Nano/Bio-materialien
2. Synthese von Nanopartikeln

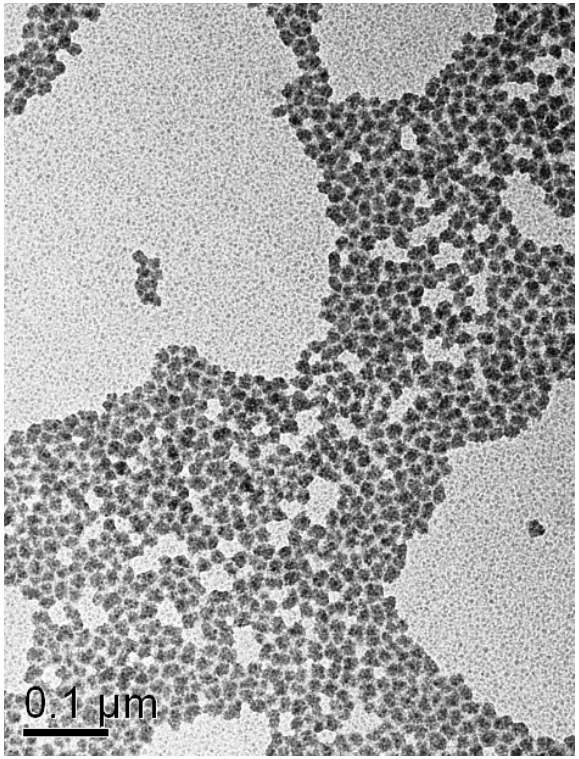
Dr. Tobias Kraus

Atoms→Clusters→Nanoparticles

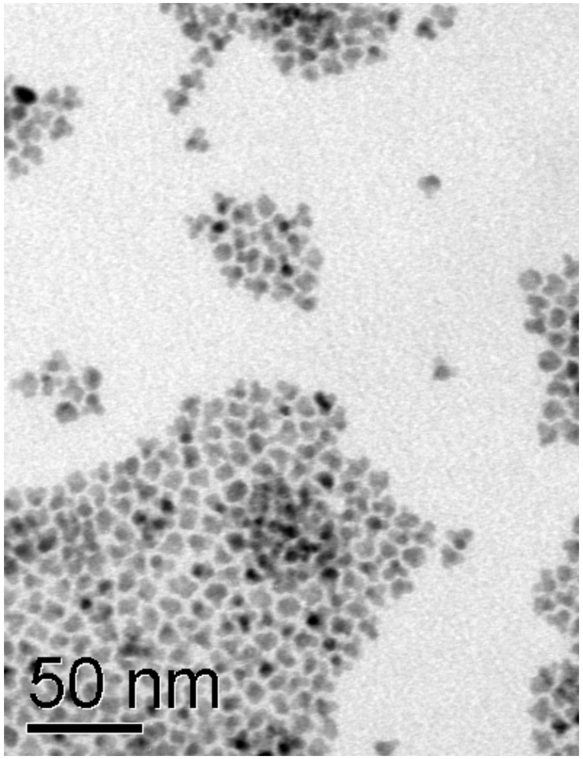
- Atoms
  - of one isotope are all identical,
  - are preserved in all chemical reactions,
  - belong to a limited set.
- Clusters (containing less than ≈500 atoms)
  - resemble large molecules,
  - often have characteristic, uniform structures,
  - are known to form from many atoms and molecules.
- Nanoparticles
  - resemble colloids and polymers,
  - have a certain polydispersity,
  - come in very many different shapes and compositions.

Nanoparticles are useful due to their availability, acceptable cost and stability: useful building blocks for materials.

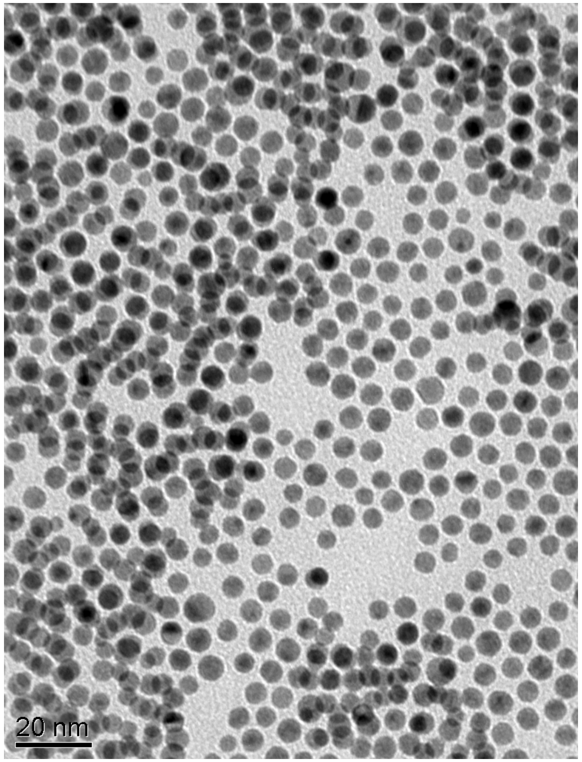
Some almost ideal nanoparticles...



