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Mean-field description of the structure and tension of curved fluid interfaces

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Mean-field Description of the Structure and Tension of Curved Fluid Interfaces

Joris Kuipers

Mean-field description of the structure and tension of curved fluid interfaces
/ J. Kuipers

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Mean-field Description of the Structure and Tension of Curved Fluid Interfaces

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 Dr. D.G.A.L. Aarts *Oxford University, UK*

“Science is what we have learned about how not to fool ourselves about the way the world is.”

- R.P. Feynman

Even a stopped clock gives the right time twice a day

List of Publications

- E. M. Blokhuis and J. Kuipers, “Thermodynamic expressions for the Tolman length” *J. Chem. Phys.* **124**, 074701 (2006) (Chapter 2)
- E. M. Blokhuis and J. Kuipers, “On the determination of the structure and tension of the interface between a fluid and curved hard wall” *J. Chem. Phys.* **126**, 054702 (2007) (Chapter 3)
- J. Kuipers and E. M. Blokhuis, “Interfacial properties of colloid-polymer mixtures” *J. Coll. Interface Sci.* **315**, 270 (2007) (chapter 5)
- E. M. Blokhuis, J. Kuipers and R. L. C. Vink, “Description of the fluctuating colloid-polymer interface” *Phys. Rev. Lett.* **101**, 086101 (2008)
- J. Kuipers and E. M. Blokhuis, “Wetting and drying transitions in mean-field theory: Describing the surface parameters for the theory of Nakanishi and Fisher in terms of a microscopic model” *J. Chem. Phys.* **131**, 044702 (2009) (chapter 4)
- J. Kuipers and E. M. Blokhuis, “Wetting to drying reversal in colloid-polymer systems” (Chapter 6, to be submitted)
- J. Kuipers, J. Groenewold and W. K. Kegel, “The Pickering Interface” (chapter 7 and appendix E, to be submitted)

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Chapter 1

Introduction

Liquids near interfaces or liquids in confinement behave substantially different than liquids in the bulk. For many years scientists have spent considerable time and effort in describing the bulk properties of matter yet the interfacial region has received considerable less attention. Several properties emerge that cannot be observed in three-dimensional bulk materials giving rise to novel types of behaviour. Furthermore, useful insights can be gained by investigating the properties of two-dimensional interfaces in systems where an accurate description of the bulk is lacking due to the complexity of the many parameters and components involved. This makes the study of the interfacial region fascinating but also a useful tool in describing new materials.

Applications are ubiquitous in every day life. Subjects as diverse as oil recovery, colloidal stability, catalysis, corrosion and even paints all involve liquids at interfaces. Important for the development of new materials, knowledge about the interfacial region aids us in understanding the physics of complex fluids and solids. Complex fluids refer to dispersions of molecular species in a fluid organized into structures with length scales relatively long (~ 10 Å) compared to typical atomistic or molecular dimensions (~ 1 Å). These structures, such as micelles, vesicles, microemulsions and so on, find their way into technological applications and serve as generic models for biological systems. To many the fascinating behaviour these complex materials exhibit is all too familiar. When applying paint we are utilizing the properties of encapsulation, while properties such as cleaning and dispersion are being utilized in soap and milk, for example.

Key in understanding the equilibrium properties of multicomponent systems is the knowledge of the free energy of the system. The minimization of the free energy balances the energetic and entropic contributions in the systems involved. Especially in complex fluids, the entropic part dominates the behaviour of the system and thermal fluctuations are often important. In contrast, knowledge about the Coulomb force between two ions usually suffices to correctly describe so called “hard materials”, like salts and metals. It is for this reason that the complex fluids involved in this thesis belong to the class of “soft materials”, i.e. materials exhibiting rich phase behaviour and which easily respond to external forces.

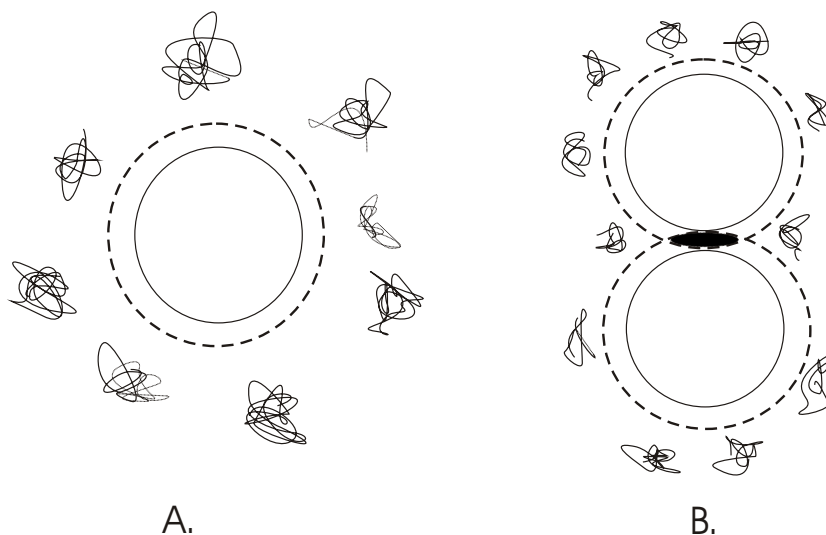


Figure 1.1 Schematic representation of depletion interaction. Non-adsorbing polymers cannot penetrate a thin shell around a colloidal particle. (A) This in turn drives the colloidal particles together thereby increasing the total volume available for the polymeric particles (B).

Recent years have seen many discoveries in the field of soft matter science. Soft matter materials exhibit both interesting equilibrium as well as rheological properties and many new types of materials are being investigated.

One such class of liquids, which received considerable attention over the last decade, are the phase-separated colloid-polymer mixtures. Colloidal particles are pushed towards each other if sufficient non-adsorbing polymer is added at the proper size ratio and this in turn drives phase separation, i.e. a fluid mixture is produced with a phase rich in colloidal particles and a phase with almost no colloidal particles. This mechanism is called depletion interaction (Figure 1.1) and was first described by Asakura and Oosawa [1] and later independently by Vrij [2]. The strength of the depletion interaction is directly proportional to the amount of polymer added and the range of interaction is determined by the size ratio of both species present. The interface between the two liquid phases exhibits an ultra-low surface tension and curvature corrections will affect the interfacial behaviour more than they would in simple systems. Thanks to the discovery of confocal microscopy, many theoretical predictions can now be tested in these systems turning the colloid-polymer mixtures into a well-studied system.

Another class of fluids, the so-called Pickering emulsions, display fascinating self-assembling properties. First discovered by Pickering [3], these emulsions form spontaneously after adding small colloidal particles to an oil-water mixture. The emulsion droplets formed are stable for many months and have a very narrow polydispersity unlike most emulsions. Figure 1.2 shows an example where a monolinolein/ styrene

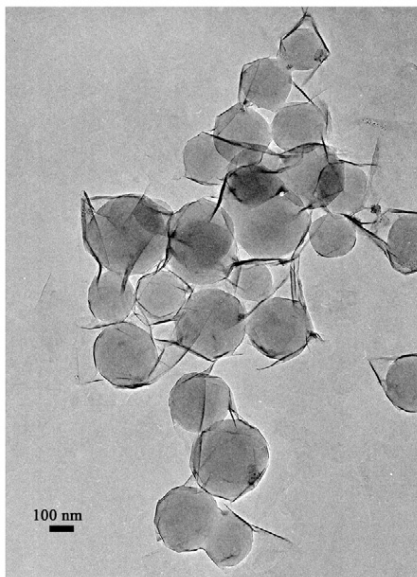


Figure 1.2 TEM image of particles from the polymerization of a 2 wt% montmorillonite-stabilized monolinolein/styrene emulsion dispersed in water. Taken from Ref. [4]

emulsion was stabilized using claylike particles. Because these emulsions do not use aggressive ionic surfactant molecules to stabilize the emulsion, these class of emulsions could be the solution for people with sensitive skin for example. From a theoretical point of view these Pickering emulsions have received considerable less attention and issues such as thermodynamical stability still remain a mystery.

As illustrated by the above examples, the field of soft matter science provides vast amounts of resources to put new ideas to use for a theoretician. By carefully examining the constituents of complex matter and their underlying relationships one aims to construct an expression for the free energy, which in turn can be used to derive all the macroscopic properties desired. This methodology is applied to several systems throughout this thesis but the focus will lay on describing the interfacial region.

The remainder of this introduction introduces the topic of fluid interfaces with some historical background and a closer look at what interfaces are and how to describe them. Then we briefly examine some of the theoretical methods devised in order to describe these inhomogeneous fluid systems, namely mean-field theory and the Helfrich surface free energy approach. We end this introduction by outlining the remainder of this thesis.

1.1 Historical Background

The field of liquid matter science is a relatively new field. During the eighteenth century increasing attention was given to the liquid phase in an attempt to describe previously unexplained phenomena, like the capillary rise of sap in trees. It was realized that in order to explain these phenomena studying the bulk properties of a fluid didn't suffice. It was the work of Pierre Simon Laplace [5] and Thomas Young [6] that led to new understandings of fluids in inhomogeneous systems. Scientists already speculated about the existence of cohesive forces within matter but it was Laplace who actually quantified it albeit in a *mean-field* manner¹. One of his most important results relates the pressure difference between the inside and outside of a liquid drop to the liquid-vapour surface tension $\sigma_{\ell v}$ and the drop's radius R :

$$\Delta p = \frac{2\sigma_{\ell v}}{R}, \quad (1.1)$$

a result what we now call *Laplace's equation*. Young used similar arguments as Laplace to obtain a relationship for the contact angle in terms of the surface tensions when a liquid or vapour touches a solid. At the point where the three phases meet the contact angle θ between the liquid-vapour (ℓv) and solid-liquid ($s\ell$) surface can be expressed via *Young's equation*,

$$\sigma_{sv} = \sigma_{s\ell} + \sigma_{\ell v} \cos \theta. \quad (1.2)$$

These equations suffice to solve all problems regarding the shape of bubbles and foams, the capillary rise (or depression) of liquids in narrow tubes and the shapes of liquids on solid surfaces.

Although these first attempts to describe the interfacial region were a great leap forward there were still some issues left unresolved. For example, Laplace assumed the interface to be sharp, an assumption which breaks down at the molecular level. Poisson, a follower of Laplace, recognized that particles in a fluid interface only interact with fluid particles on one side and that therefore a sharp density profile would imply that the fluid is not in equilibrium. According to Poisson, in equilibrium the interface should be diffuse with the width of the interface determined by the range of the attractive forces. He then went on, wrongly, to suppose that in such diffuse interfaces the surface tension must vanish [7]! Three men offered solutions to the problem of the interface, Karl Fuchs [8], Lord Rayleigh [9] and last but not least Johannes D. van der Waals [10]. van der Waals recognized the importance of minimizing a free energy opposed to the energy and stated the requirement that the free energy should always be a minimum in a system of fixed mass, temperature and volume. Especially concerning the interfacial region he was the first to adopt such an approach. By adding an additional term in the free energy depending on the square of the density gradient the resulting density profiles exhibit a nonzero interfacial thickness and a nonzero surface tension.

¹More about mean-field theory in section 1.3

van der Waals' theory long remained the best theory available for the surface layer between a liquid and its vapour. Unfortunately, many of his discoveries had to be rediscovered many years later due to decreasing attention for this field. In 1935 Landau and Lifshitz [11] basically reinvented van der Waals' theory applied to systems of magnetic domains. Then, in 1958, Cahn and Hilliard [12] independently derived the results again for the liquid-gas interface in the context of nucleation.

To understand the status of modern day treatment of interfaces we discuss two more developments that occurred during the twentieth century. The first is the derivation of an exact virial expression for the surface tension. It has long been realized that the surface tension depends on the difference between the normal and tangential components of the pressure tensor. The evaluation of the surface tension thus requires knowledge of the pressure tensor, which was first provided by Kirkwood and Buff [13] and later by Irving and Kirkwood [14]. Although there is no unique way of defining the pressure tensor, it was shown that the exact choice does not alter the value for the surface tension [15]. A natural consequence of these theories was the development of the Yvon-Born-Green equations [16], obtained by differentiating the statistical mechanical expression for the density of a certain particle with respect to the position of that particle in an inhomogeneous system. Yvon [16] was of the first to use these equations, however due to independent derivations by Born and Green the hierarchy of YBG-equations is also seen and due to contributions of Bogoliubov sometimes even as the BBGKY hierarchy.

The second development is the method of functional expansions of distribution functions. Such functionals were introduced by Lee and Yang and Green and these were soon applied to the statistical mechanics of inhomogeneous systems by Morita and Hiroike [17], Lebowitz and Percus [18], Mermin [19] and Ebner and Saam [20] among others. This eventually led to the expressions relating the surface tension to the direct correlation function $c^{(2)}(\vec{r}_1, \vec{r}_2)$, a function accounting for the direct influence between a pair of particles. Integral equations were developed in order to calculate the direct correlation function.

Furthermore, the development of the computer in the mid 20th century gave scientists a tool to actually simulate the microscopic world. Advanced simulation techniques have been developed over the years and put to use to describe many (soft matter) systems. Not only do these simulations seem to confirm many of the available theories, it also provides for an additional check for consistency of the results combined with the results obtained from experiments.

The focus in the last decades has shifted from a more fundamental to a more hybrid approach where attempts are made to accurately describe more complex systems, like polymeric and biological systems.

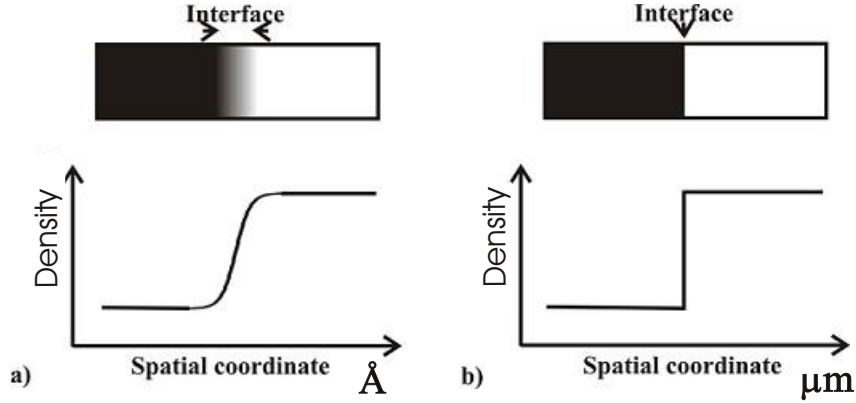


Figure 1.3 Illustration of an interface on (a) a molecular scale and (b) on a macroscopic scale.

1.2 Interfaces

The region in space which marks the boundary of two phases is called an interface. Most interfaces appear to be sharp to the naked eye but this is not the case on a molecular scale (Figure 1.3). There is a typical distance, ξ let's say, in which the concentration of particles changes from one bulk phase to another. In many systems, whether it be solid-liquid or liquid-vapour, this length is of molecular size. However, biological systems, such as phase separated biopolymer mixtures, exhibit larger interfacial thicknesses and this will lead to substantially different behaviour.

Thanks to the pioneering work of Gibbs [21], who introduced the concept of surface excess quantities, theoreticians are now able to thermodynamically describe this inhomogeneous region in space and to derive expressions for the thermodynamic quantities involved. Unfortunately, these excess quantities depend on the location of the dividing surface, the position of our mathematical description of the interface. We elaborate on this matter in chapters 2 and 3.

1.2.1 Curved Interfaces

Although Gibbs formulated a major part of the thermodynamics of curved interfaces, it was Tolman [22] who, in 1949, extended his theory for the case of spherically curved interfaces. Considering the thermodynamic description of a small liquid droplet, he found that the surface tension depends on the droplet radius R ,

$$\sigma(R) = \sigma \left(1 - \frac{2\delta}{R} + \dots \right), \quad (1.3)$$

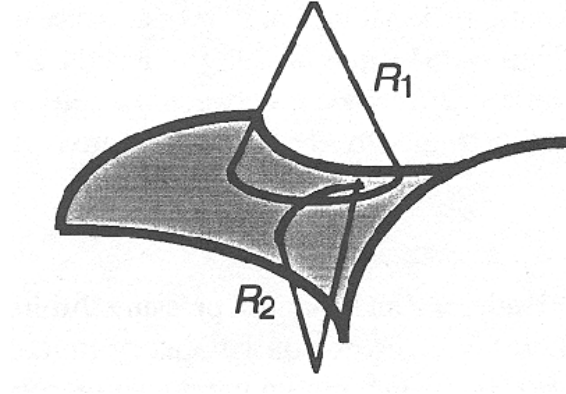


Figure 1.4 Principal radii of curvature, R_1 and R_2 .

where the coefficient to leading order in curvature, δ , is known as Tolman’s length. When the curvature is high (small droplets), curvature corrections are significant which is especially important in nucleation phenomena where the nucleation rate depends exponentially on the surface tension. The Tolman length will be discussed in chapter 2.

To describe the curvature in a point on a surface, two principal curvatures need to be introduced (see Figure 1.4). Here, R_1 and R_2 are called the principal radii of curvature. The “principal directions” corresponding to the principal radii of curvature are perpendicular to one another and perpendicular to the surface tangent plane at the point.

If we know the principal radii of curvature, we are able to calculate the total and Gaussian curvature of the surface. The total curvature is given by the sum of the two principal radii of curvature:

$$J = \frac{1}{R_1} + \frac{1}{R_2}. \quad (1.4)$$

Another useful quantity derived from the principal radii of curvature is the Gaussian curvature,

$$K = \frac{1}{R_1 R_2}, \quad (1.5)$$

which connects to the topology of the system. Both the total as well as the Gaussian curvature are intrinsic properties of the shape of the surface, independent of the coordinate system used to describe it. Note that a zero total curvature does not necessarily imply a flat surface: it simply means that the surface is *locally* flat.

1.2.2 Helfrich free energy

It was Helfrich [23] who realized that the surface free energy of arbitrarily shaped objects with large surface areas (like micelles, membranes, etc.) are well described by

an expansion to second order in curvature. If the surface tension of the membrane is low, these curvature corrections will dominate the shape and equilibrium properties. The Helfrich free energy is given by

$$F_H = \int dA \left[\sigma - 2\frac{k}{R_0}J + \frac{k}{2}J^2 + \bar{k}K \right]. \quad (1.6)$$

Here σ is the surface tension of the interface which, if the interface were to be flat, would be the only term in Eq.(1.6). For curved interfaces, three additional terms appear: the spontaneous curvature $1/R_0$, the rigidity constant of bending k (or just “rigidity”) and the rigidity constant associated with Gaussian curvature $\bar{k}$.

The spontaneous curvature $1/R_0$ indicates the preferred curvature of an interface. In other words, due to asymmetries an interface may favour one phase above the other and as a result will tend to bend towards one phase. The observed curvature of an interface may differ from the spontaneous curvature due to certain constraints. However, the equilibrium shape of the interface will always try to match the spontaneous curvature.

The bending rigidity k measures the free energy cost of bending the surface *without* stretching it. Large values for k will produce a stiffer interface whereas low values for k will produce an easily deformable interface. It is interesting to note that the radius of spontaneous curvature is also related to Tolman’s length according to

$$\sigma\delta = \frac{2k}{R_0}. \quad (1.7)$$

From this equation we can infer that the sign of the Tolman length is an indication towards which phase the interface bends when curved.

Finally, the rigidity associated with Gaussian curvature $\bar{k}$ is connected to the topology of the system. Positive values for $\bar{k}$ lead to a higher genus of the surface topology. In other words, continuous interfaces could be formed with cuttings along simple closed curves leading to structures with “holes” in them. Negative values of $\bar{k}$ lead to more closed shapes and will decrease the number of continuous structures.

Eq.(1.6) has proven its use for systems with low interfacial tension. Helfrich *et al.* [24] showed that the shapes of red blood cells were observed as the equilibrium shape of vesicles for certain values for the curvature parameters. Additionally, over the years increasing attention in the soft matter discipline has led to a number of applications of the Helfrich surface free energy [25–29].

1.3 Mean Field theory

Since we do not know the partition function of an arbitrary molecular system (and thus the free energy), scientists have to rely on approximations. One commonly employed approximation is the so called *mean-field approximation* or the assumption of the existence of a *mean molecular field* which originated in the 19th century from

the work of Laplace [5] and Rayleigh among others. The assumption made entails that the interaction of a molecule experienced by all the other molecules is replaced by an effective interaction. Although a crude approximation which renders the theory mere qualitative at best, it is often a good starting point in describing real systems. The intrinsic drawback of employing the mean-field approximation is that it fails to describe density fluctuations. In the vicinity of the critical point, where these fluctuations become especially important, the mean-field approximation breaks down completely. It is no surprise that in the field of statistical thermodynamics scientists are seeking to improve their description of a fluid's density by introducing correlation functions to account for these inhomogeneities.

Still, there are many problems which we cannot solve exactly in terms of closed expressions and even nowadays scientists have to resort to the mean-field approximation. In this thesis we will employ mean-field theory to obtain expressions for curvature parameters, phase diagrams and to gain insight in wetting/dewetting phenomena. Despite its apparent drawbacks, mean-field theory still provides useful insight in the qualitative features of a system and sometimes even semi-quantitative agreement with other experiments and/or simulations.

It is worth mentioning that alongside the mean-field approximation scientists often employ it together with the assumption of pairwise additivity, that is the assumption that the full interaction potential can be written as a sum over pair potentials. This assumption entails the neglect of many-body interactions which becomes an issue if densities are too high or in situations of spontaneous symmetry breaking: for instance when a liquid is brought into contact with an attractive substrate (chapter 4).

van der Waals [10] was one of the first to use the mean-field approximation in the field of statistical thermodynamics applying it to the liquid-vapour interface. Since his theory will be used throughout this thesis a brief summary is now presented.

1.3.1 van der Waals theory: square-gradient approach

In his thesis [10] van der Waals derived the now well-known van der Waals equation of state, relating the pressure to the fluid's density,

$$p = \frac{\rho k_B T}{1 - b\rho} - a\rho^2, \quad (1.8)$$

with ρ the density of the liquid, k_B Boltzmann's constant, T the temperature and where a and b are the usual van der Waals coefficients accounting for the attractive and repulsive interactions in the fluid, respectively. From the thermodynamic relationship $p = -(\partial F/\partial V)$, we can obtain the Helmholtz free energy density by integration:

$$f(\rho) \equiv \frac{F}{V} = \rho k_B T \ln \left(\frac{\rho}{1 - b\rho} \right) - a\rho^2. \quad (1.9)$$

For a liquid at coexistence with its vapour the thermodynamic potential of choice is the grand free energy density ²:

$$g(\rho) \equiv \frac{\Omega}{V} = f(\rho) - \mu\rho, \quad (1.10)$$

where μ denotes the chemical potential.

We now use this expression for the free energy density to describe a two-phase system at coexistence. The chemical potential is the same throughout the system $\mu = \mu_{\text{coex}}$ (just like the pressure p) and the density profile now only has a z -dependence, $\rho = \rho(z)$. For the van der Waals-model the surface grand free energy would then become

$$\frac{\Omega[\rho]}{A} = \int dz \left[\rho(z) k_B T \ln \left(\frac{\rho(z)}{1 - b\rho(z)} \right) - a\rho(z)^2 - \mu_{\text{coex}}\rho(z) + p \right], \quad (1.11)$$

with p the pressure and $A = \int dxdy$. Minimizing the above form for the free energy results in a sharp density profile $\rho(z)$, because only the bulk liquid or bulk vapour densities are found as solutions [15]. Calculating the free energy by inserting this density profile into Eq. (1.11) one obtains the surface tension, $\sigma = \frac{\Omega}{A}$. However, these density profiles yield a surface tension that is equal to zero.

To overcome this problem van der Waals added an extra term to Eq.(1.11) depending on the square of the density gradient:

$$\frac{\Omega[\rho]}{A} = \int dz \left(g(\rho) + m \left(\frac{d\rho}{dz} \right)^2 + p \right), \quad (1.12)$$

where m is a coefficient independent of ρ . Minimizing this expression using the Euler-Lagrange equation gives ³

$$2m\rho''(z) = g'(\rho). \quad (1.13)$$

Integrating this equation one gets

$$m(\rho'(z))^2 = g(\rho) + p. \quad (1.14)$$

In other words, Eq.(1.12) is a minimum when the free energy density and square-gradient terms are equal in magnitude. It is clear that this form for the free energy density will not produce sharp density profiles upon minimization; the square-gradient term would diverge!

In the vicinity of the critical point it is possible to use a simple double well form for the free energy density, $g(\rho)$,

$$g(\rho_c) = g(\rho_m) - \frac{m_c}{2\xi^2}(\rho_c - \rho_m)^2 + \frac{m_c}{(\Delta\rho)^2\xi^2}(\rho_c - \rho_m)^4, \quad (1.15)$$

²When we refer to a free energy density we mean the grand free energy density hereafter unless stated otherwise.

³ unless indicated otherwise primes indicate a differentiation towards their arguments

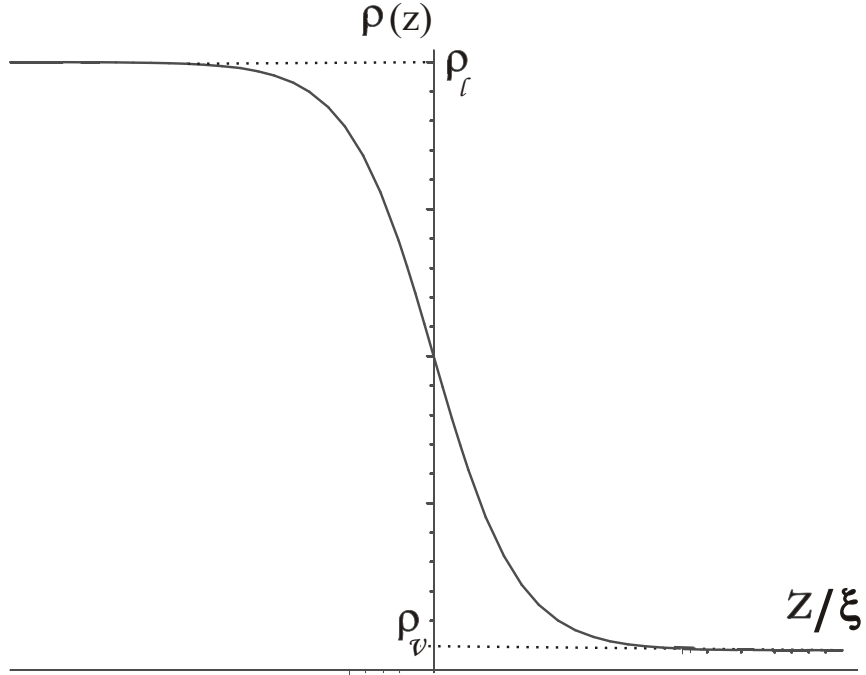


Figure 1.5 The *tanh*-density profile. The convention is that $\rho(-\infty) = \rho_\ell$.

where $\rho_m = \frac{1}{2}(\rho_\ell + \rho_v)$, $\Delta\rho = \rho_\ell - \rho_v$ and the constant m_c is given by the value of m at the critical point.

When minimizing Eq. (1.12) using Eq. (1.15) for $g(\rho)$ one finds an analytic solution for the density profile:

$$\rho(z) = \frac{1}{2}(\rho_\ell + \rho_v) - \frac{\Delta\rho}{2} \tanh\left(\frac{z}{2\xi}\right), \quad (1.16)$$

where ξ is the correlation length (the typical width of the interface), ρ_ℓ and ρ_v denote the bulk liquid and vapour densities at coexistence. Figure 1.5 displays such a density profile and one can see that values in between the bulk liquid and bulk vapour densities are found in the interfacial region. These types of density profiles yield nonzero surface tensions.

1.4 Outline of this Thesis

This thesis deals with the interfacial properties of fluid interfaces. The goal is to gain insight into the rich world of interfacial phenomena and to gain a better understanding of the important parameters describing the systems involved. Starting off with describing the interfacial properties of inhomogeneous simple fluids, later chapters will deal with describing the interfacial properties of complex fluids.

Chapter 2 deals with the leading order correction to the surface tension for curved interfaces, the Tolman length. Important for nucleation phenomena (small droplets) and curved systems the Tolman length has been extensively studied in the past but there are still some issues unresolved which will be addressed. Formal thermodynamic relations are presented and are compared with previous analyses. The magnitude of the Tolman length is determined within the context of van der Waals' square-gradient theory.

Then in chapter 3 the interfacial properties of a fluid in contact with both planar and curved hard walls are investigated. The validity of the so called wall theorem is examined and it is shown that it can break down while the requirement of mechanical equilibrium remains valid. The density profiles, surface tension and Tolman length are calculated using square-gradient theory and density functional theory with a non-local, integral expression for the interaction between molecules.

When a liquid is brought into contact with a substrate, it can either wet or partially wet the surface. These so called wetting/dewetting transitions are investigated in detail in chapter 4. Expanding the theoretical framework put down in chapter 3 to the case of attractive substrates we are able to compare the commonly applied theory of Nakanishi and Fisher with mean-field models to provide expressions for the parameters entering the theory. Wetting phase diagrams are calculated and compared with the results predicted by the theory of Nakanishi and Fisher and simulations.

Recently, phase separated colloid-polymer mixtures have received considerable experimental and theoretical attention. A sufficient amount of non-adsorbing polymeric particles effectively drives the colloidal particles together to form a phase separated mixture. The interfacial region of this multicomponent mixture is studied in detail in chapter 5. The surface tension and bending rigidity are calculated using density functional theory and a virial approach. These results are compared with simulation results.

Using the results obtained in chapter 4 we study wetting/dewetting transitions in phase separated colloid-polymer mixtures in chapter 6. We employ free volume theory in order to compare our findings with previous calculations.

Then in the final chapter 7 a theoretical treatment of the class of Pickering emulsions is presented. A theory is proposed for the surface tension in these systems in the spirit of work done in the context of microemulsions based upon Gibbs' adsorption equation.

Chapter 2

Thermodynamic Expressions for the Tolman length

ABSTRACT

The Tolman length measures the extent to which the surface tension of a small droplet deviates from its planar value. Recent thermodynamic treatments have proposed a relation between the Tolman length and the isothermal compressibility of the liquid phase at two-phase coexistence, $\delta \approx -\sigma\kappa_\ell$. In this chapter we review this analysis and show how it relates to earlier thermodynamic expressions. Its applicability is discussed in the context of van der Waals' square-gradient theory. It is found that the relation is semiquantitatively correct for this model unless one is too close to the critical point.

2.1 Introduction

When we consider a simple liquid in equilibrium with its vapour, one thermodynamic parameter, the surface tension σ , is sufficient to describe the planar interface between both phases. The grand potential for such a situation can be written as

$$\Omega = -pV_\ell - pV_v + \sigma A, \quad (2.1)$$

where V_ℓ, V_v denote the volumes of the liquid and vapour phase respectively, p is the pressure (at mechanical equilibrium the same throughout the system) and A denotes the interfacial area. The exact position of the dividing surface is not known since on a molecular scale the interface is rough and fluctuating, however the area A and total volume ($V_\ell + V_v$) in Eq. (2.1) are invariant to the choice of the dividing surface so σ in Eq. (2.1) is well-defined.

The situation for curved interfaces is somewhat different. Curved interfaces appear when considering nucleation, where small vapour/liquid droplets are being formed or when fluids are being confined, for example. The pressures in both phases are now not equal and both the sum ($p_\ell V_\ell + p_v V_v$) and A are no longer invariant anymore upon changing the location of the dividing surface.

Gibbs [30] formulated a major part of the novel thermodynamics of curved surfaces but it was Tolman [22] who took the ideas of Gibbs further and worked them out extensively for spherical surfaces. Tolman realized that the surface tension for small droplets needs curvature corrections [22]. To leading order in an expansion in curvature $1/R$, where R is given by the equimolar radius of the droplet, it is given by,

$$\Delta p = \frac{2\sigma}{R} \left(1 - \frac{\delta}{R} + \dots \right), \quad (2.2)$$

where $\Delta p = p_\ell - p_v$ is the pressure difference between the inside and outside of the drop and σ is the surface tension of the planar interface. The first term in Eq.(2.2) is the well-known Laplace equation [15] with the leading order term in curvature defining the Tolman length δ . Alternatively, one can expand the surface tension itself to leading order in curvature $1/R$ in terms of the droplet radius R :

$$\sigma(R) = \sigma \left(1 - \frac{2\delta}{R} + \dots \right). \quad (2.3)$$

Note that $\sigma(R)$ denotes the surface tension of a liquid drop with radius R , whereas σ denotes its value in the planar limit. In this definition, and the one in Eq.(2.2), the Tolman length is defined as a coefficient in an expansion in $1/R$ and therefore does not depend on R . In the literature one may find definitions of the Tolman length in which $\delta = \delta(R)$ to account not only for deviations with the planar limit to *leading order* in $1/R$, but to *all order* in $1/R$. A legitimate question then addresses the accuracy of truncating the expansion at first order [31,32]. Here, we shall not pursue this line of

research limiting our discussion strictly to the limit $\delta = \lim_{R \rightarrow \infty} \delta(R)$, so to say, keeping in mind that in this limit results should be consistent.

The definition in Eq.(2.3) shows that the surface tension deviates from its planar value when the droplet radius is of the order of Tolman's length. Since any (small) radius dependence of the surface tension influences the nucleation rate exponentially, experimental interest has come from the description of nucleation phenomena [33].

From a theoretical side the Tolman length has been studied by many people but some (still) unresolved issues arise. We will now briefly discuss four such issues.

Critical Exponents It is well established that the mean-field exponent for the Tolman length has the borderline value of zero [34]. What that implies for the behaviour of the Tolman length near the critical point for a real fluid is therefore quite sensitive to the value of the critical exponent going beyond mean-field. The Tolman length might diverge algebraically, diverge logarithmically, become zero or reach some finite value. Phillips and Mohanty [35] argued that it diverges in the same manner as the correlation length ($t^{-\nu}$), but most authors now believe that if the Tolman length diverges, it does so with an exponent close to zero [34,36,37]. Using complete scaling Anisimov [38] recently showed that the Tolman length diverges more strongly than expected upon approach to the critical point depending on the degree of asymmetry between the liquid and vapour phase. We will come back to this point in the discussion.

Sign of δ for a simple liquid Of late, much theoretical work on the Tolman length has been carried out in the context of density functional theories [31,32,39–49]. These theories give consistent results with regard to the mean-field value of the Tolman length for simple liquids: it is only weakly temperature dependent reaching a value at the critical point which is small (a fraction of a molecule's diameter) and *negative*. The few MD simulations that have been carried out for a Lennard-Jones system, however, seem to indicate that the Tolman length is *positive* although of the same order of magnitude as in the density functional theories [50–53].

Recent MD simulations furthermore indicate that the Tolman length sensitively depends on the interaction potential [54]. The discrepancy in sign and its dependence on the interaction potential is not understood. Further MD simulations should help to resolve these issues.

Mechanical expressions When obtaining the surface tension from computer simulations one often falls back to the use of mechanical expressions relating the surface tension to the integral of the difference between the normal and tangential components of the pressure tensor [15]. There is no unique choice for the pressure tensor [55] but it was shown that the actual choice did not alter the values of the surface tension [15]. In the same line of thought a similar method for the Tolman length was devised relating the surface tension to an integral of the first moment of the excess

tangential pressure of a planar interface. However, it was shown by Henderson and Schofield [56,57] that the first moment is dependent on the actual choice of the pressure tensor and this makes such a mechanical expression for the Tolman length not well defined. Later it was also shown that the Tolman length evaluated in this way using the ‘normal’ Irving-Kirkwood form for the pressure tensor is inconsistent with a more direct virial approach which avoids the use of a pressure tensor [58].

It is now well-established that the mechanical expression for the Tolman length is not well-defined [58–60]. However, in the context of *local theories*, i.e. theories in which the free energy depends only on one position, and not, as for the pressure tensor, on two positions (the positions of the two interacting molecules), the Tolman length can indeed be written as the first moment of the surface free energy density [61]. An example of such an expression is given in section 2.4.

Fluctuation route – Triezenberg-Zwanzig Examining the liquid interface from a completely different perspective, in 1972 Triezenberg and Zwanzig derived a formal expression for the surface tension expressing it in terms of the direct correlation function in the two-phase region by examining the restoring force associated with thermal fluctuations of the interface [62]. As of yet, no analog prescription for the Tolman length exists and this lead people to believe [56,59,60] that this “fluctuation route” is fundamentally different for curved interfaces than for planar ones.

It is now known that different thermodynamic conditions to induce interfacial curvature may lead to different values for curvature coefficients not only for the Tolman length, but also for the second order curvature coefficients [63,64]. From quite a different perspective, Helfrich expanded the surface free energy of an arbitrarily curved surface to second order in the curvature [23]

$$F_H = \int dA \left[\sigma - 2 \frac{k}{R_0} J + \frac{k}{2} J^2 + \bar{k} K \right]. \quad (2.4)$$

In this expression $J = \frac{1}{R_1} + \frac{1}{R_2}$, the total curvature, $K = \frac{1}{R_1 R_2}$, the Gaussian curvature with R_1 and R_2 the radii of curvature at a point on the surface. The expansion coefficients are R_0 , the radius of spontaneous curvature, k , the rigidity constant associated with bending and $\bar{k}$, the rigidity constant associated with Gaussian curvature. Many people have shown Eq.(2.4) to be a suitable choice in describing systems where the surface tension does not play a dominant role [23,26,65].

Even though it was set up in a different context, the Helfrich expansion is analogous to the expansion made by Tolman to first order and for a spherical surface (where $J = \frac{2}{R}$) comparing the first order terms in Eqs.(2.2) and ??eq:sigmaR) one finds [58]

$$\sigma \delta = \frac{2k}{R_0}. \quad (2.5)$$

This equation connects the Tolman length to the radius of spontaneous curvature. Assuming a positive rigidity ($k > 0$), a positive Tolman length would imply positive

values for R_0 which indicates a preferred curvature towards the liquid phase whereas negative values for the Tolman length would result in a tendency for the interface to curve toward the vapour phase.

The Tolman length can also be related to the *surface of tension* [15,22], the surface for which the Laplace equation holds exactly for all drop radii:

$$\Delta p = \frac{2\sigma_s}{R_s}, \quad (2.6)$$

where $\sigma_s = \sigma(R = R_s)$ is the surface tension at the surface of tension. Tolman himself showed [22] that the Tolman length could be related to the adsorbed amount at the interface at coexistence

$$\delta = \frac{\Gamma}{\Delta\rho_0}, \quad (2.7)$$

with $\Delta\rho_0 = \rho_{0,\ell} - \rho_{0,v}$ where the subscript zero denotes the value of the density at two-phase coexistence. In the next section we will show that this results leads to another definition of the Tolman length:

$$\delta = \lim_{R \rightarrow \infty} (R - R_s) = z_e - z_s, \quad (2.8)$$

where the heights z_e and z_s denote the locations of the equimolar surface and the surface of tension respectively. Although these definitions do not lend themselves well for direct numerical results without a specific microscopic model, it does connect the Tolman length to different thermodynamic quantities (radius of spontaneous curvature, adsorption, etc.).

