Nano/Bio-materialien Synthese von Nanopartikeln

## Prof. 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.
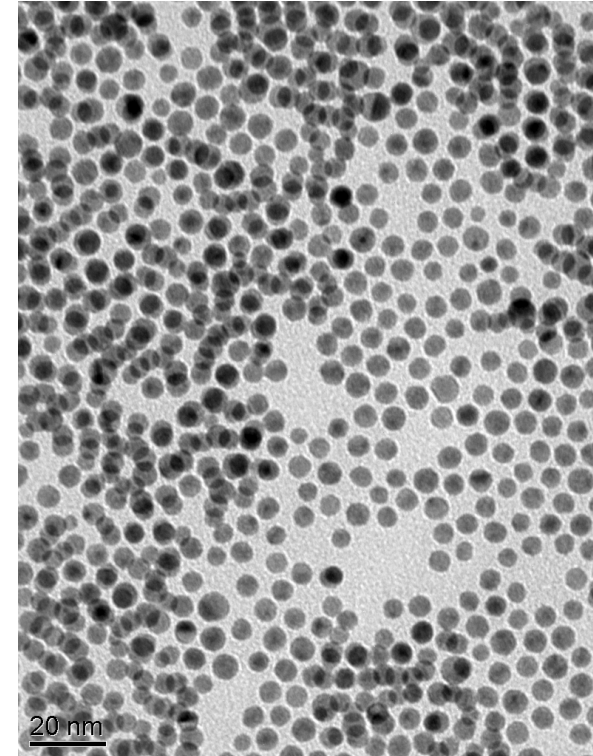
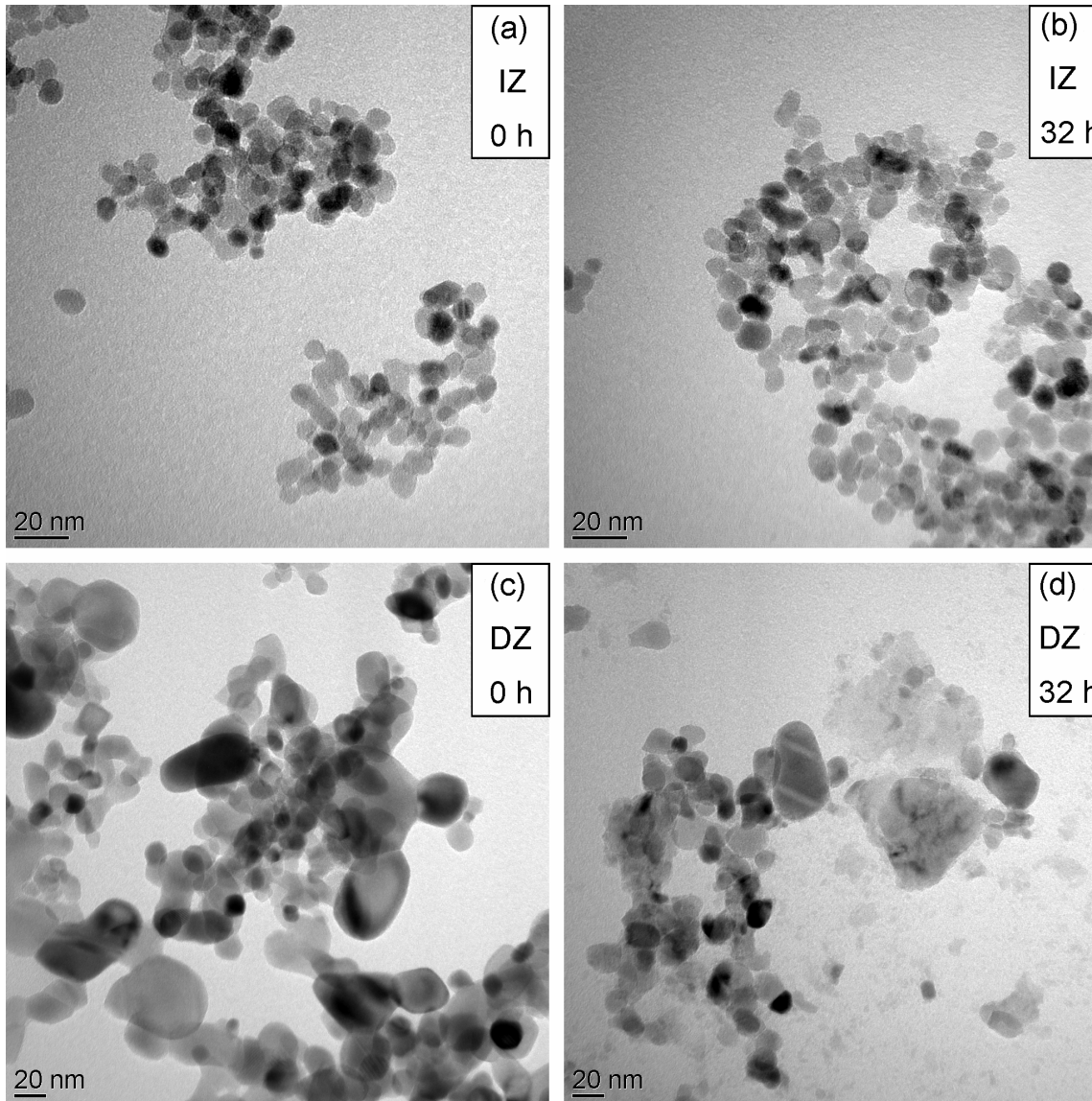# Some almost ideal nanoparticles...

