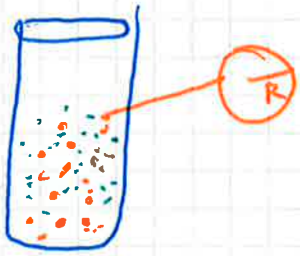
Lecture 9. Colloids

Particle cross-over scale distinguishing between colloids and granular media

To understand at what size will particles be influenced by thermal fluctuations, we will calculate the crossover scale. That is we will determine the particle radius at which thermal fluctuations can lift the particle a distance in the order of its radius in the presence of gravity.



For a brownian particle in the presence of gravity, the gravitational potential is : $V = M_{eff}\, g h$

The equilibrium distribution (i.e. the stationary solution for the F-P equation), which corresponds to the situation where random thermal forces and gravity exactly balance is:

$$P_{eq}(x) \propto e^{-U(x)/k_BT} = e^{-M_{eff} g h / k_BT}$$

So our task is to find the value of R for which the exponent of P_{eq} is ~1 for h=R. (choosing the exponent ~1 means $P(h) \sim e^{-1} \sim 0.37$, so the particle has a reasonable probability of being there).

For a particle we can write M_{eff} in terms of the density as $M_{eff} = V\Delta\rho = \underset{\substack{\uparrow \\ \text{considering} \\ \text{a spherical particle}}}{\frac{4}{3}\pi R^3}\, \Delta\rho$ where $\Delta\rho$ is the density difference between fluid and particle.

So the condition for the exponent being one is :

$$\frac{-M_{eff}\, g R}{K_B T} \sim 1 \Rightarrow R \sim \left(\frac{3K_BT}{4\pi\Delta\rho g}\right)^{1/4}$$

. considering $K_BT = 4\times10^{-21}\,J$

$g = 10\,m s^{-2}$

$\Delta\rho = 50\,kg/m^3$ (e.g. polysterene particles $\rho_p = 1050\,kg/m^3$ in water $\rho_w = 1000\,kg/m^3$)

we get :

$$R \sim \left[\frac{3}{4\pi}\left(\frac{4\times10^{-21}}{(50)(10)}\right)\right]^{1/4} \simeq \left(\frac{10^{-21}}{5\times10^{2}}\right)^{1/4} = 10^{-24/4}\,m = 1\,\mu m$$

Because of the scaling with R^4, for particles with $R > 1\mu m$, thermal fluctuations are unable to lift them appreciably. On the other hand particles of this size and smaller will be strongly affected by thermal fluctuations & much less so by gravity so they disperse.

A micron is the crossover lengthscale distinguishing

- → Granular media: Particles not affected by Brownian motion
  e.g. piles of sand, avalanches
- → Dispersions: Particles that can be viewed as a statistical physics system. (Affected by thermal fluctuations)
  e.g. colloidal systems.

A dispersion is the generic name for heterogeneous systems of particles or droplets in a fluid.

- Colloids: Dispersed solid particles. Conceptually simpler than emulsions. Main physics involves Brownian motion, sedimentation & interparticle forces. e.g. ~~droplets~~ paints, inks, coffee
- Emulsions: Fluid droplets in suspension. Interface is fluid and deformable, making their structure, dynamics & stability far richer & complex.
  e.g. mayonnaise, milk

~~Facto~~

Demo on colloids & emulsions

For this lecture we will focus on colloids.

Attractive forces between colloids

There are generally 3 mechanisms which make colloids attract each other:
- → Van der Waals interaction
- → Depletion interaction
- → Interaction resulting from the effect of their perturbation on the "vicinity".

Unless one modifies the system colloids tend to not form a stable dispersion, the attractive forces make them aggregate and stick together. Once the resulting clusters are sufficiently large they settle in the bottom or flocculate (form flakes). We will first consider the origin of the attractive forces between them and then look at how we can prevent them from sticking together.

The Van der Waals interaction

Van der Waals or "induced dipole" interactions are ubiquitous between all atoms and molecules, independent on whether they are charged or not. They arise from fluctuating atomic and molecular dipoles.

