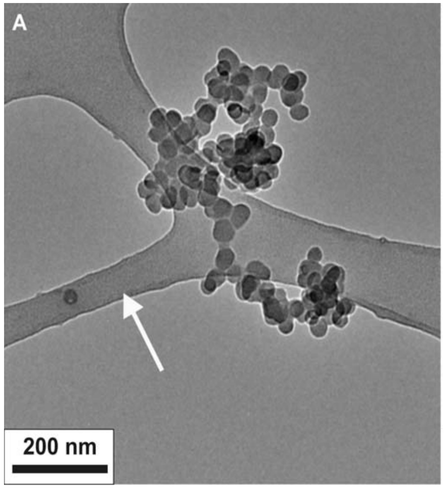
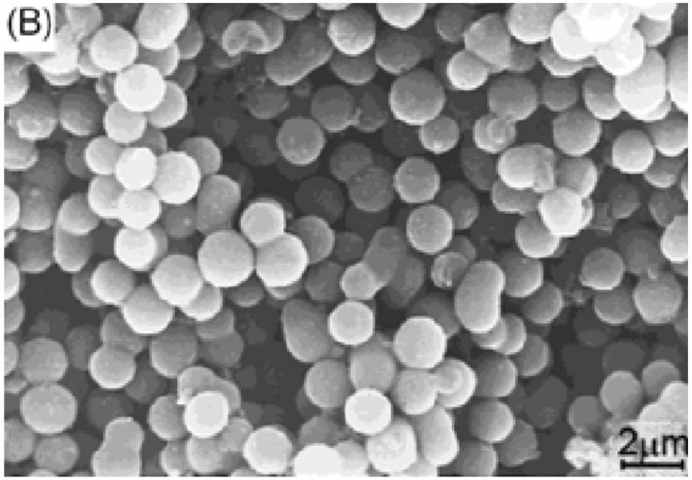
Particles and Particle Systems

Instructors: Albert Liu, Nicholas A. Kotov





Join Zoom Meeting
https://umich.zoom.us/j/91892012970

Meeting ID: 918 9201 2970
Passcode: particle

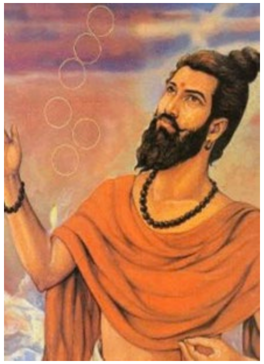
Simple Particles

Bits of History

First Particles

600 BC

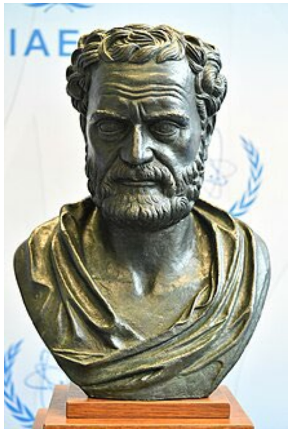
Paramanus -param�much means ultimate and 'anu' means particle.



Maharishi Kanada

460

Atoms were uniform, solid, hard, incompressible, and indestructible and that they moved in infinite numbers through empty space until stopped.



Democritus

Metal Nanoparticles

Pottery of Deruta (Umbria)

15th and 16th centuries

Recipe for the nanoparticulate glazes:

Mix copper and silver salts with vinegar, ochre, and clay and apply them to the surface of already glazed pottery.

Licurgus Cup (Italy)

Late Romans, 4th century

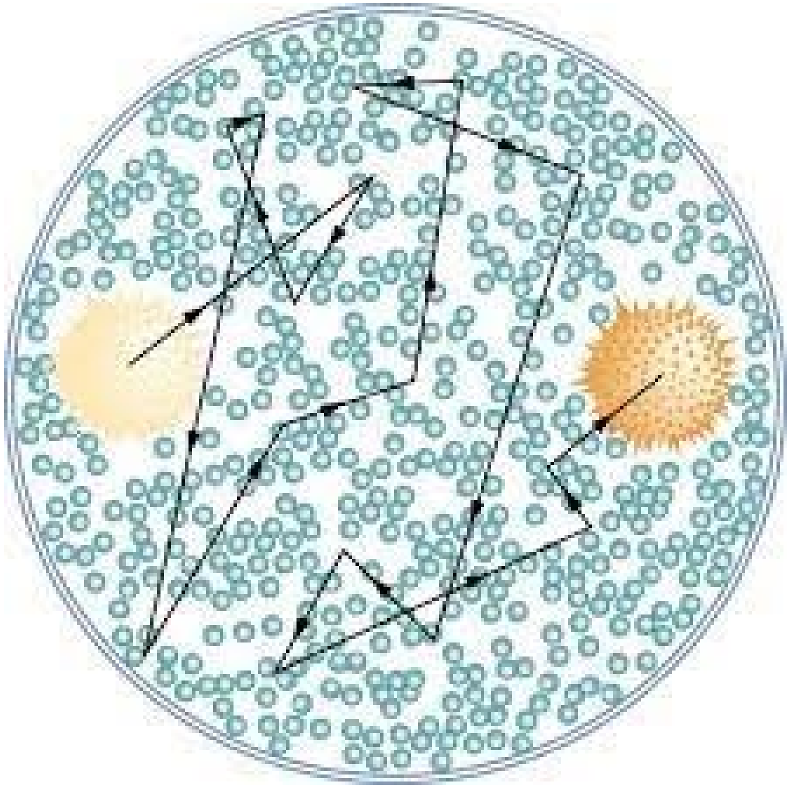
https://en.wikipedia.org/wiki/Lycurgus_Cup

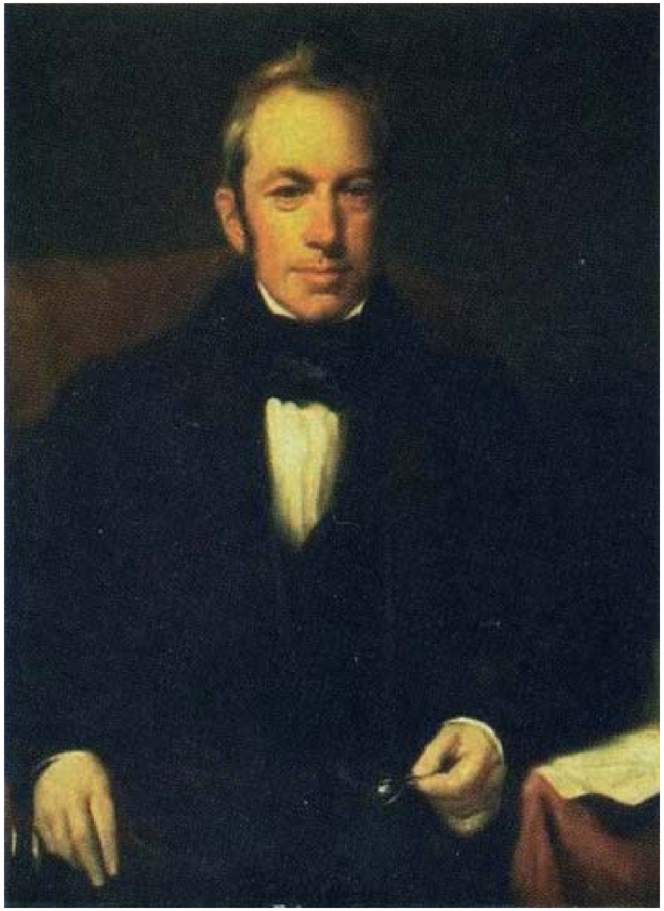
Mythical King Lycurgus tried to kill Ambrosia, a follower of the god Dionysus (Bacchus). Ambrosia was transformed into a vine that twined around the king restraining and killing him.

Microparticles in Liquids

Prof. Robert Brown

1827



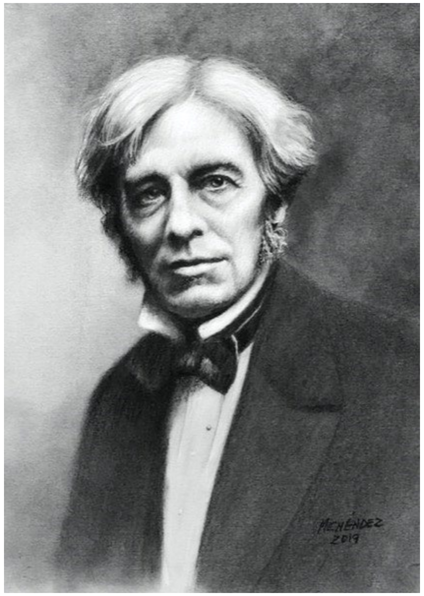


Nanoparticles in Liquids

Prof. Michael Faraday

1856

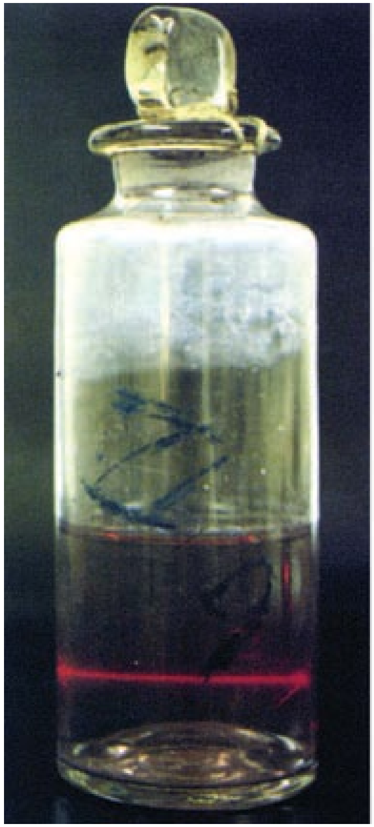
https://www.rigb.org/explore-science/explore/collection/michael-faradays-gold-colloids

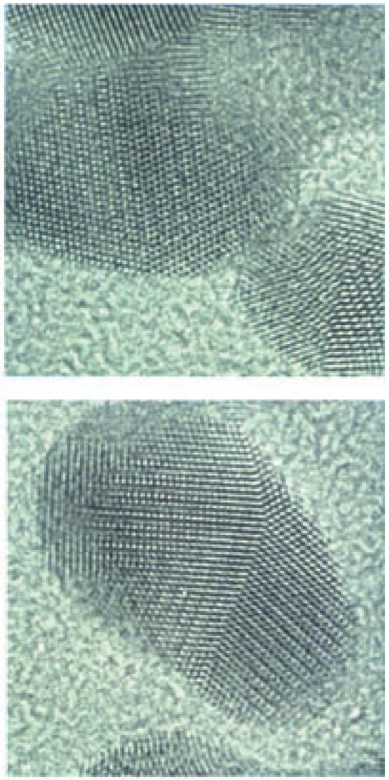


1856, Basement laboratory at the Royal Institution

Gold Nanoparticles from M. Faraday

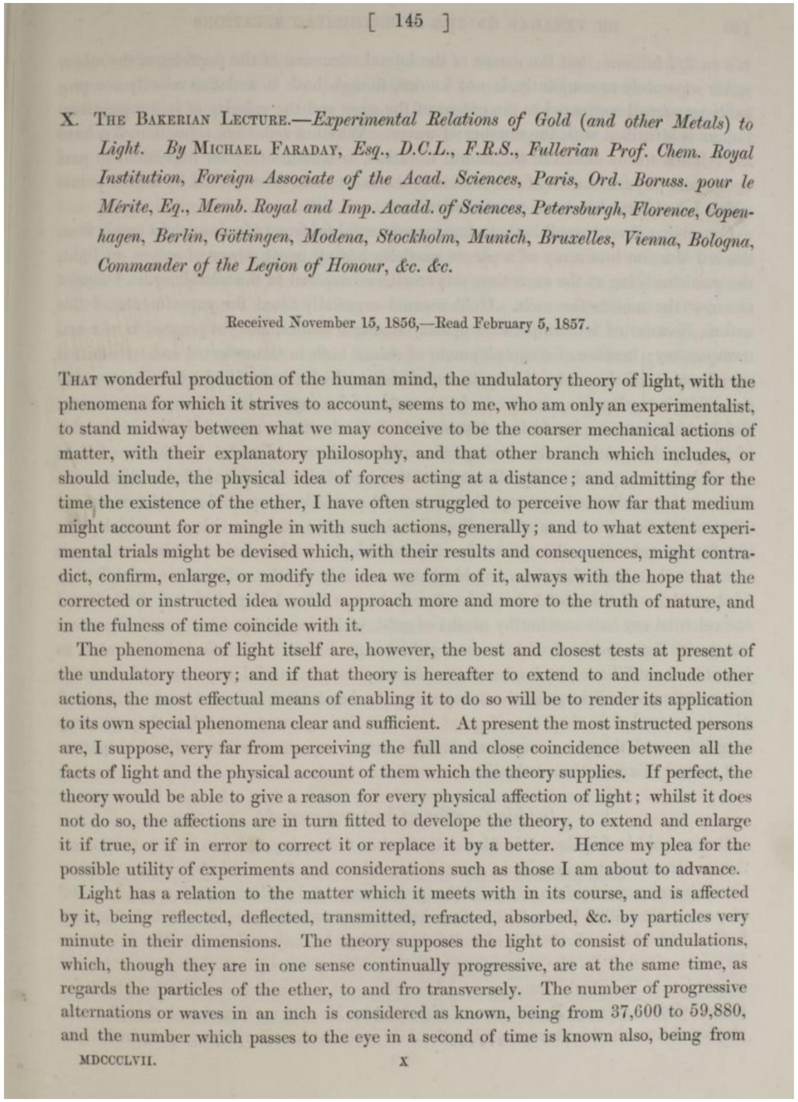
When Michael Faraday was 65 years old, he prepared pure colloidal gold using phosphorus to reduce gold chloride.





