

Polymer Mediated Interaction between Grafted Nanosheets

Supriya Gupta, Paresh Chokshi

Abstract—Polymer-particle interactions can be effectively utilized to produce composites that possess physicochemical properties superior to that of neat polymer. The incorporation of fillers with dimensions comparable to polymer chain size produces composites with extra-ordinary properties owing to very high surface to volume ratio. The dispersion of nanoparticles is achieved by inducing steric repulsion realized by grafting particles with polymeric chains. A comprehensive understanding of the interparticle interaction between these functionalized nanoparticles plays an important role in the synthesis of a stable polymer nanocomposite. With the focus on incorporation of clay sheets in a polymer matrix, we theoretically construct the polymer mediated interparticle potential for two nanosheets grafted with polymeric chains. The self-consistent field theory (SCFT) is employed to obtain the inhomogeneous composition field under equilibrium. Unlike the continuum models, SCFT is built from the microscopic description taking in to account the molecular interactions contributed by both intra- and inter-chain potentials. We present the results of SCFT calculations of the interaction potential curve for two grafted nanosheets immersed in the matrix of polymeric chains of dissimilar chemistry to that of the grafted chains. The interaction potential is repulsive at short separation and shows depletion attraction for moderate separations induced by high grafting density. It is found that the strength of attraction well can be tuned by altering the compatibility between the grafted and the mobile chains. Further, we construct the interaction potential between two nanosheets grafted with diblock copolymers with one of the blocks being chemically identical to the free polymeric chains. The interplay between the enthalpic interaction between the dissimilar species and the entropy of the free chains gives rise to a rich behavior in interaction potential curve obtained for two separate cases of free chains being chemically similar to either the grafted block or the free block of the grafted diblock chains.

Keywords—Clay nanosheets, polymer brush, polymer nanocomposites, self-consistent field theory.

I. INTRODUCTION

THE composites of polymer and nano-fillers have gained significant attention owing to phenomenal enhancement in physical and mechanical properties. While nano-fillers of varying geometries have been studied, the composites made of nanosheets, e.g. monmorillonite clay, have been subject of numerous theoretical and experimental studies in recent decades. A good dispersion of nanosheets in polymer matrix requires the polymeric chains to enter the “gallery” between the pair of clay-sheets leading to exfoliation of nano-clay particles. The one-dimensional confinement of polymer chain

between the clay-sheets is thermodynamically unfavorable due to the loss of conformational entropy of polymer chains. The most common way of improving dispersion is to functionalize the surface of the clay nanosheets by grafting polymeric chains compatible with the free chains. Wang et al. [1] examined the interaction potential between two nano-sheets grafted with polymer chains chemically identical to the polymer matrix. For this autophobic case, there exists an attractive interaction between the two nanosheets at moderate separation. The strength of this attractive potential is proportional to the grafting density and it originates from the entropy driven exclusion of free chains from the region between two nanosheets. The depletion of mobile chains occurs as the polymeric brush undergoes transition from wetted brush to dry brush when $\sigma\sqrt{N_g} > (N_g/N_f)^{3/2}$. Here, σ is the grafting density and N_g & N_f denote the degree of polymerization of grafted and free chains respectively.

In the present study, we perform SCFT calculations for the general case of grafted chain being chemically different from the free chains which introduces enthalpic effects, in addition to the entropic driven depletion interaction. The interplay between the entropic depletion and enthalpic interaction significantly alters the interparticle potential curve [2]–[5]. Further, the dispersion of nano claysheets can be enhanced by tuning the architecture of the free polymer chains. We examine a type of branched polymer, known as star polymer, in which multiple linear polymer arms are connected to a single branch point. The star polymers have compact spherical structures, which results in to decreased melting point and intrinsic viscosity compared to linear polymers of similar composition and molecular weight.

Using SCFT for interaction between two polymer brush surfaces, Singh and Balazs [6] found that the polymer architecture can effectively be used for the intermixing of polymer melt and claysheets. An increase in extent of branching improves dispersion and yields highly exfoliated structures in comparison to linear polymer chains. The experimental studies by Robello et al. [7] confirmed the theoretical finding that the exfoliation of clay nanocomposites can be achieved by using star-shaped free polymer melt chains.

