Investigation of a dilute polymer solution in confined geometries

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Abstract: The paper presents a short overview of the theoretical, numerical and experimental works on the critical behaviour of a dilute polymer solution of long-flexible polymer chains confined in semi-infinite space restricted by a surface or in a slit geometry of two parallel walls with different adsorbing or repelling properties in respect for polymers as well as in a solution of mesoscopic spherical colloidal particles of one sort or two different sorts. We discuss the application of the massive field theory approach in a fixed space dimensions $d = 3$ up to one loop order for such topics as: (a) the investigation of the elastic properties of real polymer chain immersed in a good solvent and anchored by one end to the surface and with other end being under tension of the external applied force as it is usually takes place in the single-molecule force spectroscopy experiments; (b) the calculation of the monomer density profiles, the depletion interaction potentials and the depletion forces which arise in a dilute polymer solution immersed in confined geometries, like slit of two parallel walls with different adsorbing or repelling properties in respect for polymers; (c) the investigation of monomer density profiles and the depletion forces which arise in the polymer-colloid mixtures in the case of the mesoscopic spherical colloidal particles of one sort or two different sorts. The presented results give possibility better to understand the complexity of physical effects arising from confinement and indicate about the interesting and nontrivial behavior of linear polymer chains in confined geometries and are in good qualitative and quantitative agreement with previous theoretical investigations, results of Density Functional Theory (DFT), Monte Carlo (MC) simulations and experimental data based on the single molecular atomic force spectroscopy (AFM) and the total internal reflection microscopy (TIRM). Besides, the obtained results have important practical applications for better understanding of the elastic properties of the individual macromolecules, networks, gels and brush layers as well as indicate about possibility of application in production of new types of nano- and micro-electromechanical devices.

Keywords: colloids, polymer solutions, critical phenomena, surface physics
Introduction

One of the fundamental questions of the present material science is the question about adsorption and localization processes of macromolecular chains on surfaces and in confined geometries as well as the investigation of the entropic and enthalpic elasticity of polymer materials and their mechanical stability. This is motivated by their relevance to numerous practical applications such as lubrication, adhesion, surface protection, lithography, chromatography, and biologic phenomena (polymer-membrane interactions, signal transduction), as well as in biotechnology and drug delivery. Understanding the basic principles underlying such processes is of great importance. Besides, the macroscopic characteristics of polymer materials such as fibers and plastics, are determined by the mechanical properties of individual polymer chains. In this respect very important task is the investigation of the polymer chains deformation due to the influence of external forces. As it is known, the single molecular atomic force spectroscopy (AFM) experiments on DNA, RNA or actin filaments [1–3] during last years provided information about strains and stresses which undergo biomolecules during molecular recognition between DNA and proteins or protein-induced bending of DNA and allowed to measure the energy transduction during ATP cycle in molecular motors and to investigate many other fascinating phenomena such as disentanglement of synthetic polymers [4–8] and their peeling from the surface [4, 9–11]. As it was found in [12] at low forces the intramolecular conformations of macromolecules were governed by entropic effects and at high forces the backbone deformations dominated.

In the AFM experiments on stretching of single macromolecules [12–14], one end of a
macromolecule is anchored to the surface and other end is fixed at the cantilever tip. The tip of cantilever is slowly moved away from the surface and the corresponding stretching force is measured from piconewtons up to the femtonewton resolution as a function of the distance. It should be mentioned that recently a similar procedure has been applied for measuring the forces induced during the separation of adsorbed polymers from a surface.

The development during last years of the experimental techniques, such as AFM, magnetic beads, optical tweezers or glass microneedles, which allowed to perform the structural and functional investigation of macromolecules under tension of external forces stimulated development of new theoretical approaches and models. In this contents it should be mentioned very useful the freely jointed chain (FJC) model, which was applied for description of flexible polymer chains deformations and the wormlike chain (WLC) model, which frequently was used for description of stiff biopolymers such as a double-stranded helix of DNA and biological filaments in unrestricted space. Besides, recently a parameter-free description of the polymer elasticity based on a combination of statistical mechanics and quantum mechanics was introduced in series of papers for macromolecules in unrestricted geometry. In a series of papers devoted to analytical investigation in the framework of a directed walk model the close analogy between mechanical desorption of a single polymer chain from a surface and mechanical unzipping of double-stranded DNA was mentioned.

As it is known, the critical behavior of dilute and semi-dilute polymer solutions in semi-infinite space restricted by a surface is more complicated and delicate task which requires taking into account surface effects and is described by a new set of surface critical exponents. The series of previous investigation based on renormalization group (RG) methods concentrated main attention on the investigation of the process of polymer adsorption and calculations of the respective surface critical exponents, monomer density profiles, number of adsorbed monomers on the surface and thickness of the adsorbed layer. Besides, the task of investigation of the stretching and force induced desorption of anchored to the surface polymer chains which have practical application in technological process of producing new type of polymeric materials was the subject of series recent papers. Such, for example, the theory of stretching of an end-tethered ideal chain (Gaussian chain) anchored to repulsive and inert plane was proposed in. In one of our
previous papers [32] the density functional theory (DFT) was applied for calculation of the force acting on an end-tethered ideal (Gaussian) chain and real polymer chain with the excluded volume interaction (EVI) in a good solvent anchored to repulsive surface. Unfortunately, the implementation of DFT and Monte Carlo (MC) techniques are restricted to the case of rather short polymer chains due to the computational difficulties. It stimulated us to apply the massive field theory approach (MFT) for investigation of stretching of long-flexible real polymer chain with the EVI in a good solvent anchored by one end to repulsive or inert surface [33, 34]. It should be mentioned that initially MFT approach was proposed by Parisi for infinite systems in [35] and subsequently applied to semi-infinite systems by Diehl and Shpot in [36]. Recently we applied the massive field theory approach in a fixed space dimension \(d = 3\) for investigation of a dilute polymer solution of real polymer chains with the EVI in a good solvent confined in a slit geometry of two parallel walls with different boundary conditions [37, 38] by analogy as it was proposed in [39] for two repulsive walls in the framework of the dimensionally regularized continuum version of the field theory with minimal subtraction of poles in \(\epsilon = 4 - d\) expansion, where \(d\) is dimensionality of space. Such, for example, in [37, 38] we investigated the situation of two repulsive walls (Dirichlet-Dirichlet boundary conditions (b.c.)) two inert walls (Neumann-Neumann b.c.) and mixed case of one repulsive and the other one inert wall (Dirichlet-Neumann b.c.). Taking into account the Derjaguin approximation [44] we obtained the results for the depletion interaction potentials and the depletion forces for the case of one mesoscopic colloidal particle of big size near the wall and for the case of two big colloidal particles with different adsorbing or repelling properties in respect to polymers [37, 38, 40] and compared the obtained analytical results with experimental results obtained by Rudhardt, Bechinger and Leiderer [41].

