

# Self-assembly of colloidal crystals

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Recently, there has been much progress in the self-assembly of colloidal crystals. Major advances include the growth of colloidal crystals on lithographically templated substrates, the synthesis of ordered macroporous materials starting with crystalline emulsions, the investigation of the role of entropy in hard sphere colloids in space and on earth, and the use of electrohydrodynamic forces to create ordered structures.

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Current Opinion in Colloid & Interface Science 1998, 3:5–11

Electronic identifier: 1359-0294-003-00005

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## Abbreviations

**DLVO** Deryagin-Landau-Verwey-Overbeek  
**LC** liquid crystal  
**PMMA** polymethylmethacrylate

## Introduction

The ability to control the assembly of nano- and micrometer sized particles enables the synthesis of new structures with qualitatively new applications. These applications rely on colloids and emulsions with a wide range of optical, electrical [1\*], and mechanical properties that result from both the composition and organization of their macromolecular building blocks; hence, new materials for photonics, lithography [2,3\*], ceramics, and biochemical sensors [4] are made possible. Generally, the manipulation of particles in two and three dimensions requires a deep physical understanding of both forces and instabilities in these complex fluids, and a detailed knowledge of both particle chemistry [5] and materials properties of suspending fluids [6\*\*]. Progress toward the fabrication of patterned colloids may thus be viewed broadly as the result of advances in our understanding of the natural phase behavior and novel interactions in these suspensions, and of more directed studies aimed at the design of novel structures and measurements of their properties.

This review will focus first on recent insights into phase transitions in hard-sphere and charge-stabilized systems. It will also describe novel discoveries in particle interactions that arise in suspensions which may be useful in biasing particle motion for assembly purposes. Following this we will discuss more directed work towards the creation of structures of any design, and finally we will comment on a few remaining investigations that are directed towards applications.

## Phases in natural systems

Under appropriate conditions, particles in suspension spontaneously self-assemble into macroscopic, three-dimensional, highly ordered arrays (colloidal crystals). In addition to their importance for fundamental studies of statistical mechanics [7], these fluid-solid phase transitions provide a simple way to fabricate arrays with a variety of crystal structures, including ordered planar arrays and face-centered cubic, hexagonal close-packed, AB<sub>2</sub>, and other crystal structures [8].

The advantages of the spontaneously occurring or natural approach are the ease with which it can be adapted for industrial use and the wide variety of particle species that can be manipulated. Recent examples [9,10,11\*] of the success of spontaneous self-assembly at smaller length scales include the growth of ordered, three-dimensional, fcc arrays of nanometer-sized semiconductor particles (nanoclusters) by phase separation which was highly successful. Highly ordered colloidal crystallites were grown despite the fact that the particle interactions and kinetics were not well understood. Optimal fabrication of devices will require an understanding of how to control the structure of the colloidal crystalline phase through the control of interactions among particles and particle kinetics.

The classic system for studying the effects of entropy, which plays an essential role in the spontaneous assembly process (i.e. phase transitions) is a mixture of monodisperse hard spheres. Although formation of a crystalline phase at total volume fractions greater than 0.494 was predicted [12] and observed [13] many years ago, the question has remained about whether the observed structure was the true equilibrium phase or not.

In a groundbreaking recent experiment, Zhu *et al.* [14\*\*] were able to eliminate the effects of gravity on the hard-sphere crystallization process by performing experiments on a space shuttle. Their model system consisted of  $-0.5\mu\text{m}$  diameter polymethylmethacrylate (PMMA) spheres with nearly-hard-sphere interactions among particles. The zero-gravity experiments revealed a solid phase organized in a purely random hexagonal-close-packed (rhcp) structure at volume fractions up to 0.619. This observation stands in contrast to terrestrial experiments where coexisting fcc and rhcp crystallites were observed at volume fractions less than 0.58, and a glassy state was observed at higher volume fractions [13]. The experiments reveal that gravity-induced stresses clearly alter some of the intrinsic aspects of colloidal crystallization. Computer simulations [15–17] have shown that the entropy of the fcc structure of hard spheres exceeds that of the hcp structure by between 0.001 and 0.005  $k_B$  per particle for sample

volume fractions at and below the freezing point. The rhcp structure was not considered. Finally, experiments aimed at determining directly the hard-sphere fluid equation of state [18–20] found reasonable agreement with the Carnahan-Starling equation of state which relates the pressure to particle volume-fraction in a hard-sphere fluid.

