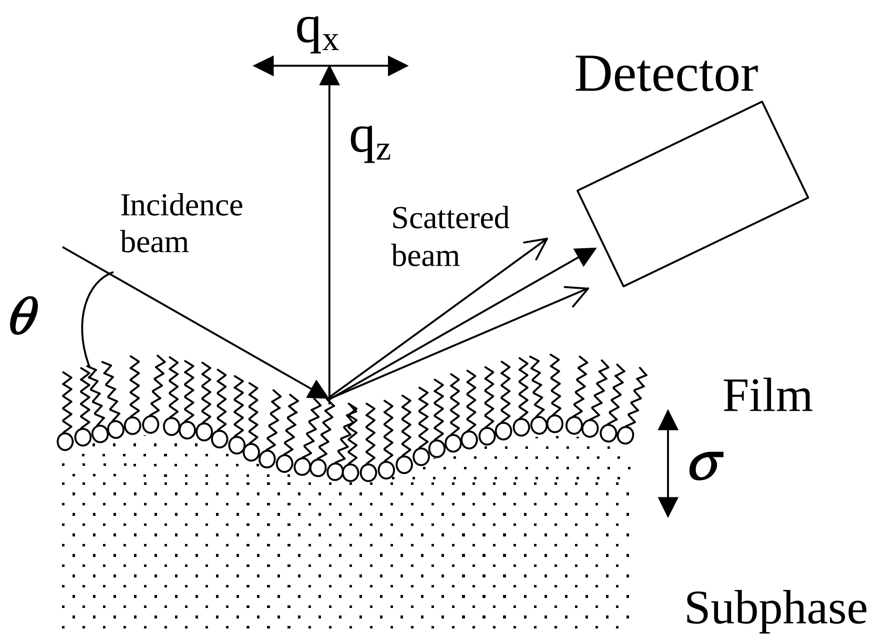
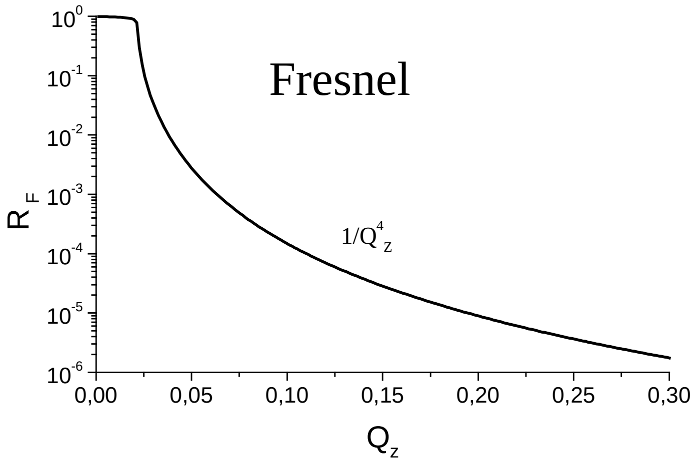
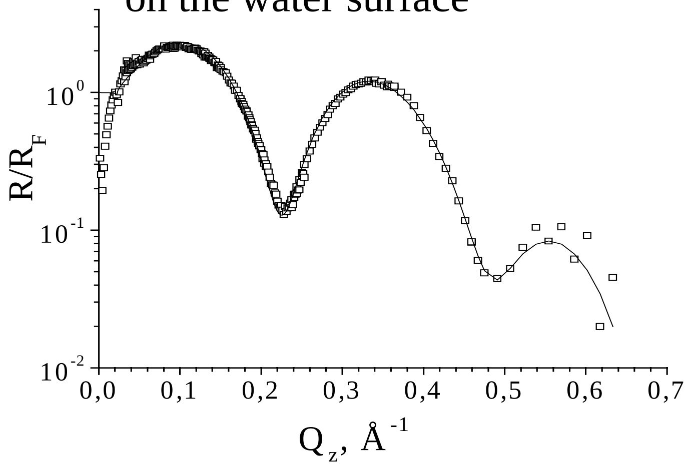
What is it X-ray reflectivity ?





Phospholipid monolayer (DSPC) on the water surface



$$I/I_0 = R_F(q_Z)\,|\Phi(q_Z)|^2\ ;\ \text{where}\ |\Phi(q_Z)| = \text{F.T.}\,[\partial\rho(z)/\partial z]$$

In case of roughness σ (identical for all interfaces) the formula should be corrected for Debye Waller factor accounting for the roughness

