Monte-Carlo simulations of star-branched polyelectrolyte micelles

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1 Introduction

Charged diblock copolymers with a long and fully charged hydrophilic part and a short hydrophobic head are attracting a great attention. In water, their hydrophobic cores tend to aggregate and they form colloidal solutions of star-branched spherical micelles. These physical systems have many applications in surface adhesion, stabilization of colloidal solutions and are also used in drug delivery processes. Due to the presence of long-range Coulomb interactions, simple scaling arguments are generally insufficient to describe their behavior. Quantitative predictions concerning the concentration profiles of monomers and counterions have been obtained through Self-Consistent-Field (SCF) models. Numerical simulations can also provide useful information. The Molecular Dynamics (MD) approach has been widely used in the study of neutral star-branched micelles and charged linear polyelectrolytes. Recently Jusuh, Likos and Löwen (JLL) applied it to star-branched polyelectrolyte micelles. They studied, at relatively low linear charge densities of the chains, the monomer and counterion profiles of one micelle and the effective interaction between two micelles. They also proposed analytical approximations to be compared with the results of MD simulations.

We focus here our attention on the problem of one isolated micelle, in a different strongly-charged regime, which is relevant for some dilute solutions of (sodium-polystyrene-sulfonate)(NaPSS)–(polyethylene–propylene)(PEP) that have been investigated through neutron scattering in our laboratory.

We use the Monte-Carlo method which, through a stochastic approach, should provide the same information as the Molecular Dynamics. Our final goal is to reach real-system sizes like stars with \( f = 54 \) arms of \( N = 251 \) monomers (27108 particles), corresponding to experimental conditions and compare with our neutron-scattering data, without any adjustable parameter. As a prelude, we first present a systematic investigation of smaller micelles within a more general theoretical framework and compare our numerical Monte-Carlo results with the predictions of scaling theories and analytical approximations.

After the description of our model and Monte-Carlo method (section 2), we study in section 3 the evolution of the structure of a micelle with \( f = 27 \) arms of \( N = 130 \) monomers as a function of the following dimensionless parameter measuring the strength of the Coulomb interaction:

\[
\zeta = \frac{|z_i|\xi}{|z_m|l_B/a}
\]

where

\[
l_B = \left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{1}{k_BT}\right)
\]

is the Bjerrum length, \( \xi = |z_m|l_B/a \) represents the “Manning parameter” which characterizes the linear charge density of polymers; \( a \) is the distance between consecutive charged monomers, \( T \) is the temperature, \( \epsilon \) the dielectric constant of the solvent and \( z_m, z_i \) are the charge densities of monomers and counterions respectively. Throughout our study \( z = -z_m = z_i > 0 \) and all monomers are charged.

The Bjerrum length is \( l_B \approx 0.71 \text{ nm} \) in water at room temperature and it can be varied through the temperature and dielectric constant. The monomer length is usually of the order of a fraction of a nanometer. \( \zeta \) is approximately 3 for sodium polystyrene sulfonate in water. It
can be increased by choosing other solvents with lower dielectric constants and/or by taking polyvalent monomers and counterions \((z > 1)\). Higher values of \(\zeta\) are thus easily accessible. Although, in our fully charged model small values of \(\zeta\), much less than 1, are at present experimentally unrealistic, it is nevertheless interesting to extend our theoretical investigations down to that range.

When the thermal energy is much larger than the Coulomb interaction \((\zeta << 1)\), most counterions are outside the micelle corona. This corresponds to the “unscreened regime” \([1,2,3,12]\). Above some threshold value \(\zeta_{\text{shp}} \approx 1/f\), a spherical condensation of counterions inside and in the vicinity of the corona is expected. In this so-called “osmotic regime” \([1,2,3]\), the spherically condensed counterions lower the interaction between branches. Both unscreened and osmotic regime have been extensively studied through mean-field analytical models \([1,2,3,12]\). Finally, when the “Manning criterion” \([10]\) \(\xi_M \approx 1/z_i\), i.e. \(\zeta_M \approx 1\), is reached, a “cylindrical condensation” of part of the counterions around the branches is superimposed to the spherical condensation. Scaling and SCF theories \([1,2,3,12]\) have predicted a linear extension of the branches with corona radius \(R_c\) proportional to \(N\) and monomer density varying roughly as \(1/r^2\), where \(r\) represents the radial distance to the center of the micelle. This has justified a “rod-like” picture of the branches. This picture has been confirmed by clear experimental evidence of the stretching of the chains \([4]\). For highly charged polymers, a Poisson-Boltzmann analysis \([15]\) has been proposed to interpret the distribution of counterions around the rod-like branches in terms of a ionic condensation \([10,15]\).

In the three latter regimes, we have compared the results of our simulations to the expectations from approximate analytical theories. The simulation of a real system of (sodium-polystyrene-sulfonate) (NaPSS)–(polyethylene-propylene)(PEP) with \(f = 54\) branches of \(N = 251\) monomers, is described in section 4, with a direct comparison to our neutron-scattering data \([4]\).

2 The Model and Monte-Carlo method

2.1 The model

We use the simple “freely-jointed chain” (or “pearl necklace”) model. Each monomer is represented by a hard core of diameter \(\sigma_m = a\). The angle between two successive monomer–monomer segments is free. We consider that the hydrophilic chain is fully ionized in water and each monomer carries a charge \((z_m e)\). This is relevant for sodium-polystyrene-sulfonate, in our experimental conditions, where the degree of ionization is generally of order 0.95. The counterions are modeled by hard spheres of diameter \(\sigma_i = a/2\), they carry a charge \((z_i e)\). For sodium-polystyrene-sulfonate \(z_i = -z_m = 1\).

