Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in Chemical Engineering

Polymer adsorption on rough surfaces

Abishek Venkatakrishnan[1,3] and Vikram Krishna Kuppa[2]

The adsorption of polymers on smooth or atomistically flat substrates has been a topic of study for decades, and such systems are well-characterized. However, there is little knowledge of the complex interfaces created by adsorption on heterogeneous surfaces: these are fundamental to numerous scientific and industrial systems, including organic optoelectronics, polymer–matrix composites, protein attachment, biomimetics, lubrication, and catalysis. Focusing on physical inhomogeneities, this paper presents an overview of the field of polymer adsorption on rough surfaces, and seeks to elucidate some of the relevant molecular mechanisms. Monte Carlo simulations are employed to study freely rotating chains adjacent to self-affine substrates, exploring the influence of surface fractal dimension and amplitude. The adsorbed polymers are characterized by density profiles and chain topologies evaluated parallel and perpendicular to the nominal surface. Our results reveal chain attachment and film structure can be controlled solely by manipulating entropic factors such as surface physical heterogeneities and adsorbate molecular weight distributions.

Addresses
[1] University of Cincinnati, United States
[2] University of Dayton Research Institute, United States

Corresponding author: Kuppa, Vikram Krishna (vikram.kuppa@gmail.com)
[3] Presently address: Raybestos Powertrain, LLC, United States.

Current Opinion in Chemical Engineering 2018, **19**:170–177

This review comes from a themed issue on **Materials engineering: Non-stick low friction materials**

Edited by **Jai Sekhar** and **Thein Kyu**

For a complete overview see the Issue and the Editorial

Available online 7th April 2018

https://doi.org/10.1016/j.coche.2018.03.001

Introduction

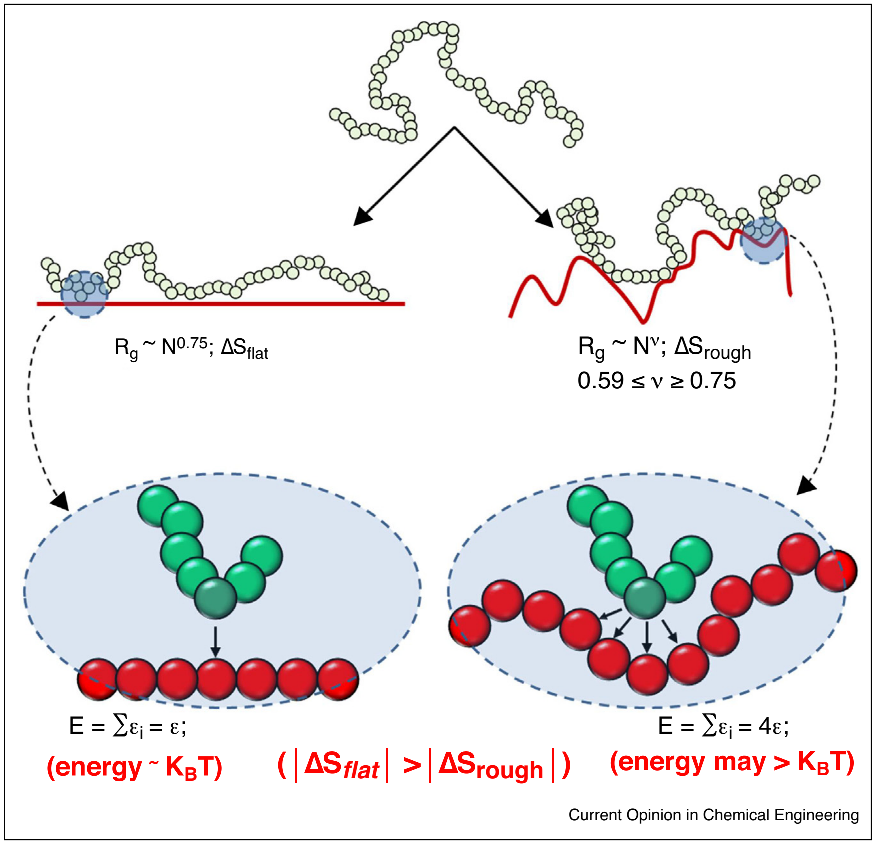
Polymer behavior and adsorption at smooth surfaces has been well studied by theory, experiment and simulation for a number of years [1•,2,3•,4•,5•,6•,7], but very little is known about chain interaction and adsorption on non-uniform surfaces. However, such complex interfaces are worthy of study and exhibit rich behavior arising from intricate relaxation processes. There exists at the present time, a considerable gap in the scientific understanding of polymer–substrate moieties. Addressing this knowledge gap will enable the rational design of a vast number of scientific and industrially relevant concerns, including protein adsorption [8], nanocomposites [9••,10] and catalysis and biomimetics [11]. Surface roughness also influences technologically significant processes like paint deposition, adhesion, substrate modification, lubrication, friction, and surface wetting and corrosion. As detailed in the Materials Genome Initiative Strategic Plan (MGI) [12], knowledge of polymer structure and morphology on realistic heterogeneous surfaces is imperative for the fabrication, design and efficient function of a range of materials manufacturing, composite processing and device fabrication technologies.

