

Excess Charge in Polyampholytes.

Y. KANTOR(*)(**)(***) and M. KARDAR(*)(* **)

(*) *Department of Physics, Massachusetts Institute of Technology
Cambridge, MA 02139, USA*

(**) *Physics Department, Harvard University - Cambridge, MA 02138, USA*

(***) *School of Physics and Astronomy, Tel Aviv University
Tel Aviv 69978, Israel*(§)

(* **) *Department of Theoretical Physics, Oxford University - Oxford OX1 3NP, UK*

(received 18 April 1994; accepted in final form 12 August 1994)

PACS. 36.20 - Macromolecules and polymer molecules.

PACS. 35.20B - General molecular conformation and symmetry; stereochemistry.

PACS. 41.10D - Electrostatics, magnetostatics.

Abstract. - Polyampholytes (PAs) are composed of (quenched) random sequences of positive and negatively charged monomers. We show that the radius of gyration of a PA strongly depends on its charge Q , and is very weakly influenced by other aspects of the sequence. For $Q < Q_c \approx \approx q_0 \sqrt{N}$, where N is the number of monomers of charge $\pm q_0$, the PA is compact, while for $Q > Q_c$ it is stretched. We explain this transition by analogy with the shape instability charged drops (where the Rayleigh charge plays the role of Q_c), and suggest a «necklace» model for the shapes of highly charged PAs.

As the building blocks of living matter, long-chain macromolecules have been the subject of intense study. Given the large number of monomers making up such chains and the variety of their interactions, finding the configuration of a particular molecule is a formidable task. It may be possible to sacrifice the specificity of the macromolecule in the hope of gleaning some general information from simplified models [1-3]. Perhaps the coarsest characteristic of a molecule is some measure of its size, such as the radius of gyration R_g . For a polymer with charged groups, the overall size is most likely controlled by the Coulomb interactions which are the strongest and with the longest range. In this paper we consider the typical size of *polyampholytes* (PAs): polymers composed of positively and negatively charged groups [4]. Even determining the size of a simple model PA, formed from charged $\pm q_0$ randomly dispersed along the chain, has proved controversial. Appealing to a Debye-Hückel (DH) attraction in analogy to electrolytes, Higgs and Joanny [5] conclude that a PA minimizes its (extensive) free energy by contracting to a compact structure. By contrast, in ref. [3], we used an analogy to the renormalization group (RG) treatment of homogeneously charged polymers [6] to conclude that the PA is stretched by the (non-extensive) energy cost of

(§) Permanent address.

typical charge fluctuations. This contradiction was partially resolved [7] by noting that the DH theory requires exact neutrality of the electrolyte, while the RG-inspired approach treats equally all possible sequences; the *typical* charge of a random sequence, $Q \approx \pm q_0 \sqrt{N}$, sufficient to modify the behavior of the PA. Monte Carlo simulations [7] indeed confirm that PAs with $Q = 0$ compactify at low temperatures, while sampling all random quenches with unrestricted Q produces an average $R_g \propto N$. Unfortunately, the broad nature of the distribution of sizes in the latter ensemble provides little information about R_g of a specific PA.

Recently, Yu *et al.* [8] investigated the volume transition in gels produced by crosslinking PAs. The screening length is quite big, enveloping a large number of monomers N . By changing the *pH* of the solution, it is possible to control the excess charge Q , within the screening length. The neutral gel is naturally the most compact. Surprisingly, the volume of the gel does not change appreciably in an interval of Q below a threshold $Q_c \approx q_0 \sqrt{N}$. Immediately beyond this threshold, the gel expands by more than an order of magnitude. This motivated us to examine the dependence of the R_g of a PA on its charge. We find that Q is a good indicator of overall size, *i.e.* PAs with quite different sequences but the same excess charge, have a narrow distribution of R_g 's. The broad distribution of R_g 's for unrestricted PAs reflects the drastic variations of size with Q . In agreement with experiments, we find that PAs are compact for small Q , and stretched when Q exceeds a critical $Q_c \approx q_0 \sqrt{N}$. We provide a (partial) justification for this transition by analogy with a charged drop which is stable at small Q , but disintegrates after Q exceeds the Rayleigh charge Q_R . This analogy further motivates a «necklace» model for highly charged PAs.

