Polymer chains in confined geometries: Massive field theory approach.

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The massive field theory approach in fixed space dimensions \(d = 3\) is applied to investigate a dilute solution of long-flexible polymer chains in a good solvent between two parallel repulsive walls, two inert walls and for the mixed case of one inert and one repulsive wall. The well known correspondence between the field theoretical \(\phi^4\) \(O(n)\)-vector model in the limit \(n \to 0\) and the behavior of long-flexible polymer chains in a good solvent is used to calculate the depletion interaction potential and the depletion force up to one-loop order. Our investigations include modification of renormalization scheme for the case of two inert walls. The obtained results confirm that the depletion interaction potential and the resulting depletion force between two repulsive walls are weaker for chains with excluded volume interaction (EVI) than for ideal chains, because the EVI effectively reduces the depletion effect near the walls. Our results are in qualitative agreement with previous theoretical investigations, experimental results and with results of Monte Carlo simulations.

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I. INTRODUCTION

Solutions of long flexible polymer chains in confined geometries such as thin films, porous media or mesoscopic particles dissolved in the solution have been extensively studied during last years, including experimental, numerical and theoretical investigations. These investigations showed that polymer solutions and binary liquid mixture in confined geometries gave rise to a new phenomena not observed in the bulk. The confinement of critical fluctuations of the order parameter in a binary liquid mixture leads to an effective long-ranged forces between the confining walls or particles immersed in fluid as it was predicted by \(^1\). It is named critical (or thermodynamic) Casimir force. Such fluctuation-induced forces are omnipresent in the nature. For example, such forces arise from the confinement of quantum fluctuations of the electromagnetic field and due to the well known quantum-electrodynamic Casimir effect \(^2\). In polymer solutions the reason for this depletion force originates from the presence of depletion zones near the confining walls or mesoscopic particles due to the additional amount of entropic energy for polymers confined within the slit or between colloidal particles. For entropic reasons the polymer chains avoid the space between the walls or two close particles. This leads to an unbalanced pressure from outside which pushes the two walls or two colloidal particles towards each other. In the case of addition of the polymer chains to the solvent of colloidal solution effective attraction between particles leads to flocculation \(^3\). Such solvent-mediated flocculation mechanism was observed experimentally for silica spheres immersed in the binary liquid mixture of water and 2,6-lutidine \(^4-6\). Improving of the experimental technique allowed recently even measure with high accuracy the depletion force between a wall and a single colloidal particle \(^7-10\). It should be mentioned, that the case of two parallel walls gives the possibility via the Derjaguin approximation \(^11\) to describe the case of big colloidal spherical particle, whose radius \(R\) is large than the radius of gyration \(R_g\) and the distance between particle and the wall \(L\). It indicates, that the investigation of the case of polymer solutions confined to geometry of two parallel walls is important not only for description of polymer solutions confined to film geometry and porous media, but it is also interesting from the point of view of investigation of behavior of big colloidal particles in polymer solutions.

During long period the interaction between polymers and colloidal particles has been modeled by approximating the polymer chains as hard spheres \(^12,13\). But, such approach does not give possibility to describe correctly behavior of small colloidal particles in polymer solution and for the case of colloidal particle of the big size the difference between theoretical predictions and experimental data are bigger than 10\%. In accordance with this more effective were approaches which took into account the chain flexibility. For example, for the case of strongly overlapping polymer chains as it has place for the case of semidilute solution, the chain flexibility is taken into account via phenomenological scaling theory \(^14,15\) or self-consistent field theory \(^16\). In the case of dilute polymer solution different polymer chains do not overlap and the behavior of such polymer solution can be described by a single polymer chain using the model of random walk (for an ideal chain at \(\theta\)-solvent) or self-avoiding walk (the real polymer chain with excluded volume interaction). The last case corresponds to the situation when solvent temperature is above the \(\theta\)-point (good solvent) and polymer coils are less compact than in the case of ideal chains. The remarkable progress in the investigation of this task was achieved by \(^17,18\) via using of dimensionally regularized continuum version of the field theory with
minimal subtraction of poles in $\epsilon = 4 - d$, where $d$ is dimensionality of the space. But, as it is easy to see\textsuperscript{18}, still there are a lot of unsolved problems and the question arises: "How to find the theory which allows to explain experimental data in a better way?". One of the methods, which up to our knowledge has not yet been applied to this task is the massive field theory approach. This method, as it was shown for the case of infinite\textsuperscript{19,20}, semi-infinite\textsuperscript{21} systems and specially for the case of dilute polymer solutions in semi-infinite geometry\textsuperscript{22} gives better agreement with experimental data and results of the Monte Carlo calculations. In accordance with this, the emphasis of the present work is on the investigation of dilute polymer solution confined to geometry of two parallel walls using the massive field theory approach in fixed dimension $d = 3$.

The most remarkable properties of fluctuation-induced forces is their universality. They are independent of most microscopic details and depend only on a few macroscopic properties such as the adsorption properties of the confining walls or shape of the particles. In accordance with this we used different combinations of confining walls, i.e. we performed calculations for the case of two repulsive walls, two inert walls and mixed case of one repulsive and one inert wall. Besides, taking into account the Derjaguin approximation\textsuperscript{11} we obtained results for colloidal particles of big radius near the wall and compare the obtained results with experimental data\textsuperscript{5}. In the case of two repulsive walls we found good agreement of our results with results of Monte Carlo simulations\textsuperscript{23,24}.

II. THE MODEL

We shall assume that the solution of polymer chains is sufficiently dilute, so that interchain interactions and overlapping between different chains can be neglected, and it is sufficient to consider the configurations of a single chain. Long flexible polymer chains in a good solvent are perfectly described by a model of self-avoiding walks (SAW) on a regular lattice\textsuperscript{25,26}. Taking into account the polymer-magnet analogy developed by\textsuperscript{27}, their scaling properties in the limit of an infinite number of steps $N$ may be derived by a formal $n \to 0$ limit of the field theoretical $\phi^4$ $O(n)$-vector model at its critical point. The average square end-to-end distance, the number of configurations with one end fixed and with both ends fixed at the distance $x = \sqrt{(\bar{x}_A - \bar{x}_B)^2}$ exhibit the following asymptotic behavior in the limit $N \to \infty$

$$< R^2 > \sim N^{2\nu}, \quad Z_M \sim q^N N^{\gamma - 1}, \quad Z_N(x) \sim q^N N^{-(2 - \alpha)},$$

respectively. $\nu$, $\gamma$ and $\alpha$ are the universal correlation length, susceptibility and specific heat critical exponents for the $O(n)$ vector model in the limit $n \to 0$, $d$ is the space dimensionality, $q$ is a non universal fugacity. $1/N$ plays a 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 a solid substrate, then the monomers interact with the surface. At temperatures, $T < T_a$, the attraction between the monomers and the surface leads to a critical adsorbed state, where a finite fraction of the monomers is attached to the wall and form $d - 1$ dimensional structure. Deviation from the adsorption threshold ($c \propto (T - T_a)/T_a$) changes sign at the transition between the adsorbed (so-named normal transition, $c < 0$) and the nonadsorbed state (ordinary transition, $c > 0$) and it plays a role of a second critical parameter. The adsorption threshold for long-flexible infinite polymer chains, where $1/N \to 0$ and $c \to 0$ is a multicritical phenomenon.

