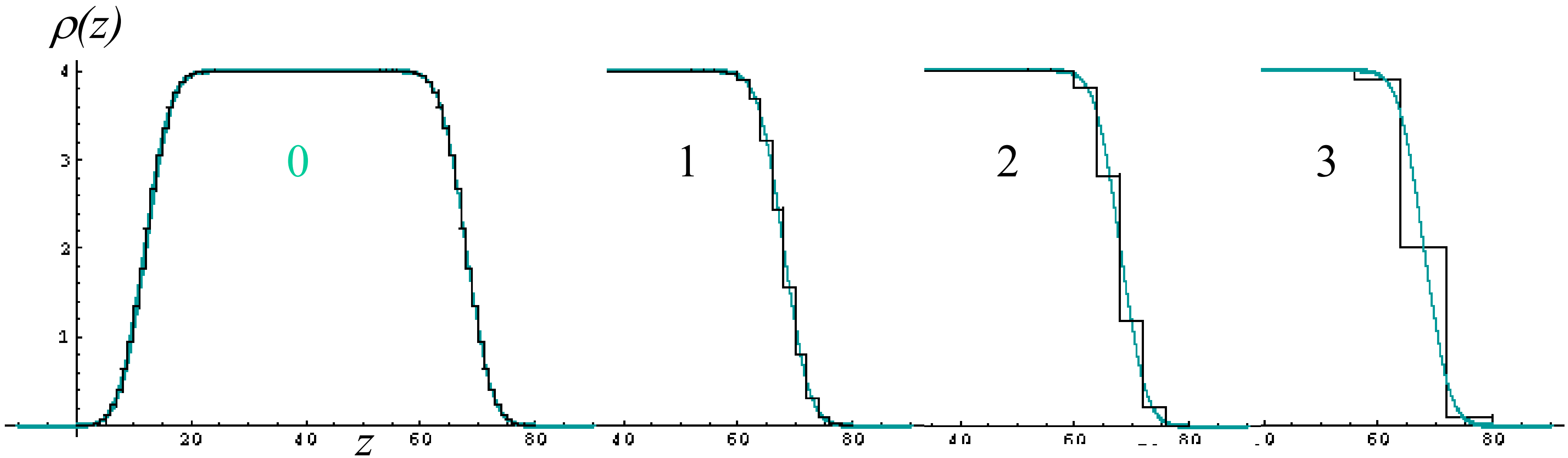


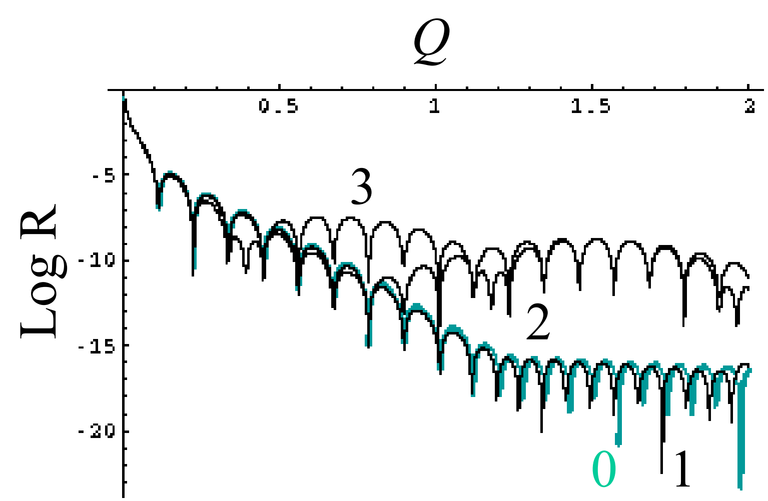
$$\mathbf{M}_n(k) = \begin{pmatrix} \cos(\kappa_n L_n) & \frac{k}{\kappa}\sin(\kappa_n L_n) \\ -\frac{\kappa}{k}\sin(\kappa_n L_n) & \cos(\kappa_n L_n) \end{pmatrix}$$

$$\kappa_n = \sqrt{k^2 - 4\pi\rho_n}$$

For binned $\rho(z)$, $r(k)$ also can be computed using the Parratt recursion formula; it's a bit more efficient than the transfer matrix and is commonly used in fitting programs.