One isolated micelle and the counterions are treated in the “primitive cell model” i.e. they are confined inside a hard-wall cube of edge \(A\), surrounding the center of the micelle. The dielectric constant is assumed to be the same inside and outside the cubic cell. This approach is relevant for low concentrations with respect to the overlap concentration \(c^\ast\) of micelles. The weak dependence of our physical results on the size \(A\) of this cubic box (provided it is larger than the diameter of the micelle) means that a more sophisticated treatment of Coulomb interactions (e.g. periodic boundary conditions and Ewald sums) is not required here.

The hydrophobic core is modeled by a hard sphere of radius \(R_{\text{core}}\) of order 5 to 20\(a\). The hydrophilic parts are attached at fixed points chosen on this sphere. Two distributions of these fixed points have been considered:

- a random distribution
- a regularized distribution with approximate equidistance between first-neighbor pairs.

The results obtained with these different distributions are practically identical and it is thus not useful to perform mean values of Monte-Carlo results over different realizations of random distributions of points on the sphere.

All distances are expressed in units of the monomer length \(a\) and the strength of the Coulomb interaction compared to \(k_B T\) is measured by the dimensionless parameter \(\zeta\) defined in equation (1).

2.2 Monte Carlo moves

For a counterion, an elementary move is chosen at random in a cube of edge \(\delta x \approx 10a\) centered around it.

For polymers we use the “pivot algorithm”, which has been shown to satisfy ergodicity \([15]\). A monomer \(P\) is chosen at random, and a unit vector \(\hat{u}\) is taken randomly in some solid angle \(\delta \Omega\) centered around the axis defined by \(P\) and the next monomer \((P + 1)\). A rigid rotation of random angle around \(\hat{u}\) is applied to the part of the polymer going from \((P + 1)\) to its end. However, beyond Manning condensation \((\zeta > 1)\), such a pivot algorithm involving only the monomers becomes inefficient since many counterions are localized around each polymer and the cost in energy to move a group of monomers away from these counterions prohibits any Monte-Carlo move.

To circumvent this problem, we have used the “partially clothed” pivot algorithm proposed by Gordon and Valleeau \([15]\). Having chosen a pivot \(P\) and the corresponding end part of the polymer, we look for all counterions at a distance less than \(d\) of this polymer part (the distance from the polymer is defined as the distance to the closest monomer). Each of these counterions is rotated in block with the part of the polymer, with a probability \(p \leq 1\). The detailed-balance equation is satisfied if, in the Metropolis scheme, we take as the probability of acceptance of the Monte-Carlo move \([18]\)

\[
P_{\text{acc}} = \min\{1, (1-p)^{n_{\text{new}} - n_{\text{old}}} \exp[-(U_{\text{new}} - U_{\text{old}})/k_B T]\},
\]

where \(n_{\text{new}}\) and \(n_{\text{old}}\) are the number of counterions at a distance less than \(d\) after and before the temptative rotation. \(U_{\text{new}}\) and \(U_{\text{old}}\) are the Coulomb energies after and before the trial move.

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In practice, we have observed that “clothed pivots” have a reasonable probability to be accepted in the Metropolis scheme if \( p > 0.9 \). Since we did not observe very important differences in the convergence to equilibrium for \( 0.9 < p \leq 1 \), we chose the value \( p = 1 \) which makes the algorithm simpler and the calculation shorter. (The choice \( p = 1 \) has also been made by Lobaskin and Linse \[19\] in similar “cluster moves” of macro-ions surrounded by a shell of small counterions). The maximum ion-polymer distance for clothed pivots has been optimized to \( d = 4a \).

To facilitate stretching and contraction of the polymer, we have also applied some small “clothed block translations” of parts of polymer in the following way. A monomer \( P \) is chosen at random. The next monomer \( (P+1) \) is moved from \( r_{(P+1)} \) to \( r'_{(P+1)} \) within a solid angle \( \delta \Omega \) centered around \( (r_{(P+1)} - r_P) \). The rest of the polymer from \( P \) to its end is translated in block by a vector \( (r'_{(P+1)} - r_{(P+1)}) \). Such moves are also combined with “cluster moves” of counterions at distance less than \( d \). Compared to pivots they have a higher probability to be accepted and a suitable combination of these both types of cluster-moves accelerates the convergence.

Our main criterion for equilibrium is the convergence of the Coulomb energy to the same stationary value starting from two drastically different initial configurations:

- Fully extended polymers with counterions distributed uniformly in the volume of the cell.
- Contracted star with polymers in the equilibrium configuration of uncharged polymer and counterions distributed uniformly in the volume of the cell.

As a typical example, Fig. 1 illustrates the convergence of the Coulomb energy, starting from these two extreme configurations for a micelle with 27 branches of 130 monomers \((2 \times 3510 \text{ particles})\) at \( \zeta = 2 \). The equilibrium was reached after \( 10^3 \) steps per particle, representing 25 hours of monoprocessor time on a Compaq RS232 parallel computer. The relevant statistical properties (distribution of monomers and counterions, form factors etc...) were measured over \( 10^3 \) further steps. A “cluster move” of a polymer part was attempted every 3 iterations (the two others being devoted to single counterion moves). The cluster moves were either pivots \((3/4 \text{ of them})\) or translations \((1/4 \text{ of them})\) as previously described. During the measure of statistical averages, each counterion was moved approximately 1300 times, about 80 pivots and 200 translations per monomer were accepted.

