Emulsions, foams, gels.
Dispersions

Dispersions are dispersed colloidal size particles (*dispersed phase*) in a *continuous phase*

<table>
<thead>
<tr>
<th>CONTINUOUS PHASE</th>
<th>Does not exist</th>
<th>泡沫，起泡液体，G/L lyosol</th>
<th>固体泡沫，xerogel，aerogel，xerosol (G/S)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DISPERSED PHASE</strong></td>
<td>• Mist</td>
<td>• Emulsion</td>
<td>• Lyogel (or gel)</td>
</tr>
<tr>
<td></td>
<td>• Fog</td>
<td>• Lyosol (L/L)</td>
<td>• Solid emulsion</td>
</tr>
<tr>
<td></td>
<td>• Spray</td>
<td></td>
<td>• Xerosol (L/S)</td>
</tr>
<tr>
<td></td>
<td>• Aerosol (L/G)</td>
<td>• Colloidal suspension</td>
<td>• Solid dispersion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Lyosol (S/L)</td>
<td>• Xerosol (S/S)</td>
</tr>
</tbody>
</table>
Enhanced aerosol concentrations cause the droplets in a cloud to be smaller and more numerous within a cloud of fixed water amount.
Carbon black aggregates
Primarily used as reinforcing filler
- Tire
- Elastomer composites
- Plastics, Pipe
- Printing Inks, Coatings

Fumed silica (silicon dioxide) aggregates
Prepared by flame hydrolysis
- Filler
- Optical uses
- Coatings

Smoke, aerosols (S/G)
Foams (G/L)

- **Sparkling liquids** (soda, sparkling water)
- Often gas bubbles are of colloidal size
- **Foams** are the concentrated G/L dispersions
Foams (G/L)

- Making foams is an energy-dependent process
  - mixing or agitation
  - bubbling a gas through a liquid
  - gas evolution (chemical or physical process)
- Foams need to be stabilized against coalescence

Foam structure of a spherical foam at 400× magnification

Foam structure of a hexagonal foam at 400× magnification

The Kelvin Problem - Filling Space with Bubbles, Kelvin's solution, the tetrakaidekahedron
Formation of foams (G/L)

\[ \Delta p = \frac{2 \gamma}{r} \]

The LAPLACE EQUATION relationship between pressure difference (\(\Delta p\)), surface tension of the liquid (\(\gamma\)) and the curvature radius (\(r\)) of the bubble

Liquid foams are made wherever gases and liquids are mixed.

Ingredients such as soap or other surfactant help to form stable films, and therefore long-lived foams.

The pressure is: \(p_C > p_A > p_B\)
as at B the curvature is \textit{negative}.
Formation of foams (G/L)

Bubbling gas into a liquid through a porous filter

• Minimum pressure required:
  \[ p = \frac{2 \gamma}{r}. \]

• At first the largest bubbles come out

• For finer bubbles, higher pressure difference should be used
The arrows show the direction of streaming, hence water will flow to these points, until they become unstable. If we add glycerol to a soap solution, the viscosity increases, and the drainage of the foam is slowed down: it takes a longer time before the foam collapses.

\[
\Delta p = \frac{2 \gamma}{r} \quad r < 0
\]

Cross section of a Plateau border and foam lamellae. (The arrows show the direction of streaming.)
Interference colors on a soap film

http://www.tcd.ie/Physics/Foams/duran.php
Stabilization of foams

Each interface is electrically charged. As the film thins, the repulsion increases.

Good emulsifying agents are also good foaming agents.

The factors which influence emulsion stability against droplet coalescence and foam stability against bubble collapse are similar.
Foam stability

• Stability of a foam film is governed by
  - *drainage*: liquid drains from the Plateau border channels until an equilibrium is reached
  - *coarsening*: gas diffuses through the liquid, small bubbles disappear while bigger bubbles grow $\rightarrow$ average bubble size increases
  - *film rupture*: if the film weakens enough, it will break. This arises mainly from the evaporation of the liquid.