The aim of the present investigations is to describe the behavior of such dilute solution of long-flexible polymer chains confined to a slit geometry of two parallel walls located at the distance $L$ one from another in $z$-direction such 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 surfaces of the system is characterized by a certain surface enhancement constant $c_i$, where $i = 1, 2$. The correspondent effective Landau-Ginzburg Hamiltonian describing such system is:

$$\mathcal{H}[\phi] = \int d^{d-1}r \int_0^L dz \left\{ \frac{1}{2} \left( \nabla \bar{\phi} \right)^2 + \frac{1}{2} \mu_0 \phi^2 + \frac{1}{4!} v_0 \left( \partial^2 \phi \right)^2 \right\} + \frac{c_{10}}{2} \int d^{d-1}r \bar{\phi}^2(r, z = 0) + \frac{c_{20}}{2} \int d^{d-1}r \bar{\phi}^2(r, z = L),$$

where $\bar{\phi}(x)$ is an $n$-vector field with the components $\phi_i(x)$, $i = 1, ..., n$ and $x = (r, z)$, $\mu_0$ is the "bare mass", $v_0$ is the bare coupling constant which characterizes the strength of the excluded volume interaction (EVI). The surfaces introduce an anisotropy into the problem, and directions parallel and perpendicular to the surfaces are no longer equivalent. In accordance with the fact that we have to deal with the slit geometry ($x = (r, 0 \leq z \leq L)$), only parallel to surfaces Fourier transforms in $d - 1$ dimensions take place. The interaction of the polymer chain with the walls is
implemented by the different boundary conditions. As it was mentioned above, we consider the case of two repulsive walls (the Dirichlet-Dirichlet boundary conditions)

$$c_1 \to +\infty, \ c_2 \to +\infty \ \text{or} \ \hat{\phi}(\mathbf{r}, 0) = \hat{\phi}(\mathbf{r}, L) = 0,$$

(2.3)

two inert walls (the Neumann-Neumann boundary conditions)

$$c_1 = 0, \ c_2 = 0 \ \text{or} \ \frac{\partial \hat{\phi}(\mathbf{r}, z)}{\partial z} |_{z=0} = \frac{\partial \hat{\phi}(\mathbf{r}, z)}{\partial z} |_{z=L} = 0,$$

(2.4)

and the mixed case of one repulsive and one inert wall (the Dirichlet-Neumann boundary conditions)

$$c_1 \to +\infty, \ c_2 = 0 \ \text{or} \ \hat{\phi}(\mathbf{r}, 0) = 0, \ \frac{\partial \hat{\phi}(\mathbf{r}, z)}{\partial z} |_{z=L} = 0.$$

(2.5)

The requirement in Eq.(2.4) describing the inert character of the walls corresponds to the fixed point of the so-named special transition$^{21,28,29}$ in field theoretical treatment.

In the present case the only relevant lengths are the average end-to-end distance $\xi_R = \sqrt{\langle R^2 \rangle} \sim N^\nu$ and the length $L$ – the distance between two walls. The properties of the system depend on the ratio $L/\xi_R$. It should be mentioned, that the present field-theoretical approach is not able to describe the dimensional crossover from $d$ to $d-1$-dimensional systems which arises for $L << \xi_R$. In this case the system is characterized by another critical temperature (see, for example, on situation in magnetic or liquid thin films) and moves to a new critical fixed point.

In accordance with this the present theory is valid for the case $L >> \xi_R$. Nevertheless, we performed some assumptions, which allowed us to describe the region $L << \xi_R$.

The well-known arguments of the polymer-magnet analogy$^{25-27,30}$ assume the correspondence between the partition function $Z_{\parallel}(x, x')$ of polymer chain with ends fixed at $x$ and $x'$ immersed in the volume containing the two parallel walls and the two-point correlation function $< \hat{\phi}(x) \hat{\phi}(x') >$ in the field theoretical field$^4 O(n)$-vector model at the formal limit $n \to 0$ in the restricted geometry:

$$Z_{\parallel}(x, x'; N, L, v_0) = \mathcal{I}C_{\mu_0} \to N (< \hat{\phi}_1(x) \hat{\phi}_1(x') > |_{n=0})$$

(2.6)

Here the r.h.s. denotes the Inverse Laplace transform $\mu^2 \to N$ of the two point correlation function for a system modelled via the corresponding Landau-Ginzburg Hamiltonian in the limit, where the number of components $n$ tends to zero. $N$ determines the number of monomers of the polymer chain and represents only an auxiliary parameter, the trace along the chain and fixes its size globally. The most common parameter in polymer physics to denote the size of a polymer chains which can be observable in experiments is $R_g^{25,26,30}$:

$$R_g^2 = \chi_d^2 \frac{R^2}{2},$$

(2.7)

where $\chi_d$ is a universal numerical prefactor which depends on the dimension $d$ of the system. For an ideal polymer chains one has $\chi_d^2 = \frac{d}{3}$ and for three dimensional case $N$ equals $R_g^2/2$. For the chains with EVI it could be obtained within a perturbation expansion$^{25}$.

The basic element in our calculations is the Gaussian two-point correlation function (or the free propagator) $< \tilde{\phi}_i(x) \tilde{\phi}_j(x') >$ in the mixed $\mathbf{p} z$ representation of the form

$$\tilde{G}_{\parallel}(\mathbf{p}, z, z'; \mu_0, c_1, c_2, L) = \frac{1}{2\kappa_0} ((\kappa_0^2 + \kappa_0(c_1 + c_2) + c_1c_2)e^{\kappa_0 L} - (\kappa_0^2 - \kappa_0(c_1 + c_2) + c_1c_2)e^{-\kappa_0 L})^{-1}$$

$$((\kappa_0^2 + \kappa_0(c_1 + c_2) + c_1c_2)e^{\kappa_0(L-|z-z'|)} + (\kappa_0^2 - \kappa_0(c_1 + c_2) + c_1c_2)e^{-\kappa_0(L-|z-z'|)})$$

$$+(\kappa_0^2 + \kappa_0(c_2 - c_1) - c_1c_2)e^{\kappa_0(L-z-z')} + (\kappa_0^2 - \kappa_0(c_2 - c_1) + c_1c_2)e^{-\kappa_0(L-z-z')}),$$

(2.8)

with $\kappa_0 = \sqrt{\mu^2 + \mu_0^2}$, where $\mathbf{p}$ is $d-1$ dimensional moment. It should be mentioned, that in the case $L \to \infty$ and $0 \leq z, z' \ll L$ (or $0 << z, z' \leq L$) the free propagator (2.8) reproduces the free propagator of the semi-infinite model (see$^{21}$).
III. THERMODYNAMICAL DESCRIPTION

We consider a dilute solution of long-flexible polymer chains with the slit and allow of the polymer coils exchange between the slit and a reservoir outside the slit. Thus the polymer solution in the slit is in equilibrium contact with an equivalent solution in the reservoir. We follow the thermodynamical description of the problem as given in $^{18}$. The free energy of interaction between the walls in such a grand canonical ensemble is defined as the difference of the free energy of an ensemble where the wall separation is fixed at finite distance $L$ and that where the walls are separated on infinite distance one from another:

$$\delta F = -k_B T N \ln \left( \frac{Z_{||}(L)}{Z_{||}(L \rightarrow \infty)} \right), \quad (3.1)$$

where $N$ is the total amount of polymers in the solution and $T$ is the temperature. $Z_{||}(L)$ is the partition function of a polymer chain located in volume $V$ containing the walls at a distance $L$:

$$Z_{||}(L) = \int_V \int_V d^d x \ d^d x' Z_{||}(x, x') , \quad (3.2)$$

with $Z_{||}(x, x')$ representing the partition function of a single polymer chain in the slit with its ends fixed at points $x$ and $x'$. For convenience we can renormalise the partition functions $Z_{||}(L)$ and $Z_{||}(L \rightarrow \infty)$ on the partition function $Z$ of one polymer chain in the volume $V$ without the walls. The volume of system $V$ can be divided into two independent subsystems $V_i$ and $V_o$ which correspond to the volume inside and outside the slit, respectively. This gives possibility to split the term $\ln(Z_{||}(L))$ into two parts

$$\frac{1}{V} \int_{V_o} d^d x (\frac{\hat{Z}_i(z)}{\hat{Z}_b} - 1) + \frac{1}{V_i} \int_{V_i} d^d x (\frac{\hat{Z}_i(z)}{\hat{Z}_b} - 1), \quad (3.3)$$

with $Z = V \hat{Z}_b$, $\hat{Z}_b = \int_{V} d^d x' Z_b(x, x')$ where $Z_b(x, x')$ is the partition function of one polymer chain in the unbounded solution with fixed ends at $x$ and $x'$ and $\hat{Z}_{o,i}(z) = \int_{V_{o,i}} d^d x' Z_{||}(x, x')$.

