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03. Colloids I

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What Are Colloids? [pln3]

Particles dipersed in some medium. The particles and the medium can be solid, liquid, or gaseous. Many combinations are realized.

Classification: [table adapted from Hamley 2007]

particles	*medium*	*type*	*realizations*
liquid	gas	liquid aerosol	fog, spray
solid	gas	solid aerosol	smoke, dust
gas	liquid	foam	foams, froths
liquid	liquid	emulsion	milk, mayonnaise
solid	liquid	sol, dispersion suspension	paints, ink, blood
gas	solid	solid foam	styrofoam, pumice
liquid	solid	solid emulsion gel	tarmac, ice cream jelly, gelatin
solid	solid	solid suspension	opal, pearl pigmented plastic

Shapes:

- liquid droplets are mostly spherical (interfacial tension balanced by pressure),
- gas bubbles are spherical at low density and tend to be polyhedral at high density (in foams),
- solid particles tend to have many different shapes,
  - compact (roughly spherical or polyhedral),
  - elongated (rod-like),
  - flat (plate-like).

Maximum size:

- solid colloids have diameter $\lesssim 1\mu$m,
- grains have diameter $\gtrsim 1\mu$m,
- motion of colloids driven by thermal fluctuations,
- motion of grains driven by mechanical agitation (e.g. shaking).

Size distribution:

- *monodispersity* (narrow distribution),
- *polydispersity* (broad distribution).

Sols:

- Solid particles dispersed in liquid.
- Preparation:
  - milling,
  - ultrasound,
  - condensation from vapor,
  - nucleation from solution.
- Challenge: control of polydispersity.
- Relation to solvent: lyophobic versus lyophilic.

Gels:

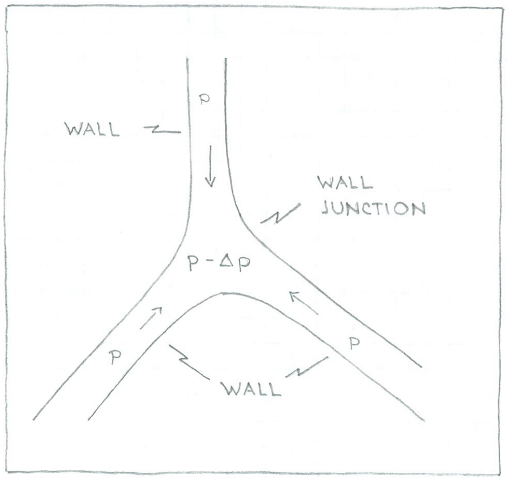
- In rheological terms gels are Bingham fluids. Dispersion medium is elastic; it does not flow.
- Sol-gel transition induced at critical concentration, perhaps assisted by chemically enhanced aggregation.
- Some gels consist of soft bridging networks grown via flocculation.
- Gels may absorb fluids due to osmotic effect and swell. Swelling saturates if network is strong or breaks up weak networks.
- Syneresis: gels may form in one structure and then age into a different, more compact structure, releasing liquid in the process.

Clays:

- Colloidal suspension of ($\sim \mu$m-sized) plate-like mineral particles.
- Formation of layered structures via adhesive VDW or H-bond forces.
- Some clays layers of water between platelets.
- Some clays have positive charges (broken covalent bonds) along edges of platelets and negative charges across flat surfaces. The charges may then produce a gel structure.

Foams:

- Gas bubbles in liquid or solid medium with shapes changing from spherical toward polyhedral as crowding increases.
- Stability of gas/liquid foams is precarious:
    1. Liquid drains, driven by gravity. Walls become thinner. Thin walls tend to pop. Interior bubbles merge and get bigger in the process. Exterior bubbles disappear.
    2. Liquid drains out of walls toward wall junctions (plateau borders), driven by surface tension. Surface tension lowers pressure at junctions relative to walls. Pressure differential induces liquid flow from walls toward junctions. Walls get thinner and junctions wider. Bubbles pop with consequences as stated.
- Gibbs-Marangoni effect: presence of surfactant molecules reduces surface tension, which slows down wall thinning.



Emulsions:

- Dispersions of immiscible liquids, homogenized e.g. by stirring, shaking, or ultrasonification.
- Homogenization increases interfacial area, which adds (positive) interfacial free energy.
- Dispersed droplets of minority liquid will merge in due time and thus lower the free energy.
- Emulsifiers (surfactant additives) reduce surface tension and thus prolong lifetime of homogenized state.

Estimate of interfacial free energy:

- N: number of droplets of minority liquid,
- R: average radius of droplets,
- γ: interfacial tension,
- $V = \frac{4\pi}{3}R^3N$: estimated total volume of droplets,
- $A = 4\pi R^2 N = \frac{3V}{R}$: estimated total interfacial area,
- $\Delta G = \gamma\frac{3V}{R}$: estimated free energy.

Some relevant facts:

- *Microemulsions* (of diameters $\sim 1-100$nm) tend to be thermodynamically more stable than *macroemulsions* (of diameters $\sim 0.1-10\mu$m).
- The same combination of substances with minority/majority reversed yields diverse products, e.g. margerine (water/oil) or milk (oil/water).
- Distinguish *dispersed* microemulsions, where only the majority liquid is connected macroscopically, from *bicontinuous* microemulsions, where both liquids form macroscopic networks.
- Colloids tend to produce non-Newtonian viscous behavior, e.g. shear thinning or shear thickening.

Stability of colloids:

- Stability against ...
  - *sedimentation* (settling at the bottom),
  - *creaming* (rising to the top),
  - *aggregation* (in the bulk).
- Types of aggregation are
  - *flocculation* (mostly reversible),
  - *coagulation* (irreversible and irregular),
  - *coalescence* (irreversible and regular).
- Monodisperse colloids tend to crystallize (coalesce) and polydisperse colloids tend to coagulate.
- Stability often is a matter of time scale.

Interactions between colloids:

- Interaction range tends to be small compared to particle size (unlike for atoms or small molecules).
- Some interaction energies tend to be large compared to $k_\mathrm{B}T$ and cause irreversible aggregation.
- Some interaction energies are controllable by modifications of the medium.

