

# Entropic force in a dilute solution of real ring polymer chains with different topological structures in a slit of two parallel walls with mixed boundary conditions\*

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Received September 5, 2023, in final form November 21, 2023

The molecular dynamics simulations were used to obtain the radius of gyration of real ring polymer chains with different topological structures consisting of 360 monomers. We focus on the entropic force which is exerted by a dilute solution of ring polymer chains of different topological structures with the excluded volume interaction (EVI) in a good solvent on the confining parallel walls of a slit geometry. We consider mixed boundary conditions of one repulsive wall and the other one at the adsorption threshold. The obtained molecular dynamics simulation results for a wide slit region demonstrate a qualitative agreement with previous analytical results for ideal ring polymers. These results could lead to interesting potential applications in materials engineering and improve understanding of some biological processes suggested in the paper. Additionally, they could be applied in micro- and nano-electromechanical devices (MEMS and NEMS) in order to reduce the static friction.

**Key words:** *soft matter, interface and surface thermodynamics, polymer behavior, phase transition, molecular dynamics simulations*

## 1. Introduction

Biopolymers such as deoxyribonucleic acid (DNA) can have in nature a ring topology. One example is the Escherichia coli (*E. coli*) bacteria, which is resistant to antibiotics. Additionally, the DNA of some viruses, such as bacteriophages  $\lambda$  that attack and destroy *E. coli* bacteria can oscillate between linear and ring topology as it was mentioned in [1, 2]. The DNA structure might depend on whether it is inside or outside the host cell. In the first case, it can switch to ring, in the other case it remains linear in mature viruses. Understanding those processes might help in the development of phage therapy. This therapy serves as an alternative to antibiotic treatments, especially for antibiotic-resistant bacteria. Besides, the measurements of the depletion force between repulsive wall and a single colloidal particle immersed in a dilute solution of nonionic linear polymer chains in a good solvent were performed in a series of papers [3–5]. The depletion force enters a complex force balance with other intercolloidal interactions such as: electrostatic repulsion and van der Waals attraction proposed by Derjaguin, Landau, Verwey, Overbeek (DLVO) or hydrophobic interaction and hydration [6–8].

Polymers are large macromolecules, consisting of a huge number  $N$  of monomers with  $N \rightarrow \infty$ , which can be well described by statistical physics methods. In 1972, de Gennes [9] introduced a concept of the

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polymer-magnet analogy for polymers in infinite space, which was later extended by Barber et al. [10] for polymers in confined geometries like semi-infinite space with surface.

In a recent paper [11], the monomer density profiles of a dilute solution of ideal ring polymers in a  $\Theta$ -solvent between two parallel walls were investigated under three different sets of boundary conditions (b.c.): Dirichlet-Dirichlet (D-D), Dirichlet-Neumann (D-N) and Neumann-Neumann (N-N). As demonstrated in [12], a dilute solution of ideal ring polymers with D-D b.c. exhibits an attractive depletion force, similar to linear polymer chains [13].

Besides, the calculations of the dimensionless depletion interaction potential and the depletion force for the case of a dilute solution of real ring polymers with the excluded volume interaction (EVI) in a good solvent for the case of D-D b.c. were obtained [12]. However, in [12] it was reported that in a dilute solution of ideal ring polymers with mixed D-N b.c., which corresponds to the situation of one repulsive and the other wall at the adsorption threshold, the respective depletion force starts to be repulsive similarly to the case of a dilute solution of real linear polymer chains with the EVI in a slit with N-N b.c. [13]. One of the examples of such systems with mixed D-N b.c. can be solution of colloidal particles, nanoparticles or ceramic nanopowders with different adsorbing and repelling properties in respect to polymers. Another example of such boundary conditions can be observed when a solution of colloidal or nanoparticles displays an opposite interaction with the polymers than the confining walls of reservoir where this polymer solution is inserted.

Unfortunately, in [12] only the case of ideal ring polymer chains was discussed analytically for the case of mixed b.c. In order to verify our analytical results in the present paper we performed molecular dynamics simulation of a dilute solution of ring polymer chains with the EVI in a good solvent confined in a slit geometry of two parallel walls with mixed boundary conditions. We discuss calculations of the radius of gyration and entropic force, which is exerted by ring polymers with different topological structures on the confining walls.

