DISPERSIONS

1. Introduction

A dispersion is a mixture of particles suspended in a liquid. Examples are blood, ceramics, concrete, grease, inks, paints, paper coatings, pesticides, and photographic “emulsions”. The particles are called the discontinuous or internal or dispersed phase. The liquid phase is called the continuous or external phase, serum, or medium. When the particles have at least one dimension less than a micron (1000 nm), they are called colloidal particles and the mixture is called a colloidal dispersion. The lower particle size limit is 1 nm (a billionth of a meter, a thousandth of a micron). Dispersions finer than this are considered molecular solutions.

The descriptor, dispersion, is sometimes used broadly to include mixtures of liquids in liquids (emulsions), gases in liquids (foams), powders in gases (dusts), and liquids in gases (aerosols).

A dispersion of submicron particles has a large liquid/solid interface. The properties of this interface are different than those of either bulk phase. Some components of the liquid may be preferentially adsorbed in the interface. These are properly called surface-active solutes but more commonly called surfactants. If these surface-active solutes are ions, then the particle acquires a net electric charge. If surface-active solutes are polymers, then a barrier to close approach is created on the particle surfaces. If an ionic component of the solid is preferentially dissolved into the liquid, then the particles also acquire an electric charge.

The smaller the particles, the more they respond to thermal fluctuations of the liquid. The randomness of thermal fluctuations creates random motion of particles called Brownian motion, after the Scottish botanist, Robert Brown. Brownian motion leads to diffusion of the particles, which in turn leads to particle–particle collisions. If the particles bounce apart after they collide, the average particle size remains the same, and the dispersion is called stable. If the particles stick when they collide, the average particle size grows with time, and the dispersion is called unstable.

A concentrated dispersion is sometimes called a slurry or a slip. Dispersions of film-forming polymer particles are called latexes. Natural rubber is a latex. Dispersibility is the ease with which a dry powder may be dispersed in a liquid.

The study of dispersions is included in the field of colloid and interface science. Understanding and controlling the conditions under which dispersions are stable or unstable is a key goal of the study of dispersions. Academic research is now mostly in departments of chemical engineering but sometimes in chemistry, physics, or material science. Journals that publish review and research articles about dispersions are included in the bibliography.

Unfortunately, the term “dispersion” is also used in colloid science to refer to a type of interparticle attractive force. This attraction is a consequence of coordinated electronic fluctuations in particles close to each other and is also referred to as London, van der Waals, Hamaker, or Lifshitz attraction after key theoretical contributors.

A word of warning: Names can be misleading. A grave error is to name a component by its putative role, wetting agent, dispersant, film former, etc. These functions are interrelated and many components participate in several roles.

2. Classification

Dispersions can be classified by the degree of dispersion, the state of the dispersed state, the dispersion medium, the interaction between the dispersed phase and the medium, and the interaction between the particles.

The degree of dispersion is generally the average particle size. If all the particles are the same size, the dispersion is called monodisperse. If the particles have a variety of sizes, the dispersion is called polydisperse. If the least dimensions of the particles are $>1\ \mu$ (1000 nm), the dispersion is called coarse. If at least one dimension of the particles is $<1\ \mu$, the dispersion is called submicron. If at least one dimension is on the order of a few nanometers, the dispersion is called nanoparticle.

The growth of particle size as particles collide and stick is called flocculation or sometimes agglomeration, and the cluster is called a floc or agglomerate. Generally flocs can be redispersed by strong agitation. However, when particles bind tightly and cannot be redispersed, the growth is called aggregation and the cluster is called an aggregate. The distinction between agglomeration and aggregation is the strength of the interparticle forces in the cluster. Aggregates are redispersed by attrition. Coagulation is the term used for the merging of emulsion drops upon contact to form a larger drop.

Dispersions are also classified by the nature of the medium; these are aqueous and nonaqueous dispersions. The former are dispersions in water, the later are dispersions in organic liquids. This distinction is made because in aqueous dispersions the role of ions is significant and in most organic liquids they are less so. Dispersions are also called polar or nonpolar based on the dielectric constant of the medium, again reflecting the role of ions.

When particle–medium interactions are weak, the dispersion is called lyophobic. When particle–medium interactions are strong, the dispersion is called lyophilic (from the Greek lyos—to loosen, phobos—a fear, and philia—an attraction). The distinction was originally used to distinguish dispersions that were sensitive to salt, lyophobic, from those that were not, lyophilic. Sensitivity to salts is also called electrocratic. Dispersions of silver halides or carbon blacks in water are lyophobic. Dispersions of albumin or gum Arabic in water are lyophilic.

The interaction between particles is a combination of attractive and repulsive forces. The attractive forces are variously called London, van der Waals, Hamaker, or Lifshitz dispersion forces, after their theories. The repulsive forces are either electrostatic, the repulsion of like-charged particles or steric, the repulsion of interpenetrating polymer layers. The attractive and repulsive forces are all dependent on interparticle distance so that the total force varies with distance. If the particles are held apart by electric forces, the dispersion is called electrostatically stabilized. If the particles are held apart by polymer coatings, the dispersions are called sterically stabilized. Sometimes dispersions are stabilized by a combination of electric charges and steric barriers. These are called electrosterically stabilized.

Lyophobic dispersions often flocculate with the addition of salt or by waiting a period of time. These dispersions are kinetically stabilized and the flocculation is irreversible. Lyophilic dispersions often flocculate with a change in temperature or solvent composition, but when the temperature or solvent composition is restored, they disperse. These dispersions are called reversible or thermodynamically stabilized.

3. Methods to Produce Dispersions

Producing a dispersion is not simple. Specialized equipment and chemicals are used, and an understanding of some fundamental principles is necessary for optimum results. To fracture particles under a micron requires applying significant stresses to small areas and so appropriate equipment is needed. Newly created interfaces have high energies and will recombine unless the adsorption of dispersant is quick enough.

3.1. Dry Grinding and Powder Flow.

Dry grinding, sometimes called micronizing, is first used to reduce particles to under a few millimeters or so. The most common equipment is the air-impact pulverizer in which particles are entrained in air streams that are directed toward walls or each other. This grinding is usually combined with a cyclone separator to recycle the large particles. Dusts of micron-sized particles can be an inhalation health hazard and an explosion and fire threat.

Liquids flow smoothly because hydrostatic pressure builds steadily with depth. Powders do not flow smoothly. They adhere to each other and to the wall. If the cohesion and adhesion is strong enough, powder can support its own weight and form bridges from wall to wall. Therefore, powder-handling equipment generally has combinations of hammers, vibrators, and air blasters to break the powder structures.

3.2. Wetting and Millbases.

The next dispersion step is wetting of the powder with liquid. Prewetting the powder is accomplished by spreading the powder as a thin film across a liquid surface and providing as much new liquid surface as possible. This new surface enhances the displacement of gas from the pigment agglomerates. Wetting agents are added to aid in the displacement of gas.

The role of the adsorbed wetting agent is to reduce the contact angle as close to zero as possible while keeping the surface tension of the liquid as high as possible. This combination produces the greatest wicking pressure as shown by the Laplace equation 1:

$$\Delta p = \frac{2\sigma_{lv} \cos \theta}{r} \tag{1}$$

where Δp is the pressure drop from the bulk of the liquid to the interface, σ_{lv} is the liquid surface tension, θ is the contact angle of the liquid on the solid, and r is the radius of the space between particles. The pressure drop depends on the product of the surface tension and the cosine of the contact angle. Many wetting agents lower the surface tension and raise the cosine of the contact angle (ie, lower the contact angle itself) so the trade-off is hard to predict.

Wetting agents are low molecular-weight surface-active solutes, hence they adsorb on particle surfaces quickly. Some powder manufacturers add wetting agents to their powders to promote fast wetting, but this added component, if not accounted for, can interfere with other properties.

Subsequent processing in high energy mills is more efficient if the prewetting is done with a minimum of liquid. Therefore most manufacturers wet pigment with a minimum of liquid to form a high volume-loaded dispersion called a millbase. This millbase is fed to the high energy mixers for subsequent particle-size reduction.

3.3. High Speed Stirrers.

The most obvious method to produce a dispersion is to stir the powder and the liquid together. All kinds of single and multiple blade mixers are available which are designed to give good circulation. Experience has shown that even the best high speed stirrers do not usually reduce the particle size below a few microns. The reason for this is that the breakup of agglomerates requires a significant shear rate (velocity gradient) on the size scale of the agglomerates. The smaller the particles, the higher the necessary shear rate. The shear rates in high speed stirrers are the ratios of

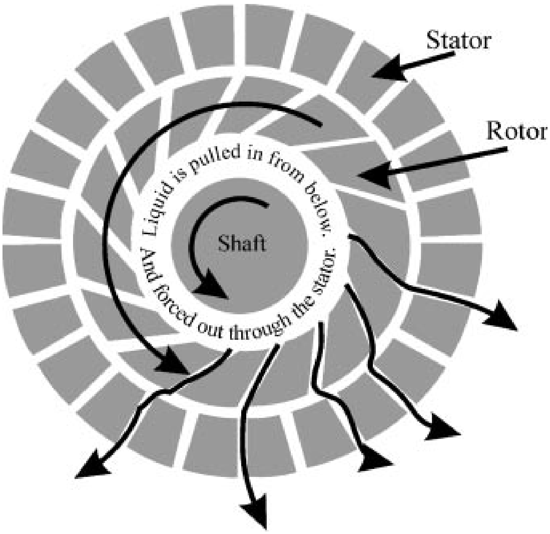

Fig. 1. A rotor-stator dispersor (1a).

their blade velocities (limited by cavitation) to the distance over which the velocities drop (approximately tens of centimeters). These are relatively low shear rates.

Much higher shear rates are attained by surrounding a spinning, slotted rotor with a shield (Fig. 1). The spinning rotor draws liquid up into itself by centrifugal forces. The liquid is forced out through slots in the stator. High shear rates are attained as the dispersion flows through the slots in the stator. It is common practice to use a blade stirrer to mix dry powder with the liquid and then a rotor-stator disperser to reduce agglomerate size to the micron range.

3.4. High Shear Mills. The key idea to produce finer and finer dispersions is to attain higher and higher shear rates. Liquid velocity is limited by cavitation. Therefore the design criterion is to force the liquid to flow through narrower and narrower gaps.

The colloid mill (Fig. 2) is constructed with a spinning rotor on a movable shaft inside a chamber. Liquid is sucked across the spinning rotor surface by centrifugal forces. The shear rate is determined by the speed of the rotor and the gap between the rotor and the chamber. To attain higher shear rates, the rotor is moved closer to the walls. The mechanical instability of the spinning rotor limits the gap to a few thousandths of an inch, but the resulting shear rate is an order of magnitude or more higher than attainable in a high speed stirrer.

Effluent from a colloid mill flows into a holding tank where it is cooled. It is customary for the holding tanks to be quite large, which means that the residence time in the holding tank is much larger than the residence time in the mill. Newly created surfaces in the mill are diluted into a tank of more stable dispersion giving surfaces time to adsorb dispersant. This use of a large holding tank in a milling process is called intermittent milling and is common in dispersion processing.

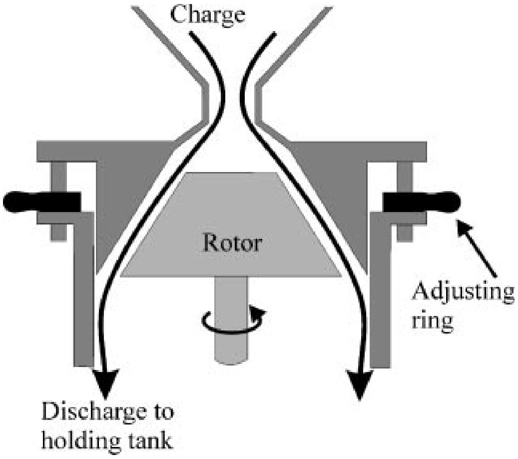

Fig. 2. Section of a vertical colloid mill (1a).

The homogenizer obtains even higher shear rates (Fig. 3). The dispersion is pumped through a narrow channel into which a plunger can be inserted. The plunger is mounted on a spring. Adjusting the flow rate to a predetermined pressure controls the mill. The deeper the plunger is into the channel, the faster the fluid flow and the higher the shear rate. The advantage of the homogenizer over the colloid mill is that there are no fast moving parts in the milling zone. Homogenizers have nearly completely replaced colloid mills.

Homogenizers come in a variety of designs. In some, the plunger is a plate rather than a cone. The advantage of this is that the plate is slightly mechanically unstable and so will vibrate when the flow rates are high. This adds another milling action. In some homogenizers the flow zone does not contain a movable

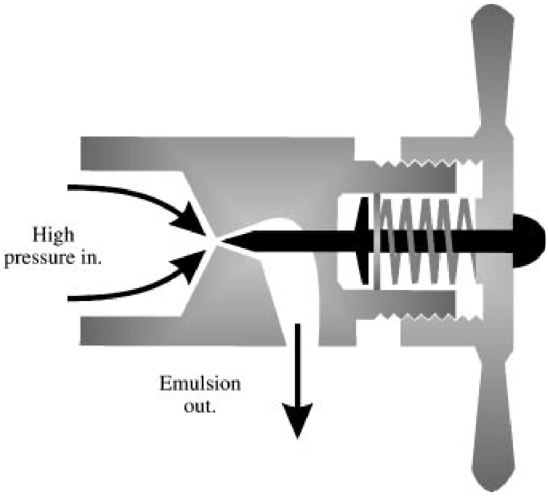

Fig. 3. Section of a single-stage homogenizer (1b).

