Chapter 6. Surface Properties of Nanoparticles

6.1 Surface Energy

Surface energy: energy required to create a unit area of new surface

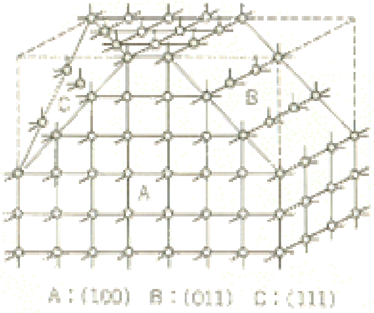
$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{n_i,T,P}$$

Can be represented roughly $\sigma = \frac{1}{2} N_b \varepsilon \rho_a$

where N_b: *number of broken bonds by forming new surface*

ε : *half of bond strength*

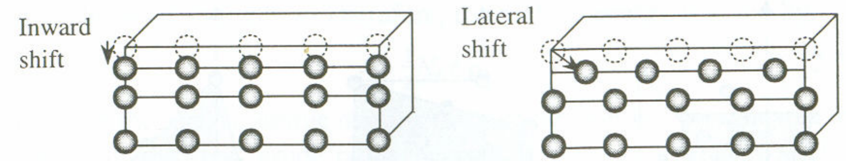
ρ_a : *surface atomic density*



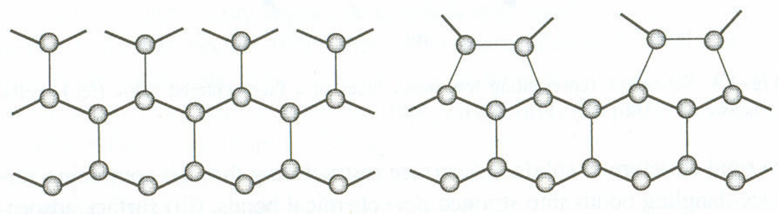
Unsaturated coordination on surfaces

Strong tendency for a solid or a liquid to minimize the total surface energy by

- Surface relaxation: inward shift of surface atoms or ions



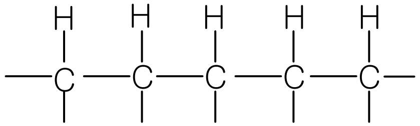
- Surface restructuring



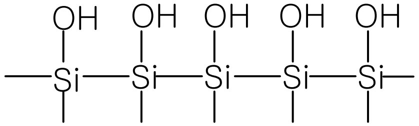
Original {100} surface

(2×1) restructured {100} surface

- *Chemical and physical adsorption on its surface*



Diamond surface



Silicon surface

    - *Surfactant*

- *composition segregation or enrichment of impurities on surfaces*

cf. Surface roughening above a transition temperature due to thermal motion

- *Combination of individual structures together to form large structures*
    - *reduce the overall surface energy*
    - *Sintering: individual structures merge together*
    - *Ostwald ripening: growth of large particles at the expense of smaller particles*
- *Agglomeration : do not alter the individual structures*
        - *The smaller agglomerates, the stronger association*

Effect of surface curvature on surface energy

Moving some mass (dV cm^3, dn molecules) from flat surface to a particle with a radius R, $dV = \frac{\pi}{2} d_p{}^2 dd_p = v_m dn$ *and* $dA = \pi d_p dd_p$

Where v_m*: molecular volume (can be* v_a *for metals)*

Work per atom moved

$$\Delta\mu = \mu_{ps} - \mu_\infty = \sigma \frac{dA}{dn} = \sigma \frac{dA}{dV / v_m}$$

$$\therefore \Delta\mu = \sigma \frac{v_m}{d_p}$$ *Young-Laplace equation*

For any curved surface

$$\Delta\mu = \sigma v_m \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

For convex surface, R_1*,* R_2*: positive: increase in surface potential*

For concave surface the reverse is true!

Form flat surface of liquid to vapor,

$$\mu_v - \mu_\infty = -kT \ln p_\infty$$

From curved surface to vapor,

$$\mu_v - \mu_c = -kT \ln p_c$$

$$\therefore \mu_c - \mu_\infty = \Delta\mu = kT \ln \frac{p_c}{p_\infty}$$

Combining with (*)

$$\ln\left(\frac{p_c}{p_\infty}\right) = \sigma v_m \frac{R_1^{-1} + R_2^{-1}}{kT}$$

Form spherical particles

$$\ln\left(\frac{p_c}{p_\infty}\right) = \frac{4\sigma v_m}{d_p kT} \qquad \textit{Kelvin equation}$$

Similarly for particles in liquid

$$\ln\left(\frac{c_c}{c_\infty}\right) = \sigma v_m \frac{R_1^{-1} + R_2^{-1}}{kT}$$

**Ostwald ripening*

- *Raising temperature to some extent promotes Ostwald-ripening…*
- *Combined sintering and Ostwald ripening lead to inhomogeneous microstructures…*

