Summary

In this thesis we simulate the crystal nucleation process in a colloidal dispersion of spherical particles with purely repulsive interaction. The main problem when studying crystal nucleation, experimentally as well as in computer simulations, is that crystal nucleation is an activated process. First, small crystal nuclei need to form spontaneously in a supersaturated solution, but unless their size exceeds a critical value, they will redissolve rather than grow. The crystal nucleation rate is the product of the probability for the formation of a critical cluster and a kinetic prefactor that describes the rate with which a critical nucleus grows. Our simulation techniques enable us to overcome this problem and to predict absolute crystal nucleation rates. In addition we are able to study the pathway for the formation of small crystal nuclei.

In chapter 2 we begin with a general introduction to how molecular simulations can be used for the calculation of a reaction rate constant. This is done in the framework of linear response theory. We focus on the main results for the reaction rate constant and the practical aspects of the numerical calculation. This formulation is applied to the special case where the barrier crossing is diffusive. The final result is applicable to the calculation of a crystal nucleation rate.

Chapter 3 summarizes classical nucleation theory (CNT) which is most commonly used to predict nucleation rates. We explicitly demonstrate that the expression for the nucleation rate is identical to that derived in chapter 2. Furthermore, we extend the formulation of CNT to a multicomponent system.

We end the first part of the thesis with chapter 4, which provides an introduction to the numerical techniques needed to predict a crystal nucleation rate. The calculation of the rate is split into two parts. First we compute the nucleation barrier and second we compute the kinetic prefactor. In all cases we perform Monte Carlo simulations, in combination with a local bond order analysis for the identification of solid particles, for the calculation of the nucleation barrier. As the formation of cluster is extremely rare we need to use umbrella sampling. The kinetic prefactor must be calculated in a separate kinetic Monte Carlo simulation.

In the second part we apply our novel techniques to colloidal dispersions of spherical particles with purely repulsive interaction. As crystallization of hard-sphere colloids has been extensively studied, this system was an obvious choice to begin with (chapter 5). This study constitutes the first example where computer simulations of crystal nucleation rates are directly compared with experiments. To our surprise, we find that our results are at odds both with the existing experiments and with CNT. We state explicitly that, according to our estimates, the computed nucleation rates are accurate to within one order of magnitude. The discrepancy with experiments must therefore be attributed to problems in the experimental data analysis. In addition we find that CNT underestimates the nucleation barrier by about 50%. Based on our barrier calculations and a precise knowledge of $\Delta \mu$ (the difference in chemical potential between the liquid and the solid phases) we deduce the liquid solid surface free energy $\gamma$ for a critical nucleus. We find that these estimates for $\gamma$ are much higher than the coexistence value, and $\gamma$ increases with density. The dependence of $\gamma$ on density was not considered in existing theories. Hence, our work poses a challenge to experimentalists and theoreticians alike. We should also
note that our calculations for the kinetic prefactor are in good agreement with a simple classical estimate. Finally, we study the structure of critical nuclei. It is known that the stable crystal structure is face centered cubic (fcc). However we find that our critical cluster constitutes a random stacking of the (111) planes of the fcc and the hexagonal closed packed (hcp) structure. This is in agreement with experimental observations and in contrast to a theoretical prediction that a fluid always crystallizes via a body centered cubic (bcc) intermediate. It can be seen as a manifestation of Ostwald’s step rule, that a liquid first nucleates in a metastable structure and only later transforms to the stable one.

