Systems involving surfactants

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Abstract. Computer simulations of amphiphilic systems are reviewed. Research areas cover a wide range of length and time scales, and a whole hierarchy of models and methods has been developed to address them all. They range from atomistically realistic models, idealized chain models, lattice spin models, to phenomenological models such as Ginzburg-Landau models and random interface models. Selected applications are discussed in order to illustrate the use of the models and the insights they can offer.

Keywords: amphiphilic systems; modeling; Computer simulations; phase behavior of amphiphiles; micelles; vesicles; interfaces; lipid bilayers; Langmuir monolayers.

I. Introduction

Surfactants can be defined very generally as substances which influence the properties of interfaces and surfaces, and which can be used to tune them. Since most materials contain a certain amount of internal interfaces, the study of such substances has attracted longstanding interest. In this chapter, we shall be concerned with a particularly efficient class of surfactants, the amphiphiles. These are molecules which contain both hydrophilic and hydrophobic units (usually one or several hydrocarbon chains), such that they “love” and “hate” water at the same
time. Familiar examples are lipids or alcohols. The effect of amphiphiles on interfacial surfaces between water and nonpolar phases can be quite dramatic. For example, tiny additions of good amphiphiles reduce the interfacial tension by several orders of magnitude. Amphiphiles are thus very efficient to promote the dispersion of organic fluids in water and vice versa. Added in larger amounts, they associate into a variety of structures, filling the material with internal interfaces, which shield the oil molecules – or in the absence of oil the hydrophobic parts of the amphiphiles – from the water. Some of the possible structures are depicted in Fig. 1. A very rich phase behavior emerges, including isotropic, but mesoscopically structured micellar and bicontinuous phases, and several ordered anisotropic phases (Fig. 2). Due to their emulsifying and self-organizing qualities, amphiphilic molecules are widely used in technology (salad dressing, detergents, soaps, oil recovery, as coating materials to stabilize colloidal systems, as nanoreactors for the preparation of nanoparticles,...) as well as by nature (milk, biological membranes, liposomes,...).

Schematic phase diagrams for binary mixtures of water with a strong amphiphile, and for ternary mixtures containing oil, water, and amphiphile, are shown in Fig. 3 (adapted from Refs. [7, 8]). Among the many interesting features of these phase diagrams, we mention in particular the existence of phases which are macroscopically isotropic and homogeneous, but structured on a mesoscopic scale. The short range order can be inferred from the form of the structure functions (obtained, e.g., by small angle neutron scattering). In the case of microemulsions, the best indicator for structure is the water-water structure function. It can be fitted very well by the expression

\[ S(q) \propto (a + gq^2 + cq^4)^{-1} \]  

(1)

For strongly structured microemulsions, \( g \) is negative, and the structure functions show a peak at nonzero wavevector \( q \). As long as \( g < 2\sqrt{ca} \), inverse Fourier transform of \( S(q) \) still reveals that the water-water correlation functions oscillate rather than
decay monotonically. The lines in phase space where this oscillating behavior sets in are usually referred to as “disorder lines”, and those where the maximum of $S(q)$ moves away from zero as “Lifshitz lines”.

Another phase which has attracted recent interest is the gyroid phase, a bicontinuous ordered phase with cubic symmetry (space group Ia3d, cf. Fig. 2 (d)[10]. It consists of two interwoven, but unconnected bicontinuous networks. The amphiphile sheets have a mean curvature which is close to constant and intermediate between that of the usually neighboring lamellar and hexagonal phases. The gyroid phase has first been identified in lipid/water mixtures[11], and has been found in many related systems since then, among other in copolymer blends[12].

In a somewhat wider sense, one can define amphiphiles as molecules in which chemically very different units are linked together. For example, the structures formed by A:B block copolymers in demixed A and/or B homopolymer melts and their phase behavior is very similar to that of classical amphiphiles in water and/or oil[13, 14]. Copolymers are used to disperse immiscible homopolymer phases in one another, but also to create new, mesoscopically structured materials with unusual and interesting properties[15].

Another interesting class of phase transitions are internal transitions within amphiphilic monolayers or bilayers. In particular, monolayers of amphiphiles at the air/water interface (Langmuir monolayers) have been intensively studied in the past as experimentally fairly accessible model systems[16, 17]. A schematic phase diagram for long chain fatty acids, alcohols, or lipids is shown in Fig. 4. On increasing the area per molecule, one observes two distinct coexistence regions between fluid phases: A transition from a highly diluted, “gas”like phase into a more condensed, “liquid expanded” phase, and a second transition into an even denser “liquid condensed” region. The latter splits into a number of distinct phases, which differ in their tilt order, positional order and orientational order of the backbones of
the (CH$_2$)$_n$ chains. In bilayers, the liquid expanded/liquid condensed transition translates into the “main transition” or the “liquid/gel” transition, where the bilayer thickness, the amphiphile mobility, and the conformational order of the chains, jump discontinuously as a function of the temperature[18]. On the ordered gel side various different phases exist, among them tilted phases and wavy phases (ripple phases). Bilayer phases are of special interest from a biological point of view, since the structure of biological membranes is coupled to the membrane functions[18].

This rich scenario and the wide range of applications of amphiphiles is reflected by an equally wide range of problems which have been addressed in studies of amphiphilic systems. In particular, the interest has focused on the following rather different classes of topics:

- The influence of amphiphiles on interfacial properties: Interfacial tension, wetting behavior, dynamical aspects such as the question how small amounts of surfactant influence the kinetics of phase separation.

- The reasons for self-assembly and the mechanisms: Necessary conditions for the aggregation into micelles, mono- or bilayers, structure of aggregates, distribution of aggregation numbers etc.

- Mesoscopic structures and phases: vesicles and vesicle shapes, structured phases and phase behavior of amphiphilic systems.

- The inner structure of monolayers and bilayers, the liquid/gel transition, tilt transitions, mixed layers etc.

A wide range of length scales and time scales is involved in these different problems, and a unified treatment of amphiphilic systems is practically impossible. On the smallest scales (up to $\leq$ 100 Å and 10-100 ns[19]), molecular dynamics simulations in atomic detail are feasible[20, 21]. They provide information on the microscopic structure and the short-time dynamics of specific systems and have the big
advantage that they allow for a direct, quantitative comparison with experiments. On the other hand, they rely heavily on the quality of the force fields. The choice of the model is the most important and the most critical step in an atomistic simulation. Other limitations come from the short accessible time scales. Phases must usually be preassembled since the times for self-assembly are very large. Hence it is difficult to decide whether a given structure is metastable or really corresponds to a true free energy minimum. Mapping out a phase diagram by a systematic variation of parameters (temperature, pressure) is generally out of reach. However, the force fields are improving, the computer technology is developing, and realistic simulations of amphiphilic systems can be pushed further and further. A large number of studies has dealt with the local properties of micelles, monolayers, and particularly of lipid bilayers. This is a rapidly growing field of research, and enormous progress has been achieved in the last few years. A brief overview over some of the activities shall be given in section 1.

Nevertheless, large scale phenomena and complicated phase diagrams cannot be investigated within realistic models at the moment, and this is not very likely to change soon. Therefore, theorists have often resorted to coarse-grained models, which capture the features of the substances believed to be essential for the properties of interest. Such models can provide qualitative and semiquantitative insight into the physics of these materials, and hopefully establish general relationships between microscopic and thermodynamic quantities.

What are the essential features of surfactant systems? An important ingredient is obviously the repulsion between water and nonpolar molecules or molecule parts, the hydrophobic force. This interaction is however highly nontrivial, and its analysis is still an active field of research[4, 22, 23]. Qualitatively, it is usually attributed to the strong orientational and positional correlations between nonpolar molecules in solution and the surrounding water molecules. The origin of the interaction is
therefore entropic: Free water forms a network of hydrogen bonds. In the neighborhood of a nonpolar solute, the water molecules reorient and replace themselves so as to maintain the highest possible number of hydrogen bonds. The associated loss of entropy accounts for the dominant contribution to the hydrophobic interaction. This effect is of course far too involved to be easily included in a simplified model for amphiphilic systems. On the other hand, we have already noted that many characteristicas of amphiphilic systems are also found in homopolymer/copolymer mixtures, where the interactions can be of very different nature. Hence the precise origin of the interactions does not seem to be important for the phenomenology, and they can conceivably be replaced by simpler potentials for most purposes.

The second important attribute of amphiphiles is their affinity to both water and oil. This aspect is retained in the microscopic models, which will be discussed in sections III and IV. Oil, water and surfactant molecules are represented by simplified pseudoparticles.

In some of these models (see section III), the surfactants are still treated as flexible chains[24]. This allows one to study the role of the chain length and chain conformations. For example, the chain degrees of freedom are responsible for the internal phase transitions in monolayers and bilayers, in particular the liquid/gel transition. The chain length and chain architecture determines the efficiency of an amphiphile and thus influences the phase behavior. Moreover, it affects the shapes and size distributions of micelles. Chain models are usually fairly universal, in the sense that they can be used to study many different phenomena.

Models of a second type (section IV) restrict themselves to a few very basic ingredients, e.g., the repulsion between oil and water and the orientation of the amphiphiles. They are less versatile than chain models and have to be specified in view of the particular problem one has in mind. On the other hand, they allow for an efficient study of structures on intermediate length and time scales, while
still establishing a connection with microscopic properties of the materials. Hence, they bridge between the microscopic approaches and the more phenomenological treatments which will be described below. Various microscopic models of this type have been constructed and used to study phase transitions in the bulk of amphiphilic systems, internal phase transitions in monolayers and bilayers, interfacial properties, and dynamical aspects such as the kinetics of phase separation between water and oil at the presence of amphiphiles.

Finally, when it comes to large scale structures and long time dynamics, it often proves useful to drop the notion of particles altogether and to resort to phenomenological models (see section V.). Here again, one can distinguish between two main lines of approaches. Ginzburg-Landau theories characterize the system by smooth “order parameters”, which stand for local, coarse-grained averages of microscopic quantities. The coarse graining length is usually not specified, but thought to be of the order of the bulk correlation length, i.e., a few molecular diameters. The order parameter fields are then distributed according to a free energy functional, which is typically constructed from symmetry considerations as an expansion in powers of the order parameter. Generic behavior is obtained as a function of the coefficients in the expansion. Unfortunately, the relation between the model parameters and the “real” parameters such as the pressure and the temperature is usually not obvious. On the other hand, Ginzburg-Landau theories have the advantage that they require relatively little input, which can in part be taken from experiments (e.g., from scattering experiments). Like the simple microscopic models, they have been applied to the study of phase behavior, interfaces, and the phase separation kinetics in amphiphilic mixtures. We will very briefly sketch the approach in section V.A. and refer to chapter 11 for a more detailed discussion.

