

# Entropic networks in colloidal, polymeric and amphiphilic systems

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## Abstract

Self-assembly in soft-matter systems often results in the formation of locally cylindrical or chain-like structures. We review the theory of these systems whose large-scale structure and properties depend on whether the chains are finite, with end-caps or join to form junctions that result in networks. Physical examples discussed here include physical gels, wormlike micelles, dipolar fluids and microemulsions. In all these cases, the competition between end-caps and junctions results in an entropic phase separation into junction-rich and junction-poor phases, as recently observed by electron microscopy and seen in computer simulations. A simple model that accounts for these phenomena is reviewed. Extensions of these ideas can be applied to treat network formation and phase separation in a system of telechelic (hydrophobically tipped, hydrophilic) polymers and oil-in-water microemulsions, as observed in recent experiments.

## 1. Introduction

Self-assembling networks and branched structures are common in both natural and synthetic materials and form under a variety of equilibrium and non-equilibrium conditions. Here, we review the theory of the structure and thermodynamic properties of equilibrium networks. This paper unifies concepts that have been previously discussed in several publications, each in different experimental contexts such as gels [1], worm-like micelles [2], microemulsions [2, 3], dipolar liquids [4] and colloids [5, 6]. In all these systems the networks consist of self-assembling, one-dimensional objects (e.g. polymer chains in the case of a gel, cylindrical micelles or microemulsions or chains of dipolar colloids). The study of network phases is of both theoretical and practical interest. From the practical point of view, gels and sol–gel systems are at the core of many industrial, biological and biomedical applications. Examples range from novel plastics and food processing to gel chromatography and tissue implants [7, 8]. There are also fundamental issues that are of interest. For example, the first-order or continuous

nature of the gelation transition in physical gels is currently under debate [8–11]. Experiments have not yet provided a clear-cut answer, because the gelation transition can be obscured by the van der Waals interaction [11, 12]. Another example is the transition of a solution of worm-like micelles to a self-assembled network that has been suggested to occur on the basis of rheological measurements; this has also been discussed theoretically [13, 14]. Network formation may also be responsible for the ‘closed-loop’ phase diagrams of dipolar and magnetic liquids and colloids [4] and of microemulsions [3]. Cryoelectron microscopy shows clear evidence of coexisting network phases in dilute microemulsions [2]. In many of the systems mentioned above, the chains themselves are self-assembled in an equilibrium manner from a large number of monomers.

This paper begins with a simple estimate of the contribution to the density and free energy of ends and junctions in a system of self-assembling chains or tubes, and shows that the junction entropy introduces an effective attraction [15, 16] (negative second-virial coefficient) that can lead to phase separation. Other work [17] has focused on flexible polymers where ring formation must be included; this is in contrast to the more rigid systems discussed here where the relevant experiments do not show the presence of many rings. (The relationship of this thermodynamic transition to the topological, connectivity transition (percolation or gelation) can be predicted in a unified manner using a modification of the  $n \rightarrow 0$  spin model for polymers as discussed in [16].) The extension of these ideas to systems with cross-links (e.g. actin gels) is also discussed. Finally, we show how entropic phase separation can also explain recent observations in a system of telechelic polymers and microemulsions that form network structures.

## 2. Competition of ends and junctions

A simple model that contains the essence of the competition between junctions (whose energy cost is  $\epsilon_f$  for the general case of  $f$ -fold junctions) and end caps (whose energy cost is  $\epsilon_1$ ) can be obtained from considerations that were originally developed to treat living polymers, micellar solutions and, recently, microemulsion networks. The starting point of the model is the probability that a chain (or cylindrical micelle or microemulsion) that began at  $\vec{r}_1$  goes through the point  $\vec{r}$ :  $\psi(\vec{r}, \vec{r}_1)$ . The probability for a monomer that is within the chain (i.e. not at one of the endpoints) to be located at a point  $\vec{r}$ , is proportional to  $\psi(\vec{r}, \vec{r}_1)\psi(\vec{r}_2, \vec{r})$  (where  $\vec{r}_1, \vec{r}_2$  are suitably chosen and later averaged over), since the presence of a monomer requires the joint probability that one end of the chain met the other end at  $\vec{r}$ . Within a mean-field model where the spatial dependence is dropped, it directly follows that the volume fraction of monomers scales like  $\phi \sim \psi^2$ . The volume fraction of ends,  $\phi_1$ , is  $\psi$  multiplied by a Boltzmann factor which accounts for the energetic cost of an end defect,  $\phi_1 \sim \psi e^{-\epsilon_1/T} \sim \phi^{1/2} e^{-\epsilon_1/T}$ . Similarly, we find that the concentration of  $f$ -fold junctions, that require the confluence of  $f$  ends, scales like  $\phi_f \sim \psi^f e^{-\epsilon_f/T} \sim \phi^{f/2} e^{-\epsilon_f/T}$ . Calculation of the free energy yields the standard result for systems governed by an interplay between the energy and entropy of topological defects: each defect, whether it is an  $f$ -fold junction or an end, contributes  $-k_B T$  to the free energy per monomer,  $g$

