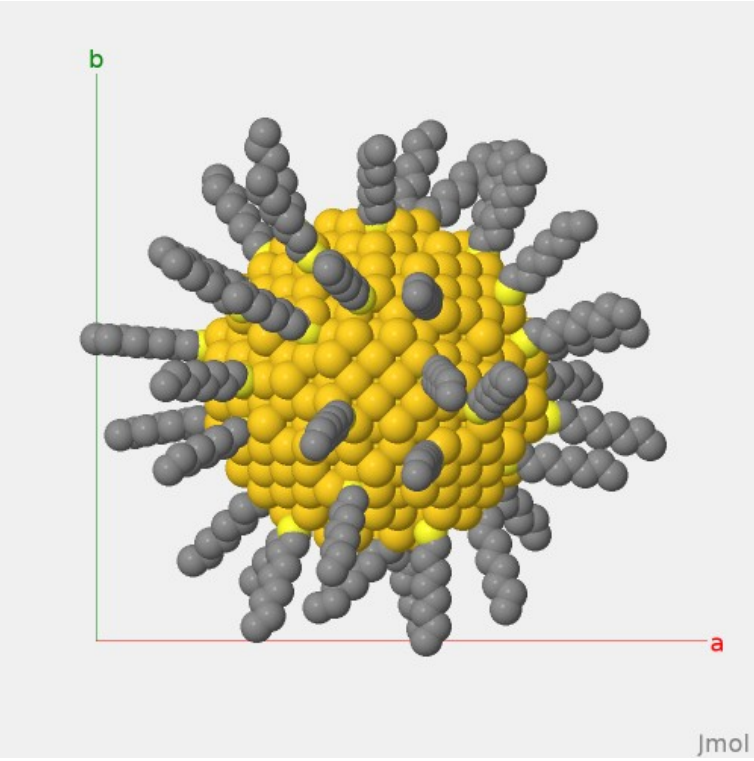
Friedrich-Alexander-Universität
Naturwissenschaftliche Fakultät

DISCUS Workshop
Refining a Nanoparticle with Least Squares Algorithm

Reinhard B. Neder
Crystallography and Structural Physics
Friedrich-Alexander-Universität Erlangen-Nürnberg

reinhard.neder@fau.de

Refining a Nanoparticle



Goal:

Refine Size/shape of ellipsoidal Gold nanoparticle decorated with a simple ligand

Basic Info:

Input data

Refinement parameters

A quick demonstration

Refining a Nanoparticle

Open in Windows Explorer: Lectures\07_Refinement\REFINE_ELLIPSOID

Start DISCUS_SUITE

You should see:

...
User macros in ...
System macros in ...
Start directory ...

suite >

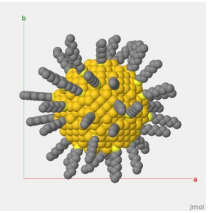
suite > **cd Lectures\07_Refinement\REFINE_ELLIPSOID**

suite > **@refine.mac**

Refining a Nanoparticle

refine.mac

```
refine
data xy, DATA/gold.grobs     ! Refine against these data
```



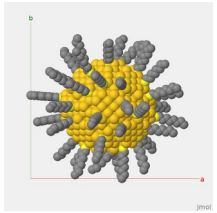
```
#Data in gold.grobs
X   Y   Sigma(x)   sigma(y)
```

Must be larger than zero!

Refining a Nanoparticle

refine.mac

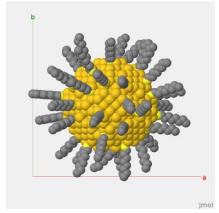
```
refine
data xy, DATA/gold.grobs     ! Refine against these data
#
newparam P_lat     , value:4.0102, range:[3.95,4.20],  &
                     status:free, points:5, shift:0.003
```

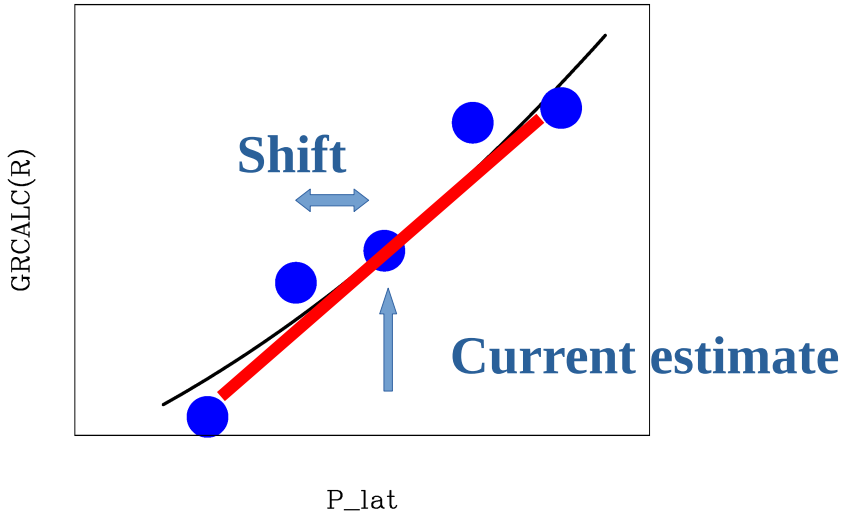


P_lat	Any valid DISCUS variable name	
value:	Initial **value** for this refinement parameter	Required
range:	Upper and lower limit [low , high] [low ,] [, high]	Optional
status:	Refine value or keep it fixed	Defaults to **free**