SiO_2



CdSe



Au

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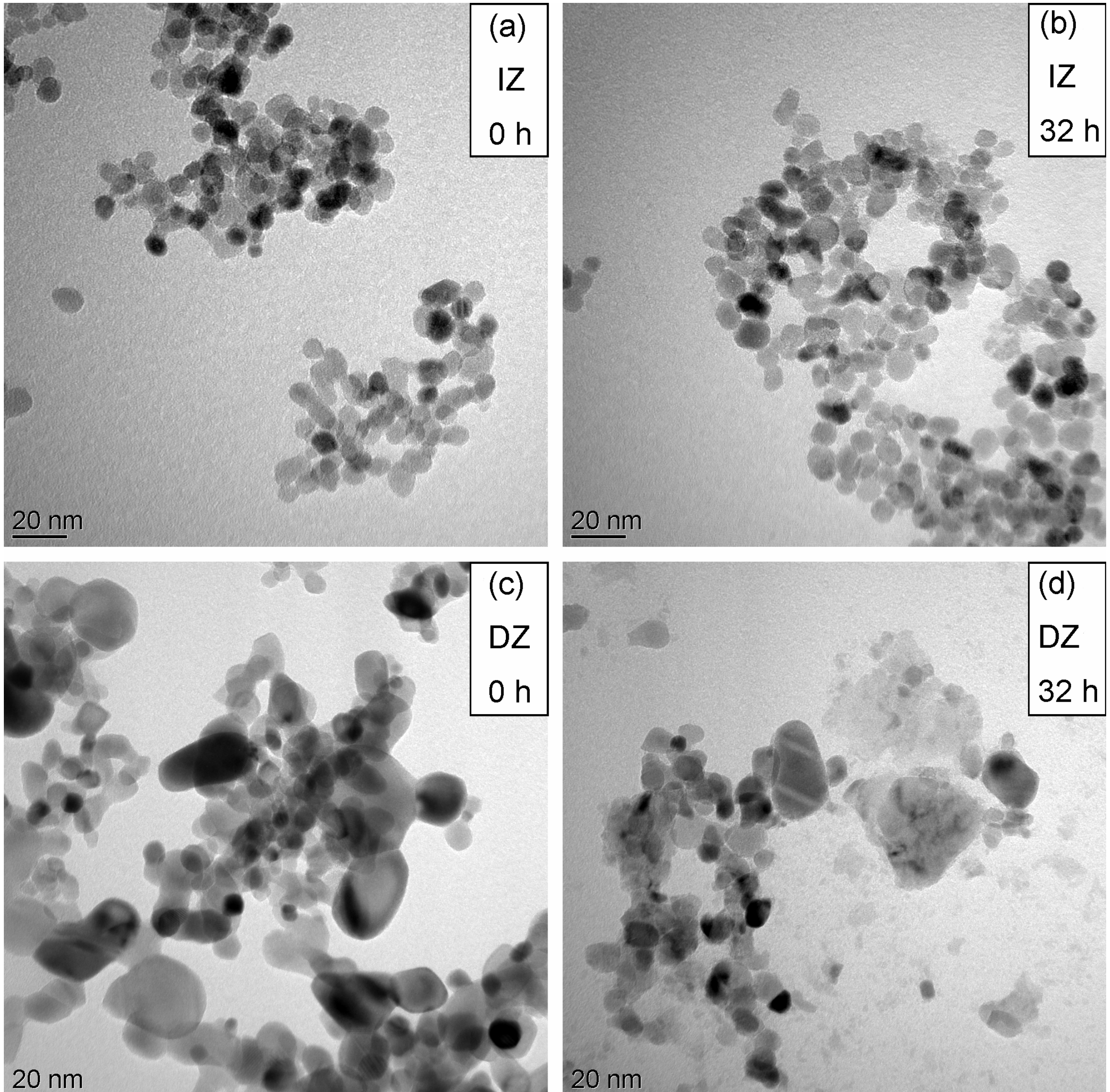
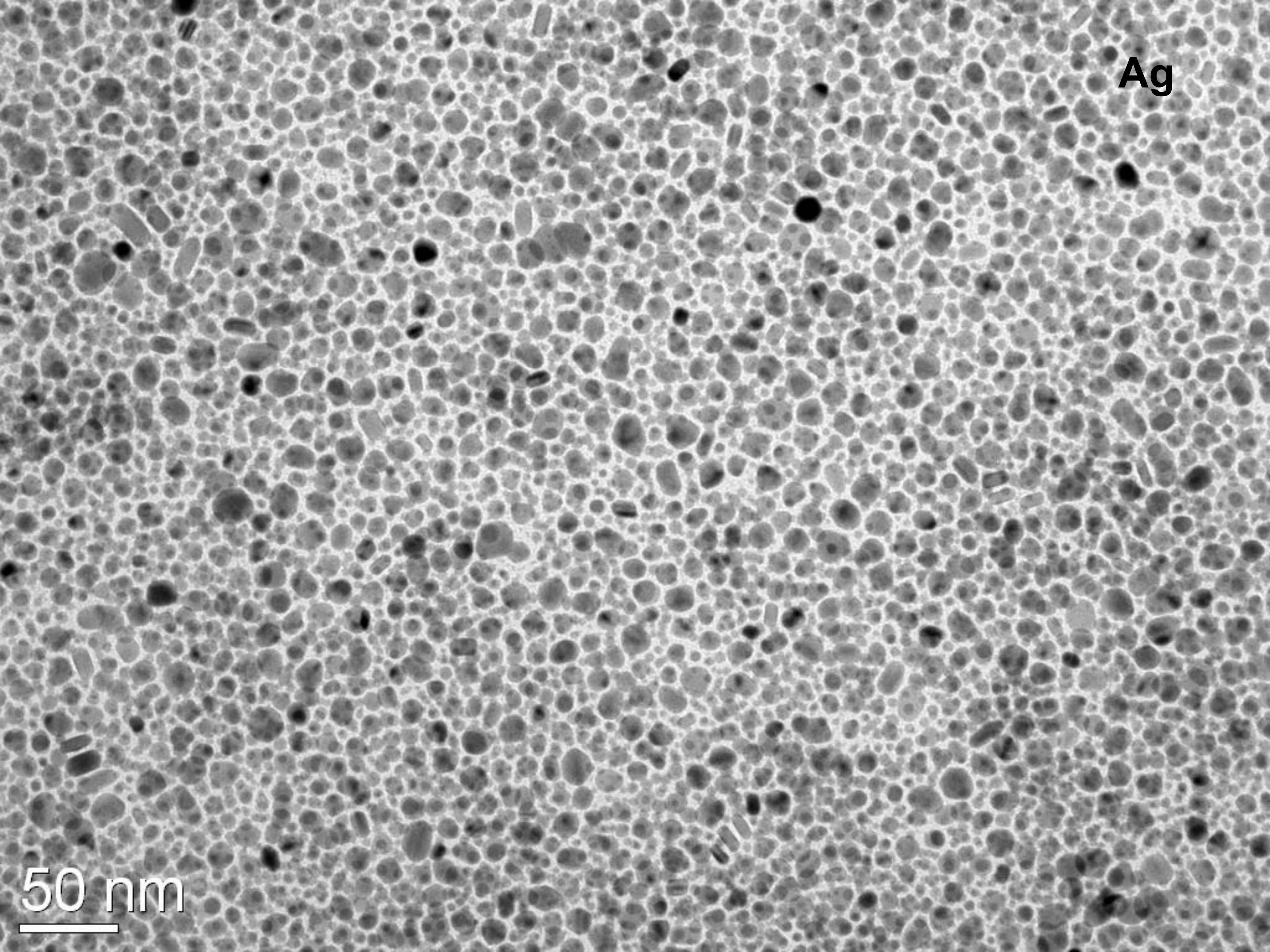
...and some less ideal nanoparticles.

