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We theoretically study the polarizability and the interactions of neutral complexes consisting of a semiflexible polyelectrolyte adsorbed onto an oppositely charged spherical colloid. In the systems we studied, the bending energy of the chain is small compared to the Coulomb energy and the chains are always adsorbed on the colloid. We observe that the polarizability is large for short chains and small electrical fields and shows a nonmonotonic behavior with the chain length at fixed charge density. The polarizability has a maximum for a chain length equal to half of the circumference of the colloid. For long chains we recover the polarizability of a classical conducting sphere. For short chains, the existence of a permanent dipole moment of the complexes leads to a van der Waal's-type long-range attraction between them. This attractive interaction vanishes for long chains (i.e., larger than the colloidal size), where the permanent dipole moment is negligible. For short distances the complexes interact with a deep short-ranged attraction which is due to energetic bridging for short chains and entropic bridging for long chains. Exceeding a critical chain length eventually leads to a pure repulsion. This shows that the stabilization of colloidal suspensions by polyelectrolyte adsorption is strongly dependent on the chain size relative to the colloidal size: for long chains the suspensions are always stable (only repulsive forces between the particles), while for mid-sized and short chains there is attraction between the complexes and a salting-out can occur.

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I. INTRODUCTION

Polyelectrolyte(PE)-colloid complexes have recently motivated a great amount of computational and analytical work [1–21]. The reason for this is not only the interesting behavior seen in such systems, but also the potential applications of them. For instance, some water-soluble paints are formed by PE-colloid complexes, in which a colloidal suspension is stabilized by adsorbed charged polymers. A better understanding of these complexes can give hints on how to avoid the precipitation of the particles from the suspension. Another example is the DNA-histone complex[1–3], whose behavior is thought to be one of the crucial factors in the packing of DNA in living cells[4].

Most of the previous work on PE-colloid complexes looked essentially at the structure and complexation behavior of the aggregates, e.g., of one PE and one macroion, [1, 5–17], one PE and many macroions [12, 14, 15, 18], one macroion and many PEs [6], or the effect of overcharging of the macroion [8, 10, 17–19]. While some works discuss the interactions between two macroions in presence of either one or more than two short PE-chains [18, 20, 21] we concentrate here on the complex formed

by one spherical colloid and one PE as a whole and look at its polarizability, as well as the effective interaction [22] between two isolated complexes. To do this we perform Monte Carlo (MC) computer simulations of one and two neutral symmetric PE-colloid complexes, i.e., systems where the charge of the PE exactly neutralizes the charge of the colloidal particle. We focus on the case where the bending energy is small compared to the energy of Coulomb coupling, i.e., the chain is always completely adsorbed on the macroion.

While the results we will show are, strictly speaking, only valid in the limit of low density of complexes and zero salt concentration, we expect these to remain qualitatively correct under more realistic conditions. As we observe in the simulations, the effect of salt at low concentrations (put into the simulations through a Debye-Hückel interaction) affects only slightly the results given for the salt-free system. Also, while both the polarizability and the interaction between complexes is very much influenced by the “microscopics” (i.e., by the structure of the chain), we will show that most of the computer simulation results can be understood using fairly simple principles, and that some of the issues related to these systems can be put on quite basic mathematics.

The paper is organized as follows: in section II we describe the model used and the computer simulation details. In section III we present the simulation results for the dipole moment in an external electrical field of one PE-colloid complex and suggest analytical expressions for the polarizability for all chain lengths. Section IV deals

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with the interaction of two of these complexes for different distances and chain lengths. We describe how the force is calculated and the results are discussed. We provide analytical results for the force for short chain lengths and long distances. Finally in section V we make some final remarks.

II. THE SIMULATION MODEL

We performed monomer-resolved Monte Carlo (MC) simulations using the model of Kremer *et al.* for single polyelectrolyte (PE) chains[23–25]. The polyelectrolyte chains are modeled as bead-spring chains of N Lennard-Jones (LJ) particles. The idea of this method was first applied on neutral linear polymers and on a single star polymer [24, 25] later also for neutral [26, 27] and charged stars polymer systems[28, 29]. For good solvent conditions, a shifted LJ potential is used to describe the purely repulsive excluded volume interaction between all N monomers:

$$V_{\text{LJ}}(r) = \begin{cases} 4\epsilon_{\text{LJ}} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] & \text{for } r \leq 2^{1/6}\sigma; \\ 0 & \text{for } r > 2^{1/6}\sigma. \end{cases} \quad (1)$$

Here, r is the distance of the interacting beads, σ is the microscopic length scale of the beads and ϵ_{LJ} sets the energy scale. We will from now on rescale all lengths with σ according to

$$\tilde{r} = \frac{r}{\sigma}. \quad (2)$$

In accordance with previous work[26, 28, 29], we have chosen for the temperature $T = 1.2\epsilon_{\text{LJ}}/k_{\text{B}}$, where k_{B} is the Boltzmann constant.

The connectivity of the bonded monomers is assured by a finite extension nonlinear elastic (FENE) potential acting between neighboring beads:

$$V_{\text{F}}(r) = \begin{cases} -\frac{1}{2}k_{\text{F}} \left(\frac{r_{\text{m}}}{\sigma}\right)^2 \ln \left[1 - \left(\frac{r}{r_{\text{m}}}\right)^2 \right] & \text{for } r \leq r_{\text{m}}; \\ \infty & \text{for } r > r_{\text{m}}, \end{cases} \quad (3)$$

where k_{F} denotes the spring constant and is set to $k_{\text{F}} = 7.0\epsilon_{\text{LJ}}$. This interaction diverges at $r = r_{\text{m}}$, which determines the maximal relative displacement of two neighboring beads. The energy ϵ_{LJ} is the same as in Eq. (1), whereas for the length scale r_{m} we have chosen the value $\tilde{r}_{\text{m}} = 2.0$.

Finally, the full Coulomb interaction $V_{\text{C}}(r)$ between all charged monomers has to be taken into account:

$$V_{\text{C}}(r_{ij}, Z_i, Z_j) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0\epsilon_r r_{ij}} \equiv k_{\text{B}}T\ell_{\text{B}} \frac{z^2}{r_{ij}}, \quad (4)$$

where Z_i and Z_j are the number of elementary charges of the interacting particles i and j , e is the elementary charge and r_{ij} the distance between the particles. In

our polymer model, every monomer has charge valence z , meaning that the total charge valence of one PE is simply given by $Z \equiv Nz$. The Bjerrum length ℓ_{B} is defined as the length at which the electrostatic energy equals the thermal energy, viz.

$$\ell_{\text{B}} = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_{\text{B}}T}, \quad (5)$$

where $\epsilon_0\epsilon_r$ is the permittivity of the solvent. For water in room temperature one obtains $\ell_{\text{B}} = 7.1\text{\AA}$. The solvent is only taken into account via the dielectric constant $\epsilon_0\epsilon_r$. In our simulations, the Bjerrum length is fixed to $\tilde{\ell}_{\text{B}} = 3.0$, which is a realistic value for typical polyelectrolytes, such as the hydrophobic sodium poly(styrene-*co*-styrene sulfonate) (NaPSS) or the hydrophilic poly(acrylamide-*co*-sodium-2-acrylamido-2-methylpropane-sulfonate).[30]