In practice, the colloidal particles used in the experiments have a distribution of particle radii (referred to as polydispersity) which is rarely less than 2 - 3% of the average radius. In order to compare our measured nucleation rates with experiments we already needed to study the effect of a small polydispersity (up to 5%) in the previous chapter. The result was that within numerical error the monodisperse and polydisperse suspensions have the same nucleation barrier at constant supersaturation $\Delta \mu$. However, experiments on hard-sphere colloids indicate that crystallization is suppressed if the polydispersity exceeds 12%. So far this has been attributed to kinetic reasons as crystallization of highly polydisperse suspensions is not excluded on thermodynamic grounds. This observation was the motivation for our second project where we further studied the crystallization kinetics for polydispersions up to 10% (chapter 6). Our calculations of the crystal nucleation barrier show that when polydispersity is increased beyond 5%, the barrier height increases rapidly at constant $\Delta \mu$. This means that the probability for the formation of a critical nucleus is decreased and crystal nucleation is suppressed. According to CNT this increase in the barrier height is attributed to an increase of $\gamma$ with polydispersity. Even more surprising is that the variation of the barrier height with supersaturation at the same polydispersity is non-monotonic. With increasing $\Delta \mu$ the barrier height first decreases then goes through a minimum and starts to increase again. Again, using the equation for the barrier height from CNT, this observation is attributed to an increase of $\gamma$ with $\Delta \mu$. The minimum of the barrier height increases rapidly with polydispersity. Our estimate for the minimum barrier height of a system of hard-sphere colloids with a polydispersity of 10% is about $30k_B T$. This implies that for a suspension of colloids with a radius of 500 nm we expect to see less than one crystallite per cubic centimeter. This has important implications for the morphology of polycrystalline colloidal materials. Vitrification at high supersaturations should yield colloidal glasses that are truly amorphous, rather than nano-crystalline. Finally we propose how our observation of the minimum in the nucleation barrier can be tested experimentally. Using a simple analysis we show that the minimum barrier height causes a minimum in the typical crystallite size at the end of a nucleation experiment. By visual inspection one can test if crystallites formed at high supersaturation are larger than those that form at lower supersaturation.

During the course of the work described above a new experiment was reported, where nucleation and growth in colloidal crystallization were studied by real-space imaging. The reported nucleation rates are much higher, and an estimate for the surface tension was much lower than the values we found in our simulations. The difference between this system and ours is that the particles were weakly charged. This inspired our next project, the crystallization of weakly charged colloidal spheres (chapter 7). We model the interaction between the charged colloids with a repulsive hard-core Yukawa potential. We study the dependence of the crystal nucleation rate as a function of supersaturation on the range and the contact value (charge on the sphere) of the interaction potential. We find that at the same volume fraction crystallization of the weakly charged spheres is much faster than for hard-spheres. This is partly due to the fact that the fluid-solid coexistence of the charged spheres occurs at lower volume fractions, which implies a higher supersaturation. In addition, we find that the charge has a strong direct effect on the nucleation barrier by lowering $\gamma$. This effect is strongest when only a weak charged is
added. Furthermore we find that the functional dependence of the barrier height as a function of supersaturation does not change considerably for different charges. This is in contrast to the experiment where only a slight dependence of the nucleation rate on supersaturation is observed. Our simulations indicate that one possible explanation is a strong density dependence of the interaction potential. Moreover, we study the structure of small crystal nuclei. All simulations are performed in a region of the phase diagram where fcc is the stable phase. However in all cases we find that the initial crystal nuclei have a bcc structure. We attribute this effect to the fact that the liquid/bcc surface free energy is lower than that of the liquid/fcc interface.

Colloids that consist of a polymethylmethacrylate (PMMA) core coated with a thin layer of poly-12-hydroxystearic (PHSA) are commonly used as a model system for hard spheres. However, due to the coating, the particles are slightly soft. In chapter 8 we study the effect that such a softness has on the phase behavior and the crystallization kinetics. In our simulations we use an interaction potential extracted from surface force measurements on that system. This potential is characterized by two parameters, the thickness and the density of the PHSA layer. We find that the freezing density measured in the experiments corresponds to a layer thickness that is about a factor two larger than the thickness measured in the surface force experiment. We suggest that this discrepancy might be due to a slight charge on the particles. Based on a comparison between the experimental and numerical results we can estimate the magnitude this charge would need to have. The charge is indeed very small (less than one electron per sphere). For the crystallization kinetics we find that the nucleation rate is increased by two orders of magnitude at constant $\Delta \mu$. While this is significant, it cannot account for the discrepancy between the nucleation rates observed in experiments and simulations (chapter 5).

Finally we apply our techniques to study crystal nucleation in a heterogeneous system. We simulate a system of hard spheres that are confined between two plane hard walls. We find that the presence of the walls narrows the density regime where the liquid is metastable with respect to the solid. Already at volume fractions less than 1% higher than coexistence spontaneous crystallization occurs, compared to about 4% in the homogeneous system. We see that the wall induces the crystal formation. First a (111) face crystal plane forms at the wall. Then it prefers to grow laterally rather than in the third dimension. The calculated barrier height of such a nucleus is about two orders of magnitude lower than an estimate based on CNT in the corresponding homogeneous system. Our simulations support arguments based on the values of the surface free energy densities which suggest that a crystal should partially wet the wall with the (111) plane. We propose that the fact that crystal formation happens at volume fractions less than 1% higher than coexistence can be used for a precise determination of the freezing point in the experimental system.