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Crossover of the effective charge in ionic thermoresponsive hydrogel particles

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We use a generalized nonlinear Poisson-Boltzmann cell model that includes excluded-volume effects to investigate whether the effective charge (Z_{eff}) of charged thermosensitive hydrogel particles increases or decreases upon the hydrogel thermal collapse. We find the existence of a crossover charge, Z^*, that separates two regimes. For hydrogel bare charges below Z^* the system shows a behavior consistent with theories based on linear approximations, i.e., Z_{eff} increases in the collapsed state. However, for bare charges above Z^*, the system enters an anomalous regime, in which Z_{eff} decreases in the collapsed state. We show that diluted hydrogel suspensions at low ionic strength are more likely to follow the anomalous behavior. Our theory provides a full physical justification for the controversial theoretical and experimental results reported in this regard, and describes how the interplay between electrostatic, excluded-volume and entropic effects affects this crossover.

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Hydrogel particles are colloids of nanometric or micrometric size formed by a cross-linked polymer network immersed in water. The chemical nature of the polymer network can be designed to endow it with the ability to reversibly swell or collapse in response to many external stimuli such as temperature, *p*H, and salt concentration, among others. The porosity of the internal polymer network provides a great permeability that can be exploited to encapsulate large amounts of small cosolutes, such as chemical reactants, drugs, proteins, or other biomolecules. These important features make hydrogels very promising biomaterials for biomedical and industrial applications, such as nano- or microreactors with tunable catalytic reaction rates [1], as selective traps for chemical separation and purification [2,3], or as nanocarriers for controlled release of biomolecules and drugs [4–8].

In many of those applications, hydrogel particles are charged, so electrostatic interactions play a decisive role. The total number of ionized groups of the hydrogel, also called bare charge, Z, becomes strongly compensated not only by the counterions distributed inside the hydrogel volume, but also by the external counterions located in the surroundings of the particle. As a result of this effect, the effective charge Z_{eff} that any other charged object experiences in the vicinity of the hydrogel is usually much smaller than the bare charge. Z_{eff} is in fact a key parameter controlling the permeation and encapsulation of charged cosolutes and the colloidal stability of hydrogels immersed in salty solutions.

However, Z_{eff} is a complex magnitude that depends on the salt concentration in the medium, temperature, the particle concentration in the suspension, and on the swelling state of the hydrogel. In addition, due to the finite size of the monomer units and ions, its value is not exclusively determined by the electrostatic interactions but also by the excluded-volume (steric) forces exerted by the polymer network and the ions. These steric forces are weak in swollen hydrogels, but become very important when the hydrogel approaches the collapsed state, as the polymer volume fraction can reach values of about $\phi_m \approx 0.5$ [9]. Previous studies performed with Monte Carlo simulations clearly indicate that steric effects are required to explain the ionic density profiles inside and around charged nanogels [10,11]. Therefore, understanding the dependence of Z_{eff} with the swelling state of thermoresponsive hydrogel particles in terms of the interplay between electrostatic and excluded-volume interactions is essential.

From an intuitive and less-rigorous point of view, the effective charge should in principle increase when the hydrogel collapses for the following two reasons. First, in a collapsed hydrogel, counterions distributed within the internal hydrogel volume become confined to a smaller volume. Therefore, the electrostatic counterion-counterion repulsion should in principle push a certain amount of them outside. Second, the excluded-volume repulsion exerted by the polymer in the collapsed state also enhances the counterion exclusion. Both effects contribute increasing the net charge of the hydrogel when it collapses.

These considerations also seem to be supported by the existent theoretical predictions. In the seminal paper by Denton [12], he used linear response theory to calculate the effective electrostatic interaction between two uniformly charged microgels of radius a immersed in a suspension of monovalent salt at concentration ρ_s with a number density of hydrogel particles of ρ_p. He found a Yukawa-like dependence for nonoverlapping hydrogels. The same prediction was also obtained by Ohshima and Kondo using the linear superposition approximation [13]

$$\beta V_{\text{eff}}(r) = l_B \frac{Z_{\text{eff}}^2 e^{2\kappa a}}{(1+\kappa a)^2} \frac{e^{-\kappa r}}{r}, \qquad r > 2a, \tag{1}$$

where $\beta = 1/k_BT$ (T is the absolute temperature and k_B the Boltzmann constant), $l_B = e^2/(4\pi\epsilon_0\epsilon_r k_BT)$ is the Bjerrum length, and $\kappa = \sqrt{4\pi l_B(Z\rho_p + 2\rho_s)}$ is the inverse of the Debye screening length. The effective charge that results from these models scales linearly with the bare charge [12,14,15]:

$$Z_{\text{eff}}^L = Z\frac{3e^{-\kappa a}}{(\kappa a)^2}(1+\kappa a)\left[\cosh(\kappa a) - \frac{\sinh(\kappa a)}{\kappa a}\right], \tag{2}$$

where superindex L refers to linear theories. According to Eq. (2), the effective charge is a decreasing monotonous function of κa. Hence, a decrease of the size induced by the hydrogel collapse will cause an increase of the effective charge. The same conclusion is found if this model is extended using integral equations within the Hypernetted Chain Closure to investigate core-shell hydrogels considering ion-ion and ion-polymer excluded-volume interactions [9,16]. In addition, a similar trend has been reported in computer simulations [10] and in experiments, which show a significant increase of the net charge and the electrophoretic mobility when hydrogel deswells [17,18].

However, all these theoretical predictions are in conflict with recent experimental observations performed in charged hydrogels at low ionic strengths, which show that the effective charge of thermoresponsive hydrogels systematically decreases with the thermal collapse, i.e., upon heating [19–21]. Therefore, in order to understand the physics behind this surprising effect, a more complete description beyond the linear response theories that includes electrostatic and steric effects is called for.

In this work, we provide an explanation for this controversy. For this purpose, we generalize the nonlinear Poisson-Boltzmann cell model to include the steric interactions exerted by the finite size of monomeric units of the polymers and ions (PBS model). The hydrogel particle is assumed to be a negatively charged semipermeable sphere of radius a whose charge groups, Z, are homogeneously distributed within its volume, so the density of charged groups as a function of the distance to the hydrogel center r is $\rho_m(r) = \frac{3Z}{4\pi a^3}\theta(a-r)$, where θ is the Heaviside step function. The hydrogel is located at the center of a spherical cell of radius R [the particle volume fraction is then $\phi_p = (a/R)^3$], and the cell is filled with a certain concentration ρ_s of monovalent salt plus the excess counterions coming from the dissociated charged groups of the hydrogel. The diameter of monomeric units, counterions, and coions are $\sigma_m = 0.8$ nm, $\sigma_+ = 0.716$ nm, and $\sigma_- = 0.33$ nm, which correspond to the standard values for poly(N-isopropylacrylamide) (PNIPAM) hydrogels and for the hydrated diameters of Na^+ and Cl^- ions. According to the PBS model, the dimensionless electrostatic potential $y(r) = \beta e\psi(r)$ obeys the following differential equation:

$$\begin{aligned}\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = 4\pi l_B[\rho_m(r) &- c_+e^{-z_+y(r)-\beta\mu_+^s(r)} \\ &+ c_-e^{-z_-y(r)-\beta\mu_-^s(r)}],\end{aligned} \tag{3}$$

where $z_+ = 1$ and $z_- = -1$ for monovalent ions, and μ_i^s ($i = +, -$) are the steric contribution to the excess chemical potential of the ions, which depend on the local volume fraction of monomeric units, counterions, and coions (ϕ_m, ϕ_+, and ϕ_-, respectively). We make use of the Boublík-Mansoori-Carnahan-Starling-Leland expression for this steric chemical potential, which is very accurate when dealing with mixtures of particles (in our case monomeric units, counterions, and coions) of dissimilar size [22–24]:

$$\begin{aligned}\beta\mu_i^s = &-\left(1 + \frac{2\zeta_2^3\sigma_i^3}{\phi^3} - \frac{3\zeta_2^2\sigma_i^2}{\phi^2}\right)\ln(1-\phi) \\ &+ \frac{3\zeta_2\sigma_i + 3\zeta_1\sigma_i^2 + \zeta_0\sigma_i^3}{1-\phi} + \frac{3\zeta_2\sigma_i^2}{(1-\phi)^2}\left(\frac{\zeta_2}{\phi} + \zeta_1\sigma_i\right) \\ &- \zeta_2^3\sigma_i^3\frac{\phi^2 - 5\phi + 1}{\phi^2(1-\phi)^3},\end{aligned} \tag{4}$$

where $\phi(r) = \sum_{i=m,+,-}\phi_i(r)$ is the total volume fraction at position r, and $\zeta_k(r) = \sum_{i=m,+,-}\phi_i(r)\sigma_i^{k-3}$. Equations (3) and (4) are solved iteratively under the constraints of a fixed number of counter- and coions inside the cell, given by $N_+ = \rho_sV_{\text{cell}} + Z$ and $N_- = \rho_sV_{\text{cell}}$, which provides the value of constants c_+ and c_-. See the Supplemental Material (part A) for a detailed description of the iterative method employed in the resolution of these equations [25].