Besides, in a series of our papers [28, 29] the universal density-force relation was analyzed by analogy as it was proposed by Joanny, Leibler, de Gennes [42] and by Eisenriegler [43]. Such, for example, in [28, 29] the corresponding universal amplitude ratio and the monomer density profiles of linear ideal and real polymer chains with the EVI in a good solvent immersed in a slit geometry of two parallel repulsive walls, one repulsive and the other one inert wall were obtained in the framework of the massive field theory approach directly in fixed space dimensions \(d = 3\). Taking into account the Derjaguin approximation [44], the monomer density profiles of a dilute polymer solution confined in a semi-infinite
space containing the mesoscopic spherical colloidal particle of big size with different adsorbing or repelling properties in respect for polymers were calculated \[28, 29\]. It should be mentioned, that the interaction of long flexible nonadsorbing linear polymers with mesoscopic colloidal particles of big and small size and different shape was the subject a series of papers \[45, 46\] based on \(\epsilon = 4 - d\) - expansion. The obtained in a series of papers \[28, 29, 37, 40, 43, 46\] results for long flexible linear polymer chains indicate that focusing on such systems leads to universal results which are independent of microscopic details and are free of nonuniversal model parameters and depend only on shapes of particles, adsorbing or repelling properties of particles in respect to polymers and ratios of three characteristic lengths of the system such as the radius of the particle, the polymer size, the distance between the particle and the wall or between two particles, respectively.

The calculation of the depletion interaction potential and the depletion force between two parallel walls in a slit geometry, or between two colloidal particles (or wall and a single colloidal particle) of arbitrary shape was performed also by other theoretical methods including the method of hard spheres \[47, 48\] and the self-consistent field theory \[49, 50\]. It should be mentioned that the theoretical investigations were verified by numerical methods \[51, 52\] using the model of RW for ideal polymer chain at \(\Theta\) - solvent and SAW for a real polymer chain with the EVI in a good solvent confined inside the slit of two repulsive walls.

In order to give answer for the question why we use for calculations the massive field theory approach \[35, 36, 53, 54\] we should notice that the above mentioned approach works directly in a fixed space dimensions \(d = 3\) and avoids the \(\epsilon = 4 - d\) - expansion. In this respect we should also recollect that in the dimensionally regularised continuum version of the field theory based on the \(\epsilon = 4 - d\) - expansion for fixed \(d < 4\) space dimensions arise infrared singularities, which manifest themselves as poles in Feynman integrals at rational values of \(\epsilon\) and accumulate at the upper critical dimension \(d^* = 4\) as the order of perturbation theory increases \[24, 26, 53, 56, 68\]. In accordance with it arises the problem of summing up these infrared singularities, which arise at small momenta and long wavelength. As was mentioned by Parisi \[35\] it should be introduced some additional hypothesis on the summation of these singularities, because any calculations based on the \(\epsilon\) - expansion and the RG in this perturbative zero-mass scheme do not contain any information about the critical behavior in the case of fixed dimension \(d < d^*\). One of such approaches, which works perfectly directly in a fixed space dimension and avoid the \(\epsilon\) -
The model

As it was mentioned in a series of papers [24, 61–63], the behaviour of long flexible polymer chains is determined by entropy and characterized by detail independence, universality and scaling. The properties of scaling and universality also take place for critical systems with surfaces [64, 65] and can be applied for the case of polymer solution in confined geometries.

In a series of our papers (see [27–29, 33, 34, 37, 38, 40]) the investigations of a dilute solution of linear polymer chains confined in semi-infinite space restricted by a surface or in a slit geometry of two parallel walls and in a solution of mesoscopic spherical colloidal particles of one sort or two different sorts were performed. We assumed that the solution of polymers is sufficiently dilute so that the interchain interactions and the overlapping between different polymers can be neglected and it is sufficient to consider the behaviour of a single polymer chain.

As it is known, the behavior of a single ideal (Gaussian) polymer chain at $\theta$-solvent can be described by a model of random walk (RW) and the behavior of long-flexible real polymer chain with the EVI in a good solvent for temperatures above the $\theta$-point by a model of self-avoiding walk (SAW). Usually in the case when the EVI between monomers becomes relevant the polymer coils are less compact than in the case of ideal chains. Taking into account the polymer-magnet analogy developed by de Gennes [61, 62], we can switch from an Edwards type model for long - flexible real polymer chains with the EVI in a good solvent to the field theoretical $\phi^4$ $O(n)$-vector model in the formal $n \to 0$ limit at the infinite number of steps (monomers) $N$. The value $1/N$ 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 interaction between the monomers and the surfaces should be taken into account. As it was noted by de Gennes [66] and by Barber et al. [67], there is a formal analogy between the polymer adsorption problem and the equivalent problem of critical phenomena in the semi-infinite $|\phi|^4$ $O(n)$-vector model of a magnet with a free surface [65, 68]. In a series of papers [69, 71]
the extensive multicanonical MC computer simulations were used in order to study the conformational behaviour of flexible polymers near an attractive surfaces and the corresponding complete solubility-temperature phase diagram was constructed and discussed.

