

Investigation of ring polymers in confined geometries

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Abstract. The investigation of a dilute solution of phantom ideal ring polymers and ring polymers with excluded volume interaction (EVI) in a good solvent confined in a slit geometry of two parallel repulsive walls and in a solution of colloidal particles of big size were performed. Taking into account the correspondence between the field theoretical ϕ^4 $O(n)$ -vector model in the limit $n \rightarrow 0$ and the behavior of long-flexible polymers, the depletion forces and the forces which exert phantom ideal ring and ring polymer with EVI on the walls were obtained in the framework of the massive field theory approach at fixed space dimensions $d=3$ up to one-loop order. Additionally, the investigation of a dilute solution of phantom ideal ring polymers in the slit geometry of two inert walls and mixed walls with one repulsive and one inert wall were performed. Taking into account the Derjaguin approximation the depletion forces between big colloidal particle and a wall as well as between two big colloidal particles were calculated. The obtained results give possibility to understand the complexity of physical effects arising from confinement and chain topology and can find practical application in new types of micro- and nano-electromechanical devices.

1. Introduction

The investigation of a dilute solution of ring polymers in confined geometries such as slit geometry of two parallel walls or inserted in a solution of mesoscopic colloidal particles is a task of great interest not only from the experimental and numerical, but also from the theoretical point of view. As it was shown in a series of atomic force microscopy (AFM) experiments [1, 2] biopolymers such as DNA very often present ring topology. Such situation takes place, for example, in the case of *Escherichia coli* (*E.coli*) bacteria with a chromosome which is not a linear polymer, but has a ring topology [3]. The biopolymers of DNA of some viruses such as bacteriophages λ that infect bacteria oscillate between linear and ring topology [4, 5]. The linear form of DNA is encountered in mature viruses, however inside of the host cell DNA of phages adopts a ring topology [6]. Besides, the physical effects arising from confinement and chain topology play a significant role in shaping individual chromosomes and in the process of their segregation, especially in the case of elongated bacterial cells [7].

Ring polymers with specified knot type were chemically synthesized a long time ago [8]. Ring topology of polymer chains has influence on statistical mechanical properties of these polymers, for example on scaling properties [9, 10] and shape [2, 11] because it restrains the accessible phase space. Looking back into the history of investigation of the statistical mechanical properties of ring polymers we should mention that it was established [12], that ring polymers with more complex knots are more compact and have a smaller radius of gyration and this decreases their ability to spread out under confinement. A series of papers [13, 14] have been devoted to the investigation of ring polymers compressed or squeezed



by a force in a slab. For example, the results of Monte Carlo simulations performed in reference [13] suggest that the knotted ring polymers will exert higher entropic forces on the walls of the confining slit than unknotted or linear polymer chains. It was stated [13] that the knotted ring polymers expanded as the width of the slit increased in contrast to the behaviour of unknotted (or linear) polymer chains whose size showed a plateau after a certain width of slit was reached. The entropic force exerted on the walls arising from confinement to a slit of a knotted ring polymer was calculated using a bead-spring model by Matthews *et al.* in [5]. It was found [5] that in the case of a narrow slit more complex knot types in a ring polymer exert higher forces on the confining walls of the slit in comparison to unknotted polymers of the same length, and for relatively wide slits the opposite situation takes place. Recently advanced Monte Carlo simulation techniques [15] have been used in order to study the effect of nanoslit confinement on topological properties of circular model DNA, which was modeled as a semi-flexible polymer chain.

Thus, at the moment most of the papers dedicated to the investigation of ring polymers compressed in confined geometries like slit or squeezed by a force in a slab of two parallel walls are performed using Monte Carlo simulation techniques, and present analytical results are not complete. The above mentioned arguments stimulate us to apply the massive field theory approach in a fixed space dimensions $d < 4$ for the investigation of ring polymers confined in the slit geometry of two parallel walls or immersed in the solution of big mesoscopic colloidal particles of different size. This method, as it was shown in the case of infinite [16, 17], semi-infinite [18, 19] systems, and confined geometry [20, 21] gives good agreement with the experimental data and with the results of Monte Carlo simulations.

