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Analytic theory of the interactions between nanocolloids mediated by reversibly adsorbed polymers

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We develop an analytic theory of the polymer mediated interactions between nanocolloids reversibly adsorbing the excluded volume polymers. This theory describes the limit of the weak adsorption where the correlation length ξ of the polymer system is much smaller than the characteristic adsorption length (colloid absorbance) α. By making use of the developed theory, we calculate the colloid immersion energy and the potential of the polymer mediated interactions as functions of the colloid radius R, the absorbance α, and the polymer volume fraction ϕ_P.

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Polymer mediated (PM) forces acting between colloids are known [1,2] to arise from the unbalanced osmotic pressure caused by the polymer density perturbations that stem from the interactions between the polymers and the colloid surfaces. These polymer-colloid interactions, therefore, play a decisive role in determining the magnitude and even the sign of the PM forces. The microscopic interactions between the polymers and the colloid surfaces can be subdivided into two main categories: repulsive entropic depletion interactions and attractive adsorption interactions. In addition, depending on the magnitude of the adsorption barrier, the polymer adsorption can be distinguished between reversible and irreversible cases, thus imposing different conditions of thermodynamic equilibrium on the colloid-polymer system. In the case of so-called reversible adsorption, the chemical potential of polymers in the depletion (enhancement) layers surrounding the colloids is equal to that of the polymers in the bulk, thus allowing a free exchange of polymers between these space domains. In the case of irreversible adsorption, polymers are kept near the adsorbing colloids by strong adsorption forces, so that the above thermodynamic equilibrium is broken. The complicated balance between the above depletion entropic and adsorption forces, as determined by the thermodynamical conditions corresponding to the adsorption case, totally determines the structure of the polymer density near colloids and the associated polymer mediated force.

In this paper, we concentrate on the study of PM interactions for the specific case of nanoscopic colloidal particles mediated by reversibly adsorbed polymers. Here we refer to the so-called protein limit [3], where the size of the particles is much less than the polymer gyration radius, so that the polymers cannot be modeled as individual soft particles interacting with colloids. The described limit of PM interactions is immediately relevant to many biologically and technologically important phenomena such as red blood cell adhesion [4], DNA mediated depletion interactions [5], and size-exclusion polymer chromatography [6]. In the diverse variety of different polymer-colloid systems exemplified by the above cases, PM interactions play the role of the driving force that causes phase separations, colloid flocculation, association, and clustering that can be effectively used in tailoring the properties of these systems in a desirable way. Understanding the underlying microscopic mechanisms of the PM forces depending on the type of adsorption interactions between the polymers and colloid surfaces thus presents a key element in predicting the macroscopic behavior of these systems in different experimental settings.

We start our analysis of the PM interaction between two colloids mediated by reversibly adsorbing polymers by giving a mathematical formulation of the self-consistent mean field theory (SCMFT) used in our study. We consider two colloids of the radius R immersed in a bath of the reversibly adsorbing polymers of the polymerization degree N. The geometry of the problem is sketched in Fig. 1. Recall that in the considered regime of the reversible adsorption, no permanent links between the polymers and the colloid surfaces are formed, so the polymers are assumed to be in thermodynamic equilibrium with the bulk polymer system far away from the colloid surfaces. SCMFT is used for determining the nonuniform density structure in the described polymer system by using the mean field potential V describing the excluded-volume interactions among polymers, of the form

$$\begin{aligned} V &= \beta^{-1} v N \rho_P \eta, \\ \eta &= N^{-1} \int_0^N Q(\vec{r},n) Q(\vec{r},N-n) dn - 1, \end{aligned} \tag{1}$$

with η obtainable from the end density Q that obeys the Edwards equation [7] of the form

$$\partial_n Q(\vec{r},n) = \nabla^2_{\vec{r}} Q(\vec{r},n) - \beta V(\rho) Q(\vec{r},n). \tag{2}$$

