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2 Abstract

Our aim here is to find the arrangemnet of nanoparticles in a diblock copolymer. Using SCFT(Self Consistent Field Theory), it was found out that by varying the size of nanoparticles, selectivity and the density of the grafted brush, we can change the arrangement of the nanoparticles. Nanoparticles align themselves either at the copolymer interface or at the centre of one of the copolymer phase. These different arrangements are obtained as a result of the change in free energy of the system i.e. competition between the entropy and the enthalpy.

3 Introduction

When nanoparticles are introduced in a diblock copolymer, self assembly of the structure take place. The spatial arrangement of the nanoparticles within the block copolymer is affected by factors such as size, shape and selectivity of nanoparticles. Chemical interactions between the particles and the block copolymer determines the position of concentration nanoparticles. Here we consider nanoparticles to be very small as compared to copolymers. Hence they are considered to be solvent molecules. As in this case we do not have to take care of the excluded volume, we use the SCFT(Self Consistent Field Theory) rather than DFT(Density Functional Theory). In this paper we examine the 3-dimensional morphologies of the lamellar copolymer phases using SCFT.

4 Problem Formulation

We will be using SCFT(Self Consistent Field Theory) to find volume fractions of A, B and the particle at all the locations in a particular volume of dimensions NXNXN.The sum of volume fractions of A, B and the particle at any point is one and is given by the equation:

$$\Phi_A(r) + \Phi_B(r) + \Phi_P(r) = 1$$

Here we have a diblock chain of N_D segments and grafted chain of $N_G = \beta N_D$ A type segments. f is the volume fraction of A in each diblock chain. Here the nanoparticles are assumed to be small enough to be approximated as solvent molecules in the system. σ denotes the number of grafted chain on each particle. SCFT uses chemical potential fields $W_1(\boldsymbol{r})$ for accounting for the interactions between different components. Free energy is minimized to obtain the equilibrium position. Free energy is given as:

$$F = \frac{1}{V}\int (N_D\chi_{AB}\Phi_A\Phi_B + N_D\chi_{AP}\Phi_A\Phi_P + N_D\chi_{PB}\Phi_P\Phi_B - W_A\Phi_A - W_B\Phi_B - W_P\Phi_P)d\boldsymbol{r} - \phi_D ln(\frac{Q_D}{V_{\phi_D}}) - \frac{\phi_{GP}}{(\alpha+\sigma\beta)} ln(\frac{Q_{GP}}{V_{\phi_{GP}}})$$

where χ_{ij} represents the Flory-Higgins interaction parameter between i and j. k_B is the Boltzmann constant, V is the system volume and $\Phi_I(\boldsymbol{r})$ represents local volume fraction of species I. $q_D(\boldsymbol{r}$,s) is the forward propagator which represents the probability of finding sN_D segments of any diblock chain at position $\boldsymbol{r}$. Similarly $q_D{}^+(\boldsymbol{r}$,s) is the backward propagator which represents the probability of finding sN_D segments from the end of any diblock chain at position $\boldsymbol{r}$.

$$\partial q_D(\boldsymbol{r},s)/\partial s = \nabla^2 q_D(\boldsymbol{r},s) - W_1(\boldsymbol{r}) q_D(\boldsymbol{r},s)$$

$$W_1(\boldsymbol{r}) = W_A(\boldsymbol{r}), 0 < s < f$$

$$W_1(\boldsymbol{r}) = W_B(\boldsymbol{r}), f < s < 1$$

$q_G(\boldsymbol{r},s)$ represents the propagator for the grafted chain.

$$\partial q_G(\boldsymbol{r},s)/\partial s = \beta\nabla^2 q_G(\boldsymbol{r},s) - \beta W_A(\boldsymbol{r}) q_G(\boldsymbol{r},s)$$

The potential fields are given by:

$$W_A = W_A + \lambda(N_D\chi_{AB}\phi_B + N_D\chi_{AP}\phi_P - W_A + X_i)$$

$$W_B = W_B + \lambda(N_D\chi_{BP}\phi_P + N_D\chi_{AB}\phi_A - W_B + X_i)$$

$$X_i = X_i + \lambda(\phi_A + \phi_B + \phi_P - 1)$$

Φ_A, Φ_B and Φ_G are given by:

$$\Phi_A(\boldsymbol{r}) = \frac{\phi_d V}{Q_d}\int_0^f q_d(\boldsymbol{r},s) q_d^+(\boldsymbol{r},s) ds + \frac{\phi_{GP}\sigma\beta V}{(\alpha+\sigma\beta)Q_{GP}}\int_0^1 q_g(\boldsymbol{r},s) q_g^+(\boldsymbol{r},s) ds$$

$$\Phi_B(\boldsymbol{r}) = \frac{\phi_d V}{Q_d}\int_f^1 q_d(\boldsymbol{r},s) q_d^+(\boldsymbol{r},s) ds$$

$$\Phi_p(\boldsymbol{r}) = \frac{\phi_{GP}\alpha V}{(\alpha+\sigma\beta)Q_{GP}} exp[-\alpha W_P(\boldsymbol{r})] q_G(\boldsymbol{r},1)^\sigma$$