2. The model and the polymer-magnet analogy

We are interested in the investigation of ring polymers confined in the slit geometry of two parallel walls and in the solution of mesoscopic spherical colloidal particles of one sort or two different sorts. We consider the dilute polymer solution, where different polymers do not overlap and the behaviour of such polymer solution can be described by a random walk (RW) of a single polymer for ideal polymer in Θ -solvent [22, 23] or self-avoiding walk (SAW) for real polymer with excluded volume interaction (EVI) in a good solvent at the temperatures above the Θ -temperature [22, 23]. Taking into account the polymer-magnet analogy developed by de Gennes [22, 23], the scaling properties of long-flexible polymers in the limit of an infinite number of steps N may be derived from a formal $n \rightarrow 0$ limit of the field theoretical ϕ^4 $O(n)$ -vector model at its critical point. In this case the $1/N$ value plays the role of a critical parameter analogous to the reduced critical temperature in magnetic systems. In the case when the polymer solution is in contact with solid substrates, the monomers interact with the surfaces. We assume that the surfaces are impenetrable. It means that the potential $U(z)$ of the interaction between the monomers of a polymer chain and a wall tends to infinity $U(z) \rightarrow \infty$ when the distance between the wall and polymer is less than the monomer size l . The deviation from the adsorption threshold ($c \propto (T - T_a)/T_a$) (where T_a is adsorption temperature) changes sign at the transition between the adsorbed (the so-called normal transition, $c < 0$) and the nonadsorbed state (ordinary transition, $c > 0$) [24, 25] and it plays the role of a second critical parameter. The value c corresponds to the adsorption energy divided by $k_B T$ (or the surface enhancement in field theoretical treatment). The adsorption threshold for long-flexible polymer chains takes place, when $1/N \rightarrow 0$ and $c \rightarrow 0$.

As was mentioned by de Gennes [22, 23], the partition function $Z(\mathbf{x}, \mathbf{x}')$ of a single polymer with two ends fixed at \mathbf{x} and \mathbf{x}' is connected with the two-point correlation function $G^{(2)}(\mathbf{x}, \mathbf{x}') = \langle \vec{\phi}(\mathbf{x}) \vec{\phi}(\mathbf{x}') \rangle$ in ϕ^4 $O(n)$ -vector model for n -vector field $\vec{\phi}(\mathbf{x})$ with the components $\phi_i(x)$, $i = 1, \dots, n$ (and $\mathbf{x} = (\mathbf{r}, z)$) via the inverse Laplace transform $\mu_0^2 \rightarrow L_0$:

$$Z(\mathbf{x}, \mathbf{x}'; N, v_0) = \mathcal{I} \mathcal{L}_{\mu_0^2 \rightarrow L_0} (\langle \vec{\phi}(\mathbf{x}) \vec{\phi}(\mathbf{x}') \rangle |_{n \rightarrow 0}) \quad (1)$$

in the limit, where the number of components of n tends to zero. The conjugate Laplace variable L_0 has the dimension of length squared and is proportional to the total number of monomers N which form the polymer chain.

The effective Ginzburg-Landau-Wilson Hamiltonian describing the system in semi-infinite ($i = 1$) or confined geometry of two parallel walls ($i = 1, 2$) is [24]:

$$\mathcal{H}[\vec{\phi}, \mu_0] = \int d^d x \left\{ \frac{1}{2} (\nabla \vec{\phi})^2 + \frac{\mu_0^2}{2} \vec{\phi}^2 + \frac{v_0}{4!} (\vec{\phi}^2)^2 \right\} + \sum_{i=1}^2 \frac{c_{i_0}}{2} \int d^{d-1} r \vec{\phi}^2, \quad (2)$$

where the conjugate chemical potential μ_0 is the "bare mass" in field - theoretical treatment, v_0 is the "bare coupling constant" which characterizes the strength of the excluded volume interaction (EVI). In the case of the slit geometry the walls are located at the distance L one from another in z -direction in such way that the surface of the bottom wall is located at $z = 0$ and the surface of the upper wall is at $z = L$. Each of the two system surfaces is characterized by a certain surface enhancement c_{i_0} , where $i = 1, 2$.

The fundamental two-point correlation function of the free theory corresponding to the effective Ginzburg-Landau-Wilson Hamiltonian equation (2) in a mixed (\mathbf{p}, z) representation is:

$$G_{ij}^{(2)}(\mathbf{p}, \mathbf{p}'; z, z') = (2\pi)^{d-1} \delta_{ij} \delta(\mathbf{p} + \mathbf{p}') \tilde{G}_{\parallel}(\mathbf{p}; z, z'; \mu_0, c_{1_0}, c_{2_0}, L), \quad (3)$$

where the free propagator $\tilde{G}_{\parallel}(\mathbf{p}; z, z'; \mu_0, c_{1_0}, c_{2_0}, L)$ of model (2) was obtained in one of our previous papers [20]. In the case when the ends of the polymer chain $\mathbf{x} = (\mathbf{r}, z)$ and $\mathbf{x}' = (\mathbf{r}', z')$ in the partition function (1) coincide, such partition function corresponds to the partition function of a phantom ring polymer, i.e. a ring polymer where we perform the summation over all possible knot structures, as it was mentioned by Eisenriegler [25]. Taking into account the above mentioned arguments the free propagator of model (2) describing a ring polymer with two coinciding ends $\mathbf{x} = \mathbf{x}'$ in the slit geometry of two parallel walls can be obtained by analogy to what was done in [20] and has a form:

$$\begin{aligned} \tilde{G}_{\parallel}(\mathbf{p}; z, z'; \mu_0, c_{1_0}, c_{2_0}, L) = & \frac{1}{2\kappa_0} \left\{ [\kappa_0^2 + \kappa_0(c_{1_0} + c_{2_0}) + c_{1_0}c_{2_0}] e^{\kappa_0 L} - [\kappa_0^2 - \kappa_0(c_{1_0} + c_{2_0}) + c_{1_0}c_{2_0}] e^{-\kappa_0 L} \right\}^{-1} \\ & \times \left\{ [\kappa_0^2 + \kappa_0(c_{1_0} + c_{2_0}) + c_{1_0}c_{2_0}] e^{\kappa_0 L} + [\kappa_0^2 - \kappa_0(c_{1_0} + c_{2_0}) + c_{1_0}c_{2_0}] e^{-\kappa_0 L} \right. \\ & + [\kappa_0^2 + \kappa_0(c_{2_0} - c_{1_0}) - c_{1_0}c_{2_0}] e^{\kappa_0(L-2z)} \\ & \left. + [\kappa_0^2 - \kappa_0(c_{2_0} - c_{1_0}) - c_{1_0}c_{2_0}] e^{-\kappa_0(L-2z)} \right\} \end{aligned} \quad (4)$$

with $\kappa_0 = \sqrt{p^2 + \mu_0^2}$, where \mathbf{p} is the value of parallel momentum associated with $d - 1$ translationally invariant directions in the system. The interaction between polymer and the walls is implemented by the boundary conditions. In the case of two repulsive walls (where the segment partition function and thus the partition function for the whole polymer tends to zero as any segment approaches the surface of the walls) the Dirichlet-Dirichlet boundary conditions (D-D b.c.) (see also [20, 24, 26]) take place: $\vec{\phi}(\mathbf{r}, 0) = \vec{\phi}(\mathbf{r}, L) = 0$ or $c_1 \rightarrow +\infty, c_2 \rightarrow +\infty$. In the case of two inert walls Neumann-Neumann boundary conditions (N-N b.c.) take place: $\frac{\partial \vec{\phi}(\mathbf{r}, z)}{\partial z} \Big|_{z=0} = \frac{\partial \vec{\phi}(\mathbf{r}, z)}{\partial z} \Big|_{z=L} = 0$ or $c_1 = 0, c_2 = 0$, and for the mixed case of one repulsive and one inert wall Dirichlet-Neumann boundary conditions (D-N b.c.) are: $\vec{\phi}(\mathbf{r}, 0) = 0, \frac{\partial \vec{\phi}(\mathbf{r}, z)}{\partial z} \Big|_{z=L} = 0$ or $c_1 \rightarrow +\infty, c_2 = 0$. The present calculations are valid for the case of wide slit limit $y \gtrsim 1$ (where $y = \frac{L}{R_x}$) and are not able to describe the case of dimensional crossover from d to $d - 1$ dimensional system which arises for $y \ll 1$. The $d - 1$ dimensional system is characterized by another critical temperature and a new critical fixed point. Nevertheless, some assumptions allowed us to describe the region of narrow slit for the case of grand canonical ensemble, as it was proposed in one of our previous papers (see reference [20]). Besides, in the case of infinitely large wall separations, the slit system decomposes into two half-space systems.

It should be mentioned that the most common parameter in polymer physics used for denoting polymers size which is observable in experiments is the radius of gyration R_g (see references [25, 27]): $R_g^2 = \chi_d^2 \frac{R_x^2}{2}$, where χ_d is a universal numerical prefactor depending on the dimension d of the system and $R_x^2 = \frac{l^2 N^{2\nu}}{3}$ (where ν is 0.5 for ideal polymers and 0.588 for real polymers with EVI). For ideal polymers the relation: $\chi_d^2 = \frac{d}{3}$ takes place and for real polymers at $d = 3$ the following takes place [27]: $\chi_3^2 = 0.958$.

3. Thermodynamic description

We consider the dilute solution of phantom ideal ring polymers and ring polymers with EVI immersed in the slit geometry of two parallel walls and allow the exchange of polymer coils between the slit and the reservoir. The polymer solution in the slit is in equilibrium contact with an equivalent solution in the reservoir outside of the slit. We follow the thermodynamic description of the problem as it was given in [20, 26] and perform the calculation in the framework of the grand canonical ensemble where the chemical potential μ is fixed. As it was shown in [26], the free energy of the interaction between the walls in the grand canonical ensemble is defined as the difference of the free energy of an ensemble where the separation of the walls is fixed at a finite distance L and where the walls are separated infinitely far from each other:

$$\delta F^R = -k_B T \mathcal{N} \ln \left(\frac{\mathcal{Z}_{\parallel}^R(L)}{\mathcal{Z}_{\parallel}^R(L \rightarrow \infty)} \right) = -k_B T \mathcal{N} \left\{ \ln \left(\frac{\mathcal{Z}_{\parallel}^R(L)}{\mathcal{Z}} \right) - \ln \left(\frac{\mathcal{Z}_{\parallel}^R(L \rightarrow \infty)}{\mathcal{Z}} \right) \right\}, \quad (5)$$

where \mathcal{N} is the total amount of polymer coils in the solution and T is the temperature. The $\mathcal{Z}_{\parallel}^R(L)$ value is the partition function of one ring polymer located in a volume V containing two walls at a distance L apart. For the sake of convenience we normalized the partition functions $\mathcal{Z}_{\parallel}^R(L)$ and $\mathcal{Z}_{\parallel}^R(L \rightarrow \infty)$ to $\mathcal{Z} = V \hat{\mathcal{Z}}_b$, where $\hat{\mathcal{Z}}_b = \mathcal{L} \mathcal{L}_{\mu_0^2 \rightarrow \frac{R_x^2}{2}} \left[\frac{1}{2\mu_0} \right]$.

