

Stretching of Polyelectrolyte Chains by Oppositely Charged Aggregates.

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Abstract. - Using Monte Carlo (MC) simulation, mean-field and scaling arguments we investigate forces between charged spherical aggregates conferred by an oppositely charged polymeric chain. At interaggregate separations comparable to the length of the chain the force is attractive due to a special type of long-range bridging attraction mediated by the polyelectrolyte chain, adsorbed to both aggregates. Beyond a certain separation (*capture separation*) there is a symmetry-breaking transition in the monomer density distribution, resulting in a preferential adsorption of the chain to one of the aggregates.

Forces between charged macromolecular aggregates mediated by oppositely charged polyelectrolyte chains made their appearance after it was recognized [1] that contrary to expectations, based on the simple electrolyte systems, the forces conferred by oppositely charged polymeric chains confined between charged macroscopic surfaces are attractive. This attraction stems from the bridging contribution of confined chains to the total force balance and is thus of different origin from correlation attraction seen in polyvalent simple-salt solutions. Whether the polyelectrolyte chains are grafted or not makes little difference in qualitative terms as far as the bridging attraction is concerned. The MC results [1] have been confirmed and extended by different mean-field calculations, based on either a generalization of the Poisson-Boltzmann theory [1,2], the application of mean-field formalism for a continuous chain [3] or lattice mean-field calculations [4]. Further MC investigations have shown that the bridging attraction in Coulombic polymer-macromolecular-aggregate systems is not limited to planar geometry but extends also to the case of interacting spherical charged aggregates [5], where polyelectrolyte chains are grafted to either surface. The attraction can be quite large, but is usually of short range. In this note we shall describe some novel features of the polymer-mediated force between spherical charged aggregates in the case that the polyelectrolyte chain is not grafted to the surface and we will show that the attraction under certain conditions can become much longer ranged.

This model situation is particularly relevant for the study of interaction between

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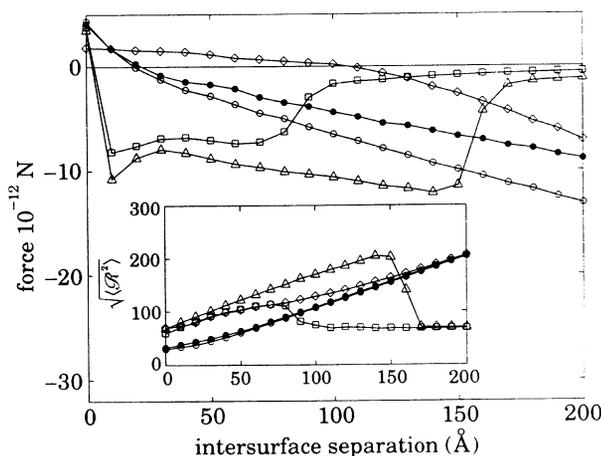


Fig. 1. – Forces between two charged spherical aggregates with a neutralising charged polymer chain. $R_A = 20 \text{ \AA}$. The length of the chain is $N = 20$ (\square) and $N = 30$ (\triangle). The inset shows the corresponding mean end-end separation of the chain $\sqrt{\langle r^2 \rangle}$. The transition from the captured regime to a symmetry-breaking leap to one of the aggregates is clearly visible. Forces between neutral aggregates with an uncharged chain with ends grafted to the surfaces of the two aggregates, $N = 20$ (\circ) and $N = 30$ (\bullet). A charged chain with ends grafted to the surfaces of uncharged aggregates, $N = 20$ (\diamond). In this case the force changes much more slowly with separation than in the case of an ideal grafted chain. The force between the aggregates is in 10^{-12} N .

polyelectrolytes and oppositely charged colloid particles, *viz.* ionic micelles or silicic-acid colloid particles [6]. These experimental studies convey the existence of electrostatically bound polyelectrolyte–colloid-particle complexes, composed of a single polyelectrolyte chain with at least two up to several tens [6] of colloid particles.