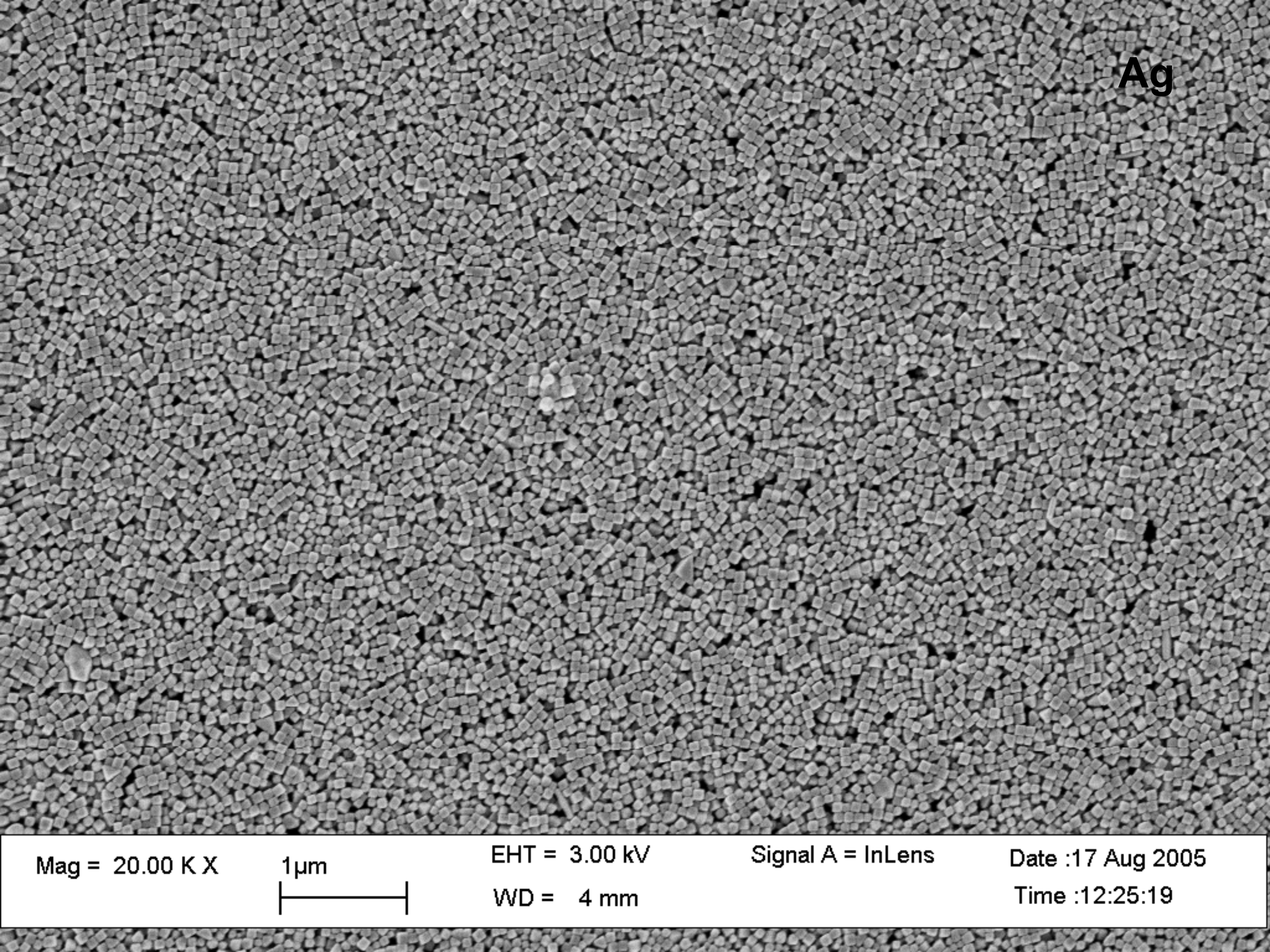


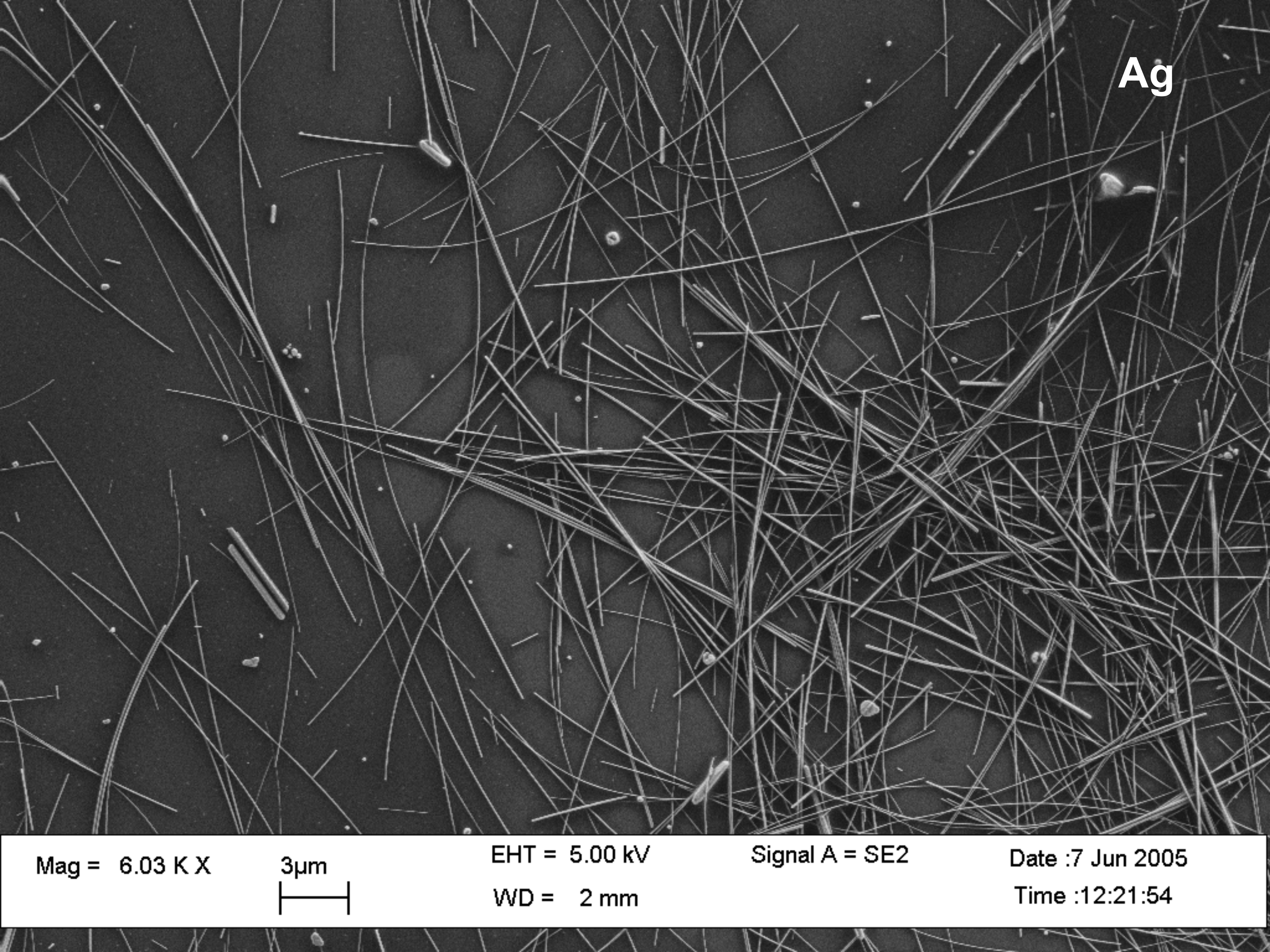
Typical features of technical nanoparticles (e.g., ZrO_2):

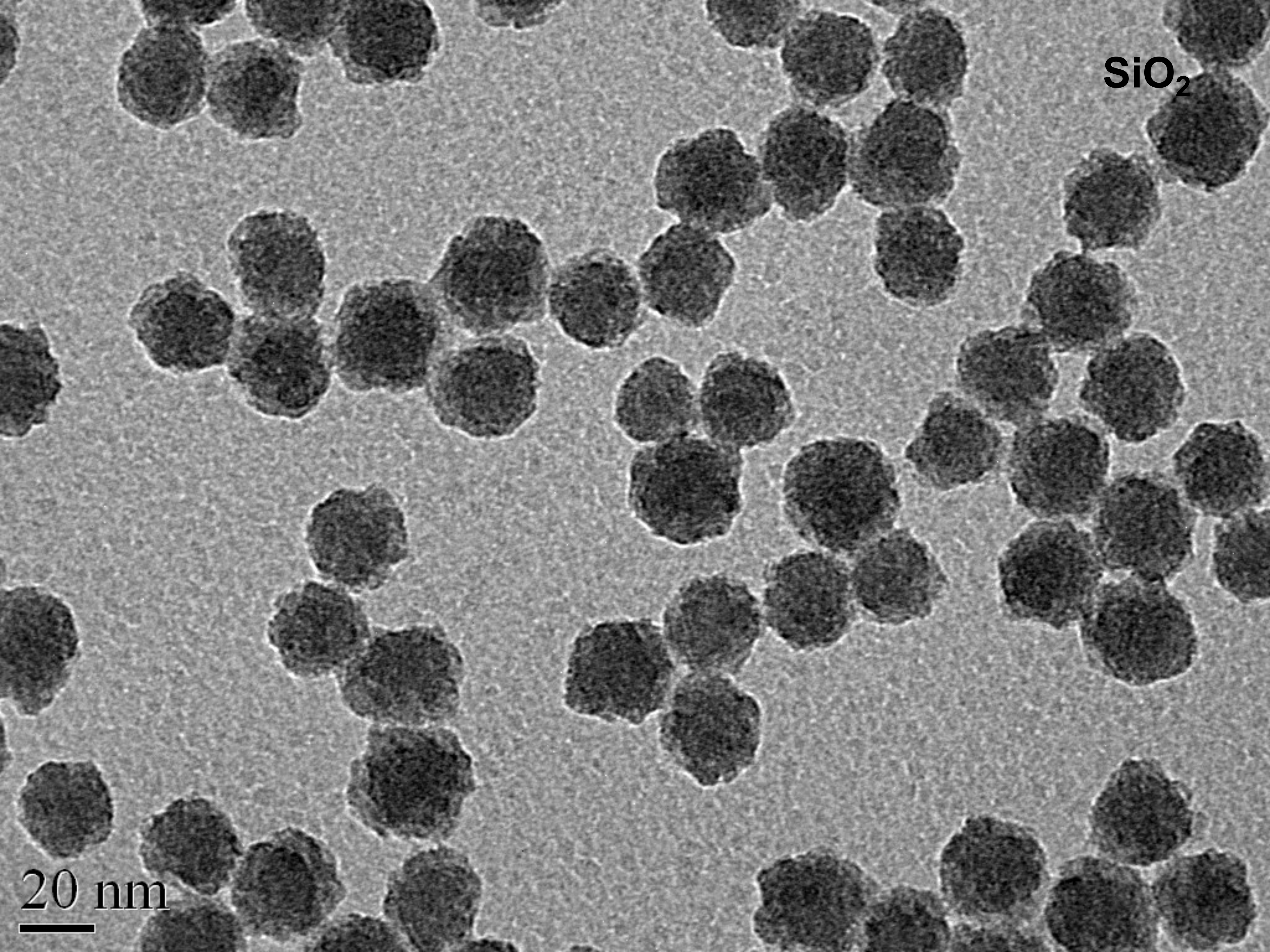
- Size distribution,
- shape distribution,
- agglomeration.