II. MODEL

The current model system consists of two parallel polymer grafted nanoclay sheets of length L , width W with a distance D along the x -axis immersed in a polymer matrix. Typically, the width of the sheets is of the order of nanometer. Polymerization index of the grafted chains is N_g and of free chains is N_f . Such systems of interacting chains, in general,

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are not analytically tractable and therefore the approximations are used to solve model equations of such systems. Here, we employ the self-consistent field (SCF) approach where the particle-particle interactions are described by an average field generated by an ensemble of chains. $q_g(\mathbf{r}, s)$, the probability of finding segment s at position \mathbf{r} , is evaluated from the modified diffusion equation

$$\frac{\partial q_g(\mathbf{r}, s)}{\partial s} = \frac{b^2}{6} \nabla^2 q_g(\mathbf{r}, s) - w_g(\mathbf{r}) q_g(\mathbf{r}, s), \quad (1)$$

where, $w_g(\mathbf{r})$ is the potential field experienced by the grafted chains.

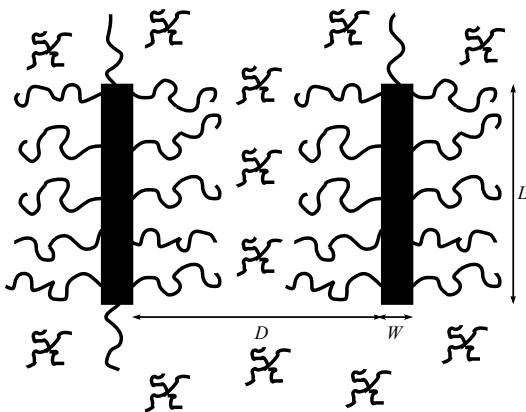


Fig. 1 Schematic of two polymer functionalized nano clay sheets immersed in a star polymer melt in two-dimensions. Note that L and W are the length and width of the clay sheets with the distance D in between them

The initial condition $q_g(\mathbf{r} = \mathbf{r}_c, 0) = 1$ and $q_g(\mathbf{r} \neq \mathbf{r}_c, 0) = 0$, and the boundary condition has been set to $q_g(\mathbf{r} = \mathbf{r}_c, s) = 0$. Here, \mathbf{r}_c indicates the surface of the nanosheets. As the two ends of the grafted chains are distinct, a backward chain propagator $q_g^\dagger(\mathbf{r}, s)$, needs to be calculated. It satisfies (1) with the right hand side multiplied by -1 with the initial condition $q_g^\dagger(\mathbf{r}, N_g) = 1$ and boundary condition $q_g^\dagger(\mathbf{r} = \mathbf{r}_c, s) = 0$.

For the star polymers, the monomer probability is given by the propagator, $q_s(\mathbf{r}, s)$, defined for any arm of the star molecule. The corresponding backward arm propagator is $q_s^\dagger(\mathbf{r}, s)$. Both propagators satisfy the modified diffusion equation similar to $q_g(\mathbf{r}, s)$ and $q_g^\dagger(\mathbf{r}, s)$ respectively, with initial and boundary conditions: $q_s(\mathbf{r}, 0) = 1$, $q_s^\dagger(\mathbf{r}, 0) = [q(\mathbf{r}, N_s)]^{ms-1}$, $q_s(\mathbf{r} = \mathbf{r}_c, s) = 0$, and $q_s^\dagger(\mathbf{r} = \mathbf{r}_c, s) = 0$. Here, ms denotes the number of arms in a star molecule. The single chain partition function of the grafted chains Q_g subjected to the mean field w_g in terms of chain propagators can be written as

$$Q_g = \int d\mathbf{r} q_g(\mathbf{r}, N_g). \quad (2)$$

The equation for the star molecule is

$$Q_s = \int d\mathbf{r} [q_s(\mathbf{r}, N_s)]^{ms}. \quad (3)$$

The mean field approximation gives the free energy of the system

$$\frac{F}{\rho_0 k_B T} = -n_g \rho_0^{-1} \ln \frac{Q_g}{V_p} - n_s \rho_0^{-1} \ln \frac{Q_s}{V_p} - \int d\mathbf{r} [\chi \phi_g \phi_s - \omega_g \phi_g - \omega_s \phi_s - \xi(1 - \phi_g - \phi_s)], \quad (4)$$

where n_g and n_s are the number of grafted and the mobile chains. $\phi_g(\mathbf{r})$ and $\phi_s(\mathbf{r})$ are the local volume fractions of the grafted and the free chains. $\xi(\mathbf{r})$ is the potential field that ensures the incompressibility in the system, k_B is the Boltzmann constant and T is the temperature. V_p is the volume of the box occupied by the polymeric chains – both grafted and free chains.

