Embedding of Colloids in Copolymer Cubic Phases: An Impurity Stabilised Crystal.

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Abstract. – We discuss the possibility of embedding colloidal solid particles in a cubic crystal of diblock copolymers. We show that the solubility of the colloids in the cores of the minority phase is enhanced, for a certain range of the particle radius, by the release of elastic tension of the polymer chains. This provides an explicit example for elastically assisted solubilization of spherical inclusions in a crystal.

Introduction. – Diblock copolymer materials are well known, due to their propensity to form ordered structures [1]. Ordering results from the competition between enthalpic effects, that tend to mutually segregate the two blocks from each other, and the global entropy of the system which would tend to favour the mixture of the molecules. The covalent linkage of the blocks impedes any segregation on a macroscopic scale, the system rather adopts a mesoscopic geometry which better satisfies the requirements of mutual exclusion and connectivity [2]. For temperatures well below the ordering transition temperature, the two blocks, denoted A and B, are strongly segregated and the interface between regions of different composition is very sharp. In this regime of strong segregation, the geometry of the crystalline structure depends only on the asymmetry f of the molecule [3]. The asymmetry is defined as the ratio of the number of (say) A-monomers to the total number of monomers in the chain $f = N_A/(N_A + N_B)$. For values of f smaller than about 0.15, the minority constituent forms spherical micelles that order as a BCC cristal in the matrix of the majority constituent. More symmetric materials, with a larger value of f, form hexagonally packed cylinders, cubic bicontinuous structures and one-dimensional stacks of lamellae [4].

The ability of copolymer blends to order results in unique mechanical, optical and structural properties. These properties can be carefully tuned by chemically tailoring the molecular architecture but also, in principle, by mixing additives which would provide an extra feature to the materials [5]. In structurally equivalent lyotropic systems, there has also recently been increased attention paid to mixtures of colloids and smectic liquid crystals (the analogues of lamellar diblock melts), particulary with magnetic particles (ferrofluids). It was

shown, for instance, that the orientation of the smectic axis in these so-called ferrosmectics can be changed by applying a magnetic field to the system[6].

In this letter we study theoretically the embedding of spherical colloidal particles in cubic phases of molten diblock copolymers. In the absence of colloids, the shorter blocks of A-monomers form a roughly spherical core, surrounded by the majority B-blocks which fill the remaining portion of the Wigner-Seitz cell. A theory for strongly segregated mesophases in diblock copolymer blends has been developed by Semenov[3]. In this approach one considers three main contributions to the free energy of the system with the approximation of a spherical shell: the stretching energies of the A and B chains, F_A and F_B, and the interfacial tension γ_{AB} between the A and B regions. Taking a spherical unit cell allows for an exact computation of the elastic energy of the chains in the core, in the strong-stretching limit[3,7]: $F_A = (\pi^2/80)(R_A^2/N_A)$, where R_A is the core radius. All energies are written in thermal units ($k_B T = 1$) and all the lengths in monomeric units ($b = 1$). The stretching contribution from the chains in the corona is calculated by assuming that all the chain ends lie in the outer surface of the corona: $F_B = (1 - f^{1/3}) \times R_A^2/(6N_A)$. The interfacial free energy is proportional to the surface per chain dividing the A and B rich regions and is controlled by the interfacial tension[3] $\gamma_{AB} \sim \chi_{AB}^{1/2}$, where χ_{AB} is the Flory interaction parameter. Thus $F_{AB} = 3\gamma_{AB} N_A/R_A$. Minimization of the total free energy $F_T = F_A + F_B + F_{AB}$ with respect to R_A gives the equilibrium radius of the core $R_A^0 = N_A^{2/3} \gamma_{AB}^{1/3}(120/\pi^2)^{1/3} \times \times [1 + 40/(3\pi^2)(1 - f^{1/3})]^{-1/3}$.

