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Immersion energy and polymer-mediated depletion interactions between nano-colloids as studied by analytic self-consistent field theory

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Abstract

By applying the Edwards self-consistent field theory, we calculate the polymer density and free energy excesses caused by the presence of nano-colloids in the excluded volume polymer system. Using the obtained results, we have calculated the depletion potential U as a function of the separation between colloids, colloid radius, polymer volume fraction, and polymer gyration radius. Upon analyzing the obtained results against the known exact asymptotic small-separation limit and scaling relations, we propose an approximate expression for U that builds upon our exact result. This expression is shown to give excellent agreement with Monte Carlo simulations. Reliability of the derived analytical expression for the depletion potential and its relation to the previous theoretical and simulation work are thoroughly discussed.

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I. INTRODUCTION

Two or more colloidal particles immersed in the system of non-adsorbing polymers change the density structure of this system, thus inducing effective entropic interactions between the immersed colloids. These polymer mediated (PMF) entropic interactions between nanoscopic colloidal particles, termed "depletion forces", are in the core of many biologically and technologically relevant phenomena such as red blood cell adhesion,[1] DNA mediated depletion interactions[2] and size-exclusion polymer chromatography.[3] Despite more than 50-year history of thorough investigations of PMF, the role of the intra- and inter-polymer interactions in the formation of the depletion/enhancement polymer layers near colloidal particles and the influence of the properties of these layers on PMF is rather poorly understood theoretically. In the first place, this lack of understanding is caused by the significant technical difficulties in associated theoretical development. Those difficulties become especially pronounced in the case of small colloid radius R-to-polymer gyration radius R_G ratios $q^{-1} \equiv R/R_G$, generally referred to as the protein limit.[4] This limit generally describes the case encountered in the majority of practically important situations, where the colloidal particles can easily penetrate polymer coils and simultaneously interact with many polymers. From the theoretical standpoint, in the described protein limit the polymers can not be modeled as individual soft particles interacting with colloids, which brings essential mathematical complications to the theoretical description of PMF. The origin of these complications stems from the many-body nature of the interactions of small "protein" colloids with polymer monomers inside polymer coils, which affect the local polymer density correlations inside these coils. The magnitude of the above polymer density correlations, in turn, is known[5,6] to significantly depend on the excluded volume interactions in the polymer system. These excluded volume interactions affected, in particular, by the solvent screening,[6] can therefore have decisive influence on the magnitude and range of the polymer mediated forces acting between nano-colloids. The present paper is intended to provide quantitative analytical understanding of the above described effects of the excluded volume interactions and polymer-to-colloid size ratio on PMF by developing the exact analytical approach based on the Edwards self-consistent mean-field theory (SCMFT).

Originally, SCMFT has been widely used[6–9] for describing the density structure of the semi-dilute polymer systems in confinement. By making use of the random mixing model for the direct correlation function of polymers,[7] SCMFT can be unified[7,10] with standard density functional theory to be successfully used in describing the density structure of dense polymer systems, such as polymer melts[7,11], polymer blends,[12] and diblock copolymers.[10] The main technical difficulty in developing SCMFT approach lies in the necessity of solving the Edwards modified diffusion equation[5] that contains the polymer density dependent self-consistent term that renders this equation essentially non-linear. To date, no exact solution of this equation is known even for the relatively simple case of a single colloid in the presence of interacting polymers. Few analytical results for the polymer density profiles near colloids, including the interpolation formula of Fleer et. al.[13] and the 'ground state' solution of Odijk[14] have been obtained by resorting to rather drastic approximations. Though being of significant practical importance, those approximate results call for more systematic analysis of the effect of finite chain length and excluded volume interactions on the structure of the depletion polymer layers formed near colloids. For instance, adopting the long chain ("ground state") approximation in Ref.[14] resulted in the conclusion that the excluded volume interactions have no effect on the nano-colloid immersion energy and structure of the depletion layer. In contrast, according to the results obtained in the present work, the excluded volume interactions cause significant corrections to the "ideal" structure of the polymer density in the vicinity of a nano-colloid. In the present theory, the significance of these corrections are quantified by introducing the "non-ideality" parameter $u \equiv Nv\rho$ that equals to the product of the polymerization degree N, polymer density ρ, and the excluded volume parameter v. Note that u can be of the order of unity or less even at very large $N \sim 10^5$, thus rendering the negligence of finite N corrections adopted in the above standard long chain ("ground state") approximation to be inadequate in many practically important cases. Note that the approach developed in the present work makes it possible to avoid not only resorting to the ground state approximation $N >> 1$, but also using any other perturbative parameters apart from $q^{-1} \equiv R/R_G$.

The described problems in the analytical description of density structure of the polymer depletion layers formed around nanoparticles carries over to the depletion forces mediated by these layers. Here we focus on the entropic depletion interactions[15] between nano-colloids mediated by interacting polymers that have been a subject of growing interest and increasing diversity due to their ability to cause phase separation (e.g. colloid flocculation) in the polymer-colloid mixtures. Despite their importance, the theoretical studies of these interactions in the protein limit are mainly restricted to the Monte-Carlo simulations,[16,17] scaling analysis[18,19] and numerical polymer self-consistent theory.[20,21] Although the above methods give very useful insight into the depletion forces, neither of them has advantages of pure analytical approach that would make it possible to explicitly elucidate a complicated interplay of the effects of the excluded volume, finite polymer length and polymer-to-colloid size ratio on the magnitude of these forces. In particular, an important relevant issue of the effect of solvent quality on the magnitude of the depletion forces acting between nano-colloids immersed in polymer solution completely falls out of the scope of existing theoretical work. The only relevant analytic solution obtained[22] in the framework of the Polymer Reference Interaction Site Model (PRISM) describes the effects of non-ideality on the depletion interactions in terms of the artificially defined polymer correlation length. Clearly, such parametric description can hardly be applied to describe the important screening effect of the solvent on the depletion interactions between nano-colloids in polymer solutions. With all its usefulness and mathematical simplicity, the described PRISM approach is based on rather drastic approximations such as representing each colloid by a single site and using "preaveraging assumption".[23] In contrast, the self consistent field theory used in the present work makes it possible to study polymer density correlations in the presence of colloids without resorting to the above artificial approximations.

In the present work, we employ SCMFT theory to describe the depletion interactions between nano-colloids immersed in the semi-dilute polymer solution. We will show that taking the protein ("small colloid") limit $q = R_G/R >> 1$ of the SCMFT equations provides seldom opportunity to obtain analytic solution of these equations without resorting to any additional (e.g. "ground state") approximations. In order to avoid terminological confusions, we explicitly define the semi-dilute solution as a relatively low monomer concentration solution with polymer densities ρ_P equal and higher than the overlap density $\rho_P^* \equiv 3/(4\pi R_G^3)$. The developed approach is therefore appropriate for describing the depletion interactions in the density regimes ranging from the chain overlap threshold to relatively high polymer densities exceeding the overlap threshold by several times. A smooth crossover between these two limiting regimes is quantified by the correlation length λ that naturally arises in our theory. The correlation length λ varies from its threshold value $\lambda = R_G$ at $\rho_P = \rho_P^*$ to polymerization degree independent strong-overlap value $\lambda = \xi$ at $\rho_P >> \rho_P^*$, ξ being the de Gennes correlation length.[6] In addition to the described semi-dilute polymer solution, the developed approach can be applied to the excluded volume (”real”) polymer system[5] in the absence of solvent. As long as this latter system can provide an adequate model of polymer melts at not very high densities, our approach can be used for the description of the depletion interactions in polymer melts. Note that care must be exercised in applying the developed SCMFT to analyzing PMF mediated by dense polymer melts, since this approach ignores the short range correlations arising from the hard-core interactions between monomers that can be important at high polymer densities. We will elaborate on this point in Sec. II devoted to the thorough description of the main guidelines of SCMFT and used approximations in relevance to the investigated physical systems.

The main aim of the present work is to develop an exact analytic approach that gives an explicit account for the above effect of the excluded volume interactions and solvent quality on the depletion forces, as described by the self-consistent field theory. As an initial step in achieving this goal, we intend to thoroughly investigate the technical aspects of the associated thermodynamic problems in Section II. In the next Section III, we calculate the quantities associated with the immersion of a single nano-colloid into polymer system, such as polymer density profile around this nano-colloid and its immersion energy. In Section IV we apply the developed approach to the investigation of the depletion potential for different solvent conditions. Section V is devoted to the comparative analysis of our analytical findings against previous results obtained by Monte Carlo (MC) simulations, scaling arguments, and field-theoretic small radius expansion method. Finally, in Section VI we conclude by giving a comprehensive description and analysis of the obtained results.