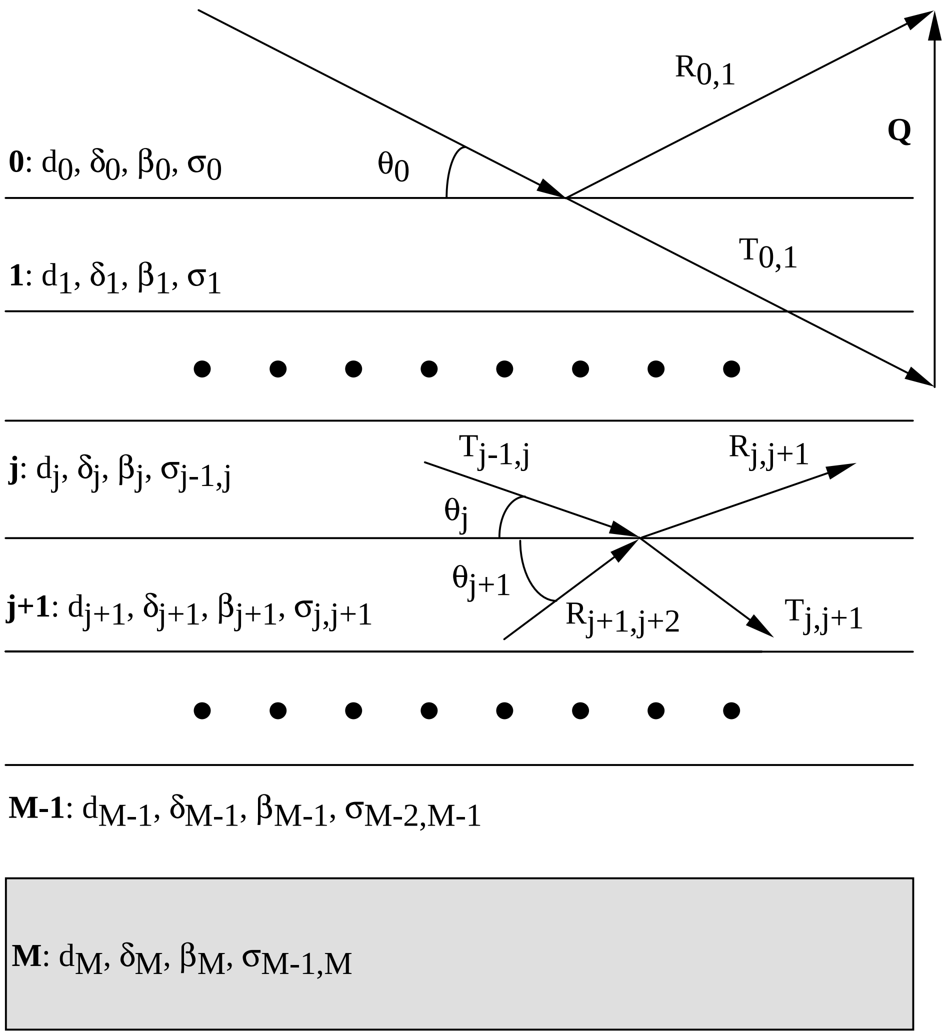
$$I/I_0 = R_F(q_Z)\,|\Phi(q_Z)|^2 \exp(-q^2_Z\,\sigma^2)$$

From specular reflectivity one can derive

- ⇨ **The electron density profile $\rho(z)$ at interface of two media**
- ⇨ **The surface/interfaces roughness σ**

Reflectivity calculation

(Parratt version)



Reflectivity is $I(\theta)=|R_{0,1}(\theta)|^2$, where $R_{0,1}(\theta)$ is calculated from recursive formula

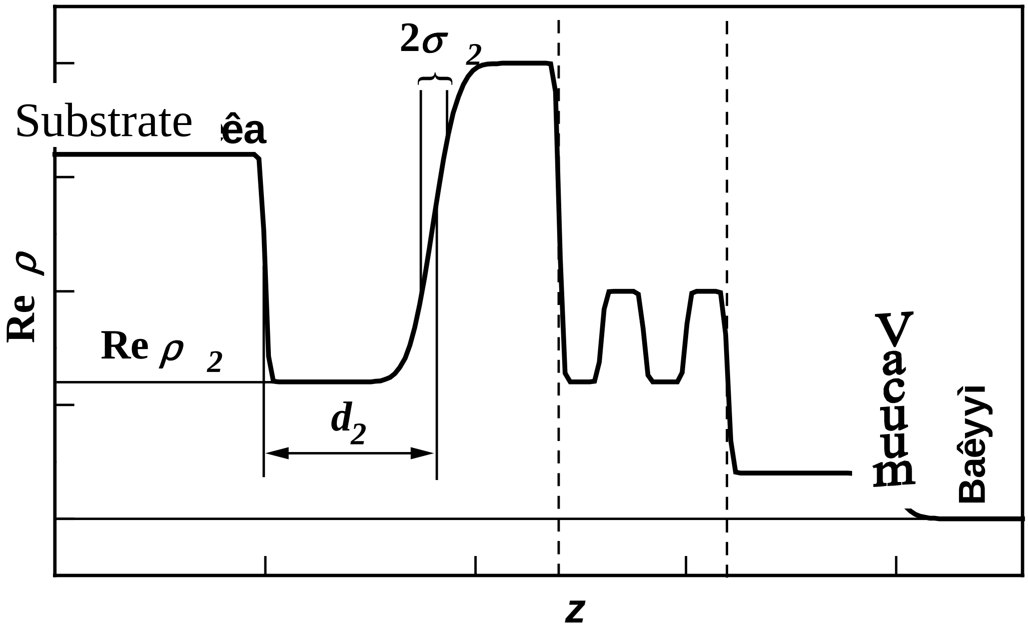
$$R_{n-1,n} = a_{n-1}^4 \cdot \left| \frac{R_{n,n+1} + F_{n,n-1}}{1 + R_{n,n+1} F_{n-1,n}} \right|$$

$R_{n,n+1}=a_n^2 \times E_n^R/E_n$, $F_{n-1,n}=(\eta_{n-1}-\eta_n)/(\eta_{n-1}+\eta_n)$, $\eta_n=(N_n^2+\cos^2(\theta))^{1/2}$, $a_n=\exp(-ik\eta_n d_n/2)$, $n=0,1,2,...,M$; $k=2\pi/\lambda$, λ- wave length, E_n , E_n^R –amplitudes of transmitted and reflected fields in the layer n, d_n – thickness of layer n, material index $N_n=1-\delta_n-i\times\beta_n$; n=M for substrate, $R_{M,M+1}=0$.

