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Abstract

Optical tweezers are employed to measure the forces of interaction within a single pair of DNA-grafted colloids in dependence of the molecular weight of the DNA-chains, and the concentration and valence of the surrounding ionic medium. The resulting forces are short-range and set in as the surface-to-surface distance between the colloidal cores reaches the value of the brush height. The measured force-distance relation is analyzed by means of a theoretical treatment that quantitatively describes the effects of the compression of the chains on the surface of the opposite-lying colloid. Quantitative agreement with the experiment is obtained for all parameter combinations.

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Surface treatment of colloidal particles and the ensuing manipulation and control of their interaction properties is a topic of high and lasting interest, on the grounds of both technological relevance and fundamental importance. Firstly, surface treatment is necessary to achieve colloidal stabilization by inducing thereby a repulsive force that acts against the ubiquitous dispersion attractions between the colloids. Two of the most common mechanisms are charge and steric stabilization, the latter being caused by grafted polymer chains. Grafting of polyelectrolyte (PE) chains on a colloid provides a natural combination of both and results to an electrosteric repulsion. Secondly, surface treatment by polymer grafting provides the possibility to tune the effective colloid interaction by ‘dressing’ the hard sphere potential with a soft tail. The range, strength and overall functional form of the soft tail can be controlled by changing the properties of the polymer brush, e.g., its grafting density, height or charge. Systems interacting by a combination of a hard sphere potential and a subsequent short-range repulsion show a tremendous variety in their equilibrium [1–4] and dynamical [5–7] properties.

Considerable work has been carried out in the study of the so-called osmotic PE-brushes [8–10], which result for high surface grafting densities and are characterized by the fact that they spherically condense the vast majority of the counterions released by the chains. These, in turn, bring about an entropic effective force between the brushes, which has been quantitatively analyzed for PE-brushes [11] and stars [12]. On the other hand, little is known for the opposite case of low surface grafting density, for which the theoretical considerations that lead to the interaction between osmotic brushes break down. In this Letter, we investigate by a combination of sensitive and accurate experiments and theoretical analysis the effective forces between spherical DNA brushes and establish a novel mechanism of interaction between those, which results from the mutual compression of PE-chains of the colloids against the surface of each other. The quantitative characteristics of the resulting forces are vastly different from those between osmotic brushes.

The experimental investigation was based on the measurement of the force-distance dependence between the brushes employing optical tweezers. Optical tweezers offer unprecedented accuracy down to the pN-domain and 3nm in measuring forces and position, respectively. By monitoring the force-distance dependencies between two grafted colloids it is possible to learn how the different physicochemical properties (molecular weight, grafting density, ionic strength of the surrounding medium) affect the effective interaction between
FIG. 1: $F(D)$ curves between DNA-grafted colloids in buffered solution (10 mM C$_4$H$_{11}$NO$_3$, pH 8.5) for grafting density $\sigma = 8.2 \cdot 10^{-5}$ nm$^{-2}$ and various bp-number $N$, indicated in the legend. Symbols: experiments; lines: theory according to Eq. (2), with the values for $L_0$ and $Z_{\text{eff}}$ given in Table I. The inset illustrates the dependence of the interaction length $\lambda_F$ on $N$ for three different values of the force.

the grafted colloids. The force $F(D)$ and the surface-to-surface separation $D$ between two identical, negatively charged DNA-grafted colloids is measured using optical tweezers in an identical set-up as used in Ref. [13].

We employed colloidal particles with a hard core radius $R_c = 1100$ nm, on which DNA-strands with various numbers of base pairs (bp) and grafting densities $\sigma$ were chemically anchored. The brush has only a slight deviation from planarity, which allows us to relate also to known facts from planar PE-brushes in what follows. The force separation dependence between DNA-grafted colloids with $\sigma = 8.2 \cdot 10^{-5}$ chains/nm$^2$ and varying molecular weights of the chains is shown in Fig. 1. By using shorter and shorter DNA-segments, the force displays a gradual transition from a soft to a hard sphere potential. The theoretical curves based on the model explained below are also incorporated. A reliable estimate for the brush thickness is deduced by determining the interaction length $\lambda_F$ at forces of 2 pN, 4 pN, and 6 pN, see inset of Fig. 1. For molecular weights between 500 bp and 1000 bp, a linear scaling is observed, in accordance with Ref. [9]. Deviations at chain length 250 bp are attributed to the relative increase of the interaction forces between uncoated surfaces.

