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Computer simulations of the conformations of strongly adsorbed chains at the solid–liquid interface

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Abstract

We have utilized molecular dynamics simulations to critically study the conformation of isolated polymer chains adsorbed on surfaces in the presence of explicit solvent. The changes in conformations of the polymer chain in good solvent as it adsorbs onto a substrate is mapped. The quasi two-dimensional pancake conformation of a well adsorbed polymer chain is confirmed. The effect of wetting characteristics of the solvent on the adsorption transition of polymer chain is also studied. We found that a non-wetting solvent aids adsorption of the polymer chain even at low sticking energies compared to wetting solvent.

Keywords: Adsorption; Chain conformation; Interface

1. Introduction

The understanding of the structure and dynamics of polymer chains near a solid substrate have been of continuing interest due to their relevance to our understanding of coatings, colloid science and more recently in the field of nanocomposites. In particular, the adsorption crucially affects the dynamics of the polymer chain, which changes from 'bulk-like' to 'surface-like' thus leading, for example, to the formation of bound polymer layers. The pioneering experiments by Granick [1] on the surface diffusion coefficient, D, of single uncharged flexible chains adsorbed at the solid–liquid interface showed that $D \sim N^{-3/2}$, where N is the polymer degree of polymerization. In contrast, a much weaker scaling, i.e. $D \sim N^{-1}$ was found by Zhang and Granick for synthetic macromolecules adsorbed on fluid phospholipid layers [2]. Experiments by Radler for double stranded DNA chains adsorbed on a fluid phospholipid bilayer show a similar scaling, $D \sim N^{-1}$ [3,4] and the in-plane chain size following the predicted scaling $R_G \sim N^{3/4}$ [3–5]. While the scaling $D \sim N^{-1}$ is expected from the Rouse model [6], it is very difficult to a-priori understand why chains adsorbed on lipid layers follow this scaling, while chains adsorbed on a hard surface have a much stronger chain length dependence.

While the dynamic consequences of chain adsorption are truly intriguing, equally important is the delineation of chain conformation on surfaces. Scaling theory predicts that chains in good solvent have dimensions $R_g \sim N^{\nu}$, where $\nu = 0.588$ in 3-d, and 0.75 in 2-d [7]. While the experimental results of Radler are consistent with these predictions, a clear understanding of chain conformations in the vicinity of the adsorption–desorption transition is important for further understanding the dynamics of chains near surfaces, and hence in controlling the organization of polymer chains on the surface.

Binder and coworkers carried out computer simulations of the adsorption of isolated polymer chains [8,9]. These studies are consistent with theory, and predict that the dilute adsorbed chain assumes a 'pancake' conformation in which the size of the chain in the direction normal to the substrate is independent of N. The in-plane size for such well adsorbed chains is known in two dimensions and a good solvent environment to be $R_{g\|} \sim N^{3/4}$. It is important to note that these simulations were performed in vacuum, i.e. by using implicit solvent. In contrast, the experimental systems correspond to a dilute polymer solution in good solvent. Since some of the hypotheses presented by Granick et al. to explain the origins of the unusual $D \sim N^{-3/2}$ scaling attribute an important role to the hydrodynamic interactions created by the presence of solvent,

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we are strongly motivated to study the adsorption of a single polymer chain in an explicit solvent.

In this paper we employ molecular dynamics simulations of a single polymer chain in explicit athermal solvent sandwiched between two attractive walls so as to explore the effects of chain adsorption on conformation. In particular, we explore the adsorption transition as a function of attraction of the polymer chain with the wall, under three different wetting conditions of the solvent: (i) 'wetting solvent' where the solvent and the polymer chain are equally attracted to the wall and (ii) 'non-wetting solvent' where the solvent-wall interactions are repulsive, while the polymer-wall interactions are attractive. These results are compared to the case of an 'implicit solvent model' where the solvent is replaced by a stochastic force acting on the polymer chain. We study the changes in the conformation and orientation of the polymer chain as it goes through the adsorption transition. We show that the conformations of the adsorbed polymer, as well as the adsorption transition parameters depend on the wetting characteristics of the solvent.