The thermodynamic and kinetic behavior of rough interfaces is very different from polymer interaction with flat substrates, Figure 1. Both entropic and enthalpic complexities arise from polymer configurational effects and contour matching with substrate curvature. The number of polymer–surface interaction sites and the distribution of interaction strengths will depend on surface structure, correlation length, physical asperities, surface fractal dimension, and on polymer length, stiffness, chemical composition and architecture. Of special interest is the manner in which nominally weak monomer–surface interactions are magnified solely due to changes in substrate topology: the resultant effects on system behavior at multiple length and time scales are still perplexing. Topological design thus assumes enormous significance, and such systems exhibit dynamic heterogeneity and unexpected structural features. The investigation of complex, fractally structured interfaces is therefore challenging.

Review of relevant literature

Polymer–substrate interfaces have been extensively studied because of their technological importance. Weak monomer–surface interactions are fairly well-understood [1•,2,3•,4•,5•,6•,7], while the more intricate case of strong adsorption [13–19] is comparatively unexplored. For both weak and strong interactions however, the overwhelming majority of studies have been performed on smooth, flat surfaces. Although useful for explaining broad trends, this assumption is invalid for most real polymer–surface interfaces. Due to the complex thermodynamics and long relaxation times, it is difficult to investigate equilibrium behavior, and there is a far smaller body of work concerning adsorption on non-uniform surfaces [20–27], mostly theoretical. There have been very few simulations and meager experimental work even though it is known that wetting is enhanced by making the surface rougher [28]. We focus below on the literature explicitly concerned with illustrating the role of substrate texture on adsorption of homopolymers.

Figure 1



Schematic illustrating how polymer adsorption is influenced by surface roughness. [Top] Near a textured substrate, chains are able to adopt conformations that are more similar to their 3-D coil structure, rather than a 2-D ‘pancake’. The entropic penalty associated with adsorption is therefore reduced. [Bottom] Enthalpic gains (monomer–surface interaction) may also be strongly dependent on roughness: For a smooth surface, a monomer interacts with only a single surface atom, and so attraction is comparable to thermal energy $E \sim k_BT$, weak interaction. For a rough surface of *identical composition*, attraction can be much stronger, even beyond simple enhancements due to higher surface area. This is because the monomer may interact with several proximal sites due to surface curvature, $E \sim 4k_BT$, strong interaction for the figure shown. Irreversible adsorption thus often results from physical heterogeneities on the surface even for weakly interacting chains.

Xu *et al.* [23] and Hone *et al.* [29] studied a sinusoidal surface profile theoretically, and calculated the adsorption of an infinitely long Gaussian chain with the ground state dominance approximation. Using Edwards’ formulation of the diffusion equation for an ideal chain in external field, Xu found enhanced adsorption on textured surfaces in comparison to smooth ones. In a similar vein, Hone considered different values of the wavelength and amplitude of the surface roughness in comparison with the thickness of the polymer layer and they were able to extract different regimes of adsorption. However, they assumed that chain crossover across the surface and attachment of the polymer on both sides of the surface is permitted. Ji and Hone [30] considered adsorption on curved surfaces from good solvents and found that interfacial tension is dependent on curvature (inner/outer surfaces of a sphere) and that for a sinusoidal grating, although kinetically hindered, it is favorable for the polymer to fill the deep holes or valleys on a rough surface.

Ball *et al.* used a mean-field argument with the ground state dominance approximation to investigate chain localization within a structured surface. They considered both sinusoidal [31] and random fractal surfaces [32]. They calculated enhanced polymer adsorption with respect to the flat surface, which was argued for in terms of the greater surface area of adsorption, and therefore larger enthalpic effects. Specifically, similar to the Hone work above, they found that highly attractive interactions (high enthalpy) led to binding of the chain at the valley depths in a curved surface, and entropic considerations favored attachment to the peaks. The existence of either state (adsorption on peaks or valleys) was determined by the interaction potential.

Douglas [33••] investigated how surface roughness affects polymer–surface interactions using an effective surface model, and renormalization group calculations. He predicted that increasing surface roughness, represented by an increase in fractal dimension, enhanced polymer–

surface interactions relative to the ideal planar surface. In contrast to Ball's work, this increase was attributed to the increased probability of interaction between monomers and surface, not due to the larger surface area. Douglas' theory also predicted the reduction in entropic penalty when chains adhere to a structured surface: the adsorption temperature is raised relative to a flat surface, thereby leading to counter-intuitive effects such as transforming a repulsive surface to attractive simply by changing its physical structure. However, the adsorption of polymer on a fractal surface is based on the assumption that the fractal has infinite extent. It would be interesting to study the same model for a finite length or extent of the fractal, and for real chains.

Baumgartner and Muthukumar [34••] studied the effect of surface roughness on the adsorption characteristics of an isolated chain using the propagator method, scaling arguments and Monte Carlo simulations. They also studied the unbinding of a polymer chain from a rough surface as the temperature is increased. The polymer chain was represented as a continuous curve of random-walk statistics without any monomer–monomer excluded volume interaction. The physically rough surface was modeled as a checker-board corrugation. Their MC simulations showed that the adsorbed state of a polymer on a rough surface exhibits three different regimes: localized, diffusive and discontinuous unbinding transition, and three temperatures corresponding to these transitions were identified. They also predicted that these temperatures would be strongly dependent on curvature, but neither curvature effects, nor random surface roughnesses were evaluated.

