RANDOMLY CHARGED POLYMERS: EXCESS CHARGE
DEPENDENCE OF SPATIAL CONFIGURATIONS

YACOV KANTOR
School of Physics & Astronomy, Tel Aviv University
69978 Tel Aviv, Israel
E-mail: kantor@orion.tau.ac.il

and

MEHRAN KARDAR
Department of Physics, Massachusetts Institute of Technology
Cambridge, MA 02139, U.S.A.
E-mail: kardar@mit.edu

ABSTRACT

Spatial configurations of randomly charged polymers, known as polyampholytes (PAs), are very sensitive to the overall excess charge $Q$. Analytical arguments, supported by Monte Carlo simulations and exact enumeration studies, lead to the following picture: For $Q < Q_c \approx q_0 \sqrt{N}$ ($q_0$ is the elementary charge, $N$ is the number of monomers in the polymer), the radius of gyration $R_g$ of the polymer decreases with decreasing temperature $T$ and the polymer becomes compact, while for $Q > Q_c$ the polymer stretches with decreasing $T$. At low $T$, the dense states are described by Debye–Hückel theory, while the expanded states resemble a necklace of globules connected by strings. At such temperatures, the transition between the dense and the expanded states with increasing $Q$, is reminiscent of the breakup of a charged drop.

1. Introduction

Statistical mechanics of randomly charged polymers, called polyampholytes (PAs), is a challenging subject because it embodies an interesting combination of long range interactions and randomness. While the physics of homogeneous polymers has a reasonably firm basis, considerably less is known about heteropolymers, although the latter present an extremely rich problem of biological significance. In this presentation we review some properties of PAs.

The spatial extent of a polymer is characterized by the critical exponent $\nu$, which relates its radius of gyration (r.m.s. size) $R_g$ to the number of monomers $N$, by the power law $R_g \propto N^\nu$. The polymer will be called “compact” if $\nu = 1/d$, where $d$ is the dimension of the embedding space, and “stretched” if $\nu = 1$. The simplest model of PAs is as a flexible chain of $N$ monomers, each of which has a charge $\pm q_0$ selected from a well defined ensemble of quenches. The polymer has a characteristic microscopic length scale $a$, such as the range of excluded volume interactions, or the nearest neighbor distance along the chain. The monomers of the PA interact both via (short range) excluded volume interactions and long range (unscreened) Coulomb
interactions. In the simplest ensemble of quenches, each monomer takes a charge $q_i = \pm q_0$ independently of all the others; i.e. $\overline{q_iq_j} = \delta_{ij}q_0^2$, where the overline indicates averaging over quenches. While the average excess charge $Q \equiv \sum_i q_i$ of such PAs is zero, a “typical” sequence has $Q$ of about $\pm Q_c$, with $Q_c \equiv q_0 N^{1/2}$. This statement, as well as the definition of $Q_c$, is unrelated to the embedding dimension $d$. However, the importance of charge fluctuations (both for the overall polymer, or for large segments of it) does depend on the space dimension. The electrostatic energy of the excess charge, spread over the characteristic size of an ideal polymer ($R_g \propto N^{1/2}$), grows as $Q^2/R_g^{d-2} \sim N^{(d-4)/2}$. This simple dimensional argument shows that for $d > 4$ weak electrostatic interactions are irrelevant. (The excluded volume effects are also irrelevant in $d > 4$.) Thus, in $d > 4$ and at high temperatures, the PA behaves as an ideal polymer with an entropy-dominated free energy of the order of $-NT$. However, on lowering temperature it collapses into a dense state, taking advantage of a condensation energy of the order of $-Nq_0^2/a^{d-2}$.

We are primarily interested in the behavior of PAs in $d = 3$. We present both numerical and analytical evidence that the behavior of PA in $d < 4$ is extremely sensitive to the value of $Q$. In particular, we show that for $Q < Q_c$ the PA assumes compact configurations, while for $Q > Q_c$ it is in an expanded state. We suggest a “necklace” model which qualitatively describes the latter state.