II. IMMERSION ENERGY AND DEPLETION POTENTIAL AS DETERMINED BY EDWARDS SELF-CONSISTENT MEAN FIELD THEORY

We start by giving mathematical formulation of the self-consistent mean field theory (SCMFT) as applied to the study of the depletion interaction mediated by real polymers. The main idea of SCMFT lies in describing the excluded-volume interactions among segments of the polymer chains by an effective potential V that in turn is self-consistently expressed through the polymer number density ρ. The relation between the density structure of polymers and the above self-consistent potential is established by the following Edwards equation[5] of the form

$$\partial_n \widehat{Q}(\overrightarrow{r}, n) = \nabla^2_{\overrightarrow{r}} \widehat{Q}(\overrightarrow{r}, n) - V(\rho)\widehat{Q}(\overrightarrow{r}, n), \tag{1}$$

where $\widehat{Q}(\overrightarrow{r}, n)$ is the coordinate $\overrightarrow{r}$-dependent end density that describes the probability to find one end of the polymer of the polymerization degree n in the point $\overrightarrow{r}$ provided that its other end is placed elsewhere in the free space Θ not occupied by hard bodies. Hereafter, all lengths are measured in the polymer segment Kuhn length b divided by $\sqrt{6}$, so that, for instance, the radius of gyration of polymer reads $R_G = \sqrt{N}$, N being the polymerization degree.

The mean-field potential V that enters Eq.(1) as an external potential serves as a vehicle to describe the excluded volume interactions in specific polymer systems. The self-consistency of the above mean field theory is achieved through considering the above potential V to be polymer density-dependent. This formally introduced dependence mimics the realistic property of polymer systems that the strength and range of the excluded volume interactions depends on the polymer density ρ. Note that along with the conceptual simplification brought in by using the above mean-field description, comes certain difficulty in correct defining the thermodynamic functions of the polymer system. In particular, care must be exercised in establishing the relationship between the free energy of polymers and the depletion potential mediated by these polymers, since V depends on the thermodynamic state of the polymer system. We will focus on the mentioned thermodynamic aspect of the problem after explicitly defining the mean field potential V.

A simplest way to specify the mean-field potential V lies through using the random mixing model[7] for excluded volume interactions that amounts to replacing the true polymer-polymer direct correlation function $c(\overrightarrow{r}, \overrightarrow{r}')$ by the model expression according to $c(\overrightarrow{r}, \overrightarrow{r}') = v\delta(\overrightarrow{r} - \overrightarrow{r}')$, $\delta(\overrightarrow{r})$ being the Dirac delta function centered at point $\overrightarrow{r}$. This approximation leads to the following expression[6,7] for the mean field potential V

$$V = \beta^{-1} v \rho, \tag{2}$$

where $\beta = (kT)^{-1}$ is the reciprocal temperature, with k and T being the Boltzmann constant and the absolute temperature, respectively, v is the excluded volume parameter[6] that quantifies the polymer excluded volume interactions, ρ is the coordinate dependent monomer number density. Note that Eq.(1) with the potential V defined by the equation Eq.(2) can be used to describe two different polymer systems. Setting $v = b^3$ in Eq.(2) leads to the mean field potential that is conventionally used[5] for describing the steric monomer excluded volume effect in polymer melts. Setting $v = b^3(1 - 2\chi)$ provides[6] the extension of this description of the excluded volume effect to the case of semidilute solutions with the interaction between polymers and solvent described by the Flory parameter χ. In this formulation, the case of purely steric interactions between polymers $v = b^3$ comes as the 'athermal' limit $\chi \to 0$ of the excluded volume parameter of the semidilute polymer solution.

Note that for practical purposes it is sometimes more convenient to use the mean-field potential $\widehat{V}$ with the subtracted 'bulk' part, defined by

$$V_{ex} = \beta^{-1} v N \rho_P \eta, \qquad \eta = \frac{\rho}{\rho_b} - 1, \tag{3}$$

where ρ_P is the bulk polymer number density defined as a density of the polymer system far away from any hard body immersed in this system and $\rho_b \equiv N\rho_P$ is the corresponding bulk monomer number density. The reduced potential V_{ex} given by Eq.(3) can be formally obtained from Eq.(1) with the potential V given by Eq.(2) by substituting the reduced end density $Q = \widehat{Q} \exp(v \rho_b n)$ into this equation, Eq.(1). It is straightforward to show that this substitution does not change the form of Eq.(1), apart from the fact that the potential V occurs to be replaced by V_{ex}.

The monomer number density ρ that enters the formula for the self-consistent field V given by Eq.(2) can be expressed[5] through the end density Q, to be written in the form

$$\rho(\overrightarrow{r}) = \rho_P \int_0^N Q(\overrightarrow{r}, n) Q(\overrightarrow{r}, N - n) dn. \tag{4}$$

Substituting the above expression for ρ into Eq.(2) turns Edwards equation in Eq.(1) into the closed integro-differential equation with respect to the end-density Q. Solving this equation for Q provides a direct route to calculating the polymer number density by the formula given by Eq.(4). The thus obtained expression for the polymer density can in turn be used for calculating the polymer-mediated potential as is described in what follows.

In order to relate the polymer number density to the immersion (solvation) energy W of a single colloid and the depletion potential U acting between two colloids one must correctly define the free energy of the polymer system in the presence of colloids. One proven way to do so, is to first determine the free energy of an ideal system and then include the non-ideal correction derived from the above described random mixing model. The free energy F_{id} of an ideal polymer system can be derived exactly, without resorting to any approximations. To simplify this derivation, it is instructive to employ the grand potential Ω_{id} of an ideal polymer system, which is conventionally defined by the negative of the logarithm of the grand partition function Ξ. The essential simplification coming from the ideality of the polymer system is that Ξ can be straightforwardly expressed through the partition function of a single polymer chain Z, to be written in the form $\Xi = \exp(Z)$. In turn, Z equals[7] to the integral of the density of the ideal polymer system over the volume Θ available to polymers divided by the polymerization degree N, which immediately leads to $\beta\Omega_{id} = -N^{-1}\int_\Theta \rho d^3r$. The free energy F_{id} can be found by applying the standard Legendre transformation that amounts to the formula

$$F_{id} = \Omega_{id} + \int_\Theta \rho(\mu - \beta^{-1}V)d^3r, \tag{5}$$

where μ is the polymer chemical potential (per monomer) and the potential V is defined by Eq.(2). It is important to note that V in Eq.(5) plays a role of the auxiliary external potential that does not represent any real external field. According to the guidelines of SCMFT, this potential, considered as an external one in Eq.(5), is to be adjusted to maximize the total grand potential of the polymer system. This adjustment leads[7] to the expression for V given by Eq.(2). However, the thus obtained potential V represents only the part of the excluded volume effect. An additional non-ideal contribution to the polymer free energy comes from the direct interactions between the monomers described in what follows.

Using the standard definition[5] of the the direct correlation function c of the monomer-monomer interactions, the non-ideal correction F_{int} to the ideal free energy F_{id} can be conventionally expressed as

$$F_{int} = 2^{-1}\int_\Theta d^3r' \int_\Theta c(\overrightarrow{r}, \overrightarrow{r}')\rho(\overrightarrow{r})\rho(\overrightarrow{r}')d^3r.$$

Applying the above described random mixing approximation $c = v\delta(\overrightarrow{r} - \overrightarrow{r}')$ and using the explicit expression for the mean-field potential V given by Eq.(2) takes the expression for the total free energy $F = F_{id} + F_{ex}$ to the form

$$F = (\mu - (\beta N)^{-1})\int_\Theta \rho(\overrightarrow{r})d^3r - (2\beta)^{-1}v\int_\Theta \rho(\overrightarrow{r})^2 d^3r. \tag{6}$$

Note that in Eq.(6), the effect of the monomer excluded volume interactions is expressed through the only parameter v. This final expression for the free energy does not contain any external field term initially introduced in Eq.(4) for an auxiliary purpose of describing the mean field representing the excluded volume interactions. It is important to note that in the case of uniform polymer system, Eq.(6) reduces to the well-known[24] mean field expression for the polymer free energy of the form $\beta F = \Theta(N^{-1}\log N^{-1}\rho_b + 2^{-1}v\rho_b^2)$, with $\beta\mu_b = N^{-1}\log(N^{-1}\rho_b) + v\rho_b$ being the per-monomer chemical potential of the uniform polymer system with density ρ_b.