Gottstein *et al.* [35••] investigated the adsorption of a single chain polymer on structured surfaces using the bond-fluctuation model. Surfaces considered were flat; stick-like (i.e. posts); pyramids; and square holes (i.e. pores). They found that the onset of adsorption starts at the same temperature for all surfaces, indicating that the surface texture does not play an important role for first contacts. A faster adsorption on the pyramidal and stick-like surfaces were observed, due to a large energy gain and an easier route to get into contact with the structured surfaces. For all surfaces, adsorbed chains showed a 2-D like scaling of radius of gyration R_g, except for the square well porous surface. Striolo studied branched polymers [36] and surfactants [37] near square-well holed surfaces using MC simulations, and found that branched chains were repelled from the surface with increasing roughness. Recently, Nowicki *et al.* [38] showed that entropy penalty for chain adsorption on fractal surfaces was highly influenced by chain length and fractal dimension.

Sung *et al.* [39] studied the adsorption of a polymer on a surface with small-scale, Gaussian-correlated undulations using a variational method. They found that the adsorption temperature was lowered, due to reduction in entropic penalties. Their results showed that increasing adsorption strength led to preferential localization of chain segments in valleys. They also demonstrated that surface correlation length plays an enormous role in determining system properties, including segment distribution, free energy, and adsorption–desorption transition. Thus for example, for a given thickness of the adsorbed chain, desorption can be induced if the surface is random below a critical length. Vilgis and coworkers [40] considered various theoretical models for the adsorption of a single ideal polymer chain on disordered surfaces, and showed that adsorption was always enhanced with respect to flat surfaces. They attributed this result to the less restricted configurational entropy for chains adjacent to a rough surface [41].

There are very few experimental works that systematically investigate homopolymer adsorption on rough surface, while considering the effect of surface roughness. Shu *et al.* [9••] studied polymer nanocomposites with textured nanoparticles, and found enhanced composite properties, attributed to better interfacial adhesion. Gupta and coworkers [42••,43••] prepared surfaces of different roughness by thermal evaporation of gold, and probed the morphology and kinetics of poly(ethylene oxide) (PEO) adhesion. Surface plasmon resonance was used to measure chain kinetics. By studying two gold surfaces with different physical features, Gupta was able to ascertain the effect of roughness on polymer behavior. Rates of absorption were higher on rough substrates than smooth. They found that with an increase in surface roughness, chains were distorted from the 2-D shape, and higher adsorption was observed. Although they show results on the roughness of the surface and demonstrate fractal behavior, the real-space AFM images of their surfaces do not seem to show self-affine properties over a range of length-scales. Thus, it would be more appropriate to consider the nature of their surface to be mounded, rather than truly fractal. Furthermore, they only studied two surface roughness values, so a complete identification of the effects of roughness is not really possible. Nevertheless, Gupta's work is of immense significance, because to our knowledge, it is the only experimental work that attempts to systematically validate theoretical predictions.

We also mention here that there are a number of papers dealing with block copolymer, or heteropolymer (e.g.: proteins) adsorption on various surfaces [8,44]. For example, recent work by Russell [45,46] has studied faceted surfaces on silicon and sapphire, created by etching of single crystals. They show that it is possible to align block copolymers (directed self-assembly) by tuning entropic effects. In all scenarios, bulk polymer behavior is recovered at a sufficient distance from the surface, dictated by interaction strength, chain size, and property of interest [1•].

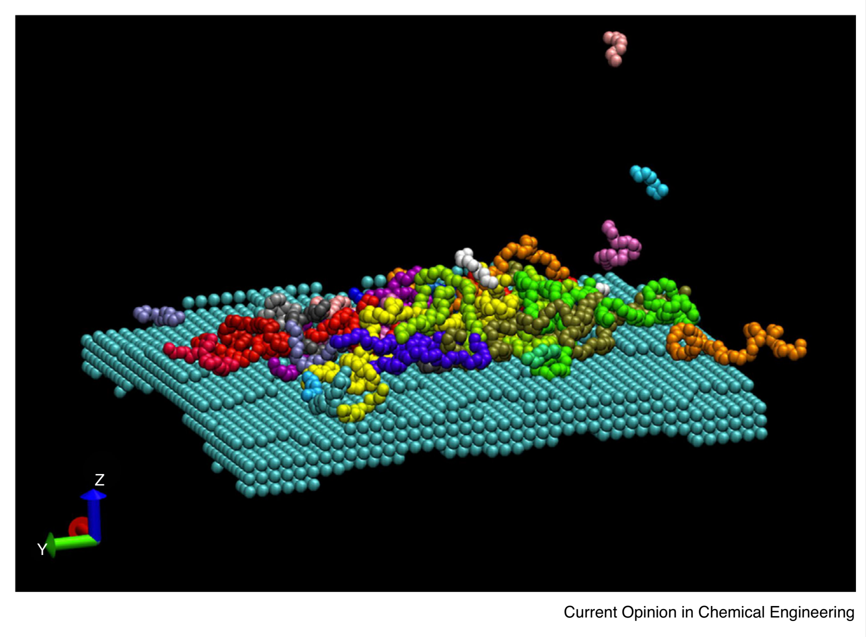
In summary, there is a surprisingly small body of literature dealing with polymer–rough surface interactions. Most of the work on this area has been theoretical, and uniformly predicts the following: enhanced adsorption on rough surfaces, lower entropic penalties, and more numerous enthalpic contacts. However, these predictions have not yet been conclusively verified, either by experiments or simulations. The effect of polydispersity on rough surface adsorption is also unclear. Increasing monomer–surface interaction also leads to irreversible adsorption, the study of which is unfeasible by conventional methods due to extremely long relaxation times.

