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Deutschsprachiges Abstract:

Di-Block Kopolymer-Sterne mit solvophilen A und solvophoben B Blöcken vereinen Eigenschaften von bereichsweise attraktiven Kolloiden und ultraweichen polymerischen Molekülen und erfreuen sich dank ihrer Selbstorganisations-Fähigkeiten eines wachsenden Interesses in der Forschungsszene der Weichen Materie. In dieser Arbeit wird eine auf einem Gittermodell basierende, großkanonische Monte Carlo Simulation eingesetzt, um das vielfältige Phasenverhalten in Lösungen von drei-, sechs- und zehnamigen Di-Block Kopolymer-Sternen mit einstellbarer Armsteifigkeit zu untersuchen. Für relative B-Block-Größen von 50% oder mehr werden flüssig-gasförmig-Phasenkoexistenzen mit kritischem Punkt beobachtet, deren Abhängigkeit von Funktionalität und Armsteifigkeit im Fokus der Untersuchungen steht. Bei sehr steifen Armen werden Systeme beobachtet, die sich im Bereich der flüssigen Phase in Hierarchien von kubischen, kolumnaren und lamellaren Flüssigkristallen organisieren. Für relative B-Block-Größen unter 50% wird ein breitgefächertes Spektrum von Mikrophasenseparations-Szenarien beobachtet, die sich über die Bildung von Gelen, sphärischen Mizellen und eine sukzessive, perlenkettenartige Formierung von sphärischen Mizellen zu wurmartigen Supermizellen erstrecken. Die Aggregationsszenarien werden mit denen von anderen kolloidalen bzw. polymerischen Teilchen verglichen und mögliche Auswirkungen auf die Rheologie gefolgert, wobei die besondere Bedeutung der Sternenarchitektur im zentralen Blickfeld steht.

Abstract

Di-block copolymer stars, featuring solvophilic A and solvophobic terminal B blocks, unite properties of both patchy colloids and ultrasoft polymeric particles, and are, due to their self-organization abilities, becoming increasingly interesting in soft matter science. This work employs lattice model Grand Canonical Monte Carlo simulations to investigate the rich phase behavior in solutions of di-block copolymer stars with functionalities $f = 3, 6, 10$ and tunable arm stiffness. For B block relative size ratios of $r \geq 50\%$, we find gas-liquid coexistence, terminating at a critical point, for which we study the influence of functionality and arm stiffness. For very rigid arms, we find that certain systems organize into hierarchized cubic, columnar and lamellar liquid crystals within the domain of their liquid phase. For B block relative size ratios of $r < 50\%$, we find a large variety of microphase separation scenarios including gel formation, spherical micelles and a successive, necklace-fashion transition of spherical micelles into wormlike super micelles. We compare the aggregation scenarios with other colloidal or polymeric particles, draw conclusions on rheological implications and stress the peculiarities of the star architecture in this respect.

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Chapter 1

Introduction

The overarching goal of Statistical Mechanics is the prediction of macroscopic properties on the basis of microscopic interactions. Real, and in particular soft matter systems, can have very complex interactions in their details. Thus it is necessary to construct generic models that capture the salient features with as much simplification as possible.

The subject of this work is the investigation of the collective behavior, structure and thermodynamics for solutions of chemically functionalized, star-shaped polymeric molecules. The main approach to investigate this subject are computer simulations - Grand Canonical Monte Carlo simulations, to be specific (abbr. as *GCMC*).

This particular GCMC is a generic approach featuring dimensionless properties and abstract descriptions. These provide a high flexibility in tuning the degree of *coarse graining* of the physical objects that are to be investigated. *Coarse graining* refers - in this case - to the abstraction and simplification of a real-world object and its physical properties, such as e.g. interactions, for the sake of a higher generality and, thus, meaningfulness of the results, and also a higher performance efficiency of the computer simulation. The idea is to intentionally neglect as many microscopic details as possible that have only little to no effect on the physical properties that are to be investigated. For instance, a macroscopic and the vast majority of mesoscopic subjects will be so marginally affected by quantum effects under most conditions that one can stick to only classical descriptions in a computer simulation thereof. For polymeric molecules, a fully atomistic description is not strictly necessary when the main interest lies in aspects such as self assembly or phase separation.

A flexible polymer chain can be modeled in freely-jointed segments of the Kuhn length [1, 2], while stiff polymers are in theory often described via the worm-like chain model [3]. However, a Monte Carlo simulation of stiff polymers can still make use of the freely-jointed chain model by considering the stiffness within energy calculations. Independent on the atomic structure of the molecule, this model is, thus, generic for both flexible and stiff polymer chains within colloidal length scales.

Therefore, the intention of this work is not the analysis of a specific molecule, but rather to draw a fundamental picture of the thermodynamics and the possible structures of the whole class of end-functionalized star polymers, and to stress the particularities of the star architecture in this respect. In Chapter 2 we will elaborate this model in detail, outline the implementation in a GCMC algorithm and give a comprehensive explanation on the method of analysis.

1.1 From hard spheres to functionalized star polymers: colloids

One of the central subjects of soft matter physics is the study of colloidal particles and their phase behavior. The reason for the tremendous interest in colloids is their unprecedented variety, flexibility and versatility for fundamental research from equilibrium structure to dynamics and flow. The successful implementation of these fundamentals into application and the industrial interest becomes obvious when considering the relevance for every day life: from food over cosmetics to industrial materials, from aerosols over gels to liquid crystals, colloids are arguably the most important field of science for any kind of crafting industry today.

Because the definition of colloids as dispersed particles in the regime between solutions (particle size $\sim 1nm$) and suspensions (particle size $\sim 1\mu m$) is very loose, the molecular nature of a colloidal particle can be quite diverse. Even a rather simple system of sterically repulsive, dispersed hard spheres of acrylic glass [4] shows a rich phase behavior, ranging from colloidal fluids over liquid crystals to a colloidal glass.

The richness of phase behavior increases with the complexity of the colloid. Two of the most important aspects that affect phase behavior and self-assembly properties are the internal structure of a colloidal particle and its functionalization. The internal structure of a colloidal particle determines its softness, elasticity and deformability. While hard spheres are by name neither soft nor deformable, and only interact by steric repulsion, objects such as dendrimers, micelles, microgels or micro-emulsions show a certain softness, elastic interactions and a limited deformability, and polymeric particles excel at all these features.

Functionalization refers to the property of a molecule to have functional groups, i.e. local groups of atoms which employ an attractive force to external particles (or the respective functional groups on those particles), where that force dominates all other interactions., for instance at DNA-coated colloids. While in chemistry, a functional group can - in general - form covalent bonds or even enter into a chemical reaction, in soft matter physics it usually refers to patches with an attractive interaction potential, featuring a repulsive component in the atomic range. These can be long range, such as for e.g. polyelectrolytes, or short range, such as the Lennard-Jones potential. Amphiphilic block copolymers in a solvent feature functional groups in their solvophobic blocks.

It should be noted, however, that in general, the term *functionalization* involves an intentional, active process of chemical decoration. For block copolymers with solvophobic blocks, the "functionalization" is a product of poor solubility. Thus, in this respect, the term is used due to analogy.

If a colloid is decorated with functional groups, and these groups lead to a significant anisotropy of the colloid's interactions, it is distinguished and specially labeled by the term "patchy colloid" and one refers to the functional groups as "patches".

Because such non-spherical, anisotropic interactions render colloids able to self-assemble into complex structures, they are investigated for the purpose as building blocks for high-tech materials. Colloids with a tetrahedral patch distribution are, for instance, considered as building blocks for diamond-symmetry structures in photonic crystals [5, 6]. The patchiness is also a crucial factor in the phase behavior. Depending on the number and position of patches, the general form of the colloid, its deformability and, thus, the relative mobility of patches, functionalized colloids can have a diverse and complex phase behavior. For hard colloids with equidistantly distributed patches [7], geometric deviations from equidistance [8], Janus particles [9, 10] or DNA-functionalized, hard colloids [11], the possible phases reach from colloidal liquids and gas-liquid coexistence with critical phenomena over gels to arrested states, colloidal glasses and a wide variety of ordered equilibrium states.

While this is already a vast variety in phase behavior, it becomes ever more complex when going to soft, patchy colloids. The ability of polymeric molecules to leave a collapsed, soft, spherical shape and deform, bend, stretch or entangle raises several aspects in phase behavior that distinguishes them from hard patchy colloids.

1.1.1 Stabilization and rheology of gelled phases

Hard, patchy colloids can associate into disordered network structures that form elastic solids, referred to as gels [12, 13]. This is not dependent on high concentrations. In fact, microgels can form in very dilute suspensions [14, 15]. These systems are especially interesting due to their dynamic effects such as adaptive local restructuring when under stress [16] and show remarkable theoretical similarities to glassy systems and polymers [17]. However, a polymeric gel is much more flexible due to the fact that colloid-colloid distances can not only change within the limits of the effective attraction range of the aggregated functional groups, but also in terms of a stretching of the whole molecule. Thus, density fluctuations on the supramolecular level (i.e. which extend over many molecular sizes) are possible, which makes an equilibrium gel state entropically much more stable. Also, such systems are much more deformable in their viscoelastic response to applied stress. The rheological properties can be quite diverse: the deformability can lead to a spatial adaption of the network to the shearing after it breaks, resulting in a decreasing viscosity, i.e. "shear-thinning". On the other hand, loops, knots and entanglement of polymeric chains within the gel during shear can dramatically increase the viscosity, i.e. "shear-thickening". Both of these non-Newtonian properties can be present for the same system, depending e.g. on the concentration [18], temperature [19] or simply the shear rate [20].

1.1.2 The ability to self-aggregate

Polymer chains featuring functional groups are very versatile tools for a large variety of applications. AB-diblock copolymers with a solvophilic A and a solvophobic B block are the most prominent type of surfactants. When in only one, pure solvent, they form spherical micelles [21], wormlike micelles [22], polymersomes [23] and liquid-gas phase separation [24]. While ABA-triblock copolymer chains with a solvophobic middle block can be used to form membranes and also polymersomes [25], an ABA architecture with solvophobic end groups will collapse into a ring shape for the case of infinite dilution. In concentrated systems, they linearly associate on the intermolecular level and form - reversible - microgels [26]. The collapse of a single molecule can also be observed in concentrated systems, when the intra-molecularly aggregated end groups of several "rings" associate on an inter-molecular level. The picture of an associated core surrounded by loops of the solvophilic chain parts gave birth to the name "flower-like micelles". Such micelles show, however, a strong tendency to form inter-micellar associations. This happens when one end-group of a single chain leaves the micelle core and becomes loose, now being able to associate with a counterpart. The result is a strong inter micellar attraction, driving the micellar solution towards gelation [27, 28]. The source of this inter micellar association, the tear-free of a single end group from the micelle core, is an entropic effect. The association of the end group with a respective free end group from another micelle, compared to an association with its own micelle core, is energetically unfavorable due to the possible number of monomer-monomer contacts. The more contact pairs of objects with attractive (negative) potential can be established, the further can the overall energy be minimized. The torn-free arm needs to associate with another micelle's core

in order to keep the association energy constant. This is only possible if the other micelles offers a free association spot by also tearing free one of its arms, which then likewise can associate with the original micelle core. This results in a strong double-bridge between these two micelles. However, what

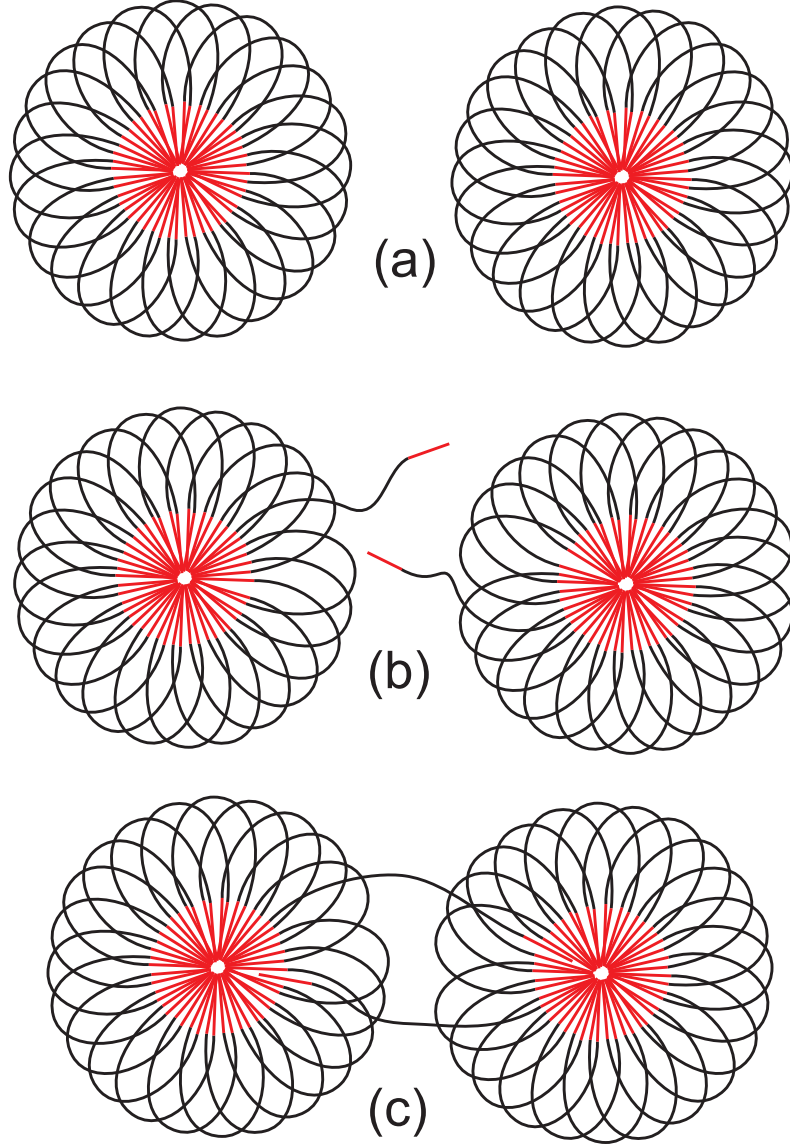


Figure 1.1: A sketch of a double-bridging between two flower-like micelles. The solvophilic polymer block is colored in black and the solvophobic block in red. (a) shows the sterically shielded micelles coexisting independently, (b) shows the two micelles tearing free one polymer chain each and (c) shows the bridged micelles.

prevents the system from totally merging micelles and forming as massive aggregates as possible, in order to maximize contact numbers, is entropy due to crowding and steric repulsion. As an antagonist of energy, entropy eschews also well organized configuration with all polymer chains bent to form isolated flower-like micelles, thus favoring more complex, interconnected structures.

As will be seen in this work, the interplay of configurational energy and the diverse aspects of entropy is complex, sometimes subtle, and can lead to an interesting and rich phase behavior.

1.2 Between single chains and patchy colloids: telechelic star polymers

The crucial role of internal structure in the phase behavior of colloidal particles like amphiphilic polymer chains is obvious, but an ABA-triblock copolymer, let alone an AB-diblock copolymer, is arguably an extreme deviation from patchy, spherical colloids. The star polymer architecture, however, offers both the softness of a polymeric molecule and a certain spherical character, as well as the option of functionalization.

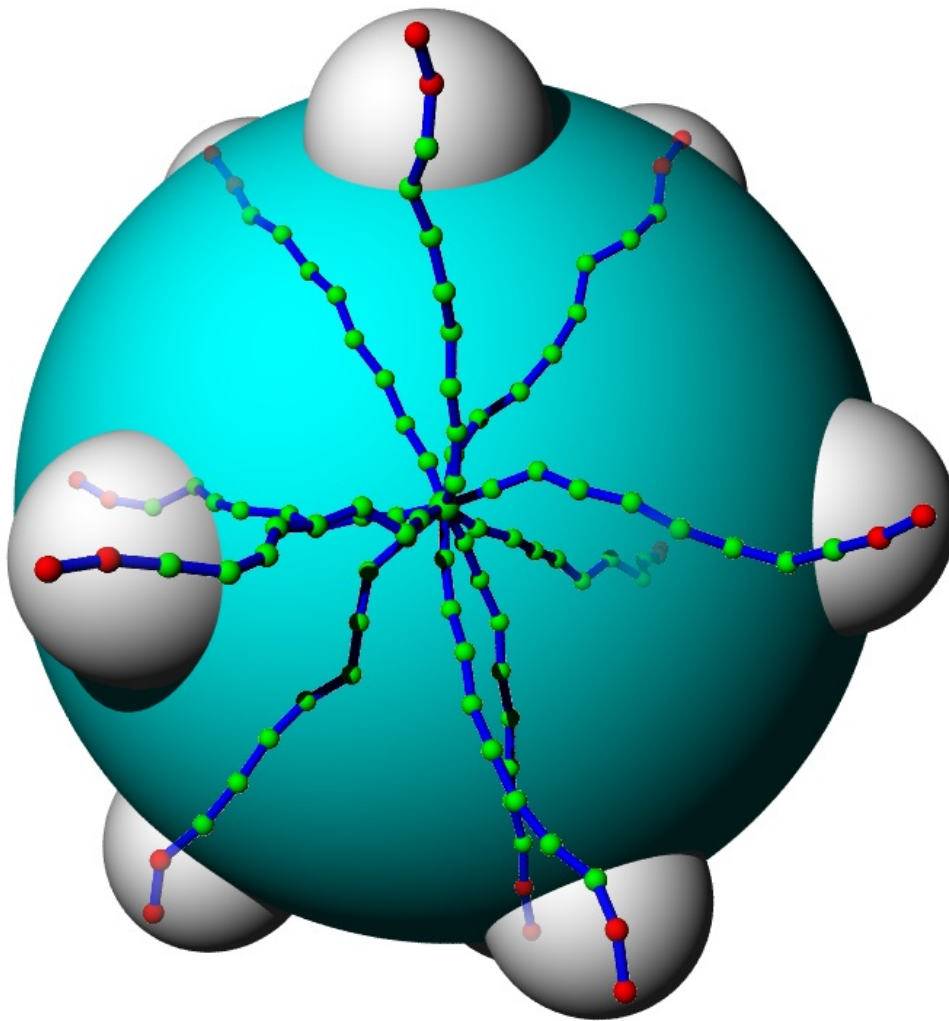


Figure 1.2: A sketch of an end-functionalized star polymer, within the terms of a Kuhn length model, and its correspondence to a patchy colloid description. Solvophilic species are shown in green and solvophobic species in red, while the bonds are colored deep blue. The light blue sphere resembles the effective colloid size and the range of steric repulsion while the white domes resemble the colloid's attractive patches.

A star polymer is formed by a number f of polymer chains that are connected at one common anchoring point. This can either be realized by a single branching (for low number of chains f) or by a sterically stabilized colloidal particle or micelle on which a number f of polymer chains are tethered or grafted (which allows much larger numbers of arms f up to hundreds or thousands). In the latter case,

it is important ensure that the core particle is much smaller than the polymer chain length to allow for a treatment of the particle as *ultrasoft* rather than *hard-core/soft-shell* [29]. After the introduction of a feasible synthesizing concept of star-branched polymers in 1962 [30], this particular polymeric architecture caught attention from both physicists and chemists. Early studies and research were reviewed in 1978 [31]. Advances in the synthesis, experimental characterization, theoretic description and computer simulation performance since then have led to considerable interest in star polymers.

Due to their excellent mechanical properties, star polymers of polystyrene-butadiene find application e.g. as stabilizers for clear resins [32] and pressure-sensitive adhesives [33, 34], in oil industry as viscosity modifiers [35], in lubricants, coatings [36, 37], binders in ink-based paints [38], and in control release drug delivery [39].

By anionic polymerization, it is possible to synthesize a branched core with up to $f = 128$ still active ends [40]. By postpolymerization linking, one can tether long chains onto this dendrimeric core [41]. Due to quite narrow molecular weight distributions of this polymerization system, a predetermined tuning of molecular weight is possible [42] and an ample degree of monodispersity in both number of arms f and degree of polymerization can be achieved.

Another way to synthesize star polymers is by a solution of diblock copolymers such as poly(ethylene-alt-propylene)-poly(ethylene oxide) (PEP-PEO) [43]. By adjusting the diblock composition and the interfacial tension, a nearly continuous tuning of the softness can be achieved, down to the aforementioned limit of a vanishing core size compared to the arm length, where a theoretical description via universal scaling as ultrasoft particles [29] is valid. The correspondence of such ultrasoft micelles to the theoretical description of a star polymer was shown by comparing the form factor of single molecules and the structure factor of concentrated systems [43]. Investigations of binary mixtures with linear polymer chains [44] further corroborate to the ultrasoft star polymer characteristics [45].

The subject of this work is a combination of the star architecture with the aforementioned chemical decoration of polymeric chains with functional groups: an end-functionalized or "telechelic" star polymer, in the remainder often abbreviated as TSP. The term *telechelic* was initially introduced in 1968 by Josef Arens [46, 47] and is used to describe the attractive nature of the arm ends. The combination of the greek words "telos" (τέλος), which means "end", and "chelos" (χείλος), which means "claw", can freely be translated as "end-functionalized". So an ABA-block copolymer with reactive or attractive A blocks can, for instance, be labeled as telechelic.

The first explicit preparation and property studies of telechelic polymer molecules dates back to 1960 [48]. The concept of telechelics drew great interest since then due to properties and applicability as grafting tools, polymeric extenders or as versatile building blocks for multiblock copolymers and other, more complex, soft material such as microgels. In recent years, great advancements have been made in the synthesis of such molecules. Worth mentioning are telechelic stars with $f = 3, 4, 5, 6$ arms of poly(L-lactide) with lipophilic pyrene terminal groups [49], which are of particular interest to medical research due to their biocompatibility (e.g. as drug-deliverers). Next to that, telechelic stars are very interesting and - as will be elaborated in this work - promising in terms of their rheological properties. In 2006, *Elkins et al.* [50] have synthesized and studied Poly(ethylene-co-propylene) star polymers, functionalized by self-complementary hydrogen-bonding sites on the arm terminals. Rheological investigations of concentrated systems in comparison to linear telechelic counterparts showed a much higher terminal relaxation time for the star architecture. Due to a highly associated structure, complex viscosity data revealed a non-Newtonian behavior for low frequencies. Similar structures have also been found for di-zwitterionic polybutadiene stars by *Vlassopoulos et al.* [51].

Experimental investigations are limited by the requirements involved in synthesizing samples and by the difficult task of bringing together macroscopic rheology and microscopic structure by means of on-the-fly measurements. However, there have been quite a number of theoretical and simulational studies on TSPs. The intra-association of higher-functionality stars leads to the possibility of multiple sites on which a number of arm terminals collapse. In the case of one single association site, the natural self-avoidance of the sterically repulsive inner blocks leads to a near-spherical, bloated shape of the molecule which has been named after its visual similarity with a water melon. Between a water melon conformation and an entirely unassociated, open star, lie certain configurations in which the molecule forms a number of sites around its anchoring center. The driving forces that determine the number of association sites and thus, the general shape, are the attraction strength and entropy. In a free energy consideration, a higher temperature leads to the dominance of entropy in this respect, and the arms remain unassociated ("open"). This single-molecule conformation behavior has been investigated by means of molecular dynamics simulations and scaling-based theory [52, 53]. In conformations with several aggregation sites, the molecule maximizes the distance between these sites due to entropy by distributing them equidistantly over the entire solid angle. The result is - again - a patchy colloidal particle with each site forming one attractive, i.e. solvophobic, patch. For instance, a conformation with four sites results in a tetrahedral patch distribution.

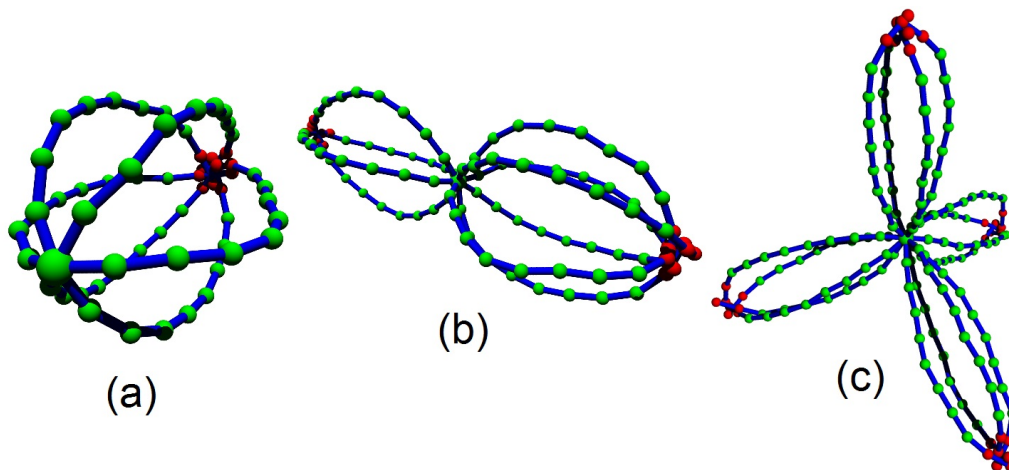


Figure 1.3: A sketch of possible collapsed, "patchy" conformations of a telechelic star polymer, within the terms of a Kuhn length model. Solvophilic species are shown in green, solvophobic species in red, while the bonds are shown in blue. (a) a "water melon" single patch conformation, (b) a "dumbbell" two patch conformation and (c) a four patch conformation resulting in a tetrahedral shape.

The single-molecule conformation can thus be used in concentrated systems to induce respective self-assembly. *Capone et al.* [54] have shown the stability of liquid crystal structures for telechelic stars of $f = 15$ arms and four patches, resulting in a diamond structure, and $f = 20$ arms and six patches, resulting in a simple cubic lattice structure.

Similar to linear diblock surfactant chains [24], the size ratio of the solvophilic A-block and the solvophobic B-block strongly determines the aggregation behavior of telechelic star polymers. In computer simulations, assuming equal relative molecular weight for both blocks, *Lo Verso et al.* [55, 56] have found for TSPs with $f = 3$ arms that when the B-block equals or exceeds the A-block in size, the concentrated system undergoes a first-order phase separation. On the other hand, when the A-block exceeds the B-block in size, the molecules form micelles. The first investigations in this work, Chapter 3, are based on these findings and extend to concentrated systems of telechelic stars with $f = 6, 10$

arms. We show that the phase separation dependence on the block size ratio holds, but find that in the intermediary case of a $\frac{60}{40}$ ratio of A- to B-block, a novel, interconnected network phase forms that coexists with enclosed micelles in the case of $f = 6$ arms. For systems of $f = 10$ arms, there are no micelles found next to the network, which is argued to be related to entropic effects on the single-molecule level.

In Chapter 4, we extend the model and focus the investigations on the role of chain rigidity in the macrophase-separation behavior. Rigid, telechelic star polymers can be realized by periodic ionization of the polymeric arms, where Coulomb repulsion drives the stars towards outstretched, open conformations. By changing salt concentration in the solvent, the ionic interactions are respectively screened and a fine-tuning of the rigidity strength can be achieved. Certain naturally stiff molecules with terminal functionalization also correspond to the rigid TSP model, such as single strands of DNA grafted onto a sufficiently small core-particle. Instead of forming micelles, such systems are more likely to form very large, highly associated structures such as gels. While in the generic model, which is the basis of all investigations within this work, the bond length corresponds to the Kuhn length of a polymeric chain, a simple increasing of the bond length in order to simulate a stiffer chain is not sufficient in this matter: in concentrated systems, volume exclusion of tightly interwoven aggregates, like micelles, and entanglement impose to a lattice model the requirement of a higher resolution of the polymer chains. The stiffness then needs to be explicitly included in the energy calculations of the Monte Carlo algorithm. A three body, angle dependent energy penalty favors conformations of stars with stiff, outstretched arms. But it leaves the chance for aggregates of heavily bent, interwoven stars, if their formation is - due to entropy and/or association energy - so favorable that the energy penalty is compensated. In this respect, arm rigidity is introduced as a third competitor, next to entropy and attraction strength, in the interplay determining the phase behavior. We investigate the effect of rigidity on the critical parameters of macrophase-separating systems of telechelic stars. We also find the emergence of hierarchies of liquid crystalline phases for very stiff TSPs and draw a thermodynamic comprehension, based on subtle manifestations of entropy.

In Chapter 5, we conclude the exploration of the rich phase behavior of telechelic stars by extending the investigations to microphase-separation scenarios with respect to arm stiffness, block size ratio and temperature regime. We find a novel form of inter-micellar aggregation in a necklace-fashion formation of large, worm-like super micelles. Indeed, the ample diversity in phase behavior goes far beyond that of non-functionalized ultrasoft particles or that of linear block-copolymers, and owes to the combination of star architecture and patchiness. The phases that we find are both interesting to investigate dynamically under shear or flow and are very promising to feature complex and unique rheological properties, which will be discussed in the outlook section in Chapter 6.

Chapter 2

Model, simulation details and method of analysis

The investigations that were performed in this work are based on a coarse-grained model of telechelic star polymers, which we will introduce in 2.1. To facilitate fast computation, we implement this model on a lattice geometry. We will cover this implementation in 2.3. To determine equilibrium configurations and obtain thermodynamic properties, we employ a Grand Canonical Monte Carlo (GCMC) simulation and consequent, statistically weighted measurements. The basic principles of a Monte Carlo simulation in the grand canonical ensemble will be introduced in 2.4. Simulating very concentrated and/or highly organized configurations, which both are of high concern in this work, often leads to extremely low acceptance rates in the regular Metropolis scheme. Hence we provide a full energetic configurational biasing to this GCMC, which will be elaborated in 2.5. In order to determine phase coexistence equilibria and to draw complete phase diagrams, results from a finite number of simulation runs are extended by histogram reweighting calculations, which will be elucidated in 2.6. Visualization of configurational snapshots was done with the program *Visual Molecular Dynamics (VMD)*, developed by the *Theoretical and Computational Biophysics Group* of the University of Illinois [57] under the UIUC open source public license. In order to classify certain aggregation scenarios, we employ a morphological analysis, based on the calculation of the *Minkowski* functionals, for which we give a comprehensive illustration in the Appendix.

2.1 Coarse-graining model

The diblock copolymer star molecule is modeled by means of a generic coarse-graining approach. While the polymeric chain constituting the star's arm can be of arbitrary degree of polymerization, we model one arm by a connection of ten generic beads that locate linearly on the underlying lattice. These should be taken as effective monomers that represents a blob, containing a polymer chain segment that, in turn, consists of a group of microscopic units [58]. While the bead conformation is self-avoiding, i.e. a single lattice site may not be occupied by more than one bead, the polymeric chain is considered fully flexible within the terms of the freely-jointed chain model (see [3]). The distance between two successive beads on the chain is the Kuhn-length [1, 2] and all bond and torsion angles are equally probable within the constraints of the lattice. This describes an *ideal, self-avoiding polymer chain*.

2.1.1 Rigidity

However, real polymers do have a certain stiffness and require energy in order to bend them. While theoretic descriptions such as the wormlike chain model define a certain persistence length (see [3]), i.e. a length scale below which the polymer chain behaves effectively like a stiff rod, it is just as well possible to extend the freely-jointed chain to be applicable to more realistic polymers with a certain bending stiffness. This can be achieved in a Monte Carlo simulation, where the overall conformational energy determines the statistical probability of a certain configuration, by adding an energetic penalty to an angle between a successive pair of bonds. We define this rigidity energy penalty as

$$E_{\text{rig}} = \alpha (1 + \cos \theta), \quad (2.1)$$

where θ denotes the angle between two successive bonds.

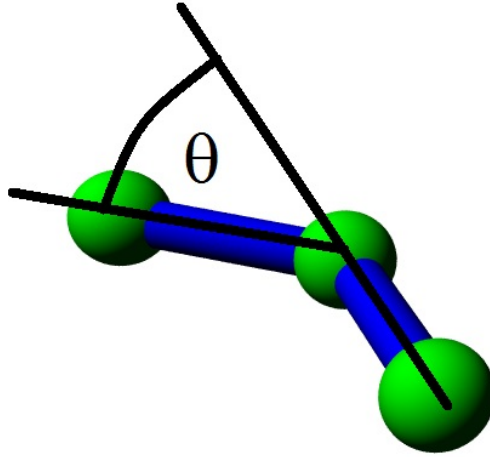


Figure 2.1: The angle between two successive bonds along a chain.

Note that θ is not the angle between the unit vectors of these successive bonds, which would be zero if the chain is straight. It is rather the angle spanned between the two joining chain segments and is, thus, $\theta = \pi$ for a straight chain at this point. In this way, the energy penalty is only non-zero for angles which deviate from the straight configuration. The maximum energy penalty that can occur is $E_{\text{rig}} = 2\alpha$ in the case of a full reversion of the chain at this point. The self-avoidance requirement, however, forbids such a full reversion in the first place. As an influential factor in the phase behavior, the rigidity can be easily tuned this way by the value of the prefactor α in equation 2.1. Setting $\alpha = 0$ fully corresponds to the self-avoiding ideal chain model, while very high values of $\alpha \approx 100$ or beyond will correspond to an object of (loosely) co-joint rods. The anchoring point of the star molecule is excluded from the rigidity calculation. All adjacent bond pairs with the anchoring point in their middle suffer no angle-dependent energy penalty. This allows for a free rotation of the chains - or rods - around the anchoring point, giving no artificially prescribed orientational correlations.

2.2 Nomenclature

In our two species model, we denote the solvophilic species of the inner A block with an H ("head" monomers), the solvophobic and effectively attractive species of the terminal B block with a T ("tail" monomers) and the functionality, i.e. the number of arms of a star molecule with f . To denote the architecture of a molecule - and also a solution of molecules of a given, fixed architecture - we use a sequence bracket notation, where $H(H_nT_m)_f$ denotes a molecule with a central H species as common anchoring point of f interconnected arms that consist of an inner block of n beads of the H species and an outer block of m beads of the T species. As a simplified parameter to describe the amphiphilicity, we denote the fraction of solvophobic beads along an arm as $r = \frac{m}{n+m}$, stated in %. As stated in 2.1, we model all chains to have a total number of $n + m \equiv 10$ beads, resulting in a handy increment of r in steps of 10%.

2.3 Lattice model

All investigations in this work are based on computer simulations of a lattice model. This model employs three options for a single lattice site, identical to three possible species: S , which denotes the solvent, H and T for the solvophilic and solvophobic species, respectively. The considered systems are *incompressible*, i.e. there are no empty lattice sites. A given cubic box of our lattice simulation consists of $V = L \times L \times L$ lattice sites, which are considered to be filled with the solvent by default. The concentration is thus defined as the total number of H and T beads within the box divided by all lattice sites. With the functionality f , ten beads per arm and one bead per molecule as anchoring point, the concentration can be written as $\phi = \frac{\mathcal{N}}{V}$, with $\mathcal{N}$ being the instantaneous number of molecules in the simulation box.

2.3.1 Interaction energies

The interactions that are considered are short range and are therefore only calculated for neighboring lattice sites on the simple cubic lattice, with a conformation number of $Z = 26$. The possible distances of interacting species are thus $\sqrt{1} = 1$, i.e. the unit cell *ledge* or miller index (100), $\sqrt{2}$, i.e. a unit cell *face diagonal* or miller index (110) and $\sqrt{3}$, i.e. a unit cell *space diagonal* or miller index (111). Despite the variation in distance, all these relative positions are just considered as *neighboring*, and result all in the same interaction energy. This is justified by the picture that a single bead is not strictly located at its lattice site, but is rather free to move within the domain of its eight adjacent unit cells. A distance based calculation of interaction potentials is not appropriate in this lattice model because of two reasons: firstly it would promote certain configurations over others, e.g. force the species with the highest interaction energy into configurations on a sub lattice of the most favorable spacing. Spherical isotropy of the interaction potentials requires, however, that there is no preferential ordering. Secondly, a distance based calculation would require the usage of float variables and non-linear calculations, whose avoidance is the very idea behind a lattice simulation. The interaction energies are therefore zero if the two considered beads are not in the same conformation cell, or, if they are, an integer multiple of a fixed energy parameter ϵ . The interaction energies of the three

species are chosen as

$$\begin{aligned}
\epsilon_{SS} &= 0 \\
\epsilon_{SH} &= 0 \\
\epsilon_{HH} &= 0 \\
\epsilon_{HT} &= 0 \\
\epsilon_{TT} &= -1 \\
\epsilon_{TS} &= 0
\end{aligned} \tag{2.2}$$

This corresponds to the Larson model for amphiphile-oil-water solutions [59, 60, 61, 62]. Assuming perfect solubility of the solvophilic species, the interaction of an H bead with an S bead is the same as that with another H bead. A non-zero value for this interaction energy would only add up to a configuration-independent constant. In a grand canonical consideration this constant only alters the chemical potential, whose numerical value is of no physical meaning and can be rigorously redefined. Thus, this constant can be set to zero by setting all interactions between H and S beads to zero. The solvophobicity of the T beads is expressed in an effectively attractive interaction potential $\epsilon_{TT} = -1$. Since all interactions involving the solvent S are, thus, zero, the species can be discarded in interaction considerations and the overall energy scale describing the system reduces to

$$\epsilon = 2\epsilon_{HT} - \epsilon_{HH} - \epsilon_{TT} = 1 \tag{2.3}$$

By that, we can define a reduced temperature for the system as

$$T^* = \frac{k_B T}{\epsilon} = k_B T \tag{2.4}$$

2.4 Grand Canonical Monte Carlo

The grand canonical ensemble uses as thermodynamic variables the Temperature T , the volume V and the chemical potential μ , which are, thus, constants for a specific simulation run. Run-averaged values such as the average concentration ϕ are thus grand canonical averages.

$$\phi = \frac{N}{V} = \frac{\langle \mathcal{N} \rangle_{\mu, V, T}}{V} \tag{2.5}$$

with $\mathcal{N}$ being the instantaneous number of molecules, i.e. stars, in the simulation box and $N = \langle \mathcal{N} \rangle_{\mu, V, T}$ being the grand canonical average of $\mathcal{N}$.

New configurations are generated via three kinds of Monte Carlo steps:

1. entire molecule insertion or deletion
2. deletion and successive regrowth of a single chain on one molecule
3. a cluster move in which a spatially isolated aggregate of possibly many molecules is being moved in a random direction over a random number of lattice sites, without change of the aggregate-internal conformation

The algorithm picks, at the beginning of each Monte Carlo step, one of these options randomly, where the probability to pick option 1 is $\mathbf{p}_1 = 0.499$, the probability to pick option 2 is $\mathbf{p}_2 = 0.5$ and the

probability for a cluster move $\mathbf{p}_3 = 0.001$. This is due to the cluster move being only a "good shake" to throw a system that might be effectively stuck in a certain region in phase space, out of its tar pit. This necessity arises only seldom, leading to a small probability for cluster moves. If option 1 is chosen, the algorithm decides by a 50/50 chance to either delete an existing or insert a new molecule. The GCMC was originally developed by *Norman and Filinov* [63] for classical fluids. For an illustrative derivation of the partition function and probability density, see [64] or [65]. Say we have a system of volume V at reduced temperature $\beta = \frac{1}{k_B T}$ with a chemical potential μ and a thermal de Broglie wavelength of Λ . The probability density to find N (not necessarily) polymeric molecules in a conformation set of coordinates $\mathbf{s}^N$ is

$$\mathcal{P}(\mathbf{s}^N, N) = \frac{\exp(\beta\mu N) V^N}{\Lambda^{3N} N!} \exp(-\beta U(\mathbf{s}^N)). \quad (2.6)$$

A canonical step in this respect, i.e. a conformation change without changing the number of molecules N , is then accepted with the Metropolis criterion

$$\text{acc}(\mathbf{s}^N \longrightarrow \mathbf{s}'^N) = \min\left(1, \exp[-\beta(U(\mathbf{s}'^N) - U(\mathbf{s}^N))]\right). \quad (2.7)$$

Note that the chemical potential plays no role at all in this step, fully corresponding to the canonical analogue.

The two grand canonical steps, i.e. a molecule insertion or deletion, respectively, is accepted with the Metropolis criteria

$$\text{acc}(\mathbf{s}^N \longrightarrow \mathbf{s}^{N+1}) = \min\left(1, \frac{\exp(\beta\mu)V}{\Lambda^3(N+1)} \exp[\beta U(\mathbf{s}^N) - \beta U(\mathbf{s}^{N+1})]\right) \quad (2.8)$$

for an insertion and

$$\text{acc}(\mathbf{s}^N \longrightarrow \mathbf{s}^{N-1}) = \min\left(1, \frac{\Lambda^3 N}{\exp(\beta\mu)V} \exp[\beta U(\mathbf{s}^N) - \beta U(\mathbf{s}^{N-1})]\right) \quad (2.9)$$

for a deletion. It should be noted that the thermal de Broglie wavelength Λ and the chemical potential μ can be combined as

$$\frac{\exp(\beta\mu)}{\Lambda^3} = \frac{\exp(\beta\mu)}{\exp(\log[\Lambda^3])} = \exp\left(\beta\left[\mu - \frac{\log(\Lambda^3)}{\beta}\right]\right) = \exp(\beta\mu^*) \quad (2.10)$$

with $\mu^* = \mu - \frac{\log(\Lambda^3)}{\beta}$ as a redefined chemical potential, where $\frac{\log(\Lambda^3)}{\beta}$ is a run-specific constant. Since the number value of the chemical potential has no physical meaning, we can rigorously redefine it and drop the thermal de Broglie wavelength from all considerations without worry.

2.5 Configurational biasing / calculus of Rosenbluth weights

With the exception of cluster moves, all MC steps feature a full-energetic configurational biasing. This includes the polymer molecule self-avoidance, interaction energies and the chain rigidity. Although highly demanding both in implementing and in computational power, the configurational biasing is in fact a speed-up for very dense solutions where totally random regrowths or insertions will almost always be rejected. The biasing technique allows for an "intelligent growth" into the most favorable

configuration while still being statistically correct with respect to Boltzmann distribution due to the way the Metropolis acceptance criterion is corrected for this biasing by Rosenbluth weights.

The concept of configurational biasing and the calculation of Rosenbluth weights is a modification to the original, "standard" Metropolis scheme [66], that was developed by *Metropolis*, the *Rosenbluths* and the *Tellers* in 1953. The Rosenbluths found particular challenge in the simulation of polymer chains on a lattice [67]. When growing a polymer chain, no matter if on a lattice or in continuous space, a regular random walk does not cover the self-avoidance inherent to polymer molecules. The problem is particularly evident on a lattice: either one allows the chain to grow regularly onto itself, which violates the self-avoidance property, or one relates an overlap of beads to a huge energy (repulsion potential), accepting a frequent rejection of moves that heavily drops computation performance. The idea was to include the self-avoidance by *biasing* the chain growth towards free lattice sites, while remaining statistically correct in terms of Boltzmann distribution. In [68], it is shown how this self-avoiding random walk scheme can be extended to arbitrary molecular systems. Here, we will sketch the scheme for the di-block copolymer stars investigated in this work and for a Grand Canonical Monte Carlo algorithm.

2.5.1 Molecule insertion

The following procedure is executed each time a new molecule is attempted to be inserted into the system:

1. A random position on the lattice is picked and checked for its occupying species. If it is occupied by an H or T species, the move is rejected right away. If the lattice is occupied by a solvent S species, for which we will in the remainder refer to as a *free* lattice site, the anchoring point is placed and its interaction energy with the surrounding $Z = 26$ lattice sites is calculated into u_1 , i.e. the total energy of bead 1.

$$u_1 = \sum_{k=1}^Z \epsilon_{1k} \quad (2.11)$$

where ϵ_{1k} is the interaction energy of the anchoring point with the species on the k th surrounding lattice site.

2. For the placement of every successive bead with index l , and one needs to distinguish two cases:

- (a) The first bead of every chain is placed without a calculation of rigidity. Rigidity is a three body- or two bond-interaction. Since with the first bead, also the first bond of the chain is placed, there is no chain rigidity to be considered, yet.

All $Z = 26$ neighboring lattice sites of the anchoring point are possible locations for the placement of the new bead, and are saved in a location set $\{\mathbf{v}\} = (\mathbf{v}_1, \dots, \mathbf{v}_{26})$. For each of these sites, the new bead is virtually set and the total energy is calculated that the bead *would have, would it be placed at that location*. If a position $\mathbf{v}_i$ is already occupied by an H or T species, the energy is set to infinity (i.e. a huge numerical value) as a result of steric repulsion. If $\mathbf{v}_i$ is free, its total energy is calculated by checking the $Z = 26$ neighbors of the virtual location for their species

$$u_l^{tot}(\mathbf{v}_i) = u_l^{int}(\mathbf{v}_i) = \sum_{j=1}^Z \epsilon_{ij}, \quad (2.12)$$

where ϵ_{ij} is the interaction energy of the virtual position $\mathbf{v}_i$ with the j th neighboring lattice site. The total energy u^{tot} is, in this case, equal to the interaction energy u^{int} since there is no rigidity to be considered.

- (b) At the placement of any other bead along a chain, rigidity needs to be considered. Thus, the total energy u^{tot} comprises both interaction energy u^{int} and rigidity energy penalty u^{rig} . The rigidity energy is dependent on the angle between two successive bonds, see eq. 2.1. This angle is calculated via the scalar product of two successive bond (unit) vectors. With the virtual position of the to-be-placed bead l being $\mathbf{v}_i$ and the positions of the two previous beads being $\mathbf{r}^{l-1}$ and $\mathbf{r}^{l-2}$, respectively, the angle Θ in eq. 2.1 is

$$\cos(\Theta) = \frac{(\mathbf{v}_i - \mathbf{r}^{l-1}) \cdot (\mathbf{r}^{l-1} - \mathbf{r}^{l-2})}{\|\mathbf{v}_i - \mathbf{r}^{l-1}\| \|\mathbf{r}^{l-1} - \mathbf{r}^{l-2}\|} \quad (2.13)$$

so the rigidity energy can be calculated by

$$u_l^{rig}(\mathbf{v}_i) = \alpha \left(1 + \frac{(\mathbf{v}_i - \mathbf{r}^{l-1}) \cdot (\mathbf{r}^{l-1} - \mathbf{r}^{l-2})}{\|\mathbf{v}_i - \mathbf{r}^{l-1}\| \|\mathbf{r}^{l-1} - \mathbf{r}^{l-2}\|} \right) \quad (2.14)$$

and the total energy of the virtual position adds up to

$$u_l^{tot}(\mathbf{v}_i) = u_l^{int}(\mathbf{v}_i) + u_l^{rig}(\mathbf{v}_i) \quad (2.15)$$

The Rosenbluth weight $\mathfrak{w}$ of the new bead is basically the sum over all Boltzmann factors of the virtual postions

$$\mathfrak{w}(l) = \sum_{i=1}^Z \exp[-\beta u_l^{tot}(\mathbf{v}_i)]. \quad (2.16)$$

Once this has been calculated, one of the virtual positions is randomly chosen for the new location, with the probability weights being the Boltzmann factors, normalized by the Rosenbluth weight

$$\mathfrak{p}(\mathbf{v}_i) = \frac{\exp[-\beta u_l^{tot}(\mathbf{v}_i)]}{\mathfrak{w}(l)}. \quad (2.17)$$

The new bead is then set at the so chosen location

$$\mathbf{r}^l = \mathbf{v}_i \quad (2.18)$$

3. Step 2 is repeated until all $M = 10f + 1$ beads of the molecule are set. Should the algorithm encounter a "dead end", i.e. a situation when there is no free lattice site for a new bead to be placed, it will place the bead onto an H or T species and, due to the infinitely large energy, save a Rosenbluth weight with value zero for this bead. This will eventually lead to a rejection of the new configuration.

Once the whole molecule has been grown this way, the *total Rosenbluth weight* is calculated by taking the product of all Rosenbluth weights, divided by the number of possible growth

directions for each bead, i.e. the number of virtual positions, being $Z \equiv 26$.

$$\mathfrak{W} = \exp(-\beta u_1) \prod_{l=2}^M \frac{\mathfrak{w}(l)}{Z} \quad (2.19)$$

where u_1 is the energy of the anchoring point from eq. 2.11¹

4. The configuration with the added new molecule is then accepted with a probability

$$\text{acc}(N \rightarrow N + 1) = \min \left(1, \frac{\exp(\beta\mu)V}{N + 1} \mathfrak{W} \right). \quad (2.20)$$

2.5.2 Molecule deletion

The molecule deletion follows the same pattern as the new molecule insertion. Since it needs to be done in reverse order, the only qualitative difference is the missing random placement of new beads. This does not alter the calculation of the Rosenbluth weights, however.

1. A random molecule is chosen to be deleted. The deletion starts at the last indexed bead, i.e. the outermost bead of the last indexed chain.
2. For every bead l , we need to distinguish, just as for the insertion algorithm, if the bead is adjacent to the anchoring point, in which case there is no rigidity to be considered.
 - (a) If the bead is not adjacent to the anchoring point, its total energy is calculated as the sum of interaction energy and rigidity energy

$$u_l^{\text{tot}}(\mathbf{r}^l) = u_l^{\text{int}}(\mathbf{r}^l) + u_l^{\text{rig}}(\mathbf{r}^l). \quad (2.21)$$

Then a set of $Z - 1 = 25$ virtual positions $\{\mathbf{v}_i^l\}$ on the lattice is generated where the bead could also have been placed (in a fictive growth process) and for each of these, the energy is calculated that the particle would have had, had it been placed at that virtual position.

$$u_l^{\text{tot}}(\mathbf{v}_i) = u_l^{\text{int}}(\mathbf{v}_i) + u_l^{\text{rig}}(\mathbf{v}_i) \quad (2.22)$$

- (b) For the first bead on every chain, i.e. the bead adjacent to the anchoring point, no rigidity is considered and the total energy comprises only the interaction energy.

$$u_l^{\text{tot}}(\mathbf{v}_i) = u_l^{\text{int}}(\mathbf{v}_i) \quad (2.23)$$

The Rosenbluth weight of the to-be-deleted bead is the sum over the Boltzmann factors of all virtual positions and of the actual, old position.

¹Note that the energy of the anchoring point u_1 is not normalized by Z . This due to the fact that the anchoring point was set right away without considering virtual positions. It can be argued that the number of virtual positions for the anchoring point is the total number of lattice sites in the box, being the volume $V = L \times L \times L$, and should, thus, be normalized by. Some documentations of configurational biasing methods actually do normalize by the volume this way. However, since the anchoring point position is picked randomly with a *uniform* distribution and there is no *biased* positioning, this is not a *weighted* positioning and is, thus, not normalized, but rather treated like an *unbiased* positioning like it is performed in the standard, unweighted Metropolis scheme. In any case, normalizing by the volume would add V into the denominator in eq. 2.20. Analog to the thermal de Broglie wavelength in Section 2.4, the volume can be "black-boxed" by a sheer redefinition of the chemical potential μ , whose numerical value has no physical meaning and can be rigorously redefined by an additive constant.

$$\mathfrak{w}(l) = \exp[-\beta u_l^{tot}(\mathbf{r}^l)] + \sum_{i=1}^{Z-1} \exp[-\beta u_l^{tot}(\mathbf{v}_i)]. \quad (2.24)$$

The bead at its actual position is then deleted. The fact that it actually *was* at that particular position is not important for the Rosenbluth sampling, only the probability distribution of all possible positions where it *could have been* set in a fictive growth process, which is covered by the Rosenbluth weight calculation.

3. Step 2 is repeated until all $M = 10f + 1$ beads of the molecule are deleted but the anchoring point, for which only the interaction energy is calculated as

$$u_1 = \sum_{k=1}^Z \epsilon_{1k}. \quad (2.25)$$

Then the total Rosenbluth weight of the deletion is calculated as

$$\mathfrak{W} = \exp(-\beta u_1) \prod_{l=2}^M \frac{\mathfrak{w}(l)}{Z} \quad (2.26)$$

and the anchoring point is deleted, as well.

4. The deletion of the molecule is accepted with probability

$$\text{acc}(N \longrightarrow N - 1) = \min \left(1, \frac{N}{\exp(\beta\mu)V} \frac{1}{\mathfrak{W}} \right). \quad (2.27)$$

2.5.3 Single chain regrowth

The insertion or deletion of a whole molecule is a rather large leap in phase space. In order to thoroughly explore phase space, a combination of grand canonical and canonical moves is appropriate, since latter resemble smaller leaps in phase space compared to the grand canonical ones. As canonical move, we perform the regrowth of a single molecule arm/chain without changing the conformation of the rest of the molecule. This regrowth is a combination of the deletion and the insertion process, and the calculated Rosenbluth weights are compared in the eventual Metropolis acceptance criterion.

