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**DENSITY FUNCTIONAL THEORY
OF NUCLEATION AND PHASE BEHAVIOR
IN BINARY FLUID SYSTEMS**

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Academic dissertation

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Preface

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Density functional theory of nucleation and phase behavior in binary fluid systems

Ismo Ilmari Napari

University of Helsinki, 2000

Abstract

Homogeneous nucleation is a fundamental mechanism of phase transformation. The nucleation process involves a formation of tiny regions of new phase in a metastable bulk matter, for example liquid-like droplets in a vapor, via thermal fluctuations. Nucleation phenomena in fluid systems are traditionally described by classical nucleation theory, which assumes that the nucleating fluctuation has the same properties as the new phase in the bulk state. The classical theory leads at its best to approximate results and can be totally erroneous in some cases. In this thesis density functional theory is applied to nucleation in nonideal binary fluid systems, which do not yield easily to the classical approach. In density functional theory the thermodynamic potentials are functions of spatially variable densities of the molecular components. The density functional method in this work is based on a division of the intermolecular potentials into repulsive and attractive parts, the latter of which are treated perturbatively. The model mixtures consist of hard spheres or chains of hard spheres with Lennard-Jones attractions.

Some binary mixtures show limited miscibility in the bulk liquid state. Phase behavior and interfacial structures in these kind of mixtures are investigated using hard sphere systems with reduced pair interaction between dissimilar components. Mutual gas-liquid nucleation of the molecular components is typically hindered in partially miscible mixtures. Similar behavior is also found in the model systems. The bulk liquid-liquid interfaces are characterized by density oscillations and a minimum in the total density.

Amphiphilic mixtures, such as water-*n*-alcohol, show enhanced mutual nucleation, although miscibility gaps are observed in the bulk liquid. This behavior is modelled by representing the alcohol molecules as chains of hard spheres with “hydrophilic” and “hydrophobic” parts. These systems are treated with an interaction site model based density functional method. The model systems also show lamellar ordering in bulk condensed states, which is observed in real mixtures with strong amphiphiles. Related ordering is seen in the structure of large molecular clusters.

This work shows that the perturbative density functional theory is a versatile tool for studying stable and unstable equilibrium states in molecular mixtures. The density functional treatment avoids the pitfalls of phenomenological approaches yet being computationally rather simple. While the results of this thesis are in accord with other theoretical and experimental studies, some predictions of nucleation in amphiphilic systems still wait for experimental confirmation.

Keywords (INSPEC): Nucleation, phase equilibrium, density functional theory.

Classification (INSPEC): A3120J, A6460Q, A6470F, A8260N

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II Ismo Napari and Ari Laaksonen, *Gas-liquid nucleation in partially miscible systems: Free energy surfaces and structures of nuclei from density functional calculations*. Reprinted with permission from J. Chem. Phys. **111** (1999) 5485–5490. Copyright 1999, American Institute of Physics.

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1 Introduction

Phase transitions are omnipresent in nature. The most familiar examples are melting of ice and condensation of water, which are readily observed in everyday life. Examples of phase transitions can be as varied as order-disorder transition in liquid crystals, ferromagnetic-paramagnetic transition in metals, and the transition of helium to a superfluid state at low temperatures. This thesis concerns first order phase transitions in fluid states of matter (gases and liquids), which, apart from their interest as fundamental physical processes, have numerous applications in atmospheric and environmental sciences, and industry [1–4].

The initiation of a phase transition occurs through a localized formation of the new phase in the old phase. Consider, for example, a vapor enclosed in a container. If the vapor pressure inside the container grows, the vapor may reach its saturation pressure, at which it can coexist with a liquid. A further increase in pressure causes the vapor to enter a metastable state, where the molecules start to agglomerate into small liquid-like droplets, which typically contain a few tens or hundreds of molecules. This formation of tiny embryos of the new phase in the old phase is called nucleation. Beyond a critical size a nucleus grows spontaneously. The energy needed to produce such a critical droplet is of major interest in nucleation studies. In practice, solid surfaces and impurities often promote the formation of nuclei. This process is called heterogeneous nucleation. The present thesis concerns homogeneous nucleation, which is caused by thermal fluctuations in the absence of foreign substances.

Although nucleation has been studied since the 18th century [5], reliable theoretical formulation of nucleation phenomena has been surprisingly difficult. The most common approach to nucleation in practical applications has been classical nucleation theory. The basic assumption in the classical theory is that the nucleus has the same thermodynamical properties as the new phase in bulk. For small molecular clusters this is clearly untrue and the sometimes disastrous predictions of the classical theory have been amply demonstrated in the experimental and theoretical work. In this thesis, density functional theory has been applied to nucleation of highly nonideal two-component (binary) fluids, which is not satisfactorily described by the classical theory. The density functional theory treats the system as an inhomogeneous fluid with all the properties arising from molecular interactions. For the present, density functional theory is only applicable to model fluids, but this work shows that nucleation of rather complex systems can be described at a qualitative level if density functional theory is used with the so-called interaction site model.

Two experimental findings have been of seminal importance to the present work. Viisanen *et al.* [6] showed that the mutual nucleation of the molecular components is hindered in vapor mixtures of n -nonane and n -alcohol: higher supersaturations than expected from ideal behavior are needed to produce critical nuclei at a given rate. In another work [7] it was found that water and n -nonane do not conucleate at all, which is understandable because water and hydrocarbons do not mix in the bulk liquid state. Nonane and alcohols do mix macroscopically

at room temperature (apart from nonane and methanol) but the mixing tendency is nevertheless reduced.

A seemingly contradictory observation was made by Strey *et al.* [8]: mutual nucleation is enhanced in water- n -alcohol systems, although nonane and higher alcohols are not fully miscible in the bulk. This can be resolved if one looks deeper in the molecular interactions. An alcohol molecule has a hydroxyl head, which is attracted to the water molecules, and a hydrocarbon tail, which is not soluble in water. This difference in the interactions causes a surface orientation of the alcohol molecules in the nuclei and, consequently, the observed enhancement of nucleation.

Molecules with a water-liking (hydrophilic) and a water-repellent (hydrophobic) part are called amphiphiles. It has been long known that strong amphiphiles tend to form structures in the bulk condensed states. For example, bilayers of amphiphilic lipid molecules are major constituents of biological membranes [9]. An amphiphile added to water or to a water-oil mixture can cause a formation of spherical or cylindrical structures or even a complicated network of tubes and handles [10]. Although various theoretical methods have been used to investigate phase equilibria in amphiphilic systems, the relationship between a given set of molecular interaction parameters and an observed phase behavior remains poorly understood.

