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Depletion interaction mediated by semiflexible polymers

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We present simple mean-field theory for the polymer-mediated depletion attraction between colloidal particles that accounts for the polymers chain stiffness. We find that, for fixed polymer radius of gyration and volume fraction, the strength of the attraction increases with increasing chain stiffness in both the dilute and semidilute concentration regime. On the contrary, the range of attraction monotonically decreases with chain stiffness in the dilute regime, while it attains a maximum in the semidilute regime. The obtained analytical expression for the depletion interaction were compared with numerical self-consistent field lattice computations and shown to be in quantitative agreement. From the interaction potential between two spheres we calculated the second osmotic virial coefficient $B_2$, which appears to be a convex function of chain stiffness. A minimum of $B_2$ as a function of chain stiffness was observed both in the numerical self-consistent field computations and the analytical theory. These findings help explain the general observation that semiflexible polymers are more effective depletants than flexible polymers and give insight into the phase behavior of mixtures containing spherical colloids and semiflexible polymers.

I. INTRODUCTION

Adding non-adsorbing polymers to colloidal dispersions has been known to often induce aggregation and phase separation. Near a colloidal surface polymers have less configurational entropy, leading to zones that are depleted of polymer. When two so-called depletion zones of adjacent colloids overlap, there is an unbalanced osmotic force between the colloidal particles and the bulk of the solution, which pushes the particles together. Thus, the non-adsorbing polymers induce an effective depletion attraction between the colloidal particles, even when all interactions in the system are repulsive.

Depletion interactions are relevant from a fundamental and practical point of view. Examples of systems in which depletion forces are operational are food formulations, biological systems, and in industrial systems such as paints. The depletion interaction due to flexible polymers is well understood in the 1950s and 1960s. Asakura and Oosawa in the 1950s and Vrij in the 1970s independently derived analytical expressions for the depletion interaction between two plates and two spheres (further called the AOV-theory) by simplifying the polymers as penetrable hard spheres. They found that the strength and range of interaction are mainly governed by two parameters: the osmotic pressure $\Pi$ of the depletants and the size of the depletion zone, also known as the depletion thickness $\delta$. AOV theory has been verified experimentally and through simulations.

Various extensions have since then been made to the original AOV-theory. These extensions include taking size dispersity into account, generalizing the depletion potential to the semidilute regime, and deriving expressions for the depletion interaction mediated by excluded volume polymers. However, in all of these extensions, the polymers are treated as being fully flexible, while in many real-world systems, the polymers have some degree of chain stiffness.

A larger polymer chain stiffness increases the effective Kuhn length $l_K$ of the polymer segments and in turn increases the gyration radius $R_g$ of the polymer in solution. Examples can be found in solutions of common biopolymers such DNA, which has a Kuhn length of tens of nanometers, and xanthan, which has a Kuhn length of several hundreds of nanometers. Additionally, because of the intrinsic stiffness, semiflexible polymers lose less configurational entropy in the vicinity of a non-adsorbing surface compared to fully flexible polymers with the same radius of gyration. This indicates that chain stiffness may have a significant effect on the depletion interaction.

Experimentally, measurements of the depletion interaction between colloidal particles in solutions of stiff chains are limited. In the work that has been done, most authors fit their experimental findings with the classical AOV-theory, without explicitly accounting for chain stiffness. Surprisingly few investigations have been done to theoretically describe the effect of chain stiffness on depletion interactions. In previous work, we showed that chain stiffness in fact can have a significant effect on the thickness of the depletion layer. In general if one keeps the radius of gyration constant, an increase of the chain stiffness results in a decrease of the depletion thickness in the dilute regime. In contrast, in the semidilute regime we observed a maximum in the depletion thickness as a function of chain stiffness. Furthermore, Peters et al. showed that, through a simple interpolation between flexible polymers and rigid rods, chain stiffness may shift the binodals of a polymer-colloid mixture several orders of magnitude in terms of the polymer concentration.

Therefore, in order to provide a more complete description, in this article we derive analytical theory that quantifies the effect of chain stiffness on the depletion interaction between two colloidal particles. Additionally, we investigate the...
consequences on the colloidal stability by analyzing the second osmotic virial coefficient $B_2$. The equations presented in this manuscript apply to both θ-solvent and good solvent conditions in a mean-field approximation. The analytical results for the interaction potentials are compared to numerical self-consistent field (SCF) computations where applicable, which are performed using the Scheutjens–Fleer formalism, extended towards semiflexible polymers\cite{Tuinier2006a}. The theory aims to advance the understanding of the interactions operational in, for example, biological systems, as many biopolymers are relatively stiff\cite{Flory1943c, Kallenbach1996a, Lu2002a}.