Recently, one such thermodynamic treatment was postulated by Bartell [66], in which an approximate expression for the Tolman length was derived in terms of the isothermal macroscopic compressibility of the liquid phase, κ_ℓ , at liquid-vapour coexistence:

$$\delta \approx -\kappa_\ell \sigma. \quad (2.9)$$

In this chapter we will show how this expression relates to previous thermodynamic expressions and we will test its validity in the context van der Waals' square-gradient theory.

In the next session we start by a review of Tolman's thermodynamic analysis and we will present a formal systematic expansion in curvature in order to link the Tolman length to the second order coefficient of the chemical potential in an expansion in curvature. In section 2.3 we will review the connection between the Tolman length and the isothermal compressibility of the liquid phase and in section 2.4 the applicability of these expressions is tested using a van der Waals liquid-vapour system as an example. We finish with some conclusions.

2.2 Thermodynamics

Figure 2.1 shows the appropriate thermodynamic conditions in a schematic way. Shown is the two-phase coexistence line as a function of chemical potential and tem-

perature along which $\mu = \mu_{\text{coex}}(T)$. At two-phase coexistence both phases have the same chemical potential and bulk pressure and there they coexist with a planar interface between them. By raising the chemical potential at constant temperature (depicted by the dashed arrow in Figure 2.1) the liquid phase will become the more stable phase. In this region we will consider the formation of a critical nucleus with an equimolar radius of R and surrounded by metastable vapour. This is the typical situation considered in the description of nucleation [33]. While making sure we do

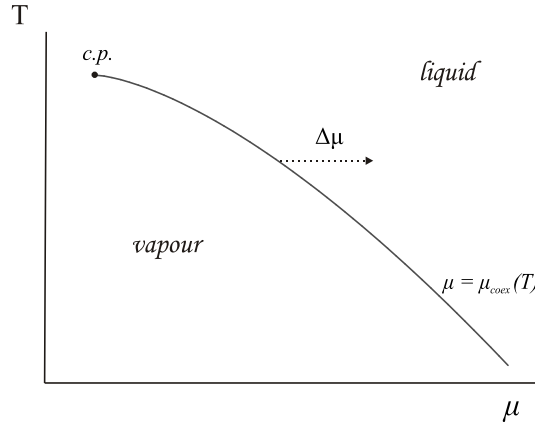


Figure 2.1 Schematic phase diagram for a liquid-vapour system as a function of μ and T . The solid line is the locus of liquid-vapour coexistence, $\mu = \mu_{\text{coex}}(T)$, ending at the critical point ($\mu = \mu_c$, $T = T_c$). The dashed line is a path in the phase diagram for fixed temperature and varying chemical potential $\Delta\mu = \mu - \mu_{\text{coex}}$, along which a liquid droplet in a metastable vapour is considered.

not cross the spinodal, the radius R is well defined in this region approaching infinity when $\mu \rightarrow \mu_{\text{coex}}$. This suggests that instead of μ we could take $1/R$ as variable to indicate the amount we are brought off-coexistence.

Thermodynamics relates the density to changes in the chemical potential when changing pressure:

$$\frac{1}{\rho} = \left(\frac{\partial \mu}{\partial p} \right)_T. \quad (2.10)$$

Alternatively, when changing the chemical potential along the path depicted in Figure 2.1, the pressure in either phase changes according to

$$dp_{\ell,v} = \rho_{\ell,v} d\mu, \quad (2.11)$$

where the subscripts ℓ, v denote the liquid or vapour phase respectively. The pressure difference across the droplet is then given by

$$d(\Delta p) = \Delta \rho d\mu, \quad (2.12)$$

This expression is valid along the whole path sketched in Figure 2.1 but we now consider the case where $\Delta\mu$ is small, i.e. we consider changes infinitesimally close to the coexistence line. Inserting Eq.(2.6) and the Gibbs adsorption equation $d\sigma_s = -\Gamma_s d\mu$ (chosen at the surface of tension) in Eq.(2.12) one finds

$$d\left(\frac{2\sigma_s}{R_s}\right) = -\frac{\Delta\rho}{\Gamma_s} d\sigma_s. \quad (2.13)$$

To leading order in $1/R_s$ this becomes

$$d\left(\frac{2\sigma}{R_s} + \dots\right) = -\left(\frac{\Delta\rho_0}{\Gamma_s} + \dots\right) d\left(\sigma - \frac{2\delta\sigma}{R_s} + \dots\right). \quad (2.14)$$

So that

$$\delta = \frac{\Gamma_s}{\Delta\rho_0}, \quad (2.15)$$

which is the same definition Tolman used in his original work [22]. Note that Γ_s is the adsorption at the surface of tension at two-phase coexistence.

To evaluate the adsorption we write out its definition in terms of the density profile $\rho_0(z)$ at two-phase coexistence,

$$\Gamma_s = \int_{-\infty}^{\infty} dz [\rho_0(z) - \rho_{\ell,0}\Theta(-z + z_s) - \rho_{v,0}\Theta(z - z_s)], \quad (2.16)$$

where $\Theta(x)$ is the Heaviside function and z_s denotes the location of the surface of tension. The coordinate z is the direction perpendicular to the (planar) interface and we adopt the convention that the integration runs from the liquid phase ($z = -\infty$) to the vapour phase ($z = \infty$). If we let z_e denote the location the equimolar surface, we have

$$\Gamma_e \equiv 0 = \int_{-\infty}^{\infty} dz [\rho_0(z) - \rho_{\ell,0}\Theta(-z + z_e) - \rho_{v,0}\Theta(z - z_e)]. \quad (2.17)$$

Subtracting these two expressions for the adsorption and carrying out the integration over z yields

$$\Gamma_s = \Delta\rho_0(z_e - z_s). \quad (2.18)$$

Inserting this into Eq.(2.15) one arrives at:

$$\delta = (z_e - z_s), \quad (2.19)$$

which is the same result as Eq.(2.8).

Starting with Eq.(2.12) one can also expand to second order in $1/R$ to obtain

$$\begin{aligned} & d\left(\frac{2\sigma}{R} - \frac{2\sigma\delta}{R^2} + \dots\right) \\ &= \left(\Delta\rho_0 + \frac{\Delta\rho_1}{R} + \dots\right) d\left(\mu_{\text{coex}} + \frac{\mu_1}{R} + \frac{\mu_2}{R^2} + \dots\right). \end{aligned} \quad (2.20)$$

After some regrouping the two leading order terms in $1/R$ are

$$\begin{aligned}\mu_1 &= \frac{2\sigma}{\Delta\rho_0} \\ \mu_2 &= -\frac{2\sigma\delta}{\Delta\rho_0} - \frac{\mu_1\Delta\rho_1}{2\Delta\rho_0}.\end{aligned}\tag{2.21}$$

The latter can be rewritten as

$$\mu_2 = -\frac{2\sigma\delta}{\Delta\rho_0} - \frac{\sigma\Delta\rho_1}{(\Delta\rho_0)^2}.\tag{2.22}$$

We now have found an expression for the Tolman length:

$$\delta = -\frac{\Delta\rho_1}{2\Delta\rho_0} - \frac{\mu_2\Delta\rho_0}{2\sigma}.\tag{2.23}$$

This derivation appeared previously in the literature starting from the free-energy density [34, 67, 68]. We give a brief summary of this alternative derivation in appendix A.

Just as a microscopic model is needed to evaluate the location of the surface of tension in order to make use of the definition in Eq.(2.19), Eq.(2.23) requires the knowledge of μ_2 in order to calculate δ . In the next section we will focus on the necessary approximations in order to link the Tolman length to the isothermal compressibility.

2.3 Relation with the isothermal compressibility of the liquid

The isothermal compressibility κ in the fluid phase reads

$$\kappa \equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T = \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial \mu} \right)_T.\tag{2.24}$$

Again we consider an infinitesimal change from two-phase coexistence along the path sketched in Figure 2.1. To leading order in $1/R$ one finds that

$$\left(\frac{\partial \rho}{\partial \mu} \right) = \frac{\rho_1}{R} / \frac{\mu_1}{R} = \frac{\rho_1}{\mu_1}.\tag{2.25}$$

Now Eq.(2.24) can be written as

$$\begin{aligned}\kappa_\ell &= \frac{1}{\rho_{\ell,0}^2} \frac{\rho_{\ell,1}}{\mu_1} = \frac{\rho_{\ell,1}\Delta\rho_0}{2\sigma\rho_{\ell,0}^2}, \\ \kappa_v &= \frac{1}{\rho_{v,0}^2} \frac{\rho_{v,1}}{\mu_1} = \frac{\rho_{v,1}\Delta\rho_0}{2\sigma\rho_{v,0}^2},\end{aligned}\tag{2.26}$$

where $\kappa_{\ell,v}$ denotes the isothermal compressibility in the bulk liquid and vapour phases respectively at coexistence. We may use Eq.(2.26) to rewrite $\Delta\rho_1 = \rho_{\ell,1} - \rho_{v,1}$ as

$$\Delta\rho_1 = \frac{2\sigma}{\Delta\rho_0} [\rho_{\ell,0}^2 \kappa_\ell - \rho_{v,0}^2 \kappa_v]. \quad (2.27)$$

Inserting Eq. (2.27) into the definition of δ in Eq. (2.23) one obtains

$$\delta = -\frac{\sigma}{(\Delta\rho_0)^2} [\rho_{\ell,0}^2 \kappa_\ell - \rho_{v,0}^2 \kappa_v] - \frac{\mu_2 \Delta\rho_0}{2\sigma}. \quad (2.28)$$

This thermodynamically exact relation describes δ in terms of the compressibility of the bulk phases instead of $\Delta\rho_1$.

The remainder of this section deals with the analysis made by Bartell [66], which in turn is inspired by a previous analysis done by Laasonen and McGraw [69], that proposes an approximate expression for the Tolman length in terms of the isothermal compressibility of only the liquid phase.

In order to understand the derivation made by Bartell [66] we turn to the integral form of Eq.(2.10) in the liquid phase:

$$\Delta\mu = \mu - \mu_{\text{coex}} = \int_{p_{\text{coex}}}^p dp \left(\frac{1}{\rho_\ell} \right). \quad (2.29)$$

When we consider infinitesimal changes from coexistence (i.e. $\Delta\mu$ small) one may approximate the bulk liquid density by its value at two-phase coexistence to leading in $1/R$ by, $\rho_\ell \approx \rho_{\ell,0}$ and use the Laplace equation for the pressure in the liquid phase, $p_\ell \approx p_v + \frac{2\sigma}{R}$ so that,

$$\Delta\mu \approx \frac{1}{\rho_{\ell,0}} \left(\frac{2\sigma}{R} + p_v - p_{\text{coex}} \right) \quad \text{correct to } \mathcal{O}\left(\frac{1}{R}\right). \quad (2.30)$$

When considering the next-to leading order term, the Laplace equation gets a correction and the liquid density becomes a function of R . We find

$$\Delta\mu \approx \frac{1}{2} \left(\frac{1}{\rho_\ell} + \frac{1}{\rho_{\ell,0}} \right) \left(\frac{2\sigma}{R} - \frac{2\sigma}{R^2} + p_v - p_{\text{coex}} \right) \quad (2.31)$$

correct to $\mathcal{O}\left(\frac{1}{R^2}\right)$.

Next, the analysis by Bartell [66] introduces two assumptions. First the vapour density is neglected. As a consequence any curvature dependence of the pressure and density in the vapour phase also disappears. One would expect this assumption to break down in the vicinity of the critical point. Second, it is argued [66] that Eq.(2.29) has a wider range of validity than just to first order in $1/R$. The result is that the Tolman length should cancel the leading curvature variation of the liquid

density. Neglecting the vapour density and equating Eqs.(2.29 and 2.30) then result in [66]

$$\delta \approx -\frac{\rho_1}{2\rho_{0,\ell}}. \quad (2.32)$$

If we now employ the same assumptions on the compressibility of the liquid phase, Eq.(2.24) we have

$$\kappa_\ell = \frac{\rho_{1,\ell}\Delta\rho_0}{2\sigma\rho_{\ell,0}^2} \approx \frac{\rho_{\ell,1}}{2\sigma\rho_{\ell,0}}, \quad (2.33)$$

which leads to [66]

$$\delta \approx -\sigma\kappa_\ell. \quad (2.34)$$

This is the expression derived in the analysis done by Bartell [66]. It can also be derived from the thermodynamically exact relation Eq.(2.23). The previous approximations imply setting $\mu_2 = 0$ and $\rho_v = 0$ in Eq.(2.23) to obtain the above result. In order to gain more insight in the validity of these approximations, especially setting $\mu_2 = 0$, we evaluate the Tolman length in the context of van der Waals' square-gradient theory in the next section.

2.4 The Tolman length using the van der Waals equation of state

In this section we turn to the explicit evaluation of the Tolman length in the context of van der Waals' square-gradient theory [15]. The grand free energy is given by the following functional form [15]:

$$\Omega[\rho(\mathbf{r})] = \int d\mathbf{r} \left[m|\nabla\rho(\mathbf{r})|^2 + g(\rho) \right], \quad (2.35)$$

where m is the usual coefficient of the square-gradient term and $g(\rho)$ is the grand free energy density for a fluid constrained to have uniform density ρ . The density profile $\rho_0(z)$ for the liquid and vapour at two-phase coexistence can be obtained by a functional minimization of Eq. (2.35). Then the surface tension and Tolman length can be expressed in terms of $\rho_0(z)$ [15, 67]:

$$\begin{aligned} \sigma &= 2m \int_{-\infty}^{\infty} dz [\rho'_0(z)]^2, \\ \sigma\delta &= 2m \int_{-\infty}^{\infty} dz (z - z_e) [\rho'_0(z)]^2, \end{aligned} \quad (2.36)$$

where the location of the equimolar surface z_e is determined by the condition in Eq.(2.17).

In order to determine the density profile a specific model for $g(\rho)$ needs to be chosen. Before we take the van der Waals equation of state, it is instructive to consider the results when one assumes for $g(\rho)$ a double parabola.

Results for double parabola as free energy The grand free energy density is given by

$$g(\rho) + p_{coex} = \begin{cases} \frac{1}{2\rho_{v,0}^2\kappa_v} (\rho - \rho_{v,0})^2 & \text{when } \rho < \rho_m, \\ \frac{1}{2\rho_{\ell,0}^2\kappa_\ell} (\rho - \rho_{\ell,0})^2 & \text{when } \rho > \rho_m, \end{cases} \quad (2.37)$$

where ρ_m is the density where the two parabola meet. The curvature of the parabola is directly related to the compressibility, $g'' = 1/(\rho^2\kappa)$. Iwamatsu [39] used this form of the free energy to determine the surface tension and the Tolman length. They obtained

$$\begin{aligned} \sigma &= \left(\frac{m}{2}\right)^{1/2} \frac{(\Delta\rho_0)^2}{(\rho_{\ell,0}\sqrt{\kappa_\ell} + \rho_{v,0}\sqrt{\kappa_v})}, \\ \delta &= \left(\frac{m}{2}\right)^{1/2} (\rho_{v,0}\sqrt{\kappa_v} - \rho_{\ell,0}\sqrt{\kappa_\ell}). \end{aligned} \quad (2.38)$$

It can be shown that the quadratic form for the free energy in Eq.(2.37) yields $\mu_2 = 0$. If one then also neglects the vapour density (i.e. $\rho_v = 0$), it immediately follows that $\delta = -\kappa_\ell\sigma$ holds for this model.

Unfortunately, this double-well form for the free energy is not able to describe the behaviour near the critical point. The free energy derived from the van der Waals equation of state *does* describe the critical point albeit in a mean-field manner,

$$g(\rho) = -k_B T \ln\left(\frac{1/\rho - b}{\Lambda^3/e}\right) - a\rho^2 - \mu_{coex}\rho. \quad (2.39)$$

Here a and b are the usual van der Waals parameters and Λ is the de Broglie thermal wavelength.

We have solved for the density profile using the above van der Waals free energy numerically and plotted the results for δ in Figure 2.2. At the critical point δ reaches a finite negative value [34, 40]

$$\begin{aligned} \delta &= -\frac{1}{12} \left(\frac{2m}{a}\right)^{1/2} \quad (T \rightarrow T_c), \\ \sigma &= \sigma_0 t^{3/2} = \frac{16a}{27b^2} \left(\frac{2m}{a}\right)^{1/2} t^{3/2}, \end{aligned} \quad (2.40)$$

where $t \equiv 1 - T/T_c$ is the reduced temperature distance to the critical point. This result may also be written as

$$\delta = -\frac{\sigma_0}{192p_c}, \quad (2.41)$$

where the critical pressure in the fluid phase according to the van der Waals model is given by $p_c = a/(27b^2)$ (this prefactor of $-1/192$ differs from that quoted in ref. [70]). The dotted curve in Figure 2.2 gives the contribution to δ derived from setting $\mu_2 = 0$ in Eq.(2.28),

$$\delta \approx -\frac{\sigma}{(\Delta\rho_0)^2} [\rho_{\ell,0}^2\kappa_\ell - \rho_{v,0}^2\kappa_v]. \quad (2.42)$$

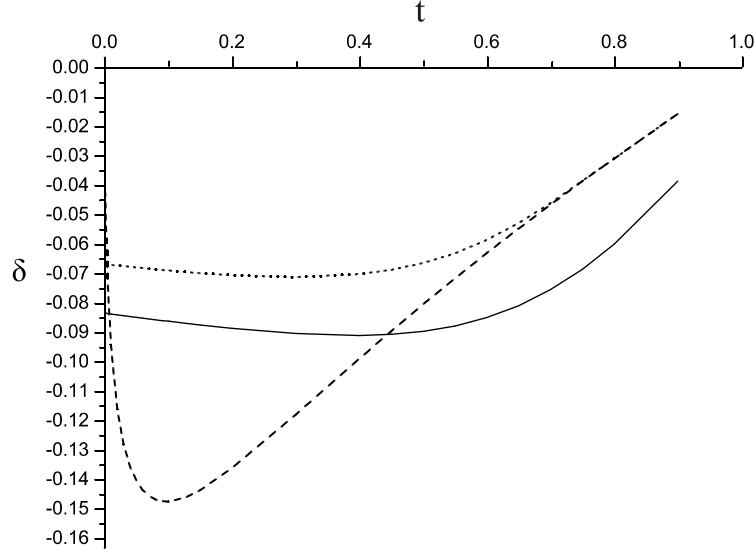


Figure 2.2 Tolman length in units of $(2m/a)^{1/2}$ as a function of reduced temperature $t \equiv 1 - T/T_c$. The solid line is the result obtained from the numerical solution of the square-gradient model using the van der Waals equation of state. The dotted line is the approximate expression for δ in Eq.(2.42). The dashed line is the approximation $\delta \approx -\kappa_\ell\sigma$ with κ_ℓ taken from the van der Waals equation of state.

One concludes from Figure 2.2 that this approximation describes the qualitative features of δ rather well and is quantitatively correct within 25% in the entire temperature range considered. Far from the critical point the vapour density becomes negligible and Eq.(2.42) reduces to the formula proposed by Bartell [66]

$$\delta \approx -\kappa_\ell\sigma. \quad (2.43)$$

This relation is shown in Figure 2.2 as the dashed line. It is clear that the approximation breaks down close to the critical point, but it is qualitatively correct far away from it. Both approximations in Eqs.(2.42) and (2.43) thus capture the order of magnitude and sign of the full mean-field solution.

2.5 Discussion

In this chapter, we have reviewed thermodynamic relations for the Tolman length. Such relations are useful in providing a framework for mathematical modeling. We saw that the surface tension itself may depend on curvature and thermodynamics gives us the tools to provide expressions for the curvature coefficients. The validity of such an expansion in curvature can be questioned (see chapter 3), but in the

case of bringing a liquid-vapour system off-coexistence by a small amount (i.e. $\Delta\mu$ small) Tolman's expansion (truncated at the first order term) provides a satisfactory description for the liquid drop.

We have investigated expressions for the Tolman length that involve the isothermal compressibility of the liquid, and tested their applicability in the context of the square-gradient model for the liquid-vapour interface. The main results of this investigation are shown in Figure 2.2. It should be kept in mind that any conclusions drawn from this Figure are made strictly in the context of the mean-field model. An important observation is that the approximate expressions for δ in Eqs.(2.42) and (2.43) do capture the order of magnitude and sign of the full mean-field solution. In these expressions the *sign* of Tolman's length is determined by the difference between the liquid and vapour phase of the symmetrized compressibility $\chi \equiv \rho^2 \kappa$; since $\chi_\ell > \chi_v$ the Tolman length is negative. This observation was first made by Iwamatsu [39] using the double-well form for the free energy density for which the approximation Eq.(2.42) holds exactly.

It is tempting to infer from the expression for δ in Eq.(2.42) the critical behaviour of Tolman's length beyond mean-field theory. The assumption then implicitly made is that the term involving μ_2 in the full expression for δ in Eq.(2.28) is sub-dominant near the critical point, or – as is the case for the square-gradient mean-field model – has the same leading critical behaviour as the contribution to δ in Eq.(2.42). The critical behaviour of the compressibility χ in the coexisting liquid and vapour phase is described by the following form [71]

$$\begin{aligned}\chi_\ell &= \chi_0 t^{-\gamma} \left(1 + \alpha_\ell t^{-\Delta} + \dots\right), \\ \chi_v &= \chi_0 t^{-\gamma} \left(1 + \alpha_v t^{-\Delta} + \dots\right).\end{aligned}\tag{2.44}$$

The leading critical behaviour of the symmetrized compressibility, as described by the prefactor χ_0 and the critical exponent $\gamma \approx 1.24$, is the same for χ_ℓ and χ_v . Since $\delta \propto \chi_v - \chi_\ell$, the critical behaviour of the Tolman length is determined by the leading order corrections as described by the dimensionless prefactors α_ℓ and α_v and the gap-exponent $\Delta \approx -0.50$ [71]. We thus find from Eq.(2.42):

$$\delta \propto t^{\mu-2\beta-\gamma-\Delta} \propto t^{-\Delta-\nu} \propto t^{-0.13},\tag{2.45}$$

where $\mu \approx 1.26$, $\nu \approx 0.63$, and $\beta \approx 0.325$ are the usual critical exponents for the surface tension, correlation length and density difference, respectively [15].

As a result we find that the Tolman length diverges weakly on approach to the critical point, which is in line with previous predictions [34, 36, 37, 53]. The result $\delta \propto t^{-\Delta-\nu}$ is also consistent with the mean-field critical behaviour for δ in the van der Waals model as given in Eq.(2.40) (i.e. $\delta \propto \text{constant}$), when one inserts the mean-field value for the exponents $\nu = 1/2$ and $\Delta = -1/2$.

As a final point we like to point out the recent results given by Anisimov [38] obtained using complete scaling [72]. Starting from the generalized Laplace equation

Eq. (2.2), the pressure difference in and outside the liquid drop is separated into a symmetric and antisymmetric part ¹:

$$\Delta p = (\Delta p)_{\text{sym}} + (\Delta p)_{\text{asym}} \quad (2.46)$$

Since the Tolman length depends on the asymmetric part only to a first approximation δ can be written as

$$\frac{2\delta}{R} \simeq -\frac{(\Delta p)_{\text{asym}}}{(\Delta p)_{\text{sym}}}. \quad (2.47)$$

In the vicinity of the critical point the pressure difference scales as $(\Delta p)_{\text{crit}} \approx \chi(\Delta\mu)^2$ and accordingly the isothermal compressibility χ (the susceptibility with respect to density fluctuations) can again be separated into a symmetric and asymmetric part. Using expressions for the susceptibility obtained earlier from complete scaling allowed for the expansion of the Tolman length valid in the vicinity of the critical point:

$$\delta \propto \text{constant}_1 t^{\beta-\nu} + \text{constant}_2 t^{1-\alpha-\beta-\nu}, \quad (2.48)$$

where $\alpha \simeq 0.109$ is a universal critical Ising exponent. Since $1 - \alpha - \beta - \nu \simeq -0.065$ the first term (only present when using complete scaling) in Eq. (2.48) diverges more strongly ($\beta - \nu \simeq -0.304^2$) and will determine the leading order behaviour upon approaching the critical point. This result implies that in highly asymmetric fluids (like high molecular weight hydrocarbons or ionic fluids) the Tolman length can easily reach a substantial magnitude.

It should be kept in mind however that faraway from the critical point the Tolman's length is only a small fraction of the molecular dimensions and in order to observe noticeable changes in the surface tension one needs a nanosize droplet.

¹The part of Δp which does not depend on which fluid phase resides within or outside the droplet is the symmetric part.

²More thermodynamic quantities like the adsorption Γ diverge as $t^{\beta-\nu}$

Chapter 3

The Interfacial structure and tension between a fluid and a curved hard wall

ABSTRACT

In this chapter the structure and tension between a fluid and a spherically shaped hard wall are investigated theoretically. Using both square-gradient theory as well as density functional theory with a nonlocal, integral expression for the interactions between molecules, the equivalence is shown for the expressions for the surface tension and Tolman length derived from these theories. Furthermore, despite the fact that these models do not obey the so called wall theorem they do fulfill the basic requirement of mechanical equilibrium. We trace the origin of this difference to the (lack of) continuity of the cavity function at the hard wall.

3.1 Introduction

This chapter deals with the situation when a liquid is brought into contact with an (infinitely) hard wall. The interplay between a fluid and a solid gives rise to new interfacial phenomena such as the formation of thin layer films, wetting/dewetting phenomena and wall induced phase separation in colloidal mixtures to name but a few. Key in understanding these interfacial phenomena is the interfacial tension between the different phases. In this chapter we will restrict our treatment by considering simple fluids interacting with structureless, hard walls.

We begin by noting that the liquid's density at the wall ρ^w is linked to the pressure p as if it were an ideal gas,

$$p = k_B T \rho^w. \quad (3.1)$$

This equation is known as the wall theorem [73], where T is the absolute temperature and k_B Boltzmann's constant. This equation can be derived by considering mechanical equilibrium between the fluid and the hard wall. It is analogous to the mechanical equilibrium present between coexisting liquid and vapour phases where $p_\ell = p_v$ with the role of the solid pressure taken over by $\rho k_B T$. Henderson [59, 74] showed that the equilibrium condition for a fluid with a curved hard wall is given by

$$-p + k_B T \rho^w = \frac{2\sigma(R)}{R} + C(R), \quad (3.2)$$

where R is the hard wall radius, $\sigma(R)$ is the radius dependent surface tension and $C(R) \equiv d\sigma(R)/dR$. The right hand side is just the Laplace pressure difference for a liquid drop in contact with its vapour [15]:

$$\Delta p = p_\ell - p_v = \frac{2\sigma}{R} + C(R). \quad (3.3)$$

As for a liquid droplet, one might expand the surface tension in $1/R$ when we consider large radii. To leading order in $1/R$ we have

$$\sigma(R) = \sigma \left(1 - \frac{2\delta}{R} + \dots \right). \quad (3.4)$$

which we already encountered as Eq.(2.3) in the previous chapter with the Tolman length δ as the leading order term in curvature [22]. Inserting this expansion into Eq.(3.3) gives

$$-p + k_B T \rho^w = \frac{2\sigma}{R} \left(1 - \frac{\delta}{R} + \dots \right). \quad (3.5)$$

The main purpose of this chapter is to investigate different expressions for the Tolman length for a fluid near a hard wall and to determine its value using density functional theories of varying degree of sophistication. In particular, we will discuss van der Waals' square-gradient theory [15] and density functional theory (DFT) with a non-local, integral expression for the interaction between molecules [75–77]. Using DFT,

Stecki *et al.* [78, 79] found a positive Tolman length, determined from a plot of $\sigma(R)$ versus $1/R$. For a system of a hard sphere fluid near a hard wall Bryk *et al.* [80] obtained a negative Tolman length, which they showed to be in good agreement results obtained with scaled particle theory (see also ref. [81]).

Our interest lays in comparing the determination of the Tolman length for the hard wall system with the determination from a liquid drop in contact with its vapour as discussed in chapter 2. We show that the Tolman length for a fluid with a hard wall can be determined from the density profile with a *planar* hard wall, just as it can in the case of a planar liquid-vapour interface [67, 82–85].

Before we evaluate the expressions for the Tolman length we deal with an important issue concerning mechanical equilibrium and the wall theorem. The Laplace equation Eq.(3.3) is derived by considering mechanical equilibrium between both the liquid and vapour phase. An important observation is that for the density functional theories considered, the Laplace equation for a liquid droplet still holds but in general, they *do not* obey the wall theorem in Eq.(3.1) or (3.2) [86]. This result has also been observed for more complex systems in contact with a hard wall [87, 88]. We show that even though the wall theorem need not always be satisfied, the condition of mechanical equilibrium remains valid. We further provide alternate expressions for the value of the density at the wall.

This chapter is organized as follows: in the next section we consider the thermodynamics necessary to study density functional theories of hard wall systems. We consider the derivation of the wall theorem for planar (Eq.(3.1)) and spherical walls (Eq.(3.2)) and show how the derivation relates to the fundamental requirement of mechanical equilibrium. In the next two sections we will explicitly consider two density functional theories: square-gradient theory and density functional theory containing an integral expression for the interaction between molecules [75–77]. We are then able to provide expressions for the surface tension and the Tolman length which are numerically evaluated. A summary of the results can be found in section 3.5.

3.2 Mechanical equilibrium and the wall theorem

There are some similarities but also important differences when considering a fluid in contact with a hard, spherically curved wall and a liquid drop in contact with its vapour [27, 59].

An important point to note is that in going from a liquid-vapour to a fluid-wall system, one essentially goes from a two-phase system towards a one-phase system for the wall is merely present as a “spectator phase” (i.e. not of influence to the thermodynamic state of the liquid surrounding it). When investigating the liquid droplet, it is either in a metastable state (the critical nucleus) or in equilibrium due to the finite size of the containing vessel. The radius of curvature is varied by changing the chemical potential μ or temperature T of the system. For a fluid in contact with a spherical wall, the system is always in equilibrium and the radius of curvature is

varied as a boundary condition.

We imagine the wall to exert infinite repulsive forces beyond some radius R so we employ the hard-wall potential:

$$V_{\text{ext}}(r) = \begin{cases} \infty, & r < R \\ 0, & r > R \end{cases} \quad (3.6)$$

This shape of the external potential leads us to define the radius R as the radial distance where the molecule's center of mass experiences an infinite repulsion.

There are authors [80] who chose R differently, like shifting the radius by a distance of $d/2$ to account for the fact that the molecule's center of mass is half a diameter away from the surface where it interacts with the hard wall. Naturally, the choice for the location of R can have no impact on all physical observable quantities, but in this case R is chosen to reflect the volume available to the liquid's molecules.

To elaborate on this matter, we consider the grand free energy of a fluid near a planar hard wall

$$\Omega = -pV_\ell + \sigma A. \quad (3.7)$$

In this expression, V_ℓ is the volume available to the liquid. If the dividing surface is now being shifted the liquid's volume is altered and the free energy is affected accordingly:

$$[d\Omega] = -pA[dh], \quad (3.8)$$

where dh is the height shift and the brackets indicate that we are considering a "notional shift" in the location of the dividing surface, which simply implies that we can redefine the location of the dividing surface without altering the physical state of the system [15]. Because Eq.(3.7) discards the solid phase we are left with a free energy which is not invariant, $[d\Omega] \neq 0$. This means we are not free to choose the dividing surface at any position but its position should be such that V_ℓ will be the actual volume of the liquid.

Even though the free energy in Eq.(3.7) is not invariant, the concept of a notional shift is useful when considering more microscopic models for the free energy. To this end, we consider a notional shift in the location of the radius of a spherically shaped hard wall. The free energy and the notional change are then given by

$$\begin{aligned} \Omega &= p \left(V - \frac{4\pi}{3} R^3 \right) + \sigma(R) 4\pi R^2, \\ [d\Omega] &= \left\{ p + \frac{2\sigma(R)}{R} + C(R) \right\} 4\pi R^2 [dR]. \end{aligned} \quad (3.9)$$

where V is the total volume of the system and the square brackets indicate we are merely considering a hypothetical shift of the dividing surface.

Now, we like to compare these expressions with a more microscopic model for the free energy. Let the free energy be a functional of the fluid's density $\rho(\mathbf{r})$. It can be

written as a sum of a term pertaining to the liquid only (Ω_ℓ) and a term describing the interaction between the wall and the fluid:

$$\Omega[\rho] = \Omega_\ell[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}). \quad (3.10)$$

If we now consider a notional change in the hard wall radius, the first term in Eq. (3.10) is unaffected and the only R -dependence stems from the external potential $V_{\text{ext}}(\mathbf{r}) = V_{\text{ext}}(r - R)$. For a spherically shaped hard wall we then have

$$\begin{aligned} [d\Omega] &= 4\pi \int_0^\infty dr r^2 \rho(r) \frac{dV_{\text{ext}}(r)}{dR} [dR] \\ &= -4\pi R^2 [dR] \int_0^\infty dr \rho(r) V'_{\text{ext}}(r), \end{aligned} \quad (3.11)$$

where we have used $dV_{\text{ext}}(r - R)/dR = -dV_{\text{ext}}(r - R)/dR = -V'_{\text{ext}}(r - R)$ and made use of the fact that $V'_{\text{ext}}(r)$ is only unequal to zero when $r = R$ for the external potential used in Eq.(3.6). Comparing Eq.(3.9) with Eq.(3.11), one finds

$$-p - \int_0^\infty dr \rho(r) V'_{\text{ext}}(r) = \frac{2\sigma(R)}{R} + C(R). \quad (3.12)$$

This equation is an important result. The analogous consideration of a notional change in the radius of a liquid droplet in contact with its vapour leads to the Laplace equation (Eq.(3.3)). For a planar interface ($R \rightarrow \infty$), Eq.(3.12) reduces to [86]

$$p = - \int_{-\infty}^\infty dz \rho(z) V'_{\text{ext}}(z). \quad (3.13)$$

In the following we shall refer to these two equations as the condition of *mechanical equilibrium*. They can be derived by considering a notional shift in the dividing surface, as we did here, but they can equally well be described by the condition of mechanical equilibrium expressed in terms of the pressure tensor $\vec{p}$ [15]

$$\nabla \cdot \mathbf{p} = -\rho(\mathbf{r}) V'_{\text{ext}}(\mathbf{r}). \quad (3.14)$$

For a planar interface, the above equation reduces to

$$p'_N(z) = -\rho(z) V'_{\text{ext}}(z), \quad (3.15)$$

where $p_N(z)$ is the normal component of the pressure tensor which reduces to the uniform pressure p in the bulk. Integrating Eq.(3.15) over z then derives Eq.(3.13).

We shall see that the conditions of mechanical equilibrium put down in Eqs.(3.12) and (3.13) are satisfied for the density functional theories considered in the next section.

One may further show that the expressions for mechanical equilibrium are closely related to the wall theorem expressed in Eqs.(3.1) and (3.2). To show this we rewrite

$$V'_{\text{ext}}(r) = -k_B T e^{V_{\text{ext}}(r)/k_B T} \frac{d}{dr} e^{-V_{\text{ext}}(r)/k_B T}. \quad (3.16)$$

The Boltzmann factor for the external potential equals the Heaviside function with its derivative being equal to the Dirac delta function. Inserting Eq.(3.16) into Eq.(3.12) we thus have

$$-p + k_B T \int_0^\infty dr n(r) \delta(r - R) = \frac{2\sigma(R)}{R} + C(R), \quad (3.17)$$

where we have introduced the so called cavity function (or y -function), $n(r)$, defined as the product of the density and inverse Boltzmann factor for the external potential,

$$n(r) \equiv \rho(r) e^{V_{\text{ext}}(r)/k_B T}. \quad (3.18)$$

Only if the cavity function is continuous at $r = R$, i.e. $n(r) = n(R^+) = \rho(R^+) \equiv \rho^w$, we are able to carry out the integration in Eq.(3.17) to arrive at Eq.(3.2):

$$-p + k_B T \rho^w = \frac{2\sigma}{R} + C(R). \quad (3.19)$$

Thus the only reason that the wall theorem is not always necessarily satisfied hinges on the continuity of the cavity function [86]. The continuity of the cavity function is a fundamental statistical property [89], but it need not necessarily hold in approximate mean-field theories. We shall see that for the density functional theories considered, the cavity function is not continuous and the wall theorem is not satisfied. An exception are the class of weighted density functional theories where the continuity of the cavity function is implied by the Euler-Lagrange equation.

As a side remark, we would like to mention the work of Lovett and Baus [90]. They presented a derivation of the wall theorem from a virial approach in such a way that nowhere in the proof one needs to rely explicitly on the continuity of the cavity function.

3.3 Square-gradient Theory

In this section we consider the square-gradient model for the free energy of a liquid near a hard wall. The free energy as a functional of density is given by

$$\Omega[\rho] = \int d\mathbf{r} \left[m |\nabla \rho(\mathbf{r})|^2 + g(\rho) + \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \right], \quad (3.20)$$

where m is the coefficient of the square-gradient term and $g(\rho)$ is the grand free energy density of a homogeneous fluid with density ρ . For explicit calculations we turn to the Carnahan- Starling form for $g(\rho)$ [91]

$$\begin{aligned} g(\rho) &= g_{\text{HS}}(\rho) - a\rho^2 \\ &= k_B T \rho \ln(\rho) - \mu\rho + k_B T \rho \frac{(4\eta - 3\eta^2)}{(1 - \eta)^2} - a\rho^2, \end{aligned} \quad (3.21)$$

where $\eta \equiv (\pi/6)\rho d^3$ and a is the van der Waals parameter to account for the interaction between molecules. The value of μ determines the bulk fluid density ρ_b and it is convenient to use ρ_b next to T as state variable. Next we turn to the determination of the density profiles in the case of a planar and a spherically shaped hard wall.