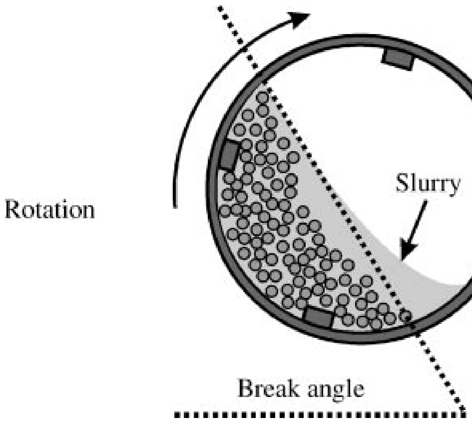

Fig. 4. Milling action in a ball mill (1c).

plunger but is tortuous. The turbulence around transitions produces high shear rates as well as cavitation.

3.5. Media Mills. High shear mills may be adequate to separate agglomerates but are not adequate to break aggregates. Media mills stir shot or rods through the dispersion to break aggregates by impact. The simplest of the media mills is the ball mill. It may be as simple as a glass jar partially filled with steel shot and placed on a roller. A pilot and manufacturing media mill is steel and is driven by a variable speed motor (Fig. 4).

The milling comes from the mass of balls cascading through the dispersion. If the rotation is too fast, the media just carry over and do not cascade. If the rotation is too slow, the media just slide slowly across the bottom and do not cascade. The proper speed is selected by listening to the mill. When the media are cascading properly, they can be heard. The proper rate of rotation varies with the viscosity of the dispersion. Since the viscosity of the dispersion varies with particle size and temperature, the rotation speed needs to be adjusted during the milling run, which also means that multiple samples cannot be put on a laboratory roller mill with the hope that all samples will get equivalent milling.

It is not unusual for ball mills to be run for several days to obtain a submicron dispersion. Energy is lost to compression and plastic flow of the particles and media moving through a viscous medium. Even the best processes are $<1\%$ efficient.

The attritor, a stirred-media mill (Fig. 5), is a significant design improvement over the ball mill. The attritor moves the media with a stirrer and holds the jar fixed, instead of moving the jar and letting the media fall. This means that the milling action is set by the speed of the stirrer, which is easy to control. The attritor has a more uniform milling action throughout the container so the particle size distributions are narrower. Additionally, the attritor is easy to cool, water is circulated through the jacket, whereas the ball mills are not. A rule of thumb is that the smaller the grinding media, the finer the grind. Attritors can be vertical or horizontal; batch, circulating, or continuous, filled with steel shot, ceramic beads, or sand, and heated or cooled.

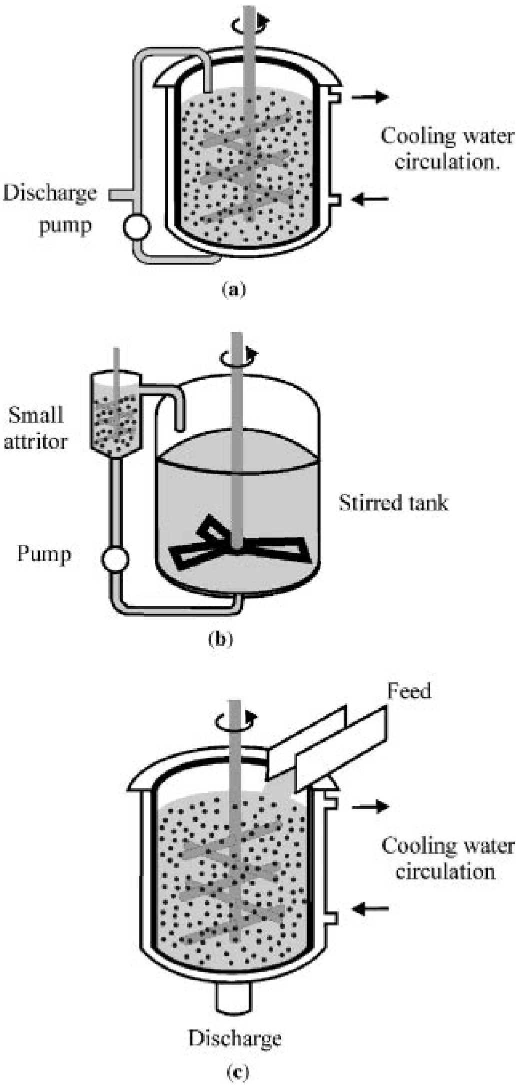

Fig. 5. Three types of attritor (**a**) batch, (**b**) circulating, (**c**) continuous (1d).

3.6. Mills for High Viscosities. The high speed stirrers, high shear mills, and impact mills only work with low viscosity dispersions. Some dispersions, such as rubber and plastic compounds, are too viscous to be made in that equipment. For these applications heavy-duty mixers are used such as three-roll mills, double-blade mixers (like dough mixers), kneaders, and screw mixers of various designs. This equipment comes with high torque motors and the ability to heat the dispersion to lower viscosity. Although the dispersions produced are adequate, none of these pieces of equipment produces a fine, submicron dispersion. That requires high shear rates unobtainable when the viscosity is too high.

Tests for the quality of these dispersions include microscopy or looking for a “calendering effect”; a sample of the dispersion is taken and reworked at as high shear stresses as possible in the laboratory. Changes in color indicate changes in the quality of dispersion (2).

3.7. Special Methods. Many dispersions, especially latex or polymeric dispersions are prepared synthetically. That is, the particles are formed *in situ* rather than by attrition. The particles may be formed by controlled nucleation and growth or the particles may be formed by dispersion or emulsion polymerization [Walbridge, Chapter 2 in (3)].

An interesting method to produce liquid–medium dispersions is to squirt liquid through a nozzle while applying a substantial electric voltage. The electric charges that are carried on the surface of the liquid film help to break large drops into smaller droplets. The technique has been demonstrated for oil in water and water in oil emulsions.

4. Chemical Processing Aids

Chemical processing aids are used to improve the wetting of the dry powder by a liquid, to stabilize newly created surfaces during milling, to stabilize particles against flocculation on long time scales, to induce flocculation when needed, to improve dispersability in polymers, and to modify the flow of dispersions. Each of these processes requires solutes to move to the particle/liquid interface, so these aids are called surface-active solutes or, more commonly, surfactants.

The first criterion for a chemical processing aid is that it accumulates at the particle/liquid interface and does this even in the presence of other materials. This process is called preferential adsorption. A solute can only be preferentially adsorbed when it displaces other molecules from the interface, including the solvent. In this sense, preferential adsorption is a kind of insolubility.

Work is required to create new particle/liquid interfaces during milling. If nothing changes after new surfaces are created, they recombine and nothing is gained. Surface-active solutes are adsorbed at the particle/liquid interface. If the adsorption of surface-active solute is slight, the particles recombine slowly. If the adsorption is substantial, the particles may not recombine for a very long time, if at all.

Surface-active solutes have specialized structures. Part of the molecule is lyophilic (solvent loving) and part of the molecule is lyophobic (solvent hating). The lyophobic portion is adsorbed at the surface and the lyophilic portion extends into the solvent. A molecule that has two such disparate moieties is called amphipathic (amphi- from the Greek for “both” and pathos for struggle). Soap is the alkali salt of an alkyl carboxylic acid and is the prototypical surface-active solute in water. The ionic carboxylic salt head groups are hydrophilic; the alkyl chains are hydrophobic. When the alkyl chain is long enough, it is adsorbed by the interface and pulls the charged, hydrophilic head group with it.

Surface-active solutes may be synthesized by combining a hydrophilic moiety with a lipophobic moiety. Table 1 lists a number of hydrophilic and lipophilic moieties, which may be combined to give solutes with different hydrophile-lipophile balance.

Table 1. **Hydrophilic and Lipophilic Moieties**

Hydrophilic		Lipophilic	
Ionic		*Hydrocarbon*	
carboxylate	$-CO_2^-$	straight-chain alkyl	(C_8–C_{18})
sulfate	$-OSO_3^-$	branched-chain alkyl	(C_8–C_{18})
sulfonate	$-SO_3^-$	alkylbenzene	(C_8–C_{16})
quaternary ammonium	R_4N^+	alkylnaphthalene	
		perfluoroalkyl	(C_6–C_8)
Nonionic		*Polymeric*	
fatty acid	$-CO_2H$	polypropylene oxide:	$H[OCH(CH_3)CH_2]_nOH$
primary alcohol	$-CH_2OH$	polysiloxane	$H[OSi(CH_3)_2]_nOH$
secondary alcohol	$-CRHOH$		
tertiary alcohol	$-CR_2OH$		
ether	$-COC-$		
polyethylene oxide:	$H[OCH_2CH_2]_nOH$		

An homologous series of dispersants of increasing alkyl chain length would be more and more surface active but less and less soluble. At some chain length, the surface activity is a maximum, which is called the Ferguson effect (Fig. 6).

Solutes can be graded in terms of how hydrophobic they are and how hydrophilic they are. This order was first proposed as a method to organize emulsifiers. Those that stabilize water-in-oil emulsions (lipophilic solutes) are assigned low numbers. These materials also stabilize dispersions in organic solvents,

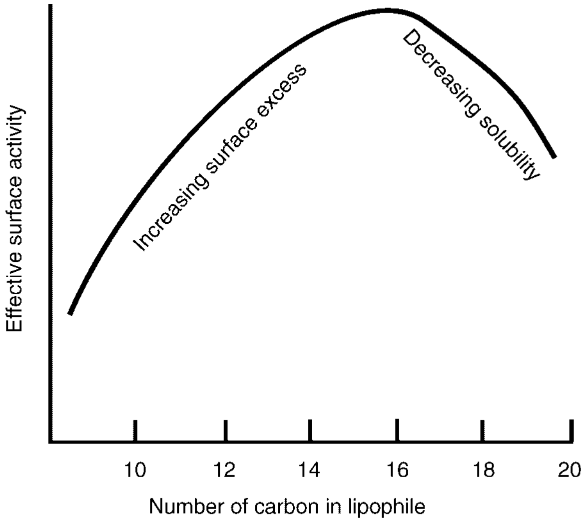

Fig. 6. The variation of effectivenss of a surface-active solute with the number of carbon atoms in the lipophile at ~60°C. Usually the alkyl chain lengths are in the order of $C_{16}>C_{14}>C_{18}>C_{12}$.

Table 2. **Graded Series of Solutes in Terms of Hydrophile–Lipophile Balance**[a]

Lipophilic end of scale				Hydrophilic end of scale	
stearane	steric acid	sodium stearate	sodium laurate	sucrose	sodium sulfate
soluble in oil; insoluble in water	soluble in oil; insoluble in water	soluble in oil; and in hot water	slightly oil-soluble; soluble in water	insoluble in oil; soluble in water	insoluble in oil; soluble in water
nonspreading on water	spreads on water	spreads on water	reduces surface tension of aqueous solutions	does not affect the surface tension in aqueous solution	increases surface tension in aqueous solution

[a] Ref. 1.

polymers, and plastics. Those that stabilize oil-in-water emulsions (hydrophilic solutes) are assigned high numbers. These materials also stabilize water dispersions. The scale is called the HLB scale for hydrophilic–lipophilic balance (Table 2).

Flocculants are also surface-active solutes, but they are designed to bind particles not disperse them. When flocculant molecules adsorbed by one particle touch a bare spot on another particle, the particles stick. This “bridging” process creates large floc structures. At excessive concentrations, flocculant molecules cover all bare surfaces, particle bridging no longer occurs, and flocs do not form.

4.1. Donor–Acceptor Interactions. Adsorption of solutes from solution by a particle surface is a complex process. Energy is required to displace solvent from both the surface-active solute and the particle surface. Energy is gained when the surface-active solute is adsorbed and the released solvent molecules mix. Adsorption is spontaneous only if the free energy decreases. If the particle is strongly wetted by the solvent or the solute is very soluble, adsorption is minimal.

Any spontaneous change is governed by changes in both entropy and enthalpy. As adsorption generally leads to a more ordered system, the entropy decreases. Therefore whether a solute will be adsorbed by a particle surface depends on a strong enthalpic interaction. Important exceptions arise with the adsorption of hydrocarbons from water. The release of water molecules increases the entropy of the system, the so-called hydrophobic effect (4). Enthalpies of interaction are studied extensively in inorganic chemistry, primarily in the formation of complexes. Adsorption can be thought of as complex formation. These heats are the sharing of electrons in one molecule with empty orbitals in another and are called donor–acceptor or Lewis acid–base interactions.

Lewis bases are electron donors. Molecules containing nitrogen atoms with unbonded electrons are the strongest bases. Oxygen-containing molecules, especially ester groups are next. Electrons on aromatic and other conjugated molecules are weak bases. Molecules containing empty low energy molecular orbitals are the strongest acids. The protons on acids and hydroxyl groups are the strongest. The hydrogens on chlorinated hydrocarbons are acidic because of the strong electron-withdrawing power of the chorine atoms attached to the same carbon atom. The silicon atoms in siloxane polymers are also acidic because they have empty *d* orbitals. The ether oxygens on the same siloxane molecules are bases.

