

Evaluation of diffraction patterns for microstructural parameters using a Monte-Carlo algorithm

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Introduction:

- theory for line broadening
- the CMWP method
- $\langle d_{\text{disl.}} \rangle$ -WSSR plots and WSSR scans
- non-linear least-squares algorithms
- the Simulated Annealing method
- the new Monte-Carlo algorithm
- stability tests of the new algorithm
- some results on ZrH samples

Theory

The Fourier coefficients of the line profiles (Warren & Averbach, 1952):

$$A(L) = A^S(L)A^D(L),$$

this means that the observed profile is the convolution of size and strain profiles.

If more physical effects and instrumental effects are simultaneously present:

$$A(L) = A_{instr.}(L)A_{size}(L)A_{disl.}(L)A_{pl.\,faults}(L)\dots,$$

$$I(2\Theta) = I_{instr.}(2\Theta) * I_{size}(2\Theta) * I_{disl.}(2\Theta) * I_{pl.\,faults}(2\Theta) * \dots$$

The size effect

If we suppose:

- spherical crystallites
- lognormal $f(x)$ size distribution density function:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \frac{1}{x} \exp \left[-\frac{\left(\log \left(\frac{x}{m} \right) \right)^2}{2\sigma^2} \right],$$

(m and σ are the two parameters of the distribution).

The size effect

The size intensity profile (Gubicza et al, 2000):

$$I^S(s) = \int_0^\infty \mu \frac{\sin^2(\mu \pi s)}{(\pi s)^2} \operatorname{erfc} \left[\frac{\log \left(\frac{\mu}{m} \right)}{\sqrt{2}\sigma} \right] d\mu,$$

where erfc is the complementary error function:

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt.$$

The Size Fourier Transform:

It can be expressed in an almost closed form which is suitable for fast numeric evaluation (Ribárik et al, 2001):

$$A^S(L, m, \sigma) = \frac{m^3 \exp\left(\frac{9}{4}(\sqrt{2}\sigma)^2\right)}{3} \operatorname{erfc} \left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \frac{3}{2}\sqrt{2}\sigma \right] - \\ \frac{m^2 \exp(\sqrt{2}\sigma)^2}{2} |L| \operatorname{erfc} \left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \sqrt{2}\sigma \right] + \\ \frac{|L|^3}{6} \operatorname{erfc} \left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} \right].$$

The strain effect

The distortion Fourier coefficients (Warren & Averbach, 1952):

$$A^D(L) = \exp\left(-2\pi^2 g^2 L^2 \langle \varepsilon_L^2 \rangle\right),$$

where

- g is the absolute value of the diffraction vector,
- $\langle \varepsilon_L^2 \rangle$ is the *mean square strain*.

The most important models for $\langle \varepsilon_L^2 \rangle$:

- Warren & Averbach (1952)
- Krivoglaz & Ryaboshapka (1963)
- Wilkens (1970)

The Wilkens dislocation theory

Wilkens introduced the effective outer cut off radius of dislocations, R_e^* , instead of the crystal diameter.

Assuming infinitely long parallel **screw** dislocations with *restrictedly random* distribution (Wilkens, 1970):

$$\langle \varepsilon_L^2 \rangle = \left(\frac{b}{2\pi} \right)^2 \pi \rho C f^* \left(\frac{L}{R_e^*} \right),$$

where f^* is the Wilkens strain function (Wilkens, 1970). Kamminga and Delhez (2000) have shown that this strain function is also valid for edge- and curved dislocations.

The distortion Fourier–transform in the Wilkens model:

$$A^D(L) = \exp \left[-\frac{\pi b^2}{2} (g^2 C) \rho L^2 f^* \left(\frac{L}{R_e^*} \right) \right].$$

The Wilkens strain function

$$f^*(\eta) = -\log \eta + \left(\frac{7}{4} - \log 2 \right) + \frac{512}{90\pi} \frac{1}{\eta} +$$

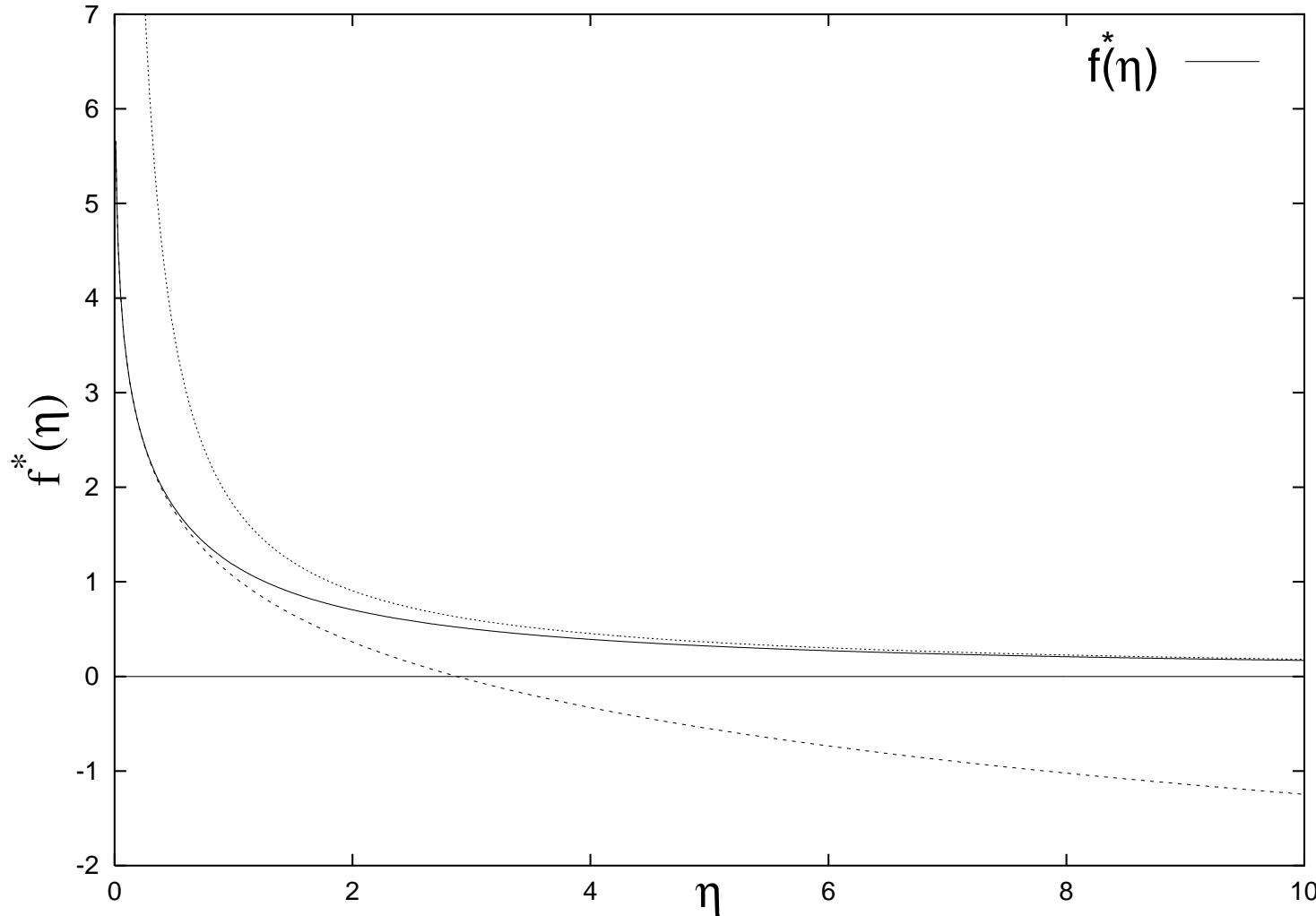
$$\frac{2}{\pi} \left[1 - \frac{1}{4\eta^2} \right] \int_0^\eta \frac{\arcsin V}{V} dV -$$

$$\frac{1}{\pi} \left[\frac{769}{180} \frac{1}{\eta} + \frac{41}{90} \eta + \frac{2}{90} \eta^3 \right] \sqrt{1 - \eta^2} -$$

$$f^*(\eta) = \frac{1}{\pi} \left[\frac{11}{12} \frac{1}{\eta^2} + \frac{7}{2} + \frac{1}{3} \eta^2 \right] \arcsin \eta + \frac{1}{6} \eta^2, \quad \text{if } \eta \leq 1,$$
$$f^*(\eta) = \frac{512}{90\pi} \frac{1}{\eta} - \left[\frac{11}{24} + \frac{1}{4} \log 2\eta \right] \frac{1}{\eta^2}, \quad \text{if } \eta \geq 1,$$

where $f\left(\frac{L}{R_e^*}\right) = f^*(\eta)$ and $\eta = \frac{1}{2} \exp\left(-\frac{1}{4}\right) \frac{L}{R_e^*}$.

The Wilkens strain function



The Wilkens function and its approximations: $-\log \eta + \left(\frac{7}{4} - \log 2 \right)$ and $\frac{512}{90\pi} \frac{1}{\eta}$.

The dislocation arrangement parameter

Wilkens introduced M^* , a dimensionless parameter:

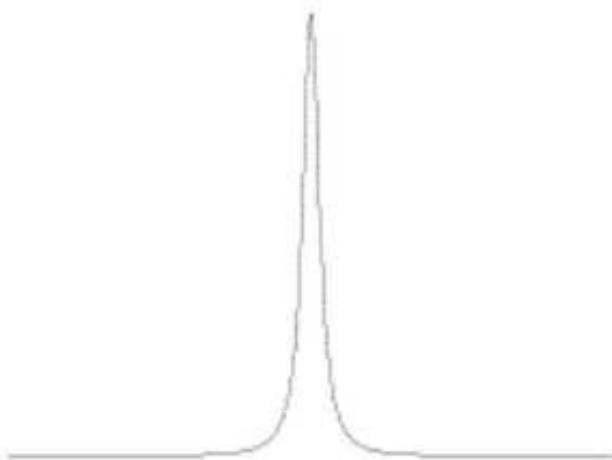
$$M^* = R_e^* \sqrt{\rho} = \frac{R_e^*}{\langle d_{\text{disl.}} \rangle},$$

where $\langle d_{\text{disl.}} \rangle$ is the average dislocation distance. The M^* parameter characterizes the dislocation arrangement:

- if the value of M^* is small, the correlation between the dislocations is strong
- if the value of M^* is large, the dislocations are distributed randomly in the crystallite

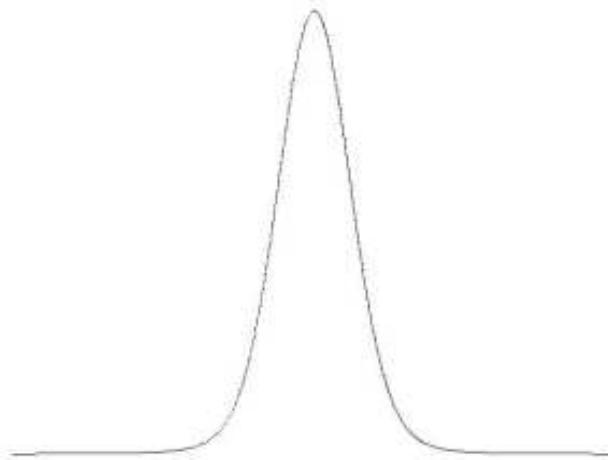
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$$R_e^* \ll \frac{1}{\sqrt{\rho}}$$

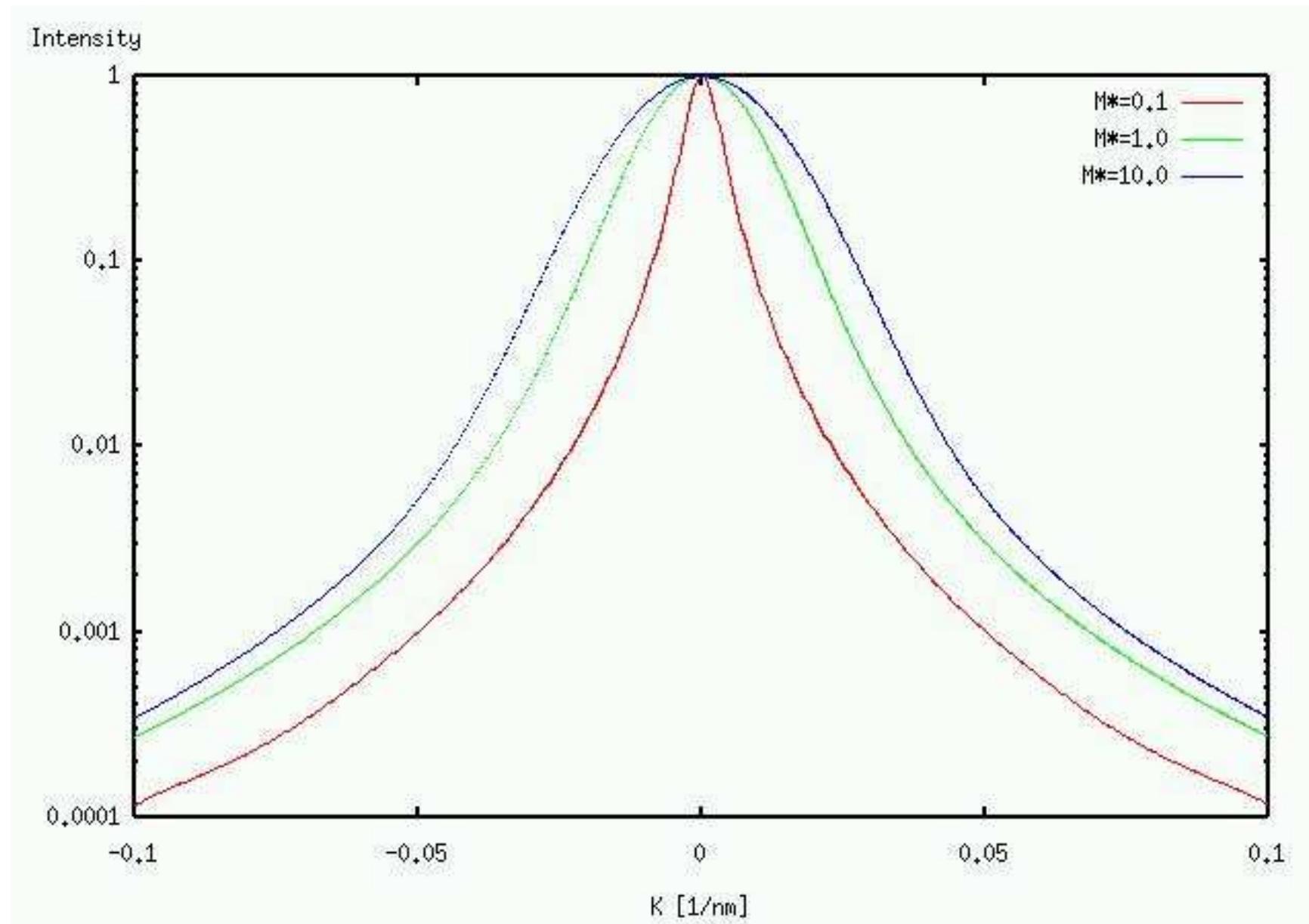
$$M^* \ll 1$$



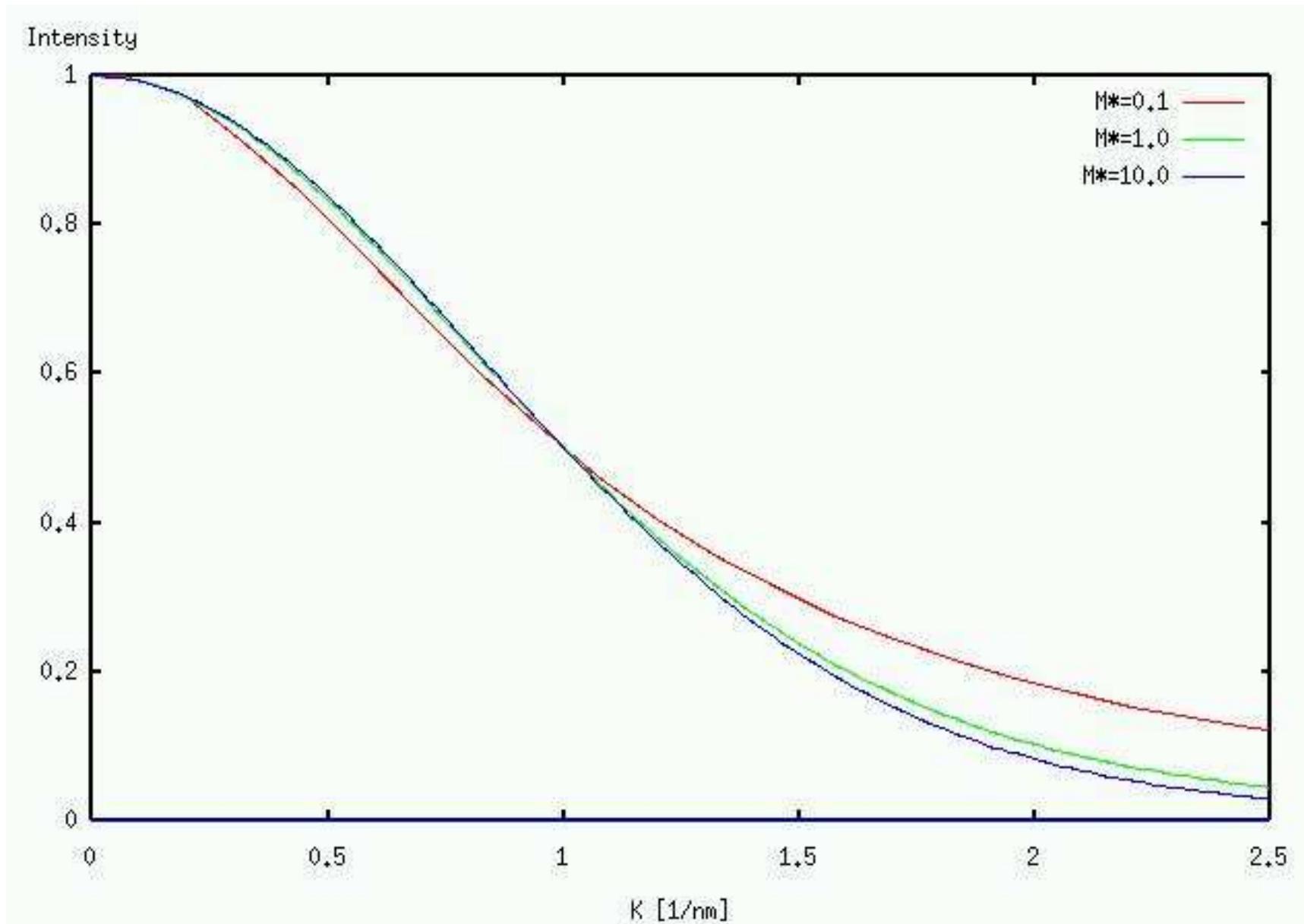
$$R_e^* \gg \frac{1}{\sqrt{\rho}}$$

$$M^* \gg 1$$

The strain profile for fixed ρ and variable M^* values:



The shape of the strain profile for fixed ρ and variable M^* values:



Strain anisotropy

According to (Ungár & Tichy, 1999), the average contrast factors of dislocations can be expressed in the following form for cubic crystals:

$$C = C_{h00}(1 - qH^2),$$

where

$$H^2 = \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2}.$$

For hexagonal crystals:

$$C = C_{hk0}(1 + a_1 H_1^2 + a_2 H_2^2),$$

where

$$H_1^2 = \frac{[h^2 + k^2 + (h+k)^2] l^2}{[h^2 + k^2 + (h+k)^2 + \frac{3}{2}(\frac{a}{c})^2 l^2]^2},$$

$$H_2^2 = \frac{l^4}{[h^2 + k^2 + (h+k)^2 + \frac{3}{2}(\frac{a}{c})^2 l^2]^2},$$

and $\frac{a}{c}$ is the ratio of the two lattice constants.