Agents of change:

- Agents of aggregation are
  - gravity, buoyancy,
  - short-range attractive forces.
- Agents of dispersion are
  - Brownian motion (thermal fluctuations),
  - electrostatic repulsion (charge stabilization),
  - modified particle surfaces (steric stabilization).

Separate topics:

- association colloids (amphiphiles)
- polymer solutions
- network colloids (porous solids)

Brownian Motion [nln63]

Early experimental evidence for atomic structure of matter. Historically important in dispute between 'atomicists' and 'energeticists' in late 19th century.

Brown 1828:
Observation of perpetual, irregular motion of pollen grains suspended in water. The particles visible under a microscope (pollen) are small enough to be manifestly knocked around by even smaller particles that are not directly visible (molecules).

Einstein, Smoluchowski 1905:
Correct interpretation of Brownian motion as caused by collisions with the molecules of a liquid. Theoretical framework of thermal fluctuations grounded in the assumption that matter has a molecular structure and with aspects that are experimentally testable.

Perrin 1908:
Systematic observations of Brownian motion combined with quantitative analysis. Confirmation of Einstein's predictions. Experimental determination of Avogadro's number.

Langevin 1908:
Confirmation of Einstein's results via different approach. Langevin's approach provided more detailed (less contracted) description of Brownian motion. Langevin equation proven to be generalizable. Foundation of general theory of fluctuations rooted in microscopic dynamics.

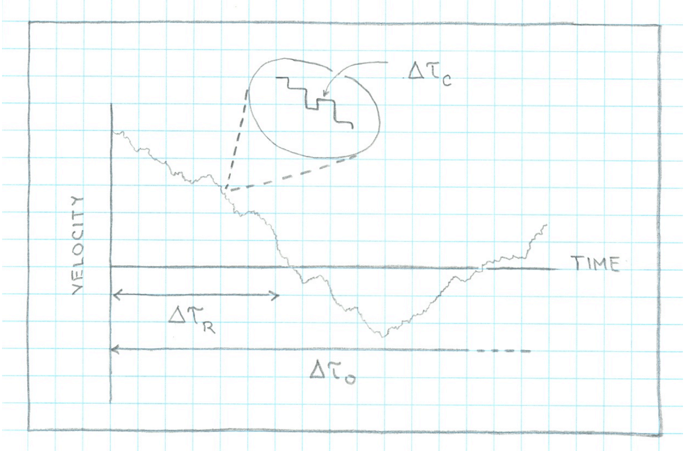
Relevant Time Scales [nln64]

Conceptually, it is useful to distinguish between *heavy* and *light* Brownian particles. For the most part, only Brownian particles that are heavy compared to the fluid molecules are large enough to be visible under a microscope.

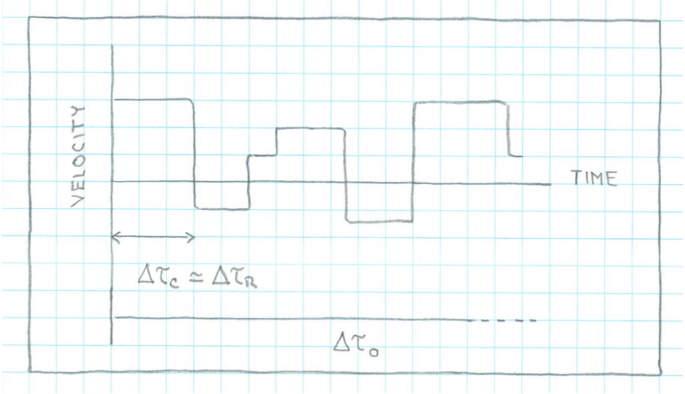
Time scales relevant in the observation and analysis of Brownian particles:

- $\Delta\tau_\mathrm{C}$: time between collisions,
- $\Delta\tau_\mathrm{R}$: relaxation time,
- $\Delta\tau_\mathrm{O}$: time between observations.

Heavy Brownian particles: $\Delta\tau_\mathrm{C} \ll \Delta\tau_\mathrm{R} \ll \Delta\tau_\mathrm{O}$.



Light Brownian particles: $\Delta\tau_\mathrm{C} \simeq \Delta\tau_\mathrm{R} \ll \Delta\tau_\mathrm{O}$.



Einstein's Theory [nln65]

Theory operates on time scale dt, where $\Delta\tau_R \ll dt \ll \Delta\tau_\mathrm{O}$.
Focus on one space coordinate: x.
Local number density of Brownian particles: $n(x,t)$.
Brownian particles experience shift of size s in time dt.
Probability distribution of shifts: $P(s)$.
Successive shifts are assumed to be statistically independent.
Assumption justified by choice of time scale: $\Delta\tau_R \ll dt$.

Effect of shifts on profile of number density:

$$n(x,t+dt) = \int_{-\infty}^{+\infty} ds\, P(s) n(x+s,t).$$

Expansion of $n(x,t)$ in space and in time:

$$n(x+s,t) = n(x,t) + s\frac{\partial}{\partial x}n(x,t) + \frac{1}{2}s^2\frac{\partial^2}{\partial x^2}n(x,t) + \cdots ,$$

$$n(x,t+dt) = n(x,t) + dt\frac{\partial}{\partial t}n(x,t) + \cdots$$

Integrals (normalization, reflection symmetry, diffusion coefficient):

$$\int_{-\infty}^{+\infty} ds\, P(s) = 1, \quad \int_{-\infty}^{+\infty} ds\, sP(s) = 0, \quad \frac{1}{2}\int_{-\infty}^{+\infty} ds\, s^2P(s) \doteq Ddt.$$

Substitution of expansions with these integrals yields diffusion equation:

$$\frac{\partial}{\partial t}n(x,t) = D\frac{\partial^2}{\partial x^2}n(x,t).$$

Solution with initial condition $n(x,0) = N\delta(x-x_0)$ and no boundaries:

$$n(x,t) = \frac{N}{\sqrt{4\pi Dt}}\exp\left(-\frac{(x-x_0)^2}{4Dt}\right),$$

No drift: $\langle\langle x\rangle\rangle = 0$.

