Colloids

Diffusion

Colloids are materials that display phase structures larger than those that display quantum effects (atomic and molecular) but small enough that the structures are sensitive to thermal fluctuations (smaller than 50 μm or the thickness of a hair), that is, colloids are affected by Brownian motion and are subject to diffusion. Particles that meet this definition of colloids range from about 5 Å to about 50 μm (a range of 100,000). Colloids can be broadly viewed as any material that displays phases that follow these restrictions at some point in their formation and contain small domains, thereby including aerosols, foams, solid foams, emulsions, solid emulsions and solid suspensions.

Diffusion is defined by Fick's law which describes the large-scale consequence of Brownian motion of molecules or particles. Molecules move by direct thermal motion while larger particles display Brownian motion due to collision of molecules that are subject to thermal motion with the particles which imparts kinetic energy to the particles. The net result is that the particles and molecules move randomly and spontaneously tracing out a random walk in space. A random walk has the feature that the average length of the walk squared is proportional to the number of steps or to the duration of the walk. Random walks follow the square root of time ($R = (2Dt)^{1/2}$ where D is the diffusion coefficient) compared to linear or ballistic walks which directly follow time ($R = ut$, where u is the velocity). Fick's first law describes the flux, J in mol/m^2s, of a diffusion material as a function of the concentration gradient, $d\phi/dx$, $(mol/m^3)/m$. The diffusion coefficent, D in m^2/s, is defined in Fick's First Law,

$$J = -D\frac{d\phi}{dt} \tag{1}$$

Fick's first law is an example of a constitutive equation and the diffusion constant is a constitutive parameter. That is, D describes the constitution of the diffusing system. Constitutive equations are phenomenological in that they are meant to describe a system but do not reflect any understanding of the system.

A fundamental understanding of the nature of a diffusing system based on a description of the mechanism of diffusion can lead to a functional form for the diffusion coefficient. Einstein suggested such an understanding for colloidal systems in his Fluctuation Dissipation Theorem. The Fluctuation Dissipation Theorem proposes that thermal fluctuations, such as thermal motion of colloidal particles, can be modeled by supposing that the particles are subject to a small force and that the bulk response to force such as through viscous dissipation can be directly substituted to understand phenomena such as Brownian motion and diffusion. For viscous motion of a spherical particle the force, F, that is necessary to cause a velocity, u, is given by,

$$F = \xi u \tag{2}$$

where ξ is a kind of drag coefficient for a small particle called the friction factor. For spheres, Stokes derived an expression for ξ,

$$\xi = 6\pi R_{sphere}\eta_{matrix} \tag{3},$$

where R_{sphere} is the radius of the spherical colloid and η_{matrix} is the viscosity of the fluid in which the sphere is suspended. The Stokes-Einstein Equation defines the diffusion coefficient for colloidal spherical particles,

$$D = \frac{kT}{6\pi R_{sphere}\eta_{matrix}}$$

(4).

Specific Surface Area
An alternative definition of colloids is simply materials with a large specific surface area that are dominated by interfacial properties. This naturally excludes atomic and molecular species that do not have a real surface and microscopic and larger materials that have specific surface areas smaller than about 1 m^2/g. This definition includes materials such as aerogels that are porous solids with nanoscale pores.

The specific surface area for a colloidal particle is proportional to 1/R since $S_V = S/V \sim R^2/R^3$. In practice the specific surface area is measured in m^2/g due to the experimental method used to determine this property. In the gas adsorption measurement a fixed mass of the colloid is placed in a degassing chamber on a scale for an extended period. The sample is then cooled and a small amount of gas is allowed to adsorb to the surface. The change in mass is recorded and the difference from the initial mass is used to determine the mass of a monolayer of gas on the colloid surface. This monolayer mass can be converted to area using a known conversion factor. Since the density of the colloidal material is often not known and because the bulk density is known to decrease for nanoscale particles the results are reported as surface area per mass. This can be converted to surface area per volume using the density. The size obtained in this way (6V/S = d_p) is called the Sauter mean diameter for the colloid and represents an equivalent spherical diameter for non-spherical particles.

Colloids and Polymers
Generally a somewhat arbitrary distinction is made between colloids and polymers primarily because polymers in solution (in the coil state) do not display a surface although they are of colloidal dimensions and are governed by diffusion. Polymers in the collapsed state, such as proteins in the native state, are colloidal particles. Colloid science predates polymer science by about 50 years so that much of solution state polymer science borrows heavily from colloid science.

Colloids and Chemical Engineering
Chemical engineers frequently encounter colloids in a wide range of industrial processes as well as in applied and fundamental research. Chemical engineers often deal with precipitation and separation of colloidal particles, flocculation and aggregation of particulates, aerosols and foams.