Once the PBS equation is solved, the effective charge of the hydrogel particle that enters Eq. (1) is obtained by solving analytically the linearized Poisson-Boltzmann equation following the renormalization prescription of Alexander *et al.* [26], assuming that the particle behaves as a hard colloid with an effective charge Z_{eff}, and using a renormalized inverse Debye screening length given by $\tilde{\kappa} = \sqrt{4\pi l_B[\rho_+(R) + \rho_-(R)]}$, where $\rho_\pm(R)$ is the number density of counter or coions at the cell border $r = R$ obtained solving the full PBS equation. The resulting effective charge can be written as [27]

$$\begin{aligned}Z_{\text{eff}} = \frac{\gamma}{\tilde{\kappa}l_B}\{&(\tilde{\kappa}^2aR - 1)\sinh[\tilde{\kappa}(R-a)] \\ &+ \tilde{\kappa}(R-a)\cosh[\tilde{\kappa}(R-a)]\},\end{aligned} \tag{5}$$

where $\gamma = 4\pi l_B[\rho_+(R) - \rho_-(R)]/\tilde{\kappa}^2$.

This method has been applied to calculate the ionic density profiles and the effective charge for two limiting swelling states of the hydrogel, namely, swollen ($a = 117$ nm at $T = 24.7\,^\circ$C) and collapsed ($a_0 = 51.4$ nm at $T = 34.9\,^\circ$C) (experimental data taken from Ref. [21] using charged PNIPAM hydrogels immersed in water). The polymer volume fraction in the collapsed state has been estimated to be $\phi_{m0} \approx 0.31$. The corresponding volume fraction for any other swelling state is $\phi_m = \phi_{m0}(a_0/a)^3$.

Figure 1 depicts a particular example of the resulting ionic volume fractions for a collapsed hydrogel particle, with and without the steric interactions (black and blue lines, respectively). As observed, taking the steric effects into account has a significant impact on the ionic distribution, as a certain amount of counterions is sterically expelled from the internal region of the hydrogel due to the reduction of the available volume. The excluded counterions then tend to accumulate at the external surface of the particle due to the electrostatic attraction. In addition, the ionic density profiles become discontinuous due to the volume exclusion caused by the polymer chains, in contrast to the smooth profiles obtained for purely electrostatic systems. This discontinuity is the consequence of assuming a uniform distribution of polymer mass and charge groups inside the hydrogel particle with a sharp interface at $r = a$, and disappears when they are replaced by a more realistic soft core-shell structure, as shown in computer

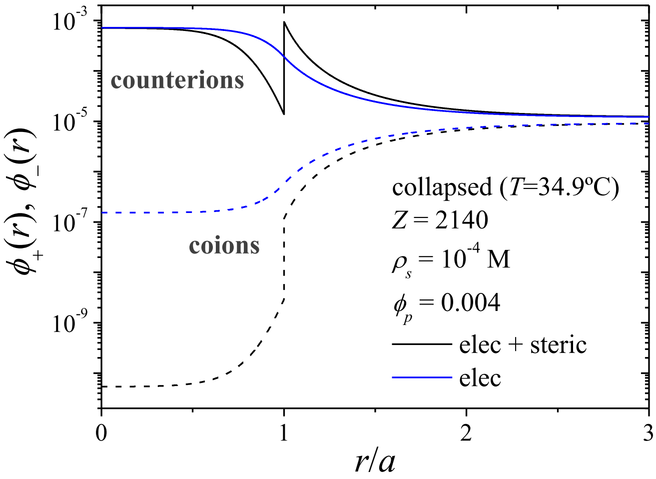

FIG. 1. Local volume fraction of counter- and coions as a function to the center of the hydrogel in the collapsed state obtained in the crossover charge for $\rho_s = 10^{-4}$ M and $\phi_p = 0.004$. Black and blue lines show the solution of the PBS equation considering and ignoring the steric interactions, respectively.

simulations [28,29]. However, the values of Z_{eff} obtained with the core-shell morphology do not deviate by more than 2% from the ones predicted by the uniform distribution, which validates the use of this simpler approximation.

