

Colloidal Suspension Rheology

Chapter 1 Study Questions

1. What forces act on a single colloidal particle suspended in a flowing fluid? Discuss the dependence of these forces on particle radius .
2. What are the interaction forces between particles in a solvent? What parameters affect their strength?
3. Discuss the range of the interparticle surface forces?
4. Explain what is meant by kinetic stability with regard to colloidal dispersions.
5. You are trying to flocculate a colloidal dispersion in a plant-size operation at 500 K using calcium oxide (CaO). In your laboratory, all you have available at the moment is sodium chloride (NaCl). At room temperature, you find that 2 mol/L NaCl is necessary to flocculate the colloidal dispersion. Estimate the concentration of CaO necessary to flocculate the dispersion in your plant operation.
6. What is the difference between the behavior of power law fluids and Bingham bodies at low stress levels?
7. What is the signature of the relaxation time for Maxwellian fluids in stress relaxation and in oscillatory experiments?
8. With regard to oscillatory shear experiments, explain the relative evolution of stress and strain curves as a function of time for (a) perfectly elastic materials, (b) perfectly inelastic (viscous) materials and (c) viscoelastic materials.
9. What is the role of a polymer in colloidal dispersion stability for
 - a) Grafted or adsorbed polymer
 - b) Dissolved, non-adsorbed polymer?
10. Discuss the characteristics of hard sphere suspension and difficulties in realizing this experimentally.
11. Define the dimensionless groups: De (Deborah number); Wi (Weissenberg number); Pe (Péclet number)
12. Why are colloidal particles defined by size limitations from nanometers to micrometers?
13. Explain the pseudo-continuum approach for calculating shear stresses and rates. What are the requirements needed to use this approach?

Chaper 1 Solutions

1. A colloidal particle under shear flow is subjected to 3 forces, which depend in different ways on particle radius as given below:

Friction force (hydrodynamics force)

$$F^h = 6\pi\eta_m aV \quad (1.2)$$

Brownian force

$$F^B \approx \frac{k_B T}{a} \quad (1.3)$$

Gravity

$$F^g = \Delta\rho V_p g = (\rho_p - \rho_m) \frac{4}{3} \pi a^3 g \quad (1.6)$$

2. We can distinguish three types of particle interaction forces:

- Dispersion forces: they are attractive forces that induce aggregation of the particles. Governing factors are: the materials comprising particles and suspending medium, particle size and shape, and the separation distance between particles.
- Surface forces: a) electrostatic forces, b) steric repulsion from grafted polymer, c) attraction from dissolved polymer (depletion force), d) effect of adsorbed polymer (bridging and steric repulsion)
 - a) Electrostatic force: generally repulsive, stabilizes the system; factors: solvent properties (ionic strength (ion valence, electrolyte concentration), pH, dielectric constant); particle properties (, surface charge density, acid-base chemistry of charge groups, adsorption capacity of the surface, shape, size, surface roughness)
 - b) Steric repulsion force from grafted polymer: repulsive, stabilizes the system; factors: quality of the solvent, grafting density and molecular weight and persistence length of polymer.
 - c) Depletion force: attractive, destabilizes the system; factors: polymer concentration, molecular weight, solvent quality
 - d) Effect of adsorbed polymer: its behavior depends on the surface coverage. For very small surface coverages flocculation by bridging might occur. At sufficiently large surface coverages steric repulsion becomes possible, similar to that for grafted polymers. An excess of polymer results in free polymer that can induce depletion flocculation.
- Hydrodynamic forces: the relative motion of particles is opposed by frictional forces caused by the viscosity of the intermediate liquid layer. The effect depends on the viscosity of the suspending fluid, the size, shape and relative position of the particles, as well as their relative velocity.

3. The range of electrostatic forces is governed by the Debye length, which is uniquely determined by the properties of the suspending medium - specifically: ionic strength (valence and concentration of the ions) and the dielectric constant. For stretched, end-grafted polymers the range of repulsion is controlled by the molecular weight and persistence length of the polymer. In case of depletion, it is the radius of gyration of the polymer that governs the range.
4. Kinetic stability or “colloidal stability” means that, given sufficient time, thermal fluctuations as well as stresses caused by flow will provide sufficient energy to overcome the energy barrier that prevents aggregation and will lead to a loss of stability. This is in contrast to thermodynamic stability, which is not time dependent. the particles to
5. According to eq. 1.13 the critical flocculation concentration n_{cfc} is proportional to T^2 and to the valence z as z^6 . Hence:

$$\frac{(n_{cfc})_{plant}}{(n_{cfc})_{lab}} = \left(\frac{T_{plant}}{T_{lab}} \right)^2 \left(\frac{z_{lab}}{z_{plant}} \right)^6$$

$$(n_{cfc})_{plant} = 2 \text{ mol} / L \left(\frac{500K}{298K} \right)^2 \left(\frac{1}{2} \right)^6 = 0.0880 \text{ mol} / L$$