$$g = -\phi_1 - \phi_f + \frac{1}{2}\phi^2 = -a_1\phi^{1/2}e^{-\epsilon_1/T} - a_3\phi^{f/2}e^{-\epsilon_f/T} + \frac{1}{2}\phi^2, \quad (1)$$

where the third term accounts for the excluded volume repulsion between chains and where  $a_1$  and  $a_3$  are numerical coefficients that depend on the detailed geometry of the system [16]. Examining the dimensionless osmotic pressure,  $p = \phi^2 \partial_\phi (f/\phi) = \frac{1}{2}\phi^2 + \frac{1}{2}(\phi_1 - (f-2)\phi_f)$ , we find two opposing, topologically induced, thermodynamic forces, a repulsion due to ends and an attraction due to junctions (for connectivity  $f > 2$ ).

For three-fold junctions ( $f = 3$ ), the junction-induced attraction is strong enough to drive a *first-order phase transition*, where the system separates into a low-density and a high-density phase. This transition is of purely entropic origin, because there are no specific interactions between the monomers. The physical reason for the transition is the higher entropy of the junction-dominated, high-density phase: although the translational entropy of the chains is lower in the high-density phase, it is overcompensated by the increase in the entropy of the self-assembled junctions, abundant in the high-density phase. For four-fold ( $f = 4$ ) and higher-functionality junctions, the junction-induced transition is too weak to drive a phase separation. In this case, the junction-induced interaction merely renormalizes the excluded volume interaction between the chains, and drives the system closer to the  $\Theta$ -point. The structural percolation transition, of course, is also present above the critical temperature of the first-order phase separation.

The nature of the phases in equilibrium depends on the temperature, but also on the rigidity of the chains and details of the junction configurations. In general, there are three possibilities:

- (i) a phase of dilute chains that coexists with a *connected network*,
- (ii) two coexisting networks, or
- (iii) the coexistence of dilute and dense phases of disjointed, branched aggregates, although not predicted by our model, is also possible.

The percolation transition from a macroscopically disconnected network to a macroscopically connected network is a topological transition that is not contained in the thermodynamics. It is, therefore, not directly related to the phase separation. The percolation transition can, however, be predicted by a unified model that combines both the thermodynamics of junction and network formation with the fluctuations of the structure, as discussed in [16].

Treatment of the spatial density variations within mean field theory [16] shows that the density–density correlation function, relevant for scattering experiments, has a simple Ornstein–Zernicke form for relatively low densities of self-assembling monomers. For higher densities, a *peak* emerges in the structure factor as a function of the scattering wavevector; this indicates the emergence of medium-range (longer range than the lattice size but not long-range order) correlations in the system. In the intermediate regime the structure factor is a monotonically increasing function of the wavevector. This is expected in any dense system: at high densities, the system has a low compressibility at long wavelengths and this suppresses the small wavevector scattering. The *absence of a peak* in the structure factor does not imply the absence of the *network*: there is a region in the phase diagram beyond the percolation line (where an infinite network exists) where there is indeed no peak in the density–density correlation function. The precise location and strength of the peak depends on the monomer density and the number of junctions present. These theoretical predictions may be related to the scattering peak observed experimentally in bicontinuous microemulsions.

