

# Nanostructure of the Interface Modified by Grafted Polymers: A Monte Carlo simulation

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## Abstract

The thermodynamic, conformational and orientational properties of polymer melts grafted on a solid substrate were obtained from a novel Monte Carlo (MC) simulation of coarse-grained model of polyethylene (PE). The interface between a non-interacting hard surface and a bulk PE melt, with all chains of which are grafted on the plane, has been studied. Different PE melts, of mean molecular length from  $C_{40}$  and  $C_{80}$ , have been investigated, at grafting densities ranging from 0.92 to 1.85 nm<sup>-2</sup>. Profiles of monomer density and free end density, bond orientation, and average monomer position along a chain were studied. Quantitative measured in the simulations are derived from the analytical self-consistent field (SCF) theory and compared with the simulation data. The conformational and orientational properties can be quite accurately described by the theory, with some discrepancies observed near the wall and at the tail of the profile. Additional results concerning thermodynamic and surface energy of the brush are also presented.

## I. Introduction

Considerable research efforts has recently gone into the study of the nanostructure and physical properties of polymers end-grafted onto a solid surface. These systems are known as polymer brushes for sufficiently high polymer densities. The properties of brush depends on the density and the type of polymer molecules. Interfaces between polymers and solids play a key role in many industrial applications as adhesives, colloidal stabilizers, and lubricants.<sup>1-3</sup> Of great importance is the practice of improving the fracture strength of interfaces through the use of a few grafted chains.<sup>4</sup> Establishing quantitative relations between chemical constitution and macroscopic properties of such systems and predicting their structure and mechanical properties is highly desirable, because this can tremendously facilitate the rational design of multiphase systems containing macromolecular chains.

Grafted polymer layers have been studied both experimentally and theoretically. Analytical Self-Consistent Field (SCF) theory gives detailed solution of the equilibrium structural properties while experiments usually can only provide more global information like thickness, concentration and the force profile between two interacting brushes. The most interesting analytical theory of grafted polymer brushes has been developed by Milner *et al.*,<sup>5,6</sup> These theories are particularly attractive because they lead to closed-form expressions for the profiles of segment density  $\psi(z)$ , monomer potential  $U(z)$ , density of free ends  $\varepsilon(z)$ , and brush height  $h$ . They also suggest universal laws for the dependence of these quantities on chain length  $N$ , grafting density  $\alpha$ , and distance from the surface  $z$  or monomer position  $i$  along the chain.

Detailed information like the polymer chain trajectory, fluctuation etc. can conveniently be obtained in a computer simulation and compared with the SCF theory. Unfortunately, little simulation work has been performed for chains with chemically realistic architectures. In this work, a novel computer simulation technique capable of probing the structure of the interface between the solid substrate and grafted polymer melts at a prescribed grafting density is developed. This simulation allows us to obtain

detailed information about the conformational, structural, and thermodynamic properties near the solid substrate, while avoiding many of the assumptions invoked in the mesoscopic, SCF models, in analytical brush theories and past simulations of bead-spring or ideal chains.<sup>7-11</sup>

