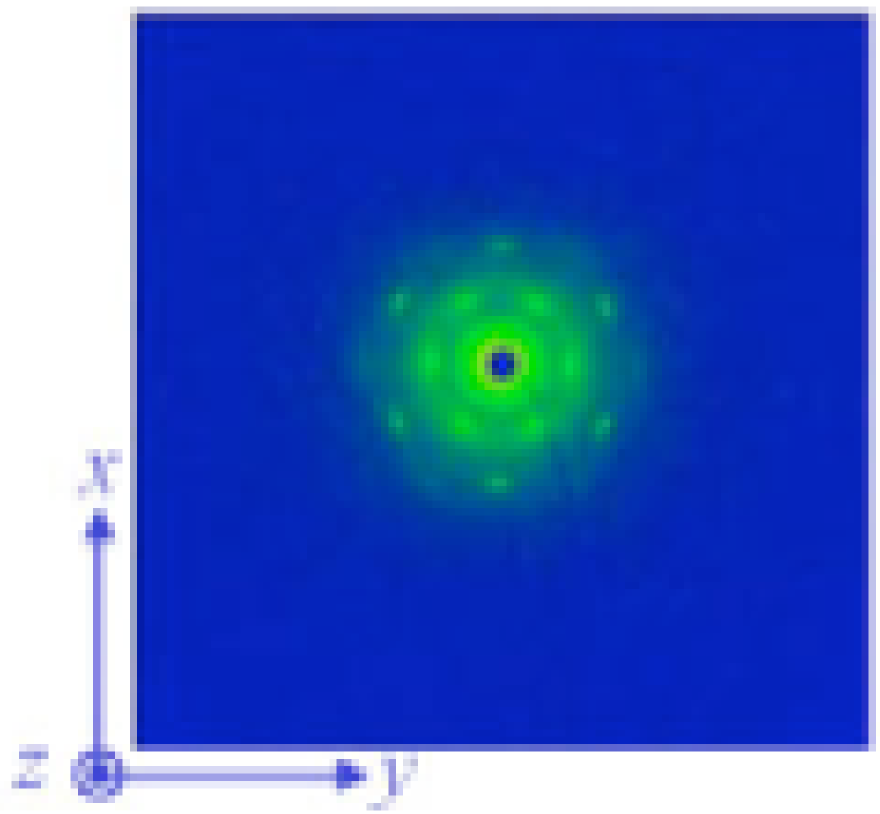
Periodic systems.

(See Roe Sect 5.5)

Repeat periods of 10-1000 Å
Degree of order usually low --> smears reciprocal lattice spots
Ordered domain size frequently small --> smears reciprocal lattice spots



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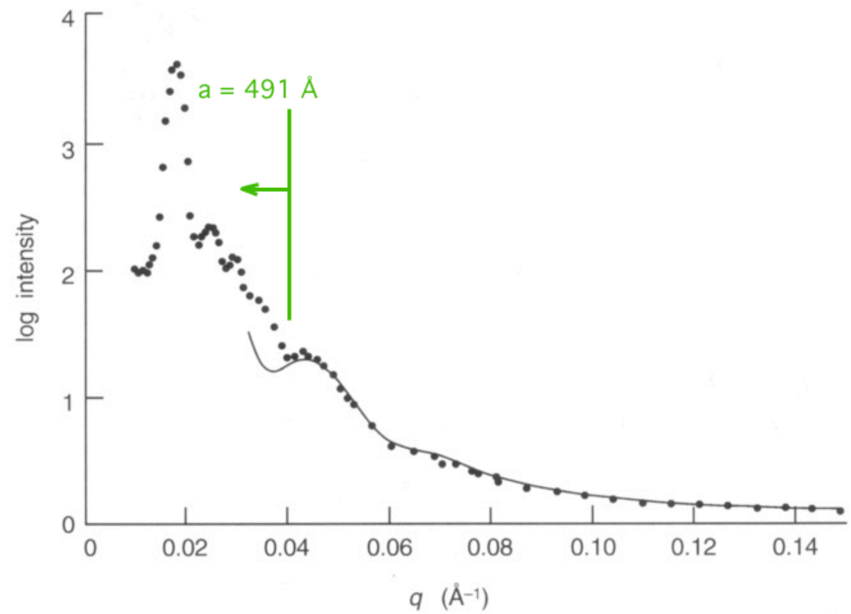

Small-angle neutron scattering intensity obtained with styrene-butadiene diblock copolymer having spherical butadiene microdomains. The peaks at very small q due to body-centered cubic structure of ordered microdomains. The solid curve is calculated intensity of independent scattering from solid spheres of mean radius 124 Å.