These ideas, originally developed to treat self-assembling systems where the number of junctions or end caps is fixed by the equilibrium and hence not conserved, are easily extended to systems where cross-link molecules are necessary for junctions to exist [1]. The total volume fraction of cross-link molecules in the system (including those contained in the junctions as well as those cross-link molecules that are free in solution) is denoted by  $c$ . In the limit where the number of junctions is dilute, the junction probability is simply proportional to the total number of available cross-link molecules,  $c - \phi_f$ , not already contained in junctions, as well as to the factors  $\phi^{f/2}e^{-\epsilon_f/T}$  as discussed above. We thus have

$$\phi_f = (c - \phi_f)a_3\phi^{f/2}e^{-\epsilon_f/T}. \quad (2)$$

Solving this for the junction probability,  $\phi_f$  in terms of the total cross-link density,  $c$ , yields

$$\phi_f = \frac{ca_3\phi^{f/2}e^{-\epsilon_f/T}}{1 + a_3\phi^{f/2}e^{-\epsilon_f/T}}. \quad (3)$$

In the equations that follow we consider the specific case of  $f = 3$ , i.e. threefold junctions.

In the general case, the number of cross-link molecules that form junctions (whose free energy is described by  $g$  above) are in equilibrium with free cross-link molecules in solution (using a simple lattice-gas model) and their number can be determined by requiring equal chemical potentials for the two types of cross-linkers. In the limit of strong but sparse junctions ( $\epsilon_f < 0$ ), the junction density saturates to the value of  $c$ , which means that in this limit all cross-link molecules form junctions. In the other limit of weak junctions,  $\phi_f \simeq ca_3e^{-\epsilon_f/T}\phi^{f/2}$ .

To predict the behaviour of the system as a function of the cross-link density  $c$ , we examine the free energy in the  $(\phi, c)$  plane. For thermodynamic stability, the appropriate [1] free energy is convex with respect to both the chain-monomer and cross-link volume fractions,  $\phi$  and  $c$ , respectively. This condition defines the spinodal line of the phase separation in the  $(\phi, c)$  plane,  $c_s(\phi)$ :

$$c_s(\phi) \approx \left( \frac{4}{3a_3} \frac{\phi^{(4-f)/2}e^{\epsilon_f/T}}{1-\phi} + \frac{a_1}{3a_3} \phi^{(1-f)/2}e^{(\epsilon_f-\epsilon_1)/T} \right). \quad (4)$$

For a given value of the monomer density  $\phi$ , at cross-link densities  $c$  lower than  $c_s(\phi)$ , the system is stable, while for  $c > c_s(\phi)$  the system separates into a dense network with many junctions, in equilibrium with a dilute phase. The dilute phase can be either a very sparse network or consist of disjointed, weakly branched clusters. In the case of weak junctions, the density of the cross-link molecules serves as a temperature-like parameter, and the location of the critical point is determined by the condition  $\frac{\partial c_s(\phi)}{\partial \phi} = 0$ . In the case of three-fold junctions this gives  $c_c \simeq (\frac{1}{2}a_1e^{-\epsilon_1/T})^{2/3}$ , independent of the junction energy  $\epsilon_f$ . Analogously, the phase separation can also be driven by increasing the monomer density  $\phi$  at fixed  $c$ . Further details including the relationship of the thermodynamic phase transition to the gelation or percolation transition can be found in [1].

### 3. Experimental applications

#### 3.1. Micelles and microemulsions

The theory outlined above was originally motivated by experiments on self-assembling networks in microemulsions and micelles. The model of self-assembling networks relates the physics of the shape transitions predicted for microemulsions to measurements of both the thermodynamics and structure. The observed, re-entrant phase separation, characterized by the closed loops, is explained as a direct result of the connected topology of the network that induces an effective attraction between junction points in the network. The topologically induced attraction, which is governed by the material-independent statistics of the junctions, explains the experimentally observed universality demonstrated by the data collapse of phase diagrams of non-ionic microemulsions [18, 19].