Diffusive mean-square displacement: $\langle\langle x^2\rangle\rangle = 2Dt$.

Smoluchowski Equation [nln66]

Einstein's result derived from different starting point.

Two laws relating number density and flux of Brownian particles:

(a) Conservation law: $\frac{\partial}{\partial t}n(x,t) = -\frac{\partial}{\partial x}j(x,t)$ (continuity equation);
local change in density due to net flux from or to vicinity.

(b) Constitutive law: $j(x,t) = -D\frac{\partial}{\partial x}n(x,t)$ (Fick's law);
flux driven by gradient in density.

Combination of (a) and (b) yields diffusion equation for density:

$$\frac{\partial}{\partial t}n(x,t) = D\frac{\partial^2}{\partial x^2}n(x,t). \tag{1}$$

Solution of (1) yields flux via (b).

Extension to include drift.

Brownian particles subject to external force $F_{\mathrm{ext}}(x,t)$.

Resulting drift velocity v, averaged over time scale dt identified in [nln65], produces drag force $F_{\mathrm{drag}} = -\gamma v$ due to front/rear asymmetry of collisions.

Damping constant: γ; mobility: γ^{-1}.

Drift contribution to flux $j(x,t)$ has general form $n(x,t)v(x,t)$.

On time scale dt of [nln65], forces are balanced: $F_{\mathrm{ext}} + F_{\mathrm{drag}} = 0$.

Drift velocity has reached terminal value: $v_{\mathrm{T}} = F_{\mathrm{ext}}/\gamma$.

(c) Extended constitutive law: $j(x,t) = -D\frac{\partial}{\partial x}n(x,t) + \gamma^{-1}F_{\mathrm{ext}}(x,t)n(x,t)$.

Substitution of (c) into (a) yields Smoluchowski equation:

$$\frac{\partial}{\partial t}n(x,t) = D\frac{\partial^2}{\partial x^2}n(x,t) - \gamma^{-1}\frac{\partial}{\partial x}\big[n(x,t)F_{\mathrm{ext}}(x,t)\big]. \tag{2}$$

The two terms on the rhs represent diffusion and drift, respectively.

Einstein's Fluctuation-Dissipation Relation [nln67]

Consider a colloid of volume V suspended in a fluid.
Excess mass: $m = V(\rho_{\text{coll}} - \rho_{\text{fluid}})$.
External (gravitational) force directed vertically down: $F_{\text{ext}} = -mg$.

Smoluchowski equation [nln66]:

$$\frac{\partial}{\partial t} n(z,t) = D \frac{\partial^2}{\partial z^2} n(z,t) + \gamma^{-1} \frac{\partial}{\partial z}\big[n(z,t)mg\big].$$

Stationary solution: $\partial n/\partial t = 0 \quad \Rightarrow \; n = n_{\text{s}}(z)$.

$$\Rightarrow \; \frac{d}{dz}\left[D\frac{dn_{\text{s}}}{dz} + \frac{mg}{\gamma}n_{\text{s}}\right] = 0; \quad n_{\text{s}}(\infty) = 0, \quad \left.\frac{dn_{\text{s}}}{dz}\right|_{z=\infty} = 0.$$

$$\Rightarrow \; n_{\text{s}}(z) = n_{\text{s}}(0)\exp\left(-\frac{mg}{\gamma D}\,z\right).$$

Comparison with law of atmospheres (thermal equilibrium state) [tex150],

$$n_{\text{eq}}(z) = n_{\text{eq}}(0)\exp\left(-\frac{mg}{k_{\text{B}}T}\,z\right),$$

implies

$$D = \frac{k_{\text{B}}T}{\gamma} \qquad \text{(Einstein relation).}$$

This is an example of a relation between a quantity representing fluctuations (D) and a quantity representing dissipation (γ).

The Einstein relation was used to estimate Avogadro's number N_{A}:

- Colloid in the shape of a solid sphere of radius a.
- Motion in incompressible fluid with viscosity η.
- Stokes' law for drag force: $F_{\text{drag}} = -6\pi\eta a v = -\gamma v$.
- Damping constant $\gamma = 6\pi\eta a$ (experimentally accessible).
- Diffusion constant D (experimentally accessible).
- Ideal gas constant $R = N_{\text{A}}k_{\text{B}}$ (experimentally accessible).
- Avogadro's number: $N_{\text{A}} = \dfrac{RT}{6\pi\eta a D}$.

Langevin's Theory [nln71]

Langevin's theory of Brownian motion operates on a less contracted level of description than Einstein's theory [nln65]. The operational time scale is small compared to the relaxation time: $dt \ll \Delta\tau_{\mathrm{R}}$. [nln64]. On this time scale inertia matters, implying that velocity cannot change abruptly. Velocity and position variables are kinematically coupled.

The Langevin equation,

$$m\ddot{x} = -\gamma\dot{x} + f(t), \tag{1}$$

is constructed from Newton's second law with two forces acting:

- drag force: $-\gamma\dot{x}$ (parametrized by mobility γ^{-1}),
- random force: $f(t)$ (Gaussian white noise/Wiener process).

Since we do not know $f(t)$ explicitly we cannot solve (1) for $x(t)$. However, we know enough about $f(t)$ to solve (1) for $\langle x^2\rangle$ as a function of time [nex118].

First step: derive the linear, 2nd-order ODE for $\langle x^2\rangle$,

$$m\frac{d^2}{dt^2}\langle x^2\rangle + \gamma\frac{d}{dt}\langle x^2\rangle = 2k_BT, \tag{2}$$

using

- the white-noise implication that the random force and the position are uncorrelated, $\langle xf(t)\rangle$,
- the equilibrium implication that the average kinetic energy of the Brownian particle satisfies equipartition, $\langle\dot{x}^2\rangle = k_{\mathrm{B}}T/m$.

