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Conformation of a single polyelectrolyte chain in the Coulombic unscreened limit

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The dimensions of single polyelectrolyte chains of increasing length are investigated with off lattice Monte Carlo simulations. It is found that the expansion factor of the mean square end to end distance α_R^2 scales with $uN^{3/2}$ for chain lengths N between 10 and 100 in the whole range of the adimensional electrostatic coupling constant u. The agreement with the predictions of the mean field theory of dilute polyelectrolyte solutions in a θ solvent without added salt is discussed. The scaling laws are verified by our experiments, which suggest also the scaling behavior of the "shape" of the chains.

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Solution properties of polyelectrolytes depend strongly on the conformational behavior of the individual polymer chains. There have been numerous theoretical studies of the behavior of single polyelectrolyte chains in various solvent conditions [1–11] but a quantitative understanding of their conformational behavior is still lacking. The main reason is the additional presence of long range repulsive Coulombic interactions to the short range polymer-solvent interactions already present in neutral polymers.

A number of theories have been suggested for describing the full range of behavior observed in dilute polyelectrolyte solutions. Very recently, a self-consistent variational mean field theory (MFT) for isolated continuous charged polymer chains originally developed by Muthukumar [10] was extended to account for all solvent conditions by Ha and Thirumalai [11]. They obtained an expression for the size of the polyion chain in terms of the parameters of the model, such as the solvent quality, the salt concentration, and the effective charge on the polymer.

In the infinite chain length limit, theories [1,6,10,11] and scaling arguments [6,12] predict that the configuration of a single polyelectrolyte chain in the unscreened Coulombic interaction limit is a rigid rod. On the other hand, a broad spectrum of configurations is expected for *finite* chains, ranging from the random coil at high temperatures (weakly charged chain) to more elongated configurations at low temperatures (strongly charged chain) [13]. However, the predictions of MFT have not been compared either with real systems or with computer experiments, even in the simplest case of free salt polyelectrolytes in a θ solvent.

In this paper, we study the dimensions of a single polyelectrolyte chain with unscreened Coulombic interactions between monomers as a function of the chain length, using Monte Carlo simulations. Our aim is to try to reproduce on a computer the simplest polyelectrolyte system analyzed already with the MFT and compare the predictions of both methods. Other solvent conditions and the effect of the charge distribution on the chain properties are planned to be reported elsewhere.

For a later comparison, we briefly review the relevant features of the MFT about the mean dimensions of the chains. Using a variational procedure, Muthukumar [10] determines analytically the configuration of a single polyelectrolyte chain as an expanded Gaussian chain with an effective step length l_1 such that the mean squared end to end distance is given by $\langle R_N^2\rangle = Ll_1$. Here $L = lN$ is the length of the chain, l is the Kuhn length of the unperturbed chain, and N is the number of statistically independent segments. When only the electrostatic interactions are present, l_1 is obtained as the solution of the equation:

$$(l_1/l)^{3/2} - (l_1/l)^{1/2} = 0.047z^{-1/2} . \qquad (1)$$

The complete solution of Eq. (1) is given in terms of the adimensional parameter $z = (4/27)\langle R_N^2\rangle_0/Q^2N_e^4$ which controls the configurational statistics of the system [13]. Here $\langle R_N^2\rangle_0$ refers to the uncharged state, Q is the Bjerrum length, and N_e is the total number of elementary charges on the chain. An alternative expression is $z^{-1} = (27/4)u^2f^4N^3$, with $u = Q/l$ the adimensional electrostatic coupling constant and $f = N_e/N$ the fraction of charged monomers.

The analytical treatment gives for the extended rod-like regime ($z \ll 1$): $\langle R_N^2\rangle^{1/2} = 0.497Lf^{2/3}u^{1/3}$ in agreement with the blob model predictions [12,14], assuming that the configuration of the chain is that of a linear sequence of Gaussian blobs. The numerical coefficient is of the same order of magnitude as that obtained by scaling arguments. Moreover, the mean squared end to end distance is a homogeneous function of its variables uf^2 and N. In fact, theory predicts that $\langle R_N^2\rangle = l^2NH(uf^2N^{3/2})$, where $H(x) \to 1$ $(x \to 0)$ and

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$H(x) \to 0.247x^{2/3}$ $(x \to \infty)$.

