

Flexible star polymer chain adsorption by a flat surface: a molecular dynamics simulation

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Abstract. In this work, we have studied the adsorption of a single flexible star polymer chain by a flat surface. The molecular dynamics simulation has been validated for the case of a free star polymer chain using the diffusion experiment. The scaling laws found are in agreement with the Flory theory predictions and the Rouse model. For the adsorption, preliminary results were obtained for chains of different sizes $N=31$ to $N=199$ and different functionalities ($f=3,4,6,8,10$). For the case of semi-flexible star polymer chains, further investigation is needed to locate the critical point of adsorption when varying the potential interaction strength between the chain and the surface.

1. Introduction

The aim of this work is to study the adsorption of a star polymer chain by a flat surface for different chain lengths and different functionalities[1] (number of arms f), and to determine how can the functionality of the chain affect the adsorption phenomena. First, we study the static and the dynamic properties of a free star polymer chain in dilute solution under good solvent conditions to get the scaling law $\tau = \tau_0 N^{2\nu+1}$ predicted by Flory[2], by measuring the gyration radius $R_g(t)$ which describes the three dimensional structure of the chain and the mean square displacement of the center of mass of the chain $g_3(t)$ which indicates that the chain is diffusing correctly in the simulation. In the second part of the work, we study the behavior of a star polymer chain attached to an attractive surface. A sufficient surface potential strength causes an adsorption transition, where the chain changes from a three dimensional structure to a bidimensional one and an expansion of the chain parallel to the surface. This behavior is well described by the parallel and perpendicular components of the gyration radius during the simulation. We will also try to determine the critical point of adsorption by measuring the number of adsorbed monomers for different chain lengths and different functionalities. The work is presented as follows: In section 2, we briefly present the model and the simulation method used in this study, the results are given and discussed in section 3. We summarize and conclude in section 4.

2. Model and simulation method

The star polymer chain is described by a coarse grained bead-spring model[3]. The interaction between two neighboring monomers is represented by the Finitely Extensible Nonlinear Elastic potential:

$$U_{FENE}(r) = \begin{cases} -\frac{1}{2}kR_{max}^2 \ln\left(1 - \frac{r^2}{R_{max}^2}\right) & r < R_{max} \\ \infty & r \geq R_{max} \end{cases} \quad (1)$$

Where $R_{max} = 1.5\sigma$ is the maximal distance between two bonded monomers and $k = 30\epsilon$ is the spring constant.

The interaction of nonbonded monomers is represented by the potential of Lennard-Jones, truncated and shifted at the minimum of the attractive part $r = 2^{1/6}\sigma$:



$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

Where $\epsilon = 1$ is the energy scale.

The interaction between the monomers and the surface is also represented by Lennard-Jones potential in the z direction:

$$U_{wall}(z) = 4\epsilon_{wall} \left[\left(\frac{\sigma}{z} \right)^{12} - \left(\frac{\sigma}{z} \right)^6 \right] \quad (3)$$

Brownian dynamics[4] is used to simulate the behavior a star polymer chain under good solvent conditions, by integrating the equation of motion:

$$m \frac{d^2 \vec{r}(t)}{dt^2} = -\nabla U(\vec{r}) - m\Gamma \frac{d\vec{r}(t)}{dt} + \vec{\eta}(t) \quad (4)$$

Here $-m\Gamma \frac{d\vec{r}}{dt}$ is the friction force and $\vec{\eta}(t)$ is a random force which corresponds to the interactions with the particles of the solvent. We have used the velocity-verlet algorithm[5] with a time step $\delta t = 0.002$ to integrate the equations of motion for a temperature $K_B T \epsilon = 1$ and a friction parameter $\Gamma = 1$. All the results are obtained in reduced units during the simulation.

3. Results

3.1. Free star polymer chain

We study the diffusion of a free star polymer chain with different lengths ($N = 31, N = 61, N = 82, N = 100, N = 200$). The properties that are measured are the mean squared displacement of the center of mass (MSQD)[6], defined as:

$$g_3(t) = \langle (\vec{r}_{cm}(t) - \vec{r}_{cm}(0))^2 \rangle \quad (5)$$

and the gyration radius defined as:

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^N \langle (\vec{r}_i - \vec{r}_{cm})^2 \rangle \quad (6)$$

Where $r_{cm}(0)$ is the center of mass at the beginning of the simulation ($t = 0$), and $r_{cm}(t)$ is the center of mass at time t .

