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Necklace model of randomly charged polymers

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Abstract

Spatial conformations of randomly charged polymers (polyampholytes (PAs)) strongly depend on their total (excess) charge Q. For Q larger (smaller) that some critical value the PA is expanded (collapsed). The transition between the collapsed and the expanded states is reminiscent of the Rayley shape instability of a charged drop. The expanded states can be approximately described using the necklace model, as a chain of interconnected compact globules. Randomness of the charge sequence along the chain modifies the simple model creating wide distribution of sizes of the "beads" of the necklace. A simple mathematical model was proposed to describe the shape of the necklace. © 1998 Elsevier Science B.V. All rights reserved.

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The importance of understanding proteins [1] has attracted much attention to the statistical mechanics of heterogeneous polymers. A particular type of heteropolymers built with a mixture of positively and negatively charged groups along their backbone are called polyampholytes (PAs). Proteins are biomolecules formed from amino-acids. Out of 20 natural amino-acids, three are positively charged (Lys, Arg, His) and two are negatively charged (Asp, Glu) [2]. A statistical study of the charge distribution along the sequences of biomolecules [3] indicates that from the point of view of electrostatic interactions the charge sequences in proteins are only weakly (anti-)correlated. Thus, the proteins can be approximately treated as *randomly* charged PAs. Experiments on PAs and polyamphilic gels [4–8] reveal an extreme sensitivity of their geometric properties on their overall charge. We will show that the presence of long-range electrostatic interactions indeed causes a rather unique behavior in such polymers: the spatial conformations of a single PA with unscreened electrostatic interactions at a low temperature T strongly depend on its total (excess) charge Q. We will demonstrate that the geometry of the system can be qualitatively described using simple models.

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We will consider a model PA consisting of N monomers. The charge of the ith monomer $q_i = \pm q_0$ is assumed to be uncorrelated with the charges of other monomers, and the charge sequence is quenched. Geometrical properties of polymers can be conveniently described by their radius of gyration (root-mean-squared size) R_g [9]. At high T, the effect of electrostatic interactions is small, and R_g is approximately equal to that of an uncharged polymer. However, upon lowering of T the PA attempts to take advantage of the presence of two types of charges along its backbone by assuming spatial conformations in which every charge is predominantly surrounded by charges of an opposite sign. If the total (excess) charge of the PA is $Q \equiv \sum_{i=1}^{N} q_i$, then the average product of the two charges selected on the sequence $\langle q_i q_j \rangle = (Q^2 - q_0^2 N)/N^2$. For instance, for a neutral PA ($Q = 0$), we have $\langle q_i q_j \rangle = -q_0^2/N$, i.e. a slightly attractive interaction. Although the attraction is very weak ($\sim 1/N$), there are $N(N-1)/2$ interacting pairs, leading to a strong overall attraction. Note, that for $Q > Q_c \equiv q_0\sqrt{N}$, the randomly selected pair will (on the average) repel. More formally, it has been shown [10,11] using $1/T$ expansion of R_g, that at high temperatures for Q greater (smaller) than Q_c the R_g increases (decreases) with decreasing T. Monte Carlo [12,13] and exact enumeration [14] studies confirm that such T-dependence of R_g persists for all temperatures.

The behavior of neutral PAs can be approximately described using a Debye–Hückel-type theory [15,16], which leads to the conclusion that at low T the polymer should collapse into a dense state with condensation energy $E_{\rm cond} \approx -Nq_0^2/a$, where a is a microscopic distance such as diameter of the monomer. In such a collapsed state, $R_g \sim N^{1/3}$. Debye–Hückel theory is not applicable to the non-neutral PAs. Nevertheless, the globular low-T state can be used as a starting point in a phenomenological description of PAs. It is plausible to assume that the energy E of a globular PA can be expressed as a sum of three terms:

$$E = -N\frac{q_0^2}{a} + \gamma S + Q^2/R_g \,. \tag{1}$$

(In this description we omit the dimensionless prefactors of order unity.) The first term in this equation represents the Debye–Hückel-type condensation energy, the second term is the surface energy (where the surface tension $\gamma \approx q_0^2/a^3$, and the surface area $S \approx a^2 N^{2/3}$), while the last term is the electrostatic energy of the globule of radius $R_g \approx aN^{1/3}$. The ability to separate the total energy into three terms in not self-evident in a random system. An exact enumeration study of all quenches and spatial conformations of PAs with $N \leqslant 13$ confirmed the accuracy of this assumption [14]: Fig. 1 depicts ground-state energies of all possible quenches of a 13-monomer PA. (The horizontal axis represents an arbitrary numbering of the quenches.) The energies are separated into seven bands, corresponding (from bottom to top) to excess charges of $Q = 1, 3, 5, \ldots, 13$. Clear separation of the bands and small fluctuations within the bands indicate that the electrostatic energy of the overall charge can be separated from the rest of formation energy. The correct N-dependence of the first two terms in Eq. (1) was also verified [14].

