Overview of X-ray Reflectivity and Diffuse Scattering from Liquid Surfaces

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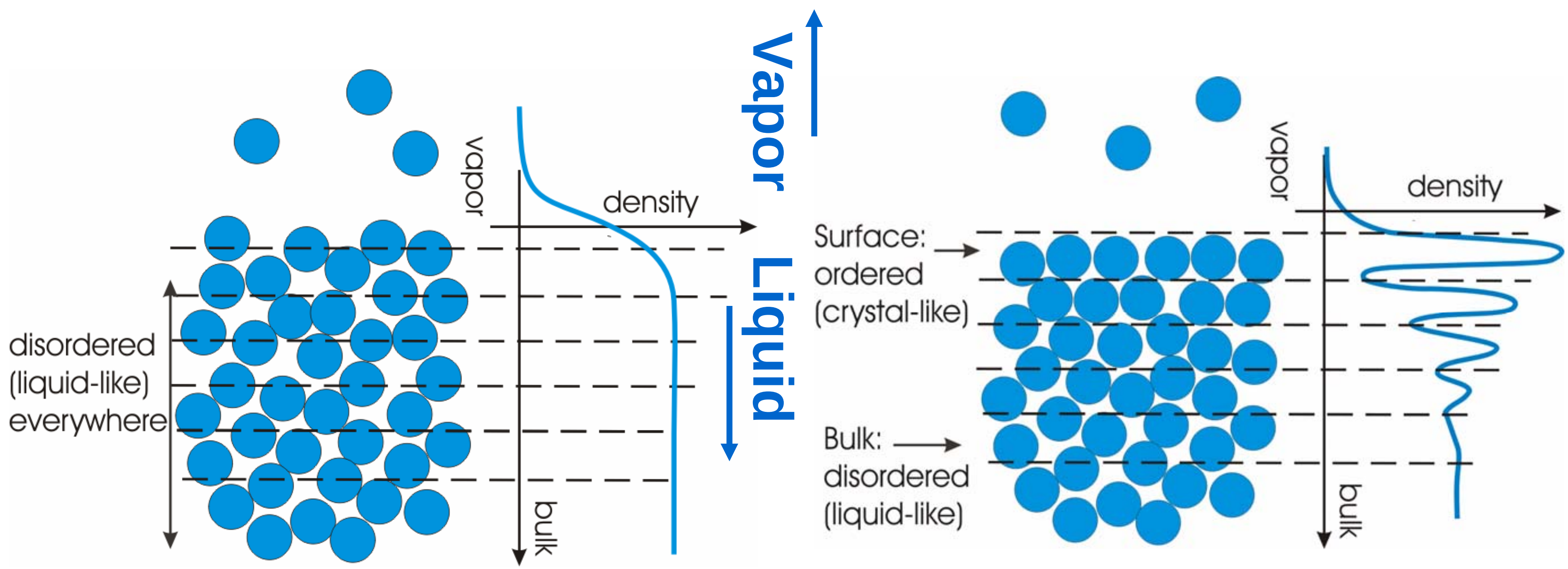
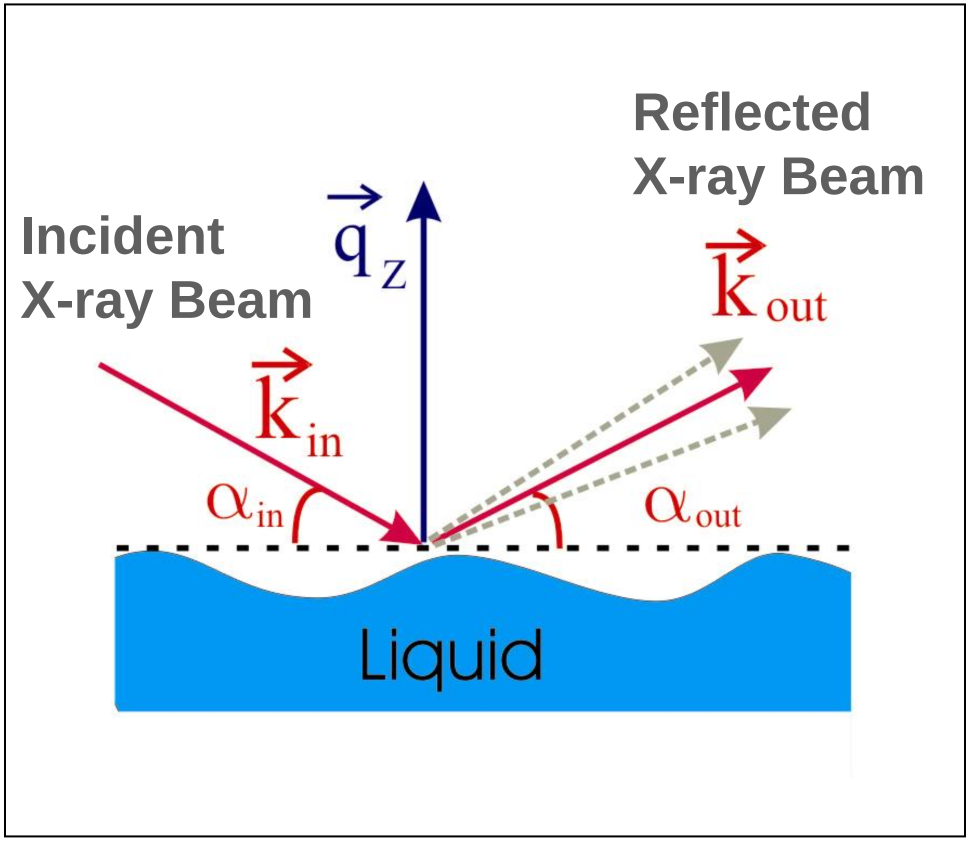
Recently discovered surface-induced layering in metallic liquids: ordering in disordered system



Disordered Interface (classical Van-der-Vaals treatment)

Ordered Interface: Surface-Induced Layering

X-ray Reflectivity: a probe of near-surface structure on atomic scale



Reflectivity from solid surfaces:

Surface profiles are static:

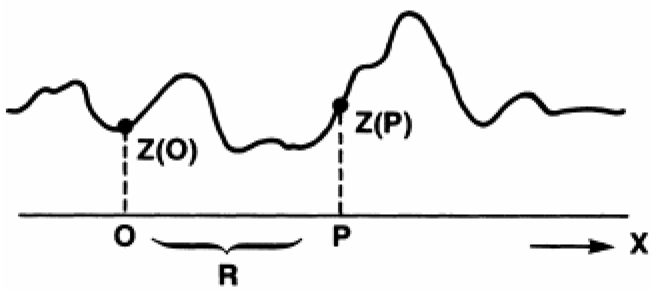
Low thermal diffuse scattering surrounding strong truncation rods/Bragg peaks

Reflectivity from liquid surfaces:

Thermal capillary fluctuations: height-height correlation function diverges logarithmically, roughness scales as ~ T/γ

Capillary fluctuations contribute to significant diffuse scattering

Scattering from rough surfaces: height-height correlation function

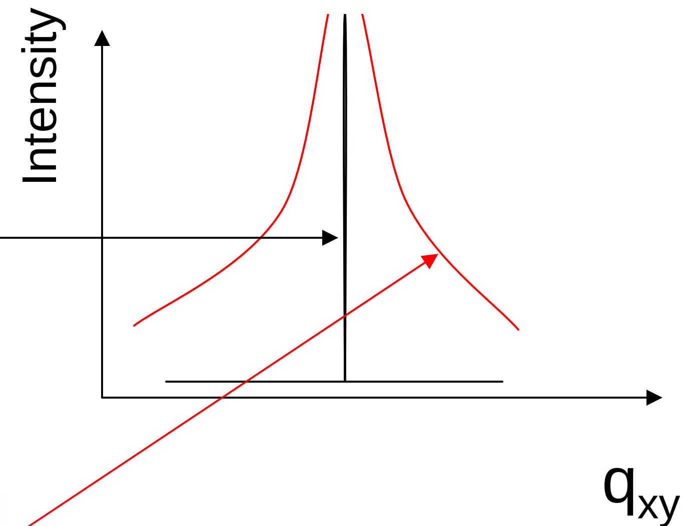


$$\langle [z(x',y') - z(x,y)]^2 \rangle = g(R)$$

$$R \equiv (x'-x, y'-y)$$

Smooth surfaces (atomically flat solids):

$$\mathrm{g(R)} = 0 \text{ and } \frac{d\sigma}{d\Omega} \approx \frac{1}{q_z^4}\delta(q_x)\delta(q_y)$$



Liquid Surfaces:

$$\mathrm{g(R)} = \mathrm{A} + \mathrm{B}\ \ln(\mathrm{R}) \text{ and } \frac{d\sigma}{d\Omega} \approx \frac{1}{q_z^4}\frac{1}{q_{xy}^{2-\eta}}$$

where $\eta = \frac{k_B T}{2\pi\gamma} q_z^2$

"capillary exponent"

Sinha et al., Phys. Rev. B 38, 2297 (1988)

Scattering from liquid surfaces

Scattering cross-section:

$$\frac{d\sigma}{d\Omega} = \frac{A_0}{\sin^2\alpha}\left(\frac{q_c}{2}\right)^4 \frac{1}{8\pi q_z^2}\left|\Phi(q_z)\right|^2 \left(\frac{1}{q_{\max}}\right)^{\eta} \frac{\eta}{q_{xy}^{2-\eta}}$$

Experimentally measured reflectivity:

$$R(q_z) = R_F(q_z)\left|\Phi(q_z)\right|^2 \int_{res} \left(\frac{1}{q_{\max}}\right)^{\eta} \frac{\eta}{q_{xy}^{2-\eta}}\, dq_x dq_y$$

Fresnel Reflectivity

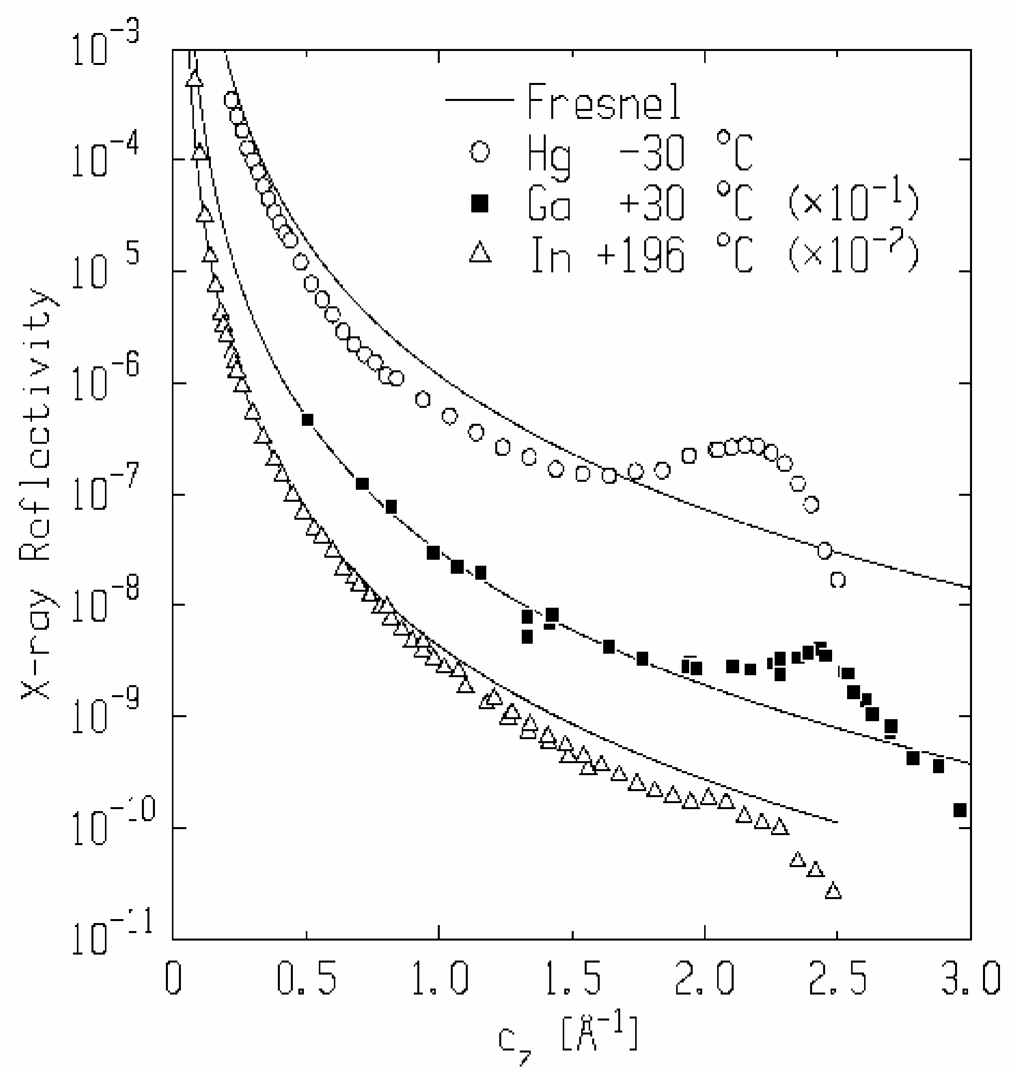
$$R(q_z) \sim \left(\frac{q_c}{2q_z}\right)^4$$

Surface Structure Factor

$$\Phi(q_z) = \frac{1}{\rho_\infty}\int dz \frac{\langle d\rho(z)\rangle}{dz}\exp(\imath q_z z)$$

Capillary exitations * Resolution function

Is layering in In weaker than in Ga and Hg?

