## Particle Distributions in a Block Copolymer Nanocomposite

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ABSTRACT: Self-consistent-field theory is used to predict the center-of-mass distribution of spherical nanoparticles embedded in the lamellar phase of a diblock copolymer melt. The calculation is performed in the dilute limit, where the particle–particle interactions have a negligible effect on the distribution. We investigate how the distribution is affected by particle radius *R*, surface affinity  $\Lambda N$ , diblock segregation IN, diblock composition *f*, and invariant polymerization index  $\overline{N}$ 

natural end-to-end length of  $aN^{1/2}$  and a physical volume of  $N/\rho_0$ , where N is the degree of polymerization, *a* is the statistical segment length, and  $\rho_0$  is the melt segment density. The dimensionless concentrations of A and B segments are still specified by

separating the statistical mechanics into two steps. First, a partial partition function

is calculated for a fixed distribution,  $\{\mathbf{R}_{\hat{a}}\}$ , of particles. Because the particles are fixed, this step can now be performed using SCFT without the polymers violating their excluded volume. Furthermore, the SCFT should provide accurate predictions so long as the block copolymer melt is well segregated (i.e., the A- and B-rich domains are relatively pure).<sup>19</sup> Next the full partition function

is evaluated by integrating over the particle coordinates. Sides et al.<sup>11</sup> performed this last step of the statistical mechanics using Brownian dynamics (BD). However, this approach is also very computational as each time step in the simulation requires a full SCFT calculation. To make the method tractable, Side et al. had to limit themselves to two dimensions and still the SCFT had to be solved on a relatively course mesh of  $72 \times 80$ , undoubtedly resulting in considerable numerical inaccuracy. Nevertheless, the general behavior of their simulation was in nice qualitative agreement with experiment.

Here we examine the particle distribution using a similar hybrid approach, where the integration over the polymer coordinates in eq 2 is performed using SCFT, but where the integration over the particle coordinates in eq 3 is evaluated in the *ideal-gas* limit. The latter limit assumes that particles are sufficiently dilute that the particle-particle interactions can be ignored, in which case the equilibrium particle distribution can be evaluated by considering an isolated particle in the effective periodic potential created by its interactions with the block copolymer matrix. Our calculation is done for the most common experimental situation of spherical nanoparticles in a block copolymer lamellar phase, as depicted in Figure 1. This simple geometry has an axial symmetry about the z axis, which greatly reduces the computational cost. Although we cannot consider the same concentration of particles as Sides et al.,<sup>11</sup> we are now able to treat true three-dimensional spherical particles, and we can do so with high numerical precision.

## **II.** Theory

This section outlines how the present theoretical technique differs from the SCFT/DFT approach of Thompson et al.<sup>14</sup> As before, the polymers are modeled as Gaussian chains with a

respectively, where f denotes the fraction of the diblock formed by A segments. Again, the particles have a center-of-mass distribution of

but now their dimensionless concentration is calculated as

where

defines the particle profile. Reference 14 assumed a step profile where P(r) switches from 1 to 0 at the particle radius *R*, whereas we now assume a gradual interface with a characteristic width of  $w_p$ 

conditions, the effective Hamiltonian of the particles is given by

where Q is the partition function of a single diblock molecule subject to the fields,  $w_A(\mathbf{r})$  and  $w_B(\mathbf{r})$ . The statistical mechanics of the particles is then evaluated according to eq 2, where the different particle configurations,  $\{\mathbf{R}_{\hat{a}}\}$ , are weighted by  $Z[\{\mathbf{R}_{\hat{a}}\}]$  $\equiv \exp(-F[\{\mathbf{R}_{\hat{a}}\}]/k_BT)$ .

Here we [(Here 0 TD10 47e-o74l-segreguated)47e-symmetricddiblockHerepoly-s

is near the middle of the B domain (e.g.,  $Z_1 \approx -0.25D$ ), its affinity for A segments pulls the two neighboring A domains into contact. As the particle is moved toward, for example, the upper z = 0 interface, it ultimately breaks contact with the lower z = -0.5D interface at  $Z_1 = -0.1256D$ , causing a discontinuous change in the morphology as illustrated by Figures 4a,b. When this happens, there is an abrupt increase in the force pulling the particle toward the center of the A domain. The force results from the deformation of the A domain, which engulfs the

transition will occur as the particle crosses the center of the B domain ( $Z_1 = -0.25D$ ) and the contact switches from one interface to the other.

