

Entropic networks in colloidal self-assembly

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A critical phase separation in self-assembling colloidal dispersions is predicted. The coexisting phases are a dilute gas of ends that coexists with a high-density liquid of branching points. Our model provides a unified explanation for the branched structures, the unusually low critical temperature and density, and the consequent two-phase coexistence ‘islands’ in both cylindrical microemulsions and dilute dispersions of dipolar particles (e.g. ferrofluids).

Keywords: network; self-assembling; dipolar fluid; ferrofluid; microemulsion

This paper presents a brief review of our recent work (Bernheim-Grosswasser *et al.* 1999; Tlusty & Safran 2000a; Tlusty *et al.* 1997, 2000) on network formation in two self-assembling systems that, under certain conditions, show aggregation into linear polymer-like structures: (i) microemulsions, dispersions of polar (water), non-polar (oil) fluids and amphiphile (Bernheim-Grosswasser *et al.* 1999; Tlusty *et al.* 1997, 2000); and (ii) dipolar fluids (Tlusty & Safran 2000a) composed of magnetic (or electrically polar) colloidal nano-particles. While the microscopic building blocks of these systems are quite different, we have shown that the global topology of these two linearly aggregating self-assembling systems, microemulsions and dipolar fluids, is similar; both are governed by two types of entropically induced defects: ends and junction points (see figure 1). The energetically favourable state of the amphiphilic molecules or magnetic colloidal particles is to aggregate in linear structures, and defects such as ends occur only due to the entropy increase caused by their introduction. Apart from terminating at an end, these linearly aggregating systems may also contain another kind of defect: junction points. When the junction points dominate over the ends, these systems self-organize to form large-scale connected networks. Our theory focuses on the topologically induced interactions within such fluctuating networks and provides a unified understanding of both their structure and thermodynamics.

This model of dilute dipolar fluids at low temperatures as self-assembling networks enables us to apply theoretical tools 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 starts or terminates at a point \mathbf{r} , $\psi(\mathbf{r})$. The probability for a chain crossing through \mathbf{r} is proportional to $\psi(\mathbf{r})^2$, since one may think of each monomer as the confluence of two chain ends. Within our mean-field model, it directly follows that the volume fraction of material in the one-dimensional aggregates scales like $\phi \sim \psi^2$. The concentration of ends is

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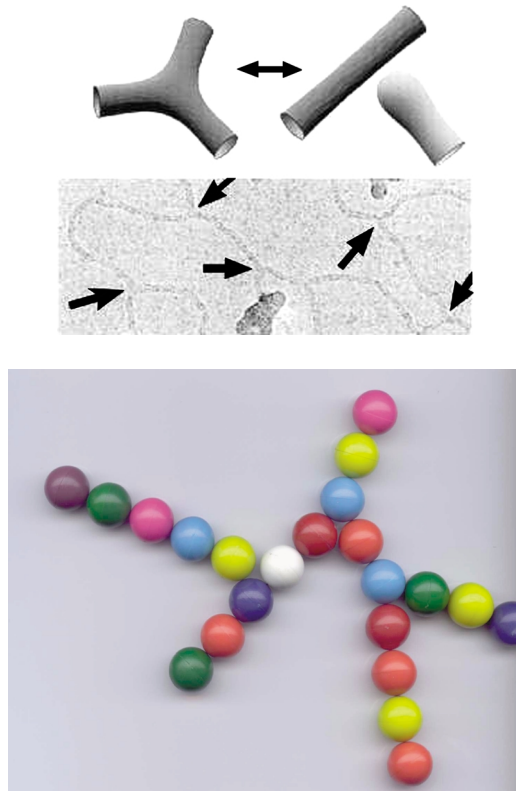


Figure 1. (a) Top: calculated shape of junction and endcap of cylindrical microemulsions; the calculations minimized (Tlusty & Safran 2000b) the curvature elastic energy of the surfactant monolayer separating the inner and outer phases (e.g. oil and water). Bottom: cryo-TEM micrographs of network microemulsions (courtesy of Grosswasser and Talmon). (b) Magnetic marbles (centimetre size) form chains that show stable network formation. The dipolar colloids discussed in the text are the nanoscale analogue of these systems and show Brownian motion and entropic effects when dispersed in solution.

ψ multiplied by a Boltzmann factor, which accounts for the energetic cost, ϵ_1 , of an end defect, $\rho_1 \sim \psi e^{-\epsilon_1/kT} \sim \phi^{1/2} e^{-\epsilon_1/kT}$. Similarly, we find that the concentration of 3-fold junctions, which requires the confluence of three ends, scales like $\rho_3 \sim \psi^3 e^{-\epsilon_3/kT} \sim \phi^{3/2} e^{-\epsilon_3/kT}$, where ϵ_3 is the energy of a junction point. The values of the end and junction point energies depend on the microscopics of the system. In microemulsions, these energies are controlled by the volume fractions and spontaneous curvature of the surfactant monolayer (Tlusty & Safran 2000b), while in dipolar fluids, these energies can be calculated from the dipole–dipole interaction (Tlusty & Safran 2000a). 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 a 3-fold junction or an end, contributes $-kT$ to the free energy per unit volume (in units of kT),

$$f = -\rho_1 - \rho_3 + \frac{1}{2}\phi^2 = -(2\phi)^{1/2}e^{-\epsilon_1/kT} - \frac{1}{3}(2\phi)^{3/2}e^{-\epsilon_3/kT} + \frac{1}{2}\phi^2,$$

where the third term accounts for the excluded volume repulsion between chains.

Examining the osmotic pressure, $p = \phi^2 \partial_\phi (f/\phi) = \frac{1}{2} \phi^2 + \frac{1}{2} (\rho_1 - \rho_3)$, we find two opposing topologically induced thermodynamic forces, a repulsion due to ends and an attraction due to junctions.

The system shows phase separation when the attraction of the dipolar junctions overcomes the repulsion due to ends and the excluded volume entropy loss. This phase separation occurs only below a critical temperature, and the critical point is defined by this critical temperature and a critical volume fraction (typically small). The nature of the phase separated, ‘liquid’ and ‘gas’ phases, is uniquely different from that of simple fluids. The basic ‘particles’ are not the individual chain segments but the topological defects—the network junctions and free ends. The liquid–gas transition is therefore analogous to the demixing of a binary fluid consisting of junctions and ends. In the low-density ‘gas’ there are more ends than junctions ($\rho_1 > \rho_3$), whereas the high-density ‘liquid’ is dominated by junctions ($\rho_1 < \rho_3$). The liquid network is connected, while the gas is composed of disconnected chains. In the phase diagram, these two regions are separated by the connectivity transition line ($\rho_1 = \rho_3$).

Because they are thermal defects, the densities of both junctions and ends decrease exponentially with decreasing temperature, leading to exponentially longer branches. The junction density, $\rho_3 \sim e^{-\epsilon_3/kT}$, decreases slower than the end density, $\rho_1 \sim e^{-\epsilon_1/kT}$, due to the lower defect energy. Therefore, in the proximity of the critical point, the junction attraction overcomes the end repulsion and the coexistence region expands. As temperature is further decreased, there are not enough junctions to balance by their attraction the excluded volume repulsion and the coexistence region narrows to very low densities.

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