Molecular dynamics of a Lennard-Jones fluid in a slit-like pore with a wall modified by a Y-shaped polymer brush

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The structural properties of a Y-shaped polymer brush at the pore wall are studied at different conditions. The pore is filled by a Lennard-Jones (LJ) fluid with a number density varying in the range ρ*=0.4-0.7 in the reduced units. The reduced temperatures in the system were chosen in the range T*=1.0-2.6. Also different values of the LJ potential describing interaction between fluid and polymer beads, ε_{01}=1.0-5.0, were checked. The new model applied in this study is similar to one used for the linear polymer brushes. The principal difference between the models consists only in the architecture of the polymers. Within the new model each of polymer molecules has an Y-shaped architecture. This architecture is presented as a three-arm star, where one of the arms is pinned to the pore wall. This three-arm star is constructed by attaching the additional chain of a length 8 to middle of the linear molecule of length 18. Therefore, the total number of beads in one polymer is 26. The obtained Y-shaped molecules were randomly placed on the pore wall with a certain surface density. The surface density of Y-shaped polymers was adjusted in such a way to get a number of polymer beads equivalent to the number of polymer beads used in the previous study for the linear polymers. Besides that, a simulation box was enlarged in X and Y directions, thus it had a size 40x40x40. A number of polymer molecules was equal to 110. The rest of peculiarities remained the same as previously for the linear polymer brush.
The simulation process was also the same as in the previous investigation. Using the method of molecular dynamics we have calculated the following characteristics: polymer and fluid density profiles, average thickness (h) of polymer brush, a radius of gyration (R_g).

The analysis of obtained results let us draw the following conclusions.

1) The temperature dependence of the average thickness (h) of a Y-shaped polymer brush can be non-monotonous (e.g. when ε_{01}=1.0), similar as it was observed for the case of linear polymer brush. The minimum of h is around T*=2.0 for all considered fluid densities. However, when ε_{01}=1.5 a qualitatively different behavior is observed, i.e. the average thickness decreases monotonously with temperature (T*=1.0-2.6). Moreover, the radius of gyration has an opposite trend, i.e. it increases monotonically with temperature. This effect is specific for a Y-shaped polymer brush and it needs more deep analysis.

2) The dependence on the parameter of LJ interaction between fluid particles and polymer beads, ε_{01}, also shows a behavior different to that observed for the linear polymer brush. For the Y-shaped polymer brush the increase of the average thickness, h, stops around ε_{01}=2.5 and then h starts to decrease. However, it is observed only at smaller densities (e.g. ρ*=0.5 and 0.6). For the density ρ*=0.7 it continues to increase after ε_{01}=2.5. It is also worth noting that the radius of gyration has qualitatively similar behavior to the average thickness at all considered fluid densities.

3) An increase of the fluid density leads to a decrease of the average brush thickness at all temperatures.

4) A form of the density profiles of Y-shaped polymer brush and fluid particles looks similar to those in the previous study with linear polymer brush. Therefore, the conclusions drawn for the case of Y-shaped polymer brush repeat those made for the case of linear polymer brush.