

Supplementary Information to: Large scale three dimensional simulations of hybrid block copolymer/nanoparticle systems.

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1 Functional derivatives on the Cahn-Hilliard equation

In equation (3) of the main text we are presented with functional derivatives of the free energy (equations 1, 5-7 and 9) with respect to the order parameter $\psi(\mathbf{r})$. In this section we show a detail derivation of these derivatives and how they result into the chemical potential μ contributions in the CDS scheme.

Firstly, we present the derivation of the short-range free energy as

$$\nabla^2 \mu_{sr} = \nabla^2 \frac{\delta F_{sr}[\psi]}{\delta \psi(\mathbf{r})} = \nabla^2 \frac{\delta}{\delta \psi(\mathbf{r})} \int \left[H(\psi) + \frac{1}{2} D(\nabla \psi)^2 \right] = \nabla^2 \frac{\partial H}{\partial \psi} - D \nabla^4 \psi \quad (1)$$

with $H(\psi)$ given by equation (8) in the main text.

The long range term in the free energy requires a more detailed explanation

$$\nabla^2 \mu_{lr} = \nabla^2 \frac{\delta F_{lr}[\psi]}{\delta \psi(\mathbf{r})} = \nabla^2 \frac{\delta}{\delta \psi(\mathbf{r})} \frac{1}{2} B \int d\mathbf{r}_1 \int d\mathbf{r}_2 G(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) \quad (2)$$

where we note $\nabla^2 G(\mathbf{r}_1, \mathbf{r}) = -\delta(\mathbf{r}_1 - \mathbf{r})$. The functional derivative results in two contributions, arising from the double integral. If we firstly take the derivative $\delta \psi(\mathbf{r}_2)/\delta \psi(\mathbf{r})$, then

$$\nabla^2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 G(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_1) \delta(\mathbf{r} - \mathbf{r}_2) = \nabla^2 \int d\mathbf{r}_1 \psi(\mathbf{r}_1) G(\mathbf{r}_1, \mathbf{r}) = - \int d\mathbf{r}_1 \psi(\mathbf{r}_1) \delta(\mathbf{r} - \mathbf{r}_1) = -\psi(\mathbf{r}) \quad (3)$$

the same contribution would arise from taking the derivative $\delta \psi(\mathbf{r}_1)/\delta \psi(\mathbf{r})$, and therefore the long range chemical potential term in the CDS scheme is simply

$$\nabla^2 \mu_{lr} = -B\psi \quad (4)$$

Finally, the coupling contribution to the chemical potential is

$$\nabla^2 \mu_{cpl} = \nabla^2 \frac{\delta F_{cpl}[\psi]}{\delta \psi(\mathbf{r})} = 2\sigma \psi_c(\mathbf{r}) [\psi(\mathbf{r}) - \psi_0] \quad (5)$$

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2 Aggregation of neutral NPs

Nanoparticles can be coated to be compatible with the interface between BCP domains, for instance, by grafting a mixed brush of homopolymers into its surface¹⁻³. Neutral NPs can greatly modify the BCP morphology after the inclusion of a considerable concentration^{1,4} of NPs. There are a multitude of sources for such morphological transitions. Using Strong Segregation Theory⁵ it has been predicted that surfactant-like NPs can lead to layer instabilities of the symmetric BCP interface.

At high concentrations the interface can be saturated with NPs, which can lead to a preference for curved interfaces that maximise the interface length. On top of that, each NP is introducing a small distortion in the surrounding BCP profile, both in the normal and parallel direction of the interface. In our coarse grained model this distortion is different from a typical capillary-interaction mechanism and is instead driven by the finite size of the interface. Each NP is introducing a small $\psi(\mathbf{r}) \sim \psi_0 = 0$ region with a length scale ξ of the order of the interface size.

In Fig. S1 we explore a fixed concentration of NPs $\phi_p = 0.4$ for a range of values of the interface width 2ξ and the lamellar periodicity H . In this parameter space, the relative size ξ/H becomes extremely relevant. Fig. S1 shows the disordered phase of BCP (asterisk) in which A and B monomers are not undergoing microphase separation. A dotted line with a constant ξ/H ratio is shown to capture the ODT line. Fig. S2 bottom right shows this disordered state.