Minimization of free energy in (4) with respect to ϕ_g , ϕ_s , ω_g , ω_s and ξ leads to the following expressions to describe the equilibrium system:

$$\phi_g(\mathbf{r}) + \phi_s(\mathbf{r}) = 1, \quad (5)$$

$$\phi_g(\mathbf{r}) = \frac{n_g \rho_0^{-1}}{Q_g} \int_0^{N_g} ds q_g(\mathbf{r}, s) q_g^\dagger(\mathbf{r}, s), \quad (6)$$

$$\phi_s(\mathbf{r}) = \frac{n_s \rho_0^{-1}}{Q_s} \int_0^{N_s} ds q_s(\mathbf{r}, s) q_s^\dagger(\mathbf{r}, s), \quad (7)$$

$$w_g(\mathbf{r}) = \chi \phi_s(\mathbf{r}) + \xi(\mathbf{r}), \quad (8)$$

$$w_s(\mathbf{r}) = \chi \phi_g(\mathbf{r}) + \xi(\mathbf{r}). \quad (9)$$

The calculations are carried out on a two-dimensional $L_x \times L_y$ box with periodic boundary conditions to represent the bulk properties. The size of the box is selected such that $L_x = L_y \gg bN_s^{1/2}$ to avoid the finite size effect. The general algorithm to solve these tedious equations consists of a random number generator to generate the initial values of the fields. The diffusion equations are then integrated using a Crank-Nicholson scheme and an alternating-direction implicit (ADI) method. ϕ_g and ϕ_s values are then evaluated (6) and (7) with the incompressibility field

$$\xi(\mathbf{r}) = \xi[1 - \phi_g(\mathbf{r}) - \phi_s(\mathbf{r})]. \quad (10)$$

Finally, the potential fields are updated till minimization of free energy. These steps are repeated until the relative free energy changes at each iteration are reduced to 10^{-4} .

III. RESULTS AND DISCUSSION

A. Linear Polymer Matrix

First, we examine the case of polymer matrix composed of linear polymeric chain chemically dissimilar to the grafted polymers. The interaction between the two polymers is denoted by the Flory's interaction parameter χ .

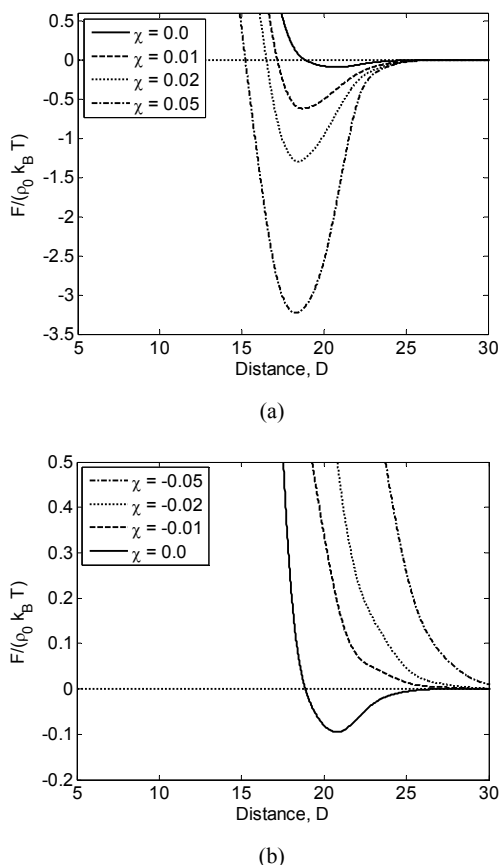


Fig. 2 Inter-particle potential curve as a function of separation showing the effect of interaction parameter χ with the system parameters $N_g = N_f = 50$, $\sigma = 0.25$, $L = 31$ and $W = 3$

Fig. 2 depicts the stabilizing and the destabilizing effect of the interaction parameter on the interparticle free energy curves. For polymer matrix containing two nanosheets functionalized with polymeric chains chemically identical to the free chains, that is $\chi = 0$, the interaction potential is repulsive at short separation and shows depletion attraction for moderate separations [1]. The repulsion at short separation is attributed to the overlapping of two layers of grafted polymers on the nanosheets. The attraction at intermediate distance originates from the combination of depletion of free chains and the enforcement of incompressibility constraint. The depletion is caused by the loss of conformational entropy of free polymeric chains when confined between two sheets. The free chains are expelled out in order to gain the entropy creating depletion related attraction between two sheets to maintain incompressibility.