## II. Model and Simulation

The simulation employs the bridging technique that allows the interconversion between a fully atomistic representation of a structure in continuous space and a coarse-grained version of the same structure in the discrete space of a high coordination lattice.<sup>12</sup> This method has been recently employed to study the surface properties of various systems such as polymer nanofilm<sup>13-14</sup>, nanofiber<sup>15-17</sup> and nanoparticle.<sup>18</sup> The coarse-grained representation retains every second carbon atom on a lattice with  $10i^2 + 2$  sites in shell  $i$ . We study monodisperse grafted polymers, each chain containing  $N$  ethylene units, with  $20 < N < 40$ . The solid substrate was located at  $z = 0$  and  $z = M$ , where  $M > N$ . Beads were not allowed to move from  $z = 0$  to  $-1$ . The total number of available surface sites is  $40 \times 40$  (surface area =  $86.6 \text{ nm}^2$ ). We choose periodic boundary conditions in the  $x$  and  $y$  directions, while the two boundary in  $z$  direction are treated as hard impenetrable walls. The grafting density ( $\sigma$ ) is from  $0.92$  to  $1.85 \text{ nm}^{-2}$ . To model the PE chain, Rotational Isomeric State (RIS) formalism is used to model the short-range intramolecular interactions. The original RIS model for PE developed by Abe *et al.*<sup>19</sup> is modified for the coarse-grained model. Long-range intra- and intermolecular interaction among nonbonded units are incorporated into the simulations using the Lennard-Jones potential for ethylene units with  $\epsilon/k_B = 185 \text{ K}$  and  $\sigma = 0.44 \text{ nm}$ .<sup>20</sup> The second virial coefficient expression is utilized to assign an average interaction energy for each neighboring shell around a lattice site.<sup>21</sup> The system temperature is set to  $450 \text{ K}$ . Single bead and pivot moves on the lattice are accepted according to the Metropolis MC algorithm.<sup>22</sup> Analysis is obtained as an ensemble average of the subsequent  $10^6$  Monte Carlo Step (MCS) after equilibration. A snapshot is taken every  $10,000$  MCS during this period for analysis of the static properties.

## Results and Discussions

### A. Local melt density

Figure 1 presents the  $z$  variation of the density  $\rho$  of the  $C_{80}$  PE melt simulated, all chains of which are grafted on a hard substrate, as a function of  $\sigma$ . For the grafting densities studied,  $\rho(z)$  exhibits two zones of reduced density corresponding to two boundaries: the substrate/melt and the melt/vacuum interfaces. In contrast, the density practically remains constant in the bulk region independent of  $\sigma$ . The reduced  $\rho(z)$  values near the solid are mainly entropic origin caused by the presence of the boundary that limits the number of available conformation assumed by each grafted chain. The variable lattice model calculations<sup>23-24</sup> also showed the development of a reduced-density zone of width close to  $0.6 \text{ nm}$ , very similarly to the result in Fig. 1. The sigmoidal shape and the width of the profile at the upper boundary in Fig. 1 is typical of a melt/vacuum interface. The identification of the two zones where the melt density attains reduced values relative to the bulk demonstrates its power in elucidating some of the silent features underlying the structural and thermodynamic properties of grafted polymeric systems. These results

are in contrast to the usual practice in analytical or numerical theoretical models of grafted melts which, in their majority, invoke the assumption of a constant density everywhere in the interfacial region.

### B. Conformational properties

Information about the conformational properties can be extracted by studying the average chain conformational path defined as the average height  $\langle z(i) \rangle$  of backbone atom  $i$  above the grafting surface. Fig. 2 shows the reduced mean height  $\zeta(s)$  defined through  $\zeta(s) = \langle z(i) \rangle / \langle z(1) \rangle$  as a function of scaled coordinate  $s = i/N$ .  $\zeta(s)$  is an increasing function of atom ranking position  $s$  which means that, on the average, grafted chains develop upward without any back folding. According to analytical brush theories,<sup>5-6</sup> this graph should lead to a universal curve, independent of  $\sigma$ . All curves are seen to superimpose reasonably well with the SCF result,  $\zeta(s) = \sin(s\pi/2)$ , and fall approximately on a single curve implying  $\langle z_i \rangle$  is a function of  $i/N$  only. Despite their similarity, two universal curves present slightly quantitative differences especially for small  $N$  and  $\sigma$ . These can be attributed to: (a) analytical theory is based on the most probable trajectory, i.e., the trajectory that minimize the free energy of the brush; the rest of the conformational paths are neglected. In contrast, in the present simulations, the mean path is calculated as an ensemble average over all conformational path realized by all chains. (b) the molecular model in the simulations is much more detailed than that on which the theory is formulated.