In our simulations, the polyelectrolyte is modeled as an off lattice random walk of N segments. Electric charges are assigned to the $N+1$ monomers on the backbone: the chain is fully charged ($f = 1$) and each monomer interacts with every other monomer separated a distance r_{ij} through an unscreened Coulombic potential $V_{ij} = u/r_{ij}$. Here V_{ij} and r_{ij} are measured in units of k_BT and the Kuhn length l, respectively (k_B, Boltzmann constant and T, temperature) [15].

Ensemble-average chain properties were determined by Metropolis Monte Carlo sampling over the configurational space of the polyelectrolyte. For each simulation at fixed u, the initial configuration was either a random walk or some final equilibrium configuration obtained from a previous run at lower u. The reptation algorithm [16] was used to generate successive chain conformations. After approximately N^2 reptation cycles, the new configuration is uncorrelated with the original one. Chain configurations were recorded every m times N^2 cycles, the appropriate factor m was chosen for each chain length (see Table I), and chain properties were averaged over the total number of sets of selected configurations.

We calculated the mean squared end to end distance of chains with N = 10, 20, 40, 60, and 100 segments, for several values of the adimensional coupling constant u. We restricted our analysis to $u < 1$, below the value describing the Manning condition for counterion condensation ($u = 1$), which was absent in our simulation. The organization of the simulation is shown in Table I. Our results are shown in Fig. 1. The average dimensions of chains with the same length grow as the electrostatic interaction parameter increases, displaying a transition between the random walk configurations $\langle R_N^2 \rangle = N$ as $u \to 0$ (we set $l = 1$ as scale length in our simulations), to more extended configurations as $u \to 1$. Our results are similar to those reported by Higgs and Raphael [17] using another simulation procedure.

In order to compare our results with the MFT predictions, we look for the relation between the simulation parameters u and N at one particular state of the system. We define a state of the system as the set of configurations of chains of different lengths that share the same value of the expansion factor of the mean squared end to end distance, α_R^2 $(= \langle R_N^2 \rangle / \langle R_N^2 \rangle_0)$. We select one particular expanded Gaussian state, defined as $\alpha_R^2(u, N) = \frac{4}{3}$ [13] as our testing sample. We reproduce in Fig. 2 the corresponding solutions. The best fit gives $u = (2.68 \pm 0.11)N^{-(1.52 \pm 0.02)}$, in excellent agreement with the MFT result ($uN^{3/2} = 3.133$). It is recognized [10,11] that numerical constants are not very important to the theory, but our results give confidence to the whole relevant parameter z or $uN^{3/2}$.

TABLE I. Total number of Monte Carlo (MC) cycles, m factors for the selection of initial and successive configurations for statistics and total number of sets (of cycles) for averaging. Two configurations of a set are mN^2 cycles apart.

N	Total MC cycles	Initial m	Successive m	Number of sets
10	102 500	25	5	200
20	205 000	12.5	5	100
40	408 000	5	2.4	100
60	408 000	2.22	1.11	100
100	520 000	2	1	50

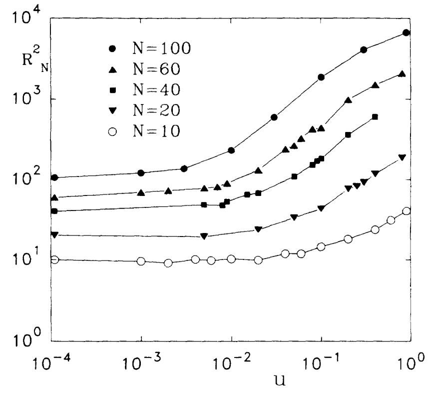

FIG. 1. Mean square end to end distances of the chains $\langle R_N^2 \rangle$ as a function of the adimensional electrostatic coupling constant, for several chain lengths.

We plot in Fig. 3 the expansion factor α_R^2 versus the mean field scaling variable $uN^{3/2}$. All the results fall on the same curve, demonstrating the universal behavior of our simulation performed at different chain lengths. The MFT result is also shown in Fig. 3 for comparison. The agreement between numerical and analytical results is complete for $uN^{3/2} < 2$. A systematic departure of our simulation data from above the MFT prediction is evident for values $uN^{3/2} > 10$.

We notice that the asymptotic behavior $\alpha_R^2 \to (uN^{3/2})^{2/3}$ is reached by MFT only from values $uN^{3/2} > 1000$; this abscissa is reached in our simulations only for the longest chain ($N = 100$) and $u \to 1$; one wonders if longer chains would be needed to reproduce an ideal rodlike regime.