The purpose of this thesis is twofold. The foremost aim is to apply density functional theory to partially immiscible model systems and compare the results with the experimental works of water- n -nonane, n -nonane- n -alcohol, and water- n -alcohol mixtures. On the other hand, the same theoretical method is applied to study the properties of bulk phases and their interfaces, which are then related to the nucleation behavior of the model systems. The calculations are extended to encompass strong amphiphiles in order to shed some light on systems showing structured phases.

This thesis is organized as follows: In section 2 a phenomenological description of phase equilibrium and metastable states is given. Phase behavior of partially miscible mixtures and amphiphilic systems is explored in some detail. A description of gas-liquid nucleation is provided in the context of classical nucleation theory. In section 3 several theories of inhomogeneous fluids are reviewed. A detailed account of the density functional theory used in this thesis is given. The molecular models and their application to the density functional formalism are presented. The original research papers are reviewed in section 4. Conclusions are given in section 5. The original papers are appended at the end.

2 Phase behavior of fluids

2.1 Stable and metastable states

Under suitable conditions, two or more phases can coexist in a stable thermal equilibrium [11]. The equilibrium conditions require that the coexisting phases must have a common pressure

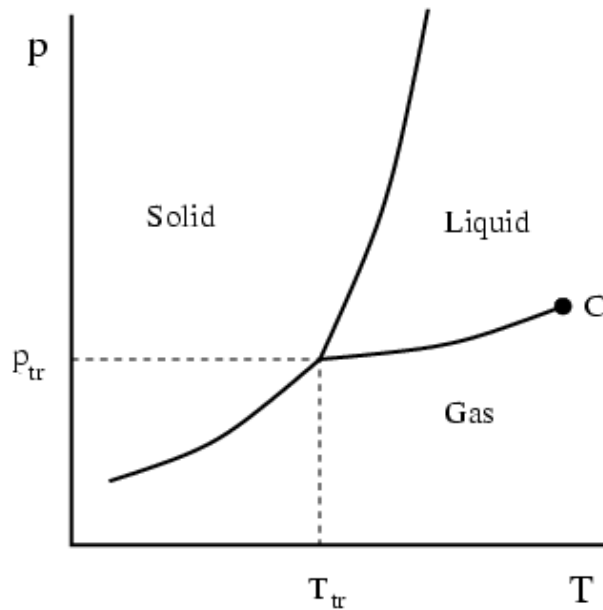


Figure 1: Coexistence lines of gas, liquid, and solid phases of a one-component system. Triple point is indicated by p_{tr} and T_{tr} . Gas-liquid critical point is denoted by C.

p and temperature T . Furthermore, the chemical potential μ must have the same value in all parts of the system. Because chemical potential is a function of both pressure and temperature, the last requirement implies that for a one-component (unary) system a unique coexistence line can be drawn in the p - T plane as shown in Fig. 1. At a certain point three phases have common values of p , T , and μ , which is the definition of the triple point.

In addition to pressure and temperature, a system consisting of C different particle species is defined by $C - 1$ mole fractions x_i of the components. Not all of these variables are independent at coexistence. The number of independent variables or the number of thermodynamic degrees of freedom f is given by the Gibbs phase rule

$$f = C - P + 2, \quad (1)$$

where P is the number of coexisting phases. For example, gas-liquid equilibrium ($P = 2$) in a binary system ($C = 2$) has $f = 2$; thus, the coexistence is defined by a surface in the p - T - x space.

A system in a stable equilibrium is in a state of maximum entropy. However, when the system is moved away from coexistence, it can still be stable with respect to small fluctuations, which means that the system corresponds to a local maximum of entropy. Such states are called metastable. Metastable states are peculiar to the first order phase transitions. Transformations from one phase to another can be classified into different orders according to the lowest order of the derivatives of the Gibbs free energy which are discontinuous in the transition. The chemical potential $\mu = \partial G / \partial N$ is always continuous, but the other derivatives, entropy $S = \partial G / \partial T$ and volume $V = \partial G / \partial p$, are discontinuous in a first order transition. In a second order transition S

and V are continuous, but their derivatives are not. This work only considers phase transitions of the first order.

Stable and metastable states in unary fluid systems can be understood by considering the isothermal pressure p and free energy F as a function of volume V as shown schematically in Figs. 2(a) and 2(b), respectively. The points A and E have equal pressures and a common tangent $(\partial F/\partial V)_{T,N} = -p$. The tangent intersects the vertical axis at $F = G$ ($V = 0$) and, since $G = \mu N$, points A and E have a common chemical potential. This means that the fluids at A and E are in equilibrium in accord with the conditions stated above. They define the binodal line of vapor-liquid coexistence as shown in Fig. 2(c).

Phase stability in a one-component system requires that the system is stable with respect to density fluctuations. The stability condition is then written as

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{1}{V\kappa_T} > 0, \quad (2)$$

where κ_T is the isothermal compressibility. Away from stable equilibrium, condition (2) holds on the branches AB and ED, which in fluid systems correspond to metastable superheated liquid and supercooled vapor, respectively. The stability condition is first violated when the isothermal compressibility diverges, which means that the pressure has a stationary point and the free energy an inflection point. This occurs on the spinodal, which is indicated by B and D in Fig. 2. In the region between B and D the system is unstable with respect to infinitesimal fluctuations. The relaxation from an unstable state to a stable state is called spinodal decomposition.

Binary systems exhibit metastability with respect to the gas-liquid transition in a similar manner as unary systems. However, one must also consider stability with respect to concentration fluctuations in the liquid state, in which case the relevant stability condition at a constant temperature and pressure is

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p} > 0. \quad (3)$$

When condition (3) is violated one speaks of diffusional or material instability. This kind of instability is observed in mixtures showing limited miscibility in the bulk liquid state.

The preceding discussion on metastable phase equilibria relies on the assumption that the equation of state (pressure) can be continued from the one-phase region to the two-phase region between A and E. Although this assumption lacks a firm statistical mechanical basis [3], there is evidence from perturbation theory [13] and computer simulations [14] that such a constrained one-phase fluid indeed exists under metastable and even unstable conditions.