The proposed in \[24, 27–29, 33, 34, 37–40\] calculations were performed for the case when the surfaces were impenetrable. It means that the corresponding potential \(U(z)\) of the interaction between the monomers of a polymer chain and a wall tends to infinity \(U(z) \to \infty\) when the distance between a wall and polymer chain is less than 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, \(c > 0\)) \[24, 65\] 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. It should be mentioned that the adsorption threshold for long-flexible polymer chains takes place when \(1/N \to 0\) and \(c \to 0\). In the case when a polymer solution is confined in a slit geometry of two parallel walls the properties of the system depend on the ratio \(L/\xi_R\), where \(L\) is the distance between two walls and \(\xi_R = \sqrt{\langle R^2 \rangle} \sim N^{\nu}\) is the average end-to-end distance, as it was shown in a series of papers \[28, 29, 37–39\]. Taking into account the polymer-magnet analogy \[61, 62\], the respective partition function \(Z(x, x')\) of a single polymer chain with two ends fixed at \(x\) and \(x'\) is connected with the two-point correlation function \(G^{(2)}(x, x') = \langle \vec{\phi}(x) \vec{\phi}(x') \rangle\) in \(\phi^4\) \(O(n)\)-vector model for \(n\)-vector field \(\vec{\phi}(x)\) with the components \(\phi_i(x), i = 1, ..., n\) \((x = (r, z))\) via the inverse Laplace transform \(\mu_0^2 \to L_0\): \(Z(x, x' \ N, v_0) = \mathcal{L}_{\mu_0^2 \to L_0} \langle \vec{\phi}(x) \vec{\phi}(x') \rangle |_{n \to 0}\) in the limit, where the number \(n\) of components tends to zero \[24, 28, 37, 61, 63\]. The conjugate Laplace variable \(L_0\) has the dimension of length squared and is proportional to the total number of monomers \(N\) of the polymer chain: \(L_0 \sim l^2 N\).

The effective Ginzburg-Landau-Wilson Hamiltonian describing the system of a dilute polymer solution confined in semi-infinite \((i = 1)\) or confined geometry of two parallel walls \((i = 1, 2)\) is \[65\]:

\[
\mathcal{H}[\vec{\phi}, \mu_0] = \int d^d x \left\{ \frac{1}{2} \left( \nabla \vec{\phi} \right)^2 + \frac{\mu_0^2}{2} \vec{\phi}^2 + \frac{v_0}{4!} \left( \vec{\phi}^2 \right)^2 \right\} + \sum_{i=1}^{2} \frac{c_i a}{2} \int d^{d-1} r \vec{\phi}^2, \tag{1}
\]
where the variables $\mu_0$ plays the role of chemical potentials (or "bare mass" in field-theoretical treatment), $v_0$ is the "bare coupling constant" which characterizes the strength of the EVI between any monomers of polymer chain. The case $v_0 = 0$ corresponds to the situation of an ideal polymer chain when only monomer - monomer interactions between consecutive monomers along the chain take place. In the case of a 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 located at $z = L$. Each of the two system surfaces is characterized by a certain surface enhancement constant $c_{i0}$, where $i = 1, 2$. The model defined in (1) is restricted to translations parallel to the bounding surfaces. Thus, only parallel Fourier transformations in $d - 1$ dimensions with respect to "parallel" coordinates $r$ take place.

The interaction between the polymer chain and the walls is implemented by the different boundary conditions. In a series of our papers we performed investigations for different boundary conditions. Such, for example, when we discussed the processes of adsorption and desorption on the surface of a dilute solution of polymer chains [27] and stretching anchored to the surface long-flexible real polymer chain with the EVI in a good solvent for temperatures above the $\theta$-point [33, 34], we performed calculations for the case of repulsive wall and wall where the adsorption threshold takes place (so-called [24] "inert" wall). In the case of repulsive wall (i.e. where the segment partition function and thus the partition function for the whole polymer chain $Z(x, x'; L_0)$ tends to 0 as any segment approaches the surface of the wall: $z, z' \to 0$) Dirichlet boundary condition takes place: $\vec{\phi}(r, z) = 0$ at $z = 0$. This corresponds to the fixed point boundary condition: $c \to +\infty$ of the ordinary transition of the field theory. In the case of inert wall the fields $\vec{\phi}(r, z)$ satisfy Neumann boundary conditions: $\left. \frac{\partial \vec{\phi}(r, z)}{\partial z} \right|_{z=0} = 0$. The requirement, describing the inert wall corresponds to the fixed point $c = 0$ of the so-called special transition [36, 65, 68] in the field theoretical treatment.

Besides, in a series of papers [28, 29, 37, 38, 40] we performed investigation of a dilute polymer solution of linear polymer chains immersed in a slit geometry of two repulsive walls, two inert walls, and for the mixed case of one repulsive and the other one inert wall. The situation of two repulsive walls corresponds to the Dirichlet-Dirichlet boundary
conditions (D-D b.c.) (see also [37–39]):

\[ \vec{\phi}(r, 0) = \vec{\phi}(r, L) = 0 \quad \text{or} \quad c_1 \to +\infty, \quad c_2 \to +\infty. \] (2)

The case of two inert walls corresponds to the Neumann-Neumann boundary conditions (N-N b.c.) (see also [37, 38]):

\[ \frac{\partial \vec{\phi}(r, z)}{\partial z} \bigg|_{z=0} = \frac{\partial \vec{\phi}(r, z)}{\partial z} \bigg|_{z=L} = 0 \quad \text{or} \quad c_1 = 0, \quad c_2 = 0, \] (3)

and for the mixed case of one repulsive and the other one inert wall, the Dirichlet-Neumann boundary conditions (D-N b.c.) takes place [37, 38]:

\[ \vec{\phi}(r, 0) = 0, \quad \frac{\partial \vec{\phi}(r, z)}{\partial z} \bigg|_{z=L} = 0 \quad \text{or} \quad c_1 \to +\infty, \quad c_2 = 0. \] (4)

The performed calculations are valid for the case of wide slit limit \( y \geq 1 \) (where \( y = \frac{L}{R_x} \)), but they are not suitable 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, as it takes place, for example, in magnetic or liquid thin films. Nevertheless, some assumptions allowed us to describe the region of narrow slit, as it was proposed in one of our papers (see Ref. [37]). In the case of infinitely large wall separations, the slit system decomposes into two half-space systems.

