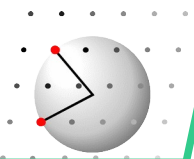
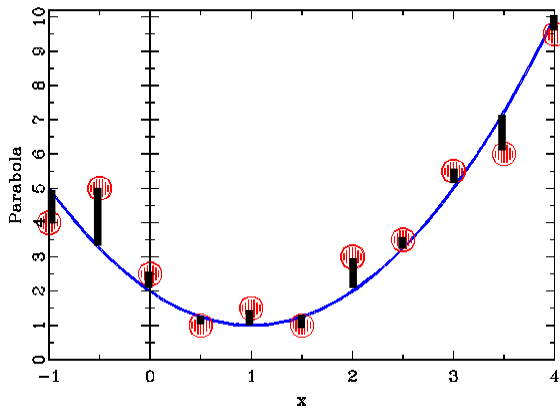


tutorial session VII

refinement





● experimental data

Model: $y = a x^2 + b x + c$

what are **best** a , b , c ?

smallest deviations between data and model

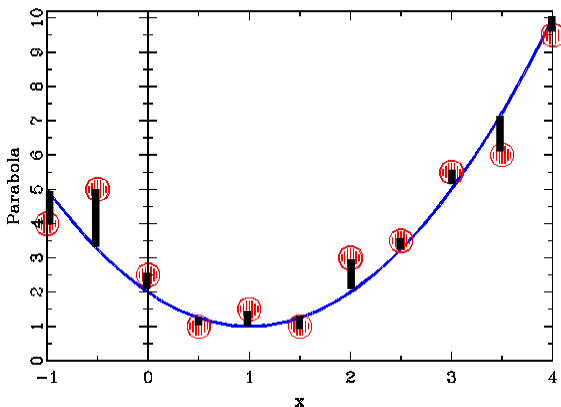
$$R_w = \sqrt{\frac{\sum_j w_j (y_{j,obs} - y_{j,calc})^2}{\sum_j w_j y_{j,obs}^2}}$$

weighted Residual

$y_{j,obs}$ observed values

$y_{j,calc}$ calculated values

w_j weight = $1/\sigma_j^2$



● experimental data

Model: $y = a x^2 + b x + c$

what are **best** a , b , c ?

least squares fit start with estimates a , b , c

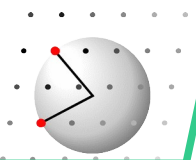
calculate derivatives:

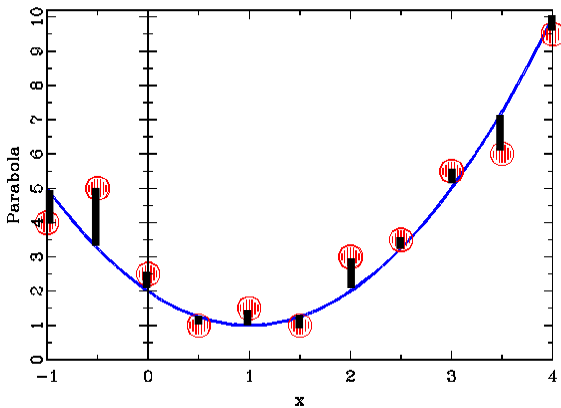
$$\left\{ \begin{array}{l} \partial y / \partial a = x^2 \\ \partial y / \partial b = x \\ \partial y / \partial c = 1 \end{array} \right.$$

obtain better estimates of a , b , c

derive lattice constants, atom positions ...

powder pattern calculated
analytically ==> Rietveld





● experimental data

Model: $y = a x^2 + b x + c$

what are **best** a , b , c ?

Monte Carlo techniques simulated annealing Reverse Monte Carlo

start with estimates a , b , c

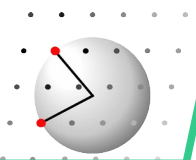
“randomly” vary a , b , c until a good fit
is obtained

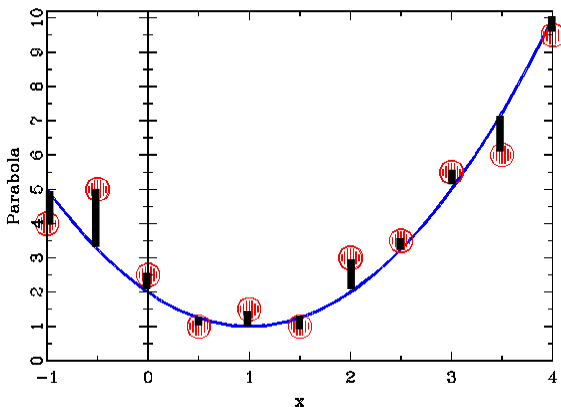
create list of atom positions

“randomly” modify atom positions within crystal

shift atoms, switch two atoms ...

refine by comparing
calculated powder pattern
to experimental pattern





● experimental data

Model: $y = a x^2 + b x + c$

what are **best** a, b, c ?

Genetic Algorithms Evolutionary Algorithms

start with **N sets** of estimates a, b, c ; calculate R

derive M ($M \geq N$) new sets of parameters a, b, c

compare fit of new sets to old sets

keep better parameter sets

create parameter sets: lattice constants, atom positions, defects...

build crystal

refine by comparing
calculated powder pattern
to experimental pattern



least squares fit

requires analytical derivable expression

$I(\mathbf{h}) = G(a, b, c, \alpha, \beta, \gamma, r_j, B_j, N_j, \text{strain, size, profile})$

