

# Colloid based crystalline and amorphous structures

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**Abstract.** These notes are intended to summarise the content of a talk given by the author at the conference "From Physical Understanding to Novel Architectures of Fuel Cells" (21–25 May 2007, Trieste, Italy). A few basic concepts of colloidal science and the simple DLVO theory are introduced in order to provide the reader with a crude understanding of colloidal interactions. Without going into numerical details, this insight leads directly to a generic phase diagram of colloids in terms of which processes of structure formation can be illustrated. A few real examples of synthesised colloid based crystalline and amorphous structures will be shown in the presentation. The highlight will be a recently fabricated porous amorphous structure designed for the application in fuel cell electrodes. It is the authors intention not to give detailed explanations on recent improvements in colloidal science but to qualitatively illustrate how principles of colloidal science can be applied in the development of, e.g., novel fuel cell architectures.

## 1. Definition of terms

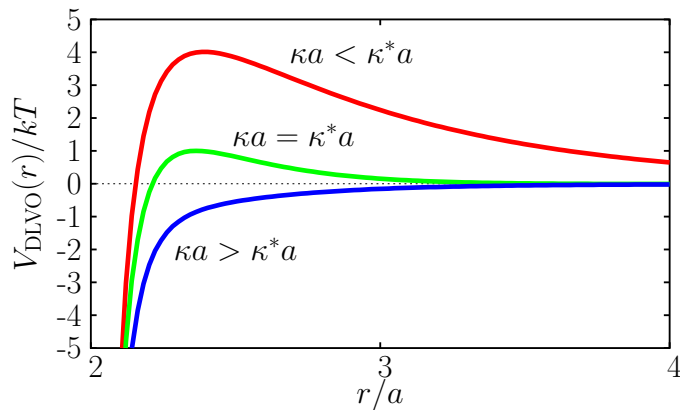
Colloid science [1] as a discipline of chemistry, to which also physicists, geologists, and agronomists contributed, exists for more than a century now. Hence it is understandable that definitions within colloidal science have been changing with time and that there is not always common agreement upon terms. Here some basic definitions are given as they will be used in the following; however, the reader should not assume that other colloid scientists use the same definitions.

*Colloidal particles* are defined as entities of size  $1\text{nm} - 1\mu\text{m}$  which are dissolved in a molecular solvent [1]. Neither do colloidal particles need to be solid nor is the molecular solvent necessarily a liquid: The colloidal particles of emulsions, e.g., milk, are liquid droplets, and the solvent of an aerosol, e.g., smoke, is a gas [1]. Colloidal particles should, according to the above definition, be considered as single units which are to be distinguished from the molecular solvent. The lower bound of their size implies that colloidal particles are sufficiently *large* such that colloidal *length* and *time scales* are well *separated* from molecular length and time scales. This property offers the possibility of a coarse grained description which takes only the colloidal degrees of freedom, e.g., position and orientation, explicitly into account. The upper bound of the size is not sharply defined as it represents the property that the colloidal particles are sufficiently *small* such that *Brownian motion* is relevant. Several examples of colloidal particles of spherical [2, 3, 4], rodlike [5, 6, 7], platelike [8, 9, 10], and cubic [11, 12, 13] shape will be shown in the presentation.

Traditionally the system comprising colloidal particles and the molecular solvent is termed a *colloid*. Note that scientists (including me) sometimes use the word "colloid" as an abbreviation for "colloidal particle". However, in this contribution the terms *colloid* and *colloidal particle* should be distinguished. If the *gravitational length*  $\frac{kT}{|\Delta m|g}$ , where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\Delta m$  is the buoyancy mass of a colloidal particle with respect to the solvent, and  $g$  is the acceleration due to gravity, is large as compared to the system size, the colloidal particles will be distributed almost homogeneously due to Brownian motion. In this case the colloid is termed *colloidal dispersion*. In contrast, if the gravitational length is not large as compared to the system size, the colloidal particles will sediment either to the bottom ( $\Delta m > 0$ ) or to the top ( $\Delta m < 0$ ) of the vessel. Then the colloid is called *colloidal suspension*.

## 2. Colloidal interactions

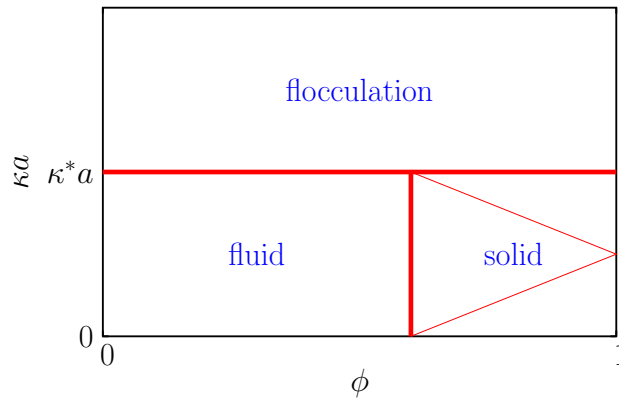
In order to understand the properties of colloids it is necessary to consider the interactions between the constituting particles. Within a coarse grained description one may formulate effective interactions between colloidal particles only. The solvent properties are thereby accounted for by parameters such as the Hamaker constant, the effective charge, the Debye length, or the hydrodynamic radius of the colloidal particle [14, 1]. The precise description of effective colloidal interactions is an important topic