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1st:

$$\rho(\mathbf{r}) = \rho_u(\mathbf{r}) * z(\mathbf{r})$$

$\rho_u(\mathbf{r})$ = scattering length density for single repeated motif
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and:

$$I(\mathbf{q}) = |F(\mathbf{q})|^2 \, |Z(\mathbf{q})|^2$$

(Fourier transform of convolution of 2 fcns = product of their transforms)

$Z(\mathbf{q})$ describes the reciprocal lattice
$F(\mathbf{q})$ is the "structure factor"

Periodic systems.

Consider lamellar morphology (membranes, folded-chain crystallites, etc.)

If one stack of well-ordered lamellae:

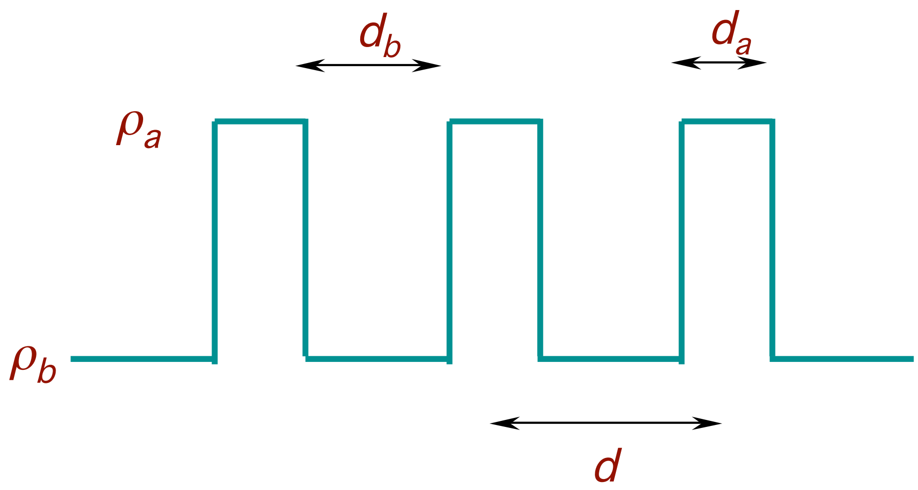
saxs --> array of points along line in reciprocal space

If many randomly oriented stacks:

saxs --> isotropic pattern (rings)

Periodic systems.

Ideal 2-phase lamellar structure



$$\rho(x) = \rho_u(x) * z(x/d)$$

$$z(x) = \sum_{n=-\infty}^{n=\infty} \delta(x - n)$$

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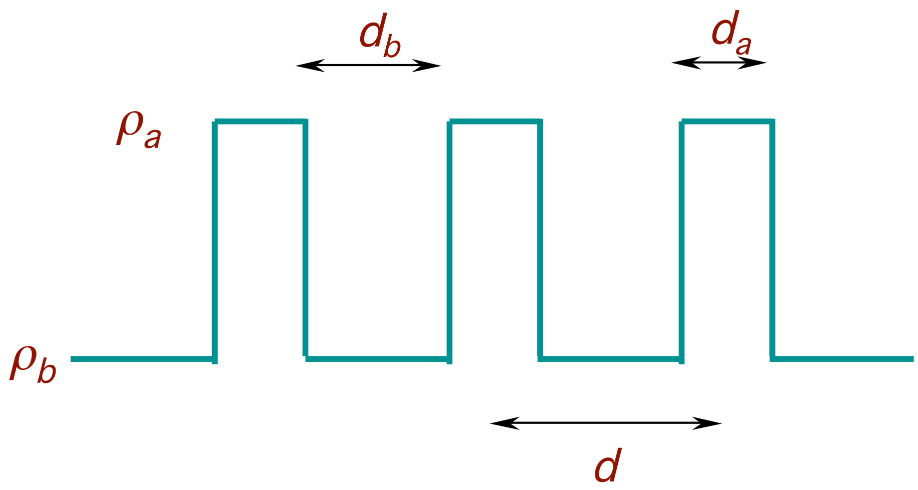