Recall that for a permanent dipole $\underline{\mu}$ in an electric field $\underline{E}$ the potential energy is:

$$U = -\underline{\mu} \cdot \underline{E}$$

the minus sign shows that the energy is minimal when the dipole is pointing in the same direction as E.

If an atom does NOT have a permanent dipole, the presence of an electric field will generally induce a dipole moment:

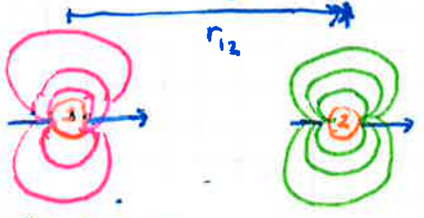
$$\underline{\mu}_{ind} = \alpha \underline{E}$$ where $\alpha \equiv$ polarizability of the atom

As a result the energy associated with the induced dipole is:

$$U_{ind} = -\int^{E} dE' \mu_{ind} = -\int_0^{E} \alpha E' dE' = -\frac{1}{2}\alpha E^2 = -\frac{1}{2}\mu_{ind} E$$

We will now consider two identical atoms a distance r_{12} apart in the absence of an external field. Even if the atoms don't have a permanent dipole moment, due to quantum mechanical fluctuations they have a fluctuating dipole moment.

For simplicity we will assume that atom 1 has ~~seen as~~ at some instant a fluctuating dipole moment μ_1 pointing towards atom 2:



atom #1 has an instantaneous fluctuating dipole moment $\underline{\mu}_1$

The field generated by $\underline{\mu}_1$ is:

$$E_{ind} = \frac{2\mu_1}{4\pi\varepsilon_0 r^3}$$

Atom 2 comes into the field E_{ind} of atom 1, which induces a dipole $\underline{\mu}_2$ at atom 2. This dipole is:

$$\mu_2 = \alpha E_{ind}$$

This dipole then becomes the source of an electric field

$$E^*_{ind} = \frac{2\mu_2}{4\pi\varepsilon_0 r^3} = \frac{2\alpha E_{ind}}{4\pi\varepsilon_0 r^3}$$

$$= \frac{2\alpha}{4\pi\varepsilon_0 r^3} \cdot \frac{2\mu_1}{4\pi\varepsilon_0 r^3}$$

Putting this all together E^*_{ind} now is "felt" by atom 1. Since E^*_{ind} points in the same direction as μ_1, it lowers the energy according to

$$U_{ind} = -\frac{1}{2}\mu_{ind} E$$ so in this case

$$U_{1,2} = -\frac{1}{2}\mu_1 E^*_{ind}$$ gives the interaction energy of the pair due to fluctuations of atom 1

And using the expression for E^*_{ind} we find:

$$U_{12} = -2\alpha \frac{\mu_1^2}{(4\pi\varepsilon_0)^2 r_{12}^6} \quad \textcircled{*}$$

since the dipole μ_1 is fluctuating we still need to average over the magnitude and direction of μ_1. We also need to add $U_{2,1}$ from fluctuations of atom 2 as well. In any case, the energy is always lowered and taking into account these considerations we get an expression of the form ⊛ with μ_1^2 replaced by $\langle\mu_1^2\rangle$ with a slight correction from the angular average.

In order of magnitude the dipole fluctuations will be $\langle\mu_1^2\rangle = \mathcal{O}(ea)^2$ where a is the size of the atom and e the fundamental charge. The polarizability α is typically $\mathcal{O}(4\pi\varepsilon_0 a^3)$. In any case, due to these dipole fluctuations, two atoms generally attract with a power law interaction:

$$\boxed{U_{1,2} = -C\left(\frac{a}{r_{12}}\right)^6 \quad \text{Van der Waals attraction}}$$

where C is a positive constant, [C] = energy
order of magnitude of C $\mathcal{O}$(several eV)
comparable to the binding energy of an atom

so far we considered the VdW interaction between 2 atoms or molecules in free space. If we now consider a solvent, the constant C will depend on the difference in polarizabilities and the dielectric constant, which is frequency dependent. A full analysis includes the frequency dependence and involves an integral over all fluctuating frequencies. Even with all of this taken into account the effective potential will be of the form $U_{1,2}$, although the value of C will be different for molecules in a solvent compared to molecules in free space.