Second step: Integrate (2) twice using

- initial conditions $\langle x^2\rangle_0 = 0$ and $d\langle x^2\rangle_0/dt = 0$,
- Einstein's fluctuation-dissipation relation $D = k_{\mathrm{B}}T/\gamma$,
- the fact that (2) is a 1st-order ODE for $d\langle x^2\rangle/dt$.

The result reads

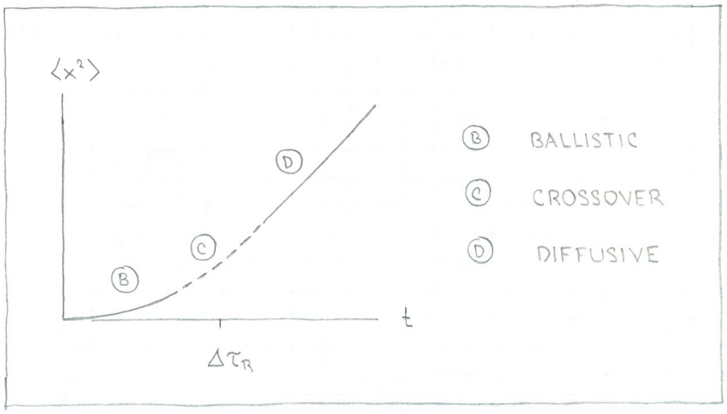
$$\langle x^2\rangle = 2D\left[t - \frac{m}{\gamma}\left(1 - e^{-\gamma t/m}\right)\right]. \tag{3}$$

Within the framework of Langevin's theory, the relaxation time previously identified [nln64] is

$$\Delta\tau_{\rm R} = \frac{m}{\gamma}.$$

This relaxation time separates short-time *ballistic* regime from a long-time *diffusive* regime:

- $t \ll \dfrac{m}{\gamma}: \quad \langle x^2\rangle \sim \dfrac{D\gamma}{m}t^2 = \dfrac{k_BT}{m}t^2 = \langle v^2\rangle t^2,$
- $t \gg \dfrac{m}{\gamma}: \quad \langle x^2\rangle \sim 2Dt.$



Applications and variations:

▷ Mean-square displacement of Brownian particle [nex56] [nex57] [nex118]

▷ Formal solution of Langevin equation [nex53]

▷ Velocity correlation function of Brownian particle [nex55] [nex119] [nex120]

Brownian Motion of Particles with Shapes [pln40]

Langevin equation: $m\ddot{x} = -\gamma\dot{x} - \dfrac{dU}{dx} + f$.

- $m\ddot{x}$: inertia, ignorable in diffusive regime,
- $-\gamma\dot{x}$: drag force,
- $-dU/dx$: force from external potential,
- f: white-noise random force, $\langle f(t)f(t')\rangle = 2\gamma k_\mathrm{B}T\delta(t-t')$.

Overdamped motion: $\gamma\dfrac{dx}{dt} = -\dfrac{dU}{dx} + f$.

Particles with several degrees of freedom and external potential $U(x_1,\ldots,x_n)$ experience three kinds of generalized forces:

- conservative force: $F_i^{(\mathrm{c})} = -\partial U/\partial x_i$,
- dissipative force: $F_i^{(\mathrm{d})} = -\sum_j \gamma_{ij}\dot{x}_j$,
- random force: f_i with $\langle f_i(t)f_j(t')\rangle = 2\gamma_{ij}k_\mathrm{B}T\delta(t-t')$.

Attributes of generalized friction coefficients:

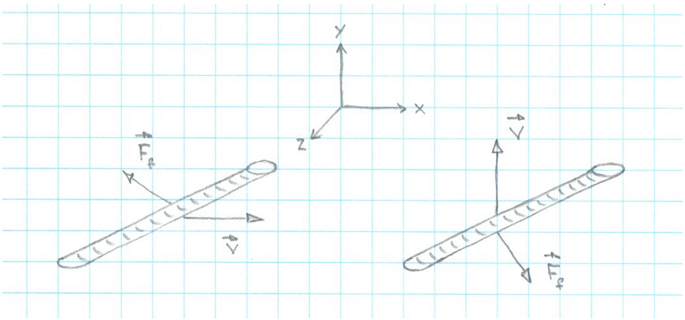
(1) $\gamma_{ij} = \gamma_{ji}$: effects are reciprocal,
(2) $\sum_{ij}\gamma_{ij}\dot{x}_i\dot{x}_j \geq 0$: dissipative work is non-negative.

In hydrodynamics, Eqs. (1) are named *Lorentz* reciprocal relations and in statistical mechanics *Onsager* reciprocal relations.

Reciprocal effects applied to rod-like particles and to particles with chirality are discussed on the next page.

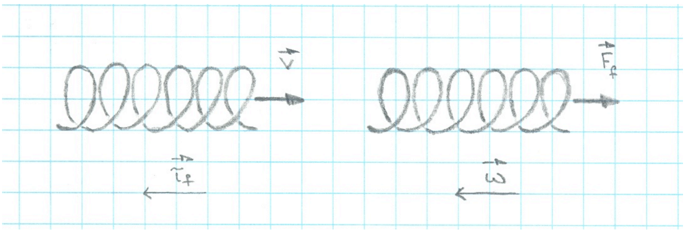
Consider a rod-like particle. When it moves in x-direction (y-direction) it experiences a drag force in the direction shown on the left (right). Reciprocity (1) implies the following relation between components of forces and velocities:

$$\frac{F_{\mathrm{f}y}}{v_x} = \frac{F_{\mathrm{f}x}}{v_y}.$$



Consider a particle with helical shape. When it moves with velocity $\vec{v}$ it experiences a torque $\vec{\tau}_{\mathrm{f}}$. When it rotates with angular velocity $\vec{\omega}$ about its axis it experiences a force $\vec{F}_{\mathrm{f}}$. Reciprocity (1) implies the following relation between (generalized) forces and velocities:

$$\frac{\tau_{\mathrm{f}}}{v} = \frac{F_{\mathrm{f}}}{\omega}.$$



[extracted from Doi 2013]