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$$|F(q)|^2 = 4(\Delta\rho/q)^2 \sin^2 (d_a q/2)$$

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(Fourier transform)^2 of $z(x/d)$ is reciprocal lattice w/ period $2\pi/d$

Sharp Bragg-type peaks occur at $q = 2\pi n/d$
w/ intensity ~ $(n)^{-2} \sin^2 (\pi n \phi_a)$

(can get volume fractions of phases from intensities)

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Peaks are δ-fcn sharp if structure is ideal

Non-ideal structures --> peak broadening

Periodic systems.

2-phase structure w/ variable thickness lamellae

lamellae parallel
lamellae thickness varies
no correlation in thickness of neighboring lamellae

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2-phase structure w/ variable thickness lamellae

lamellae parallel
lamellae thickness varies
no correlation in thickness of neighboring lamellae
probability of thickness of A lamellae betwn *a* & *a + da* is

$$p_a(a)\,da$$

similar for B lamellae

Then, as before:

$$A(q) = \sum_{j=1}^{N} A_j(q)$$

Periodic systems.

2-phase structure w/ variable thickness lamellae

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$$A(q) = \sum_{j=1}^{N} A_j(q)$$

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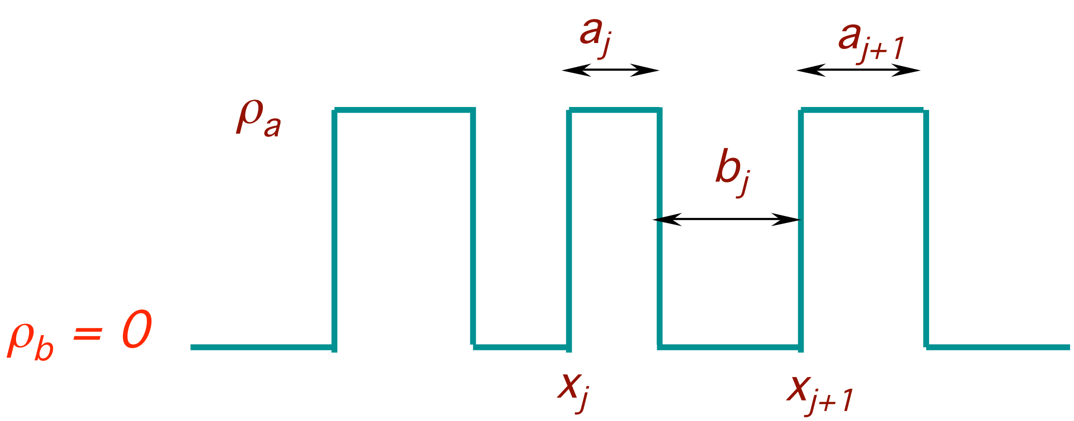

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$$I(q) = \sum_{j=1}^{N} A_j A_j^* + \sum_{j=1}^{N} \sum_{m=1}^{N} (A_j A_{j+m}^* + A_{j+m} A_j^*)$$ (*N* very large)

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$$\Sigma A_j A_j^* = (\Delta\rho/q)^2 \, \Sigma \, (2 - \exp(-iqa_j) - \exp(iqa_j))$$

$$\Sigma A_j A_j^* = (\Delta\rho/q)^2 N (2 - \langle \exp(-iqa_j) \rangle - \langle \exp(iqa_j) \rangle)$$

Periodic systems.