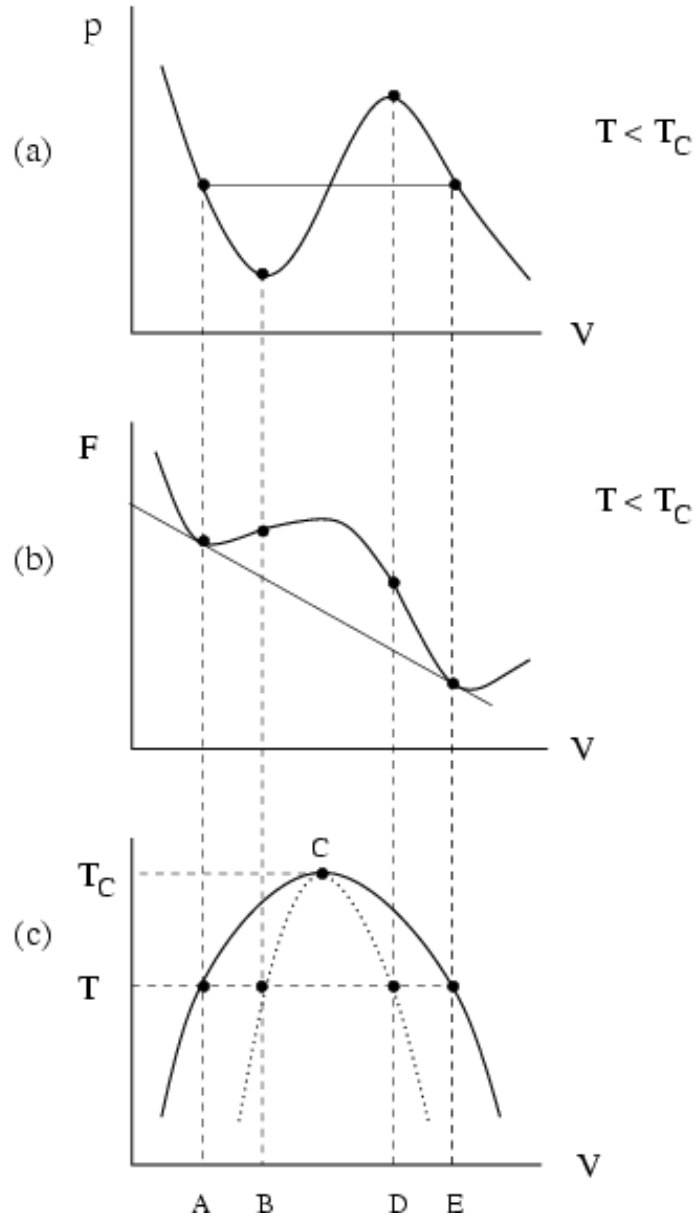


Figure 2: (a) Pressure p and (b) free energy F as function of volume V of a one-component system below the critical temperature T_C . (c) Phase diagram with the critical point at C. A and E indicate the equilibrium liquid and vapor, respectively. B and D are the limits of stability (spinodal). Coexistence (binodal) is shown as a full line in the phase diagram and spinodal with a dotted line. Adapted from Ref. 12.

2.2 Liquid-liquid immiscibility in binary mixtures

Binary fluid systems exhibit far more diverse phase behavior than unary fluids, which typically only show coexistence between vapor and liquid. The phase diagrams can also have more complex shapes because of the additional degree of freedom. Regardless of the apparent complexity, a rather reliable description of phase behavior of binary systems can be obtained from van der Waals-type “one-fluid” equations of state if the molecules have approximately isotropic interaction potentials. An extensive classification of the equilibrium behavior of binary van der Waals mixtures can be found in an article by van Konynenburg and Scott [15]. However, recent studies have shown that even simple models can yield new and surprising results [16–18].

A typical feature absent from unary systems is the coexistence between two demixed liquids. The attractive interaction between dissimilar molecular components in a binary system is usually weaker than the attraction between similar components. Sometimes the mutual dislike prevents the components from mixing in all proportions: the system has a miscibility gap in the composition space. The two liquid mixtures at these limiting compositions are in a stable equilibrium with each other.

Phase diagrams depicting liquid-liquid equilibrium can be created by plotting the miscibility gap as a function of temperature or pressure. The two principal types of phase diagrams are shown in Fig. 3. In the simplest case the phase diagram resembles an inverted parabola (Fig. 3(a)). The immiscible region ends at an upper critical solution temperature (UCST), above which the liquid is fully miscible. The widening of the gap with decreasing temperature results from the interplay of energy and entropy [19]. In equilibrium, the system minimizes its free energy $F = U - TS$, where U is internal energy, S is entropy, and T is temperature. At low temperatures the entropic term has little effect and minimizing free energy is practically the same as minimizing internal energy, which is related to the interaction energies between the particles. At high temperatures the entropic term dominates and the liquid becomes miscible.

Figure 3(b) shows another kind of liquid-liquid phase diagram, which is a closed loop with an UCST and a lower critical solution temperature (LCST). The preceding discussion also applies to the upper part of this diagram, but it does not explain the disappearance of the miscibility gap at low temperatures. The closed-loop behavior is usually related to strong associating forces, which typically are hydrogen bonds in real liquids. Hydrogen bonds depend on the orientation of the molecules and break easily at high temperatures. At low temperatures the hydrogen bonds are stable over appreciable time scales, which results in lowering of energy and entropy of the system. However, the energetic contribution has a greater effect than the entropic contribution and, thus, mixing is favored.

In contrast to unary systems, a binary mixture at three-phase coexistence still has one degree of freedom. This makes it possible to plot a line of triple points in x - T or x - p plane. In **paper I** vapor-liquid-liquid triple lines are presented for partially miscible Lennard-Jones fluids.