SiO$_2$

50 nm
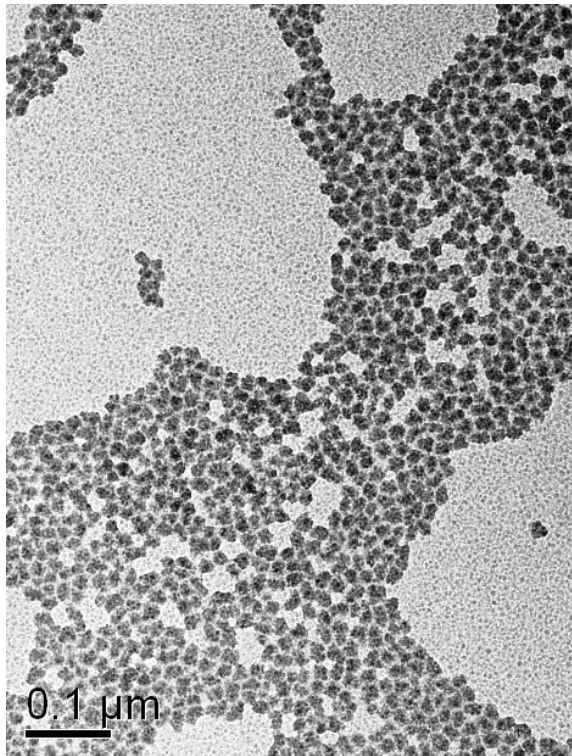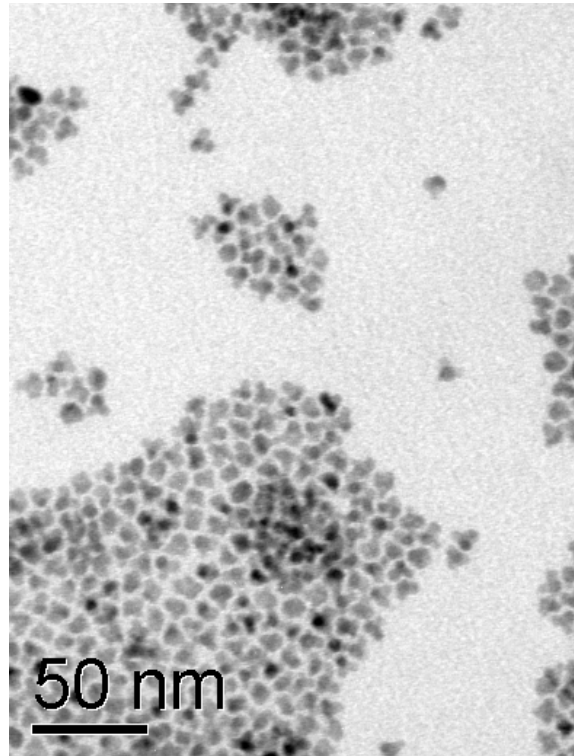
CdSe

Au

...and some less ideal nanoparticles.

(a) IZ 0 h
20 nm

(b) IZ 32 h
20 nm

(c) DZ 0 h
20 nm

(d) DZ 32 h
20 nm

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

- Size distribution,
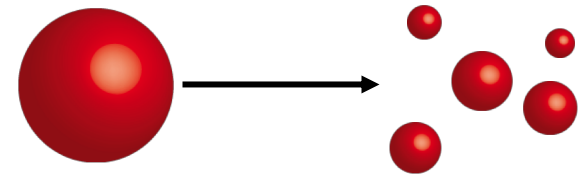- shape distribution,
- agglomeration.

Dissociation vs. association

Particles can be formed either
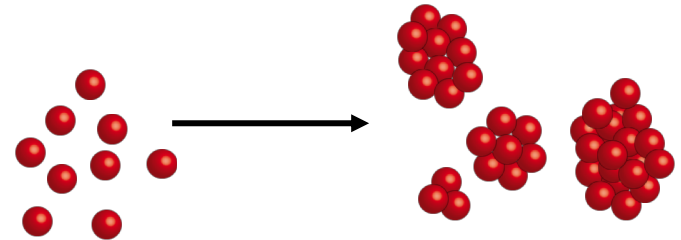– top-down or
– bottom-up.