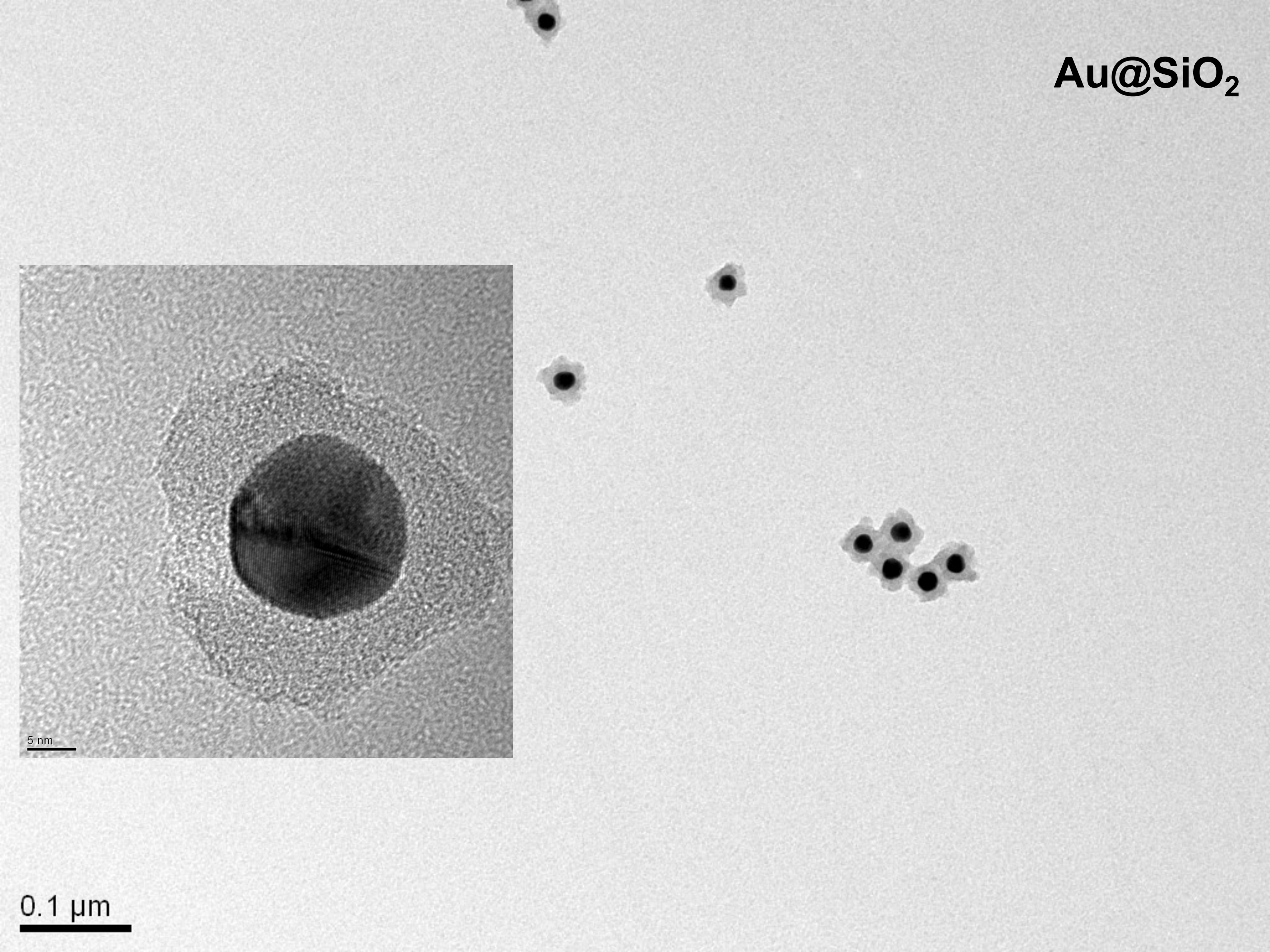

CdTe
0.1 μm


Ag
50 nm


Ag
Mag = 20.00 K X
1µm
EHT = 3.00 kV
WD = 4 mm
Signal A = InLens
Date :17 Aug 2005
Time :12:25:19


Ag
Mag = 6.03 K X
3µm
EHT = 5.00 kV
WD = 2 mm
Signal A = SE2
Date :7 Jun 2005
Time :12:21:54


SiO_2
20 nm


Au@SiO$_2$
5 nm
0.1 µm

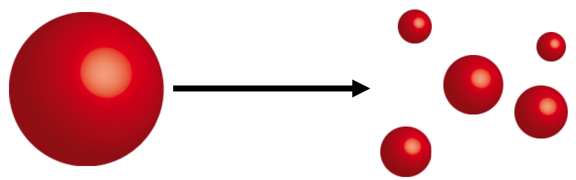
Dissociation vs. association

Particles can be formed either

- top-down or
- bottom-up.

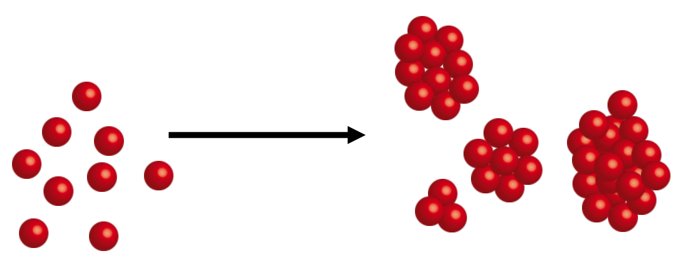
Top-down: Grind long enough!

- Mechanical disintegration,
- Radiation-assisted disintegration,
- Chemical disintegration (etching).



Bottom-up: Stop fast enough!

- Precipitation from solutions,
- Condensation of gas phases,
- Decomposition of solvated species,
- Decomposition of vapors.