It should be mentioned that the depletion force for linear polymer chains was studied previously with various numerical methods [14–16]. Shorter polymer chains ( $32 \leq N \leq 512$ ) were modelled using computationally expensive off-lattice Monte Carlo method [14, 15]. The problem of the modelled short chains was overcome with the on-lattice pruned-enriched Rosenbluth method (PERM), which was used in three spatial dimensions to study the systems of long flexible linear polymer chains ( $N \leq 80000$ ) trapped between two parallel walls [16]. The ideal polymer chains were modelled as random walks (RW) and real polymers with the EVI in a good solvent as self-avoiding-walks (SAW). The depletion effects were studied in [17] for self-avoiding polymers within the framework of Langevin dynamics, where they discussed the competition between depletion attraction and enhanced viscous friction as two competitive crowding-induced effects.

The statistical mechanical properties of ring polymer chains in a slit with D-D b.c. were investigated in a series of papers [18, 19]. As it was shown in [18, 19], when the complexity and compactness of ring polymers increases, then the radius of gyration decreases at the same time. It makes ring polymers less mobile in the systems without driving forces, as it was shown in [20]. It should be noted that in the limit  $N \rightarrow \infty$ , the influence of knots on polymer properties is much smaller. Thus, the average size of ring polymers is proportional to  $N^\nu$ , where  $\nu$  is the Flory exponent.

The calculations of the entropic forces in a dilute solution of ring polymers under confinement of two parallel repulsive walls (D-D b.c.) obtained with the molecular dynamics simulations in [19] showed that polymers with more complex knots in the narrow slits produce higher entropic forces exerted on the wall than the unknotted knots. The opposite relation is observed for relatively wide slits. Significant differences in free energy and in metric properties between freely jointed polymers and unknotted ring polymers were discussed in [21]. It was shown [21] that the polymers with knots might present different qualitative properties due to steric effects. The knotting probability as it was shown in [22] using the method of self-avoiding polygons depends on the polymer length and on the magnitude of the excluded volume effects. Taking into consideration the complexity of biological systems one could expect that the diversity of the structures and types of polymers could induce the creation of some knots. It was shown that nematic ordering (effective stiffening of DNA) induces the formation of torus knots in phage capsids [23].

In biological eukaryotic organisms, chromosomes separate during cell division. Centrosomes, primarily composed of centrioles, organize the structure of these dividing cells. So, centrioles are key

ingredients in the proper separation process of the parent cell into the child cells. However, there are species that lack centrioles, and a remarkable example being mutant flies (*Drosophila melanogaster*) that do not have these structures and yet can normally develop until a certain life stage [24, 25]. This means that despite the lack of centrioles, the cells have successfully divided a great number of times. Centrioles are abundant organelle in biological cells except a few taxonomic groups such as coniferes (Pinophyta). One could imagine that depletion effects, which create additional forces in constrained systems could play some role in this or in similar biological mechanisms.

In mammalian cells, protein synthesis on the rough endoplasmic reticulum (ER) results in proteins either passing into the ER lumen, interweaving through the membrane, or becoming transmembrane proteins. The flat shape of the ER locally resembles a slit space, akin to a polymer in a slit geometry, where protein is attached to one side of it. One of the examples of translationally active cells are liver cells. When analyzing the biological cells, we can find direct analogies to the behaviour of polymers in a slit geometry between two parallel walls. Ribosomes on the ER surface have some density so that they are spaced approximately at a distance between two membranes in ER sheets, approximating the situation of a dilute polymer solution between two parallel walls with mixed b.c. with one repulsive and one attractive wall (D-N b.c.). Considering the emerging proteins can form various loops or knots in their structure due to their length. They can transfer interactions from one ER wall to the other one, reinforcing the analogy of proteins as polymers in a slit geometry.