Colloidal gold - 10^7×

P. P. Edwards, J. M. Thomas, Gold in a Metallic Divided State—From Faraday to Present-Day Nanoscience, *Angew. Chem.* **2007**, 46, 5480.



[145]

X. The Bakerian Lecture.—*Experimental Relations of Gold (and other Metals) to Light.* By Michael Faraday, *Esq., D.C.L., F.R.S., Fullerian Prof. Chem. Royal Institution, Foreign Associate of the Acad. Sciences, Paris, Ord. Boruss. pour le Mérite, Eq., Memb. Royal and Imp. Acadd. of Sciences, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, Munich, Bruxelles, Vienna, Bologna, Commander of the Legion of Honour, &c. &c.*

Received November 15, 1856,—Read February 5, 1857.

That wonderful production of the human mind, the undulatory theory of light, with the phenomena for which it strives to account, seems to me, who am only an experimentalist, to stand midway between what we may conceive to be the coarser mechanical actions of matter, with their explanatory philosophy, and that other branch which includes, or should include, the physical idea of forces acting at a distance; and admitting for the time the existence of the ether, I have often struggled to perceive how far that medium might account for or mingle in with such actions, generally; and to what extent experimental trials might be devised which, with their results and consequences, might contradict, confirm, enlarge, or modify the idea we form of it, always with the hope that the corrected or instructed idea would approach more and more to the truth of nature, and in the fulness of time coincide with it.

The phenomena of light itself are, however, the best and closest tests at present of the undulatory theory; and if that theory is hereafter to extend to and include other actions, the most effectual means of enabling it to do so will be to render its application to its own special phenomena clear and sufficient. At present the most instructed persons are, I suppose, very far from perceiving the full and close coincidence between all the facts of light and the physical account of them which the theory supplies. If perfect, the theory would be able to give a reason for every physical affection of light; whilst it does not do so, the affections are in turn fitted to develope the theory, to extend and enlarge it if true, or if in error to correct it or replace it by a better. Hence my plea for the possible utility of experiments and considerations such as those I am about to advance.

Light has a relation to the matter which it meets with in its course, and is affected by it, being reflected, deflected, transmitted, refracted, absorbed, &c. by particles very minute in their dimensions. The theory supposes the light to consist of undulations, which, though they are in one sense continually progressive, are at the same time, as regards the particles of the ether, to and fro transversely. The number of progressive alternations or waves in an inch is considered as known, being from 37,600 to 59,880, and the number which passes to the eye in a second of time is known also, being from

MDCCCLVII. X

M. Faraday, The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light, Philos. Trans. R. Soc. Lond., 147 (1857) 145-181.

Gold Nanoparticles from M. Faraday

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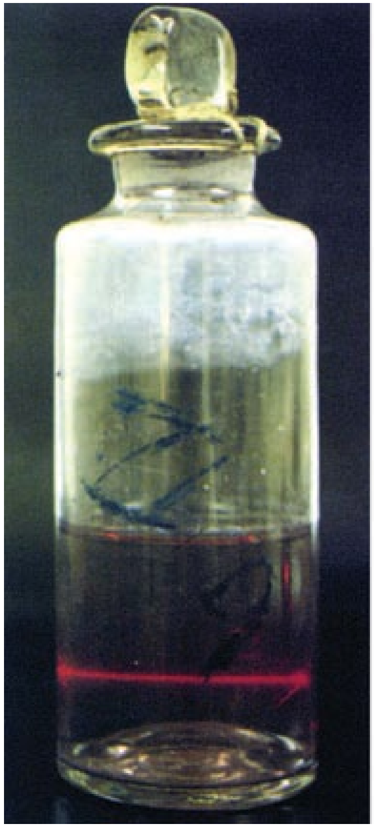
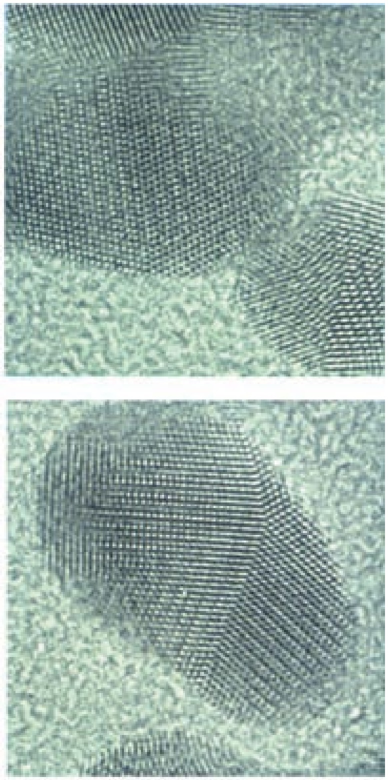




Colloidal gold - $10^7\times$

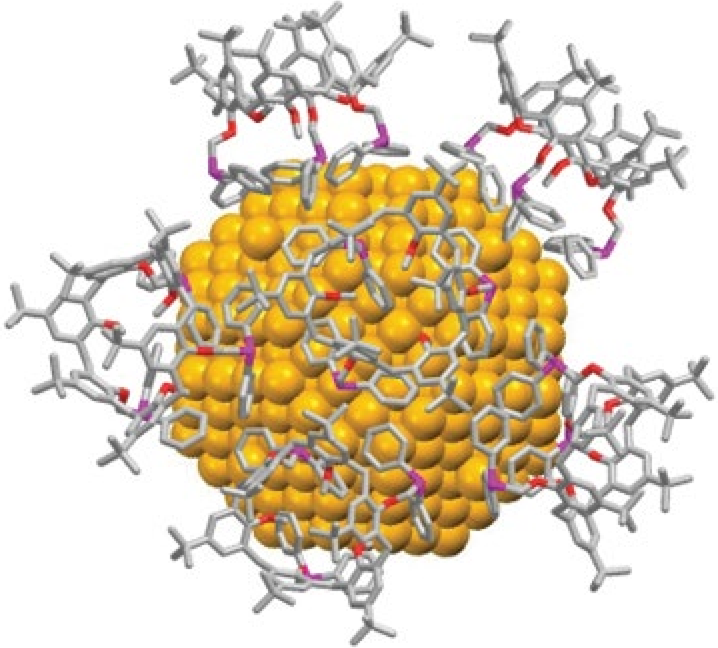


Image courtesy of Prof. Jeong-Myeong Ha/UC Berkeley

P. P. Edwards, J. M. Thomas, Gold in a Metallic Divided State—From Faraday to Present-Day Nanoscience, *Angew. Chem.* **2007**, 46, 5480.

Particle-Wave Dualism

Prof. Louis De Broglie **1923**

$$\lambda_{dB} = h/p$$

All particles are waves!

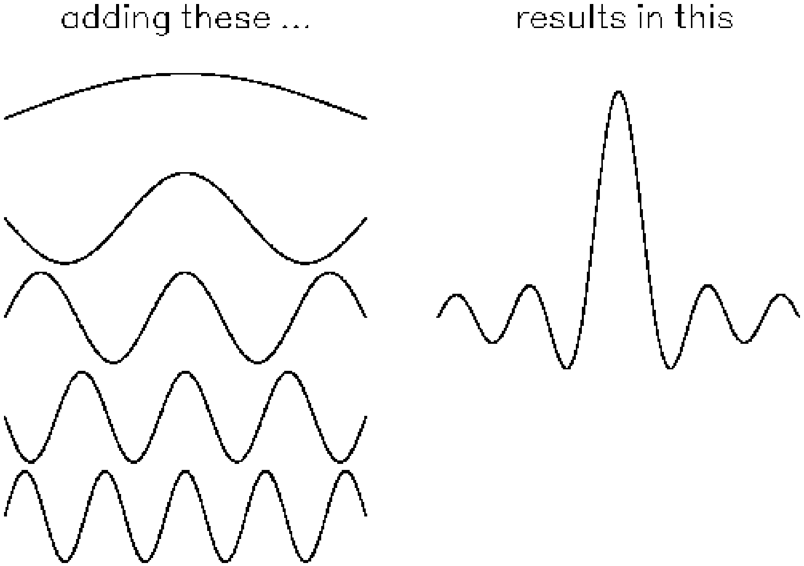
λ_{dB} = **de Broglie wavelength**

h = **Planck's Constant**
6.63 × 10^{-34} Joule·second

p = **momentum of particle**
= mass × velocity

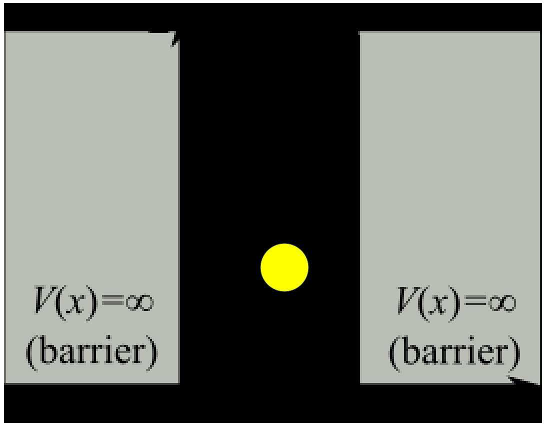
$E = p^2/2m$
m – particle mass

$E = (h/\lambda)^2/2m$



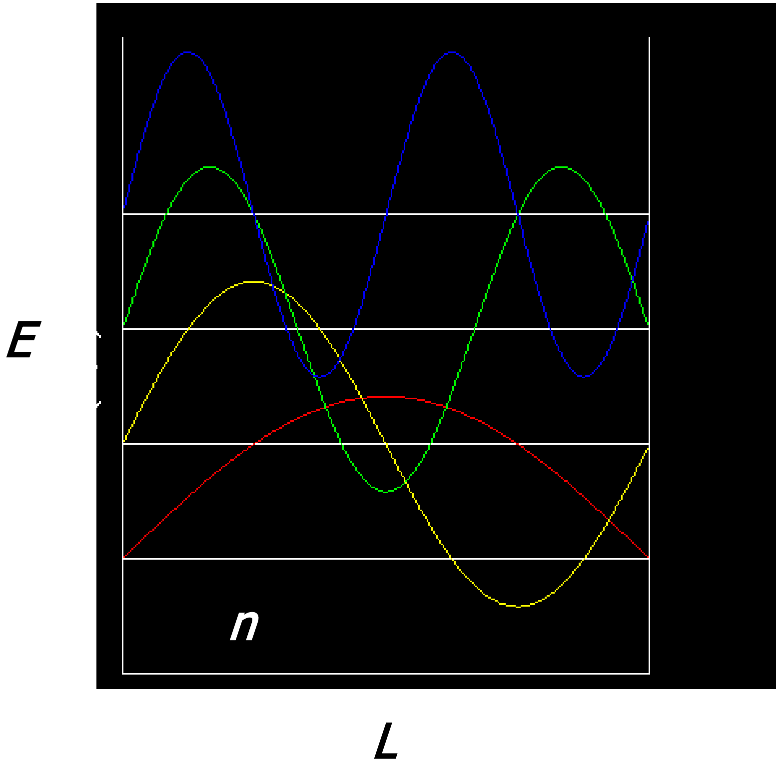
http://physics.weber.edu/carroll/honors/duality.htm