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,
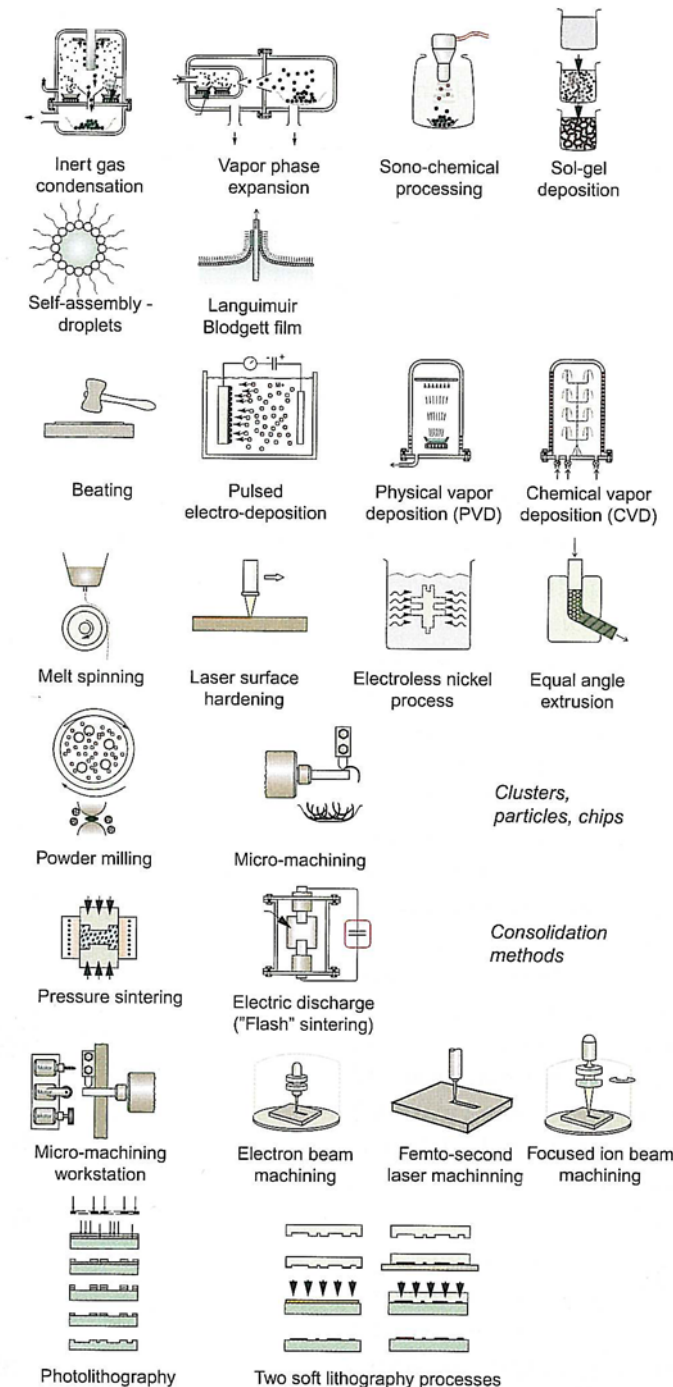– Decomposition of vapors.

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).

Inert gas condensation

Vapor phase expansion

Sono-chemical processing

Sol-gel deposition

Self-assembly - droplets

Languimuir Blodgett film

Beating

Pulsed electro-deposition

Physical vapor deposition (PVD)

Chemical vapor deposition (CVD)

Melt spinning

Laser surface hardening

Electroless nickel process

Equal angle extrusion

Powder milling

Micro-machining

Clusters, particles, chips

Pressure sintering

Electric discharge ("Flash" sintering)

Consolidation methods

Micro-machining workstation

Electron beam machining

Femto-second laser machinning

Focused ion beam machining

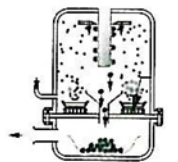Photolithography

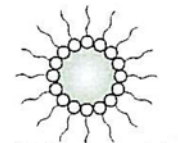Two soft lithography processes

Bottom-up processes

Bottom-up: Limit growth

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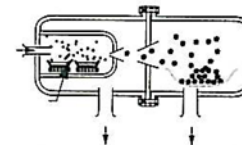nanoparticles have formed,
for example using

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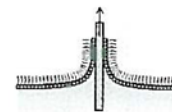- Removal from reactive region,
- Emulsion droplets,
- Templates.