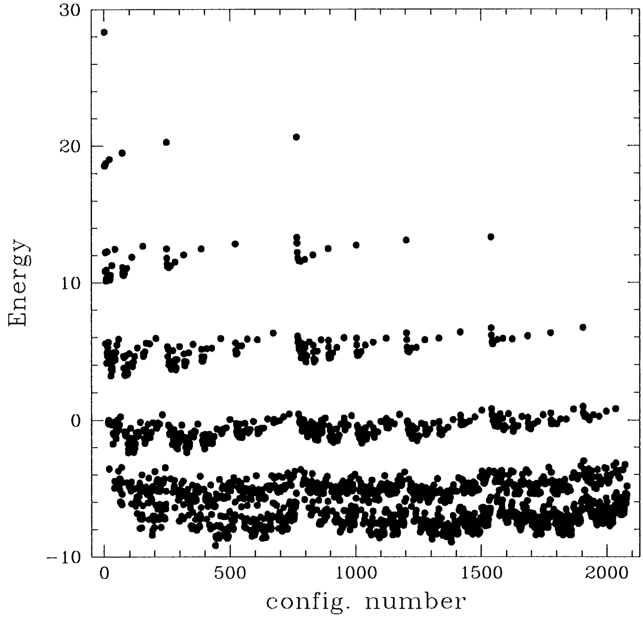

Fig. 1. Energies of the ground states [14] of all distinct (i.e. unrelated by symmetry transformations) quenches (arbitrarily numbered from 1 to 2080) of PAs with $N = 13$.

If the volume of the globule remains constant, i.e. the first term in Eq. (1) does not change, then the optimal shape of the globule can be obtained by minimizing the sum of surface and electrostatic energies. Note, that for spherical shape both terms are proportional to $N^{2/3}$. The problem is analogous with the well-known problem of a charged liquid drop [17,18] and with charged-drop model of the atomic nucleus [19–21]. (The former case treats a conducting drop, while the latter case corresponds to a uniformly charged drop.) For a drop with volume $V = \frac{4}{3}\pi R^3$, one can define a dimensionless parameter

$$\alpha \equiv \frac{Q^2}{16\pi R^3\gamma} = \frac{Q^2}{\sqrt{12V\gamma}} \equiv \frac{Q^2}{Q_R^2}, \tag{2}$$

which determines the shape of the drop. The *Rayleigh charge* $Q_R \equiv 12V\gamma \approx q_0\sqrt{N}$ coincides with Q_c. It can be shown [14] that the elongated (spheroidal) shape of a conducting drop has lower energy than the spherical shape for $\alpha > 0.899$. Although spheroidal shape has lower energy, it is not the absolute energy minimum. A drop can further lower its energy by splitting into several equal drops. In particular, a uniformly charged drop will split into two drops for $\alpha > 0.3$. A polyampholyte with excess charge Q can imitate such a splitting by forming a *necklace* of several charged globules connected by narrow necks. If the total length of such conformation is h ($ha^2 \ll R^3$), then the splitting will reduce the electrostatic energy to Q^2/h. However, creation of the necks connecting the globules will increase the surface energy by γah. Optimizing the total energy we find: $h\sim Q$. This picture has been independently confirmed by MC simulations [22] of *homogeneous* weakly charged polymers. Since such polymers do not condense into globular shape, and attractive short-range interaction has been added to ensure the condensation. Formation of necklace has been observed with increasing Q.

Unlike the homogeneous case, in PAs the condensation energy is created by all the (positive and negative) charges of the sequence. However, the main difference between the PA and the homogeneously charged polymer is the *randomness*. Splitting a random sequence of charges into two equal parts will *not* split the total excess charge into half: on the contrary, the excess charges of two subchains can have either the same or opposite signs. Monte Carlo studies indicate [12,13] that low-T configurations consist of few almost neutral globules connected by charged necks, or even of a single almost neutral globule with charged tails sticking out of it. It is not clear whether there is just one well-defined low-T conformation, or several conformations of very different shapes with similar energies [23].