Contrary to that, in the left-most part of Fig. S1 we can observe a region of blue dots representing high hexagonal close packed colloidal ordering. In this region the colloids are forming an almost unique percolating cluster. In this region the BCP domains (originally lamellar for $N_p = 0$) are broken down into smaller, irregularly shaped domains. For higher values of R/H we can observe an important morphological transition in the BCP from irregularly-shaped domains to elongated BCP-rich domains with alternating black/white domains. In this region the NPs are expelled from the interface between domains in order to create a NP-rich areas which are macrophase-separating from the BCP. This is represented by squares in Fig. S1. It is important to differentiate between BCP domains (black or white) and BCP-rich domains. In BCP-rich domains the density of colloids is low and microphase-separation of the block copolymer domains is occurring. In the squares region, the number of BCP-rich domains becomes low, while the number of NP-rich domains is higher.

NP phase separation from the BCP melt suggests a strong incompatibility between these two elements of the mixture. This region is clearly occurring with larger values of R/ξ . As mentioned before, the extend of the NP distortion is controlled by the size of ξ . On top of that, a higher value of R/H leads to an enhanced distortion which is longer ranged. It depends not only on the short range interfacial term in the free energy but also on the long range B term. The orientation of the BCP domains is normal to the NP-rich areas, as expected for a non-selective hard wall⁶. Furthermore, our results are considerably comparable with BCP/Homopolymer blends, as described by a two order parameter model using CDS⁷. We are, in essence, describing a ternary mixture of A-*b*-B/C component blend. A further morphological change occurs as the ratio R/H is again increased: the BCP-rich number of domains continues to lower and the NPs undergo order to disorder transition, in which they are now diffusively moving in a disordered BCP background. In this regime the ξ/H indicates the system is closer to the ODT and thus the BCP can easily find local disorder near NP-rich areas (NPs induce mixing in its surroundings). The higher available space leads to a disordered phase for the NPs, which behave as liquids. Finally, in this regime the BCP tends to form a single BCP-rich domain which is elongated as it tends to maximise the number of perpendicular black/white domain boundaries with the NP-rich domains.

3 Supplementary material description

Video *supp-video.avi* shows the time evolution towards the steady state in Figure 10 of the main text.

References

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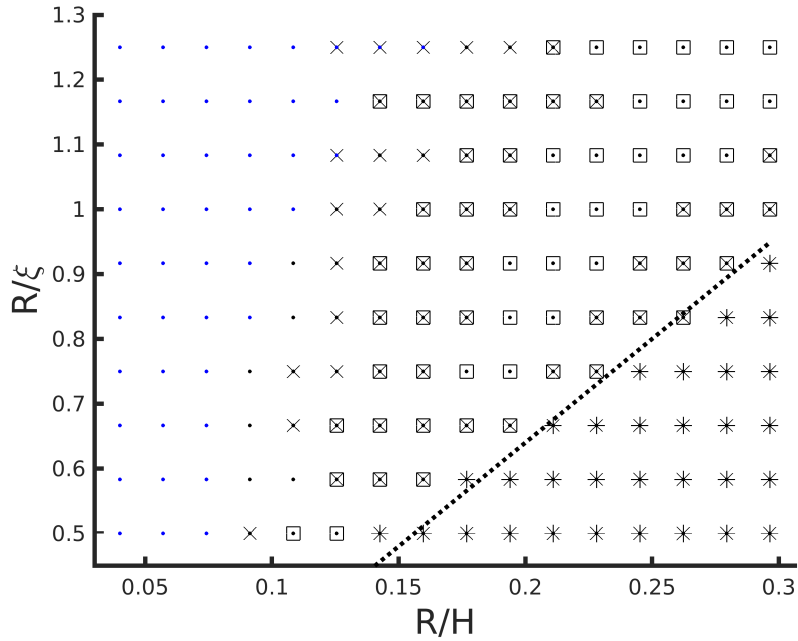


Figure S1: Phase behaviour of a mixture of lamellar-forming BCP with a fixed concentration $\phi_p = 0.4$ of interface-compatible nanoparticles. Symbols represent the following: A single black point represents a simulation point. On top of that, a blue dot marks values such that colloidal hexagonal order parameter $\Psi_6 > 0.4$, ie, when the colloids are hexagonally arranged. If the number of BCP-rich areas is smaller than 20, a square is used. An additional cross indicates a number of colloidal clusters larger than 7. Asterisks stand for disordered BCP phase along with a fluid-like arrangement of colloids.