fastest algorithm

defects, very small size difficult

Monte Carlo techniques simulated annealing Reverse Monte Carlo

slow algorithm

requires modification of an existing crystal

structural parameters derived from model

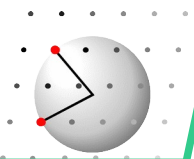
Genetic Algorithms

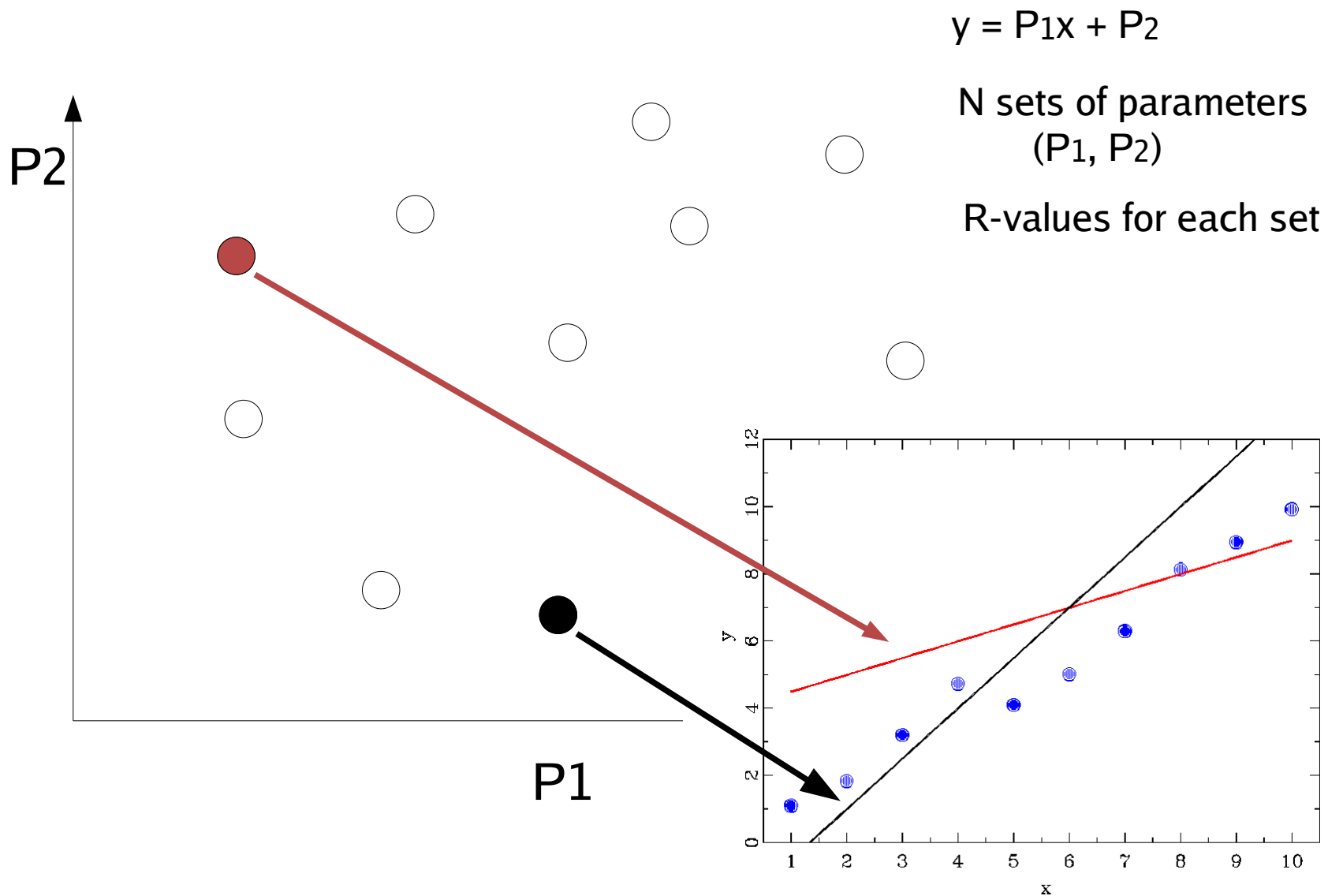
slow algorithm

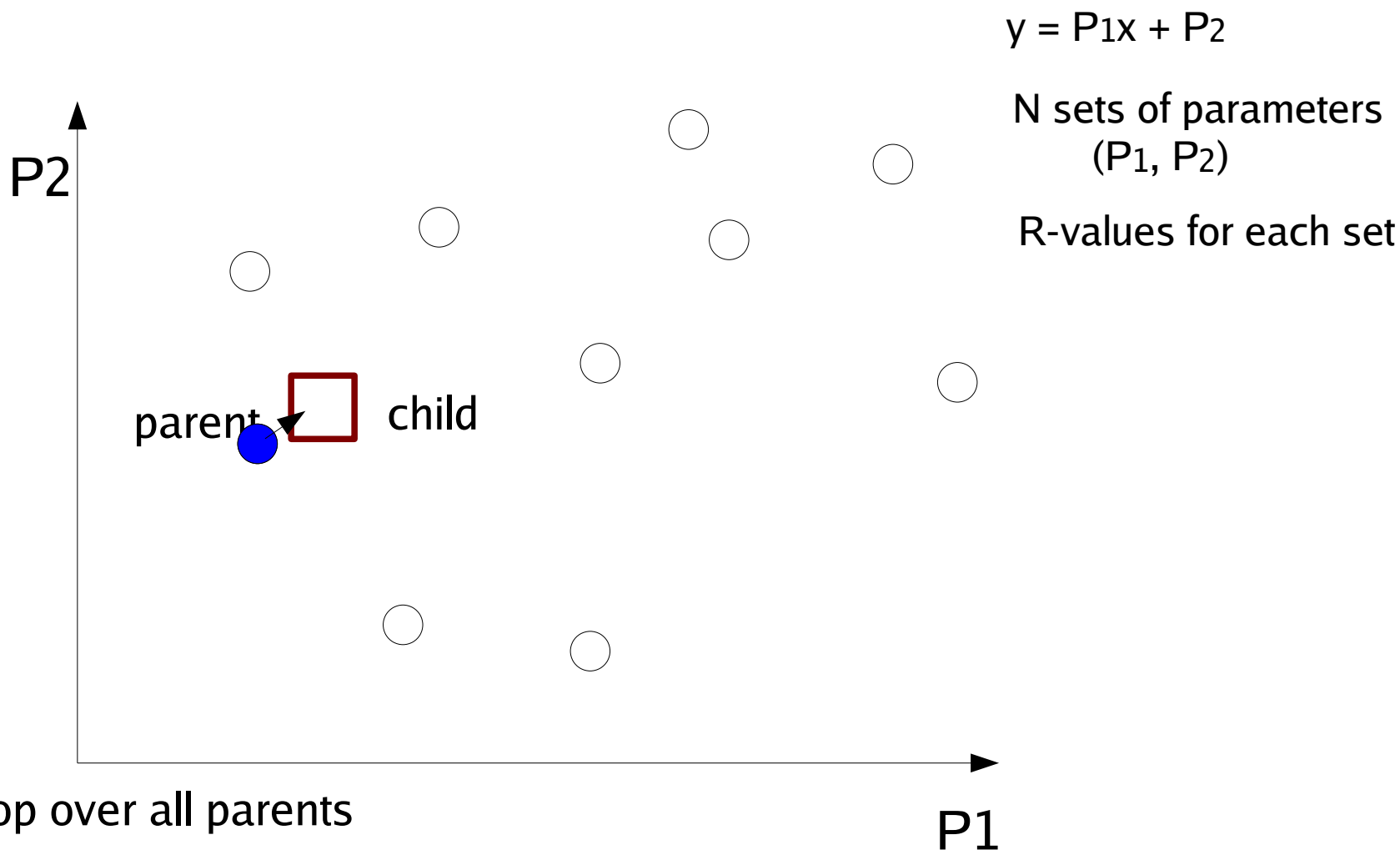
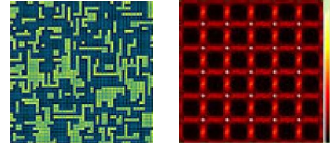
Evolutionary Algorithms

