Collapse of Polyelectrolyte Macromolecules by Counterion Condensation and Ion Pair Formation: A Molecular Dynamics Simulation Study

Roland G. Winkler, Michael Gold, and Peter Reineker
Abteilung Theoretische Physik, Universität Ulm, 89069 Ulm, Germany

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The conformational properties of single polyelectrolyte chains of various lengths in the presence of counterions are investigated by molecular dynamics simulations. For Coulomb interaction strengths below the critical value for Manning condensation, the molecular chain exhibits an increase of the radius of gyration and of the end-to-end distance with increasing interaction strength. Above this critical value, counterions condense on the chain and ion pairs are formed. The ion pairs possess a net attraction such that beyond a certain interaction strength the chain with the condensed ions collapses into a dense coil. The scaling behavior of the radius of gyration and the end-to-end distance with changes in the number of bonds is discussed for various Coulomb interaction strengths. [S0031-9007(98)05910-9]

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Charged macromolecules (polyelectrolytes and polyampholytes) constitute a large class of materials which are particularly important for biological systems. Among these proteins and nucleic acids are well known. A variety of theoretical studies have been undertaken to elucidate the structural properties of such molecules [1–4] and to gain insight into the coil to rod transition behavior. However, to predict the conformational properties of a charged macromolecule is a very complex problem due to the long range nature of the Coulomb interaction. This is particularly true for highly charged chains, where the interaction with the counterions has to be taken into account. Recent experimental and theoretical studies demonstrate that the condensation of counterions and the formation of ion pairs significantly influence the conformation of a chain [5–7]. The Coulomb interaction and the counterions add new length scales to those of the neutral polymer. This complicates scaling theories and other theoretical approaches considerably. Thus, a microscopic understanding of the underlying physical phenomena is currently only possible by computer simulations.

To elucidate the conformational properties of highly charged polyelectrolytes in the presence of counterions, we performed a series of molecular dynamics simulations. We particularly investigated the distribution of the counterions for various interaction strengths between the chain molecule and the ions. For highly charged chains all the counterions are condensed on the chains, and compact globules are formed. As demonstrated below, the formation of ion pairs associated with dipole moments is essential for the collapse of the chain.

In this Letter, we present simulation results for a polyelectrolyte chain without salt but taking into account the counterions explicitly. The chain comprises N ($N - 1$ being the number of bonds) harmonically bound mass points. The excluded volume interaction between the masses of the chain and with an equal number of counterions is taken into account by a purely repulsive Lennard-Jones potential. In addition, each monomer of the chain carries a charge e and the counterions a charge $-e$. Hence, the charges of the total system compensate each other. The charged particles interact by the full Coulomb potential. The solvent is replaced by a dielectric background. The system is placed in a cubic box, and periodic boundary conditions are applied to keep the density $\varrho_{\text{mon}} = \varrho_{\text{ion}} = 2.16 \times 10^{-5}/\sigma^3$ constant. The long range Coulomb interaction in the infinite periodic system is taken into account by the Ewald sum [8]. In order to study the scaling behavior with respect to the chain length for various charge strengths, we simulated chains of $N = 8$, 16, 32, and 64 mass points. To maintain a narrow distribution of bond lengths, we used the bond spring constant $k_b = 5000\epsilon/\sigma^2$, where ϵ is the energy and σ the characteristic length scale of the Lennard-Jones potential. This parameter yields a standard deviation which is smaller than 2% of the equilibrium bond length $l = 2^{1/6}\sigma$.

The strength of the Coulomb interaction is determined by the Bjerrum length $\lambda_B = e^2/\varepsilon k_B T$, where ε is the dielectric constant of the solvent. In the simulation a normalized quantity is used as a measure of the interaction strength between the charges: $\tilde{\lambda} = e^2/\varepsilon\epsilon\sigma$. The simulation covers the interaction range $0 \leq \tilde{\lambda} \leq 23.6$, i.e., from a chain in good solvent to a totally collapsed chain. Thus, our simulations go beyond previous simulations, where either weakly charged or noncollapsed chains were considered [9,10].

We performed constant temperature simulations based on the Langevin equation. The temperature is chosen as $k_B T = 1.2\epsilon$, the damping constant as $\gamma = 1/\tau$, where τ is the time unit of the simulation, and the time step as $2 \times 10^{-3}\tau$. In order to achieve a reasonable statistics up to 16 runs per chain and charge strength were performed each of 10^6 time steps.