Rendering penalty

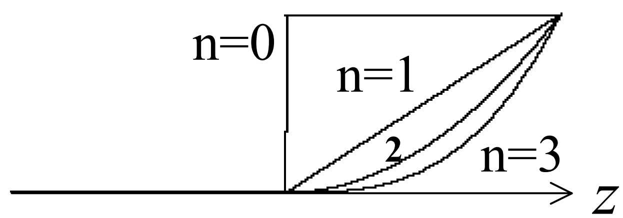


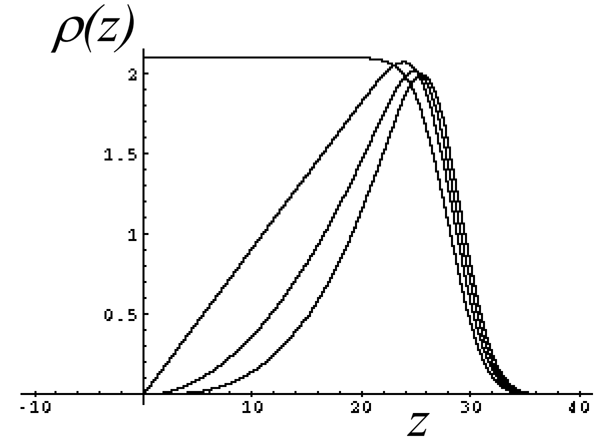


To avoid serious rendering penalty, use $\Delta z \le Q_{\max}$.

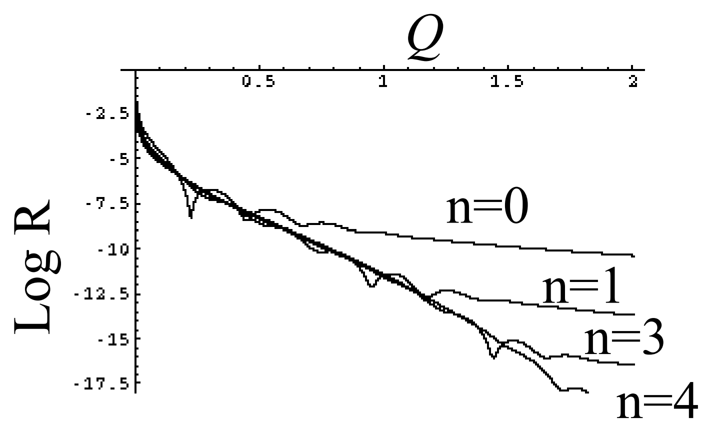
Edge features of $\rho(z)$ determine large-Q behavior of $R(Q)$.

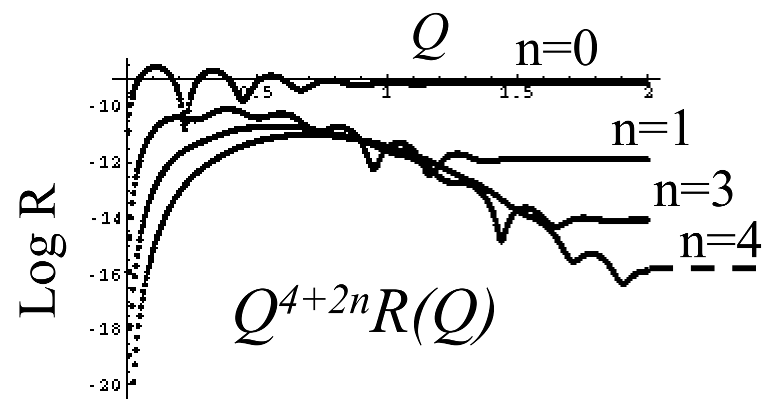
$$\Delta\rho(z) \propto z^n \mathrm{UnitStep}(z)$$





$$R(Q) \sim Q^{-2(n+2)} \text{ as } Q \rightarrow \infty$$





The "sharpest" edge in $\rho(z)$ determines $R(Q)$ as $Q \rightarrow \infty$

...usually the single-crystalline substrate.