Understanding and predicting which molecules are adsorbed requires considering the balance of acid–base interactions between all three components: the surface, the solute, and the solvent.

4.2. Creation of Surface Charge.

Some surface-active solutes are also ionic. For example, soaps are the alkali salts (sodium or potassium) of alkyl carboxylic acids. When soaps dissolve in water they dissociate into a cation, the positively charged sodium or potassium ion, and an anion, the negatively charged alkyl carboxylate. The cations are quite hydrophilic, but the carboxylate anion is substantially hydrophobic. These anions find a lower energy state by adsorbing onto the particle surface, which partially removes the hydrophobic alkyl chain from the water. The anions are also adsorbed at the water/air interface and reduce surface tension. The anions also will form micelles if their concentration is above the critical micelle concentration. The adsorption of the anions by the particle surface gives the particle a net negative charge. Charged particles repel each other and are less likely to flocculate.

The surface-active solutes that form ions in solution are called ionic. The surface-active solutes whose anions are adsorbed are called anionic surfactants. Anionic surfactants create negatively charged particles. The surface-active solutes whose cations adsorb are called cationic surfactants. Cationic surfactants create positively charged particles. Those surface-active solutes that do not dissociate into ions are called nonionic. Nonionic surfactants do not confer charge to particles.

Some solids have ionic groups on their surfaces. Silica and alumina are examples. These surfaces can add or loose protons, which results in a net surface charge that changes with pH. The pH at which the sign of the charge on particles changes from positive to negative is called the point of zero charge (PZC). Other solids such as silver halides are also charged by the adsorption or desorption of ions. For example, silver chloride particles are positive in the presence of excess silver ions and negative in the presence of excess chloride ions. The ions that control the charge on the particle are called potential-determining ions.

4.3. Creation of Steric Barriers.

When molecules are adsorbed by a solid surface, they coat the surface. Small, uncharged molecules on the particle surface have no effect on whether particles stick during collisions because the strength of the dispersion force attraction is strong at short separations. However, if the molecule is large, ie, polymeric, then the surface coating may be thick enough to keep particles far enough apart that dispersion forces do not hold them together. This produces a stable dispersion. The adsorbed polymer film is called a steric barrier and the resulting stabilization is called steric stabilization.

The essential requirement for a good steric stabilizer is that it forms a thick adsorbed film. Homopolymers are not good steric stabilizers since, if they are adsorbed, they will adsorb flat against the surface. The exceptions are some naturally occurring polymers whose molecular weights are so high that the time required for them to uncoil and lay flat is long. Such polymers were originally called protective colloids since they prevented flocculation of dispersions during freeze–thaw cycles.

Copolymers are better steric stabilizers. Some of the monomer units in the copolymer need to have a chemistry (acid–base) that binds the polymer to the solid. The rest of the polymer needs to be soluble in the solvent. As a rule of thumb, $\sim$10% of the monomer units should act as anchor sites. The more efficient molecular designs for copolymers are block copolymers since a lesser proportion of anchoring groups is needed.

The most efficient steric barriers are obtained by grafting the polymer to the particle surface. When the polymer is chemically attached to the surface, it can have a chemistry that is strongly solvated. The strongly solvated chains are highly extended and the molecular weight needed to obtain a thick film is less.

4.4. Selection of Dispersion Aids.

The general principles are understood: The surface-active solute needs to adsorb to the particle surface. It must have a stronger affinity for the particle than the solvent. If the surface-active solute is ionic, then enough must adsorb to produce a high enough electric charge to keep the particles apart. If the surface-active solute is nonionic, then it must have a high enough molecular weight to form a thick enough surface coating to keep particles apart (see the section Steric Repulsion).

A good start at selecting dispersing aids is from the experience of colleagues who have prepared similar formulations. By examining what dispersants have worked before or what ones are described in patent literature, clues are found about classes of materials to try. The important information is not the trade name but rather the chemical composition. Another source of information is McCutcheon's *Emulsifiers &* Detergents, an annual trade publication from which information in Table 3 is taken (5). Common dispersants are also described by Conley (6) and shown in Table 4. Nelson has suggested a short list of trial dispersants of six anionics, a cationic, three nonionics and two block copolymers [(7), p. 164], as well as a general selection scheme [(7), Appendix C]. Technological books give many practical examples [Chapter 6 in (8), (9)]. Edited technological books have chapters on dispersions of specific pigments (2). Surfactant kits containing small quantities of common dispersants are available from commercial suppliers.

The Daniel flow point test is commonly used to pick efficient dispersants. A small amount of pigment is titrated with a solution of the candidate dispersant. The mix is stirred with a spatula after each aliquot is added. The dispersant requiring the least addition to make a free-flowing paste is considered best (10).

4.5. Flocculants.

Flocculation is the formation of clusters of particles called flocs. Flocs usually settle quickly and are easy to filter. Flocs can be redispersed by relatively weak mechanical forces. Aggregation is the formation of clusters of particles that cannot be redispersed except with strong mechanical forces. For efficient filtration and drying, open structures are wanted so flocculation is preferred. Fine particles in wastewater are efficiently removed by sedimentation after they are flocculated.

One method to induce flocculation is to remove the stabilizing mechanism, not necessarily by removing the dispersant. If the particles are stabilized by electric charge, then neutralizing the charge by adsorbing ions of the opposite charge flocculates the dispersion. A dispersion may be flocculated by adding enough salt to shield the electric fields around charged particles. This shielding allows particles to approach each other closely enough to be trapped by dispersion forces.

Table 3. **Commonly Used Emulsifiers, Detergents, and Dispersants**

Chemical class	Application
1. *Anionic*	
alkyaryl sulfonates	detergents, emulsifiers
fatty alcohol sulfates	detergents, emulsifiers
lignosulfonates	dispersants
alkali soaps of tall oil	anionic emulsifiers
alkali soaps of rosin	anionic emulsifiers
dialkylsulfosuccinates	wetting agents
polyphosphate	dispersing agent
tetrasodium pyrophosphate (TSPP)	dispersing agent
trisodium orthophosphate	dispersing agent
2. *Cationic*	
alkyltrimethylammonium chloride	emulsifier, corrosion inhibitor, textile softener, antibacterial agent, detergent
3. *Nonionic*	
alkanolamides	detergents, foam stabilizers
glyceryl esters	emulsifiers
ethylene-oxide condensates of alkylphenols	emulsifiers
ethoxylated alkylphenols	detergents, wetting agents, emulsifiers, dispersants
ethoxylated fatty esters	food emulsifiers (oil in water)
fatty esters	food emulsifiers (water in oil)
polyalkylsuccinimides	oil-soluble dispersants
lecithins	oil-soluble dispersants
metal soaps	oil-soluble dispersants

Changing the solvent composition or temperature collapses polymer layers. This reduces the thickness of adsorbed layers and allows the flocculation of the sterically stabilized dispersions. If the solvent composition can be changed to solubilize the polymer, the dispersion will also flocculate.

Adding a polymer to the system that binds particles together is a method to flocculate. If the polymer is adsorbed by two particles close together, that polymer is a good flocculant. Several approaches work.

First, if the polymer has a high enough molecular weight, has a chemical composition that binds to the solid, and is used at a low enough concentration that it does not cover most of the particle surface, it will flocculate the dispersion.

Table 4. **Common Dispersants**[a]

Class	Examples
salts of inorganic acids	phosphates, polyphosphates, silicates, aluminates, and borates
salts of organic polyacids and copolymers with polyethers	polyacrylates and their salts
nonionics containing Lewis bases	dihydric alcohols, poly(ethylene amines), alkanolamines, polyethyleneoxides
amphiphilic nonionics	polyethyleneoxide-*co*-polypropyleneoxides, Triton X-100

[a] Ref. 6.

The same molecule will adsorb on two particles tying them together. An example is a high molecular weight cationic polymer such as polyacrylamide. Most aqueous dispersions are negatively charged so a cationic polymer is adsorbed strongly. The higher the molecular weight, the more likely the polymer is to bridge the space between two particles.

Second, if the polymer is a triblock copolymer with the ends strongly attracted to the particle surface but the middle soluble in liquid, then it can form bridges between particles. An example is a copolymer of polypropyleneoxide (insoluble in water) and polyethyleneoxide (soluble in water) with the PEO in the middle and PPO at both ends.

A key factor in the use of flocculants is control of the dosage. The optimum dosage is lower than the dosages used for dispersants. Polymer flocculants work when they are able to connect bare surfaces on two particles. If their concentration is too high, they cover the particle surfaces and no bridges are formed. If the flocculant works by charge neutralization, too high a dosage just reverses the sign of the charge on the particle and redisperses it.

A general guide in the evaluation of both flocculants and dispersants is to test over a wide range of concentrations, especially for polymers. At too low a concentration, many dispersants can be adsorbed on two particles simultaneously and act as flocculants. Similarly, at too high a concentration, many flocculants cover all the particle surfaces and act as dispersants.

4.6. Selective Flocculation. Selective flocculation is used to separate selected particles from mixed-particle dispersions. The original use was to separate valuable minerals, such as iron, copper and tungsten, from the gangue with which they are mixed. More recent uses are for the separation of low and high density cholesterol and in the separation of treated paper from pulp (11). When the dispersed particles are all finely divided, either the valuable component or the gangue can be flocculated and separated by sedimentation. Sometimes the valuable component can be flocculated and then separated by bubbling air. This is called froth flotation.

4.7. Flushing. Flushing is the direct transfer of dispersed particles from one liquid to another. Flushing is commonly used to transfer pigment particles from the water dispersion in which they are synthesized to an oil phase. Flushing avoids drying the pigment and the problems associated with aggregation. Flushing is often done at high pigment loadings and is surprisingly sudden. The aqueous dispersion is mixed with the oil or low molecular weight polymer in a large, low speed blender to form an oil in water emulsion. After some time the pigment particles suddenly transfer from one liquid to the other, seemingly simultaneously, leaving a water-white aqueous solution. The process is likely the gradual build up of pigment at the oil/water interface until the emulsion becomes unstable. As droplets coalesce, the pigment is transferred to the bulk of the oil phase and the water separates. [(12) p. 348f] Flushed pigments are easier and less expensive to formulate into inks and coatings. Flushing is also a purification step. Much of the transfer technology is proprietary (2).

High volume loaded pigment dispersions in resins are called pigment chips. They are manufactured by dispersion into molten resin at high shear, often on two- or three-roll mills. Pigments provided as concentrated dispersions in low viscosity liquids are called master batches.

5. Dispersed Particles

5.1. Particle Motion. *Brownian Motion, Diffusion, Fractals, and Sedimentation Equilibrium.* The pressure of a gas against the walls of its container is a clear indication of the motion of the gas molecules; the higher the temperature, the faster the motion. Liquid molecules are also in constant random motion, but this is not so obvious and it took the molecular thermodynamic theory of Boltzmann to explain it. Einstein realized the connection between Boltzmann's molecular theory and observations of Brownian motion and derived an expression for the diffusion constant, D, of dispersed particles as a function of particle radius, a, and the liquid viscosity, η,

$$D = \frac{kT}{6\pi\eta a} \tag{2}$$

where k is Boltzmann's constant and T is the absolute temperature. When the particle is not spherical, a is called the equivalent hydrodynamic radius. This equation was verified independently by Svedberg and Perrin who won Nobel prizes in 1926, one in chemistry and the other in physics. The triumph was experimental verification of Boltzmann's molecular hypothesis and the explanation of Brownian motion. The apparent speed of a particle, its displacement over a time, t, is given by

$$v_{\text{apparent}} = \sqrt{\frac{6D}{t}} \tag{3}$$

where v_{apparent} is the apparent speed, D is the particle diffusion coefficient given by equation (2) and t is the time between measurements of position. A striking property of equation (3) is that the speed of the particle appears faster and faster the shorter the time between observations. This is an example of a fractal object (a fractal object is one whose shape appears similar at different magnification). Another fractal object is the roughness of a particle surface. As the magnification is increased, the number of observed surface features increases and the higher the surface area of the particles appears to be. Floc structures can be thought of as fractal. At each stage of growth, larger and larger flocs join. The structure becomes more open as it grows.

Sedimentation Equilibrium. Brownian motion causes particle diffusion. Gravity causes particles to settle. If a stable, dilute dispersion is left to equilibrate at constant temperature it should form a concentration gradient, most concentrated at the bottom and decreasing exponentially with height. By using Boltzmann's equation for concentration of particles as a function of potential energy (positive when particles are above the bottom) the concentration of particles, n, is found as a function of height, h

$$n = n_0 \exp\left(\frac{V\Delta\rho g}{kT}\, h\right) = n_0 \exp\left(-\frac{4\pi a^3\Delta\rho g}{3kT}\, h\right) \tag{4}$$

where n_0 is the concentration of particles at the bottom, V is the volume of a particle, $\Delta\rho$ is the density difference between the particle and the liquid, g is the acceleration due to gravity, k is Boltzmann's constant, T is the absolute temperature, and a is the radius of the particle. The inverse of the coefficient of h in the exponent is called the characteristic height, h_0:

$$h_0 = \frac{3kT}{4\pi a^3 \Delta\rho g}$$

or (5)

$$h_0\ (\mu m) = \frac{0.100}{a^3 \Delta\rho}$$

at 25°C when a is in μm and ρ is in g/cm^3. A dispersion of 0.10-μm radius particles in water with a density of 2 g/cm^3 would have an equilibrium height of only about 100 μm. Even stable particles settle to the bottom. The only reason all dispersions do not settle is that they are not left to equilibrate. Very little energy is needed to mix a colloidal dispersion so external thermal fluctuations and vibrations keep them uniformly mixed.