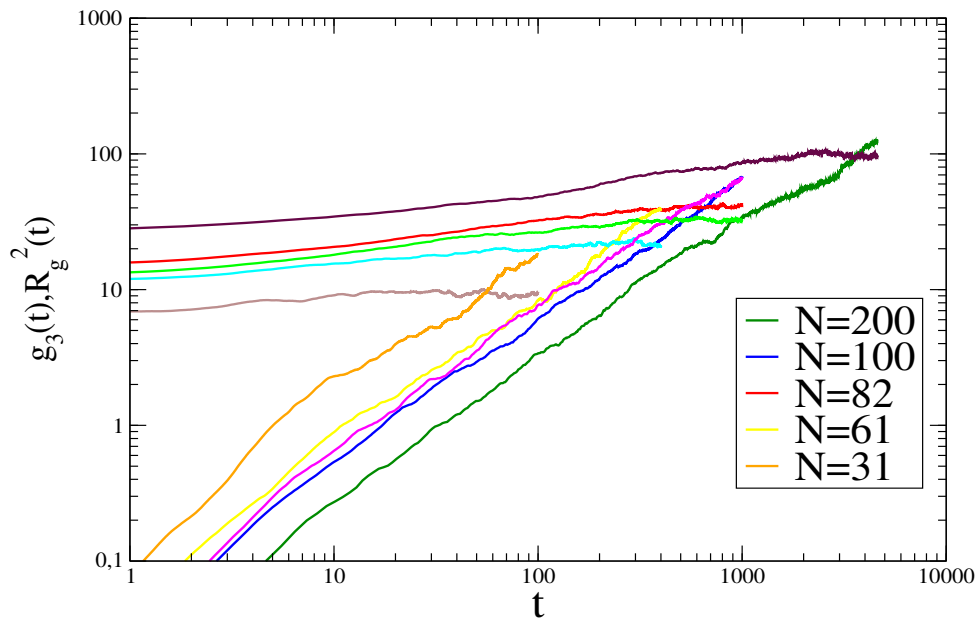


Figure 1: MSQD and gyration radius as a function of time in log-log scale

In figure 1, we observe two phases, the ballistic phase, where the chain has a viscoelastic behavior ($t < \tau$), and a diffusif phase where the chain simply diffuse in the solvent ($t > \tau$)

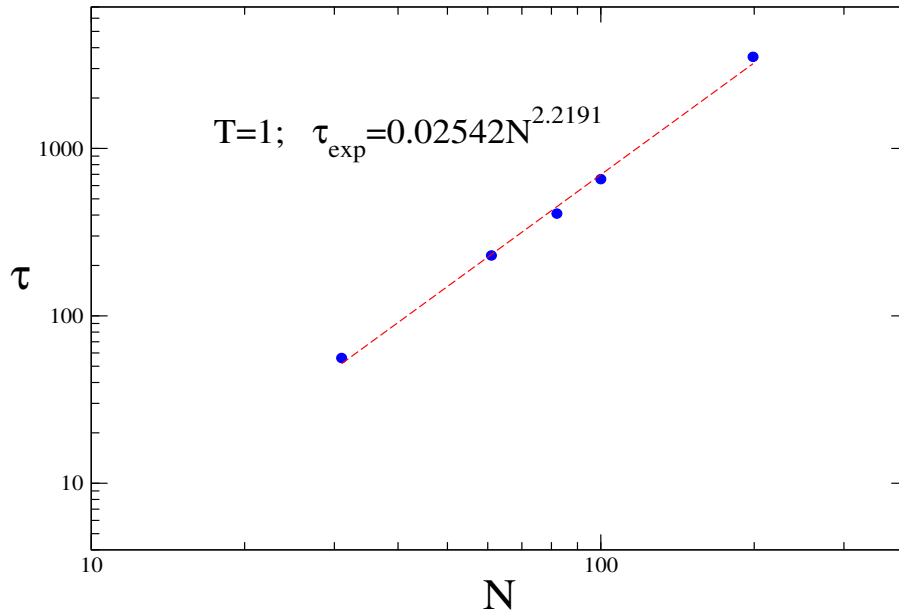


Figure 2: Relaxation time τ as a function of star polymer chain length N

By making a fit of type $y = AX^B$, we obtain the scale law:

$$\tau_{exp} = 0.02542 \times N^{2.2191} \quad (7)$$

From figure 2, we can see from the fit that the Flory formula $\tau = \tau_0 N^{2\nu+1}$ is satisfied where $\nu = \frac{3}{5}$. Since the scale law is confirmed, our molecular dynamics code is reliable to study the adsorption phenomena.

3.2. Star polymer chain attached to an attractive surface

The adsorption of star polymer chain is studied by attaching the end monomer of the last arm of the chain to the surface, the process of adsorption occurs when the strength of the attractive surface potential is sufficiently big, the star polymer makes a transition from a three dimensional structure to a two dimensional one. This transition can be observed by measuring the ratio $\frac{R_{g\perp}}{R_{g\parallel}}$ where $R_{g\perp}$ and $R_{g\parallel}$ are respectively the perpendicular and the parallel components of the gyration radius:

$$\langle R_{g\perp}^2 \rangle = \frac{1}{N} \sum_{i=1}^N \sum_{j>i}^{N-1} \langle (z_i - z_j)^2 \rangle \quad (8)$$

and

$$\langle R_{g\parallel}^2 \rangle = \frac{1}{N} \sum_{i=1}^N \sum_{j>i}^{N-1} \langle (x_i - x_j)^2 + (y_i - y_j)^2 \rangle \quad (9)$$

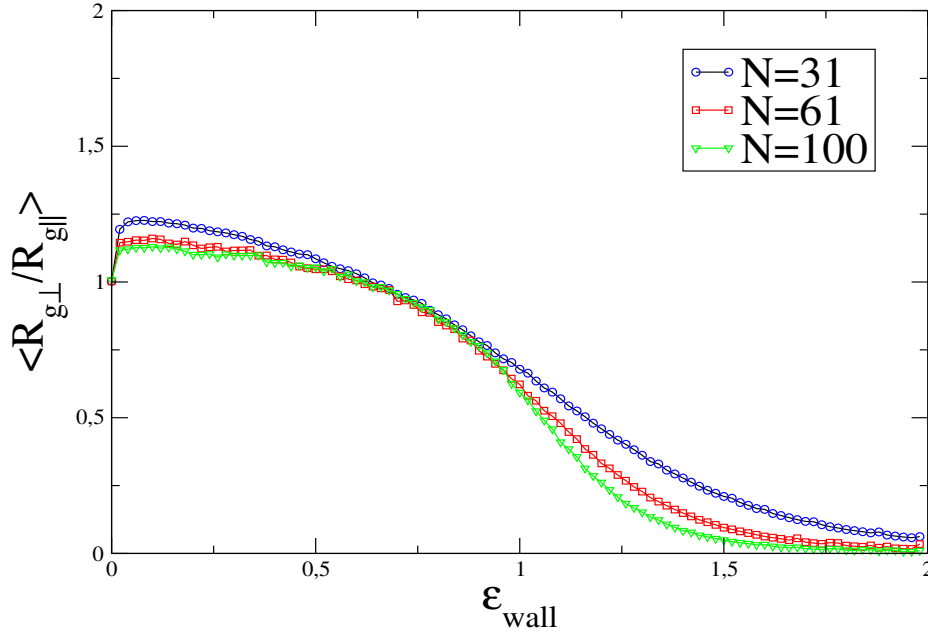


Figure 3: The ratio of perpendicular and parallel gyration radius parts as a function of ϵ_{wall} for different lengths N for a three arms star polymer chain

Figure 3 shows that for low potential strength of the surface ($\epsilon_{wall} \ll 1$), the chain behaves like a free polymer chain, and for high values of ϵ_{wall} , the $R_{g\parallel}$ increases, which means that the chain is spreading onto the surface. The transition phase appears for a critical ϵ_{wall} value, this corresponds to the area where the curves for $N = 31$, $N = 61$, $N = 100$ overlaps. The critical point of adsorption is lower than 1 and approximately ($\epsilon_{wall} \simeq 0.94k_bT$). For $\epsilon_{wall} \leq 0.5$, the ratio is higher than 1, the chain is in the distortion phase. The chain is in the adsorption phase for $0.5 < \epsilon_{wall} \leq 1$. $R_{g\parallel}$ dominates for $\epsilon_{wall} > 1$ and this can be interpreted as a post-adsorption relaxation phase .

