Polymer Dynamics Simulation at Nanometer Scale in a 2D Diffusion Model

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In this study the polymer transport dynamics in a 2D lattice model is investigated. The dependence of the polymer escape time through a nanometer pore on the stiffness and the monomers number of the polymer is demonstrated. We have also proved the major effect of superimposed electric field on the polymer translocation.

Keywords: 2D lattice model, Langevin equation, nanopore, transport phenomena, translocation time

Polymers translocation through a nanopore plays a critical role in many biological processes. For example the motion of DNA and RNA molecules across nuclear pores, gene swapping, and protein transport through membrane channels, involve the motion of biopolymers across membranes [1, 2]. When a polymer molecule moves through a nanometer pore, the electric current in the system nearly vanishes because the polymer blocks the flow of free ions through the channel [3].

The translocation of a polymer through a nanometer pore faces a large entropic barrier due to the loss of a great number of available configurations. In order to overcome the barrier and to speed up the translocation, an external field or interaction is often introduced.

The possible driving mechanisms include an external electric field, a chemical potential difference, or selective adsorption on one side of the membrane [4].

The molecular simulations have a central role in computer-aided pharmaceutical products design. Brownian dynamics simulation is the most used molecular simulation method for the biopolymers transport processes simulation. The movements of particles which follow Brownian motion are described by Langevin equation.

Theoretical part

The Langevin equation is a popular model for macromolecular simulations, because it is computationally less demanding than ordinary Newtonian molecular dynamics [5, 6].

The general expression of Langevin equation under consideration [6, 7] is given by>

$$\begin{cases} dx = vdt \\ dv = M^{-1}F(x)dt - \gamma v dt + \sqrt{2\gamma k_B T} M^{-1/2} dW(t) \end{cases} \quad (1)$$

where x is the displacement vector, v is the velocity vector, t is the time, M is a diagonal matrix of masses, $F(x)$ is the collective force vector, γ is the friction coefficient, k_B is the Boltzmann constant, T is absolute temperature and $W(t)$, $t > 0$, is a collection of independent standard Wiener processes.

Regarding the standard Wiener process, we remember that

- $W(0) = 0$ with probability 1,
- $W(t+\Delta t) - W(t)$, $\Delta t > 0$, is independent of $W(\tau)$ for $\tau < t$ and is Gaussian with mean zero and variance Δt.

Therefore, it is of great importance to theoretically investigate the polymer transport under an electric force $\boldsymbol{F_1}$, generated by an external electric field of intensity E.

In the present numerical simulations, the polymer chains are modeled as bead-spring chains of **L**ennard-**J**ones (***LJ***) particles with the **F**inite **E**xtension **N**onlinear **E**lastic (***FENE***) potential,[]. Both excluded volume and Van de Walls interactions between beds are modeled by a repulsive ***LJ*** potential $U_1(r)$ between all bead pairs >

$$U_1(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon, & r \le 2^{1/6}\sigma; \\ 0, & r > 2^{1/6}\sigma, \end{cases} \quad (2)$$

where σ is the diameter of a bead, and ε is the depth of the potential. The connectivity between beads is modeled as a ***FENE*** spring, respectively $U_2(r)$ potential, with:

$$U_2(r) = -\frac{1}{2}kR_0^2 \ln\left(1 - r^2/R_0^2\right) \quad (3)$$

where r is the separation between connected beads [8].

The second Newton's law and the superposition principle for each bead lead to the following equation:

$$m\frac{d^2\vec{r}}{dt^2} = \vec{F}_{c,i} + \vec{F}_{f,i} + \vec{F}_{r,i} \quad (4)$$

where m is the monomer's mass, $\vec{F}_{c,i}$ is the conservative force, $\vec{F}_{f,i}$ is the frictional force and $\vec{F}_{r,i}$ is the random force [5].

The behaviour of viscous circumstance is included in the frictional force, which has the value

$$\vec{F}_{f,i} = -\gamma\vec{v}_i \quad (5)$$

for an individual monomer. In this equation γ is the friction coefficient and v_i is the monomer's velocity.

The conservative force $F_{c,i}$ in the Langevin equation consists of several terms

$$\vec{F}_{c,i} = -\nabla\left(U_1 + U_2\right) + \vec{F}_1 \quad (6)$$

The external electric force F_1 is vectorially expressed as

$$\vec{F}_1 = q\vec{E} \quad (7)$$

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where q is the electric charge of monomer and E is the electric field vector in the direction perpendicular to the wall.

The general dynamics of each monomer results from the random bombardment of solvent molecules. In this conception the monomer motion is a Brownian motion, evidently. The random force $F_{r,i}$ can be calculated using the fluctuation-dissipation theorem:

$$\langle F_{r,i}(t)\rangle = 0;$$
$$\langle F_{r,i}(t)\times F_{r,j}(t')\rangle = 6k_B T\gamma\delta_{ij}\delta(t-t'). \quad (8)$$

Results and discussions

Here we study the problem of polymer translocation through a nanopore in the presence of an external electric force. For this purpose, we use the two-dimensional (2D) model with single-segment diffusion moves. To overcome the entropic barrier without artificial restrictions, we consider a polymer which is initially placed in the middle of the pore, and study the escape time τ required for the polymer to completely exit the pore on either end.

