Università degli Studi di Trieste
Dipartimento di Ingegneria e Architettura
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Scienza e Tecnologia dei Materiali Ceramici

Modulo 2: Materiali Nanostrutturati

- Lezione 3 -

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5 μm

Previous lecture: Review

- Mechanisms of minimization of the surface energy
  - Surface mechanisms
  - Mechanisms at the level of the individual nanostructure
  - Mechanisms at the scale of the ensamble of nano-objects: aggregation, sintering, Ostwald ripening → Gibbs-Thompson

This lecture: Content

- Nanoparticles
  - Approaches to the stabilization of nanostructures (the example of nanoparticles)

Where are we?

3. Fabbricazione

- Approcci "bottom-up":
  - Building blocks (nanocristalli: wells and films, wires, dots; carbon based nanostructures: fullerenes, graphenes, etc.)
  - Proprietà dei building blocks
  - Metodi di fabbricazione (deposizione di film, aerosol, sospensioni colloidali, epitassia controllata, etc.)
  - Assemblaggio (self assembly bioassistito, self assembly via polimeri, eterostrutture, Marangoni, …)

- Approcci "top-down"
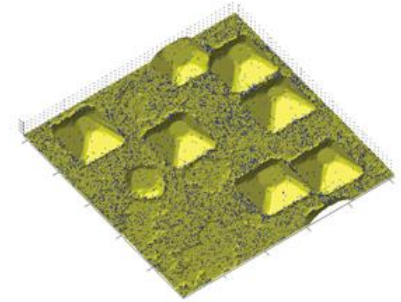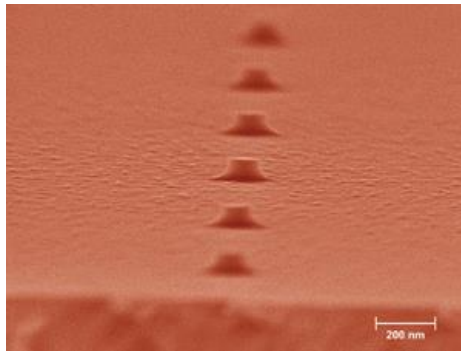 - Litografia, ball milling, ion implantation, thin film layers + thermal treatment, etc.

5 µm

Approaches to nanoparticle synthesis

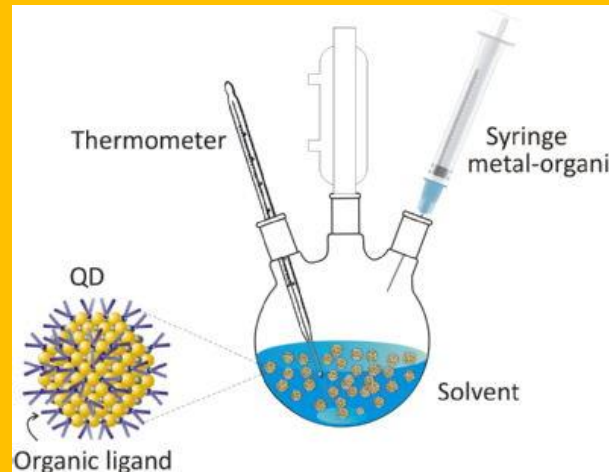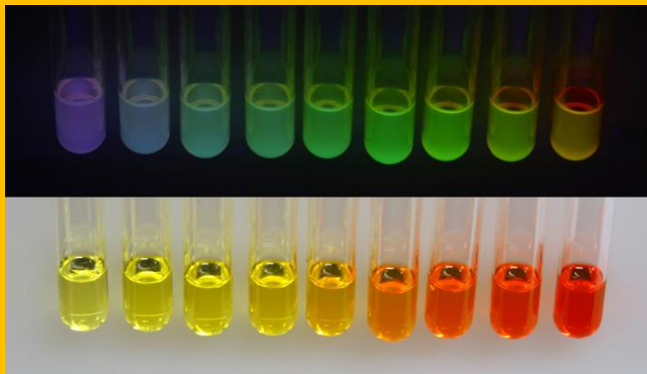- **Self-assembled nanocrystals**

1) A on B   A   Increasing Growth   100 Å

(i)   (ii)