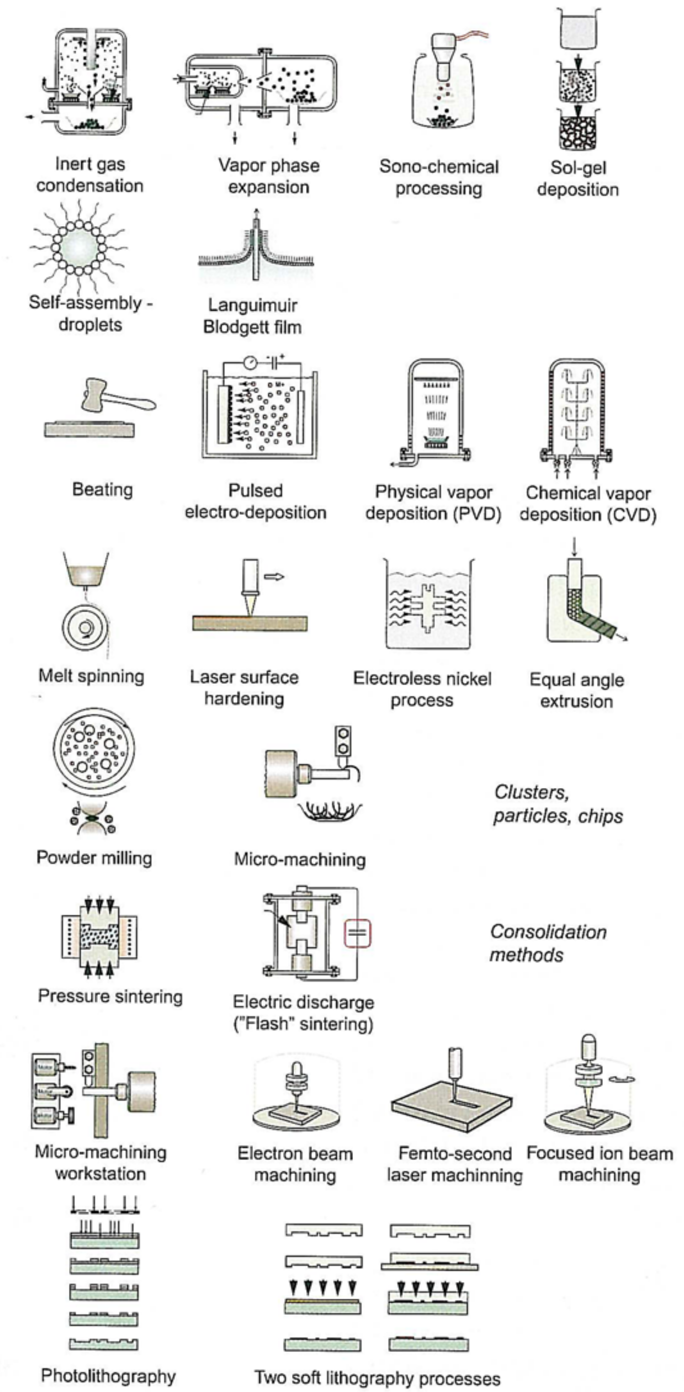


Top-down processes

Top-down: Concentrate energy sufficiently

Energy has to be introduced at sufficiently small scales, e.g. through

- Milling spheres (powder milling),
- Laser beams (laser ablation),
- Electron beams (electron beam patterning),
- Acoustic waves (ultrasonic processing).

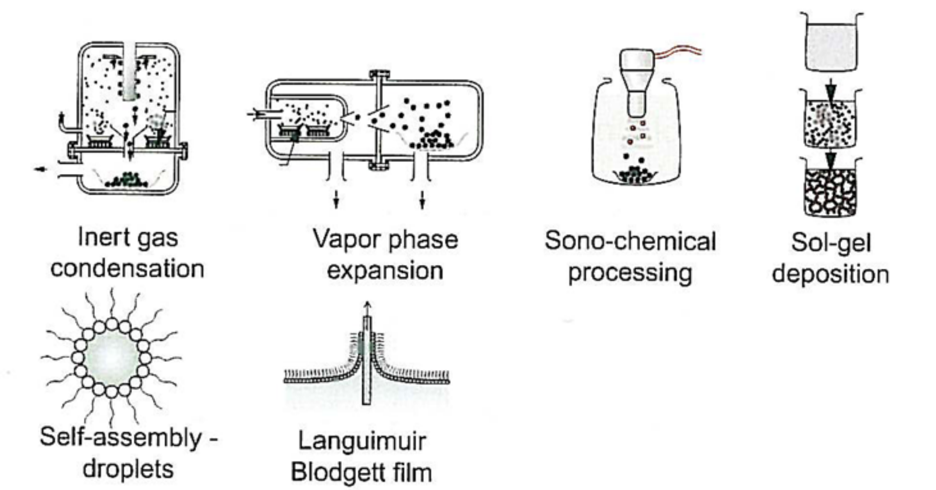


Bottom-up processes

Bottom-up: Limit growth

Growth has to be stopped after nanoparticles have formed, for example using

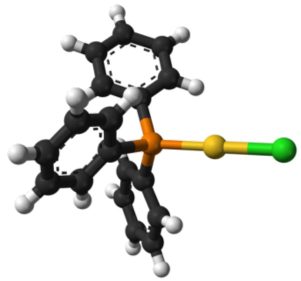
- Surfactants,
- Reduction of concentration,
- Temperature change,
- Removal from reactive region,
- Emulsion droplets,
- Templates.



Solution-based particle synthesis

Supersaturation can originate from

- precipitation after ion reaction,
- precipitation after pH change,
- hydrolysis (sol-gel processes),
- electrochemical action,
- reduction, e.g. by alcohols, hydrides, P,
- oxidation, e.g. by H_2O_2,
- thermal decomposition ("solvothermal").



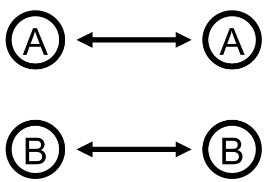
Surfactants that stabilize the particles include

- alkylsulfonates and alkylamines (ionic surfactants),
- Triton, Tween and alike (anionic surfactants),
- thiols and phosphines,
- diblock copolymers and polyelectrolytes.


Fluka
Cyclohexane
Cyclohexan
Aceton
Acetone
Acetone
21.2
55.0
20.8
55.0
BOY
116

Rules of attraction

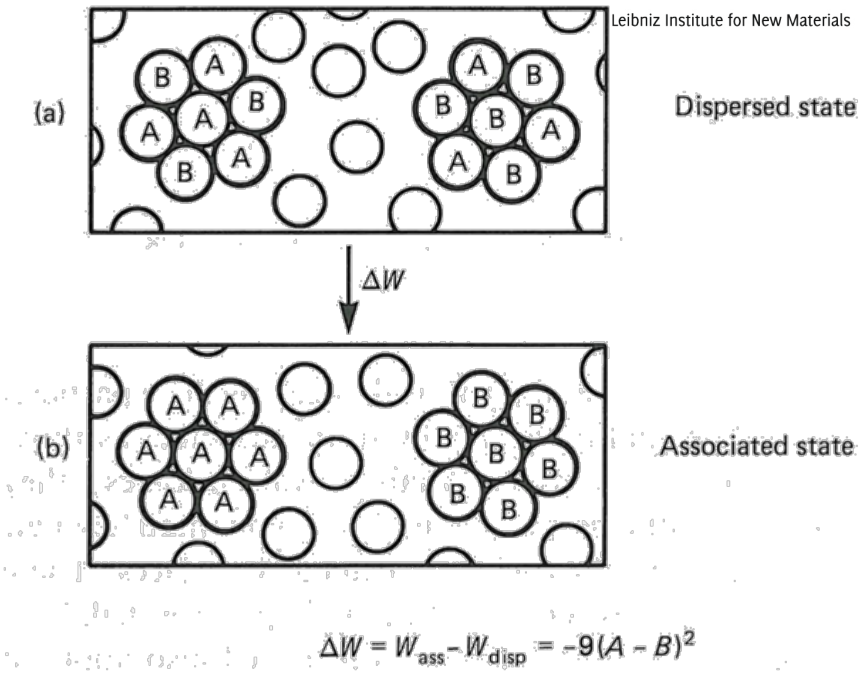
Why do particles agglomerate?