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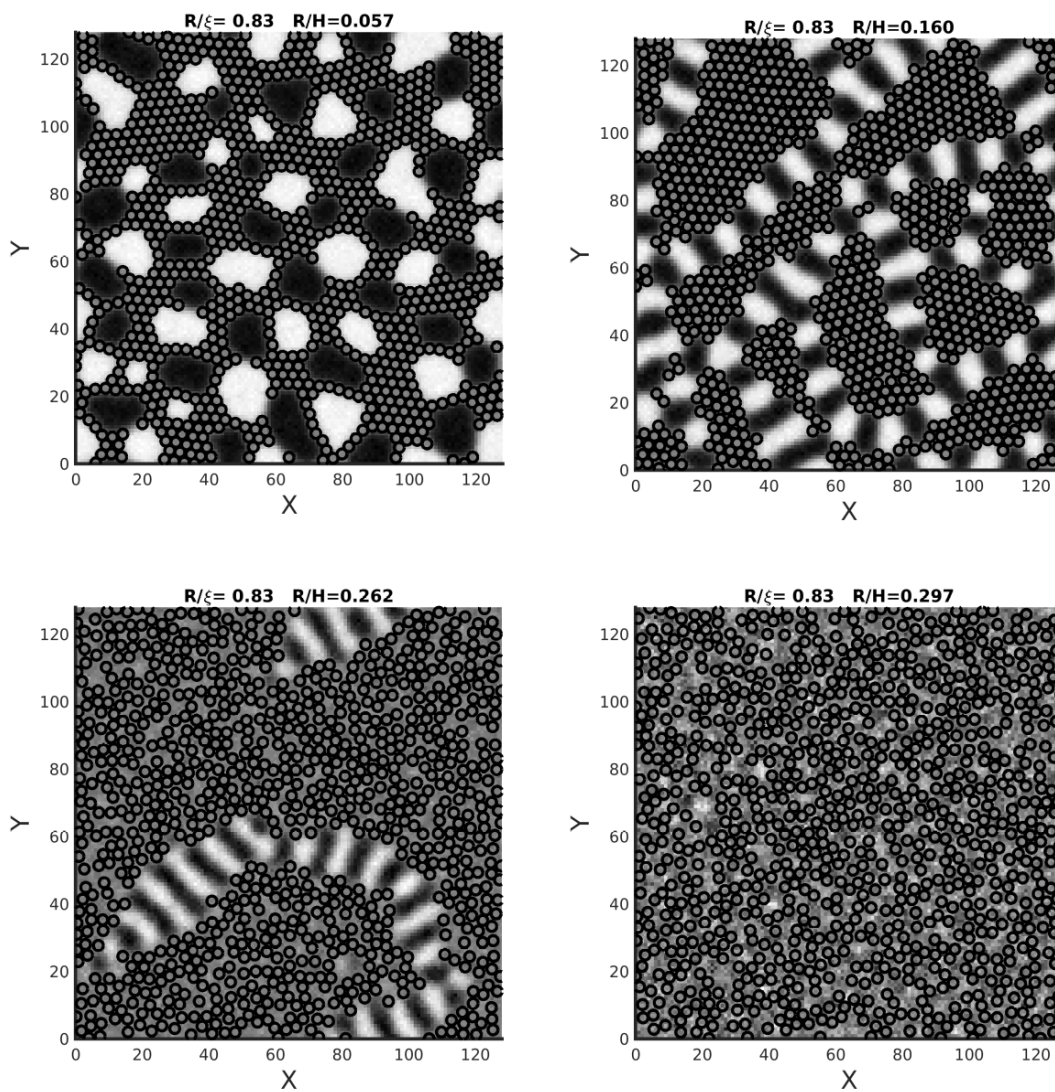


Figure S2: Four instances of lamellar-forming BCP mixed with a fixed concentration of interface-compatible nanoparticles. The size of the lamellar periodicity H is tuned with respect to the NP size.