1. A random molecule is picked, of which a random arm is selected to be regrown.
2. The beads of the arm are deleted successively, similar to the deletion process step 2. A bead's total energy is calculated as the sum of interaction energy and rigidity energy

$$u_l^{tot}(\mathbf{r}^l) = u_l^{int}(\mathbf{r}^l) + u_l^{rig}(\mathbf{r}^l). \quad (2.28)$$

The set of $Z - 1 = 25$ virtual positions $\{\mathbf{v}_i^l\}$ on the lattice is generated. For each, the energy is calculated that the particle would have had, had it been placed at that virtual position.

$$u_l^{tot}(\mathbf{v}_i) = u_l^{int}(\mathbf{v}_i) + u_l^{rig}(\mathbf{v}_i) \quad (2.29)$$

The Rosenbluth weight of the to-be-deleted bead is, analog to the deletion step 2,

$$\mathfrak{w}^{old}(l) = \exp[-\beta u_l^{tot}(\mathbf{r}^l)] + \sum_{i=1}^Z \exp[-\beta u_l^{tot}(\mathbf{v}_i)]. \quad (2.30)$$

3. Step 2 is repeated until all beads but the first of the arm are deleted.
4. For the last bead on the arm, i.e. the bead adjacent to the anchoring point, no rigidity is considered and the total energy of both actual and virtual position comprises only the interaction energy.

$$u_1^{tot}(\mathbf{v}_i) = u_1^{int}(\mathbf{v}_i) \quad (2.31)$$

$$u_1^{tot}(\mathbf{r}^1) = u_1^{int}(\mathbf{r}^1) \quad (2.32)$$

where the Rosenbluth weight is

$$\mathfrak{w}^{old}(1) = \exp[-\beta u_1^{tot}(\mathbf{r}^1)] + \sum_{i=1}^{Z-1} \exp[-\beta u_1^{tot}(\mathbf{v}_i)]. \quad (2.33)$$

and the total Rosenbluth weight of the old configuration is

$$\mathfrak{W}^{old} = \prod_{l=1}^{10} \frac{\mathfrak{w}^{old}(l)}{Z}. \quad (2.34)$$

Then the first bead of the arm is deleted.

5. The new arm is grown, where the first bead needs to be distinguished in the calculation from all the following beads
 - (a) The new, first bead is - again - placed without calculation of rigidity. A set of $Z = 26$ virtual positions $\{\mathbf{v}_i\}$ at the lattice sites surrounding the anchoring point is generated and their energy is calculated as

$$u_l^{tot}(\mathbf{v}_i) = u_l^{int}(\mathbf{v}_i) = \sum_{j=1}^Z \epsilon_{ij}, \quad (2.35)$$

where ϵ_{ij} is the interaction energy of the virtual position $\mathbf{v}_i$ with the j th neighboring lattice site.

- (b) For every other bead, rigidity is considered and the total energy is

$$u_l^{tot}(\mathbf{v}_i) = u_l^{int}(\mathbf{v}_i) + u_l^{rig}(\mathbf{v}_i) \quad (2.36)$$

The Rosenbluth weight is in both cases calculated as

$$\mathfrak{w}^{new}(l) = \sum_{i=1}^Z \exp[-\beta u_l^{tot}(\mathbf{v}_i)]. \quad (2.37)$$

One of the virtual positions is randomly, with respect to the Rosenbluth-normalized Boltzmann distribution, chosen for the new location. The probability for each virtual position $\mathbf{v}_i$ is

$$\mathbf{p}(\mathbf{v}_i) = \frac{\exp[-\beta u_l^{\text{tot}}(\mathbf{v}_i)]}{\mathbf{w}(l)}. \quad (2.38)$$

The new bead is then set at the so chosen location

$$\mathbf{r}^l = \mathbf{v}_i. \quad (2.39)$$

6. Step 5 is repeated until all beads of the new arm are set. The total Rosenbluth weight of the new configuration is calculated as

$$\mathfrak{W}^{\text{new}} = \prod_{l=1}^{10} \frac{\mathbf{w}^{\text{new}}(l)}{Z} \quad (2.40)$$

7. The new configuration is accepted over the old one with probability

$$\text{acc}(\text{old} \rightarrow \text{new}) = \min \left(1, \frac{\mathfrak{W}^{\text{new}}}{\mathfrak{W}^{\text{old}}} \right). \quad (2.41)$$

2.6 Histogram reweighting

Run-specific constants in a GCMC are the temperature T or the reduced temperature T^* , the chemical potential μ and the simulation box volume V . The grand canonical ensemble respects variation in pressure p and the number of particles $\mathcal{N}$ and thus allows for concentration fluctuations². This allows for the sampling of macrophase coexistence within a single simulation run, even if the two phases have different densities, like it is the case for a gas-liquid phase coexistence. If the free energy barrier between states of each phase is sufficiently low, a Monte Carlo algorithm can overcome it and the overall concentration in the simulation box changes from a low one (for the gaseous phase) to a high one (for the liquid phase) or vice versa. When close to the critical point of a first-order phase transition, the concentration fluctuation becomes theoretically infinitely large due to the divergence of susceptibility at a critical point, in this case the isothermal compressibility

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T. \quad (2.42)$$

A histogram of e.g. molecule number N and internal energy U of any fluctuating simulation run includes information not only on a point, but a finite *volume* in phase space, within the limits of the fluctuating variables. For any full set of thermodynamic properties that is sampled during the course of this simulation, the histogram gives a statistical approximation to the probability to find a system of given species under the condition of the constant grand canonical variables T (or β), μ and V in exactly this configuration, i.e. with values for pressure p , concentration ϕ , energy U and so on. However, it is also possible to conjecture from the statistics of a system within the limits of its fluctuations, to the thermodynamic properties *beyond* the limits of these fluctuations. This way, it is possible to determine e.g. complete phase diagrams over a broad range of the respective variables on the basis of only a finite (and rather small) number of actual simulation runs.

²In the remainder of this work we may sometimes use the terms "density" and "concentration" or "volume fraction" equivalently. Because there is no information about the molecular weight of the polymeric molecules or the solvent, this is sloppy. However, the picture of an "empty" box at concentration zero, with only solvent beads on the lattice sites, which is then filled by star molecules, is intuitively analog to means of a density.

In 1988, *Ferrenberg and Swendsen* presented a method to obtain from a single Monte Carlo run, complete thermodynamic information on a first-order phase transition in a classic 2D Ising spin model [99]. A year later, they presented how to further optimize this concept by combining the information of several Monte Carlo runs [100]. This concept is often referred to as the *Ferrenberg-Swendsen-patching* and has been applied to phase transitions of non-discrete models, as well. *Wilding*, for instance, showed in 1995 how to use this concept for first-order phase transitions in fluids [69, 70, 71].

Here we will elaborate the usage of what is in general now referred to as *histrogram reweighting* in the context of a Grand Canonical Monte Carlo simulation, which has been reviewed and demonstrated by *Panagiotopoulos* in 1998 [101]. The basic idea in this respect is to gather data from a single run to provide information over a broad regime of thermodynamic variables. This is done via the calculation of a universal probability density, based on free energy calculus. One can then use this probability distribution to predict the thermodynamics of the system at an arbitrary configuration in phase space. To increase the quality and range in phase space of this prediction, a technique of patching histograms at different locations in phase space is demonstrated. This can be combined with finite size scaling arguments for a critical phenomenon of known universality class, e.g. Ising, to iteratively predict a configuration which best matches this universality class and, thus, gives a fairly good estimate of the location of a critical point.

2.6.1 Guess from a single histogram

With the grand canonical variables T , μ and V constant, two fluctuating variables which are easy to measure in our GCMC are the molecule number N and the total configurational energy E , which is already measured during the process of configurational biased Monte Carlo, see section 2.5. The GCMC measures the instantaneous molecule number $\mathcal{N}$ and total energy E within a Markovian interval and writes them down in a respective histogram $f(\mathcal{N}, E)$. The probability of a system at temperature $\beta = \frac{1}{k_B T}$ and chemical potential μ to have $\mathcal{N}$ molecules and the total configurational energy E is

$$\mathbf{p}(\mathcal{N}, E; \mu, \beta) = \frac{f(\mathcal{N}, E) \exp(\beta E - \beta \mu \mathcal{N})}{\sum_{\mathcal{N}, E} f(\mathcal{N}, E) \exp(\beta E - \beta \mu \mathcal{N})}. \quad (2.43)$$

Having obtained a histogram $f(\mathcal{N}, E)$, one can use this probability distribution to make a "guess" for the system at temperature β^* and chemical potential μ^* via

$$\mathbf{p}(\mathcal{N}, E; \mu^*, \beta^*) = \frac{\mathbf{p}(\mathcal{N}, E; \mu, \beta) \exp[(\beta^* - \beta)E - (\beta^* - \beta)(\mu^* - \mu)\mathcal{N}]}{\sum_{\mathcal{N}, E} \mathbf{p}(\mathcal{N}, E; \mu, \beta) \exp[(\beta^* - \beta)E - (\beta^* - \beta)(\mu^* - \mu)\mathcal{N}]}. \quad (2.44)$$

The denominator is an estimate of the partition function, in this case, over the range of fluctuations of $\mathcal{N}$ and E in the performed GCMC run. The quality of this guess is strongly dependent on the statistical reliability of the run, and only valid for phase space regions within the range of fluctuations. However, one can extend this idea by taking into account several runs at different β and μ , that have a certain degree of overlap in both $\mathcal{N}$ and E .

2.6.2 Patching multiple histograms

The theoretical probability to find the system with a particle number $\mathcal{N}$ at total energy E is given by

$$f(\mathcal{N}, E) = \frac{\Omega(\mathcal{N}, V, E) \exp(-\beta E + \beta \mu \mathcal{N})}{\Xi(\beta, \mu, V)} \quad (2.45)$$

with the partition functions of the microcanonical ensemble $\Omega(\mathcal{N}, V, E)$ and the grand canonical ensemble $\Xi(\beta, \mu, V)$. Since these partition functions are values derived from the thermodynamic limit and can never completely be calculated by means of finite simulations, one needs to relate them to actual *measurable* variables. The thermodynamic potential related to the microcanonical partition function is the entropy $S(\mathcal{N}, V, E)$

$$S(\mathcal{N}, V, E) = k_B \ln (\Omega(\mathcal{N}, V, E)). \quad (2.46)$$

Resolving eq. 2.45 to $\Omega(\mathcal{N}, V, E)$ leads to

$$\Omega(\mathcal{N}, V, E) = f(\mathcal{N}, E) \exp(\beta E - \beta \mu \mathcal{N}) \Xi(\beta, V, \mu) \quad (2.47)$$

$$\ln (\Omega(\mathcal{N}, V, E)) = \ln (f(\mathcal{N}, E)) + \beta E - \beta \mu \mathcal{N} + \ln (\Xi(\beta, V, \mu)) \quad (2.48)$$

$$\frac{1}{k_B} S(\mathcal{N}, V, E) = \ln (f(\mathcal{N}, E)) + \beta E - \beta \mu \mathcal{N} + C \quad (2.49)$$

where $C = k_B \ln (\Xi(\beta, V, \mu))$ is constant for a specific run.

Thermodynamics requires the entropy $S(\mathcal{N}, V, E)$ to be a continuous function over almost all of phase space, the exception being first-order phase transitions. Putting this aside for now, we require two runs at different temperature T and chemical potential μ to share the same, system-inherent thermodynamic potential. When the two runs are compared by means of their $\mathcal{N}$ and E histograms, and they have sampled at least a few pairs $(\mathcal{N}, E)$ in common, we can require the entropy in this area of overlap in the $\mathcal{N}$ - E -plane to be unique and continuous. In order to achieve this, one needs to patch the two entropy functions from two histograms $f_1(\mathcal{N}, E)$ and $f_2(\mathcal{N}, E)$ onto another by tuning the constant C in eq. 2.49.

Ferrenbergs and Swendsens work [100] is based on a spin system, where they related the patching of a number of runs to the free energy as the shared thermodynamic potential. In our case, using instead entropy, the derivation is entirely analogous. For a given number of independent runs $i = 1, \dots, R$, assuming they have the same statistical efficiency and are all Markovian, i.e. independent, the composite probability of a system at temperature $\beta = \frac{1}{k_B T}$ and chemical potential μ to have $\mathcal{N}$ molecules and the total configurational energy E is

$$\mathbf{p}_R(\mathcal{N}, E; \mu, \beta) = \frac{\sum_{i=1}^R f_i(\mathcal{N}, E) \exp(\beta E - \beta \mu \mathcal{N})}{\sum_{i=1}^R \exp(\beta_i E - \beta_i \mu_i \mathcal{N} + C_i) \sum_{\mathcal{N}, E} f_i(\mathcal{N}, E)}. \quad (2.50)$$

The set of constants $\{C_i\}$ can be determined by

$$\exp(C_i) = \sum_E \sum_{\mathcal{N}} \mathbf{p}_R(\mathcal{N}, E; \mu, \beta) \quad (2.51)$$

and equations 2.50 and 2.51 are iterated until convergence is achieved. This iteration and the evaluation of the "weights" $\{C_i\}$ is what gives the procedure the name "histogram reweighting". After this process, the composite probability distribution $\mathbf{p}_R(\mathcal{N}, E; \mu, \beta)$ can be utilized to derive all thermodynamic quantities within the region of phase space that is covered by the combined fluctuations of all

R runs, and, in principal, even beyond. The density, for instance, is given by

$$\langle \rho \rangle_{\mu, \beta} = \frac{1}{V} \sum_E \sum_{\mathcal{N}} \mathfrak{p}_R(\mathcal{N}, E; \mu, \beta) \mathcal{N}. \quad (2.52)$$

The composite probability distribution utilizes approximations of the partition function. Depending on the overall statistical quality, especially at the extreme values of each run's fluctuations, the correctness of the approximated partition function is subject to statistical uncertainties. Furthermore, it only contains information on phases that have explicitly been sampled. Particularly at low temperatures, the free energy barriers that are involved with the nucleation of new phases become increasingly large. Even if the grand canonical variables would lead to the new phase, it might not be possible for the Monte Carlo simulation to sample it. Since this is the case on both sides of the free energy barrier, this leads not only to wrong statistics, but also to ambiguities in the sampled states, depending on the initial conditions of runs that attempt to sample close to or within the domain of the free energy barrier. This problem is known as *hysteresis* and is not only subject to macrophase coexistence, but also to microphase nucleation such as micellization. Using the histogram reweighting in the context of multiple phase transitions, thus, requires special care. The free energy barriers become smaller at higher temperatures and hysteresis effects diminish. In order to correctly sample nucleation processes at low temperatures, it is reasonable to use a higher temperature as initial condition for the MC simulation, and gradually decrease it to end up at the "correct" side of the underlying free energy barrier - a technique generally known as *annealing*.

2.6.3 Sampling of phase coexistence

As stated in 2.6.2, a first-order phase transition leads to a discontinuity in the thermodynamic potential whose continuity is required for the reweighting. Indeed, the reweighting is not reliable within the region of a phase coexistence. There is, however, a literal *workaround* to obtain the coexistence line of a first-order phase transition. If one performs runs only outside of phase coexistence regions, discontinuities are entirely avoided. By circumventing the critical point at the supercritical level, i.e. where the phase transition is of higher order and no discontinuity of the thermodynamic potential is encountered, it is possible to patch runs of the (sub-critical) gaseous phase together with runs of the respective (sub-critical) liquid phase and obtain data of both phase regions in one reweighting process. However, this will not provide enough information to draw a complete phase diagram since there is no information on the phase coexistence region. The critical point of the first-order phase transition is also the threshold where the discontinuity from inside the coexistence region vanishes. The reweighting is therefore still valid and reliable at this point. Since we are simulating on a finite volume here, divergence of the correlation length is not possible since all fluctuations are limited by the box size. A run at the critical point, however, does provide information on both branches of the underlying binodal in such sufficiency that a *supercritical path* of overlapping runs, including a few close to the critical point, will give an accurate phase envelope that does not suffer from metastable intermediary states that are related to large free energy barriers such as in the phase coexistence region.

To ensure that such a supercritical path is, indeed, supercritical, one can use the histogram reweighting formalism to get a very good estimate of the location of the critical point. In 1992, *Bruce and Wilding* [102, 103] have presented an approach that involves concepts of finite-size scaling theory [72, 73].

The order parameter of our one-component fluid is given by

$$M \sim \mathcal{N} - sE \tag{2.53}$$

with a field-mixing parameter s . Using the composite probability distribution $\mathfrak{p}_R(\mathcal{N}, E; \mu, \beta)$ from 2.6.2, we can transform it to

$$\mathfrak{p}_R(M; s, \mu, \beta) \tag{2.54}$$

and use a convex optimization iteration to find a set of parameters $\{s, \mu, \beta\}_{crit}$ that leads to a distribution $\mathfrak{p}_R(M)$ that has the least deviation from the (numerically given) three-dimensional Ising universality class. A run at values μ_{crit} and β_{crit} then is as close to the critical point as can be provided by the combined concepts of histogram reweighting and finite-size scaling.

Chapter 3

Self-assembly scenarios of block copolymer stars

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*We examine the self-organization scenarios of star-shaped AB-block copolymers, consisting of a solvophilic A-block and a solvophobic B-block, in which f such blocks are chemically anchored on a common center on their A-parts, leaving the B-blocks exposed on their exterior. We employ a lattice model and we perform Grand Canonical Monte Carlo simulations for the case $f = 6$, varying thereby the percentage of attractive monomers as well as the concentration of stars. In agreement with previous studies on the low-functionality case $f = 3$ [F. Lo Verso, A. Z. Panagiotopoulos, and C. N. Likos, *Phys. Rev. E* **79**, 010401(R) (2009)], we find that when the majority of monomers in the star are attractive, macrophase separation between two fluid phases at different concentrations of stars occurs below a system-dependent critical temperature. When the majority of monomers is repulsive, novel forms of self-organization arise, which include not only well-defined spherical micelles but also the coexistence of a multiply-connected percolating cluster with smaller micelles having a well-defined size. The morphological characteristics and the sizes of the ensuing aggregates are quantitatively analyzed and a critical comparison with the case $f = 3$ and $f = 10$ is presented.*

3.1 Introduction

Advances in the synthesis and fabrication of complex colloids have brought about the emergence of a large variety of novel colloidal systems in the last years. Whereas hard colloidal particles without internal degrees of freedom and lacking chemical "decoration" on their surface have been the subject of extensive studies in the past, new and exciting classes of emerging complex colloids include soft particles such as star polymers, dendrimers, microgels and polyelectrolytes on the one hand [74, 75, 76, 77, 47] or hard, patchy colloids, which carry dipoles [78, 79, 80] or associating sites on their surface on the other [81, 5, 82]. The self-assembly scenarios, the structural and dynamical properties, as well as the flow- and shear-characteristics of complex colloids are much richer than those of their simpler counterparts, and they constitute a broad and developing new field of research in soft matter science. The existence of multiple and, in many cases, fluctuating degrees of freedom of these colloids, in addition to the position and momentum of their centers of mass, renders the problem of coarse-graining of complex colloids very challenging; in fact, even the choice of the relevant degrees of freedom to be kept at a coarse-grained description is not *a priori* clear, since competing interactions and agents are present in a complex molecule. In particular, when dealing with *block-copolymers*, a suitable coarse-graining that keeps track of both chemical species and maintains at least one degree of freedom per block is crucial in providing a realistic description of the various self-association phenomena in the system [83, 58, 84, 85, 86, 87]. In this work, we consider a particular class of complex colloidal particles, which combine characteristics and features of both softness and patchiness. The system of interest is a collection of star-shaped AB-diblock copolymers with a number of arms (functionality) f , which are covalently anchored on a common point. The architecture is such that the self-avoiding, solvophilic A-blocks lie at the interior of the star, whereas the attractive, solvophobic monomers are exposed on its periphery [88, 89, 90]. At the level of a *single* molecule (limit of infinite dilution), these molecules can self-organize in a variety of ways [52, 53]. Whereas at sufficiently high temperatures, for which the attractions between the B-monomers are washed out by thermal effects, the stars are open, lowering the temperature brings about a collapse of the same onto so-called *water-melon* configurations. In the latter, either all f chains physically associate on an attractive ball that lies opposite to the point of chemical anchoring or, as f grows, they break up into partial water melons, each consisting of a number $f_p < f$ of chains whose attractive ends have collapsed onto attractive balls. As such, block copolymer stars (alternatively termed also *telechelic star polymers*, TSP) are soft, penetrable colloids due to their polymeric nature, and at the same time patchy colloids, due to the possible existence of multiple association sites on their periphery, arising from the aforementioned multiple water-melon configuration [53]. In contrast to the usual, hard patchy colloids, however, a coarse-graining of telechelic star polymers by means of their center of mass and fixed association sites (patches) on their surface, is physically inadequate: indeed, since the patches are formed by the self-association of flexible objects (the stars' arms), which can recombine and rearrange, in a concentrated solution the intra-association of the arms will most likely be replaced by inter-association of arms of different stars [20, 51, 26, 91, 92, 93, 94]. Therefore, a full description of the architecture of the molecules should be kept in any model that attempts to predict the many-body behavior of telechelic stars at finite concentrations.

To strike a compromise between the computationally very expensive task of modeling and simulating realistically telechelic stars in concentrated solution, and the requirement of maintaining the salient features of the system, we opt for working with a lattice model, which greatly reduces computational complexity without coarse-graining the system too much. Our interest lies in exploring the role of

both the competing interactions and association mechanisms and that of the star functionality on the self-organization of telechelic star solutions, on the structure of the ensuing phases and on the possible implications on the rheological properties of the same. In previous work, we had focused on the very low functionality case, $f = 3$, exploring thereby the effects of the attractions and the degree of polymerization of the arms [55, 56]. The existence of a dual scenario of macrophase separation against micellar formation has been established, depending crucially on the fraction of attractive monomers. Here, we extend our previous investigations to higher functionalities, $f = 6$ and $f = 10$, for which already at the single-molecule level differences with the $f = 3$ case have been established, in the sense that multiple water-melon configurations are stable instead of the single water-melon ones. By applying state-of-the-art Grand Canonical Monte Carlo (GCMC) computer simulations, accompanied with finite-size scaling and histogram-reweighting techniques, we examine the phase behavior of $f = 6$ and $f = 10$ telechelic stars and we establish the similarities as well as important differences with the case $f = 3$. In particular, we find that although the borderline between phase separation and microphase structuring still lies at about a fraction of 50% attractive monomers, the microphase structured assemblies of $f = 6$ and $f = 10$ telechelic stars show differences from those of functionality $f = 3$. Indeed, we find for the $f = 6$ block copolymer stars a new microstructured phase, in which percolating clusters coexist with isolated micelles. The rest of the paper is organized as follows: in Sec. 3.2 we briefly describe our system and related model. Moreover we give few details concerning the simulation techniques we employed in our study. In Sec. 3.3 we discuss in detail the interplay between phase separation and micellization for low functionality telechelic stars ($f = 3$ and $f = 6$) as well as the inter-molecular aggregation structures. In particular, we analyze how the phase behavior and aggregation processes depend on the percentage of attractive monomers as well as on the concentration of stars. In Sec. 3.4 we discuss the phase behavior of block copolymer stars with $f = 10$ in order to further generalize the results obtained in the previous section. Finally, in Sec. 3.5 we summarize and draw our conclusions.

3.2 Interaction model and method of analysis

As already discussed in the introduction, the phase behavior and inter- and intra-molecular aggregation properties of telechelic star polymers is, in addition to the thermodynamic parameters of temperature and chemical potential, determined by a number of molecular parameters. The most fundamental ones are the functionality, the degree of polymerization and the size ratio of the block composition as well as the strength of interaction between the functional groups. More subtle factors are, for instance, the elasticity and bending rigidity of the polymer arms. When dealing with concentrated solutions, it is necessary to reduce the degrees of freedom of the system, in order to make extensive parameter studies via numerical simulations possible in a reasonable amount of time. Following the scheme described in Ref. [55], we employ a Grand Canonical Monte Carlo simulation (GCMC) on a three-dimensional cubic lattice with a coordination number of 26, to ensure the flexibility of the chains, and periodic boundary conditions in all three directions. The relative position vectors for the bonded and nonbonded interactions are $(1, 0, 0)$, $(1, 1, 0)$, $(1, 1, 1)$ together with the additional vectors arising from the point-group symmetry operations of the cubic lattice [95, 96]. Consistently with the grand canonical ensemble, the volume $V = L \times L \times L$ is fixed for a single simulation. However, different box sizes $L = 30, 40, 50$ have been studied, depending on the number of monomers per molecule, and also with the goal of verifying the absence of finite size effects. The instantaneous number of monomers in

the system is denoted $\mathcal{N}$, whereas $N \equiv \langle \mathcal{N} \rangle_{\mu, V, T}$ stands for the expectation value of the same in the simulated grand-canonical ensemble with chemical potential μ and volume $V = L^3$; thereby, $\phi = N/V$ is the average monomer concentration.

Based on previous investigations [55, 56], we applied for the monomer-monomer interactions the Larson model for amphiphile-oil-water systems [59, 60, 61, 62], where the three treated species are solvophilic head monomers (H), solvophobic tail monomers (T) and solvent molecules (S). Since the interaction parameters of the H and S species are considered as the same, the overall energy contribution of lattice sites occupied by these species is a constant. Thus, the interaction energies can be set to $\epsilon_{HH} = \epsilon_{HT} = 0$ and $\epsilon_{TT} = -1$, so that the overall energy parameter describing the system is $\epsilon = 2\epsilon_{HT} - \epsilon_{HH} - \epsilon_{TT} = 1$ and the reduced temperature can be defined as $T^* = k_B T / \epsilon$. To identify the most important molecular parameters for a particular system, i.e. functionality, degree of polymerization and block composition, we label the stars as $H(H_n T_m)_f$, meaning that the f arms are chemically linked at an anchoring point consisting of a H monomer, and that each arm is composed as stated in the parentheses, namely of n inner H monomers and m outer T monomers. The functionalities we studied in detail here are $f = 6$ and $f = 10$, with a total number of monomers per arm $k = n + m = 10$ and various block compositions (n, m) obeying the latter sum. As in Ref. [55], the GCMC simulation employs a mixture of molecule insertion/deletion, single chain regrowth and cluster moves. In the case of an insertion, the molecule center, i.e. the anchoring monomer, is placed randomly on an unoccupied lattice site. The following molecule growth as well as the single chain regrowth step are performed using the *athermal* configurational-bias sampling method [97, 98], in order to improve efficiency in dense system configurations. Insertions and removals of TSPs or individual arms of the latter were performed computing the Rosenbluth weight for each growth step [97]. The simulation length, i.e. the number of equilibration and MC steps, ranged from a total of 10^6 to 10^9 MC, depending on the region of the phase diagram to investigate.

In order to determine whether a system undergoes a macrophase separation, we employed the size dependence of the coexistence curve obtained by histogram-reweighting [24]. Data for the histograms for $\mathcal{N}$ as well as the internal energy $\mathcal{U}$ for a given system size were combined using the Ferrenberg-Swendsen algorithm [99, 100, 101]. The coexistence curve of a truly macrophase separating system is independent of the simulation box size. For the estimation of critical points in case of fluid-fluid phase separation, we used finite size scaling methods [102, 104]. To identify and characterize the aggregation patterns that occur for non macrophase separating systems, we employed a morphological analysis of the systems using the Minkowski functionals [105, 106, 107] and cluster size histograms. For further details see Refs. [55, 56].

3.3 Block copolymer stars with functionality $f = 6$

The main purpose of the present manuscript is to clarify the effect of the functionality on the aggregation scenarios of dense solutions of telechelic diblock copolymer stars. For this goal, we fixed in the first place the number of monomers per arm to the value $k = 10$. In our previous study on the single telechelic star [52, 53], with only one functional group per chain, we proved the tendency of the TSP to form a single, collapsed, *water-melon* structure. This possibility is influenced by parameters such as the temperature, the number of monomers per chain and the number of chains. It is important to remind here once again that for short chains at fixed temperature the single water-melon conformation becomes unfavorable when increasing the number of arms [53]. Evidently, the intra-molecular asso-

ciation strongly influences the mechanisms of inter-association between molecules in dense solutions and the appearance of network formations. In this context, a crucial range of functionalization is $6 \leq f \leq 10$: molecules within this range of f start to prefer to intra-associate in partial water-melon structures instead of a single one. In this section we focus on stars with $f = 6$.

3.3.1 Phase separation

The parameter we varied here is the percentage of attractive monomers per chain. For a high number of stickers (terminal T-units) per molecule, we investigated the fluid-fluid phase coexistence curve. When the length of the attractive block is at least equal to the length of the repulsive block, the systems phase separate. In Fig. 3.1 we present the coexistence curves obtained for $m \geq 5$. The trend is exactly the same we encountered for the systems $H(H_n T_m)_3$, full symbols in Fig. 3.1. Increasing m , the critical temperature as well as the critical concentration increase. Essentially the reason is that an increase in f causes a strengthening of the effective attractions. At any rate, the growth of T_c^* is not proportional to f , since indeed there is also a corresponding increase of the repulsions from the inner part. For $m = n$ the coexistence curve is relatively flat.

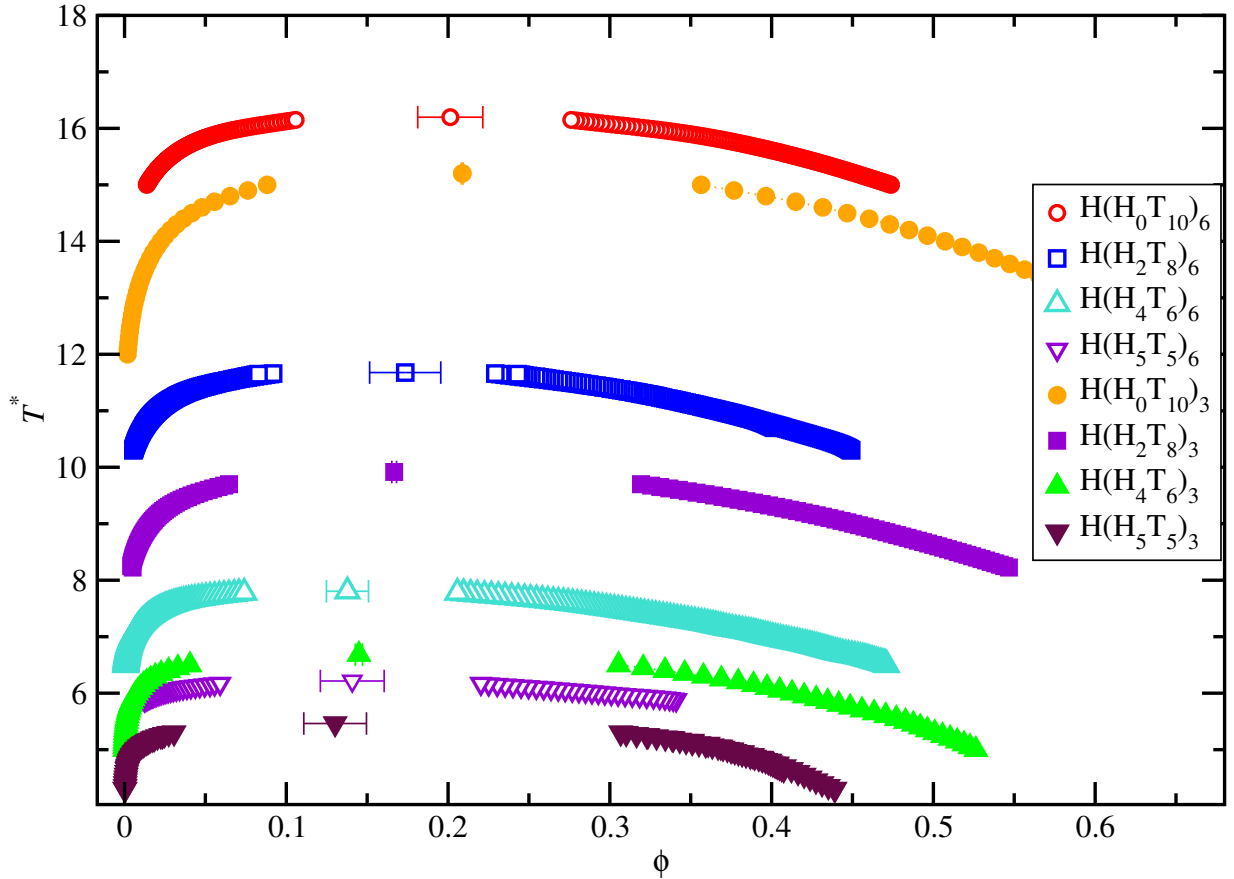


Figure 3.1: Phase coexistence boundaries of telechelic star block copolymers for different block compositions. The figure shows the comparison between different functionalities: $f = 3$ and $f = 6$.

When the number of repulsive monomers exceeds that of the attractive ones, no macroscopic phase separation takes place, since the pseudo-coexistence curve we obtain dramatically depends on the lattice size. From this analysis as well as from the results discussed in Ref. [56], we conclude that the limiting case of disappearance of the macroscopic phase separation seems to be 50% of attractive monomers, independently of f and k .

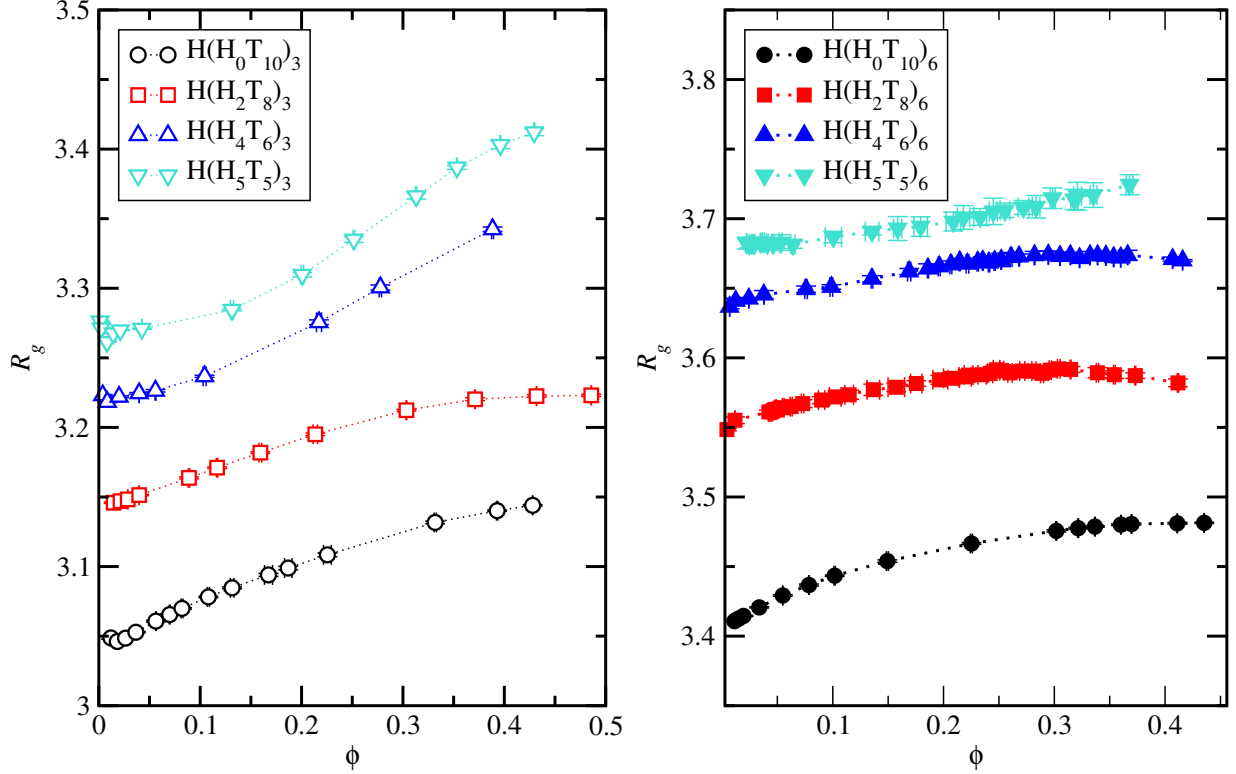


Figure 3.2: The radius of gyration R_g of the stars as a function of the concentration for different systems. Left panel: $f = 3$, $T^* = 15.25$, $T^* = 10.25$, $T^* = 6.9$, $T^* = 5.8$, for $n = 0, 2, 4, 5$ respectively. Right panel: $T^* = 16.6$, $T^* = 11.98$, $T^* = 8.1$, $T^* = 6.5$ for $n = 0, 2, 4, 5$ respectively.

In order to study in more detail the conformation of the molecules for phase separating systems, we have measured the gyration radius R_g of the same as a function of the monomer concentration ϕ . In Fig. 3.2, right panel, we show the typical monotonic behavior of R_g as a function of monomer concentration ϕ : as the concentration of the solution increases, the molecules start to create inter-connections and aggregates, with a consequent stretching of the chains, so that the molecules grow in average size. In Fig. 3.2, left panel, we also show the corresponding results for $f = 3$. The main behavior is the same for both functionalities. However, for $f = 6$ the rate of increase is smaller due to the interplay between intra- and inter-molecular aggregation: indeed the higher number of arms brings about partial intra-molecular association already at low density. This effect partially inhibits the global stretching of the chains. Here, the temperature is fixed to the same value considered for the morphological analysis i.e., slightly supercritical: $T^* = 16.6$, $T^* = 11.98$, $T^* = 8.1$, $T^* = 6.5$, for $n = 0, 2, 4, 5$ respectively.

The multiply connected structures typical of high densities of the phase separating systems can be analyzed in terms of the Minkowski functionals. As in our previous studies [55, 56] we calculated the exposed area per volume, V_1/V , the integral mean curvature density V_2/V as well as the Euler characteristic per site, V_3/V . A detailed analysis of the trends of the morphological coefficients varying

the composition of the arms will be given in the next subsection. Here, and in Fig. 3.3, we focus on the Euler characteristic per site, V_3/V , for $m \geq 5$.

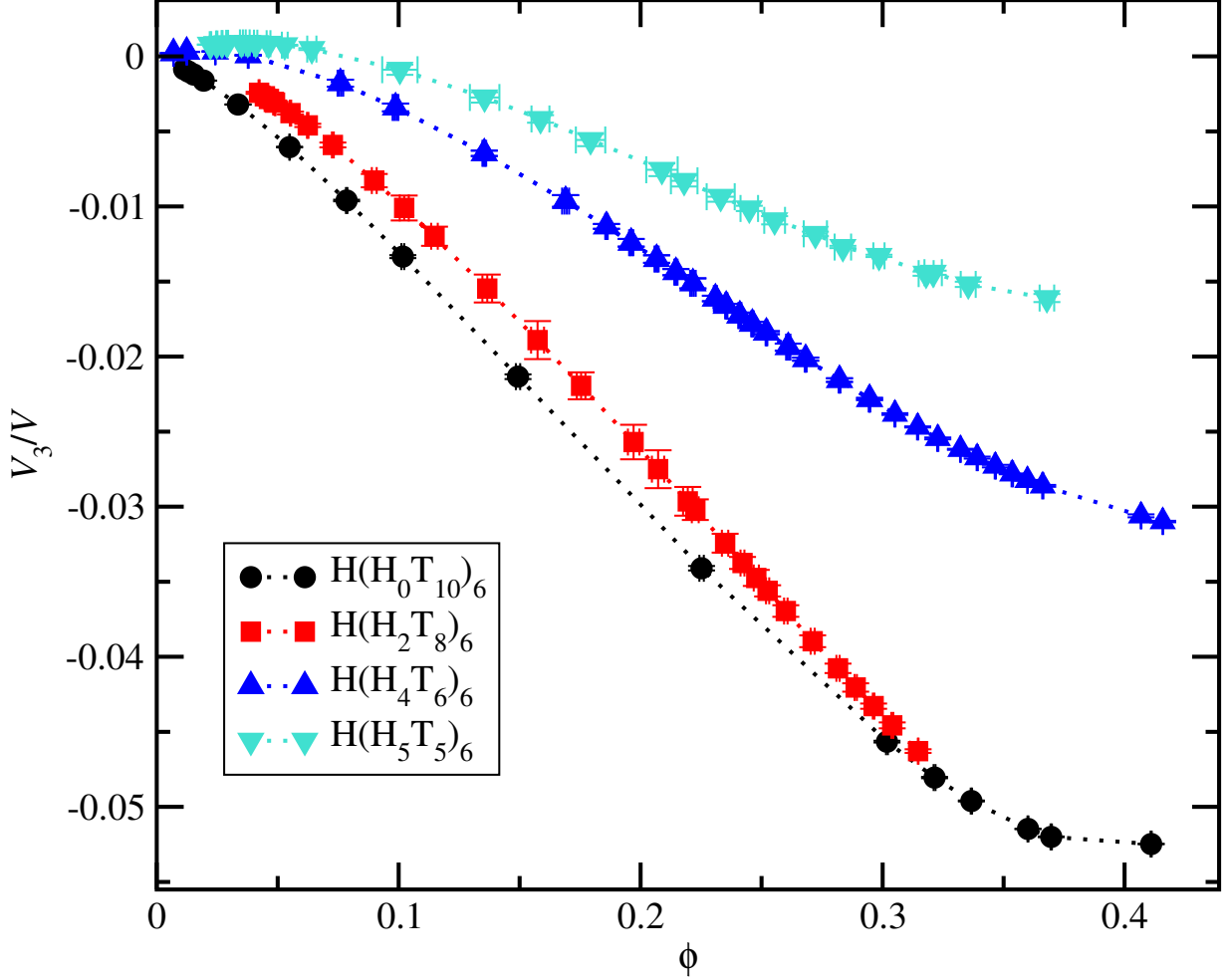


Figure 3.3: Euler Minkowski functional of phase-separating, six-functional, telechelic star block copolymer solutions with $k = 10$ monomers per arm. $T^* = 16.6$, $T^* = 11.98$, $T^* = 8.1$, $T^* = 6.5$ for $n = 0, 2, 4, 5$ respectively.

The negative values of the Euler characteristic point to percolating, bicontinuous structures formed in the dense phase of the system. Exactly as in the case $f = 3$, the hollow, spongy nature of the fluid, featuring a large number of tunnels ($V_3 < 0$) diminishes as the number of stickers becomes lower. In particular, phase separation results into a negative Euler characteristic V_3 at sufficiently high monomer densities. The negative values of this quantity start at higher and higher densities decreasing the percentage of attractive monomers per chain. In both cases, $f = 3$ and $f = 6$, as the number of solvophilic heads increases, the curves move closer and closer to the $V_3/V = 0$ axis. The study of the morphological coefficients we have done confirms that the phase separation depends only on the block-copolymer composition and not on f .

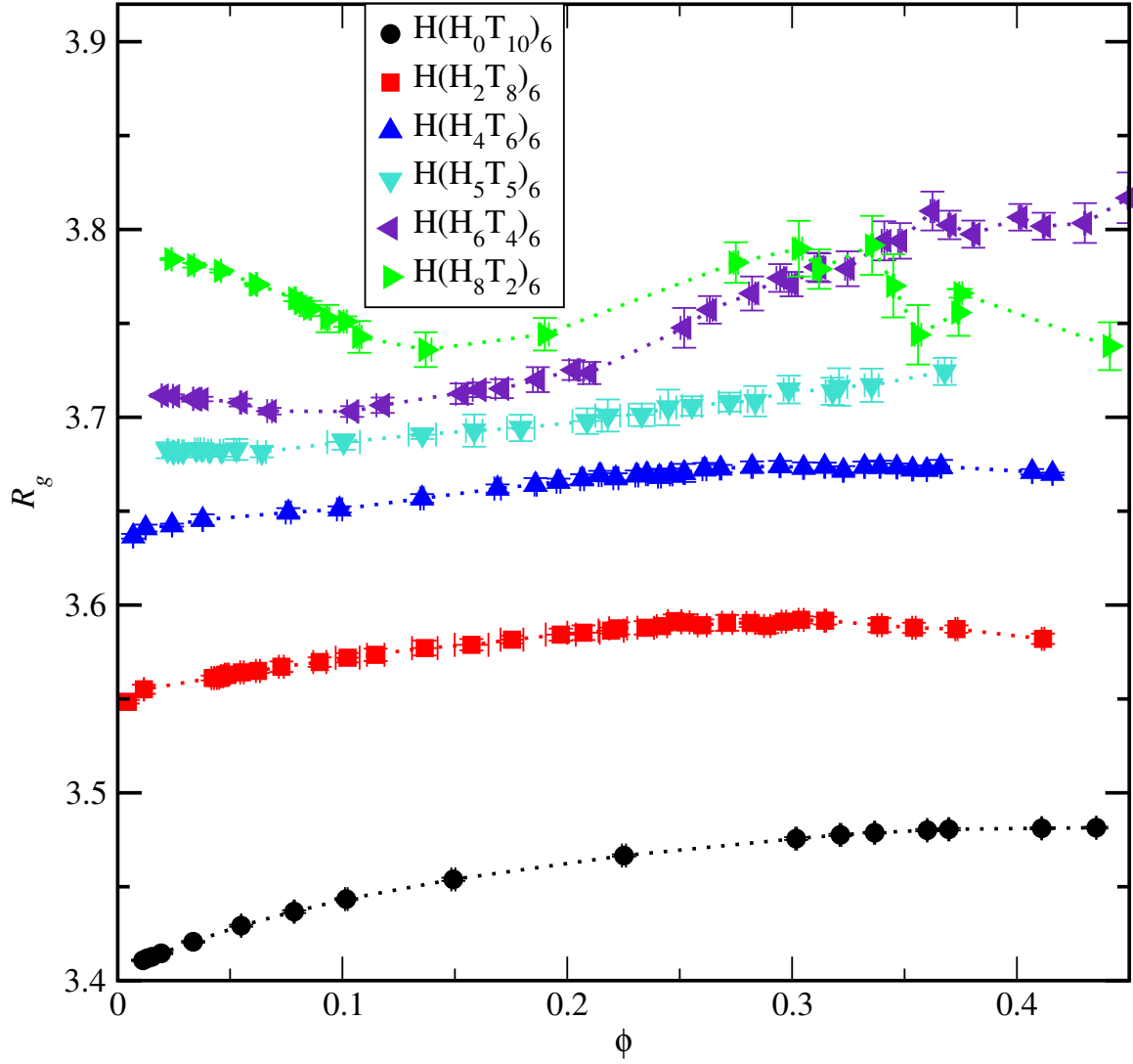


Figure 3.4: The dependence of the gyration radius of the block copolymer stars, R_g , on the monomer concentration ϕ for $f = 6$ and compositions as indicated in the legend. The corresponding T^* temperatures are: $\text{H}(\text{H}_8\text{T}_2)_6$: $T^* = 2.4$, $\text{H}(\text{H}_6\text{T}_4)_6$: $T^* = 4.9$, $\text{H}(\text{H}_5\text{T}_5)_6$: $T^* = 6.5$, $\text{H}(\text{H}_4\text{T}_6)_6$: $T^* = 8.1$, $\text{H}(\text{H}_2\text{T}_8)_6$: $T^* = 11.98$, $\text{H}(\text{H}_0\text{T}_{10})_6$: $T^* = 16.6$.

3.3.2 Micellization and aggregation phenomena

As we discussed in the previous sections, for $n > m$ the coexistence curves show a dependence on the lattice size which is a typical signature of the lack of phase separation [24]. Although here the critical point is only apparent, we proceed for the system $\text{H}(\text{H}_6\text{T}_4)_6$ similarly to the case of phase-separating systems and we focused on a range of temperatures slightly supercritical. Besides consistency reasons, in this way we reduce possible hysteresis effects. For the $\text{H}(\text{H}_8\text{T}_2)_6$ -system, we focus on a temperature that is half the one of the $\text{H}(\text{H}_6\text{T}_4)_6$ -case, in proportionality to the reduction of the attractive ends. In this regime ($n > m$), the aggregation mechanisms are quite sensitive to the arm numbers. As a preliminary criterion, which demonstrates the differences between the cases $n > m$ and $n \leq m$, we plot in Fig. 3.4 the dependence of the gyration radius R_g on the monomer concentration ϕ for all systems with functionality $f = 6$ examined. It is evident from the non-monotonic shape of the curve for the $\text{H}(\text{H}_8\text{T}_2)_6$ -system and its comparison with those of the phase separating systems ($n \leq m$) that a macrophase separation cannot hold for this case and that indeed a different aggregation scenario is

at play. In fact, it has been shown in Ref. [56] that for $f = 3$, this shape is caused by the formation of well-characterized spherical micelles, as will also be demonstrated for the case $f = 6$ in what follows. The dependence of R_g on ϕ for the $\text{H}(\text{H}_6\text{T}_4)_6$ -system is more peculiar and the types of aggregation present in that system will be discussed separately.

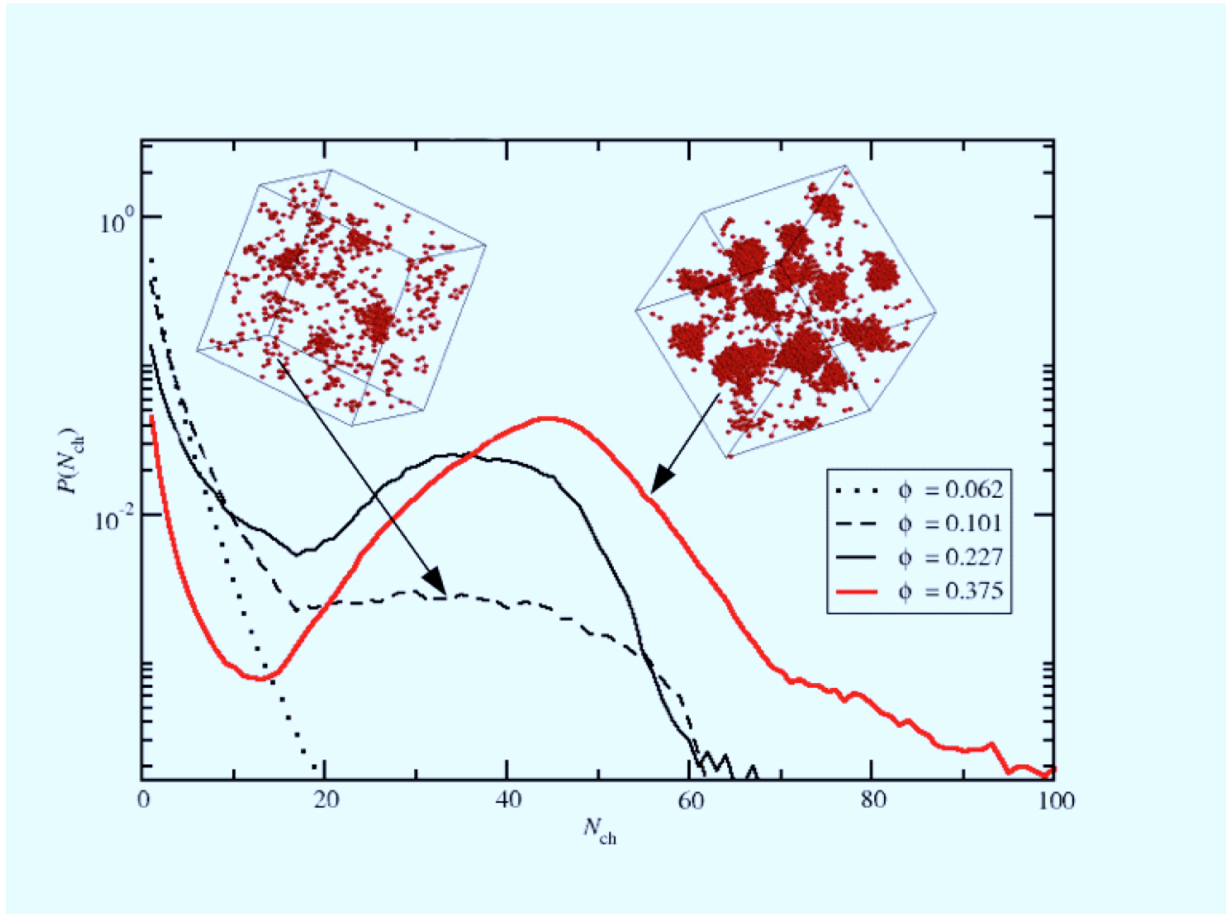


Figure 3.5: Probability density $P(N_{\text{ch}})$ for finding clusters that contain N_{ch} chains, and for different overall monomer concentrations, indicated in the legend. The histograms are for an $\text{H}(\text{H}_8\text{T}_2)_6$ system at $T^* = 2.4$. The insets show simulation snapshots of the end monomers at the quoted values of the concentration increasing from left to right.

