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Long-Ranged Attractive Forces Induced by Adsorbed Dendrimers: Direct Force Measurements and Computer Simulations

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Interaction forces between charged interfaces in the presence of oppositely charged dendrimers are studied by experiment and simulation. The experiments involve direct force measurements with an atomic force microscope (AFM) between two negatively charged colloidal particles in the presence of adsorbed, positively charged globular dendrimers. The simulations are carried out by treating the macroions explicitly, while the small salt ions are treated implicitly through the Debye—Hückel approximation. The system undergoes overcharging, and at the isoelectric point long-ranged attractive electrostatic forces are present. The range of the attraction is on the order of half the Debye length at high salt concentration, but it becomes smaller at low salt concentration. Away from the isoelectric point, repulsive electrostatic forces are observed due to diffuse layer overlap. A semiquantitative agreement between experiment and simulation is obtained, despite the fact that the simple theoretical model does not involve any adjustable parameters. This study provides for the first time detailed comparison between experimental and simulation data of interaction forces between colloidal particles in the presence of multivalent macroions and monovalent salt ions.

Introduction

Since ion—ion correlations were recognized to be essential for a correct description of electrolyte solutions and electrical double layers,[1–3] remarkable activity has developed in this field.[4–12] Two spectacular manifestations of ion—ion correlations are the occurrences of charge inversion and attractive forces between equally charged colloids. While charge inversion with small multivalent ions has been known for a long time,[13] its relation to ion—ion correlations was recognized much later.[14] Attractive electrostatic forces between two identical interfaces were predicted on theoretical grounds,[8,9,15,16] but only recently have similar forces been reported experimentally.[10] However, it remains unclear whether such forces exceed van der Waals forces and how they compare to theoretical predictions.

Oppositely charged linear polyelectrolytes may equally induce charge inversion of water—solid interfaces.[8,17–21] The adsorption of polyelectrolytes is usually accompanied by coadsorption of small ions. Nonelectrostatic interactions might be equally important, and one finds that the attractive forces are stronger than the van der Waals forces near the isoelectric point (IEP).[17–19] However, systems involving linear polyelectrolytes are complicated by conformational transitions on the surface and slow kinetics of surface rearrangements.[17,22]

In the present letter, we study the charge reversal induced by poly(amidoamine) (PAMAM) dendrimers experimentally by direct force measurements and theoretically by computer simulations based on a simple model including the particles, dendrimers, and salt. These branched macroions are highly positively charged in acidic conditions, and they adsorb strongly on negatively charged interfaces.[23–25] Their charge can be varied by the dendrimer generation, making a wide range of electrostatic couplings accessible (see Table 1). Their globular architecture restricts the conformational space, making them an ideal model system of highly charged macroions. While PAMAM dendrimers are known to induce charge inversion of negatively charged colloids,[24,25] attractive forces in these systems have not been studied so far.

Experimental Section

Direct force measurements between negatively charged colloidal particles with adsorbed PAMAM dendrimers were carried out

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Table 1. System Parameters Obtained from Experiments and Used in Simulations[a]

generation	adsorbed amount Γ_{IEP} ($\times 10^{-3}$ nm^{-2})	bare charge[b] Z	effective charge[b] Z_{eff}
G4	8.78	126	4
G6	3.37	510	10
G8	1.48	2046	23
G10	0.42	8190	81

[a] The adsorbed amount at IEP measured by electrophoresis Γ_{IEP}. The bare charge Z is calculated from the covalent structure of the dendrimers, while the effective charge Z_{eff} was obtained from eq 7. [b] Expressed in units of the elementary charge.