Particle Motion with An Applied Force. The viscous drag on a sphere as is moves through a liquid is given by Stokes' equation:

$$F_{\text{viscous}} = 6\pi\eta a v \tag{6}$$

where η is the viscosity of the fluid (Pa-s), a is the particle radius and v is the velocity of the particle. Whenever a force is applied to a particle, it will accelerate. As the velocity increases, the viscous drag increases. The particle reaches a steady state, a terminal velocity, when the applied force and the viscous drag are equal.

The terminal velocity, v_t, is

$$v_t = \frac{F_{\text{applied}}}{6\pi\eta a} \tag{7}$$

When particles settle, the applied force is gravitational so the terminal velocity for a freely settling particle is

$$v_t^{\text{gravity}} = \frac{2a^2 \Delta\rho g}{9\eta} \tag{8}$$

The rate of sedimentation decreases as the square of the particle radius; the smaller the particles, the slower they settle. When particles flocculate, their size increases and the rate of sedimentation goes up accordingly. If the particles and the medium have the same density, the particles do not settle.

When the particles are in a centrifuge, the applied force is centrifugal, so the terminal velocity is

$$v_t^{\text{centrifuge}} = \frac{2a^2 \Delta\rho R \omega^2}{9\eta} \tag{9}$$

where R is the distance from the center of the centrifuge to the position the particle concentration is being measured and ω is the angular velocity of the centrifuge. The efficiency of a centrifuge increases linearly with its size but with the square of its angular velocity. Therefore increasing the speed of the centrifuge is more significant than making the centrifuge larger.

When an electric field is applied to a charged particle the terminal velocity is the electrophoretic velocity:

$$v_t^{\text{electrophoretic}} = \frac{2D\epsilon_0 \zeta E}{3\eta} \tag{10}$$

where D is the dielectric constant, ε_0 is the permittivity of free space, ζ is the surface potential, and E is the electric field at the surface of the particle. (This field can be different than the applied field because of ion shielding. See the section Particle Charge.) Note that, in this approximation, the electrophoretic velocity does *not* depend on particle size. The approximation is good in nonaqueous dispersions where the ion concentration is low. Equation (10) can be used to determine the surface potential by measuring the electrophoretic velocity at a known electric field.

5.2. Optical Properties.

Light is a traveling electric and magnetic wave. As light passes through a particle, the electric field moves the electrons in the particle. The electric field is sinusoidal so that the electrons accelerate back and forth. This oscillation of electrons produces light. The light scattered by particles is the light generated by the oscillating electrons. It is not light reflected off a particle. Most particles have little magnetic susceptibility so the interaction with the magnetic field of the light is ignored. The scattered light that is seen by eye or is measured by a detector comes from the summation of the electric fields emanating from all the illuminated electrons. The wavelength of visible light varies from ~400 nm (0.4 μm) in the blue to ~700 nm (0.7 μm) in the red.

Dilute Dispersions. In a dilute suspension, as would be used in particle sizing, the detector "sees" light singly scattered from individual particles. Three particle size ranges are important. (*1*) When all particles are much less than the wavelength of light, ie, less than ~100 nm, Rayleigh theory is applicable. (*2*) When particles are about the wavelength of light, ie, ~100–1000 nm, Mie theory is applicable. (*3*) When all particles are much greater than the wavelength of light, ie, greater than ~1000 nm, Fraunhofer theory is applicable (Fig. 7).

Rayleigh Theory–Particles Small Compared to the Wavelength of Light. Rayleigh developed this first quantitative theory for the scattering of light to explain the blue of the sky. He obtained two important results, first, the intensity of light varies as the sixth power of the particle size, and second, it varies inversely with the fourth power of the wavelength:

$$I \sim \frac{a^6}{\lambda^4} \tag{11}$$

where a is the radius and λ is the wavelength. The strong dependence on particle size (Fig. 7) explains the appearance of scattering just as particles are forming

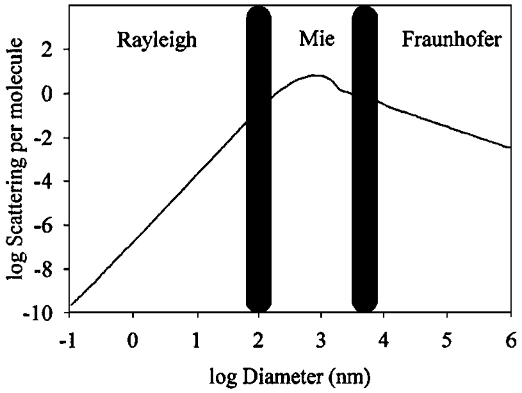

Fig. 7. Scattering of visible light per water molecule (14).

during precipitation (the Tyndall effect). The inverse dependence on the wavelength explains the blue of the sky: White light contains all wavelengths. As it passes through the atmosphere, the short wavelength blue light is scattered more strongly than the longer wavelength red light. In essence, the atmosphere glows blue. This blue glow can be confirmed by noticing that the landscape looks bluer the greater the distance.

Mie Theory–Particles about the Wavelength of Light. When the particle size is about the same as the wavelength of light, the electric field varies across the particle, which means that the total intensity of the scattering will be a strong function of the size of the particle and the direction of observation. This finding is illustrated in Figure 8(**b**) for a 500-nm diameter polystyrene particle.

Fraunhofer Diffraction–Particles Larger Than the Wavelength of Light. When the particle size is large compared to the wavelength of light, the scattered light begins to look like the light through a lens. For a spherical lens, the scattered light is a series of concentric rings in the forward direction. Figure 8(**c**) shows the scattering in the plane of the laser light. In two dimensions, the forward scattering lobes are rings of light. The detectors used for Fraunhofer scattering are concentric rings placed directly in the path of the laser beam (with an opening for the unscattered light to pass.)

Quasielastic Light Scattering—Particles Equal To or Less Than the Wavelength of Light. The data taken for Rayleigh, Mie, and Fraunhofer scattering are the time-average intensities as a function of scattering angle. The data taken for quasielastic light scattering is the time variation of the scattered light at a fixed scattering angle. The time scale is of the order of microseconds and longer. The light scattered at any angle is the sum of the light scattered from all the particles in the scattering volume in that direction. The intensity at any instant depends on the relative positions of the particles. Some will be at a position where their scattered light constructively interferes. Others will be at a position where their scattered light destructively interferes. As the particles move by Brownian motion, their relative positions change so the intensity of scattered light changes. The smaller the particles, the faster they diffuse, and

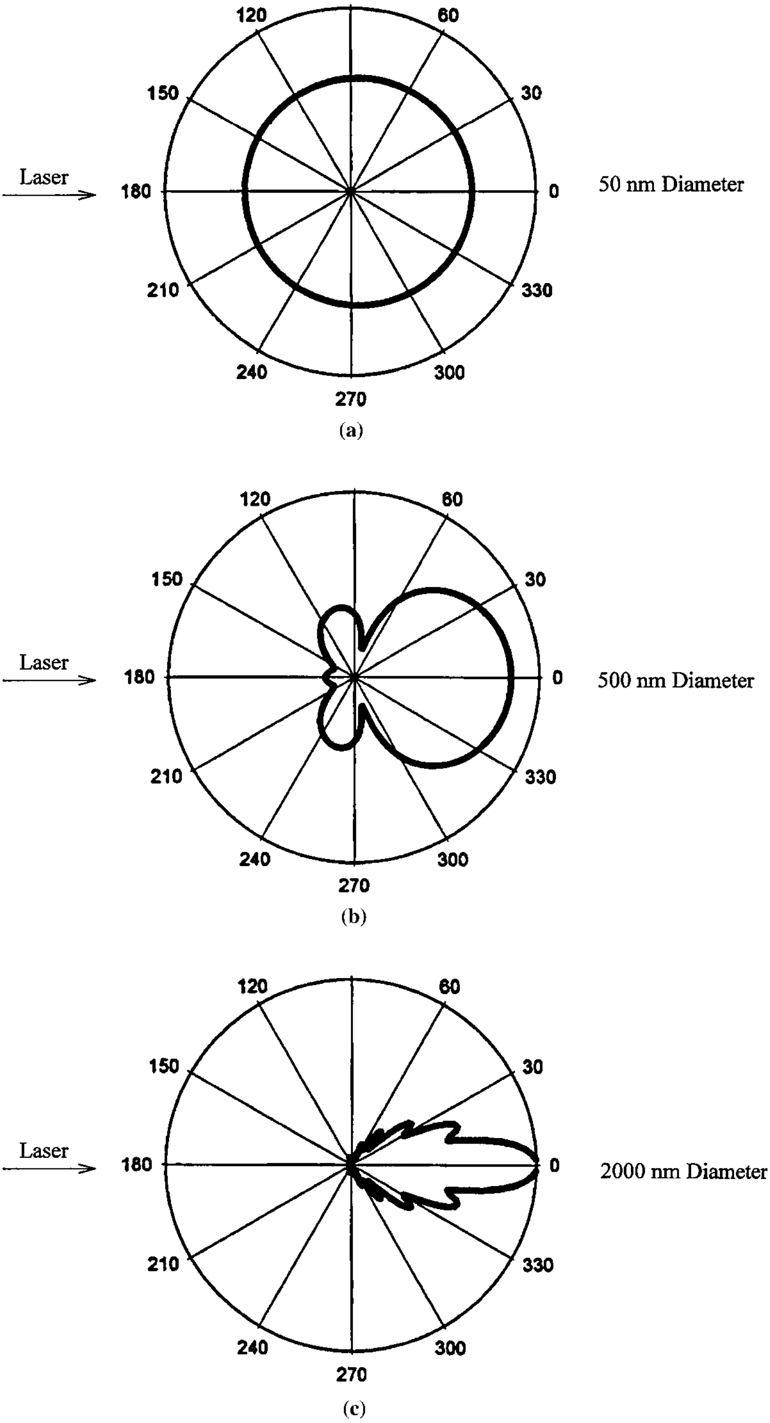

Fig. 8. Angular dependence of scattered intensity for polystyrene spheres suspended in water. The arrows indicate the direction of the incident polarized laser light. Each diagram has been scaled in the forward direction to make comparisons [(1), p. 8].

the faster the intensity of light varies with time. An analysis of the variation of intensity with time gives the diffusion coefficient, and hence average particle size. This technique is so accurate for monodisperse particles that it is used as the calibration standard for all other sizing techniques.

Concentrated Dispersions. In a concentrated dispersion generally and in a dried coating especially, light passing through is scattered and partially absorbed by many particles. A single photon takes a tortuous route through the dispersion and undergoes multiple scattering. A common analysis is by the Kubelka-Munk theory that treats light scattering in concentrated systems as a series of rates. The first is for the fraction of light back scattered from each layer and the second is for fraction of light absorbed in each layer. The total back scattered intensity sums the rates over the thickness of the sample.

Other useful information about dispersions at high particle concentrations models the multiple scattering of light as a diffusive spreading similar to a random walk. The intensity of light changes as interparticle spacing changes because of constructive and destructive interference. The time-dependence of the intensity of the scattered light, called diffusing wave spectroscopy, is most sensitive to the smallest motions as these are the most correlated. The technique analyses the time dependence of the intensity of the scattered light on a shorter time scale than quasielastic light scattering and after multiple scattering events. The results give information about interparticle forces rather than particle size.

5.3. Particle Size. *Microscopy.* The most common measurement made on a dispersion is the average particle size. The most certain technique is microscopy if applicable. Questions about shapes, size distributions, and even variable compositions can be answered with pictures. No other technique approaches this level of information. The limitation of microscopy is its lower size limit. Since the wavelength of light is ~500 nm it is not possible to form an image of a particle much less than ~1 μm. Particles smaller than that scatter enough light to appear in the image, but their outlines are not distinct enough to know their size. Ultramicroscopy is the use of a microscope and dark-field illumination to count the number of particles in a known volume of liquid. It can detect very much smaller particles but does not identify their size. The average size is estimated from the number of particles, their density, and the known mass concentration.

Shorter wavelengths enable the imaging of smaller particles. Ultraviolet (uv) light is difficult to focus, but the short wavelengths of the electron microscope are fine. Particle size can be determined easily to the nanometer range. The limitation is that the electron microscopy is a vacuum technique so that dispersions dry out before the image is taken. This always raises questions about what the dispersion looked like before it dried. A useful technique, freeze–etch electron microscopy, is to freeze the sample quickly enough to prevent any motion. In the electron microscope the size of primary particles can usually be determined.

Sampling and Sample Preparation. In most dispersions the particle sizes are small enough, the concentration high enough, and the stirring good enough that sampling is not the problem it is for dry powders. The sample preparation challenge for dispersions is that they usually need to be diluted before the common particle-sizing techniques can be used. If a dispersion is diluted with pure solvent, the concentration of all the soluble species change. This may lead to desorption of the stabilizing surface-active solutes and allow the particles to flocculate. The proper procedure is to dilute the dispersion in the serum of the dispersion. A common technique is to make up a solution with all the components of the formulation added. Another technique is to filter or centrifuge the dispersion and use the particle-free serum to dilute the sample. An exception is for light scattering measurement. The particle concentration has to be quite low so that even if the diluted sample is unstable, the time scale of flocculation may be longer than needed for the measurement.