Planar and twin faults:

The peak profile is the sum of a delta function and shifted and broadened Lorentzian profile functions

- the FWHM and shift value of the Lorentzians depend on the density of faults
- hkl -dependence: DIFFaX software (Treacy et al., Proc. Roy. Soc., 1991)

The parameters were systematically calculated for each fundamental types of planar faults by Levente Balogh (see: L. Balogh, PhD thesis, Eötvös University, 2009).

CMWP-fit

This method is

- in fact: a Whole Powder Pattern fitting method
- it's a microstructural method: the unit cell is NOT refined

The aim is microstructure in terms of:

- size
- strain

Microstructural parameters

CMWP-fit provides:

- size: m, σ
- dislocations: ρ, M, q (or a_1, a_2)
- planar faults: α

The theoretical intensity pattern

$$I_{theoretical} = BG(2\Theta) + \sum_{hkl} I_{MAX}^{hkl} I^{hkl}(2\Theta - 2\Theta_0^{hkl}),$$

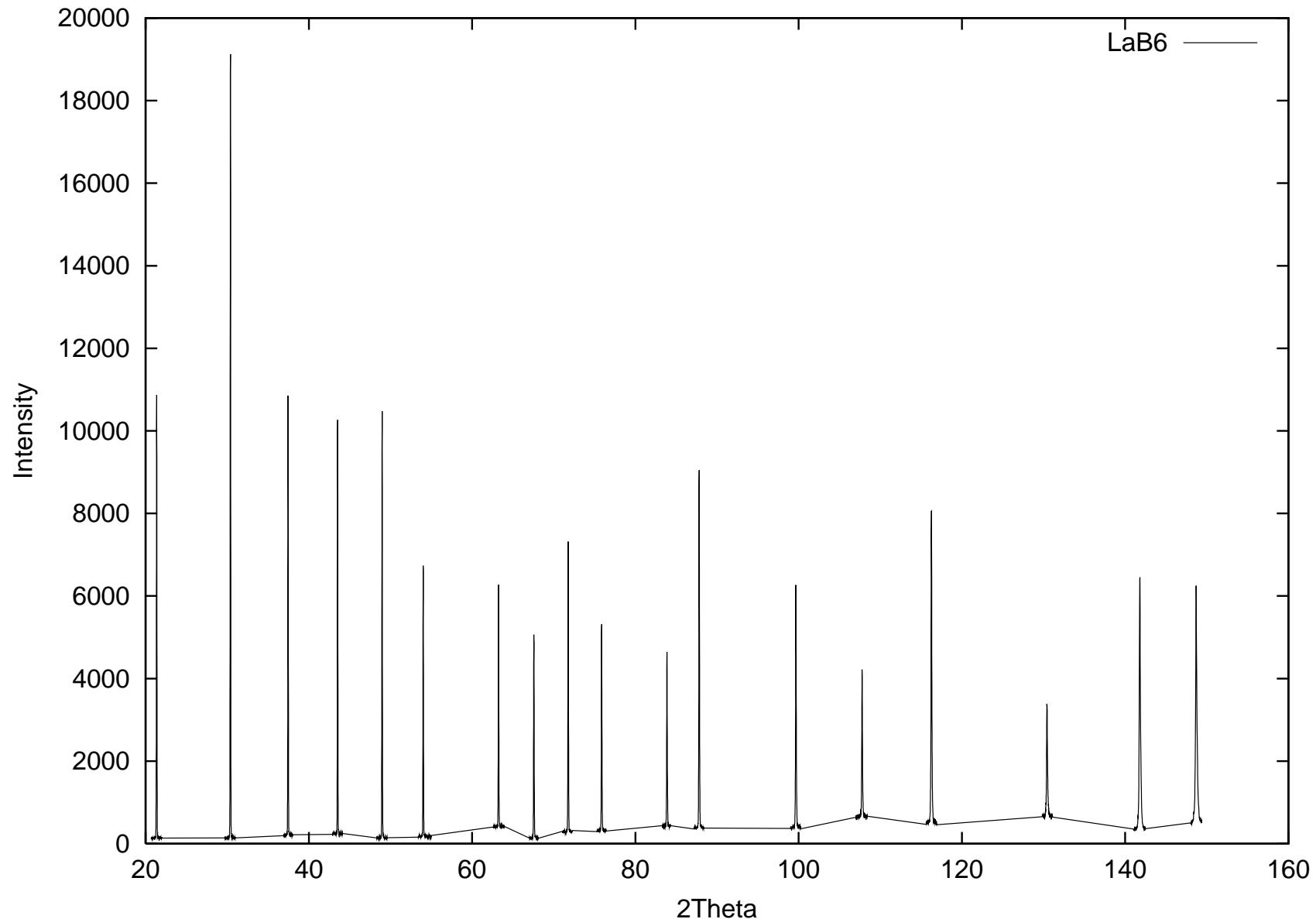
where:

$$I^{hkl} = I_{instr.}^{hkl} * I_{size}^{hkl} * I_{disl.}^{hkl} * I_{pl.\text{faults}}^{hkl},$$

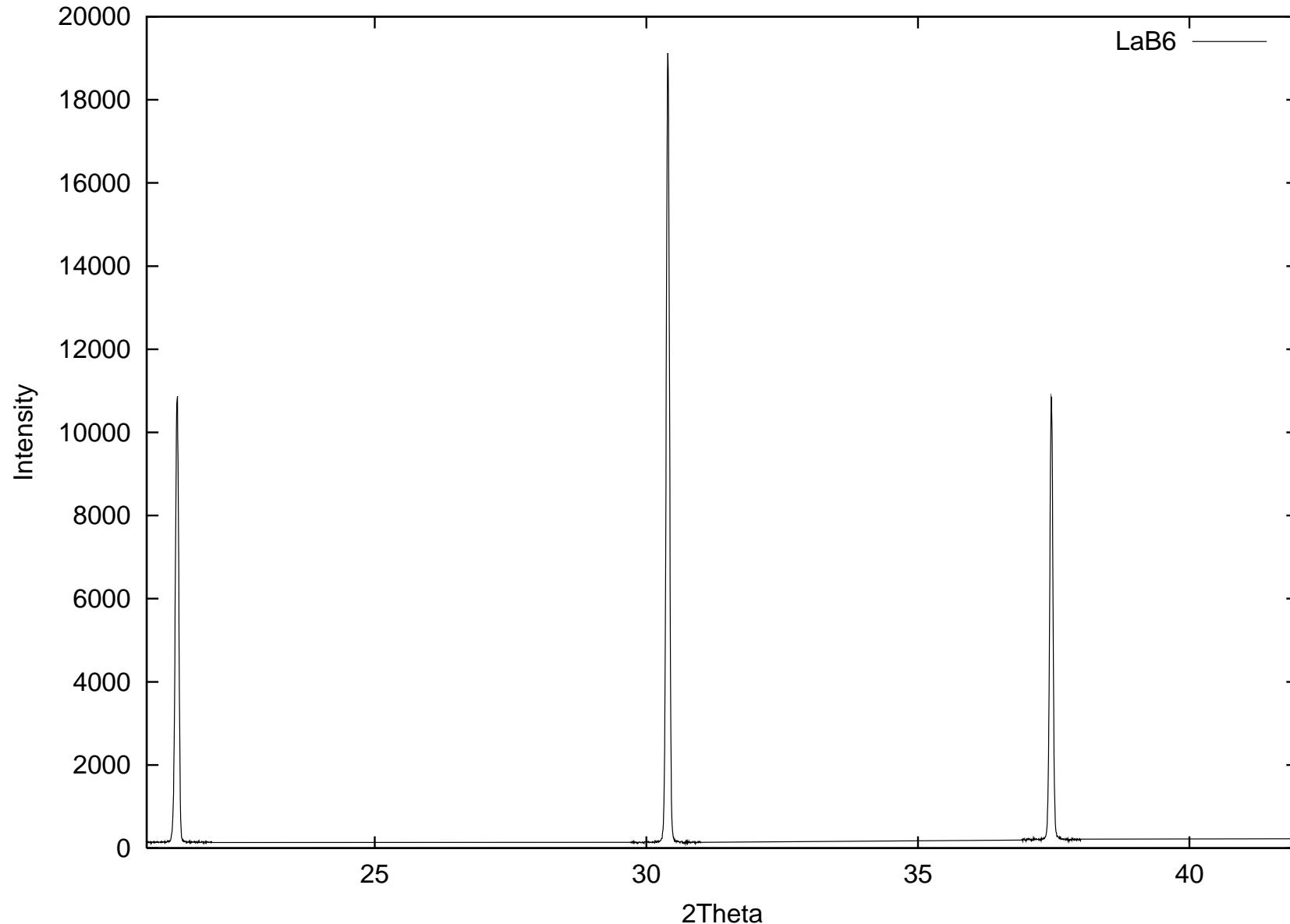
$I_{instr.}^{hkl}$: *measured* instrumental profile which is directly used

The measured and theoretical patterns are compared using a nonlinear least-squares algorithm, the fitted parameters are the microstructural parameters (no individual profile parameters are used).

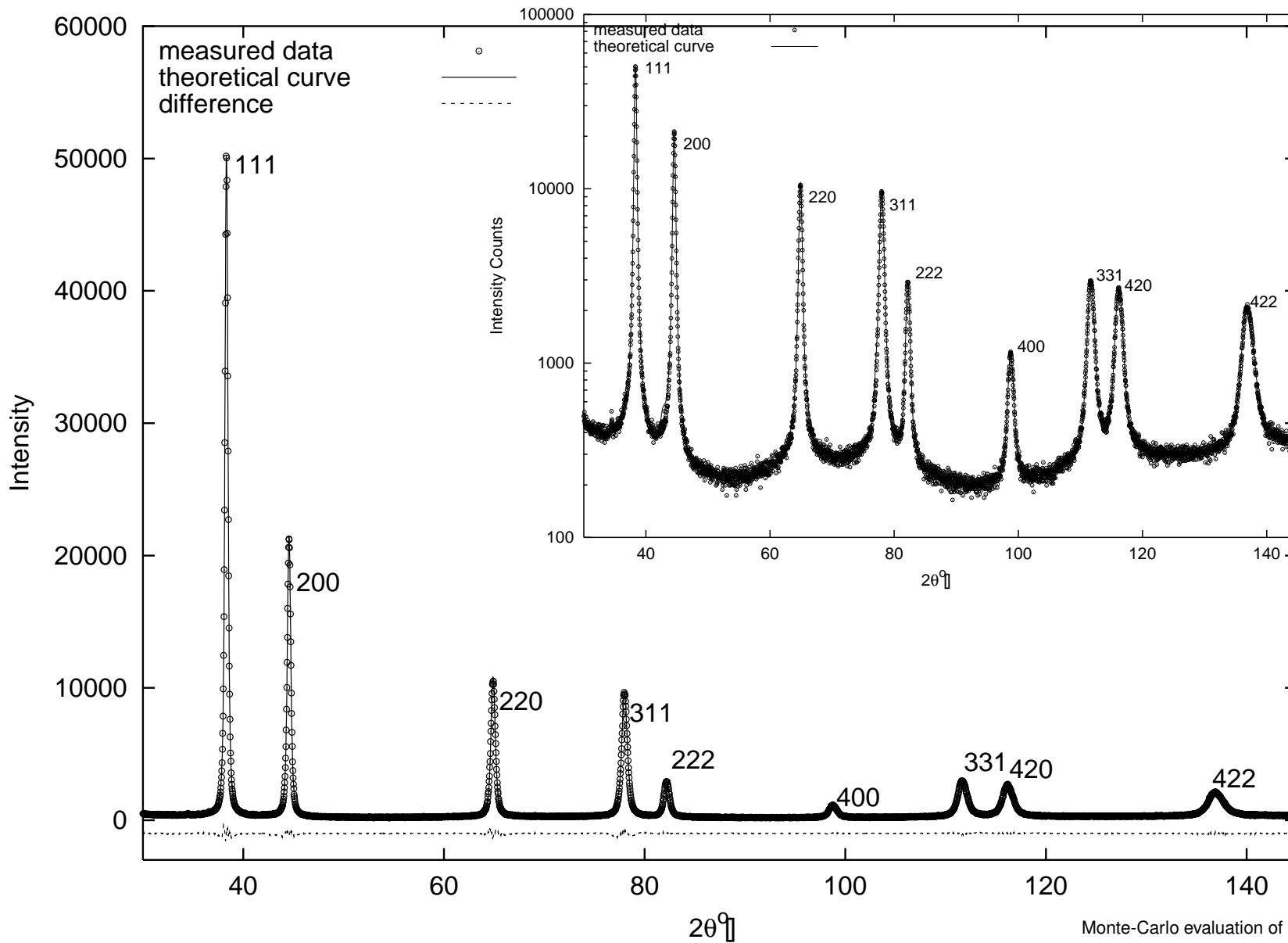
Instrumental pattern of LaB₆



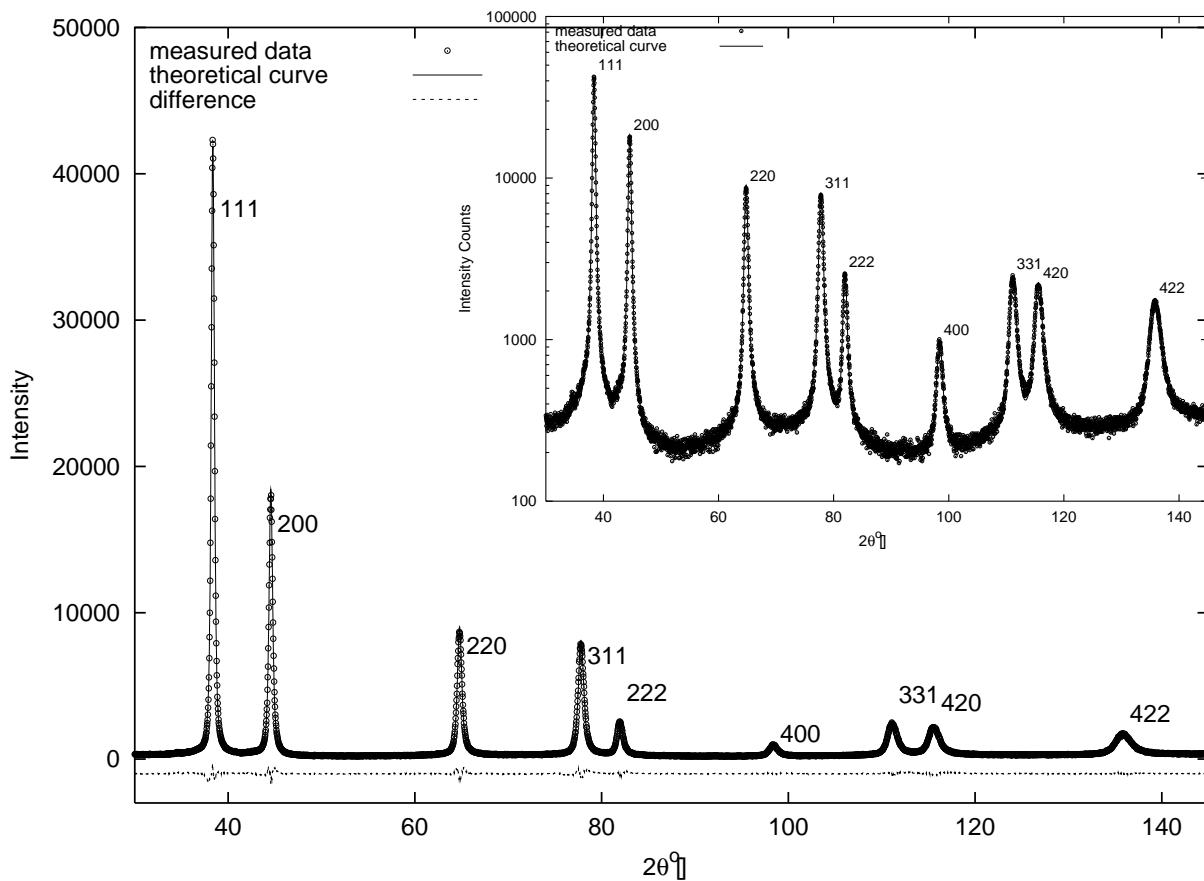
Instrumental pattern of LaB₆



Al-3Mg ball milled 3 h.



Al-6Mg ball milled 6 h.



