

ADSORPTION AND WETTING BEHAVIOR OF POLYMER DROPLETS THROUGH SIMULATIONS AND EXPERIMENTS

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ABSTRACT

Different structural compositions of a homopolymer droplet residing on a substrate may have marked effects on the wetting behavior of droplets under poor solvent conditions. In this work Monte Carlo computer simulations were utilized to probe the behavior of homopolymer droplets adsorbed at solid surfaces as a function of the number of chains making up the droplets and varying droplet sizes. One of the most striking results of the present analysis is the differences in the wetting and underlying adsorption mechanism between droplets comprising a single chain and droplets comprised of multi-chains.

INTRODUCTION

The adsorption of polymers onto a surface and the wetting of a surface by polymers are longstanding problems relating with a wide range of applications.^{1,2,3} For example, in surface coating and paint technology, the adsorption of polymers onto surfaces will determine the quality of spreading of the paint or coating. In adhesives, the adsorption of the adhesive polymer on the solid determines the strength of adhesion.⁴ Polymer-interface problems and thin polymer films is an area of extended studies both theoretical and experimental, where adsorption has been thoroughly studied.^{5,6,7,8}

Wetting of a surface by a polymer droplet and the underlying mechanism of adsorption of the polymer chains contained within the droplet differ essentially from those of low-molecular-mass substances. The differences are associated with the macromolecular size as well as with conformational aspects of the polymer chain (i.e., structure, functionality, etc). In addition the effect of the substrate and the environment render the problem of understanding and/or control the behavior of a polymer substance onto a surface a complicated issue.

The picture of single and multi-chain adsorption in good/theta solvents is well established.⁹ On the other hand, in poor solvents, a non-trivial interplay between effective monomer-monomer and monomer-surface interaction determines the chain conformation and the problem is very complicated. With the present work we aim to provide useful information concerning unexplored issues of adsorption under poor solvent conditions.¹⁰

MODELS AND SIMULATION METHOD

Single polymer chains and multi-chain droplets were simulated on a simple cubic lattice under poor solvent conditions next to an adsorbing surface located at $z = 0$, defining the horizontal. Monte Carlo (MC) simulations were performed in the canonical (NVT) statistical ensemble. To sample different configurations, Local Monte Carlo (LMC) moves respecting lattice positions and chain connectivity were employed.

We employed a coarse grained model whereby each monomer was reduced to a point, constrained on the vertices of the cubic lattice with lattice constant α ($\alpha = 1$) and associated through an effective well potential with other non-consecutive contact monomers (exempt first neighbors) and the substrate when it is at a distance of one lattice site apart (i.e., only segments at $z=1$ experience this potential). The monomer-monomer energy is denoted by $-E$, while the monomer-substrate energy by $-E_w$. Both energies are attractive so they attain negative values. In the present work, we explore $E = 0.45$ and $E_w = 0.3$ and 0.416 , in units of $k_B T$, where k_B is Boltzmann constant and T the absolute temperature. For a given chain, E implicitly determines the solvent quality, with increasing absolute values corresponding to decreasing solvent quality, $E = 0$ being the athermal solvent.¹¹

Droplets of three different sizes were simulated, namely of a total number of $N_T = 1000$, $N_T = 5000$, and $N_T = 10000$ monomers. Each system comprised a variable number of chains, n , of equal length (i.e., number of monomers), N . The number of chains in a droplet ranged from $n=1$ to as many as possible on the condition that the droplet maintained cohesion and its chains did not dissociate. It is noted here that for short enough chains it was entropically favourable to break apart from the original cluster. All $[N_T, N, E_w]$ combinations are shown in Table 1 (E is constant). Simulation details, as well as information about the force are given in our corresponding publications.^{10,7}

Table 1. The entirety of simulated droplets. Each $[N_T, N, E_w]$ combination uniquely specifies a droplet and the statistical ensemble to which that corresponds. ■ $E_w = 0.3$; ● $E_w = 0.416$. Systems for which a segregated state was statistically favoured are denoted by 's'. Chain lengths that were not permissible by division to give an integer number of chains in a droplet are denoted by 'n/a'.