To estimate the precision in the simulation, we have made 20 samples for each run. The results with error bars are presented in figure 4 for the case of a star polymer with three arms ($f = 3$) and a chain length $N = 61$

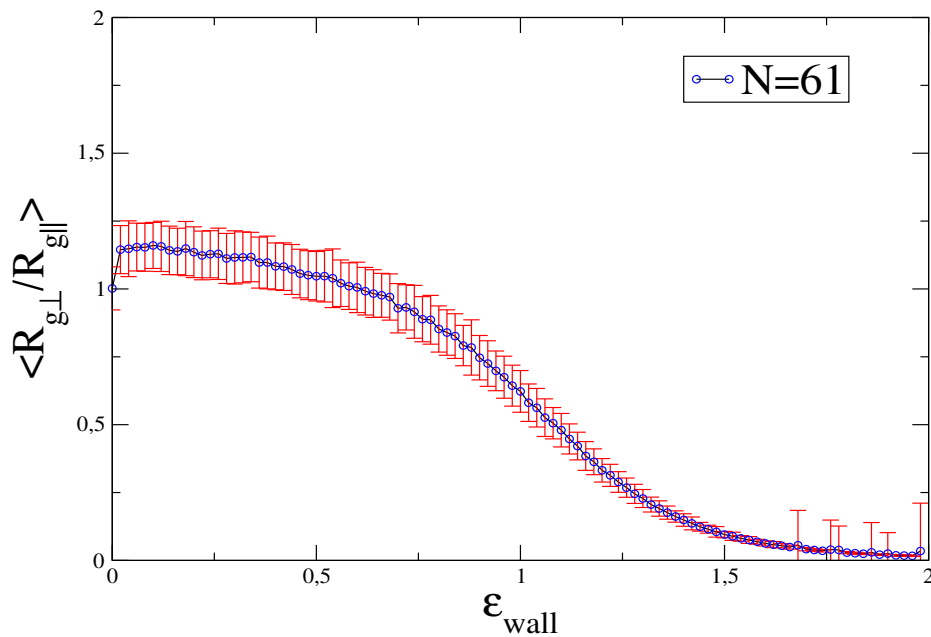


Figure 4: The ratio of perpendicular and parallel gyration radius parts as a function of ϵ_{wall} for $N = 61$ for a three arms star polymer chain. Error bars are obtained by calculating the standard deviation over 20 samples.

We have also calculated the rate of adsorption Θ which is the number of the monomers adsorbed n_c divided by the total number of monomers N .