The other class of phenomenological approaches subsumes the random surface theories (section V.B). These reduce the system to a set of internal surfaces, sup-
posedly filled with amphiphiles, which can be described by an effective interface Hamiltonian. The internal surfaces represent either bilayers or monolayers – bilayers in binary amphiphile-water mixtures, and monolayers in ternary mixtures, where the monolayers are assumed to separate oil domains from water domains. Random surface theories have been formulated on lattices and in the continuum. In the latter case, they are an interesting application of the membrane theories, which are studied in many areas of physics, from general statistical field theory to elementary particle physics[26]. Random surface theories for amphiphilic systems have been used to calculate shapes and distributions of vesicles, and phase transitions[27, 28, 29, 30, 31].

We close these introductory remarks with a few comments on the methods which are actually used to study these models. They shall for the most part only be mentioned very briefly. In the rest of this chapter, we will focus mainly on computer simulations. Even those shall not be explained in detail, for the simple reason that the models are too different and the simulation methods too many. Rather, we refer the reader to the available textbooks on simulation methods, e.g., Ref. [32, 33, 34, 35], and discuss only a few technical aspects here. In the case of atomistically realistic models, simulations are indeed the only possible way to approach these systems. Idealized microscopic models have usually been explored extensively by mean field methods. Even those can become quite involved for complex models, especially for chain models. One particularly popular and successful method to deal with chain molecules has been the self-consistent field theory. In a nutshell, it treats chains as random walks in a positional dependent chemical potential, which depends in turn on the conformational distributions of the chains in some self-consistent way. A recent survey of the method can be found in Ref. [36]. Self-consistent field approaches provide extremely good descriptions of polymer blends (for which they have been developed originally), since macromolecules have many contacts with other molecules and therefore show mean-field type behavior almost everywhere.
in phase space. In the case of short chain surfactants in low molecular weight solvents, the quantitative predictions are not quite as satisfactory. In particular, the stability of self-assembled aggregates can be overestimated by several orders of magnitude\cite{37}. However, the local structure in the aggregates, local density profiles etc., are still in reasonable agreement with Monte Carlo simulations\cite{37, 40}. Self-consistent field theories have been used to study micelles\cite{37, 38}, bilayers\cite{38, 39, 40} and monolayers\cite{41, 42, 43}. More details on the technique are given in chapter 9 of this book.

The first step to study phenomenological theories (Ginzburg-Landau theories and membrane theories) has usually been to minimize the free energy functional of the model. Fluctuations are then included at a later stage, e.g., using Monte Carlo simulations. The latter shall be discussed in section V and in chapter 11.

II. Simulations in atomic detail

Even among the so-called realistic simulations, there are still very different levels of coarse-graining. A full quantum chemical and ab-initio treatment of a system as complex as amphiphilic systems is practically impossible. Hence they are usually studied by classical molecular dynamics in combination with empirical interaction potentials, which have been optimized by fitting them to experimental data (structural data, latent heat of first order transitions etc.) and/or to ab-initio data (substructures of molecules). The functional form of these potentials may have little or nothing to do with the underlying physics of the interactions. For example, the forces between atoms of different chains are usually taken to be pairwise additive, even if the underlying interactions are nonadditive dispersion forces\cite{4}. One has thus some freedom in the choice of the potentials, and many different forms are available. Hydrogen atoms are sometimes not included explicitly, but adsorbed into the more “important” neighbor atoms (united atom models vs. full atomic detail). Bond an-
gles and bond lengths are sometimes constrained to take fixed values (constrained models vs. fully flexible models). Complicated head groups are sometimes replaced by simpler structures. The models also differ in the way charges and partial charges are treated. Some models do not include electrostatic interactions at all, \textit{i.e.}, they have no $1/r$ terms in the potentials. Others do, but truncate them at a certain distance, and still others deal with them in full by Ewald summation methods\cite{44}. Whether or not interactions are truncated obviously makes a difference\cite{43}. One could hope that the long range character of the interactions is not essential for the physics of amphiphilic systems, in which case one empirical potential is as promising as the other, as long as they all have been optimized independently. Note that long range interactions are ignored in most of the more idealized treatments of amphiphilic systems. On the other hand, a careful treatment of the electrostatic interactions is crucial to reproduce the peculiarities of water, such as the dielectric properties\cite{46}.

After these introductory \textit{caveats}, we review some of the work that has been done in realistic simulations of amphiphilic systems.

Perhaps the first simulation of a system with amphiphiles is due to Kox in 1980\cite{47}, a model of a lipid monolayer. A number of simulations of monolayers at air/substrate interfaces have followed\cite{48, 49, 50, 51, 52, 53, 54, 55, 56, 57}, which have been able to reproduce cooperative tilt effects of the hydrocarbon chains and tilt transitions as well as backbone ordering and different rotator phases\cite{50, 55}. Moreover, they have provided valuable insight on the density profiles and the distribution of defects in the chains\cite{53, 55}. The simulations are usually done at constant volume. In one case, the Gibbs ensemble is used to study the phase coexistence between the “gas” phase and the “liquid expanded” phase\cite{56} (In the Gibbs ensemble, two boxes are simulated in parallel, and particles can be exchanged between the boxes\cite{57}. The two boxes are thus at pressure and chemical potential equilib-
rium: Coexisting phases can be monitored in systems which contain no disturbing interfaces.) In most of the models, the amphiphiles are supported by a uniform continuum substrate, which could be water or any other polarizable material, on the hydrophilic side, and in contact with vacuum (“air”) on the hydrophobic side. The work of Alper et al. [49] focuses on the influence of an amphiphilic layer on a water substrate, therefore the water is treated explicitly. A few recent studies have also probed amphiphiles at oil/water interfaces [58, 59, 60] with explicit oil molecules; much work clearly remains to be done here. Rice and coworkers have investigated special systems, such as monolayers of fluorinated amphiphiles [61] and monolayers on Cs [62] and ice [63].

Bilayers have received even more attention. In the early studies, water has been replaced by a continuous medium like in the monolayer simulations [64, 67, 66]. Today’s bilayers are usually “fully hydrated”, i.e., water is included explicitly. Simulations have been done at constant volume [68, 69, 70, 71, 72, 73] and at constant pressure or fixed surface tension [74, 75, 76, 77, 78, 79]. In the latter case, the size of the simulation box automatically adjusts itself as to optimize the area per molecule of the amphiphiles in the bilayer [33]. If the pressure tensor is chosen isotropic, bilayers with zero surface tension are obtained. Constant (positive) surface tension can be enforced by choosing an anisotropic pressure tensor, which is smaller in the directions parallel to the bilayer [75, 77, 78]. A comparison of different simulation methods, different ensembles, different water models, and different hydrocarbon models, has been made recently by Tielemann and Berendsen [78].

Whereas the main challenge for the first bilayer simulations has been to obtain stable bilayers with properties (e.g., densities) which compare well with experiments, more and more complex problems can be tackled nowadays. For example, lipid bilayers were set up and compared in different phases (the fluid, the gel, the ripple phase) [76, 77, 80, 81]. The formation of large pores and the structure of
water in these water channels has been studied\cite{80, 81}, and the forces acting on lipids which are pulled out of a membrane have been measured\cite{82}. The bilayer systems themselves are also becoming more complex. Bilayers made of complicated amphiphiles such as unsaturated lipids have been considered\cite{83, 84}. The effect of adding cholesterol has been investigated\cite{85, 86}. An increasing number of studies are concerned with the important complex of lipid/protein interactions\cite{87, 88, 89} and, in particular, with the structure of ion channels\cite{90, 91, 92}.

The third class of systems which have been investigated relatively extensively by simulations in atomic detail are micelles. Again, the first studies have ignored the water molecules and simply considered the conformations of amphiphiles which are confined into a shell of given spherical geometry\cite{93, 94}. Later studies focus on the stability of (preassembled) micelles in water, on the structure and mobility of the amphiphiles, and on the degree of water penetration into the hydrophilic shell and the hydrophobic core\cite{73, 95, 96, 97, 98, 99}. Reverse micelles have also been considered, as well in vacuum as in an explicit oil environment\cite{100, 101}. Simulations of more complex self-assembled structures are still in their infancy. Watanabe and Klein have investigated cylindrical hexagonal phases using simulation cells with appropriate boundary conditions\cite{102}. The structure of the cylinders turns out to be comparable to that of spherical micelles in many respect (water penetration, conformational properties etc.). More recently, Kong et al\cite{103} have employed a simplified amphiphile model (ethoxy head group chains attached to a hydrocarbon continuum) to study the water-induced interactions between lamellae in a lamellar phase. They conclude that water restructuring plays an important part in stabilizing the lamellar phase.
III. Idealized chain models

In coarse grained microscopic models, the amphiphiles, oil and water molecules are still treated as individual particles, but their structure is very much simplified. Molecular details are largely lost. For reasons of computational efficiency, coarse grained models are often formulated on a lattice. This obviously introduces the danger of lattice artefacts; as we shall see, lattice models have nevertheless been used successfully in the study of various phenomena and turn out to be extremely powerful. Off-lattice models are computationally more costly, but do not impose an a priori anisotropy on space, and are attracting growing interest.

III.A. Lattice models

The most complex and powerful coarse grained models are those which retain the chain character of the amphiphile molecules.

In a class of “realistic” lattice models, hydrocarbon chains are placed on a diamond lattice in order to imitate the zigzag structure of the carbon backbones and the trans and gauche bonds. Such models have been used early on to study micelle structures[104], monolayers[103], and bilayers[100]. Levine and coworkers have introduced an even more sophisticated model, which allows to consider unsaturated C=C bonds and stiffer molecules such as cholesterol: A monomer occupies several lattice sites on a cubic lattice, the saturated bonds between monomers are taken from a given set of allowed bonds with length $\sqrt{5}$, and torsional potentials are introduced to distinguish between “trans” and “gauche” conformations[107, 108].