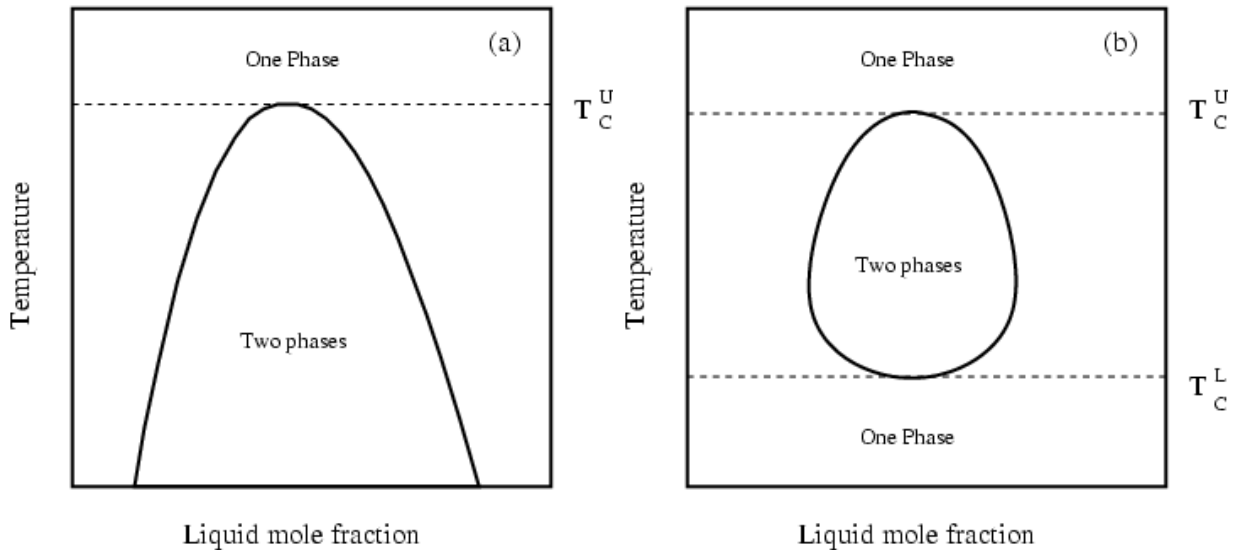


Figure 3: Typical liquid-liquid phase diagrams of binary fluid mixtures. (a) A phase diagram with an upper critical solution temperature (UCST) at T_C^U . (b) A closed loop phase diagram with an UCST and a lower critical solution temperature (LCST) at T_C^L . Above UCST and below LCST the liquid is fully miscible.

2.3 Amphiphilic systems

Interesting phase behavior can be observed in binary mixtures containing an amphiphilic component [10, 20]. In the context of aqueous solutions, an amphiphile is a molecule which has a water soluble hydrophilic head and a water insoluble hydrophobic tail. Because of the hydrophobic part, amphiphiles are not very soluble in water. As a result, amphiphiles tend to concentrate on surfaces, which leads to reduction of surface tension. Amphiphiles with this property are called surfactants. In the absence of surfaces or when the surface becomes saturated, the hydrophobic tails induce microscopic phase separation, which is the reason for the self-assembling properties of amphiphilic systems.

In water-rich solutions, amphiphiles form spherical aggregates called micelles, in which the hydrophilic heads lie on the surface and the hydrophobic tails point towards the center. The hydrophobic parts of the amphiphilic molecule are thus shielded from unfavorable interactions with water molecules. Vesicles are another kind of spherical aggregates, which consist of a surfactant bilayer that separates a pocket from the surrounding fluid. With increasing amphiphile concentration a variety of so-called modulated phases are observed. The amphiphiles in these phases are arranged into hexagonally packed cylinders (Fig. 4(a)) or into stacked bilayers with the water molecules dispersed between the hydrophilic heads (Fig. 4(b)). In some systems, bilayers of amphiphiles divide the water into distinct regions, which is called the sponge phase. At high amphiphile concentrations the inverse hexagonal phase and inverse micelles, where the roles of the head and tail of the amphiphile are reversed, can be found.

Simple equations of state are not adequate to describe phase equilibria in amphiphilic mixtures, because the density distributions exhibit local variations even in the bulk state. Previous

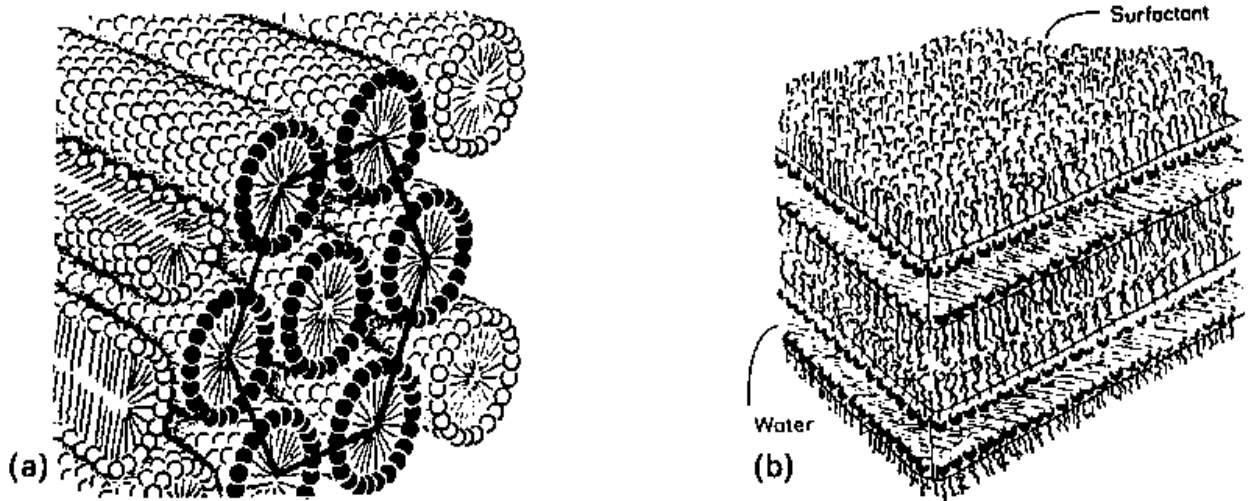


Figure 4: A schematic representation of (a) hexagonal and (b) lamellar phases (from Ref. 10).

theoretical models of amphiphilic systems have been based mostly on lattice, Ginzburg-Landau and membrane theories [10], although density functional theory has been applied to describe membranes, vesicles, and micelles in binary systems [21] and micelles and lamellar phases in ternary systems [22]. In these studies the molecules were composed of spherical components. In **paper IV** isotropic liquid–lamellar liquid–vapor triple lines in binary mixtures with non-spherical amphiphiles are determined using density functional theory and interaction site model. The same theoretical approach is applied in **papers III** and **V** to investigate gas-liquid nucleation in amphiphilic systems.

2.4 Nucleation

While a system in the metastable region is stable with respect to small fluctuations, bigger fluctuations will inevitably lead to phase separation. Determining the properties of the critical fluctuation just on the brink of growing and shrinking is the main objective of nucleation research. In fluid systems the critical fluctuation is a tiny liquid droplet in a supersaturated vapor (gas-liquid nucleation), a bubble of gas surrounded by metastable liquid (bubble nucleation or cavitation), or a liquid droplet in a liquid of another composition (liquid-liquid nucleation). The following discussion on the phenomenology of nucleation pertains mostly to gas-liquid nucleation, but it can be extended to the other cases as well.