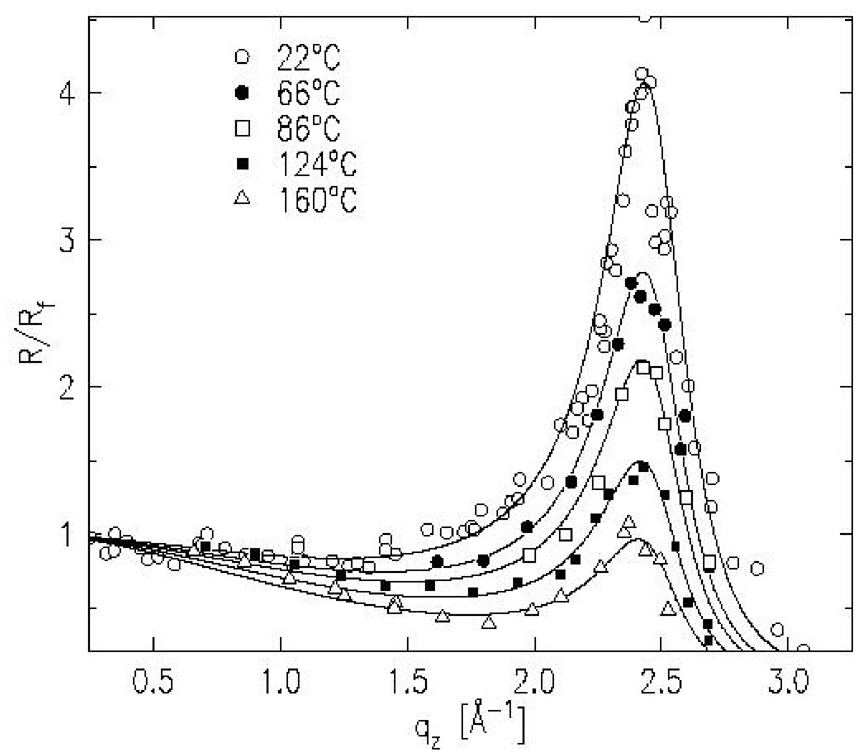


- Quasi-Bragg peak is evidence of layering
- Layering for In appears to be weaker than for Hg and Ga
- After thermal effects are removed, surface structure factor is <u>the same</u> for all three metals!

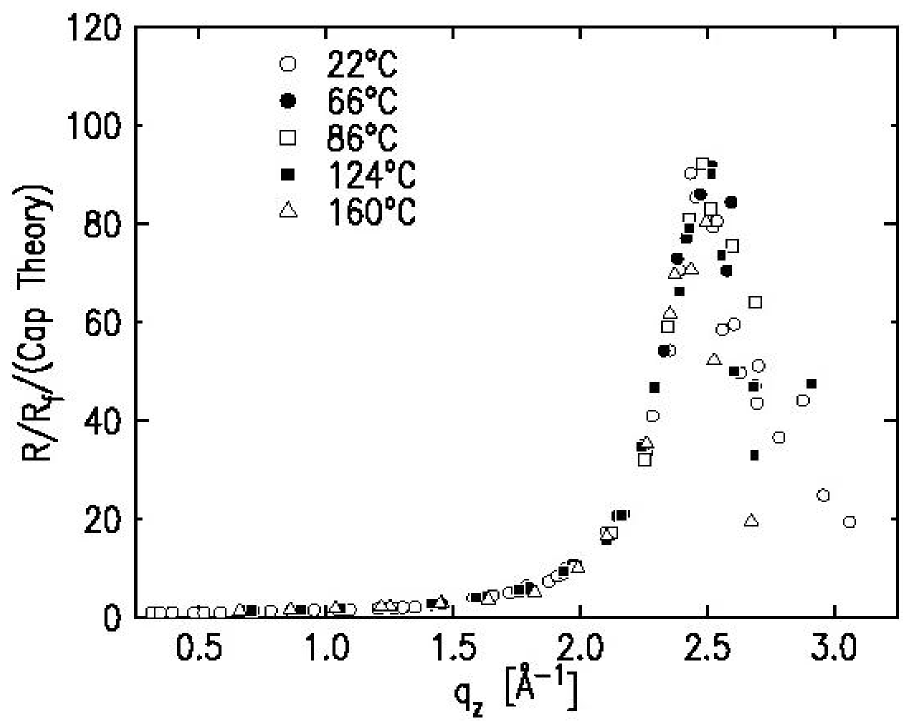
Tostmann et al., Phys. Rev. B **59**, 783 (1999)

Capillary excitations are T-dependent, intrinsic surface structure is NOT!

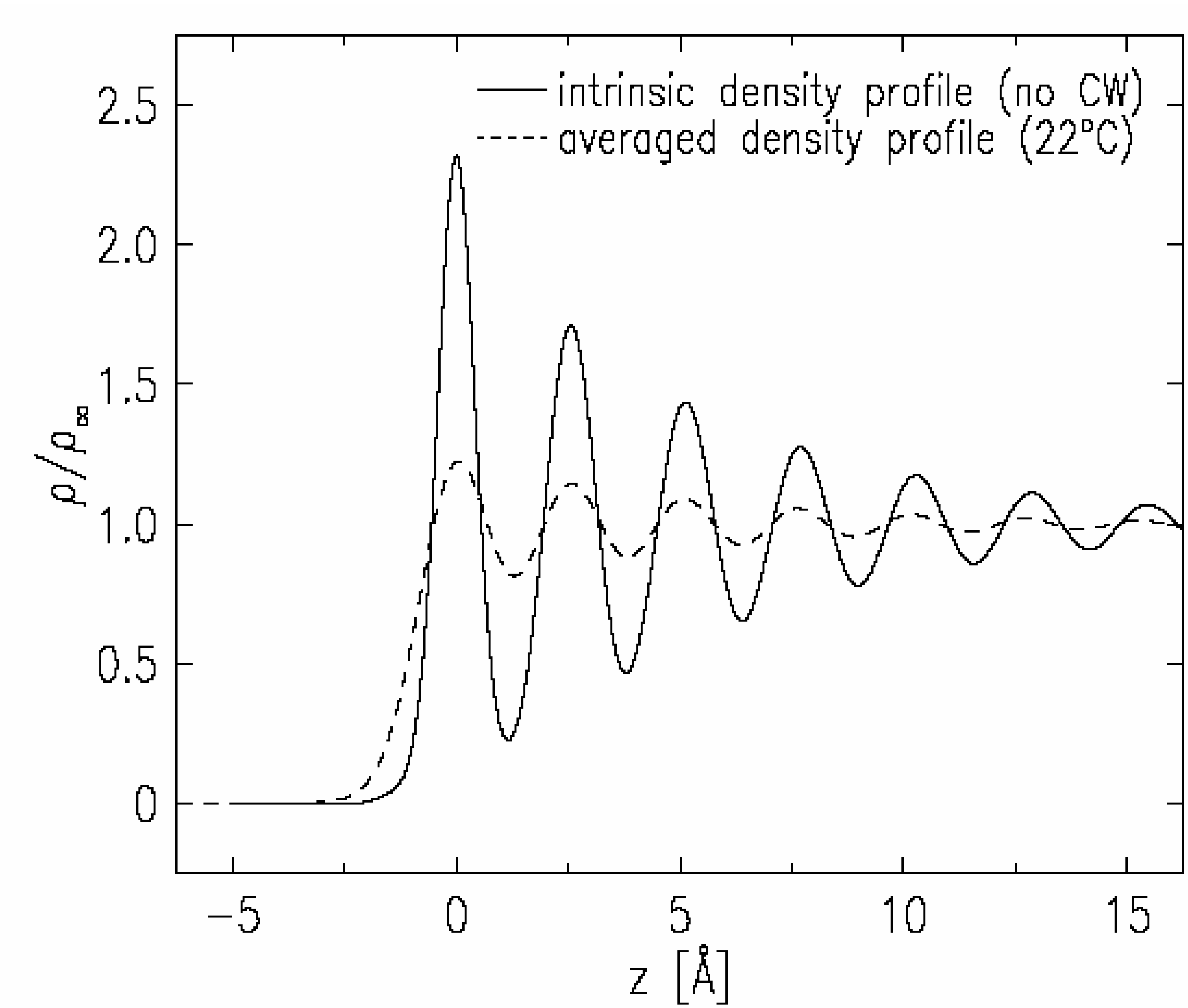
Fresnel-normalized Reflectivity (Ga):



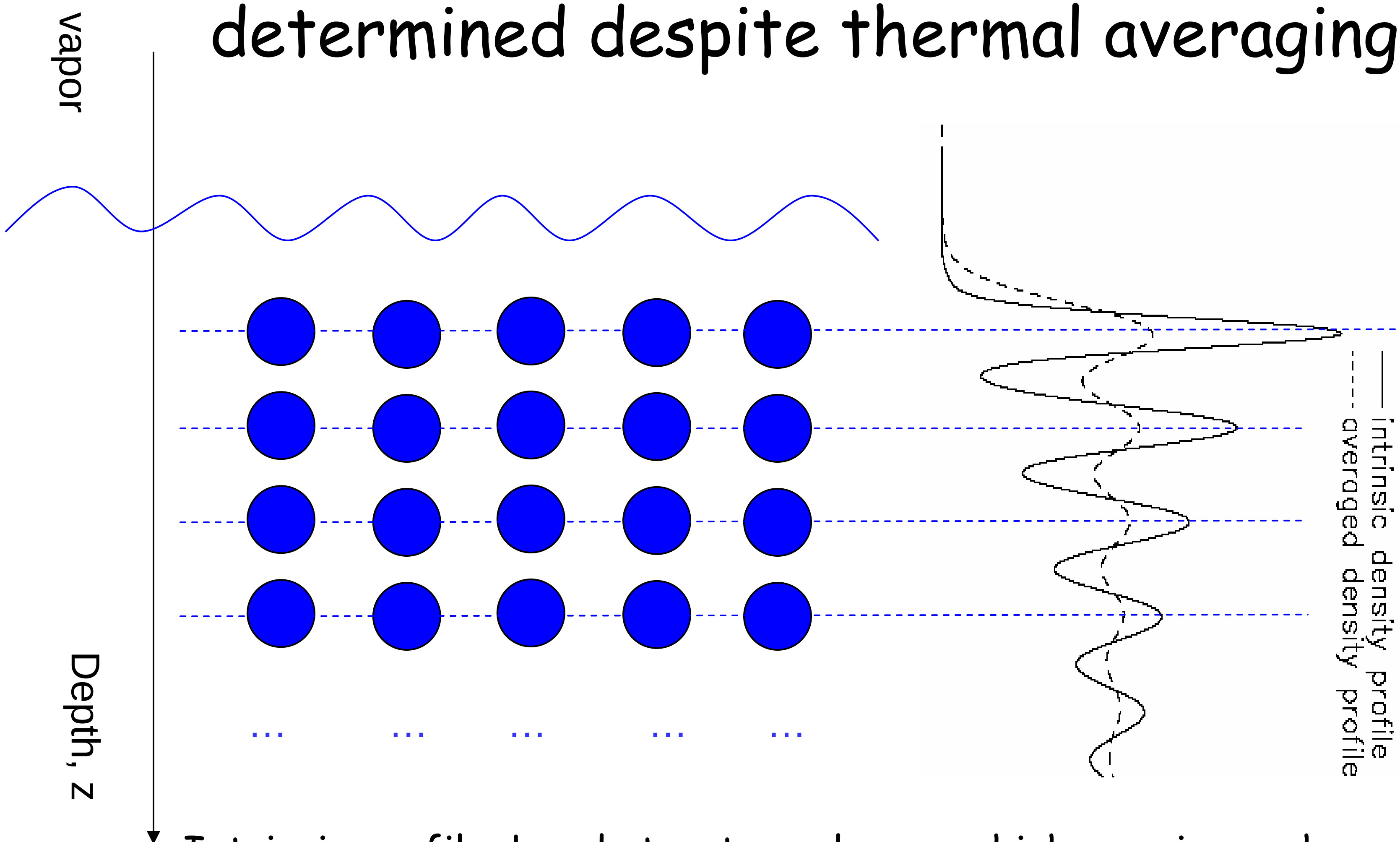
Surface-Structure Factor: (thermal fluctuations removed)