[pex22] Colloidal regime on Earth and in space

Consider a dispersion of solid particles with diameter σ and excess density $\rho = 1\text{g/cm}^3$ in a fluid medium at room temperature. In the following we investigate two measures that demarcate a colloidal regime, $\sigma < \sigma_c$, from a granular regime, $\sigma > \sigma_c$. One measure involves the Earth's gravitational field, the other does not.
(a) The first measure uses the barometric formula for the height distribution of dispersed particles at thermal equilibrium as a criterion. Calculate the average height $\langle h \rangle$ of particles with diameter σ. In the colloidal regime we must have $\langle h \rangle > \sigma$. Estimate σ_c.
(b) For the second measure we use Brownian motion in water and the Einstein-Stokes expression for the diffusion constant. For the colloidal regime we demand that the particle diffuse a distance greater than its diameter every second (on average). Estimate σ_c again and compare with the the estimate derived from the other measure.
(c) How long (in years) would a grain with $\sigma = 1\text{mm}$ take to diffuse across the distance of its diameter when propelled by Brownian motion in water at room temperature?

[adapted from D. Frenkel in Hu and Shi 2011]

Solution:

Van der Waals Attraction Between Colloids [pln42]

Quantum mechanical perturbation theory predicts attractive force between (neutral) atoms due to fluctuating electric dipole moments.

Effective VdW potential:

$$V(r) = -\frac{C}{r^6}, \quad C = \frac{3}{4}\left(\frac{1}{4\pi\epsilon_0}\right)^2 \alpha^2\hbar\omega,$$

where α is the electric polarizability and $\hbar\omega$ the ionization energy.

Consequence: adhesive force between objects of mesoscopic or macroscopic size with strength depending on size and shape of objects and on distance between them.

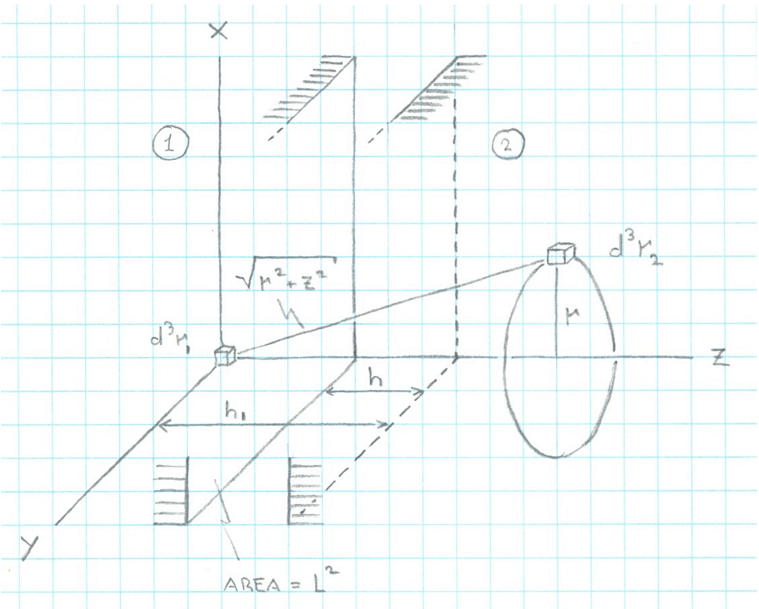
Generic expression for interaction energy:

$$U_{12} = -\int d^3r_1\,\rho(\vec{r}_1)\int d^3r_2\,\rho(\vec{r}_2)\,\frac{C}{|\vec{r}_1-\vec{r}_2|^6},$$

where $\rho(\vec{r})$ is the atomic number density.

Applications to simple cases:

- two large objects with parallel flat surfaces [pex23],
- two solid objects of spherical shape close to each other [pex24].



Comments:

- Assumption of pairwise additivity neglects many-body effects, i.e. collective nature of fluctuations.
- Assumption of instantaneity neglects retardation effects, i.e. dynamic nature of fluctuations.
- Retardation effects weaken adhesive force at large distances:
  - ▷ $\sim r^{-6} \to r^{-7}$ (microscopically).
  - ▷ $\sim h^{-2} \to h^{-3}$ (mesoscopically).
- Assumption of unpolarized space between colloids neglects effects of dispersion medium.
- Casimir effect represents alternative derivation of adhesive force in terms of vacuum fluctuations of elcetromagnetic field in the space between colloids.

[extracted from Jones 2002]

[pex23] Adhesive force between flat colloidal surfaces

The (attractive) van der Waals interaction between atoms is a consequence of correlated quantum fluctuations, effectively a coupling between induced electric dipoles. The interatomic potential energy inferred from a quantum mechanical perturbation calculation reads

$$V(r) = -\frac{C}{r^6}, \quad C \doteq \frac{3}{4}\left(\frac{1}{4\pi\epsilon_0}\right)^2 \alpha^2 \hbar\omega,$$

where α is the polarizability and $\hbar\omega$ the ionisation energy. This microscopic interaction gives rise to an adhesive force between mesoscopic and macroscopic object. That adhesion plays a significant role in colloids of various shapes and sizes.
Consider the idealized situation of two semi-infinite volumes of colloidal matter (colloids 1 and 2) with flat surfaces separated by a distance h. Calculate the adhesive interaction energy between these two objects. Start from the generic expression,

$$U_{12} = -\int d^3r_1\, \rho_1(\mathbf{r}_1) \int d^3r_2\, \rho_2(\mathbf{r}_2) \frac{C}{|\mathbf{r}_1 - \mathbf{r}_2|^6},$$

where ρ_1, ρ_2 (here assumed constant) are the atomic number densities in the two colloids, respectively. Pick one atom in colloid 1 and integrate d^3r_2 using cylindrical coordinates. The result is a function of the distance between the selected atom (on colloid 1) and the surface (of colloid 2). The integration d^3r_1 over a semi-infinite slab of cross sectional area L^2 then produces a result of the form $U_{12} = L^2 u(h)$. Show that the adhesive energy per unit area can be written in the form

$$u(h) = -\frac{A_H}{12\pi h^2}, \quad A_H = \pi^2 \rho_1 \rho_2 C,$$

where A_H is known as the Hamaker constant.