The interaction between one PE and a spherical macroion of radius R_0 is modeled as follows: a monomer in distance r to the center of the colloid has a repulsive interaction $V_{\text{LJ}}^{\text{m}}(r)$ of the truncated and shifted Lennard-Jones type

$$V_{\text{LJ}}^{\text{m}}(r) = \begin{cases} \infty & \text{for } r \leq R_0; \\ V_{\text{LJ}}(r - R_0) & \text{for } r > R_0, \end{cases} \quad (6)$$

and an attractive Coulomb interaction $V_{\text{C}}(r, -Z, z)$, i.e., electrostatic interaction between a monomer of charge valence z and an opposite charge at the center of the macroion with valence $Z = Nz$, which exactly neutralize the charge of the polyelectrolyte. Naturally, the repulsive interaction between two macroions each with charge valence Z in distance r is given by $V_{\text{C}}(r, Z, Z)$. At a later stage we will include the effect of added salt by using a Debye-Hückel (screened) interaction, via

$$V_{\text{DH}}(r_{ij}, Z_i, Z_j) = \ell_{\text{B}} \frac{Z_i Z_j \exp[-\kappa(r_{ij} - R_i - R_j)]}{\beta r_{ij} (1 + \kappa R_i)(1 + \kappa R_j)} \quad (7)$$

where R_i and R_j are the hard core radii of the two interacting particles, in particular R_0 for the macroions and zero for the monomers and κ is the inverse screening length [31]. With $\beta = 1/k_{\text{B}}T$ we denote the inverse thermal temperature. κ is related to the salt concentration via

$$c_{\text{s}} = \kappa^2/2N_{\text{A}}\ell_{\text{B}}, \quad (8)$$

where N_{A} is Avogadro's number.

In this work, we focus our attention on the case where the bending energy of the chain is small compared to the Coulomb energy of the complex. A good estimate of the bending energy of a chain with persistence length l_{p} (isolated chain) and contour length l wrapped around a macrosphere to build a complex with radius R is given by

$$E_{\text{bend}} = k_{\text{B}}T \frac{l_{\text{p}}l}{2R^2} \quad (9)$$

This should be small compared to the Coulomb energy, what yields

$$2Z^2 \frac{\ell_B R}{l_p l} \gg 1 \quad (10)$$

as the condition for a complete adsorption of the chain. We measured the persistence length of an isolated chain by calculating the bondvector correlations in dependence of the contour distance between the bonds and determining the typical decay length. We find a linear dependence $l_p \approx l/2$ for a wide range of contour lengths if no intrinsic stiffness is applied. Inserting this scaling relation in (10) and using $Z \approx \tilde{l}z$ gives us a simple estimate for the wrapping state for chains with no intrinsic stiffness

$$4z^2 \tilde{l}_B \tilde{R} \gg 1. \quad (11)$$

Another limit where desorption can take place if the Coulomb coupling is small compared to the thermal fluctuations, e.g., the macroion is very big compared to the chain size. There is a complete adsorption of the chain onto the colloid if the electrostatic attraction is larger than the thermal fluctuations

$$Z^2 \frac{\ell_B}{R} \gg 1. \quad (12)$$

Although this adsorption is, strictly speaking, a metastable state (cf. Manning condensation picture), the unbinding probability becomes exponentially small as the charge of the PE is increased. In our simulations, and in agreement with previous works, the PE has always stayed at the close vicinity of the colloidal particle, since the parameters are chosen such that Eq. (10) and Eq. (12) are always satisfied.

Increasing chain stiffness has great influence on polarizability and interaction of these complexes. Some possible effects will be discussed briefly by introducing a simple harmonic coupling between the bonds of one PE

$$V_{\text{bond}} = \sum_{i=2}^{N-1} k_{\text{ang}} (\alpha_i - \alpha_0)^2, \quad (13)$$

where α_i is the angle formed between the connecting vectors of bonds i and $i-1$ and the bonds i and $i+1$. We choose an equilibrium angle $\alpha_0 = \pi$ and examine the effects of increasing chain stiffness by enhancing the bonding constant k_{ang} . Unless when explicitly mentioned, k_{ang} is always chosen to be zero.

We applied the standard MC Metropolis algorithm [32] where one MC step consists of a trial move of every monomer. The macroions were kept on fixed places. The acceptance rate for one MC sweep was approximately 50 percent. For faster equilibration and better statistics we introduced full chain moves where the whole PE is rotated around the closest macroion. Details describing these technic can be found in [33, 34]. Our systems were simulated without any cell in an infinitely wide space

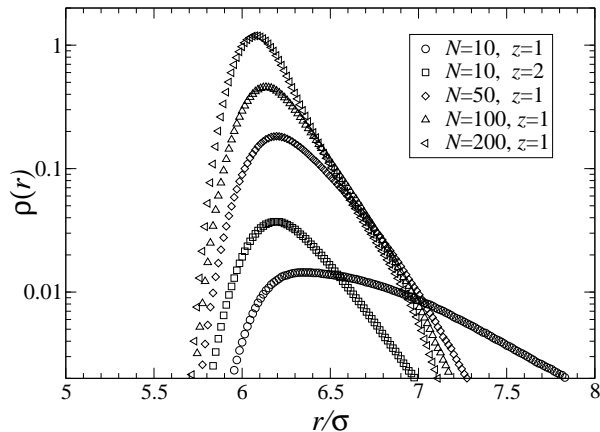


FIG. 1: Density profile of the monomers of one chain adsorbed to a spherical colloid with radius $\tilde{R}_0 = 5$ for different monomer numbers N and different number of charges per monomer z plotted versus the distance \tilde{r} to the center of the colloid. With increasing N and z the monomers move closer to the center and the effective complex radius R decreases. See Fig. 2 for simulation snapshots of one isolated complex.

where the full accurate Coulomb interaction without an cutoff is taken into account. We observed that only at low Coulomb coupling or large intrinsic stiffness the thermal fluctuations lead to an uncoupling of chain and colloid due to gain of entropy. After a long equilibration time (typically of 1.5×10^5 to 2×10^5 MC steps), the different observables were averaged over runs with 10^6 to 10^7 MC steps.

III. POLARIZABILITY OF A SINGLE COMPLEX

In this section we study the polarizability of a single complex consisting of one PE-chain with contour length l and linear charge density $\tau = Ze/l$ ($Z = Nz$) which is adsorbed onto a spherical colloid with radius R_0 and charge valence Z . In order to calculate the contour length in the simulation, we measure the mean distance between neighboring monomers: for a monomer charge $z = 1$ we obtain $l \approx N\sigma$ and for $z = 2$ we obtain $l \approx 1.2N\sigma$, i.e., $\tau\sigma = \tilde{\tau} = 1$ for $z = 1$ and $\tilde{\tau} = 0.83$ for $z = 2$. In what follows we will extensively use as a parameter the ratio between the PE length and the *effective* diameter of the complex ($2R$)