Inert gas condensation

Vapor phase expansion
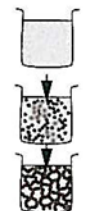
Sono-chemical processing

Sol-gel deposition

Self-assembly - droplets

Languimuir Blodgett film
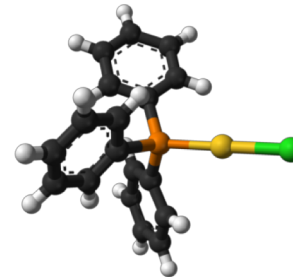
Solution-based particle synthesis

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,
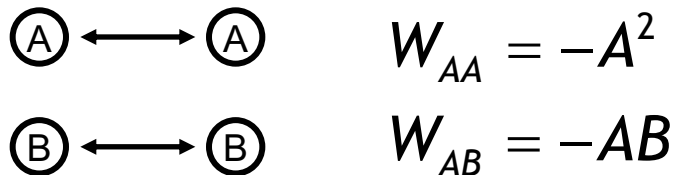- thermal decomposition ("solvothermal").

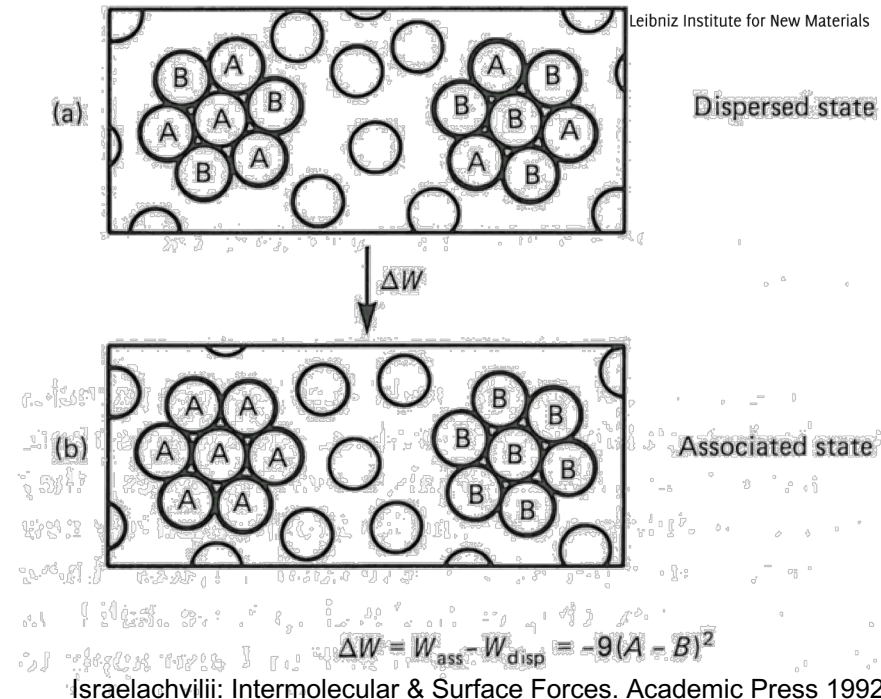Surfactants that stabilize the particles include
- alkylsulfonates and alkylamines (ionic surfactants),
- Triton, Tween and alike (anionic surfactants),
- thiols and phosphines,
- diblock copolymers and polyelectrolytes.

Rules of attraction

Why do particles agglomerate?

$$A \longleftrightarrow A \qquad W_{AA} = -A^2$$

$$B \longleftrightarrow B \qquad W_{AB} = -AB$$

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

(a) Dispersed state

ΔW

(b) Associated state

$$\Delta W = W_{ass} - W_{disp} = -9(A - B)^2$$

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	[-]

Rules of attraction

Why do particles agglomerate?

