Effective charge, collapse and the critical point of a polyelectrolyte chain

Arindam Kundagrami and M. Muthukumar
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

The charge of a polyelectrolyte (PE) controls myriads of phenomena in biology, biotechnology, and materials science, but still remains elusive from an understanding. Considering the adsorption of counterions on an isolated PE chain, an analytical expression for the effective charge - valid for all chain flexibility, for variable salt, in good solvents at all conditions, in poor solvents in the expanded (coil) state away from the critical point, and for gels, brushes and other PE systems in their expanded state - is derived. Phase boundaries and the critical point for the 1-st order collapse transition, induced cooperatively by counterion adsorption and chain conformations, are calculated self-consistently. The size of the PE chain is found to be a single-valued function of charge.

PACS numbers: 36.20.-r, 36.20.Ey, 47.57.Ng, 82.35.Rs

The net charge of a polyelectrolyte (PE) chain in salty aqueous solutions is the most fundamental albeit elusive entity faced in systems containing charged polymers. Manifestations of charged polymers, whether m-RNA, ss- or ds-DNA, proteins, polysaccharides, or synthetic analogs such as polystyrene sulfonates, and the ways in which they fold conformationally and move in solutions depend crucially on their charge. These conformational fluctuations of PE chains under external stimuli are of critical importance to numerous biological and synthetic processes. A charged chain assumes in a good solvent a much larger dimension\[1, 2\] than an uncharged self-avoiding-walk (SAW) chain due to electrostatic repulsion between like-charged monomers. This repulsive force resists the collapse of the PE in a poor solvent, but only up to a certain degree of hydrophobicity, beyond which it assumes similar to neutral chains a dimension way below the Gaussian value.\[3, 4\] Additionally, the PE has its counterions some of which adsorb (i.e., condense) on the monomers and modulate the effective charge. An optimization between electrostatic binding energy and translational entropy controls this effective charge which, in turn, affects the size of the chain and vice versa. Therefore, a self-consistent procedure is necessitated to calculate the size and the effective charge of the PE molecule.

A number of theories\[5\] addressed the size dependency of a PE chain (or a PE gel\[6\]) on its effective charge, which is taken as a fixed parameter independent of its size. However, a fixed finite charge is incompatible to a collapsed PE chain in poor solvents as it leads to severe electrostatic energy penalty. Variable PE charge was addressed\[7\] within the Oosawa model assuming rod-like chains. A three-state model\[8\] earlier self-consistently calculated the size and charge with the free counterions partitioned into two domains - one within and the other outside the radius of gyration ($R_g$) of the PE. A successful analysis\[9\] of collapse due to counterion correlations in good solvents, however, failed to include the counterion adsorption effects and the right experimental trends. A theory that captures counterion adsorption, intra-chain electrostatic repulsion, and polymer conformational changes in a self-consistent way is yet to emerge.

Experiments\[10, 11\] and simulations\[12\] have indisputably demonstrated that a PE chain at a specific poorness of the solvent collapses to a globule. However, the stability of the exciting intermediate pearl-necklace phase\[13\], made of globules and elongated chain parts co-existing in a single chain, remains a controversial\[12\] issue. In this letter we analyze the variational theory of counterion adsorption\[2, 14\], and derive an analytical expression for the charge of a flexible PE chain in good solvent conditions. Further, we determine the condition for collapse of the PE chain in a poor solvent and calculate the phase boundaries for this first-order coil-globule transition induced cooperatively by counterion adsorption and solvent poorness. Temperature controls both the solvent quality and the Coulomb strength. This formalism, fundamentally different from the Manning condensation theory\[15\], accounts for the interplay between chain conformations and counterion adsorption from a neutralizing plasma, as well as for the “oily” chemical nature of the polymer backbone. Addressing such interplay is crucial to understand the transformations between expanded and contracted polymer conformations encountered in a multitude of life processes, and to further explore a possible decoupling of charge and size. The simplest candidate of coil-globule transition to exhibit the new paradigm is used to elucidate ideas pertinent to the swelling of ionic gels, behavior of charged polymers at surfaces and interfaces, and assemblies such as viruses.