Experimentally, a supersaturated vapor state is achieved by heating a liquid pool (thermal diffusion cloud chamber), adiabatically cooling a vapor by fast expansion (expansion chamber), or mixing two or more gas flows (mixing chamber) [1,2,23–25]. Several variants of these methods exist. The measurable quantity obtained from experiments is the nucleation rate

$$J = K \exp\left(-\frac{\Delta\Omega^*}{k_B T}\right), \quad (4)$$

where $\Delta\Omega^*$ is the formation energy of the critical nucleus and K is a kinetic prefactor. In theoretical studies it is often convenient to consider the formation energy directly, because it can in principle be obtained from equilibrium thermodynamics without any need for kinetic treatment of nucleation.

Phenomenological description of nucleation is usually based on the time-honoured classical nucleation theory (see e. g. Ref. 5). The work of nucleus formation can be thought to consist of the energy needed to produce an interface between the old and the new phase and the energy gained from the transfer of a unit volume of the system to the new phase. The total formation energy of the critical nucleus is written as

$$\Delta\Omega^* = n^* \Delta\mu + A^* \gamma, \quad (5)$$

where n^* is the total number of molecules in the nucleus, A^* is the area of the nucleus, and γ is the surface tension of the planar vapor-liquid interface. The difference in chemical potential between liquid and vapor phases is given at the ideal gas limit by

$$\Delta\mu = -k_B T \ln \frac{p}{p_e}, \quad (6)$$

where p and p_e are the pressures of the supersaturated and saturated vapor, respectively. Assuming spherical and incompressible nucleus, the radius of the droplet R^* is obtained from the Kelvin equation

$$\Delta\mu + \frac{2\gamma v}{R^*} = 0, \quad (7)$$

where v is the molecular volume. Equations (5)–(7) can readily be extended to binary or multicomponent systems [26, 27].

The classical description rests on the so-called capillarity approximation, which states that the nucleus has the same properties as the new phase in bulk and that the interfacial tension of the curved interface is the same as that of the planar interface. Obviously, these assumptions do not hold for small critical nuclei. The predictions of the classical theory are fairly accurate in gas-liquid nucleation of nonpolar substances [5], but in polar vapors [28] and especially in bubble nucleation [29, 30] the classical theory fails badly. This partial success of the classical theory is somewhat coincidental [31]. The curvature dependence of surface tension is omitted, which decreases the work of formation. On the other hand, the nucleation barrier does not vanish at spinodal, as it should, which increases the nucleation work. These two factors cancel each other at some (often experimental) range of temperatures. It has been demonstrated that if the range of the attractive potential were slightly larger, the classical theory would be in gross error [29].

For nonideal binary mixtures the classical theory can give results which are not only er-

roneous but also unphysical [32–34]. For instance, the classical theory is unable to predict the composition of the nucleus in water-alcohol systems, because the nucleus exhibits a strong surface segregation. The calculated formation energy can then increase with increasing vapor-phase activity (or chemical potential), which contradicts the nucleation theorem [35, 36]

$$\left(\frac{\partial\Delta\Omega^*}{\partial\mu_i}\right)_{T,\mu_j} = -\Delta n_i^*, \quad (8)$$

where μ_i is the chemical potential of component i in the surrounding phase and Δn_i^* is the excess number of molecules of i in the critical nucleus. Even worse, the interfacial tension is not available at all liquid compositions for partially miscible mixtures (such as water and higher alcohols), which seriously hampers the usefulness of the classical theory.

The failure of classical nucleation theory (and several revisions, which are reviewed in Ref. 2) has been an incentive to studies based on microscopic approaches. In principle, Monte Carlo and molecular dynamics simulations should provide optimal tools for studying nucleation in systems with complex interactions. However, computer simulations are limited by the rarity of the nucleation events and the small volume of the simulation box. To date, only a few simulations of binary nucleation in fluid systems have been performed [37–40].

During the last decade, the statistical mechanical density functional theory has become increasingly popular in binary nucleation studies [32, 33, 41–43]. In density functional theory the microscopic degrees of freedom of the system are reduced to density distributions. In essence then, the system is considered as an inhomogeneous fluid with the density distributions depending on spatial coordinates. This ensures that the structure of the interface is properly taken into account. Also, no assumptions are made of the properties of the critical nucleus, which eliminates the need to refer to the bulk values of the new phase in nucleation calculations. Unfortunately, quantitatively correct results for real molecules are not obtained from the density functional method as yet, because the molecular models must be kept rather simple for computational reasons.

3 Density functional theory

3.1 Theories of inhomogeneous fluids

Many of the liquid-state theories based on distribution or correlation functions can be applied to study phase behavior and interfacial properties of fluids [44–47]. The most famous of these is the Born-Green-Yvon (BGY) equation [44],

$$\nabla_1 \ln \rho_i(\mathbf{r}_1) = \frac{1}{k_B T} \sum_j \int d\mathbf{r}_2 \rho_j(\mathbf{r}_2) g_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \nabla_2 \phi_{ij}(\mathbf{r}_1, \mathbf{r}_2), \quad (9)$$

which is the first member of the BGY hierarchy of equations. In Eq. (9) ρ_i is the one-particle density distribution of the molecular component i , $g_{ij}^{(2)}$ is the pair distribution function, and ϕ_{ij} is the pair potential between the molecular species i and j .

Another integral equation which has been applied to liquid-vapor and liquid-liquid interfaces in binary systems [48] is the Lovett-Mou-Buff-Wertheim (LMBW) equation [49, 50],

$$\nabla_1 \ln \rho_i(\mathbf{r}_1) = \sum_j \int d\mathbf{r}_2 c_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \nabla_2 \rho_j(\mathbf{r}_2), \quad (10)$$

where $c_{ij}^{(2)}$ is the direct correlation function. The pair distribution and correlation functions are themselves functions of the density distributions and hence they must be first calculated for the homogeneous fluid and then approximated somehow at interfaces. While possible for bulk fluid-fluid interfaces, this method is cumbersome in nucleation calculations, because the densities at the center of nucleus are not known in advance.