The Monte Carlo (MC) procedure is identical to that of ref. [7]. We use self-avoiding chains on a cubic lattice of spacing a , with electrostatic interactions $U_{ij}(r) = q_i q_j / \sqrt{2a^2 + r^2}$ for every pair $\langle i, j \rangle$ of charges at a distance r ; where $q_i = \pm q_0$ with signs specific to a particular quench. We examined the dependence of polymer size on both temperature T , and excess charge Q ; always averaging over 10 *different* quenches. Equilibration times were sufficiently long to ensure that statistical uncertainties of thermal averages were smaller than the differences between quenches [9]. Figure 1 depicts the temperature dependence of R_g^2 for 64-monomer chains. The number near each curve indicates the charge Q/q_0 . At very high temperatures, electrostatic interactions are unimportant and the chains behave as self-avoiding walks, with $R_g \propto N^\nu$ and $\nu = 0.588$. As T is lowered, the effects of interactions

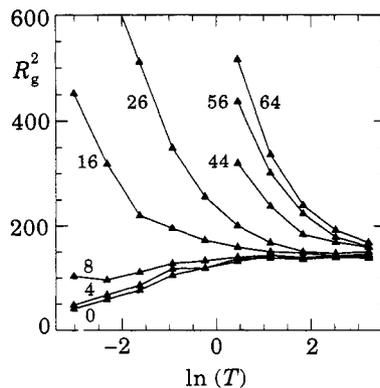


Fig. 1. $-R_g^2$ (in units of a^2) as a function of T (in units of q_0^2/a) for several values of the excess charge Q for a 64-monomer chain. Each point is an average over 10 quenches. Independent quenches are used at different temperatures. The numbers near each curve indicate Q/q_0 .

are first observed for the strongly charged polymers at $T_Q \approx Q^2/R_g \sim Q^2/N^\nu$ (measured in energy units). This follows from the estimate of Q^2/R_g for the electrostatic energy of a typical configuration. However, for weakly charged polymers, with $Q < q_0\sqrt{N}$, the main interaction is between the non-homogeneities in the charge distribution. The energy of a typical density fluctuation, $q(Q - q)/R_g \approx -q_0^2 N/R_g$ for $q \approx q_0\sqrt{N}$ exceeds Q^2/R_g and such PAs start to deviate from their infinite- T behavior at $T'_Q \approx q_0^2 N/R_g \sim q_0^2 N^{1-\nu}$. These arguments also suggest that on lowering T , the size of PAs with large Q increases (since the Coulomb energy of excess charge is repulsive), while R_g decreases for PAs with small Q (since the charge fluctuation energy is attractive). This is confirmed by a (high temperature) perturbative expansion of the radius in the strength of the interaction as in ref. [7]. The first correction is proportional to $\overline{q_i q_j} = (Q^2 - q_0^2 N)/N^2$ for $i \neq j$, and the change in the behavior of R_g occurs for $Q_c \approx q_0\sqrt{N}$.

Are the *averages* in fig. 1 a meaningful measure of the PA size? Figure 2 depicts histograms of the distribution of R_g^2 at $T = 0.05q_0^2/a$ for several values of Q . Since thermal fluctuations are small, this histogram represents the differences between quenches. Note that the distributions are fairly narrow; their widths not exceeding the distance between their averages. Thus the location of a point in fig. 1 provides a good measure of $R_g^2(Q)$, without need for any additional reference to the details of the sequence. If this function is known, the average of R_g^2 for *unrestricted* quenches is simply obtained from $R_g^2(\text{random}) = \int_0^\infty dQ R_g^2(Q) P(Q)$, where $P(Q) \propto \exp[-Q^2/2q_0^2 N]$ is the probability density of an excess charge Q . In previous work [7], we found that the distribution of $R_g^2(\text{random})$ was very broad. The current results indicate that this follows simply from the strong dependence of R_g^2 on Q , rather than a large scatter of R_g^2 among different quenches with similar Q . Exact enumeration studies of ground states of PAs [9] confirm that this conclusion also applies to (anti-) correlated sequences such as studied in ref. [10].

The curves in fig. 1 have a monotonic T -dependence. This suggests that the line separating

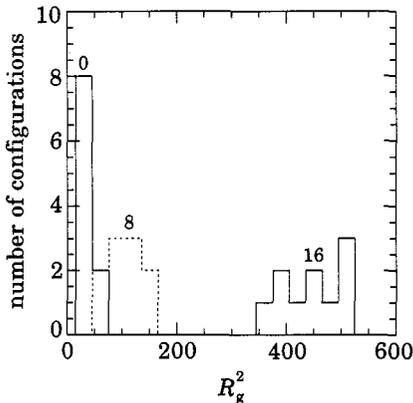


Fig. 2.