We commence with the case of the $\text{H}(\text{H}_8\text{T}_2)_6$ -system, which has relatively long solvophilic blocks and short stickers. In Fig. 3.5 we plot the histograms of the number of chains, N_{ch} , participating in a micellar cluster, $P(N_{\text{ch}})$. Here, a cluster is defined by all terminal monomers that are found within the distance set by the coordination of the lattice, rendered as red spheres in the snapshots of Fig. 3.5. In this representation, the onset of micellization is marked by the development of a shoulder in the corresponding distribution, which extends out to the aggregation number g_0 of the micelles. From the figure, we can determine a micellar functionality about $g_0 \simeq 45$, which grows very slowly with ϕ . We remind here that for $\text{H}(\text{H}_8\text{T}_2)_3$ the probability density revealed the appearance of cluster maxima at aggregation numbers which are integer multiples of the fundamental micellar size. On the other hand for $\text{H}(\text{H}_8\text{T}_2)_6$ we do not see any such harmonics, i.e., there is a continuous, exponentially falling distribution of micellar cluster aggregates, instead of the predominance of singlets, doublets and triplets found in the case $f = 3$. We conjectured that the micelle-micelle interaction here is *patchy*, in the sense that part of the attractive surface of the micelle is more exposed in the $f = 6$ case. To

materialize the $f = 3$ micellization shapes, the chains would indeed have to stretch themselves too much to cover the surface of the micelle uniformly. The exposed attractive micellar core favors a further increase of the micelle size with the concentration, in a quasi-continuum fashion. Once again the collapse of the single-molecule arms in multi-water melon structures, instead of a single water melon, has important consequences for the inter-association mechanism.

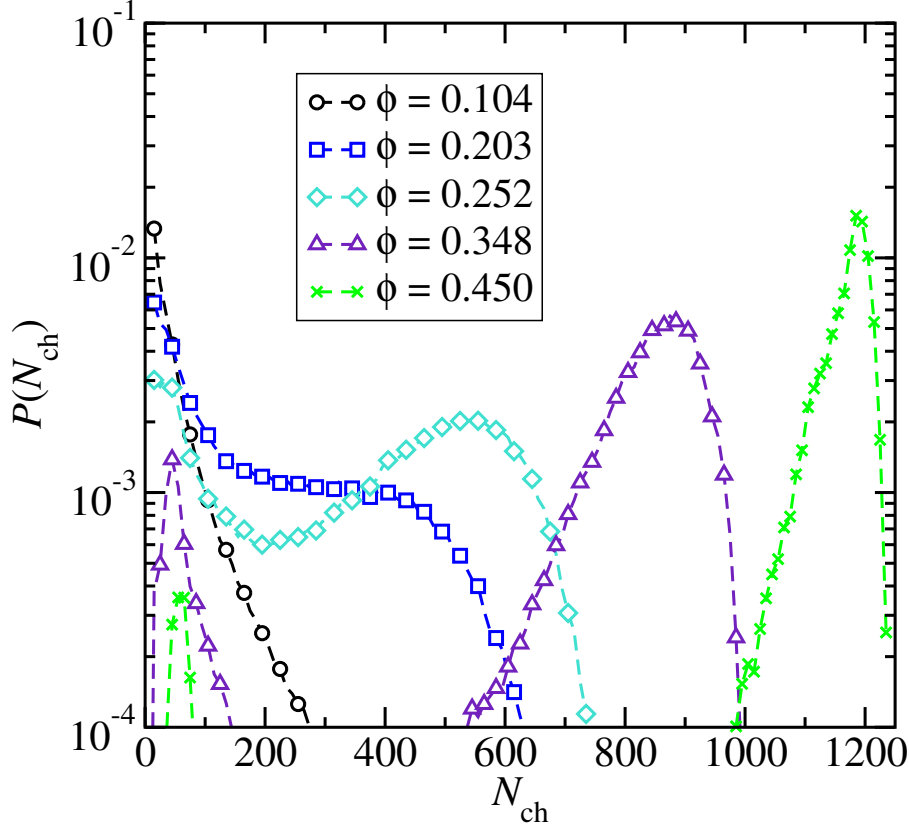


Figure 3.6: Probability density $P(N_{\text{ch}})$ for finding clusters that contain N_{ch} chains, and for different overall monomer concentrations, indicated in the legend. The histograms are for an $\text{H}(\text{H}_6\text{T}_4)_6$ -system at $T^* = 4.9$.

We proceed now to the very interesting case $\text{H}(\text{H}_6\text{T}_4)_6$, for which the gyration radius data (Fig. 3.4) indicate some form of aggregation that is intermediate between macrophase separation and formation of well-defined micelles. In fig. 3.6 we show the $P(N_{\text{ch}})$ for different overall monomer concentrations. Here the characteristic shoulder, which signals the onset of the micellization, appears at very high monomer concentration, $\phi \simeq 0.2$, as compared with the $\text{H}(\text{H}_8\text{T}_2)_6$ -system or systems with $f = 3$ [55]. Increasing the concentration, and around $\phi \simeq 0.3$, two distinct peaks in the distribution show up: the first peak is centered around $N_{\text{ch}} = 50$, and its position does not move increasing the density, whereas the second peak is on the high side of chain numbers N_{ch} and keeps moving to higher and higher values as the density grows. It is clear that the behavior of the system with $n = 6$, and $f = 6$ arms is not typical of a micellization scenario. In fact, the $\text{H}(\text{H}_6\text{T}_4)_6$ -system does not form usual micelles but rather a volume-spanning, percolating network, as witnessed by the huge number of chains for which the right peak shows. At the same time, on the left side, a ϕ -independent peak shows up after the percolation transition, which corresponds to micelles forming in the voids left by the percolating matrix. This interpretation is corroborated by the comparison with the results from $L = 40$. In Fig. 3.7, we plot $P(N_{\text{ch}})$ for different overall monomer concentrations and different lattice sizes. The

comparison between $L = 30$ and $L = 40$ fully confirms the above considerations: for a given ϕ above percolation, the high-peak position depends on L . In fact, the ratio of the locations of the peaks roughly scales as $(40/30)^3$, confirming that the density of monomers for which the peaks appear is fixed and spanning the whole system. We emphasise, however, that the left peak has a position that does not depend on L , pointing to localized micelles with $g_0 \simeq 50$. The explanation lies on the fact that, as for the H_8T_2 -case, the surfaces of the aggregates of the attractive monomers are less spherical than for $f = 3$ and at the same time they expose naked attractive parts to other aggregates, which enhance the formation of percolating clusters. However, the voids contained in such a percolating structure offer a natural size for the growth of monodisperse micelles (left peak).

The fact that the $\text{H}(\text{H}_6\text{T}_4)_3$ system forms well-defined spherical micelles whereas the system with the same block composition but a higher functionality, $\text{H}(\text{H}_6\text{T}_4)_6$, does not, requires some physical explanation. The formation of a spherical micelle requires that all the chains of a given number of stars collapse onto a common core, leaving at the exterior of the micelle the anchor points together with the f solvophilic segments of chains that they carry. Whereas this is favorable for a small chain number, $f = 3$, this is evidently not the case for $f = 6$, since the collapse of all chains on the same core would require the stretching and crowding of a larger number of self-avoiding connected segments. This is not the case for the $\text{H}(\text{H}_8\text{T}_2)_6$ -system because here the self-avoiding blocks are *longer*, and thus the entropic penalty for collapse of the short attractive blocks on a common micellar core is not too high and the formation of micelles pays off. The above interpretation, if true, should hold even more so for the case $f = 10$, and indeed it does, as we will demonstrate in the following section.

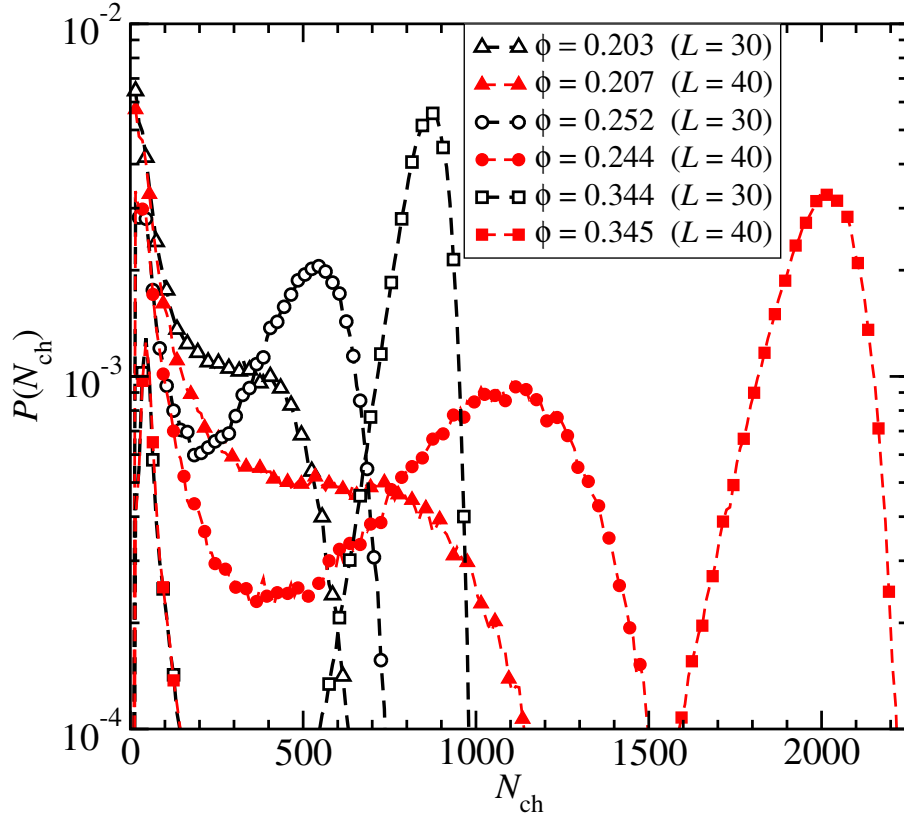


Figure 3.7: Probability density $P(N_{\text{ch}})$ for finding clusters that contain N_{ch} chains, and for different overall monomer concentrations and lattice size, as indicated in the legend. The histograms are for an $\text{H}(\text{H}_6\text{T}_4)_6$ system at $T^* = 4.9$.

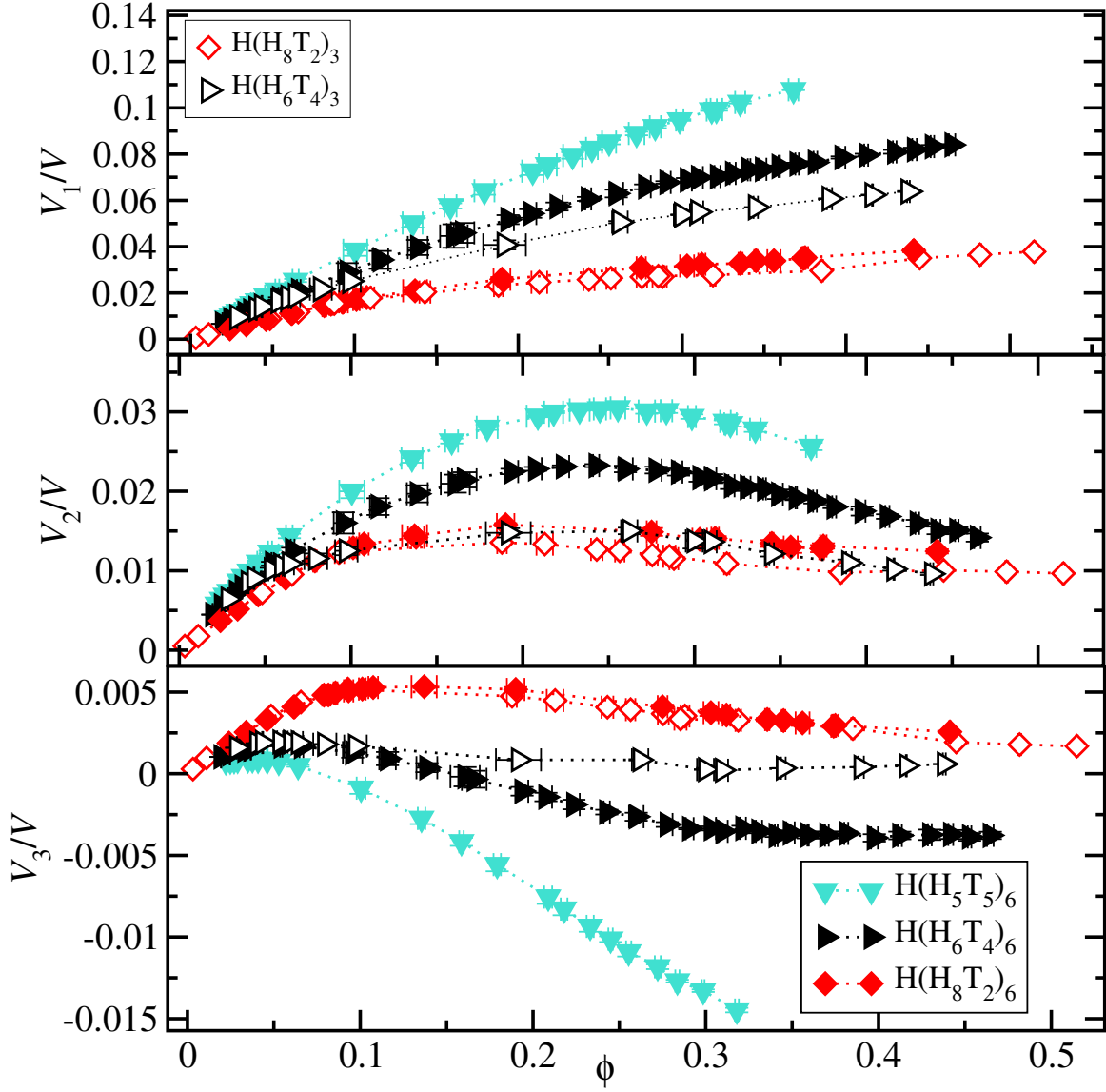


Figure 3.8: Minkowski functionals of phase-separating, six-functional and tri-functional, telechelic star block copolymer solutions with $k = 10$ monomers per arm. Full Symbols: $T^* = 6.5, 4.9, 2.4$ for $n = 5, 6, 8$ respectively and $f = 6$. Empty Symbols: $T^* = 4.4$ and 2.3 for $n = 6, 8$ respectively and $f = 3$.

To complete our analysis and further corroborate our conclusions, we calculated the morphological Minkowski coefficients and compared all of them with the lower functionality case, $f = 3$: results can be seen in Fig. 3.8. In the figure we plotted also the borderline case, namely $H(H_5T_5)_6$, above which we obtain macrophase separation. For the systems $H(H_8T_2)_3$ and $H(H_8T_2)_6$, the results are very similar, despite the difference in the functionality ($f = 3$ vs. $f = 6$). However, between the systems $H(H_6T_4)_3$ and $H(H_6T_4)_6$ significant differences show up, underlying the crucial role of the star functionality on the morphologies of the resulting, non-phase separating aggregates. First, the value of the exposed surface area V_1 , which increases monotonically with the number of sticky groups per molecule, is higher for $f = 6$ than for $f = 3$. The formation of spherical micelles ($f = 3$) results into a reduction of the exposed area with respect to the more irregular shape of the aggregates conjectured for $f = 6$. The comparison of the integral mean curvature, V_2/V , between the cases $H(H_6T_4)_3$ and $H(H_6T_4)_6$ also carries the signature of the different forms of self-aggregation of the two systems, albeit in a more subtle fashion. In the former case, the integral mean curvature per site first increases as a function of ϕ and then it decreases slightly, as a result of the emergence of connections between the micelles, since the narrow necks connecting the latter have a negative contribution to it. Note, however, that since not all micelles form connections to each other, this drop is weak. In the latter case, the integral mean curvature first rapidly grows, as a consequence of the size- and shape-polydispersity of the many isolated, irregular clusters that form, up to the concentration $\phi \cong 0.2$, at which the system starts percolating. Beyond that point, the network formed by the stars contains regions of both positive and negative principal radii of curvature, resulting to a rapid drop of the integral mean curvature, which is rather akin to the shape of this curve for the phase-separating, $H(H_5T_5)_6$ -system. Most telling is the comparison between $f = 3$ and $f = 6$ for the Euler characteristic V_3 . Here, we obtain clearly negative values for this quantity for the $H(H_6T_4)_6$ -system at high concentrations, whereas the same quantity remains positive for the $H(H_6T_4)_3$ -system. This behavior fully agrees with the picture we drew on the basis of the histogram analysis, see Figs. 3.6,3.7. Indeed it holds that $\mathcal{V}_3 = \mathcal{N}_D + \mathcal{N}_C - \mathcal{N}_T$, where $\mathcal{N}_D$ is the number of disconnected components, $\mathcal{N}_C$ the number of cavities and $\mathcal{N}_T$ the number of tunnels. A negative value at high density can be expected for the volume-spanning, percolating network, described by the right side peak seen in Figs. 3.6 and 3.7. Finally, it is instructing to compare the Euler characteristic of the $H(H_6T_4)_6$ and $H(H_5T_5)_6$, reminding ourselves of the fact that the latter shows macrophase separation. Here we see that the morphologies of the dense aggregates for both systems are similar, in the sense that in both cases we obtain bicontinuous structures (negative Euler characteristic), however the phase-separating system is more spongy than the percolating one.

3.4 The case of functionality $f = 10$

We further increased the arm number to $f = 10$ and we studied the interplay between phase separation and micellization as before. We analysed first the borderline case, namely $n = m = 5$, and we found once again fluid-fluid phase coexistence with a higher critical temperature than for the lower functionality cases of the same block composition. In the context of the phase behavior that we found for the case $f = 3$ and $f = 6$, we omit here the study of systems of higher sticker numbers and focus on the phase behavior when the number of attractive monomers further decreases. While for $H(H_5T_5)_{10}$ the coexistence curves for different lattice sizes $L = 30, 40$ nicely overlap, see Fig. 3.9, the system $H(H_6T_4)_{10}$ shows heavy lattice-size dependence. Thus once again, for $n > m$, macrophase separation breaks down and – similar to the case $H(H_6T_4)_6$ – the system shows a continuous range of aggregate

sizes that spreads to higher and higher values increasing the density, i.e. in response to an increase in the chemical potential.

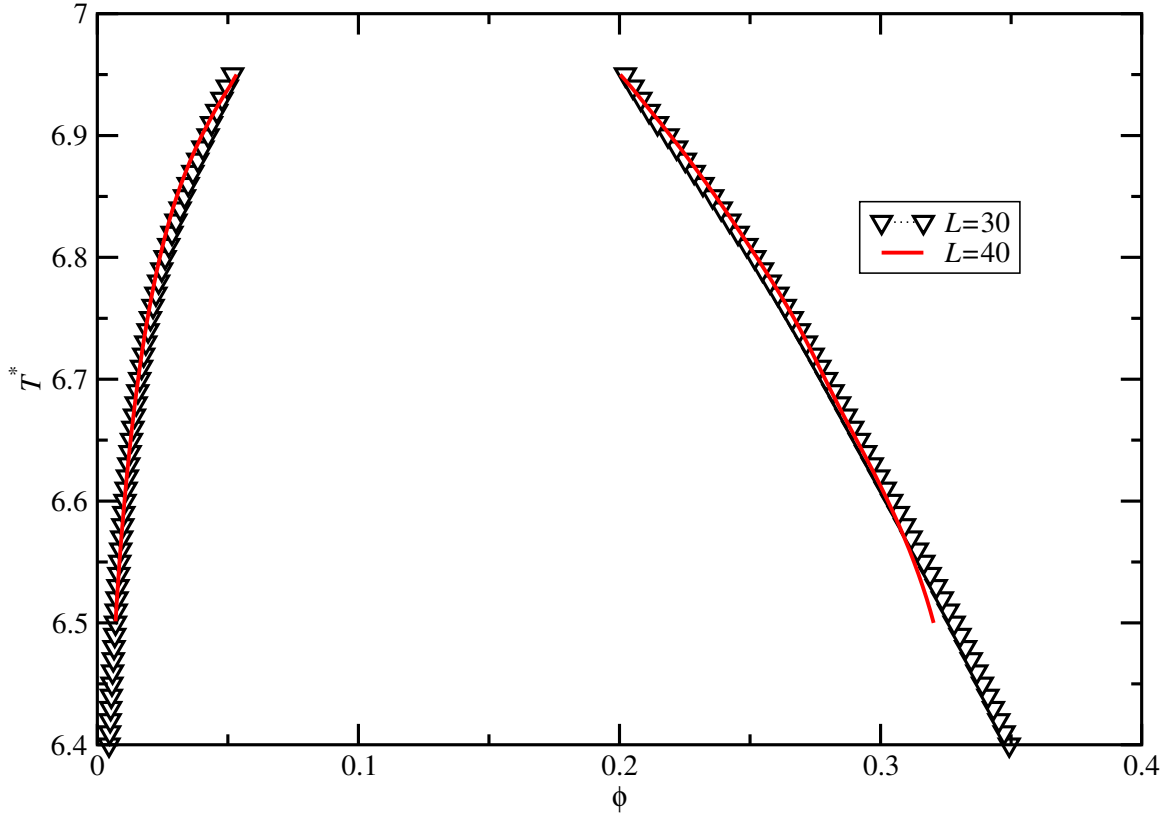


Figure 3.9: Phase coexistence boundaries of $H(H_5T_5)_{10}$ telechelic star block copolymers for two different lattice sizes used. The agreement between the two results is a confirmation that the system has a true, macroscopic phase separation.

Above a threshold density, the system builds up a multiply-connected network, see Fig. 3.10, whose percolating nature can be seen in the lattice size dependence of the peaks in Fig. 3.11. However, in comparison to $H(H_6T_4)_6$, the system here lacks for the presence of smaller micelles with well-defined size in the gaps of the network, see Figs. 3.11 and 3.12.

Nevertheless, this does not mean that for $f = 10$ usual micellization is not possible at all. Similar to the $f = 6$ case, the usual, spherical micelles show up when the number of solvophilic monomers is further increased. In Fig. 3.13 we show the cluster histograms of the $H(H_8T_2)_{10}$ -system. Evidence can be seen for the formation of well-defined micelles above a critical micellization concentration, in full similarity to the $H(H_8T_2)_6$ -case. However, the histograms for these two systems, despite the fact that both offer evidence for the formation of micelles, show differences. In the $f = 10$ case, the peak corresponding to the micelle size is far less sharp and shows a tail for higher cluster sizes, indicating not only the occurrence of two connected micelles, but also the bonding of micelles with smaller aggregates, such as single molecules. Comparing the $H(H_nT_m)_6$ and the $H(H_nT_m)_{10}$ -systems we can deduce that for the same block composition, but for higher functionality, aggregates such as micelles are far less isolated to their immediate surrounding. A star *on the surface of a micelle*, where all the arms stick into the micelle, suffers from heavy repulsion near the anchoring point, the more arms try to grow into the same solid angle and reach into the micelle. Such a configuration becomes

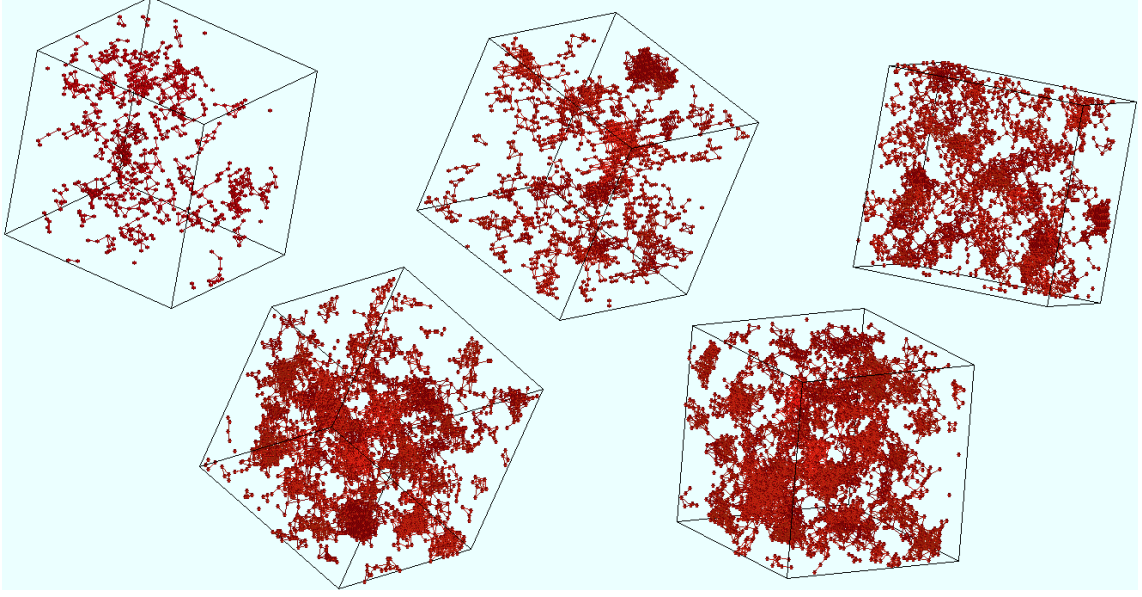


Figure 3.10: Typical aggregate structures of end-monomers for $H(H_6T_4)_{10}$ -system increasing the density, at $T^* = 5.3$: from the left to right, first line we have $\phi = 0.06, 0.13, 0.19$ second line $\phi = 0.24, 0.27$.

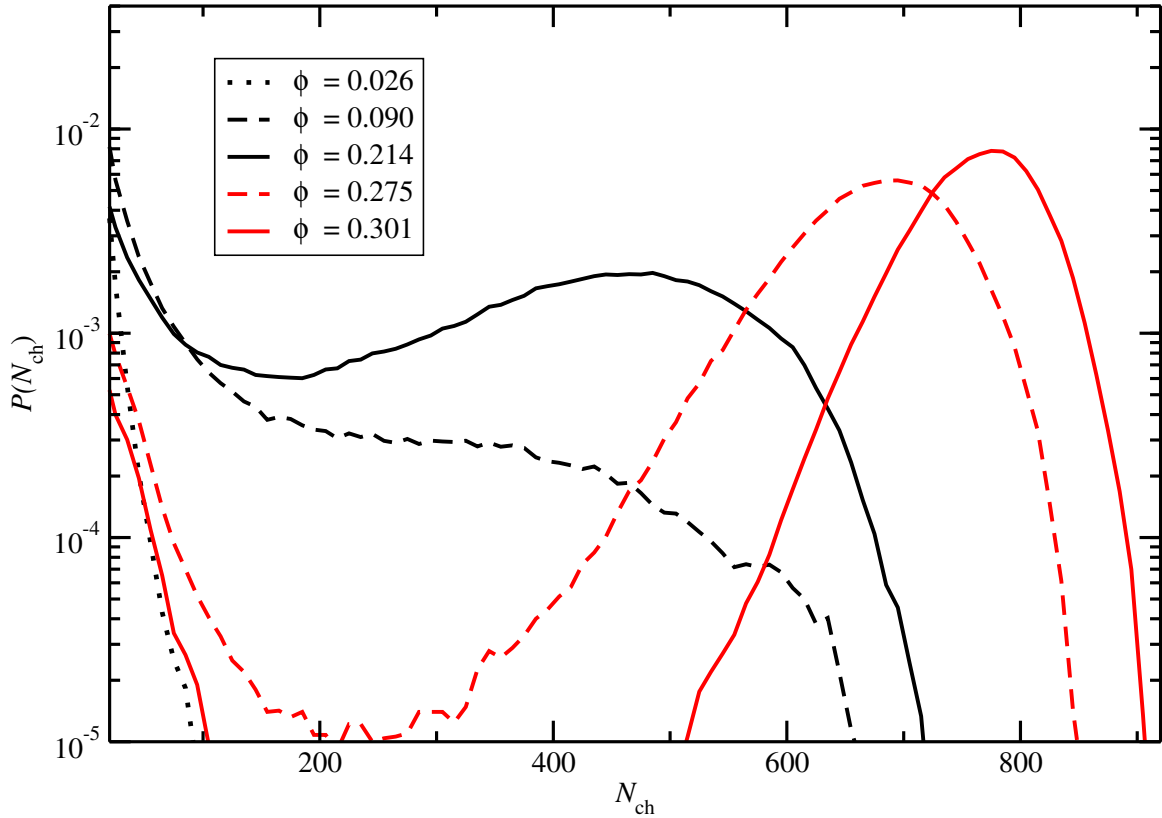


Figure 3.11: Probability density $P(N_{ch})$ for finding clusters that contain N_{ch} chains, and for different overall monomer concentrations. The histograms are for an $H(H_6T_4)_{10}$ system at $T^* = 5.3$.

less and less probable against configurations where a few arms grow apart and form bonds outside of the micelle, leading for instance to the broadening of the histogram in $H(H_8T_2)_{10}$ or merging into the surrounding percolating network in $H(H_6T_4)_{10}$.

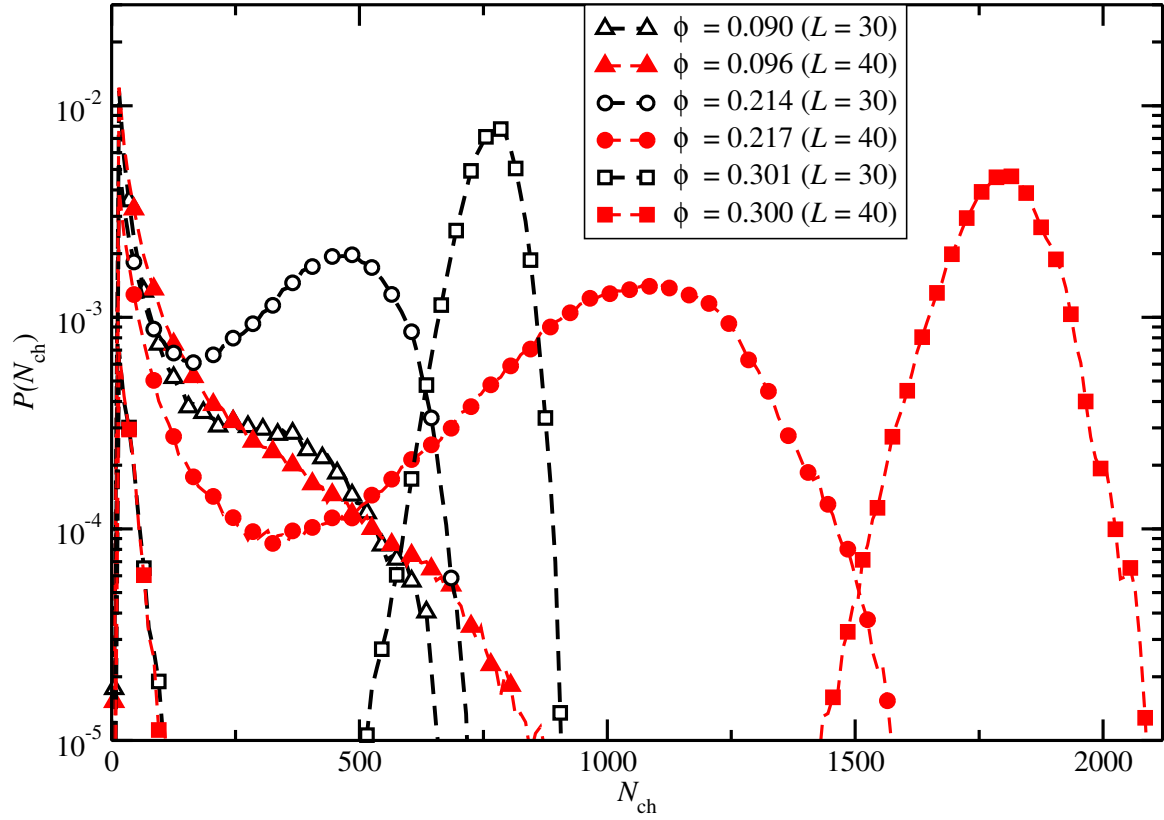


Figure 3.12: Probability density $P(N_{\text{ch}})$ for finding clusters that contain N_{ch} chains, and for different overall monomer concentrations and lattice size, as indicated in the legend. The histograms are for an $\text{H}(\text{H}_6\text{T}_4)_{10}$ system at $T^* = 5.3$.

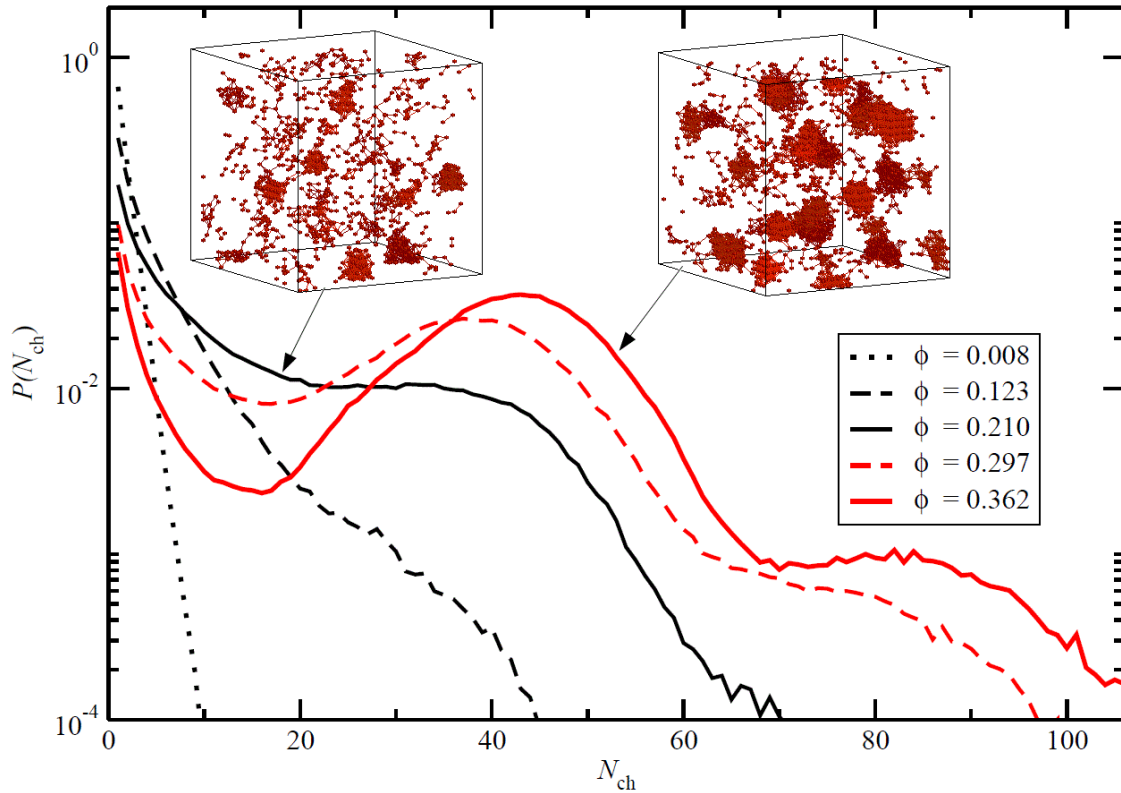


Figure 3.13: Probability density $P(N_{\text{ch}})$ for finding clusters that contain N_{ch} chains, and for different overall monomer concentrations, as indicated in the legend. The histograms are for an $\text{H}(\text{H}_8\text{T}_2)_{10}$ system at $T^* = 2.6$.

3.5 Conclusions

The work presented in this paper comes forward to complete a picture regarding the problem of self-organization of telechelic, small functionality block copolymer stars that has started emerging from previous investigations on the same problem, mainly concerned with the case of functionality $f = 3$ [55, 56]. In particular, we have established that the functionality is *irrelevant* as far as macrophase separation is concerned, at least in the range $f \leq 10$ and for a moderately small number of monomers per arm ($k = 10, k = 20$). Here, one needs, within the employed Larson model, a majority of attractive units to bring about phase coexistence and the associated critical point. Although the model is simplified in its form, and for real telechelic stars the inter-monomer interactions are expected to be more complicated, we expect that the result of the independence of phase separation on f will hold for more realistic models as well.

On the other hand, the self-organization of non-phase-separating systems does have a crucial and delicate dependence on functionality. Whereas for $f = 3$ stars well-defined, spherical micelles form for all systems in which the majority of monomers are self-avoiding, for $f = 6$ and $f = 10$ the novel and intermediate scenario of the formation of percolating networks has been established here, for the cases $\text{H}(\text{H}_6\text{T}_4)_6$ and $\text{H}(\text{H}_6\text{T}_4)_{10}$. These aggregates form a natural bridge between full macroscopic phase separation and formation of spherical micelles, which is recovered when the number of terminal stickers is further reduced, i.e. for the $\text{H}(\text{H}_8\text{T}_2)_6$ and $\text{H}(\text{H}_8\text{T}_2)_{10}$ cases. We believe that the signature of the possibility that system-spanning networks can form at finite concentration lies already at the fact that configurations of multiple water-melons are possible for $f = 6$ and $f = 10$ at infinite dilution

[53].

Further work on these interesting systems with the goal of exploring their intriguing self-organization properties is currently under way on two different and complementary directions. On the one hand, sticking with the case of low degree of polymerization, it is interesting to know what is the effect of chain stiffness and elasticity on the hitherto explored scenarios, within the framework of the Larson lattice model. On the other hand, the opposite extreme of degrees of polymerization in the range of thousands or even tens of thousands of monomers should be studied in an off-lattice model. Here, the extremely high computational cost requires the use of suitable blobbing techniques, which allow to group a large number of monomers within a single soft blob. This method has already been applied to the system at hand for a variety of functionalities and compositions, bringing about a host of possible self-organized structures, and it will be the subject of a future publication [54, 108].

Chapter 4

Phase behavior of rigid, amphiphilic star polymers

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*We determine the phase behavior of rigid, amphiphilic diblock copolymer stars in solution, by employing a lattice model and applying Grand Canonical Monte Carlo simulations as well as histogram reweighting techniques. previous studies on these systems [C. Koch et al., Molecular Physics, 2011, **109**, 3049] have found that for fully flexible chains with a moderate functionality ranging from $f = 3$ to $f = 10$ and with a solvophilic A-block smaller than or equal to the solvophobic B-block, the solution undergoes a liquid-gas macrophase separation with a well-defined critical point. We find that the introduction of chain rigidity alters the critical parameters: the higher the stiffness, the higher the critical temperature T_c and the lower the critical density ϕ_c . Furthermore, we find that for high rigidities and densities beyond ϕ_c , the molecules arrange in cubic, columnar and lamellar ordered phases whose domain of stability depends on molecular architecture and block incompatibility. For even higher densities the system remelts again into another fluid phase. The resulting rich phase diagrams of star polymers that feature amphiphilicity and high rigidity are a manifestation of the character of these hybrid molecules as polymer-based, soft patchy colloids.*

4.1 Introduction

The self-assembly behavior of functionalized soft colloids and the technological advances in their fabrication have attracted a great deal of attention within the soft matter community in the last years. Studies on systems of complex colloids, such as hard patchy colloids with a small number of attractive patches [81], star-branched polyelectrolytes [75], single-strand DNA-coated colloids [109, 110], microgels [77], dendrimers [76], block copolymer brushes [58] or star polymers [44] have demonstrated the enormous richness of the self-assembly properties of these systems. *Amphiphilic star polymers*, also termed *diblock copolymer stars* or *telechelic star polymers* (TSP's), are an additional, versatile example of complex colloids. They result when a number f (functionality) of AB-diblock polymer chains are covalently anchored with their solvophilic A-block ends to a common, likewise solvophilic point, so that the solvophobic B-blocks lie at the periphery, exposed to the solvent environment.

Depending on physical conditions of the solution (e.g., temperature and concentration) and their chemical or architectural properties (e.g., functionality, degree of amphiphilicity), TSP's can resemble

soft, penetrable colloidal particles with a chemical decoration, i.e., they constitute *functionalized, patchy colloids* due to the presence of the B-blocks forming association sites on the periphery. The capability of TSP's to adjust their sizes to concentration [56] and the inherent orientational degrees of freedom of their chains, which are free to attach their patchy parts to others in a variety of ways, thus gives rise to a wide range of inter-aggregation scenarios [56, 52, 53, 55]. As such, TSP's go beyond a coarse-grained model of a spherical patchy colloid with variable radius: the attractive tails of the block copolymers can assume configurations in which some or even all of them aggregate, rendering the molecule able to merge its patches [52, 53]. In that case, dramatic deviations from sphericity emerge, as all polymer chains (the arms of the molecule) protrude into the same solid angle. The latter configuration, termed *water-melon structure* is assumed by isolated TSP's at sufficiently low temperatures, depending on the degree of amphiphilicity [52, 53]. Such conformations survive also at finite concentrations, in cases where the solvophilic, repulsive A-block is longer than the solvophobic, attractive B-block, in which case the system tends to micellize [55]. In the opposite case of a longer B-block, macrophase separation between a gas and a liquid takes place, terminating at a critical point [55].

The complexity of the system calls for a coarse-grained approach, based on some minimal model, capable of capturing the underlying physics. A too blunt approach that would render the TSP-molecules as spherical particles with isotropic attractions would lead to a loss of information, obscuring crucial aspects of the phase behavior. The choice of a suitable approach of coarse-graining these molecules is not *a priori* clear, since there is a subtle competition of quite a few interactions. In particular, the influence of chain entropy is often very elusive, which makes the coarse-graining problem very challenging every time a new degree of freedom is introduced to the system. previously employed approaches include lattice models [55, 56, 111] as well as an off-lattice approach in which a local coarse-graining at the level of the multiblob approach has been performed [54].

In all prior work, attention has been devoted to the case of fully flexible polymers; the effects of a finite bending rigidity on the structure and thermodynamics of concentrated solutions of amphiphilic star polymers have not been investigated thus far. Studies of the effects of flexibility on fully attractive *chains* have shown a correlation between increasing the bending stiffness and the critical temperature at which the liquid-gas phase separation terminates [96]. In the case of amphiphilic chains, the competition between bending energy, molecular interaction and entropy brings forward a host of new effects, whereby it not only determines the size of regular micelles [112], but also the occurrence of cylindrical phases, lamellar phases [113] or liquid crystals [114]. Similar phases have been observed for flexible block copolymers in the semidilute regime, by means of the multiblob coarse-graining approach [85, 83], and for diblock copolymer melts with one block possessing orientation-dependent segmental interactions, by means of a self-consistent field theory [115].

While the formation of such phases for single surfactant chains is broadly understood, the phase behavior of a star architecture is far more subtle and it has hardly attracted any attention up to now. Hsu *et al.* [116] have considered a model of colloidal particles decorated with stiff DNA strands that associate with the strands of *other* colloids but not with those of *the same* colloid. This situation is brought about by the double constraint of not only strand rigidity but also anchoring rigidity on the colloid, which enforces a tetrahedral arrangement of the four strands. Under these conditions, it has been established in Ref. [116] that the system shows a cascade of liquid-gas transitions and an associated hierarchy of interpenetrating networks. However, the rigid TSP's we consider in this work display exclusively bending rigidity along their arms, which are otherwise completely free to rotate

around their common anchoring point. Under these circumstances, the emergence of ordered phases, in addition to the usual liquid-gas transition is plausible for sufficiently high values of the rigidity and for a sufficient degree of amphiphilicity, as will be shown in what follows. The loss of translational entropy associated with the emergence of spatial order is, in this case, compensated by a reduction in bending energy penalty, since spatial order allows for a better accommodation of the attractive terminal groups without the associated bending-energy cost that disordered phases carry.

In this work, we extend our studies of moderate functionality, fully flexible TSP's [111] by introducing a bending rigidity to the arms of the molecule. While the phase behavior is still strongly determined by the stars' architecture and the interplay of the competing interactions, the energy penalty for a heavily bent arm is a crucial new element, giving rise to ordered phases. To cover a wide range of molecular architectures, and taking into account the fundamental role of both competing interactions and functionality on the phase behavior of fully flexible TSP's [111], we focus at low to moderate values of the functionality $f \in \{3, 6, 10\}$. The size ratios of the solvophobic B-block to the solvophilic A-block range from 100% (i.e., fully attractive molecules) down to 50%, whereas the values for the bending rigidity reach from a fully flexible chain over weak stiffness up to very heavy energy penalties for bent arms, stiffening the stars practically to co-joint rod particles.

The rest of the paper is organized as follows. In section 4.2 we introduce the terminology and illustrate our lattice model, the technical details of the Grand Canonical Monte Carlo (GCMC) algorithm and the essential data analysis techniques, i.e., histogram reweighting, finite size scaling and morphological analysis. In section 4.3 we investigate and discuss the effects of rigidity on the critical behavior of fully attractive stars. In section 4.4 we extend the investigations to amphiphilic systems and identify the occurrence of ordered phases beyond the critical concentration, while in section 4.5 we study these phases in detail for one particular system and draw a complete phase diagram of this system. In section 4.6 we discuss the results, draw conclusions and conjecture from that how rigidity might affect other architectures of amphiphilic star polymers. Some more technical aspects of the problem related to the influence of the finite-size of the simulation box on the ordered phases are relegated to the Appendix.

4.2 Model, simulation techniques and method of analysis

The analysis of the phase behavior and self-assembly properties of diblock copolymer stars investigated in this work is based on simulations of a lattice model. Phase boundaries and structural properties are determined by both thermodynamic and morphometric approaches. The number of diblock polymer chains which are co-joint to a common anchoring point to form a TSP-molecule is called functionality f . We cover moderate values of $f \in \{3, 6, 10\}$. All chains have a fixed number of $k = 10$ segments, representing 10 monomers per arm. It should be noted, however, that these need not be true monomers; they are rather effective ones, that can represent small groups of microscopic units blobbed together into an effective one, which is represented by an either flexible or stiff blob [86]. To keep this in mind, we refer to the generic particles as *beads*, staying within the terms of the abstract, effective model. We label each system in a unique fashion in the following way: solvophilic beads are identified with the letter H ('heads') and solvophobic beads with the letter T ('tails'). The central anchoring point is always of H -type; accordingly, a particular molecule, as well as the concentrated system of the same, is labelled as $H(H_n T_m)_f$, where the first H represents the anchoring point and the sequence brackets describes one of f arms, where the inner A-block consists of n heads (omitted when $n = 0$) and the

outer B-block of m tails, with $n + m \equiv k = 10$. Finally, the subscript f denotes the functionality of the stars.

Starting from systems that feature fully attractive arms, i.e., $H(T_{10})_f$, we go over the amphiphilic cases $H(H_2T_8)_f$ and $H(H_4T_6)_f$ to systems where the A- and B-blocks are of the same size, i.e., $H(H_5T_5)_f$. The latter case has been found in our previous studies [55, 111] to be the threshold case where fully flexible TSP's still undergo liquid-gas phase separation below a certain critical temperature. Increasing the length of the solvophilic A-block further, i.e., for the $H(H_6T_4)_f$ and $H(H_8T_2)_f$ -cases, macrophase separation abruptly disappears and instead the solution shows the formation of bicontinuous, percolating network structures and/or micellization, depending on the value of the functionality f . In this work, we stay below the aforementioned threshold and only investigate the effects of rigidity on systems which, in the fully flexible case, show gas-liquid macrophase separation terminating at a critical point.

The inter-bead effective interaction is modeled by means of the Larson scheme for amphiphile-oil-water solutions [59, 60, 61, 62]. Within the framework of this model, a lattice site can be occupied by one of three species, namely a solvent molecule (S), a solvophilic head (H) or a solvophobic tail (T), and there are no empty sites (incompressibility condition). The interaction energies of the solvent and the solvophilic species are chosen to be the same $\epsilon_{SS} = \epsilon_{HS} = \epsilon_{HH} = 0$. We further choose $\epsilon_{HT} = 0$, for the interaction between head and tail monomers, and $\epsilon_{TT} = -1$, for the interaction between tail monomers, the negative value of the latter expressing the propensity of solvophobic beads to establish contacts to one another. The overall energy scale describing the system is therefore $\epsilon = 2\epsilon_{HT} - \epsilon_{HH} - \epsilon_{TT} = 1$, so that the reduced temperature can be defined as $T^* = k_B T / \epsilon$. As in previous work [56, 55], we employ a simple-cubic lattice to place the beads, in which both bonding and interactions extend up to the third nearest neighbor of any site; the effective coordination of the cubic lattice is therefore $Z = 26$. The model contains *no elasticity contributions*: although the ratios of third- to second- to first-neighbor distances are $\sqrt{3} : \sqrt{2} : 1$, there is no difference in the stretching energies for bonding of sequential monomers along these three directions. Periodic boundary conditions are applied in all spatial directions using the minimum image convention.

The rigidity is modeled by introducing an energy penalty when the angle between two successive bonds along a chain deviates from the value π . The stiffness of the chain is tuned by a prefactor α and the energy penalty is written as

$$E_{rig} = \alpha (1 + \cos \theta), \quad (4.1)$$

where θ is the angle between two successive bonds along a chain.¹ A straight-line segment is thus not penalized, while a right angle one is penalized by a value of $E_{rig} = \alpha$, up to a hypothetical maximum bending of zero degrees with a penalty of $E_{rig} = 2\alpha$, although this cannot occur in our lattice model since we do not allow overlap of two beads on the same lattice site. We emphasize, however, that this rigidity pertains only to the bonds along any chain of the star and it is absent at the anchoring point of the f chains on the central bead; there, the connections are fully flexible. At odds with the model of Ref. [116], the TSP's of our model feature no prescribed orientational correlations between their chains.

We employ Grand Canonical Monte Carlo (GCMC) simulations: the volume $V = L \times L \times L$ of the simulation box is fixed for a single run, and we have employed in most cases box sizes $L = 30$; however,

¹Note that in some cases Eq. (4.1) is written as $E_{rig} = \alpha(1 - \cos \theta)$, since the angle θ is defined there through the relation $\theta = \cos^{-1}(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_{i+1})$ with the unit *vectors* $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_{i+1}$ between successive bonds. Here, we rather adopt the convention of defining θ as the angle spanned by the straight line segments of two successive bonds, having its apex at their shared joint.

to check for finite-size effects and to ascertain that critical points are genuine ones, we have also run simulations with box sizes ranging from $L = 20$ up to $L = 60$ (all lengths expressed in units of the lattice constant). The chemical potential μ and the temperature T are run-specific constants as well, so that the average volume fraction of the beads, $\phi = N/V$, of a single run is calculated from the grand canonical expectation value $N \equiv \langle \mathcal{N} \rangle_{\mu, V, T}$ of the instantaneous number $\mathcal{N}$ of molecules in the simulation box.

A mixture of MC steps is implemented, namely insertion and deletion of an entire molecule, the deletion and regrowth of single chains of one molecule as well as moving of an aggregated cluster of molecules. With the exception of the latter, all MC steps feature a full-energetic configurational biasing, taking into account both the interaction energies between the terminal groups and the rigidity when placing or removing a bead. This biasing turns out to be very effective when simulating at high monomer concentrations ($\phi > 0.4$), where the presence of multiple neighboring molecules forces the molecule under growth to assume heavily bent configurations that are unfavored by the rigidity and would most certainly be rejected if the rigidity had only been considered in the Metropolis acceptance check. Thus, both rigidity and interaction energy are biased *on the fly* and the Rosenbluth factors are kept and taken into account in the Metropolis acceptance criterion [65].

