Static and dynamic properties of inverse patchy particles

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Course on “Soft Matter Self-Assembly”
Varenna, June 29$^{\mathrm{th}}$ 2015

Outline

1. Introduction
2. Model
3. Results
4. Conclusions & Outlook

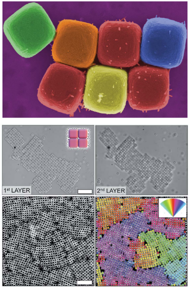
Anisotropy driven self-assembly

Examples for colloidal self-assembly driven by anisotropy

- anisotropy in shape
- dipolar or multipolar particles
- anisotropy in surface patterns (“patchy particles”)
- anisotropy in surface charge (“inverse patchy particles”)
- …

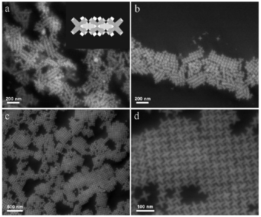
Anisotropy driven self-assembly – Example No. 1

anisotropy in shape



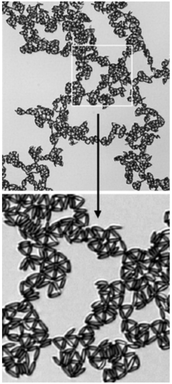
cubes

L. Rossi *et al.*, Soft Matter **7**, 1439 (2011)



octapods

W. Qi *et al.*, Nano Letters **12**, 5299 (2012)

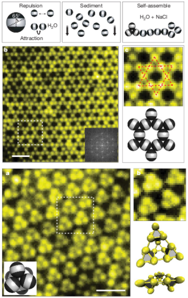


ellipsoids

B. Madivala, J. Fransaer, J. Vermant, Langmuir **25**, 2718 (2009)

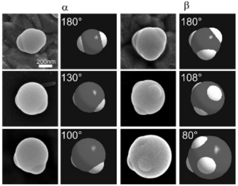
Anisotropy driven self-assembly – Example No. 2

anisotropy in surface pattern (”patchy particles”)



hydrophobic poles – charged equators
(triblock Janus particles)

Q. Chen, S.C. Bae, and S. Granick, Nature **496**, 381 (2011)

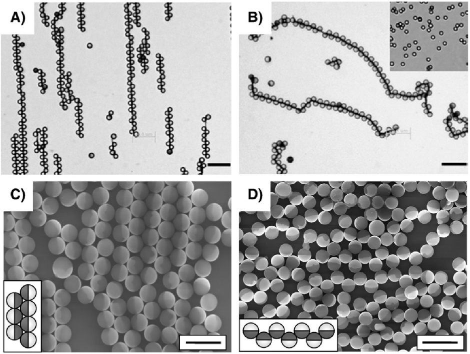


colloids with well-controlled bond angles

D.J. Kraft, J. Groenewold, W.K. Kegel, Soft Matter **5**, 3823 (2009)

Anisotropy driven self-assembly – Example No. 3

multipolar particles



one (or two) magnetic patches

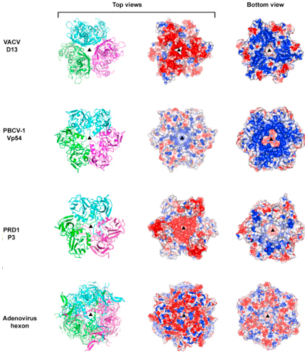
I. Kretzschmar and J.H. Song, Curr. Opin. Colloid Interface Sci. **16**, 84 (2011)

Anisotropy driven self-assembly – Example No. 4

heterogeneously charged particles

polyelectrolyte stars
adsorbed on a charged colloid

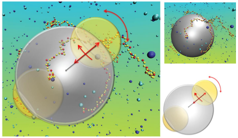
Virus capsids, proteins



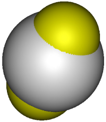
virus capsids, proteins

Inverse patchy particles

colloidal particles with heterogeneously charged surfaces:



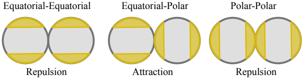
microscopic models



inverse patchy colloid

(IPC)

- negatively charged colloids with a small number of extended, positive regions (or vice versa)
- extended, soft and possibly long-ranged patches
- axially symmetric quadrupoles
- competition between
  - (a) repulsion (of like-charge regions)
  - (b) attraction (of unlike-charge regions)



