


Small Angle X-ray Scattering (I)

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Scattering at Low Angles

Inhomogeneous Density Distribution Over Large Distance (nm scale)

$$s = 1/D \text{ (or } q = 2\pi/D) \text{ (\AA}^{-1}\text{)}$$

$$s = 0.001 - 0.1 \text{ \AA}^{-1} \quad D (10 \sim 1000 \text{ \AA})$$

$$2\theta = 0.008-8, \quad \lambda = 1.542 \text{ \AA}$$

$$s = |\vec{s}| = \frac{2\sin\theta}{\lambda}$$

- *Morphological information of multiphase system:
Domain (Particle) Size, Distribution, Surface
Area, Interface Thickness*
- *Density Fluctuation*
- *Supramolecular Ordered Structure (nanometer scale)*

Fundamental Theories

- X-ray scattering from the electron density distribution in sample
- Small angle scattering for the large distance

$$f(\vec{s}) = \int_{V_r} \rho(\vec{r}) e^{2\pi i \vec{r} \cdot \vec{s}} d\vec{r}$$

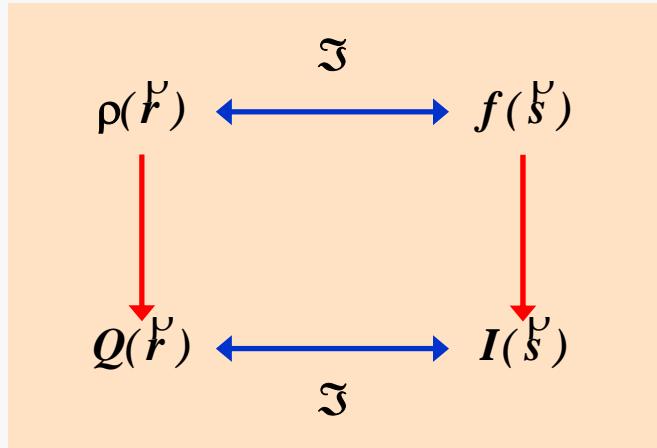
$$I(\vec{s}) = f(\vec{s}) \cdot f^*(\vec{s})$$

$$I(s) = |\mathfrak{F}\{\rho(x)\}|^2$$

$$\left| \frac{-}{s} \right| = \frac{2 \sin \theta}{\lambda} = \frac{1}{d} \quad \quad \left| \frac{-}{q} \right| = \frac{4 \pi \sin \theta}{\lambda}$$

$$I(\vec{s}) = \mathfrak{F}\{Q(\vec{r})\}$$

$$Q(\vec{r}) = \mathfrak{F}^{-1}\{I(\vec{s})\}$$



$f(\vec{s})$: Amplitude of scattered X-ray

$I(\vec{s})$: Scattered intensity

$\rho(\vec{r})$: Electron density function

$Q(\vec{r})$: Patterson function ($\rho(\vec{r}) * \rho(-\vec{r})$)

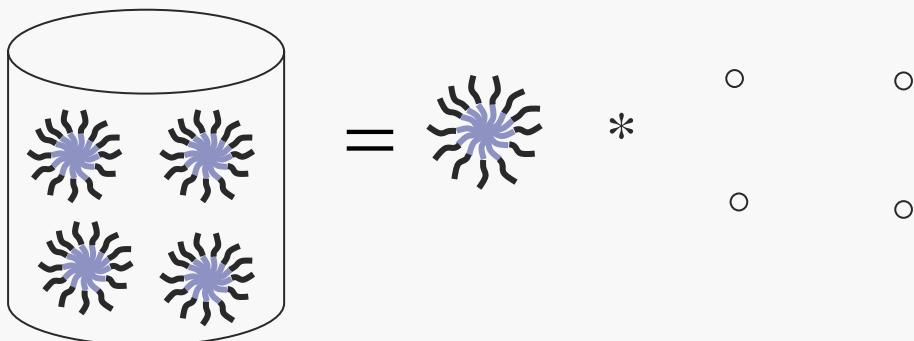
\mathfrak{F} : Fourier transform

Convolution

$$\{f * g\}(\vec{r}) \equiv \int_{-\infty}^{\infty} f(\vec{u}) g(\vec{r} - \vec{u}) d\vec{u}$$

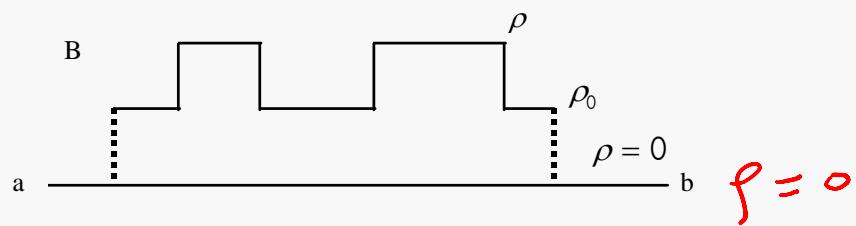
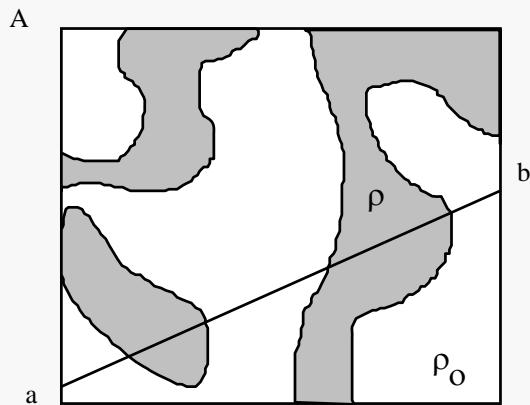
$$f * g(-\vec{r}) \equiv \int_{-\infty}^{\infty} f(\vec{u}) g(\vec{r} + \vec{u}) d\vec{u}$$

$$\Im\{f * g\} = \Im\{f\} \cdot \Im\{g\}$$



Two Phase System

Sharp boundary



Model of two phase system (A) and electron density distribution follow up line a-b (B).

Patterson Function

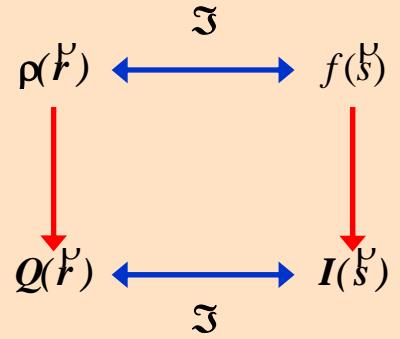
$$I(\bar{s}) = \mathfrak{I}\{Q(\bar{r})\} \quad Q(\bar{r}) = \mathfrak{I}^{-1}\{I(\bar{s})\}$$

$$Q(\bar{r}) = \rho(\bar{r}) * \rho(-\bar{r}) = \int \rho(\bar{a}) \rho(\bar{r} + \bar{a}) d\bar{a}$$

$$\begin{aligned} Q(\bar{r}) &= \int_0^\infty (\eta(\bar{a}) + \rho_0)(\eta(\bar{r} + \bar{a}) + \rho_0) d\bar{a} & \eta(\bar{r}) &= \rho(\bar{r}) - \rho_0 \\ &= \int \eta(\bar{a}) \eta(\bar{r} + \bar{a}) d\bar{a} + C \end{aligned}$$

$$I(\vec{s}) = \mathfrak{I}\{\eta(\vec{r}) * \eta(-\vec{r})\} + \mathfrak{I}\{C\}$$

$$I_{obs}(\bar{s}) = \mathfrak{I}\{\eta(\bar{r}) * \eta(-\bar{r})\}$$



$$I_{obs}(\bar{s}) = \mathfrak{I}[Q_\eta(\bar{r})] \Leftrightarrow Q_\eta(\bar{r}) = \mathfrak{I}^{-1}\{I_{obs}(\bar{s})\}$$

Derivation

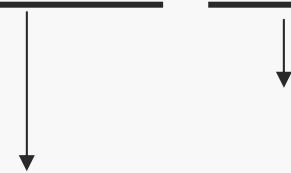
$$I(s) = \Im \left\{ \int \rho(u) \rho(u+r) du \right\}$$

$$\eta(u) = \rho(u) - C$$

$$\begin{aligned} \int \rho(u) \rho(u+r) du &= \int [\eta(u) + C] [\eta(u+r) + C] du \\ &= \int \eta(u) \eta(u+r) du + C \int \eta(u) du + C \int \eta(u+r) du + C^2 \int du \\ &= \int \eta(u) \eta(u+r) du + C' \end{aligned}$$

$$I(s) = \frac{\Im \left\{ \int \eta(u) \eta(u+r) du \right\}}{\overline{}}$$

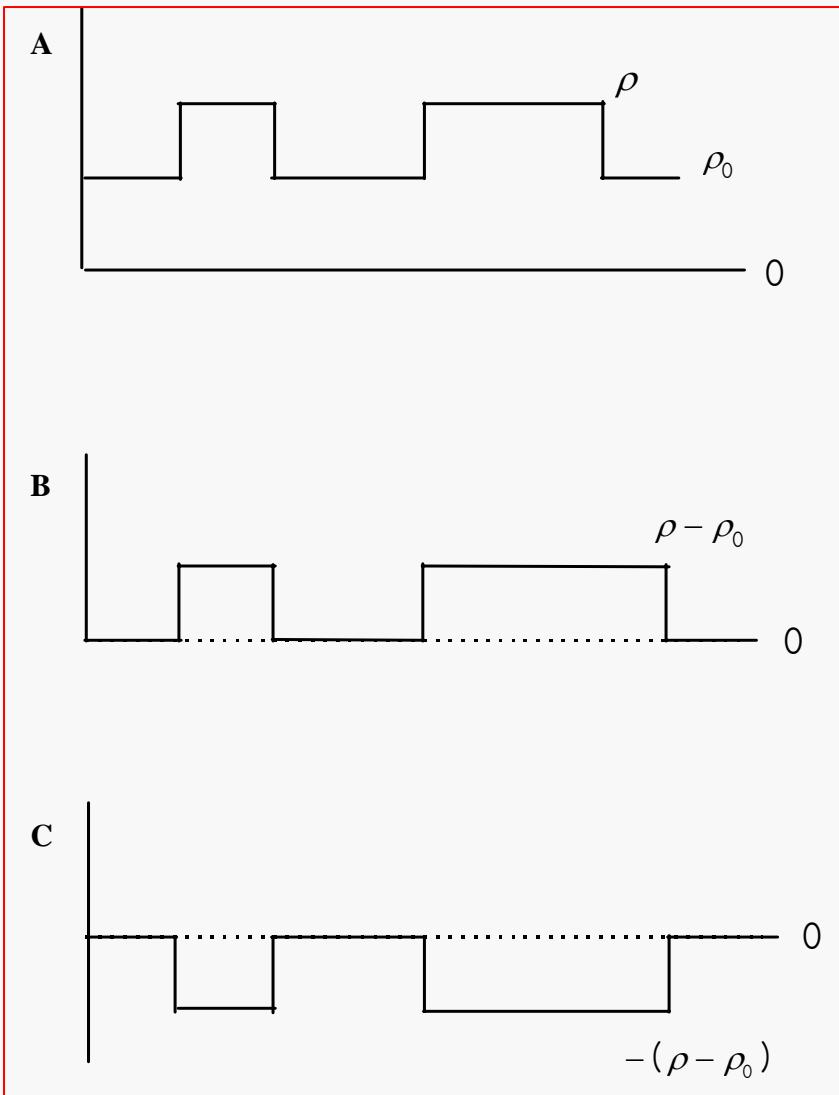
$$+ \frac{\Im \{ C \}}{\overline{}}$$



delta function at $s=0$

$$I_{obs}$$

Babinet's Reciprocity Principle



All produces identical I_{obs}

Correlation Function and Patterson Function

$$\gamma(\bar{r}) = \frac{\eta(\bar{r}) * \eta(-\bar{r})}{\int_0^\infty [\eta(\bar{r})]^2 d\bar{r}} = \frac{\int_0^\infty \eta(\bar{a}) \eta(\bar{r} + \bar{a}) d\bar{a}}{\int_0^\infty \eta(\bar{a}) \eta(\bar{a}) d\bar{a}} = \mathfrak{I}^{-1}\{I_{obs}(\bar{s})\} \cdot \frac{1}{\langle \eta^2 \rangle V}$$

For an isotropic system $\left| \vec{s} \right| = s, \quad \left| \vec{r} \right| = r$

$$\gamma(r) = \mathfrak{I}^{-1}\{I_{obs}(s)\} \frac{1}{\langle \eta^2(u) \rangle V} = \frac{\int s^2 I_{obs}(s) \frac{\sin 2\pi r s}{2\pi r s} ds}{\int s^2 I_{obs}(s) ds}$$

Pair Distance Distribution Function (PDDF) $P(r) = r^2 \gamma(r)$

Invariant

Integration of Intensity

$$\int_0^\infty I_{obs}(\bar{s}) d\bar{s} = \int_0^\infty I_{obs}(\bar{s}) e^{2\pi i \bar{s} \bar{r}} d\bar{s}, \quad \bar{r} = 0$$

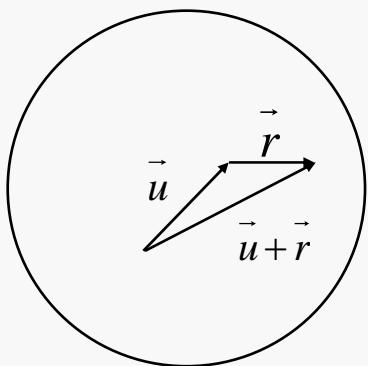
$$\Im^{-1} [I_{obs}(\bar{s})], \quad \bar{r} = 0$$

$$\langle \eta^2 \rangle V \cdot \gamma(0) = \langle \eta^2 \rangle V$$

Integration of intensity =
average density difference * scattering volume

Meaning of Correlation Function

$$\frac{\int_0^{\infty} \eta(\bar{a})\eta(\bar{r}+\bar{a})d\bar{a}}{\int_0^{\infty} \eta(\bar{a})\eta(\bar{a})d\bar{a}}$$



$$\rho(r) = \begin{cases} \rho & \text{inside} \\ 0 & \text{outside} \end{cases}$$