Phase Determination and The Inverse Problem

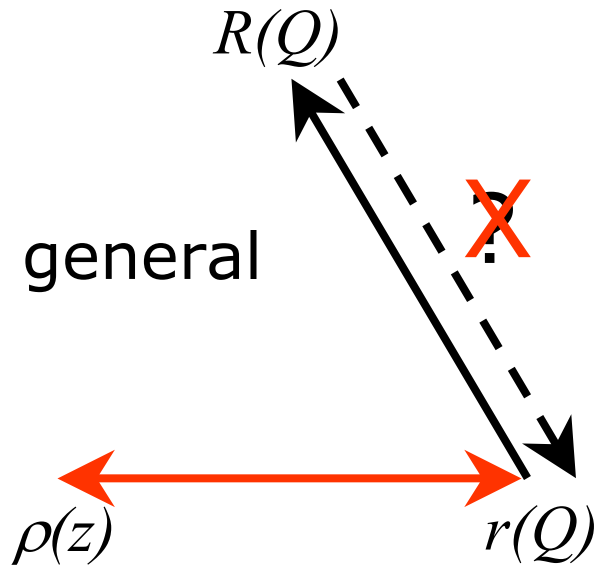
(“phase-inversion”)

1) Obtain $r(k)$ from reflectivity measurements
2) Obtain $\rho(z)$ from $r(k)$

1) Obtain *r(k)* from reflectivity measurements

Recall:

…in general

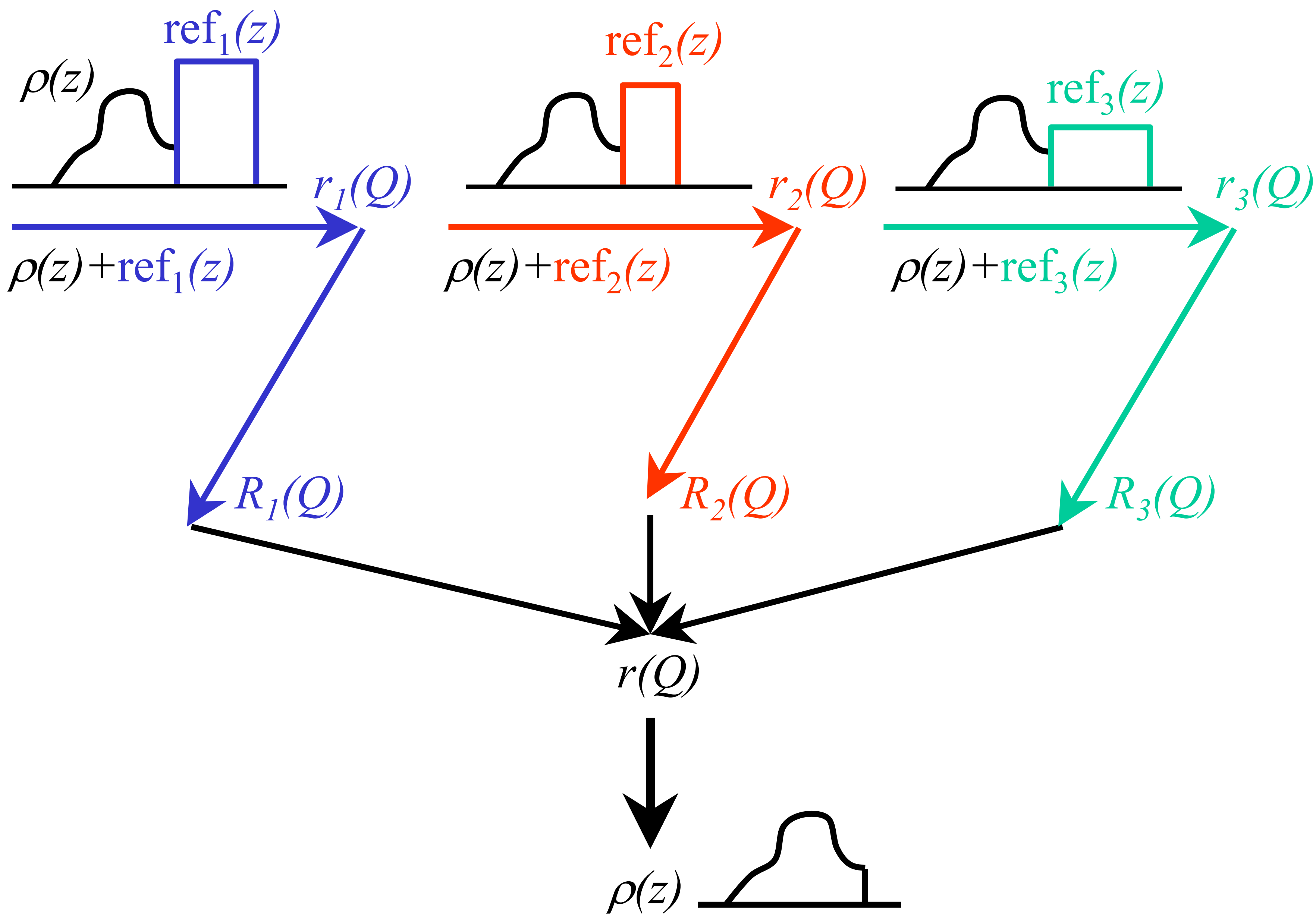


There exist large families of $\rho(z)$ which produce the different $\boldsymbol{r(Q)}$ … *but exactly the same* $\boldsymbol{R(Q)}$.

