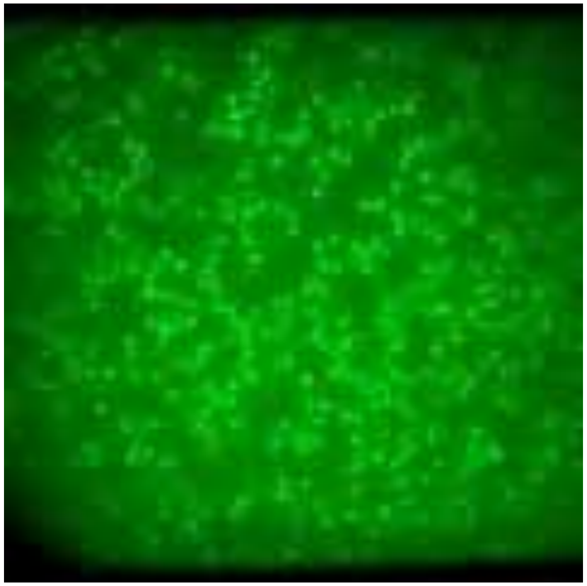

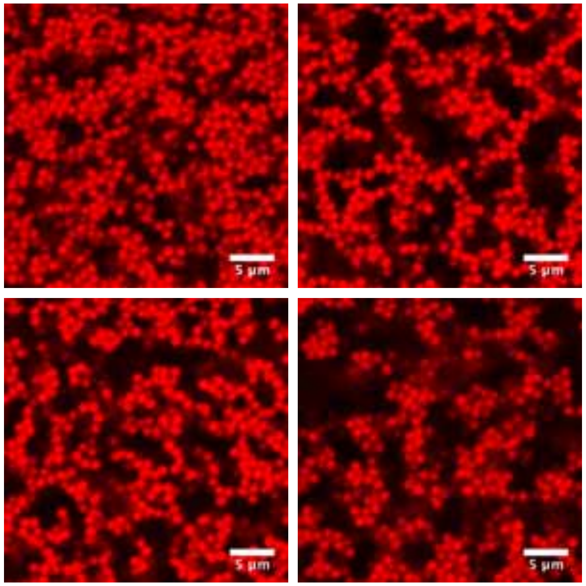

Colloidal gels

Multiscale approaches to their structure and rheology

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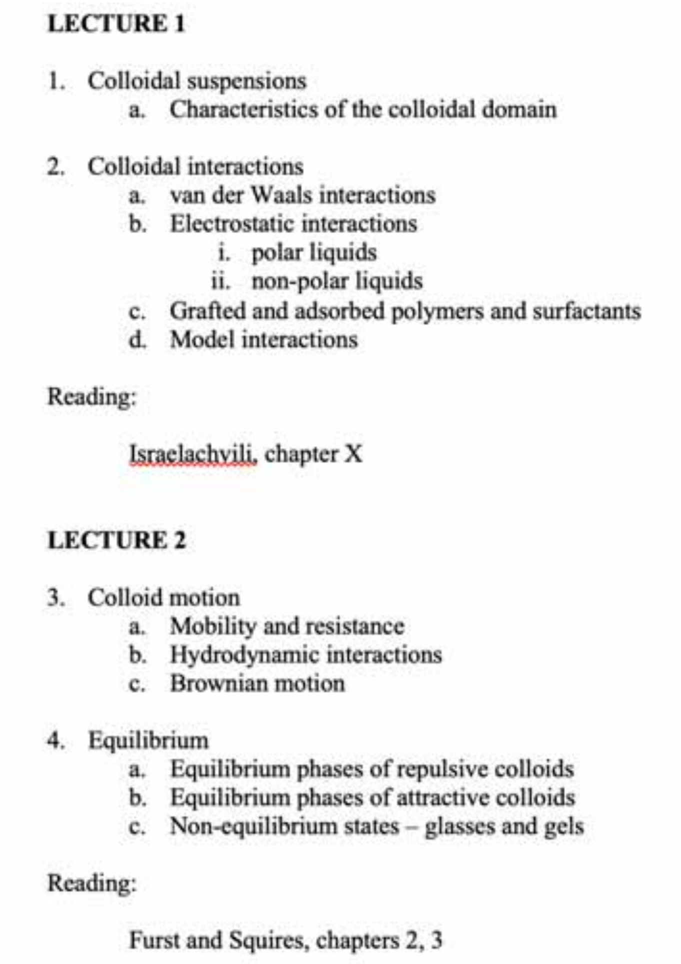
Department of Chemical and Biomolecular Engineering
University of Delaware

Lab Navier — École des Ponts
September 2022

Overview and schedule

Course goal: Highlight the key physical phenomena driving colloidal gelation and gel properties and discuss experimental methods to study their structure and rheology, with an emphasis on methods that enable an understanding of the connections between different length scales.



LECTURE 1

1. Colloidal suspensions
    a. Characteristics of the colloidal domain

2. Colloidal interactions
    a. van der Waals interactions
    b. Electrostatic interactions
        i. polar liquids
        ii. non-polar liquids
    c. Grafted and adsorbed polymers and surfactants
    d. Model interactions

Reading:

Israelachvili, chapter X

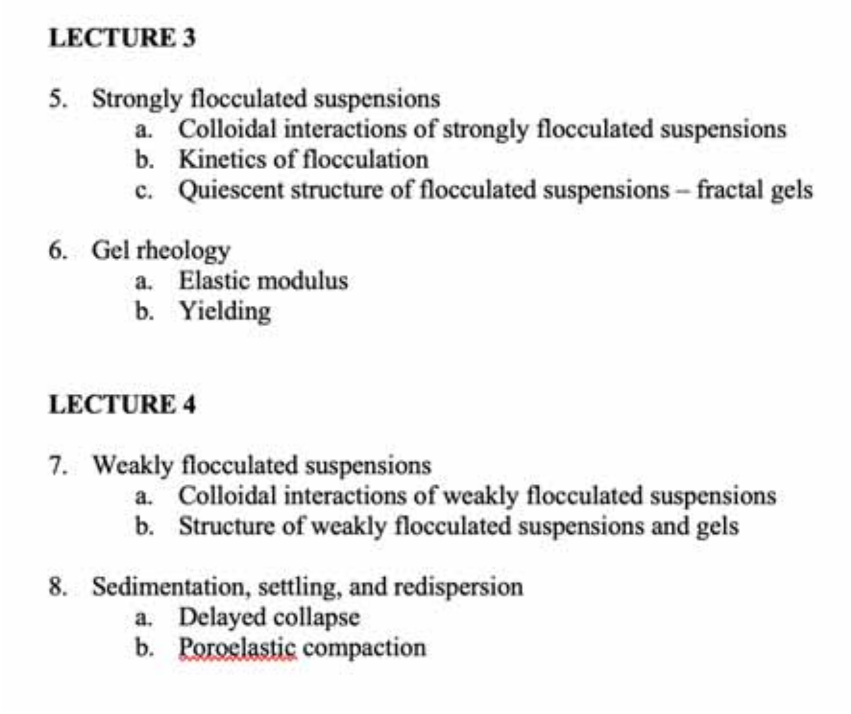
LECTURE 2

3. Colloid motion
    a. Mobility and resistance
    b. Hydrodynamic interactions
    c. Brownian motion

4. Equilibrium
    a. Equilibrium phases of repulsive colloids
    b. Equilibrium phases of attractive colloids
    c. Non-equilibrium states – glasses and gels

Reading:

Furst and Squires, chapters 2, 3



LECTURE 3

5. Strongly flocculated suspensions
    a. Colloidal interactions of strongly flocculated suspensions
    b. Kinetics of flocculation
    c. Quiescent structure of flocculated suspensions – fractal gels

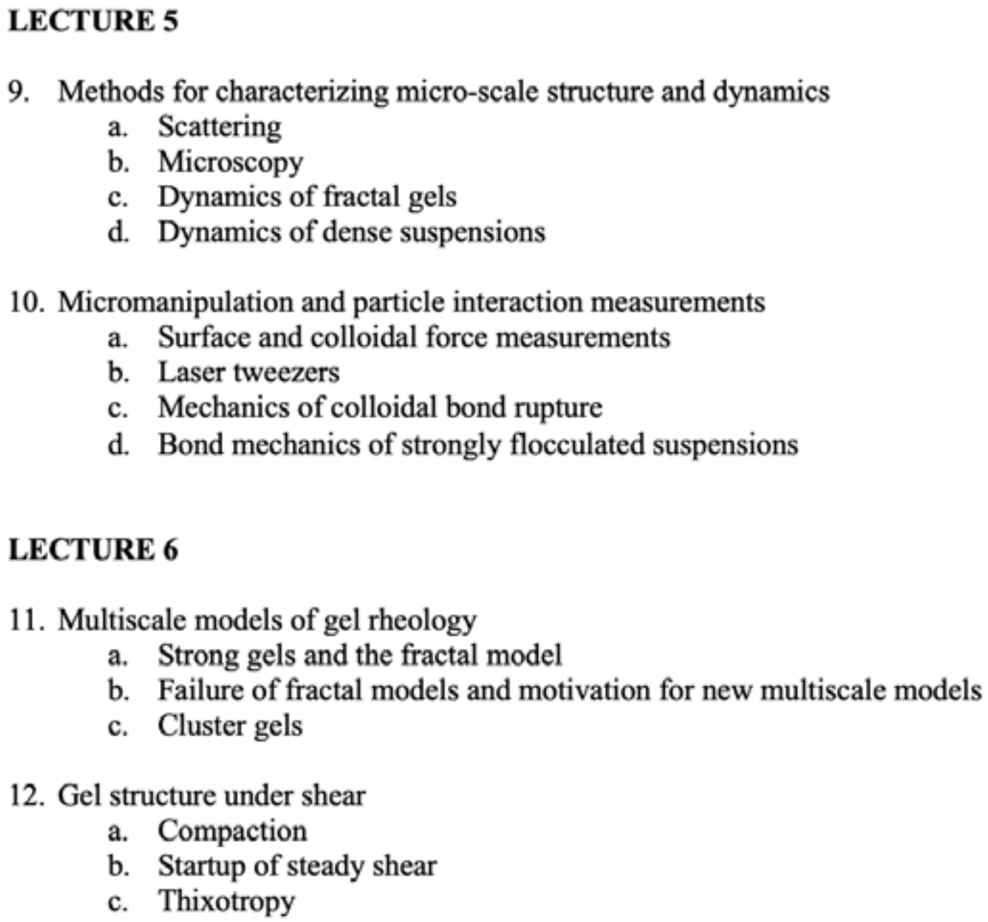
6. Gel rheology
    a. Elastic modulus
    b. Yielding

LECTURE 4

7. Weakly flocculated suspensions
    a. Colloidal interactions of weakly flocculated suspensions
    b. Structure of weakly flocculated suspensions and gels

8. Sedimentation, settling, and redispersion
    a. Delayed collapse
    b. Poroelastic compaction

Overview



LECTURE 5

9. Methods for characterizing micro-scale structure and dynamics
    a. Scattering
    b. Microscopy
    c. Dynamics of fractal gels
    d. Dynamics of dense suspensions

10. Micromanipulation and particle interaction measurements
    a. Surface and colloidal force measurements
    b. Laser tweezers
    c. Mechanics of colloidal bond rupture
    d. Bond mechanics of strongly flocculated suspensions