Here, $Q(\vec{r},n)$ is the coordinate $\vec{r}$-dependent end density that describes the probability to find one end of the polymer of the polymerization degree n in the point $\vec{r}$ provided that its other end is placed elsewhere in the free space Θ not occupied by hard bodies. ρ_P is the bulk polymer number density defined as a density of the polymer system far away from any hard bodies immersed in this system, and $\rho_b \equiv N\rho_P$ is the corresponding bulk monomer number density; $\beta = (kT)^{-1}$ is the reciprocal temperature, with k and T being the Boltzmann constant and the absolute temperature, respectively; v is the excluded volume parameter [8] that quantifies the polymer excluded volume interactions. Note that the excluded volume parameter v that enters the right-hand side (r.h.s.) of Eq. (2) is defined by $v = b^3(1 - 2\chi)$ for the incompressible semidilute

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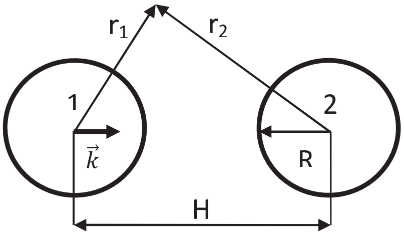

FIG. 1. Sketch of the geometry of the considered problem.

[8] polymer solution considered in the present work, with the interaction between polymers and solvent described by the Flory parameter χ. 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, while $\chi = 1/2$ describes the case of a θ solvent [8]. 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 the polymer reads $R_G = \sqrt{N}$, N being the polymerization degree.

Note that the Edwards equation given by Eq. (2) is the second-order partial differential equation that must be supplemented by appropriate boundary conditions (BCs) that describe the adsorption interactions between the polymers and colloid surfaces. In the presence of these attractive interactions, one can no longer use the standard Dirichlet BC $Q(\vec{r},0) = 0$ that describes only purely entropic repulsion between the colloid surfaces and the polymers. Instead, we impose a BC of the form

$$\partial_{\vec{m}}[|\vec{r} + x\vec{m}|Q(\vec{r} + x\vec{m},n)] + \alpha^{-1}|\vec{r} + x\vec{m}| \times Q(\vec{r} + x\vec{m},n)|_{x=L} = 0 \tag{3}$$

on each colloid surface, where $\vec{m}$ is the positive unit normal to the colloid surface, $\partial_{\vec{m}} \equiv \vec{m}\nabla$ is the directional derivative, $\vec{r}$ is the position vector of the colloid center, and x is the distance to the colloid surface. The coefficient α that has the dimension of length quantifies [9] the strength of the adsorption interactions between the polymers and the colloid surfaces. L is the range of the adsorption potential that is assumed to be of the order of the monomer unit length, which justifies including L in the effective particle radius $R + L$ in the considered diffusion limit $L \sim b \ll R$.

Following the pioneering work of de Gennes in Ref. [10], BCs similar to that expressed by Eq. (3) are often used to describe the infinitesimally narrow adsorption potential that can be represented by a δ function in the simplest case of the planar adsorbing surface [8]. For the case of curved adsorbing surfaces, the corresponding BC turns out [11] to be dependent on the curvature radii of this surface, rendering the choice of BC appropriate to the specific geometry highly nontrivial. The BC given by Eq. (3) specific to the considered spherical geometry has been derived in Ref. [12] upon analyzing the solution of the Edwards equation given by Eq. (2) in the presence of an infinitesimally narrow finite range potential. Note that the use of the actual short-range adsorption potential in the above derivation of the BC is unavoidable since this potential proves to be nonrepresentable by a δ function, in contrast to its planar counterpart. According to the implicit equation for α derived in Ref. [12], near the adsorption threshold $u \equiv L\sqrt{\beta A} \sim \pi/2$ describing the case of weak adsorption, the expression for α simplifies to $\alpha = 4L/[\pi(2u - \pi)]$, A being the strength of the adsorption potential. Alternatively, the characteristic length α can be related [12] to the absorbance defined as the characteristic width of the density enhancement layer formed around the adsorbing colloid.

Note that the use of the boundary condition given by Eq. (3) implies that the adsorption ability of the colloid surface is sufficient to overcome the entropic barrier imposed by entropic repulsion of polymers, as indicated by the appearance of the surface bound states [12].

