

# Enhanced Structure at the Interface Between the Polymer Matrix and Spherical Nanoparticles in Polymer Based Nanocomposites

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## ABSTRACT

The effect of a curved solid wall on the conformations of long, flexible polymer chains is studied in a dense polymer system by means of lattice Monte Carlo simulations. The differences with respect to the flat interface case are discussed. In the athermal limit the wall does not perturb the atom number density, which is constant throughout the volume of the polymer, however the chain end density is higher at the wall compared to the bulk and the bonds are preferentially oriented parallel to the interface. The intensity of these effects decreases with increasing wall curvature. These conclusions preserve qualitatively in presence of energetic interactions. The density at the wall decreases and the chain end segregation increases with increasing cohesive energy in the bulk polymer. The chain mobility is much lower in the close vicinity of the wall compared to the bulk. This effect increases with increasing wall curvature, which suggests that the experimentally observed reduction in chain mobility with filler radius has, in part, an entropic origin.

**Keywords:** Nanocomposites, Chain dynamics, Bound polymer layer.

## 1 INTRODUCTION

The allowable conformations of polymer chains are restricted in the neighborhood of impenetrable interfaces. The structure of the polymer is determined by the energetics of the interaction with the wall, by the cohesive energy in the bulk polymer, and by the loss in configurational entropy when the chain approaches the interface. The entropic force due to the reduction in the number of accessible chain configurations drives the chain away from the interface. The excluded volume effect in the bulk, and an attractive interaction with the wall promote the opposite trend. These issues have been studied extensively for the flat wall, experimentally [1,2,3], as well as analytically [4,5,6] and by means of simulations [7,8,9]. In the immediate vicinity of a flat impenetrable wall, the polymer chains are preferentially aligned in the direction parallel to the interface and have reduced mobility. The degree of alignment depends on the details of the energetic interaction with the wall. The volume of polymer affected by the presence of the interface (or the thickness of the “bound polymer layer”) is generally estimated to correspond to about two bulk gyration radii.

The present study addresses the effect of the wall curvature on the structure and mobility of polymer chains. Both the thermal (energetic interactions between polymers are considered) and the athermal (purely entropic case) conditions are considered. The investigation is based on computer simulations of idealized polymer chains confined by spherical impenetrable particles. The radius (curvature) of the fillers is kept as a parameter.

This work is part of an effort to understand the structural origins of the exceptional mechanical properties exhibited by polymer-based nanocomposites with ceramic nanofillers [10,11]. These materials show significantly enhanced stiffness and strength compared to the similar material filled with regular micron size ceramic particles. Most importantly, a gain in these properties does not compromise ductility, as is typically the case with conventional materials.

## 2 SIMULATION PROCEDURE

The study is performed by means of lattice Monte Carlo (MC) simulations. The simulation cell is shown in Figure 1. The volume surrounding a spherical particle of radius  $R$  (forbidden region) is filled with a monodisperse population of polymer chains of length  $N = 100$  bonds. The united atom model is used for the chains. The beads are freely rotating but no overlaps are permitted and the bond angles are defined by the underlying lattice. The polymers occupy a bcc lattice that fills the allowable volume. The dimension of the cell was taken  $L=50$  lattice units. Periodic boundary conditions are used.

Simulations in both thermal and athermal conditions are performed. No energetic interactions are imposed in the athermal case and the system is purely entropic. In the thermal case, the beads interact through a Lennard-Jones potential truncated at  $R_c = 2.5$ . No interaction with the filler particle is imposed in either case.

The simulation cell is filled with chains of the desired length and at the desired atom number density,  $\rho = 0.9$ , by performing self avoiding random walks (SAW) on the bcc lattice. No energetic interactions are considered in this phase. Once the simulation cell is filled with chains, the system is evolved by a MC procedure. Since the SAW mimics the athermal case, the initial chain structure corresponds to high temperature conditions. When considering energetic interactions, a slow “cooling” procedure needs to be applied before the structure is sampled at the desired temperature, in order to avoid trapping due to limited kinetics.

Two types of moves are performed with equal probability: the “slithering snake” or “reptation,” and the “crack shaft” move. The simulation evolves at constant number of atoms and constant volume. The polymer structure and chain mobility are obtained by averaging over time and over a number of replicas ( $N_c = 10$ ) of the system in order to reduce statistical noise.