3.3.1 Planar hard wall

For a planar hard wall the grand free energy per unit surface area is given by

$$\frac{\Omega[\rho]}{A} = \int_{-\infty}^{\infty} dz \left[m[\rho'(z)]^2 + g(\rho) + \rho(z)V_{\text{ext}}(z) \right]. \quad (3.22)$$

Then, the infinite repulsion of the hard wall is taken into account in two steps. First, we consider the following form for the external potential:

$$V_{\text{ext}}(z) = \begin{cases} k_{\text{B}}TV_0, & z < 0 \\ 0, & z > 0 \end{cases} \quad (3.23)$$

where V_0 is a very large constant. Second, we take the limit $V_0 \rightarrow \infty$. The Euler-Lagrange equation to minimize the free energy in Eq.(3.22) reads

$$2m\rho''(z) = g'(\rho) + V_{\text{ext}}(z). \quad (3.24)$$

This differential equation indicates that because $V_{\text{ext}}(z)$ is discontinuous around $z = 0$, the second derivative of the density profile is discontinuous. However, the profile itself is continuous:

$$\rho(0^-) = \rho(0^+) = \rho^w, \quad \rho'(0^-) = \rho'(0^+). \quad (3.25)$$

Integrating the Euler-Lagrange equation in Eq. (3.24) gives

$$m\rho'(z)^2 = \begin{cases} g(\rho) + c_1, & \text{for } z > 0 \\ g(\rho) + k_{\text{B}}TV_0\rho(z) + c_2, & \text{for } z < 0 \end{cases} \quad (3.26)$$

The two integration constants $c_{1,2}$ are determined by the behaviour of the density profile in the two bulk regions far from the interface. For $z \rightarrow \infty$,

$$g(\rho_b) = -p \Rightarrow c_1 = p. \quad (3.27)$$

The fluid density in the solid region is extremely small, i.e. $\rho_s \simeq \exp(-V_0) \rightarrow 0$. This means that for $V_0 \rightarrow -\infty$,

$$g(\rho_s) \simeq k_{\text{B}}T\rho_s \ln(\rho_s) \rightarrow 0 \Rightarrow c_2 = 0. \quad (3.28)$$

The Euler-Lagrange equation becomes

$$m\rho'(z)^2 = \begin{cases} g(\rho) + p, & \text{for } z > 0 \\ g(\rho) + k_{\text{B}}TV_0\rho(z), & \text{for } z < 0. \end{cases} \quad (3.29)$$

Due to the fact that the first derivative is continuous at $z = 0$, we have the condition that

$$g(\rho^w) + p = g(\rho^w) + k_{\text{B}}TV_0\rho^w \Rightarrow \rho^w = \frac{p}{k_{\text{B}}TV_0} \rightarrow 0. \quad (3.30)$$

Thus we conclude

$$\rho^w = 0. \quad (3.31)$$

This result is clearly not in accord with the wall theorem in Eq.(3.1). However, we could have anticipated this result in hindsight: it is similar to the condition that the wavefunction is zero at the boundaries when solving Schrödinger's equation for a single particle in a box.

So the density profile obtained from square-gradient theory does not satisfy the wall theorem. One may verify however, that the square-gradient model does *not* violate the condition of mechanical equilibrium:

$$p \stackrel{?}{=} - \int_{-\infty}^{\infty} dz \rho(z) V'_{\text{ext}}(z) = \int_{-\infty}^{\infty} dz \rho(z) k_B T V_0 \delta(z) = k_B T V_0 \rho^w, \quad (3.32)$$

which is indeed the case on the account of Eq. (3.30). That the nature of the cavity function is discontinuous for the square-gradient model may also explicitly be inferred from its definition in Eq.(3.18) and the expression for the density at the wall in Eq.(3.30):

$$\begin{aligned} n(0^-) &\simeq \frac{p}{k_B T V_0} e^{V_0} \rightarrow \infty, \\ n(0^+) &\simeq \frac{p}{k_B T V_0} \rightarrow 0. \end{aligned} \quad (3.33)$$

The full fluid density profile can now be determined taking the limit $V_0 \rightarrow \infty$. For $z < 0$, we have that $\rho(z) = 0$, whereas for $z > 0$ the density profile is obtained by solving the differential equation in Eq.(3.29) subject to the boundary condition in Eq.(3.31). Note that this implies that while for *finite* V_0 the first derivative of the density profile is always continuous in $z=0$, in the limit of $V_0 \rightarrow \infty$ it is not:

$$\rho'(0^-) = 0, \quad \rho'(0^+) = \sqrt{\frac{p}{m}}. \quad (3.34)$$

It is interesting to compare the density profile obtained in the square-gradient model with the so-called Nakanishi-Fisher model [92], which is designed to describe the interaction of a fluid with a wall. Using this model, Nakanishi and Fisher were able to construct a rich wetting phase diagram in terms of two fluid-wall interaction parameters, h_1 and g [92]. Besides the presence of (attractive or repulsive) fluid-wall interactions, an important difference with the analysis presented here is that the infinite “hardness” of the wall for $z < 0$ is taken into account simply by limiting the integration of the free energy to the region $z > 0$. The result is that if we were to set the interaction with the wall to zero ($h_1 = 0, g = 0$), one obtains for the density profile $\rho(z) = \rho_b$, everywhere. The Nakanishi-Fisher model is designed specifically to describe the interactions of a fluid with a wall. It is, however, not suited to describe the limit where those interactions vanish.

The applicability of the Nakanishi-Fisher model can also be regarded as a matter of length scales. Suppose we construct a square-gradient model in which the interaction with the wall is described by an interaction potential with a certain shape and range for $z > 0$, and which is strictly infinite for $z < 0$. The density profile calculated

from such a model could be described in terms of the Nakanishi-Fisher parameters for distances far (compared to the interaction range) from the wall, but, nearing the wall, the density profile necessarily approaches zero. This approach is the basis of what is covered in chapter 4.

The situation is similar to the theoretical description of a polymer solution in contact with a wall. In the theoretical treatment by de Gennes [93,94], the interaction with the wall is modeled by the “extrapolation length” ($1/d$), which is analogous to the parameter h_1 in the Nakanishi-Fisher model. Setting $1/d=0$ then again results in a flat monomer density profile. This result is to be contrasted with the analysis by Eisenriegler, who considers a polymer in contact with a purely hard wall, and obtains the boundary condition of vanishing monomer density at the wall [95].

3.3.2 Spherically shaped hard wall

To determine the radius dependent surface tension $\sigma(R)$ and thus Tolman’s length, we next consider the spherically shaped hard wall. In spherical coordinates the free energy is given by

$$\Omega[\rho] = 4\pi \int_0^\infty dr \, r^2 [m\rho'(r)^2 + g(\rho) + \rho(r) V_{ext}(r)], \quad (3.35)$$

with the Euler-Lagrange equation

$$2m \rho''(r) = -\frac{4m}{r} \rho'(r) + g'(\rho) + V_{ext}(r). \quad (3.36)$$

The presence of the infinitely hard wall again leads to the boundary condition $\rho(R) = \rho^w = 0$. The radius dependent surface tension $\sigma(R)$ is calculated by inserting the density profile determined by the above differential equation into the free energy:

$$\sigma(R) = \int_0^\infty dz \left(1 + \frac{z}{R}\right)^2 [m[\rho'(z)]^2 + g(\rho) + p], \quad (3.37)$$

where we have introduced $z \equiv r - R$ as the (radial) distance to the wall. To determine the Tolman length, we expand $\sigma(R)$ and the density profile in $1/R$:

$$\rho(z) = \rho_0(z) + \rho_1(z) \frac{1}{R} + \dots \quad (3.38)$$

The derivation of explicit expressions for σ and $\delta\sigma$ in terms of the density profile follows very closely the analogous derivation in ref. [67] (outlined in part in Appendix A) of these coefficients for a spherical liquid-vapour surface. The only distinction lies in the fact that the integration over the volume now runs from $z=0$ to $z=\infty$, which is to be expected, and that there is no term associated with μ_1 , the leading order term in an expansion in $1/R$ of the chemical potential. The latter is a direct consequence

of the fact that the chemical potential in the fluid is constant, *independent* of the radius R .

From the analysis in ref. [67], we conclude that the surface tension of the planar interface and Tolman length are thus given by

$$\begin{aligned}\sigma &= 2m \int_0^\infty dz [\rho'_0(z)]^2, \\ \delta\sigma &= -2m \int_0^\infty dz z [\rho'_0(z)]^2.\end{aligned}\tag{3.39}$$

In the next section, these expressions are used to calculate σ and $\delta\sigma$.

3.4 Density functional theory

We showed that, for the model considered in the previous section, the density at the wall is identically zero. This is a direct consequence of the presence of the square-gradient term which gives an infinite contribution to the free energy when the density profile is discontinuous. To allow for such a discontinuity, it therefore seems appropriate to describe the interactions between molecules with the full, non-local integral term [75, 76]:

$$\begin{aligned}\Omega[\rho] &= \int d\vec{r} [g_{hs}(\rho) + \rho(\vec{r}) V_{ext}(\vec{r})] \\ &\quad + \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 U(r_{12}) \rho(\vec{r}_1) \rho(\vec{r}_2),\end{aligned}\tag{3.40}$$

where $g_{hs}(\rho)$ is given by the expression in Eq.(3.21) and $U(r_{12})$ is the attractive part of the interaction potential between molecules at a distance $r_{12} \equiv |\vec{r}_2 - \vec{r}_1|$. For explicit calculations, we take it to be of the following form [96]:

$$U(r_{12}) = \begin{cases} 0 & \text{when } r_{12} < d, \\ -A (d/r_{12})^6 & \text{when } r_{12} > d, \end{cases}\tag{3.41}$$

to mimic London-dispersion forces. By comparing the free energy in Eq.(3.20) to Eq.(3.40), making a gradient expansion in the latter, one may express the parameters a and m in terms of A and d :

$$\begin{aligned}a &= -\frac{1}{2} \int d\vec{r}_{12} U(r_{12}) = \frac{2\pi}{3} A d^3, \\ m &= -\frac{1}{12} \int d\vec{r}_{12} U(r_{12}) r_{12}^2 = \frac{\pi}{3} A d^5.\end{aligned}\tag{3.42}$$

It is convenient to express lengths in units of d and energies in units of a/d^3 . The reduced temperature thus becomes $T^* \equiv k_B T d^3/a$.

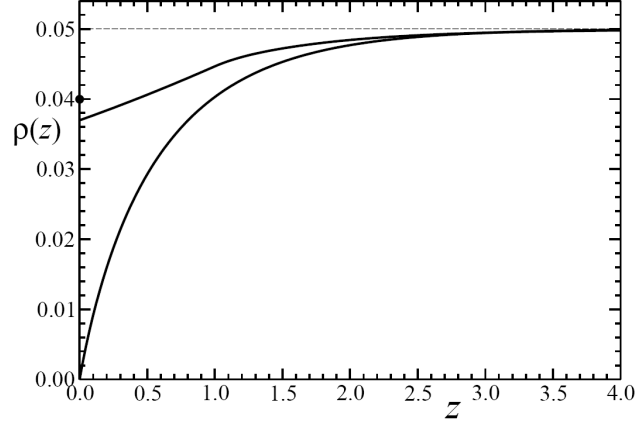


Figure 3.1 Density profiles, $\rho(z)$ (in units of $1/d^3$), as a function of wall distance, z (in units of d), determined by square-gradient theory (lower solid curve) and density functional theory (upper solid curve). In this example is $T^* = 0.16$ and $\rho_b = 0.05$ (dashed line). The solid point indicates the wall density predicted by the wall theorem (Eq.(3.1)).

3.4.1 Planar hard wall

Again we turn to the planar case first. The free energy is then:

$$\begin{aligned} \frac{\Omega[\rho]}{A} &= \int_{-\infty}^{\infty} dz [g_{hs}(\rho) + \rho(z) V_{ext}(z)] \\ &\quad + \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} d\vec{r}_{12} U(r_{12}) \rho(z_1) \rho(z_2), \end{aligned} \quad (3.43)$$

with the Euler-Lagrange equation:

$$g'_{hs}(\rho) + V_{ext}(z_1) + \int d\vec{r}_{12} U(r_{12}) \rho(z_2) = 0. \quad (3.44)$$

For $z < 0$ the density profile $\rho(z) = 0$, and for $z > 0$ one may solve the above integral equation numerically. A typical density profile is shown in Figure 3.1. One finds that, in contrast to the square-gradient model, the density at the wall, ρ^w , is not equal to zero, but it is also not equal to the value given by the wall theorem in Eq.(3.1). For the interaction potential in Eq.(3.41), this observation was already made by van Giessen, Bukman and Widom [96]. In Appendix B, we show that the wall density is, instead, determined by

$$p = -g_{hs}(\rho^w) + \rho^w g'_{hs}(\rho^w) \equiv p_{hs}(\rho^w). \quad (3.45)$$

This formula was first presented by Parry and Evans [97], but there it was derived strictly in the context of the Sullivan model [75] for the interaction potential between fluid molecules. The analysis in Appendix B shows that this result is independent of the precise form of the interaction potential. The point we like to stress, however, is that, as for the square-gradient model, the condition of mechanical equilibrium, Eq.(3.12) or Eq.(3.13), remains satisfied. This is shown explicitly in Appendix B. Again, the conclusion is that for this model the cavity function is not continuous at the wall.

3.4.2 Spherically shaped hard wall

To determine the radius dependent surface tension, we now turn to the spherically shaped hard wall. In spherical coordinates the free energy is then

$$\begin{aligned} \Omega[\rho] = & 4\pi \int_0^\infty dr r^2 [g_{hs}(\rho) + \rho(r) V_{ext}(r)] \\ & + 2\pi \int_0^\infty dr_1 r_1^2 \int d\vec{r}_{12} U(r_{12}) \rho(r_1) \rho(r_2), \end{aligned} \quad (3.46)$$

with the Euler-Lagrange equation now given by

$$g'_{hs}(\rho) + V_{ext}(r_1) + \int d\vec{r}_{12} U(r_{12}) \rho(r_2) = 0. \quad (3.47)$$

The radius dependent surface tension $\sigma(R)$ is derived by inserting the density profile determined by the above differential equation into the free energy:

$$\begin{aligned} \sigma(R) = & \int_0^\infty dz \left(1 + \frac{z}{R}\right)^2 [g_{hs}(\rho) - a\rho_b^2 + p] \\ & + \frac{1}{2} \int_0^\infty dz_1 \left(1 + \frac{z_1}{R}\right)^2 \int d\vec{r}_{12} U(r_{12}) [\rho(r_1)\rho(r_2) - \rho_b^2]. \end{aligned} \quad (3.48)$$

To obtain explicit expressions for σ and $\delta\sigma$, one must again expand $\sigma(R)$ and the density profile in $1/R$. The derivation follows very closely the analogous derivation in ref. [40] of these coefficients for a spherical liquid-vapour surface. Following ref. [40], one finds

$$\begin{aligned} \sigma &= -\frac{1}{4} \int_{-\infty}^\infty dz_1 \int d\vec{r}_{12} U(r_{12}) r_{12}^2 (1 - s^2) \rho'_0(z_1) \rho'_0(z_2), \\ \delta\sigma &= \frac{1}{4} \int_{-\infty}^\infty dz_1 \int d\vec{r}_{12} U(r_{12}) r_{12}^2 (1 - s^2) z_1 \rho'_0(z_1) \rho'_0(z_2). \end{aligned} \quad (3.49)$$

The above expression for σ is similar to the Triezenberg-Zwanzig [62] formula for the surface tension.

The integration over z_1 in Eq.(3.50) runs over the entire volume, including the region of inhomogeneity. It therefore includes the singular contribution from the derivative of the density profile, $\rho'(z)|_{\text{sing}} = \rho^w \delta(z)$. For numerical evaluation it is necessary to limit the integration to the liquid region and explicitly take into account the singular contribution. This leads to

$$\begin{aligned}
 \sigma &= -\frac{1}{4} \int_{0^+}^{\infty} dz_1 \int_{0^+}^{\infty} d\vec{r}_{12} U(r_{12}) r_{12}^2 (1-s^2) \rho'_0(z_1) \rho'_0(z_2) \\
 &\quad - \frac{\rho^w}{2} \int_{0^+}^{\infty} d\vec{r}_{12} U(r_{12}) r_{12}^2 (1-s^2) \rho'_0(sr_{12}) \\
 &\quad - \frac{(\rho^w)^2}{8} \int d\vec{r}_{12} U(r_{12}) r_{12}, \\
 \delta\sigma &= \frac{1}{4} \int_{0^+}^{\infty} dz_1 \int_{0^+}^{\infty} d\vec{r}_{12} U(r_{12}) r_{12}^2 (1-s^2) z_1 \rho'_0(z_1) \rho'_0(z_2) \\
 &\quad + \frac{\rho^w}{4} \int_{0^+}^{\infty} d\vec{r}_{12} U(r_{12}) r_{12}^3 s(1-s^2) \rho'_0(sr_{12}), \tag{3.50}
 \end{aligned}$$

where the lower limit, 0^+ , indicates that the integrals are strictly limited to the regions $z_1 > 0$ and $z_2 > 0$. The above expression for σ , with the singular part explicitly evaluated, is closely related to formula (45) derived by Parry and Evans in ref. [97]. In Figure 3.2 we show, as the solid curves, the Tolman length (in units of d), numerically determined using the expressions in Eq.(3.50), as a function of bulk density at two temperatures, one below and one above T_c . Also drawn in Figure 3.2, as the dashed curves, are the results for δ derived from the square-gradient model (Eq.(3.39)) for the same set of parameters. The curves are qualitatively similar to the DFT results and about a factor of 2 larger. Above T_c the Tolman length is negative, less than a molecule's diameter, and it exhibits a maximum as a function of the fluid's bulk density. Below T_c the density range is limited by the densities of the coexisting liquid and vapour phase (ρ_ℓ and ρ_v , vertical dashed lines). On the vapour side, nothing spectacular happens: the Tolman length is negative and in size less than a molecule's diameter. On the liquid side, however, on approach to the coexistence density, the Tolman length diverges.

An interpretation for the divergence of the Tolman length was provided by Evans and coworkers [98–100]. They showed that a “wetting” layer of vapour is formed between the liquid and the hard wall when the coexistence density is approached on the liquid side. It was demonstrated that a cross-over radius R_c exists such that when $R < R_c$, *non-analytic* contributions to the surface tension $\sigma(R)$ are present. The cross-over radius R_c depends critically on the distance to the coexistence density: $R_c \equiv 2\sigma_{\ell v}/(\Delta\rho\Delta\mu)$, with $\sigma_{\ell v}$ the liquid-vapour surface tension at coexistence, $\Delta\rho = \rho_\ell - \rho_v$

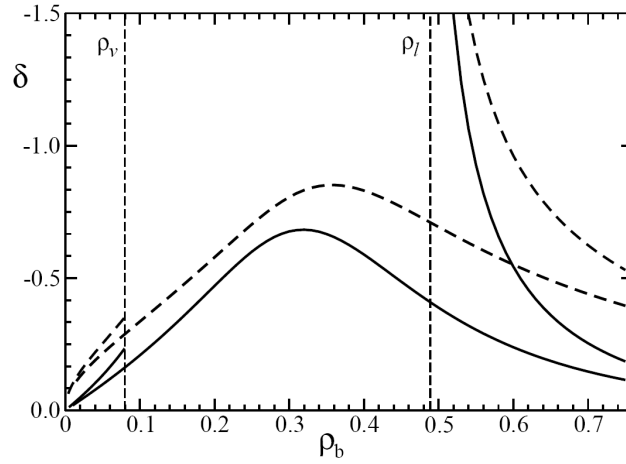


Figure 3.2 Tolman length, δ (in units of d), as a function of bulk density, ρ_b (in units of $1/d^3$), determined by square gradient theory (dashed curves) and density functional theory (solid curves) at two temperatures, one below $T_c^* = 0.18015455\dots$ ($T^* = 0.16$), and one above T_c ($T^* = 0.20$). The curves below T_c are those on either side of the vertical dashed lines which are the limiting bulk densities at coexistence, $\rho_v = 0.0795594\dots$ and $\rho_\ell = 0.4887348\dots$. The curves above T_c are those that span the entire density range.

the liquid-vapour density difference, and $\Delta\mu = \mu - \mu_{coex}$ the chemical potential distance to liquid-vapour coexistence. The consequence is that while the Tolman length itself remains well-defined on approach to the coexistence density, its “usefulness” in the expansion of $\sigma(R)$ in $1/R$ is restricted to an increasing limited interval, $0 < 1/R < 1/R_c$.

Furthermore, *at* coexistence, we have $1/R_c = 0$ and the expansion breaks down completely. The leading order correction to the surface tension is not of the Tolman length-form ($1/R$); the precise expression to replace the Tolman correction is given in refs. [99] and [100] both for short-ranged forces as well as algebraically decaying interaction forces between fluid molecules. The Tolman length itself is no longer well-defined in the limit $\mu \rightarrow \mu_{coex}$, which manifests itself in the divergence of δ as featured in Figure 3.2. One may show that the divergence of δ follows the divergence of the thickness of the intruding wetting layer. This implies that $\delta \propto \ln(\Delta\mu)$ for the short-ranged forces of the square-gradient model [99] (dashed line); whereas $\delta \propto (\Delta\mu)^{-1/3}$, for the dispersion forces of the DFT [100] (solid line).

It may also be convenient to express σ and $\delta\sigma$ in terms of the density profile itself – and not its derivative – to avoid any singular contribution coming from $\rho'_0(z)$:

$$\sigma = \frac{1}{4} \int_0^\infty dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) \rho_0(z_1) \rho_0(z_2),$$

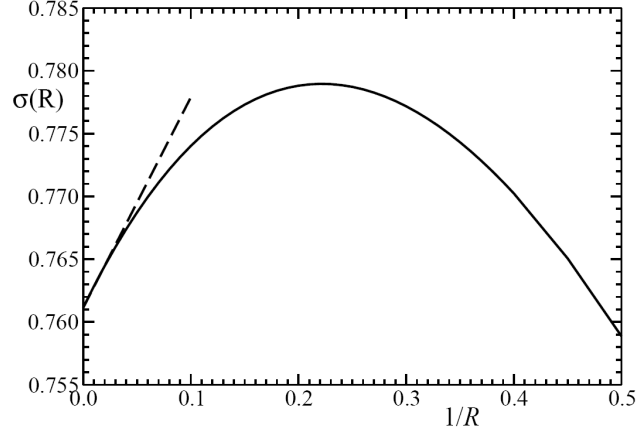


Figure 3.3 Radius dependent surface tension, $\sigma(R)$ (in units of $10^{-3} a/d^5$), as a function of the reciprocal radius, $1/R$, of a spherical hard wall, determined by density functional theory. In this example is $T^* = 0.16$ and $\rho_b = 0.05$. The dashed line is $\sigma(1 - 2\delta/R)$ with σ and δ obtained from the planar density profiles (Eq.(3.50) or Eq.(3.51)).

$$\begin{aligned} \delta\sigma = & -\frac{1}{8} \int_0^\infty dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) \\ & \times (z_1 + z_2) \rho_0(z_1) \rho_0(z_2). \end{aligned} \quad (3.51)$$

As we show in Appendix C, these expressions can either be derived from the more general virial expressions for σ and $\delta\sigma$ [28, 83, 101], which are valid also beyond the mean-field approximation, or they can be derived by repeated partial integration from Eq.(3.50). For the results shown in Figure 3.2, we have checked that Eqs.(3.50) and (3.51) give the same value for σ and $\delta\sigma$, within numerical accuracy. As a further check on our numerical results, we have verified that the Tolman length calculated from Eq.(3.50) (or Eq.(3.51)), expressed in terms of the density profile of the planar interface, is equal to the Tolman length obtained directly from the expansion of the radius dependent surface tension, $\sigma(R) = \sigma - 2\delta\sigma/R + \dots$. In Figure 3.3, we show $\sigma(R)$ calculated using Eq.(3.48) with the density profile determined from numerically solving the differential equation in Eq.(3.47). The shape of the graph is quite similar to that obtained in refs. [78] and [81] at low densities. The limiting slope of $\sigma(R)$ near $1/R=0$ ($-2\delta\sigma$) agrees with the value calculated from Eq.(3.50) (dashed line).

3.5 Summary

We have determined density profiles, surface tension and Tolman length for a fluid in contact with a hard wall using the square-gradient model and density functional

theory with a non-local, integral expression for the interaction between molecules. Even though both these models yield equilibrium density profiles which do not satisfy the wall theorem, we showed that they do obey the basic requirement of mechanical equilibrium, thus giving credence to the predictions made.

The expressions for the surface tension and Tolman length are similar to those derived for a liquid-vapour interface [40, 67]; in particular the Tolman length may again be expressed in terms of the density profile of the planar interface. Furthermore, for the density functional theory, we showed the equivalence between the Triezenberg-Zwanzig-like expression and Kirkwood-Buff-like expression for δ .

Qualitatively, the two models yield similar (numerical) results for the Tolman length as a function of bulk density and temperature: the Tolman length is negative and, generally, less than the molecule's diameter. These results are similar to density functional theory results for the Tolman length of a liquid droplet surrounded by the vapour phase.

An exception is the behaviour of the Tolman length on approach to the coexistence density on the liquid side of the phase diagram. Here, the Tolman length diverges, as predicted by Evans and coworkers [98–100], due to the formation of a “wetting” layer of vapour between the liquid and the hard wall.

Chapter 4

Wetting and Drying transitions in mean-field theory

ABSTRACT

The theory of Nakanishi and Fisher (*Phys. Rev. Lett.* **49**, 1565 (1982)) describes the wetting behaviour of a liquid and vapour phase in contact with a substrate in terms of the surface chemical potential h_1 and the surface enhancement parameter g . Using density functional theory, we derive molecular expressions for h_1 and g and compare with earlier expressions derived from Landau lattice mean-field theory. The molecular expressions are applied to compare with results from density functional theory for a square-gradient fluid in a square-well fluid-substrate potential and with molecular dynamics simulations.

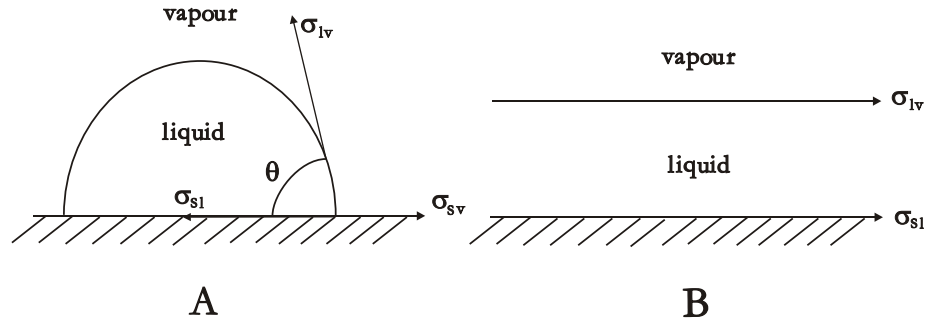


Figure 4.1 Schematic representation of a partial (A) and complete wet state (B).

4.1 Introduction

When two bulk liquid phases or a liquid in coexistence with its vapour are brought into contact with a substrate (solid wall) two situations can arise: either one of the two phases completely wets the substrate, that is one layer of liquid will cover the entire substrate (complete wet state), or one of the two phases will partially wet the substrate and form little droplets on it (partial wet state). This is schematically depicted in Figure 4.1. Changing a thermodynamic variable such as temperature may induce a transition between the two situations. This wetting transition was independently investigated by Cahn [102] and by Ebner and Saam [103]. Since then there has been a lot of experimental and theoretical work done on the nature and aspects of wetting transitions [86,92,104–113]. Among all these theories, the Nakanishi-Fisher model [92] has played a pivotal role in shaping our understanding of the wetting phase diagram.

4.1.1 The model of Nakanishi and Fisher

In the Nakanishi-Fisher model, the free energy Ω describes the free energy of a fluid (liquid and or vapour) phase in contact with a solid wall. Just like in chapter 3, the solid wall is assumed to be present as a so-called ‘spectator phase’ (the solid is unaffected by the fluid’s thermodynamic state) and this leads to the exclusion of the fluid in the region $z < 0$, where z is the direction perpendicular to the wall. The free energy is a functional of the fluid’s density $\rho(z)$:

$$\frac{\Omega[\rho]}{A} = \int_0^\infty dz \left\{ m[\rho'(z)]^2 + g(\rho) \right\} - h_1 \rho(0) + \frac{g}{2} \rho(0)^2, \quad (4.1)$$

where $A = \int dx dy$ is the surface area. The first term approximates the fluid’s free energy by a simple square-gradient expression with coefficient m and bulk free energy density $g(\rho)$. For explicit calculations, we consider for $g(\rho)$ the Carnahan-Starling

form [91]:

$$g(\rho) = g_{\text{hs}}(\rho) - a\rho^2 = k_{\text{B}}T\rho \ln(\rho) + k_{\text{B}}T\rho \frac{(4\eta - 3\eta^2)}{(1 - \eta)^2} - \mu\rho - a\rho^2, \quad (4.2)$$

where $\eta \equiv (\pi/6)\rho d^3$ with d being the molecular diameter, a is the usual van der Waals parameter to account for the attractive interactions between molecules, μ is the chemical potential, T is the absolute temperature and k_{B} Boltzmann's constant.

The last two terms in Eq.(4.1) account for the interaction of the fluid with the wall in terms of two phenomenological parameters, h_1 and g , which are termed the *surface chemical potential* and *surface enhancement parameter*, respectively. In terms of these two parameters, Fisher and Nakanishi located the crossover between first and second order transitions and reported prewetting transitions for a fluid off-coexistence [92]. The assumption implicitly made is that the fluid-wall interaction is short-ranged so that these terms only depend on the fluid's density in the direct vicinity of the wall, $\rho(0) \equiv \rho(z = 0^+)$. For a fluid interacting with the substrate through long-ranged London dispersion forces, $V_{\text{wall}}(z) \propto 1/z^3$, this assumption may very well be questioned.

To determine the surface tension, one minimizes the free energy in Eq.(4.1) leading to the following Euler-Lagrange equation for $\rho(z)$ [15]:

$$2m\rho''(z) = g'(\rho), \quad (4.3)$$

with the boundary condition:

$$2m\rho'(0) = -h_1 + g\rho(0). \quad (4.4)$$

The surface tension is then calculated by inserting $\rho(z)$ into the free energy and subtracting the pressure contribution from the bulk at $z \rightarrow \infty$, $p = -g(\rho_b)$, where ρ_b is the bulk fluid density:

$$\sigma = \int_0^\infty dz \left\{ m[\rho'(z)]^2 + g(\rho) + p \right\} - h_1\rho(0) + \frac{g}{2}\rho(0)^2. \quad (4.5)$$

Our goal in this chapter is to understand the molecular origin of the two parameters h_1 and g in terms of the full shape of the interaction potential of the interaction between the fluid and the wall. For instance, setting the model parameters to zero in the Nakanishi-Fisher model ($h_1 = 0$ and $g = 0$) results in constant density profiles at the value of the bulk density which is not expected if a fluid is brought in contact with a hard wall. To appreciate this point, we first investigate in Sections 4.2 and 4.3 two routes to derive the Nakanishi-Fisher free energy expression: the Landau mean-field lattice model and density functional theory (DFT), providing us with a molecular interpretation of the model parameters h_1 and g . In section 4.4 the molecular expressions for h_1 and g are used to compare with results from a simple square-gradient model of a fluid interacting with the substrate through an attractive square-well potential. We end with a discussion of results.

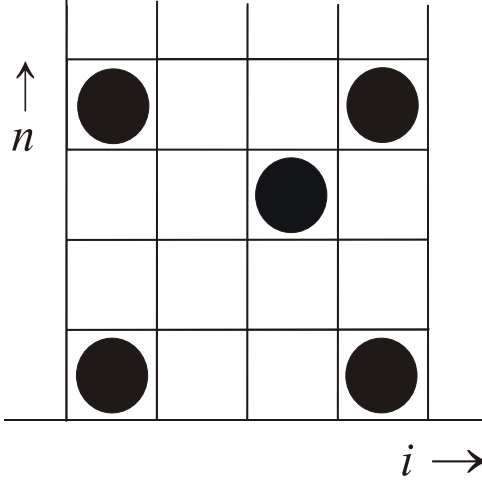


Figure 4.2 Schematic representation of the Landau cell model. Each lattice site i in layer n can be singly occupied or empty.

4.2 Landau mean-field lattice model

The majority of studies regarding interfacial behaviour have their roots in Landau mean-field theory. It is typically derived from a continuum limit of spin models with short-ranged molecular interactions and thus provides an interpretation of the microscopic parameters entering the theory [114]. In this section, to set the stage for the derivation using density functional theory in section 4.3, we briefly discuss the usual derivation of the microscopic expressions for h_1 and g in terms of the lattice interaction parameters [92, 107, 108, 115].

In Landau theory one assumes a semi-infinite set of discrete lattice sites, arranged in equally spaced layers labeled by an index $n = 1, 2, 3, \dots$. Each lattice site is occupied by a single molecule or remains vacant (see Figure 4.2). The free energy for a molecule in the bulk is given by:

$$\frac{d^3}{k_B T V} \Omega(\Phi) \equiv g(\Phi) = \Phi \ln(\Phi) + (1 - \Phi) \ln(1 - \Phi) - \tilde{\mu} \Phi - \chi \Phi^2, \quad (4.6)$$

where χ is the interaction parameter between neighboring molecules and where $\Phi \equiv N d^3/V$ is the volume fraction of molecules, with d the lattice spacing (set equal to the molecular diameter), N the number of molecules and V the system's volume.

For a fluid interacting with a solid wall, the volume fraction depends on the layer index, $\Phi = \Phi_n$, with the interaction between neighboring molecules given by

$$U_{\text{int}} \propto -\chi \Phi_n [\lambda \Phi_{n-1} + (1 - 2\lambda) \Phi_n + \lambda \Phi_{n+1}], \quad (4.7)$$

where $1/\lambda$ is the total number of nearest neighbors; for a cubic lattice $1/\lambda = 6$. This expression is valid only when $n \geq 2$. In the first layer ($n = 1$) the number of neighbors

is reduced by the wall since the wall excludes all molecules for $n \leq 0$. Furthermore, one often allows for the interaction between two molecules that both lie in the first layer to be enhanced by a factor $(1 + D)$. For $n=1$, one thus has:

$$U_{\text{int}} \propto -\chi \Phi_1 [(1 - 2\lambda)(1 + D)\Phi_1 + \lambda\Phi_2]. \quad (4.8)$$

The total free energy for the lattice system is then:

$$\begin{aligned} \frac{d^2 \Omega[\Phi_n]}{A k_B T} = & \sum_{n=2}^{\infty} \{ g(\Phi_n) - \lambda\chi \Phi_n [\Phi_{n-1} - 2\Phi_n + \Phi_{n+1}] \} \\ & + g(\Phi_1) - \lambda\chi \Phi_1 \left\{ \left[-2 + \frac{(1-2\lambda)}{\lambda} D \right] \Phi_1 + \Phi_2 \right\} - \chi_s \Phi_1, \end{aligned} \quad (4.9)$$

where the final term is added to account for the interaction of the molecules in the first layer with the wall with strength χ_s .

The Euler-Lagrange equation that minimizes Eq.(4.9) reads:

$$g'(\Phi_n) = \begin{cases} 2\lambda\chi [\Phi_{n-1} - 2\Phi_n + \Phi_{n+1}] & \text{when } n \geq 2, \\ 2\lambda\chi \left\{ \left[-2 + \frac{(1-2\lambda)}{\lambda} D \right] \Phi_1 + \Phi_2 \right\} + \chi_s & \text{when } n = 1. \end{cases} \quad (4.10)$$

Now, it is convenient to introduce an *apparent* value for Φ_0 so that one can extend the Euler-Lagrange equation in Eq.(4.10) to include the case $n=1$ [107, 115]. It directly follows that one should define Φ_0 as:

$$\Phi_0 \equiv \frac{(1-2\lambda)}{\lambda} D \Phi_1 + \frac{\chi_s}{2\lambda\chi}. \quad (4.11)$$

The surface tension is derived by inserting into Ω the profile Φ_n that follows from the Euler-Lagrange equation and subtracting of the bulk contribution. One then has, using Eq.(4.11):

$$\tilde{\sigma} \equiv \frac{d^2 \sigma}{k_B T} = \sum_{n=1}^{\infty} [g(\Phi_n) + \tilde{p} - \lambda\chi \Phi_n (\Phi_{n-1} - 2\Phi_n + \Phi_{n+1})] - \frac{\chi_s}{2} \Phi_1. \quad (4.12)$$

where $\tilde{p}$ is the (reduced) bulk pressure. This can also be written as:

$$\tilde{\sigma} = \sum_{n=1}^{\infty} \left[\lambda\chi (\Phi_{n+1} - \Phi_n)^2 + g(\Phi_n) + \tilde{p} \right] - \chi_s \Phi_1 + \lambda\chi \left[1 - \frac{(1-2\lambda)}{\lambda} D \right] \Phi_1^2. \quad (4.13)$$

Next, we approximate the lattice model by taking the continuum limit. This means that we replace $\Phi_n \rightarrow \Phi(x)$, where $x \equiv z/d = x_0 + n$. In the continuum limit, we then have that:

$$\Phi_{n+1} - \Phi_n \approx \Phi'(x), \quad \Phi_{n-1} - 2\Phi_n + \Phi_{n+1} \approx \Phi''(x). \quad (4.14)$$

Furthermore, we shall define $\Phi_1 \rightarrow \Phi(0)$, which implies that $x=n-1$, but one might consider a more judiciously chosen location of the solid wall. However, since it is not our goal to accurately approximate the lattice model, we shall not pursue this line.

In the continuum limit, the Euler-Lagrange equation in Eq.(4.10) becomes:

$$g'(\Phi) = 2\lambda\chi \Phi''(x). \quad (4.15)$$

With $\Phi_0 = \Phi_1 - (\Phi_1 - \Phi_0) \approx \Phi(0) - \Phi'(0)$, the boundary condition in Eq.(4.11) is given by:

$$\Phi'(0) = \left[1 - \frac{(1-2\lambda)}{\lambda} D\right] \Phi(0) - \frac{\chi_s}{2\lambda\chi}. \quad (4.16)$$

Finally, the expression for the surface tension in Eq.(4.13) becomes:

$$\tilde{\sigma} = \int_0^\infty dx \left\{ \lambda\chi [\Phi'(x)]^2 + g(\Phi) + \tilde{p} \right\} - \chi_s \Phi(0) + \lambda\chi \left[1 - \frac{(1-2\lambda)}{\lambda} D\right] \Phi(0)^2. \quad (4.17)$$

This expression for the surface tension is identical to the Nakanishi-Fisher expression in Eq.(4.5) when the following identifications are made:

$$\begin{aligned} \frac{m}{d^5 k_B T} &= \lambda\chi, \\ \frac{h_1}{d k_B T} &= \chi_s, \\ \frac{g}{d^4 k_B T} &= -2(1-2\lambda)\chi D + 2\lambda\chi. \end{aligned} \quad (4.18)$$

One finds that h_1 is directly related to χ_s which is to be expected. The identification for g is somewhat more subtle. It is the sum of *two* terms, one term due to the enhanced interaction between molecules near the wall as described by D , and one term that is present even in the absence of any enhancement.