2. Properties of Polyampholytes

2.1. Neutral Heteropolymers: Short–Range vs. Long–Range Interactions

It is interesting to compare and contrast the behaviors of heteropolymers with short and long range interactions. Consider a polymer represented by a self–avoiding chain carrying a quenched sequence of random charges which interact only at short distances, with similar charges repelling each other and the opposite charges attracting. In $d = 3$, at high temperatures $T$, the presence of such short range interactions does not influence the behavior of the polymer and it behaves as a self–avoiding walk (SAW). If $Q$ is small, i.e. the positive and negative charges are almost balanced, upon decrease of temperature, charges of opposite sign are more likely to be in the vicinity of each other. This introduces an effective attraction which increases in strength with decreasing temperature, and at a certain temperature the polymer collapses into a globule, as in a regular $\theta$–transition. When the imbalance $Q$ between the two types of charges increases, the transition temperature decreases, as demonstrated in Fig. 1a, and for sufficiently large imbalance the transition disappears altogether. Since the behavior of the system varies very gradually with increasing $Q/N$, it does not really matter whether the ensemble of chains consists only of quenches with exactly vanishing $Q$, or is obtained by independently choosing each $q_i = \pm q_0$ with equal
probability. In the latter case $Q$ may deviate from zero by an amount of order $q_0N^{1/2}$; such fluctuations have a negligible contribution to $Q/N$ for large $N$.

The long range Coulomb interactions in random PAs are always relevant at $d < 4$. An approximate treatment using a Debye–Hückel type theory leads to the conclusion that a PA minimizes its free energy by assuming a configuration in which positive charges are predominantly surrounded by negative charges, causing screening as in a regular electrolyte. A detailed calculation suggests the following picture: At a finite $T$, the PA can be divided into segments containing $n$ monomers each, where $n$ defines the length scale at which electrostatic interactions become of order $T$, i.e. $Q^2(n)/R_g(n) \sim q_0^2n/(an\nu_0) = T$ in $d = 3$, where $\nu_0 \approx 0.59$. The overall configuration is then composed of $n$–mer blobs: Inside the blob the PA behaves as an uncharged polymer, while the blobs form a compact structure resembling an electrolyte. The resulting PA is compact (i.e., has $R_g \sim N^{1/3}$) at all temperatures, with a $T$–dependent density. On the other hand, scaling arguments assume that the $N$–dependence of the $R_g$ of a random PA is determined from the relation $Q^2/R_g \sim q_0^2N/R_g \approx T$, leading to the conclusion that $R_g \sim N$ in $d = 3$. This apparent contradiction is resolved by noting that the spatial configurations of PAs are extremely sensitive to the overall charge $Q$. In particular, it can be shown that there is a critical charge $Q_c = q_0N$, such that for $Q < Q_c$ the PAs are compact, while for $Q > Q_c$ they are stretched. The diagram in Fig. (b) indicates such separation between contracted and expanded regimes of the PA. In the following subsections we shall present different arguments.
Fig. 2. Low $T$ configuration of 64–monomer PAs with (a) $Q = 12$, and (b) $Q = 0$. Dark and bright shades indicate opposite charges.

and numerical results supporting this conclusion.

2.2. Polyampholytes with Excess Charge: High Temperature Arguments

For $d < 4$, electrostatic interactions are relevant and the high temperature phase is no longer a regular self–avoiding walk. At high $T$, the behavior of the polymer can be explored perturbatively. For the ensemble of uncorrelated charges ($\mu_i\mu_j = 0$), the lowest order $(1/T)$ correction to the quench–averaged $R_g^2$ vanishes. However, restricting the ensemble to yield fixed $Q$, slightly modifies the quench–averaged charge–charge correlations. In particular, the two–point correlation function becomes $\frac{q_i q_j}{N^2} = \frac{(Q^2 - Q_c^2)}{N^2}$ for $i \neq j$. This small (order of $1/N$) correction to the correlation function causes a significant change in $R_g^2$ due to the long range nature of the Coulomb interaction. A $1/T$–expansion has a first order term proportional to $Q - Q_c$. Thus the size of a PA tends to decrease upon lowering temperature if $Q$ is less than $Q_c$, and increases otherwise.

Confirming the $1/T$–expansion, a strong $Q$–dependence of $R_g$ has been seen in Monte Carlo simulations. It has been shown that for $Q < Q_c$ the PA contracts with decreasing $T$, while for $Q > Q_c$ it expands. Fig. depicts low temperature equilibrium configurations of two PAs, one of them has $Q$ slightly larger than $Q_c$ and is strongly stretched, while the other has $Q = 0$ and forms a globule. The two behaviors are separated by the vertical line at the top of the phase diagram in Fig. b. It should be noted that the arguments leading to location of this line are independent of $d$, as long as $d < 4$. 
2.3. Polyampholytes with Excess Charge: Low Temperature Arguments