We investigate a solution containing charged spherical aggregates as well as oppositely charged polymers in a dilute limit, when $C_{\text{polymer}} < C_{\text{aggregate}}$, where C stands for the concentration. Though the concentration of the polymer is small, we furthermore assume that the chains are long enough so that on the average they compensate the charge residing on the aggregates. Our discussion is based on a cell model version of this system that contains in the lowest order two aggregates of radius R_A with a charge e each, plus a chain N beads long with charge e_0 per monomer, $e = -(1/2)Ne_0$. This is also the simplest situation seen in a polyelectrolyte–colloid-particle complexation experiment [6]. We thus neglect all non-pairwise additive contributions to the thermodynamic averages, effects of small counterions as well as salt. The chain is described in the framework of the coarse-grained bead spring model with a configurational Hamiltonian

$$\mathcal{H}(N) = \frac{3kT}{2l^2} \sum_{i=1}^{N-1} (\mathbf{r}(i+1) - \mathbf{r}(i))^2 + \frac{1}{2} \sum_{i,j=1}^N u(\mathbf{r}(i), \mathbf{r}(j)) + \sum_{i=1}^N \phi_{\text{ex}}(\mathbf{r}(i)), \quad (1)$$

where $u(\mathbf{r}(i), \mathbf{r}(j)) = e_0^2 u_C(|\mathbf{r}(i) - \mathbf{r}(j)|)$ and $\phi_{\text{ex}}(\mathbf{r}(i)) = -ee_0 u_C(|\mathbf{r}(i) - \mathbf{R}_1|) - ee_0 u_C(|\mathbf{r}(i) - \mathbf{R}_2|)$, with $|\mathbf{R}_1 - \mathbf{R}_2| = D + 2R_A$. $u_C(r)$ is the Coulomb interaction between unit point charges, D is the intersurface separations between the aggregates and R_A is their radius. Instead of working with the effective bond length, l , we choose the parameter $R_{\text{min}}^3 = e_0^2 l^2 / 3kT4\pi\epsilon\epsilon_0$. All the symbols not specifically defined are standard. We now use eq. (1) as a basis for a MC simulation with $R_{\text{min}} = 6 \text{ \AA}$, $R_A = 20 \text{ \AA}$ and $N = 20, 30$, values that are

consistent with observables in real systems [6]. An equilibration and a production run consisted of approximately 10^6 configurations per particle, with the final accuracy in the force data always better than 1%. The forces were computed by algorithms described elsewhere [5]. The simulation results for forces are presented in fig. 1, together with configurational properties of the chain as represented by the average end-end separation, $\sqrt{\langle \mathcal{R}^2 \rangle}$.

The behaviour of the force, f , between aggregates as a function of D suggests several different regimes corresponding to different physical mechanisms determining f . First of all if D is large enough compared to the mean end-end separation of an isolated chain ($D \geq 90 \text{ \AA}$, see fig. 1) the polymer chain remains preferentially adsorbed to a single aggregate. Since our simulation cell is electroneutral, the adsorption of the chain to a single aggregate leads to a charge reversal on the «dressed» aggregate. The dimensions of the adsorbed chain in this limit of D depend solely on the geometrical features of the adsorbing surface and lead in our case to $\sqrt{\langle \mathcal{R}^2 \rangle} \sim R_A$, being much smaller than $\sqrt{\langle \mathcal{R}^2 \rangle}$ in the bulk (*i.e.* for a free chain with $N = 20$ the bulk $\sqrt{\langle \mathcal{R}^2 \rangle}$ is about 120 \AA). In this limit of D the force between the two aggregates is an electrostatic attraction decaying as D^{-2} and is due to the charge reversal on the «dressed» aggregate.