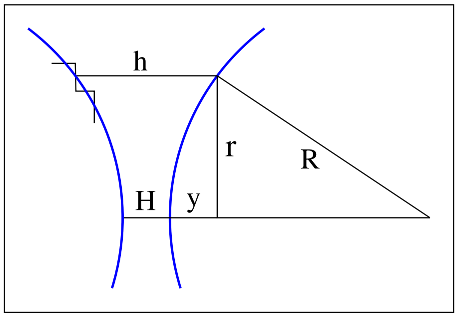
[adapted from Jones 2002]

Solution:

[pex24] Adhesive force between spherical colloids (Derjaguin approx.)

Use the result, $u(h) = -A_H/12\pi h^2$, for the adhesive energy per unit area between parallel flat colloidal surfaces from [pex23] as the starting point for the calculation of the adhesive energy, $U(H)$, between two spherical colloids of radius R at a distance H between nearest points. The Derjaguin approximation assumes $H \ll R$ and replaces the spherical surfaces in the vicinity of the nearest points by two staircases of rings with radius r and width dr. Each pair of rings with equal radius is treated as a pair of flat surfaces subject to an adhesive force per area equal to that derived in [pex23]. Adding up the forces for all such pairs of rings yields the total force, $F(H)$, between the spherical colloids, from which the adhesive interaction potential, $U(H)$, can be inferred directly. Show that the Derjaguin approximation predicts

$$U(H) = -\frac{A_H R}{12H}.$$



Solution:

[pex25] Ionized colloidal surface: diffuse layer of counter-ions and co-ions

Consider a flat, positively charged colloidal surface. The liquid dispersion medium is an electrolyte, containing equal average number densities, n_0, of positively charge co-ion and negatively charged counter-ions. The electric field outside the colloid (at $x > 0$) will be screened by a differential, $n_-(x) - n_+(x) > 0$, in the density of counter-ions over the density of co-ions. The thermodynamic equilibrium state thus stabilized by the electrostatic forces between the colloidal surface and the mobile ions in the dispersion medium is governed by the Poisson equation,

$$\frac{d^2\psi}{dx^2} = -\frac{\rho(x)}{\epsilon},$$

where $\psi(x)$ is the electrostatic potential, $\epsilon \doteq \epsilon_r\epsilon_0$ is the permittivity of the liquid,

$$\rho(x) = q\big[n_+(x) - n_-(x)\big],$$

is the charge density with empirical constant q. The number densities, in turn, depend on the potential via the familiar Boltzmann exponentials,

$$n_\pm(x) = n_0 \exp\left(\mp\frac{q\psi(x)}{k_BT}\right).$$

(a) Show that the electrostatic potential thus satisfies the differential equation,

$$\frac{d^2\psi}{dx^2} = \frac{2qn_0}{\epsilon}\sinh\left(\frac{q\psi(x)}{k_BT}\right).$$

Introduce scaled quantities $\bar{\psi}(\bar{x}) \doteq \psi(x)/\psi_0$, $\bar{x} \doteq x/x_D$, to infer the universal (i.e. non-parametric) differential equation, $\bar{\psi}'' = \sinh(\bar{\psi})$, for the function $\bar{\psi}(\bar{x})$. Identify ψ_0 and x_D in terms of q, n_0, ϵ, k_BT. The characteristic length scale x_D is known as the Debye screening length.
(b) Search for a numerical solution $\bar{\psi}(\bar{x})$ with boundary value $\bar{\psi}(0) = 1$ that is monotonically decreasing and approaches $\psi(\infty) = 0$. Plot that solution for $0 < \bar{x} < 5$. In a separate panel, plot scaled versions of the densities, $n_+(x)$, $n_-(x)$, and $\rho(x)$, inferred from that solution.
(c) Compare the numerical solution from (b) with the Debye-Hückel solution $\bar{\psi}_{DH}(\bar{x}) = e^{-\bar{x}}$ of the linearized differential equation. Plot $\bar{\psi}_{DH}(\bar{x}) - \bar{\psi}(\bar{x})$ for $0 < \bar{x} < 5$. Comment on your findings.

Solution:

Zeta Potential [psl8]

The electric field of a negatively charged colloid suspended in an electrolyte is screened by counter-ions. The double layer consists of (i) the surface charge and (ii) a layer of counter-ions with co-ions mixed in. The outer layer has a (sharply defined) Stern part and a diffuse part.

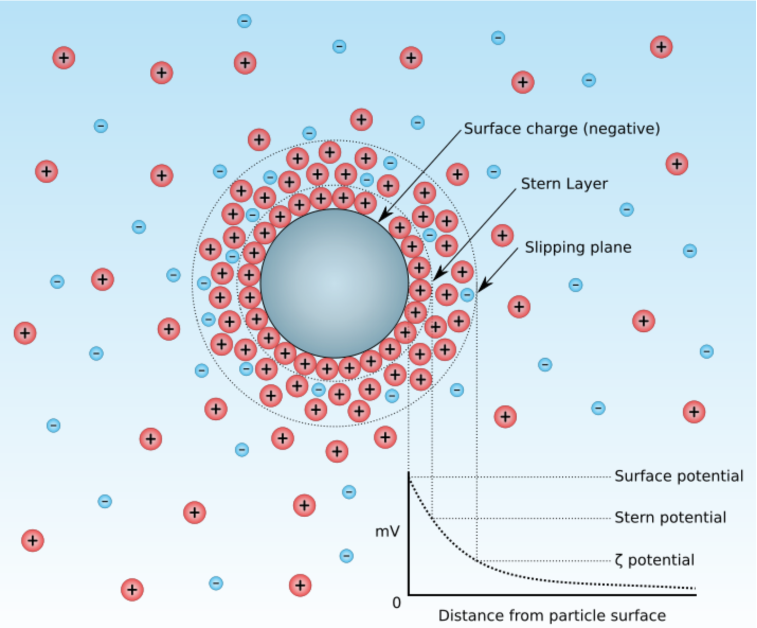
The moving colloid drags along a cloud of ions of radius R_s. The magnitude $V(R)$ of the electrostatic potential decreases monotonically with increasing radius R [pex25]. Its value at R_s is the ζ-potential: $V(R_s) = \zeta$.