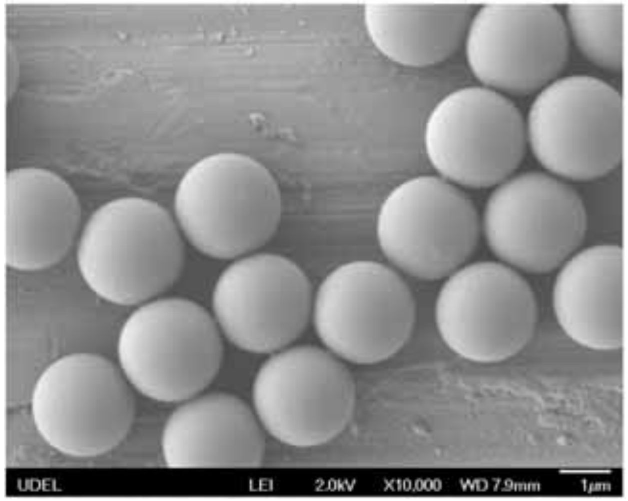
LECTURE 6

11. Multiscale models of gel rheology
    a. Strong gels and the fractal model
    b. Failure of fractal models and motivation for new multiscale models
    c. Cluster gels

12. Gel structure under shear
    a. Compaction
    b. Startup of steady shear
    c. Thixotropy

Colloid science

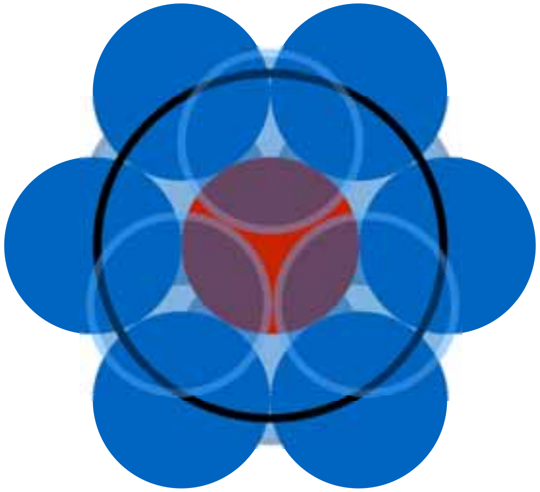
What is a colloid?



polystrene latex, 1.8μm diameter

The IUPAC definition of a colloid is a ``state of subdivision such that... particles dispersed in a medium have at least one dimension between approximately 1 nm and 1 μm…"

A colloid is *large enough* to be much larger than the atoms or molecules around it (or inside it), but *small enough* that it exhibits some properties of the molecular scale (e.g. Brownian motion).



12 nearest neighbors in an fcc crystal (0.74)

$$\frac{4}{3}\pi(2a)^3 - \frac{4}{3}\pi a^3 = \frac{28}{3}\pi a^3$$

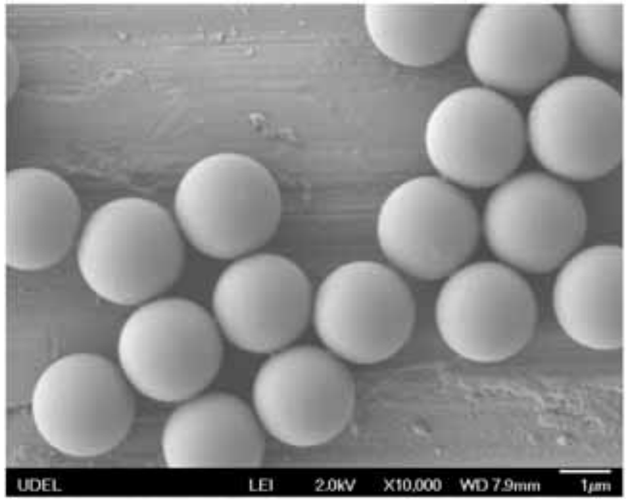
How many H_2O molecules if $2a = 1\ \mu\mathrm{m}$?

$$\bar{V} = 3 \times 10^{-29}\ \mathrm{m}^3$$

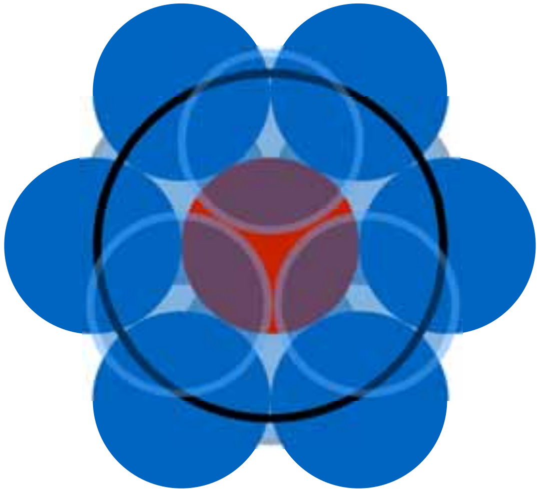
$$V/\bar{V} = 1.2 \times 10^{11}\ \text{molecules}$$

$$\bar{V}^{-1/3} \sim 3.1\text{Å}$$

What is a colloid?



polystrene latex, 1.8μm diameter



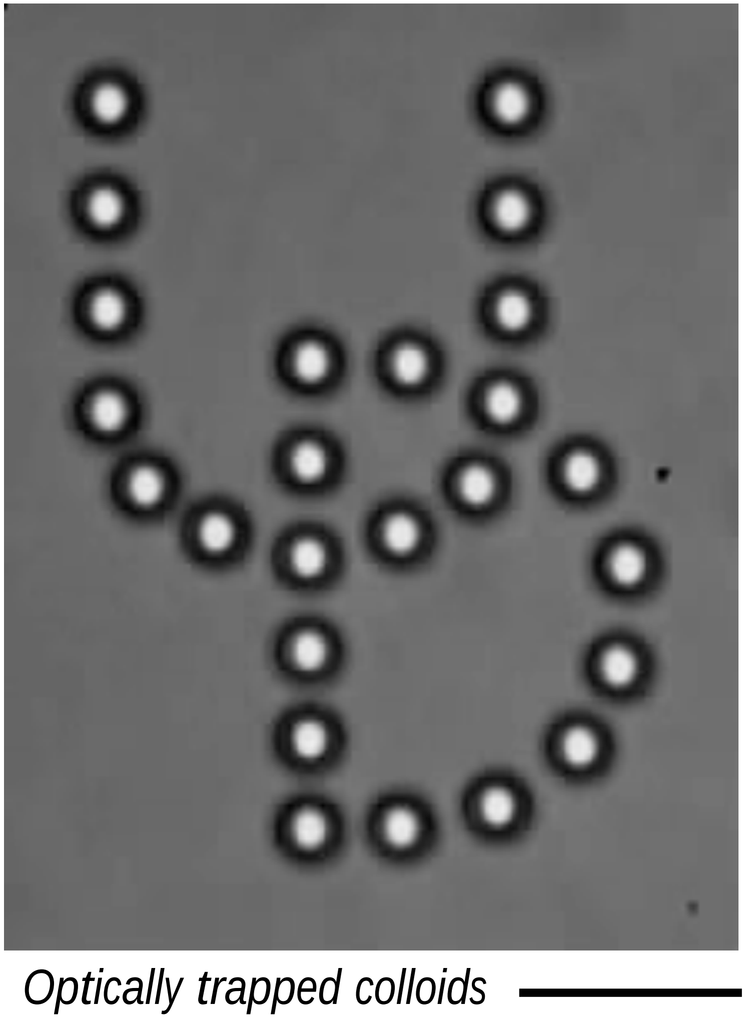
The IUPAC definition of a colloid is a ``state of subdivision such that... particles dispersed in a medium have at least one dimension between approximately 1 nm and 1 μm…"

A colloid is *large enough* to be much larger than the atoms or molecules around it (or inside it), but *small enough* that it exhibits some properties of the molecular scale (e.g. Brownian motion).

Therefore:

- Continuum mechanics (inside and outside)
- Continuum electrodynamic properties (dielectric constant, index of refraction, etc.)

Brownian motion



Optically trapped colloids

Time scales

		$2a = 100\ \text{nm}$	$1\,\mu\text{m}$	$10\,\mu\text{m}$
Vorticity	$\tau_\eta = \frac{a^2}{\nu} = \frac{a^2\eta_s}{\rho_s}$	2.5 ns	250 ns	
Inertial	$\tau_I = \frac{2\rho_p}{9\rho_s}\tau_\eta$	0.6 ns	60 ns	
Brownian	$\tau_B = \frac{\pi\eta a^3}{kT}$	0.1 ms	100 ms	100 s

$$\nu \approx 10^6\,\text{m}^2/\text{s}$$

$$kT = 4.1 \times 10^{-21}\ \text{J}$$

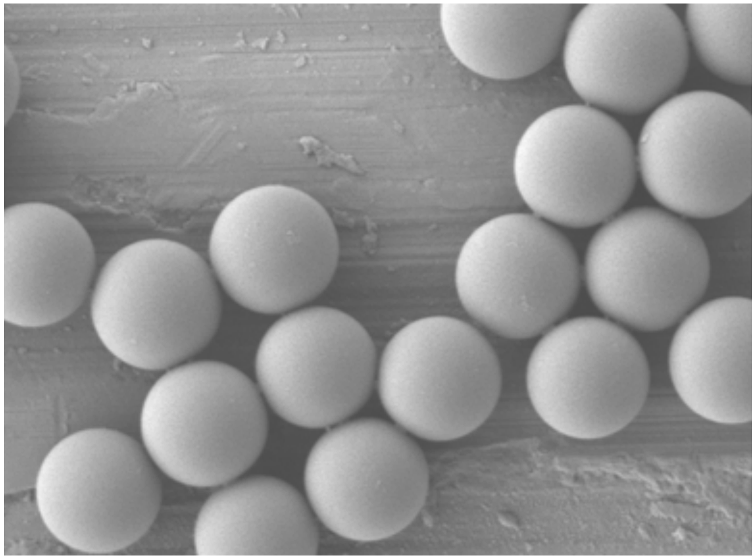
Force and energy scales

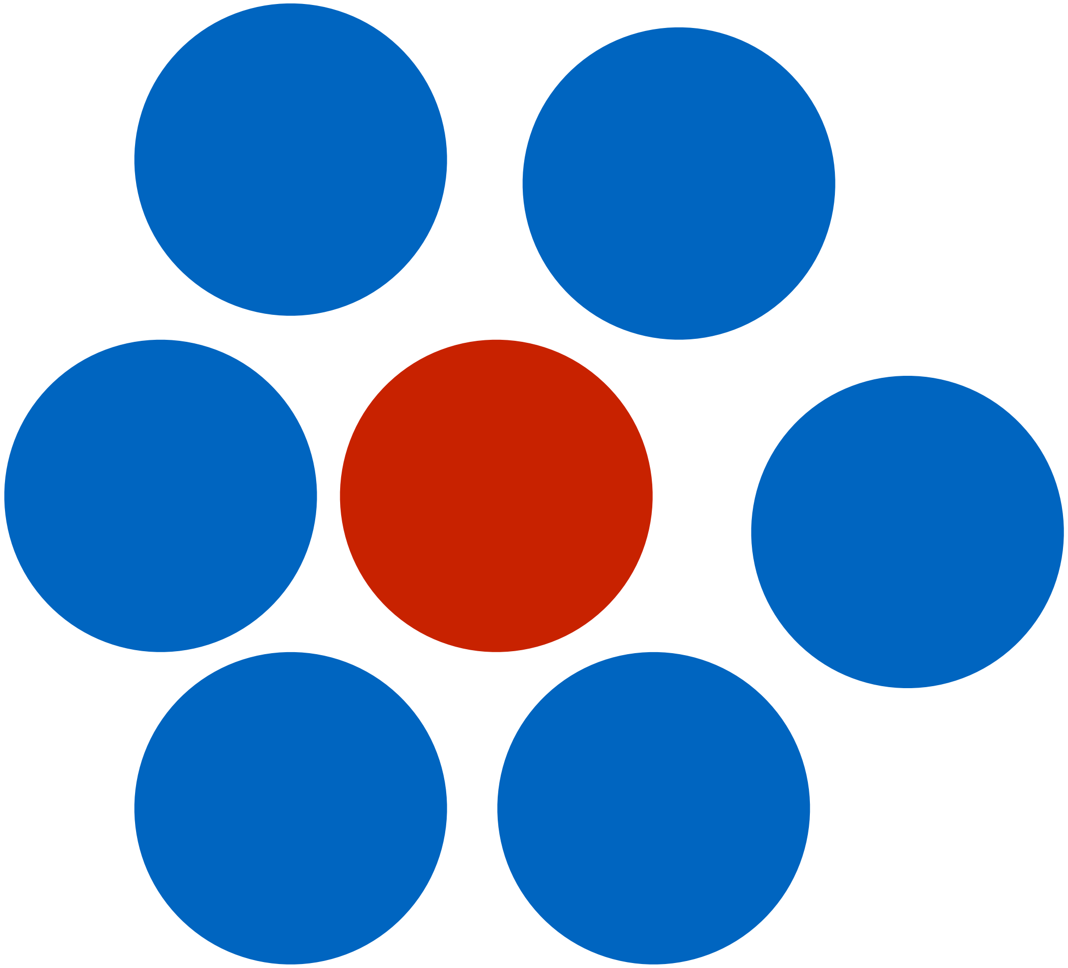
$$kT = 4.1 \times 10^{-21}\ \mathrm{J}$$