The above expression for the free energy can be used to derive all the thermodynamic functions of the polymer system in the presence of colloids, with the effect of the excluded volume interactions taken into account. In the reminder of this section, we will focus on the derivation of the immersion energy W of a single colloid and the polymer mediated depletion potential U acting between two colloids. The immersion energy W (at infinite dilution) is defined as the work needed to reversibly bring a colloid from the infinity to its actual position in the polymer system, while maintaining constant chemical potential. Similarly, the potential of the depletion interaction $U(H)$ acting between two colloids mediated by polymers that are maintained in thermodynamic equilibrium is defined as the work needed to reversibly bring these bodies from infinite separation to a separation distance H. In the above both cases, this work can be evaluated as an excess grand potential $\Delta\Omega$ caused by the presence of colloids in polymer system. The grand potential Ω of the polymer system can be straightforwardly derived from the expression for the free energy given by Eq.(6) by applying standard Legendre transformation. In the absence of an external field, the appropriate Legendre formula reads

$$\Omega = F - \mu \int_\Theta \rho(\overrightarrow{r})d^3r, \tag{7}$$

which immediately leads to the following expression for Ω

$$\Omega = -(\beta N)^{-1} \int_\Theta \rho(\overrightarrow{r})d^3r - (2\beta)^{-1}v \int_\Theta \rho(\overrightarrow{r})^2 d^3r. \tag{8}$$

Note that for homogeneous polymer system, the grand potential Ω given by Eq.(8) reduces to the negative of the osmotic pressure $P_b = N^{-1}\rho_b + 2^{-1}v\rho_b^2$ multiplied by the volume Θ available to polymers, as should be expected. The excess grand potential (relative to the bulk system) is thus determined by the formula

$$\Delta\Omega = \Omega + P_b\Theta = -(\beta N^{-1}) \int_\Theta (\rho(\overrightarrow{r}) - \rho_b)d^3r - (2\beta)^{-1}v \int_\Theta (\rho(\overrightarrow{r})^2 - \rho_b^2)d^3r. \tag{9}$$

According to the definitions of the immersion energy W and the depletion potential U given right above Eq.(7), the obtained excess grand potential $\Delta\Omega$ given by Eq.(9) can be directly identified with W and $-U$ in the corresponding cases. For further references, it is therefore instructive to give a simplified form of the expression in Eq.(9) for the case when the polymer density only slightly deviates from the bulk density ρ_b. Up to the leading order in the difference $\rho - \rho_b$, this expression reads

$$\beta\Delta\Omega = -(1+u)\rho_b N^{-1} \int_{\Theta} \eta(\overrightarrow{r})d^3r, \tag{10}$$

where we have introduced the important parameter of non-ideality $u = vN\rho_b$ that describes the combined effect of the excluded volume interactions and finite polymer length (degree of polymerization). Eq.(10) expresses the excess grand potential through the reduced density η defined in Eq.(2). In order to obtain η one has to solve Edwards equation in Eq.(1) for the end density Q for given locations of the colloids in polymer system and then use the thus obtained Q in the definition of ρ given by Eq.(4). Solving Edwards equation in the presence of boundary conditions imposed by hard colloids is therefore a main stage of calculating the colloid immersion energy and depletion potential. This calculation will be described in the next two sections for the cases of one and two colloids immersed in the polymer system, respectively.

III. IMMERSION FREE ENERGY AND POLYMER DENSITY PROFILE AROUND A SINGLE NANO-PARTICLE

As has been mentioned in the previous section, the excess density η given by Eq.(4) is the key quantity that determines the excess grand potential caused by the presence of a particle. η can in turn be expressed through the end density Q, which can be obtained as the solution of the Edwards equation given by Eq.(1) in the presence of the boundary condition that describes the interaction of polymers with the particle surface. For the case of purely entropic interaction between the particle and polymers, this condition reduces[5] to the standard Dirichlet boundary condition that amounts to the condition that the end density Q must be zero at any point of contact of the polymers with the particle surface.

As a first step of calculating the end density, we will solve the Edwards equation given by Eq.(1) in the leading order in the particle radius R. By imposing the standard initial condition[5] $Q(\overrightarrow{r}, 0) = 1$ that describes the equiprobable distribution of the free polymer ends in the space not occupied by the particles, one can write the spherically symmetric solution of the Edwards equation in the form

$$Q = 1 - \frac{R\psi(x,n)}{r}, \tag{11}$$

where r is the radial variable in the reference frame with the origin placed in the center of the particle and $x = r - R$ is the distance from the particle surface. The first term in the right hand side (r.h.s.) of Eq.(11) gives the end density of the polymers in the bulk, and the second term corrects for the presence of the particle. The structure of this second term results from the property of the Laplacian ∇^2 in the spherical coordinate system that can be expressed as $\nabla^2(\psi(r)/r) = (\partial_r^2\psi(r))/r$.

In the absence of the excluded volume interactions ($v = 0$) the function ψ reduces to the well known[25,26] expression of the form

$$\psi(n,x) = \mathrm{erfc}(x/(2\sqrt{n})) \tag{12}$$

that is exact for any R.

Substituting the expression for the end density given by Eq.(11) and linearizing with respect to R results in the following equation for the function $\psi(n,x)$

$$(\partial_n - \partial_x^2)\psi = -2uf(x), \tag{13}$$

where the function f is given by the expression

$$f(x) = N^{-1}\int_0^N \psi(n,x)dn. \tag{14}$$

The Dirichlet boundary condition and the initial condition $Q(\overrightarrow{r},0) = 1$ imposed on the solution of the Edwards equation given by Eq.(1) causes the function ψ to satisfy the following boundary and initial conditions

$$\psi(n,0) = 1, \qquad \psi(0,x) = 1. \tag{15}$$

Note that according to Eq.(13), the expression for the polymer excess density

$$\eta = \left(1 - \frac{Rf(x)}{r}\right)^2 - 1, \tag{16}$$

that is exact up to the leading order in R is given solely in terms of the function f. In order to calculate η one therefore has to first solve simultaneous equations Eq.(13) and Eq.(14) for this function.

According to the above derivation, in the leading order in R the problem of calculating the end density Q reduces to the boundary value problem for the function ψ described by Eqs.(13-15). This problem can be further simplified by reducing the partial differential equation given by Eq.(13) to the integral equation with respect to the function f. For this purpose one must invert the differential operator $\partial_n - \partial_x^2$ in the left hand side of Eq.(13) in the presence of the boundary and initial conditions given by Eq.(15). The result reads

$$\psi = \operatorname{erfc}(\frac{x}{2\sqrt{n}}) - 2u \int\limits_0^n \int\limits_0^\infty dy f(y)(\kappa(x-y,t) - \kappa(x+y,t))dt, \tag{17}$$

where $\kappa(x,n) = (2\sqrt{\pi n})^{-1} \exp(-x^2/4n)$ is the Gaussian defined as the solution of the potential-free Edwards equation, Eq.(1), with the imposed initial condition of the form $\kappa(x,0) = \delta(x)$.

Substituting the expression for ψ given by Eq.(17) into the definition of the function f in Eq.(14), one arrives at a closed linear integral equation for f of the form

$$f(x) = N^{-1} \int\limits_0^N \operatorname{erfc}(2^{-1} n^{-1/2} x) dn - 2uR_G^{-1} \int\limits_0^\infty f(y) T(x,y) dy, \tag{18}$$

where the kernel $T(x,y) = T_0(x-y) - T_0(x+y)$ of the integral in the right hand side of Eq.(18) is expressed through the function T_0 that is given by the expression $T_0(x) = (2/3)\pi^{-1/2}(1+x^2)e^{-(4N)^{-1}x^2} - x\,(1+2x^2/3)\operatorname{erfc}(x)$.