model derived from structural parameters

rough concept must exist



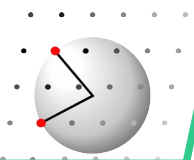


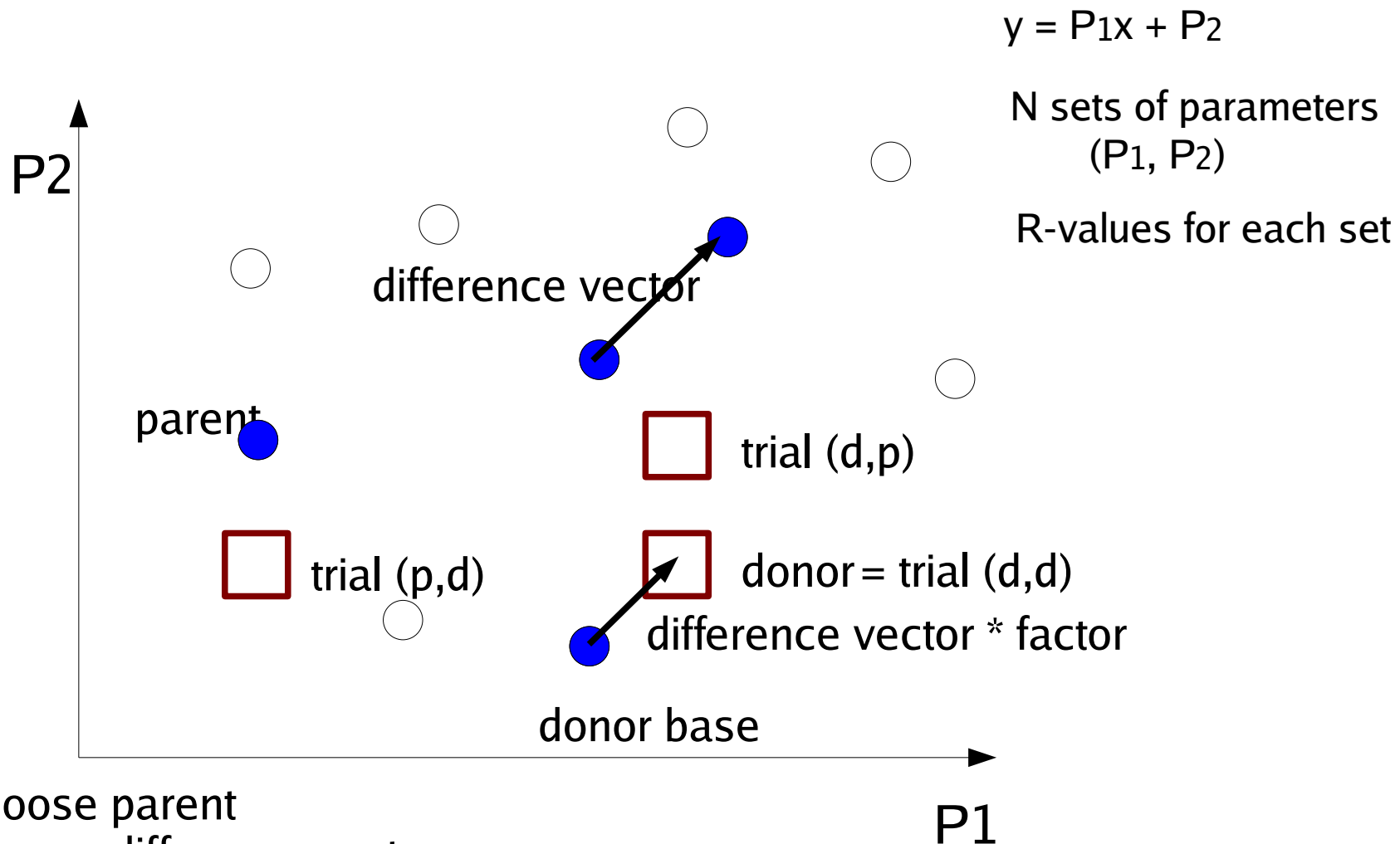


loop over all parents

“randomly” modify parameter values

compute cost function for all children, keep better of parent(s)/child(ren)





choose parent
 choose difference vector
 add to donor base to get donor
 cross-over between parent and donor

generic refinement program; part of discus_suite

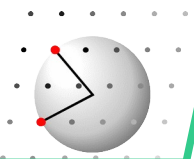
identical command language as DISCUS/KUPLOT

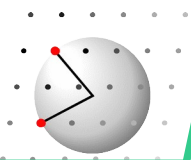
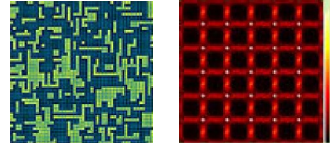
initialization commands