In the thermodynamical limit (as $N, V \rightarrow \infty$) the contribution from the first term in (3.3) disappear and the reduced free energy of interaction $\delta f$ per unit area $A = 1$ of the confining walls may be written as:

$$\delta f = \frac{\delta F}{n_p k_B T} = L - \int_{V_i} d^d x (\frac{\hat{Z}_i(z)}{\hat{Z}_b} - 1) + \int_{V_{HS}} d^d x \left( \frac{\hat{Z}_{HS_1}(z)}{\hat{Z}_b} - 1 \right) + \int_{V_{HS}} d^d x \left( \frac{\hat{Z}_{HS_2}(z)}{\hat{Z}_b} - 1 \right), \quad (3.4)$$

where $n_p = N/V$ is the number density of the polymer chains in the bulk solution and

$$\hat{Z}_{HS_i}(z) = \int_{V_{HS}} d^d x' Z_{HS_i}(x, x'), \quad (3.6)$$

with $i = 1, 2$ and $Z_{HS_i}(x, x')$ denoting the corresponding partition functions for a polymer chain in a half space with two fixed ends at points $x$ and $x'$. The functions $\hat{Z}_i(z)$ and $\hat{Z}_{HS_i}(z)$ depend only on the $z$-coordinates perpendicular to the walls. The reduced free energy of interaction $\delta f$, according to (3.5), is a function of the dimension of a length and dividing it by another relevant length scale (namely that for the size of the chain in the bulk, e.g. $R_z$) yields a universal dimensionless scaling function

$$\Theta(y) = \frac{\delta f}{R_z}, \quad (3.7)$$

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

$$\Gamma(y) = - \frac{d(\delta f)}{dL} = - \frac{d\Theta(y)}{dy} . \quad (3.8)$$
The total grand canonical free energy $\Omega$ of the polymer solution with the slit is:

$$\Omega = -n_p k_B T A L \varpi$$  \hspace{1cm} (3.9)

with

$$\varpi = \frac{1}{T} \int_0^L dz \frac{\hat{Z}_s(z)}{\hat{Z}_b}.$$  \hspace{1cm} (3.10)

Taking into account (3.5) and (3.9) we can write for unit surface area $A = 1$:

$$\frac{\Omega}{n_p k_B T} = f_b L + f_{s_1} + f_{s_2} + \delta f,$$  \hspace{1cm} (3.11)

with the reduced bulk free energy per unit volume $f_b = -1$ and the reduced surface free energy per unit area

$$f_{s_i} = \int_{\nu_{s_i}} dz \left( 1 - \frac{\hat{Z}_{hs_i}(z)}{\hat{Z}_b} \right).$$  \hspace{1cm} (3.12)

Further for convenience we can introduce $X$, the total system susceptibility in the form

$$X = \frac{1}{V} \int_{V} d^d x d^d x' < \hat{\varphi}_I(x) \hat{\varphi}_I(x') >.$$  \hspace{1cm} (3.13)

This definition is consistent with the bulk susceptibility for the unbounded space given as $X_b = \frac{1}{m^2}$ to all orders of perturbation theory (e.g.20). $\hat{Z}_b$ being the Inverse Laplace transform of $X_b$ and $\hat{Z}_b = 1$ to all orders as well. Accordingly to (2.6) and (3.13) we can rewrite (3.5) in the form

$$\delta f = \mathcal{I} \mathcal{L}_{\mu^2 \rightarrow R_s^2/2} \left\{ L (X_b - X_{||}) - \mathcal{Y}_1 - \mathcal{Y}_2 \right\},$$  \hspace{1cm} (3.14)

where $X_{||}$ denotes the total susceptibility for a slit geometry and $\mathcal{Y}_i$ with $i = 1, 2$ give two half-space (HS) contributions such that $f_{s_i} = \mathcal{I} \mathcal{L}_{\mu^2 \rightarrow R_s^2/2} \{ \mathcal{Y}_i \}$ (see Appendix A).

IV. CORRELATION FUNCTIONS AND RENORMALIZATION CONDITIONS

Correlation functions which involve $N'$ fields $\phi(x_i)$ at distinct points $x_i (1 \leq i \leq N')$ in the bulk, $M_1$ fields $\phi_I(r_{j_1}, z = 0) = \phi_{s_1}(r_{j_1})$ at distinct points on the wall $z = 0$ and $M_2$ fields $\phi_2(r_{j_2}, z = L) = \phi_{s_2}(r_{j_2})$ at distinct points on the wall $z = L$, and $I$ insertions of the bulk operator $\frac{1}{\hat{Z}} \hat{\phi}^2(X_k)$ at points $X_k$ with $1 \leq k \leq I$, $I_1$ insertions of the surface operator $\frac{1}{\hat{Z}} \hat{\phi}^2_s(R_l)$ at points $R_l$ with $1 \leq l \leq I_1$ and $I_2$ insertions of the surface operator $\frac{1}{\hat{Z}} \hat{\phi}^2_s(R_l)$ at points $R_l$ with $1 \leq l \leq I_2$, have the form

$$G^{(N', M_1, M_2, I_1, I_2)} \left( \{x_i\}, \{r_{j_1}\}, \{r_{j_2}\}, \{X_k\}, \{R_{l_1}\}, \{R_{l_2}\} \right) =$$

$$\left< \prod_{i=1}^{N'} \phi(x_i) \prod_{j_1=1}^{M_1} \phi_{s_1}(r_{j_1}) \prod_{j_2=1}^{M_2} \phi_{s_2}(r_{j_2}) \prod_{k=1}^{I} \frac{1}{\hat{Z}} \hat{\phi}^2(X_k) \prod_{l_1=1}^{I_1} \frac{1}{\hat{Z}} \hat{\phi}^2_s(R_{l_1}) \prod_{l_2=1}^{I_2} \frac{1}{\hat{Z}} \hat{\phi}^2_s(R_{l_2}) \right>. \hspace{1cm} (4.1)$$

Here, the symbol $< ... >$ denotes averaging with Hamiltonian (2.2). The free propagator of a Gaussian chain in slit geometry in the mixed $p, z$ representation has the form (2.8), as was mentioned above.