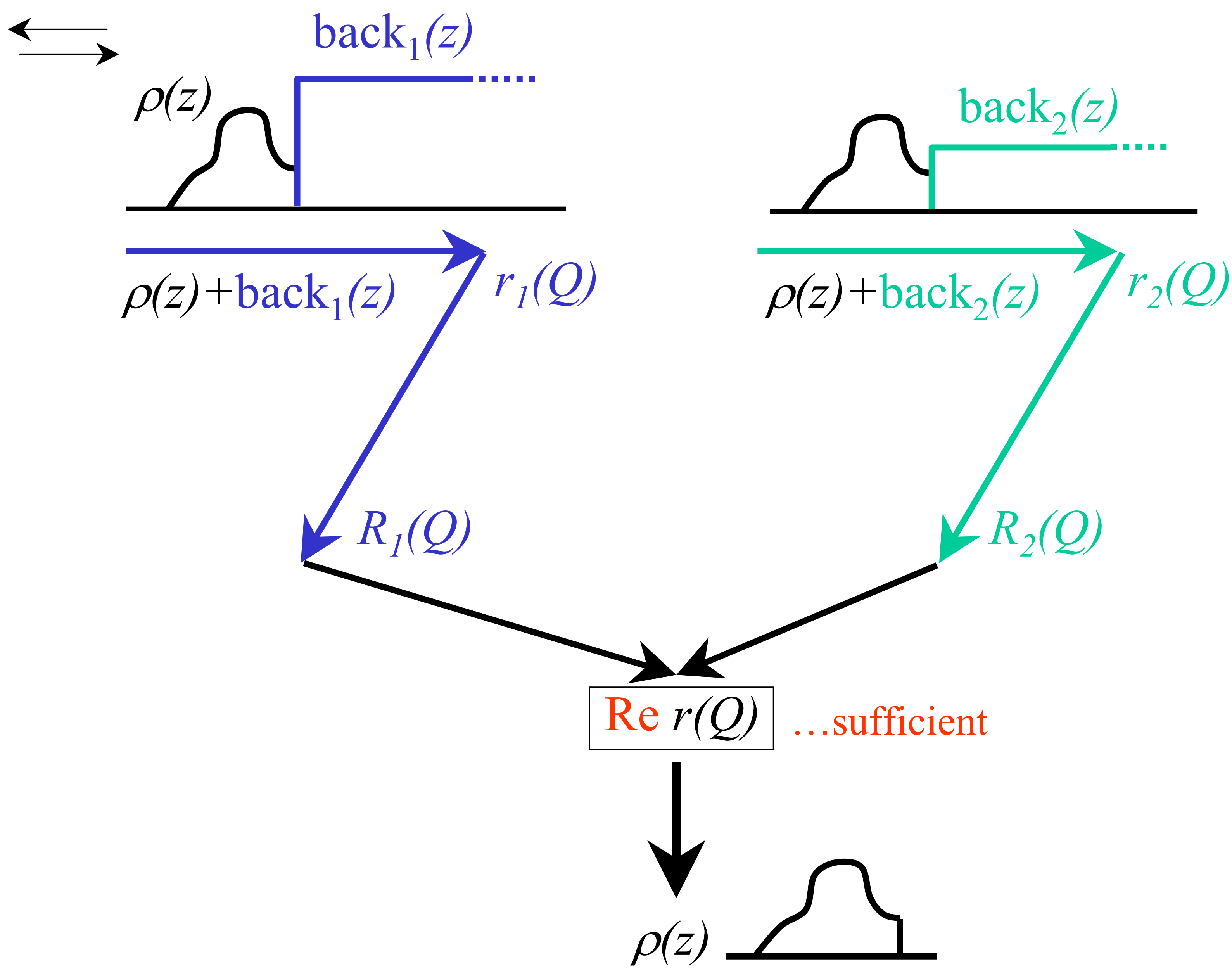
However, multiple measurement strategies exist for finding $r(Q)$.