- **Lithography**

200 nm
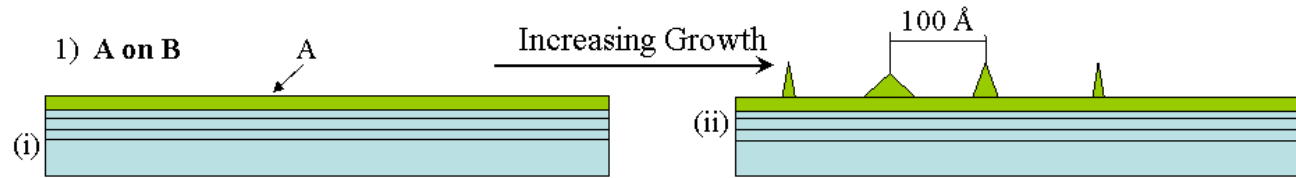
- **Colloidal nanocrystals**

Thermometer   Syringe metal-organic

QD

Solvent

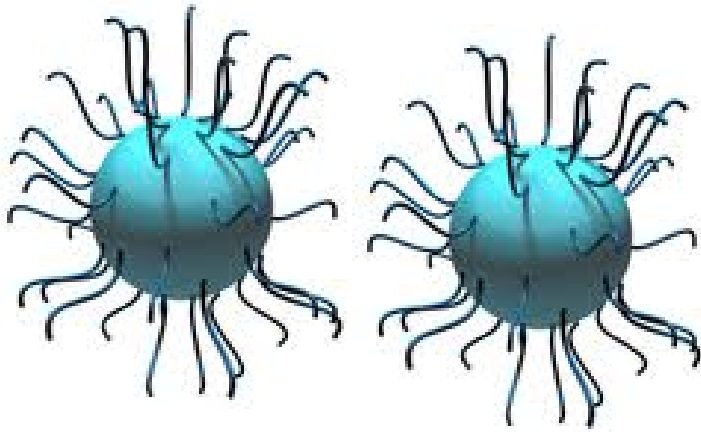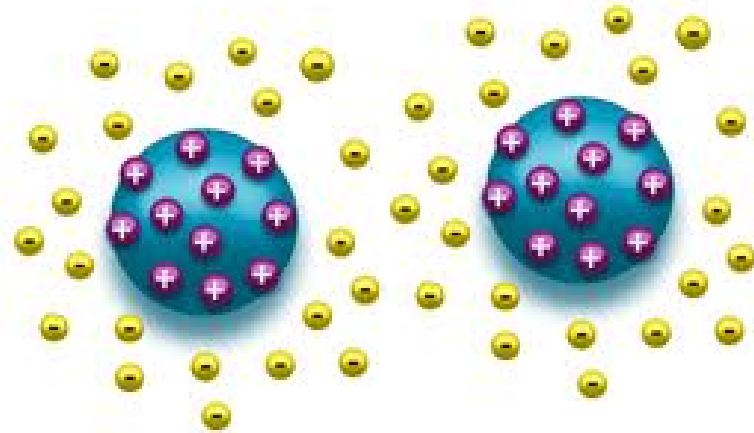Organic ligand

We focus on this!

