Report of summer student program from 25.7.2007 to 18.09.2007

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Contents

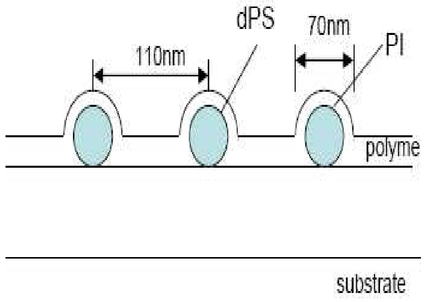

Figure 1: schematic structure of polymer

1 Introduction

During the summer student program at DESY I was assigned to the workgroup of Stephan Roth. In the 2 month of the program it was my task to analyze data of a GiSAXS (Grazing incident small angle x-ray scattering) experiment.
The aim of this experiment was to compare different kind of metal nano-clusters. Copper and gold were evaporated onto a thin film of polymer. The method that was used for the investigation was μGiSAXS (micro Grazing incident small angle x-ray scattering). In particular it was my business to evaluate the data taken from the copper nano-particles.

2 Sample preparation and properties

The samples consist of a gradient with nanometer-sized metal clusters on top of a polymer film. The properties of nanometer-sized particles strongly depends on their size. At length scales larger than the nanometer regime the wavelength of light absorbed by the material and the plasmon-frequency are fixed properties. With decreasing size surface effects begin to rise and could not longer be neglected. At some point the absorption of light is dominated by the plasmon frequency, while the plasmon frequency itself is a function of the size and shape of the nano particles. Additionally a color effect is visible, meaning that the absorbed wavelength also depends on the angle of observation.
This technic for instance is interesting for security features and the production of solar cells. In the application area of security it is essentially to know the shape and size and further more to control the growth of the nano particles, to end up with the possibility to built films of nano particles with very well known properties. Such films could be used as security feature to mark e.g. cash cards. To verify the original you have to know the wavelength absorbed under a certain angle. For copying such a marker you need therefor the information of the clusters properties. In solar cells this technic could be used to achieve a higher absorption. Through the possibly to tune the absorption wavelength a higher

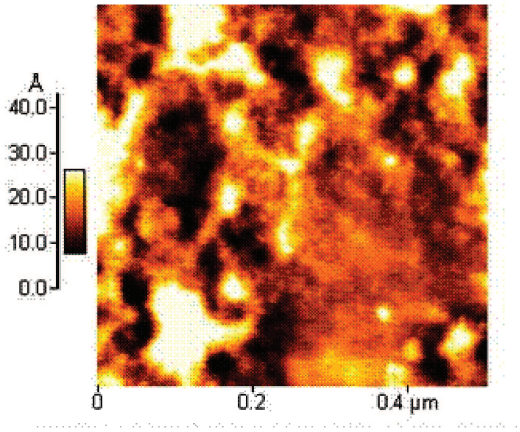

Figure 2: afm picture of the surface of the copper sample

	dPS	PI
M_W	2,3	152
M_W/M_N	1,05	1,04

Table 1: mass prosperities of the polymers in kilo dalton

efficiency can be achieved.
A specific attribute of the sample was the polymer film. This polymer was a blend of deuterised polystyrol (dPS) and polystyrene (PI) with a ratio of $5,5:4,5$. The masses of the polymer are shown in table 1. The polymer was brought on the silicon waver via spin-coating forming a 40nm thick film. Due to the mixture of this polymers the film showed a structure and was not plane. A sketch is seen in figure 1. The surface shows hills with beads of polystyrol covered with a thin polystyrene film. The hills had a diameter of 70nm and a distance of about 110nm.

A block of copper served as base material for the copper clusters, which were brought on to the surface due to thermal evaporation. The block was heated in a vacuum chamber and vapor of copper forms. The copper vapor than settles down on the polymer forming clusters. The gradient was achieved by shadowing one part of the polymer. A afm picture of the sample surface is shown in figure 2. The question in this study was how does metal nano-particles replicates the surface structure of the polymer blend. The analyze of the gold film was done in a former work by Alexey Veligzhanin.