\vec{u} and $\vec{u} + \vec{r}$ (inside the particle): $\gamma(\bar{r}) = 1$

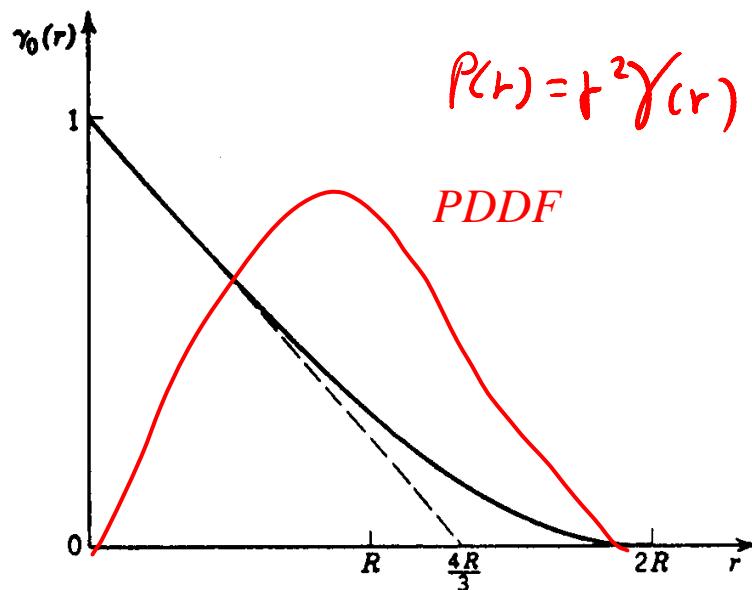
$\vec{u} + \vec{r}$ (outside the particle): $\gamma(\bar{r}) = 0$

γ depending on particle shape and size,
representing the probability of finding of a point $u + r$ within the particle

Correlation function of sphere
of radius R

$$\gamma(r) = 0 \quad r > 2R$$

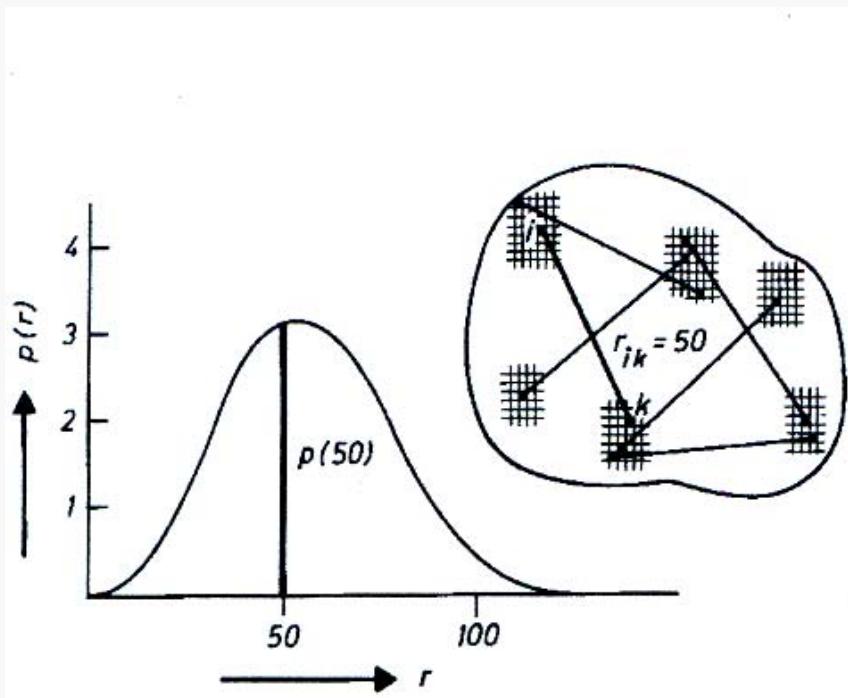
$$\gamma(r) = 1 - \frac{3}{4} \frac{r}{R} + \frac{1}{16} \left(\frac{r}{R} \right)^3$$



Pair Distance Distribution Function

$$P(r) = r^2 \gamma(r)$$

Probability finding scattering elements separated by r

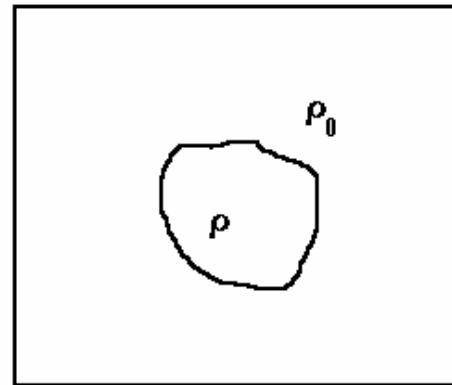


Particle Scattering (single particle)

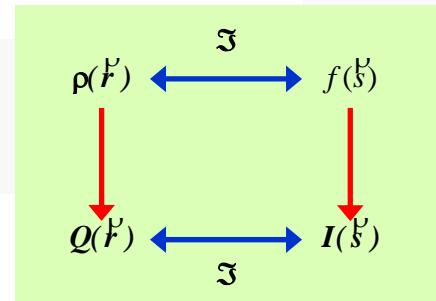
$$\eta(\vec{r}) (\equiv \rho(\vec{r}) - \rho_0) = (\rho - \rho_0) \sigma(\vec{r})$$

$\sigma(\vec{r}) \begin{cases} 1 & \text{inside} \\ 0 & \text{outside} \end{cases}$ form factor

$$f(s) = \Im \{(\rho - \rho_0) \sigma(r)\} = (\rho - \rho_0) F(s)$$



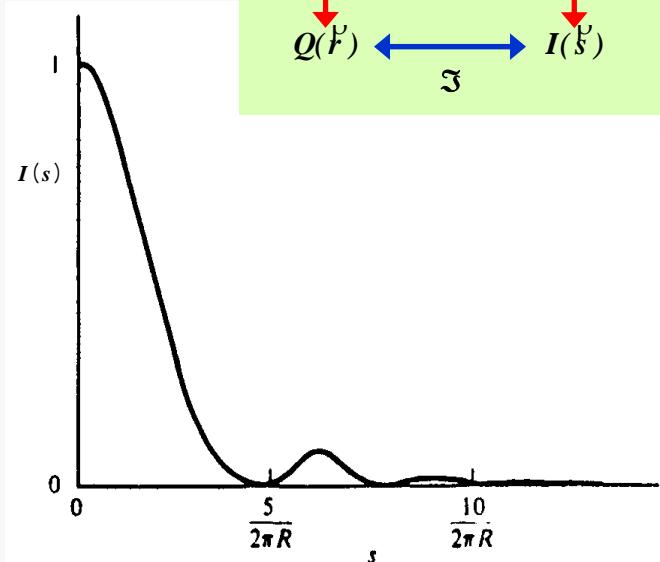
$$I_{obs}(\bar{s}) = \Im \{\eta(\bar{r}) * \eta(-\bar{r})\} = (\rho - \rho_0)^2 |F(\bar{s})|^2$$



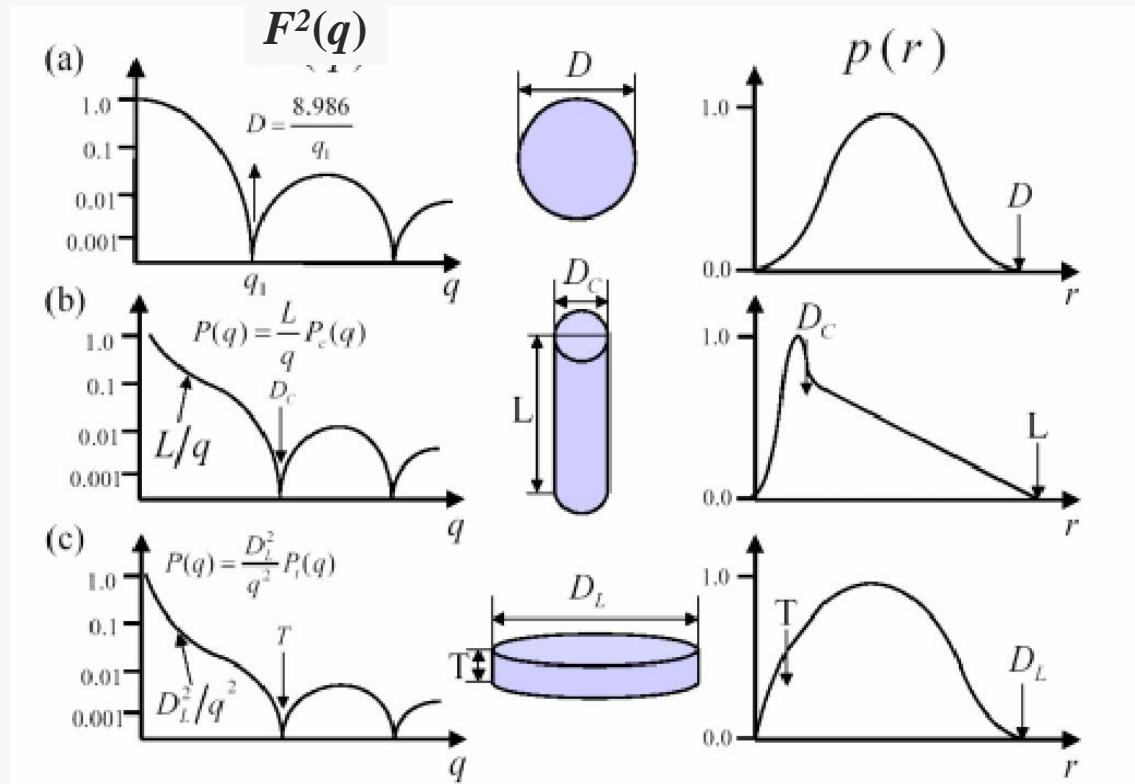
For Spherical Particles

$$I_{obs}(s) =$$

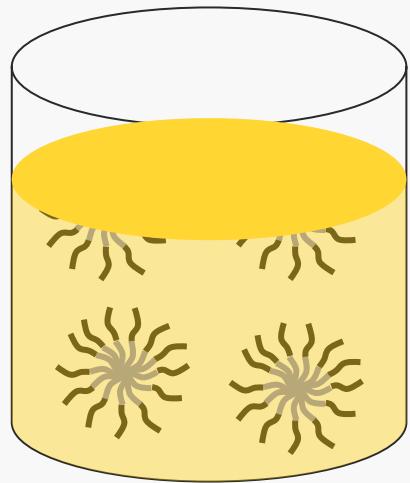
$$(\rho - \rho_0)^2 \frac{4}{3} \pi R^3 \left[3 \frac{\sin(2\pi R s) - 2\pi r s \cos(2\pi R s)}{(2\pi R s)^2} \right]$$



Particle Scattering Pattern and PDDF



Particle Scattering



convolution

↓

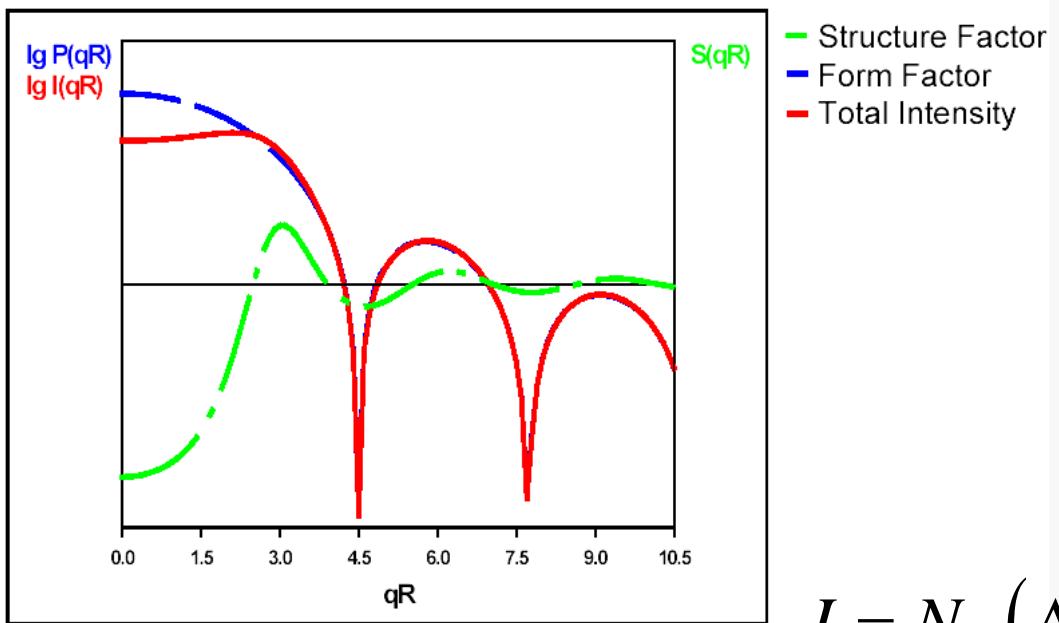
\otimes

$I = N_p \left(\Delta\rho_p \right)^2 F^2(q) S^2(q)$

Form Factor Structure Factor

The diagram illustrates the convolution process in particle scattering. On the left, a cylinder contains four polymer particles. An equals sign followed by a convolution symbol (\otimes) indicates the calculation of the intensity I . The intensity is the result of convolving the form factor $F^2(q)$ (represented by a starburst) with the structure factor $S^2(q)$ (represented by a collection of blue dots). Red arrows point from the labels "Form Factor" and "Structure Factor" to their respective components in the equation.