The critical points have been determined as follows: first, a concentration-scan was performed by running simulations at a given temperature and increasing gradually the chemical potential, looking for density jumps that signal the existence of a first-order (condensation) phase transition. Successively repeating this for higher temperatures lowers the magnitude of the jump, eventually ending in a small regime in the (T, μ) plane, where strong concentration fluctuations are observed. This region is sampled to a sufficient number of runs and the density- and energy-fluctuations are analyzed using a finite-size-scaling approach, in which the limiting critical distribution of the density (i.e. concentration) is matched with that of the Ising universality class [102]. Minimizing the Ising curve deviation for values of T and μ provides the necessary parameters for an extensive simulation run in which the critical point is sampled. Repeating the procedure for different box sizes ascertains that the critical point is a genuine one [24].

The total number of MC steps, i.e., equilibration plus sampling ones, range from orders of magnitude of 10^6 for very dilute systems, such as the gaseous branch of a macrophase separation binodal, up to 10^9 for very dense systems and critical points. Determination of the latter requires very good statistics in order to adequately cover the range of fluctuations, which is imperative for the calculations of coexistence curves. The latter were calculated using the histogram-reweighting method [21], i.e., by sampling the instantaneous molecule number $\mathcal{N}$ as well as the internal energy $\mathcal{U}$, and combining them according to the Ferrenberg-Swendsen algorithm [99, 100, 101]. For a particular system, the resulting coexistence curves for two different box sizes were compared since they are identical for a truly macrophase-separating system, while for a pseudo-critical point, the binodal narrows for larger simulation box sizes [24]. Possible ordered phases and aggregation phenomena beyond the liquid-gas macrophase separation were found, identified and characterized by a direct visual of simulation box snapshots, cluster size histograms and a detailed morphological analysis. The latter provides a very robust signature of the existence of ordered phases at the high-concentration regime in the form of jumps or kinks of the morphometric coefficients of the mixture at certain density regimes. To obtain those, we performed selected, supercritical, isothermal runs at fixed Volume V , varying chemical potential μ and calculating the Minkowski functionals [105, 106, 107] of the aggregates formed by the T -beads of the solution.

4.3 Fully attractive telechelic star polymers with rigidity

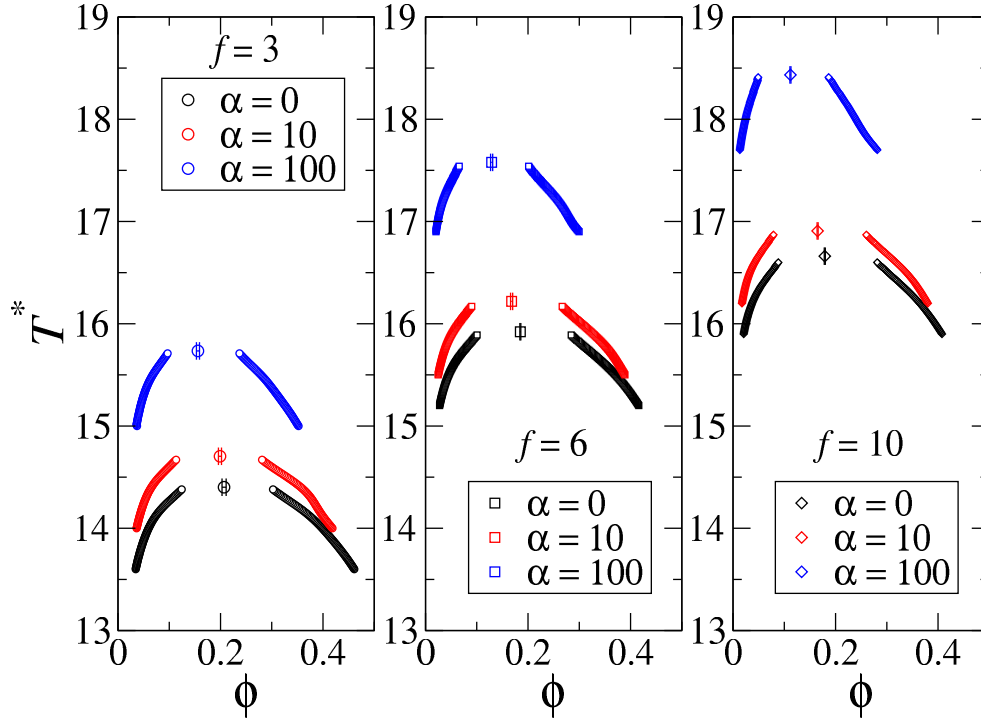


Figure 4.1: The gas-liquid binodals of $H(T_{10})_f$ -systems, $f = 3, 6, 10$ for different values of the bending rigidity α , as indicated in the legends. The critical points are shown with error bars and are direct simulation results. The coexistence curves are results from histogram reweighting calculations.

We commence our investigations with the systems $H(T_{10})_{f=3,6,10}$, which all represent f fully attractive chains, anchored together at a common solvophilic head H . Indeed, this is the simplest case to begin with, since fully-flexible TSP's up to a amphiphilicity of $H(H_5T_5)_f$ have shown to undergo macrophase separation with a well-defined critical point, and it is interesting to examine the evolution of the phase diagrams of these systems upon growing rigidity of the arms, keeping all other interactions in the model fixed. previous studies on the effects of rigidity on fully attractive *linear* chains [96, 117, 118, 119, 120, 121], which also undergo a macrophase separation, have shown that an increase in either chain stiffness or in chain length decrease the critical concentration while increasing the critical temperature. In fact, it can be argued that the increase in the chain rigidity is equivalent, in its effect, with a growth of the chain length of a fully flexible chain. As rigidity grows, chains assume increasingly directional configurations, exposing thereby their attractive monomers to those from other chains. This state of affairs enhances the possibility (and the associated energy gain) of interchain associations. Combined with the decreasing entropic term due to orientational fluctuations, an increase in the critical temperature with bending stiffness results [96].

These trends from linear chains are fully confirmed for the case of the star architecture as well. In Fig. 4.1 we show the phase separation binodals of the $H(T_{10})_f$ -systems, $f = 3, 6, 10$, where a systematic increase in the critical temperature T_c^* and a concomitant decrease in the critical bead concentration ϕ_c upon increasing α can be seen. This is the same trend as the one seen for fully flexible TSP's upon

increasing the arm monomer number [56]; in fact, doubling the arm monomer number from $k = 10$ to $k = 20$ brings about an increase in T_c^* by about two units [56], almost the same as an increase of α from $\alpha = 0$ to $\alpha = 100$ for fixed $k = 10$. A relative increase of T_c^* by about $\sim 10\%$ for the $H(T_{10})_3$ system can be seen when going from $\alpha = 0$ to $\alpha = 100$. At the same time, a fully attractive chain with a length of $k = 32$ monomers shows an increase in the critical temperature of $\sim 12\%$ for the same change of its rigidity [96]. Since the star molecule has a total of $k = 31$ monomers of which 30 are attractive, the effect of the rigidity on the increase in critical temperature has a remarkable correspondence between the two architectures. Furthermore, comparing the value of the critical temperature itself for the $H(T_{10})_3$ star and the $k = 32$ bead single chain [96], for both extreme values $\alpha = 0$ and $\alpha = 100$, that of the single chain is roughly $\sim 6.3\%$ higher than that of the star. This value is remarkably close to the fraction of attractive beads of the two models, which is $\frac{32}{30} \approx 6.7\%$. We conjecture that in the architectural change from a single chain to the most rudimentary star of $f = 3$, the critical temperature is primarily determined by the number of attractive beads, rather than the architecture itself.

The above conclusions do not hold for higher functionalities, in which the effects of the star architecture are much more pronounced. The critical temperature is higher for the $f = 6$ case and again higher for $f = 10$, but not proportional to the total number of beads on the molecule. Moreover, even for the case $f = 3$, and at odds with the similarity to the stiff chains for the evolution of the binodal, we have not found any ordered phases for fully attractive star polymers. For the stability of nematic or smectic phases, architecture does matter and fully attractive stars do not sustain them, at least not within a range of a few temperature units around T_c^* that we investigated. On the contrary, a host of ordered phases are stabilized by the simultaneous presence of rigidity *and* amphiphilicity, as we will demonstrate in the following sections.

The structure of the fluid phase formed by the TSP's can be characterized in a number of ways. Although it is customary to consider the pair correlation function or its inverse-space counterpart, the structure factor, these quantities deliver information about *pair correlations only*. Here, we employ a different, morphometric approach, which is robust and more suitable in bringing forward quantitative characteristics of the spatial organization of the molecules, and in particular of their associating, attractive end-beads. For this purpose, we surround each lattice site by the Wigner-Seitz cell of the cubic lattice, i.e., by an elementary cube having the size of the lattice constant; evidently, this construction is space-filling. We then denote each such cell that surrounds a site occupied by a T -monomer as 'full' and all others that surround H -beads or empty (solvent) sites as 'empty'. The resulting spatial pattern of filled cells can be characterized by the four Minkowski functionals [105, 106, 107], all normalized over the box volume V : the occupied volume, ν_0/V , the exposed surface area ν_1/V , the integral mean curvature ν_2/V and the Euler characteristic ν_3/V . Average values of the same over many system realizations, $\nu_i \equiv \langle \nu_i \rangle$, $i = 0, 1, 2, 3$, can be calculated during the simulation and their dependence on ϕ delivers information on the structure of the fluid. In what follows, we limit our analysis to $i = 1, 2, 3$, since the quantity ν_0/V is equal to the volume fraction of terminal monomers and thus trivially related to ϕ by a system-dependent proportionality constant.

Results for a representative, fully attractive TSP-system (i.e., for $f = 3$) are shown as a function of ϕ in Fig. 4.2, for temperature $T^* = 1.1 T_c^*$. The form of the curves is quite similar for all systems, independently of f and, in addition, the curves are largely insensitive to the value of the bending rigidity α . We discuss thus their generic shapes and the implications of their ϕ -dependence for the structure of the fluids.

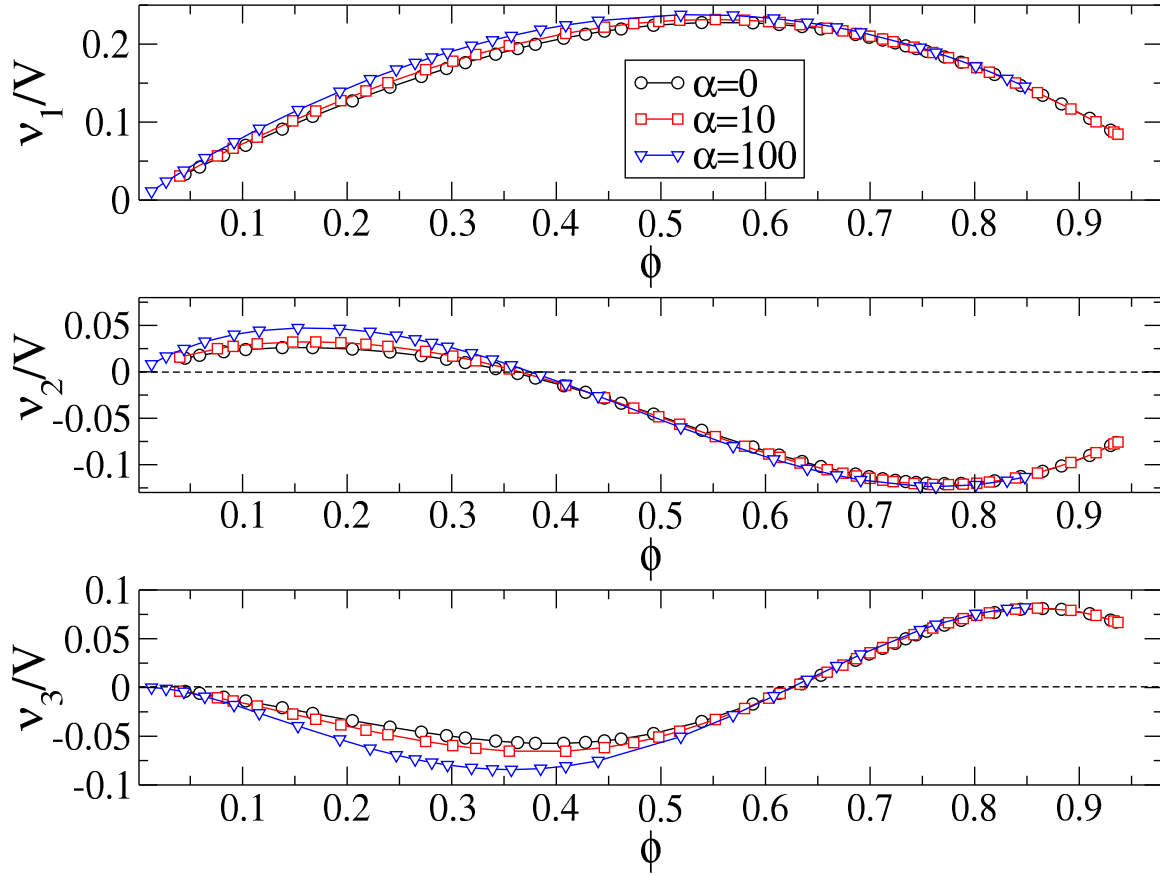


Figure 4.2: The box-volume-normalized Minkowski morphological coefficients of the system $H(T_{10})_3$, plotted against the monomer volume fraction ϕ at temperature $T^* = 1.1 T_c^*$. From top to bottom, the exposed area v_1/V , the integral mean curvature v_2/V and the Euler characteristic v_3/V . Values of the bending rigidity α as indicated in the legends.

The coefficient ν_1 describes the free surface of the entirety of T beads in the box. A constant slope for low concentrations is an indicator of a gaseous phase in which all molecules roam independently, while the decrease of the slope as ϕ grows stems from enhanced intermolecular associations. A saturation is reached for the fluid phase in which most of the molecules aggregate. For high concentrations, the fluid phase becomes ever denser and fills remaining voids, thus reducing the slope below zero. At the limit $\phi \rightarrow 1$, the lattice is *almost* full with terminal monomers and only the anchoring points, which are of H -type contribute to the cells that are termed ‘empty’ for the purposes of the morphometric analysis. The system thus attains in this case a ‘swiss cheese’ configuration and the exposed area equals the total area of the cubes that surround the anchoring points.

The coefficient ν_2 describes the integral mean curvature in three spatial dimensions. The positive values at low concentrations denote purely convex aggregates of tail beads in the gaseous solution. The maximum and the ensuing negative slope when increasing concentration are due to the negative contribution from emerging, locally concave forms, especially when two convex clusters meet, merge and connect via a narrow neck. The negative contribution is further amplified when the concentration increases and T -monomer clusters grow further, eventually enclosing cavities in their interior. The latter effect is dominating for high concentrations $\phi > 0.4$. At very high concentrations, $\phi > 0.8$, the solvent cavities start to get filled and their negative contribution vanishes, thus driving the value of

ν_2 upwards again.

The Euler characteristic is a topological signature of the pattern and in three dimensions it takes the form

$$\nu_3 = \mathcal{N}_D + \mathcal{N}_C - \mathcal{N}_T, \quad (4.2)$$

where $\mathcal{N}_D$ is the number of disconnected aggregates, $\mathcal{N}_C$ the number of enclosed cavities and $\mathcal{N}_T$ the number of perforations, i.e., tunnels that percolate through the system. The negative values that the Euler characteristic obtains for low- and moderate-concentrations are typical for systems that form bicontinuous, spongy structures. On increasing the concentration, two competing mechanisms are at place: on the one hand, the increasing intermolecular associations create more tunnels, thus driving ν_3/V to more negative values. On the other, as space is filled, tunnels start closing and the Euler characteristic attains a negative minimum at which its trend is reversed: the perforations fade away and leave isolated cavities within the bulk structure, thus driving the value of ν_3 to positive values. At the limit $\phi \rightarrow 1$, the Euler characteristic per site approaches the value $(kf + 1)^{-1}$, i.e., the volume fraction of the cavities formed by the H -type anchoring points.

We argue that the form of the three morphological coefficients is a quasi-universal property of macrophase-separating TSP-systems. The differences due to changes in the bending rigidity are small and they become visible only in the dilute or semidilute regimes for the case of very high stiffness, $\alpha = 100$. Moreover, the dependence of the morphological coefficients on ϕ takes, for all cases of fully attractive TSP's, the form of smooth curves – at least within the limitations of the sampling points we considered along the concentration axis. This constitutes a morphological implication of the fact that the system remains within the same, uniform phase, along the whole concentration path. The situation is different in case additional and, in particular, ordered phases intervene along the way, as we will demonstrate in the following sections. Accordingly, we can make use of possible ‘anomalies’ in the evolution of the morphological measures with ϕ , such as kinks or jumps, as signatures for the emergence of spatial order.

4.4 Amphiphilic telechelic star polymers with rigidity

We now introduce amphiphilicity to the system by turning the first few beads on a chain solvophilic, i.e, of the H -type. As these heads H have the same interaction energies as the solvent species, there is no direct interaction potential between them, except from volume exclusion. However, entropy drives the heads apart, as they try to explore all possible neighboring sites. All fully flexible amphiphilic systems with relative block sizes between 20% solvophilic, [i.e., $H(H_2T_8)_f$] up to an even ratio of half solvophilic/half solvophobic blocks, [i.e., $H(H_5T_5)_f$], undergo macrophase separation and it has been found [111] that a higher relative size of the solvophilic block lowers the critical temperature as well as the critical concentration. This is due to entropy effects, which are more pronounced for a larger inner block: the less attractive sites a molecule has, the lower the temperature needed to suppress intramolecular association in the liquid phase that lead to critical fluctuations that terminate liquid-gas coexistence. At the same time, the repulsion from the inner block increases the radius of gyration and the effective molecule size, lowering thus the monomer concentration in which the molecules associate into a fluid phase.

When rigidity is introduced, the entropic contribution to the free energy diminishes. As for the case of the fully attractive TSP's, this pushes the critical temperature up again. In Figs. 4.3, 4.4, and 4.5 we plot the coexistence curves of several amphiphilic systems up to rigidity values of $\alpha = 10$. The

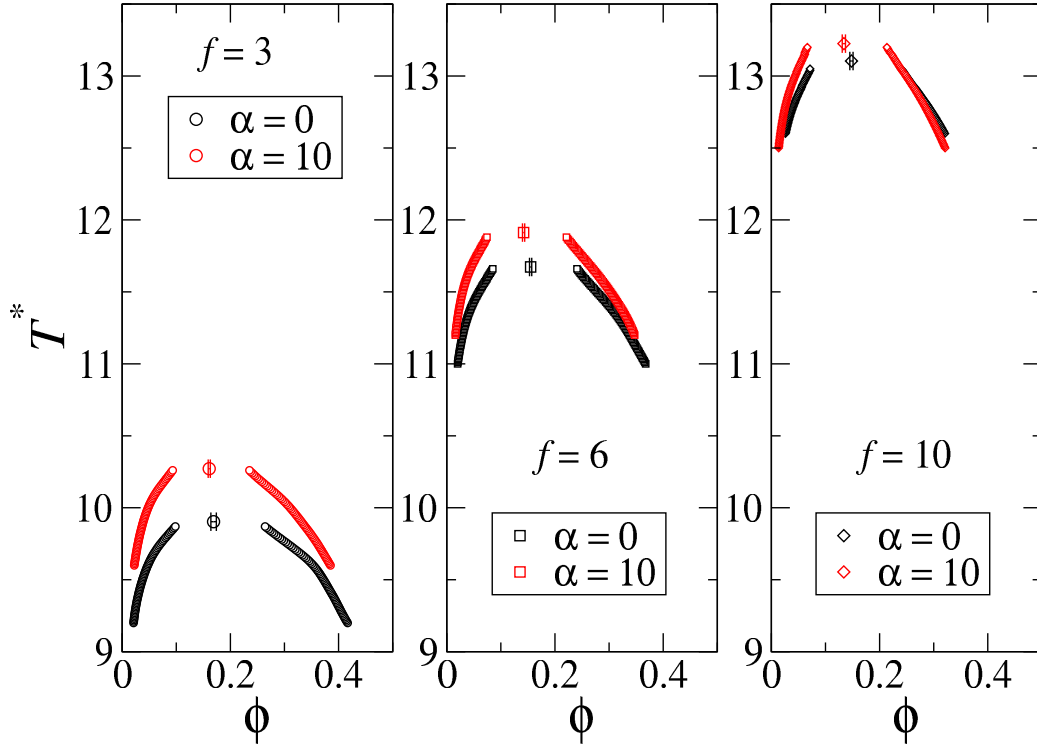
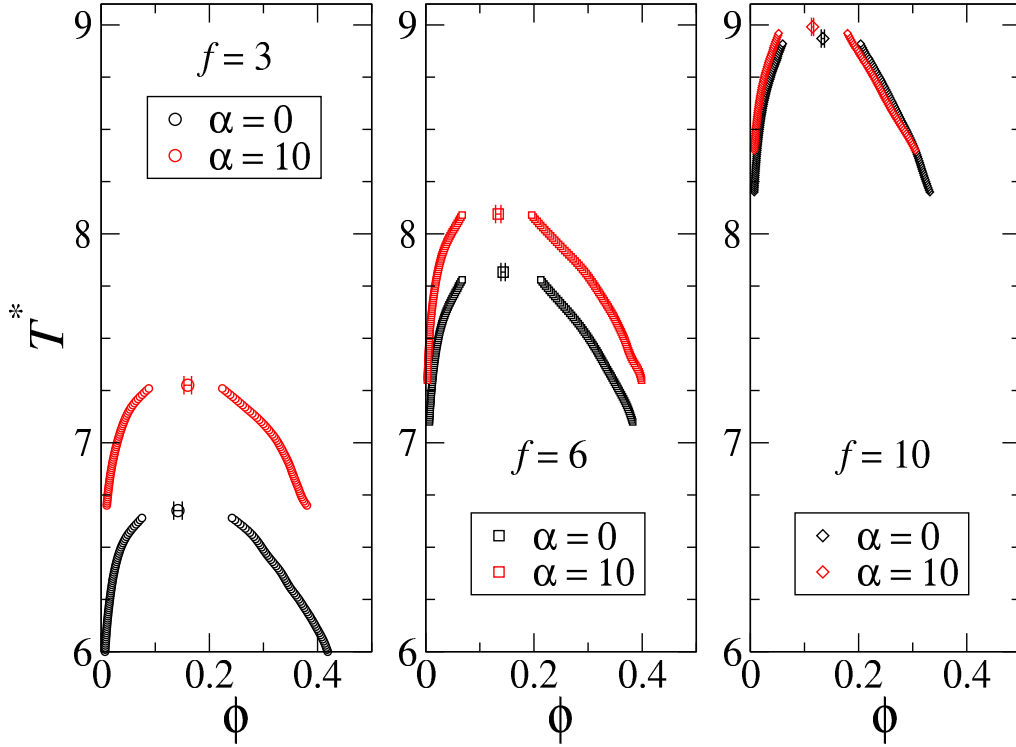


Figure 4.3: The phase separation binodals of the systems $H(H_2T_8)_f$ for $f = 3, 6$, and 10 as indicated in the headings and for bedding rigidities $\alpha = 0, 1$, and 10 as indicated in the legends. The case $\alpha = 100$ is omitted here, since ordered phases show up for high rigidities (see the text).

case $\alpha = 100$ is discussed separately. The trend that was already observed for fully attractive single chains [96] and fully attractive stars in section 2 holds: the critical temperature increases with α and the critical concentration drops, with the exception of the $f = 3$ -systems for which it does not appear to change within the error bars.

The morphological coefficients of a representative amphiphilic system, $H(H_2T_8)_3$ are shown in Fig. 4.6 for rigidities $\alpha = 0, 1, 10$, and 100 . The curves for rigidities $\alpha = 0, 1$, and 10 show the same qualitative form as the fully attractive stars, which we argued to be universal for macrophase separating systems. A slight stretching of all curves in comparison with those shown in Fig. 4.2 can be seen: for instance, the x -axis intersect of the Euler characteristic ν_3/V occurs at $\phi \cong 0.625$ for the system $H(T_{10})_3$, while it lies at $\phi \cong 0.78$ for the system $H(H_2T_8)_3$. This stretching is due to the fact that the morphologies of *just* the T -bead clusters are calculated. The latter system possesses $\frac{8}{10}$ of the total number of T beads of the former, thus it needs $\frac{10}{8}$ times the number of molecules to build a morphologically similar aggregate as $H(T_{10})_3$, which is precisely the factor of the present stretching. An additional manifestation of this can be seen, e.g., at the $\phi \rightarrow 1$ extrapolation of the surface area term, v_1/V . Here, the isolated head groups of the $H(H_2T_8)_3$ -system are bigger than those of the $H(T_{10})_3$ -system and they thus have a larger exposed area to the rest of the system, which is reflected at the higher extrapolated value of this quantity at the limit of full lattice occupancy. Note that this fact is obscured at the Euler characteristic, since this is a topological signature and it simply counts the number of

Figure 4.4: Same as Fig. 4.3 but for the $H(H_4T_6)_f$ -case.

cavities in this limit, which is a scale-invariant, topological measure.

Apart from these quantitative changes, the morphological measures of the low- and moderate-rigidity amphiphilic systems do not show any significant difference from those of their fully attractive counterparts and the curves for $\alpha = 0, 1$, and 10 are smooth functions of ϕ . The situation is markedly different for the high rigidity case, $\alpha = 100$. Here, a deviation from the universal shape and a kink/jump can be seen in Fig. 4.6, occurring at $\phi \cong 0.4$ and $\phi \cong 0.62$, respectively – both most pronounced for the surface area v_1/V and the Euler characteristic v_3/V . These are signatures of first-order phase transitions, so we resorted to visual inspection and a concomitant cluster analysis of the aggregates to identify the new phases that show up in the system. In the region $0.4 < \phi < 0.62$, an ordered, lamellar phase shows up, which remelts into a very dense fluid for $\phi > 0.62$. The typical structure of the lamellar phase can be seen in snapshots in fig. 4.8: the H -parts of the molecules self-organize into parallel planes, which are separated by planes in which the fully stretched T -parts of the arms interpenetrate and come into contact. No other ordered phases were detected for the $H(H_2T_8)_f$ and for the $H(H_4T_6)_f$ -systems.

Both the appearance of an ordered lamellar phase and its remelting at high monomer concentrations require some physical explanation. We begin with the former issue. Consider first the liquid phase at moderate values of the concentration, $\phi \approx 0.3$. Its morphological signature shows that it is a bicontinuous, spongy phase with many tunnels perforating the pattern formed by the inter-associating terminal monomers. For flexible molecules, upon compression of the system, the patterns formed by the terminal parts can have variable thickness and the interface separating them from the H -regions

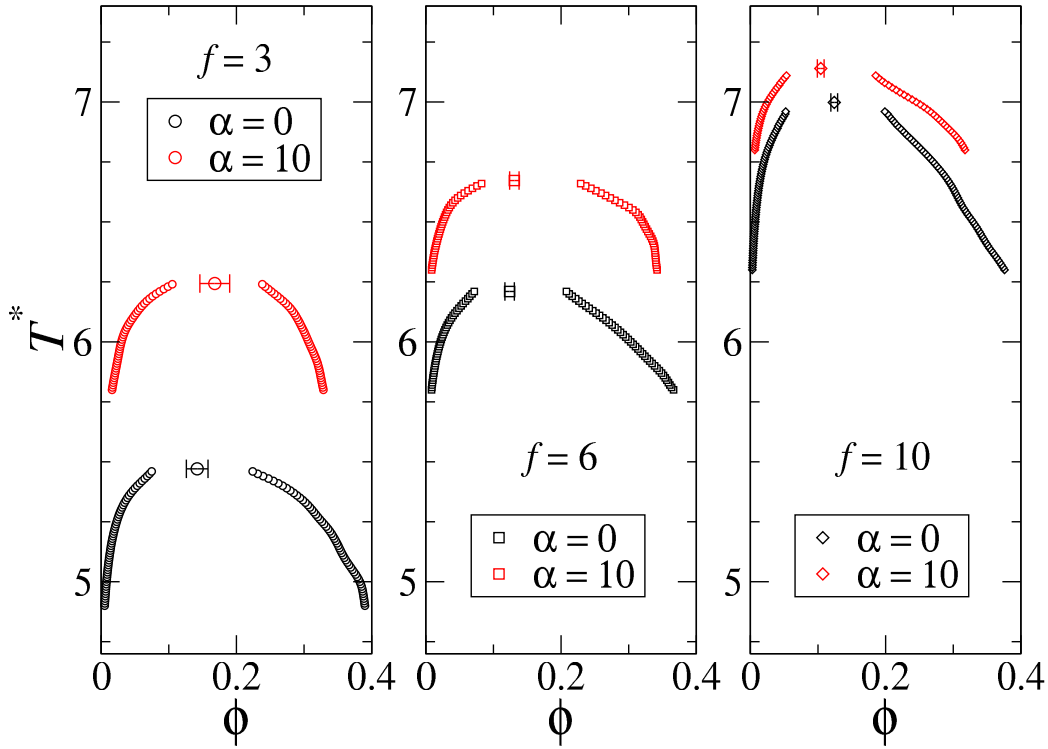


Figure 4.5: Same as Fig. 4.3 but for the $H(H_5T_5)_f$ -case.

can fluctuate, since the chains are flexible and they can backfold and compactify. This possibility is not available to the most rigid system, since it would carry a high energy cost. Accordingly, the system chooses the strategy of sacrificing a part of its translational entropy, restricting the molecules to an essentially two-dimensional configuration in the lateral direction of the lamellar planes, and gaining the energetic advantage of maximizing the contacts between the fully stretched, attractive parts of the chains, which now occupy the region in the interior of equidistant, lamellar planes. The signature of the lamellae is clearly visible in the plateau of the surface-area term, v_1/V , at the upper panel of Fig. 4.6. Moreover, as the terminal monomers compactify within the lamellae as ϕ grows, they eliminate small tunnels in this region, driving the Euler characteristic towards higher values and even bringing about a saturation of the same at approximately zero value for $0.58 < \phi < 0.62$ – see the bottom panel of Fig. 4.6. Although the lamellar phase offers the system a very suitable opportunity to self-organize under the restrictions imposed by amphiphilicity and rigidity, it cannot persist to arbitrarily high values of the monomer concentration due to the incompatibility between close-packing coordination and star functionality. Eventually, thus, at sufficiently high values of ϕ , the system returns to an amorphous phase that closely resembles the structure and morphology of its flexible counterparts.

The above considerations regarding the stability of the lamellar (or, more generally, ordered) phases put emphasis on one important factor – the rigidity of the chains. However, this is *not* sufficient by itself, as can be easily verified by the fact that for fully attractive TSP's no such ordered phase has been detected. The *additional* factor is a sufficient degree of amphiphilicity. To appreciate this, consider a typical lamellar phase shown, e.g., in Fig. 8, and imagine gradually shrinking the extent of the

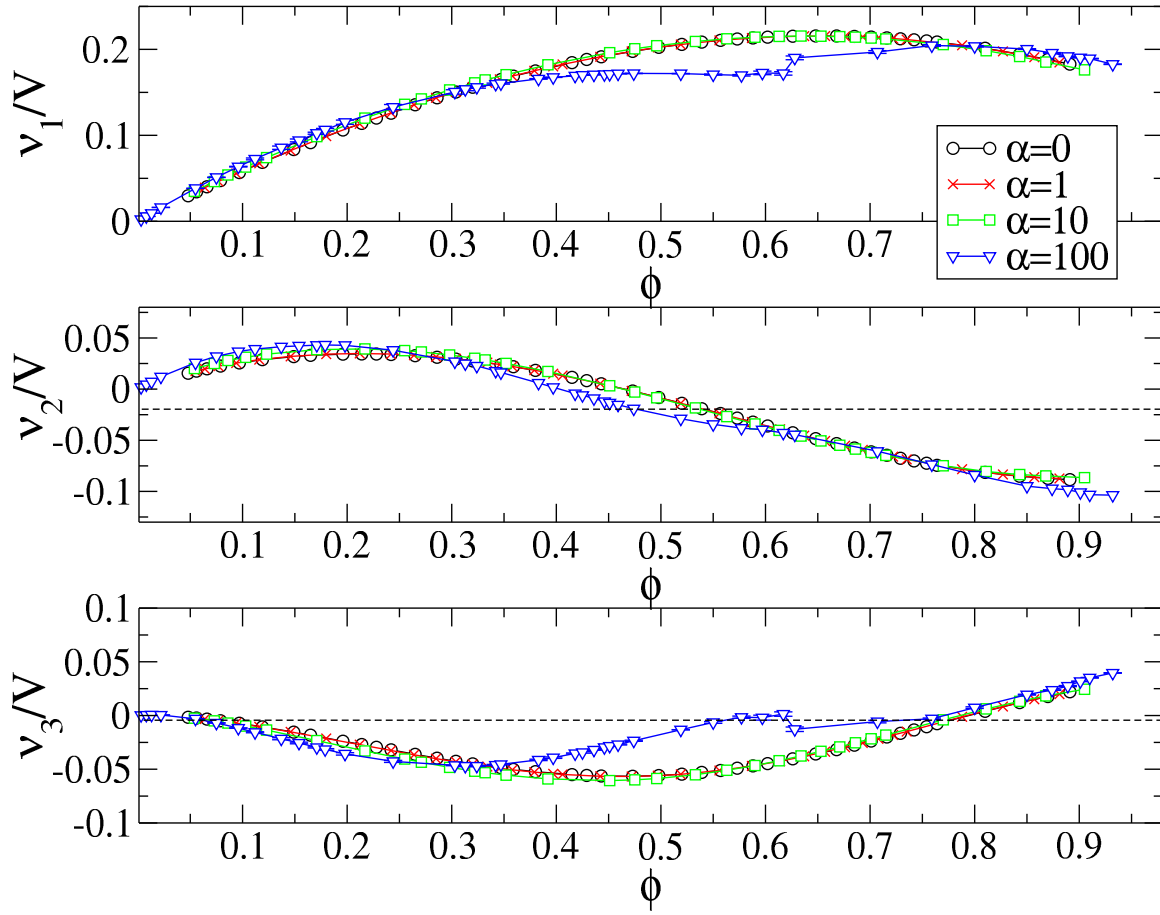


Figure 4.6: The box-volume-normalized Minkowski morphological coefficients of the system $H(H_2T_8)_3$, plotted against the monomer volume fraction ϕ at temperature $T^* = 1.1 T_c^*$. From top to bottom, the exposed area v_1/V , the integral mean curvature v_2/V and the Euler characteristic v_3/V . Values of the bending rigidity α as indicated in the legends.

solvophilic sheets, so that at the end only the central bead of the stars is of the H -type. Imagine now an undulation on the lamellar planes perpendicular to their extension, which on the one hand gives the star centers additional translational entropy and on the other it causes a perforation of the solvophilic planes by the solvophobic, stretched chains. Since in this case the remaining solvophilic planes are thin and sparse, this perforation does not result into a significant energy loss due to missed T -monomer contacts and therefore the putative lamellar phase becomes unstable. Indeed, this is precisely what has been found for the fully attractive, $H(T_{10})_f$ -stars: there, the stable phase is a uniform fluid with full, three-dimensional translational freedom for the star centers. It is thus a combination of rigidity and sufficient degree of block-incompatibility that must cooperate in order to make the solvophilic planes sufficiently dense and thick, so that a perforation by T -blocks brings with it a sufficiently high energetic penalty, stabilizing thereby the lamellar phase.

These considerations are quantitatively confirmed in our simulations, in which we found that by making the molecules more amphiphilic, i.e., by going from $H(H_2T_8)_f$ - to $H(H_4T_6)_f$ -ones, the region of stability of the lamellar phase grows. It follows, then, that the most amphiphilic systems considered here, namely the $H(H_5T_5)_f$ -ones, hold the highest promise of featuring an interplay between gas-liquid phase separation and, possibly, a number of ordered phases. We examine in detail such a representative case in the following and we draw a semi-quantitative phase diagram based on runs at selected points

in the temperature-concentration plane.

4.5 Ordered phases for strong amphiphilicity and high chain rigidity

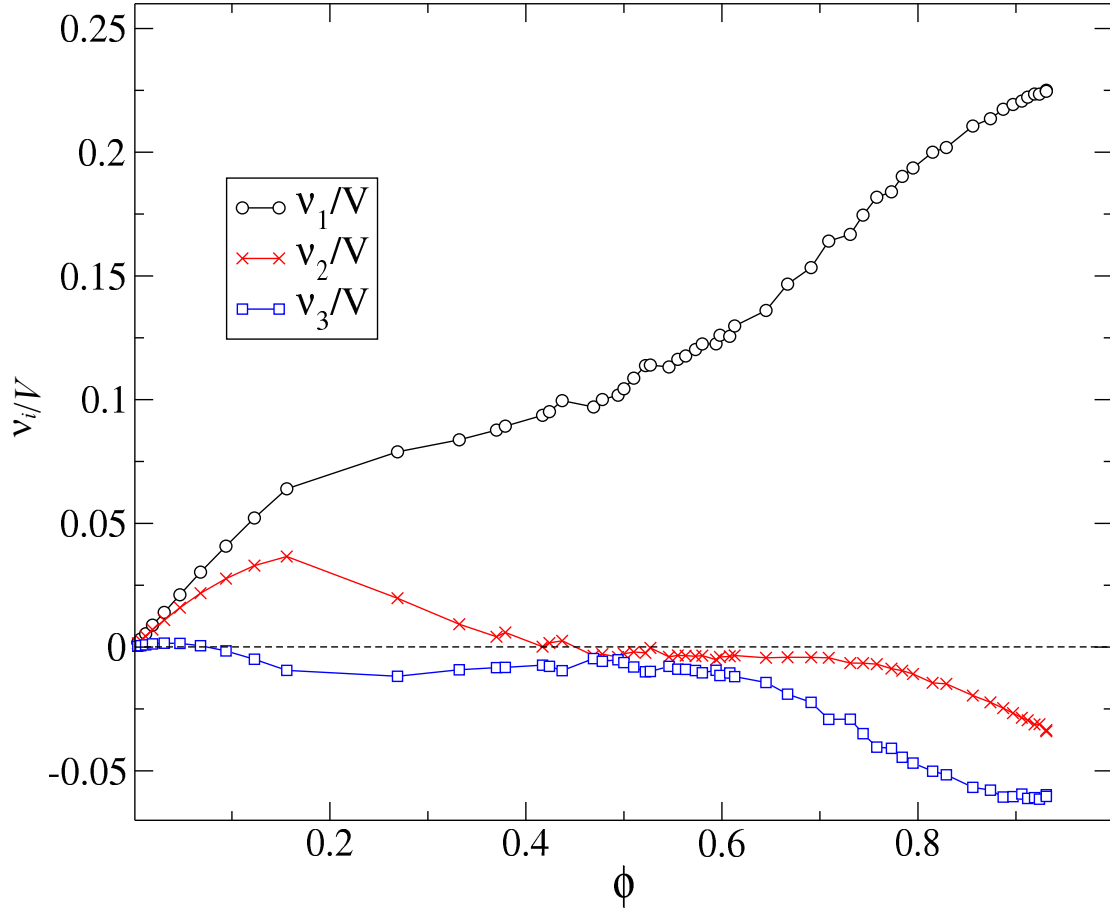


Figure 4.7: The Minkowski functionals per unit volume plotted against monomer volume fraction ϕ , for the system $H(H_5T_5)_3$ and rigidity $\alpha = 100$ at temperature $T^* = 9$.

As a representative of strongly amphiphilic molecules with high rigidity, we consider here in some detail the $H(H_5T_5)_3$ -system with $\alpha = 100$. Our simulations for the other two $H(H_5T_5)_f$ -systems, $f = 6, 10$, as well as those for the ordered phases of the $H(H_2T_8)_f$ - and the $H(H_4T_6)_f$ -systems will be discussed in the context of our findings for this particular system.

We commence by considering the morphological measures at a slightly supercritical temperature $T^* = 9$, shown in Fig. 4.7. In comparison with the preceding results, we establish that these curves display very wide ranges of ‘anomalous’ behavior with many kinks/jumps, covering a range of concentrations ϕ between, roughly, 0.2 and 0.7. Visual inspection of the simulation snapshots revealed the existence of as many as three different ordered phases on the high-density side of a (narrow) gas-liquid binodal. The presence of ordered phases predestines any attempts of histogram reweighting for lower temperatures to fail. However, we were able to find for all amphiphilic systems at rigidity $\alpha = 100$ a point with critical molecule number fluctuations. By running simulations sufficiently close to this critical point, we could avoid sampling of ordered phases, thus being able to draw a small piece of the binodal using histogram reweighting. Starting from the dense branch of the resulting binodal, we kept volume V and temperature T fixed and increased the chemical potential μ . By direct visual of simulation snapshots

we identified three ordered phases: a cubic lattice, a columnar phase and a lamellar phase, before the system remelts at high concentrations.

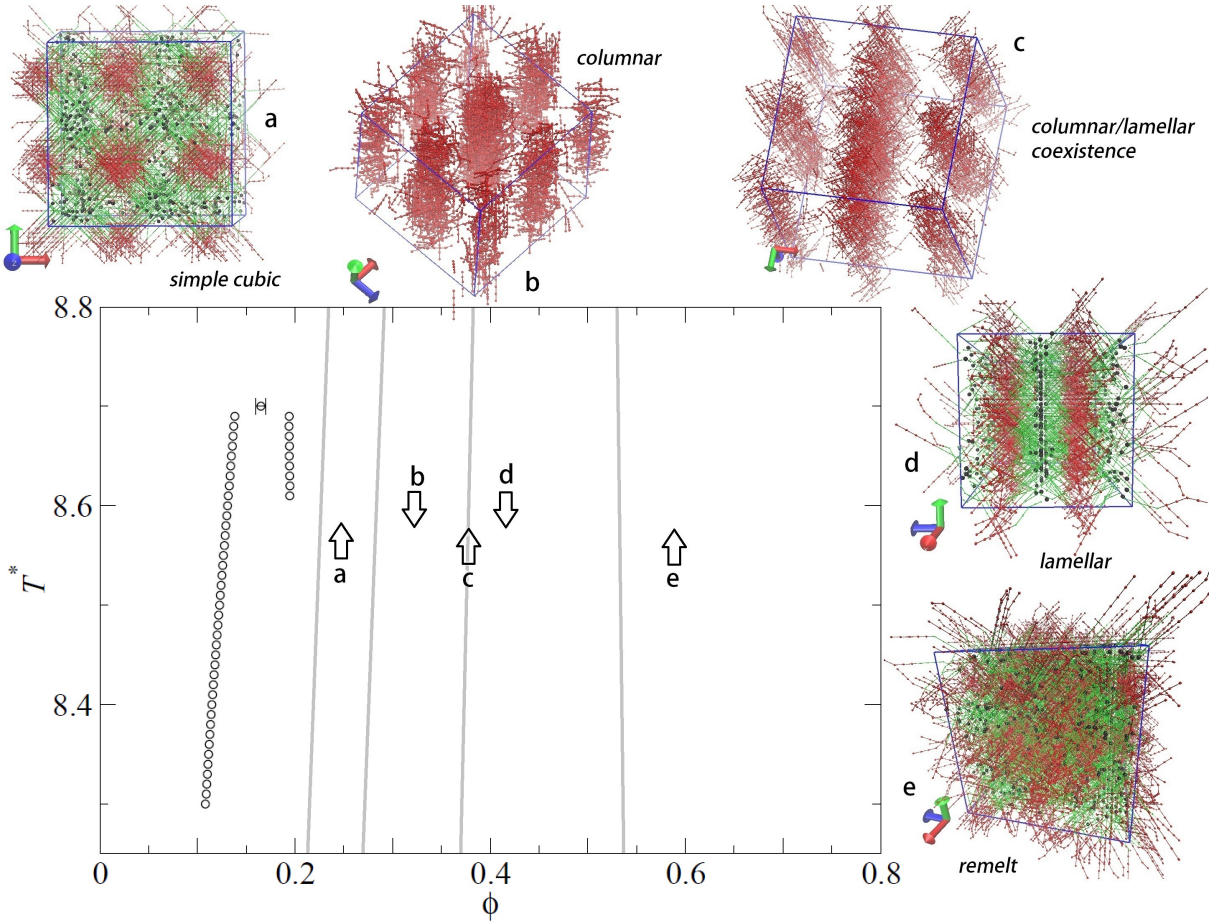


Figure 4.8: A semi-quantitative phase diagram of the $H(H_5T_5)_3$ -system. Open circles denote the gas-liquid binodal terminating at a critical point, and they have been calculated by the histogram-reweighting method. Gray lines are rough phase boundaries (guides to the eye) between the phases denoted by the arrows and they have been drawn using the procedure explained in the text. The snapshots are taken at the points a - e on the phase diagram and they show the molecular arrangement at the ordered phases (a , b , d), at a mixed columnar-lamellar phase (c) and at the high-concentration remolten fluid (e). In the snapshots, outer-block T -beads are colored red, inner-block H species are colored green and anchoring points are colored black. In snapshots b and c we only show the T -species for visual clarity.

The presence of the finite-size box as well as issues of compatibility between the cubic box and the symmetries of ordered phases make the task of calculating free energies of the ordered phases very demanding and we refrain from it in this work. Our purpose is not to draw detailed phase diagrams that include the ordered phases but rather to draw general, semi-quantitative conclusions about the shape and the topology of the phase diagram. For this purpose, we have limited ourselves to visual inspection and morphological characterization of the phases at selected temperatures, complemented with physical argumentation. Concomitantly, we draw in Fig. 4.8 a ‘hybrid phase diagram’ that includes the phase separation binodal (which is based on proper free energy calculations) combined with drawings of the regions of stability of the ordered phases that were based on the considerations sketched above. In Fig. 4.8 we show, in addition, snapshots of the ordered phases. All snapshots were taken from simulations at temperature $T^* = 8.6$ and a box volume of $V = 40 \times 40 \times 40$ lattice sites.

In snapshot *a* of Fig. 4.8, taken at concentration $\phi = 0.253$, the molecules orient in such a way that the *T* species form spherical clusters that self-assemble in a cubic lattice. Within each red, spherical cluster of terminal monomers the chains are stretched and the system attains an ordered microphase separation between its incompatible *H*- and *T*-beads. In trying to understand the propensity of the system to form a phase in which translational invariance is broken in all three spatial dimensions, particular attention has to be paid in two different sources of entropy inherent in the system: the translational entropy of the molecular centers on the one hand and the combinatorial entropy that arises from the different possibilities that a star has to throw its arms towards any of its neighboring *T*-monomer blobs. The number of these possibilities, in turn, depends on the location of the molecular center within the simple-cubic lattice formed by the attractive blobs.

Due to the rigidity of the arms, it is extremely rare that more than one arm of a molecule aggregate within the same cluster. This happens for molecules whose anchoring point is located between two clusters that are nearest neighbors, i.e., around the clusters' simple cubic lattice near locations $(\pm \frac{d}{2}, 0, 0)$ and permutations, whereby d is the lattice constant of the cubic lattice formed by the *T*-clusters. Most of the anchoring points are located between two next-nearest neighbors on the lattice, i.e. near locations $(\pm \frac{d}{2}, \pm \frac{d}{2}, 0)$ and permutations or between next-next-nearest neighbors, i.e., $(\pm \frac{d}{2}, \pm \frac{d}{2}, \pm \frac{d}{2})$. While in the former case, each molecule is centered between four surrounding clusters, in the latter it is centered between eight. Since configurations in which two or even three arms aggregate into the same cluster are entropically and energetically unfavored, the position with four surrounding clusters leaves opportunity for one arm to leave its cluster and switch to another. With eight surrounding clusters, the degree of freedom for the arms to switch clusters is maximized, thus the anchoring points prefer to locate in the body center of the cluster lattice's unit cell. Note that in our model, there is no 'elasticity' of chain bonds, i.e. although a bonding vector $(1, 1, 1)$ is longer than a bond $(1, 1, 0)$ let alone $(1, 0, 0)$, there is no energetic difference between the three cases. When the anchoring points locate at the body center, the arms have to stretch more than e.g. a molecule with the anchoring point at the face center. An energetic penalty for intense stretching will qualitatively shift the population of anchoring points towards the face centers.

The above discussion brings forward two physically relevant points: on the one hand it demonstrates that the relative density of anchoring points at certain positions within the cubic lattice is directly influenced by the combinatorial entropy gain that a molecule has at these positions with respect to the location of its rigid arms. On the other hand, however, it also demonstrates that the localization of the star centers in the lattice is *weak*. Contrary to the case of usual, colloidal solids of hard particles, the star centers are *not* confined to small cages formed by their nearest neighbors – a state of affairs that incurs a significant loss of translational entropy. Here, we are dealing with a delocalized, diffusive solid, akin to the 'cluster crystals' that are stabilized by ultrasoft repulsive particles or mixtures thereof [122, 123, 124, 125, 126, 127, 128, 129, 130]. Accordingly, the space explored by the stars within the cubic phase still extends over all three spatial directions: although the superlattice formed by the attractive clusters and the anchoring points has the form of two interpenetrating simple-cubic lattices (forming together a bcc- or CsCl-structure) a star can wander from one lattice site to another and it can even position itself in interstitial regions.

Upon increase of concentration, the *T*-clusters of the cubic phase grow in size due to steric constraints and their boundaries start thus coming closer to one another. This gives rise to an instability upon which neighboring clusters deform and merge along one of the three equivalent crystallographic directions, giving thus rise to a columnar phase, shown at snapshot *b* of Fig. 4.8, taken at concentration

$\phi = 0.328$. The anchoring points prefer here locations at the geometrical center between four neighboring columns of T clusters. Locations between two neighboring columns are much less likely. Once more, the reason comes from combinatorial entropy: in the latter case the molecule has to give more than one arm into the same column, whereas in the former there are more possibilities available. In the columnar structure full translational invariance is restored in the direction parallel to the columns. Upon increasing the concentration further, the instability scenario simple cubic $\rightarrow$ columnar sketched above repeats itself, driving now a columnar $\rightarrow$ lamellar transition. In snapshot *c* of Fig. 4.8, taken at concentration $\phi = 0.385$, we show a state of coexisting columns and a lamella. In snapshot *d* of Fig. 4.8, taken at concentration $\phi = 0.410$, the lamellar phase is stable. The anchoring points locate halfway between two neighboring lamellae of T clusters. It should be noted that in such a lamellar phase, the molecules have two-dimensional freedom of movement without the necessity for any arm to leave its respective cluster. At the same time, the combinatorial possibilities for locating the arms into lamellar planes are reduced, since each star can throw its arms only to two immediately neighboring planes. Finally, at sufficiently high concentrations, the lamellar phase remelts into a liquid, see snapshot *e* of Fig. 4.8, taken at concentration $\phi = 0.585$.

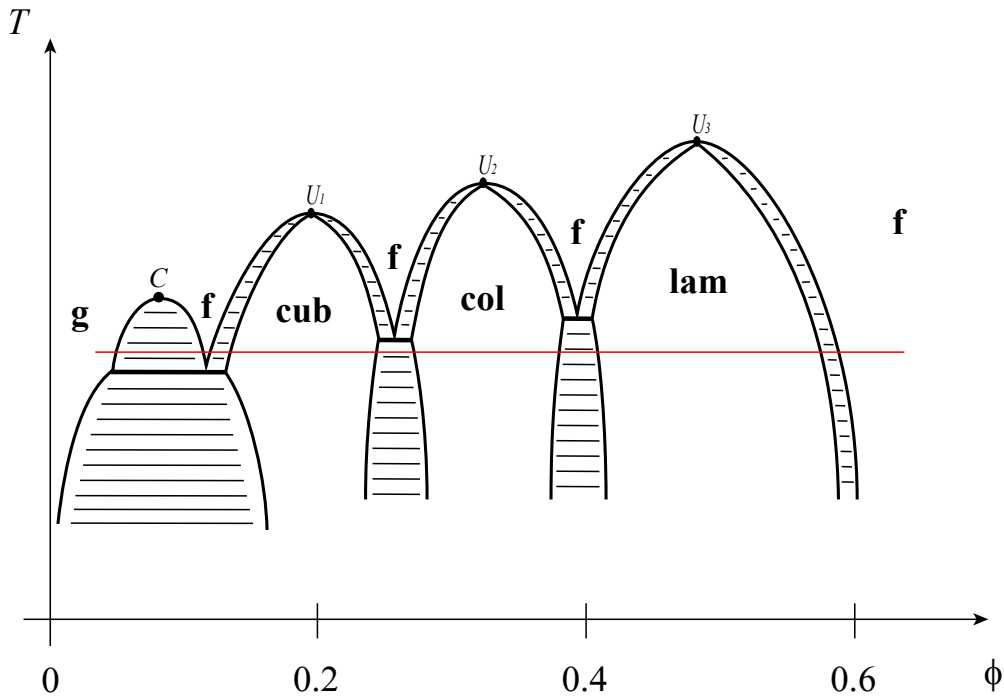


Figure 4.9: Sketch of the topology of the phase diagram of the system $H(H_5T_5)_3$. The critical temperature is $T_c^* = 8.7$ while the upper stability temperatures of the ordered phases at points U_1 , U_2 , and U_3 all lie at, roughly, $T^* \approx 10$, increasing slightly from point U_1 to point U_3 . The red line indicates the temperature at which the snapshots of figure 4.8 have been obtained. The symbols **g** and **f** denote the regions of stability of the gas and the fluid, whereas the symbols **cub**, **col** and **lam** correspond to the cubic, columnar and lamellar phases, respectively.