The outline of this manuscript is as follows. First, we derive analytical results for the depletion interaction induced by semiflexible polymers. This theory is based upon extensions of known analytical theory for the depletion interaction between flat plates and spheres for flexible polymers. Next, we present the results of our analytical theory, and compare it to Scheutjens-Fleer Self-Consistent Field (SF-SCF) lattice computations. Furthermore, we discuss the implications for the polymer chain stiffness dependence of the second virial coefficient. Lastly, the main findings are summarized.

For a detailed explanation of the SCF computations, we refer the reader to earlier work\cite{Tuinier2006a, Fleer2006b}. All length scales including the radius of gyration $R_g$, Kuhn length $k$, colloid radius $a$ and distance between two colloidal particles $h$ are expressed in terms of the bond-length $l$. Furthermore, all interaction potentials are expressed dimensionless in terms of $Wl^2/k_BT$ for plates and $W_c/k_BT$ for spheres.

**II. THEORETICAL SECTION**

**A. Interaction between two plates**

The interaction potential $W(h)$ between two plates at a distance $h$ can be calculated using the extended Gibbs adsorption equation\cite{Tuinier2006a, Fleer2006a}:

$$-\left(\frac{\partial W(h)}{\partial \mu}\right)_h = \Gamma(h) - \Gamma(\infty), \quad (1)$$

where $\mu$ is the chemical potential of the polymers, $\Gamma(h)$ is the adsorbed amount of polymers when the plates are at a distance $h$ and $\Gamma(\infty)$ is the adsorbed amount at infinite plate separation. Integration of eq. (1) and applying the Gibbs-Duhem relation yields\cite{Tuinier2006a}:

$$W(h) = -\int_0^{\phi_b} \left[\Gamma(h) - \Gamma(\infty)\right] \frac{1}{\phi_b} \left(\frac{\partial \Pi_b}{\partial \phi_b}\right) d\phi_b, \quad (2)$$

where $\phi_b$ is the bulk monomer volume fraction and $\Pi_b$ is the osmotic pressure of the polymer solution (in units of $k_BT/l^3$), given by the mean-field Flory-Huggins equation\cite{Flory1942}:

$$\Pi_b = -\ln(1 - \phi_b) - \left[1 - \frac{1}{N}\right] \phi_b - \chi \phi_b^2, \quad (3)$$

with $\chi$ the Flory-Huggins interaction parameter and $N$ the number of monomers per polymer chain, related to the radius of gyration as $R_g = \sqrt{Nk_b/6l_k}$, where $N_k$ is the number of Kuhn segments $N_k = N/l_k$, thus, $R_g = \sqrt{Nl_k/6}$. One may then show that $W(h)$ is equal to\cite{Tuinier2006a}:

$$W(h) = -\int_0^{\phi_b} \left[2\delta - h + hX(h)\right] \frac{\partial \Pi_b}{\partial \phi_b} d\phi_b, \quad (4)$$

where $\delta$ is the depletion thickness at one isolated wall and $X(h)$ is the modified Cassasa distribution coefficient\cite{Cassasa1959} of a solution of non-adsorbing polymers between two plates with regards to the external bulk solution:

$$X(h) = \frac{8}{\pi^2} \sum_{n=1,3,5...} \frac{1}{n^2} \exp \left[-n^2\pi^2 \left(\frac{\delta}{2\hbar}\right)^2\right]. \quad (5)$$

In eq. (6a) $\xi$ is the (bulk) correlation length in units of the bond length $l$, and $k$ is a numerical constant\cite{Tuinier2006a}:

$$\frac{1}{\delta^2} = \frac{1}{\delta_0^2} + \frac{1}{l_k} (k\xi)^2, \quad (6a)$$

$$\delta_0^2 = \frac{\pi}{4R_g^2}, \quad (6b)$$

$$\frac{1}{\xi^2} = -3\ln(1 - \phi_b) - 6\chi \phi_b. \quad (6c)$$

In the dilute limit eq. (4) is equivalent to the classical expression of Asakura and Oosawa for ideal polymers\cite{Asakura1954}.

Tuinier and Fleer showed\cite{Tuinier2006a} that for flexible polymers, the integration in eq. (4) may be approximated through an effective interaction distance $\delta_i$. Insertion of $\delta_i$ in eq. (5) then yielded a simplified expression which was in quantitative agreement with SF-SCF computations:

$$W(h) = -\Pi_b \left[2\delta_i - h + hX(h)\delta_i \rightarrow \delta_i\right]. \quad (8)$$

In this manuscript we depart from the ansatz that the distribution coefficient of a solution of semiflexible polymers is similar to that of a flexible polymer, such that the expression for $X(h)\delta_i \rightarrow \delta_i$ still holds. Our approach is motivated by the observation that the Green’s function (and therefore partition function) of a semiflexible polymer may be mapped onto the partition function of a flexible polymer in a simple but efficient manner\cite{Tuinier2006a}. Next, we derive an expression for the effective interaction distance $\delta_i$ for semiflexible polymers.

