

Supplementary information to Co-assembly of Janus nanoparticles in block copolymer systems

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May 27, 2019

A Estimating the energetic coupling of a JNP in the interface

If we consider a flat interface in a diblock copolymer, and a JNP with a two faces such as $\psi_+ = -\psi_-$, that is, it is a symmetric two-faced particle, we expect that as long as $\bar{\psi}_0 > 0$ the nanoparticle will segregate to the interface. Furthermore, the JNP will orient in such a way that the positive face will be completely situated in the positive region of the flat interface. Let's consider a flat vertical interface such that $\psi(x)$ and a nanoparticle that is assumed to be in the $x = 0$ with an orientation given by the normal vector \mathbf{n} . This vector points into the positive part of the JNP and in the equilibrium it should point also into the positive part of the phase-separated BCP. Nonetheless, we can expect that if the random fluctuations due to the brownian motion are dominant over the anisotropy of the particle, then we would observe a low degree of orientational order.

Let's estimate the energy that is needed to undergo a flip, that is, for a particle to go from a \mathbf{n} to a $-\mathbf{n}$. Let's begin by calculating the equilibrium coupling free energy

$$F_{cpl}(\mathbf{n}) = \sigma \int d\mathbf{r} \psi_c(r/R) [\psi(\mathbf{r}) - \psi_0(x)]^2 \quad (1)$$

we can't analytically predict the form of the flat interface in the presence of a nanoparticle, nonetheless, let's assume that particle weakly distorts the interface, therefore

$$\psi(x) \sim \psi_{eq} \tanh\left(\frac{x}{\sqrt{2}\xi}\right) \quad (2)$$

for an interface characterized by a size ξ .

$$F_{cpl}(\mathbf{n}) = \sigma \int_0^R dr r \psi_c(r/R) \int_0^{2\pi} d\phi [\psi(x) - \psi_0(x)]^2 \quad (3)$$

we can make the obvious non-dimensional changes such as $\psi \rightarrow \psi_{eq}\psi$, $r \rightarrow rR$ and

$$\bar{\xi} \equiv \xi/R \quad (4)$$

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we can also observe that we can break the angular integral into the to semicircles. Both integrals are equal, then

$$F_{cpl}(\mathbf{n}) = 2\sigma R^2 \psi_{eq}^2 \int_0^1 dr r \psi_c(r/R) \int_{\pi/2}^{3\pi/2} d\phi \left[\tanh\left(\frac{r \cos(\phi)}{\sqrt{2\xi}}\right) - \psi_0 \right]^2 \quad (5)$$

let's also take the limit $\bar{\xi} \rightarrow \infty$ which means that we are in a regime in which the particle size is small compared with the interface size.

$$F_{cpl}(\mathbf{n}) = 2\sigma R^2 \psi_{eq}^2 \int_0^1 dr r \psi_c(r/R) \int_{\pi/2}^{3\pi/2} d\phi \left[\frac{r \cos(\phi)}{\sqrt{2\xi}} - \psi_0 \right]^2 \quad (6)$$

which result in

$$F_{cpl}(\mathbf{n}) = 2\sigma R^2 \psi_{eq}^2 \left[\frac{1}{4} \pi A_3 \bar{\xi}^{-2} + \frac{4A_2}{\sqrt{2}} \psi_0 \bar{\xi}^{-1} + \pi A_1 \psi_0^2 \right] \quad (7)$$

where

$$A_n = \int dr r^n \psi_c(r) \quad (8)$$

Now, if we want to obtain the energetic difference needed to induce a flip, we need to calculate $\Delta F = F(\mathbf{n}) - F(-\mathbf{n})$, for which we have to calculate the coupling energy of a flipped state. But we can also notice that changing $\mathbf{n} \rightarrow -\mathbf{n}$ is equivalent to change $\psi_0 \rightarrow -\psi_0$. Therefore, as we subtract in the energetic difference, only the odd powers of ψ_0 remain, then

$$\Delta F_{cpl} = \frac{16 A_2}{\sqrt{2}} \sigma R^2 \psi_{eq}^2 \frac{\psi_0}{\xi} \quad (9)$$

This equation, although is the result of many strong approximations, maintains the reasonable idea that the energetic cost of a flip is proportional to ψ_0 , which means that if we have an isotropic particle $\psi_0 = 0$, the cost is zero. Similarly, larger particles are more difficult to flip, which again is expected.

We can compare this with the thermal energy scale, such that

$$\chi_{orient} = \frac{\Delta F_{cpl}}{k_B T} = \frac{16 A_2}{\sqrt{2}} \sigma R^2 \psi_{eq}^2 \frac{\psi_0}{\xi k_B T} \quad (10)$$

B Comparison Between JNP and Isotropic (Neutral) at Interfaces. Effect on BCP morphology.

Similarly to what is done in Figure 5 in the main text for lamellar-forming BCP in the presence of JNP/Homogeneous neutral NPs, we can study the effect of JNP on the morphology of a cylinder-forming BCP with $f_0 = 0.35$. In order to characterise the effect of JNP, we explore the fraction ϕ_p of particles in the system. Moreover, neutral isotropic NPs are also simulated in order to compare the behaviour of two different types of particles. In order to track the effect of NPs at interfaces, we compute the number of BCP domains (positive + negative domains). This is a broad measurement of the morphology of the system, with lamellar BCPs having the lower number of domains (ideally, two).