The polymer structure next to the wall is monitored by dividing the polymer volume in bins in the radial direction,  $r$ , and by taking advantage of the spherical symmetry of the problem. The thickness of each bin is taken to be equal to one unit cell of the bcc lattice. The number density is computed in each bin for both the overall atomic population and for the chain end atoms. The average bond orientation is evaluated based on the second Legendre polynomial  $P_2^b = \frac{1}{2}(3 \cos^2 \theta_b - 1)$ , where the angle  $\theta_b$  is made by the bond vector with the radial direction at the current site (Fig. 1). For a random orientation of bonds,  $P_2^b$  vanishes, while a preferential orientation in the tangential direction leads to negative  $P_2^b$  values. The orientation is also computed for chain segments of length  $N_s = 8$  using a similar definition of segment orientation,  $P_2^s$ . The angle  $\theta_s$  is made by the end-to-end vector of the segment (between atoms  $i$  and  $i + N_s$ ) and the radial vector passing through atom  $i$ . The segment is conventionally assigned to the bin in which atom  $i$  resides.

The atom/bond mobility is evaluated based on the mean square displacement (or the diffusion coefficient) of beads. An atom was typically followed for 1000 MCS.

Further details of the procedure are presented in [12].

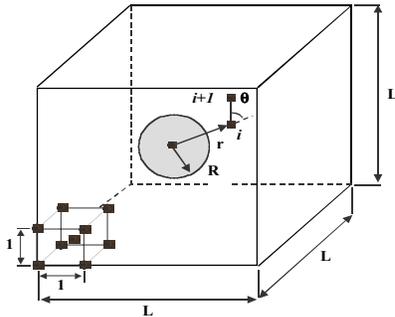


Figure 1: Schematic representation of the model.

### 3 RESULTS

The analysis is focused on two issues: the dependence of the molecular structure of the polymer in the vicinity of the interface on wall curvature, and the influence of the presence of the curved wall on chain mobility. The understanding of the polymer structure is expected to provide insight in the effect of fillers on the local material properties of the polymer matrix. The analysis of chain mobility is to reveal the physical origins of the scaling of

chain dynamics with filler size, as observed in polymer-based nanocomposites.

#### 3.1 Polymer Chain Conformations

The polymer structure was studied on the scale of a bond in the vicinity of curved and flat surfaces for various filler radii,  $R$ . In the athermal limit, it was observed that the presence of the solid wall does not influence the atom number density within the accuracy of the present calculations (the statistical noise is below 2%). In the thermal case and in absence of an attractive force between the polymers and the filler, the density in the immediate vicinity of the wall is slightly lower than that in the bulk. A similar effect was previously reported in the literature [13] for the flat wall.

In the athermal case, enrichment in chain end density of about 13% is seen in the atomic layer next to the wall, with the opposite effect manifested in the next layer. The thickness of the polymer layer affected by the presence of the wall is no larger than two bond lengths. Such an entropy driven effect was repeatedly reported in the literature [14,15] for the flat wall. This effect is more pronounced in the thermal case, and increases in magnitude with decreasing temperature.

The bonds are seen to be preferentially oriented in the direction parallel to the wall, in both cases, with and without energetic interactions in the polymer matrix being considered. The effect is limited to the first two bins in the immediate neighborhood of the wall. The result suggests that, when measured on the bond scale, the thickness of the “perturbed polymer layer” is rather limited. The preferential bond orientation is weakly sensitive to the presence of energetic interactions, which suggests that it is essentially a geometric effect.

The scaling of these parameters with the chain length was investigated. The bond orientation is rather insensitive to the chain length, while the chain end segregation increases significantly with this parameter (Fig. 2).