# Stabilization of nanostructures

Steric repulsion

Electrostatic repulsion

Electrostatic stabilization

1. Formation of charges on the surface of a solid particle in a polar solvent:

- Preferential ion adsorption
- Dissociation of surface charged species
- Substitution of surface ions
- **Accumulation or loss of electrons at the surface (next slide)**
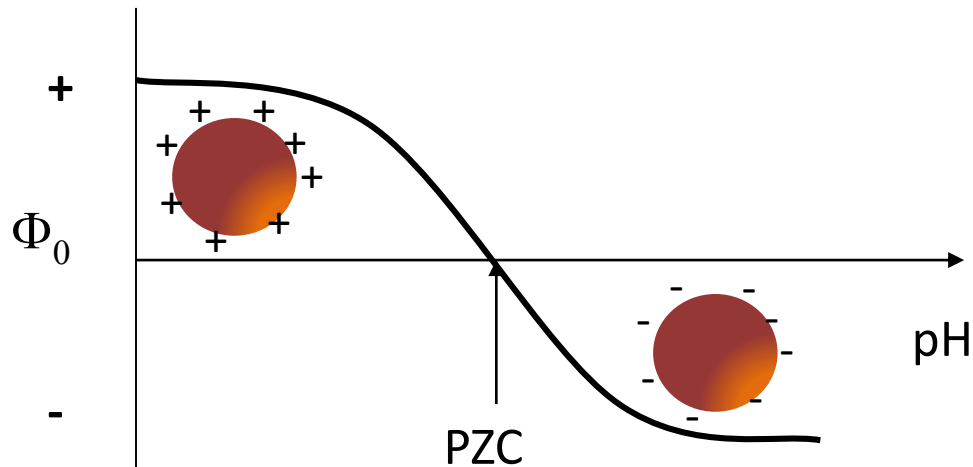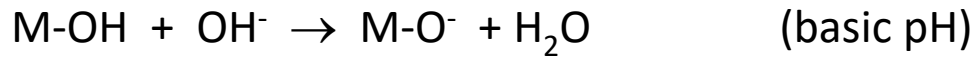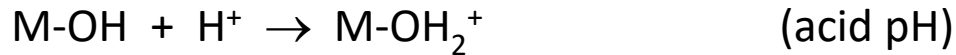- **Adsorption of charged species (figures below)**
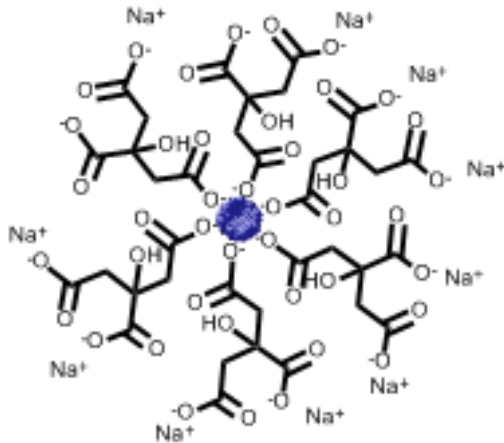
Citrate-capped metal
nanoparticle
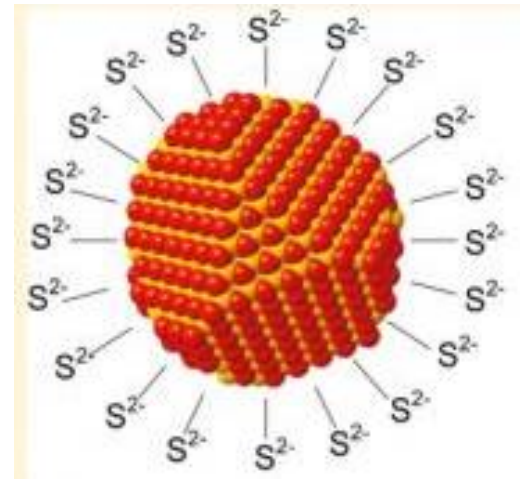
Sulphur-capped metal
chalcogenide nanoparticle

Electrostatic stabilization

Accumulation or loss of electrons at the surface: e.g. hydrated oxides in water

$M\text{-}OH + H^+ \rightarrow M\text{-}OH_2^+$ (acid pH)

$M\text{-}OH + OH^- \rightarrow M\text{-}O^- + H_2O$ (basic pH)

Mineral	pzc
Fe_2O_3, $FeOOH$	6-8
TiO_2	4-6
SiO_2	2-3
MnO2	2-4
Al_2O_3, $AlOOH$	8-10
PbS, CdS	2-3
proteins	6-8
Latex particles (COOH)	4-6

Φ_0

PZC

«Point of Zero Charge»

sensitive to adsorbed ions and molecules,
cristallinity of the particles and ionic strength
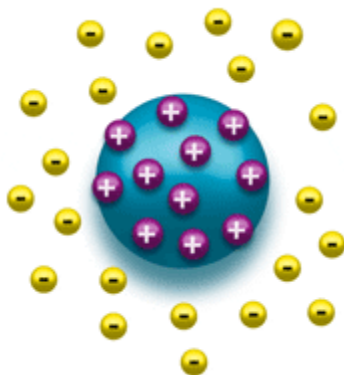
Electrostatic stabilization