Results and discussion

Recently, we proposed a path enabling equilibrium simulations of strongly adsorbed polymer interfaces [47••]. Here we exploit this accomplishment by identifying the molecular mechanisms that govern polymer properties next to attractive and rough surfaces. We employ Monte Carlo molecular simulations in the ($NnVT\mu$) ensemble. Polymer chains are represented by freely rotating chains, that is, with bond and angle potentials governing intrachain interactions, but without dihedrals. Polymer entities as well as surfaces are represented by spherical beads that interact via standard Lennard–Jones style potentials, representing non-bonded dispersive interactions: polymers are linear chains, while surfaces are represented by a network. Polymer–polymer bead interactions ($\varepsilon_{\text{monomer–monomer}}$) were set to 0.1kT, representing the interaction under good solvent conditions, while polymer–surface parameters ($\varepsilon_{\text{monomer–surface}}$) were set at 0.125 kT, and a system temperature of 1 kT. Simulation results are presented here in reduced units [48]: further details and protocols are available in our earlier work [47••,49••] and others [50]. Essentially, the simulation setup mimics the adsorption of polymers, dissolved in a good solvent, onto a textured, rough surface. Figure 2 shows a snapshot of the simulation box constructed to perform MC simulations. It is evident from the figure that some polymer chains (colored strings) are attached to the surface. This occurs via physical adsorption of the polymer, and is not due to any chemical bonding. Some smaller chains (top right of the figure) are desorbed from the surface.

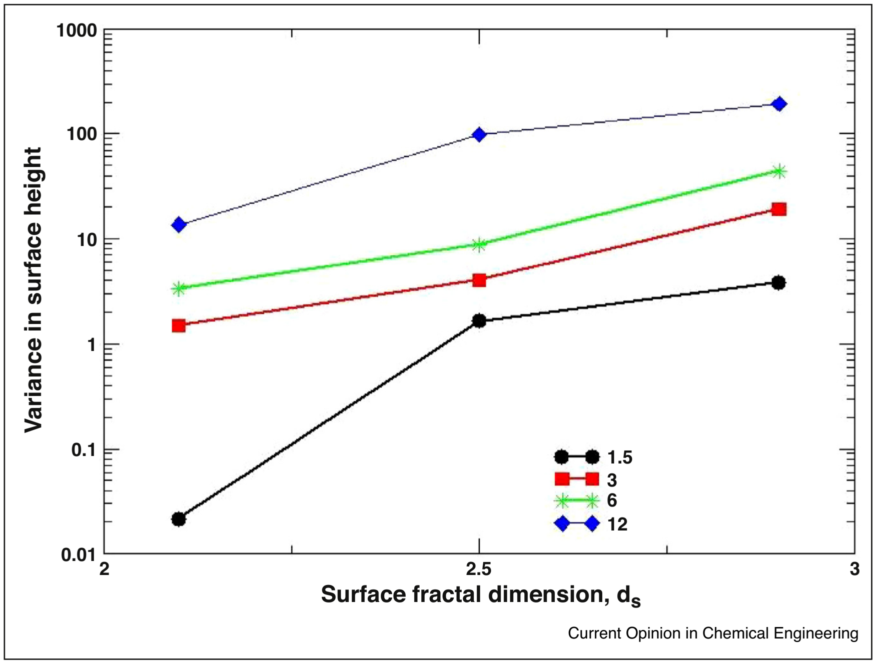
Self-affine fractal surfaces were constructed using a diamond-square algorithm [51], to vary the heights of the peaks: the surfaces were spread out along the XY plane, with normal along the Z-direction (height). Twelve different substrates were generated, with varying values of amplitude ($A(\sigma)$ = 1.5, 3, 6, 12, where σ is the diameter of a monomer or surface bead) and fractal dimension (d_s = 2.1, 2.5, 2.9). Increasing either the amplitude or fractal dimension (or both) lead to an increase in the physical heterogeneity (AKA texture, AKA roughness) of the surface [52], as shown in Figure 3. Each of these twelve surfaces were studied independently with the

Figure 2



Snapshot of the simulation box designed for studying polymer adsorption on rough surfaces. Cyan spheres show the substrate on which the different polymers — colored differently — are adsorbed.