The translocation time is defined as the time interval between the entrance of the first segment into the pore and the exit of the last segment. In figure 1, the two distinct situations regarding the polymer's positions are put in evidence. In this sense, the polymer escape time through the nanometer hole is the time in which the polymers geometry changes between the two limit situations.

Using the method described by Ermak and Buckholtz [9], the 2D Langevin Equation can be integrated in time. In other words, the general Brownian motion equation for a particle under an external electric field can be easily solved by a discrete method, implementable in a programming language. The differential equations are required to be approximated by the difference equations [10] which compute the velocity and location of the particles, becoming equations (9) and (11).

The recurrence relation of the particle's velocity is

$$v(t+t_s) = v_0\left(1-e^{-\gamma t_s}\right)+\frac{F_0}{m\gamma\left(1-e^{-\gamma t_s}\right)}+B_1 \quad (9)$$

where t_s is the time step and the term B_1 satisfies the equation:

$$\langle B_1^2\rangle = 3\frac{k_B T}{m}(1-e^{-2\gamma t_s}) \quad (10)$$

The recurrence relation of the particle's location is:

$$x(t+t_s) = r_0+\frac{1}{\gamma}\left(v+v_0-2\frac{F_0}{m\gamma}\right)\left(1-e^{-\gamma t_s}\right)\left(1+e^{-\gamma t_s}\right)+$$
$$+\frac{F_0}{m\gamma t_s}+B_2 \quad (11)$$

where the term B_2 satisfies the equation:

$$\langle B_2^2\rangle = 6\frac{k_B T}{m\gamma} \quad (12)$$

For the transport to take place [11] several conditions should be fulfilled:

- the first monomer from the chain should be found at the pore entrance;
- an external electric field should be applied to "push" the polymer through the pore from CIS to TRANS zone;
- the polymer shouldn't "tie" itself at the pore entrance.

Not respecting the last condition would result in blocking the translocation.

In our simulation, the first monomer lies exactly at the pore entrance. Due to the existence of an external electric field, the first monomer is pulled through the nanopore from CIS to TRANS zone. In the absence of the external field, the translocation is extremely slow, even impossible. The bigger the external force resulted from the electric field action, the highest the probability that the polymer to translocate the pore.