## 2. The model

The present paper is devoted to the investigation of a dilute solution of real ring polymers with the EVI in a good solvent confined in a slit geometry with two parallel walls with mixed b.c. In a dilute solution, different polymer chains do not overlap, so such polymer solution can be well described by the statistics of a single polymer chain. The polymer chain is confined in the slit between parallel walls at  $z = 0$  and  $z = L$ . The walls are impenetrable, so the potential tends to infinity  $U \rightarrow \infty$  at walls. The short-range attractive potential is different from zero only over a distance comparable with the effective monomer linear dimension  $\tilde{l}$ . The single ideal polymer chain in a  $\Theta$ -solvent can be modelled by random walk (RW) with the Flory critical exponent  $\nu = 0.5$ . The real polymer chain with the EVI in a good solvent for temperatures  $T$  above the  $\Theta$ -point can be modelled by self-avoiding walk (SAW) with the Flory exponent  $\nu = 0.588$ .

We performed molecular dynamics (MD) simulation using LAMMPS (Large-scale Atomic Molecular Massively Parallel Simulator) for ring polymers consisting of 360 monomers. The neighbouring beads interactions were modelled with FENE potential, the monomer repulsion was modelled with 12-6 Lennard-Jones (LJ) potential and the monomer-wall interaction with 9-3 LJ potential [26]. We used Verlet integration algorithm with  $\Delta t = 0.005$  and the Langevin thermostat, which helped us to keep temperature  $T = 1$  constant. Simulations were equilibrated for  $10^7$  steps and the simulation data collected over  $2 \cdot 10^7$  steps. The results for the force were taken from 10 separate simulations for each of the slit widths used. Additionally, based on a similar system, we calculated the radius of gyration for each of the knot topologies. The calculations were performed for the adsorption temperature  $T = 2.30$  [27]. We used a model similar to [28]. The interaction between the non-neighbouring monomers was modelled with the 12-6 Lennard-Jones potential:

$$U_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (2.1)$$

for  $r \leq r_{\min} = 2^{\frac{1}{6}}\sigma$  with  $\sigma = 0.7/2^{\frac{1}{6}} = 0.6236$ , where  $r_{\min}$  is the extremum obtained from  $dU_{\text{LJ}}(r)/dr = 0$ . The potential was truncated  $U_{\text{LJ}}(r) = 0$  for  $r > r_{\min}$  and shifted with  $U_{\text{LJ,sh}}(r) = U_{\text{LJ}}(r) - U_{\text{LJ}}(r_{\min})$  in order to get  $U_{\text{LJ,sh}}(r_{\min}) = 0$ . The interaction between monomers and walls was modelled with Lennard-Jones 9-3 potential [26]:

$$U_{\text{LJ}}^{\text{wall}}(z) = \epsilon_w \left[ \frac{2}{15} \left( \frac{\sigma}{z} \right)^9 - \left( \frac{\sigma}{z} \right)^3 \right], \quad (2.2)$$

where  $\epsilon_w$  is equal 1.0,  $z \leq z_c$  setting  $z_c = z_{\min}$  being obtained from the condition  $dU_{\text{LJ}}^{\text{wall}}/dr = 0$ . So  $z_{\min} = (2/5)^{1/6}\sigma = 0.5353\sigma$  for the repulsive wall and for the attractive wall, the potential was truncated at  $z_c = 4.5\sigma$ . Shifting and truncation were performed for those potentials according to  $U_{\text{LJ,sh}}^{\text{wall}}(z) = U_{\text{LJ}}^{\text{wall}}(z) - U_{\text{LJ}}^{\text{wall}}(z_c)$ . The bonds were simulated with Finitely Extensive Nonlinear Elastic (FENE) potential [29]:

$$U_{\text{FENE}}(r) = -\frac{KR_0^2}{2} \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right], \quad r < R_0, \quad (2.3)$$

where  $R_0 = 1.0$  and  $K = 40.0$ , while for  $r > R_0$  the potential  $U_{\text{FENE}}(r) = 0$ . We performed simulations for linear, ring polymers:  $3_1, 6_1, 7_1, 9_1, 10_{124}$  and twist knots with  $n = 20$  number of twists.