4.3 Density functional theory

In this section, we consider density functional theory with the full, non-local integral term to describe the interactions between molecules and show how it can be cast into the form of the Nakanishi-Fisher expression. The starting expression for the free energy functional reads [116]:

$$\Omega[\rho] = \int d\vec{r} [g_{\text{hs}}(\rho) + \rho(\vec{r}) V_{\text{ext}}(\vec{r})] + \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 U(r) \rho(\vec{r}_1) \rho(\vec{r}_2), \quad (4.19)$$

where $g_{\text{hs}}(\rho)$ is given by the expression in Eq.(4.2) and $U(r)$ is the *attractive part* of the interaction potential between molecules at a distance $r \equiv |\vec{r}_2 - \vec{r}_1|$. The external potential $V_{\text{ext}}(\vec{r}) = V_{\text{ext}}(z)$ models the interaction of the fluid with the solid wall. We shall assume that it is infinitely hard when $z < 0$, and given by some short-ranged (usually attractive) interaction $V_{\text{ext}}(z) = V_{\text{wall}}(z)$ for $z > 0$. As a result of the infinite

repulsion, we have that $\rho(z) = 0$ when $z < 0$, and we can limit the integrations in Eq.(4.19) to the region $z > 0$:

$$\frac{\Omega[\rho]}{A} = \int_0^\infty dz [g_{\text{hs}}(\rho) + \rho(z) V_{\text{wall}}(z)] + \frac{1}{2} \int_0^\infty dz_1 \int_{z_2 > 0} d\vec{r}_2 U(r) \rho(z_1) \rho(z_2). \quad (4.20)$$

Next, we consider the gradient expansion for $\rho(z_2)$:

$$\rho(z_2) = \rho(z_1) + z_{12} \rho'(z_1) + \frac{z_{12}^2}{2} \rho''(z_1) + \dots \quad (4.21)$$

The gradient expansion does not take into account that $\rho(z_2) = 0$ when $z_2 < 0$. To accommodate for this, it turns out to be convenient to extend the integration over z_2 in Eq.(4.20) and subtract the difference:

$$\begin{aligned} \frac{\Omega[\rho]}{A} &= \int_0^\infty dz [g_{\text{hs}}(\rho) + \rho(z) V_{\text{wall}}(z)] + \frac{1}{2} \int_0^\infty dz_1 \int d\vec{r}_{12} U(r) \rho(z_1) [\rho(z_1) + \dots] \\ &\quad - \frac{1}{2} \int_0^\infty dz_1 \int_{z_2 < 0} d\vec{r}_2 U(r) \rho(z_1) [\rho(z_1) + \dots]. \end{aligned} \quad (4.22)$$

The final term in this expression, as well as the term containing $V_{\text{wall}}(z)$, only contributes *near the wall*. In the spirit of the Nakanishi-Fisher model, we may therefore approximate $\rho(z) \approx \rho(0)$ in both these terms. With this approximation, together with the gradient expansion, one thus has:

$$\begin{aligned} \frac{\Omega[\rho]}{A} &= \int_0^\infty dz \left\{ m[\rho'(z)]^2 + g_{\text{hs}}(\rho) - a\rho(z)^2 \right\} \\ &\quad + \rho(0) \int_0^\infty dz V_{\text{wall}}(z) - \frac{\rho(0)^2}{2} \int_0^\infty dz_1 \int_{z_2 < 0} d\vec{r}_2 U(r), \end{aligned} \quad (4.23)$$

where we have defined

$$a \equiv -\frac{1}{2} \int d\vec{r}_{12} U(r) \quad \text{and} \quad m \equiv -\frac{1}{12} \int d\vec{r}_{12} r^2 U(r). \quad (4.24)$$

The integration over $\vec{r}_{12}$ is restricted to the region $r > d$. This is not explicitly indicated; instead, we adhere to the convention that $U(r) = 0$ when $r < d$.

Comparing Eq.(4.23) to the Nakanishi-Fisher free energy in Eq.(4.1), we are finally left with the following expressions for the surface interaction parameters h_1 and g :

$$\begin{aligned} h_1 &= - \int_0^\infty dz V_{\text{wall}}(z), \\ g &= - \int_0^\infty dz_1 \int_{z_2 < 0} d\vec{r}_2 U(r) = -\frac{1}{4} \int d\vec{r}_{12} r U(r). \end{aligned} \quad (4.25)$$

The structure of these expressions is similar to the results from the Landau model. The parameter h_1 is directly related to (the integral of) the wall-fluid interaction potential. For attractive interactions, h_1 is positive and wetting transitions are expected to occur with increasing h_1 . The expression for g is given directly in terms of the interaction potential between fluid molecules. In this case, there is no enhancement factor – the interaction between molecules is not different at the surface than in the bulk region – and the only contribution to g comes from the ‘missing’ fluid-fluid interaction next to the hard wall. Since $U(r) < 0$ (it is the *attractive* part of the interaction between fluid molecules), one has that $g > 0$ thus opposing wetting.

The absence of an enhancement factor is the consequence of the assumption of pairwise additivity of the interaction between molecules. In general, one might include three- or many-body effects occurring near the hard wall and consider a more general form for the interaction potential between molecules:

$$U(\vec{r}_1, \vec{r}_2) = U(r) + \Delta U(\vec{r}_1, \vec{r}_2). \quad (4.26)$$

The term $\Delta U(\vec{r}_1, \vec{r}_2)$, which accounts for the deviation from pairwise additivity, then leads to the existence of an additional contribution in the expression for g , which may be either positive or negative. It is this term that is represented by the enhancement factor D in the Landau mean-field lattice model.

In square-gradient theory, it is assumed that the fluid-fluid interactions as described by $U(r)$ are generally short-ranged. One may therefore assume that the attractive interaction does not extend significantly beyond the diameter d . In that case, Eqs.(4.24) and (4.25) lead to the following expressions for the parameters m and g in terms of the van der Waals parameter a :

$$m = \frac{ad^2}{6} \quad \text{and} \quad g = \frac{ad}{2}. \quad (4.27)$$

With these values for m and g , one may construct the wetting phase diagram as predicted by the Nakanishi-Fisher model. In Figure 4.3, the solid lines are the loci of wetting ($h_{1,W}$) and drying ($h_{1,D}$) transitions as a function of temperature. The wetting and drying transitions turn from first to second order transitions at so-called *tricritical points*, indicated by the open circles, on approach to the liquid-vapour critical point (solid circle). In Table 4.1 we have listed numerical values for the locations of the critical point and the tricritical points in the wetting phase diagram for the various theories discussed here. The advantage of the Nakanishi-Fisher model is that it is relatively simple to locate wetting and drying transitions and determine whether they are of first or second order. Especially the determination of the *nature* (order) of the transition is notoriously difficult in experiments, simulations and more sophisticated density functional theory calculations [117–119]. It is therefore useful to investigate the results of the Nakanishi-Fisher model to establish a first order approximation, while recognizing that more sophisticated density functional theory calculations should give more accurate results.

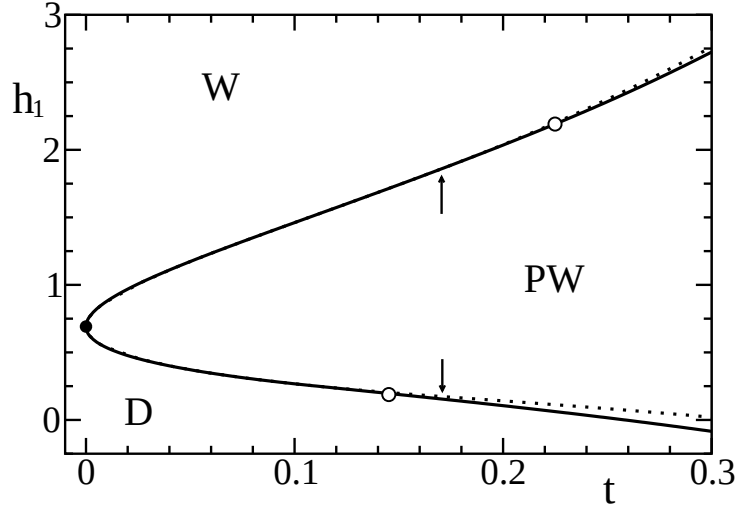


Figure 4.3 Wetting phase diagram for the Nakanishi-Fisher model in terms of the surface chemical potential h_1 (in units of $k_B T d$) as a function of the reduced temperature $T^* = k_B T d^3 / a$. The symbols W, PW, D mark the wetting, partial wetting and drying region, respectively. The upper solid line is the locus of wetting transitions whereas the lower solid line is the locus of drying transitions. Open circles on these solid lines mark the locations of the tricritical points where the wetting/drying transition changes from first to second order in the direction of the liquid-vapour critical point (solid circle). The dashed lines are approximate results for the wetting and drying transitions based on the ρ^4 -form of the free energy in Eq.(4.28).

Furthermore, the Nakanishi-Fisher model has the advantage that analytical expressions for h_1 and g at the wetting and drying transitions may be obtained assuming proximity to the critical point, replacing the Carnahan-Starling form for $g(\rho)$ by a ρ^4 -form:

$$g(\rho) = \frac{m}{(\Delta\rho)^2 \xi^2} (\rho - \rho_v)^2 (\rho - \rho_\ell)^2. \quad (4.28)$$

Minimizing the free energy in Eq.(4.1) using this form for $g(\rho)$ leads to the well-known tanh-profile for the liquid-vapour interface:

$$\rho(z) = \rho_c - \frac{\Delta\rho}{2} \tanh\left(\frac{z}{2\xi}\right), \quad (4.29)$$

where ξ is the bulk correlation length, $\rho_c = \frac{1}{2}(\rho_\ell + \rho_v)$ and $\Delta\rho = \rho_\ell - \rho_v$. Inserting this expression for the interfacial density profile into Eq.(4.5), one obtains for the surface tension of the liquid-vapour interface:

$$\sigma_{\ell v} = \frac{m(\Delta\rho)^2}{3\xi}. \quad (4.30)$$

	critical point		tricritical wetting		tricritical drying	
	T^*	ε, h_1	T^*	ε, h_1	T^*	ε, h_1
NF	0.180155	0.691490	0.139639	2.190712	0.160824	0.255710
NF (ρ^4)	0.180155	0.691490	0.149415	1.860343	0.149415	0.173383
SQW	0.180155	0.893475	0.1478	2.4613	0.1248	0.0190

Table 4.1 Listed are numerical values for the locations of the critical and tricritical points obtained in the various models (NF is the Nakanishi-Fisher model and SQW is the square-gradient fluid interacting with the substrate through a square-well potential). The location is given by the reduced temperature $T^* = k_B T d^3 / a$ and the surface interaction parameter ε (in units of $k_B T$) or h_1 (in units of $k_B T d$).

The surface tensions for the solid-liquid and solid-vapour interfaces are obtained by minimizing Eq.(4.1) taking into account the boundary condition at the substrate, Eq. (4.4), and inserting the corresponding density profiles into Eq.(4.5). Using Young's equation, $\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cos(\theta)$, one is then able to determine whether the surface is (partially) wet or dry upon changing h_1 and g [92]. For a second order wetting or drying transition, one explicitly has:

$$\begin{aligned}
 g &= \frac{2m}{\xi} = \frac{6 \sigma_{lv}}{(\Delta\rho)^2}, \\
 h_{1,W} &= g \rho_\ell = \frac{6 \sigma_{lv} \rho_\ell}{(\Delta\rho)^2}, \\
 h_{1,D} &= g \rho_v = \frac{6 \sigma_{lv} \rho_v}{(\Delta\rho)^2}.
 \end{aligned} \tag{4.31}$$

The loci of the wetting and drying transitions determined using the ρ^4 -form for $g(\rho)$ are drawn in Figure 4.3 as the dashed lines. The correspondence near the critical point is good as to be expected. The corresponding tricritical points for both the wetting and drying transitions are located at a reduced temperature of $T^* = k_B T d^3 / a = 0.149415$, which is in between the tricritical point temperatures obtained using the full Carnahan-Starling form for $g(\rho)$ (see Table 4.1).

In the next section, we compare the wetting phase diagram in Figure 4.3 to the wetting phase diagram obtained for a square-gradient fluid interacting with the substrate through an attractive square-well potential.

4.4 Square-gradient fluid in a square-well potential

In this section our goal is to show how the results of the Nakanishi-Fisher model can be used together with Eq.(4.25) to predict the wetting phase diagram of more complicated density functional theories. As an example, we determine the wetting phase diagram for a square-gradient fluid interacting with the substrate through an attractive square-well potential.

Within the square-gradient approximation, the free energy of a fluid in the presence of an external potential takes on the form:

$$\frac{\Omega[\rho]}{A} = \int_{-\infty}^{\infty} dz \left\{ m[\rho'(z)]^2 + g(\rho) + \rho(z) V_{\text{ext}}(z) \right\}, \quad (4.32)$$

where it is reminded that $g(\rho) = g_{\text{hs}}(\rho) - a\rho^2$ (Eq.(4.2)). For the external potential, we take the following square-well form:

$$V_{\text{ext}}(z) = \begin{cases} V_0 & \text{when } z < 0, \\ -\varepsilon & \text{when } 0 < z < d, \\ 0 & \text{when } z > d, \end{cases} \quad (4.33)$$

where the limit $V_0 \rightarrow \infty$ is considered. One may show that in this limit one has [104, 105, 120]:

$$\rho(z = 0^+) = 0. \quad (4.34)$$

With the observation that $\rho(z) = 0$ in the whole region $z < 0$, the density profile that minimizes the free energy in Eq.(4.32) is obtained from solving the following differential equations (with $\rho(0) = 0$ as boundary condition):

$$m\rho'(z)^2 = \begin{cases} g(\rho) + p - \varepsilon\rho(z) + \varepsilon\rho_d & \text{when } 0 < z < d, \\ g(\rho) + p & \text{when } z > d, \end{cases} \quad (4.35)$$

where we have defined $\rho_d \equiv \rho(d)$.

Solutions for the density profile are obtained numerically using the fourth order Runge Kutta method [121]. Two different types of solutions are found: density profiles that are monotonically increasing and density profiles that exhibit a maximum. In Figure 4.4 a typical example of two such solutions is shown.

The surface tension is obtained by inserting the density profile into the expression for the free energy in Eq.(4.32). When the profile monotonically increases, the surface tension is given by

$$\sigma = -\varepsilon d\rho_d + 2m^{\frac{1}{2}} \int_0^{\rho_d} d\rho [g(\rho) + p - \varepsilon\rho + \varepsilon\rho_d]^{\frac{1}{2}} + 2m^{\frac{1}{2}} \int_{\rho_d}^{\rho_b} d\rho [g(\rho) + p]^{\frac{1}{2}}, \quad (4.36)$$

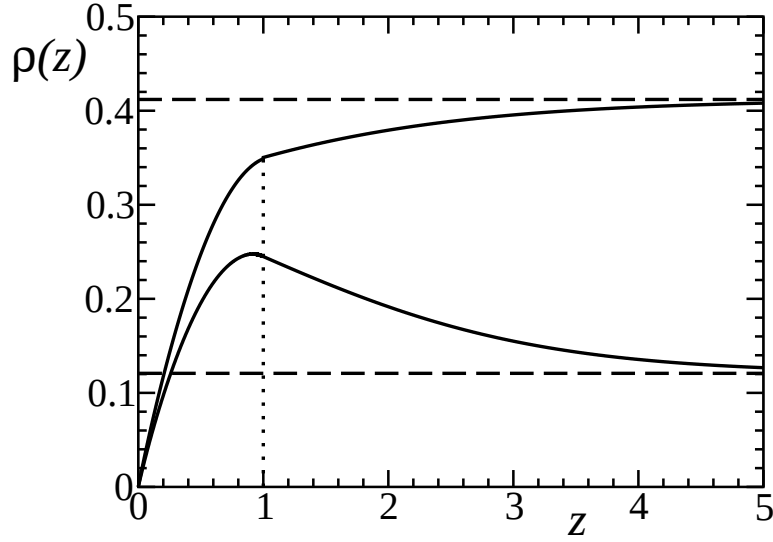


Figure 4.4 Density profiles $\rho(z)$ (in units of $1/d^3$) as a function of z (in units of d) for the square-gradient fluid interacting with the substrate via a square-well potential at a temperature $T^* = k_B T d^3/a = 0.17$ and depth of the attractive well $\varepsilon/k_B T = 1.2$. The horizontal dashed lines mark the values of the bulk liquid and vapour densities.

with ρ_b denoting the bulk fluid density far from the substrate which can be either ρ_ℓ to give σ_{sl} or ρ_v to give σ_{sv} . When the profile exhibits a maximum, say at $z = z_{\max}$, the surface tension is given by

$$\begin{aligned} \sigma = & -\varepsilon d \rho_d + 2m^{\frac{1}{2}} \int_0^{\rho_{\max}} d\rho [g(\rho) + p - \varepsilon\rho + \varepsilon\rho_d]^{\frac{1}{2}} \\ & + 2m^{\frac{1}{2}} \int_{\rho_d}^{\rho_{\max}} d\rho [g(\rho) + p - \varepsilon\rho + \varepsilon\rho_d]^{\frac{1}{2}} + 2m^{\frac{1}{2}} \int_{\rho_b}^{\rho_d} d\rho [g(\rho) + p]^{\frac{1}{2}}, \quad (4.37) \end{aligned}$$

with $\rho_{\max} = \rho(z = z_{\max})$.

With the surface tensions thus determined, using Young's equation for the contact angle, we are again able to determine the wetting phase diagram which is shown in Figure 4.5. The solid lines are the loci of wetting and drying transitions as a function of temperature, with the tricritical points indicated by the open circles (see Table 4.1 for numerical values).

To compare these results with the Nakanishi-Fisher model, we use the fact that the interaction is short-ranged, giving $m = ad^2/6$ and $g = ad/2$ (Eq.(4.27)), and that $h_1 = \varepsilon d$ for the square-well potential (Eq.(4.25)). The wetting and drying transition lines obtained from the theory of Nakanishi and Fisher are shown in Figure 4.5 as the dashed lines, with the corresponding tricritical points indicated by open squares. Reasonable agreement between the two models is obtained; the wetting transition line

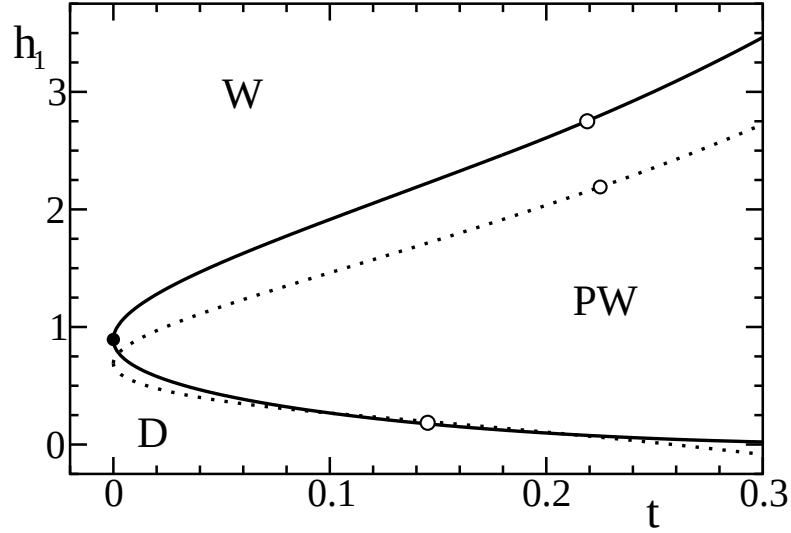


Figure 4.5 Wetting phase diagram for the square-gradient fluid interacting with the substrate via a square-well potential in terms of the square-well depth ε (in units of $k_B T$) as a function of the reduced temperature $T^* = k_B T d^3/a$. As in Figure 4.3, the symbols W, PW, D mark the wetting, partial wetting and drying region, respectively, the solid lines are the loci of wetting and drying transition, and the open circles mark the locations of the tricritical points. The dashed lines are the Nakanishi and Fisher model results of Figure 4.3, with $h_1 = \varepsilon d$, with the corresponding tricritical points indicated by the open squares.

obtained in the square-well model is somewhat above the Nakanishi-Fisher wetting line, whereas the location of the drying transition line seems to be in better agreement. The locations of the wetting transition tricritical points are comparable but the (temperature) location of the drying tricritical points differ significantly, indicating that the locus of the drying transition is very sensitive to the details of the model.

When the transition is of second order (close to the critical point), the location of the wetting ($\varepsilon = \varepsilon_W$) or drying transition ($\varepsilon = \varepsilon_D$) is determined by the following integral condition:

$$m^{\frac{1}{2}} \int_0^{\rho_b} d\rho [g(\rho) + p - \varepsilon\rho + \varepsilon\rho_b]^{-\frac{1}{2}} = d, \quad (4.38)$$

where ρ_b is either ρ_ℓ or ρ_v to determine ε_W or ε_D , respectively. This equation can be used to, numerically, determine the shape of the wetting phase very accurately. In an expansion in $t \equiv 1 - T/T_c$, with T_c the critical point temperature, one obtains:

$$\frac{\varepsilon_c}{k_B T} \equiv \frac{\varepsilon_W + \varepsilon_D}{2 k_B T} \simeq 0.893475 + 1.7328 t + \dots,$$

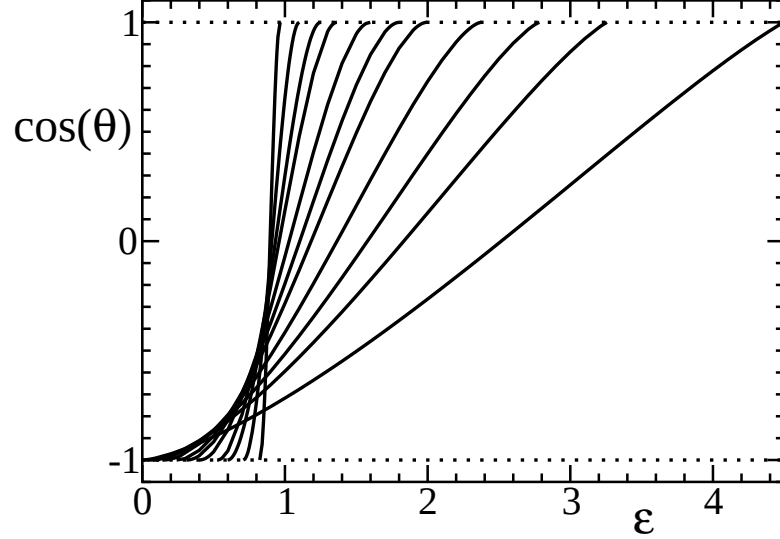


Figure 4.6 Cosine of the contact angle for the square-gradient fluid interacting with the substrate via a square-well potential versus the square-well depth ε (in units of $k_B T$) for various wetting isotherms: $T^* = k_B T d^3 / a = 0.18, 0.179, 0.177, 0.175, 0.17, 0.165, 0.16, 0.15, 0.14, 0.13, 0.11$, from left to right.

$$\frac{\Delta \varepsilon}{k_B T} \equiv \frac{\varepsilon_W - \varepsilon_D}{k_B T} \simeq 4.8793 t^{\frac{1}{2}} + \dots \quad (4.39)$$

In Figure 4.6, the contact angle of the square-gradient fluid interacting with the substrate through a square-well potential is shown for a number of different isotherms. It can be inferred from Figure 4.6 that $\cos(\theta)$ jumps discontinuously from -1 to 1 at the critical point, located at $\varepsilon \simeq 0.893475$ (see Table 4.1). Near the critical point, the behaviour of the contact angle as a function of the well-depth between the limits $\varepsilon_D < \varepsilon < \varepsilon_W$ can be analytically determined, yielding:

$$\cos(\theta) = \frac{3 \varepsilon_W \varepsilon_D (\varepsilon_W + \varepsilon_D) - \varepsilon_W^3 - \varepsilon_D^3 - 12 \varepsilon_W \varepsilon_D \varepsilon + 6 (\varepsilon_W + \varepsilon_D) \varepsilon^2 - 4 \varepsilon^3}{(\varepsilon_W - \varepsilon_D)^3}. \quad (4.40)$$

In terms of $\Delta \varepsilon$ and the critical value ε_c this rearranges to

$$\cos(\theta) = 3 \left(\frac{\varepsilon - \varepsilon_c}{\Delta \varepsilon} \right) - 4 \left(\frac{\varepsilon - \varepsilon_c}{\Delta \varepsilon} \right)^3. \quad (4.41)$$

The same scaling form for the fundamental behaviour of the contact angle close to the critical point is to be expected if one considers, for example, the Nakanishi-Fisher model replacing ε by h_1 .

4.4.1 Simulation results by van Swol and Henderson

Although it is not the goal in this chapter to come to a numerically accurate description of simulation results for wetting and drying, it is perhaps interesting to compare

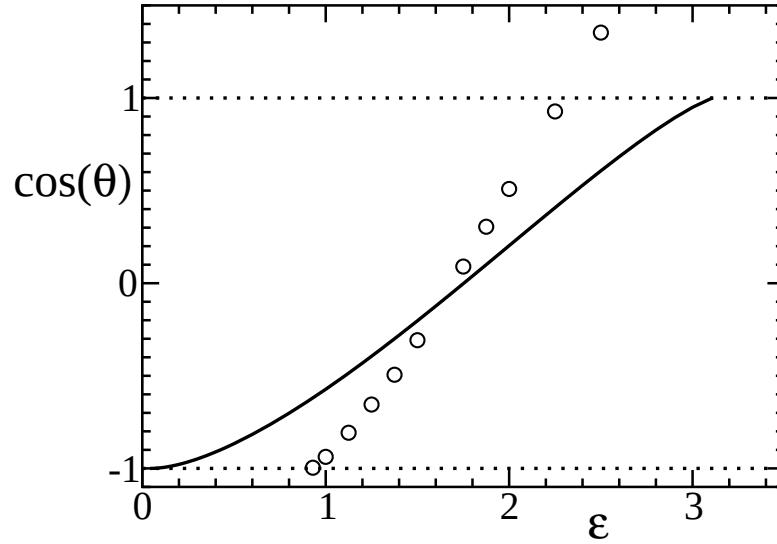


Figure 4.7 Cosine of the contact angle versus the square-well depth ε (in units of $k_B T$) for the simulation results of Ref. [86, 111] (open circles) and the Nakanishi-Fisher model with $h_1 = \varepsilon d/2$ and $T^* = 0.134$.

with Molecular Dynamics (MD) simulations carried out by van Swol and Henderson, already some 15 years ago [86, 111]. In these simulations the wetting phase behaviour and interfacial structure of a square-well fluid adsorbed at a square-well wall was investigated. The simulations are performed along a single isotherm at liquid-vapour coexistence, which the authors report to be at $T/T_c = 0.738$. To compare with the liquid-vapour coexistence using the Carnahan-Starling expression for the bulk free energy, different criteria can be used to fix the location in the liquid-vapour phase diagram. Here we have chosen to fix the liquid-vapour bulk density difference $\Delta\rho$ to the value obtained in the simulations. This gives $T/T_c = 0.745$ ($T^* = 0.134$) and for the bulk densities $\rho_v d^3 = 0.027$ and $\rho_\ell d^3 = 0.642$, which are comparable to the densities obtained in the simulations, $\rho_v d^3 = 0.033$ and $\rho_\ell d^3 = 0.648$.

The MD simulation results by van Swol and Henderson are plotted in Figure 4.7 as the open circles. The data clearly suggest that the wetting transition is of first order, although it is indicated by the authors that the simulations near the wetting transition are somewhat less reliable due to the unacceptably long simulation runs [86, 111]. The determination of the order of the drying transition is (notoriously) difficult and it was concluded that it is either second order or very weakly first order.

To compare with the Nakanishi-Fisher model, we first use Eq.(4.24) and Eq.(4.25) for the square-well interaction potential between fluid molecules to determine that $m = (211/760) ad^2$ and $g = (195/304) ad$. Furthermore, we use Eq.(4.25) for the square-well interaction potential between the fluid and the substrate to determine that $h_1 = \varepsilon d/2$. The resulting behaviour of the contact angle versus ε is shown as the solid in line in Figure 4.7. Both the wetting and drying transition is of first order, in

line with the simulation results. A striking difference between the simulation results and the Nakanishi-Fisher model is the location of the drying transition. For the Nakanishi-Fisher model, but also for the square-gradient model with the square-well fluid-substrate interaction and more sophisticated density functional theories [86,111], the drying transition occurs at a value of h_1 , or equivalently ε , that is close to zero at moderate temperatures not too close to the critical point. In the simulations, however, the substrate remains dry not until a large (threshold) value for the attractive surface interaction parameter (h_1 or ε) is reached.

4.5 Discussion

As long as the interaction potential between a liquid and a substrate is short-ranged – an assumption which may not be appropriate in the case of long-ranged London dispersion forces – the theory of Nakanishi and Fisher provides an excellent starting point in describing wetting behaviour. We have used density functional theory to derive microscopic expressions for the surface parameters h_1 and g that are present in the Nakanishi and Fisher model. One finds that the parameter h_1 captures the interaction of the substrate with the liquid: increasing the strength of the attractive interaction (larger values of h_1) promotes wetting. The enhancement parameter g is generally determined by the sum of two contributions: (1) due to the fact that the interaction potential between fluid molecules might be enhanced near the substrate as compared to the bulk, (2) due to the lack of fluid molecules for $z < 0$. Even when the fluid-fluid interaction potential is translationally invariant, as it is in the density functional theory considered here, one therefore has a non-zero, positive value for g so that the term *enhancement* parameter is somewhat misleading.

As an example, we have determined the wetting phase diagram for a square-gradient fluid interacting via a short-ranged square-well potential in terms of the square-well depth and temperature. Loci of wetting and drying transitions are obtained on which tricritical points are located where the order of the transition changes from first to second order (see Table 4.1). Using the microscopic expressions for the surface parameters h_1 and g , the phase diagram is compared to the phase diagram from the theory of Nakanishi and Fisher. One finds that the shape of the phase diagrams are comparable (see Figure 4.5) but that the nature of the drying transition depends sensitively on the details of the model considered.

The square-gradient model is in many ways too simplistic to describe wetting phenomena in a *quantitative* way, especially away from the critical point [122,123]. It is unfit to describe the phenomenon of surface layering [124] that is present in integral theories [125] and which also has been observed in Monte Carlo simulations [126]. Furthermore, the square-gradient model always leads to a zero density at a hard wall, which is inconsistent with the wall theorem [73,120]. However, the square-gradient model *does* have the advantage of being simple enough to be able to unambiguously determine the *order* of the wetting and drying transitions – something that is very

difficult or even impossible to do in more sophisticated density functional theories – thus allowing for a direct test of our microscopic expressions for h_1 and g by making the comparison with the theory of Nakanishi and Fisher.

Chapter 5

Interfacial properties of colloid-polymer mixtures

ABSTRACT

In this chapter the interfacial properties of demixed colloid-polymer mixtures are analyzed. Using density functional theory and a virial approach we calculate the surface tension and bending rigidity of the interface between the demixed fluid phases. Our results are compared with computer simulations and experiments.

5.1 Introduction

It is well-known that the addition of non-adsorbing polymer to a colloidal suspension can lead to phase separation. This is due to an effective attraction between colloidal particles arising from the exclusion of polymer in the depletion zones between them [1, 2]. This phase separation has been observed experimentally [127–130] and described theoretically [1, 2, 131–133]. The fluid-fluid interface between the demixed phases possesses an ultra-low surface tension (in the order of $\mu\text{N/m}$ [134]), common for (bio)polymer systems. de Hoog and Lekkerkerker [135] reported surface tensions of a silica/poly(dimethylsiloxane) mixture which are of the same magnitude. The fluctuations of such an interface have also been studied experimentally by the same group [136]. These fluctuations can be described in terms of capillary wave theory (CWT). It is known that for fluctuations with short wavelengths corrections on CWT may be present, which can be described in terms of the bending rigidity. Especially in systems with low interfacial tensions the bending rigidity becomes important and may even dominate the behaviour of the surface. Recently Scholten *et al.* [137] proposed a calculation of the bending rigidity by estimating the interfacial thickness using experimentally determined surface tensions. They found for a near critical gelatin/dextran system bending rigidities in the order of 200-1000 $k_B T$. Vink *et al.* [138] performed Monte Carlo simulations to determine the spectrum of capillary wave-type interfacial excitations. From the spectrum one is able to determine the bending rigidity and surface tension. In this chapter we will calculate the surface tension and bending rigidity for a demixed colloid-polymer system and compare with experiments and simulation results.

In order to obtain values for the bending rigidity both deep inside the two-phase region as well as near the critical point, the free energy needs to be determined. We follow the work of Gast and Hall [131] who employed second order thermodynamic perturbation theory in order to obtain the phase diagrams. Further applications can be found in refs. [139, 140]. Equipped with the free energy obtained from perturbation theory the interfacial properties can be calculated. We employ a square-gradient theory similar to the work of Brader *et al.* [141]. To complete our theoretical investigation we have adopted a virial approach to the interfacial properties.

This chapter is outlined as follows. First the perturbation theory will be briefly summarized in section 5.2. Then, in section 5.3, the methods for calculating the surface tension and bending rigidity will be treated. We finish with some conclusions in section 5.4.

5.2 Perturbation theory

We consider a system composed of N spherical colloids of diameter σ_c in a bath of ideal polymers, which are in equilibrium with a polymer reservoir at fixed chemical potential μ_p and density ρ_p . The colloids are assumed to interact through a non-

electrostatic and pairwise additive intermolecular potential $u(r)$, which is a function of the intermolecular distance r . We follow the theoretical description by Gast *et al.* [131] by describing this system using perturbation theory. In perturbation theory the interaction potential is decomposed into a reference potential with well-known properties and a perturbation potential:

$$u(r) = u_{\text{HS}}(r) + u_{\text{dep}}(r). \quad (5.1)$$

The reference potential is the hard sphere potential:

$$u_{\text{HS}}(r) = \begin{cases} \infty, & r < \sigma_c \\ 0, & r > \sigma_c \end{cases} \quad (5.2)$$

and the perturbation potential is given by the depletion potential [1]:

$$\frac{u_{\text{dep}}(r)}{k_{\text{B}}T} = -\eta_p \frac{(1+q)^3}{q^3} \left\{ 1 - \frac{3r}{2(1+q)\sigma_c} + \frac{r^3}{2(1+q)^3\sigma_c^3} \right\}, \quad \sigma_c < r < \sigma_c + \sigma_p \quad (5.3)$$

with the polymer to colloid size ratio $q = \sigma_p/\sigma_c$, $\eta_p = \frac{\pi}{6}\rho_p\sigma_p^3$, k_{B} Boltzmann's constant and T the temperature. The presence of polymers is only apparent through the form of the depletion potential. Its magnitude is proportional to the uniform polymer density - or rather the polymer fugacity but since we consider ideal polymers, $z_p = \rho_p$. Effectively, the system can thus be regarded as a one-component system in which the resulting free energy is a function of colloidal density only.

In perturbation theory the interaction potential is written as $u(r) = u_{\text{HS}}(r) + \lambda u_{\text{dep}}(r)$ where λ is a small parameter which is “switched on” by changing it from $\lambda = 0$ to $\lambda = 1$. The free energy is then determined by considering the logarithm of the N -particle partition function expanded around $\lambda = 0$:

$$\ln Z_N = \ln Z_N|_{\lambda=0} + \lambda \left(\frac{\partial \ln Z_N}{\partial \lambda} \right)_{\lambda=0} + \frac{\lambda^2}{2} \left(\frac{\partial^2 \ln Z_N}{\partial \lambda^2} \right)_{\lambda=0} + \mathcal{O}(\lambda^3). \quad (5.4)$$

When the perturbation expansion is carried out to second order we find for the Helmholtz free energy:

$$\frac{F}{Nk_{\text{B}}T} = \frac{F_{\text{HS}}}{Nk_{\text{B}}T} + \frac{\rho_c}{2k_{\text{B}}T} \int d\mathbf{r} g_{\text{HS}}(r) u_{\text{dep}}(r) - \frac{\rho_c^2}{4k_{\text{B}}T} \left(\frac{\partial \rho_c}{\partial p} \right)_{\text{HS}} \int d\mathbf{r} g_{\text{HS}}(r) u_{\text{dep}}^2(r), \quad (5.5)$$

where $\rho_c = N/V$ is the colloidal number density, $g_{\text{HS}}(r)$ the radial distribution function of hard spheres, $\left(\frac{\partial \rho_c}{\partial p} \right)_{\text{HS}}$ the bulk compressibility of the reference system and F_{HS} the free energy of the hard sphere reference system. The Carnahan-Starling expression [91] is used for the free energy of the fluid phase. The evaluation of the second order term in the λ -expansion requires the knowledge of the three and four body distribution functions of the reference system. Because of the difficulty arising

Quantity	Type	Reference
<i>Fluid phase</i>		
Helmholtz free energy	Carnahan Starling	[143]
Radial distribution function	Percus-Yevick	[144]
	Verlet-Weis improvement	[145]
<i>Solid phase</i>		
Helmholtz free energy	Hall	[146]
Radial distribution function	Kincaid-Weis	[147]

Table 5.1 Sources for the hard-sphere reference states

in calculating this term it is approximated using the macroscopic compressibility approximation devised by Barker and Henderson [142]. Substitution of the perturbation potential Eq.(5.3) into Eq.(5.5) then gives:

$$\begin{aligned} \frac{F}{Nk_B T} = \frac{F_{\text{HS}}}{Nk_B T} - 12\eta_c \eta_p \left(\frac{1+q}{q} \right)^3 \int_1^{1+q} dx x^2 g_{\text{HS}}(x) \left\{ 1 - \frac{3x}{2(1+q)} - \frac{x^3}{2(1+q)^3} \right\} \\ - 6\eta_c \eta_p^2 \left(\frac{1+q}{q} \right)^6 \left(\frac{\partial \rho_c}{\partial p} \right)_{\text{HS}} k_B T \int_1^{1+q} dx x^2 g_{\text{HS}}(x) \left\{ 1 - \frac{3x}{2(1+q)} - \frac{x^3}{2(1+q)^3} \right\}^2, \end{aligned} \quad (5.6)$$

where $x = r/\sigma_c$.