In Fig. 2 we show the $F(D)$ dependence on the concentration and valency of added salt, using the ionic strength $I = (\sum_i c_i z_i^2)/2$ as a parameter, where the sum is carried over all salt ions of concentration $c_i$ and valency $z_i$. In order to eliminate possible uncertainties due to variations among the colloids, the experiments for the data shown in Fig. 2 were carried
FIG. 2: $F(D)$ dependence for various ionic strengths $I$ and types of salt. (a) NaCl; (b) CaCl$_2$; (c) LaCl$_3$. Here, $N = 1000$ bp and $\sigma = 8.2 \cdot 10^{-5}$ nm$^{-2}$. Symbols: experiment; lines: theory according to Eq. (2), $L_0$ and $Z_{\text{eff}}$ are given in Table I.

out with one single pair of colloids for which the solvent is exchanged. With increasing salt concentration the force-separation dependence becomes shorter-ranged, reflecting the transition from an osmotic to a salted brush [13] and the concomitant shrinkage of the latter. The trends are the same independently of the counterion valency (NaCl, CaCl$_2$, and LaCl$_3$). As for the salt-free case, we obtain an estimate for the brush thickness as the interaction length $\lambda_F$ at the force of 2 pN; results for this quantity are shown in Fig. 3. The slope of the brush thickness versus ionic strength is close to $0.3 \pm 0.05$, in good agreement with the scaling law [8]. The transition from the osmotic to the salted brush takes place when the external salt content equals the counterion concentration inside the brush. A contact between the solid surfaces of the particles is not observed at low salt concentration ($< 1$ mM NaCl) and high forces (up to 100 pN) in accordance with known results for planar brushes [14].

In order to gain a deeper understanding of the underlying physical mechanisms that give rise to the measured forces, we rely on recent theoretical and simulational work on star-branched polyelectrolytes and the related system of spherical polymer brushes [11, 12, 15].
It has been shown [12] that the main physical mechanism giving rise to a (soft) repulsion between star-shaped polyelectrolytes comes from the entropic contribution of the counterions that are spherically trapped within the star’s corona. This consideration has been extended to spherical brushes, which possess a rigid, colloidal core. An analytical expression for the entropic effective interaction, $V_{\text{en}}(D)$, between two brushes at surface-to-surface distance $D$ has been derived, reading [11]:

$$\beta V_{\text{en}}(D) = N_{\text{trap}} \left\{ \frac{D + 2R_c}{2RK} \ln^2 \left( \frac{D + 2R_c}{2R} \right) + 2R_c \left[ \frac{2}{RK} - \frac{1}{L_0} \right] \ln \left( \frac{R_c}{R} \right) + \ln \left( \frac{2L_0}{RK} \right) \right\},$$

(1)

where $K = 1 - 2R_c/R + x(1 - \ln x)$, $x \equiv (D + 2R_c)/2R$. Further, $\beta = (k_B T)^{-1}$ is the inverse temperature, $N_{\text{trap}}$ represents the number of spherically trapped ions, $L_0$ is the equilibrium brush height and $R = R_c + L_0$. The entropic force is given as $F_{\text{en}}(D) = -\partial V_{\text{en}}(D)/\partial D$.