**1. Interaction distance $\delta_i$**

To obtain the effective interaction distance, we follow the approach of Tuinier and Fleer\cite{Tuinier2006a} who showed that $\delta_i$ can be calculated from:

$$\delta_i = \frac{\Omega(\infty)}{\Pi_b}, \quad (9)$$
where $\Omega(\infty)$ is the grand potential at infinite plate separation (in units of $k_B T / \ell^2$):

$$\Omega(\infty) = \int_0^\infty [\Pi_b - \Pi(z)] dz,$$

with $\Pi(z)$ the local osmotic pressure profile next to one wall. A Taylor expansion of eq. (3) in $\varphi$ gives:

$$\Pi_b = \frac{\ell_k}{6R_b^2} + \frac{(1 - 2\chi)\varphi_b^2}{2} + \frac{\varphi_b^3}{3} + \cdots,$$

$$\Pi(z) = \frac{\varphi(z)\ell_k}{6R_b^2} + \frac{(1 - 2\chi)\varphi(z)^2}{2} + \frac{\varphi(z)^3}{3} + \cdots,$$

where we take for $\varphi(z)$ the expression of Martens et al.\textsuperscript{36} for semiflexible polymers:

$$\varphi(z) = \varphi_b \tanh \left( \frac{z + \delta_{sf}}{\delta} \right)^2,$$

with $\delta_{sf}$ accounting for the semiflexibility of the polymer chains:

$$\delta_{sf} = \sqrt{\frac{\ell_k^2 (\ell_k - 1)^2}{4(\ell_k + 3)(\ell_k + 1)}}.$$

We can split eq. (10) into $n$ separate integrals:

$$\Omega(\infty) = \frac{\ell_k \varphi_b}{6R_b^2} c_1 + \frac{(1 - 2\chi)\varphi_b^2}{2} c_2 + \frac{\varphi_b^3}{3} c_3 + \cdots,$$

with

$$c_n = \int_0^\infty \left[ 1 - \tanh \left( \frac{z + \delta_{sf}}{\delta} \right)^2 \right] dz,$$

which may be solved analytically:\textsuperscript{48}

$$c_n = \delta \sum_{k=1}^n \frac{1 - \tanh \left( \frac{\delta_{sf}}{\delta} \right)^{2n-2k+1}}{2n - 2k + 1},$$

where $c_1 = \delta_{sf}$, the depletion thickness for semiflexible polymers next to a flat wall:\textsuperscript{36}

$$c_1 = \delta_{sf} = \delta \left[ 1 - \tanh \left( \frac{\delta_{sf}}{\delta} \right) \right].$$

In the dilute limit, we find that the first term of eq. (14) is leading and thus in this limit $\delta = \delta_{sf}$. However, for higher concentrations, higher order terms become increasingly important; thus, the interaction range $\delta$ in this case is larger than $\delta_{sf}$\textsuperscript{20}.

The derivation performed in this section is for polymers which are strongly depleted from the surface, as eq. (12) is only valid in this regime. However, in real systems, there can be a small, but significant adsorption energy between the surface and the polymer segments, effectively shifting the concentration profile towards the surface. Taking this into account is possible using the methodology outlined by Fleer and Skvortsov\textsuperscript{49}. One may derive an effective extrapolation length as a function of the adsorption energy and add this to eq. (12).

### B. Interaction between two spheres

In contrast to the flat-plate result, no analytical expression for the distribution coefficient between two spheres is known for flexible chains, although approximations exist\textsuperscript{30,31}. Therefore, the approach used in the previous section can not be applied. In this section, we use two different methods. The first is more in line with the original work of Asakura and Oosawa and Vrij\textsuperscript{2,4}, but extended towards the semidilute regime\textsuperscript{20}. The second is based on the Derjaguin approximation of equation eq. (4).