Now if we consider the VdW interactions between colloids, we have objects consisting of lots of molecules different from the solvent molecules. We can write the effective VdW interaction between two colloidal particles 1 and 2 a distance h apart:

$$\boxed{U(h) = -\sum_{\underline{r}_1}\sum_{\underline{r}_2} C\left(\frac{a}{r_{12}}\right)^6}$$

sum of all VdW interactions of the constituent atoms.
where $\underline{r}_1, \underline{r}_2$ are the positions of all the atoms in colloid 1 and 2 respectively

This effective VdW interaction can be worked out for different cases by converting the sums to integrals.

In the case of two semi-infinite slabs separated by a distance h:

$$U_{vdw}(h) = \frac{-H\,A}{12\pi\,h^2}$$

where [H] = energy is the Hamaker constant

For two spheres of radius R:

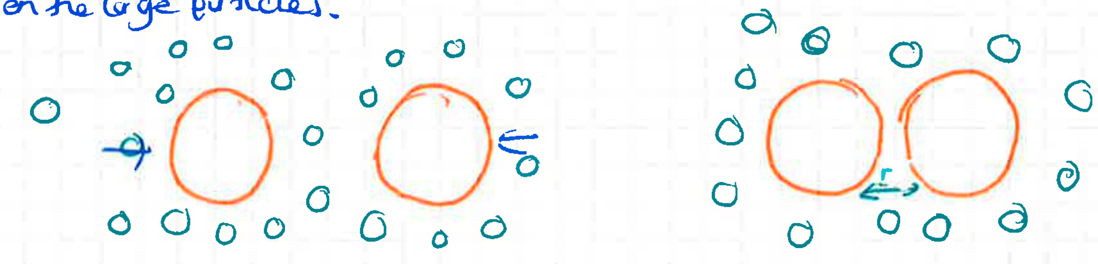
$$U_{vdw}(h) = \frac{-HR}{12h}, \quad \text{for } h \ll R$$

i.e. in the limit when two spheres are very close.

In general even though the precise functional form of U_{vdw} depends on the shapes & orientations of particles, the important result is that mesoscopic objects generally attract each other with a slowly varying power law potential.

Depletion interaction

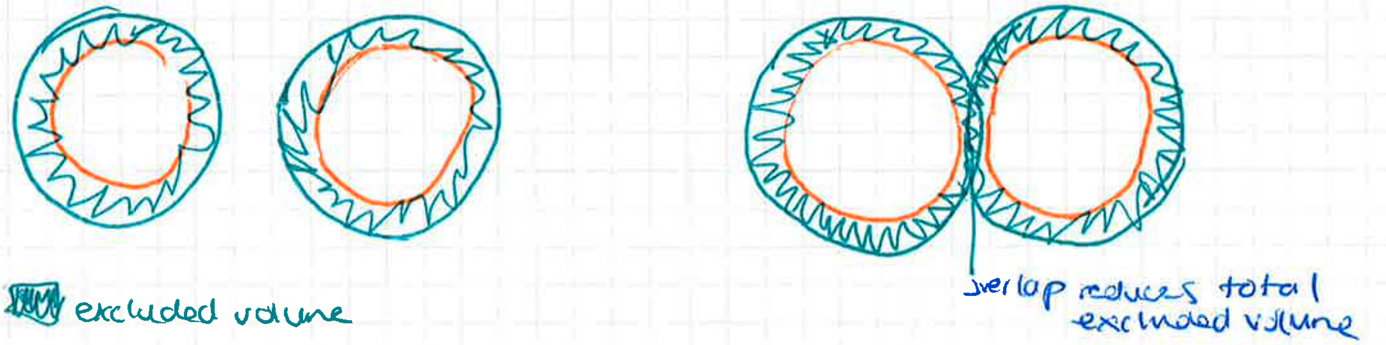
When 2 large particles in a thermal bath of smaller ones approach one another a distance comparable to the size of the smaller ones, these smaller particles will be excluded from the zone between the large particles.



r < 2R where R is the radius of small o particles

If the distance between large particles is $r < 2R$ (where R is the radius of the smaller particle) the smaller particles will be excluded from the region between large particles. The result of this is that large particles will feel a net pressure inward from the small particles ⇒ there is an effective attractive force with a range of the order 2R (size of small particles).