The total free energy of the system consisting of an isolated flexible PE chain with ionizable monomers, counterions, and the added salt ions (all monovalent) in high dilution is taken to be\[2\]
\[
F = F_1 + F_2 + F_3
\]

where,
\[
F_1 = \frac{N k_B T}{N} \left( f_m - \alpha \right) \log \left( 1 - \frac{\alpha}{f_m} \right) + \alpha \log \left( \frac{\alpha}{f_m} \right),
\]
\[
F_2 = \frac{N k_B T}{N} \left( f_m - \alpha + \frac{\tilde{c}_s}{\tilde{\rho}} \right) \log \left( \frac{\tilde{\rho}(f_m - \alpha) + \tilde{c}_s}{\tilde{\rho}} \right) + \frac{\tilde{c}_s}{\tilde{\rho}} \log \tilde{c}_s - \left( f_m - \alpha + 2 \frac{\tilde{c}_s}{\tilde{\rho}} \right),
\]
\[
F_3 = -\frac{2}{3} \sqrt{\pi} \frac{\tilde{\rho}^{3/2}}{\bar{\rho}} \left( \tilde{\rho} \left( f_m - \alpha \right) + 2\tilde{c}_s \right)^{3/2},
\]

and the other outside the radius of gyration ($R_g$) of the PE. A successful analysis\[9\] of collapse due to counterion correlations in good solvents, however, failed to include the counterion adsorption effects and the right experimental trends. A theory that captures counterion adsorption, intra-chain electrostatic repulsion, and polymer conformational changes in a self-consistent way is yet to emerge.
\[
\frac{F_4}{Nk_B T} = -\alpha \tilde{l}_B \delta,
\]
\[
\frac{F_5}{Nk_B T} = \frac{3}{2N} \left( \tilde{l}_1 - 1 - \log \tilde{l}_1 \right) + \frac{4}{3} \frac{3}{2\pi} \sqrt[3]{\frac{N}{l_1^0}} \Theta_0(a),
\]
\[
+ \frac{w_3}{Nl_1^0} + 2\sqrt{\frac{2}{N}} l_1^0 \frac{N}{l_1^0} \frac{l_1^0}{l_1^0} \Theta_0(a), \quad \text{where}
\]
\[
\Theta_0(a) = \frac{\sqrt{\pi}}{2} \left( \frac{2}{a^{3/2}} - \frac{1}{a^{3/2}} \right) \exp(\text{erf}(\sqrt{a} + \frac{1}{3a}) + \frac{1}{2} \left( \frac{1}{a^2} \right) - \frac{\sqrt{\pi}}{2a^{3/2}}.
\]

with the contributions being due to, respectively, the entropy of mobility along the chain backbone of adsorbed counterions (\(F_1\)), the translational entropy of the free ions (\(F_2\)), fluctuations in densities of all mobile ions (\(F_3\), as in the Debye-Hückel theory), adsorption (Coulomb) energy of the bound pairs (\(F_4\)), and the free energy of the chain\(^{14}\) (\(F_5\)) resulting from its connectivity (conformational entropy), the excluded volume (two-body), steric (three-body), and screened electrostatic interactions between monomers. Here \(f_m = N_e/N, \alpha = M/N, \) with \(N, N_e,\) and \(M\) being the numbers, respectively, of monomers, of ionizable monomers, and of adsorbed counterions, \(k_B\) the Boltzmann constant, and \(T\) the temperature. \(\tilde{c}_s = c_s l_0^0 / \Omega, \) and \(\tilde{\rho} = \rho l_0^0 / \Omega\) with \(c_s, l_0,\) and \(\Omega\) being, respectively, the number of salt cations, the length of a monomer (Kuhn step length for a flexible polymer), and the volume of the system.

\[
\tilde{k} = \sqrt{4\pi \tilde{l}_B \left( \rho \left( f_m - \alpha \right) + 2\tilde{c}_s \right)}
\]
is the dimensionless inverse Debye length. Here, \(\tilde{k} = k l_0,\) and \(\tilde{l}_B = C_1/T\) is the dimensionless Bjerrum length with \(C_1 = e^2/4\pi k_B \epsilon_0 \epsilon_0 l_0,\) where \(e, \epsilon_0,\) and \(\epsilon\) are the electron charge, vacuum permittivity, and the solvent dielectric constant, respectively. \(\delta = (d l_0 / \epsilon_0 d)\) with \(\epsilon_1,\) and \(d\) being, respectively, the local dielectric constant\(^2\)\(^{10}\), and the ion-pair separation. Further, \((R^2) = N l_1 \equiv N^2 l_1^0 = 6r_0^2\) with \(l_1 = l_1 / l\) and \(f = (N_e - M) / N_m = f_m - \alpha. \Theta_0(a) = 2 / 15(a \ll 1, 1 / 3a(a \gg 1)\) is a cross-over function\(^2\)\(^{14}\) of \(a \equiv k^2 N l_1^0 / 6\).

