

Kapitel 9

Summary

In this work the freezing behavior of n-alkanes was investigated. These substances were chosen because they show the very rare phenomenon of surface freezing.

An variable temperature electrodynamic balance was designed to examine the nucleation behavior of small droplets without the influence of wall contact. An discharge charger was developed which allows to charge droplets via ion attachment. This made it possible to carry out such investigations for the first time on non-polar organic substances.

Supercooling temperatures of n-alkanes with carbon numbers ranging from 14 to 17 were examined. On the average a supercooling temperature of 9 °C was observed. This is much higher than the supercooling previously observed in bulk samples and contradicts the common assumption that alkanes exhibit a solid monolayer at the air interface and therefore cannot be supercooled at all. This supercooling is, however, lower than the mean supercooling of 15 °C reached so far in emulsions.

Nucleation rates were measured for alkane droplets with carbon numbers of 15 and 17 at supercoolings from 8.8 to 9.8 °C. A linear function between the logarithmic nucleation rates and the supercooling was fitted on the data. This fit makes it possible to calculate the supercooling of samples with different volumes at the same freezing probability. Alkane droplets in emulsions have much smaller droplet volumes than the droplets analyzed in this work. The supercooling difference resulting from this effect is 2.3 °C. This can not explain the observed difference of 6 °C.

$C_{15}H_{32}$ showed a different freezing kinetics than expected for pure homogeneous nucleation. An induction time of several seconds was observed before freezing star-

ted. Therefore more complex nucleation mechanisms and their effect on the nucleation kinetics had to be considered.

It was shown that the existence of a solid monolayer not inevitably leads to instantaneous crystallization, although the size of a critical nucleus is exceeded. If the layer is completely closed a new activation energy is needed for the formation of the next layer.

The assumption of a growing surface layer can explain the observed behavior of the $C_{15}H_{32}$ droplets. With the increase of the surface layer also the probability for the nucleation on this existing layer increases. A theoretical solution for the nucleation differential equations assuming a time variable partial volume is given in this work and reproduces the observed data very well.

In the last years surface freezing was also observed in other organic liquids like alcohols. The existence of a solid layer could be characteristic for molecules with long chains and weak interaction. It would therefore be reasonable to extend the nucleation measurements on other levitated organic droplets which also show surface freezing. Currently the nucleation behaviour of alcohol/water droplets is investigated in our laboratory. The nucleation rates at low alcohol concentrations correspond to the nucleation rates measured for water. Since the alcohol concentrates at the surface, we are investigating the minimum concentration at which the surface layer influences the nucleation.