(4 zeptajoules)

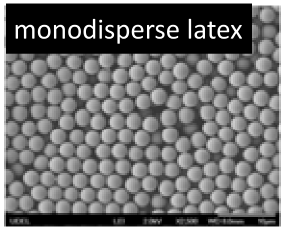
	$2a =$	$1\ \mathrm{nm}$	$1\ \mu\mathrm{m}$
Brownian force	$F_B = \dfrac{kT}{a}$	10^{-12} N	10^{-15} N
Brownian stress	$\sigma_B = \dfrac{kT}{a^3}$	10^{3} Pa	10^{-6} Pa

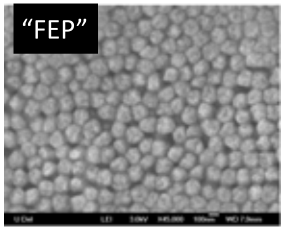
A colloid?

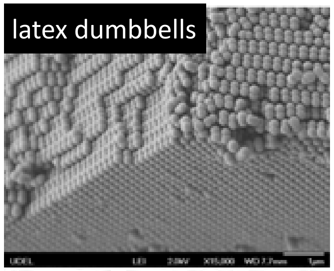


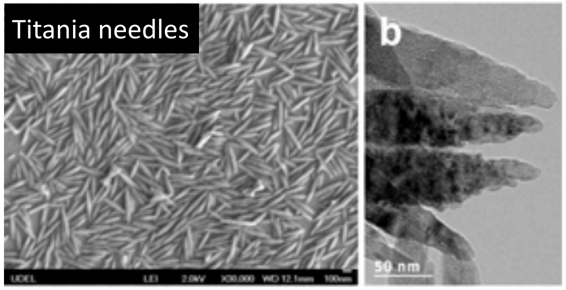


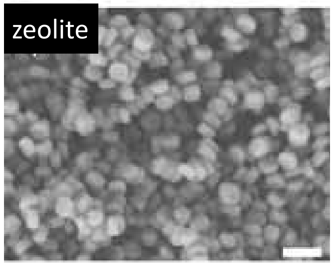
Examples of colloids

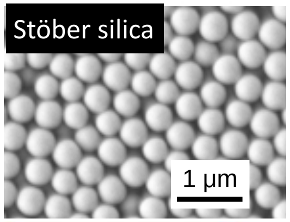

monodisperse latex

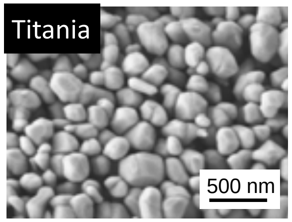

“FEP”


latex dumbbells

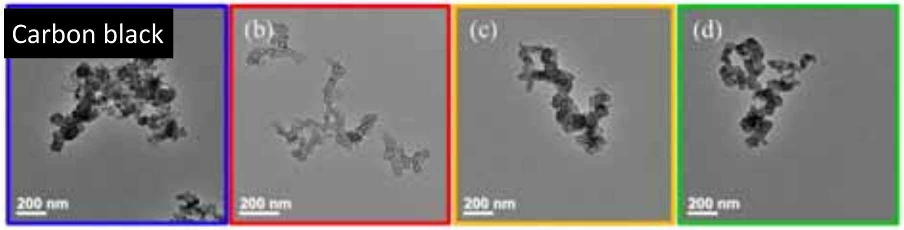

Titania needles


zeolite


Stöber silica


Titania


Solid wax

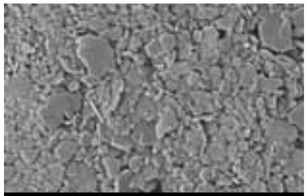

Carbon black

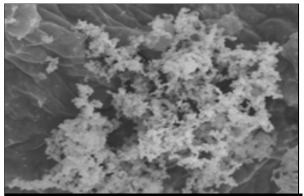
Acicular, prolate

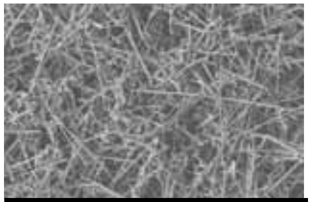
Plate-like, oblate

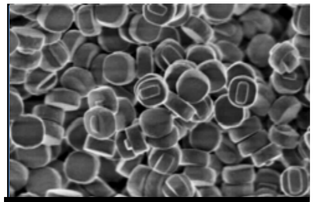
Irregular, faceted

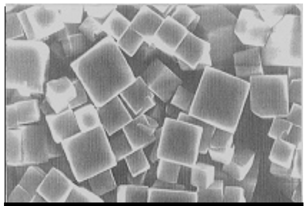

Precipitated $CaCO_3$

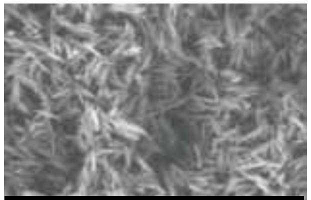

Kaolin

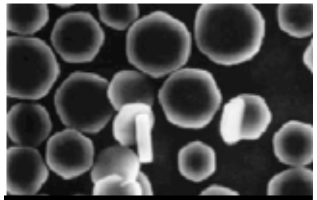

Fumed silica

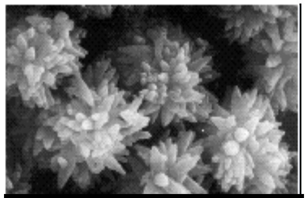

SiC whiskers


Oblate SiO_2


Lead sulfide


$Fe_20_3(0H)$ (Goethite)


Al_2O_3 (Gibbsite)

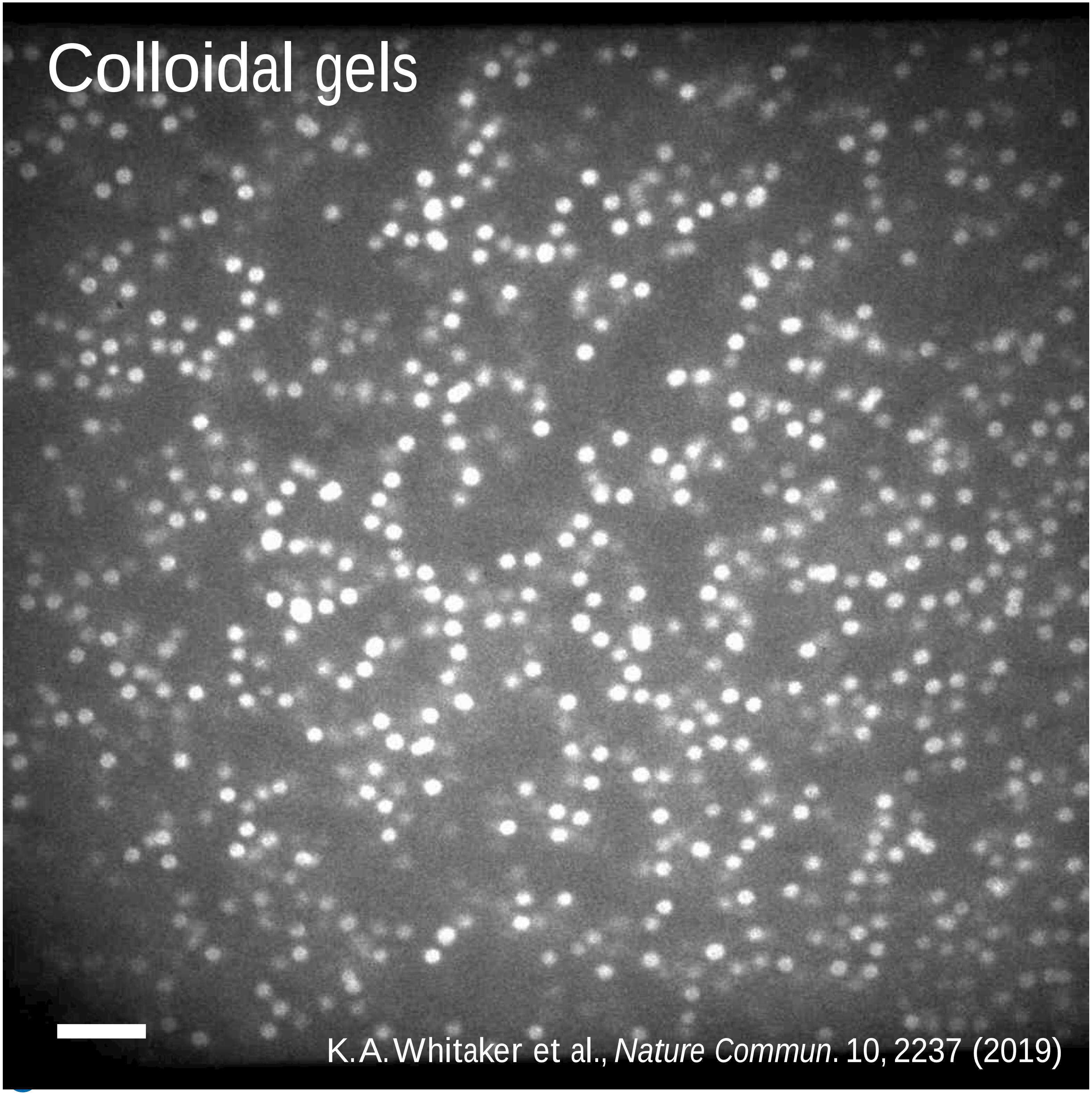

Precipitated $CaCO_3$

Rough / smooth
Monodisperse / polydisperse
Isotropic / anisotropic
Uniform / patchy
Prolate / oblate