Fluctuation-averaged density profile is not a meaningful way of describing liquid surfaces



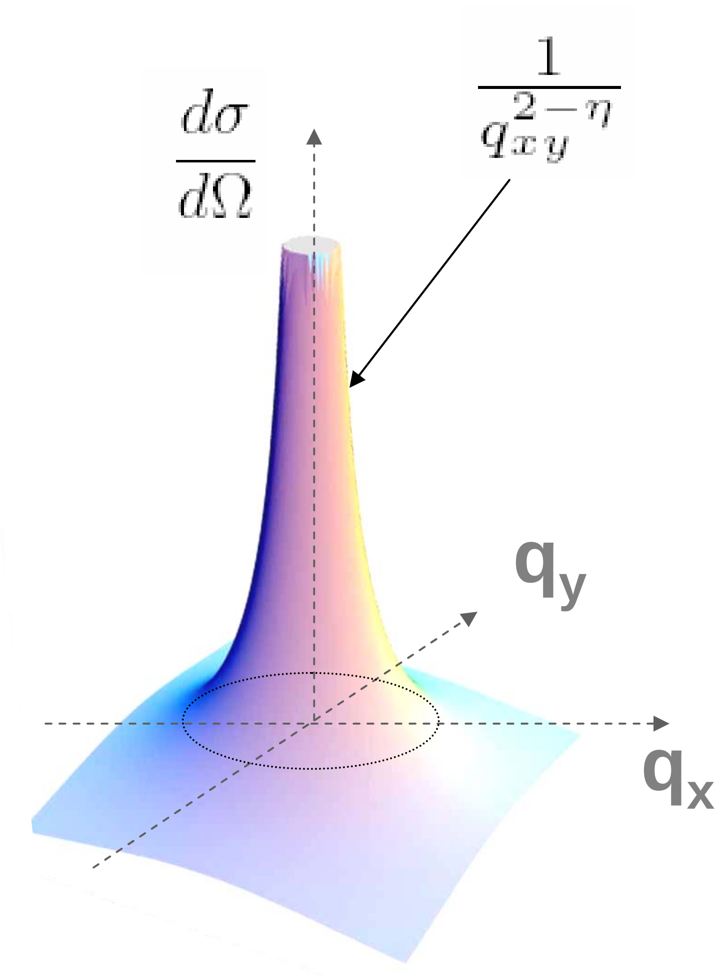
Intrinsic (local) density profile can be determined despite thermal averaging



Intrinsic profile: Local structure along z, which remains unchanged and fluctuates conformally with respect to the surface.

Average profile: ensemble average of intrinsic profiles smeared out by thermal surface fluctuations

Analysis of capillary contributions is needed to determine intrinsic structure

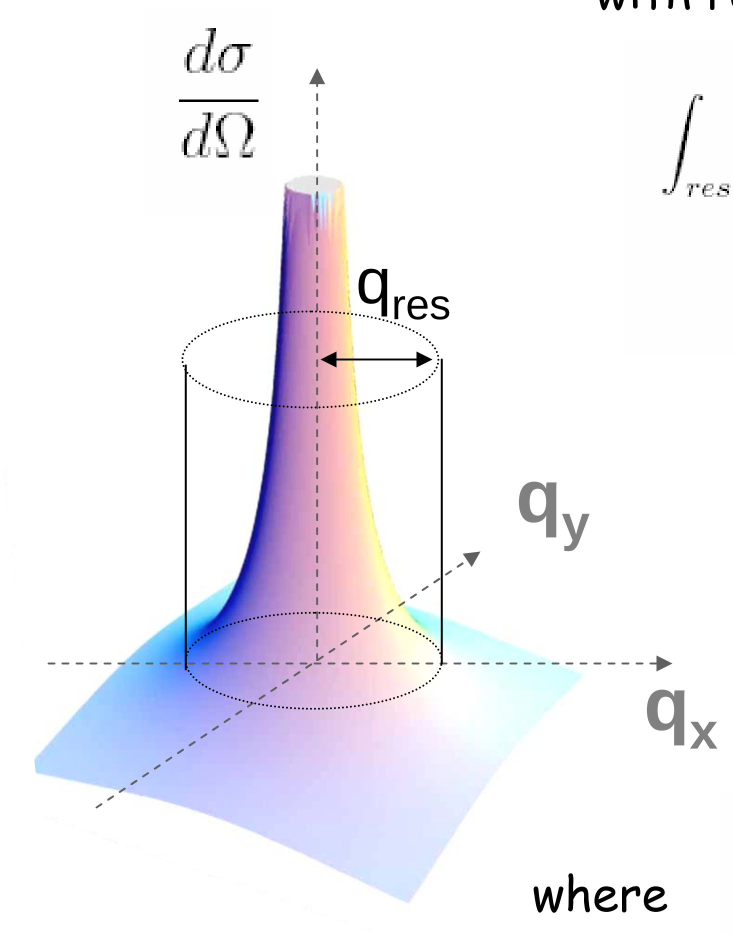


Need to convolve the function with the experimental resolution function in q_{xy}

Singularity at $q_{xy}=0$ represents specular reflection

Power-law decay for large q_{xy} are known as diffuse scattering "tails"

Simple analytic solution exists for isotropic "circular" resolution function



If resolution function is simple symmetric circle with radius q_{res}:

$$\int_{res}\frac{1}{q_{xy}^2}\left(\frac{q_{xy}}{q_{\max}}\right)^\eta d^2q_{xy} = \left(\frac{1}{q_{\max}}\right)^\eta \int_{q_r}\int_\phi \frac{1}{q_r^{2-\eta}} q_r dq_r d\phi =$$

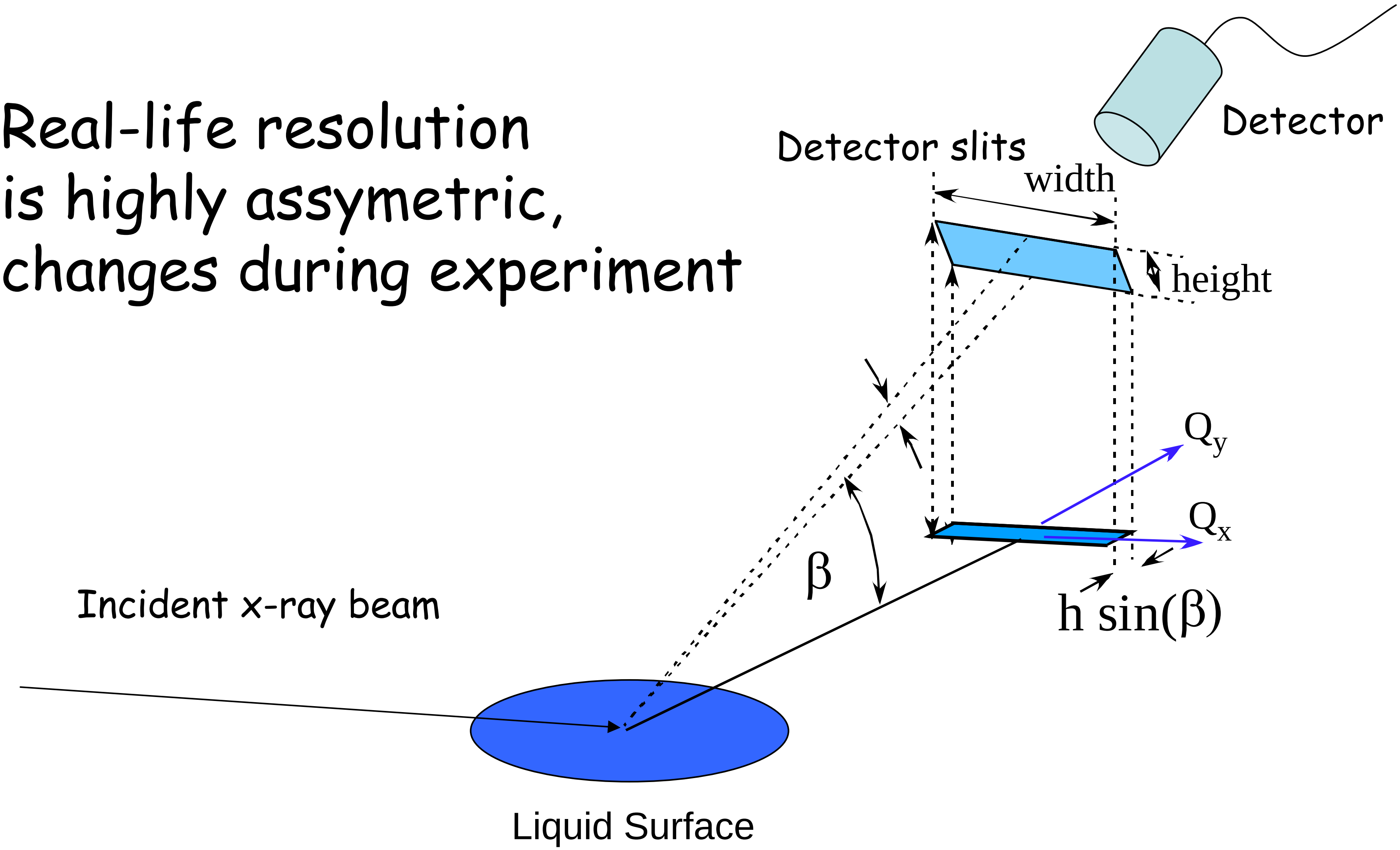
$$= \frac{2\pi}{q_{\max}{}^\eta}\int_{q_r}\frac{1}{q_r^{1-\eta}}dq_r d\phi = \frac{2\pi}{q_{\max}{}^\eta}\frac{q_r^\eta}{\eta}\bigg|_0^{q_{res}} = \frac{2\pi}{\eta}\left(\frac{q_{res}}{q_{\max}}\right)^\eta$$

Therefore:

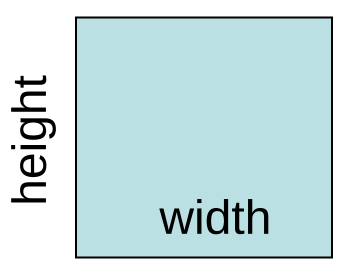
$$\frac{R(q_z)}{R_F(q_z)} = |\Phi(q_z)|^2\left(\frac{q_{\rm res}}{q_{\max}}\right)^\eta = |\Phi(q_z)|^2\exp[-\sigma_{\rm cw}^2 q_z^2]$$

where $\sigma_{\rm cw}^2 = \frac{k_B T}{2\pi\gamma}\ln\left(\frac{q_{\rm res}}{q_{\max}}\right)$ is a "capillary roughness"

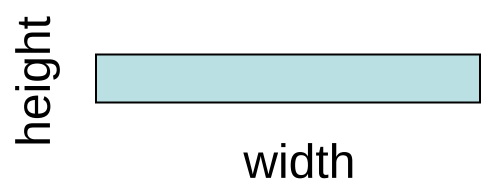
Real-life resolution is highly assymetric, changes during experiment