Refining a Nanoparticle

Least-Squares needs derivatives: $\partial Grcalc / \partial P\_lat = value$





Refine calculates derivatives numerically

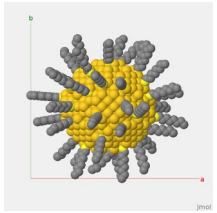
More **points**: better accuracy for derivative; yet more computation time

Larger **shift**: Necessary for parameters that change the function in discreet steps
For continuous parameters, a smaller shift gives better estimate

Refining a Nanoparticle

refine.mac

```
refine
data xy, DATA/gold.grobs     ! Refine against these data
#
newparam P_lat     , value:4.0102, range:[3.95,4.20],  &
                     status:free, points:5, shift:0.003
```

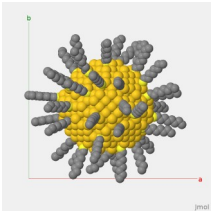


P_lat	Any valid DISCUS variable name	
value:	Initial **value** for this refinement parameter	Required
range:	Upper and lower limit [low , high] [low ,] [, high]	Optional
status:	Refine value or keep it fixed	Defaults to **free**
points:	number of points for derivative	Defaults to **3**
shift:	Relative parameter change	Defaults to **0.003**

Refining a Nanoparticle

refine.mac

```
refine
data xy, DATA/gold.grobs     ! Refine against these data
#
newparam P_lat     , value:4.0102, range:[3.95,4.20],  &
                status:free, points:5, shift:0.003
#
set cycle,  25              ! Maximum cycle number
set relax, start, 2.000 ! Start value for Lambda parameter
```

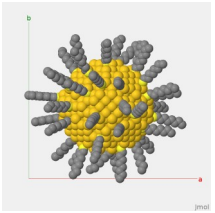


relax: Control how much a parameter is changed from cycle to cycle
Large LAMBDA => small changes

Refining a Nanoparticle

refine.mac

```
refine
data xy, DATA/gold.grobs     ! Refine against these data
#
newparam P_lat     , value:4.0102, range:[3.95,4.20],  &
                status:free, points:5, shift:0.003
#
set cycle,  25              ! Maximum cycle number
set relax, start, 2.000 ! Start value for Lambda parameter
#
set conver, dchi:0.5, pshift:0.005, conf:0.90, chisq:1.1
#set conver, status:off
```



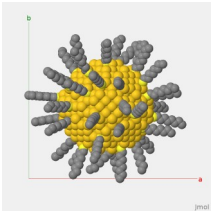
convergence: Control termination criteria converged if:

- **dchi**: If chi^2 changes by less
- **pshift**: If largest relative parameter change is less
- **conf**: If confidence number is larger
- **chisq**: If chi^2 is less

Refining a Nanoparticle

refine.mac

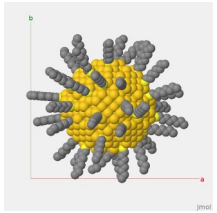
```
refine
data xy, DATA/gold.grobs    ! Refine against these data
newparam P_lat     , value:4.0102, range:[3.95,4.20],  &
                status:free, points:5, shift:0.003
set cycle,  25             ! Maximum cycle number
set relax, start, 2.000 ! Start value for Lambda parameter
set conver, dchi:0.5, pshift:0.005, conf:0.90, chisq:1.1
#
run discus_main.mac, plot:k_inter.mac
```



run: start calculation, use macro *discus_main.mac* to calculate
optionally show current status with plot macro k_inter.mac

Refining a Nanoparticle

discus_main.mac



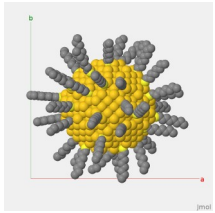
```
branch discus          ! 1st line must branch
#
calc_calc_calc         ! calculate desired function
#
branch kuplot          ! Sidestep into kuplot
load xy, CALC/gold.grcalc  ! Make sure calculated function is
#                          ! last data set
exit                   ! back to DISCUS
exit                   ! BACK TO REFINE
finished               ! Special REFINE command to indicate End of
```

Slave macro must start with a branch.
Last data set in kuplot must be the calculated function.
Exit back to refine.
The **finished** command indicates to refine that this is the end of the slave macro

Refining a Nanoparticle

k_inter.mac

```
reset                          ! We are in kuplot already
load xy, DATA/gold.grobs       ! Original data
load xy, CALC/gold.grcalc      ! Calculated function
kcal sub, 1, 2                 ! Difference Obs-Calc
r[0]= min(-1,nint(min(ymin[1],ymin[2]) - ymax[3]))
ccal add, wy, 3, r[0]          ! Shift difference curve down
scale xmin[1], xmax[1], ymin[3]*1.025, max(ymax[1],ymax[2])*1.025
mark 5, 5                      ! Scale section and place markers
lcol 3, black                  ! Difference curve in black
plot                           ! Display actual graph
rval 1, 2, dat                 ! Display R-value
exit                           ! Back to refine
```



Plot macro automatically starts within kuplot.
May do a reset within kuplot.
Exit back to refine.

Refining a Nanoparticle

Open in Windows Explorer: Lectures\
07_Refinement\
REFINE_ELLIPSOID

Start DISCUS_SUITE

You should see:

...
User macros in ...
System macros in ...
Start directory ...

suite >

suite > **cd Lectures\07_Refinement\REFINE_ELLIPSOID**

suite > **@refine.mac**

Try with : different start values
small values for shift => cover, diameter

Refining a Nanoparticle