Fig. 2. – Histograms of the distribution of (ten) values of R_g^2 (measured for $N = 64$ at $T = 0.05q_0^2/a$) for several values of Q/q_0 , indicated near the histograms.

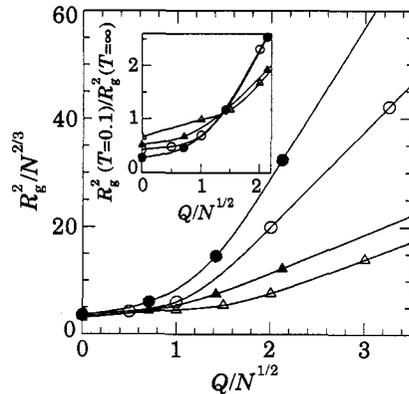


Fig. 3.

Fig. 3. – R_g^2 at $T = 0.1q_0^2/a$ scaled with $N^{2/3}$ in the main figure, and with R_g^2 of uncharged system (*i.e.* at $T = \infty$) in the inset, as a function of scaled charge Q/q_0 for chain lengths $N = 16$ (open triangles), 32 (full triangles), 64 (open circles), and 128 (full circles).

compact and extended states in the (Q, T) -plane is roughly straight, starting from $Q = Q_c = q_0 \sqrt{N}$ at infinite T . To test this hypothesis, we considered the Q - and N -dependence of the radius of gyration for chains of lengths $N = 16, 32, 64, 128$. To achieve good thermal averages, simulations were performed at $T = 0.1q_0^2/a$ and not at the lowest temperature in fig. 1. The dependence of R_g^2 on Q is depicted in fig. 3; the vertical axis is scaled so as to remove the trivial N -dependence for $Q = 0$. The charges on the horizontal axis are scaled to $Q/Q_c(N)$ for all polymer lengths. Although R_g^2 is a monotonically increasing function of Q , its variations are not gradual: for small Q the radius barely depends on Q , while beyond a certain threshold an extremely fast increase begins. This feature is further amplified at low temperatures: the low-charge polymers get smaller, while the charged ones increase in size. Figure 3 strongly suggests that the transition from compact to stretched configurations at low temperatures still occurs for $Q \approx Q_c$. In fact, the inset of fig. 3 plots $R_g^2(T = 0.1q_0^2/a)/R_g^2(T = \infty)$, showing that the curves become steeper with increasing N and intersect at $Q/N^{1/2} \approx 1.4q_0$. This implies that for $Q > 1.4Q_c$ the PAs at low T are more stretched than self-avoiding walks.

To explain these results, we start with the empirical observation that the neutral PA compactifies to more or less a spherical shape. This suggests an energy (or more correctly a quench averaged free energy) that grows with the number of monomers as $E(Q = 0) = -\varepsilon_c N + 4\pi R^2 \gamma$, where $\varepsilon_c \propto q_0^2/a$ is the energy gain per particle, and $R \approx aN^{1/3}$ is the radius in the collapsed state. A positive surface tension, $\gamma \approx q_0^2/a^3$, accounts for the spherical shape of such PAs. If we now uniformly add a charge Q to each configuration, its energy increases by Q^2/R . Therefore, $E(Q) \leq -\varepsilon_c N + 4\pi R^2 \gamma + Q^2/R$, the inequality indicating that the system can reduce its energy by rearranging the charges. We would like to find the rearrangements that minimize the energy. For the sake of generality, we shall consider $Q \propto q_0 N^\beta$, with emphasis on the most relevant case of $\beta = 1/2$. (Directed PAs with $Q \propto N^3$ have been studied by [11].) To gain some insight into the behavior of PAs we shall explore analogies to charged drops. In the following paragraphs we briefly discuss the shape of a charged *conducting* drop. This analogy is most appropriate for an annealed version of the problem in which the charges are free to move along the polymer chain. (Here, the term «annealed» means that the charges along the chain are mobile, although their sum is fixed. This differs from the definition used in ref. [12].) We then go on to consider the shape of a charged *insulating* drop (immobile charges), and finally conclude with applicability of such arguments to quenched PAs.