Parratt L.G. Physical Review., 1954, v.95, p.359

Scattering density profile parameterization.

$$\Gamma = \left\{ N_m , \left\{ d_{mj} , \rho_{mj} , \sigma_{mj} \right\}_{j=1}^{M_m} \right\}_{m=1}^{G}$$



Calculation of reflectivity R

Matrix of the structure:

$$\mathbf{A} = \prod_{m=1}^{G} \mathbf{U}_m \ \mathbf{A}_m^{N_m} \ \mathbf{W}_m : \quad R = \left| \frac{a_{21}}{a_{11}} \right|^2$$

Power of the matrix **Y** (det **Y** = 1):

$$\mathbf{Y}^N = \begin{pmatrix} y_{11} T_{N-1}(x) - T_{N-2}(x) & y_{12} T_{N-1}(x) \\ y_{21} T_{N-1}(x) & y_{22} T_{N-1}(x) - T_{N-2}(x) \end{pmatrix} ,$$

$$x = (y_{11} + y_{22}) / 2 ,$$

$$T_N(x) = \frac{\sin[(N+1) \arccos x]}{\sqrt{1 - x^2}} .$$

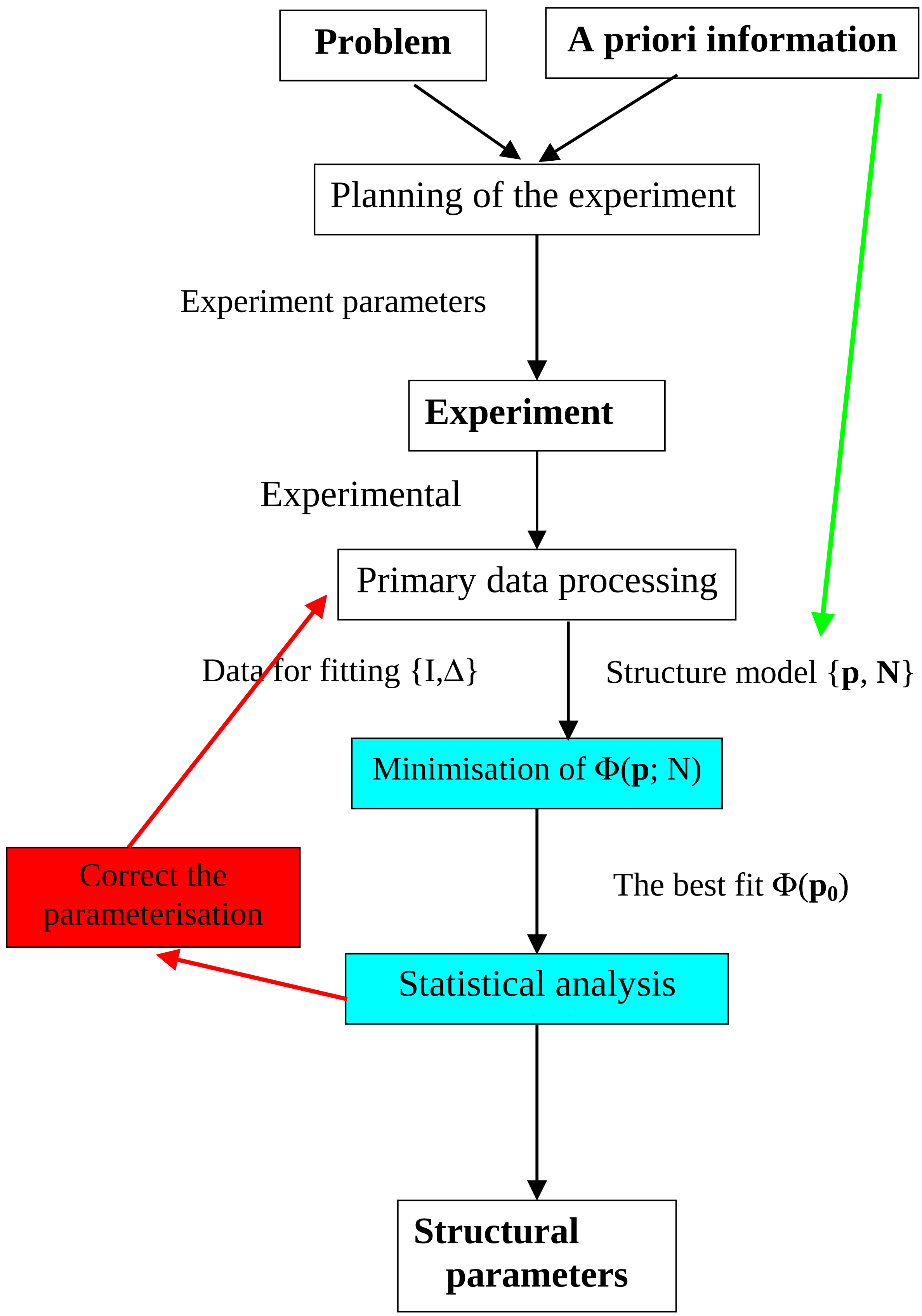
Matrix of a layer:

$$\mathbf{A}_k = \left\| \begin{matrix} [1 - (r_k^F)^2]^{-1/2} \exp(-ib_k d_k) & r_k^F [1 - (r_k^F)^2]^{-1/2} \exp(ib_k d_k) \\ r_k^F [1 - (r_k^F)^2]^{-1/2} \exp(-ib_k d_k) & [1 - (r_k^F)^2]^{-1/2} \exp(ib_k d_k) \end{matrix} \right\| ,$$

