Chapter 1

Introduction

What are colloids? The word origin *kolla* (glue) and *eidos* (form, shape) suggests to some extent the connection to the field of soft matter within statistical physics, but it does not capture the rich variety of phenomena and properties. The term *colloidal*, in general, describes a class of particles with size from a few nanometers to typically a few microns that are dispersed in a medium. More than one hundred years ago colloids played an important role in the development of the idea of the discontinuous structure of matter, or, that is to say to the existence of atoms. In 1905 A. Einstein predicted that small particles visible by a microscope due to thermal molecular motions are subject to Brownian motion [1]. A few years later J. Perrin experimentally confirmed the kinetic theory and thereby showed the existence of atoms [2]. From sedimentation experiments he could determine Avogadro's number N_A, or equivalently, the Boltzmann constant k_B. In 1926 J. Perrin and in 1925 R.A. Zsigmondy received the Nobel Prize for their work on the discontinuous structure of matter and the heterogenous nature of colloid solutions, respectively. In the following period, atoms, the quantum character of matter, and the nucleus became of increasing interest. It took several decades until the study of colloidal systems underwent a recent renaissance based on the development of experimental techniques, the availability of extensive computer simulations, and well-developed theoretical approaches. The latest developments allow one to consider colloids as model atoms [3,4] because they provide tunable interparticle interactions and the underlying length and time scales allow one to directly study aspects of atomic systems. Moreover, from a technological point of view, the relevance of micro- and nanostructured materials and the presence of colloids in nature and everyday life motivates study of this rich field. Colloids can be found, for instance, in paint, in blood, and in many industrial processes.

The solvent in which the colloidal particles are immersed can itself consist of a variety of particles such as atoms, ions, macromolecules, polymers, and other species of colloids. The interaction between the colloidal particles is affected by the properties of the solvent and can be described by an effective interaction that originates from integrating out the degrees of freedom of the solvent. This requires a good understanding of the solvent behavior to consider its contribution to the effective interaction. In order to achieve this, we study the behavior of mixtures of colloids such as spherical particles, polymer coils, needles and platelets in various situations: in the bulk we benefit from the model character of colloids and achieve a means to handle the tunable nature of their mutual interactions; at planar walls additional surface contributions give rise to further effects; in confinement the phase behavior of the fluid will affect the force on the confining walls; analogously, the solvent properties might strongly influence the interaction between two fixed big colloids at close distance.

From an experimental point of view, colloidal mixtures are of appealing size and well-developed experimental techniques allow one to synthesize and study particles of different size and shape. It is possible to choose particles that are matched in density and refractive index and to study systems with vanishing dispersion forces. Electrostatic or steric stabilization yields particles with a strong short-ranged repulsion and a weak long-ranged interaction. From a theoretical point of view, such colloids [5,6] are successfully described by the hard-core model. Hard-sphere fluids are widely studied and theory provides very accurate results when compared with computer simulations. One example is the equation of state for the one-component hard-sphere fluid [7,8]. The construction of a theory for mixtures is more demanding, particularly for mixtures of particles of different species. For mixtures of hard spheres and ideal polymer Asakura and Oosawa [9,10] and independently Vrij [11] introduced a successful model that serves as a starting-point for various approaches. Several different routes have been developed to describe the structure and thermodynamics of such mixtures. Density functional theory (DFT), integral equation theory and perturbation theory allow us to select an approach most suitable for a given physical situation. In DFT [12] the framework of fundamental measure theory (FMT) provides a successful reference model to treat particles with interactions that are dominated by strong repulsion [13]. Within FMT it is possible to add to the hard-sphere fluid additional species that together act as a depletion agent [14]. Upon integrating out the degrees of freedom of the depletion agent, the solvent effects can be mapped onto the effective interaction between the remaining particles. For hard-sphere solvents [15–18] and different kinds of soft particles [19–22] this method has been applied successfully. The effective one-component treatment in some cases is simpler to treat as compared to the full mixture and one may employ different routes which often involve a perturbation theory.

If the solvent is composed of a mixture of small colloids c, modeled as hard spheres, and ideal polymer p the solvent exhibits phase separation between a colloid-rich and a colloid-poor phase. In such systems fluid–fluid demixing can be experimentally observed by confocal microscopy [23], and the rich phase behavior of mixtures of colloids and depletion agent has been observed by other experimental techniques [23–31]. When two big colloids of type b are immersed into a colloid-polymer (cp) mixture then the mapping of the solvent onto an effective one-component system of particles of the species b has to deal with a rich phenomenology. Computer simulations provide insight into the properties of colloidal mixtures, but if the particle sizes are highly asymmetric the different length and time scales of the problem lead to slow convergence and simulations have to be performed with care [32–34]. In contrast, density functional theory for such mixtures is well developed and various inhomogeneous situations, such as fluids near planar walls [22], confined in narrow slits [35] or in porous media [36] have been studied.