Solving the Edwards equation given by Eq. (2) supplemented by the boundary conditions, Eq. (3), for Q and substituting the result into the second equality in Eq. (1), one finds the excess polymer number density η. η in turn is to be related to the immersion energy W of a single colloid and the potential U of PM forces acting between two colloids. W and U can be identified [12,13] with the excess grand potential,

$$\Delta\Omega = -\rho_b(\beta N)^{-1}\int_{\Theta}[(1 + vN\rho_b)\eta(\vec{r}) + vN\rho_b\eta(\vec{r})^2/2]d^3r, \tag{4}$$

caused by the presence of, respectively, one and two colloids in the polymer system. Note that the above identification, $W = \Delta\Omega$ ($U = \Delta\Omega$), relies on the fact that $\Delta\Omega$ describes the minimal work needed to reversibly bring one (two) colloids from infinity to its actual position in the polymer system while maintaining thermodynamic equilibrium with the bulk polymers as described by uniform density ρ_P.

To avoid essential mathematical difficulties associated with solving the nonlinear differential equation (2), different approximation schemes are often used, which rely on the nature of the considered limiting cases. For the sake of simplicity, in the present work we consider the asymptotic limit $N \gg 1$ only, which describes the most practically important case in which the gyration radius of polymers R_G is larger than all the relevant length scales. Mathematically, taking this limit can be formalized by replacing the n-dependent end density $Q(\vec{r},n)$ by its n-independent asymptotic form $q(\vec{r})$. The resulting equation reads

$$\nabla^2 q = 2\xi^{-2}q(q^2 - 1), \tag{5}$$

where $\xi \equiv (v\rho_b/2)^{-1/2}$ is the correlation length [7]. Note that the asymptotic end density q satisfies the same boundary condition, Eq. (3), which has been initially derived for the true end density Q. Despite the above simplification, the complicated geometry associated with the boundary conditions specified on the surfaces of two spherical colloids makes the analytic solution of Eq. (5) prohibitively complicated. However, in some limiting cases, this equation can be reduced to the linear differential equation that can be solved analytically even in the described complicated geometry. In this paper, we concentrate on one such limiting case, known as the "weak adsorption" limit [8], where the colloidal particles are assumed to cause only slight density perturbations in the polymer system. In terms of the used notations, this limit can be formulated as $\alpha^{-1}\xi \ll 1$, which simply states that the adsorption strength quantified through the inverse adsorption length α^{-1} is much smaller than the screening effect of the excluded volume quantified through the Edwards length ξ. Taking this limit is equivalent to assuming [8] that q deviates only slightly from its bulk value 1, which immediately reduces Eq. (5) to its linearized form,

$$\nabla^2 q = 4\xi^{-2}(q-1), \tag{6}$$

which represents the spatial behavior of the above deviation correction $q-1$ up to the leading order in $\alpha^{-1}\xi$. In contrast to the nonlinear equation given by Eq. (5), its linear counterpart in Eq. (6) can be solved analytically in the considered limit of weak adsorption. For the case of a single colloid, the exact solution of the *linearized* equation given by Eq. (6) reads

$$\begin{aligned} q_1(\vec{r}) &= 1 + R(q_s-1)r^{-1}e^{-2(r-R)/\xi}, \\ q_s &= \left(1+\frac{\xi}{2R}\right)\left(1-\frac{\xi}{2\alpha}\right)^{-1}, \end{aligned} \tag{7}$$

where $r = |\vec{r}|$ is the distance from the center of the colloid and q_s is the value of the end density on the surface of the colloid.