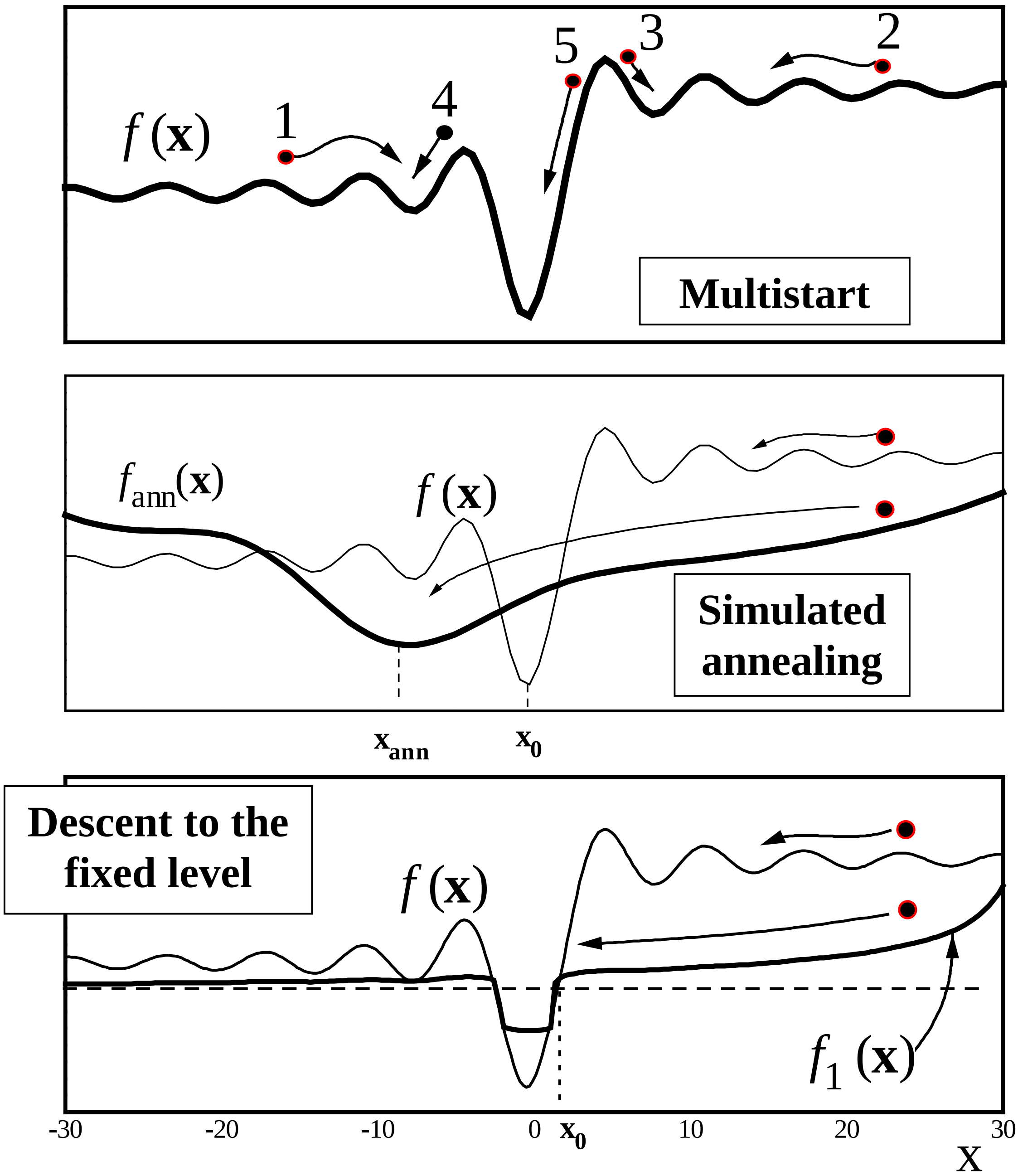
$$b_k = 1/2 \cdot \sqrt{Q^2 - 2\pi \rho_k} , \quad Q = \frac{4\pi}{\lambda} \sin \theta ,$$

$$r_k^F = \frac{b_k - b_{k+1}}{b_k + b_{k+1}} \cdot \exp(-2 b_k b_{k+1} \sigma_k^2) , \quad k = 1, \ldots N_t .$$

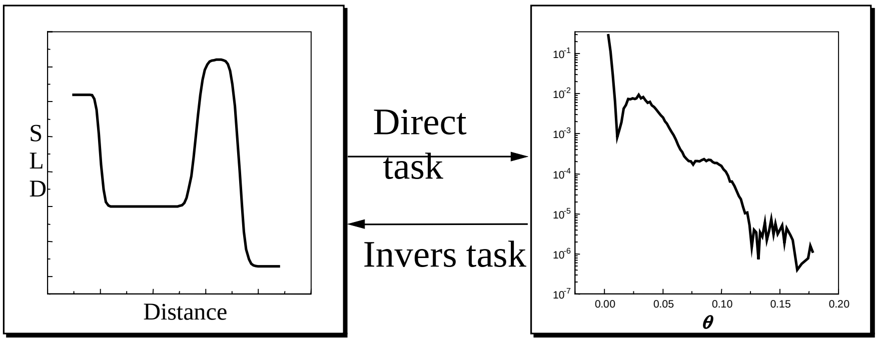
Generalized scheme of reflectivity data treatment

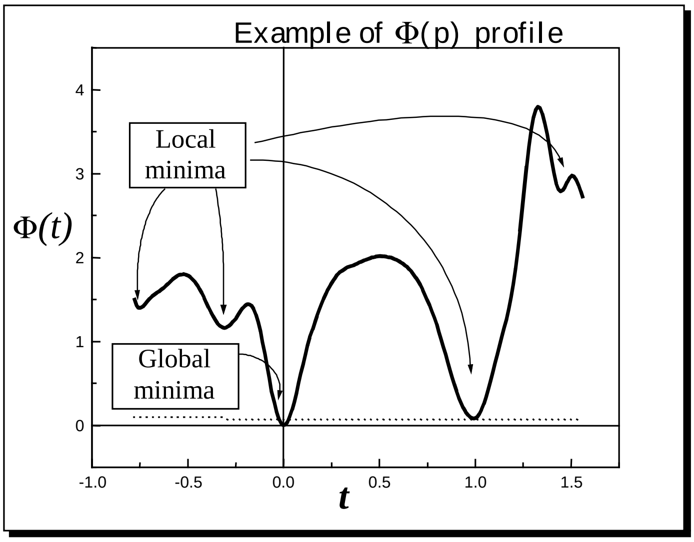


Some techniques of global minimization



The objective function minimization





The objective function of fitting Φ(p)

$$\Phi(\mathbf{p}) = \frac{B}{L - P} \cdot \sum_{c=1}^{C} \sum_{l=1}^{L_c} \left(\frac{I_{\exp}(Q_{cl}) - S_c \; I(Q_{cl}, \Gamma(\mathbf{p}))}{\Delta_{cl}} \right)^2 ,$$