Mixing hard spheres of two different sizes induces a controllable entropic attraction between two larger particles—a force sometimes called the ‘depletion’, or ‘excluded-volume’. Although the underlying entropic mechanism has been approximately understood for many years in the context of colloidal particles mixed with smaller polymers, only recently has it been systematically investigated for mixtures of hard spheres of two different sizes. For example, it has been shown experimentally [21,22<sup>••</sup>,23] and theoretically [24,25] that among mixtures of hard spheres the larger ones ( $\sim 0.2$ – $1.0\ \mu\text{m}$  diameter) form an rhcp crystalline phase even when the total volume fraction in the sample is as low as 0.2.

In addition, the formation of a disordered dense phase at high volume fractions has been tied to a hidden fluid-fluid spinodal (instability point) in colloid-polymer mixtures and in protein solutions [26].

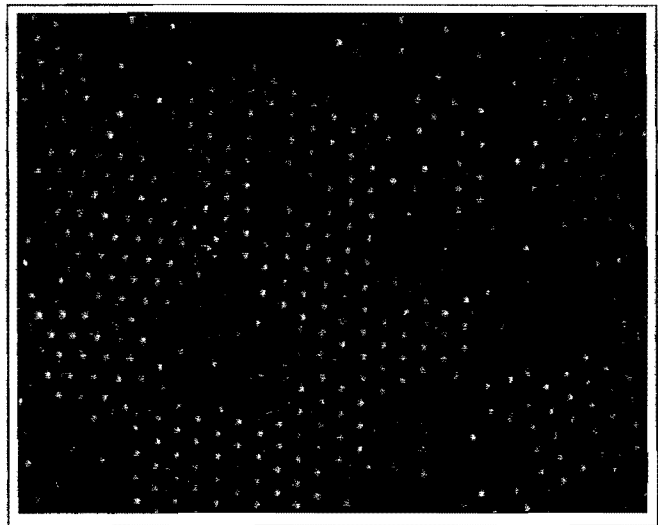
Perhaps more useful for the purposes of assembly was the discovery that larger, more ordered crystallites of the same bulk structure nucleate and grow on flat surfaces at lower volume fractions than in the bulk [21,22<sup>••</sup>,27]. The ‘entropic wetting’ arises because the gain in volume accessible to the smaller particles is greater when a large sphere approaches a wall than when two large spheres approach one another in the bulk. Further understanding of the thermodynamic effects of walls and of other confinement geometries have come from experiments [21,28] and theory [28–31]. Phase separation near corners and walls may improve the size, order and alignment of crystallites [22<sup>••</sup>].

Precise measurements of the interaction between pairs of hard spheres surrounded by smaller ones (JC Crocker, AD Dinsmore, AG Yodh, unpublished data; [32,33]) shed important light on predictions [34,35] about the structure of the smaller particles in suspension, and will enable the phase behavior to be related to the microscopic forces.

The phase behavior of charge-stabilized suspensions has generally been modeled within the context of Deryagin-Landau-Verwey-Overbeek (DLVO) theory (see [36] and references therein). Colloidal particle scattering experiments by Wu and van de Ven [37<sup>•</sup>] show good agreement with DLVO theory at high ionic strength, once the effect of the spheres ‘hairy’ polymer layer are taken into account. Detailed studies of colloidal hydrodynamics also conform closely to the standard theory [38<sup>•</sup>]. Two recent experiments, however, have uncovered anomalous phases in charge-stabilized suspensions. Larsen and Grier

[39,40<sup>•</sup>] and Murray [41] used electrophoretic forces to create long-lived, isolated crystallites in an otherwise dilute suspension (Figure 1). If the long-range interactions were entirely repulsive, these crystallites should melt two orders of magnitude faster than was observed. Tata *et al.* [42<sup>•</sup>] used confocal microscopy to image large, stable voids inside a dense fluid or crystalline colloid phase. Both results strongly suggest that the pair interactions in dense suspensions can have a long-ranged attractive component in contradiction to the standard DLVO [8] theory which predicts no long-range attraction.

Figure 1



Video micrograph of metastable colloidal crystallites. The white and black spots are images of  $0.65\ \mu\text{m}$  diameter colloidal spheres in two different focal planes. If such crystals were the result of purely repulsive interactions, the crystals should rapidly break apart into their constituent particles. Reproduced with permission from [39].