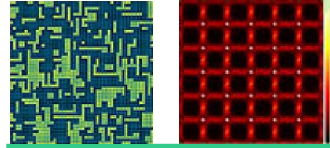
loop

system external calculation

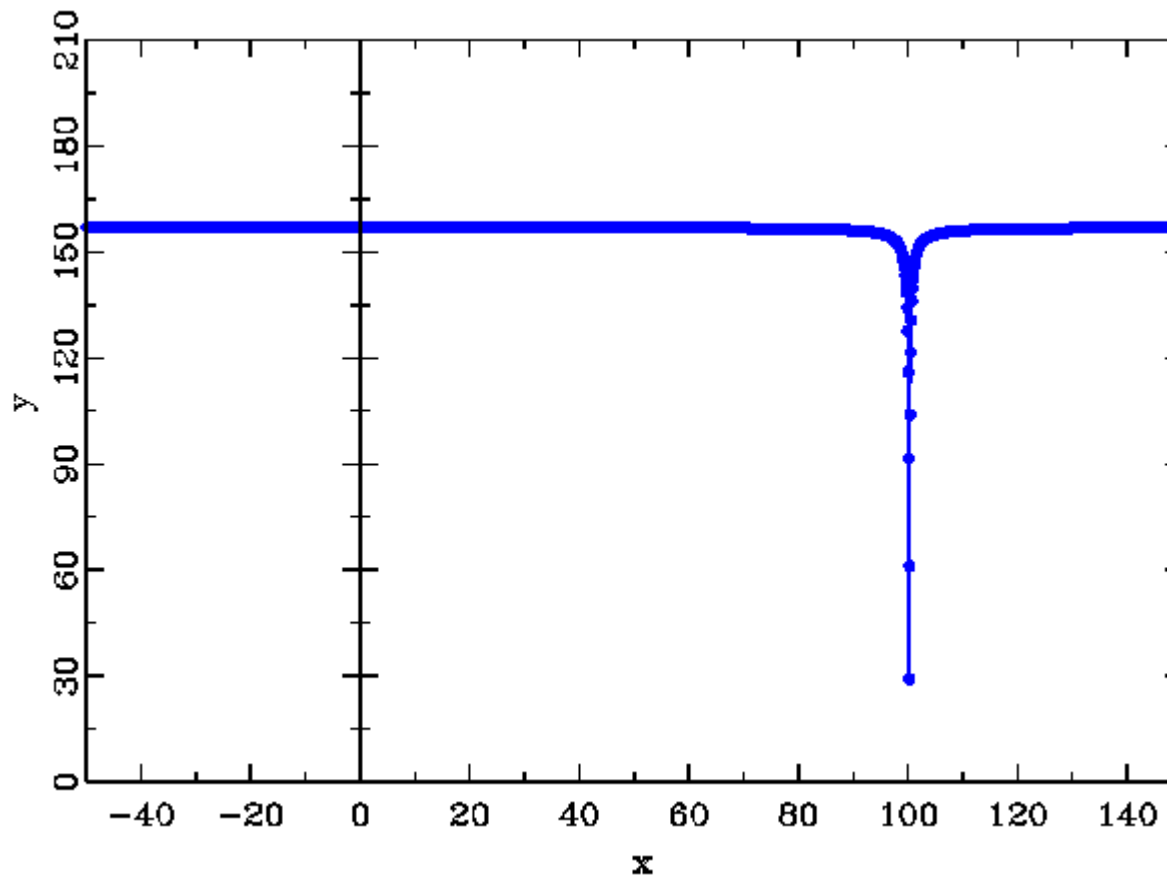
compare



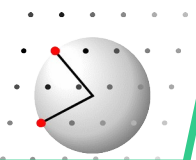


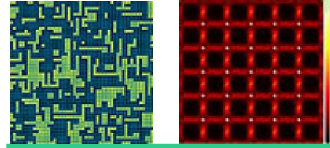


1. Example

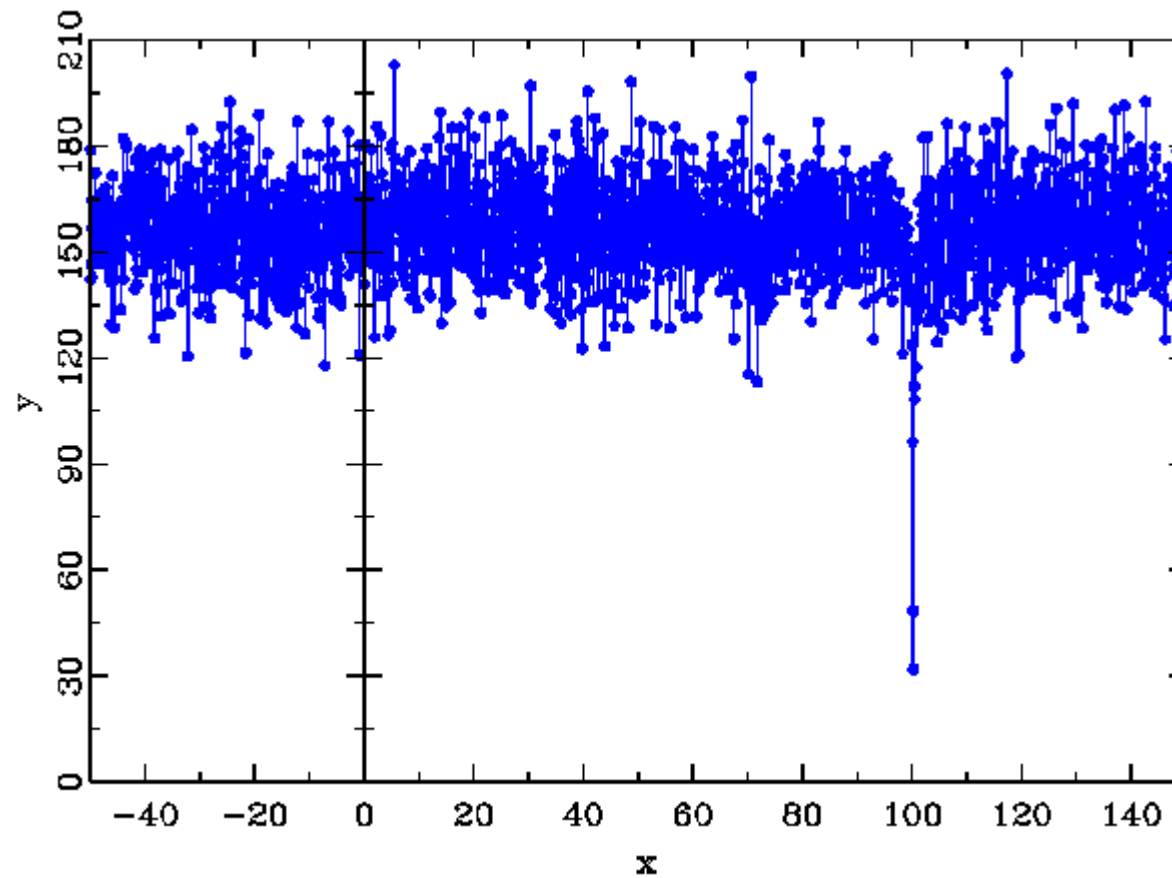


$$100 * \arctan \left(\frac{|x - 100.23|}{0.05} \right)$$

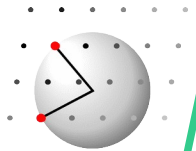




1. Example noisy data



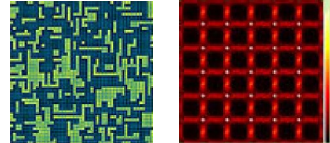
$$100 * \arctan \left(\frac{|x - 100.23|}{0.05} \right)$$