It should be mentioned, that the only relevant length of the model is the average end-to-end distance \( <R^2> \sim N^{2\nu} \), and \( <R_x^2>_{\text{bulk}} = <R_y^2>_{\text{bulk}} = <R_z^2>_{\text{bulk}} = <\frac{R^2}{d}>_{\text{bulk}} \)

where \( R_x, R_y, R_z \) are the projection of the end to end distance \( R \) onto the direction of \( x, y, z \) axis and \( \nu \) - is Flory exponent which is 1/2 for ideal polymer chain and 0.588 for real polymer chain with the EVI.

**Calculation of the average stretching force**

A series of papers [31–34] were devoted to the investigation of stretching anchored to the surface long-flexible linear polymer chain with the EVI in a good solvent for temperatures above the \( \theta \)-point. The difference in the strain-force and the force-strain dependences,
which corresponds to the $f$ ensemble and $Z$ ensemble, respectively, was discussed in [31]. As it was mentioned in [31], in $Z$ ensemble stretching usually was performed via an increase in the end-to-end distance and in the case of $f$ ensemble the stretching was provided by the external force field. It was established, that the relation between strain and force is similar for the both ensembles for the case of ideal polymer chain and for the case of real polymer chain with the EVI in a good solvent the difference diminishes in the limit of infinite number of monomers $N \to \infty$.

In general, the average stretching force which is applied to the free end (which is situated in the layer on the distance $z'$ from the surface) of the polymer chain anchored by other end to the surface at $z = 0$ can be calculated and has a form:

$$
\frac{f(z')}{k_B T} = -\frac{\partial}{\partial z'} \ln Z(z = 0, z'; N).
$$

(5)

This force is analogous to the well known Pincus force [62].

Such in the case of ideal polymer chain anchored by one end to repulsive surface the result for the average stretching force has a form [33, 34]:

$$
< f_{id \text{ord}}(\zeta) > R_z k_B T = -\frac{1}{\zeta}(1 - \zeta^2),
$$

(6)

where $\zeta = \frac{z'}{R_z}$. The case of real polymer chains is more complicated, because the EVI should be taken into account. Thus, after performing the mass $\mu_0^2 = \mu^2 + \delta \mu$ and the surface enhancement $e_0 = c + \delta c$ renormalizations of the correspondent correlation functions and after vertex normalization of the coupling constant $v_0 = v\mu$, as it is usually accepted in the massive field-theory approach of semi-infinite systems in fixed space dimensions $d = 3$ (see [28, 36, 72]), the respective result for the average stretching force applied to free end of real polymer chain with the EVI in a good solvent anchored by other end to repulsive surface was obtained [33, 34] in accordance with Eq.5:

$$
< f_{\text{ord}}(\zeta) > R_z k_B T = -\frac{1}{\zeta}(1 - \zeta^2 + \tilde{v}^* \frac{\zeta}{4} e^{-4\zeta^2}(1 + \frac{1}{4\zeta^2})).
$$

(7)

It should be mentioned that the calculations were performed at the correspondent stable fixed point $\tilde{v}^* = 1$ obtained from resummed beta functions $\beta(\tilde{v})$ of the underlying bulk
field theory in one-loop order.

In a similar way were performed the calculations for the average stretching force applied to free end of polymer chain anchored to inert surface. Thus, for the case of ideal chain we obtained [33, 34]:

\[
\frac{< f_{id}^{sp}(\zeta) >}{k_B T} = \zeta.
\]  

The obtained in Eq.(8) result indicates that in the case when free end of polymer chain moves away from the inert surface, the average stretching force increases linearly. Taking into account the massive field - theory approach at fixed \( d = 3 \) dimensions [36, 73], the correspondent average stretching force applied to free end of real polymer chain with the EVI in a good solvent anchored by other end to inert surface was obtained in [33, 34]:

\[
\frac{< f_{sp}^{real}(\zeta) >}{k_B T} = \zeta \left(1 + \frac{\tilde{v}^*}{16}\right).
\]  

It should be mentioned that the results obtained in the framework of the present calculation scheme for the average stretching force in the case of ideal polymer chain anchored to repulsive and inert surfaces (see Eq.(6) and Eq.(8)) coincide with the results obtained by Skvortsov et. al [31] for Gaussian chain model. The comparison of our results Eq.(6) and Eq.(8) (see also [33, 34]), and the results obtained by Skvortsov et al. in [31] is possible to observe in Figure 1. Our results for the stretching force applied to anchored to the repulsive surface ideal chain marked as black and blue dashed lines for number of monomers \( N=50 \) and \( N=500 \), respectively, and the results obtained by Skvortsov et al. in [31] for Gaussian chain are shown as orange triangles and green circles, respectively. We took into account that the projection of the end-to-end distance on the \( z \) axis is:

\[
R_z^2 = < R_z^2 >_{bulk} = b^2 \frac{N^{2\nu}}{3} \quad \text{and} \quad \nu = 1/2 \quad \text{for ideal chain}, \quad b \quad \text{is the effective segment length of the polymer model under consideration.} \]

It should be mentioned, that Figure 1 contains also our results obtained in the framework of the massive field theory (MFT) approach at fixed space dimensions \( d=3 \) for the case of real polymer chain with the EVI in a good solvent with \( N=50 \) (orange solid line) and with \( N=500 \) (green solid line) anchored to repulsive surface. Unfortunately, in [31] the situation of real polymer chains anchored to the surface was not discussed and only the task of finding stretching force applied to the ends of real polymer chain in a good solvent immersed in unrestricted space was discussed. In a similar
FIG. 1: Comparison of the massive field theory (MFT) results obtained for the average stretching force applied to free end of ideal and real polymer chain anchored to repulsive surface as function of $k = z'/bN$ and the results obtained by Skvortsov et al. [31] for Gaussian chain for number of monomers $N = 50$ and $N = 500$. The results obtained in the framework of both methods for ideal chain (Gaussian chain) coincide.

way we compared our results with the ones obtained in [31] for the average stretching force applied to an ideal chain anchored to inert surface and found complete agreement (see [33, 34]). As it is known [18, 31, 62], the force extension relation for real polymer chain with the EVI in a good solvent without surface reduces to the Pincus deformation law: $z \sim N \left( \frac{h}{k_B T} \right)^{1/\nu}$. The presence of the surface should modify the force extension relation.