2. Double layer

Driving forces for order:
- Charge at the surface
- → Electrostatic interaction with charged species in solution
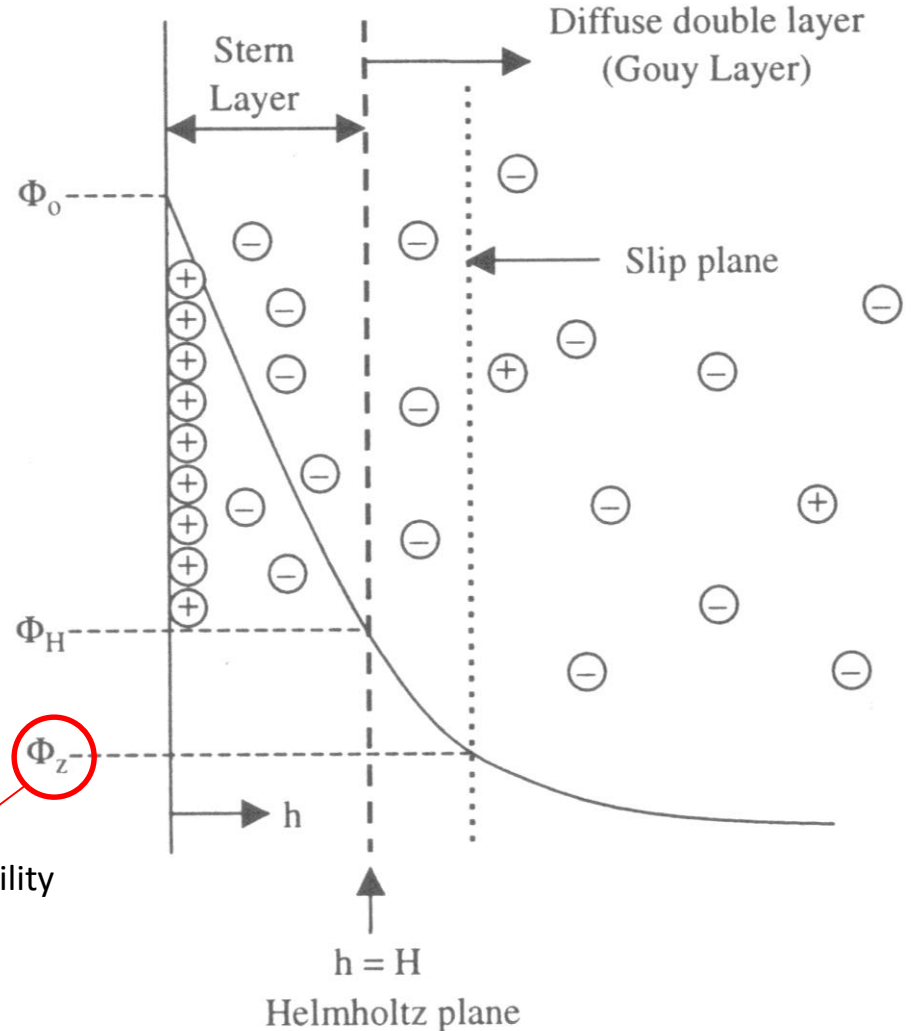
Driving forces for disorder (homogenization):
- Brownian motion
- Entropy

Counterions distribute in a **double layer**

«zeta potential»