Monte Carlo results indicate that PAs with $Q = 0$ form dense globules at low temperatures. We can use this observation as a starting point for the investigation of the dependence of low-$T$ shapes on $Q$ in $d = 3$. The energy (or rather the quench–averaged free energy) of the PA is phenomenologically related to its shape by

$$E = -\epsilon_c N + \gamma S + \frac{bQ^2}{R}. \quad (1)$$

The first term is a condensation energy proportional to the volume (assumed compact) and $\epsilon_c \sim q_0^2/a$, the second term is proportional to the surface area $S$ (with a surface tension $\gamma \sim q_0^2/a^3$), while the third term represents the long–range part of the electrostatic energy due to an excess charge $Q$ ($b$ is a dimensionless constant of order unity). The correctness of separating the energy into the 3 terms appearing in Eq. (1) is not self–evident in random systems. A justification for the assumptions implicit in this equation is provided by an exact enumeration study of the ground states of PAs defined on a lattice. Fig. 3 depicts the ground state energies of all 2080 possible quenches for 12–step (13–atom) chains. (The horizontal axis represents an arbitrary numbering of the quenches.) The energies are clearly separated into 7 bands, corresponding to excess charges of $Q = 1, 3, 5, \cdots, 13$. (There is only one quench with $Q = 13$.) While each band has a finite width, we see that the energy of a PA can be determined rather accurately by only specifying its net charge $Q$, while the additional details of the quench appear only in the width of the band.

The optimal shape is obtained by minimizing the overall energy in Eq. (1). The first term is the same for all compact shapes, while the competition between the surface and electrostatic energies is controlled by the dimensionless parameter

$$\alpha \equiv \frac{Q^2}{16\pi R^3 \gamma} = \frac{Q^2}{12V \gamma} \equiv \frac{Q^2}{Q_R^2}. \quad (2)$$

Here, $R$ and $V$ are the radius and volume of a spherical drop of $N$ particles, and we have defined the Rayleigh charge $Q_R$. We note that in the case of PAs, $Q_R \approx q_0 N^{1/2} = Q_c$. The behavior of a system described by Eq. (1) has been analyzed in the past in the contexts of charged conducting drops, as well as liquid drop models of atomic nuclei. If one restricts the possible shapes of a globule to spheroids, then one finds that for sufficiently large values of $\alpha$ (of order one or more), the energy of the system can be decreased by distorting the drop into a prolate spheroidal shape. Both MC simulations and experimental results indicate that for $Q < Q_R$, the $R_g$ of PA at low temperature is almost independent of $Q$, while it increases extremely fast as a function of $Q$ for larger charges.
The transition between compact and expanded states with increasing $Q$ is represented by the vertical line at the bottom of the diagram in Fig. 3b. The presence of this line signifies the instability of the spherical shape, but provides no indication of what the stable state of the PA looks like. This question is taken up in the following section. It should be stressed, that although both high and low temperature arguments seem to provide a consistent picture of transition between compact and extended states, the equality between $Q_c$ and $Q_R$ depends on the space dimension. For $d < 3$ ($d > 3$) $Q_R$ increases with $N$ slower (faster) than $Q_c$, and therefore the high-$T$ criterion will not coincide with the low-$T$ limit.

3. The Necklace Model

3.1. Uniform Charges

Although the ellipsoidal globule may have a lower energy than the spherical one, the former is not the minimum energy configuration of a charged drop: A uniformly charged drop minimizes its energy by splitting into two equal, infinitely removed, droplets for $\alpha > 0.3$, and the number of such droplets increases with $\alpha$. Obviously, the PA must maintain its connectivity. We can constrain the overall shape to remain singly connected by linking the droplets via narrow tubes of total length $L$ and diameter $a$. As long as $La^2 \ll R^3$, most of the charge remains in the spheres. The total electrostatic energy is proportional to $Q^2/L$, while the surface energy cost grows as...
\(\gamma aL;\) equating the two gives \(L \propto Q.\) For large \(Q,\) the PA will look like a *necklace* of globules connected by narrow strands. The configuration depicted in Fig. 2a indeed bears some resemblance to such a necklace.

It should be noted that \(R_g\) in this simplified discussion is proportional to the typical charge \(Q,\) and therefore proportional to \(N^{1/2}.\) This serves as an indication that the quench–averaged configurations are not compact. The picture has one important shortcoming for PAs: it assumes that the excess charge is uniformly distributed along the chain and disregards the strong charge fluctuations. It thus applies to such problems as an alternating sequence of charges to which some additional charge has been added, or to a weakly charged homogeneous polymer in which the attraction (and, therefore, the condensation energy) is provided by a different mechanism, such as short range attractions.