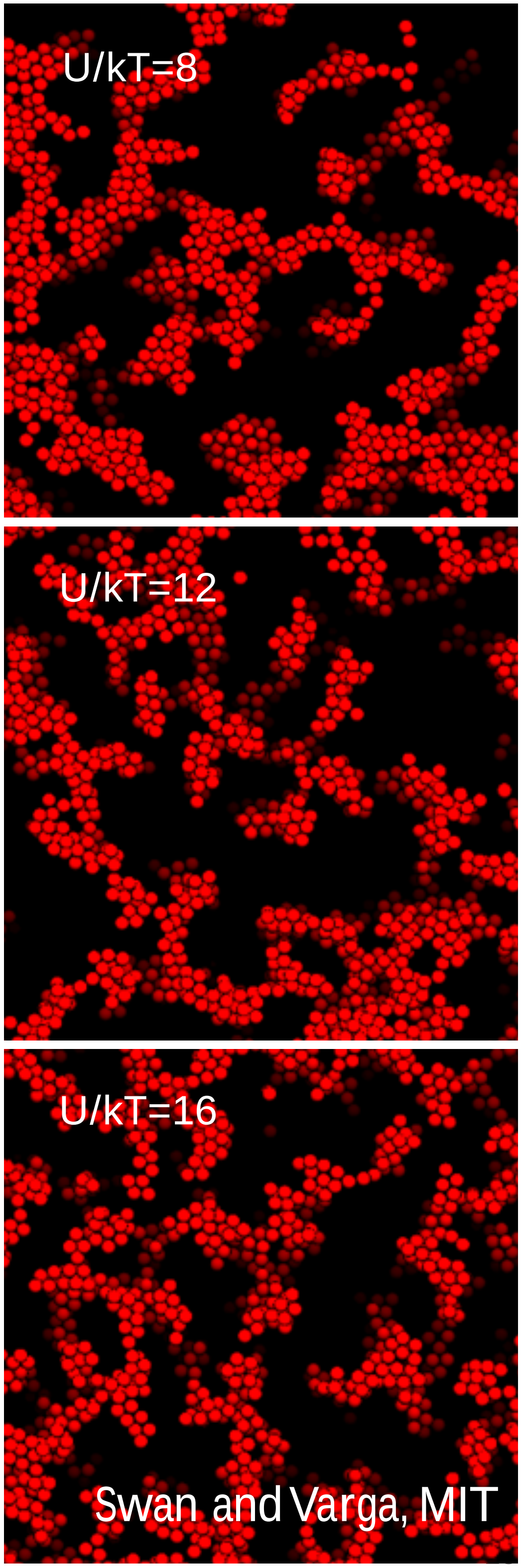
What is a colloidal gel?

- An elastic solid with a yield stress composed of…
- Percolated microstructure
- and (incompressible) solvent

Colloidal gels



K.A. Whitaker et al., *Nature Commun*. 10, 2237 (2019)



Swan and Varga, MIT

Fundamental and economic significance

- Colloidal suspensions with attractive interparticle interactions include colloid-polymer mixtures, colloids with screened electrostatic interactions, protein solutions at low temperatures.

- Exhibit a wide range of equilibrium and non-equilibrium behavior

- This affects the stability and shelf-life of consumer products, foods, agrochemicals, pharmaceuticals, coatings, paints, etc.

- Generalizable / predictable behavior to aid development and engineering?

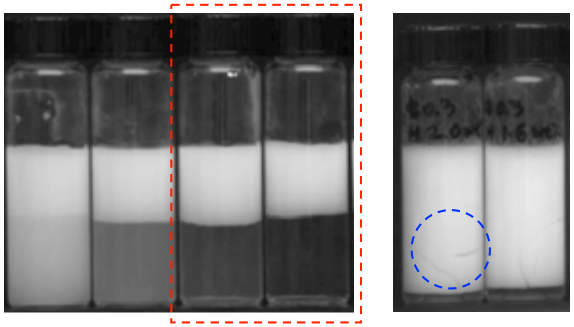
Examples of equilibrium and non-equilibrium behavior

Phase separation

Stable, homogeneous dispersion

Thickening / gelation

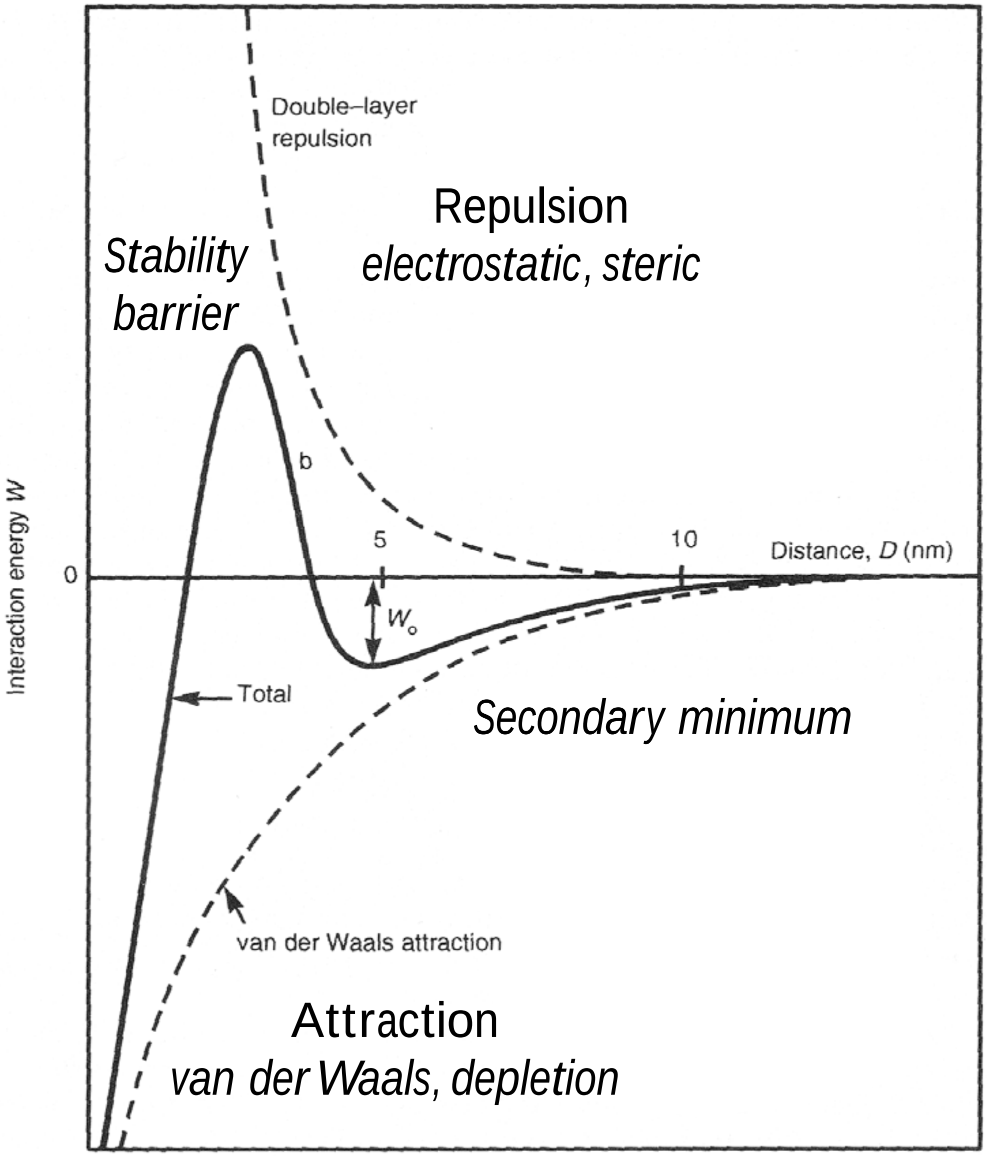
Consolidation / sedimentation



Colloidal interactions and stability

Colloidal interactions

Israelachvili, *Intermolecular and Surface Forces*, 3rd ed., Academic Press, New York, 2007.



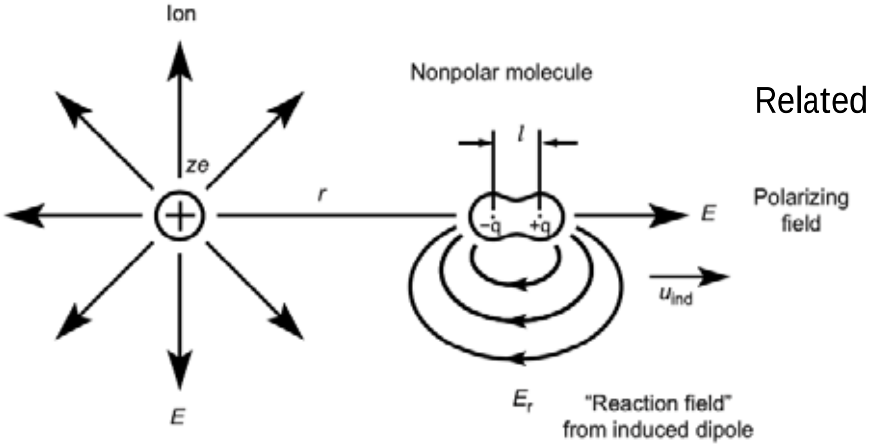
Stability barrier

Repulsion
electrostatic, steric

Secondary minimum

Attraction
van der Waals, depletion

van der Waals interactions



Related to the polarizability of molecules

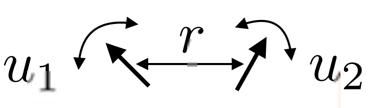
$$u_{\text{ind}} = ql = \alpha E$$

$$E_r = -2\alpha E/4\pi\epsilon\epsilon_0 r^3 = -2\alpha(ze)/(4\pi\epsilon\epsilon_0)^2 r^5$$

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\epsilon\epsilon_0)^2 r^5$$

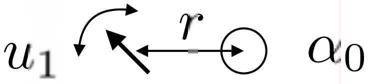
$$w(r) = -\int_\infty^0 F dr = -\alpha(ze)^2/2(4\pi\epsilon\epsilon_0)^2 r^4$$

Keesom interaction
angle-averaged dipole-dipole



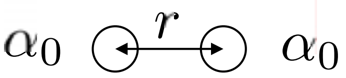
$$w(r) = \frac{-u_1^2 u_2^2}{3(4\pi\epsilon\epsilon_0)^2 kT}\left(\frac{1}{r^6}\right)$$

Debye interaction
rotating dipole-induced dipole



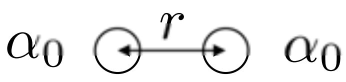
$$w(r) = \frac{-u_1^2 \alpha_0}{(4\pi\epsilon\epsilon_0)^2}\left(\frac{1}{r^6}\right)$$

London interaction
induced dipole-induced dipole



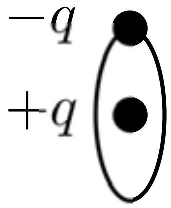
$$w(r) = \frac{-3\alpha_0^2 h\nu}{4(4\pi\epsilon_0)^2}\left(\frac{1}{r^6}\right)$$

London dispersion interaction



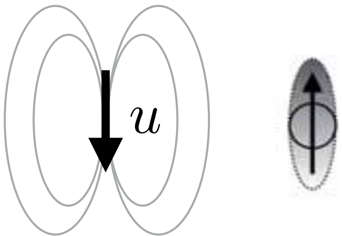
$$w(r) = \frac{-3\alpha_0^2 h\nu}{4(4\pi\epsilon_0)^2}\left(\frac{1}{r^6}\right)$$

Bohr atom



momentary dipole

$$\mathcal{O}(10^{-16})\,\mathrm{s}$$



$$\mathbf{E} = \frac{1}{4\pi\epsilon_0 r^3}\left(3\hat{\mathbf{x}}\hat{\mathbf{x}} - \mathbf{I}\right)\cdot\mathbf{u}$$

$$\nu \sim 3.3 \times 10^{15}\,\mathrm{s}^{-1}$$

$$I = h\nu$$

First ionization potential
of Bohr atom based on
its “orbital frequency”

- “Long-range” interaction 0.2-10nm
- Usually attractive, special cases repulsive
- Brings together molecules and weakly aligns
- <u>Not</u> pairwise additive