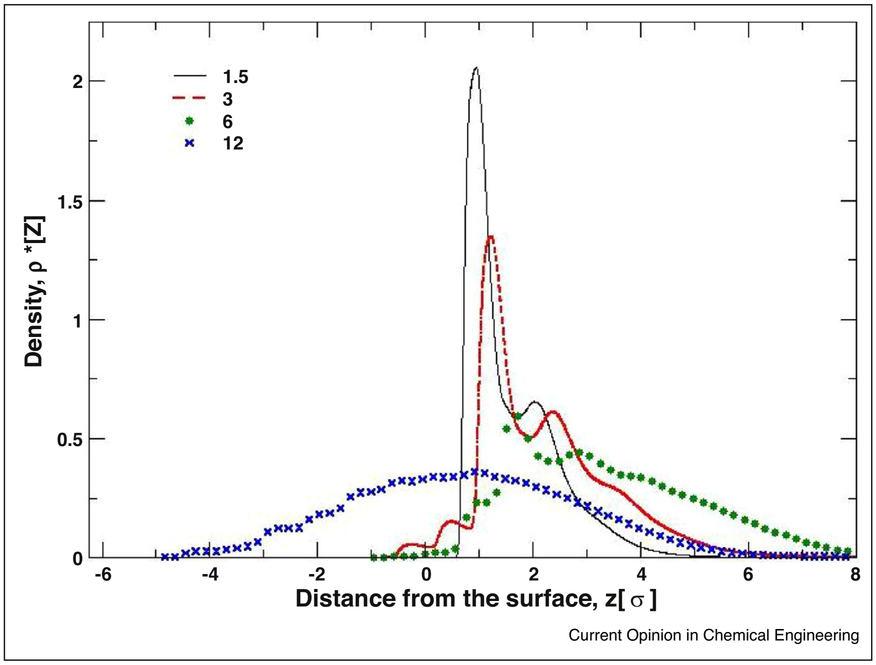
Figure 3



Current Opinion in Chemical Engineering

Variance in the heights of the beads constituting the various surfaces generated and studied in this research plotted against surface fractal dimension, for different amplitudes. Changing either the fractal dimension, or the amplitude or both resulted in different value of the roughness.

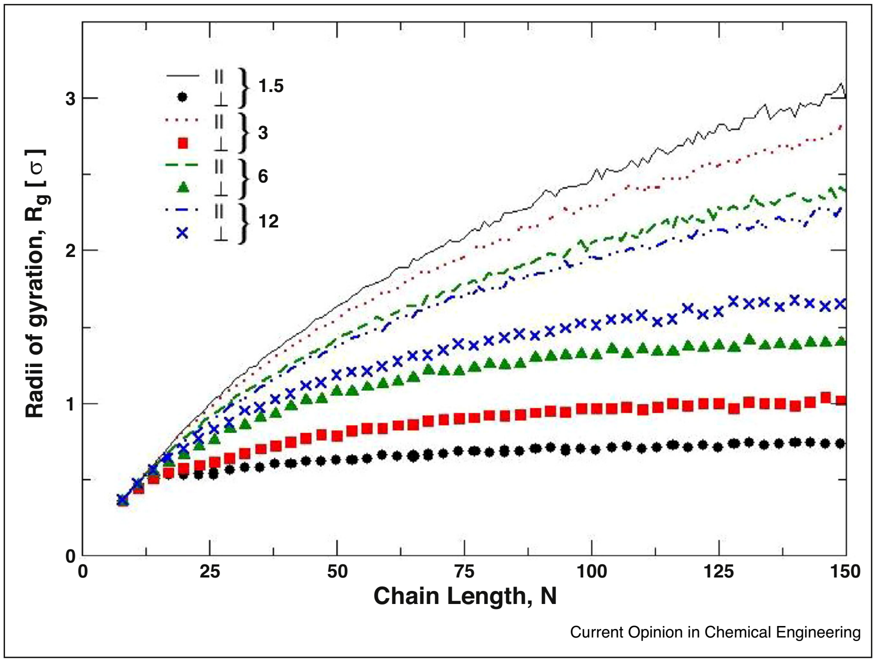
Figure 4



Current Opinion in Chemical Engineering

Density profile of polymer beads adsorbed onto substrates of different roughness amplitudes (black line, 1.5σ; red dashed line, 3σ; green circles, 6σ; blue crosses, 12σ) at a fractal dimension of 2.5.

Figure 5



Radius of gyration (R_g) in units of bead diameter (σ) as a function of chain length for polymers adsorbed onto substrates of fractal dimension 2.5, for different amplitudes.

same adsorbate, comprised of 2043 monomer beads distributed amongst 48 chains, each of which had allowed lengths between 8 and 1000 monomers. The chains were permitted to physically adsorb onto the surfaces in the simulations, and after equilibration of the system, the structure and chain statistics were investigated.

