

Colloidal Stability and Complex Fluids Design

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Introduction

In this lab, we will explore the fundamentals of dispersion and emulsion stability, and apply our understanding to design stable emulsions and suspensions. “Dispersion” refers to a mixture where one phase is dispersed within another. Suspensions refer to solid particles in liquid media, while emulsions consist of liquid droplets in a second, immiscible liquid. In each case the particles or droplets are on the colloidal size scale, ranging from the nanometer range up to microns or even 10’s of microns. On the macroscopic scale dispersions may appear homogeneous.

Both dispersions and emulsions are classes of materials designated as ‘complex fluids,’ so named because of the coexistence of two (or more) phases of matter within the mixture. Other examples include polymeric and liquid crystalline materials, foams (gas in liquid), aerosols (liquid in gas) and even granular materials (solid in gas). Complex fluids abound in everyday items, including shampoo (polymeric liquid), shaving cream (foam), toothpaste (suspension), meringue (foam), milk and mayonnaise (emulsions), paint (suspension), and even electronic displays (liquid crystals or suspensions).

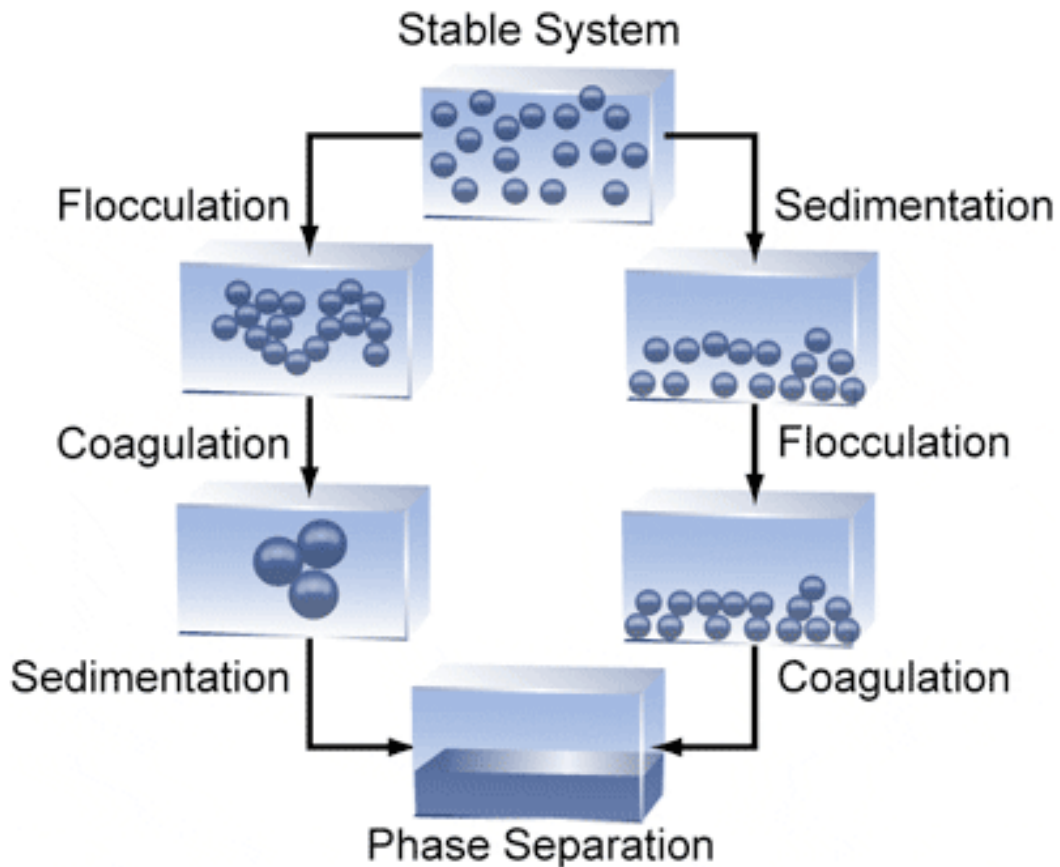
COMPLEX FLUID	Dispersed Phase	Suspending Phase	Examples
Suspension	Solid	Liquid	Paint, coffee
Emulsion	Liquid	Liquid	Salad dressing, milk
Foam	Gas	Liquid	Soap suds, ice cream
Solid Foam	Gas	Solid	Bread, insulation
Aerosol	Liquid	Gas	Hair spray, perfume
Granular Materials	Solid	Gas	Sandpiles, sugar
Polymer Materials	Polymers	Liquid	Jello, detergent

In these materials, thermal energy scales dominate and determine both the microscopic and macroscopic behavior of the materials. As a result, the mechanical properties may be solid-like under some conditions, and liquid-like under other conditions. Important parameters in determining properties of complex fluids include

- concentration of the dispersed phase
- temperature
- applied stress
- dielectric constant of the solvent
- pH and ionic strength
- interparticle interactions.