$$x \equiv \frac{l}{2R}. \quad (14)$$

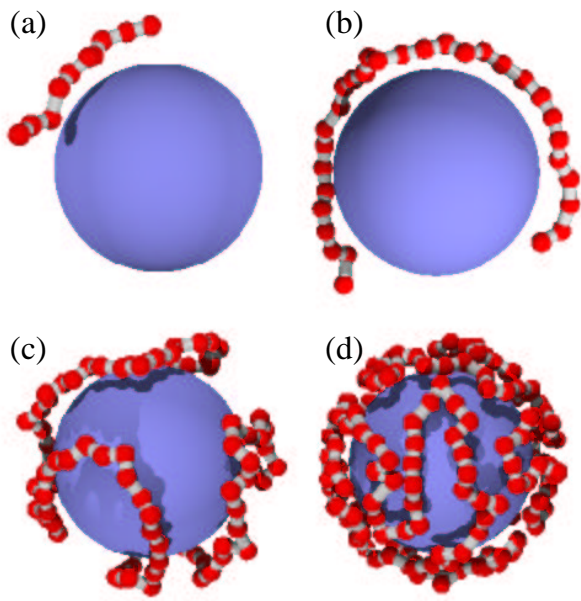


FIG. 2: Computer simulation snapshots of a PE adsorbed to a spherical colloid with radius $\tilde{R}_0 = 5$ for (a) $N = 10$, (b) 30, (c) 100 and (d) 200 monomers. The number of elementary charges per monomer is $z = 1$. The monomers are rendered as dark spheres with diameter σ .

For $x = \pi$ the chain length is equal to the circumference of the complex. For a chain much thinner than the colloid radius and at low temperatures, the effective radius R should be given by $R \approx R_0$. However, since in our simulations the monomers have a size that is comparable to the colloidal particle, this effective radius is approximately $R \approx R_0 + \sigma$, with some dependence on the number of monomers in a chain and on the charge of each monomer, as can be seen in Fig. 1. In this figure, we show the density profile $\rho(r)$ of the monomers surrounding a colloid with radius $\tilde{R}_0 = 5$ for chains with different number of monomers N and different monomer charges $z = 1, 2$. As one would expect, a higher Coulomb coupling between the PE and the colloid (through a higher total charge in the PE) leads to a reduction of the effective radius of the complex, here assumed to be at the maximum of the monomer distribution. Simulation snapshots are shown in Fig. 2 for systems with different numbers of monomers and no external field. As already mentioned, the dependence of R on the parameters of the PE is so weak that it can be assumed for all practical purposes to be a constant for a wide range of chain lengths. In the following we will choose $\tilde{R} = 6.3$ for short chains $x \lesssim \pi$ and $\tilde{R} = 6.1$ for long chains $x \gtrsim \pi$ as effective complex radius, for a fixed colloid radius $\tilde{R}_0 = 5.0$. We checked that all forthcoming results obtained from the simulations are independent of the chosen radius of the colloid. All theoretical results in this and the following section should hold generally for all colloid sizes.

We start our analysis with chains which are short compared to the size of the colloid, viz. $x < \pi$. In this regime the PE-colloid complex has always a nonvanishing instantaneous dipole moment, since the center of charge of the chain cannot coincide with the center of the colloid. We define the dipole moment \vec{P} of the complex as

$$\vec{P} = \frac{Ze}{N} \sum_{i=1}^N (\vec{r}_i - \vec{R}_c), \quad (15)$$

where \vec{R}_c is the vector pointing to the center of the colloid and \vec{r}_i is the position of monomer i . Notice that, with this definition, the magnitude of \vec{P} is given by Ze times the distance between the center of the colloid and the center of charge of the PE-chain. It is easy to show that the mean dipole moment of a thermally fluctuating rigid dipole with length d and charge Ze in an electrical field E is

$$P = Ze d \left(\coth(\beta Ze d E) - \frac{1}{\beta Ze d E} \right), \quad (16)$$

where P is the magnitude of \vec{P} and $\beta \equiv 1/k_B T$. Introducing the rescaled dimensionless dipole moment

$$P^* = \frac{P}{\sigma e} \quad (17)$$

and electric field

$$E^* = \beta \sigma e E \quad (18)$$

one can rewrite Eq. (16) as

$$P^* = Z \tilde{d} \left(\coth(Z \tilde{d} E^*) - \frac{1}{Z \tilde{d} E^*} \right), \quad (19)$$

where $\tilde{d} = d/\sigma$. For low temperatures or strong electrical fields $Z \tilde{d} E^* \gg 1$, the mean dipole moment saturates to $P^* = Z \tilde{d}$, while for small fields $Z \tilde{d} E^* \ll 1$ and we recover the well known result

$$P^* = \frac{Z^2 \tilde{d}^2}{3} E^*. \quad (20)$$

For the case of a chain adsorbed onto a spherical colloid, the center of charge of the chain is on average somewhere between the center of the colloid and its surface. Assuming that the chain can be approximately described by a circular arc fluctuating on the surface of the colloid (see eg. Fig. 2(b)), the distance between the center of the colloid and the center of charge of the chain is given by

$$\tilde{d} = \tilde{R} \frac{\sin(x)}{x}, \quad (21)$$

where $\tilde{R} = R/\sigma$. Our model is assumed to work for chains shorter than the circumference of the sphere, i.e. Eq. (21) holds for $0 < x < \pi$.

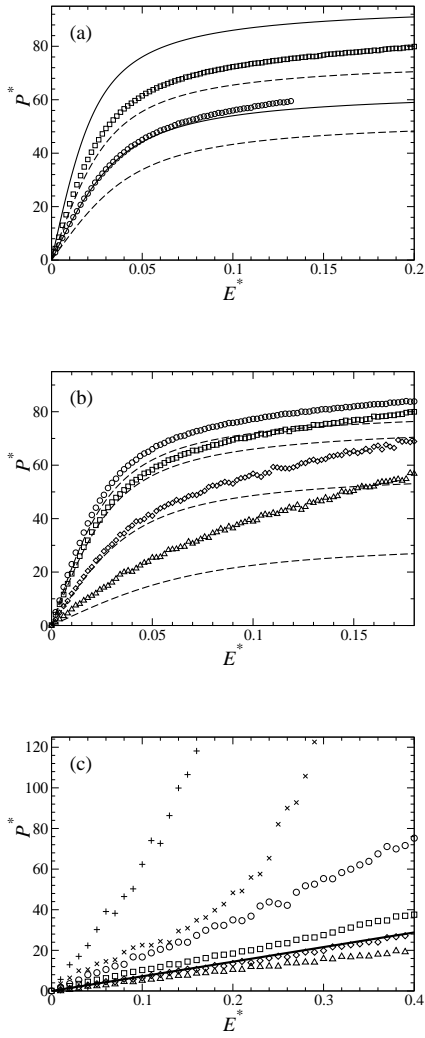


FIG. 3: Dimensionless dipole moment $P^* = P/\sigma e$ of one PE-colloid complex versus the dimensionless external electrical field $E^* = \beta\sigma e E$ for different chain lengths, $z = 1$ and a colloidal radius $\tilde{R}_0 = 5$. Symbols are computer simulation results, lines are theoretical results. Plot (a) shows the scaled chain lengths $x = 0.79$ (circles) and $x = 1.19$ (squares). The dipole moment increases with x . Lines are the theoretical results, Eq. (19), using $\tilde{d} = \tilde{R}$ (solid) or the effective dipole length $\tilde{d} = \tilde{R} \sin(x)/x$ (long dashed). Plot (b) shows the results for $x = 1.59$ (circles), $x = 1.99$ (squares), $x = 2.38$ (diamonds), $x = 2.78$ (triangles). Note that the dipole moment now decreases with increasing x . The long dashed lines is theory as used in (a). Plot (c) shows the results for $x = 4.10$ (circles), $x = 8.20$ (squares), $x = 16.40$ (diamonds), $x = 24.60$ (triangles). The solid line is the dipole moment of a conducting sphere with radius $\tilde{R}_{cs} = 6.1$ according to $P^* = \alpha_{cs} E^*$, where α_{cs} is given by Eq.(24). In (c) we also show the effect of increasing chain stiffness for $x = 4.10$. The harmonic coupling is quantified by $\beta k_{\text{ang}} = 4.0$ (crosses) and $\beta k_{\text{ang}} = 5.0$ (plusses).