### 3. Results







Taking into account the dependence of the radius of gyration on the topological structure, we investigated the effect of the complexity of the polymer on the entropic forces arising in the confined geometry. We investigated the behaviour of ring polymer chains such as unknotted  $0_1$  or with knots  $3_1, 6_1, 7_1, 9_1, 10_{124}$  (according to the standard Alexander-Briggs notation  $c_p$ ) and twist knot with [30]  $n = 20$  (see table 1). The  $3_1$  knot is the example of one of the simplest non-trivial topologies also called trefoil knot. In this notation, the  $c$  is the number of crossings, whereas the subscript  $p$  corresponds to the order among all knots with the same number of crossings, which can be an arbitrarily assigned number.

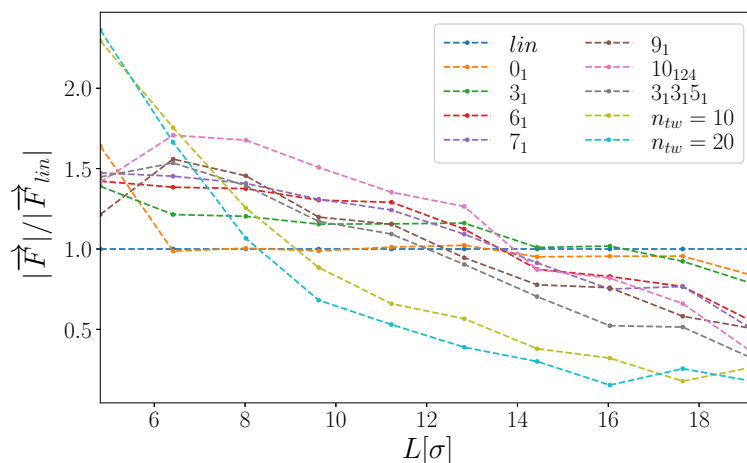
We calculated the radii of gyration for each knot type using MD simulations at an adsorption temperature of  $T = 2.30$  [27]. The obtained results are presented in table 1. One can notice that for the least complicated polymers like  $3_1$ , the radius of gyration is the highest, while for the most complicated ring polymer with the twist knot  $n = 20$  it has the lowest value, which is an expected observation.

Additionally, we performed molecular dynamics simulations of the model and calculated the entropic forces for different topological structures of ring polymer chains with the excluded volume interaction confined in a slit geometry of two parallel walls where one is attractive and the other one is repulsive. As it is known, the entropic force measures the polymer interaction with the confining walls.

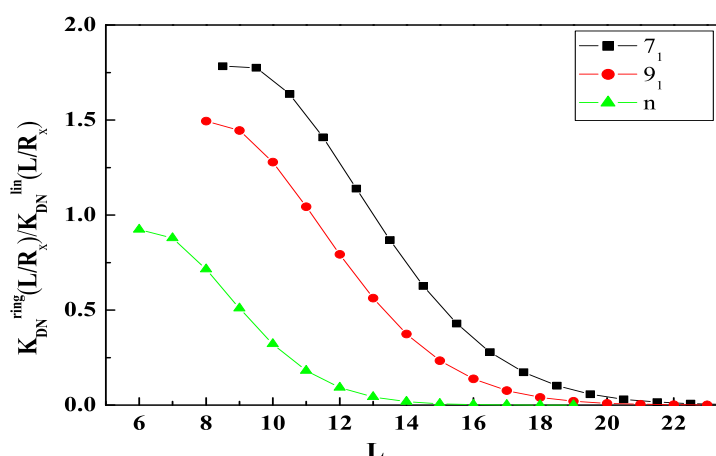
The results of simulations are presented in figure 1 and some analytical results for a wide slit region based on the results obtained in [12, 13] can be found in figure 2 for qualitative comparison reasons. We can observe from figure 1 that as the distance between the walls increases, the entropic forces nonlinearly approach zero. As it is possible to see from the results presented in figure 1, the ratio of the entropic forces for ring polymers decreases with an increase of the slit width and with an increase of the complexity