The basic assumption underlying the derivation of Eq. (1) above is that of no interdigitiation between the two brushes: as the surface-to-surface distance $D$ becomes smaller than $2L_0$, the chains of each brush retract to the half-space in which the respective colloidal core lies. The experimental data at hand, however, cannot be described by the force derived from the entropic contribution of Eq. (1), because the resulting forces have a completely different $D$-dependence than the experimental ones (see, e.g., Fig. 4). This is a clear indication that a different physical mechanism is at play for the system at hand. The rather small grafting density of the brushes brings about a different possibility, namely the mutual interdigitation of the brushes up to a surface-to-surface separation $L_0$ and the subsequent compression of the chains opposite to the hard colloidal core for smaller distances. This mechanism has been clearly identified and quantitatively analyzed in Ref. [15], in which interactions of star-branched polyelectrolytes with hard, planar surfaces have been discussed. Taking into account that chains from both brushes get compressed against the core of the opposite brush, the expression for the compression contribution to the effective brush-brush interaction reads for $d \ll D \leq L_0$ as

$$\beta V_{\text{c}}(D) = \frac{(Z_{\text{eff}} N)^2 \lambda_B}{D} \times \left\{ 2 \ln \left( \frac{D}{d} \right) + \left( \frac{D}{L_0} \right)^3 \left[ \ln \left( \frac{L_0}{d} \right) - 1 \right] \right\}.$$

(2)

Here, the Bjerrum length $\lambda_B = \beta e^2/\epsilon$ denotes the distance at which the electrostatic...
FIG. 3: Double-logarithmic plot of the interaction length for a force $F = 2$ pN versus the ionic strength of the added salt. Here, the molecular weight of the grafted DNA is $N = 1000$. Different types of symbols correspond to different salt valencies. The dashed line of slope $-1/3$ indicates theoretical scaling law predictions for comparison.

energy equals the thermal energy and has the value $\lambda_B = 7.18 \, \text{Å}$ for water at 300 K. Further, $d$ is the typical diameter of individual arms of the two interacting brushes, having for DNA the value $d = 18 \, \text{Å}$ [16, 17]. Again, the compression contribution to the force is given as $F_c(D) = -\partial V_c(D)/\partial D$ and it can be easily checked that $F_c(D)$ vanishes at $D = L_0$. Contrary to the entropic contribution, which sets in when the coronae overlap, i.e., at $D = 2L_0$, the compression contribution requires that the grafted chains of one brush touch the core colloid of the other and thus it is nonvanishing in the range $D \leq L_0$.

The brush height $L_0$ used in the theoretical calculation of the forces is read off from experiment and it is thus no free fit parameter. The ‘effective ion valency’ $Z_{\text{eff}}$ appearing in Eq. (2) is treated as a fit parameter to the experimental data; nevertheless, it is constrained by certain physical considerations based on known facts on the propensity of DNA strands to adsorb and strongly condense counterions on their grooves. Indeed, as it has been shown experimentally [18, 19], DNA can strongly condense about 90% of counterions, which already sets a rough upper limit of 0.1 for this effective valency; additional factors, such as weak adsorption of salt counterions inside the brush, are expected to push $Z_{\text{eff}}$ to even lower values. All parameter combinations for the various DNA-grafted colloids are shown in Table I.

The experimental forces shown in Figs. 1 and 2 are very well described by the compression force; there are still ‘tails’ for $D > L_0$ that can be discerned, and which correspond to small contributions from the entropic force, Eq. (1). The purpose of this work lies in the
TABLE I: The physical parameters of the employed DNA-grafted colloids and the effective valency $Z_{\text{eff}}$ employed in the theoretical modeling of each system.

| Figure | $\sigma$ [nm$^{-2}$] | Base pairs | $I$ [mM] | $L_0$ [nm] | $Z_{\text{eff}}$ |
|--------|----------------------|------------|---------|-----------|---------------|
| 1      | $8.2 \cdot 10^{-5}$  | 250        | 100     | 0.227     |
|        |                      | 500        | 130     | 0.115     |
|        |                      | 750        | 180     | 0.104     |
|        |                      | 1000       | 280     | 0.091$^b$ |
| 2(a)   | $8.2 \cdot 10^{-5}$  | 1000       | 0.0     | 280       | 0.081$^c$    |
|        |                      |            | 0.1     | 150       | 0.088        |
| 2(b)   | $8.2 \cdot 10^{-5}$  | 1000       | 3.3     | 110       | 0.078        |
|        |                      |            | 10.0    | 90        | 0.061        |
|        |                      |            | 100.0   | 40        | 0.018        |
| 2(c)   | $8.2 \cdot 10^{-5}$  | 1000       | 0.03    | 180       | 0.079        |
|        |                      |            | 0.3     | 130       | 0.077        |
|        |                      |            | 30.0    | 40        | 0.036        |
| 4      | $1.8 \cdot 10^{-4}$  | 1000       | 0.0     | 280       | 0.078$^c$    |
|        | $5.9 \cdot 10^{-5}$  | 1000       | 0.6     | 190       | 0.068        |
|        | $2.0 \cdot 10^{-5}$  | 1000       | 6.0     | 70        | 0.067        |