For example, from the results obtained in the framework of the dimensionally regularised field theory with $\epsilon$-expansion in [26] for the case of real polymer chain immersed in a slit of two parallel walls with different boundary conditions and anchored by one or two ends to surface follows, that the correspondent stretching force will be proportional to $1/z'$ for both cases of Neumann and Dirichlet boundary conditions. This result is in disagreement with the result obtained by [31] for the case of ideal (Gaussian) chain anchored to inert surface (Neumann b.c.), where average force is proportional to extension $z'$. In [43] was mentioned, that the force extension relation for the case of polymer chain anchored to the surface should be different for two limiting cases $z' << R_z$ and $z' >> R_z$. But, unfortunately in [43] detailed analysis for these cases was not performed. The detailed analysis of our results, obtained in Eq. (7) shows, that in the case $z' << R_z$ (or $\zeta << 1$) we obtain that the average stretching force $\frac{<f(\zeta)>}{k_B T}$ for long - flexible real polymer chain anchored to the
repulsive surface is proportional to $1/z'$, which is in agreement with scaling arguments of Flory theory and theory of Pincus blobs adsorbed on the surface \[18, 74\]. In the intermediate case, when $z' = R_z$ the $1/z'$ dependence of the stretching force is still valid. In the case $z' \gg R_z$ (or $\zeta \gg 1$) we come to the dependence $\frac{< f(\zeta) >}{k_B T} \sim \zeta^{1-\nu}$. The analysis of our results for the average stretching force in the case of real polymer chain anchored to inert surface Eq.(9) is in agreement with the result obtained in \[31\] for Gaussian chain anchored to inert surface, where the average stretching force is proportional to extension $z'$. Besides, we observed good qualitative agreement of the obtained analytical results with experimental results based on the AFM measurements \[4, 14\] as it was shown in \[33\].

In \[34\] the comparison of the analytical results obtained in the framework of the massive field theory approach and the results obtained in the framework of DFT approach and Monte Carlo (MC) calculations \[32\] were performed (see Figure 2(a) and Figure 2(b)). It should be mentioned that in order to do this comparison we introduced some changes of variables, as it was mentioned in \[34\]. We assumed, that $t = z'/N$, then the result obtained in Eq.(6) for the average stretching force has the form:

$$< \frac{f_{\text{ideal}}(t)}{k_B T} > = -\frac{1}{Nt} (1 - \frac{t^2 N d}{b^2}). \tag{10}$$

The correspondent expression for the average stretching force in the case of real polymer chain with the EVI anchored by one end to the repulsive surface as function of $t = z'/N$ is:

$$< \frac{f_{\text{real}}(t)}{k_B T} > = -\frac{1}{Nt} (1 - \frac{t^2 A d}{b^2} + \frac{\tilde{v}^*}{4} e^{-\frac{4t^2 A d}{b^2} (1 + \frac{b^2}{4t^2 A d})}), \tag{11}$$

where $A = \frac{N^2}{N^{\text{EVI}}}$ and $A \approx 6.67$ for N=10, $A \approx 11.81$ for N=20. Figures 2(a) and 2(b) present comparison of the obtained in the framework of the massive field - theory approach results for the average stretching force (see Eq.(10), Eq.(11)) and the results obtained in the framework of DFT approach and MC calculations \[32\] for different numbers of monomers N=10 and N=20, respectively. The comparison of the results presented in Figures 2(a) and 2(b) indicates that the obtained in the framework of DFT and MC methods results are in good agreement with the analytical results obtained with use the massive field theory approach for the region of small applied forces when deformation of polymer chain is not bigger than linear extension of polymer chain in this direction, $z'/R_z \leq 1$. Besides, the
FIG. 2: Comparison of the massive field theory results obtained for the average stretching force applied to free end of ideal and real polymer chain anchored to repulsive surface as function of $t = z'/N$ and the results of DFT and MC simulations [32] for: (a) $N = 10$; (b) $N = 20$ with $b=1$

better agreement between our analytical results and the results obtained in the framework of DFT and MC is observed in the case, when the number of monomers increases and polymer chain becomes longer. It should be mentioned, that in the case of strong deformations of polymer chain the Gaussian distribution does not give good results for the stretching force and in this case the calculations should be performed with taking into account Langevin distribution function. This task is more complicated and should be investigated separately, such as requires more delicate treatment, specially for the case of real polymer chains anchored to the surface. In general, it should be mentioned, that the obtained results have important practical applications for better understanding of the elastic properties of the individual macromolecules, networks, gels and brush layers.

**Dilute solution of ideal and real polymer chains in a slit geometry of two parallel walls**

The task of investigation of a dilute solution of ideal and real polymer chains with the EVI in a good solvent immersed in a slit geometry of two parallel walls situated at a distance $L$ one from another with different boundary conditions was the subject of series papers [37–39]. The thermodynamic description of the problem proposed in [39] assumed that the polymer solution in the slit is in equilibrium contact with an equivalent solution in the reservoir outside the slit and allowed for the exchange of polymer coils between the slit and
the reservoir. As it was shown in \cite{37, 39}, the free energy of the interaction between the 
walls in such a 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:

\[
\delta F = -k_B T \tilde{N} \ln \left( \frac{Z_{\parallel}(L)}{Z_{\parallel}(L \to \infty)} \right) = -k_B T \tilde{N} \left\{ \ln \left( \frac{Z_{\parallel}(L)}{Z} \right) - \ln \left( \frac{Z_{\parallel}(L \to \infty)}{Z} \right) \right\}, \tag{12}
\]

where \(\tilde{N}\) is the total amount of polymer coils in the solution and \(T\) is the temperature. 
The \(Z_{\parallel}(L)\) value is the partition function of one polymer located in a volume \(V\) containing 
two walls at the distance \(L\). It should be mentioned that the partition functions \(Z_{\parallel}(L)\) and 
\(Z_{\parallel}(L \to \infty)\) were normalized on the function \(Z = V \hat{Z}_b\), where \(\hat{Z}_b = I L \mu^2 \frac{1}{2} \pi_0 \left[ 1 - \frac{\mu^2}{2} \right] \).