Rigid and strongly amphiphilic stars of low functionality feature a very rich scenario of phase behavior:

starting from a liquid-gas coexistence (which terminates at a critical point), they go over to a phase with a fully broken translational symmetry upon increase of the concentration: a three-dimensional, diffusive, delocalized crystal, akin to the cluster crystals formed by general classes of ultrasoft repulsive particles. Upon further concentration increase, translational invariance is restored gradually, in a step-by-step fashion: the crystal transforms into a columnar phase in which symmetry is broken only in two spatial directions, then the columnar phase to a lamellar one, in which symmetry is broken only in one direction, and, finally, the system remelts into a uniform phase. This scenario, in turn, is reminiscent of the complementary class of ultrasoft particles, which show freezing and remelting as density grows, albeit not in the stepwise fashion mentioned above. The most prominent example of this class is the Gaussian core model [131, 132, 133, 134, 135, 136, 137, 138], for which a fluid $\rightarrow$ fcc $\rightarrow$ bcc $\rightarrow$ fluid sequence has been established to happen at sufficiently low temperatures.

Apart from the liquid-gas binodal, the phase boundaries shown in Fig. 4.8 have been drawn in a semi-quantitative way, and they have been based on simulation runs in the temperature region $8 \leq T^* \leq 10$: visual inspection of the resulting phases has been employed to identify phase changes in those temperatures and the points have been connected by the straight, gray lines. Of course, this procedure is bound to suffer both from finite-size and from hysteresis-effects, thus the phase boundaries shown there are a guide to the eye. Raising the temperature to values $T^* \cong 12$, all ordered phases disappear and the system remains in the uniform, fluid state throughout the whole concentration range. This finding is physically intuitive: at this range of temperatures, thermal effects dominate over the terminal-bead attractions and the stars resemble fully solvophilic (but rigid) star polymers of low functionality. In the absence of intermolecular association, no ordered phases are expected here. At much higher temperatures, even rigidity will be washed out and thus we return to the well-known case of low- f , flexible star polymers, which indeed do not crystallize [139] for $f \leq 34$. Since the phase boundaries separating ordered phases of *different* spatial symmetry cannot terminate at critical points and since such phases must be everywhere separated from one another in the phase diagram, it follows that the resulting phase diagram must be of the reentrant type: in the (T, μ) -plane the phase boundaries must be lines that have a maximum along the temperature-axis and turn around, much like the phase boundaries for high- f star polymer solutions [139], for the Gaussian model [136, 137, 138] or for the Hertzian model [140]. In the (T, ϕ) plane the same topology is preserved but the lines broaden to accommodate the density jumps at coexistence. Based on these considerations, and on quantitative information from the simulations, we draw in Fig. 4.9 a sketch of the phase diagram of the $H(H_5T_5)_3$ -system, which features, apart from the gas-liquid critical point C , three maximum temperature order-disorder points U_1 , U_2 , and U_3 . At these points, the region of stability of the ordered phase right below them shrinks to a single ϕ -value and above them the fluid phase is stable. The topology of the phase diagram is very similar to that of high- f , flexible, self-avoiding star polymer solutions with the addition of the gas-liquid coexistence. Here, however, the multitude of ordered phases is brought about by the interplay between intermolecular association, amphiphilicity, and arm rigidity.

Finally, we return to the ordered phases of the other rigid ($\alpha = 100$) TSP's considered in this work. The $H(H_2T_8)_f$ - and $H(H_4T_6)_f$ system feature only a lamellar (stable) phase, whose region of stability grows with amphiphilicity. The columnar and the cubic phases were also absent or unstable for the case of the $H(H_5T_5)_{10}$ -system. We argue that this lies in the fact that the number of neighboring T -clusters into which a star can throw its rigid arms (4 for the columnar and at most 8 for the cubic phase) at this case is inferior to the star's functionality, thus forcing the latter to place at some arms

into the same cluster, an option that is entropically unfavorable and energetically expensive, since some arms will have to bend so as to run parallel to one another. Finally, and for essentially the same reasons, we found no columnar phase for the $H(H_5T_5)_6$ -system, whereas the cubic phase of the same was stable, but very distorted. Whether these systems can form other ordered phases that are incompatible with the cubic simulation box is an open question that would require fluctuating box shapes to be implemented and lies beyond the scope of this work.

4.6 Conclusions

We have shown that the introduction of rigidity on amphiphilic star polymers has similar effects on the gas-liquid separation of these systems as it has on surfactant chains. Rigidity increases the effective molecule size and thus decreases the concentration on which a fluid phase forms, effectively narrowing binodals of liquid-gas phase separating systems. The intra-molecular energy demand that rigidity imposes in order to maintain the same level of conformational freedom as a fully flexible molecule implies a higher critical temperature in comparison.

At high rigidities, gas-liquid phase separation is complemented by the formation of ordered phases. The interplay of entropy and configurational energy has a heavy impact on the phase behavior: At moderate concentration just above the fluid phase, the system minimizes the surface of terminal T bead clusters by forming spherical clusters and aligning them on a simple cubic lattice. Unless a molecule disconnects from a cluster, which is highly unfavored, the molecule is stuck at its position within the system. Increasing the concentration, the system forms columnar T clusters that align on a cubic lattice. While still attempting to minimize the cluster surface, the columnar alignment allows for a one dimensional configurational freedom for the molecules. Accordingly, a two dimensional configurational freedom is ensured for higher concentrations when the system forms a lamellar phase. Since there is no ordered phase that allows for full three-dimensional configurational freedom, driving the concentration further leads to a remelt of the system into another bicontinuous fluid phase. The variety of ordered phases and their stability depends crucially on the simultaneous effects of three factors: the star architecture, the incompatibility of the blocks of the chains and the high rigidity of the same. The resulting phase diagrams are rich, featuring a topology that is akin to those of ultrasoft spherical particles with re-entrant melting scenarios [141] but the ordered phases formed have strong similarities with cluster phases built by the complementary class of ultrasoft interactions [141]. It is remarkable that crystallization into periodic lattices can be induced in this case even for extremely low-functionality stars, $f = 3$.

It is promising to extend the model by introducing bond elasticity that might affect the structure or even the forming of the ordered phases. Also, we have only investigated systems so far that have previously shown to be macrophase separating. Investigations on how rigidity will affect micellar phase properties will give further insight into the subtle interplay between configurational entropy and molecular properties, thus further extending the big picture of thermodynamics of complex colloidal particles. Our results can be experimentally tested by using short-chain diblock stars with high bending rigidity. Possible candidates are block-copolymer-grafted nanoparticles [142, 143] for which the chain rigidity emerges either by the short chain length or, e.g., by grafting rigid polymers such as functionalized polyelectrolytes [144] or polypeptides [145] on nanoparticles.

4.7 Appendix: Finite-size effects on ordered phases

Ordered phases in a simulation box with periodic boundary conditions are likely to be affected by finite size effects: their properties like periodic length will be subject to the finite box size. To ascertain that the appearance of the lamellar phases is not an artifact of the cubic box and to obtain information on the lamellar spacing, we ran a series of simulations of this phase for the system $H(H_5T_5)_3$ for different cubic simulation box sizes L . It should be noted that the investigations in what follows are easily generalized for the columnar or cubic phases. The lamellar phase only has a periodicity in one dimension, while for the columnar and cubic, the periodicity is symmetric in two and three dimensions, respectively. Moreover, since the effective coordination of the underlying lattice is $Z = 26$, the discussion on the lamellar phases also carries over to $f = 6$ and to $f = 10$.

The molecules have a maximum extension of 21 lattice sites. A box size of e.g. $L = 20$ thus still allows for configurations in which the molecule directly interacts with its own periodic image, which leads to unwanted and unphysical correlation effects. We remind that the model allows for growth along any of the $(1, 0, 0)$ -, $(1, 1, 0)$ - and $(1, 1, 1)$ -crystallographic directions of the underlying lattice without stretching penalty. The simulation box is oriented parallel to the $(1, 0, 0)$ -direction and the lamellae orient parallel to any of the box faces. Within the overlap regions of the T -tails, thus, terminal monomers of a given star can have contacts either with those of another star positioned directly opposite to it at the next plane, the chains extending along the $(\pm 1, 0, 0)$ -directions and permutations thereof, or with those of stars located along face- or body diagonals of the lattice. In all cases, the projected length of the chains in the direction perpendicular to the lamellar planes is the same.

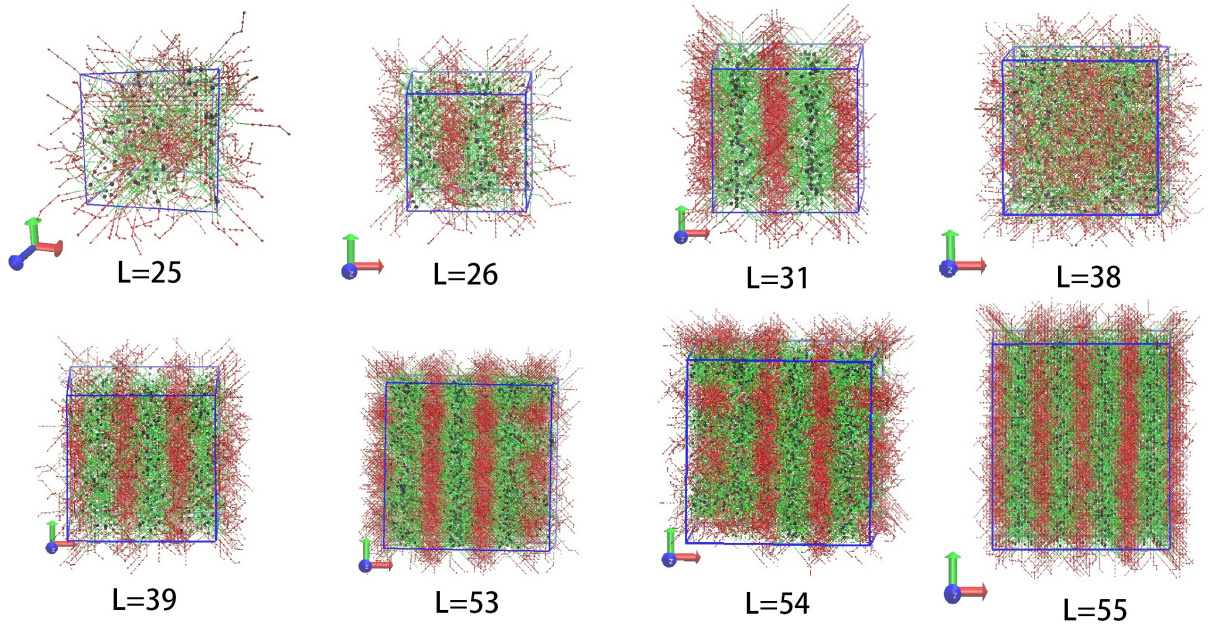


Figure 4.10: Simulation snapshots of a $H(H_5T_5)_3$ system at $T^* = 8.6$ for different box sizes. The molecules are rendered as in Fig. 4.8.

Consider the anchoring points of two stars lying opposite to one another and shifted laterally by one lattice point along the lamellar planes. Since each chain possesses $k = 10$ monomers, and given the 50% fraction of attractive monomers, the two chains will have full contacts between all of their terminal monomers when their distance is $\ell = 16$ lattice points. This is the ‘zero-temperature’ optimal distance but thermal fluctuations cause some broadening in the positions of the anchoring points and

occasional kinks in the chain directions, so that we anticipate the lamellae to be stable in a finite simulation box for a small range of separations around this value. The smallest simulation box that can accommodate a fully stretched TSP without inducing self-interactions with its periodic image has size $L = 21$. We ran a series of simulations for box sizes ranging from $L = 20$ to $L = 60$. In Fig. 4.10 we show representative simulation snapshots from these runs. The number of lamellar sheets found in the simulation for various sizes L of the box are summarized in Table 4.7.

We found no ordered phases for box sizes below $20 \leq L \leq 25$. At $L = 26$, the system forms two very coarse lamellae with interlamellar spacing $\ell = 13$. The anchoring points feature a high spread around the lamella center and most of the arms do not extend at their maximum. Increasing the box size, the lamellae become more sharply aligned and positional fluctuations diminish, as seen for the case $L = 31$ in Fig. 4.10. An inter-lamellar spacing $\ell = 16$ sets in, which maximizes the number of aggregated terminal T beads onto an arm from the opposite lamella while being fully stretched. Such sharply aligned lamellae were accordingly also found for box sizes $L = 47$ and $L = 48$, close to the next multiple of $\ell = 16$. Increasing the box size beyond $L = 32$ slides the T -contacts apart, and a competition sets in between fewer lamellar sheets with larger ℓ and more of the same with a smaller ℓ -value. The box size $L = 38$ is an interesting case, since it is twice the value $\ell = 19$ and almost three times the value $\ell = 13$, both of them featuring two T -contacts for oppositely positioned stars. The competition between these two scenarios leads to a breakdown of the ordered phase, as can be seen in Fig. 4.10 for $L = 38$. At $L = 39$, a three-lamellae state with $\ell = 13$ is favored over a heavily stretched two-lamella scenario with $\ell = 19$. The next case in which this competition shows up is for box sizes $L = 53$ and $L = 54$, both close to two competing scenarios: four lamellae with $\ell = 13$ or three lamellae with $\ell = 19$. In this case, the competition does not lead to a breakdown into a disordered phase. Instead, the system builds up two quite sharp lamellae (in the box center in the snapshots) while the third is in constant competition to be split up in two (at the edges of the snapshots). This leads to a large spread of the latter lamella, perforations and in the case of $L = 54$, to a breakdown only of the third lamella, while at $L = 55$, the four-lamellae state becomes stable.

Conjecturing from these investigations values for the most likely lamella distance in the bulk is a challenging task, but it is obvious from above that the molecules prefer states with a certain degree of conformational freedom over the fully stretched states. Since rigidity drives the stiff arms into a widely stretched configuration, states seem to be the most favorable that do not require the arms to bend in order to maximize the number of aggregated T beads while at the same time leaving as much freedom as possible for the molecule centers. We argue that this is the case for a lamella distance $\ell \cong 15$ and we establish that $\ell = 13$ and $\ell = 19$ are the lower- and upper limits of mechanical stability for the inter-lamellar separation.

L	N_{lam}
20 – 25	0 (disorder)
26 – 36	2
38	0 (disorder)
39 – 52	3
53	3/4
54	3/4
55 – 60	4

Table 4.1: The number of lamellar sheets N_{lam} of the $H(H_5T_5)_3$ -system (right column) formed at temperature $T^* = 8.6$ for different values of the size L of the simulation box (left column).

Chapter 5

Microphase separation scenarios

*Studies on the phase behavior of end-functionalized diblock copolymer stars on the basis of Grand Canonical Monte Carlo Simulations have been conducted. Previous studies on macrophase separating scenarios [C. Koch et al., Soft Matter, **9**, 7424 (2013).] were extended to systems expected to nucleate microphase aggregates, i.e. solutions of diblock copolymer stars with a solvophobic outer block smaller than the solvophilic inner block. The low functionality case $f = 3$ as well as the intermediate case $f = 6$ are investigated, both in the fully flexible case and with an arm stiffness employed. We find rich and complex microphase separation scenarios that cover microgels, spherical micelles, liquid crystalline ordering of micelles and a novel form of inter-micellar aggregation in a necklace-fashion formation of large, worm-like supermicelles. We propose a comprehensive relation of the phase behavior to the thermodynamic interplay of molecule architecture, chain stiffness, temperature and entropy both on a microscopic and a mesoscopic level. We stress the peculiarities of the star architecture in this respect and emphasize its micellization properties that unite characteristics of both diblock surfactant and triblock telechelic copolymer chains.*

5.1 Introduction

Up to this point, we have investigated the phase behavior of telechelic star polymers with special regard to first-order phase transitions, their critical parameters and the limits of critical phenomena when changing the molecule architecture and/or arm stiffness. We have found for the most fundamental star architecture, i.e. a three arm star $f = 3$, as well as for stars of higher functionality $f = 6$ or $f = 10$ that the limiting case for macrophase separation is always a relative terminal B block size of $r = 50\%$. For a given architecture $H(H_n T_m)_f$, the parameter r denotes the fraction of solvophobic beads along an arm as $r = \frac{m}{n+m}$, stated in %. If the terminal B block comprises at least half of the stars' arms, $r \geq 50\%$, macrophase separation occurs. The same limit is found for telechelic triblock copolymer chains [24], which we can roughly relate within the terms of our model to a telechelic star of functionality $f = 2$ (where one needs to consider that a star polymer additionally has one more H bead at the anchoring point). Due to this correspondence, a more general investigation on the role of the star architecture in comparison to telechelic (THT) triblock copolymer chains and diblock (HT) surfactant chains is called for, and will elaborate the peculiarities of the star architecture with respect to both macro- and microphase separation scenarios.

With a smaller B block, i.e. $r < 50\%$, telechelic stars of functionality $f = 3$ collapse in infinite dilution and form micelles at a concentration above a certain cmc (i.e. critical micelle concentration), respectively. These micelles can associate into *harmonics*, i.e., multiple-micelle-sized aggregates, whose

chance of occurrence decreases exponentially with their size [56]. Doubling the functionality to $f = 6$ does not affect the limit of $r = 50\%$, where macrophase separation still occurs (see section 3.3). The higher functionality leads to an increase in critical temperature, which we related to a higher thermal energy needed to provide the same level of fluctuations. At $r = 40\%$, the macrophase separation is superseded by a continuous phase transition from sol to gel. At densities beyond $\phi \approx 0.3$, spherical micelles form in the voids inside the - already percolated - gel network phase, and remain stable there. Further increasing the functionality to $f = 10$ (see section 3.4), the limiting relative B block size of $r = 50\%$ for the macrophase separation still holds, and at $r = 40\%$, the continuous sol-gel transition is yet again found. However, there is no formation of stable micelles that coexist with the gel phase. For both $f = 6$ and $f = 10$, a smaller relative B block size r causes the sol-gel transition to be superseded by spherical micelle formation. The micelles in the $f = 10$ system show a propensity to associate with each other or with free stars in the environment (see fig. 3.13), which we argued to be related to steric repulsion near the anchoring points. A star of higher functionality is a lot more crowded around the anchoring point and thus has an increased propensity to have one arm leave the micelle and reorient to the opposite direction, away from the micelle. Once this arm establishes a connection to a nearby cluster, it binds the micelle to that cluster. This binding acts against steric repulsion. It is no longer possible for the micelle to drift away from that cluster in order to increase entropy. Given this circumstance, an association of the micelle core with the cluster is favorable to minimize interaction energy. If this cluster is another micelle, the result will be a "super micelle" of double the characteristic micelle size, i.e. a first order harmonic. But if this cluster is the bulk of a gel system, the micelle will be consumed by the gel network. We argue that this is the case for the $f = 10$ system with a B block size of $r = 40\%$, where the stable "void micelles" from the respective $f = 6$ case are no longer present (see fig. 3.11).

This principle demonstrates a remarkable coherence of the behavior of single telechelic stars and concentrated solutions thereof. For single molecules, open "burst" conformations have been found along with fully collapsed "watermelon" conformations as well as intermediate, partly collapsed states where the arms of one star associate in several sites. The number of these sites has been found to increase with functionality f [54]. At the same temperature T^* , e.g. a single star of a relative B block size of $r = 40\%$ forms one or two patches for $f = 6$ and three or more for $f = 10$. This is an effect of repulsion due to crowding around the anchoring point and is found again in the above mentioned principle that determines micelle stability in concentrated systems. A higher functionality increases the repulsion at the anchoring point, driving single stars to form more association sites and stars in concentrated solutions to more and more avoid stable micellar aggregates.

For all these systems, phase behavior can be comprehended by the determining interplay of temperature, interaction energy and entropy, both on an intra- and inter-molecular level. The introduction of rigidity in chapter 4 has shown to bring a fourth factor into this interplay. Rigidity increases the effective molecule size, thus decreasing critical densities. It also imposes an additional intra-molecular energy demand that needs to be compensated by a higher temperature in order to provide critical fluctuations. Finally, a very high rigidity also allows for the formation of cubic, columnar and lamellar ordered phases. In chapter 4, we only studied stiff TSPs down to a relative B block size ratio of 50%. Yet to be investigated is the effect of rigidity on systems of smaller B block size, i.e., systems that, for the full flexible case, feature microphase-separation scenarios. Based on the investigations in chapter 3 and the preliminary conclusions stated above, the most important aspects that are to be considered are the propensity of stiff TSPs to arrange in ordered phases and the decreased entropic cost of straight

arm-configurations. Since the energy penalty for bending promotes straight arm configurations and thus minimizes entropy gain by steric repulsion of "jiggling" close-by chains, very narrow arrangements of straight arms are, in principal, possible. This interplay of rigidity and entropy is of special concern in the context of the above mentioned micelle stability considerations that closely relate to the behavior of TSPs in infinite dilution. At a certain stiffness, entropic effects due to steric repulsion within a single star will decrease so much that the propensity of the star to form multiple association sites is lost. All arms of this star will then collapse onto a single association site, while the arm stiffness reduces an entropic "bloating" to a typical watermelon. For an illustration, see figure 5.1. The resulting molecule configuration is quite narrow and effectively makes the star a colloidal particle with surfactant properties, thus drastically stabilizing micelle formation in concentrated systems, which is illustrated in figure 5.2.

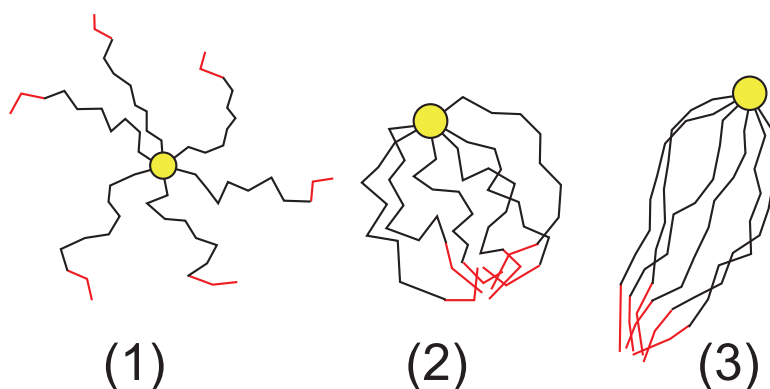


Figure 5.1: A sketch of three different conformations for a single TSP. (1) an open "burst" star due to strong steric inter-arm repulsion, (2) a collapsed "watermelon" in which inter-arm repulsion "bloats" the shape, and (3) a rigid TSP, collapsed into an elongated, effectively surfactant conformation.

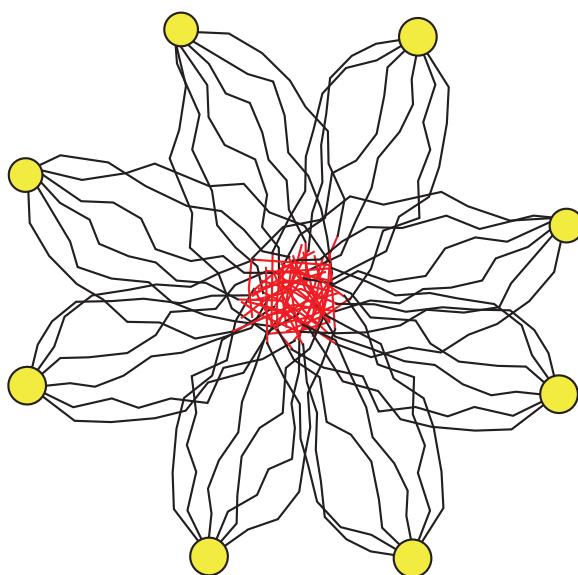


Figure 5.2: A sketch of multiple effective surfactant TSPs, associating to a micelle.

It should be noted that there is a qualitative difference between micelles of diblock surfactant copolymer chains and telechelic star polymers. While the effectively repulsive corona of a micelle of diblock copolymer chains is isotropically formed by independently moving solvophilic ends of polymeric chains,

repelling each other, the corona of a micelle of telechelic star polymers is formed by a distribution of anchoring points in which the solvophilic polymer chains converge, thus drastically deviating from the isotropic distribution. This is illustrated in figure 5.3.

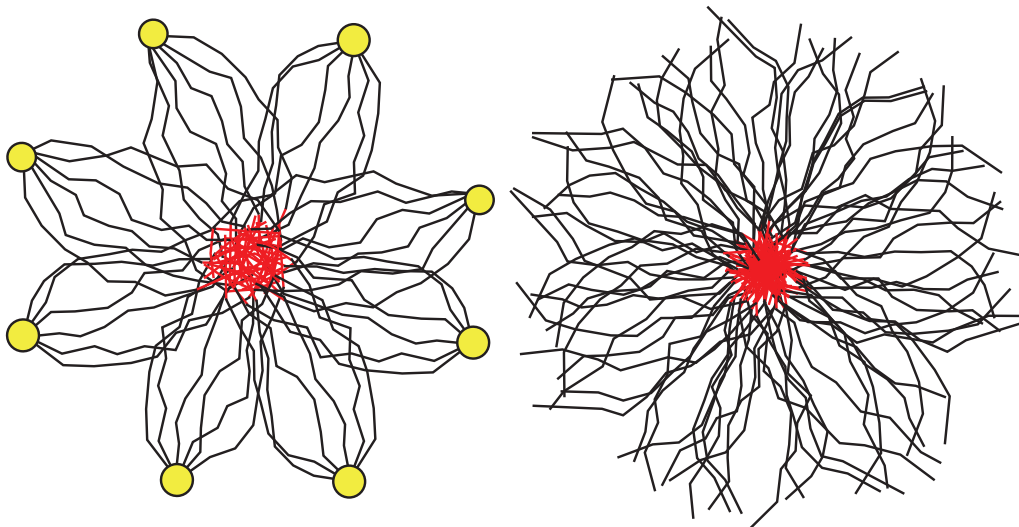


Figure 5.3: A sketch showing a micelle of telechelic star polymers (left) and a micelle of diblock copolymer surfactants (right). Solvophilic blocks are colored black and solvophobic blocks are colored red.

Hence, there is no purely independent movement of chains in the corona. The anchoring leads to a collective character of movement, for instance when there is an elastic interaction between two micelles coming close enough to get into range of each other's steric repulsion. Compared to an isotropic corona without this collective character, the chance is much higher that a micelle with an anchored corona exposes a spot of the micelle core, opening up the opportunity for the two micelles' cores to get close enough for an aggregation, ultimately leading to the formation of "harmonics", i.e. aggregates of multiple micellar size. Such an association of two micelles is illustrated in figure 5.4.

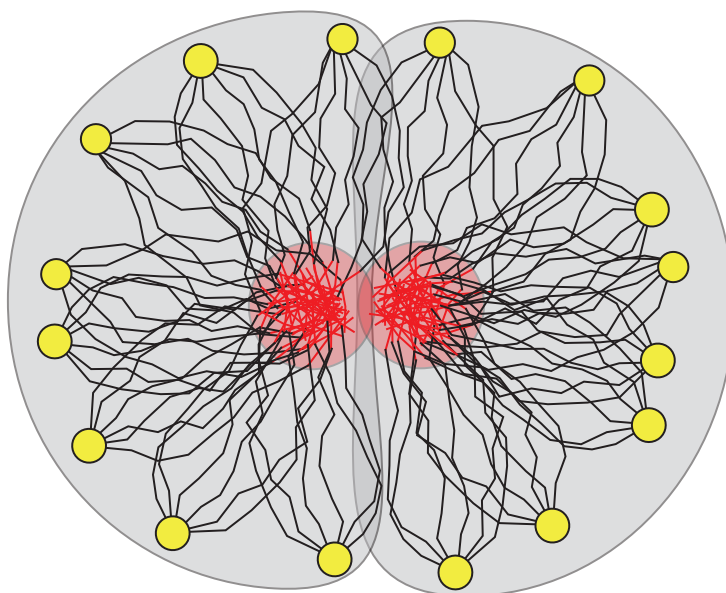


Figure 5.4: A sketch showing two micelles of telechelic star polymers that bend aside their coronae so that their cores can associate, forming a micellar aggregate of double the characteristic micelle size, i.e. a first order harmonic. The shaded regions are only guides to the eye.

Rigidity has no influence on the isotropy of a micelle corona of diblock copolymer surfactants. A single chain is more tightly held in its conformation within the corona and will not "jiggle" so much due to entropic fluctuations and steric repulsion as might be the case for a micelle of fully flexible chains. However, the overall distribution of chains in the corona is even over the whole solid angle. In a micelle of telechelic star polymers, with an anchored corona, rigidity will increase the narrowing of the stars' conformation in the corona and thus dramatically promote the anisotropy and exposure of openings to the micelle core. Consequently, we expect micelles of telechelic star polymers to show an increasing propensity of inter-micellar aggregation into super micelle harmonics, when rigidity is increased.

Furthermore, the entropic cost involved with a folding aside of the micelle corona scales naturally with the relative size of the corona compared to the micelle core. Since the parameter r gives the relative solvophobic B block size, a lower value of r means a larger micelle corona. This scaling is illustrated in figure 5.5.

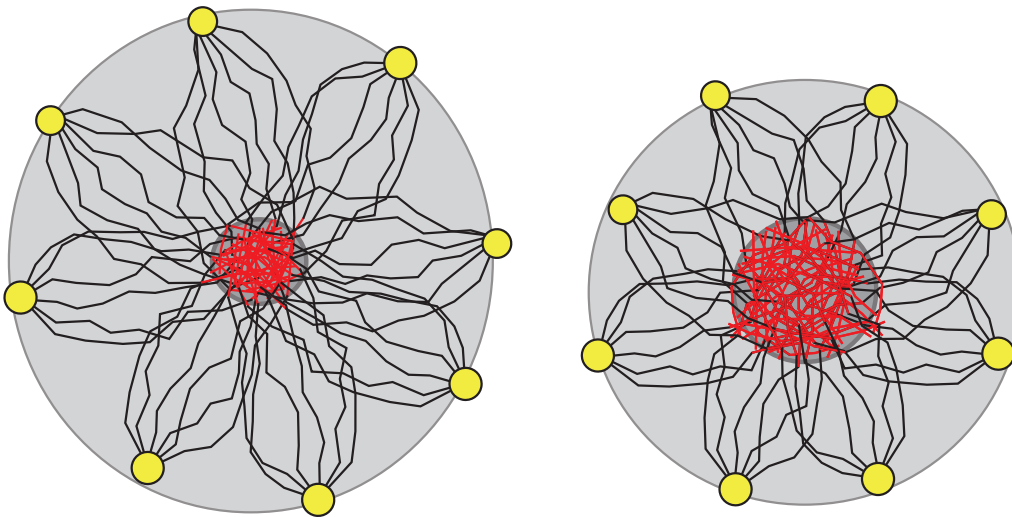


Figure 5.5: A sketch showing two micelles of telechelic star polymers with different block size ratios. The left micelle is formed by TSPs with a low relative B block size $r \approx 20\%$ and thus has a larger solvophilic corona, while the right micelle is formed by TSPs with a higher $r \approx 40\%$ and thus has a smaller solvophilic corona. The shaded regions are guides to the eye.

The entropic cost for an inter-micellar core association is therefore expected to be lower for TSP systems featuring smaller solvophilic, and thus repulsive, A blocks. TSPs of higher r are also expected to show a higher propensity to form super micelle aggregates as outlined above.

It has also been found for single telechelic stars that there is a reversible conformation change from the "watermelon" into the "burst" state when the temperature T^* is increased [52]. The role of temperature in the microphase separation scenarios of rigid TSPs is therefore to be investigated more thoroughly. Indeed, we find rich scenarios of microphase separation behavior, including the formation of networks, spherical micelles, a necklace-fashion formation of worm-like supermicelles and several scenarios of liquid crystalline ordering.

While the configurational biasing techniques outlined in 2.5 allow us to extend investigations to very high concentrations, the focus of this chapter lies in the low functionality case $f = 3$ and the intermediate case $f = 6$, both in the fully flexible case $\alpha = 0$ and with an employed arm stiffness of $\alpha = 10$. We refrain in this chapter from investigations on systems of functionality $f = 10$, since the qualitative effects of functionality become already clear when comparing $f = 3$ and $f = 6$ systems. By no

means do we intend to draw a quantitative analysis of the phase behavior. The results in the present chapter provide an insight into the novel, rich and complex microphase separation behavior that is brought about by the star architecture, especially in contrast to solutions of diblock and telechelic triblock copolymer chains and with respect to its significance in rheological considerations, which we will elaborate in the conclusions in section 5.8.

5.2 The $H(H_6T_4)_3$ -system

5.2.1 Flexible stars

For the system $H(H_6T_4)_3$, it has been found [55] that spherical micelles with a well defined characteristic size form at low concentrations. These micelles are not perfectly sterically shielded by their corona of solvophilic A-blocks. In the cluster size histograms, the occurrence of "harmonics", i.e. integer multiples of the characteristic micelle size, witness the inter-aggregation of couples, triples, etc. of spherical micelles into supermicelles, see figure 5.6. The size of these, however, is bounded at the third and fourth harmonic. It is not favorable for the system to merge more than this number of micelles into a large aggregate because of the entropic cost involved when folding aside the solvophilic corona. Increasing the concentration of this system eventually leads to a percolation, as where the coexisting micelles, supermicelles and remaining single star molecules associate into a system spanning cluster. This cluster has a very broad size distribution without any significant sizes or size changes, and grows continuously when increasing the concentration.

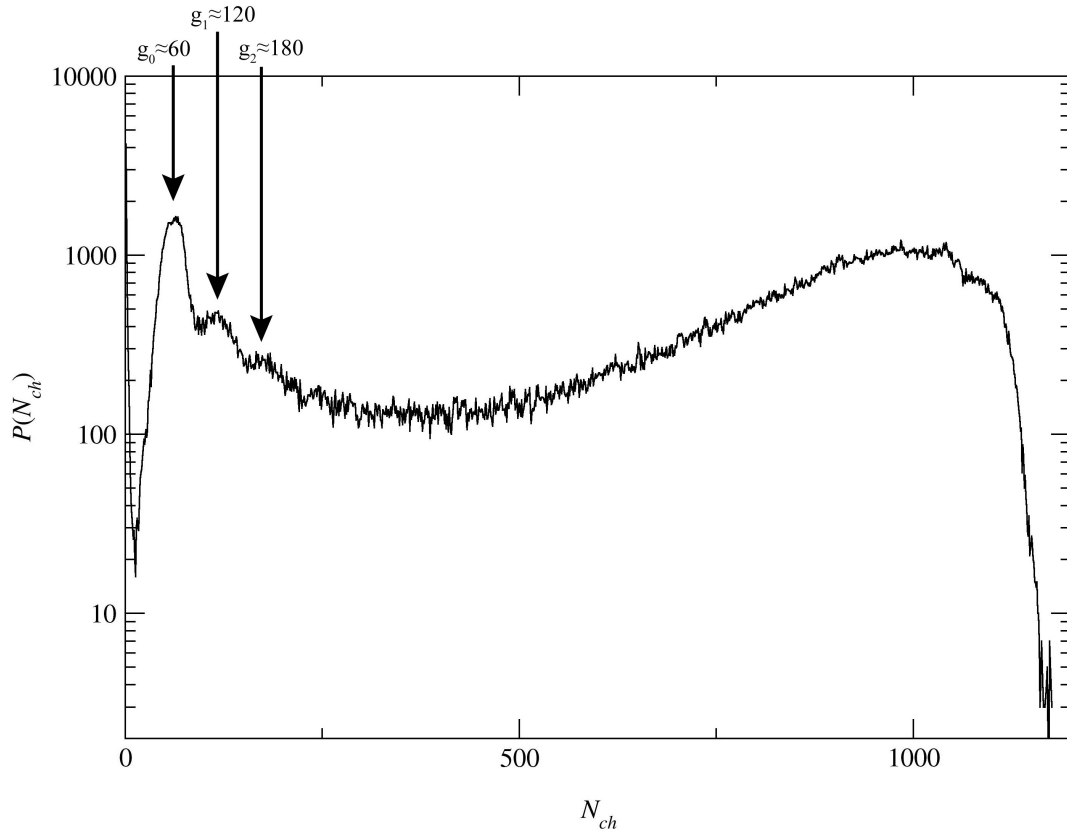


Figure 5.6: Cluster size distribution of a $H(H_6T_4)_3$ system at concentration $\phi = 0.423$, temperature $T^* = 4.6$ and average total molecule number $\langle N \rangle = 369 \Leftrightarrow \langle N_{ch} \rangle = 1107$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

Our recent investigations, however, have shown that, when lowering the system temperature down to $T^* = 4.0$, significant peaks of harmonics arise in the cluster size histograms in figure 5.7. These harmonics extend over the full width of cluster sizes up to percolation size.

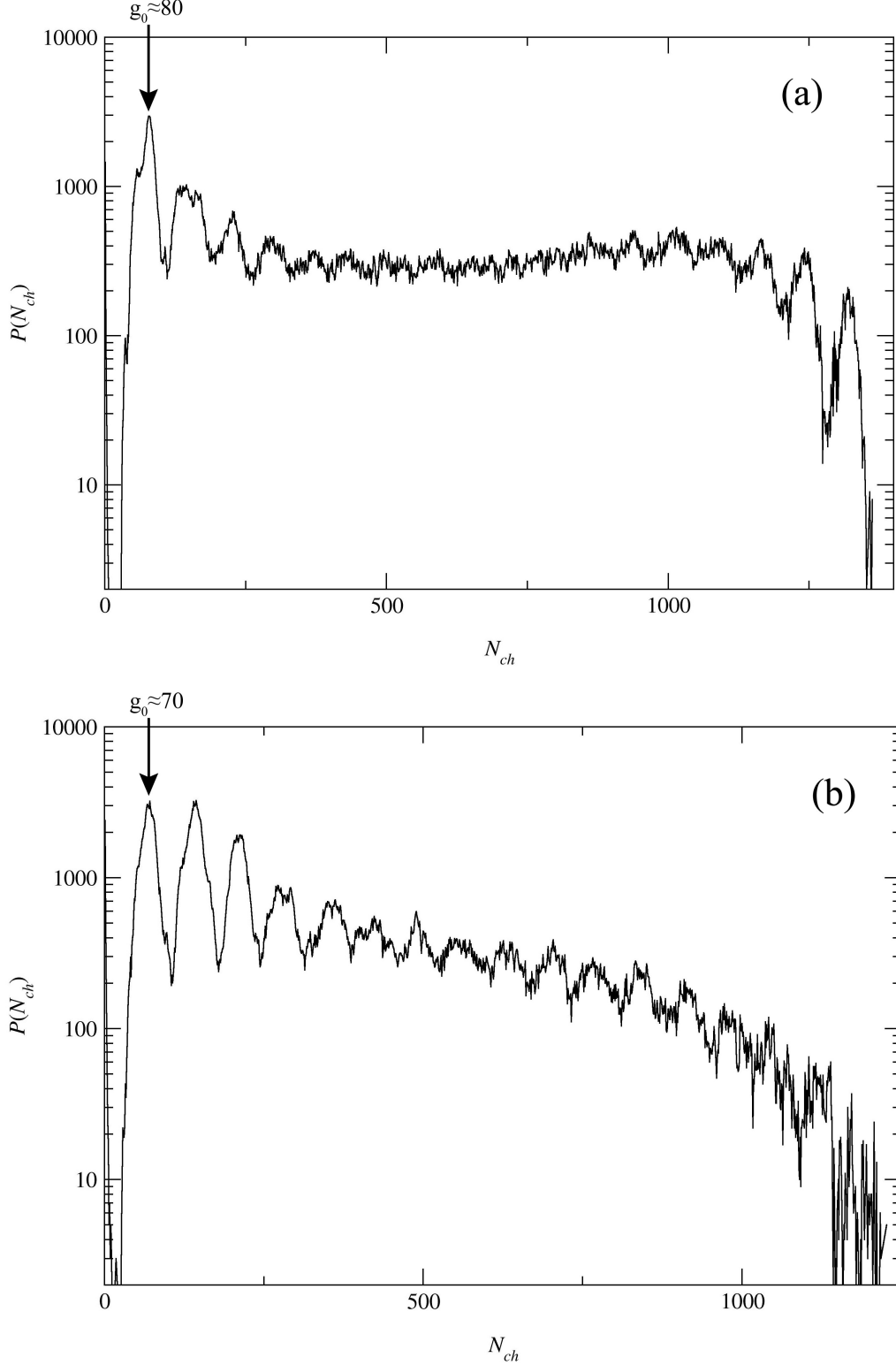


Figure 5.7: Cluster size distribution of a $H(H_6T_4)_3$ system, (a) $\phi = 0.502$, $T^* = 4.2$, $\langle N \rangle = 437 \Leftrightarrow \langle N_{ch} \rangle = 1311$, (b) $\phi = 0.455$, $T^* = 4.0$, $\langle N \rangle = 395 \Leftrightarrow \langle N_{ch} \rangle = 1185$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

In general, lowering a system's temperature enhances the propensity of attractive particles to maximize the number of their associations. We argue that in this case, the lower temperature drives the micelles to sacrifice the aforementioned entropic cost involved in the inter-aggregation of several micelles. We further argue that the peaks in fig. 5.7 are inherent to a super micelle association principle in which coexisting, stable spherical micelles fold aside their corona in order to be able to associate in a dumbbell fashion, thus increasing the number of attractive beads in contact and further minimizing the overall energy. Additional micelles can then associate in the same way onto either far end of the dumbbell, creating a super micelle "necklace". This fashion is illustrated for three micelles of TSPs in figure 5.8 and for a large group of micelles in figure 5.9.

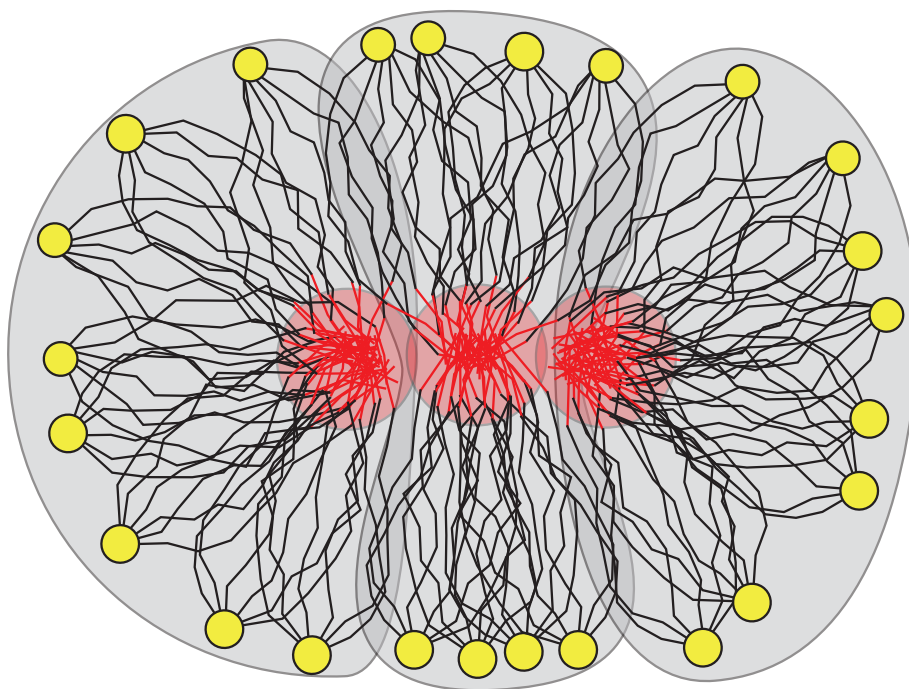


Figure 5.8: A sketch of three micelles associating into a triple harmonic aggregate. The shaded regions are guides to the eye.

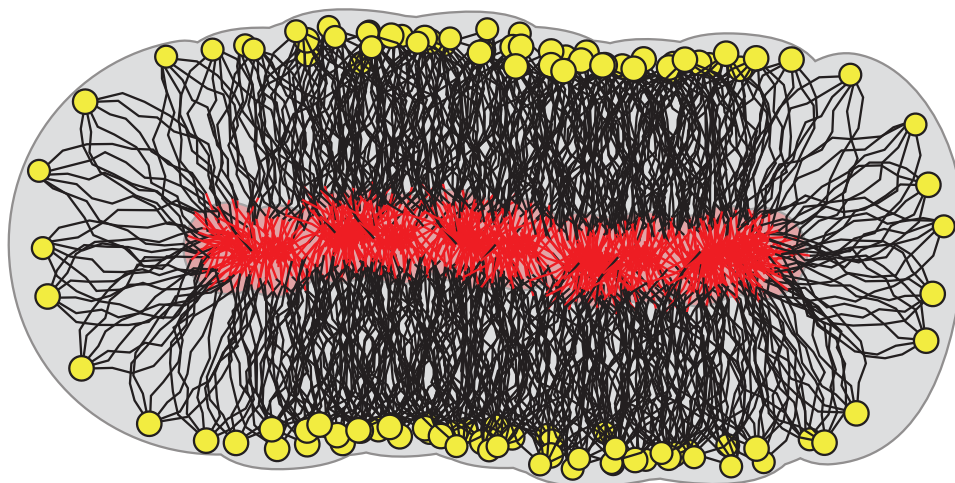


Figure 5.9: A sketch of a worm-like super micelle, formed from a necklace-fashioned association of spherical micelles. The shaded regions are guides to the eye.

Note that this super micelle exhibits a one dimensional growth. A three-dimensional super micelle growth is unfavorable by the fact that micelles inside the core of such an aggregate can not get rid of their solvophilic corona, which limits the size of a spherical, purely solvophobic cluster. However, the consideration of a two dimensional equivalent is justified, in which the micelles fold aside their coronae so to expose an equatorial ring for association and thus forming a membrane-like super micelle. We argue that, although such a scenario would certainly further minimize aggregational energy, the cost in entropy involved is too high and makes it highly unfavorable. We have not observed such a scenario in the range of systems investigated, but make some presumptions on this in the outlook section.

The supermicelles that we found, after forming up in a necklace-like fashion, further maximize the number of associated B-block beads while minimizing the surface of their cluster: Dumbbells and necklaces deform into worm-like micelles (for an illustration see figure 5.10) that grow in total length with increased concentration, as can be seen in snapshots in figure 5.11.

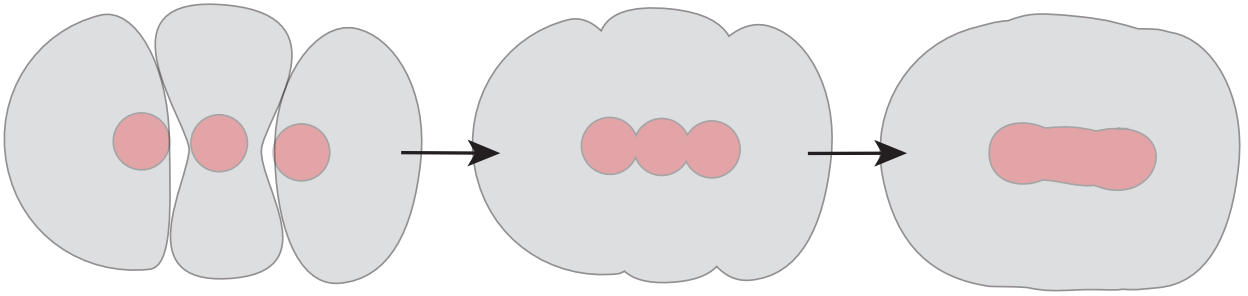


Figure 5.10: A sketch of three micelles associating into a triple harmonic aggregate and subsequently deforming into a smooth worm shape.

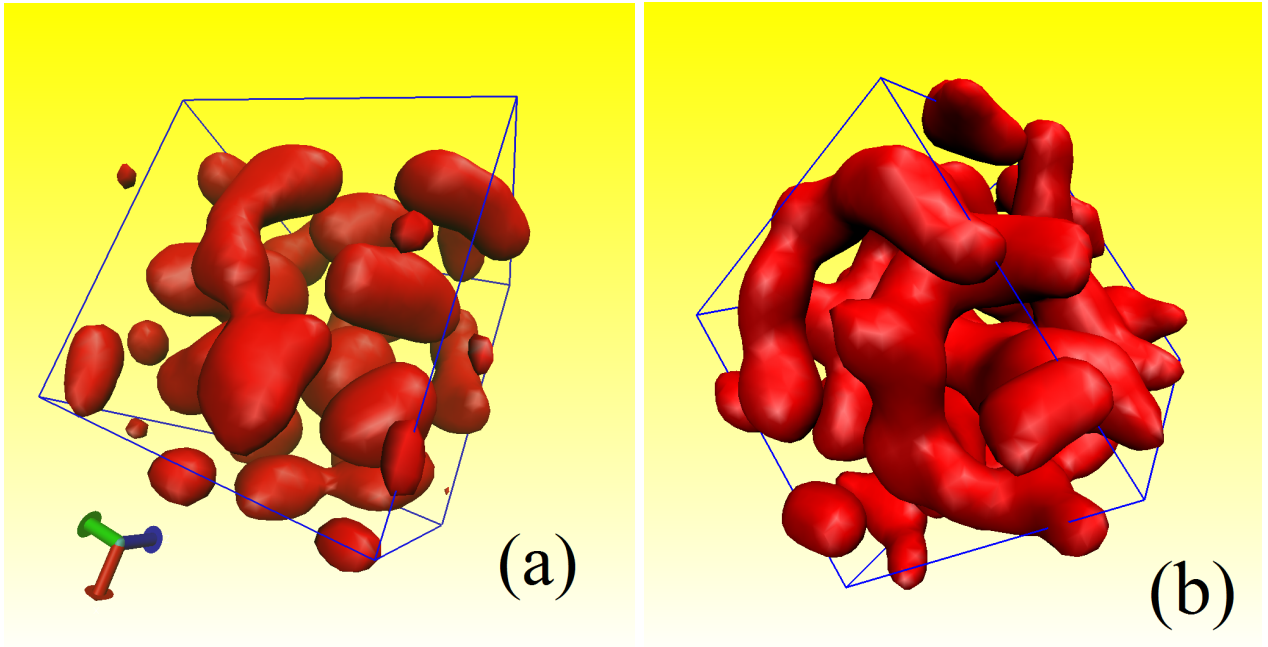


Figure 5.11: Snapshots of a $H(H_6T_4)_3$ system. (a) $\phi = 0.455$, $T^* = 4.0$, (b) $\phi = 0.694$, $T^* = 4.0$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

For high concentrations, these worms also form cross links and eventually a percolating network. At

concentrations $\phi \approx 0.7$ (see fig.5.11, right picture), the network comprises all molecules within the system.