Types of Distributions. Particle-size distributions can be expressed in several ways. The distribution may be a histogram or continuous function. The distribution may be a probability function such that the amount of particles in some size range is given by the integral of the function over that size range. Or the distribution could be cumulative with the probability function being the fraction of particles less that a certain size. The probability distribution is the derivative of the cumulative distribution. These functions are illustrated in Figure 9.

A further distinction is whether the distribution is a number distribution or a mass distribution. The number distribution is the number of particles in some interval. The mass distribution is the mass of particles in some interval. Size distributions from microscopy are number distributions since the number of particles in each size range is counted. Size distributions from sieving are mass distributions since the mass of particles in each size range is measured. The number distribution and mass distribution are different for the same sample

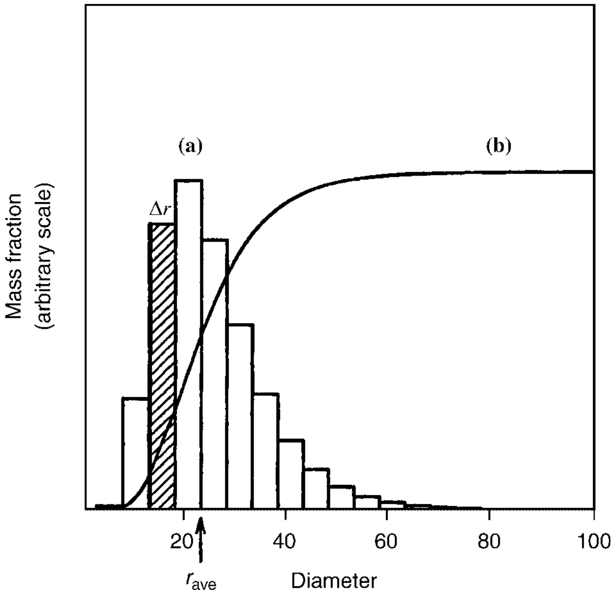

Fig. 9. A probability size distribution (**a**) and its corresponding cumulative function (**b**). The hatched area in the histogram is the fraction of particles within the range Δr. The midpoint of the cumulative distribution is the average particle size.

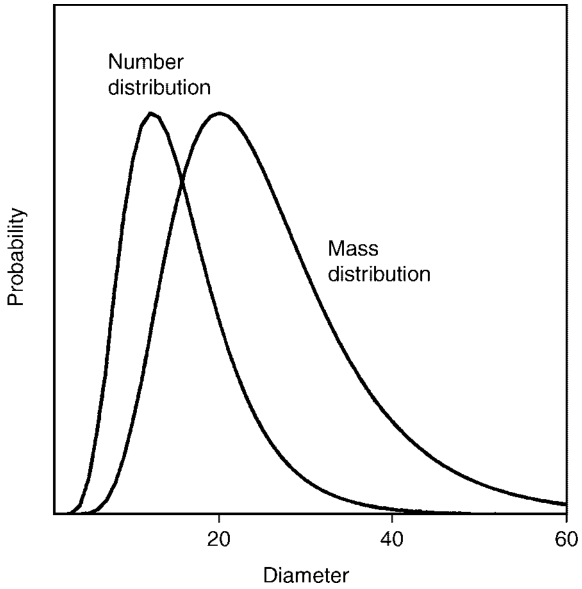

Fig. 10. A schematic comparing the number and the mass distribution for a given sample.

(Fig. 10). The number-average size is less than the mass-average size. The difference between the two can be quite large so that it is important when reporting particle sizes to identify the kind of distribution being reported.

Shape and Porosity. The shapes of particles in a dispersion are difficult to determine. The least ambiguous technique is microscopy. The optical microscope can be used for particles greater than a micron or so. The electron microscope can be used for smaller particles as long as care is taken that the particle shapes do not change with sample preparation and measurement. This is usually only possible for hard particles such as metals and metal oxides.

Shape sometimes influences rheological measurements. The presence of needle-like particles can produce dilatant flow. As the shear rate increases, the rotation of the needles in the flow field sweeps out larger volumes and the dispersion appears to have a higher viscosity. Plates flowing at low shear rates can orient in the direction of the flow and show optical birefringence in reflected light.

The porosity of particles is usually determined by mercury porosimetry that measures the pressure at which mercury can be forced into pores, the smaller the pore, the higher the required pressure. The porosity of aggregates can be measured by determining the critical volume fraction, the amount of liquid just necessary to fill the voids in the aggregates and the spaces between them. This test is standard for the characterization of carbon blacks known as the DBP (dibutyl phthalate) number and is the volume of DBP that can be added to a mass of carbon black before it begins to flow uniformly.

5.4. Sizing by Flow. *Sedimentation and Centrifugation.* The terminal velocity of a freely settling particle is given by equation (8). Velocities are not easy to measure directly. The usual procedure is to shake the dispersion,

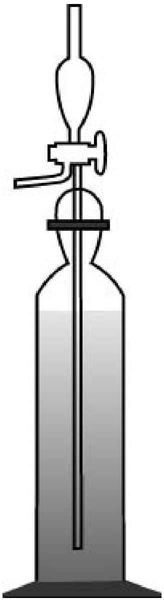

Fig. 11. In the Andreason sedimentation pipette, the cylinder is filled with homogeneous dispersion. The concentration at the sampling depth is measured as a function of time (14).

pour it into a glass cylinder, and let it settle. The concentration of the dispersion is measured at a known distance from the top of the liquid as a function of time (Fig. 11). The concentration does not change as long as each particle that settles out of the sensing zone is replaced by one of the same size settling into the sensing zone from above. This steady state continues until all of the largest particles have settled from the top of the liquid through the sensing zone. Then the concentration drops. The distance from the top of the liquid divided by the time it takes for the concentration to first start to change gives the sedimentation velocity of the largest particles. From that velocity and the known density difference between the particle and the liquid, the equivalent spherical radius can be calculated. The experiment continues until all the particles have fallen past the sensing zone. The data give a cumulative distribution of particle masses (or volumes).

A particularly useful method to determine concentration during sedimentation is to measure the speed of sound through the dispersion (16). The speed of sound is high as it passes through solids and slow through liquids. The time that sound takes to traverse a dispersion is linear in the volume fraction of components up to high volume concentrations and so is simple to analyze. Further, sound travels easily through pipes, tank walls, and opaque dispersions so the technique is applicable to many practical processes.

The practical lower size limit for sedimentation is roughly a few microns. The reason is that mechanical and thermal fluctuations disturb the dispersion and cause currents sufficiently strong to interfere with the settling of the small particles.

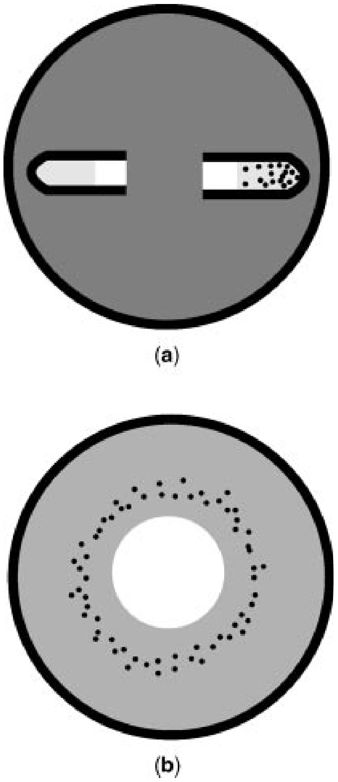

Fig. 12. Two types of disk centrifuges. (**a**) A disk centrifuge containing the sample on one cuvette and a blank in the second. (**b**) A disk centrifuge in which the sample is injected on top of the liquid inside a spinning disk. Both centrifuges have a stationary optical sensor near the outside edge of the sample.

To make particles settle faster a centrifuge is used. The centrifugal velocity of particles freely settling is given by equation (9). The velocity increases with distance from the center of rotation. Nevertheless, the method is similar to sedimentation in that the concentration is measured at a known distance from the top of the dispersion [Fig. 12(**a**)]. The data give a cumulative distribution of particle masses (or volumes).

A second type of disk centrifuge is available [Fig. 12(**b**)]. This centrifuge uses a clear, hollow disk. The spinning disk is filled with serum for the dispersion and a sample of the dispersion is injected onto the top of the spinning fluid. A density gradient is usually created on the top of the spinning fluid so that particles will settle smoothly from the injected volume into the serum. The detector does not sense any particles until the largest settle from the top to the sensing volume. Each size particle passes the detector at different times. Therefore, the data give a probability distribution of particle masses (or volumes). These are more accurate data than the cumulative distribution measured on the homogenous-start centrifuges, but the need for a density gradient makes the technique more difficult.

Hydrodynamic Chromatography and Field-Flow Fractionation. Liquid flowing slowly down a capillary tube (a few or few tens of microns in diameter, a few meters long) has a parabolic velocity profile, the maximum in the center of the tube, falling off quadratically toward the wall, and zero at the wall. Particles in the liquid are moving at the velocity of the liquid. The particles will diffuse to all positions across the tube. Smaller particles are able to move closer to the walls of the tube so they sometimes move at the slowest velocities. Therefore, on the average, larger particles move down the tube faster than smaller ones. The sample is fractionated by size. The usual detector is a uv spectrophotometer to minimize size-dependent scattering effects. The walls are carefully treated so that particles do not adhere. This limits the solvents that can be used. Aqueous dispersions are usually analyzed. The instrument is calibrated with standard-size polystyrene beads.

Field-flow fractionation is a set of techniques that combine flow down a tube or channel with a force field applied perpendicular to the flow. The most common technique uses centrifugation. A sample is injected into a flowing stream that runs into a centrifuge spinning up to ~30,000 rpm. Rotating seals allow the liquid to flow into the moving centrifuge disk. The centrifuge disk has a capillary channel machined in it. As the centrifuge spins, the larger particles are pushed to the outside edge. The liquid flowing at the outside edge is slower than liquid nearer the center of the channel, therefore the large particles take longer to move through the centrifuge. In practice, the flow is steady and the centrifugation is ramped to optimize separation.

5.5. Sizing by Single Particle Detection.

Photozone and Electrozone Detection. A simple particle-sizing technique is to pass a dilute suspension through a small sensing volume so that only one particle is in the sensing zone at a time. A light is mounted opposite to an optical detector and the cross-sectional area of each particle is measured as it passes through the sensing volume (Fig. 13). This technique is called photozone detection. Photozone

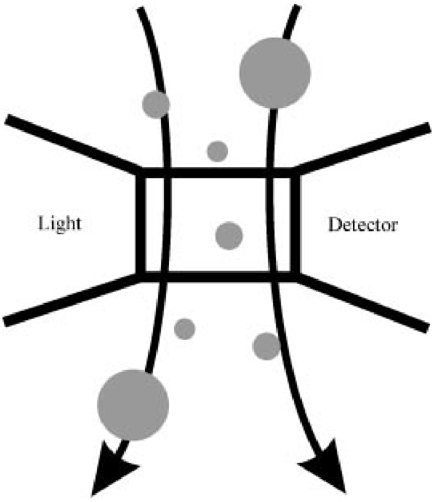

Fig. 13. The optical sensing and the flow pattern of a dispersion in a typical photozone counter (15).

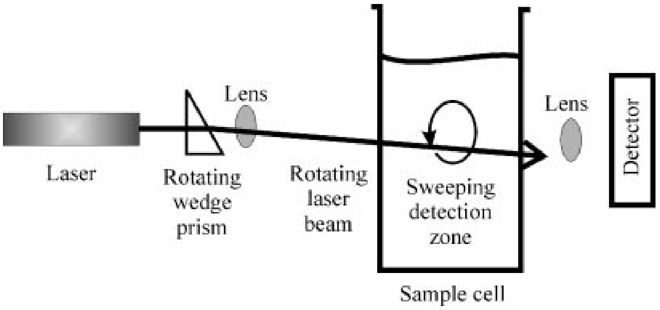

Fig. 14. The basic optics for the time-of-transition particle-sizing technique (17).

detection generates a number distribution of cross-sectional areas. The lower detection limit is ~1 μm equivalent radius below which the amount of light blocked by the particle is not equal to the cross-sectional area.

An electrozone counter detects a particle in the sensing volume by a change in the electric current flowing between two electrodes. The equipment is often called a Coulter counter after its inventors (two brothers of that ilk). The magnitude of the loss in current is proportional to the volume of the particle. The electrozone counter returns a number distribution of volumes. The technique is only applicable to aqueous dispersions because the electrical conductivity of the liquid must be high. A common use of electrozone detection is the determination of white and red cell counts in blood.

Time-of-Transition. The time-of-transition method counts particles by sweeping a focused laser beam through the medium (Fig. 14). A highly focused laser beam is passed through a rotating wedge prism and illuminates a well-defined volume in the dispersion. The dispersion flows through the illuminated volume and the particles are counted by a photodiode. The particle size is calculated from the time a particle scatters light and the velocity of the scanning beam. This method is applicable only for particles greater than ~2 μm. Many corrections are needed to take into account the different ways a light beam could cross a particle so the sizes reported are not accurate. The optics can be attached to a fiber optic probe so that the technique can be used in flowing systems and without dilution.