Results for the neutral chains are well known. In particular, the end-to-end distance and the radius of gyration obey the scaling law $R^2 \sim R_g^2 \sim N^{2\nu}$ with $\nu \approx 0.6$. Intuitively, it is obvious that an increase of the charges causes a stretching of a chain due to a repulsion of the charged monomers. However, from the theory of Manning condensation it is known that for Bjerrum lengths $e^2/\varepsilon k_B T \geq 1l$, where l is the distance between charged units along the chain, counterions start to condense [11]. The condensation leads to a screening of the charges of the chain, and its conformation is changed. Up to now there is no systematic study of the conformational changes of a chain due to screening by counterion condensation. From the simulations in Ref. [3] it is obvious that the chain dimensions shrink with increasing $\tilde{\lambda}$ beyond the condensation value $\tilde{\lambda}\epsilon/k_B T \approx 1$. The analytical theories of Odijk [12] and Skolnick and Fixman [13] are only applicable in the rod limit. But for $\tilde{\lambda}\epsilon/k_B T > 1$ chains are no longer rodlike.

Our simulations confirm the intuitive picture for increasing $\tilde{\lambda}$. Figure 1 exhibits an increase of the radius of gyration R_g with increasing interaction strength. At $\tilde{\lambda} \approx 1$–$2$ the maximum value of R_g is reached, and the chains start to collapse again. The collapse finally stops, and a limiting value is assumed, which is below the value of the chain in a good solvent. The changes of the end-to-end distance R and the radius of gyration with increasing chain length can well be described by the scaling relations $R^2 \sim (N-1)^{2\nu_e}$ and $R_g^2 \sim (N-1)^{2\nu_g}$. In contrast to a chain in a good solvent, the exponents ν_e and ν_g are different, at least for $\tilde{\lambda} > 10$. The dependence on the charge strength is shown in Fig. 2. Starting from the value in good solvent, the exponents increase with $\tilde{\lambda}$, reflecting the stretching of the chain. The end-to-end distance approximately reaches the value of a rodlike chain ($\nu_e = 1$). The exponent of the radius of gyration, however, is below that value. Generally, up to $\tilde{\lambda} \approx 10$, ν_g is smaller than ν_e. For $\tilde{\lambda} > 10$ the situation is reversed. The intersection point between the two curves could correspond to a chain in a θ solvent. At approximately the same charge strength, the curves of Fig. 1 intersect. However, to finally decide whether all curves of Fig. 1 intersect in one point, more simulations are required. The exponent $\nu_g \approx 0.3$ at large $\tilde{\lambda}$ corresponds to the value of a chain in bad solvent. However, $\nu_e \approx 0.25$ is below that value. Obviously, compact globules are formed, where the end points are less free than for chains in a bad solvent. The scaling exponents can very well be extracted from the respective data, and simulations of chains of length $N = 128$ for certain charge strengths confirm the above results. An estimate of the errors based upon the standard deviations of the average of the 16 performed runs yields relative uncertainties below 10%. The chain lengths used in the simulations correspond to experimentally relevant molecular weights, if a model chain segment is imaged on a real chain section and we expect that the obtained scaling behavior would also be observed in an experiment.

The breakdown of a universal scaling behavior is also evident from the investigation of the static structure factor $S(k)$. If a unique length scale exists in a problem, simple dimensional analysis leads to the power law dependence $S(k) \sim k^{1/\nu}$ for sufficiently long chains [14], and the structure factor is a universal function of the product kR_g. The analysis of the chain structure factor confirms this behavior for zero charges, but exhibits that the scaling is only valid for $kR_g < 1.5$ as long as $\tilde{\lambda} > 0$. For larger scattering vectors significant differences of the structure factors for the various chain lengths are found. However, for large k values a scaling regime is obtained for $\tilde{\lambda} < 7$. From this regime a scaling exponent can be extracted, particularly for those systems where we simulated chains up to length $N = 128$. But these exponents are equal to or smaller than ν_g and ν_e. This behavior clearly indicates the existence of different (at least two) length scales in the system [3].

As is obvious from, e.g., Fig. 1, the condensation of counterions changes the conformation of a

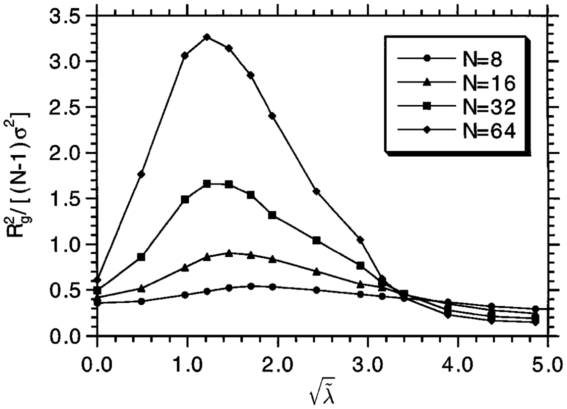

FIG. 1. Squared radius of gyration divided by the number of bonds as a function of the square root of the interaction strength for various chain lengths N.