Actually, the configurations of our longest chains in the high $uN^{3/2}$ limit are already well elongated. In fact, the asphericity parameter $\langle A \rangle$, introduced by Rudnick and Gaspari [18] as a measure of the departure of fractal objects from sphericity, has been used to investigate the shape of the chains. $\langle A \rangle$ ranges from zero for spherically symmetric objects to 1 for extremely elongated objects.

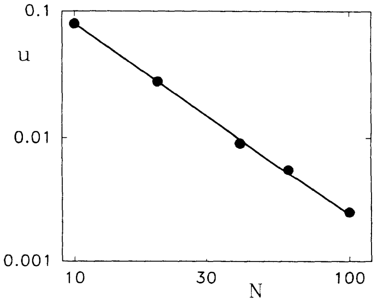

FIG. 2. Roots of the equation $\alpha_R^2(u, N) = \frac{4}{3}$ for chain lengths N = 10, 20, 40, 60, and 100. The solid line represents the best fit, as explained in the text.

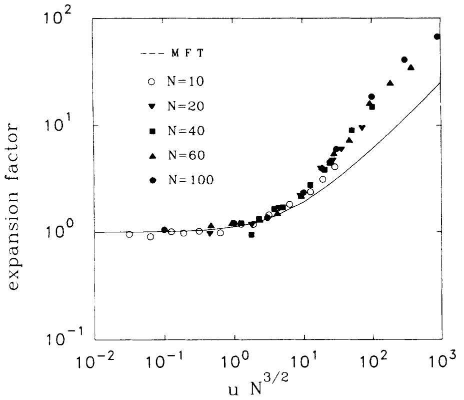

FIG. 3. Expansion factor α_R^2 of the mean square end to end distance versus $uN^{3/2}$. All the data from simulation lie on a single master curve. The solid line corresponds to the mean field theory prediction (see the equation in the text).

At the maximum attainable value of u ($= 0.9$), the calculated asphericity for chain lengths $N \geq 40$ is larger than 0.96, while the shortest chain ($N = 10$) reaches only an asphericity value of 0.73. Even if this number is well above the random walk estimate, $\langle A \rangle_{\mathrm{RW}} = \frac{10}{19}$ [18], it is still far from an acceptable value of an unambiguously defined rod configuration. We conclude that finite chains with lengths higher than 40 can reach the asymptotic rodlike regime at physically realizable values of u, just below the threshold of Manning condensation.

Moreover, the maximum value of the abscissa of our master curve for $N = 10$ is $uN^{3/2} = 28.5$. The corresponding asphericities of other chains are 0.71, 0.75, and 0.72 for $N = 20$, 40, and 60, respectively, suggesting an additional scaling law for the asphericity parameter with $uN^{3/2}$.

Regarding the comparison of our simulations with the predictions of the MFT, we recall that the system we have chosen to analyze is the simplest one to perform this task because the corresponding MFT is exactly soluble. In fact, the expansion factor is known analytically in the *whole* range of the scaling variable $uN^{3/2}$ [13]. Any other system—including electrostatic screening or excluded volume interactions, for instance—loses that property and the details of the approach to scaling are generally not addressed in the literature. Our simulations confirm the full validity of the MFT for *low* values of the scaling variable $uN^{3/2}$, where the chain behaves as an expanded Gaussian coil. The nontrivial scaling laws predicted by the theory are only obtained for long chains and our present numerical results give insight about the appropriate meaning of the term "long chains" to reach the rodlike regime. From the nature of the approximations involved in the theory, it is not expected that MFT could give a good description of the polyelectrolyte in the extended rod limit. Nevertheless, our Monte Carlo calculations for the longest chains agree with the global prediction of the theory, such as the power law exponent, but demonstrate that the MFT—formulated as in Refs. [10,11]—underestimates the dimensions of the polyelectrolyte in the more extended configurations regime. We state that any realistic calculation of physical properties with the MFT in this regime must take into account this limitation of the theory.

We conclude that our Monte Carlo simulations demonstrate the universal behavior of the expansion factor of finite polyelectrolyte chains whose monomers interact only through pure Coulombic forces. Short chains preserve their Gaussian behavior in the whole range of the scaling variable $uN^{3/2}$, whose upper limit is imposed by the physically allowed values of the electrostatic coupling constant u. Longer chains, even if they do not reach the exact asymptotic behavior, show elongated (almost-rod) structures approaching the familiar picture depicted by high molecular weight polyelectrolytes in solutions without added salt.

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