Most lattice models however abstract from the details of the hydrocarbon chain structure. The “monomers” of the model chains are then conceived as effective monomers, which represent several (CH$_2$) (or other) units in the molecules. One particularly popular lattice model has been introduced by Larson et al[24, 109]: In this model, oil and water molecules occupy single sites of a cubic lattice, and am-
phiphiles are chains made of “tail” monomers $T$ and “head” monomers $H$, which are identical to the oil and water particles, respectively. The amphiphile monomers are connected by bonds with one of the 26 nearest or diagonally nearest neighbors. Since the lattice is entirely filled with either oil, water, or amphiphile, one only has one independent (dimensionless) interaction parameter $w/k_BT$, the relative repulsion between oil and water particles or tail and head monomers. The interaction range is chosen such that particles interact with their nearest neighbors and diagonally nearest neighbors, i.e., the coordination number is again 26. The phase behavior of the model is solely controlled by the architecture of the amphiphile. It has been studied for a number of systems by Larson himself and others\[109, 110, 111, 112, 113\] and turns out to be amazingly multifarious. Perhaps the most spectacular achievement of the model is that it seems to exhibit a gyroid phase\[112\] (cf. Fig. 2 (d)). In a narrow concentration region, and if the size of the simulation box matches closely the preferred spacing of the gyroid unit cell, the amphiphiles self-assemble spontaneously into a gyroid upon cooling. This may not be conclusive evidence that the gyroid is actually the phase with the lowest free energy in an infinitely extended system, but it nevertheless demonstrates impressively the power of simple lattice models. Some phase diagrams\[112\] for binary water/amphiphile systems are shown in Fig. 3. Their topology resembles that of experimental phase diagrams, i.e., the gyroid phase intrudes between the hexagonal phase and the lamellar phase, as an intermediate between a state where the amphiphilic sheets have high local curvature (the hexagonal phase), and one without local curvature (the lamellar phase).

The Larson model and Larson-type models have been widely used to study micelles\[111, 114, 115, 116, 117, 118\], amphiphiles at oil/water interfaces\[121, 122, 118\], bilayers\[117, 123\] and various other problems\[124, 125, 126, 127, 128\]. The models differ from each other in the range of the interactions and in the treatment of the amphiphile monomers. Other than in Larson’s original model, most authors
include only nearest neighbor interactions, sometimes in combination with a different underlying lattice \cite{120}. Some models stay with Larson’s simplifying assumption that the amphiphile monomers are identical to oil or water particles \cite{37, 119, 120}, but most of them equip the amphiphiles with new types of particles, often even allowing for more than two different monomer species. A popular description going back to Stauffer and coworkers \cite{114} and to Bernardes and coworkers \cite{113, 123} adopts the language of the Ising model and assigns a spin $S = -1$ to oil particles, a spin $S = +1$ to water particles, and an integer spin ranging between -1 and +2 to surfactant monomers. The interaction energy is described by a Hamiltonian $\mathcal{H} = -\epsilon \sum_{<ij>} S_i S_j$, where the sum $<ij>$ runs over nearest neighbor sites on the lattice. Bernardes has demonstrated, that amphiphile with the architecture $(+1, 0, -1, -1, -1, -1)$ or $(-1, -1, -1, -1, 0, 1, 1, 0, -1, -1, -1)$ (two-tailed amphiphiles) can spontaneously self-assemble into vesicles \cite{125, 126}. A snapshot of such a vesicle is shown in Fig. 6.

A particularly simple lattice model has been utilized by Harris and Rice \cite{129} and subsequently by Stettin et al \cite{130} to simulate Langmuir monolayers at the air/water interface: Chains on a cubic lattice which are confined to a plane at one end. Haas et al have used the bond-fluctuation model, a more sophisticated chain model which is common in polymer simulations, to study the same system \cite{131}. Amphiphiles are modeled as short chains of monomers, which occupy a cube of eight sites on a cubic lattice, and are connected by bonds of variable length \cite{132}. At high surface coverage, Haas et al report various lattice artefacts. They conclude that the study of dense surfactant monolayers calls for the use of off-lattice models, especially if one is interested in phenomena such as collective tilt etc. Nevertheless, the bond-fluctuation model can be a useful tool in other contexts. For example, Müller and Schick \cite{133} have employed it to study the formation and the structure of pores in amphiphilic bilayers. From the bilayer undulations, they were able to extract the
bilayer tension, and from the distribution of pore sizes, they could deduce the line tension of the pore edges. Fig. 7 shows an example of a pore. It is found to be “hydrophilic”, i.e., the amphiphiles around the pore rearrange themselves so as to shield the bilayer core from the unfavorable solvent.

Last in this section on lattice chain models, let us cite the somewhat different approach of Jennings et al. [134], who model the amphiphiles as single site particles on a lattice, but surround them with long hydrophobic chains (of chain length up to $N = 80$). Their study focusses on the influence of amphiphiles on the conformations of nonpolar polymers. They report phenomena such as amphiphile induced polymer collapse and the stabilization of lamellar phases.

Lattice models have the advantage that a number of very clever Monte Carlo moves have been developed for lattice polymers, which do not always carry over to continuum models very easily. For example, Nelson et al use an algorithm which attempts to move vacancies rather than monomers [120], and thus allows to simulate the dense cores of micelles very efficiently. This concept cannot be applied to off-lattice models in a straightforward way. On the other hand, a number of problems cannot be treated adequately on a lattice, especially those related to molecular orientations and nematic order. For this reason, chain models in continuous space are attracting growing interest.

### III.B. Chain models in continuous space

The usual structure of off-lattice chain models is reminiscent of the Larson models: The water and oil particles are represented by spheres (beads), and the amphiphiles by chains of spheres which are joined together by harmonic springs

$$U_{ij}^b = k_b/2 \left(|\vec{r}_i - \vec{r}_j| - b\right)^2. \quad (2)$$

Here a hard or smooth cutoff $b^c$ is sometimes imposed, such that

$$U_{ij}^b = \infty \quad \text{for} \quad b - b^c < |\vec{r}_i - \vec{r}_j| < b + b^c,$$
in order to ensure that the beads cannot move arbitrarily far apart from each other. Spheres of type $i$ and $j$ often interact via truncated and shifted Lennard-Jones potentials

$$U_{ij}^{LJ}(r) = \begin{cases} 4\epsilon_{ij} \left[ (\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6} \right] + C_{ij} & r < R_{ij}^c \\ 0 & \text{otherwise} \end{cases}$$

where $C_{ij}$ is chosen such that $U_{ij}^{LJ}(r)$ is continuous everywhere. In most cases the interaction parameter $\epsilon_{ij}$ is chosen species-independent, $\epsilon_{ij} \equiv \epsilon$, and the “sign” of the interaction is controlled by the cutoff length $R_{ij}^c$: Purely repulsive interactions between hydrophilic and hydrophobic units are obtained by choosing $R_{ij}^c = 2^{1/6}\sigma_{ij}$. For the attractive interactions, $R_{ij}^c = 2.5\sigma$ (most common) or $2\sigma$ is often used. In addition, a bending potential is sometimes introduced which favors chain stretching and makes the chains stiffer. A model of this kind has first been introduced by Smit et al[135] and later employed to explore the interplay of micelle formation and amphiphile adsorption at an oil/water interface[136, 137], the self-assembly of micelles in general[138, 139, 140, 141], and that of bilayers[141]. In the case of binary systems, the model can be further simplified by ignoring the solvent particles. Even then, one can still observe and study self-assembling micelles very well[142, 143, 144].

The different surfactant models vary mostly in details. Karaborni et al[139] explore the influence of different chain architectures on the micelle shapes. Inserting spacers between hydrophobic tails in a double tailed amphiphile turns out to transform former spherical micelles into threadlike micelles. (A similar result was observed by Maiti and Chowdhury in the Larson model[118].) Götz and Lipowsky[141] replace the repulsive interactions between hydrophilic and hydrophobic beads by the softer potential $U = 4\epsilon(\sigma/r)^9$ and introduce spontaneous tilt angles in the bending potential in some of their simulations. Harries et al[140] and von Gottberg et al[142] connect the beads by rigid rods, i.e., choose an infinitely large spring constant $k_b$. Bhatthacharya et al[143] compare nonionic surfactants with ionic surfactants and model the latter by including an additional Yukawa-type electrostatic interaction.
$U(r) \propto \exp(-\kappa/r)$ between the head groups. Perhaps not surprisingly, the charged micelles show a much stronger ordering tendency than the neutral micelles.

A few groups replace the Lennard-Jones interactions by interaction of a different form, mostly ones with a much shorter interaction range [144, 145, 146]. Since most of the computation time in an off-lattice simulation is usually spent on the evaluation of interaction energies, such a measure can speed up the algorithm considerably. For example, Viduna et al use a potential, in which the interaction range can be tuned,

$$U^M(r) = E_{ij}\left[e^{-2\alpha(r-\sigma)} - 2e^{-\alpha(r-\sigma)}\right] - C \quad \text{for } r < R_c$$

(Morse potential). The constant $C$ is defined such that $U^M(r) = 0$ at the cutoff distance $R_c$. The interaction range is determined by the parameter $\alpha$, which Viduna et al choose very large, $\alpha = 24$. Hence the cutoff distance can be made small ($R_c = 1.25\sigma$ in [144]). This model has first been used by Gerroff et al [147] and is discussed in some detail in chapter 9 of this book.

Bead spring models without explicit solvent have also been used to simulate bilayers [40, 145, 146] and Langmuir monolayers [148, 149, 150, 151, 152]. The amphiphiles are then forced into sheets by tethering the head groups to two dimensional surfaces, either via a harmonic potential, or via a rigid constraint.

Baumgärtner and coworkers [145, 146] study lipid-protein interactions in lipid bilayers. The lipids are modeled as chains of hard spheres with heads tethered to two virtual surfaces, representing the two sides of the bilayer. Within this model, Baumgärtner [147] has investigated the influence of membrane curvature on the conformations of a long embedded chain (a “protein”). He predicts that the protein spontaneously localizes on the inner side of the membrane, due to the larger fluctuations of lipid density there. Sintes and Baumgärtner [149] have calculated the lipid-mediated interactions between cylindrical inclusions (“proteins”). Apart from the usual depletion interaction at contact, they find that the lipids induce a net attractive force between the inclusions over the much wider range of $\sigma < r < 6\sigma$, ...
where \( \sigma \) is the diameter of a lipid bead.

Simulations of monolayers have focused on internal phase transitions, \emph{e.g.}, between the expanded phase and the condensed phases, between different tilted phases etc. These phenomena cannot be reproduced by models with purely repulsive interactions. Therefore, Haas \textit{et al} \cite{148, 149} represent the amphiphiles as stiff Lennard-Jones chains, with one end (the head bead) confined to move in a plane. In later versions of the model \cite{150, 151, 152}, the head bead interactions differ from those of the tail beads: They are taken to be purely repulsive, and the head size is variable.

