SMS-618, Particle Dynamics, Fall 2003 (E. Boss, last updated: 10/29/2003)
Aggregation Dynamics

Aggregation

Formal definitions:

- Aggregation- A collection of units or parts into a mass or whole.
- Flocculation- aggregation resulting from linking/bridging of several particles by a polymer chain.
- Coagulation- aggregation induced by electrolyte addition (e.g. due to suppression of electrostatic charge fields around clays).

Both coagulation and flocculation are used interchangeably with 'aggregation' in the oceanographic literature.
In *fresh* water electrostatic charges keep small particles from aggregating. In sewage treatment plants, the addition of a coagulating agent (Alum) reduces the electrostatic charges promoting coagulation (in rivers this is done by salts). Flocculation is enhanced by mixing, further promoting aggregation The net effect is in removal of the suspended material that would otherwise stay in suspension.

Particulate aggregation is a major process regulating particulate flux to depth, and changes in the particulate size distribution. Aggregates are also believed to provide micro-environments with physical-chemical conditions enabling processes not possible outside the aggregate (see colloid lecture). We have covered aggregation settling in the particle settling lecture.

Aggregation equation and the mathematics of aggregation.

In order for aggregation to occur particles have to be brought together and then to stick to each other. There are three dominant mechanisms by which particles in the ocean are brought together:

1. Brownian motion-random motion of particles causes them to bump into each other.
2. Fluid Shear-faster moving fluid pushes a particle against a particle close by that moves in a slower moving fluid.
3. Differential settling-faster settling particle overtake a slower settling particle.

In all cases we model the rate of collisions between particles of type i (of concentration C_i) and type j (C_j)as follows:
Rate of collision = $\beta_{ij} C_i C_i$
$[C_i, C_j] = 1/L^3$, and thus $[\beta_{ij}] = L^3/T$.
β_{ij} is called an aggregation kernel. Each mechanism for collision has a different coagulation kernel (βij). The total kernel is the sum of all.

We can simplify the computation of the kernels by neglecting the details of the flow around each other (termed 'rectilinear kernels').

In that case (see Fig. 1 for relative contribution of the different kernels):

A. $\beta_{ij,Brown}=2\pi(D_i+D_j)(K_i+K_j)$

where $K_i=k_BT/(3\pi\mu D_i)$ is the Brownian diffusion coefficient and D_i the particles' diameter.

B. $\beta_{ij,Shear}=G\,(D_i+D_j)^3/6$, where G is the shear due to the mean flow.

where G is the shear rate. When the flow is turbulent, $G=0.16(\varepsilon/\nu)^{1/2}$, where ε is the turbulent kinetic energy dissipation rate and ν the kinematic viscosity. For particles as big or bigger than the Kolmogorov scale $(\nu^3/\varepsilon)^{1/4}$, $\beta_{ij,Shear}=1.08\varepsilon^{1/3}(D_i+D_j)^{7/3}$(Hill et al., 1992).

C. $\beta_{ij,Diff.Sed.}=\pi(D_i^2+D_j^2)|w_i-w_j|/4$,

where w_i is the particle settling (rising) velocity.

In all cases, the encounter rate is equal to the product of a combined cross-sectional area ($=\pi(D_i^2+D_j^2)/4$) and a relative velocity between the particles.