2. Simulation model and procedure

The simulation model consists of a single polymer chain in the presence of explicit solvent sandwiched between two analytically flat walls. The lateral size of the system is a square of size L, while the distance between the walls is set to $M=13$, where σ is the unit for length (see below). We shall systematically check our results for finite size effects by varying L, but we shall not vary M since this quantity does not appear to affect the structure of well adsorbed chains considered here. The polymer chains are represented by the bead-spring model of Kremer and Grest [10–13]. Most of our simulations considered a single chain with $N=80$ beads, but we also considered chains of size $N=30$, 40, 60 and 120 in a few selected cases. Interactions between all pairs of chain monomers are described by a purely repulsive potential derived by truncating and shifting a Lennard–Jones [LJ] potential at its minimum: $U(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]+\varepsilon$ for $r<2^{1/6}\sigma$, and $U(r)=0$ for $r>2^{1/6}\sigma$. This potential is also known as the WCA potential [14]. All lengths are reported in units of σ. Adjacent bonded monomers via a FENE potential in addition to the LJ potential, which constrains the bond length to ~ 1.

The size of the solvent molecules is the same as the monomers in the polymer chain. To make the solvent athermal, the interactions between solvent–solvent, solvent–monomer and monomer–monomer are equal and described by the same truncated-shifted LJ potential explained above. In all the simulations with different simulation cell sizes, the total number of particles in the system are adjusted such that the reduced density, $\rho^*=\rho\sigma^3=0.74$ where ρ is the monomer number density. A simple velocity rescaling thermostat is used in all simulations with an explicit solvent to set the temperature $T=\varepsilon/k_{\mathrm{B}}$, where k_{B} is Boltzmann's constant. Finally, in all simulations we used an MD time step equal to 0.005τ, where $\tau=(\varepsilon/m\sigma^2)^{1/2}$. Periodic boundary conditions are applied in the directions parallel to the walls.

The walls are modeled as analytically smooth. The energy of interaction of a monomer with the wall is divided into two parts: the first originates from the inner 3-d LJ continuum semi-infinite solid, while the second is from a 2-d continuum plane immediately exposed to the solution. Thus, we follow the ideas of Steele [15] and integrate the interactions between all particles in the wall and the monomer of interest. We choose to use this model since it is computationally more efficient than considering a wall composed of explicit atoms. The density of the interior 3-d layer is $\rho_{\mathrm{B}}\sigma^3=1.05$, which corresponds to the density of a crystalline, closed packed (fcc) arrangement of monomers. The density of the planar 2-d layer is $\rho_{\mathrm{s}}\sigma^2=0.94$, corresponding to the density of a (111) fcc plane. These integrated potentials have attractive and repulsive parts, one from the 3-d continuum solid and one from the 2-d surface layer. The 2-d contribution to the repulsive part is,

$$U_{Nj}^{\mathrm{2Dr}}=\frac{4\pi\varepsilon\rho_{\mathrm{s}}\sigma^{12}}{5z^{10}} \tag{1}$$

where, z is the separation distance between the center of the solvent/monomer and the surface of the wall. Similarly, the 3-d contribution is,

$$U_{Nj}^{\mathrm{3Dr}}=\frac{4\pi\varepsilon\sigma^{12}\rho_{\mathrm{B}}}{45(z-\sigma/2)^{9}} \tag{2}$$

The $\sigma/2$ factor accounts for the fact that in our model the 3-d continuum starts $\sigma/2$ below the 2-d continuum plane. For the attractive part the 2-d contribution is

$$U_{Nj}^{\mathrm{2Da}}=\frac{4\pi\varepsilon\rho_{\mathrm{s}}\sigma^{6}}{2z^{4}} \tag{3}$$

while the 3-d contribution is

$$U_{Nj}^{\mathrm{3Da}}=\frac{4\pi\varepsilon\rho_{\mathrm{B}}\sigma^{6}}{6(z-\sigma/2)^{3}} \tag{4}$$

The total potential is the summation of the 2-d and 3-d contributions for both the repulsive and attractive parts. The attraction (or well depth) is manipulated by multiplying the total potential with a prefactor, K_{p}. The higher the value of K_{p}, the stronger is the attraction between the wall and solvent/monomer. All the results will be shown in terms of the well depth, ε_{w}, of the wall-monomer interaction, which is determined by the prefactor K_{p}.

For 'solvent-wetting' conditions, the interactions between the solvent and wall are same as those between a monomer and the wall. Thus, a solvent and the monomers are equally attracted to the wall. The driving force for adsorption is due to the effectively larger number density of the polymer chain with respect to the solvent due to a shorter monomer–monomer distance along the polymer chain caused by the FENE attractive potential.