Generally, \(F = \sum_i F_i\) must be minimized self-consistently with both \(f\) and \(\tilde{l}_1\) to obtain the equilibrium values of the variables. We note that \(f\) features in \(F_5\) only in the fourth term that describes the long-range electrostatic interactions between charged monomers. However, the adsorption energy (\(F_4\)) related to the short-range ion-pair electrostatic attraction is more significant to \(F_5\) and shows a greater variation with \(f\) in most conditions. At low salt both the logarithmic and the linear terms in \(F_2\) will dominate the \(f^{3/2}\) term in \(F_3,\) and at high salt the variation of \(F_3\) with \(f\) is negligible. The full numerical analysis confirms these predictions, and allows us to propose an adiabatic approximation in which the chain free energy (\(F_3\)) is decoupled from the rest. Then \(F_{ad} = F_1 + F_2 + F_3\) are the relevant contributions that determine the effective charge \(f.\) This

adiabatic approximation, however, progressively fails for lower molecular weights, higher \(\tilde{l}_B\)’s and lower \(\delta\)’s (\(F_5\) becomes important and comparable to \(F_4\) in those cases), but, otherwise, remains applicable for a reasonably wide range of experimental conditions, especially at low and very high salts. Within adiabatic approximation, therefore, \(F_{ad}\) does not contain the expansion factor and we can minimize over only \(\alpha\) to obtain the effective charge.

\[
\frac{\partial F_{ad}}{\partial \alpha} = 0 \quad \text{gives us, using} \quad f = f_m - \alpha,
\]

\[
f = \frac{-\left( \tilde{c}_s + e^{-\delta l_B} \right) + \sqrt{\left( \tilde{c}_s + e^{-\delta l_B} \right)^2 + 4 \tilde{\rho} f_m e^{-\delta l_B}}}{2 \tilde{\rho}}
\]

(\(f_m = 1\) for a fully ionizable chain). The present model is immediately related to experimental systems, where the “oily” backbone of the polymer presents heterogeneities in the dielectric function of the medium. Eq. \(^2\)\(^{14}\) is the expression for the effective charge of an isolated PE chain, regardless of its flexibility, at all conditions in a good solvent, and in the expanded (coil) state away from the critical point in a poor solvent. This closed form analytical
expression, as a function of the monomer density, maximum ionizability, salt concentration, the Bjerrum length (temperature and the bulk dielectric constant), and the dielectric mismatch parameter $\delta$, is reported for the first time in literature. $\delta = C_2 c_0$ has a non-universal constant $C_2 = (\varepsilon d)^{-1}$, which can be determined from experiments using Eq. (2). Further, the contributions to $F_{\text{ad}}$ only depend on the number of ionizable monomers inside a polymeric system, not on the size and shapes of the chains. In addition, the effective charge depends only on the average monomer density $\rho$ (in volume $\Omega$), but not explicitly on the molecular weight ($N$). The generality of the effective charge expression warrants its validity for gels, brushes, and any other PE system in dilute solutions, as long as with changing $f$ the variation in the adsorption energy for bound counterions ($F_4$) is more significant to the variation of the intra-chain electrostatic interaction energy (term 4 in $F_3$). For denser systems, higher counterion adsorption is expected in order to minimize the intra-chain repulsive energy. The size of the chain in the adiabatic (or expanded) state is determined by minimizing $F_3$ with respect to $l_1$, using the $f$ from Eq. (2).

When the chain collapses ($l_1 \leq 1$, the Gaussian value) in a poor solvent away from the critical point, the chain collects most of its counterions reducing the effective charge and the electrostatic penalty, and the two- and three-body interaction terms dominate the free energy ($F_3$). Here we employ the neutral chain approximation in which we assume $f \approx 0$ or $\alpha = f_m$, and only $F_3$ (with the fourth term in it being zero) survives. This approximation breaks down (verified numerically) progressively closer to the critical point where the electrostatic interactions between monomers become comparable to the excluded volume and steric interactions. However, away from the critical point $\partial F_3/\partial l_1 = 0$, in conjunction with $l_1 \leq 1$ in the collapsed state, yields the expansion factor

$$\tilde{l}_1 = \left( \frac{3}{2} \right)^{\frac{1}{2}} 2 \pi \left( \frac{w_3}{w} \right)^{\frac{1}{2}} N^{-\frac{1}{2}} = 2.274 \left( \frac{w_3}{w} \right)^{\frac{1}{2}} N^{-\frac{1}{2}}. \tag{3}$$