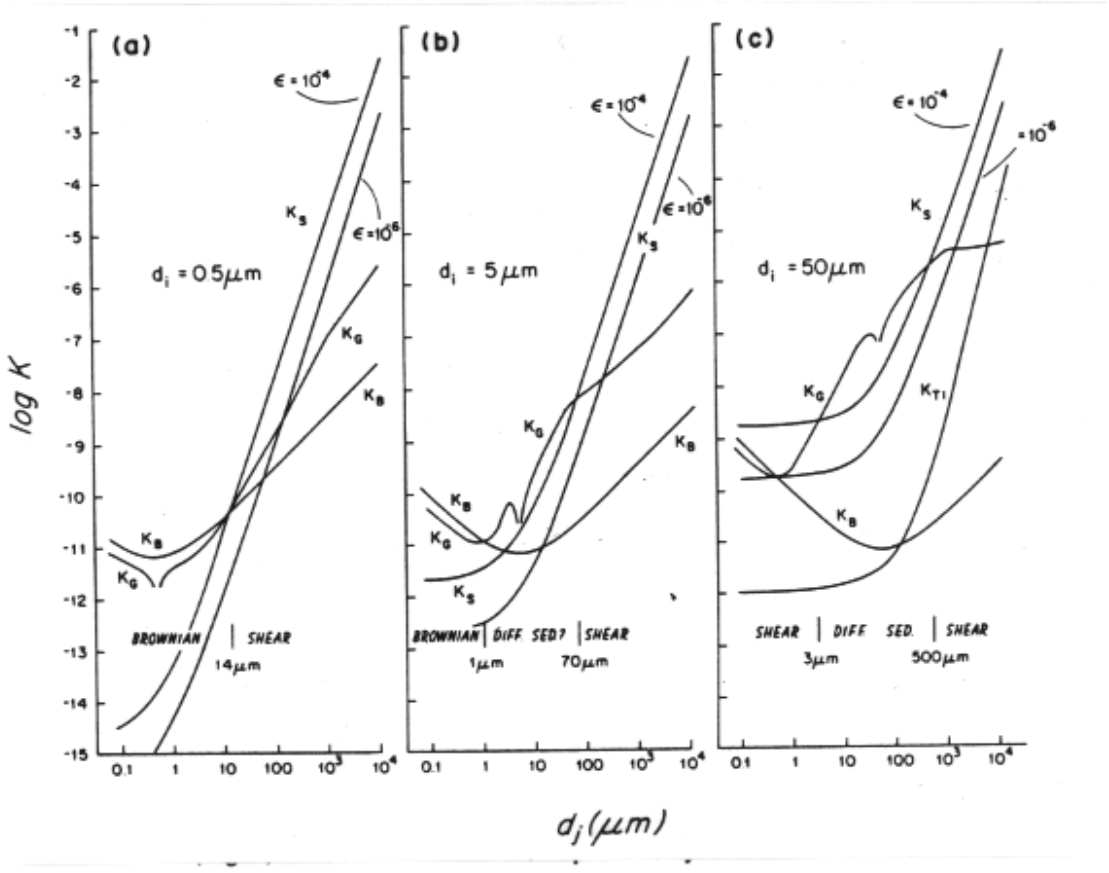

Figure 1. Coagulation kernels (βij, here denoted by K) for shear (K_S, two different ε), Brownian motion (K_B) and differential settling (K_G), for a given particle d_j interacting with a given particle d_i. From McCave (1984).

A more sophisticated formulation takes into account the changes in flow around the larger particle (termed 'curvilinear kernels'). Usually Stokes settling is assumed for differential settling. More sophisticated formulations include flow through porous spheres and fractal behavior of particles. The more accurate rates are slower than the simple approximations.

The kernel has to be multiplied by a 'stickiness' factor (or 'sticking probability), the likelihood that the particles will stay together after collision. This parameter is often denoted by α and is often assumed (due to lack of observations) not to vary with type of collision or size of particles involved. It is often used as a 'tuning' factor to match models and observations.

When particle collide they make a particle with a new mass and a new size. Keeping track of all the sizes of particles is not trivial because volume and size increase at different rates.

The differential formulation of the aggregation process reads:

$$\frac{dN(D,t)}{dt} = \frac{1}{2}\int_0^D \alpha(D_1, D-D_1)\beta(D_1, D-D_1)N(D_1,t)N(D-D_1,t)dD_1 - \int_0^\infty \alpha(D_1,D)\beta(D,D_1)N(D_1,t)N(D,t)dD_1 \quad (1)$$

N(D,t) is the differential number concentration of particles of diameter D, α denote the sticking efficiency and β is the combined coagulation kernel. The first term on the RHS is a source denoting aggregation of small particle into a larger particle of size D and the second term denote loss of material into larger size fractions. This equation is most often discretized into discrete size bins in the oceanographic literature.