Stadler \textit{et al} have performed Monte Carlo simulations at constant pressure of this model, and calculated the phase behavior for various different head sizes. It turns out to be amazingly rich. The phase diagram for chain length \( N = 7 \) and heads of size \( 1.2\sigma \) (\( \sigma \) being the diameter of the tail beads) is shown in Fig. 8. A disordered expanded phase is found as well as several condensed phases with different tilt order – a phase without collective tilt, one with tilt towards nearest neighbors, and one with tilt towards next nearest neighbors. Particularly unexpected is a phase with a superstructure (LC-mod), where the direction of tilt is modulated and points on average towards an intermediate between nearest neighbors and next nearest neighbors. The heads in the condensed phases are arranged on a hexagonal lattice, which is distorted in the direction of tilt. In order to avoid shear stress in the system, it is thus crucial to let fluctuate not only the size of the simulation box, but also its shape. Moreover, huge hysteresis effects were observed at some of the phase boundaries, and the free energies of the competing phases had to be calculated by thermodynamic integration methods \cite{35} in order to locate the phase boundaries. Configuration snapshots of the expanded phase and the modulated condensed phase are shown in Fig. 9.

The modulated phase disappears for head sizes smaller than \( 1.14\sigma \). Modulations of this kind have not been observed in experiments so far. However, Stadler \textit{et al}
argue that the intensity of the satellite peaks which would be indicative of the superstructure is so low, that they could not possibly be detected in X-ray measurements with the usual experimental resolution. Phases with intermediate tilt directions have been reported\cite{16,17}.

To complete this overview over chain models, we mention the dimer models, which represent the amphiphiles by just two units attached to each other\cite{153,154,155,156,157}. They have been used to study curved bilayers\cite{153}, the kinetics of phase separation between oil and water at the presence of surfactants\cite{153}, and some aspects about self-assembled micelles\cite{154,157} (see below).

III.C. An application: Micelle shapes and size distributions

As has probably become obvious already, the study of micelles has been one of the big topics in simulations of systems with surfactants. We have cited many of the related publications in the previous sections. Here, we shall discuss some special aspects of micelle simulations in order to illustrate the use of idealized chain models for this type of problem.

The first important step in a micelle simulation obviously consists in defining a “micelle”. In simulations of systems with short range interactions, this can be done in a relatively straightforward way: Molecules are said to form an aggregate if they are in contact with each other, \textit{i.e.}, if they interact. After having set this straight, one can proceed to measure the concentration of \textit{free}, \textit{i.e.}, noninteracting surfactants as a function of the total surfactant concentration. In self-assembling systems, it saturates very soon after a first regime of linear increase, and stays constant or even decreases slightly\cite{142} thereafter. Similarly, the chemical potential of the surfactant as a function of the surfactant concentration exhibits a marked kink, and turns from initial increase almost into a constant\cite{154,119}. The concentration at which this happens is called the critical micelle concentration (CMC). The sharp changes at the CMC can be understood from the competition between the translational entropy
of the free surfactants and the energy, which their hydrophobic tails gain in the
micelles due to the reduced number of unfavorable water contacts. Let us consider
surfactants which are part of an aggregate with the aggregation number \( N \), and
neglect the interactions between aggregates. Since the aggregates are at equilibrium
with each other, the chemical potential at temperature \( T \) can be written as \[ \mu = \mu_0^N + k_B T/N \ln (f_N X_N/N) \] for all \( N \), where \( \mu_0^N \) denotes the mean interaction free energy in the aggregate, and
the second term describes its translational entropy. Here \( X_N \) is the volume fraction
of amphiphiles in an aggregate of size \( N \), and the activity coefficient \( f_N \) is of order
one. From eqn. (5) one concludes immediately
\[ f_N X_N = N \left[ f_1 X_1 e^{(\mu_1^0 - \mu_0^N)/k_B T} \right]^N. \]
Note that \( \mu_1^0 > \mu_0^N \), since the surfactants gain energy in the aggregates. Large
aggregates can therefore be expected to dominate at surfactant concentrations larger
than
\[ (X_1)_{CMC} \approx e^{(\mu_1^0 - \mu_1^0)/k_B T}. \]
Beyond the CMC, surfactants which are added to the solution thus form micelles,
which are at equilibrium with the free surfactants. This explains why \( X_1 \) and \( \mu \) level
off at that concentration. Note that even though it is called “critical”, the CMC
is not related to a phase transition. Therefore, it is not defined unambiguously. In
the simulations, some authors identify it with the concentration where more than
half of the surfactants are assembled into aggregates\[14\]; others determine the
intersection point of linear fits to the low concentration and the high concentration
regime, either plotting the free surfactant concentration vs. the total surfactant
concentration \( \Phi \)\[13\], or plotting the surfactant chemical potential vs. ln(\( \Phi \))\[19\].

We turn to the discussion of micelle size distributions and micelle shapes. In
order to proceed with the analysis, one needs an expression for the interaction free
energy $\mu^0_N$ of surfactants in aggregates of size $N$. Following Israelachvili [4], we assume that the amphiphiles pack closely into aggregates, occupying a fixed volume per amphiphile $v$, and that $\mu^0_N$ is simply given by the surface free energy of the aggregates:

$$\mu^0_N = \frac{\gamma}{a} (a - a_0)^2 + \tilde{\mu}^0,$$

where $\gamma$ is the interfacial tension, $a$ the surface area per molecule, and $a_0$ the optimal head group area. In the case of spherical micelles, the surface area is given by $a = (36\pi v^2)^{1/3} N^{-1/3}$. The free energy (8) has a minimum at the aggregation number $M = 36\pi v^2/a_0^3$, and can be expanded around this minimum to yield

$$\mu^0_N = \text{const.} + \frac{\gamma a_0}{9M^2} (N - M)^2.$$

(9)

Inserting this into eqn. (6), one obtains a size distribution for spherical micelles which is approximately Gaussian,

$$X^S_N \propto e^{-\frac{1}{2} \sigma^2} \quad \text{with} \quad \sigma = \sqrt{\frac{9k_BT M}{2\gamma a_0}}.$$

(10)

Hence the sizes of spherical micelles are distributed around a most probable aggregation number $M$, which depends only on molecular details of the surfactants in this simplest approximation. Indeed, micelle size distributions at concentrations beyond the CMC have shown a marked peak at a given aggregation number in many simulations [3, 11, 14, 17, 19, 38, 144, 154, 157].

Larger aggregates have seldom spherical geometry, but tend to form cylindrical micelles. In this case, the diameter of the cylinders can usually be adjusted such that the head groups can cover their optimal head group area $a_0$, and the interaction free energy per surfactant reduces to the constant $\tilde{\mu}^0$. The size distribution for cylindrical micelles is then exponential in the limit of large $N$,

$$X^C_N \propto e^{-N\alpha} \quad \text{with} \quad \alpha = -\ln(f_1X_1) - (\mu^0_1 - \tilde{\mu}^0)/k_BT.$$

(11)

At small $N$, correction terms come into play which account for the ends of the cylinders. In particular, the aggregation number of cylindrical micelles in this simple
picture must always be larger than $M$, the most probable aggregation number of a spherical micelle. Putting everything together, the expected size distribution has a peak at $M$ which corresponds to spherical micelles, and an exponential tail at large $N$ which is due to the contribution of cylindrical micelles.

That this is indeed so, has been demonstrated nicely by Nelson et al\cite{120} in extensive simulations of the Larson model. Fig. 10 shows an example of a micellar size distribution for $H_2T_2$ surfactants in an aqueous environment, at 7.5 % surfactant volume fraction. The main peak is fitted to a Gaussian distribution (10), and the tail to an exponential distribution of the form (11),

$$X_N \propto f(N) \exp(-\alpha N),$$

where the prefactor $f(N)$ interpolates smoothly between $f(N) = 0$ at $N = M$ and $f(N) = 1$ at $N \gg M$. The results confirm clearly the predicted exponential decay at large $N$. The shape of the micelles can be studied directly by comparing the different eigenvalues of the radius of gyration tensor of the aggregates. Nelson et al find that they are approximately equal, as long as the aggregation number is smaller than the most probable size $M \approx 40$. Beyond that value, the largest eigenvalue grows linearly to become much larger than the other two. This observation is consistent with the picture that the peak of the distribution is generated by spherical micelles, and the tail by spherically capped cylindrical micelles.

Whereas the evolution from spherical to cylindrical shapes as a function of aggregation number appears to be gradual in the simulations of Nelson et al, Viduna et al report a rather dramatic transition at a well-defined aggregation number in their off-lattice simulations of $H_2T_2$ micelles. The eigenvalues of the radius of gyration tensor are shown as a function of the aggregation number in Fig. 11. At this choice of parameters, the micelle size distribution exhibits a peak at $N \approx 28$. The shape parameters seem rather unaffected by this, one barely notices that the largest eigenvalue begins to increase a little bit faster than the other two. In contrast, at $N \approx 47$, it rises abruptly and attains a larger value, where it seems to level off.
again. This interesting “shape transition” clearly deserves further investigation in the future.

Other questions which will have to be studied in more detail refer to the role of micelle interactions. Note that they are not included in the approximate analysis sketched above. Von Gottberg *et al.[142]* have argued that excluded volume interactions between micelles are responsible for the slight decrease of $X_1$ at higher surfactant concentrations, which has been observed in many simulations[119, 142, 144]. Bolhuis and Frenkel[157] have studied the influence of intermicellar interactions on the micelle size distributions within a simple model, which approximates the micelles as hard spheres of variable size. Their results indicate that the interactions affect the size distribution in a way which is equivalent to shifting the chemical potential to an effectively lower value.

**IV. Lattice spin models and others**

Whereas chain models still allow for a relatively unified treatment of various aspects about amphiphilic systems, such as their bulk phase behavior and the properties of monolayers and bilayers, this is not true any more for the even more idealized models at the next level of coarse graining. These usually have to be adapted very specifically to the problem one wishes to study.

One particularly favored class of models have been models of Ising type, which represent the particles by states on sites or bonds of a lattice. Those intended to describe bulk amphiphilic systems have been reviewed recently by Gompper and Schick in Ref. [1], and those developed for monolayers and bilayers by Dammann *et al.* in Ref. [158]. Hence we shall only briefly recall their main features here, and focus on the discussion of their use in computer simulations.
IV.A. Bulk systems

Lattice models for bulk mixtures have mostly been designed to describe features which are characteristic of systems with low amphiphile content. In particular, models for ternary oil/water/amphiphile systems are challenged to reproduce the reduction of the interfacial tension between water and oil at the presence of amphiphiles, and the existence of a structured disordered phase (a microemulsion), which coexists with an oil rich and a water rich phase. We recall that a “structured” phase is one in which correlation functions show oscillating behavior. Ordered “lamellar” phases have also been studied, but they are much more influenced by lattice artefacts here than in the case of the chain models.