The number of accepted pivots as a function of the position of the pivoting point \( P \) is represented in Fig. 2. Close to the core of the micelle, the number of accepted moves is low (of the order of 10 per monomer). Nevertheless, it grows roughly exponentially as a function of the position of monomer \( P \) and statistics becomes acceptable beyond a few tens of monomers.

The size \( \delta x \) of the cubic box for elementary counterion displacements was \( 10a \), and the elementary solid angle \( \delta \Omega \) for pivot rotations was fixed to \( 2 \pi \times 10^{-2} \) steradians. We have also tried some simulation with \( \delta \Omega \) increasing with the distance to the core of the micelle, without any substantial improvement of the rate of convergence to equilibrium.
3 General results

3.1 The theoretical model studied

We present here some theoretical results concerning the variations of the monomer and counterion profiles as a function of the dimensionless parameter $\zeta$ [cf. equation (1)] measuring the strength of the Coulomb interaction with respect to $k_BT$.

We consider two micelles with numbers of monomers and branches smaller than those corresponding to the experimental system studied in the next section:

(i) $N = 130$ and $f = 6$
(ii) $N = 130$ and $f = 27$

The radius of the core $R_{\text{core}}$ is chosen to be small compared to the radius of the micelle corona and has thus a little influence on the corona. We take in all cases $R_{\text{core}} = 5a$. The influence of the boundary conditions was investigated by comparing the results obtained with two different sizes of the cubic cell: $A = 320a$ and $A = 640a$.

We vary the dimensionless parameter $\zeta$ keeping the ratios $A = A/a$, $R_{\text{core}} = R_{\text{core}}/a$ and $\sigma_i = \sigma_i/a$ constant. We start from a low value $\zeta_0 = 0.005$ and increase it by steps. At each new step $\zeta_{n+1}$ we take as initial state of the Monte-Carlo calculation the equilibrium state obtained at the preceding one $\zeta_n$. The system is thus progressively "annealed", which provides a faster convergence to equilibrium at each step. As a typical test for equilibrium we compare in Fig. 1 the energy obtained in that way at $\zeta = 2$ starting from the equilibrium configuration at $\zeta = 1$ to the results obtained with far-from-equilibrium arbitrary initial configurations. After 1000 iterations the differences between all curves are of the order of the fluctuations.

We calculate the mean values of the radial distributions of monomers and counterions. The deviations of these distributions from the monomer distribution corresponding to fully extended arms are better emphasized by considering, in terms of $\tilde{r} = r/a$, the dimensionless quantities:

$$\rho_{\{m,i\}}(\tilde{r}) = \frac{4\pi}{f} \tilde{r}^2 a^3 c_{\{m,i\}}(\tilde{r})$$

where $c_{\{m,i\}}(\tilde{r})$ represent the local volume densities. For a micelle with fully extended arms, $\rho_m$ should be 1 for $R_{\text{core}} < \tilde{r} < R_{\text{core}} + N$ and 0 elsewhere.

3.2 Monomer profile as a function of $\zeta$

For $N = 130$, $f = 27$ and $A = 320$, typical monomer and counterion profiles at represented in Figs. 3a, 3b and 3c at weak coupling ($\zeta = 0.02$), intermediate coupling ($\zeta = 0.2$) and strong coupling ($\zeta = 3$) respectively. Corresponding snapshots of the micelle are shown in Fig. 4.

The variations of the radius of gyration $R_g$ and of the corona radius $R_c$ as a function of $\zeta$ are shown in Fig. 5 (circles). The corona radius $R_c$ is defined here as the abscissa of the maximum of the free-end distribution, which is approximately gaussian (see Fig. 6). It also roughly coincides with the rightmost inflexion point in the concentration profile $\rho_m(\tilde{r})$.

We have studied the influence of boundary conditions by doubling the size $A$ of the cubic cell (crosses). $R_c$ and $R_g$ are very weakly dependent on boundary conditions. Relative difference of the order of a few percent at most are observed at maximum stretching ($\zeta$ of order 1). We conclude that it is not useful to investigate more sophisticated treatments of Coulomb interaction like these corresponding to periodic boundary conditions with Ewald sums.

The influence of the number of arms is seen in Fig. 5 by comparing our results with a small number of arms $f = 6$ (diamonds) to the results with $f = 27$ (circles). It is only important at weak coupling.

The Figs. 3, 4 and 5 show clearly, as a function of $\zeta$, three different regimes. These three regimes are governed by changes in the behavior of the counterions, which are expected from mean-field theories.

3.3 The "unscreened regime".

At weak coupling $\zeta << 1$, the contribution of the counterions to the entropy dominates the electrostatic energy. The local volume density $c_i$ of counterions is roughly constant in the cell: $c_i \approx f N/A^3$ and from equation (4) $\rho_i \approx 4\pi N \sigma^2 / A^3$. If $A$ is larger than $R_c$, the fraction of counterions in the micelle corona is small and the electrostatic interactions between branches are weakly screened.