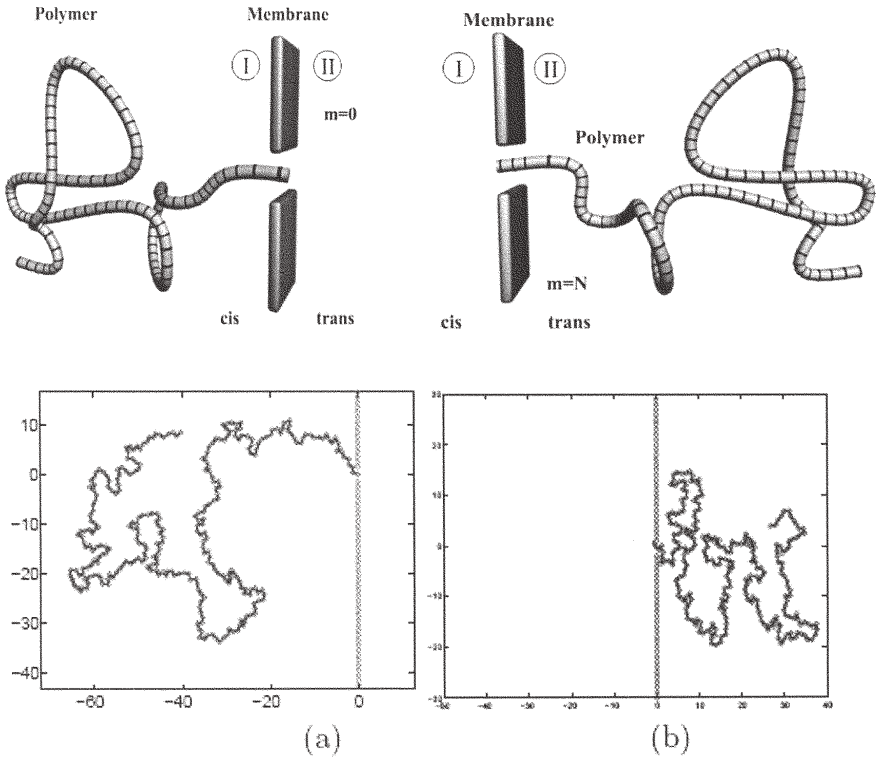

Fig.1 a) Polymer is found in CIS zone , b) Polymer is found in TRANS zone

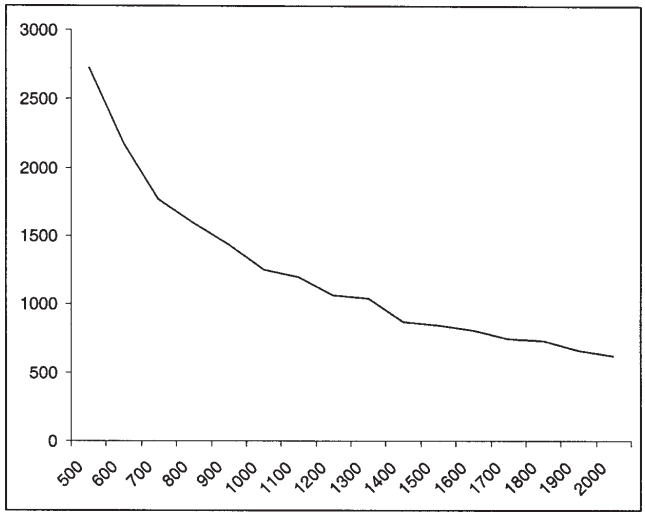

Fig 2. The external force influence on the translocation time (N = 5 monomers)

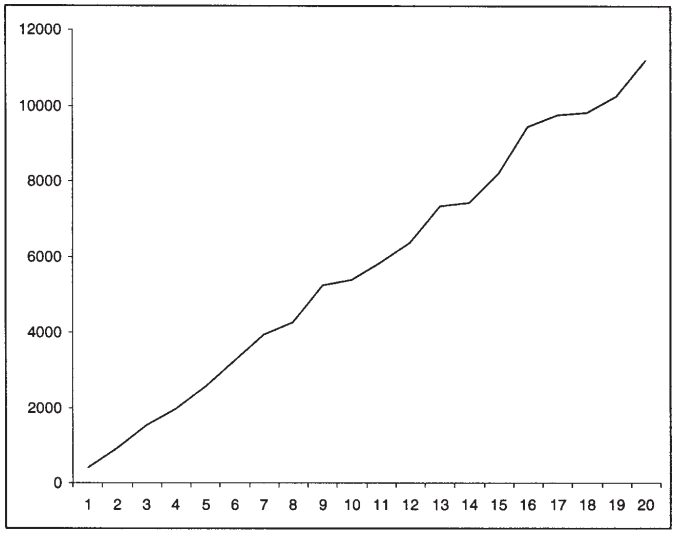

Fig 4. The influence of the monomers number *N* on the translocation time at high external forces

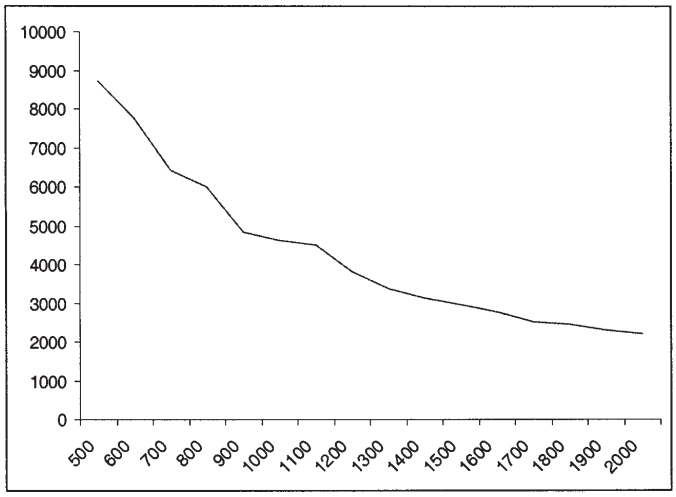

Fig 3. The external force influence on the translocation time (N = 16 monomers)

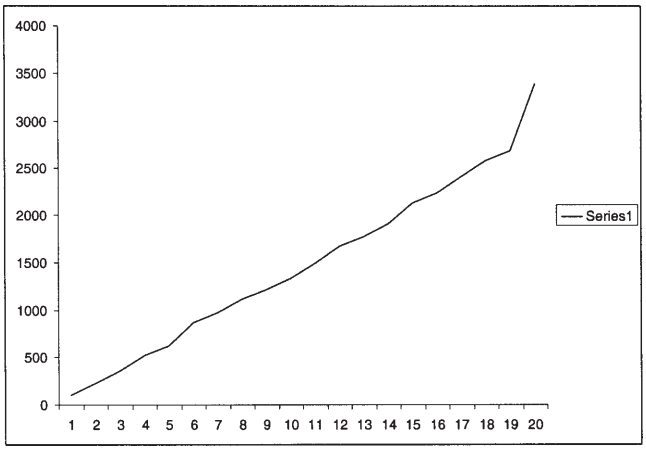

Fig 5. The influence of the monomers number *N* on the translocation time at low external forces

One of the objectives of this study is to evaluate the external force influences on the polymer translocation time. The simulation results are presented in the graphs from the figures.

Conclusions

The polymer transport dynamics in a 2D lattice model (by focusing on the time of polymer translocation through a nanometer pore) has been investigated.

Obviously the polymer escaping time is function of the monomers number. The smaller the monomers number is, the quicker the polymer's passing time.

In particular, we were interested in the effect of superimposed electric field on the polymer translocation. The dependence of the translocation dynamics on the stiffness and the monomers number of the polymer is also considered. It was proved that the external force resulted from the electric field action has an important role in the transport process.

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