3 μGiSAXS at BW4

GiSAXS (grazing incident small angle x-ray scattering) is a technique which is suited to analyze surface structures as well as buried structures. The sensitivity

for the surface and the buried structures are due to the penetrating of the wave vector component perpendicular to the surface. The wave impinges the sample under a very small angle, lower than the critical angle of the material. The wave penetrates the sample and is thereby scattered lateral before it is reflected.
The scattering process could be understood by the two-phase model. In general small angle scattering is used for samples without a crystalline structure. Because of that the positions of the particles that the incoming wave are scattering are not relevant. Mainly the shape and the electron density are important. So the sample can be divided up to N homogenies particles imbedded in a matrix with a scattering amplitude

$$I(q) = I_O T | \int_{V_S} \sum_j \rho_j(\vec{r}) \exp(-i\vec{q}\vec{r}) d\vec{r}|^2 \frac{d\sigma}{d\Omega_{Thomsen}} \tag{1}$$

(V_S=volumen sample, ρ_j=scatering length density , j= Number of particles)

With the consideration that the matrix and the particles have different density and atomic form factors the result is that the scattering intensity depends on the difference in the spatial electron density fluctuations.

$$I(\vec{q}) \propto N \Delta\rho^2 V^2 |3 \frac{\sin qR - qR\cos(qR)}{(qR)^3}|^2 \tag{2}$$

($\Delta\rho^2$=difference in scattering length density, R= particle radius)

For further explanation see [1].
The interest by GiSAXS experiments lies in the diffuse scattered x-rays in the off specular beam area in regimes of tenth of degrees. The diffuse scattering is due to the roughness of the sample which has its origin in this case mainly through the clusters on top of it. The measurements were done at BW4 of HASYLAB. The gradient was scant in steps of ??? 5nm????. In order to decrease the diameter of the beam to be able to scan the sample a set of beryllium lenses were used focusing the beam down to a size of B=(65 x 35) μm^2. A wavelength of 0,138nm was used and the sample detector distance was 1.955m. A schematic sketch is shown in figure 4. A monochromatic x-ray beam impinges the sample under a small angle and is reflected and scattered. Mostly the diffuse scattered intensity is a much smaller then the directly reflected so that there is a beam stop to be used. In order to protect the detector and also to increase the signal to noise ratio due to an higher acquisition time. For further reference of BW4 see [5]. A typical picture of the scattering pattern is shown in figure 3.
For the analysis two cuts were taken: one in horizontal direction and one in vertical. The so called "detector cut " , vertical direction, gives information about the structure perpendicular to the surface, e.g. the hight of the clusters or the roughness. The horizontal cut called "out of plane cut" gives information about structures in the lateral direction, e.g. distances and diameter of the clusters.

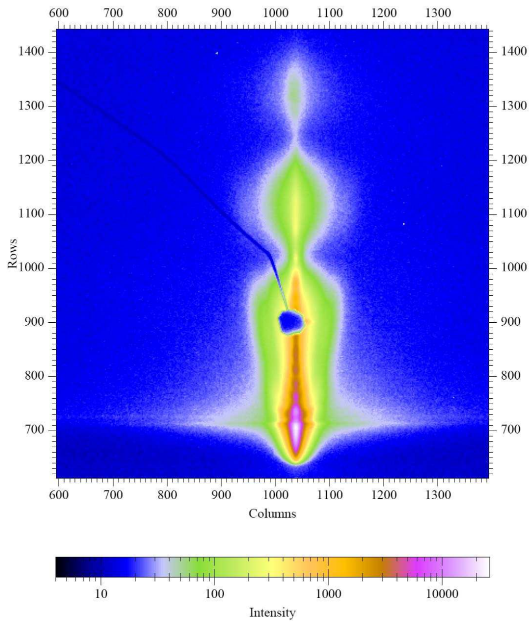

Figure 3: typical scatter pattern

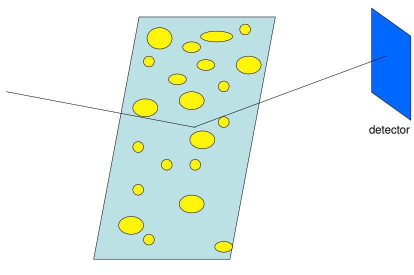

Figure 4: schematic sketch of GiSAXS, incoming beam from the left, the gradient is increasing from the bottom of the sketch to the upper end