GENERATION	fixed filename, contains current generation number, refinement size
DIFFEV/Parameter.*	contains the complete refinement history,
DIFFEV/Parameter.Rvalue	Development of R-value
DIFFEV/Parameter.P_length	Development of Parameter named P_length path/name is set by user, extension fixed
DIFFEV/Summary.Rvalue	contains a refinement summary, Development of R-value
DIFFEV/Summary.P_length	Development of Parameter named P_length path/name is set by user, extension fixed





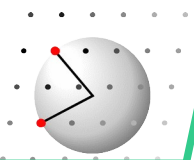
kpara Rvalue plots changes of parameters 0 to... as function of refinement cycle

parameter Rvalue
or actual parameter names

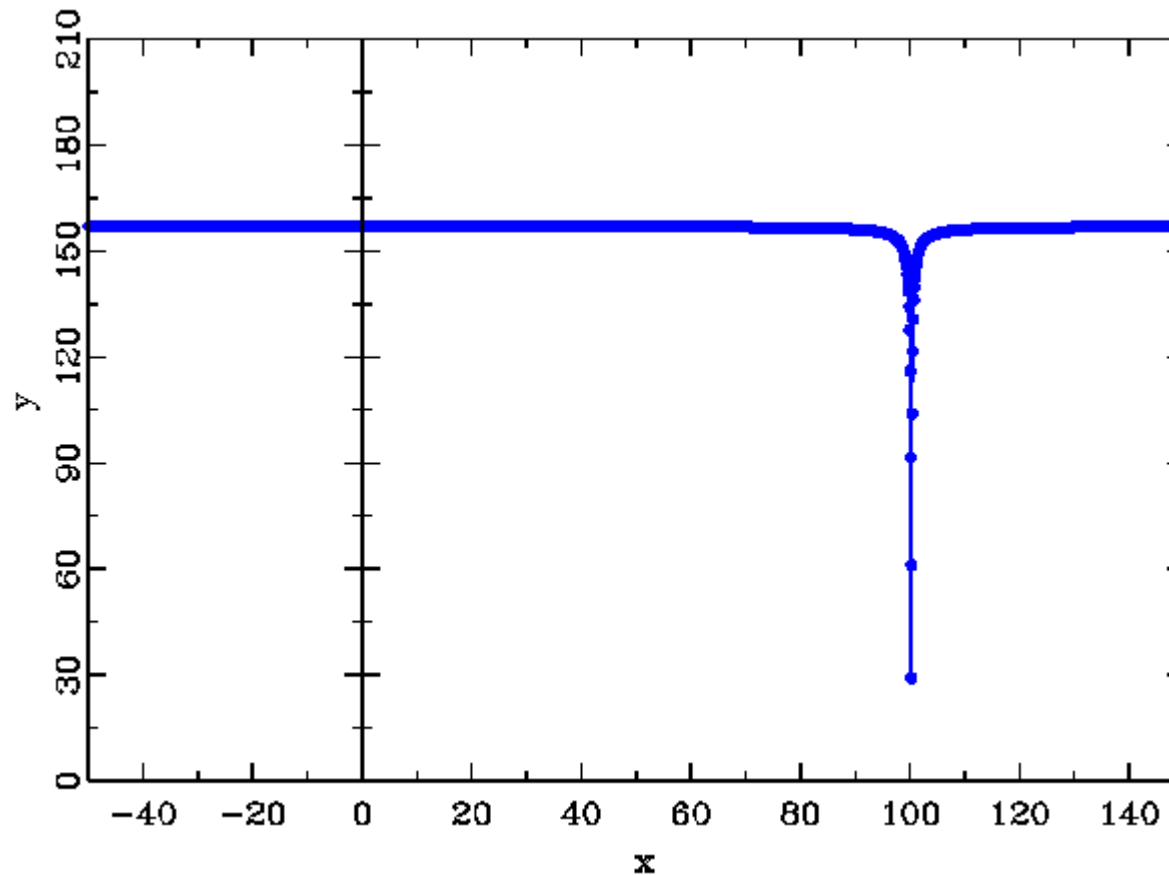
@ksingle.mac 1 plots the current best match to the data; or the 2nd ...