For instance, foams like shaving cream can behave like solids while at rest under the influence of gravity only, but yield easily under applied stress, as when rubbed between one's fingers.

Aside from the chemical properties consumers expect from products, including for instance cleaning and dyeing abilities, industries devote research and development funds to design stable formulations with long shelf-lives. If you ask the virtual agent on Hellmanns.com "how should I store mayonnaise" it responds: "Your mayonnaise should be refrigerated after opening. Storage conditions (temperature) will affect product quality. High temperatures will accelerate the loss of fresh flavor and exposure to cold (near freezing temperatures) can change the consistency, texture, and thickness and may cause separation..." While slightly separated mayonnaise is still edible and can be stirred to re-suspend, few people would buy it.



The cartoon above illustrates possible pathways and mechanisms leading to separation in dispersions. In suspensions, aggregation and sedimentation can lead to complete separation of the solid phase. In emulsions, when the suspended liquid is less dense than the solvent, as with oil-in-water emulsions, separation is driven by the buoyancy of the suspended drops, which rise to the top in a process called creaming. In the next section we will consider forces which can provide dispersion stability.

Interparticle Interactions

Dispersion stability is determined by the sum of forces between particles or drops. The forces playing an important role in colloidal stability are mainly electrostatic interactions, van der Waals forces, and entropic forces. While electrostatic and entropic forces can be either attractive or repulsive, van der Waals forces are always attractive.

Force	Attractive/Repulsive	Range
Electrostatic	Attractive (opposite charges) or Repulsive (like charges)	Short-, medium-, or long-ranged (based on solvent dielectric constant and ionic strength)
van der Waals, dispersion	Always attractive	Long-ranged
Entropic	Attractive (e.g. depletion) or Repulsive (e.g. steric)	Short-ranged

van der Waals forces arise from interactions between dipoles, and include contributions from fixed-dipole interactions and induced-dipole interactions. Interactions between two induced-dipoles are referred to as London dispersion forces. Dispersion forces are more ubiquitous than fixed-dipole interactions, and can only be reduced by matching the refractive index of the suspending and dispersed phases. van der Waals interactions are long-ranged; the van der Waals force between two spheres of radius r is given by

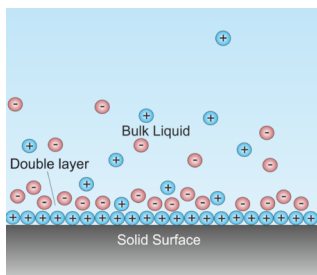
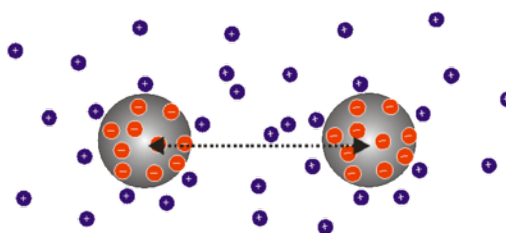
$$F = A / 12r$$

where A is the material-dependent Hamaker constant.

Electrostatic forces obey Coulomb's law:

$$F = kq_1q_2 / r^2$$

where q is the charge on two objects separated by r , and k is the Coulomb constant. Coulomb's law illustrates that electrostatic interactions ($1/r^2$) are shorter-ranged than van der Waals ($1/r$).



When charged particles are dispersed in liquids, the electrostatic force is screened by counter-ions in suspension. Oppositely charged counterions from solution will build up near the surface of the charged particles and create an electric double layer. The concentration of ions around the charged particle decays with distance away from the solid surface. The cartoon shows an example of a negatively charged solid immersed in a liquid.

The characteristic thickness of the electric double layer is given by the Debye length, or screening length, κ^{-1} , defined as

$$\kappa^{-1} = (\epsilon_r \epsilon_0 k_B T / 2 N_A e^2 I)^{1/2}$$

where ϵ_r is the dielectric constant of the medium, ϵ_0 the permittivity of free space, N_A Avogadro's number, e the elementary charge, and I the ionic strength.