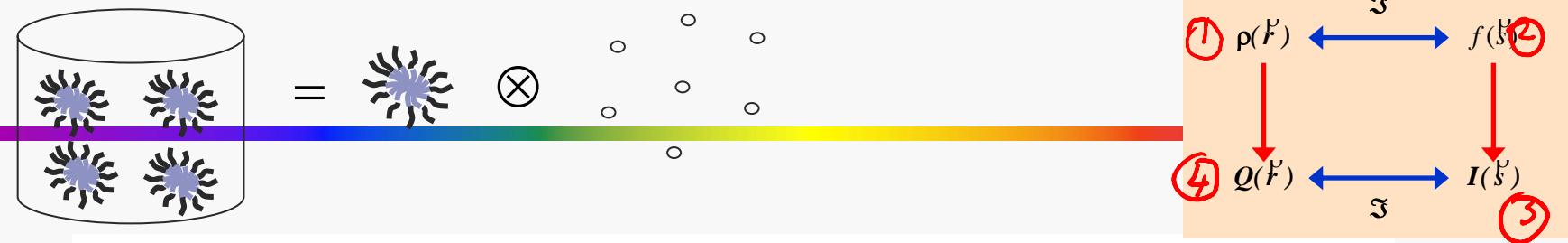
$S(q) \approx 1$ for dilute solution



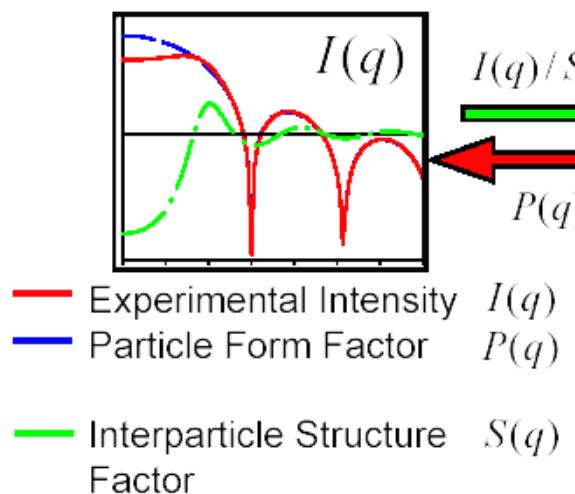
$$I = N_p \left(\Delta \rho_p \right)^2 F^2(q) S(q)$$

Form Factor *Structure Factor*

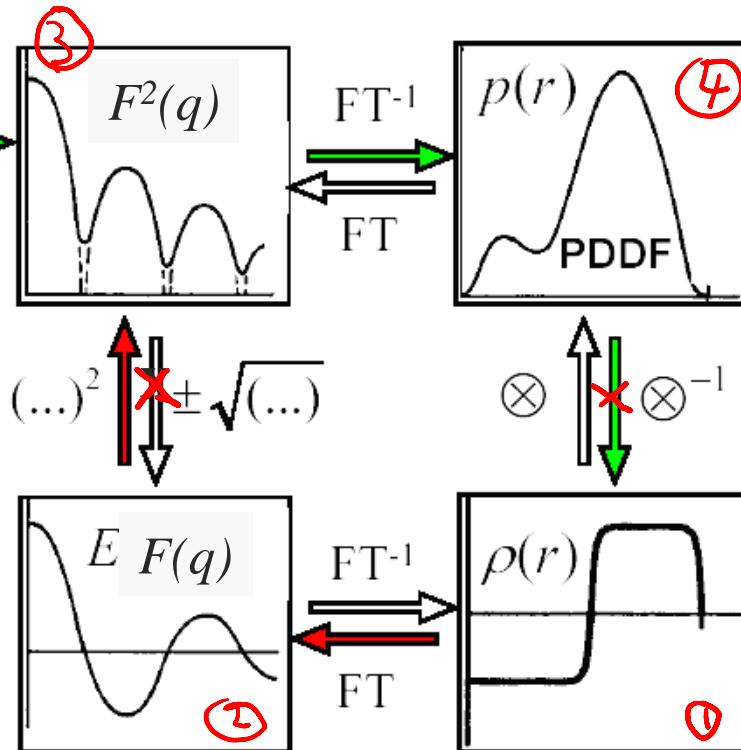
$S(q) \approx 1$ for dilute solution



Dense system

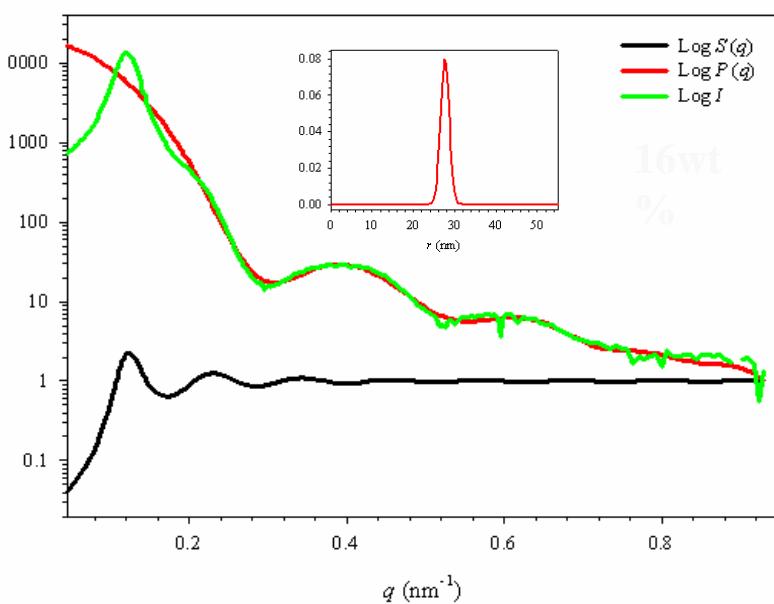
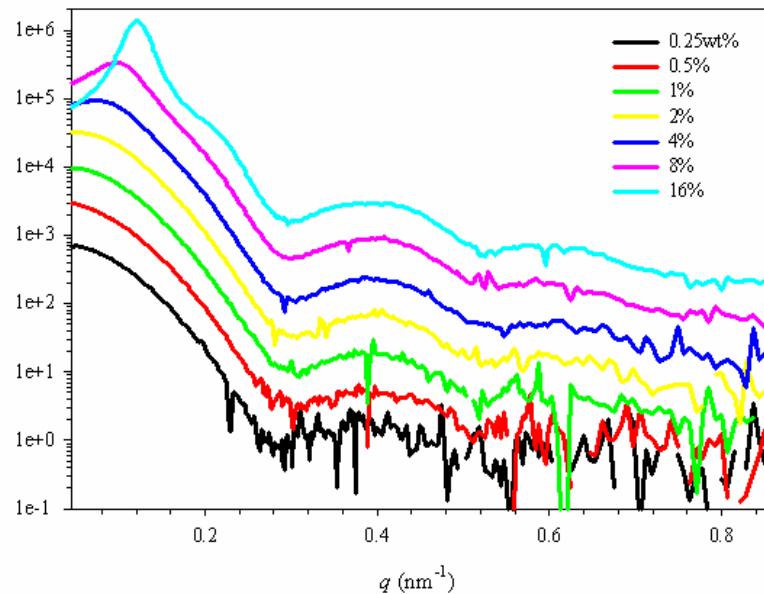


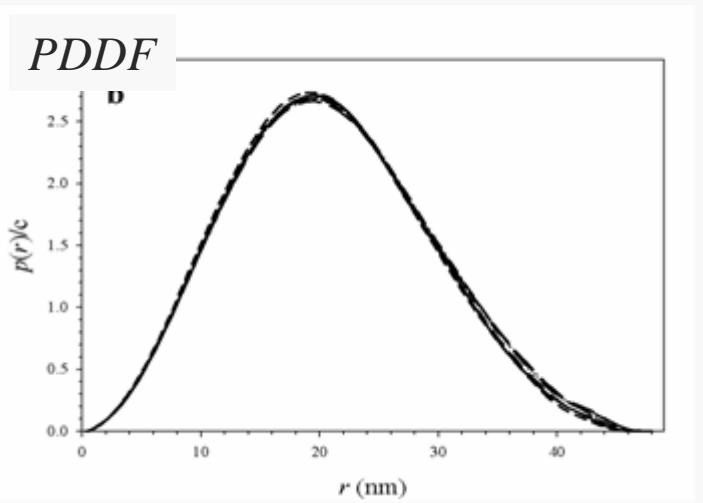
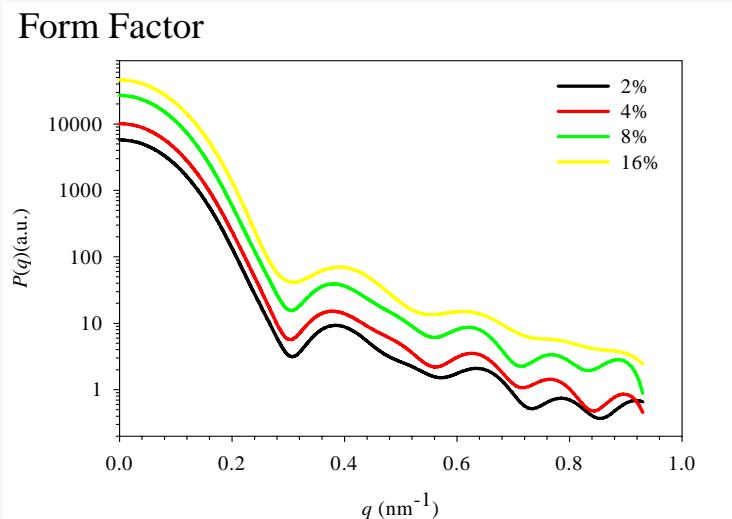
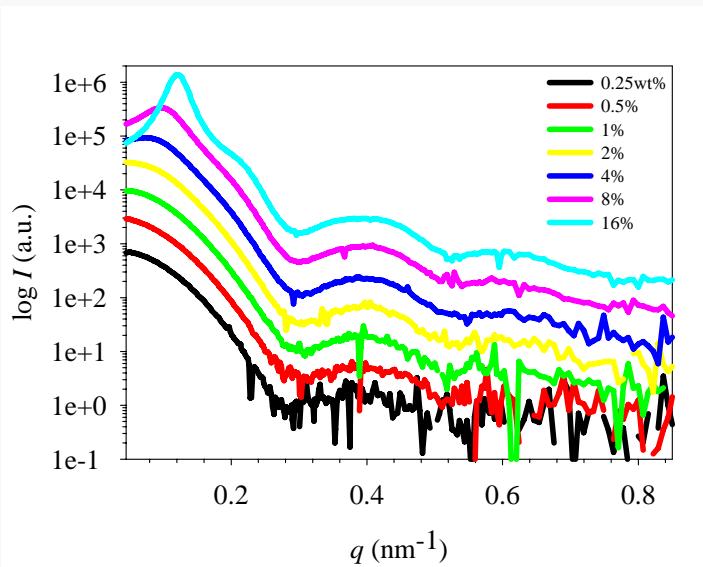
Dilute system



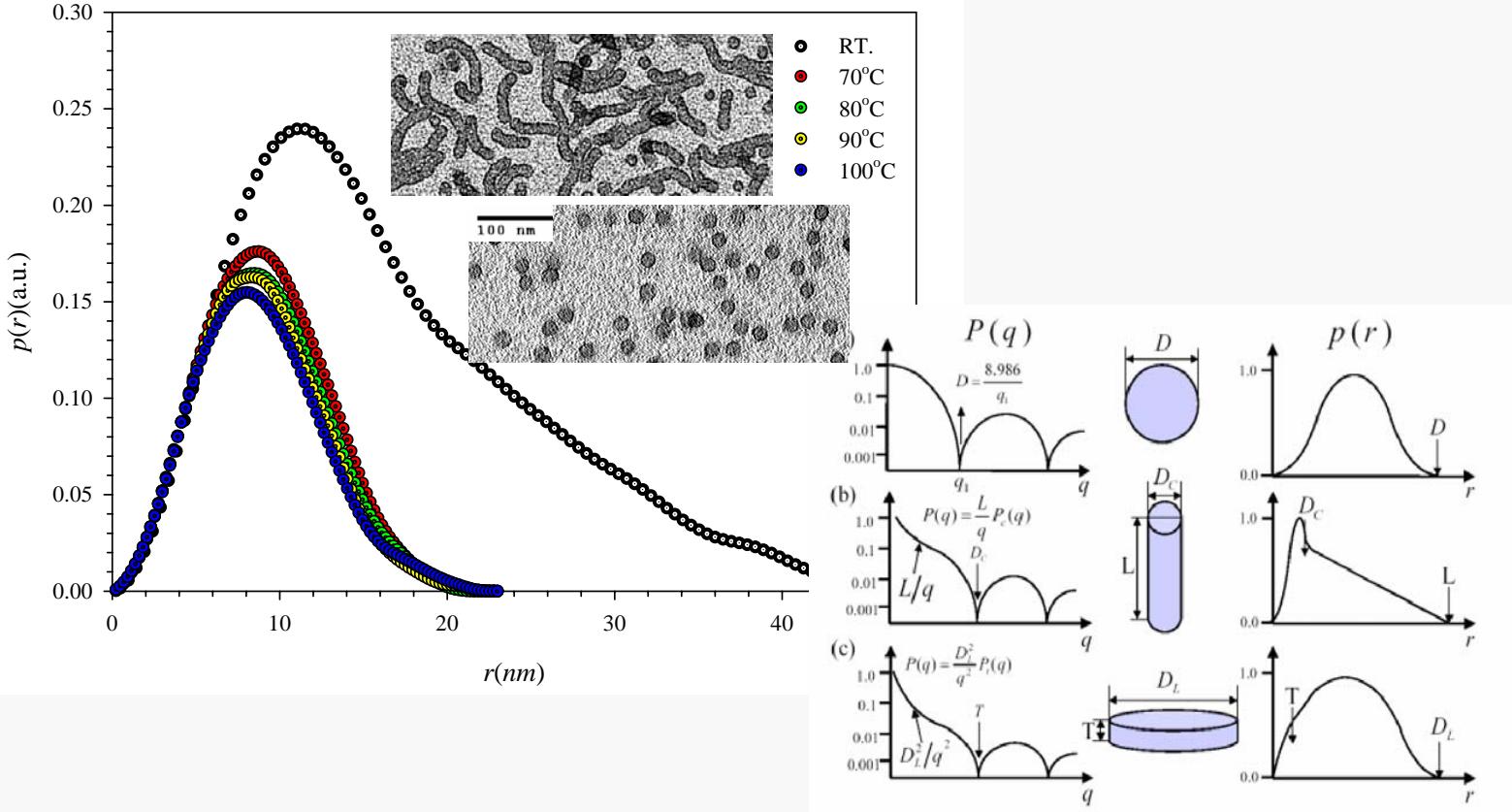
█ Interpretation
█ Modelling

PS(12k)-*b*-PVP(11.8k) solutions in toluene





**PDDF of PS(12K)-*b*-P4VP(11.8K),
with different concentration levels up to 16 wt %.**



S.Y.Park

Guinier Approximation

$$I_{obs}(s) = N \langle \eta^2 \rangle V^2 e^{-\frac{4}{3} \pi^2 R_g^2 s^2}$$

$$\ln I_{obs}(s) = \ln N V^2 \langle \eta^2 \rangle - \frac{4}{3} \pi^2 R_g^2 s^2$$

R_g : radius of gyration

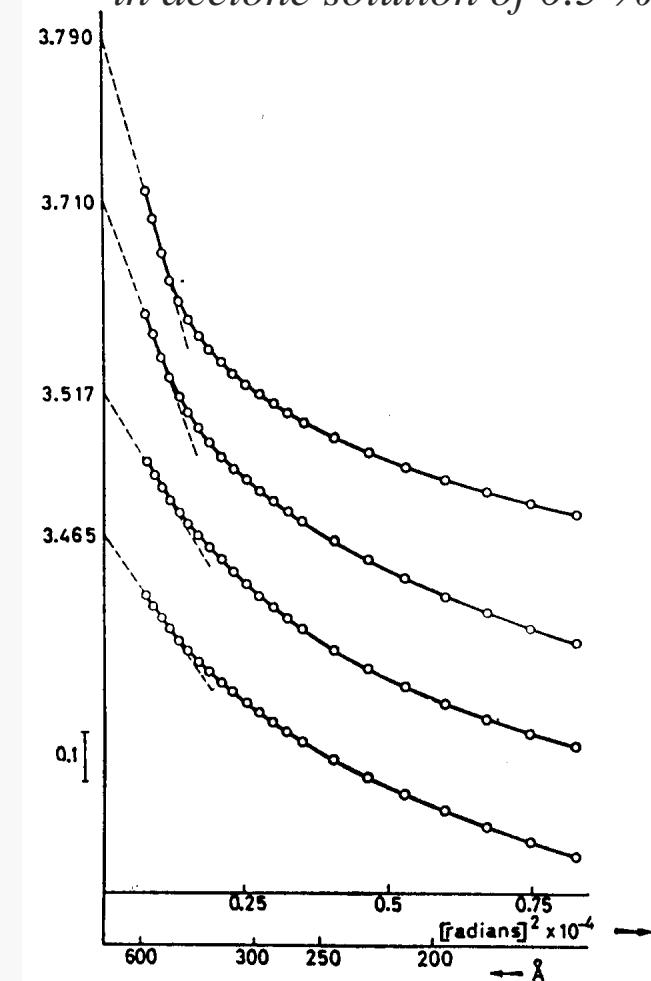
V : scattering volume

R_g from the slope

$$I(0) = N V^2 \langle \eta \rangle^2$$

- Applicable only at very small angles
- Must be sufficiently dilute

Guinier plot of cellulose nitrate in acetone solution of 0.5 %.