With the charge on the surface of a freely suspended *conducting* spherical drop of radius R , the non-extensive contribution to the energy is $E'(Q) = 4\pi R^2 \gamma + Q^2/(2R)$. As Q increases, the shape of the drop may change. The surface energy of an uncharged drop, $E'(0) = 4\pi R^2 \gamma$, sets the overall energy scale of the problem, while the dimensionless parameter,

$$\alpha \equiv Q^2/(16\pi R^3 \gamma) \equiv Q^2/Q_R^2,$$

determines its shape. (Q_R is the Rayleigh charge of the drop.) Note that the above estimates of γ and R for the model PA lead to $Q_R \approx Q_c$. We shall initially consider only deformations in shape that maintain the integrity of a single drop. Such deformations of a charged conducting drop, and related problems, have been considered by many authors [13]. It was noted by Rayleigh [14] that for $\alpha > 1$ the charged sphere is locally unstable and must thus become distorted. The problem was also studied by Taylor [15] who considered distortions into prolate spheroids. For spheroids, the energy and shape can be determined by minimizing a trial energy with respect to the eccentricity, e . We can show [9] that for $\alpha > 0.899$ the energy of the spheroid is smaller than that of the sphere, and the drop deforms into a strongly elongated shape. This qualitative similarity to the experimental results [8], and to fig. 3 is

encouraging. While the drop strongly elongates for finite α , it maintains a finite aspect ratio. Gutin and Shakhnovich [16] recently reached a similar conclusion by assuming that the charged PA distorts into a cylindrical shape with one long dimension R_{\parallel} , and two short dimensions R_{\perp} which are related by volume conservation: minimizing estimates of $E(Q)$ for such shapes leads to $R_{\parallel} \sim N^{(4\beta-1)/3}$, *i.e.* no significant stretching for $\beta = 1/2$. Another recent study by Dobrynin and Rubinstein [17] relaxes the constant volume constraint and also reaches the conclusion that there is an onset of stretching for $\beta = 1/2$, although a completely stretched state is reached only for $\beta = 2/3$, when the Coulomb energy becomes extensive.

However, the spheroidal shape *is not* a local energy minimum [15] as the strongly elongated spheroid is unstable to a variety of perturbations [13]. Experimentally, for $\alpha > 1$ the drop disintegrates into smaller ones. Indeed if splitting of a continuum droplet is allowed, its energy can be reduced to $E'(0)$. This is achieved by splitting away from the original drop an infinite number of infinitesimal droplets which contain all the charge but have vanishing total electrostatic energy, surface area and volume, and removing them to infinity. Even if the particles are required to stay connected (to maintain the connectivity of a chain), the system may be able to reduce its energy by expelling its charge in the form of a finger. Balancing the Coulomb energy (Q^2/L) of a finger of length L , with a condensation energy $\varepsilon_c L/a$, indicates $L \propto Q$. Such fingers appear spontaneously if their cost (roughly $Q\sqrt{\varepsilon_c/a}$) is less than the Coulomb energy of the uniformly charged sphere, Q^2/R , *i.e.* for $Q > R\sqrt{\varepsilon_c/a}$. Thus, the typical *annealed* PA has a protruding finger of length $L \propto N^{\beta}$ for $\beta > 1/3$. However, since the weight of the finger is small, it does not effect the scaling of R_g^2 for $\beta < 5/9$. Such annealed PAs have large spanning sizes without appreciably greater R_g .

Now consider an opposite limit where the charge is uniformly distributed along the polymer, mimicked by a droplet of charged *insulator*. The sum of electrostatic and surface energies for a spherical drop is $3Q^2/(5R) + 4\pi R^2\gamma$. Unlike the conducting case, energy cannot be lowered by expelling charge into small drops or fingers (since distortions of charge and volume are now connected). However, for $\alpha > 0.293$ a drop can reduce its energy by splitting into two equal drops separated by an infinite distance. Additional splittings occur for larger charges; the optimal number of droplets increasing linearly with α . We can again constrain the overall object to remain singly connected by attaching the droplets with narrow tubes of total length L and diameter a . As long as $L \ll aN$, most of the charge remains in the spheres. Equating the total electrostatic energy, $\propto Q^2/L$, to the condensation cost, $\varepsilon_c L/a$ (or a surface energy of γaL in the continuum parlance) leads to $L \propto Q$. Not surprisingly, the tubes in this case behave much the same as the fingers for the conducting polymer. However, whereas the surface tension in the conducting case results in one big central drop, for the insulating case the droplets are separated as in a necklace. The radius of gyration is now of the same order as the span of the necklace, L . The «neckless» model should also describe any collapsed polymer that is charged beyond Q_c , including those obtained from anti-correlated [10] or alternating [18] sequences.