$^a$Except for this value for $Z_{\text{eff}}$, which is still of the order 0.1, all other lie below the threshold 0.1 mentioned in the text. Note, however, that here $L_0$ deviates from linear scaling with $N$, as mentioned before, and this fact may affect the precise $Z_{\text{eff}}$-value.

$^b$Here, different colloids were used than in the cases marked with the superscript $^c$ below, which explains the deviation between the corresponding experimental results and the concomitant difference in the $Z_{\text{eff}}$-values.

$^c$In these two cases, the same colloids were used, yet the measured forces show minimal differences set by experimental accuracy. The theoretical values of $Z_{\text{eff}}$ are then slightly different between these two cases.
FIG. 4: Effective force-distance curves for DNA-grafted colloids at different grafting densities $\sigma$, fixed molecular weight $N = 1000$ bp and no added salt. Symbols: experiment; lines: theory. For the lowest $\sigma$, the solid line also includes an entropic contribution to force, derived from Eq. (1), which is illustrated by the dashed line.

understanding of the compression-induced forces, thus we have not attempted a detailed description of the tails, especially since the magnitudes of the resulting forces there lie at the limit of experimental accuracy. We show nevertheless for the lowest grafting density in Fig. 4 a typical example of the combination of compression and entropic contributions that results into an excellent description of the forces. Here, a number of $N_{\text{trap}} = 1100$ spherically trapped counterions was employed, which is in good agreement with the simulation results of Ref. [20]. There, planar PE-brushes were simulated and for a grafting density very close to the lowest one in Fig. 4, it was found that about 10% of the counterions are outside the brush. As the vast majority of the remaining 90% is Manning-condensed on the rods, a very small relative number of about 1000 spherically condensed ones, results, in agreement with the value of $N_{\text{trap}}$ mentioned above. For the higher grafting densities shown in Fig. 4, the entropic contribution seems to be negligible.

Summarizing the results shown in Figs. 1, 2, and 4, it can be surmised that the compression force resulting from Eq. (2) yields a very good description of a large variety of experimental data. The effective valency $Z_{\text{eff}}$ from Table I always lies in the physically expected region and shows the expected dependence on salinity, decreasing with ionic strength $I$. Note that already the fact that the resulting forces from theory lie at the pN-domain is a nontrivial feature, in view of the fact that quantities of vastly different order of magnitude in SI (Bjerrum length, Boltzmann constant, brush height and DNA-diameter) are involved in determining its numerical value.
We have measured and theoretically described the forces between spherical DNA-brushes with low grafting density. The physical system at hand provides a convincing verification of the importance of the PE-compression mechanism [15], in sharp contrast to most hitherto studied systems, which were dominated by counterion entropy. Therefore, it has been demonstrated that the present systems are colloids whose effective interaction is short-range, i.e., tunable in terms of its extension and strength by changing the number of base pairs involved, the ionic strength and grafting density. The quantitative characteristics of the resulting effective force are unique: whereas for neutral, densely grafted brushes the force scales as $F(D) \sim D^{-1}$ for $D \ll L_0$ [21, 22], here a dependence $F(D) \sim D^{-2}\ln(D/d)$ for $d \ll D \ll L_0$ results. On the other hand, for $D \lesssim L_0$, we obtain $F(D) \sim |D - L_0|$. Future work should focus on the study of concentrated solutions of such brushes, including crystal- and glass formation, and the analysis of these in terms of the effective interaction derived in this work.

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