- patches can be "addressed" by external (electric) fields
- see also: A.L. Božič and R. Podgornik, JCP **138**, 074902 (2013)

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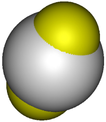
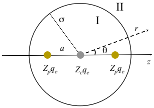
The coarse grained model (1)

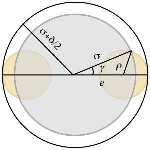
two-step coarse graining procedure



coarse-graining (1)



coarse-graining (2)



microscopic model

Debye-Hückel model

coarse-grained model

remarks:

- ○ coarse-graining (1): mathematically involved
- ○ coarse-graining (2): introducing big and small interaction spheres

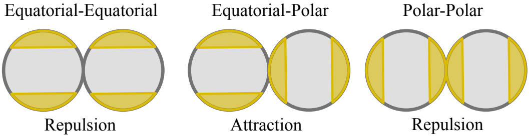
- coarse-grained model is rather simple and thus amenable to simulations
- double coarse-graining and model can be easily generalized to more complex scenarios (e.g., three and more patches)
- double coarse-grained model reproduces faithfully the symmetry of the microscopic model

The coarse-grained model (2)

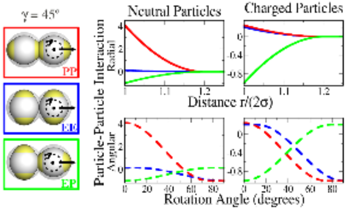
ansatz for the coarse grained pair potential:

$$U(r_{ij}, \Theta_i, \Theta_j, \Theta_{ij}) = \underbrace{w_{\mathrm{BB}}}_{\text{geometry}} \underbrace{u_{\mathrm{BB}}}_{\text{energy}} + w_{\mathrm{BS}} u_{\mathrm{BS}} + w_{\mathrm{SS}} u_{\mathrm{SS}}$$

- geometry:
  $w_{\mathrm{BB}}, w_{\mathrm{BS}}, w_{\mathrm{SS}}$ are the overlap volumes of the big ('B') and the small ('S') spheres
- energy:
  $u_{\mathrm{BB}}, u_{\mathrm{BS}}, u_{\mathrm{SS}}$ are energy parameters, adapted to the analytic expression by considering three standard particle arrangements:



Coarse-grained potentials (example)

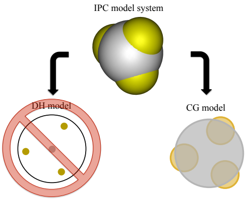


neutral and charged particles

opening angle: 45°

Advantages of mapping procedure

- simple model amenable to be investigated by simulations
  collective behaviour of our model IPCs
- model can be easily generalized to more complex scenarios:
  - three-patch IPCs



  - asymmetric patch decoration

see also:

E. Bianchi, G.K., and C.N. Likos, Soft Matter **7**, 8313 (2011)
M. Stipsitz, G.K., and E. Bianchi, JCP (submitted)

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Results – overview

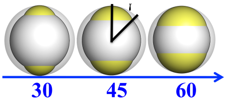
- self-assembly of IPCs under external influence
  - spatial confinement
  - external electric field
- ordered bulk phases
  - bulk phase diagram
  - (hybrid) layer formation (preliminary data)
- some experimental impressions

self-assembly under external influence

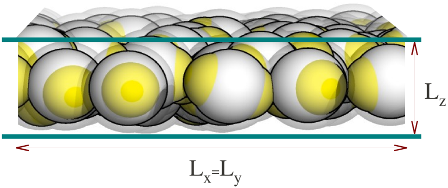
Self-assembly under external influence – system

particles:

- overall neutral ('n') and charged ('c') particles
- different opening angles of the patches (30°, 45°, 60°)

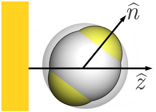


geometry:



confined geometry

(tight vs. loose confinement)



particle-wall interaction

obtained in a suitably adapted coarse-graining procedure [cf. interparticle interactions]

Self-assembly – overview

QUESTIONS:

effect of ...