#### 1. The AOV approach

We assume that the polymer concentration profile is a Heaviside step function given by:

$$\varphi(z) = \begin{cases} 0 & z \leq \delta_{sf} \\ \varphi_b & z > \delta_{sf} \end{cases},$$

where $z$ is the distance from the surface of the colloidal particle and $\delta_{sf}$ the depletion thickness of a semiflexible polymer around a sphere\textsuperscript{36}:

$$(1 + \frac{\delta_{sf}}{a})^3 = 1 + \frac{3\delta_{sf}}{a} \left[ 1 - \tanh \left( \frac{\delta_{sf}}{\delta} \right) \right] - \frac{9\delta_{sf}^2}{\pi a^2} \ln \frac{\delta}{\delta_{sf}},$$

where $\ln$ is the dilogarithm defined as $\ln(x) = -\int_0^x \frac{\ln(1 - u)}{u} du$. The depletion potential is then given by\textsuperscript{20}:

$$W_s(h) = -\int_0^{\varphi_b} V_{ov} \left( \frac{\partial \Pi_b}{\partial \varphi_b} \right) d\varphi_b,$$

where $V_{ov}$ is the overlap volume of two depletion zones\textsuperscript{4}:

$$V_{ov} = \begin{cases} \frac{a}{6} (2\delta_{sf} - h)^2 (6a + 4\delta_{sf} + h) & h \leq 2\delta_{sf} \\ 0 & h > 2\delta_{sf} \end{cases},$$

with $a$ the colloid radius.

#### 2. The Derjaguin approximation

The second approach to obtain an expression for the depletion interaction between two spheres is using the Derjaguin approximation\textsuperscript{52}. Derjaguin realised that when the range of interaction is much smaller than the size of the spheres, the interaction potential between two spheres can be approximated from the interaction potential between two plates as

$$W_s(h) = \pi a \int_h^\infty W(h) dh.$$  

It turns out that in the case of the depletion interaction due to non-adsorbing polymers, an exact solution to this integral is
possible. Here we highlight the main results, the full derivation is given in appendix A. After insertion of eq. (4) and performing the integration, one obtains:

\[ W_c(h) = \Pi_0 \pi a \left[ \delta (\delta - h^2/2 + h^2 X(h) \delta \rightarrow \delta \right. \right.

\[ + \pi \delta^2 Y(h) \left. \right] \]

(23)

where \( X(h) \) is given by eq. (5) and \( Y(h) \) is defined as:

\[ Y(h) = \sum_{n=1} \frac{(-1)^n}{n} \text{erfc} \left( \frac{nh}{\sqrt{\pi} \delta} \right). \]

(24)

Equation 23 is shown to be consistent with an approximation obtained by Eisenriegler\(^{53}\) for ideal polymers, see appendix A eq. (A11).

3. Second osmotic virial coefficient

Finally, our aim is to understand the effect of chain stiffness of the non-adsorbing polymers on the colloidal stability, which can be probed through the second osmotic virial coefficient \( B_2 \). Using hard spheres as the reference, the second osmotic virial coefficient can be expressed as:

\[ B_2 = 4 \nu_c + 2 \pi \int_0^\infty (2a + h)^2 \left[ 1 - e^{-W_c(h)} \right] dh, \]

(25)

where \( \nu_c \) is the volume of the colloidal spheres. In the limit of \( \phi_b = 0, \) \( W_c(h) \) vanishes and the classical hard-sphere limit \( B_2 = 4 \nu_c \) is recovered.

4. SF-SCF calculations

To validate the analytical theory in the previous sections we compare the theoretical predictions with numerical SF-SCF lattice computations. The SF-SCF theory can be regarded as a gradient-extended Flory-Huggins mean-field theory.\(^{39}\) It allows for the inclusion of for example chain stiffness\(^{42}\) and electrostatics\(^{54}\). In SF-SCF, space is discretized in \( M \) layers of thickness equal to the monomer length \( l \), the solvent molecules have the same size \( l \) and volume \( l^3 \) as the monomers. Each component in the system is characterized by a corresponding volume fraction at every location \( \phi(z) \) and a segment potential \( u(z) \). The core idea of SF-SCF theory is that

\[ \phi \{ u(z) \} \leftrightarrow u \{ \phi(z) \}, \]

(26)

under the constraint that

\[ \sum_i \phi_i(z) = 1, \]

(27)

where the sum is taken over all components in the system. Given an initial guess, the free energy of the system is minimized to fulfill the self-consistent condition eq. (26), yielding the partition function and volume fractions of all components. All relevant thermodynamic parameters can then be calculated.

To calculate the interaction potential between two plates we use a planar lattice with coordination number 6 and gradients in the direction perpendicular to the surface. A solid surface is placed at the lower boundary of the lattice and a mirror boundary condition is used as the upper boundary condition. By decreasing the lattice size \( M \) stepwise one then calculates the interaction potential from the grand potential as \( W(h) = \Omega(h) - \Omega(\infty) \), where due to the mirror boundary condition \( h = 2M \).

To describe the interaction potential between two spheres we employ the method first described by Wijmans, Leermakers and Fleer\(^{55}\). Whereas this method was first only feasible for short polymers \( N < 200 \) and small spheres with radius \( a < 10 \), advances in computational power allow us to calculate the interaction potential between two spheres mediated by polymers with \( N > 1000 \) and \( a > 40 \). We use a cylindrical lattice with coordination number 6 and concentration gradients in both the axial and radial direction and place a spherical particle with radius \( a \) in the centre of the coordinate system. Using a mirror boundary condition at the last lattice site we may use symmetry and a decrease of the axial lattice size to obtain the interaction potential between two identical spheres. For a detailed explanation we direct the reader to Ref. 55.