It is important to note that the above solution $q_1(\vec{r})$ of the linearized equation given by Eq. (6) is valid for any radius R of the colloid. Still, care must be exercised in using this formally exact solution, since it has restricted validity with respect to the relation between the parameters ξ and α. This restriction can be mathematically expressed as $\alpha \in (-\infty,0] \cup (\xi/2,\infty)$, which enforces the physical requirement that the surface end density q_s must be positive for any α and ξ. Note that the above restriction does not impose any additional constraints on the validity of Eq. (7) in the cases of physical interest considered in the present work. Specifically, the above condition evidently covers the limit of weak adsorption $\xi \ll \alpha$ where, up to the leading order in ξ, the surface end density reduces to $q_s = 1 + \xi(R^{-1}+\alpha^{-1})/2$. Note that in the weak adsorption limit $\xi \ll \alpha$, the deviation correction expressed by the second term on the r.h.s. of Eq. (7) is positive at any R, α, and ξ so that the adsorption of polymers always leads to the enhancement of the polymer density in the vicinity of the colloid. In the limiting case of nonadsorbing polymers described by the limit $\alpha \to 0$, q_s tends to 0 as $\alpha \to 0$, so that q_1 in Eq. (7) reduces to the solution $q_1 = 1 - Rr^{-1}e^{-2(r-R)/\xi}$ of the linearized equation in Eq. (6) obtained in Ref. [13]. In addition, taking the limit $R \to \infty$ of the r.h.s. of Eq. (7) gives the end density $q_1^{\infty}(\vec{r}) = 1 + (\alpha^{-1}\xi/2)\exp[-2(r-R)/\xi]$ of the polymers in the presence of the planar adsorbing surface that can be directly obtained as a leading term of the expansion of the exact solution [8,14] of the planar version of Eq. (7) in ξ/α.

In the case of two colloids with the centers separated by the distance H, it is instructive to look for the solution of Eq. (6) in the form of the linear combination of the exponential terms similar to the last term on the r.h.s. of Eq. (7) that satisfies the boundary condition given by Eq. (3). The corresponding solution reads

$$\begin{aligned} q_2(\vec{r}) &= 1 + R(q_s-1)\left(1 - RH^{-1}(q_s-1)e^{-2H/\xi}\right)^{-1} \\ &\quad\times\left(\frac{e^{-2(r_1-R)/\xi}}{r_1} + \frac{e^{-2(r_2-R)/\xi}}{r_2}\right), \end{aligned} \tag{8}$$

where q_s is defined in Eq. (7), and r_1 and r_2 are the distances from the point $\vec{r}$ to the centers of the first and second colloids, respectively. Similarly to its one-colloid counterpart given by Eq. (7), the end density given by Eq. (8) correctly reproduces the corresponding expression describing the case of nonadsorbing polymers considered in Ref. [13], which can be formally obtained from Eq. (8) by taking the limit $\alpha, q_s \to 0$. However, due to the more complicated geometry of the two-colloid problem, Eq. (8) has more restricted validity with respect to the colloid radius R in comparison with the above one-colloid counterpart given by Eq. (7). Formally speaking, the above expression for q_2 satisfies the boundary condition, Eq. (3), only in the asymptotic limit of the "protein" colloids $R \ll H$. Fortunately, this formal restriction can be avoided in the semianalytical calculation of the PM potential based on Eq. (8) discussed in what follows.

To derive the immersion energy W and the potential of the PM interactions U, we substitute the obtained expressions for the end density given by Eqs. (7) and (8) into the expression for the excess grand potential $\Delta\Omega$ given by Eq. (4) to write

$$\beta W = -3\phi_P R_G^{-1} R(q_s-1) \tag{9}$$

and

$$\beta U = -6\phi_P (HR_G)^{-1} R^2 (q_s-1)^2 e^{-2H/\xi}, \tag{10}$$

respectively. Here, ϕ_P is the polymer volume fraction defined by $\phi_P = (4\pi/3)R_G^3\rho_P$, and q_s is defined in Eq. (7). Similarly to the expression for the polymer end densities in the presence of one and two colloids given by Eqs. (7) and (8), respectively, Eqs. (9) and (10) can be straightforwardly reduced to their nonadsorbing polymer and weakly adsorbing polymer limits. According to the explanations given right below Eq. (7), those limits can be obtained, respectively, by setting $q_s = 0$ and $q_s = 1 + \xi(R^{-1}+\alpha^{-1})/2$ on the r.h.s. of Eqs. (9) and (10). Note that the limit of nonadsorbing polymers derived from Eqs. (9) and (10) by setting $q_s = 0$ $(\alpha = 0)$ correctly reproduces the corresponding expressions for the colloid immersion energy and the depletion potential obtained in Ref. [13].