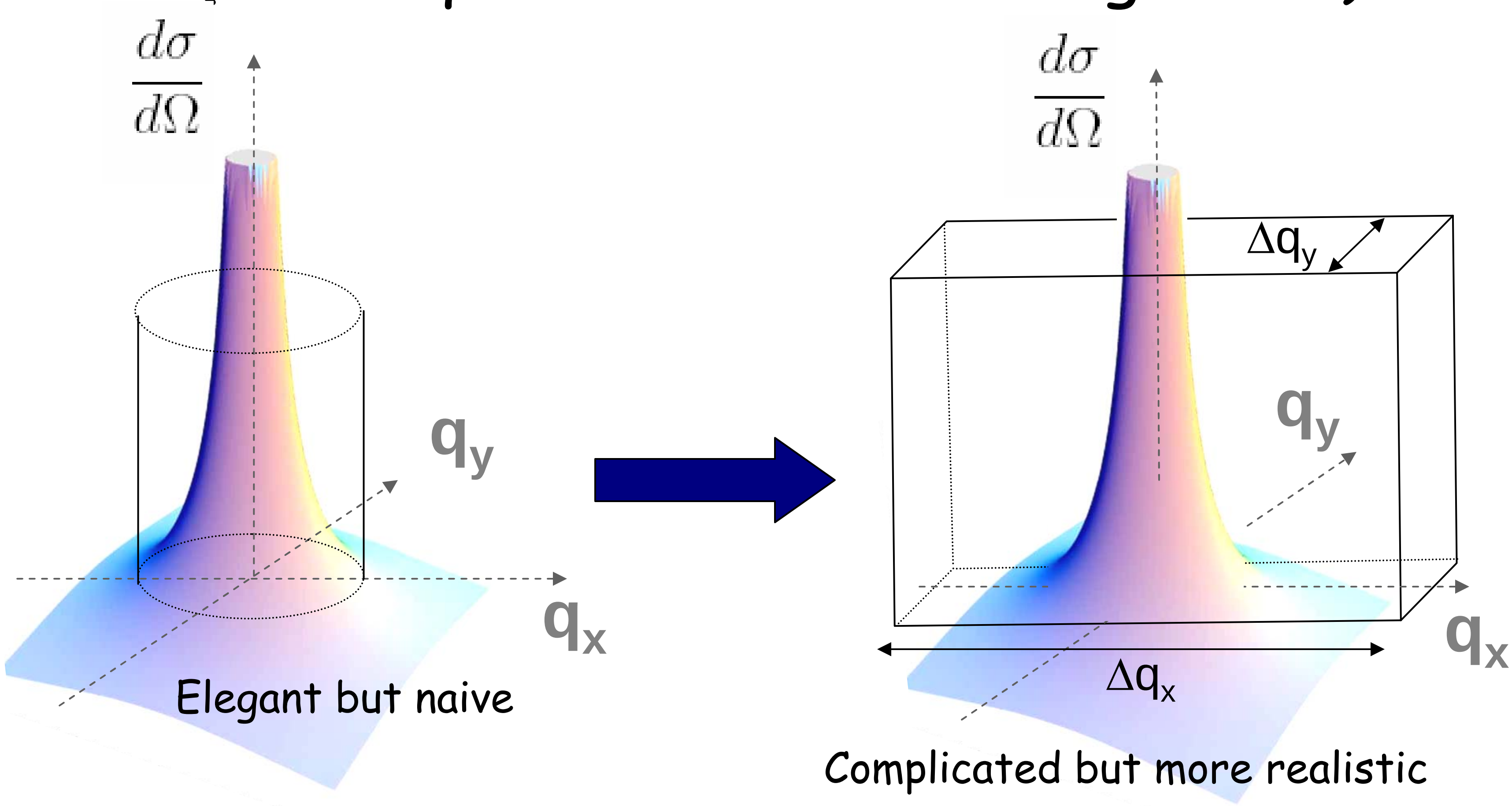
Slits in real space, aspect 1:1



Slits in momentum space, aspect 10:1
(for β=6 degrees)



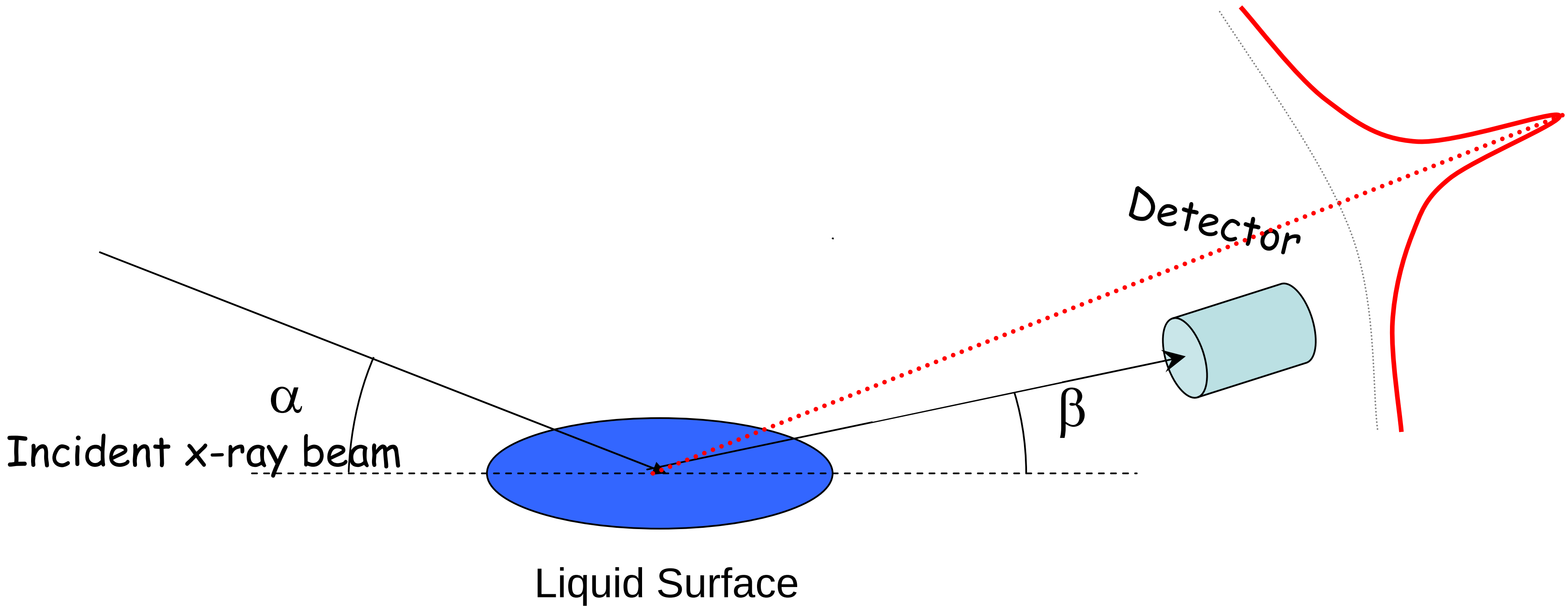
A box is a more realistic resolution function (but requires numerical integration)



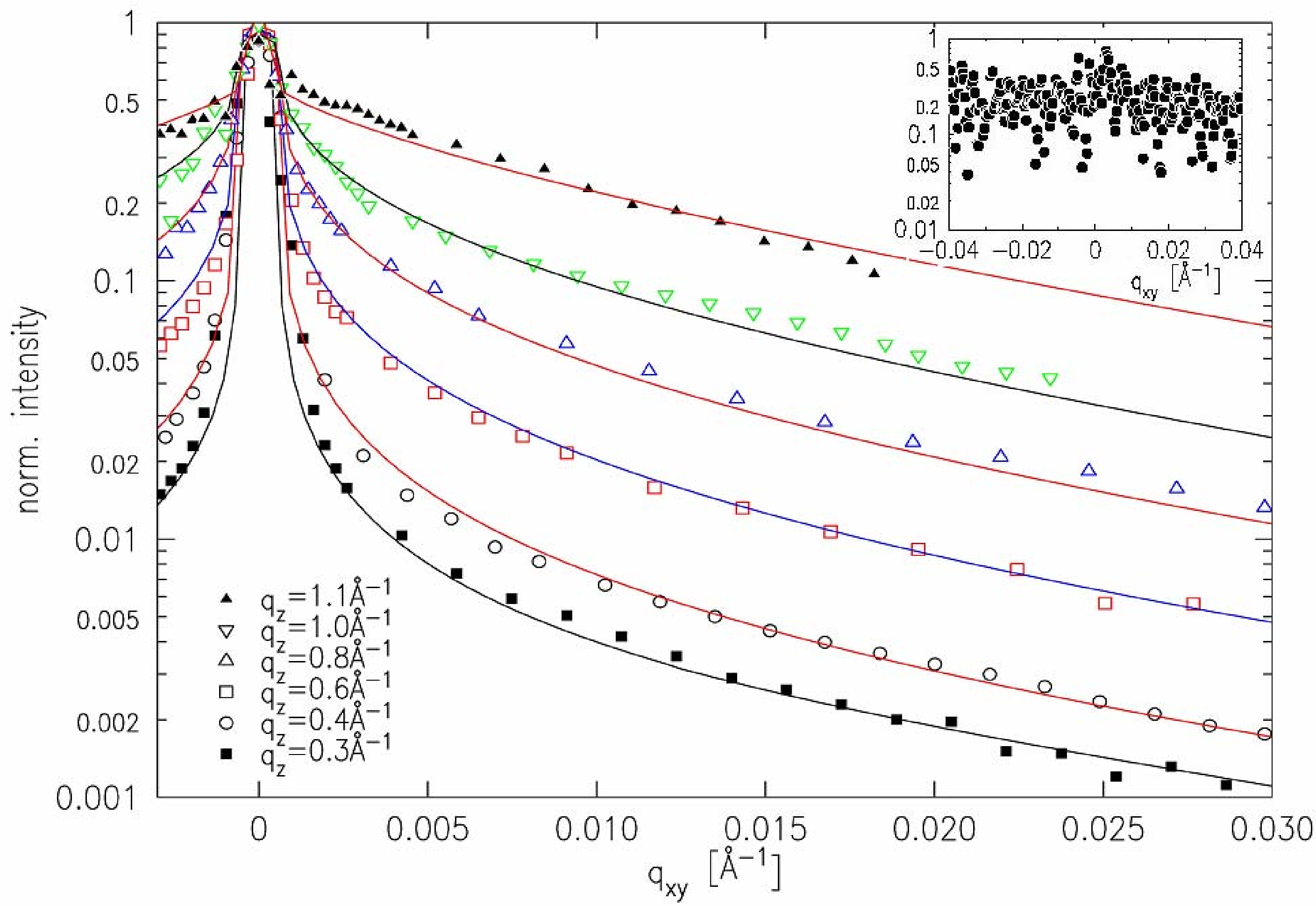
Further corrections: sample curvature, beam divergence, incident slits, Gaussian or Lorenzian-like beam shape profile, etc.

(Usually secondary for most practical purposes)

Reflectivity scans $\alpha=\beta$, varied simultaneously
Diffuse scattering scans, only β is varied

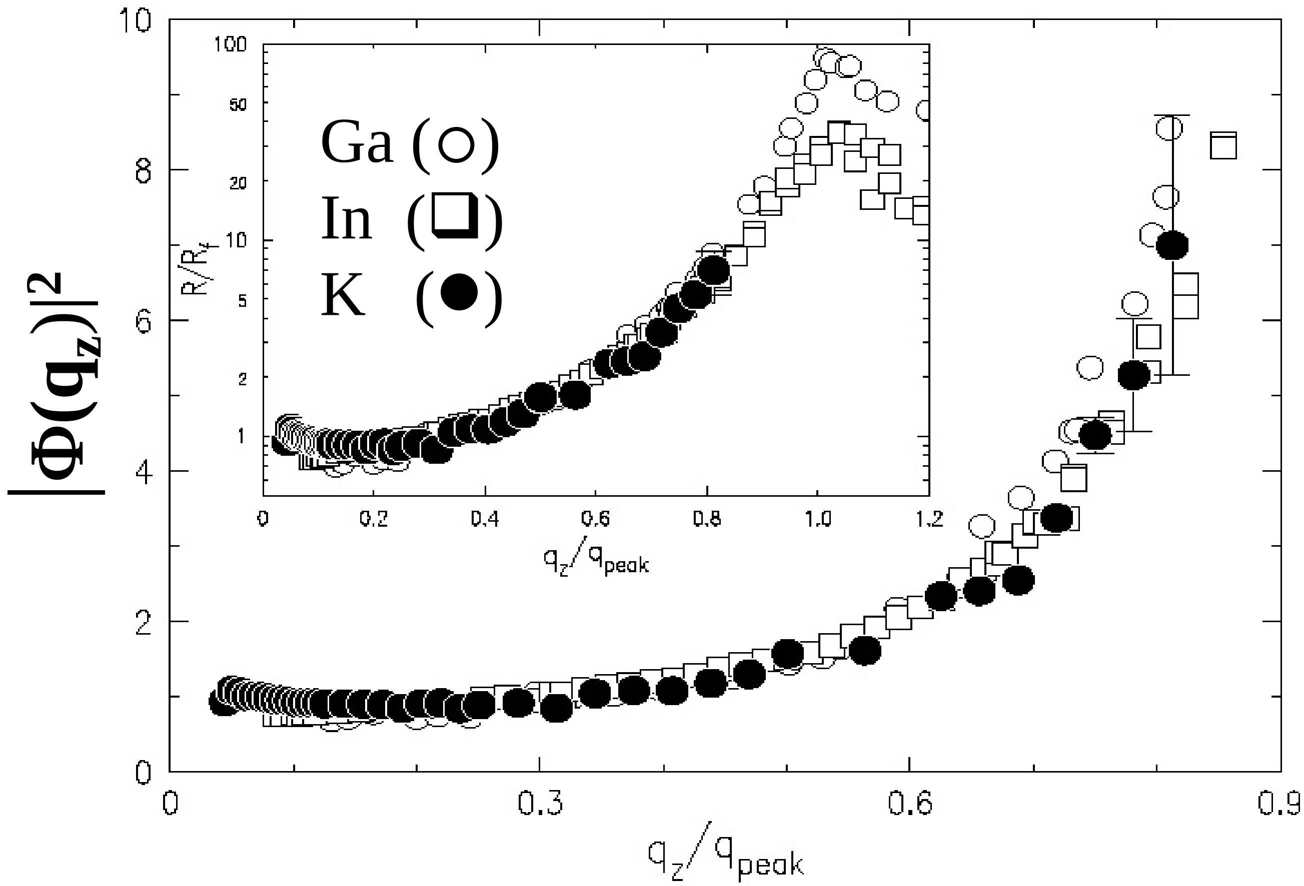


Capillary excitations well-accounted for in liquid potassium (up to a η-limit)