Porod Law (for high scattering angle, Porod region)

For spherical particle

$$I_{obs}(s) = \frac{\rho - \rho_0}{8\pi^3} \left[\frac{4\pi R^2}{s^4} + \frac{1}{\pi s^6} + \frac{4R}{s^5} \sin 4\pi R s + \left(\frac{4\pi a^2}{s^4} - \frac{1}{\pi s^6} \right) \cos 4\pi R s \right]$$

when s is large

$$I_{obs}(s) = \frac{\rho - \rho_0}{8\pi^3} \frac{A}{s^4}$$

A is surface area of the particle

Satisfies regardless of particle shape, size and concentration

Surface area A can be obtained from the plot of $s^4 I_{obs}(s)$ vs. s

This is also used for intensity fit at high angles

Condensed Multi-phase

ρ_1, ρ_2 : densities of particle and matrix

ϕ_1, ϕ_2 : volume fractions $\rho_0 = \rho_1 \phi_1 + \rho_2 \phi_2$ average density

$$\eta(r) = \rho(r) - \rho_o$$

$$\langle \eta^2 \rangle = \Delta\rho^2 \phi_1 \phi_2 \quad \Delta\rho = \rho_1 - \rho_2$$

$$I_{obs}(\vec{s}) = \langle \eta^2 \rangle V \Im\left\{ \gamma(\vec{r}) \right\} = \Delta\rho^2 \phi_2 \phi_1 V \cdot \Im\left\{ \gamma(\vec{r}) \right\}$$

$$I_{obs}(s) = \underbrace{2\pi(\Delta\rho)^2 \phi_1 \phi_2}_\text{①} V \cdot \underbrace{\Im\left\{ \gamma(r) \right\}}_\text{②}$$

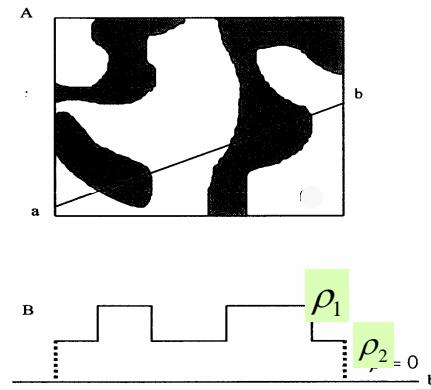
Invariant

$$\int I_{obs}(\vec{s}) d\vec{s} = \int I_{obs}(s) e^{i2\pi \vec{r} \cdot \vec{r}} ds \quad (\vec{r} = 0)$$

$$\underbrace{(\Delta\rho)^2 \phi_1 \phi_2}_\text{③} V \gamma(\vec{r}), \quad \vec{r} = 0$$



$$(\Delta\rho)^2 \phi_1 \phi_2 V$$



Surface Area

$$\gamma'(0) = -\frac{1}{4\phi_1\phi_2} \frac{A}{V}$$

Interface Thickness

$$\rho_{sharp}(r)$$

$$h(r)$$

$$\rho_{diffuse}(r)$$

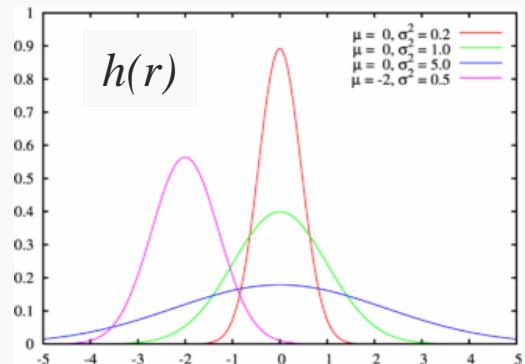
$$\rho_{diffuse}(r) = \rho_{sharp}(r) * h(r)$$

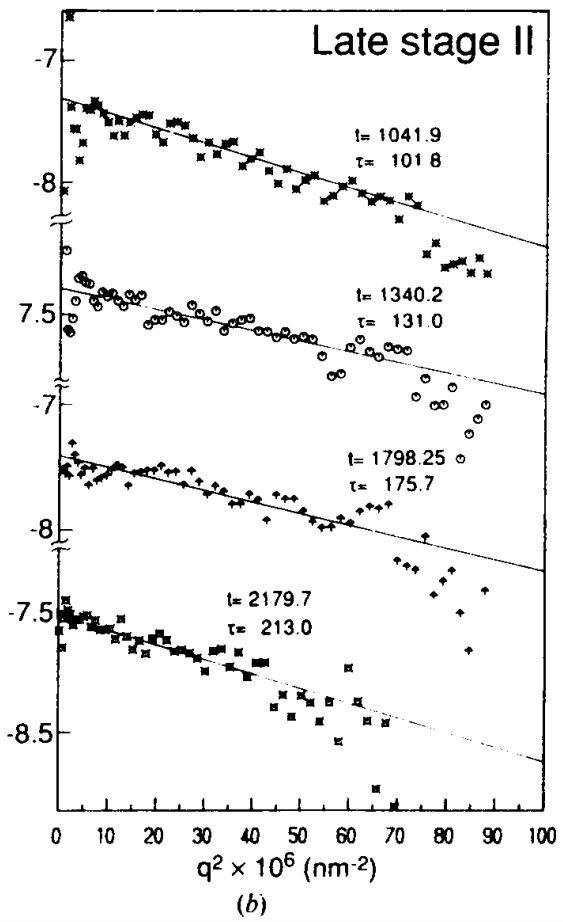
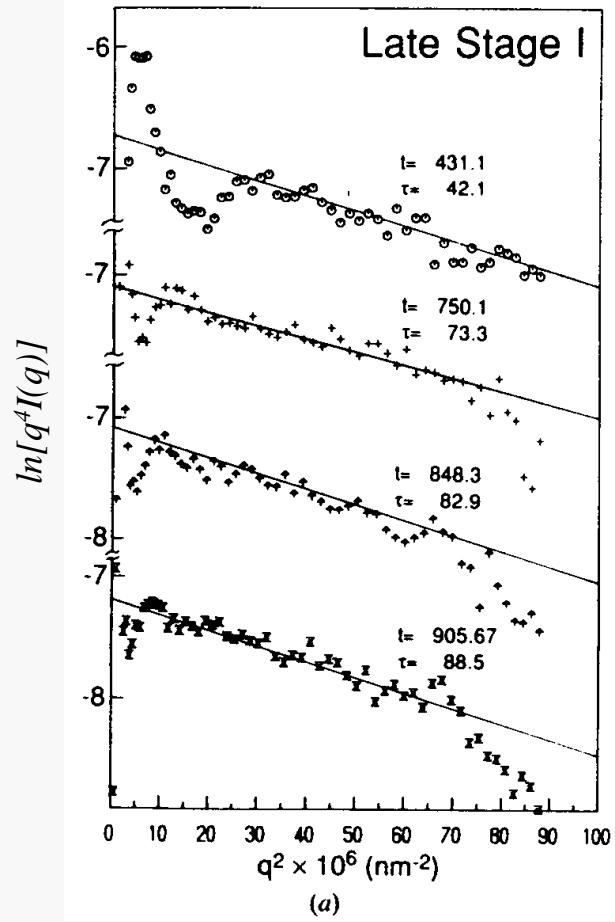
$$h(r) = \frac{1}{(\sqrt{2\pi}\sigma)^3} \exp\left(-\frac{r^2}{2\sigma^2}\right)$$

$$I_{diffuse}(\vec{s}) = I_{sharp}(\vec{s}) \left| \Im\left\{ h(\vec{r}) \right\} \right|^2 \quad \left| \Im\left\{ h(\vec{r}) \right\} \right|^2 = e^{-4\pi^2\sigma^2 s^2}$$

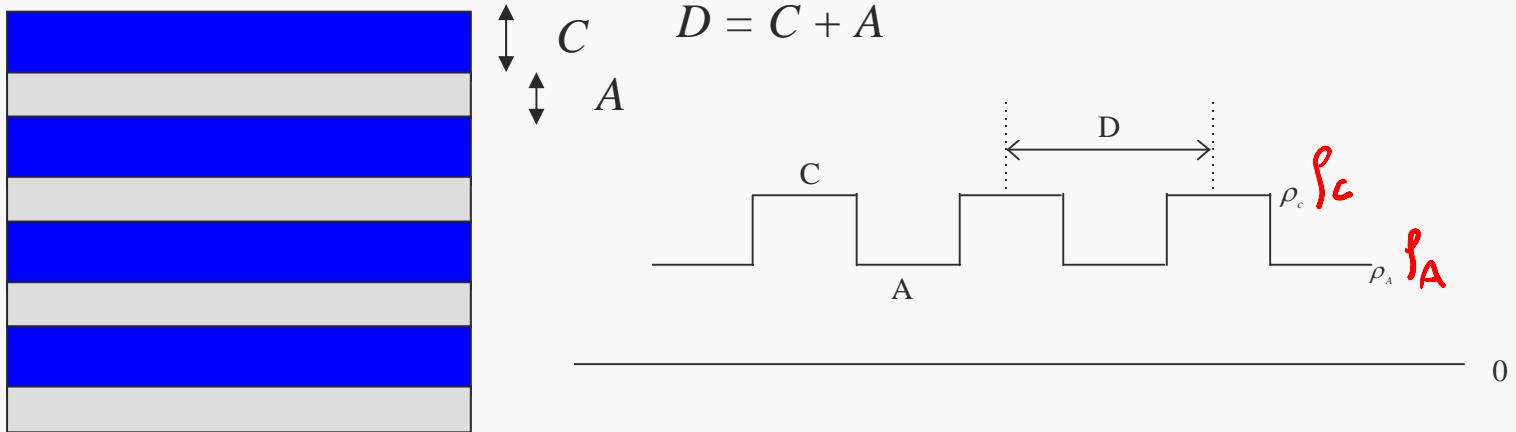
$$I_{diffuse}(s) = I_{sharp}(s) e^{-4\pi^2\sigma^2 s^2} \sim I_{sharp}(s) (1 - 4\sigma^2\pi^2 s^2)$$

$$I_{diffuse}(s) \sim \frac{1}{8\pi} (\Delta\rho)^2 \frac{A}{s^4} (1 - 4\sigma^2\pi^2 s^2) \quad \textit{Porod region}$$



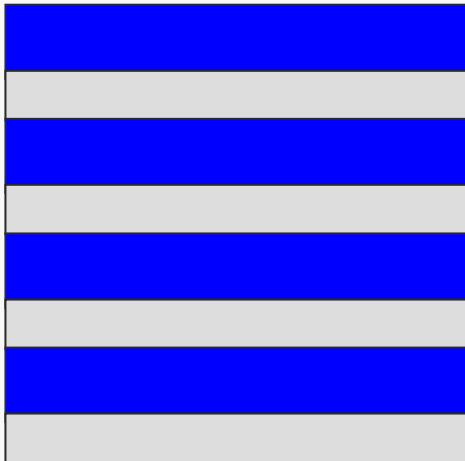
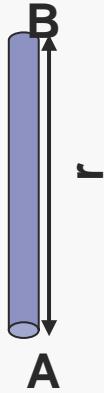


Polymer Crystals (*lamellae*)



$$I_{1obs}(s) = 4\pi s^2 I_{obs}(s)$$

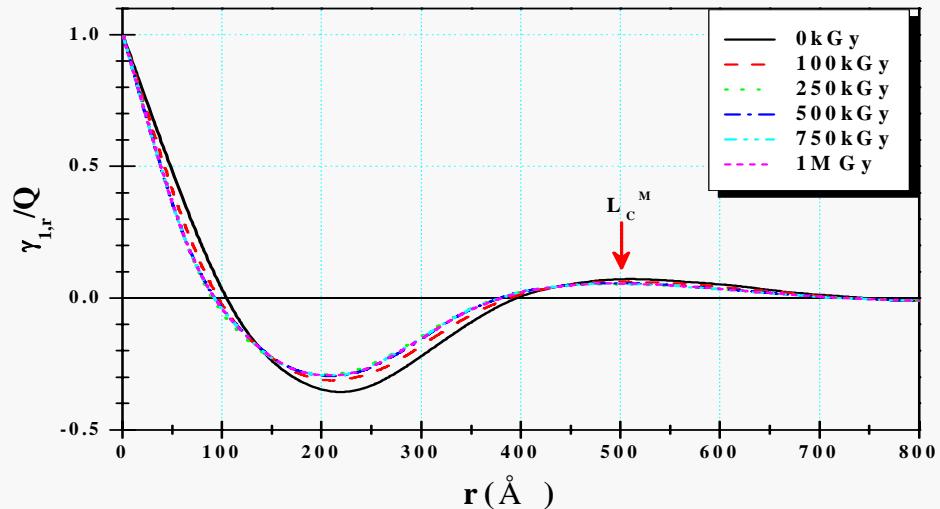
Correlation Function



$$\eta_A, \eta_B (\eta = \rho - \langle \rho \rangle)$$

$$\gamma_1(r) = \frac{\int \eta(r+u)\eta(u)du}{\langle \eta^2 \rangle} = \frac{\langle \eta_A \eta_B \rangle}{\langle \eta^2 \rangle}$$