**Table 1.** The radius of gyration for different types of knottings obtained by molecular dynamics simulations.

Knot type	Illustrative image	Radius of gyration
$3_1$		4.0893
$6_1$		3.5128
$7_1$		3.4318
$9_1$		3.2817
$10_{124}$		3.2355
Twist knot with $n=20$		2.8073

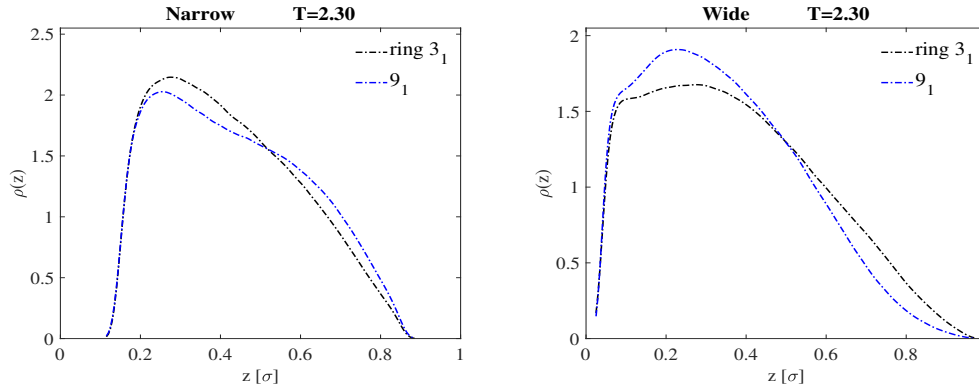


**Figure 1.** (Colour online) The ratio of entropic forces for a single real ring polymer chain to the force for real linear polymer chain in a slit geometry with one adsorbing wall and the other repulsive one obtained by molecular dynamic simulation.



**Figure 2.** (Colour online) The entropic force ratio of specific knotted ideal ring polymers ( $7_1, 9_1, n_{tw} = 20$ ) to the linear ones obtained analytically on the basis of the analytical results presented in [12, 13] for a wide slit region.

of the polymer topology for a wide slit region. Generally, the real ring polymers with the EVI have a greater absolute value of the forces than ideal polymer chains, which is an interesting observation from the theoretical point of view. It suggests that the excluded volume effects have a significant impact on the properties of polymer solution. As we can see from figure 3, the monomer density profiles of ring polymers with different topological structures have higher values near the attractive wall and decrease nonlinearly in the direction towards the repulsive wall. Moreover, one can observe that for a narrow slit (left side), the polymers with less complicated structure have a higher density near the attractive wall (at  $z = 0$ ) than more complicated ones. The opposite behaviour is observed near the repulsive wall. For a wide slit, the relation of densities to polymer complexity across the slit is contrary compared to the narrow case. It results in a smaller probability of contact between entangled polymer and this wall. The consequence of this could be that for a wide slit region, the degree of force generation due



**Figure 3.** (Colour online) The monomer density profiles for temperature  $T = 2.30$  in narrow and wide slit for two selected knots:  $3_1$  and  $9_1$  obtained using molecular dynamic simulations. The slit width  $z$  is on the horizontal axis and is scaled to 1. Narrow slit corresponds to the width of  $4.81\sigma$  ( $L < 2R_g$ ) and wide slit corresponds to  $19.24\sigma$  ( $L > 2R_g$ ) [28].

to fluctuations and contact between the walls is significantly reduced. Thus, it could be understandable that with an increase of the distance between the walls the influence of the interactions of polymer with walls becomes negligible. The obtained value of the monomer density is expected to control the force exerted by the polymer on the confining walls. The comparison of figure 3 and figure 1 demonstrate a close correlation between the two above mentioned quantities.

In figure 2, we present the analytical results of entropic force ratios for the given topologies  $7_1$ ,  $9_1$  and  $n_{tw} = 20$  to force for linear polymer in a wide slit obtained on the basis of the results presented in [12, 13]. The results suggest that in a wide slit, the forces decrease with an increase of the complexity of the polymer topology. These results are in a qualitative agreement with the results obtained by molecular dynamic simulations presented in figure 1 when we look at the right side of the graph, where the wide slit region is located. Besides, as it is possible to see from figure 1, each type of ring polymer topologies has its own crossing point of the ratio being higher or lower compared to the linear polymer chain, which is shown with the line at the value 1.0. It can be seen on the left-hand side of figure 1, that the more complex is the knot, the larger force ratio it has compared to a linear polymer, whereas on the right-hand side of figure 1 we observe that for the wide slits, the relation is opposite. Thus, it means that the more complex is the polymer, the smaller force ratio it has.