Another way to view this is as an excluded volume interaction. We can think of the larger particles having an excluded volume region around them, which the smaller particles cannot enter due to their finite radius. When the 2 large particles come together the total excluded volume is reduced. A decrease in the excluded volume enhances the entropy of the small particles and hence induces an attractive interaction.



When the excluded volume is decreased, the small particles have more room to explore entropically

Excluded volume interactions are not very strong, they are on the order of $k_B T$.

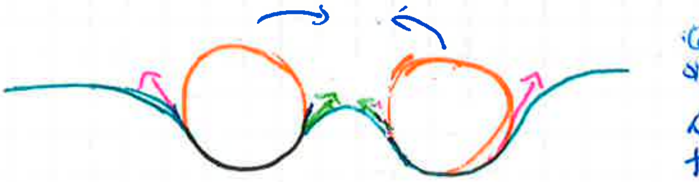
Induced attractive interaction due to perturbations of the surrounding media

Colloidal particles "perturb" their environment. Once introduced in a solvent, they effectively change the surrounding's packing, density, composition, orientational correlations, etc. When these perturbations fall off smoothly away from the colloidal particle, this usually leads to an effective attractive interaction.

The origin of the effective attractive interaction is that if a particle affects property W in its neighborhood, then clearly another particle of the same type will "feel happier" in the neighbourhood of the original one, where property W is already affected in a way it likes. So this leads to a perturbation-induced attraction. The precise nature of the attraction depends very much on the problem under consideration, so the strength and range of this interaction is system specific.

Pickering effect

Colloids are attracted to the fluid interface simply because they reduce its area, so
Colloids are attracted through each other through the deformation of the interface.



Particles deform the fluid interface, as they come together, the contact angle on the inside ↗↖ differs from the ~~[illegible]~~ angle on the other side of the particle ↖↗ giving rise to a driving force that brings particles together.

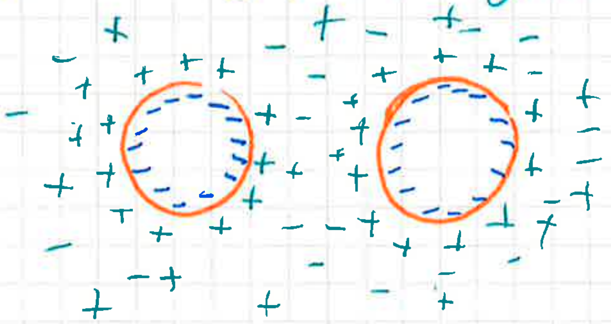
We have seen that in general colloidal particles tend to attract each other ~~[illegible]~~ hence forming aggregates or floculates instead of staying dispersed. Having discussed the origin of the attractive interaction, we can now see what strategies can be applied to counteract these interactions.

Since we have both electrostatic + steric attractive interactions, we need to engineer repulsive interactions of the same kind to stabilize dispersions.

Electrostatic stabilization

One way to stabilize colloids against VdW interaction is to charge them to get repulsive electrostatic forces.

The effective interaction between particles of the same charge will not be a $1/r$ Coulomb potential since their charges get screened by ions in a solution.



these negatively charged particles attract positive ions in the solution. This "second layer" of charge leads to a screening of the Coulomb potential over a distance K^{-1}
This distance depends on the concentration of ions in the solute.

This screening is the so called Debye-Hückel screening.