• Foam stability
  - *unstable foams* are mainly from aqueous solution of short chain amphiphilic compounds
  - *metastable* foams are made from longer chain species
Foam inhibition and breaking

- **Foam inhibitors**: added before the foam forms, they displace or foaming agents or solubilize the foaming agents (into micelles)

- **Foam breaking**: mechanical-, shock- or compression waves, ultrasonics, rotating discs, heating, electrical sparks

- **Antifoams**: added to existing foams, in the form of small droplets, which spread on the lamellae, thinning and breaking them.
With an antifoam on one surface, electrostatic stabilization is lost.

The Laplace pressure is low, because of the negative curvature, hence water will flow away, until the foam becomes unstable.

**Antifoams** - added to existing foams, in the form of small droplets, which spread on the lamellae, thinning and breaking them.
Applications

• Chemical processing.
• Food products, such as whipped cream and chocolate mousse.
• Toiletries, such as shaving foam and hair mousse.
• Household cleaning products, such as oven cleaner and limescale remover.
• Fire extinguishers.
Further examples

- **Marshmallow**: foam formed from egg white, gelatin, and sugar.
- **Ice cream**: refrigerated and aerated at the same time. Ice crystals and fat crystals form the matrix. ([http://www.foodsci.uoguelph.ca/deicon/icstruc.html](http://www.foodsci.uoguelph.ca/deicon/icstruc.html))
- **Dynamic foams**: cakes, sponges, bread, meringues, soufflés. Bubbles change at various stages of preparation.
- **Foams on drying**, especially in distillation columns. A foam blanket at the surface acts as an insulating layer, causing overheating.
- **Metallic slags foam**: probably because of the high viscosity. Cooling stabilizes the foam.
- **Paper making**: Caused by lignin, resin, and fatty acids in wood, sulfate soaps from pitch. Also, sizing materials, dyes, fillers, oxidized starch, proteins, etc act as profoamers.
- **Beer**: foam should not affect taste, but it remains important. Too little, beer looks "flat". Sources of foam: entrained air by pouring, in the pressurizing, and from dissolved carbon dioxide. Mostly stabilized by proteins. Protein-polysaccharide complexes are especially stabilizing.
Fire fighting with foams

Firefighting Foams
• For fire protection against fire from petroleum products and other chemicals.
• Against airplane and automotive fires.
• Foam is made in a self-aspirating branchpipe: high pressure pushes the water + foaming agent down a pipe, aspirating air, foaming because of the turbulence (about 1mm bubbles) and is thrown from about 15 to 75 m.

Main types:
• Protein foam liquid - solution of hydrolyzed protein
• Liquid made from various perfluorinated surfactants (high performance, non-biodegradable)
• Mixtures of perfluorinated surfactants with proteins
Immobilization with foams

- To retard evaporation. Improve insulation.
- For fumigants (chemicals toxic to fungi), insecticides, contraceptives, to keep them in place.
- Applying thin layers, such as adhesives or etching formulations, dyes or bleaches.
- Capture of aerosols..
- Aqueous foam is an excellent suspending medium for paper fibers. Pseudo plasticity enables dispersion of long fibers. At low shear stress the fibers are "frozen" in position. Enables the use of long fibers which otherwise orient on coating.
Solid foams (G/S)

● Solid foams are cellular materials, i.e. materials which are made up from a framework of solid material surrounding gas-filled voids (bubbles). Solid foams can be 100 times lighter than the equivalent solid material.

● Natural solid foams include wood, bone and sea sponges.

● Bee's honeycomb is an analogic (but not colloidal) two-dimensional cellular structure:
Solid foams (G/S)

• Recent developments in metal foams (especially aluminum) have produced a new class of lightweight materials, which are excellent energy absorbers. This property is useful in reducing the impact of a car, plane or train crash.

• Other applications of solid foams include:
  - Cushioning materials in furniture.
  - Structural materials such as sandwich board.
  - Insulating materials, such as cavity wall insulation. Honeycomb concrete.
  - Packaging materials, such as expanded polystyrene.
  - Several food items are (at least partly) solid foams, such as bread, cake and other snack foods.
Emulsions (L/L)

- An *emulsion* is a dispersed, liquid in liquid (L/L) system in which the phases are immiscible or partially miscible.