This implies that $R_g^2 \sim R_g^2 (\theta) \tilde{l}_1^2 \sim N l_0^2 N^{-1/3}$, or $R_g \sim N^{1/3}$, which is the compact globule limit. Note that $w$ must be negative to have a collapse ($l_1 \leq 1$). Now, exactly at collapse the binodal (equal chemical potential) states are, respectively, the $f = 0$ (collapsed) and $f \neq 0$ (expanded). Note that for the present situation, chemical potential is the free energy per monomer. Equality of chemical potentials of the components in these two phases having zero osmotic pressure achieved in equilibrium in a dilute solution yields, using Eq. (2) to determine the free energy at collapse,

$$\frac{1}{Nk_B T} \left\{ (F_1 + F_2 + F_3) \bigg|_{\alpha = \alpha^c} - (F_1 + F_2 + F_4) \bigg|_{\alpha = f_m} \right\} + 4 \left( \frac{3}{2\pi} \right)^{3} \left( \frac{1}{w_3} \right)^{3} \left( 1 - \Theta_{\ell}/T \right)^{2} = 0 \tag{4}$$

where, $\alpha^c$ satisfies Eq. (2), and the dependency of $w$ on $T$ is given as $w = (1 - \Theta_{\ell}/T)$. Considering the temperature dependency of the Bjerrum length, $l_B = C_1/T$, simultaneous solutions of $T$ and $\alpha^c$ in Eqs. (2) and (4) give us the temperature and the effective charge of the expanded chain at collapse.

![FIG. 2: Salt induced collapse of a fully ionizable polyelectrolyte chain. Fixed parameters are: $N = 1000$, $\tilde{c} = 0.0005$, $\delta = 3.0$, Ionizability $f_m = 1.0$, $\Theta_{\ell} = 400K$, $T = 300K$, and therefore, $l_B = 3.0$, and $w = -0.333$. Critical values are: $\tilde{c}_1 = 0.00305$, $w_1 = 0.46$, $l_1 = 0.9$, and $f^* = 0.051$. Dotted curves are the analytical result [Eq. (2)] in the expanded state.]

The above approximations which simplify the analysis by decoupling the chain free energy with rest and allow us to obtain the closed form expression of charge [Eq. (2)] fail near the critical point where $f$ is substantially higher than zero. Therefore, to obtain the critical point and the phase boundaries, we minimize the total free energy (sum of all five components) numerically with respect to both variables (i.e., $f$ and $l_1$). The critical point and the phase boundaries for the temperature induced collapse of a fully ionizable chain in salt-free conditions are presented in Fig. 1. The unique feature of this calculation is to take temperature as the only independent variable, thus rendering $w$ and $l_B$ as dependent functions through, respectively, the relations $w = 1 - \Theta_{\ell}/T$, and $l_B = 18000/c T l_0$, assuming that the Bjerrum length in water at room temperature is $\sim 0.75$ nm, and the Kuhn length ($l_0$) is $\sim 0.25$ nm [keeping in mind a polymer of type sodium polyethylene glycol (PEG)].
ternized poly-2-vinylpyridine) is reduced keeping the mixture of 1-propanol and 2-pentanone containing quater-

cative behavior with a purely collapse induced collection of electrostatic energy penalty. One may contrast this coop-
gible with rampant counterion adsorption minimizing the in the expanded state helps counterion adsorption which collapse are mutually cooperative processes in the case clearly suggests that counterion condensation and chain
effect of ion-pairs that reduces the two-body interaction parameter only slightly without significantly affect-
ing the phase boundaries is ignored. The phase boundary clearly suggests that counterion condensation and chain
collapse are mutually cooperative processes in the case of a varying Coulomb strength. Lowering temperature in the expanded state helps counterion adsorption which reduces the effective charge and hence the resistance to collapse. Once the collapse occurs, charge becomes negligible with rampant counterion adsorption minimizing the electrostatic energy penalty. One may contrast this coop-
erative behavior with a purely collapse induced collection of counterions, where only the solvent quality (for the mixture of 1-propanol and 2-pentanone containing quar-
ternized poly-2-vinylpyridine) is reduced keeping the the Coulomb strength (Bjerrum length times dielectric con-
stant) virtually unchanged. Similar measurements of size and ionic conductivity as the temperature is varied would validate the major concepts presented in this letter.