Single size model—logistic equation.

Much insight into aggregation can be found through a very simple model. Suppose the smallest particle involved is a phytoplankton with a specific growth rate of μ. Assume they are within a finite well mixed container, and that the biggest size aggregate contains only two cells. The conservation equation for the single phytoplankton class reads:

$$\frac{dC}{dt} = \mu C - \alpha\beta C^2, \quad (2)$$

where β is the aggregation kernel and α the sticking efficiency. This is the famous logistic equation. It has a stable solution when $C_{attractor}=\mu/\alpha\beta$. If $C > C_{attractor}$ the process of aggregation acts to reduce *C*. If $C < C_{attractor}$, the process of growth acts to increase *C*. Thus aggregation is very sensitive to concentration. When the concentration is high it acts fast to reduce it to the point where the concentration is too low for aggregation to impact much the remaining of the non-aggregated particles. If the particles are inert (μ=0, or $C >> \mu/\alpha\beta$),

$$\frac{dC}{dt} = -\beta C^2 \rightarrow C = \frac{C_0}{1+\alpha\beta C_0 t}.$$

The result of which depends strongly on the initial concentration. The concentration is decreased to half when $t=1/\alpha\beta C_0$. However, after twice that time, at $t=2/\alpha\beta C_0$, it decreases by only another 1/6 of the original concentration (1/3 of what it was at $t=1/\alpha\beta C_0$).

The model above (2) can easily be modified to include settling in a mixed-layer (of depth h_{ml}) by setting with $\mu_{effective}=\mu-w_s/h_{ml}$, in the above analysis. A steady state exists only when $\mu>w_s/h_{ml}$, i.e. there is more growth then settling loss.

'Equilibrium' particulate size distributions and aggregation.

Under some restrictive dynamics the particle size distribution (PSD) can be shown to reflect the dominating coagulation mechanism. Hunt (1982) demonstrates that if

1. The PSD is in a dynamic steady state (equilibrium) where small particles are constantly supplied into a size bin and constantly removed on the large end by settling. Thus for each size interval there is a balance between flux of material in and out.
2. Only one coagulation mechanism is dominant at a given particle size. We consider interaction that occur only with particles of similar size, regions (in size domain) exist where only one coagulation mechanism dominate (e.g. Brownian motion for submicron particles, shear coagulation for 2-10μm and differential settling for particles bigger than 50μm, see Figure 1).
3. Efficiency of particle sticking (α) is independent of size.
4. Each coagulation mechanism can be represented by a single parameter:
   Browinian: $K=k_BT/\mu$ $[L^3T^{-1}]$
   Shear: G $[L^3D^{-3}T^{-1}]$
   Differential sedimentation: $S=g(\rho_p-\rho_{fluid})/\mu$ $[L^3D^{-4}T^{-1}]$

The volume flux through each size class is denoted by E $[D^3L^{-3}T^{-1}]$, where D is the particles characteristic size, L the fluid length scale and T the fluid time scale.

The PSD has the functional form $N=N(D,E,K,G,S)$ $[L^{-4}]$.
By dimensional analysis we find:
Browinian: $N(D)=A(E/K)^{1/2}D^{-2.5}$
Shear: $N(D)=A(E/G)^{1/2}D^{-4}$
Differential sedimentation: $N(D)=A(E/S)^{1/2}D^{-4.5}$