Particle in a Box Model



m – particle mass

$$E_n = h^2 n^2/(8mL^2)$$

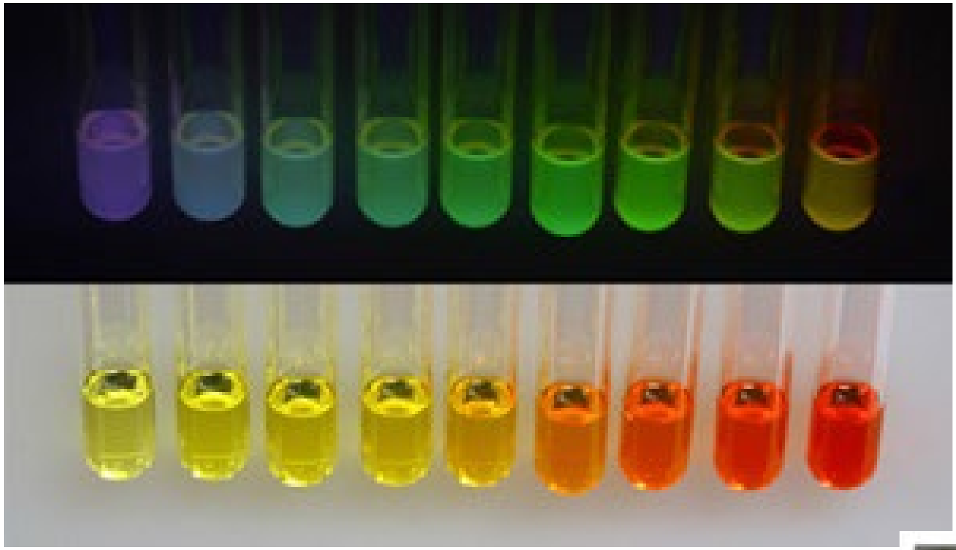


$$\psi(x,t) = [A \sin(kx) + B \cos(kx)] \exp(-i\omega t)$$

k – wavenumber, *ω* - angular frequency

$$E = h\omega/2\pi = h^2k^2/8\pi\cdot m$$

Examples

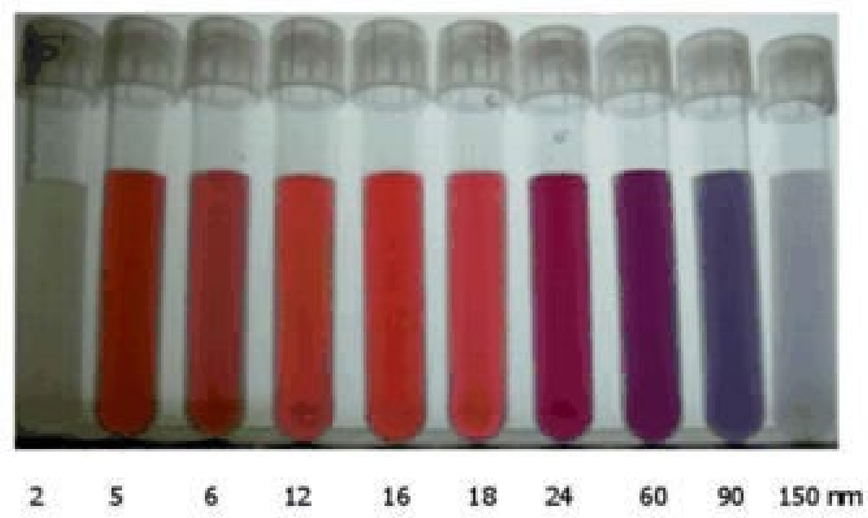


1.5 nm

8.5 nm

CdSe nanoparticle

Gold nanoparticle



Metal Nanoparticles

Gold nanoparticles

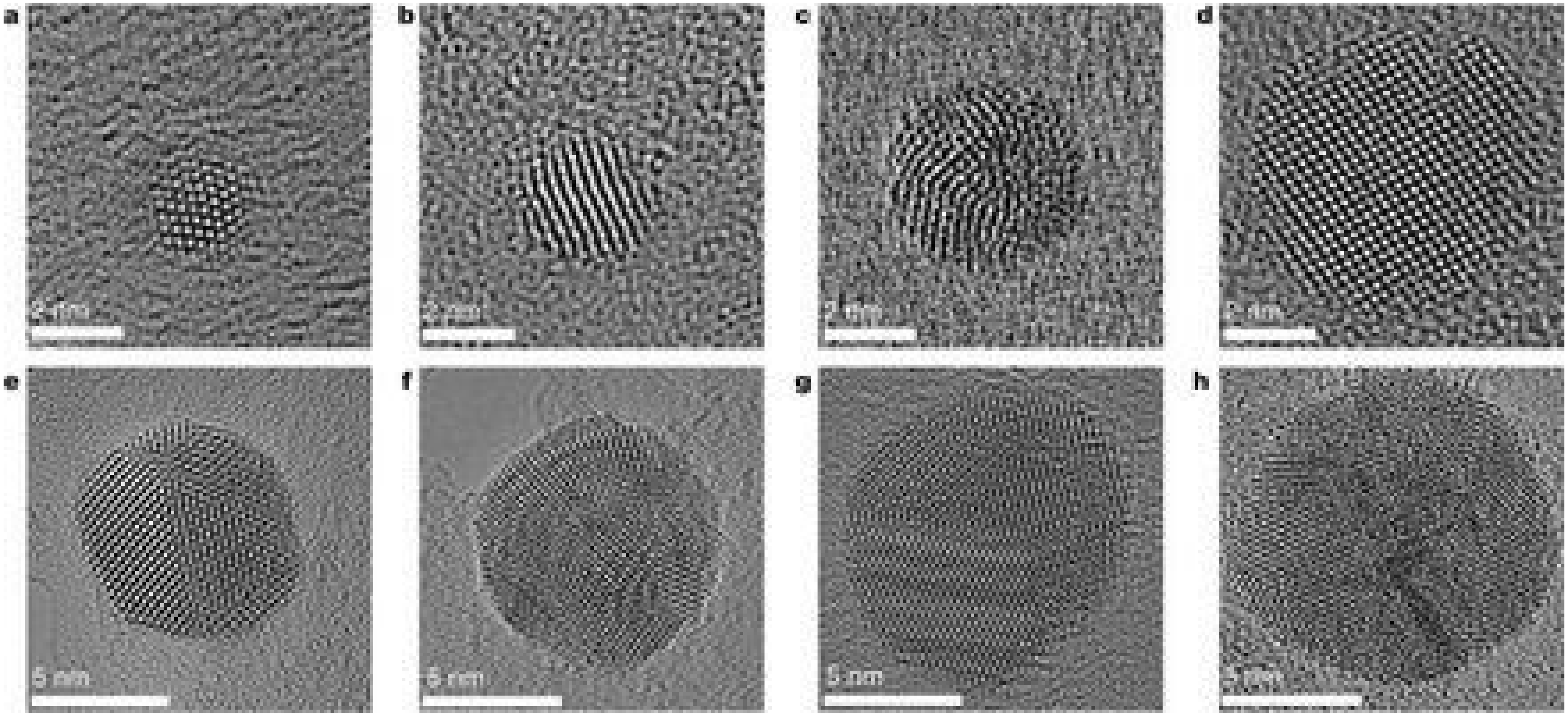
Nanocomposix.com

Noble metal nanoparticles
(Au, silver, alloys, complex particles)

Nanocomposix.com

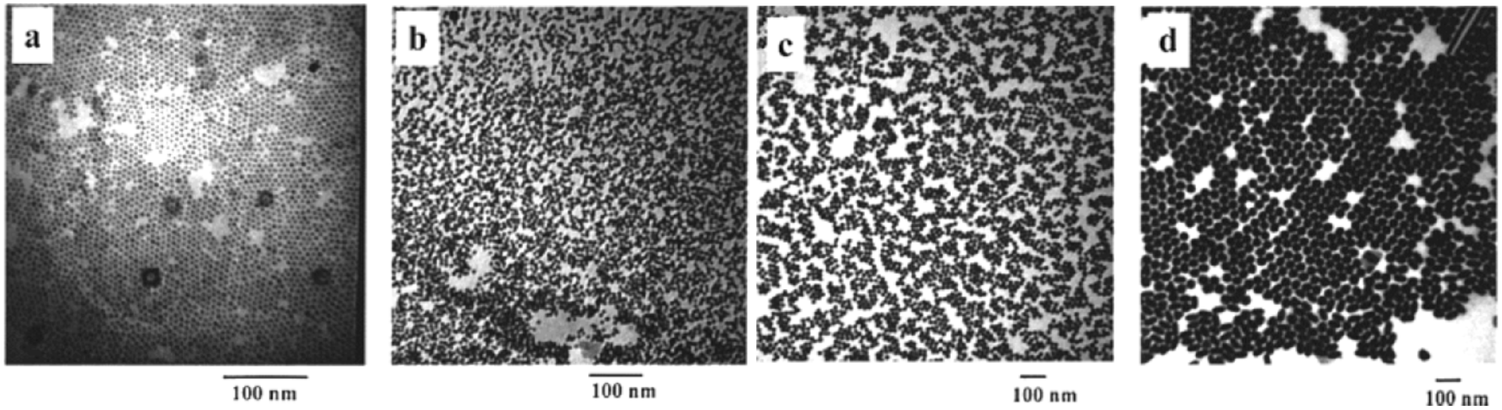
Similarly to semiconductor particles oscillatory motion of charge is the key to understanding their properties

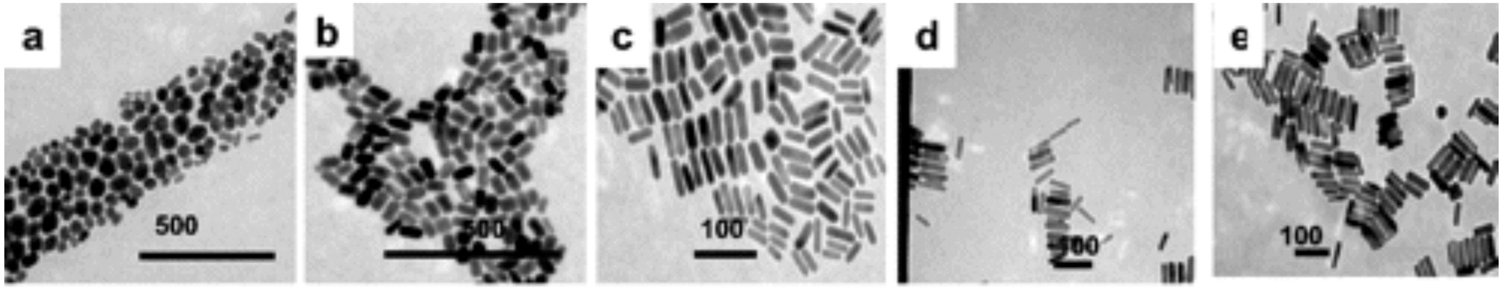
Gold Nanoparticles

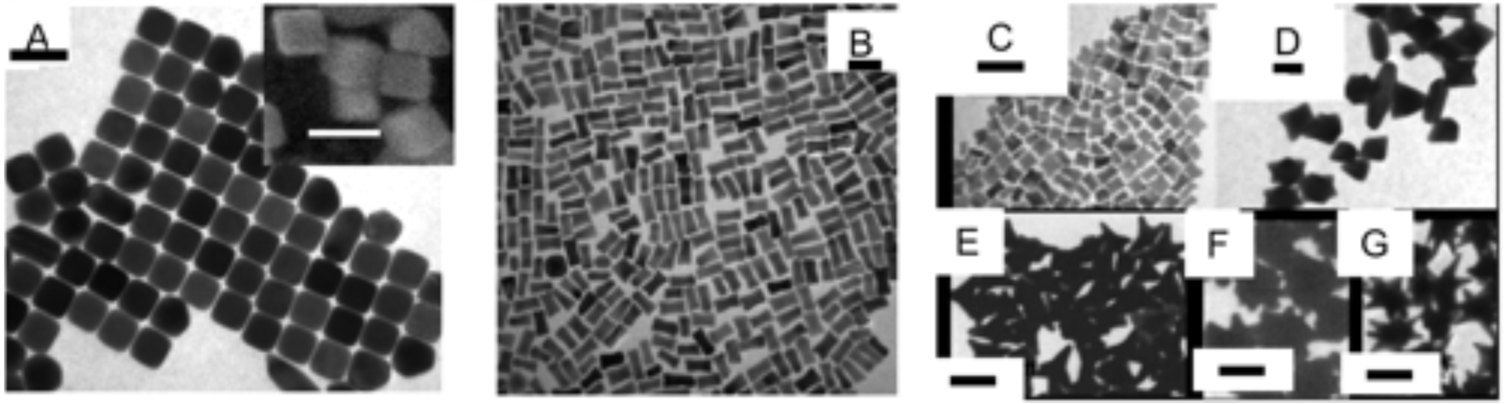


Quantum plasmon resonances of individual metallic nanoparticles, Jonathan A. Scholl,
Ai Leen Koh, Jennifer A. Dionne, Nature, 483, 421–427