These results have compounded a recent controversy [43,44] regarding the form of electrostatic colloidal interactions. A few years ago, the first direct video microscope measurements of such interactions found either a purely repulsive DLVO-like interactions between isolated spheres [43] or an interaction with an anomalous long-ranged attractive tail among particles near glass walls [44]. The latter result was taken as evidence in favor of a competing interaction theory [45], due to Sogami and Ise, which is similar to DLVO at short range but which predicts a long-ranged attractive component at long range under some circumstances [46]. A recent, crucial experiment [47<sup>•</sup>] has clarified these earlier results [43,44] while confirming the breakdown of DLVO theory in some systems. The results of Crocker and Grier's [47<sup>•</sup>] experiment clearly shows that the Sogami and Ise theory is inconsistent with the pair interaction of isolated spheres and that the attractions seen in earlier experiments [44] were induced by the confining glass walls of the thin

sample cell. They point out that the DLVO theory, while verified for dilute suspensions, may not be applicable to dense suspensions. Furthermore, they conjecture that the unexplained attractions seen in dense suspensions and near walls may be related; the surrounding spheres in one case playing a role similar to the walls in the other case. They conjectured that the attractive interactions seen in dense suspensions arise because the surrounding charged spheres playing a role analogous to the charged walls. Theoretical work to understand the long-range attraction has proceeded rapidly [48–50,51\*,52\*]. Carbajal-Tinoco and Grier [51\*] applied the liquid structure theory to calculate the finite volume fraction pair interaction and found that a long-ranged attractive tail appeared as the volume fraction was increased. In a direct calculation within the DLVO formalism, van Roij and Hansen [52\*] discovered an effective attraction due to a van der Waals-like instability in the free energy in a narrow region of phase space, bracketing the conditions studied by Larsen and Grier [40\*].

### Novel interactions

Techniques for organizing particles also arise from the creation of systems with new particle–particle and particle–substrate interactions. For example, the depletion effect has been used to organize particles around microscopic structure etched into inert substrates. Recent experiments have demonstrated that the large particles in suspension are repelled from the edge of a terrace [53\*], attracted to an inside corner [22\*\*], and pushed along a wall of changing radius of curvature [54\*], simply because of the presence of much smaller particles in the suspension. Such techniques, which illuminate the interplay of entropy and surface texture, position particles at predetermined locations and push particles in specified directions in suspension. The entropic concepts have been extended to include interactions with softer membranes where the interplay between the depletion effect and the membrane bending rigidity can lead to vesicle shape transitions and new membrane mediated particle–particle interactions [54\*].

Poulin *et al.* [55\*] reported a novel class of colloidal interactions that arose when the host fluid was anisotropic. In this case, micron-size water droplets were dispersed in a nematic liquid crystal (LC). Alignment of the LC molecules at the surfaces of the particles created strain in the nematic director that induced a dipole-like interaction among the particles and pushed them into a line. The self-organization was switched on and off by heating or cooling the host LC through its isotropic–nematic transition temperature.

Finally, experiments employing ‘electrohydrodynamic’ effects in electrolytic cells have revealed more about lateral interparticle forces that arise between particles on the electrode surfaces [56,57]. Formation of two-dimensional arrays of micron- and nanometer-sized particles resulting from these forces was observed over a range

of applied voltages and accompanying currents [58\*] and the mechanisms underlying these long-ranged attractive forces has been suggested to arise from electric-field induced fluid flow around the particles [59\*]. The use of this mechanism, along with patterns on the substrates to induce crystallites of controlled shape and position, was demonstrated [59\*] and the controlled growth of three-layer domains achieved [58\*].

### Assembly of designed structures

Several epitaxial techniques have been used to apply monolayers of particles onto a substrate. Repetition of such a process can result in a multi-layer structure in which the composition of the layers can be independently controlled [60\*,61\*]. One very general procedure is to attach linker molecules (such as polycations, thiols, and silanes) to a flat substrate. The particles then stick to the linker molecules, forming a very stable, though typically disordered and not very dense layer. Linker molecules have also been used to make ordered three-dimensional arrays. These techniques have been reviewed in [62\*\*,63\*].