5.6. Sizing by Light Scattering. For particles less than ~100-nm Rayleigh theory is used. The turbidity of the dispersion, τ, is determined by measuring the attenuation of light

$$\tau = -\frac{1}{L}\ln\left(\frac{I}{I_0}\right) \tag{12}$$

where I is the intensity of the transmitted light, I_0 is the incident light intensity, and L is the path length. The average particle size is calculated by the relation:

$$d^3 = \frac{\lambda^4}{4\pi^4\rho}\left(\frac{n^2+2}{n^2-1}\right)^2\left(\frac{\tau}{c}\right) \tag{13}$$

where d is the average diameter, λ is the wavelength of the incident light, ρ is the density of the particles, n is the ratio of the refractive indices of the particles to that of the medium, and c is the mass concentration of the particles. This relation assumes the particles are transparent spheres and so is not generally accurate, but is practically useful.

Fraunhofer diffraction is used for particles greater than ~ 1 μm. The usual measurement records the scattering intensity simultaneously at a series of forward scattering angles. This enables a nearly instantaneous determination of the size distribution. The size distribution can be determined as a function of time, even on a flowing system. Rates of flocculation are easily measured by Fraunhofer diffraction.

Quasielastic light scattering (QELS) is used for particles less that ~ 1 μm. QELS is so accurate for monodisperse spheres that it is used to measure the size of the latex standards that are used to calibrate all other techniques. As long as the scattered light intensity is strong enough, QELS can be used down to the nanoparticle range of a few nanometers. The mathematical representation of the time dependence of the scattered light intensity is called the autocorrelation function. For monodisperse spheres the autocorrelation function decays exponentially with a decay constant proportional to the diffusion coefficient. For a polydisperse system, the autocorrelation function is a sum of exponentials. These data can usually be deconvoluted to give some information about the size distribution.

5.7. Sizing by Acoustic Scattering and Absorption. Light is a traveling transverse wave (the oscillations are perpendicular to the direction of propagation). Sound is a traveling longitudinal wave (the oscillations are parallel to the direction of propagation.) Light scattering depends on the electric and magnetic properties of matter. Acoustic scattering depends on the mechanical and thermal properties of matter. The similarity is that both are the scattering of waves. If the scattering of light gives particle size information so does acoustic scattering, although they depend on different material properties. The advantage of light scattering is that it depends practically only on one material property, the ratio of the refractive index of the particle to that of the medium. One advantage of acoustic scattering is that data can be taken as a function of wavelength. This means that, for any particle size, the wavelength of sound can be adjusted to bring the scattering data into a range appropriate to theory. A second advantage is particle sizing can be done on concentrated dispersions so dilution is usually not necessary. A third advantage is that the dispersions and even the containers can be opaque. Acoustic particle size analysis of a flowing dispersion inside a steel pipe has been successfully demonstrated. The disadvantage of acoustic absorption is that it requires knowing many mechanical and thermal properties of particles and the medium that are hard to obtain. Povey (16) provides extensive theoretical and practical information.

5.8. Particle Charge. *In Aqueous Dispersions.* Particles dispersed in water acquire charge chiefly by the preferential adsorption of surface-active ions, usually anions, or by dissociation of surface ionogenic groups.

What is usually inferred is the electric potential caused by the charge on the particle. This potential is called the zeta potential. The most common method to measure the zeta potential is to apply an electric field and measure the velocity of the particle. When the concentration of ions in solution is low, ie, a low ionic strength, the zeta potential, ζ, is given by the Hückel equation:

$$\zeta = \frac{3\eta v}{2ED\epsilon_0} \tag{14}$$

where η is the solvent viscosity, v is the velocity of the particle, E is the magnitude of the electric field, D is the dielectric constant of the medium and ε_0 is the permittivity of free space. When the concentration of ions in solution is high, the zeta potential is given by the Smoluchowski equation:

$$\zeta = \frac{\eta v}{ED\epsilon_0} \tag{15}$$

The calculation of the surface potential for intermediate ionic strengths is provided by O'Brien and White in the form of graphs generated by a computer program (18).

Initially electrophoretic measurements were made by timing the motion of the particles while viewing them through a microscope, hence the technique was called microelectrophoresis. More recently the motion of the particles is measured by laser Doppler velocimetry and the technique is called laser Doppler microelectrophoresis.

If the particles are large, then they settle too fast to measure their electrophoretic motion. A corresponding technique is to hold the particle stationary, say by holding them in a packed bed between two porous plugs and measure the velocity of the medium when an electric field is applied. This is called electroosmosis.

Similarly, particles can be allowed to settle and the generated electric field measured. This is called the sedimentation potential. Or the particles could be held stationary and the liquid forced past them. The electric field generated is called the streaming potential. The analysis of each of these variants is similar. Once the velocity is known, either by measuring it or creating it, and the electric field is known, either by measuring it or creating it, then the zeta potential can be calculated.

Titrations of Surface Charges. The number of acid or base functional groups in a latex dispersion can be determined by potentiometric (pH) or conductiometric titration. The later is simpler and preferred. An anionic dispersion is titrated with a base, usually sodium hydroxide and back-titrated to determine the reversibility of the reaction. Cationic dispersions are titrated with acids. The end points (multiple if strong and weak acid groups are present) are determined by the inflection points in the data. The titrations are done under an inert atmosphere and at constant ionic strength.

In Nonaqueous Dispersions. Measurements of surface potentials in nonaqueous dispersions are no different that in aqueous dispersions. Care needs to be taken to avoid space charge, a charge accumulation in some part of the apparatus or sample, because it changes the electric field. For example, an accumulation of ions at an electrode can neutralize the applied electric field. Particles would not move because there was no electric field not because they were uncharged. Some of the early misunderstanding about whether dispersed particles in nonpolar solvents could have any charge was due to this error. The ease of generating space charge in low conductivity media is shown by explosions during petroleum processing and the need for grounding straps for containers of organic solvents (19).

Electroacoustic Techniques. When an ac electric field is applied to a dispersion of charged particles, the particles move in response to the field. As long as the frequency is less than ~1 MHz or so, the particle motion is in phase with the applied electric field. If the particles have a different density than the medium, the oscillatory motion of the particles creates an acoustic wave of the same frequency. The higher the charge on the particles, the faster they move, and the higher is the amplitude of the acoustic wave. The charge on the particles is calculated from the amplitude of the acoustic wave.

A similar experiment is to apply an acoustic wave to a dispersion of charged particles and measure the generated electric wave. This later experiment is called the colloid vibration potential. Both of these techniques work quite well on dispersions without having to dilute them.

If frequencies substantially >1 MHz are used, then the particles have too much inertia to stay in phase with the applied signal. The larger the particles, the more out of phase. Therefore measuring both the amplitude and the phase of the response gives information about the particle charge size simultaneously (20,21).

6. Flow of Dispersions

Quantitative information on how a dispersion flows under various conditions is useful in optimizing manufacturing steps such as coating, draining, and pumping. Rheology (from the Greek rheos, a stream) is the study of flow. A rheological test is often used as a quality control or quality assurance test in manufacturing. The effectiveness of many products depends on proper flow, eg, cosmetics, paints, and lubricants. Rheology is the tool of choice for an analysis of the interactions of components of a dispersion.

The fundamental flow equation was proposed by Newton and is a relation between the stress applied and the resulting flow:

$$\tau = \eta\dot{\gamma} \tag{16}$$

where τ is the shear stress (tangential force per unit area, Pa), $\dot{\gamma}$ is the shear rate perpendicular to the applied stress (velocity per unit distance, s^{-1}), and η is the viscosity coefficient (Pa·s). Figure 15 shows a schematic of the shear stress and corresponding shear rate for the flow of liquid between two parallel plates. The higher the viscosity coefficient, the higher the shear stress needs to be to achieve the same shear rate (flow).

The viscosity coefficient is sometimes called the internal friction because the stronger the internal structure, the higher the stress required for equivalent flow. When the concentration of particles is high or they are flocculated, the viscosity coefficient is high. Rheology is an important diagnostic tool to study the interaction between particles in a dispersion. For example, when salt is added

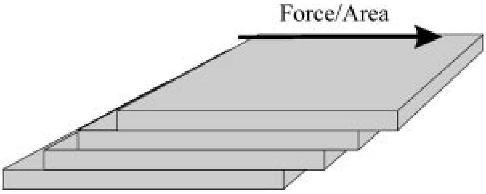

Fig. 15. The flow of a liquid between two parallel plates. A force per unit area is applied to the top plate (shear stress). The bottom plate is stationary. The velocity of the liquid flow decreases from a maximum at the top plate to zero at the bottom plate. The shear rate is the change in velocity with distance between the plates.

to an electrocratic dispersion, the particles form flocs that create an internal structure and a corresponding increase in viscosity. When the shear stress is high enough to break flocs apart, the internal structure is decreased and the viscosity coefficient drops. Rheology is used to identify useful dispersants and flocculants, their optimum concentrations, their sensitivities to other components, or sensitivity to ionic strength, temperature, or pressure.

6.1. Effect of Particle Interactions. If the viscosity coefficient is constant over all shear rates and shear stresses then the fluid is called Newtonian [Fig. 16(**c**)]. This implies that the structure of the fluid does not change with flow. Simple fluids such as organic solvents are Newtonian fluids. However, dispersions are mixtures of phases and it is rare that their internal structures remain the same no matter what the flow. The most common observation is a decreasing viscosity with increasing shear stress or shear rate [Fig. 16(**a**)]. Such a flow is called shear thinning. This decrease in viscosity implies that internal structure is being destroyed. The usual explanation is that flocs are being broken apart. If the structure has some minimum shear stress before it starts to flow, it is said to have a yield point and the flow is called plastic [Fig. 16(**b**)].

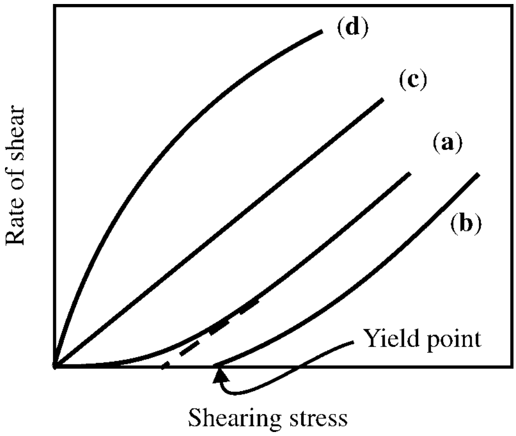

Fig. 16. Flow curves showing (**a**) a loss in structure with increasing stress, shear thinning, (**b**) a loss in structure with increasing stress after a region of no flowing below a yield point, plastic flow, (**c**) no change in internal structure with increasing stress, Newtonian flow, and (**d**) an increase in structure with increasing stress, dilatant flow.

Figure 16(**d**) shows a fourth type of rheogram, the increase in structure with flow called dilatant flow. Dilatancy is seen in well-stabilized dispersions at higher shear rates when the particles cannot flow around each other fast enough and a structure begins to form. Dispersions of needle-like particles are also dilatant when rotating needles cannot avoid each other as they are sheared.

Many empirical equations have been proposed to model non-Newtonian flow. For shear-thinning liquids, the experimental data often fit a power law:

$$\tau = k_{\mathrm{PL}}\dot{\gamma}^{1-n} \tag{17}$$

where k_{PL} is an empirical constant and n is called the flow or power-law index. The power-law index is zero for Newtonian dispersions, positive for shear thinning dispersions, and negative for dilatant dispersions. When the dispersion has an apparent yield point at low shear stresses, the data often fit a modified power-law equation:

$$\tau = \tau_0 + k_1\dot{\gamma}^{1-n} \tag{18}$$

where τ_0 is the yield point. The yield point can be thought of as the strength of whatever structure the dispersion has at rest. The power-law index is a measure of how that structure disintegrates with increasing flow. The empirical constants are useful in understanding the effects of various components on the dispersion.

6.2. Effect of Volume Fraction. A key particle parameter is its volume fraction, not its mass fraction. The variation in flow of a dispersion with volume fraction also has several useful empirical equations. Einstein showed that for a hard-sphere dispersion (no interparticle attraction) at low volume concentrations, Φ, the viscosity, η, is

$$\eta = \eta_0(1 + 2.5\Phi) \tag{19}$$

where η_0 is the medium viscosity. Deviations from this equation (ie, coefficients different than 2.5) are measures of interparticle interactions. At higher volume loadings, multiple-body interactions become important. Many empirical equations have been proposed for higher volume fractions. Most are based on the idea of a limiting volume fraction corresponding roughly to closest packing, Φ_{max}:

$$\eta = \eta_0\left(1 + \frac{2.5\Phi}{\Phi_{\mathrm{max}} - \Phi}\right) \tag{20}$$

The critical pigment volume concentration, CPVC, is the concentration of pigment just low enough that all the air is eliminated from the dispersion. At the CPVC many mechanical properties of paint systems have abrupt changes such as density, tensile strength, porosity, reflectance, and hiding power [(22), p. 172].

6.3. Effects of Polymers. Most commercially important dispersions are pigment dispersions in polymer solutions. The polymers usually have two roles, first to aid in the stabilization of the dispersion as steric surface-active solutes and second to be film formers when the formulation is dried. One polymer is often not optimum for both roles so complex formulations are developed.