### C. Distribution of monomers

Fig. 3 shows the probability distribution of monomers along a chain for  $C_{80}$  at  $\sigma = 1.39 \text{ nm}^{-2}$ . Interestingly, the end monomers can be anywhere in the brush. Thus there is a systematic deviation from the SCF theory which predicts no end bead at  $z = 0$ . The SCF also suggests a scaling plot of  $\rho_i(z)h \sin(i\pi/2N)$  versus  $z / \{h \sin(i\pi/2N)\}$ . Within the statistical accuracy of the simulation results, the curves obtained coincide, suggesting the existence of a master curve. However, the functional form of the master curve predicted is somewhat different than that of the curve derived by analytical theories. The comparison is poor for the region to the left of the maximum in the distributions which are rather concave in opposite to the SCF results. However, previous lattice Monte Carlo simulations<sup>9-10</sup> obtained distributions which were convex for small  $z / \sin(\frac{i\pi}{2N})$ . This may due to finite stretching of monomers as been shown by SCF theory. For larger values of  $z$ , the distribution decay more slowly than SCF prediction in agreement with other MD<sup>7-8</sup> and MC simulations.<sup>9-10</sup>

### D. Orientation

The profiles of the first-rank order parameter (from carbon atom  $i$  to  $i+2$ )  $\langle P_i(\cos\theta) \rangle = \langle \cos\theta \rangle$  are calculated as a function of  $N$  and  $\sigma$  where  $\theta$  is the angle formed between a chord vector and  $z$  axis. The positive order parameter was found even at the outer edges of the grafted layer which demonstrate that, on average, the grafted chains

develop outwards exactly as was inferred by the continuous increase of the function  $\langle z(i) \rangle$  for large  $i$ . From the SCF theory, the profiles of the function  $\lambda_1 = \frac{\langle r_1(\cos\theta) \rangle}{\sigma}$  should exhibit a universal behavior, independent of  $N$  and  $\sigma$  as  $\lambda_1 = \cos\left(\frac{i\pi}{2N}\right)$ . The data show a rough collapse except for monomers near the wall. This is expected since SCF theory does not take into account for the short range order effects near the wall. The MC data indicate the brush is less stretched but the stretching is quite uniform over the entire brush.

### E. Thermodynamics

The interaction energy of polymer brushes can be calculated directly from on-lattice energetics. Fig. 4 shows the profiles of short-range intramolecular (from the RIS model) and long-range intermolecular (discretized Lennard-Jones potential for PE on 2nd lattice) and the total energies as a function of  $z$ . The short-range energy drops, while the long-range energy increases at the interfacial region, the overall result being a slight increase in the total energy. Compared to the free surface region, intramolecular interaction decreases more for the beads closer to grafting surface as polymer chains adopt more *trans* conformation. The deviation from the bulk values starts at *ca.* 3 nm from the free surface which is broader than that from the grafted surface (*ca.* 1 nm).

The potential energy part of the surface energy,  $\gamma$ , can also be estimated using the equation:  $\gamma = (E_{\text{brush}} - \langle E_{3D} \rangle) / \text{area}$ . Here,  $E_{\text{brush}}$  and  $\langle E_{3D} \rangle$  denote the average potential energies of the polymer brush and bulk, respectively. The surface energy of this brush is 21.5 erg/cm<sup>2</sup>. The simulated<sup>13</sup> and experimental<sup>25</sup> values of thin film are 22.2 and 23.4 erg/cm<sup>2</sup> respectively.

### Conclusions

A methodology is presented for the study of grafted polymer melts through the coarse-grained PE model using lattice MC simulations. Equilibration of the melt configurations was made possible with the very efficient MC algorithm. PE melt systems consisting of grafted chains as long as C<sub>80</sub> were studied in a broad range of grafting densities. For melts consisting of only grafted chains, our simulation data verified many universal laws suggested by the analytical brush theories. However, the exact functional dependencies of certain descriptors of the brush conformational and structural characteristics on chain length and grafting density seem to be different from those derived analytically.