$$Ⓐ \longleftrightarrow Ⓐ \qquad W_{AA} = -A^2$$

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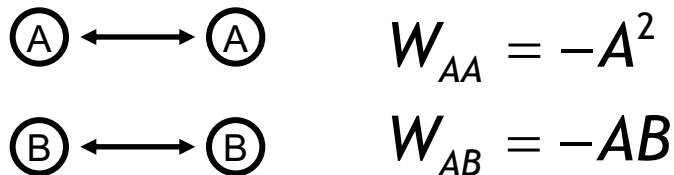
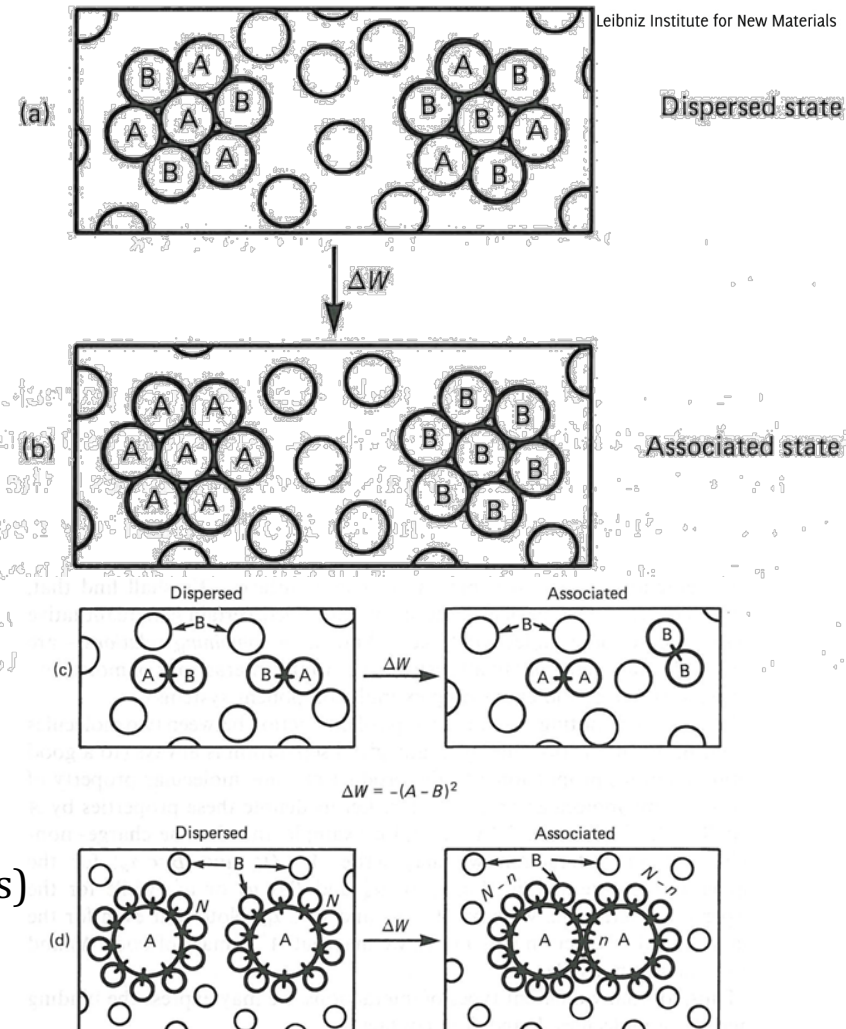$$\Delta W = W_{ass} - W_{disp} = -n(A-B)^2$$

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.

(a) Dispersed state

ΔW

(b) Associated state

(c) Dispersed → Associated

$\Delta W = -(A-B)^2$

(d) Dispersed → Associated

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.

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

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

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

a …	Activity	[mol/m³]
A …	Cluster surface area	[m²]
c …	Concentration	[mol/m³]
C_c …	Cluster molar density	[mol/m³]
R …	Particle radius	[m]
R_g …	Gas constant	[J/K mol]
T …	Temperature	[K]
V …	Cluster volume	[m³]
ΔG …	Free energy change	[J]
γ_{cl} …	Cluster surface energy	[J/m²]
S …	Supersaturation	[-]

Nucleation

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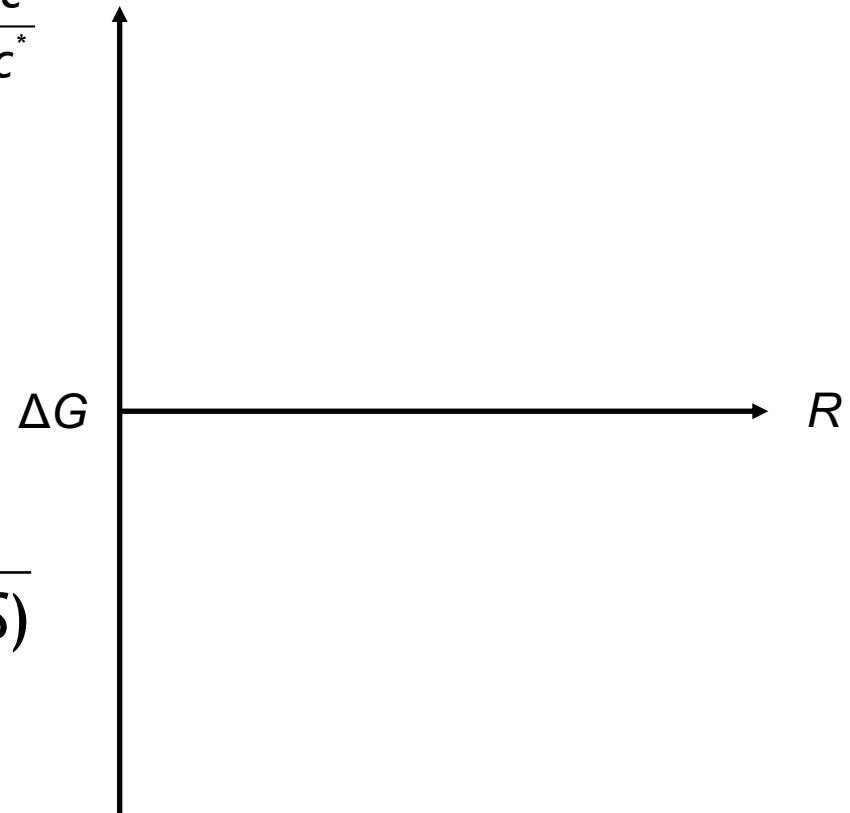Homogeneous nucleation: small particles "pop up". How?