In Fig. 3 we compare the dipole moment of a complex in an external field for various chain lengths and $z = 1$ as a function of the external field from computer simulations and from Eq. (19). Note that $\tilde{R}_0 = 5$ and the effective radius is assumed to be $\tilde{R} = 6.3$ for $x \lesssim \pi$. For the theoretical effective dipole length \tilde{d} , we use the result from Eq. (21) when $0 \lesssim x \lesssim \pi$ and Eq. 10 is satisfied. If Eq. 10 is not fulfilled, the chain is essentially a straight rod that touches the sphere—in this case, the effective length of the dipole is simply given by R . On the other hand, for $x \gtrsim \pi$ the chain cannot be approximated by a two-dimensional circle and Eq. (19) breaks down.

The polarizability α of the complex is defined as the slope of its dipole moment as a function of the electric field

$$\alpha = \frac{dP^*}{dE^*}. \quad (22)$$

The behavior of α is shown in Fig. 3: in the regime of small electric fields, the polarizability is constant, here we are in the linear response regime, see Eq. (20). In the regime where the interaction energy between the dipole and the applied field largely exceeds the thermal energy ($ZdE^* \gg 1$) the polarizability becomes very small; this latter behavior is not surprising, since in this regime the dipole is essentially pointing towards the field, and thermal fluctuations which tend to destroy this alignment at small fields become unimportant. In our simulations we never really reach the point where the polarizability becomes zero since at some point the field is strong enough to induce the unbinding of the chain from the colloidal particle. Plot (a) shows the dipole moment for two short chains, viz. $x = 0.79$ and $x = 1.19$. Notice that the system with former value of x is very well described by P with $d = R$, while the latter tends to approach the dipole moment which uses d given by Eq. (21). The reason for this is the fact that in the system with smaller x the polyelectrolyte has a bending energy of the order of the Coulomb energy of the complex, see Eq. (10), and the system behaves more like a rigid rod in contact with a sphere than as a circular arc, as described by Eq. (21). The curve for $x = 0.79$ in (a) stops abruptly since the critical field for the desorption is reached.

Longer chains lead to a decrease of the polarizability at small fields as can be seen in plot (b) of Fig. 3, where we plot $x = 1.59, 1.99, 2.38$ and 2.78 . This effect is a result of the dislocation of the center of charge of the chain to a position that is closer to the center of the colloid, according to Eq. (21). Note that complexes with medium-sized chains tend to approximately exhibit dipole moment of a circular arc on a sphere. However, complexes with long chains, $x \gtrsim \pi$ tend to have a linear response to a wider range of the applied field (see plots (b) and (c)), which is a consequence of the fact that larger chains have more charge at fixed charge density, and so the fields needed to deviate from a linear law are larger; also, the fact that longer chains have more possible conformations leads to a qualitative change in the response of the complex, and

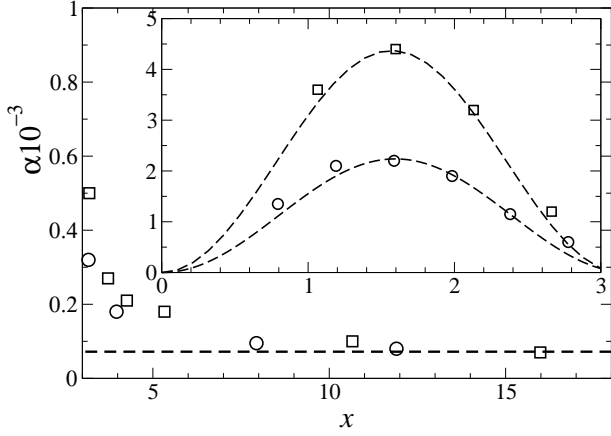


FIG. 4: Dimensionless polarizability α versus the scaled chain length x at small applied fields. The symbols denote the simulation, the dashed lines are the theoretical results from Eq. (23) (inset) and Eq. (24) for charges per monomer $z = 1$ (circles) and $z = 2$ (squares). The colloid radius is $\tilde{R}_0 = 5$.

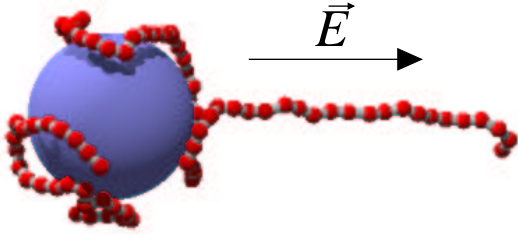


FIG. 5: Simulation snapshot of a PE-colloid complex in an external electrical field E . The chain has an intrinsic stiffness due to the harmonic coupling Eq. (13). The bonding constant is $\beta k_{\text{ang}} = 4.0$, the number of monomers is $N = 100$, $E^* = 0.4$, $z = 1$, and $\tilde{R}_0 = 5.0$.

a simple model as the one used above is no longer valid.

Let us have a closer look at the polarizability for small fields and short chains. Inserting Eq. (21) into (20), one obtains, for small fields, the dimensionless polarizability of the complex as a function of the PE-chain length and charge density

$$\alpha = \frac{4\tilde{\tau}^2 \tilde{R}^4}{3} \sin^2(x). \quad (23)$$

where the linear charge density τ has been rescaled such that $\tilde{\tau} = \sigma\tau$. For a fixed τ , this polarizability shows a maximum at $x = \pi/2$ for a chain with length equal to half the circumference of the colloid and vanishes for $x = \pi$, when a chain has a full circumference. Indeed,

this behavior predicted by theory is very close to in the computer simulation results in the inset of Fig. 4, where we plot α for small fields for a colloid with fixed radius $\tilde{R}_0 = 5$ and $\tilde{R} = 6.3$ and monomer charges $z = 1$ and $z = 2$.

In the cases where the complex contains a long chain $x \gtrsim \pi$, the polarizability Eq. (23) loses its validity. Note that in this case, the chain is wrapped around the sphere more than one time and one expects a small or vanishing dipole moment. Because the monomers tend to distribute themselves on average more or less homogeneously throughout the surface of the sphere, one could expect the response of the PE-colloid complex to electric fields to become similar to the response of a neutral conducting sphere, which has a dimensionless polarizability given by (see. e.g., [35])

$$\alpha_{cs} = \frac{\tilde{R}_{cs}^3}{\tilde{\ell}_B} \quad (24)$$

where R_{cs} is the radius of the sphere and $\tilde{\ell}_B = \ell_B/\sigma$. Not surprisingly, in the limit of very large chains $x \gg \pi$ this latter result is recovered, as shown in Fig. 4. For this comparison we have chosen $\tilde{R}_{cs} = 6.1$ for the effective sphere radius. Note that the simulation results for long chains are independent of the linear charge density in agreement with Eq. (24).