Note that in contrast to the expressions for the colloid immersion energy W given by Eq. (9), the expression for the PM potential U in Eq. (10) is valid only up to the leading order in the colloid radius. In this limit, the formula for the PM potential given by Eq. (10) allows for a simple interpretation that can be elucidated by representing this formula as

$$\begin{aligned} \beta U &= -\left(\beta W \rho_P^{-1}\right)^2 K_0(H/R_G), \\ K_0(x) &= (2\pi)^{-1}\rho_P R_G^{-3} x^{-1} e^{-2x/\lambda}, \end{aligned} \tag{11}$$

where $\lambda \equiv \xi/R_G$ is the reduced polymer correlation length that depends on the overlap degree of the polymer coils in the polymer solution. Note that λ decays from 1 at the overlap threshold (corresponding to the semidilute solution boundary) to 0 at strong overlaps, thus presenting a convenient dimensionless parameter amenable to evaluations of the overlap degree for each particular system of the excluded volume polymers.

Two important remarks as to the derived expression for the PM potential, Eq. (10), are in order here. First, according to this expression, U is always negative, which corresponds to the attraction between colloids. In addition, the absolute magnitude of U increases upon increasing the inverse absorbance α^{-1} and decreases upon increasing the correlation length ξ. The former trend is caused by the fact that α^{-1} quantifies the adsorption strength of the colloid that imposes the enhanced bridging effect [15], which is known to play in favor of increasing the strength of PM interactions. The latter, opposite trend of decreasing the strength of the PM interaction upon increasing the correlation length ξ can be attributed to increasing the excluded volume screening effect that suppresses these interactions. Secondly, the form of Eq. (11) suggests that in the protein limit of small colloids, the potential of PM forces factorizes into the terms that describe the colloid immersion energies and the correlation function of the homogeneous (bulk) system of the excluded volume polymers. Note that this form of PM potential has similar structure as that obtained [13,16] for the case of purely entropic repulsion between the surface of protein colloids and polymers.

Note that the described simple factorization of the expression for the PM potential U into the immersion energy W and the correlation function K_0 provides a convenient route to practical use of this expression. In fact, in the considered limit $\xi \ll \alpha$, the correlation function of the excluded volume polymers K_0 turns out to be independent of the nature of the adsorption interactions between the colloid and these polymers. The effect of weak adsorption of polymers to the surfaces of small colloids leading to the appearance of the PM interactions exhibits itself only in the dependence of the colloid immersion energy on the adsorption strength quantified through the parameter α. In other words, the approximate expression for U given by Eq. (11) gives a possibility to reduce the two-colloid problem of calculating the polymer mediated interaction potential to the one-colloid problem of determining the colloid immersion energy. The accuracy of this approximate expression can therefore be easily improved by using the refined correlation function K_0 that is free of the limitations of the used SCMFT approach. For instance, the polymer-colloid interaction-independent polymer correlation function K_0 can be deduced from a comparison between the results of the Monte Carlo simulations and the theoretical formula for the depletion potential U_D along the lines of our previous work in Ref. [13]. Note that the analytic expression obtained in Ref. [13] for the correlation function of the form

$$K = \sigma_g \rho_P H^{-3} (H/R_G)^{\frac{5}{3}} \exp[-(2H/\lambda R_G)^{\frac{5}{6}}] \qquad (12)$$

leads to a good agreement between the simulations and the theoretical predictions for U_D, which proves the adequateness of Eq. (12) for the case of the excluded volume polymers. The second ingredient of the expression for the PM potential in Eq. (11), the colloid immersion energy W, can be calculated numerically for arbitrary values of the correlation length ξ, the absorbance α, and the colloid radius R. These calculations are much less computationally intensive in comparison with the corresponding exact solution of the Edwards equation in bispherical geometry imposed by the presence of two colloids. This significant simplification, outlined above, is achieved at a cost of restricting the validity of the results to the protein limit $R <\sim \xi$ only, which establishes the hierarchy of length scales $R \ll \xi \ll \alpha$ describing the domain of parameters where the used approximation works best.