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.

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

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

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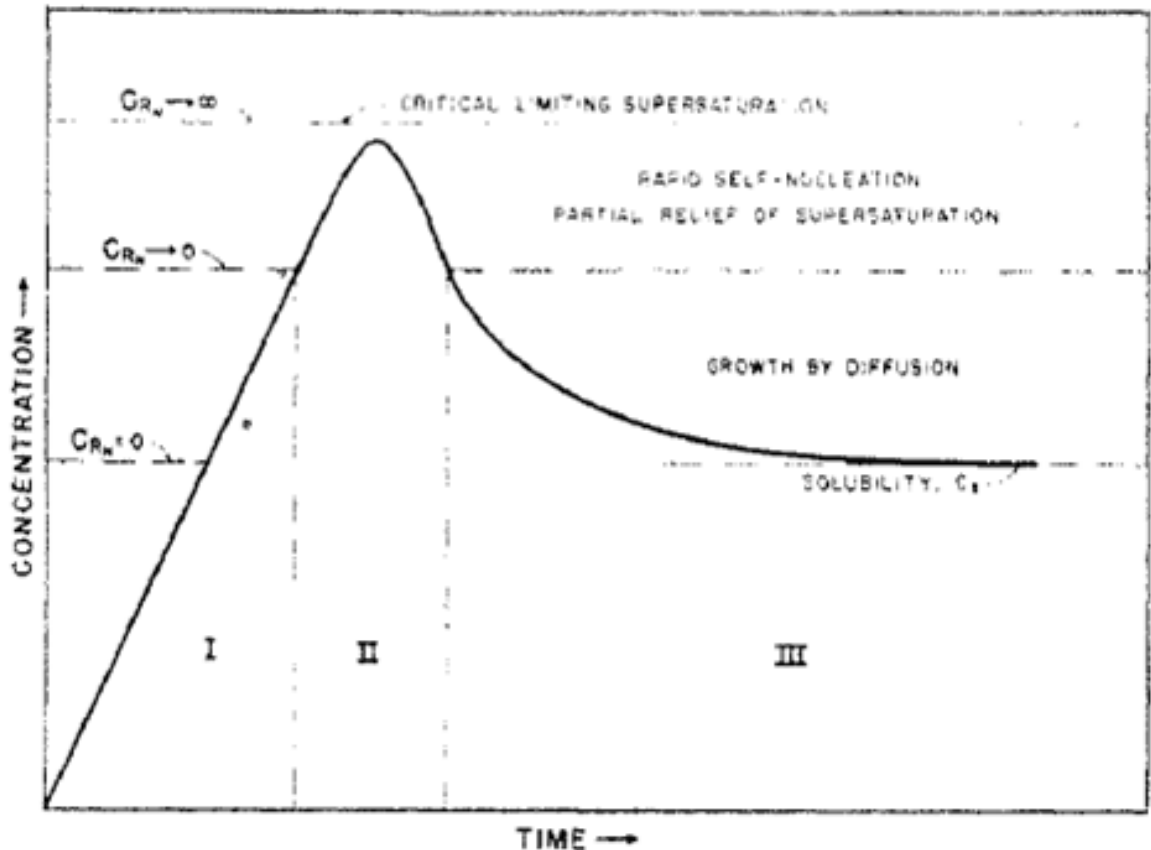
ΔG ⟶ R