Increasing the temperature to $T^* = 4.6$, harmonics of high order, up to the network size, gradually vanish, see e.g. figure 5.6, while the overall morphology of the system remains worm-like, see figure 5.12. Higher thermal fluctuations destabilize larger aggregates in the sense that, the larger the aggre-

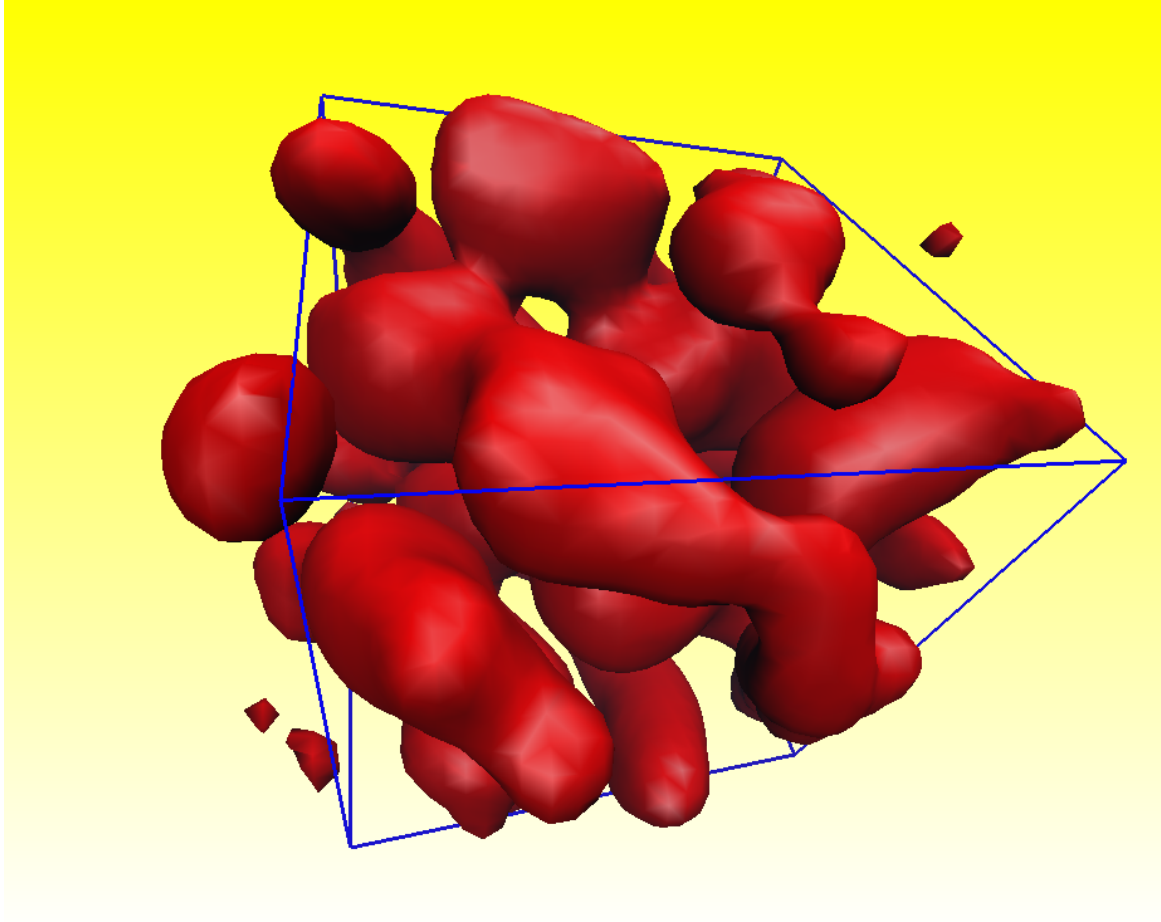


Figure 5.12: Snapshots of a $H(H_6T_4)_3$ system at concentration $\phi = 0.618$ and temperature $T^* = 4.6$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown. The entire system is connected and solvophobic species form one system spanning cluster.

gate, the higher the likelihood that the affected molecules frequently expose spots of the micelle core and open a chance for small aggregates or even single, free stars, to associate with the super micelle. Consequently, the cluster size does not grow only in steps of the significant micelle size, but rather in the smallest possible steps, i.e. single chain associations, which flattens out the histograms. Thus, we argue that also for higher temperature, although the harmonics in the cluster size histograms are missing up to the network size, the super micelle association principle is the same.

5.2.2 Rigidity

Investigating the $H(H_6T_4)_3$ system with an employed bending rigidity on the molecules' arms, the harmonics in the cluster size histograms become even more pronounced, see figure 5.13, upper plot. ¹

¹Note that the reduced temperature of the fully flexible systems investigated above is lower than that of the rigid systems investigated in the following. A comparison of flexible and stiff systems at the same reduced temperature is not

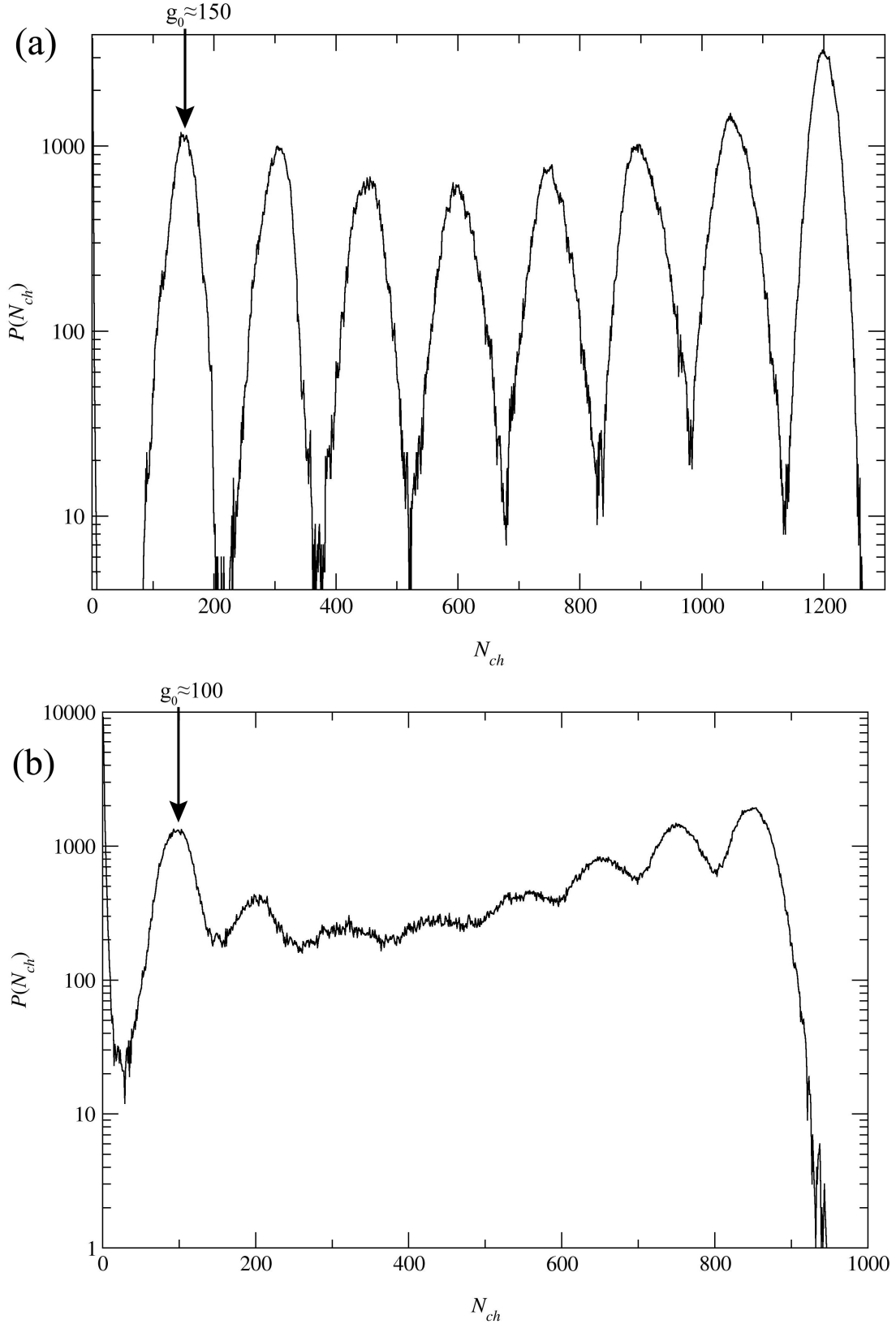


Figure 5.13: Cluster size histograms of a $H(H_6T_4)_3$ system with an arm rigidity of $\alpha = 10$. (a) $\phi = 0.463$, $T^* = 5.4$, $\langle N \rangle = 403 \Leftrightarrow \langle N_{ch} \rangle = 1209$, (b) $\phi = 0.335$, $T^* = 5.6$, $\langle N \rangle = 291 \Leftrightarrow \langle N_{ch} \rangle = 873$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

meaningful, since the energy penalty exerted by the rigidity demands a higher temperature to induce a similar level of fluctuations.

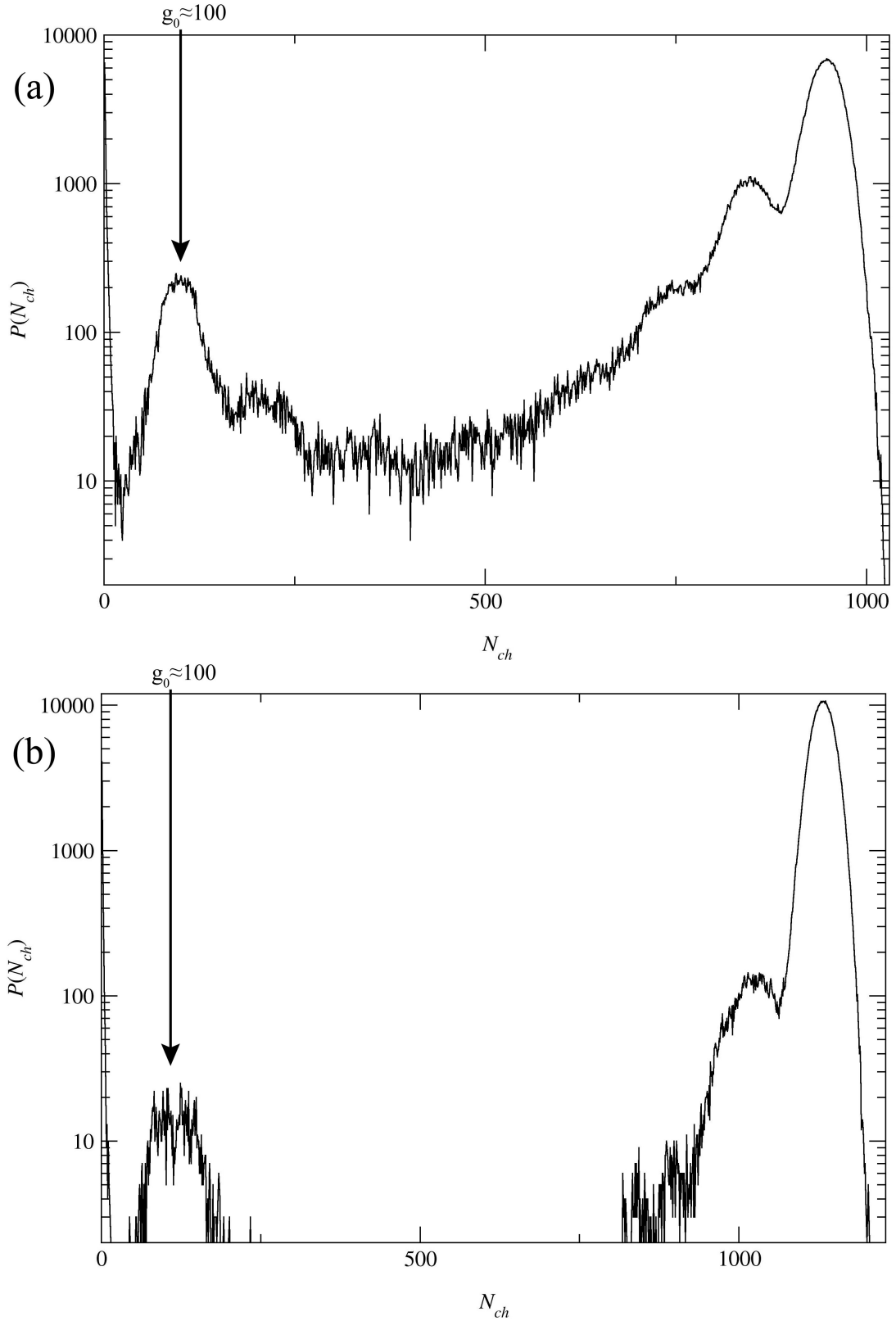


Figure 5.14: Cluster size histograms of a $H(H_6T_4)_3$ system with an arm rigidity of $\alpha = 10$. (a) $\phi = 0.370$, $T^* = 5.8$, $\langle N \rangle = 322 \Leftrightarrow \langle N_{ch} \rangle = 966$, (b) $\phi = 0.399$, $T^* = 6.0$, $\langle N \rangle = 381 \Leftrightarrow \langle N_{ch} \rangle = 1140$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

When increasing the temperature, in figure 5.13 one can see that intermediate cluster sizes are suppressed by a factor of ~ 5 compared to single micelles or the largest aggregates in the system, and in figure 5.14, increasing the temperature further, this suppression evolves to a gap in the cluster size his-

tograms. The harmonics are always discernible. However, higher temperatures make the intermediate aggregate sizes less probable in favor for the single micelles (first peak on the left) or large aggregates that cover the majority of present molecules (utmost right peak).

While for the $H(H_6T_4)_3$ system, rigidity strongly stabilizes the necklace-fashion forming of worm-like micelles in general, combining it with higher temperatures further promotes the formation of very large, percolating aggregates. Stiff molecule arms reduce steric repulsion effects in the worm-like micelle corona, thus making it quite flexible. At the same time, a high temperature flattens the influence of interaction energy on configurational probabilities, easing the urge of maximizing T bead contacts and cluster surface minimization. With this urge decreased and a high flexibility, the worm-like micelles gain entropy by bending and are much more likely to form energetically unfavorable cross-links, resulting in large, fractal aggregates.

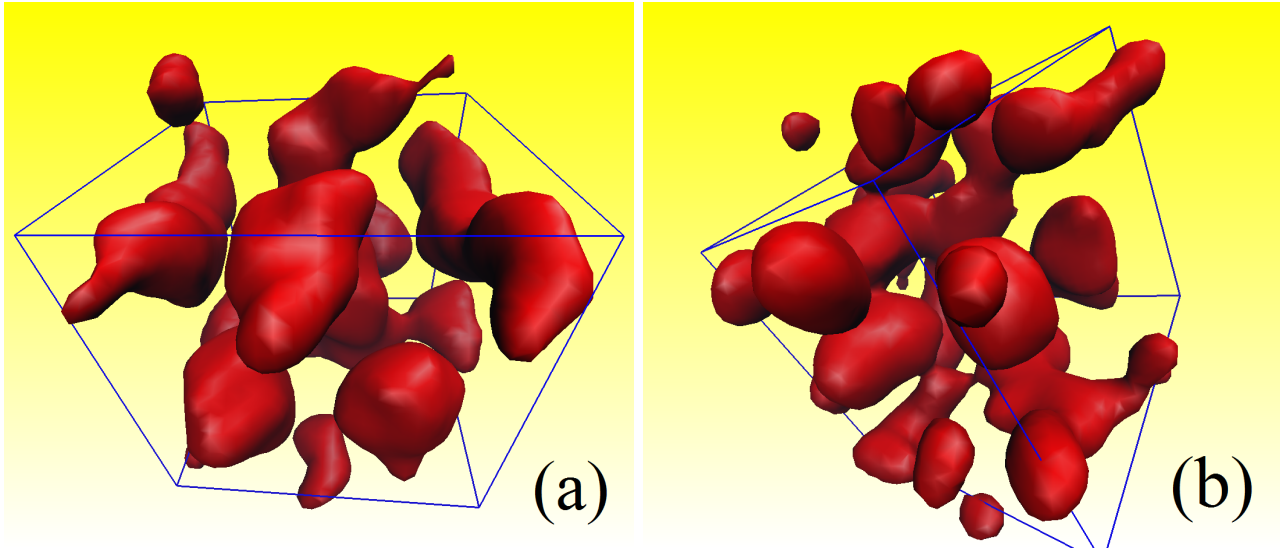


Figure 5.15: Snapshots of a $H(H_6T_4)_3$ system. (a) $\phi = 0.442$, $T^* = 5.2$, (b) $\phi = 0.438$, $T^* = 6.0$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

In fig. 5.15, the left picture shows a conformation at temperature $T^* = 5.2$ with the conformation in the right picture being at $T^* = 6.0$, both at about the same concentration $\phi \approx 0.44$. While in the left picture, one can distinguish intermediate aggregates like single micelles, coexisting worms and other supermicelles, the conformation on the right is basically one big, fractal aggregate of associated micelles and supermicelles. Note that even narrow bottleneck connections, however unfavorable in terms of solvophobic surface minimization, are no rarity.

Although we did not undertake a quantitative analysis of orientational characteristics on the super micelle conformations, it should be noted that systems at lower temperatures, where intermediate sized worm-like micelles are most prominent, do seem to have a preferential nematic ordering, while the system-spanning aggregates at higher temperatures lack any kind thereof. This promises interesting viscoelastic properties to which we will come back in the outlook section.

5.3 The $H(H_6T_4)_6$ -system

5.3.1 Flexible stars

In the fully flexible case, doubling the number of arms, compared to the former case $H(H_6T_4)_3$, leads to a similar percolating network formation, but we find no micellization prior to this network, i.e. at concentrations below the percolation threshold. At temperature $T^* = 4.9$, we only find the presence of single micelles next to the network, and decreasing down to $T^* \approx 4.6$, we also find the first harmonics of the significant micelle size next to the network, see figure 5.16. Corroborating to our previous investigations in chapter 3, both the single micelles and small supermicelles remain stable, but arrested in the voids that are left by the gel network.

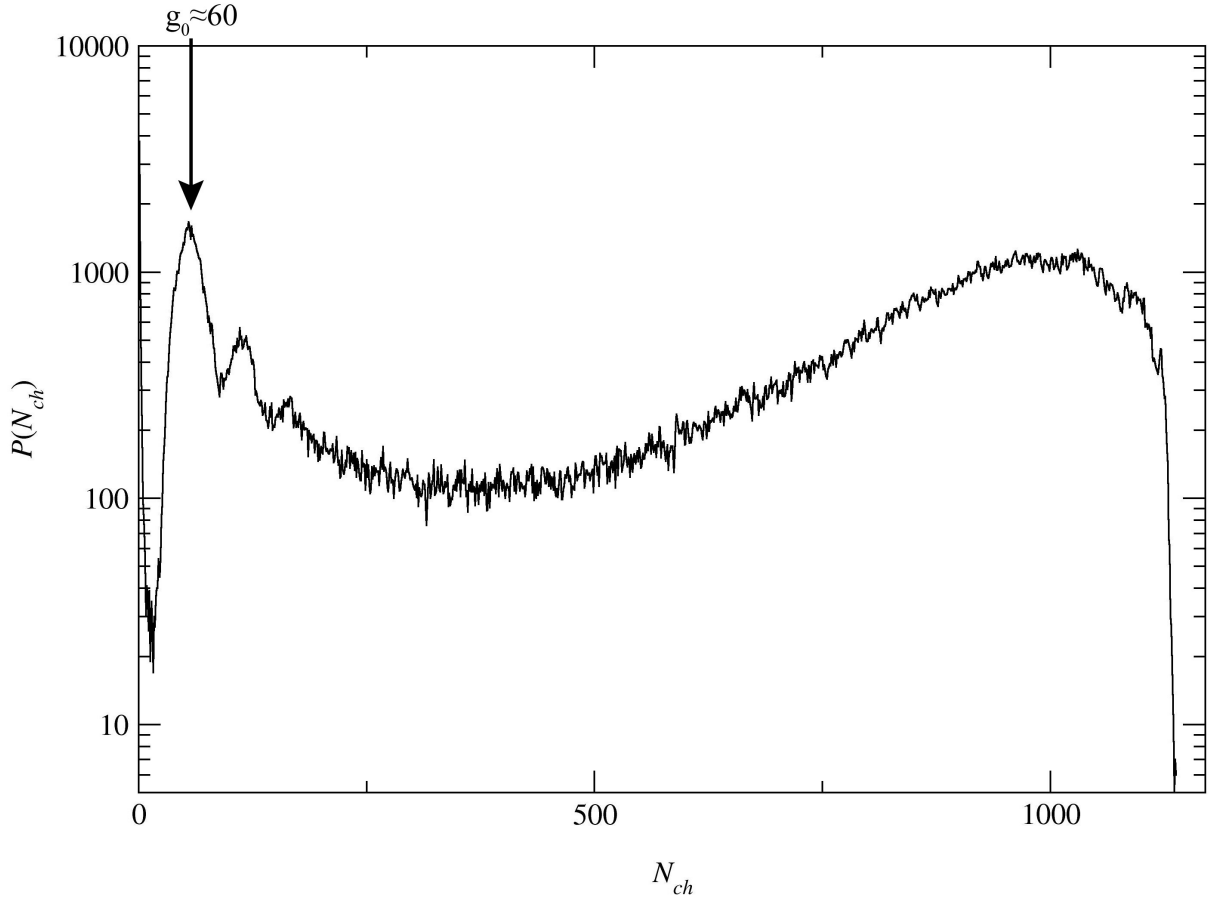


Figure 5.16: Cluster size distribution of a $H(H_6T_4)_6$ system at concentration $\phi = 0.412$, temperature $T^* = 4.6$ and average molecule number $\langle N \rangle = 182 \Leftrightarrow \langle N_{ch} \rangle = 1092$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

In contrast to the $H(H_6T_4)_3$ case, where the critical micelle concentration lies below the percolation concentration, in the $f = 6$ system, when successively increasing the concentration, the micellar aggregates form only after the formation of the percolating network. We argue that there is no general tendency of the $f = 6$ stars to form micelles, but that they are, instead, only formed when free stars are trapped inside a void of the gel network and can not protrude into the solvophobic interior of the latter. In order to anyhow maximize the number of solvophobic beads in contact, they turn to one another and form micelles.

This argument is supported by simulations on the same molecules in infinite dilution, performed by B. Capone et al. in [54], in which a $H(H_6T_4)_6$ star is right beyond the threshold where it does not

form a single solvophobic patch towards which all arms protrude into the same solid angle, but two patches lying on opposite sides of the anchoring point. Where single stars of $p = 1$, i.e., that tend to form only one patch in infinite dilution, are predestined to form micelles when at higher concentration, stars of $p > 1$, i.e., that would rather form several patches when in infinite dilution, are most likely to form an extended network. This is the case here, the majority of the system comprises a fractal, percolating macrogel network phase. Only after the formation of such a network is it possible that spherical micelles are formed by additional stars, for which it is necessary to be externally driven into micellization by environmental properties such as the soft steric confinement of the network voids, and an absence of any other accessible nearby association sites.

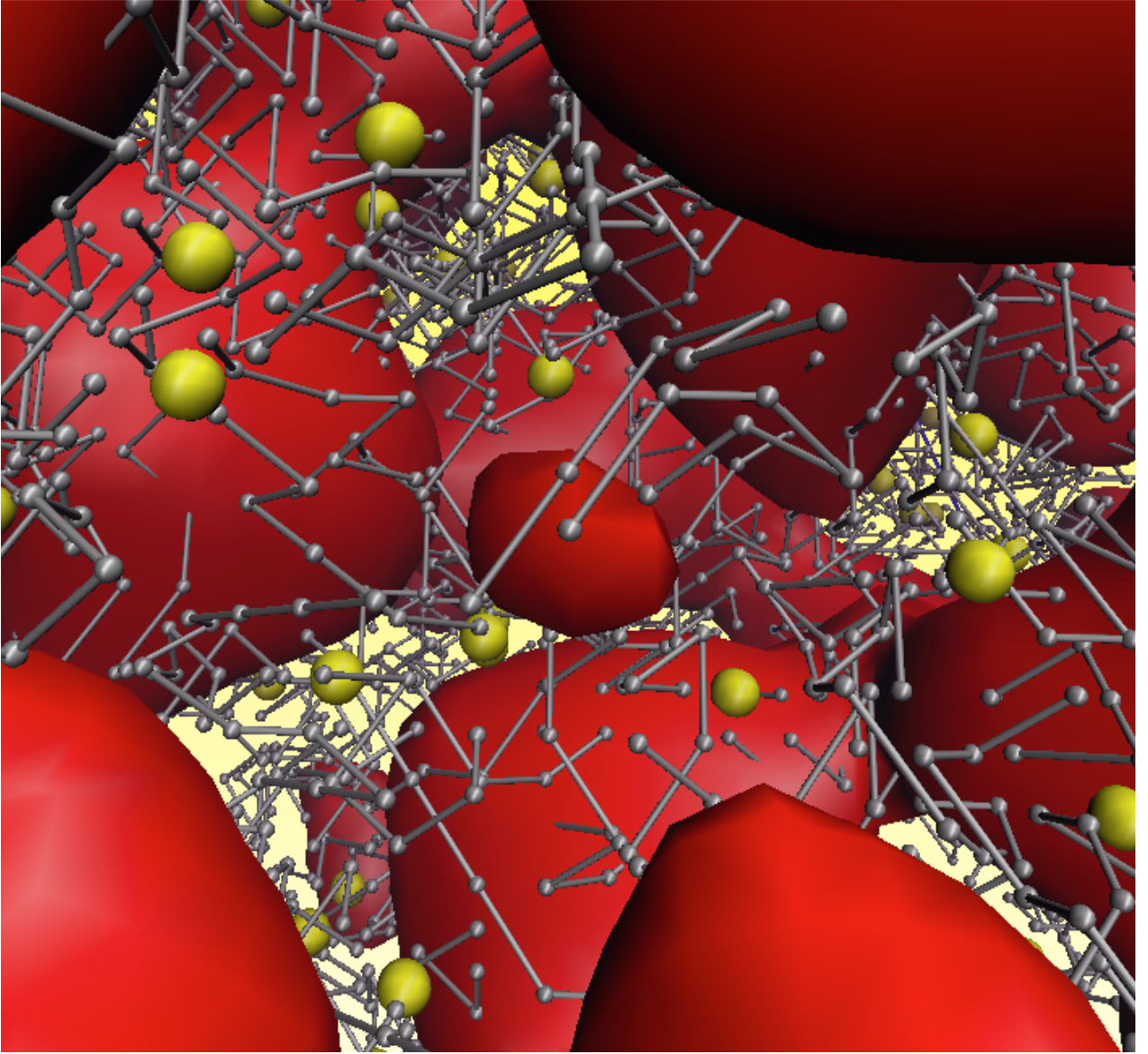


Figure 5.17: A single micelle, trapped in a void left by a percolating network. The snapshot was taken from a $H(H_6T_4)_6$ system at concentration $\phi = 0.427$ and temperature $T^* = 5.0$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. The grey beads and bonds represent the solvophilic A-block and the yellow beads represent the solvophilic anchoring points.

In figure 5.17, such a micelle is visualized for a $H(H_6T_4)_6$ system. The micelle is trapped in a void that is left by the surrounding percolating bulk. The attractive core of this bulk is shielded by the

solvophilic species, leaving no way for the micelle to associate with the bulk. However, the tendency of the stars in this system to form several patches is eased when one arm from within the micelle leaves its core, reaches out towards the surrounding bulk and manages to penetrate the solvophilic shielding. In exchange, one molecule belonging to the bulk shielding may tear free one of its own arms and associate with the micelle core where the arm of the micelle, that had just associated with the network bulk, has left a free association site. The micelle position and characteristic size remain the same, but the micelle is now towed via two chemical connections, "anchoring point bridges", to the bulk, see figure 5.18.

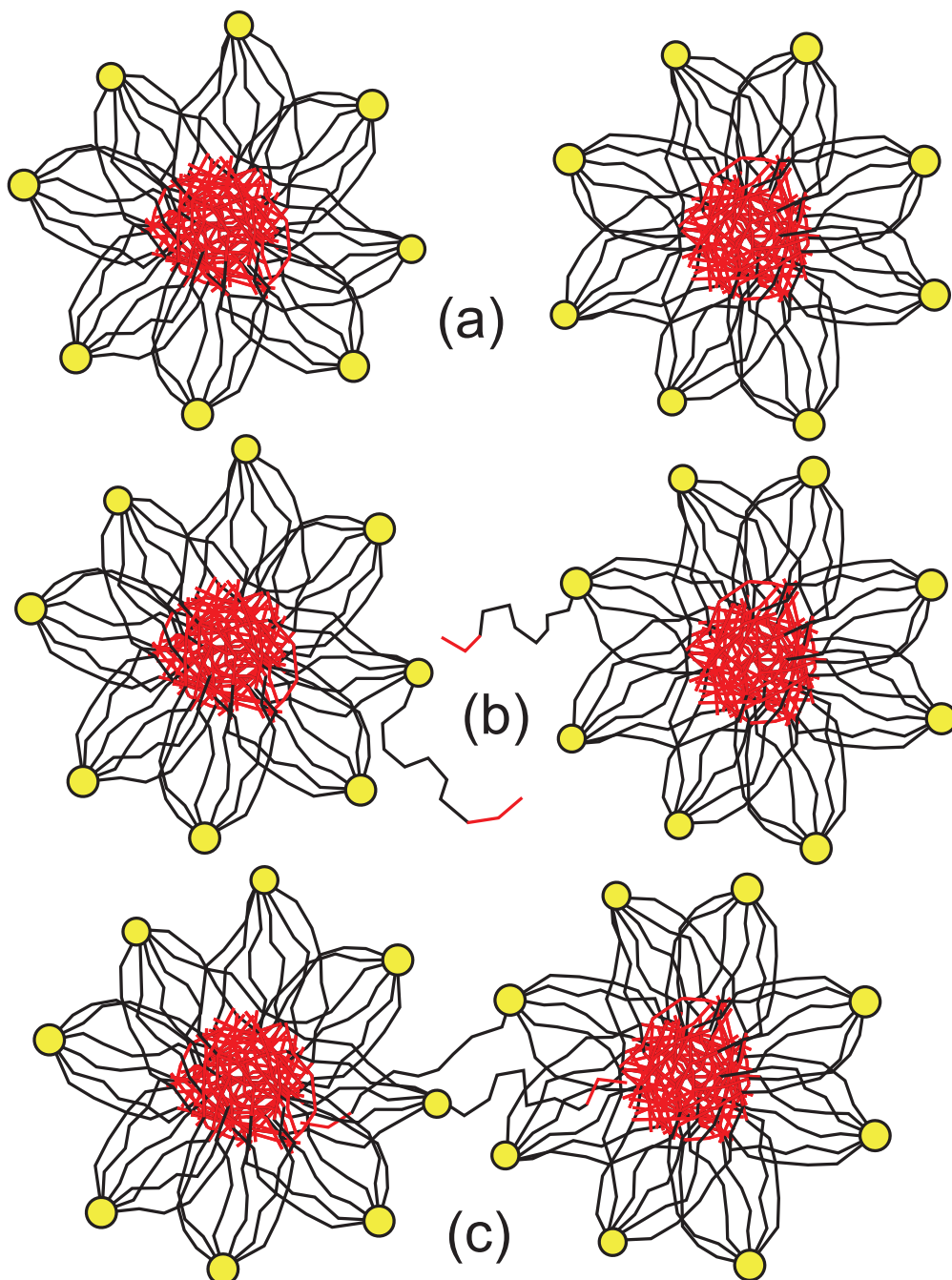


Figure 5.18: A sketch of two micelles of TSPs forming an anchoring point double bridge. (a) the micelles approach each other, (b) each micelle tears free one arm and (c), the arms associate to the respective other micelle, forming two chemical bridges over the anchoring points of the stars that contribute to the association.

In the following we will elaborate the role of chemical connections via anchoring point bridges in the $H(H_6T_4)_6$ system at lower temperature. At $T^* = 4.0$, the split in the cluster size distribution does not hold. Instead, we find a broad distribution of aggregate sizes, see figure 5.19 and a snapshot thereof in figure 5.22. This distribution survives for a very broad range of concentrations $0.2 \leq \phi \leq 0.6$.

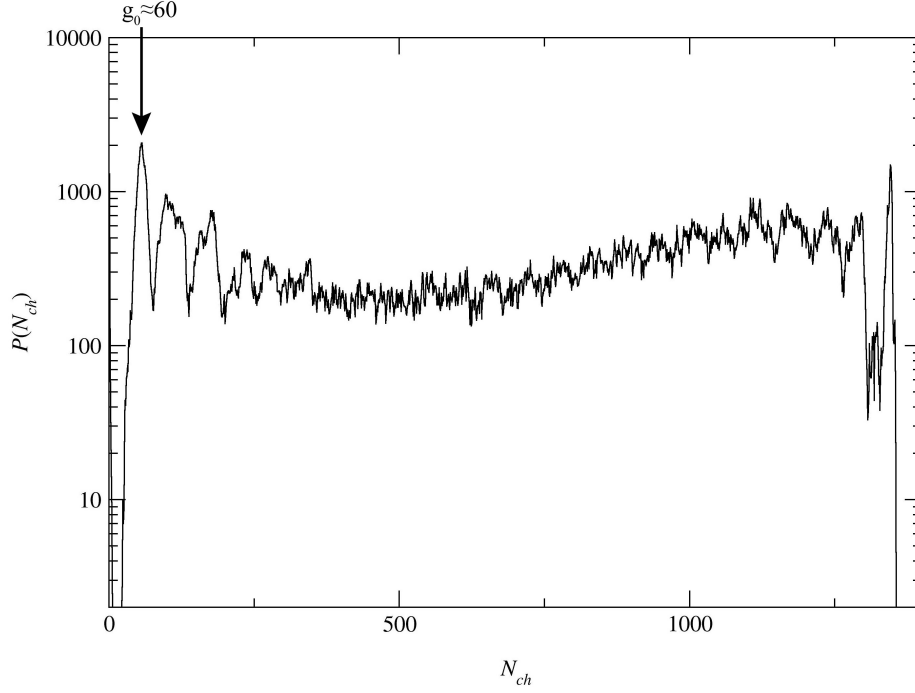


Figure 5.19: Cluster size distribution of a $H(H_6T_4)_6$ system at concentration $\phi = 0.501$, temperature $T^* = 4.0$ and average molecule number $\langle N \rangle = 221 \Leftrightarrow \langle N_{ch} \rangle = 1326$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

Furthermore, at concentration $\phi = 0.01$, we find a critical micelle concentration, see figure 5.20, that lies below the network percolation threshold of $\phi_{perc} \approx 0.2$.

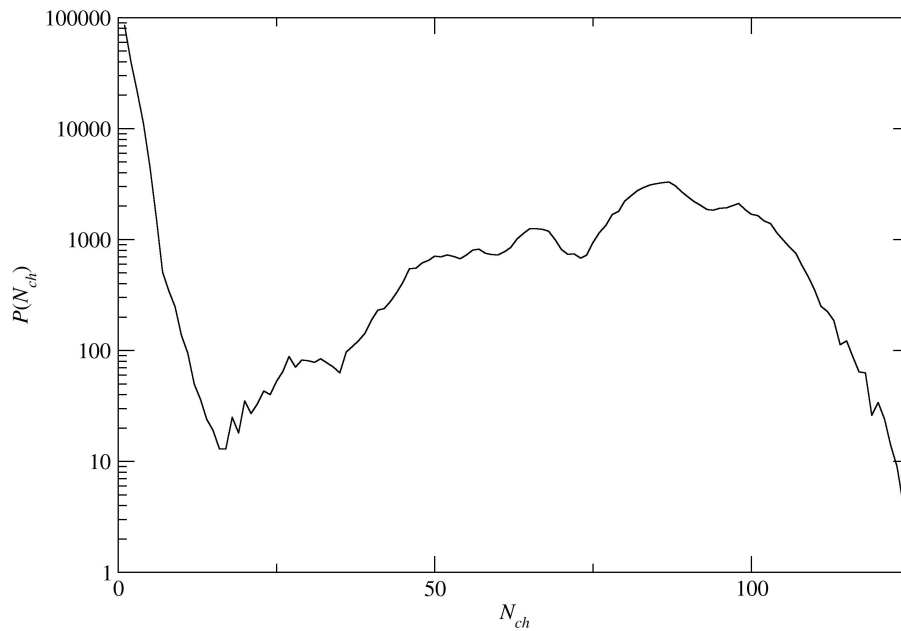


Figure 5.20: Cluster size distribution of a $H(H_6T_4)_6$ system at concentration $\phi = 0.010$, temperature $T^* = 4.0$ and average molecule number $\langle N \rangle = 15 \Leftrightarrow \langle N_{ch} \rangle = 90$.

One could argue that this is nevertheless evidence of micelles and harmonics, only heavily distorted by hysteresis effects or lack of equilibration. Equilibration was never under 50×10^6 MC steps for these systems and hysteresis effects have been diminished by combining histograms of multiple simulations with different initial configurations.

We instead propose the following. Due to an increased effect of attractions, the patchiness of a TSP decreases with decreasing temperature [52]. Lowering the temperature of a system of network-forming $p = 2$ dumbbell TSPs will at some point bring the system to a point where the TSPs assume configurations of $p = 1$ and $p = 2$ with similar probabilities. Assume only free stars in concentration, each with the tendency to form one or two solvophobic patches with near-equal probability, making the system effectively a mixture of watermelons and patchy dumbbells, and the ability to change patchiness between the two options. A micelle of these stars would have the same significant size, no matter if it is formed by stars with only one patch or double the number of stars when they have two patches and only one contributes to the micelle core, see figure 5.21. Thus, the first peak in the

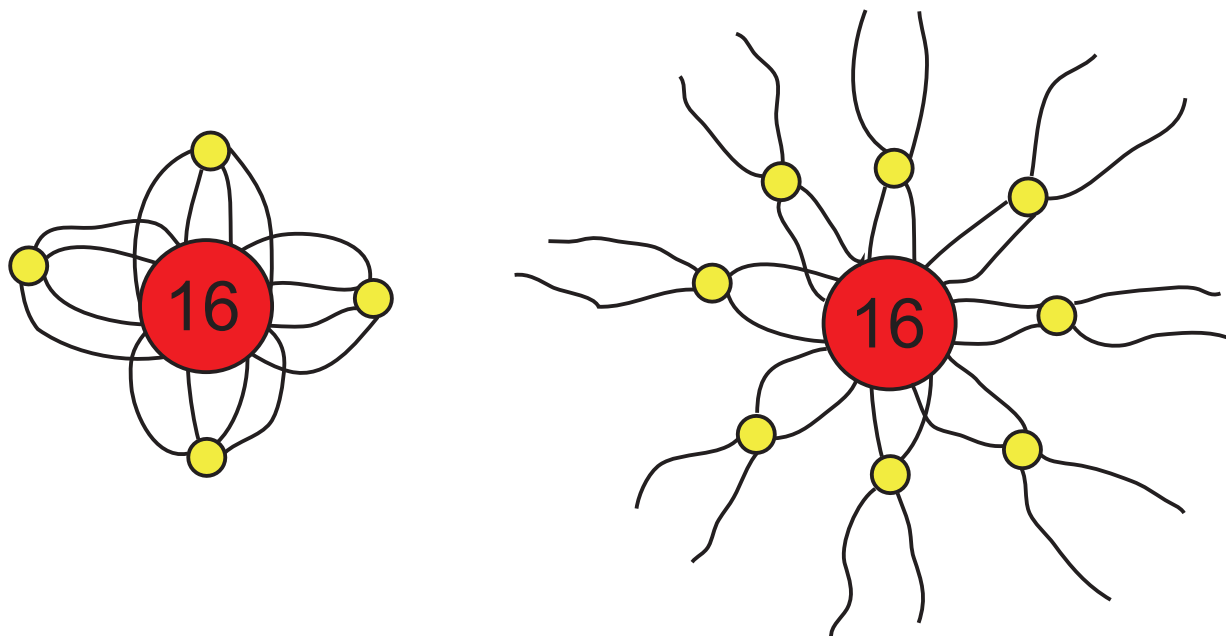


Figure 5.21: Sketch of two micelles, formed by TSPs of functionality $f = 4$. The micelle on the left is formed by four stars of patchiness $p = 1$, where all arms contribute to the micelle core. The micelle on the right is formed by double the number of stars, i.e. eight stars, where only two of the four arms of each star contribute to the micelle core. The characteristic micelle size is the same in both cases $g_0 = 16$. The micelle on the right, however, is eightfold linked via chemical anchoring point bridges.

cluster size distribution (figure 5.19) refers to the fundamental micelle that is shielded by a solvophilic corona. If there are stars with two patches contributing to the micelle, the patch facing away from the micelle is predestined to associate with close stars or even other two-patch-stars from the very same micelle, thus forming another aggregate which is then chemically associated to the micelle via a polymeric bridge over some stars' anchoring points. In this fashion, a tightly connected network of unassociated micelles is formed.

Increasing the concentration, this network gets so dense that it becomes favorable to sacrifice some entropy, fold aside the corona and merge micelles into supermicelles. This is made evident by the first harmonics in the cluster size distribution. However, the formation of worm-like micelles in a necklace-like fashion, like it was the case for the $H(H_6T_4)_3$ system, is suppressed by the extensive

chemical connections. In the case that a large super micelle is formed, it is more likely that this super micelle grows bigger not by the merging with another micelle, but by successive assimilation of single arms. This arm leaves a neighboring micelle, flips to its stars' other patch on the opposite side and fills up bottleneck association sites of the super micelle in order to minimize its cores surface. This flipping is inherent to stars of higher functionality and the two-patchiness of the $H(H_6T_4)_6$ stars in infinite dilution. In this way, large supermicelles do not grow in multiples of the significant micelle size, like it was the case for $f = 3$, but rather continuously.

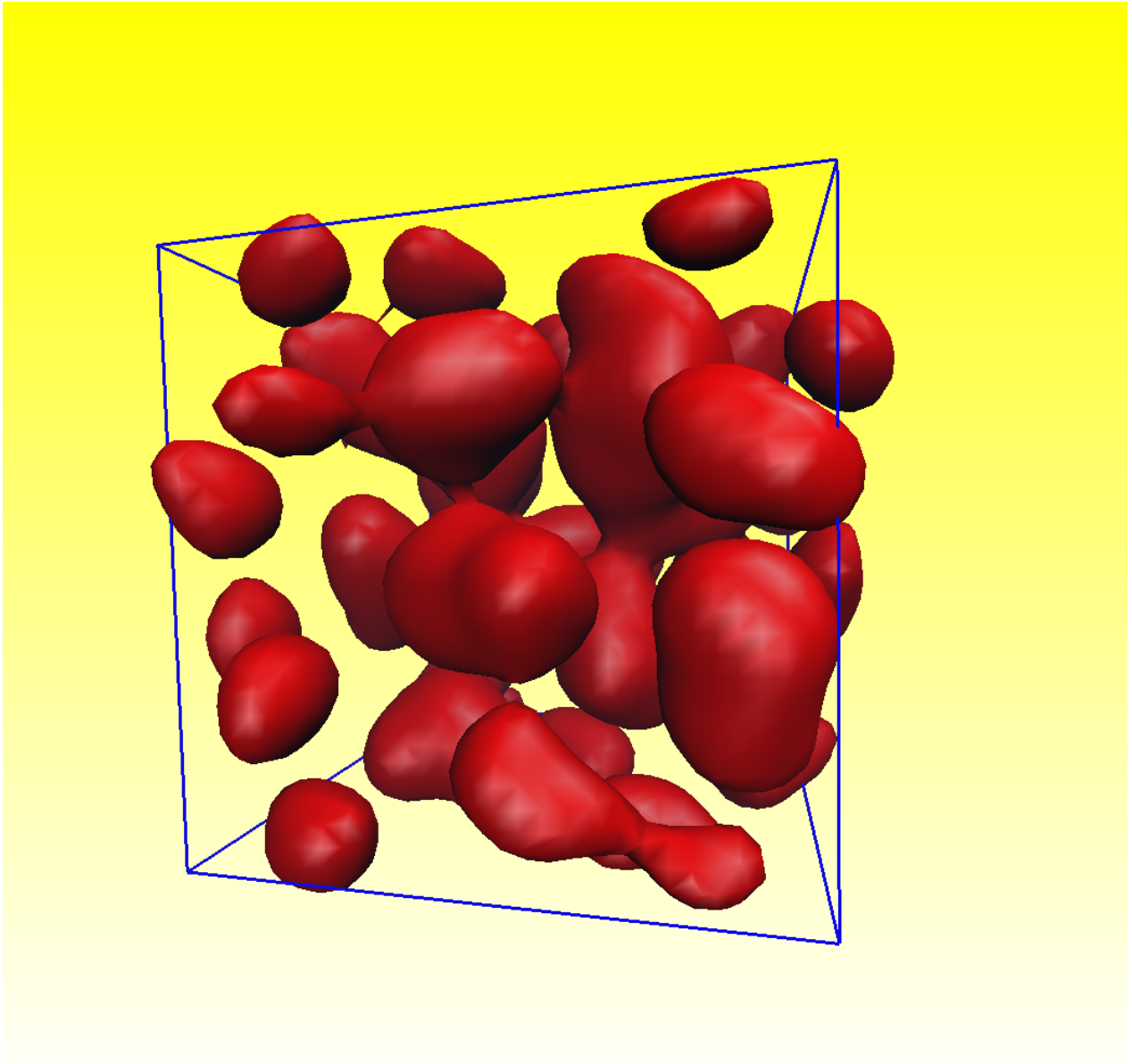


Figure 5.22: Snapshot of a $H(H_6T_4)_6$ system at concentration $\phi = 0.501$ and temperature $T^* = 4.0$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

5.3.2 Rigidity

Applying a bending stiffness to the $H(H_6T_4)_6$ system stabilizes the formation of worm-like micelles in a necklace-like fashion in a similar way as it did for the $H(H_6T_4)_3$ system. The cluster size histograms show multiple harmonics that are most pronounced at lower temperatures, see figure 5.23.

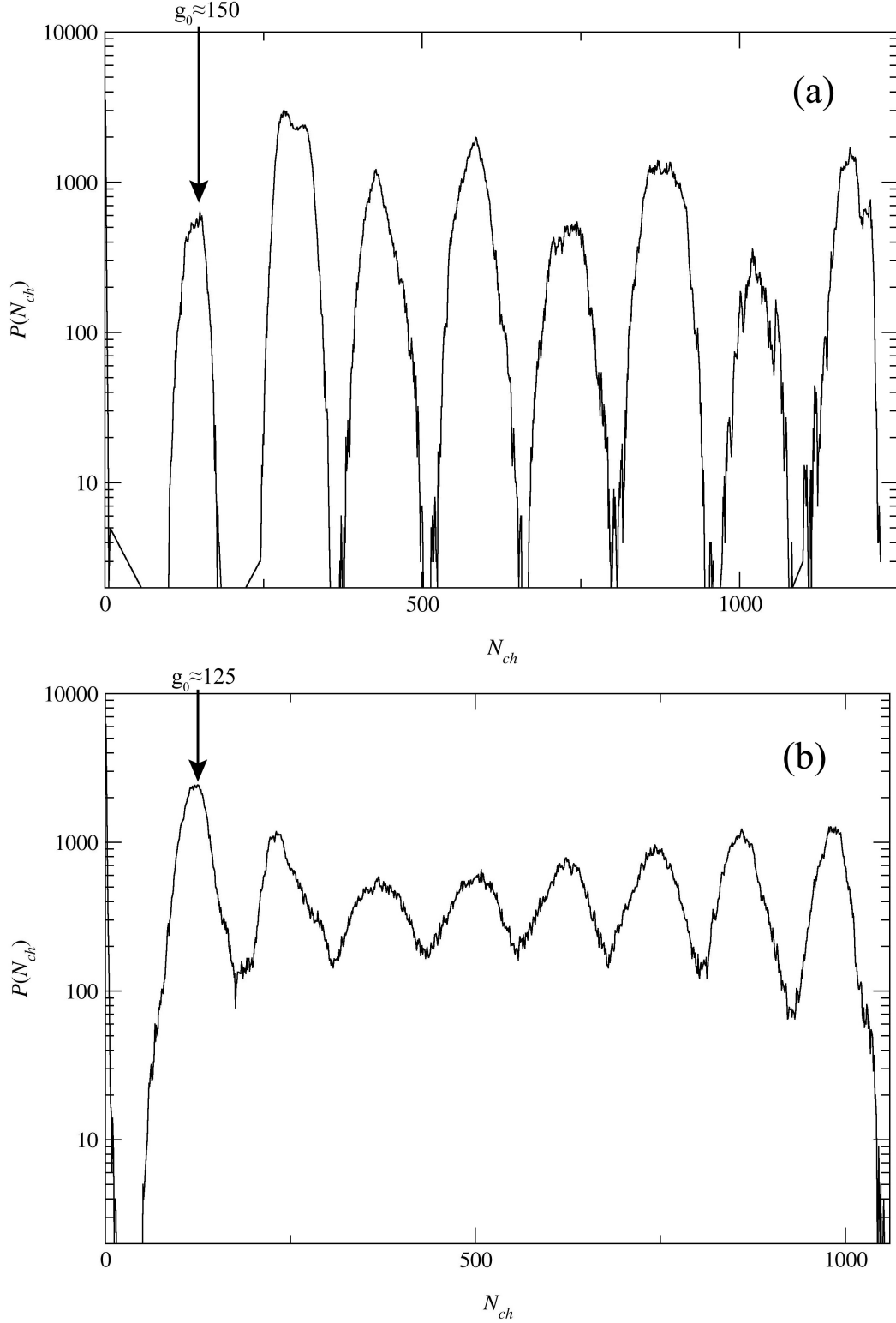


Figure 5.23: Cluster size histograms of a $H(H_6T_4)_6$ system with an arm rigidity of $\alpha = 10$. (a) $\phi = 0.444$, $T^* = 5.2$, $\langle N \rangle = 196 \Leftrightarrow \langle N_{ch} \rangle = 1176$, (b) $\phi = 0.375$, $T^* = 5.4$, $\langle N \rangle = 165 \Leftrightarrow \langle N_{ch} \rangle = 990$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

With the picture of a micellar network formation in mind that we drew in 5.3.1, one needs to realize that the flipping of arms for a single star, out of a single attractive patch and onto another patch, is due to steric repulsion of the A-blocks and the entropy gain when one or more arms can move towards a yet free solid angle. As already pointed out on pages 77 and 87, for stiff arms, this entropy gain is much lower than for fully flexible arms, since one single arm is already held in a much tighter configuration by the employed rigidity. Rigidity promotes for a single star a collapse to a narrow $p = 1$ watermelon conformation. While this means for very dilute systems that the one patch-configuration will survive up to much higher temperatures, this also means for a concentrated system that regular micellization and, thus, the formation of worm-like micelles in a necklace-like fashion is the evident scenario. Snapshots (see figure 5.24) further confirm this:

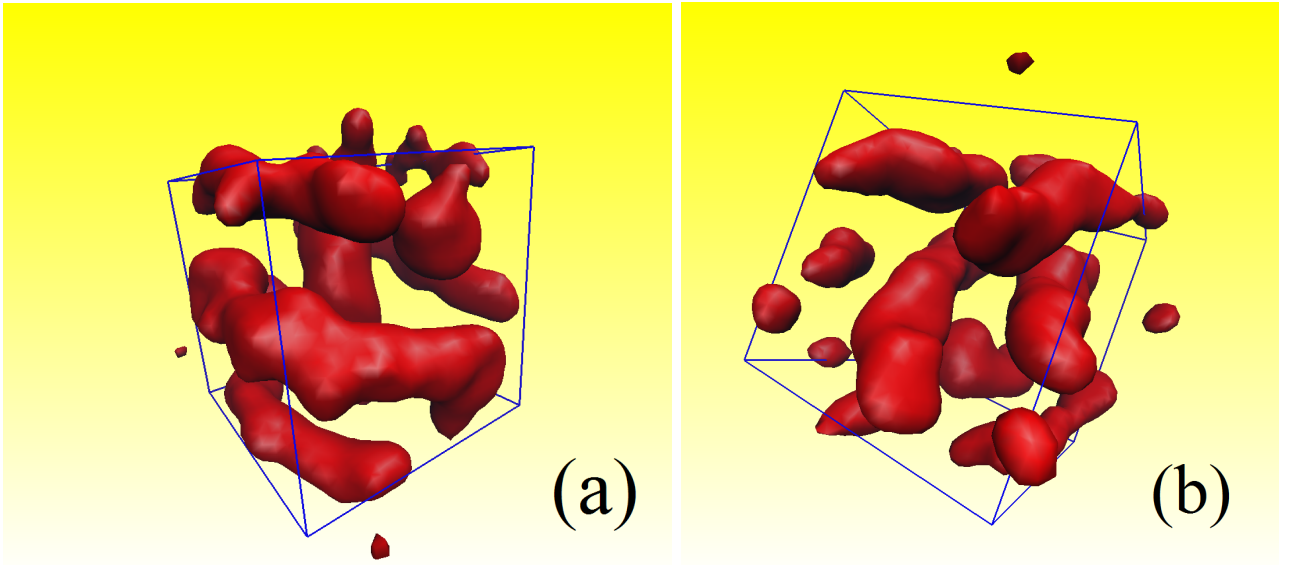


Figure 5.24: Snapshots of a $H(H_6T_4)_6$ system with an arm rigidity of $\alpha = 10$. (a) $\phi = 0.444$, $T^* = 5.2$, (b) $\phi = 0.427$, $T^* = 5.4$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

5.4 The $H(H_8T_2)_3$ -system

5.4.1 Flexible stars

In a star with only $r = 20\%$ attractive B-block size ratio, all effects of the solvophilic A-block are more pronounced. In accordance with previous investigations [55] and our results from chapter 3, this system forms stable, spherical micelles of well-defined size. Compared to the $H(H_6T_4)_3$ system, however, the size ratio of the micelle corona to the core is much higher, for an illustration see figure 5.5. Folding aside of the corona is necessary for an aggregation of two micelles in order to get the two micelle cores into contact. For large ratios of the corona to the core size, this folding has a much higher entropic cost. Next to that, the number of additional associations that can be gained by inter-aggregating micelles is much lower compared to the case $r = 40\%$, where a micelle core is naturally much bigger in size, see e.g. figure 5.5. Also, a hypothetical worm-like micelle would have a much higher persistence length than one of a $r = 40\%$ system. A bending of the worm-like micelle leads to a compression of the corona, which is penalized due to steric repulsion. Thus, a larger corona relative to the micelle core will lead to stiffer, straighter worm-like micelles, which are eschewed by entropy. Due to all these reasons, the formation of supermicelles is a lot less favorable in this system, which results in histograms that feature significant cluster sizes only up to the first harmonic, see figure 5.25. Drastically reducing the temperature, the influence of entropy on the aggregation mech-

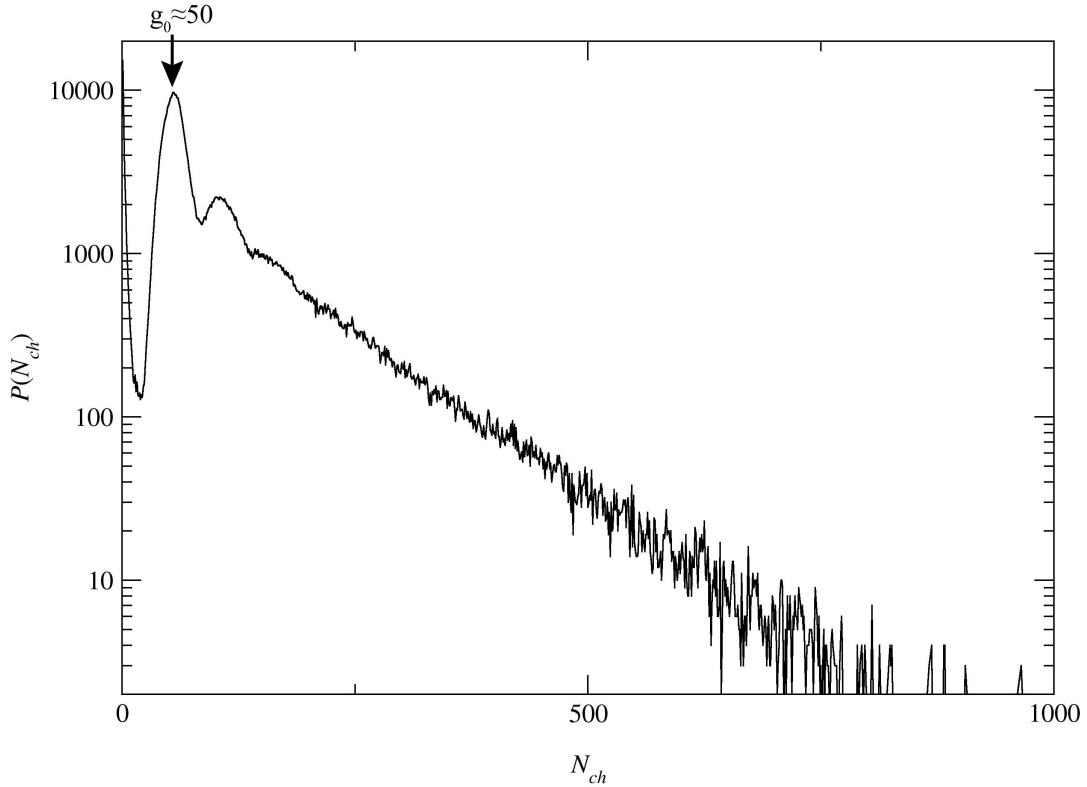


Figure 5.25: Cluster size histograms of a $H(H_8T_2)_3$ system at concentration $\phi = 0.587$, temperature $T^* = 3.0$ and average molecule number $\langle N \rangle = 511 \Leftrightarrow \langle N_{ch} \rangle = 1533$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

anisms is reduced and the attractions become the most determining factor. Entropy is overcome and inter-micellar associations of higher order are more favorable. A third and - possibly - fourth harmonic can be found, as can be seen in figure 5.26.