| $N_T \backslash N$ | 100 | 125 | 200 | 250 | 400 | 500 | 650 | 1000 | 1250 | 2000 | 2500 | 5000 | 10000 |
|--------------------|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|-------|
| 1000 | ss | ■ s | ■ s | ■ ● | n/a | ■ ● | n/a | ■ ● | n/a | n/a | n/a | n/a | n/a |
| 5000 | ss | ■ s | ■ ● | ■ ● | n/a | ■ ● | n/a | ■ ● | ■ ● | n/a | ■ ● | ■ ● | n/a |
| 10000 | ■ s | ■ s | ■ ● | ■ ● | ■ ● | ■ ● | ■ ● | ■ ● | ■ ● | ■ ● | ■ ● | ■ ● | ■ ● |

RESULTS AND DISCUSSION

According to Table 1 the $N=100$ and the $N=10000$ single chain droplet are examples of the two ends of a series of simulated droplets containing a constant total number of monomers, $N_T = 10000$, and varying number of chains, $n = 1, 2, 4, \dots, 80, 100$, corresponding to respective chain lengths $N = 10000, 5000, 2500, \dots, 125, 100$.

Starting with the single chain droplet, in Figure 1 the perpendicular and the parallel to the surface components of the radius of gyration for $N = 1000$, $N=5000$ and $N = 10000$ droplets are presented. It is observed that for an overall increase of N by one order of magnitude (from $N = 1000$ to $N = 10000$), a rather weak increase of R_{gz} for both substrates happens. This weak dependence is compatible with an increase of R_{gxy} by approximately 2 times, showing that the monomers of each chain are preferentially distributed laterally and this is more pronounced at stronger adsorption conditions. Moreover, the R_{gz} dependence on N becomes weaker with increasing N (slope decreases), in agreement with our previous simulation study, where it was found that the thickness of a single chain adsorbate becomes independent of N as N increases.⁷

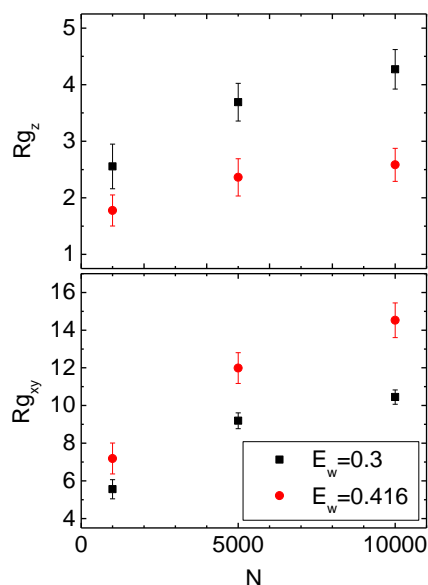


Figure 1. Perpendicular, R_{gz} , and horizontal, R_{gxy} , components of the radius of gyration of single-chain droplets as a function of chain length, N , for $N = N_T = 1000, 5000$, and 10000 under weak, $E_w = 0.3$ (black squares), and strong, $E_w = 0.416$ (red circles), adsorption in poor solvent conditions, $E=0.45$. (Figure from ref. 10)

In the following single chain versus multi-chain droplet behavior are juxtaposed. Figure 2 shows the wetting state of a droplet consisting of one (1) chain of $N=10000$ monomers compared to that of a droplet consisting of one hundred (100) chains of $N=100$ monomers. The total number of monomers is the same, as is their chemical identity, and the volume of the droplets. However, their shape is different. The single chain attains a flatter, pancake-like shape, while the multi-chain droplet attains a more globular shape.

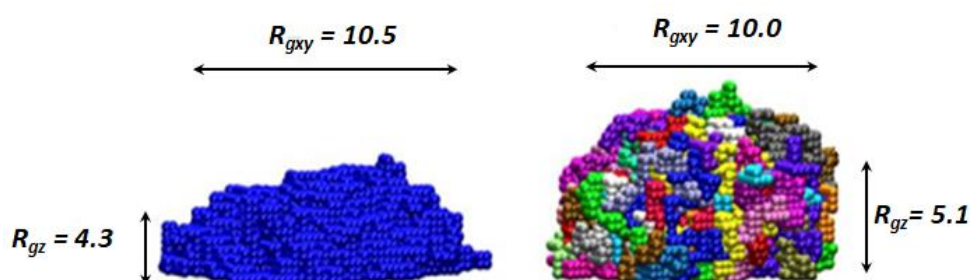


Figure 2. A droplet consisting of 1 chain of $N=10000$ monomers (left) and a droplet consisting of 100 chains of $N=100$ monomers (right) residing on a weakly attractive substrate, $E_w=0.3$, in poor solvent conditions, $E=0.45$. Horizontal, R_{gxy} , and vertical, R_{gz} , components of the radii of gyration of the combined system of chains at equilibrium wetting conditions.