with an atomic force microscope (AFM; MFP-3D, Asylum Research) mounted on an inverted optical microscope (Figure 1). Suspensions of sulfate latex particles of 3.1 μm in diameter were mixed with PAMAM dendrimer solution adjusted to pH 4 with HCl, and the ionic strength was adjusted with KCl. The degassed suspensions were left to react overnight. Subsequently, particles were deposited from the aqueous suspension on glass substrates previously functionalized with 3-(ethoxydimethylsilyl)-propyl amine. One of the particles was attached to a similarly functionalized tip-less cantilever in the fluid cell by rolling and pressing it against the substrate with the AFM. The particle on the cantilever was centered above another particle on the substrate through the interference pattern observed in the optical microscope. The force constants of the cantilevers were determined by three different methods, and the contact point was determined from the onset of the constant compliance region.[26] The force F was measured as a function of the surface separation h. To improve the signal-to-noise ratio, about 100 force curves recorded upon approach were averaged. The measured force curves were normalized to the effective radius $R_{\text{eff}} = R_1 R_2 / (R_1 + R_2)$ where respective radii of the spheres R_1 and R_2 were determined by optical microscopy. A similar technique was used to study forces induced by linear polyelectrolytes.[27] Since particle suspensions are being used, the dendrimer dose can be controlled very precisely. Nevertheless, because of the enormous sensitivity of force profiles near the IEP, such attractive force profiles often showed a minor repulsive part. This repulsive force was extracted by fitting the force at larger distances with the expected van der Waals and double-layer force profiles, which was approximated by a simple exponential. Attractive forces were obtained by subtracting the repulsive double-layer part and yielded well reproducible attractive force profiles. An analogous approach was used to correct such repulsive forces earlier.[10] For comparison, van der Waals forces were measured between bare latex particles at their IEP near pH 3 in 1 M KCl. These forces are consistent with the expected van der Waals constant of 9×10^{-21} J for polystyrene[28] and an inward shift of the plane of origin of about 1 nm. Such a shift is expected on the basis of the finite thickness of the adsorbed dendrimers.

The dendrimer adsorption was probed by electrophoresis. The fact that the adsorption of the dendrimers to the latex particles is quantitative was verified by counting the individual dendrimers adsorbed to the particle surface (see Figure 1). Complete adsorption was equally reported in a similar systems.[19,25] Adsorbed dendrimers were imaged in air with an AFM (Nanoscope III, Vecco) in tapping mode on particles deposited on filtration membranes of 1.2 μm of pore size. Given the known molecular mass, the surface number density was converted to the adsorbed mass and found to be equal to the added dendrimer dose within experimental error.
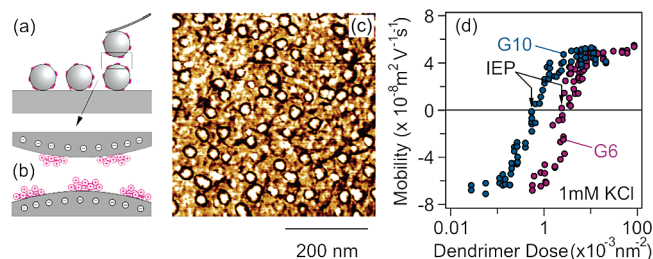

Figure 1. (a) Schematic representation of the experimental setup and (b) the detailed interaction geometry. (c) Flattened phase AFM image of adsorbed G10 dendrimers on the latex particles used. (d) Electrophoretic mobility of G6 and G10 dendrimers as a function of the dendrimer dose in 1 mM KCl at pH 4 measured with a velocimetry setup.

Simulations

The system is modeled with Monte Carlo (MC) simulations as two planar, uniformly charged surfaces. While the highly charged dendrimers are treated explicitly, the small ions in the electrolyte solution are treated on a Debye–Hückel (DH) level. The model assumes a uniform background screening of the electrolyte solution as well as a uniform dielectric constant. The dendrimers are modeled as point charges, interacting with the isotropically screened Coulomb interaction

$$\beta u_{\text{dd}}(r) = \lambda_B Z_{\text{eff}}^2 \frac{\exp(-\kappa r)}{r} \tag{1}$$

where r is the distance between the dendrimers bearing an effective charge Z_{eff} expressed in units of the elementary charge, κ^{-1} is the Debye screening length, and λ_B is the Bjerrum length equal to 0.72 nm in water at room temperature. The interaction between a dendrimer and a charged surface is given by integrating eq 1 over the surface yielding

$$\beta u_{\text{ds}}(z) = 2\pi \lambda_B \sigma Z_{\text{eff}} \frac{\exp(-\kappa z)}{\kappa} \tag{2}$$

where z is the distance of the dendrimer normal to the charged interface, and σ is the surface charge density expressed in units of elementary charge per unit area. The interaction energy per unit area of the parallel charged surfaces is obtained from eq 2 as

$$\beta u_{\text{ss}}(h) = 2\pi \lambda_B \sigma^2 \frac{\exp(-\kappa h)}{\kappa} \tag{3}$$

where h is the surface–surface separation. The total energy is obtained by summing these contributions for typically 100–800 dendrimers in a periodic box with lateral dimensions varying between 220 to 840 nm, depending on the dendrimer generation. At each separation, 10^5 MC steps were performed, a tenth of them for equilibration. The MC steps included single displacement of the dendrimers and collective movement of all the dendrimers on one of the surfaces relative to the other. Dendrimers were constrained to the surfaces in the simulations, since one experimentally finds that the adsorption is quantitative. Under these conditions, finite size effects are unimportant, and it is straightforward to apply the canonical MC procedure[29] for a given