$$W_{AA} = -A^2$$

$$W_{AB} = -AB$$

$$\Delta W = W_{ass} - W_{disp} = -n(A-B)^2$$



Israelachvilii: Intermolecular & Surface Forces. Academic Press 1992

A …	Interaction due to component A [J$^{1/2}$]
W_{AA} …	Free energy change due to A-A interaction [J]
n …	Number of bonds [-]

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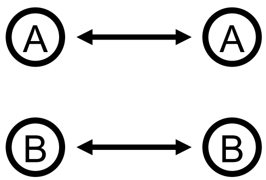


$$W_{AA} = -A^2$$

$$W_{AB} = -AB$$

$$\Delta W = W_{ass} - W_{disp} = -n(A-B)^2$$

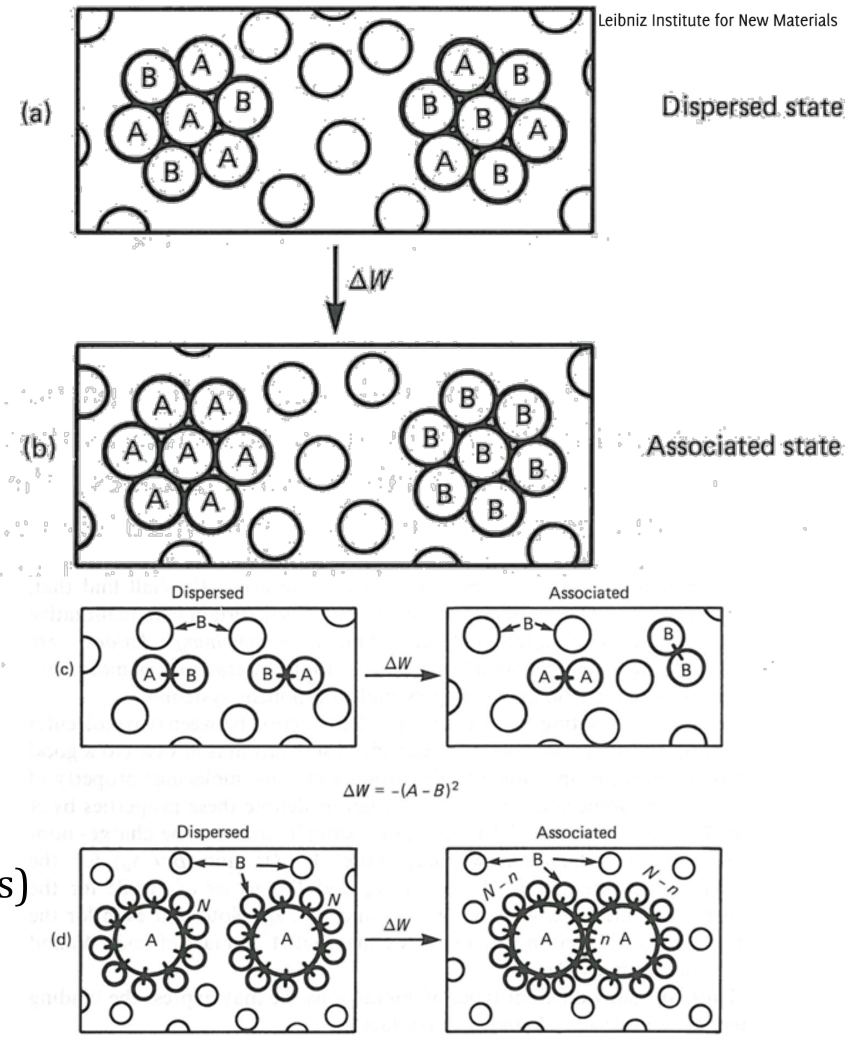
Many interactions follow multiplicative rules.

Most important example: **van der Waals**

Exceptions include

- Coulomb forces,
- Hydrogen bonds.

→ free particles (atoms, molecules, nanoparticles) will often form aggregates even in multi-component mixtures.



Israelachvilii: Intermolecular & Surface Forces. Academic Press 1992

Nucleation

Heterogeneous nucleation: small particles grow.
Homogeneous nucleation: small particles “pop up”. How?

The driving force is supersaturation S:

$$S = \frac{a}{a^*} \approx \frac{c}{c^*}$$

Now keep in mind entropy and see what changes when a cluster forms.

$$\Delta G_A = A\gamma_{Cl} \propto R^2$$

$$\Delta G_V = -VC_c\mathrm{R_g}T\ln(S) \propto R^3$$

$$\left.\frac{\partial \Delta G}{\partial R}\right|_{R_{crit}} = 0 \Rightarrow R_{crit} = \frac{4\gamma_{cl}}{\mathrm{R_g}TC_c\ln(S)}$$

a …	Activity	[mol/m^3]
A …	Cluster surface area	[m^2]
c …	Concentration	[mol/m^3]
C_c …	Cluster molar density	[mol/m^3]
R …	Particle radius	[m]
$\mathrm{R_g}$ …	Gas constant	[J/K mol]
T …	Temperature	[K]
V …	Cluster volume	[m^3]
ΔG …	Free energy change	[J]
γ_{cl} …	Cluster surface energy	[J/m^2]
S …	Supersaturation	[-]

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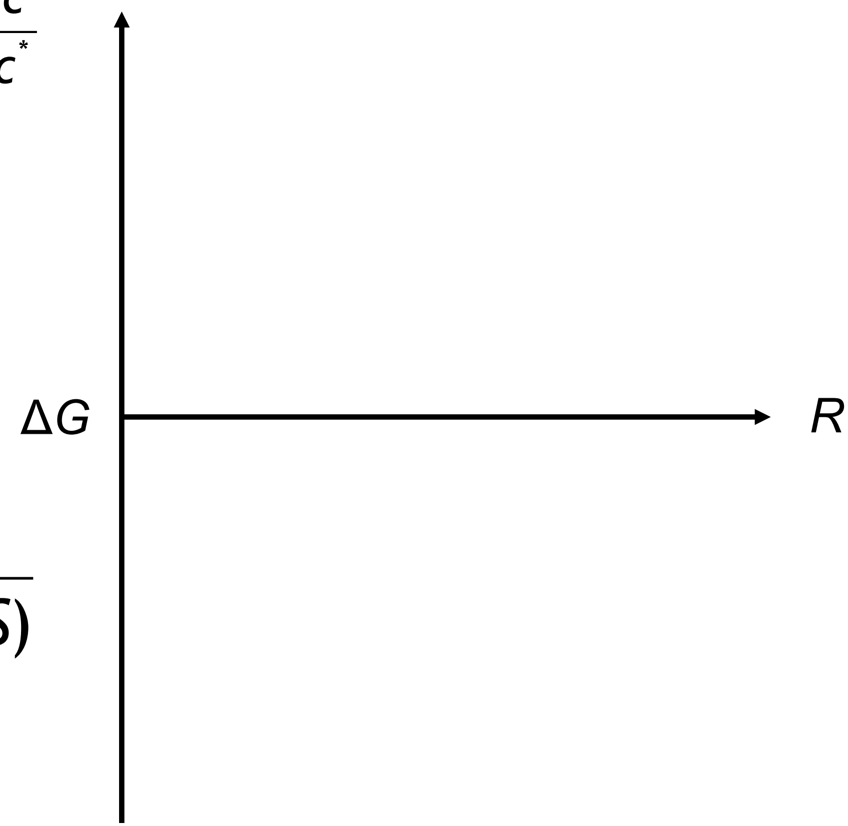