The main difficulty in solving the integral equation given by Eq.(18) stems from the fact that the integration over x in the r.h.s. of this equation is performed over the half space $x > 0$. In order to avoid the associated mathematical difficulties that arise from this fact, we will first reduce the above integral to the equivalent form of the integral over the full space $-\infty < x < \infty$. In performing this reduction, we use the important symmetry property of the kernel $T(x,y)$ that can be expressed in the form $T(-x,y) = -T(x,y)$. By making use of this symmetry property, on can easily show that the function f satisfies the identity $f(-x) = 2 - f(x)$, which can be straightforwardly derived directly from Eq.(18). The above two symmetry identities results in the following identity $(1 - f(-x))T(-x,y) = (1 - f(x))T(x,y)$ that can be straightforwardly used in order to bring Eq.(18) to the form

$$f(x) = f_0(x) - 2uR_G^{-1} \int\limits_{-\infty}^\infty f(y) T_0(x-y) dy, \tag{19}$$

where the function f_0 can be most conveniently expressed in the form of the integral

$$f_0(x) = N^{-1} \int\limits_0^N \operatorname{erfc}\left(\frac{x}{2\sqrt{n}}\right)\left(1 + 2u\left(1 - \frac{n}{N}\right)\right) dn.$$

Note that analytically taking the integral in the above expression for f_0 leads to quite cumbersome expression that we do not show here for the sake of brevity.

In contrast to the integral equation given by Eq.(18), the obtained Eq.(19) can be straightforwardly solved by first reducing this to the linear equation for the Fourier transform $\widehat{f}$ of the function f, solving this equation for $\widehat{f}$ and transforming back to the coordinate x-space. The result of these tedious but straightforward manipulations reads

$$f(x) = 1 - \frac{2}{\pi} \int\limits_0^\infty \frac{\sin kx (D_1(k^2 R_G^2) + uD(k^2 R_G^2))}{k(1 + uD(k^2 R_G^2))} dk, \tag{20}$$

where $D(x) = 2(e^{-x} + x - 1)/x^2$ is the Debye function, and $D_1(x) = (1 - e^{-x})/x$.

Substituting the above expression for f into Eq.(20), one arrives at the following expression for the function ψ that describes the decay of the polymer end density with increasing the distance from the particle surface.

$$\psi = \frac{2}{\pi} \int\limits_0^\infty \frac{\sin kx (1 - e^{-k^2 n})}{k(1 + uD(k^2 R_G^2))} dk. \tag{21}$$

Note that setting $u = 0$ in the above expression allows for the analytic integration that takes ψ given by Eq.(21) to its ideal limit described by Eq.(12). For non zero values of the non-ideality parameter u the analytic integration is not possible, so one has to resort to numerical evaluation of ψ.

The end density Q and the excess polymer density η can be expressed through the calculated functions f and ψ using the equations given by Eq.(11) and Eq.(16), respectively. Integrating the excess density η over the volume available to polymers and substituting the result into Eq.(10) one arrives at a simple expression for the excess grand potential $\Delta\Omega$ on the form

$$\Delta\Omega \equiv W = 3\phi_P (\beta R_G)^{-1} R, \tag{22}$$

where $\phi_P = 4\pi\rho_P R_G^3/3$ is the polymer volume fraction.

According to the explanations given right above Eq.(9), the calculated excess grand potential $\Delta\Omega$ is to be identified with the energy cost W (minimal work) that is needed to bring the particle from the infinity to the initially homogeneous polymer system with the chain density $\rho_P \equiv 3(4\pi R_G^3)^{-1}\phi_P$. Interestingly, the colloid immersion energy W given by Eq.(22) does not depend on the excluded volume parameter v, so that the effect of the non-ideality of the polymer chains does not appear in the leading order in R. Moreover, expressing the immersion energy in the equivalent form $W = 2\pi\rho_b b^2 R/3$ shows that the only parameter describing the polymer system that enters W is the monomer number density ρ_b. Consequently, the immersion energy W does not depend on the polymerization degree N at fixed monomer bulk density ρ_b.

The colloid radius dependence of the immersion energy W given by Eq.(22) is in agreement with the simple result $W_O \sim R/R_G$ of a scaling analysis performed by Odijk in Ref. [14] for a small colloid interacting with Gaussian polymer coils. However, due to the approximate nature of this analysis, the above scaling result misses the important prefactor $3\phi_P \equiv 2\pi\rho_b b^2 R_G/3$ calculated in our exact approach. This exact prefactor takes into account the effect of monomer density ρ_b and removes the dependence of W on the polymerization degree N at fixed ρ_b. These exact dependencies of our result for W on ρ_b and N can be explained by observing that the immersion energy of a small colloid does not depend on the size of much larger polymer coils. Rather, it depends only on the local monomer density quantified by ρ_b, as has been concluded from the structure of Eq.(22) at the end of the previous paragraph.

It is instructive to compare the obtained analytic results with the available predictions of the Scheutjens-Fleer (SF) numerical approach described in Ref.[13]. This comparison is performed in Fig. 1 that shows the monomer number density profiles around spherical colloids for several values of the colloid radius R. As can be clearly seen from this Figure, the reduced number density $\rho/\rho_b \equiv 1 + \eta$ calculated by Eq.(16) with the function f given by Eq.(20) shows very good agreement with the numerical solution of the SF self-consistent equations performed at $N = 1000$, $\chi = 0.4$ for small colloid radii $R = b; 3b$. For these two cases, our theory shows slightly better agreement with the SF results than the interpolation expression derived in Ref.[13], of the form

$$\rho = \rho_b \left(\frac{x + R\tanh(x\delta)}{x + R} \right)^2, \qquad \delta = \sqrt{\left(\frac{\pi}{4R_G^2} + \frac{v\rho_b}{2} \right)}, \tag{23}$$

represented by the dotted curves in Fig.1. The observed good agreement between the analytic theory and SF numerical results slightly deteriorates for larger colloid radius $R = 10b$

thus empirically setting the limit of validity of the used in our theory small radius expansion to approximately $q \equiv R_G/R >\sim 1000^{0.59}/10 \approx 6$. It is interesting to note that the interpolation formula (FST) given by Eq.(23) shows just the opposite trend giving better predictions for larger colloid radii. The demonstrated overall good agreement between the results of the analytical and numerical theories speaks in favor of the adequateness of the developed approach to the described case of small colloids.

Finally, its worth noting that the obtained expression for W formally coincides with the well-known[19] asymptotically exact result for the colloid immersion energy of the form $W_{SC} = A_g N^{-1} \rho_b R^{3-1/\nu} R_G^{1/\nu}$ specialized to the case of the Gaussian polymers as described by the corresponding exponent $\nu = 1/2$. The universal constant A_g in the above expression that is obtained with help of the renormalization group theory evaluates to 18.4 for the excluded volume polymers, which makes the main difference with the present result that estimates the corresponding coefficient as $4\pi \equiv 12.57$. Interestingly, the above result for W_{SC} is also N-independent at fixed monomer number density ρ_b, which independently corroborates our main conclusion drawn from the above analysis of Eq.(22). We will get back to the analysis of the above expression for W_{SC} in Section V where we intend to compare our findings with previous theories.

IV. DEPLETION INTERACTION BETWEEN NANO-PARTICLES

In this section we apply the mathematical formalism developed in the previous section in order to investigate the depletion potential acting between two nano-particles with the effect of the excluded volume taken into account. We consider two spherical particles of the radius R with the centers separated by a distance H. The particles are immersed into a good polymer solution as described by the Flory parameter[6] $0 < \chi < 1/2$. We chose to work in the reference frame with the origin placed in the center of one of the particles hereafter referred to as the 'first' particle. For the sake of notational convenience, we introduce the position vectors $\overrightarrow{r_1}$ and $\overrightarrow{r_2}$ pointer away from the particle centers to the point described by the position vector $\overrightarrow{r}$. In the chosen reference frame, the vectors $\overrightarrow{r_1}$ and $\overrightarrow{r_2}$ are given by the expressions $\overrightarrow{r_1} = \overrightarrow{r}$ and $\overrightarrow{r_2} = \overrightarrow{r} - H\overrightarrow{k}$, respectively, $\overrightarrow{k}$ being the unit vector pointed away from the center of the first particle to the center of the second particle.