## 4. Conclusions

The results of MD simulations are presented in figure 1 for the ratio of the entropic forces. This is a ratio of the entropic forces of real ring polymer chains with the EVI for different topologies to the entropic force of a linear polymer chain. These findings align with the analytical results for a dilute solution of ideal ring polymer chains, as shown in figure 2. The analytical results are based on the research presented in references [12, 13]. From the obtained numerical and analytical results, we see that the depletion force, which arises in a dilute solution of ring polymer chains with different topological structures confined in a slit geometry with mixed D-N b.c. is repulsive. Those results are interesting from the point of view of their application to nano- or micro-electromechanical systems (NEMS and MEMS), because it allows one to reduce the static friction due to the depletion repulsion, which prevents them from malfunction.

In nanotechnology, the repulsion between confining walls in a dilute solution of real ring polymer chains with mixed D-N boundary conditions has practical applications. It helps preventing the agglomeration of nanoparticles and ceramic nanopowders. Additionally, it reduces the static friction between these particles. It can be used for the creation of a new generation of nano- and micro-electromechanical devices. Preventing the creation of nanoparticle agglomerates is a very important task in the nanotechnology and electronic industry in order to reduce the sizes of manufactured devices.

Our numerical study indicates that polymers with different topological structures exhibit varied force ratios in relation to the slit size. Such a behavior may play a significant role in biological systems. As depicted in figure 1, more complex knots (or structures) exert larger force ratios for narrow slits. By contrast, in the region of wider slits, these ratios are smaller compared to the linear polymer case. Simulation results show a nonlinear decrease in the force ratio for the most intricate cases, such as the twisted polymer with 20 twists, which is more pronounced than in other scenarios.

The molecular dynamic simulation outcomes suggest that the effect of polymer complexity on the force ratio might arise from the increasing steric effects due to the dense spatial packing of polymers with intricate knots. These complex knots have limited spatial penetration due to fluctuations and are inherently stiffer. This suggests that in wide slits, the interaction with the opposite side may be limited, thereby reducing the force exerted on the opposite wall. The density profiles of polymers with varying knot structures are discussed in [28], where it was demonstrated that the wide slit space penetration diminishes with the knot complexity, see figure 3. Conversely, in narrow slits, where the distance is short, both complex and simple polymers can directly influence the opposite slit sides [28].

In recent papers [31, 32], using the tube model it was shown that the sizes of polymer knots (measured in monomer size units) are influenced by the confinement. Under strong confinement conditions, the knot sizes decrease. A comparison of the free energy required to form a knot in a free space versus under the confinement revealed that the free energy around the knot intersections increases, forcing the monomers out of the knot to decrease the overall free energy of the chain. Our findings show that strongly confined polymers with more complex knots exert larger forces on the walls. Similar to prior findings, it is plausible that the increased forces exerted by knots may also be linked to the enlarged free energies at the knot intersections.

The dual nature of evolutionarily conserved slit proteins may have broader implications in the organism development. For instance, they have been shown to guide the tracheal development of *Drosophila melanogaster* [35]. We highlight a potential mechanism that might switch between interacting and non-interacting walls, achievable by merely altering the polymer's conformation in the medium. In the case of two repulsive walls, the polymer chain stays in the middle of the slit. However, in the case of a slit with mixed b.c., when one wall is attractive and the other one is repulsive, the polymer prefers to stay near the attractive wall. In the mixed case, changing the topology of the chain can have a much higher impact on the space penetrated by itself due to the thermal fluctuations compared to the nonadsorbing case.