In the present study, we consider the free chains to be chemically non-identical to the grafted chains, thus bringing the enthalpic contribution in to the picture. Fig. 2 (a) shows the role of positive χ parameter representing the case of free polymer and grafted polymer to be chemically incompatible. Here, the grafting density is kept high at $\sigma = 0.25$ and other parameters are $N_g = N_f = 50$, $L = 31$, and $W = 3$. In this case, unfavourable enthalpic interaction between the grafted

and free chains leads to stronger depletion of free polymer chains from the region between two nanosheets which, in turn, results in a stronger attractive potential in comparison to the autophobic case with $\chi = 0$. As the interaction parameter increases, the degree of incompatibility increases and stronger depletion of free polymer chains take place. It is seen that the depth of the attraction well increases with increase in positive χ parameter. The broadness of the well is also noticed with for higher χ parameter. The higher incompatibility is akin to grafted chains surrounded by poor solvent, which in turn leads to thinner height of the grafted layer. Thus, the overlapping of grafted layers occurs at shorter distance.

For the case when the grafted polymers interact favourably with the free chains, indicated by negative values of χ parameter, Fig. 2 (b) shows the interaction potential curve. In this case, the loss of entropy due to confinement, which is responsible for depletion of free chains, is compensated by the favourable enthalpic interaction between grafted and free chains. In order to maximise the contacts between two types of chains, the free chains penetrate in to the region between the claysheets. This results in to a wet brush which helps improve the dispersion. When the enthalpic contribution to the free energy curve dominates the entropic contribution, there exists no depletion of free chains leading to purely repulsive interaction between the clay nanosheets. The purely repulsive nature of interaction curve is indicative of exfoliation of clay nanocomposites. For stronger negative value of χ parameter, the range of repulsion tends to increase mainly due to thicker height of grafted layer. This study shows that the strength of attraction well can be tuned by altering the compatibility between the grafted and the mobile chains.

B. Star Polymer Matrix

Next, we alter the architecture of the polymer matrix chain to star type branched polymer. Here, total number of Kuhn monomers in polymer, N_s , are divided in to ms number of arms each containing N_s/ms Kuhn monomers. The grafted polymer chain is linear with degree of polymerization being N_g . Fig. 3 compares the distribution of grafted monomers for linear and five-armed star polymer keeping $N_g = N_s = 100$, $\sigma = 0.25$, $L = 31$, $W = 3$, and $D = 33$.

Fig. 4 plots the monomer compositions for both the grafted and free chain as a function of distance in the region between two nanosheets. Four profiles are plotted for different architectures of the free chains in terms of variable ms , the number of arms. For a fixed degree of polymerization of the free chains, as the number of arms, ms , increases, the volume fraction of mobile monomers, belonging to star molecules, increases in the region between two nanosheets. Thus, the depletion of free chains becomes weaker for the star polymer in comparison to the linear polymer. This is attributed mainly to the small size of star molecule permitting it to be confined between claysheets without significant loss of conformational entropy.

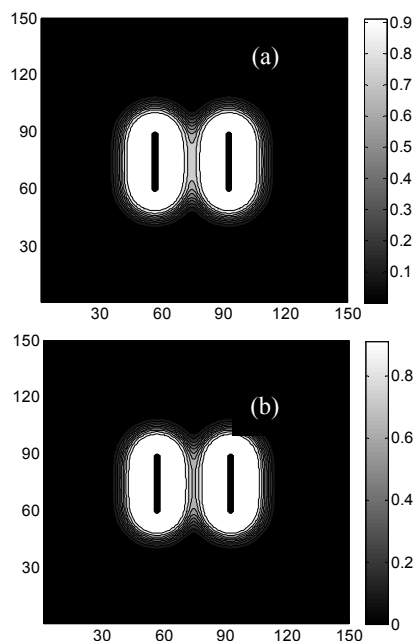


Fig. 3 Monomer density distribution of the grafted chains with $N_g = N_s = 100$, $\sigma = 0.25$, $L = 31$, $W = 3$, $D = 33$ for (a) $ms = 1$, and (b) $ms = 5$

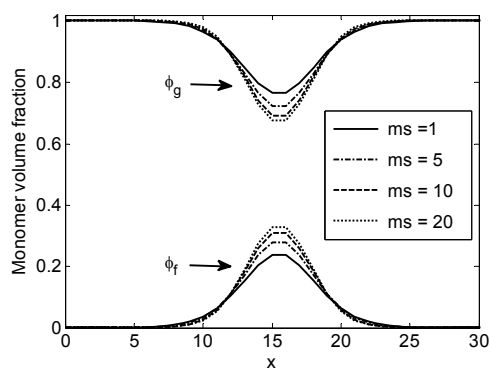


Fig. 4 Monomer density profiles of the grafted and the free chains with $N_g = N_s = 100$, $\sigma = 0.25$, $L = 31$ and $W = 3$ for various polymer chain architectures along the x direction

For two interacting nanosheets placed in a polymer melt, we calculate the interaction energy $F/\rho_0 k_B T$ for a given separation distance D . The interaction potential is given by

$$\frac{F}{\rho_0 k_B T} = F(D) - F(\infty). \quad (11)$$

$F(\infty)$, the reference state is the state where the two grafted sheets are far separated so that the monomer density distributions in the grafted layer on a nanosheet is uninfluenced by the presence of the other sheet.