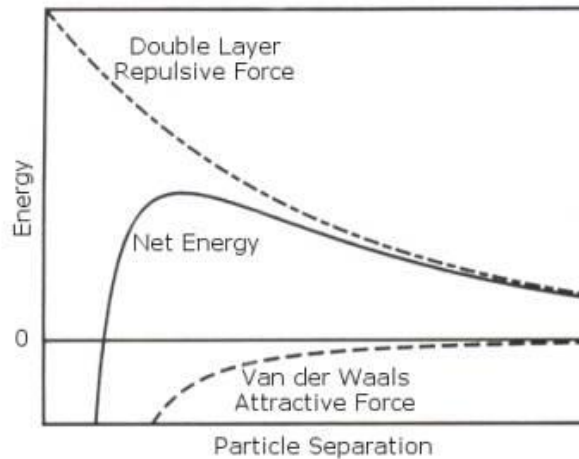Determines the stability of a colloid

Electrostatic stabilization
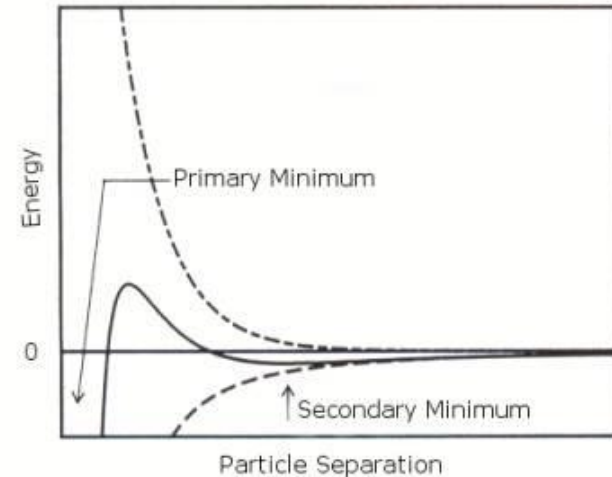
3. DLVO Theory

Interaction between charged particles in a liquid: balance between
- Electrostatic repulsion (depends on zeta potential)
- Van der Waals (dipole) attraction

**Strong electrostatic repulsion (high zeta potential)**
→No aggregation

If secondary minimum forms
→ Weak aggregation possible

| Zeta potential [mV]	Stability behavior of the colloid
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

LOOK AT RECENT (2015) WORK BY Nick Kotov, showing that DLVO approximations are actually not valid for nanoparticles. Granularity at the atomic-molecular level make the forces at play «non-additive»

Steric stabilization
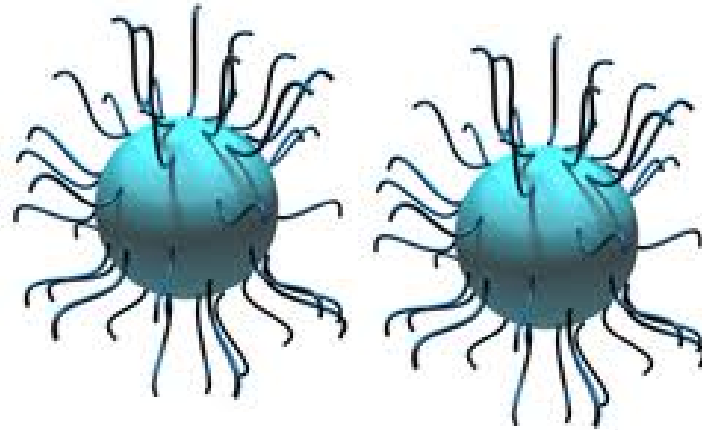
Addition of molecules («capping agents», «ligands», «surfactants») on the surface of the nanoparticle

In most cases organic molecules:

Oleic acid

Mercaptopropionic acid

citrate
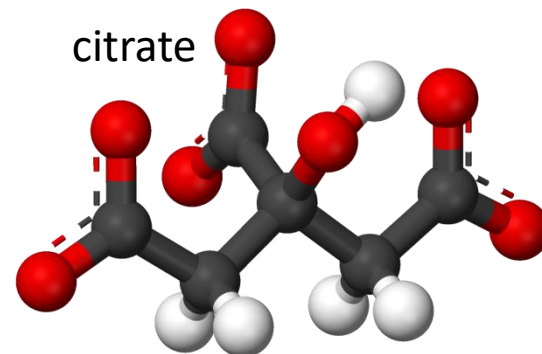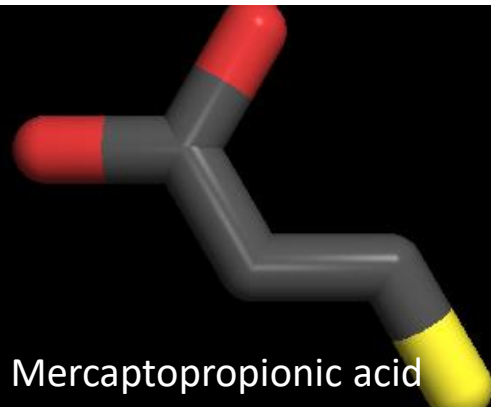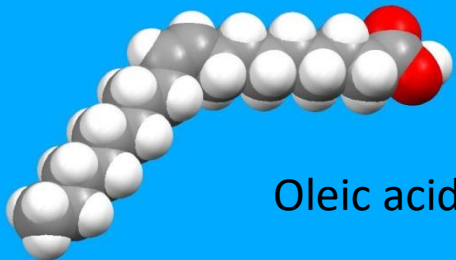
Steric stabilization