As it was mentioned in \cite{37, 39}, the corresponding reduced free energy of interaction \(\delta f\) 
per unit area \(A = 1\) for the case of linear polymers confined in the slit geometry of two 
parallel walls after performing Fourier transform in the direction parallel to the surfaces 
and integration over \(d^{d-1}r\) can be obtained:

\[
\delta f = \frac{\delta F}{n_p k_B T}. \tag{13}
\]

Here \(n_p = \tilde{N}/V\) is the polymer density in the bulk solution. The reduced free energy of 
interaction \(\delta f\), according to Eq.\,(13), 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 \textit{depletion interaction potential}: 

\[
\Theta(y) = \frac{\delta f}{R_x}, \tag{14}
\]

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:

\[
\Gamma(y) = - \frac{d(\delta f)}{dL} = - \frac{d\Theta(y)}{dy}. \tag{15}
\]

In \cite{37, 38} during the investigation of ideal and real polymer chains with the EVI in a good 
solvent immersed in a slit geometry of two parallel walls with D-D b.c. Eq.\,(2) (the case of 
two repulsive walls) we obtained that if both \(c_1\) and \(c_2\) are positive, the depletion
interaction potential $\Theta_{DD}(y)$ is negative and hence the walls attract each other due to the depletion zones near repulsive walls. It should be mentioned, that the obtained in the framework of the massive field theory approach at fixed space dimensions $d = 3$ results for the dimensionless scaling function of the depletion interaction potential and the depletion force for ideal and real polymer chains in a slit geometry of two repulsive walls are in good quantitative agreement with the previous theoretical results obtained in Ref. [39] via using the dimensionally regularized continuum version of the field theory with minimal subtraction of poles in $\epsilon = 4 - d$ expansion (see Figure 3(a)). The obtained analytical results indicate that the reduction in the depletion effect due to the EVI is weaker within the massive field theory approach as compared to the results obtained using the $\epsilon$ - expansion. For the dimensionless scaling function of the depletion interaction potential in the case of ideal polymer chain immersed in a slit geometry of two inert walls, which corresponds to N-N b.c. Eq.(3) in [37, 38] we obtained $\Theta_{NN}(y) = 0$. It corresponds to the fact that ideal chains do not loose free energy inside the slit in comparison with free chains in unrestricted space. The entropy loss is fully regained by surface interactions provided by two walls. In the case of real linear polymer chain with the EVI in a good solvent immersed in a slit geometry of two inert walls we obtained (see [37, 38]) that resulting force becomes repulsive due to excluded volume effects between monomers of polymer chain. In the case of one repulsive and the other one inert wall, which corresponds to D-N b.c. Eq.(4) we obtained in [37] that $\Theta_{DD}(2y) \approx 2\Theta_{DN}(y)$ for ideal polymer chains. This result is intuitively clear, because the depletion zone is formed only near the lower wall, i.e. near the wall with Dirichlet b.c. The upper wall with Neumann b.c. does not contribute at all to the induced depletion interaction. Thus, in [37, 38] the results for the dimensionless scaling functions of the depletion interaction potential and the depletion force were obtained for ideal and real linear polymer chains with the EVI in a good solvent confined in a slit geometry of two parallel walls with D-N b.c. Besides, in [37, 38] the asymptotic region of wide slit with $y \geq 1$ and narrow slit with $y << 1$ were discussed. In the case of narrow slit with $y << 1$ the asymptotic solution for the depletion force in the case of two repulsive walls and for the case of one repulsive and the other one inert wall simply becomes $\Gamma_{DD(DN),narrow}(y) \approx -1$ (see 37) for ideal polymer chains. These results can be understood phenomenologically. In our units the quantities $\Theta$ and $\Gamma$ were normalized to the overall polymer density $n_p$. So, the above results simply indicate that
FIG. 3: (a) The dimensionless scaling functions of $\Gamma_{DD}(y)$ for linear polymer chain in a slit geometry of two repulsive walls (see [37, 38]) in comparison to the results obtained in [39]; (b) Comparison of the analytical results obtained in [37, 38] for the reduced canonical force and the results obtained by MC simulations for a trapped polymer between two repulsive walls [51, 52]. The plots for ideal chain (exact) and real polymer chain with the EVI (wide slit) represent the results of our calculations in the framework of MFT. The first SAW (MC) are the results obtained by [51]. The curves depicted as RW (MC) and the second SAW (MC) are the results obtained in the narrow slit limit by [52] for random walks and self avoiding walks.

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. No chain has remained in the slit. It is reasonable in the case of repulsive walls in the limit of narrow slits. The above mentioned arguments were used in order to obtain the leading contributions to the depletion effect as $y \to 0$. We can state that in the case of very narrow slits polymers would pay a very high entropy to stay in the slit or even enter it. It is due to the fact that the phase space containing all possible conformations is essentially reduced by the squeezing confinement to the size $\frac{d-1}{d}$ times its original size (for an unconfined chain). Therefore, as it was shown in [37], the ratio of partition function of polymer chain in the slit and the free chain partition function vanishes strongly as $y \to 0$. 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 polymers with the EVI.

Besides, in [37, 38] we obtained very good agreement of our analytical results for the reduced canonical force $Lk_BT$ and the results obtained by Hsu and Grasberger [52] based on the lattice MC algorithm on a regular cubic lattice in three dimensions, as it is possible to see on Figure 3(b). In general the canonical free energy can be obtained via the
Legendre transform from the grand canonical one in the thermodynamic limit ($\tilde{N}, V \to \infty$) (for details see [37]).