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surface−surface separation h. A similar strategy was used to study interaction between two colloidal particles in the presence of dendrimers.[30]

The pressure p between the surfaces is calculated and sampled in the simulations, and the free energy per unit area follows by integration as

$$W(h) = \int_{h}^{\infty} p(h')dh' \qquad (4)$$

and converted to the normalized force curves by invoking the Derjaguin approximation

$$F/R_{\text{eff}} = 2\pi W(h) \qquad (5)$$

The surface charge density of the latex particles of $\sigma \simeq -0.034 \text{ nm}^{-2}$ was obtained from the measured force curve for two bare latex surfaces at 1 mM ($\chi = 0$), and the fact that the particles are negatively charged was inferred from electrophoresis.

Results

The normalized force curves F/R_{eff} are shown for PAMAM G6 dendrimers in Figure 2 at 1 mM. The top graphs refer to doses below and at the IEP, while the lower graphs show data at and beyond this point. The corresponding parameters are given in Tab. 1. With increasing dose, the strength of the repulsion decreases, and the forces become purely attractive at the IEP. Comparison with electrophoretic mobility data confirms that purely attractive forces occur precisely at the IEP (see Figure 1). For large dendrimer doses, the strength of the repulsion increases again. The dendrimer dose is reported as the charging parameter

$$\chi = \frac{\Gamma}{\Gamma_{\text{IEP}}} \qquad (6)$$

where Γ is the number of adsorbed dendrimers per unit area and Γ_{IEP} the same quantity at IEP. One has $\chi = 0$ for the bare latex, $\chi = 1$ at the IEP, and $\chi > 1$ for an overcharged system. The effective charge of the dendrimers Z_{eff} was determined from the charge neutralization condition ($\chi = 1$)

$$Z_{\text{eff}}\Gamma_{\text{IEP}} + \sigma = 0 \qquad (7)$$

and the experimentally measured dose at the IEP (Table 1). The resulting effective charges agree with recent estimates from repulsive forces involving silica substrates.[31]

Because of the linearity of DH theory, the magnitude of σ is underestimated with respect to the bare surface charge. Similarly, the estimated effective dendrimer charges Z_{eff} are much smaller than the bare charges Z (see Tab. 1). This choice is consistent with used interaction potentials, which are based on DH theory. The fact that interactions can be modeled with DH theory only when one uses effective charges, which are much smaller than bare charges, was equally reported in other systems.[32,33] The high charging ratios observed for PAMAM dendrimer adsorption on

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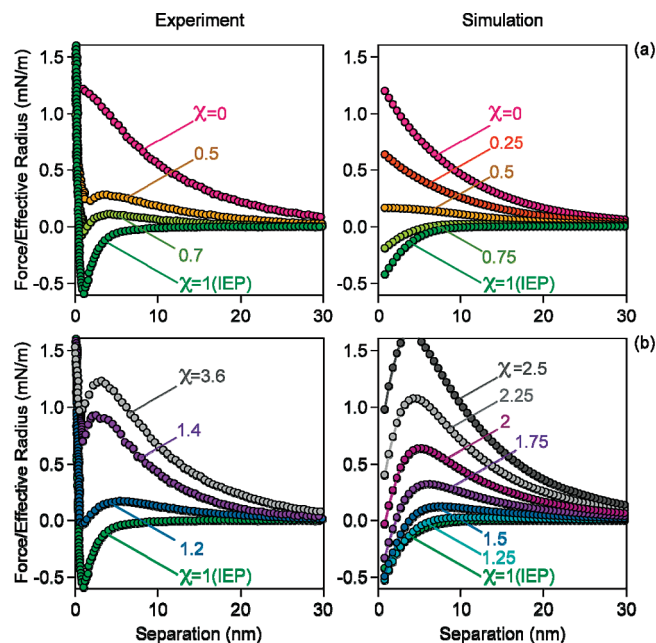
Figure 2. The forces between negatively charged latex particles in the presence of positively charged G6 dendrimers at an ionic strength of 1.0 mM and pH 4. Experimental data (left) are compared to simulation results (right). (a) Results shown are below and (b) above the IEP.

latex particles equally point toward the fact that $Z_{\text{eff}} \ll Z$ for adsorbed dendrimers.[25]

Simulations and experiments reveal very similar trends (see Figure 2). With increasing dendrimer dose, the strength of the repulsion decreases. This repulsive force is due to diffuse layer overlap. Its range is given by the Debye length κ^{-1} and its magnitude by the surface charge.[31] At smaller distances, a short-ranged attractive force appears. At the IEP, only the attractive force remains operational. Beyond the IEP, the repulsive force due to diffuse layer overlap sets in again, and the attractive force weakens. The agreement between experiment and simulation is not quantitative. However, given the complexity of the experimental system and the presence of no adjustable parameters, the agreement is remarkable. The hard-core repulsion interaction between the walls is not shown in the simulation data, but the corresponding short-ranged repulsion is visible in the experiment.