How strong? *Consider two atoms with*

$$\frac{\alpha_0}{4\pi\epsilon_0} = 1.5 \times 10^{-30}\,\mathrm{m}^3$$

$$I = h\nu = 2 \times 10^{-18}\,\mathrm{J}$$

$$r \sim \sigma \approx 0.3\,\mathrm{nm}$$

$$w(\sigma) = -4.6 \times 10^{-21}\,\mathrm{J}$$

$$\approx 1\,\mathrm{kT}$$

van der Waals interactions

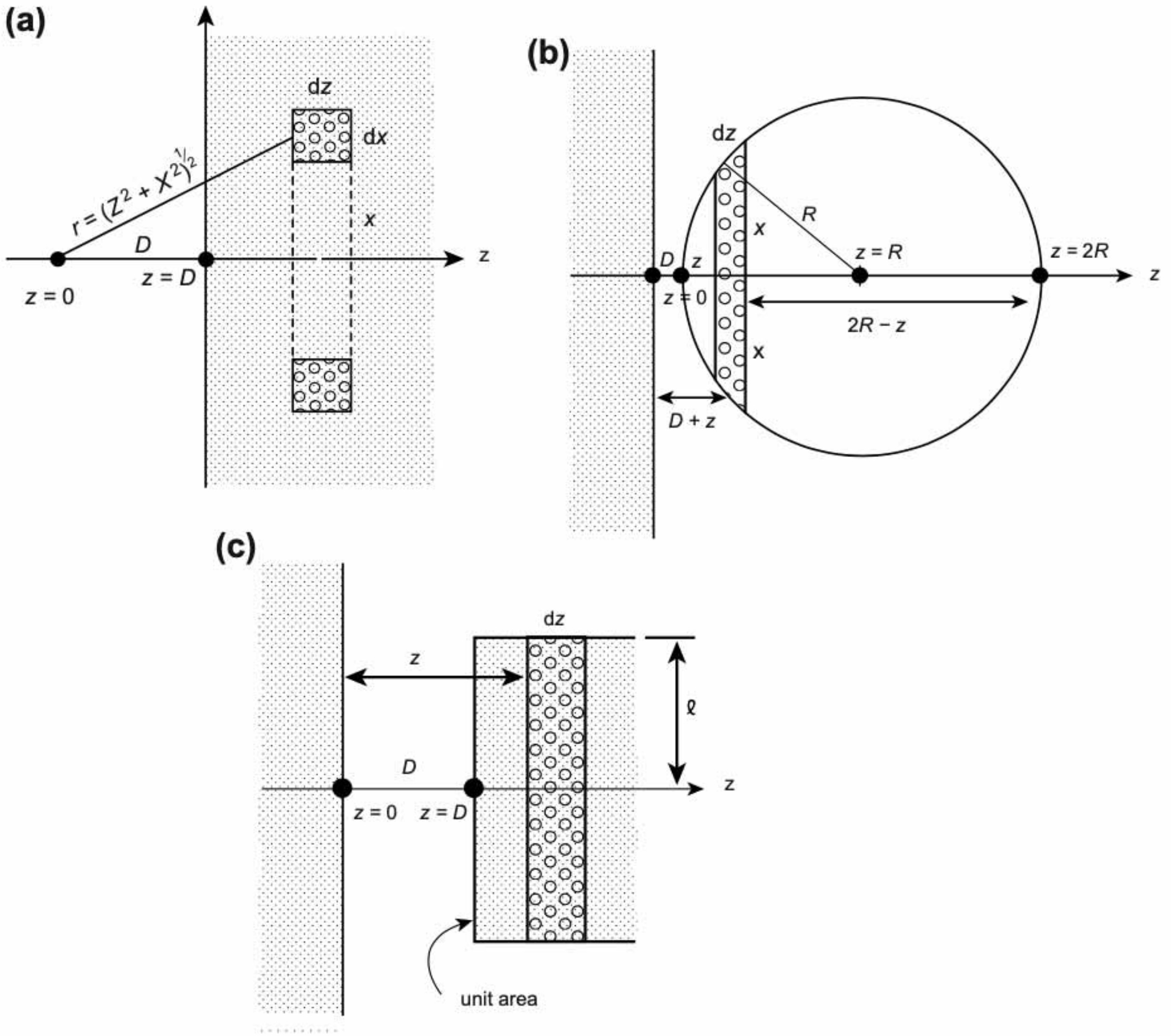
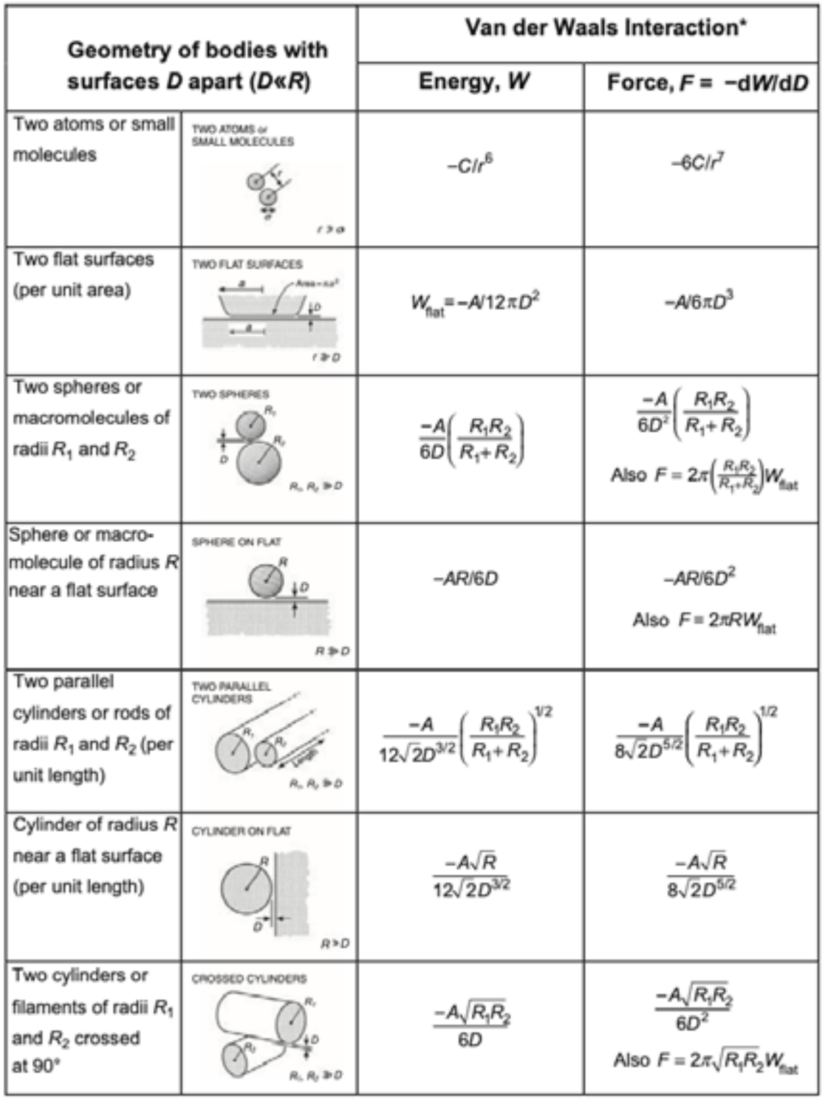


FIGURE 11.2 Methods of summing (integrating) the interaction energies between molecules in condensed phases to obtain the interaction energies between macroscopic bodies. **(a)** Molecule near a flat surface or "wall." **(b)** Spherical particle near a wall ($R \gg D$). **(c)** Two planar surfaces ($l \gg D$).

van der Waals attraction



Geometry of bodies with surfaces D apart ($D \ll R$)		Van der Waals Interaction*	
		Energy, W	Force, $F = -dW/dD$
Two atoms or small molecules	TWO ATOMS or SMALL MOLECULES $r \gg \sigma$	$-C/r^6$	$-6C/r^7$
Two flat surfaces (per unit area)	TWO FLAT SURFACES Area $= \pi a^2$ $r \gg D$	$W_{flat} = -A/12\pi D^2$	$-A/6\pi D^3$
Two spheres or macromolecules of radii R_1 and R_2	TWO SPHERES $R_1, R_2 \gg D$	$\frac{-A}{6D}\left(\frac{R_1R_2}{R_1+R_2}\right)$	$\frac{-A}{6D^2}\left(\frac{R_1R_2}{R_1+R_2}\right)$ Also $F = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)W_{flat}$
Sphere or macromolecule of radius R near a flat surface	SPHERE ON FLAT $R \gg D$	$-AR/6D$	$-AR/6D^2$ Also $F = 2\pi R W_{flat}$
Two parallel cylinders or rods of radii R_1 and R_2 (per unit length)	TWO PARALLEL CYLINDERS $R_1, R_2 \gg D$	$\frac{-A}{12\sqrt{2}D^{3/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$	$\frac{-A}{8\sqrt{2}D^{5/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Cylinder of radius R near a flat surface (per unit length)	CYLINDER ON FLAT $R \gg D$	$\frac{-A\sqrt{R}}{12\sqrt{2}D^{3/2}}$	$\frac{-A\sqrt{R}}{8\sqrt{2}D^{5/2}}$
Two cylinders or filaments of radii R_1 and R_2 crossed at 90°	CROSSED CYLINDERS $R_1, R_2 \gg D$	$\frac{-A\sqrt{R_1R_2}}{6D}$	$\frac{-A\sqrt{R_1R_2}}{6D^2}$ Also $F = 2\pi\sqrt{R_1R_2}W_{flat}$

FIGURE 13.1 Van der Waals interaction energy W and force F between macroscopic bodies of different geometries in terms of their Hamaker Constant, A. Negative F implies attraction (A positive); positive F means repulsion (A negative). The Hamaker constant A is defined as $A = \pi^2 C\rho_1\rho_2$ where ρ_1 and ρ_2 are the number of atoms per unit volume in the two bodies and C is the coefficient in the atom-atom pair potential (top row). More rigorous methods for calculating Hamaker constants are described in Sections 13.4 and 13.5. For other geometrics, see Parsegian (2006).

A_H *Hamaker constant*

$$w(r) = -C/r^6$$

$$A_H = \pi^2 C \rho_1 \rho_2$$

$$A_H = (0.4\text{–}4) \times 10^{-19}\ \text{J}$$

Interaction between spheres (more rigorous)

$$\Phi_{\text{vdw}}(h) = -\frac{A_H}{12}\left\{\left(\frac{4a^2}{4ah+h^2}\right) + \left(\frac{2a}{2a+h}\right)^2 + 2\ln\left[1 - \left(\frac{2a}{2a+h}\right)\right]\right\}$$