Let us now discuss possible effects of an increasing intrinsic stiffness of the chain. For short chains we observe an increasing polarizability if the harmonic coupling is strong enough to decrease the curvature of the chain around the spherical macroion meaning that the bending energy reaches values of the order of the Coulomb energy.

The center of charge of the PE is less close to the colloid center and the effective dipole length increases. As an upper limit the maximal dipole moment is then given by Eq. (3) inserting $d = R$, with R effective complex radius. However, for the case, where the bending energy comes close to the Coulomb energy, we observe that the chain decouple easily from the colloid and no bound complex is formed.

More interesting is the behavior for long chains. For long chains with a large bending energy and no electrical field, so called one-tail or two-tail configurations sets in [1, 5, 13, 15, 16]. Here part of the PE is still adsorbed on the colloid while one or two rigid parts are stretched away from the macroion to lower the bending energy and so minimize the total energy. In an electrical field the one tail configuration is obviously promoted due to the strong dipolar interaction with the external field, see Fig. 5 for a simulation snapshot. We make the following observation in our simulation: if the chain is fully adsorbed on the colloid the polarizability is still given by Eq. (24) independent of the higher chain stiffness, only the effective complex radius increases slightly due to a less tight wrapping around the colloid. But for a sufficiently strong chain rigidity a small external electrical field can now pull

a part of the chain in direction of the chain to lower the bending and dipole energy and a dipolar one tail configuration is formed. Two examples of the dipole moment are shown in Fig. 3 (c) for $x = 8.34$, $\beta k_{\text{ang}} = 4.0$ and $\beta k_{\text{ang}} = 5.0$. For small fields the chain is fully adsorbed and the polarizability is the same as for the $\beta k_{\text{ang}} = 0$ case. Then the increased stiffness leads to a continuous unwrapping in the one-tail configuration and the polarizability increases dramatically due to formed dipole. Further increasing of the electrical field lengthens the tail and eventually decoils the chain from the colloid. The longer the tail, the larger is the dipole moment and the polarizability increases with growing field until complete desorption is accomplished. A snapshot for an one-tail complex in an electrical field E is shown in Fig. 5.

Finally, adding salt obviously increases the polarizability as the range and strength of the Coulomb attraction between PE and the colloid is screened and the effective complex radius grows. We take the presence of salt into account by using a Debye-Hückel potential between the monomers (and ignoring any polarizability due to the salt), going up to a salt concentration of $c_s \approx 1.0\text{M}$. We observe that Eq. (23) for short chains and Eq. (24) for long chains still hold as long a stable complex is formed but with a slightly larger effective radius R or R_{cs} , respectively.

IV. EFFECTIVE INTERACTION BETWEEN TWO COMPLEXES

We now turn to the interaction between two complexes at distance r . The effective force acting on the center of one colloid in the simulation is calculated as follows: consider two spherical colloids with radius R_0 and center-to-center distance r , which means that they have a surface-to-surface distance of $s = r - 2R_0$. The energy of one colloid in presence of one monomer at distance r^m is the sum of Coulomb attraction and short-ranged LJ-repulsion

$$V_{\text{mon}}(r^m) = V_C(r^m, -Z, z) + V_{\text{LJ}}^m(r^m). \quad (25)$$

After a sufficiently long equilibration time, the force F_m of all monomers acting on one of the colloids is measured by performing the statistical average

$$F^m(r) = \left\langle \sum_{i=1}^M \sum_{j=1}^N \nabla_r V_{\text{mon}}(r_{ij}^m) \right\rangle, \quad (26)$$

where the sum in i goes over all M PE-chains and the sum in j considers all N monomers of each chain. r_{ij}^m is the distance of monomer j from the i th PE-chain to the center of the considered colloid. The brackets in Eq. (26) denote ensemble statistical average. We obtain the total force between the colloids in distance r by adding the direct repulsive Coulomb force between the colloidal particles, viz. $Z^2 e^2 / 4\pi\epsilon_0\epsilon_r r^2$. The total force can be then divided into two contributions,

$$F(r) = F_C(r) + F_{\text{LJ}}(r). \quad (27)$$

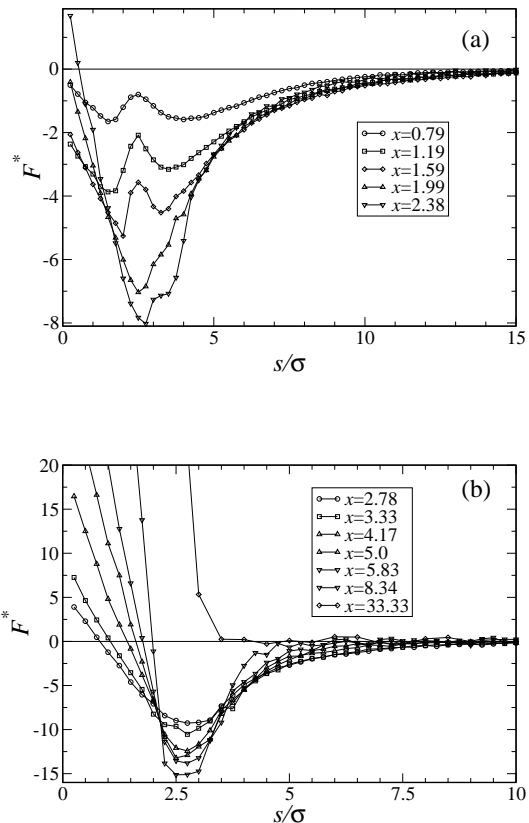


FIG. 6: Simulation results of the dimensionless force $F^* = \beta \sigma F$ between two PE-colloid complexes versus the surface-surface distance \tilde{s} for different chain lengths x and $z = 1$. The colloid radius is $\tilde{R}_0 = 5.0$. Lines are guide to the eye. Plot (a): short chains $x \lesssim \pi$. Plot (b): long chains $x \gtrsim \pi$.

where

$$F_C(r) = \frac{Z^2 e^2}{4\pi\epsilon_r r^2} + \left\langle \sum_{i=1}^M \sum_{j=1}^N \nabla_r V_C(r_{ij}^m, Z, z) \right\rangle \quad (28)$$

is the Coulomb force due to the electrostatic attraction of all monomers and the electrostatic repulsion of the second colloid and

$$F_{\text{LJ}}(r) = \left\langle \sum_{i=1}^M \sum_{j=1}^N \nabla_r V_{\text{LJ}}(r_{ij}^m) \right\rangle \quad (29)$$

resulting from the excluded volume interaction of the monomers through the aforementioned Lennard-Jones potential. Since this force is essentially a hard-core exclusion force, one can consider this as describing the interaction due to gain and loss of entropy. For this reason we call it entropic force.