LaMer's model of distribution

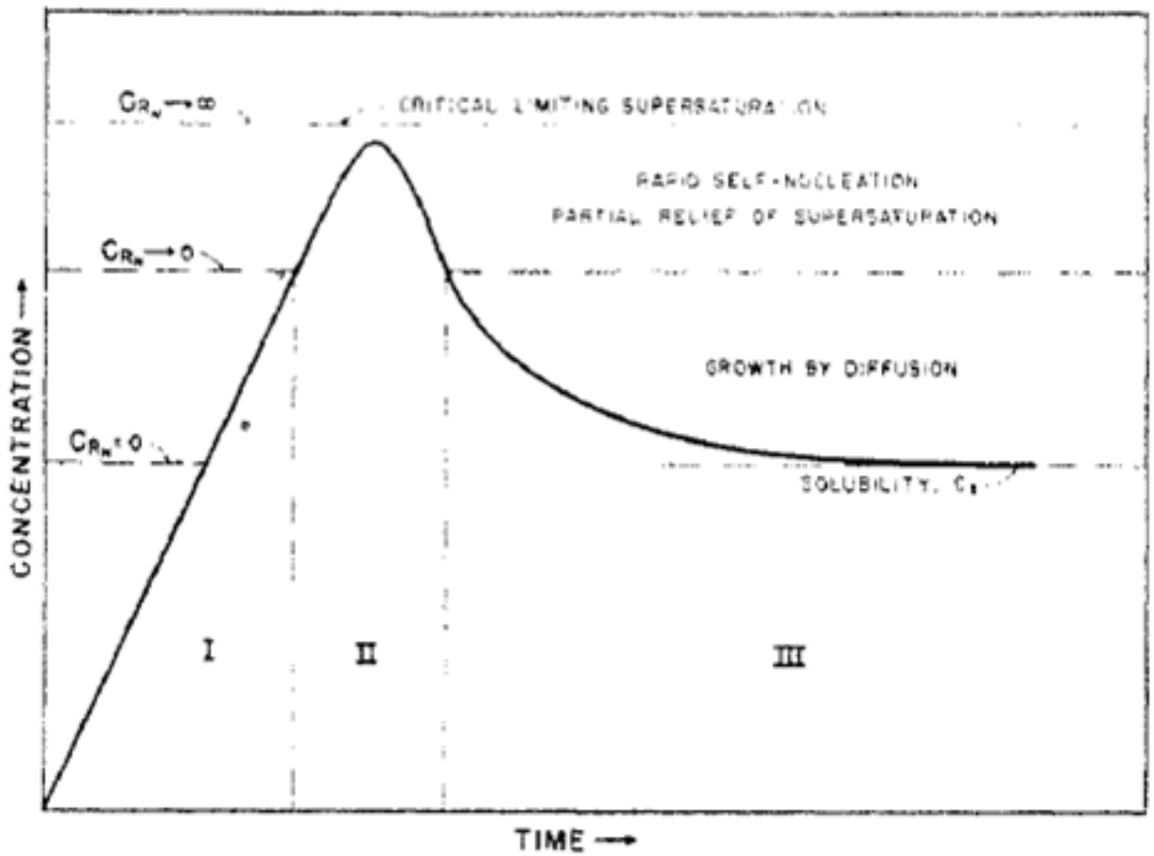
The experimentalists *did* find monodispersed particles even in batch reactors, however!

LaMer and Dinegar, *JACS* **1950**, 72, 4847-

LaMer suggested (in 1950):

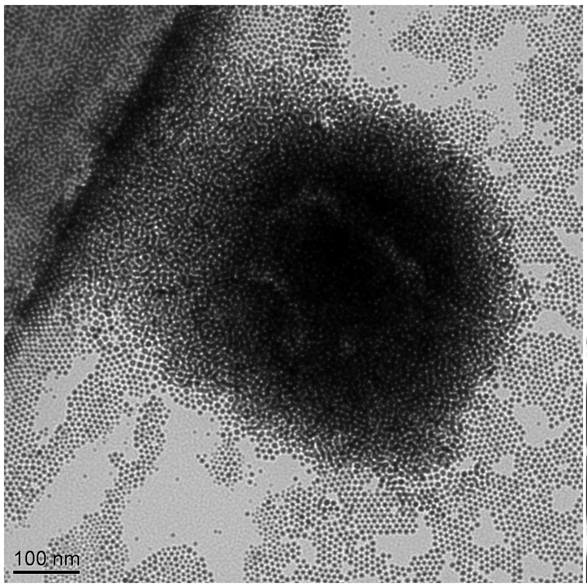
- initial burst forms nuclei,
- exclusive growth follows.

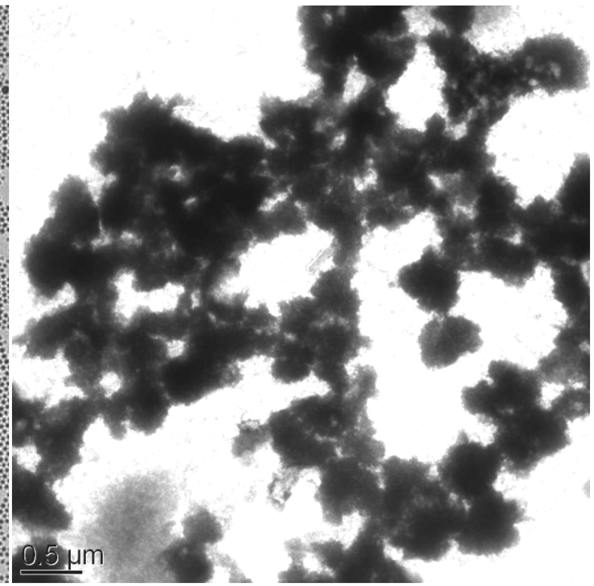
→ Narrow distribution.



Nanoparticle stability and agglomeration

Nanoparticles often agglomerate:





Gold nanoparticles, 6 nm core, sterically stabilized (Philip Born, INM)

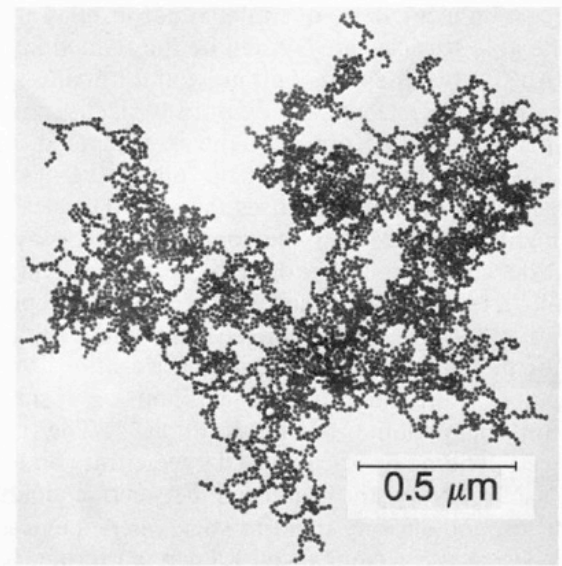


FIG. 1. TEM image of typical gold colloid aggregate. This cluster contains 4739 gold particles.