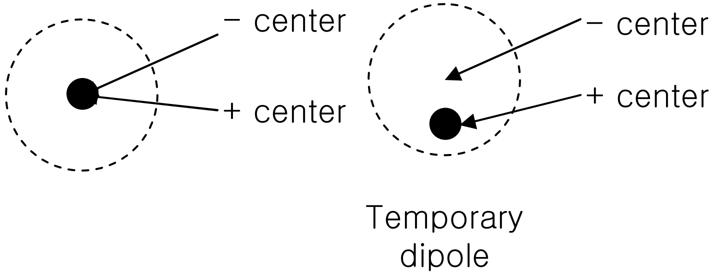
6.2 Particle-Particle Interaction

(1) van der Waals force

- Attractive force between temporary dipoles and induced dipoles ("universal" force)

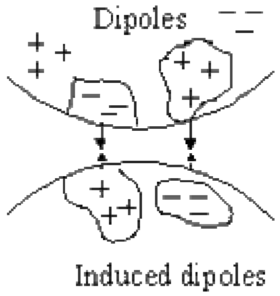
Starting from instantaneous (temporary) dipoles in an atom

“Universal” force



** Attraction potential:*

- Obtained by integrating the forces between all dipole pairs in two bodies



$$\Phi_A = -\frac{A}{6}\left\{\frac{d_p^{\,2}/2}{S^2+2d_pS}+\frac{d_p^{\,2}/2}{S^2+2d_pS+d_p^{\,2}}+\ln\left(\frac{S^2+2d_pS}{S^2+2d_pS+d_p^{\,2}}\right)\right\}$$

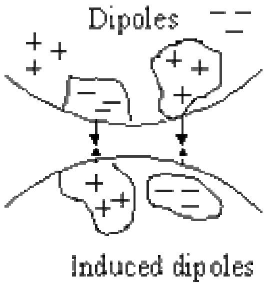
where A: Hamaker constant (~10^{-19}~10^{-20}J)

when $S \ll d_p/2$

$$\Phi_A = -\frac{Ad_p}{24S}$$

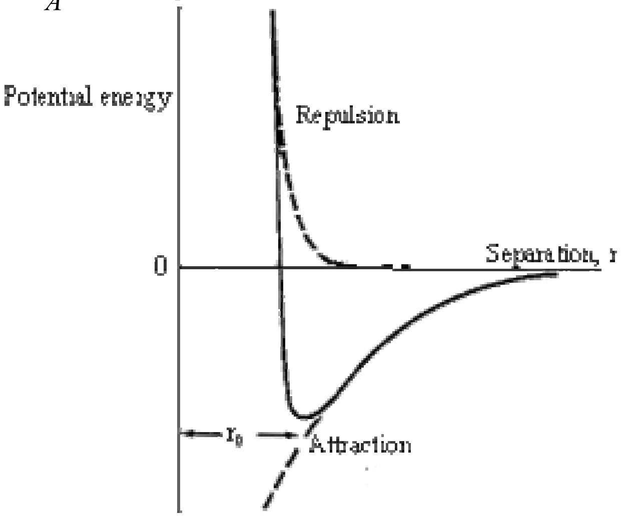
Hamaker constants (A) of materials

Interacting solids			*Hamaker constant, $A(10^{-20}\ J)$*	
solid	*media*	*solid*	*Calculated*	*Measured*
Quartz	*Vacuum (air)*	*Quartz*	6.5	5–6
Mica	*Vacuum (air)*	*Mica*	10	13.5
Metals	*Vacuum (air)*	*Metals*	30–50	–
PTFE	*Vacuum (air)*	*PTFE*	3.8	–
Quartz	*Water*	*Quartz*	8.83	–
Mica	*Water*	*Mica*	2.0	2.2
PTFE	*Water*	*PTFE*	0.33	–
(Air)	*Water*	*(Air)*	3.7	–
Quartz	*Water*	*(Air)*	–1.0	–



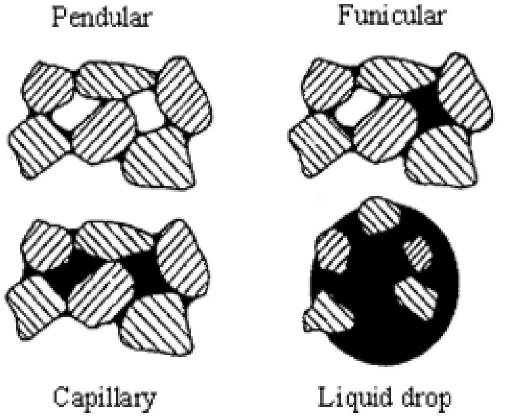
cf. Molecular attraction potential $\Phi_A \propto S^{-6}$