4 IsGiSAXS

The program used for data analyzing was IsGiSAXS programmed by Remi Lazzari from the Institute des NanoSciences de Paris. This program is capable of one dimensional as well as two dimensional fitting. The program is was especially developed for GiSAXS to analyze nano-structures on top substrates. This includes islands on surfaces as well as buried structures or e.g. covered spheres. For the numerical calculations the scattering cross section is decomposed in two parts: the form factor of the particle and the interference function. For the size-distance coupling there are different approximations implemented: Decoupling Approximation (DA), local Monodisperse Approximation (LMA) and Size-Spacing Correlation Approximation (SPCA). The form factor for the particles is be given in the distorted wave born approximation (DRAB) and is mainly the fourier transform of the particle shape. The interference function is cable of characterizing uncorrelated particles, a paracrystal with a loss of long range order as well as regular or defective lattices. In the DA approximation it is assumed that the type of scatters and their position is not correlated so that the pair correlation function only depends on relative position of the of the scatters. In the LMA the scattering wight for each molecule is replaced by the mean value over the size distribution. Here it is supposed that the size is only slowly varying across the sample.
In the SPCA, which was used in this analyzes, size dispersed particles are aligned along a paracrystel. The distance d_n with a probability $p(d_n)$ at which a particle is placed thereby depends linearly on the size of two neighboring particles

$$< d_n >= D + \kappa[R_{n-1} + R_n - 2 < R_n >] \tag{3}$$

So the particles are lined up with a distance D on the paracrystal while the parameter κ (size-distance cupeling parameter) is describing the misalignment relatively to particle size.
For the shape of the cluster particles was a cylindric form used. To account for different sized particles a bimodal distribution was fitted. To the cluster structure with the greater radius it will be denoted as particle 1 and to the smaller one to particle 2. For the program are 3 files necessary. The data file (.dat) where the data of the experiment was in. Then input file (.inp) where all values of the parameters for the theoretical curve are to be placed. And at least the fit file (.fit) where IsGiSAXS is told which parameter is to be fitted. A typical input and the header of the data file are in the appendix. Altogether thirteen parameters were fitted. The scaling factor of the curve also as the shift factor, which considers the underground radiation. Then there was the radius of particles fitted and their dispersion of radius. Also the hight and the dispersion of hight was fitted. For the paracrystel the peakposition D and the with W was fitted along with the size distance cupeling parameter κ.

5 Typical proceeding

As starting values for a fit served the values attained by the former fit. Then curve was compared to the new data. Then mostly a new scaling and shifting was done. Afterwards the probability of the two particles was fitted and in the following the radii and hight. The further steps depend on how the fitted curve and the data corresponds. When the loop of the out-plane-cut was not matching the dispersions of the radii were fitted. But then it must be paid attention that the oscillation in the detector-cut are not smeared out if the dispersion get too high. The inclination of the out of plane scan in regime of small q values could be affected by the size distance cupeling parameter κ as well as the strength of the oscillation in the regime of high q values in the detector scan. The grid parameters (D,W) are mostly effecting the loop in the out of plane scan. It could be observed when D gets larger that the inclination flattens as well as hight of the Yoneda-peak is affected. Also during fitting the scaling parameters must ne adjusted. Partially it happened that one parameter, especially the grid parameters (D,W), were divagating, after the adjustment of the scaling this behavior was corrected and they were convergent. It could also observed that mostly the value of w was larger than the distance D, what makes no sense, this could be fixed through increasing the scaling factor. The scaling factor had therefor also an big influence on the dispersion of the radius σ_r. So at the beginning it looked as if the scaling factor was a relatively uncritical parameter it showed up that it has a great import influence on the fitting.
A general procedure was not established because of a strong interference of the parameters so every time it depend on the graph was would be the next step. In some cases the fitted curve with new parameters had a worse correspondence so old values had to be kept. Also there could sometime no progress be observed so values had to be changed by hand. Then mostly in one of the cuts there was a better correspondence to experimental data. Then this value was kept fix and it was tried to get a better achievement due fitting a connected parameter.
In the fits done by me the dispersion of hight was always kept fix to a value of 10^{-4} because with a greater value the oscillations in the detector cut at high q values were smeared out. And fitting of this parameters was not successful.