$$\Theta = \frac{n_c}{N} \quad (10)$$

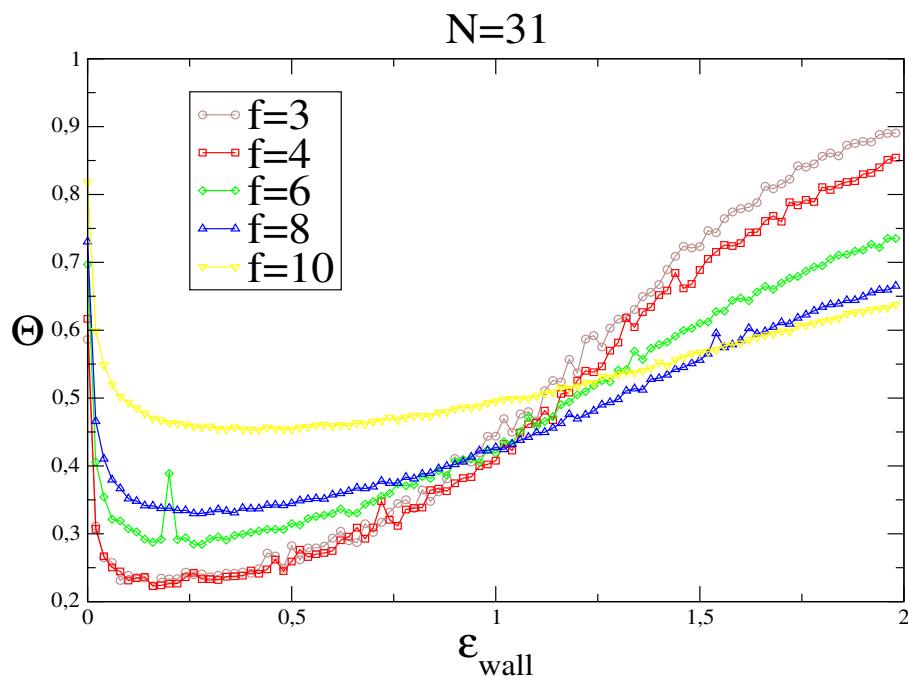


Figure 5: The rate of adsorption for a star polymer with $N = 31$ monomers and different functionalities (number of arms) as a function of ϵ_{wall}

From figure 5, we found that the functionality is a major factor which affect the number of adsorbed

monomers. For $f = 3$, 88% of monomers are adsorbed at the end of the simulation, and only 63% of monomers are : < 1.3

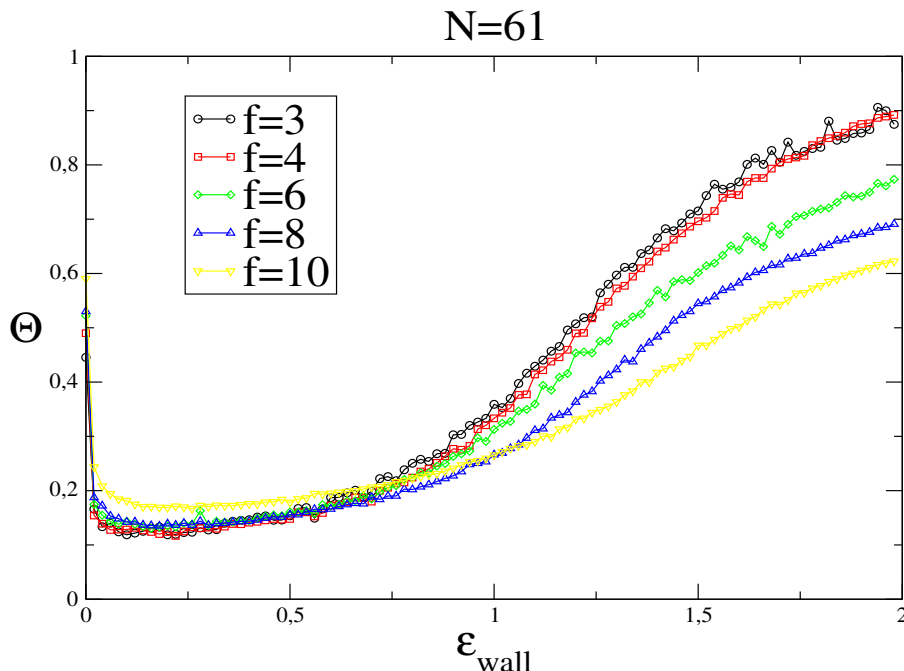


Figure 6: The rate of adsorption for a star polymer with 61 monomers and different functionalities (number of arms) in function of ϵ_{wall}

Figure 6 shows the same experiment for a chain length $N = 61$. For $f = 3$ and $f = 4$, 90% of the monomers are adsorbed, and only 62% of the monomers are adsorbed for $f = 10$, the critical adsorption point is located in $0.5 < \epsilon_{wall} < 0.8$.

4. Conclusion and perspectives

In this work, we have studied the behavior of a flexible star polymer chain attached to a flat surface. The critical point of adsorption has been approximately located by varying the strength of the interaction potential between the star polymer chain and the surface for different chain lengths and different functionalities. In a future work, it is interesting to estimate more exactly the critical point of adsorption by calculating the variation of energy of the chain as a function of the potential strength between the polymer chain and the surface and also look forward the behavior of semiflexible star polymer chains in contact with a surface and see if the critical point of adsorption changes by varying the degree of stiffness of the chain.

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6. References

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