Taking into account that surface fields $\phi_{s_i}(r_{j_i})$ and surface operators $\frac{1}{\hat{Z}} \hat{\phi}^2_s(R_{l_i})$ with $i = 1, 2$ scale with scaling dimensions that are different from those of their bulk analogs $\phi(x_j)$ and $\frac{1}{\hat{Z}} \hat{\phi}^2(X_j)$ (see21), the renormalized correlation functions involving $N'$ bulk fields and $M_1$ surface fields on the wall $z = 0$ and $M_2$ surface fields on the wall $z = L$, $I$ bulk operators, $I_1$ and $I_2$ surface operators can be written as

$$G^{(N', M_1, M_2, I_1, I_2)}_{R} (\mu, v, c_1, c_2, L) =$$

$$Z_{\phi}^{-(N' + M_1 + M_2)} Z_{\phi}^{I_1} Z_{\phi}^{I_2} Z_{\phi_{s_1}}^{I_1} Z_{\phi_{s_2}}^{I_2} G^{(N', M_1, M_2, I_1, I_2)} (\mu_0, v_0, c_{10}, c_{20}, L), \hspace{1cm} (4.2)$$
where $Z_\phi$, $Z_1$, $Z_2$ and $Z_{\phi^2}$, $Z_{\phi^2_1}$, $Z_{\phi^2_2}$ are correspondent UV-finite (for $d < 4$) renormalization factors. The typical bulk and surface short-distance singularities of the correlation functions $G^{(N',M_1,M_2)}$ can be removed via mass shift $\mu_0^2 = \mu^2 + \delta \mu^2$ and surface-enhancement shifts $c_0 = c_1 + \delta c_1$, respectively. The renormalizations of the mass $\mu$, coupling constant $v$ and the renormalization factor $Z_\phi$ are defined by standard normalization conditions of the infinite-volume theory. In order to adsorb UV singularities located in the vicinity of the surfaces, a surface-enhancement shifts $\delta c_i$ are required. In this connection the new normalization conditions should be introduced. It is obvious, that in the limit $L \to \infty$ we should have

$$
\lim_{L \to \infty} \left[ \tilde{G}_R^{(0,2,0)}(p;\mu,v,c_1,c_2,L)|_{p=0} \right] = \frac{1}{\mu + c_1},
\lim_{L \to \infty} \left[ \tilde{G}_R^{(0,0,2)}(p;\mu,v,c_1,c_2,L)|_{p=0} \right] = \frac{1}{\mu + c_2}.
$$

(4.3)

For the renormalization factors $Z_i$, $Z_{\phi^2_i}$, where $i = 1, 2$ we obtain, respectively

$$
\lim_{L \to \infty} \left[ \frac{\partial}{\partial p^2} \tilde{G}_R^{(0,2,0)}(p;\mu,v,c_1,c_2,L)|_{p=0} \right] = -\frac{1}{2\mu(\mu + c_1)^2},
\lim_{L \to \infty} \left[ \frac{\partial}{\partial p^2} \tilde{G}_R^{(0,0,2)}(p;\mu,v,c_1,c_2,L)|_{p=0} \right] = -\frac{1}{2\mu(\mu + c_2)^2}.
$$

(4.4)

and

$$
\lim_{L \to \infty} \left[ \tilde{G}_R^{(0,2,0,0,1,0)}(p,p;\mu,v,c_1,c_2,L)|_{p,p=0} \right] = \frac{1}{(\mu + c_1)^2},
\lim_{L \to \infty} \left[ \tilde{G}_R^{(0,0,2,0,1)}(p,p;\mu,v,c_1,c_2,L)|_{p,p=0} \right] = \frac{1}{(\mu + c_2)^2}.
$$

(4.5)

In the limit $L \to \infty$ all these conditions yield exactly the same shifts $\delta c_i$ and renormalization factors as in the semi-infinite case. It is intuitively clear that in the case of two inert walls or mixed walls situated on big, but finite distance $L$ with $L \gtrsim R_g$ such that the chain is still not deformed too much from its original size in the bulk, the shift of $c_0^{ap} \to c_0^{sp}$ may depend on the presence of the other surface and hence on the size of the slit. So, in the case of $L \gtrsim R_g$ (or $\mu L \gtrsim 1$) from (2.8) and (4.3) we obtain new conditions

$$
\lim_{L \mu \gtrsim 1} \left[ \tilde{G}_R^{(0,2,0)}(p;\mu,v,c_1,c_2,L)|_{p=0} \right] = \frac{1}{\mu + c_1} \left( 1 + \frac{2\mu}{\mu + c_1} \frac{\mu - c_2}{\mu + c_2} e^{-2\mu L} + O(e^{-4\mu L}) \right),
\lim_{L \mu \gtrsim 1} \left[ \tilde{G}_R^{(0,0,2)}(p;\mu,v,c_1,c_2,L)|_{p=0} \right] = \frac{1}{\mu + c_2} \left( 1 + \frac{2\mu}{\mu + c_2} \frac{\mu - c_1}{\mu + c_1} e^{-2\mu L} + O(e^{-4\mu L}) \right).
$$

(4.6)

The above mentioned conditions (4.6) give one-loop order corrections to the respective surface-enhancement shifts $\delta c_i$ of semi-infinite theory in the case of large, but finite wall separation $L$. In accordance with this for the case of mixed walls we obtain

$$
\delta c_1^{S-O} = \delta c_1 + \Delta^{(S-O)}
$$

(4.7)

with corrections of order $O(e^{-2\mu L})$

$$
\Delta^{(S-O)} = \frac{\mu}{4} \left( \frac{1}{\mu L} + C_E + \ln 8 - 3 + \ln \mu L - e^{4\mu L} E_i(-4\mu L) \right) e^{-2\mu L}.
$$

(4.8)

In the case when both walls are inert, the modified surface enhancement shifts are

$$
\delta c_i^{S-S} = \delta c_i + \Delta^{(S-S)}
$$

(4.9)

with

$$
\Delta^{(S-S)} = -\Delta^{(S-O)} - \mu \left( \ln 2 - \frac{1}{2} \right) e^{-2\mu L}.
$$

(4.10)

The above mentioned corrections $\delta c_i$ are UV singular for $d = 3$ dimensions. They provide the singular parts of the counterterms that cancel the UV singularities of correspondent correlation functions by analogy as it took place for semi-infinite systems (see). The above mentioned corrections $\Delta^{(S-O)}$ and $\Delta^{(S-S)}$ are finite in $d \leq 4$ dimensions.
V. RESULTS FOR GAUSSIAN CHAINS

Let us consider at the beginning the Gaussian model for ideal polymer chains \((v_0 = 0)\). As mentioned above it corresponds to the situation of a polymer chain under \(\Theta\)-solvent conditions.

For general case of arbitrary \(c_1\) and \(c_2\) on the confining walls we obtain for the reduced free energy of interaction:

\[
\delta f = -\mathcal{I} L_{\mu^2 \rightarrow R^2/2} \left\{ \frac{1}{\mu^3} \left[ (\mu + c_1)(\mu + c_2)e^{\mu L} - (\mu - c_1)(\mu - c_2)e^{-\mu L} \right]^{-1} \times \right. \\
\left. \left\{ 4c_1c_2 - (\mu(c_1 + c_2) + 2c_1c_2)e^{\mu L} + (\mu(c_1 + c_2) - 2c_1c_2)e^{-\mu L} \right\} + \frac{1}{\mu^3} \left( \frac{c_1}{\mu + c_1} + \frac{c_2}{\mu + c_2} \right) \right\}. \tag{5.1}
\]

First, consider the case of the Dirichlet-Dirichlet (D-D) boundary conditions (2.3) on the confining surfaces. Taking the limits \(\frac{c_1}{m} \to \infty, \frac{c_2}{m} \to \infty\) yields:

\[
\Theta_{D,D}^{D}(y) = -4y \mathcal{I} L_{\tau \rightarrow (2y^2)^{-1}} \left( \frac{1}{\tau^{3/2} 1 + e^{2\sqrt{\tau}}} \right), \tag{5.2}
\]

where \(\tau = \mu^2 L^2\) and \(y = \frac{\mu L}{\delta f}\). The result indicates that if both \(c_i\) being positive, the depletion interaction potential is negative and hence the walls attract each other due to the depletion zones near repulsive walls. The inverse Laplace transform can only be performed numerically (the plot is shown in Figure 1) or may be expanded for asymptotic values of \(\sqrt{\tau}\). The obtained results for ideal polymer chains in slit of two repulsive walls are in agreement with previous theoretical results obtained in Ref.18. But, it should be mentioned, that on plotting these functions the authors of18 used a rescaled variable \(\sqrt{2}R_x\), which was not mentioned there.