$$\gamma_1(r) = \frac{\int I_I(s) \cos 2\pi rs ds}{\int I_I(s) ds}$$



Correlation and Interface Distribution Functions Analysis on Lamellar Structure

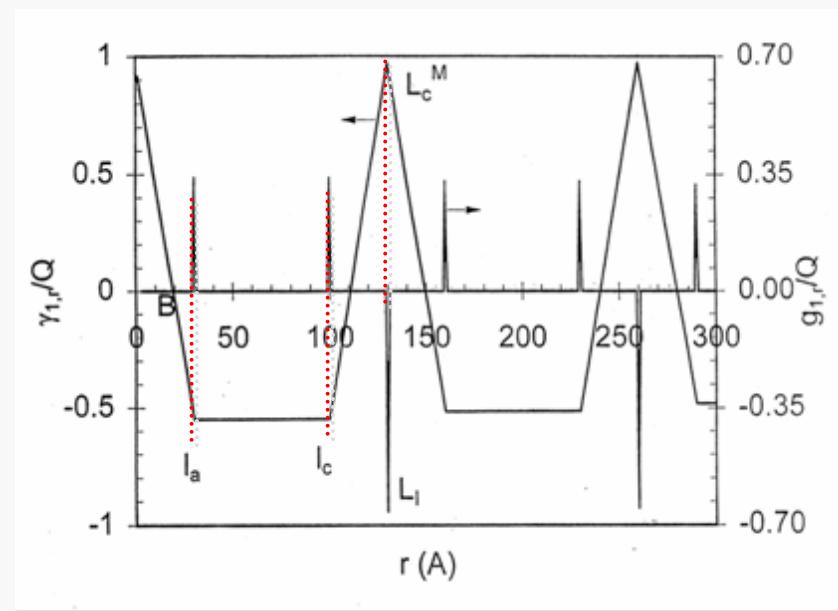
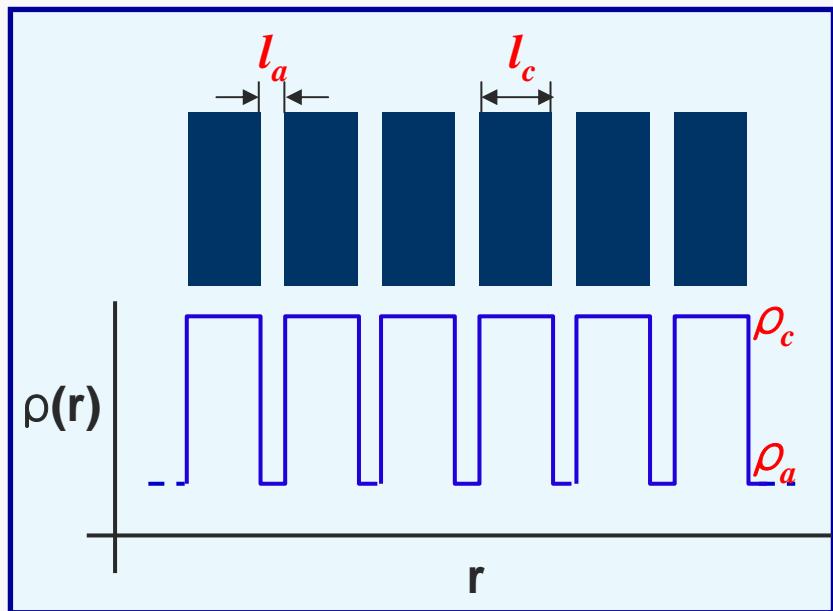
Examples of various arbitrary model

$$Z''(r) = \frac{2}{r_e^2 (2\pi)^2} \int_0^\infty \left[\lim_{q \rightarrow \infty} q^4 I(q) - q^4 I(q) \right] \cos qr dq$$

Ideal Two Phase Model

$$I_{ideal} = \Im(\rho_{ideal} * \rho_{ideal})$$

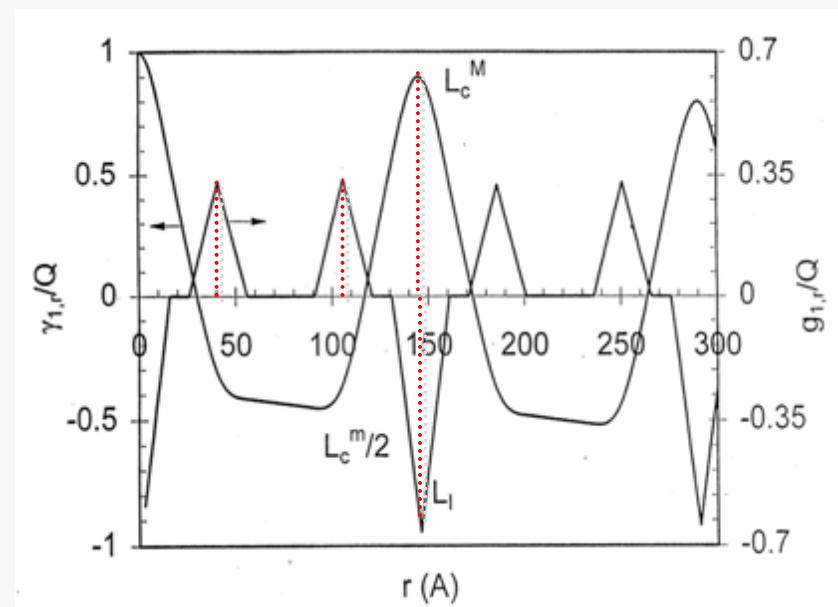
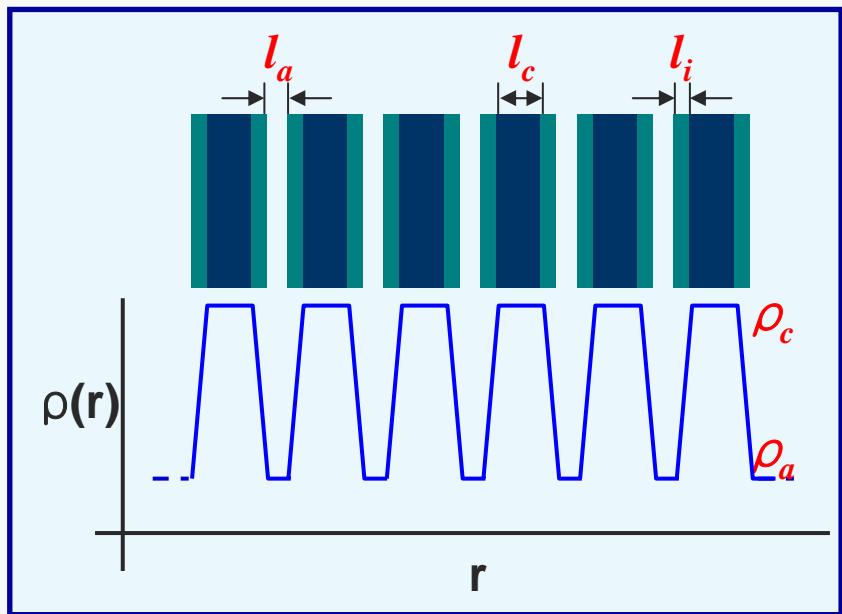
$l_c=100\text{\AA}$, $l_a=30\text{\AA}$, finite no. of lamellae in the stack is 20



Model With Interface (I)

The ideal two phase model with a finite crystal amorphous transition zone

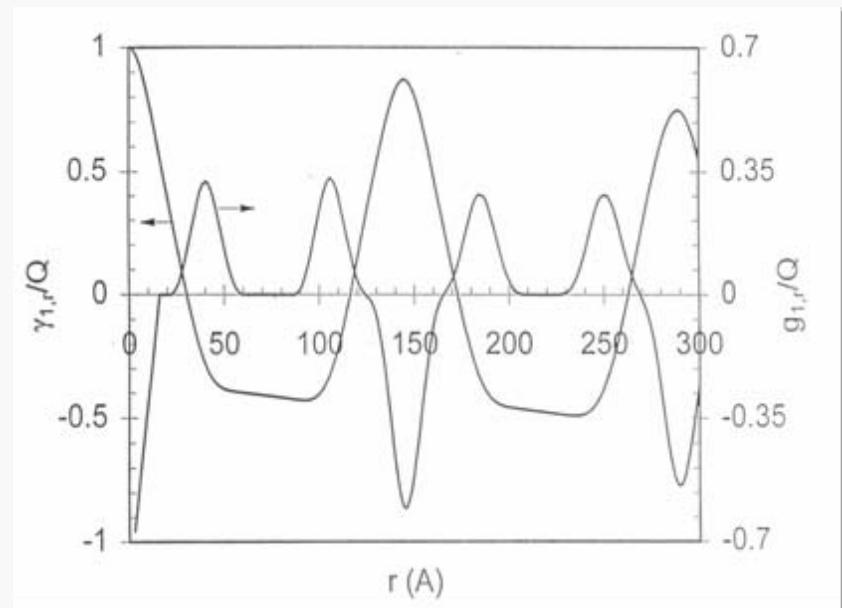
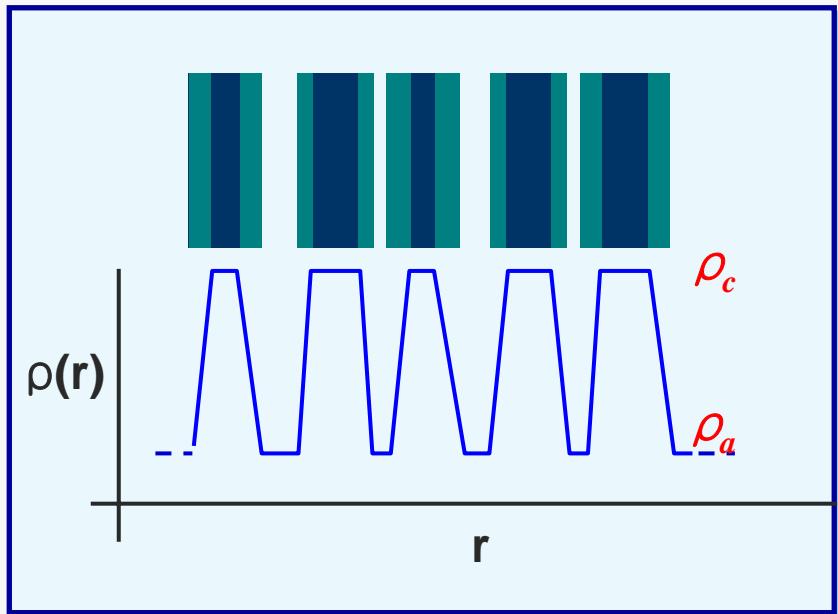
$$l_c=100\text{\AA}, l_a=30\text{\AA}, l_i=12\text{\AA}$$



Model With Interface (II)

Distribution of lamellar and amorphous layer sizes

$$l_c = 90\text{\AA}, w_c = 10\text{\AA}, l_a = 25\text{\AA}, w_a = 10\text{\AA}, l_i = 15\text{\AA}, w_i = 1\text{\AA}$$



$$L_{model} = L_c^M \geq L_c^m \quad \text{for } w_2 \leq w_1$$

$$L_{model} = L_c^M \leq L_c^m \quad \text{for } w_2 \geq w_1$$

2 ; thicker phase

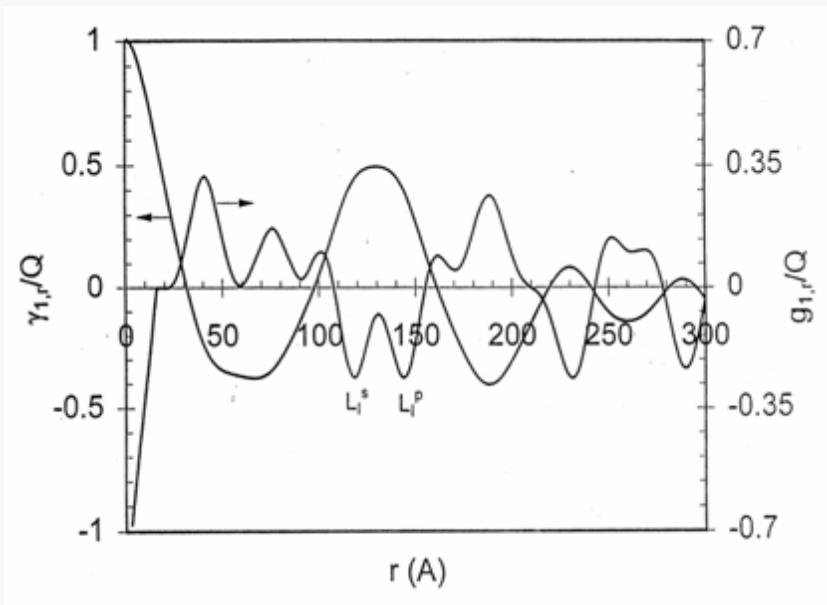
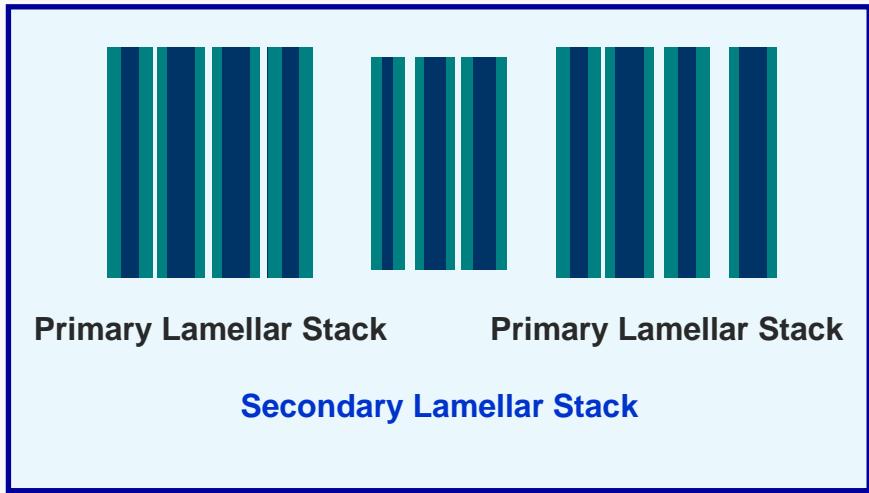
w ; width of the thickness distribution

L_{model} ; average long spacing in the model

Dual Lamellar Stack Model

Stack 1 $I_c=90\text{\AA}$, $w_c=10\text{\AA}$, $I_a=25\text{\AA}$, $w_a=10\text{\AA}$, $I_i=15\text{\AA}$, $w_i=1\text{\AA}$

Stack 2 $I_c=60\text{\AA}$, $w_c=10\text{\AA}$, $I_a=25\text{\AA}$, $w_a=10\text{\AA}$, $I_i=15\text{\AA}$, $w_i=1\text{\AA}$