Diversity of Gold Colloids



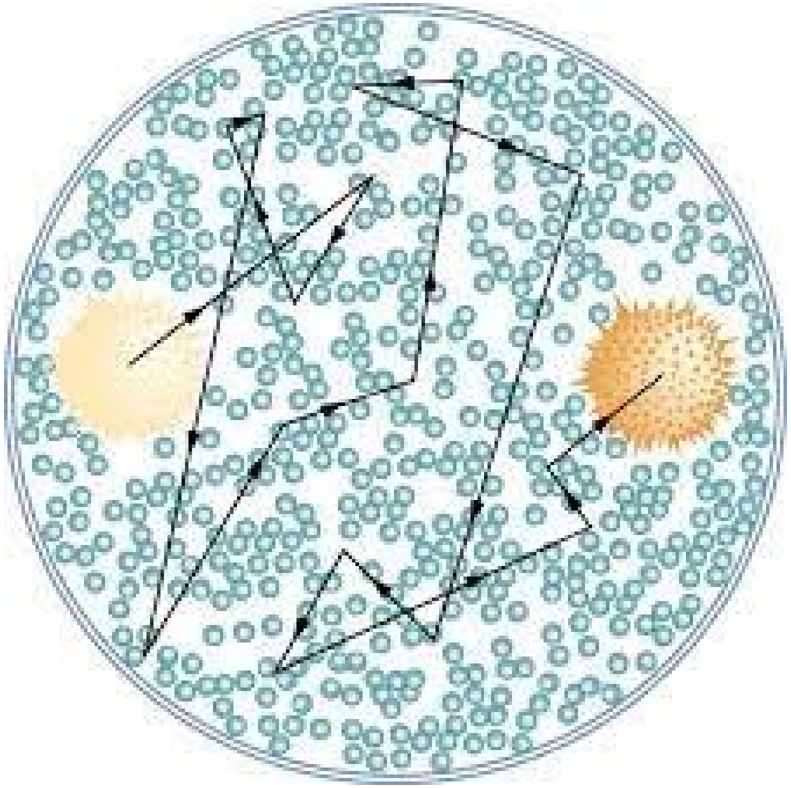


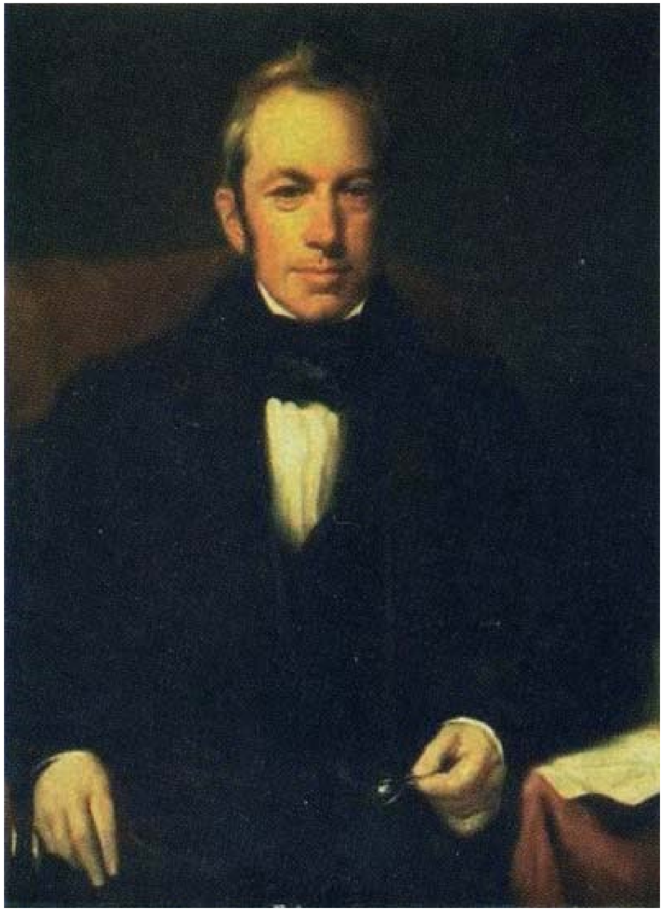


Microparticles in Liquids

Prof. Robert Brown

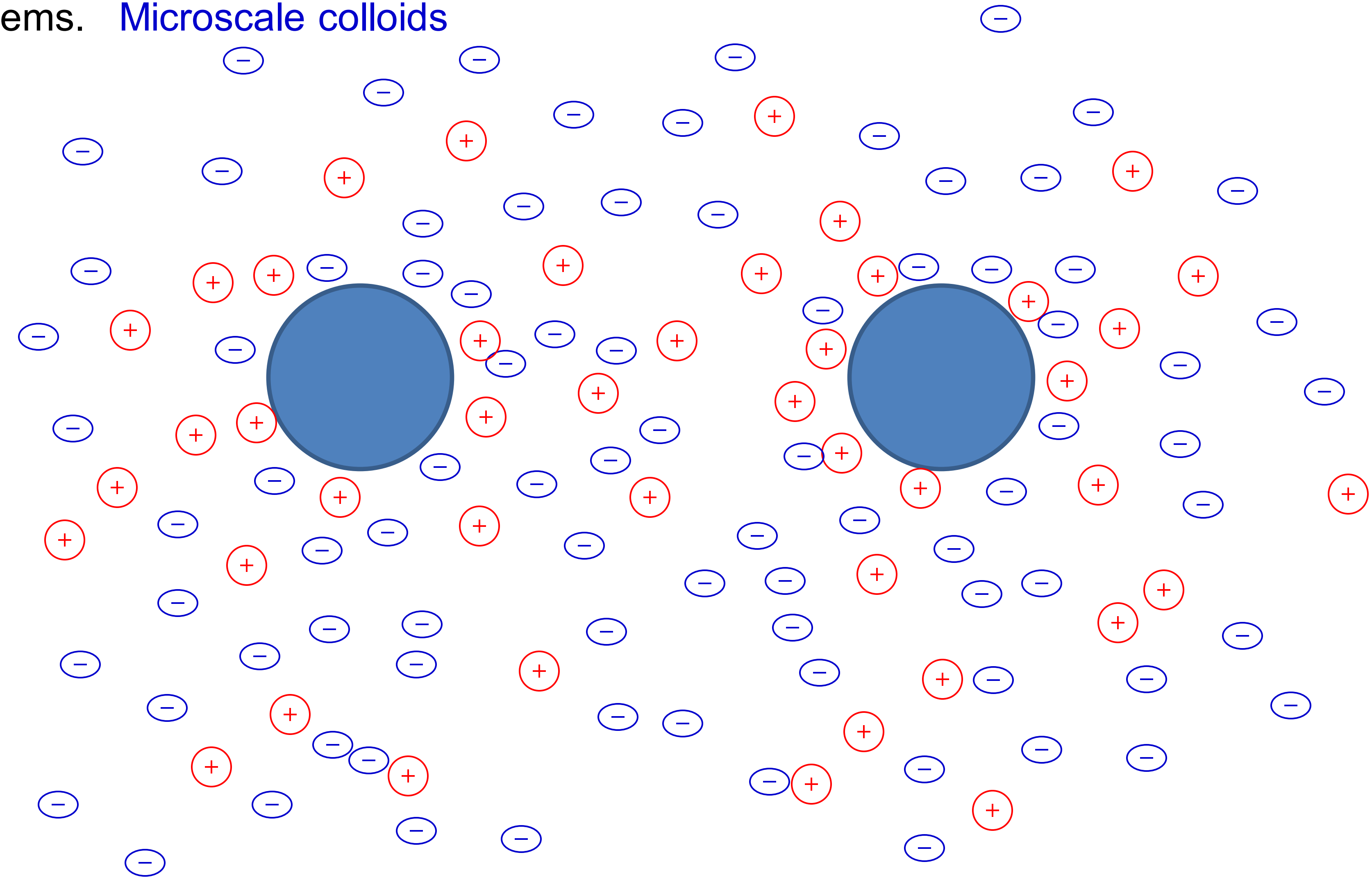
1827





DLVO Theory

Derjaguin, Verwey, Landau and Overbeek (1940s) - theory of the stability of colloidal systems. Microscale colloids



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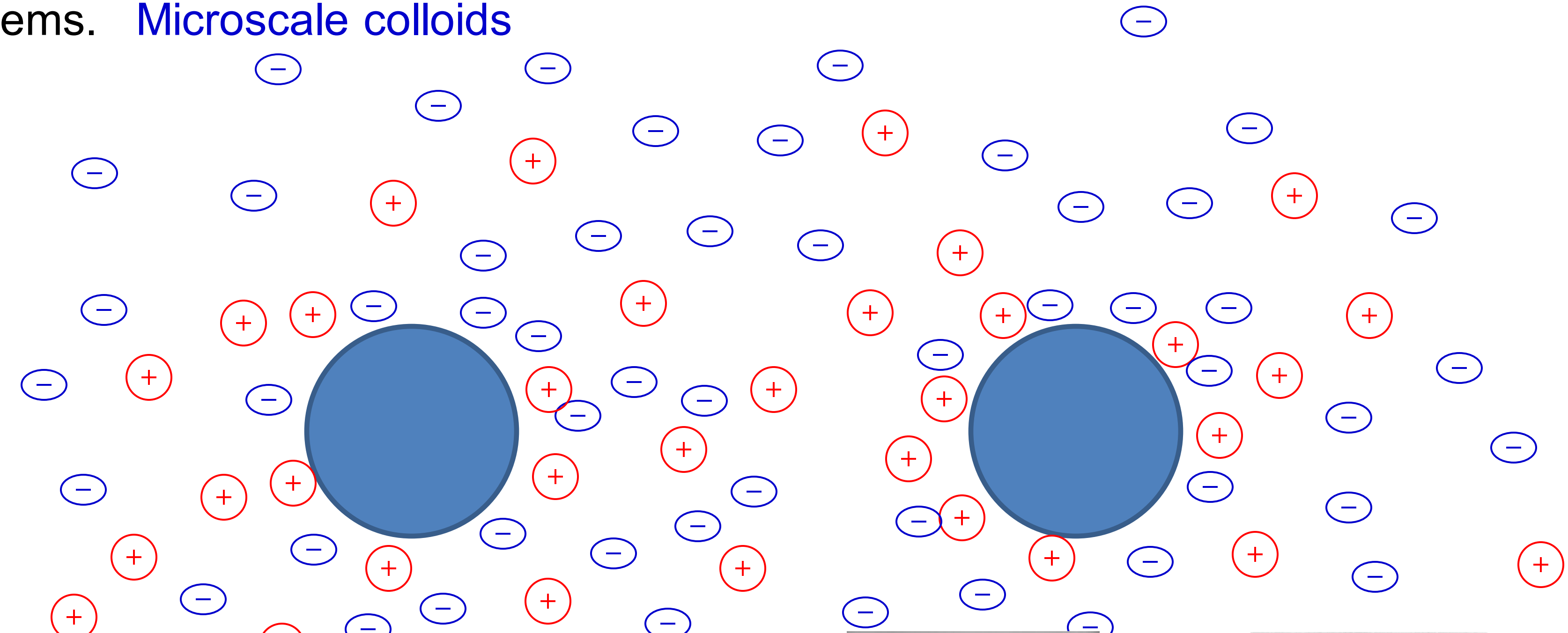
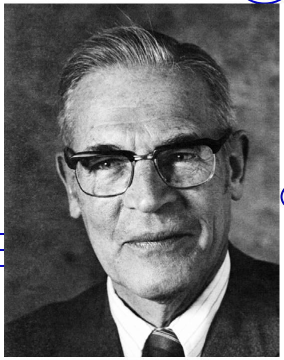
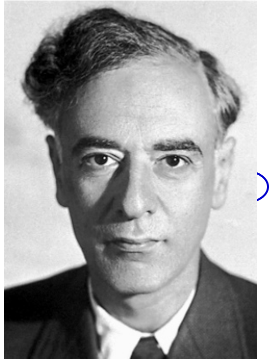