To explicitly evaluate the free energy one needs to model the radial distribution function $g_{\text{HS}}(x)$. Following Gast *et al.* [131] we have taken the expression by Smith and Henderson [148] with the modification suggested by Verlet and Weis [145]. As was shown by Gast *et al.*, the resulting expression for the free energy exhibits a liquid-vapour-like transition. Phase boundaries may be determined by equating the chemical potential and pressure in both the liquid and vapour phases:

$$\mu_c = \left(\frac{\partial f}{\partial \rho_c} \right)_{T,N}, \quad (5.7)$$

and

$$p = -f + \mu_c \rho_c, \quad (5.8)$$

where f denotes the free energy density: $f = F/V$.

We have determined the phase diagrams for a range of values for the polymer to colloid size ratio, $q = 0.8, 0.9, 1.0$. The results are presented in Figure 5.1. Even though our main interest lies within the interfacial properties of the fluid-fluid interface, we have included in these phase diagrams the solid-fluid transition. The determination of this transition requires knowledge of the radial distribution function and free energy of the solid phase, which we have taken from ref. [146]. Table 5.1 summarizes the type of expressions used to calculate the phase diagrams.

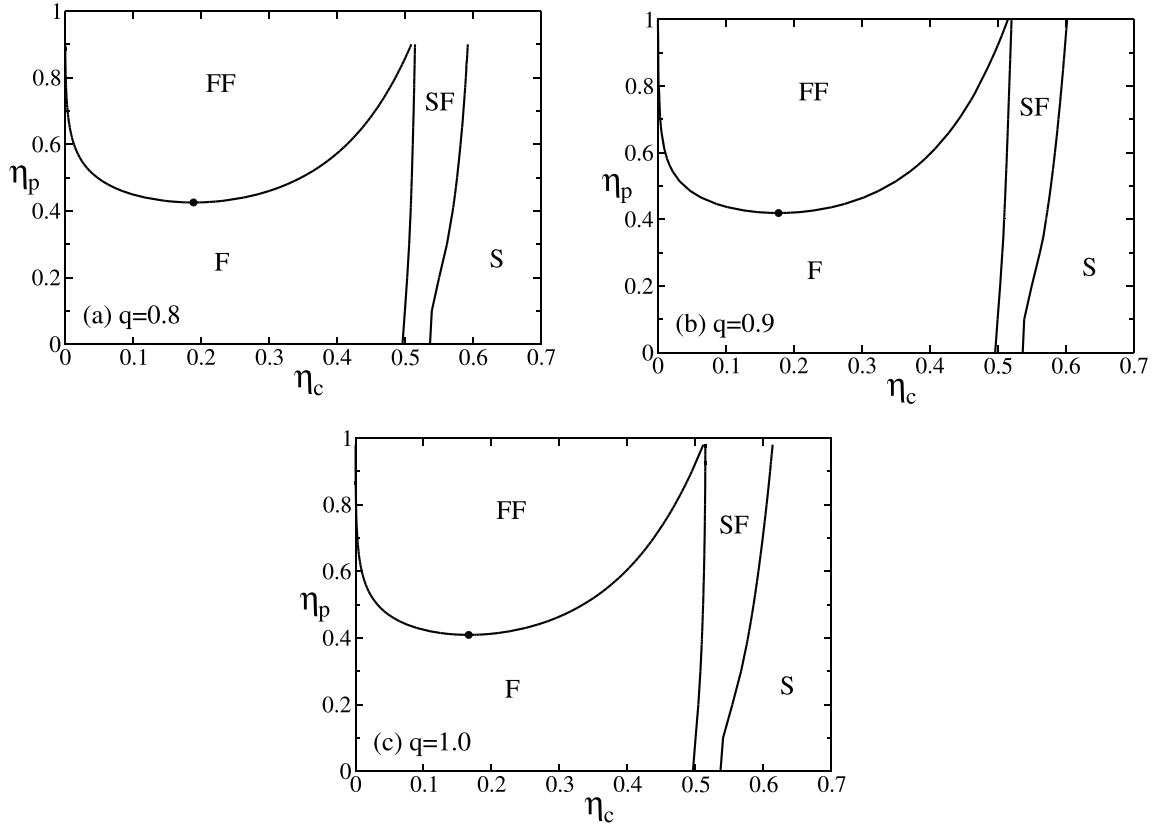


Figure 5.1 Phase diagrams as a function of colloidal (η_c) and polymer (η_p) volume fractions for three values of the polymer to colloid size ratio ($q = 0.80 - 1.0$). The solid point indicates the location of the critical point between the fluid two-phase region (FF) and the fluid single phase region (F). Also shown are the solid-fluid two-phase region (SF) and the solid single phase region (S).

For small size ratios the fluid fluid phase separation is preempted by phase coexistence between a high density solid and a single low density phase. Upon increasing the size ratio the fluid-fluid phase separation becomes stable ($q \sim 0.27$) with a critical point and triple point, the phase diagram being not unlike those of simple liquids with the polymer density playing the role of inverse temperatures ($T \sim 1/\eta_p$).

5.3 Calculation of interfacial properties

We now turn to the calculation of the interfacial properties of the colloid-polymer mixture. First, the calculation of the surface tension will be treated. Then, we turn our attention to the calculation of the bending rigidity. Comparisons with experiments and simulations are made.

5.3.1 Surface tension

We shall adopt two different approaches to the calculation of the surface tension. The first is the usual square-gradient model in which we relate the coefficient of the square-gradient to the depletion potential. Using this model the leading behaviour of the surface tension in the vicinity of the critical point is investigated. The second approach is a virial approach that uses the Kirkwood-Buff expression for the surface tension.

Square-gradient theory

In square-gradient theory the grand free energy is written as a functional of the colloidal density ρ_c :

$$\Omega[\rho_c] = \int d\mathbf{r} \left[m |\nabla \rho_c(\mathbf{r})|^2 + f(\rho_c) - \mu_c \rho_c(\mathbf{r}) \right], \quad (5.9)$$

where $f(\rho_c)$ is the Helmholtz free energy density for a fluid constrained to have density ρ_c , μ_c the colloidal chemical potential at coexistence and m denotes the usual coefficient of the square-gradient term. The explicit form of $f(\rho_c)$ is given by Eq.(5.6) using the relation $\rho_c \frac{F}{Nk_B T} = \frac{F}{V k_B T} = f$. The coefficient m is given by

$$m(\rho_c) = \frac{k_B T}{12} \int d\mathbf{r} r^2 c^{(2)}(r; \rho_c), \quad (5.10)$$

where $c^{(2)}(r; \rho_c)$ is the pair direct correlation function of a uniform colloidal system. For simple liquids $m(\rho_c)$ is largely insensitive to the choice of approximation for $c^{(2)}(r; \rho_c)$, however for the short-ranged attractive depletion potential this is not the case. We approximate the direct correlation function by setting it zero inside the hardcore region ($r < \sigma_c$) and equal to

$$c^{(2)}(r; \rho_c) = -\frac{u_{dep}(r)}{k_B T} g_{HS}(r; \rho_c), \quad (5.11)$$

when $r > \sigma_c$. This form may be inferred from extending Eq.(5.5) to inhomogeneous systems neglecting the second order term and making a gradient expansion. The square-gradient coefficient thus becomes

$$m(\rho_c) = -\frac{1}{12} \int d\mathbf{r} r^2 u_{dep}(r) g_{HS}(r; \rho_c). \quad (5.12)$$

This expression is closely related to the calculation by Brader and Evans [141] who set $c^{(2)}(r) = \frac{-u_{dep}(r)}{k_B T}$ for $r > \sigma_c$ so that the resulting square-gradient coefficient is independent of the colloidal density.

By considering a planar interface $\rho_c(\mathbf{r}) \equiv \rho_{c,0}(z)$ (which we shall denote as $\rho_0(z)$) minimizing Eq.(5.9) leads to the usual expression for the surface tension, σ :

$$\sigma = 2 \int_{-\infty}^{\infty} dz m(\rho_c) [\rho_0']^2. \quad (5.13)$$

This equation can be rewritten:

$$\sigma = \int_{\rho_c^V}^{\rho_c^L} d\rho_c [m(\rho_c) (f(\rho_c) - \mu_c \rho_c + p)]^{1/2}, \quad (5.14)$$

where (ρ_c^V, ρ_c^L) denote the values of the colloidal density at coexistence for the vapour and liquid phases, respectively. Using Eq.(5.14) we have determined the surface tension. The results are shown as the open circles in Figure 5.2 for two values of q as a function of the variable $\Delta\eta \equiv \eta_c^L - \eta_c^V$.

In the vicinity of the critical point it is possible to approximate $f(\rho_c)$ by the well-known double well form of the free energy:

$$f(\rho_c) = f(\rho_m) - \frac{m_c}{2\xi^2}(\rho_c - \rho_m)^2 + \frac{m_c}{(\Delta\rho)^2\xi^2}(\rho_c - \rho_m)^4, \quad (5.15)$$

where $\Delta\rho \equiv (\rho_c^L - \rho_c^V)$, $\rho_m \equiv \frac{1}{2}(\rho_c^L + \rho_c^V)$. The constant m_c is given by the value of m evaluated at the critical point and ξ is the bulk correlation length which may according to Eq.(5.15) be related to the fourth derivative of the free energy with respect to the density at the critical point, $f_c^{(4)}$:

$$\xi = \sqrt{\frac{24m_c}{(\Delta\rho)^2 f_c^{(4)}}}. \quad (5.16)$$

Minimizing the free energy functional Eq.(5.9), using this form for $f(\rho_c)$, results in the well known tanh-form of the density profile:

$$\rho_0(z) = \rho_m - \frac{\Delta\rho}{2} \tanh\left(\frac{z}{2\xi}\right). \quad (5.17)$$

The surface tension near the critical point can now be calculated by substituting this profile into Eq.(5.13) to obtain:

$$\sigma = \frac{m_c(\Delta\rho)^2}{3\xi} = \frac{1}{36}\sqrt{6m_c f_c^{(4)}}(\Delta\rho)^3 \propto (\Delta\eta)^3, \quad (5.18)$$

which gives the scaling for the surface tension in these types of density functional theories. This scaling result is shown as the dashed line in the inset of Figure 5.2.

Virial expression

We like to compare the results for the surface tension with other models which are applicable not only near the critical point, i.e. where the bulk correlation length is small compared to the range of interaction. A rigorous expression for the surface tension is the Kirkwood-Buff formula, which expresses σ in terms of the interaction potential $u(r)$ and the pair density of the planar interface $\rho_0(z_1, z_2, r)$ [101]:

$$\sigma = \frac{1}{4} \int dz_1 \int d\mathbf{r}_{12} u'(r) r (1 - 3s^2) \rho_0^{(2)}(z_1, z_2, r), \quad (5.19)$$

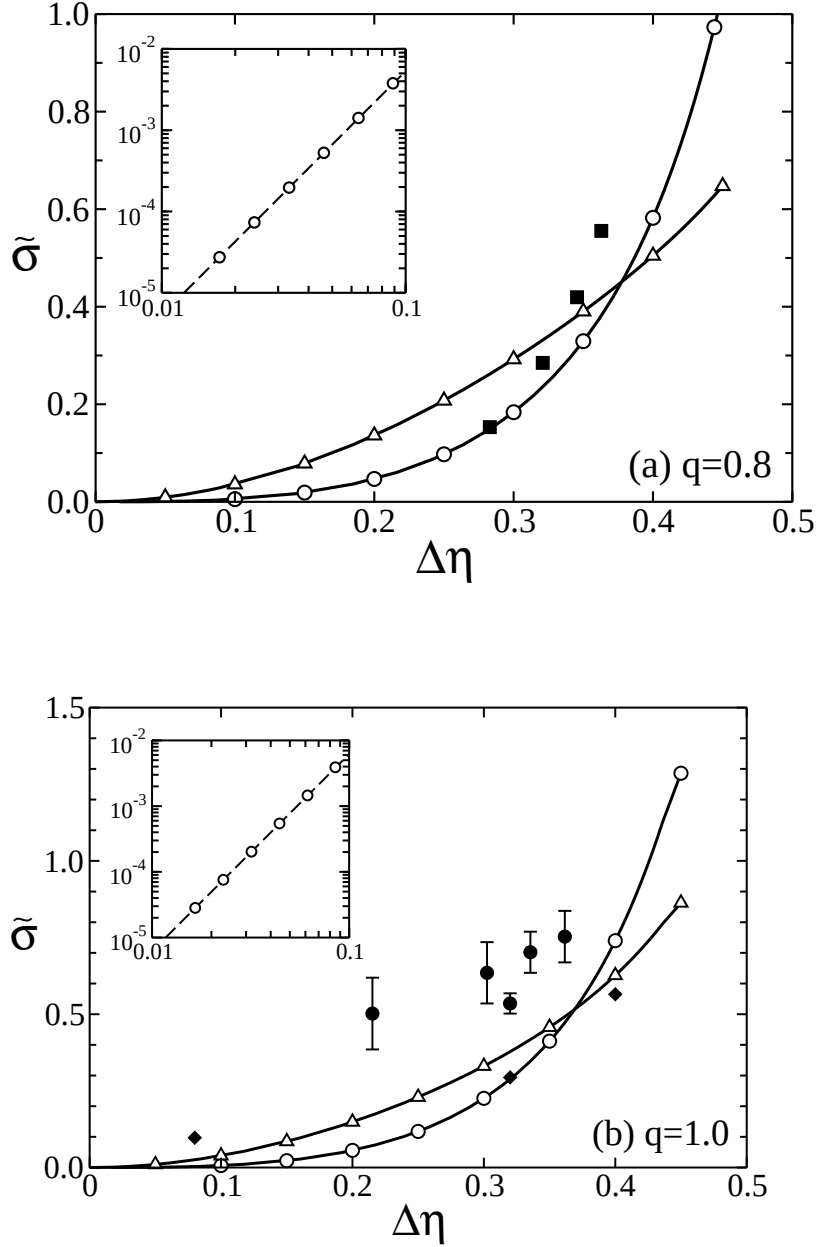


Figure 5.2 Surface tension σ (in units of $k_B T / \sigma_c^2$) as a function of the bulk colloidal volume fraction difference, $\Delta\eta \equiv \eta_c^L - \eta_c^V$ for (a) $q=0.80$ and (b) $q=1.0$. The open circles are the results from square-gradient theory (Eq.(5.14)); open triangles are the results from the virial expression (Eq.(5.23)). The inset shows the square-gradient results for the surface tension close to the critical point together with the scaling relation $\sigma \propto (\Delta\eta)^3$ (dashed line). The filled squares in (a) are the results for σ from the simulations by Vink [138] (see Table 5.2). The filled circles in (b) are the experimental results by de Hoog and Lekkerkerker [135], where we used the experimental estimate $\sigma_c \approx \sigma_p \approx 26$ nm.

where $r \equiv |\mathbf{r}_{12}|$, $s \equiv \cos(\theta_{12})$ and $z_2 \equiv z_1 + sr$. The Kirkwood-Buff expression relies on the assumption that the intermolecular potential can be written as a sum over the interaction energy between pairs of particles. To evaluate this expression, we shall assume that far from the critical point the vapour density is low compared to the liquid density. First, we assume that the pair density can be written as a product of the densities and the pair correlation function in the bulk liquid $g_{\text{HS}}(r; \rho_c^L)$:

$$\rho_0^{(2)}(z_1, z_2, r) \approx \rho_0(z_1)\rho_0(z_2)g_{\text{HS}}(r; \rho_c^L). \quad (5.20)$$

Furthermore, we assume that the range of intermolecular interactions is greater than the interfacial width so we can replace the density profiles in the above expression by a step profile $\rho_{0,\text{bulk}}(z)$:

$$\rho_{0,\text{bulk}} = \rho_{0,\text{bulk}}(z) = \rho_c^L \theta(-z) + \rho_c^V \theta(z), \quad (5.21)$$

where $\theta(z)$ is the Heaviside function.

With these assumptions the surface tension reduces to the one derived by Fowler [149]:

$$\sigma = \frac{\pi}{8}(\Delta\rho)^2 \int_0^\infty dr u'(r) r^4 g_{\text{HS}}(r; \rho_c^L). \quad (5.22)$$

When applying this formula to our model interaction potential, care must be taken of the discontinuity in the integrand at $r = \sigma_c$. By making use of the continuity of $n(r) = g(r) \exp(u(r)/k_B T)$ the integration can be split in a singular and continuous part:

$$\sigma = -\frac{\pi}{8}(\Delta\rho)^2 k_B T \sigma_c^4 g_{\text{HS}}(\sigma_c^+) + \frac{\pi}{8}(\Delta\rho)^2 \int_{\sigma_c}^\infty dr u'_{\text{dep}}(r) r^4 g_{\text{HS}}(r; \rho_c). \quad (5.23)$$

The surface tension evaluated using this expression is shown in Figure 5.2 as the triangulated curves for two different values of q . Furthermore, we have added in Figure 5.2a ($q = 0.8$) simulation results of Vink *et al.* [138] as filled squares. In Figure 5.2b ($q = 1.0$) the experimental results of de Hoog and Lekkerkerker [135] are shown as the filled circles. They obtained the surface tension by employing a spinning drop technique. As can be seen the experimental results seem to overestimate the theoretical predictions over the entire density range whereas the simulation results are closer to the theory.

5.3.2 Bending rigidity

The bending rigidity measures the energy cost of bending an interface without stretching it. It is formally defined by the Helfrich expansion of the free energy [23]:

$$F = \int dA \left[\sigma - \frac{2k}{R_0} J + \frac{k}{2} J^2 + \bar{k} K \right], \quad (5.24)$$

where σ is the surface tension of the planar interface; R_0 , the radius of spontaneous curvature, k , the rigidity constant of bending and $\bar{k}$, the rigidity constant of bending associated with Gaussian curvature. The total curvature J and the Gaussian curvature K are defined as

$$J = \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \quad K = \frac{1}{R_1 R_2}, \quad (5.25)$$

with R_1 and R_2 are the principle radii of curvature on the surface. The Helfrich equation is the starting point for most experimental [25, 26] and theoretical work [27–29] dealing with curved surfaces. It may also be used to describe thermal fluctuations around a planar equilibrium surface. The reader is referred to [64, 67] for a comprehensive review on this subject.

In this chapter we are interested in calculating the bending rigidity for the colloid-polymer system. Since the surface tension in these systems is very low, the bending rigidity may play an important role in describing the behaviour of the surface. First, the bending rigidity is determined using square-gradient theory close to the critical point. Second, it is examined far from the critical point using a virial approach. Our goal is to compare with results from computer simulations by Vink *et al.* [138].

Square-gradient theory

The bending rigidity may be determined from the square-gradient expression in Eq.(5.9) by expanding it to second order in curvature $1/R$ and comparing the result with the form of the Helfrich equation in Eq.(5.24). One finds the following expression:

$$k = \int_{-\infty}^{\infty} dz \left\{ -m\rho'_0 \rho_{s,1} - \mu_{s,1} z [\rho_0 - \rho_{0,\text{bulk}}] - \frac{\mu_{s,1}}{4} [\rho_{s,1} - \rho_{1,\text{bulk}}] - 2\mu_{s,2} [\rho_0 - \rho_{0,\text{bulk}}] \right\}, \quad (5.26)$$

where subscripts $s, 1$ and $s, 2$ refer to the first and second coefficients in an expansion in $1/R$ for a spherical surface. Calculation of the bending rigidity using square-gradient theory thus requires knowledge of $\rho_{s,1}(z)$. Near the critical point the free energy form of Eq.(5.15) may be used to derive the following expression:

$$\rho_{s,1}(z) = \Delta\rho\xi \left(\frac{1}{3} - \frac{\pi^2}{12 \cosh(z/2\xi)} \right). \quad (5.27)$$

The rigidity constant near the critical point can now be calculated by inserting the expressions for $\rho_0(z)$ and $\rho_{s,1}(z)$ in Eq.(5.26) and using $\mu_{s,1} = 2\sigma/\Delta\rho$ to obtain [67]:

$$k = -\frac{1}{9}(\pi^2 - 3)m_c(\Delta\rho)^2\xi = -\frac{2}{9}(\pi^2 - 3)\sqrt{\frac{6m_c^3}{f_c^{(4)}}}\Delta\rho \propto \Delta\eta. \quad (5.28)$$

Virial expressions

Statistical mechanical expressions analogous to the Kirkwood-Buff formula for the surface tension have been derived for the rigidity constant k . Two equivalent expressions were found [83]:

$$k = \frac{1}{4} \int dz_1 \int d\mathbf{r}_{12} u'(r) r \{ (1 - 3s^2) [2\rho_{c,2}^{(2)}(z_1, z_2, r) + z_1 z_2 \rho_0^{(2)}(z_1, z_2, r)] + \frac{r^2}{16} (1 + 6s^2 - 15s^4) \rho_0^{(2)}(z_1, z_2, r) \} \quad (5.29)$$

$$k = \frac{1}{8} \int dz_1 \int d\mathbf{r}_{12} u'(r) r \{ (1 - 3s^2) [(z_1 + z_2) \rho_{c,1}^{(2)}(z_1, z_2, r) - z_1 z_2 \rho_0^{(2)}(z_1, z_2, r)] - \frac{r^2}{8} (1 + 6s^2 - 15s^4) \rho_0^{(2)}(z_1, z_2, r) \}, \quad (5.30)$$

where subscripts $c, 1$ and $c, 2$ refer to the first and second coefficients in an expansion in $1/R$ for a cylindrical surface. The azimuthal dependance of the pair density is ignored. Besides the approximations made in calculating the surface tension of a flat profile (pairwise additivity and the pair density approximation (Eq. (5.20)) one more approximation is introduced for the calculation of the bending rigidity. We have assumed the pair density of the curved interface to be the same as that of the planar interface, i.e. $\rho_{c,1}^{(2)}(z_1, z_2, r) = 0$ and $\rho_{c,2}^{(2)}(z_1, z_2, r) = 0$. With these assumptions the two equations in Eq.(5.29) both reduce to

$$k = \frac{-\pi}{192} (\Delta\rho)^2 \int_0^\infty dr u'(r) r^6 g_{\text{HS}}(r). \quad (5.31)$$

Again care must be taken of the discontinuity of the integrand around $r = \sigma_c$. Making use of the continuity of $n(r) = g(r) \exp(u(r)/k_B T)$ the integral is again split into a singular and regular part:

$$k = \frac{\pi}{192} (\Delta\rho)^2 k_B T \sigma_c^6 g_{\text{HS}}(\sigma_c^+) - \frac{\pi}{192} (\Delta\rho)^2 \int_0^\infty dr u'_{\text{dep}}(r) r^6 g_{\text{HS}}(r). \quad (5.32)$$

The extended capillary wave model

Here we compare the theoretical expressions for the bending rigidity to recent computer simulations by Vink *et al.* [138]. In these simulations the spectrum of height fluctuations of a planar interface is analysed for a model polymer-colloid mixture. To understand the role played by the bending rigidity in describing these fluctuations, we first turn to the (extended) capillary wave theory (CWT) [150–152].

In CWT one of the key assumptions is the existence of a smooth interface described by the height profile $h(\mathbf{r}_{||})$ written in terms of the lateral coordinates $\mathbf{r}_{||} = (x, y)$. The notion of such a smooth interface breaks down when the wavelength of the transversal capillary fluctuations of the interface is becoming very short, say of the order of the diameter of the particles. Deep inside the two-phase region, the capillary fluctuations are usually of long wavelengths and the concept of a smooth surface is valid.

η_p	η_c^V	η_c^L	$\tilde{\sigma}$	$\tilde{k}$
0.9	0.0141	0.2970	0.1532	-0.046
1.0	0.0062	0.3271	0.2848	-0.071
1.1	0.0030	0.3485	0.4194	-0.093
1.2	0.0018	0.3647	0.5555	-0.12

Table 5.2 Shown are the values of the surface tension σ (in units of $k_B T / \sigma_c^2$) and the bending rigidity k (in units of $k_B T$) as a function of polymer density η_p . Also shown are the vapour and fluid densities at two-phase coexistence (respectively η_c^V and η_c^L).

We start our investigation by considering the energy cost ΔF of having an undulated surface with respect to a flat one. The energy cost can be expressed in terms of the surface tension σ , bending rigidity k and the change in surface area $\Delta A \approx (1 + \frac{1}{2} |\nabla h|^2) d\mathbf{r}_{||}$:

$$\Delta F \equiv F - \sigma A = \frac{1}{2} \int d\mathbf{r}_{||} [\sigma |\nabla h|^2 + k (\Delta h)^2], \quad (5.33)$$

where the height fluctuations are assumed to be small $|\nabla h| \ll 1$ and gravity is assumed to be negligible. One may show that Eq. (5.33) depends on the definition of the height function $h(\mathbf{r}_{||})$; the surface tension is not affected by the exact choice of this function whereas the bending rigidity is. As long as one is consistent in this choice the CWT model still provides us with valuable information regarding the bending rigidity. The Fourier transform of Eq.(5.33) is given by

$$\Delta F[h(\mathbf{q})] = \frac{1}{2} \int \frac{d\mathbf{q}}{(2\pi)^2} [\sigma q^2 + k q^4] h(\mathbf{q}) h(-\mathbf{q}), \quad (5.34)$$

where $q \equiv |\mathbf{q}|$, $\mathbf{q} \equiv (q_x, q_y) = (\frac{2\pi n}{L}, \frac{2\pi m}{L})$ with $(n, m) = 0, 1, 2, \dots$ and L the system size. The capillary spectrum can be obtained by calculating thermal averages to obtain the height-height correlation function $S(q) \equiv \langle h(\mathbf{q}) h(-\mathbf{q}) \rangle$:

$$S(q) = \int d\mathbf{r}_{||} e^{i\mathbf{q} \cdot \mathbf{r}_{||}} \langle h(\mathbf{r}_{1,||}) h(\mathbf{r}_{2,||}) \rangle = \frac{k_B T}{\sigma q^2 + k q^4} \equiv \frac{k_B T}{\sigma(q) q^2}, \quad (5.35)$$

where $\mathbf{r}_{||} = \mathbf{r}_{12,||} \equiv \mathbf{r}_{2,||} - \mathbf{r}_{1,||}$. Equation (5.35) should be interpreted as the limiting form of the capillary wave spectrum for $q \rightarrow 0$.

Vink *et al.* [138] used grand canonical Monte Carlo simulations to visualize capillary waves. Using a block analysis method they were able to obtain the Fourier amplitudes of the capillary waves as a function of q . In order to obtain σ and k from the spectrum the Fourier amplitudes are fitted in an expansion in q^2 . Figure 5.3 shows the surface tension ($\tilde{\sigma} \equiv \sigma \sigma_c^2 / k_B T$) as a function of q^2 using the results of Vink. The bending rigidity is determined from a linear fit of $\sigma(q) = \sigma + k q^2$ (solid lines). The values for k obtained in this way together with the bulk properties of the state points

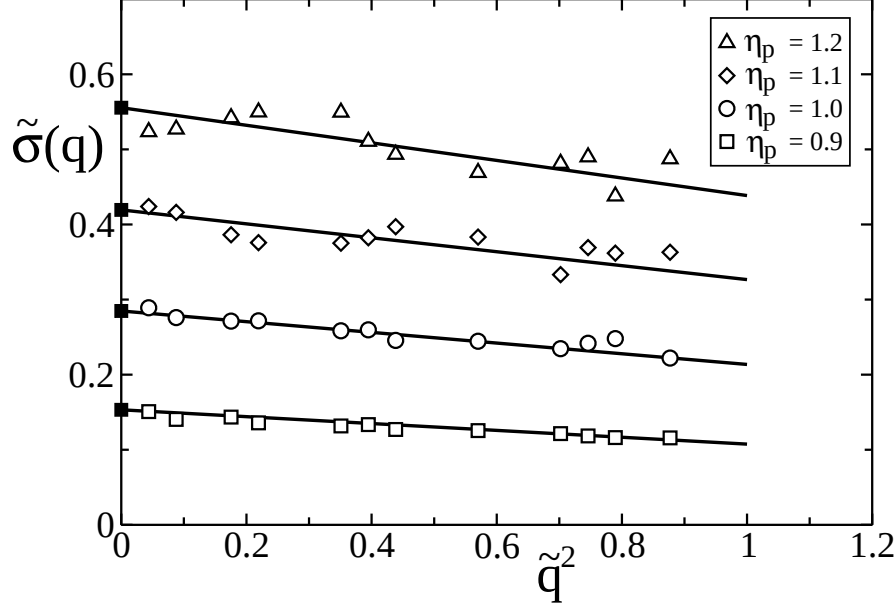


Figure 5.3 Wavevector dependent surface tension $\sigma(q) \equiv k_B T / q^2 S(q)$ (in units of $k_B T / \sigma_c^2$), as a function of q^2 (in units of σ_c^2) for various polymer volume fractions $\eta_p = 0.9-1.2$. The open symbols are the simulation results by Vink *et al.* taken from Figure 11 in ref. [138]. The solid lines represent linear fits of the form $\sigma(q) = \sigma + kq^2$, in which σ is fixed to its planar value (filled squares, see Table 5.2). The values for the rigidity constant k obtained from the fit are listed in Table 5.2.

used in their work are listed in Table 5.2 and shown as the filled squares in Figure 5.4. The dashed curve represents the square-gradient calculation (Eq.(5.28)) and the rigidity obtained using the virial route (Eq.(5.32)) as the triangulated curve.

It seems clear that although the order of magnitude is the same, the square-gradient route does not lend itself well for calculating the bending rigidity. Furthermore, both simulations and theory predict negative values for k .

5.4 Discussion

We have adopted different approaches in calculating the interfacial properties of a phase separated colloid-polymer mixture within the context of an effective one-component model. The interface between both phases has a much lower surface tension compared to regular liquid surfaces. Both square-gradient theory and virial theory confirm this picture. The experimental results of de Hoog and Lekkerkerker [135]

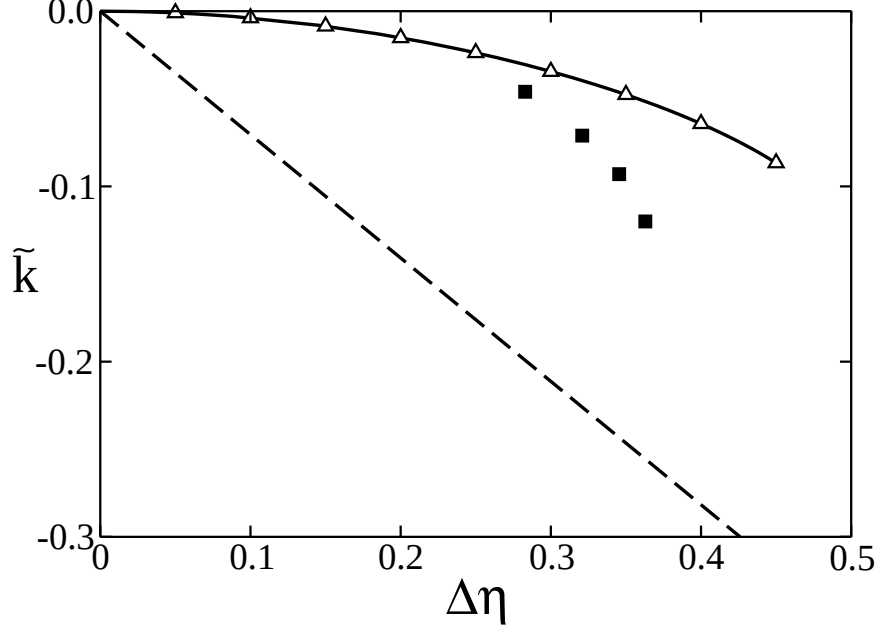


Figure 5.4 Rigidity constant of bending k (in units of $k_B T$) as a function of the bulk colloidal volume fraction difference, $\Delta\eta \equiv \eta_c^L - \eta_c^V$ for $q=0.80$. The open triangles are the results from the jkl expression (Eq.(5.32)); the dashed line is the scaling relation $k \propto \Delta\eta$ (Eq.(5.28)). The filled squares are the results from the simulations by Vink obtained from the fit in Figure 5.3 (see Table 5.2).

do agree qualitatively but show higher values for the surface tension than predicted by theory. Furthermore, theory predicts a rapid decrease of the surface tension: $\sigma \sim (\eta_c^L - \eta_c^V)^3$ whereas the experiments show a weak decrease. As can be inferred from the inset in Figure 5.2, near the critical point the surface tension vanishes with the mean-field critical exponent ($\mu/\beta = 3$) expected when employing a density functional theory. Far from the critical point, virial theory is expected to be more reliable which would indicate that the square-gradient results overestimate the surface tension in that regime. Letting the coefficient in the square-gradient expansion depend on density shifts the values for the surface tension to somewhat higher values compared to the calculation previously done by Brader *et al.* [141].

The bending rigidity is calculated in the region close to the critical point and deep into the two-phase region using two different theoretical models. Both theories predict negative values of the bending rigidities which seems to be in correspondence with the data from the simulations of Vink *et al.* [138]. Both theories also show the bending rigidities tending towards zero upon approaching the critical point. Using a mean-

field method one would expect the bending rigidity to scale as $k \propto k_B T$. It should be noted, however, that the mean-field expressions are inherently of approximate nature and should be tested using exact microscopic expressions. Whether an expansion in curvature is suited to calculate the bending rigidity is still subject of debate. When the interaction decays algebraically, higher order coefficients in the curvature expansion of the surface free energy, which depend on higher moments of the interaction potential, will become infinite at some point. In systems with a Lennard-Jones potential for example, an additional logarithmic term appears in the q -expansion for the surface tension. Our depletion potential has a cut-off at $r = \sigma_c + \sigma_p$ so our curvature-expansion of the free energy converges for radii larger than the cut-off distance and will lead to finite coefficients. From the Kirkwood-Buff like expressions (Eqs.(5.29)) we derived explicit values for the bending rigidity. In doing so, some approximations are made regarding the pair density. The statistical mechanical route seems to give results which agree more closely with the simulation results. Deep in the two-phase regime where the interaction range is longer than the bulk correlation length and thus the typical interfacial width, such a statistical mechanical description is better suited in describing the bending rigidity compared to square-gradient theory.

Chapter 6

Wetting in colloid-polymer systems

ABSTRACT

The wetting of a phase-separated colloid-polymer mixture in contact with a hard wall is analyzed using free volume theory in a Nakanishi-Fisher type approach. We present results for the wetting phase diagram for several model approximations. Our analysis is compared with a previous analysis by Aarts *et al.* (*J. Chem. Phys.* **120**, 1973 (2004)). We find that there is cross-over from wetting to drying at a threshold value for the colloid-polymer size ratio and that the transitions reported are close to the critical point and of second order in nature.

6.1 Introduction

The class of phase separated colloid-polymer mixtures has received a great deal of interest over the past decades. In the previous chapter we have analyzed the interfacial properties of a phase separated colloid-polymer mixture in a way similar to the theoretical explanations first offered by Asakura and Oosawa [1] and independently by Vrij [2] where the polymer degrees of freedom are integrated out thus describing the mixture as if it merely consists of colloids in a homogeneous ocean of identical non-interacting polymers.

The first attempts to explicitly include the polymer degrees of freedom, thus allowing for polymer partitioning between the coexisting phases were done by Lekkerkerker *et al.* [132] in the form of free volume theory. In free volume theory the (effective) interaction between colloids is given by

$$W = U_c - \Pi_p(\mu_p)V_{\text{free}}(\vec{r}_c). \quad (6.1)$$

Here the interaction is split up in two parts, a bare colloid interaction potential U_c and a term due to the influence of the polymer particles with $\Pi(\mu_p)$ the osmotic pressure of a pure polymeric system expressed in terms of the polymer chemical potential μ_p and $V_{\text{free}}(\vec{r}_c)$ the free volume available in which the polymers can move. Clearly, Eq.(6.1) is of a many body nature since the free volume (depending on positions of all colloidal particles $\vec{r}_c$) depends on the mutual overlap of the excluded volumes of all the colloidal particles.

Both extensive computer simulations [153–155] as well as exact solutions in one dimension [156–158] seem to validate a free volume approach. Since its conception (where the polymer particles were treated in an ideal manner) people sought to improve the description of the polymers. Instead of listing the numerous improvements made over the years the author refers to an excellent review written by Fuchs and Schweizer [159].

Of fundamental interest is the wetting behaviour of colloid-polymer mixtures. It was in 2002 that Brader *et al.* [160] reported on a wetting transition for mixtures in contact with a planar hard wall for size ratio $q \equiv \frac{2R_g}{d} = 0.6$ (with R_g, d denoting the radius of gyration and colloidal diameter, respectively) using density functional theory. They believed the transition was of first order but they did not find any prewetting transitions. In addition to a wetting transition also layering transitions were found which are absent in classical squared-gradient theories. These results were confirmed by Monte Carlo simulations carried out by Dijkstra and van Roij [161] for size ratio $q = 1.0$. Yet here too, the authors did not find any prewetting lines indicative of first order behaviour. Later experiments were carried out which confirm the existence of a wetting transition [162,163]. The experimental determination of the location of the wetting transition proved difficult arising from difficulties in measuring contact angles.

In 2004 Aarts *et al.* [164] investigated the colloid-polymer mixture employing free volume theory and investigated the wetting behaviour in the spirit of Nakanishi and

Fisher [92]. The polymers were modeled both as ideal as well as excluded volume interacting particles. They derived expressions linking the Nakanishi-Fisher model parameters to the microscopic parameters entering the theory. In this chapter we retrace their derivation and show that an additional parameter appears in the description of the surface enhancement parameter g .

Our goal in this chapter is to investigate the wetting behaviour of the phase separated colloid-polymer system within the context of both free volume theory and the theory of Nakanishi and Fisher. First, in section 6.2 free volume theory is presented where we truncate the expression for the free volume at the second level in the density. Then, in section 6.3, we use introduce several approximations in the spirit of Nakanishi and Fisher in order to link the parameters to the microscopic expression for the free energy derived in section 6.2. We are then able to calculate the wetting phase diagrams for ideal and excluded volume interacting (EVI) polymers and compare with the calculation performed by Aarts *et al.* [164]. We end with some conclusions.