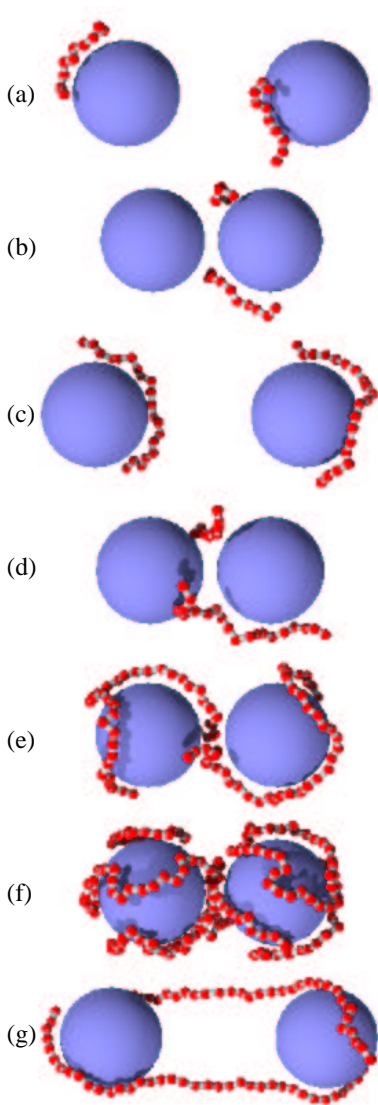


FIG. 7: Snapshots of two interacting PE-colloid complexes with colloid radius $\tilde{R}_0 = 5$, $z = 1$, chain length x and surface-to-surface distance s . From top to bottom: (a) $x = 0.79$, $\tilde{s} = 8.0$; (b) $x = 0.79$, $\tilde{s} = 1.5$; (c) $x = 1.59$, $\tilde{s} = 10.0$; (d) $x = 1.59$, $\tilde{s} = 1.5$; (e) $x = 4.10$, $\tilde{s} = 2.5$; (f) $x = 8.20$, $\tilde{s} = 2.0$; (g) $x = 3.28$, $\tilde{s} = 11.25$, $\beta k_{\text{ang}} = 4.0$

Based on the previous discussion on the polarizability of a single complex, one can essentially expect two distinct regimes for the interaction between two equal symmetric complexes, viz. when the chains are short and when the chains are long. Fig. 6 summarizes our results, where the dimensionless force $F^* = \beta \sigma F$ is plotted for systematical increase of x and $z = 1$ as a function of s , the surface-to-surface distance. Negative forces mean attraction while positive forces mean repulsion. See Fig. 7 for some typical simulation snapshots. Notice that for short chains, a long-range attractive tail is present. This is consistent, as we will demonstrate, with a dipolar in-

teraction between the complexes. For longer chains, this long range tail disappears, and only a strong short-range attraction (also present for shorter chains) survives. In the limit of very long chains, only a repulsive steric interaction is present. We discuss these results in more detail in the following.

A. Short chains

In the previous section we showed that the complexes with short chains respond like permanent dipoles to electric fields. When interacting with each other, it is reasonable to expect that in such case a dipole-dipole interaction shows up, at least at large separations between complexes. One way of estimating this long-range tail is by looking at the interaction between two fluctuating permanent dipoles $P = Zed$ with length d as given by Eq. (21) expressed through the so called Keesom energy [36]

$$\beta v(r) = \frac{1}{3} \frac{Z^4 \tilde{l}_B^2 \tilde{d}^4}{\tilde{r}^6}. \quad (30)$$

After some algebra one obtains for the interaction energy between two PE-colloid complexes with $0 \lesssim x \lesssim \pi$

$$\beta v(r) = -\frac{16 \tilde{l}_B^2 \tilde{\tau}^4 \tilde{R}^8}{3 \tilde{r}^6} \sin^4(x). \quad (31)$$

where r is the distance between the dipole and the polarizable object. Accordingly, the attractive force acting on the polarizable object is

$$F^*(r) = -\frac{32 \tilde{l}_B^2 \tilde{\tau}^4 \tilde{R}^8}{\tilde{r}^7} \sin^4(x). \quad (32)$$

We easily see that the electrostatic interaction has a maximum of strength for a length $x = \pi/2$ according to the behavior of the polarizability of one isolated maximum. Another remarkable feature is the strong dependence on the complex radius which goes with the eighth power for a fixed x . A comparison of expression (32) with the long distance tail of the force between the complexes is done in Fig. 8 for different chain lengths and charge densities, leading as expected to a nice agreement. As theoretically predicted the simulations show a maximal dipole interaction for a length $x \approx \pi/2$.

In order to obtain some insight into the conformational properties of the interacting complexes we introduce the order parameter

$$\phi = \frac{\vec{P}_1 \cdot \vec{P}_2}{|\vec{P}_1| |\vec{P}_2|}, \quad (33)$$

which is the normalized dot product between the two dipole moments of each complex. For a dipole-dipole interaction $-1 \leq \phi \leq 1$ should be positive as both dipoles show in the same direction. Negative values of ϕ mean

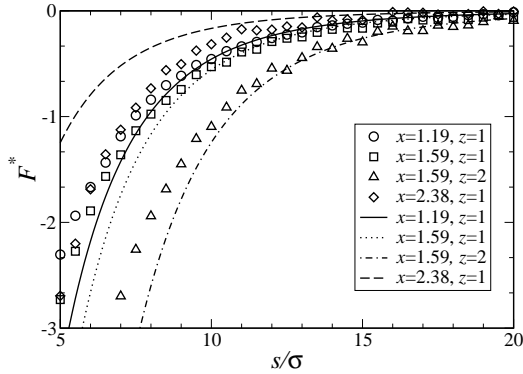


FIG. 8: Interaction force between two PE-colloid complexes for long distances and short chains ($x \lesssim \pi$). The plot shows a comparison made between the analytical expression Eq. (32) for the dipole-dipole interaction (lines) and the computer simulation results (symbols) for colloids with size $\tilde{R}_0 = 5$ and various chains lengths x and monomer charge z .

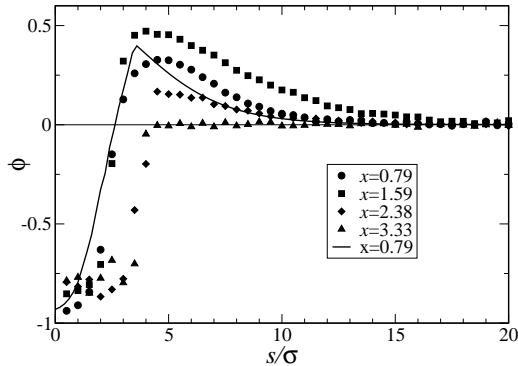


FIG. 9: Simulation results (symbols) of the order parameter ϕ versus the surface-to-surface distance of two PE-colloid complexes with $\tilde{R}_0 = 5.0$, $z = 1$, and different chain lengths. The solid line is the numerical solution of the toy model sketched in Fig. 10 for $x = 0.79$.

that the dipoles are on average pointing in opposite directions. By studying the average distance between the center of charge of the chains in our simulations, we found that every time ϕ becomes negative the monomers accumulate between the colloids, meaning that each dipole moment points in direction of the other complex in average.

Fig. 9 shows ϕ as a function of separation for different chain lengths with $z = 1$ at fixed complex radius. As expected, for short chains and large distances, ϕ is positive:

the dipoles of the two complexes basically point in the same direction and produce the dipole-dipole interaction as discussed above. Note that the largest values for ϕ are obtained for complexes with chains with $x = 1.59$, a value close to $x = \pi/2$ where the polarizability is maximal. Typical configurations in the dipole-dipole regime are shown in Fig. 7 (a) and (c) where the order parameter ϕ has positive values. A relatively sharp transition from positive to negative values of ϕ is observed for distances $\tilde{s} \approx 4$ for all values of x .