The phase behavior of the colloid-polymer (cp) mixture with monodisperse components is widely studied for various types of depletion agents [23,24,26–29,31,37–39] including spherical polymers, needles, and platelets. A pure hard-sphere fluid exhibits a fluid–solid phase separation at sufficiently high packing fractions [40]. Adding a depletion agent d favors the phase separation and widens the region in the phase diagram with metastable and unstable states while the regions with the stable fluid and the stable solid phase shrink. Moreover, for mixtures of colloids (diameter σ_c) and a spherical depletion agent (diameter σ_d) with a symmetric size ratio $q = \sigma_d/\sigma_c \simeq 1$ a fluid–fluid phase separation is stable with respect to crystallization. By introducing polydispersity, i.e., species with a continuously varying size or shape distribution, the mixture shows even richer phase behavior that has been demonstrated in experiment [30, 41] and theory [42–50]. For the cp mixture with monodisperse particles, a recent approach based on FMT [51] provides a good starting-point to introduce polydispersity because multi-component mixtures with different size or geometry can be considered from the outset. It is not known a priori how polydispersity, for example introduced by varying size or shape of the depletion agent particles, affects the phase behavior. By introducing different length scales the phase diagrams can possess two fluid–fluid critical points [52–55]. The distinct length scales are typically introduced directly via the interparticle interaction potential. Here, we address the question whether similar effects can be seen, if the length scales are introduced in terms of a bimodal size distribution of the depletion agent.

In contact with walls a colloid-polymer mixture exhibits a complex surface phase behavior. Within the Asakura-Oosawa-Vrij (AOV) model for the mixture for weak size asymmetry, a series of layering transitions and a wetting transition have been found [22]. When confined in narrow slit-like pores, depending on the interaction of the confining planar walls, a fluid can undergo capillary condensation [56–58] or evaporation [59, 60]. In experiments, narrow pores can be studied using the surface force apparatus [61,62] or two mica plates [63–65]. In theoretical calculations for the AOV model both capillary condensation and evaporation have been observed [35,66]. Combining the results for the AOV mixture at a single wall and in a narrow pore, we address the question in which range of the slit-width of the pore the various effects compete. One can expect a competition between the gas phase, the layering phase and the liquid phase. Since the confined fluid exerts an excess pressure on the confining walls, we study how the layering transitions and capillary condensation affect forces between the walls of a slit-like pore.

In order to study mixtures of different species one can in some cases consider the full mixture, i.e., each species explicitly. In many cases this approach is complicated and demanding. If one is mainly interested in the behavior of one component of the mixture then it is convenient to integrate out the degrees of freedom of the remaining species. Although this procedure is restricted to particular situations, e.g., asymmetric size ratios for hard-sphere mixtures, one ends up with a problem that is simpler to treat. The resulting effective interaction potentials between the remaining particles capture the influence of the solvent in addition to the direct interaction. Effective interactions between two particles or between a particle and a wall are widely studied for simple solvents. In the case of a hard-sphere solvent one obtains a depletion potential with oscillatory decay [18, 67]. In the case of an ideal polymer solvent, the interaction potential is of finite range and known even exactly [9,10]. The effective interaction potentials have been studied in other systems, e.g., for charged particles [68], for long-ranged and for soft interactions [19,69]. Once the effective interaction is known, integral equation techniques or perturbation theory can be employed to study the structure and the phase behavior of the effective one-component fluid.

For solvents with rich phase behavior the mapping onto an effective interaction potential is more complicated. The structure, the thermodynamic properties, and the phase behavior of the colloid-polymer mixture described by the AOV model of one colloid and one polymer component are widely studied. For that reason, the colloid-polymer mixture provides an appropriate model to introduce a complex solvent in a colloidal suspension of big particles. When a big colloid is brought close to a wall or a second big particle then the solvent-mediated interaction must reflect the rich behavior of the solvent and it is evident that integrating out the degrees of freedom of the solvent particles becomes a challenging task. In particular, near the phase coexistence of the solvent one will face rich phenomenology.