Figure 4 shows the density profiles of the polymer phase adsorbed onto surfaces of different amplitudes, at a d_s of 2.5. For the smallest amplitude (1.5), the density profile is orthodox, and is similar to those observed for other polymer–surface studies [53–55]. As the amplitude of surface heights (and thus, its roughness) increases, we observe profiles with more peaks ($A = 3$), before finally transitioning ($A = 6$) to a broad distribution spread across the entire corrugated structure ($A = 12$). With higher roughness, there is a greater surface area for the polymer to attach to, and thus the polymer phase is increasingly spread out over the entire available area. It is important to note that the relatively ordered structure resulting from adsorption on the smooth surface (sharp first peak, corresponding to the first neighbors, and the secondary shell) are masked when considering higher roughness values. This is due to the stochastic, fractally complex nature of the surface, which leads to diffuse and uncorrelated adsorption patterns. In these results, there is no difference between the different surfaces and the polymers, apart from the roughness of the substrates: all interactions and parameters are the same.

To further examine the role of roughness on adsorption, ensemble averaged radii of gyration (R_g) of all polymer chains in the system as a function of chain length are shown in Figure 5 at a d_s of 2.5, for different amplitudes. The R_g is indicative of chain structure and conformation, and in order to delineate adsorption and spreading, components of the R_g both parallel to the nominal surface (II) and perpendicular (⊥) are calculated. For the smoothest surface, chains tend to lie flat, that is, they are adsorbed along the surface and spread out laterally, as demonstrated by the higher parallel values of R_g. However, as the roughness increases, the discrepancy between the orthogonal components is reduced, and for the highest amplitude (i.e. roughest surface at this d_s) the difference is quite small. This structural data confirms the results indicated by the density profiles of Figure 4, demonstrating that as the substrate loses its purely two-dimensional character and gains three-dimensional attributes, the polymer chains follow suit and adsorb in a commensurate manner.

Conclusions

Interfaces such as those engendered when polymers adhere to rough surfaces exhibit complex thermodynamic and kinetic behavior. Such systems exhibit dynamic heterogeneity and unexpected structural features. The investigation of convoluted, fractally structured interfaces is therefore onerous. The paucity of work in the field is indicative of both the opportunities and challenges in studying this topic, and this manuscript surveys the literature on homopolymer adsorption on rough surfaces. Our research on Monte Carlo simulations reveals fundamental insights into the role of roughness on polymer structure. Although the normal way of controlling polymer adhesion to substrate is by changing enthalpy through surface chemistry, our results indicate that interfacial structure can be tuned via entropy-dependent parameters, while maintaining chemical composition. This provides a crucial lever in enabling surface engineering in situations where chemical modification is not possible or desirable.

Acknowledgements

VKK gratefully acknowledges support of this work from the Hanley Sustainability Institute and its Summer Scholarship Grant at the University of Dayton, and the National Science Foundation grant NSF CMMI-1636036.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. • Fleer GJ, Cohen Stuart MA, Scheutjens JMHM, Cosgrove T, Vincent B: *Polymers at Interfaces*. Chapman & Hall; 1993.
Seminal book on polymer adsorption.

2. Rubinstein M, Colby RH: *Polymer Physics*. Oxford University Press; 2003.

3. • Scheutjens JMHM, Fleer GJ: **Statistical theory of the adsorption of interacting chain molecules. 1. Partition function, segment density distribution, and adsorption isotherms**. *J Phys Chem* 1979, **83**:1619-1635.
Pioneering work on adsorption.

4. • Scheutjens JMHM, Fleer GJ: **Statistical theory of the adsorption of interacting chain molecules. 2. Train, loop, and tail size distribution**. *J Phys Chem* 1980, **84**:178-190.
See annotation to Ref. [3•].

5. • de Gennes PG: **Polymer solutions near an interface: adsorption and depletion layers**. *Macromolecules* 1981, **14**:1637-1644.
See annotation to Ref. [3•].

6. • De Gennes P: **Polymers at an interface; a simplified view**. *Adv Colloid Interface Sci* 1987, **27**:189-209.
See annotation to Ref. [3•].

7. Frantz P, Granick S: **Kinetics of polymer adsorption and desorption**. *Phys Rev Lett* 1991, **66**:899-902 http://www.ncbi.nlm.nih.gov/pubmed/10395766.

8. Rechendorff K, Hovgaard MB, Foss M, Zhdanov VP, Besenbacher F: **Enhancement of protein adsorption induced by surface roughness**. *Langmuir* 2006, **22**:10885-10888 http://dx.doi.org/10.1021/la0621923.

9. •• Shu S, Husain S, Koros WJ: **A general strategy for adhesion enhancement in polymeric composites by formation of nanostructured particle surfaces**. *J Phys Chem C* 2007, **111**:652-657 http://dx.doi.org/10.1021/jp065711j.
Experimental work showing how roughness enhances polymer attachment to fillers.

10. Oh H, Green Peter F: **Polymer chain dynamics and glass transition in athermal polymer/nanoparticle mixtures**. *Nat Mater* 2009, **8**:139-143.

11. Slocik JM, Naik RR: **Probing peptide–nanomaterial interactions**. *Chem Soc Rev* 2010, **39**:3454-3463 http://dx.doi.org/10.1039/b918035b.

12. **Subcommittee on the Materials Genome Initiative**. *Materials Genome Initiative Strategic Plan: Draft for Public Comment* 2014.