The main issue of interest here is the dependence of the various parameters defining the polymer structure on the wall curvature (filler radius). The results are shown in Fig. 2 for the athermal case and for selected systems with energetic interactions. Results obtained for the flat wall are included for reference. The entropic force leading to chain end segregation is more important in the flat wall case. This is a consequence of the fact that the spherical excluded volume of the filler particle has a weaker effect in reducing the number of allowable chain configurations compared to the much more constraining flat wall. This entropic driving force decreases with increasing wall curvature. The chain end segregation is more pronounced when considering energetic interactions, as mentioned above (isolated data point in Fig. 2). The vertical arrows represent the particle radius for which  $R$  equals the radius of gyration of the respective chain. The data points on the left of the arrows correspond to chain coils “smaller” than the filler, while

those on the right correspond to the filler particle being smaller.

The filler radius influences the degree of bond orientation in the neighborhood of the interface, with the maximum effect being observed for the flat wall. As already mentioned, adding energetic interactions (cohesive energy only) has no major effect on this parameter. The thickness of the polymer layer in which bonds are preferentially oriented is independent of chain length and particle size.

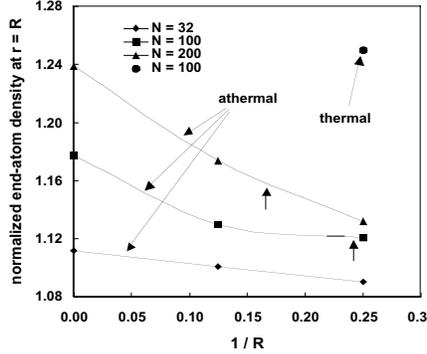


Figure 2a: Effect of wall curvature on chain end segregation.

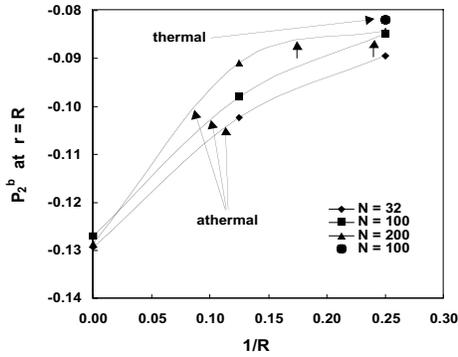


Figure 2b: Effect of wall curvature on preferential bond orientation in the immediate vicinity of the interface.

### 3.2 Chain Mobility

The chain mobility was evaluated as a function of the distance from the wall and for the athermal system only. The mean square atomic displacement during the MC evolution of the system is used as a measure of mobility. The diffusion coefficient may be derived from this quantity in the long time limit through  $\langle (r(s)-r(0))^2 \rangle = 2D_r s$  and  $\langle (t(s)-t(0))^2 \rangle = 4D_t s$ , where  $D_r$  and  $D_t$  are the diffusion coefficients in the radial and tangential direction, respectively. We refer here to the mean square atomic displacement rather than to the diffusion coefficient since only the short time response is of interest. As in the previous analysis, the polymer volume about the particle is divided in spherical bins, each bin having a thickness of 2. The atom trajectories are traced for about 1000 MCS and are assigned to the bin in which they reside at time zero.

It is observed that the mobility of the atoms located in the first bin next to the wall is significantly lower (about

half) than that in the bulk. However, the mobility in the second bin, at a distance roughly equal to one gyration radius from the wall, is similar to that in the bulk. Furthermore, the bulk is isotropic, as it should, with the mobility in the radial and tangential directions being equal.

Interestingly, the mobility in the tangential direction in the first bin is seen to be higher than that in the radial direction. To elucidate the origins of this effect, the trajectory of a chain was traced in a long simulation. It was observed that, although the pre-imposed probability of moves in the MC procedure is similar for reptation and crack-shaft moves, the chain as a whole diffuses by reptation. Considering that the bonds are preferentially oriented in the tangential direction in the first bin, it results that the beads move predominantly in this direction.

The effect of the wall curvature on bead mobility was further investigated. Figure 3 shows the normalized mean square displacement in both directions, measured at time  $t = 1000$  MCS, and as a function of the particle radius. The normalization is made with the values of the respective parameters in the bulk. As mentioned above, the mobility in the close vicinity of the wall is much smaller than in the bulk and depends on wall curvature. Increasing wall curvature leads to a reduction in mobility in both tangential and radial directions.