kpar_par -1,1,0 plots parameters 1 versus R-value for the current generation

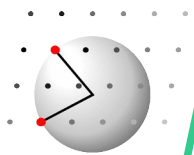
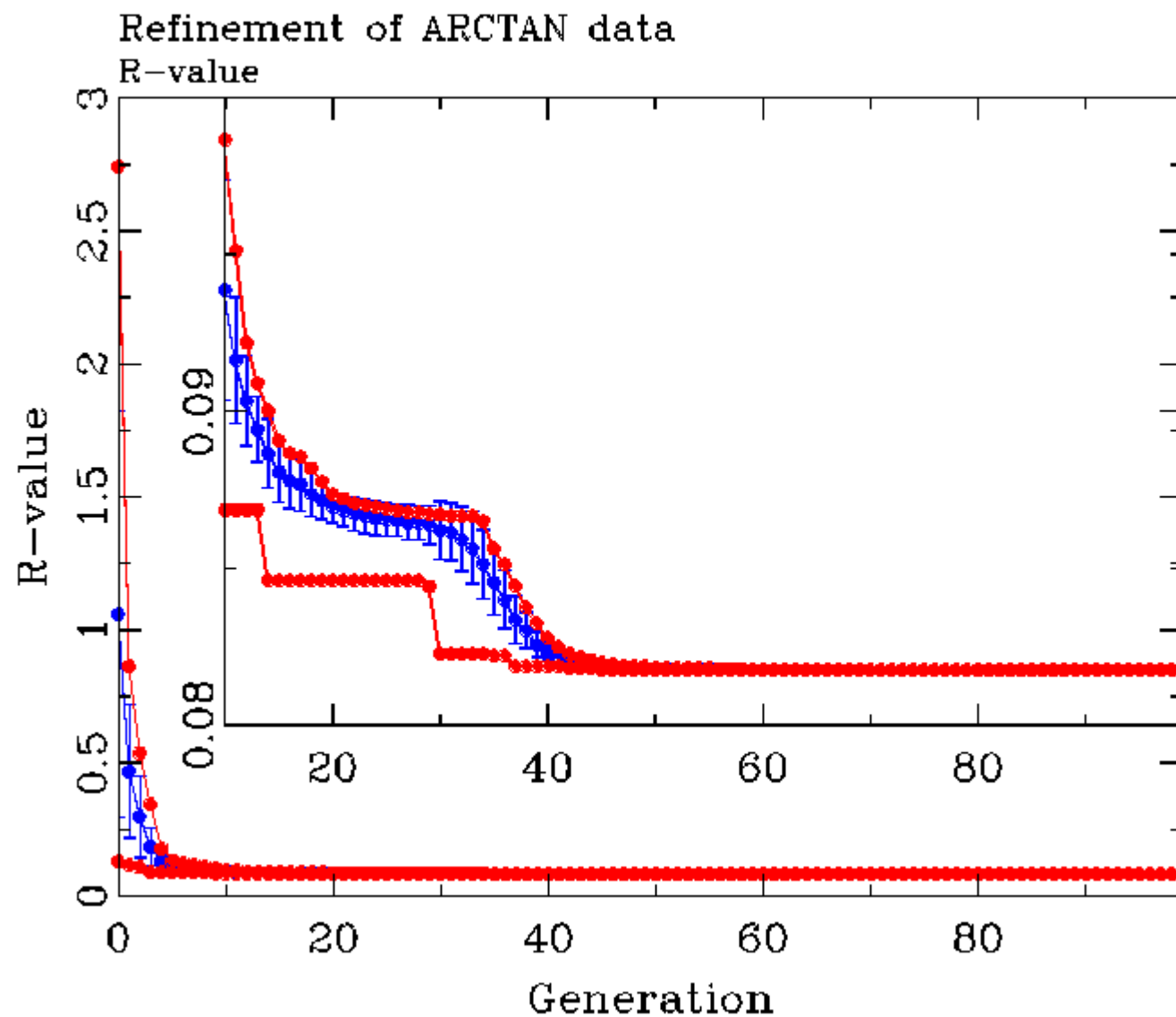
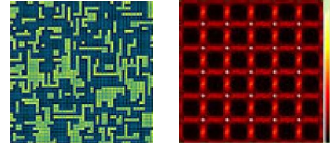
1st argument: generation number -1 for latest
2nd argument: parameter name along y-axis
3rd argument: parameter name along x-axis
0 = R-value
1,... actual parameter names
-1 = number of the child in the population

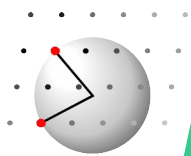
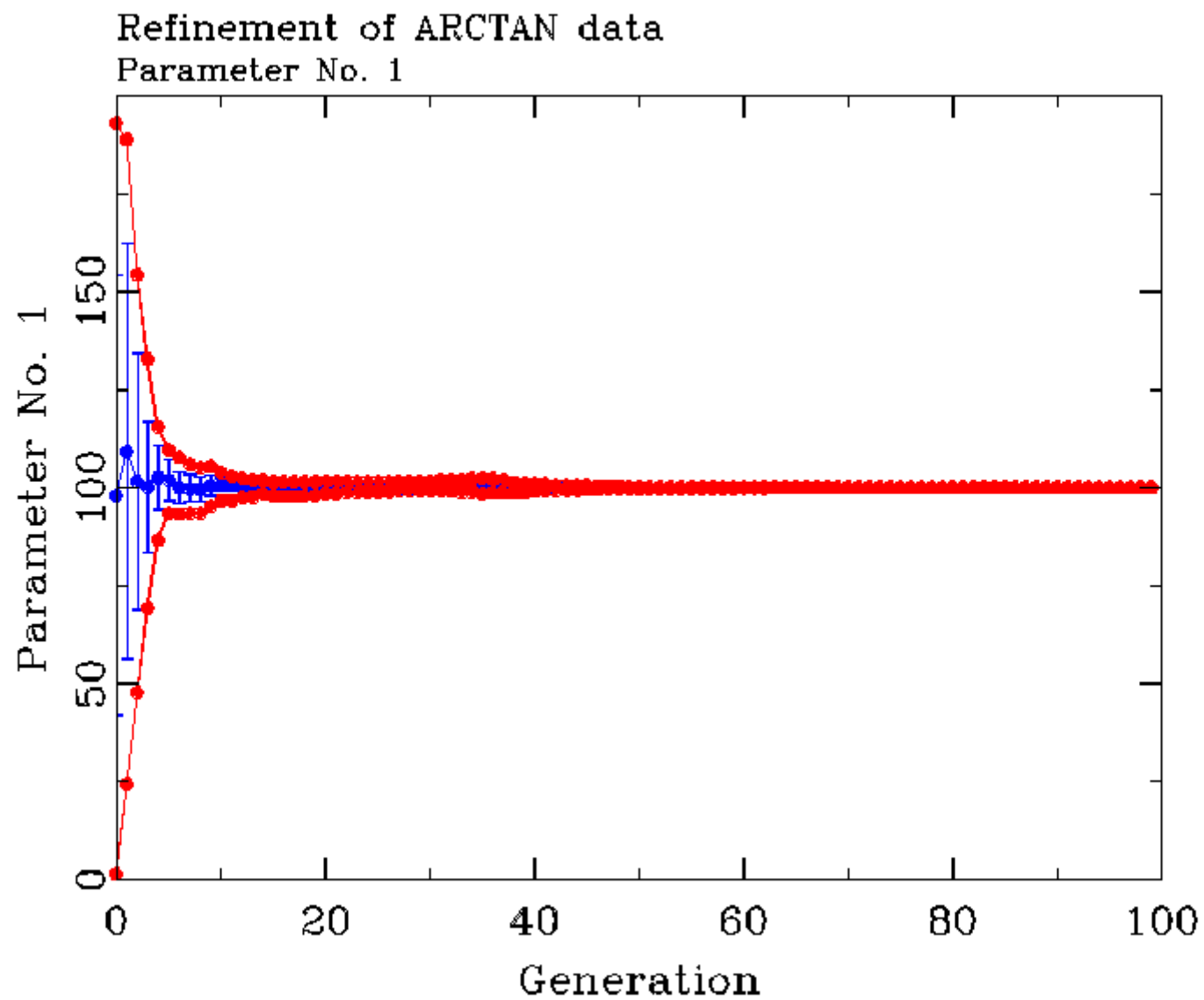
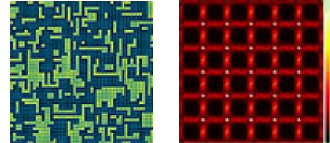