13. Johnson HE, Granick S: **Exchange kinetics between the adsorbed state and free solution: poly(methyl methacrylate) in carbon tetrachloride**. *Macromolecules* 1990, **23**:3367-3374 http://dx.doi.org/10.1021/ma00215a026.

14. Guiselin O: **Ireversible adsorption of a concentrated polymer solution**. *Eur Lett* 1992, **17**:225-230.

15. Granick S: **Perspective: kinetic and mechanical properties of adsorbed polymer layers**. *Eur Phys J E Soft Matter* 2002, **9**:421-424 http://dx.doi.org/10.1140/epje/i2002-10100-7.

16. Cohen Stuart MA, Fleer GJ: **Adsorbed polymer layers in situations**. *Annu Rev Mater Sci* 1996, **26**:463-500 http://www.annualreviews.org/doi/pdf/10.1146/annurev.ms.26.080196.002335 (accessed April 1, 2014).

17. O'Shaughnessy B, Vavylonis D: **Irreversible adsorption from dilute polymer solutions**. *Eur Phys J E* 2003, **11**:213-230.

18. O'Shaughnessy B, Vavylonis D: **Non-equilibrium in adsorbed polymer layers**. *J Phys Cond Matt* 2005, **17**:R63-R99.

19. O'Shaughnessy B, Vavylonis D: **Irreversibility and polymer adsorption**. *Phys Rev Lett* 2003, **90**:56103-56104.

20. Gorbunov AA, Zhulina EB, Skvortsov AM: **Theory of adsorption of macromolecules in cylindrical pores and at surfaces of cylindrical shape**. *Polymer (Guildf)* 1982, **23**:1133-1142 http://dx.doi.org/10.1016/0032-3861(82)90367-6.

21. Ligoure C, Leibler L: **Decoration of rough surfaces by chain grafting**. *Macromolecules* 1990, **23**:5044-5046 http://dx.doi.org/10.1021/ma00225a029.

22. Zhou H, Yang L, You W: **Rational design of high performance conjugated polymers for organic solar cells**. *Macromolecules* 2012, **45**:607-632 http://dx.doi.org/10.1021/ma201648t.

23. Xu X, Sun X, Yang Y: **Polymer adsorption between a rough surface and a flat surface for an ideal long chain**. *Acta Polym* 1995, **46**:145-151 http://onlinelibrary.wiley.com/doi/10.1002/actp.1995.010460208/abstract.

24. Nowicki W: **Structure and entropy of a long polymer chain in the presence of nanoparticles**. *Macromolecules* 2002, **35**:1424-1436 http://dx.doi.org/10.1021/ma010058d.

25. Skau KI, Blokhuis EM: **Polymer adsorption on curved surfaces: finite chain length corrections**. *Macromolecules* 2003, **36**:4637-4645 http://dx.doi.org/10.1021/ma021787b.

26. Hershkovits E, Tannenbaum A, Tannenbaum R: **Polymer adsorption on curved surfaces: a geometric approach**. *J Phys Chem C* 2007, **111**:12369-12375 http://dx.doi.org/10.1021/jp0725073.

27. Hershkovits E, Tannenbaum A, Tannenbaum R: **Scaling aspects of block co-polymer adsorption on curved surfaces from nonselective solvents**. *J Phys Chem B* 2008, **112**:5317-5326 http://dx.doi.org/10.1021/jp7097894.

28. Bonn D, Eggers J, Indekeu J, Meunier J, Rolley E: **Wetting and spreading**. *Rev Mod Phys* 2009, **81**:739-805 http://dx.doi.org/10.1103/RevModPhys.81.739.

29. Hone D, Ji H, Pincus PA: **Polymer adsorption on rough surfaces. 1. Ideal long chain**. *Macromolecules* 1987, **20**:2543-2549 http://dx.doi.org/10.1021/ma00176a038.

30. Ji H, Hone D: **Polymer adsorption on rough surfaces. 2. Good solvent conditions**. *Macromolecules* 1988, **21**:2600-2605 http://dx.doi.org/10.1021/ma00186a049.

31. Ball RC, Blunt M, Barford W: **Can surface bound states be induced by interfacial roughness?** *J Phys A Gen Phys* 1989, **22**:2587-2595 http://dx.doi.org/10.1088/0305-4470/22/13/049.

32. Blunt M, Barford W, Ball R: **Polymer adsorption and electron binding on rough and fractal surfaces**. *Macromolecules* 1989, **22**:1458-1466 http://dx.doi.org/10.1021/ma00193a076.

33. •• Douglas JF: **How does surface roughness affect polymer–surface interactions?** *Macromolecules* 1989, **22**:3707-3716 http://dx.doi.org/10.1021/ma00199a035.

Theory on polymer adsorption on fractal surfaces.

34. •• Baumgärtner A, Muthukumar M: **Effects of surface roughness on adsorbed polymers**. *J Chem Phys* 1991, **94**:4062 http://dx.doi.org/10.1063/1.460656.

Theory and simulation of polymer adsorption on checker board-like rough surfaces.