Fig. 5 shows the interaction potential curves between two nanosheets for polymer matrix chains with varying number of arms. Upon increasing number of arms in a star polymer with a fixed degree of polymerization, depth of attraction well decreases. This is due to the weaker depletion of free chains

for the increasingly compact star molecules. Thus, the stability of the dispersion is enhanced by changing the architecture of free chains from linear to star polymer. The stabilizing effect of chain architecture in controlling the interactions between the polymer grafted nano claysheets can be utilized to improve the dispersion.

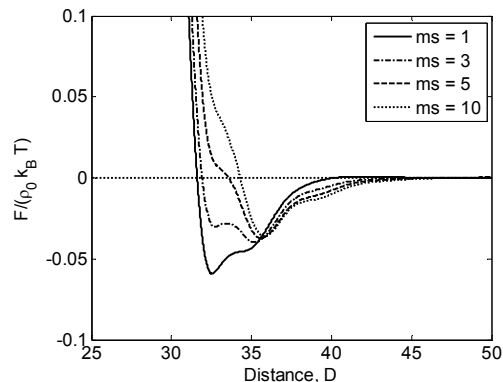


Fig. 5 The interparticle interaction between two polymer functionalized nanosheets as function of separation between them for various chain architectures with system parameters $N_g = N_s = 100$, $\sigma = 0.25$, $L = 31$ and $W = 3$

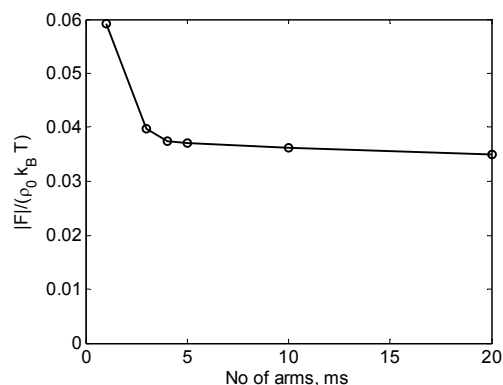


Fig. 6 Strength of attractive interactions between two polymer grafted nanosheets as a function of number of arms, ms , with the system parameters $N_g = N_s = 100$, $\sigma = 0.25$, $L = 31$, $W = 3$ and $D = 33$

The strength of the attraction well with the interaction parameter is shown in Fig. 6. It demonstrates that the strength of attraction well decreases as the number of arms of the free chains increases. After a certain number of number of arms, the depth of the attractive potential is found to be uninfluenced by the number of arms. Fig. 7 depicts the similar stabilizing role of chain architecture for degree of polymerization $N_g = N_s = 50$, keeping grafting density $\sigma = 0.25$.

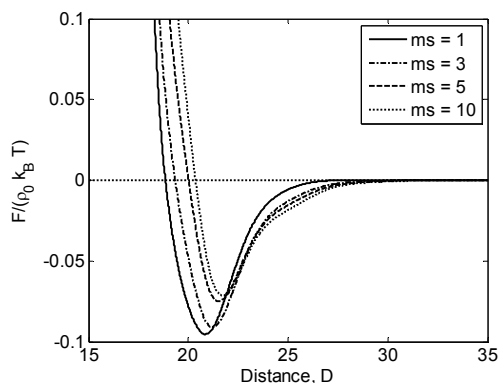


Fig. 7 The interparticle interaction between two polymer functionalized nanosheets as function of separation between them for various chain architectures with system parameters $N_g = N_s = 50$, $\sigma = 0.25$, $L = 31$ and $W = 3$

IV. CONCLUSION

The interaction potential between two nano-clay sheets grafted with linear polymer chains mediated by a polymer matrix is estimated using SCFT. For the matrix comprising of linear polymeric chains, we investigated the role of compatibility of free chains with the grafted chain, measured in terms of Flory's χ parameter. The favourable enthalpic interaction between the grafted and mobile chains tends to suppress the attraction potential at intermediate distance resulting in to purely repulsive interaction, indicative of exfoliated structure. For free chains chemically identical to the grafted chains, the quality of dispersion can be enhanced by modifying the architecture of free chains from linear to multiple-armed star molecule.

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