In figure 1 we can observe the number of domains in dependence of the fraction of particles in the system. While at low concentrations both types of particles disturb the BCP morphology, they do so in different rates. Neutral (isotropic) nanoparticles are segregated to the interface but during the phase separation process easily create elongated domains, in contrast to the circular domains that would be found in the pure block copolymer case. This leads to less domains (several small circular domains are now joined in one larger domain). While JNPs are also segregated to the interface, and also disturb the phase separation process, its effect is more moderate. We can compare the left-most and second left-most snapshots corresponding to the same ϕ_p . JNP are well dispersed within the system and are less prone to induce larger elongated BCP domains. For this reason, the number of domains is always larger in the JNP case, as compared with the neutral case. In both cases the curve is decreasing for the initial range of ϕ_p .

Both curves reach a minimum at a different ϕ_p^* which represents the point in which the BCP resembles a lamellar-forming BCP the most. As explained in figure 7, symmetrical JNP and neutral JNP tend

to create new interface in which to anchor. Previous work¹ have described how neutral particles in a highly asymmetrical BCP results in a lamellar-like morphology for the majority phase of the BCP (white domains in this figure), while the minority blocks are confined to smaller domains surrounded by NPs. JNP do not tend to aggregate as much, due to their two-face nature there is a preference to form elongated domains (see bottom, right-most snapshot).

Finally, at very high concentrations of particles the global behaviour depends less on the initial condition, with the NPs dominating the morphology of the system. Again, the JNP are more prone to form elongated domains with zero curvature, as their preference is to form side-to-side configurations within the monolayers of nanoparticles.

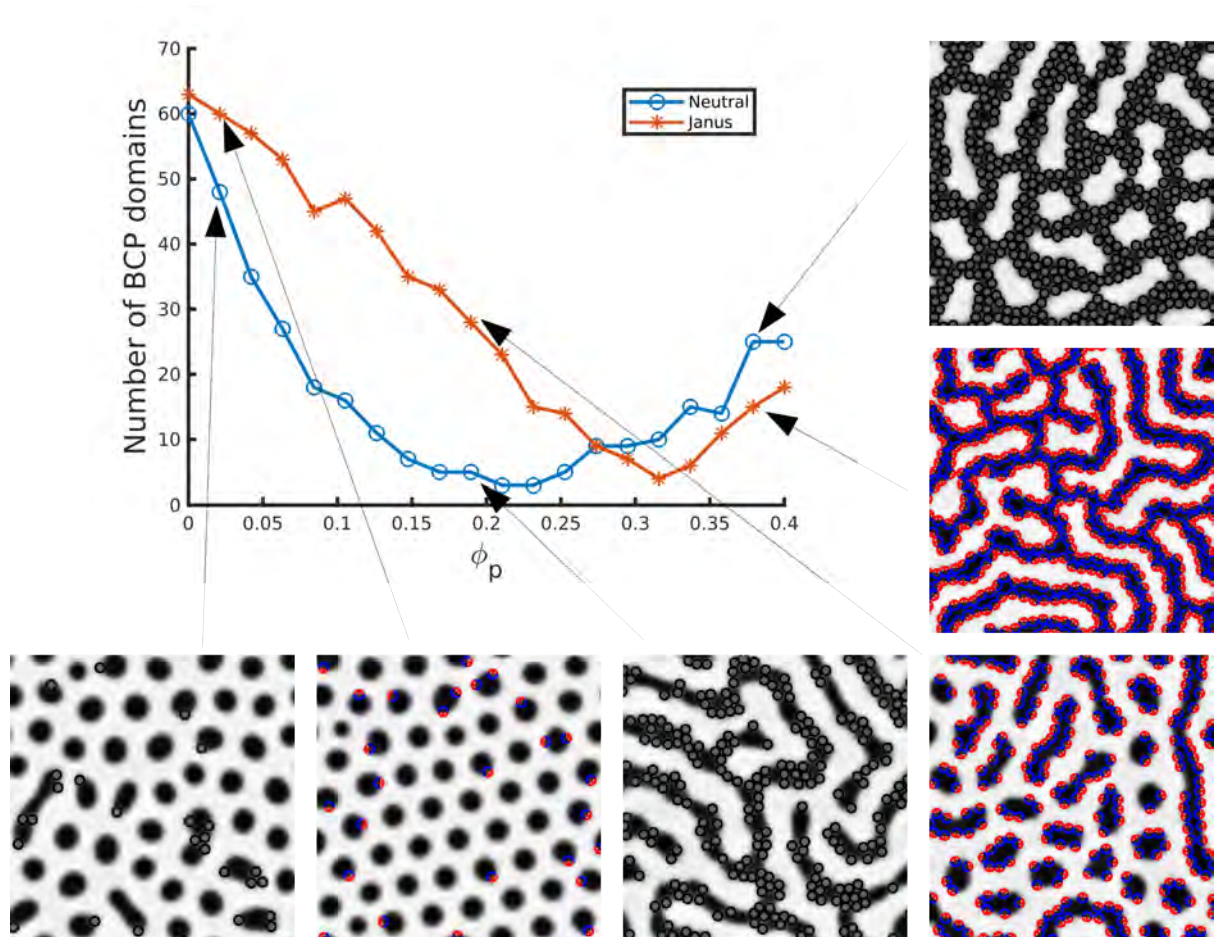


Figure 1: Number of BCP domains ($N_A + N_B$) in the presence of JNP and isotropic neutral nanoparticles. Snapshots of representative simulations are related with an arrow. Please refer to the colour version to see the positive/negative face of the Janus nanoparticles.

References

- [1] J. Diaz, M. Pinna, A. V. Zvelindovsky and I. Pagonabarraga, *Advanced Theory and Simulations*, 2018, **1**, 1800066.