Lennard–Jones(6–12) potential



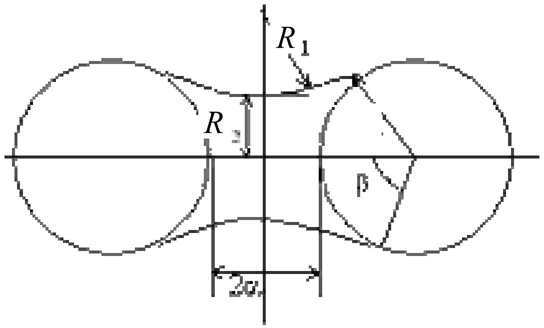
(2) Liquid-bridge

Formation of water- film bridge between two particles condensed from water vapor



Classification of liquid bridges between particles

- For pendular state



Assuming complete wetting $F = 2\pi R_2\sigma + \pi {R_2}^2\sigma\left(\frac{1}{R_1} - \frac{1}{R_2}\right)$

From geometric consideration $F = \frac{\pi d_p \sigma}{1 + \tan(\beta/2)}$

If contact, $R_2 >> R_1$, $F = \pi d_p \sigma$

** Relative humidity vs. liquid bridge*

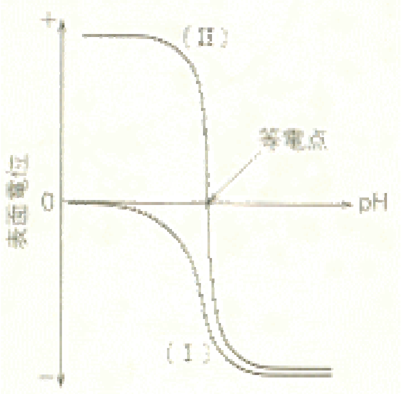
$$\ln\left(\frac{p_c}{p_\infty}\right) = \sigma v_m \frac{{R_1}^{-1} + {R_2}^{-1}}{kT}$$ *Kelvin equation*

(3) Electrostatic repulsion in liquid media

<u>Surface charge density</u>

Surface charging mechanisms in liquid

- *Preferential adsorption of ions*
- *Dissociation of surface charged species*
- *Isomorphic substitution of ions*
- *Accumulation or depletion of electrons at the surface*
- *Physical adsorption of charged species on to the surface*



Surface charge varies pH of the medium:

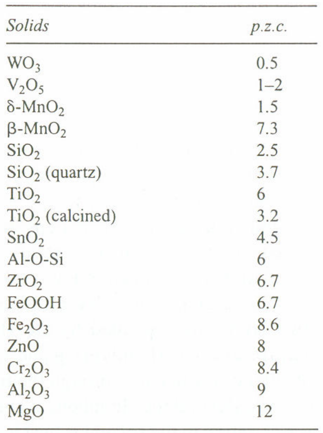
- *Point of zero charge (pzc)*

For oxides, pH < pzc: positively charged and vice versa ($pH = -\log[H^+]$)

$$E_0 = \frac{2.303RT(pzc - pH)}{F}$$

At room temperature

$$E_0 \sim 0.06(pzc - pH)$$



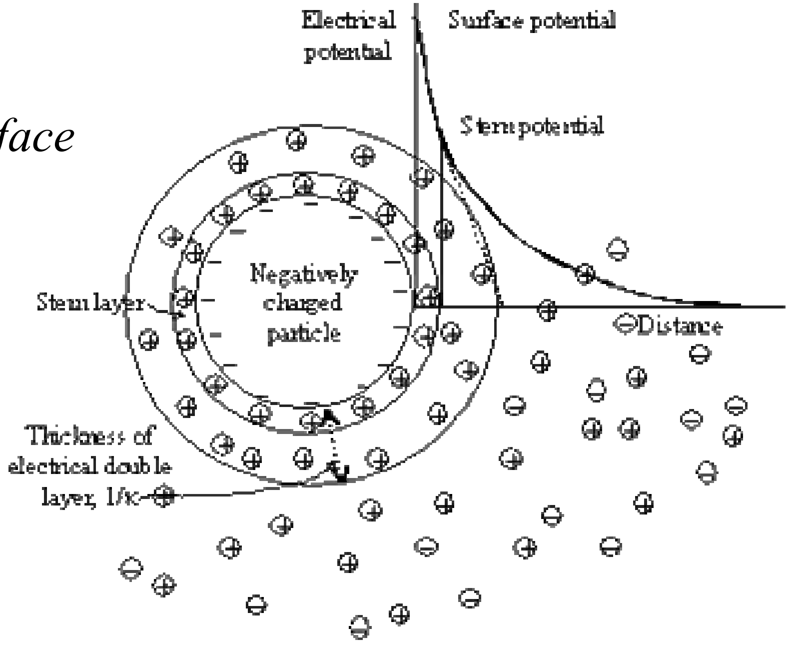
Solids	*p.z.c.*
WO_3	0.5
V_2O_5	1–2
δ-MnO_2	1.5
β-MnO_2	7.3
SiO_2	2.5
SiO_2 (quartz)	3.7
TiO_2	6
TiO_2 (calcined)	3.2
SnO_2	4.5
Al-O-Si	6
ZrO_2	6.7
FeOOH	6.7
Fe_2O_3	8.6
ZnO	8
Cr_2O_3	8.4
Al_2O_3	9
MgO	12