In order to investigate whether the effective charge increases or decreases when the hydrogel collapses, we plot Z_{eff} as a function of Z for $\rho_s = 10^{-4}$ M at the swollen and collapsed states. The particle volume fractions in the swollen and collapsed states are $\phi_{p,\text{swollen}} = 0.046$ and $\phi_{p,\text{coll}} = 0.004$, respectively. Figure 2(a) clearly shows that Z_{eff} strongly deviates from the linear dependence and tends to reach a saturation value, especially for the collapsed state. This kind of behavior has been reported previously in the literature for both hard and permeable (soft) colloids as a consequence of the strong nonlinear coupling arising in highly charged systems [26,30–33]. In fact, Z_{eff} represents the net charge of the hydrogel dressed by the electric double layer inside and outside the particle. These results also show that the exclusion of counterions from the internal volume of the hydrogel caused by the steric effect leads to higher values of Z_{eff}.

The most important result of this work is shown in Fig. 2(b), which spans the region of small Z. As observed, the curves for swollen and collapsed states intersect at the so-called *crossover charge*, Z^* [red diamonds in Fig. 2(b)]. For $Z < Z^*$ the collapsed hydrogel has an effective charge larger than the swollen one, as predicted by the linear theories. However, for hydrogels with high enough bare charge, $Z > Z^*$, we find the opposite trend, i.e., the effective charge in the swollen state is larger, and the difference with respect to the collapsed state becomes more pronounced by increasing Z. This anomalous result does not require the presence of steric interactions. In fact, ignoring the steric contribution in the PBS equation also leads to the same result but with a smaller crossover charge due to the enhanced permeation of counterions inside the hydrogel, which induces a more efficient screening of the bare charge. In the regime of very small Z, the solution without steric forces converges to the prediction obtained with purely electrostatic linear theories [see Eq. (2)].

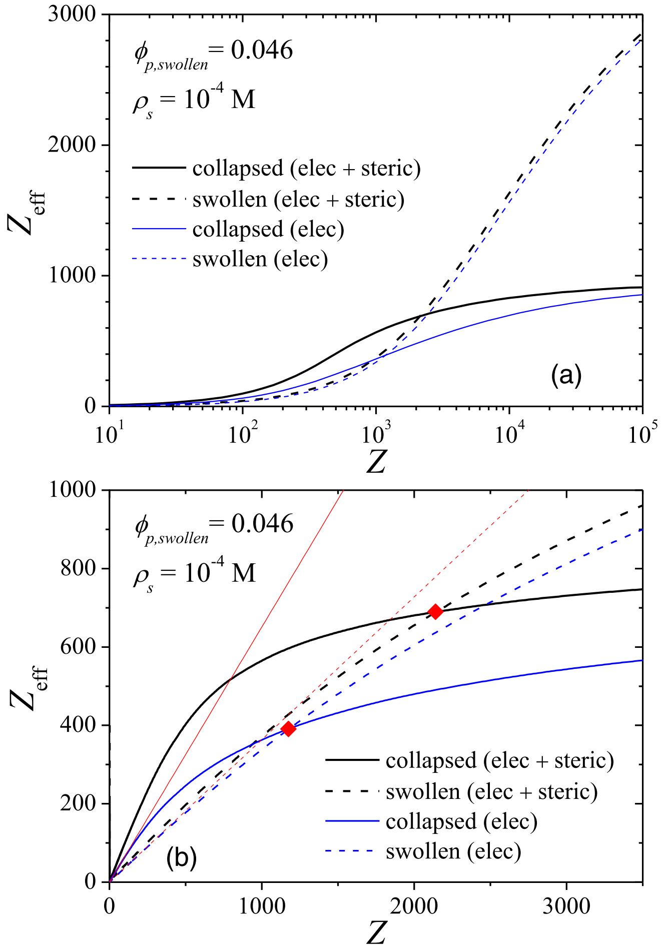

FIG. 2. (a) Effective charge of the hydrogel in the collapsed and swollen states as a function of the bare charge for $\rho_s = 10^{-4}$ M and $\phi_{p,\text{swollen}} = 0.046$. (b) Same as (a), but magnifying the region of small Z to clearly show the crossover (red diamonds). Red solid and dashed lines are the theoretical prediction using linear response theories [see Eq. (2)] for the collapsed and swollen states, respectively.

Therefore, at this point we can already provide an answer to the main question of this work: the effective charge of hydrogels in the collapse is smaller than the one for swollen only for values of the bare charge sufficiently large, above Z^*.

The existence of this crossover can be rationalized in terms of the physical meaning of Z_{eff}, i.e., a renormalized charge that estimates the bare charge of the particle plus the ionic cloud inside and around the hydrogel. Let us suppose that the hydrogel particle shrinks maintaining constant its effective charge (which means that the ions trapped inside and condensed at the hydrogel surface do not diffuse away). First, this provokes an increase of the electrostatic energy of the particle since the same charge is confined within a smaller volume. Second, the hydrogel collapse also involves a decrease of translational entropy, as the ions are also more constrained. Finally, the strong confinement also originates a significant increase of the excluded-volume free energy exerted by the ions and the polymers inside the hydrogel. All three of these effects lead to an increase of the free energy that the system tries to avoid. For weakly charged hydrogels (Z small), the entropic effect dominates over the electrostatic one, as the entropy can be

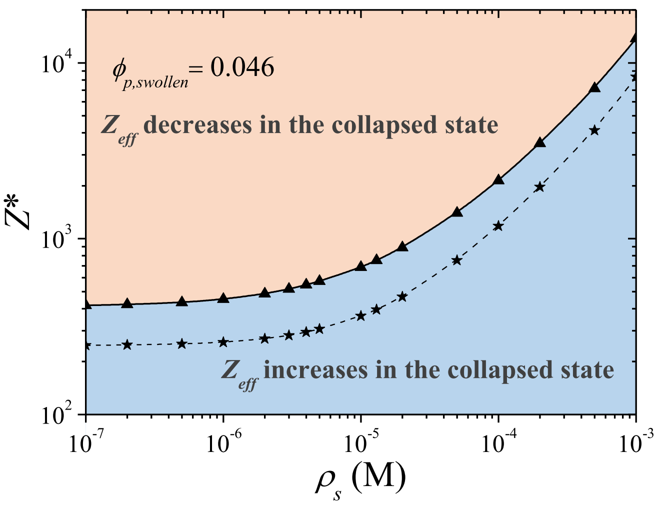

FIG. 3. Crossover charge, Z^*, as a function of the electrolyte concentration for $\phi_{p,\mathrm{swollen}} = 0.046$. Solid and dashed lines show the prediction considering and ignoring the steric interactions, respectively.

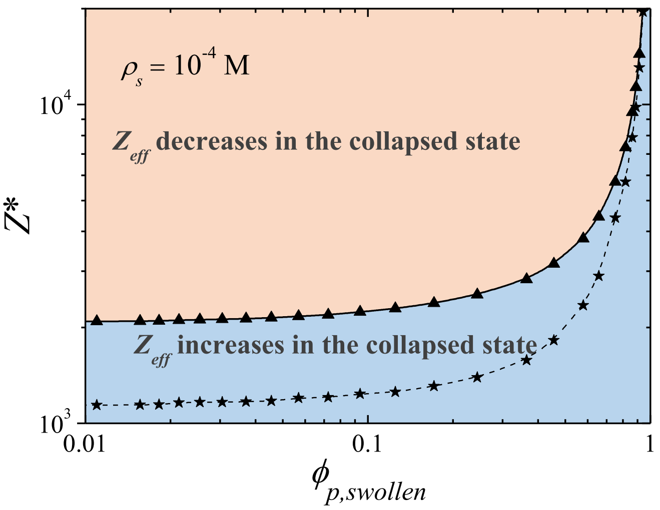

FIG. 4. Crossover charge, Z^*, as a function of volume fraction of hydrogel (in the swollen state) for $\rho_s = 10^{-4}$ M. Solid and dashed lines show the prediction considering and ignoring the steric interactions, respectively.

substantially raised if part of the counterions are released to the bulk suspension, which leads to an increase of the effective charge of the hydrogel. However, as we increase Z, the electrostatic cost of releasing counterions becomes large enough to counteract both the decrease in entropy and the increase of the enhanced steric repulsion. Hence, strongly charged hydrogels tend to absorb as many counterions as possible to reduce the effective charge at all costs. The crossover charge, Z^*, represents the bare charge at which entropic and steric effects are just canceled by the electrostatic contribution. See Supplemental Material (part B) for further insight regarding the dependence of Z_{eff} with the hydrogel swelling state below and above the crossover [25].