In the unscreened limit, the self-consistent field arguments proposed a long time ago for linear polyelectrolytes by de Gennes et al. [13] have been straightforwardly generalized to star-branched polyelectrolytes [11]. Let us consider a chain whose first unit is placed at the origin. The $n$-th unit is at an average distance $r(n)$ and feels two forces:

- In a simple gaussian model, there is an elastic force which tends to contract the chain:

$$F_e = \frac{3k_B T}{a^2} \frac{d^2 r}{dn^2}. \quad (5)$$

- If we assume equal stretching of the $f$ chains of a star, i.e. all chain ends are at the same distance $R_c$ from the origin, the spherical region at distance smaller than $r(n)$ contains a mean charge $Q = n f z_m e$. Applying Gauss theorem, there is an electrostatic force:

$$F_e = \frac{f(z_m e)^2}{4\pi \varepsilon \varepsilon_0} \frac{1}{r(n)^2}. \quad (6)$$

Writing the equilibrium between the two forces, one obtains the following dimensionless equation:

$$\frac{d^2 u}{dx^2} + \frac{1}{3} \frac{x}{u^2} = 0 \quad (7)$$

with $x = n/N$ and $u = r/(Nd)$ where the length scale $d$ is:

$$d = a \left( \frac{f z_m e}{\varepsilon_0 a} \right)^{1/3} \quad (8)$$
Fig. 3. Density profiles of monomers (black) and counterions (grey) in the three different regimes: a) uncondensed regime ($\zeta = 0.02$); b) spherically condensed regime ($\zeta = 0.2$); c) Manning-condensed regime ($\zeta = 3$). Here $N = 130$, $f = 27$ and $\tilde{A} = 320$.

Fig. 4. Snapshots of the micelle in equilibrium corresponding to the three regimes considered in Fig. 3 respectively. The three snapshots are represented at the same scale.
Fig. 5. Variation of the corona radius $R_c$ and radius of gyration $R_g$ as a function of the dimensionless parameter $\zeta$ for: (i) $f = 27, \tilde{A} = 320$ (circles); (ii) $f = 27, \tilde{A} = 640$ (crosses); (iii) $f = 6, \tilde{A} = 320$ (diamonds). $N = 130$ in all cases. The Manning threshold is indicated by the dash-dotted vertical line $\zeta \approx 1$. The dashed and dotted vertical lines indicate different threshold values for spherical condensation corresponding to (i), and (iii) respectively. The horizontal arrow on the left indicate the limiting values of the corona radius corresponding to neutral stars with $f = 27$ arms of $N = 130$ monomers.

Fig. 6. Distribution of branch ends for $\zeta = 0.02$. The Monte-Carlo results (full line) are fit by a gaussian (dashed line): $1/\sqrt{2\pi}(\tilde{\sigma})\exp[-(\tilde{r} - \tilde{R}_c)^2/2\tilde{\sigma}^2]$ with $\tilde{R}_c = 66.33$ and $\tilde{\sigma} = 5.31$.

Fig. 7. Monomer profiles in the “unscreened” regime. Full lines: $N = 130$ and $f = 27$ for three $\zeta$-values, $\zeta = 0.005$ (lowest maximum), $\zeta = 0.01$ and $\zeta = 0.02$ (highest maximum). Dotted lines: $N = 130$ and $f = 6$ for $\zeta = 0.01$ and $\zeta = 0.02$. The gray dashed line indicates the solution of Eq. 7.
The boundary conditions are $u(0) = 0$ and $du/dx = 0$ at $x = 1$. Taking $f = 1$ in the previous algebra is nothing else than De Gennes et al. equations [13].

The center to end distance of the chains is thus proportional to $Nd$:

$$R_c \approx f^{1/3} \zeta^{1/3} Na$$

(9)

(we take $z_i = -z_m$).

These simple scaling arguments lead to a stretching of the chains which is proportional to the number $N$ of monomers. They have justified a so called "rod-like" picture of the branches.

In Fig. 5, the slope $d \log R_c/d \log \zeta$ is smaller than 1/3, the value expected through the previous scaling arguments. The dependence of $R_c$ on $f$ is also weaker than predicted by equation (9). At very weak coupling, we obtain (see Fig. 5) $R_c(f = 27)/R_c(f = 6) \approx 1.35$ compared to the expected scaling: $(27/6)^{1/3} = 1.65$. The explanation is that when $\zeta$ is low enough to ensure that very few counterions are inside the corona, the excluded volume effects (which are not taken into account in the previous scaling arguments) become significant. The value of $R_c$ has a lower limit which is given by the scaling law for neutral stars [24]:

$$R_{c, neutral} \approx a f^{1/5} N^{3/5}$$

(10)

This limiting value for $N = 130$ and $f = 27$, within our pearl-necklace model is indicated in Fig. 5. Our lowest value for $R_c$ shows an inflexion towards this asymptote.

Close to the core, our monomer profiles can be roughly scaled on a universal curve by plotting $\rho_m(R_c - R_{core})/Na$ as a function of $(r - R_{core})/(R_c - R_{core})$ (i.e. the integral of each curve is normalized to 1) and compared to the solution of Eq. 7 given in Fig. 2 of Ref. [1] (see Fig. 7). Close to the core, our Monte-Carlo results agree qualitatively with the solution of equation (7) which gives a roughly constant profile of $\rho_m$ (i.e. $a^2 c_m(\tilde{r}) \approx \tilde{r}^{-2}$). At $R_c$, equation (7) leads to some unphysical divergence, which is smoothed in more refined SCF models taking into account the fluctuations of the chain ends [13]. Nevertheless a substantial increase of $\rho_m$ near $R_c$ remains in these SCF models, as well as in our simulation.