I. IDEAL AND REAL POLYMER CHAINS IN A SOLUTION OF MESOSCOPIC SPHERICAL PARTICLES

The task of a great importance is investigation of a dilute solution of ideal and real polymer chains with the EVI in a good solvent immersed in the solution of mesoscopic colloidal particles or nanoparticles. The interaction of long flexible nonadsorbing linear polymer chains with mesoscopic particles of big or small size with different shape was the subject of investigation in a series of papers [45, 46]. In our papers [37, 38, 40] we focused attention on the investigation of the depletion interaction potential and the depletion force for two cases: (1) between a big spherical colloidal particle of radius $R$ and the wall; (2) 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 a dilute solution of ideal and real linear polymer chains with particles and walls is implemented by the corresponding boundary condition. The difference between the forces with and without the particle (or particles) yields the depletion interaction potential of the particle with the wall (or between two particles). Taking into account the Derjaguin approximation [44], which describes the sphere of the big colloidal particle of the radius $R$ (with $R >> L$ and $R >> R_x$) by a superposition of immersed plates (see Figure 4(a)) 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 $\rho$ - is the width of the fringe itself we performed in [37, 40] the calculations of the depletion interaction potential $\Phi(\tilde{y})/n_p k_B T$ and the depletion force $-\frac{1}{n_p k_B T} \frac{d\Phi(\tilde{y})}{d\tilde{y}}$ between the colloidal particle and the wall in a dilute solution of linear polymer chains. We also used some modifications of the Derjaguin approximation for the calculation of the depletion interaction potential and the depletion force in the case of two big spherical colloidal particles with different radii $R_1 \neq R_2$ when $R_i >> L$ and $R_i >> R_x$, $i = 1, 2$. In this case we took into account that the distance $h(\rho)$ is equal to:

$$h(\rho) = a + R_1 - \sqrt{R_1^2 - \rho^2} + R_2 - \sqrt{R_2^2 - \rho^2},$$

where $a$ - is the nearest distance from the particle to other particle (see Figure 4(b)). Thus, the depletion interaction potential $\Phi(\tilde{y})/n_p k_B T$ can be written in the form: $2\pi \tilde{R} R_x \int_{\tilde{y}}^{\infty} dy \Theta(y)$ with $\tilde{y} = a/R_x$ where $\tilde{R} = R$. 


for the case of the big spherical colloidal particle of radius $R$ near the wall and 
$\tilde{R} = R_1 R_2 / (R_1 + R_2)$ for the case of two big spherical colloidal particles with different radii $R_1 \neq R_2$. Taking into account the results for the depletion interaction potential

\begin{equation}
\Phi(\tilde{y}) / n_p k_B T \quad \text{(see [37, 38])}
\end{equation}

we performed calculation of 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) has the following form [40, 59]:

\begin{equation}
- \frac{1}{n_p k_B T} \frac{d\Phi^{id}(\tilde{y})}{d\tilde{y}} = 2\pi R^2 \tilde{R} \vartheta^{id}(\tilde{y}),
\end{equation}

where the results for the corresponding scaling functions $\vartheta^{id}(\tilde{y})$ for the case of a dilute solution of ideal polymer chains are presented in Figures 5(a)-5(c) by blue lines with blue circles, respectively. It should be mentioned that in a similar way we performed calculations for the depletion force between the mesoscopic colloidal particle of big size and the wall (or between two big spherical colloidal particles of different radii) induced by a dilute solution of real polymer chains with the EVI in a good solvent. The obtained results for the corresponding dimensionless scaling functions $\vartheta^{EVI}(\tilde{y})$ of the depletion force in the case of real polymer chains with the EVI in a good solvent immersed in the solution of big spherical colloidal particles are presented in Figures 5(a)-5(c) by orange lines with orange triangles, respectively (see also [40]). It should be mentioned that in this situation we also distinguished two cases at the calculation of the depletion interaction potential and the depletion force: (1) between a big spherical colloidal particle of radius $R$ and the wall; (2) between two colloidal particles of big sizes with different radii $R_1$ and $R_2$. Besides, we took into account different adsorbing or repelling properties between the mesoscopic colloidal particle and the wall (or between two big spherical colloidal particles) with respect to
FIG. 5: The dimensionless scaling functions of $\vartheta(\tilde{y})$ for a dilute solution of linear polymers immersed between the big spherical colloidal particle and the wall (or between two big spherical colloidal particles) for the case of (a) D-D b.c.; (b) N-N b.c.; (c) D-N b.c.

polymers in the solution which were implemented by taking into consideration the different boundary conditions.

As it is possible to see from the obtained results (see Eq.16) the absolute value of the depletion force between the mesoscopic spherical colloidal particle and the wall is bigger than for the case of two 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, the corresponding depletion force is twice smaller than for the case of the particle near the wall.

The improvement of the experimental technique allowed to measure with high accuracy the depletion force between a wall and a single colloidal particle [41, 75, 76]. In one of our previous papers [37] the good qualitative agreement between analytical results obtained in the framework of the massive field theory approach at fixed space dimensions $d = 3$ and the experimental results obtained by Rudhardt, Bechinger and Leiderer [41] by means of total internal reflection microscopy techniques (TIRM) for the depletion interaction potential between the spherical colloidal particle of big radius $R = 1.5\mu m$ and the wall of the container immersed in the dilute solution of nonionic linear polymer chains were obtained in the case when the radius of gyration was used as freely adjustable parameter (we assumed that $R_{g}^{fit} = 0.13\mu m$) (see Figure 6).
FIG. 6: Comparison of the massive field theory (MFT) results obtained for the the depletion interaction potential $\Phi(a)$ with the experimental results obtained by means of total internal reflection microscopy techniques [41], where $a$ is the closest distance between the particle and the wall. In the experiment [41] the radius of colloidal particle was assumed to be $R = 1.5\mu m$ and the radius of gyration has been determined by means of small angle scattering experiments ($R_g = 0.101\mu m$).