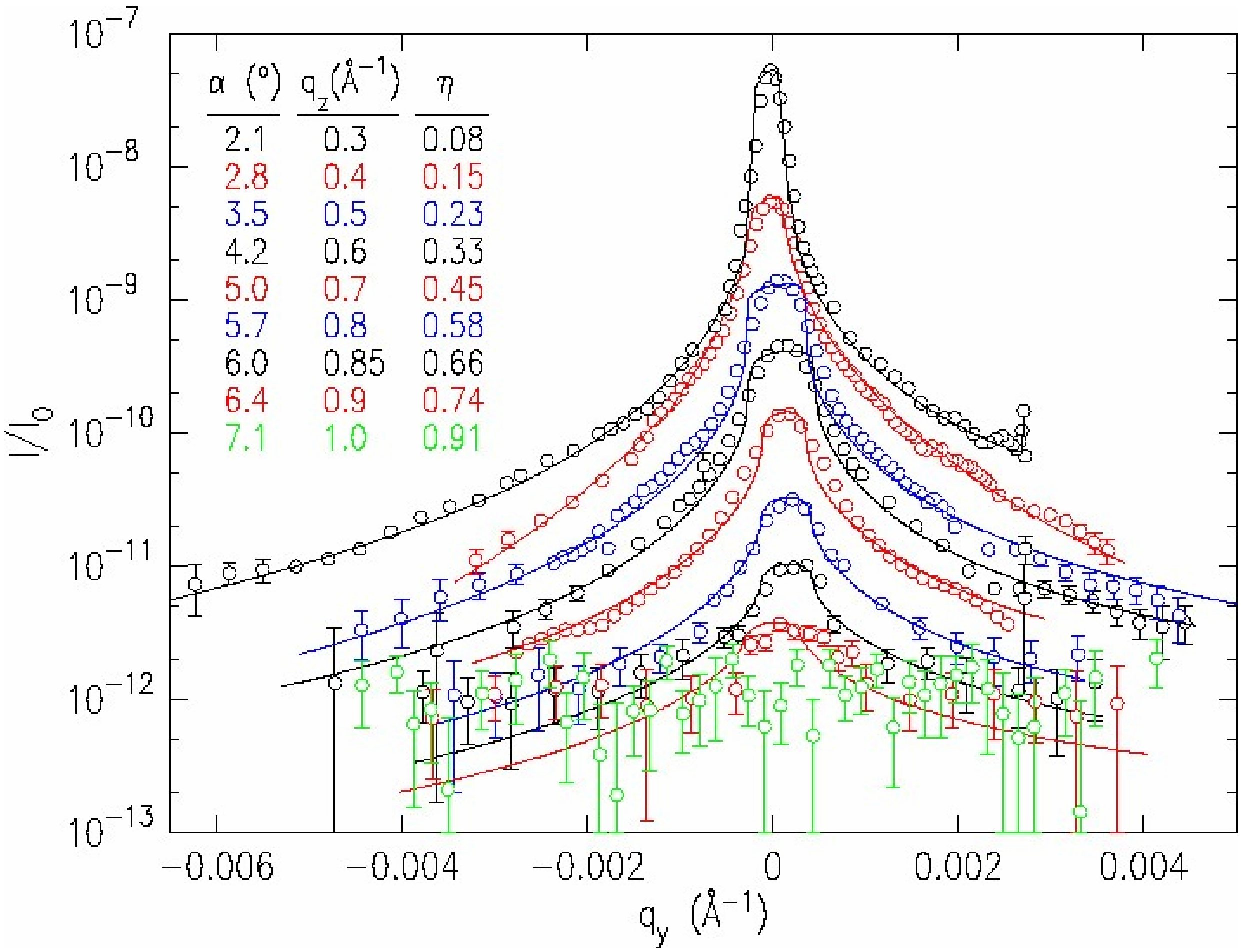
O.G. Shpyrko et. al, Phys. Rev. B **67**, 115405 (2003)

Metallic properties define layering, not high surface tension (liquid K, cont'd):



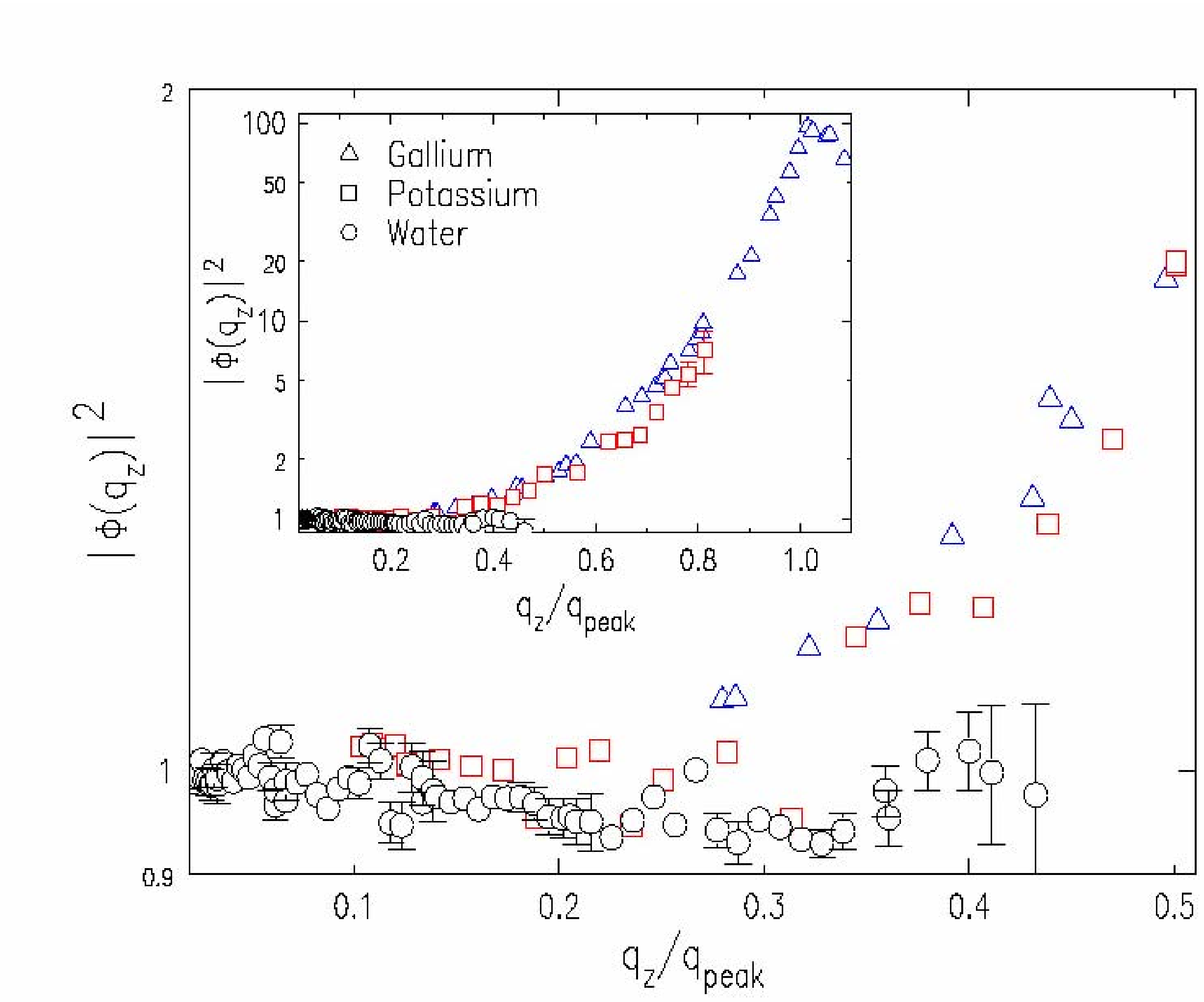
O.G. Shpyrko et al., Phys. Rev. B **67**, 115405 (2003)

Similar study can be done for surface of liquid water – until η ~1



O.G. Shpyrko et al., Phys. Rev. B **69** 245423, (2004)

Water shows no sign of layering



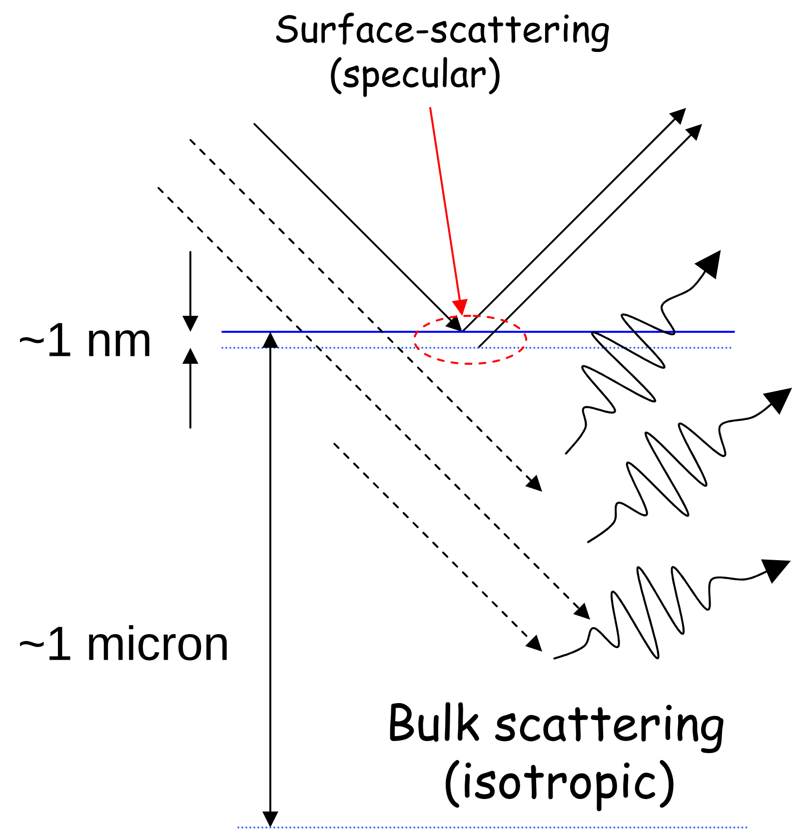
O.G. Shpyrko et al., Phys. Rev. B **69** 245423, (2004)

Specular singularity is essential for x-ray reflectivity technique

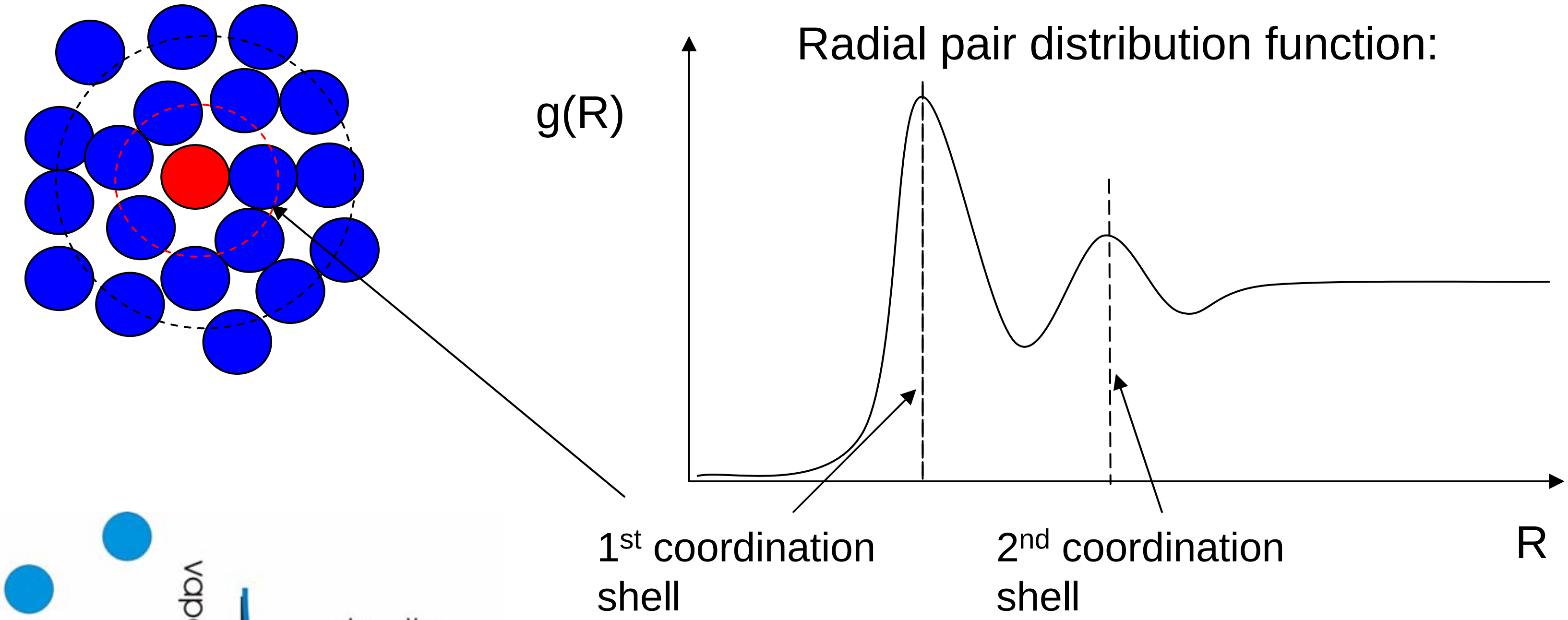
Specular singularity contains surface-sensitive information and can be separated from *isotropic* bulk background