3.4 The “osmotic regime” with spherical condensation of counterions

Increasing $\zeta$ we expect a “spherical condensation” of a part of the counterions inside and in the vicinity of the corona. This occurs when the Coulomb energy of a counterion in the field created by the charged monomers:

$$(z_m N f) z_i e^2/(4\pi \epsilon_0 R_c)$$

at the limit of the corona radius is of the order of $kT$, i.e. for

$$\zeta_{sph} \approx 1/f$$

(at this level of approximation we take $R_c \approx Na$). The condensation of ions near the surface of an impenetrable charged sphere [11] has been formulated in an analogous way to the cylindrical condensation of ions around a charged rod studied by Manning [14]. The more complex problem of counterion condensation in a penetrable micelle has been studied through Self-Consistent Field methods [12,13]. It can also be formulated in a simpler way through a Poisson-Boltzmann analysis. The Poisson-Boltzmann equation can be solved numerically for a penetrable sphere of radius $R_c$ with charge density

$$c_m(r) = f N/(4\pi R_c r^2)$$

inside a spherical cell of volume $A^3$. The Fig. 8 compares the Monte-Carlo to the Poisson-Boltzmann results for the osmotic coefficient $\phi$. The osmotic coefficient is defined as the ratio of the osmotic pressure to its value corresponding to a uniform repartition of the ions in the cell. The osmotic pressure is equal to $k_B T$ times the local ionic density at the edge of the cell.

There is a clear change of slope of $\phi(\zeta)$ at a point which can be defined as the crossover to the condensed regime. For different numbers of arms and cell sizes, we deduce the crossover to the spherically condensed regime at the following values $\zeta_{sph}$:

- $\zeta_{sph} \approx 0.15$ for $f = 6$, $\tilde{A} = 320$
- $\zeta_{sph} \approx 0.03$ for $f = 27$, $\tilde{A} = 320$
- $\zeta_{sph} \approx 0.08$ for $f = 27$, $\tilde{A} = 640$

($N = 130$ in the three cases). At fixed $\tilde{A}$, $\zeta_{sph}$ varies in $1/f$. 
Fig. 9. Radial distribution of counterions ($N=130$) as a function of $\zeta$ for different numbers of arms: (a) $f=6$ and $A=320$, (b) $f=27$ and $A=320$, and different cell sizes: (c) $f=27$ and $A=640$. The arrows indicate a common inflexion point at $r \approx R_c/\alpha$. Since in that $\zeta$ range $R_c$ is roughly constant, the abscissa of this inflexion point remains constant.

In Fig. 9, we show that at the thresholds defined above, there is a drastic change of the counterion profile. Below $\zeta_{sph}$, the local density $c_i$ of counterions is roughly constant $c_i \approx fN/A^3$ leading to a quadratic behavior of $\rho_i$. Above the threshold, the curves $\rho_i$ show an inflexion point at $\tilde{r} \approx R_c/\alpha$. Since in that $\zeta$ range $R_c$ is roughly constant, the abscissa of this inflexion point remains constant.

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For $\zeta >> 1/f$, most of the counterions are inside the micelle corona (see Fig. 9). This regime has often been called “osmotic” by reference to the osmotic pressure of counterions inside the corona.

The range $1/f << \zeta < 1$ corresponds to the largest stretching of the star with a flat maximum in the curve $R_c(\zeta)$ (see Fig. 5).

3.5 The “Manning condensed” regime

For larger $\zeta$ values, beyond the “radial condensation” of counterions in the micelle corona, we expect the superposition of a “cylindrical condensation” of counterions around each branch of the micelle. This phenomenon is clearly
"cylindrical condensation" is seen in Fig. 3c and Fig. 4c. The Manning criterion for this scenario is: 

$$\xi_M = 1/|z|$$

which corresponds to the threshold value $$\zeta_M = 1$$.

The Fig. 10 represents an enlargement of the last decade in Fig. 5. The corona radius $$R_c$$ presents a flat maximum at 0.5 < $$\zeta < 1$$ and decreases at $$\zeta > 1$$. At this stage, it is interesting to compare our approach with the Molecular Dynamics study by JLL, where $$\zeta$$ has been fixed to 3, but where only one monomer out of three, four or six is charged. The “charge fraction” $$\alpha$$ is thus varied from $$\alpha = 1/3$$ to $$\alpha = 1/6$$ whereas it is $$\alpha = 1$$ in our model. The relevant Manning parameter which characterizes the linear charge density of the polymer is $$\zeta = z_m l_B / b$$, where $$b = a/\alpha$$ is the distance between consecutive charged monomers. In Fig. 10 we have plotted some of JLL results, as a function of $$\zeta' = \alpha \zeta$$. The fact that from $$\alpha = 1/6$$ to $$\alpha = 1/3$$ their corona radius increases indicates that they have not reached the Manning condensed regime at $$\alpha = 1/6$$ and $$\alpha = 1/4$$. They are just reaching it near $$\alpha = 1/3$$.

At $$\zeta >> 1/f$$, (near the broad maximum of $$R_c$$ and in the Manning condensed regime), the monomer profiles are only very weakly dependent on $$f$$. In Fig. 11, we compare the monomer profiles for different values of the number of branches $$f = 6, 27, 54$$. The number of monomer per branch is $$N = 130$$, the radius of the hydrophobic core is $$R_{core} = 5$$ and the size of the cell is $$A = 320$$. The Fig. 12 represents the variation of the gyration radius as a function of the number of branches $$f$$.

The last decade in Fig. 5 and its enlargement in Fig. 10 show that, in our fully charged model ($$\alpha = 1$$), beyond the Manning threshold, the corona radius $$R_c$$ decreases in $$\zeta^{-1/3}$$. This is quite a new result. Both this exponent and the independence of $$R_c$$ on $$f$$ can be interpreted with the following simple arguments.

For $$\zeta > 1$$, there is a cylindrical condensation of a fraction of counterions along the branches. The model proposed by Manning, considers that a fraction $$(1 - 1/\zeta)$$ of the counterions condenses around the branches in such a way that the monomers get an effective charge $$\alpha_{eff} z_m$$.
with an effective charge fraction
\[ \alpha_{\text{eff}} = \frac{1}{\zeta}. \]

The remaining fraction \( 1/\zeta \) of counterions are only spherically condensed and distributed between the branches. We assume that \( f \) is sufficiently high \( (\zeta > > 1/f) \) to neglect the fraction of “free” counterions outside the corona. Taking a spherical distribution in \( 1/r^2 \), we obtain the following effective ion density:
\[ c_{\text{eff}}^i(\tilde{r}) = \frac{1}{4\pi a^2 R_c} \frac{fN}{|z_i|}. \]

The corresponding “effective” screening length is
\[ \kappa_{\text{eff}}^{-1}(\tilde{r}) = \left[ 4\pi l_B z_i^2 c_{\text{eff}}^i \right]^{1/2} = a\tilde{r} \left[ f \frac{|z_i|}{|z_m|} \frac{Na}{R_c} \right]^{-1/2}. \]

Since we restrict our study to \( |z_i| = |z_m| \), it is independent of \( \zeta \). The “effective” screening length roughly keeps the same value it reaches at the Manning condensation threshold \( \zeta = 1 \). At a radial position \( r \), the mean transverse distance between two neighboring branches is roughly \( 4a\tilde{r}f^{-1/2} \). It exceeds the screening length by a factor larger than 4. Hence we can neglect the electrostatic interactions between branches. Since the polymers are relatively extended, the excluded volume interactions between branches are also weak. This is the reason why the monomer profiles are so weakly dependent on \( f \).

To justify the \((-1/3)\) exponent, we consider one branch in the familiar electrostatic “blob” picture\[13\]. Let us represent a branch as a succession of \( N/m \) blobs of size \( l \), each containing \( m \) monomers. As far as the size of a blob is smaller than the screening length \( \kappa_{\text{eff}}^{-1} \), the electrostatic energy of a blob is
\[ E_c = \left( \alpha_{\text{eff}} z_m e m \right)^2 / (4\pi \varepsilon \varepsilon_0 l). \]

Its elastic energy from entropic origin is
\[ E_e = \frac{3}{2}k_BT l^2 / (ma^2). \]

Minimizing the sum \( E_c + E_e \) with respect to \( m \), we obtain:
\[ (l/ma) = \left[ \frac{4}{3} \left( \alpha_{\text{eff}} z_m l_B \right)^{1/3} \right] = \left[ \frac{4}{3} \frac{|z_m|}{|z_i|} \right]^{-1/3} \]

and the length of the branch is
\[ R_c = (N/m)l = Na \left[ \frac{4}{3} \frac{|z_m|}{|z_i|} \right]^{-1/3}. \]

Since in the present study \( |z_m| = |z_i| \), \( R_c \) is proportional to \( \zeta^{-1/3} \) \[23\].

At high \( \zeta \), Schiessel and Pincus\[24\] predicted a collapse of the polymers with the following arguments. When the Coulomb energy dominates over the entropic contribution, each counterion is practically fixed to a monomer and forms an electric dipole. The attraction of dipoles should lead to a transition towards a collapse of the star. Up to \( \zeta = 10 \) our results follow a \( \zeta^{-1/3} \) power law, and we do not observe any precursor of this effect.

The Manning picture allows us to make some approximate mapping of our model at \( \alpha = 1, \zeta = 3 \) onto the model of JLL at \( \alpha = 1/3 \) and the same \( \zeta = 3 \). In our model, at

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**Fig. 13.** A blow-up over the last 80 monomers of one branch in Fig. 3c. Large spheres are fully charged monomer. Small spheres with diameter 1/2 of the large ones are counterions with an effective charge fraction \( \alpha_{\text{eff}} = 1/\zeta \). The remaining fraction \( 1/\zeta \) of counterions are only spherically condensed and distributed between the branches.

**Fig. 14.** Snapshots of the same branch at equal time intervals during measurement of thermodynamic quantities. The portion of space explored corresponds to a cone of solid angle \( 4\pi/\zeta \) steradians. The sphere at the top represents the hydrophobic core.
Fig. 15. Density of counterions at a radial distance \( \tilde{r} \) from the micelle center and a transverse distance from the nearest branch \( \tilde{d} \). The results of the Monte-Carlo simulation (symbols) are compared to those of a Poisson-Boltzmann approximation (continuous lines). (a) Circles and dotted line: \( \tilde{r} = 20 \); (b) stars and dashed line: \( \tilde{r} = 40 \); (c) diamonds and full line: \( \tilde{r} = 70 \). Here, \( \zeta = 3 \), \( N = 130 \), \( f = 27 \) and \( \tilde{A} = 320 \).

\[ \zeta = 3, \text{ due to Manning condensation}, \quad (1 - 1/\zeta) = 2/3 \text{ of the counterions condense on the monomers. The remaining effective charge fraction of monomers is thus } \alpha_{\text{eff}} = 1/3 \text{ and the other one third of the counterions is only spherically condensed inside the corona. This effective model is thus close to the real situation studied by JLL at } \alpha = 1/3 \text{ and } \zeta = 3. \]

The arrow in Fig. 10 shows a very nice agreement of the corona radii corresponding to this mapping. This is a strong evidence of the relevance of Manning’s picture.