6 Outcomes

Altogether 5 fits could be done successfully. The evaluated radii and distances are shown in the figures 5 and 6. The gradient decreases with increasing number of layer. The distances of the particles were calculated with the approximation

$$d = D + 2 \cdot \kappa \cdot R \tag{4}$$

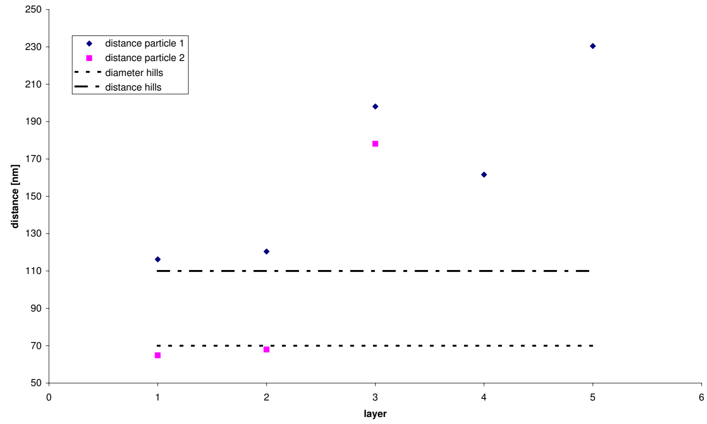

Figure 5: distances of the particles with plotted distances and diameter of the polymer hills

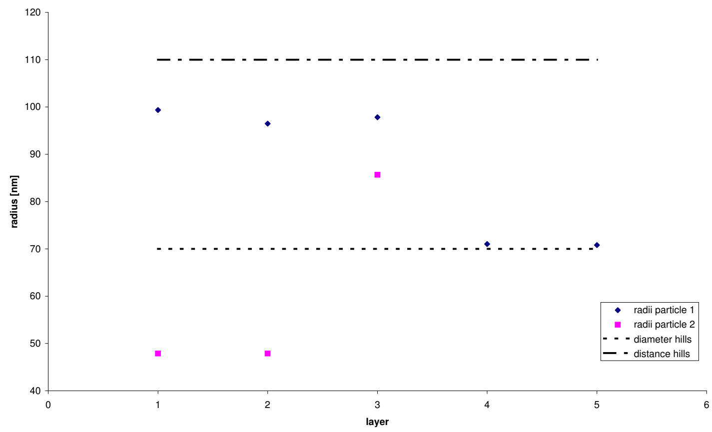

Figure 6: radii of the particles with plotted distances and diameter of the polymer hills

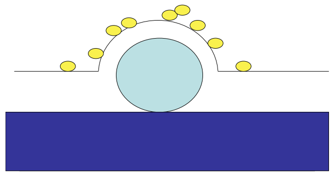

Figure 7: schematic growing of nano particles, beginning of progress

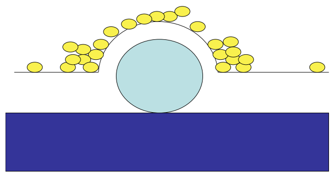

Figure 8: schematic growing of nano particles, progress with increasing layer thickness

7 Conclusion

It seems as if with an increasing in thickness the morphology of the polymer layer is slightly replicated. The data is indicating that in the layer 1 and 2 the tiny islands are growing around the hills of the polymer, because distance of the particle 2 is nearly as big as the diameter of the polymer hills. The the big particles instead seems to growing on top of the hills because their distance is comparable to the distance of the hills. With decreasing thickness the distance between the particles enlarge while the diameter of the different particles is getting smaller. At layer 4 there seem to be no more copper or at least less copper. The radius of the particles approaches 70nm which is the size of thew polymer hills. At this stage they seem to be the origin of the scattered intensity. It is interesting that the distance of the particles showing another behavior. The distance between them is not corresponding to the distance of the beads.
So i would conclude that growth process is as follows. First the hills of the polymer are covered with a film of copper with increasing layer thickness there is an excess creation at transition from the hill to flat layer. And there are formed two different particles. The growing is sketch in the figure 7 and 8.

Outlook In order to get better agrement of the fitted parameters it could bring an advantage to make the calculations with an polymer bead covered with a copper film for the big particles. This idea is based on the fact that is seems that the big particles cover the polymer hills. In order to include the scattering from the polymer structure, which is not included in the fitting yet, the described model could be used.