35. •• Gottstein W, Kreitmeier S, Wittkop M, Goritz D, Gotsis F: **Mont e Carlo simulations of the adsorption of a single polymer chain on rough surfaces**. *Polymer* 1997, **38**:1607-1613.

MC simulation of polymer adsorption on surfaces with stick-like, pyramidal and square hole defects.

36. Striolo A, Prausnitz JM: **Adsorption of branched homopolymers on a solid surface**. *J Chem Phys* 2001, **114**:8565-8572 http://dx.doi.org/10.1063/1.1362317.

37. Striolo A: **Adsorption of model surfactant like copolymers on nanopatterned surfaces**. *J Chem Phys* 2006, **125**:94709-94719 http://dx.doi.org/10.1063/1.2346676.

38. Nowicki W, Nowicka G, Dokowicz M, Mańka A: **Conformational entropy of a polymer chain grafted to rough surfaces**. *J Mol Model* 2013, **19**:337-348 http://dx.doi.org/10.1007/s00894-012-1546-5.

39. Sung W, Sung J, Lee S: **Effect of surface undulation on polymer adsorption**. *Phys Rev E* 2005, **71**:31805-31811 http://dx.doi.org/10.1103/PhysRevE.71.031805.

40. Vilgis TA, Heinrich G: **Disorder-induced enhancement of polymer adsorption — a model for the rubber–polymer interaction in filled rubbers**. *Macromolecules* 1994, **27**:7846-7854 http://dx.doi.org/10.1021/ma00104a047.

41. Huber G, Vilgis TA: **Polymer adsorption on heterogeneous surfaces**. *Eur Phys J B* 1998, **3**:217-223 http://dx.doi.org/10.1007/s100510050306.

42. •• Huang Y-W, Gupta VK: **Effects of physical heterogeneity on the adsorption of poly(ethylene oxide) at a solid–liquid interface**. *Macromolecules* 2001, **34**:3757-3764 http://dx.doi.org/10.1021/ma001780z.

Experimental work on polymer adsorption on rough surfaces.

43. •• Huang Y-W, Gupta VK: **Influence of polymer flux and chain length on adsorption of poly(ethylene oxide) on physically heterogeneous surfaces**. *Langmuir* 2002, **18**:2280-2287 doi:papers2://publication/doi/10.1021/la011529s.

See annotation to Ref. [42••].

44. Balazs AC, Huang K, Lantman CW: **Adsorption of triblock copolymers on rough surfaces**. *Macromolecules* 1990, **23**:4641-4647 http://dx.doi.org/10.1021/ma00223a023.

45. Hong SW, Voronov DL, Lee DH, Hexemer A, Padmore HA, Xu T, Russell TP: **Controlled orientation of block copolymers on defect-free faceted surfaces**. *Adv Mater* 2012, **24**:4278-4283 doi:papers2://publication/doi/10.1002/adma.201201279.

46. Hong SW, Huh J, Gu X, Lee DH, Jo WH, Park S, Xu T, Russell TP: **Unidirectionally aligned line patterns driven by entropic effects on faceted surfaces**. *Proc Natl Acad Sci* 2012, **109**:1402-1406 http://dx.doi.org/10.1073/pnas.1115803109.

47. •• Kuppa VK: **Molecular weight distribution effects on the structure of strongly adsorbed polymers by Monte Carlo simulation**. *J Chem Phys* 2012, **136**:214902-214913 http://dx.doi.org/10.1063/1.4725544.

Details of MC simulation technique used in this study, applied to strong polymer adsorption.

48. Allen MP, Tildesley DJ: *Computer Simulations of Liquids*. Clarendon Press; 1992.

49. •• Kuppa VK, in't Veld PJ, Rutledge GC: **Monte Carlo simulation of interlamellar isotactic polypropylene**. *Macromolecules* 2007, **40**:5187-5195.

Details of MC simulation technique used in this study.

50. Mavrantzas VG, Boone TD, Zervopoulou E, Theodorou DN: **End-bridging Monte Carlo: a fast algorithm for atomistic simulation of condensed phases of long polymer chains**. *Macromolecules* 1999, **32**:5072-5096.

51. Fournier A, Fussell D, Carpenter L: **Computer rendering of stochastic models**. *Commun ACM* 1982, **25**:371-384 http://dx.doi.org/10.1145/358523.358553.

52. Zhao Y, Wang G-C, Lu T-M: *Characterization of Amorphous and Crystalline Rough Surface: Principles and Applications*. Academic Press; 2001.

53. Gupta S, Koopman DC, Westermann-Clark GB, Bitsanis IA: **Structural patterns and molecular mobility inside the interface between an fcc solid and liquid n-octane**. *Chem Engr Sci* 1994, **49**:2907-2920.

54. Gupta S, Koopman DC, Westermann-Clark GB, Bitsanis IA: **Segmental dynamics and relaxation of n-octane at solid–liquid interfaces**. *J Chem Phys* 1994, **100**:8444-8453.

55. Chremos A, Glynos E, Koutsos V, Camp PJ: **Adsorption and self-assembly of linear polymers on surfaces: a computer simulation study**. *Soft Matter* 2009, **5**:637-645 http://dx.doi.org/10.1039/b812234b.