The cloud of counter-ions impedes the mobility μ of the colloids. This effect is captured by models for the ζ-dependence of μ.

The ζ-potential is a measure for the effective repulsion between charged colloids. Charge stabilization remains effective if $\zeta \gtrsim 25\text{mV}$.

The ζ-potential can be measured indirectly via

- streaming currents: colloids driven through capillary with charged walls.
- electrophoresis: augmented retardation force due to cloud of ions.
- electro-osmosis: motion of counter-ions along charged surfaces.



[image from Wikipedia]

Charge Stabilization of Dispersion [pln43]

Surface of colloidal particles can acquire charge via

- ionization through contact with medium,
- physical interactions,
- chemical reactions.

Stability status of dispersion determined by balance between

- van der Waals attractive force,
- partially screened electrostatic repulsion.

Two-parameter DLVO model:[1]

$$V(r) = be^{-r} - \frac{a}{r},$$

where the parameters a, b are scaled in units of $k_\mathrm{B}T$ and the distance r in units of the Debye screening length r_D.

The DLVO model does not take into account any short-range repulsion of the hard-core type.

Depending on the parameter range this model predicts equilibrium states in the form of

- a stable dispersion,
- flocculation (reversible aggregation),
- coagulation (irreversible aggregation).

Aggregation of either kind is likely to lead to sedimentation or creaming.

The parameter regimes are identified in [pex26] and illustrated below.

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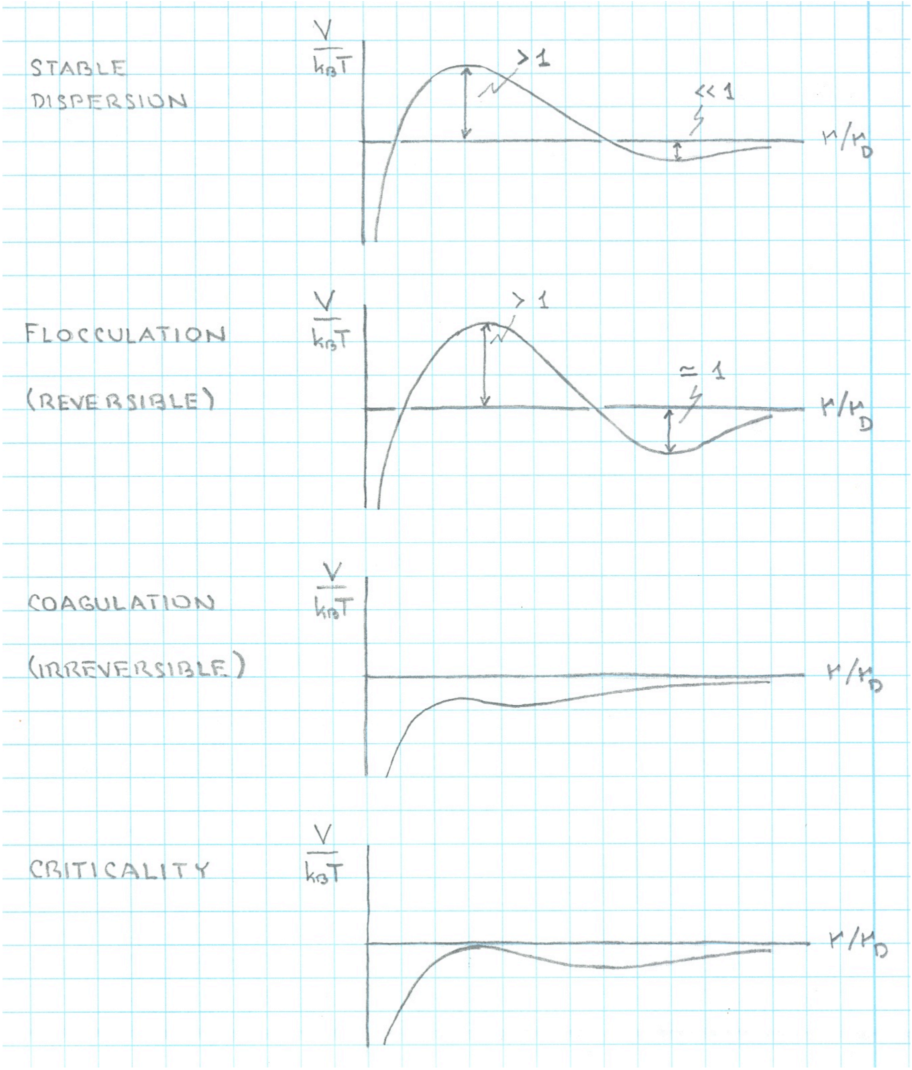
[1] named after Derjaguin, Landau, Verwey, and Overbeek.