The most senior among the lattice models is the Widom model, which has been formulated already in 1968 in its first version by Wheeler and Widom[159]. The water, oil and amphiphile molecules are represented by (1,1), (-1,-1) and (1,-1) bonds, respectively, on a two state Ising lattice. Hence oil and water are always separated by amphiphiles by construction. If the particles are taken to be non-interacting otherwise, the model maps directly onto the Ising model with nearest neighbor interactions, where the role of the temperature is assumed by the chemical potential of the amphiphile. The resulting phase diagram is well-known, one finds a region of oil/water coexistence and a critical point. In order to obtain more complex phase behavior, interactions between particles have to be added. For example, a penalty is often imposed on amphiphiles which meet at their one end. This introduces additional terms into the equivalent Ising Hamiltonian,

$$
\mathcal{H} = -h \sum_i \sigma_i - J \sum_{ij} \sigma_i \sigma_j - 2M \sum_{ij} \sigma_i \sigma_j - M \sum_{ij} \sigma_i \sigma_j
$$

(12)

where the second sum runs over nearest neighbors, the third over next nearest neighbors, and the fourth over fourth nearest neighbors. The first two terms drive the volume fraction of oil, water and amphiphile in the system, the third term incorporates some sort of “bending energy” of the amphiphilic sheets, and the last
term an interaction between sheets. The model exhibits a region of coexistence between oil and water rich phases, a region with various ordered phases, and a disordered structured phase. In the simple version (12), the transition between the oil/water region and the disordered region is continuous, hence the model does not recover three phase coexistence. However, this can be remedied by including suitable additional bond interactions[160]. The phase behavior of the model has been investigated in detail in Monte Carlo simulations, in particular by Stauffer and coworkers[160, 161, 162]. Chowdhury and coworkers have used it to study various other aspects of amphiphilic systems, such as the effect of confinement on a microemulsion[163], the lifetime, stability and rupture of Newton black films[164], and the roughness of an amphiphilic film[165].

Even though the basic idea of the Widom model is certainly very appealing, the fact that it ignores the possibility, that oil/water interfaces are not saturated with amphiphiles, is a disadvantage in some respect. The influence of the amphiphiles on interfacial properties cannot be studied on principle; in particular, the reduction of the interfacial tension cannot be calculated. In a sense, the Widom model is not only the first microscopic lattice model, but also the first random interface model: Configurations are described entirely by the conformations of their amphiphilic sheets.

As an alternative, Alexander[166] has proposed a model which places the oil and the water on lattice sites and distributes the amphiphiles on the bonds. The interactions between two neighboring oil and/or water particles depend on whether or not the connecting bond is occupied by an amphiphile. As long as the amphiphiles themselves do not interact with each other, the sum over possible bond states can be carried out independently, and the model turns out to be equivalent to an Ising model with temperature dependent interactions. Hence this simplest version does not capture the specific properties of amphiphilic systems, and additional amphiphile interactions have to be included. A variety of different interaction terms have been
implemented: bending energies, edge energies, corner energies, special penalties if amphiphilic sheets meet or cross each other etc. Different versions of the model have been explored in Monte Carlo simulations by Ebner and coworkers\cite{167} and Stockfisch and Wheeler\cite{168}. The model displays lamellar phases, and three phase coexistence between an oil rich, a water rich and a disordered phase with intrinsic structure. Moreover, the amphiphiles were shown to reduce the interfacial tension between oil and water by a factor of up to 1000\cite{168}. The interfacial tension was determined with the histogram method of Binder\cite{169}, which shall be discussed in more detail below.

More recently suggested models for bulk systems treat oil, water and amphiphiles on equal footing and place them all on lattice sites. They are thus basically lattice models for ternary fluids, which are generalized to capture the essential properties of the amphiphiles. Oil, water and amphiphiles are represented by Ising spins $S = -1, 0$ and $+1$. If one considers all possible nearest neighbor interactions between these three types of particles, one obtains a total number of three independent interaction parameters, and two independent chemical potentials. In Ising language, the most general Hamiltonian then reads

$$H = -\sum_{ij} \left[ J S_i S_j + K S_i^2 S_j^2 + C(S_i^2 S_j + S_j^2 S_i) \right] - \sum_i \left[ H S_i - \Delta S_i^2 \right],$$

which is exactly the Hamiltonian of the Blume-Emery-Griffiths model\cite{170}. Balanced systems with intrinsically identical oil and water particles are described by the set of parameters $C = 0$ and $H = 0$.

The first extension of this model, which accounts for the special character of the amphiphiles, has been the three component model, introduced by Schick and Shih in 1987\cite{171}. They simply add an additional triplet interaction

$$H_{amp} = -L \sum_{ijk} S_i (1 - S_j^2) S_k,$$

between triplets $(ijk)$ of sites in a line. At $L < 0$, this term imposes a energy penalty.
if an amphiphile is sitting between two oil or two water particles, and offers an extra energy reward if an amphiphile separates oil from water. The model exhibits a structured disordered phase, which may coexist with an oil-rich and a water-rich phase in three dimensions, and ordered “lamellar” phases. It has been examined in detail by mean field theories and other analytical methods[1], but relatively seldom by computer simulations[172, 174].

In order to illustrate the type of questions which can be addressed within such an idealized lattice model, we show a histogram of the normalized order parameters $M = \sum_i S_i/N$ and $Q = \sum_i S_i^2/N$ ($N$ being the system size) in Fig. 12[174] for a point in phase space, where oil- and water-rich phases coexist with a structured microemulsion, The peaks corresponding to the three phases are readily identified at $M \approx \pm 1$ and $M = 0$. Moreover, one discerns a broad band at $Q \approx 0.94$ which extends over nearly the whole range of $M$. The story behind this plot is the following: Based on mean field arguments, Gompper and Schick[173] had made the prediction that a structured microemulsion should not wet the oil/water interface. This is indeed observed in systems with strongly structured microemulsions; however, it is not always true for weakly structured microemulsions[177]. One reason had already been pointed out by Gompper and Schick[173]: long range van der Waals forces shift the wetting transition beyond the structured side of the disorder line. Other factors which usually influence phase transitions are fluctuations. The Monte Carlo study[174] aimed to elucidate this latter aspect.

Having obtained a set of histograms like Fig. 12 for different system sizes, (using histogram reweighting methods[173] in larger systems), the procedure was as follows: Assuming that the main contribution to the valleys between the peaks arises from configurations which contain two interfaces separating one phase regions, the interfacial tension between those phases is given by[163]

$$\gamma/k_B T = -\frac{1}{2A} \ln(N_{\text{min}}/N_{\text{max}}) \quad (15)$$
where $A$ is the interfacial area. The interfacial tensions $\gamma_{om}$ and $\gamma_{wm}$ between the oil or water rich phase and the microemulsion can thus be extracted directly from the valleys between the peaks at $M = \pm1$ and $M = 0$. Furthermore, one estimates the number of amphiphiles needed to form just two sheets of amphiphiles, and realizes that the corresponding configurations are just those which belong to the band at $Q = 0.94$. Hence the direct interfacial tension $\gamma_{ow}$ between the oil- and the water-rich phase can be calculated from the area under that band. The microemulsion wets the oil/water interface if $\gamma_{ow} < \gamma_{om} + \gamma_{wm}$. Note that the numbers obtained for the interfacial tensions with this method are subject to strong finite size corrections, which have to be analyzed carefully.

For the system studied in [174], it turns out that the oil/water interface is not wetted by the microemulsion, even though the latter is weakly structured. Hence fluctuations do shift the wetting transition beyond the disorder line. This has been explained later by Schmid and Schick as the effect of capillary wave fluctuations of the interface positions [176]. The amphiphiles in [174] are found to reduce the total interfacial tension by a factor of 100, a value which is consistent with experimental results for comparably weak amphiphiles [177].

The example illustrates, how Monte Carlo studies of lattice models can deal with questions, which reach far beyond the sheer calculation of phase diagrams. The reason why our particular problem could be studied with such success lies of course in the fact that it touches a rather fundamental aspect of the physics of amphiphilic systems – the interplay between structure and wetting behavior. In fact, the results should be universal and apply to all systems where structured, disordered phases coexist with non-structured phases. It is this universal character of many issues in surfactant physics, which makes these systems so attractive for theoretical physicists.

After this short intermezzo, we turn back to introduce the last class of lattice
models for amphiphiles, the vector models. Like the three component model, they are based on the three state Ising model for ternary fluids; however, they extend it in a way that they account for the orientations of the amphiphiles explicitly: Amphiphiles (sites with $S = 0$) are given an additional degree of freedom $\vec{\tau}_i$, a vector with length unity, which is sometimes constrained to point in one of the nearest neighbor directions, and sometimes completely free. It is set to zero on sites which are not occupied by amphiphiles. A possible interaction term which accounts for the peculiarity of the amphiphiles reads

$$H_{\text{amph}} = -J \sum_{ij} (\sigma_i \vec{r}_{ji} \cdot \vec{\tau}_j + \sigma_j \vec{r}_{ij} \cdot \vec{\tau}_i),$$  \hspace{1cm} (16)$$

where $\vec{r}_{ij}$ denotes the vector which connects the site $i$ to the site $j$. The new interaction thus awards an energy bonus if an amphiphile points towards a water molecule or away from an oil molecule. As long as the $\tau_i$ do not interact with each other, one can get rid of them by integrating them out exactly. However, this generates a set of temperature dependent multiplet interactions, which are not necessarily easier to handle\cite{1, 178}. Probably the first Monte Carlo simulation of such a model (for a binary water/amphiphile system) has been performed by Halley and Kolan\cite{179} in 1988. Later, ternary systems were studied in two dimensions by Slotte\cite{178} and Laradji et al.\cite{180}, and in three dimensions by Gunn and Dawson\cite{181}, Matsen et al.\cite{182} and Linhananta\cite{183}. Fig. 13 shows a phase diagram of Matsen et al. As the previously discussed models, vector models display lamellar phases, regions of oil/water coexistence and a structured microemulsion. Fluctuations are found to have a particularly destabilizing effect on the lamellar phase\cite{180, 182}, and to increase, in turn, the region of stability of the microemulsion. This has a significant effect on the topology of the phase diagram in both two and three dimensions. In two dimensions, phase coexistence between the lamellar phase and the oil- and water-rich phases is entirely suppressed, and the lamellar phase is separated from the oil/water coexistence region by a microemulsion channel at all temperatures.
Matsen[184] has conjectured that this should generally be the case for microemulsion models in two dimensions, and argued that as a consequence, two dimensional models also fail to produce a triple line of coexistence between an oil-rich, a water-rich and a disordered phase, as soon as the surfactant is efficient enough to produce a lamellar phase. Hence fluctuations suppress three phase coexistence of oil, water and microemulsions in two dimensions. In three dimensions, the effect is just opposite. The mean field phase diagram corresponding to Fig. 13 does not exhibit three phase coexistence. By stabilizing the microemulsion, the fluctuation unveil a region of three phase coexistence, which would otherwise be covered by the coexistence region between the lamellar phase and the oil/water-phases.