For small distances, ϕ becomes negative for all systems studied. As mentioned before, this means that the centers of charge of the chains are located somewhere between the colloids, something that turns out to be always true as $\tilde{s} \lesssim 4$. This can also be seen in snapshots for close distances of the complexes as for instance in Figs. 7(b) and (d).

In order to obtain a better understanding of the small distance behavior of the force for complexes with short chains, Fig. 6 (a), consider the toy model depicted in Fig. 10. Here the chains are modeled as hard spheres with effective diameter a . Each sphere sticks to one colloid and can only move on the surface of the macro sphere with radius R_0 . One small sphere belonging to one colloid can not penetrate into the other complex, and the center-to-center distance between the colloids is r . In this case, the effective complex radius is $R = R_0 + a/2$.

As previously shown, complexes with short chains behave like rigid dipoles with length d which is dependent of the chain contour length l . Hence, in our toy model the complex has a dipole moment in direction from the center of the colloid to the center of the small sphere with an effective length d and charge Z . For distances $r > 2(R_0 + a)$ this model shows a simple dipole-dipole attraction, whereas for smaller distances the dipole-dipole attraction is modified by the restricted number of available configurations.

One can find the force between the complexes for this toy model by numerically solving the partition sum and calculating the free energy as a function of the distance r . The results for a chain length $x = 0.79$ is plotted in Fig. 11 together with the corresponding simulation data. According to the results from the previous section we use $\tilde{d} = 6.3$. We use the diameter of the small spheres a as a fit parameter, which should in any case be of the order of the monomer size. This parameter does not affect the dipole-dipole interaction, being only important when the deviations from the pure dipole-dipole interaction sets in. For $x = 0.79$ and $z = 1$ we used $\tilde{a} = 3.6$. This model leads to a qualitative agreement for the short range behavior of the force, as depicted in Fig. 11: while the scale of the force is larger for the toy model, the minima and maxima are located at approximately the right distances. In other words, this means that the behavior observed for the force at small distances and for small chains (a force with two minima) is at least partially explained by the restriction of the number of available configurations of a system that is still essentially composed by two interact-

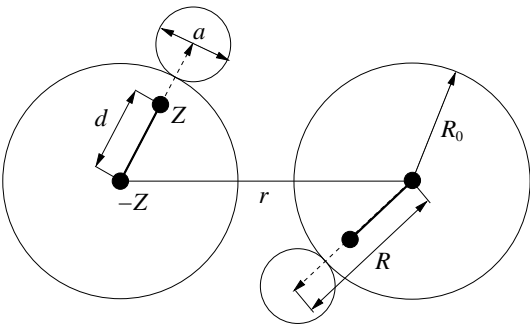


FIG. 10: Schematic representation of the toy model for two PE-colloid complexes at distance r for short chain lengths ($x \lesssim \pi$). One complex behaves like a dipole with charge Z and length d (dumbbells). The short chain is modeled as a simple sphere sticking on the surface of the colloid in distance $R = R_0 + a/2$ where R_0 is the colloid radius and a is the effective diameter of the fluctuating chain.

ing dipoles.

It is also interesting to study the behavior of the order parameter ϕ of our toy model solved for the length $x = 0.79$ and $z = 1$ also plotted in Fig. 9. The qualitative behavior in dependence of the distance is quite the same as in the simulation. At $\tilde{s} \approx 4.5$ the dipole-dipole regime breaks down and ϕ descends to negative values for closer distances s . The negative value of ϕ means that in our toy model both small spheres are located mainly between the macroions for distances. One is lead to conclude that due to the excluded volume interaction of the small sphere/chain with the macrosphere the dipole-dipole interaction is disturbed and the the spheres/chains locate themselves between the macroions, contrary to what happens in the dipole-dipole interaction regime.

B. Long chains

Increasing the chain length we observe a deep short ranged attraction as plotted in Fig. 6 (b) which is in agreement with previous studies[20, 21, 37]. The depth of attraction initially grows with increasing chain length while the range of attraction shrinks. Further increasing of the chain length leads to a pure repulsion of the complexes. The attraction is essentially of entropic origin, as the comparison between the Coulomb force F_C and the entropic force F_{LJ} as defined in Eq. (28) and (29) shown in Fig. 12 demonstrates: for $x = 3.28$ (large chain) the entropic force clearly dominates over the Coulomb. For distances comparable to some monomer lengths the chain is able to gain entropy by bridging the two colloids with some parts of the chain, as seen for instance in snapshots Figs. 7(e) and (f). In agreement with the absence of the dipole-dipole interaction between the complexes, note that for chains with $x > \pi$, only zero or negative

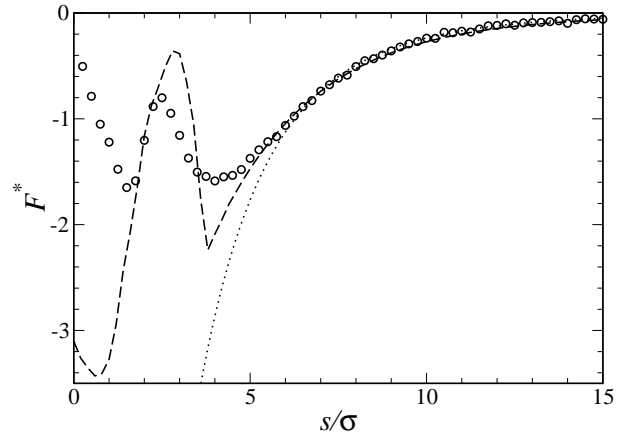


FIG. 11: Interaction force between two PE-colloid complexes with a short chain $x = 0.79$ and $z = 1$. Simulation results (circles) are compared to the numerical solution of the toy model depicted in Fig. 10 (dashed line) and the analytical result for the dipole-dipole interaction (dotted line).

values of ϕ are observed: at short enough distances, the chains bridge between the colloids, otherwise the complexes basically ignore each other and no long-range force is present.

Not surprisingly, for small distances the attraction of two long chains is indistinguishable from the behavior of one chain with the combined length of the two chains, as depicted in Fig. 13, where the force between two complexes with chains with $x = 4.10$ is compared with the force between colloids in the presence of only one chain with $x = 8.20$. The force is the same for small distances $\tilde{s} < 5$ where the entropic bridging regime is found. The linear long ranged attraction of the single chain system is due to an energetic bridging already observed and discussed in Refs. [21] and [20].