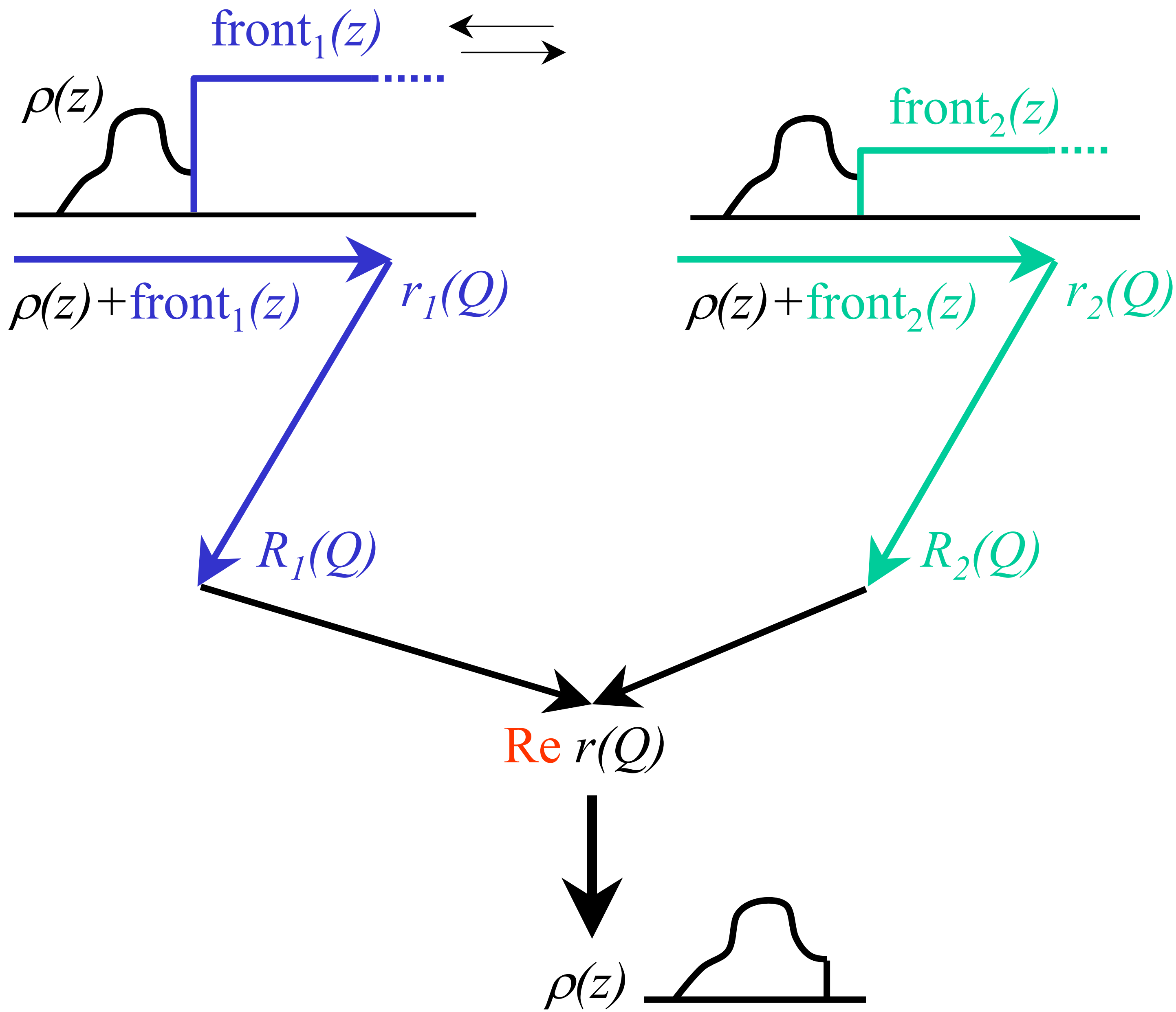
The idea is to combine the unknown $\rho(z)$ with <u>known</u> “reference” $\rho(z)$.