Gold nanoparticles, 14.5 nm core, charge-stabilized (Weitz/Oliveira, Exxon)

Particle stabilization

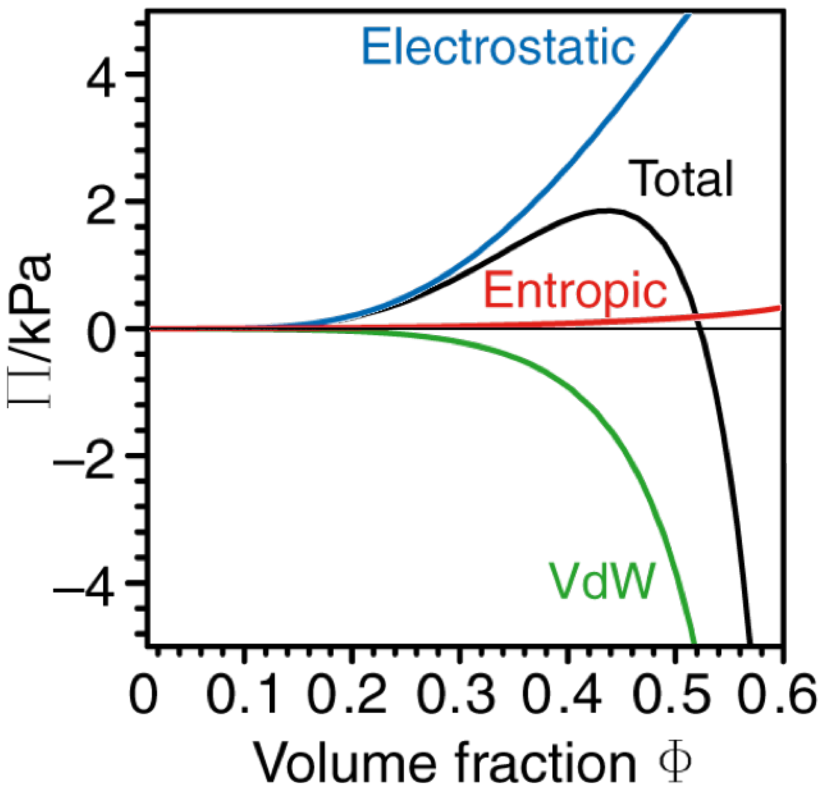
How can we make stable nanoparticle suspensions?

a) Use the exceptions from the rule:
non-attractive interactions.
"Coulombic/electrostatic" stabilization.

b) Make sure it costs lot of entropy for the particles to aggregate:
"steric/entropic" stabilization.

c) Try to make agglomeration very slow:
"metastable" suspension.

Electrostatic stabilization



Spherical gold crystals, 60 nm diameter,
at an ionic strength of 1 mmol/L.

Example:
60-nm gold nanocrystals with

- diameters on the order of Debye lengths,
- about 10 times stronger van der Waals interaction than polymers,
- large surfaces.

DLVO theory describes their stability.

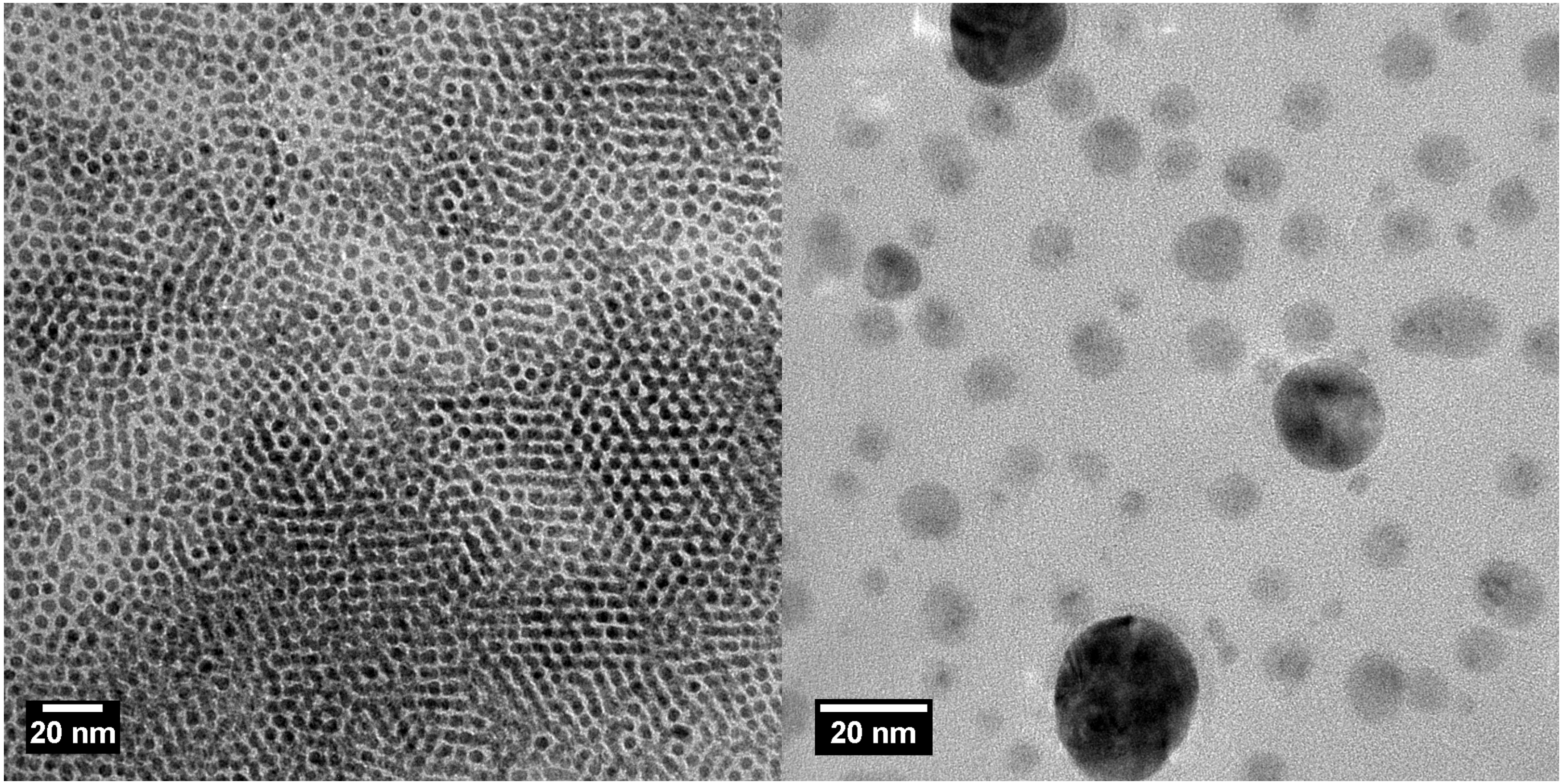
Steric stabilization

Adsorbed polymers cause strong, long-ranged repulsion.

The origin of the repulsion is entropy:
exclusion limits the possible configurations of the chains.

Ostwald ripening

A common problem beyond agglomeration is ripening:



Ag NPs, stabilized using oleic acid/oleyl amine, by Karsten Moh (INM)

Facts to keep in mind

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Nanoparticles

- are smaller than 100 nm in all dimensions,
- can be formed by dissociation or association processes (how? why?),
- are often polydispersed, but narrow size distributions can be obtained e.g. through LaMer's mechanism,
- generally attract each other (why?), which limits stability,
- have to be stabilized to be conveniently used (how?).