As the separation is decreased ($D \leq 80 \text{ \AA}$) we observe that $\sqrt{\langle \mathcal{R}^2 \rangle}$ rises sharply. The sharpness of this transition depends on the number of monomers in the chain, being almost discontinuous for $N > 40$, while scaling approximately as the separation D , see insert in fig. 1. There is thus a limiting separation D_c , $D_c \sim 80 \text{ \AA}$ for $N = 20$ ($D_c \sim 150 \text{ \AA}$ for $N = 30$) at which the behaviour of the end-end extension of the chain switches from scaling $\sqrt{\langle \mathcal{R}^2 \rangle} \sim R_A$ to $\sqrt{\langle \mathcal{R}^2 \rangle} \sim D$. This switch in the dimension of the chain is accompanied by a symmetry-restoring transition of the monomer density with respect to both aggregates. A related phenomenon can be observed for a chain with one end fixed at a separation D from an adsorbing planar wall that becomes captured by it at a certain critical value of the separation, wherefrom the designation «capture distance» introduced by Johner *et al.* [7]. In our case we shall refer to a chain adsorbed in part to both aggregates as being «captured»⁽¹⁾. Capturing of the chain affects also the force between aggregates that it mediates; it becomes more attractive and depends approximately linearly on the separation (fig. 1). Only at very small separation does this form of attraction give way to a stronger repulsive force reflecting the crowding of the polymer in the region between the aggregates.

The breakdown of the total force into its components indicates, table I, that the attraction seen in the captured regime is due mainly to the bridging contribution. The Coulombic correlation and the direct Coulombic force are almost compensating. This is true for both chain lengths investigated. For comparison we included also two simulation results for uncharged chains of different lengths ($u(\mathbf{r}(i), \mathbf{r}(j)) = 0$) into fig. 1 as well as table I. The chain in this case is grafted by its two ends to both surfaces. The corresponding net force is much less attractive at small separations, which is due mostly to the larger ideal (osmotic) contribution to the total force, stemming from the crowding of monomers in the mid-surface region. Also the force scales differently with the length of the chain in this case. For a captured chain the longer the chain the larger the attraction (as exemplified by the $N = 20$ and $N = 30$ simulations). The grafted uncharged chain confers less attraction as it becomes

(1) The «capturing» of the polymer chain described above, being an equilibrium phenomenon, is quite distinct from the much more complicated problem of dynamical particle capture [8] that we do not address here.

TABLE I. - *The osmotic, bridging, Coulomb correlation and direct Coulombic contributions [5] to the total force between two aggregates at intersurface separation $D = 70 \text{ \AA}$, $R_A = 20 \text{ \AA}$. The symbols have the same meaning as in fig. 1.*

$D = 70 \text{ \AA}$	Osmotic	Bridging	Coulombic	Direct	Total
□	4.1	-14.2	0.5	2.4	- 7.2
△	4.4	-16.5	-12.4	14.5	-10.0
○	11.1	-15.6	0.0	0.0	- 4.5
●	16.1	-19.1	0.0	0.0	- 2.9
◇	6.1	-15.3	9.9	0.0	0.7

longer (this is clearly connected with the osmotic contribution to the total force). Even if we add electrostatic interactions between the monomers, but not with the aggregates, to the grafted chain, its behaviour does not mimic the captured chain.

The osmotic, bridging, Coulomb correlation and direct Coulombic contributions [5] to the total force between two aggregates at intersurface separation $D = 70 \text{ \AA}$, $R_A = 20 \text{ \AA}$. The symbols have the same meaning as in fig. 1.