Three-measurement method:



Two-measurement method:





front$_1(z)$
$\rho(z)$
$\rho(z)$+front$_1(z)$
$r_1(Q)$
$R_1(Q)$
front$_2(z)$
$\rho(z)$+front$_2(z)$
$r_2(Q)$
$R_2(Q)$
Re $r(Q)$
$\rho(z)$

2) Obtain $\rho(z)$ from $r(k=Q/2)$

First, from the known $r(k)$, *construct*

$$G(2z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{-2ikz} r(k)\,dk$$

… and consider the Born approximation:

$$r(k) \approx r_{BA}(k) = \frac{4\pi}{2ik}\int_0^L \mathrm{e}^{2ikz}\rho(z)\,dz$$

$$G(2z) \approx G_{BA}(2z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{-2ikz} r_{BA}(k)\,dk$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{-2ikz}\left[\frac{4\pi}{iQ}\int_0^L \mathrm{e}^{2ik\zeta}\rho(\zeta)\,d\zeta\right]dk = -8\pi\int_0^z \rho(\zeta)\,d\zeta$$

$$\text{So then,}\quad \rho(z) = \frac{-1}{8\pi}\frac{dG_{BA}(2z)}{dz}$$

Thus in the BA, we retrieve $\rho(z)$ from the Fourier transform of $r(k)$ ... no surprise. In general, construct:

$$G(z+\zeta)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{e}^{-ik(z+\zeta)}r(k)dk$$

Then, with $\mathrm{G}(z+\zeta)$ as input, solve the GLM equation:

$$K(z,\zeta)+G(z+\zeta)+\int_{-z}^{z}K(z,\zeta')G(\zeta'+\zeta)d\zeta'=0$$

for $K(z,\zeta)$, and then, finally

$$\boxed{\rho(z)=\frac{1}{2\pi}\frac{dK(z,z)}{dz}}$$

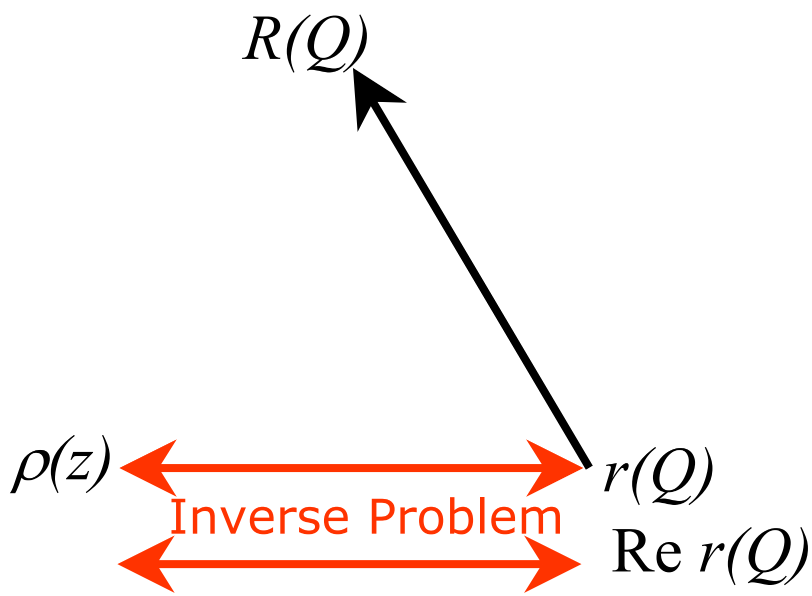
as if $K(z,z)$ where $G_{BA}(2z)$.

A side note: for our $\rho(z)$

$$G(z+\zeta)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{e}^{-ik(z+\zeta)}r(k)dk$$

$$=\frac{2}{\pi}\int_0^{\infty}\cos[k(z+\zeta)]\underbrace{\mathrm{Re}\,r(k)}_{\text{2 measurements}}dk=-\frac{2}{\pi}\int_0^{\infty}\sin[k(z+\zeta)]\,\mathrm{Im}\,r(k)dk$$

Thus knowledge of $\mathrm{Re}\,r(k)$ is sufficient for inversion.



Surround variation phase inversion:

1) Determine $\operatorname{Re} r(Q)$ from by surround variation:

2 reflectivity measurments

2) Compute $G(z+\zeta) = \dfrac{2}{\pi}\displaystyle\int_0^{\frac{Q_{max}}{2}} \cos[k(z+\zeta)]\operatorname{Re} r(k)\,dk$

3) Solve $K(z,\zeta) + G(z+\zeta) + \displaystyle\int_{-z}^{z} K(z,\zeta')G(\zeta'+\zeta)\,d\zeta' = 0$

Then $\rho(z) = \dfrac{1}{2\pi}\dfrac{dK(z,z)}{dz}$

Q-range truncation effects:

$$G(x) = \frac{2}{\pi}\int_0^{Q_{max}/2} \cos(kx)\,\mathrm{Re}\,r(k)\,dk$$