An alternative description of inhomogeneous fluids is based on approximate free energy functionals [12, 44, 45, 47, 51]. The fundamental fact behind this approach is that the free energy functional $F[\rho_i]$ is uniquely determined by the density distributions and it corresponds to the free energy in the usual thermodynamic sense if the densities are replaced by the equilibrium densities [51]. The free energy functional thus has a central role when calculating thermodynamic properties of the system such as grand potential, pressure, interfacial tension, etc.

The earliest form of approximate free energy functionals originates from the classic work of van der Waals [52], although it is better known from the more modern exposition of Cahn and Hilliard [53]. Van der Waals postulated that the free energy density $f = F/V$ can be divided into two parts: the free energy density of the homogeneous fluid f_u and a free energy cost from the spatial variations of the density. The second term is proportional to the square of the density gradient $(\nabla\rho)^2$. For mixtures the free energy density is written as [47]

$$f = f_u + \frac{1}{2} \sum_{i,j} K_{ij} \nabla \rho_i(\mathbf{r}) \nabla \rho_j(\mathbf{r}), \quad (11)$$

where the coefficients K_{ij} can be related to the interaction energies of the particles.

Density gradient expansions are realistic only in situations where the densities are slowly varying, e. g. close to spinodal. On the other hand, a density functional theory based on a perturbative expansion of the intermolecular pair potentials is capable of describing steeply varying densities. This kind of perturbation theory has been the principal tool in the nucleation studies of inhomogeneous fluids since it was applied to nucleation in Yukawa fluids by Oxtoby and Evans [29]. The perturbation approximation has been used in the present thesis to study nucleation as well as planar fluid-fluid interfaces in simple and complex binary fluid mixtures.

3.2 Perturbation approximation

Intermolecular potentials can usually be divided into steeply repulsive and smoothly varying attractive parts. The idea behind the perturbation approaches of classical fluids is the observation that the repulsive potential is mainly responsible for the structure of the fluid and the attractive potential holds the fluid at a specified density [44]. The intermolecular potential is then written as a sum of a repulsive or “reference” part to which an attractive perturbation is added.

Consider a multicomponent mixture in which the pairwise additive intermolecular potentials are decomposed as

$$\phi_{ij} = \phi_{ij}^R + \lambda\phi_{ij}^A. \quad (12)$$

Here ϕ_{ij}^R is the reference potential, ϕ_{ij}^A is the attractive potential, and λ is a small coupling parameter. Varying λ from 0 to 1 gradually switches on the perturbation. It can be shown that the Helmholtz free energy of this system is exactly [47]

$$F = F^R + F^A, \quad (13)$$

where F^R is the free energy of the reference system and

$$F^A = \frac{1}{2} \sum_{i,j} \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}' \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') g_{ij}^{(2)}(\mathbf{r}, \mathbf{r}', \lambda) \phi_{ij}^A(|\mathbf{r} - \mathbf{r}'|) \quad (14)$$

is the free energy contribution from the attractive interactions. In Eq. (14) $\rho_i(\mathbf{r})$ is the one-particle density distribution of the component i and $g_{ij}^{(2)}(\mathbf{r}, \mathbf{r}', \lambda)$ are the pair distribution functions of the perturbed system.

In homogeneous fluids, approximations exist for the pair distribution function, and they can be extended to inhomogeneous systems [47]. However, if the attractive potential is long ranged compared to the interparticle separations, $g_{ij}^{(2)}$ can be set to unity [44]. This so-called van der Waals approximation has been made in this thesis.

The free energy of the reference system can be written as

$$F^R = F^I + F^E, \quad (15)$$

where F^I is the ideal gas part

$$F^I = k_B T \sum_i \int d\mathbf{r} \rho_i(\mathbf{r}) \ln \rho_i(\mathbf{r}) \quad (16)$$

and F^E is the excess free energy arising from the interactions between particles in the reference

system, which in this work is a mixture of hard spheres. The excess free energy is obtained from the Carnahan-Starling formulas [54], although other expressions could be used as well [47].

The excess free energy in fluid systems is often assumed to depend only on the local densities of the hard spheres. However, close to dense boundaries, such as hard walls, the liquid phase is highly structured, which requires a nonlocal treatment of the reference system. In the weighted density approximation (WDA) of Tarazona [55, 56], the excess free energy is given by

$$F^E = k_B T \int d\mathbf{r} \Psi[\bar{\rho}_i(\mathbf{r})] \rho_s(\mathbf{r}), \quad (17)$$

where $\rho_s(\mathbf{r}) = \sum_i \rho_i(\mathbf{r})$ is the total density and Ψ is the excess free energy per molecule. The weighted densities $\bar{\rho}_i$ are given by

$$\bar{\rho}_i(\mathbf{r}) = \int d\mathbf{r}' w_i(|\mathbf{r} - \mathbf{r}'|) \rho_i(\mathbf{r}') \quad (18)$$

with a weighting function

$$w_i(r) = \left(\frac{3}{\pi d_i^4} \right) (d_i - r) \Theta(d_i - r), \quad (19)$$

where d_i is the hard sphere diameter of the component i and Θ is the Heaviside step function. More general forms of excess free energy functionals and weighting functions are reviewed in Ref. 47. If the weighting function is chosen to be the Dirac delta function, Eq. (17) reduces to the free energy in the local density approximation (LDA). Subtle differences in the structure of liquid-liquid interfaces are found between LDA and WDA in **paper I**.

The equilibrium density distributions are those which minimize the grand potential functional [51]

$$\Omega = F - \sum_i \mu_i \int d\mathbf{r} \rho_i(\mathbf{r}). \quad (20)$$

Thus, the equilibrium densities are found by setting

$$\frac{\delta \Omega}{\delta \rho_i(\mathbf{r})} = 0 \quad (21)$$

and solving the resulting Euler-Lagrange equations. Iterative method of solution is used in this work. For planar interfaces the iteration necessarily converges to a stable solution. The density profiles of the critical nucleus are somewhat harder to obtain, because the critical nucleus is in an unstable equilibrium with the surrounding medium. In **paper I** the equations are solved in canonical ensemble, which ensures convergence for a system with a fixed number of particles [57]. Solutions in grand canonical system (fixed chemical potentials) are obtained in **papers II-V** using the method presented in **paper II**.