3.2. Effects of Randomness

We now illustrate the difficulties caused by randomness for the case of an unrestricted PA. Since \(\overline{Q^2} = \overline{q_0^2 N}\), where the overline denotes an average over the ensemble of all quenches, we have \(\overline{\alpha} = 1.\) A uniformly charged drop is unstable to splitting already for \(\alpha \approx 0.3,\) and thus a typical random PA is expected to form several globules connected by narrow tubes. Now consider splitting sequences of \(N\) monomers with total charge constrained by a particular \(\alpha\) into two equal subchains of charges \(Q_1\) and \(Q_2.\) It is easy to show that each segment has \(\overline{\alpha_{\text{subchain}}} = (1 + \alpha)/2,\) while the mean product of the charges is \(\overline{Q_1 Q_2} = \overline{q_0^2 N(\alpha - 1)/4.}\) The subchains have, on average, values of \(\alpha\) close to unity. Also, for \(\alpha = 1,\) the average value of the product of charges vanishes. We thus have the paradoxical situation in which most spherical shapes are unstable, while there is on average no energetic gain in splitting the sphere into two equal parts.

Therefore, charge inhomogeneities drastically modify the necklace picture. The resulting PA is probably still composed of rather compact globules connected by a (not necessarily linear) network of tubes. The globules are selected preferentially from segments of the chain that are approximately neutral (or at least below the instability threshold), while the tubes are from subsequences with larger than average excess charge. It can be shown that the probability of finding a very large neutral segment in a random sequence of charges is large, i.e. it is possible to build a configuration consisting of one very large neutral globule with highly charged “tails” sticking out of it.

While the necklace model provides a convenient starting picture for the behavior of PAs, it does not encompass the entire complexity of the problem. The probability distribution of the \(R_g\) of the ground states of PAs obtained from exact enumeration study has a large peak for small \(R_g,\) indicating that most of the configurations are compact, as well as a slowly decaying tail at large \(R_g.\) This tail represents the
expanded configurations, and determines the behavior of the quench–averaged $R_g$. Indeed, for $N \leq 13$ we found that 80% of all quenches can be classified as compact, i.e. their $R_g$ increases as $N^{1/3}$, while the remaining 20% have quench–averaged $R_g$s increasing with $N$ at least as fast as that of a SAW.

We can summarize our current knowledge of the behavior of random PAs as follows: The exact enumeration and Monte Carlo studies confirm that random PAs have (on the average) expanded spatial conformations, although further work is needed to verify whether $\nu = 1$. The necklace model provides a useful qualitative view of the ground state configurations. Further studies are needed to put the model on a more quantitative basis.

4. Acknowledgements

This work was supported by the US–Israel BSF grant No. 92–00026, and by the NSF through grant No. DMR–94–00334 at MIT’s CMSE.

5. References

1. P.G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca (1979).
2. D.L. Stein, Proc. Natl. Acad. Sci. USA 82, 3670 (1985); J.D. Bryngelson and P.G. Wolynes, Proc. Natl. Acad. Sci. USA 84, 7524 (1987); H.S. Chan and K.A. Dill, Physics Today 46(2), 24 (1993); T. Garel and H. Orland, Europhys. Lett. 6, 307 (1988); E.I. Shakhnovich and A.M. Gutin, Europhys. Lett. 8, 327 (1989); M. Karplus and E.I. Shakhnovich, in *Protein Folding*, ed. by T.E. Creighton, ch.4, p. 127, (Freeman & Co., New York, 1992).
3. Y. Kantor and M. Kardar, Europhys. Lett. 28, 169 (1994).
4. P.G. Higgs and J.-F. Joanny, J. Chem. Phys. 94, 1543 (1991); J. Wittmer, A. Johner and J.F. Joanny, Europhys. Lett. 24, 263 (1993).
5. Y. Kantor, H. Li, and M. Kardar, Phys. Rev. Lett. 69, 61 (1992); Y. Kantor, M. Kardar, and H. Li, Phys. Rev. E49, 1383 (1994).
6. Y. Kantor and M. Kardar, Europhys. Lett. 14, 421 (1991).
7. Y. Kantor and M. Kardar, Europhys. Lett. 27, 643 (1994); Y. Kantor and M. Kardar, Phys. Rev. E51, 1299 (1995).
8. Y. Kantor and M. Kardar, Phys. Rev. E52, in press (1995).
9. X.-H. Yu, A. Tanaka, K. Tanaka, and T. Tanaka, J. Chem. Phys. 97, 7805 (1992); Yu X.-H., Ph. D. thesis, MIT (1993).
10. J.M. Victor and J.B. Imbert, Europhys. Lett. 24, 189 (1993).
11. Y. Kantor and D. Ertaş, J. Phys. A27, L907 (1994); D. Ertaş and Y. Kantor, Phys. Rev. E, submitted (1995).