In Fig. 2 we present the phase boundaries for the salt induced collapse of a fully ionizable PE at 300K, at which the solvent is poor (note, $\Theta_t = 400K$). This shows that room temperature collapse of polymer of type NaPSS in water is possible in the presence of salt but unlikely at salt-free conditions (Fig. 1) unless solvent poorness is drastically enhanced. There are remarkable quali-
tative similarities between salt and temperature induced collapse (Fig. 1). The main ideas of the phase transitions, arising from the coupling between counterions and poly-
mer conformations, are also valid for the volume transitions of PE gels and brushes. New experiments monitoring the counterion density inside the gels and brushes will stimulate a fundamental understanding of this important class of soft materials. One finally notes that computer simulations ignore the dielectric heterogeneity present in real experimental polymeric systems. Equivalently, a low value of $\delta$ in our theory for which the counterion ad-
sorption is weak raises the possibility of a necklace-like structure. Experiments, however, see rough spheri-
cal objects with substantial incorporation of counterions within them, as predicted by our model.

We thank Rajeev Kumar for stimulating discus-
sions. This work was supported by NIH Grant No. 5R01HG002776 and National Science Foundation (NSF) Grant No. 0605833.

* corresponding author: muthu@polysci.umass.edu

[1] M. Beer, M. Schmidt, and M. Muthukumar, Macromolecules 30, 8375 (1997); M. J. Stevens and K. Kremer, J. Chem. Phys., 103 1669 (1995); R. G. Winkler, M. Gold, and P. Reineker, Phys. Rev. Lett. 80, 3731 (1998); S. Liu and M. Muthukumar, J. Chem. Phys. 116, 9975 (2002).
[2] M. Muthukumar, J. Chem. Phys. 120, 9343 (2004).
[3] C. Williams, F. Brochard, and H. L. Frisch, Ann. Rev. Phys. Chem. 32, 433 (1981); T. M. Birshtein and V. A. Pyramitsyn, Macromolecules, 24, 1554 (1991); I. M. Lifshitz, A. Y. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys., 50, 68 (1978).
[4] M. Muthukumar, J. Chem. Phys. 81, 6272 (1984).
[5] C-Y. Shew and K. Yoshikawa, J. Chem. Phys. 126, 144913 (2007); B-Y. Ha and D. Thirumalai, Phys. Rev. A 46, R3012 (1992); A. Dua and T. A. Vilgis, Europhys. Lett. 71, 49 (2005); C-Y. Shew and A. Yethiraj, J. Chem. Phys. 110, 667 (1999); H. Schiessel and P. Pincus, Macromolecules 31, 7953 (1998); H. Schiessel, Macromolecules 32, 5673 (1999).
[6] T. Tanaka et al., Phys. Rev. Lett. 45, 1636 (1980).
[7] A. V. Dobrynin and M. Rubinstein, Macromolecules 34, 1964 (2001).
[8] E. Y. Kramarenko, A. R. Khokhlov, and K. Yoshikawa, Macromol. Theory. Simul. 9, 249 (2000); V. V. Vasilevskaia, A. R. Khokhlov, and K. Yoshikawa, 9, 600 (2000); E. Y. Kramarenko, I. Y. Erukhimovich, and A. R. Khokhlov, 11, 462 (2002).
[9] N. V. Brilliantov, D. V. Kuznetsov, and R. Klein, Phys. Rev. Lett. 81, 1433 (1998).
[10] V. V. Vasilevskaia et al., J. Chem. Phys. 102, 6595 (1995); M. Ueda and K. Yoshikawa, Phys. Rev. Lett. 77, 2133 (1996); K. Yoshikawa et al., Phys. Rev. Lett. 76, 3029 (1996); A. Yamada et al., Appl. Phys. Lett. 86, 223901 (2005); S. Wang and J. Zhao, J. Chem. Phys. 126, 091104 (2007).
[11] P. Loh et al., Macromolecules 41, 9352 (2008).
[12] R. Chang and A. Yethiraj, Macromolecules 39, 821 (2006); G. Reddy and A. Yethiraj, 39, 8536 (2006).
[13] A. V. Dobrynin, M. Rubinstein, and S. P. Obukhov, Macromolecules 29, 2974 (1996); H. J. Limbach, C. Holm, and K. Kremer, Europhys. Lett. 60, 566 (2002); L. J. Kirwan, G. Papastavrou, and M. Borkovec, Nano Lett. 4, 149 (2004).
[14] M. Muthukumar, J. Chem. Phys. 86, 7230 (1987).
[15] G. S. Manning, J. Chem. Phys. 51, 924 (1969).
[16] E. L. Mehler and G. Eichele, Biochemistry 23, 3887 (1984).