We now describe an ideal equilibrium situation, where the cubic phase is in contact with a reservoir of colloidal particles, which might freely migrate to their equilibrium positions: the cores of the minority A-phase, the corners of the Wigner-Seitz cells in the majority B-phase.... We consider here the case where the embedded solid colloids occupy the core of the minority phase (see fig. 1), and will briefly discuss the effects of embedding in other locations. In addition to the asymmetry f two new parameters now enter in this configuration: the radius of the colloidal particles R_c and the difference of interfacial tensions $\Delta\gamma = \gamma_{cA} - - \gamma_{cv}$, where γ_{cA} and γ_{cv} are, respectively, the colloid/polymer-A and colloid/reference-phase interfacial tensions. The reference phase is taken with respect to some reservoir or the B-phase, whichever presents the lower interfacial tension with respect to the colloidal surface. We neglect any elastic effects provoked by the inclusion of particles in the majority phase and do not consider translational entropy contributions because they are negligible in the limit of long chains and large particles. Adopting the same approximations and calculation
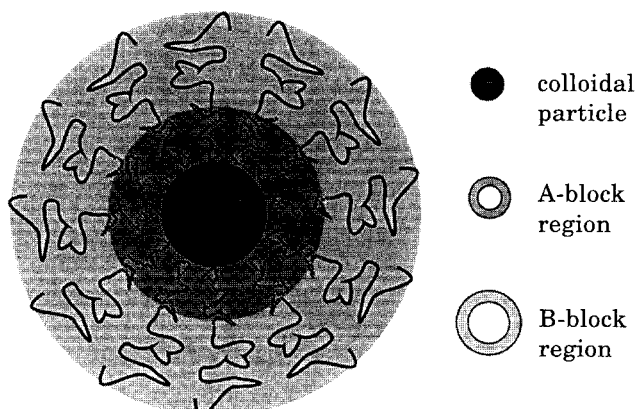

colloidal particle

A-block region

B-block region

Fig. 1. – Schematic representation of the embedding of the colloidal particles in the cubic phase of diblock copolymers.

methods described above [3,7] for the pure cubic copolymer phases, one gets for the mixed configuration the following expression for the total free energy per chain:

$$\frac{F_T(\alpha, \beta)}{N_A^{1/3} \gamma_{AB}^{2/3}} = \frac{\pi^2}{80} \left[\frac{120}{\pi^2 + 40/3(1 - f^{1/3})} \right]^{2/3} \frac{\varrho^2}{\alpha^2} \left[\frac{1 + 15\alpha^2 - 6\alpha^5 - 10\alpha^3}{1 - \alpha^3} + \frac{40}{3\pi^2}(1 - f^{1/3}) \right] +$$

$$+ \left[\frac{\pi^2 + 40/3(1 - f^{1/3})}{120} \right]^{1/3} \frac{3\alpha}{\varrho} \frac{1 + \beta\alpha^2}{1 - \alpha^3}, \qquad (1)$$

where we have introduced the rescaled variables $\alpha = R_c/R_A$, $\beta = \Delta\gamma/\gamma_{AB}$ and $\varrho = R_c/R_A^0$. A straightforward numerical minimization with respect to α gives the equilibrium radius $R_A = = R_c/\alpha$ of the structure and the energy per chain at the minimum $F_T^{\min}(\varrho, \beta)$. The solubility of the colloidal particles in the cores of the cubic phase can be represented, for a given asymmetry f, in a two-dimensional phase diagram $[\beta, \varrho(f)]$. We stressed here the fact that the ratio of the size of the colloid to the unperturbed core radius depends on the copolymer asymmetry f. The solubility lines correspond to equal energies of a cubic phase with embedded colloids and a cubic phase without embedded colloids $F_T^{\min}(\varrho, \beta) = F_T^{\min}(\varrho = = 0, \beta = 0)$. The $[\beta, \varrho(f)]$ solubility diagram is presented in fig. 2 for values of f in the range of asymmetry where the cubic phase is known to be the stable phase $0 < f < 0.12$.

There are two distinct regions in the solubility diagram, depending on the sign of β. For negative values of β the interfacial tension between the colloid and the core of the cubic phase is always lower than the interfacial tension between the colloid and the reference phase. Very small particles (which only slightly distort the copolymer matrix) will thus always be solvated by the core of the cubic phase. Particles of increasing size will, however, contribute to a larger distortion of the copolymer structure, leading to a β-dependent maximum size that can be embedded into the cubic crystal. Not surprisingly, the maximum soluble size increases when one approaches the conditions for total wetting ($\beta \le -1$).