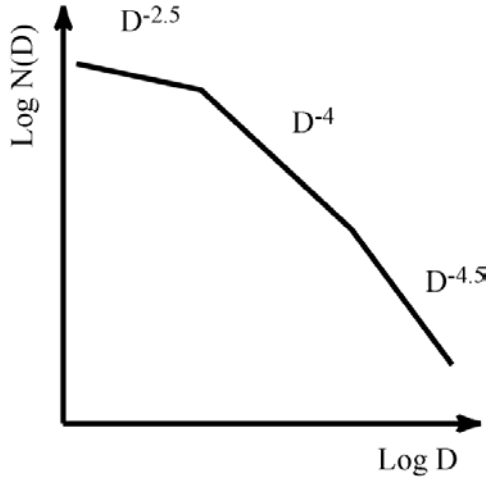

Figure 2. Illustration of the equilibrium spectra at different size range. After George Jackson's lectures on modeling coagulation in the oceans http://oceanography.tamu.edu/%7Eecomodel/People/George/george.html

Diffusion limited vs. encounter limited aggregation.

Two mechanisms can reduce aggregation:

a. Reduction in the efficiency of sticking, α.
b. Reduction in the encounter rate.

When α is limiting, particles have to encounter several time before forming an aggregate. The observed aggregate in this case are more condensed (higher fractal dimension). In encounter limited aggregation, particles stick upon encounter forming very porous aggregates (low fractal dimension).

Disaggregation:

Aggregates are believed to disaggregate when shear levels exert forces that are stronger than the forces holding the aggregate together. Those shear forces/stresses may be due to either sinking in a calm environment or turbulent shear within the water.
The diameter of the smallest turbulent eddies is regulated by the Kolmogorov microscale: $d = 2\pi(\nu^3/\varepsilon)^{1/4}$, where ε is the energy dissipation rate and ν the kinematic viscosity. Aggregates that are bigger than this scale will be sheared between several eddies potentially breaking up, while those smaller can maintain their shape.
Hill and McCave, 2001, point to the uniformity in sinking speeds of large aggregate (~1mm/sec) as indicative that in most cases it is shearing associated with sinking that regulates aggregate size. At these velocities the Re number of aggregates is O(1). Large aggregates are often seen to have tear-drop shapes suggesting that hydrodynamic control of their shape is occurring.
For $Re \ll 1$ the drag force (F_D) exerted on the aggregate is proportional to U_{sink}. For $Re \gg 1$ the drag force is proportional to U_{sink}^2. Thus, the higher the Re number (either by increasing U_{sink} or the diameter, D), the higher the drag force increase as function of U_{sink}. The torque on the aggregate is proportional to $D*F_D$ increasing (nonlinearly) with size and sinking speed.
Two type of dissagregation process are:

1. Floc erosion—small particles are removed from larger flocs.
2. Floc splitting—breakup of flocs into roughly equal sized daughter fragments.

Hill (1996) present evidence that splitting dominates the breakup of flocs, and that flocs smaller than O(100μm) are not subject to significant breakage. The formulation of disaggregation is presented and discussed in Hill and Newell (1995) and Hill (1996).
See: http://tnweb.tn.utwente.nl/vlfre/PROJECTS/prtolpekin.html for a project on aggregation and disaggregation of colloids by shear.

Issues with the terms in the equations and their application to 'real life'.

Some limitation of the aggregation model:

1. The assumption of a single monomer from which all aggregates are composed.
2. A single fractal dimension characterizing all aggregates.

3. Limited knowledge of the sticking efficiency value and its dependence on size and coagulation mechanism (values observed vary from 0.001 to 1, Alldredge et al., 1990).
4. Limited of understanding of aggregate's breakup.
5. Limited understanding of aggregate sinking dynamics.

References:

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Appendix: Fractals

Aggregates are fractals. This means that their mass (m_F) relates to their size (d_F) with an exponent that is smaller than 3:

$$m_F \propto d_F^{D3}, \quad D3<3.$$

The fractal dimension is measured by plotting the mass of aggregates of similar composition as function of size. The excess density of the fractals (needed to calculate the buoyancy force) can be computed from above as:

$$\rho_F - \rho_{fluid} = (\rho_r - \rho_{fluid})\{d_F/d_r\}^{(D3-3)}$$

where ρ_r and d_r denote, respectively, the density and diameter of the building block of the aggregate. Since D3<D, the density of aggregates decreases with size.