Now we proceed to the case of two inert walls, what corresponds to the Neumann-Neumann (N-N) boundary conditions (2.4). For the free energy of interaction we obtain

\[
\Theta_{N,N}^{N}(y) = 0. \tag{5.3}
\]

This corresponds to the fact that ideal chains do not loose free energy inside the slit in comparison to the free chains in unrestricted space. The entropy loss is fully regained by the surface interactions provided by the two walls.

Taking the limits \(\frac{c_1}{m} \to \infty, \frac{c_2}{m} \to 0\) in accordance with (2.5) (the Dirichlet-Neumann (D-N) boundary conditions) from (5.1) we obtain:

\[
\Theta_{D,N}^{D}(y) = -2y \mathcal{I} L_{\tau \rightarrow (2y^2)^{-1}} \left( \frac{1}{\tau^{3/2} 1 + e^{2\sqrt{\tau}}} \right). \tag{5.4}
\]

This result can only be evaluated numerically and is plotted in Figure 2. Let’s consider different asymptotic regions of \(y\).

Wide slits \((y >> 1)\):

In the case \(\mu L >> 1\) from (5.2) we obtain for two repulsive walls:

\[
\Theta_{D,D}^{D}(y) \approx 4y \left\{ \mathrm{erfc} \left( \frac{y}{\sqrt{2}} \right) - \frac{1}{y} \sqrt{\frac{2}{\pi}} \exp \left( -\frac{y^2}{2} \right) \right\} - 8y \left\{ \mathrm{erfc} \left( \sqrt{2} y \right) - \frac{1}{y \sqrt{2\pi}} \exp \left( -2y^2 \right) \right\}. \tag{5.5}
\]

The force (3.8) becomes

\[
\Gamma_{D,D}^{D}(y) \approx -4 \mathrm{erfc} \left( \frac{y}{\sqrt{2}} \right) + 8 \mathrm{erfc} \left( \sqrt{2} y \right). \tag{5.6}
\]

And for one repulsive and one inert wall we have:

\[
\Theta_{D,N}^{D}(y) \approx 4y \mathrm{erfc} \left( \sqrt{2} y \right) - \frac{4}{\sqrt{2\pi}} \exp \left( -2y^2 \right), \tag{5.7}
\]

which implies

\[
\Gamma_{D,N}^{D}(y) \approx -4 \mathrm{erfc} \left( \sqrt{2} y \right). \tag{5.8}
\]
These approximating functions are presented on Figures 1 and 2, respectively.

**Narrow slits \((y \ll 1)\)**

In the case of narrow slit \(\mu L \ll 1\) the asymptotic solution for (5.2) reads:

\[
\Theta_{D,D}(y) \approx -\frac{4}{\sqrt{2\pi}} + y.
\]  

(5.9)

and the force simply becomes \(\Gamma_{D,D}(y) \approx -1\).

For the depletion interaction potential (5.4) we get:

\[
\Theta_{D,N}(y) \approx -\frac{2}{\sqrt{2\pi}} + y.
\]  

(5.10)

For the force we have again \(\Gamma_{D,N}(y) \approx -1\).

These results can be understood phenomenologically. In our units the quantities \(\Theta\) and \(\Gamma\) are normalized to the overall polymer density \(n_p\). So, the above results simply indicate that the force is entirely induced by the 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. Unfortunately, the narrow slit regime is beyond the validity of our approach in the presence of EVI, as mentioned above. But, the above mentioned arguments can be 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 the chains 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 a size \(\frac{d-1}{d}\) times its original size (for an unconfined chain). Therefore, the ratio of partition function of polymer chain in slit and free chain partition function vanishes strongly as \(y \to 0\), which implies directly the function \(\omega\) in (3.10). Setting \(\omega = 0\) and using only the corresponding surface contributions and the bulk contribution \((f_b = -1)\) in (3.11) must lead to the same asymptotic limits in the narrow slit regime. The advantage of this procedure is that no expansion necessary and it should be equally valid in the EVI-regime.

In Figures 1, 2 and 3 the depletion interaction potential \(\Theta(y)\) and depletion force \(\Gamma(y)\) are plotted for all boundary conditions. As expected, the results for mixed walls are located in between the results of two inert walls and those of two repulsive walls.

**VI. RESULTS FOR GOOD SOLVENT**

In good solvent the EVI between chain monomers play a crucial role so that the polymer coils occupy the bigger volume and are less compact than in the case of ideal polymer chains. The influence of EVI on the depletion functions can be obtained in the framework of the massive field theory approach in fixed dimensions \(d = 3\) up to one-loop order expansion of the two-point correlation functions \(G^{(2,0,0)}\) restricted in slit geometry (2.2). The bare total susceptibility \(\chi^{bare}_{||}\) (see (3.14)) for the slit geometry in accordance with (3.13), (3.10) and (4.1) is:

\[
\chi^{bare}_{||}(\mu_0, v_0, c_{10}, c_{20}, L) = \frac{1}{L} \int_0^L \int_0^L dz dz' \left\{ \tilde{G}_{||}(p = 0, z, z'; \mu_0, c_{i0}, L) - \frac{n + 2}{6} v_0 \int_0^L dz'' \int_{q} \tilde{G}_{||}(p = 0, z, z''; \mu_0, c_{i0}, L) \tilde{G}_{||}(q, z'', z''; \mu_0, c_{i0}, L) \tilde{G}_{||}(p = 0, z'', z'; \mu_0, c_{i0}, L) \right\}. 
\]

(6.1)

The two HS contributions denoted by \(\Upsilon_i\) (see (3.14)) can be obtained in accordance with (3.12) similarly to (6.1) with the propagators of semi-infinite system. Some details for the calculation of these quantities for zero-loop and one-loop order for different surface critical points of interest (ordinary, special) are presented in the Appendix A.

**A. Two repulsive walls**

Lets consider first the case of D-D boundary conditions (2.3) on each of the two surfaces. In this case no surface divergences appear in the calculation of the correlation functions and any surface renormalization is not necessary at
all. Each surface term \( f_s, i = 1, 2 \) contributes:

\[
f_s^D = \sqrt{\frac{2}{\pi}} \left( 1 - \frac{\ln \frac{9}{8}}{4} \right) R_x.
\] (6.2)

After performing the standard mass and coupling constant renormalization and additive subtraction at zero momentum all divergent terms disappear and the correspondent function \( X_{\|,ren}^{D,D} \) can be obtained. In order to be concise, we do not present here the complicated form for \( X_{\|,ren}^{D,D} \) and just discuss the limiting cases of wide and narrow slit regimes.

**Wide slits** \( (y \gtrsim 1) \):

\[
\Theta(y) = \frac{\delta f}{R_x y} = \frac{\delta f}{L}.
\]

\[
\Gamma(y) = \frac{1}{L}.
\]

**Narrow slits** \( (y \ll 1) \):

Following the simple argument obtained from the discussion of the exactly solvable ideal chain model the entire slit
contribution $\omega$ (3.10) to the reduced free energy of interaction $\delta f$ in (3.11) is simply set to zero and the depletion effect is only calculated from the bulk and surface contributions. In this limit the depletion potential becomes:

$$\Theta(y) \approx y - \frac{2\sqrt{2}}{\sqrt{\pi}} \left( 1 - \frac{\ln 3}{4} \right).$$ (6.5)

and the force again is unity. In Figure 1 one can follow how the two regimes come to match in the crossover regime $y \approx 1$. The lowest order expansion in case of wide slits would not be able to show this matching. With these two approximations we are in the position to present a rather complete picture of the problem in comparison to the approach given in $^{18}$.

B. One repulsive / One inert wall

This case has not been studied so far in any approach. Since we are now dealing with an inert wall, the surface renormalization should be taken into account. Again, the full result for the renormalized total susceptibility in a slit system $X_{\text{ren}}$ has complicated form and we discuss just limiting cases of wide and narrow slits.