Electric potential at the proximity of particle surface

- *Distribution of electric potential around solid surface*
  - *Coulombic force or electrostatic force*
  - *Entropic force, dispersion*
  - *Brownian motion*
- *Electrical double layer*

  Around a charged particle:

  - *Stern layer : layer of adsorbed counter ions*
  - *Diffuse layer: layer of ions in a balance between electrostatics and diffusion caused by thermal motion.*



* *Electrical potential* $E \propto e^{-\kappa(h-H)}$

where $\kappa = \sqrt{\dfrac{F^2 \sum_i c_i {z_i}^2}{\varepsilon_r \varepsilon_0 RT}}$

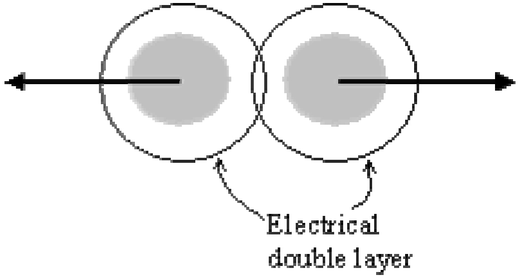
Where κ *: inverse of the thickness of electrical double layer*
h : distance from the surface
H : Stern layer thickness
F : Faraday constant
c_i *: bulk ion concentration*
z_i*: ionic valence*
ε_0*: permittivity of vacuum*
ε *: dielectric constant of the solvent*

In water,

$$\kappa = 3.29 \times 10^{9} z_i \sqrt{c_i}$$

where c_i*: mol/cm*^{3}

Electrical repulsion between two equally sized spherical particles



$$\Phi_R = \pi \varepsilon_r \varepsilon_0 d_p E_0{}^2 e^{-\kappa S}$$

where S: the nearest distance from surface to surface

(4) DLVO Theory (Deryagin - Landau and Vewey Overbeek) theory - In liquid media

** Assumptions*

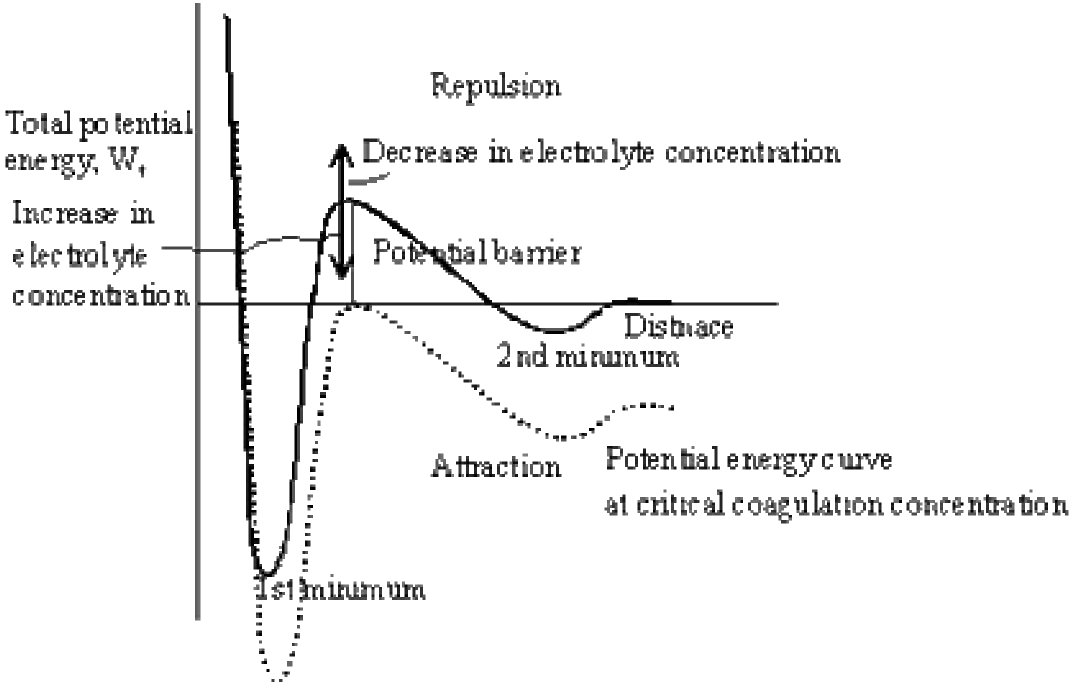
Dilute dispersion (no interference)

No other forces besides van der Waals force and electrostatic potential

Uniform surface property

$$\Phi = \Phi_A + \Phi_R$$

** Total potential between two particles*



- *To increase dispersion of particles*
  - *Increase the surface charge or zeta potential .*

    e.g. by adsorption of citrate and chloride ions for gold and hexametaphosphate ion for sulfide semiconductor nanoparticles
  - *Decrease the ionic strength of the dispersing medium.*