Results of the
CMWP fit:

$$m = 21 \text{ nm}$$

$$\sigma = 0.36$$

$$\rho = 10^{16} \text{ m}^{-2}$$

$$M = R_e \sqrt{\rho} = 1.3$$

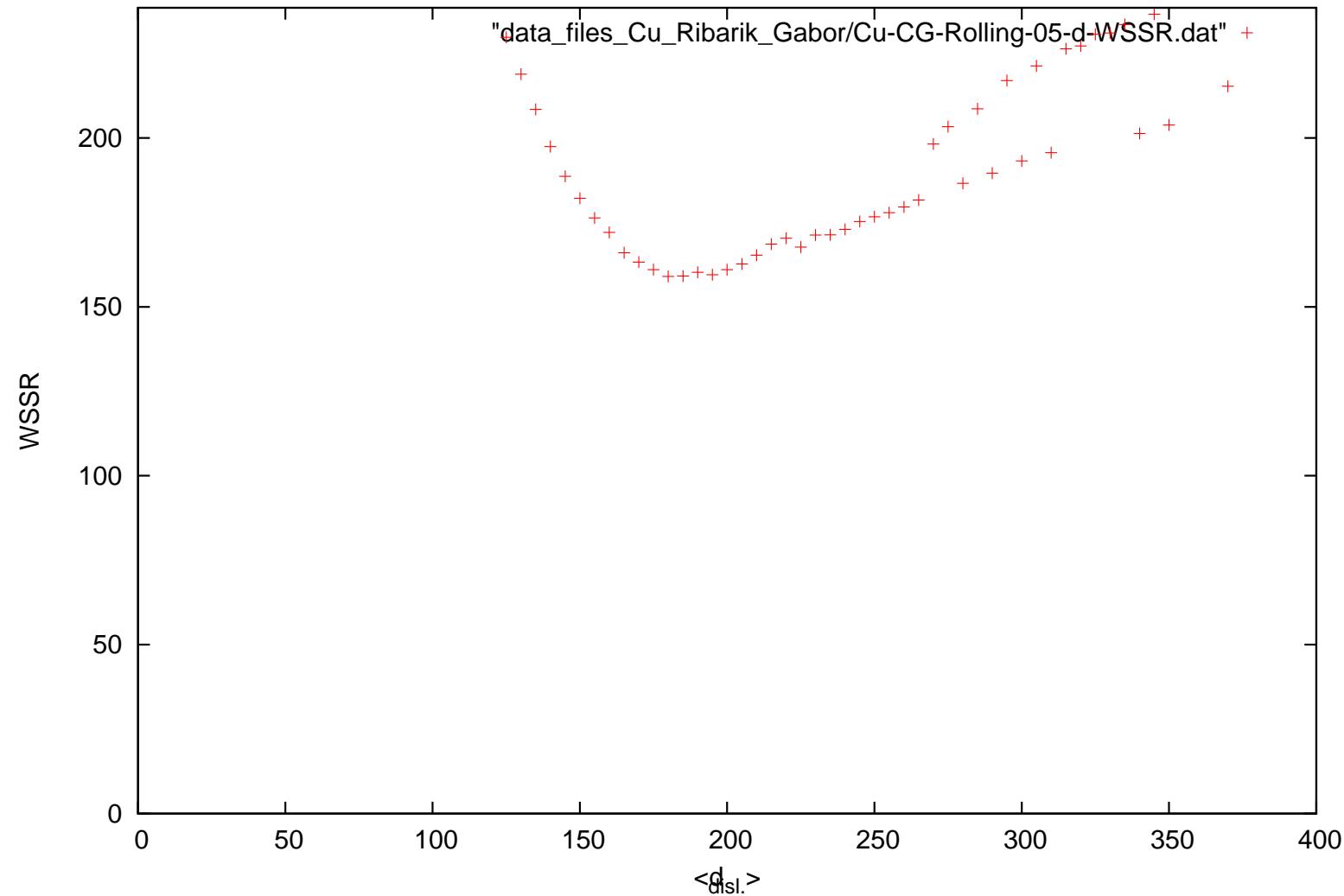
$$q = 1.3$$

WSSR

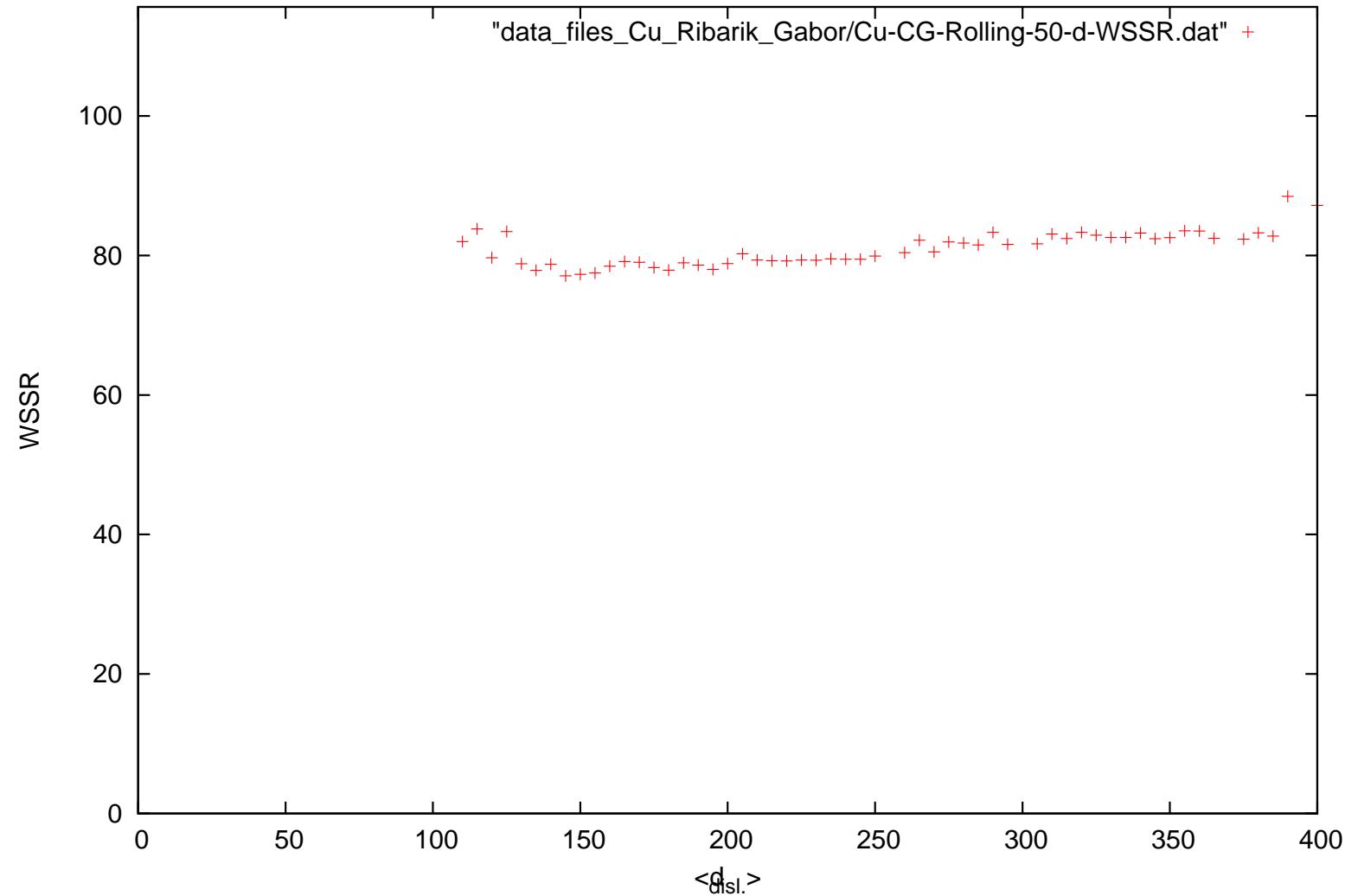
The definition of the WSSR (Weighted Sum of Squared Residuals) in the case of uniform weights:

$$WSSR = \sum_{i=1}^{i=N_{data}} (I_{(K)}^{measured} - I_{(K)}^{theoretical})^2$$

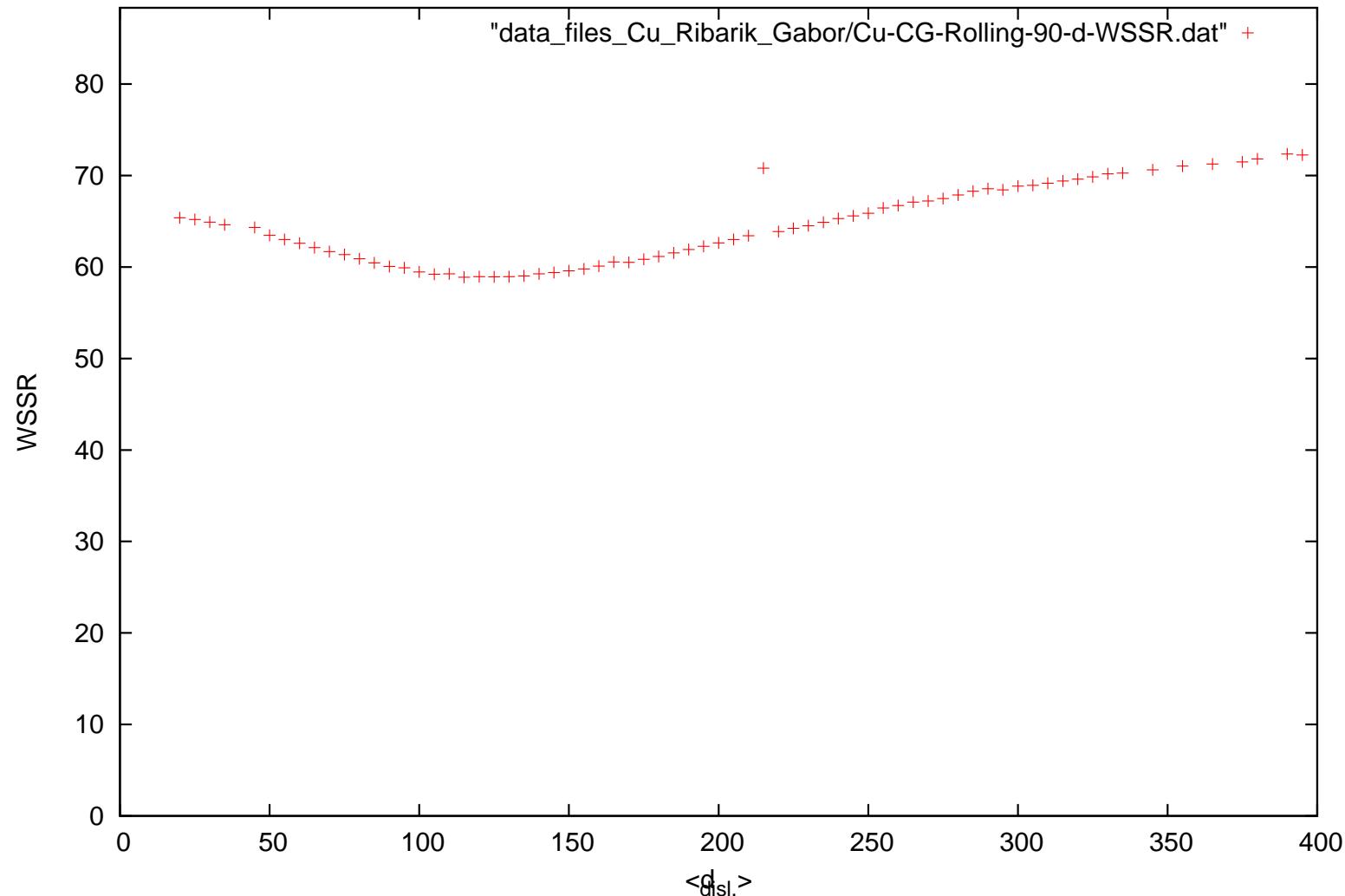
$\langle d_{\text{disl.}} \rangle$ -WSSR plots: Cu-CG-Rolled 5%



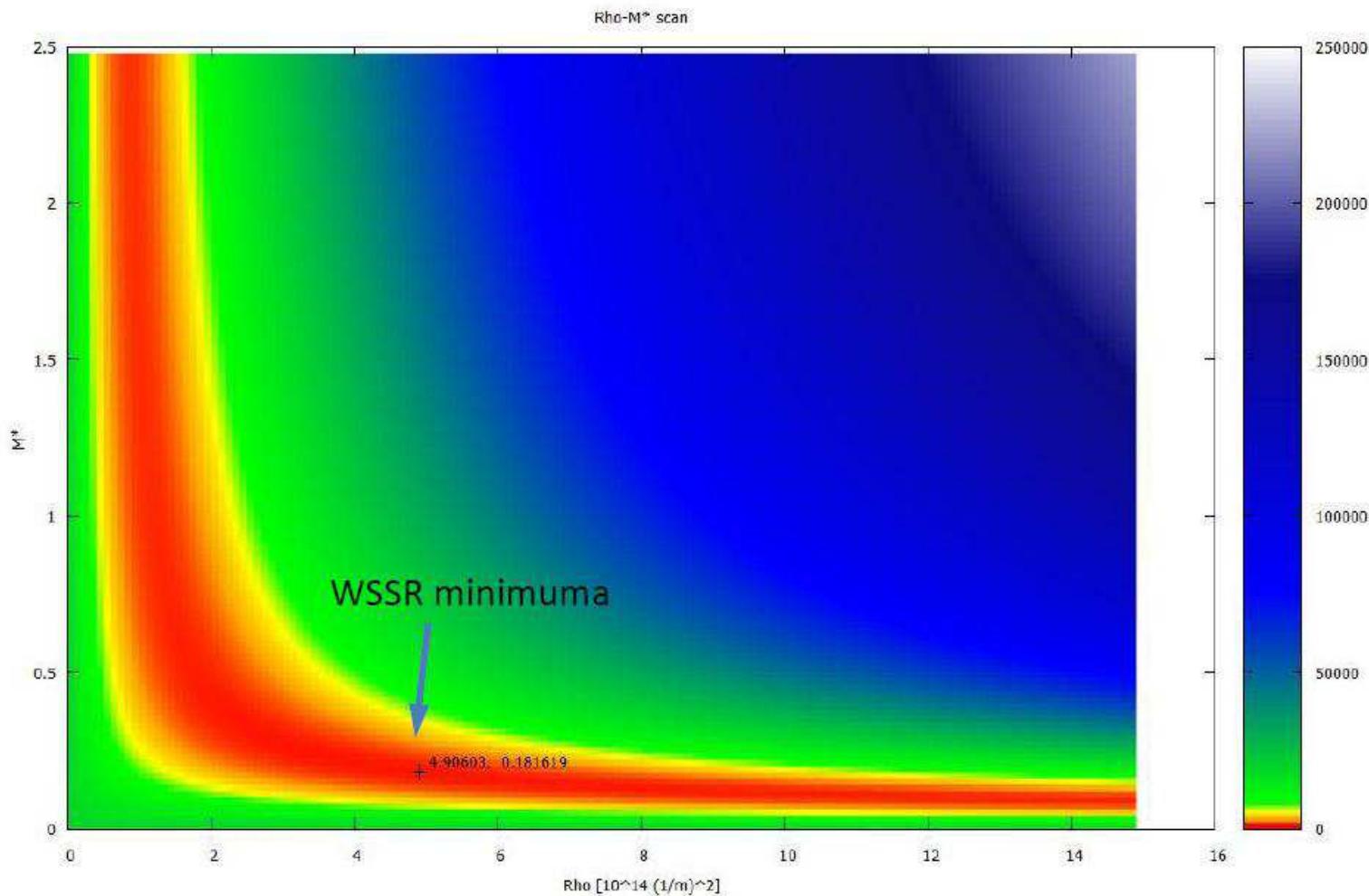
$\langle d_{\text{disl.}} \rangle$ -WSSR plots: Cu-CG-Rolled 50%



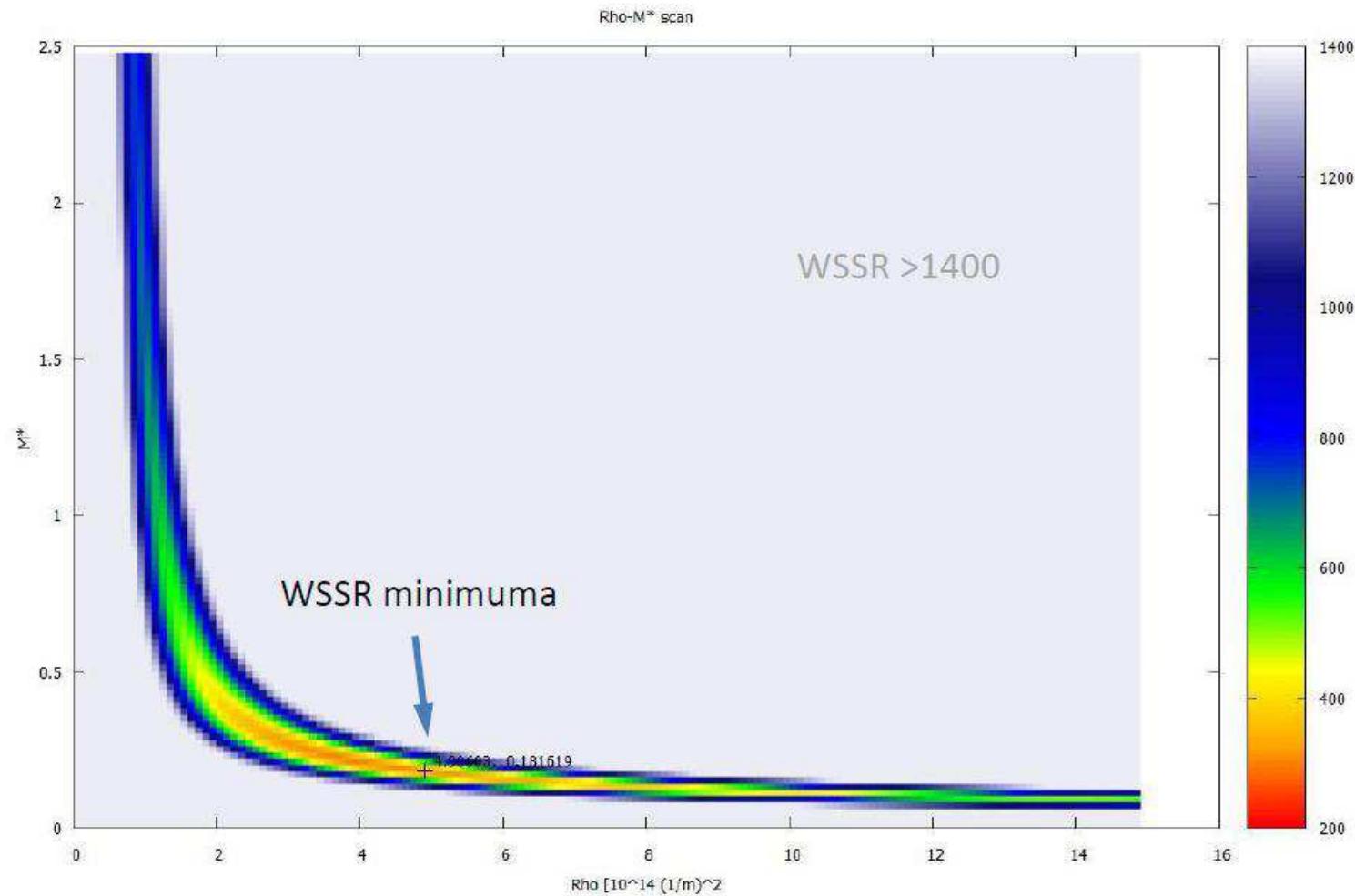
$\langle d_{\text{disl.}} \rangle$ -WSSR plots: Cu-CG-Rolled 90%