In order to quantify the shape of the adsorbed polymer droplet and, therefore, describe its wetting state or contact angle the ratio of the perpendicular to the parallel component of the radius of gyration, R_{gz}/R_{gxy} , is calculated. A lower ratio denotes increased wetting (i.e., smaller thickness), whereas a higher ratio denotes decreased wetting (i.e., larger thickness). Weaker, $E_w=0.3$, and stronger, $E_w=0.416$, adsorbing substrates for a series of droplets with $N_T=10000$ are

presented in Figure 3. As reasonably expected, droplets exhibit a higher R_{gz}/R_{gxy} , or decreased wetting, on the weaker adsorbing substrate, $E_w=0.3$, and a lower R_{gz}/R_{gxy} , or increased wetting, on the stronger adsorbing one, $E_w=0.416$. An remarkable observation is that the droplet comprising the single chain, $N=10000$, lies flatter and wets the substrate more than the multi-chain droplet that attains a more globular shape and wets the substrate less. Furthermore, most multi-chain droplets share a common R_{gz}/R_{gxy} value. Trends are similar for both substrate types, $E_w=0.3$ and $E_w=0.416$, whereas the difference between the single chain and the multi-chain droplets is more pronounced in the latter case.

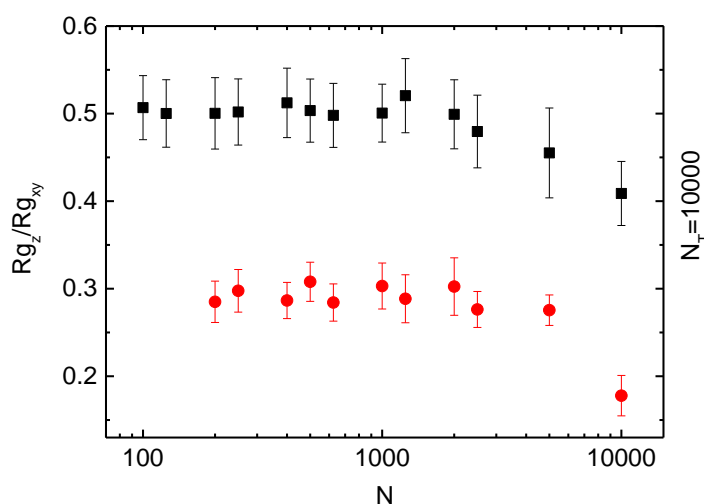


Figure 3. Ratio of the perpendicular to parallel component of the radius of gyration, R_{gz}/R_{gxy} , of droplets as a function of the molecular weight, N , of the constituent chains, for $N_T=10000$, under weak, $E_w=0.3$ (black squares), and strong, $E_w=0.416$ (red circles), adsorption in poor solvent conditions, $E=0.45$.

CONCLUSIONS

Polymer dewetting at a solid surface involves the formation of sessile droplets; the polymer chains are confined in a spherical cap between the solid substrate and the free polymer surface. We used Monte Carlo computer simulations to investigate the behavior of polymer droplets on solid surfaces as a function of the number of chains making up the droplets (keeping the total number of monomers constant) and varying droplet sizes (changing the total number of monomers). The wetting behavior was analyzed via the ratio of the perpendicular to the parallel component of the effective radii of gyration of the droplets. We investigated in depth the conformational behavior of the polymer chains within the droplets. Significant differences in the wetting behavior were observed: Single polymer chain droplets were found to lie flatter and wet the substrate more than chemically identical multi-chain droplets of the same size (same total number of monomers), which attain a more globular shape and wet the substrate less. This marked difference in the wetting behavior is in good agreement with atomic force microscopy (AFM) experiments.^{10,5} In conclusion we have demonstrated that conformational arrangements within droplets affect wetting behavior in an unexpected but predictable way and could be used to control the shape of the polymer droplets on solid surfaces.

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