- Both the dispersed phase (droplets) and the continuous phase (serum or medium) are liquid.

- Main types depending on the nature of the discontinuous and continuous phases
  - *oil in water* (O/W): dispersed phase is apolar
  - *water in oil* (W/O): dispersed phase is polar
  - *bicontinuous*: there is no clear dispersed phase, both phases are continuous
The globules of the dispersed liquid are generally between 0.1 μm and 10 μm, and so are larger than the particles found in sols.
Types of emulsions

- Identification of the type of the emulsion
  - Generally, an O/W emulsion has a creamy texture and a W/O emulsion feels greasy
  - The emulsion mixes readily with a liquid which is miscible with the dispersion medium
  - The emulsion is readily colored by dyes which are soluble in the dispersion medium
  - O/W generally have a much higher electrical conductivity than W/O emulsions

- The liquid with the greater phase volume need not necessarily be the dispersion medium!
  - Above 74% there is either a phase inversion or the droplets are deformed to polyhedral shape.
Terminology

• Macroemulsions
  - At least one immiscible liquid dispersed in another as drops whose diameters generally exceed 10 µm.
  - The stability is improved by the addition of surfactants and/or finely divided solids. Considered only kinetically stable.

• Miniemulsions
  - Emulsion with droplets between 0.1 and 10 µm, reportedly thermodynamically stable.

• Microemulsions
  - Emulsion with droplets below 100 nm.
  - Thermodynamically stable, transparent solution of micelles swollen with solubilizate. Microemulsions usually require the presence of both a surfactant and a cosurfactant (e.g. short chain alcohol).
Terminology

- **Creaming**: less dense phase rises
- **Inversion**: internal phase becomes external phase
- **Ostwald ripening**: small droplets get smaller while larger ones grow
- **Flocculation**: droplets stick together
- **Coalescence**: droplets combine into larger ones

The most important physical property of an emulsion is its stability
Emulsifiers form an adsorbed film around the dispersed droplets and prevent their coalescence. Emulsifiers are soluble, to different extent, in both phases.

- Drops without emulsifiers flocculate and coalesce spontaneously. In general, emulsions are thermodynamically unstable
  \[ \Delta G = \gamma \Delta A < 0 \]

- Emulsifiers adsorb to the surface of the droplets. If the work of desorption of the emulsifier is high, the coalescence is prevented, and the emulsions are thermodynamically stable.
  \[ \Delta G = \gamma \Delta A + \text{work of desorption} > 0 \]
Making emulsions

• Mode of action of making emulsions
  - Fluid streams at high velocities are forced against each other resulting in cavitation, turbulence, and shear.

• Emulsification proceeds in two steps
  - mechanical mixing
  - stabilization

• Main methods
  - Method of phase inversion
  - High speed mixers
  - Condensation methods: solubilize an internal phase into micelles
  - Electric emulsification
  - Intermittent milling
Emulsifiers

• Surface active materials
  - Carbohydrates: Acacia gum (gum arabic), tragacanth, agar, pectin → for o/w emulsions.
  - Proteins: gelatin, egg yolk, casein → for o/w emulsions.
  - High molecular weight molecules: stearyl alcohol, cetyl alcohol, glycercyl monostearate → for o/w emulsions, derivatives of cellulose, Na carboxymethyl cellulose, cholesterol → for w/o emulsions. Polyethylene glycol
  - Wetting Agents: Anionic, Cationic, Nonionic

• Finely divided solids (Pickering stabilization)
  - Bentonite, clays
  - Silica (fumed)
  - Metal hydroxides (magnesium hydroxide, aluminum Hydroxide) → for o/w emulsions
  - carbon black → for w/o emulsions
Emulsion stability

- The term “emulsion stability” can be used with reference to three different phenomena –
  - creaming (or sedimentation)
  - flocculation
  - breaking of the emulsion due to the droplet coalescence.
- Eventually the dispersed phase may become a continuous phase, separated from the dispersion medium by a single interface.
- The time taken for phase separation may be anything from seconds to years, depending the emulsion formulation and manufacturing condition.
Emulsion stability