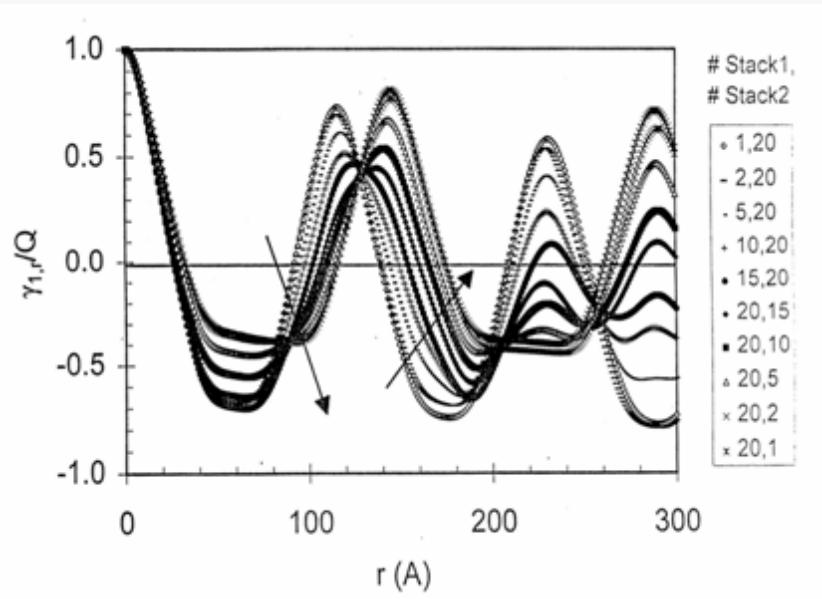
$$L_c^M \geq L_I, \quad L_c^m \geq L_I$$

$$L_c^M \geq L_c^m \geq L_I \quad \text{for } w_2 \leq w_1$$

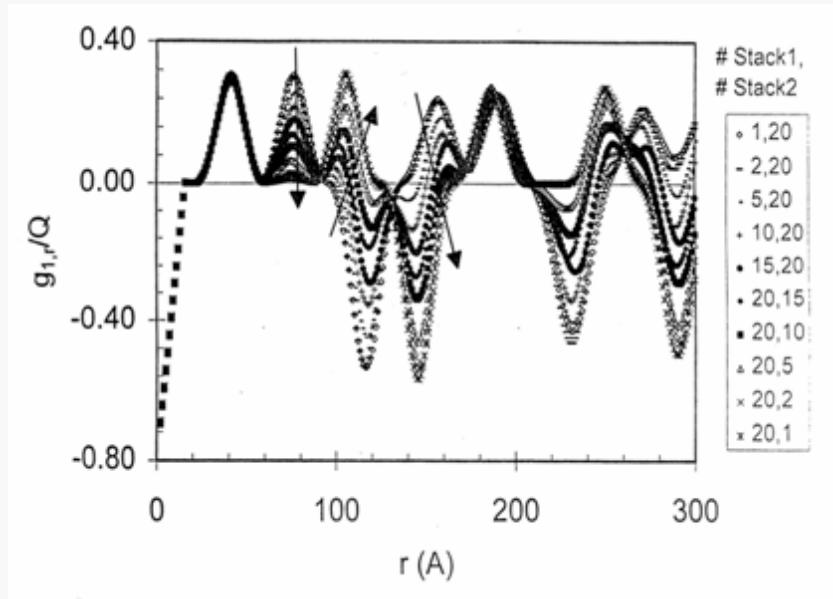
$$L_c^m \geq L_c^M \geq L_I \quad \text{for } w_2 \geq w_1$$

Examples

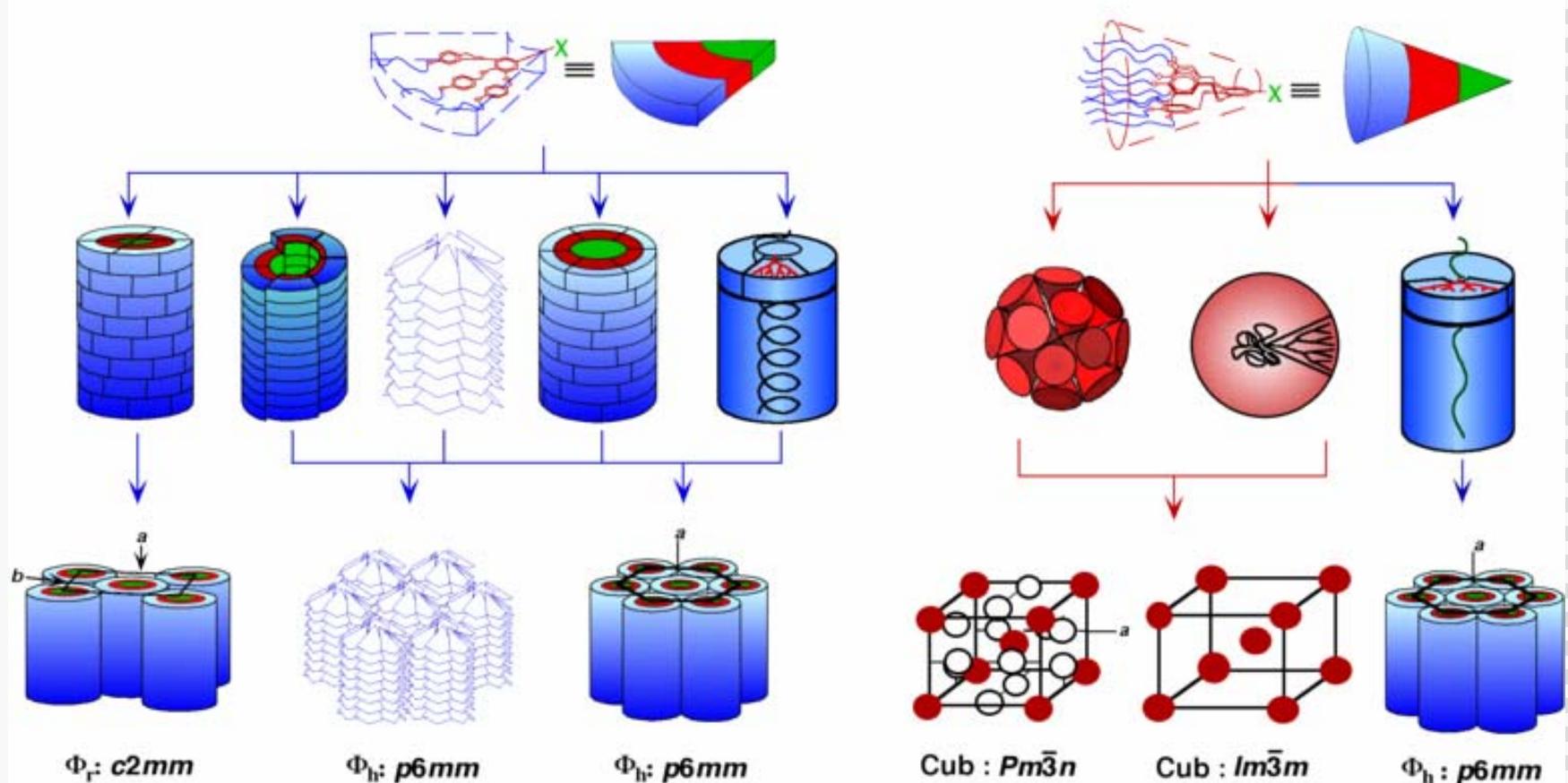
Correlation function



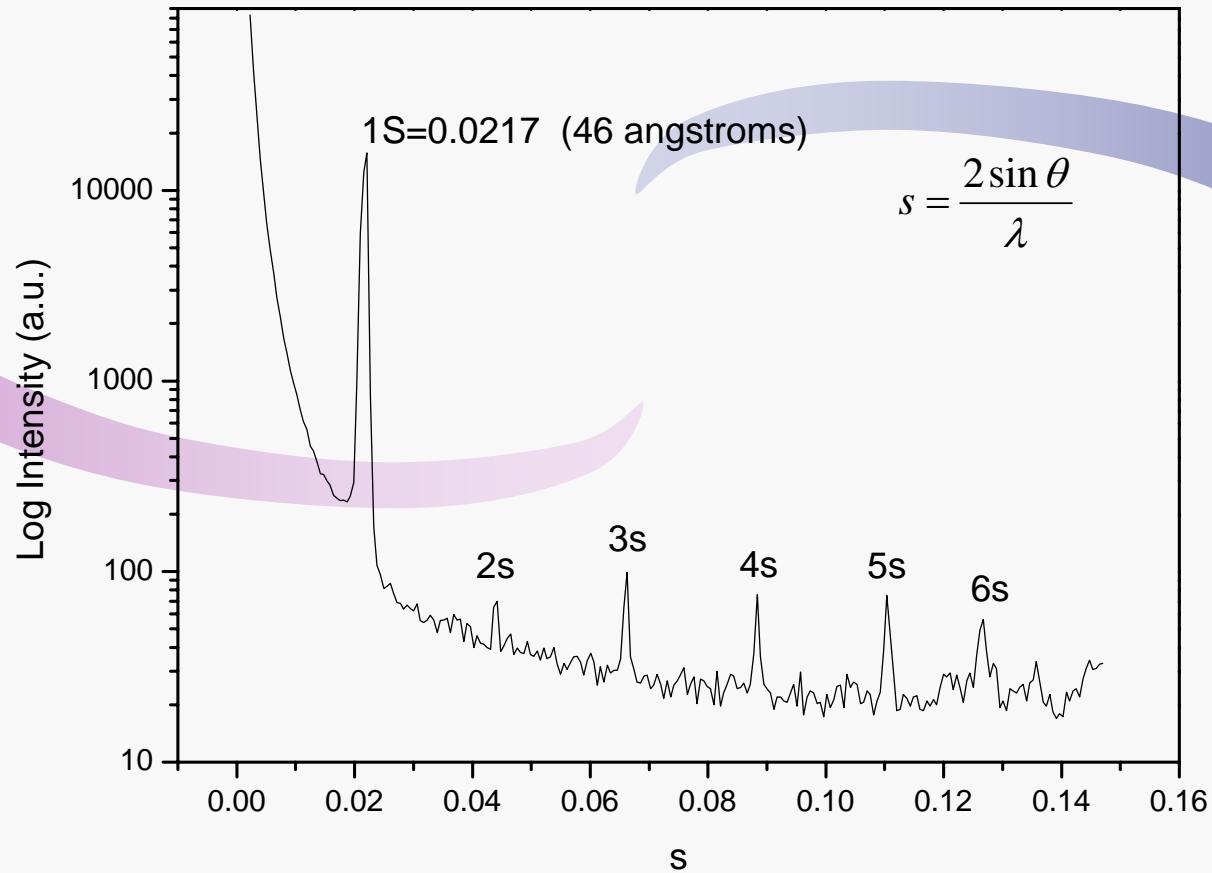
Interface distribution function



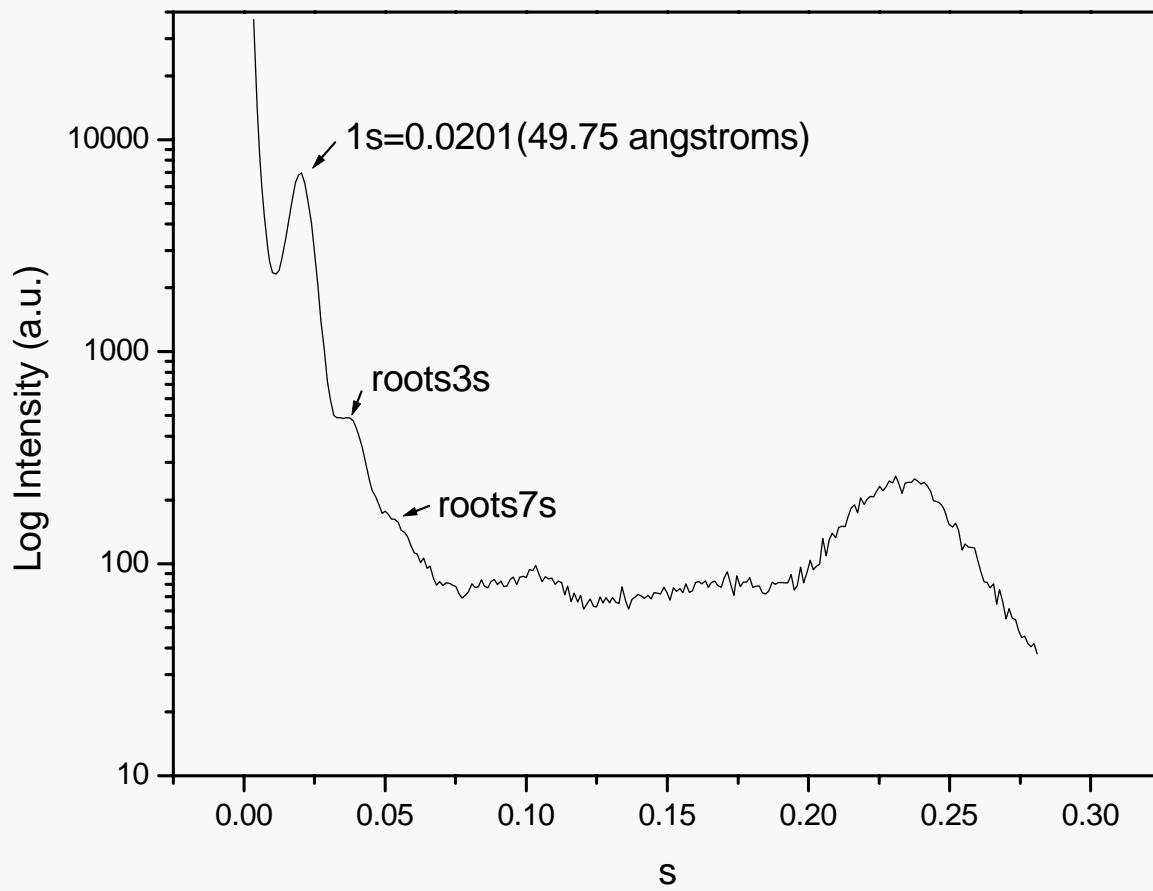
Nanostructures



Lamella



Hexagonal cylinder

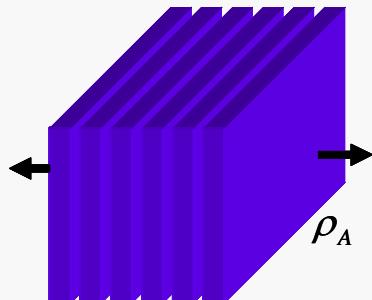
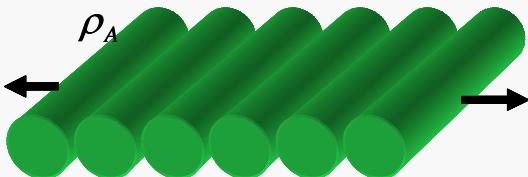