As compared to the considered case of one particle, the case of two particles involves more complicated geometry consideration, which brings added difficulty into the associated mathematical development. In order to deal with these complications, it is instructive to work with the Laplace transform of the end density $\widetilde{Q}(s) = \int_0^\infty Q(n)e^{-sn}dn$. Note that the solution of the Edwards equation for the end density Q given by Eq.(1) must be symmetric with respect to the plane equidistanced from the centers of the particles. This symmetry requirement causes that the Laplace transform of the end density takes the following form

$$\widetilde{Q} = s^{-1} - R\left(1 - \frac{Rs\widetilde{\psi}(x_1)}{H}\right)\left(\frac{\widetilde{\psi}(x_1)}{|\overrightarrow{r_1}|} + \frac{\widetilde{\psi}(x_2)}{|\overrightarrow{r_2}|}\right), \tag{24}$$

where $\widetilde{\psi}$ is the Laplace transform of the function $\psi(x)$ given by Eq.(21), $x_{1,2} = |\overrightarrow{r_{1,2}}| - R$ denote the distances from the corresponding particle surfaces to the point $\overrightarrow{r}$ and the function $\psi(x)$ satisfies the same equations, Eqs.(13)-(14), and the boundary and initial conditions, Eq.(15), as in the case of single particle. The form of the prefactor of the second term in the brackets in the r.h.s. of Eq.(24) ensures that the end density Q satisfies Dirichlet boundary condition on the surfaces of each particle.

Substituting the Laplace transform of the end density given by Eq.(24) into Eq.(4) for the number density ρ, integrating over the space variable according to the formula given by Eq.(10), and taking the inverse Laplace transform, one arrives at the following expression for the excess grand potential

$$\beta\Delta\Omega = 8\rho_P R^2 R_G^4 H^{-1} \int_0^\infty \frac{kD(k^2R_G^2)\sin kH}{1 + uD(k^2R_G^2)}dk \tag{25}$$

As has been explained right above Eq.(9), the excess grand potential given by Eq.(25) can be directly associated with the negative of the potential U of the depletion force acting between colloids. In reduced notations, this potential reads

$$U = -\frac{6\phi_P}{\pi h q^2} \int_0^\infty \frac{kD(k^2)\sin kh}{1 + uD(k^2)}dk, \tag{26}$$

where we have introduced reduced separation between particles $h = H/R_G$. Recall that for semi-dilute solvent conditions the non-ideality parameter $u = v\rho_b N$ is related to the Flory parameter χ that describes the interaction between polymers and solvent molecules by $u = N\rho_b b^3(1-2\chi)$. Note that for θ-conditions described by the equality $\chi = 1/2$, Eq.(26) reduces to the well-known[27–29] expression for the leading-order term of the depletion potential acting between nano-colloids in the presence of non-interacting polymers, of the form

$$U = 8\rho_b b^3 q^{-2}(6N)^{-1/2}\left(\pi^{1/2}e^{-h^2/4} - \pi(h^{-1} + 2^{-1}h)\mathrm{erfc}(2^{-1}h)\right). \tag{27}$$

According to the obtained expression for the depletion potential given by Eq.(26), the whole effect coming from the interaction among polymers is described by the term proportional to u in the denominator of the fraction under the integral in the r.h.s. of Eq.(26). Therefore, the excluded volume interactions always play in favor of reducing the absolute magnitude of the depletion potential. In order to verify this statement, in Fig. 2 we have plotted the depletion potential U given by Eq.(26) as a function of the reduced separation between colloids $(H - R_G)/R_G$ for the polymer volume fraction $\phi_P = 0.43$, colloid radius $R = 10b$ and several values of the Flory parameter χ. This Figure quantitatively corroborates the above conclusion that the stronger the screening of the polymer excluded volume interaction by the solvent, the weaker the effect of these interactions on the depletion potential. For the chosen values of ϕ_P and R, the largest difference between the values of the depletion potential U calculated in the boundary cases $\chi = 0$ and $\chi = 1/2$ reaches the order of magnitude of U evaluated at $\chi = 0$.

For the convenience of practical use, it is instructive to derive simplified version of the exact expression given by Eq.(27) that would make it possible to explicitly elucidate dependence of U on the involved parameters. The integral in the r.h.s. of Eq.(27) can be easily performed by resorting to the widely used[5] approximation for the Debye function of the form $D(x) \approx 2/(2+x)$. This results in the following simple approximation for the depletion potential

$$\beta U = -\frac{4\pi\rho_b b^2 R^2}{3H}\exp\left(-\frac{H}{\lambda}\right), \tag{28}$$

where the parameter $\lambda = R_G\xi_E(2\xi_E^2 + R_G^2)^{-\frac{1}{2}}$ that naturally arises in the above calculation can be interpreted as the correlation length that describes smooth crossover from the dilute polymer densities to high densities $\rho_P >> \rho_P^*$ significantly exceeding the overlap threshold density ρ_P^*. This crossover can be elucidated by analyzing the form of the correlation length λ that varies from its dilute limit $R_G/\sqrt{2}$ to the dense limit expressed by the N-independent Edwards correlation length[6] $\xi_E = b(2\sqrt{3v\rho_b})^{-1}$. We will return to the above discussion of the correlation length λ in the next Section, where we will compare different strategies of defining λ for arbitrary degrees of the chain overlap.

Another important conclusion can be drawn from the form of the expression given by Eq.(28). Similarly to Eq.(27), this expression is given by the product of the N-independent at-contact depletion potential $\beta U_c = -4\pi\rho_b b^2 R^2/(3H)$ and N (R_G) dependent exponential factor that describes the decay of the depletion potential with increasing the separation H. As will be shown in Section V this structure of the depletion potential is in agreement with the exact asymptotic form of the depletion potential at small separations and Monte Carlo simulations.

The expression for U given by Eq.(26) describes the desirable leading term of the depletion potential calculated in the protein limit $q >> 1$. As will be shown in the next section, this expression has quite tractable structure that can be qualitatively understood by scaling analysis.

V. COMPARISON WITH PREVIOUS WORK

Very useful insight into the behavior of the depletion potential as a function of the separation between colloids H is provided by the previous theories based on the field-theoretical small radius (”short distance”) expansion (FT)[19] and scaling analysis (SC).[18]. It is therefore instructive to compare our findings for the colloid immersion energy W and the depletion potential U obtained in the previous sections from the exact solution of the self-consistent Edwards equation with the above result. Recall the results for W and U obtained in Ref.[19] for these quantities

$$\beta W_{sc} = A_g \rho_P R^3 q^{\frac{1}{\nu}}, \qquad \beta U_{sc} = (\beta W \rho_P^{-1})^2 K(h), \tag{29}$$

where A_g is the universal (i.e. independent on the gyration radius) constant and ν is the Flory exponent that respectively evaluate to $A_g = 18.4$ and $\nu = 0.59$ for the excluded volume polymers; $K(h)$ is the normalized polymer density correlation function in the bulk polymer solution with chain number density $\rho_P = \rho_b/N$. It is important to note that R_G in Eq.(29) stands for the polymer gyration radius of the corresponding bulk polymer system, so that for the excluded volume polymers R_G scales[6] as $N^{3/5}$ rather than $N^{1/2}$. In the limit $H << R_G$, $K(h)$ is known[19,30] to assume the form

$$K_0(h) = \rho_P \sigma_g H^{-3} h^{\frac{1}{\nu}}, \tag{30}$$

where $\sigma_g = 0.069$ is the universal constant obtained by the renormalization group method.[31]