(i) wall charge Z_w
(ii) particle charge: 'n' vs. 'c'
(iii) confinement
(iii) patch width: 30° vs. 45°

... on self-assembly scenarios

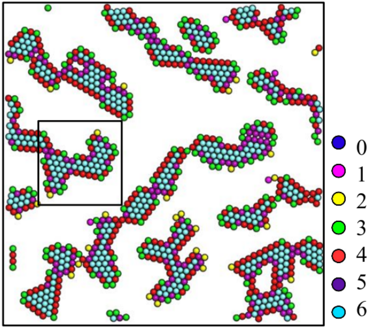
typical parameters:

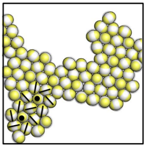
- opening angle 60°:
  $Z_\mathrm{c} = -20/9 Z_\mathrm{p}$ (charged)
  $Z_\mathrm{w} = 0.05 Z_\mathrm{p}$

Self-assembly – effect of wall charge (1)

state of reference

- neutral particles
- neutral wall



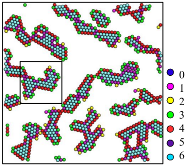


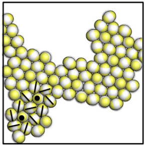
- microcrystalline gel
- triangular structure
- flower-like pattern

Self-assembly – effect of wall charge (2)

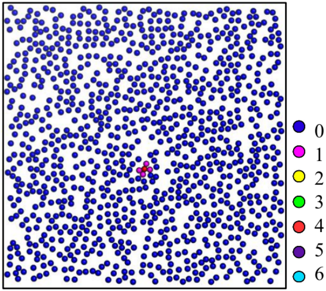
state of reference

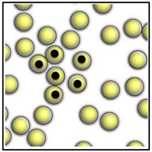
- neutral particles
- neutral wall





- neutral particles
- charged wall (as the equator) $[Z_{\mathrm{w}} = 0.05 Z_{\mathrm{p}}]$



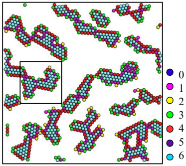


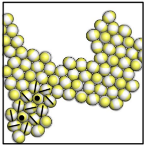
fluid (or gas) of (upright) monomers

Self-assembly – effect of wall charge (3)

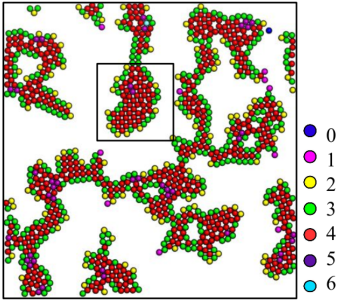
state of reference

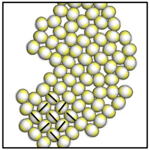
- neutral particles
- neutral wall





- neutral particles
- charged wall (as the patches) [$Z_{\mathrm{w}} = 0.05 Z_{\mathrm{p}}$]



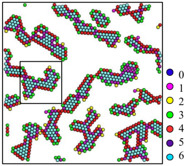


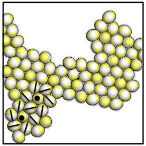
- microcrystalline gel
- square structure
- T-like pattern

Self-assembly – effect of particle charge (1)

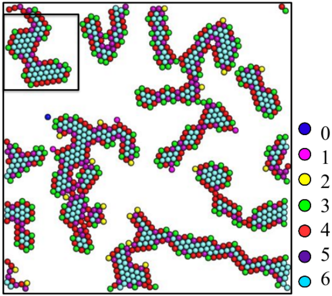
state of reference

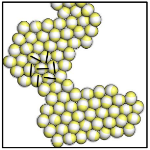
- neutral particles
- neutral wall





- charged particles (as the equator)
- neutral wall

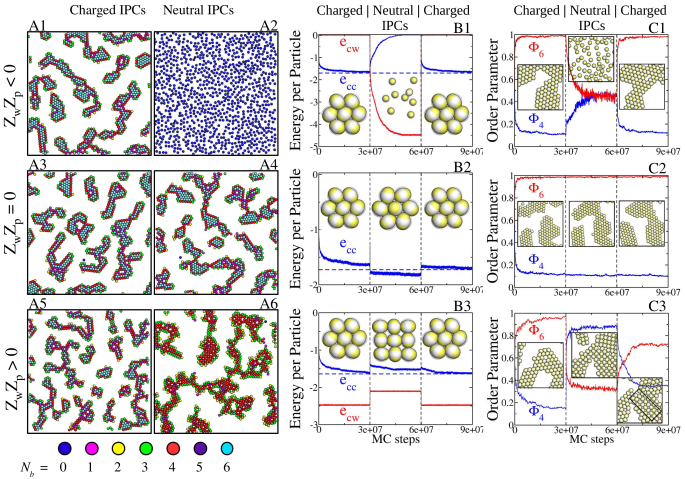




- microcrystalline gel
- triangular structure
- grain-like pattern

Self-assembly – effect of particle charge (2)

