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Colloidal interactions obtained from total
internal reflection microscopy measurements
and scattering data

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Abstract

The scattering of radiation can be used to extract information about the interactions between colloidal ($10^{-7} - 10^{-3}$ cm radius) particles suspended in liquids. As colloidal interactions incorporate entropic effects they are weak and while system specific they are governed by a number of general mechanisms. Colloidal interactions can be studied to some extent by direct measurements or more indirectly by inferring information from measurements of some property of the system.

In this thesis the principal experimental technique has been total internal reflection microscopy (TIRM), which is a very sensitive scattering technique. It allows for measurements of interaction energies between a single colloidal sphere and a flat surface in the area of 10^{-21} Joules. TIRM has been applied to show that high concentrations of non-ionic surfactant, often used at low concentrations to sterically stabilize colloidal particles, can cause particles to become physically attached by some bridging structure between the surface and particle. Another common stabilization mechanism widely used in colloidal systems is charge stabilization, whereby dissociated surface charges result in repulsion between particles and surfaces at low concentrations of electrolyte. Using TIRM a wide range of electrolytes and ionic strengths have been investigated, showing that the range of repulsion is given by the so-called Debye length for almost all situations that can be studied by TIRM. The exception is shown to be higher concentrations of 2:2 electrolytes, like MgSO_4 and ZnSO_4 , in which repulsions are longer-ranged than expected.

At high electrolyte concentrations attractive van der Waals interactions become important. When the interaction involves surfaces or particles of two different materials with a solvent with properties in-between those of the two materials, it is possible that the van der Waals interaction can become repulsive. Some support for this occurring in polar solvent mixtures under special conditions has been obtained by TIRM.

Small colloidal particles can be used to induce effective interactions between larger particles and surfaces. A widely studied mechanism is depletion, which results from the imbalance in osmotic pressure when two surfaces come close enough together to exclude the small "depletant" spheres from the gap in between. TIRM was used to study the effect of concentration of charged depletant spheres and electrolyte on the depletion-like structural interactions between a large colloidal sphere and a flat surface. At high depletant concentrations an attraction is observed followed by a repulsive barrier as a function of separation distance, which is modeled using integral equation theory. Integral equation theory has also been used in modeling the interactions between oil-swollen surfactant micelles, so-called microemulsion droplets, based on non-ionic surfactant in water. Small-angle X-ray scattering data for a range of droplet concentrations were shown to be well described by a model based on an effective hard-sphere interaction, i.e. a short-ranged highly repulsive interaction, which is an example of an indirect method of obtaining information on colloidal interactions.

Keywords: Total internal reflection microscopy, colloidal stability, van der Waals interaction, Debye length, surfactants, depletion, scattering