For further development it is important to emphasize that the above formulas for W_{SC} and U_{SC} are valid for arbitrary degrees of overlap among the polymer coils in semi-dilute polymer solution. This fact is thoroughly explained in Ref. [19], so here we restrict ourselves to proving that Eq.(29) reduces to the well known result[32] $\beta W_{dG} = a(R/\xi_\infty)^{3-1/\nu}$ of de Gennes for the immersion energy in the limit of strong overlap among polymer coils. This proof relies on the fact that ξ_∞ that represents the correlation length of strongly overlapped polymer coil system at high polymer volume fractions $\phi_P \equiv 4\pi\rho_P R_G^3/3 >> 1$, is polymerization degree independent even at small monomer densities $\rho_b \sim \rho_P R_G^{1/\nu}$ corresponding to the semidilute conditions. This fact determines the exponent $m = -\nu/(3\nu - 1)$ in the scaling relation[6] $\xi_\infty \sim R_G(4\pi\rho_P R_R^3/3)^m$ for the polymer correlation length ξ_∞ in the above strong overlap limit $\phi_P >> 1$. The above scaling relation can be conveniently expressed in the form

$$\xi_\infty^{1/\nu-3} = 4\pi\rho_P R_G^{1/\nu}/3 \sim \rho_b \tag{31}$$

that clearly shows that ξ_∞ is indeed polymerization degree independent. Substituting $\rho_P R_G^{1/\nu}$ derived from Eq.(31) into the r.h.s. of the first equation in Eq.(29) one recovers the above de Gennes result $\beta W_{dG} = a(R/\xi_\infty)^{3-1/\nu}$ with the coefficient $a = 3A_g/4\pi$. Making the same substitution into the r.h.s. of the second equation in Eq.(29) results in

$$K_0(H) = \frac{4\pi\rho_P^2\sigma_g}{3}\left(\frac{\xi_\infty}{H}\right)^{3-1/\nu}, \tag{32}$$

which, up to the prefactor proportional to ρ_P^2, coincides with the scaling result of Sear.[18] Note that the derived strong-overlap asymptotic forms of the immersion energy W_{dG} and correlation function given by Eq.(32) rely on the scaling relation for the correlation function ξ_∞ given by Eq.(31) that is only valid in the limit $\phi_P >> 1$. In the vicinity of the overlap threshold, where the correlation length is polymerization-degree dependent, one has to use universal relations given by Eq.(29) valid for arbitrary $\phi_P \geq 1$.

Note that despite its high accuracy in predicting at-contact depletion potential $U(H = 2R)$,[19] the above expression for U_{sc} in Eq.(29) fails[19] to give a correct prediction for the depletion potential at large separations $H >\sim R_G$. Since the exact correlation function of the semi-dilute polymer solution is generally unknown, in order to describe the case of separations of the order or larger than the gyration radius $H \sim R_G$ one has to resort to simplifying approximations. To describe the strong-overlap limit of the polymer correlation length at large separations $H >> \xi_\infty$, a simple mean-field expression for $K_E \sim \exp(H/\xi_E)/\xi_E$ derived by Edwards[5] is frequently used, where $\xi_E = b/\sqrt{12 v \rho_b}$ is the N-independent Edwards correlation length.[6] Note that ξ_E provides a mean-field counterpart of the scaling result of de Gennes given by Eq.(31), which explicitly takes into account quality of the solvent. The above expression for K_E, however, does not reduce to the exact asymptotic limit[18] given by Eq.(32) for small separations $H <\sim \xi_\infty$, thus failing to adequately describe the depletion potential at small separations $H << R_G$. Summarizing the above arguments, the existing FT and SC theories[18,19] are only capable of describing the above limiting cases of small ($H << R_G, \xi$) and large ($H >> \xi, R_G$) separations, respectively, which cannot be unified to adequately describe the intermediate case $H \sim R_G, \xi$. It is therefore instructive to derive an approximate expression built upon the exact self-consistent result for U, Eq.(26), which would provide a consistent description for arbitrary ratios H/R_G and give the correct asymptotic form K_0 at $H << R_G$.

Quite interestingly, the exact, up to the leading order in R, expressions for the colloid immersion energy W and the depletion potential U respectively given by Eqs.(22) and (26) can be formally presented in the same form as that of their FT counterparts given by Eq.(29). This direct analogy can be elucidated by recognizing the fact that the FT result for the immersion energy W_{sc} reduces to its exact counterpart W given by Eq.(22) upon substituting the Gaussian exponent $\nu = 1/2$ and the constant $A_g = 4\pi \sim 12.57$ into the expression for W_{sc} in Eq.(29). The same holds true for the FT result for the depletion potential U_{sc} written in the form given in Eq.(29), provided that the correlation function K in the r.h.s. of the second equality in Eq.(29) is taken in the form

$$K_{ex}(h) = \frac{\sigma_g \rho_P}{\pi H^3} \int\limits_0^\infty \frac{D(k^2 h^{-\frac{1}{\nu}}) k \sin k}{1 + u D(k^2 h^{-\frac{1}{\nu}})} dk. \tag{33}$$

It is straightforward to check that substituting the Gaussian exponent $\nu = 1/2$ and the new value of the universal constant $\sigma_g = (2\pi)^{-1} \sim 0.16$ into the expression for K_{ex} given by Eq.(33) takes the above expression for U_{sc} back to the form of its exact counterpart U. Moreover, in the limit of small separations $H << R_G$, correlation function K_{ex} given by Eq.(33) reduces to the desirable exact asymptotic expression given by Eq.(30).

As a conclusive step of the above comparative analysis of the results of the FT and the present self-consistent field theory, we shall propose a "hybrid" expression for the depletion potential. This expression reduces to both the self-consistent result given by Eq.(26) and the above described FT results upon choosing an appropriate Flory exponent ν and the complex universal constant $A_g^2 \sigma_g$. Substituting correlation function K_{ex} given by Eq.(33) into the expression for U_{sc} given by the second equality in Eq.(29) results in the above "hybrid" expression for the depletion potential of the form

$$\beta U = -\frac{4A_g^2\sigma_g\rho_P R^6}{\pi H^3}\left(\frac{R_G}{R}\right)^{\frac{2}{\nu}}\int\limits_0^\infty \frac{D(k^2h^{-\frac{1}{\nu}})k\sin k}{1+uD(k^2h^{-\frac{1}{\nu}})}dk. \tag{34}$$

The above expression for U, Eq.(34), combines the advantages of the present self-consistent approach that is capable of describing the separation dependence of U for arbitrary relations between H and R_G, and findings of FT that explicitly take into account the semi-dilute nature of the polymer solution at $H << R_G$. Recall that this expression is constructed in such a way that substituting the values $\nu = 1/2$ and $A_g^2\sigma_g = 8\pi$ into Eq.(35) gives the expression for the depletion potential derived from the exact solution of the Edwards equation in Section IV. On the other hand, taking the limit $H << R_G$ takes U expressed by Eq.(34) to the form given in Eq.(29) with the asymptotically exact correlation function K_0 given by Eq.(30). Interestingly, the exact value of the coefficient $A_g^2\sigma_g = 18.4^2\times 0.069 = 23.36$ known[19] from the renormalization group theory is pretty close to its self-consistent theory counterpart $A_g^2\sigma_g = 8\pi = 25.13$, which adds to the accuracy of Eq.(34) in bridging between the above FT and SCMFT results.

In order to gain better understanding of the separation dependence of the above hybrid depletion potential, one has to investigate the integral term in the r.h.s. of Eq.(34). In order to simplify the analysis of this approximate expression, here we employ rather drastic but widely used approximation[5] for the Debye function of the form $D(x) = 2/(2+x)$. Using this approximation makes it possible to perform the integration in the r.h.s. of Eq.(34) analytically, leading to a simple expression for U of the form

$$\beta U = -\frac{3A_g^2\sigma_g\phi_P}{4\pi}\left(\frac{R^2}{HR_G}\right)^{3-\frac{1}{\nu}}\exp\left(-\left(\frac{H}{\lambda}\right)^{\frac{1}{2\nu}}\right), \tag{35}$$

where we have introduced the characteristic length of the depletion interaction $\lambda \equiv R_G(2(1+v\rho_b N))^{-\nu}$. Note that according to the above definition, the deviation of λ from the dilute-limit correlation length[5] $\lambda_G \equiv R_G/2$ is totally defined by the value of the non-ideality parameter $u \equiv Nv\rho_b$. If the value of this parameter is large enough, λ reduces to the well known[5] N-independent expression for the strong-overlap limit of the correlation length $\xi_E = b(2\sqrt{3v\rho_b})^{-1}$ mentioned in the above.