Boris Derjaguin


Theodoor Overbeek


Evert Verweij


Lev Landau

B.W. Ninham, B. V. Derjaguin and J. Theo. G. Overbeek. Their Times, and Ours. *Substantia* 2019, 3(2): 65-72.

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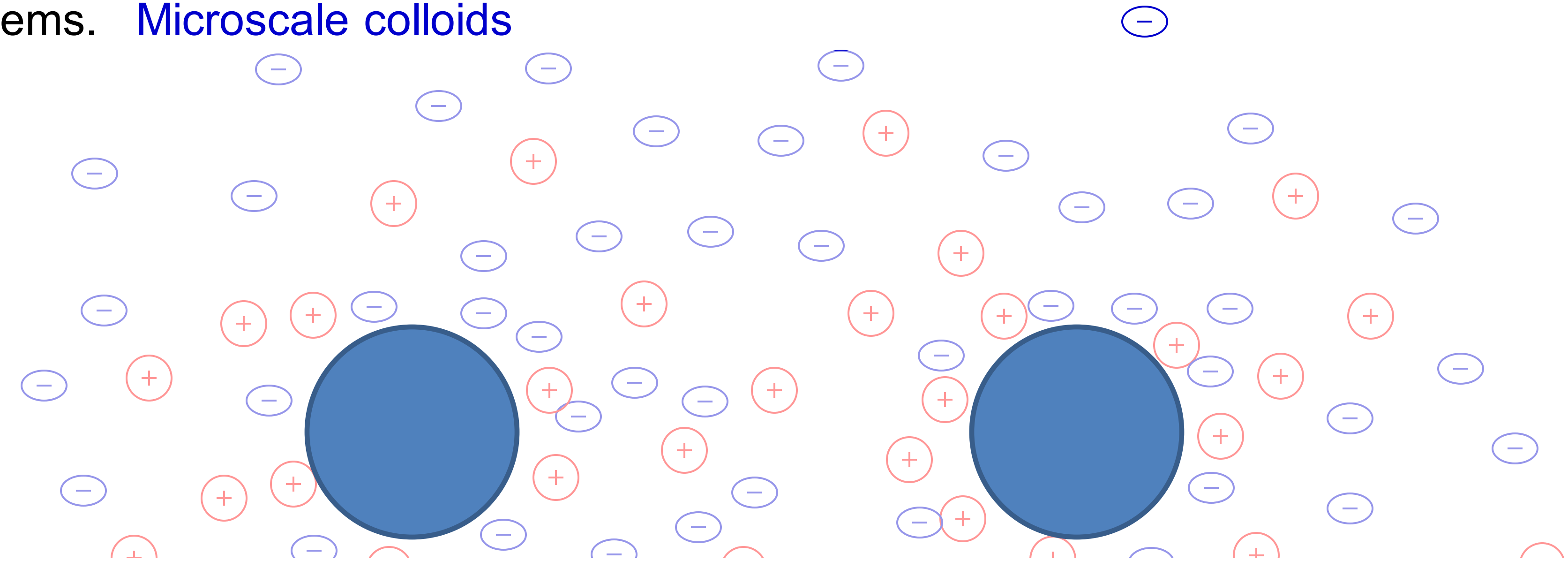

Total potential energy of the two colloidal particles is

$$V_T = V_{el} + V_{vdW}$$

Derjaguin, B. and Landau, L. D. (1941) Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes Acta Phys. Chim., 14, 633-662.

Derjaguin, B. (1939) A theory of interaction of particles in presence of electric double-layers and the stability of lyophobe colloids and disperse systems, Acta Phys. Chim., 10, 333-346.

Verwey, E. J. W. and Overbeek, J. T. G. (1948) Theory of Stability of Lyophobic Colloids. Elsevier Amsterdam.

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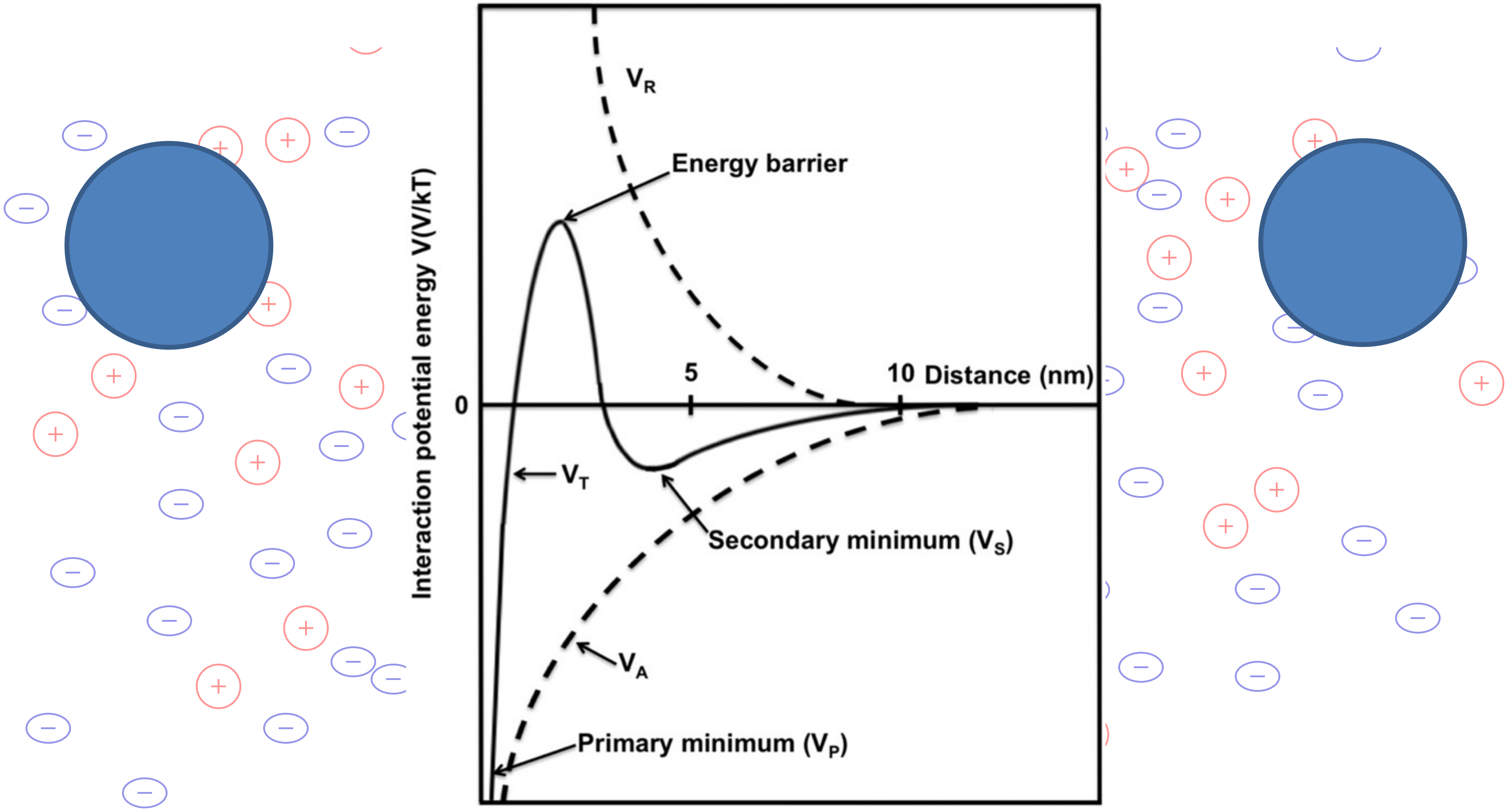

E. Piacenza et al, Stability of biogenic metal(loid) nanomaterials related to the colloidal stabilization theory of chemical nanostructures, Critical Reviews in Biotechnology, 2018 38:8, 1137-1156

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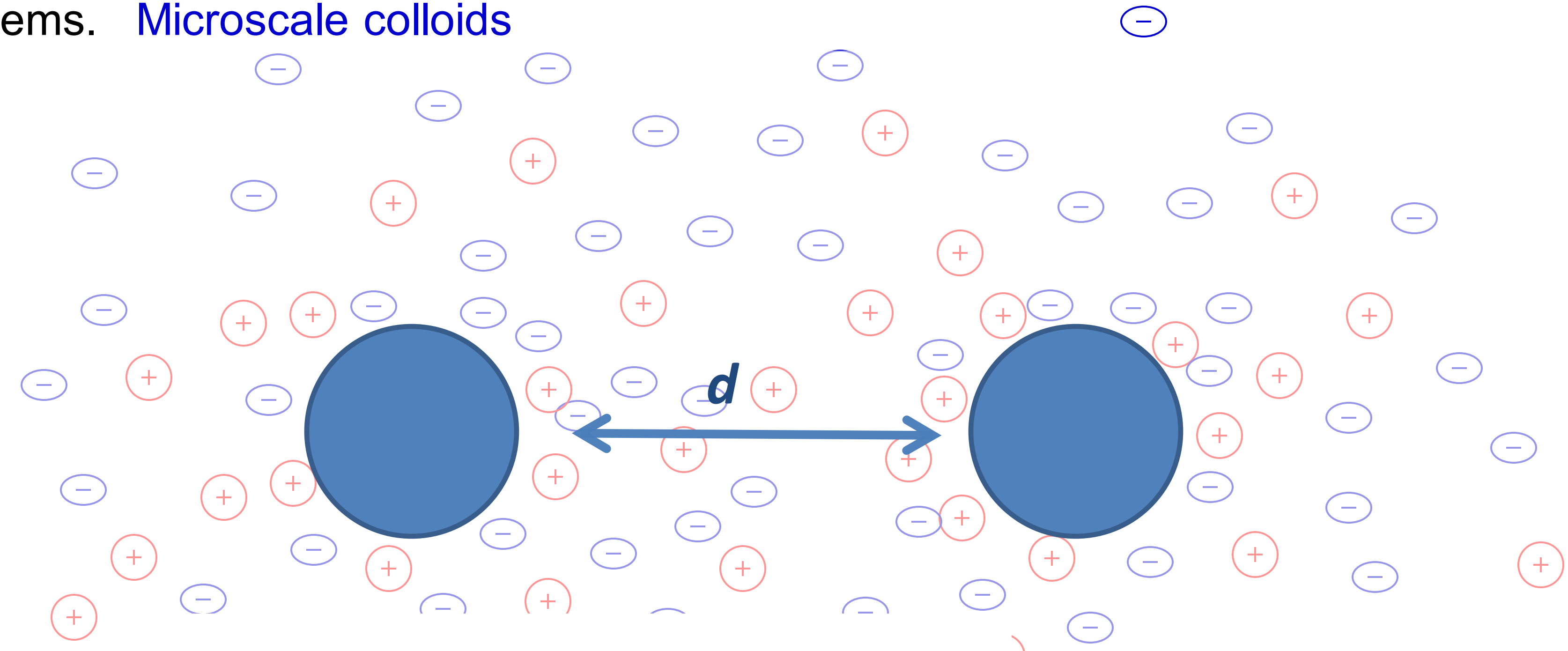