It must be noted that the SF-SCF theory is a mean-field theory, which implies that the polymer chains in the bulk behave as Gaussian chains. For theta-solvent conditions this is accurate, however, for good-solvent conditions fluctuations are not accurately accounted for. The scaling exponents for the correlation length and radius of gyration obtained from SF-SCF thus differ from methods such as renormalization group theory and simulations.\(^{56,57}\) Nevertheless, qualitative trends obtained from the SF-SCF computations are in line with those from simulations.\(^{40,58}\)

III. RESULTS AND DISCUSSION

A. Interaction between two plates

First we investigate the effect of increasing the chain stiffness on the depletion interaction as predicted by eq. (8) and compare this to numerical SF-SCF computations. In fig. 1 results are plotted for a solution containing polymers with \( R_g = 50 \) and \( \phi_b = 0.005 \) (semidilute) and \( \phi_b = 10^{-7} \) (dilute). The radius of gyration is kept constant by varying the number of monomers using \( N = 6R_g^2/l_G \) (thus varying the contour length). As can be seen, there is good agreement between eq. (8) and the numerical SF-SCF computations for a wide range of chain stiffnesses. At intermediate plate separations the analytical results slightly overestimate the magnitude of the depletion potential. The slight overestimation can be expected from our simple approximation, as the distribution coefficient of a semiflexible polymer solution is shown\(^{59,60}\) to be much more involved, compared to eq. (5). In dilute conditions (panel B) there is close agreement. In summary, our approximation provides a simple yet semi-quantitative analytical expression for the interaction potential \( W \) and the distribution coefficient \( X \).
The general effect of chain stiffness in both the dilute and semidilute regimes is an increase in the magnitude of the contact potential (panels A and B). This can be explained by the fact that at a given \( \phi_b \), the osmotic pressure increases with increasing \( l_K \) for solutions containing polymers with the same \( R_g \), because the polymer number density increases. The range of interaction shows different behavior in the dilute and semidilute regimes, as can be observed in fig. 1 panels C and D. In the dilute concentration regime the range of interaction decreases with increasing chain stiffness, while it relatively increases in the semidilute regime.

A consequence of increasing the chain stiffness while keeping the radius of gyration constant at a constant segment volume fraction \( \phi_b \), is that the polymer concentration relative to the overlap concentration (\( c^* / c^* \)) also increases. Since \( c^* \propto N / R_g^3 \), where if one increases the chain stiffness while keeping \( R_g \) constant, \( N \) scales as \( N \propto 1/l_K \), such that at constant \( \phi_b \), we find \( c^* / c^* \propto l_K \). One may interpret these results as performing experiments with three different polymers with a similar radius of gyration, at the same mass concentration, but with a different chain stiffness (and different molar masses).

On a general note, the depletion interaction in solutions of semiflexible polymer was shown by Forsman and Woodward to have a weak repulsive regime at intermediate surface separations. The height and location of the repulsive tail was shown to be a function of chain stiffness and may result in a phenomena known as depletion stabilization. While not shown in fig. 1 this region is also visible in the SF-SCF computations and was investigated for flexible polymers using SF-SCF by van der Gucht et al. As shown by Semenov, the repulsive part of the interaction potential is due to the depletion of chain ends at the midplane. Our analytical theory does

FIG. 1. The interaction potential between two plates in a solution of non-adsorbing semiflexible polymers as a function of the interplate separation for \( R_g = 50 \), \( \chi = 0 \) and various values of the chain stiffness. The radius of gyration is kept constant by varying the contour length (\( N = 15000, 1500 \) and \( 600 \), for \( l_K = 1, 10 \) and \( 25 \), respectively). Interaction potentials are shown for both semidilute \( \phi = 0.005 \) (A and C) dilute \( \phi = 10^{-7} \) (B and D) conditions. The symbols are numerical SF-SCF calculations and the solid curves are calculated using eq. (8).
It is of interest to find an approximate expression for this maximum. Inspection of eq. (14) indicates that the maximum of $\delta_d$ would be at approximately the value of $l_K$ where $\delta_1$ also has a maximum. In appendix B we show $l_{K,\text{max}} \approx \frac{\delta_0^3}{\xi} - \delta_0^2/(2\xi^2)$. Using the parameters from fig. 2 we find $l_{K,\text{max}} \approx 28$, which is in agreement with the numerical SF-SCF calculations.