Electrostatic interactions in oil are extremely different than in aqueous systems. The low dielectric constant of non-polar media makes charge separation extremely energetically costly (i.e. this is why salt doesn't dissolve in oil). As a result, charged moieties in non-aqueous suspensions readily aggregate via strong attractive electrostatic forces. At the same time, whenever like charges can be stabilized in non-polar media, the resulting electrostatic repulsion is also very strong. Electrostatic interactions in non-polar media are also very long-ranged, due to the extremely low concentration of counter-ions in solution.

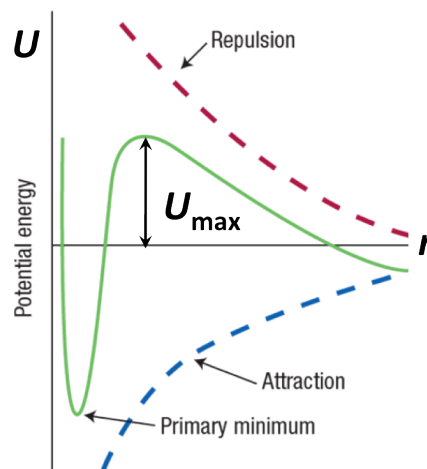
Entropic forces may also play a role in colloidal stability, and include forces such as steric repulsion and depletion attraction, both of which are short-ranged and essentially due to excluded-volume interactions. Steric stabilization consists of grafting polymer "brushes" onto the surface of colloids to prevent close approach of the particles and thereby prevent aggregation from occurring. Steric hindrance or "steric protection" are often exploited by organic and synthetic chemists to stop unwanted side reactions. Attractive depletion interactions arise from the presence of smaller particles or large polymers in suspensions of larger spheres. Due to excluded volume considerations, there exists a region around each of the larger spheres which the depletants are unable to occupy; the size of this region is roughly the size of the depletant particles. Aggregation of the large spheres minimizes the total excluded volume in the sample, maximizing the space available to the smaller depletant particles and thereby decreasing the entropy of the system.

Dispersion Stability

The ubiquitous nature of attractive van der Waals interactions causes colloids to aggregate. In aqueous suspensions, the main mechanisms of providing stability to colloids involve electrostatic or steric stabilization. We will focus on electrostatic stabilization, as it allows us to discuss surface charges, the zeta potential, and electrostatic screening lengths. The reduction of salts in suspension, adjustments to pH, and polymer or surfactant additives can all help to prevent aggregation of nanoparticles.

DLVO theory, so named for the theorist Derjaguin, Landau, Verway and Overbeek, captures the concept of colloidal stability given the sum of attractive van der Waals interactions and repulsive electrostatic interactions. The cartoon shows an example

of a DLVO interparticle potential $U(r)$, with the attractive force shown in blue (scaling as $1/r$), the repulsive force shown in red (scaling as $1/r^2$) and the sum in green. DLVO potentials have a deep minimum at particle contact r_0 , with a large repulsive barrier upon closer approach ($r < r_0$) due to excluded volume interactions. Depending on the relative strengths of the forces, the resultant potential could have an energetic barrier and even a secondary minimum, both located at $r > r_0$. While thermodynamic equilibrium occurs at the global minimum of the potential, when all particles have aggregated, the height of the energetic barrier U_{\max} can prevent the system from reaching equilibrium for very long times.



Dispersion stability is closely related to particle surface charge. In this module we will measure both particle or droplet size as well as electrophoretic mobility, which relates to surface charge. As particles grow or droplets coalesce, they are more likely to either sediment or cream until full separation occurs. Measurements of particle size as a function of time can help assess dispersion stability on the microscopic scale even before the onset of macroscopic sedimentation or creaming.

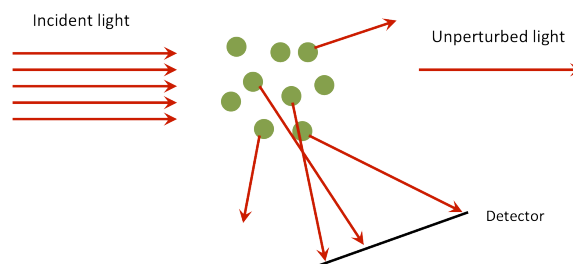
Instrumentation

Dynamic Light Scattering

This module makes use of light scattering techniques to measure particle or droplet size as well as surface charge. Dynamic light scattering is based on a measurement of diffusive time scales in a system, from which particle size may be calculated. Particles experiencing Brownian motion do not travel in ballistic fashion, but rather explore their surroundings via a random walk. The area explored by a particle in one second is represented by the diffusion constant D , which has units of area per time:

$$D = [L^2]/[T]$$

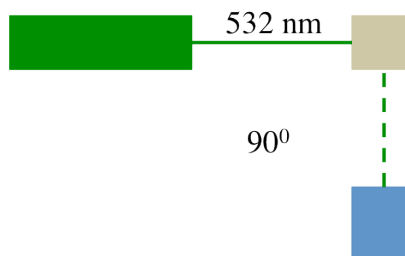
In this experiment, a laser of wavelength λ is shined incident onto a sample suspension. Photons scattering off of the particles in suspension are collected by a detector placed at an angle θ from the incident light. The time scale τ of diffusive motion through the path of



the laser is determined by high-speed correlations of the scattered light signal. The length scale for the diffusive motion is determined by the geometry of the instrument, wavelength of light used and the solvent of the sample, as given by the scattering vector q :

$$q = 4\pi n \sin (\theta/2) / \lambda$$

where n is the index of refraction of the solvent. Note that q has units of 1/length. The cartoon shows a schematic where the incident light is $\lambda = 532$ nm and the detector is placed at $\theta = 90^\circ$. For an aqueous sample measured with these instrument parameters, $q \sim 2 \times 10^7$ (1/m). D is measured by



$$D = 1/q^2\tau$$

and is independent of assumptions regarding particle shape. By assuming spherical particles, we can extract particle size a from the measurement of D using the Stokes-Einstein relation

$$D = k_B T / 6\pi\eta a$$

where k_B is the Boltzmann constant, T the temperature, and η the solvent viscosity.

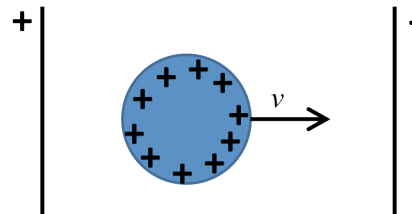
In addition to particle size measurements, the scattered light intensity can be recorded and used as an indication of dispersion stability against sedimentation or creaming. As the particles either sediment below the path of the incident laser light or rise above it, the scattered light intensity decreases as an indication of the reduced particle concentration in the path of the beam.

Electrophoretic Mobility

When placed in an electric field, charged particles will migrate to the oppositely-charged electrode. For charged particles suspended in a fluid, the electrophoretic force $F_{el} = EQ$, where Q is the total surface charge, is balanced by the viscous drag $F_v = 6\pi\eta a v$, resulting in a constant drift velocity v .

With a measurement of the velocity v of charged particles in a field of strength E , the electrophoretic mobility μ can be calculated, defined as:

$$\mu = v/E$$



Electrophoretic mobility measurements done with light scattering instrumentation exploit a principle similar to the Doppler shift. The incident beam is split into a

reference signal and a portion which passes through the electric field. While particles throughout the sample are undergoing Brownian motion, the particles subject to the field are diffusing with drift velocity v . Comparing the phase shift of the signal with respect to the reference beam allows for a measurement of v . Most instruments measuring electrophoretic mobility use a technique known as “Phase Analysis Light Scattering” (PALS).

Determined along with μ is the zeta-potential ζ , which is defined as the electric potential just beyond the first layer of counterions in the electric double layer around the particle. The true surface potential on the particle is generally greater than ζ . The two quantities are related to each other through the use of Henry’s equation

$$\mu = 2\varepsilon\zeta f(\kappa a) / 3\eta$$

where ε is the dielectric constant of the solvent. The choice of the constant $f(\kappa a)$ is determined by the nature of the solvent and a comparison of particle size to screening length κ . In aqueous dispersions, ionic strengths are generally high, and give rise to short screening lengths. Often, $a > \kappa$, and $f(\kappa a) = 1.5$, in the Smoluchowski limit of the Henry equation. Due to the energetic ease of charge separation in aqueous suspensions, it is often difficult to access the regime $a < \kappa$ unless non-polar solvents are used. In this case, $f(\kappa a) = 1$, in what is known as the Huckel limit.

Further Reading

- Colloidal Dispersions. W.B. Russel, D.A. Saville and W.R. Schowalter. Cambridge University Press (1995).
- Colloidal Dispersions: Suspensions, Emulsions, and Foams. Ian D. Morrison and Sydney Ross. Wiley & Sons (2002).
- Principles of Colloid & Surface Chemistry. Paul C. Hiemenz and Raj Rajagopalan. Marcel Dekker (1997).
- Light Scattering by Small Particles. H. C. van de Hulst. Dover Books of Physics (1981).
- Dynamic Light Scattering. B. J. Berne and R. Pecora. John Wiley (1976).