The solubility of polymers is sensitive to other components, especially other polymers. The general rule is that two polymers are not both soluble. Even small molecules change the solubility of polymers since they act like a second solvent. Surface-active solutes and polymers often form complexes in solution with surprising results (23). The polymer chain can be thought of as a kind of one-dimensional surface. Surface-active solutes can solubilize polymers in the same manner that they disperse lyophobic particles.

At low polymer concentrations, particle–particle interactions can dominate the flow. If polymers are adsorbed, they can stabilize dispersions, hence lower viscosity. If the polymers adsorb simultaneously onto two particles, they are flocculants and raise viscosity.

At high polymer concentrations, the polymer solution rheology can dominate the flow. If the viscosity is high enough, especially in liquid polymers, the viscosity does not change significantly whether the particles flocculate or not.

6.4. Time-Dependent Flow. Shear thinning and dilatancy arise from structural changes in the dispersion. The loss of structure from shear thinning rebuilds as particles reflocculate, but the recovery may be slow. Built-up structure from dilatancy takes time to dissipate. A complete picture of the flow of dispersions accounts for the time structures take to form and to relax. These times can be important practically. For example, the loss of structure in paint when a brush pushes it against the wall is necessary for a smooth coating, but if the structure does not recover quickly once the brush is removed, the paint runs down the wall.

Some materials do not flow steadily after stress is applied, they merely stretch and stop. This phenomenon is called elastic flow. Rubber bands are elastic. The internal structure of a dispersion can be thought of as elastic; it changes to a new structure with stress and then relaxes to the initial structure after the stress is removed. If the relaxation time is significant, then the flow of a dispersion is both viscous and elastic and is called viscoelastic flow.

One experiment is to measure the rheogram starting at low stresses, increase the stress either to break structure (shear thinning) or to create structure (dilatancy), and then monitor the return to equilibrium by slowly decreasing the stress. Slow recovery would be detected on the rheogram by a hysteresis (Fig. 17). This slow recovery of structure is called thixotropy. Some literature incorrectly uses thixotropy as a synonym for shear thinning, but thixotropy implies a time effect. When the dispersion is dilatant, a hysteresis in the rheogram is called rheopexy.

The limitation to experiments like that shown in Figure 17 is that the experiment has to be rerun for a variety of recovery times in order to understand or predict behavior. A more systematic approach is to measure flow as a function of frequency rather than a function of time. A sinusoidal stress is applied to the dispersion and the flow measured. The amplitude of motion gives information about the viscous flow and the phase gives information about the elasticity. The analysis of viscoelasticity is simplified if the stress is small enough that the strains are linear. This is easy to do for polymers and the measurement is called linear viscoelasticity.

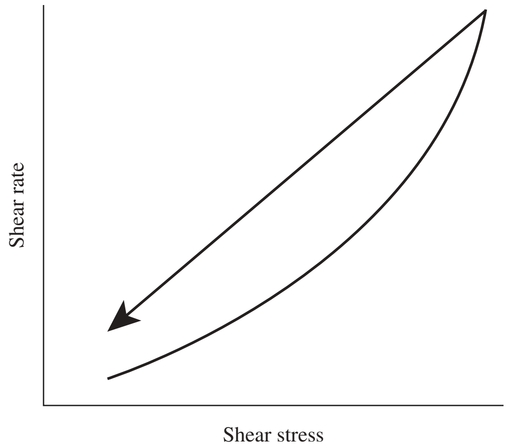

Fig. 17. Thixotropy is the slow recovery of structure of a shear-thinning dispersion as the applied stress is reduced. This hysteresis loop shows a nearly Newtonian flow after the stress is reduced, which implies that the structure broken has not reformed on the time scale of the measurement.

However, the structures in dispersions are brittle, that is, they break with only a small strain, so the experiment is difficult. A useful technique generates a small-amplitude torsional shear strain at one point in a dispersion and measures the speed of propagation of the shear wave through the dispersion (24).

7. Stability of Dispersions

Dispersed particles collide with each other frequently because of Brownian motion. If the particles stick when they collide, the dispersion is called unstable and the process is called flocculation. If the particles separate after a collision then the composition of the dispersion remains constant and the dispersion is called stable.

7.1. Stability Ratio. If particles flocculate at a rate determined by Brownian motion, the time for one-half of the particles to stick together, $t_{1/2}$, is

$$t_{1/2} = \frac{3\eta}{4kTn_0}\,W \tag{21}$$

where η is the viscosity, k the Boltzmann constant, T the absolute temperature, n_0 the number of particles per unit volume, and W the stability ratio given by

$$W = 2a \int_{2a}^{\infty} \exp\left(\frac{U}{kT}\right) \frac{dr}{r^2} \tag{22}$$

where a is the particle radius and U is the interparticle energy as a function of interparticle distance, r. When the particles repel, U is positive, W is >1, and the half-life is longer. The half-life is experimentally measured by the change in

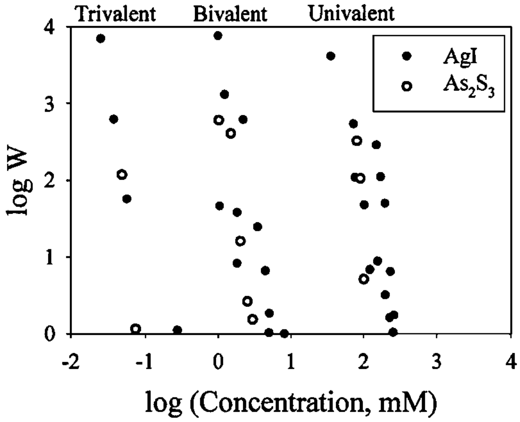

Fig. 18. Effect of electrolyte concentration on the stability ratio of various lyophobic dispersions. The three groups of lines refer to univalent, bivalent, and trivalent electrolytes (from the right) (25).

particle size. Therefore *W* can be calculated by equation (21) and *U* estimated from equation (22).

Theories for the stability of dispersions are one the most popular academic topics in colloid chemistry. An early interest was that rapid flocculation of model dispersions indicated a long-range interparticle force of unknown origin. Another interest arose from the experimental observation that the concentration of ions sufficient to flocculate a dispersion varied with the sixth power of the valency of the ions with the same sign charge as the particle, a rule now referred to as the Schulze-Hardy rule (Fig. 18).

A theoretic approach to explaining these observations was developed independently by Derjaguin and Landau in the USSR and Verwey and Overbeek in the Netherlands and is called the DLVO theory. The central idea is that interaction between two charged particles can be calculated by adding the forces of attraction to the electrostatic forces of repulsion. The forces of repulsion are principally two: electrostatic repulsion between similarly charged particles, and the steric repulsion between particles as their polymer-coated surfaces are pushed together.

Forces of Attraction. Experimental evidence gotten by measuring the stability ratio of carefully cleaned dispersions gave information about the inherent attraction particles have for each other in suspension. The first theory to explain this interaction was due to Hamaker.

Hamaker modeled the attraction between two particles as the sum of the attraction between the molecules in each particle. Molecules were known to attract each other from equations such as the van der Waals equation of state for imperfect gases. London showed that this attraction depended of the coordination of electron motion in molecules as they approach one another. The coordinated electronic motion lowered the total energy. Hamaker's final formulae have three components. First, they contain a distance dependence since the strength of molecular interactions vary with distance. Second, they contain a material-dependent term that reflects molecular properties. London showed this property is the electric polarizability of the molecule. Third, different particle shape, eg, spheres, plates, cones, etc, require different equations.

For two equal spheres of radius, a, the Hamaker equation for the free energy of interaction is

$$\Delta G^d = -\frac{A}{6}\left[\frac{2a^2}{R^2-4a^2}+\frac{2a^2}{R^2}+\ln\left(1-\frac{4a^2}{R^2}\right)\right] \tag{23}$$

where A is the Hamaker constant and R is center-to-center interparticle distance. When the distance between the particle surfaces, $H = R - 2a$, is small equation (23) has the approximate form:

$$\Delta G^d = -\frac{Aa}{12H} \tag{24}$$

The Hamaker constant for a particular particle in a particular fluid is calculated from the Hamaker constant from the particle–particle interaction through a vacuum, A_{11}, the liquid–liquid interaction A_{22}, and the interaction between the particle and the liquid, A_{12} by the following:

$$A_{121} = A_{11} + A_{22} + 2A_{12} \tag{25}$$

The values for A_{11} and A_{22} are obtained from tables [eg, (1)]. Another excellent source for Hamaker constants is to search the World Wide Web. The value for A_{12} is estimated by

$$A_{12} \simeq (A_{11}A_{22})^{1/2} \tag{26}$$

Lifshitz improved the theory by showing how to calculate the attraction between particles based on measurable optical properties rather than calculations based on molecular properties. The idea is that the optical spectrum of a particle, that is the absorption coefficient as a function of wavelength, corresponds to the resonant electron fluctuations that coordinate between particles. An application of Lifshitz theory only requires knowing the static dielectric constant, the absorption coefficient and wavelength of the strongest uv or visible absorption, and an average absorption coefficient and wavelength in the infrared (ir). Figure 19 shows the agreement between the measured force and the force calculated from Lifshitz theory for rutile particles dispersed in water. Lifshitz constants are more accurate than Hamaker constants.

Electrostatic Repulsion. The mechanisms by which a particle acquires electric charge are discussed above. The dispersion as a whole has no electric charge. The liquid contains the counterions. These counterions are mobile so they are pulled by electrostatic forces towards the oppositely charged particle surfaces. They are also subject to random thermal fluctuations of the solvent. This thermal fluctuation (also the source of Brownian motion) acts to counterbalance the diffusion of counterions to the particle surfaces. The net result is a distribution of counterions around a charged particle surface. The concentration of counterions is highest near the particle surface and decreases roughly

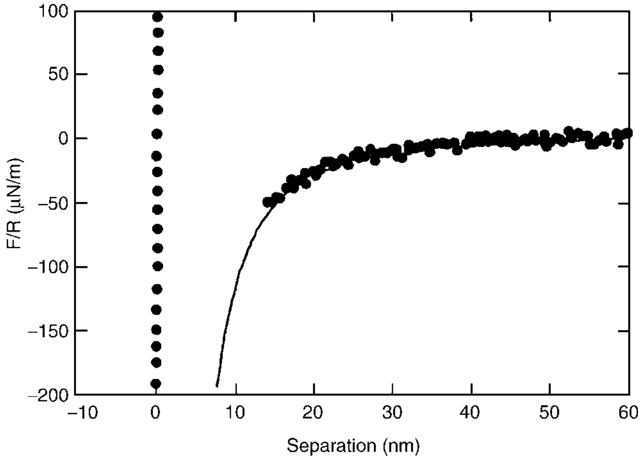

Fig. 19. Force-separation data taken at the isoelectric point of rutile on the atomic force microscope. The full curve is the theoretical interaction using Lifshitz theory (26).

exponentially away from the surface. The electric potential decays in the same manner. The exponential decay constant, κ, is given by

$$\kappa = \sqrt{\frac{4e^2}{D\epsilon_0 kT} I} \tag{27}$$

where e is the electronic charge, D the dielectric constant of the liquid, ε_0 the permittivity of free space, k the Boltzmann constant, T the absolute temperature, and I the ionic strength of the liquid. The ionic strength of the liquid is

$$I = \frac{1}{2}\sum n_{i0} z_i^2 \tag{28}$$

where n_{i0} is the concentration of the ith ion far from the particle surface and z_i is the charge on the ion. The important observation is that the decay of the electric potential away from the particle goes exponentially with the ionic strength and the ionic strength is sensitive to highly charged ions. The effect of calcium, magnesium, iron, and aluminum ions on dispersion stability is important.

The decay constant, κ, has units of inverse distance. The inverse of κ is a distance and is commonly called the Debye length or the approximate "thickness" of the electrical double layer.

When two electrically charged particles approach each other, their electrical double layers overlap. Since the double layers have the same sign charge, it requires work to push the particles closer. It is the higher potential energy that two particles have as they approach each other that helps to keep them apart. This repulsive potential energy, ΔG^r is given by

$$\Delta G^r = \frac{64 n_0 \pi a k T \gamma^2}{\kappa^2} \exp\left[-\kappa(R-2a)\right] \tag{29}$$

where γ is a function of the zeta potential, ζ:

$$\gamma = \tanh\left(\frac{ze\zeta}{4kT}\right) \tag{30}$$

An important observation about equation (29) is that the zeta potential appears only in the preexponential factor. The ionic strength appears in both the preexponential factor and the exponent, but the exponent is the dominant term. Therefore variations in ionic composition of a dispersion, which can be over several orders of magnitude, often overwhelm variations in zeta potential.

DLVO Theory. Adding the energy of attraction, equation (23), to the energy of repulsion, equation (29), gives the total energy of interaction between two charged spheres in terms of the Hamaker-Lifshitz constant, A, the particle radius a, the zeta potential, ζ, (as part of the γ term), and the ionic strength, I, (as part of the κ term), and the distance between the spheres, R:

$$\Delta G^d = \frac{64 n_0 \pi a k T \gamma^2}{\kappa^2} \exp\left[-\kappa(R-2a)\right] - \frac{A}{6}\left[\frac{2a^2}{R^2-4a^2} + \frac{2a^2}{R^2} + \ln\left(1-\frac{4a^2}{R^2}\right)\right] \tag{31}$$

Equation (31) appears daunting but actually is quite useful. Figure 20 shows the interaction between two 200-nm diameter titania particles with zeta potentials of -100 of mV at various electrolyte concentrations.