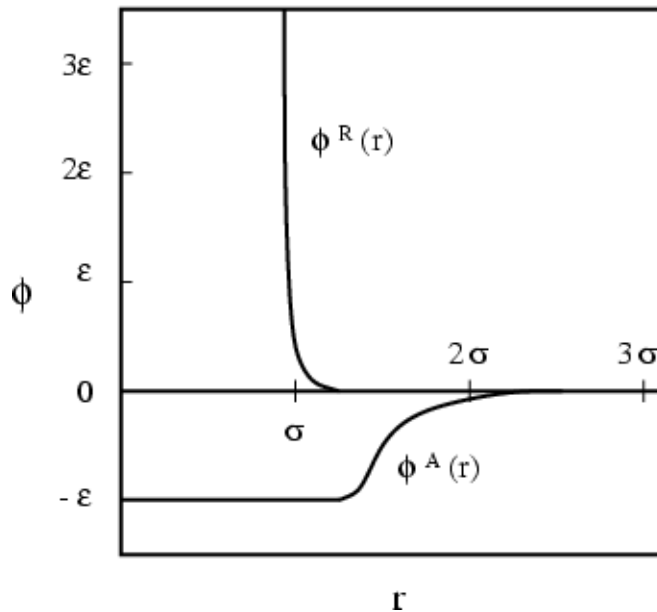


Figure 5: WCA separation of the intermolecular LJ pair potential into a repulsive part $\phi^R(r)$ and an attractive part $\phi^A(r)$. Redrawn from Ref. 59.

3.3 Lennard-Jones system

The success of the perturbation approach relies on the assumption that the perturbation potential is slowly varying in space. Although other possibilities exist [58], in this thesis the perturbative part is considered to be given by the attractive tail of the Lennard-Jones (LJ) potential,

$$\phi_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right], \quad (22)$$

where ϵ_{ij} are the energy and σ_{ij} the length parameters between molecule species i and j , respectively. The division into the repulsive and attractive parts is somewhat arbitrary. In this work the separation of Weeks, Chandler, and Andersen (WCA) [59] has been used, which for a LJ fluid is written as (see Fig. 5)

$$\phi^R(r) = \begin{cases} \phi(r) - \phi(r_m) & \text{if } r < r_m, \\ 0 & \text{if } r \geq r_m, \end{cases} \quad (23)$$

$$\phi^A(r) = \begin{cases} \phi(r_m) & \text{if } r < r_m, \\ \phi(r) & \text{if } r \geq r_m, \end{cases} \quad (24)$$

where $r_m = 2^{1/6}\sigma$ is the location of the minimum of the LJ potential. The properties of the reference system in this separation are not well known; therefore, the reference system is replaced by a system of hard spheres. Reasonable agreement with computer simulations is obtained if the hard sphere diameter d is chosen properly [58, 59].

The length and energy parameters in Eq. (22) are defined by

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) + \Delta_{ij}, \quad (25)$$

$$\epsilon_{ij} = (1 - k_{ij})\sqrt{\epsilon_{ii}\epsilon_{jj}}, \quad (26)$$

where Δ_{ij} and k_{ij} are mixing parameters. If $\Delta_{ij} = k_{ij} = 0$, the familiar Lorentz and Berthelot rules are obtained. If $\Delta_{ij} = 0$, the mixture is said to be additive, otherwise it is non-additive. This work only considers additive mixtures.

The choice of parameters k_{ij} is crucial in regard to the mixtures in this thesis. Values $k_{ij} > 0$ reduce the attractive interaction between unlike molecular species, while values $k_{ij} < 0$ enhance it. If the factor $1 - k_{ij}$ is small enough, the system exhibits partial immiscibility in the bulk liquid state.

3.4 Interaction site model

The molecular model described in the preceding section suffers from an obvious shortcoming. Although many of the phenomena observed in partially immiscible mixtures have been successfully modeled using systems consisting of spherical molecules, the real molecules in these systems usually are highly non-spherical, e.g. long hydrocarbon chains. The inadequacy of the simple LJ model is especially felt in amphiphilic mixtures, where the strength and nature of the interaction depends on the position and orientation of the water molecule with respect to the chain molecule.

An ingenious way to model complex molecules in the context of density functional theory was introduced by Chandler *et al.* [60,61]. The theory is based on the interaction site formalism, in which the molecules are made up of smaller units with intramolecular constraints set between these so-called interaction sites. The free energy of a system consisting of n interaction sites is written in the local density approximation as [60–62]

$$F = F^I + F^E + F^B + F^A, \quad (27)$$

where the free energy contributions are

$$F^I = k_B T \sum_{i=1}^n \int d\mathbf{r} \rho_i(\mathbf{r}) \ln f_i(\mathbf{r}), \quad (28)$$

$$F^E = k_B T \int d\mathbf{r} \Psi[\rho_i(\mathbf{r})]\rho_s(\mathbf{r}), \quad (29)$$

$$F^B = -k_B T \int \dots \int \left[\prod_{i=1}^n d\mathbf{r}_i f_i(\mathbf{r}_i) \right] s^{(n)}(\{\mathbf{r}_{i+1} - \mathbf{r}_i\}), \quad (30)$$

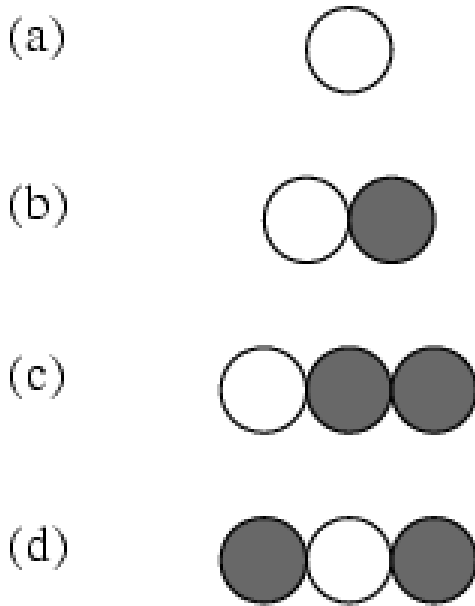


Figure 6: The model molecules. (a) A monomer. (b) A dimer. (c) A trimer with the “monophilic” site (enhanced mutual attraction with monomers) at the end position. (d) A trimer with the “monophilic” site at the mid position. The “monophobic” sites (reduced mutual attraction with monomers) are depicted as grey spheres.

$$F^A = \frac{1}{2} \sum_{i,j=1}^n \int \int d\mathbf{r} d\mathbf{r}' \phi_{ij}^A(|\mathbf{r} - \mathbf{r}'|) \rho_i(\mathbf{r}) \rho_j(\mathbf{r}'). \quad (31)$$

Following the notation of the previous section, F^I is the ideal gas part, F^E is the contribution from the reference system, and F^A arises from the perturbation potential. Equation (27) differs, however, from the free energy functional (13) in two respects. First, it is not only a functional of the site densities ρ_i but also of the “site activities” [63] f_i (for non-bonded components $f_i = \rho_i$). Hence, the corresponding grand potential functional is minimized with respect to both ρ_i and f_i . Secondly, the decrease in entropy due to the bonding between the interaction sites is taken into account by the free energy term F^B , where $s^{(n)}$ is an intramolecular correlation function. The bonded molecules in this thesis are hard sphere dumbbells (dimers) or rigid chains of three hard spheres (trimers) as depicted in Fig. 6. Then, the correlation function is the Dirac delta function or a product of two delta functions.