6.2 Second order free volume theory

The system under consideration is that of a mixture of colloidal particles, described as hard spheres with a diameter d , and ideal polymers, with radius R_g , that is in contact with a hard wall. The distribution of the colloidal particles is given by a position dependent density $\rho(\vec{r})$, whereas the N_p polymers are assumed to be uniformly distributed throughout the volume available V_{av} , i.e. the volume not occupied by the hard spheres or by the hard wall. The expression for the free energy of such a system is given by:

$$\Omega[\rho(\vec{r}), n_p] = \int d\vec{r} [g_{hs}(\rho) + \rho(\vec{r}) V_{wall}(\vec{r}) + g_{id}(n_p)], \quad (6.2)$$

where $n_p \equiv N_p/V$ with V the system's volume, and where the colloid-wall interaction potential, $V_{wall}(\vec{r})$, is taken to be purely repulsive. For the colloid, hard-sphere bulk free energy density $g_{hs}(\rho)$, we consider the Carnahan-Starling form [91]:

$$g_{hs}(\rho) = k_B T \rho \ln(\rho) + k_B T \rho \frac{(4\eta - 3\eta^2)}{(1 - \eta)^2} - \mu \rho, \quad (6.3)$$

where $\eta \equiv (\pi/6) \rho d^3$, μ is the chemical potential of the colloidal particles, T is the absolute temperature and k_B Boltzmann's constant. The usual (grand) free energy expression for an ideal gas consisting of N_p (polymer) particles in a volume V_{av} is given by

$$\Omega_{id}(N_p) = k_B T N_p \ln(N_p/V_{av}) - k_B T N_p - \mu_p N_p, \quad (6.4)$$

where we have elected to absorb the term involving the thermal wavelength into the chemical potential μ_p . The polymer free energy density is then given by:

$$g_{id}(n_p) \equiv \frac{\Omega_{id}(N_p)}{V} = k_B T n_p \ln(n_p/\alpha(\rho)) - k_B T n_p - \mu_p n_p, \quad (6.5)$$

where we have defined the available volume fraction $\alpha(\rho) \equiv V_{\text{av}}/V$, and where it is explicitly indicated that the available volume depends on the distribution of the colloidal particles as described by $\rho(\vec{r})$. The minimization of the free energy in Eq.(6.2) with respect to the polymer density n_p gives:

$$n_p = \alpha(\rho) e^{\mu_p/k_B T} \equiv \alpha(\rho) n_p^r. \quad (6.6)$$

Here we have introduced the parameter n_p^r as the equivalent polymer density of a polymer reservoir having the same chemical potential, μ_p [132].

Substituting this expression for n_p into the free energy in Eq.(6.2), which is now a functional of the colloid distribution alone, one has:

$$\Omega[\rho] = \int d\vec{r} [g_{\text{hs}}(\rho) + \rho(\vec{r}) V_{\text{wall}}(\vec{r}) - k_B T n_p^r \alpha(\rho)]. \quad (6.7)$$

In general, the available volume in a system of hard spheres, $\alpha(\rho)$, is a complicated function of the density for which several approximations can be made. Here, we consider for $\alpha(\rho)$ the expansion in ρ truncated at second order:

$$\alpha(\rho) = 1 - \rho(\vec{r}_1) V(\vec{r}_1) + \frac{1}{2} \int d\vec{r}_2 V_{\text{overlap}}(\vec{r}_1, \vec{r}_2) \rho(\vec{r}_1) \rho(\vec{r}_2) + \dots, \quad (6.8)$$

where the volumes $V(\vec{r})$ and $V_{\text{overlap}}(\vec{r}_1, \vec{r}_2)$ have a strict geometrical interpretation: $V(\vec{r})$ is the volume unavailable to the polymer due to the presence of a single hard sphere at position $\vec{r}$ and $V_{\text{overlap}}(\vec{r}_1, \vec{r}_2)$ is a correction to $V(\vec{r})$ due the fact that the total volume available to the polymer increases when the excluded volumes of the two hard spheres located at $\vec{r}_1$ and $\vec{r}_2$ overlap (see Figure 6.1).

It is clear that the volumes $V(\vec{r})$ and $V_{\text{overlap}}(\vec{r}_1, \vec{r}_2)$ depend on the distance to the hard wall. This is best demonstrated graphically. We consider z as the coordinate orthogonal to the wall with the $z=0$ plane defined as the plane of closest proximity of the colloidal particles to the wall, i.e. $\rho(z)=0$ when $z<0$. We can divide $V(\vec{r})=V(z)$ in a bulk contribution with a correction term in the vicinity of the hard wall (see Figure 6.1a):

$$V(z) = V_0 - V_1(z), \quad (6.9)$$

where, from geometrical considerations, one may show that

$$\begin{aligned} V_0 &= \frac{\pi}{6} d^3 (q+1)^3, \\ V_1(z) &= \frac{\pi}{24} d^3 \left[2(q+1)^3 - 3(q+1)^2 \left(\frac{2z}{d} + 1 - q \right) + \left(\frac{2z}{d} + 1 - q \right)^3 \right], \end{aligned} \quad (6.10)$$

with the polymer-colloid size ratio parameter q defined as:

$$q \equiv \frac{2R_g}{d}. \quad (6.11)$$

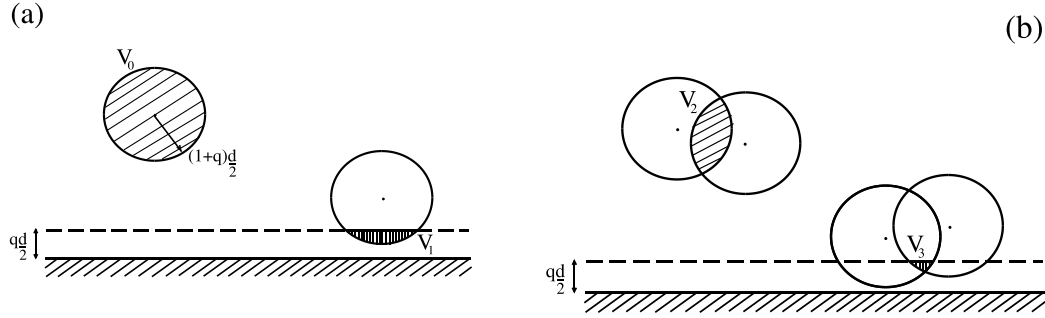


Figure 6.1 Schematic representation of the volumes excluded to the polymer due to the presence of the colloidal particles (spheres) and the hard wall (dashed line at a distance of $R_g = qd/2$ from the wall). The shaded regions show the volumes V_0 , V_1 , V_2 , and V_3 defined below. (a) shows the excluded volume $V(z)$ due to the presence of a *single* colloidal particle; far from the wall $V(z)$ equals V_0 but close to the wall ($0 < z < qd$) the excluded volume is less by an amount $V_1(z)$ due to the overlap with the volume excluded by the hard wall. (b) shows that the total excluded volume of *two* colloidal particles is less by an amount V_{overlap} when the two particles are sufficiently close to each other ($d < r < (1 + q)d$). Far from the wall V_{overlap} equals $V_2(r)$ but close to the wall V_{overlap} is itself less by an amount $V_3(z_1, z_2, r)$ due to the overlap with the volume already excluded by the hard wall.

The volume correction $V_1(z)$ is only unequal to zero in the interval $0 < z < qd$. A similar division can also be made for the overlap volume $V_{\text{overlap}}(\vec{r}_1, \vec{r}_2) = V_{\text{overlap}}(z_1, z_2, r)$ (see Figure 6.1b):

$$V_{\text{overlap}}(z_1, z_2, r) = V_2(r) - V_3(z_1, z_2, r). \quad (6.12)$$

From geometrical considerations, one may show that

$$V_2(r) = \frac{\pi}{12} d^3 \left[2(q+1)^3 - 3(q+1)^2 \left(\frac{r}{d} \right) + \left(\frac{r}{d} \right)^3 \right], \quad (6.13)$$

with $d < r < (1 + q)d$. A similar analytical formula for $V_3(z_1, z_2, r)$ does not exist and explicit values for it have to be determined numerically.

The result of the truncation of $\alpha(\rho)$ in Eq.(6.8) to second order is that the free energy is reduced to that of a single component – the colloidal particles with density $\rho(\vec{r})$ – with the influence of the polymer *only* captured by the presence of the external field $V(\vec{r})$ and an effective interaction between the colloidal particles equal to $-k_B T n_p^r V_{\text{overlap}}(\vec{r}_1, \vec{r}_2)$. In the bulk region, $V_{\text{overlap}}(z_1, z_2, r)$ is equal to the excluded volume $V_2(r)$, so that this effective interaction is equal to the usual depletion interaction potential, $U_{\text{dep}}(r) = -k_B T n_p^r V_2(r)$,

$$U_{\text{dep}}(r) = -k_B T \frac{\eta_p}{2q^3} \left[2(q+1)^3 - 3(q+1)^2 \left(\frac{r}{d} \right) + \left(\frac{r}{d} \right)^3 \right], \quad (6.14)$$

where we have introduced $\eta_p \equiv (\pi/6) n_p^r d^3 q^3$.

Next, we substitute the expression for $\alpha(\rho)$ in Eq.(6.8) into the expression for the free energy in Eq.(6.7), using Eqs.(6.9) and (6.12). In doing so, we omit the constant contribution to the free energy $-k_B T n_p^r$ and absorb the term containing V_0 in a modified chemical potential. Our final expression for the free energy then reads:

$$\begin{aligned} \frac{\Omega[\rho]}{A} = & \int_{-\infty}^{\infty} dz [g_{\text{hs}}(\rho) + \rho(z) V_{\text{wall}}(z)] + \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} d\vec{r}_{12} U_{\text{dep}}(r) \rho(z_1) \rho(z_2) \\ & - k_B T n_p^r \int_{-\infty}^{\infty} dz \rho(z) V_1(z) + \frac{1}{2} k_B T n_p^r \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} d\vec{r}_{12} V_3(z_1, z_2, r) \rho(z_1) \rho(z_2), \end{aligned} \quad (6.15)$$

where $A = \int dx dy = \int d\vec{r}_{\parallel}$ is the surface area.

6.3 Nakanishi-Fisher model approximation

In the Nakanishi-Fisher model [92], the free energy of a fluid (liquid or vapor) phase in contact with a solid wall is given by:

$$\frac{\Omega[\rho]}{A} = \int_0^{\infty} dz \left\{ m[\rho'(z)]^2 + g(\rho) \right\} - h_1 \rho^w + \frac{g}{2} (\rho^w)^2. \quad (6.16)$$

The first term approximates the fluid's free energy by a simple squared-gradient expression with coefficient m and bulk free energy density, $g(\rho)$. The last two terms account for the interaction of the fluid with the wall in terms of two phenomenological parameters, h_1 and g , which are termed the *surface chemical potential* and *surface enhancement parameter*, respectively. The assumption implicitly made is that the fluid-wall interaction is short-ranged so that these terms only depend on the fluid's density in the direct vicinity of the wall, $\rho^w \equiv \rho(z=0^+)$.

The goal in this section is to make several approximations to the free energy in Eq.(6.15) to cast it in the Nakanishi-Fisher form in Eq.(6.16), where, now, the 'liquid phase' refers to the phase relatively rich in colloids and the 'vapor phase' refers to the phase relatively poor in colloids.

First, as a result of the fact that $\rho(z)=0$ when $z<0$, we limit the integrations in Eq.(6.15) to the region $z>0$:

$$\begin{aligned} \frac{\Omega[\rho]}{A} = & \int_0^{\infty} dz g_{\text{hs}}(\rho) + \frac{1}{2} \int_0^{\infty} dz_1 \int_{z_2>0}^{\infty} d\vec{r}_{12} U_{\text{dep}}(r) \rho(z_1) \rho(z_2) \\ & - k_B T n_p^r \int_0^{\infty} dz \rho(z) V_1(z) + \frac{1}{2} k_B T n_p^r \int_0^{\infty} dz_1 \int_{z_2>0}^{\infty} d\vec{r}_{12} V_3(z_1, z_2, r) \rho(z_1) \rho(z_2). \end{aligned} \quad (6.17)$$

The last two terms in Eq.(6.17) only contribute *near the wall*, so that, following Nakanishi-Fisher, we may approximate $\rho(z) \approx \rho(0^+) = \rho^w$ in both these terms. For

the second term, containing the depletion potential, we like to consider a gradient expansion which implies for $\rho(z_2)$:

$$\rho(z_2) = \rho(z_1) + z_{12} \rho'(z_1) + \frac{z_{12}^2}{2} \rho''(z_1) + \dots \quad (6.18)$$

The gradient expansion, however, does not take into account the fact that $\rho(z_2) = 0$ when $z_2 < 0$. To accomodate for this, it is convenient to extend the integration over z_2 for the second term in Eq.(6.17) and subtract the difference:

$$\begin{aligned} \frac{1}{2} \int_0^\infty dz_1 \int_{z_2>0} d\vec{r}_{12} U_{\text{dep}}(r) \rho(z_1) \rho(z_2) &= \frac{1}{2} \int_0^\infty dz_1 \int d\vec{r}_{12} U_{\text{dep}}(r) \rho(z_1) [\rho(z_1) + \dots] \\ &\quad - \frac{1}{2} \int_0^\infty dz_1 \int_{z_2<0} d\vec{r}_{12} U_{\text{dep}}(r) \rho(z_1) [\rho(z_1) + \dots]. \end{aligned} \quad (6.19)$$

Again, the final term in this expression only contributes *near the wall* so that we may approximate $\rho(z) \approx \rho^w$ in this term. With the gradient expansion for the first term on the right-hand-side of Eq.(6.19), one then has for the free energy:

$$\begin{aligned} \frac{\Omega[\rho]}{A} &= \int_0^\infty dz \left\{ m [\rho'(z)]^2 + g_{\text{hs}}(\rho) - a \rho(z)^2 \right\} - k_B T n_p^r \rho^w \int_0^\infty dz V_1(z) \\ &\quad + k_B T n_p^r \frac{(\rho^w)^2}{2} \int_0^\infty dz_1 \int_{z_2>0} d\vec{r}_{12} V_3(z_1, z_2, r) - \frac{(\rho^w)^2}{2} \int_0^\infty dz_1 \int_{z_2<0} d\vec{r}_{12} U_{\text{dep}}(r). \end{aligned} \quad (6.20)$$

where we have defined

$$a \equiv -\frac{1}{2} \int d\vec{r}_{12} U_{\text{dep}}(r) \quad \text{and} \quad m \equiv -\frac{1}{12} \int d\vec{r}_{12} r^2 U_{\text{dep}}(r). \quad (6.21)$$

Using the explicit expression for $U_{\text{dep}}(r)$ in Eq.(6.14), the coefficients a and m are readily calculated to yield

$$\begin{aligned} a &= k_B T d^3 \eta_p \frac{\pi}{12} (12 + 15q + 6q^2 + q^3), \\ m &= k_B T d^5 \eta_p \frac{\pi}{240} (40 + 70q + 56q^2 + 28q^3 + 8q^4 + q^5). \end{aligned} \quad (6.22)$$

Now, comparing Eq.(6.20) to the Nakanishi-Fisher form for the free energy in Eq.(6.16), we identify $g(\rho) = g_{\text{hs}}(\rho) - a\rho^2$ and we obtain the following expressions for the surface interaction parameters h_1 and $g \equiv g_1 + g_2$:

$$\begin{aligned} h_1 &= k_B T n_p^r \int_0^\infty dz V_1(z), \\ g_1 &= - \int_0^\infty dz_1 \int_{z_2<0} d\vec{r}_{12} U_{\text{dep}}(r) = -\frac{1}{4} \int d\vec{r}_{12} r U_{\text{dep}}(r), \\ g_2 &= k_B T n_p^r \int_0^\infty dz_1 \int_{z_2>0} d\vec{r}_{12} V_3(z_1, z_2, r) = k_B T n_p^r \int_0^\infty dz_1 \int_0^\infty dz_2 \int d\vec{r}_{\parallel} V_3(z_1, z_2, r). \end{aligned} \quad (6.23)$$

One finds that the parameter h_1 is directly related to (the integral of) the colloid-wall interaction potential. In this case the interaction is attractive resulting in a *positive* value of h_1 thus promoting wetting of the wall by the liquid phase (the phase rich in colloidal particles). Eq.(6.23) also shows that the expression for g is the sum of *two* terms, g_1 and g_2 . The contribution g_1 is due to the ‘missing’ colloid-colloid interactions for $z_2 < 0$, whereas the contribution g_2 is due to the *enhancement* of the colloid-colloid interactions in the vicinity of the wall (see chapter 4 of this thesis). Both contributions to g are positive thus *opposing* wetting of the wall by the liquid phase. The subtle interplay between the surface parameters h_1 and g therefore determines the precise shape of the wetting phase diagram to be determined next.

Using the explicit form for the depletion potential in Eq.(6.14), the coefficients h_1 and g_1 are readily calculated to yield

$$\begin{aligned} h_1 &= k_B T d \eta_p \left(1 + \frac{q}{2}\right), \\ g_1 &= k_B T d^4 \eta_p \frac{\pi}{140} (70 + 105 q + 63 q^2 + 21 q^3 + 3 q^4). \end{aligned} \quad (6.24)$$

The value of g_2 can only *numerically* be determined for arbitrary q ($g_2 = 0$ when $q < 1/4$), although it should be mentioned that Aarts *et al.* [164] calculated its exact value for the special case $q = 1$:

$$g_2 = k_B T d^4 \eta_p \frac{27\pi}{140} \quad (q = 1). \quad (6.25)$$

For other values of q , the integral in Eq. (6.23) needs to be evaluated and we follow the methodology applied by Bellemans [165]. We find that the numerical results for g_2 can be well-represented by the following phenomenological formula

$$g_2 = k_B T d^4 \eta_p \frac{6}{\pi q^3} \left(q - \frac{1}{4}\right)^{\frac{11}{2}} (c_0 + c_1 q + c_2 q^2 + c_3 q^3 + c_4 q^4). \quad (6.26)$$

With $c_0 = 1.5841$, $c_1 = -0.74308$, $c_2 = 1.2372$, $c_3 = -0.68784$, and $c_4 = 0.15422$, this formula fits the numerical results to within 0.1% in the interval $0.251 < q < 1.5$.

With explicit expressions for the surface parameters h_1 and g , we are now able to determine the locations of wetting and drying transitions as a function of the parameter η_p for various colloid-polymer size ratio's. In Figure 6.2 the resulting colloid-polymer phase diagram is shown. The solid circles mark the locations of the critical points whereas open circles denote the locations of the wetting and drying transitions; numerical values for the locations of these points are listed in Table 6.1. It is found that the wetting and drying transitions occur close to the critical point and that there is a cross-over from wetting to drying as q increases at $q = 0.935$ (determined by the condition $h_1 = g \phi_c$). Due to the closeness to the critical point, all wetting and drying transition are of *second order*. Only at an extremely low colloid to polymer size ratio, $q = 0.040$, is the wetting transition of first order.

q	critical point		wetting
	η	η_p	η_p
0.4	0.130444	1.114511	1.198394 (W)
0.6	0.130444	0.907018	0.931551 (W)
0.8	0.130444	0.747829	0.750864 (W)
1.0	0.130444	0.623602	0.624142 (D)
1.2	0.130444	0.525229	0.532058 (D)

Table 6.1 Listed are numerical values for the location of the critical point and the wetting or drying transition. All wetting and drying transitions are of second order

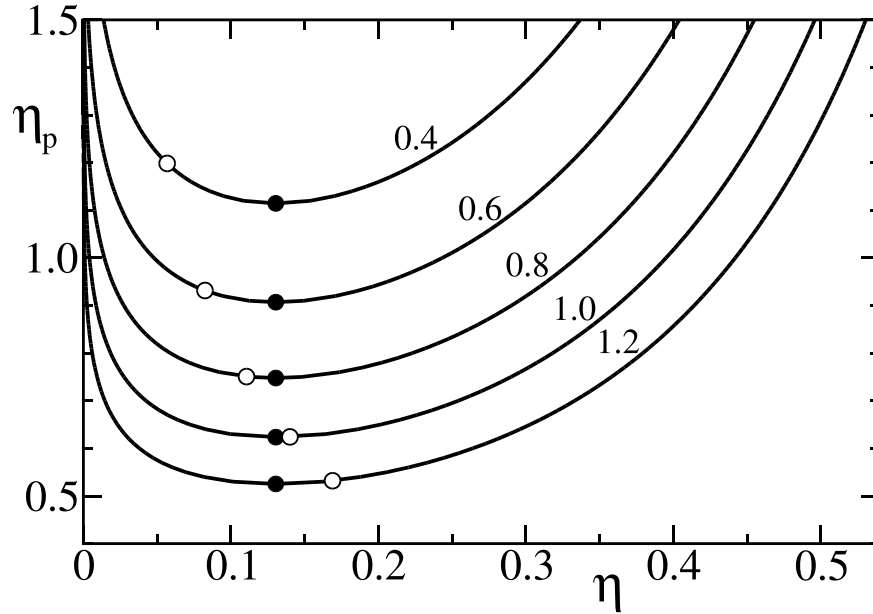


Figure 6.2 Colloid-polymer phase diagram shown as a function of η and η_p for various values of the colloid-polymer size ratio parameter q . Solid circles mark the locations of the critical points; open circles mark the locations of the wetting and drying transitions. Results are obtained for an ideal polymer solution using the truncated form for $\alpha(\rho)$.

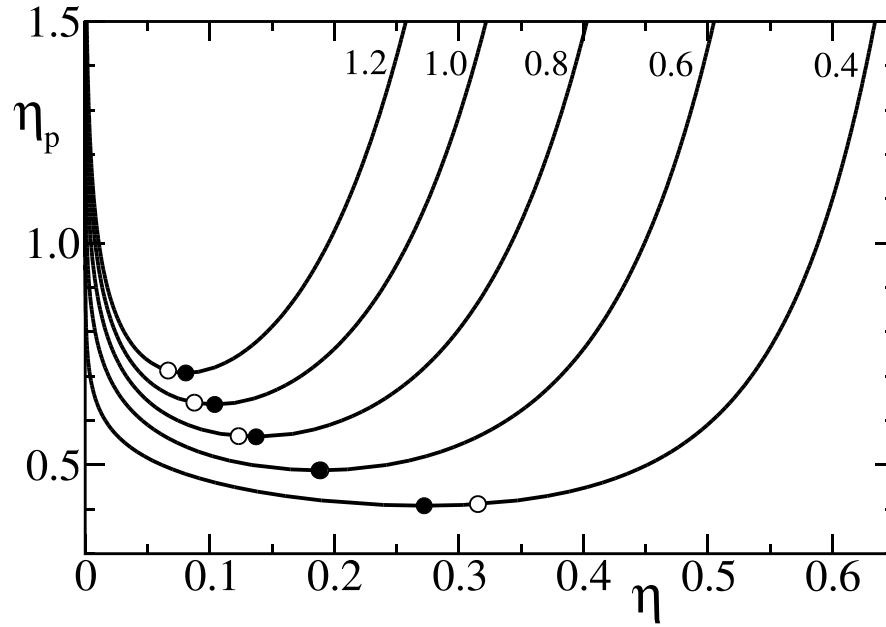


Figure 6.3 Colloid-polymer phase diagram shown as a function of η and η_p for various values of the colloid-polymer size ratio parameter q . Solid circles mark the locations of the critical points; open circles mark the locations of the wetting and drying transitions. Results are obtained for an ideal polymer solution using the full expression for $\alpha(\rho)$.

6.3.1 Direct comparison with the results by Aarts *et al.*

The reason that the wetting and drying transitions are so close to the critical points is due to the fact that the value of g is rather large. In comparison with the results by Aarts *et al.* [164], the largeness of g results from the contribution g_1 which was neglected in their analysis. However, we argue that this is an important contribution and, in fact, $g_1 \ll g_2$ (for example, $g_2/g_1 = 10\%$, for $q=1$).

The phase diagram in Figure 6.2 was calculated using the truncated form for the available volume fraction $\alpha(\rho)$. In order to be able to show the influence of taking the contribution g_1 into account, we directly follow the analysis by Aarts *et al.* [164] and calculate the wetting phase diagram for ideal polymers and for polymers with excluded volume interactions (EVI) using the full form for the available volume fraction $\alpha(\rho)$ by Lekkerkerker *et al.* [132]. The equations used here and by Aarts *et al.* [164, 166] are explicitly listed in appendix D. We rederive the phase diagram results by Aarts *et al.* with only the location of the wetting and drying transitions now different due to the different value of g . The resulting colloid-polymer phase diagrams are shown in Figure 6.3 for ideal polymers and in Figure 6.4 for EVI polymers. Again, the solid circles mark the locations of the critical points whereas open circles denote the locations of the wetting and drying transitions; numerical values for the locations of

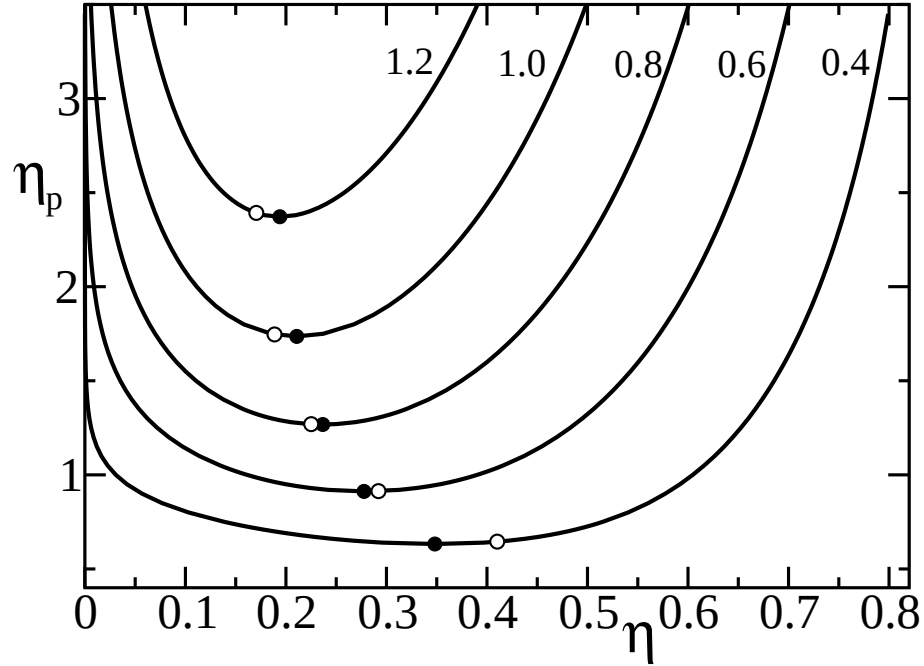


Figure 6.4 Colloid-polymer phase diagram shown as a function of η and η_p for various values of the colloid-polymer size ratio parameter q . Solid circles mark the locations of the critical points; open circles mark the locations of the wetting and drying transitions. Results are obtained for a polymer solution with excluded volume interactions (EVI) using the full expression for $\alpha(\rho)$.

these points are now listed in Table 6.2.

Results are similar to those shown in Figure 6.2: wetting and drying transitions are of second order and are located close to the critical point. Again, a cross-over from wetting to drying occurs but now as q decreases. This sequence is opposite to that in Figure 6.2 which is probably due to the fact that the q -dependence of the whole shape of the phase diagram is also reversed: in Figure 6.2 the value of η_p at the critical point decreases with increasing q whereas it increases in Figures 6.3 and 6.4.

6.3.2 Numerical solution for the contact angle

We also like to mention the result of numerically solving the Euler-Lagrange equation that minimizes the free energy in Eq.(6.15) directly *without* making the Nakanishi-Fisher approximation. This route is numerically very tedious and has the disadvantage that it is difficult to draw definite conclusions about the order of the wetting transition obtained.

The Euler-Lagrange equation that minimizes the free energy in Eq.(6.15) is given

q ₀	full $\alpha(\rho)$ – ideal polymers			full $\alpha(\rho)$ – EVI polymers		
	critical point		wetting	critical point		wetting
	η	η_p	η_p	η	η_p	η_p
0.4	0.272212	0.408071	0.411790 (D)	0.3481	0.6322	0.6450 (D)
0.6	0.187800	0.487896	0.487900 (D)	0.2777	0.9121	0.9134 (D)
0.8	0.137267	0.563368	0.564951 (W)	0.2366	1.2678	1.2694 (W)
1.0	0.104001	0.636412	0.640473 (W)	0.2107	1.7358	1.7463 (W)
1.2	0.080806	0.707456	0.712921 (W)	0.1940	2.3717	2.3920 (W)

Table 6.2 Listed are numerical values for the location of the critical point and the wetting or drying transition. All wetting and drying transitions are of second order

by:

$$\begin{aligned}
& g'_{\text{hs}}(\rho) + V_{\text{wall}}(z_1) + \int d\vec{r}_{12} U_{\text{dep}}(r) \rho(z_2) \\
& - k_{\text{B}}T n_p^r V_1(z_1) + k_{\text{B}}T n_p^r \int d\vec{r}_{12} V_3(z_1, z_2, r) \rho(z_2) = 0.
\end{aligned} \tag{6.27}$$

As a result of the infinite repulsion of the hard wall, we have that $\rho(z)=0$ when $z < 0$. The range of values for z_1 in the Euler-Lagrange equation may therefore be limited to the region $z_1 > 0$, where $V_{\text{wall}}(z_1) = 0$. The resulting Euler-Lagrange equation is solved numerically for the density profile $\rho(z)$. In Figure 6.5 a typical example of two density profiles obtained are shown.

The accuracy of the solution for the density profile obtained may be tested by considering the limiting value of $\rho(z)$ at the hard wall, $\rho^{\text{w}} \equiv \rho(0^+)$, which should obey the following generalized wall theorem:

$$\begin{aligned}
p &= -g_{\text{hs}}(\rho^{\text{w}}) + \rho^{\text{w}} g'_{\text{hs}}(\rho^{\text{w}}) + k_{\text{B}}T n_p^r \int_{0^+}^{\infty} dz \rho(z) V_1'(z) \\
&+ k_{\text{B}}T n_p^r \int_0^{\infty} dz_1 \int d\vec{r}_{12} V_3(z_1, z_2, r) \rho(z_1) \rho'(z_2).
\end{aligned} \tag{6.28}$$

Finally, the surface tension of the fluid in contact with the hard wall needs to be determined. The surface tension is defined as the excess (surface) free energy

$$\begin{aligned}
\sigma &= \int_0^{\infty} dz [g_{\text{hs}}(\rho) + p - k_{\text{B}}T n_p^r \rho(z) V_1(z)] \\
&+ \frac{1}{2} \int_0^{\infty} dz_1 \rho(z_1) \int_0^{\infty} dz_2 \rho(z_2) \int d\vec{r}_{\parallel} U_{\text{dep}}(r)
\end{aligned}$$

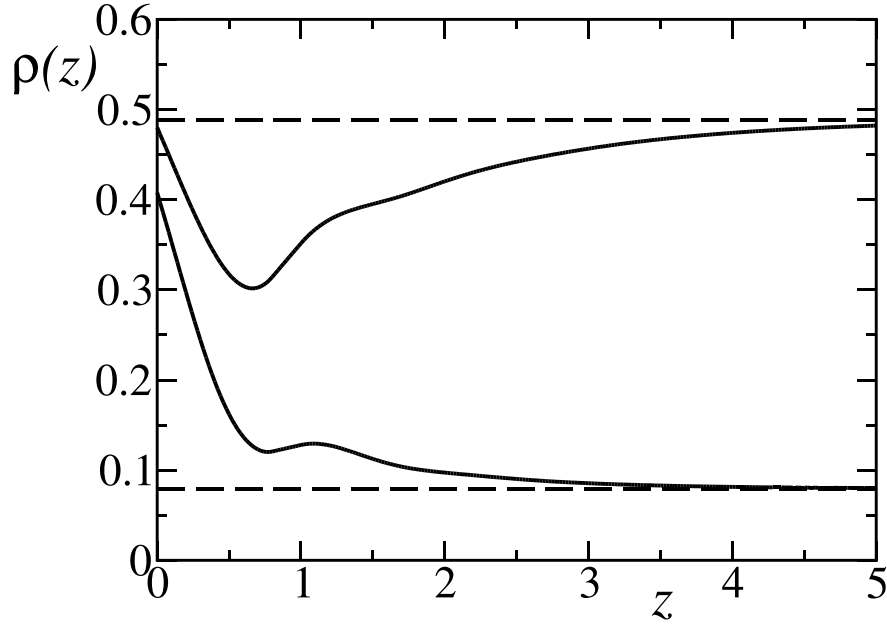


Figure 6.5 Density profiles $\rho(z)$ (in units of $1/d^3$) as a function of z (in units of d) for $q=0.8$ and at a temperature $T^*=k_B T d^3/a=0.16$ ($\eta_p=0.842$). The horizontal dashed lines mark the values of the bulk liquid and vapor densities.

$$+\frac{1}{2} k_B T n_p^r \int_0^\infty dz_1 \rho(z_1) \int_0^\infty dz_2 \rho(z_2) \int d\vec{r}_\parallel V_3(z_1, z_2, r). \quad (6.29)$$

Using Young's law and inserting the different density profiles into Eq.(6.29) enables us to calculate the contact angle. In Figures 6.7 and 6.6 we show the behaviour of the contact angle versus temperature $T^*=k_B T d^3/a$ obtained using the numerical solution of Eq.(6.27) and the model of Nakanishi and Fisher, respectively.

Only wetting transitions are found in the numerical solution of Eq. (6.27) upon approaching the critical point (at $T^* \approx 0.1816$) over the entire temperature range considered, yet increasing the size ratio lessens the wettability of the substrate as can be inferred from Figure 6.6. From the results obtained from the Nakanishi-Fisher form depicted in Figure 6.7 we observe a wetting reversal: with increasing values for q the nature of the transition changes from wetting to drying. Furthermore, for size ratios far from the cross-over (at $q \sim 0.93$) the location of the transition is further away from the critical point than the wetting transitions obtained from the numerical solution of Eq. (6.27) which all seem to be closer to a similar temperature.

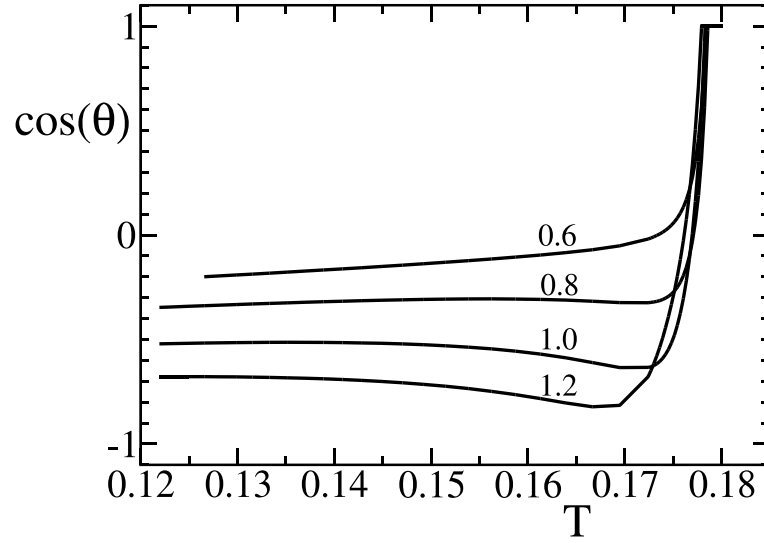


Figure 6.6 Cosine of the contact angle versus temperature $T^* = k_B T d^3 / a$ obtained from numerically solving Eq.(6.27) for various values of the colloid-polymer size ratio parameter q .

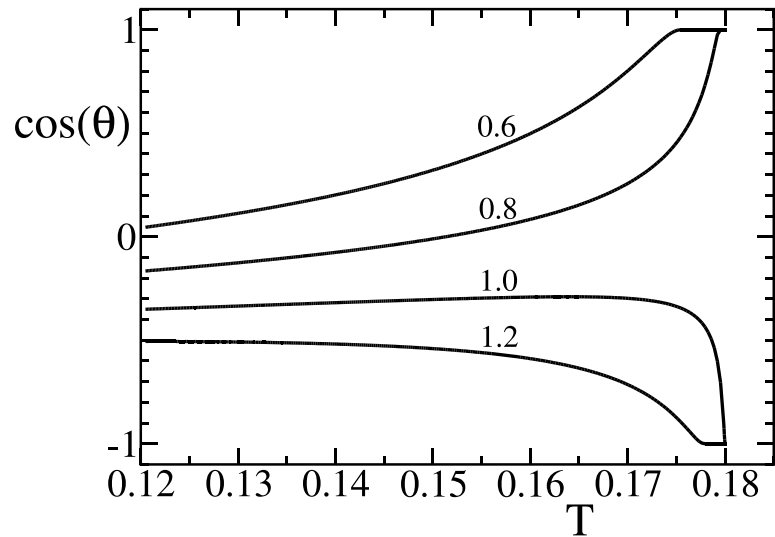


Figure 6.7 Cosine of the contact angle versus temperature $T^* = k_B T d^3 / a$ obtained using the Nakanishi-Fisher model for various values of the colloid-polymer size ratio parameter q .

6.4 Discussion

Because the depletion interactions governing the phase separation in colloid-polymer mixtures are short-ranged in nature the theory of Nakanishi and Fisher provides a good starting point in discussing wetting phenomena. The expressions for the surface parameters h_1 and g in Eq. (6.23) are an important result. They are derived by casting the free energy obtained from second order free volume theory into the Nakanishi-Fisher form. Analogous to the derivation in chapter (4) h_1 is connected to the wall-fluid interaction potential where larger values for h_1 will promote wetting. The surface enhancement parameter g is composed of two parts: one term is a direct consequence of the absence of molecules in the half-space $z < 0$ (g_1) and the other term is due to an *enhancement* of the colloidal interactions in the vicinity of the hard wall (g_2).

The wetting phase diagram obtained using second order free volume theory where the polymers act as ideal particles displays a remarkable feature: there is a cross-over at $q = 0.935$ where the wetting transitions change into drying transitions upon raising the size ratio. All wetting and drying transitions reported are of second order and lay close by the critical point. First order wetting transitions were only reported for extreme low values of q . It is found that out of the two contributions to g , g_1 is the main contributor and for all size ratios considered in this work $g_1 \gg g_2$.

Aarts *et al.* [164] calculated the wetting phase diagram where they have used the full shape for the free volume $\alpha(\rho)$. The polymeric particles were both modeled as ideal as well as excluded volume interacting chains. However, in their work they neglected the contribution from g_1 to the surface enhancement parameter g . Just as is the case when employing a truncated free volume theory, here too g_1 is the main contributor to g and it cannot be neglected. In the appendix we have derived expressions for the model parameters analogous to the work of Aarts *et al.* and we have recalculated the wetting phase diagrams both for ideal as well as excluded volume interacting polymers. Aarts *et al.* found a first order wetting transition far away from the critical point. We found wetting transitions of second order which lay in the vicinity of the critical point similar to the wetting phase diagrams obtained using the truncated form of free volume theory. Again a cross-over from wetting to drying occurs but now with *decreasing* the size ratio. Allowing for excluded volume interactions widens the coexistence region and shifts the binodals to higher values of η_p , yet the same qualitative trend is found in the wetting behaviour compared to the case of ideal polymers.