- *To coagulate particles*
  - *Reduce the surface charge by the displacement of the adsorbed anions by a more strongly bound neutral molecule or cation*

    e.g. adding pyridine to gold sol.
  - *Add electrolytes to the media*

**Critical coagulation concentration (CCC)*

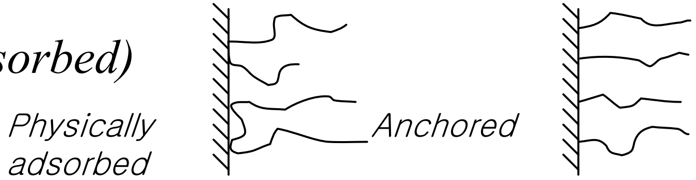
- *From* $\Phi = 0$ *and* $\frac{d\Phi}{dS} = 0$

- *Solving two equations simultaneously for* c_i

$$ccc = \frac{107(\varepsilon_0 \varepsilon_r)^3 k^5 T^6 \sigma^4}{A^2 (Z_i e)^6}$$

(5) Steric stabilization in liquid media

** Physically adsorbed vs. anchored (chemically adsorbed)*

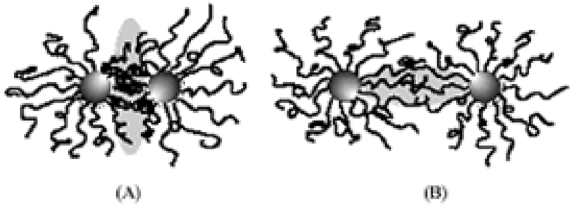


** Morphologies of polymers adsorbed on particle surface*

- The goodness is determined by the nature of polymer-solvent interaction and temperature

- Prevention of agglomeration by polymer molecules adsorbed physically or chemically on particle surface*

Entropic effect $\Delta G = \Delta H - T\Delta S > 0$



Osmotic effect: exclusion of solvent between two approaching particles

**Electrostatic vs. steric stabilization*

Electrostatic stabilization	*Steric stabilization*
Kinetic stabilization	*Thermodynamic stabilization*
Applicable to dilute particle systems	*Applicable to high concentration possible*
Sensitive to electrolyte	*Insensitive to electrolyte*
Unsuitable to multiple phase system	*Suitable to multiple phase system*

-Polymers adsorbed also serve as a diffusion barrier to suppress polydisperse growth of particles.

6.3 Surface modification of nanoparticles

- *to promote the stability of the particles in liquid media*
- *to alter hydrophillicity of particle surface to hydrophobicity*
- *to couple biomaterials for biological purpose (recognition, delivery, manipulation)*
- *to produce building blocks for assembly (devices)*
- *to obtain functional nanoparticles (core-shell structure)*[1]

** Types of surface modification*

  - *Anquored /Adsorbed: in-situ/ post-treatment*
  - *Core-shell: coating via heterogeneous nucleation route*

(1) Surface modifiers

- Surfactants

- Coupling agent (silane)

- Polymers

** Choice of surface modifier*

  - Depending on where to be used

  In general,

  - requires balance between adsorption vs. affinity to the solvent (good solvent)

** Natural polymer stabilizers: gelatin, agar, cellulose acetate, cellulose nitrate, cyclodextrins*

- Synthetic polymer stabilizers:

  - vinyl polymers with polar side groups

    e.g. polyvinylpyrrolidone, polyvinyl alcohol

  - vinyl pyrrollidone - vinyl alcohol copolymer (Ag)

- *Combined effect of electrostatic and steric stabilizations:*
    - *Charged particles with nonionic polymers*
    - *Poly electrolytes attached to uncharged particles*

        long-chain alkylammonium cations and surfactants
- *Recent trend*
    - *Use of relatively small ligand*

        *Sulfonated triphenylphosphine, alkanethiol**

* *Silane: compounds containing silicon-hydrogen bonds,* SiH_4

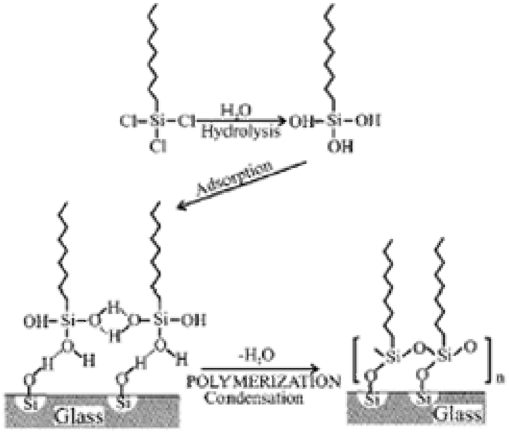
Trichlorosilane: $HSiCl_3$

disilane: H_3SiSiH_3

methylsilane: CH_3SiH_3

methyldichlorosilane: CH_3SiHCl_2

triethylsilane: $(C_2H_5)_3SiH$



Hydrolysis with their molecules and surface

* *Thiol: sulfur analogous of alcohol*

"mercaptan"

2-mercaptoethanol: $HSCH_2CH_2OH$

Mercaptoacetic acid: $HSCH_2COOH$

1-amino-2-propanethiol: $H_2NCH_2CH(SH)CH_3$

Thiophenol: C_6H_5SH

- Dithiol:

1,2-ethanedithiol: $HSCH_2CH_2SH$

(2) Methods of surface modification

- Insitu

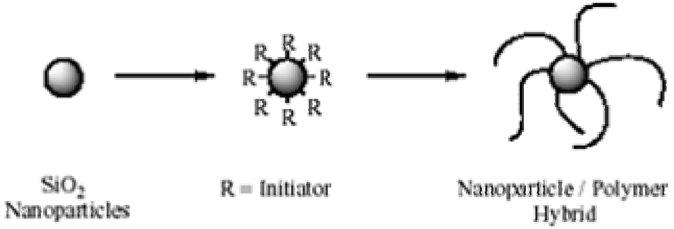
Preparation from precursor+ polymer solution

Simultaneous preparation for NP and polymer

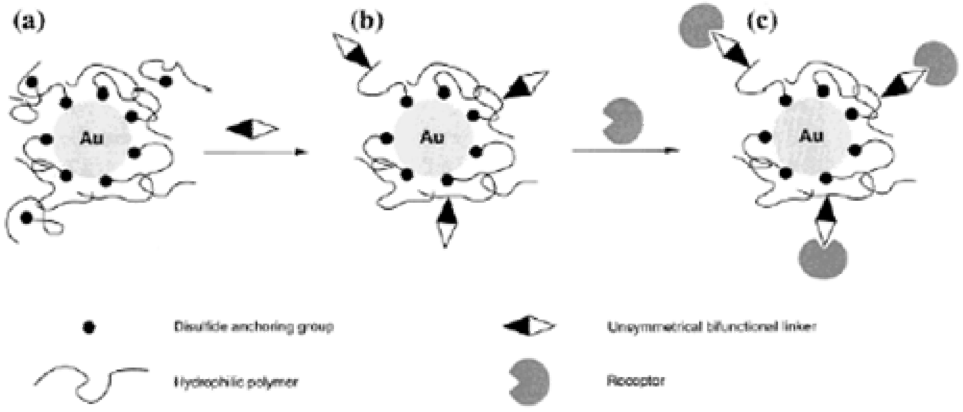
Preparation from single precursor

- Post-treatment

Grafting by polymerization from surface-immobilized initiators)



Grafting to:



*Stepwise "grafting-to" derivatization of gold surfaces. (a) Fixation of the **polymer with disulfide anchoring** groups. (b) Activation of the polymer*

*Stepwise "grafting-to" derivatization of gold surfaces. (a) Fixation of the **polymer with disulfide anchoring** groups. (b) Activation of the polymer*

*by **unsymmetrical bifunctional linker** groups. (c) Functionalization of the polymer by **receptors**. Step b is omitted when "activated" polymers are used.*

6.4 Application of Dispersed Nanoparticles

(1) Catalysts

* *Advantage of nanoparticle catalysts*

- *very large surface area: "atom economy"*
- *enhanced* ***intrinsic chemical reactivity***
  - *edge and corner effect*
  - *anion / cation vacancies*
  - *distorted in bonding patterns*

* *Catalyst materials*

Metals : Pt (or Pd), Au based, other metals (Cu, V, Rh)

Nonmetallic : MgO, MoS_2, CeO_{2-x}, NiO, Cr_2O_3, Fe_2O_3, Fe_3O_4, Co_3O_4, and β-$Bi_2Mo_2O_9$

* *Forms of* ***dispersed*** *nanoparticle catalysts*

- *Homogeneous catalysts: acids, bases, capped nanoparticles*
- *Heterogeneous catalysts*
  - *dispersed on* ***highly porous support****(400m^2/g-600m^2/g)*
    Porous silica, titania, alumina, zeolites

(2) Biomedical applications

<u>Characteristics of biomaterials:</u>

- specific and strong complementary interactions

antibody-antigen

nucleic acid-DNA

hormone-receptor

Preparation of ***biomatertial - nanoparticle conjugates***

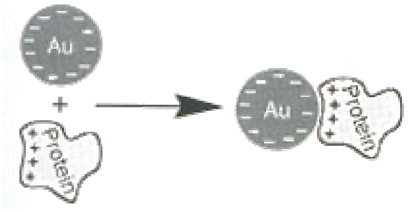
- Nanoparticles

- ***latex/ gold/ semiconductor/ magnetic*** *nanoparticles*

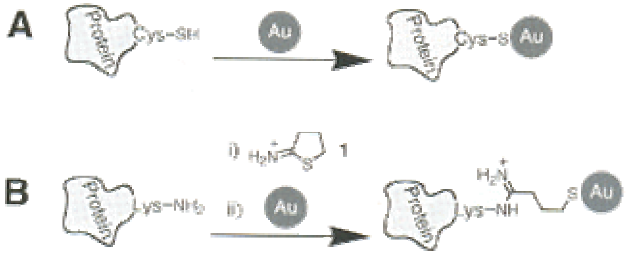
- Preparation

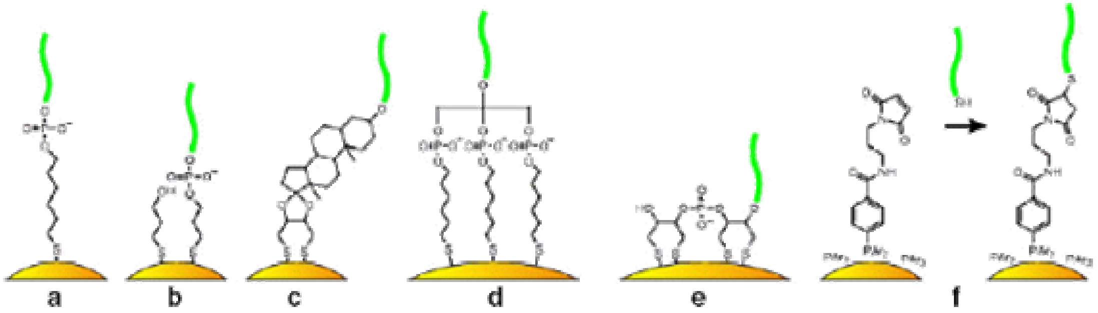
- ***electrostatic adsorption***

Au-citrate(-) + protein(+)



- *chemisorption of* ***thiol-derivatized biomaterials***





Methods for conjugating ***oligonucleotides*** *to* ***gold*** *nanoparticles. (a)* ***Thiol****-modified and (b)* ***disulfide-modified*** *oligonucleotides spontaneously bind to gold nanoparticle surfaces. Asymmetric disulfide modification adds an additional* ***mercaptoalcohol ligand*** *to the Au surface, but the density of oligonucleotides formed on the nanoparticle surface is the same as for thiol-terminal oligonucleotides. (c)* ***Di*** *and (d)* ***tri-sulfide modified*** *conjugates. (e)* ***Oligothiol****-nanoparticle conjugates. Although four thiol connections are shown, any number are possible via sequential addition of a commercial dithiane phosphoramidite during solid-phase oligonucleotide synthesis. (f) Oligonucleotide conjugates from* ***Nanoprobes' phosphine -modified*** *nanoparticles*

Applications

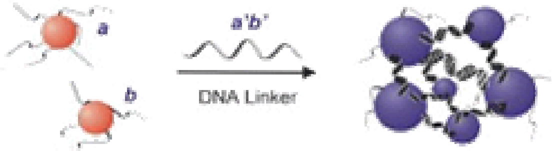
For Nanoparticle-DNA, see

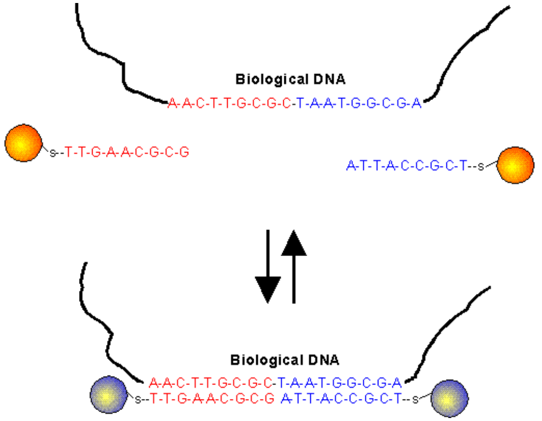
http://www.ipht-jena.de/BEREICH_3/english/molnano/pdf/36.pdf

For Biomaterial-functionalized magnetic nanoparticles, see

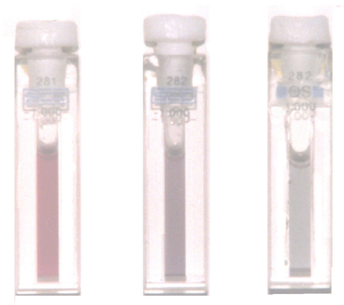
http://www.biomagres.com/content/1/1/2

- ***Reporter*** *for biochemical information (labeling, sensor)*



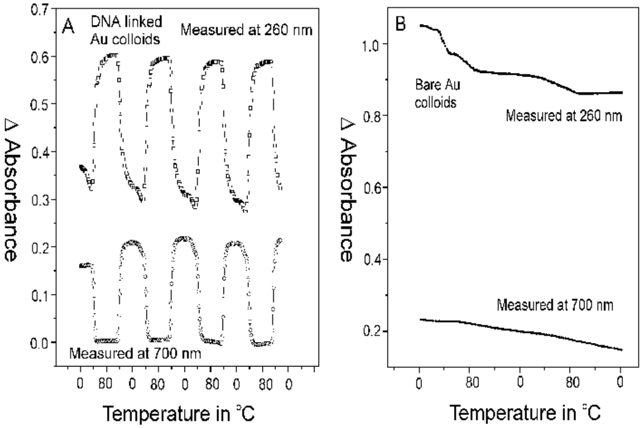


This scheme illustrates how a targeted portion of biological DNA can be used as the linker molecule to aggregate DNA modified colloids. Applications of this described system include ***sequence specific gene detection and DNA separation methodologies.***



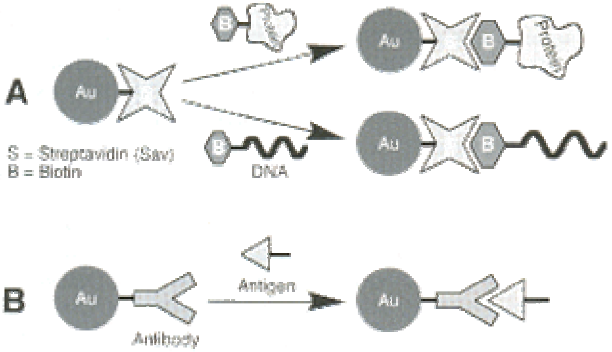
Cuvettes containing the DNA modified Au colloids and linking strands.