The excess free energy per molecule Ψ is calculated from the Carnahan-Starling formulas for isolated hard spheres [54]. More accurate equations of state designed for non-spherical bodies [64,65] could be used to allow for the excluded volume effects introduced by the bonded molecules. However, these considerations do not have any qualitative effect on the interfacial properties [62] or nucleation [63].

The principal asset of the interaction site model is in its relative simplicity. Minimizing the grand potential functional leads to a system of Euler-Lagrange equations, which are solved in a similar manner as in the case of non-bonded hard spheres. Although the exact orientational profiles are not obtained from this theory, the orientations are still implicitly present in the

density distributions.

Previously, interaction site model based density functional theory has been used to investigate behavior of polyatomic molecules near hard walls [66] and in slit-like pores [67], surface tension of molecular fluids [68], thin surfactant films at liquid-vapor interfaces [62], orientational ordering of diblock copolymers [69], and nucleation of hard-sphere dumbbells [63] and chains [70]. Very recently, a similar monomer-dimer model as in this work was used in an interaction site study of nucleation in micellar solutions [71]. **Paper IV** of this thesis concerns with the formation of lamellar phases in monomer-dimer mixtures. In **papers III** and **V** an examination of gas-liquid nucleation in amphiphilic monomer-dimer and monomer-trimer systems is presented.

4 Review of the papers

Paper I is a study of interfacial phenomena in partially miscible binary mixtures consisting of identical Lennard-Jones components with spherical hard cores. Vapor-liquid and liquid-liquid phase diagrams are presented for two systems with different degree of miscibility. The weighted density approximation (WDA) and the local density approximation (LDA) are compared. The WDA is capable of showing density oscillations at interfaces at low temperatures. The LDA yields higher interfacial tensions than the WDA, but the difference is small. In liquid-liquid nucleation the LDA gives somewhat higher nucleation barriers with a notable difference only for large clusters.

Paper II investigates gas-liquid nucleation in partially miscible Lennard-Jones systems. Mixtures with symmetric and asymmetric interaction parameters are compared. Nucleation in these systems is hindered compared to an idealized mixture. Both systems have a region in the activity space where two kinds critical nuclei form with unequal formation energies. An earlier method of finding the formation energy of a noncritical cluster is extended to binary systems, which is then used to construct a free-energy surface around a critical cluster. The method is further applied to prove that the layered droplets found in the asymmetric system are not critical clusters. Elongated nuclei with a phase-separated structure has been observed in some earlier studies. In this paper, an argument based on classical nucleation theory suggests the noncriticality of these clusters.

Paper III explores gas-liquid nucleation in an amphiphilic system using density functional theory with the interaction site model. The mixture is composed of single hard spheres (monomers) and two tangential hard spheres (dimers). One end of the dimer is strongly attracted to monomers, while the attraction between the other end and monomers is greatly reduced. Although the combined attractive energy of the dimer molecule is somewhat reduced from the Berthelot mixing rule, nucleation is enhanced in this system. The enhancement is shown to result from the surface activity and orientation of the dimers. The layered nuclei

found in this system are proven to be critical clusters.

Paper IV is a study of lamellar phases in monomer-dimer systems. A complete phase diagram is calculated for the system studied in **paper III** showing vapor–isotropic liquid–lamellar liquid triple lines in the mole fraction–temperature plane. The lamellar phase ends at two tricritical points. Various choices for the energy parameters are investigated. The calculated density profiles show that the thickness of the dimer bilayer in the lamellae is almost constant at different parts of the phase diagram; hence, the mole fraction in the lamellar phase is primarily determined by the concentration of the monomers.

Paper V presents a thorough investigation of gas-liquid nucleation in monomer-dimer and monomer-trimer systems with reduced mutual interaction and with equal-sized hard sphere sites and rigid bonds. Systems with and without an amphiphilic component are compared. Enhanced mutual nucleation is only observed in mixtures with asymmetric amphiphiles. In systems with non-amphiphilic components or with symmetric amphiphiles no orientational ordering in the critical nuclei is seen. A monomer-trimer system resembles closely the observed behavior of water- n -alcohol mixtures. Layered clusters are also detected in this system. The transition from ordinary to layered nuclei is indicated by a discontinuity in the formation energy or in its derivative with respect to mean activity.

5 Conclusions

This thesis is a contribution to the understanding of phase behavior, interfacial properties, and nucleation in binary fluid mixtures starting from molecular-level interactions. Particular emphasis is given to gas-liquid nucleation in mixtures showing limited miscibility in the bulk liquid state. The fluids are modelled using attracting hard spheres as molecules or as building blocks of more complex molecules. The systems are treated perturbatively in the framework of density functional theory.

Fluids consisting of hard-core Lennard-Jones molecules with isotropic interactions are used to study planar interfaces in partially miscible systems. The interfacial structures are found similar to those in other theoretical studies. Gas-liquid nucleation in these systems is shown to qualitatively resemble water- n -nonane and n -nonane- n -alcohol mixtures. However, this model is incapable of explaining the observed enhancement of mutual nucleation in water- n -alcohol mixtures. The enhanced nucleation is successfully modelled using the interaction site model.

In addition to gas-liquid nucleation, this thesis shows that the interaction site model can be used to study, for example, lamellar phases in strongly amphiphilic systems. The model amphiphiles are very simple: molecules consisting of two or three hard spheres. Even so, the available interaction parameter space is extensive, and only a few systems are investigated in this work. Quite possibly, studies of molecules with different energy parameters and unequal hard

sphere diameters will reveal phenomena not reported earlier. This, along with investigations of more complex molecules, is left for future work.

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