Mathematical treatment of X-ray scattering

$$I(s) = |\Im\{\rho(x)\}|^2$$

$$s = \frac{2\pi \sin \theta}{\lambda} = \frac{1}{d}$$

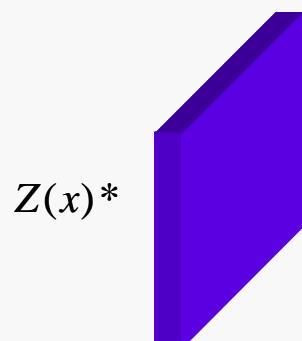
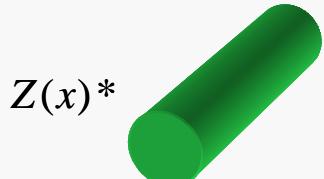
$$\begin{aligned}\rho(x) &= \rho_A(x) * Z(x) \\ \Im\{\rho(x)\} &= \Im\{\rho_A(x) * Z(x)\} \\ &= \Im\{\rho_A(x)\} \cdot \Im\{Z(x)\} \\ &= F(S) \cdot Z(S)\end{aligned}$$

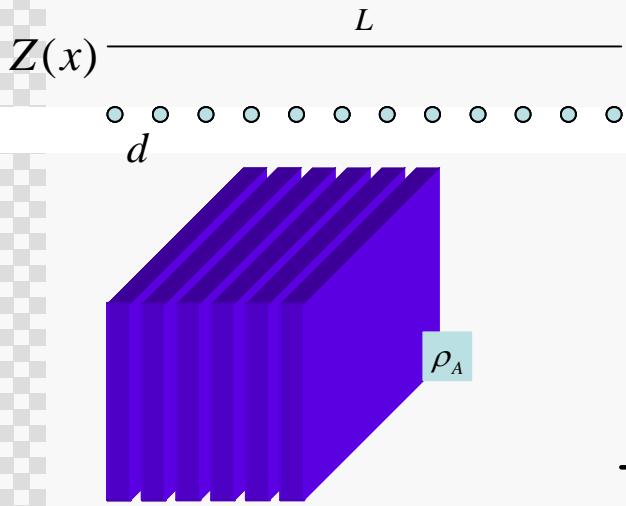


$$Z(x) \equiv \sum_{n=-\infty}^{+\infty} \delta(x - nd)$$



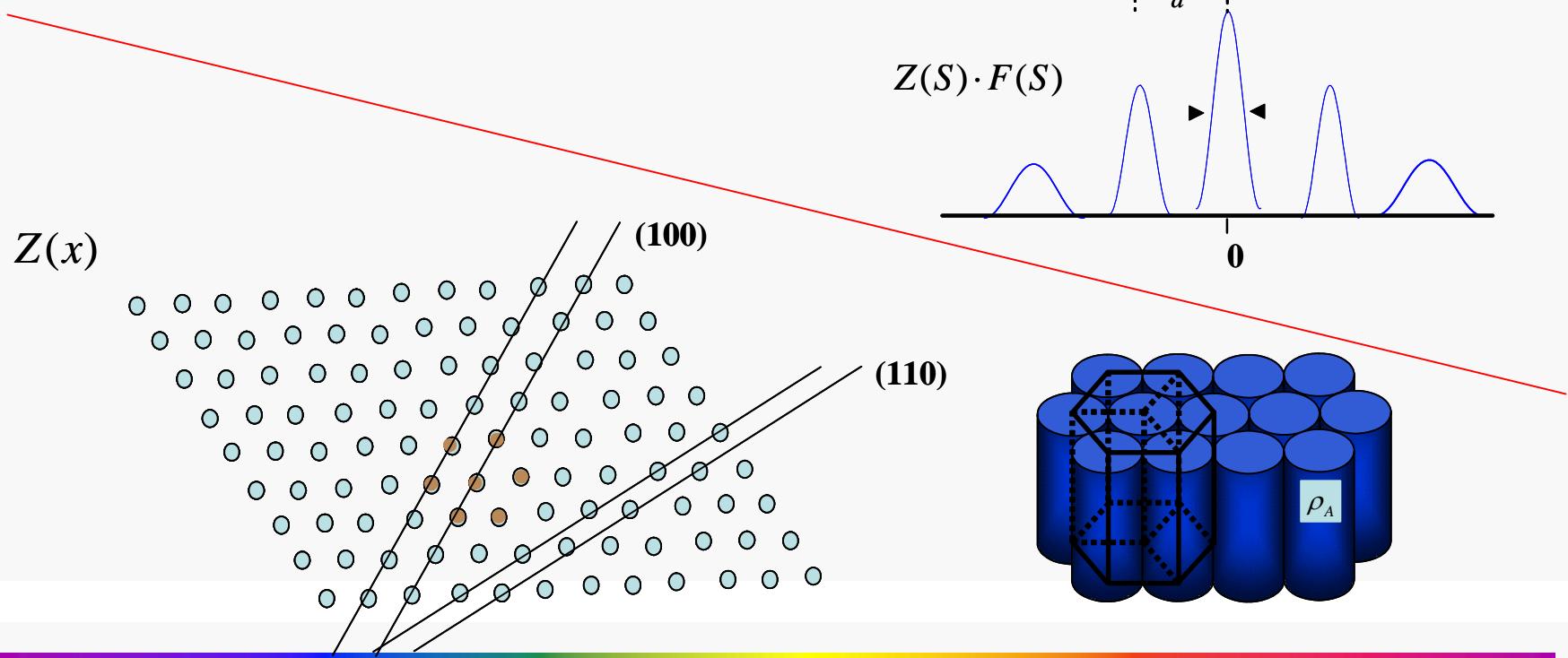
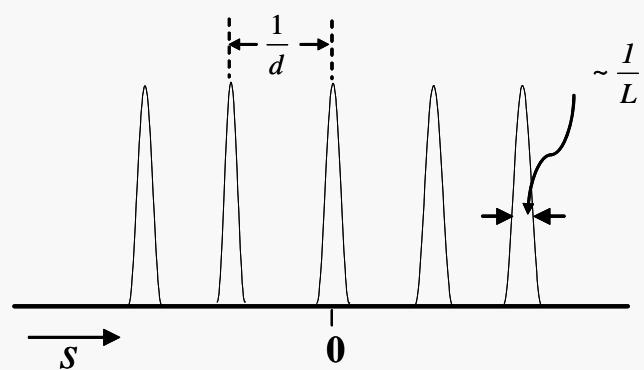
$$\rho(x) = Z(x) * \rho_A$$



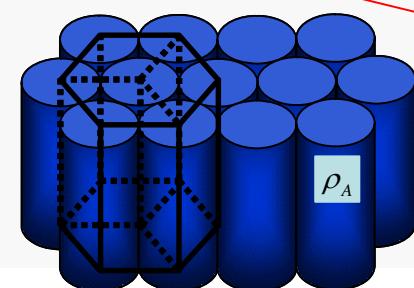
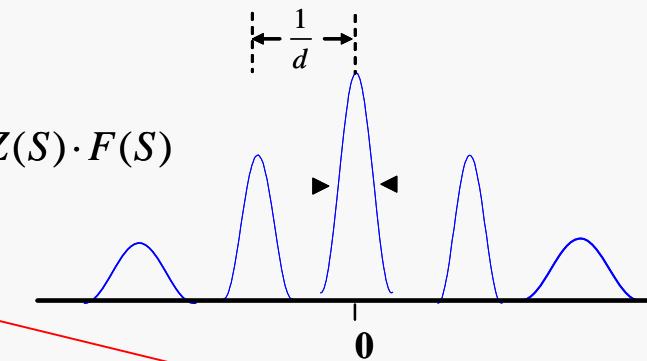


$$Z(S) = \Im\{Z(x)\}$$

$$F(S) = \Im\{\rho_A(x)\}$$



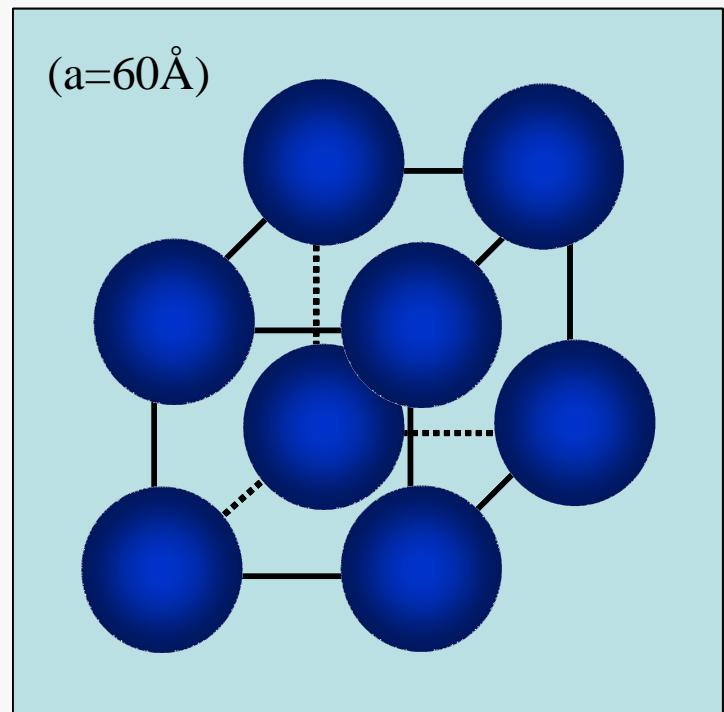
$$Z(S) \cdot F(S)$$



Sphere cubic packing

h	k	l	s²	s	order	d
1	0	0	2.78E-04	0.016667	1	60.00
1	1	0	5.56E-04	0.02357	$\sqrt{2}$	42.43
1	1	1	8.33E-04	0.028868	$\sqrt{3}$	34.64
2	0	0	0.00111	0.033333	$\sqrt{4}$	30.00
2	1	0	0.00139	0.037268	$\sqrt{5}$	26.83
2	1	1	0.00167	0.040825	$\sqrt{6}$	24.49
2	2	0	0.00222	0.04714	$\sqrt{8}$	21.21
2	2	1	0.0025	0.05	$\sqrt{9}$	20.00
2	2	2	0.00333	0.057735	$\sqrt{12}$	17.32
3	0	0	0.0025	0.05	$\sqrt{9}$	20.00
3	1	0	0.00278	0.052705	$\sqrt{10}$	18.97
3	1	1	0.00306	0.055277	$\sqrt{11}$	18.09
3	2	0	0.00361	0.060093	$\sqrt{13}$	16.64
3	2	1	0.00389	0.062361	$\sqrt{14}$	16.04

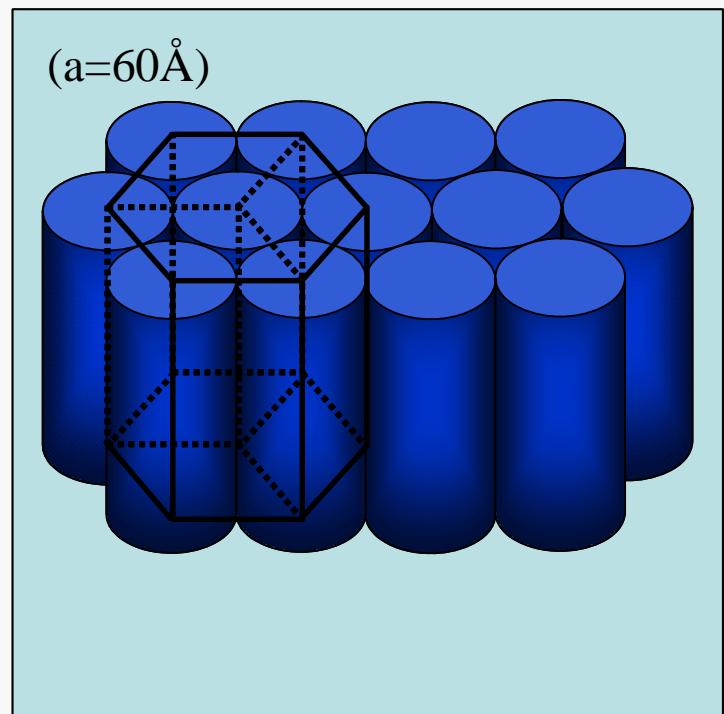
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$



Columnar hexagonal packing

h	k	l	s²	s	order	d
1	0	0	0.00037	0.019245	1	51.96
1	1	0	0.001111	0.033333	$\sqrt{3}$	30.00
2	0	0	0.001481	0.03849	$\sqrt{4}$	25.98
2	1	0	0.002593	0.050918	$\sqrt{7}$	19.64
2	2	0	0.004444	0.066667	$\sqrt{12}$	15.00
3	0	0	0.003333	0.057735	$\sqrt{9}$	17.32
3	1	0	0.004815	0.069389	$\sqrt{13}$	14.41
3	2	0	0.007037	0.083887	$\sqrt{19}$	11.92
3	3	0	0.01	0.1	$\sqrt{27}$	10.00
4	0	0	0.005926	0.07698	$\sqrt{16}$	12.99
4	1	0	0.007778	0.088192	$\sqrt{21}$	11.34
4	2	0	0.01037	0.101835	$\sqrt{28}$	9.82
4	3	0	0.013704	0.117063	$\sqrt{37}$	8.54
4	4	0	0.017778	0.133333	$\sqrt{48}$	7.50

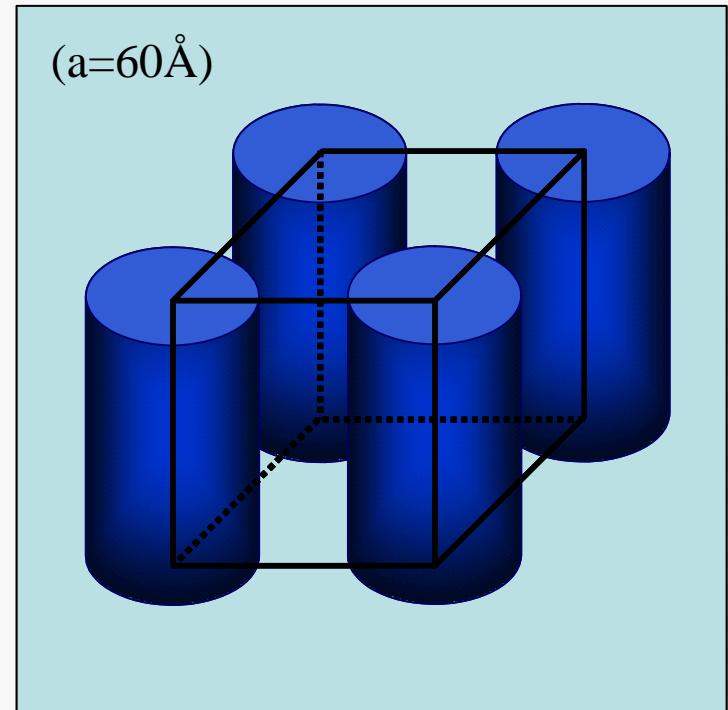
$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$