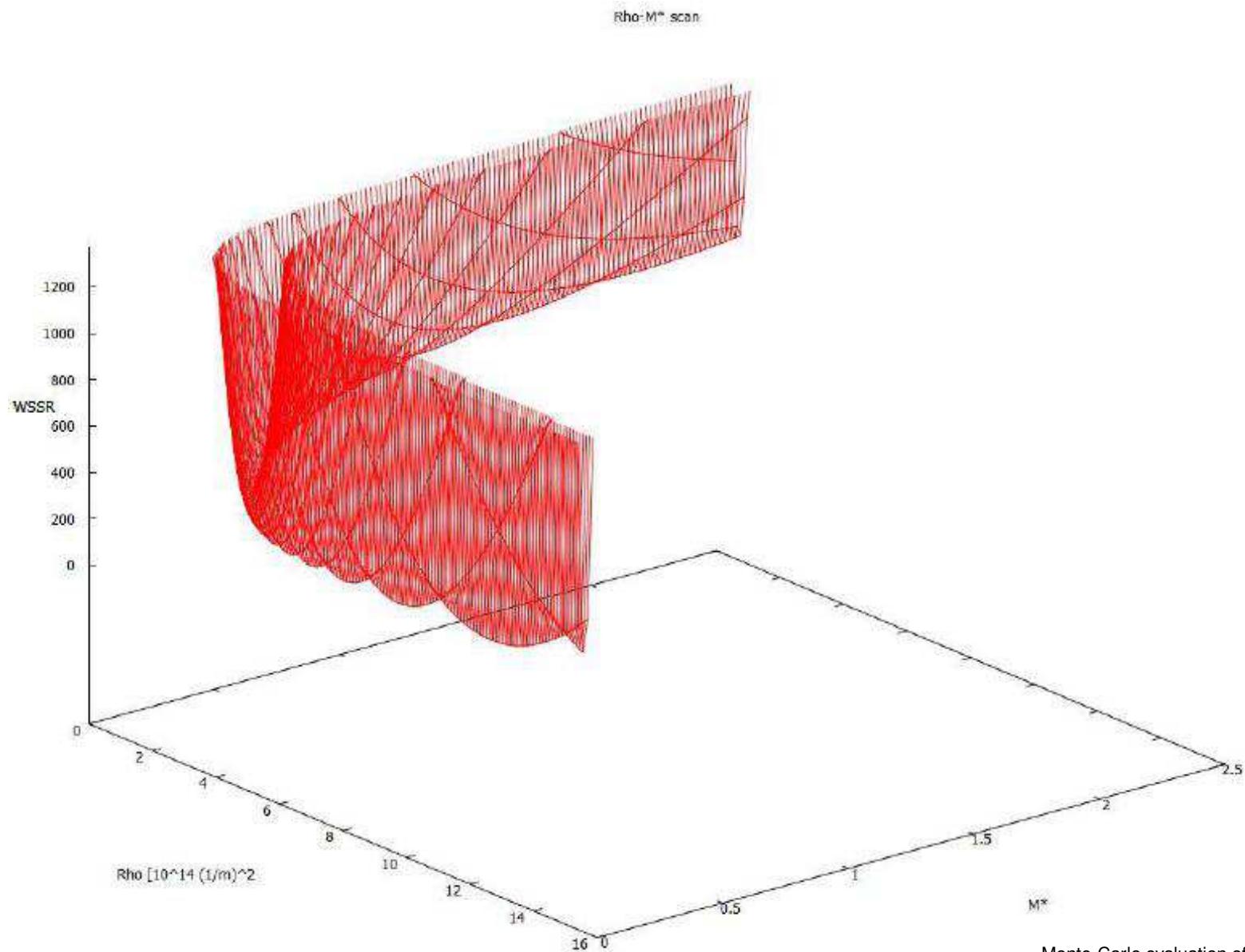
ρ - M^* scan of Cu sample



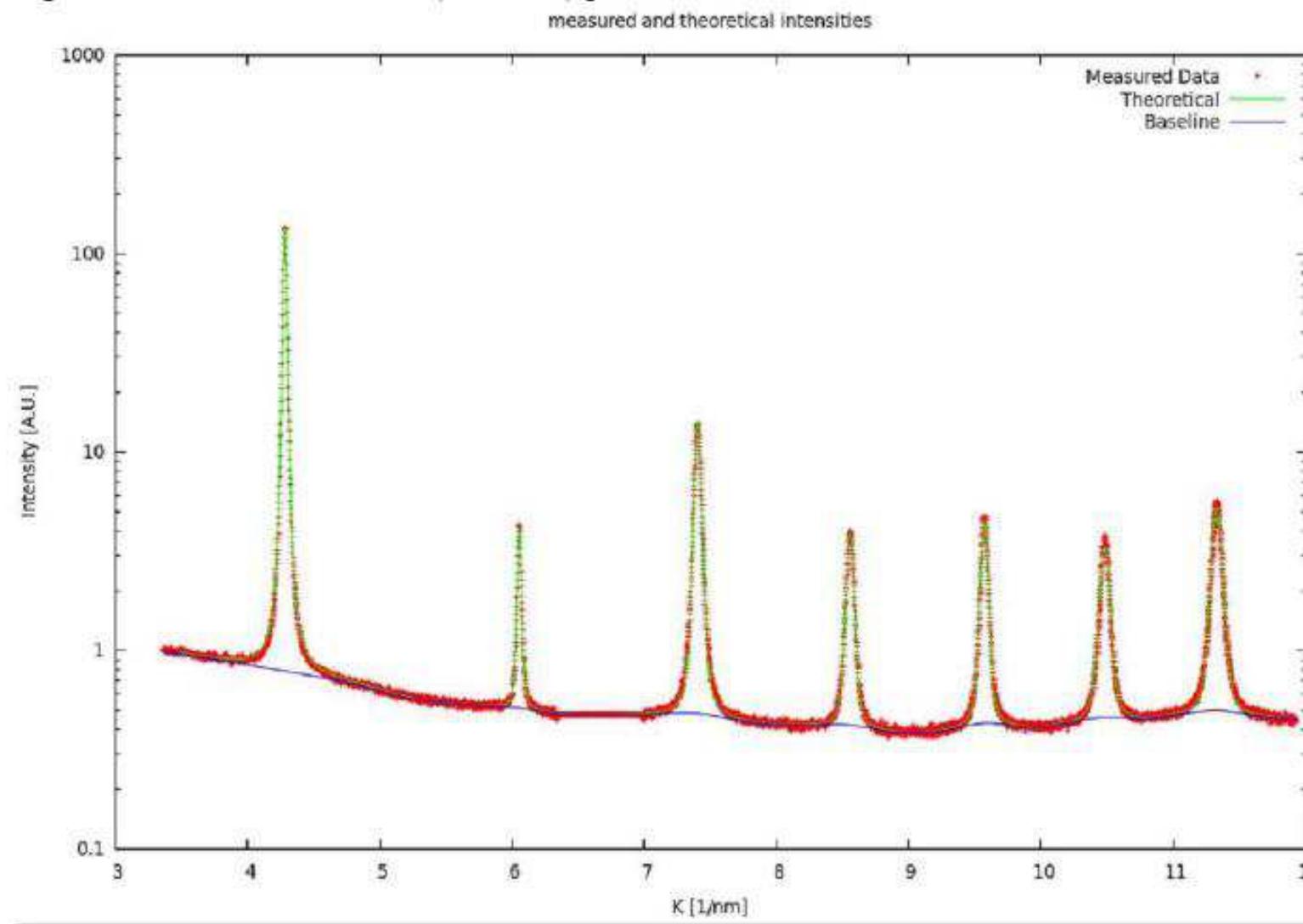
ρ - M^* scan of Cu sample



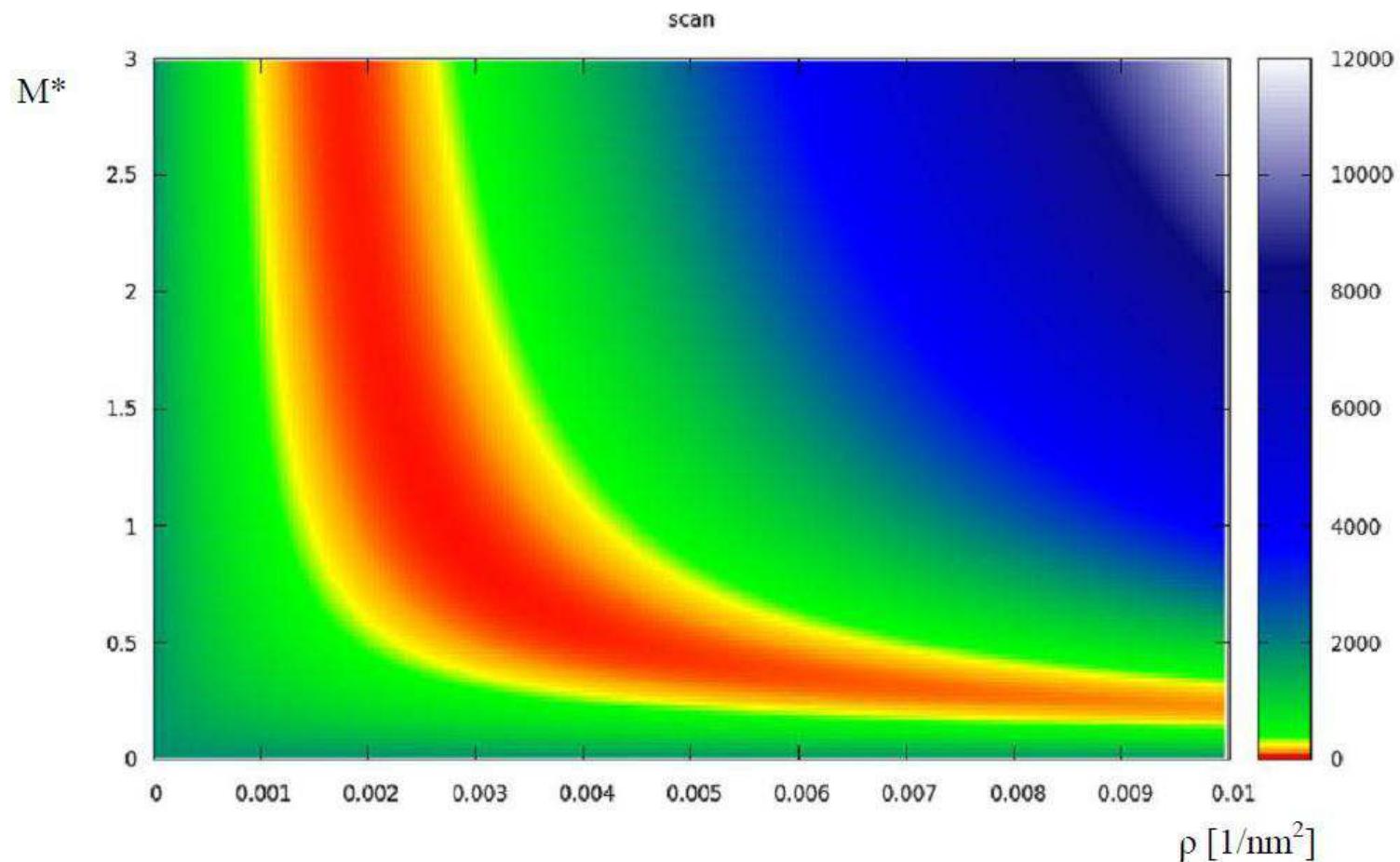
ρ - M^* scan of Cu sample



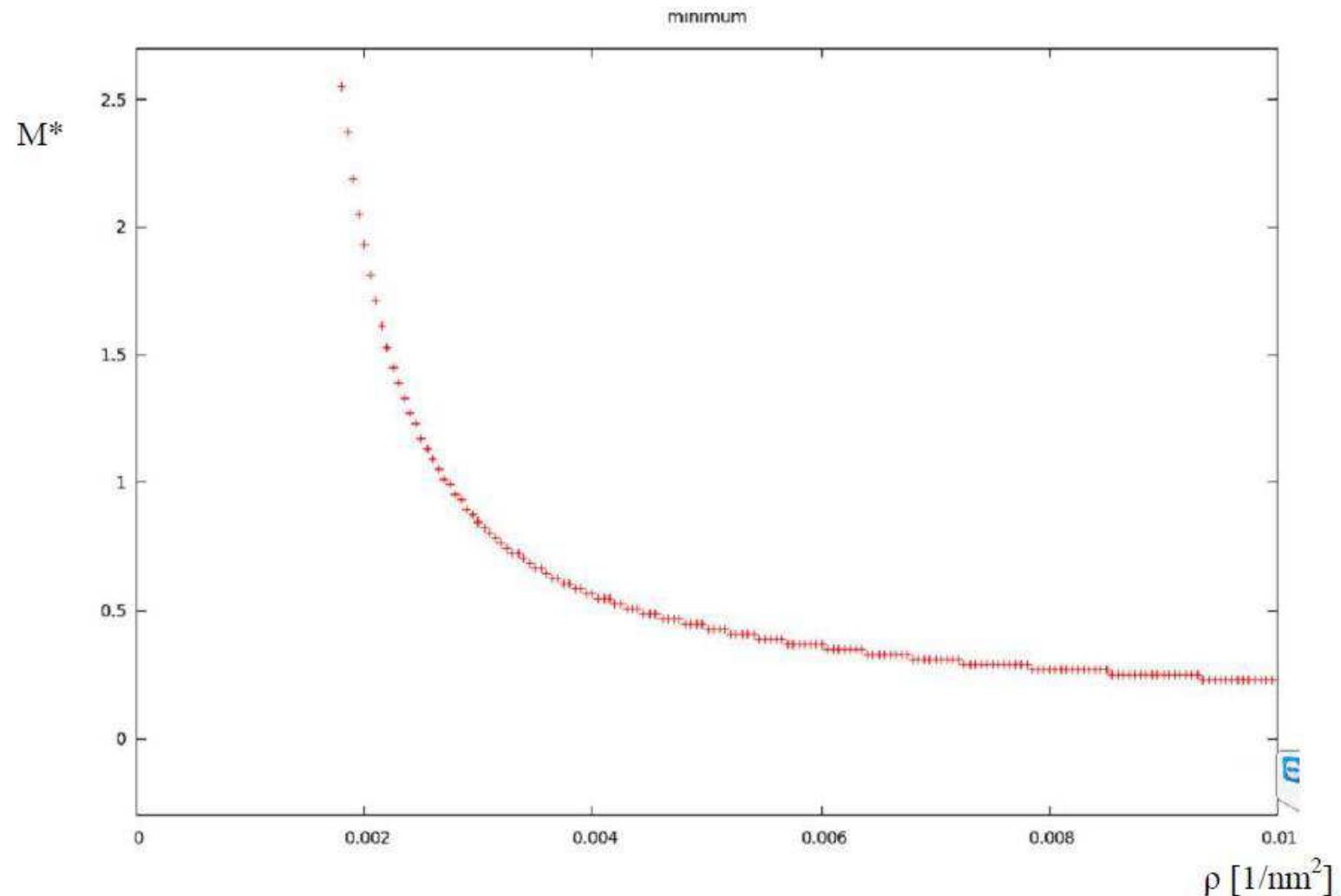
CMWP fit of Nb sample



ρ - M^* scan of Nb sample

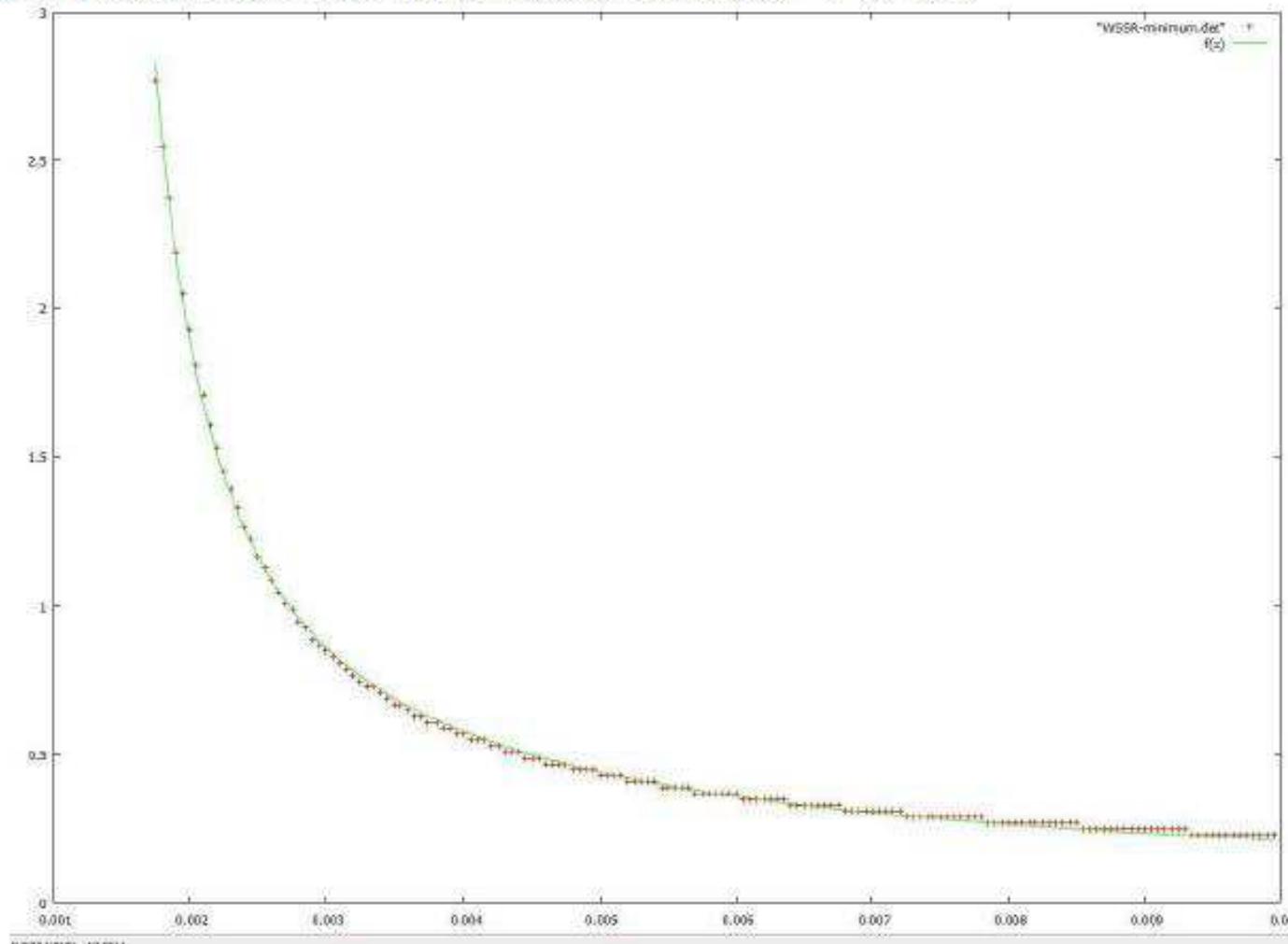


ρ - M^* minimum curve of Nb sample



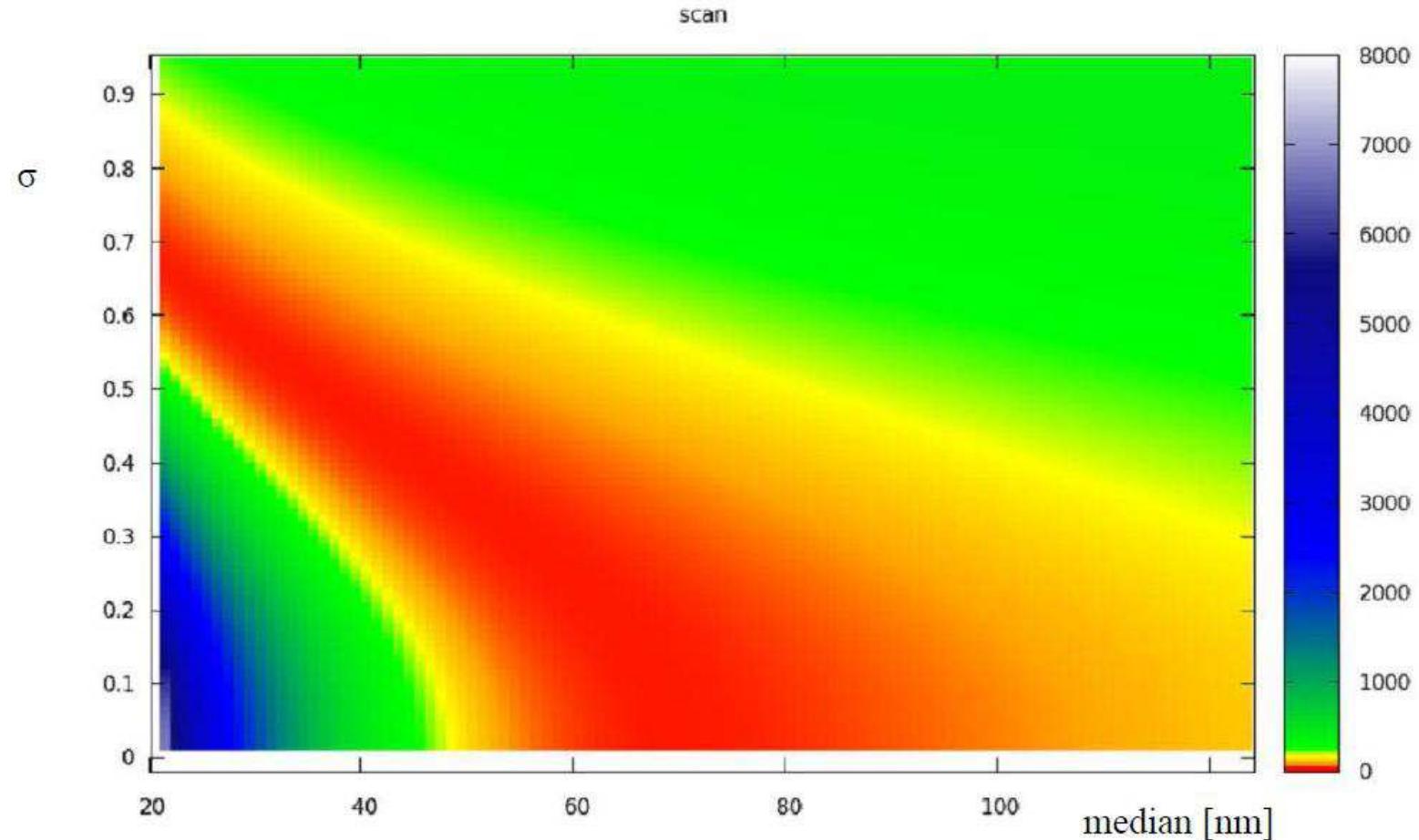
ρ - M^* fit of Nb sample

Figure 8. The minimum valley fitted with function: $f(x) = a^*(x-b)^n$

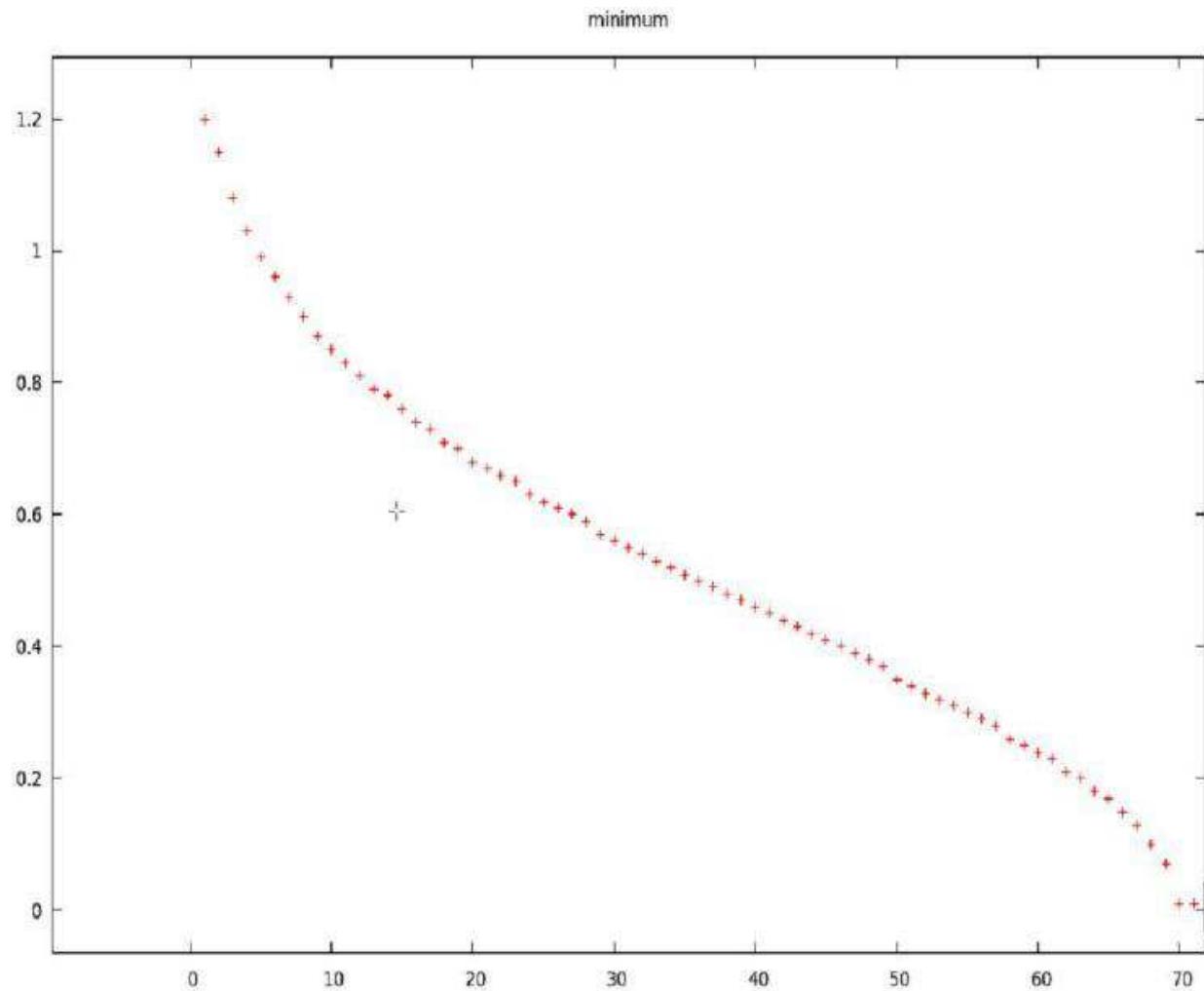


fitted parameters: $a=0.0038$, $n=-0.85$, $b=0.0013$

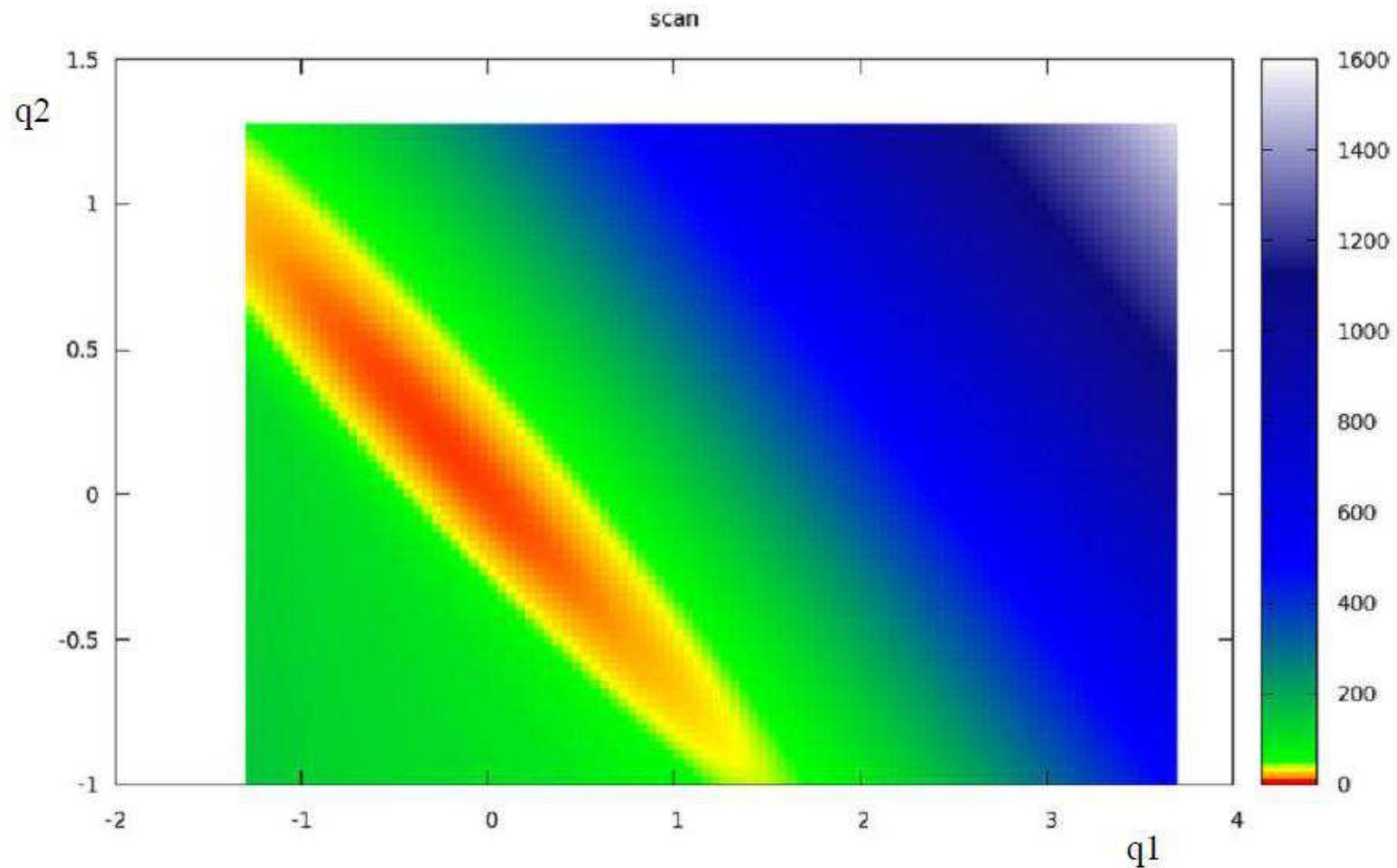
$m\text{-}\sigma$ scan of Nb sample



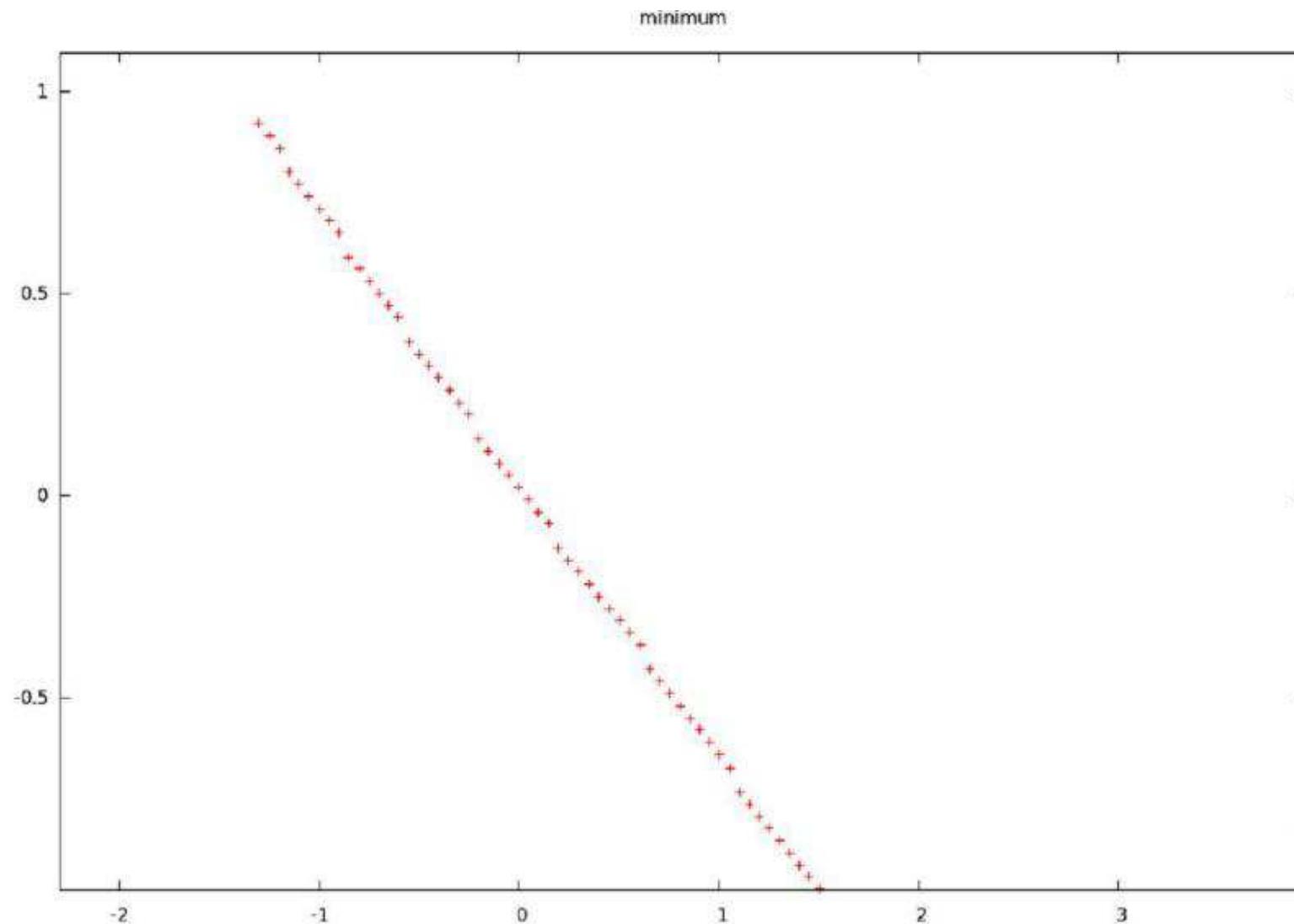
m - σ minimum curve of Nb sample



q_1 - q_2 scan of Nb sample



q_1 - q_2 minimum curve of Nb sample



Non-linear least-squares algorithms

- Gauss-Newton, conjugate gradient algorithms (iterative methods based on Taylor-expansion)
- Marquardt-Levenberg algorithm: a scalable step is used

These methods can find only the local minimum. Some of the global optimization algorithms:

- Simulated annealing method
- Monte-Carlo methods

Monte-Carlo methods

A random generator number is used for probing the parameters. Compared to the brute force method (systematic scanning) it requires much less calculations to obtain a (less detailed) map the parameter space. It can be used iteratively, e.g. the new parameters are searched in the proximity of the previous ones.