FIG. 16. Radial density of counterions. The Monte-Carlo results are compared to the Poisson-Boltzmann approximation (dashed line). Here, \( \zeta = 3 \), \( N = 130 \), \( f = 27 \) and \( \tilde{A} = 320 \).

Up to now, radial distributions of counterions were only considered. In the Manning regime, it is of prime interest to study the cylindrical distribution of counterions around one branch. Defining the distance \( d \) of a counterion to the closest branch as the distance to the closest monomer we have measured the mean value of the radial density \( n(r, d) \), \( n(r, d) \delta r \delta d \) representing the number of counterions at distance between \( d \) and \( (d + \delta d) \) from a branch and at distance between \( r \) and \( (r + \delta r) \) from the center of the micelle.

The Fig. 15 represents the density \( n(\tilde{r}, \tilde{d}) \) of counterions at distance \( \tilde{d} = \tilde{d}a \) from the closest branch and at a distance \( \tilde{r}a \) from the center of the micelle for three values of \( \tilde{r} \): close to the core (\( \tilde{r} = 20 \)), in the middle (\( \tilde{r} = 40 \)) and close to the edge of the corona (\( \tilde{r} = 70 \)). We chose \( \zeta = 3 \), well above the Manning threshold, \( N = 130 \), \( f = 27 \) and \( \tilde{A} = 320 \).

It is interesting to compare these results to those expected from a “rod-like” picture of the arms and a Poisson-Boltzmann approach for the distribution of counterions.

Fig. 17. Number \( \nu(\tilde{d}) \) of counterion per monomer at distance less than \( \tilde{d} \) from the closest branch, for different values of the dimensionless parameter \( \zeta \). Here \( N = 130 \), \( f = 27 \) and \( \tilde{A} = 320 \). The change of curvature between \( \zeta = 0.5 \) and \( \zeta = 1.5 \) corresponds to Manning condensation. The Manning threshold \( \xi = 1/z_i \) is reached at \( \zeta \approx 1 \). A logarithmic dependence of \( \nu \) on \( \tilde{d} \) is expected at \( \xi = 1/z_i \), from a Poisson-Boltzmann approximation in a “rod-like” picture. For each value of \( \zeta \) in the Manning condensed regime, the arrow indicates the distance at which the “effective charge parameter” \( \alpha_{\text{eff}} = 1 - \nu \) leads to \( \xi_{\text{eff}} = 1/z_i \).
The Manning threshold is to plot in log-linear coordinates the Monte-Carlo results of Fig. 3c.

There is a change of curvature of the lines between \( \nu / \nu_i \) between 3 and 2 and \( \nu / \nu_i \) at distance less than \( \tilde{d} \) < 0.02. The radius of the rod is chosen to 0.75\( \sigma \), which corresponds to the sum of the hard-core radius of monomer and counterion. The height of the core is equal to the radius of a sphere of volume \( A \).

The calculation took only one minute on a computer

...and counterions (grey line) for a micelle with 54 branches of 251 monomers.

The density profiles of monomers and counterions are plotted in Fig. 19. The corona radius is \( R_{\text{cor}} \approx 4.5 \text{ nm} \approx 18 \sigma \). The monomer size for (NaPSS_4) moiety is \( A = 25 \text{ nm} \). Taking \( l_B = 0.71 \text{ nm} \) as the Bjerrum length of pure water at room temperature, the dimensionless parameter \( \zeta \) is evaluated to \( \zeta = l_B/a = 2.8 \). The concentration is \( 0.25c^* \) where \( c^* \) represents the overlap concentration. Our cubic cell was chosen such that its volume represents the mean volume occupied by one micelle in the solution i.e. \( A = 560 \).

4.2 Monomer and counterion profiles

The density profiles of monomers and counterions are plotted in Fig. 19. The corona radius is \( R_{\text{cor}} \approx 4.5 \text{ nm} \approx 18 \sigma \). The monomer size for (NaPSS_4) moiety is \( A = 25 \text{ nm} \). Taking \( l_B = 0.71 \text{ nm} \) as the Bjerrum length of pure water at room temperature, the dimensionless parameter \( \zeta \) is evaluated to \( \zeta = l_B/a = 2.8 \). The concentration is \( 0.25c^* \) where \( c^* \) represents the overlap concentration. Our cubic cell was chosen such that its volume represents the mean volume occupied by one micelle in the solution i.e. \( A = 560 \).
4.3 Form factor, comparison to experimental results

The monomer-monomer form factor obtained through the Monte-Carlo simulation, with the parameters described in subsection 4.1 is shown in Fig. 20 (dashed line). It is close to the monomer-monomer form factor obtained though neutron scattering except in the range $q \approx \pi/R_{\text{core}}$ where the size of the core has a large influence on the spectrum. Another Monte-Carlo calculation with a slightly smaller core $R_{\text{core}} = 12a$, (full line) was performed. It is in a better agreement with the neutron scattering results.