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## References

1. A. Halperin, M. Tirrell and T. P. Lodge, *Adv. Polym. Sci.* 100, 31, (1991).
2. S. T. Milner, *Science* 251, 905, (1991)
3. B. Zhao and W. J. Brittain, *Progress in Polymer Science*, 25, 677, (2000).
4. C. L. Clarke, R. A. L. Jones, J. L. Edwards, K. R. Shull, and J. Penfold, *Macromolecules* 28, 2042 (1995).
5. S. T. Milner, T. A. Witten, and M. E. Cates, *Macromolecules* 21, 2610 (1988).
6. S. T. Milner, T. A. Witten, and M. E. Cates, *Macromolecules* 22, 853 (1989).
7. M. Murat and G. S. Grest, *Macromolecules* 24, 704 (1991).
8. G. S. Grest and M. Murat, *Macromolecules* 26, 3108 (1993).
9. R. Toral and A. Chakrabarti, *Macromolecules* 23, 2016 (1990).
10. P. Y. Lai and K. Binder, *J. Chem. Phys.* 95, 9288 (1991).
11. I. M. Neelov and K. Binder, *Macromol. Theory Simul.* 4, 119 (1995).
12. J. Baschnagel, K. Binder, P. Doruker, A.A. Gusev, O. Hahn and K. Kremer *et al.*, Bridging the gap between atomistic and coarse-grained models of polymers, *Adv Polym Sci* 152, 41, (2000).
13. P. Doruker and W.L. Mattice, *Macromolecules* 31, 1418, (1998).
14. V. Vao-soongnern, P. Doruker, W. L. Mattice, *Computational Studies, Nanotechnology, and Solution Thermodynamics of Polymer Systems*, M. D. Dadmun, W. A. Van Hook, D. W. Noid, Y. B. Melnichenko, B. G. Sumpter, Eds., Kluwer Academic/Plenum Publishers, New York, 117, (2001).
15. V. Vao-soongnern, P. Doruker and W.L. Mattice, *Macromol. Theory Simul.* 9, 1 (2000).
16. V. Vao-soongnern and W. L. Mattice, *Langmuir*, 16, 6757, (2000).
17. V. Vao-soongnern and W. L. Mattice, *Macromol. Theory Simul.* 9, 570, (2000).
18. V. Vao-soongnern and W. L. Mattice, *Macromol. Theory Simul.* 10, 553, (2001).
19. A. Abe, R.L. Jernigan and P.J. Flory, *J Am Chem Soc* 88, 631 (1966).
20. J. O. Hirschfelder, C. F. Curtiss, B. B. Bird, *Molecular Theory of Gases and Liquids*; Wiley, New York, 1954.
21. J. Cho and W.L. Mattice, *Macromolecules* 30, 637 (1997).
22. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *J Chem Phys* 21, 1087 (1953).
23. D. N. Theodorou, *Macromolecules* 22, 4589 (1989).
24. D. N. Theodorou, *Macromolecules* 22, 4578 (1989).
25. S. Wu, *J. Colloid Interface Sci.* 31, 153 (1969).

## List of Figures

Figure 1 (a) Density profile as a function of the distance from the grafting plane of  $C_{80}$  PE melt all chains of which are grafted on a hard substrate, at  $\sigma = 0.92, 1.39$  and  $1.85 \text{ nm}^{-2}$ . In all simulations,  $T = 450 \text{ K}$ .

Figure 2 The normalized mean height  $\zeta(s)$  plotted as a function of the normalized bead coordinate  $s$  along chain contour, of the fully grafted  $C_{80}$  PE melt at  $\sigma = 0.92, 1.39$  and  $1.85 \text{ nm}^{-2}$ , and of  $C_{40}, C_{60}$  and  $C_{80}$  at  $\sigma = 1.85 \text{ nm}^{-2}$ . The solid line corresponds to the prediction of the Milner *et al.* theory.

Figure 3 The scaled distribution probability for  $i$ th monomer of the fully grafted  $C_{80}$  PE melt at  $\sigma = 1.85 \text{ nm}^{-2}$ . The points correspond to  $i/N = 0.2$  ( $\blacksquare$ ),  $0.4$  ( $\square$ ),  $0.6$  ( $\times$ ),  $0.8$  ( $\blacktriangle$ ) and  $1.0$  ( $\Delta$ ).

Figure 4 The average short-range, long-range and total energy of the system (normalized by number of beads and volume in each bin) as a function of distance from the grafting substrate of the fully grafted  $C_{80}$  PE melt at  $\sigma = 1.85 \text{ nm}^{-2}$ .