For positive values of β the interfacial tension between the colloid and the core of the cubic
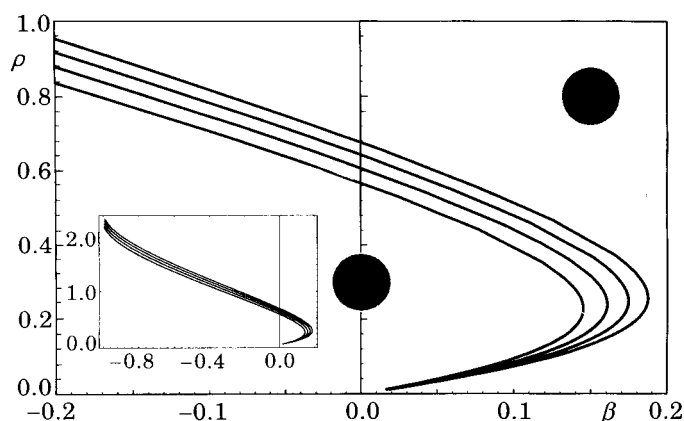

Fig. 2. – Phase diagram for the embedding of solid spherical particles into a cubic mesophase of diblock copolymers. Colloids can be embedded in region II of the phase diagram. ϱ is the ratio of the particle radius to the radius of the cores of the copolymer mesophase in the absence of colloids. β is a measure of the difference in interfacial energies between the particle and the core chains, and between the particles and some reference phase. Simple interfacial tension balance would lead to solubilization only for negative β values. Different border lines correspond to different copolymer asymmetries f. From left to right one has $f = 0.05$, 0.075, 0.1, 0.125.

phase is larger than the interfacial tension between the colloid and the reference phase. On the simple grounds of the interfacial-tension balance, one would expect a zero solubility for the colloids. However, particles in an appropriate size range may liberate enough elastic energy in the cores of the cubic phase to compensate the adverse balance of interfacial tensions. This leads, in the positive β-side of the solubility diagram, to the appearance of a characteristic re-entrant shape. For a given asymmetry value f, there exists thus a maximum value of β above which it becomes impossible to embed particles of any size in the cores of the cubic phase. Note also that the lower branch of the re-entrant phase diagram should not hold for arbitrary small particles which would then need to be treated as solvent molecules.

An exact calculation of the embedding of particles in the majority matrix is a much more difficult task, because the distortion field imposed by the particles is no longer spherical. The embedded particles are expected to be located at the positions where they increase less (or release more) elastic energy of the polymer chains, the interfacial-energy contribution being independent of the position. For a body-centred cubic structure this could correspond, for instance, to the vertices of the Wigner-Seitz cell that has the form of a truncated octahedron, but other locations are also possible. We recall, however, that the phase diagram for diblock copolymer chains is calculated within the spherical approximation for the Wigner-Seitz cell which neglects all the geometrical details associated with the symmetry of the problem. Within this approximation, for instance, the energies of the body-centred cubic and face-centred cubic crystals are the same. Consistently, we first consider the embedding of the particles in the majority phase to result in the addition of an extra shell of particles to the spherical unit cell, which would have no effect in the elastic energy. In this case the results for the solubility diagram in fig. 2 strictly apply, the outer region in the diagram corresponds to a system where the particles are embedded in the B-matrix or expelled from the crystal, depending only on the relative values of the interfacial tensions. Of course, this also implies that the phase diagram in fig. 2 also describes the solubility of colloidal particles in the cores of diblock copolymer micelles in a polymeric solvent.

Corrections to the spherical approximation have been proposed in the literature for the hexagonal phase [8]. These corrections take into account the deviations from the uniform angular distribution for chain stretching. They originate in the space filling constraints of the chains in a non-circular Wigner-Seitz cell and always lead to a small increase of the total elastic energy. The corresponding value of asymmetry for which the lamellar hexagonal phase transition occurs is only changed by a factor of 4%. In spite of the absence of a similar calculation for three-dimensional structures, it is reasonable to assume that such corrections would also lead to a small increase of the stretching energy of the chains in the matrix. Similarly, because of the non-spherical form of the distortion imposed by the inclusion of the particles, we also speculate the total contribution of such distortion to the elastic energy to be positive. If this is the case, the solubility diagram presented in fig. 2 would then correspond to a lower-bound estimate of the region in parameter space where the embedding of the colloids is thermodynamically favourable.

In conclusion, we studied theoretically the embedding of spherical solid particles in a cubic phase of diblock copolymers. We showed that for diblocks with a given asymmetry the embedding depends both on the relative sizes of the colloids and polymer cores, and on the wettability of the particles by the shorter blocks of the copolymer. We found also that embedding can be achieved even for an adverse balance of interfacial tensions, because solid particles in an appropriate size range release some elastic tension of the copolymer chains in the cores of the structure. Cubic phases of diblock copolymers can thus be viewed as a special class of crystal that promotes the solubilization of spherical inclusions. Study of embedding of inclusions with other geometries in spherical, cylindrical and smectic mesophases of diblock copolymers is currently under way.

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