Following the thermodynamic description proposed in [20, 26] the corresponding *reduced free energy of interaction* δf per unit area, $A = 1$, for the case of ring polymer confined in the slit geometry of two parallel walls after performing Fourier transform in the direction parallel to the surfaces and integration over $d^{d-1}r$ may be written in the form:

$$\delta f^R = \frac{\delta F^R}{n_p k_B T} = L - \int_0^L dz \frac{\hat{\mathcal{Z}}_I^R(z)}{\hat{\mathcal{Z}}_b} + \int_0^\infty dz \left(\frac{\hat{\mathcal{Z}}_{HS_1}^R(z)}{\hat{\mathcal{Z}}_b} - 1 \right) + \int_0^\infty dz \left(\frac{\hat{\mathcal{Z}}_{HS_2}^R(z)}{\hat{\mathcal{Z}}_b} - 1 \right). \quad (6)$$

Here $n_p = \mathcal{N}/V$ is the polymer density in the bulk solution, the functions $\hat{\mathcal{Z}}_I^R(z)$ and $\hat{\mathcal{Z}}_{HS_i}^R(z)$ are equal to: $\hat{\mathcal{Z}}_I^R(z) = \mathcal{L} \mathcal{L}_{\mu_0^2 \rightarrow L_0} G^{(2)}(\mathbf{p} = 0; z, z)|_{n \rightarrow 0}$, and $\hat{\mathcal{Z}}_{HS_i}^R(z) = \mathcal{L} \mathcal{L}_{\mu_0^2 \rightarrow L_0} G_{HS_i}^{(2)}(\mathbf{p} = 0; z, z)|_{n \rightarrow 0}$, where $G^{(2)}(\mathbf{p} = 0; z, z)$ and $G_{HS_i}^{(2)}(\mathbf{p} = 0; z, z)$ with $i = 1, 2$ are correlation functions of model (2) describing the system in the slit geometry of two parallel walls and in semi-infinite geometry, respectively. The *reduced free energy of interaction* δf^R , according to equation (6), is a function of the dimension of length and dividing it by another relevant length scale, for example, the size of polymer in bulk, e.g. R_x yields a universal dimensionless scaling function for the *depletion interaction potential*:

$$\Theta^R(y) = \frac{\delta f^R}{R_x}, \quad (7)$$

where $y = L/R_x$ is a dimensionless scaling variable. The resulting scaling function for the *depletion force* between two walls induced by the polymer solution is denoted as:

$$\Gamma^R(y) = -\frac{d(\delta f^R)}{dL} = -\frac{d\Theta^R(y)}{dy}. \quad (8)$$

As it is known [25], the force exerted on the surfaces of a confining slit by polymer is equal to the *depletion force* with opposite sign: $K^R(y) = \frac{d(\delta f^R)}{dL}$.

4. Phantom ideal ring polymer in the slit geometry of two parallel walls

Let's consider at the beginning the case of phantom ideal ring polymer under Θ -solvent condition trapped in the slit geometry of two parallel walls situated at the distance L one from another. According to

equations (7) and (8) in the wide slit region $L/R_x \gtrsim 1$ (or $y \gtrsim 1$) for the dimensionless scaling functions for the *depletion interaction potential* $\Theta^R(y)$ and the *depletion force* $\Gamma^R(y)$ between two repulsive (or inert) walls induced by the dilute solution of ideal ring polymers we obtain:

$$\Theta_{DD}^{R,id}(y) = -2ye^{-2y^2}, \quad \Gamma_{DD}^{R,id}(y) = 2e^{-2y^2} - 8y^2e^{-2y^2}. \quad (9)$$

The universal dimensionless scaling functions for the *depletion interaction potential* and the *depletion force* in the case of one repulsive and one inert wall (D-N b.c.) in the limit $y \gtrsim 1$ has a form:

$$\Theta_{DN}^{R,id}(y) = 2ye^{-2y^2}, \quad \Gamma_{DN}^{R,id}(y) = -2e^{-2y^2} + 8y^2e^{-2y^2}. \quad (10)$$

We obtained that phantom ideal ring polymers due to the complexity of chain topology and from entropical reasons prefer to escape from the space not only between two repulsive walls but also in the case of two inert walls. As a result, the attractive *depletion force* arises between the walls. As it is possible to see from equation (10), the scaling function for the *depletion force* in the case of mixed boundary conditions becomes repulsive in the region $y \gtrsim 1$.