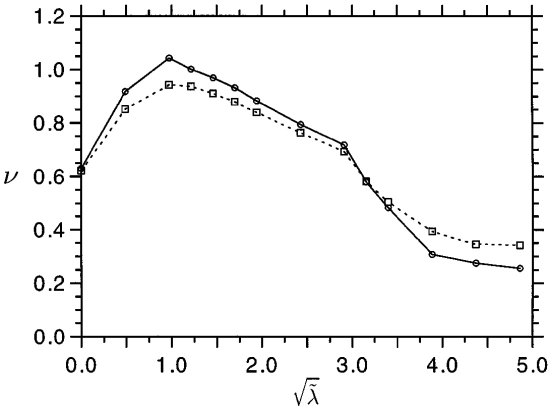

FIG. 2. Scaling exponents ν_e (○) of the end-to-end distance $R^2 \sim (N-1)^{2\nu_e}$ and ν_g (□) of the radius of gyration $R_g^2 \sim (N-1)^{2\nu_g}$, respectively, as a function of the interaction strength.

macromolecule. The question then is as follows: What is the interaction along the chain which leads to the chain collapse, and how are the ions distributed along the chain? To clarify these questions we studied the distribution of the counterions with respect to the chain. Figure 3 depicts the number of counterions (N_{ion}) within a distance $r = 1.5\sigma$ perpendicular to the chain for various interaction strengths $\tilde{\lambda}$ and chain lengths. At $\tilde{\lambda} \approx 1$ condensation sets in and proceeds until all ions are condensed. The curves for the various chain lengths deviate from each other. For a given $\tilde{\lambda}$ the amount of counterions within 1.5σ of a chain increases with increasing chain length. According to standard ideas, a chain of a given fraction of charges will ultimately be stretched with increasing chain length due to the long range nature of the Coulomb interaction [1]. From our simulations we conclude that this is no longer true for chains in the presence of counterions. The increase of the counterions seen in Fig. 3 leads to a screening of the charges of the chain such that the dimensions (R^2, R_g^2) of the chain increase according to power laws with exponents approximately given in Fig. 2. This certainly holds for even longer chains because screening does not occur only due to counterions within a distance of 1.5σ from a chain. The increase of the Coulomb interaction within the chain with increasing chain length is balanced by a similar increase of the Coulomb interaction with the counterions.

For small interaction strengths $\tilde{\lambda} < 2$, the charges are rather mobile along the chain. This obviously follows from the monomer-counterion pair distribution function $g_{\text{mon-ion}}$ presented in Fig. 4 for the chain of $N = 32$ particles. The ion-ion pair distribution function, as well as the distribution function of ions perpendicular to the chain, supports this conclusion. However, with increasing interaction strength the ions begin to localize at certain positions along the polymer chain. For $\tilde{\lambda} > 6$ there is already a preference for monomer-ion distances $r \approx \sigma$ (cf. Fig. 4). With increasing interaction strength the peak at $r = \sigma$ becomes more and more pronounced which is an indication for the localization of the ions on the chain and the formation of ion pairs. The distribution function of the ions along the chain contour finally shows that the counterions are localized in between two successive monomers with a distribution which is much smaller than the bond length. Since the number of counterions is equal to the number of monomers, one counterion is localized at one of the chain ends causing an increased density of ions there as well as an attractive force between the chain ends. It is this condensation of the ions which causes $\nu_e = 0.25$ in the collapsed state.

The condensation causes a screening of the Coulomb interaction between the chain monomers. If the charges are completely screened, one might expect chain scaling behavior similar to that of a chain in a good solvent (Debye-Hückel model). From the simulation, however, we find the scaling behavior of a collapsed molecule, which requires an attractive interaction between the new units of the chain formed by monomers and condensed ions. Comparing the density and reduced temperature $T^* = k_B T \epsilon a / e^2$, where a is the diameter of the particles, of our simulations with results for the phase behavior of a restricted primitive model (RPM) [15,16] we see that our systems are far from the vapor-gas coexistence curve and correspond to a gas of ions. The density $\varrho^* = \varrho a^3 = 6.1 \times 10^{-5}$ is far below the critical density $\varrho_c^* = 0.023\text{–}0.035$. The temperature $T^* = (k_B T/\epsilon) a / \sigma \tilde{\lambda} = 0.057$ (here we used $\tilde{\lambda} = 23.6$) is approximately equal to the critical temperature $T_c^* = 0.052\text{–}0.056$ for cluster formation. This estimation expresses the fact that the connectivity of the chain is essential for the collapse of the system. A gas of ions at the same density would not form a compact colloidal structure. This is confirmed by computer simulations. After cutting the bonds the original compact structure (for $\tilde{\lambda} = 23.6$) is evaporating at a constant temperature ($k_B T = 1.2\epsilon$). Because of the bonds, however, the charge density is inhomogeneous,