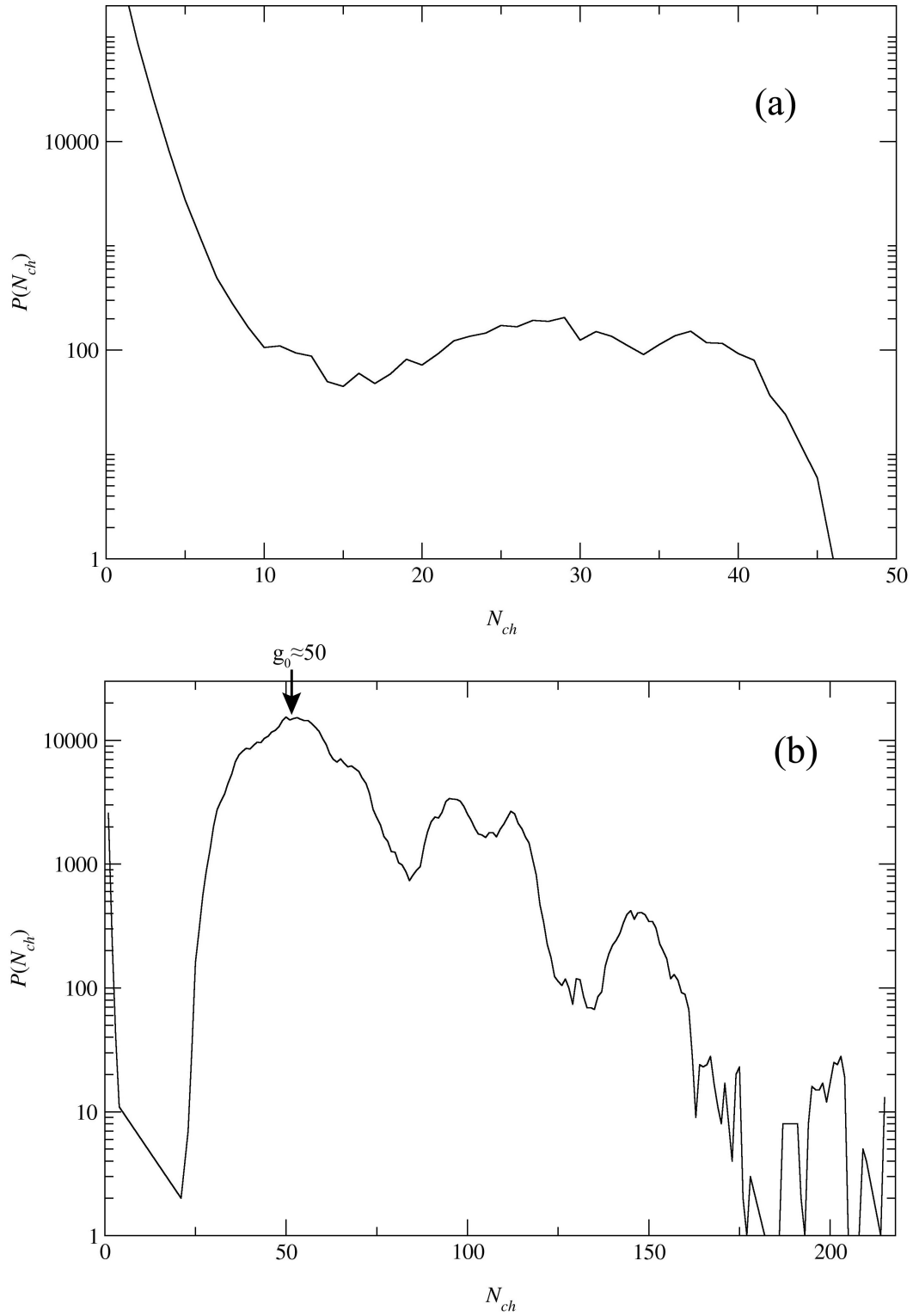


Figure 5.26: Cluster size histograms of a $H(H_8T_2)_3$ system. (a) $\phi = 0.02$, $T^* = 2.0$, $\langle N \rangle = 16 \Leftrightarrow \langle N_{ch} \rangle = 48$, the characteristic "shoulder" of a system at the threshold to micellization, (b) $\phi = 0.591$, $T^* = 2.0$, $\langle N \rangle = 518 \Leftrightarrow \langle N_{ch} \rangle = 1554$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

At low temperatures, this system shows no percolation transition. The micelles are stable up to arbitrarily high concentrations. Increasing the temperature, however, opens all star molecules and makes micellization impossible. Entropy dominates over the surface minimization of the solvophobic species and, thus, a living network is continually formed, which percolates at $\phi \approx 0.4$ (see figure 5.27)

and is compressed to a bicontinuous fluid phase at high concentrations, see e.g. a snapshot in figure 5.28.

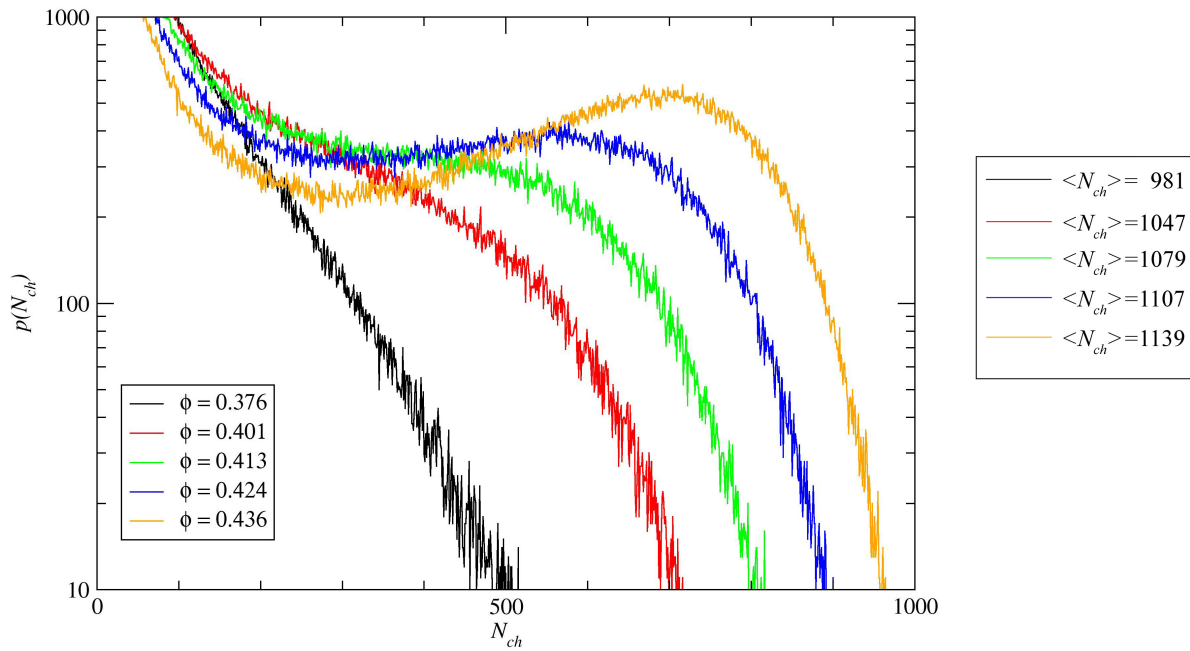


Figure 5.27: Cluster size histograms of a $H(H_8T_2)_3$ system at temperature $T^* = 4.0$ and different concentrations.

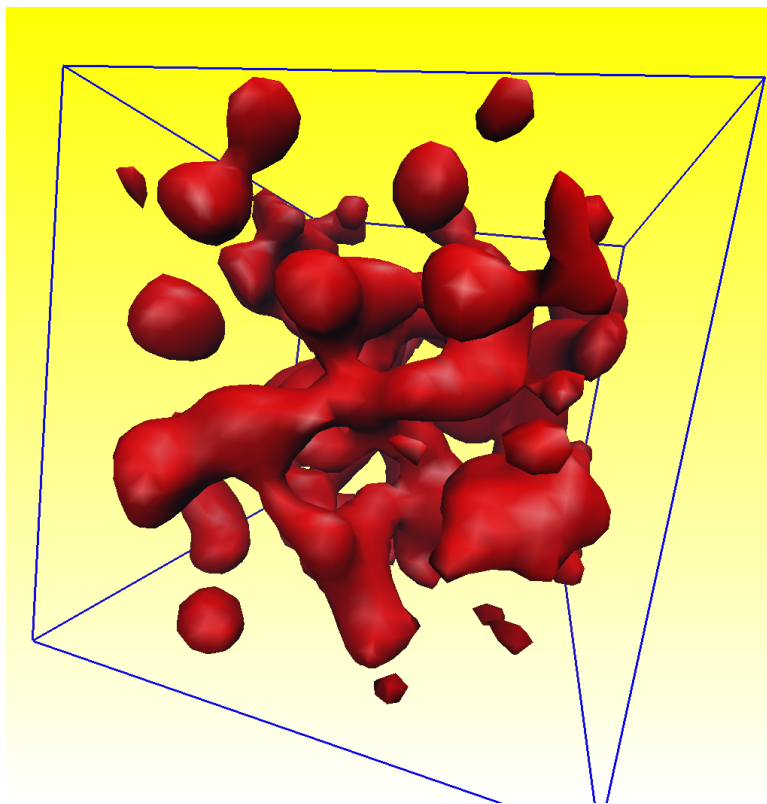


Figure 5.28: Snapshot of a $H(H_8T_2)_3$ system at concentration $\phi = 0.489$ and temperature $T^* = 4.0$.

5.4.2 Rigidity

As was the case for the $r = 40\%$ systems, applying a bending rigidity to the arms of the $H(H_8T_2)_3$ system reduces the entropic cost of an inter-micelle aggregation. We observed necklace-like formation of supermicelles up to the fifth harmonic at moderate temperatures of $T^* = 3.2$, see the histograms in figure 5.29 and the respective snapshots in figure 5.30 and 5.31.

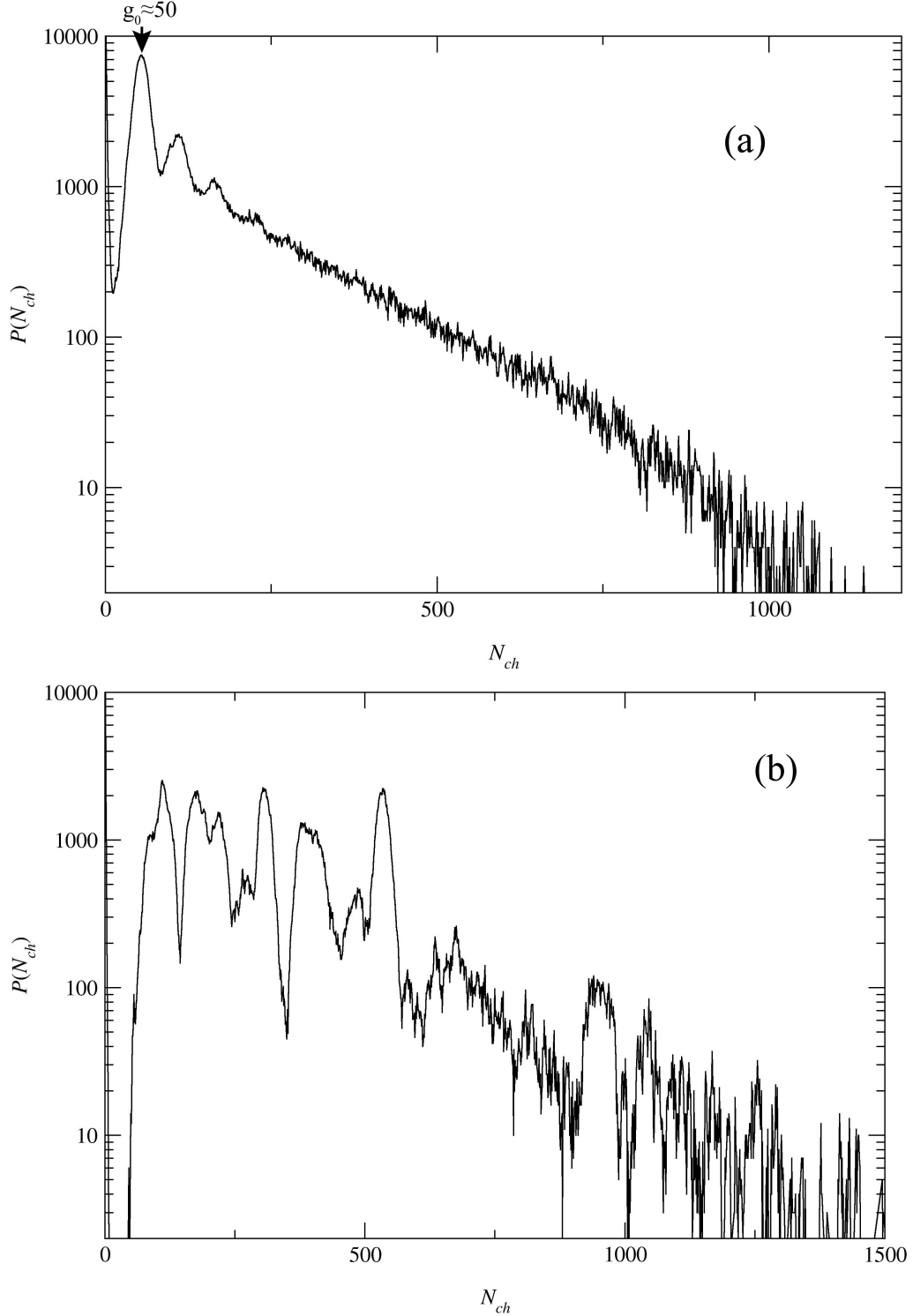


Figure 5.29: Cluster size histograms of a $H(H_8T_2)_3$ system with an arm rigidity of $\alpha = 10$. (a) $\phi = 0.508$, $T^* = 3.2$, $\langle N \rangle = 442 \Leftrightarrow \langle N_{ch} \rangle = 1327$ (b) $\phi = 0.620$, $T^* = 3.2$, $\langle N \rangle = 540 \Leftrightarrow \langle N_{ch} \rangle = 1620$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

For high concentrations, the harmonics become less pronounced and the histogram is heavily distorted. This is the case when the system becomes so dense that there is no more space for free stars to form another micelle. They then, instead, bring one or more arms into association with an existing micelle or super micelle, thus changing its cluster size. Consequently, significant sizes in the histogram are smeared out.

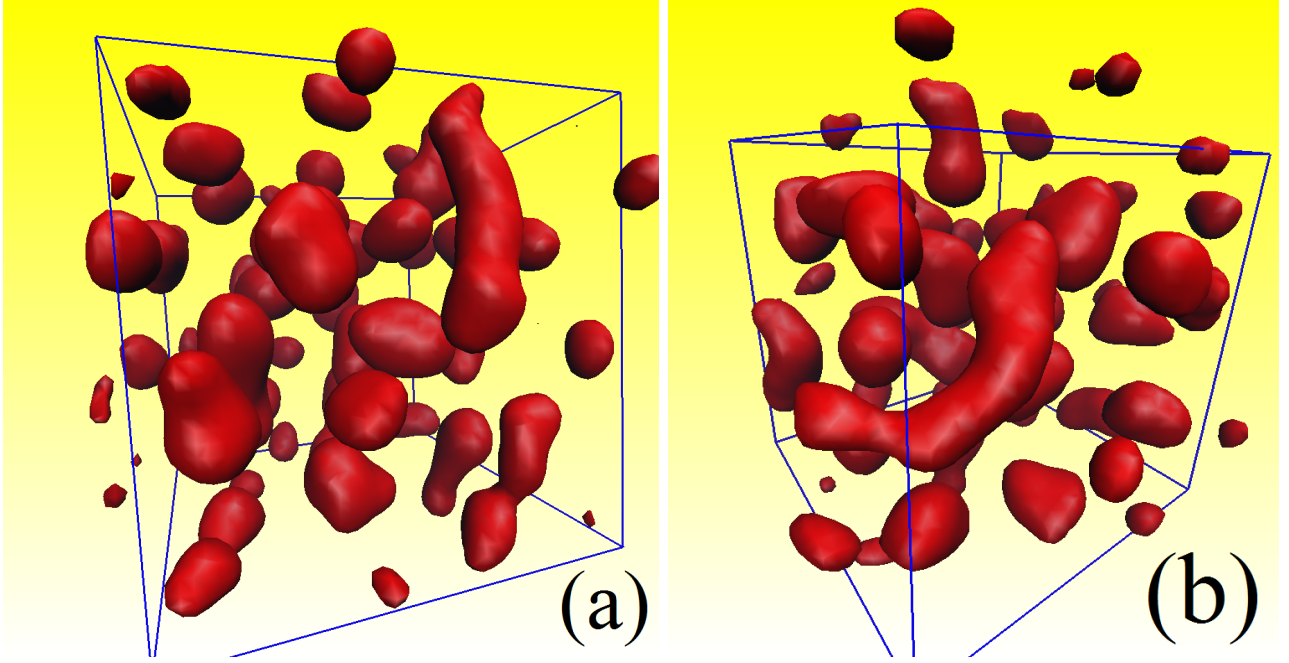


Figure 5.30: Snapshots of a $H(H_8T_2)_3$ system with an arm rigidity of $\alpha = 10$ at concentration $\phi = 0.508$ and temperature $T^* = 3.2$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

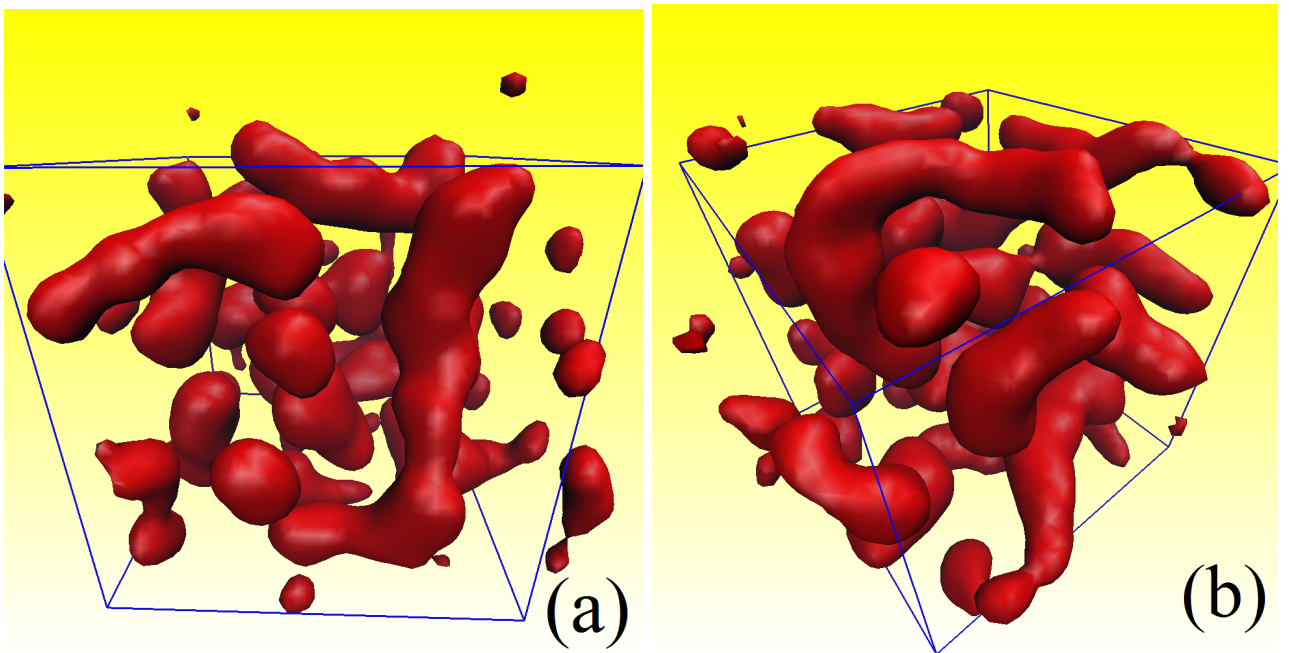


Figure 5.31: Snapshots of a $H(H_8T_2)_3$ system with an arm rigidity of $\alpha = 10$ at concentration $\phi = 0.620$ and temperature $T^* = 3.2$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

There is no formation of a system spanning cluster. The application of rigidity promotes the formation of worm-like micelles that show - in contrast to the $r = 40\%$ systems - little tendency to form cross links. The majority of supermicelles comprises well defined worms that quite heavily bend and even entangle ².

In contrast to the fully flexible $H(H_8T_2)_3$ system, rigidity promotes the formation of worm-like micelles due to a strong reduction in the sterically repulsive effects in the micelle coronae. The reduction makes the coronae more flexible and allows for both folding aside to expose the core and for compression. In contrast to systems of $r = 40\%$ (see section 5.6), there is no significant effect of rigidity on the fundamental micelle size g_0 , which would increase the density of the corona and decrease its compressibility. Thus, an easier core exposure promotes the very formation of supermicelles, while an easier corona compression allows for worm-like micelles to bend more excessively.

Aggregate bending is essential when considering entropy. Since rigidity penalizes bending of a molecule's arms, it dampens entropy manifestation on an intra-molecular scale. However, we have already seen for the hierarchies of ordered phases in chapter 4.5 that the introduction of rigidity only shifts entropy towards other opportunities of disorder in the system. In this case, the eased worm bending due to corona compression creates a large variety of similarly probable system states, and thus leads to entropy manifesting in an excessive bending of the worm-like micelles in the system. Overall, the system sacrifices entropy on an intra-molecular scale to gain entropy on a supra-molecular scale. This trade off enables the formation of worm-like micelles in the first place.

This is an extremely interesting aspect when considering rheological properties. For the fully flexible $H(H_8T_2)_3$ system, we have found that the formation of percolating clusters is possible at sufficiently high temperature and concentration. A highly concentrated micelle sol is stable at low temperature. Increasing the temperature, the entropic effects in the micelle corona become so strong that the micelles melt and the formation of a fractal percolating network is favored. Rigidity decreases the entropic effects in the micelle corona, thus stabilizing micelle aggregation. A much higher temperature is needed to melt these stabilized micelles and allow for a percolation transition. Similar to the increasing effect on the critical temperature of macrophase separating systems (see 4.4), rigidity increases the necessary temperature for strong enough fluctuations to allow for a melt of the micelles and a consequent gelation.

In experiment, a tunable rigidity can be realized for instance by periodic ionization of the polymer chains and control of the screening strength by tuning the salinity. At given high concentration, the sol-gel transition and thus, the rheological properties can therefore not only be tuned by changing the system temperature, but also at constant temperature by tuning the rigidity via e.g. salinity, so that micelle formation is stabilized sufficiently that the percolation transition is suppressed.

²Occasionally, a worm gets so long while being very straight that it reaches out of the simulation box and, due to periodic boundary conditions, comes back in on the other side to bite its own tail and self-associate. However, the histograms show a clear trend of decreasing probability for long necklaces, which indicates that such a one dimensional percolation is a finite size artifact. We only found such percolating worms for box sizes $L = 30, 40$ and never in a box of length $L = 50$, which is also a strong hint that there is no percolation in this system whatsoever.

5.5 The $H(H_8T_2)_6$ -system

5.5.1 Flexible stars

Similar to the fully flexible $H(H_8T_2)_3$ systems, for $H(H_8T_2)_6$ spherical micelles are stable and super micelle formation is only found at concentrations above $\phi \approx 0.5$, up to the third harmonic, see figure 5.32. This complements our investigations in chapter 3, in which we did not investigate such high concentrations and, thus, found no harmonics.

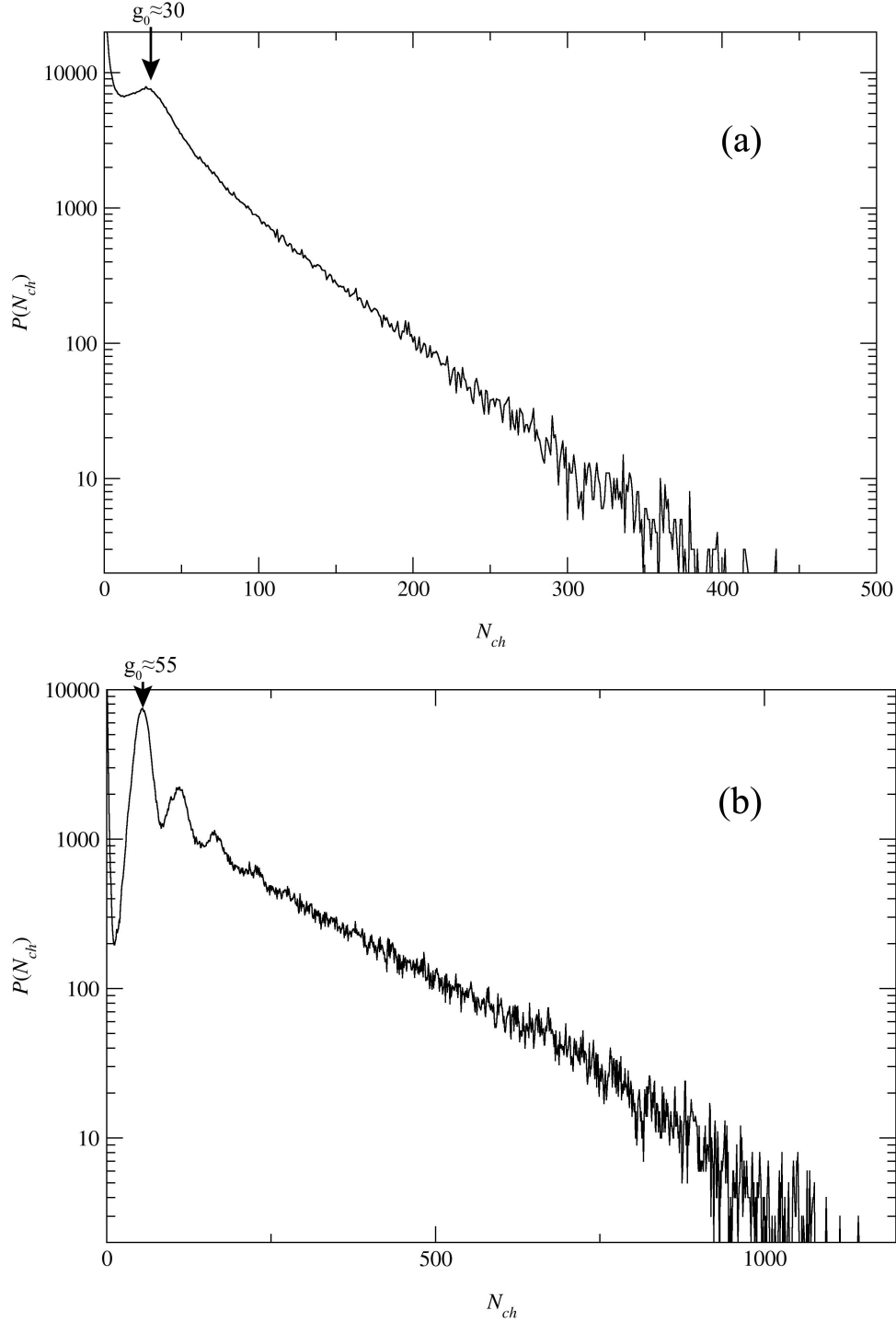


Figure 5.32: Cluster size histograms of a $H(H_8T_2)_6$ system. (a) $\phi = 0.365$, $T^* = 3.0$, $\langle N \rangle = 161 \Leftrightarrow \langle N_{ch} \rangle = 969$, (b) $\phi = 0.599$, $T^* = 3.0$, $\langle N \rangle = 265 \Leftrightarrow \langle N_{ch} \rangle = 1590$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

Also alike $H(H_8T_2)_3$, the $f = 6$ case allows for a percolation in the form of a fractal network, when the temperature is increased over the threshold where all micellar aggregates melt.

Although the higher functionality might suggest that - similar to the $r = 40\%$ cases - the stars in this system form two attractive patches instead of one, and thus, could form a tightly connected micellar network similar to $H(H_6T_4)_6$ system, this is not the case. A micellar network, when increasing the concentration, will eventually merge into a dense, bicontinuous fluid. For this system, however, even at very high concentrations, the micellar aggregates are so well sterically shielded that no system spanning cluster is found. Increasing the temperature, a such a phase is only found beyond the melting point of micelles. From that, we argue that, to drive the stars in this system to flip arms away from their single patch to form a second one and thus form a network of patchy micelles would require a temperature which is beyond the melting of micellar aggregates.

5.5.2 Rigidity

As in all investigated systems, the application of rigidity to the stars' arms promotes the formation of worm-like micelles, the reason being, once more, the reduced effect of entropy on the stars' coronae and, thus, their enhanced ability to form inter-micellar associations, see figure 5.33.

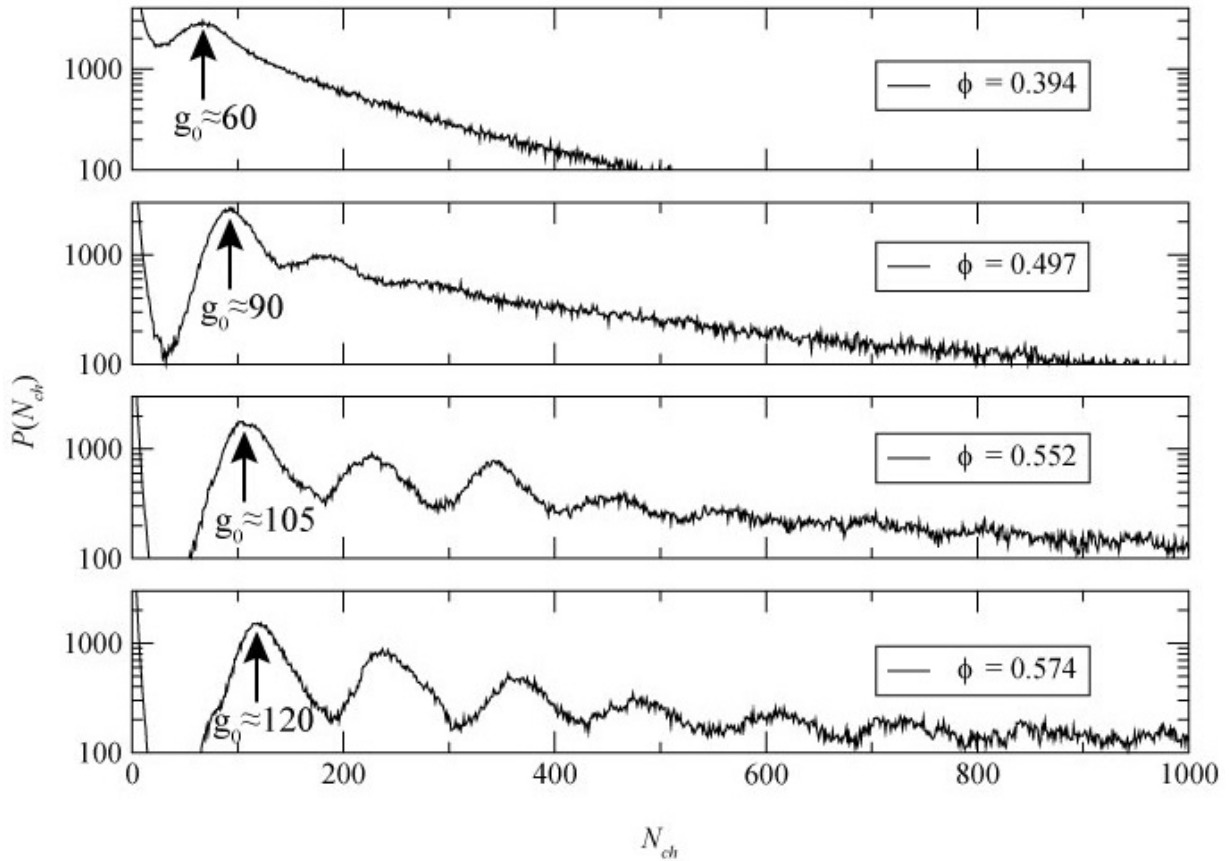


Figure 5.33: Cluster size histograms of a $H(H_8T_2)_6$ system with an arm rigidity of $\alpha = 10$ at temperature $T^* = 4.0$. The g_n values denote the aggregate sizes of harmonics and will be subject of section 5.6.

What is really outstanding for this system is the occurrence of ordered phases. For a temperature range $3.6 \leq T^* \leq 3.8$, the worm-like micelles that form start to arrange in a columnar hexagonal ordering at concentrations $\phi \approx 0.6$, as can be seen in figure 5.34.

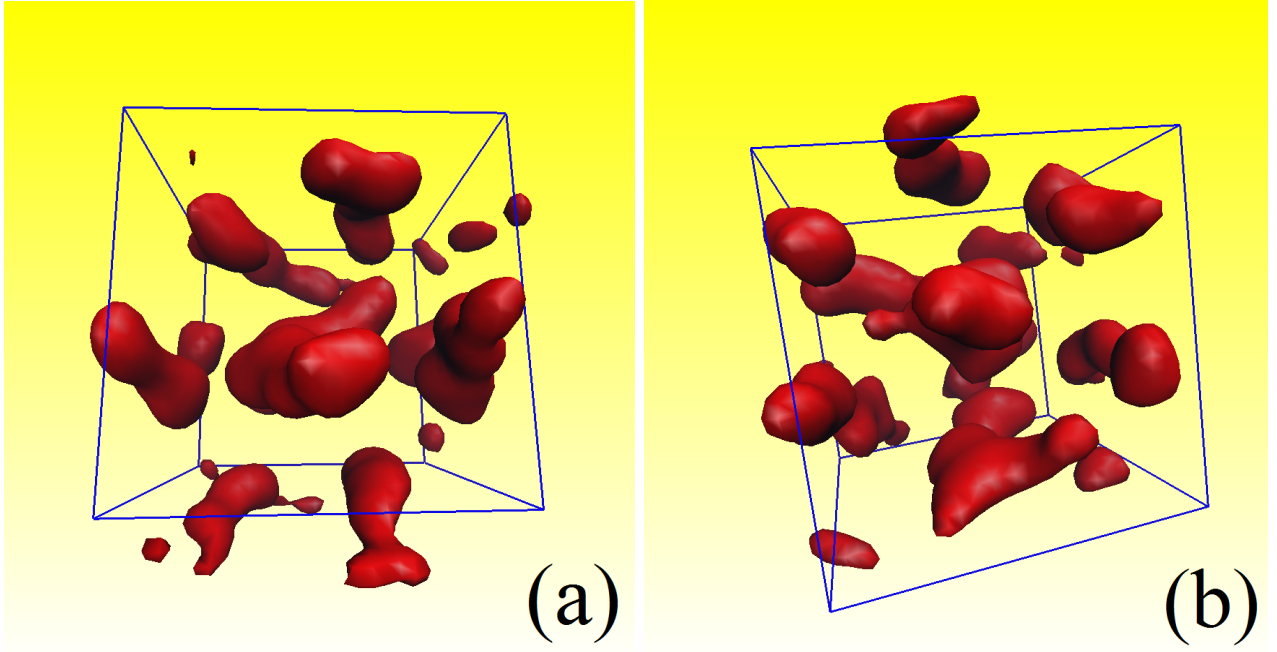


Figure 5.34: Snapshots of a $H(H_8T_2)_6$ system with an arm rigidity of $\alpha = 10$. (a) $\phi = 0.626$, $T^* = 3.6$, (b) $\phi = 0.639$, $T^* = 3.8$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

For higher concentrations, additional micelles form, the columns start to associate with one another and the ordering breaks down into a fractal network. Also, we have used a finite size simulation with periodic boundary conditions. Hence, the hexagonal ordering is highly dependent on a suitable box size, which is why we have only observed it in simulations with a box of $L = 30$ lattice sites.

However, the mere tendency of the system to arrange in an ordered phase is witnessed also in simulations of other box sites, where, instead, we found the micelles to arrange on a cubic lattice.

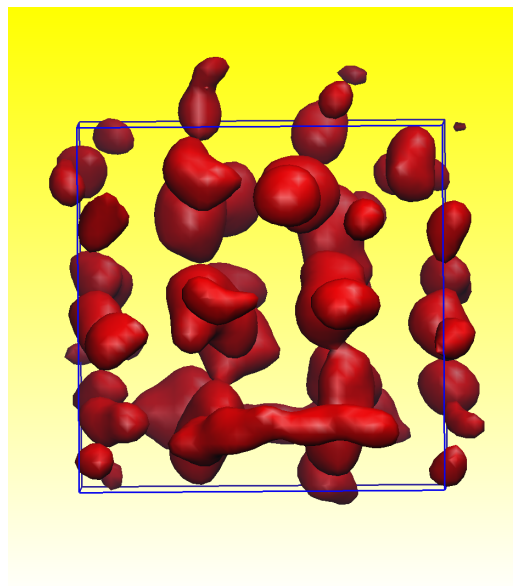


Figure 5.35: Snapshots of a $H(H_8T_2)_6$ system with an arm rigidity of $\alpha = 10$ at concentration $\phi = 0.519$ and temperature $T^* = 3.6$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

As seen in figure 5.35 at a somewhat lower concentration, $\phi = 0.519$, spherical micelles try to arrange in a standard cubic lattice while at the same time trying to form supermicelles. Thus, neighboring micelles on the cubic lattice associate quite frequently into small worms. With higher concentration, these worms grow, bend, form cross links and/or 90° angles and rearrange due to their inherent persistence length, eventually leading to system spanning aggregates and completely destroying the ordering, see fig.5.36.

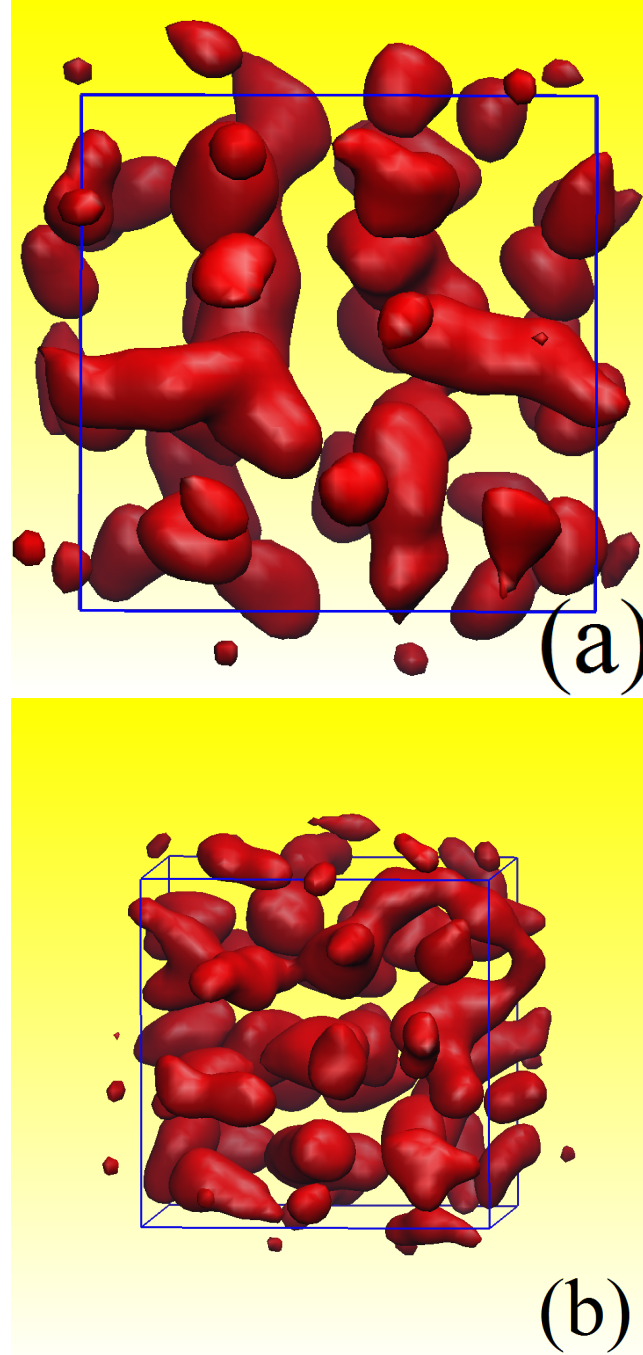


Figure 5.36: Snapshots of a $H(H_8T_2)_6$ system with an arm rigidity of $\alpha = 10$. (a) $\phi = 0.574$, $T^* = 3.6$, (b) $\phi = 0.710$, $T^* = 3.6$. The red shapes are a geometrical encasing of clusters of associated solvophobic tail beads. Solvophilic species are not shown.

5.6 Fundamental micelle size

Up to now, we have stated that arm stiffness and a consequent narrowing in the shape of collapsed TSP conformations stabilizes micelle (and super micelle) formation. The narrow configuration makes a collapsed TSP an effective surfactant colloid that suffers quite little from steric effects. Next to the mere stabilization of micelle formation, this also affects the number of molecules that form a single micelle.

A comparison of the cluster size histograms of the $H(H_6T_4)_3$ system at different temperatures and rigidities shows that there is a change in the fundamental micelle size g_0 , given by the number of chains, i.e. molecule arms, that contribute to the micelle core. From figures 5.7 and 5.13, we get a micelle size of $g_0 \approx 70$ for the flexible and $g_0 \approx 150$ for the rigid system. The smaller size of a stiff and, thus, narrow collapsed TSP compared to a bloated, flexible one, and the reduced steric repulsion, allow for a much denser assembly of the TSPs when forming a micelle, as is illustrated in figure 5.37.

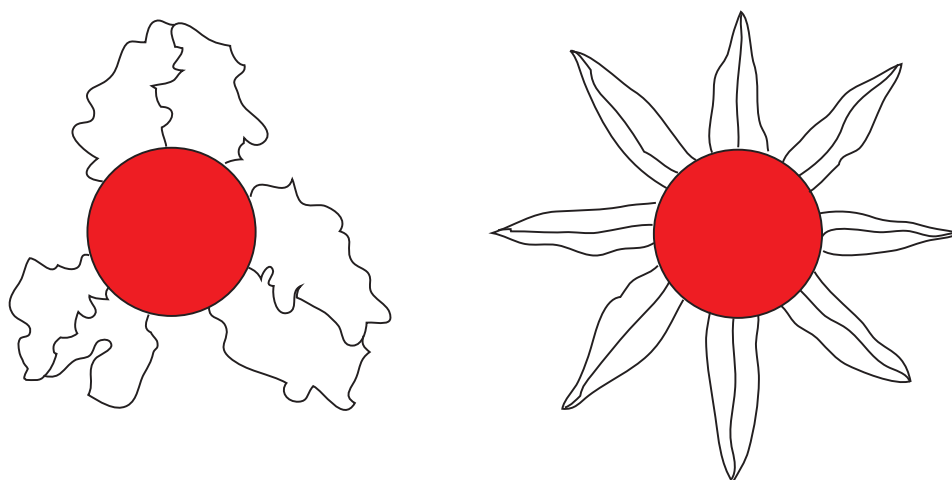


Figure 5.37: A very simplified sketch of two micelles formed by flexible (left) and stiff TSPs (right), respectively. The blue area resembles the micelle core while the black lines resemble the anchored, inner A blocks.

This difference in the fundamental micelle size is particularly interesting with respect to the higher ability of micelles of rigid TSPs to associate to supermicelles. Despite the fact that the mere arm density in the corona is much higher for a micelle of rigid TSPs, it is still more capable of heavy foldings and flexings in the corona that are required for inter-micellar associations.

There is also a notable increase in the fundamental micelle size for the same system when increasing the concentration. This change is not linear. For all our investigations, the fundamental micelle size g_0 is quite stable above the critical micelle concentration ϕ_{cmc} up to concentrations of about $\phi \approx 0.4$. In the concentration regime $0.4 < \phi < 0.6$, a drastic increase of g_0 is found, which can lead to a doubling of g_0 for concentrations beyond $\phi = 0.6$. Figure 5.33 documents the change in g_0 for this concentration regime for a rigid $H(H_8T_2)_6$ system.

This concentration dependence of the fundamental micelle size is another effect of the propensity of TSPs to fold a micelle corona in order to expose the micelle core for associations. At higher concentration, the micelle solution becomes so dense that the formation of another micelle is hindered by a lack of free space. Additional molecules due to an increase in concentration seek association in order to minimize interaction energy and are thus absorbed by the micelles that are already present. Micelles of diblock surfactant chains are in general saturated at a concentration-independent, specific

characteristic micelle size and feature a strong steric shielding against further associations to the micelle core. In contrast, the concentration-dependent absorption of additional molecules in the case of micelles of telechelic stars is enabled by the flexibility of the anisotropic - i.e. anchored - corona inherent to the star architecture. For an illustration, see figure 5.38.

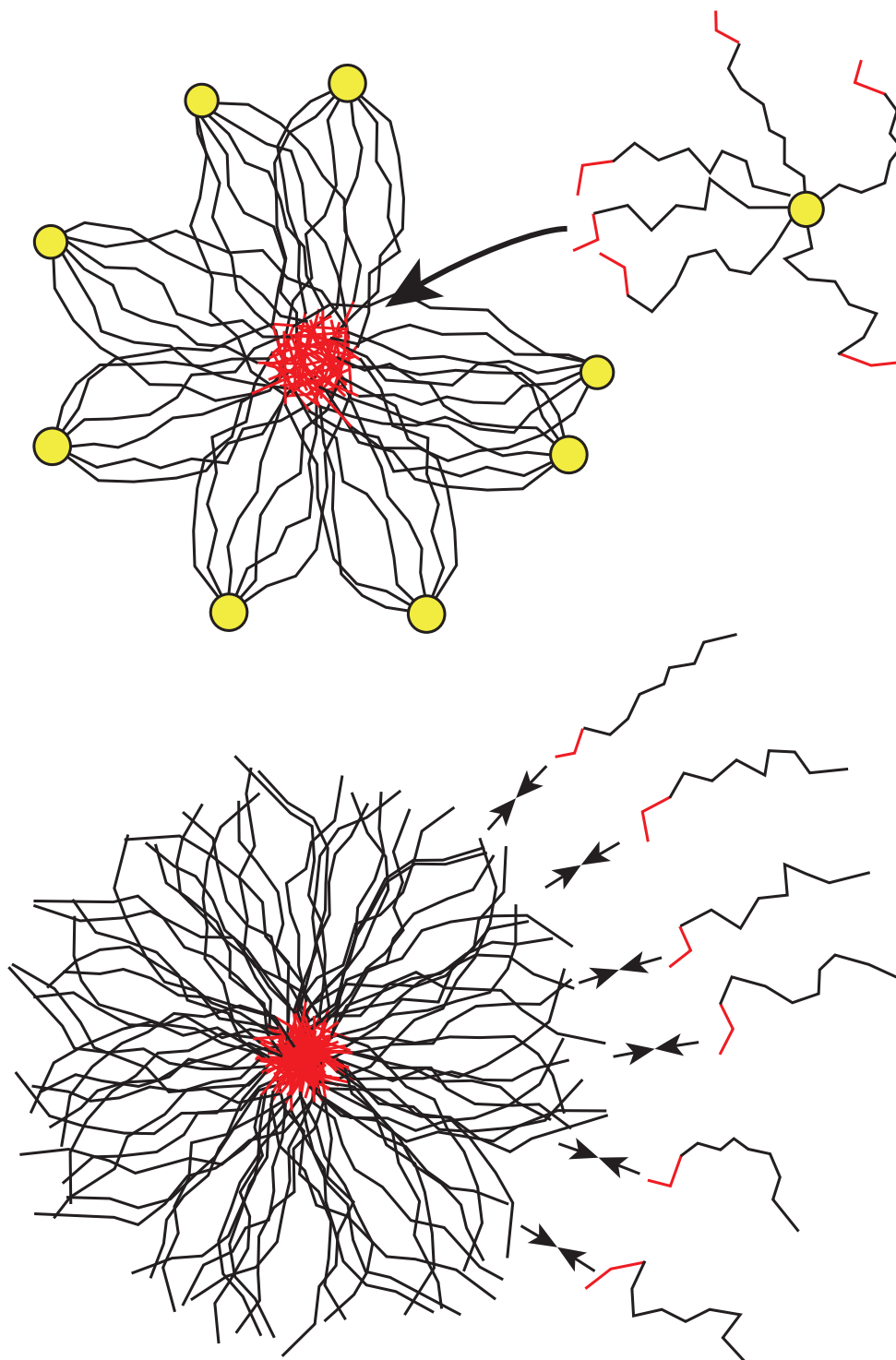


Figure 5.38: A sketch of a TSP micelle and a surfactant chain micelle, both in the interaction with respective nearby single molecules. The arrows visualize the effective attraction and repulsion, respectively.