The region of narrow slit corresponds to the situation of $L/R_x \ll 1$ (or $y \ll 1$). We can state that in the case of very narrow slit with two repulsive walls the ring polymers would pay a very high entropy to stay in the slit or even enter it. The contribution from the partition function of polymer chain in the slit $\frac{1}{L} \int_0^L dz \frac{\hat{Z}_I^R(z)}{\hat{Z}_b}$ in equation (6) vanishes strongly as $y \rightarrow 0$. Taking into account in the case of narrow slit of two repulsive walls only the corresponding bulk and the surface contributions in equation (6) gives possibility to obtain the asymptotic solutions for the scaling functions $\Theta_{DD}^{R,id}(y)$ and $\Gamma_{DD}^{R,id}(y)$ in the form: $\Theta_{DD,narr}^{R,id}(y) \approx y - \frac{\sqrt{2\pi}}{2}$, and $\Gamma_{DD,narr}^{R,id}(y) \approx -1$. The quantities Θ and Γ are normalized to the overall polymer density n_p . So, the above results simply indicate that the force is entirely induced by free chains surrounding the slit, or, in other words, by the full bulk osmotic pressure from the outside of the slit. It means that in the case of narrow slit with two repulsive walls no chain has remained inside the slit. The advantage of the proposed procedure is that no expansion is necessary in this case of narrow slit region and it should be equally valid for polymer chains with EVI. In figures 1(a) and 1(b) we present the results for the force K^R (as functions of L for different values of the radius of gyration R_g) which exerts phantom

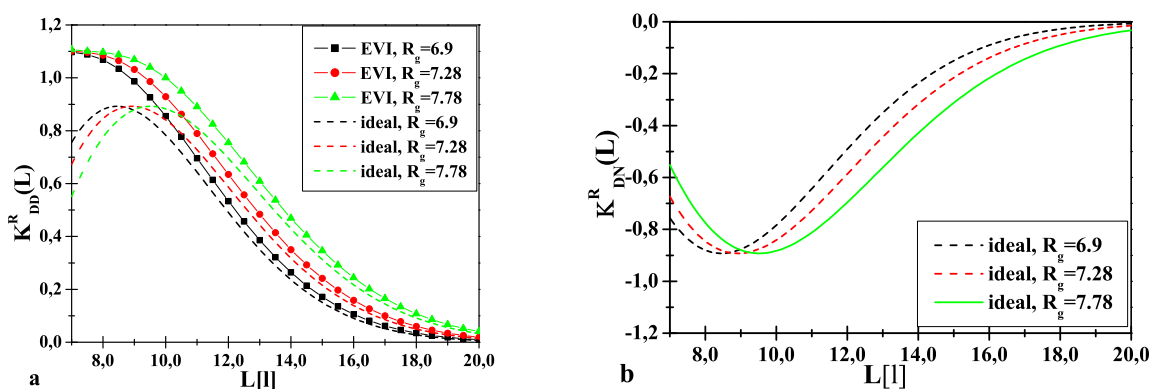


Figure 1. The force $K^R(L)$ for phantom ideal ring polymer and ring polymer with EVI in a good solvent immersed between: *a*) two repulsive walls; *b*) one repulsive and other one inert wall for different values of the radius of gyration R_g .

ideal ring polymer on the confining two repulsive (or two inert) walls and two mixed walls, respectively. It should be mentioned that calculations, presented in figure 1(a) and figure 1(b), were performed for different values of the radius of gyration [5]: $R_g(12_1) = 6.9 \pm 0.01[L]$, $R_g(9_1) = 7.28 \pm 0.01[L]$, and $R_g(6_1) = 7.78 \pm 0.01[L]$ which correspond to the ring polymers with different knot types: $12_1; 9_1; 6_1$, where C_p is a standard notation [29], C denotes the minimum number of crossings in any projection on a plane and p is used in order to distinguish knot types with the same C . It should be mentioned that region of validity of the obtained results for the entropically induced forces K^R for phantom ideal ring polymers [see figure 1(a), figure 1(b)] is defined by the value of $y = L/R_x \gtrsim 1$ with $R_x = \sqrt{2}R_g$.