Affinity between solvent and polymer capping agents:
- «Good solvent»: chain expands (e.g. oleic acid in octadecene)
- «Bad solvent»: chain contracts

Table 2.5. List of some solvents with their dielectric constants.

| Solvent	Formula	Dielectric constant	Type
Acetone	C_3H_6O	20.7	Aprotic
Acetic acid	$C_2H_4O_2$	6.2	Protic
Ammonia	NH_3	16.9	Protic
Benzene	C_6H_6	2.3	Aprotic
Chloroform	$CHCl_3$	4.8	Aprotic
Dimethylsulfoxide	$(CH_3)_2SO$	45.0	Aprotic
Dioxanne	$C_4H_8O_2$	2.2	Aprotic
Water	H_2O	78.5	Protic
Methanol	CH_3OH	32.6	Protic
Ethanol	C_2H_5OH	24.3	Protic
Formamide	CH_3ON	110.0	Protic
Dimethylformamide	C_3H_7NO	36.7	Aprotic
Nitrobenzene	$C_6H_5NO_2$	34.8	Aprotic
Tetrahydrofuran	C_4H_8O	7.3	Aprotic
Carbon tetrachloride	CCl_4	2.2	Aprotic
Diethyl ether	$C_4H_{10}O$	4.3	Aprotic
Pyridine	C_5H_5N	14.2	Aprotic

Steric stabilization

Types of interaction between polymer capping and particle surface
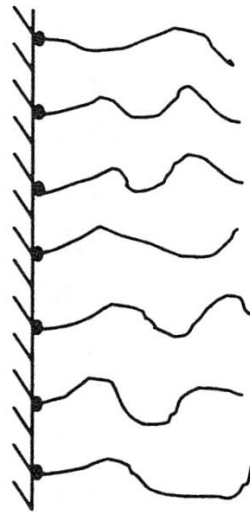
Anchored   Absorbed
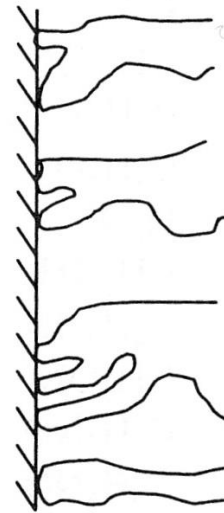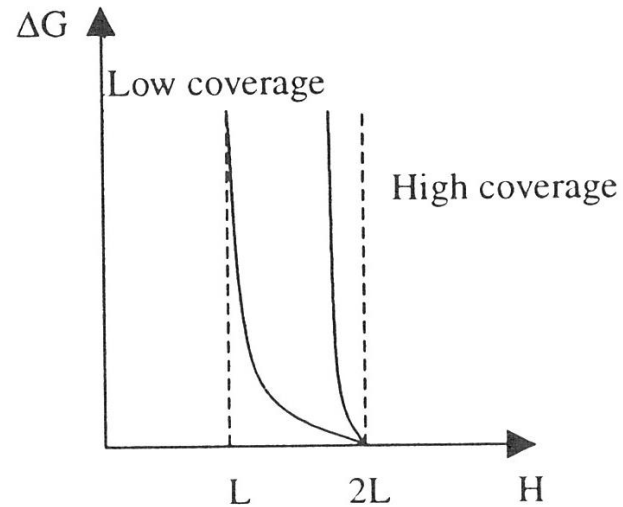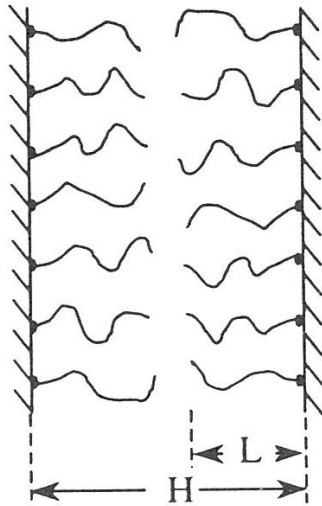
Steric stabilization
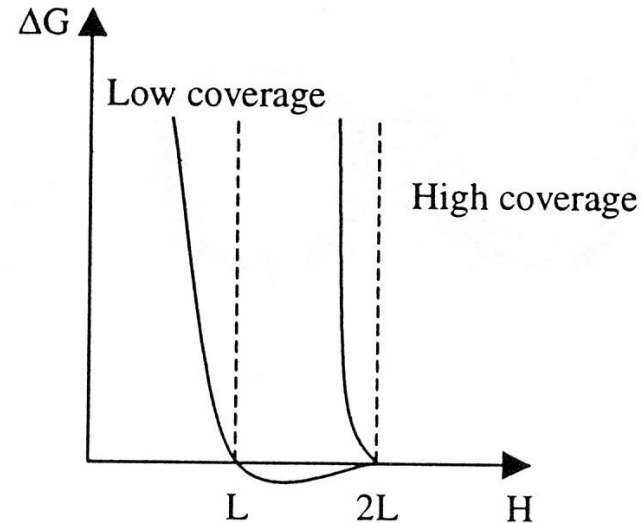
$$\Delta G = \Delta H - T\Delta S$$