One can also observe a decreasing micelle size with increased temperature. Comparing e.g. figures 3.5 (red curve) and 5.32 (a), which show histograms of a $H(H_8T_2)_6$ system at about the same concentration $\phi \approx 0.37$, but at different temperatures $T^* = 2.4$ and $T^* = 3.0$, we find a drastic decrease in the micelle size from $g_0 \approx 45$ at $T^* = 2.4$ down to $g_0 \approx 30$ for $T^* = 3.0$.

Comparing figures 5.13 (b) and 5.14, for the same (rigid) system $H(H_6T_4)_3$, we find that the increase in concentration is balanced out by an increase in temperature and the micelle size remains stable, i.e. $g_0(T^* = 5.6, \phi = 0.335) \approx g_0(T^* = 5.8, \phi = 0.370) \approx g_0(T^* = 6.0, \phi = 0.399) \approx 100$, while a combined higher concentration and lower temperature in figure 5.13 (a) results in a much higher micelle size of $g_0(T^* = 5.4, \phi = 0.463) \approx 150$.

A higher temperature flattens the effects of internal energy such as rigidity on Boltzmann statistics, driving a system into even energetically unfavorable configurations (such as bent arms opposed to the rigidity energy penalty) in order to gain entropy. This further points out the contrary roles of temperature and rigidity with respect to the effect on phase behavior. Even very rigid molecules become flexible when temperature is sufficiently high while the employment of rigidity increases the temperature demand for a system to reach a certain level of fluctuations, like we have seen for the critical temperature of rigid TSPs in chapter 4.

5.7 Summary table

	$\alpha = 0$		$\alpha = 10$	
	high T^*	low T^*	high T^*	low T^*
$H(H_6T_4)_3$	spherical micelles, supermicelles up to few harmonics; percolation into amorphous, system spanning aggregate	necklace-fashioned worms; percolation into system-spanning, multiply cross-linked worm network	stabilization of super micelle formation, even size distribution	worm length increases with decreasing temperature; worms order nematically; percolation into fractal aggregate of still discernible micelles and supermicelles
$H(H_6T_4)_6$	no micelles at low ϕ ; percolation into system spanning, bicontinuous network; at high ϕ micelles form within the soft confinement of network voids	formation of chemically tightly connected micellar network; increasing ϕ leads to super micellar aggregation, heavily hindered by chemical connections	necklace super micelle formation due to reduced entropic penalty when folding aside micellar corona	promoted formation of long worms
$H(H_8T_2)_3$	micelles melt, continuous formation of fractal network via small, non-micellar cluster associations	micelles, supermicelles up to very few harmonics; no percolation transition	necklace-like super micelle formation up to fifth harmonic; histogram is smeared out at high ϕ due to lack of space for further micelles, thus forcing single star associations	promoted formation of long worms; no percolation, no formation of cross-links; at high ϕ a dense, entangled worm solution is formed
$H(H_8T_2)_6$	above the melting point of micelles: percolation transition into fractal network of small, non-micellar cluster	very high cmc at $\phi_{cmc} \approx 0.3$, supermicelles only up to third harmonic, no percolation	stabilization of necklace-like supermicelles, up to 7th and 8th harmonic at high ϕ	promoted formation of worms; worms arrange in hexagonal ordering in appropriate box size; in other box sizes, micelles arrange on cubic lattice and associate with increasing ϕ

5.8 Summary and conclusions

Extending the investigations on macrophase separating systems performed in chapter 4, the microphase separating scenarios give a yet deeper insight to the aggregation behavior of telechelic star polymers and the links between their behavior in infinite dilution and in concentrated systems. A broad picture can be drawn from which one can comprehend the aggregation behavior with respect to an interplay of system temperature, interaction energies, rigidity and entropy both on a microscopic, i.e. the steric repulsion effects of the inner A blocks, and on a mesoscopic scale, i.e. formation, distribution, orientation and ordering of aggregates such as micelles.

While in infinite dilution, a single telechelic star polymer tries to bring its arms' terminal B blocks into association and thus collapses into configurations with one or more association sites, a consistent behavior is observed in concentrated systems. For a concentrated system of TSPs under given thermodynamic conditions, let p be the number of association sites that a single TSP out of the system would form in infinite dilution. Stars that would form a single association site (i.e. a "watermelon" configuration, $p = 1$), when put into concentrated solution under the same thermodynamic conditions, are very likely to assemble into micellar aggregates. This does not only cover spherical micelles, but also supermicelles that arise from inter-association of several spherical micelles, see e.g. $H(H_8T_2)_3$ (section 5.4). One dimensional aggregates, so called "worm-like micelles" are formed this way in a fashion that resembles a pearl-necklace assembly, see e.g. $H(H_6T_4)_3$ (section 5.2). The formation of these worm-like micelles highly profits from low temperature, see e.g. $H(H_6T_4)_3$ (section 5.2), and/or a high arm stiffness, see e.g. $H(H_6T_4)_3$ (section 5.2.2, figures 5.13 and 5.14), $H(H_8T_2)_6$ (section 5.5.2), since both reduce the impact of intra-molecular entropic effects on a single star's conformation in favor of microphase aggregation. If entropy on a single star level is sacrificed and inter-micellar aggregation into necklace structures is performed, the resulting worm-like supermicelles can bend and entangle, re-manifesting the sacrificed intra-molecular entropy on a supra-molecular level, see e.g. $H(H_8T_2)_3$ (section 5.4.2, figure 5.31), $H(H_6T_4)_6$ (section 5.3.2, figure 5.24).

At high concentrations, the worms can form cross-links and eventually aggregate into a system-spanning and highly cross-linked, percolating network, see e.g. $H(H_6T_4)_3$ (section 5.2, figure 5.11). Although we have also found nematic ordering of worm-like micelles, see $H(H_6T_4)_3$ (section 5.2.2, figure 5.15), for some systems, one dimensional percolation based on the nematic ordering is probably a finite simulation box size effect and is rather unlikely to happen in the thermodynamic limit, see $H(H_8T_2)_3$ (section 5.4.2). However, we have also found systems in which worm-like micelles arrange hexagonally into a columnar liquid crystal that is stable over a certain temperature range, see $H(H_8T_2)_6$ (section 5.5.2).

In all our investigations, while certainly other aggregation structures are plausible, the way of "watermelon" ($p = 1$) TSPs to micellize was always from spherical micelles to necklace-fashioned formation of one dimensional, worm-like supermicelles. Still, the stability of all micellar aggregates depends strongly on the behavior of the TSPs in infinite dilution. Either by a high functionality f and/or by high temperature, intramolecular entropic effects of steric repulsion at the inner A blocks can drive a single star to form more than one association site $p > 1$, in which case the attractive sites distribute around the star's center to form a patchy colloid. In concentration, such stars are unlikely to form stable micelles that are completely shielded by a solvophilic corona of TSP A blocks. Such a micelle needs additional stabilizing effects like a steric environmental confinement employed by e.g. a surrounding gel phase, see e.g. $H(H_6T_4)_6$ (section 5.3.1, figure 5.17).

The most prominent behavior of TSPs with $p > 1$ in concentration is to follow the same behavior as

in infinite dilution and give in to intra-molecular entropic effects of steric repulsion at their A blocks, forming multiple association sites. Aggregation of these molecules in concentration leads to associations that are not completely shielded by a solvophilic corona, but are connected via chemical bridges formed by the stars' center blocks. These aggregates may have no characteristic size and constitute a living network, reflected in a flat cluster size distribution, see e.g. $H(H_6T_4)_6$ (section 3.3.2, figure 3.6), $H(H_6T_4)_{10}$ (section 3.4, figure 3.11). We have also observed network formation based on micellar aggregates with a characteristic size, see $H(H_6T_4)_6$ (section 5.3.1, figures 5.19 and 5.22), in which case the "micelle core" is comprised by only one patch of a number of TSPs, while they orient their remaining patches away from the micelle core, effectively forming a highly "patchy micelle" that acts as a building block for resulting networks. Increasing such a system's temperature beyond the melting temperature of these micelles leads to the living network-formation of non-micellar clusters outlined above, see e.g. $H(H_8T_2)_6$ (section 5.3.1).

In both living network and micelle network scenario, we observe a continuous formation of linked structures, rather than a certain gelation transition, starting at quite low concentration. Regarding the role of TSPs as soft, deformable, patchy colloids outlined in the introduction in section 1.2, this behavior remarkably corresponds to microgel formation in solutions of hard patchy colloids [14, 15]. For high concentrations, however, the additional flexibility and deformability of TSPs, compared to hard patchy colloids, allows for the bending of the star molecules in order to merge most association sites to further minimize interaction energy. This eventually leads to the formation of system-spanning, amorphous, bi-continuous aggregates, constituting a very dense fluid, see e.g. $H(H_6T_4)_6$ (section 3.3.2, figure 3.6), $H(H_6T_4)_{10}$ (section 3.4, figures 3.11 and 3.10), $H(H_8T_2)_3$ (section 5.4, figure 5.28).

There have been some experimental studies on telechelic star polymers, their aggregation behavior and rheology in recent years. In 1996, *Pitsikalis et al.* [146] prepared three-arm telechelic polybutadiene stars via anionic polymerization and studied their association behavior in dilute solution by dynamic light scattering. Performing X-ray scattering and dynamic rheological measurements, *Vlassopoulos et al.* found these three-arm molecules to collapse to watermelon configurations [51] or few-star soft spherical aggregates [20]. The latter can have a few free arms, rendering them able to inter-connect and form transient networks, which were studied in their linear viscoelastic response.

As yet there have been no studies on micelle nucleation of TSPs. Indeed, the propensity to aggregate into worm-like micelles via a necklace-fashion outlined in this work, is a novel discovery.

However, as of 1990, there have been quite some studies of telechelic (*THT*) triblock copolymers, their effects on oil-in-water microemulsions and pre-assembled micelles and the formation and viscoelasticity of transient networks formed by the telechelic polymer chains interconnecting microemulsion droplets [147, 148]. *Meier et al.* [149] demonstrated in 1996 that water-soluble, hydrophobically end-functionalized polymer chains can be used to interconnect vesicles or living cells to create hydrogel networks. *Bagger-Jørgensen et al.* (1997) [150] as well as *Appell et al.* (1998) [151] have investigated the effects of hydrophobically end-capped poly(ethylene oxide) ("PEO") on globular micelles in a ternary mixture of water, decane and ethylene glycol dodecyl ether surfactants. Both studies found competing effects of micelle attraction and repulsion, the first due to bridging by the telechelic chains when their hydrophobic ends connect to two different micelles, the latter due to a steric decoration of micelles when both ends of a telechelic chain connect to the same micelle and the hydrophilic inner block forms a loop at the micelle corona.

In 2007, *Ramos et al.* [152] performed similar investigations on the addition of telechelic PEO to a

surfactant system of worm-like micelles, for which they found the same competition of a short ranged steric repulsion due to loop decoration and an inter-micellar attraction due to linking telechelic chains. Nakaya–Yaegashi *et al.* [153] extended these studies in 2008 by investigations on the linear viscoelasticity of these bridged worm-like micelles. They found two elastic moduli: a slow mode that relates to a transient network of entangled but sterically repulsive worm-like micelles and a fast mode that relates to a transient network of telechelic chains linking the worm-like micelles.

We argue that telechelic star polymers, as investigated in this work, unite features of both diblock surfactant chains and telechelic triblock chains. The ability to collapse into watermelon conformations allows TSPs to fully associate with a micellar aggregate and further decorate it with a solvophilic shell, adding to the short-range steric repulsive interactions. By tuning the system's temperature or the molecules' rigidity (by e.g. changing the solvent salinity in case of an ionic realization of rigidity), the intra-molecular repulsive interactions of the stars' A blocks can be used to "open" the watermelon conformations and enable the TSPs to act as telechelic linkers between micelles, similar to triblock copolymer chains.

On top of being a first extensive study on the microphase behavior of telechelic star polymers, the novelty of this work is added by the fact that a solution of TSPs is a *monodisperse* system that features both micellization effects of surfactant molecules and attractive effects of telechelic linkers. From a rheological point of view, our results are also promising that solutions of TSPs with tunable rigidity could potentially bear similar viscoelastic properties as mixtures of spherical and/or worm-like micelles with telechelic linkers like e.g. those investigated by Nakaya–Yaegashi *et al.* [153].

Chapter 6

Conclusions and Outlook

In this work, we have performed a first extensive study on the phase behavior of end-functionalized diblock copolymer stars, also labelled *telechelic star polymers*. For both macro- and micro-phase separating scenarios, our investigations have achieved novel findings that allow us to draw a conclusive picture from which the peculiar features of solutions of telechelic star polymers can be comprehended: In infinite dilution, single telechelic star polymers have been found to either remain in an open configuration, a "star burst", or to collapse into conformations where the terminal blocks form p association sites, making the molecule an effective patchy colloid with patchiness p . In the case $p = 1$, all of the star's arms collapse onto a single association site opposite to the star's anchoring point, making the molecule an effective surfactant colloid, labelled as "watermelon" conformation.

The patchiness p is dependent on the ratio between hydrophobic attraction of the terminal blocks and steric repulsion of the hydrophilic inner blocks, crowding at the anchoring point. This ratio is dependent - within the conception of our work - on the system temperature T^* , the star's functionality f , the relative size ratio of the polymer blocks r and the stiffness of the polymer arms α . Higher temperature screens out attraction potentials in Boltzmann statistics and thus promotes repulsion, favoring higher p . A higher functionality leads to a denser crowding around the anchoring point, also promoting repulsion, favoring higher p . A higher relative terminal block size r increases attractive forces, favoring lower p . Finally, a higher arm stiffness reduces steric repulsion between the inner blocks due to intra-molecular entropy, leading to lower p .

These dependencies hold for concentrated systems, and the patchy behavior in infinite dilution plays an important role in understanding the thermodynamic effects that determine the phase behavior of solutions of telechelic star polymers. For a relative terminal block size of $r \geq 50\%$, we observe macrophase separation with a well defined critical point for all investigated functionalities, i.e. $f = 3, 6, 10$, and no arm stiffness, i.e. $\alpha = 0$. In order to achieve critical fluctuations, interactions must be screened out to a certain degree by thermal energy. Thus, the critical temperature scales with both functionality f and relative terminal block size r , see figure 3.1. The introduction of arm rigidity imposes another internal energy to the system that needs to be compensated by thermal energy in order to achieve critical fluctuations. Increasing the rigidity parameter α thus raises the critical temperature. It also decreases the critical density due to the fact that stiffer arms lead to a larger effective size of the stars, see section 4.3.

For very high values of the rigidity parameter α , we observe the occurrence of liquid-crystalline ordered phases next to a liquid-gas phase separation. In the exemplary system $H(H_5T_5)_3$, starting from the liquid phase above the critical concentration and further increasing the concentration, the system

rearranges as a simple cubic, then a columnar, then a lamellar phase, before it remelts again into a dense fluid for very high concentrations, see figures 4.8 and 4.9. This hierarchy of liquid crystals, we argue, is due to a subtle interplay of interaction energy minimization, translational entropy, i.e. degrees of freedom for molecule movement, and a combinatorial entropy that is found in the ability of telechelic stars to flip their arms between association sites in the crystal lattice, maintaining the liquid crystalline ordering.

For relative terminal block sizes $r < 50\%$, solutions of TSPs are subject to microphase separation, in which the role of the behavior of single molecules becomes particularly important. TSPs that collapse into a watermelon conformation in infinite dilution, i.e. $p = 1$, are predestined to form micelles as in this conformation, they can effectively be treated as surfactant colloids. Rigidity has been found to promote micelle nucleation due to a decrease in intramolecular steric effects and a consequent narrowing of the watermelon conformation, see figures 5.1 and 5.2.

Since the corona of a micelle of TSPs is formed by the hydrophilic inner blocks, the anchoring that comes with the star architecture leads to an anisotropy of the sterically repulsive shielding of the micelle. Molecule arms are not as free as the hydrophilic corona of a micelle of diblock surfactant chains, and arms belonging to the same star behave collectively when steric interactions between multiple micelles are considered. Micelles of TSPs show a strong propensity to form inter-micellar associations which we relate to the increased ability to fold aside parts of the micelle corona to expose the micelle core for aggregation. This folding and thus, the very ability for inter-micellar aggregation, is promoted by the collective corona behavior inherent to the star architecture, which, in turn, is particularly strong for rigid molecule arms.

Spherical micelles associate into supermicelles this way, which we found to prefer a one-dimensional growth in a necklace fashion, leading to large, worm-like supermicelles, see section 5.2. Since the corona of these worm-like micelles is inherited from the spherical micelles, it is similarly flexible due to the chain anchoring, enabling the worms to bend, entangle and even form cross-links, see section 5.4. The system gains a large variety of probable configurations this way, adding a large contribution to entropy, which was sacrificed by a large amount due to intra-molecular stretching and intra-micellar folding, both involved in the formation of the worm-like micelles in the first place.

For TSPs of $p > 1$, i.e. that would form more than one terminal bead association site in infinite dilution, sterically shielded, independent spherical micelles are no possible aggregation scenario since that requires Janus-like surfactant molecules. We argue, nevertheless, that micelles can be formed by such TSPs of, for instance, $p = 2$ in a fashion that is illustrated in figure 5.21. Such micelles are tightly connected via *anchoring point bridges* to a micellar network that can percolate to a macrogel phase, see section 5.3.1. Although stable, non-connected spherical micelles are also found coexisting in the voids that are left by such a macrogel phase, we argue that their stability is only enabled by the lack of nearby association sites and the steric confinement of the surrounding bulk, see sections 3.3.2 and 5.3.1.

An increase in temperature promotes intra-molecular steric effects and for high enough temperature, a molecule will increase its patchiness up to an entirely uncollapsed "burst" state. For concentrated systems, this means that micellar aggregates melt and single molecules with multiple patches coexist, forming transient networks. Increasing the concentration in such a system results in a continuous formation of amorphous structures and a percolation transition to a bicontinuous fluid, similar to the behavior of a macrophase separating system at a supercritical path.

We have shown that the phase behavior of a polymeric particle is raised by a large variety when going from a mere surfactant chain to the star architecture. Our findings on macrophase separating systems give an insight to the complex interplay of thermodynamic effects that determine critical effects and can also drive the system into hierarchies of liquid crystals, for which we have stressed the crucial role of different manifestations of entropy. For the microphase separating systems, our novel findings on the necklace-like formation of worm-like supermicelles and the formation of tightly connected micellar networks are promising especially from an experimental point of view. Investigations on both worm-like micelles and telechelic linkers have been performed in the past. However, our work has shown that telechelic star polymers combine micellization abilities of surfactant molecules and network building abilities of telechelic linkers in a monodisperse solution. Next to their promising role as building blocks for soft materials that has been stressed before [54], they are also promising to yield rich and interesting rheological properties. Especially the realization of a controllable arm rigidity by e.g. periodic ionization of the polymer arms and a tuning of the solvent salinity could bear TSP molecules, whose patchiness (in infinite dilution) can be controlled by both temperature and salinity. This can then be used to induce the various aggregations that we outlined in chapter 5.

The dynamic behavior under shear and flow of all systems investigated in this work will be subject of theoretical and simulational studies in the future.

Chapter 7

Appendix

We give here a short outline on the morphometrical analysis that we use in chapters 3 and 4 to describe the morphology of clusters formed by the terminal beads of telechelic star polymers.

7.1 Minkowski functionals

The analyses is based on the calculation of a set of *Minkowski functionals*. In functional analysis, *Minkowski functionals* are a generalization of a *norm*, and are thus a tool to describe distances in mathematical space. They can be used to describe the general morphology of a point set $X = \{x_i; i = 1, \dots, N\}$ in Euclidean space $\mathbb{E}$, by extending it to a voluminous set. Considering spherical balls $B_r(x_i) = \{x \in \mathbb{E}^3; \|x - x_i\| \leq r\}$ with radius r around the points x_i , the union $\mathcal{B}(r) = \bigcup_{i=1}^N B_r(x_i)$ of balls around all points from set X will be a set consisting of overlapping ("clustering") and non-overlapping balls, which can be analyzed by means of integration. The general idea is that a set of $d+1$ numbers can be uniquely associated to a certain morphology in d -dimensional space. For a more detailed elaboration, see [154, 155].

Consider a closed and convex subset K in Euclidean space $\mathbb{E}$ with a regular boundary $\partial K \in \mathcal{C}^2$ (a "closed body") and let R_1 and R_2 be the principal radii of curvature. This body has a volume V and a surface area

$$F = \int_{S^2} R_1 R_2 d\sigma \quad (7.1)$$

Say we vary both radii by a small number ϵ and thus create another convex body K_ϵ that consists of all points within a distance ϵ from K , and call it a *parallel body* of K . The volume of K_ϵ can be calculated as

$$V_\epsilon = V + \int_0^\epsilon F_{\epsilon'} d\epsilon' \quad (7.2)$$

where F_ϵ is the surface area of K_ϵ , given as

$$F_\epsilon = \int_{S^2} (R_1 + \epsilon)(R_2 + \epsilon) d\sigma \quad (7.3)$$

With the integral mean curvature H of K

$$H = \frac{1}{2} \int_{\partial K} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) df \quad (7.4)$$

the integral Gaussian curvature G of K

$$G = \int_{\partial K} \left(\frac{1}{R_1 R_2} \right) df \quad (7.5)$$

and the surface area F of K given by equation 7.1, the surface area F_ϵ and volume V_ϵ of K_ϵ can be written as an expansion with respect to ϵ as

$$\begin{aligned} F_\epsilon &= \int_{S^2} (R_1 + \epsilon)(R_2 + \epsilon) d\sigma \\ &= F + 2 \cdot H \cdot \epsilon + G \cdot \epsilon^2 \end{aligned} \quad (7.6)$$

$$\begin{aligned} V_\epsilon &= V + \int_0^\epsilon F_{\epsilon'} \\ &= V + F \cdot \epsilon + H \cdot \epsilon^2 + \frac{G}{3} \cdot \epsilon^3 \end{aligned} \quad (7.7)$$

The theorem of Gauss-Bonnet (see e.g. [156]) relates the integral Gaussian curvature G to the *Euler characteristic* χ of a (closed) Riemannian manifold, given by the compact body K , as

$$G(K) = 4\pi\chi(K) \quad (7.8)$$

where $\chi = 1$ for a convex body.

We define from the coefficients of the expansion 7.7 the four Minkowski functionals in $d = 3$ Euclidean space as

$$\mathcal{W}_0 = V \quad (7.9)$$

$$3\mathcal{W}_1 = F \quad (7.10)$$

$$3\mathcal{W}_2 = H \quad (7.11)$$

$$\mathcal{W}_3 = \frac{G}{3} = \frac{4\pi}{3}\chi \quad (7.12)$$

To comprehend the factors of three in this definition, consider as a simple example a ball in $d = 3$ dimensional Euclidean space with radius R . A change of the radius by a number ϵ will affect the ball volume by

$$V_\epsilon = \frac{4\pi}{3}(R + \epsilon)^3 \quad (7.13)$$

An expansion with respect to ϵ leads to

$$\frac{4\pi}{3}(R + \epsilon)^3 \quad (7.14)$$

$$= \frac{4\pi}{3}(R^3 + 3R^2\epsilon + 3R\epsilon^2 + \epsilon^3) \quad (7.15)$$

$$= \underbrace{\frac{4\pi}{3}R^3}_{\mathcal{W}_0} + 3 \cdot \underbrace{\frac{4\pi}{3}R^2}_{\mathcal{W}_1} \cdot \epsilon + 3 \cdot \underbrace{\frac{4\pi}{3}R}_{\mathcal{W}_2} \cdot \epsilon^2 + 3 \cdot \underbrace{\frac{4\pi}{3}}_{=\frac{4\pi}{3}\chi=\mathcal{W}_3} \cdot \epsilon^3 \quad (7.16)$$

$$= \underbrace{\frac{4\pi}{3}R^3}_V + \underbrace{4\pi R^2}_F \cdot \epsilon + \underbrace{4\pi R}_H \cdot \epsilon^2 + \frac{4\pi}{3}\chi \cdot \epsilon^3 \quad (7.17)$$

So we can write this in a more general form as

$$V_\epsilon(K) = \sum_{\alpha=0}^{d-3} \binom{d}{\alpha} W_\alpha(K) \cdot \epsilon^\alpha \quad (7.18)$$

Equation 7.18 is known as *Steiner's formula* and is the general definition of the Minkowski functionals of convex bodies in d -dimensional space.

The generalization to non-convex bodies such as the "ball clusters" described in the beginning of this section can be found in a work of *Hadwiger* [157]. While Minkowski functionals feature some important algebraical properties such as *additivity*, *continuity* and *motion invariance*, *Hadwiger* also shows in [157] that any additive, continuous and motion invariant functional on a subset of d -dimensional Euclidean space $\mathbb{E}^d$ can be written as a linear combination of the $d + 1$ Minkowski functionals on $\mathbb{E}^d$, making them a powerful mathematical tool in geometrical description.

7.2 Euler characteristic

The Euler characteristic χ is a topological invariant to describe topological spaces' shape and structure. It is based on the historical finding of *Leonard Euler* that any convex polyhedron obeys the rule

$$\chi = V - E + F = 2 \quad (7.19)$$

where V is the number of vertices (corners), E the number of edges and F the number of faces of the subject polyhedron. While at first, it was only used for geometrical investigations on polyhedra, it is possible to compute the Euler characteristic for general surfaces, for which they need to be described as CW-complexes, i.e. one must find a polygonization of the surface. For compact sets, it satisfies an additivity known as the inclusion-exclusion principle:

$$\chi(K_1 \cup K_2) = \chi(K_1) + \chi(K_2) - \chi(K_1 \cap K_2) \quad (7.20)$$

which can be illustrated with Venn diagrams as shown in figure 7.1.

$$\chi(\text{yellow circle} \cup \text{blue circle}) = \chi(\text{yellow circle}) + \chi(\text{blue circle}) - \chi(\text{intersection})$$

Figure 7.1: A Venn diagram showing the additivity principle of the Euler characteristic χ .

From that, one can derive the general relation for compact sets

$$\chi = I + C - T \quad (7.21)$$

where I denotes the number of disconnected compounds, C the number of enclosed cavities in the compounds and T the number of tunnels, i.e. perforations in the compounds. For a detailed elaboration, see [158].

A few examples:

1. The Euler characteristic of two disjoint spheres is 2, since we have two compounds $I = 2$, no cavities $C = 0$ and no tunnels $T = 0$.
2. The Euler characteristic of a torus is 0, since we have only one compound $I = 1$, no enclosed cavities $C = 0$, but a full perforation of the compound $T = 1$, giving $\chi = 1 + 0 - 1 = 0$.
3. The Euler characteristic of a lantern is $\chi = 1$, since there is only one compound $I = 1$, a cavity to hold the candle $C = 1$ and a perforation between the vessel and the handle $T = 1$, giving $\chi = 1 + 1 - 1 = 1$.
4. The Euler characteristic of a block of swiss cheese can be positive or negative. We definitely have only one compound $I = 1$, and while the number of entirely enclosed cavities ("cheese holes") add to χ , the number of full perforations, i.e. joint cheese holes that stretch through the whole block in one dimension, will be subtracted from χ .
5. The Euler characteristic of a fishing net will be negative by a large number $\chi \ll 0$, since there is only one compound $I = 1$, no cavity $C = 0$, but a whole lot of perforations $T \gg 1$.

7.3 Implementation on a 3D cubic lattice

A lattice model, while bringing the advantage of high computing performance, also poses some serious physical issues that need special consideration. The Hamiltonian, in general, depends on the underlying lattice, and needs to be calculated with respect to any lattice site and its neighbors (withing interaction range), see e.g. the Ising model.

Within the terms of the model used in this work, the Wigner-Seitz cell of any lattice site contains one of three possible species, and interactions with the $Z = 26$ surrounding Wigner-Seitz cells are taken into account for the model Hamiltonian in terms of interactions. A cluster of a certain species is represented by a set of Wigner-Seitz cells, of which any one is in contact with at least one other. This contact can be either a shared cell *face*, a cell *edge* or a cell *corner*. Thus, in order to describe the morphology of a cluster, the calculation of the Minkowski functionals, which were defined for *regular* subsets in $\mathbb{E}^d$, needs to be formulated for sub-dimensional embeddings in $\mathbb{E}^3$.

Following the heuristic approach we outlined for a spherical ball in equations 7.13 ff., we can calculate the Mikowski functionals of a closed body K by expanding the volume V_ϵ of its parallel body, i.e. the set of all points within a distance $\leq \epsilon$ from K . For a closed cube C with edge length a , we get

$$V_\epsilon(C) = \underbrace{a^3}_{\mathcal{W}_0(C)} + \underbrace{6a^2}_{3\mathcal{W}_1(C)} \cdot \epsilon + 3 \underbrace{\pi a}_{\mathcal{W}_2(C)} \cdot \epsilon^2 + \underbrace{\frac{4\pi}{3}}_{\mathcal{W}_3(C)} \cdot \epsilon^3 \quad (7.22)$$

Equivalently for a two-dimensional square Q with edge length a we get

$$V_\epsilon(Q) = \underbrace{0}_{\mathcal{W}_0(Q)} + \underbrace{2a^2}_{3\mathcal{W}_1(Q)} \cdot \epsilon + \underbrace{2\pi a}_{3\mathcal{W}_2(Q)} \cdot \epsilon^2 + \underbrace{\frac{4\pi}{3}}_{\mathcal{W}_3(Q)} \cdot \epsilon^3 \quad (7.23)$$

and eventually for the volume of the parallel body of a $d = 1$ embedding P

$$V_\epsilon(P) = \underbrace{0}_{\mathcal{W}_0(P)} + \underbrace{0}_{\mathcal{W}_1(P)} \cdot \epsilon + \underbrace{\pi a}_{3\mathcal{W}_2(P)} \cdot \epsilon^2 + \underbrace{\frac{4\pi}{3}}_{\mathcal{W}_3(P)} \cdot \epsilon^3 \quad (7.24)$$

In [105], *Likos et al.* demonstrate a partition of a cluster on a simple cubic lattice into closed polyhedra, which, in turn, are considered as a union of the disjoint collection of their vertices, open edges, faces and interior. By making use of the additivity, continuity and motion invariance, the Minkowski functionals of lattice morphologies can be calculated on the basis of this partition.

Bibliography

- [1] P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press (1953).
- [2] H. Kuhn, H. D. Försterling and D. H. Waldeck, *Principles of Physical Chemistry*, Wiley, Hoboken (2009).
- [3] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford Univ. Press (2003).
- [4] P. N. Pusey and W. van Megen, *Nature* **320**, 340 (1986).
- [5] E. Bianchi, R. Blaak and C. N. Likos, *Phys. Chem. Chem. Phys.* **13**, 6397 (2011).
- [6] M. Maldovan and E. Thomas, *Nat. Mater.* **3**, 593 (2004).
- [7] G. Doppelbauer, E. Bianchi and G. Kahl, *J. Phys.: Condens. Matter* **22**, 104105 (2010).
- [8] G. Doppelbauer, E. G. Noya, E. Bianchi and G. Kahl, *Soft Matter* **8**, 7768 (2012).
- [9] K.-H. Roh, D. C. Martin and J. Lahann, *Nat. Mater.* **4**, 759 (2005).
- [10] A. Walther and A. H. E. Müller, *Chem. Rev.* **113**, 5194 (2013).
- [11] L. Di Michele and E. Eiser, *Phys. Chem. Chem. Phys.* **15**, 3115 (2013).
- [12] S. Corezzi, C. De Michele, E. Zaccarelli, D. Fioretto and F. Sciortino *Soft Matter* **4**, 1173 (2008).
- [13] E. Zaccarelli, *J. Phys.: Condens. Matter* **19** 323101 (2007).
- [14] J. Colombo, A. Widmer-Cooper and E. Del Gado, *PRL* **110**, 198301 (2013).
- [15] E. Del Gado and W. Kob, *Phys. Rev. Lett.* **98**, 028303 (2007).
- [16] A. Fierro, E. Del Gado, A. de Candia and A. Coniglio, *J. Stat. Mech.* L04002 (2008).
- [17] C. De Michele, E. Del Gado and D. Leporini, *Soft Matter* **7**, 4025 (2011).
- [18] T. Uneyama, S. Suzuki and H. Watanabe, *Phys. Rev. E* **86**, 031802 (2012).
- [19] M. J. Glassmann, J. Chan and B. D. Olsen, *Adv. Func. Mat.* **23**, 1182 (2013).
- [20] D. Vlassopoulos, M. Pitsikalis and N. Hadjichristidis, *Macromolecules* **33**, 9740 (2000).
- [21] M. A. Floriano, E. Caponetti and A. Z. Panagiotopoulos, *Langmuir* **15**, 3143 (1999).
- [22] M. Cates and S. J. Candau, *J. Phys.: Condens. Matter* **2**, 6869 (1990).
- [23] Y. L. Lin, H. Y. Chang, Y. J. Sheng and H. K. Tsao, *Soft Matter* **9**, 4802 (2013).

- [24] A. Z. Panagiotopoulos, M. A. Floriano and S. K. Kumar, *Langmuir* **18**, 2940 (2002).
- [25] C. Krumm, C. P. Fik, M. Meuris, G. J. Dropalla and J. C. Tiller, *Macromol. Rapid Commun.* **33**, 1677 (2012).
- [26] G. T. Gotzamanis, C. Tsitsilianis, S. C. Hadjiyannakou, C. S. Patrickios, R. Lupitskyy and S. Minko, *Macromolecules* **39**, 678 (2006).
- [27] T. A. Witten, *J Phys (Paris)* **49**, 1055 (1988).
- [28] S. T. Milner and T. A. Witten, *Macromolecules* **25**, 5495 (1992).
- [29] C. N. Likos, *Physics Reports* **348**, 267 (2001).
- [30] M. Morton, T. E. Helminiak, S. D. Gadkary and F. Bueche, *J. Polym. Sci.* **57**, 471 (1962).
- [31] B. J. Bauer and L. J. Fetters, *Rubber Chem. Tech.* **51**, 406 (1978).
- [32] P. Dreyfuss, L. J. Fetters and D. R. Hansen, *Rubber Chem. Tech.* **53**, 728 (1980).
- [33] O. L. Marrs and L. O. Edmunds, *Adhesives Age* **14**, 15 (1971).
- [34] O. L. Marrs, F. E. Naylor and L. O. Edmunds, *J. Adhes.* **4**, 211 (1972).
- [35] R. J. Sutherland and R. B. Rhodes, *U.S. Pat.* **5**, 369, 564 (1994).
- [36] J. A. Simms, *Proceedings of International Conference on Organic Coating Science Technology, New Paltz, NY*, 423 (1992).
- [37] J. C. Chen, *European Pat.*, **EP 389791** (1990).
- [38] M. Uchama, *Japanese Pat.*, **9,919,196** (1994).
- [39] N. A. Peppas, T. Nagai and M. Miyajima, *Pharm. Tech. Jpn.* **10**, 611 (1994).
- [40] J. Roovers, L.-L. Zhou, P. M. Toporowski, M. van der Zwan, H. Iatrou and N. Hadjichristidis, *Macromolecules* **26**, 4324 (1993).
- [41] G. S. Grest, L. J. Fetters, J. S. Huang and D. Richter, *Adv. Chem. Phys.* **XCIV**, 67 (1996).
- [42] N. Hadjichristidis, A. Guyot and L. J. Fetters, *Macromolecules* **11**, 668 (1978).
- [43] J. Stellbrink, G. Rother, M. Laurati, R. Lund, L. Willner and D. Richter, *J. Phys.: Condens. Matter* **16**, 3821 (2004).
- [44] B. Lonetti, M. Camargo, J. Stellbrink, C. N. Likos, E. Zaccarelli, L. Willner, P. Lindner and D. Richter, *Phys. Rev. Lett.* **106**, 228301 (2011).
- [45] C. N. Likos, H. Löwen, M. Watzlawek, B. Abbas, O. Jucknischke, J. Allgaier and D. Richter, *Phys. Rev. Lett.* **80**, 4450 (1998).
- [46] J. Arens, *J. Bull. Chim. Soc. Fr.*, 3037 (1968).
- [47] F. Lo Verso and C. N. Likos, *Polymer* **49**, 1425 (2008).
- [48] C. A. Uraneck, H. L. Hsieh and O. G. Buck, *J. Polym. Sci.* **46**, 535 (1960).

- [49] M. Danko, J. Libiszowski, T. Biela, M. Wolszczak and A. Duda, *J. Polym. Sci. Part A Polym. Chem.* **19**, 4586 (2005).
- [50] C. L. Elkins, K. Viswanathan and T. E. Long, *Macromolecules* **39**, 3132 (2006).
- [51] D. Vlassopoulos, T. Pakula, G. Fytas, M. Pitsikalis and N. Hadjichristidis, *J. Chem. Phys.* **111**, 1760 (1999).
- [52] F. Lo Verso, C. N. Likos, C. Mayer and H. Löwen, *Phys. Rev. Lett.* **96**, 187802 (2006).
- [53] F. Lo Verso, C. N. Likos and H. Löwen, *J. Phys. Chem. C* **111**, 15803 (2007).
- [54] B. Capone, I. Coluzza, F. G. Lo Verso, C. N. Likos and R. Blaak, *Phys. Rev. Lett.* **109**, 238301 (2012).
- [55] F. Lo Verso, A. Z. Panagiotopoulos and C. N. Likos, *Phys. Rev. E Rapid Commun.* **79**, 010401 (2009).
- [56] F. Lo Verso, A. Z. Panagiotopoulos and C. N. Likos, *Faraday Discuss.* **144**, 143 (2010).
- [57] W. Humphrey, A. Dalke and K. Schulten, *J. Molec. Graphics* **14**, 33 (1996).
- [58] B. Capone, C. Pierleoni, J. P. Hansen, and V. Krakoviack, *J. Phys. Chem. B* **12**, 3629 (2009)
- [59] R. G. Larson, L. E. Scriven and H.T. Davis, *J. Chem. Phys.* **83**, 2411 (1985).
- [60] R. G. Larson, *J. Chem. Phys.* **89**, 1642 (1988).
- [61] R. G. Larson, *J. Chem. Phys.* **91**, 2479 (1989).
- [62] R. G. Larson, *J. Chem. Phys.* **96**, 7904 (1992).
- [63] G. E. Norman and V. S. Filinov, *High Temp. (USSR)* **7**, 216 (1969).
- [64] D. Frenkel, *Molecular Dynamics Simulations of Statistical Mechanics Systems*, Proceedings of the 97th Int. "Enrico Fermi" School of Physics (1986).
- [65] B. Smit, *Molec. Phys.* **85**, 153 (1995).
- [66] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *J. chem. Phys.* **21**, 1087 (1953).
- [67] M. N. Rosenbluth and A. W. Rosenbluth, *J. chem. Phys.* **23**, 356 (1955).
- [68] J. I. Siepmann, *Molec. Phys.* **90**, 1145 (1990).
- [69] N. B. Wilding, *Phys. Rev. E* **52**, 602 (1995).
- [70] N. B. Wilding, *Phys. Rev. E* **55**, 6624 (1997).
- [71] N. B. Wilding, F. Schmid and P. Nielaba, *Phys. Rev. E* **58**, 2201 (1998).
- [72] A. E. Ferdinand and M. E. Fisher, *Phys. Rev.* **185**, 832 (1969).
- [73] M. E. Fisher and M. N. Barber, *Phys. Rev. Lett.* **28**, 1516 (1978).

- [74] C. N. Likos, *Soft Matter* **2**, 478 (2006).
- [75] A. Jusufi and C. N. Likos, *Rev. Mod. Phys.* **81**, 1753 (2009).
- [76] B. M. Mladek, G. Kahl, and C. N. Likos, *Phys. Rev. Lett.* **100**, 028301 (2008).
- [77] D. Gottwald, C. N. Likos, G. Kahl, and H. Löwen, *J. Chem. Phys.* **122**, 074903 (2005).
- [78] T. Stirner and J. Sun, *Langmuir* **21**, 6636 (2005).
- [79] J. Fornleitner, F. Lo Verso, G. Kahl, and C. N. Likos, *Soft Matter* **4**, 480 (2008).
- [80] A. Chremos and C. N. Likos, *J. Phys. Chem. B* **113**, 12316 (2009).
- [81] E. Bianchi J. Largo, P. Tartaglia, E. Zaccarelli, and F. Sciortino, *Phys. Rev. Lett.* **97**, 168301 (2006).
- [82] A. B. Pawar and I. Kretzschmar, *Macromol. Rapid. Commun.* **31**, 150 (2010).
- [83] J. J. Molina, C. Pierleoni, B. Capone, J. P. Hansen, and I. S. S. de Oliveira, *Mol. Phys.* **107**, 535 (2009).
- [84] C. Pierleoni, C. I. Addison, J.-P. Hansen, and V. Krakoviack, *Phys. Rev. Lett.* **96**, 128302 (2006).
- [85] B. Capone, J. P. Hansen, and I. Coluzza, *Soft Matter* **6**, 6075 (2010).
- [86] B. Capone, I. Coluzza, and J. P. Hansen, *J. Phys.: Condens. Matter* **23**, 194102 (2011).
- [87] C. Gross and W. Paul, *Soft Matter* **6**, 3273 (2010).
- [88] F. Ganazzoli, Y. A. Kuznetsov, and E. G. Timoshenko, *Macromol. Theory Simul.* **10**, 325 (2001).
- [89] R. Connolly, E. G. Timoshenko, and Y. A. Kuznetsov, *J. Chem. Phys.* **119**, 8736 (2003).
- [90] R. Connolly, E. G. Timoshenko, and Y. A. Kuznetsov, *Macromolecules* **37**, 7381 (2004).
- [91] M. Pitsikalis and N. Hadjichristidis, *Macromolecules* **28**, 3904 (1995).
- [92] E. Eiser, J. Klein, T. A. Witten, and L. J. Fetters, *Phys. Rev. Lett.* **82**, 5076 (1999).
- [93] A. G. Zilman and S. A. Safran, *Eur. Phys. J. E* **4**, 467 (2001).
- [94] G. Floudas, S. Pispas, N. Hadjichristidis, and T. Pakula, *Macromol. Chem. Phys.* **202**, 1488 (2001).
- [95] A. Z. Panagiotopoulos, V. Wong, and M. A. Floriano, *Macromolecules* **31**, 912 (1998).
- [96] M. A. Floriano, V. Firetto, and A. Z. Panagiotopoulos, *Macromolecules* **38**, 2475 (2005).
- [97] D. Frenkel, G. C. A. M. Mooji, and B. Smit, *J. Phys.: Condens. Matter* **4**, 3053 (1992).
- [98] J. J. de Pablo, M. Laso, J. I. Siepmann and U. W. Suter, *Mol. Phys.* **80**, 55 (1993).
- [99] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett.* **61**, 2635 (1988).
- [100] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett.* **63**, 1195 (1989).

- [101] A. Z. Panagiotopoulos, *J. Phys.: Condens. Matter* **12**, R25 (2000).
- [102] A. D. Bruce and N. B. Wilding, *Phys. Rev. Lett.* **68**, 193 (1992).
- [103] N. B. Wilding and A. D. Bruce, *J. Phys.: Condens. Matter*, **4**, 3087 (1992).
- [104] N. B. Wilding, *Phys. Rev. E* **51**, 2079 (1985).
- [105] C. N. Likos, K. R. Mecke and H. Wagner, *J. Chem. Phys.* **102**, 9350 (1995).
- [106] N. Hoffmann, F. Ebert, C. N. Likos, H. Löwen, and G. Maret, *Phys. Rev. Lett.* **97**, 078301 (2006).
- [107] N. Hoffmann, C. N. Likos and H. Löwen, *J. Phys.: Condens. Matter* **18**, 10193 (2006).
- [108] B. Capone, I. Coluzza, R. Blaak, F. Lo Verso, and C. N. Likos, *New J. of Phys.* **15**, 095002 (2013).
- [109] D. Nykypanchuk, M. M. Maye, D. van der Lelie, and O. Gang *Nature* **451**, 549 (2008).
- [110] S.Y. Park, A. K. R. Lytton-Jean, B. Lee, S. Weigand, G. C. Schatz, and C. A. Mirkin, *Nature* **451**, 553 (2008).
- [111] C. Koch, C. N. Likos, A. Z. Panagiotopoulos, and F. Lo Verso, *Mol. Phys.* **109**, 3049 (2011).
- [112] V. Firetto, M. Floriano, and A. Z. Panagiotopoulos, *Langmuir* **22** 6514 (2006).
- [113] S. Foerster, A. K. Khandpur, J. Zhao, F. S. Bates, I. W. Hamley, A. J. Ryan, and W. Bras, *Macromolecules* **27**, 6922 (1994).
- [114] G. J. T. Tiddy, *Phys. Rep.* **57**, 1 (1980).
- [115] W. Zhao, T. P. Russell, and G. M. Grason, *J. Chem. Phys.* **137**, 104911 (2012).
- [116] C. W. Hsu, J. Largo, F. Sciortino, and F. W. Starr, *Proc. Nat. Acad. Sci. U.S.A.* **105**, 13711 (2008).
- [117] K. W. Wojciechowski, D. Frenkel, and A. C. Brańka, *Phys. Rev. Lett.* **66**, 3168 (1991).
- [118] K. W. Wojciechowski, A. C. Brańka, and D. Frenkel, *Physica A* **196**, 519 (1993).
- [119] H. Fynenever and A. Yethiraj, *J. Chem. Phys.* **108**, 1636 (1998).
- [120] J. M. Polson and D. Frenkel, *J. Chem. Phys.* **109**, 318 (1998).
- [121] A. Galindo, C. Vega, E. Sanz, L. G. MacDowell, E. de Miguel, and F. J. Blas, *J. Chem. Phys.* **120**, 3957 (2004).
- [122] B. M. Mladek, D. Gottwald, G. Kahl, M. Neumann, and C. N. Likos, *Phys. Rev. Lett.* **96**, 045701 (2006).
- [123] C. N. Likos, B. M. Mladek, D. Gottwald, and G. Kahl, *J. Chem. Phys.* **126**, 224502 (2007).
- [124] D. A. Lenz, R. Blaak, C. N. Likos, and B. M. Mladek, *Phys. Rev. Lett.* **109**, 228301 (2012).
- [125] A. J. Archer, C. N. Likos, and R. Evans, *J. Phys.: Condens. Matter* **16**, L297 (2004).

- [126] S. D. Overduin and C. N. Likos, *Europhys. Lett.* **85**, 26003 (2009).
- [127] A. J. Moreno and C. N. Likos, *Phys. Rev. Lett.* **99**, 107801 (2007).
- [128] D. Coslovich, L. Strauss, and G. Kahl, *Soft Matter* **7**, 2127 (2011).
- [129] D. Coslovich, M. Bernabei, and A. J. Moreno, *J. Chem. Phys.* **137**, 184904 (2012).
- [130] M. Montes-Saralegui, A. Nikoubashman, and G. Kahl, *J. Phys.: Condens. Matter* **25**, 195101 (2013).
- [131] F. H. Stillinger, *J. Chem. Phys.* **65**, 3968 (1976).
- [132] F. H. Stillinger and T. A. Weber, *J. Chem. Phys.* **68**, 3837 (1978).
- [133] F. H. Stillinger and T. A. Weber, *Phys. Rev. B* **22**, 3790 (1980).
- [134] F. H. Stillinger, *J. Chem. Phys.* **70**, 4067 (1979).
- [135] F. H. Stillinger, *Phys. Rev. B* **20**, 299 (1979).
- [136] F. H. Stillinger and D. K. Stillinger, *Physica A* **244**, 358 (1997).
- [137] A. Lang, C. N. Likos, M. Watzlawek, and H. Löwen, *J. Phys.: Condens. Matter* **12**, 5087 (2000).
- [138] S. Prestipino, F. Saija, and P. V. Giaquinta, *Phys. Rev. E* **71**, 050102 (2005).
- [139] M. Watzlawek, C. N. Likos, and H. Löwen, *Phys. Rev. Lett.* **82**, 5289 (1999).
- [140] J. C. Pámies, A. Cacciuto, and D. Frenkel, *J. Chem. Phys.* **131**, 044514 (2009).
- [141] C. N. Likos, A. Lang, M. Watzlawek, and H. Löwen, *Phys. Rev. E* **63**, 031206 (2001).
- [142] Y. Chen, *Macromolecules* **45**, 2619 (2012).
- [143] B. V. S. Iyer, I. G. Salib, V. V. Yashin, T. Kowalewski, K. Matyjaszewski, and A. C. Balazs, *Soft Matter* **9**, 109 (2013).
- [144] M. Rikkou-Kalourkoti, E. Kassi, and C. S. Patrickios, *J. Polym. Sci. Pol. Chem.* **50**, 665 (2012).
- [145] S. Junnila, N. Houbenov, A. Karatzas, N. Hadjichristidis, A. Hirao, H. Iatrou, and O. Ikkala, *Macromolecules* **45**, 2850 (2012).
- [146] M. Pitsikalis, N. Hadjichristidis and J. W. Mays, *Macromolecules* **29**, 179 (1996).
- [147] C. Quellet, H.-F. Eicke, G. Xu and Y. Hauger, *Macromolecules* **23**, 3347 (1990).
- [148] M. Odenwald, I.-F. Eicke and W. Meier, *Macromolecules* **28**, 5069 (1995).
- [149] W. Meier, J. Hotz and S. Günther-Ausborn, *Langmuir* **12**, 5028 (1996).
- [150] H. Bagger-Jørgensen, L. Coppola, K. Thuresson, U. Olsson and K. Mortensen, *Langmuir* **13**, 4204 (1997).
- [151] J. Appell, G. Porte and M. Rawiso, *Langmuir* **14**, 4409 (1998).
- [152] L. Ramos and C. Ligoure, *Macromolecules* **40**, 1248 (2007).

- [153] K. Nakaya–Yaegashi, L. Ramos, H. Tabuteau and C. Ligoure, *Journal of Rheology* **52**, 359 (2008).
- [154] J. Schmalzing and M. Kerscher, *Generation of Cosmological Large-Scale Structure* **503**, 255 (1997).
- [155] K. R. Mecke, T. Buchert, and H. Wagner, *Astronomy and Astrophysics* **288**, 697 (1994).
- [156] J. M. Lee, *Riemannian Manifolds: An Introduction to Curvature*, Springer (1997).
- [157] H. Hadwiger, *Vorlesungen über Inhalt, Oberfläche und Isoperimetrie*, Springer, (1957).
- [158] H. Hadwiger, *J. Reine Angew. Math.* **194**, 101 (1955).