Hamaker constants

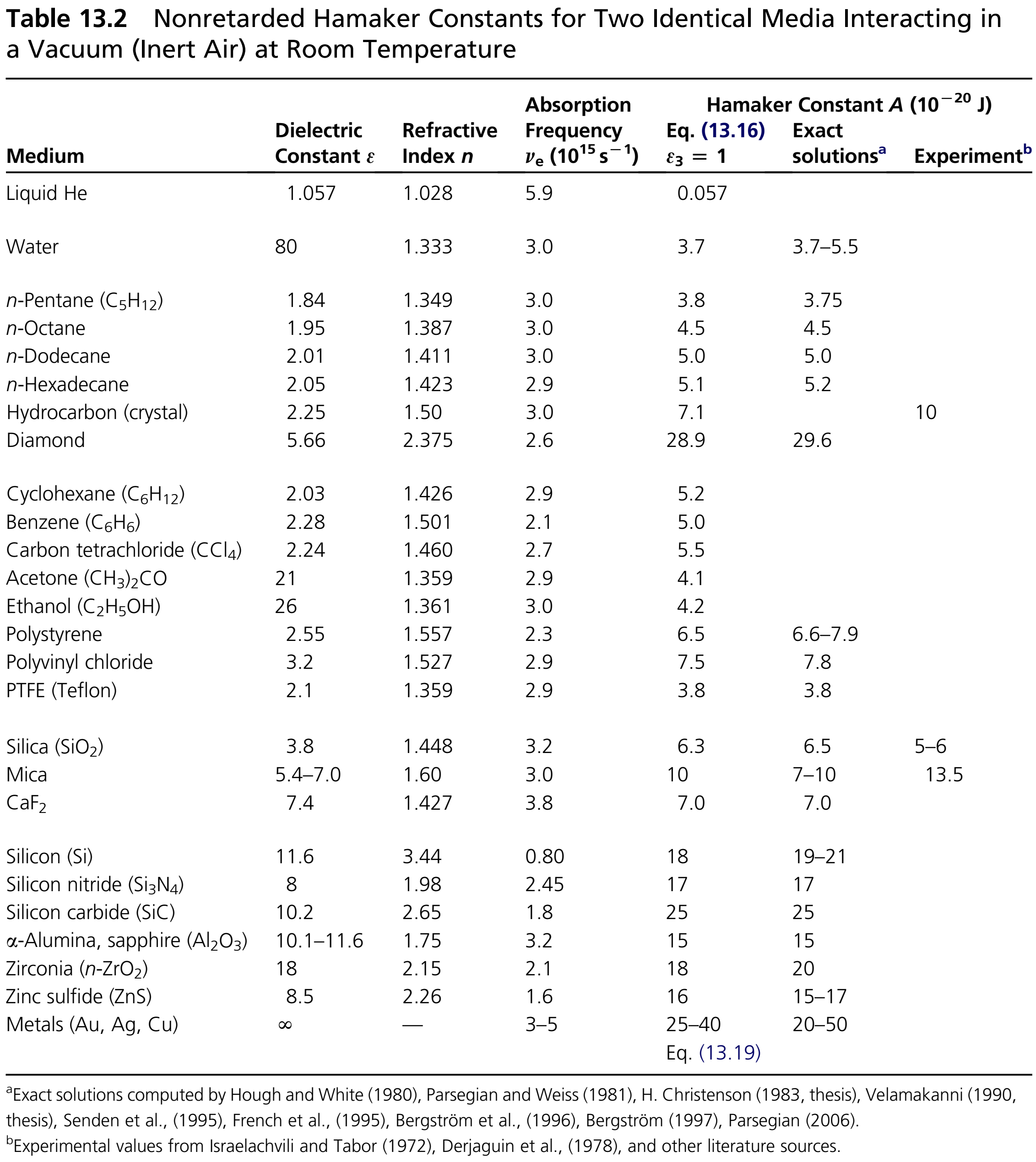


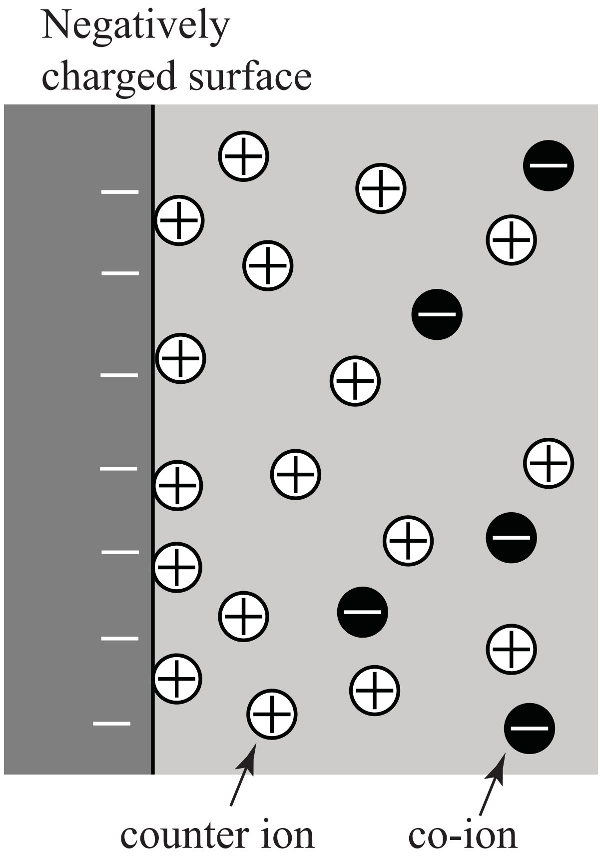
Table 13.2 Nonretarded Hamaker Constants for Two Identical Media Interacting in a Vacuum (Inert Air) at Room Temperature

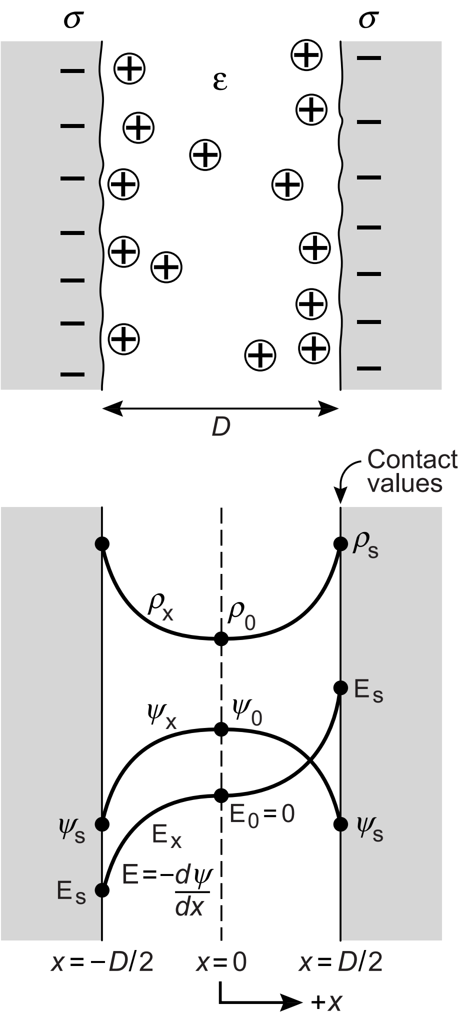
				Hamaker Constant A (10^{-20} J)		
Medium	**Dielectric Constant ε**	**Refractive Index n**	**Absorption Frequency ν_e ($10^{15}\ s^{-1}$)**	**Eq. (13.16) $\varepsilon_3 = 1$**	**Exact solutions[a]**	**Experiment[b]**
Liquid He	1.057	1.028	5.9	0.057		
Water	80	1.333	3.0	3.7	3.7–5.5	
n-Pentane (C_5H_{12})	1.84	1.349	3.0	3.8	3.75	
n-Octane	1.95	1.387	3.0	4.5	4.5	
n-Dodecane	2.01	1.411	3.0	5.0	5.0	
n-Hexadecane	2.05	1.423	2.9	5.1	5.2	
Hydrocarbon (crystal)	2.25	1.50	3.0	7.1		10
Diamond	5.66	2.375	2.6	28.9	29.6	
Cyclohexane (C_6H_{12})	2.03	1.426	2.9	5.2		
Benzene (C_6H_6)	2.28	1.501	2.1	5.0		
Carbon tetrachloride (CCl_4)	2.24	1.460	2.7	5.5		
Acetone ($(CH_3)_2CO$)	21	1.359	2.9	4.1		
Ethanol (C_2H_5OH)	26	1.361	3.0	4.2		
Polystyrene	2.55	1.557	2.3	6.5	6.6–7.9	
Polyvinyl chloride	3.2	1.527	2.9	7.5	7.8	
PTFE (Teflon)	2.1	1.359	2.9	3.8	3.8	
Silica (SiO_2)	3.8	1.448	3.2	6.3	6.5	5–6
Mica	5.4–7.0	1.60	3.0	10	7–10	13.5
CaF_2	7.4	1.427	3.8	7.0	7.0	
Silicon (Si)	11.6	3.44	0.80	18	19–21	
Silicon nitride (Si_3N_4)	8	1.98	2.45	17	17	
Silicon carbide (SiC)	10.2	2.65	1.8	25	25	
α-Alumina, sapphire (Al_2O_3)	10.1–11.6	1.75	3.2	15	15	
Zirconia (*n*-ZrO_2)	18	2.15	2.1	18	20	
Zinc sulfide (ZnS)	8.5	2.26	1.6	16	15–17	
Metals (Au, Ag, Cu)	∞	—	3–5	25–40 Eq. (13.19)	20–50	

[a] Exact solutions computed by Hough and White (1980), Parsegian and Weiss (1981), H. Christenson (1983, thesis), Velamakanni (1990, thesis), Senden et al., (1995), French et al., (1995), Bergström et al., (1996), Bergström (1997), Parsegian (2006).

[b] Experimental values from Israelachvili and Tabor (1972), Derjaguin et al., (1978), and other literature sources.

Electrostatic repulsion





Poisson equation

$$-\epsilon\epsilon_0\nabla^2\psi = ze\rho$$

Boltzmann distribution

$$\rho = \rho_0 e^{-ze\psi/kT}$$

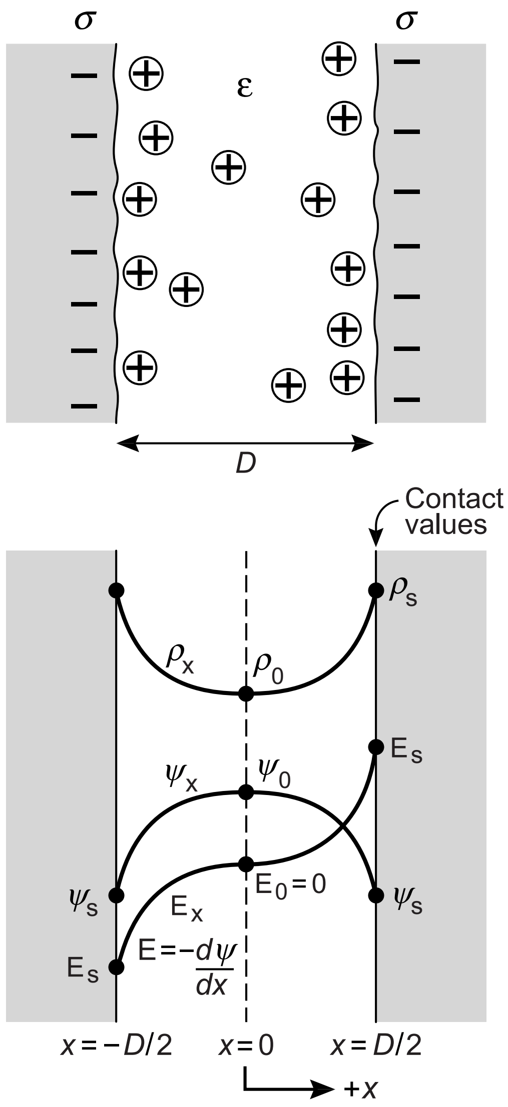
Poisson-Boltzmann equation

$$\nabla^2\psi = -(ze\rho_0/ - \epsilon\epsilon_0)e^{-ze\psi/kT}$$

Israelachvili, Intermolecular and Surface Forces, 3rd ed., Academic Press, New York, 2007.

Russel, Saville, and Schowalter. Colloidal Dispersions. Cambridge University Press, New York, 1989.