STABLE DISPERSION
V/k_BT
> 1
<< 1
r/r_D
FLOCCULATION (REVERSIBLE)
V/k_BT
> 1
≃ 1
r/r_D
COAGULATION (IRREVERSIBLE)
V/k_BT
r/r_D
CRITICALITY
V/k_BT
r/r_D

[pex26] Colloidal stability, flocculation, and coagulation

Consider a dispersion of charged colloids in an electrolyte. The macrostate of this system is governed by the balance of the screened electrostatic repulsion and the van der Waals attraction. The two interactions are here represented, respectively, by the two terms in the potential,

$$V(r) = be^{-r} - a/r,$$

where the energy constants $a, b > 0$ are to be interpreted in units of k_BT and r is the distance between colloids in units of the Debye screening length. This potential, which ignores the inevitable hard-core repulsion, assumes the limiting values $V(0) = -\infty$ and $V(\infty) = 0$ independent of a, b.
(a) Show that $V(r)$ only has local extrema (a maximum followed by a minimum) if the ratio a/b is smaller than a certain threshold c_1. Find the value of c_1.
(b) Show that the local maximum becomes non-negative if $a/b < c_2 < c_1$. Find the value of c_2.
To prevent (irrevesible) coagulation, the local maximum must significantly exceed unity. The macrostate then represents a stable dispersion if the depth of the local minimum is sufficently shallow. A local minimum of depth significantly exceeding unity leads to (reversible) flocculation provided the height of the local maximum at shorter distance is significantly larger than the depth of the minimum at longer distance.
(c) Plot $V(r)$ for $0 < r < 10$ with values for a, b chosen and identified to represent the following cases: (i) a potential with $a/b = c_1$, representing a coagulated state, (ii) a potential with $a/b = c_2$, still representing a coagulated state, (iii) a potential representing a state of stable dispersion, (iv) a potential representing a flocculated state.

Solution:

Steric Stabilization [pln44]

Colloidal dispersions can be stabilized by polymer chains grafted to colloidal surface.

Forms of attachment:

- attachment by chemical bond,
- lyophobic attachment (e.g. block copolymer with one block insoluble in dispersion medium).

Types of grafting:

- *brushes*: high density grafting with polymers strongly interacting,
- *mushrooms*: low-density grafting with polymers weakly interacting.

The effective repulsive force is in part osmotic in character and in part due to brush elasticity.

Grafted polymers tend to weaken vdW attraction between colloids. In poor solvents grafted polymers may enhance attractive force.

Depletion interaction: Attractive force between colloids resulting from reduced osmotic pressure.

For example, when polymers coils (globules of volume density n_{g}) of smaller size than colloidal particles are added to the dispersion medium, there exists a depletion zone near the surface of colloids. The osmotic pressure, $p_{\mathrm{osm}} = n_{\mathrm{g}} k_{\mathrm{B}} T$, is then reduced in the depletion zone and produces an effective attraction between colloids with overlapping depletion zones.

Quantitative analysis for specific geometry: [pex27].

[pex27] Depletion interaction potential between spherical colloids

Consider a colloidal dispersion with monodisperse, spherical colloids of radius a. If the dispersion medium also contains globules of radius $L << a$, they produce an attractive depletion interaction between the colloids. It is of osmotic origin and can be written in the form

$$\Phi_{dep}(r) = -p_{osm}V_{ex}, \quad p_{osm} = n_g k_B T,$$

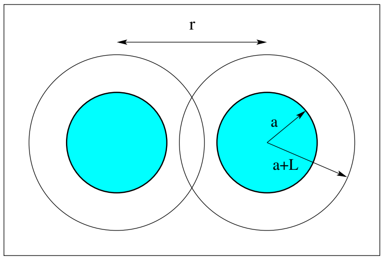
where the second equation with volume density n_g of globules is van 't Hoff's approximation for the osmotic pressure. It is adequate for low globule concentration. The volume V_{ex} from which globules are exluded when the distance r between two colloids is smaller than $2(a+L)$ is that of the lense-shaped region shown.

(a) Use the results of [pex21] to show that

$$V_{ex} = \frac{4\pi}{3}(a+L)^3\left[1 - \frac{3r}{4(a+L)} + \frac{r^3}{16(a+L)^3}\right].$$

(b) Plot $\Phi_{dep}(r)/p_{osm}V_0$ versus scaled distance $r/2(a+L)$, where $V_0 = (4\pi/3)(a+L)^3$.

[adapted from [Jones 2002]



Solution:

[pex50] Spherical aggregates of colloids

Consider a colloidal dispersion with a tendency for aggregation. The differential in mass density between colloids and dispersion medium is so small that any effects of gravity can be ignored. The colloids are monodisperse and have volume v. The interfacial energy $E_{int} = 4\pi r^2\gamma$ between aggregate and dispersion medium adds to the cost of aggregation. Therefore, if the energy of association for one colloid to an aggregate of infinite size is ϵ_∞ then the energy of association of m colloids to one spherical aggregate is $\epsilon_m = \epsilon_\infty + E_{int}/m$ for each of these colloids.
(a) Show that this energy of association can be written in the form

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{m^{1/3}}, \quad \alpha \doteq \frac{4\pi\gamma}{k_B T}\left(\frac{3v}{4\pi}\right)^{2/3}. \tag{1}$$

The parameter α decreases with increasing T not only because of the factor T in the denominator but also because the interface tension γ is expected to decrease. As in [pex40]-[pex42] we use the expression

$$X_m \propto m \exp\left(\frac{m(\mu - \epsilon_m)}{k_B T}\right), \quad m = 1, 2, \ldots \tag{2}$$

for volume fractions of size-m aggregates at thermal equilibrium.
(b) Infer from expressions (1) and (2) the relation

$$X_m = m\left[X_1 e^{\alpha}\right]^m e^{-\alpha m^{2/3}}, \tag{3}$$

by eliminating the chemical potential μ.
(c) Construct a Mathematica program that computes the concentration of size-m aggregates, X_m, and the total concentration of colloidss, $\phi \doteq \sum_m X_m$, as functions of the variable α and the parameter X_1 (the concentration of colloids in dispersion). Use a cut-off m_{max} in the sum large enough that its effect on the results is negligible. The concentration of aggregated colloids is $X_{agg} \doteq \phi - X_1$. Use the ParametricPlot option of Mathematica to produce curves of X_1 and X_{agg} versus ϕ. Use several values of the energy constant in the range $1 < \alpha < 7$. For each choice of α, zoom into the range of ϕ where interesting physical phenomena take place such as (more or less abrupt) changes in the concentrations of free and aggregated colloids.
(d) Identify data points for the critical aggregation concentration (CAC). Try to fit these data point to a model expression for $\phi_c(\alpha)$.

[adapted from Jones 2002]

Solution: