Electronic supplementary information (ESI) for the article "Oscillatory structural forces between charged interfaces in solutions of oppositely charged polyelectrolytes"

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Experimental

Materials. Silica microspheres were purchased from Bangs Laboratories Inc., USA. They have a mean diameter of 5.04 µm and a polydispersity of 8%, which represents the coefficient of variation. Poly-L-lysine hydrobromide (PLL) with a molecular mass of 167 kg/mol and polydispersity index below 1.2 was obtained from Alamanda Polymers (USA). Poly(2-vinylpyridine) (P2VP) with a molecular mass of 245 kg/mol and polydispersity below 1.15 was purchased from Polymer Standards (Germany). Linear polyethylenimine (LPEI) with an approximate molecular mass of 250 kg/mol was obtained from Polysciences, Inc. (USA). For all the experiments PLL, P2VP, and LPEI were dissolved at different concentrations in ultrapure water (Milli-Q, Millipore). By addition of dilute HCl, the pH was adjusted to 4.0 for the experiments with PLL, and to 3.0 for the experiments with PEI and P2VP. Smaller silica particles were also purchased from Bangs Laboratories and used for the electrophoresis measurements. For the latter particles, the manufacturer report a specific surface area of $6.2 \text{ m}^2/\text{g}$ and a mean diameter 0.49 µm. The latter value is in good agreement with the value of 0.47 µm, which was measured by dynamic light scattering (Zetasizer Nano ZS, Malvern) in 1.0 mM NaCl solution of pH 4.0 at a particle concentration 100 mg/L. All experiments were carried out at room temperature of $20\pm3^\circ$ C.

Direct force measurements. Forces between pairs of silica microparticles were measured with particles sintered to a quartz slide (Plano GmbH, Germany) and particles attached to tip-less AFM cantilevers of dimensions 2×35×350 µm (MicroMasch, Tallin, Estonia). The quartz slides were cleaned for 20 minutes in boiling piranha solution, which is a mixture of 96% sulfuric acid and 30% hydrogen peroxide in a volume ratio 3:1, and then rinsed in ultrapure water. The silica microparticles were then sprinkled over the slide, and the slide was sintered at a temperature 1150°C for 3 hours. The cantilevers were cleaned with ethanol, then in ultrapure water, and finally treated in air plasma (PDC-32G, Harrick, New York) for 15 minutes. The clean cantilever was then mounted in the AFM, immersed in a drop of glue, and then the silica microparticle was attached to the glue. Finally, the cantilever was sintered in the same way as the quartz slides. The sintering process leads to firm attachment of the microparticles to the slide and to the cantilever. At the same time, the particles shrink to a diameter of about 4.4 µm and their roughness is reduced to about 0.8±0.1 nm. The latter parameter was determined by AFM imaging. The cantilevers have a spring constant of 0.32 N/m and a resonance frequency around 23 kHz in air. The cantilever spring constant was determined with the method described by Sader et al.¹ This method uses the lateral dimensions of the cantilever, its frequency response, and has an accuracy of about 10%. The forces were obtained from the deflection of the cantilever by means of the Hooke's law. Forces between the silica microparticles were measured in the liquid AFM cell. The AFM cantilever was mounted in the fluid cell containing the slide with the attached particles, and the cell was then filled with the polyelectrolyte solution. The two particles were then manually brought into contact, and centered in the optical microscope. After an equilibration time of about 10 minutes, about 150 approach and retraction curves were recorded. Contact was assumed to be reached when the normalized force reached the value of 5 mN/m. This load is sufficient to reach contact between silica surfaces.² The resulting force curves were down sampled, and the force profiles were averaged. The resulting noise level in the measured force was about 2 μ N/m and the distance resolution about 0.2 nm.

Electrophoresis. Electrophoretic mobility was measured in suspensions of silica particles of 0.49 μ m at a particle concentration of 87 mg/L and different concentrations of PLL. The measurements were performed with the Zetasizer Nano ZS (Malvern) with a He-Ne laser of a wavelength of 633 nm. The mobility was converted to the electrokinetic potential (ζ -potential) with the Smoluchowski model.³