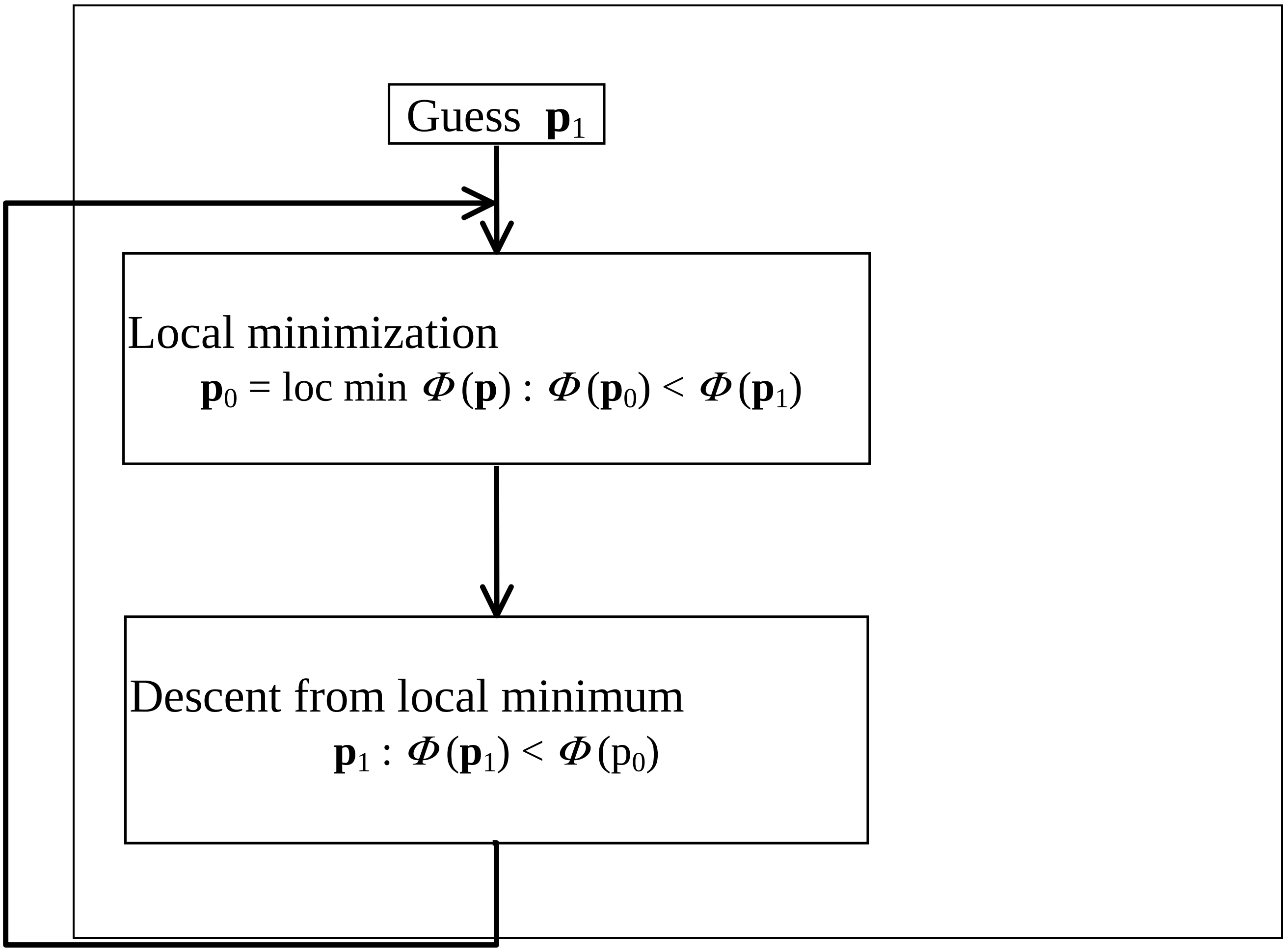
$$L = \sum_{c=1}^{C} L_c , \quad B = \left(\sum_{c=1}^{C} \sum_{l=1}^{L_c} \left(\frac{I_{\exp}(Q_{cl})}{\Delta_{cl}} \right)^2 \right)^{-1} ,$$

$$S_c = \frac{\displaystyle\sum_{l=1}^{L_c} \frac{I_{\exp}(Q_{cl}) \cdot I(Q_{cl}, \Gamma(\mathbf{p}))}{\Delta_{cl}^2}}{\displaystyle\sum_{l=1}^{L_c} \frac{\left(I(Q_{cl}, \Gamma(\mathbf{p}))\right)^2}{\Delta_{cl}^2}} .$$

The domain of minization

$$\Omega = \left\{ \mathbf{p} : \left\{ p_k^{\min} < p_k < p_k^{\max} \right\}_{k=1}^{P} \right\}$$

<u>Method of successive descent from local minima</u> ($\Phi^* = \Phi(\mathbf{p}_0)$)



Modification of the objective

$$\Phi_1 = \frac{\Phi(\mathbf{p}) - \Phi(\mathbf{p_0})}{\left\| \mathbf{p} - \mathbf{p_0} \right\|^{\alpha}}$$