6. When the shear stress tends to zero for a power law fluid the viscosity tends to infinity, but at each finite value of the shear stress there will be a non-zero shear rate. In materials with a yield stress, such as the Bingham body, the shear rate remains zero until a finite value of the stress, the yield stress, is reached.
7. In linear stress relaxation experiments (stress evolution after a sudden application of a sufficiently small strain) on Maxwellian fluids the stress decays exponentially in time. The relaxation time is the characteristic time of this exponential. In oscillatory experiments the storage and loss moduli become equal at the frequency $1/\tau$.
8. a) Perfectly elastic materials will have their stress and strain curves in phase with one another.
b) For perfectly viscous materials the stress should be in phase with the strain rate. As the strain rate is the derivative of the strain, it is in sinusoidal motions shifted by 90 degrees with respect to the strain. Hence the same applies to the stress.
c) Viscoelastic materials will exhibit an oscillatory stress with a phase shift between 0 and 90 degrees. The stress components in phase with the strain yield the elastic modulus, while those shifted by 90 degrees yield the viscous modulus.

9.
 - a. Grafted or adsorbed polymer: The dispersion can be stabilized by steric repulsion due to grafted/adsorbed polymer. With sufficient graft density and molecular weight, the steric repulsion can prevent particles from aggregating. However, if the adsorbed amount is not sufficient, it can cause aggregation by bridging flocculation.
 - b. Dissolved/ non-adsorbed polymer: Dissolved, non-adsorbed polymer can induce an attraction between particles via the depletion force. This potential arises from the exclusion of polymers from the region between the particles when they are in close approach. The potential is proportional to the osmotic pressure of the polymer in solution and to the volume of the region between the particles from which polymer is excluded. It depends on the concentration of polymer in solution relative to the overlap concentration and on the radius of gyration of the polymer.
10. In hard sphere suspensions the only interparticle interactions are excluded-volume interactions. The interaction potential is either zero when there is no contact between particles, or infinite when the particles are in contact. As a result, monodisperse Brownian hard sphere dispersions do not exhibit the usual gas-liquid-solid phase transitions that are typical for simple liquids. For the same reason they are also considered to be thermodynamically athermal: the phase diagram is independent of temperature. In reality, dispersion forces will always be present, meaning that a true hard sphere potential will never be realized. Even if dispersion forces are minimized, perfect spherical geometries are rarely attained. Additionally, the surface structure of the particle will be important, as it is unlikely that the surface morphology is smooth as expected for a hard sphere particle.
11.
 - a. $De = \tau / t$: where τ refers to the stress relaxation time, and t refers to the characteristic time of the flow. The Deborah number can be generally defined as the ratio of a characteristic relaxation time of the fluid (τ) to a characteristic time of the flow. It thus indicates the relative importance of elastic phenomena. At lower Deborah numbers, the material behaves in a more fluid-like manner, with an associated Newtonian viscous flow. At higher Deborah numbers, the material behavior changes to a non-Newtonian regime, increasingly dominated by elasticity, demonstrating solid-like behavior
 - b. $Wi = \gamma\dot{\lambda}$: Weissenberg number is the product of a characteristic time of the fluid and the shear rate. For shear flow, it is equivalent to the De number.

- c. $Pe = \dot{\gamma} / (D_o / a^2)$: is the ratio of the timescale for Brownian motion to the timescale for shear flow. This sets the importance of the flow relative to the ability of Brownian motion to maintain/restore the equilibrium microstructure.
12. The size limitations help validate the assumptions used in colloid science. The smaller size limit ensures that the mass of the particle is significantly larger than the molecules comprising the suspending fluid. This validates the assumption that the suspending medium can be considered a continuum. The larger size limit ensures that thermal forces are still significant in determining the motion of the colloidal particle and that gravitational settling will not remove particles from the dispersion.
13. The pseudo-continuum approach assumes that the colloidal system is actually homogenous on the length scale of observation, i.e. the heterogeneous nature of the sample is ignored. The shear stresses and shear rates are calculated from the force and velocity on the plates in the same manner as a homogenous fluid. By assuming constant average values for stress and shear rate, the heterogeneous sample is theoretically replaced with a pseudo-continuum. In order to use this approach, the dynamic and kinetic parameters need to be averaged over a sufficiently large statistical sample of the suspension. The dimensions of the heterogeneities (i.e. the particles or their aggregates) must be significantly smaller than the size of the material. Additionally, if the shear rate varies significantly with position on this length scale, no statistical average can be made and the approach cannot be used.