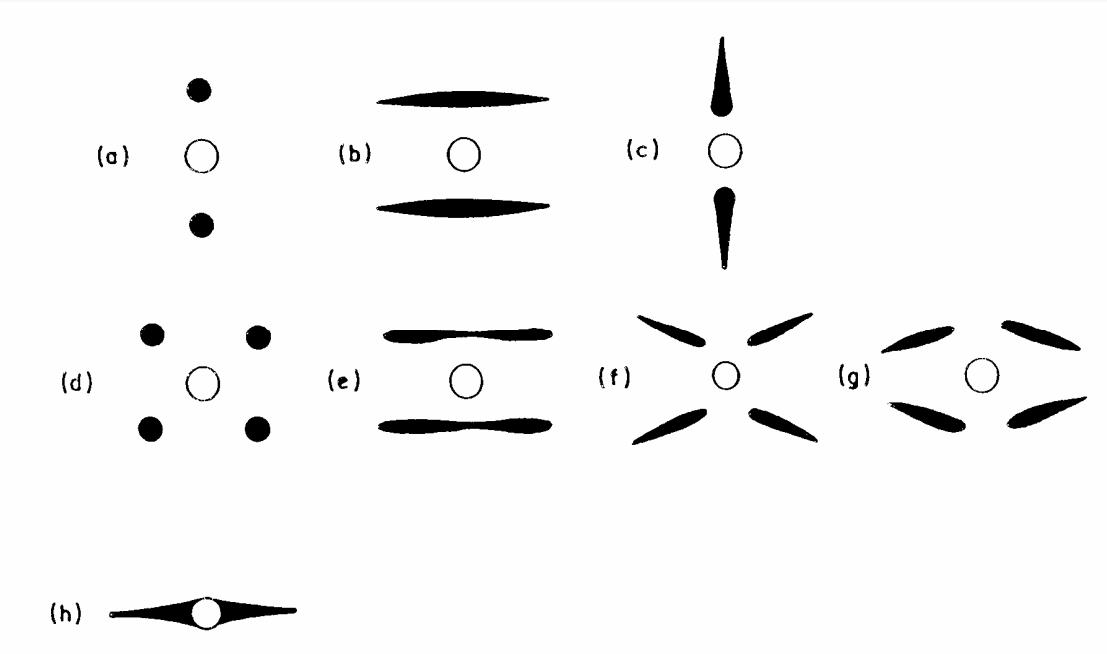
Columnar quadratic packing

<i>h</i>	<i>k</i>	<i>l</i>	<i>s</i>²	<i>s</i>	order	<i>d</i>
1	0	0	0.000278	0.016667	1	60.00
1	1	0	0.000556	0.02357	$\sqrt{2}$	42.43
2	0	0	0.001111	0.033333	$\sqrt{4}$	30.00
2	1	0	0.001389	0.037268	$\sqrt{5}$	26.83
2	2	0	0.002222	0.04714	$\sqrt{8}$	21.21
3	0	0	0.0025	0.05	$\sqrt{9}$	20.00
3	1	0	0.002778	0.052705	$\sqrt{10}$	18.97
3	2	0	0.003611	0.060093	$\sqrt{13}$	16.64
3	3	0	0.005	0.070711	$\sqrt{18}$	14.14
4	0	0	0.004444	0.066667	$\sqrt{16}$	15.00
4	1	0	0.004722	0.068718	$\sqrt{17}$	14.55
4	2	0	0.005556	0.074536	$\sqrt{20}$	13.42
4	3	0	0.006944	0.083333	$\sqrt{25}$	12.00
4	4	0	0.008889	0.094281	$\sqrt{32}$	10.61

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$



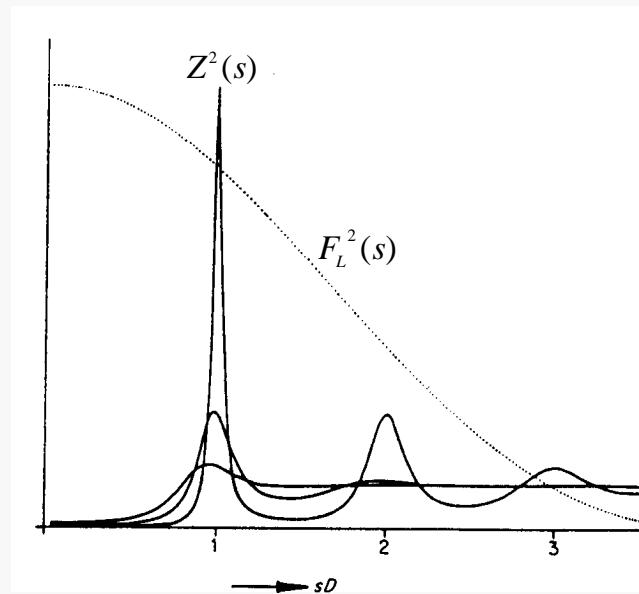
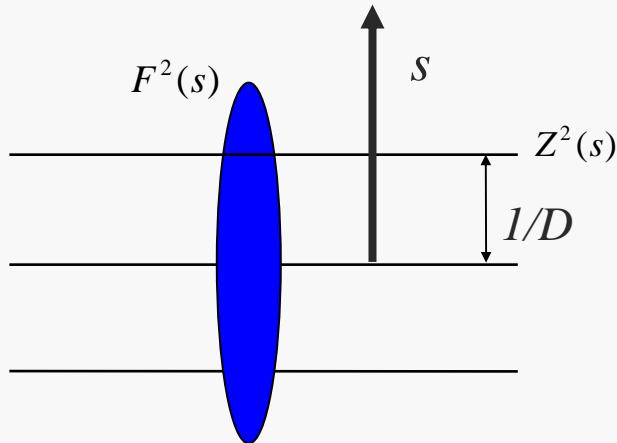
Oriented Lamellar Patterns

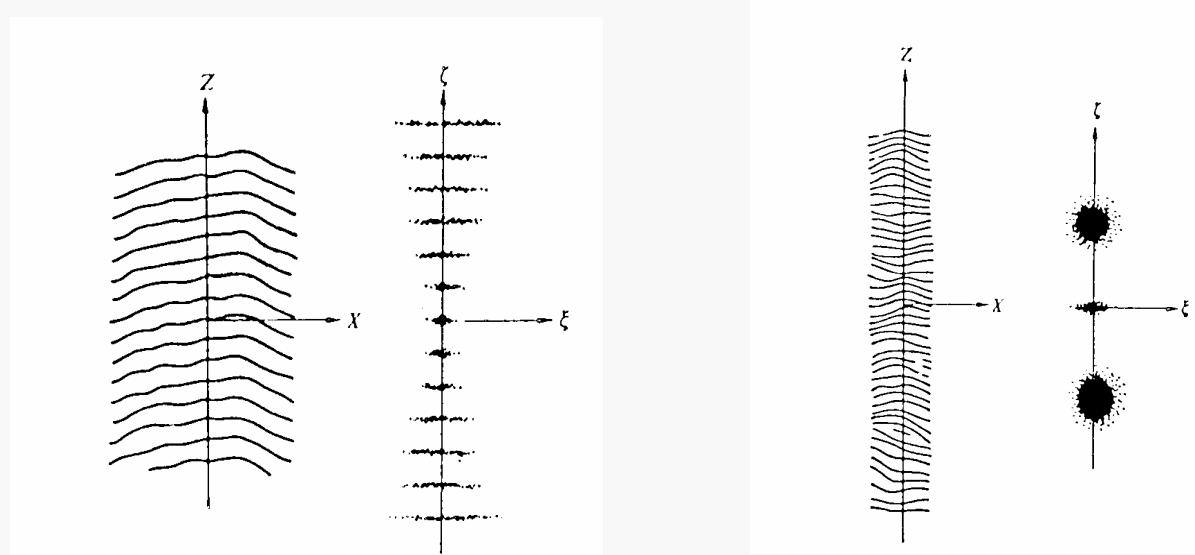
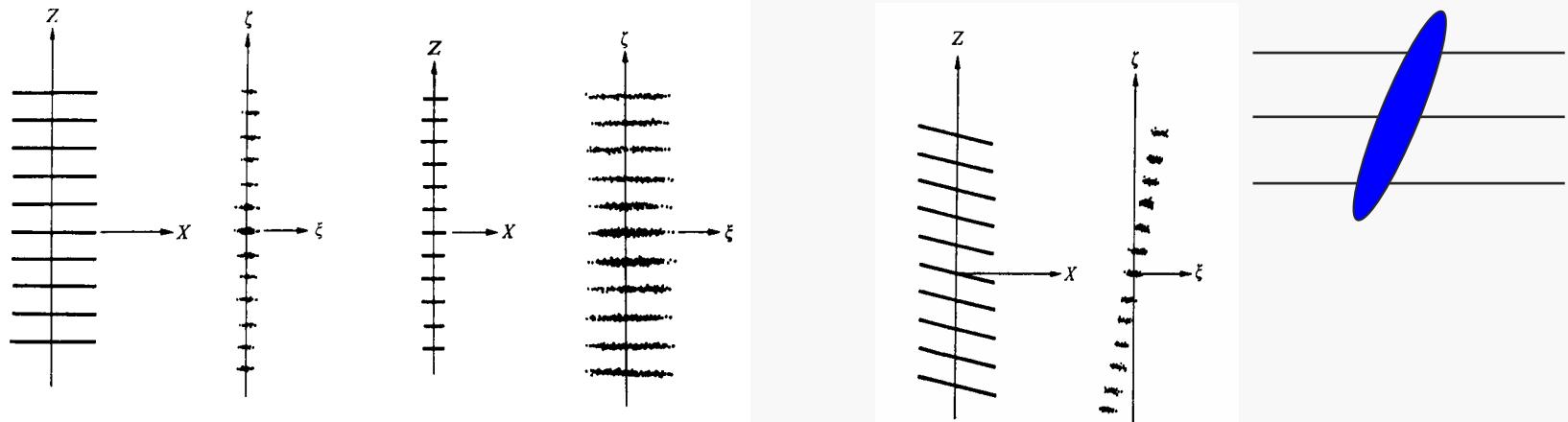


$$\begin{aligned}\rho(x) &= \rho_A(x) * Z(x) \\ \Im\{\rho(x)\} &= \Im\{\rho_A(x) * Z(x)\} \\ &= \Im\{\rho_A(x)\} \Im\{Z(x)\} \\ &= F(S) Z(S)\end{aligned}$$

* 

$$I_{obs}(s) = (F^2(s) \cdot Z^2(s))$$





Density Fluctuation

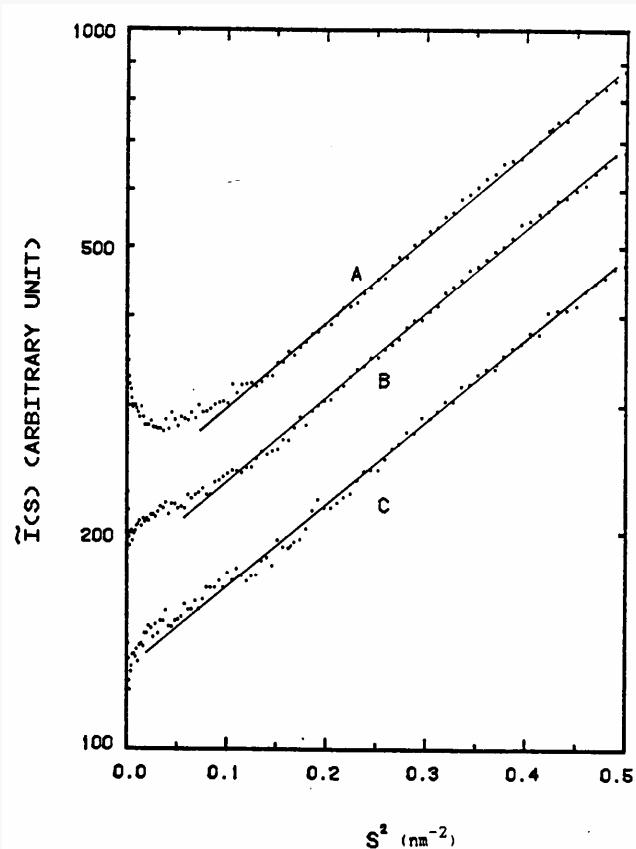
$$Fl(V) = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle}$$

$$Fl(V) = \int_{Vr} \frac{1}{\rho_0} I(s) \frac{1}{V} (\sum^2(s)) ds$$

Ruland (1975)

$$Fl(\infty) = \frac{1}{\rho_0} I(0)$$

$$Fl(\infty) = \rho \kappa T \beta_T$$



Optimization of Collection Time (Error Analysis)

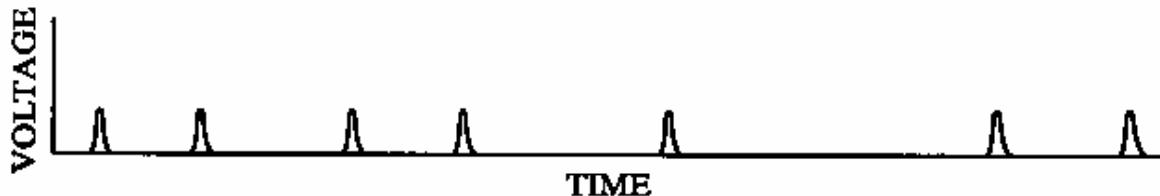


Figure 6-12 Randomly spaced voltage pulses produced by a detector.

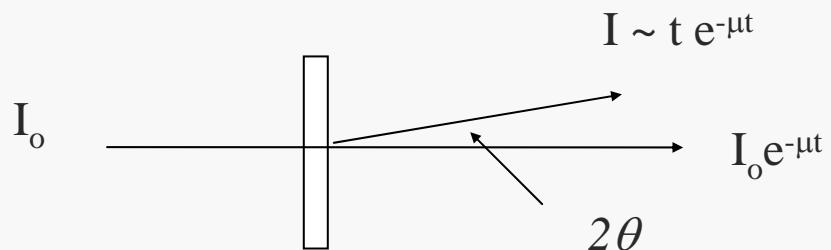
Poisson distribution

$$P(N) = \frac{(nt)^N e^{-nt}}{N!} \quad \begin{aligned} nt &: \text{average value} \\ P(N) &: \text{probability of having } N \text{ count in a given time } t \end{aligned}$$

$$\pm \frac{\sqrt{N}}{N} \quad \textbf*Relative error possessed in the count } N*$$

number of pulses counted	standard deviation (%)	collection time (sec)
1,000	3.2	1
10,000	1.0	10
100,000	0.3	100

Optimum Sample Thickness (Transmission Geometry)



t, μ : Thickness, Linear Absorption Coefficient

$$I_{obs}(s) \sim t \cdot e^{-\mu t}$$

$$t_{opt} = \frac{1}{\mu}$$