It is instructive to derive the strong-overlap limit of the above expression for the depletion potential given by Eq.(35). Substituting the appropriate correlation length $\lambda = \xi_\infty$ into this expression and using the relation between R_G and ξ_∞ given by Eq.(31), one arrives at the following expression for the depletion potential describing the limit $\phi_P >> 1$

$$\beta U_\infty = -\frac{3A_g^2\sigma_g}{4\pi}\left(\frac{R^2}{H\xi}\right)^{\frac{4}{3}}\exp\left(-\left(\frac{H}{\xi}\right)^{\frac{5}{6}}\right). \tag{36}$$

For the sake of generality, in Eq.(36) we have omitted the subscript ∞ that describes only specific scaling approximation for the strong-overlap limit ξ of the correlation length. ξ in Eq.(36) has a status of the N-independent strong-overlap limit of the generally unknown true correlation length of the semi-dilute polymer solution, which is not restricted to its specific scaling form given by Eq.(31). Note that the above expression for U_∞ depends on the polymer density only through the correlation length ξ, as is should be expected in the limit of strong overlap of the chain coils, where all properties are solely determined by this correlation length.[6]

Note that similarly to the FT result given by Eq.(29), the expression for the depletion potential given by Eq.(35) has a structure of a product of the squared reduced immersion energy $\beta W\rho_P^{-1} = A_g R^{3-1/\nu}R_G^{1/\nu}$ and the negative of the correlation function K. The correlation function K that enters Eq.(35) therefore has the form

$$K = \sigma_g\rho_P H^{-3}(H/R_G)^{\frac{1}{\nu}}\exp\left(-H/\lambda\right)^{\frac{1}{2\nu}}. \tag{37}$$

It is straightforward to check that K given by Eq.(37) reduces to the above mentioned known mean-field expression[5] for Gaussian polymers ($\nu = 1/2$) with the mean-field correlation length ξ replaced with its finite polymer length counterpart $\lambda = R_G(2(1+\upsilon\rho_b N))^{-\nu}$. On the other hand, introducing the Flory exponent $\nu = 3/5$ into the above expression for K ensures the correct asymptotic form of the correlation function at small separations $H << R_G$ given by Eq.(30) for the semi-dilute regime. It is important to note that Eq.(35) shows slightly slower exponential decay ($\sim \exp{(H/\lambda)^{5/6}}$) of the depletion potential U with increasing the separation H than the scaling result for U derived in Ref.[18] by making use of the Edwards mean field correlation function described right below Eq.(30).

Alternatively to using the above specific definition, the characteristic length λ can be treated as an adjustable parameter that can be derived from plausible arguments. One feasible way to evaluate λ is to apply the compressibility sum rule[31] for the correlation function K written in the form

$$\int K(H)d^3H = \beta^{-1}\rho_P\left(\frac{\partial\Pi}{\partial\rho_P}\right)^{-1}, \tag{38}$$

where Π is the osmotic pressure of the bulk polymer system. Substituting the correlation function K given by Eq.(37) with $\sigma_g = (2\pi)^{-1}$ into Eq.(38) results in simple explicit expression for λ in terms of Π, of the form

$$\lambda = R_G \left(4\nu\beta \frac{\partial \Pi}{\partial \rho_P} \right)^{-\nu} . \tag{39}$$

Note that using the Gaussian exponent $\nu = 1/2$ and mean field expression[24] $\beta\Pi = \rho_P + \upsilon\rho_b^2/2$ for the osmotic pressure, takes Eq.(39) back to the form $\lambda = (2(1+u))^{-1/2}$ obtained in the above.

A clear advantage of the expression given by Eq.(39) is in the possibility to obtain more precise evaluation for λ by using more advanced expression for the polymer osmotic pressure in terms of the polymer density. One such highly accurate expression is given[31] by the renormalization group theory. A few estimates for λ for several values of the polymer volume fraction based on this expression are shown in Table 1. In what follows, we will compare these estimates against the corresponding values of λ obtained from the fit of the calculated depletion potential to the results of the previous Monte Carlo (MC) simulations.

An important remark as to the validity of Eq.(35) is in order here. Specifically, care must be exercised when using this expression for evaluating the depletion potential U at small separations $H >\sim 2R$. This is because the exact self-consistent counterpart of this expression for U is derived by making use of the expansion in series of polymer-colloid size ratio q^{-1}, which implies that R is assumed to be the smallest length in the system. This reservation as to the validity of the used small colloid radius expansion in the limit of small separations $H >\sim 2R$ that equally refers to the above FT and SC results, is confirmed by the comparison of the present theoretical findings with the results of MC simulations obtained in Ref.[16]. Moreover, a detailed analysis of this simulations shows that the depletion potential U experiences exponential decay with decreasing the separation in the whole range of the studied H, rather than power law decay $\sim H^{-2\nu}$ predicted by the SCMFT, FT and SC theories. This exponential decay of U observed in MC simulations is not in agreement with the obtained approximate expression given by Eq.(35), FT result given by Eqs.(29,30) and scaling estimate[18] $U \sim (R/\xi)^{8/3}((R/\xi)^{4/3} - 1)^{-2}\xi H^{-1} \exp(-H/\xi)$ evaluated at small and intermediate separations $H <\sim R_G$.

Interestingly, however, that Eq.(35) excellently fits to the above MC simulation data if one replaces the prefactor of the exponential in the r.h.s. of Eq.(35) with its contact value calculated at $H = 2R$. This replacement takes Eq.(35) to the form

$$\beta U_A = -\kappa\phi_P \exp\left(-H/\lambda\right)^{\frac{1}{2\nu}}, \qquad \kappa = 3(4\pi)^{-1} A_g^2 \sigma_g (2q)^{\frac{1}{\nu}-3}. \tag{40}$$

Given the parameters used in the simulations in Ref.[16], the polymer-colloid size ratio evaluates to $q \equiv R_G/R = (2000)^{0.59}/10 = 8.9$, which results in the coefficient κ taking the value of 0.11. Substituting this exact value of κ into the first equality in Eq.(40) and using λ as an adjustable parameter we have fitted the above results of the Monte Carlo simulations for several values of the polymer volume fraction ϕ_P shown in Table 1. The results of this fitting procedure are shown in Fig. 3. As is clearly seen from this Figure, the exponential form of the expression for U given by Eq.(40) with λ given in the second column of Table 1 for respective values of ϕ_P excellently fits to the simulation results. Given the approximate nature of the expression for U_A in Eq.(40), it is instructive to check how the adjusted values of λ compare against those derived from the compressibility sum rule given by Eq.(39). Recall that in calculating those latter values we use the known[31] highly accurate renormalization group theory expression for the osmotic pressure Π. The results of this comparison are shown in Table 1. According to this Table, the predictions of Eq.(39) slightly underestimate the values of λ extracted from the fit of the depletion potential U_A given by Eq.(40) to the simulations for the polymer volume fraction $\phi_P = 0.43$ that corresponds to the case of dilute polymer solution. For larger values of $\phi_P = 1.29, 2.58, 5.16$ that describe the semi-dilute regime, the agreement between the calculated and fitted values of λ is very good. This overall good agreement speaks in favor of that Eq.(40) with plausible values of λ given in Table 1, provides adequate description of the MC results in the whole range of separations H and polymer densities ρ_P. Moreover, Eq.(40) give very accurate estimate for the at-contact ($H = 2R$) value of U that excellently agrees with the simulation results without using any adjustable parameters.

Despite the fact that the expression for the depletion potential U_A given by Eq.(40) shows very good agreement with the results of the MC simulations, this expression cannot be credited for being systematically derived from the results of our rigorous self-consistent approach. This expression therefore has a status of the interpolation formula that circumstantially provides very good description of the simulation results. The expression for the depletion potential U_A given by Eq.(40) builds upon approximate formula for U given by Eq.(35) with refined prefactor of the exponential, so that this prefactor gives correct limit

$H >\sim 2R$. We therefore attribute the remarkably good agreement between predictions of Eq.(40) and MC simulations to the fact that the former expression for U_A properly describes the above small separation limit, that appears to be not properly handled by either SCMFT, FT theories or scaling arguments.

VI. RESULTS AND DISCUSSION

In the present work we have calculated the polymer density and free energy excesses caused by the presence of nano-colloids in the excluded volume polymer system and the depletion interaction acting between nano-colloids in this system, by making use of the Edwards self consistent mean field theory.

One clear advantage of the present approach lies in the fact that, in contrast to the field-theoretic method and scaling arguments, this approach makes it possible to analytically calculate the coordinate dependent polymer density in the presence of colloids. This advantage is achieved at a cost of resorting to the small colloid radius perturbative solution of the Edwards equation, Eq.(1), owing to the complexity of this equation associated with the presence of the non-linear self-consistent term describing the excluded volume interactions.