References

[1] 27. IFF-Ferienkurs, Streumethoden zur Untersuchung kondensierter Materie, Vorlesungsmanuskripte

[2] S.V. Roth, H. Walter, M. Burghammer,C. Riekel,B.Lengeler,C.Schroer,M.Kuhlmann,T.Walther, A.Sehrbrock, R.Dominik, P.Müller-Buschbaum, Appl. Phys. Lett. 88, 021910 (2006)

[3] S.V. Roth, H. Walter, M. Burghammer,C. Riekel,P.Müller-Buschbaum, A.Diethert and P. Panagiotou, App. Phys. Lett. Volume 82 N. 12

[4] P.Müller-Buschbaum, Anal. Bioanal. chem. (2003) 376:3-19

[5] S.V. Roth, H. Walter, B.Lengeler, C.Schroer, M.Kuhlmann, P.Müller-Buschbaum, R.Döhrmann, I. Kröger, and R. Gehrke, review of scientific instruments 77, 085106 (2006)

A header of data file

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#       copcu_00006_0011
#       Weight. Scale   factor. Shift   factor
        5.00E-01        1       F       0       F
        0.00E+00        100000  0       100000
        F       F       F       F
#       DeltaOmega(deg).        DeltaOmega(deg)
        0.00E+00        0
#       Fitted, Sin(2Thetaf),   Sin(Alphaf),    Intensity,      Error   bars
F       0.0000100       -0.0253663      30.0000100      5.4772265
T       0.0000100       -0.0253259      30.0000100      5.4772265
T       0.0000100       -0.0252854      31.0000100      5.5677653
T       0.0000100       -0.0252449      37.0000100      6.0827634
.
.
.
################################################################################
################
#       Parallel        cut     at      alphaf=0.464deg
#       copcu_00006_0011
#       Weight, Scale   factor, Shift   factor
        5.00E-01        1.00E+00        F       0.00E+00        F
        0.00E+00        1.00E+05        0.00E+00        1.00E+05
        F       F       F       F
#       DeltaOmega(deg),        DeltaOmega(deg)
        0.00E+00        0.00E+00
#       Fitted, Sin(2Thetaf),   Sin(Alphaf),    Intensity,      Error   bars
F       -4.194E-02      5.341E-03       1.000E-05       3.162E-03
T       -4.190E-02      5.341E-03       1.000E-05       3.162E-03
T       -4.186E-02      5.341E-03       1.000E-05       3.162E-03
T       -4.182E-02      5.341E-03       1.000E-05       3.162E-03
T       -4.178E-02      5.341E-03       1.000E-05       3.162E-03
T       -4.173E-02      5.341E-03       1.000E-05       3.162E-03