<u>Descent condition (go away from $\mathbf{p}_0$)</u>

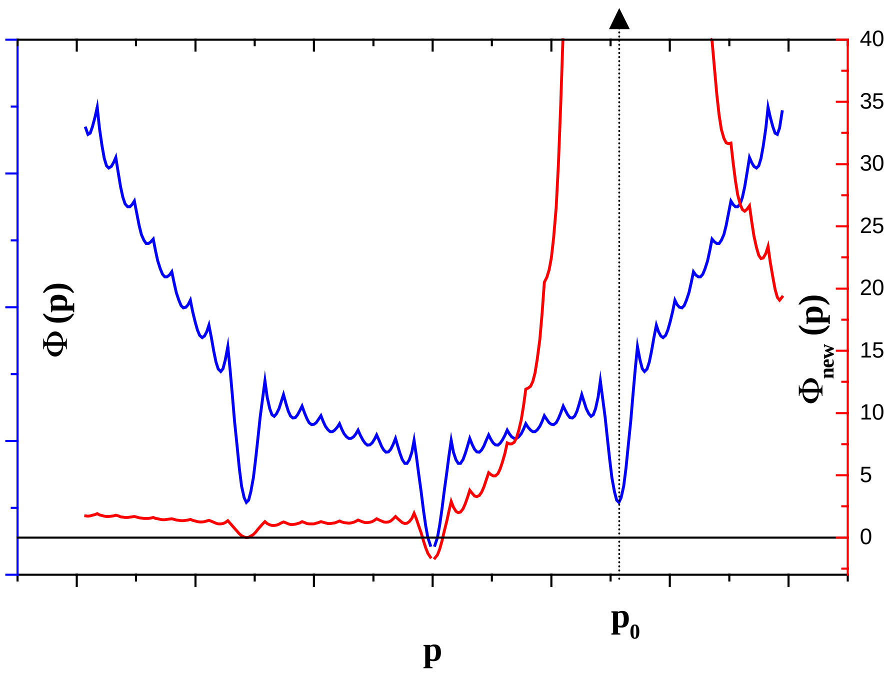
$$\left((\nabla \Phi_1(\mathbf{p})) \bullet (\mathbf{p} - \mathbf{p}_0) \right) < 0 \; ;$$

$$\alpha > \frac{1}{2} \left(\frac{\nabla \Phi(\mathbf{p})}{\Phi(\mathbf{p}) - \Phi(\mathbf{p_0})} \right) \bullet (\mathbf{p} - \mathbf{p_0})$$

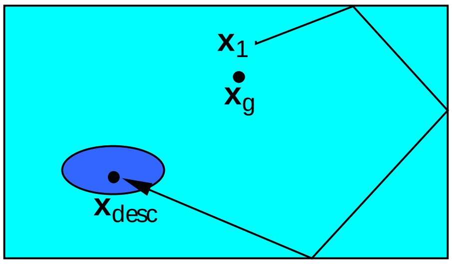
Geometric interpretation of the objective function modification.

modified objective function

$$\Phi_{new} = \frac{\Phi(\mathbf{p}) - \Phi(\mathbf{p_0})}{(\mathbf{p}-\mathbf{p_0}\ ,\mathbf{p}-\mathbf{p_0})^{\alpha}}$$