In rough ER in cells, such as those in translationally active liver cells, protein translation is a continuous, steady-state process. This process may help maintain the rough ER's structure, which is characterized by elongated, flat disks dispersed throughout the cell volume. Any disruption in this translation stream or changing the interaction properties of polymers, due to adding the knots, could morphologically impact the size of the lumen of ER structure. Such structural changes might result in a potential risk of the cell malfunction. On the other hand, as was indicated in [36], the ER plays a pivotal role in the axon development and presynaptic differentiation. In other words, such ER structural changes due to polymer switching to the knotted forms, might impact the stability of ER, which could further lead to a potential reduction of neural network development.

In summary, ring polymer solutions under mixed boundary conditions exhibit distinct behaviours compared to those in homogenous environments. Given the vast range of conditions in biological systems, introducing these interactions from an entropic perspective could provide deeper insights into cellular-scale biological processes. Simplifying these intricate systems might involve employing coarse-grained methods or effective fields to incorporate entropic or depletive effects, complementing classical approaches. It might help to improve the understanding of the models such as the protein transport or behaviour inside the ER. Moreover, acknowledging these interactions could be pivotal in comprehending the neuroplasticity aspects, specifically presynaptic differentiation and axon development, as indicated in [36]. Additionally, this knowledge has potential applications in devising new materials for drug delivery systems, such as micelles, whose behavior might deviate due to entropic or depletive factors compared to standard lab conditions. Overall, considering entropic or depletion interactions in biological systems can enrich our comprehension of these intricate processes.

Ambivalent nature of evolutionary conserved slit proteins might have wider importance in organism development. It was shown that it can guide tracheal development of *Drosophila melanogaster* [35]. We show potentially one of the mechanisms, which could lead to switching between interacting and

noninteracting walls, which could be done by just changing the conformation of the polymer in the medium, which results in smaller or larger space penetrated by thermally fluctuating polymer that is adsorbed on one of the sides of the slit. The polymer systems in mixed interaction environment can present an interesting behaviour from theoretical and numerical perspective due to thermal fluctuations and some spatial constraints, which in mesoscopic or microscopic scale may exhibit new phenomena. This is just like mentioned earlier in rough ER of cells in general and liver cells in particular. Such interactions due to a constant stream of translational process of proteins belong to the system of one adsorbed and another repelled polymer. This system can be imagined to be in a state resembling the steady state, which could help in keeping the structure of rough endoplasmic reticulum. The ER has long and flat disks that are in the bulk of the cell volume. Any deviation in such stream of polymer translation could have morphological consequences in the cells structure and thus increase the risk of cell malfunction. Like it was shown in [36], the ER plays an important role in axon development and presynaptic differentiation. Moreover, if we assume that rough ER width is around 20–30 nm, then switching conformation by entangling it could switch between interacting and non-interacting states with two walls at the same time.

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## Ентропійна сила в розведеному розчині справжніх ланцюгів кільцевих полімерів з різними топологічними структурами в щілині двох паралельних стінок зі змішаними граничними умовами

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Моделювання методом молекулярної динаміки було використано для розрахунку радіуса гірації справжніх ланцюжків із кільцевих полімерів з різними топологічними структурами, що містять 360 мономерів. Автори зосереджуються на ентропійній силі, з якою розведений розчин ланцюжків кільцевого полімеру різних топологічних структур з взаємодією виключеного об'єму (EVI) діє у хорошому розчиннику на обмежуючі паралельні стінки з щільною геометрією. Розглядаються змішані граничні умови, коли одна стінка є відштовхуючою, а інша – на границі адсорбції. Отримані результати молекулярної динаміки для області широкої щілини показують якісне узгодження з попередніми аналітичними результатами для ідеальних кільцевих полімерів. Ці результати можуть мати цікаве потенційне застосування у матеріалознавстві та розширювати наше розуміння деяких біологічних процесів, про які йдеться у статті. Крім того, це може бути застосовано в мікро- та наноелектромеханічних пристроях для зниження ефекту статичного тертя.

**Ключові слова:** м'яка речовина, термодинаміка інтерфейсів та поверхонь, поведінка полімерів, фазовий перехід, молекулярна динаміка водневї зв'язки

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