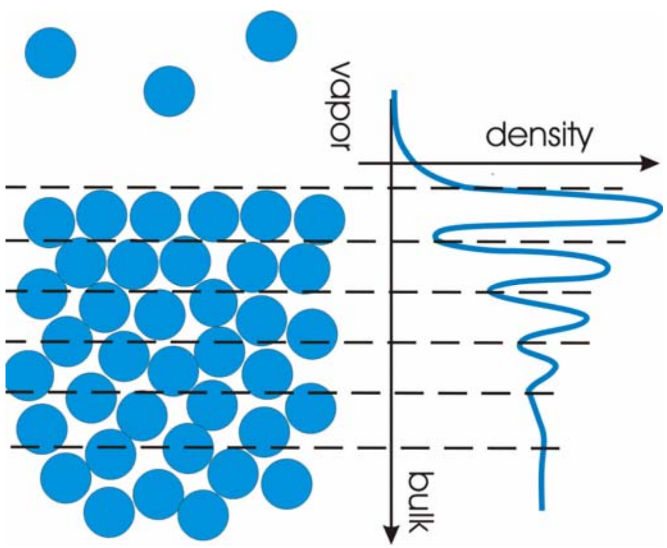
Otherwise scattering from ~ micron thick bulk would dominate ~ 1 nanometer thick near-surface region by a factor of 1,000!

But how important is bulk scattering analysis?



Closed-packed liquid bulk structure is similar to layered surface profile

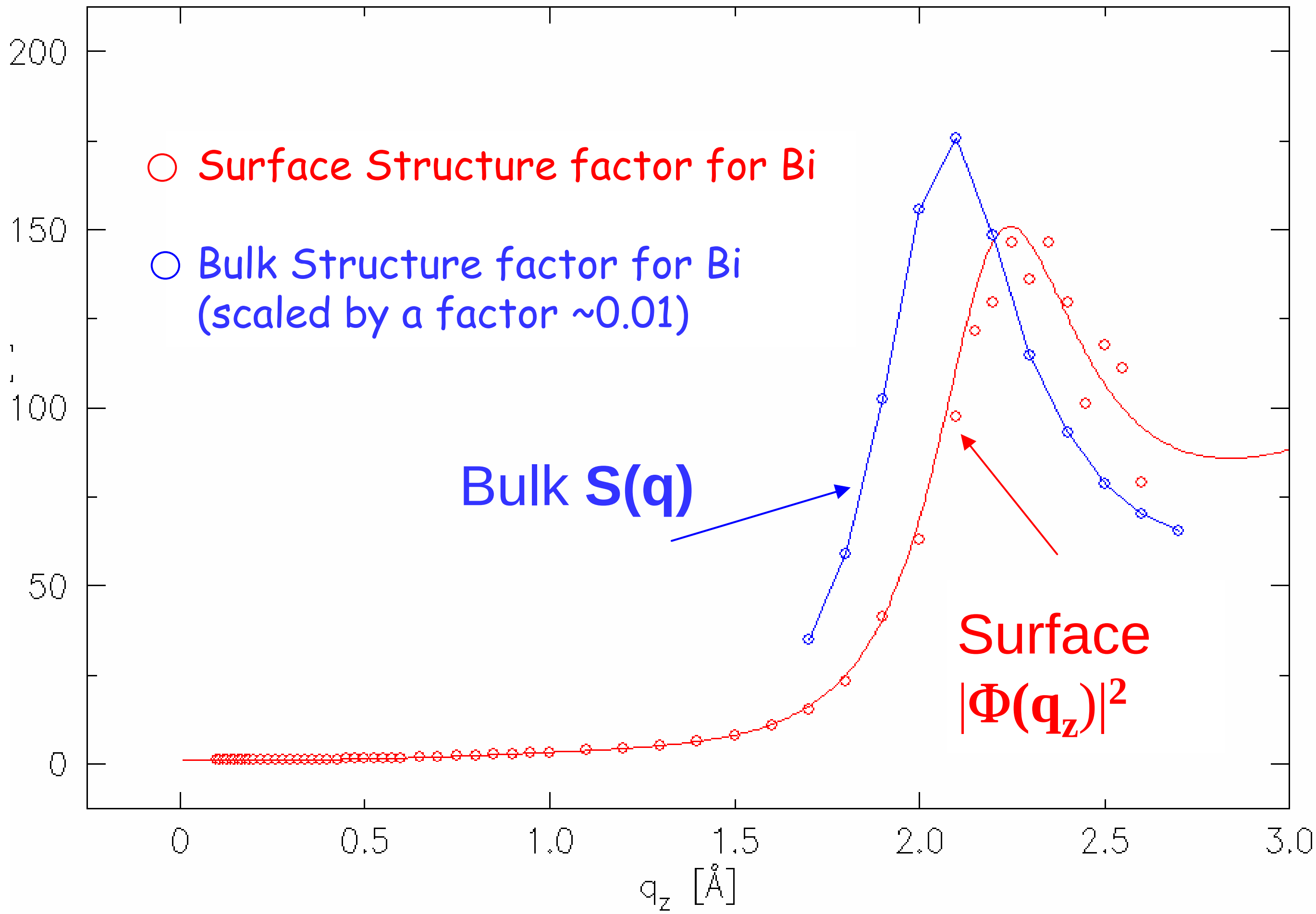




Note the similarity between radial atomic pair distribution function in liquid/amorphous bulk and layering density profile.

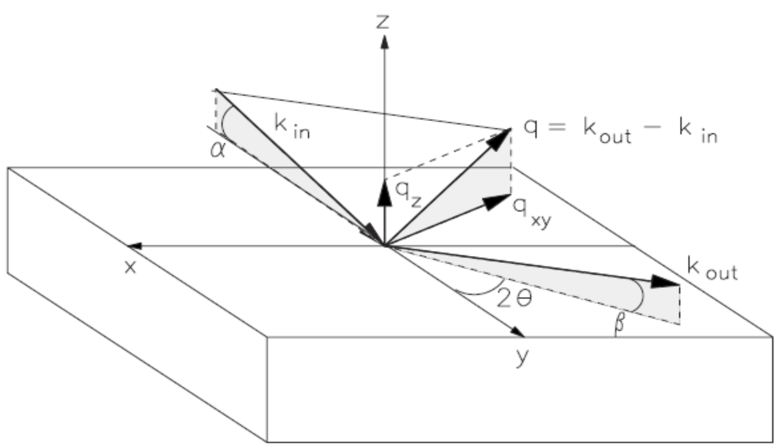
Important difference: layering is correlated only along surface normal, bulk structure is isotropic.

Bulk and surface structure factors have similar shapes, q-positions



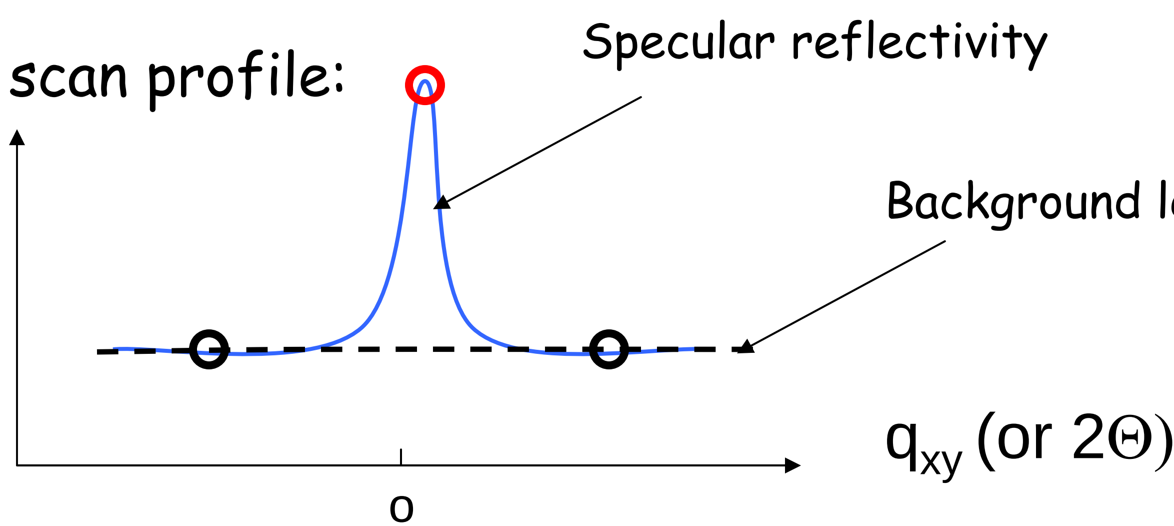
Data from most recent measurement at ChemMat-CARS, July 2005 (unpublished)

Bulk background is subtracted by azimuthal off-specular measurement

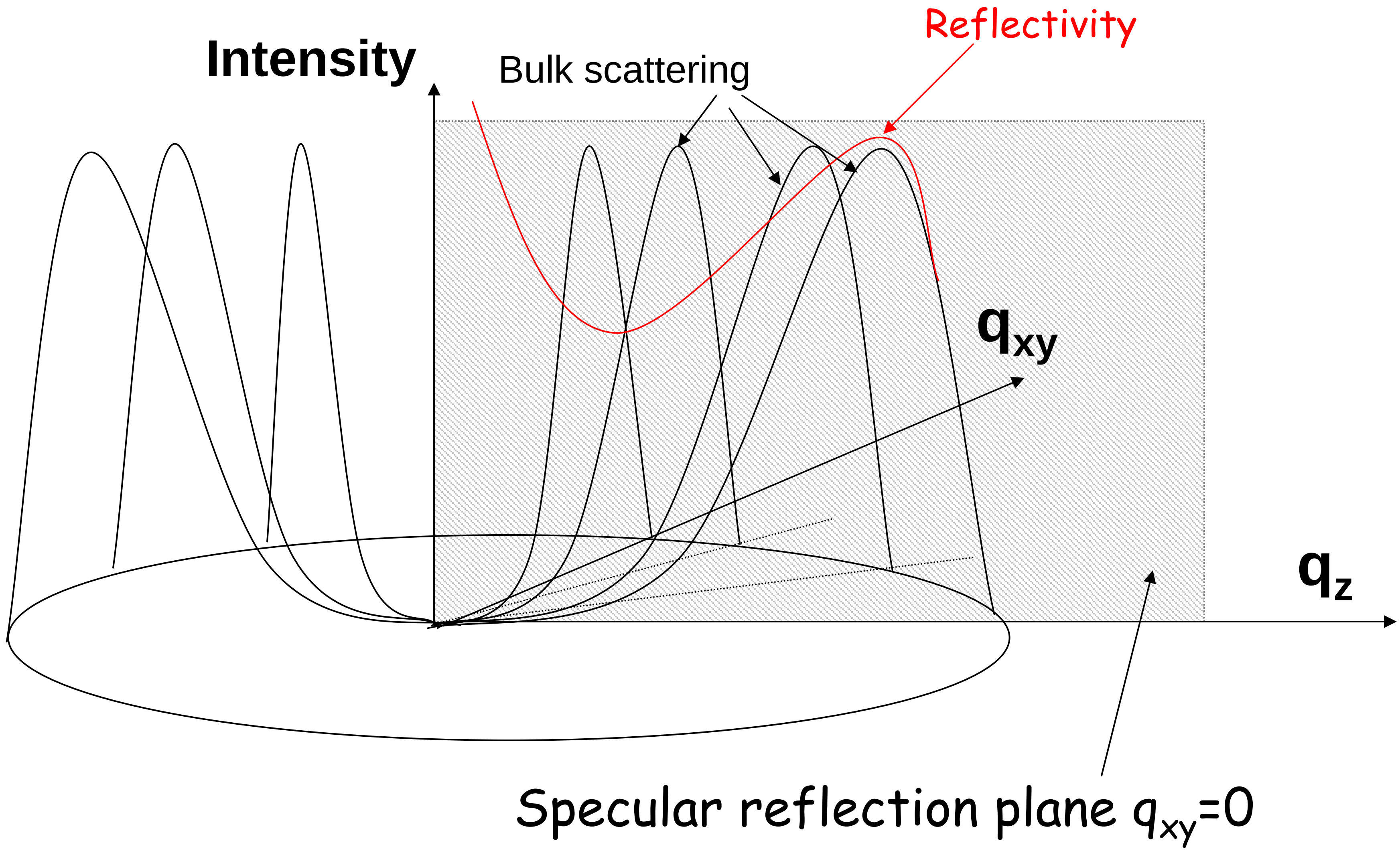


Recipe:
Measure background off specular plane (for example, move 2θ to non-zero position).