For complexes with very long chains only a pure repulsion is observable, see eg. $x = 33.33$ in Fig. 6 (b). If the chain is long enough to cover the whole surface of the macroion no bridging is possible due to the electrostatic repulsion between the approaching chain and the shell of monomers around the macroion. A simple theoretical estimate for the critical length when pure repulsion occurs is obtained by equating the available surface of the spherical complex $A = 4\pi R^2$ with the area $A = l\sigma$ of the covering chain with length l and thickness σ , which yields

$$x_c = 2\pi R/\sigma. \quad (34)$$

We compared above estimate for two different complex radii $R \approx 3.0$ and $R \approx 6.0$ with simulation results and

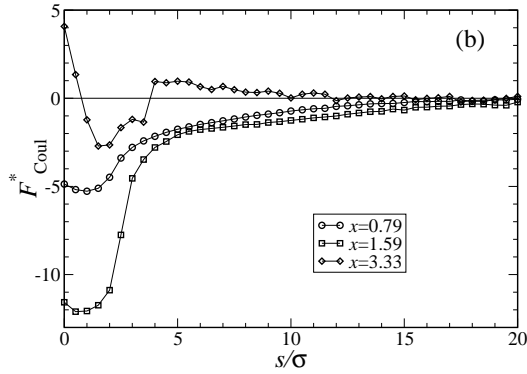
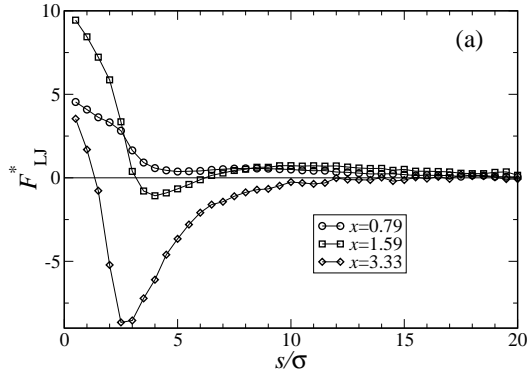


FIG. 12: Plot (a): simulation results of the entropic part of the force $F_{LJ}^* = \beta \sigma F_{LJ}$ defined in Eq. (29) for different chain lengths and $z = 1$. The colloid radius is $\tilde{R}_0 = 5.0$. Plot (b): simulation results for the Coulombic part of the force $F_C^* = \beta \sigma F_C$ Eq. (28) using the same parameters as in plot (a). Lines are guide to the eye.

found $x_c \approx 15$ and $x_c \approx 33$ which is very close to the theoretical results $x_c = 18.85$ and $x_c = 37.70$. See Fig. 6 (b) for examples for the force between two complexes with a colloid radius $\tilde{R}_0 = 5$.

C. Effects of chain stiffness or salt

Increasing chain stiffness has an enormous influence on the interaction for all chain lengths. The mechanism of interaction changes completely as now the rigid chains try to bridge between the colloids to lower their bending energy which now is not neglectable comparable to the electrostatic energy. Simulation results for increasing chains stiffness are shown in Fig. 14 for a chain length $x = 3.28$. At a critical distance the chains bridge from one colloid to the other as shown in the snapshot in Fig. 7 (g). We checked that the isolated complex with

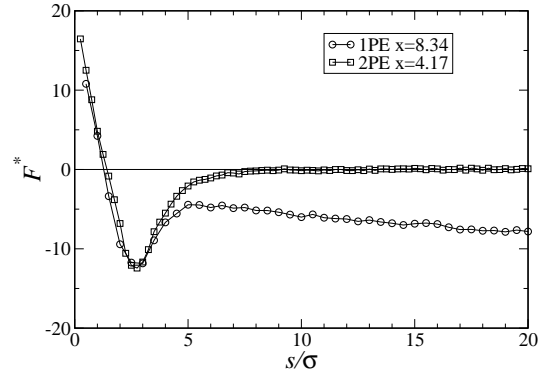


FIG. 13: Simulation results of the force between two colloids with $\tilde{R}_0 = 5.0$ carrying two chains of length $x = 4.17$ (squares) and one chain with doubled length $x = 8.34$ (circles). The monomer valence is $z = 1$. Lines are guide to the eye.

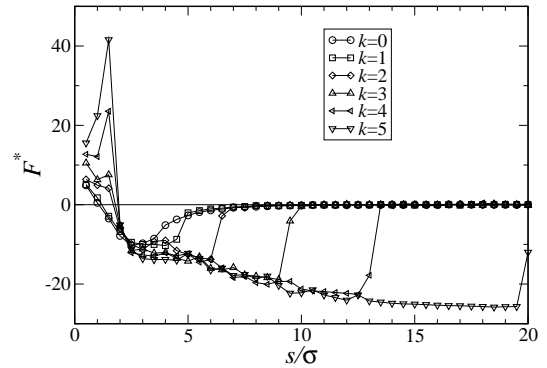


FIG. 14: Simulation results of the force between two PE-colloid complexes for a fixed chain length $x = 3.33$, $z = 1$, and different rigidity $k = \beta k_{\text{ang}}$ according to Eq. (13). Lines are guide to the eye.

this length and bonding parameters shows always a complete adsorption of the PE to the charged sphere and no one- or two-tail configurations. The functional behavior of the force is linear for a wide range of the distance. This is similar to the interaction of two colloids with only one chain, see Fig. 13 discussed in Ref. [21] where the sharing of the chain was named energetic bridging as one chain is then able to neutralize both colloids and lower the electrostatic energy. In our similar case with two chains the bridging is due to lowering of the bending energy of the rigid chains.

Adding salt shows no surprising behavior of the interactions for all chain length. The shape and qualitative

behavior of the force remains the same for low salt concentration, only the magnitude of attraction decreases. As expected, the interaction of short chains is more affected by adding salt since the long-range attraction is due to electrostatic interaction which are now screened. Here differences already occur for a salt concentration of $c_s \approx 0.05\text{M}$ and the long-ranged attraction vanishes completely for $c_s \approx 0.2\text{M}$ (measured for $x = 1.59$ and $z = 1$). The interaction of long chains has entropic origin and remains unaffected till c_s exceeds values of approximately 0.1M for a chain length $x = 5.0$ and $z = 1$. For values of $c_s \approx 1.0\text{M}$ still a weak attraction is observed.

V. FINAL REMARKS

In summary, we studied the polarizability and interaction of PE-colloid complexes for the case where the chain is fully adsorbed on the macroion. The polarizability is strong for small chains and small electrical fields and has a maximum for chain length comparable to the circumference of the colloid. It can theoretically be described in terms of a thermally fluctuating dipoles with an effective length which depends on the chain length. For chains longer than the circumference of the macroion the polarizability is of the order of the polarizability of a classical conducting sphere with radius of complex size. The interaction shows a van der Waals like attraction for short chains and a deep short ranged attraction for midsized chains. Exceeding a critical chain length x_c the interaction is completely repulsive.

One of the interesting conclusions that one can draw from this work concerns the stability of colloidal suspensions which are stabilized by adsorption of polyelec-

trolytes. While for chains which are very long compared to the size of the particles $x > x_c$ this is indeed an effective mechanism of stabilization (as shown in Fig. 6 for $x = 33.33$, where the forces are always repulsive or zero), complexes with chains with a length comparable with the colloidal size exhibit a short range attraction due to the so-called bridging between the particles. However, for chains that are smaller than the colloid, a long-range attraction is present and one should expect such suspensions to behave like dipolar fluids[38]. This shows that the stabilization of colloidal suspensions by polyelectrolyte adsorption is strongly dependent on the chain size relative to the colloidal size: for long chains the suspensions are always stable (only repulsive forces between the particles), while for mid-sized and short chains there is attraction between the complexes and a salting-out can occur. Although our studies were essentially done for isolated, strongly charged and symmetric complexes these conclusions should hold in more realistic situations where the chains have some polydispersity and the complexes are at relatively high concentrations, since the only key point is the existence of the complexes.

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