The captured regime ($D < D_c$) can be characterized by the competition of two force mechanisms. First there is the bridging attraction stemming from the first term in the Hamiltonian, eq. (1), being entropic in origin. The second contribution to the total force comes from energetic considerations, since pulling the aggregates apart presupposes partial sliding of the adsorbed polymer off the surface of the aggregates, exposing more of the bare charge on the surfaces that in its turn draws the oppositely charged chain again back to the surfaces. The net effect of the two mechanisms is an effective elastic force that scales proportionally with the length of the chain. The osmotic contribution to the total force, proportional to the mid-plane density [5] and always repulsive, is significantly smaller for the captured chain than for the uncharged chain whose ends only are constrained to remain on the (different) surfaces, thus making the effective interaction more attractive at small separations. At larger separations, when the grafted chain undergoes large traction, the attraction conferred in this way becomes larger than in the captured regime.

In fact, more extensive simulations for different length chains [9] lead to the empirical conjecture that the polyelectrolyte-mediated attraction below the capture limit can be roughly described by a scaling form of

$$f \sim - \frac{kT}{l} a' \left(\frac{D}{l} + b' N^\zeta \right), \quad (2)$$

where the constants a' and b' depend on R_A , while $\zeta \approx 1$. Furthermore the mean end-end separation in this limit behaves as

$$\sqrt{\mathcal{R}^2} \sim D. \quad (3)$$

The difference between the force described by eq. (2) and pure elastic forces is substantial and must be due to different physical causes. We shall try to elucidate them by presenting rough theoretical analyses of the polyelectrolyte-mediated force. Above the capture limit the behaviour of the force is recognizable and follows $f \sim -c/D^2$, with the dimension of the chain scaling as $\sqrt{\mathcal{R}^2} \sim R_A$.

In the mean-field approach the properties of an N -monomer chain follow from the Green's

function defined as $\mathcal{G}(\mathbf{r}, \mathbf{r}'; N) = \sum_i \exp[-E_i N] \Psi_i(\mathbf{r}) \Psi_i(\mathbf{r}')$, where the eigenfunctions are solutions of the Schrödinger equation

$$\left[-\frac{l^2}{6} \nabla^2 - u_C(|\mathbf{R}_1 - \mathbf{r}|) - u_C(|\mathbf{R}_2 - \mathbf{r}|) \right] \Psi_i(\mathbf{r}) = E_i \Psi_i(\mathbf{r}). \quad (4)$$

$u_C(r)$ is just the interaction potential between the polymer beads and the two macroions assumed to be point charges. Polymer self-interaction is obviously not included in the above analysis which is its major shortcoming. A lowest-order solution of the above equation gives for the interaction free energy

$$F = -kT \iint d^3r d^3r' \mathcal{G}(\mathbf{r}, \mathbf{r}'; N) \approx -\frac{36}{e} kT \frac{N^4 \lambda_B^3}{l^3} D \exp\left[-\frac{3N\lambda_B}{l^2} D\right], \quad (5)$$

where F is the free energy of the chain as a function of $D = |\mathbf{R}_1 - \mathbf{R}_2|$ and $\lambda_B = \frac{e^2}{4\pi\epsilon\epsilon_0 kT}$.

Even in this very simplified mean-field analysis one is thus able to demonstrate that a polyelectrolyte chain in an attractive field of two oppositely charged macroions confers an effective attraction to them. The N -scaling as well as the D -dependence of the polymer mediated attraction suggested by eq. (5) are not consistent with MC results presumably due to the fact that the polymer self-interaction has not been included into the analysis.

Adding self-interactions between polyelectrolyte charges to the above analysis is a difficult task, but can nevertheless be approached in a rough manner through a revealing scaling «calculation». In the most simple scaling analysis the free energy for a chain captured by the two aggregates has the form

$$F \sim aM^2 - 2bNM + kT \left(\frac{D}{l}\right)^{1/(1-\alpha)} (N-M)^{-\alpha/(1-\alpha)}. \quad (6)$$