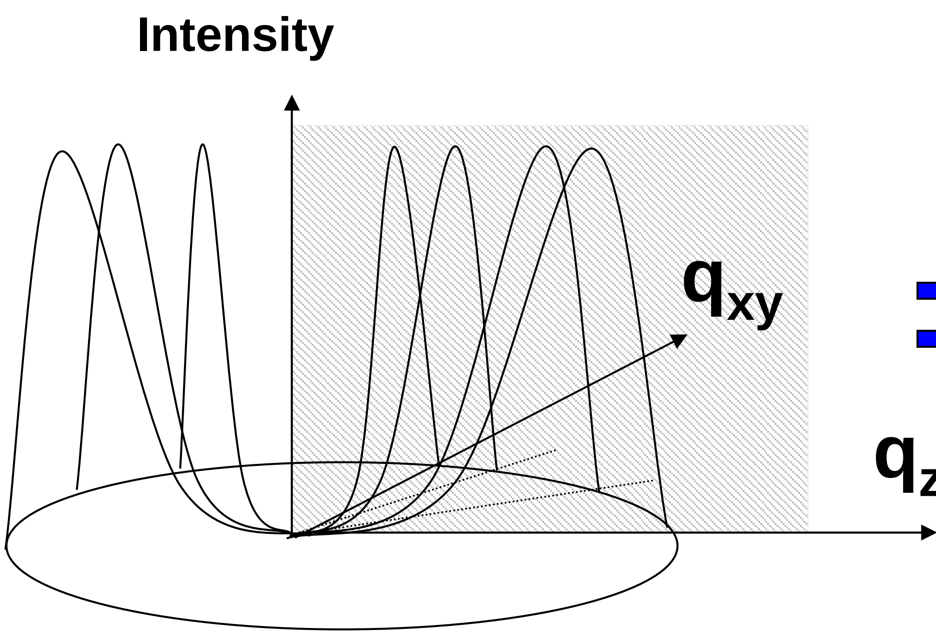
Expected scan profile:



Bulk scattering is isotropic with respect to q

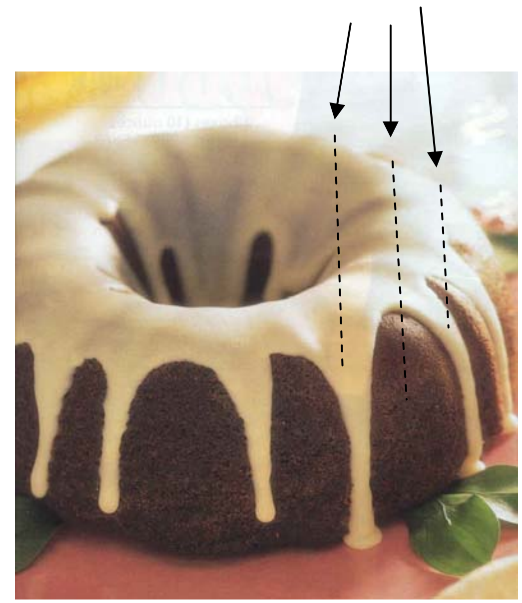


Bulk scattering profile in momentum space



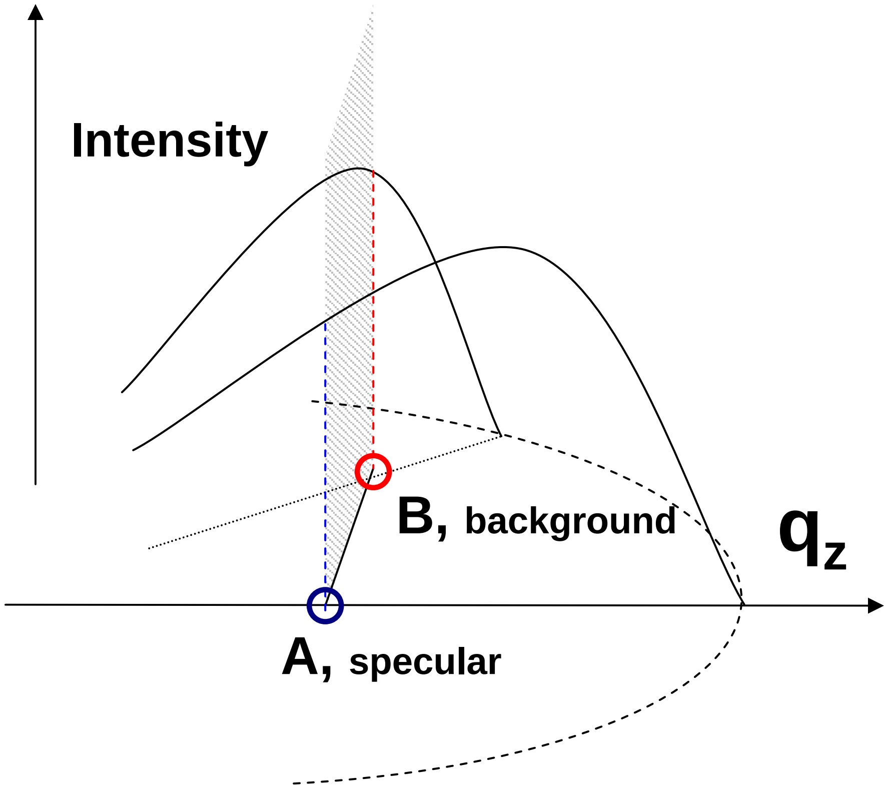
Shape of bulk scattering profiles in q_z-q_{xy} space

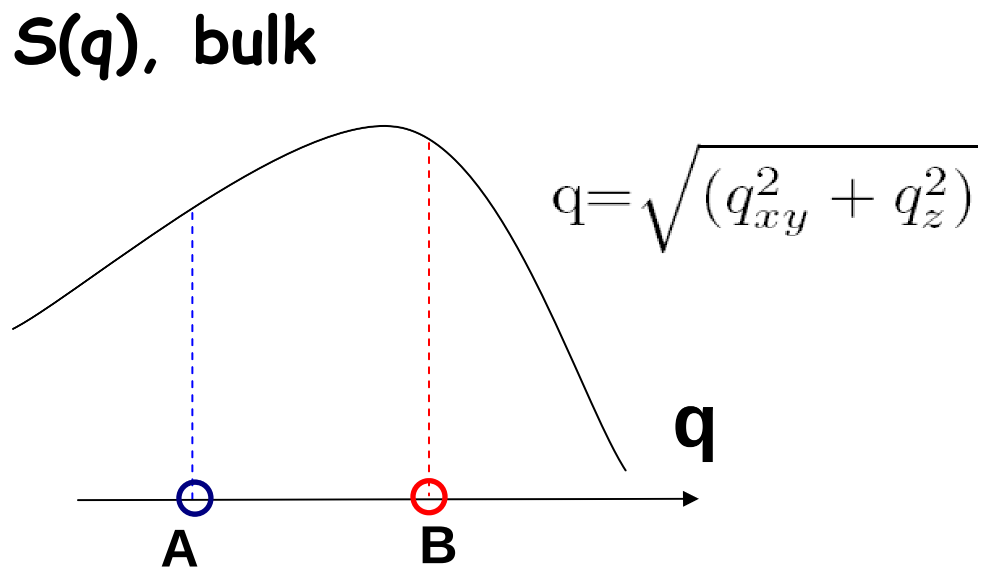
Think about these cuts:



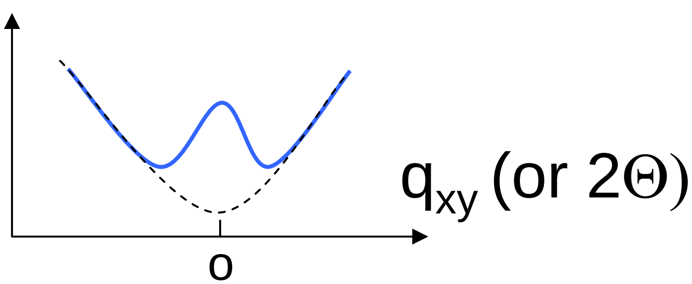
Donut / Bunt-cake
(hmmmm… donuts…)

“Cutting the Donut”