For the 'non-wetting solvent' the wall-solvent interactions include only repulsive terms given by Eqs. (1) and (2). The polymer monomer-wall interactions are the same as described previously with both the repulsive and attractive parts, except that only the attractive part is multiplied by the prefactor, K_p.

A third class of models incorporates only implicit solvent, i.e. we use the polymer-wall potentials the same as for the wetting solvent case. However, no solvent is considered. The temperature is maintained by the application of additional stochastic forces acting independently on all monomers (mimicking collisions with the solvent). A corresponding viscous drag is also added. The viscous drag parameter is adjusted to a value such that the mean free path of the polymer chain is a small fraction of the monomer size. The amplitude of the stochastic noise via the dissipation fluctuation theorem is such that the temperature is set to $T^* = T/(\varepsilon/k_B) = 1.0$.

We equilibrated all structures over time intervals of around 3–4 million time steps. Such equilibrated structures are then used as starting structures for production runs of 50–100 millions MD steps over which we collect the structural data. Since the end-to-end distance correlation function decayed to zero over a time scale of three million MD time steps, we are convinced that our simulations characterize the true equilibrium states of these systems.

3. Results and discussion

3.1. Wetting solvent

3.1.1. Chain size

Here we present structural characteristics of a single polymer chain, $N=80$, adsorbed to the solid–liquid interface in the presence of a wetting solvent. First, we address the issue of system size so as to address finite size effects [16–19] as well as the computing time requirements. Fig. 1 shows a plot of the radius of gyration component normal to the wall, $R_{g\perp}$, for a range of L (10, 15, 20, 24, 30, 40). For $\varepsilon_w=6.3$ and $L=10$, where $c=N/ML^2=0.8$, the polymer chain monomers exhibit significant crowding on the interface. This leads to a relatively large $R_{g\perp}$ value, reflecting the fact that the chain segments desorb so as to reduce crowding and also to gain entropy. In fact, at this system size, the polymer chain desorbed in two out of the five realizations studied (over a 50 million MD step run). The value in the plot corresponds to the average over the three cases in which the polymer chain stays adsorbed. The $R_{g\perp}$ value decreases to a constant value ~0.6 for all $L>20$. At this system size the radius of gyration parallel to the interface also becomes size independent (not shown). This demonstrates that finite size effects on the static properties of the polymer chain can be minimized for $L>20$.

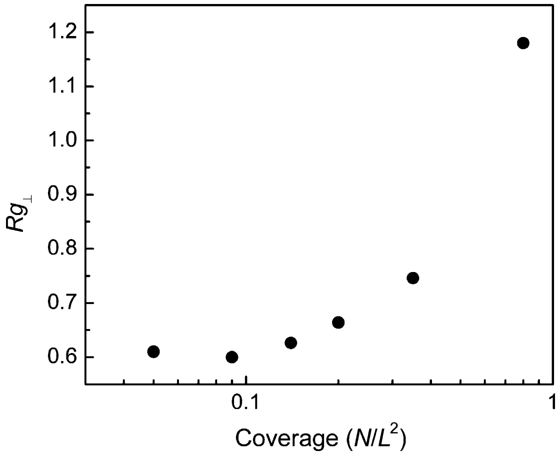

Fig. 1. The radius of gyration component normal to the wall, $R_{g\perp}$, of polymer chain length, $N=80$ for a selection of system sizes, L. The value of $R_{g\perp}$ decreases to a constant value ~0.6 with increasing L for $\varepsilon_w=6.3$.

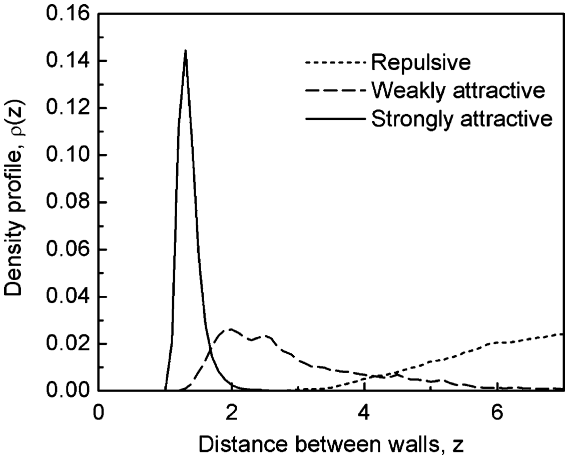

Fig. 2. The density profile, $\rho(r)$, of the center of mass of the chain ($N=80$) as a function of distance from the wall. Three cases are shown: repulsive, weakly attractive and strongly attractive walls ($\varepsilon_w=0$, 3.15 and 6.3).