The surface contribution for a repulsive wall coincides with (6.2) and for inert wall we have:

$$f_s^N = \frac{2\ln 2 - 1}{8} \sqrt{\frac{2}{\pi}} R_x.$$ (6.6)

Wide slits ($y \gtrsim 1$):

For the total susceptibility up to $O(e^{-2\mu L})$ order we obtain:

$$X_{\text{ren}}^{\text{OS}} \approx \frac{L}{\mu^2} - \frac{1}{\mu^3} \left( 1 + \frac{2\ln 4 - \frac{3}{2}}{4} \right) + \frac{e^{-\mu L}}{\mu^3} \left( \frac{2\ln 4 - 3 - 1}{2} \right) + \frac{e^{-2\mu L}}{\mu^3} \left( \frac{31 - 2C_E}{8} - \ln 3 - \frac{7}{4} - \frac{3}{4\mu L} \right)$$

$$+ \frac{e^{-3\mu L}}{4} \text{Ei}(-\mu L) - \frac{e^{-4\mu L}}{2} \text{Ei}(-4\mu L) - \frac{e^{-5\mu L}}{2} \text{Ei}(-5\mu L).$$ (6.7)

In comparison to the result for ideal chains (5.4) where the lowest order term, contributing to the total susceptibility in the wide slit limit is of order $O(e^{-2\mu L})$, now the additional term of order $O(e^{-3\mu L})$ appears.

---

**FIG. 2:** The functions $\Theta(y)$ and $\Gamma(y)$ for one repulsive and one inert wall with and without excluded volume interactions (EVI)

In this case the depletion interaction potential becomes:

$$\Theta(y) \approx \frac{1}{2} \left( \ln \frac{16}{3} - 1 \right) \left( y \text{erfc} \left( \frac{y}{\sqrt{2}} \right) - \frac{y^2}{2} \exp \left( -\frac{y^2}{2} \right) \right) + \frac{55}{96y} \text{erfc} \left( \sqrt{2} y \right)$$

$$+ \frac{1}{4} \left( \frac{229}{12} - C_E - \ln 1152 \right) \left( 2y \text{erfc} \left( \sqrt{2} y \right) - \frac{y^2}{\sqrt{\pi}} \exp \left( -2y^2 \right) \right) + \frac{y}{8} \mathcal{I}_x \left( \frac{\ln \tau}{\tau^{3/2}} e^{-2\sqrt{\tau}} \right).$$ (6.8)
The Figure 2 presents the depletion interaction potential $\Theta(y)$ and the force $\Gamma(y)$. It clearly indicates that in comparison to ideal chains the depletion effect is stronger in the regime of wide slits.

**Narrow slits ($y' \ll 1$):**
Following again the thermodynamic argument, $\omega$ is set to zero and only bulk and surface contributions are taken into account in (3.11). One gets:

$$\Theta(y) \approx y - \left(1 + \frac{2 \ln \frac{4}{3} - \frac{1}{4}}{4}\right) \sqrt{\frac{2}{\pi}},$$

(6.9)

which is also slightly below the depletion potential in comparison to the case of ideal chains (see Figure 2). The depletion force is unity.

Both approximations for wide, as well as for narrow slits suggest the depletion effect to be stronger in the case of excluded volume interactions than for ideal polymer chains (see Figure 2).

**C. Two inert walls**

In order to obtain the renormalized total susceptibility for a system confined by two parallel inert walls we have to apply the surface renormalization scheme suggested by\textsuperscript{21} for both surfaces at their surface critical point $c_{i}^{sp}$. Starting from (6.1) we obtain for the renormalized total susceptibility:

$$\chi_{SS}^{||} L = \frac{L}{\mu^2} - \frac{1}{2\mu^3} \left(\ln 2 - \frac{1}{2} - \ln \left(1 - e^{-2\mu L}\right)\right).$$

(6.10)

The surface contribution has already been presented in (6.6). Lets consider the asymptotic expansion for wide slits $\mu L >> 1$. Taking into account the surface (6.6) and the bulk contributions, the result for the depletion interaction potential becomes:

$$\Theta(y) \approx \frac{1}{\sqrt{2\pi}} e^{-2y^2} - y \text{erfc} \left(\sqrt{y}\right).$$

(6.11)

This function and its derivative for the force are plotted in Figure 3.

![Figure 3: The functions $\Theta(y)$ and $\Gamma(y)$ for two inert walls with and without excluded volume interactions (EVI). Here we introduced notations: $\delta_{c_{semi}} = \delta_{c_{i}}$ and $\delta_{c_{slit}} = \delta_{c_{i}}$ with $i = 1, 2$.](image)

It is obvious that only the wide slit approximation can be applied here since the usual argument for the narrow slit approximation is no more valid and $\omega$ does not necessarily vanish.

Interestingly, the depletion force turns out to be positive and the walls are repelled from each other. This means that the chains rather like to stay in between the slit than leave it. This in turn means that the chains gain enough energy from attractive interactions on the walls, which forces them to exert their loss of entropy (due to the confinement) onto the walls instead of leaving the slit.
It is very instructive to have a more general look on the terms appearing in the free energy of interaction. If now we take into account the new normalization conditions for surface-enhancement constants for slit geometry (see Eqs. (4.6)-(4.10)), which assume that we have big, but finite wall separation $L$, the $\delta f$ can be written as:

$$\delta f = 2 I L \mu^2 \int \frac{S_i}{\mu^4} \left( \delta c_{S-S} - \delta c_i \right) - I L \mu^3 \frac{\ln \left( 1 - e^{-2\mu L} \right)}{2\mu^3}.$$ (6.12)

Here $\delta c_{S-S}$ is the surface-enhancement constant shifts for slit geometry which appears in the case of finite walls separation and $\delta c_i$ is surface-enhancement constant shift in the case of infinite walls separation. In the presented approach the same renormalization of critical values $c_0$ was used and equally the same shifts to the renormalized values were obtained. So the first term on the r.h.s. just disappeared on the assumption that the surface-enhancement constant shift on one surface is not affected by the presence of the second one.

In fact this assumption could be doubted and an additional shift through the influence of the second wall (coupling effect between the two walls) may appear. Since the interaction potential itself is purely local, such a coupling effect can only be mediated through the chain conformations. As a result the number density of monomers near the walls might differ in comparison to a semi-infinite constraint and also the shift of the critical point (due to excluded volume interactions) can change. As already proposed in this in turn would require a different renormalization scheme for the surface critical point, where this coupling effect is to be taken into account. The results of calculations for a slightly modified surface renormalization scheme which takes into account the finite surface separation $L$ are introduced in the Appendix B and are presented in Figure 3 as well.

VII. COMPARISON TO PREVIOUS WORK

A. Theoretical approach

As was mentioned in the Introduction, the remarkable progress in the investigation of the influence of EVI on the depletion interaction and depletion force between two repulsive walls was achieved by via using of dimensionally regularized continuum version of the field theory with minimal subtraction of poles in $\epsilon = 4 - d$, where $d$ is dimensionality of the space. Figure 4 presents comparison of our results obtained in the framework of massive field theory at fixed dimensions $d = 3$ for the case of two repulsive walls and results obtained in.