change in particle charge



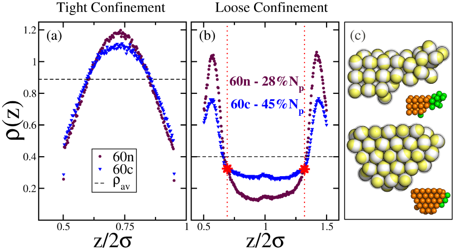
reversible

reversible

not fully reversibel

Self-assembly – effect of confinement

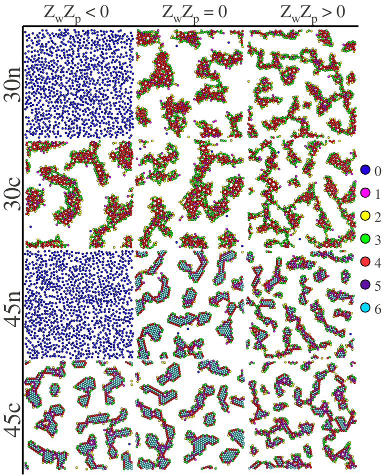
impact of confinement: tight vs. loose confinement:

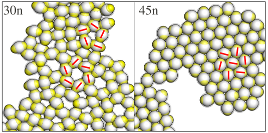


density profiles snapshots

Self-assembly – effect of the patch width

particles with patch widths of 30º and 45º





bulk phase

Ordered bulk phases – No. 1

calculation of the full phase diagram

- Monte Carlo simulations
  - thermodynamic integration schemes (à la Frenkel-Ladd)
  - accurate but time consuming (spatial and orientational degrees-of-freedom)
- theoretical concepts (i)
  - using concepts from based on association theory
  - computationally attractive but not sufficiently accurate

Yu.V. Kalyuzhnyi, E. Bianchi, S. Ferrari, and G.K., JCP **142**, 114108 (2015)
S. Ferrari, E. Bianchi, Yu.V. Kalyuzhnyi, and G.K., JPCM **27**, 234104 (2015)

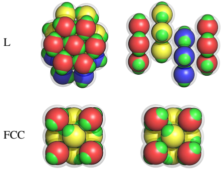
- theoretical concepts (ii)
  - extending the self-consistent phonon approach (K.S. Schweizer *et al.*)
  - currently developed, conclusive statements on accuracy and reliability not yet available

M. Stipsitz, E. Bianchi, and G.K. (in preparation)

Ordered bulk phases – No. 2

ordered candidate structures

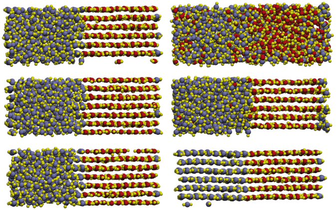
("educated guess" via optimization tools)



methods

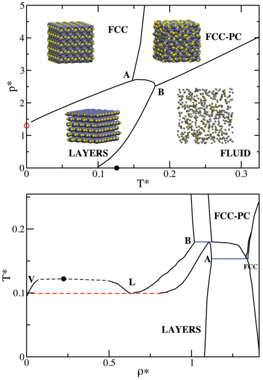
- Monte Carlo simulations
- thermodynamic integration

simulation snapshots



phase diagram

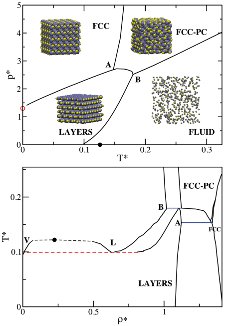
slightly overcharged
opening angle $\gamma = 39^{\text{o}}$
low screening conditions