Literature Examples

- C Cametti, P Codastefano, P Tartaglia. “[Aggregation kinetics in model colloidal systems: a light scattering study](#)” *JCIS* **131** 2 (1989).
- Z Meng, SM Hashmi, M Elimelech. “[Aggregation rate and fractal dimension of fullerene nanoparticles](#),” *JCIS* **392** (2013).
- CM Sorensen. “[Light scattering by fractal aggregates: a review](#),” *Aerosol Science & Technology* **35** 2 (2001).
- Y Zhou and GV Franks. “[Flocculation mechanism induced by cationic polymers investigated by light scattering](#).” *Langmuir* **22** 16 (2006).
- PW Zhu and DH Napper. “[The effects of different electrolytes on the fractal aggregation of polystyrene latexes](#),” *Colloids & Surfaces A* **98** (1995).

Pre-Lab Discussion Questions

- 1) What measurement parameters or instrumental considerations most strongly determine the lower limit on measurable particle sizes in a dynamic light scattering measurement?
- 2) If electrostatic forces exactly balance viscous drag forces in an electrophoretic mobility measurement, then μ is directly related to Q , the total surface charge on the surface of a particle. For what types of samples, or under what circumstances could this hold true? What could complicate an estimate of Q ?
- 3) Discuss some sample preparation considerations in advance of your first measurements. What assumptions are involved in the data analysis and theory? How do these affect sample prep? Might there be guidelines for the appearance of a sample (by eye)?
- 4) Given the effort expended on creating stable suspension and emulsion formulations, what kind of circumstances might actually require separation? Propose some mechanisms for inducing or reversing separation in a complex fluid.

Experiments

In this lab you will prepare several formulations of suspensions and emulsions, and measure initial particle size and zeta potential, as well as dispersion stability over the course the 2-week module. Supplemental measurements will include pH, conductivity, and UV-vis absorption to confirm that the samples do not strongly absorb at 532 nm.

Light scattering measurements will be performed to measure size and mobility. For sizing measurements, use a collection duration of 30s, and measure 20-30 data points for statistical analysis on each of your samples. For all light scattering measurements you will need to look up the index of refraction and viscosity of your solvents.

After your initial measurements in Week 1, you should make predictions regarding the stability of your formulations for the next week. **Clearly label all samples**, as they will be stored during the week between the lab sessions. Lab notebooks will be assessed at the end of Week 1 and beginning of Week 2 to check your work.

During Week 2, you will again assess dispersion stability. Based on the observed stability of your formulations from Week 1, you will make one or two additional dispersions, this time designed to aggregate and sediment or cream within a few hours. Measure particle size as a function of time for at least an hour, maintaining a collection time of 30s per measurement.

Dispersion Formulation

Assess the importance of electrolyte concentration and valence on the stability of silica colloids in water. [10 samples]

Starting suspension: Ludox silica beads or zinc oxide nanorods [*choose one*]

Dilutions: dilute to 0.1% and 0.05% by weight [*choose one*]

Electrolytes: KNO_3 , CaCO_3 [*choose one*]

Electrolyte concentration: 1, 3, 10, 30, 100 mM

Emulsion Formulation

Assess the importance of sample formulation (surfactant concentration) on the initial droplet size of your emulsions, as well as electrolyte concentration on the zeta potential. [10 samples]

Aqueous Phase: SDS or CTAB in DI water [*choose one*]

Surfactant concentration: 0.1, 0.5, 1 mg/mL [*choose one*]

Electrolyte: NaCl, MgCl_2 [*choose one*]

Electrolyte concentration: 1, 3, 10, 30, 100 mM

Oil phase: mineral oil

Prepare samples with 3% oil phase; homogenize for 3 minutes before measurement. Dilute by a factor of 10 if sample is too turbid.

Lab Report & Discussion

(1) Present your results from Week 1 in order to illustrate and discuss the importance of sample composition in determining electrophoretic mobility and droplet size. Include calculations of ionic strength in addition to electrolyte concentration. Estimate surface charge given measurements of electrophoretic mobility; discuss the relevance of these estimates given the variation of ionic strengths.

(2) Compare your predictions from Week 1 to the observations made in Week 2. Were the formulations you predicted to be stable actually stable? If not, why not? Discuss separation of the dispersions and estimate a typical sedimentation and creaming time for a single particle and drop.

(3) In presenting your results from Week 2, discuss the shape of $a(t)$, particle growth over time. Aggregation can occur through diffusion-limited or reaction-limited mechanisms, each of which exhibits different growth dynamics: in DLA particle size grows with a power law in time, while for RLA growth is exponential. Given the amount of time you measured your sample and the observed growth, can you identify the aggregation mechanism?