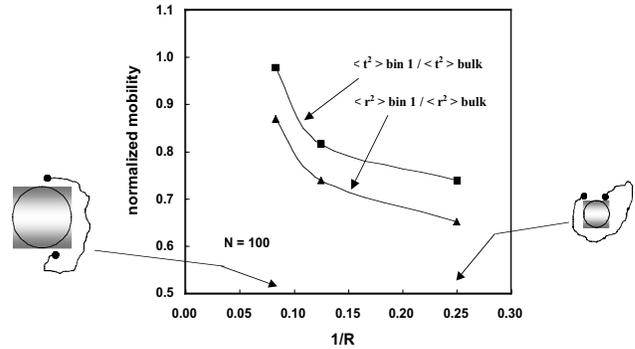


Figure 3: Variation of the normalized chain mobility in the radial and tangential directions with the wall curvature, in the first bin next to the wall. The normalization is made with the bulk mobility. The two insets show schematically the chain wrap-around phenomenon, which is proposed here as the physical mechanism leading to reduced chain mobility with decreasing filler size. The effect occurs when the chain radius of gyration is of the same order of magnitude with the filler radius.

This result is significant since it correlates with the observed reduction in chain mobility with decreasing filler size in nanocomposites (size effect). This experimental observation was attributed to the confining effect of the wall on the chains, i.e. the physical picture derived from the analysis of the flat wall configuration was extended to the case of a composite filled with nanoscale spherical particles. Here we suggest that the physics in this case is different. The intuitive picture is shown schematically in

Fig. 3. When the chain radius of gyration is smaller than the filler radius, the chains coil next to the interface, just as in the case on a flat wall. This leads to a reduction in mobility, especially in the radial direction. By contrast, when the two radii are comparable, the chains wrap around the filler, which leads to a dramatic loss of mobility in both radial and tangential directions.

In order to validate this physical picture, the end-to-end distance of chains located at various distances from the filler was computed. It was observed that when the chain radius of gyration is smaller or comparable to the filler radius, a significant fraction of the chains have their center of mass within the filler. This is, of course, impossible in the flat interface case, and becomes geometrically possible only when  $R_g/R > 1$ . This conclusion is further supported by the large increase in length of the end-to-end vector of chains having their center of mass within the particle. The swelling is more pronounced in the case of the larger particle ( $R = 8$ ,  $R_g = 4$ ). In this case, the chain does not completely surround the filler. The particle of radius  $R = 2$  is smaller than the bulk radius of gyration of the chain and hence may be fully contained within a chain, swelling being less important. Finally, this observation justifies in part the increased strength of polymer-based nanocomposites filled with particles having diameters on the order of the chain radius of gyration.

#### 4 CONCLUSIONS

The polymer structure and mobility in the vicinity of a curved impenetrable interface was studied by means of lattice Monte Carlo simulations. Systems with purely entropic interactions as well as with cohesive interactions in the polymer were considered. It was observed that the atom number density is not affected by the presence of the wall, being constant throughout the polymer, while chain ends segregate at the wall. The chain end segregation effect is more pronounced for long chains and for the flat wall. The chain end density depends on the presence of energetic interactions, the driving force for segregation increasing with increasing cohesive energy in the bulk polymer.

The wall induces preferential bond and chain segment orientation in the direction tangential to the wall. This effect is essentially insensitive to the details of the energetic interactions. The thickness of the perturbed polymer layer depends on the probing metric, being one bond length when the structure is probed on this scale, and larger, when the probing is performed on the chain segment scale. This suggests that experimental measurements of the perturbed polymer volume in a nanocomposite or a polymeric thin film depend on the radiation wavelength used for probing.

The mobility measured on the bond scale is affected by the presence of the wall in the immediate neighborhood of the interface only. Increasing particle curvature leads to a reduction in mobility in both the radial and tangential directions. It is shown that particles with a radius smaller than the bulk radius of gyration of the polymer chain act as

effective entanglement sites. The chain mobility is affected over a distance of about two radii of gyration from the wall. The chain wrap-around mechanism is proposed to explain, in part, the experimentally observed reduction in chain mobility with filler radius and the dramatic loss of mobility in nanocomposites in which the mean chain radius of gyration is comparable with the filler size.

#### ACKNOWLEDGMENT

This work was supported by the National Science Foundation through grant CMS 9908025 and by the Office of Naval Research through grant N00014-01-1-0732

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