LaMer's model of distribution

The experimentalists *did* find monodispersed particles even in batch reactors, however!
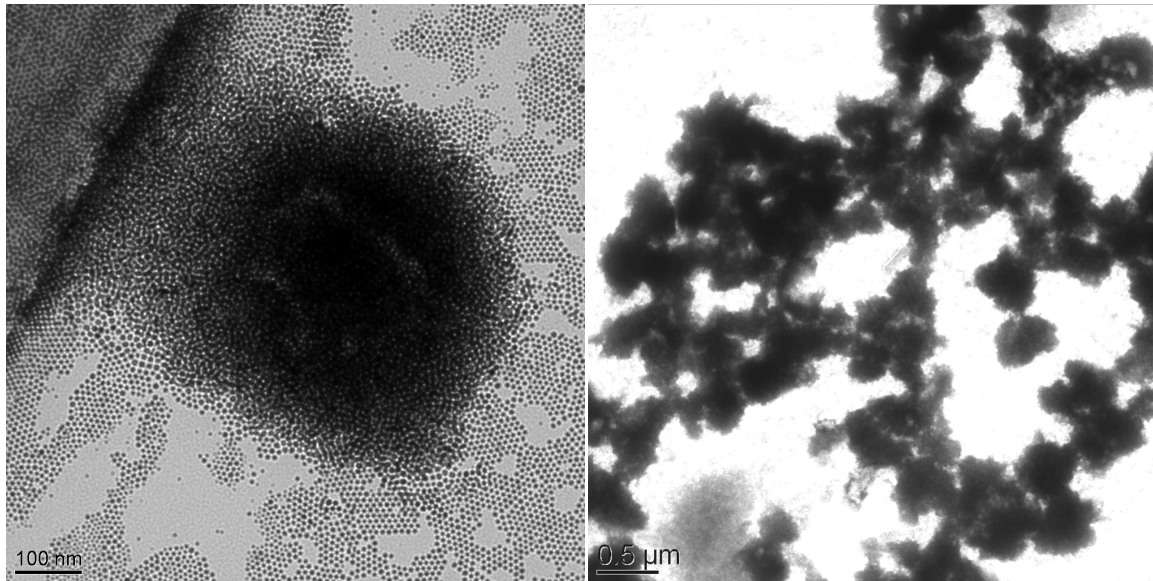
LaMer and Dinegar, *JACS* **1950**, 72, 4847-

LaMer suggested (in 1950):

- initial burst forms nuclei,

- exclusive growth follows.

→ Narrow distribution.

Nanoparticle stability and agglomeration

Nanoparticles often agglomerate:

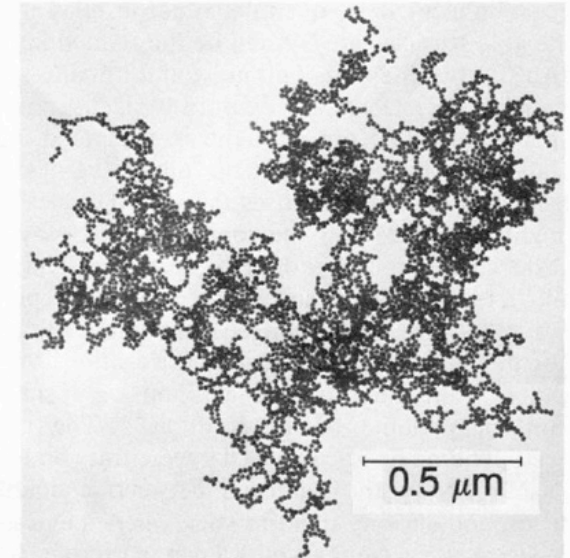Gold nanoparticles, 6 nm core, sterically stabilized (Philip Born, INM)

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.
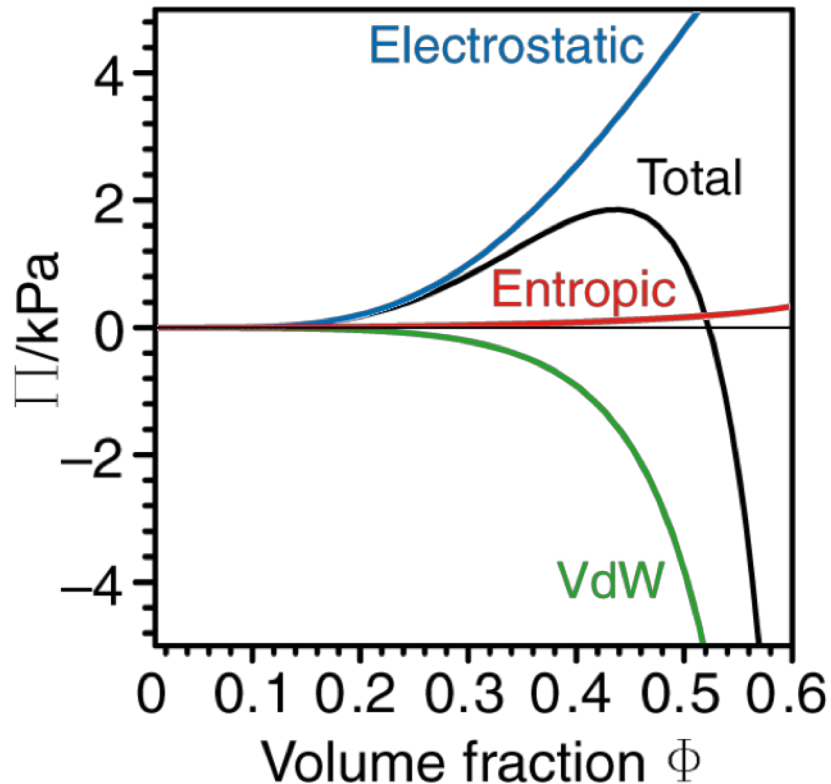
Example:

60-nm gold nanocrystals with

- diameters on the order of Debye lengths,

- about 10 times stronger van der Waals interaction than polymers,

- large surfaces.

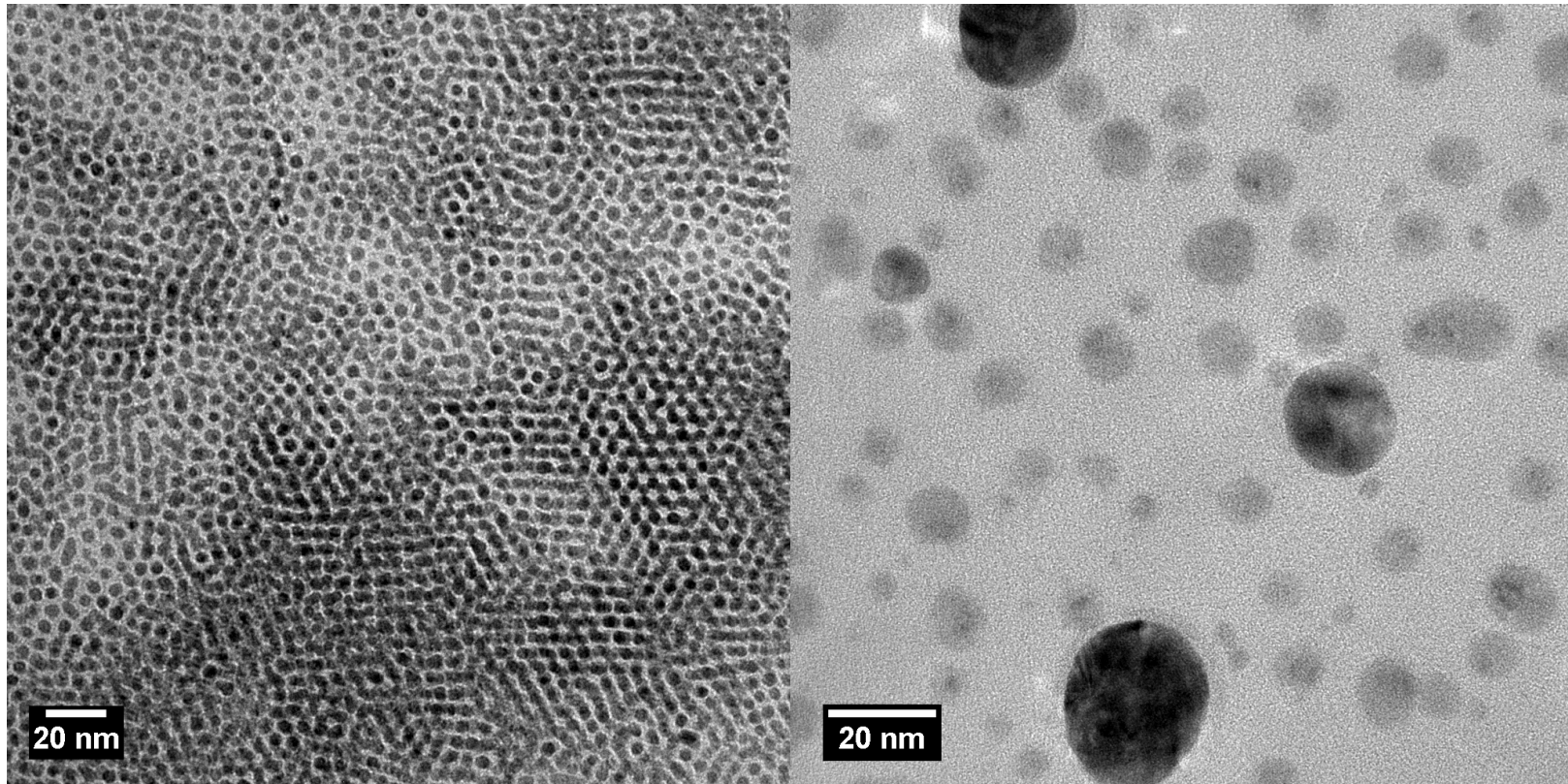DLVO theory describes their stability.

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

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?).