While the exact treatment of electrostatic interactions is not possible, we can pose a simplified problem which captures some essential features of this necklace model, e.g., we may ask what the typical size L of the largest neutral (or weakly charged) segment in a random sequence of N charges will be. In order to answer this question, we investigated [24,25] the size distribution of the largest Q-segments (segments with a total charge Q) in such N-mers. This problem can be mapped to a one-dimensional random walk (RW): the sequence of charges $\{q_i=\pm 1\}$, is mapped into a sequence of unit steps in the positive or negative directions along an axis. The sequence of charges with vanishing total charge now corresponds to a RW which returns to the origin after N steps, while a neutral segment inside the sequence of charges corresponds to a loop inside the RW. Similarly, a segment with charge Q corresponds to a segment (in the corresponding RW) whose end is displaced by Q units from its beginning.

In the large N limit, the problem can be described in terms of a probability density $p(\ell,q)$, where $\ell\equiv L/N$ and $q\equiv Q/\sqrt{N}$ are the reduced length and charge, respectively. This probability density was investigated using Monte Carlo and exact enumeration methods, as well as by analytical arguments [24,25]. Fig. 2 depicts the dependence of p on both its variables. It has been shown that the function $p(\ell,0)$ has an essential singularity in the $\ell\to 0$ limit, and diverges as $1/\sqrt{(1-\ell)}$ in the limit $\ell\to 1$. For our purposes, it is important to note that the typical neutral segment in a random sequence is very large ($L\approx\frac{3}{4}N$). Thus, it is not surprising that the low-energy states of a random quench frequently look like one large weakly charged globule with sticking out charged tails.

The problem of largest Q-segment is closely related to the problem of self-avoiding walks (SAWs). While the physical problem of charged PAs naturally creates a one-dimensional RW, we can generalize the problem to a d-dimensional walk. Now the elementary charges become vectors, and we are looking for the longest segment which produces a prescribed displacement. (If the prescribed displacement vanishes, then we are looking for the longest loop.) Not surprisingly, the problem becomes trivial for

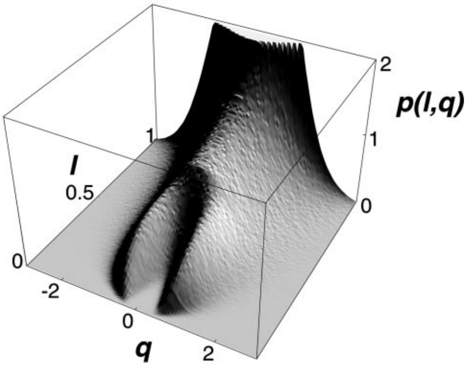

Fig. 2. Probability density of largest Q-segments as a function of reduced charge q and reduced length ℓ. The results have been obtained from MC simulations [24,25].

$d > 4$, where $p(\ell,0) = \delta(\ell)$, i.e. the largest loops have negligible length compared with the length of the walk. However, for $d<4$, the function p has a non-trivial shape which has been calculated using Monte Carlo methods [24,25]. The probability density $p(\ell,0)$ can be derived from the partition function of a modified SAW in which self-avoiding interactions are operating only between monomers separated by distance (measured along the walk) larger than ℓN. This problem could be treated using the standard renormalization group methods.

The largest Q-segment problem significantly oversimplifies the actual problem of PA. Nevertheless, its results capture some qualitative features of the low-temperature conformations. Slightly, better results can be obtained by considering problems of several segments (e.g. searching for two separate neutral segments with the largest sum of lengths) in the same random sequence with simplified surface energies (which depend only on the length of a segment) and simplified Coulomb interactions (which depend only on overall charges and distances between the segments). Preliminary results show an improved agreement with the results observed in the numerical studies of PAs. While such simple models increase our understanding of the ground states of PAs, we do not expect them to resolve such questions as the scaling relation between the quench-averaged R_g and N. The typical excess charge created by a random sequence is of the order of Q_R, i.e. the averaging over an ensemble of quenches is performed exactly at the point where R_g depends very strongly on Q, and therefore the resulting average may depend on minute details of the statistics.

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