**Figure 1.** Colloidal interaction potential within DLVO theory  $V_{\text{DLVO}}$  as a function of the distance  $r$  between two spherical colloidal particles of radii  $a$ . The curves correspond to different values for the Debye length  $\kappa^{-1}$ . Small values of  $\kappa a$  lead to a high potential barrier which prevents colloidal particles from getting trapped in the global potential minimum at contact ( $r = 2a$ ). In contrast, for large values of  $\kappa a$  the barrier is too small or vanishes and the colloidal particles aggregate practically irreversibly. Some critical intermediate value  $\kappa a = \kappa^* a$  corresponds to the boundary between both regimes.

in the theory of colloids. However, here it is not intended to cover recent progress within these investigations but to show how knowledge of colloidal interactions lead to information on the phase behaviour which in turn suggest, e.g., methods to fabricate crystalline or amorphous structures.

Consider the traditional DLVO theory of colloidal interaction as an example [15, 1]. It describes colloidal interactions between spherical colloidal particles on the basis of three contributions: the hard-core interaction which prevents the colloidal particles from overlapping, the attractive London-van der Waals interaction, and the repulsive screened Coulomb interaction due to electrical charges on the surfaces of the colloidal particles. Figure 1 displays the colloidal interaction potential within DLVO theory  $V_{\text{DLVO}}$  as a function of the distance  $r$  between two spherical colloidal particles of radii  $a$ . The colloidal interaction potential depends on various control parameters from which the Debye length  $\kappa^{-1}$  has been chosen as an example.  $\kappa^2$  is proportional to the ionic strength within the molecular solvent. Hence one can readily tune  $V_{\text{DLVO}}$  by varying the salinity. Small values of  $\kappa a$ , i.e., low salt concentration, lead to a high potential barrier which prevents colloidal particles from coming close enough by means of Brownian motion to getting trapped in the global potential minimum at contact ( $r = 2a$ ). However, if  $\kappa a$ , i.e., the salt concentration, is too large the barrier is too small or it vanishes completely. Under these conditions the colloidal particles *flocculate* practically irreversibly by forming aggregates. The two regimes are separated from one another by some critical intermediate value  $\kappa a = \kappa^* a$  for which the barrier height compares to the excitation energy a colloidal particle typically gains due to Brownian fluctuations.



**Figure 2.** Generic phase diagram of spherical colloidal particles within DLVO theory. For sufficiently large values of  $\kappa a$  flocculation of the colloid occurs. For small values of  $\kappa a$  the colloidal particles at small packing fraction  $\phi$  form a fluid whereas the colloid is a crystal or an amorphous solid at large packing fraction.

There are examples of real colloids which are well described by DLVO — some even quantitatively. However, other colloids do not fit into the framework because, e.g., the flocculation for these systems is reversible upon decreasing the salinity. For such instances extensions of the original DLVO theory have been proposed in the past. Here the illustrative DLVO theory is assumed to be at least qualitatively valid. Recalling the fact that fluids of hard spheres undergo a fluid-solid phase transition at a sufficiently large packing fraction  $\phi$  one expects a colloidal phase diagram which is generically of the form of Fig. 2. For sufficiently large values of  $\kappa a$  flocculation of the colloid occurs where the flocs are usually of amorphous, fractal structure. For small values of  $\kappa a$  the colloidal particles at small packing fraction  $\phi$  form a fluid structure which in some cases reveals as a gel. For large packing fractions solid structures, including colloidal crystals and amorphous solids such as glasses, are formed. The actual phase diagram of a given colloid exhibits the structures and the conditions under which they form.

### 3. Applications

The formation of some crystalline or amorphous structure in terms of a phase diagram such as in Fig. 2 usually consists of the preparation of a colloidal fluid from which afterwards the solvent is removed thereby increasing the packing fraction  $\phi$  of the colloidal particles. The resulting structure depends sensitively on details of the process of formation, e.g., on the path in the phase diagram and on the rates. Some experimental results of colloidal crystals [16, 17, 18] as well as amorphous solids [19] will be shown during the presentation.

Colloidal crystals [20, 21, 22] can exhibit crystal structures which do not occur as ionic crystals because for binary colloids there is no constraint on the stoichiometry due to electrical neutrality as it is the case for ionic systems; the electrical neutrality in colloids is guaranteed by the counterions.

Very recently the formation of a porous amorphous structure has been achieved which is intended to be applied to fuel cell electrodes [23]. This structure is based on the self-assembly of carbon nano tubes which are decorated with Pt-nanoparticles. The porous structure is conductive for fluids whereas the self-assembled nano tubes lead to a high electrical conductivity. More details will be given in the presentation.

#### 4. Summary

Colloidal science offers many possibilities to fabricate interesting crystalline and amorphous structures for applications such as fuel cell electrodes [23]. However, the formation processes are challenging as there are many parameters to be controlled which sensitively influence the resulting structure. Continued intensive experimental and theoretical investigations of the underlying colloidal interaction potentials will guide the development.

#### Acknowledgments

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