Factors favoring **emulsion stability**

1. Low interfacial tension
2. Steric stabilization. Mechanically strong interfacial film (proteins, surfactants, mixed emulsifiers are common. **Temperature is important**)
3. Electrical double layer repulsions (at lower volume fractions)
4. Relative small volume of dispersed phase
5. Narrow size distribution
6. High viscosity (simply retards the rates of creaming, coalescence, etc.)
7. Reduced gravitational separation: reduced density difference, reduced droplet size, increased continuous phase viscosity
Emulsion inversion

- Emulsion inversion is the change of a given emulsion type to an other type (e.g. o/w $\rightarrow$ w/o)
- Generally it proceeds by the action of:
  - temperature
  - concentration
  - change of the composition of the phase(s)
Increasing the concentration of droplets (A) make them get closer until they “pinch off” into smaller, opposite type of emulsion (B).

**Making of butter**

- Cow’s milk is a fairly dilute, not very stable *O/W* emulsion, with about 4% fat.
- *Creaming* produces a concentrated, not very stable *O/W* emulsion, about 36% fat.
- Gentle *agitation*, particularly at 13–18°C, inverts it to make a *W/O* emulsion about 85% fat.
- *Drainage*, addition of salt, then thorough *mixing* produces
  - Butter (solid phase)
  - Buttermilk (liquid phase)
## Typical food emulsions

<table>
<thead>
<tr>
<th>Food</th>
<th>Emulsion type</th>
<th>Dispersed phase</th>
<th>Continuous phase</th>
<th>Stabilization factors, etc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice cream</td>
<td>O/W</td>
<td>Butterfat (cream) or vegetable, partially crystallized fat. Volume fraction of air phase: 50%</td>
<td>Water and ice crystals, milk proteins, carbohydrates (sucrose, corn syrup) Approx. 85% of the water content is frozen at –20 oC.</td>
<td>The foam structure is stabilized by agglomerated fat globules forming the surface of air cells. Added surfactants act as “destabilizers” controlling fat agglomeration. Semisolid frozen phase</td>
</tr>
<tr>
<td>Butter</td>
<td>W/O</td>
<td>Buttermilk: milk proteins, phospholipids, salts. Volume fraction: 16%</td>
<td>Butterfat triglycerides, partially crystallized and liquid oils; genuine milk fat globules are also present.</td>
<td>Water droplets distributed in semisolid, plastic continuous fat phase.</td>
</tr>
</tbody>
</table>
### Typical food emulsions

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</tr>
</thead>
<tbody>
<tr>
<td><strong>Margarine and related Products (low calorie spread)</strong></td>
<td>W/O</td>
<td>Water phase may contain cultured milk, salts, flavors. Droplet size: 1 – 20 μm Volume fraction: 16 – 50%</td>
<td>Edible fats and oils, partially hydrogenated, of animal or vegetable origin. Colors, flavor, vitamins.</td>
<td>The dispersed water droplets are fixed in a semisolid matrix of fat crystals; surfactants added to reduce surface tension/promote emulsification during processing.</td>
</tr>
<tr>
<td><strong>Mayonnaise</strong></td>
<td>O/W</td>
<td>Vegetable oil. Droplet size: 1 – 5 μm. Volume fraction: minimum 65% (U.S. food standard.)</td>
<td>Aqueous solution of egg yolk, salt flavors, seasonings, ingredients, etc. pH: 4.0 – 4.5</td>
<td>Egg yolk proteins and phosphatides. Lecithin (O/W), cholesterol (W/O)</td>
</tr>
<tr>
<td><strong>Salad dressing</strong></td>
<td>O/W</td>
<td>Vegetable oil. Droplet size: 1 – 5 μm. Volume fraction: minimum 30% (U.S. food standard.)</td>
<td>Aqueous solutions of egg yolk, sugar, salt, starch, flavors, seasonings, hydrocolloids, and acidifying ingredients. pH: 3.5 – 4.0</td>
<td>Egg yolk proteins and phosphatides combined with hydrocolloids and surfactants, where permitted by local food law.</td>
</tr>
</tbody>
</table>
Hydrophilic-lipophilic balance (HLB)