GOOD SOLVENT

Low coverage: for H < 2L there is interpenetration of the polymers → $\Delta S < 0$
High coverage: for H < 2L compression of the polymers $\Delta G > 0$

Steric stabilization

$$\Delta G = \Delta H - T\Delta S$$

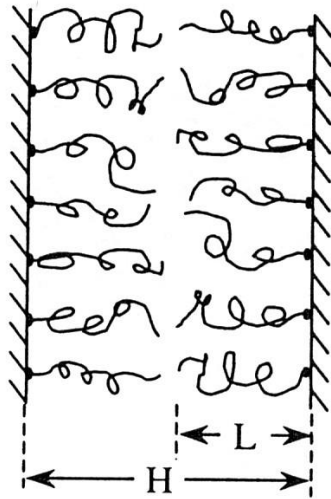**BAD SOLVENT**

Low coverage
- For L < H < 2L there is interpenetration of the polymers → more entanglement is promoted → $\Delta S > 0$ and **$\Delta G < 0$**
- For H < L: compressive forces → $\Delta G > 0$

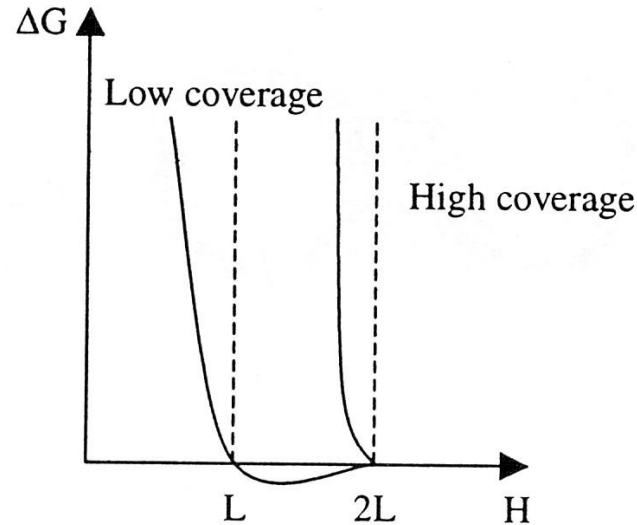High coverage: for H < 2L there are compressive forces → $\Delta G > 0$

Stabilizzazione sterica

CATTIVO solvente

$\Delta G = \Delta H - T\Delta S$

(a)

(b)

Fig. 2.21. Schematic of interactions between polymer layers: (a) the schematic of two approaching polymer layers and (b) the Gibbs free energy as a function of the distance between two particles.

Scarso ricoprimento: per L<H<2L interpenetrazione dei polimeri che promuove ulteriore attorcigliamento $\Delta S>0$, per H<L forze repulsive $\Delta G>0$
Buon ricoprimento: per H<2L compressione dei polimeri $\Delta G>0$

Advantages/disadvantages

Electrostatic

- Does not need special surface chemistry
- Electrostatically stabilized particles cannot be redispersed if they aggregate
- Can be used for only diluted suspensions
- Difficult to apply to multiple phase systems
- Cannot be applied to electrolyte sensitive systems

Steric

- Sterically stabilized particles can be redispersed if they aggregate
- Can be used even for very concentrated suspensions
- Can be applied to multiple phase systems
- Can be applied to electrolyte sensitive systems
- Can be used as an aid to control the synthesis
- Needs addition of chemical species at the surface

Electrosteric stabilization

(a)