The effective electric potential of the interaction between particles is given by the Debye-Hückel equation:

$$\nabla^2 \Phi(\underline{r}) = K^2 \Phi(\underline{r}) \quad \text{with } K^2 = \frac{2e^2c}{\varepsilon_0 \varepsilon_r K_B T}$$

. K plays the role of an inverse screening length.
with e = elementary charge
c = concentration of ions in solvent
ε_0 = permittivity of vacuum
$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$ relative permittivity of material.

If we solve this equation in 1D we get:

$$\Phi_{DH}(r) = \frac{e\, e^{-Kr}}{4\pi \varepsilon_0 \varepsilon_r r} = \frac{e\, e^{-r/\lambda_D}}{4\pi \varepsilon_0 \varepsilon_r r}$$

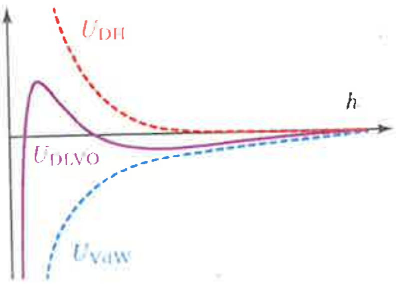
where $\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r K_B T}{2ce^2}}$ is the Debye screening length.
characteristic distance over which electrostatic interactions are screened by mobile ions in the solution.

λ_D sets the range of the electrostatic repulsion between particles

The expression for Φ_{DH} is for a point charge, if we now consider a the Debye-Hückel potential around a sphere of charge Ze we get:

$$\text{Sphere: } \Phi_{DH}(r) = \frac{Ze}{4\pi \varepsilon_0 \varepsilon_r (KR+1)} \frac{e^{-(r-R)/\lambda_D}}{r}$$

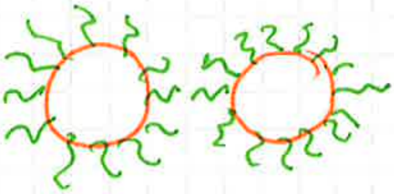
The figure below shows the effective interactions between colloids according to the DLVO theory in which interactions are modelled by combining the attractive Van der Waals potential with the repulsive screened Debye-Hückel potential



Steric stabilization by grafting polymers onto the surface

One way to stabilize colloids at short range against attractive forces is to put "bumpers" on them. i.e attach a polymer to their surface that prevents them from getting too close.

The interaction between the polymer and the solvent has to be tuned by the choice of either to optimize their length and density such that they form a polymer brush. i.e. they interact 'favorably' with the solvent and don't "collapse onto themselves".



Here polymers are not shown to scale, usually brushes are 10-20nm, so relatively thin compared to ~~bare~~ colloids

Non-Newtonian rheology of colloidal dispersions.

We had discussed that ~~the~~ colloidal dispersions were ~~per~~ prototypical examples of non-Newtonian fluids.

In general the flow behavior of colloidal suspensions will depend on:

→ particle interactions: Electrostatic, vdW, steric
→ particle concentration: In crowded suspensions particles interact more

We can ~~see~~ imagine how these interactions can give rise to the non-Newtonian behavior of colloids:

- shear thinning: Particle networks 'break apart' under shear and flow easily.
- shear thickening: Particles form transient clusters under stress, resisting flow.

The Péclet number gives us an estimation of when ~~an~~ external shearing will result in non-Newtonian behavior of a colloidal dispersion. This ~~number~~ dimensionless number compares advective vs diffusive transport, in this case:

$$Pe = \frac{\dot{\gamma} R^2}{D} \quad ; \text{ where } \dot{\gamma} = \text{shear rate}$$

R^2 = radius of colloid

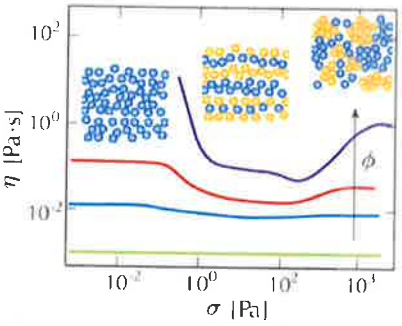
D = diffusion coefficient given by Stokes-Einstein relation.

$$= \frac{\dot{\gamma}\, t_{diff}}{2} \qquad \frac{\text{timescale of diffusion}}{\text{timescale advection}} \qquad \left(D = \frac{K_B T}{6\pi \eta R} \right)$$

where $t_{diff} \simeq 10 R^3 (s/\mu m^3)$ time we estimated it takes for a particle to diffuse its radius at room temp.