- *Reversible hybridization*



A) Absorbance vs. temperature/time profile for ***DNA/colloid hybridized materials****. At low temperatures the Au colloids aggregate due to the hybridization of "linking" DNA. At high temperatures (80 degrees Centigrade), the colloids are dehybridized and form a dark red solution. The temperature vs. time profile shows that this is* ***a reversible process****. B) Same analysis of an aqueous solution of* ***unmodified Au colloids****.*

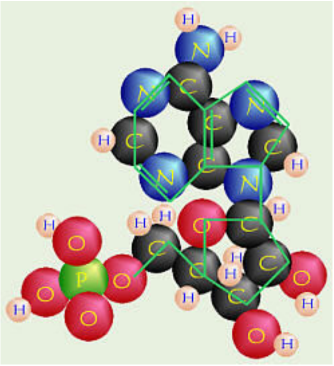
- ***Capturer*** *for bioseparation of molecules or cells*



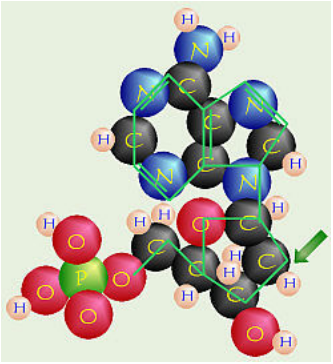
- *Drug carrier*
- *Gene carriers*

* ***DNA (deoxyribonucleic acid)*** http://library.thinkquest.org/18617/index-java_frames.html

- ***Nucleotide*** *molecules*

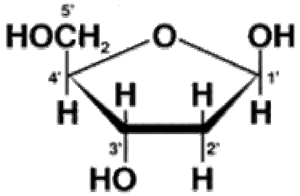


Nucleotide

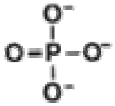


Deoxynucleotide

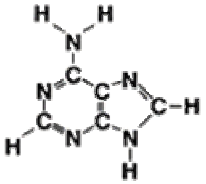
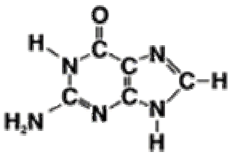
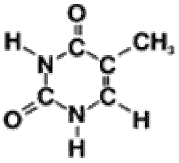
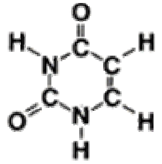
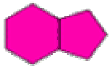
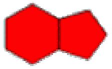
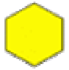
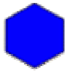
Deoxyribose sugar



Phosphate group



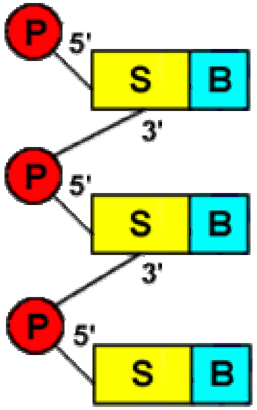
Nucleotide bases

Base	Adenine (A)	Guanine (G)	Thymine (T)	Cytosine (C)
Purine/ Pyrimidene	Purine	Purine	Pyrimidene	Pyrimidene
Chemical Structure *				
Simplified Representation				

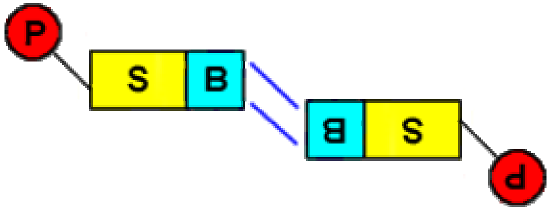
* C = Carbon, N = Nitrogen, O = Oxygen.
A single line between atoms is a single bond.
A double line between atoms is a double bond.

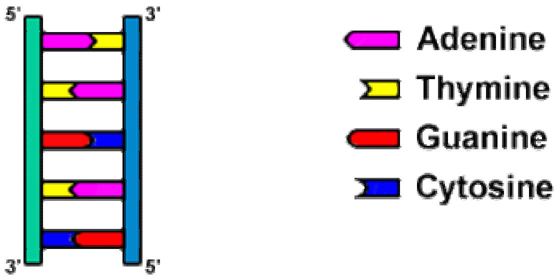
- *Structures*

Helix



Base paring





Compacted double stranded (helix) nucleotides nanowires