At large chain stiffness, both the dilute $\phi_b = 10^{-7}$ and semidilute $\phi_b = 0.005$ curves of the interaction distance seem to tend towards the same curve, indicating a concentration independent limit. While our analytical theory is not quantitative in this region, it does provide a qualitative explanation for this observation. Inspection of eq. (6a) shows that in the large chain stiffness limit, for $l_K \xi^2 \gg \delta_b$, $\delta = \delta_b$. Additionally, when $\rho_d \gg \delta_b$, all terms of a higher order than 1 in eq. (14) effectively vanish, yielding that $\delta_1$ will have a concentration independent slope, and asymptotically approaches the dilute interaction distance in the limit of $l_K \rightarrow \infty$.

For real systems though, due to the fact that $\delta_b = \Omega(\infty)/\Pi_b$, $\delta_1,\phi_b,1 < \delta_1,\phi_b,2$ for $\phi_b,1 > \phi_b,2$. Thus the effective interaction distance at higher concentrations is always smaller than the interaction distance at lower concentrations.

On a general note, the free energy gain of confinement-induced nematization of the semiflexible polymer chains is not taken into account in both the analytical expression for the depletion thickness and the SF-SCF calculations. It has been shown that the effective ordering parameter of the polymer chains increases with decreasing interplate separation and increasing chain stiffness at high concentrations. We expect that the confinement-induced nematization results in a decrease of the effective depletion thickness at the point of overlap, effectively making the depletion thickness itself a function of the interplate separation. As alignment of the polymer chains with the plates increases the polymer concentration between the two plates, we expect the magnitude to increase, while the range of the depletion interaction decreases, compared to our predictions.

### B. Interaction distance $\delta_1$

We may compare our analytical results for $\delta_1$ with the numerical SF-SCF calculations by investigating $-W(0)/(2\Pi_b)$ as $W(0) = -2\Pi_b \delta_1$ which follows from eq. (8). In fig. 2 we plot the interaction distance $\delta_1$ as a function of the Kuhn length for $\phi_b,1 = 10^{-7}$ (dilute) and $\phi_b,2 = 10^{-2}$ (semidilute) for a solution of polymers with $R_g = 50$ and $\chi = 0$. The radius of gyration is again kept constant by varying the contour length of the polymers. Again, the analytical predictions agree well with the SF-SCF calculations, to a comparable degree as fig. 1. At large chain stiffness we find some small deviations from the SCF results, which can be attributed to the upper limit of validity of eq. (12), which was shown to be $l_K \lesssim \sqrt{3}/2R_g$.

We observe entirely different behavior in the dilute regime, compared to the semidilute regime. In the dilute regime, the interaction distance is a monotonically decreasing function of chain stiffness. In contrast, in the semidilute regime the interaction distance is a concave function of chain stiffness, having a maximum. This effect was also observed for the depletion thickness $\delta_d$,

### C. Interaction between two spheres

In fig. 3 the interaction potential between two spheres of radius $a = 20$ (A) and $a = 40$ (B) mediated by a solution of polymers with $R_g = 20$, $\phi_b = 0.005$ and various values of the Kuhn length as indicated. The radius of gyration is kept constant by varying the contour length of the polymers. The size ratio between the polymers and colloids $q = R_g/a$ is $q = 1$ (A) and $q = 0.5$ (B). The symbols are the results from the 2D SF-SCF computations, the solid curves are the predictions of the AOV approach (eq. (20)) and the dashed curve is the Derjaguin approximation (eq. (23)).

We find similar trends as for the flat plate case; a decrease in the contact potential and an increase in the range of interaction when the chains are stiffer at fixed $R_g$. As expected the depletion attraction increases upon increasing the sphere radius. This follows directly from eq. (23), showing that the contact potential scales linearly with the colloid radius. As can be seen in both fig. 3 A and B, the AOV approach to the deple-
FIG. 3. The interaction potential between two spheres for \( a = 20, q = 1 \) (A), and for \( a = 40, q = 0.5 \) (B) as a function of the distance between the colloidal particles for \( R_g = 20, \chi = 0 \) and various values of \( I_K \) as indicated. The solid curves are calculated using the AOV approach, eq. (20) and the dashed curves are the Derjaguin approximation predictions of eq. (23).

D. Implications for colloidal stability

From the interaction potentials \( W_s(h) \) between two spheres, the second osmotic virial coefficient \( B_2 \) can be calculated using eq. (25). In fig. 4 we show results for \( B_2/v_c \) for \( a = 40, R_g = 20, \varphi_b = 0.005 \) as a function of the relative chain stiffness \( R_g/I_K \). The general effect of increasing the chain stiffness (a decrease in \( R_g/I_K \)) is a lowering of the osmotic virial coefficient, as both the range of the interaction and the contact potential increase in magnitude with increasing chain stiffness. This observation indicates that for comparable coil size, stiffer polymers are more effective depletants.