As a test we have also calculated the contact angle behaviour for different values of the temperature and size ratio by numerically solving the Euler-Lagrange equation in Eq.(6.27) and by solving the Nakanishi-Fisher model. In the model of Nakanishi and Fisher, wetting reversal is observed from wetting to drying upon increasing q in accordance with the results obtained from both free volume theory and free volume theory with a truncated expression for the free volume. The contact angle behaviour upon solving the Euler-Lagrange equation in Eq. (6.27) does not show this feature

(Figure 6.6) and only wetting transitions were found upon approaching the critical point. However, upon raising the size ratio the wettability decreases as in accordance with the model of Nakanishi and Fisher.

The fact that all wetting (or drying) transitions reported in this chapter lay close in the vicinity of the critical point certainly could provide an explanation as to why wetting transitions in colloid-polymer mixtures are hard to observe in practice, yet more sophisticated theories are needed in order to make better predictions.

Chapter 7

Pickering Stabilisation

ABSTRACT

In this chapter we investigate the interfacial properties of Pickering emulsions. Based upon findings that indicate these emulsions to be thermodynamically stable, we devise a thermodynamic theory assuming the droplets to be stable inspired by a theory originally derived for swollen micelles.

7.1 Introduction

It is well known that oil ¹ does not mix with water unless when vehemently shaken or when an emulsifying agent is added. The ordinary emulsions then formed, abundant in many food and daily life products, are characterized by big polydisperse oil drops which eventually will demix due to drop coalescence. In order to stabilise these emulsions the oil and water mixtures are usually exposed to prolonged periods of mechanical agitation and emulsifiers are added in the form of surfactants which adsorb to the bare oil-water interface thus preventing drop coalescence.

Another class of emulsions, the microemulsions, are characterized by a small stable droplet size in the order of ~ 100 Å. The small size of the droplets explains the colorless appearance of these emulsions. Unlike ordinary emulsions, microemulsions are usually obtained upon mixing the ingredients² without the requirement of the high shear conditions necessary to stabilize ordinary oil-water emulsions yet are considered thermodynamically stable, i.e. microemulsions are a distinct thermodynamic phase. Depending on the type of surfactant and concentration of the components involved several microemulsion phases exist: water-in-oil droplets, oil-in-water droplets and even bicontinuous structures are known to be formed.

In the classical Pickering emulsion [3], the emulsion is stabilised by the adsorption of small colloidal particles at the oil-water interface. Opposed to the case of surfactant stabilised emulsions, where the shape and chemical properties of the surfactant molecules determine the emulsifying behaviour, in Pickering emulsions the oil droplet is stabilised by a reduction of the bare oil-water interface by adsorption of small particles. The parameter of choice here to describe these Pickering emulsions is the contact angle of the adsorbed particles. It has been shown that for contact angles in the range $30^\circ - 90^\circ$ oil-in-water emulsions are formed, whereas larger values of the contact angle lead to water-in-oil emulsions. Stabilising emulsions using nanoparticles is not limited to the class of Pickering emulsions. In commercial products, particle attachment is controlled by using both surfactants and colloidal particles which lead to a new class of emulsions. Recently, people even succeeded stabilising *foams* using nanoparticles [167, 168]. Stabilising foams, however, is an active process, i.e. one also has to supply sufficient (mechanical) energy to prepare these particle-stabilised foams.

For a long time, the stabilisation of the Pickering emulsion was attributed to a *kinetic* barrier resulting from a viscosity increase of the continuous medium between the Pickering droplets, or to the mechanism of particle adsorption itself. Recently, Sacanna *et. al.* [169] reported on a monodisperse emulsion created from water, oil and nanoparticles. The oil phase was of the methacrylate type and the nanoparticles employed were all charged but varied in nature (silica, iron-oxide and cobalt-ferrite). Under the appropriate conditions these constituents self-assemble into stable,

¹“Oil” and “water” are generic terms: one should read oily phase and the water phase which both could contain many components.

²In general oil, water, surfactant and co-surfactant.

monodisperse droplets with diameters in the range of 30 – 150 nm. As in the case of microemulsions, these Pickering emulsions form without the need for any mechanical agitation. This observation in combination with the fact that one observes a spontaneous evolution towards one droplet size after mixing leads to the speculation that the Pickering emulsion is a *thermodynamically stable* state just like in microemulsions.

From another recent study [170] we can infer that Pickering emulsions are most stable when the Pickering droplets are homogeneously covered by nanoparticles. This implies that the Pickering drops should be large (> 100 nm) since small droplets cannot be covered completely. Any “bare” parts of the oil-water interface will lead to drop coalescence/flocculation over time since the system always strives to minimize the total interfacial area of the oil-water interface. This means that Pickering emulsions in which the droplets are small are expected to destabilize (e.g. by creaming) over time.

The goal in this chapter is to analyze the Pickering emulsion using a theory originally derived for microemulsions. By using the Gibbs adsorption equation we derive expressions for the surface tension and compare with the experiments done by Sacanna *et al.* [169]. We end with some conclusions.

7.2 Thermodynamics

In what follows we largely follow the analysis presented by Ruckenstein [171]. We assume water to be the continuous phase and the Pickering droplets to consist of the dispersed oil phase. In order to simplify the analysis it will be assumed that

- the colloidal particles are only soluble in the continuous phase or are adsorbed on the surface of the Pickering droplet.
- the Pickering droplets are spherical with radius R and are uniform in size

In our system we keep the volume V , total amount of particles N_i of component i and the temperature T fixed, so that the thermodynamic potential of choice is the Helmholtz free energy. It reads

$$F = \sigma A + \sum_i \mu_i N_i - p_1 V_1 - p_2 V_2 + F_{\text{ent}}, \quad (7.1)$$

where i marks a summation over the components (in this case water, oil and colloid), V_1, V_2 are the volumes of the continuous and dispersed phases respectively with pressures p_1, p_2 and F_{ent} is due to the dispersion of the drops in the medium and is entropic in nature. The surface tension σ is the surface tension of the oil-water interface coated by the colloidal particles which we will assume to depend on the radius of the Pickering droplet $\sigma = \sigma(R)$. In appendix E we present a detailed analysis of the surface tension in a Pickering droplet.

From the free energy we can construct the phase diagram but here we focus on the equilibrium properties of N_p Pickering droplets.

If $\phi = \frac{4\pi}{3} \frac{N_p}{V} R^3$ denotes the volume fraction of the Pickering droplets, then the interfacial area per unit volume is $A/V = 3\phi/R$. Using this constraint we then have for the free energy density

$$f \equiv \frac{F}{V} = \sigma \frac{3\phi}{R} + \sum_i \mu_i \rho_i - p_1 \phi_1 - p_2 \phi_2 + f_{\text{ent}}, \quad (7.2)$$

where the partial volumes fractions ϕ_1 and ϕ_2 are related to the volume fraction of Pickering droplets by $\phi_1 = 1 - \phi$ and $\phi_2 = \phi$. The pressures in the continuous phase and inside the drop are related according to Laplace's law $p_2 = p_1 + 2\sigma/R$. The equilibrium drop radius R_e can be determined by using

$$\left(\frac{\partial f}{\partial R_e} \right)_{N_i, p_1, T} = 0. \quad (7.3)$$

Performing the differentiation one obtains

$$-\frac{3\phi}{R_e^2} \sigma(R_e) - p_1 \left(\frac{\partial \phi_1}{\partial R_e} \right) - p_2 \left(\frac{\partial \phi_2}{\partial R_e} \right) + \left(\frac{\partial f_{\text{ent}}}{\partial R_e} \right) = 0. \quad (7.4)$$

Using Laplace's law and noting that $\phi_1 + \phi_2 = 1$, this can be rewritten as

$$-\sigma(R_e) \left[\frac{2}{R_e} \left(\frac{\partial \phi}{\partial R_e} \right) + \frac{3\phi}{R_e^2} \right] + \left(\frac{\partial f_{\text{ent}}}{\partial R_e} \right) = 0. \quad (7.5)$$

Note that the surface tension now depends on the drop's radius R . Since in general $d\phi/dR \ll \phi/R$ we can rewrite Eq.(7.5) to [171]:

$$-\frac{3\phi}{R_e^2} \sigma(R_e) + \left(\frac{\partial f_{\text{ent}}}{\partial R_e} \right) = 0. \quad (7.6)$$

This equation determines the equilibrium drop's radius R_e to be determined next. The above treatment is valid only if the Pickering drop's radius R_e is sufficiently large compared to the interfacial thickness. In order to calculate the equilibrium radius of the Pickering droplets we now turn to the calculation of the interfacial tension.

7.2.1 Calculating the Interfacial Tension

We employ an approach which models the interfacial layer as a (curved) surface film. Such a film is characterised by the surface tension σ_{ow} of the water/solvent phase and a surface pressure $\pi(T, A)$ which in general will depend on the temperature T and area per adsorbed colloid A . This quantity is experimentally accessible due to the relation $A = 1/\Gamma$ with Γ the adsorption of colloidal particles. We then have that the surface tension of the film with the adsorbed particles can be calculated from

$$\sigma = \sigma_{ow} - \pi. \quad (7.7)$$

The Gibbs adsorption equation reads

$$d\pi = -d\sigma = \sum_i \Gamma_i d\mu_i. \quad (7.8)$$

In the following we consider the formation of droplets at constant external pressure and temperature and consider the surface excess of oil and water to be negligible. Double layer effects are also ignored at the moment. The adsorption equation now becomes

$$d\pi = \Gamma_c d\mu_c. \quad (7.9)$$

Furthermore, when the concentration of colloids c in the bulk is sufficiently small, its chemical potential can be written as

$$\mu_c = \mu_c^\ominus + k_B T \ln c / c^\ominus, \quad (7.10)$$

where $\mu_c^\ominus$ is the standard chemical potential, $c^\ominus$ a reference bulk concentration, k_B is Boltzmann's constant and c the concentration of colloids in the bulk³. If we now combine Eq. (7.9) and Eq. (7.10) one obtains

$$\Gamma_c = \frac{1}{k_B T} \frac{d\pi}{d \ln c}. \quad (7.11)$$

This equation relates the adsorbed amount of colloids to the surface pressure. In order to calculate the surface tension we thus need information regarding the surface pressure π . Here we use Szyskowski's equation given by [172]

$$\pi = \alpha \ln \left(\frac{c}{\beta} + 1 \right), \quad (7.12)$$

where α, β are constants. Several choices can now be made for the surface excess amount of colloids. Here we take a Langmuir isotherm [173],

$$\Gamma_c = \Gamma_c^\infty \frac{c}{k + c}, \quad (7.13)$$

where Γ_c^∞ is the adsorption at closest packing and k is a temperature dependent rate function [174]. It is related to the heat of adsorption via

$$k = k^\ominus \exp \left(\frac{\Delta\mu_{\text{ads}}}{k_B T} \right), \quad (7.14)$$

where $k^\ominus$ is the molarity of water ($k^\ominus = 33.35$ molecules / nm^{-3}) and $\Delta\mu_{\text{ads}}$ is the chemical potential difference for a colloidal particle due to adsorption (a negative quantity in general). Eq. (7.13) is derived by neglecting any interactions between the adsorbed colloidal particles but does describe a monolayer reasonably well [175]. One

³Formally the activity a should replace c . However, here we treat the emulsion as ideal.

of the striking features follows from the fact that the constants α and β appearing in Szyskowski's equation Eq. (7.12) are related to Γ_c and k :

$$\begin{aligned}\alpha &= k_B T \Gamma_c^\infty \\ \beta &= k.\end{aligned}\tag{7.15}$$

With all the model parameters defined, inserting Eq. (7.12) into Eq. (7.7) gives

$$\sigma = \sigma_{ow} - k_B T \Gamma_c^\infty \ln\left(\frac{k+c}{k}\right),\tag{7.16}$$

with k defined in Eq.(7.14).

Inserting expression (7.16) for the surface tension into Eq.(7.6) one obtains:

$$\sigma_{ow} - k_B T \Gamma_c^\infty \ln\left(\frac{k+c}{k}\right) - \frac{R_e^2}{3\phi} \left(\frac{\partial f_{\text{ent}}}{\partial R_e}\right) = 0.\tag{7.17}$$

This equation minimizes the free energy in Eq. (7.2). The bulk concentration of colloids c can be determined by considering the condition of mass balance. Denoting by $n_c = N_c/V$ the number of colloids per unit volume in the *entire system*, one can write

$$\frac{3\phi}{R} \Gamma_c + c(1 - \phi) = n_c.\tag{7.18}$$

Now using this expression in Eq. (7.13) and solving for c one obtains

$$\begin{aligned}c &= \frac{1}{2R(\phi - 1)} (-3\phi \Gamma_c^\infty + n_c R + R\phi k - Rk \\ &+ (9\phi^2 (\Gamma_c^\infty)^2 - 6\phi \Gamma_c^\infty n_c R - 6\phi^2 \Gamma_c^\infty k R + 6\phi \Gamma_c^\infty k R \\ &+ n_c^2 R^2 - 2n_c \phi k R^2 + R^2 \phi^2 k^2 - 2n_c k R^2 - 2R^2 k^2 \phi + R^2 k^2)^{1/2}).\end{aligned}\tag{7.19}$$

Since the derivative of the dispersion entropy is much smaller than the oil-water surface tension, we can ignore the last term in Eq. (7.17). With this approximation one obtains

$$R_e = \frac{3\phi \Gamma_c^\infty \Lambda^{-1} (\Lambda - 1)}{k [(1 - \phi)(1 - \Lambda)] + n_c},\tag{7.20}$$

where

$$\Lambda \equiv \exp(\sigma_{ow}/\Gamma_c^\infty k_B T),\tag{7.21}$$

Note that this result differs slightly from the one obtained in ref. [171] due to a different choice for the mass constraint.

One of the main features of this theory is the fact that the surface pressure π is radius dependent. This in turn causes the surface tension to depend on the radius, which is a direct consequence of the fact that the distribution of colloids between the continuous phase and the droplets depends on the surface area of the droplets which itself depends on R_e .

In the next section we test this model on the type of emulsions created by Sacanna *et al.* [169].

7.3 Testing the model on the work of Sacanna *et al.*

In the work by Sacanna *et al.* [169] the surface tension of the TPM-water interface was reported as $1.9 k_B T / nm^2$ (spinning drop) and the concentration of colloids was $C = 1.2 \cdot 10^{-24} g / nm^{-3}$. The magnetite crystal structure is of the inverted spinel type where the unit cell has a dimension of $\sim 15 \text{ \AA}^3$ [176]. The average diameter of the colloids is $11 nm$ so each colloid consists of $4.6 \cdot 10^4 Fe_3O_4$ molecules. The molecular weight of the colloids is therefore estimated as $M = 1.1 \cdot 10^7 g mol^{-1}$. The concentration of colloids n_c can now be calculated using

$$n_c \equiv \frac{N_c}{V} = \frac{C}{M} N_A = 6.6 \cdot 10^{-8} nm^{-3}, \quad (7.22)$$

where N_A denotes Avogadro's constant.

Now instead of using a Langmuir isotherm, let us consider the following. Since the amount of free colloidal particles in the bulk is low [169], we may neglect the amount in the bulk as a first order approximation: $\Gamma_c \approx n_c R / 3\phi$, i.e. all the colloids adsorb onto the interface. We then have

$$R \approx \frac{3\phi \Gamma_c}{n_c}. \quad (7.23)$$

With this additional approximation Eq. (7.6) becomes

$$\sigma_{ow} - k_B T \frac{n_c R_e}{3\phi} - \frac{R_e^2}{3\phi} \left(\frac{\partial f_{ent}}{\partial R_e} \right) = 0. \quad (7.24)$$

Again neglecting the entropy term and solving for R_e one finds

$$R_e = \frac{3\phi \sigma_{ow}}{n_c k_B T}. \quad (7.25)$$

This is the same result as in Ref. [177], where it was derived using an ideal gas approximation for the adsorption isotherm (i.e. Henry's law). The volume fractions of added oil should be similar to the final volume fraction of Pickering drops. The typical value of the volume fraction of Pickering drops is $\phi \sim 0.002$ [178] so one finds $R_e = 1.7 \cdot 10^5 nm$, which overestimates the experimental finding of $R \approx 50 nm$ [169] by three orders of magnitude.

From this finding we can infer that in order to reduce the bare oil-water interface by adsorption of colloids, the Pickering drops need to be very large. In the case of microemulsions the adsorption of surfactants (and co-surfactants) can reduce the bare oil-water interface much more efficiently, resulting in an effective surface tension of zero. Here, the oil-water interface is also reduced but apparently not as much as in microemulsions and the oil-water surface tension still dominates the interfacial behavior.

Next, we examine the situation of close-packed layers of colloids.

7.3.1 Close Packing

It is well-known that the droplets in Pickering emulsions are coated with a close-packed layer of colloidal particles. The adsorption at close packing Γ^∞ is related to the molecular area at closest packing A_0 via $\Gamma^\infty = 1/A_0$. For typical nonionic surfactants $A_0 \sim 50 - 100 \text{ \AA}^2$ [179]. Using this relationship Eq. (7.16) becomes

$$\frac{\sigma}{k_B T} = \frac{\sigma_{ow}}{k_B T} - \frac{1}{A_0} \ln\left(\frac{k+c}{k}\right), \quad (7.26)$$

with c given in Eq. (7.19). We have plotted the surface tension for several values of Γ_c and ϕ in Figure 7.1.

The model predicts larger drops for increasing values of the volume fractions of Pickering drops. If the Pickering drops can adsorb more colloidal particles the surface tension drops faster to lower values and on average larger drops will be formed. This confirms the picture that the reduction of the tension in the bare oil-water interface due to adsorption of the colloids is the primary driving force behind the stabilization mechanism. As can be inferred from Figure 7.1 the model is rather insensitive to changes in the volume fraction.

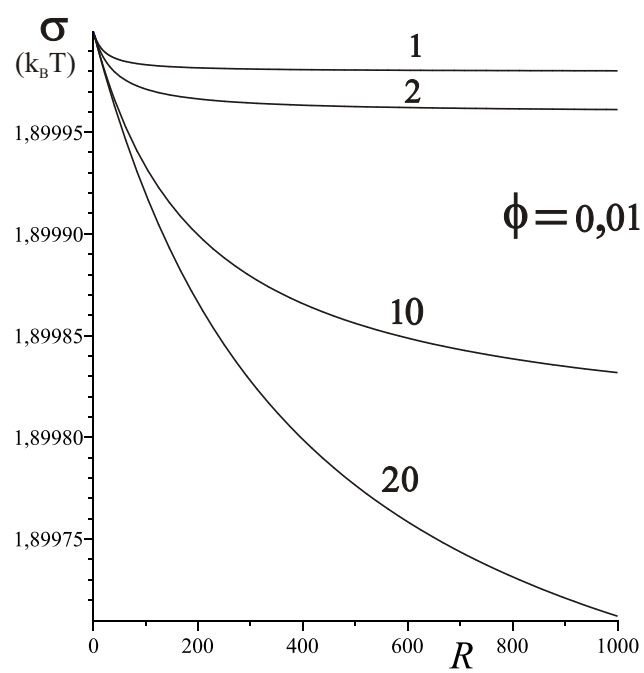
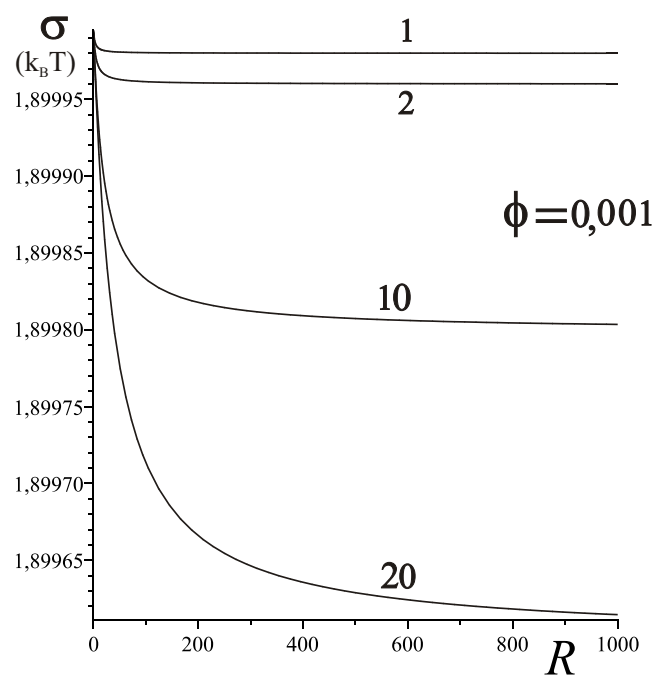
In Figure 7.2 the surface tension is plotted versus the bulk concentration of colloids. It is an empirical rule that in surfactant systems the surface tension scales linearly with $\log c$ for concentrations well below the cmc (i.e. in this regime the surface pressure may be transformed to $\pi \sim \alpha \ln(c/\beta)$). For low concentrations of colloids the surface tension shows linear behavior as can be seen in Figure 7.2. To the author's knowledge no experimental results for the surface tension as a function of magnetite concentration exists, so whether this surfactant approach is applicable in Pickering emulsions remains an open question.

Better agreement may be obtained if some data becomes available from experiments like better values for the adsorption energy, measurements of the volume fraction of drops and adsorption isotherms for magnetite on water/TPM interfaces. Despite the model's simplicity it does reproduce the essential features as observed in experiments.

7.4 Discussion

It was shown that if Pickering drops are thermodynamically stable the theory devised for swollen micelles could act as a good starting point for the theoretical description of Pickering emulsions. The key part of the theory is the introduction of a radius dependent surface tension. This has its origin in the fact that the colloids can be distributed between the continuous and dispersed phases and the latter is uniquely defined by the drop's radius R .

When comparing our model to the Pickering emulsions in the work of Sacanna *et al.* [169], still too many assumptions have to be made in order to make an accurate



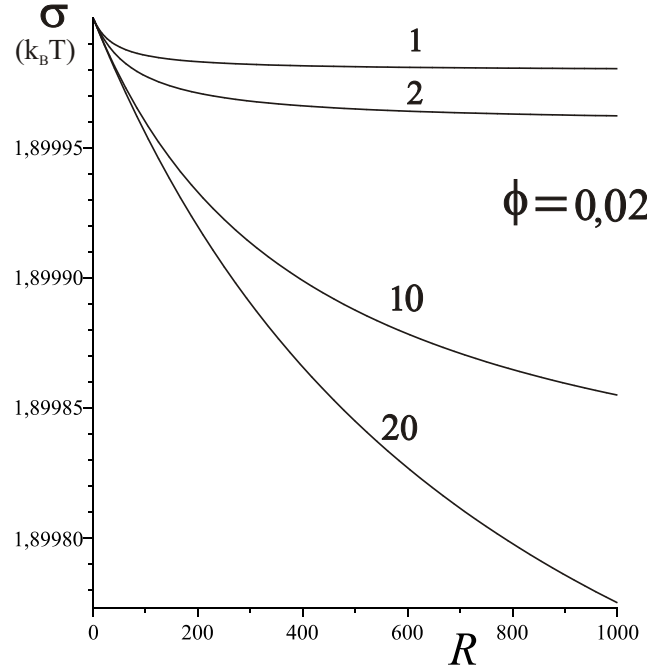


Figure 7.1 Surface Tension (in units of $k_B T/nm^2$) as function of the droplet radius for different values of Γ_c (in units of nm^{-2}) for values of $\phi = 0.001$, 0.01 and $\phi = 0.02$. We have taken $k = 33 \exp(-10)nm^{-3}$ and $n_c = 6.6 \cdot 10^{-8} nm^{-3}$.

comparison. Many parameters entering the theory still need to be determined experimentally before we can put them to use. Still, despite the approximations made and using the data available we do find that the model predicted Pickering droplets are of the same order in size. This agreement brakes down however, when we use Henry's law for the adsorption. It would be of special interest to see what the model predicts when adsorption isotherms become available for these kind of systems.

We have calculated the interfacial tension and found that it decreases with increasing R . It should be noted that these radii merely serve to reflect the different stages of the adsorption process and are not to be considered *equilibrium* radii. To obtain the equilibrium radius the free energy F_0 of a reference state needs to be constructed and compared with the free energy presented in this chapter. Only by minimizing the difference between both free energies one obtains the equilibrium droplet shape.

Both in Pickering emulsions and microemulsions (for which the original theory was derived) the reduction of the bare oil-water interface is the driving force towards aggregation. The observation that both the reduction of the surface tension is not that pronounced combined with the fact that Eq. (7.25) overestimates the radius implies that, opposed to the case of microemulsions, the bare oil-water interface still plays a non-negligible role in Pickering emulsions.

This model is far from complete. We have ignored double layer effects which,

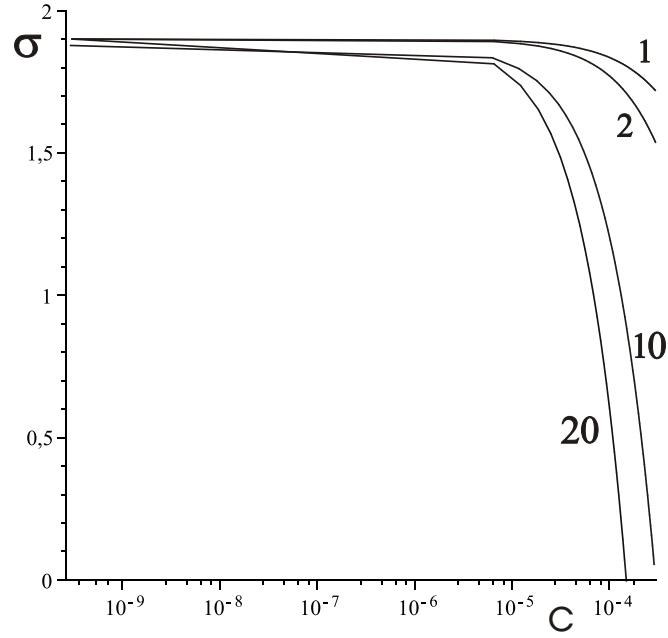


Figure 7.2 Surface Tension (in units of $k_B T / nm^2$) as function of the bulk concentration colloids c (in units of nm^{-3}) for different values of Γ_c (in units of nm^{-2}). Here $k = 33 \exp(-10) nm^{-3}$, $\phi = 0.001$ and $n_c = 6.6 \cdot 10^{-8} nm^{-3}$.

especially when constructing the phase diagram, will be important in describing the interactions between drops. Furthermore, the assumption of the nonexistence of interparticle interactions is especially expected to break-down at high surface coverages. Yet, the rationale here is that the colloidal particles adsorb strongly to the interface in a monolayer and we expect the interparticle interactions here to be smaller than in surfactant systems for which the theory was originally derived.

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Appendix A

Alternative thermodynamic derivation of the Tolman length in terms of the free energy density

In this Appendix an alternative thermodynamic derivation of Eq.(2.23) in terms of the free energy density is given. Our derivation [34, 67] starts with the grand free energy per volume $g \equiv \Omega/V$ which is the appropriate free energy at fixed μ , V , and T . In particular, we consider $g(\rho)$ which is the grand free energy density of a hypothetical fluid *constrained* to a certain density ρ . A typical shape for $g(\rho)$ is shown in Figure A.1. Only at its minimum (minima) does $g(\rho)$ have a clear physical meaning as the

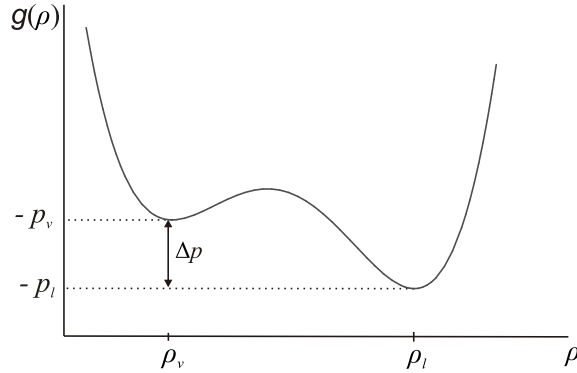


Figure A.1 Typical shape of the grand free energy density $g = \Omega/V$ as a function of density. It describes the situation of a liquid droplet (with $\rho = \rho_\ell$ and $p = p_\ell$) in a metastable vapour phase (with $\rho = \rho_v$ and $p = p_v$)

(metastable) equilibrium state. The density at the minimum defines the equilibrium density and the corresponding value of $g_{min} = -p$, owing to the thermodynamic

relation $\Omega = -pV$. In the example depicted in Figure A.1, there are two minima corresponding to a stable liquid phase and a metastable vapour phase:

$$\begin{aligned} g'(\rho_\ell) &= g'(\rho_v) = 0, \\ g(\rho_\ell) &= -p_\ell, \\ g(\rho_v) &= -p_v. \end{aligned} \quad (\text{A.1})$$

To explicitly investigate the variation of the free energy with chemical potential, we consider the Helmholtz free energy density $f \equiv F/V$:

$$g(\rho) = f(\rho) - \mu\rho. \quad (\text{A.2})$$

The minimization equations in Eq.(A.1) then become:

$$f'(\rho_\ell) = f'(\rho_v) = \mu, \quad (\text{A.3})$$

$$f(\rho_\ell) - \mu\rho_\ell = -p_\ell, \quad (\text{A.4})$$

$$f(\rho_v) - \mu\rho_v = -p_v. \quad (\text{A.5})$$

Next, we expand in $1/R$. The leading order and next to leading order term of the expansion of Eq.(A.5) give

$$\begin{aligned} f'(\rho_{\ell,0}) &= f'(\rho_{v,0}) = \mu_{coex}, \\ f''(\rho_{\ell,0})\rho_{\ell,1} &= f''(\rho_{v,0})\rho_{v,1} = \mu_1. \end{aligned} \quad (\text{A.6})$$

Next, we consider $\Delta p = p_\ell - p_v$ with p_ℓ and p_v given in Eqs.(A.6) and (A.7). A systematic expansion to second order in $1/R$ gives:

$$\begin{aligned} \Delta p &= f(\rho_v) - \mu\rho_v - f(\rho_\ell) + \mu\rho_\ell = f(\rho_{v,0}) - \mu_{coex}\rho_{v,0} - f(\rho_{\ell,0}) + \mu_{coex}\rho_{\ell,0} \\ &+ \frac{1}{R} [f'(\rho_{v,0})\rho_{v,1} - \mu_{coex}\rho_{v,1} - \mu_1\rho_{v,0} - f'(\rho_{\ell,0})\rho_{\ell,1} + \mu_{coex}\rho_{\ell,1} + \mu_1\rho_{\ell,0}] \\ &+ \frac{1}{R^2} \left[f'(\rho_{v,0})\rho_{v,2} - \mu_{coex}\rho_{v,2} - \mu_2\rho_{v,0} - \mu_1\rho_{v,1} + \frac{1}{2}f''(\rho_{v,0})(\rho_{v,1})^2 \right. \\ &\left. - f'(\rho_{\ell,0})\rho_{\ell,2} + \mu_{coex}\rho_{\ell,2} + \mu_2\rho_{\ell,0} + \mu_1\rho_{\ell,1} - \frac{1}{2}f'(\rho_{\ell,0})(\rho_{\ell,1})^2 \right] + \dots \end{aligned} \quad (\text{A.7})$$

The zeroth order term vanishes since $p_{\ell,0} = p_{v,0} = p_{coex}$ at coexistence. Using Eq.(A.8) in the remaining terms one has

$$\Delta p = \frac{2\sigma}{R} - \frac{2\delta\sigma}{R^2} + \dots = \frac{\mu_1\Delta\rho_0}{R} + \frac{1}{R^2} \left[\mu_2\Delta\rho_0 + \frac{\mu_1}{2}\Delta\rho_1 \right] + \dots \quad (\text{A.8})$$

Comparing the corresponding terms in the expansion in $1/R$ one recovers the results in Eqs.(2.21) and (2.23).

Appendix B

Verification of mechanical equilibrium

In this section we derive Eq.(3.45) and explicitly verify the validity of mechanical equilibrium, Eq.(3.13), for the density functional theory of section 3.4. Both results are derived from the Euler-Lagrange equation given in Eq.(3.44):

$$g'_{hs}(\rho) + V_{ext}(z_1) + \int d\vec{r}_{12} U(r_{12}) \rho(z_2) = 0. \quad (\text{B.1})$$

We first derive Eq.(3.13). This is done by multiplying all the terms in the above Euler-Lagrange equation by $\rho'(z_1)$ and subsequently integrating them over z_1 :

$$\begin{aligned} & \int_{-\infty}^{\infty} dz_1 g'_{hs}(\rho) \rho'(z_1) + \int_{-\infty}^{\infty} dz_1 V_{ext}(z_1) \rho'(z_1) \\ & + \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2) = 0. \end{aligned} \quad (\text{B.2})$$

It is important that the integration includes the region of discontinuity at $z=0$, which we have assured by taking the lower limit of the integration at $z_1 = -\infty$. The first term gives:

$$\int_{-\infty}^{\infty} dz_1 g'_{hs}(\rho) \rho'(z_1) = [g_{hs}(\rho)]_{z_1=-\infty}^{z_1=\infty} = -p + a \rho_b^2. \quad (\text{B.3})$$

The second term gives:

$$\int_{-\infty}^{\infty} dz_1 V_{ext}(z_1) \rho'(z_1) = - \int_{-\infty}^{\infty} dz_1 V'_{ext}(z_1) \rho(z_1). \quad (\text{B.4})$$

The last term gives:

$$\int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2) \quad (\text{B.5})$$

$$\begin{aligned}
&= \left[\int d\vec{r}_{12} U(r_{12}) \rho(z_1) \rho(z_2) \right]_{z_1=-\infty}^{z_1=\infty} \\
&\quad - \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho(z_1) \rho'(z_2) \\
&= -2a\rho_b^2 - \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2) = -a\rho_b^2.
\end{aligned}$$

We have used $1 \leftrightarrow 2$ symmetry to write the integral expression in the last line as (minus) the same term on the left-hand side. Adding all three terms in Eqs.(B.3)-(B.5), one recovers the condition for mechanical equilibrium, Eq.(3.13).

Next, we derive Eq.(3.45). This is achieved by, again, multiplying all the terms in the Euler-Lagrange equation in Eq.(B.1) by $\rho'(z_1)$ but now the integration over z_1 is limited to the fluid region:

$$\begin{aligned}
&\int_{0^+}^{\infty} dz_1 g'_{hs}(\rho) \rho'(z_1) \\
&\quad + \int_{0^+}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2) = 0.
\end{aligned} \tag{B.6}$$

The first term now gives:

$$\begin{aligned}
\int_{0^+}^{\infty} dz_1 g'_{hs}(\rho) \rho'(z_1) &= [g_{hs}(\rho)]_{z_1=0^+}^{z_1=\infty} \\
&= -p + a\rho_b^2 - g_{hs}(\rho^w).
\end{aligned} \tag{B.7}$$

The second term gives:

$$\begin{aligned}
&\int_{0^+}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2) \\
&= \left[\int d\vec{r}_{12} U(r_{12}) \rho(z_1) \rho(z_2) \right]_{z_1=0^+}^{z_1=\infty} \\
&\quad - \int_{0^+}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho(z_1) \rho'(z_2) \\
&= -2a\rho_b^2 + \rho^w g'_{hs}(\rho^w) \\
&\quad - \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho(z_1) \rho'(z_2),
\end{aligned} \tag{B.8}$$

where we have made use of Eq.(B.1) with $z_1 = 0^+$ inserted. A subtle point in this derivation is that the integration over $\vec{r}_{12}$ is over whole space while the integration

over z_1 is limited to the fluid region and does not include the region of the wall discontinuity. This breaks the $1 \leftrightarrow 2$ symmetry. In order to restore the symmetry, we have therefore extended the integration over z_1 to the entire volume in the last term. Interchanging $1 \leftrightarrow 2$ in this last term:

$$\begin{aligned}
& - \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho(z_1) \rho'(z_2) \\
& = - \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2) \\
& = \rho^w g'_{hs}(\rho^w) - \int_{0^+}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2),
\end{aligned} \tag{B.9}$$

where we have used that the singular contribution to $\rho'(z_1)|_{\text{sing}} = \rho^w \delta(z_1)$, and again used Eq.(B.1) for $z_1 = 0^+$. Recognizing that the last line contains the same term as the left-hand side in Eq.(B.8), with a minus sign, we thus conclude for the second term in Eq.(B.6):

$$\begin{aligned}
& \int_{0^+}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \rho'(z_1) \rho(z_2) \\
& = -a \rho_b^2 + \rho^w g'_{hs}(\rho^w).
\end{aligned} \tag{B.10}$$

This result is added to the result in Eq.(B.7) to arrive at Eq.(3.45):

$$p = -g_{hs}(\rho^w) + \rho^w g'_{hs}(\rho^w). \tag{B.11}$$

Note that this derivation does not make any assumption on the precise form of the interaction potential $U(r_{12})$ other than that it should be sufficiently short-ranged.

Appendix C

Virial expressions for the surface tension and Tolman length

The virial expressions [28, 83, 101] for the surface tension and Tolman length of a liquid-vapour interface are given by

$$\begin{aligned}\sigma &= \frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) \rho^{(2)}(z_1, z_2, r_{12}) \\ \delta\sigma &= -\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) \\ &\quad \times (z_1 + z_2) \rho^{(2)}(z_1, z_2, r_{12}),\end{aligned}\tag{C.1}$$

where $\rho^{(2)}(z_1, z_2, r_{12})$ is the pair density correlation function for the planar liquid-vapour interface. The first of the above expressions is known as the Kirkwood-Buff formula for the surface tension [101]. By making the following mean-field approximation for the pair density

$$\rho^{(2)}(z_1, z_2, r_{12}) \approx \rho_0(z_1) \rho_0(z_2),\tag{C.2}$$

we arrive at the expressions for σ and $\delta\sigma$ in Eq.(3.51):

$$\begin{aligned}\sigma &= \frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) \rho_0(z_1) \rho_0(z_2), \\ \delta\sigma &= -\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) \\ &\quad \times (2z_1 + sr_{12}) \rho_0(z_1) \rho_0(z_2),\end{aligned}\tag{C.3}$$

where it is reminded that $z_2 = z_1 + sr_{12}$, with $s = \cos\theta_{12}$. The expressions for σ and $\delta\sigma$ in Eqs.(C.1) and (C.3) are independent of the type of interface; the difference

only comes about in the precise form of the pair density (Eq.(C.1)) or density profile (Eq.(C.3)). For the case of the wall-fluid interface, that we consider here, we have that $\rho_0(z)=0$ for $z<0$, so that we might also set the lower limit of the z_1 -integration to $z_1=0$. It is, however convenient, to leave the integration over the entire volume.

Our goal is to show the equivalence of the expressions for σ and $\delta\sigma$ in Eq.(C.3) with those in Eq.(3.50). We shall limit ourselves to the derivation of the expression for $\delta\sigma$, however. The derivation of the expression for σ follows in an analogous way.