It is interesting to compare the simulated and experimental results to straightforward analytical approximations at low and high $q$.

(i) At low $q$, ($q < \pi/R_{\text{core}}$), the form factor can be reasonably approximated by that of a $1/r^2$ spherical distribution of monomers from $r = R_{\text{core}}$ to $r = R_c$ and zero otherwise:

$$F^{\text{sp}}(q) = \left[ \frac{\text{Si}(qR_c) - \text{Si}(qR_{\text{core}})}{qR_c} \right]^2 (11)$$

where $\text{Si}(z)$ represents the SineIntegral function. The thin dashed and dotted lines represent this function for $R_{\text{core}} = 12a$ and $R_{\text{core}} = 18a$ respectively. Up to $qa \approx 0.1$ they closely follow the corresponding Monte-Carlo simulations (heavy full and dashed lines). At $q \approx \pi/R_{\text{core}}$ large oscillations appear in the function $-\text{Si}(qR_{\text{core}})$, the first of them being responsible for a dip observed in the simulation. Close to this dip, the form factor is very sensitive to the size of the core. We find that our simulation with $R_{\text{core}} = 12$ is closer to the experimental results than that with $R_{\text{core}} = 18$. The interface between the hydrophobic core and the hydrophilic branches might happen to be not so smooth and as well defined as assumed in our model. For example, some hydrophilic monomers may be trapped inside the outer part of the core, leading to a lower effective core radius.

(ii) At high $q$, the branches can be approximated by rods of length $L = R_c - R_{\text{core}}$ with negligible thickness. The corresponding form factor is:

$$F^{\text{rod}}(q) = \frac{1}{L} \left\{ \frac{2}{qL} \text{Si}(qL) - \left[ \frac{\sin(qL/2)}{qL/2} \right]^2 \right\} (12)$$

The thin full line represents this function with $L = R_c - R_{\text{core}} = 156a$ corresponding to our Monte-Carlo estimate. At large $q$, $F^{\text{rod}}(q) \approx [1/fq(R_c - R_{\text{core}})]$ and the position of this line of slope (-1) in logarithmic coordinates gives a nice estimate of the corona radius. In conclusion the corona radius obtained through our Monte-Carlo simulation is in agreement with the experimental value.

The peak observed in the experimental data at $qa \approx 0.02$ arises from long-range correlations between micelles, mostly due to the remaining uncondensed charges. It is a collective effect which, of course, is absent in our model. The concentration is $c = 5 \times 10^{-3}g/cm^3$. The corresponding $q$ wave vector characterizing the inter-micelle correlations is $q \approx 2\pi(cN/fM)^{1/3}$ where $M = 5.7 \times 10^4$ is the molar mass of one diblock copolymer and $N$ the Avogadro number. We obtain $qa \approx 0.016$ in reasonable agreement with the position of the peak.

5 Conclusion

Monte-Carlo simulations appear to be a useful tool for understanding the complex structure of highly charged
copolymer urchin-like micelles. As the Coulomb coupling is increased, three different regimes can be distinguished. i) At low coupling, the freely-jointed polyelectrolyte branches become stretched due to the monomer-monomer repulsion and the micelle swells. The monovalent counterions are not sensitive to the low micellar charge and are uniformly distributed inside the cell. ii) At intermediate coupling, the arms are almost fully stretched and most of the counterions are trapped inside or in close vicinity of the micelle. This spherical condensation is due to the presence of many, although weakly charged, branches in the same micelle. iii) At large coupling, a classical ionic condensation appears locally around each highly charged branch which adds to the previous one. The effective post-condensation monomer charge decreases, the monomer-monomer repulsion weakens and the micelle deswells. These Monte-Carlo results agree with Poisson-Boltzmann analyses in different geometries and nicely reproduce small-angle neutron scattering data. The influence of intrinsic chain rigidity, and the role of ion-ion correlation in presence of multivalent counterions will be investigated in future papers.

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21. JLL consider $b = R_e/(N\alpha)$ rather than $b = a/\alpha$. The relevant question is: how to extend the Manning concepts from a perfect cylindrical rod to a wiggling chain. We consider that the cylindrical picture remains valid at small length scale (of the order of ten monomers) and that our local definition $b = a/\alpha$ is more relevant that the global one $b = R_e/(N\alpha)$, which incorporates the large scale wiggles of the chain shown in Fig. 13 (see footnote [23]). Nevertheless, taking $b = R_e/(N\alpha)$ instead of $b = a/\alpha$ merely shifts in Fig. 10 the data of JLL as well as ours from a factor $Na/R_e$ and does not affect our general discussion.
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23. This blob picture in the “Manning condensed” regime, with effective charge renormalization, is identical to that proposed by Schiessel and Pincus [24] for dilute solutions of polyelectrolytes, except that we consider a renormalizing factor: $\alpha_{eff} = 1/\zeta = a/l_B$ while their equation (2) corresponds, with our notations, to $\alpha_{eff}^P = (R_e/N)/l_B$ and leads to the exponent -1 instead of (-1/3). We are left with the same question as the one risen in footnote [21] about how to define the “Manning parameter” for an imperfect rod. In Fig. 10, our Monte Carlo results for $R_e$ show a (-1/3) exponent. This indicates that our “local” picture is the most relevant.
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