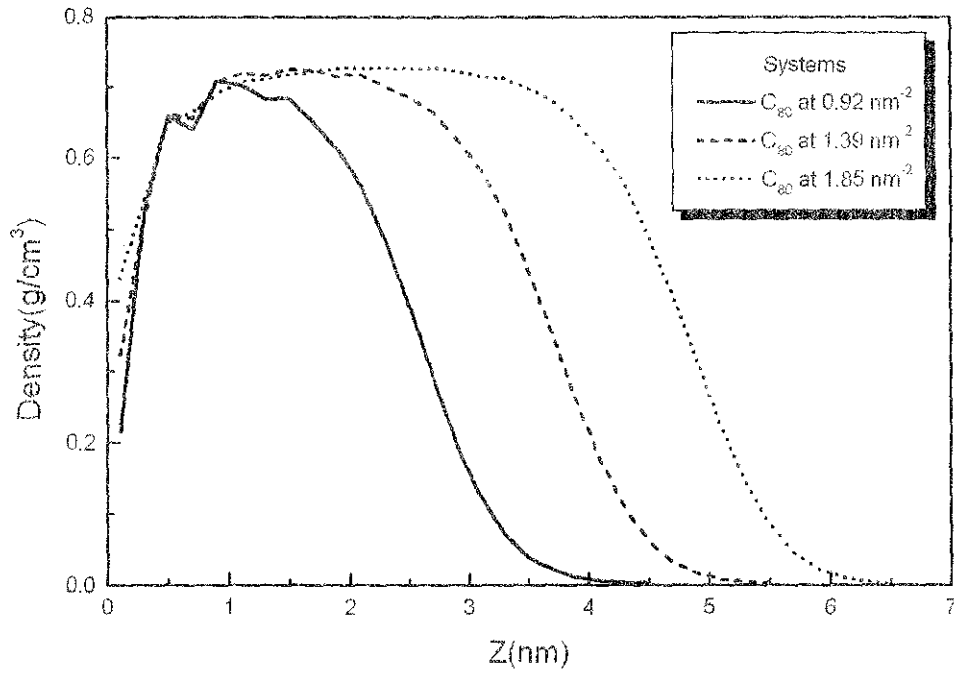


Figure 1

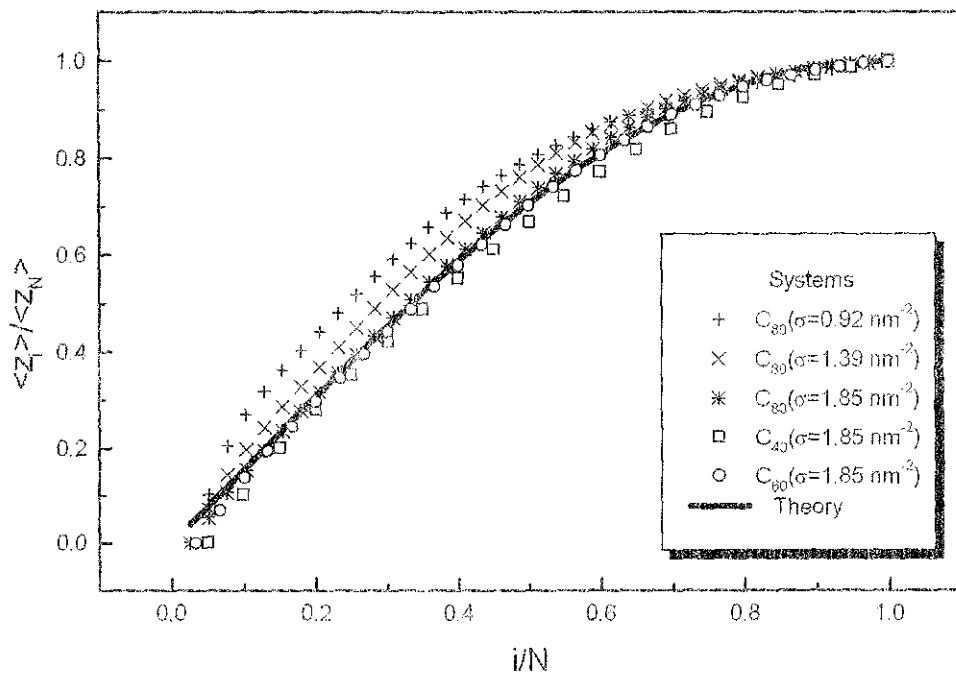


Figure 2