5. Dilute solution of ring polymers with EVI in the slit of two repulsive walls

As a next step let's consider the dilute solution of ring polymers with EVI in a good solvent immersed in the slit geometry of two parallel repulsive walls. As it is known [22, 23], in a good solvent the effects of the EVI between monomers play a crucial role so that the polymer coils occupy large space and are less compact than in the case of ideal polymers. The influence of the EVI on the depletion functions and corresponding partition functions can be obtained via using perturbation treatment in the framework of the massive field theory approach in a fixed space dimensions $d = 3$ up to one-loop order approximation in the presence of confining slit geometry of two parallel repulsive walls. The calculation of the partition functions $\tilde{\mathcal{Z}}_i^R(z)$ and $\tilde{\mathcal{Z}}_{HS_j}^R(z)$ which allows to obtain the reduced free energy of interaction δf^R in equation (6) are connected with the calculation of the correlation functions $G^{(2)}(\mathbf{p} = 0; z, z)$ and $G_{HS_i}^{(2)}(\mathbf{p} = 0; z, z)$ with $i = 1, 2$, where the terms describing the EVI effects are taken into account via using perturbation treatment. The above mentioned correlation functions were renormalized in accordance with the renormalization scheme proposed in references [18, 20]. In order to make the theory UV finite in RG sense directly in $d = 3$ space dimensions we perform the standard mass renormalization $\mu_0^2 = \mu^2 - \delta\mu_0^2$ with $\delta\mu_0^2 = \frac{(n+2)}{6} \frac{v_0}{(2\pi)^{d-1}} \int \frac{d^{d-1}q}{2\kappa_q}$ and the coupling constant renormalization $v_0 = \mu v$ of the corresponding correlation functions by analogy to what was proposed by Parisi [17]. Besides, the surface enhancement renormalization $c_{j_0} = c_j + \delta c_j$ of the correlation functions in the case of D-D b.c. reduces to an additive renormalization as it took place in the case of semi-infinite geometry [18] and slit geometry (see reference [20]). In order to be concise, we do not present here the results of the complicated calculations and just discuss the limiting cases of wide and narrow slit regimes. The corresponding expression for the universal dimensionless scaling function for the *depletion interaction potential* can be written in the form:

$$\Theta_{DD}^{R,EVI}(y) = -2ye^{-2y^2} + \frac{\tilde{v}}{2} \left(\sqrt{2\pi} \operatorname{erfc}[\sqrt{2}y]D + e^{-2y^2}B(y) \right), \quad (11)$$

where we introduced $D = \frac{1}{4} [10 - 2i \ln 2 - 2\psi^{(0)}(-\frac{1}{2}) + \sqrt{\pi}\psi^{(0)}(\frac{1}{2}) - 2\gamma_E]$, $B(y) = 2y\sqrt{\pi}\psi^{(0)}(-\frac{1}{2}) - \frac{1}{y}$ and $v = b_n\tilde{v}$, with $b_n = \frac{6}{n+8} \frac{(4\pi)^{3/2}}{\Gamma(1/2)}$ at space dimensionality $d = 3$ and the limit $n \rightarrow 0$ was assumed. It should be mentioned that $\gamma_E = 0.577$ is the Euler's constant, $\psi^{(0)}(z)$ - is the digamma function, and $\operatorname{erfc}[z] = 1 - \operatorname{erf}[z]$ is the complementary error function. The calculations were performed at the corresponding stable fixed point $\tilde{v}^* = 1$ obtained from resummed beta functions of the underlying bulk field theory in the framework of one-loop approximation scheme. Taking into account equations (8) and (11), the result for the *depletion force* between two repulsive walls is:

$$\Gamma_{DD}^{R,EVI}(y) = 2e^{-2y^2} - 8y^2e^{-2y^2} - \frac{\tilde{v}}{2}e^{-2y^2} \left[\frac{1}{y^2} + 2\sqrt{\pi}\psi^{(0)}\left(-\frac{1}{2}\right) - D - 4yB(y) \right]. \quad (12)$$

The obtained results for the scaling functions $\Gamma_{DD}^R(y)$ between two repulsive walls in the dilute solution of phantom ideal ring polymers and ring polymers with EVI are presented in table 1.

In the region of very narrow slit $y \ll 1$ the *depletion potential* becomes:

$$\Theta_{DD,narr}^{R,real}(y) \approx y - \frac{\sqrt{2\pi}}{2} + \frac{\tilde{v}}{8} \left(\ln 2 - \frac{1}{2} \right) \sqrt{2\pi}$$

and the *depletion force* is: $\Gamma_{DD,narr}^{R,real}(y) \approx -1$.

Table 1. The dimensionless scaling function for the *depletion force* Γ_{DD}^R between two repulsive walls as function of $y = L/R_x$

y	1.3	1.5	1.7	1.9	2.1
ideal ring	-0.3922	-0.1777	-0.0652	-0.0197	-0.0049
ring with EVI	-0.3912	-0.1750	-0.0638	-0.0192	-0.0048

In figure 1(a) we present the results for the entropically induced force K^R (as a function of L for different values of the radius of gyration R_g) which exerts ring polymer with EVI on the confining two repulsive walls. We observed that in the wide slit region ring polymers with less complex knot types (with bigger radius of gyration) in a ring topology exert higher forces on the confining walls. Our results for entropically induced force K^R are in agreement with previous results obtained by Matthews *et al.* [5] using a bead-spring model.

