9 Summary

Liquid water is different from other liquids in many respects. Because of these anomalies and due to the tremendous importance of water in nature and economy, water has been attracting considerable research interest for a long time. This interest persists unvaried even in our days since many details in the behaviour of water are not yet completely understood.

Water in the metastable supercooled liquid state is an important constituent of the upper troposphere and lower stratosphere. In these regions cirrus clouds are formed which are of great influence on the earth's radiation balance. Homogeneous nucleation of ice in deeply supercooled water is a major mechanism in the formation of cirrus clouds.

Because only molecules of the metastable phase itself are involved in the homogeneous formation of the germs, this process is governed solely by the structure and dynamic of the liquid. Hence the investigation of homogeneous nucleation can give further clues how water "works".

Electrodynamically levitated supercooled liquid droplets are very suitable objects in order to study homogeneous nucleation. This method appears to have several advantages over alternative strategies. The further elaboration of these superior experimental features has been a key issue of the work presented in this thesis. The observation of homogeneous nucleation is aggravated or even made impossible in many cases by the competing heterogeneous nucleation. The latter nucleation mechanism can be excluded by levitation more reliably than by other methods.

Within the project reported in this thesis, an apparatus for the measurement of nucleation rates has been constructed. The central part of the setup consists of a coolable electrodynamical trap. The experimental setup was designed particularly to fulfil the requirements which arise with the measurement of rates of homogeneous nucleation in deeply supercooled levitated liquid droplets.

During the construction of the experimental setup many experiences collected in the former project (see [Kräm99]) could be taken into account and led to several improvements. Due to the very compact design and the small inner volume there are clearly defined thermal conditions inside the new trap. The failure-free operation of the droplet generator can now be accomplished easier than before, since the droplet generator is not mounted inside the cooled trap anymore but rather outside at room temperature. This is a prerequisite for a fully computer-controlled operation of the apparatus which allows an increased number of repetitions of the single freezing experiment. Because nucleation is governed by statistical laws, a large number of repetitions leads to a higher significance of the results.

The volume of each single droplet is measured through analysis of the spatial intensity distribution of the scattered laser light and permanently recorded during the experiment as a function of time. Therefore the particle ensemble under investigation is characterized with high precision. This has to be considered as a major advantage over alternative methods (supercooling of emulsions, aerosols etc.).

Within the frame of this thesis homogeneous nucleation in supercooled H_2O has been studied between 239.4 K and 239.7 K. In this temperature range the only until now reported data for nucleation rates were measured in an aerosol chamber by *DeMott* and *Rogers* [RoDe90]. There is good consistency between the data of this group and our own data. However, the measured rates are approximately two orders of magnitude higher than the results from the function published by *Pruppacher* [Prup95] and the results from the function of *Jeffery* und *Austin* [JeAu99].

The homogeneous nucleation of ice in supercooled D_2O has been studied *for the first time* in levitated supercooled droplets. In the range between 243.7 K and 244.7 K the rate of nucleation has been measured. A large discrepancy appears between our nucleation rates and the only until now published data for supercooled D_2O (*Taborek* 1985, [Tabo85]). However, there are profound doubts about the reliability of *Taborek*'s data [Prup95].

The investigated temperature intervals were chosen in such a way that the nucleation times lasted up to 3 min. This means that the supercooled state was maintained in average for a *substantially longer* period than in earlier measurements [Kräm99]. In contradiction to theoretical expectations, pronounced deviations from the expected statistical behaviour were observed for freezing events with longer nucleation times. Obviously the number N_u of unfrozen droplets *does not* decay purely exponentially with time within an ensemble of N_0 supercooled droplets. In addition, there seems to be a temperature-dependent induction period of slowly rising nucleation rate in the case of heavy water. The reasons for this discrepancy between theory and experiment could not be explained solely on the basis of the available data up to now. It cannot be excluded that the described phenomena are related to so far unknown properties of supercooled water. Our observations point toward the existence of different modifications of supercooled water being in equilibrium with each other. This hypothesis is supported by hints from other experiments [BeFu98]. The observed time dependence of the nucleation rate may be caused by the slow re-equilibration of the system after the temperature jump.