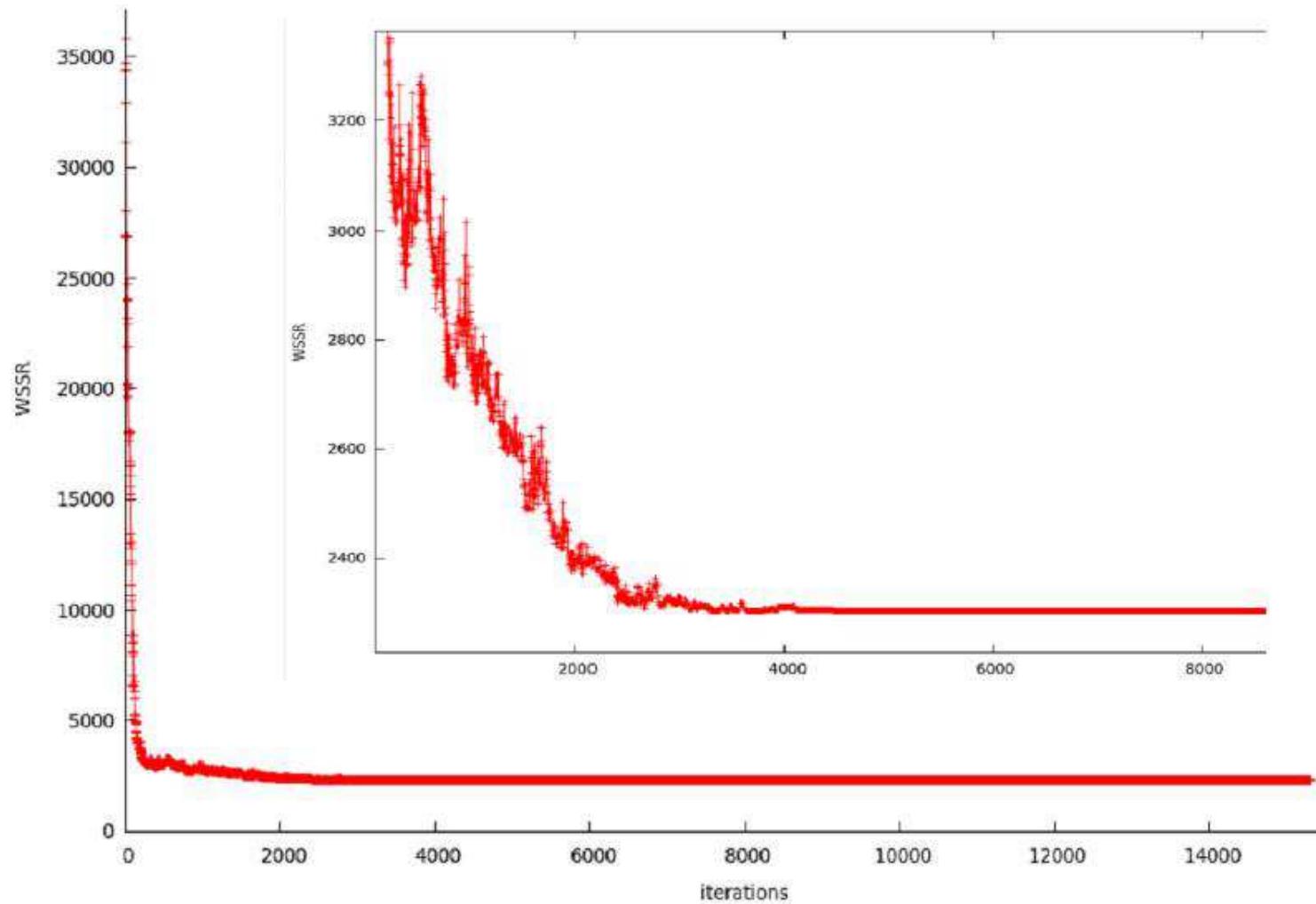
Simulated Annealing method

It's a Monte-Carlo method. The smaller WSSR is always accepted. The larger WSSR is accepted with the following probability (T is a “temperature” parameter):

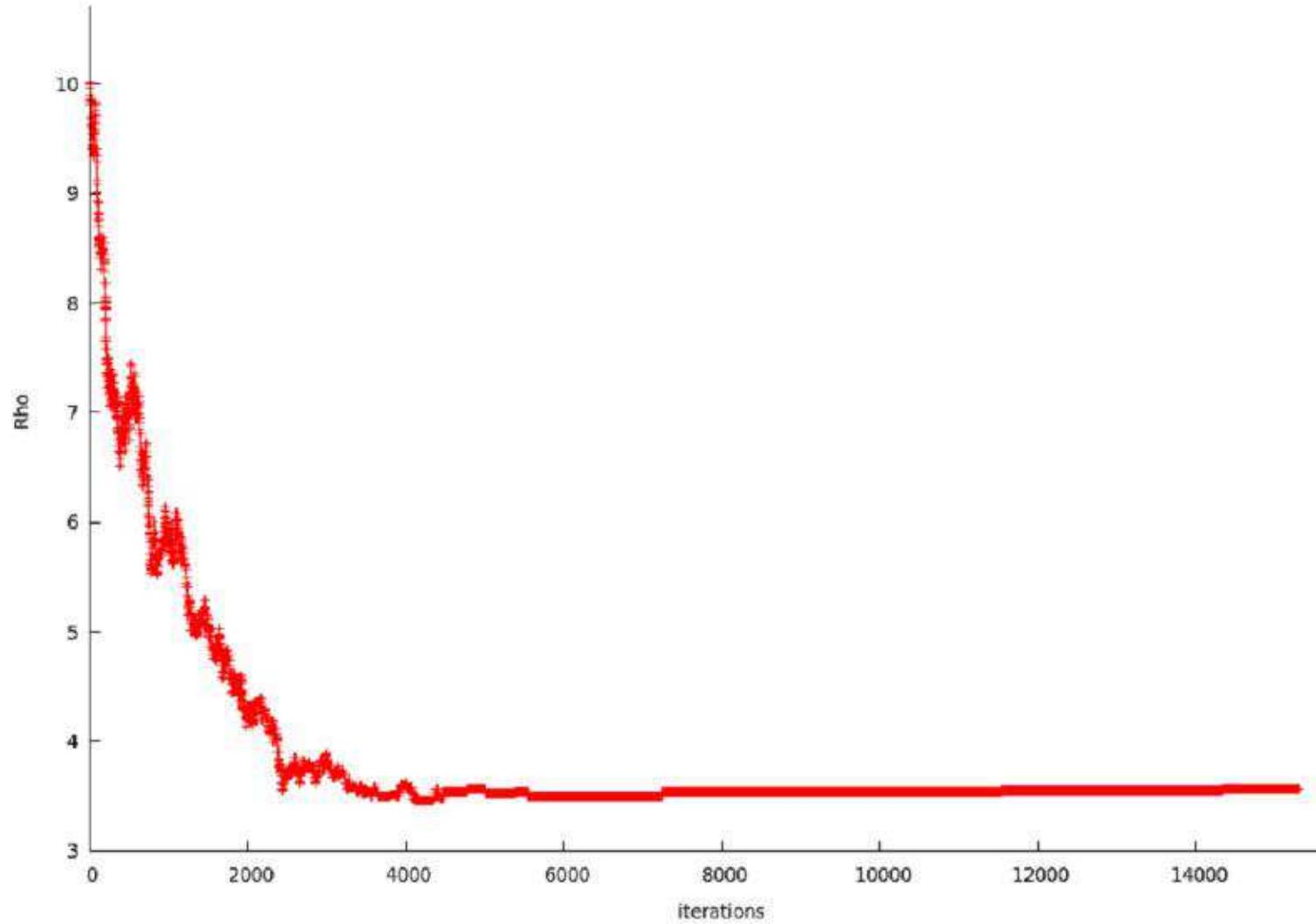
$$\exp\{(WSSR - WSSR') / T\}$$

The parameter T is “cooled down” (decreased) during the fit until it reaches a minimum value T_{min} . Its name is coming from annealing in metallurgy (controlled cooling of a material to increase the size of its crystals and reduce defects), as the temperature is cooled down, the system finds the global minimum of the thermodynamic free energy.

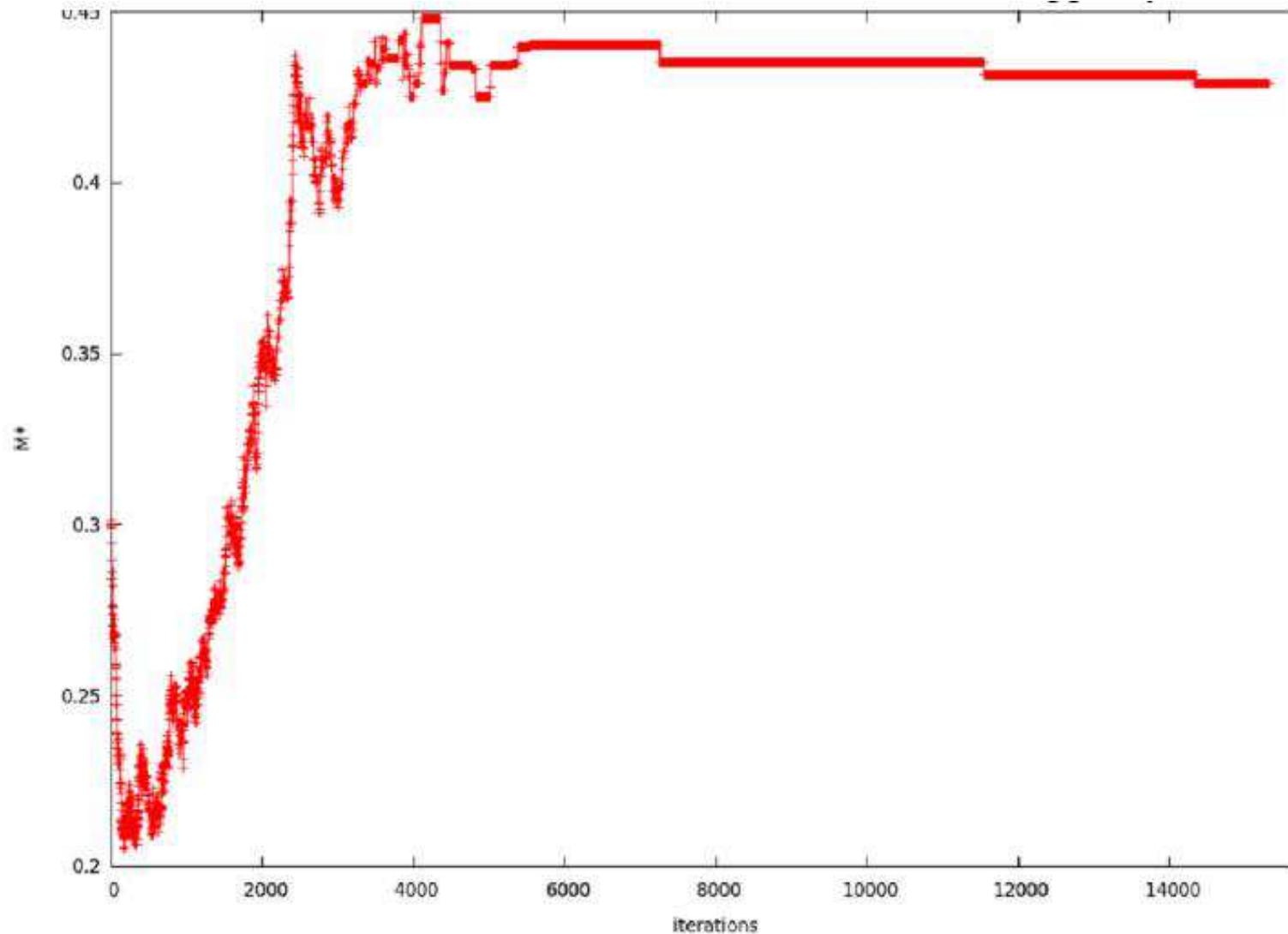
SA method: WSSR evolution



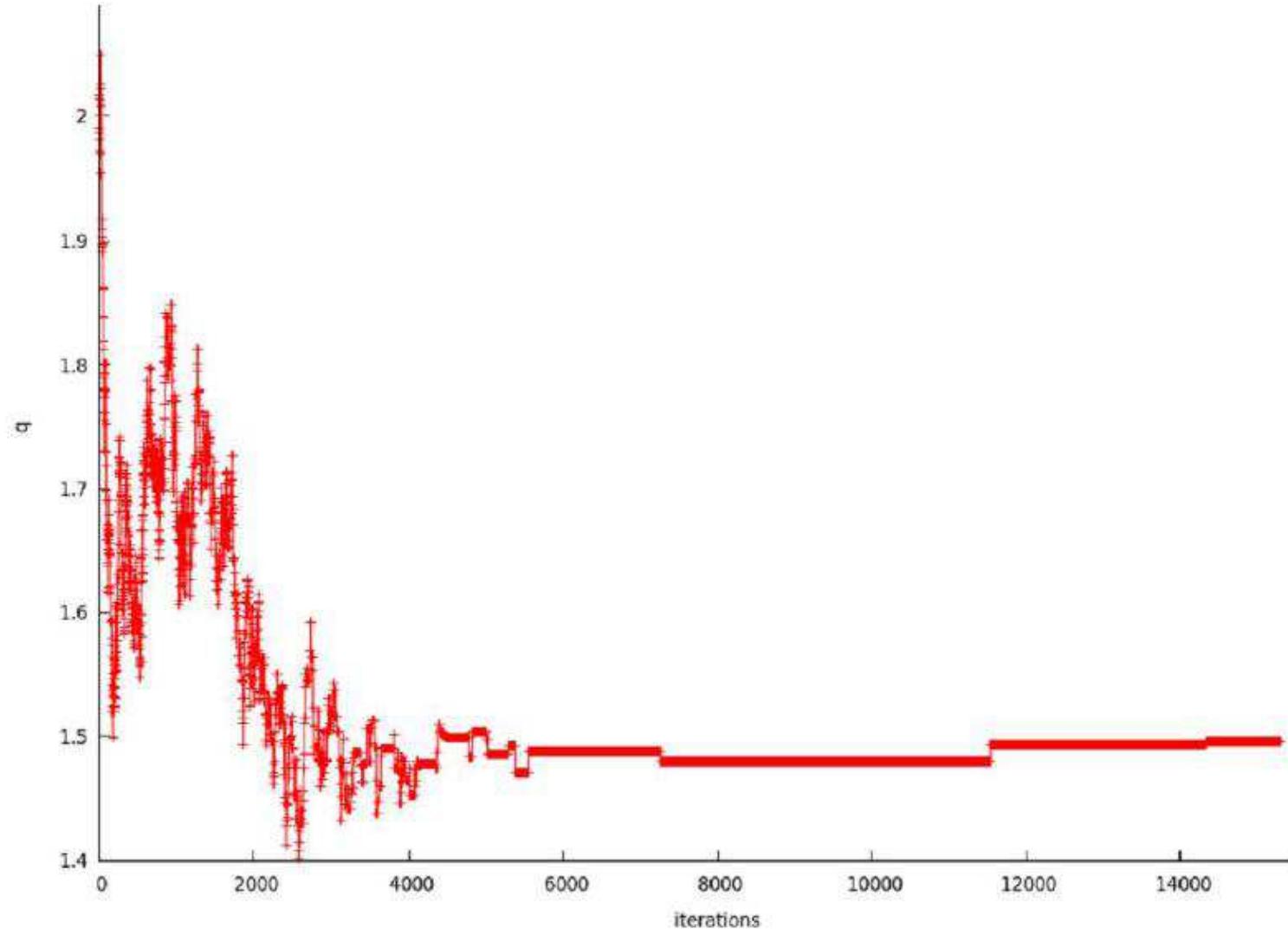
SA method: ρ evolution



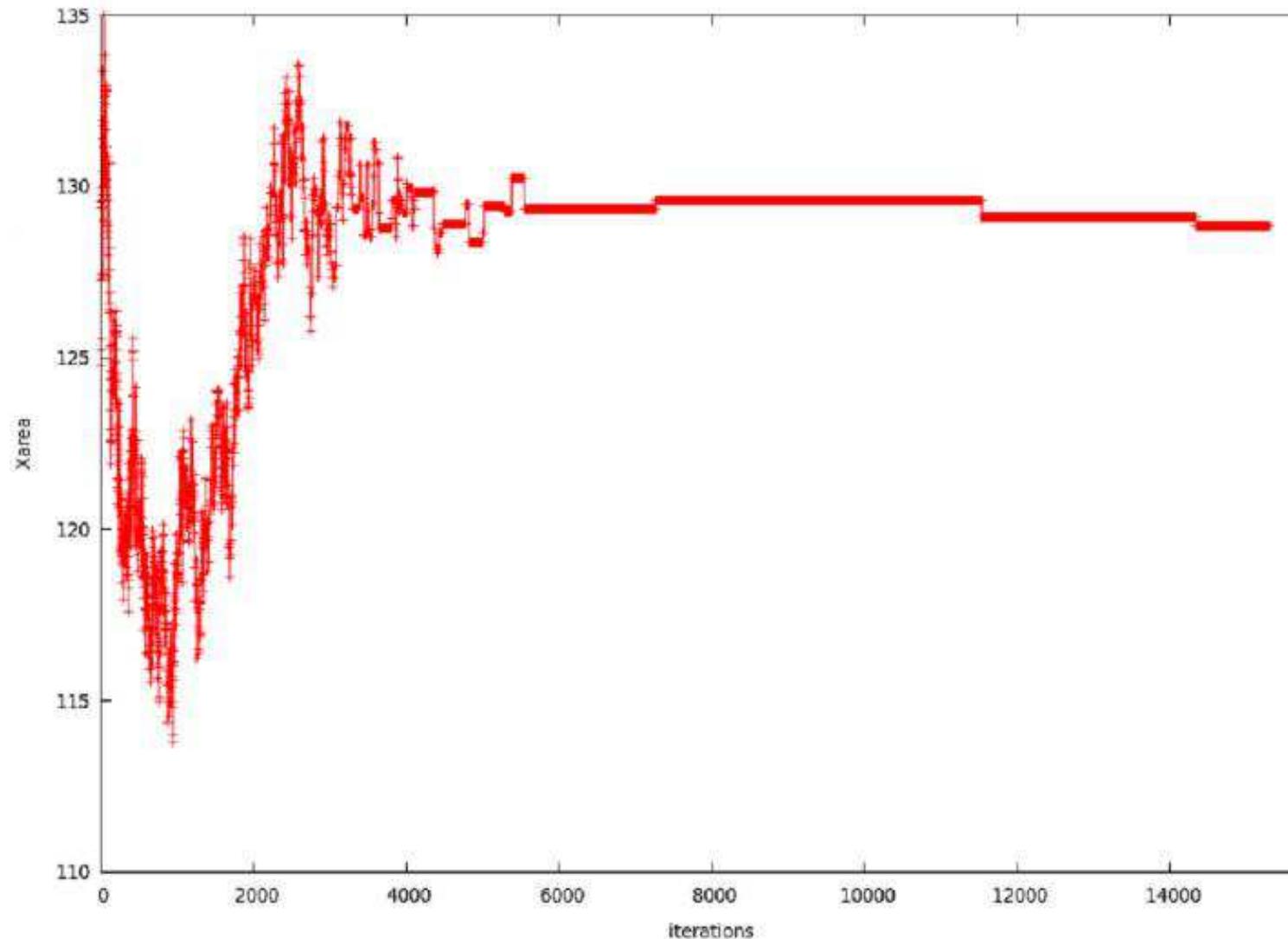
SA method: M^* evolution



SA method: q evolution



SA method: $\langle x \rangle_a$ evolution



The new Monte-Carlo method

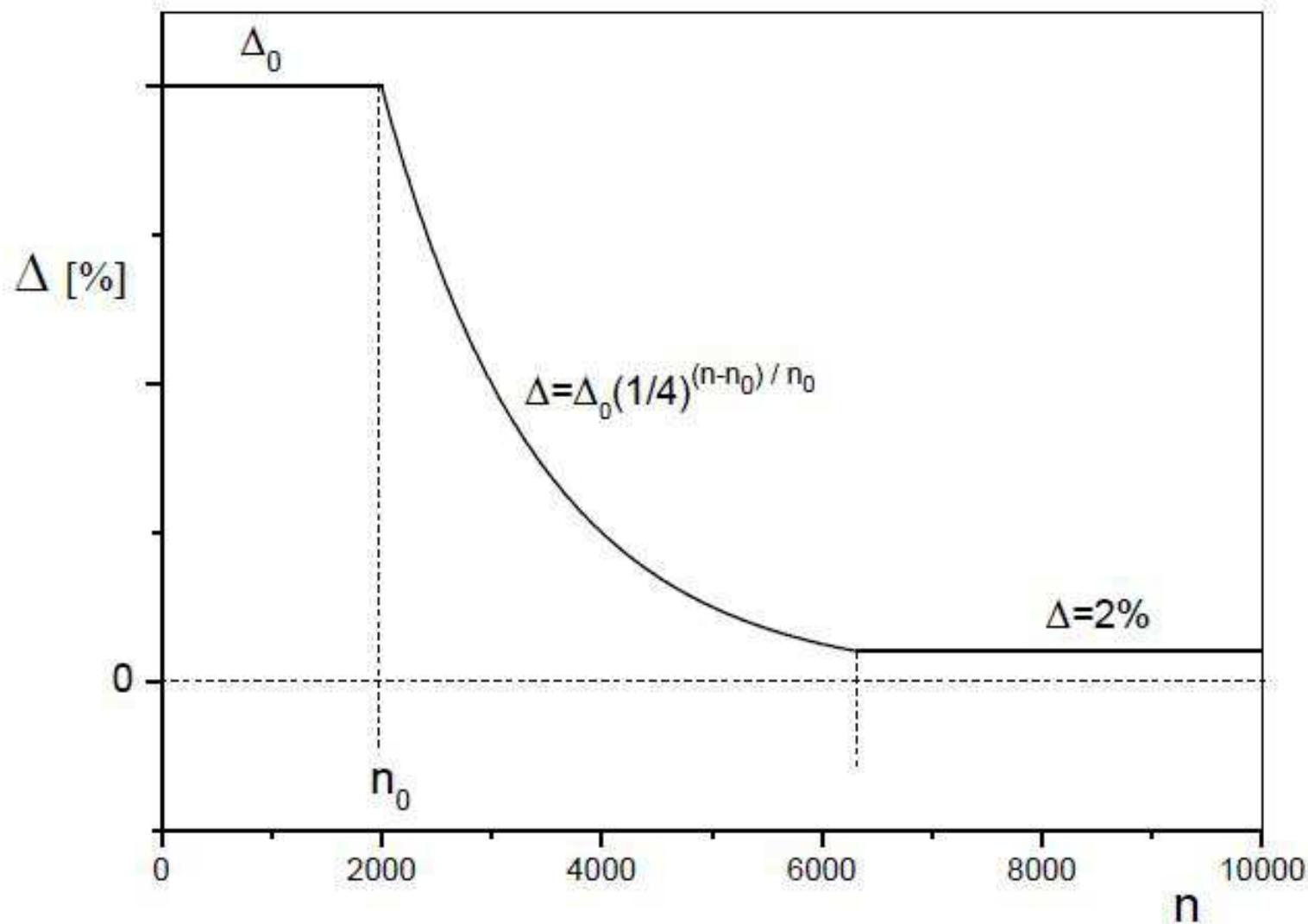
The fitting parameters are the following physical parameters: m , σ , q (or a_1 , a_2), ρ and M^* . Fitting ρ and M^* provides better results (less scattering) than fitting $\langle d_{\text{disl.}} \rangle$ and R_e^* . Each parameter has a minimum and maximum value which cannot be bypassed. The new parameter values are searched in the proximity of the previous ones:

$$a_n^i \in [a_m^i + \Delta^i ; a_m^i - \Delta^i]$$

The Δ parameter's definition:

$$\Delta_n^i = \begin{cases} \Delta_0^i & , \text{ha } n \leq n_0 \\ \Delta_0^i \cdot (1/4)^{\frac{n-n_0}{n_0}} & , \text{ha } n > n_0 \\ 2\% & , \text{ha } \Delta_n^i < 2\% \end{cases}$$

The evolution of the Δ parameter



The new Monte-Carlo method

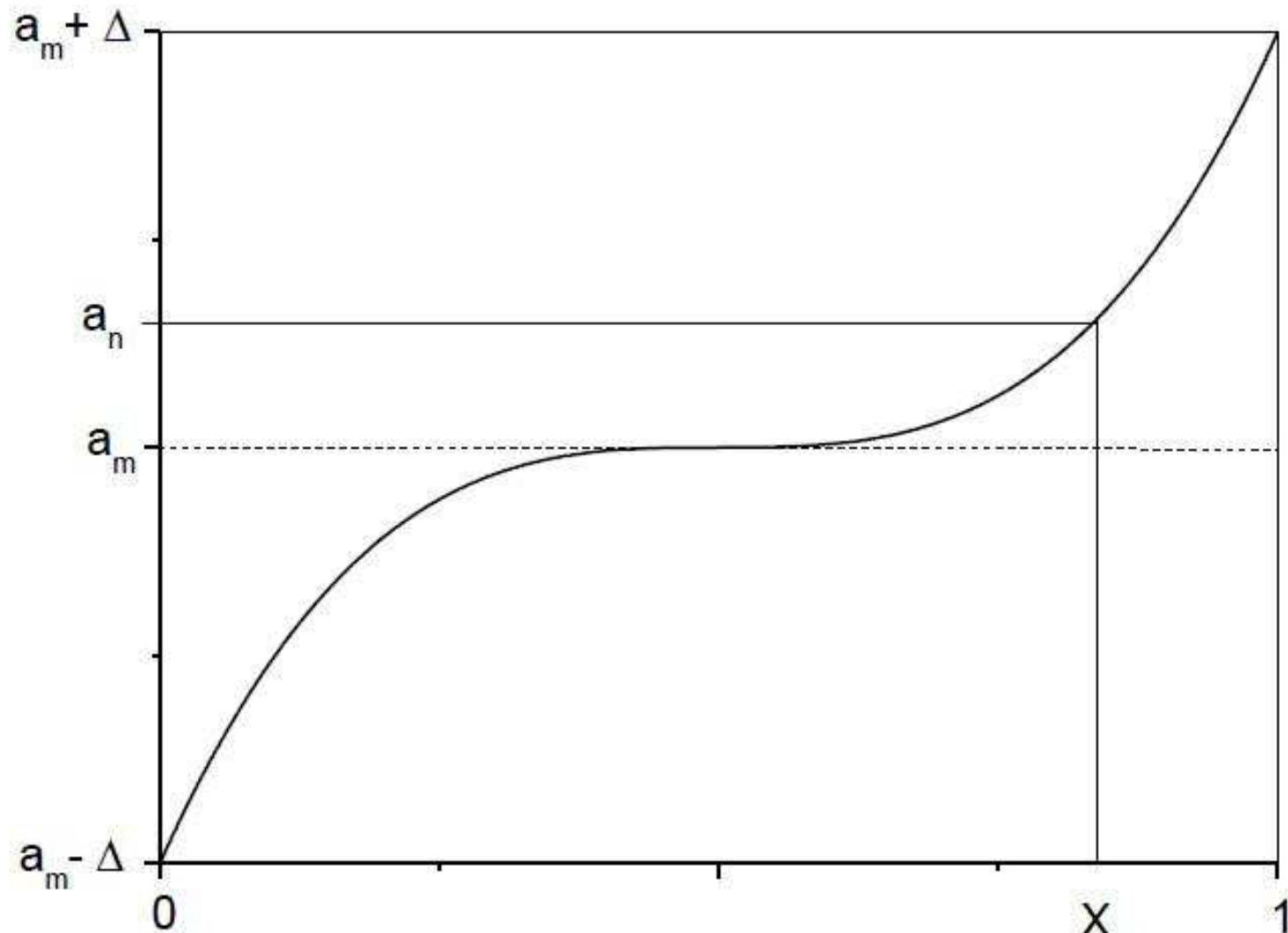
The new parameters are deviated to the previous ones using a cubic probability function:

$$a_n^i = \Delta_n^i \cdot (2x_n^i - 1)^3 + a_m^i$$

where $x_i \in [0, 1]$ is a random number. The condition for accepting the new parameters:

$$a_{m+1}^i = \begin{cases} a_n^i, & WSSR^n < WSSR^m \\ a_m^i, & WSSR^n \geq WSSR^m \end{cases}$$

The cubic probability function



The new Monte-Carlo method

- determination of the *confidence intervals*: if $WSSR > WSSR_{best}$ AND $WSSR < 1.025 \cdot WSSR_{best}$ then the parameters are remembered and *the errors* corresponding to a 2.5% confidence level are determined for all parameters (the errors in the positive and negative direction can be different)
- *convergence criteria*: number of steps should reach $3n_0$ AND confidence level statistics should be at least 100. At the end the MC fit is always followed by a ML fit.
- *the peak intensities and peak positions* are fitted at every 500 steps after the number of steps has reached n_0 using the Marquardt-Levenberg algorithm (all parameters are fitted and the same limits are applied)

Example for parameter errors

a	=	1.1531	(0.92364–1.374)
b	=	21.725	(19.792–23.468)
c	=	0.34766	(0.30318–0.38179)
d	=	66.312	(60.552–85.871)
e	=	0.27925	(0.23091–0.31104)

Confidence level statistics: 160

Errors for a (value: 1.1531): -19.9%, +19.2%

Errors for b (value: 21.725): -8.9%, +8.03%

Errors for c (value: 0.34766): -12.8%, +9.82%

Errors for d (value: 66.312): -8.69%, +29.5%

Errors for e (value: 0.27925): -17.3%, +11.4%

Stability of the MC scan

```
1.sol:Final (best) WSSR value from MC scan: 11347
2.sol:Final (best) WSSR value from MC scan: 11340
3.sol:Final (best) WSSR value from MC scan: 11404
4.sol:Final (best) WSSR value from MC scan: 11374
5.sol:Final (best) WSSR value from MC scan: 11355
6.sol:Final (best) WSSR value from MC scan: 11340
7.sol:Final (best) WSSR value from MC scan: 11347
8.sol:Final (best) WSSR value from MC scan: 11354
9.sol:Final (best) WSSR value from MC scan: 11335
10.sol:Final (best) WSSR value from MC scan: 11337
```

Stability of the final results

```
1.sol:final sum of squares of residuals : 11333.9
2.sol:final sum of squares of residuals : 11333.9
3.sol:final sum of squares of residuals : 11333.9
4.sol:final sum of squares of residuals : 11333.9
5.sol:final sum of squares of residuals : 11332.9
6.sol:final sum of squares of residuals : 11332.9
7.sol:final sum of squares of residuals : 11333.9
8.sol:final sum of squares of residuals : 11333.9
9.sol:final sum of squares of residuals : 11333.9
10.sol:final sum of squares of residuals : 11333.9
```

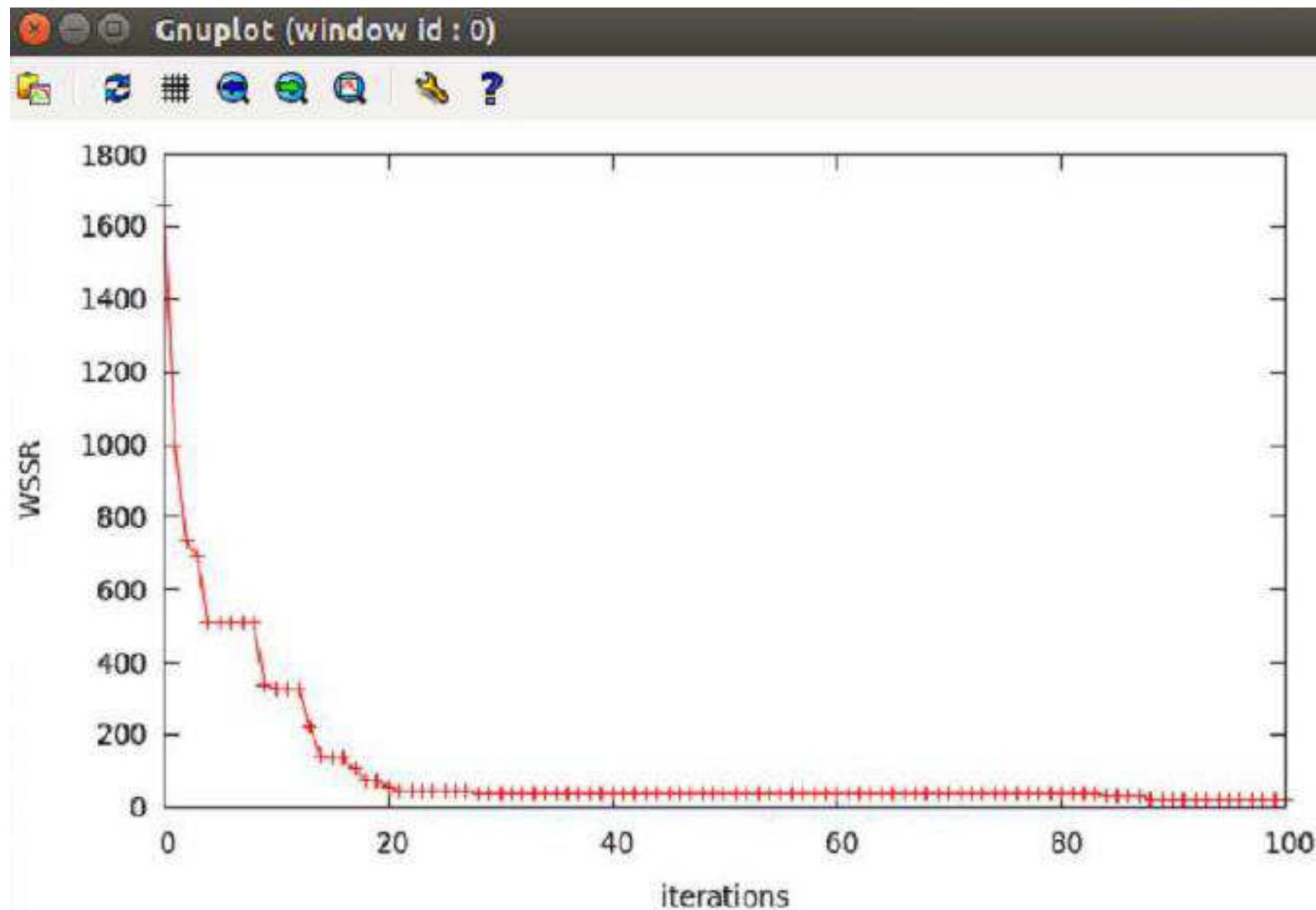
Stability of ρ from MC scan

1.sol:d	=	67.357	(60.83–87.647)
2.sol:d	=	66.718	(54.784–72.845)
3.sol:d	=	58.621	(46.825–60.909)
4.sol:d	=	61.071	(53.869–64.286)
5.sol:d	=	71.738	(66.664–80.551)
6.sol:d	=	72.085	(65.768–87.398)
7.sol:d	=	63.617	(48.022–67.695)
8.sol:d	=	65.589	(59.505–72.337)
9.sol:d	=	66.94	(56.841–82.475)
10.sol:d	=	66.312	(60.552–85.871)

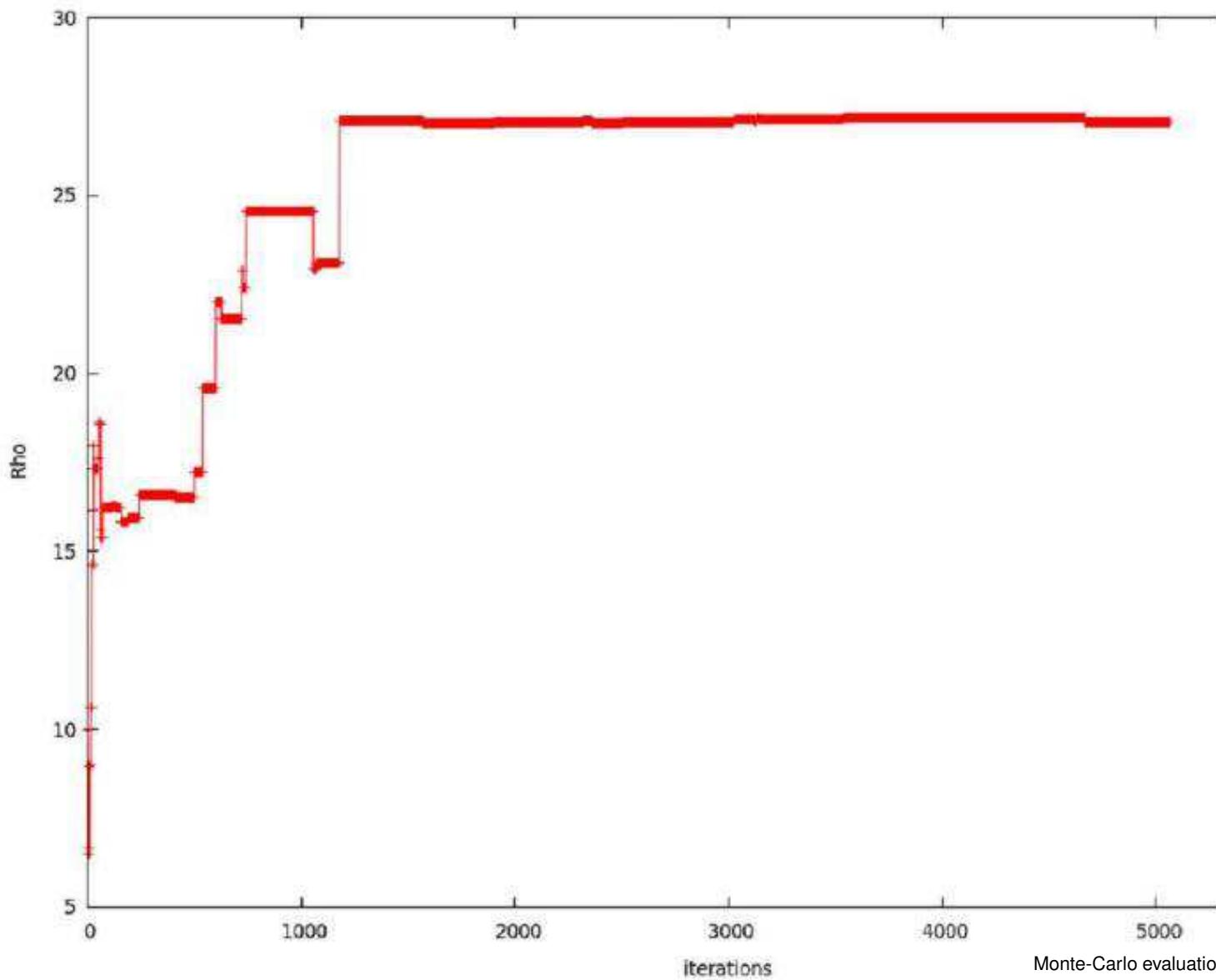
Stability of the final ρ value

```
1.sol:rho=d/1e4=0.0067762 (1/nm) ^2  
2.sol:rho=d/1e4=0.00677642 (1/nm) ^2  
3.sol:rho=d/1e4=0.00677669 (1/nm) ^2  
4.sol:rho=d/1e4=0.00677671 (1/nm) ^2  
5.sol:rho=d/1e4=0.00685561 (1/nm) ^2  
6.sol:rho=d/1e4=0.0068558 (1/nm) ^2  
7.sol:rho=d/1e4=0.0067759 (1/nm) ^2  
8.sol:rho=d/1e4=0.00677664 (1/nm) ^2  
9.sol:rho=d/1e4=0.00677638 (1/nm) ^2  
10.sol:rho=d/1e4=0.00677656 (1/nm) ^2
```