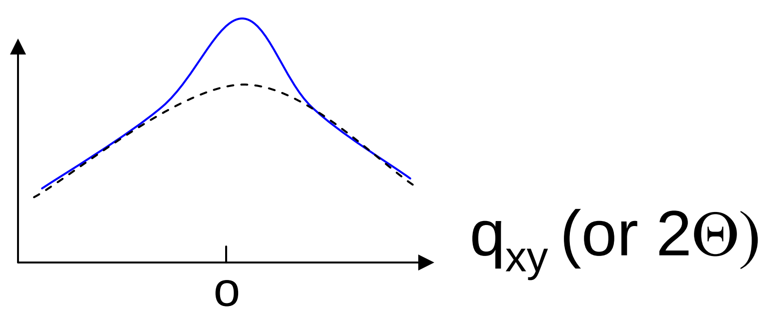




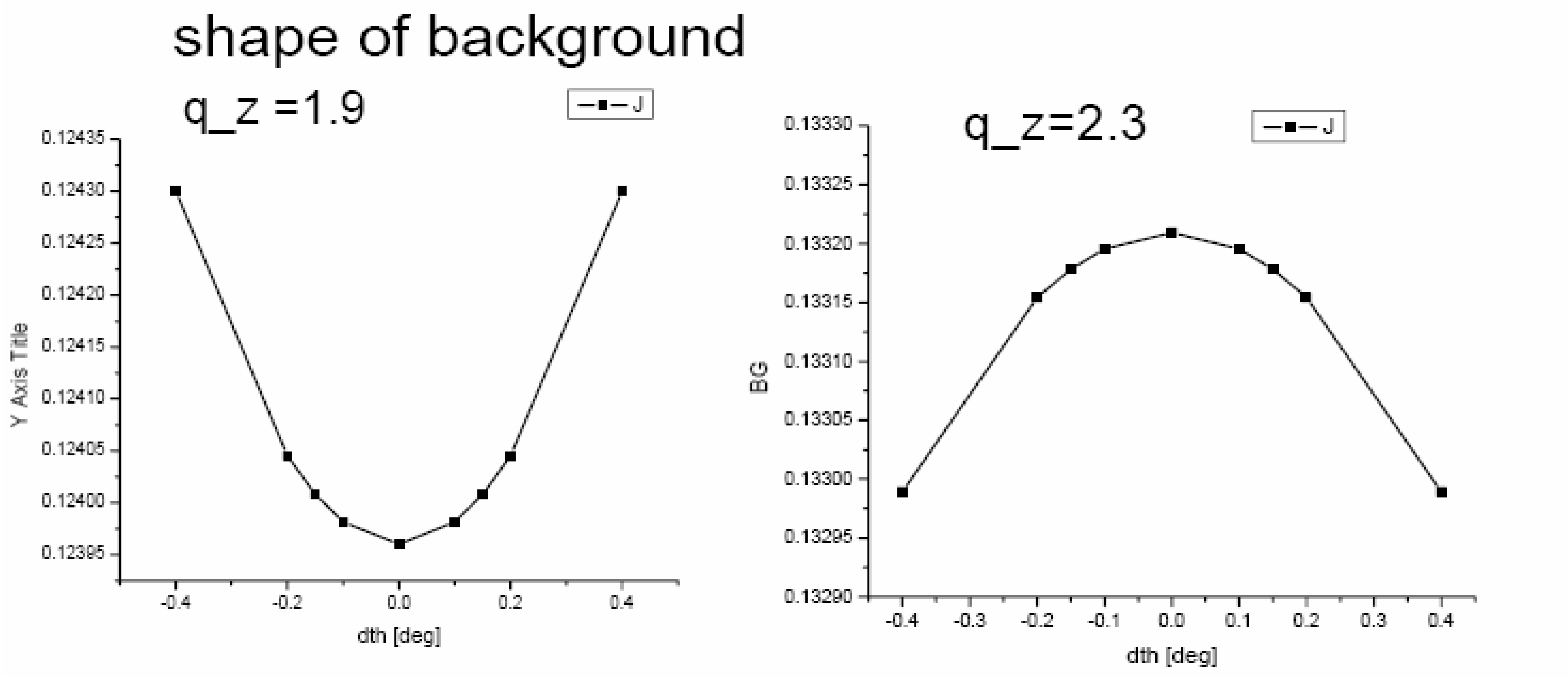
Below S(q) peak



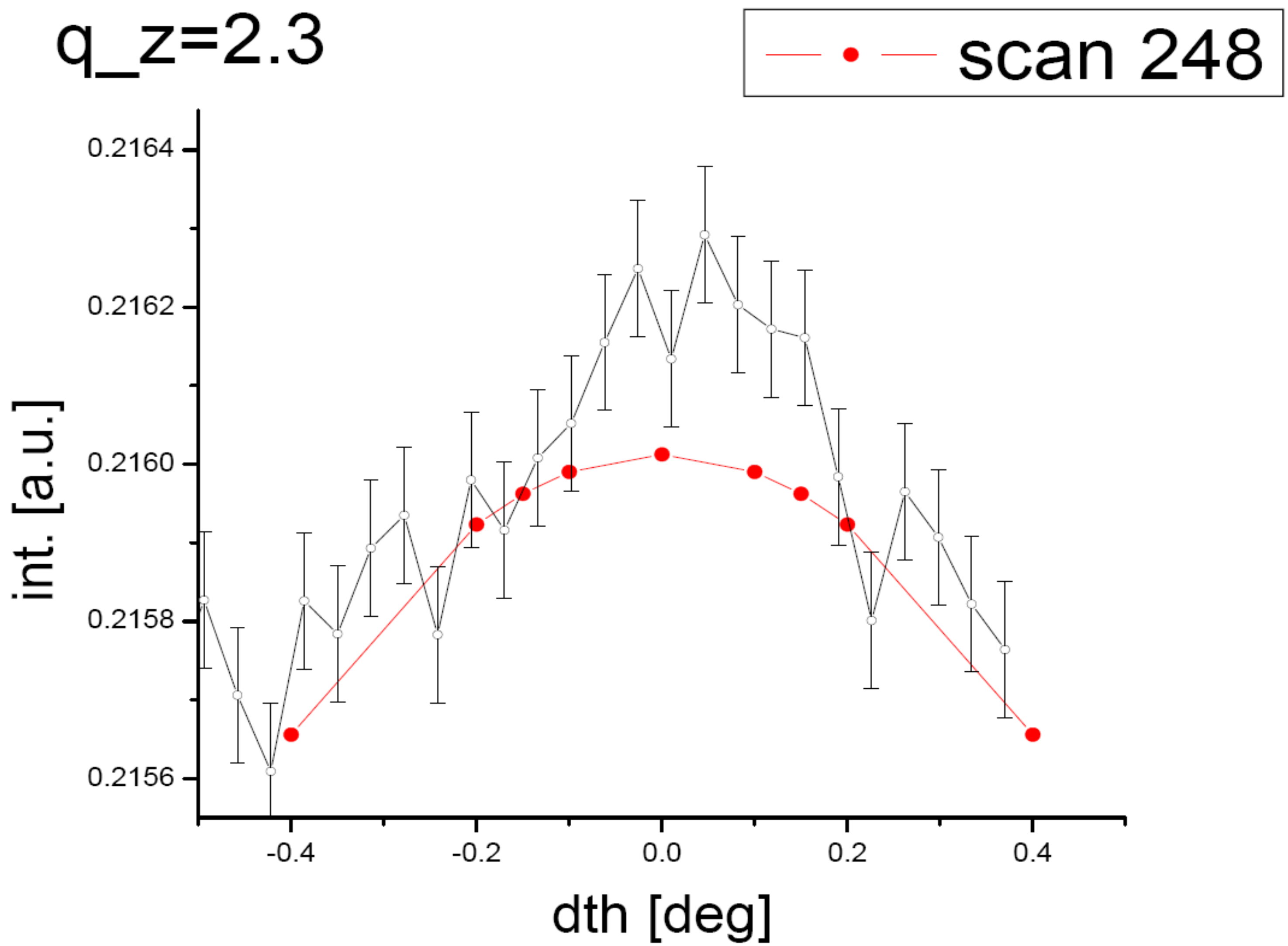
Above S(q) peak



2θ background scans can be simulated based on experimentally measured S(q)

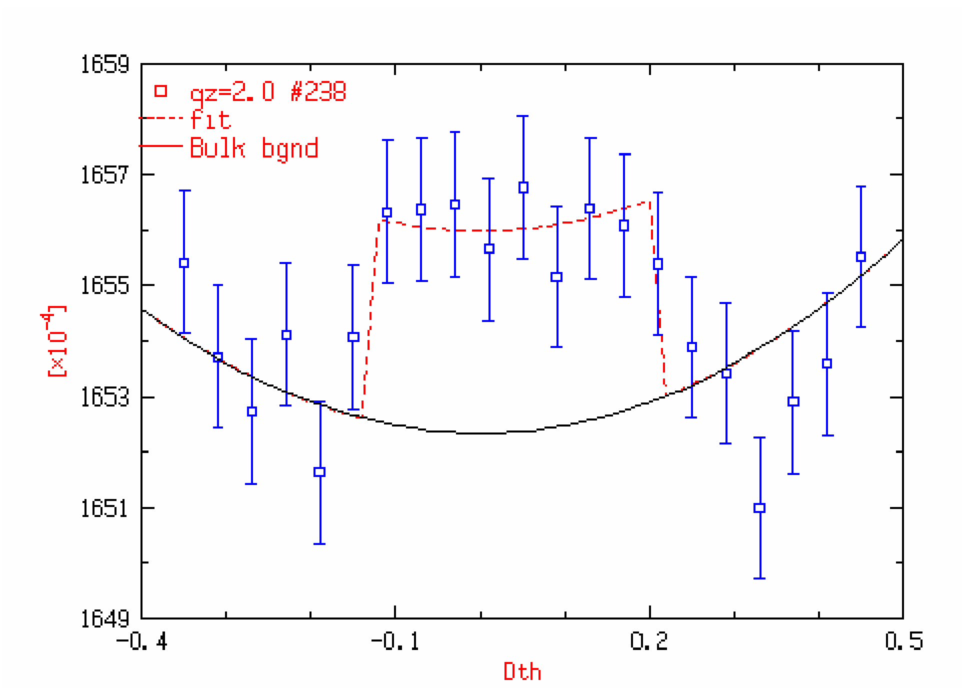


Data from the most recent measurement at ChemMat-CARS, July 2005 (unpublished)

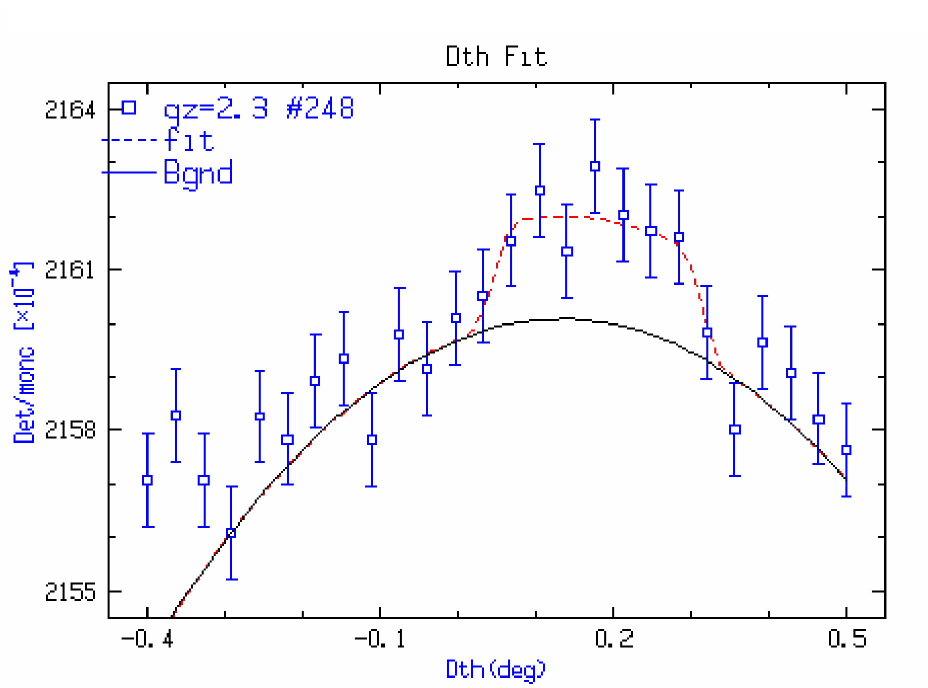


Data from the most recent measurement at ChemMat-CARS, July 2005 (unpublished)

Shape of background scans switches from concave to convex



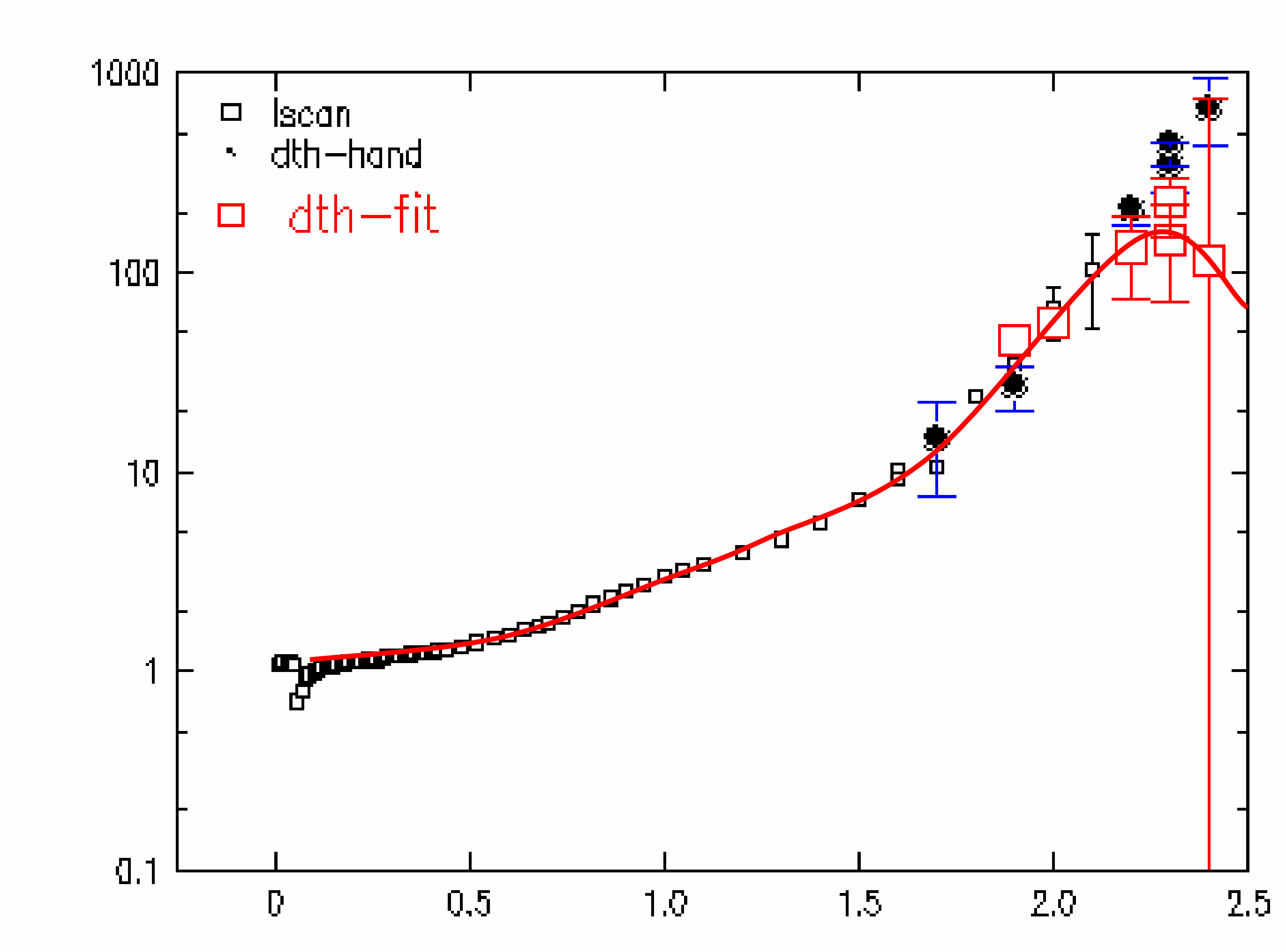
Below layering peak position



Above layering peak position

Data from the most recent measurement at ChemMat-CARS, July 2005 (unpublished)

“Donut-slice” analysis corrects surface structure factor for Bi in a meaningful way



Data from the most recent measurement at ChemMat-CARS, July 2005 (unpublished)

Summary:

Dynamics (capillary excitations) and structure can be deconvolved by careful analysis of diffuse scattering

Resolution effects are crucial!

At high η specular singularity disappears (reflectivity can no longer be observed)

Bulk scattering is not completely isotropic – important at high Q_z