The first term corresponds to Coulombic self-interaction of the M beads of the whole chain that are adsorbed ($a \sim R_A^{-1}$), the second one to the Coulombic interaction between the adsorbed parts of the chain and the charges on the aggregates (the system is overall electroneutral), while the last one describes the stretching [7] of the part of the chain that occupies the space between the aggregates. α is the usual scaling exponent associated with the swelling of the chain, $\sqrt{\mathcal{R}^2} \sim N^\alpha$. While writing down eq. (6) we disregarded the detailed structure of the adsorption layer, assuming that all the adsorbed monomers are located right at the surface, and used only the roughest scaling forms for the different parts of the free energy [10]. In order to get the equilibrium force, we first of all have to minimize F with respect to M , *i.e.* $\partial F/\partial M = 0$. The general form of this minimization condition is untractable, but there are revealing limiting cases that yield to simple analysis. For $M < N$ at sufficiently large separations, we obtain approximately $M \sim N(1 - g_0^{1-\alpha} N^{\alpha-2} (D/l))$, where we introduced $g_0 = kT\alpha/((1-\alpha)2b)$. The ensuing force assumes in this limit the approximate form

$$f = -\frac{\partial F}{\partial D} \sim -2a \frac{g_0^{2(1-\alpha)} N^{2(\alpha-1)}}{l^2} D - kT \frac{g_0^{-\alpha} N^\alpha}{(1-\alpha)l} \left(1 - \frac{a}{b} \alpha\right). \quad (7)$$

Expression eq. (7) for the force describes a long-range attraction, extending over separations of the order of the length of the chain, terminating abruptly at $D = D_c \sim lN^{2-\alpha} g_0^{\alpha-1}$, where the symmetry-breaking transition occurs. The scaling of the attractive force with D and N is completely consistent with simulation results, eq. (2). The ansatz equation (6) is not valid directly for an electrostatically stiffened chain ($\alpha = 1$), but on the other hand it is clear that

for $\alpha \leq 1$ the force equation (7) is just of the form eq. (2), with $\rho = \alpha$. At $D = D_c$, the attractive force will cease to exist and the chain will make a symmetry-breaking jump to one of the spheres, quite in a similar way as in the more simple planar uncharged case [7] where the force in the captured regime is a constant and where the adsorbing potential is short ranged.

There is clearly a difference between the force, eq. (7), and the result given by Johner *et al.* for a chain captured by a planar wall. The difference can be traced back to the first term in the energy equation (6). This term can indeed be omitted in the case of a planar adsorbing wall with a large surface area at small surface coverages of the adsorbing polymer; it can however not be left out in the case of an adsorbing particle with a finite surface area.

It is important to realize at this point that the origin of the force just described is not in the stretching of the chain, as one would expect in an ordinary type of bridging attraction acting between planar walls [1]. Surprisingly, most of the force stems from the energy of the interaction between the chain and both aggregates (the first two terms in eq. (6)), that changes with separation since the length of the chain in contact with (or in close proximity to) the spheres (*i.e.* M) changes with separation. In view of this partitioning of the force among the different contributions to the free energy of the system, we propose to call this type of polymer-mediated interaction *energetic bridging* as opposed to ordinary bridging, which is mainly entropic in nature and operates in infinite planar systems. As the energetic bridging essentially stems from the requirement on electroneutrality of the whole (model) system it is specific to electrostatic (long-range) interactions. The restrictions imposed on the polyelectrolyte-colloid-particle complexes by the electroneutrality have been clearly noted also in experiments [6].

The most important distinction between the two bridging forces is their range. While entropic bridging extends only to separations comparable to the average monomer-monomer separation [5] (in the case of charged spheres with compensating charged grafted polymer chains), the energetic bridging extends over separations comparable to the length of the polymer chain and is comparable in strength to the entropic bridging at its maximum. Energetic bridging should be important always when a single charged chain has to compensate the charge residing on two (or more) aggregates [9], thus whenever the concentration of the polymer is small compared with the concentration of the aggregates but its length is of the order of D . In the opposite case, several short chains could adsorb to the surface of a single sphere thus preventing the emergence of energetic bridging, leaving, however, the entropic bridging at small separations intact.

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