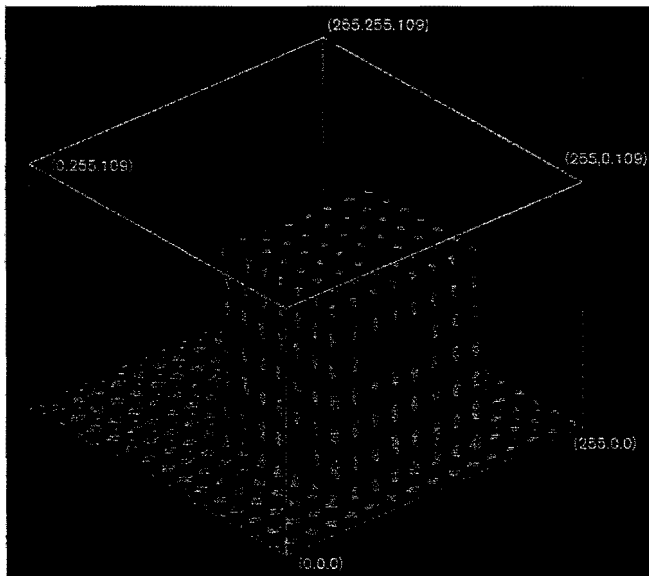
Ordered monolayers have been made by a combination of evaporation and capillary forces. In this process [64\*\*], an evaporation front passes over a hydrophilic substrate at a controlled rate. Dispersed particles are pulled to the drying front by convection, then deposited there when the drying film becomes very thin. Capillary forces subsequently pull the particles together into a close-packed triangular array. This methodology is known as the convective assembly technique. In a related technique, ordered films of nanoclusters have been made by allowing a drop of solution to dry on a carbon grid (see [10,11\*] and references) by spin-drying it [1\*,62\*\*]. The van der Waals forces that typically hold the particles to the substrate in these cases are generally not as strong as the bonds formed by other techniques, but they can be augmented by subsequent addition of linker molecules. The addition of poly(allylaminehydrochloride) to fix a monolayer of gold particles has been reported [58\*].

Dinsmore and co-workers [22\*\*,65] have shown that the convective assembly technique can be used to make three-dimensional AB<sub>2</sub> crystals up to five layers in thickness. The key is to make the particles sufficiently hydrophilic so that, when the convective assembly process is repeated, the water forms a thin film on the first layer of particles. Then, as the water evaporates, the particles that form the second layer are pulled into the interstices of the first layer. In this way, the particles in each layer are in registry with the underlying layer.

An ideal technique of colloidal assembly would allow microscopic particles to be assembled into a three-dimensional crystal starting from an arbitrary surface pattern. One such technique was beautifully demonstrated by van Blaaderen *et al.* [66\*\*]. They used electron-beam lithography to etch holes in a 500 nm thick layer of PMMA.

Silica spheres of diameter 1050 nm were then admitted to the sample. Slow sedimentation of these particles into the etched holes led to the formation of a two-dimensional ordered array. Starting from the (100) or (110) face, fcc crystals several millimeters thick were grown (Figure 2). The technique should allow hcp crystals to be fabricated starting from a plane of the hcp lattice that has no twinning possibilities. The work [66\*\*] is also notable for its use of fluorescence confocal microscopy and fluorescent particle, which provide images of resulting structure (including defects) with high resolution even at significant depth inside the sample, and to investigate how strain in the first layer of the lattice forces the crystal structure to relax to the stable rhcp structure.