3.1.2. Adsorption transition

In Fig. 2 we plot the number density profile, $\rho(z)$, of the center of mass of the chain (averaged over the total production run) as a function of distance from the wall, z. Three different values of $\varepsilon_w=0$, 3.15 and 6.3, respectively, are shown. Since the two walls are identical the density profiles from the two walls should be the same: to improve the statistical quality of the data we have averaged the data from the two halves, and we show data only from one half of the system.

For $\varepsilon_w=0$, there is a single peak at the center of the film, and the polymer density profiles decay to zero near the walls. Since a chain loses roughly 1 k_BT on adsorption (associated with entropic loss on confinement), the chain is depleted from the surface in the absence of a favorable energetic gain on adsorption. At $\varepsilon_w=3.15$ the peak at the center disappears, but two new broad peaks develop in the vicinity of the walls. For this attraction strength the polymer chain actually undergoes multiple adsorption and desorption events. This is caused by a close balance between energy related attraction and entropic repulsion. For stronger wall attraction ($\varepsilon_w=6.3$) the chain is effectively irreversibly adsorbed on the wall, and the density approaches zero at the center. This does not mean that the chain will never be desorbed, but that the residence time for such conditions is very large. In fact, during our MD simulation run time we never observe a chain desorption event. There are two important messages here. First, the chain in solvent can undergo an adsorption transition even in the presence of a solvent that is nominally of identical structure and interactions. Second, the adsorption transition is rounded and may not be regarded as a phase transition. This result is almost certainly due to the finite size of the polymer chains in question, as well as due to the fact that we considered isolated polymer chains.

3.1.3. Change in conformation on adsorption

It's a well-established fact that the typical shape of a three dimensional polymer chain is ellipsoidal rather than spherical [20–23]. It will be interesting to investigate the change in shape as a function of the adsorption state of the chain molecule. The shape of a polymer coil is characterized by the eigenvalues (or principal moments) $\lambda_1^2 < \lambda_2^2 < \lambda_3^2$ of the radius of gyration tensor, Q, defined as

$$Q_{\alpha,\beta} = \frac{1}{2N^2} \sum_{i,j=1}^{N} [r_{i,\alpha} - r_{j,\alpha}][r_{i,\beta} - r_{j,\beta}] \qquad (5)$$

where, r_i represents position of the ith monomer along the chain, α, $\beta = 1,2,3$ denote Cartesian components. The sum of these three eigenvalues equals gives the square of the radius of gyration, R_g^2.

In Fig. 3 we plot the value of the smallest eigenvalue, λ_1, and the radius of gyration in the direction normal to the wall plane, $R_{g\perp}$, as a function of attraction strength parameter, ε_w. We observe that both $R_{g\perp}$ and λ_1 decrease monotonically with increasing ε_w. The steepest change corresponds to the region around $\varepsilon_w \sim 4.2$. Furthermore, λ_1 becomes essentially equal to $R_{g\perp}$ for $\varepsilon_w > 5.25$. This demonstrates that, upon adsorption, the polymer chain assumes a pancake conformation and with its shortest axis normal to the wall. This conclusion is verified by our calculation of the ensemble averaged directional cosine, $\langle \cos^2\theta \rangle$, where $\cos\theta$ is a dot product between the unit eigenvector corresponding to λ_1 and the z axis (representing the normal to the wall). We find that this quantity changes from about 0.33 (random orientation) for non-adsorbed chains to one for adsorbed chains. This result verifies that the axis corresponding to λ_1, the shortest eigenvalue, becomes normal to the surface on strong adsorption.