Note that Fig. 13 has still little similarity with the experimental phase diagram of ternary amphiphilic systems, Fig. 3b. In particular, the region of three phase coexistence is not confined between an upper and a lower critical endpoint, as in the experiments. This is however not surprising, since the lower critical endpoint is probably caused by orientational ordering in the water molecules, i.e., the increasing structure of the hydrogen bond network. In order to account for this effect, Matsen et al.[185] have proposed a vector model which attaches vector degrees of freedom to both the amphiphile and the water molecules. They were able to calculate a mean field phase diagram which is indeed remarkably similar to the experimental phase diagram for weak amphiphiles. The model has not been studied in Monte Carlo simulations so far.

A somewhat different type of vector model has been studied by Emerton, Boghosian and coworkers[186] in a set of recent papers. It is a lattice gas model, i.e., the sites of a (triangular) lattice can also be empty. Amphiphiles are assigned a dipole vector, and all particles are given a “velocity” $\vec{v}_i$, which points in one of the lattice directions. The dynamics of the system is described by collision processes: Particles move along the direction of their velocity, collide, and are redistributed according
to a Boltzmann weight under consideration of various conservation laws. The interaction energies are fairly complicated and shall not be spelled out here. The basic feature of the model is that it includes hydrodynamic interactions and allows to study dynamical phenomena under conditions of conserved momentum. At equilibrium, it exhibits the usual phases, lamellae, droplets and bicontinuous structures. It has mainly been used to investigate nonequilibrium phenomena, such as the kinetics of phase separation, shear induced phase transitions etc.

Before moving on to the bilayer and monolayer models, we briefly discuss a few idealized microemulsion models in continuous space. In general, off-lattice models on this level of coarse graining have attracted much less interest than lattice models. Gunn and Dawson\cite{187} have studied a mixture of Lennard-Jones spheres (water) and Gay-Berne ellipsoids (amphiphile) as a model for a binary amphiphile/water mixture (The Gay-Berne potential is a distorted Lennard-Jones potential). An additional interaction similar to (16) between amphiphiles and water is added in order to mimic the amphiphilic nature. The system is simulated under constant pressure and constant temperature conditions. It exhibits a crystalline lamellar phase, a fluid lamellar phase, and a disordered liquid crystal. Unfortunately, Gunn and Dawson do not seem to have pursued their studies of this model. Drouffe et al\cite{188} have studied self assembly into two dimensional layers using a two dimensional model of hard spheres, which are decorated with interacting intrinsic “orientations” $\vec{n}$. Two dimensional aggregation into ring vesicles has also been examined by Saito and Morikawa\cite{189} within a hard rod model. Recently, de Miguel and Telo da Gama\cite{190} have introduced a model which borrows elements from Drouffe’s model and from the lattice vector models: Particles are represented by hard spheres of equal diameter $\sigma$, with attractive (species dependent) van der Waals potentials. In addition, amphiphiles are given an extra dipole moment, which interacts with water and oil particles with a potential which is again reminiscent of the vector model
potentials (10),

\[ V_{ani} = \pm \epsilon (\sigma / r)^6 (\vec{n} \cdot \vec{r} / r). \]  

(17)

The model has not been studied very intensely so far, in particular, none of the features which are characteristic for amphiphilic systems have been recovered yet. However, it is close enough to the successful vector models and simple enough that it might be a promising candidate for off-lattice simulations of idealized amphiphilic systems in the future.

**IV.B. Bilayer and monolayer models**

Whereas microscopic models for bulk systems incorporate the amphiphilic character and often the orientational properties of the surfactants as basic ingredients, models for bilayers and monolayers are constructed to reproduce internal transitions, such as the gel-fluid transition, and therefore concentrate on rather different aspects of the surfactant structure.

For example, Scott *et al*\[191\] take interest in the ripple phase in bilayers and have constructed a lattice model which assigns two integer degrees of freedom to each site (“lipid”) on the lattice: One Ising spin \( \sigma = \pm 1 \), which describes possible orientations of the head group, and one integer \( n \in \{0, \pm 1, \pm 2, \ldots \} \), which represents the displacement of the molecules perpendicular to the bilayer plane. Using a complicated Hamiltonian, borrowed from the chiral clock model, they indeed find a ripple phase with properties which are in decent agreement with experimental data. The interplay of head group orientation and ripple formation in lipid bilayers has also been studied by Schneider and Keller within a coarse-grained lipid model\[192\].

Other studies have been concerned with transitions between condensed phases in Langmuir monolayers. Tilting phase transitions have been studied in some detail within models of grafted rigid rods\[193, 194, 195\]. Swanson *et al*\[196\] study a fluid of up to 4096 particles with fourfold symmetry in order to model rotator phase
transitions. These are transitions from a state where the amphiphile tails are locked into each other, to a state where they are free to rotate around. Interestingly, a hexatic phase is found, in which positional correlations decay exponentially, but the correlations between the orientations of the bonds connecting nearest neighbors decay only algebraically. Many condensed monolayer phases are indeed believed to be hexatic\cite{16}.

Most monolayer and bilayer studies focus on the gel-fluid transition, where the internal (conformational) degrees of freedom of lipids are important. In the most widely studied lattice model, the ten-state Pink model\cite{197}, they are built in as intrinsic degeneracies. The Pink model assigns one of ten states, denoted $m$, to every site (lipid) on a triangular lattice. Every state corresponds to a set of conformations: The lowest state $m = 1$ to the (unique) all-trans configuration, the states $m = 2−9$ to almost ordered chains with a few isolated chain defects, and the highest state $m = 10$ to a completely disordered chain. Every state is characterized by its degeneracy $D_m$ ($D_1 = 1, D_m \approx 4−100$ for $m = 2−9, D_{10} \approx 400.000$), its energy $\epsilon_m$, and the area $A_m$ covered by the lipids. The latter is approximated by $1/d_m$, the inverse chain length in the state $m$. With this identification, $D_m$, $\epsilon_m$, and $A_m$ are single chain properties which can be calculated within an appropriate microscopic chain model. One further defines the occupation variable $L_{im}$, which takes the value 1 if the lipid $i$ is in the state $m$, and 0 otherwise. The Pink Hamiltonian is then written as

$$H_{pink} = \sum_i \sum_{m=1}^{10} (\epsilon_m + \Pi A_m) L_{im} - \frac{J_0}{2} \sum_{ij} \sum_{m,n=0}^{10} I_{im} I_{jn} L_{im} L_{jn},$$

(18)

where $\Pi$ is an effective lateral pressure, $J_0$ the strength of the van der Waals interaction between neighbor chains, and $I_{im} I_{jn}$ an interaction matrix which accounts for the conformations of the chains and the distance between two chains, and can also be calculated from microscopic single chain properties. In practice, the model parameters have often been chosen so as to describe phospholipid monolayers and bilayers. The interactions between the monolayers in bilayer sheets are usually ig-
nored. If one is not interested in a quantitative comparison with experiments, one can choose to study a simplified version of the model. For example, the two-state Doniach model\cite{198} distinguishes between only two states, one ordered state with $\epsilon_0 = 0$, and one highly degenerate state with $\epsilon_1 > 0$. The interactions are such that only ordered lipids are capable of interacting with each other. A similarly simple model has been studied by Jerala et al\cite{199}.

The Pink model is found to exhibit a gel-fluid transition for lipids with sufficiently long chains, which is weakly first order. The transition disappears in bilayers of shorter lipids, but it leaves a signature in that one observes strong lateral density fluctuations in a narrow temperature region\cite{200, 201}. In later studies, the model has been extended in many ways in order to explore various aspects of gel-fluid transitions\cite{202}. For example, Mouritsen et al\cite{203} have investigated the interplay between chain melting and chain crystallization by coupling a two-state Doniach model or a ten-state Pink model to a Potts model. (The use of Potts models as models for grain boundary melting has been suggested by Sahni et al in 1983\cite{204}: Every Potts state is then identified with a different domain orientation.) More recently, Nielsen and coworkers\cite{205} have approached the same problem in a different fashion, and placed the lipids on a random lattice rather than on a regular lattice. The random lattice was constructed as a network of hard disks on a plane, tethered to each other such that the tethers cannot exceed a given maximum length. The model has been simulated at constant pressure with a suitably adapted version of the dynamic-triangulation algorithm, which will be discussed in detail in section IV.B.

The interactions between lipids are taken to depend both on their conformational state and on their distance, which introduces very naturally a coupling between the conformation of the lipids and that of the random lattice. If this coupling is weak, the gel-fluid transition takes place at a higher temperature than the crystallization transition. However, the two transitions can be brought to concur if the coupling is
chosen large enough.

Note that large density fluctuations are suppressed by construction in a random lattice model. In order to include them, one could simply simulate a mixture of hard disks with internal conformational degrees of freedom. Very simple models of this kind, where the conformational degrees of freedom only affect the size or the shape of the disks, have been studied by Fraser et al\textsuperscript{206}. They are found to exhibit a broad spectrum of possible phase transitions.

Zhang et al\textsuperscript{207} have discussed the effect of intermonolayer coupling on the gel-fluid transition. They find that any kind of coupling usually drives the transition to be more strongly first order. In other studies, the model has been generalized to incorporate hydrogen bonding and hydration in bilayers\textsuperscript{208}. Moreover, it has been extended to include several molecular species, such that binary mixtures of lipids\textsuperscript{209, 210} and mixtures of cholesterol and lipids\textsuperscript{203} could be studied. Special attention has been given to lipid-protein interactions\textsuperscript{211, 212, 213}. Proteins in bilayers have been reviewed recently by Mouritsen\textsuperscript{214}.

V. Phenomenological models

The last class of models, which are widely used to describe amphiphilic systems, are the phenomenological models. As opposed to all the previous models, they totally ignore the fact that amphiphilic fluids are composed of particles, and describe them by a few mesoscopic quantities. In doing so, they offer the possibility to clarify the interrelations between different behaviors on a very general level, and to study universal characteristics which are independent of the molecular details.

As already mentioned in the introduction, phenomenological models for amphiphilic systems can be divided into two big classes: Ginzburg-Landau models and random interface models.
V.A. Ginzburg-Landau models

Ginzburg-Landau theories of amphiphiles have been reviewed at various places\[1, 25\], among other in chapter 11 of this book. Hence we shall be brief in this subsection.