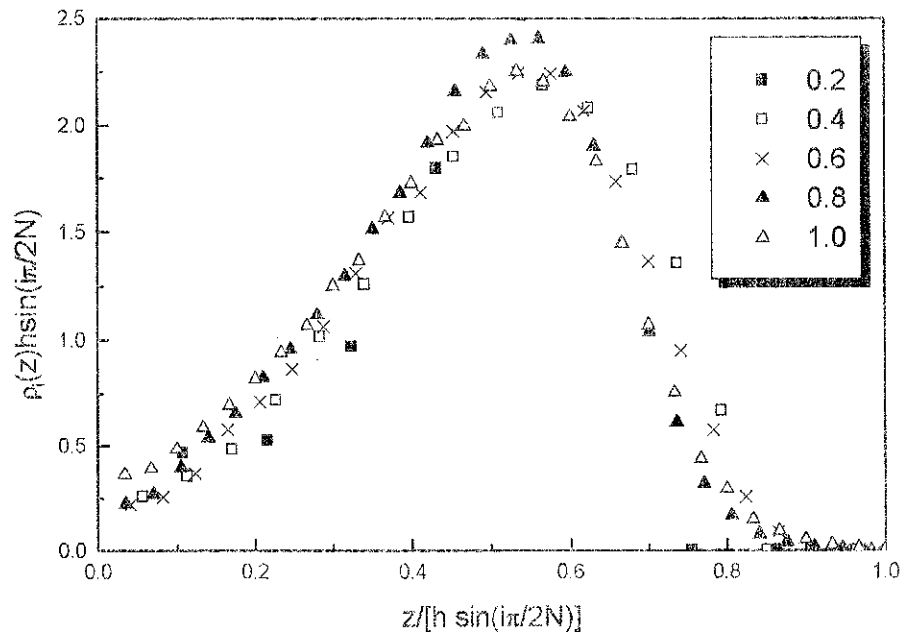


Figure 3

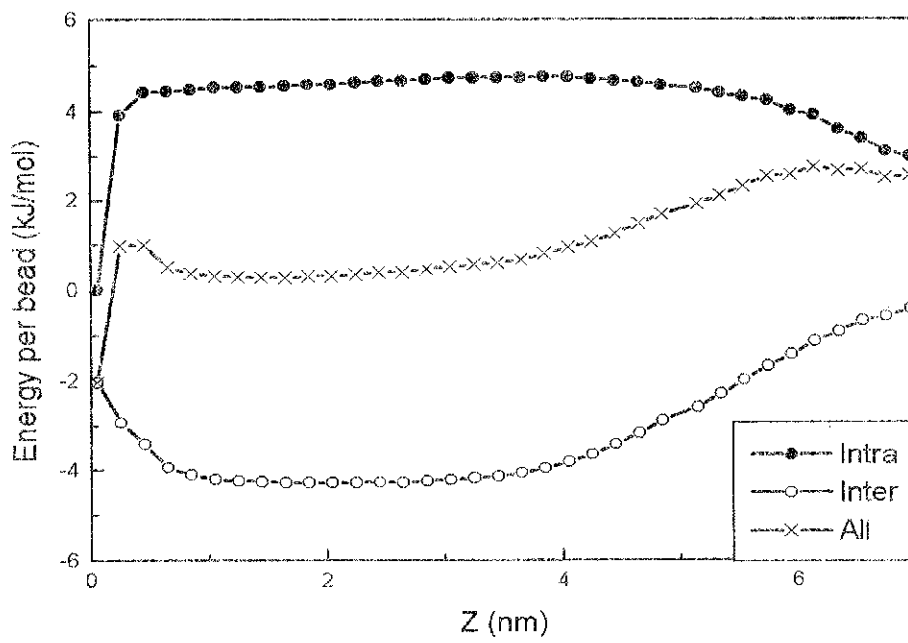


Figure 4