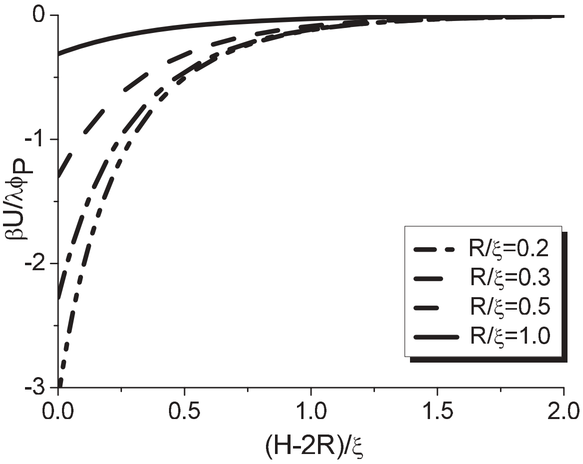

FIG. 2. Reduced PM potential for several values of the reduced colloid radius R/ξ and the selected value of the reciprocal adsorption length $\xi/\alpha = 0.1$.

The above outlined calculation of the PM potential based on the numerical evaluation of the immersion energy W and the analytic result for the correlation function given by Eq. (12) are illustrated in Fig. 2. Note that the reduced correlation length λ and the polymer volume fraction ϕ_P used in parametrizing the PM potential U are not independent. For the considered case of the excluded volume polymers, these parameters can be related by using the evaluation procedure described in detail in Ref. [13]. This evaluation shows that $\phi_P \lambda$ is the increasing function of ϕ_P that varies between 0.2 at the overlap threshold $\phi_P = 1$ and 0.39 at $\phi_P = 5$. The at-contact reduced PM potential $\beta U(H = 2R)$, therefore, reaches the order of unity at small colloid radii $R \sim 0.2\xi$, and it decreases by a factor of 10 upon increasing the colloid radius up to the order of the correlation length ξ. Note that the described dependence of the magnitude of the PM potential on the colloid radius shows just the opposite trend in comparison with the purely entropic depletion potential that increases with R. This difference stems from different dependencies of the colloid immersion energy W on its radius R for the above cases of nonadsorbing and adsorbing polymers. In the case of nonadsorbing polymers that mediate purely entropic depletion interactions, the main factor that affects the strength of these interactions is the colloid surface area, so that W turns out to be proportional to R. For the case of reversibly adsorbed polymers, the main factor affecting the immersion energy is the strength of the adsorption interactions, so that even small colloids can change considerably the polymer density structure in their vicinity at large enough α^{-1}. Interestingly, in the case of nonadsorbing polymers, the increasing power dependence of W on R overrides [13] the decreasing power dependence of the correlation function $K(H = 2R)$ described by Eq. (12), so that the resulting at-contact depletion potential $U_D \sim W(R)^2 K(H = 2R)$ increases with increasing R. In contrast, for the considered case of adsorbing polymers, the mentioned decreasing power dependence $K(H = 2R)$ is the main factor contributing to the R dependence of $U(H = 2R)$ in the limit $R \ll \xi$. This results in the observed decreasing $U(H = 2R)$ with increasing R for adsorbing polymers, which is solely due to the decreasing H dependence of the correlation function $K(H)$ given by Eq. (12).

In summary, we obtained an analytic expression of the potential of the PM interaction between nanocolloids mediated by reversibly adsorbing polymers. An adequate description of the adsorption interactions between the polymers and colloid surfaces has been achieved through using the boundary condition that correctly describes the case of reversible polymer adsorption onto nanosized "protein" colloids. The obtained analytic expression for the PM potential can be effectively used to investigate the thermodynamic properties of polymer-nanocolloid mixtures in dependence on the affinity of the colloid surface for polymers quantified by the adsorption length α incorporated in the above BC. In particular, the present results for the PM potential shown in Fig. 2 raise yet another interesting question if the PM interactions mediated by adsorbing polymers can induce the phase separation of the colloid-polymer system. It is well known [16] that inducing this separation by mixing nonadsorbing polymers with small nanocolloids is hardly possible. According to our results, the presence of the adsorption interactions between the colloids and polymers can drastically change this picture and lead to colloid-polymer demixing even at small R and large enough α^{-1}. A more detailed discussion of the colloid-polymer phase diagram based on the calculated PM potential intended to rigorously answer the above question will be reported elsewhere.

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