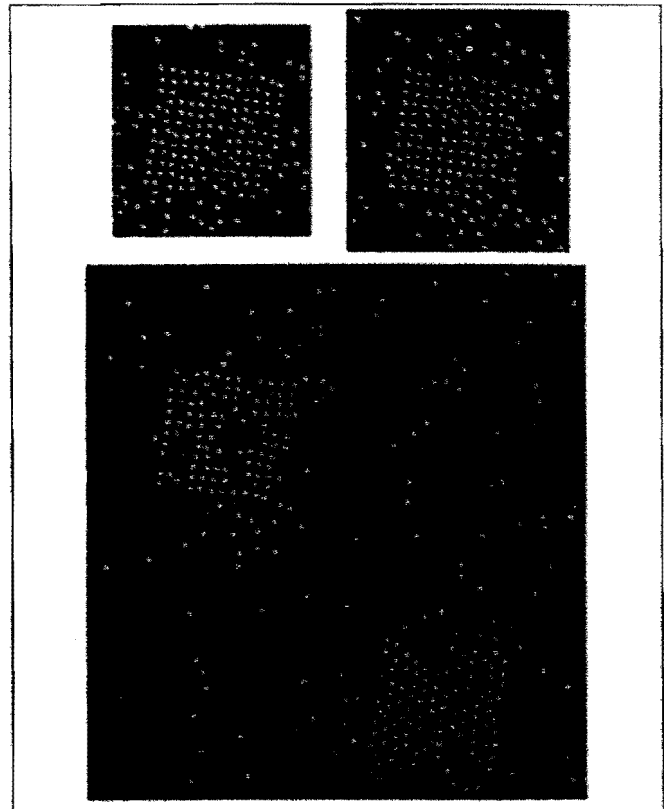
Figure 2



Confocal microscope image of a section of a close-packed, three-dimensional fcc crystallite of 1  $\mu\text{m}$ -diameter silica spheres in a water-glycerol mixture [64\*\*]. The core of each colloidal sphere contained fluorescent dye and is visible in the image. The crystallite was grown atop 0.5  $\mu\text{m}$  deep holes etched into an inert polymer (PMMA) substrate. Reproduced with permission from [66\*\*].

Dinsmore ([22\*\*]; AD Dinsmore *et al.*, unpublished data) have developed a similar approach in which sub-micron colloidal particles are fixed to a substrate with ionic bonds to form a monolayer of arbitrary structure. Electron-beam lithography is used to make tiny holes (<50 nm) in PMMA, which are used as a pattern, then filled with cationic poly-L-lysine. The result is an array of 50 nm diameter spots of exposed poly-L-lysine; the particles electrostatically attracted to the poly-L-Lysine will stick to these spots. The substrate is then dipped into a polystyrene suspension. Particles fill up the lattice sites forming two-dimensional arrays (Figure 3).

Figure 3



Optical monographs of 0.46  $\mu\text{m}$  diameter polystyrene spheres assembled in two-dimensional patterns made by electron-beam lithography ([22\*\*,65]; AD Dinsmore *et al.*, unpublished data). Shown are  $12 \times 12$  arrays of various symmetries using amino-silane glue molecules.

The synthesis of inverse structures, or ordered 'macro-porous' materials is described in a spectacular recent paper by Imhof and Pine [6\*\*]. Briefly, the authors first create a monodisperse emulsion of oil-in-formamide [67], and then they disperse the emulsion in a metal oxide sol. The emulsion self-assembles into a colloidal crystal, and the system is made to gel. After the gel has aged, the sample is washed, dried, and heated to remove the droplets and other organics. The result is an ordered inverse colloid with hardened inorganic material surrounding monodisperse, spherical cavities. The technique has been demonstrated in titania, zirconia and silica hosts, with varying hole sizes and concentrations [6\*]. The resulting materials may find use as photonic structures as well as novel catalytic supports and lightweight materials.

### Toward applications

The 3-D dielectric periodicity of the ordered microspheres gives rise to band structure effects for photons analogous to electronic band structure in semiconductors.

Perhaps the greatest applications would arise from a full photonic band gap, analogous to an electron band

gap in semiconductors [68\*\*,69\*,70]. Kitson *et al.* [71\*] lithographically fabricated a two-dimensional array of silver dots and successfully demonstrated the first full photonic band gap in the visible range in two dimensions. Anderson and Giapis [72] have shown that reducing the symmetry of a two-dimensional lattice by the addition of smaller rods leads to structures with wider photonic band gaps. No full gaps in the visible spectrum have been reported to date in three-dimensional materials, but experiments by Watson and co-workers have mapped the photonic band structure of fcc [73] and bcc [74] crystals with a low refractive-index contrast and have shown that defects in a colloidal crystal can widen the stop bands along particular directions [75\*]. Recent calculations have shown that band gaps can be opened or widened by using materials with a large magnetic susceptibility [76] or with an intensity-dependent refractive index [77-79]. In a related demonstration of an optical switch, Pan *et al.* [80\*] made a crystal of refractive-index-matched particles that contained a dye that absorbed light from a pump beam. This adsorbed light increased the sample's temperature and refractive index. The pump pulse therefore switched on the Bragg scattering of an incident probe beam thus redirecting the probe and rendering the sample effectively opaque. In a similar spirit, Jethmalani and Ford [81] have embedded a colloidal crystal in an elastomeric matrix so that the lattice spacing (hence, the wavelength of Bragg-scattered light) can be reversibly stretched up to 30%.

Finally, assembly at the nanometer level was recently used to create high densities of ~20 nm holes and dots in silicon nitride coated silicon [82\*]. The patterns, which were derived from the transfer of spherical and cylindrical microdomains in diblock copolymer thin films, provide a qualitatively new methodology to create the smallest lithographic structures to date.