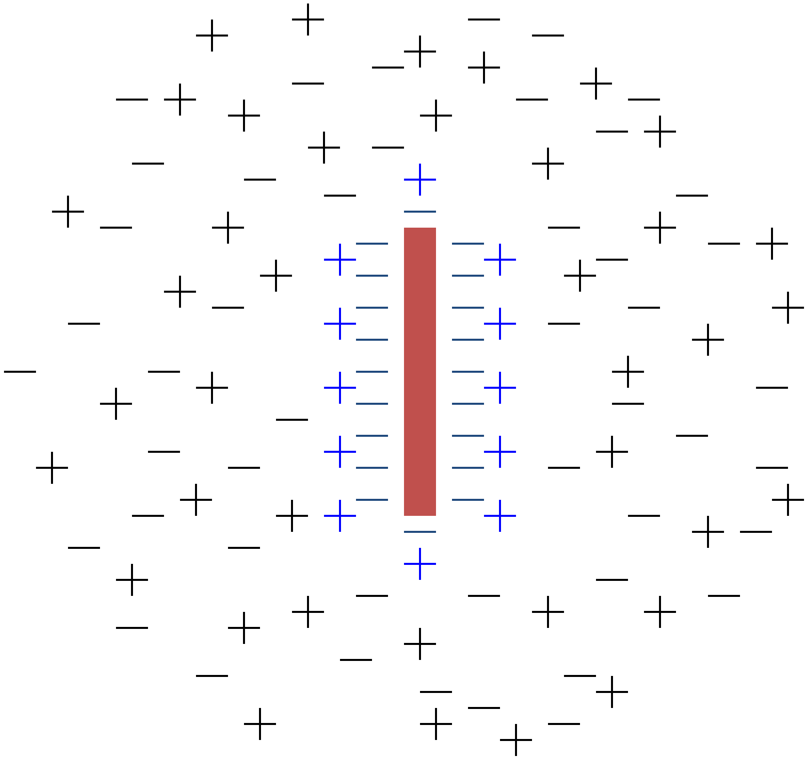
Van der Waals energy: $\mathbf{V_{vdW}}$

$$V_{vdW}(d) = -H/(12\pi d^2)$$

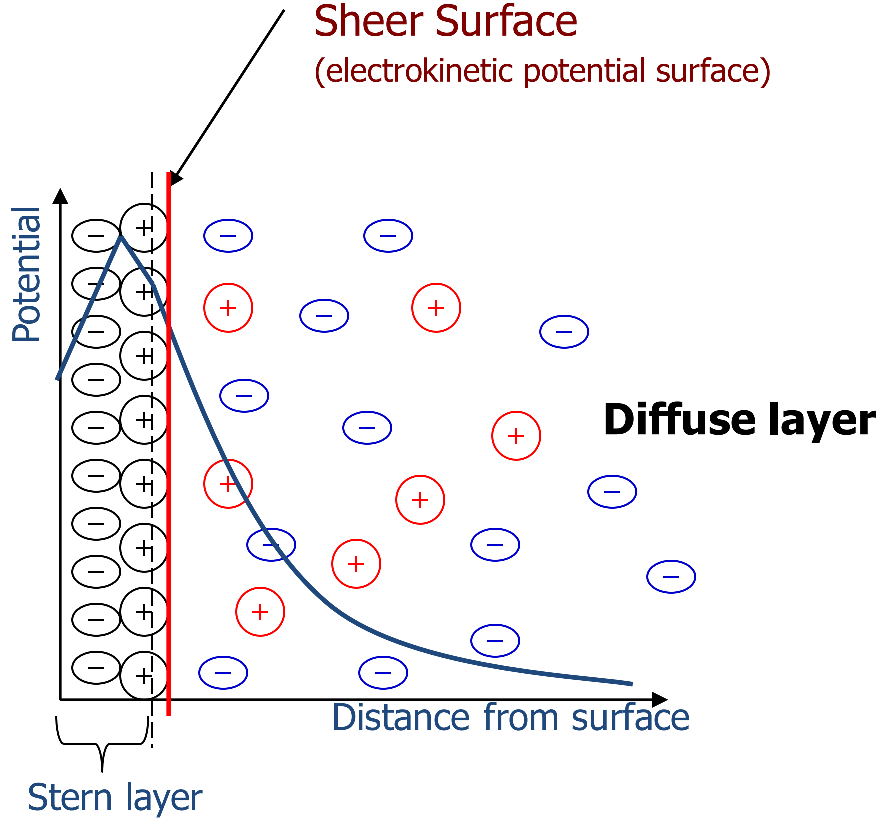
H – Hamaker constant

Metals and semiconductors	$10 — 40 \cdot 10^{-20}$ J
Organic molecules	$1 — 10 \cdot 10^{-20}$ J

Electrostatic Interactions



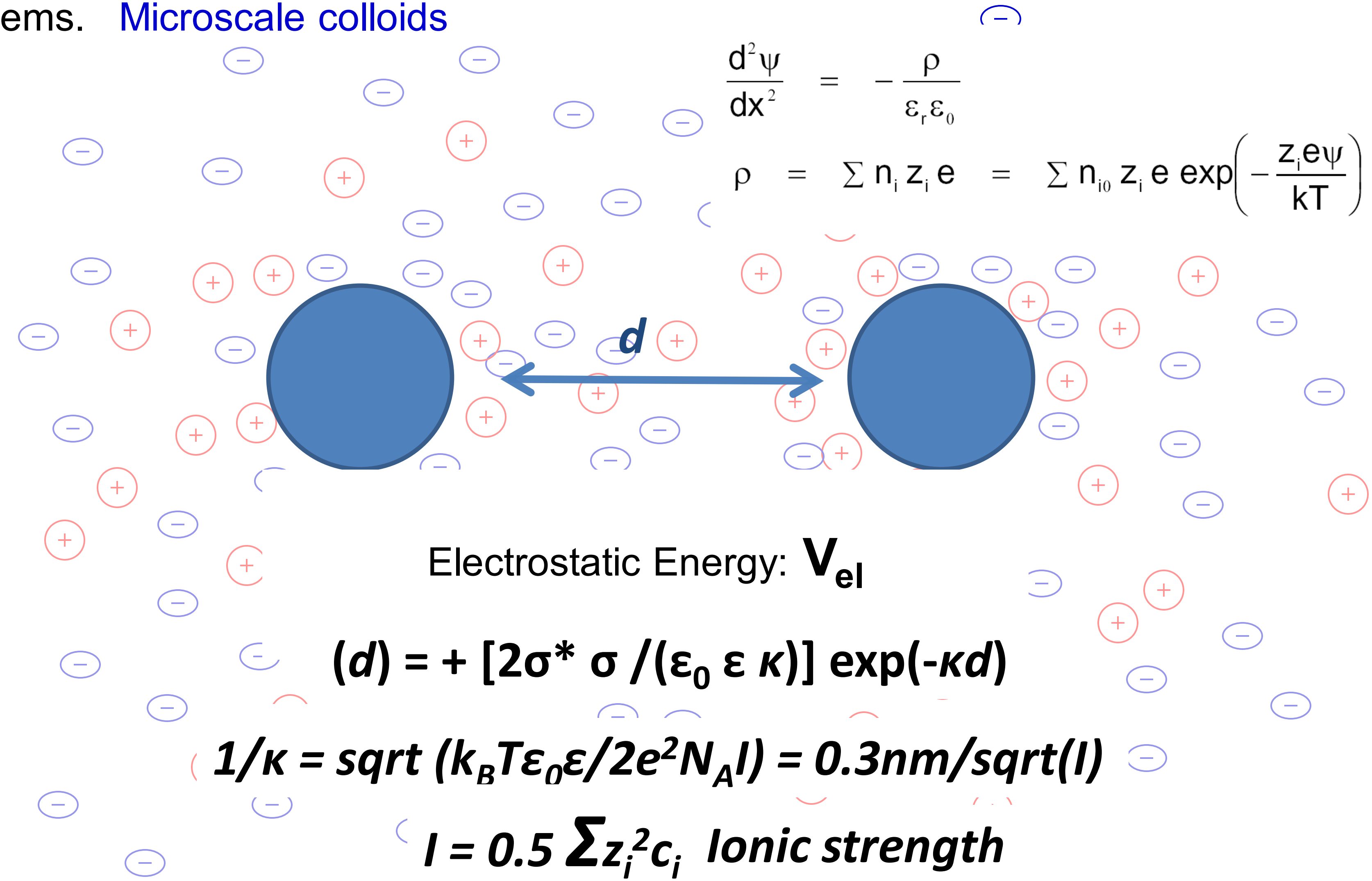
Zeta potential, ζ , is the potential at the slippage surface (sheer surface)



Double electric layer = Stern layer+ Diffuse layer
Stern layer is immobile, strongly adsorbed
Diffuse layer is mobile, thermally fluctuating

DLVO Theory

Derjaguin, Verwey, Landau and Overbeek (1940s) - theory of the stability of colloidal systems. Microscale colloids



$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon_r \varepsilon_0}$$

$$\rho = \sum n_i z_i e = \sum n_{i0} z_i e \exp\left(-\frac{z_i e \psi}{kT}\right)$$

Electrostatic Energy: $\mathbf{V_{el}}$

$$\mathbf{(\mathit{d}) = +\ [2\sigma^*\ \sigma\ /(\varepsilon_0\ \varepsilon\ \kappa)]\ \exp(-\kappa \mathit{d})}$$

$$\mathbf{1/\kappa = sqrt\ (k_B T \varepsilon_0 \varepsilon / 2e^2 N_A I) = 0.3nm/sqrt(I)}$$

$$\mathbf{I = 0.5\ \Sigma z_i^2 c_i}$$ ***Ionic strength***

DLVO Theory

Derjaguin, Verwey, Landau and Overbeek (1940s) - theory of the stability of colloidal systems. Microscale colloids