![FIG. 4: The functions $\Theta(y)$ and $\Gamma(y)$ for two repulsive walls in comparison to](image-url)

The results obtained in the framework of both analytical methods are in quantitative agreement. But, one notes that the reduction of the depletion effect due to excluded volume interactions is less stronger within the massive field approach as compared to an $\epsilon$-expansion in one-loop order. It should be noted, that we extended our results up to the next $e^{-2\mu L}$ order. This allowed us to obtain good matching with approximating results in narrow slit limit (see Figures 1,2 for $\theta(y)$).
B. Simulations

One of the possibilities to test reliability of the obtained analytical results is to compare them to results obtained by Monte Carlo simulations. In this section we compare our results with results of MC calculations obtained by\textsuperscript{23} and\textsuperscript{24} for a single polymer chain trapped inside a slit of two repulsive walls, what corresponds to a canonical ensemble. The canonical free energy can be obtained via a Legendre transform from the grand canonical one in the thermodynamical limit \((N, V \rightarrow \infty)\) in the form:

\[
F(N_l) = \Omega[\mu(N_l)] + \mu(N_l)N_l,
\]

with \(\Omega\) from (3.9).

Thus the reduced canonical force for a one polymer chain \(N_l = 1\) can be written as its dimensionless counterpart:

\[
\frac{K L}{k_B T} = \frac{1}{\omega} \frac{d}{dL} (L \omega).
\]

It should be mentioned, that both Monte Carlo algorithms (see\textsuperscript{23} and\textsuperscript{24}) differ very much from each other in the range of analyzed slit widths and chain lengths of the simulated polymers. In\textsuperscript{23} an off-lattice bead and spring model for the self-avoiding polymer chain in \(d = 3\) dimensions trapped between two parallel repulsive walls at distance \(D\) has been studied by Monte Carlo methods, using chain lengths up to \(N \leq 512\) (number of monomers in the chain) and distances \(D\) from 4 to 32 (in units of the maximum spring extension). It was stated that the total force \(K\) exerted on the walls is repulsive and diverges for the case of narrow slit as

\[
\frac{K L}{k_B T} \sim \left(\frac{L}{R_g}\right)^{-1/\nu},
\]

where \(R_g\) is the radius of gyration of the polymer chain in unrestricted geometry.

In Ref.\textsuperscript{24} a lattice Monte Carlo algorithm on a regular cubic lattice in three dimensions, with \(D\) lattice units in \(z\)-direction and impenetrable boundaries was applied. The other directions obeyed periodic boundary conditions. The proposed MC simulations\textsuperscript{24} are based on the analytical result obtained by\textsuperscript{17} for the scaling behavior of partition function for a chain confined to a slit geometry of width \(D\):

\[
Z_N(D) \propto \left(\mu_\infty + aD^{-\frac{\nu}{2}}\right)^{-N} N^{\gamma_2-1} D^{\left(\frac{\gamma_2-\gamma_3}{\nu}\right)},
\]

for \(N, D \rightarrow \infty\), but \(D \ll N^\nu\), where \(\mu_\infty\) is the critical fugacity per monomer and \(\gamma_d\) is the universal exponent (see (2.1)) dependent on the space dimension \(d\) and the parameter \(a\) is a universal amplitude. The critical fugacity means the averaged inverse number of possible steps at each site. In\textsuperscript{24} universal amplitudes and exponents for the partition function of a chain trapped in the slit with respect to that of a free chain have been obtained through analyzing the statistics for different \(D\) and number of chain monomers up to \(N \leq 80\,000\). Also both cases of ideal chains (modeled as a simple random walk (RW)) and chains with excluded volume interactions (modeled via self-avoiding walks (SAW)) have been studied. In the case of an ordinary random walk on a regular cubic lattice in three dimensions one has obviously \(\mu_\infty = \frac{1}{2}\) and \(\gamma_d=3 = 1\). In the case of a SAW on such a lattice it is clear that at least \(\mu_\infty \geq \frac{1}{3}\). From Eq. (7.4) one may obtain the force exerted onto the walls in units of \(k_B T\) as:

\[
\tilde{K} = k_B T \frac{d}{dD} \ln \left(Z_N(D)\right).
\]

In the limit \((D \ll N^\nu, N, D \rightarrow \infty)\) \(\tilde{K}\) becomes:

\[
\tilde{K} = k_B T \left(\frac{Na}{\nu \mu_\infty} D^{1-\frac{\nu}{2}}\right).
\]

One should note that all functions here are in terms of dimensionless length scales, the number of lattice sites (\(D\) and \(N\)). In order to compare with our results it must be translated into terms of \(L\) and \(R_g\). Apparently \(L = uD\), with \(u\) denoting the lattice spacing, and the reduced, dimensionless force reads:

\[
k = \frac{\tilde{K} D}{k_B T} = \frac{a}{\nu \mu_\infty} \left(\frac{6}{\chi_d}\right)^{1/3} \left(\frac{L}{R_g}\right)^{-1/3},
\]
where we take into account the general relation (e.g.\textsuperscript{25}):

\[ R_g^2 = \chi \frac{b^2 N^{2\nu_3}}{6} \]  

(7.8)

in \( d = 3 \) dimensions. Parameter \( b \) denotes the (effective) segment length of the polymer model under consideration. In the case of RW and SAW on a cubic lattice one has simply \( b = u \) because the segment length in these models is naturally provided by the lattice parameter \( u \). In\textsuperscript{24} the universal amplitude \( a \) for the case of ideal chains was found

\[ a \approx 0.2741, \]  

which is very close to the exact value, computed analytically in\textsuperscript{17}, of \( a = \frac{\pi^2}{36} \). Taking into account that for ideal chain \( \nu = 0.5, \chi_d = 1 \) and \( \mu_\infty = \frac{1}{6} \) the force becomes:

\[ k_{id} = 2 \pi^2 \left( \frac{L}{R_g} \right)^{-2}. \]  

(7.9)

In Figure 5 this asymptotic behaviour for narrow slits is clearly recovered by our results for ideal chains, where the narrow slit limit is valid. By contrast, for a SAW in Ref.\textsuperscript{24} was suggested the value \( a \approx 0.448 \). Taking into account the values for \( \nu \approx 0.588, \chi_3 \approx 0.958^{25} \) and \( \mu_\infty \approx 0.2135 \) the reduced force can be written as

\[ k_{saw} \approx 16.95 \left( \frac{L}{R_g} \right)^{-1.7}. \]  

(7.10)

The result Eq.(7.10) is presented in Figure 5 in its regime of validity and compared to our theoretical results for a trapped chain with EVI, which are valid for the wide slit regime. As it easily can be see from Figure 5, the result (7.10) very well fit to our predictions in wide slit limit. Also, in Figure 5 the results obtained by the authors of Ref.\textsuperscript{23} are plotted and one notes a qualitative agreement to our predictions. One of the possible reason for the remaining deviations with results of Ref.\textsuperscript{23} is that the chain in the MC simulation is too short in order to compare with results of field-theoretical calculations. It should be noted, that at the moment no simulations concerning two inert walls or one inert/ one repulsive wall exist.

C. Experiment

In Ref.\textsuperscript{8} an experimental study of the depletion effect between a spherical colloidal particle immersed in a dilute solution of nonionic linear polymer chains and a wall of the container through total internal reflection microscopy was
analyzed. Using the Derjaguin\textsuperscript{11} approximation we could compare our theoretical results with experimental data in the case when the radius of the spherical colloid particle $R$ is much larger than radius of gyration $R_g$ and the closest distance $a$ between particle and the surface. The deviation of the experimental setup to the presented theoretical approach connected with the fact that the second wall is not plane but curved. Summing up the depletion potential per volume unit for the case of two plane surfaces in the margins of the curved volume allows to estimate the depletion effects in the case of a sphere and a wall. In the experiment by\textsuperscript{8} the radius of gyration was measured as $R_g = 0.101 \, \mu m$ and the colloidal particle was reported to have a radius $R = 1.5 \, \mu m$. Straightforward application of the Derjaguin\textsuperscript{11} approximation yields:

$$\frac{\phi_{d\epsilon pl}(a)}{n_p k_b T} = 2\pi R^2 \frac{a_R \beta}{x} \int_{a}^{R_x} dy \left(R + a - R_x y \right) \Theta(y),$$

(7.11)

with $a$ the minimal distance between the sphere and the wall. Since in the range of $y$ the last two terms in the parenthesis are much smaller in comparison to the first one we can assume that:

$$\frac{\phi_{d\epsilon pl}(a)}{n_p k_b T} \approx 2\pi R R^2 \int_{a}^{\infty} dy \Theta(y).$$

(7.12)

The experimental data in comparison to our theoretical prediction are plotted in Figure 6. It should be mentioned, that our results obtained in the framework of the massive field theory are situated slightly closer to the experimental data than previous theoretical results obtained in the framework of the dimensionally regularized continuum version of the field theory with minimal subtraction of poles in $\epsilon = 4 - d$\textsuperscript{18}. Unfortunately, this shift is not enough in order to obtain quantitative agreement with experimental data. But, the obtained theoretical curves in Figure 6 are in qualitative agreement with experimental data. The quantitative discrepancy can be removed if we use the radius of gyration as adjusting parameter by analogy as it was done in\textsuperscript{18}. From another side this indicate about importance of further theoretical investigations of depletion interaction potential and depletion force in the crossover region from wide to narrow slit.