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after this point, as is observed in fig. 4. It is interesting to investigate these findings with, for example, density functional theory\textsuperscript{30} or PRISM\textsuperscript{35} calculations. We do expect that the minimum as a function of chain stiffness is preserved; however, within the limitations of our mean-field results the precise location of the minimum may vary.

IV. CONCLUDING REMARKS

In this paper we showed how chain stiffness affects the polymer-mediated depletion interaction between two plates and two spheres. We presented an extension of mean-field theory for flexible polymers by including a theoretical expression\textsuperscript{36} for the concentration profile of a semiflexible polymer solution next to a non-adsorbing surface. The results from our analytical expressions semi-quantitatively describe the interaction potentials as obtained from self-consistent field computations in the case of two interacting flat plates and two spheres.

In the dilute regime, when the chain stiffness increases at constant radius of gyration, the range of attraction decreases, while the magnitude of the contact potential increases. This effect was observed in both the interaction between two plates and two spheres. In contrast, in the semidilute regime, the range of the depletion interaction was shown to exhibit a maximum value upon increasing the chain stiffness. From the pair potentials between two spheres we calculated the second osmotic virial coefficient $B_2$. The general effect is that stiffer polymers are more effective depletants. At high chain stiffness, a minimum in $B_2/v_c$ was observed both analytically and in the numerical SF-SCF calculations, which may have important implications for the phase behavior of colloid-polymer mixtures. Although our analytical results were shown to provide accurate predictions of the interaction potentials up to high chain stiffness, the calculated $B_2$ curves quantitatively deviated at $R_s/l_k < 2$, providing a limit to the validity of our simple analytical mean-field theory. It must be stressed that the results presented in this article are valid within a mean-field treatment of polymer solutions, which has its limitations. Both the self-consistent field calculations and the analytical expressions do not account for fluctuations. Therefore, the exact scaling exponents differ from those used in the present work. However, extensions to account for chain swelling and using the correct scaling exponents for the osmotic pressure are straightforward\textsuperscript{12} and should be used when comparing the theory with experimental results. At least semi-quantitatively, the results shown here may be of help in explaining the interactions and phase stability in mixtures of colloids and semiflexible polymers.

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DATA AVAILABILITY STATEMENT

The data used in this manuscript is available from the corresponding author upon request.

AUTHOR DECLARATIONS

The authors have no conflicts to disclose.

Appendix A: An exact solution to the Derjaguin approximation for the depletion interaction due to non-adsorbing polymers

Derjaguin derived that the interaction between two spheres is related to the interaction between two plates as:

$$W_c(h) = \pi a \int_0^\infty W(\tilde{h})d\tilde{h}, \quad (A1)$$

which upon insertion of eq. (8) gives:

$$W_c(h) = -\Pi_0 \pi a \int_0^\infty [2\delta h - h(1 - X(\tilde{h})_{\delta \to \delta})] d\tilde{h}, \quad (A2)$$

From integrating each term individually yields:

$$f(\tilde{h}) = 2\delta h - \frac{\tilde{h}^2}{2} + \int \tilde{h} X(\tilde{h})_{\delta \to \delta} d\tilde{h}, \quad (A3)$$

where the last part of the right-hand side can be integrated analytically using the Casassa sum eq. (5):

$$\int \tilde{h} X(\tilde{h})_{\delta \to \delta} d\tilde{h} = \frac{8}{\pi^2} \sum_{n=1,3,5,...} \frac{1}{n^2} e^{-n^2\pi^2(\frac{\delta}{2})^2} d\tilde{h}, \quad (A4)$$

which upon integrating each term individually yields:

$$\int \tilde{h} X(\tilde{h})_{\delta \to \delta} d\tilde{h} = \frac{8}{\pi^2} \sum_{n=1,3,5,...} \frac{\tilde{h}^2}{n} e^{-n^2\pi^2(\frac{\delta}{2})^2} + \ln(2)\pi\delta^2$$

$$-\delta^2 \tilde{h} + \pi\delta^2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \text{erfc} \left( \frac{n\tilde{h}}{\sqrt{\pi}\delta} \right), \quad (A5)$$

where erfc is the error function complement. One may recognize $X(\tilde{h})_{\delta \to \delta}$ in eq. (A5) and thus rewrite it as:

$$\int \tilde{h} X(\tilde{h})_{\delta \to \delta} d\tilde{h} = \frac{\tilde{h}^2}{2} X(\tilde{h})_{\delta \to \delta} + \ln(2)\pi\delta^2 - \delta^2 \tilde{h}$$

$$+ \pi\delta^2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \text{erfc} \left( \frac{n\tilde{h}}{\sqrt{\pi}\delta} \right). \quad (A6)$$
Hence, the total expression for the integral of the flat-plate potential $A_3$ is given by:

$$f(\tilde{h}) = \ln(2) \pi \delta_i^2 + \delta_i \tilde{h} - \frac{\hbar^2}{2} (1 - X(\tilde{h})_{\delta \to \delta_i})$$

$$+ \pi \delta_i^2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \text{erfc} \left( \frac{nh}{\sqrt{n} \delta_i} \right).$$