The attractive forces at the IEP ($\chi = 1$) from experiment and simulations are compared for different ionic strengths and generations in Figure 3. The data suggest that the range and strength of the attraction increases with decreasing salt level, and at low salt level the attractive force becomes independent of ionic strength and approaches universal algebraic decay.[16] By analyzing the simulated pair distribution functions of the macroions, we find that their correlations become increasingly important with decreasing separation distance. Therefore, the observed attraction is related to lateral correlations of the macroions. However, the range of the calculated attractive forces is larger than the one observed experimentally. We suspect that this disagreement originates from the fact that, in the simulations, the macroions may freely arrange on the surface, while in the experiment, the surface mobility of the dendrimers is strongly reduced, resulting in a glass-like arrangement as observed by AFM (see Figure 1). This inherent disorder is expected to lead to a less efficient registry of the respective surfaces, and smaller ranges of interaction. While some authors have reported a range of half a
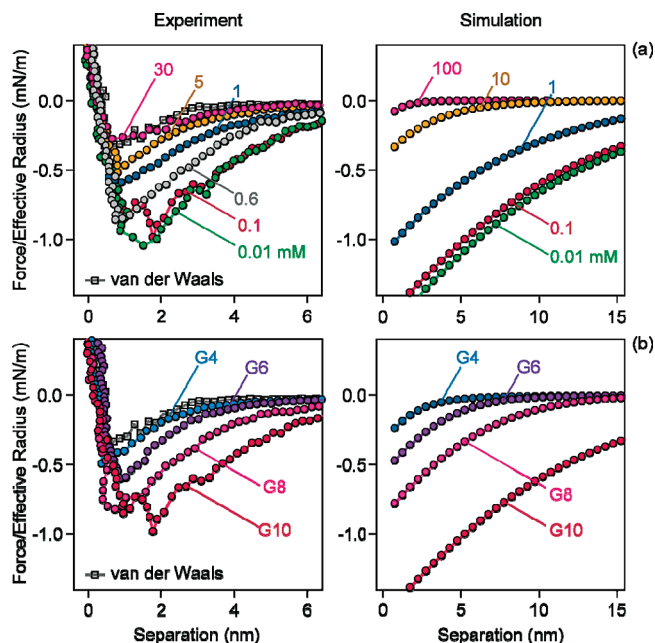
Figure 3. Attraction between negatively charged latex particles neutralized by positively charged dendrimers at IEP. Experimental data (left) for doses given in Table 1 are compared to simulation results (right). (a) Results for different ionic strengths for G10 dendrimers at pH 4.0, while the solution with ionic strength of 0.01 mM has a pH of 5.0. (b) Results for different dendrimer generations at an ionic strength of 0.1 mM and pH 4. The measured van der Waals forces between bare latex particles are shown as well (left).

Debye length for such attractive interactions,[34] other studies[35,36] confirm the present finding that the range of the attraction can be much smaller, especially at low salt concentration. The finite size

of the dendrimers is probably of little importance, as they flatten substantially upon adsorption.[31] Nevertheless, the resulting granularity of the surfaces as well as the inherent surface roughness become important at small distances. The charge regulation effects by release or uptake of counterions[37] might further obscure the comparison with simulation, which treats the dendrimers as simple point charges with a constant effective charge. Finally, van der Waals forces contribute to the experimental results, but they are not considered in the simulations. However, independent measurements confirm that van der Waals forces are much weaker than the attractive forces observed and are merely relevant for the weakest attractive forces reported (see Figure 3). A similar situation was equally reported for inhomogeneously charged particles in the presence of polyelectrolytes.[21]

Conclusion

We conclude that the experimentally observed interaction forces between colloidal particles during the charge inversion by charged dendrimers can be rationalized semiquantitatively with electrostatic interactions only. The model treats the particle surfaces and macroions explicitly, while the salt ions are treated on a mean-field level within the DH approximation. The model is solved by MC simulation techniques, and rationalizes the experimentally observed charge reversal and attractive forces near the IEP without adjustable parameters. These attractive forces exceed van der Waals forces and clearly originate from correlation effects between the two interacting layers of adsorbed dendrimers. We suspect that the present results are generic, and that charge reversal and interaction forces induced by highly charged macroions are dominated by electrostatics.

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