II. THE UNIVERSAL DENSITY-FORCE RELATION AND THE MONOMER DENSITY PROFILES

One of the most remarkable theoretical predictions proposed by Joanny, Leibler and de Gennes [42] states that the monomer density profile of a dilute solution of long flexible linear polymer chains bounded by a planar repulsive wall has a depletion region of mesoscopic width of order of the coil size $R_x \approx N^\nu$ (where $N$ is the number of monomers per chain), and for the distances $z$ from the wall that are small compared to this width but bigger than microscopic lengths of monomer size $\tilde{l}$ the profile increases according to the law

$$\rho(z) \sim z^{1/\nu}$$

with Flory exponent $\nu$. The critical exponent $\nu$ is equal $1/2$ for ideal polymer chains and $\nu \approx 0.588$ for real polymer chains with the EVI in a good solvent. As it was mentioned in [42], the monomer density close to the wall is proportional to the force per unit area which the polymer solution exerts on the wall. In a paper [43] a complete quantitative expression for the universal density-force relation was obtained for the first time by Eisenriegler on
the basis of $\epsilon$- expansion up to first order. The validity of the above mentioned density-force relation for the different cases of a single polymer chain with one end (or both ends) fixed in the half space bounded by the wall, a single chain trapped in the slit geometry of two parallel walls, for the case of dilute and semi-dilute solution of free polymer chains in a half space and for the case of polymer chain in a half space containing a mesoscopic particle of arbitrary shape was discussed.

The interaction of long flexible nonadsorbing linear polymer chains with mesoscopic colloidal particles of big and small size and different shape was the subject a series of papers [45, 46]. The above mentioned universal density-force relation was verified by simulation methods using an off-lattice bead-spring model of a polymer chain trapped between two parallel repulsive walls [51] and by the lattice Monte Carlo (MC) algorithm on a regular cubic lattice in $d = 3$ dimensions [52]. In a series of our papers [28, 29] the universal density-force relation was analyzed by analogy as it was proposed by Eisenriegler [43] and the corresponding universal amplitude ratio was obtained in the framework of the massive field theory approach directly in fixed space dimensions $d = 3$. It allowed us to obtain in a series of our papers [28, 29] the monomer density profiles of ideal and real linear polymer chains with the EVI in a good solvent immersed in a slit geometry of two parallel repulsive walls, one repulsive and the other one inert wall. The obtained in a series of our papers [28, 29] results indicate that in the case of two repulsive walls the maximum of the layer monomer density is situated in the middle of the slit at $L/2$. In the case of one repulsive and the other one inert wall the maximum of the layer monomer densities is near the distant inert wall. Besides, the monomer density profiles of a dilute polymer solution confined in a semi-infinite space containing the mesoscopic spherical colloidal particle of big size with different adsorbing or repelling properties in respect for polymers were calculated (see [28, 29]).

**III. CONCLUSIONS**

Summarizing the obtained in a series of papers [31–34] results we should mention that the performed investigations have important practical applications for better understanding of the elastic properties of the individual macromolecules, networks, gels and brush layers. The obtained in the framework of the massive field theory approach results for the
stretching force are in good agreement with the experimental results based on AFM measurements \cite{4,14} as it was shown in \cite{33} and with the results obtained in the framework of DFT and MC methods \cite{32} for the region of small applied forces when deformation of polymer chain is not bigger than linear extension of polymer chain in this direction. Besides, the better agreement between the analytical results and the results obtained in the framework of DFT and MC methods is observed in the case, when the number of monomers increases and polymer chain becomes longer. In the case of strong deformations of polymer chain the Gaussian distribution does not give good results for the stretching force and in this case the calculations should be performed with taking into account Langevin distribution function.

Besides, the results obtained in \cite{28,29,37-40,43} indicate that for the entropic reasons, the polymer chains avoid the space between two repulsive walls in a slit geometry or between two close colloidal particles with repelling properties in respect to polymers. In confined dilute polymer solutions are present the depletion regions near the confining walls or mesoscopic particles due to an additional amount of entropic energy for polymers. It leads to an unbalanced pressure the outside which pushes the two repulsive walls or two such colloidal particles towards each other. As a result the attractive depletion force arises between two repulsive walls or two close colloidal particles with repelling properties. Completely different behavior is observed for the case of a dilute polymer solution of long-flexible linear polymer chains confined in a slit of two inert walls (the walls where the adsorption threshold takes place). One of the remarkable results which we obtained in \cite{37,38} shows that the depletion force in the case of two inert walls becomes repulsive for the case of linear real polymer chains with the EVI in a good solvent. This result is very important from practical point of view, because it means that in such systems we observe reduction of the static friction and as a result such systems can be used for producing of new types of nano- and micro-electromechanical devices.

The performed in a series of papers \cite{37,38,40,43,45,46} investigations for long flexible linear polymer chains immersed in a solution of mesoscopic colloidal particles of big or small size with different shape indicate that focusing on such systems leads to universal results which are independent of microscopic details and depend only on shapes of particles, adsorbing or repelling properties of the confining walls in respect to polymers and ratios of three characteristic lengths of the system such as the radius of the colloidal
particle, the polymer size, the distance between the colloidal particle and the wall or between two mesoscopic colloidal particles, respectively. In general, the analysis of the obtained in the framework of the massive field theory approach at fixed space dimensions $d = 3$ results for the surface critical exponents $[27]$, the monomer density profiles $[28, 29]$, the stretching force in the case of anchored to the surface ideal or real linear polymer chain with the EVI in a good solvent $[33, 34]$, as well as the results of calculations of the dimensionless depletion interaction potential and the depletion force which arise in a dilute polymer solution immersed between two parallel walls in a slit $[37, 38]$ or between colloidal particle and the wall (or between two colloidal particles) $[37, 40]$ indicates about very good agreement between the results of this analytical method and other theoretical methods $[25, 31, 39, 43]$. Besides, as it was possible to observe in a series of our papers $[28, 29, 33, 34, 37, 38]$ there is a very good agreement between our analytical results and numerical results based on MC calculations or DFT approach $[32, 52]$, and the experimental results obtained by different techniques such as AFM experiment $[4, 14]$ and total internal reflection microscopy (TIRM) $[41]$. All this confirm that the massive field theory approach at fixed space dimensions $d < 4$ is a promising candidate for description of critical behavior of other complex systems in confined geometries.

IV. AUTHOR CONTRIBUTIONS

Z.Usatenko performed calculations, write the review paper and prepared part of figures. K.S. Danel search for the literature, prepared reference list and part of figures.

V. CONFLICT OF INTERESTS

The authors declare no conflict of interests.

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