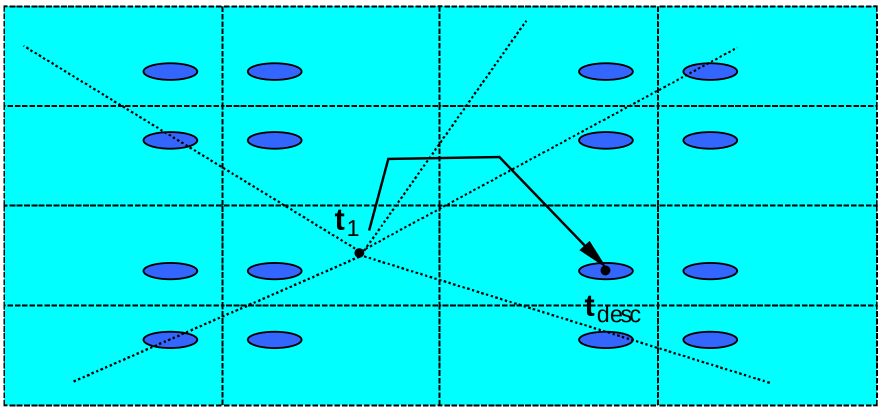


Trajectory of the probing point

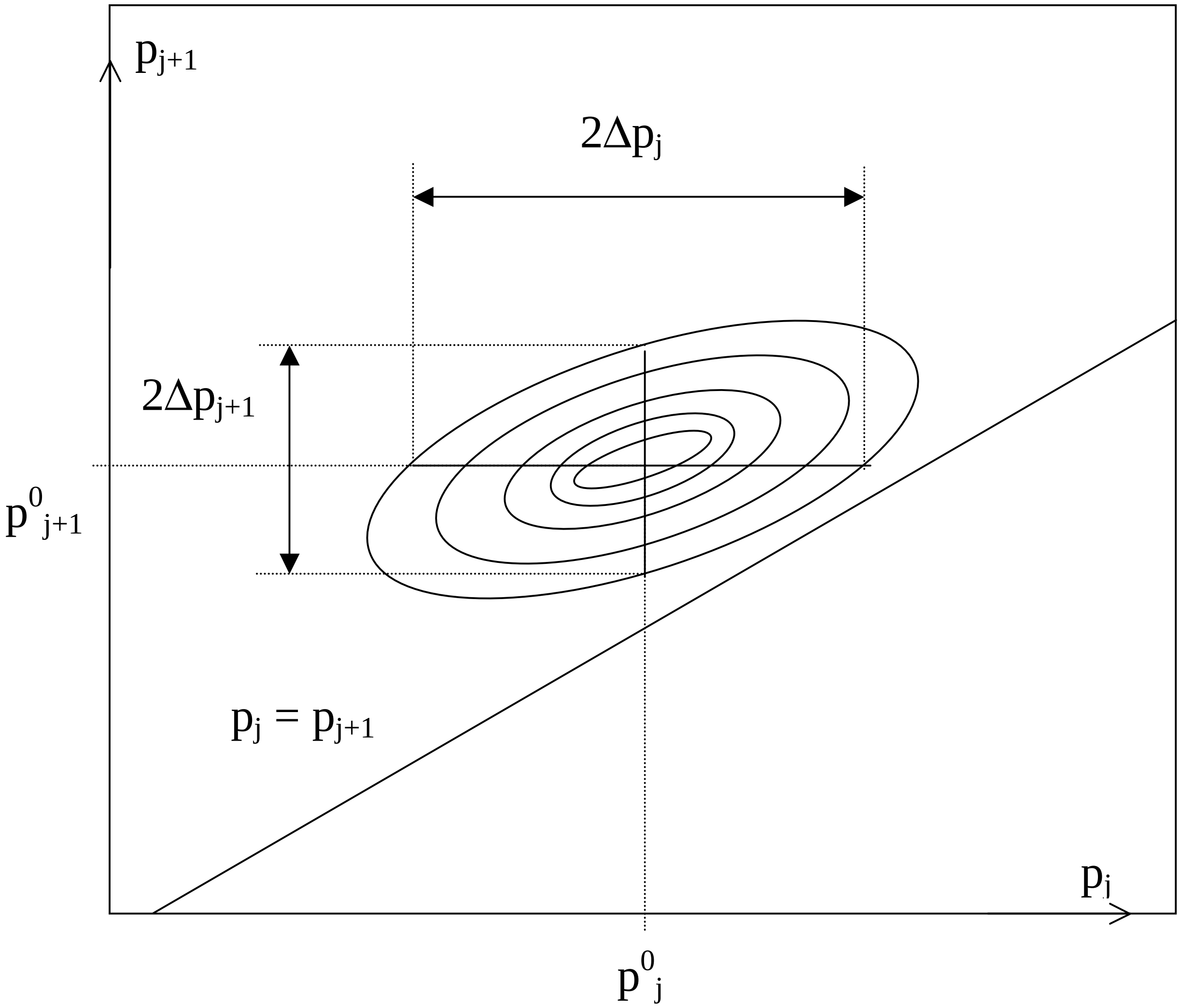


Periodic extention of the domain of interest

$$p_k = \frac{p_k^{max} + p_k^{min}}{2} + \frac{p_k^{max} - p_k^{min}}{2} \sin t_k \ , k = 1, \ldots , P.$$



Geometric interpretation of the hypothesis
about equivalence of two parameters



ellipsis are confidence domain.
Δp^0_j and Δp^0_{j+1} are confidence intervals
line $p_j = p_{j+1}$ is hypothesis

Hypothesis is accepted when its intersection with the confidence domain is not empty with certain confidence level.

Statistical analysis

Matrix of equations **X** and inverse covariance matrix $\mathbf{C}^{-1}$

$$X_{ij} = \sqrt{B}\,\frac{S_i(\mathbf{p}_0)}{\Delta_i}\,\frac{\partial I(Q_i,\Gamma(\mathbf{p}))}{\partial p_j}\bigg|_{\mathbf{p}=\mathbf{p}_0},$$

$$\mathbf{C}^{-1} = \left(\mathbf{X}^{\mathbf{T}}\mathbf{X}\right)^{-1}.$$

Significance of parameters. Testing hypothesis

$$d_j = 0;$$
$$\sigma_j = 0;$$
$$\operatorname{Im}\rho_j = 0;$$
$$\operatorname{Re}\rho_j = \operatorname{Re}\rho_{j-1};\ \operatorname{Re}\rho_j = \operatorname{Re}\rho_{j-1}$$

Statistics:

$$F_1 = \frac{(u_j - \mu)^2}{\Phi_g\cdot\left(\mathbf{C}^{-1}\right)_{jj}},$$

$$F_2 = \frac{(u_j - u_{j-1})^2}{\Phi_g\cdot\left(\left(\mathbf{C}^{-1}\right)_{jj} + \left(\mathbf{C}^{-1}\right)_{j-1,j-1} - 2\left(\mathbf{C}^{-1}\right)_{j,j-1}\right)}.$$

Criteria of the hypothesi acceptence: $F_j < F_j(w_0)$.

$F_j(w_0)$ - is quantile of confidence level w_0 for $F_{1,L-P}$ distribution

Accuracy evaluation. Confidence interval:

$$\Lambda_j(w_0) = [\,p_{0j} - \gamma\cdot\sqrt{\Phi_g\cdot(\mathbf{C}^{-1})_{jj}},\ p_{0j} + \gamma\cdot\sqrt{\Phi_g\cdot(\mathbf{C}^{-1})_{jj}}\,]$$

γ- is quantile of confidence level w_0 for Student's distribution with (L-P) degrees of freedom

Fisher's criterion (F-distribution)

How compare two model and made a choice between them ?

If two models $\mathbf{p}_1$ (with rank M_1) and $\mathbf{p}_2$ (with rank M_2) obtained independently on the base of N_1 and N_2 trials, accordingly, then to check up hypothesis about its equality useful to use ratio of residues

$$H_F = \frac{\Phi_{M_1}(\mathbf{p}_1)}{\Phi_{M_2}(\mathbf{p}_2)}$$

Statistic theory says that H_F obeys to, so called, *F*-distribution with (N_1-M_1) and (N_2-M_2) degrees of freedom. This distribution is known also as Fisher's criterion. *F*-distribution value for H_F gives probability that residues $F_{M1}(\mathbf{p}_1)$ and $F_{M2}(\mathbf{p}_2)$ of two model are not equal, and therefore lets make assumption about models

F-distribution is

$$F_{m,n}(x) = \frac{\Gamma\left(\frac{m+n}{2}\right)}{\Gamma\left(\frac{m}{2}\right)\Gamma\left(\frac{n}{2}\right)} \int_0^x \frac{\alpha^{\frac{m}{2}-1}}{(\alpha+1)^{\frac{m+n}{2}}} d\alpha$$

In accordance with Fisher's criterion two model are statistically identical if the value of its statistics (the residues ratio) is lower than the quantile of the $F_{N1,N2}$ distribution. This quantile is defined by the confidence level w_0 and numbers of model parameters N1 and N2 (N1 < N2).

How verify hypothesis about parameters correlation ?