6. Ring polymers in a solution of mesoscopic spherical colloidal particles

Let's consider the situation of the dilute solution of ring polymers immersed in the solution of mesoscopic colloidal particles. We focus our attention on the investigation of the depletion interaction for two cases: (a) between a big spherical colloidal particle of radius R and the wall; (b) between two colloidal particles of big sizes with different radii R_1 and R_2 and different adsorbing or repelling properties with respect to polymers in the solution. The interaction of the dilute solution of ring polymers with particles and walls is implemented by the corresponding boundary condition, as it was mentioned above. The difference between the forces with and without the particle (or particles) yields the depletion interaction of the particle with the wall (or between two particles). Taking into account the Derjaguin approximation [30], which describes the sphere of the big colloidal particle of the radius R (with $R \gg L$ and $R \gg R_x$) by a superposition of immersed plates with local distance $h(\rho) = a + R - \sqrt{R^2 - \rho^2}$ from the wall, where a is the nearest distance from the particle to the wall and ρ is the width of the fringe itself we performed calculations of the *depletion force*: $\frac{-d(\Phi^R(\tilde{y})/n_p k_B T)}{d\tilde{y}}$ between colloidal particle and the wall in a dilute solution of ring polymers. In the case of two big spherical colloidal particles with different radii $R_1 \neq R_2$ when $R_i \gg L$ and $R_i \gg R_x$, $i = 1, 2$ we also can use the Derjaguin approximation for calculation of the *depletion force* with some modification and taking into account that $h(\rho) = a + R_1 - \sqrt{R_1^2 - \rho^2} + R_2 - \sqrt{R_2^2 - \rho^2}$, where a , in this case, is the nearest distance from the particle to other particle. It should be mentioned, that the *depletion interaction potential* $\Phi^R(\tilde{y})/n_p k_B T$ is equal to: $2\pi\tilde{R}R_x^2 \int_{\tilde{y}}^{\infty} dy \Theta^R(y)$ with $\tilde{y} = a/R_x$ where $\tilde{R} = R$ for the case of the big particle of radius R near the wall and $\tilde{R} = R_1 R_2 / (R_1 + R_2)$ for the case of two particles with different radii $R_1 \neq R_2$.

Taking into account the results for the scaling function $\Theta^R(y)$ between two parallel repulsive (D-D b.c.) and inert (N-N b.c.) walls [see equation (9)] or for the mixed case of D-N b.c. [see equation (10)] induced by the dilute solution of ideal ring polymers in accordance with [30] for the *depletion interaction potential* $\Phi^R(\tilde{y})/n_p k_B T$ between the big spherical colloidal particle and the wall (or between two big spherical colloidal particles) we obtain:

$$\frac{\Phi^{id}(\tilde{y})}{n_p k_B T} = \pm \pi R_x^2 \tilde{R} \eta^{id}(\tilde{y}), \quad (13)$$

where $\eta^{id}(\tilde{y}) = -e^{-2\tilde{y}^2}$. The sign “+” corresponds to the case of D-D b.c. or N-N b.c. and the sign “-” to the case of D-N b.c. Based on the *depletion interaction potential* we can calculate the *depletion force* for

certain b.c.'s. The *depletion force* between the big spherical colloidal particle and the wall (or between two big spherical colloidal particles) for the case of D-D b.c. or N-N b.c. and for the mixed case of D-N b.c. has the following form:

$$-\frac{d}{d\tilde{y}} \frac{\Phi^{id}(\tilde{y})}{n_p k_B T} = \pm 2\pi R_x^2 \tilde{R} \vartheta^{id}(\tilde{y}), \quad (14)$$

where $\vartheta^{id}(\tilde{y}) = -2\tilde{y}e^{-2\tilde{y}^2}$ and the sign “+” corresponds to D-D b.c. or N-N b.c. and the sign “-” to the case of D-N b.c. In a similar way taking into account equation (11) we performed calculations for the *depletion force* between the big colloidal particle and the wall (or between two big spherical colloidal particles of different radii) induced by the dilute solution of ring polymers with EVI in a good solvent. The obtained results for the corresponding scaling function $\vartheta^{EVI}(\tilde{y})$ for the *depletion force* in the case of D-D b.c. induced by the dilute solution of ideal ring polymers and ring polymers with EVI in a good solvent are presented in table 2.

Table 2. The dimensionless scaling function $\vartheta(\tilde{y})$ for the *depletion force* which arises between the big spherical colloidal particle and the wall (or between two big spherical colloidal particles) in the case of D-D b.c. as function of $\tilde{y} = a/R_x$.

\tilde{y}	1.3	1.5	1.7	1.9	2.1
ideal ring	-0.0885	-0.0333	-0.0105	-0.0028	-0.0006
ring with EVI	-0.0873	-0.0326	-0.0103	-0.0027	-0.0006