We now repeat our calculation for a strongly segregated block copolymer melt of IN = 40, where the increased interfacial tension swells the domain spacing to  $D = 1.95aN^{1/2}$ . Figure 8 shows the variation in free energy as  $R = 0.2aN^{1/2}$  particles of

and large domains are shown in parts b and c of Figure 10, respectively. The difference is fairly minimal, but the particles are somewhat more localized in the smaller domain for f = 0.4. This should be expected given that a smaller A domain implies less volume over which the particles can move without contacting a B domain.

## **IV. Discussion**

Our study provides the most quantitatively reliable predictions to date for the particle distributions in a block copolymer nanocomposite. Not only does it fully respect the excluded volume of the particles, the particles are modeled as true threedimensional spheres and the numerical calculations are performed with high precision. However, the predictions are restricted to low particle concentrations because the statistical mechanics over the particle coordinates,  $\mathbf{R}_{a}$ , in eq 3 are treated in the ideal-gas limit. This restriction will be most serious when the distribution,  $\rho_{\rm P}(\mathbf{r})$ , is narrow and the particles are essentially arranged in two-dimensional planes. For the approximation to remain valid, the total cross-sectional area of the particles,  $n_p \partial R^2$ , must be much smaller than the total interfacial area, 2V/D, of the block copolymer. This requires that the particle volume fraction satisfies

For typical experimental particle sizes (e.g.,  $R/D \sim 0.1$ ), we expect that our predicted distributions,  $\rho_{\rm P}(z)$ , will be reasonably accurate for particle volume fractions of less than 1%.

For these low concentrations, it is unlikely that there would be any significant deviation of the lamellar period, D, from that of the neat diblock copolymer melt,<sup>8</sup> as we have assumed in our present calculation. Nevertheless, it could be interesting to calculate the leading order correction for nonzero  $\bar{\phi}_{\rm P}$ .<sup>17</sup> Provided the particles still remain sufficiently dilute, the partition function in eq 3 can still be evaluated in the ideal-gas limit as a function of the domain size. The corrected equilibrium period would then be obtained by minimizing the resulting free energy,  $F = k_{\rm B}T$ ln Z.

For more concentrated particles, the shape of  $\rho_{\rm P}(\mathbf{r})$  would begin to depend on  $\overline{\phi}_{\rm P}$ .<sup>7</sup> To predict the change in the distribution, one would have to go beyond the ideal-gas approximation and account for the effective particle-particle interactions by a cluster expansion or an appropriate density functional theory. Of course, this would be much more complicated than for classical gases because of the periodic background potential and the fact that the effective interaction between two particles depends on their actual positions,  $Z_1$  and  $Z_2$ , as well as their lateral separation. Apart from the special case of when the particles are aligned in the z direction, a numerically accurate calculation would be highly computational. Reister and Fredrickson<sup>25</sup> have evaluated these effective interactions, but only for cylindrical and planar objects oriented parallel to the lamellae. As a simple approximation, one could ignore the effect of the block copolymer matrix and just include the direct hardcore interaction, which for spheres is only a function of their separation.

The virtue of the hybrid approach introduced by Sides et al.<sup>11</sup> and used here is that it prevents the polymers from entering the excluded volume of the particles,  $\hat{\phi}_{\rm P}(\mathbf{r})$ . Provided that the width of the particle profile in eq 7 is narrow (i.e.,  $w_{\rm p} \ll aN^{1/2}$ ), the entropic penalty of restricting the polymer configurations is well approximated by<sup>13</sup> This penalty should be relatively constant, assuming that the particles remain reasonably dispersed. However, this is not the case in the SCFT/DFT approach,<sup>14–16</sup> where the polymers are effectively excluded from the average particle positions. In that case, the entropic penalty is still approximated by eq 13, but with  $\hat{\phi}_{\rm P}(\mathbf{r})$  replaced by its thermodynamic average,  $\phi_{\rm P}(\mathbf{r})$ . Consequently, the entropic penalty in the SCFT/DFT calculations increases as the particles become more localized, which leads to an unphysical mechanism that broadens the particle distribution.

The violation of the excluded volume also impacts the particle-polymer interaction,  $\rho_0 \int d\mathbf{r} \left[ I_{AP} \right]$