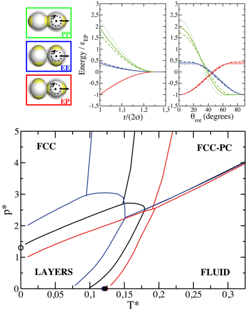
E.G. Noya, I. Kolovos, G. Doppelbauer, G. K., E. Bianchi, Soft Matter **10**, 8464 (2014)

Ordered bulk phases – No. 3

phase diagram: impact of the patch size



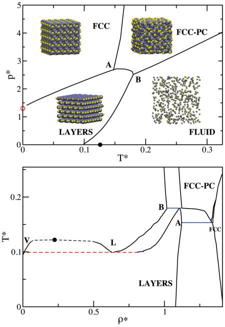
reference phase diagram



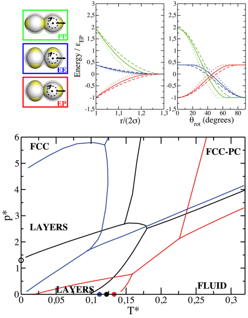
small patch, big patch

Ordered bulk phases – No. 4

phase diagram: impact of the interaction range



reference phase diagram



short ranged, long ranged

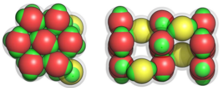
E.G. Noya and E. Bianchi, JPCM **27**, 234103 (2015) (hybrid) layered structures

(Hybrid) layered structures (preliminary data) – No. 1

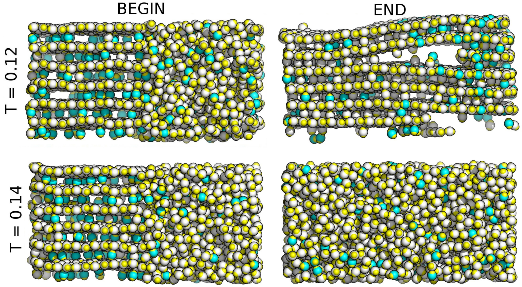
system

neutral (or sightly overcharged)
opening angle $\gamma = 45^{\text{o}}$
(optimum coverage for strong equatorial-polar bonding)
low screening conditions

(predicted) ordered
ground state configuration



simulation snapshots



(Hybrid) layered structures (preliminary data) – No. 2

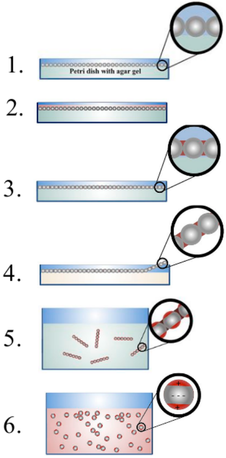
observations so far:

- observed phases:
  - low temperature: ordered phase
  - intermediate temperature: hybrid crystal-liquid phase – interlayer particles are mobile
  - high temperature: system melts
- different types of dynamics:
  diffusion coefficient, dynamic correlation functions show characteristic differences for the different types of particles (particles within the layers vs. interlayer particles)
- strong tendency to form layered structures:
  even more pronounced when particles are overcharged

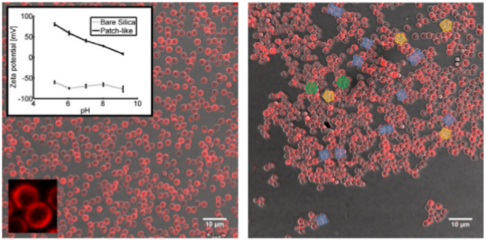
S. Ferrari, E. Bianchi, and G.K. (in preparation) experimental impressions

Experimental realization – No. 1

synthesis

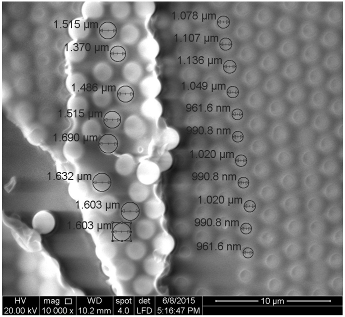


snapshots



(a) (b)

Experimental realization



asymmetric patch decoration (top and bottom view)

P.D.J. van Oostrum, M. Hejazifar, C.-M. Niedermayer, and E. Reimhult, JPCM **27**, 234105 (2015)