7. Conclusions

The present investigations show that the scaling functions for the *depletion interaction potential* and the *depletion force* between two repulsive or two inert walls [see equations (9),(11),(12) and table 1] or in a mixed case of one repulsive and one inert walls [see equation (10)] induced by the dilute solution of phantom ideal ring polymers and real ring polymers with EVI are characterized by completely different behavior than in the case of the dilute solution of linear polymer chains immersed in the slit geometry of two parallel walls [see [20]]. We would like to recollect that in the case of linear ideal polymer chains in confined geometry of two inert walls, in reference [20] we obtained that the scaling functions for the *depletion interaction potential* and the *depletion force* were equal to zero. The obtained in the present paper results indicate that ring polymers due to the complexity of chain topology and from entropical reasons prefer to escape from the space not only between two repulsive walls but also in the case of two inert walls. As a result, the attractive *depletion force*, that arises, decreases as the width of slit increases. Besides, the *depletion force* between one repulsive and one inert walls induced by the dilute solution of ideal ring polymers becomes repulsive in the region $y \gtrsim 1$. Similar behaviour was observed for binary liquid mixture confined in the slit geometry of two parallel walls with mixed boundary conditions as it was shown in [28]. Such behaviour of the dilute solution of phantom ideal ring polymers in confined geometries of two parallel walls with mixed boundary conditions can be used for the production of new types of micro- and nano- electromechanical devices, because it allows to reduce the static friction in such systems. As it is possible to see from table 1, the absolute value of the scaling function for the *depletion force* between two repulsive walls for the dilute solution of ring polymers with EVI is smaller than for the dilute solution of ideal ring polymers in the region of validity of the obtained results, e.g. for $y \gtrsim 1$.

In order to compare our results with the results obtained in the framework of other methods we performed calculations of the entropically induced forces K^R exerted by ring polymer on the surfaces of the confining slit. The results for the forces K^R exerted by ring polymers on two repulsive, two inert and for the mixed case of one repulsive and one inert walls as functions of L for different values of

R_g are presented in figure 1(a) and figure 1(b), respectively. We observed that in the wide slit region ring polymers with less complex knot types (with bigger radius of gyration) in a ring topology exert higher forces on the confining repulsive walls [see figure 1(a)] at the same length L . As it is possible to see from figure 1(b) in the mixed case of one repulsive and one inert walls in the wide slit region the opposite is true. Figure 2 presents the ratio $K_{DD}^R(L)/K_{DD}^{lin}(L)$ of the force for ring polymers K_{DD}^R and the corresponding force for linear polymers K_{DD}^{lin} in the slit geometry of two parallel repulsive walls as function of the distance L (in l units) between the walls for different values of the radius of gyration. As it is possible to see from figure 2 our results for the ratio of the resulting entropic forces $K_{DD}^R(L)/K_{DD}^{lin}(L)$ are in good qualitative agreement with the previous results obtained by Matthews *et al.* (see figure 2 in [5]) in the framework of bead-spring model. The difference between our results and the results obtained by Matthews *et al.* arises due to the fact that in [5] calculations were performed for relatively short polymers with polymer length of order $N \sim 300$ units for different values of the radius of gyration. The force $K^{lin}(L)$ was obtained from the results presented in one of our previous papers [20]. Besides, taking into account the Derjaguin approximation [30] we obtained the results for the *depletion*

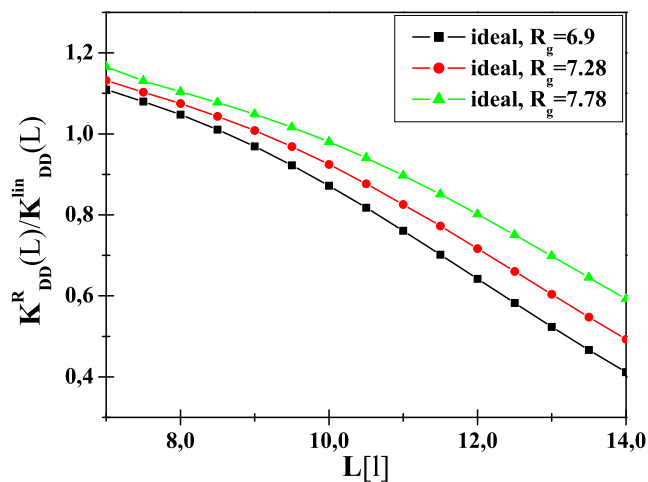


Figure 2. The ratio $K^R(L)/K^{lin}(L)$ of the force for ring polymers and the force for linear polymers in the slit geometry of two parallel repulsive walls as function of the distance L (in l units) between the walls for different values of the radius of gyration R_g .

interaction potential and the *depletion force* for the dilute solution of ring polymers immersed in the solution of mesoscopic spherical colloidal particles. We performed investigations of the depletion effect for mesoscopic colloidal particles with different radii and different adsorbing or repelling properties with respect to ring polymers in the solution. As it is possible to see from the obtained in equation (14) and table 2 results the absolute value of the depletion force between the spherical colloidal particle and the wall is bigger than for the case of two spherical colloidal particles. This feature is universal and does not depend on the boundary condition type. In the case when two colloidal particles have the same radius ($R_1 = R_2$), the corresponding *depletion force* is twice smaller than for the case of particle near the wall. Further analytical and experimental investigations of the dilute and semidilute solutions of ring polymers with EVI immersed in the slit geometry of two inert walls or mixed walls is a task of great interest and is currently under consideration.

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