2-phase structure w/ variable thickness lamellae

Now:

$$\langle \exp(-iqa_j)\rangle = \int_{-\infty}^{+\infty} \exp(-iqa_j)\, p_a(a)\, da$$

$$= P_a(q) = \text{Fourier transform of } p_a(a)$$

After further similar manipulations:

$$I(q) = 2N\,(\Delta\rho/q)^2\, Re\,[(1 - P_a)\,(1 - P_b)/\,(1 - P_a P_b)]$$

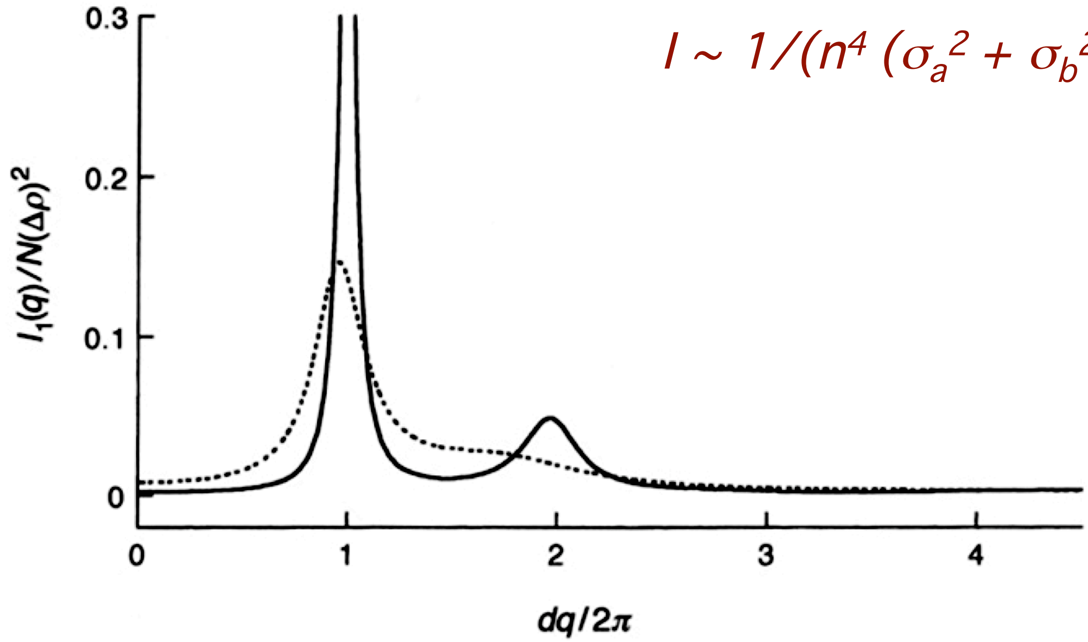
If $p_a(a)$ known or assumed, can calc $I(q)$

Periodic systems.

2-phase structure w/ variable thickness lamellae

Example

Suppose p_a, p_b Gaussian:



$I \sim 1/(n^4\ (\sigma_a^{\ 2} + \sigma_b^{\ 2}))$

Scattering intensity $I_1(q)$ from stack of parallel lamellae of alternating phases A and B, in which thicknesses of lamellae vary according to Gaussian probability functions. Solid line: $\phi_a = 0.3$, $\sigma_a = 0.15d_a$, $\sigma_b = 0.15d_b$. Broken line: $\phi_a = 0.3$, $\sigma_a = 0.3d_a$, $\sigma_b = 0.3d_b$.

Periodic systems.

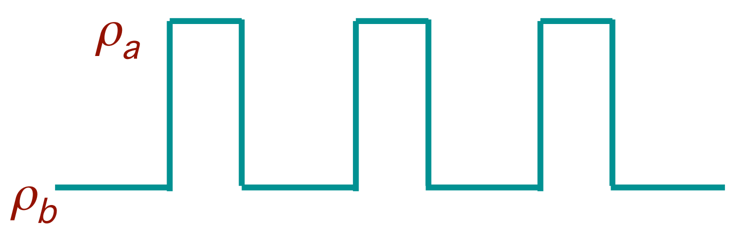
2-phase lamellar structures - correlation functions