5 Numerical Methods

We solve our model by using the SCFT method. for using this method, first of all we assume the values of chemical potential between each pair of species as a function of time. We assumed the potential for a laminar state. We further proceed by finding the value of propagator $q_D(r,s)$ (which represents the probability of finding the sN_D segment of the diblock chain at position r) by using modified diffusion equation:

$$\partial q_D(\boldsymbol{r},s)/\partial s = \nabla^2 q_D(\boldsymbol{r},s) - W_1(\boldsymbol{r}) q_D(\boldsymbol{r},s)$$

$$W_1(\boldsymbol{r}) = W_A(\boldsymbol{r}), 0 < s < f$$

$$W_1(\boldsymbol{r}) = W_B(\boldsymbol{r}), f < s < 1$$

These equations are solved by using the pseudo spectral method where the equation simplifies to:
$q_{n+1} = R_{\Delta s} q_n$
$R_{\Delta s} = e^{-w\Delta s/2} e^{\Delta s\nabla^2} e^{-w\Delta s/2}$
This is solved in Matlab using Fourier Transformation. The initial values are taken as $q_D(\boldsymbol{r},0) = 1$ and $q_D^+(\boldsymbol{r},1) = 1$. To do this we take the fourier transform of first term, multiplying it with the second term, taking the inverse fourier transform of the product and then multiplying it with the third term. The similar equation is solved for grafted polymer chain propagator using the initial conditions $q_g(\boldsymbol{r},0) = 1$ and $q_g^+(\boldsymbol{r},s) = exp[-\alpha W_P(\boldsymbol{r})] q_G(\boldsymbol{r},1)^{\sigma-1}$. The equation solved for grafted

chain propagator is :

$\partial q_G(\boldsymbol{r},s)/\partial s = \beta\nabla^2 q_G(\boldsymbol{r},s) - \beta W_A(\boldsymbol{r}) q_G(\boldsymbol{r},s)$

Now after getting the value of new q, we substitute their values in equations

$\Phi_A(\boldsymbol{r}) = \frac{\phi_d V}{Q_d}\int_0^f q_d(\boldsymbol{r},s)q_d^+(\boldsymbol{r},s)ds + \frac{\phi_{GP}\sigma\beta V}{(\alpha+\sigma\beta)Q_{GP}}\int_0^1 q_g(\boldsymbol{r},s)q_g^+(\boldsymbol{r},s)ds$

$\Phi_B(\boldsymbol{r}) = \frac{\phi_d V}{Q_d}\int_f^1 q_d(\boldsymbol{r},s)q_d^+(\boldsymbol{r},s)ds$

$\Phi_p(\boldsymbol{r}) = \frac{\phi_{GP}\alpha V}{(\alpha+\sigma\beta)Q_{GP}} exp[-\alpha W_P(\boldsymbol{r})] q_G(\boldsymbol{r},1)^\sigma$

to get local densities of different components A, B and the grafted particle. Also, we find the partition functions Q_D and Q_GP using the following equations:

$Q_d = \int d\boldsymbol{r} q_d(\boldsymbol{r},1)$
$Q_{GP} = \int d\boldsymbol{r} exp[-\alpha W_P(\boldsymbol{r})] q_G(\boldsymbol{r},1)^\sigma$

These values are substituted in the expressionof free energy for calculation of free energy. These values are stored in a file.
Now, using these values of local densities and partition functions, we find the minimum value of potential field using the expressions:

$W_A = W_A + \lambda(N_D\chi_{AB}\phi_B + N_D\chi_{AP}\phi_P - W_A + X_i)$
$W_B = W_B + \lambda(N_D\chi_{BP}\phi_P + N_D\chi_{AB}\phi_A - W_B + X_i)$
$X_i = X_i + \lambda(\phi_A + \phi_B + \phi_P - 1)$

This gives us new values of potential fields. These new values are used again in an iteration to again calculate values of propagator, local densities, free energy and potential until the total free energy of our particle approaches zero. At each iteration a graph is plotted for density of particle A, B or grafted particle with position (x=N/2).

6 Results and Discussion

The iteration time for 3 dimensional morphologies of the arrangement of the nanoparticles was very long. This constricted us to run our program to a very small number of iterations and thus, get the exact results. We were able to obtain the laminar arrangement to some extent. This can be depicted by the figure as:

As we increase the size of the nanoparticles, there is a tendancy of these particles to change their position from the copolymer interfaces to the centre of A domain(only if the nanoparticles are grafted with A). This transition is a result of the competition between the entropy and enthalpy of a sysytem. Also, on increasing density of the grafted polymer brush(either by increasing the chain length or by increasing number of grafted polymer on each particle) the nanoparticles move from copolymer interfaces to the centre of A domains. This is because on incresing the grafting density, shielding increases and as a result of this nanoparticles prefer sites in the centre of A domain(only if nanoparticles are grafted with A).