Interaction potential between spheres



Constant potential surfaces

$$U_{\mathrm{el}}(h) = 2\pi\epsilon\epsilon_0(kT/ze)^2 a\Psi_s^2 \ln\left[1+e^{-\kappa h}\right]$$

Debye length

$$\kappa^{-1} = \left(\frac{kT\epsilon\epsilon_0}{2Ie^2}\right)^{\frac{1}{2}}$$

Ionic strength

$$I = \frac{1}{2}\sum_{i=1}^{N} z_i^2 n_{s,i}$$

$$n_{s,i} = 1000 N_A c_{s,i}$$

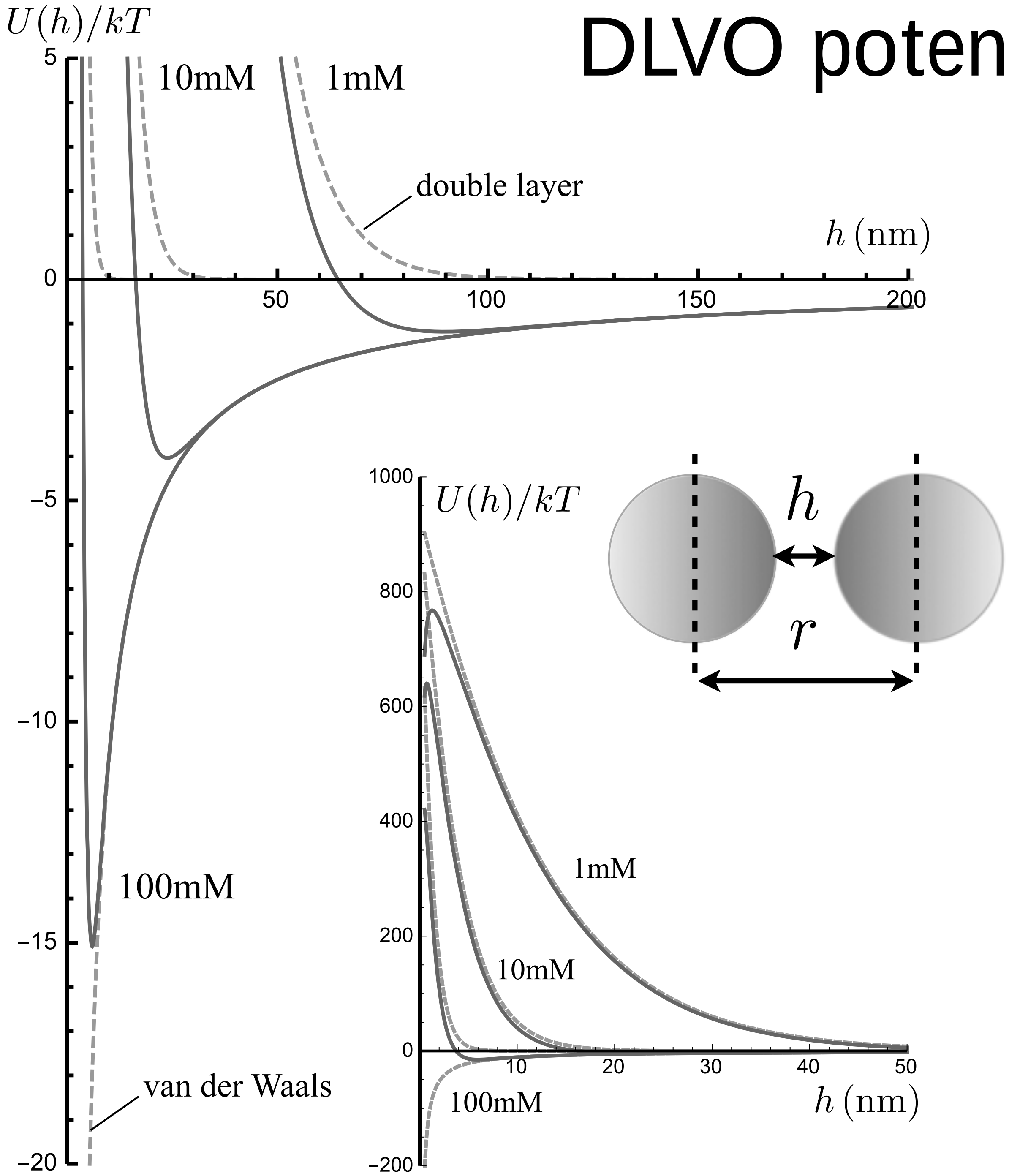
NaCl (mM)	κ^{-1} (nm)
0.1	31
1	9.7
10	3.1
100	0.97

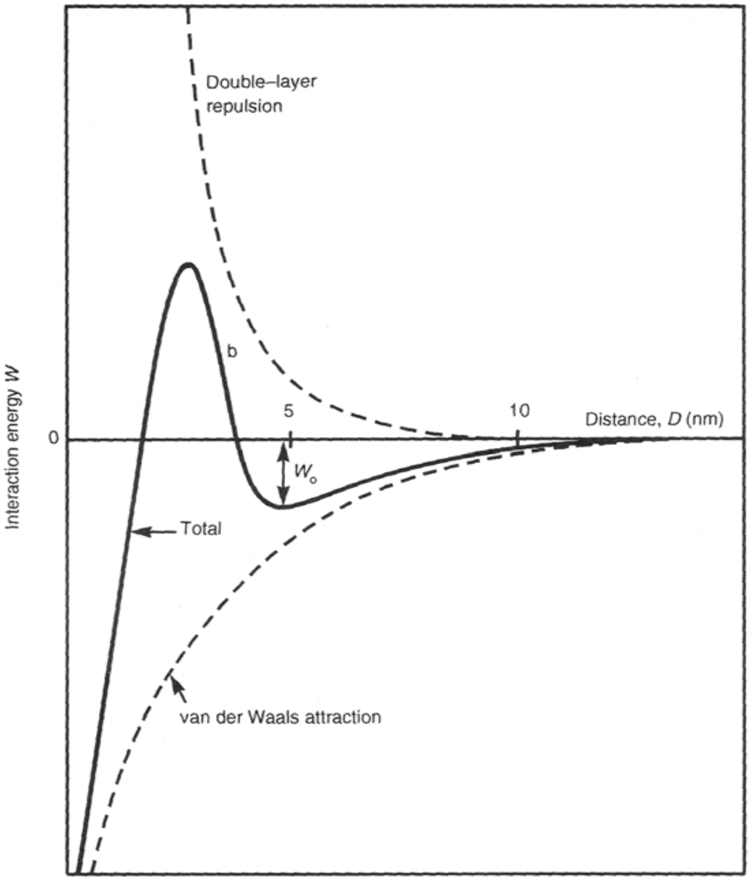
in water, R.T.

DLVO potential

$$U(h) = U_{\mathrm{vdw}}(h) + U_{\mathrm{el}}(h)$$

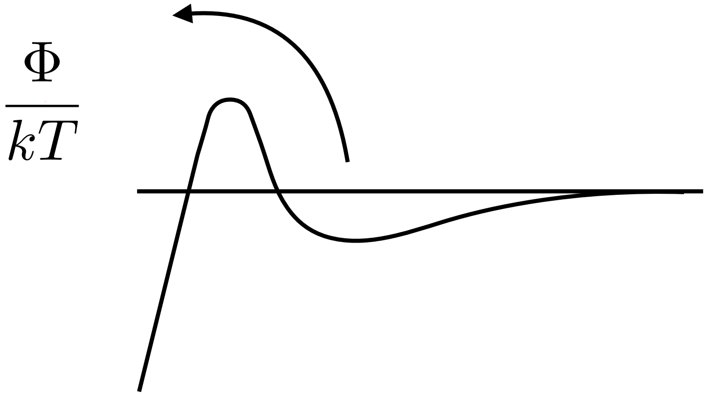
1µm diameter polystyrene, -50mV





Israelachvili, 2007

Kinetic stability



$$t \sim \left(\frac{3\pi a^3 \eta}{k_B T}\right) \exp(\Phi_{\mathrm{max}}/k_B T)$$

$$e^1 \approx 2.7$$

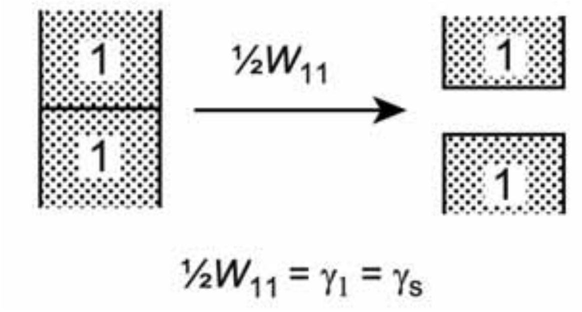
$$e^5 \approx 150$$

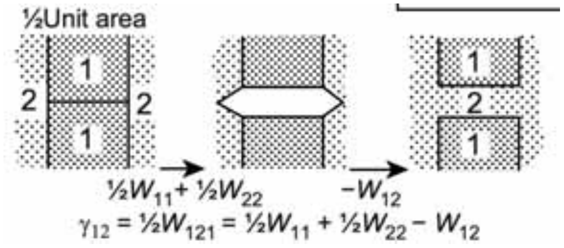
$$e^{10} \approx 2 \times 10^4$$

		$2a = 100$ nm	$1\ \mu$m	$10\ \mu$m
Brownian	$\tau_B = \frac{\pi \eta a^3}{kT}$	0.1 ms	100 ms	100 s

Cohesion

When particles come into contact, they are held by strong van der Waals forces





$$W_{SL} = \frac{1}{2} W_{SS} + \frac{1}{2} W_{LL} - \gamma_{SL}$$

Then

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL}$$

Young equation

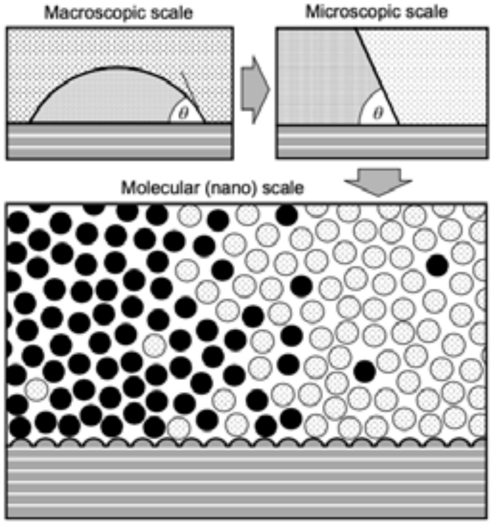
$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta$$

Young-Dupré equation

$$W_{SL} = \gamma_L (1 + \cos\theta)$$

Alternately,

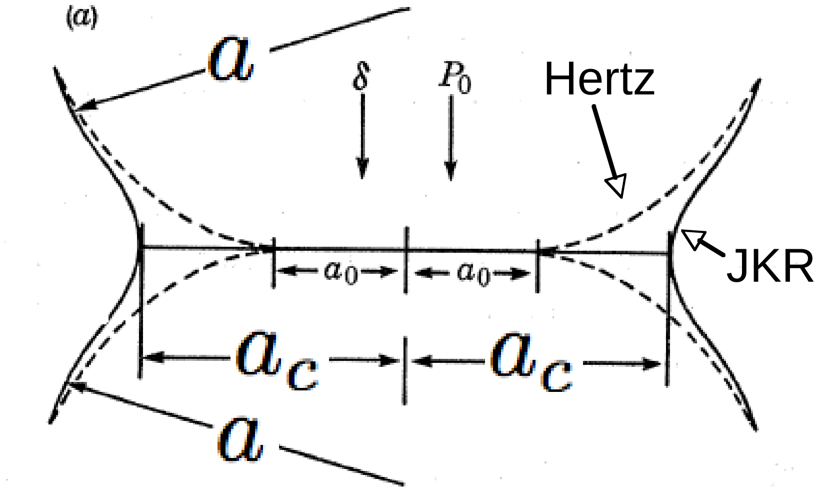
$$\gamma_S \approx \frac{A_H}{12\pi D_0^2}$$



Adhesion between elastic particles
JKR Theory

Johnson, Kendall and Roberts, Proc. R. Soc. London, Ser. A 324, 301 (1971).

$$P_0 = 0 \qquad a_c = \left[\frac{3\pi a^2 W_{SL}}{2K}\right]^{1/3}$$



Surface adhesion energy:

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL}$$

$$W_{SL} = \gamma_L(1+\cos\theta_0) \approx 93\mathrm{mJ/m^2}$$

Young-Dupré eqn

where[1] $\theta_0 = 73.7 \pm 0.3^\circ$

$\gamma_L \approx 72 - 73\mathrm{mN/m}$

Elastic modulus: $K = \frac{2E}{3(1-\nu^2)}$

$K \approx 2.5\mathrm{GPa}$ [2]

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[1] Kwok et al. J. Colloid Interface Sci. 206, 44 (1998).
[2] Jarvis and Scheiman, J. Phys. Chem. 72, 74 (1968).