The simplest correlation between parameters is linear correlation.

$$\mathbf{A}\mathbf{p}_{\text{opt}} = \mathbf{v}$$

Where **A** is known matrix *n* x *m* (*n* number of independent parameters) and **v** is known vector (with rank *n)*. In case of linear correlation is possible build statistic as

$$F_A = \frac{RSS_A - RSS}{n\ \Phi_M(\mathbf{p}_{opt})} = \frac{(\mathbf{A}\,\mathbf{p}_{opt} - \mathbf{v})^{\mathbf{T}}\left(\mathbf{A}\mathbf{C}^{-1}\mathbf{A}^{\mathbf{T}}\right)^{-1}(\mathbf{A}\,\mathbf{p}_{opt} - \mathbf{v})}{n\ \Phi_M(\mathbf{p}_{opt})}$$

which also obeys to *F*-distribution with *m* and N-M degrees of freedom
RSS_A and *RSS* are χ^2 value for model with correlation and with out correlation.

Example of use the program *REFLAN*

Modeling of scattering by system Si/SiO_2/4 x (PS/PBMA)

polystyrene / polybuthylmethacrylate copolymer films spin-coated on Si substrates

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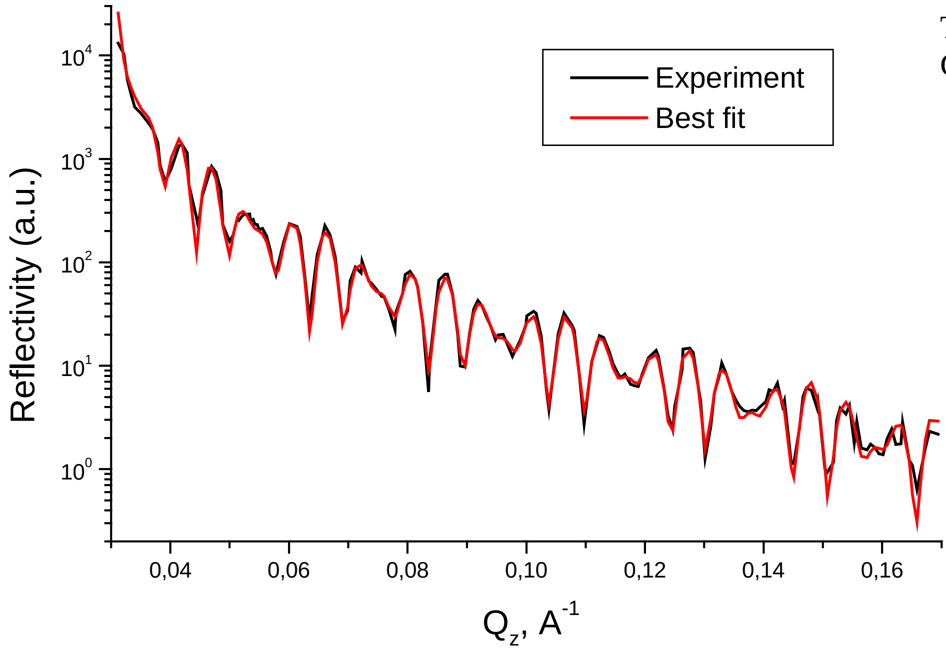
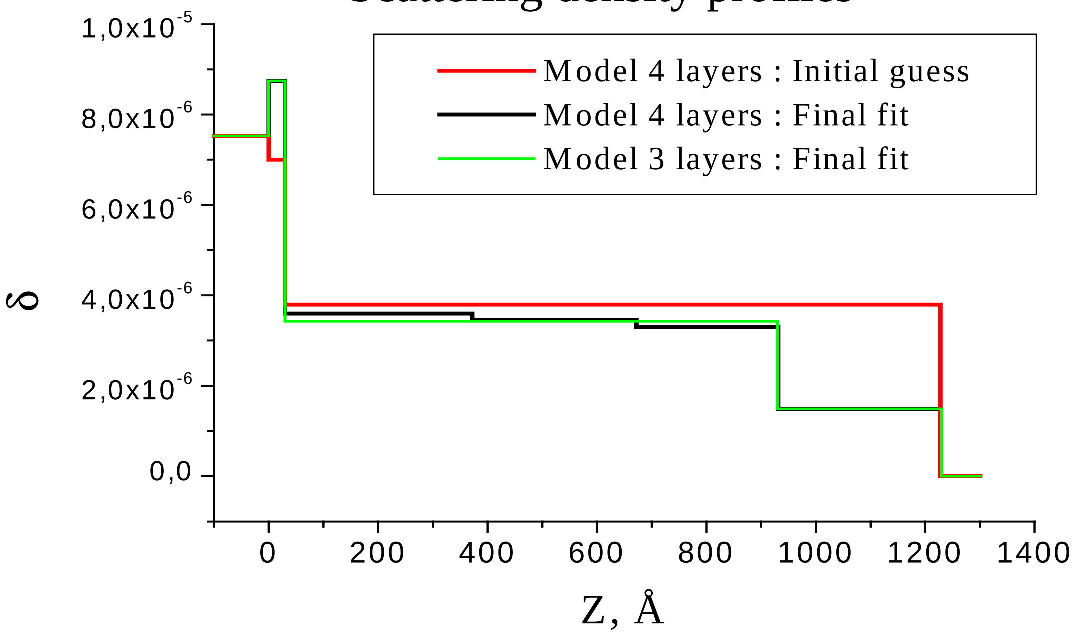


Thesis of
G. VIGNAUD

Scattering density profiles



Confidence intervals (confidence level $w_0 = 0.68$):

$\rho_4 = 1.49 \cdot 10^{-6} \pm 0.4 \cdot 10^{-6}$, $d_4 = 300 \pm 15$ A.

$\rho_3 = 3.43 \cdot 10^{-6} \pm 0.3 \cdot 10^{-6}$, $d_3 = 900 \pm 5$ A;

$\rho_2 = 8.74 \cdot 10^{-6} \pm 2.1 \cdot 10^{-6}$, $d_2 = 30 \pm 5$ A;