From particle dispersions to rational arrangements

Tobias Kraus, Structure Formation Group, Leibniz-Institute for New Materials
GAFOE 2013, 28 April 2013, Beckman Center, Irvine, USA
Introduction

Structure formation by interacting proteins

Proteins

- Typical 10-100 kDa (~10-100 nm)
- Made of C, H, O mostly
- Stable dispersion in water
- Functional combinations: „quaternary structures“

- Specific interactions
- Binding sites
- Precise arrangements

Actin + Myosin

David Goodsell
(RCSB Protein DB)

Alain Viel, Robert A. Lue
(Harvard University)
Introduction

Structure formation by interacting nanoparticles

Nanoparticles
- Typical sizes 1-100 nm
- Made of almost anything you want
- Stable dispersion in solvent
- Functional combinations with polymers: „hybrid materials“
- „Polydispersity“
- Unspecific interactions
- No binding sites
- Random agglomerates

Niels de Jonge and Tobias Kraus, unpublished
Introduction

State of the art in particle-based materials

Silver in Epoxy
(Epotek)

Silver nanowires
(INM)

PbS in P3HT:PCBM
(Sandro F. Tedde and Hans Cerva, Siemens AG Corporate Technology)
Introduction

Example: x-ray detector

- Make scintillating nanoparticles (that glow upon x-ray adsorption),
- Embed them in a photovoltaic polymer,
- Create a “soft” photodetector for radiography.

Vision:
Solution-processed photodetector with integrated x-ray absorber
Introduction

Structure formation by interacting nanoparticles

- Assemble nanoparticles with the precision of proteins
- Design the microstructure of particle-based materials

Kraus, *Chemical Monthly* 141 (2010) 1267
Contents

(Why we think this will work)

Structural control through **shells**
- Ligands, not core materials, dominate morphology
  → Concept independent of core material

Particle **clusters** in emulsion droplets
- Clusters are known to be free energy minima
  → Particle can find even complex free energy minima

**Wet Coating 2.0**
- Regular assemblies in simple coating processes
  → Concept compatible with industry standards
Contents

1. Shells
2. Clusters
3. Coating 2.0
Shell dominates agglomerate structure

Structure of the shell: ligands

Electron microscopy:

Powerpoint particle:

More realistic (simulation):

T. Djebaili, J. Richardi, S. Abel and M. Marchi, “Atomistic Simulations of the Surface Coverage of Large Icosahedral Gold Nanocrystals”, submitted

Dodecanethiol ligand

9 nm

Au
Shell dominates agglomerate structure

Temperature-induced agglomeration

- Make a stable dispersion of gold particles in heptane.
- Cool it to instability.
- Follow the particles' assembly.
- Look at the morphology of the superstructures.
Shell dominates agglomerate structure

Temperature-induced agglomeration

Approximate averaged hydrodynamic radius from dynamic light scattering [nm]

Born and Kraus, *PRE*, manuscript in review
She dominates agglomerate structure

Temperature-induced agglomeration

Approximate averaged hydrodynamic radius from dynamic light scattering [nm]

Time [s]

Born and Kraus, *PRE*, manuscript in review
Shell dominates agglomerate structure

Temperature-induced agglomeration

Born and Kraus, *PRE*, manuscript in review
Shell dominates agglomerate structure

Temperature-induced agglomeration
But: no order under any conditions!

Modify experiment: agglomerate at higher temperatures.
Shell dominates agglomerate structure

Octadecane monolayer

Shell dominates agglomerate structure

Octadecane monolayer

Hexadecane monolayer

Shell dominates agglomerate structure

Octadecane monolayer

Hexadecane monolayer

Dodecane monolayer

Ligand shells melt

Shell dominates agglomerate structure for unpolar nanoparticle dispersions.

Cores interact through **van der Waals** forces
- Van der Waals is weakly T-dependant
  → Cores do not cause sharp transitions

Ligands **interact** with solvent
- Particle interactions are dominated by this interaction
  → as in Proteins, solvent-molecule interactions dominate superstructures

Ligands **change conformation** with temperature
- Particle packing in agglomerates depends on conformation
  → as in Proteins, molecular conformation translates into arrangement
Contents

1. Shells

2. Clusters

3. Coating 2.0
Particle clusters

Emulsion-assisted particle assembly

Procedure:

- Mix particles in hexane with surfactant and water,
- Emulsify oil phase by shear or ultrasound,
- Gently evaporate hexane,
- Obtain stable dispersion of supraparticles.
### Supraparticles

#### Structures

<table>
<thead>
<tr>
<th>TEM</th>
<th>Theoretical Projection</th>
<th>Theoretical 3D rendering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 47, Structure: IC</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 nm</td>
</tr>
<tr>
<td></td>
<td>n = 78, Structure: IC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 160, Structure: FC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 190, Structure: MD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 228, Structure: IC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 255, Structure: IC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 755, Structure: MD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 807, Structure: IC*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 971, Structure: IC*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 1609, Structure: IC</td>
<td></td>
</tr>
</tbody>
</table>

Supraparticles are proof that nanoparticles find minima

Particles find a **unique minimum** that is known to be optimal
- Just as proteins, they settle in free energy minima
  → Engineering minima lets you engineer structure

**Confinement** seems to aid assembly
- Only in confined volume do particles find the minimum
  → as in cells, confinement apparently favours regular assembly
Wet coating 2.0

Structural control in standard coating processes:

- Doctor blading
- Dip coating
- Slot-die coating
- Spray coating

How do we transfer the results?

- Lab-scale coaters with in-situ observation.
- Analysis of particle trajectories and liquid geometry.
- Structural control at realistic speeds.
Wet coating 2.0

Structural control in standard coating processes

Doctor blading    Dip coating    Slot-die coating    Spray coating

How do we transfer the results?

• Lab-scale coaters with in-situ observation.
• Analysis of particle trajectories and liquid geometry.
• Structural control at realistic speeds.
Convective and capillary assembly

Sun and nanowires
Gold nanocrystals, 60 nm, printed on silicon
Contents

(Why we think this will work)

Structural control through *shells*
- Ligands, not core materials, dominate morphology
  → Concept independent of core material

Particle *clusters* in emulsion droplets
- Clusters are known to be free energy minima
  → Particle can find even complex free energy minima

Wet Coating 2.0
- Regular assemblies in simple coating processes
  → Concept compatible with industry standards
The team:

Philip Born, Christina Bauer, Jonas Becker, Daniel Brodoceanu, Jona Engel, Dominik Gerstner, Johann Lacava, Anika Weber, Anne Wonn
Collaborations: Tihamer Geyer (UdS), Patrick Huber (TUHH), Heiko Wolf (IBM), ...
Funding: DFG, DAAD, BMBF, AiF, INM
Thank you!