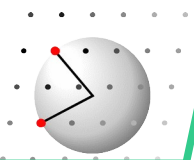
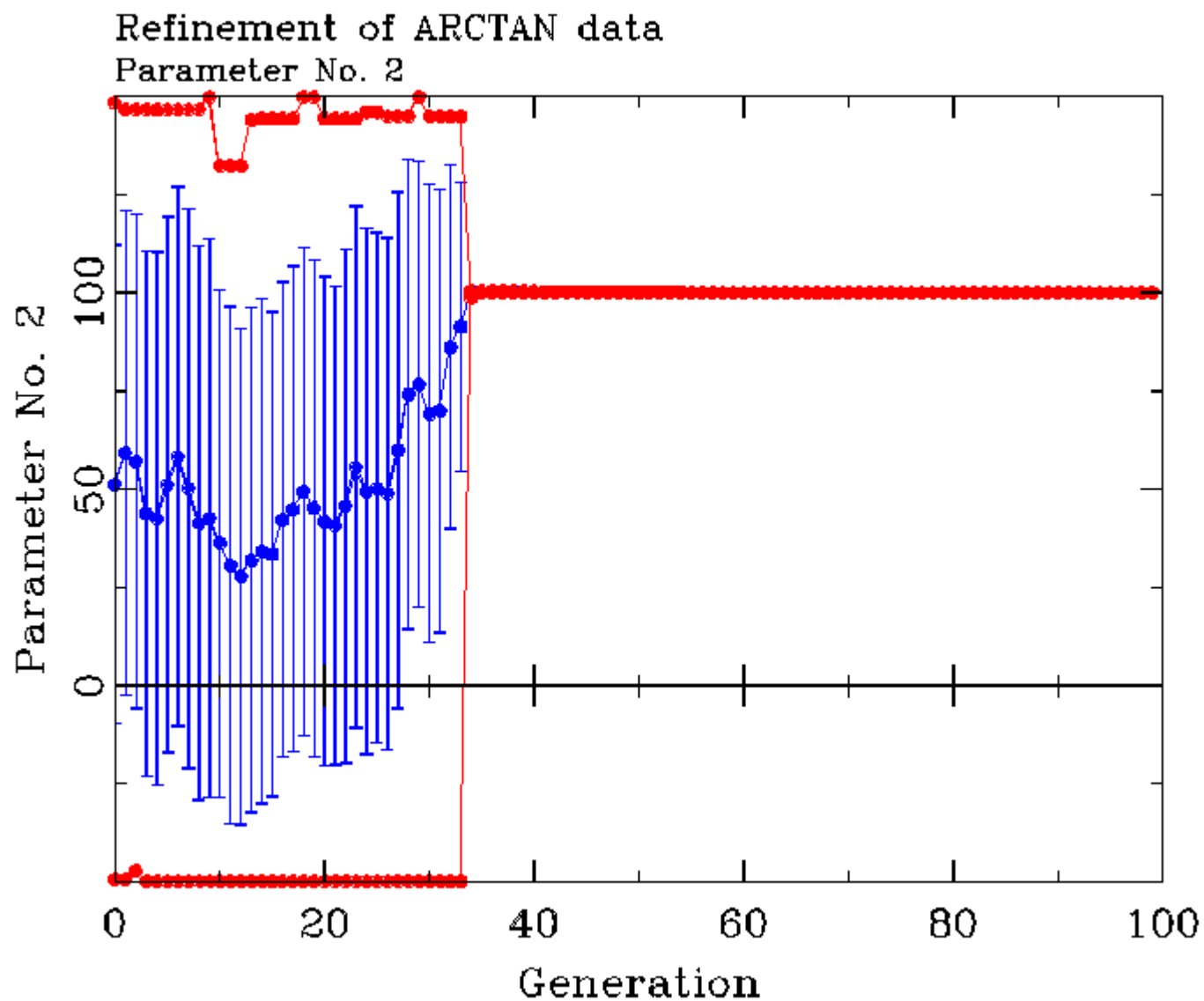
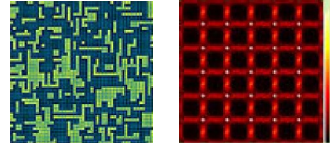
Sample function