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon_r\varepsilon_0}$$

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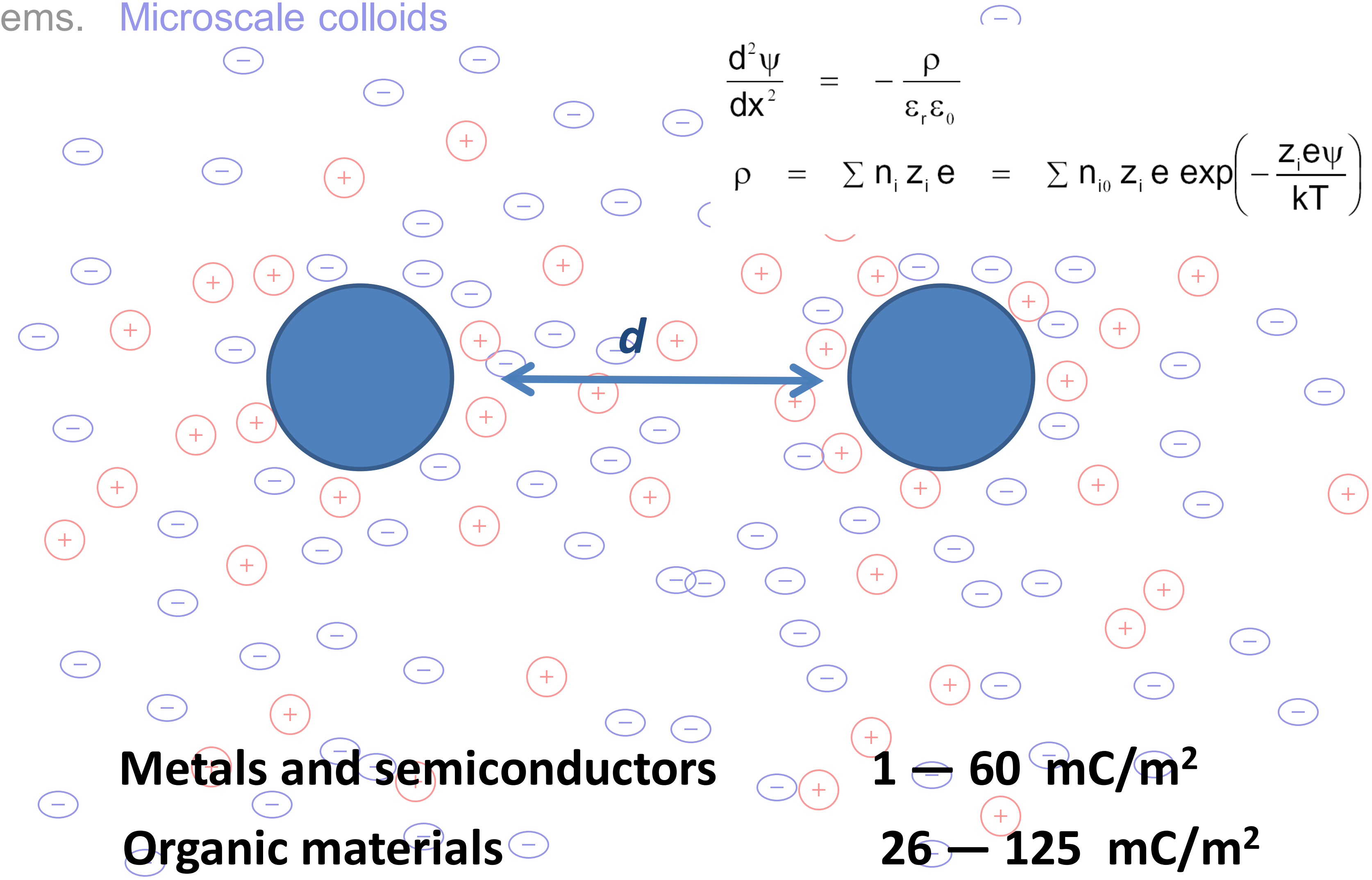
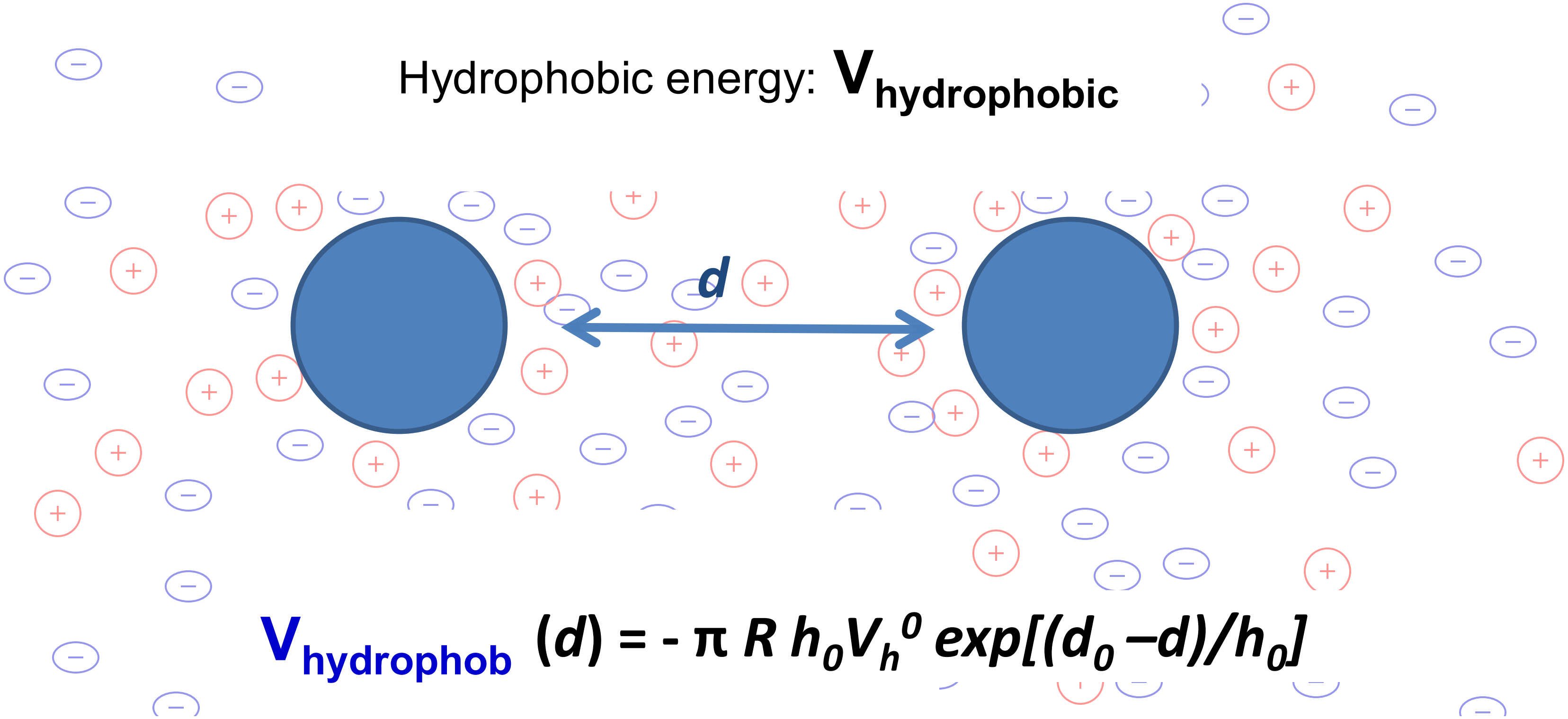


Metals and semiconductors	**1 — 60 mC/m²**
Organic materials	**26 — 125 mC/m²**

Extended DLVO Theory

Microscale particles from inorganic materials:
Metals and semiconductors typical for nanoscale colloids

Hydrophobic energy: $V_{\text{hydrophobic}}$



$$V_{\text{hydrophob}}\ (d) = -\ \pi\ R\ h_0 V_h^0\ exp[(d_0 - d)/h_0]$$

R – particle radius

V_h^0 - the acid-base free energy per unit area

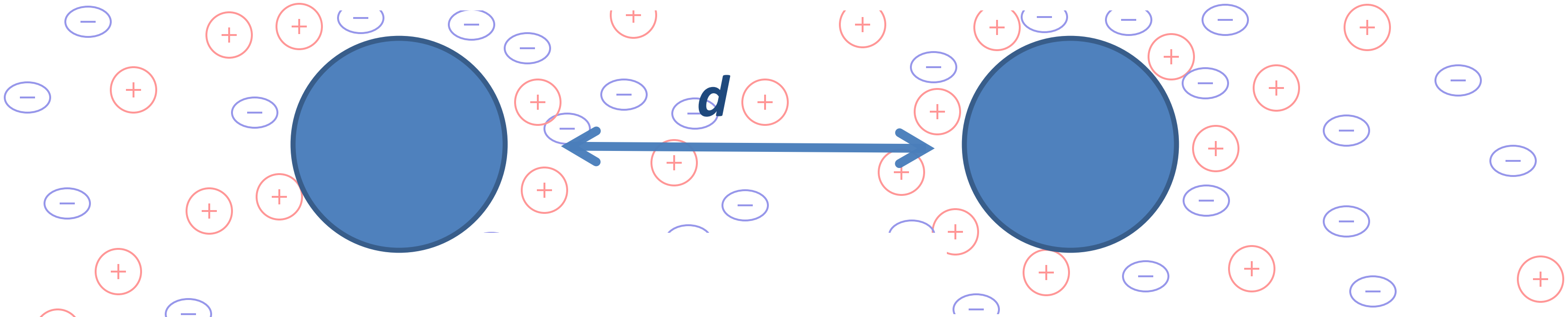
d_0 – minimal equilibrium contact distance

h_0 - decay length (from 0.2 nm to 13 nm, widely accepted 1 nm)

Extended DLVO Theory

Microscale particles from inorganic materials:
Metals and semiconductors typical for nanoscale colloids

Hydrophobic energy: $V_{hydrophobic}$



$V_{hydrophob}$ ~ θ contact angle with water

Metals and semiconductors	**5 - 20 degrees**
Organic materials	**20-120 degrees**

Extended DLVO Theory: Hydrophobic forces

Total potential energy of the two colloidal particles is

$$V_T = V_{el} + V_{vdW} + V_{hydrophob}$$

$$V_{el}\,(d) = +\,[2\sigma^{*}\,\sigma\,/(\varepsilon_0\,\varepsilon\,\kappa)]\;exp(-\kappa d)$$

$$V_{vdW}\,(d) = -\,H\,/(12\pi\,d^2)$$

$$1/\kappa = sqrt\,(k_B T\varepsilon_0\varepsilon/2e^2 N_A I) = 0.3nm/sqrt(I)$$

$I = 0.5\,\Sigma z_i^2 c_i$ Ionic strength

$$V_{hydrophob}\,(d) = -\,\pi\,R\,h_0 V_h^0\,exp[(d_0 - d)/h_0]$$

Extended DLVO Theory: Hydrophobic forces

Total potential energy of the two colloidal particles is

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$$I = 0.5\ \Sigma z_i^2 c_i \quad \text{Ionic strength}$$

$$V_{hydrophob}\ (d) = -\ \pi\ R\ h_0 V_h^0\ exp[(d_0 - d)/h_0]$$

R – particle radius

V_h^0 - the acid-base free energy per unit area

d_0 – minimal equilibrium contact distance

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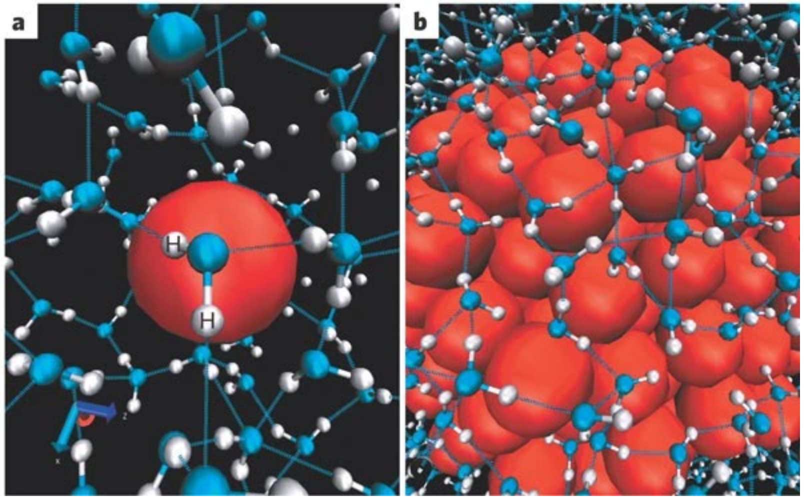
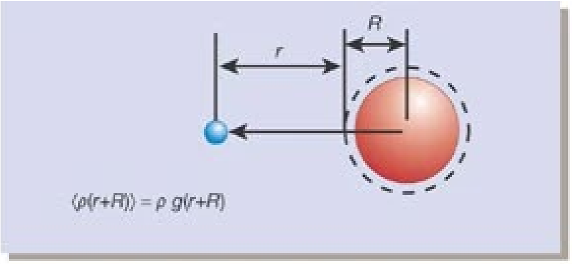
J. Yao et al, A Method of Calculating the Interaction Energy between Particles in Minerals Flotation, *Mathematical Problems in Engineering* Volume 2016, ID 8430745, http://dx.doi.org/10.1155/2016/8430745

Nature of Hydrophobic Interactions

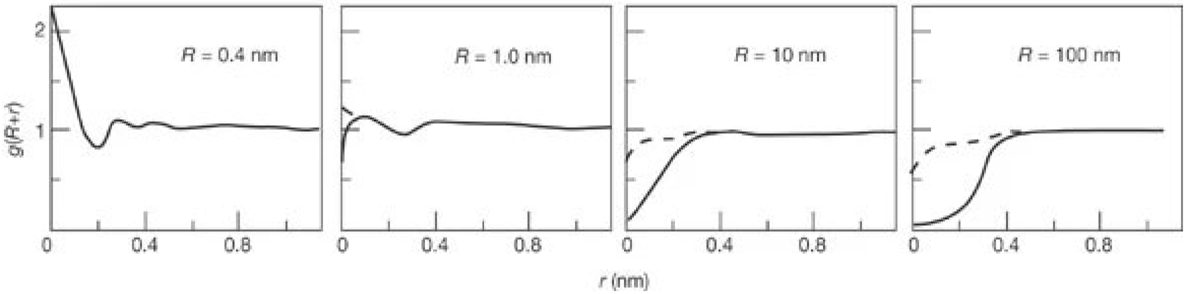


The blue and white particles represent the oxygen (O) and hydrogen (H) atoms. The dashed lines indicate hydrogen bonds.