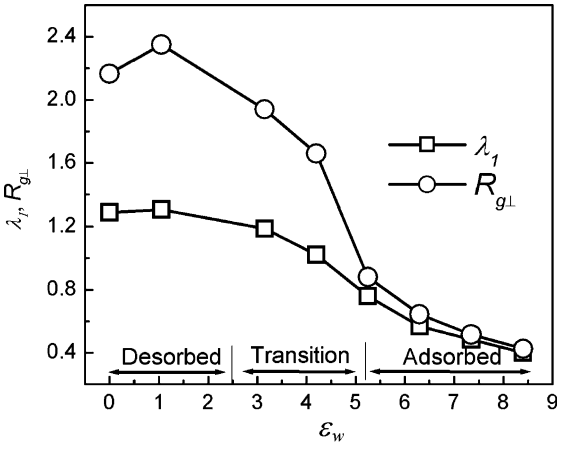

Fig. 3. The eigenvalue, λ_1, that represents the shortest axis of the polymer chain ($N = 80$) and the radius of gyration component normal to the wall, $R_{g\perp}$, plotted as a function of increasing attraction with the walls, ε_w. We see a monotonical decay suggesting a transition from desorbed chains to fully adsorbed chains.

Table 1

Shape factors, *sfi*, where [$i = 1,2,3$] and radius of gyration, for chain length $N = 80$, at various degrees of attraction, ε_w, with the wall

ε_w	sf_1	sf_2	sf_3	R_g^2
0.00	0.058 ± 0.001	0.167 ± 0.0075	0.774 ± 0.015	28.5 ± 0.5
1.05	0.059 ± 0.003	0.176 ± 0.004	0.765 ± 0.02	29.0 ± 1.0
3.15	0.040 ± 0.001	0.147 ± 0.0075	0.813 ± 0.015	35.6 ± 1.0
4.20	0.025 ± 0.001	0.143 ± 0.006	0.832 ± 0.004	41.4 ± 1.0
5.25	0.013 ± 0.001	0.140 ± 0.0075	0.847 ± 0.015	45.5 ± 2.5
6.30	0.006 ± 0.0003	0.142 ± 0.010	0.851 ± 0.020	51.5 ± 3.0
7.35	0.005 ± 0.0007	0.160 ± 0.010	0.835 ± 0.020	51.9 ± 3.5
8.40	0.003 ± 0.0003	0.172 ± 0.010	0.824 ± 0.020	49.9 ± 3.0

The transition of a polymer chain to a pancake type conformation can be further characterized via shape factors defined as ratios of $\lambda_1^2 : \lambda_2^2 : \lambda_3^2$ to R_g,

$$sf_i = \frac{\langle \lambda_i^2 \rangle}{\langle R_g^2 \rangle} \qquad (6)$$

where, $i = 1, 2, 3$. For spherical molecules $sf_i = 1/3$, whereas for a long rod shaped molecules $sf_1 = sf_2 = 0$ and $sf_3 = 1$. The analytical expressions for (sf_1, sf_2, sf_3) gives (0.059, 0.165, 0.776) for self avoiding walk (SAW) statistics in three dimensions [24,25]. Our simulations for desorbed chains ($\varepsilon_w = 0$) give shape factor values of (0.058, 0.167, 0.774), which are consistent with literature [26] estimates.

Table 1 shows the values of sf_i for different ε_w. The value of sf_1 decreases with increasing chain affinity to the surface. Correspondingly, both sf_2 and sf_3 increase, demonstrating a change from the ellipsoidal shape in bulk solution to an elliptical disk on adsorption to a 2-d surface. Throughout the adsorption 'transition' the sf_2/sf_3 ratio is constant (within simulation uncertainties), indicating that the change in shape of the polymer chain on adsorption is isotropic with respect to both principal directions in the plane of the surface. Finally, Table 1 shows that there is an increase of radius of gyration, R_g, as the polymer is adsorbed on the surface.

To further establish that the chain becomes an elliptical disk on adsorption we note the following prediction based on scaling theory. First, the chain size normal to the surface becomes independent of N, the chain degree of polymerization. Further, for a self-avoiding walk the in-plane dimensions must scale as $R_{g\parallel} \sim N^{0.75}$. We have varied N in the range of 30–120 in a series of simulations for a single value of $\varepsilon_w = 6.3$ which corresponds to strong adsorption. Fig. 4 demonstrates that the size normal to the wall ($= \lambda_1$ for adsorbed chain) is essentially chain size independent and equal to 0.57 ± 0.03 for all chain lengths. Both the in-plane dimensions, λ_2, λ_3, scale as $N^{3/4}$. Thus, our adsorbed polymer chain obeys all the characteristics of a pancake type conformation.