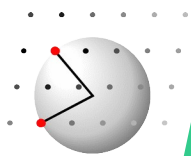
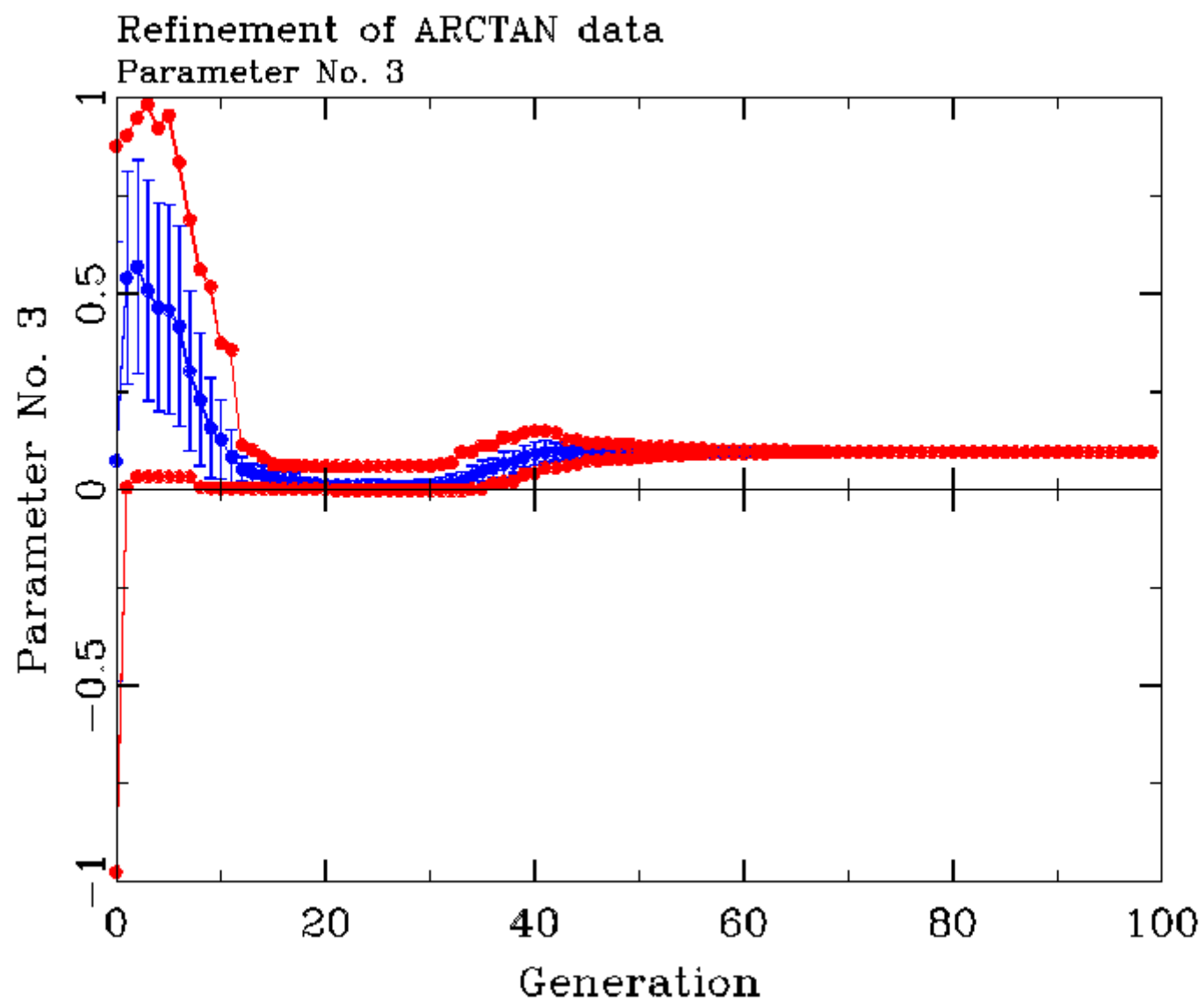
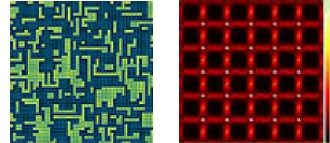


$$150 * \arctan \left(\frac{|x - 100.23|}{0.05} \right)$$

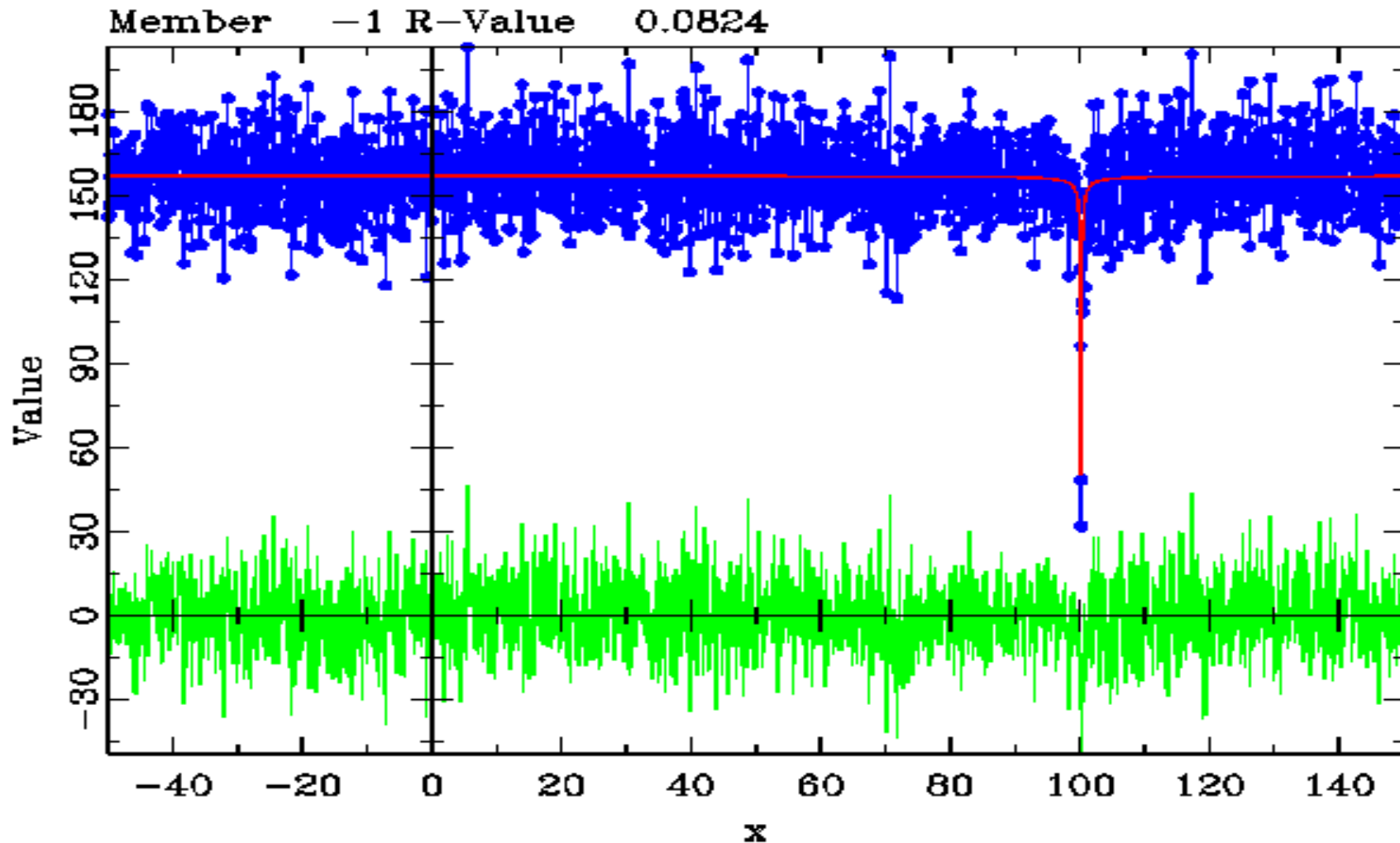








Sample function



$$99.93 * \arctan \left(\frac{|x - 100.23|}{0.049} \right)$$