The space-filling size of the hydrophobic (red) particle in **a** is similar to that of a methane molecule. The hydrophobic cluster in **b** contains 135 methane-like particles that are hexagonally close-packed to form a roughly spherical unit of radius larger than 1 nm. In both cases, the water molecules shown are those that are within 0.8 nm of at least one methane-like particle



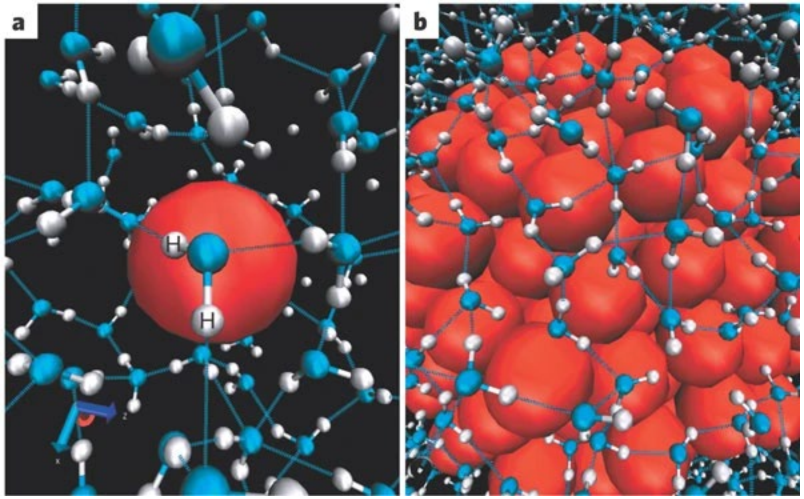
R is the distance of closest approach between the centre of a water molecule (red circle) and the centre of the cavity (blue circle). The lines representing *g*(*R*+*r*), the density, <*ρ*(*r*+*R*)> relative to that of the bulk water, *ρ*.



Solid lines refer to the ideal hydrophobic solute, which expels water from the sphere of radius *R*. Dashed lines refer to the case where the cavity also interacts with water by means of a van der Waals attraction typical of that between water and a spherical cluster of oil.

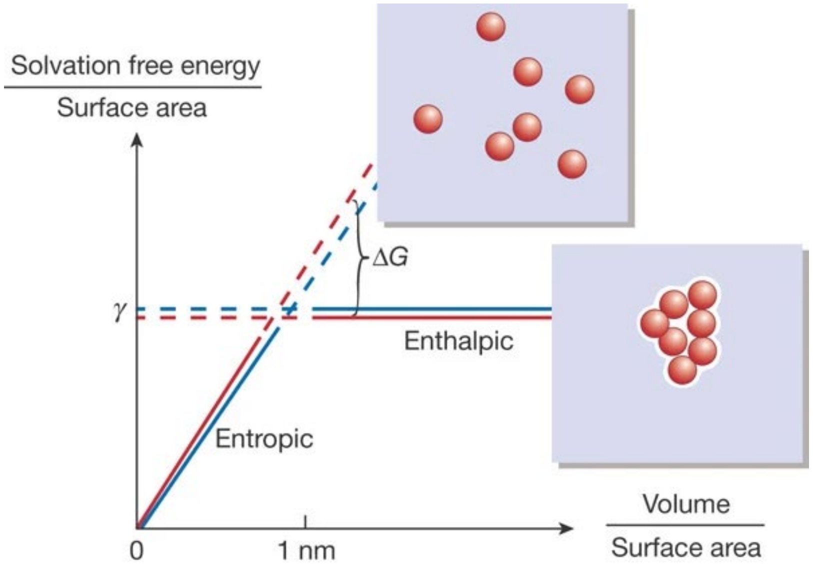
David Chandler, Interfaces and the driving force of hydrophobic assembly *Nature* 2005, 437, 640–647

Nature of Hydrophobic Interactions



The blue and white particles represent the oxygen (O) and hydrogen (H) atoms. The dashed lines indicate hydrogen bonds.

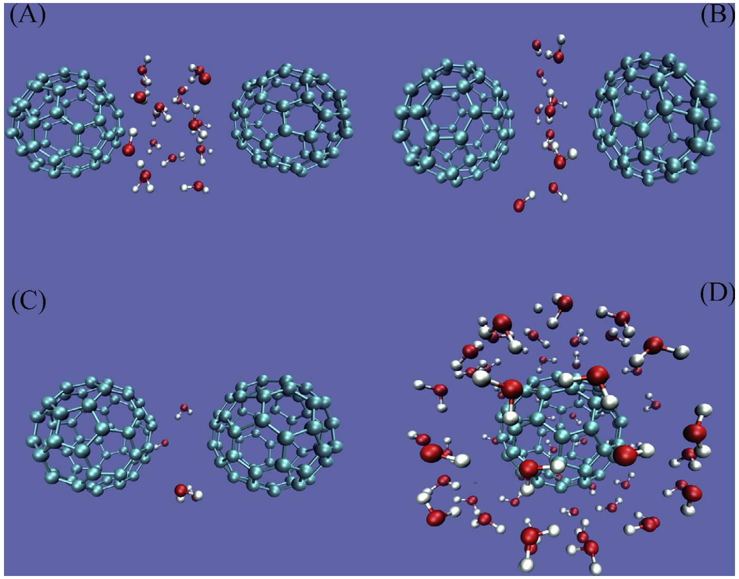
The space-filling size of the hydrophobic (red) particle in **a** is similar to that of a methane molecule. The hydrophobic cluster in **b** contains 135 methane-like particles that are hexagonally close-packed to form a roughly spherical unit of radius larger than 1 nm. In both cases, the water molecules shown are those that are within 0.8 nm of at least one methane-like particle



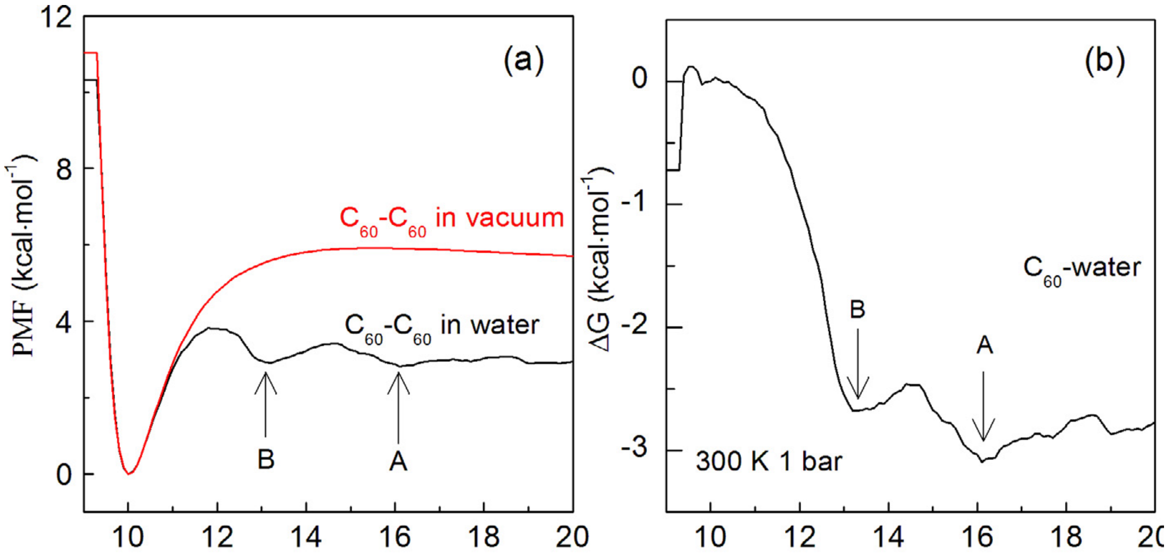
The horizontal and sloping lines indicate the behaviour of the solvation free energy for the assembled and disassembled cluster, respectively. Red lines indicate the free energies at a higher liquid temperature; blue lines indicate the free energies at a lower temperature. The liquid–vapour surface tension is indicated by γ. ‘Volume’ and ‘surface area’ denote the volume excluded to water, and the solvated surface area of that volume, respectively.

David Chandler, Interfaces and the driving force of hydrophobic assembly *Nature* 2005, 437, 640–647

Hydrophobic Interactions and Hydration Shells



Snapshots of water molecules between C_{60} fullerenes at various distances:
(A) 16 Å, (B) 13 Å, and (C) 11.2 Å. The interfacial water of C_{60} fullerene is shown in (D).

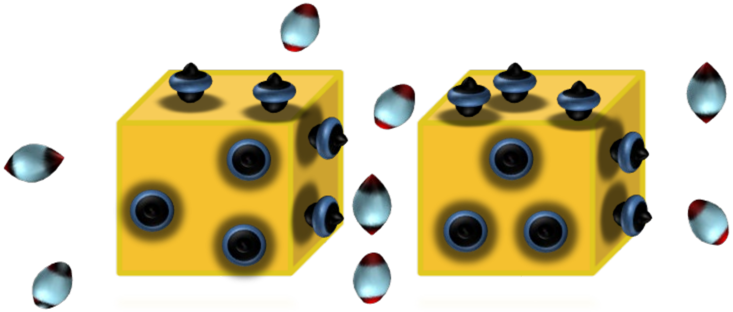


The potential of mean force (PMF) between C_{60} fullerenes in water and under vacuum. (b) The water-induced PMF between C_{60} fullerenes in water.

Q. Sun∗, X.W. Su, C.B. Cheng, The dependence of hydrophobic interactions on solute size, *Chemical Physics,* **2019***,* 516, 4 Pages 199-205

Non-Additivity of NP Interactions

How much do we know about the interactions between nanoparticles?

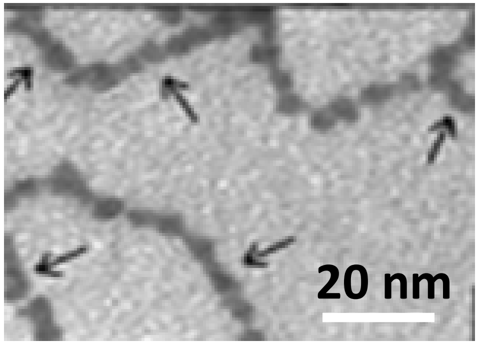


$$V_T = V_{el}(d) + V_{vdW}(d) + V_{hydrophob}(d)$$

$$V_T \neq V_{el}(d) + V_{vdW}(d) + V_{hydrophob}(d)$$

C.A. Silvera Batista, R.G.Larson, N.A.Kotov, Non-additivity of Nanoparticle Interactions, *Science*, 2015, DOI: 10.1126/science.1242477

Non-Additivity of NP Interactions



Molecular scale corrugation and multiscale re-configurability of NPs and their immediate vicinity leads to non-additivity.

Smallness of gaps between NPs (circa NP diameter) cause non-additivity of interactions

DLVO is inapplicable for gaps <20 nm.

C.A. Silvera Batista, R.G.Larson, N.A.Kotov, Non-additivity of Nanoparticle Interactions, *Science*, 2015, DOI: 10.1126/science.1242477

Thank you!