7 Conclusion

The arrangement of nanoparticles in the diblock copolymer is largely affected by 3 paramaters. First one is the size. As size of nanoparticle increase, they will come to centre of A domains. Next is the grafting density. As we increase the grafting density on nanoparticles, they move towards centre of A domains.

We can also find other arrangements of the nanoparticles by changing the fraction of A and B in diblock copolymer and obtain cylindrical and spherical arrangements of the nanoparticles. We may need to change the initial condition of potential field for obtaining these profiles in a lesser time.

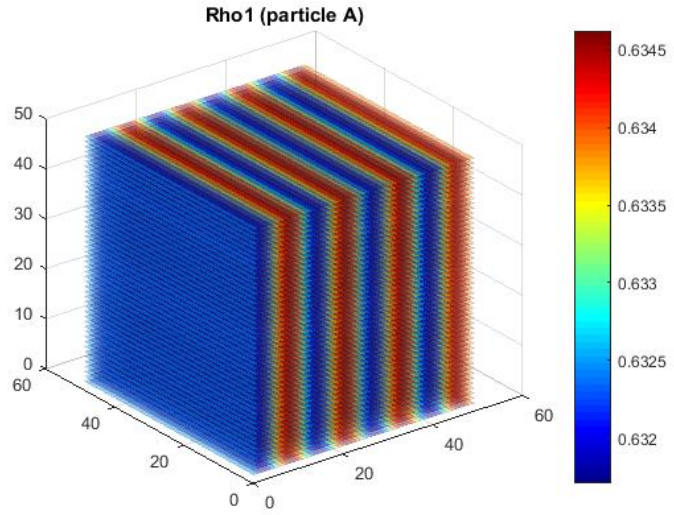

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Figure 1: Density of particle A with position at iteration no. 102

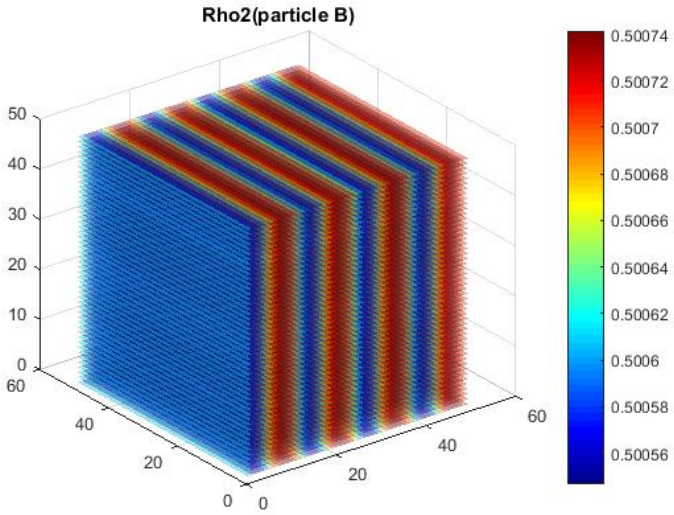

Figure 2: Density of particle B with position at iteration no. 102

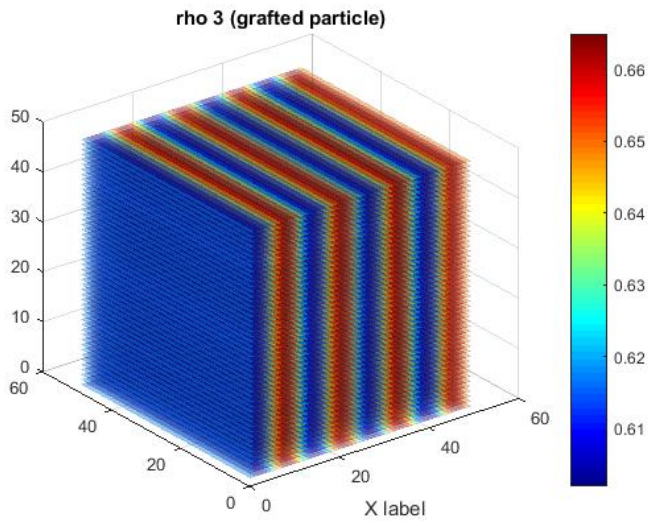

Figure 3: Density of grafted particle with position at iteration no. 102

Numerical method based on SCFT has been used to find the arrangement of nanoparticles in the diblock coplymer. The equations being a non linear one can yield more than one solution. So different initial conditions have been used to obtain different arrangements. Here we have used intial conditions for potential to give us results for laminar arrangement. This technique has been modified a little bit to obtain convergence faster. This technique mainly involves minimisation of free energy to obtain the most stable configuration.

8 References

[1]Xu, G. K., and X. Q. Feng. "Position transitions of polymer-grafted nanoparticles in diblock-copolymer nanocomposites." Express Polym. Lett 5 (2011): 374-383.
[2]Wikipedia