                                        Page 1
```

B input file

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#########################################
#   GISAXS SIMULATIONS : INPUT PARAMETERS
#########################################

# Base filename
100907a_copcu_00006_0012_result0
###########################  Framework and beam  parameters
###########################################
# Framework,  Diffuse,  Multilayer, Number of index slices,
Polarization
           DWBA           SSCA    0        25 ss
# Beam Wavelenght  :  Lambda(nm), Wl_distribution, Sigma_Wl/Wl,
Wl_min(nm), Wl_max(nm), nWl,  xWl
                       1.380E-01          none   0.000E+00   1.380E-
01   1.380E-01         1   0.000E+00
# Beam Alpha_i     :  Alpha_i(deg), Ai_distribution, Sigma_Ai(deg),
Ai_min(deg), Ai_max(deg), nAi, xAi
                       0.620E+00          none   0.000E+00   7.780E-
01   7.780E-01         1   0.000E+00
# Beam 2Theta_i    :  2Theta_i(deg), Ti_distribution, Sigma_Ti(deg),
Ti_min(deg), Ti_max(deg), nTi, XTi
                       0.000E+00          none   0.000E+00   0.000E+
00   0.000E+00         1   0.000E+00
# Substrate        :  n-delta_S,  n-beta_S, Layer thickness(nm), n-
delta_L, n-beta_L, RMS roughness(nm)
                       5.974E-06   1.551E-07   4.00000E+01 2.900-06
0.005E-06   0E+00
# Particle         : n-delta_I, n-beta_I, Depth(nm), n-delta_SH, n-
beta_SH
                       2.103E-05   0.521E-06   0.000E+00   8.000E-04
2.000E-08
################################ Grid parameters
#####################################################
# Ewald mode
 T
# Output angle (deg) :   Two theta min-max, Alphaf min-max, n(1), n
(2)
                       -1.000E+00   1.000E+00   0.62   0.62       200
1
# Output q(nm-1)     :  Qx min-max, Qy min-max, Qz min-max, n(1), n
(2), n(3)
                      -1.000E+00   1.000E+00  -1.000E+00   1.000E+00
-2.000E+00   0.000E+00       200       200         1
#################################   Particle parameters
#################################################
# Number of different particle types
           2
# Particle type, Probability
                    cylinder   3.7989E-01
                    cylinder   6.2011E-01
# Geometrical parameters : Base angle (deg), Height ratio, FS-radii/R
                       5.473E+01   1.000E+00   1.000E+00   8.000E-01
8.000E-01
                       5.473E+01   1.000E+00   1.000E+00   8.000E-01
8.000E-01
# Shell thicknesses (nm) : dR, dH, dW
                       0.000E+00   0.000E+00   0.000E+00
                       0.000E+00   0.000E+00   0.000E+00
# H_uncoupled, W_uncoupled
 T F
 F F
# Size of particle     : Radius(nm), R_distribution, SigmaR/R,
      Rmin(nm), Rmax(nm), nR, xR
                       4.98609E+01       gaussian   0.296744
```

```
1.000E-05   2.415E+03        30   3.000E+00
                       2.38621E+01       gaussian   0.169421
       1.000E-05   2.501E+02        30   3.000E+00
# Height aspect ratio  : Height/R, H_distribution, SigmaH/H, Hmin/R,
Hmax/R, nH, xH, rho_H
                      1.17925E-01        gaussian   1.11620E-04
2.396E-02   2.998E+02        50   3.000E+00   0.000E+00
                       0.144638            gaussian   7.48703E-04
1.996E-02   2.004E+02        50   3.000E+00   0.000E+00
# Width aspect ratio   : Width/R, W_distribution, SigmaW/W, Wmin/R,
Wmax/R, nW, xW, rho_W
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00   1.000E+00         1   0.000E+00   0.000E+00
                       1.000E+00           none   0.000E+00   1.000E+
00   1.000E+00         1   0.000E+00   0.000E+00
# Particle orientation : Zeta(deg), Z_distribution, SigmaZ(deg), Zmin
(deg), Zmax(deg), nZ, xZ
                       0.000E+00           none   0.000E+00   0.000E+
00   0.000E+00         1   0.000E+00
                       0.000E+00           none   0.000E+00   0.000E+
00   0.000E+00         1   0.000E+00
#################################### Lattice parameters
#################################################
# Lattice type

1DDL
#  Interference function : Peak position D(nm), w(nm), Statistics,
Eta_Voigt, Size-Distance coupling, Cut-off
                      16.9421E+00   7.03313    gau   5.000E-01
0.999761   1.000E+04
# Pair correlation function : Density(nm-2), D1(nm), sigma(nm)
                       5.272E-01   2.500E+01   1.000E+02
# Lattice parameters : L(1)(nm), L(2)(nm), Angle(deg, Xi_fixed
                       1.000E+01   1.000E+01   9.000E+01   F
                    Xi(deg), Xi_distribution, SigmaXi(deg), Ximin
(deg), Ximax(deg), nXi, xXi
                       0.000E+00           none   0.000E+00   0.000E+
00   0.000E+00         1   0.000E+00
                    Domain sizes DL(nm), DL_distribution, SigmaDL/DL,
DLmin(nm), DLmax(nm), nDL, XDL
                       2.000E+03   2.000E+04           none   0.000E+
00   0.000E+00   2.000E+03   2.000E+04   2.000E+03   2.000E+04
1         1   0.000E+00   0.000E+00
# Imperfect lattice : Rod description, Rod shape
                     rec_ellip       cau       cau
                    Correlation lenghts(nm),  Rod orientation(deg)
                       3.000E+03   1.000E+03   0.000E+00   9.000E+01
# Paracrystal : Probability description
                         ellip
                    Disorder factors w(nm), DL-statistical
distribution and rod orientation (deg)
                       5.000E-01   5.000E-01   5.000E-01   5.000E-01
                         cau       cau       cau       cau
                       0.000E+00   9.000E+01   0.000E+00   9.000E+01
# Pattern  :  Regular pattern content, Number of particles per
pattern
                           F         2
                     Positions xp/L, Debye-Waller factors B11/L1
B22/L1 B12/L1
                       0.000E+00   0.000E+00   0.000E+00   0.000E+00
0.000E+00
                       5.000E-01   5.000E-01   0.000E+00   0.000E+00
0.000E+00
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