Chapter 4 Study Questions

1. Describe the different electroviscous effects by which the presence of electrostatic charge on the particle surface affects the suspension viscosity.
2. What is the physical meaning of the separation length in charge-stabilized suspensions?
3. How do electrostatic interparticle forces affect the zero shear viscosity and shear thinning?
4. How does the ionic strength of the suspending medium affect the yield stress of an electrostatically stabilized suspension?
5. Why is the limiting high frequency viscosity insensitive to the salt concentration.
6. Compare the effects of electrostatic and steric stabilization for dilute and concentrated suspensions.
7. Compare the viscoelastic behavior of electrostatically and sterically stabilized suspensions.

Chapter 4 Answers

1. Three different electroviscous effects can be distinguished. The primary electroviscous effect is the result of ions fluid motion during around a particle being convected by the fluid motion during flow. This will distort the distribution of ions in the double layer which in turn gives rise to electric stresses. Consequently, energy dissipation and viscosity will increase. As no particle interaction is required, this effect can occur in dilute systems. As suspensions become more concentrated, secondary electroviscous effects become important. Like-charged particles in close proximity to one another will repel each other, keeping larger distances between particles and pushing each other across streamlines. This effect can significantly increase the viscosity of the suspension. Finally, tertiary electroviscous effects occur in suspensions where polyelectrolytes are grafted or adsorbed onto particle surfaces. Here the interparticle repulsion is a combination of electrostatic and steric effects, which are coupled as the molecular configuration of the polyelectrolyte, and hence its steric effects, are determined by the electrostatic ones.

2. Electrostatic forces between like-charged particles are repulsive and tend to push particles further apart than would be the case in Brownian hard sphere systems. The balance between the potential of the electrostatic forces and Brownian energy k_BT will determine the interparticle distances and hence $g(r)$. The distance from the particle surface where the two energies become equal is the separation length L. It becomes then difficult for particles to penetrate to smaller interparticle distances and L determines the nearest neighbor location. This distance is closely related to the Debye screening length and can be calculated from the solution properties (eqn. 4.6).

3. Electrostatic repulsion between like-charged particles means that there is additional volume around the hard sphere core particle where a second particle cannot be located. This is determined by the separation length L. It creates essentially an effective hard sphere radius and effective volume fraction that are greater than those of the hard particle itself and accordingly, increases the zero shear viscosity. This effective volume fraction can be estimated using this length (eqn. 4.9). As for Brownian forces, the relative importance of electrostatic interparticle forces relative to the shear forces decreases as the strength of the flow increases, explaining the shear thinning of such systems. A cross-type of model (eqn. 4.12) can be used to model the shear thinning viscosity. Note that the high shear viscosity is, in general, insensitive to the presence of the electrostatic repulsion so shear thinning can be more extreme for charge-stabilized dispersions.

4. The yield stress refers to the minimum stress level that must be applied for a suspension to flow (see Section 9.4.2). For electrostatically stabilized systems the repulsive interparticle forces create a larger effective volume fraction that increases with the charge or decreasing ionic strength. Thus, charge-stabilized dispersions can crystallize at much lower volume fractions than hard spheres. The screened volume around the particles, as characterized by the Debye screening length κ^{-1}, decreases with increasing ionic strength, resulting in a lower effective volume fraction and hence, yield stress. Increasing

the ionic strength will melt the crystal (or glass) and adding too much salt can destabilize the suspension, which will then affect the yield stress differently (see Chapter 6).

5. As is the case for Brownian hard spheres, the limiting high frequency viscosity reflects the purely hydrodynamic stresses, which are not directly affected by the electrostatic repulsion forces. There will be a small effect of the electrostatic forces altering the pair distribution function, but this effect is generally small concerning the high frequency viscosity.

6. In dilute suspensions, flow distorts the distribution of ions around, and as a result electric stresses arise which increases the viscosity. This effect (the primary electroviscous effect) is, however, small and the intrinsic viscosity is therefore close to that of hard spheres. In contrast, suspensions that are sterically stabilized can show a more substantial increase in suspension viscosity: the suspending medium does not easily flow through the polymer stabilized layer, resulting in an increase in apparent particle volume, and an increase in viscosity. In concentrated suspensions both types of stabilization cause an effective increase in volume fraction as compared to Brownian hard spheres. Differences arise from the dense brush in sterically stabilized systems. It causes a steeper and more short range repulsion, in contrast with the longer tail of electrostatic interparticle potentials. The softer potential will make that the similarity with hard spheres (i.e. mapping by effective volume fraction) deviate earlier for case of electrostatic stabilization, although deviations will also happen for sterically stabilized ones with relatively thick brushes. The shorter range of the repulsion, requiring overlap of the brushes, results in a higher maximum packing fraction for the zero shear viscosity, when expressed in core volume fraction, than would normally be the case for electrostatic stabilization. Finally, in the limit of high shear rates (no shear thickening), the electrostatic effects are negligible, whereas the brush still affects the hydrodynamic interactions by increasing the excluded volume.

7. Both types of forces will dramatically increase the viscoelasticity relative to hard spheres for concentrated dispersions. Potential repulsion forces are elastic interparticle forces that can contribute substantially to the dynamic moduli once the potentials of neighboring particles overlap. A high frequency limiting moduli will depend strongly on the range and strength of the electrostatic forces. Because of the long range electrostatic potentials the "concentrated" suspension behavior and solid-like behavior (yield stresses) can be reached often at lower core volume fractions than for sterically stabilized systems. However, the limiting high frequency viscosity is close to that of Brownian hard spheres at the same core volume fraction. In a sterically stabilized suspension the brushes should be overlapping to crease a measurable plateau modulus, which also causes higher values of the limiting high frequency viscosity. In both cases the dynamic moduli should resemble those of a modified Maxwell fluid (see section 1.2), with a characteristic peak in G''. However, because of the much larger high frequency viscosities the drop in G'' might largely disappear under the G''-ω curve of the high frequency regime for sterically stabilized suspensions. In comparing the two types of stabilizing forces, the high

frequency modulus of the sterically stabilized suspensions in general increases much more rapidly with concentration than that for electrostatically stabilized suspensions.