In experiments, the re-entrant phase separation is accompanied by a decrease in the interfacial tensions between the coexisting phases by three to five orders of magnitude [20, 21]. Sottmann and Strey [19, 22] have shown that the tension curves also exhibit universal scaling. The theory outlined here can be extended [3] to calculate the scaling of the ultra-low interfacial tension as a function of the spontaneous curvature and show that this is a direct outcome of the network topology which leads to two-phase and three-phase coexistence. We also

predict the related wetting transition, in accord with experiment. For the micellar systems [2], the observations of phase coexistence of dilute and dense network phases resolves a long-standing puzzle: the cylindrical micelles elongate as one approaches the critical point for phase separation, but the critical point is reached before the cylinders have grown enormously. This is perfectly consistent with the network model where the phase separation occurs for finite cylinders since it is driven by the network entropy and an infinite correlation length for junction density fluctuations—not cylinder length. The observed universality of the transitions in microemulsions in both oil-in-water and water-in-oil systems also points to the entropic nature of the effective attraction that leads to the coexistence of two types of networks. It is not necessary to invoke chemical, van der Waals or hydrogen bonding attractions between the cylinders to understand the transition.

The existence of networks in microemulsions and cylindrical micelles has been directly verified by cryogenic transmission electronic microscopy (cryo-TEM) measurements [2]. The images strongly support the prediction that the critical phase separation in both microemulsions and micelles is into two coexisting networks that differ in their density of junctions [2]. The cryo-TEM measurements also confirmed that at the boundaries of the bicontinuous regime the networks break up into disconnected cylindrical globules [2]. The results show that junctions are preferred at low values of the spontaneous curvature while ends are preferred at larger spontaneous curvature due to their curved spherical cap. The crossover between these two regimes heralds the formation of a connected network [16, 23] via the topological, percolation transition discussed above. The anomalous re-entrant nature of this phase separation results from the non-monotonic dependence of the defect energy on system parameters [3].

### 3.2. Dipolar fluids

The same topologically induced attraction responsible for network formation and entropic phase separation in microemulsions and micelles can lead to a liquid–gas transition in dipolar fluids. We have found [4] that in zero external magnetic field, three-fold junctions have defect energies that are lower than those of the end-caps and the dipolar chains therefore tend to form networks. This difference in energy increases as the particles become more anisotropic (e.g. spherocylinders [24, 25]). There is some preliminary evidence for branched structures from simulations and experimental studies of ferrofluids [26–28]. The attraction and phase separation in our network formalism are not related to the individual dipolar spheres, but rather to the topological defects of the chains—the network junctions. The proposed phase separation, which is driven by effective attraction within the fluctuating networks, results in an equilibrium between two dipolar networks with differing densities of junction points.

Simulation studies of dipolar fluids in the low-temperature dilute regime encounter severe numerical difficulties due to the strongly collective nature of the thermal fluctuations that imposes very long relaxation times. Despite these difficulties, recent studies [29] have found some preliminary evidence supporting our suggestion that junction attraction is indeed the mechanism underlying the liquid–gas transition of dipolar systems. Experiments are more difficult to interpret [30, 31], since in addition to the anisotropic, dipolar interactions that favour chain formation, there exist isotropic, van der Waals attractions between the colloidal particles. These can give rise to the usual liquid–gas phase separation that can obscure the network formation and closed-loop coexistence curve [4]; careful balance of the isotropic attractions and repulsions in these systems, perhaps by the addition of polymers or charged groups to the colloidal particles, may facilitate measurements that focus mainly on the effects of the anisotropic, dipolar interactions. This may allow observations of network formation and the entropic phase separations discussed above.

### 3.3. Cross-linked systems: actin gels

Networks of actin filaments are an important example of networks of rigid chains joined by cross-link molecules. In *in vitro* experiments on solutions of actin filaments, cross-linked with  $\alpha$ -actinin it was found that the system undergoes a continuous, non-thermodynamic transition from an entangled network of branched clusters to a ‘microgel’ [32]. This transition manifests itself by a sharp increase in viscosity, and can be interpreted in terms of percolation and formation of a connected network. At lower temperatures, it was found that the system undergoes a first-order phase separation into a dilute solution of short chains in equilibrium with a dense network consisting primarily of bundles of actin filaments, tightly bound by cross-linkers. The observed phase separation agrees with the predictions outlined in [1] and the bundle formation might be attributed to nematic interactions between actin filaments.