How can we relate the above discussion to the quenched PA? The immobile charges are likely to produce a necklace of compact beads joined by narrow strings once the Rayleigh charge has been exceeded. However, it may be possible for the random PA to reduce its energy (compared to a homogeneous one) by taking advantage of charge fluctuations along its sequence: the strings will be constructed of segments with a larger excess charge than the average, while the beads are from segments closer to neutral. Thus, $R_g \propto Q$ may underestimate the size of the PA. The necklace picture may be hard to quantify if the beads and strings have a broad distribution of sizes. The following argument seems to suggest an upper bound to the total length of the strings L (and hence for R_g). The string segments must lose at least a portion of the condensation energy associated with compact beads. Since this energy loss can only come from a reduction in the Coulomb energy, we have

$L < aQ^2 / (\epsilon_c R) \propto N^{2z-1/3}$. Thus, while the quenched PA is certainly extended beyond the Rayleigh instability, it seems difficult to justify $R_g \propto N$. However, we began the discussion with rather robust assumptions on the condensation energy ($\propto N$) and surface energy ($\propto N^{2/3}$), while the end-result involved energies of order $N^{1/2}$. Consequently, an accurate estimate of the stretching of the quenched PA requires a more detailed knowledge of its energy spectrum. A full understanding of the behavior of PAs is yet to be attained.

* * *

We would like to thank B. I. HALPERIN for bringing the importance of surface tension to our attention, and D. ERTAS for helpful discussions. This work was supported by the US-Israel BSF grant No. 92-00026, by the NSF through No. DMR-87-19217 (at MIT's CMSE), DMR 91-15491 (at Harvard), and the PYI program (MK).

REFERENCES

- [1] BRYNGELSON J. D. and WOLYNES P. G., *Proc. Natl. Acad. Sci. USA*, **84**, 7524 (1987).
- [2] SHAKHNOVICH E. I. and GUTIN A. M., *Europhys. Lett.*, **8** (1989) 327.
- [3] KANTOR Y. and KARDAR M., *Europhys. Lett.*, **14** (1991) 421.
- [4] TANFORD C., *Physical Chemistry of Macromolecules* (Wiley, New York, N.Y.) 1961.
- [5] HIGGS P. G. and JOANNY J.-F., *J. Chem. Phys.*, **94** (1991) 1543.
- [6] PFEUTY P., VELASCO R. M. and DE GENNES P. G., *J. Phys. (Paris) Lett.*, **38** (1977) L-5.
- [7] KANTOR Y., KARDAR M. and LI H., *Phys. Rev. E*, **49** (1994) 1383.
- [8] YU X.-H., TANAKA A., TANAKA K. and TANAKA T., *J. Chem. Phys.*, **97** (1992) 7805; YU X.-H., Ph.D. Thesis, MIT (1993).
- [9] KANTOR Y. and KARDAR M., submitted to *Phys. Rev. E*.
- [10] WITTMER J., JOHNER A. and JOANNY J. F., *Europhys. Lett.*, **24** (1993) 263.
- [11] DERRIDA B. and HIGGS P. G., in *Proceedings of Surface Disordering, Growth, Roughening and Phase Transitions* (Les Houches, Nova Science, New York, N.Y.) 1992.
- [12] RAPHAEL E. and JOANNY J. F., *Europhys. Lett.*, **13** (1990) 623.
- [13] See, e.g., GRIGOR'EV A. I. and SHIRYAeva S. O., *Ž. Tekh. Fiz.*, **61** (1991) 19 (*Sov. Phys. Tech. Phys.*, **36** (1991) 258) and references therein.
- [14] LORD RAYLEIGH, *Philos. Mag.*, **14** (1882) 184.
- [15] TAYLOR G., *Proc. R. Soc. London, Ser. A*, **280** (1964) 383.
- [16] GUTIN A. M. and SHAKHNOVICH E. I., preprint (1994).
- [17] DOBRYNIN A. V. and RUBINSTEIN M., preprint (1994).
- [18] VICTOR J. M. and IMBERT J. B., *Europhys. Lett.*, **24** (1993) 189.