The height of the peak in the potential energy curve determines the stability of the dispersion. As long as the electrolyte concentration is less that ~3 mM, this dispersion is stable. Higher electrolyte concentrations flocculate the dispersion. The negative values of the potential energy at longer distances corresponds to a secondary minimum into which the particles can settle as a loosely held floc

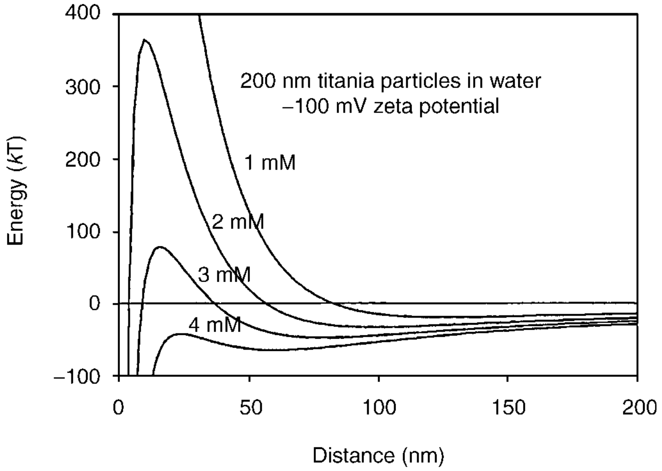

Fig. 20. Total potential energy of interaction (in units of kT) between two titania spheres in water with a Hamaker constant of 7×10^{-20} J and a surface potential of -100 mV at various concentrations of 1-1 electrolyte (1, p. 392).

structure, possibly producing a yield point if the particle concentration is high enough.

Equation (31) can be used to calculate the concentration of counterions just sufficient to eliminate any barrier to flocculation. That concentration of electrolyte is called the critical coagulation concentration, CCC. The dependence of the CCC on the magnitude of the charge on the counterions is given by

$$CCC \sim \frac{1}{z^6} \tag{32}$$

That is, the concentration of counterions necessary to flocculate a dispersion goes as the inverse sixth power of the charge on the ions. Only a very small concentration of ions with high electric charge is sufficient to flocculate a dispersion. DLVO theory explains the Schulze-Hardy rule (see Fig. 18).

DLVO theory treats the serum as a continuous material and the ions as point charges, which is only a first approximation. The first correction is to take into account the size of the ions because close to the surface their concentration is limited by their size. Similarly, the molecular nature of the medium becomes important when distances are short, especially for polymers. The details of the structures formed between solvent molecules and the particle or surface-active solutes can be important, especially in biological systems. These are called solvation or structural forces and are an area of active research.

Steric Repulsion. Steric stabilization is sometimes called polymer stabilization and in the older literature, lyocratic or lyophilic stabilization. The essential idea is that particles covered with a polymeric layer cannot approach any closer together than permitted by the interpenetration of the polymer layers. If the polymer layers are solvated, they extend some distance from the surface of the particles. Even when extended, and hence at low concentration, the polymer layers do not interpenetrate for the same reasons they are soluble in solution. Energy is required to push solvent molecules away from the polymer chains. This can also be expressed theoretically in terms of osmotic pressure. Interpenetrating polymer layers are at a higher osmotic pressure than polymers in solution so solvent diffuses in and separates the particles.

A simple, but useful, theory of polymer stabilization starts with the idea that as long as adsorbed polymer layers hold the particles far enough apart that the energy of attraction is small compared to kinetic energy, then the particles will not flocculate when they collide. This can be expressed mathematically by

$$kT > \frac{Aa}{12H} \tag{33}$$

where equation (24) has been used. If t_0 is the thickness of polymer layer on each particle, then the requirement for steric stabilization is

$$t_0 \geq \frac{aA}{24kT} \tag{34}$$

The usefulness of this expression is shown in Figure 21 where the polymer thickness required on a particle to provide steric stabilization for various dispersions as a function of particle size is shown.

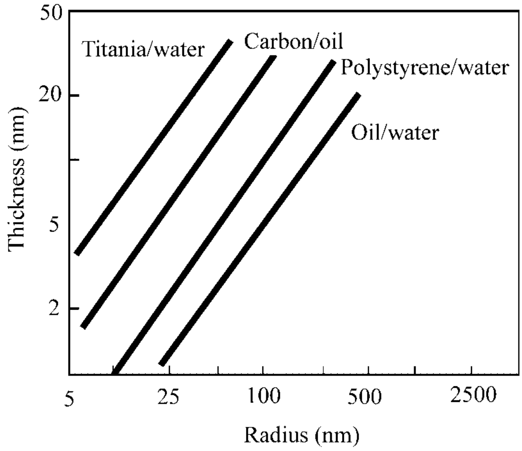

Fig. 21. Polymer thickness, t_0, on equal spherical particles to prevent flocculation at 25°C for several dispersions as a function of particle radius (1, p. 399).

The thickness of a polymer on a solid surface can be estimated by using the radius of gyration of the polymer in solution. The rationale for this is that polymers are only surface active when they are just soluble in solution. If they are too soluble, they do not adsorb. If they are too insoluble, then not enough can be dissolved in the liquid. These are theta conditions for the polymer. Calculations and measurements are available to estimate their size.

Polymer phase diagrams report the solubility ranges of polymers in different solvents as a function of temperature. The general principle is that a polymer can only be a steric stabilizer if it is soluble at that temperature, and pressure and solvent composition. If the polymer is not soluble, then particles flocculate on collision for the same reasons that polymer precipitates from solution. Therefore, sterically stabilized dispersions are only stable in the one-phase regions of the polymer phase diagram (27). An important practical consideration is to know where the critical temperatures are in relation to manufacture and use. For example, a polymer that stabilizes well at lab temperatures will not be a good stabilizer if it is used above its critical solution temperature.

Tests for Stability. The most versatile test for dispersion stability is rheology. Rheological measurements detect interparticle forces. As these forces change with time or process conditions or chemistry, the flow will change.

Sedimentation is another easy test for dispersion stability. Flocs settle faster than primary particles because they are larger. Filtration is also a possible test. A flocculated dispersion filters easily and leaves a thick filter cake. This loose sediment usually has a yield point. A stable dispersion either passes completely through the filters or clogs them with tightly packed sediment. This tightly-packed sediment is usually dilatant.

A test for flocs is to use a Hegman "fineness of grind" gauge. The dispersion is spread into a calibrated, tapered well. The top surface is examined carefully to see at what depth flocs first appear at the surface.

A particularly useful test for electrostatic stabilization is to measure the CCC, how much salt can be added to the dispersion before it flocculates. This measurement is done easily with a series of beakers, each containing the dispersion to be tested and each with a different salt concentration. Another method is to freeze and thaw a dispersion. As ice crystals form, salt and particles are forced into the remaining volume. Ultimately, just before the dispersion freezes completely, the salt concentration is high enough to flocculate the dispersion. When thawed the dispersion usually does not redisperse. To stabilize dispersions from freeze–thaw cycles, formulators often add high molecular weight polymers. These are called protective colloids because they protect particles from flocculating on freeze–thaw.

Sterically stabilized dispersions are sensitive to temperature changes since the solubility of polymers is sensitive to temperature. This finding can be used to advantage in manufacturing since flocculated dispersions are easier to purify and concentrate. The dispersions can be restabilized by a return to the initial conditions of temperature or solvent composition. If a dispersion redisperses easily after flocculating, the dispersion was at least partially sterically stabilized.

8. Model Dispersions

Dispersions in which all the particles are the same size are called monodisperse. Monodisperse dispersions are important for testing theories but also for their interesting optical and electronic properties. Monodisperse colloids have been produced by Zsigmondy (gold sols), La Mer and Dinegar (sulfur), Watillon and Dauchot (selenium), Ottewill and Woodbridge (silver halides), Matijević (metal oxides), and Vanderhoff, Ugelstad, and El-Aasser (polymers).

Charged, monodisperse dispersions, carefully prepared at low ionic strength and high volume loadings, settle into well-ordered structures. The order of these structures causes Bragg diffraction and the dispersions are brightly iridescent. The study of the phase behavior of monodisperse dispersions has been used to study theories of phase transitions (28).

CITED PUBLICATIONS

1. I. D. Morrison and S. Ross, *Colloidal Dispersions: Suspensions, emulsions, and foams*; John Wiley & Sons, Inc., New York, 2002. (a) page 120, (b) page 122, (c) page 124, (d) page 126.
2. G. Battersby in R. B. McKay, ed., *Technical Applications of Dispersions*, Marcel Dekker, New York, 1994, p. 223.
3. Th. F. Tadros, ed., *Particle/Medium Dispersions*, Academic Press, London, 1987.
4. D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, Academic Press, New York, 1983.
5. MC Publishing, Glen Rock, N.J.
6. R. F. Conley, *Practical Dispersion: A Guide to Understanding and Formulating Slurries*, VCH Publishers, New York, 1996.
7. R. D. Nelson, Jr., *Dispersing Powders in Liquids*, Elsevier, Amsterdam, The Netherlands, 1988.
8. E. Kissa, ed., *Dispersions: Characterization, Testing, and Measurement*, Marcel Dekker, New York, 1999.

9. R. A. Williams, ed., *Colloid and Surface Engineering: Applications in the Process Industries*, Butterworth Heinemann, Oxford, 1992.
10. F. K. Daniel, *J. Paint Tech.* **38**, 534 (1966) .
11. Y. A. Attia, in R. A. Williams, ed., *Colloid Science and Engineering: Applications in the Process Industries*, Butterworth Heinemann, Oxford, 1992.
12. E. K. Fischer, *Colloidal Dispersions*, John Wiley & Sons, Inc., New York, 1950.
13. C. F. Bohren, Optics, Atmospheric, in *Encyclopedia of Applied Physics*, 1995, Vol. 12, p. 405, Figure 7.
14. Z. K. Jelínek, *Particle Size Analysis*, John Wiley & Sons, Inc., New York, 1970; p. 77.
15. T. Allen, ed., *Particle Size Measurements*, 5th ed., Chapman and Hall, New York, 1997, p. 253.
16. M. J. W. Povey, *Ultrasonic Techniques for Fluids Characterization*, Academic Press, New York, 1997.
17. B. B. Weiner, W. W. Tscharnuter, and N. Karasikov, *ACS Symp. Ser.* **693**, 88 (1998).
18. R. W. O'Brien and L. R. White, *J. Chem. Soc., Faraday Trans. 2* **74**, 1607 (1978).
19. A. Klinkenberg and J. L. van der Minne, *Electrostatics in the Petroleum Industry: The Prevention of Explosion Hazards*, Elsevier, New York, 1958.
20. S. G. Malghan, ed., *Electroacoustics for Characterization of Particulates and Suspensions*, NIST Spec. Pub. 856, US Gov. Printing Office, Washington, D.C., 1993.
21. R. J. Hunter, *Colloids Surf. A, Physico. Eng. Aspects* **141**, 37 (1998).
22. T. C. Patton, *Paint Flow and Pigment Dispersion, a Rheological Approach to Coating and Ink Technology*, 2nd ed., John Wiley & Sons, Inc., New York, 1979.
23. K. Holmberg, B. Lindman, B. Jönsson, and B. Kronberg, *Surfactants and Polymers in Aqueous Solution*, 2nd ed., John Wiley & Sons, Inc., New York, 2002.
24. J. W. Goodwin, in Ref. 3, p. 217.
25. J. Th. G. Overbeek, in H. R. Kruyt, ed., *Colloid Science*, Vol. 1, Elsevier, New York, 1952, p. 320.
26. I. Larson, C. J. Drummond, and D. Y. C. Chan, *J. Am. Chem. Soc.* **115**, 11885 (1993).
27. M. D. Croucher and M. L. Hair, *Macromolecules* **11**, 874 (1978).
28. W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, Cambridge, 1989.

GENERAL REFERENCES

A. W. Adamson and A. P. Gast, *The Physics and Chemistry of Surfaces*, 6th ed., John Wiley & Sons, Inc., New York, 1997.

B. Dobiáš, X. Qiu, and W. von Rybinski, eds., *Solid–Liquid Dispersions*, Marcel Dekker, New York, 1999.

P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, 3rd ed., Marcel Dekker, New York, 1997.

S. Ross and I. D. Morrison, *Colloidal Systems and Interfaces*, John Wiley & Sons, Inc., New York, 1988.

M. Takeo, *Disperse Systems*, Wiley-VCH, New York, 1999.

JOURNALS

Advances in Colloid and Interface Science, Elsevier Science B. V., Amsterdam, The Netherlands.

Colloid and Surfaces A: Physicochemical and Engineering Aspects, Elsevier Science B. V., Amsterdam, The Netherlands.

Current Opinion in Colloid and Interface Science, Elsevier Science B. V., Amsterdam, The Netherlands.

Journal of Colloid and Interface Science, Academic Press, New York.

Journal of Dispersion Science and Technology, Marcel Dekker, New York.

Langmuir, American Chemical Society, Washington, D.C.

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