To this end, a network of rigid filaments can be viewed very roughly as an assembly of rods of average length  $\bar{l}$ , the mean distance between the junctions. According to the Onsager theory [33], the rods tend to align in parallel when their volume fraction exceeds  $\phi_c \simeq \text{constant} \times \frac{1}{7}$ . The total length of all the segments is proportional to the total volume of monomers in the system. Consequently, for three-fold junctions,  $(\frac{3}{2}N_f + \frac{1}{2}N_1)\bar{l} = N$ ; the factor  $\frac{1}{2}$  corrects for the double counting of each segment and  $N_f$ ,  $N_1$ , and  $N$  are the number of junctions, end caps, and monomers in the system. Converting to the volume fractions of junctions, ends and monomers,  $\phi_f$ ,  $\phi_1$  and  $\phi$  respectively,  $\bar{l} = \frac{2\phi}{3\phi_f + \phi_e}$ . We conclude from the theory [1] that for

$$c < (2\phi^2 - \phi^{1/2}a_1e^{-\epsilon_f/T})/(3a_3\phi^{3/2}e^{-\epsilon_f/T}) \quad (5)$$

one might expect the onset of nematic alignment of the filaments, which results in the formation of the bundles, due to the presence of the junctions.

## 4. Networks in polymer–microemulsion systems

A novel experimental system described in [5] is the network formed when spherical microemulsion droplets of oil in water are mixed with telechelic polymers. The polymers are composed of a hydrophilic backbone chain with one hydrophobic sticker attached to each end. The great advantage of such a system is that variation of the polymer and droplet concentration and size offers control over the system parameters, such as the number of nodes and connections among them.

Due to the hydrophobic interaction, it is energetically preferable for the chain ends to reside inside the hydrophobic core of the microemulsion droplets, and to a first approximation one can neglect the very small number of free hydrophobic chain ends in contact with water and assume that all the polymer ends reside within the droplets. Thus, a given polymer chain can either connect two neighbouring droplets (which we shall term a ‘bonding chain’), or loop on a single droplet, so that both of its ends reside inside the same drop [5]. The free energy difference between a looped polymer and a bonding one is largely determined by the difference in the number of spatial configurations available to a looped polymer compared with one that forms a bond between two drops. In principle, the bonding polymers can be stretched to different degrees, depending on the distance between the bonded droplets. However, it turns out that the stretching of the polymers does not modify the qualitative features of thermodynamic behaviour of the system [6].

It has been found experimentally that as the ratio of the number of the polymers to the number of droplets is changed, the system undergoes two independent transitions:

- (i) a continuous fluid to gel transition, attributed to a formation of an infinite network

- (ii) a first-order thermodynamic phase transition, where the system separates into a dense system of tightly connected droplets, in equilibrium with a phase of dilute droplets, decorated with polymer loops [5].

The fluid to gel transition can be related to a model of site-bond percolation on a lattice that has already been applied to study gelation [35]. The site-bond percolation model provides a qualitative indication of the fluid–gel transition, but cannot be applied in a quantitative manner to the polymer–droplet system since it is intrinsically off-lattice. The percolation transition is a change in the topology, or connectedness, of the system and cannot be predicted from the thermodynamics.

We have shown that the thermodynamics can be understood by a simple model that counts the polymer–droplet configurations [6]. In particular, this approach allows one to understand the first-order phase separation observed in the experiment. The physical origin of the phase separation as the number of polymers per droplet increases can be understood as a balance between the translational entropy of the droplets with the configurational entropy of the polymer connections among the droplets. As the ratio of the number of droplets to the number of polymers decreases, there are fewer ways that the droplets can be connected by polymers; this contribution to the entropy thus decreases. At some point, the system prefers to separate into two phases: one with a high density of highly connected droplets (with relatively low translational entropy) but where the configurational entropy associated with the number of polymer bonds is large, and another phase of dilute droplets whose translational entropy is high, decorated with polymer loops and where very few droplets are connected by polymers. The configurational entropy of this latter phase is low. We emphasize here that this transition is exclusively entropic in nature; there are no direct interactions between either the droplets or the polymers. The predicted phase diagram is in good qualitative agreement with the experiments.

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