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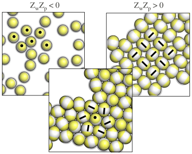
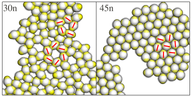
Conclusions

- particles with heterogeneously charged surfaces are characterized by a complex interplay between attraction and repulsion
- system shows strong tendency to form spatially and orientationally ordered microcrystalline gel structures





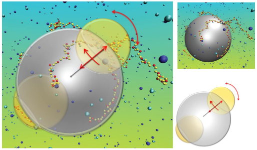
- subtle changes of external parameters (pH, wall charge, ...) can drastically change the morphology and the size of the aggregates

for details see:

E. Bianchi, C.N. Likos, and G.K., ACS Nano **7**,, 4657 (2013)
E. Bianchi, C.N. Likos, and G.K., Nano Letters **14**, 3412 (2014)

Outlook

- extension to mobile patches



see also: E. Bianchi, B. Capone, G.K., and C.N. Likos, Faraday Discussions (in press)

- investigations of dynamic properties (dynamical arrest):
  - disentangle dynamical slowing down of spatial and orientational degrees-of-freedom
  - molecular dynamics simulations and mode coupling theory

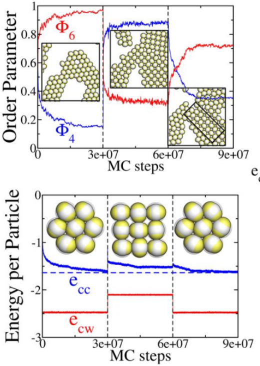
Thank you!

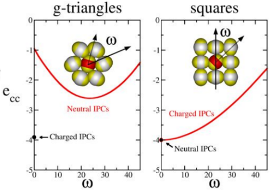
Emanuela Bianchi (TU Wien)
Christos N. Likos (Universität Wien)
Eva G. Noya (CSIC, Madrid)
Günther Doppelbauer (former TU Wien)
Ismene Kolovos (TU Wien)
Silvano Ferrari (TU Wien)
Yurij V. Kalyuzhnyi (Lviv)
Monika Stipsitz (TU Wien)
Barbara Capone (Universität Wien)

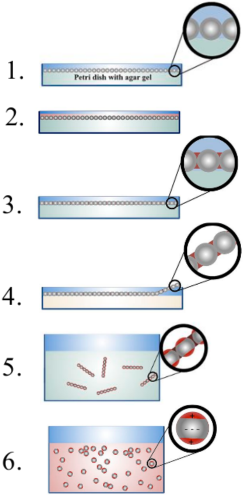
financial support:

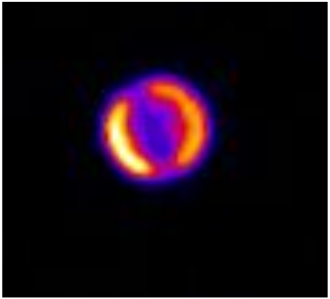
FWF — Der Wissenschaftsfonds.

COMPLOIDS — comploids EQUILIBRIUM AND DRIVEN

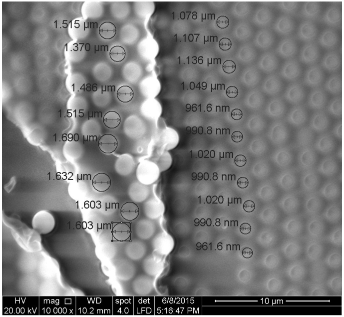

Order Parameter
Φ_6
Φ_4
MC steps
0
3e+07
6e+07
9e+07
Energy per Particle
e_{cc}
e_{cw}
MC steps


g-triangles
squares
ω
e_{cc}
Neutral IPCs
Charged IPCs
Charged IPCs
Neutral IPCs
ω
ω





P. van Oostrum, M. Hejazifar, C.-M. Niedermeyer, and E. Reimhult


1.515 µm
1.370 µm
1.486 µm
1.515 µm
1.690 µm
1.632 µm
1.603 µm
1.603 µm
1.078 µm
1.107 µm
1.136 µm
1.049 µm
961.6 nm
990.8 nm
1.020 µm
990.8 nm
1.020 µm
990.8 nm
961.6 nm
HV
20.00 kV
mag
10 000 x
WD
10.2 mm
spot
4.0
det
LFD
6/8/2015
5:16:47 PM
10 µm