(7)

Lastly we take the limits $\tilde{h} \to h$ and $\tilde{h} \to \infty$ to obtain the full expression for the Derjaguin approximation. Note that the asymptotic limit of $X(\tilde{h})_{\delta \to \delta_i}$ around $\tilde{h} \to \infty$ is given by $X(\tilde{h})_{\delta \to \delta_i} = 1 - 2\delta_i/h$, which when inserted in eq. (7) yields:

$$\lim_{\tilde{h} \to \infty} f(\tilde{h}) = \ln(2) \pi \delta_i^2,$$

(8)

where we used that $\lim_{x \to -\infty} \text{erfc} x = 0$. The total expression for the Derjaguin approximation to the flat plate result is then given by:

$$W_s(h) = \Pi_0 \pi a \left[ \delta_i h - \frac{h^2}{2} (1 - X(h)_{\delta \to \delta_i}) \right]$$

$$+ \pi \delta_i^2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \text{erfc} \left( \frac{nh}{\sqrt{n} \delta_i} \right).$$

(9)

Analysis of eq. (9) shows that the contact potential $W_s(0)$ is given by:

$$W_s(0) = -\Pi_0 \pi a \ln(2) \pi^2 \delta_i^2,$$

(10)

since $\text{erfc}(0) = 1$ and $\sum_{n=1}^{\infty} \frac{(-1)^n}{n} = -\ln(2)$. One may compare this result for $W_s(0)$ with an expression obtained by Eisenriegler, who, using an expansion in $h$, found the following analytical expression for the Derjaguin approximation for ideal polymers:

$$W_{sEisenriegler}(0) = -\Pi_0 \pi a \ln(2) \pi^2 \delta_i^2 R_s^2.$$  

(11)

Using $R_s^2 = \frac{\pi}{3} \delta_i^2$, and the fact that in the dilute regime for $l_K = 1$, $\delta_i = \delta_0$ eq. (10) and eq. (11) are identical.

### Appendix B: The maximum of $\delta_{sf}$ as a function of $l_K$

In the semidilute concentration regime, there is a maximum in the depletion thickness as a function of the Kuhn length $l_K$ at a constant $R_s$, see Ref. 36. In this previous paper we did not supply an analytical approximation for this maximum which is given here. First, we rewrite eq. (17) as

$$\delta_{sf} = \frac{\delta_0}{\sqrt{1 + \frac{\delta_i^2}{K_K^2}}} \left[ 1 - \tanh \left( \frac{p_{sf} - \delta_0}{\delta_0} \right) \right].$$

(1)

For $p_{sf} \ll \delta_0/\sqrt{1 + \frac{\delta_i^2}{K_K^2}}$ one can use the approximation

$$\tanh x \approx x,$$

(2)

giving:

$$\delta = \frac{\delta_0}{\sqrt{1 + \frac{\delta_i^2}{K_K^2}}} - \frac{p_{sf}}{}.$$

Next, we perform a Taylor expansion of the square root in the denominator $\sqrt{1 + x^2} \approx 1 + x^2/2$ and use the large $l_K$ limit of $p_{sf}(l_K \gg 1) \approx l_K/2 - 3/2$ to obtain:

$$\delta \approx \frac{\delta_0}{\sqrt{1 + \frac{\delta_i^2}{K_K^2}}} - \frac{l_K}{2} + \frac{3}{2}.$$  

(3)

From eq. (3) it follows that $\delta$ attains a maximum value for:

$$l_{K,\text{max}} \approx \frac{\delta_0}{\delta_i} - \frac{\delta_i^2}{2 K_K^2},$$

(4)

which is accurate within a few percent as compared to numerical results obtained from eq. (17) or SF-SCF calculations up to $\phi_b = 0.01$.


\[ \phi_b = 0.005 \]

\[ \phi_b = 10^{-7} \]
$q = 1 \quad \varphi_b = 0.005$

Depletion potential $W_s(h)$

Sphere separation $h$

A

$q = 0.5$

Depletion potential $W_s(h)$

Sphere separation $h$

B
$\varphi_b = 0.005$

$q = 0.5$

$B_2/V_c$

$R_g/l_K$

$\leftarrow$ increasing stiffness