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# Structural properties of self-assembled polymeric micelles

Kell Mortensen

At present, the thermodynamic understanding of complex copolymer systems is undergoing important developments. Block copolymers aggregate in selective solvents into micelles of various form and size depending on molecular architecture and interaction parameters. The micelles constitute the basis for a variety of novel mesophases, including biocontinuous phases and networks of ordered cross-linking micelles. Research has focused on structural studies of block copolymer systems, using small-angle scattering of X-rays and neutrons.

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Current Opinion in Colloid & Interface Science 1998, 3:12–19

Electronic identifier: 1359-0294-003-00012

© Current Chemistry Ltd ISSN 1359-0294

## Abbreviations

AB	Diblock copolymer composed of an A and a B block
ABA	Symmetric triblock copolymer composed of A and B blocks where the A block is soluble in the relevant solvent
BAB	Symmetric triblock copolymer composed of A and B blocks where the B block is soluble in the relevant solvent
c	copolymer concentration
EO <sub>m</sub>	poly(ethylene oxide) with <i>m</i> monomers
<i>I</i>	scattering intensity
PBO	poly(butylene oxide)
PDMS	poly(dimethyl siloxane)
PE	poly(ethylene)
PEB	poly(ethylene butylene)
PEE	poly(ethyl ethylene)
PEO	poly(ethylene oxide)
PEP	Poly(ethylene propylene)
PI	poly(isoprene)
PIB	poly(isobutylene)
PO <sub>n</sub>	poly(propylene oxide) with <i>n</i> monomers
PPO	poly(propylene oxide)
PS	poly(styrene)
<i>q</i>	scattering momentum transfer
$\phi$	micellar volume fraction
$\phi_c$	critical micellar volume fraction for hard-sphere crystallization

## Introduction

The physical properties of amphiphilic macromolecules constitute a rich topic which, in recent years, has attracted interests within both applied and basic science [1–3, 4\*\*–7\*\*]. Currently, the field is extremely active, and a concise review of recent progress can include only limited aspects of the recent results.

When block copolymers are mixed in a solvent which dissolves only one of the blocks, the molecules self-associate into specific structures to avoid direct contact

between solvent and the blocks which are insoluble. This self-association gives rise to a wide range of phase behavior, including the formation of micelles of various forms and sizes, complexly structured microemulsions, and liquid crystalline phases. A variety of block copolymers, including blocks of poly(styrene) (PS), poly(isoprene) (PI), poly(ethylene) (PE), poly(ethylene propylene) (PEP), and poly(ethylene butylene) (PEB), have been studied in this context when dissolved in selective organic solvents. In aqueous solutions, block copolymers based on poly(ethylene oxide) (PEO), as the water-soluble block have been investigated to a large extent. The insoluble or less-soluble blocks have, for example, been poly(propylene oxide) (PPO), poly(dimethyl siloxane) (PDMS), poly(butylene oxide) (PBO), PS, and poly(isobutylene) (PIB). In this paper I will review some of the recent progress on complex block copolymer systems, where the main focus has been on structural studies based on small-angle scattering of X-rays and neutrons.

## Block copolymer self-association into micellar aggregates

It is well established that a variety of block copolymers of AB or ABA type form micelles in solvents, which are thermodynamically good for the A block and precipitants for the B block. Such micelles constitute a liquid dispersion of hard-sphere interacting units. BAB copolymers may also form individual micelles, but this implies that all polymer chains start and end in the same micellar core having the middle A-block dispersed into the liquid. It is more likely that such micelles form interconnected networks, where cores are connected by the soluble A-polymer block, as shown schematically in Figure 1.

## Critical micellization temperature and concentration

In general, micellization of block copolymers assumes an equilibrium between molecularly dispersed copolymers (unimers) and multimolecular aggregates (micelles). The thermodynamic approach for describing the aggregation process has been calculated based on lattice models with the mean-field Flory–Huggins type of segmental interactions [8, 9\*].

Ideal model systems for studying the micellization process and micellar interactions are aqueous systems of block copolymers composed of PEO with either PPO or PBO, because at low temperatures all these polymers are hydrophilic, but at higher temperatures PPO and PBO become hydrophobic. At low temperature aqueous solutions of PEO–PPO–PEO and PEO–PBO–PEO therefore appear as unimers. Structural studies based on scattering [5\*\*] and <sup>1</sup>H-NMR relaxation [10] indicate that the PEO–PPO–PEO unimers resemble unimolecular micelles