3.2. Effect of the wetting characteristics of the solvent

The conformation of an adsorbed polymer chain is dependent on several parameters such as the interaction

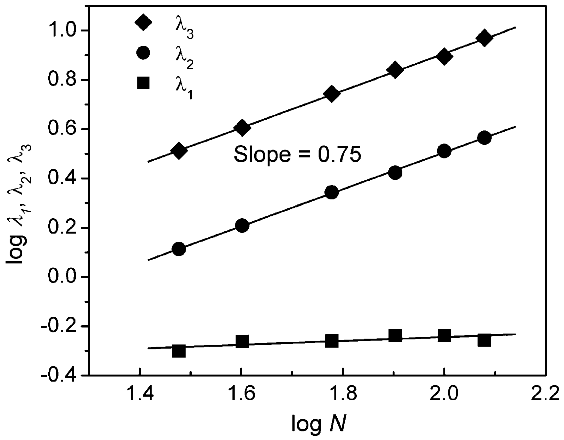

Fig. 4. The values of the three eigenvalues, λ_1, λ_2, and λ_3, of the polymer radius of gyration tensor as a function of the chain length on a log–log plot. For all chain lengths the wall interaction parameter is $\varepsilon_w = 6.3$. The smallest eigenvalue is essentially chain size independent, while the two other eigenvalues exhibit $R_{g\parallel} \sim N^{0.75}$ characteristic of self-avoiding walks in two dimensions.

strength between the substrate and polymer, the Flory χ parameter, and the wetting characteristics of the solvent. The polymer chains adsorbs easily from a poor solvent. Here we assess the effect of wetting characteristics of the solvent on polymer adsorption.

In the wetting solvent case described in the previous section, the monomers which make up the polymer chains and the solvent atoms are identical in size and interactions. To contrast this situation, we now consider the case where the polymer wets the surface, while the solvent is non-wetting (repulsive solvent-wall interactions). As shown in Fig. 5, the adsorption transition is shifted to very small values of $\varepsilon_w \sim 0.15$ in the case of the non-wetting solvent. In contrast, the adsorption transition occurred in the vicinity of $\varepsilon_w \sim 4.2$ for the wetting solvent. This result reflects that the entropic barrier to adsorption can be overcome by relatively weak energetic gains on adsorbing chains, a result which is consistent with the notion that a chain loses roughly $1k_BT$ on adsorption in entropic effects. The adsorption transition of the polymer chain in implicit solvent lies between the wetting and non-wetting solvent.

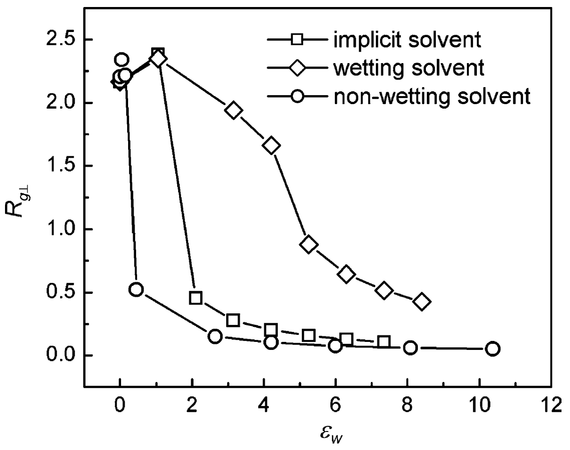

Fig. 5. The radius of gyration component normal to the wall, $R_{g\perp}$, for $N = 80$, is plotted for non-wetting solvent, vacuum solvent and wetting solvent as a function of increasing attraction with the walls.

4. Summary and conclusions

Our simulations mapped the structural changes of a single polymer chain as it adsorbs from solution on to a substrate. In particular, we demonstrated how a three-dimensional ellipsoidal polymer chain transforms into a two-dimensional elliptical (pancake) disk on adsorption. For well-adsorbed chains the thickness of this ellipse is independent of the chain length. Also, the increasing attraction to the substrate results in a decrease in the thickness of the ellipse accompanied by a lateral spreading of the chain and an increase of the radius of gyration. For well-adsorbed polymer chains the radius of gyration normal to the surface, $R_{g\perp}$, becomes equal to the shortest eigenvalue of the radius of gyration tensor. This demonstrates that the adsorbed polymer chain reorients itself with the shortest axis normal to the substrate.

We also showed that the adsorption transition is dependent on the wetting properties of the solvent. A non-wetting explicit solvent leads to a strong adsorption at low polymer-surface attraction strength.

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