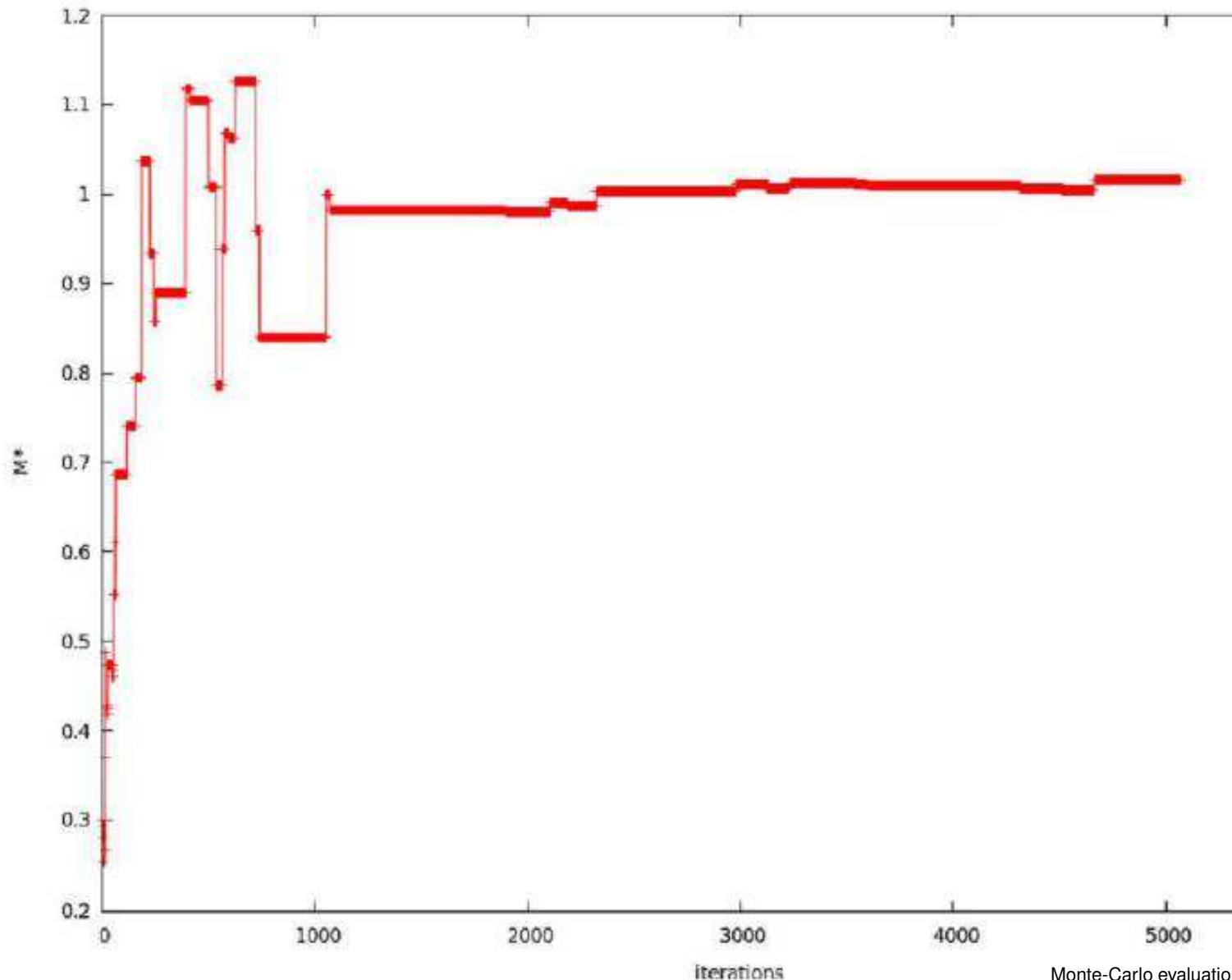
MC method: WSSR evolution



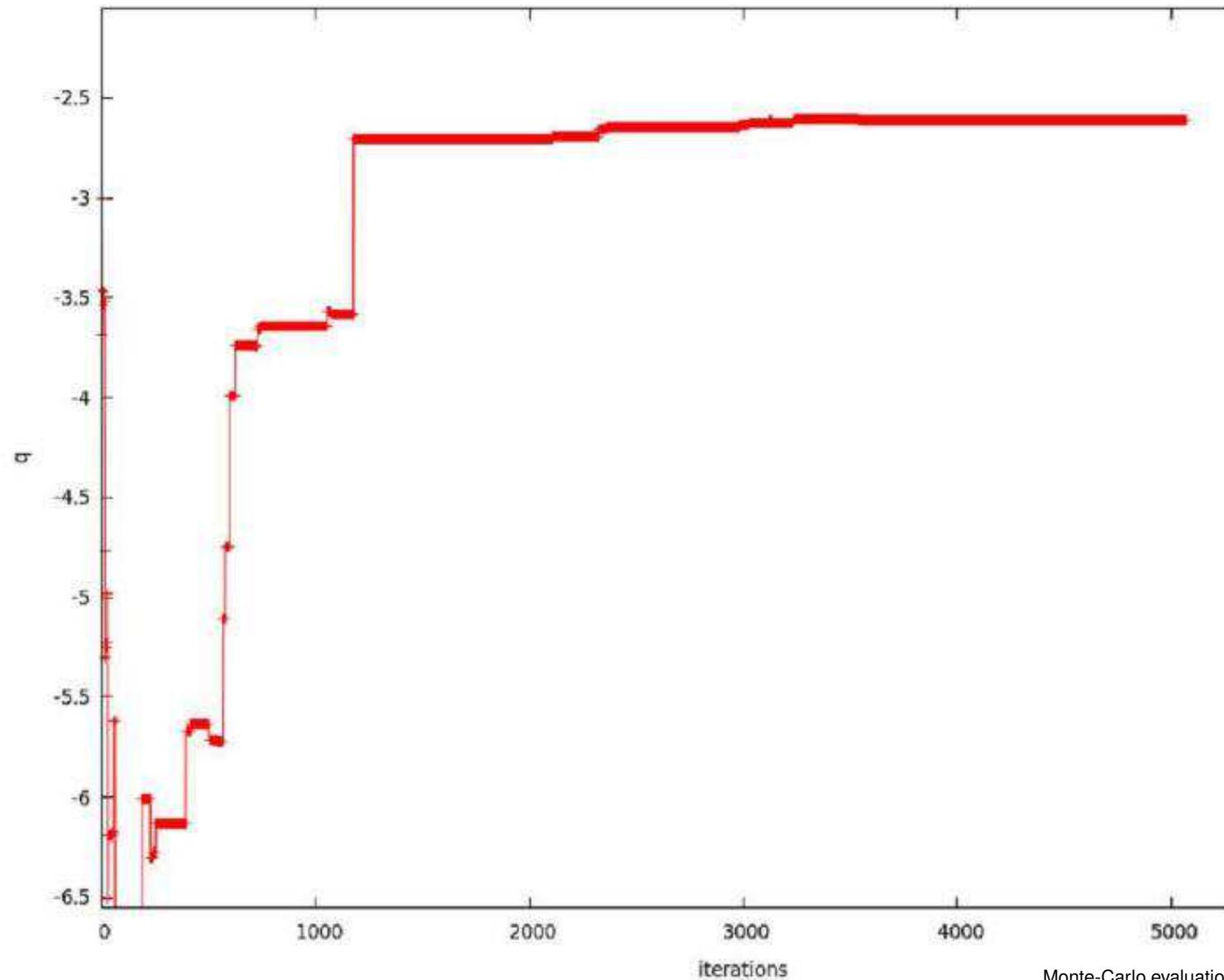
MC method: ρ evolution



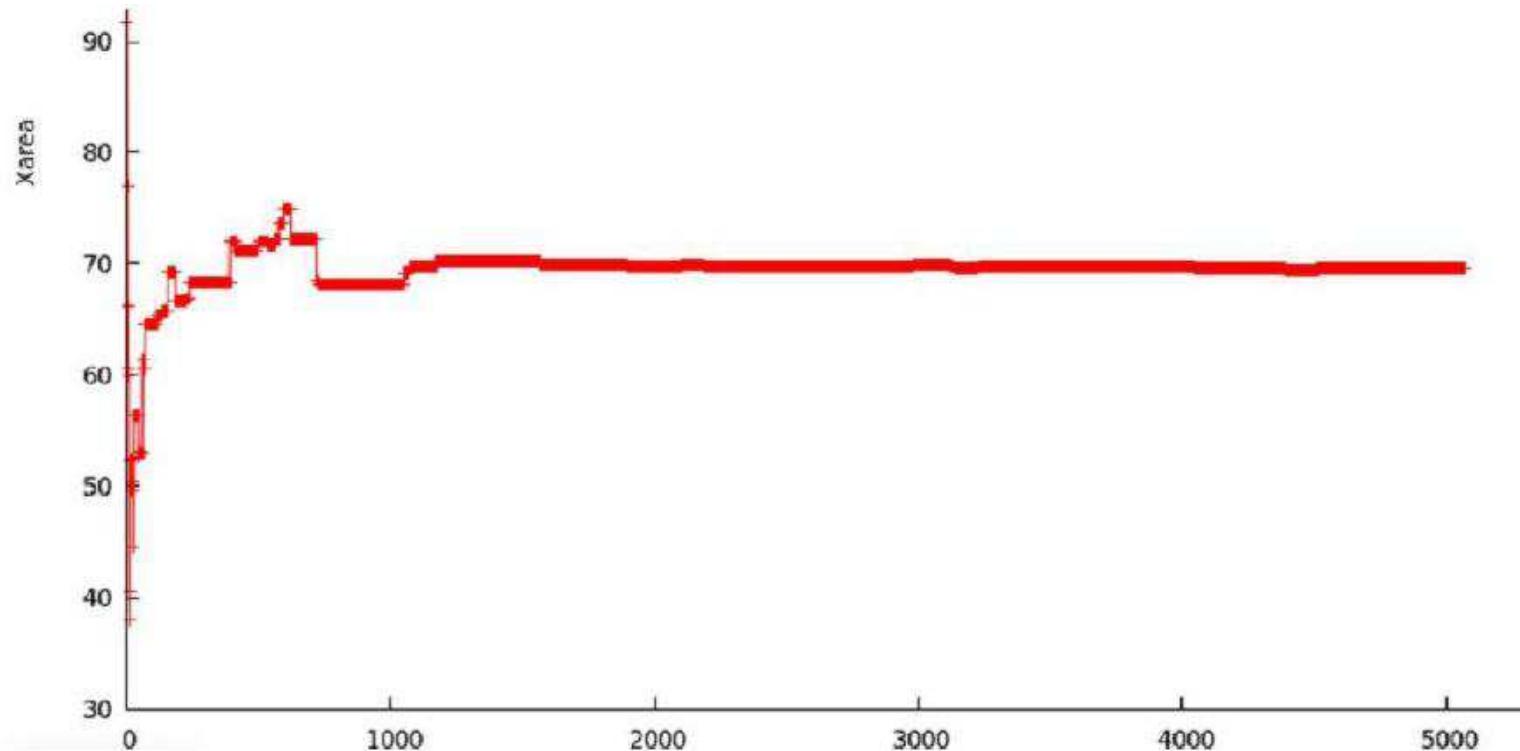
MC method: M^* evolution



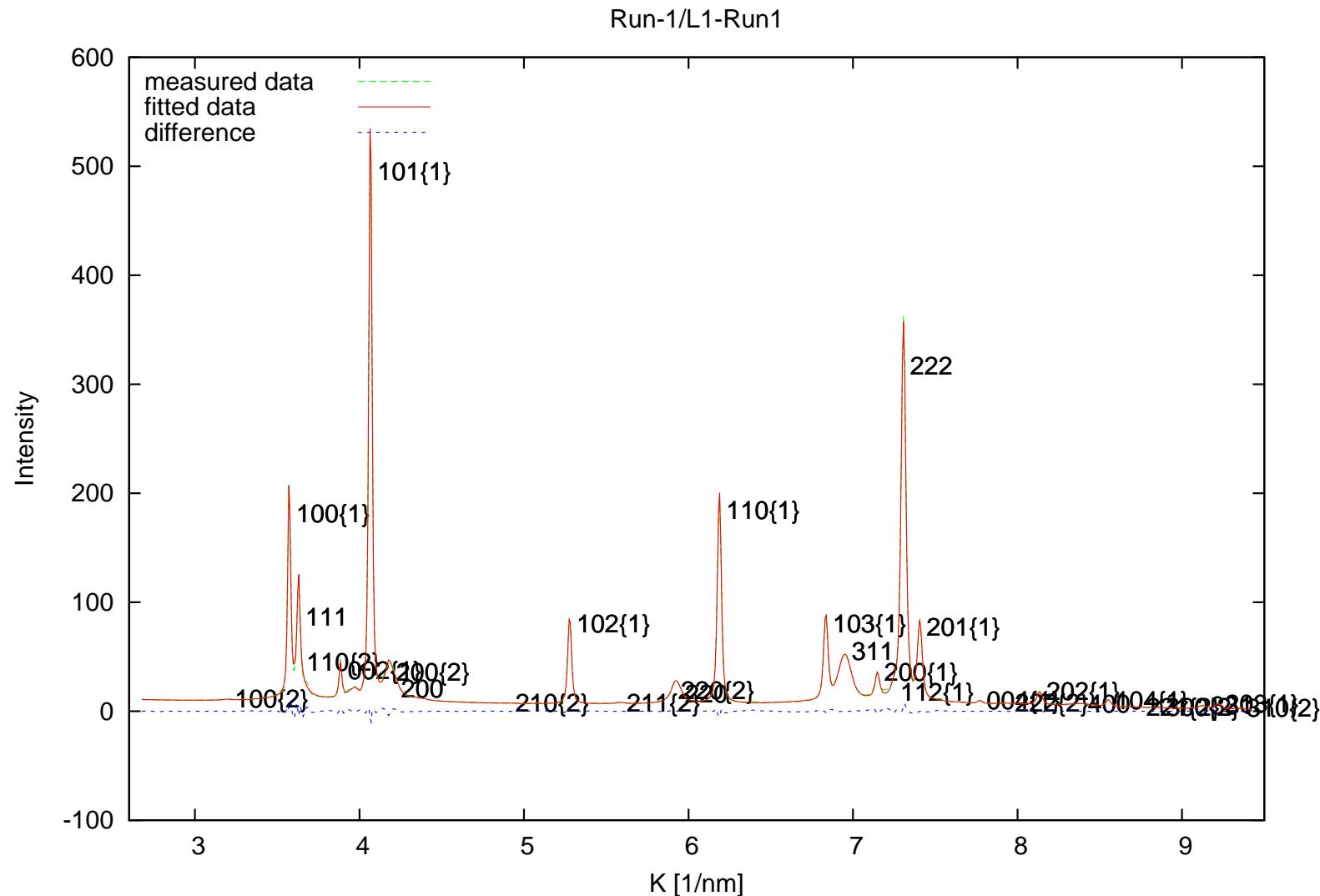
MC method: q evolution



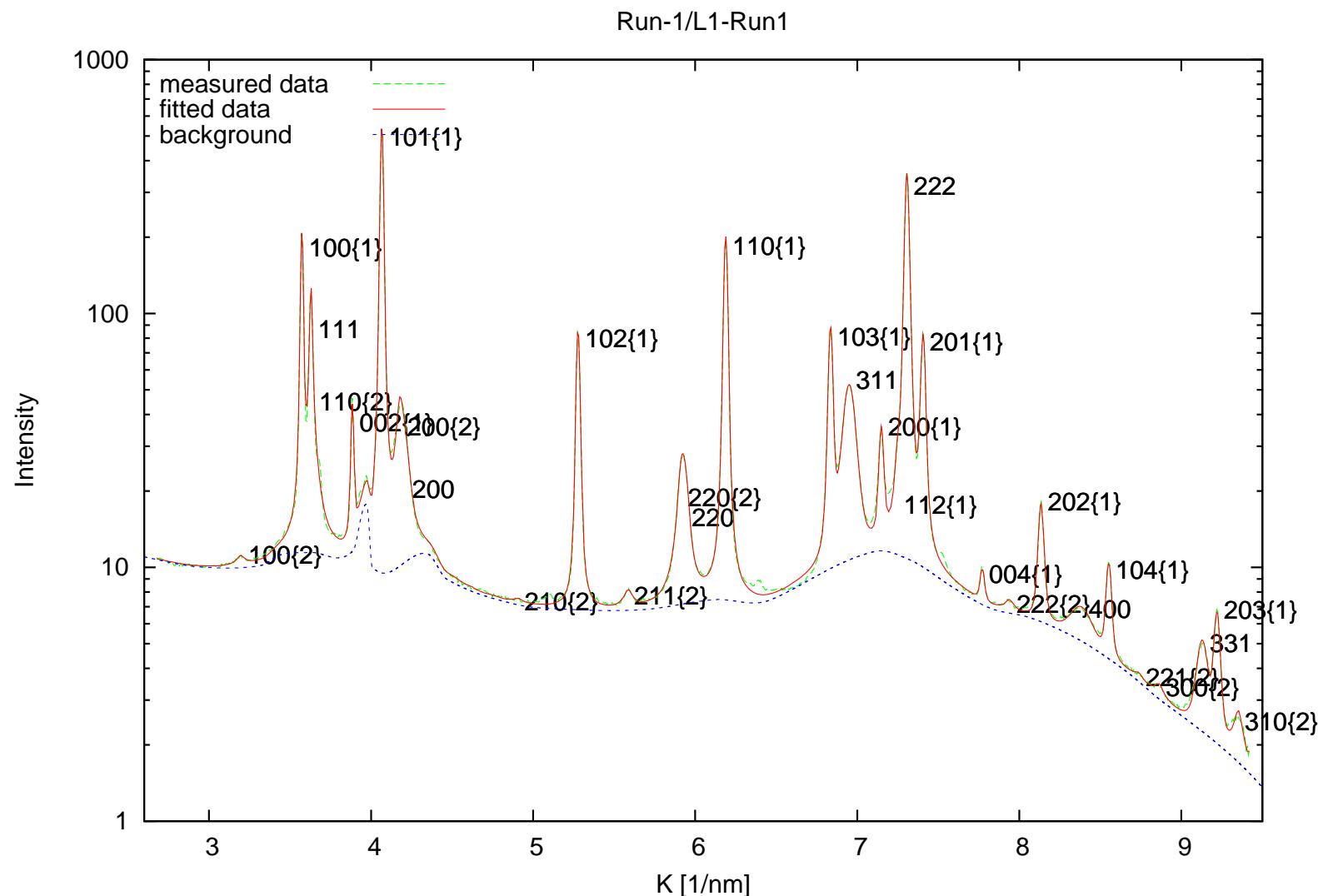
MC method: $\langle x \rangle_a$ evolution



MC fitting of ZrH samples



MC fitting of ZrH samples



Thank you for your attention!