DMT and JKR theories

Derjaguin, B., Muller, V. & Toporov, Y., *J. Colloid Interface Sci.* 53, 314–326 (1975)
Tabor, D. *J. Colloid Interface Sci.* 1977, 58, 2--13.

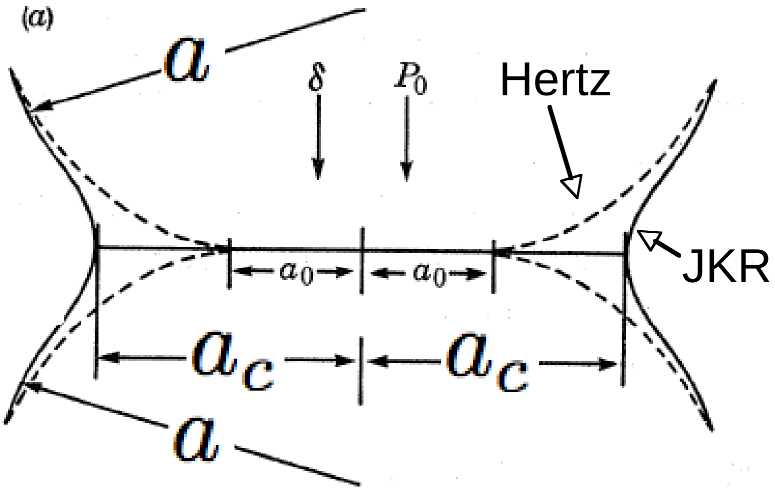
$$\lambda = \left(\frac{2W^2 a}{9K^2 h^3}\right)^{1/3}$$

	Contact radius	Tabor #	
JKR model	$a_c = \left(\frac{3\pi a^2 W}{2K}\right)^{1/3}$	$\gg 1$	
DMT model	$a_c = \left(\frac{\pi a^2 W}{2K}\right)^{1/3}$	$\ll 1$	
PMMA	$40\mathrm{nm}$	1.9	$K = 2.5\,\mathrm{GPa}$
silica	$10\mathrm{nm}$	0.4	$K = 23\,\mathrm{GPa}$

$$2a = 1\mu\mathrm{m}, W \sim 100\mathrm{mJ/m}^2, h \sim 0.3\mathrm{nm}$$

Energy holding particles together

Johnson, Kendall and Roberts, Proc. R. Soc. London, Ser. A 324, 301 (1971).



With $a_c \approx 40\,\mathrm{nm}$ $\quad W_{SL} \approx 93\,\mathrm{mJ/m^2}$

$$U(h=0) \sim 4.7 \times 10^{-15} J$$

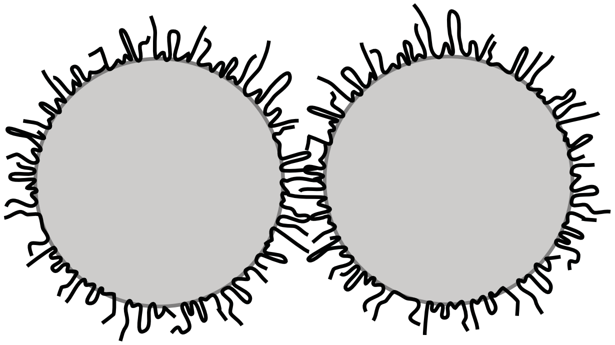
$$U(h=0) \sim 10^{-16} J \sim 10^3\,\mathrm{kT}$$

We should calculate the force!

Steric forces

D. H. Napper. *Polymeric Stabilization of Colloidal Dispersions*. Academic Press, New York, 1983.

Adsorbed and grafted polymers
Homopolymers and co-polymers



For chemically-grafted polymers:

$$\Phi_p = \begin{cases} \Phi_0 \left[-\ln y - \frac{9}{5}(1-y) + \frac{1}{3}(1-y^3) - \frac{1}{30}(1-y^6) \right], & 0 < y < 1 \\ 0 & y \geq 1 \end{cases}$$

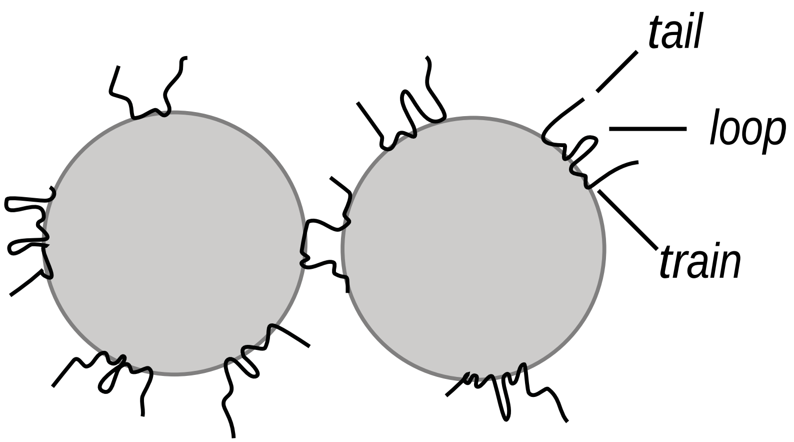
$$y = h/2L = (r - 2a)/2L$$

$$\Phi_0 = \left(\frac{\pi L \sigma_p k_B T}{12 N_p l^2} \right) a L^2$$

L	contour length
N_p	degree of polymerization
l	segment length
ϕ_p	surface graft fraction

Bridging interactions

Adsorbed polymer, protein at lower surface coverage



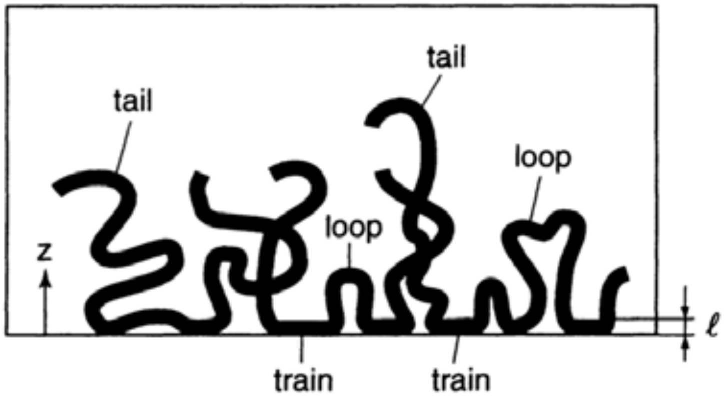
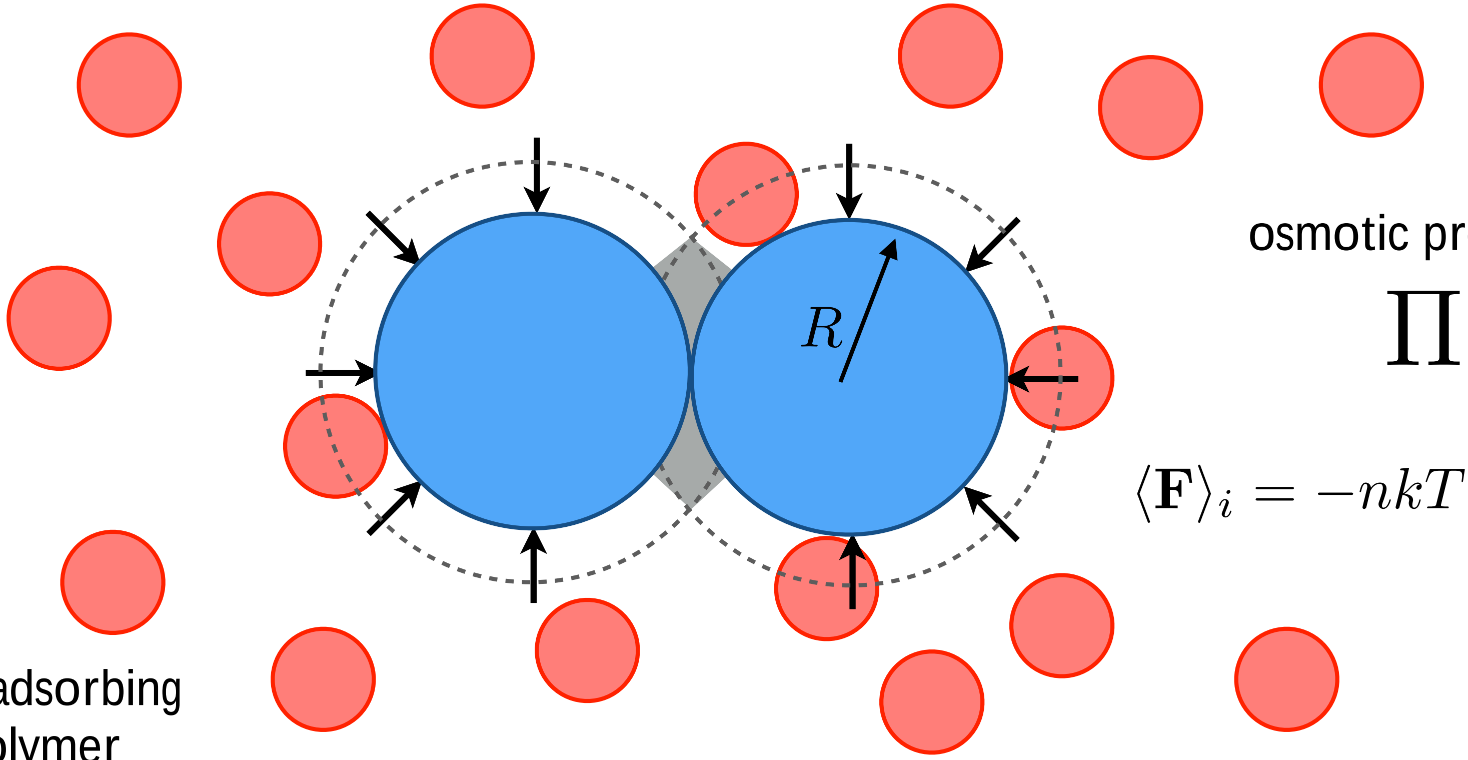


FIGURE 2.3.1. Pictorial representation of an adsorbed polymer layer. Loops, tails, and trains are indicated.

G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T .Cosgrove, B.Vincent. Polymers at Interfaces. New York, 1993.

Depletion attraction

Asakura, S. & Oosawa, F. J Chem Phys 22, 1255–1256 (1954).
Vrij, A. Pure Appl. Chem. 48, 471–483 (1976).



osmotic pressure

$$\Pi$$

$$\langle \mathbf{F} \rangle_i = -nkT \oint \mathbf{n}_i g \, dS_i$$

non-adsorbing polymer

$$\frac{U(r)}{k_B T} \approx \phi_p \left\{ 1 - \frac{3r}{4R(1+R_g/R)} + \frac{1}{2}\left[\frac{r}{2R(1+R_g/R)}\right]^3 \right\}$$

Depletion potential