Calculation of double layer forces

Forces between identical spheres of radius R were calculated within the Poisson-Boltzmann (PB) approximation. Within the Derjaguin approximation, the normalized force can be expressed as³

$$\frac{F(h)}{R_{\rm eff}} = 2\pi \int_{h}^{\infty} \Pi(h') dh'$$
⁽¹⁾

where R_{eff} is the effective radius and $\Pi(h)$ is the pressure acting between two planar walls with the same surface properties as the particles that are separated with a distance *h*. Double layer forces are found by solving the Poisson-Boltzmann (PB) equation^{3,4}

$$\frac{d^2\psi}{dx^2} = -\frac{q}{\varepsilon_0\varepsilon} \sum_i z_i c_i e^{-z_i\beta q\psi}$$
(2)

where $\psi(x)$ is the electrostatic potential, which depends on the position x in between the plates, c_i are the bulk number concentrations of ions of type *i* and valence z_i , *q* is the elementary charge, ε_0 is the permittivity of vacuum, ε is the dielectric constant the electrolyte solution, and $\beta = 1/(k_B T)$ whereby k_B is the Boltzmann constant and *T* is the absolute temperature. The plates are assumed to be positioned at $x = \pm h/2$. This equation is solved numerically with the boundary conditions^{4,5}

$$\pm\varepsilon_0 \varepsilon \frac{d\psi}{dx}\Big|_{x=\pm h/2} = \sigma - C_{\rm in}[\psi(\pm h/2) - \psi_{\rm dl}]$$
(3)

where σ is the surface charge density, ψ_{dl} is the diffuse layer potential, and C_{in} is the inner capacitance. The former to parameters are related with the charge potential relationship⁴

$$\sigma = \operatorname{sgn}(\psi_{dl}) \left[2k_{\mathrm{B}} T \varepsilon_{0} \varepsilon \sum_{i} c_{\mu} (e^{-z_{i} \beta q \psi_{dl}} - 1) \right]^{1/2}$$
(4)

where sgn(x) is the sign function. The regulation parameter is given by^{5,6}

$$p = \frac{C_{\rm dl}}{C_{\rm dl} + C_{\rm in}} \tag{5}$$

where the diffuse layer capacitance is given by

$$C_{\rm dl} = \frac{\partial \sigma}{\partial \psi_{\rm dl}} = \operatorname{sgn}(\psi_{\rm dl}) \left(\frac{q^2 \varepsilon_0 \varepsilon}{2k_{\rm B}T}\right)^{1/2} \frac{\sum_i z_i c_i (e^{-z_i \beta q \psi_{\rm dl}} - 1)}{\left[\sum_i c_i (e^{-z_i \beta q \psi_{\rm dl}} - 1)\right]^{1/2}}$$
(6)

The regulation parameter assumes simple values for the boundary conditions of constant potential (CP, p=0) and constant charge (CC, p=1). The double layer pressure is then calculated as^{3,4}

$$\Pi = k_{\rm B} T \sum_{i} c_i \left(e^{-z_i \beta q \psi} - 1 \right) - \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{d\psi}{dx} \right)^2 \tag{7}$$

The calculations assume a temperature of 20°C and set $\varepsilon = 80$ as appropriate for water.

Table S1. Reported structural oscillatory forces in various polyelectrolyte solutions. The data include poly(L-lysine) (PLL), linear polyethylenimine (LPEI), poly(2-vinylpyridine) (P2VP), poly(styrene sulfonate) (PSS), poly(acylic acid) (PAA), and linear poly(2-acrylamido-2-methylpropanesulfonate) (LPAMPS) together with estimated crossover concentrations and they are shown in Fig. 4.

Polyelectrolyte	Molar Mass	Estimated Crossover
PLL ^a	167	0.50 ^{b,7}
LPEI ^a	250	0.123 ^c
P2VP ^a	245	0.070 ^c
PSS ^{d,8}	4.2	870 ^{<i>b</i>,9}
	6.5	360 ^{<i>b</i>,9}
	13.2	88 ^{<i>b</i>,9}
	32	15 ^{<i>b</i>,9}
	75.6	$2.7^{b,9}$
	2300	$0.0029^{b,9}$
PSS ^{<i>d</i>,10}	6.4	370 ^{<i>b</i>,9}
	30	$17^{b,9}$
	200	$0.38^{b,9}$
PSS ^{<i>d</i>,11}	46	$7.2^{b,9}$
PAA ^{<i>d</i>,12}	33	$0.54^{b,12}$
	99	$0.058^{b,12}$
PAA ^{<i>d</i>,13}	30	$0.63^{b,12}$
LPAMPS ^{d,14}	858	0.018 ^c

^{*a*}Present work. ^{*b*}Crossover concentrations are obtained based on data given in the reference. ^{*c*}Crossover concentrations are extracted from the scaling relation shown in Fig. 4. ^{*d*}Wavelength extracted from the force measurements in the reference given.

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