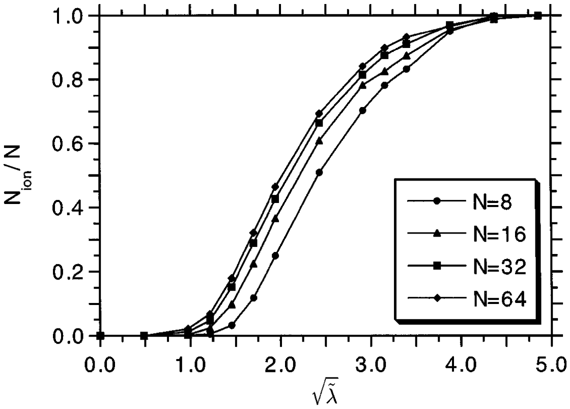

FIG. 3. Fraction of ions within a distance of $r < 1.5\sigma$ perpendicular to a chain molecule as a function of the interaction strength and for various chain lengths.

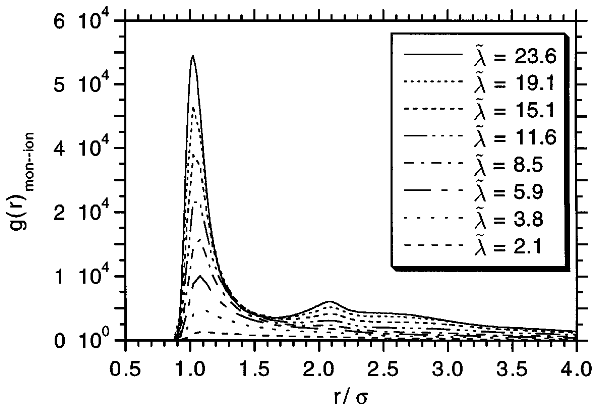

FIG. 4. Pair correlation function between chain monomers and counterions for various interaction strengths $\tilde{\lambda}$.

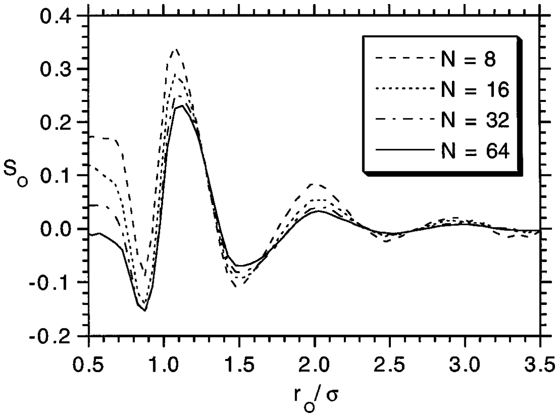

FIG. 5. Dipole orientational order parameter for various chain lengths.

and the local charge density is sufficiently high to induce a collapse of the whole system.

To account for the attractive interaction along the chain, we expect that the formation of ion pairs is associated with the appearance of dipole moments. The existence of ion pairs is obvious from the distribution of counterions discussed above (Figs. 3 and 4). Numerically, the dipoles were determined as follows: Starting at a chain end monomer, the nearest counterion was determined and a dipole moment assigned to that pair. We then jumped to the next monomer and again determined the nearest counterion leaving out the one(s) already built into other dipoles. Since the number of monomers is equal to the number of ions, we are able to build dipoles incorporating all particles by that procedure. To study the relative orientation of the various dipoles, we determined the orientation order parameter $S_O = (3\langle\cos^2\theta\rangle - 1)/2$ as a function of their separation r_O, where θ is the angle between the dipoles. From Fig. 5 we conclude that there are indeed dipoles which assume preferred orientations, particularly at a distance of one bond length. The orientation depends upon the chain length for short chains, but approaches a limiting curve which is close to the one for $N = 64$ as our simulations for a chain of length $N = 128$ demonstrate. Considering the cosine of the relative angle itself, we find that dipoles separated by $r_O \approx 1\sigma$ are aligned preferentially antiparallel, whereas those at distances $1.5 < r_O < 2$ are aligned preferentially parallel. Using the concept of dipoles may help to understand the collapse of the discussed systems.

In conclusion, the current simulations exhibit features of counterion condensation which reach beyond the Manning condensation theory. In particular, we observe a scaling behavior of the radius of gyration and the end-to-end distance which cannot be explained by simple theories and is a consequence of the complex interplay between the increase of the chain length and the screening due to the counterions. For highly charged chains we find that counterion condensation leads to an inhomogeneous charge distribution and the formation of ion pairs. The resulting attractive interaction (e.g., dipole-dipole) leads to a collapse of the whole chain into a very compact structure. It is exactly this behavior which is responsible for the collapse of polymer chains and gels after extra ionization [5–7].

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