Using the above described advantage of our approach, we have calculated the density profile of polymers in the vicinity of a single colloid and compared our findings, Eqs.(16,20), against the results of Scheutjens-Fleer numerical procedure.[13] This comparison is illustrated in Fig. 1 that shows good agreement between the theory and SF results for small colloid radii $R = b, 3b$, and satisfactory agreement for larger colloid radius $R = 10b$. This result empirically sets limitations of the validity of our approach to $q = R_G/R >\sim 6$, which naturally stem from the nature of the developed theory that relies on the small colloid radius expansion.

By making use of the above small colloid radius expansion of the excess polymer density in the presence of colloids, we have calculated the leading terms of the colloid immersion energy W and the depletion potential U given by Eq.(22) and Eq.(26), respectively. Based on these results, we have shown that the role of the excluded volume interactions in the formation of the depletion layers near colloids can be quantified by a single complex parameter $u = v\rho_b N$. For a typical polymer system this parameter can be of order of unity even at large polymerization degrees N, which put in question the adequateness of the popular approximation scheme known as "ground state theory"[6] to describing the depletion interactions. Interestingly, similarly to what is observed in one-chain polymer system,[14] the above excluded volume parameter u cancels out in the final expression for the colloid immersion energy W in the leading order in q^{-1}, thus eliminating the excluded volume effect on W. W is shown to be proportional to the monomer bulk density, the only relevant parameter describing polymer system that affects the colloid immersion energy in the limit $q >> 1$.

Similarly to its ideal counterpart given by Eq.(27), the calculated leading term of the depletion potential U given by Eq.(26) is shown to be proportional to the squared colloid radius. In contrast to the linear dependence of U on the polymer volume fraction ϕ_P observed for ideal polymers (cf. Eq.(27)), the depletion potential mediated by the excluded volume polymers shows intricate non-linear dependence on ϕ_P. Since this dependence cannot be expressed in simple analytic form, we have investigated the depletion potential given by Eq.(26) graphically, by plotting this potential for several values of the Flory-Huggins parameter χ that quantifies the effect of solvent screening on the polymer excluded volume interactions. According to this plot shown in Fig. 2, the effect of the excluded volume leads to the suppression of the depletion force acting between colloids. Since the screening effect of the solvent diminishes the polymer excluded volume interactions, increasing χ results in increasing the absolute magnitude of U at fixed polymer volume fraction ϕ_P and colloid radius R.

In order to improve the applicability of the developed approach to realistic polymer systems, we proposed a "hybrid" expression for the depletion potential U expressed by Eq.(35). This "hybrid" expression builds upon rescaling the parametric dependence of our exact result, Eq.(26), on the polymer-colloid size ratio q and the reduced separation $h = H/R_G$ according to the rules $q \to q^{2\nu}$, $h \to h^{2\nu}$. Setting the introduced exponent ν to its Gaussian value $\nu = 0.5$ takes the above "hybrid" expression back to our exact self-consistent field theory result given by Eq.(26). Using the Flory exponent $\nu = 0.59$ in Eq.(35) leads to U having the well known correct small-separation asymptotic form given in Eq.(34) for the semi-dilute good solvent conditions. In the proposed "hybrid" form, our expression for the depletion potential agrees with the results of the small radius field-theoretic expansion,[19] scaling arguments,[18] and properly describes the at-contact depletion potential obtained by MC simulation[16] without using any adjustable parameters.

Despite the above good agreement with previous work, the derived "hybrid" expression shows more rapid decay of the depletion potential with increasing the separation H between colloids than that observed in MC simulations in Ref.[16]. Excellent agreement with these simulation results can be achieved by the slight modification of the expression for U given by Eq.(35) that amounts to replacing the prefactor in this expression by its at-contact value taken at $H = 2R$. This modification results in the expression for the depletion potential U_A given by Eq.(40) that has a status of the interpolation formula that bridges the asymptotic limits of small $H << R_G$ and large $H >> R_G$ separations between colloids. The fact that the above interpolation formula gives more adequate description of the above MC simulations than the present self-consistent, field-theoretic and scaling results can be attributed to that this formula better describes the small separation limit $H \sim 2R$. In this limit, MC simulations show exponential decay $U \sim \exp\left(-h^{2\nu}\right)$ rather than power law decay $U \sim H^{-2\nu}$ predicted by all the above theories at $H <\sim R_G$.

We have to note that the above comparison between the theory and simulations should not be considered conclusive, since this is based on analyzing the only available instance of the MC simulations performed in the protein limit. Only more extensive simulations of the depletion interaction in this limit can reveal if the above excellent agreement with the interpolation formula given by Eq.(40) is circumstantial or not. In all cases, the derived hybrid expression for the depletion potential, Eq.(35), appears to provide a solid basis for investigating the depletion interactions in different settings. This expression can also serve for constructing different approximations or interpolation formulas for practical use, similar to the expression for U_A given by Eq.(40).

VII. ACKNOWLEDGMENTS

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Captions to figures and tables

Fig.1: Comparison of the calculated polymer density profile near a single colloid against the predictions of the Scheutjens-Fleer numerical approach (Ref.[13]) and the interpolation formula obtained in Ref.[13] for several values of the colloid radius. Polymer volume fraction and Flory-Huggins parameter are set to $\phi_P = 0.43$ and $\chi = 0.4$, respectively.

Fig.2: Polymer depletion potential as a function of the reduced separation between colloids for several values of the Flory-Hugging parameter. Polymer volume fraction and the colloid radius are set to $\phi_P = 0.43$ and $R = 10b$, respectively.

Fig.3: Comparison of the Monte Carlo simulations of the depletion potential with the predictions of Eq.(40) for several values of the polymer volume fraction and the colloid radius $R = 10b$.

Table 1: Comparison of the values of the characteristic length λ extracted from fitting the Monte Carlo results by Eq.(40) against predictions of Eq.(39)

Figures

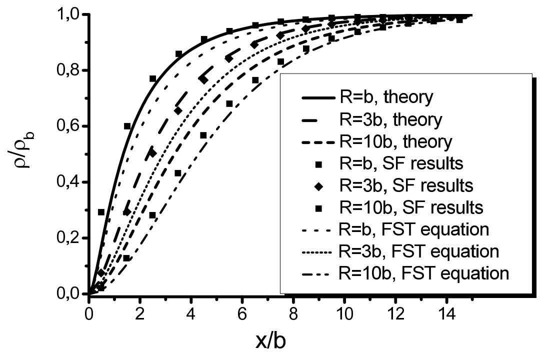

FIG. 1:

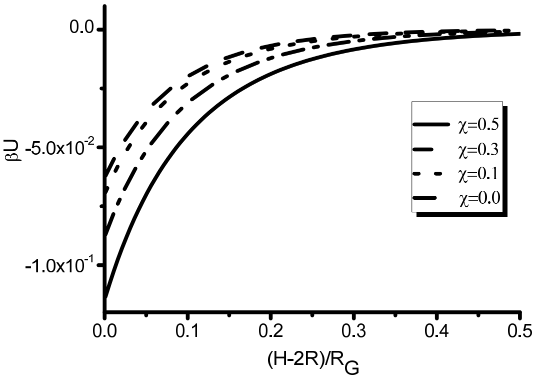

FIG. 2:

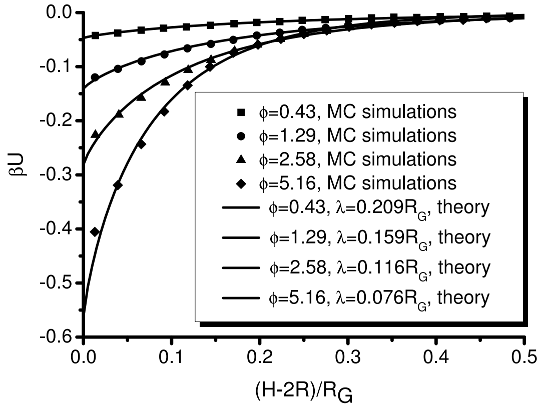

FIG. 3:

Tables

ϕ_P	λ/R_G from fit	λ/R_G from Eq.(39)
0.43	0.209	0.344
1.29	0.159	0.189
2.58	0.116	0.118
5.16	0.076	0.070