\section*{VIII. CONCLUSIONS}

Using the massive field theory approach directly at fixed dimensions $d = 3$ we calculated the depletion interaction potential and depletion force between two repulsive, two inert and one repulsive and one inert walls confining a dilute solution of long flexible polymer chains. The obtained calculations for all cases of polymer-surface interactions were performed for the ideal chain and real polymer chain with excluded volume interactions in the wide slit regime.
Besides, we used some assumptions which allowed us to estimate the depletion interaction potential in the region of narrow slit. Our results are obtained up to the next $e^{-2\mu L}$ order in comparison with results of $\epsilon$-expansion\textsuperscript{18}. Our investigations include modification of renormalization scheme for the case of two inert walls (or mixed walls) situated on big, but finite distance $L$ with $L \gtrsim R_g$ such that the polymer chain is still not deformed too much from its original size in the bulk. The obtained results indicate that the reduction of the depletion effect due to excluded volume interactions is less stronger within the massive field theory approach as compared to the dimensionally regularized continuum version of the field theory with minimal subtraction of poles in $\epsilon = 4 - d$\textsuperscript{18} in one-loop order. We found very good agreement with Monte Carlo simulation data\textsuperscript{24} and\textsuperscript{23} for the case of two repulsive walls. Taking into account Derjaguin approximation we obtained good qualitative agreement with experimental data\textsuperscript{8} for the depletion potential between a spherical colloidal particle of big radius and repulsive wall. From comparison of obtained theoretical results and experimental data we can see that the results obtained in the framework of the massive field theory are situated slightly closer to experimental data. But, this shift is not enough in order to obtain good quantitative agreement with experiment. Interesting fact is that even the taking into account the excluded volume interaction between the monomers of the polymer chain do not resolve completely this problem. One of the possible ways to find a good agreement could be connected with further theoretical investigation of crossover region from wide to narrow slit.

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Appendix A: The surface contributions

To calculate the function $\Upsilon$ defined in Eq.(3.14), we need the free propagator for a semi-infinite system confined by a surface at $z = 0$. This free full propagator has a form\textsuperscript{21}:

\[
\tilde{G}^*_{ij,HS}(\mathbf{p}, \mathbf{p}', z, z'; \mu_0, c_0) = (2\pi)^{d-1}\delta_{ij}\delta(\mathbf{p} + \mathbf{p}')\tilde{G}_{HS}(\mathbf{p}, z, z', \mu_0, c_0),
\]

with

\[
\tilde{G}_{HS}(\mathbf{p}, z, z', \mu_0, c_0) = \frac{1}{2\kappa_0} \left( e^{-\kappa_0|z-z'|} + \frac{\kappa_0 - c_0}{\kappa_0 + c_0} e^{-\kappa_0(z+z')} \right),
\]

where $\kappa_0 = \sqrt{\mu^2 + \mu_0^2}$.

In the zero-loop order we have:

\[
\Upsilon_i = \frac{1}{\mu^3} \frac{c_i}{\mu + c_i}.
\]

In one-loop order the calculation for Dirichlet boundary conditions on the surface (or $\frac{c}{m} \to \infty$) yields after renormalization in fixed dimensions $d = 3$:

\[
\Upsilon^D = \frac{\hat{\nu}}{\mu^3} \left( 1 - \frac{n + 2}{n + 8} \hat{\nu} \ln \frac{9}{8} \right).
\]

And for Neumann boundary conditions ($c = 0$) after renormalization we obtain:

\[
\Upsilon^N = \frac{\hat{\nu}}{\mu^3} \left( \ln 2 - \frac{1}{2} \right) \frac{n + 2}{n + 8},
\]

where we introduced rescaled renormalized coupling constant $\hat{\nu}$ in the form: $\hat{\nu} = \frac{\Gamma(n/2)}{(4\pi)^{n/2}}\nu$. The correspondent fixed point in one-loop order approximation is $\hat{\nu}^* = 1$. 
Appendix B: The case of finite slit separation for two inert walls

Taking into account the new \( \delta c_{i}^{S,S} \) (see Eq.(4.9)) we can calculate \( \delta f \) in accordance with Eq.(6.12) for the case of big, but finite slit separation \( L \). We obtain:

\[
\delta f \approx \mathcal{I}_L \mu^2 \rightarrow \frac{\mu^3}{2} \left( \frac{\Delta^{(S,S)}}{\mu^4} + \frac{e^{-2\mu L}}{2\mu^3} \right).
\]  \hspace{1cm} \text{(A2.1)}

After substitution of \( \Delta^{(S,S)} \) from (4.10) the result for \( \delta f \) is:

\[
\delta f \approx - \mathcal{I}_L \mu^2 \rightarrow \frac{\mu^3}{2} \left\{ \left( \frac{1}{\mu L} + C_E + 7 \ln 2 - 6 + \ln \mu L - e^{4\mu L} \text{Ei}(-4\mu L) \right) \frac{e^{-2\mu L}}{2\mu^3} \right\}.
\]  \hspace{1cm} \text{(A2.2)}

If we carry out the inverse Laplace transform, the result for \( \Theta(y) \) in the wide slit limit is:

\[
\Theta(y) \approx - \frac{C_E + 7 \ln 2 - 7}{2} \left( \sqrt{\frac{2}{\pi}} e^{-y^2} - 2y \text{erfc} \left( \sqrt{2} y \right) \right) - \frac{1}{4y} \text{erfc} \left( \sqrt{2} y \right)
\]
\[
- \frac{y}{4} \mathcal{I}_L \tau \rightarrow \frac{1}{2y} \left( \frac{e^{-2\sqrt{\tau}}}{\tau^{3/2}} \ln \tau \right) + \frac{y}{2} \mathcal{I}_L \tau \rightarrow \frac{1}{2y} \left( \frac{e^{2\sqrt{\tau}}}{\tau^{3/2}} \text{Ei} \left( -4\sqrt{\tau} \right) \right).
\]  \hspace{1cm} \text{(A2.3)}

In contrast to (6.11) this expression is indeed negative. Thus, if we perform calculations for the depletion interaction potential and the depletion force including big, but finite slit separation \( L \) we obtain, that force for the case of two inert walls change character and becomes attractive. In Figure 3 the depletion interaction potential and the depletion force obtained in the framework of this alternative renormalization scheme with \( \delta c_{\text{slit}} \) are plotted in comparison to the results obtained via the original renormalization using \( \delta c_{\text{semi}} \). Here we introduced for convenience the following notations: \( \delta c_{\text{semi}} = \delta c_i \) and \( \delta c_{i}^{S,S} = \delta c_{\text{slit}} \) with \( i = 1,2 \).

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