If $Pe \ll 1$ ⇒ Brownian motion dominates
particles diffuse faster than the shear can advect them
Fluid is Newtonian or ~Non newtonian

If $Pe \gg 1$ ⇒ Shear dominates
particles are advected faster than they can diffuse
Fluid is Non-newtonian (either shear thinning or thickening).



Playing with colloids as model systems.

***Colloidal aggregates**. Due to their interactions colloids will have a natural tendency to aggregate. Particles will diffuse around until they "hit" one or others and then stick together forming ~~an~~ ever growing clusters.
This process is known as diffusion limited aggregation DLA. The structures formed by this process are fractals.

These structures are scale invariant, which means that the pattern repeats at all scales, and the object has a self-similar power law structure characterized by its fractal dimension.

For an ordinary homogeneous bulk material, the density $\rho(r)$ is constant, so the total mass $M(r)$ of the particles within a radius r goes as:

$$M(r) = \int_{r' < r} \rho(r')\, d^d r' \sim r^d$$

For fractal aggregates, the particle density falls off with with the distance r as a power law:

$$\rho(r) \sim r^{d_f - d} \Leftrightarrow M(r) \sim r^{d_f}$$ ~~which~~ where d_f is the fractal dimension.

Fractals with $d_f < d$ are "fluffy" as the density of particles within a ball of radius r falls off as: $\frac{M(r)}{r^d} \sim r^{d_f - d}$ which becomes very small as r grows.

Video: Fun with fractals

*** Colloidal glasses**: when polydispersity of a colloidal dispersion is ~~big~~ significant, the formation of ordered phases is suppressed and the colloids tend to get stuck in some random configuration as their volume fraction increases, forming a colloidal glass.

Hallmark of glass-forming molecular materials is that ~~when~~ starting from a liquid state, as materials cool down, the viscosity is found to increase exponentially fast as the temperature is decreased. A typical empirical law fitted to data is:

$$\frac{\eta}{\eta_0} = e^{[CT_0/(T - T_0)]}$$ where C is a constant

This relation suggests a divergence at $T = T_0$, but it's not possible to get to $T = T_0$ because once the viscosity reaches values of $O(10^{12}\ \mathrm{Pa \cdot s})$ the liquid doesn't flow on human timescales. So the question of whether a true phase transition with divergent lengthscale at a finite temperature T_0 underlies this behavior is still open.

In colloidal glasses, temperature is not relevant. But similar behavior is observed as a function of volume fraction ϕ

$$\frac{\eta}{\eta_0} = e^{[C\phi/(\phi_0 - \phi)]}$$

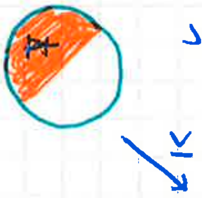
where ϕ_0 is the maximum packing

As the density goes up particles are more and more in each other's way so they get jammed as the density approaches the jamming density ϕ_J.

Video: Colloidal glasses. Bringing glass physics into focus.

Colloids as active matter

Active matter seeks to describe the emergent patterns that arise from the interactions of self-propelled particles. Initially this field was motivated by examples of living matter, e.g. flocks of birds, swarming of bacteria. But since it was discovered that colloidal particles can be made into microswimmers, it has become clear that colloidal particles ~~[illegible]~~ provide a versatile system to model active matter.



Janus particle: Colloidal particle coated on one side with Platinum. Platinum is a good catalyst so in a solution with hydrogen peroxide, the hydrogen peroxide reacts on the platinum side pushing the particle forward.

Fun fact: Name of this particles comes from the Roman god Janus who was often portrayed with two faces.

Video: Global symposium on Janus Particles