The basic idea of a Ginzburg-Landau theory is to describe the system by a set of spatially varying “order parameter” fields, typically combinations of densities. One famous example is the one-order-parameter model of Gompper and Schick\[173\], which uses as only variable $\phi$ the density difference between oil and water, distributed according to the free energy functional

$$\mathcal{F}\{\phi\} = \int d\vec{r} \left[ c(\Delta \Phi)^2 + g(\phi)(\nabla \phi)^2 + f(\phi) \right].$$

Here the functions $g(\phi)$ and $f(\phi)$ are defined in a suitable way to produce the desired phase behavior (see chapter 11). The amphiphile concentration does not appear explicitly in this model, but it influences the form of $g(\phi)$ – in particular, its sign. Other models work with two order parameters, one for the difference between oil and water density and one for the amphiphile density. In addition, a vector order-parameter field sometimes accounts for the orientational degrees of freedom of the amphiphiles\[1\].

The equilibrium phase behavior of models of this kind has been investigated by various methods, including Monte Carlo sampling methods\[215, 216\], since these allow to account for fluctuation effects in a complete and straightforward way. However, the vast majority of computer simulations which have been dealing with Ginzburg-Landau models has employed them to study nonequilibrium phenomena. In particular, the phase separation kinetics at the presence of surfactants has attracted much interest. It was mostly investigated in two dimensions by Langevin simulations\[217, 218, 219, 220, 221\]. The differences lie in the particular form of the Ginzburg-Landau model, and in the dynamical system which is examined. For example, Pätzold and Dawson\[218\] include hydrodynamic effects and couple the system to Navier-Stokes equations, whereas most other groups consider a simpler
relaxation dynamics, with or without conserved order parameters. Kawakatsu et al take special interest in situations where the surfactant molecule is much larger than the oil or water, i.e., a polymer. Therefore they work with a hybrid models, which treats the surfactants as particles, and the difference of oil and water density by a Ginzburg-Landau field\[220\]. Related models due to the same authors represent all particle densities by continuous fields, but include long range interactions between the surfactants, or extend the original hybrid model in other ways\[221\].

The phase separation process at late times \( t \) is usually governed by a law of the type \( R(t) \propto t^n \), where \( R(t) \) is the characteristic domain size at time \( t \), and \( n \) an exponent which depends on the universality class of the model and on the conservation laws in the dynamics. At the presence of amphiphiles however, the situation is somewhat complicated by the fact that the amphiphiles aggregate at the interfaces and reduce the interfacial tension during the coarsening process, i.e., the interfacial tension depends on the time. This leads to a pronounced slowing down at late times. In order to quantify this effect, Laradji et al\[217, 222\] have proposed the scaling ansatz

\[
R(t) = t^n f(\rho_s^x t) \quad \text{with} \quad x = 1/n \quad \text{in two dimensions.} \tag{20}
\]

The function \( f \) incorporates the screening effect of the surfactant, and \( \rho_s \) is the surfactant density. The exponent \( x \) can be derived from the observation that the total interface area at late times should be proportional to \( \rho_s \). In two dimensions, this implies \( R(t) \propto 1/\rho_s \) and hence \( x = 1/n \). The scaling form (20) was found to describe consistently data from Langevin simulations of systems with conserved order parameter (with \( n = 1/3 \))\[217\], systems which evolve according to hydrodynamic equations (with \( n = 1/2 \))\[218\], and also data from molecular dynamics of a microscopic off-lattice model (with \( n = 1/2 \))\[153\]. The data collapse has not been quite as good in Langevin simulations which include thermal noise\[218\].

Langevin simulations of time-dependent Ginzburg-Landau models have also been
performed to study other dynamical aspects of amphiphilic systems\cite{223, 224}. An attractive alternative approach are the Lattice-Boltzmann models, which take proper account of the hydrodynamics of the system. They have been used recently to study quenches from a disordered phase in a lamellar phase\cite{225, 226}.

**V.B. Random interfaces**

Random interface models for ternary systems share the feature with the Widom model and the one-order-parameter Ginzburg-Landau theory\cite{19} that the density of amphiphiles is not allowed to fluctuate independently, but is entirely determined by the distribution of oil and water. However, in contrast to the Ginzburg-Landau approach, they concentrate on the amphiphilic sheets. Self-assembly of amphiphiles into monolayers of given optimal density is premised, and the free energy of the system is reduced to effective free energies of its internal interfaces. In the same spirit, random interface models for binary systems postulate self-assembly into bilayers and introduce an effective interface Hamiltonian to study the conformations of the bilayers.

For fluid membranes, in which neighbor relations are not maintained, the free energy of a membrane is often written in the form\cite{27, 30}

$$\beta \mathcal{H} = \int dS \left[ \sigma + \lambda_S H + 2\kappa H^2 + \bar{\kappa}K \right].$$

(21)

Here $dS$ denotes a surface element, $H$ the local mean curvature, and $K$ the local Gaussian curvature. They are derived from the two local radii of curvature $R_1$ and $R_2$ via $H = (1/R_1 + 1/R_2)/2$, and $K = 1/(R_1R_2)$. The parameter $\sigma$ drives the total amount of interface in the system and is thus in a sense related to the chemical potential of the amphiphiles – it can also be interpreted as an interfacial free energy or a negative spreading pressure. The second term $\lambda_S$ generates a preferred radius of curvature towards one side of the membrane, hence it breaks the symmetry of the two sides. The parameters $\kappa$ and $\bar{\kappa}$ denote the bending rigidity and the saddle-splay
modulus, respectively. Note that the integral over the last term depends solely on the topology of the interfaces according to the Gauss-Bonnet theorem,

\[ \int dSK = 2\pi \chi_E, \quad \text{with} \quad \chi_E = 2(c - g), \quad (22) \]

where the Euler characteristic \( \chi_E \) counts the number of closed surfaces \( c \) (including cavities) minus the number of handles \( g \).

How can one simulate such a system?

A relatively simple approach suggests itself if the interfaces are known to be almost flat. In that case, the interface position can be described by a single-valued function \( z(x, y) \), where \( (x, y) \) are cartesian coordinates on a flat parallel reference plane. The functional (21) can be approximated by

\[ \beta \mathcal{H} = \int dx \, dy \left[ \frac{\sigma}{2} (\nabla z)^2 + \frac{\kappa}{2} (\Delta z)^2 \right] \quad (23) \]

(Monge representation\([1, 27]\)). Due to the underlying cartesian coordinates, the discretization of this Hamiltonian is straightforward. Obviously, the Hamiltonian (23) does not really need to be studied by Monte Carlo simulations, since it can be solved exactly. However, things become more interesting if one considers stacks of interacting membranes\([227, 228, 229]\), or fluid membranes with locally varying elastic properties\([230]\).

The model (23) is simple to study, but unfortunately not very widely applicable. In general, one is more interested in situations where the interfaces are free to fold around and to assume every possible conformation. A second possible approach is to switch over to a lattice formulation. This has been done by a number of groups\([231, 232, 233]\). The resulting models are very similar to the Widom or Alexander model. As a first step, random surfaces are composed from plaquettes on a lattice. In models for ternary systems\([231, 232]\), these have to be closed, but they may be open in models for binary systems\([233]\) (there is no reason why a bilayer should not end somewhere). Then, a Hamiltonian is introduced for these random surfaces.
which imposes penalties on plaquettes who meet at a right angle, who share a link with more than one other plaquette, etc. – in the case of open surfaces also for edges and seams. A particularly elegant form has been used by Likos et al.\cite{232}: They construct the Hamiltonian as a sum over the four Minkowski functionals in three dimensions, \textit{i.e.}, the volume, the area, the total mean curvature, and the Euler characteristic\cite{234}. If the surfaces are closed, the Hamiltonian can then be mapped in a straightforward way onto an Ising model on the dual lattice, which has various pair and multiplett interactions. Since the models are so similar to the lattice models of section IV.A., their phase behavior is comparable as well. One finds ordered phases, three phase coexistence and a structured microemulsion in ternary systems, and a sponge phase in the binary system.

Thus random interfaces on lattices can be investigated rather efficiently. On the other hand, much analytical work has concentrated on systems described by Hamiltonians of precisely the type (21), and off-lattice simulations of models which mimic (21) as closely as possible are clearly of interest. In order to perform such simulations, one first needs a method to generate the surfaces \{S\}, and second a way to discretize the Hamiltonian (21) in a suitable way.

A widely used method to generate surfaces is the dynamic random-triangulation algorithm\cite{233,236}, which we have already mentioned in section II.B.. Surfaces are modeled by triangular networks of spherical beads, linked by tethers of some given maximum length \(l_0\). The tethers define the neighbor relations on the surface. In order to generate self-avoidance, the beads are equipped with hard core interactions, and the maximum tether length is chosen smaller than \(\sqrt{3}\sigma\), where \(\sigma\) denotes the bead diameter\cite{237}. The Monte Carlo algorithm involves two different types of steps\cite{158}: Regular attempts of moving single beads or clusters of beads in space, and attempts to change the connectivity of the network, \textit{i.e.}, to redistribute the tethers between the chains\cite{158}. The latter is done by randomly cutting tethers and
reattaching them between the four beads which form two neighboring triangles\[235, \ 236\], as illustrated schematically in Fig. 14. Updates of the bead positions are subject to the constraint that the maximum tether length must not exceed $l_0$, and connectivity updates have to comply in addition with the requirement, that at least three tethers are attached to one bead, and that two beads cannot be connected to each other by more than one tether. Otherwise, attempted updates are accepted or rejected according to a standard Metropolis prescription.

The next task is to discretize the surface integral (21). In most simulations, all terms except for the third one are dropped: The average interfacial area is determined by the choice of the number of beads and the maximum tether length; including the first term would only make sense in a “grandcanonical” ensemble, where beads can be added and removed. The last term ($2\pi \chi E$ according to eqn. (22)) can be evaluated much more accurately by other methods than by an integral over some approximate expression for the Gaussian curvature. Finally, the amphiphilic layers are usually assumed to be intrinsically symmetric, which eliminates the second term. The remaining term is the bending penalty on the mean curvature $H$. It is usually approximated by\[238\]

$$\int dS \ 2\kappa H^2 \approx \lambda \sum_{\alpha\beta} (1 - \bar{n}_\alpha \bar{n}_\beta) + 2\pi \kappa \chi E, \quad (24)$$

where $\bar{n}_\alpha$ is the unit normal vector of triangle $\alpha$, and the sum runs over all neighbor triangle pairs. This expression is commonly employed in simulations of stiff fluid membranes. However, it has the disadvantage that the relationship between $\lambda$ and $\kappa$ is not clear. Comparing ideal spheres, for example, one obtains $\lambda = \sqrt{3}\kappa$\[240\], whereas a similar calculation yields $\lambda = 2\kappa/\sqrt{3}$ for the case of cylinders. In order to avoid this problem, Gompper and Kroll\[241\] have recently argued that a more appropriate discretization of the bending free energy should be based directly on

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the square of the local mean curvature:

\[ \int dS \ 2\kappa H^2 \approx \frac{\tau}{2} \sum_{ij} \frac{1}{\sigma_i} \left[ \sum_{j(i)} \sigma_{ij}(\vec{R}_i - \vec{R}_j) \right]^2, \tag{25} \]

with \( \tau \approx \kappa \), where \( i \) runs over all sites, \( j \) over all neighbors of \( i \), \( \vec{R}_i \) denotes the position of bead \( i \) and \( l_{ij} \) the length of the bond connecting \( i \) with \( j \). The other quantities are related to the dual lattice, which is created from the intersections of the perpendicular bisectors of the bonds: \( \sigma_{ij} \) is the length of the dual bond which bisects \( l_{ij} \), and \( \sigma_i = \sum_{j(i)} \sigma_{ij} l_{ij} / 4 \) the area of the dual cell of site \( i \). Note that \( \sigma_{ij} \) is not necessarily positive.