(b)
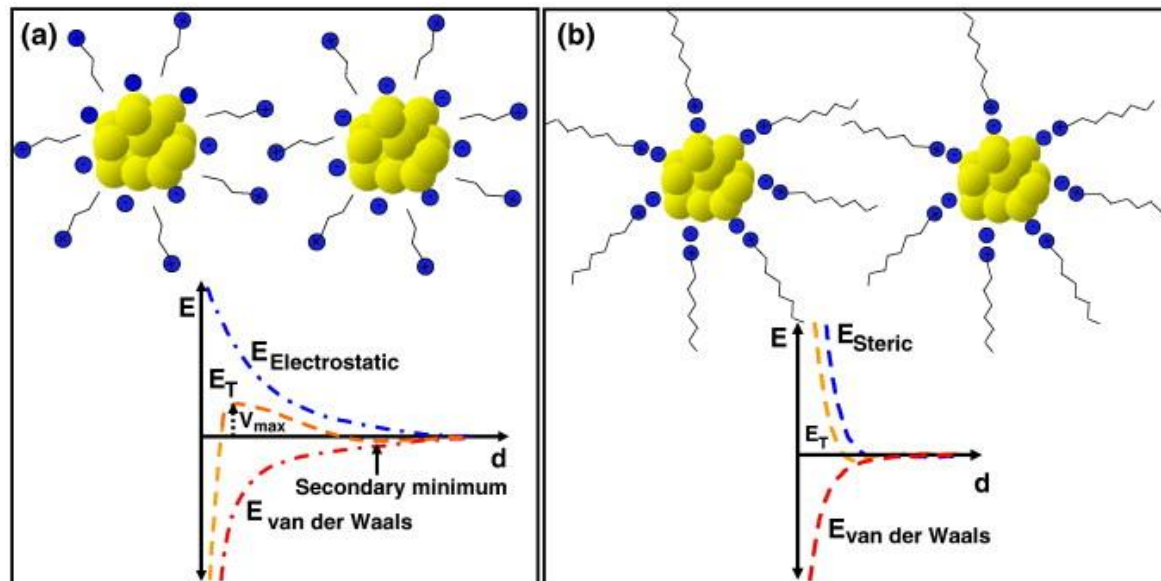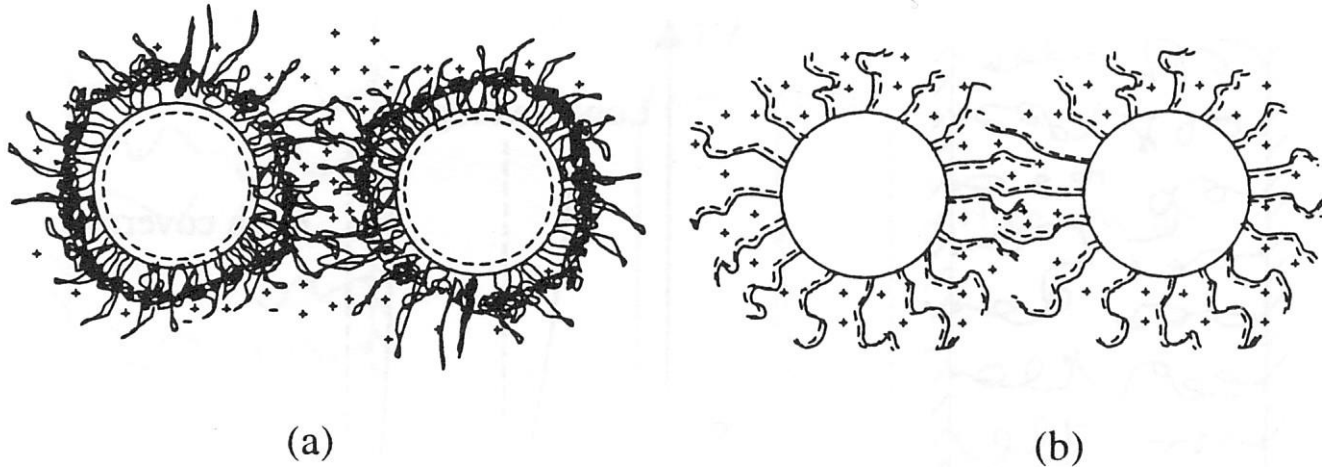
Fig. 2.22. Schematic representation of electrosteric stabilization: (a) charged particles with nonionic polymers and (b) polyelectrolytes attached to uncharged particles.