Summary

This thesis is primarily concerned with the (equilibrium) description of the structure and tension of curved fluid interfaces. Many everyday applications make use of the fascinating properties of the interfacial region; topics range from food, coatings and detergents to subjects as diverse as oil recovery. All of these applications involve liquids at interfaces and the main goal of this thesis is to gain better understanding of the fluid interfacial region.

The introductory chapter 1 aims to give a brief review of the concepts underlying this thesis. A brief overview of the historical developments is presented followed by a brief introduction about interfaces in general. Special attention is given to the case of curved interfaces and we introduce the Helfrich free energy for curved surfaces. Furthermore, the topic of the mean-field approximation is introduced together with van der Waals’ theory for the liquid-vapour system.

From a thermodynamic point of view, curvature of the interface can be induced only in two ways: either a fluid (or vapour) is brought off-coexistence (the case of nucleation) or an external potential in the system forces the interface to be curved (e.g. a liquid near a hard wall or in a confined space). In both cases, the surface tension depends on this curvature. Under the circumstances that an expansion in curvature is valid, the now well-known Tolman’s length, defined as being the leading order term in such an expansion, proves to be a good description for a small nucleating drop. In chapter 2 it was shown that for the case of a nucleating drop van der Waals’ model predicts a negative Tolman length, slightly diverging upon approaching the critical point. We have shown that far away from the critical point Bartell’s compressibility approximation captures the behaviour predicted by van der Waals’ theory both in sign and magnitude.

The theoretical investigation of a curved fluid interface near a solid hard wall is presented in chapter 3. The difference with an ordinary curved interface (e.g. a nucleating droplet) is in the way one establishes the curvature: here it enters as a boundary condition. We show that the condition of mechanical equilibrium is always valid when calculating density profiles, but that the so-called wall theorem need not always be satisfied. We trace this observation due to the lack of continuity of a statistical mechanical function, called the cavity function, at the wall. The Tolman length can again be expressed in terms of planar density profiles just as in the case of a nucleating droplet. On approach to the critical point from the liquid side, the Tolman
length diverges due to the formation of a “vapour” layer on the solid surface. It should be noted that in general one has to keep in mind that on approach to coexistence the curvature expansion breaks down and the Tolman length itself is then no longer well-defined.

In chapter 4 we extend our analysis of a fluid in contact near a hard wall in the spirit of Nakanishi and Fisher. By using expressions derived from Landau lattice mean-field theory and density functional theory we are able to derive microscopic expressions for the surface chemical potential $h_1$ and surface enhancement parameter $g$. The surface chemical potential is a direct measure of the substrate-fluid interaction strength. It is found that the surface enhancement parameter $g$ consists of two parts: (1) due to the lack of molecules behind the wall and (2) due to the possible enhancement of the interaction potential of fluid molecules near the substrate. Using these expressions we found that the wetting phase diagram of a square-well fluid interacting with the substrate via a square-well potential compares well with the original model of Nakanishi and Fisher. The main advantage of employing a square-gradient model (despite its apparent drawbacks), is that, unlike more sophisticated theories, the order of the wetting or drying transitions can be unambiguously determined.

In chapter 5 we investigate the the interfacial properties of colloid-polymer mixtures theoretically by employing an effective one-component model in which the polymeric degrees of freedom are integrated out and thus effectively reducing this system to a system of colloids interacting in a mean-field way with the polymers. For our calculations we employ square-gradient theory and a virial approach. We have calculated the surface tension for the phase separated colloid-polymer mixture where have improved on the original calculations performed by Gast et al. by introducing a density dependent square-gradient coefficient. This modification leads to somewhat higher values for the surface tension compared to earlier theoretical studies done by Brader, where this modification was left out. This finding is more in line with the experimental results. We have also calculated the bending rigidity and found that it is negative and decreases in magnitude upon approach to the critical point using both theoretical methods. Employing a virial route for calculating the bending rigidity the magnitude is less and decreases less fast in the vicinity of the critical point compared to the linear scaling relationship derived from square-gradient theory, more in line with the simulation results of Vink et al. This finding indicates that a virial route lends itself more in calculating the bending rigidity.

Combing the ideas of the previous two chapters, chapter 6 deals with wetting/dewetting in colloid-polymer mixtures in a Nakanishi-Fisher type approach. In order to compare with similar work done by Aarts et al. the colloid-polymer mixture was described by employing free volume theory with several model approximations. It was found that all wetting and drying transitions are of second order in nature and lay close by the critical point. For all size ratios considered it was found that the main contribution to the surface enhancement parameter stems from the missing fluid part in the half-space $z < 0$, with $z = 0$ marking the location of the solid wall, opposed to the contribution from the enhancement of the interaction between fluid molecules
near the substrate. Depending on the choice for the approximation of the free volume term there is cross-over from wetting to drying (or drying to wetting) at a polymer to colloid size ratio $q = 0.935$. This cross-over behaviour is not found when abandoning the Nakanishi-Fisher approximation and numerically solving for the density profiles, although the wettability does decrease when raising the size ratio.

The final chapter 7 describes the interface of a Pickering droplet. Modeling the interface within the context of the swollen micellar model devised by Ruckenstein, we found the model overestimates the size order of the drops encountered in Pickering emulsions and this mainly because the model is too simplistic to produce quantitative results. Due to the semi-empirical nature of the theory and the lack of experimental data (colloidal adsorption energies, adsorption isotherms, volume fraction of colloidal particles in the bulk, etc.) only qualitative trends for Pickering emulsions can be predicted. Nevertheless, just as in the case of microemulsions here too the bare oil-water interface is reduced however colloids are less surface active than typical surfactants, so it is expected that the oil-water surface tension still plays a dominating role.

Modeling the interface using the capillary part of the free energy we find that in both two and three dimensions the adsorbance of a single colloid does not influence the pressure difference between the inside and the outside of the drop but does lower its free energy. Both the laws of Laplace and Young still hold in this case. The model needs to be extended, however, to allow for colloidal interactions in order to describe a fully covered Pickering droplet.