Figure 3 depicts the dependence of Z^* as a function of the concentration of monovalent salt (solid line). The curve separates two well-defined regimes. In the upper region Z_{eff} decreases in the collapsed state whereas it increases in the lower region. For very dilute electrolyte suspensions (close to the salt-free limit) the crossover charge tends asymptotically to a salt-independent constant value determined by the excess counterions coming from the dissociation of the hydrogel charged groups. When increasing the salt concentration, Z^* grows and finally tends to follow a linear dependence with ρ_s. This implies that, for large electrolyte concentrations, only strongly charged hydrogels will decrease Z_{eff} upon collapsing. In other words, given a fixed bare charge Z, there exists a critical salt concentration, ρ_s^*, so that Z_{eff} exhibits the anomalous behavior (i.e., decreases in the collapsed state) for $\rho_s < \rho_s^*$. This result may also be understood in terms of the interplay between electrostatic and entropic contributions. Indeed, increasing ρ_s screens the electrostatic interactions, which reduces the electrostatic free energy cost of releasing counterions, raising the value of Z^* required to reach the anomalous regime. This theoretical prediction also explains why the normal behavior is precisely observed for moderate to large electrolyte concentrations, whereas the opposite anomalous trend occurs for diluted electrolyte solutions. Neglecting the steric interactions leads to a similar behavior of Z^*, but shifted to smaller values due to the enhanced counterion permeation inside the hydrogel (dashed line in Fig. 3).

The dependence of the crossover charge with the particle volume fraction is shown in Fig. 4 for $\rho_s = 10^{-4}$ M including and neglecting the excluded-volume interactions (solid and dashed lines, respectively). In the limit of very diluted hydrogel suspensions, the crossover charge converges to its asymptotic value. Conversely, for particle volume fractions close to 1, the hydrogel collapse leads to a significant increase of the available volume outside the particle, which in turn implies an important entropy gain when counterions migrate from the internal to the external volume of the hydrogel. This effect raises the value of Z^*, as a larger electrostatic free energy term is required to compensate this entropy increase. Again repulsive ion-ion and ion-polymer steric interactions shift the crossover charge to larger values compared to the prediction obtained without excluded-volume effects.

In conclusion, we make use of a generalized nonlinear Poisson-Boltzmann cell model that includes ion-ion and ion-polymer steric interactions to investigate whether the effective charge of thermosensitive charged hydrogel particles increases or decreases upon collapsing. Our theoretical predictions clearly show the existence of a crossover bare charge, Z^*. For $Z < Z^*$ (weakly charged hydrogels) the effective charge increases in the collapsed state, whereas for $Z > Z^*$ (strongly charged hydrogels) the opposite behavior is found. This crossover cannot be deduced from theories based on linear response or linear superposition approximations. The existence of this crossover provides a physical explanation to the anomalous experimental observations reported at sufficiently low electrolyte concentrations, which show a decrease of the hydrogel effective charge upon collapsing [19–21]. We also demonstrate that concentrated suspensions at relatively high salt concentration are more likely to increase the effective charge in the collapsed state. Conversely, the effective charge of diluted suspensions at low ionic strength tends to decrease after the thermal hydrogel collapse.

Finally, it should be emphasized that although excluded-volume effects are not strictly necessary to justify the existence of the crossover charge, they do contribute to increasing its value in a significant amount compared to the predictions obtained with a purely electrostatic framework. Therefore, any attempt to quantitatively determine the hydrogel effective charge must incorporate these effects, especially for swelling states close to the collapsed conformation.

As future work, we would like to suggest that experimentalists perform systematic measurements of the effective charge by varying the salt concentration in suspensions of ionic thermoresponsive hydrogel particles, which would allow the determination of the crossover charge.

Further investigations will include the elastic and solvent free energy of the hydrogel particle to incorporate the effect of the bare charge, electrolyte concentration, and particle volume fraction on the swelling response of the hydrogel [33–36]. Nevertheless, we anticipate that hydrogel swelling will not modify the value of Z^* in a really significant way. Indeed, as reported in Fig. 3, the crossover charge is in general reached at low electrolyte concentrations (below 10^{-3} M) even for strongly charged hydrogels. Earlier experimental observations and theoretical calculations have shown that such low electrolyte concentration is not enough to induce the collapse of a swollen hydrogel particle, which occurs at salt concentrations of the order of 0.1–1 M [33]. For this reason, the shift of Z^* due to this effect is expected to be small, and the conclusions reached in this Rapid Communication regarding the possibility to detect experimentally this crossover can be maintained, even if the swelling response is not included in the model.

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