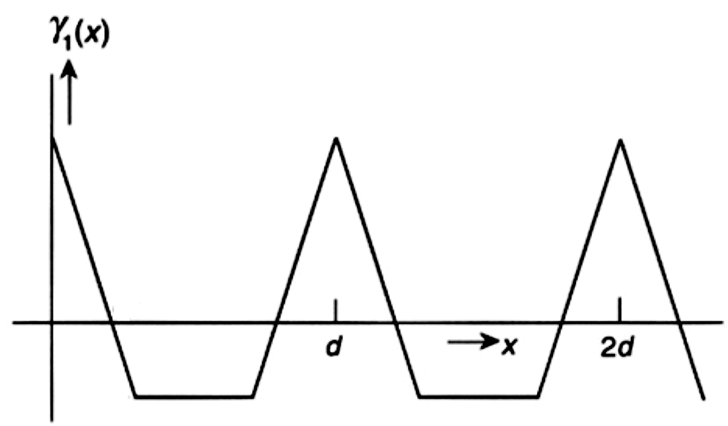
Can get Γ_{obs} from Fourier transform of $I(q)$ & compare with

$$\Gamma_{model}(x) = \int \eta(u)\, \eta(u + x)\, du$$

$$\eta_a = \rho_b - \langle\rho\rangle = \Delta\rho\, \phi_b$$

$$\eta_b = \rho_b - \langle\rho\rangle = \Delta\rho\, \phi_a$$





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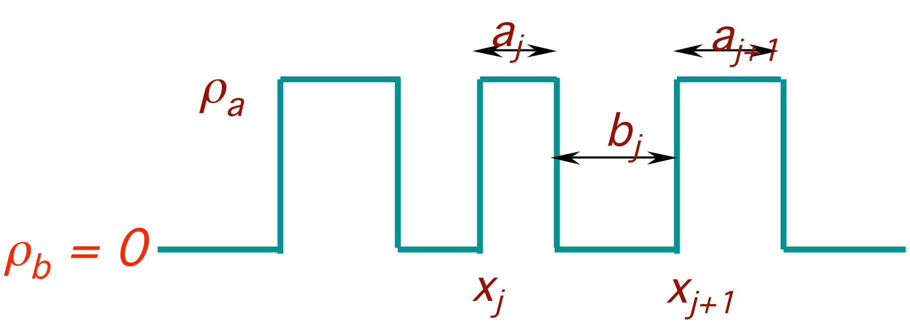
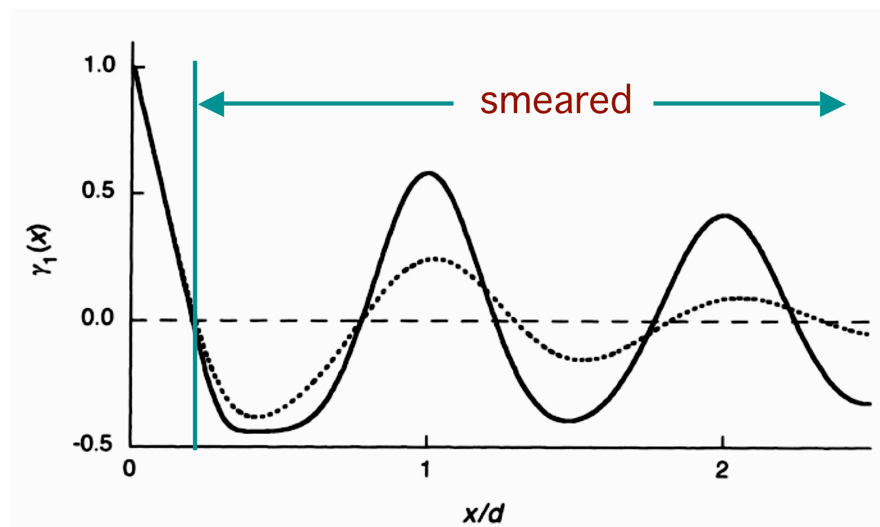
If thicknesses of lamellae vary (Gaussian):





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If lamellae/lamellae transitions not sharp, self correlation peak rounds