As yet, models for fluid membranes have mostly been used to investigate the conformations and shapes of single, isolated membranes, or vesicles. In vesicles, a pressure increment \( p \) between the vesicle’s interior and exterior is often introduced as an additional relevant variable. An impressive variety of different shapes has been found, including branched polymer-like conformations, inflated vesicles, dumbbell shaped vesicles, and even stomatocytes. Fig. 15 shows some typical configuration snapshots, and Fig. 16 the phase diagram for vesicles of size \( N = 247 \), as calculated by Gompper and Kroll.

The collapsed polymer-like state is characterized by specific scaling laws, e.g., the average volume of the vesicle is proportional to the number of beads, \( \langle V \rangle \propto N \). Other scaling laws apply in other regions of the phase diagram. For the case of zero pressure increment, \( p = 0 \), and moderate bending rigidity, a scaling ansatz of the form

\[ \langle V \rangle = N^{3/2} \theta(\sqrt{A}/\xi) \tag{26} \]

has been proposed, where \( \sqrt{A} = \sqrt{N} \) is the area of the vesicle, and \( \xi \propto \exp(4\pi/3\kappa) \) its persistence length. If the scaling law (26) holds, simulation data for different vesicle sizes \( N \) should collapse on one curve, if \( \langle V \rangle N^{-3/2} \) is plotted versus \( \sqrt{N} \exp(-4\pi\kappa/3) \). This is indeed the case. Scaling laws are
extremely sensitive tools which allow to study various phenomena very accurately. For example, it has been predicted\textsuperscript{243} that the bending rigidity $\kappa$ is softened by fluctuations on large length scales $l$

$$\kappa(l) = \kappa - \frac{\alpha}{4\pi} \ln(l/a_0),$$

where $a_0$ is a microscopic cutoff length, and $\alpha$ a universal constant. By a careful scaling analysis of volume fluctuations in the limit of large bending rigidity, Gompper and Kroll have been able to verify this prediction\textsuperscript{241}.

A number of recent studies consider more complex systems, such as freezing vesicles\textsuperscript{246} (freezing can be induced by reducing the tether length), or mixed membranes which contain more than one component\textsuperscript{247, 248}. The possibility that a membrane may break up and form pores has also been considered\textsuperscript{249}.

In all of these investigations, the topology of the simulated object was kept fixed (spherical). Current work is devoted to study systems with variable topology, where vesicles can fuse and break up. Such models will probably be very useful to study bicontinuous states, and the evolution of them into states of isolated vesicles and droplets\textsuperscript{250, 251}.

V.C. Conclusions

We have attempted to give an overview over the wide spectrum of topics which are currently investigated in amphiphilic systems, and over the multitude of simulation methods and simulation models which have been used to explore them. Amphiphilic systems have been studied on length scales ranging from a few Angstrom to micrometers, and over a similarly wide range of time scales. Hence a whole hierarchy of models have been developed, each of which covering a different length scale, and devised to address a different type of problem. We have also attempted to give a feeling for the many interesting questions which are still open and/or under current investigation. Amphiphilic systems turn out to be an immensely rich playground for
researchers, which has something to offer for almost everybody: for the materials
scientist, the physical chemist, the biologist, the condensed matter physicist, and
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Self-assembled structures in amphiphilic systems: Micellar structures (a) and (b) exist in aqueous solution as well as in ternary oil/water/amphiphile mixtures. In the latter case, they are swollen by the oil on the hydrophobic (tail) side. Monolayers (c) separate water from oil domains in ternary systems. Lipids in water tend to form bilayers (d) rather than micelles, since their hydrophobic block (two chains) is so compact and bulky compared to the head group, that they cannot pack into a sphere very well\[4\]. At small concentrations, bilayers often close up to form vesicles (e). Some surfactants also form cylindrical (wormlike) micelles (not shown).
Figure 2:

Selected structured phases in amphiphilic systems: Again, these phases are present in both ternary oil/water/amphiphile mixtures and binary systems of water and amphiphile. In the first case, the dashed lines represent monolayers which separate oil from water domains, in the second case, they represent in (a) and (b) bilayers, in (c) and (d) surfaces of amphiphile aggregates. Specifically, we show a macroscopically isotropic, but microscopically structured bicontinuous phase, called sponge phase ($L_3$ structure) in the binary mixture and bicontinuous microemulsion in the ternary mixture (a); the lamellar phase $L_α(b)$; the hexagonal phase $H_1(c)$; and the gyroid phase $G$ (d). The different shading in (d) distinguishes between the two constituting networks of the gyroid. See text for more explanation.
Figure 3:
Fig. 3

Schematic phase diagrams of amphiphilic systems with good anionic amphiphiles (a) for a binary water/amphiphile mixture (adapted from Strey et al 1990[7]), and (b) for a ternary mixture at an oil/water ratio of 1:1 (adapted from Kahlweit et al 1986[8]). Here $L_\alpha$ denotes the lamellar phase, $H_1$ the hexagonal phase and $V_1$ a phase with cubic symmetry, presumably a gyroid phase. In the binary system (a), $L_3$ represents the sponge phase and $L_1, L_2$ two other isotropic liquid phases. Shading indicates regions of two phase coexistence. In the ternary system, the symbol $1\Phi$ labels a single phase region, $2\Phi$ a region of two phase coexistence between an oil-rich and a water-rich phase, and $3\Phi$ a region of three phase coexistence with an additional amphiphile rich “middle phase”. In systems with strong amphiphiles, the coexisting middle phase is usually a structured microemulsion (cf. Fig. 2).
Figure 4:

Phase diagram of Langmuir monolayers at low and intermediate surface coverage (schematic). Not shown are the various phases on the condensed side at high surface coverage.
Figure 5:

Phase diagrams of binary amphiphile/water systems in the Larson model. The amphiphile structures are (a) $H_4T_7$, (b) $H_4T_6$, (c) $H_4T_4$ and (d) $H_6T_4$. $H$ denotes the hexagonal phase, $L_\alpha$ the lamellar phase, $G$ the gyroid phase, $BCC$ a phase with spherical micelles in body-centered cubic arrangement, and $R$ a rhombohedral-like mesh phase. From Larson 1996[112].
Figure 6:

Configuration snapshot of a spontaneously formed vesicle from double-tailed amphiphiles in the Larson model. (a) entire vesicle (b) vesicle cut in half in order to show its inner side. Black circles represent head particles (+1), grey circles tail particles (-1), white circles the neutral connecting particles (0). From Bernardes 1996[26].
Figure 7:

Snapshot of a bilayer conformation with a pore in the bond-fluctuation model. The dark spheres represent head particles, the light spheres tail particles. Around the pore, the amphiphiles rearrange so as to shield the bilayer interior from the solvent. From Müller and Schick 1996 [133].
Figure 8:

Phase diagram of a Langmuir monolayer in a model of grafted stiff Lennard-Jones chains. LE denotes a disordered expanded phase, LC-U a condensed phase with untilted chains, LC-NN and LC-NNN condensed phases with collective tilt towards nearest neighbors and next nearest neighbors, respectively, and LC-mod a phase which has a superstructure and an intermediate direction of tilt. From Stadler and Schmid 1998[151].
Figure 9:

Configuration snapshots of the monolayer in Fig. 8 (a) in the disordered expanded phase LE, (b) in the condensed modulated phase LC-mod. From Stadler and Schmid 1998[15].
Figure 10:

Micelle size distribution for $H_2T_2$ surfactants within the Larson model. The dashed lines show fits to the expected form for spherical micelles (main peak) and cylindrical micelles (tail). Inset shows the tail of the distribution on a semi-logarithmic plot to demonstrate the exponential decay predicted for the cylindrical micelles. From Nelson, Rutledge and Hatton 1997 [120].
Figure 11:

Eigenvalues of the radius of gyration tensor (dots: largest, squares: middle, triangles: smallest) of micelles vs. aggregation number $N$ in an off-lattice model of $H_2T_2$ surfactants. The micelle size distribution for this particular system has a peak at $N \approx 28$. From Viduna, Milchev and Binder 1998[144].
Figure 12:

Histogram of $Q$ and $M$ in the three component model at three phase coexistence. Parameters are $C = H = 0$, $K = 0.5$, $\Delta = -7$, $L = -5$ in units of $J$, and temperature $k_B T / J = 2.78$. System size is $12 \times 12 \times 24$. See text for further explanation. From Schmid and Schick 1994[174].
Figure 13:

Phase diagram of a vector lattice model for a balanced ternary amphiphilic system in the temperature vs. surfactant concentration plane. \( W+O \) denotes region of coexistence between oil- and water-rich phases, \( D \) a disordered phase, \( L_1 \) an ordered phase which consists of alternating oil, amphiphile, water and again amphiphile sheets, and \( L_F \) an incommensurate lamellar phase (not present in mean field calculations). The data points are based on simulations at various system sizes on an fcc lattice. From Matsen and Sullivan 1994[182]. Copyright 1994 by the American Physical Society.
Figure 14:

Schematic sketch of a connectivity update in the dynamic triangulation algorithm.
Figure 15:

Conformations of fluid vesicles for different values of the bending rigidity and pressure increment. (a) branched polymer (b) inflated vesicle (c) prolate vesicle (d) stomatocyte. From Gompper and Kroll 1995[243]. Copyright 1995 by the American Physical Society.
Phase diagram of fluid vesicles as a function of pressure increment $p$ and bending rigidity $\lambda$. Solid lines denote first order transitions, dotted lines compressibility maxima. The transition between the prolate vesicles and the stomatocytes shows strong hysteresis effects, as indicated by the error bars. Dashed line (squares) indicates a “transition” from metastable prolate to metastable diskshaped vesicles. From Gompper and Kroll 1995[243].