This thesis is structured as follows. In Chapter 2 we present a brief introduction into the basic principles used throughout the thesis, including some thermodynamic foundations, density functional theory with focus on fundamental measure theory, and free-volume theory. In Chapter 3 we present results for the bulk phase behavior of a mixture of colloids and a depletion agent. We also introduce a general approach in which the depletion agent can be polydisperse. In the case of bimodal distributions we find a novel phase and complex phase diagrams with two stable critical points. The phase behavior of a monodisperse colloid-polymer mixture in confined geometry is treated in Chapter 4. There we describe the competition between layering transitions found at a single hard wall and capillary condensation, which can be found in narrow slits. The influence of the solvent phase behavior on the interaction between the walls is also studied. The interaction between a big colloid and a planar hard wall in a solvent of an AOV mixture is presented in Chapter 5. We study the behavior of a colloid-polymer mixture close to phase coexistence near two big colloids and near one ellipsoidal particle in Chapter 6. We conclude in Chapter 7.

Chapter 2

Statistical Mechanics of Colloidal Mixtures

In this chapter we give an introduction to the framework and basic principles that we use for treating colloidal mixtures. Starting from the elementary grounds of equilibrium thermodynamics we describe their basic quantities and concepts. We briefly review density functional theory (DFT), which allows us to treat inhomogeneous classical fluid mixtures. Originally, DFT has been developed by Hohenberg and Kohn [70] to study electronic systems at temperature $T = 0$ and was generalized by Mermin [71] to non-zero, positive temperature, $T > 0$. Several approaches to describe non-uniform classical fluids, such as integral equation techniques, variational principles, diagram representations of the grand partition function expansions and cluster theory, have been developed at the same time [72–75] but it took more than ten years until the density functional formalism was introduced to describe inhomogeneous classical fluids [76, 77]. Refs. [12] and [78] give an excellent review to foundations of this topic and Ref. [79] provides a recent overview to a wide range of applications of density functional theory. One of the main issues within DFT is to find reliable approximations for the free energy that take into account the interparticle interactions. For a particular kind of colloids, which exhibit strong short-ranged repulsion and weak long-ranged interactions, the core contribution in the interparticle interaction potential can be modeled by a hard-core reference system and the potential tail can be treated in a perturbative manner [80]. For colloids with very weak or vanishing long-ranged interactions the pure hard-core model provides a suitable approximation. Within that model the temperature scales out, as $\beta V(r)$ only takes the values 0 or ∞, and the behavior of the system is driven by entropy. Mixtures of particles with hard-core potentials can be described within fundamental measure theory (FMT) going back to the work of Rosenfeld [13]. It is possible to base the FMT on different equations of state [67, 81–83]. We present an outline of the main ideas for that approach. Within the same framework we can add to the hard-sphere colloids another species, say a polymer substance or colloidal rods, which acts as a depletion agent [14, 84]. A recent approach [51] which combines FMT and the free-volume theory (FVT) allows us to treat bulk phase behavior of colloids in a sea of arbitrarily shaped depletion agent [37] and is presented at the end of this chapter.

2.1 Thermodynamics and phase transitions

From a phenomenological point of view classical statistical systems in equilibrium are described by a small number of variables. In the case of bulk, or equivalently homogeneous, systems such as colloidal mixtures of ν components i connected to a heat bath and particle reservoirs the temperature T, the volume V and the chemical potentials μ_i are sufficient. In the grand canonical ensemble the thermodynamic potential is given by

$$\Omega(T, V, \{\mu_i\}) = -pV, \tag{2.1}$$

where p is the bulk pressure. In the canonical ensemble with fixed particle numbers N_i the corresponding Helmholtz free energy $F(T, V, \{N_i\})$ is related to Ω by

$$\Omega = F - \sum_i \mu_i N_i. \tag{2.2}$$

In the description of colloids throughout the current work we focus on a model in which temperature scales out due to particle interaction potentials $\beta V_{ij}(r) = \infty$ in the range of $r < \sigma_{ij} = (\sigma_i + \sigma_j)/2$, where σ_i is the diameter of component i, and 0 otherwise. The thermodynamic properties based on such type of interactions are determined by entropy alone. Hence we omit relations based on a variation of T. Both the grand potential Ω and the Helmholtz free energy F play a central role in the description of the phase behavior of colloidal mixtures. In the homogeneous case the pressure p and the chemical potentials μ_i are given by

$$p = -\frac{\partial F}{\partial V}\Big|_{T,\{N_i\}} \tag{2.3}$$

and

$$\mu_i = \frac{\partial F}{\partial N_i}\Big|_{T,V}. \tag{2.4}$$

Two different bulk phases α and β, which for example differ from each other by their densities $\rho_i = N_i/V$, $i = \alpha, \beta$, can coexist if their pressures and chemical potentials are equal: $p^\alpha = p^\beta$ and $\mu_i^\alpha = \mu_i^\beta$. The equation of state describes the relation between