As a first step, the expression for $\delta\sigma$ in Eq.(C.3) is partially integrated over r_{12} . The boundary term vanishes and one finds that:

$$\begin{aligned}\delta\sigma &= \frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) (1 - 3s^2) \\ &\quad \times (3z_1 + 2sr_{12}) \rho_0(z_1) \rho_0(z_2) \\ &+ \frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) sr_{12} (1 - 3s^2) \\ &\quad \times (2z_1 + sr_{12}) \rho_0(z_1) \rho'_0(z_2). \end{aligned} \quad (\text{C.4})$$

The integrand in the first term in Eq.(C.4) is written as the derivative with respect to s :

$$\begin{aligned}(1 - 3s^2) (3z_1 + 2sr_{12}) \\ = \frac{d}{ds} \left[3z_1 s(1 - s^2) + \frac{r_{12}}{2}(1 + 2s^2 - 3s^4) \right]. \end{aligned} \quad (\text{C.5})$$

This result is used to partially integrate the first term in Eq.(C.4) over s . Combining the result with the second term in Eq.(C.4) gives:

$$\begin{aligned}\delta\sigma &= -\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \\ &\quad \times \left[4z_1 sr_{12} + r_{12}^2(1 + s^2) \right] \rho_0(z_1) \rho'_0(z_2). \end{aligned} \quad (\text{C.6})$$

Next, we use $1 \leftrightarrow 2$ symmetry

$$\begin{aligned}\delta\sigma &= -\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) \\ &\quad \times \left[-4z_1 sr_{12} + r_{12}^2(1 - 3s^2) \right] \rho'_0(z_1) \rho_0(z_2). \end{aligned} \quad (\text{C.7})$$

Again, the integrand is written as the derivative with respect to s

$$\begin{aligned}-4z_1 s + r_{12}(1 - 3s^2) \\ = \frac{d}{ds} \left[2z_1 (1 - s^2) + sr_{12}(1 - s^2) \right], \end{aligned} \quad (\text{C.8})$$

which is used to perform yet another partial integration:

$$\begin{aligned} \delta\sigma &= \frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) r_{12}^2 (1 - s^2) \\ &\quad \times (2z_1 + sr_{12}) \rho'_0(z_1) \rho'_0(z_2). \end{aligned} \quad (\text{C.9})$$

Finally, we note that the sr_{12} -term is antisymmetric when we interchange $1 \leftrightarrow 2$, so this term vanishes. We are then left with the result for $\delta\sigma$ anticipated in Eq.(3.50):

$$\begin{aligned} \delta\sigma &= \frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r_{12}) r_{12}^2 (1 - s^2) \\ &\quad \times z_1 \rho'_0(z_1) \rho'_0(z_2). \end{aligned} \quad (\text{C.10})$$

In connection with the symmetry-argument used to derive Eq.(C.10) from Eq.(C.12), we should mention a subtle point with regard to the similar term present in the expression for $\delta\sigma$ in Eq.(C.3). Here too, one could wonder whether the same argument can be used to show that this term is zero and replace the term $(2z_1 + sr_{12})$ by $2z_1$. This turns out not to be correct. The reason is that the integral over z_1 in Eq.(C.3) is *conditionally convergent*: the integrand is zero at $z_1 \rightarrow \infty$ only when *first* the integral over s is taken. To make the integral explicitly convergent, it is therefore customary to subtract of the bulk contribution [180]:

$$\begin{aligned} \delta\sigma &= -\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) \\ &\quad \times (2z_1 + sr_{12}) \left[\rho_0(z_1) \rho_0(z_2) - \rho_b^2 \Theta(z_1) \right]. \end{aligned} \quad (\text{C.11})$$

The consequence, however, is that the presence of this bulk term breaks the $1 \leftrightarrow 2$ symmetry with the result that the sr_{12} -term in the above expression is not zero, as an explicit calculation shows:

$$\begin{aligned} &-\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) sr_{12} \\ &\quad \times \left[\rho_0(z_1) \rho_0(z_2) - \rho_b^2 \Theta(z_1) \right] \\ \stackrel{1 \leftrightarrow 2}{=} &\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) sr_{12} \\ &\quad \times \left[\rho_0(z_1) \rho_0(z_2) - \rho_b^2 \Theta(z_2) \right] \\ = &\frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) sr_{12} \\ &\quad \times \left[\rho_0(z_1) \rho_0(z_2) - \rho_b^2 \Theta(z_1) \right] \end{aligned}$$

$$\begin{aligned} & + \frac{\rho_b^2}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U'(r_{12}) r_{12} (1 - 3s^2) s r_{12} \\ & \quad \times [\Theta(z_1) - \Theta(z_2)] \\ = & \frac{\rho_b^2}{60} \int d\vec{r}_{12} U'(r_{12}) r_{12}^3. \end{aligned} \tag{C.12}$$

Appendix D

Full $\alpha(\rho)$ and excluded volume interactions

In this appendix, instead of truncating the available volume fraction $\alpha(\rho)$ to second order in an expansion in ρ , we use the full expression as given by Lekkerkerker [132]:

$$\alpha(\rho) = (1 - \eta) \exp\left[-\frac{A\eta}{1 - \eta} - \frac{B\eta^2}{(1 - \eta)^2} - \frac{C\eta^3}{(1 - \eta)^3}\right], \quad (\text{D.1})$$

where it is reminded that $\eta = (\pi/6) \rho d^3$. The coefficients A , B , and C depend on q as:

$$A = 3q + 3q^2 + q^3, \quad B = \frac{9}{2}q^2 + 3q^3, \quad C = 3q^3. \quad (\text{D.2})$$

The colloid-polymer phase diagram can be determined replacing $g(\rho) = g_{\text{hs}}(\rho) - a\rho^2$ by the full expression

$$g(\rho) = g_{\text{hs}}(\rho) - k_{\text{B}}T n_p^r \alpha(\rho). \quad (\text{D.3})$$

A further modification, which is due to Aarts *et al.* [164], has the goal of taking the polymer excluded volume interactions (EVI) into account thus improving on the approximation of treating the polymers as ideal. Here, we list the formulas used by Aarts *et al.* in connection with this modification which consists of several steps.

First, q as it appears in the colloid-colloid depletion interaction is replaced by a polymer density dependent $q_{\text{dep}}(\eta_p)$ [166]

$$q_{\text{dep}}(\eta_p) = \left(1 + 3a q_0 (\xi_d^*)^{1/2} + 3b q_0^2 \xi_d^* - 3c q_0^3 (\xi_d^*)^{3/2}\right)^{1/3} - 1. \quad (\text{D.4})$$

Here, the polymer-colloid size ratio parameter is denoted as $q_0 \equiv 2R_g/d$ and a , b and c are numerical constants:

$$\begin{aligned} a &= \frac{1}{4\sqrt{\pi}} \left[6 + 3\ln(2) + \pi - \frac{2\pi}{3}\sqrt{3}\right] \approx 1.0710, \\ b &= \frac{53}{36} - \frac{5\pi}{8} + \frac{\pi}{4}\sqrt{3} \approx 0.8691, \\ c &= \frac{1}{9\sqrt{\pi}} \left[-\frac{551}{15} + \frac{1673\pi}{16} - 40\pi\sqrt{3}\right] \approx 0.0399 \end{aligned} \quad (\text{D.5})$$

The polymer density dependence of q_{dep} enters through the bulk correlation length parameter $\xi_d^* \equiv \xi_d^2/R_g^2$, with ξ_d the bulk correlation length. The explicit form for ξ_d^* is taken from renormalization group results by Schäfer for a monodisperse polymer system in the excluded volume limit [181]:

$$\xi_d^*(\hat{s}) = \frac{w^{4\nu-2}}{0.805} \times \frac{0.636 - 0.265 w^{-1} \xi^{(1)}(W_R)}{1 + W_R[1.728 - 0.299 w^{-1} J_1(W_R)]}, \quad (\text{D.6})$$

where $\hat{s} \equiv \eta_p/1.169$, the Flory exponent $\nu = 0.588$, and where the functions $\xi^{(1)}(W_R)$ and $J_1(W_R)$ are given by

$$\begin{aligned} \xi^{(1)}(W_R) &= \frac{-0.6382 + 0.1059 W_R + 0.00115 W_R^2}{1 + 0.6900 W_R + 0.01647 W_R^2} (1 + 0.00288 W_R)^{-1/2}, \\ J_1(W_R) &= \int_0^\infty dx \sqrt{x} \left(\frac{e^{-x} - 1 + x}{x^2 + 2W_R(e^{-x} - 1 + x)} \right)^2. \end{aligned} \quad (\text{D.7})$$

The variables w and W_R are determined from $\hat{s}$ by solving

$$\frac{n_0}{c_0} \tilde{u} \hat{s} = (1 - w^2) w^{2-6\nu} \quad \text{and} \quad W_R = c_0 n_0 \left(\frac{1}{w^2} - 1 \right). \quad (\text{D.8})$$

with $n_0 = 0.53$, $c_0 = 1.2$, and $\tilde{u} = 8.107$.

As a second step, the osmotic pressure of the polymers is considered no longer ideal and replaced by the osmotic pressure of polymers with excluded volume interactions. The result is that the expression for $g(\rho) = g_{\text{hs}}(\rho) - k_B T n_p^r \alpha(\rho)$ in Eq.(D.3) is replaced by

$$g(\rho) = g_{\text{hs}}(\rho) - \int_0^{n_p^r} dn_p^r \left(\frac{\partial \Pi}{\partial n_p^r} \right) \alpha(\rho; q_{\text{dep}}), \quad (\text{D.9})$$

where it is reminded that the available volume fraction $\alpha(\rho)$ now depends on the polymer density η_p since we have replaced q by $q_{\text{dep}}(\eta_p)$. Notice that for an ideal polymer system $(\partial \Pi / \partial n_p^r) = k_B T$ so that Eq.(D.9) reduces to Eq.(D.3).

The explicit form for the osmotic pressure is also taken from renormalization group results by Schäfer for a monodisperse polymer system in the excluded volume limit:

$$\frac{1}{k_B T} \left(\frac{\partial \Pi}{\partial n_p^r} \right) = 1 + 3.073 \hat{s} \left(\frac{1 + 3.80 \hat{s} + 5.67 (\hat{s})^2}{1 + 1.73 \hat{s}} \right)^{0.309}. \quad (\text{D.10})$$

We have now all the ingredients to determine the polymer-colloid phase diagram by numerical integration of Eq.(D.9).

Finally, we determine the parameters that are necessary for locating the wetting transition within the Nakanishi-Fisher model. The squared-gradient parameter m

and the surface parameter g_1 only depend on the colloid-colloid depletion potential and are evaluated from the following integrals

$$\begin{aligned} m &= \frac{d^5}{q_0^3} \int_0^{\eta_p} d\eta_p \left(\frac{\partial \Pi}{\partial n_p^r} \right) \frac{\pi}{240} q^3 (40 + 70 q + 56 q^2 + 28 q^3 + 8 q^4 + q^5), \\ g_1 &= \frac{d^4}{q_0^3} \int_0^{\eta_p} d\eta_p \left(\frac{\partial \Pi}{\partial n_p^r} \right) \frac{\pi}{140} q^3 (70 + 105 q + 63 q^2 + 21 q^3 + 3 q^4), \end{aligned} \quad (\text{D.11})$$

where $q = q_{\text{dep}}(\eta_p)$ in both integrations and where we have replaced n_p^r by $\eta_p = (\pi/6) n_p^r q_0^3 d^3$ as integration parameter.

The surface parameters h_1 and g_2 not only depend on the colloid-colloid depletion distance parameter q but also on the colloid-wall depletion distance parameter q_{wall} which is derived from Eq.(D.4) by considering the $q_0 \rightarrow 0$ limit:

$$q_{\text{wall}} = a q_0 (\xi_d^*)^{1/2}. \quad (\text{D.12})$$

The surface parameters h_1 and g_2 are now evaluated from the following integrals

$$\begin{aligned} h_1 &= \frac{d}{q_0^3} \int_0^{\eta_p} d\eta_p \left(\frac{\partial \Pi}{\partial n_p^r} \right) q^3 \left(1 + \frac{q}{2} \right), \\ g_2 &= \frac{d^4}{q_0^3} \int_0^{\eta_p} d\eta_p \left(\frac{\partial \Pi}{\partial n_p^r} \right) \frac{6}{\pi} \left(q - \frac{1}{4} \right)^{\frac{11}{2}} (c_0 + c_1 q + c_2 q^2 + c_3 q^3 + c_4 q^4), \end{aligned} \quad (\text{D.13})$$

where now we need to replace q by $q = (q_{\text{dep}} + q_{\text{wall}})/2$ in both integrations.

Appendix E

A detailed description of the interface in Pickering Emulsions

This Appendix aims to describe the Pickering drops in terms of the capillary part of the free energy. Model calculations in two and three dimensions are presented.

Consider a solution with N Pickering droplets. The temperature T and the total volume V are fixed. Each Pickering drop contains n adsorbed colloidal particles with radius a . The free energy F_H of a single Pickering drop with radius R can be written as

$$F_H = \sum_i \sigma_i A_i - p_{\text{in}} V_{\text{in}} - p_{\text{out}} V_{\text{out}} + \sum_j \mu_j N_j \quad (\text{E.1})$$

where i labels a sum over the interfaces, i.e. $i = \{co, cw, ow\}$ and $j = \{\text{colloid, oil, water}\}$ a sum over the components. It is useful to consider the grand potential $F = F_H - \sum_j \mu_j N_j$. The free energy can now be written as

$$F = \sigma_{co} A_{co} + \sigma_{cw} A_{cw} + \sigma_{ow} A_{ow} - \Delta p V_d, \quad (\text{E.2})$$

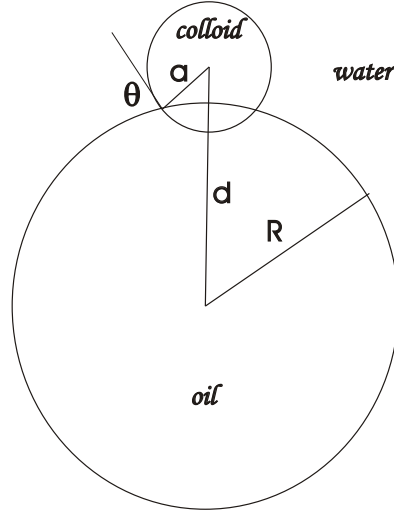
where A_{co} , A_{cw} and A_{ow} denote the surfaces of the colloid-oil, colloid-water and oil-water surfaces respectively and Δp is the pressure difference between the inside and outside of the drop where V_d is the volume available *inside* the drop. We assume the droplet to be in thermodynamic equilibrium, i.e. the chemical potentials μ_j is uniform for all components (i.e. $d\mu_i = 0$).

E.1 2 D description

Consider the oil as a circle with radius R onto which n colloidal particles are adsorbed with radius a as depicted in Figure E.1. The contact angle θ is determined by wettability of the colloidal particle. The distance between the centers of the colloidal particle and the oil drop is labeled d .

The free energy of this system can be written as

$$F = \sigma_{co} L_{co} + \sigma_{cw} L_{cw} + \sigma_{ow} L_{ow} - \Delta p A_{\text{oil}}, \quad (\text{E.3})$$

**Figure E.1** A 2D Pickering drop

here A_{oil} is the area unoccupied by colloids.

The corresponding interfacial lengths read [182]

$$\begin{aligned}
 L_{co} &= 2na \arccos\left(\frac{d^2 - R^2 + a^2}{2da}\right) \\
 L_{cw} &= 2\pi na - 2na \arccos\left(\frac{d^2 - R^2 + a^2}{2da}\right) \\
 L_{ow} &= 2\pi R - 2na \arccos\left(\frac{d^2 - a^2 + R^2}{2dR}\right).
 \end{aligned}
 \tag{E.4}$$

The area of the bare oil-water interface is given by

$$\begin{aligned}
 A_{\text{oil}} &= \pi R^2 - n \left(a^2 \arccos\left(\frac{d^2 - R^2 + a^2}{2da}\right) + R^2 \arccos\left(\frac{d^2 - a^2 + R^2}{2dR}\right) - \right. \\
 &\quad \left. \frac{1}{2} \sqrt{(-d + a + R)(d + a - R)(d - a + R)(d + a + R)} \right).
 \end{aligned}
 \tag{E.5}$$

With these expressions the free energy per colloid per unit length of interface per colloid becomes

$$\begin{aligned}
 g \equiv \frac{F}{2na} - \pi \sigma_{cw} &= \Delta \sigma \arccos\left(\frac{d^2 - R^2 + a^2}{2da}\right) + \sigma_{ow} \frac{R}{a} \left(\frac{\pi}{n} - \arccos\left(\frac{d^2 - a^2 + R^2}{2dR}\right) \right) \\
 &\quad - \Delta p \left(\frac{\pi R^2}{2na} - \frac{1}{4a} \sqrt{(-d + a + R)(d + a - R)(d - a + R)(d + a + R)} \right).
 \end{aligned}
 \tag{E.6}$$

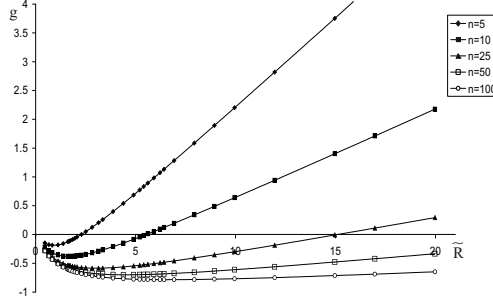


Figure E.2 2D free energy for a Pickering drop with $\Delta\sigma = 0, \sigma = 1$ as a function of $\tilde{R} = R/a$ for different values of n .

where we have introduced $\Delta\sigma \equiv \sigma_{\text{co}} - \sigma_{\text{cw}}$.

Since we consider noninteracting colloids we may treat the separation d and radius of the drop R as independent variables. We are then able to minimise Eq. (E.6) using the conditions

$$\left(\frac{\partial g}{\partial R}\right)_d = \left(\frac{\partial g}{\partial d}\right)_R = 0. \quad (\text{E.7})$$

As a result we find that the droplet radius which minimises Eq.(E.6) is given by

$$R = \frac{-a\Delta\sigma \pm (a^2\Delta\sigma^2 + \sigma_{\text{ow}}^2(d^2 - a^2))^{1/2}}{\sigma_{\text{ow}}} \quad (\text{E.8})$$

where the $\pm$ indicates which of the two phases (oil, water) is present inside the drop. The contact angle in Figure E.1 is related to d, R and a via the geometrical relationship

$$\cos(\theta) = \frac{d^2 - R^2 - a^2}{2aR}. \quad (\text{E.9})$$

If we now substitute our result for R into Eq. E.9 one obtains

$$\Delta\sigma = \sigma_{\text{ow}} \cos \theta, \quad (\text{E.10})$$

e.g. Young's law. As a further result of the minimisation we find

$$\Delta p = \frac{\sigma_{\text{ow}}}{R}, \quad (\text{E.11})$$

which is the two dimensional analogue of Laplace's equation. An equivalent statement is that the adsorbed particles will not adjust the pressure inside the drop. Because interactions between colloids are not included, this model is only correct in the case $n = 1$. It can be shown that the free diverges for larger values of n for small droplet radii due to the fact that the volume available to the oil phase can become negative.

For small values the effect of adsorbing colloidal particles is to lower the free energy for all values of $\Delta\sigma \in [-1, 1]$.

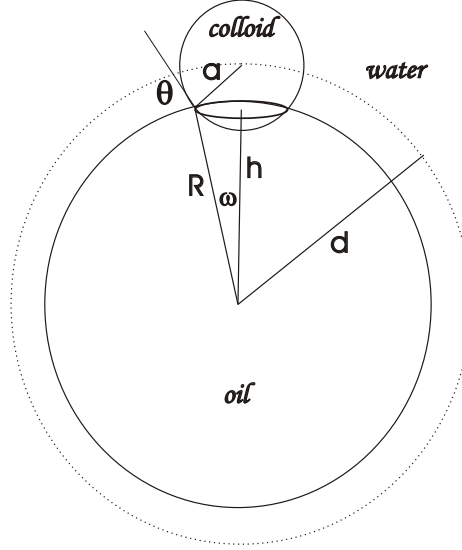


Figure E.3 3D Drop

E.2 3 D description

Figure E.3 depicts the conditions in three dimensions. Like in the two-dimensional description a denotes the colloidal radius, R the radius of the oil-water meniscus and d is the distance between the centers of the drop and particle. In three dimensions the three phase contact line takes the form of a circle which has a radius of $a \sin(\theta - \omega) = (R^2 - h^2)^{1/2}$ where h is given by the distance between the center of the circle and the drop center. The angles ω and θ are defined in Figure E.3. Note that for a flat ($R \rightarrow \infty$) oil-water interface the distance between the particle and the interface is given by $a \cos \theta$. At finite R , that distance is given by $a \cos(\theta - \omega) = d - h$.

In this three dimensional description the free energy ¹ is given by

$$F = \sigma_{co}A_{co} + \sigma_{cw}A_{cw} + \sigma_{ow}A_{ow} - \Delta p V_{oil}. \quad (\text{E.12})$$

This expression is analogous to Eq. (E.3) with the straightforward replacement of interfacial lengths by areas and the area available to the oil-phase by V_{oil} , the volume available.

The expressions for the areas A are given by:

$$\begin{aligned} A_{co} &= 2\pi n a^2 (1 + \cos(\omega - \theta)) = 2\pi n a^2 \left(1 + \frac{d - h}{a}\right) \\ A_{cw} &= 2\pi n a^2 (1 - \cos(\omega - \theta)) = 2\pi n a^2 \left(1 - \frac{d - h}{a}\right) \\ A_{ow} &= 4\pi R^2 - 2\pi n R^2 (1 - \cos \omega) = 4\pi R^2 - 2\pi n R^2 \left(1 - \frac{h}{R}\right). \end{aligned} \quad (\text{E.13})$$

¹ignoring the effects from line tension

$$(E.14)$$

The height h can be expressed in terms of d, R and a by the relationship

$$h = R - \frac{(a - R + d)(a + R - d)}{2d}. \quad (E.15)$$

The volume available in the oil phase is given by [183]

$$V_{\text{oil}} = \frac{4\pi}{3}R^3 - \frac{n\pi}{12d}(R + a - d)^2(d^2 + 2da - 3a^2 + 2dR + 6aR - 3R^2). \quad (E.16)$$

These expressions lead to the following form of the free energy per unit area per colloid

$$g \equiv \frac{F}{2\pi na^2} - \sigma_{co} - \sigma_{cw} = -\Delta\sigma \frac{d - h}{a} + 2\sigma_{ow} \frac{R^2}{a^2} \left(\frac{1}{n} - \frac{1}{2} \left(1 - \frac{h}{R} \right) \right) - \frac{\Delta p V_{\text{oil}}}{2\pi na^2}, \quad (E.17)$$

where we have introduced $\Delta\sigma = \sigma_{co} - \sigma_{cw}$.

Again using our formalism when $n = \text{constant}$ and using

$$\left(\frac{\partial g}{\partial d} \right)_R = \left(\frac{\partial g}{\partial R} \right)_d = 0 \quad (E.18)$$

we find for the drop radius

$$R = \frac{-a\Delta\sigma \pm (\Delta\sigma^2 a^2 + \sigma_{ow}^2 (d^2 - a^2))^{1/2}}{\sigma_{ow}}. \quad (E.19)$$

where the positive root refers to oil-in-water emulsions and the negative one to water-in-oil. Inserting this expression into E.9 leads to

$$\cos(\theta) = \frac{\Delta\sigma}{\sigma_{ow}}, \quad (E.20)$$

which is Young's law again. As a further result of the minimisation we find

$$\Delta p = \frac{2\sigma_{ow}}{R}, \quad (E.21)$$

i.e. the well-known Laplace equation. Just as in the two-dimensional case the pressure difference between the inside and outside of the drop is unaffected by the adsorption of colloidal particles, and this in turn is a direct consequence of the absence of inter-particle interactions (only correct for the situation when $n = 1$) in this model.

In Figure E.4 we have plotted g/V_{oil} as a function of R for different values of $\Delta\sigma$. Unlike the two-dimensional case if $\Delta\sigma > 0$ the free energy goes through a maximum. If $\Delta\sigma < 0$ the free energy is slightly raised compared to the bare surface and there is

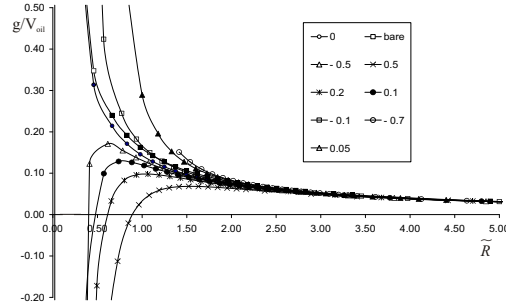


Figure E.4 3D free energy for a Pickering drop for several values of $\Delta\sigma$ as a function of $\tilde{R} = R/a$. Except for the bare surface the curves are for $n = 1$.

no maximum. The symmetrical case $\Delta\sigma = 0$ resembles the case of the bare surface only here the free energy is lowered again.

An analysis of the interface of a Pickering drop was presented using the capillary part of the free energy. Minimising the proposed free energy with respect to the drop's radius results in Laplace's law and Young's law in both two and three dimensions. Clearly, the fact that the colloidal particles are (partially) wetted by both phases explains the strong adsorption of these particles as is found in experiments.

The neglect of interparticle interactions at the interface is of course subject to scrutiny and in future work this needs to be incorporated. One could for example add an additional hard-sphere like term to the free energy taking into account the colloid-colloid interactions. Still, this model is exact for the case of single adsorbed colloid where it is found that it will lower the drop's free energy. The main finding is that Laplace's law still holds in this case. This implies that the adsorbed colloid exerts no influence on the pressure inside the drop. This would definitely change if the description is expanded to allow for colloidal interactions. The change in drop volume would then also couple to the amount of adsorbed colloids and Laplace's law would in that case break down.

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.

Algemene Samenvatting

In deze samenvatting zal ik het verrichte onderzoek van de afgelopen vier jaar op een eenvoudige manier presenteren. Men dient hierbij te realiseren dat het onderzoek van theoretische aard is, d.w.z. we pogen een verklaring te zoeken achter het hoe en waarom van zaken gebruikmakend van theoriën zoals thermodynamica en statistische mechanica.

Vloeistofoppervlakken treffen we aan bij talloze applicaties: verf, voedselproductie, coatings, wasmiddelen en zelfs bij toepassingen zoals het verwijderen van olie of in de nanotechnologie. Het doel van het onderzoek is kennis te vergaren over hoe deze vloeistofoppervlakken zich gedragen toegepast in verschillende systemen.

De titel van het proefschrift laat zich vertalen als “De gemiddelde veldbeschrijving van de structuur en spanning van gekromde vloeistofoppervlakken.” De rol van de gemiddelde veldbeschrijving staat centraal in dit proefschrift. Hiermee wordt een theorie bedoeld die de interactie die een molecuul ondervindt ten gevolge van alle individuele moleculen om hem heen *benaderd* door de invloed van al die deeltjes te beschrijven met een gemiddelde interactie. Ondanks het feit dat deze benadering soms niet goed op gaat geeft deze theorie vaak een goed startpunt om een bepaalde waarneming te verklaren.

We zijn nu in staat om met behulp van deze gemiddelde veldtheorie eigenschappen van het vloeistofoppervlak uit te rekenen, zoals de oppervlaktespanning (hoeveel energie kost het om het oppervlak uit te rekken) of de buigingsrigiditeit (hoeveel energie kost het om het oppervlak te buigen *zonder* te strekken). Deze methodologie zal worden toegepast op een aantal verschillende systemen.

In hoofdstuk 2 en 3 kijken we naar een simpele vloeistof met het bijbehorende gas. Als we water bijvoorbeeld laten koken, zal er spontaan in het water gas (waterdamp) worden gevormd, omdat bij die temperatuur gas de thermodynamisch meest stabiele fase is. In het begin ontstaat een gasbelletje en het oppervlak van zo’n groeiend gasbelletje is sterk gekromd. Het blijkt zo te zijn dat de oppervlaktespanning voor rechte oppervlakken niet hetzelfde is als voor gekromde oppervlakken. De kromtecorrectie op de oppervlaktespanning wordt de Tolman lengte genoemd, naar zijn ontdekker R. C. Tolman. In hoofdstuk 2 berekenen we de Tolman lengte in de context van een gemiddelde veld theorie ontwikkeld door de Nederlandse natuurkundige J. D. van der Waals. Het blijkt dat om de Tolman lengte uit te rekenen kennis over het dichtheidsprofiel van het *ongekromde* oppervlak voldoende is. We vinden dat in dit

model de Tolman lengte negatief is en klein (ordegrootte $\sim$ nm). Bij coëxistentie, het punt waarbij beide fases dezelfde vrij energie hebben, gaat de expansie die de Tolman lengte definieert niet meer op.

In hoofdstuk 3 berekenen we de Tolman lengte voor een vloeistofoppervlak nabij een harde wand. Ook al is de situatie hier iets anders dan in het geval van een groeiend belletje, de Tolman lengte kan in principe op dezelfde manier uitgerekend worden. De beide modellen die we gebruiken leveren dezelfde soort resultaten op: de Tolman lengte is ook hier negatief en kleiner dan de typische doorsnede van een molecuul. Tevens laten we zien dat het “walltheorem”² onder verschillende modelbenaderingen niet op hoeft te gaan, maar er altijd aan de voorwaarde van mechanisch evenwicht voldaan wordt.

Wanneer een vloeistof op een oppervlak wordt aangebracht zijn er twee situaties mogelijk. Of de vloeistof bedekt heel het oppervlak of de vloeistof vormt druppels op het oppervlak. Door het systeem te veranderen (we modificeren het oppervlak, verhogen de temperatuur, etc.) is het mogelijk dat er een overgang plaats vindt tussen beide situaties. Dit onderwerp staat centraal in hoofdstukken 4 en 6. In hoofdstuk 4 beschouwen we de bevochtiging van oppervlakken in de context van de theorie van Nakanishi en Fisher. In deze theorie wordt de substraat-vloeistof interactie door twee parameters gemodelleerd: een oppervlakte chemische potentiaal, welke de substraat-vloeistof interactie beschrijft en een oppervlakte *enhancement* parameter die de verandering in interactie tussen moleculen nabij het oppervlak beschrijft. In hoofdstuk 4 leiden we uitdrukkingen af voor deze modelparameters en zijn zo in staat andere theorieën te vergelijken met de theorie van Nakanishi en Fisher. Voor het “square-gradient” model hebben we het wetting fasediagram uitgerekend. We vinden dat dicht bij het kritieke punt de overgangen van tweede orde zijn. In hoofdstuk 6 bestuderen we de bevochtiging in colloid-polymeer mengsels.

Colloid-polymeer mengsels verdienen de afgelopen jaren nogal wat aandacht van de wetenschappelijke gemeenschap. Zo’n mengsel is voor te stellen als een vloeistof waarin zich grote harde bollen bevinden (colloïden) en polymeren die in oplossing zich meer gedragen als kluwen slietvormige moleculen. Voegt men nu polymeren toe aan een oplossing met colloïdale deeltjes (die niet adsorberen aan de colloïden) dan treedt er fasescheiding op, d.w.z. de vloeistof scheidt in een fase rijk aan colloïdale deeltjes en arm in polymeer en vice versa. Het vloeistofoppervlak wat we hier aan treffen heeft een ultralage oppervlaktespanning en mede hierom worden correcties op de oppervlaktespanning belangrijk om de eigenschappen van een dergelijk systeem goed te kunnen begrijpen.

In hoofdstuk 5 bestuderen we de colloid-polymeer mengsels en berekenen middels een gemiddelde veldtheorie de oppervlaktespanning en de buigingsrigiditeit uit. De oppervlaktespanning heeft dezelfde ordegrootte als gevonden in experimenten. De buigingsrigiditeit is experimenteel lastig te bepalen en ook de theoretische route is

²Theorema welke stelt dat de dichtheid in de directe nabijheid van de wand uitgerekend kan worden alsof de vloeistof zich zou gedragen als een gas zonder interacties.

niet eenvoudig. Een schalingsrelatie afgeleid met behulp van square-gradient theorie levert een negatieve rigiditeit, lineair proportioneel met het colloïdale dichtheidsverschil tussen beiden fasen. Een andere route, de zogeheten viriaalroute, levert ook een negatieve rigiditeit op en de resultaten gebruikmakend van deze route levert meer overeenstemming met eerder uitgevoerde computersimulaties.

De wetting eigenschappen van colloid-polymeer mengsels in de context van het model van Nakanishi en Fisher worden beschreven in hoofdstuk 6. De analyse is veelal gelijk aan die in hoofdstuk 6, maar ditmaal maken we gebruik van free volume theory om de eigenschappen van het colloid-polymeer mengsel mee te beschrijven. Dit stelt ons in staat onze bevindingen te vergelijken met de analyse van Aarts en medewerkers aan hetzelfde systeem. We vinden in een van de Nakanishi Fisher modelparameters een term die mist in het werk van Aarts, waardoor het wetting fasediagram er rigoreus anders uit komt te zien. Ten eerste vinden we, als we de grootteverhouding tussen de colloïden en polymeren vergroten een omslag van wetting naar drying³. Tevens vinden we vrijwel alleen maar tweede orde faseovergangen in tegenstelling tot het werk van Aarts, allen dicht in de nabijheid van het kritieke punt. Een numerieke berekening zonder de expliciete aanname die gedaan wordt in het model van Nakanishi en Fisher vertoont geen omslag van wetting naar drying, maar het opvoeren van de grootteverhouding vermindert wel het wetting vermogen van het colloid-polymeer mengsel.

Het laatste hoofdstuk in dit proefschrift beschrijft het grensvlak aangetroffen in zogeheten Pickering emulsies. Vloeistoffen die niet oplosbaar in elkaar zijn (bijvoorbeeld water en olie) kunnen gemengd worden met behulp van emulgatoren, i.e. moleculen met een affiniteit voor beide fasen. Zonder emulgatoren zijn emulsies niet stabiel en ontmengen na verloop van tijd. In een Pickering emulsie wordt het mengsel gestabiliseerd met behulp van colloïdale deeltjes als ijzeroxide, magnetiet en dergelijke in tegenstelling tot moleculen zoals in standaard emulsies. De colloïden adsorberen aan het olieoppervlak en vormen zo een Pickering druppel waarin de oliefase wordt afgeschermd van het water.

In hoofdstuk 7 berekenen we de grootte van Pickering druppels zoals waargenomen in het werk van Sacanna in de context van een model van Ruckenstein oorspronkelijk afgeleid voor microemulsies⁴. We vinden een te hoge ordegraad van de Pickering druppels. De oorzaak hiervan ligt aan de simpliciteit van het model. De reductie van de grensvlakspanning ten gevolge van de adsorptie van colloïdale deeltjes wordt beschreven door Gibbs' adsorptievergelijking. Net als in microemulsies wordt ook hier het olie-water oppervlak gereduceerd door adsorptie van colloïden. Echter, dit effect blijkt in Pickering emulsies niet zo belangrijk als in microemulsies, waardoor gesteld kan worden dat het olie-water oppervlak hier een belangrijke rol blijft spelen.

³een macroscopische laag gas bedekt nu het oppervlak, i.e. het tegenovergestelde van wetting

⁴Een ander type emulsie waarbij de olie-in-water (water-in-olie) druppels doorgaans heel klein zijn.

Curriculum Vitae

The author was born on October 16, 1982 in Roosendaal, the Netherlands. After finishing high school in 2000 at “Titus Brandsmacollege”, Dordrecht, he went on to study Chemistry at the University of Leiden. He obtained his Masters degree in 2005 in the Theoretical Chemistry group of the Leiden Institute of Chemistry. He wrote his master’s thesis entitled “Investigating the Platinum nanowire” under supervision of prof. dr. M.C. van Hemert. In 2005, he started his Ph.D. in the Colloid & Interface Science group in Leiden under supervision of dr. E.M. Blokhuis with whom he already participated in a small research project as part of his Bachelor research. During his Ph.D. the author participated in Ph.D. schools in Han-sur-Lesse (“Han sur-Lesse winterschool”) and Cargèse (“Dynamics of Soft Matter”). The author attended the Complex Fluids meeting in Santa Fe and participated in poster sessions in Bonn (“Jülich Soft Matter meeting”) and at the “Vloeistoffen & Grensvlakken” meeting in Lunteren. The author presented his work orally in his research group and at the “Vloeistoffen & Grensvlakken” meeting in Lunteren.

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Het werk als promovendus in de vakgroep Colloïden & Grensvlakken de afgelopen vier jaar is mij uitstekend bevallen. Het eindeloze geduld, groot inzicht in zaken en de aangename persoonlijkheid van Edgar Blokhuis was een grote inspiratiebron. De derde verdieping van de hoogbouw in het Gorlaeus kenmerkt zich door een gemixte omgeving met uiterst diverse collegae bij wie ik voor alles en nog wat terecht kon. Memorabel zijn de talrijke discussies met themas variërend van het geloof (toen Ahmed er nog was), het goede van een veganistische leefwijze zoals Hana R. Marsden die aanhangt of de kloof tussen links en rechts politiek Nederland. Gelukkig waren er zelfs collegas in de vorm van Frank Versluis en Agur Sevink die bereid waren deze discussies buiten in de regen verder te voeren onder het genot van wat rookwaar!

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Tijdens mijn promotie heb ik volop de kans gekregen om de wetenschappelijke wereld beter te leren kennen door het volgen van verschillende conferenties. Zodoende heb ik veel van de wetenschappers opgenomen in de referentielijst een keer in het echt ontmoet en ben in aanraking gekomen met vele mede promovendi uit zowel binnen- als buitenland. In het bijzonder ben ik dankbaar voor de keren dat ik met Jan Groenewold en Willem Kegel in Utrecht kon samenwerken in het laatste jaar: een samenwerking voortvloeiend uit een geslaagde zomerschool in Corsica.

Buiten de academia ben ik aan het nobele schaakspel begonnen en dit bracht mij bij het Leidsch Schaakgenootschap (LSG). Het is een fijne gewaarwording dat ik hier sinds 2005 periodiek terecht kan om de geest wat noodzakelijke afleiding te verschaffen. Al mijn vrienden in mijn oude stad Dordrecht: bedankt voor de gezelligheid en lijpheid! In het bijzonder een woord van dank richting Coen van der Kamp aan wie ik de omslag te danken heb. Zonder jouw creatieve geest was dit niet gelukt. Hier in Leiden heb ik veel gelachen met Maarten en Erwin en was dat nog vele jaren van plan te doen.

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