• A practical (arbitrary) scale defining the relative balance between hydrophilic and lipophilic character of a surfactant
• Used mainly for non-ionic detergents
• Two definitions in use
  - *Griffin's method*: $\text{HLB} = 20 \times \frac{M_h}{M}$ (where $M_h$ is the molar mass of the hydrophilic part of the molecule and $M$ the molar mass of the whole molecule)
  - *Davies' method*: $\text{HLB} = 7 + n_h - n_l$ ($n_h$: number of hydrophilic groups, $n_l$: number of lipophilic groups)

http://www.snowdriftfarm.com/what_is_hlb.html
## HLB values: applications

$$\text{HLB} = 7 + (\text{number of hydrophilic groups}) - (\text{number of lipophilic groups})$$

<table>
<thead>
<tr>
<th>Applications by HLB</th>
<th>Dispersibility in water by HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-6</td>
<td>For W/O emulsions</td>
</tr>
<tr>
<td></td>
<td>&lt;3</td>
</tr>
<tr>
<td>7-9</td>
<td>wetting agents</td>
</tr>
<tr>
<td></td>
<td>3-6</td>
</tr>
<tr>
<td>8-15</td>
<td>For O/W emulsions</td>
</tr>
<tr>
<td></td>
<td>6-8</td>
</tr>
<tr>
<td>13-15</td>
<td>Detergents</td>
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<td></td>
<td>8-10</td>
</tr>
<tr>
<td>15-18</td>
<td>Solubilizers</td>
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<tr>
<td></td>
<td>10-13</td>
</tr>
<tr>
<td></td>
<td>&gt;13</td>
</tr>
</tbody>
</table>

Ionic detergents may have much higher HLB values:

- SDS has a HLB of 40
Variation of type and amount of residual emulsion with HLB number of emulsifier.

(antagonistic action)

The nature of the emulsifying agent determines the type of emulsion
Physical properties of emulsions

- **Identification** of “internal” and “external” phases (W/O or O/W)
- **Droplet size and size distributions** – generally greater than 1 µm
- **Concentration of dispersed phase** – often quite high. The viscosity, conductivity, etc, of emulsions are much different than for the continuous phase.
- **Rheology** – complex combinations of viscous, elastic and viscoelastic properties.
- **Electrical properties** – useful to characterize structure.
- **Multiple phase emulsions** – drops in drops in drops in drops, ...
Emulsification by particles (Pickering emulsions)

Each interface needs a different HLB value. The curvature of each interface is different.

Almost all particles are only partially wetted by either phase. When particles are “adsorbed” at the surface, they are hard to remove – the emulsion stability is high. Crude oil is a W/O emulsion and is very old!!

(Pickering stabilization)

Bentonite clays tend to give O/W whereas carbon black tends to give W/O emulsions
Multiple phase emulsions

- “Drops in drops”
- More and more studied and used
- Great potential in drug-delivery

http://www.rsc.org/delivery/_ArticleLinking/DisplayArticleForFree.cfm?doi=b501972a&JournalCode=SM
Methods of breaking emulsions

- First, determine the type (O/W or W/O). Continuous phase will mix with water or oil.
- Chemical demulsification, i.e. change the HLB
  - Add an emulsifier of opposite type (antagonistic action).
  - Add agent of opposite charge.
- Freeze-thaw cycles.
- Add electrolyte. Change the pH. Ion exchange.
- Raise temperature (HLB depends on the temperature)
- Apply electric field.
- Filter through fritted glass or fibers.
- Centrifugation.
1. As temperature is increased, ethoxylated surfactants become less water-soluble, because the hydrogen bonding between the oxygen of ethylene oxide and the hydrogen of water is inhibited. The molecules are more mobile and cloudiness results.

2. Inversion $O/W \rightarrow W/O$, oil is separated out.

The oil-in-water emulsions measure just 100 – 300 nanometers, are of very low viscosity and can thus be applied by spraying.

Scanning electron microscope can provide a visual representation of the phase inversion: [http://www.chemistrymag.org/cji/2001/03c058pe.htm](http://www.chemistrymag.org/cji/2001/03c058pe.htm)