

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

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In our investigation we considered a system of a Lennard-Jones fluid confined in a slit-like pore with a wall modified by a linear polymer brush. We are aimed to study distributions of polymer beads composing the brush as well as a fluid density profiles in the pore at different conditions: temperature, amount of a fluid, interaction between fluid and polymer beads. Therefore, a series of molecular dynamics simulations are performed and the corresponding structural characteristics for polymer and fluid components are obtained and analyzed. Among of them there are polymer and fluid density profiles, average thickness (h) of polymer brush, a radius of gyration (R_g) and an end-to-end distance (R_{1N}) of polymer chains. We have checked a system at different temperatures in the range $T^*=1.0-2.6$. The number density of fluid in reduced units, $\rho^*=N/V$, was changed from 0.4 to 0.7. The parameters of Lennard-Jones (LJ) interaction between polymer beads, ϵ_{00} , and between fluid particles, ϵ_{11} , were kept constant and equal to $\epsilon_{00}=\epsilon_{11}=1.0$, while fluid-polymer interaction LJ parameter ϵ_{01} was varied in the range $\epsilon_{01}=1.0-5.0$. The interaction of all particles in the system with the pore walls are of a hard-core type. The distance between walls is large enough to get a bulk-like region in the middle region of the pore, in our case it is $L=40\sigma$, where $\sigma=1.0$ – LJ diameter of particles in the system, which is the same both for the polymer beads and fluid particles. The length of polymer chains in the brush is 18 beads. The bonds between polymer beads are described by the FENE potential with the parameters $K=50.0$ and $R_0=1.3\sigma$. All potentials of interaction used in our study are cut off at the distance $r_{cut}=3.0\sigma$. The polymer chains are distributed randomly at one of the two walls of pore. A number of polymer chains is taken equal to 102 and it corresponds to the surface density 0.1 in reduced units.

The simulations were performed in a few stages. First stage is preliminary equilibration of a system at a low temperature ($T^*=1.0$) using simple rescaling of particle velocities. The second one is the equilibration in the NVT ensemble at the required temperature ($T^*=1.0-2.6$) with the Nose-Hoover thermostat applied. The third stage is used for a production of results and it is performed in the NVE ensemble.

The obtained results allow us to draw the following conclusions:

- 1) An increase of the fluid density leads to a decrease of the thickness of polymer brush. The radius of gyration and the end-to-end distance of polymer chains also decreases when the fluid density increases.
- 2) The non-monotonous dependence of the considered characteristics (h , R_g and R_{1N}) on temperature with a distinct minimum is observed for the case $\epsilon_{01}=1.0$. For each of the characteristic the position of the minimum is different. Therefore, for the radius of gyration it is located around $T^*=1.8$, for the end-to-end distance it is about $T^*=2.0$ and for the brush thickness it is $T^*=1.2$. If to consider higher values of the parameter of interaction ϵ_{01} , for instance $\epsilon_{01}=1.5$, one can see that non-monotonous behavior of the temperature dependence is not so prominent and it is shifted to the lower temperatures.
- 3) An increase of the interaction parameter ϵ_{01} leads to the dramatic growth of the h , R_g and R_{1N} . However, while for the brush thickness, h , increases monotonically and almost linearly in the range $\epsilon_{01}=1.0-5.0$, the radius of gyration, R_g , and the end-to-end distance, R_{1N} , have the maximum in $\epsilon_{01}=3.0$ with a subsequent small lowering.
- 4) The analysis of density profiles for the polymer brush and the fluid shows that the increase of ϵ_{01} promotes layering effects for polymer chains and fluid particles near the pore wall, while an increase of temperature suppresses them. Also an increase of ϵ_{01} leads to a condensation of fluid on the wall, i.e. the local density of fluid close to the pore wall increases. On the contrary, a local fluid density decreases near the pore wall if the temperature increases.
- 5) It is observed that for the case of $\epsilon_{01}=1.0$ at the temperature $T^*=1.0$ the polymer chains form droplets, which is clearly seen at snapshots obtained from the system configurations.