

Monte Carlo simulations of polymer conformations at the bulk/membrane interface

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In a membrane filtration process small particles are permeating through the membrane while larger particles are being retained. Although very large particles will never permeate through a pore, flexible polymer coils are able to unroll themselves and penetrate the pore despite the fact that their coil size is larger than the pore size.

From the early 1980s on, people used the scaling theory developed by de Gennes [1] to predict the partitioning of polymers between a pore and a bulk phase and their behaviour in tubes under ideal conditions. Many Monte Carlo simulations have been performed to validate the theory. Recently large polymer chains in the vicinity of narrow pore openings were found to

be able to enter the pore by deforming themselves [2,3]. Simulations on polymer brushes showed that polymers can deform themselves in a similar way: part of the chain is stretched and part of it resides in a coil-like state, resembling a “flower” [4,5]. Interestingly, these flower conformations can also be observed for large DNA molecules in a weak electric field entering regions where the pore radius is smaller than the polymer radius of gyration [6,7].

The main issue we try to answer is: what happens to the conformation of a flexible polymer chain in the transition from the bulk to a membrane pore and we try to quantify this deformation.

The simulations are carried out on a lattice and are a combination of the Bond fluctuation model [7] and a configurational bias method [8].

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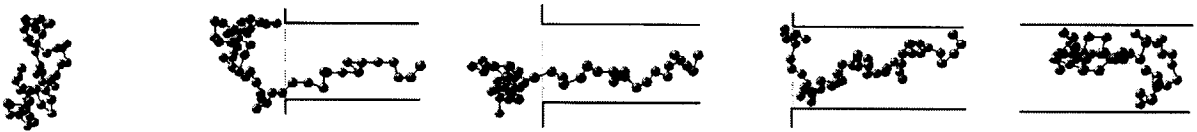


Fig. 1. Snapshots of polymer conformations in small pores. In the bulk (left) the polymers have a coil-like conformation. Increasing degrees of confinement result in partial stretching of the polymer (flower conformation) until the polymer is completely confined (right).

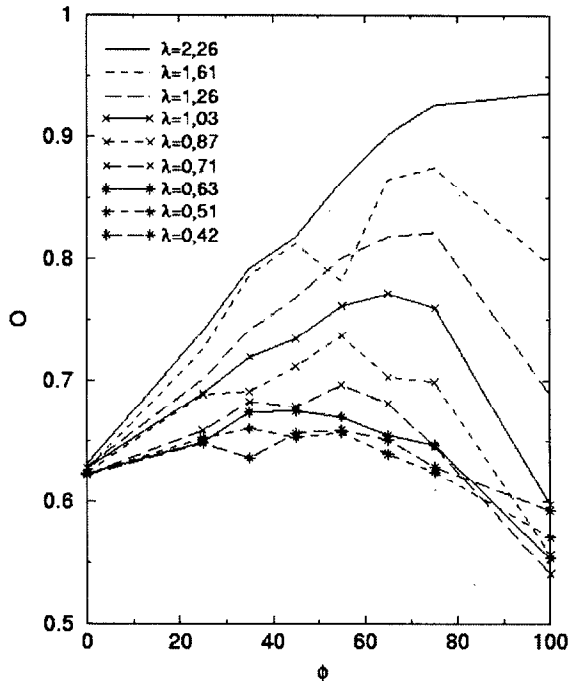


Fig. 2a. The asphericity O of the polymers as a function of the degree of confinement ϕ for various pore radii.

The results of our simulations show that on average the polymers adopt very different conformations depending on their degree of confinement — the fraction of monomers inside the pore (Fig. 1). In the bulk the polymer adopts a coil-like conformation. When the polymer is partially inside the pore, the polymer stretches and relaxes again when it is completely confined. Partially confined chains adopt a flower-type conformation; the stem of the flower is inside the pore while the segments outside the pore remain in the coil-like state: the crown. These changes in

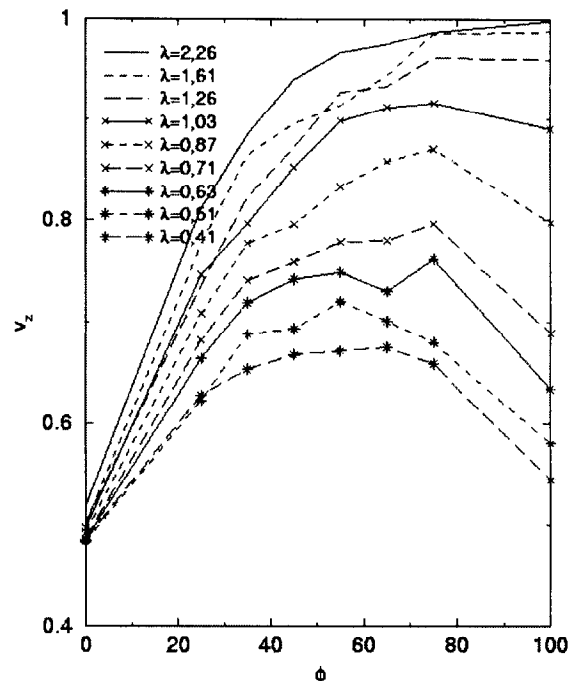


Fig. 2b. The projection of the main principle axis of the radius of gyration v_z as a function of the degree of confinement ϕ for various pore radii.

conformations can be quantified using the radius of a gyration tensor. When this tensor is diagonalised, the Eigen values and eigenvectors give the information about the shape. A related quantity like the “asphericity” O is calculated to quantify the deviation from a perfect sphere ($O=0$) (Fig. 2a). The projection of the main principle axis of the radius of gyration tensor on the pore direction does not give information about the shape, but it does indicate in which direction the deformed polymer points (Fig. 2b).

The parameter λ in Figs. 2a and 2b is the radius of gyration divided by the pore radius. Large λ values (small pores) result in high asphericities and extreme alignments to the pore direction. Large pores show less extreme deformations. Fig. 2 shows that with increasing degree of confinement the polymer stretches along the pore direction. Only after 60% of all monomers has entered the pore does the stretched conformation relax back to adopt a (deformed) coil-like conformation (see also Fig. 1). These results indicate that in the permeation process the polymer disentangles its coiled conformation, and next enters the pore to finally regain its coiled shape. At present we are working on the calculation of the free energy barrier associated with this phenomenon.

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